Plasticization

and Plasticizer Processes

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Norbert A. J. Platzer,
Symposium Chairman

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Advances in Chemistry Series

Robert F. Gould, ***Editor***

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications.

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PREFACE

Plasticizers are often called servants of the resin industry because they serve to soften hard and brittle resins into flexible and pliable products. Of all the resin servants, they are certainly the oldest, as some of them have been used with natural resins far before the first synthetic resin was invented. Their origin dates back to ancient times when the first sailors added oil to pitch when calking their ships.

The plasticizer industry represents a giant servant. In 1964, production passed the one billion pound mark. When compared with the plastics industry, plasticizers have only been surpassed by the polyolefins, the vinyls, and the styrene resins. All other plastics are smaller, such as the phenolics, alkyds, melamines, ureas, polyesters, or epoxies.

As servants, plasticizers are more neglected than their masters, the resins themselves. Less has been said and written about them. The Division of Industrial and Engineering Chemistry felt that plasticization and plasticizer processes are important enough to hold a two-day symposium on this subject. This volume contains the papers presented at the symposium during the Spring of 1964—National ACS Meeting in Philadelphia.

Plasticizers seem to have an importance equal to plasticized resins and should be considered as a spouse rather than as servant. This couple, resin plus plasticizer, is equally responsible for the physical properties of the plasticized product, its processing performance, and its cost. In selecting a plasticizer, one must consider compatibility, efficiency, permanence, and economy. Compatibility depends upon polarity, structural configuration, and size of molecule. Efficiency depends upon the solvating effect. Permanence depends upon volatility and susceptibility to extraction. And economy depends upon raw materials and conversion costs.

Plasticization is the process in which the plasticizer molecules neutralize the secondary valence bonds, known as van der Waal's force between the polymer molecules. It increases the mobility of the polymer chains and reduces the crystallinity. These phenomena become evident in reduced modulus or stiffness, increased elongation and flexibility, and lowering of the brittle or softening temperature of the plasticized product. The effect of plasticizers on polymers is the subject of the first chapter by E. H. Immergut and H. F. Mark.

Reducing the glass transition temperature by blending high boiling solvents with polymers is considered as external plasticization and discussed by M. C. Shen and A. V. Tobolsky. Reducing the glass transition temperature through copolymerization is considered as internal or self-plasticization. K. Ueberreiter, who created these terms 24 years ago, has recently found a second transition temperature: the side group transition. Polymers and plasticizers must have side groups of high mobility in order to have plasticizing qualities. This and other observations, such as the relation between rate of dissolving and solubility are discussed in Ueberreiter's chapter.

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In his chapter, "Mobility of Plasticizers in Polymers," R. Kosfeld describes his recent finding that a portion of a liquid plasticizer remains in the liquid-like state in the plasticized resin even below its glass transition temperature.

For many years, it has been known that a small quantity of plasticizer acts as an antiplasticizer for polyvinyl chloride (PVC). During a recent search for effective plasticizers for polycarbonate, W. J. Jackson and J. R. Caldwell found several groups of compounds which acted as antiplasticizers. They increased the tensile modulus and strength and reduced the elongation of polycarbonate films. In contrast to plasticizers, these antiplasticizers affected glass transition temperature quite differently. Their mechanism is explained by the fact that they either increase crystallinity or reduce the mobility of the polymer chain through the bulkiness of their molecules.

Plasticizers represent a large family. There are 300 different plasticizers known, of which one hundred are commercially produced—liquid and solid, monomeric, and polymeric. Plasticizers are generally grouped into phthalates, phosphates, low temperature diesters, polymeric or permanent plasticizers, epoxides, and others.

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U. S. Plasticizer Production 1964

	Million Pounds	*Average Price ¢/lb.*
Phthalates	650	16
Phosphates	80	29
Epoxides	74	29
Low temperature diesters (adipates, azelates, sebacates)	70	34
Polymer	65	42
All others	96	. .
		. .
Total	1035	22

Phthalic ester plasticizers represent by far the largest plasticizer group because of their good performance and economy. In 1964 they accounted for 63% of the total plasticizer production and 46% of their dollar sales. Three chapters of this book describe novel processes for phthalic esters. The chapter by S. J. Fusco and co-workers deals with the oxonation of linear olefins resulting in primary alcohols of a high degree of linearity. Phthalate esters of these linear alcohols exhibit an improved performance in PVC compounds. The chapter by L. O. Raether and H. R. Gamrath reports a novel and economic process for phthalic esters by the reaction of phthalic acid with olefins and without isolating the alcohol and even without adding water. The chapter by A. Coenen reveals new catalyst systems for the esterification of phthalic acid with an alcohol.

Phosphates represent the second largest plasticizer group. They accounted for 8% of the total plasticizer production and 16% of total sales. Tricresyl phosphate continued to hold the lead with production increasing 13% and sales increasing 19%, whereas triphenyl phosphate remained practically constant. Epoxides and low temperature diesters each accounted for 7% of the total plasticizer market. Epoxidized tallates are frequently replaced by low temperature diesters along with epoxidized soya oil. From the low temperature diesters, adipates and azelates showed a sharp increase, whereas the sebacates decreased. Polymeric plasticizers accounted for 6% of the plasticizer production and enjoy a better than average growth rate. New developments in this area are given in the chapter by H. Hopff.

Because of the many different plasticizers, it frequently becomes important to analyze the composition of a plasticizer extracted from a plastic. A chromatographic method has been developed for analyzing plasticizers by D. Braun and is described in his chapter.

Plasticizers are used in combination with cellulosics, vinyls, acrylic, and styrene resins, as well as polyvinylacetate, polyamides, polycarbonate, and other synthetic and natural resins. Because PVC consumes about 70% of all plasticizers produced, the plasticizer market is closely related to the vinyl resins production. During the last ten years, the vinyl market grew at an average rate of 18% per year and has reached 1.6 billion pounds in 1964. The growth in vinyl resins and plasticizer production was paralleled by a drop in resin price and a shift towards more effective and less expensive plasticizers.

Chlorinated normal paraffins represent a family of low cost secondary plasticizers for PVC with better properties than chlorinated waxes and are discussed in D. H. Rotenberg's chapter. The interaction between PVC and plasticizers and the effect on mechanical, thermal, and electrical properties are the subjects of the following two chapters by M. C. Shen and A. V. Tobolsky, H. Breuer and R. Kosfeld, and by R. D. Deanin and co-authors. Large quantities of plasticizers are used in vinyl plastisols. A novel instrument to measure the gelling characteristics of plastisols is described in A. Hill's chapter. Vinyl organosols will find greater uses in protective coatings, via fluidized-bed spray coating techniques.

Little plasticizer is used commercially with styrene polymers. To investigate the interaction between ethylene oxide and vinyl aromatic polymers has been the objective of J. Moacanin and co-workers.

The book closes with two chapters on the plasticization and antiplasticization of polycarbonate by A. Conix and L. Jeurissen and G. W. Jackson and J. R. Caldwell, respectively. It would have been possible to include more examples of the interaction between polymers and plasticizers, for instance on the effect in lacquers, in latices, or adhesives. Some are mentioned in the first chapter.

The scope of this book has not been to list all available plasticizers and their combinations with all different kind of resins. For this, we have to refer to the text books and trade literature. The intention of this book and of the symposium has been to report on new developments in the field of plasticization and plasticizer processes. Nobody else would have been more qualified than the authors of these chapters who are experts in this field. It is our hope that this book may lead the reader closer to the achievements of these experts.

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Springfield, Mass.
April 5, 1965

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1

Principles of Plasticization

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Plasticization, in general, refers to a change in the thermal and mechanical properties of a given polymer which involves: (a) lowering of rigidity at room temperature; (b) lowering of temperature, at which substantial deformations can be effected with not too large forces; (c) increase of the elongation to break at room temperature; (d) increase of the toughness (impact strength) down to the lowest temperature of serviceability. These effects can be achieved: (1) by compounding the given polymer with a low molecular weight compound or with another polymer: and (2) by introducing into the original polymer a comonomer which reduces crystallizability and increases chain flexibility.

A plasticizer is usually defined in terms of the desired properties of a given polymer–plasticizer system. Thus, for coatings or films, it might be defined as a compound that gives flexibility, shock resistance, hand or feel, etc. For an elastomeric material a plasticizer changes the properties by reducing stiffness and permitting easier processing–i.e., milling, mixing, etc., or at least allows this at lower temperatures. For many molded, extruded, and calendered plastics, it is a compound that imparts a desirable degree of flexibility over a broad range of use temperatures and lowers the brittle point (temperature at which the material becomes brittle).

Unfortunately there seems to be no way at present absolutely to characterize the behavior of a plasticizer in terms of some fundamental property. The reason is that the behavior of the plasticizer is intimately tied up with the polymer to which it is added, and the polymer, in turn, depends greatly on its previous history. For example, one can prepare two samples of film from the same batch of polymer; yet, by drawing one to a greater extent, it will increase in crystallinity owing to better orientation of the chains, and the effect of the plasticizer will, therefore, be quite different. Whereas one can use molecular orbital calculations to predict, for in-

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stance, antioxidant behavior (because oxidation involves electron transfer, and can therefore be put on a quantitative basis) there is no similarly well defined quantitative interaction with plasticizers.

Types of Plasticizers

There are two main groups of plasticizers: internal and external plasticizers.

Internal Plasticizers. These are actually a part of the polymer molecule—e.g., a second monomer is copolymerized into the polymer structure, thereby making it less ordered, and therefore, more difficult for the chains to fit closely together. This softens the polymer–i.e., lowers the glass temperature (T_g) or the modulus. Usually the internal plasticizer is a monomer whose polymer has good low temperature properties. A few representative values of T_g or T_b (brittle temperature) for homopolymers and copolymers are shown in Table I:

Table I. Effect of Internal Plasticization

Polystyrene	T_g = 100°–105°C.	Poly(vinylidene chloride)	T_g = −18°C.
Polyacrylonitrile	T_g = 105°–130°C.	Poly(vinyl chloride)	T_g = 82°–89°C.
Polybutadiene	T_b = −68°C.	Poly(vinyl acetate)	T_g = 30°C.
Styrene–Butadiene Copolymer (25 : 75)	T_b = −66°C.	Vinylidene chloride–Vinylchloride Copolymer (85 : 15)	T_g = −5°C.
Butadiene–Acrylonitrile Copolymer (75 : 25)	T_b = −50°C.	Vinylchloride–Vinylacetate Copolymer (85 : 15)	T_g = 63°C.

T_g = glass temperature.
T_b = brittle temperature.

Internally plasticized systems consisting of simple random copolymers, designed for use in flexible plastic articles, generally have an unsatisfactorily narrow use temperature range, since they soften more sharply than analogous externally plasticized systems or polyblends (mixtures of two or more polymers).

Another type of internal plasticization involves the introduction of side chains (either substituents or grafted branches). This effect is well known with the polyacrylates and polymethacrylates (*27*) (Figure 1), and is caused by lowering of the forces between the polymer chains owing to the bulkiness of the substituent groups. The reason for the minimum in the curve is that side chain crystallization occurs as the substituent chain increases beyond a certain length. Another example of internal plasticization is the alkylation of polyamides (*29*) which gives elastic fibers by lowering crystallinity and T_g through reduction of intermolecular forces. These fibers were the forerunners of the present elastic fibers such as Lycra, Vyrene, and others.

External Plasticizers. The external plasticizers are the most important as far as commercial application is concerned. This is because they provide more satisfactory combinations of properties and allow the manufacturer more formulating flexibility than if the plasticizer were added during the polymerization process.

External plasticizers, are compounds of low vapor pressure which, without chemical reaction, interact with the polymer, mainly at elevated temperature, by means of their solvent, or swelling power.

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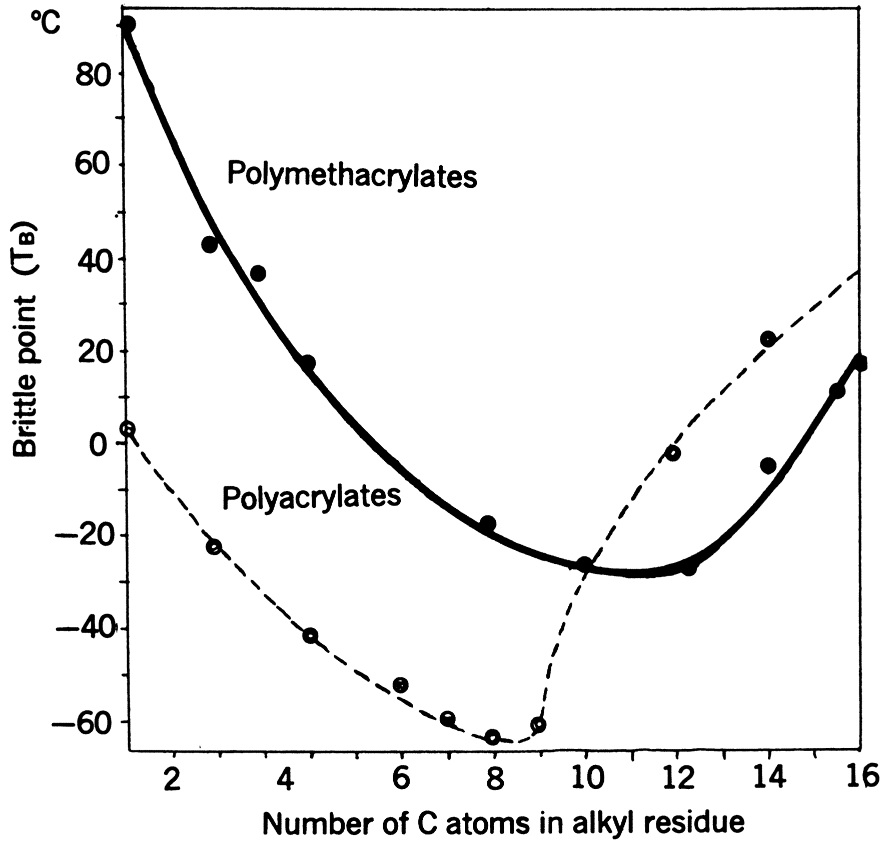

Figure 1. Brittle point of n-alkyl esters of polyacrylic and polymethacrylic acid (27)

A distinction should be made between solvent plasticizers and nonsolvent plasticizers. With an amorphous polymer, any plasticizer is a solvent plasticizer—i.e., under suitable conditions the polymer would eventually dissolve in the plasticizer. With a crystalline or semicrystalline polymer, there are some compounds which enter both the crystalline (ordered) and the amorphous (disordered) regions. These are true plasticizers–sometimes they are called primary plasticizers. If, on the other hand, only the amorphous regions are penetrated, the compound may be considered as a nonsolvent plasticizer, also known as a secondary plasticizer, or softener. Such softeners are used sometimes as diluents for the primary plasticizer.

Factors Opposing Plasticization

Intermolecular Forces. It is the principal function of the plasticizer to interpose itself between the polymer chains. The main obstacles to this endeavor are the attractive forces between the polymer molecules, which depend on the chemical and physical structure of the polymer.

However, it is also important to consider the intermolecular forces between the plasticizer molecules themselves and between plasticizer and polymer. Unless all these interactions–i.e., plasticizer–plasticizer, plasticizer–polymer, and polymer-polymer–are the same order of magnitude, there can be no plasticizing action.

The following describes the various possible intermolecular forces.

DISPERSION FORCES. These exist between all polar or nonpolar molecules. They result from the attraction between atoms, arising from interaction between small dipoles, induced in one atom by those formed by the nucleus and electrons of the other atom. Dispersion forces constitute a major component of the total intermolecular forces only with nonpolar systems–e.g., benzene and polyethylene or polystyrene.

INDUCTION FORCES. These arise when a molecule with a permanent dipole caused by a polar group (C–Cl, C=O, $C–NO_2$), induces a dipole in a neighboring molecule. This effect is particularly strong with aromatics because of the high polarizability of the easily displaced π-electrons–e.g., low molecular weight esters and polystyrene, or benzene and poly (vinyl acetate).

DIPOLE–DIPOLE INTERACTIONS. These occur between two molecules, both of which contain polar groups, after mutual orientation of the dipoles such as $+-\ \ +-$ and $\begin{smallmatrix}+ & -\\ - & +\end{smallmatrix}$. The interaction of ester group-containing plasticizers with polymers, such as poly (vinyl chloride), or cellulose nitrate, are representative examples.

HYDROGEN BONDS. With molecules containing OH or NH groups, such as water, acids, amines, polyamides, poly(vinyl alcohol), cellulose, etc., intermolecular, and sometimes also intramolecular H-bond formation results. This is a rather strong interaction, and plasticizers capable of similarly strong interaction with the polymer molecules will be required for such materials. It is important here to consider also the distance between the H bonds along the polymer chain. The more closely spaced they are, the more they will oppose plasticizer penetration. On the other hand, with increasing temperature, the intermolecular attraction due to H bonds decreases markedly because increased Brownian motion works against the required orientation of the molecules.

The following table of cohesion energies (*21*) indicates the intermolecular forces involved with various polar and nonpolar molecules.

Table II. Specific Molar Cohesion of Polymers (*21*)

Polymer	*Groups responsible for lateral attraction*	*Specific molar cohesion (cal.)*
Polyethylene	CH_2	1000
Polyisoprene (Rubber)	CH_2, CH_3	1300
Polychloroprene	CH_2, CCl	1600
Poly(vinyl chloride)	CH_2, CCl	2600
Poly(vinyl acetate)	CH_2, $COCH_3$	3200
Polystyrene	CH_2, C_6H_5	4000
Poly(vinyl alcohol)	CH_2, OH	4200
Cellulose acetate	OH, $COCH_3$	4800
Cellulose	OH, COC	6200
Polyamides	CH_2, CONH	5800
Silk fibroin	CHR, CONH	9800

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Crystallinity. Polymer chains which possess a regular structure, not only chemically but also sterically, are able to crystallize under suitable conditions, either from the melt, or from solution. This means that the chain molecules change from a coiled and disordered state to a tightly folded, aligned, and ordered state (Figure 2).

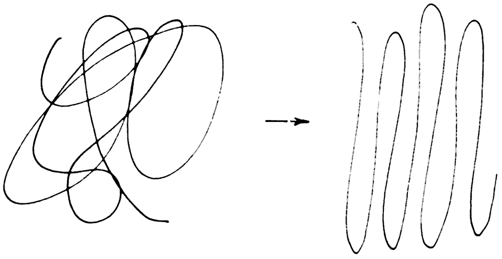

Figure 2. Crystallization of a chain molecule

While, in recent years, many laboratories have demonstrated that nearly every synthetic polymer can crystallize in the form of "single crystals" (*13*) consisting of lamellae formed by regular chain folding (Figure 3), it is clear that extreme conditions–i.e., very slow crystallization or very dilute solutions, are required for these structures to form. Under normal conditions, such as those encountered in any industrial process, the polymer usually crystallizes in the form of less ordered, large structures, called spherulites.

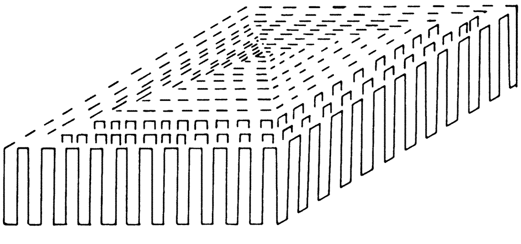

Figure 3. Schematic representation of a polymer single crystal, illustrating the principle of chain folding (13)

However, with naturally occurring macromolecules, such as cellulose, the older "fringed micelle" concept is believed to apply. This represents a crystalline polymer, (it would be more correct to speak of semicrystalline or partially crystalline polymers since a material consisting of chain molecules can never be completely ordered), made up of ordered (crystalline) domains interspersed with disordered (amorphous) domains, so that each polymer chain passes through several crystalline and amorphous regions (Figure 4).

It is readily apparent from Figures 2, 3, and 4 that a plasticizer molecule will have much more difficulty in penetrating the crystalline regions, where there is a

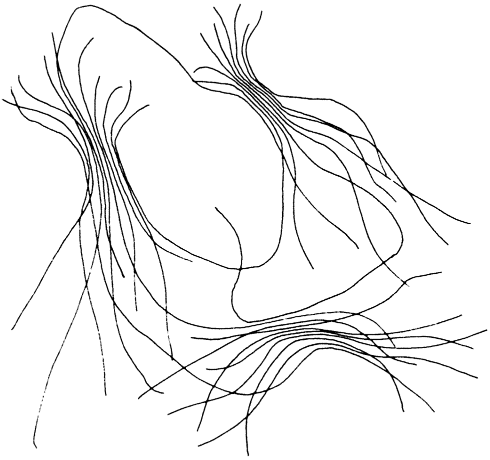

Figure 4. Schematic presentation of a partially crystalline material ("fringed micelle")

minimum of free space between the polymer chains, than the amorphous regions. Crystallinity should, therefore, be considered as a factor opposing plasticization.

Plasticizer Requirements

In addition to such general requirements as low volatility, temperature stability, light stability, little, or no odor, etc., there are a number of more basic requirements.

One of these has already been mentioned, namely, that all the intermolecular forces involved (between plasticizer and plasticizer, between polymer and polymer, between plasticizer and polymer) be of the same order of magnitude.

There are three other important criteria.

Solvent Power. The plasticizer should, in most cases, have a high degree of solvent power for the polymer.

With crystalline polymers, only a solvent type plasticizer will be able to penetrate both the ordered and the disordered regions, whereas a nonsolvent plasticizer (softener) will only be able to enter the amorphous regions.

It should be realized, however, that when a low molecular weight compound penetrates the crystalline regions certain properties which depend on crystallinity –e.g., tensile strength, and modulus–will deteriorate. With materials where these properties are of prime importance, it may therefore be more advantageous to use only a secondary plasticizer, or softener.

Compatibility. The plasticizer should be compatible with the polymer system over both the processing and the use temperature ranges; and it is desirable that subsequent exposure of the plasticized article to common substances or conditions, such as water, oil, oxygen, or sunlight, should not disturb the compatibility balance.

Factors affecting compatibility, in addition to polarity, are the size (molecular weight) and shape of the plasticizer. An example of good compatibility due to similar chemical structure (polarity, shape, size) is the oldest known plasticizer–

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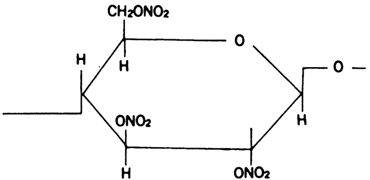
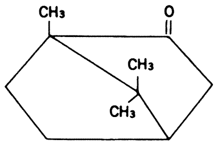
polymer system: camphor and cellulose nitrate. It is readily apparent from Figure 5 that plasticizer and polymer have a similar chemical structure.



Cellulose Nitrate



Camphor

Figure 5. Cellulose nitrate and camphor, illustrating similarity between polymer and plasticizer

Efficiency. The term "plasticizer efficiency" is used to relate a desirable modification of the properties of a given product to the amount of plasticizer required to achieve this effect. For example, the efficiency of various plasticizers in "plasticizing" a given polymer may be expressed in terms of the depression of the glass temperature by a given mole, or volume fraction of plasticizer. Therefore, there is no absolute value for the efficiency of a certain plasticizer, and the relative efficiency of different plasticizers will depend on which polymer property is used to measure plasticizer efficiency.

In addition to size and molecular weight, one of the most important factors which determines plasticizer efficiency is the rate of diffusion of the plasticizer in the polymer matrix. In view of the dynamic solvation–desolvation between the plasticizer molecules and the polymer chains, the higher the diffusion rate, the greater the efficiency of the compound as a plasticizer. However, high diffusion rates are usually encountered with small molecules; the smaller the plasticizer molecule, the greater its volatility and, therefore, the rate at which it is lost from the plasticized product.

Permanence. The permanence of a plasticizer–i.e., its tendency to remain in the plasticized material, depends on the size of the plasticizer molecule and on its rate of diffusion in the polymer. The larger the plasticizer molecule, the lower its vapor pressure, or volatility and, therefore, the greater its permanence. This accounts for the popularity of certain polymeric plasticizers, such as polyesters, in spite of their relatively high price. Other factors, such as polarity and hydrogen bonding, will also, of course, affect the vapor pressure of the plasticizer.

The rate of diffusion of the plasticizer molecules within the polymer matrix will also determine plasticizer permanence. Unfortunately, while a high rate of diffusion provides for greater plasticizer efficiency, it results in low plasticizer permanence.

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The choice of a plasticizer, therefore, usually involves a compromise since the requirements for good solvent power, compatibility, efficiency, and permanence, cannot all be met simultaneously. This has been clearly illustrated by Boyer (*1*) with the aid of the diagram in Figure 6.

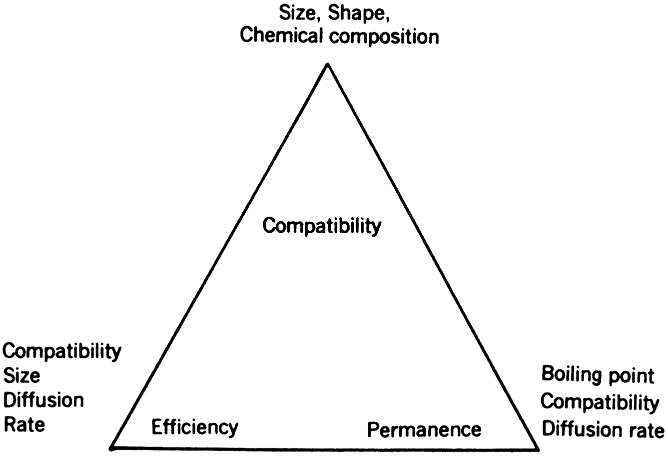

Figure 6. Schematic representation of relationships between three important properties of the plasticizer: compatibility, efficiency, and permanence (1)

Measurement of Plasticizer Properties

We will concentrate here on some measurements of fundamental properties, rather than on technical tests developed for specific products, or end uses.

Solvent Power and Compatibility. We will consider four methods for measuring the solvent power and compatibility of a plasticizer: the Flory-Huggins μ value, the cohesive energy density, viscosity measurements, and cloud point measurements.

FLORY-HUGGINS μ. The Flory-Huggins μ value measures the interaction between polymer and solvent (plasticizer). It derives from the so-called "lattice theory," which represents a statistical approach to the behavior of polymer molecules in solution (*10*, *14*, *15*, *16*, *22*). The μ value may be experimentally determined for any polymer–plasticizer system (where the plasticizer can dissolve the polymer) by osmotic pressure measurements according to the relation:

$$\frac{\pi}{c_2} = \frac{RT}{M_2} + \frac{RTd_1}{M_1 d_2^2}(0.5 - \mu)c_2 + \cdots$$

where π = osmotic pressure
R = gas constant
T = absolute temperature
d_1, d_2 = density of solvent and polymer, respectively
M_1, M_2 = molecular weight of solvent and polymer, respectively
c_2 = concentration of polymer

Thus from a plot of π/c_2 *vs.* c_2 one obtains μ directly from the slope. A "good"

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solvent–i.e., one with high solvent power, shows a large slope on the π/c_2 *vs.* c_2 plot, whereas a "poor" solvent–i.e., one with low solvent power–shows a small slope, and in some cases, even a negative slope. This is illustrated in Figure 7.

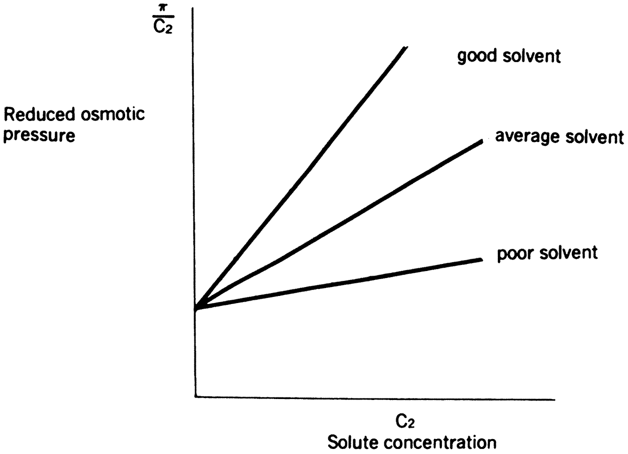

Figure 7. Typical osmotic pressure results illustrating the effect of solvent power

Since the slope is proportional to (0.5–μ), rather than to μ, a "good" solvent has a μ value much smaller than 0.5–i.e. about 0.2–whereas a "poor" solvent has a μ value of approximately 0.5. For μ values greater than 0.55, the liquid may be considered a nonsolvent.

The μ value may also be determined from swelling measurements of slightly cross-linked samples of the polymer (*12*). This method is based on a theory developed by Flory and Rehner (*11*). It does not require the polymer to be completely soluble in the plasticizer and avoids the need for osmotic pressure measurements which, even under the most favorable conditions, require considerable skill.

According to this method, the sample is calibrated by calculating the volume fraction of the polymer, v_2, from the weight changes, or the dimensions of the sample, after immersion in a liquid for which μ is known (this is the case for many polymer–solvent systems). From v_2 and μ, one obtains M_c, the average molecular weight between cross-links, according to the relation:

$$\mu v_2^2 = -\ln(1 - v_2) - v_2 - \rho_2 V_1 v_2^{1/3}/M_c$$

where ρ_2 = density of the polymer, and V_1 = molal volume of solvent. Having thus determined M_c, swelling measurements are carried out in the plasticizer to obtain v_2, and then μ can be calculated from the above equation.

The swelling method has been used successfully in a classic study by Doty and Zable (*7*) to evaluate the interaction of various plasticizers with poly(vinyl chloride). Figure 8 shows the μ values of a series of dialkyl phthalates as a function of their molecular weight. It can be seen that dibutyl, dihexyl, and dioctyl phthalate have low μ values–i.e., high solvent power for poly(vinyl chloride), (PVC), whereas the higher and lower esters have high μ values, and therefore low solvent power.

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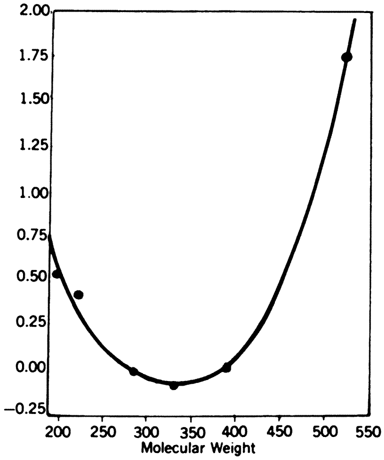

Figure 8. Dependence of the interaction parameter μ on the molecular weight of a homologous series of dialkyl phthalates in PVC (7)

Cohesive Energy Density. The cohesive energy density (*CED*) was defined in 1931 by Scatchard as the energy of vaporization per unit volume. Hildebrand then proposed the square root of the cohesive energy density as a numerical value identifying the solvent power of specific solvents.

Solubility will occur if the free energy of mixing, ΔF, is negative–i.e., $\Delta F = \Delta H - T\Delta S < 0$. Since ΔS, the entropy of mixing, is usually large and always positive for polymer–solvent systems, the sign of ΔF will be determined by the sign and magnitude of ΔH, the heat of mixing.

For cases where $\Delta H > 0$, according to Hildebrand and Scatchard,

$$\Delta H = \phi_s \phi_p (\delta_s - \delta_p)^2$$

where ϕ_s and ϕ_p are the volume fraction of solvent and polymer, respectively, and δ_s, δ_p are the solubility parameters of the solvent and the polymer.

The solubility parameter, δ, is defined by the relation

$$\delta = (\Delta E/V)^{1/2} = (CED)^{1/2}$$

For cases where there is strong interaction between solvent and polymer, such that ΔH is negative, the polymer will dissolve since ΔF will be < 0. However if there is no strong polymer–solvent interaction, ΔH being positive, the magnitude of ΔH determines whether or not the liquid will dissolve the polymer. This means that only liquids for which ΔH will be very small will be solvents for the polymer, and the smaller ΔH, the better the solvent. In fact, if $\Delta H = 0$, ΔF must be negative, and solution is certain. Thus, in selecting a suitable solvent, one tries to have $\Delta H = 0$ by trying to make the term $(\delta_s - \delta_p) = 0$. In other words, one attempts to choose a liquid with a solubility parameter (or cohesive energy density) as close to that of the polymer as possible.

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Tables III and IV show some representative δ values of polymers and organic liquids (*5*).

Table III. Solubility Parameter δ of Polymers (*5*)

Polymer	δ
Teflon	6.2
Polyethylene	7.9
Polyisobutylene	8.1
Polyisoprene	8.3
Polybutadiene	8.6
Polystyrene	9.1
Poly(vinyl acetate)	9.4
Poly(methyl methacrylate)	9.5
Poly(vinyl chloride)	9.7
Polyethylene glycol terephthalate	10.7
Cellulose nitrate	11.5
Poly(vinylidene chloride)	12.2
Nylon (6,6)	13.6
Polyacrylonitrile	15.4

Table IV. Solubility Parameter δ of Common Solvents (*5*)

Solvent	δ
Ethyl ether	7.4
Carbon tetrachloride	8.6
Xylene	8.8
Toluene	8.9
Ethyl acetate	9.1
Benzene	9.2
Methyl ethyl ketone	9.3
Cyclohexanone	9.9
Acetone	10.0
sec-Butyl alcohol	10.8
n-Butyl alcohol	11.4
Cyclohexanol	11.4
n-Propyl alcohol	11.9
Ethyl alcohol	12.7
Nitromethane	12.7
Ethylene glycol	14.2
Methanol	14.5
Glycerol	16.5
Water	23.4

The δ values for liquids are calculated according to the relation $\delta = (\Delta E/v)^{1/2} = [(\Delta H - RT)/(M/d)]$

where ΔH = latent heat of vaporization
T = absolute temperature
R = gas constant
M = molecular weight
d = density

If ΔH is not known, it can be calculated fairly accurately by Hildebrand's equation: $\Delta H = 23.7\ T_{bp} + 0.020\ T_{bp}^2 - 2950$ where T_{bp} is the boiling point in °K.

For polymers, δ cannot be calculated according to the above relations because the polymer is not volatile–i.e., it has no boiling point or ΔE of vaporization. There are two methods of overcoming this problem. The δ can be determined experimentally by determining solubility (or swelling of slightly cross-linked samples) in a series of liquids of known δ. The δ of the polymer is then the midpoint of the range of δ

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values of the liquids in which the polymer dissolves. For the cross-linked samples, one takes the δ value of the liquid in which maximum swelling occurs.

The alternative method is to calculate δ for the polymer from the structural formula and the density of the polymer by using the molar attraction constants tabulated by Small (*28*).

Table V. Molar Attraction Constants (*28*)

Group	*G*	*Group*	*G*
$-CH_3$	214	$-O-$	70
$-CH_2-$	133	CO	275
$-CH<$	28	COO	310
$>C<$	−93	CN	410
$CH_2=$	190	Cl	270
$-CH=$	111	Br	340
$>C=$	19	I	425
$CH\equiv C-$	285	CF_2	150
$-C\equiv C-$	222	S	225
$-C_6H_5$	735	SH	315
$-C_6H_4-$	658	ONO_2	440
		Si	−38

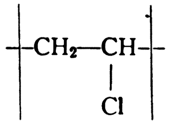
Assuming the additivity of these constants, δ can be calculated according to the relation:

$$\delta = d\,\Sigma G/M$$

where d is the density, ΣG is the sum for all the atoms and groupings in the polymer repeat unit, and M is the molecular weight.

As an example, the calculation of δ for PVC is as follows:

$d = 1.4$
$M = 62.5$



$$\left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right]$$

$1\ CH_2 = 133$
$1\ CH = 28$
$1\ Cl = 270$
$\Sigma G = 431$

$$\delta = \frac{1.4 \times 431}{62.5} = 9.66$$

as compared to an experimental value of 9.7 ± 1.0.

This approach is very useful for polymer–plasticizer systems, and especially for cases where polymeric plasticizers, which evidently cannot be treated as volatile liquids, are being considered.

Viscosity Measurements. Although in typical polymer–plasticizer systems, the polymer is the major component, it is possible to use the viscosity of dilute polymer solutions as a measure of the solvent power of the liquid for the polymer. Thus, liquids with high solvent power for the polymer cause a stretching out of the chain molecules, whereas a liquid of poor solvent power causes the chains to coil up. This is because, in the liquid with poor solvent power, the segments of the polymer chain (the monomer units) prefer to stay close to each other, while in a good solvent, interaction between polymer segments and solvent molecules is preferred.

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Since the viscosity of a polymer solution is determined by the resistance offered to the flow of the liquid by the polymer molecules, viscosity measurements may be used to obtain information about the degree of coiling of the chain molecules and, therefore, about the solvent power of the plasticizer for the polymer. The more coiled up the polymer chain, the less the resistance it presents to the flow of the solution, and, therefore, the lower the viscosity. This will be the case for a plasticizer with poor solvent power, whereas for a plasticizer with a high degree of solvent power for the polymer, the polymer chains are stretched out, thereby offering strong resistance to flow resulting in a high dilute solution viscosity.

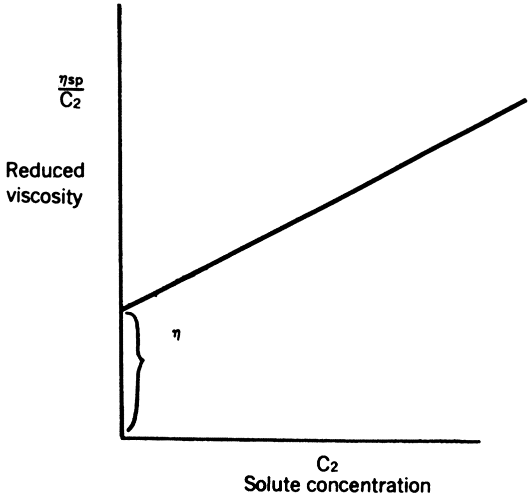

Figure 9. Typical viscosity plot

To obtain a quantity which is independent of the concentration of the solution, one determines the reduced viscosity, η_{sp}/c, for a series of concentrations and then extrapolates to zero concentration (Figure 9). The intrinsic viscosity, $[\eta]$, is obtained from the intercept at the ordinate.

The different viscosities are related to each other as follows:

Specific viscosity $= \eta_{sp} = (\eta_{solution} - \eta_{solvent})/\eta_{solvent}$

Reduced viscosity $= \eta_{red} = \eta_{sp}/c$

Intrinsic viscosity $= [\eta] = [\eta_{sp}/c]\ \lim_{c = 0}$
(or Limiting Viscosity Number)

Table VI gives intrinsic viscosities of PVC in a series of dialkyl phthalates (*34*). These results lead to the same conclusions as the μ value determinations of Doty and Zable illustrated in Figure 8.

It should be pointed out that some workers (*19*) have used viscosities based on molar, rather than weight, concentrations, but this does not seem significantly to affect the qualitative conclusions drawn from the viscosity experiments.

There is one other way (*8*) in which viscosity measurements can be used to

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determine the solvent power of a plasticizer for a certain polymer. This consists in preparing a suspension of the polymer in the plasticizer (1% by weight polymer), and determining the viscosity of the suspension as a function of temperature. As the temperature is raised, the viscosity goes through a maximum which occurs at the temperature where the suspension becomes a true molecular solution–i.e., where the plasticizer becomes a solvent. The higher the solvent power of the plasticizer for the polymer, the lower the temperature at which the maximum viscosity occurs (T_{max}).

Table VI. Intrinsic Viscosity of PVC in Dialkyl Phthalates (*34*)

$T = 80°C.$

Alkyl Residue	$[\eta]$
Methyl	0.39
Ethyl	0.46
n-Propyl	0.69
n-Butyl	1.04
n-Octyl	0.76

THE CLOUD POINT. If a plasticizer is incompatible with the polymer, a gradual "sweating out" of the plasticizer from the plasticized material–i.e., phase separation occurs. Since this is fairly slow, a more rapid evaluation of plasticizer compatibility can be obtained by determining the cloud point. This is the temperature, T_c, at which a dilute homogeneous solution of the polymer in the plasticizer becomes cloudy (turbid) on cooling (*18*). The cloudiness signifies that phase separation is taking place–i.e., that the polymer is no longer compatible with the plasticizer. The more compatible the plasticizer and polymer are, the lower will be the temperature to which the solution can be cooled before it becomes cloudy.

Table VII gives T_c values for solutions of PVC and poly(vinyl acetate) in a series of dialkyl phthalates (*34*).

Table VII. Cloud Point Values (T_c) for PVC and Poly(vinyl acetate) in Dialkyl Phthalates (2% conc.) (*34*)

	T_c = (°C.)	
Alkyl Residue	*PVAc*	*PVCl*
Methyl	−25	70
Ethyl	<−30	40
n-Propyl	10	~5
n-Butyl	20	−10
n-Amyl	45	<−10
n-Hexyl	90	
n-Heptyl	170	

Plasticizer Efficiency. All the above-mentioned methods are useful for evaluating the solvent power and compatibility of plasticizers; but none really measures quantitatively the efficiency of the plasticizer in "plasticizing" the polymeric product into which it is incorporated. Thus, it is the plasticizer's function to reduce the forces between the macromolecules and thereby increase chain mobility, which, in turn, leads to a "softening" or "plasticization" of the polymeric material. Therefore, any experimental method which permits measurement of chain mobility

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(translation and rotation of atoms, groups, segments, and whole chain molecules) also measures plasticizer efficiency.

THE GLASS TEMPERATURE. Determining the glass temperature, T_g, is the most important of the methods that measure chain mobility. The glass temperature, also called the second-order transition temperature, is the temperature at which a polymeric substance turns into a "glass" on cooling. To put it quite simply, it is the temperature above which the substance is soft and below which it is hard.

T_g can be determined by studying the temperature dependence of a number of physical properties such as specific volume, refractive index, specific heat, etc. *First-order transitions*, such as the melting of crystals, give rise to an abrupt change or discontinuity in these properties. However, when a polymeric material undergoes a *second-order transition*, it is not the primary property (the volume), but its first derivative with respect to temperature, (the coefficient of expansion), which becomes discontinuous. This difference between a first and second-order transition is illustrated in Figure 10.

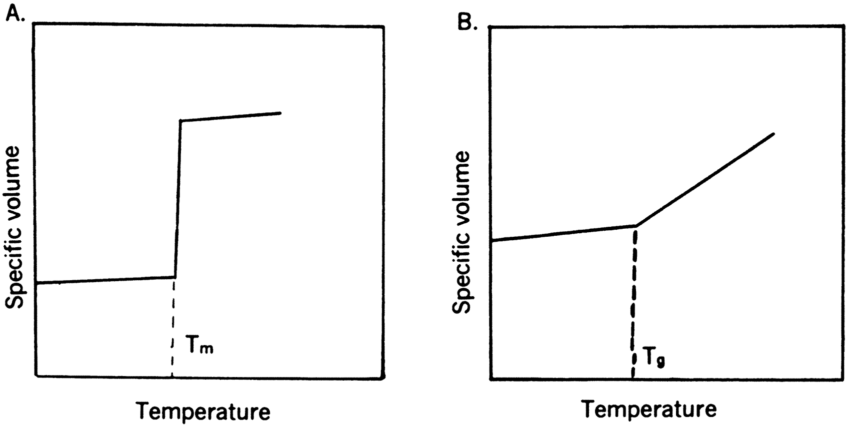

Figure 10. Schematic representation of first-order transition (A), and second-order transition (B)

Table VIII lists some representative T_g values of unplasticized polymers. Very flexible polymers such as polyethylene, polyisoprene, polybutadiene, have low T_g values, whereas polymers with stiff backbone chains and bulky side groups, such as poly(methyl methacrylate) and polystyrene, have a high T_g. Clearly, it is a polymer with a high T_g value where plasticization is most needed and where a significant lowering of T_g owing to the plasticizer may be expected.

Table IX shows the effect of two chemically very different organic liquids on the glass temperature of polystyrene (*2*). Ethylbenzene, with a chemical structure very similar to that of the polystyrene monomer unit, greatly lowers T_g and therefore, is a much more efficient plasticizer for polystyrene than paraffin oil, with its completely aliphatic structure.

It should be pointed out here that determining T_g is not completely unambiguous since the exact value depends somewhat on the cooling rate of the

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polymer during the measurement. Thus, T_g will be slightly lower for a slowly cooled than for a rapidly cooled material. However, the brittle temperature, T_b, which, as its name implies, is the temperature at which, on cooling, a material becomes brittle and breaks under certain specified conditions, will depend even more on extraneous factors, such as sample thickness, methods of flexing or impact, rate of measurement, etc., and is therefore not as characteristic of the material itself as T_g.

Table VIII. Glass Temperatures of Various Polymers

Polymer	*T_g(°C.)*
Silicone rubber	−123
Polyethylene	−110
Polybutadiene	−85
Polyisoprene	−70
Poly(*n*-butyl acrylate)	−56
Poly(ethyl acrylate)	−22
Polypropylene	−18
Poly(methyl acrylate)	5
Poly(*n*-butyl methacrylate)	22
Poly(vinyl acetate)	30
Poly(ethyl methacrylate)	65
Poly(vinyl chloride)	82
Polystyrene	100
Poly(methyl methacrylate)	105

Table IX. Effect of Plasticizer on T_g of Polystyrene (*2*)

Plasticizer	*% Plasticizer*	*T_g*
Ethylbenzene	0	82
	3	68
	5	50
	10	22
Paraffin Oil	0	80
	3	75
	10	56
	20	49
	50	43

Finally, several empirical equations exist which permit calculation of the glass temperature of a plasticized polymer if the composition of the mixture and the T_g values of the polymer and plasticizer are known (*4*).

DYNAMIC MECHANICAL TESTS. Plasticizer efficiency, can be measured, not only be the lowering of T_g, but also by temperature dependence of typical dynamic mechanical properties, such as modulus and damping.

Dynamic mechanical tests measure the response of a material to a periodic force or its deformation by such a force. One obtains simultaneously an elastic modulus (shear, Young's, or bulk) and a mechanical damping. Polymeric materials are viscoelastic–i.e., they have some of the characteristics of both perfectly elastic solids and viscous liquids. When a polymer is deformed, some of the energy is stored as potential energy, and some is dissipated as heat. It is the latter which corresponds to mechanical damping.

While there are many methods for measuring modulus and damping, one of the simplest involves using a torsion pendulum (*23*, *24*, *25*) as illustrated in Figure 11.

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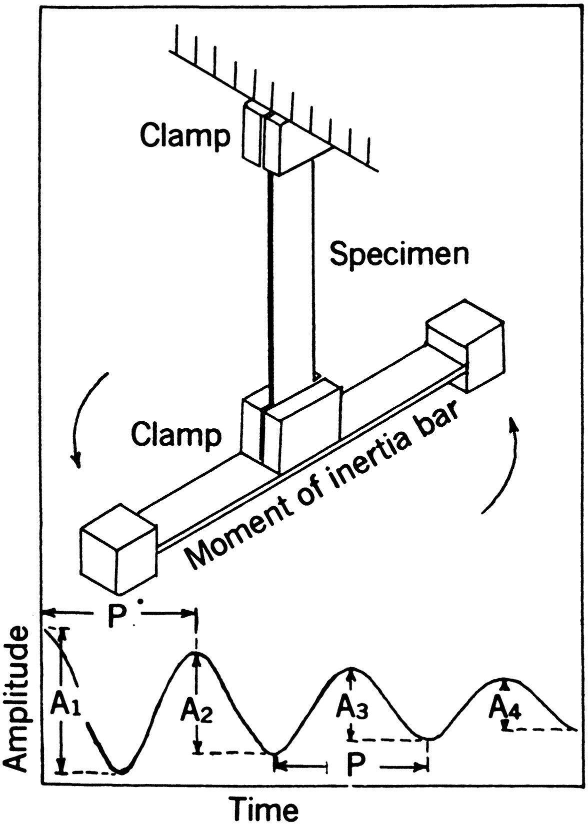

Figure 11. Schematic diagram of a torsion pendulum for measuring dynamic shear modulus and damping. A typical damped oscillation curve is illustrated at the bottom of the figure (25)

The shear modulus, G, is given by the relation:

$$G = \frac{5.588 \times 10^{-4}\, LI}{CD^3 \mu P^2} \text{ (p.s.i.)}$$

where L = Specimen length (inches)
C = Specimen width (inches)
D = Specimen thickness (inches)
P = Period of oscillations (seconds)
I = Polar moment of inertia of the system (pounds-sq. in.)
μ = a shape factor, which is a function of (C/D)

The damping, expressed as the logarithmic decrement, Δ, is calculated from the rate at which the amplitude of the oscillation decreases according to the equation:

$$\Delta = \ln (A_1/A_2) = \ln (A_2/A_3) = \cdots$$

where A_1 = amplitude of 1st oscillation,
A_2 = amplitude of 2nd oscillation, etc., (Figure 11).

It must be pointed out that the definition of the damping term depends on the method used. It is, therefore, necessary to express damping in terms of a complex modulus in order to be able to make comparisons. Thus:

$$G^* = G' + iG''$$

where G^* is the complex modulus, G' is the real part of the shear modulus, $i = \sqrt{-1}$, and G'' is the imaginary part of the modulus.

The imaginary part of the modulus, also called the loss modulus, is a damping term which determines the dissipation of energy as heat upon deformation. G''/G' is called the dissipation factor and is proportional to the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle.

We may now express the damping term of the torsion pendulum experiment in terms of the dissipation factor by the simple equation (an approximation which holds for most cases):

$$\Delta = \pi(G''/G')$$

For methods which measure Young's modulus, E, instead of the shear modulus, G, the analogous term for the damping is given by:

$$E''/E' = \tan \delta$$

where E' is the real part of the modulus, E'' is the imaginary part of the modulus (the loss modulus), and δ is the phase angle between the stress and the strain.

Figure 12 shows typical modulus and damping curves for an uncross-linked, amorphous polymer (a copolymer of styrene and butadiene) (*25*).

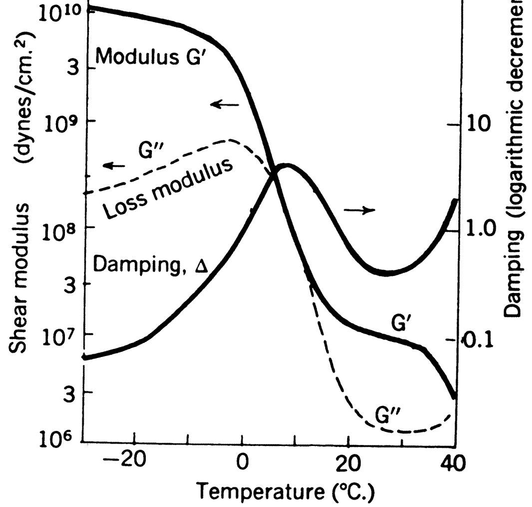

Figure 12. Typical dynamic behavior of uncrosslinked amorphous polymers. The material is a copolymer of styrene-butadiene (25)

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In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

Figure 12 shows, that in the neighborhood of the glass transition temperature there is a sudden drastic change in the modulus curves and a maximum in the damping curve. Hence, modulus and damping are properties that can be used to determine second-order transitions and, therefore, plasticizer efficiency. Thus, plasticizers will lower the temperature at which the maximum (or the sudden change in modulus) occurs, and the magnitude of this temperature shift, ΔT, will be a measure of plasticizer efficiency.

Table X shows such ΔT values for a series of plasticizers in a copolymer of styrene (28%) and butadiene (72%) (*3*).

Table X. Efficiency of Various Plasticizers in Lowering T_g of Styrene-Butadiene Copolymer (*3*)

Plasticizer	ΔT (°*C.*)
Dibutyl sebacate	9
Dibutyl phthalate	24
Hydrocarbon oils	25–30
Dioctyl adipate	37
Dioctyl sebacate	38

It should be pointed out that the temperature at which the damping maximum occurs depends on the frequency of the measurement: the higher the frequency, the higher the temperature. (This is quite analogous to the effect of the cooling rate on the T_g value obtained from volume–temperature measurements as discussed in the previous section).

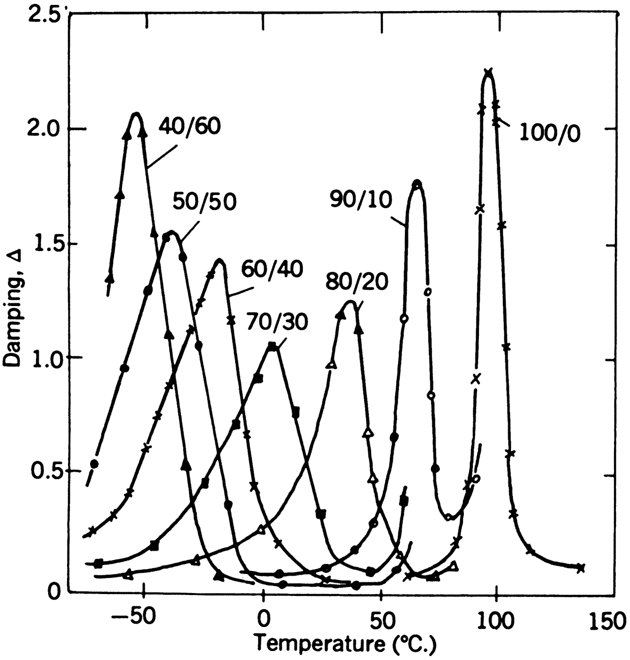

Figure 13. Mechanical damping of PVC plasticized with diethylhexyl phthalate (30)

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The temperature of maximum damping also depends on the concentration of plasticizer (Figure 13) (*30*), and comparisons of different plasticizers must, therefore, be made at the same concentrations.

DIELECTRIC MEASUREMENTS. Plasticizer efficiency can also be determined by measuring the electrical dissipation factor (damping) which is given by:

$$\epsilon''/\epsilon' = \tan \delta$$

where ϵ' is the dielectric constant and ϵ'' is the electrical loss factor. The temperature at which tan δ goes through a maximum corresponds to the temperature at which the mechanical damping is at a maximum. Lowering of this temperature by the plasticizer is, therefore, a measure of plasticizer efficiency.

Table XI shows ΔT values obtained from dielectric measurements (*34*, *35*, *36*).

Table XI. Efficiency of Various Plasticizers in Lowering T_g of PVC (*34*, *35*, *36*)

Plasticizer (*mole fraction = 0.1*)	*T* (°*C.*)
Diethyl phthalate	67
Di-*n*-butyl phthalate	76
Di-*n*-hexyl phthalate	82
Di-*n*-octyl phthalate	91
Di-*n*-decyl phthalate	98
Di-*n*-dodecyl phthalate	105

The analogy between the mechanical and the electrical damping measurements is also borne out by the effect of plasticizer concentration on the temperature of maximum damping as shown in Figure 14 (*31*, *32*, *33*).

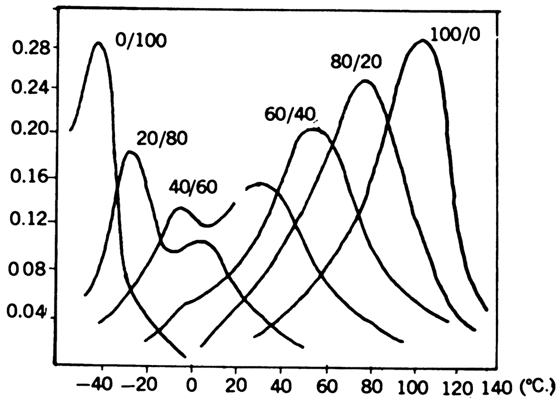

Figure 14. Electrical damping (tan δ) as a function of temperature for poly(vinyl acetate) plasticized with benzyl benzoate (31, 32, 33)

NUCLEAR MAGNETIC RESONANCE (*NMR*). One of the newest physical methods, which has been applied successfully to study the effect of plasticizers on T_g, is nuclear magnetic resonance (*20*).

However, since this work will be discussed by R. Kosfeld (p. 49–60) it is sufficient here simply to mention the method.

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Plasticizer Efficiency as a Function of Plasticizer Structure

The following general results are intended to present some of the more important conclusions concerning the relationship between plasticizer action and plasticizer structure.

Effect of Plasticizer Concentration. It is generally agreed that ΔT–i.e., the lowering of T_g–for most systems is directly proportional to the plasticizer concentration in the polymeric material. While some investigators (*37*) have insisted on using molar concentrations, it was later shown that weight concentrations can be used for comparisons of plasticizer efficiency in most cases (*34*, *17*).

Effect of Plasticizer Molecular Weight. Plasticizer efficiency, being a function of many factors, including molecular flexibility, shape, and polarity, which themselves vary from member to member in a homologous series, is a complex function of molecular weight. Generally, with a given polymer such as polyvinyl chloride, for each plasticizer family such as the phthalates, adipates, or sebacates, there is a range of molecular weights within which plasticizer efficiency is optimum. The effect is illustrated in Table XIII (cloud point criteria) and in the lower diagram of Figure 15. Comparison of the upper and lower diagrams shows that, whereas the depression of T_g per mole of plasticizer increases with molecular weight,

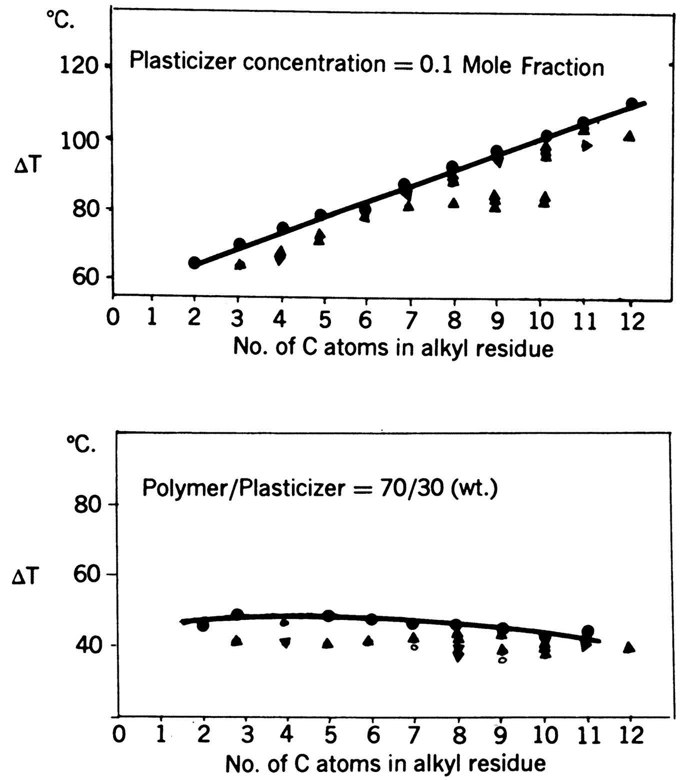
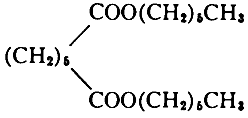
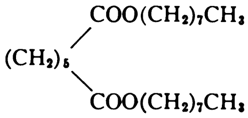
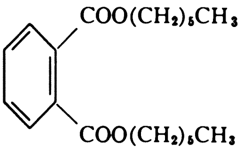
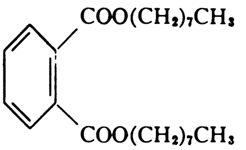
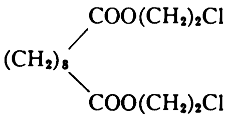
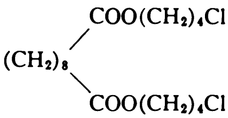
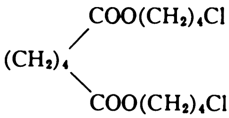
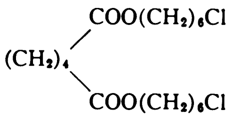
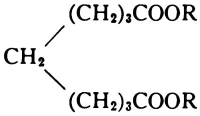
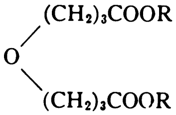
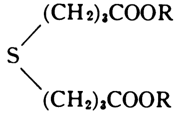


Figure 15. Plasticizer efficiency of a homologous series of dialkyl phthalates with PVC (*35*)

per unit weight of plasticizer the efficiency decreases somewhat for the higher phthalates.

Table XII. Comparison of Plasticizers for PVC (*36*)

	Plasticizer	Molecular Weight	η Plasticizer, Centipoise, T, 20°C.	Max. Solution Temperature T_{max}°C.	Turbidity T°C.	Plasticizer Efficiency ΔT°C.	
						Mole Fraction, 0.1	Weight Ratio 70:30
A		328	9.8	131	−30	99	90
B		384	15.0	147	~+50	107	93
C		334	30.5	104	<−70	82	71
D		390	39.7	117	<−70	91	71
E		327	+49 m.p.	135	not miscible	86	73
F		383	39.9	121	<−12	93	73
G		327	29.5	112	−50	83	69
H		383	36.7	114	<−11	92	73

I		R =						
		n-Butyl	300	8.2	120	−20	97	87
		n-Hexyl	356	12.3	137	−2	107	88
		n-Octyl	412	17.4	155	+110	113	80
J		R =						
		n-Butyl	302	8.1	117	< −74	93	80
		n-Hexyl	358	12.2	140	< −70	100	77
		n-Octyl	414	17.6	157	−30	~105	~80
K		R =						
		n-Butyl	318	11.5	108	< −75	96	80
		n-Hexyl	374	16.8	124	−40	104	76
		n-Octyl	430	23.8	140	−12	110	84

(1) Plasticizer A is better than plasticizer C as far as plasticizer efficiency is concerned, but C is better than A as far as solvent power and compatibility are concerned.

(2) G is better than F in solvent power and compatibility but worse in efficiency.

(3) H is better than G and F better than E (i.e., the further the Cl atom is removed from the ester group) in plasticizer efficiency.

(4) Comparing I, J, and K, it can be seen that incorporation of the more polar O and S improves solvent power and compatibility without loss of efficiency.

Effect of Polar Groups. To achieve good compatibility, polar plasticizers must be used with polymers containing polar groups. The smaller the distance between the polar groups along the polymer chain, the higher must be the plasticizer polarity to overcome the forces between the polymer molecules. However, if the forces between the plasticizer molecules become stronger than the plasticizer–polymer interactions, (as found with glycerol and PVC), then no plasticization occurs.

It was also found that better plasticization occurs if the polar group is on an aliphatic molecule (because of its greater mobility) rather than on an aromatic molecule.

Some of these polarity effects are illustrated in Table XII.

Table XIII. Cloud Point, T_c, of PVC (5%) in Various Plasticizers (*34*, *35*, *35*)^y

$A[COO(CH_2)_y - H]_2$	*1*	*2*	*3*	*4*	*6*	*8*	*10*	*12*
A = C_6H_4	110	95	60	48	< −70	< −70	−23	5
A = C_2H_4	90	67	< −73	−70	−36	+15		
A = C_6H_{12}		−2		−45	−22	+10		

Effect of Plasticizer Shape. Extended plasticizer molecules such as aliphatic chains with a high degree of flexibility, usually lower T_g or T_c much more than bulky plasticizer molecules, such as those containing ring structures. However, Table XIII shows that the comparison between aliphatic and aromatic ester plasticizers is also determined by the length of the alcohol residues and by separation between the ester groups.

Effect of Branching. A comparison of branched *vs.* linear plasticizer molecules usually shows that the linear molecules are more efficient in lowering T_g than the branched molecules. This effect is shown in Figure 15, where the open circles represent the branched phthalates and the full circles, the corresponding linear compounds. The branched esters give lower ΔT values in every case.

Effect of Internal Mobility (Flexibility). It seems that the internal mobility or flexibility of the plasticizer molecule plays an important, if not the most important, role in determining plasticizer efficiency. This appears to be true irrespective of the polymer which is being plasticized, unless there are overriding physical factors involved, such as polymer crystallinity. In general, the lowering of T_g will be proportional to the temperature difference between $(T_g)_{Polymer}$ and $(T_g)_{Plasticizer}$. This is illustrated in Table XIV. This table also shows that if the polymer itself is quite flexible, such as polychloroprene (Neoprene), the plasticizer efficiency is quite small, and may even result in negative ΔT values.

Table XIV. Plasticizer Efficiency of Ester Plasticizers in Different Polymers (*35*)

Polymer	*Dimethyl cyclohexyl-o-phthalate* $T_{pl} = +6°$	*Tricresyl-phosphate* $T_{pl} = -30°$	*Di-n-hexyl-o-phthalate* $T_{pl} = -57°$	*Di-n-butyl-adipate* $T_{pl} = -85°$
Styrene/AN (T_p = +151°) (copolymer)	52°	61°	74°	90°
PVC (T_p = +116°)	38°	50°	70°	83°
PVAc (T_p = +84°)	19°	29°	43°	58°
Polychloroprene (T_p = −9°)	−9°	0°	16°	32°

T_p = temp. in °C. of tan δ max (10^5 cycles/sec.) of the pure polymer.

T_{pl} = temp. in °C. of tan δ max (10^5 cycles/sec.) of the plasticizer.

$T_{70/30}$ = temp. in °C of tan δ max (10^5 cycles/sec.) of the mixture 70/30 (by weight) of polymer–plasticizer.

$$\tan \delta = \frac{E''}{E'} = \frac{\text{energy lost due to heat}}{\text{recoverable energy}} = \text{damping}$$

Plasticization of Natural Polymers

Almost everyone thinks of plasticization in terms of synthetic polymers. However, this phenomenon is also important with natural polymers, and it seems that this aspect has been neglected too long. We would, therefore, like to conclude this chapter by giving a few examples of plasticization phenomena in natural polymers.

One example is the plasticizing effect of water on fibers. Thus, if cellulose is regenerated in the form of filaments (rayon), the tensile strength of the fiber produced will depend greatly on the crystallinity of the material. The crystallinity in turn, depends on the conditions under which the cellulose is regenerated and, the slower the regeneration–i.e., the spinning process–the higher the crystallinity. However, the economics of rayon production are such that the manufacturer cannot afford to spin slowly enough to achieve maximum crystallinity, giving the cellulose chains time enough to orient and organize themselves into the most ordered state possible.

It has recently been shown (*26*) that rayon can be subjected to an after treatment, consisting of a very brief exposure to steam, which greatly increases the crystallinity. The water acts as a typical plasticizer by reducing the interaction forces–i.e., the hydrogen bonds–between the cellulose chains; this allows them to rearrange themselves so that greater order (crystallinity) is achieved. Table XV shows the increase in crystallinity that can be obtained in this manner. (Similar effects are also known with synthetic fibers–e.g., 6,6–Nylon).

Table XV. Effect of Steam on Crystallinity of Rayon (*26*)

Temperature (°C.)	*Time (min.)*	*Crystallinity (%)*	*Crystallinity Increase (%)*
Untreated sample	—	24.5	0
110	5	28.7	4.2
130	5	29.4	4.9
150	5	32.5	8.0
170	5	35.9	11.4
190	5	35.1	10.6
210	5	42.2	17.7

Another example of plasticization, or more correctly the loss of plasticizer, is the change in the swelling of rat tail tendon (collagen) as a function of the age of the rat (*6*, *9*). It was found that swelling is reduced with increasing age, which implies that greater fibrillar organization–i.e., better crystallization, has taken place. This may well be caused by the reduction of the interfibrillar spaces, resulting in a squeezing-out of the plasticizer, water.

It is hoped that these few examples dealing with natural polymers will arouse some interest in those concerned with plasticization and will perhaps make them look more closely at the work and findings of the biophysicist and the molecular biologist. It may well be that, by investigating plasticization in natural polymers, more light will be shed on the mechanism of plasticization in synthetic polymers.

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2

Glass Transition Temperature of Polymers

Effect of Plasticizer, Chain Ends, and Comonomer

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The effect of low concentrations of plasticizer, chain ends, or comonomer on the glass transition temperature of a polymer can be described by a linear equation with respect to the weight fraction. Over the entire range of composition, these effects can be described approximately by a quadratic equation. The interrelation of all of these equations is discussed and considered.

Incorporating a plasticizer into a polymer almost always leads to a lowering of the glass transition temperature of the polymer. Two empirical equations have been proposed relating the glass transition temperature depression to the diluent content. The first one (*4*) is:

$$T_g = T_{g1} - kw_2 \tag{1}$$

where T_g and T_{g1} are the glass transition temperatures of plasticized and unplasticized polymers, respectively, w_2 is the weight fraction of the diluent, and the coefficient, k, varies from 200° to 500° K. for different diluents in polystyrene. Equation 1 is valid at relatively low dilution if the diluent and polymer are compatible (*3*, *10*, *11*, *13*).

However, when it is desirable to cover the entire region of diluent concentration, a parabolic function is required to account for the deviation from linearity at higher dilution. The second empirical equation (*7*) is as follows:

$$T_g = T_{g1} w_1 + T_{g2} w_2 + Kw_1w_2 \tag{2}$$

In Equation 2, T_{g2} is the glass transition temperature of the pure plasticizer, w_1 is the weight fraction of the pure polymer, and K is an empirical constant that ranges from −100° to −300°K. T_{g1} and T_{g2} are expressed in degrees Kelvin. For other polymers, for instance polymethyl methacrylate (*7*), values of K range from +58° to −300°K.

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By putting $w_1 = 1 - w_2$ in Equation 2 and neglecting the term of order w_2^2, one obtains a linear equation which can be compared with Equation 1. This results in

$$k = T_{g1} - T_{g2} - K \tag{3}$$

Values of k can be obtained directly from experimental results using Equation 1. Values of K are then computed from Equation 3. Both k and K for polystyrene and several plasticizers (*7*) are shown in Table I.

Table I. Coefficients for $T_g - W_2$ Correlation[a]

Plasticizer	M_2, *grams*	T_{g2}, °K.	k, °K.	K, °K.	$c_p' \times 10^{-4}$ (*calc.*)	$c_p \times 10^{-4}$ (*expt.*)
β-Naphthal salicylate	385	243.5	−220	−105	8.5	6.3
Tricresyl phosphate	368	217	−280	−130	9.1	9.5
Phenyl salicylate	335	208.5	−280	−138	9.3	7.7
Methyl salicylate	272	169.5[b]	−350	−161	9.5	9.7
Carbon tetrachloride	154	161.5	−280	(−83)	(4.3)	3.8
n-Butyl acetate	125	123.4	−450	−215	5.6	5.0
Nitrobenzene	123	177.5	−340	−159	4.2	3.7
Chloroform	118	132.5	−340	−114	4.0	4.9
Ethyl acetate	97	118.5	−580	−340	5.6	5.9
Toluene	92	111.5	−420	−173	3.9	4.9
Dichloromethane	85	109.5	−380	−131	3.2	3.4
Methyl acetate	83	108.5	−580	−330	4.8	4.8
Benzene	78	173.5	−420	−235	3.3	3.6
Carbon disulfide	44	99.5	−560	−301	2.5	2.3

[a] Recalculated from (*4*). T_{g1} in this study was 358.5°K., indicating that its molecular weight was $\sim 10^{-4}$. T_{g1}^* is 373°K. for an "infinite" molecular weight polystyrene (*13*).

[b] This value and subsequent ones in this column are given in (*6*), where they were obtained by an extrapolation technique.

If we take K for polystyrene as having an average value of −150°K., then Equation 3 is a somewhat useful equation for making a rough estimate of the glass transition temperature of a plasticized polymer:

$$T_g \approx T_{g1} - (T_{g1} - T_{g2} + 150)w_2 \tag{4}$$

Many theories (*2*, *6*, *8*, *17*) have been proposed to explain the lowering of T_g by plasticizer. These all result in equations of form 1. Seemingly this would allow an a priori calculation of k in terms of molecular quantities. However, this is not the case; all the expressions involve quantities which cannot be evaluated without

Table II. Equations for Glass Transition Temperature of Plasticized Polymers

Author	*Approach*	*Equation*	*k*	*Lit. cited*
Fujita and Kishimoto	Isofree volume	$T_g = T_{g1} - (\beta/\alpha)w_2$	β/α[a]	(*7*)
Boyer and Spencer	Iso-viscous	$T_g = T_{g1} - \frac{BRT^2}{2E} w_2$	$\frac{BRT^2}{2E}$[b]	(*8*)
Kauzmann and Eyring	Viscous flow	$T_g = a - bw_2$[c]	b	(*8*, *10*)
Zhurkov	Active group	$T_g = T_{g1} + \frac{2nRT}{uN}$	$\frac{-2kT^2(n_1M_1 + n_2M_2)}{uNM_2}$[d]	(*11*)

[a] β = Contribution of diluent to the increase of free volume.

[b] B = Constant; R = gas constant; T = absolute temperature; E = activation energy for viscous flow.

[c] a,b = constants

[d] n = number of diluent molecules; n_1 = number of moles of polymer; n_2 = number of moles of diluent; k = Boltzmann's constant; u = binding energy per node; N = number of active groups.

reference to the experimental facts. A compilation of these proposed equations is given in Table II.

Effect of Chain Ends

It is interesting to compare Equation 1 with another equation, which was used to describe the decrease of T_g with decreasing molecular weight of the polymer. Based on isofree volume and viscous flow concepts, the following semiempirical equation was derived (*5*):

$$T_g = T_{g1}^* - c/\overline{M}_n \qquad (5)$$

where T_{g1}^* is the T_g of an "infinite" polymer, $\overline{M}_n$ is the number average molecular weight of the polymer whose glass transition temperature is T_g, and c is a constant which depends on the polymer involved. In the case of polystyrene, c was originally estimated to be 1.8×10^5. Later more extensive data (*15*) showed that

$$c = 6.9 \times 10^4$$

The quantity, c can be interpreted by the following equation (*14*):

$$c = 2\,N\,\phi/\alpha \qquad (6)$$

where N is the Avogadro's number, ϕ is the free volume per chain end, and α is the difference between the thermal expansion coefficients above and below the glass transition temperature.

One of the major ideas concerning the lowering of glass transition temperature by adding plasticizer or by decreasing molecular weight is that both of these effects result from an increase in the fractional free volume. If so, it is interesting to treat these two effects in a uniform manner. Let us suppose that the molecules of low molecular weight plasticizer should be treated as part of the polymer mixture. The number average molecular weight of the plasticized mixture is defined as $\overline{M}_{n,p}$:

$$\overline{M}_{n,p} = 1/[(w_1/M_1) + (w_2/M_2)] \qquad (7)$$

Substituting into Equation 5, we obtain

$$T_g = T_{g1}^* - c_p\left(\frac{w_1}{M_1} + \frac{w_2}{M_2}\right) \qquad (8)$$

Where w again represents weight fraction; M is molecular weight; and subscripts 1 and 2 refer to polymer and plasticizer, respectively. We use the notation, c_p here to indicate that the constant may vary from one plasticizer to another. Figure 1 shows a plot of T_g *vs.* $1/\overline{M}_n$ for several polystyrene-plasticizer systems. If M_1 is very much larger than M_2, Equation 7 becomes

$$T_g = T_{g1}^* - c_p w_2/M_2 \qquad (9)$$

Hence for small values of w_2, comparison with Equations 2 and 3 yields

$$c_p' = M_2\,(T_{g1}^* - T_{g2} - K) \qquad (10)$$

Table I shows values of c_p' computed from Equation 10 and c_p obtained experimentally from Equation 8. The agreement is fairly good.

To carry this analogy a step further, lowering the molecular weight of polymer can be regarded as adding chain ends as a "plasticizer" to create larger fractional

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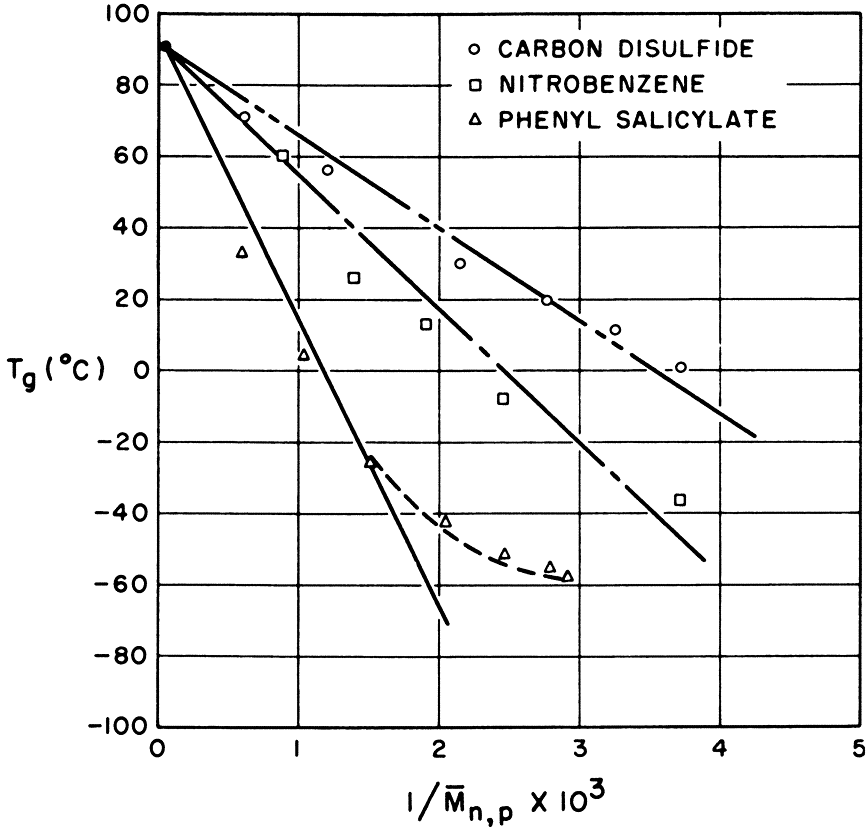

Figure 1. Glass transition temperature of plasticized polystyrene vs. reciprocal of the number average molecular weight of the mixture (6)

free volume. Since each chain possesses two chain ends, $M_2 = 2M_0$, where M_0 is the molecular weight of the monomer. Looking at the effect of chain ends in this manner, c in Equation 5 can be assigned the following definition by comparing Equations 5 and 10:

$$c = 2M_0\,(T_{g1}^* - T_{g2} - K') \tag{11}$$

where T_{g2} now represents the glass transition temperature of the dimer. K', which is the value of K appropriate to the chain ends, can be computed from Equation 11 taking $c = 6.9 \times 10^4$; $T_{g1}^* = 373$°K.; and $T_{g2} = 195$°K. The value of K' is equal to -180°K.

We now utilize Equation 2 to describe the effect of chain ends on lowering T_g. Thus,

$$T_g = T_{g1}^*\,w_1 + T_{g2}\,w_2 + K'\,w_1\,w_2 \tag{12}$$

Values of T_g, obtained by using Equation 12 with $K' = -180$°K. and w_2 equals weight fraction of chain ends, fits the observed values (*13*) of T_g *vs.* $\overline{M}_n$ very well over the entire range for degrees of polymerization ranging from 2 to 900 (Figure 2).

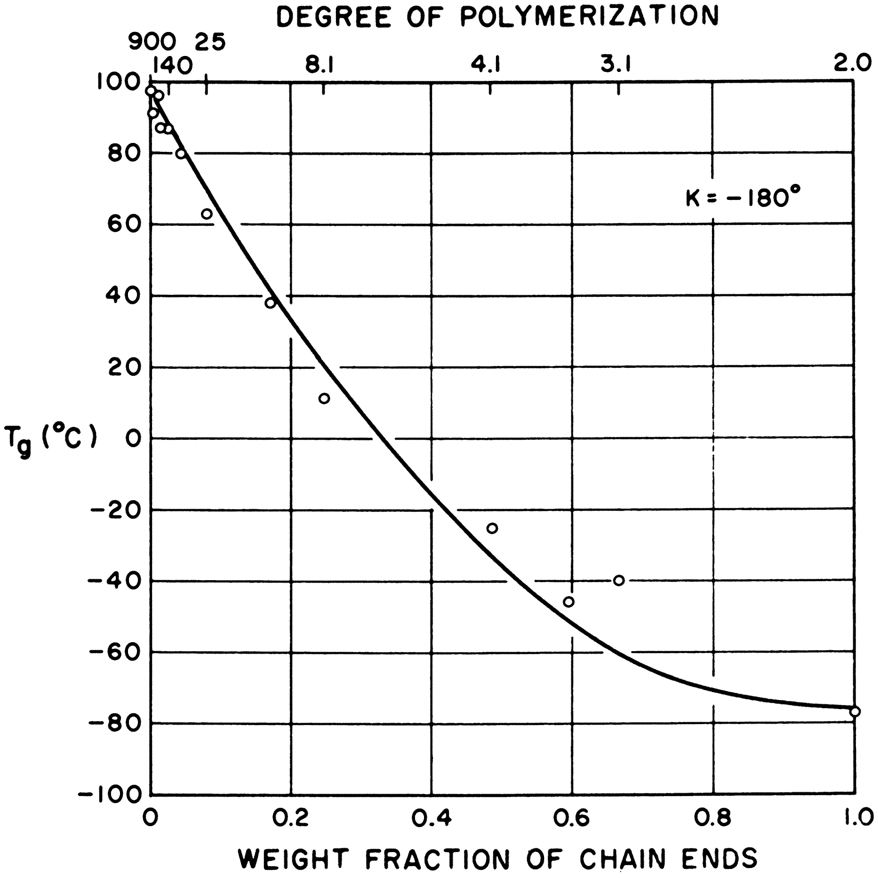

Figure 2. Glass transition temperature of polystyrene vs. weight fraction of chain ends (13)

It is worth noting that if we substitute Equation 6 into Equation 9, equating chain ends to plasticizer molecules, we obtain

$$T_g = T_{g1} - \frac{2N\phi}{\alpha M_2} w_2 \tag{13}$$

or

$$T_g = T_{g1} - (\beta/\alpha)\, w_2 \tag{14a}$$

where

$$\beta = 2N\phi/M_2 = N\phi/M_0 \tag{14b}$$

Now the definition of ϕ is generalized to include the free volume per plasticizer molecule. Equation 14*a* is equivalent to the one proposed by Fujita and Kishimoto (*6*) for the effect of plasticizer on T_g as shown in Table II. Originally β was defined

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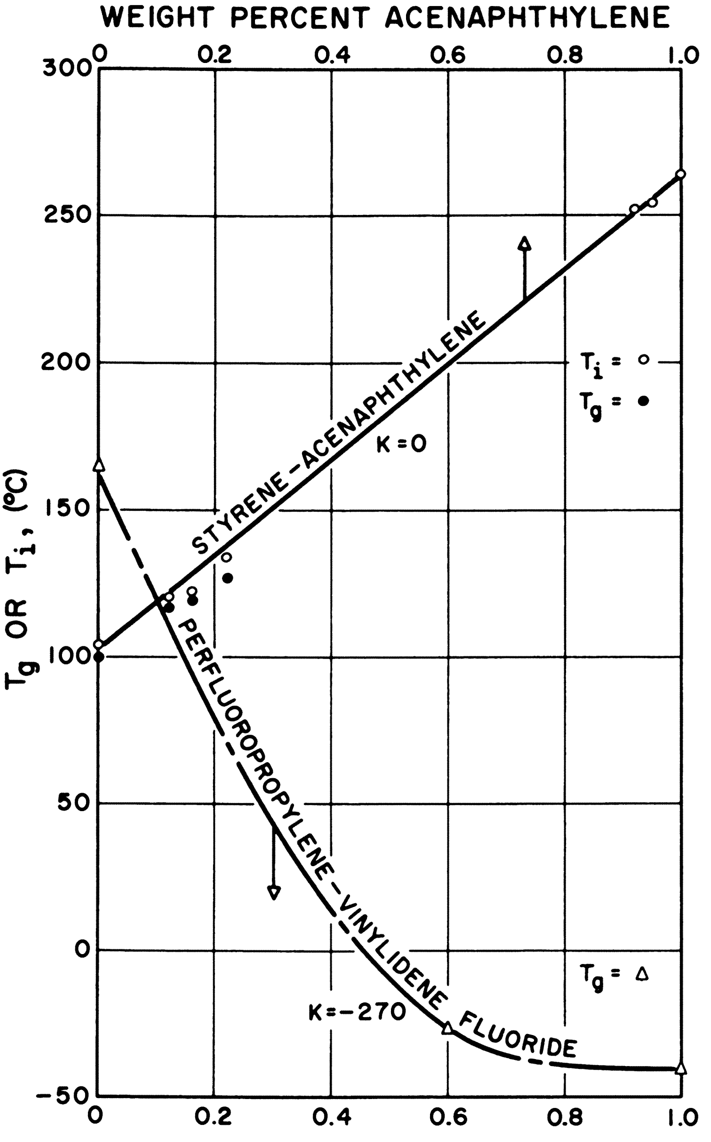

Figure 3. Glass transition temperature of copolymers vs. weight fraction of monomer units (14)

T_i is the temperature at which the 10-second Young's modulus is 10^9 dynes/sq. cm. It is usually a few degrees higher than T_g

as "the contribution of diluent to the increase of free volume," in agreement with Equation 14*b*. This consistency in results is gratifying but perhaps to be expected, since these theories are both based on free volume concepts.

Effect of Comonomer Units

The following equation has been proposed as an empirical equation for the glass transition temperature of certain copolymers:

$$T_g = T_{g1} w_1 + T_{g2} w_2 \qquad (15)$$

where *w*'s refer to weight fractions of comonomers. Equation 15 is, of course, a special case of Equation 2 with $K = 0$. However, linearity in T_g copolymer composition curves are not always observed, hence Equation 2 should give a better fit to the experimental data. Values of *K* may range from positive to negative. Figure 3 shows a linear relationship for the styrene-acenaphthylene copolymers (*12*) indicating a *K* value of zero. A value of −270°C. was obtained for *K* in the vinylidene fluoride–perfluoropropylene copolymer system, which seems reasonable in comparison with the *K* values of plasticized polymers. Positive values of *K* exist for copolymers but are quite rare (*16*).

The use of Equation 2 for copolymer systems in analogy with plasticized systems is particularly apt for the "static mechanism" of plasticization (*1*), which suggests that diluents can be regarded as being attached to the polymer chain. Ideally speaking, the effect of this type of plasticization would be to convert the polymer molecule into a copolymer of plasticized and unplasticized segments. Conversely, change of chemical structure of the polymer chain by copolymerization can be regarded as changing T_g by "internal plasticization" (*14*). If we regard the free volume theory as being applicable to interpretation of glass transition temperatures, it is not surprising that similar equations describe the effect of chain end concentration, effect of plasticizer, and effect of copolymerization. Probably the similarity in equations would result from other theoretical interpretations also.

In summary, the equations proposed for lowering T_g in plasticized polymers and the lowering of T_g due to decreasing molecular weight show certain consistencies. Further analogies can also be drawn with the changing of T_g via copolymerization. From an empirical point of view the two very simple equations, 1 and 2, give a reasonably good and unified description for all these effects. For none of these cases, however, do we have a completely satisfying a priori theory.

It would also be interesting to explore the consequences of Equation 2 for the various cases discussed here if weight fractions were replaced by volume fractions and by mole fractions.

Recently Kovacs (*9*) suggested that a discontinuity in the dependence of T_g on composition is to be expected. This is not inherent in Equation 2, and an experimental test of this suggestion is in order.

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The Elastic Range of Polymers and Its Change by Plasticization

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Thermal diffusivity and conductivity measurements of polymers show two transitions, the main glass transition and a new, sidegroup transition. Sidegroups with a very low transition temperature cause plasticization of the polymer. Thermal measurements prove that good plasticizers have a structure similar to polymers; they possess bulky anchor groups and rotatable side chains which by their free rotation in the liquid state create a great number of isomers. These are a great barrier to nucleation, permitting an easy glass formation. The elastic range of polymers is the temperature interval between the glass transition- and the flow-temperature. Good solvents in contrast to bad ones diminish the extension of this range even if added only in small amounts. Dissolution measurements are a powerful tool for judging plasticizers.

The phenomenon of plasticization has been known almost as long as the use of plastics, but for a long time no distinction was made between plasticization by copolymerisation and plasticization by addition of a solvent. The definitions of internal and external plasticization were given when this difference was recognized (*9*). The specific influence of the end groups, which create locations of higher mobility and, therefore, lower the freezing point of crystallizing polymers (*5*) and the glass transition temperature, led to the term "self-plasticization" (*10*). We will now study some experimental results which enable us to recognize the side group transitions in polymers and lead to an understanding of the mobility of polymer systems caused by "side group plasticization" which is another form of self-plasticization.

Side Group Transitions

Thermal diffusivity measurements of polymers were made for the first time by

Ueberreiter and collaborators (*12*, *13*, *14*) but have remained relatively unknown. In their earlier work the authors tried to calculate the heat conductivity λ from these thermal diffusivity measurements by means of the relation

$$\lambda = (a \times c_p)/v$$

where a is the thermal diffusivity, c_p the specific heat, and v the specific volume.

Since the specific heat and volume had to be determined separately while undergoing rapid changes in the glass transition region, the value of λ in this region was not very dependable. In order to determine a more accurate value of λ, a new instrument was constructed which measures both thermal diffusivity, a, and heat conductivity, λ, with very great precision. The results of such measurements are given in Figure 1 showing the curves of the thermal diffusivity, a, (the non-stationary measurement) and the heat conductivity, λ, (the stationary measurement) of a short chain polymer, methyl methacrylate. The thermal diffusivity curve is in the same form as those in the earlier publications (*12*, *13*, *14*) indicating two transitions: the glass transition at 60°C. and a new transition at 110°C. which is much smaller but very definite. The heat conductivity curve is similar to the thermal diffusivity curve and also exhibits both transitions.

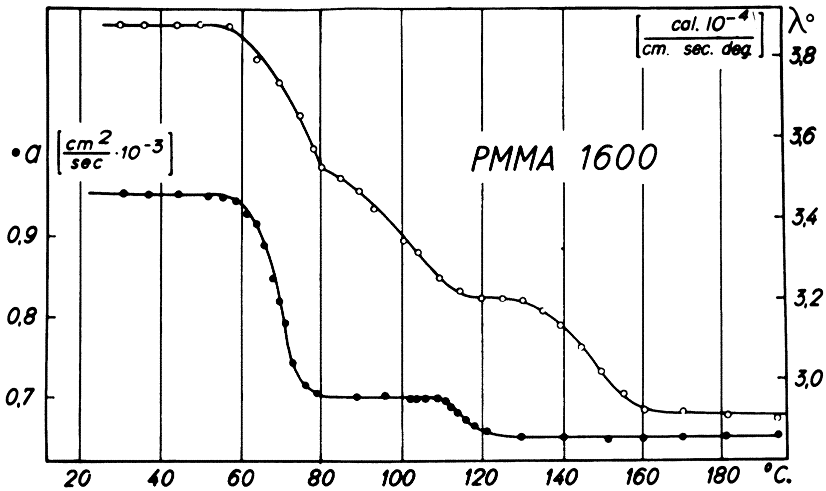

Figure 1. Thermal Diffusivity (*a*) *and Heat Conductivity* (λ) *of Poly*(*methyl methcarylate*). $T_G = 60°C.$ $T_{Side\ group} = 110°C.$

Much controversy still remains as to whether or not the glass transition has an effect on the heat conductivity. Figure 1 proves that it does (T_G = 60°C.); the curve is very reproducible. The circles indicate the error range and the values, therefore, are very dependable. Details will be given in a later publication. In the earlier papers (*12*, *13*, *14*) the new transition above the glass transition was interpreted as showing the flow temperature of the polymer. But measurements of the flow temperatures show that this transition lies, not in the elastic, but in the liquid range. Therefore, I would like to assume that this transition is caused by the rotation of the side groups. A proof for this explanation has been presented both by investigating polymers without side groups and by very precise measurement of the specific heat in the neighborhood of this new transition, indicating a very small but distinct jump in the c_p curve (*15*).

Glass Transition

One can now define an additional kind of plasticization—the plasticization of the polymer system owing to its rotating side groups. It is well known that polymer systems can be distinguished as rubbers, thermoplasts, or temperature resistant. Consider now a poly(isobutylene) molecule. This molecule consists of a paraffinic skeleton chain with methyl groups attached along its length. Methyl groups fixed to a paraffinic chain have a hindered but still relatively free rotation. Poly (isobutylene), therefore, is a rubber, the methyl groups are "plasticizers"; the transition temperature of the side groups is −20°C. (determined from thermal diffusivity measurements) while the transition temperature of the chain units is −70°C.

It seems unlikely that the transition temperature of the side groups can be much higher than the glass temperature of the larger chain units. But it must be realized that the side group transition above T_G is a free rotation to torsional vibration transition, being a transitional mode in the sense of Saito (*7*); the side groups have almost completely free rotation above this transition temperature but only torsional vibrations below it. The polymer structure is not affected as much by this transition as by the transitional mode of the chain units. This fact is indicated by the small change of the specific heat.

On the other hand the chain units with their side groups have freedom of only torsional vibrations above the glass temperature of the polymer and lose this freedom if cooled below this temperature. Side groups should also exihibit a torsional vibration to vibration transition, but the temperature of this transition is very difficult to detect and lies well below the main glass transition temperature of the polymer. Figure 1 gives with PMMA an example of these two transitions determined by thermal diffusivity or heat conductivity measurements. We observe the rotational transition of the ester side groups at 110°C. and the torsional vibration transition (the glass transition of the polymer) of the chain units at $T_G = 60°C$. These measurements will indicate the correlation of the transition effect to the greater structural changes occurring at the glass temperature T_G.

Polar groups (PMMA) or larger side groups (polystyrene) have a smaller plasticization effect and create thermoplasts. The "side group plasticization" is impossible if bulky ring systems are attached to the paraffinic main chain which, due to steric hindrance, are unable to rotate and thus create polymers which are highly temperature resistant. Their glass temperature is almost in the degradation region (polyvinyl carbazole).

Similarity of Good Plasticizers to Polymer Systems

Heat conductivity and thermal diffusivity measurements have proved to be very good detectors of the different kinds of transitions in macromolecules. External plasticizers must have high mobility in order to have plasticizing qualities, but they also must have high vapor pressure to prevent vaporization from the polymer matrix in which they are embedded. These two properties can be ensured by plasticizing the plasticizers themselves by attaching rotating side groups. This

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objective was almost automatically accomplished by choosing liquids which have good plasticizer qualities, for example, dimethoxyethyl phthalate.

The thermal diffusivity and heat conductivity curves for this substance are shown in Figure 2 and bear a striking resemblance to the curves in Figure 1. Again we have two transitions: the glass transition at −84°C. followed by a sharp decrease in the thermal diffusivity and a small transition in the heat conductivity. At approximately −20°C. in the liquid range we observe a further transition which is easily recognized in both properties, thermal diffusivity and heat conductivity. This transition is caused by internal rotation of parts of the plasticizer molecule, presumably the ester groups. These rotating groups act as "plasticizers" of this system and are connected by an anchor group, the phthalate molecule. The phthalate molecule, therefore, plays the role of the paraffinic chain in polymers and the ester group plays the role of the side groups in polymers. Hence, a larger molecule forms a system of much higher mobility.

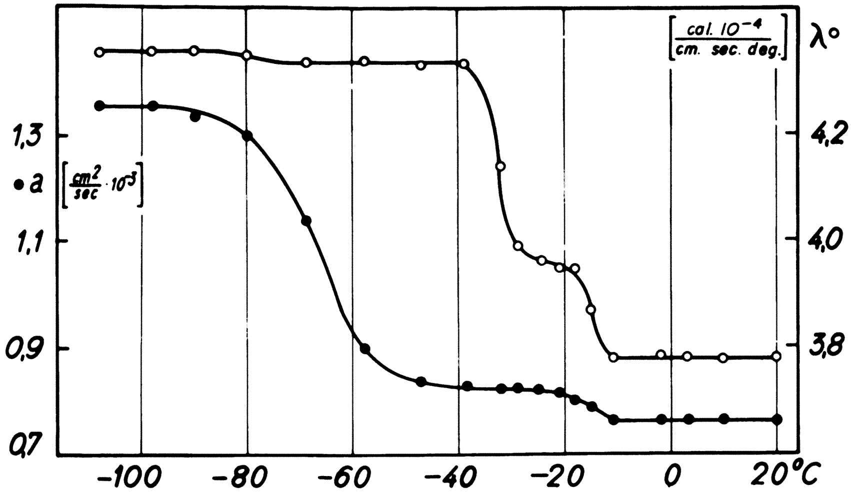

Figure 2. Thermal Diffusivity (a) and Heat Conducitity (λ) of Dimethoxyethyl phathalate. $T_{Side\ group} = -20°C.$

All phthalates, phosphates, and so on show the same phenomenon of internal plasticization by their own rotatable ester ends. The large size of the molecule guarantees it against low volatility and makes it very suitable for plasticization.

Glass Formation of Phthalates

It is usually very difficult to transform a liquid into a glass since nearly all liquids or melts crystallize when undercooled. The question as to which liquids can be undercooled has recently been discussed by Turnbull (*8*). From a more chemical standpoint Zachariasen's ideas are well accepted (*20*). He states that a glass can be formed if the liquid contains a structural network in the temperature range near the melting point. This network must be broken in order to form crystal nuclei and this is not possible if the liquid is undercooled too much, thus preventing nucleation

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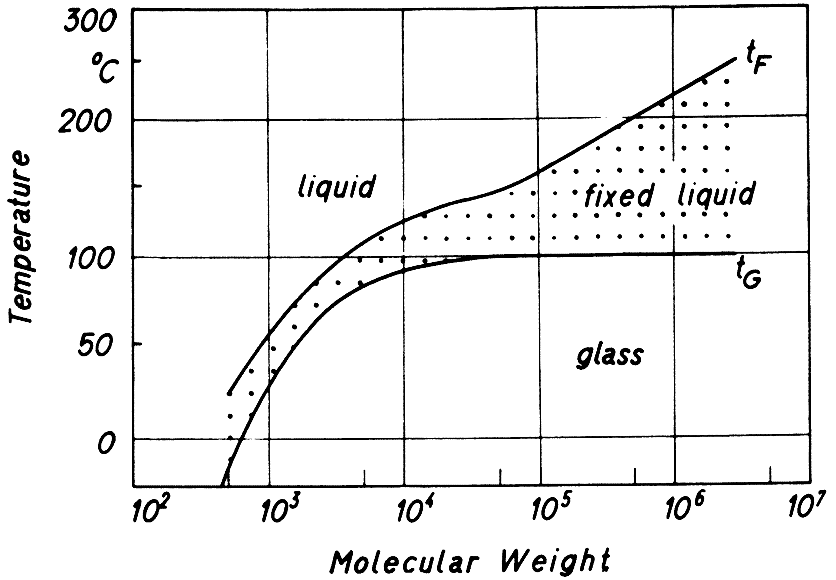

Figure 3. Phase Diagram of Polystyrene

in the glass transformation range. The network can consist of ionic bonds as in silicate glasses and of hydrogen bonds in alcohols and similar compounds (*6*).

Most of the commercial plasticizers have a different principle of glass formation which has not yet been clearly explained. They contain side groups like the ester groups in phthalates, but the ester group attached to the phthalate molecule cannot rotate freely below a certain temperature in the liquid range owing to the hindrance of the two C=O groups of the ester end. This hindrance causes the transition described above in the liquid range at a temperature where the free rotation of the side groups ceases. Therefore, a mixture of isomers is created which can be easily undercooled. The hindering potential for rotation of the ester ends in phthalates is quite high as indicated by the relatively high transition temperature which is above the melting point in the liquid range. This is caused by the hindering potential of the two C=O groups. Here is a further reason for glass formation: creation of an isomer mixture resulting from hindered internal rotation of larger parts within a molecule, which keeps crystal nuclei of the same kind from forming.

Elastic Range of Polymers

The molecular movements of the chain determine the elastic range of polymers. In this unique state of rubber like elasticity there is freedom of the micro-Brownian motion of the chain units and a high relaxation time for the macro-Brownian motion of the entire chain. This state can be described as a liquid with a fixed structure (*16*).

The liquid state is defined by freedom of both micro- and macro-Brownian motion; the solid, glassy state on the other hand allows no freedom of structural changes at all below a temperature at the lower end of the glass transformation range where the freezing phenomenon has ceased (*17*). The elastic range can be determined by defining two limiting temperatures: the flow temperature as the

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upper limit separating this state from the liquid, and the glass temperature as lower limit indicating the transition into a solid.

Elastic Range and the State Diagram

The lower limit of the elastic range, the glass transition temperature, can be easily determined by refractometric, volumetric, or other well known methods. The upper limit suffers from an exact definition; the transition from the fixed liquid to the liquid state occurs without transformation. But as the viscosity decreases exponentially with the temperature it is very convenient to define a "flow-temperature" by penetrometer measurements. If the rate of temperature rise is kept constant, this temperature is reproducible within 1° or 2°C. The penetrometer indicates a temperature where macroscopically one would call the substance "liquid."

Typical state diagrams which have been obtained by measuring the flow and the glass temperature are shown in Figures 3 and 4. They show the extension of the liquid, elastic, and solid states as a function of the chain length of the polymers, polystyrene and poly(methyl methacrylate) (*18*). These figures indicate that PST is less elastic than PMMA. We can recognize the change of polymer to oligomer character which happens in a molecular weight range of 0.5–1 × 10^5. Below these chain lengths the extension of the elastic range becomes so small that the typical polymer character disappears. These diagrams, therefore, are very useful for characterizing a polymer.

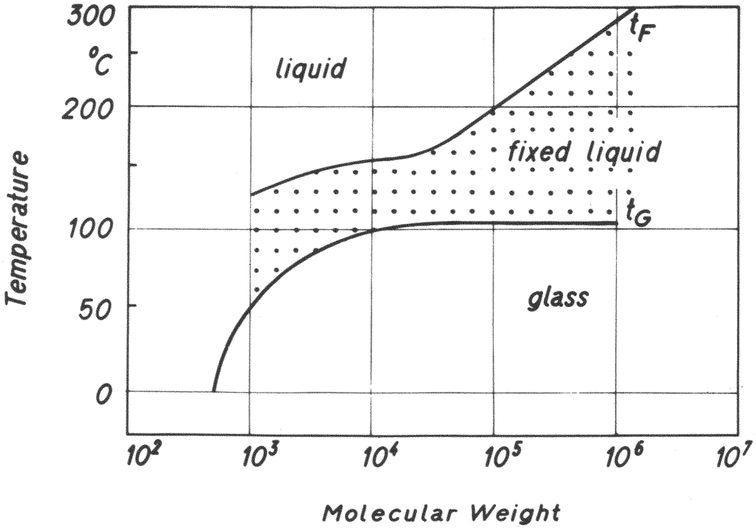

Figure 4. Phase Diagram of Poly(methyl methacrylate)

Change of Elastic Range

The same state diagram can be taken as a function, not of the chain length, but of the amount of plasticizer which is added to a polymer of given molecular weight. A new type of penetrometer, which uses a penetrating rod, has been constructed for

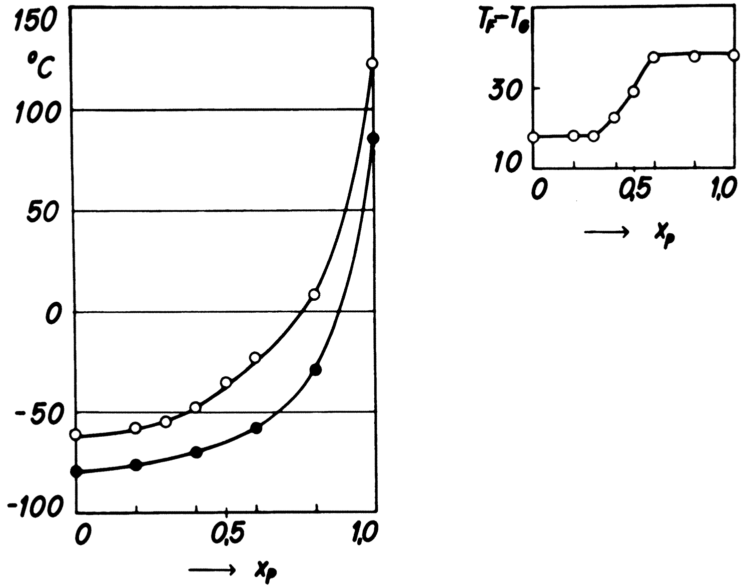

Figure 5. Glass (open circles) and Flow (full circles) Temperatures and their Difference of Dinonyl Phthalate Solutions with X_p mole % Polystyrene

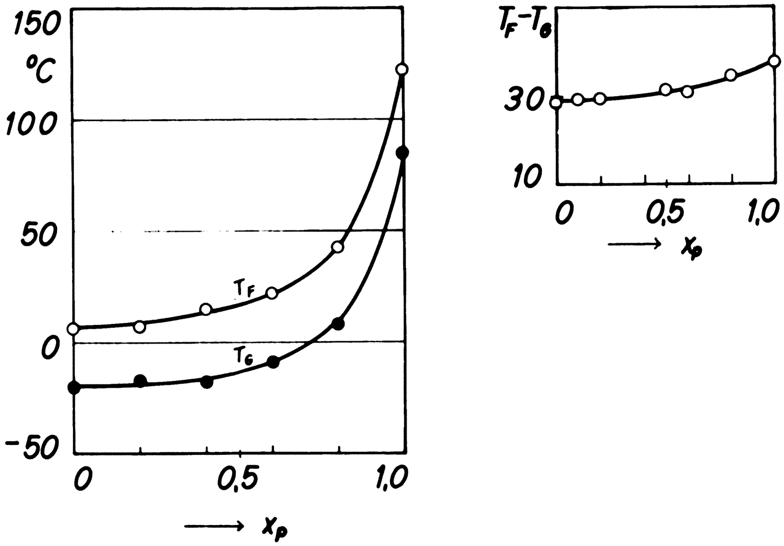

Figure 6. Glass (open circles) and Flow (full circles) Temperatures and their Differences of Hexachlorodiphenyl Solutions with X_p mole % Polystyrene

this purpose. Two typical examples are shown in Figures 5 and 6. Polystyrene of a long chain length (the glass temperature of the pure sample has the limiting value) was mixed with various amounts of di-*n*-nonyl phthalate (Figure 5) and with hexachlorodiphenyl (Figure 6). The concentration of the plasticizers is given in mole fractions in order to have a better comparison for molecules of different chemical constitution. Although the curves of T_G and T_F against the polymer content (X_p) seem to be very similar, those curves which indicate the extension of the fixed liquid range expressed by the difference of the limiting temperatures, (flow temperature and glass temperature $T_F - T_G$) show a remarkable difference: the phthalate maintains the extension of the elastic range up to concentrations of almost 0.5 mole % of plasticizer while hexachlorodiphenyl changes the structure of the polymer from the very beginning.

These diagrams, therefore, have already fulfilled one purpose: to serve as a further tool for selecting plasticizers. An explanation of this behavior is suggested: a very good solvent is probably able to break the cohesion points between polymer chains and thereby reduce the relaxation times of the macro-Brownian motions, leading to a strong decrease of the flow temperature. This influence seems to be greater than that of the plasticizer in lowering the glass temperature.

To test theory one must work with solutions for which adequate thermodynamic data exist. Figure 7 contains the state diagram of the same polystyrene with mixtures of methyl isobutyl ketone and Figure 8 with toluene. The similarity of Figure 7 with Figure 5, and Figure 8 with Figure 6 is striking. The ketone is a thermodynamically poor solvent for polystyrene and, therefore, cannot disturb the polymer structure at very small concentrations. The good solvent, toluene, enters

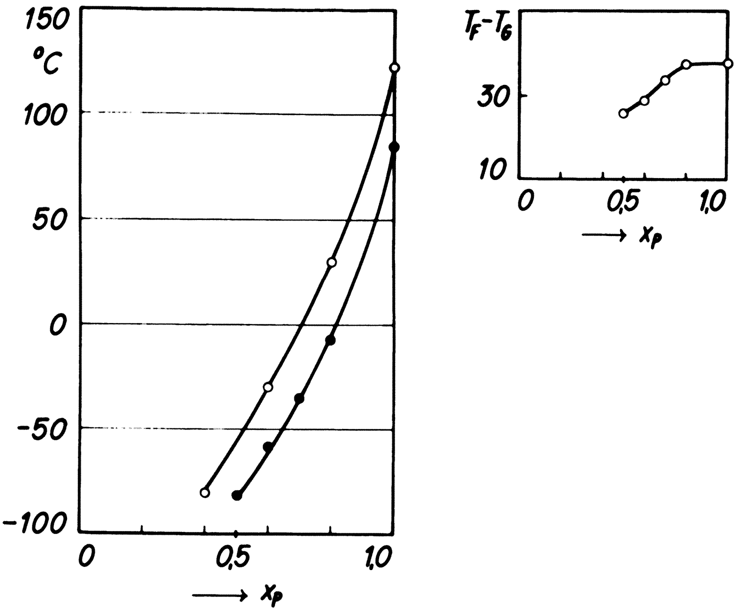

Figure 7. Glass (open circles) and Flow (full circles) Temperatures and their Difference of Methyl Isobutyl Ketone Solutions with X_p mole % Polystyrene

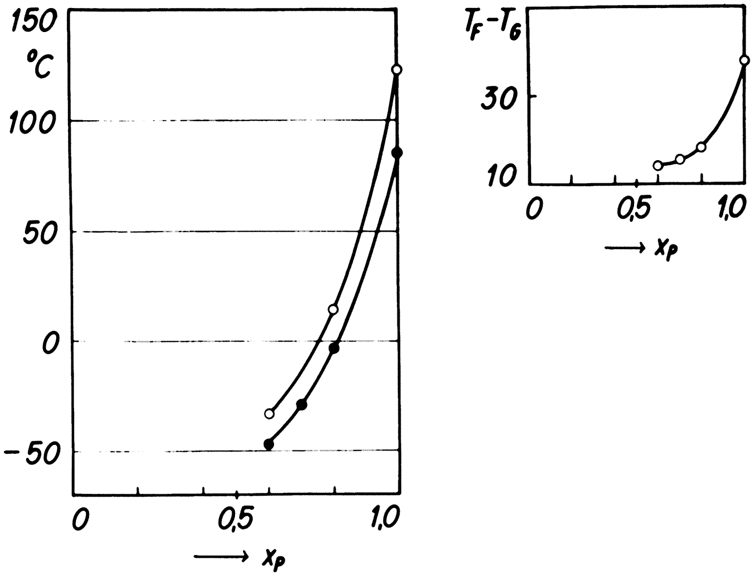

Figure 8. Glass (open circles) and Flow (full circles) Temperatures and their Difference of Toluene Solutions with X_p mole % Polystyrene

into the polymer structure and separates the contact points of the polymers, thereby diminishing the fixed liquid range.

Thus, it is important to determine the extension of the elastic range in selecting plasticizers. Figure 9 gives some examples which show that the plasticizers investigated differ widely in their ability to change the polymer structure. Similar curves are obtained for other polymers and plasticizers. These few examples will only indicate the procedure. We can see that the thermodynamic property of a solvent, serving as a plasticizer, allows us to predict the degree of change of the polymer structure. But, of course, a plasticizer must enter the polymer structure within a tolerable amount of time. The plasticizer's kinetic properties determine the time element.

Kinetic and Thermodynamic Behavior of Solvent

Measurements of the dissolution velocity of polymers have been made by my collaborator, F. Asmussen (*4*). In making these measurements we have used a new microscopic method which will be published later. This method gave us insight into both the thermodynamic and the kinetic character of a solvent from the same measurement. The term "good solvent" has not been completely defined until now since the thermodynamic and kinetic characters have not been considered separately. But we have found that one thermodynamically good solvent enters into the polymer very slowly while another thermodynamically poor solvent penetrates the polymer structure with great velocity. The thermodynamic affinity, which can be expressed numerically by the second virial coefficient or by the Huggins constant, is a function primarily of the chemical constitution of the solvent molecule, as already described (*19*). Its kinetic behavior depends largely upon the shape of the molecule and, therefore, in a group of chemically related substances, is a function of the molecular weight.

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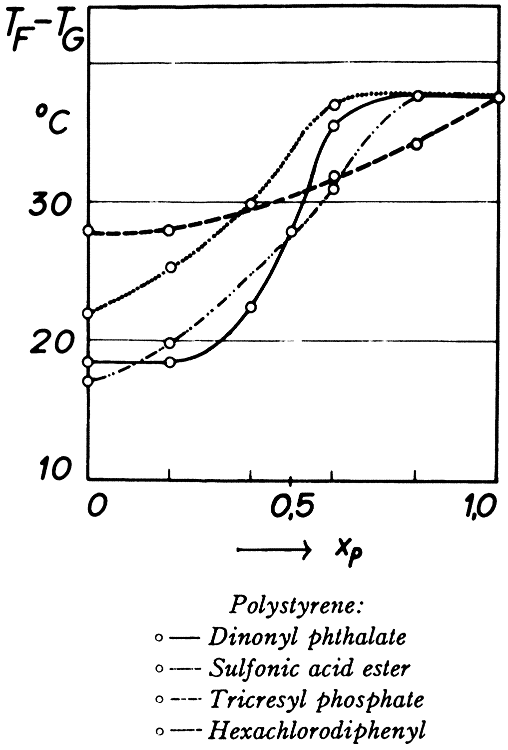

Figure 9. The Extension $T_F - T_G$ of the Elastic Range of Plasticized Polystyrene

Dissolution Measurements

Dissolution measurements under the microscope give several results which will be discussed separately. The first and most evident result is the penetration velocity of the solvent into the polymer. In order to judge the influence of the solvent's chemical constitution on the polymer we have chosen a number of phthalic acid esters which differ only in their ester groups and which are well known plasticizers. The polymer was a vinyl chloride–vinyl acetate (87:13) copolymer. The following plasticizers have been tested, (the abbreviations are indicated)

Dimethyl phthalate	M
Diethyl phthalate	A
Dibutyl phthalate	B
Di-isobutyl phthalate	IB
Benzyl butyl phthalate	BB
Methoxyethyl phthalate	MOA
Ethyl hexyl phthalate	AH
Dinonyl phthalate	N
Didecyl phthalate	Z

The penetration velocity is influenced mainly by the viscosity of the plasticizer. We can conclude this from Figure 10 which shows the dependence of penetration velocity, $\dot{s}$, expressed in cm. sec.$^{-1}$, on the viscosity of the solvent, expressed in centipoises. The penetration velocity (measured at 120°C.) decreases rapidly with increasing viscosity of the plasticizer. The measurements were made at 20°C. If both measurements are made at the same temperature a similar curve is obtained (to be published). The kinetic behavior, therefore, is determined mainly by the plasticizer mobility.

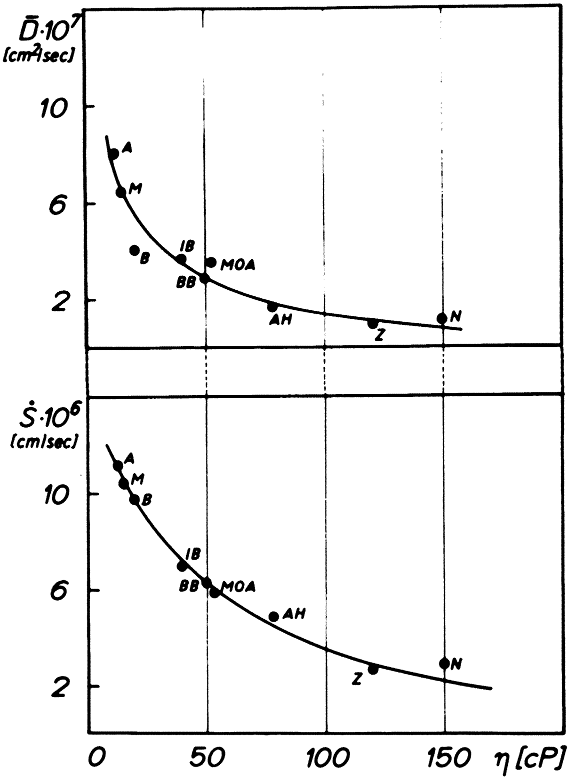

Figure 10. Velocity of Penetration ($\dot{s}$) and Mean Coefficient of Diffusion ($\bar{D}$) of Phthalates in the Polymer, PVC – PVC (87:13)

In our earlier work we found that the kinetic property depends on geometrical shape. To test this fact again we plotted the mean coefficient of diffusion against the molecular weight of the phthalates investigated. Since their chemical nature is almost the same, the molecular weight implicitly reflects the size of the plasticizers. The result can be seen in Figure 10 and proves the reliability of the assumption. The various values of D form a falling curve with increasing molecular weight or size of the plasticizer.

Thermodynamic Quality and Surface Layer

We aimed to draw more conclusions from these dissolution measurements also by measuring the thermodynamic properties. This was done quantitatively by

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measuring the thickness of the surface layer of the dissolving polymer. As already discussed in earlier papers (*2*) this layer has quite a complicated nature if the polymer is below its glass transition temperature. Above T_G the swollen surface layer consists of only two parts: the elastic layer and the liquid layer. The rubberlike or shorter "gel" layer of the total surface layer is a good measure of the solvent's thermodynamic quality, in our case a plasticizer. The influence of the thermodynamic quality on the gel layer can be predicted by our previous experience with results of the extension of the elastic range. If a thermodynamically good plasticizer tends to distrupt the polymer structure by separating its points of contact, it should do the same during the dissolution process and thereby diminish the extension of the gel layer. This prediction is justified as we can see from Figure 11. In this figure the extension of the gel layer is expressed as a kind of volume fraction, $\varphi_{gel} = \delta_{gel}/\delta_{total}$, where the δ's are the thicknesses of the gel or total surface layer, which are equivalent to volumes since the samples are of equal thickness. The other variable, the Huggins constant χ, is a measure of thermodynamic quality as indicated by Flory (*5*) and measured by Anagnostopoulos (*1*) with the help of critical dissolution temperatures of PVC. Using his values it is clear that both values describe the thermodynamic quality; increasing Huggins constants belong to increasing φ_{gel} values since both variables increase as the thermodynamic quality of the solvent decreases. Further insight into the functional dependence of φ_{gel} and χ will be gained when our own χ values become available (*4*)

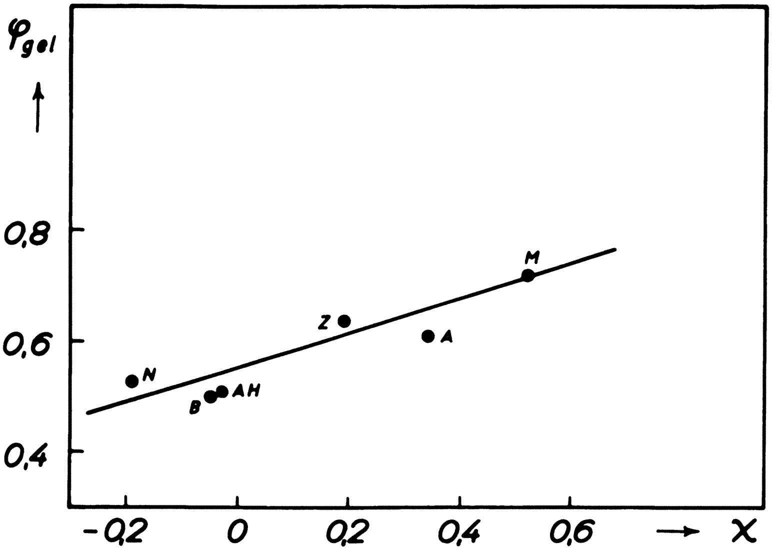

Figure 11. Extension of the Gel Layer (φ_{gel}) and Huggins' Constant (χ) of Phthalates in the Polymer, PVC–PVA.

Although chemical constitution obviously plays the major role in determining the thermodynamic quality of a solvent, the influence of steric properties on solvent quality remains an open question. In order to answer this question we have plotted our dissolution-measurement-indicator for thermodynamic quality—the gel fraction φ_{gel}—against the molecular weight which stands for the size of the molecule (Figure

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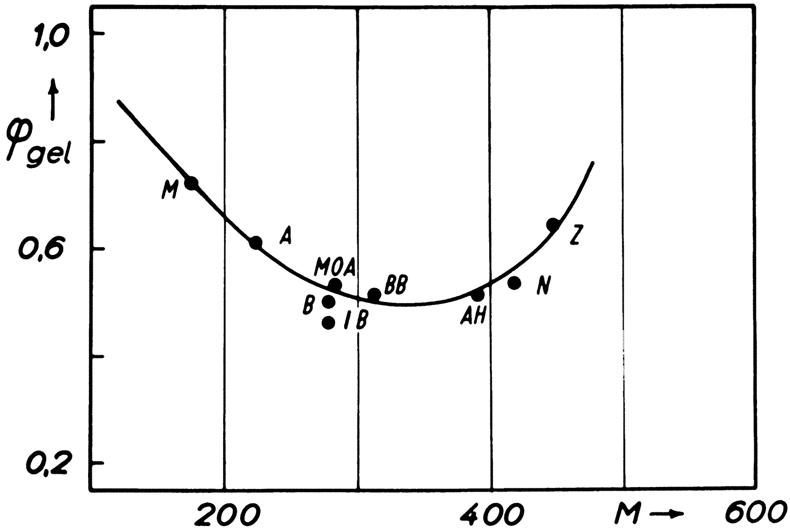

Figure 12. Extension of the Gel Layer (φ_{gel}) and Molecular Weight (M) of Phthalates in the Polymer, PVC–PVA

12). The values are from the same dissolution measurements of the phthalates. It seems at first surprising: the curve has a minimum and, therefore, the solvent power or thermodynamic quality has a maximum as φ_{gel} decreases if the solvent power increases. The C=O group is apparently a necessary factor for dissolving PVC but it must be shielded to some extent in order to be fully effective. A methyl group alone on the other side is too small. If the side chain becomes longer the shielding effect reaches a maximum efficiency but finally becomes too strong and causes a decrease in solvent power again at very long side chains.

Ketones, which are solvents for polystyrene, exhibit similar behavior. Acetone is a relatively poor solvent, methyl ethyl ketone is much better, and the ketones with longer paraffinic ends are finally no longer solvents.

Dissolution measurements under the microscope, therefore, are a powerful tool for selecting solvents or plasticizers. Measurements of elastic range extension give insight into structural changes caused by plasticizers. Thermal diffusivity and heat conductivity measurements are recommended to detect side group and other transitions in polymers and other substances.

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Mobility of Plasticizers in Polymers

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The structure and molecular mobility are the main factors which determine the macroscopic behavior of high polymers. In many cases, however, it is very difficult to obtain detailed information about molecular processes. This is especially true for binary systems where one of the components shows a high glass-transition temperature (macromolecule) and the other a low (plasticizer). The system polystyrene-plasticizer has been investigated within a larger range of temperature to study the behavior of the plasticizer. The results show that even below the glass-transition temperature a certain number of plasticizer molecules are in a "liquid-like" state. Analogous results occur in investigating the temperature dependence of volume by means of refractive-index measurements or in x-ray investigations.

All physical properties of high polymers in the solid state are determined by the cooperation of primary valences of the macromolecules and secondary valences between them.

It has long been known that the physical properties of a polymeric solid can be influenced largely by the addition of organic liquids, the plasticizers. Their effect is caused by their influence on the secondary valences or van der Waals forces which act between the chains, and on the steric flexibility of the individual chains which depends essentially on the structure of the polymer itself. The addition of a plasticizer always lowers the glass temperature, T_g, and it is interesting to study this effect in order to get information on the molecular interaction (behavior) of the plasticizer and polymer. Before dealing with this problem the "freezing-in" and the "glass state" of polymers will be discussed briefly.

Freezing and Glass State

Lowering the temperature of a liquid of a high or low molecular weight substance changes it from the fluid to the crystalline, or the glassy state. Although the

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change from melt to crystal is a true phase transition from one equilibrium to another, the change from liquid to glass cannot be called a phase transition as defined by thermodynamics. (Partially crystallized compositions are special cases and should be excluded.) Both transitions can be followed by the change of volume, V, and heat content, H (enthalpy), with temperature.

In Figure 1 the volume V, or the enthalpy H, are schematically plotted *vs.* temperature. By lowering the temperature of the liquid phase (upper right hand side of the figure), both decrease steadily. If crystallization occurs at the temperature T_s, volume and enthalpy decrease abruptly. The state of an undercooled liquid can be reached if crystallization is somehow suppressed at T_s, as shown in the upper curve of Figure 1. Upon further cooling, this curve shows an inflection at T_g, indicating a smaller temperature coefficient of V and H.

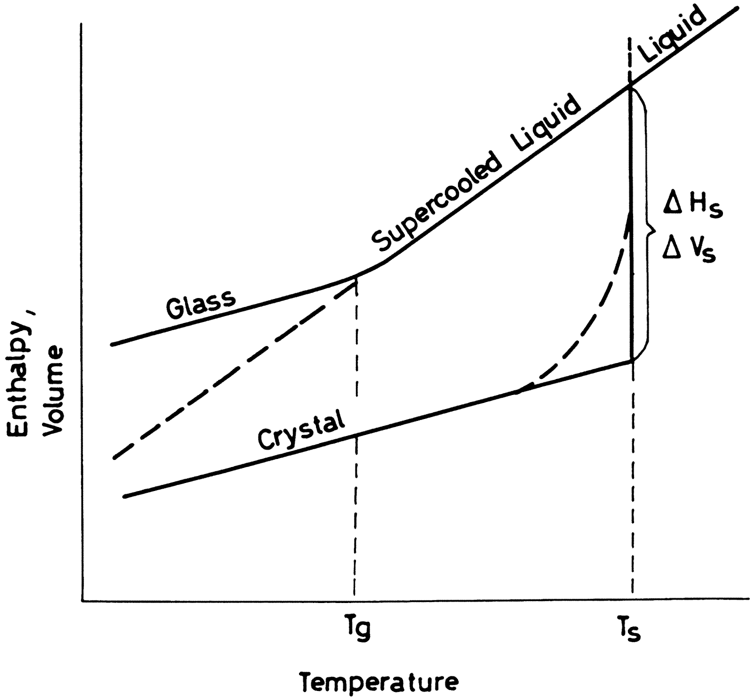

Figure 1. Schematic presentation of volume and enthalpy as functions of temperature in the liquid, crystalline, and glassy state. T_s, melting temperature, T_g, glass temperature, H_s, heat of melting, V_s, specific volume difference between crystal and melt.

Below T_g the material is in the glassy state. Compared with the crystal the glass shows a larger specific volume and heat content, but both quantities have a smaller temperature coefficient than in the melt (*8*). The transition from melt to glass is often called a transition of the second order (*2, 3*) since it is not accompanied by finite changes of volume and enthalpy, but only by changes of their temperature coefficients.

In general, ordinary substances which can be frozen-in by supercooling will not convert to the glass state when cooled infinitely slowly, whereas for substances

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undergoing second-order transition at the thermodynamically-fixed temperature, T_u, a transition occurs, especially when cooled slowly.

It can also be observed that, just below the transition temperature, T_u, the specific heat and the expansion coefficient respectively, are higher than above T_u. When changing to the glass state the reverse behavior has always been observed (*14*). Furthermore, the entropy of a glass is positive at 0°K. However, the entropy of a substance going through a real transition of the second-order is zero according to Nernst's Third Law of Thermodynamics, as inner equilibrium is achieved (*4*). [*See also* Kauzman (*9*) and Davies and Jones (*1*).]

Pure Polymers. Using a simplified model the transition from the melt to the glassy state can be demonstrated as in Figure 2 (*7*). At a temperature above T_g the "empty space" between the molecules is filled by the translational, rotational, and vibrational motions of the molecules. Their average distance is relatively large compared with their diameter. Therefore, the energy barriers counteracting the translational displacements are low, and the molecules can move easily past one another. This is the state of melt (Figure 2a). With lowering temperature the average kinetic energy of the molecules decreases, and the distances between them also decrease. Consequently the intermolecular forces become dominating, the energy barriers grow, and the translatory motions of the molecules past each other become smaller. Within the freezing range the distances between the molecules are of the order of their diameters. At the points of contact the energy barriers are very high and the molecular motion is greatly hindered. In the glassy state the microbrownian movement of the chain segments is at a standstill.

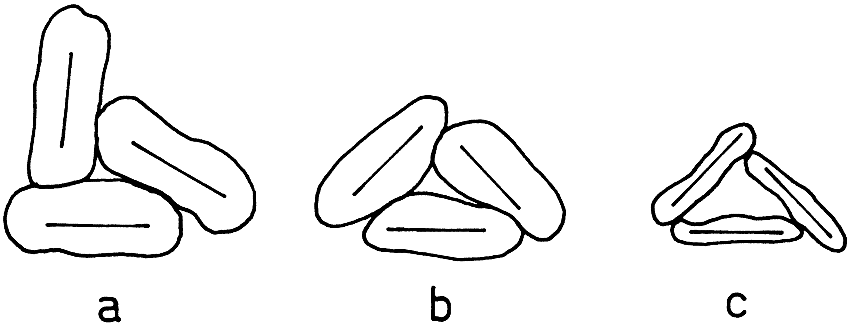

Figure 2. Schematic presentation of the freezing process and glass structure. The width of the rod-like molecules and segments, respectively, represents the amplitude of the oscillator.

(a) $T > T_g$ *Structure of melt; space completely filled.*
(b) $T = T_g$ *Changed position of molecules; space still filled.*
(c) $T < T_g$ *Position of molecules as a* T_g*; forming of a cavernous glass structure.*

No rearrangement of the molecules is possible upon further cooling i.e., the arrangement prevailing at the glass temperature is nearly fixed, and only the amplitudes of the oscillations may further decrease (Figure 2c). Therefore it can be understood, that in the glass state, submicrosopic cavities exist which have been, in fact, discovered by the x-ray examinations of cellulosic fibers (*5*).

Plasticized Polymers. As mentioned above the glass transition temperature T_g is lowered by adding certain organic liquids, the so called plasticizers. The illustration of polymers above T_g by means of a model remains valid also for plasticized systems. The configuration that is built up at the transition from the melt to the glass, in this case, remains below the glass temperature, too. Thus, we have an extended structure containing "holes."

In the melt of a two-component system, polymer–plasticizer, the segments of a macromolecule and the molecules of the plasticizer are arranged in such a way that almost no holes exist (Figure 3a). In the glass state such an arrangement is no longer possible, leaving the macromolecules in a structure with holes. The molecules of the plasticizer may remain more or less mobile in these holes (Figure 3b). Since the macromolecular chains are immobile and the expansion coefficient is small, the plasticizer molecules may possess a liquidlike mobility in the spongy matrix of the frozen glass.

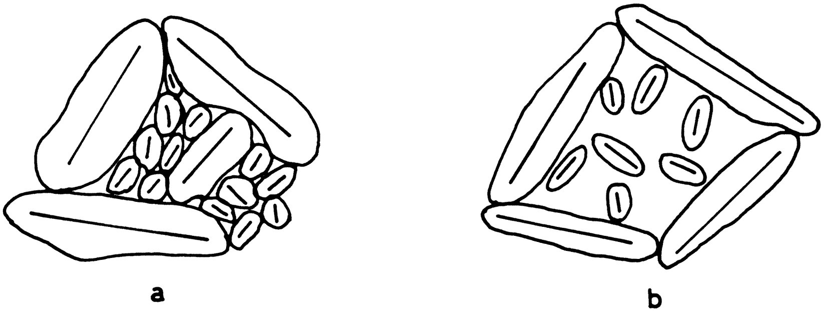

Figure 3. Schematic presentation of a composed phase consisting of macromolecules and plasticizer molecules.

(a) $T > T_g$ Structure of an equilibrium melt; space completely filled.
(b) $T < T_g$ Forming of a cavernous structure; the holes are filled with more or less freely mobile plasticizer molecules.

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Examination of Plasticizer Behavior in the System Polystyrene-Plasticizer

The models in Figures 2 and 3 show that a part of the low molecular weight liquid obviously separates the polymer chains from each other, thus facilitating segment mobility. Another part of it fills the cavities and displays almost liquid state behavior in them. This rather simplified model of the glass structure has been verified in some by nuclear magnetic resonance experiments.

In a polymeric solid it was found that the line width ΔH of the absorption curve decreases with increasing temperature with a distinct reduction occurring near the glass transition point. This is shown in Figure 4 for polystyrene and polymethylmethacrylate where the line width is plotted *vs.* temperature.

The molecular interpretation of this result is as follows: above the glass temperature T_g the molecular segments are in vigorous motion and change their positions frequently. Hence, the average nuclear spin interaction is reduced to a minimum. This causes a narrow absorption line. As the kinetic motion of the molecules is decreased by cooling, the frequency of position changes is reduced, and

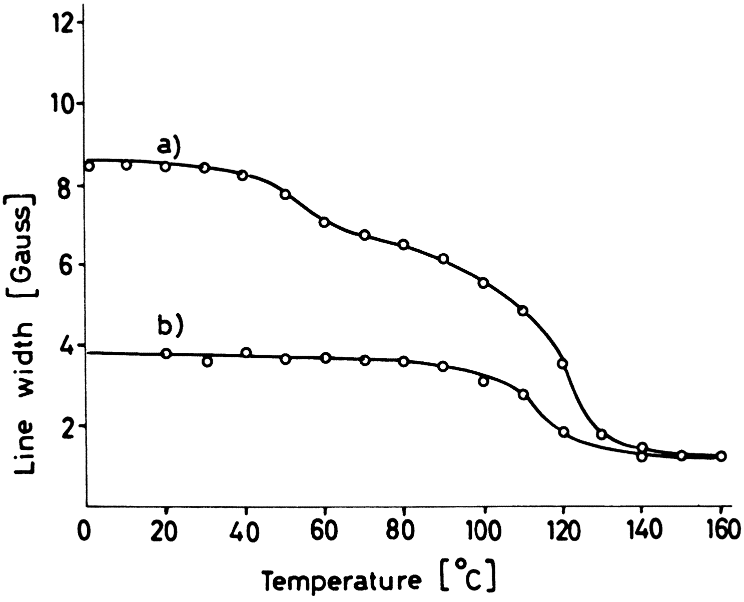

Figure 4. Line width vs. temperature for (a) Polystyrene; (b) Poly-(methyl methacrylate).

the nuclear magnetic interaction increases, which leads to a broadening of the line. Below T_g the width can be nearly constant (*see* polymethylmethacrylate) but secondary movements–e.g., hindered rotations, can result in further changes of the line width and the second moment, respectively (*see* polystyrene).

Plasticizer Behavior in the Polymer

The behavior of plasticizers in a polymer has already been examined by Würstlin (*16*) with dielectric measurements. However, this method is not sensitive enough to detect the plasticizer behavior in the system at small plasticizer concentrations. Luther and Weisel (*12*) have also pointed out this fact as a result of their DC measurements of PVC–plasticizer systems. The following measurements deal with the behavior of plasticizers in polystyrene.

Compared with "bound" plasticizer, the "free" plasticizer should have a distinctly higher mobility and thus be measurable by nuclear resonance experiments. In order to detect the plasticizer mobility unmistakably, we have chosen as plasticizers, compounds which contain protons on the one hand, and compounds which do not contain protons on the other. This made it possible to distinguish the behavior of the plasticizer and the polymer in the nuclear resonance experiments (*10, 11*).

Adding the proton-free solvent carbon tetrachloride to polystyrene, one observes the relationship between line width and temperature as shown in Figures 5a and 5b. For the system polystyrene with 21.5% carbon tetrachloride the absorption curves for various temperatures are plotted against the field strength (*2*) in gauss. As the temperature decreases, the line broadens, as shown more clearly in

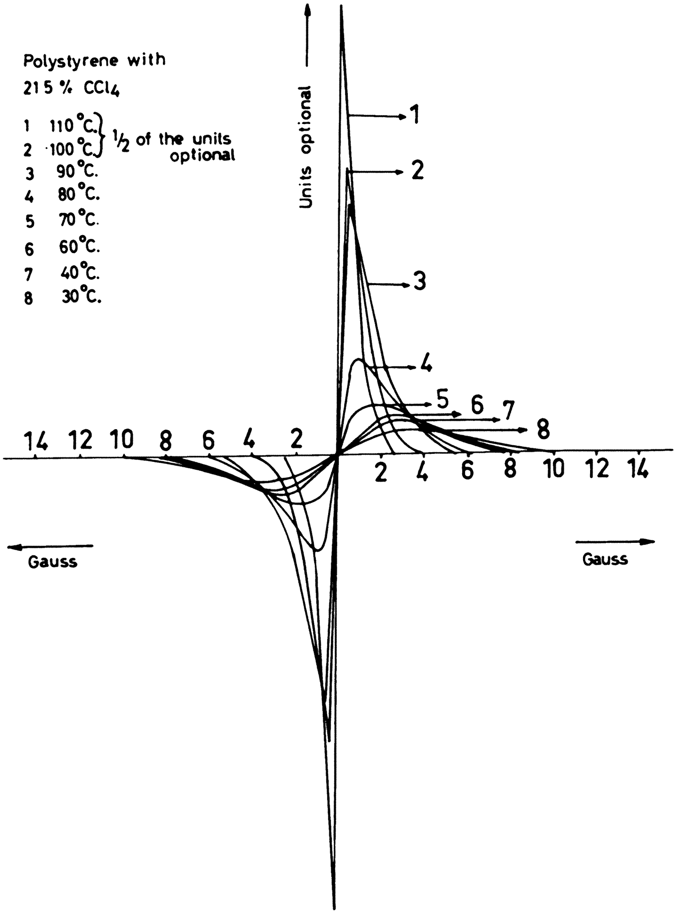

Figure 5a. Differentiated absorption curves of the system Polystyrene with 21.5% CCl_4. Parameter is the temperature; ordinate units optional.

Figure 5b. According to the plasticizer content a shift to lower temperatures occurs, corresponding with a decrease of the glass temperature.

The investigation of samples, which were plasticized with proton-containing solvents, like dichloromethane or benzene, does not show equally simple absorption curves. Together with a broad component, a superimposed narrow component has now been found. Figure 6a shows the absorption curve for the system of polystyrene with 5.5% dichloromethane, Figure 6b for the same system the line width-temperature relationship for the narrow as well as the broad component. This type of curve remains unaltered even below the glass temperature. However, the intensity of the small component, attributable to the plasticizer, decreases with lower temperatures. At about 60° below glass temperature the narrow component is absorbed by the broad one. The temperature dependance of the line width in the system polystyrene-benzene is shown in Figure 7.

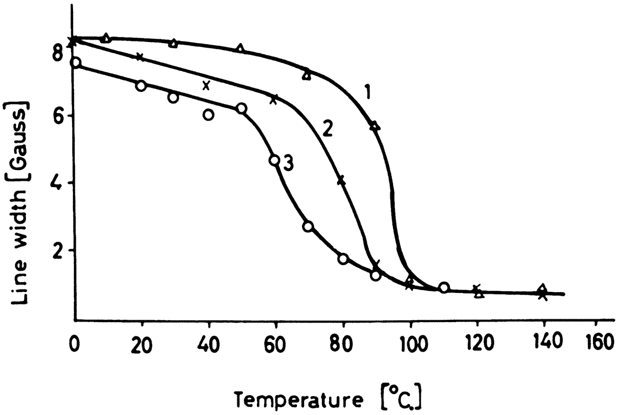

Figure 5b. Line width vs. temperature for the system Polystyrene–CCl_4.

(1) Polystyrene with 10.6% CCl_4.
(2) Polystyrene with 15.2% CCl_4.
(3) Polystyrene with 21.5% CCl_4.

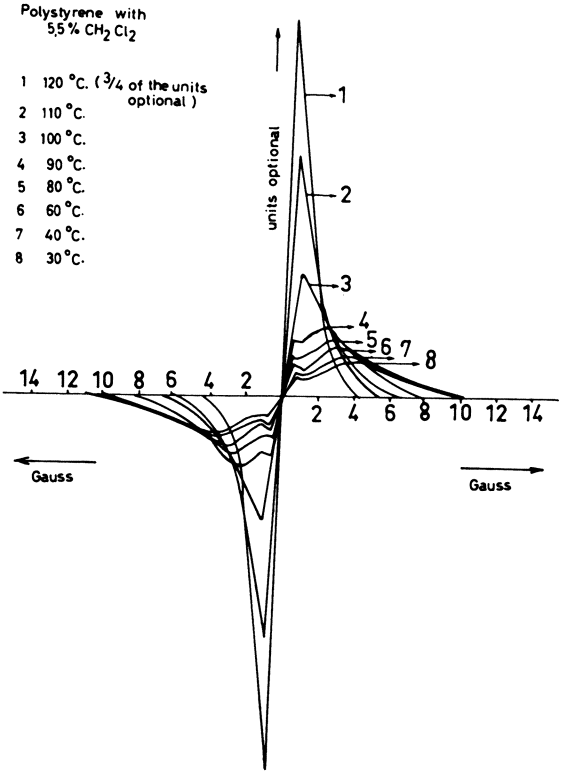

Figure 6a. Differentiated absorption curves of the system Polystyrene with 5.5% CH_2Cl_2. Parameter is the temperature; ordinate units optional.

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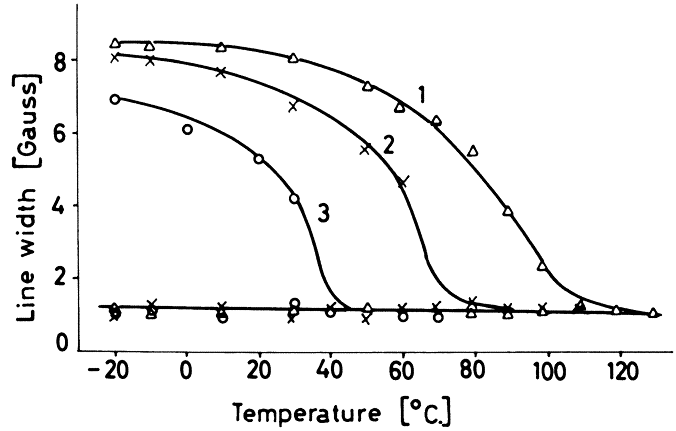

Figure 6b. Line width vs. temperature for the system Polystyrene–CH_2Cl_2.

(1) Polystyrene with 5.5% CH_2Cl_2.
(2) Polystyrene with 11.0% CH_2Cl_2.
(3) Polystyrene with 15.7% CH_2Cl_2.

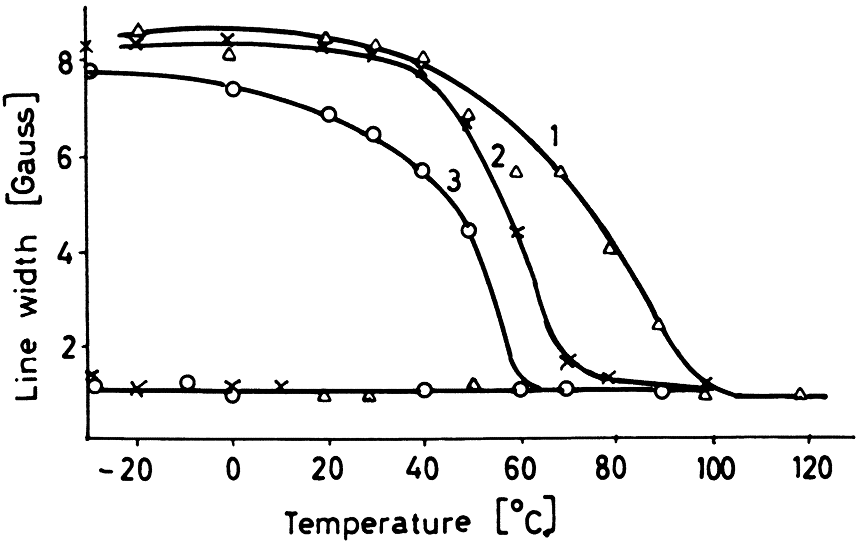

Figure 7. Line width vs. temperature for the system Polystyrene–C_6H_6.

(1) Polystyrene with 5.5% C_6H_6.
(2) Polystyrene with 10.0% C_6H_6.
(3) Polystyrene with 15.5% C_6H_6.

From these measurements it follows that the solvent molecules are in a liquidlike state even below glass temperature. This indicates that the solvent molecules are mobile within the numerous cavities of the polymer as in a liquid. With decreasing temperature more and more of them are fixed against each other and against the chain segments, until finally all plasticizer molecules are immobilized.

Temperature Dependance of the Free Plasticizer Below the Freezing Temperature

The area below the absorption curve is proportional to the number of protons in the sample which permits the decrease of "free" plasticizer to be calculated from the change of this area upon cooling. For each sample the area below the curve is constant, regardless of whether the absorption is narrow or broad. Below the glass temperature the narrow component of the absorption curve can be attributed to the plasticizer, whereas the broad component represents the glassy polymer and that part of the plasticizer which is already immobilized.

Samples containing different plasticizers are comparable if referred to the same number of protons. If p is the number of protons in the base molecule of the polymer and w is the number of protons in the molecule of the plasticizer, then

$$\frac{F_w/w}{F_w/w + F_p/p} = \frac{f_w}{f_w + f_p}$$

is the base-mole-fraction of the "free" plasticizer in the polymer. F_w and F_p are the areas of the narrow and the broad components of the absorption curve, respectively, obtained by using a planimeter.

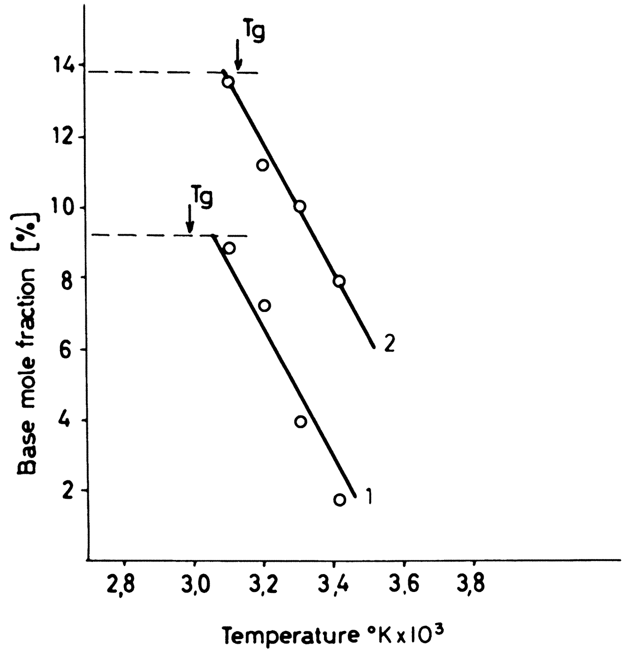

Figure 8. Decrease of the "free" plasticizer (chloroform) below the glass temperature vs. the temperature.
(1) Polystyrene with 10.5% $CHCl_3$.
(2) Polystyrene with 15.5% $CHCl_3$.

In this manner the decrease of the "free" plasticizer is plotted against temperature for chloroform (Figure 8) and for benzene (Figure 9), the decrease in free

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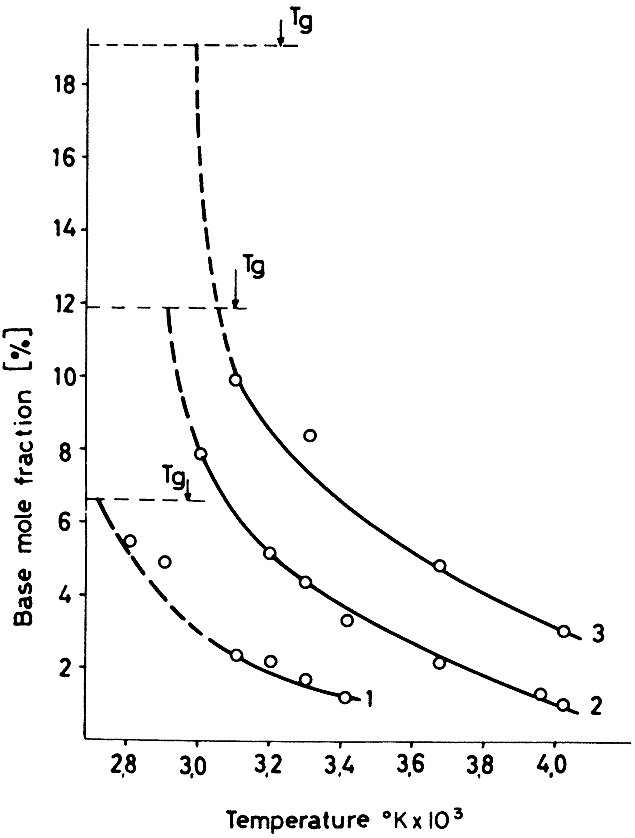

Figure 9. Decrease of the "free" plasticizer (benzene) below the glass temperature vs. the temperature.

(1) Polystyrene with 5.1% C_6H_6.
(2) Polystyrene with 10.0% C_6H_6.
(3) Polystyrene with 15.5% C_6H_6.

plasticizer at the beginning is steeper for benzene than for chloroform. This different behavior could probably be explained by the geometric form of the plasticizer molecules; spherical molecules should have greater mobility against each other than disc-shaped ones. Chloroform is an example for the first case, benzene for the second.

Comparison of NMR Absorption with Diffusion Rates

From diffusion measurements it is known that the translatory mobility of solvent molecules in polymers changes abruptly at the glass temperature. Below T_g the diffusion constants are of the order of 10^{-12} to 10^{-14}sq. cm./sec., above T_g of the order of 10^{-4} to 10^{-8}sq. cm./sec. (*13*). We have found that even below the glass temperature, plasticizer molecules may perform rather rapid motions, preferably rotatory motion. If the plasticizer has long aliphatic side chains, as with phthalates, rotating motions in the side chains should also result in a narrow absorption line. Then it is no longer possible to distinguish between free and bound plasticizer.

We stress at this point that our experimental results seem to contradict the results and thermodynamic deductions by Jenckel and Gorke (*6*) and also by Rehage (*15*). The conclusions of these authors are based essentially on studies of volume and refractive index which show that a few degrees below the freezing temperature the entire binary system is frozen in. This result seems to contradict our studies which have shown that the plasticizer is still mobile far below the freezing temperature of the binary system. But according to its definition, the phase is macroscopic and its state therefore should be determined by given values of macroscopic variables, such as volume, temperature, and composition. But this is not the case. In the course of time one still observes changes (after-effects) which indicate microscopic incidents. Therefore, without any distortion of the macroscopic homogenity of a phase, there exist mobile as well as immobile microscopic areas.

The Concept of Glass Structure

We shall conclude with some remarks on the structure of glassy polymers. If one frequently speaks of glass structures, this does not mean that there exists one definite glass structure similar to a crystal. In a macromolecular solid–e.g., the polystyrene–plasticizer system, entirely different glasses are obtainable, the macroscopic composition of which is always the same (*8*). In Figure 10 the full

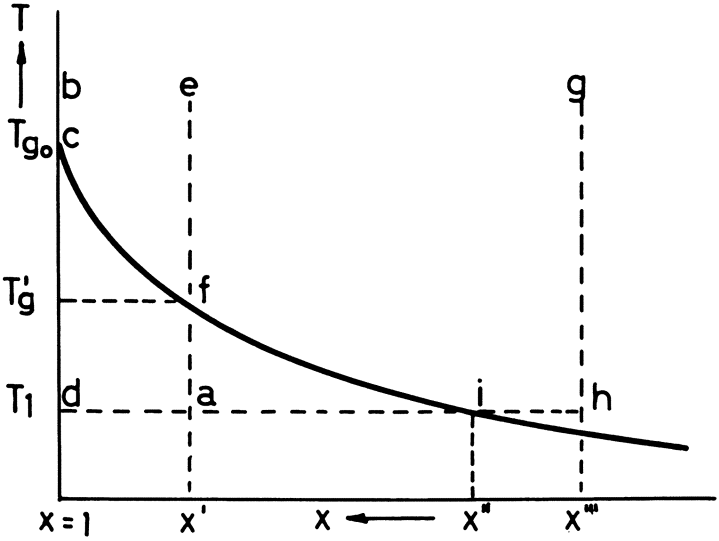

Figure 10. Forming of a glass structure in a composed glass. The curve c-f-i shows the correlation between glass temperature and the plasticizer concentration. According to the sequence history (see text) the structure of the glass with the composition x' *and the temperature* T_1 *is described by the coordinates of the glass point f,* ($x = x'$, $T_{g'}$) *or the glass point i,* ($x = x''$, T_1) *respectively;* $x = 1$ *corresponds to the pure polymer.*

curve schematically shows the correlation between glass temperature and plasticizer content. A glass of the composition x' at the temperature T_l (point a) may, in principle, be obtained by the following methods:

1. By first cooling the melt of the pure polymer until the glass temperature T_{g0} is reached and then further to the temperature T_l (point "d"). At T_l the solvent is allowed to diffuse into the solid until point "a" is reached. The glass structure is determined by $T = T_{g0}$ and $x = 1$, as well as the sequence history b–c–d–a.
2. A solvent-containing melt is cooled to T_g. Then the system is frozen to a glass (Point "f"). Further cooling to the temperature T_l leads again to a glass at the point "a" where the glass structure is given by $T = T_g$, and $x = x'$ and by the sequence history e–f–a.
3. A third possibility is to cool a solvent-containing melt starting from "g" to T_l (point "h"). By subsequently removing the solvent, the system reaches at $x = x''$ the glass state. By further removing the solvent, the composition x' and again point "a" is reached. Now we have a glass which is defined in the structure by $T = T_l$ and $x = x''$ as well as the sequence history g–h–i–a.

These glasses differ macroscopically in volume and, therefore, in structure. This mental experiment intends to point out, that correctly speaking, there does not exist a glass of definite structure. A glass of the composition x' at the temperature T_l can be produced in different ways which result in glasses of different structure. The characteristic behavior of the plasticizer in its molecular interaction with the chain molecules determines structure and macroscopic behavior of the glass.

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Linear Oxo Phthalate Plasticizers

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Oxonation of linear alpha olefins gives primary alcohols of a high degree of linearity. From this process it is possible to obtain odd-numbered, as well as even-numbered, carbon atom alcohols. These represent a new type of plasticizer raw material in the United States since such alcohols are not commercially available from natural sources, the conventional oxo process, or the ethylene growth process. Phthalate esters of these alcohols exhibit the improved performance in PVC compounds expected of linear alcohols.

The vinyl compounder can choose from a large number of plasticizers when formulating for specific performance. Almost inevitably, however, he turns to phthalates for the major portion of his plasticizer system since they offer a good balance of performance characteristics and are generally among the least expensive primary plasticizers available. When the poly(vinylchloride) industry was relatively new, its demands for plasticizers were met by products such as dibutyl phthalate and dioctyl phthalate (from 2-ethylhexanol). It soon became evident, that if the PVC industry were to expand, better plasticizers were needed to meet increasingly severe performance requirements. This, in turn, meant a need for new alcohols and acids since ester type plasticizers met the new performance requirements best.

Oxo Synthesis

The demands for new alcohols were to a considerable extent satisfied by the commercialization of the oxo synthesis in the United States (*1*). The synthesis involves reaction of an olefin with carbon monoxide and hydrogen to produce an aldehyde, which is reduced subsequently to a primary alcohol. From branched chain feeds such as pentene, heptene, nonene, and tetrapropylene–hexyl, isooctyl, isodecyl, and tridecyl alcohols have been made available to the plasticizer industry in large volume. These alcohols are mixtures of branched chain isomers owing to the branched nature of the olefin feed. (Oxo hexyl alcohol contains about ⅓ 1-hexanol).

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Plasticizer manufacturers have long recognized the desirable features of straight chain alcohols as plasticizer raw materials, but until recently, they depended entirely on limited production from natural sources for these products. Presently, mixtures of straight chain alcohols of even carbon number are available at commercially attractive prices from the ethylene growth process (*2*), but the pure alcohols are still too expensive generally to interest the plasticizer manufacture.

Alternate products of a high degree of linearity can be produced by oxonation of linear alpha olefins. By this process, one can obtain alcohols of any desired chain length, including the odd-numbered ones. Except for tridecyl alcohol, odd-numbered alcohols in the plasticizer range are not currently produced in volume at attractive prices in the United States.

For our study, individual samples of linear alpha olefins, containing from six to eleven carbons, were subjected to oxo synthesis to produce primary alcohols containing from 7 to 12 carbons. Analysis of the alcohols showed them to contain on the average 50% or more of the straight chain primary alcohols; the remaining alcohols were also primary and consisted mainly of the 2-methyl isomers. To distinguish between 100% straight chain on the one hand, and 100% branched chain on the other, we call these new alcohols "linear."

Phthalate esters of these linear alcohols were prepared by standard esterification techniques, and no problems were encountered in producing light-colored esters comparable to commercial phthalate plasticizers. For convenience, the plasticizers tested and the controls were given the code names listed in Table I.

Table I.

Code Name	*Plasticizer*
DHP	Dihexyl phthalate
DL7P	Di "linear" heptyl phthalate
DOP	Di-2-ethylhexyl phthalate
DIOP	Di-isooctyl phthalate
DNOP	Di-*n*-octyl phthalate
DL8P	Di "linear" octyl phthalate
DL9P	Di "linear" nonyl phthalate
DIDP	Di-isodecyl phthalate
DNDP	Di-*n*-decyl phthalate
DL10P	Di "linear" decyl phthalate
DL11P	Di "linear" undecyl phthalate
DL12P	Di "linear" dodecyl phthalate
DTDP	Ditridecyl phthalate

Performance Characteristics of Phthalates

Method. The plasticizers listed in Table I were incorporated in the following test formulation.

Polyvinyl Chloride Resin	100
Barium Cadmium Stabilizer	2.5
Stearic Acid	0.5
Plasticizer	50

The compounds were mixed on a two-roll mill at 320°F. for 8 minutes, then molded into test plaques at 340°F. and 1500 p.s.i. Samples for mechanical testing, hardness, compatibility, and Clash-Berg temperature were 0.075 inch thick while carbon black volatility and extractions were performed on 0.010 inch films. All testing was in accordance with ASTM specifications, and results are summarized in Tables II through V.

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Results The data in Table II offer the opportunity to compare phthalates of four different eight-carbon alcohols. The performance differences are perhaps greater than would be expected from such simple variations in skeletal makeup. The most notable differences are in volatility and low temperature properties, but other minor differences also exist. Greater linearity leads to increased efficiency (as measured by the 100% modulus), lower volatility, better flexibility at low temperatures, and better resistance to soapy water. In most circumstances, the "linear" alcohol phthalates are quite similar to straight chain phthalates. This is to be expected in view of the close similarity of structures. (The true value of a plasticizer system must, of course, consider not only performance but price. Thus, high efficiency can sometimes be a disadvantage when costs on a pound volume basis are calculated. In other words, a less efficient plasticizer often gives the lowest compound pound volume cost.)

Table II. Performance of Various Octyl Phthalates

Plasticizer	*DOP*	*DIOP*[a]	*DL8P*	*DNOP*
Original Properties				
Ultimate tensile, p.s.i.	2860	2850	2900	2790
Ultimate elongation, %	270	270	280	280
100% modulus, p.s.i.	1915	1970	1795	1750
Hardness, shore "A"	78	79	78	78
Aged 7 days at 100°C.				
(Turntable oven—1000 fpm)				
Tensile retained, %	100	102	100	102
Elongation retained, %	70	80	89	95
Volatility, wt.% lost	8.2	7.0	4.5	2.9
Aged 7 days at 113°C.				
(Turntable oven—1000 fpm)				
Tensile retained, %	103	105	105	107
Elongation retained, %	27	40	63	83
Volatility, wt.% lost	18	15.5	11	7.9
Compatibility, ⅜" Loop Test Exudation, 1 day	None	None	None	None
Carbon Black volatility, wt.% 24 hours at 70°C.	1.5	1.4	1.3	1.2
Clash-Berg, T_f, °C.	−26	−24	−31	−35
Soapy water extraction, wt.% 20 Hours at 70°C.	3.2	3.3	2.8	2.3
Hexane extraction, wt.% 1 hour at 23°C.	23	23	23	24

[a] Contains 0.1 wt.% Bisphenol A.

The general conclusions drawn in considering the octyl phthalates hold equally well for the decyl phthalates. Here, however, the "linear" alcohol phthalate is even closer in performance to the straight chain alcohol phthalate. Both the straight chain and the linear product are somewhat less compatible than the conventional oxo phthalate but have higher efficiency, lower volatility, and better flexibility at low temperatures.

Since there were no commercially available phthalate plasticizers comparable to the linear heptyl and nonyl derivatives, they were bracketed between the even numbered oxo phthalates for comparison. Table IV shows that DL7P was the most efficient of all the plasticizers tested and is superior to DHP and DIOP in low temperature flexibility. It is considerably less volatile than DHP and only slightly

Table III. Performance of Various Decyl Phthalates

Plasticizer	*DIDP*[a]	*DL10P*	*DNDP*
Original Properties			
Ultimate tensile, p.s.i.	2895	2885	2860
Ultimate elongation, %	265	275	285
100% modulus, p.s.i.	2110	2010	1940
Hardness, shore "A"	81	81	80
Aged 7 days at 121°C. (Turntable oven—1000 fpm)			
Tensile retained, %	102	102	101
Elongation retained, %	66	89	92
Volatility, wt.%	11.8	6.7	4.7
Aged 7 days at 136°C. (Turntable oven—1000 fpm)			
Tensile retained, %	122	110	106
Elongation retained, %	11	64	78
Volatility	19	12.8	9.3
Compatibility, 3/8" Loop Test Exudation 1 day	Light	Moderate	Moderate
Carbon Black volatility, wt.% 24 hours at 70°C.	1.4	1.2	1.3
Clash-Berg, T_f, °C.	−27	−33	−37
Soapy water extraction, wt.% 20 hours at 70°C.	0.6	0.5	0.5
Hexane extraction, wt.% 1 hour at 23°C.	25	25	25

[a] Contains 0.1 wt.% Bisphenol A.

Table IV. Performance of Various (Hexyl to Decyl) Phthalates

Plasticizer	*DHP*	*DL7P*	*DIOP*[a]	*DL9P*	*DIDP*[a]
Original Properties					
Ultimate tensile, p.s.i.	2885	2800	2850	2920	2895
Ultimate elongation, %	270	285	270	275	265
100% modulus, p.s.i.	1750	1680	1970	1980	2110
Hardness, shore "A"	75	75	79	78	81
Aged 7 days at 100°C. (Turntable oven—1000 fpm)					
Tensile retained, %	100	101	102	99	103
Elongation retained, %	28	58	80	95	100
Volatility, wt.%	17.8	10.9	7.0	2.0	2.2
Aged 7 days at 113°C. (Turntable oven—1000 fpm)					
Tensile retained, %	78	131	105	99	101
Elongation retained, %	4	3	40	85	93
Volatility, wt.%	23.4	21	15.5	5.6	5.1
Compatibility, 3/8" Loop Test Exudation 1 day	None	None	None	None	Light
Carbon Black volatility, wt.% 24 hours at 70°C.	4.2	2.5	1.4	1.2	1.4
Clash-Berg, T_f, °C.	−26	−29	−24	−30	−27
Soapy water extraction, wt.% 20 hours at 70°C.	11.5	8.6	3.3	0.7	0.6
Hexane extraction, wt.% 1 hour at 23°C.	12	20	23	25	25

[a] Contains 0.1 wt.% Bisphenol A.

poorer than DIOP in this respect. At equal efficiency the volatility difference between DL7P and DIOP would be very small. The DL9P is about as efficient as

Table V. Performance of Various (Decyl to Tridecyl) Phthalates

Plasticizer	*DIDP*[a]	*DL11P*	*DL12P*	*DTDP*[b]
Original Properties				
Ultimate tensile, p.s.i.	2895	2795	2820	2840
Ultimate elongation, %	265	270	265	250
100% modulus, p.s.i.	2110	2000	2095	2270
Hardness, shore "A"	81	83	88.0	90.0
Aged 7 days at 121°C. (Turntable oven—1000 fpm)				
Tensile retained, %	102	102	100	99
Elongation retained, %	66	99	96	88
Volatility, wt.%	11.8	3.6	2.8	3.9
Aged 7 days at 136°C. (Turntable oven—1000 fpm)				
Tensile retained, %	122	103	101	102
Elongation retained, %	11	86	87	81
Volatility, wt.%	19.0	7.3	4.9	7.2
Compatibility, 3/8" Loop Test Exudation 1 day	Light	Heavy	Very Heavy	Heavy
Carbon Black volatility, wt.% 24 hours at 70°C.	1.4	0.9	1.1	1.2
Clash-Berg, T_f, °C.	−27	−35	−40	−27
Soapy water extraction, wt.% 20 hours at 70°C.	0.6	0.1	0.6	0.5
Hexane extraction, wt.% 1 hour at 23°C.	25	27	29	27

[a] Contains 0.1 wt.% Bisphenol A.
[b] Contains 0.5 wt.% Bisphenol A.

DIOP and only slightly more volatile than DIDP. It has very good low temperature flexibility and resistance to soapy water and is more compatible than DIDP.

For the same reasons cited above, the "linear" undecyl and dodecyl phthalates were compared to DIDP and DTDP. Linear undecyl phthalate (DL11P) demonstrates some rather impressive performance characteristics in relation to the materials against which it was compared. It has excellent permanence for a monomeric plasticizer, very good low temperature properties, and outstanding resistance to soapy water. The same statements are generally true of DL12P, except that it was the least compatible of the plasticizers tested and probably would be used best in combinations with more compatible plasticizers.

Conclusions

In summary, it can be said that even-numbered "linear" oxo phthalates are superior in performance to the corresponding conventional oxo phthalates, and in most respects, closely approach the performance of the completely straight chain alcohol phthalates. Odd-numbered linear alcohols produce phthalates which impart some unique combinations of performance properties to vinyl that were previously available only by using composites of several plasticizers.

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6

Acid-Olefin Esterification

Process for o-Phthalate Ester Plasticizers from Olefins

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A manufacturing process for producing orthophthalate esters derived from alkyl acid orthophthalates and olefins has been developed and demonstrated on the pilot plant scale. Process variables include choice of reactants, stoichiometry, reaction kinetics, recycle of recovered materials and the fate of the perchloric acid catalyst. Some physical properties of the ortho-phthalate esters have been determined and several of the esters have been evaluated as plasticizers for polyvinyl chloride. The composite data show that the acid-olefin esterification process provides commercially acceptable plasticizers for polyvinyl chloride.

Approximately 80% of the plasticizers used in this country today fall into one category with regard to chemical structure: they are esters of organic carboxylic acids. These range from esters of monocarboxylic acids such as benzoic, through the esters of the difunctional phthalic and adipic acids, to esters of tri- and even tetrafunctional acids, such as trimellitic and pyromellitic. It is therefore not surprising with such esters possessing the necessary performance requirements to act as plasticizers for a variety of resins, that their commercial development should be based on classical processes which yield products of consistent quality with favorable economics. Such processes have been based on the classical esterification of these desired carboxylic acids with a variety of commercially available alcohols. By examination of the raw materials used in production of the alcohols which subsequently enter into this esterification reaction, it can be seen that in many cases olefins are the precursors to these very alcohols. Thus, in preparing a typical plasticizer ester such as diisooctyl phthalate, the alcohol used is prepared by oxonation of the corresponding heptene. Since oxonation of the olefin involves addition of the elements of water, which must subsequently be removed by esterification, this chain of events, theoretically at least, contains an unnecessary processing step. The elimination of this step by direct esterification should thereby provide a more economically attractive method for preparing these esters.

The direct esterification of olefins with carboxylic acids is not a new reaction. This process has been used commercially for some time in the production of various solvents and vinyl monomers. Until now little was known, however, on the application of this technique to the preparation of higher molecular weight esters such as those used as resin plasticizers. In a previous paper (*2*) on this subject, we described in detail the experimental results which led to the choice of catalyst, acid, and olefins which were suitable for preparation of plasticizer-type esters by direct esterification. This previous work may be summarized as follows: the acid component of the reaction should be soluble in the olefin to be esterified, should be a fairly strong acid, relatively low in molecular weight, and the resulting ester should possess the necessary chemical and physical properties characteristic of resin plasticizers. A particular group of acids met these requirements very well; this group is the primary alkyl acid *o*-phthalates. The olefin component also has a corresponding set of criteria, as follows: the olefin should be C_6 or higher; it should predominate in types I ($RCH=CH_2$) and II ($RCH=CHR$); it should contain a minimum of non-reactive diluents, and it should show an economic advantage over the corresponding alcohol as a raw material for preparation of the esters. The catalyst for the reaction should be a strong proton donor; it should possess a large anion with wide charge distribution; it should be soluble in the media, and it should not cause excessive side reaction. Catalysts satisfying these requirements in all respects were 72% perchloric acid and boron trifluoride (as the etherate).

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Primary and Side Reactions

Having thus established the necessary requirements for the raw materials which enter into the direct esterification of olefins, the processing conditions required to obtain the desired product in acceptable quality were studied in detail. Figure 1 illustrates the primary reactions which occur during this direct esterification of olefins, using partial esters of *o*-phthalic acid as the carboxylic acid. Included also are the side reactions which occur during the processing. Ideally, of course, one would desire a clean reaction with no side reactions, and the minimization of side reactions was the objective of the process study. It was found desirable for several reasons to maintain an essentially anhydrous system throughout this reaction because of the very detrimental side reaction numbers 4 and 5 as shown in Figure 1. The tendency of the partial ester to yield the anhydride and the alcohol further detracts from the primary reaction by the subsequent reaction of the alcohol with another mole of the half-ester to give the diester and a mole of water. This mole of water then reacts with the anhydride to yield the very insoluble *o*-phthalic acid. This was found to form a heterogeneous system due to the gross insolubility of *o*-phthalic acid in the medium, and also to inhibit the catalytic activity of the catalyst. The removal of *o*-phthalic acid from the reaction media by precipitation destroys the stoichiometry of the desired reaction and its formation must, therefore, be eliminated. We found that this could be carried out by the use of two expedients: (1) the reaction temperature used was also the reflux temperature of the olefin, and the olefin, therefore, acted as an azeotropic agent to remove any water as it was formed, and (2) charging of an excess of phthalic anhydride originally to promote the half-esterification as opposed to the acid-ester decomposition reaction. Using these two expedients, the system remains anhydrous and the

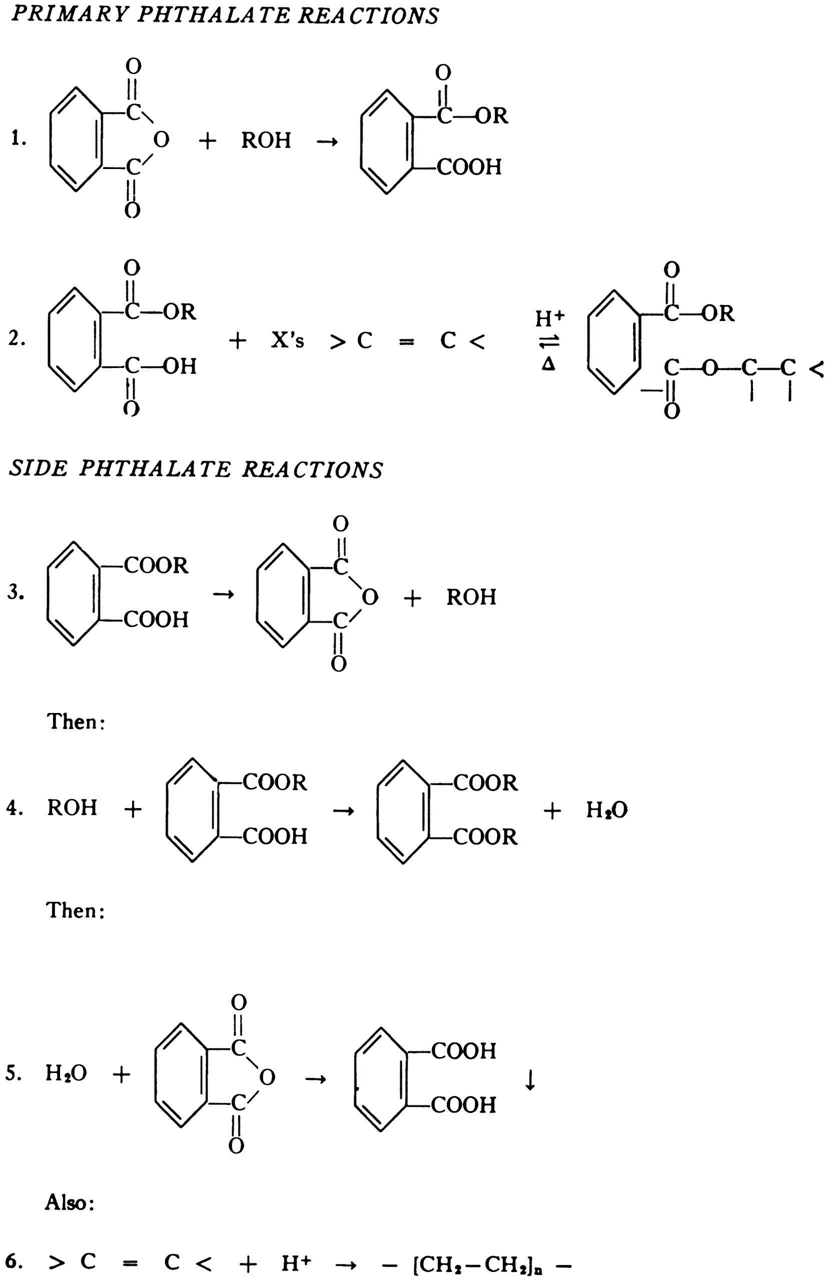

Figure 1.

In Plasticization and Plasticizer Processes; Platzer, N.;
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increase in yield over the system in which the *o*-phthalic acid is precipitated is substantial.

As is normally the case with esterification reactions, an equilibrium situation exists in this particular series, and Reaction 2, with respect to its degree of completion is dependent upon the concentration of the olefin in the reaction medium. We studied the effect of the olefin excess in the reaction on yield of ester and found that at levels less than 50%, the yields based on the acid-ester components were considerably less. With olefin excesses larger than 50%, the rate of the primary reaction, that is formation of the diester, was decreased. We therefore determined that an olefin excess of about 50% favored the primary reaction (number 2) as opposed to the secondary reaction in which the olefin can undergo polymerization in the acid media.

We also studied the effect of catalyst concentration on the reaction and determined that the reaction could take place without catalysis, but that its speed was highly dependent upon the concentration of catalyst, both in the case of 72% perchloric acid and in the case of the boron trifluoride etherate. A workable level for the perchloric acid catalyst was found to be in the order of 3–4 grams per mole of the acid-ester charge. A catalyst level for the boron trifluoride etherate of 40 grams per mole of the acid component charge was satisfactory.

The effect of reaction temperature was studied in some detail, and its role in the formation of the primary reactions as opposed to the side reactions was determined. At reaction temperatures lower than 80°C. the reaction is slower by a considerable factor, especially when compared with the reaction carried out at, say, 50°C. At higher temperatures, the side reactions are favored and the most prevalent side reactions which occur are those illustrated in Figure 1 as numbers 3 and 6.

A study of the completion of reaction *vs.* time was also made on the direct esterification of a typical olefin with a primary alkyl acid *o*-phthalate. By titration of the reaction mass with 0.5*N* sodium hydroxide, we determined the rate of reaction using standard conditions of catalyst level, reaction temperature and olefin excess as previously described. The acid value reached a minimum and longer time cycles did not reduce this to any great extent.

Experimental

Upon completion of this study of the effect of processing conditions upon the speed and yield of the reaction, we were able to devise a standard experimental procedure for the direct esterification of olefins. This is shown in the experimental details given in Figure 2. An excess of the anhydride and the primary alcohol of choice were heated with agitation to form the acid-ester. Upon completion of the half-esterification and on cooling the batch temperature to less than 100°C., the olefin, at a 50% molar excess, and the perchloric acid catalyst were charged. The mass was held at 80°C. ±2°C. under reduced pressure (in the case of butyl acid *o*-phthalate and caprylene) until a titration of the reaction mass showed residual acidity to be less than 70 meq./100 grams. Throughout the reaction, the distillate was sent through a water separator and the separated olefin returned to the reaction vessel as practically dry olefin. Approximately 8 hours after addition of the olefin a quantity of alcohol was added to the reaction vessel to convert the excess anhydride to the partial ester for subsequent recovery. When the reaction

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was complete, the crude ester was washed with a mixture of water and sodium hydroxide to remove unreacted acid-ester and catalyst. This acid-ester was recovered by acidification of the alkaline wash and recycled into succeeding esterification batches. The acid-free diester was then steam-stripped to remove unreacted olefin, and this material was entirely suitable for re-use as recycle material. When the olefin was caprylene, evaluation of composition of the recovered olefin showed the same ratio of 1-octene to 2-octene as the starting material. The ester was then decolorized, dried, and filtered. By this procedure, the conversion based on alkyl acid *o*-phthalate was 82.5%. The yield of phthalic anhydride was about 90% in the case of esterification of caprylene with butyl or 2-ethylhexyl acid *o*-phthalate.

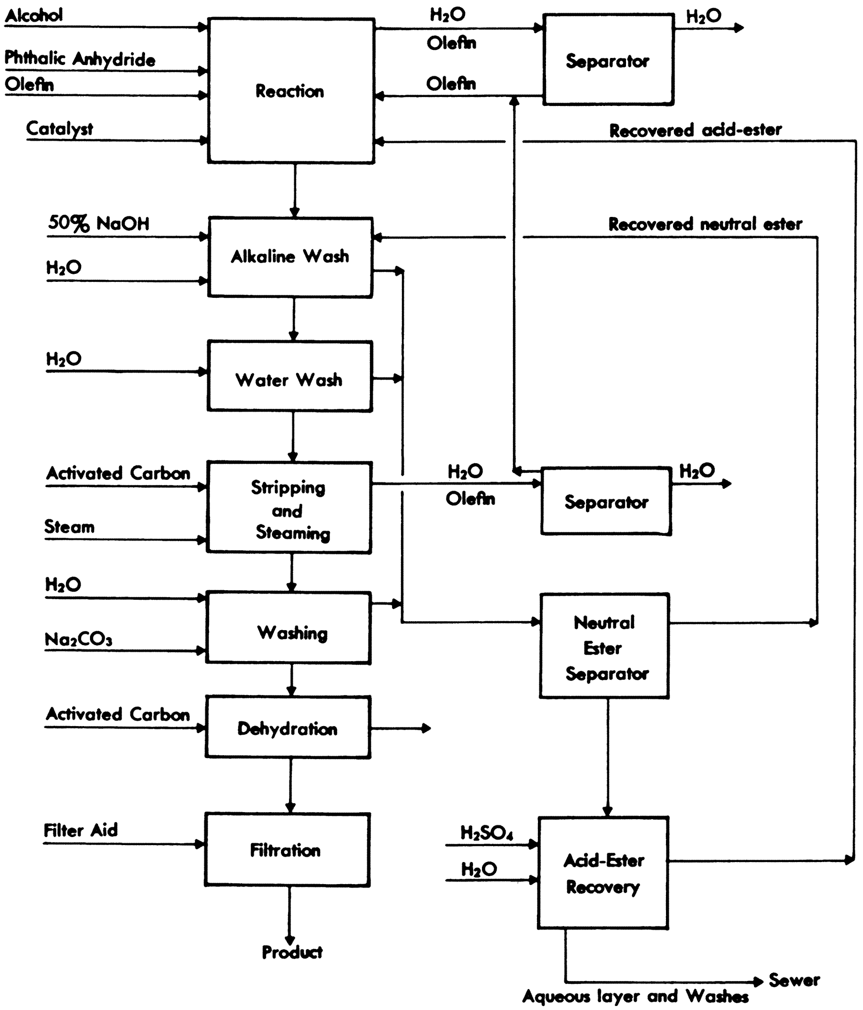

Figure 2. Process flow diagram for olefin esterification

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Upon establishment of a standard procedure, which had demonstrated the ability to obtain high yields of esters in reasonable times by direct esterification of olefins, we undertook a study to determine the utility of the reaction with respect to the various types of both acid-ester and olefin raw materials which were commercially available. Table I shows the summation of this work and the extension of the reaction to a variety of acid-esters and olefins. The acid-esters ranged from methyl, the lowest molecular weight, to isodecyl acid *o*-phthalate, the highest molecular weight version. The olefins ranged from 2-pentene, to 1-octadecene, an olefin of the Type I variety which, in this case, was derived from dehydration of 1-octadecanol. In all cases, the products were obtained in high purity when using the refining technique already described, and the conversions (based on acid-ester) ranged from a low of 67% with 2-pentene and butyl acid *o*-phthalate to a high of 84% with 2-ethylhexyl acid *o*-phthalate and caprylene. Caprylene is a mixture of 1- and 2-octene derived from the cracking of castor oil fatty acids, whereas the other olefins are essentially pure materials of the structure indicated by their chemical nomenclature. We also determined that the olefin need not necessarily be the pure 1-olefin but that various quantities of both aromatic and/or aliphatic diluents, such as toluene or aliphatic hydrocarbons such as octane, etc., did not to any great extent decrease conversion to ester.

Evaluation

The evaluation of a large series of the esters derived from olefin esterification was carried out with respect to their performance as plasticizers for PVC resin. This evaluation indicated to us that two particular esters justified further effort regarding larger scale production than laboratory size batches. Processes and subsequent pilot plant demonstrations were therefore developed and demonstrated for the esterification of caprylene with normal butyl acid *o*-phthalate, and the esterification of caprylene with 2-ethylhexyl acid *o*-phthalate. In both cases, the larger scale operations very closely approximated the experience obtained in the laboratory study with respect to time cycles, yields, and product quality. The number of batches prepared in the pilot plant demonstration was large enough to show (1) the efficacy of recycling recovered materials, and (2) consistent product quality with only minor batch-to-batch variations. Our pilot plant experience was based on preparation in 50-gallon glass-lined equipment scaled to yield approximately 200 pounds of finished ester per batch.

Table I. o-Phthalate Esters from Alkyl Acid o-Phthalates and Olefins

			Ester Properties	
Alkyl Acid o-Phthalate (A)	*Olefin*	*Ester Conversion on (A), %*	*Sp. Gr. 25/25°C.*	$N^{25°}D$
Ethyl	1-Octadecene	71.4	0.9347	1.4754
Methyl	1-Hexadecene	68.2	. . .	1.4785
Methyl	1-Tetradecene	70.9	0.9843	1.4738
n-Propyl	1-Dodecene	74.9	0.9692	1.4795
2-Ethylhexyl	1-Octene	76.0	0.978	1.4836
n-Butyl	Caprylene	82.5	1.0058	1.4850
2-Ethylhexyl	Caprylene	84.1	0.978	1.4820
Isodecyl	Caprylene	80.8	0.9823	. . .
n-Butyl	2-Pentene	67.2	1.030	1.4880

At this point the use of 72% perchloric acid, which is our preferred catalyst, may be some cause for concern. This very strong oxidizing agent has been cited as the cause for many mishaps and damaging explosions. A study was therefore undertaken to determine the malefic behavior of the perchloric acid catalyst in this reaction by the use of differential thermal analyses (*1*). In this study the thermal stability of a series of synthetic samples spiked with 72% perchloric acid was measured. Materials tested ranged from olefin perchloric acid systems (homogeneous and two-phase) to such materials as the finished ester and mineral oil spiked with 72% perchloric acid. One series of runs was made with 2 cc. of 72% perchloric acid mixed with 5 cc. of caprylene (homogeneous system) and 2.5 cc. of 72% perchloric acid plus 5 cc. of dodecene (two-phase system). The latter mixture was the least stable of all systems encountered. However, even this sample did not reach a rate of heat evolution of one calorie per kilogram per minute until roughly 120°C. to 125°C., and then was evolving heat at a rate of 1000 calories per kilogram per minute at 176°C. The mass exploded at 180°C. to 190°C. In all cases of heat evolution encountered with the raw materials, the reaction mass, and the finished product, the rate of heat gradually increased rather than exhibiting a sudden uncontrollable exothermic reaction owing to any oxidative instability with the perchloric acid. A sample of olefin esterification reaction mass, using butyl acid *o*-phthalate and caprylene was obtained immediately after addition of the perchloric acid catalyst. This material was found to be stable thermally up to 200°C., at which temperature, the test was discontinued. A duplicate sample, aged for several days before determination of its thermal stability, also failed to show any large heat evolution up to 200°C. The thermal stability of two additional reaction masses was studied and neither gave an indication of any noticeable heat evolution up to 200°C. The samples consisted of: (1) reaction batch made with recycled materials just after addition of the standard charge of perchloric acid and (2) an aliquot of (1) aged for one week prior to determination of its thermal stability. Both samples were additionally spiked with several times the normal amount of catalyst. These recycle materials were prepared in the presence of Monel metal (Monel TM International Nickel Co.). Along with these two samples, a study was made on a mixture of 0.3 grams of sodium perchlorate and 0.6 grams of 1-octene. No exothermic reaction was observed up to 195°C. at which point the test was discontinued.

Perchloric Acid

In addition to the analysis of the thermal stability of the perchloric acid organic reaction media mixtures, a procedure was worked out to determine the fate of the perchloric acid by chlorine analysis of the batch, effluent streams, etc. Preliminary analyses on selected process samples showed no tendency for perchloric acid to concentrate in recycle material and therefore build up in the reactor. A total of less than 1% of the initial charge of perchloric acid (total chlorides calculated as perchloric acid) was found in the combined recovered acid-ester and olefin fractions. Less than 1% of the initial charge of perchloric acid was found in the finished ester. The analytical method used was an oxygen bomb decomposition, followed by titration of chlorides with 0.01N silver nitrate, using a recording automatic titrator. The eventual fate of the perchloric acid catalyst was

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evaluated on the basis of a total chlorine balance. The results determined as percent of total chlorine charged are shown in Table II.

Table II. Chlorine Analysis of Process Streams

91.3%	In combined washes. 84.3% in first and second washes. 1.4% in acid-ester wash. 5.6% in third wash.
0.4%	In recovered, washed acid-ester.
0.8%	In recovered caprylene.
6.4%	In stripped, steamed, filtered ester prior to decolorization. (7.1% in washed crude, prior to stripping.)
0.5%	In finished goods.
99.4%	Total Chlorine Balance

The data show that the half-ester, the caprylene recycle material and finished goods each contain less than one % of the original perchloric acid charge determined as chlorides. Preliminary analysis with samples both from laboratory and pilot plant operations indicated that there was no serious perchloric acid carry-back encountered with recycle of recovered acid-ester and unreacted caprylene. We therefore assumed that no hazardous build up of perchloric acid in the reaction step would be expected. The results of these studies may be summarized as follows:

(1) No danger from explosion or adverse temperature effects exists if the process as previously described is strictly followed.

(2) Experimental data show that the perchloric acid is extracted by the aqueous washes and subsequently leaves the process in effluent streams, and that, therefore, no measurable hazardous build up in the reaction step would be expected.

The esters prepared by the direct esterification of olefins were designed, as we mentioned at the outset, for potential use as plasticizers for PVC resin. Several

Table III. o-Phthalate Esters from Olefins as Plasticizers for Polyvinyl Chloride

					Water Extraction,	
Plasticizer	*From Olefin*	T_f°*C.*	*Vol., % Plast. Lost*	*Kerosene Extraction, % Plast. Lost*	*% Sol.*	*% Absrd.*
n-Butyl pentyl phthalate	1- and 2-Pentene	−32	33	9	0.55	0.99
n-Butyl octyl phthalate	1- and 2-Octene	−35	23	10	0.24	1.35
n-Butyl nonyl phthalate	2,6-Dimethyl heptene	−25	2	11	0.1	0.95
n-Butyl decyl phthalate	1-Decene	−39	9	12	0.10	0.82
2-Ethylhexyl octyl phthalte	1- and 2-Octene	−39	5	71	0.05	0.25
Di-*n*-butyl phthalate	—	−40	45	9	0.26	0.38
Di-2-ethylhexyl phthalate	—	−41	4	60	0.01	0.22

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typical esters were evaluated as plasticizers by normal techniques used in plasticizer screening evaluation and the results of these studies are shown in Table III. Each plasticizer was compounded with a commercial grade of polyvinyl chloride and with a commercial stabilizer equivalent to 0.5 part per 100 parts of resin. The concentration of plasticizer was 40% on resin. The composition was fluxed on a differential speed roll mill and the resulting mass was heat transformed under pressure to form a sheet from which the test specimens were die cut. Thereafter, standard ASTM testing techniques were used. As can be seen from the table, the *o*-phthalate esters prepared from olefins are essentially equivalent as plasticizers to those prepared from alcohols and are commercially acceptable plasticizers based on the tests herein described. Esters prepared from alcohols are included and used for comparison purposes. These are commercially available products which presently enjoy multi-million pound–per–year markets.

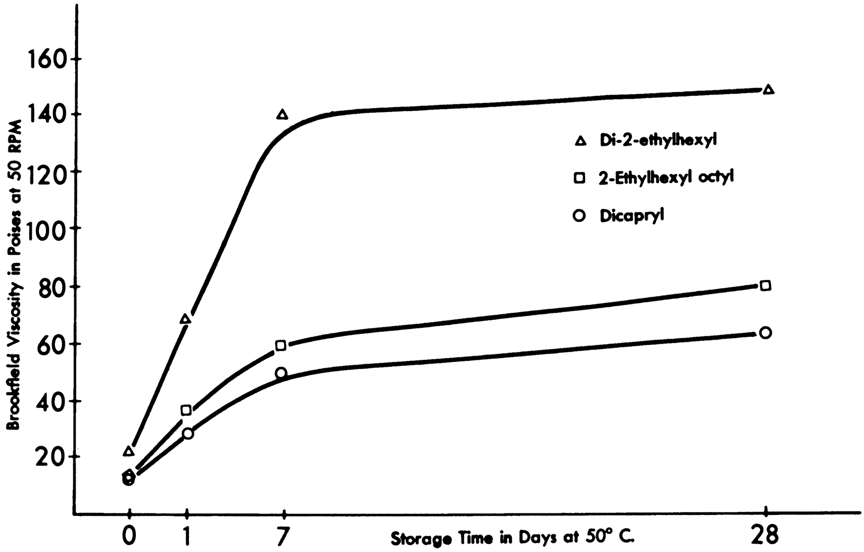

Figure 3. Viscosity stability of polyvinyl chloride-o-phthalate ester compositions

Another very important property of plasticizers for PVC resins is the ability to act as a dispersing medium for polyvinyl chloride plastisols. The performance of the particular plasticizer in a plastisol application depends to a great extent on a property known as its viscosity stability. The stability of the plastisol to viscosity build up is the manifestation of the solvating effects of the plasticizer, and thus, those materials with higher solvating efficiency tend to display an increase in plastisol viscosity on standing. Figure 3 is the plot of the viscosity stability of PVC *o*-phthalate ester plastisol compositions and, in essence, compares the alcohol-derived plasticizers with that of the olefin-derived plasticizer. The data show that dicapryl *o*-phthalate, a secondary alcohol ester, exhibits good viscosity stability while di-2-ethylhexyl *o*-phthalate exhibits a considerable viscosity increase over 28-day storage period at 50°C. The viscosity stability of the plasticizer prepared from the reaction between 2-ethylhexyl acid *o*-phthalate and caprylene also shown on the graph displays a viscosity stability very similar to that of the commercially available and accepted dicapryl *o*-phthalate.

As a result of this work, we have drawn the following conclusions. Direct esterification of olefins to yield high molecular weight esters suitable for use as resin plasticizers is technically feasible provided certain requirements of the raw materials and catalyst are satisfied. The reaction is applicable to a wide range of alkyl acid *o*-phthalates and a variety of olefins. Optimum processing conditions have been determined, and the effect on ester conversion of time, temperature, catalyst concentration, etc., is known. When perchloric acid is used as the esterification catalyst, it is essentially quantitatively removed in the process effluent, thus preventing any dangerous buildup of this strong oxidizing agent. Esters prepared by direct esterification of olefins possess the necessary properties to perform satisfactorily as plasticizers for polyvinyl chloride resins. In more specific applications, the olefin-derived esters exhibit a good level of viscosity stability for utility in polyvinyl chloride plastisols.

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7

Preparation of Ester Plasticizers by Amphoteric Catalysis

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In manufacturing esters of o-phthalic acid, stearic acid, and benzoic acid, various amphoteric oxides and oxide hydrates of metals of the Ist, IInd, IIIrd, IVth, and VIIth group of the periodic table are used—partly with alkaline substances—as esterification and transesterification catalysts. The reaction goes by homogeneous catalysis through formation of six-ring chelate addition compounds of the metals. Contrary to proton-induced reactions, no by-products such as olefins and ethers are formed. Consequently, it can be run, even at the boiling temperatures of the alcohols, without any entrainers. At a 99.95% conversion, this method yields colorless esters. The alcohols can be re-used more than a hundred times. Costs for materials, utilities, and labor are summarized for commercial production.

In studying the patent literature concerning the manufacture of ester plasticizer we conclude that, although the esterification reaction can be catalyzed simply by using acid compounds, special measures are required to obtain useful end products. Concentrated sulfuric acids and their acid salts, besides aryl sulfonic acids and phosphoric acids, are primarily used as catalysts (*1*, *2*, *7*, *8*, *9*, *13*, *20*, *21*, *24*, *25*, *26*, *28*). In order to esterify carefully, the temperature is kept as low as possible by choosing auxiliary liquids with a low boiling point to remove the reaction water. To achieve a sufficient speed of esterification, comparatively high additions of acid catalysts are used. To produce a colorless ester, the acid-catalyzed reaction is carried out in the presence of oxygen-consuming compounds such as phenols, amines, or salts of metals belonging to the transition series, of low valence. This can be achieved also by using sulfurous acid. Obviously, the color is frequently improved in a later process, either physically, by vacuum distillation, or chemically by oxidative or reductive decomposition of the coloring impurities.

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In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

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The Hüls Process

The Hüls esterification method later described is based on the following factors: no acid catalysts are used for esterification; instead, substances or substance mixtures which react in a neutral or alkaline way in the presence of water are used. Since strong inorganic acids with a dehydrating and oxidating effect are not a part of the esterification components, it is easier to obtain colorless esters with this method than with that usually employed.

Thus, the above mentioned additives, as well as the refining of the esters, can be eliminated. The use of auxiliary liquids is also unnecessary. The esterification process patented in the Federal Republic of Germany in 1951 (*6*) now makes it possible (besides other processes developed on a similar basis (*16*, *22*)) to produce plasticizer esters of excellent quality, simply and cheaply. In this connection we should like to mention the use of titanic acid esters as esterification and transesterification catalysts known since 1955 (*29*), and 1951 (*15*).

Discovery. Many years ago tests were conducted to clear up an operating disturbance. Among others, silicic acid, iron hydroxide, and aluminum hydroxide were examined for their influence during the esterification reaction. It was discovered that the latter substance greatly increased the esterification speed (while continuously separating the reaction water distilling off)—as compared to the test batch without a catalyst. Tests with other solids, the results of which cannot be included here, showed that the discovered catalytic effect can only be noticed when amphoteric compounds are used. These compounds are among the metal hydroxides of group I, II, III, and IV of the periodic system, and also among the sulfides of group V from which the following can be mentioned: Cu, Mg, Zn, Al, Ga, In, Tl, Sn, Pb, As, Sb. However, the alkaline oxides and hydroxides of metals belonging to the first and second group were ineffective, for example, the alkali metals and alkaline earth metals beginning with calcium. But, the oxides of the third and fourth group, reacting merely as acids, proved equally inactive, catalytically, for example, those of boron and silicon.

With regard to the catalytic effectiveness and cheapness of the compounds examined, aluminum hydroxide was most interesting. That is why subsequent tests concentrated on this substance.

Dissolved Catalyst Effects. First, it was assumed that the catalysis would proceed heterogeneously and would take place on the surface of the solid catalyst only, limited to a minimum temperature of about 180°C. The most favorable course during technical esterification is obtained with a slow and constant temperature increase, and the catalyst becomes considerably less effective under a slight decrease of temperature. Since a temperature decrease of only a few degrees does not greatly influence the esterification speed, we assumed that only certain surface centers of the amphoteric solids are important for the catalysis. Examining the reaction mixture for aluminum in solution brought the expected result that less than 5 p.p.m. of aluminum could be detected after the solid catalyst had been filtered off. However, this examination unexpectedly showed that the catalytic effect is the result of only this small quantity in solution. This is shown by the fact that an esterification batch, in which the solid had been removed after a reaction period of one hour, took almost the same course with respect to time as did the original esterification with the suspended aluminum hydroxide.

Method. In the course of each experiment 148 grams of phthalic acid anhydride were brought to boil under normal pressure with 500 grams of 2-ethylhexanol in a 1-liter glass bulb with reflux condenser and a water separator. The increasing consumption of acid, which is determined by a regular control of the acid number, is the criterion of conversion. At the beginning of the experiment the reaction temperature is 180° C., rising to 210° C. by the end of the experiment. Aluminum hydroxide, 1% by weight relative to phthalic anhydride, is added as catalyst, as it is obtained in the technical Bayer process. In the clear reaction solution, which is filtered as hot as possible, aluminum was determined by photometric evaluation of the absorption spectrum of the oxychinolate.

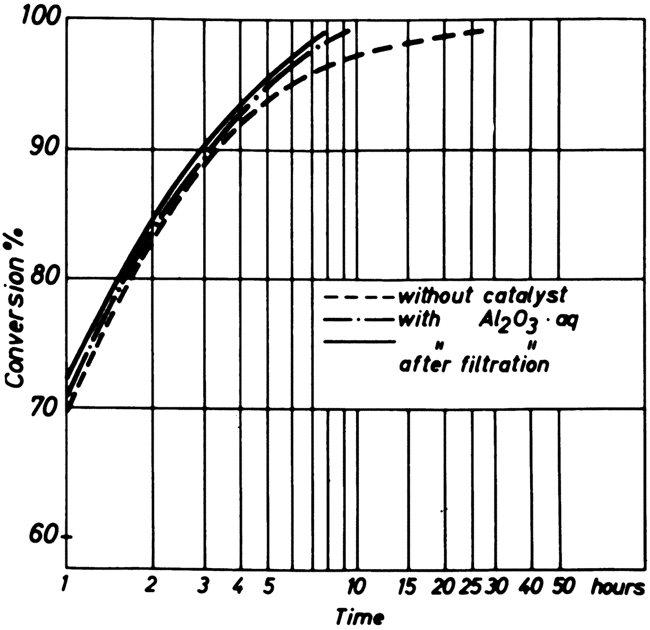

Figure 1. Esterification with and without $Al_2O_3 \cdot aq$. catalyst.

Results and Discussion

Figure 1 shows the conversion in relation to time. The uncatalyzed reaction has a conversion of 99% after 25 hours; the catalyzed reaction reached the same stage after 8 hours. The third curve shows the reaction course of a batch which, after having been esterified with a solid catalyst for one hour, continued after removal of the catalyst. This followed a course similar to that of the catalyzed reaction.

Efficiency of Small Amounts of Alkali. Obviously Dr. Hueter and Mr. Hentschel (*19*), chemists of the VEB Deutsches Hydrierwerk Rodleben, also thought that the catalysis was a surface reaction, that the catalyst is not used up, and therefore can be used over and over again. Extending our patent they obtained protection for a special solid-form of the catalyst in 1957. They covered the addition of alkali according to a method which had been previously covered by the patent for CWH in 1951.

In systematically testing the various amphoteric hydroxides for their catalytic effect, alkali was also added. As a result, the hydroxides of the trivalent metals in particular increased considerably in activity. When sodium hydroxide is used the amount required, relative to phthalic anhydride, is 0.1% part by weight and 10% parts by weight of the aluminum hydroxide. It is fed as a concentrated alkali solution.

In the presence of alkali metal the solubility of aluminum in the reaction mixture increases considerably, and it is undoubtedly the dissolved part of the metal which catalyzes the esterification in a homogeneous reaction. When the residue is filtered off, this time after a reaction period of 45 minutes, the esterification proceeds at the same speed as without filtration. The filtered residue can be used effectively again and again so that, in the case of the alkali-activated catalysis, it may be denied that only specific active regions of the solid catalyze the reaction.

Figure 2 clearly shows the differences with the alkali free esterification; the conversion depends on time almost exponentially; a change of the reaction course after removal of the solid is not noticed. The esterification was followed up to 99.9% conversion.

The content of aluminum in the reaction solution was determined at 50 p.p.m., the content of sodium at 100 p.p.m. Up to 95% conversion, the metal content in solution did not change, but at the end of the esterification about 50% of the aluminum had separated as an insoluble substance, and only 10% of the original concentration of the alkali still existed in solution. After removing the remaining alcohol and brightening the plasticizer with adsorbents, the content of the two metals lies with 0.07 p.p.m. sodium and 0.1 aluminum at the limit of detectability. The sodium was determined by flame photometry; the determination of aluminum is discussed later.

If it is true that only the small dissolved part of the added solid is effective, the addition of soluble aluminum and sodium compounds in much smaller quantities

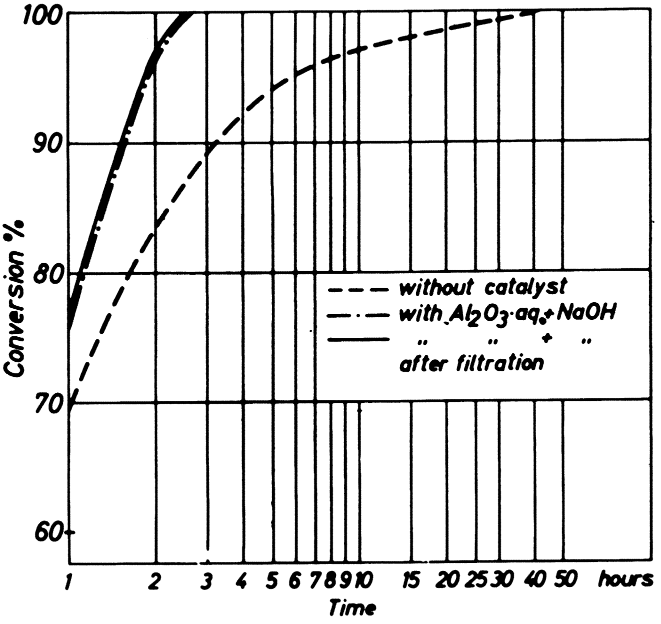

Figure 2. Esterification with and without alkaline Al_2O_3·aq. catalyst.

should have the same catalytic effect. This is actually the case. Here, mainly the alcoholates of the quoted metals are effective.

Temperature. The temperature of the reaction is important, for it is only above 180°C. that all catalysts and catalyst combinations are fully effective. With a reaction temperature of 160°C. and the use of an aluminum–sodium combination, for instance, the esterification, as compared to that of the purely thermal procedure, is 4.5 times faster; it is 20 times faster at 200°C. In order fully to use the catalytic effectiveness of aluminum hydroxide in case of alcohols with a boiling point below 180°C., it is necessary to work with the appropriate high pressure.

Catalytic Effect of Other Additives. Table I illustrates the catalytic effectiveness of different additives.

Table I. Catalytic Effect of Additives

Catalyst	*without*	$Al_2O_3\cdot$ *aq*	Al_2O_3 + *NaOH*	$Pb(OH)_2$	$Sn(OH)_2$	$Zn(OH)_2$	Sb_2S_3	H_2SO_4[b]	H_3PO_4[b]
Esterification-time, hours	45	7	2.5	4.5	7[a]	5[a]	7[a]	2.5	25
Color value mg. iodine/100 ml.	3–4	2	2	2–3	1	2–3	5	7	4

[a] To 99.6% conversion.
[b] 0.2% relative to Phthalic Anhydride.

During the appropriate tests phthalic anhydride was smoothly esterified with 2-ethylhexanol in the mole ratio 1:4. The reaction temperature rose to 200°C. after about 15 minutes, then rose slowly up to 210°C. till the end of the esterification. Table I shows the esterification time in hours after 99.9% conversion, while continuously removing the reaction water, according to the acid number relative to monooctyl phthalic acid. Furthermore, it indicates the ester colors according to the iodine scale in milligrams iodine/100 ml., whereby 1 mg. iodine/100 ml. can be more or less compared with a dye number of 120 APHA. Since, the values are obtained with the same starting materials, it is possible to compare the color numbers. They show that with the same times, the amphoteric catalysis achieves better colors than in the reaction course containing catalytically effective acids.

Furthermore, with amphoteric catalysis, no olefins or ethers are formed, which means that the dehydration of the ester alcohol is completely suppressed. This advantage becomes particularly important during the conversion of secondary alcohols, as during the formation process of di-cyclohexylphthalate.

Presumable Reaction Mechanism

In trying to formulate a reaction mechanism for the catalysis, the well known reaction of aluminum alcoholates with carboxylic anhydrides was used as a basis (*14*). For example, phthalic anhydride, maleic anhydrides, and carbon dioxide, will react so that the acid anhydride pushes itself between the metal atom and the alkoxy groups, thus separating them. This results in forming neutral aluminum salts of the monoalkyl carboxylic acids. It is possible, of course, for the conversion to proceed incompletely, having two alkoxy groups bound to the aluminum, thus having only 1 mole of acid anhydride react on 1 mole of aluminum alcoholate.

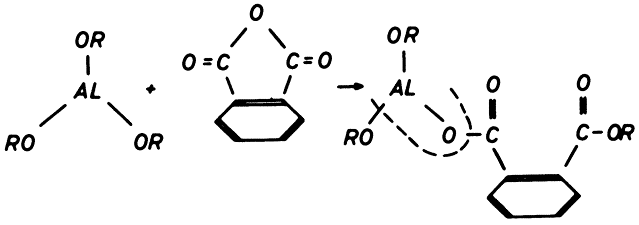

Figure 3. Reaction between alcoholate and phthalic anhydride.

Starting, for example, from aluminum tributylate, it is possible to distill pure phthalic acid dibutyl ester from this compound which results from an incomplete conversion, by heating it to 180°–200°C.—the usual esterification temperature. Regarding other esterification reactions, the gel-like reaction residue of the above decomposition is catalytically just as effective as aluminum hydroxide. However, this conversion does not serve as a basis for the reaction mechanism. One reason for this is that adding alkali during the formation of the addition compound led to the saponification of the ester grouping; on the other hand, it is questionable whether the oxide residue, left from the decomposition of the addition compound after splitting off the ester, will be able to bind alcohol again as alcoholate.

A reaction mechanism quite similar to the Claisen–Tishchenko and Meerwein–Pondorf–Verley reactions assumes tetravalent aluminum in an anionic complex and is more likely to correspond to the requirements.

If, for example, when manufacturing dioctyl phthalate, the reaction partners and the catalyst combination $Al_2O_3 \cdot aq. + NaOH$ are both present, it can be taken for granted that monoalkylphthalic acid anions and sodium cations exist.

As the first step of the catalyzed reaction series, the aluminum hydroxide suspended in the reaction liquid forms an aluminum complex with the acid anion, aluminum having the coordination number four in this complex.

Owing to its high organic content, the anion is soluble in the mixture of excess alcohol and monoalkylphthalic acid. The formation is stimulated by the tendency of the electron deficient aluminum to form an octet. The formation of such anions with tetravalent aluminum is certain for the aluminum alcoholates.

Therefore, it is not misleading to regard the above hypothetical intermediate stage as a complex formulated derivative of the alcohol soluble sodium aluminate $Al_2O_3 \cdot Na_2O \cdot 4H_2O$. The reaction is likely to continue in the following way: with a reaction temperature of 180°C. and higher, a hydroxy group of the aluminum is replaced by an alkoxy group in equilibrium; then finally, the alkoxy group approaches the positively polarized carbon of the carboxyl group, thus giving origin to the phthalic acid dialkyl ester. The remaining sodium and aluminum cations reform the original complex with monoalkylphthalic acid.

If, while formulating the theory, the valency angles are considered, and the alkoxy group is marked as a chain, the relationship to the six-ring complexes (*4*) formulated in the reaction of Meerwein–Pondorf–Verley and Claisen–Tishchenko is at once clear.

Contrary to the former reaction scheme, the six-ring structure of the intermediate compound leads to the assumption that the reaction, with a shifting of

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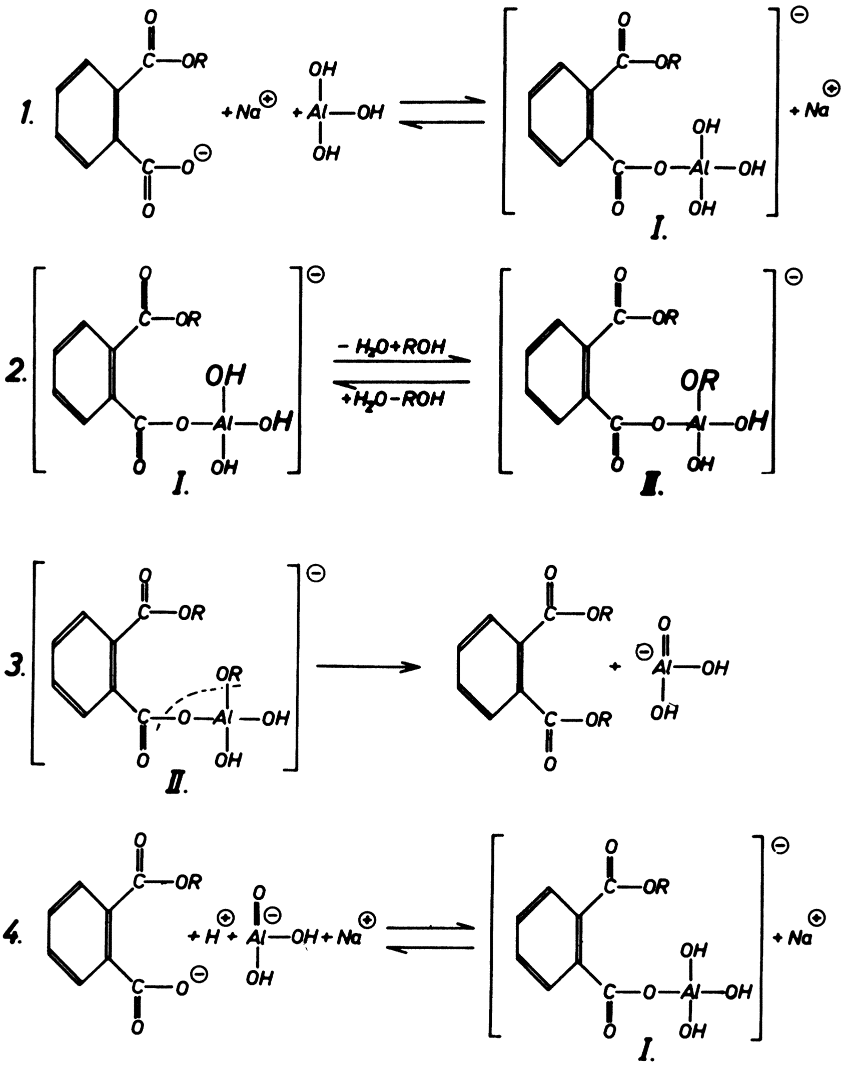

Figure 4. Presumed reaction mechanism.

synchronous electrons, results in a migration of an alkyl group, and not of an alkoxy group.

Transesterification

The next structural formula illustrates the course of a transesterification which proceeds smoothly and quickly if it is catalyzed with soluble aluminum salts found in the reaction medium, for instance, with basic aluminum stearate. In contrast to the conventionally catalyzed transesterifications by alkali alcoholate, the presence of free carboxylic acid does not have a negative effect. The catalyst

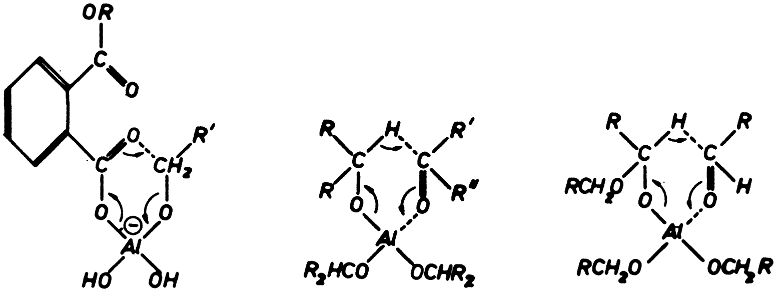

Figure 5. Hypothetical intermediary term II as six-ring complex.

is not sensitive to acid, as shown by the fact that the remaining acid is also esterified during the transesterification.

The anion is irrelevant for the catalysis. However, it participates in the reaction by producing ester. This fact confirms the correctness of the proposed reaction mechanism under discussion. If, for instance, *n*-butyl benzoate reacts with 2-ethylhexanol in the presence of a large quantity of basic aluminum stearate, distinctly detectable quantities of 2-ethylhexyl stearate can be found in the reaction product, and an equivalent amount of benzoic acid is found in the filtered aluminum precipitate.

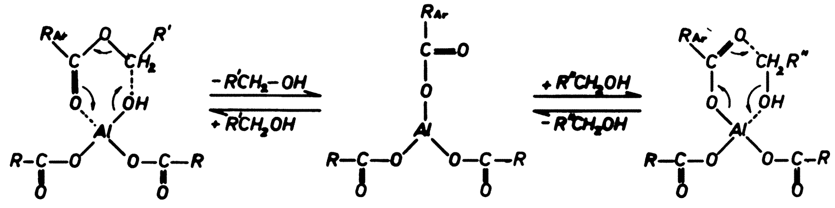

Figure 6. Transesterification.

R_{AR} = *Aryl* R' = *Butyl*

R = *Stearyl* R'' = *Octyl*

Other Metal Compounds

If, in these formulations, the aluminum, with its electron sextet and its tendency to form an electron octet, is decisive for the reaction course, the question naturally arises whether such a formulation also applies to the other metals which are catalytically effective. The answer is positive, returning to the starting point of the considerations, that is, to the existence of the complex $Na(Al(OH)_4)$. It becomes evident that similar addition compounds actually exist with other metals which are catalytically effective. Literature (*10*, *17*, *18*) on the subject describes among others, $HZn(OH)_3$, $H_2Pb(OH)_6$, nd $H_2Sn(OH)_6$.

If the study is extended beyond the hydroxy complexes to the alkoxy complexes (*17*), the following must be mentioned:

$HZn(OR)_3$ $H_2Mg(OR)_4$

$HFe(OR)_4$ $H_2Be(OR)_4$

In our structural formulas, zinc with its three ligands could, without any fundamental difficulty, take the place of the aluminum with four ligands. In this connection, attention may be drawn to the technical ethyl acetate synthesis according to Tishchenko, in which the catalytically active aluminum may be replaced in part, or even wholly, by zinc.

According to our findings, all soluble metal compounds of an amphoteric nature are effective esterification catalysts. If, when concluding the theoretical considerations, the amphoteric nature of the metals is described as their ability to function as cations in salts, and also to form anionic hydroxy or alkoxy complexes, this offers the possibility of using the reaction mechanism just discussed for all effective metals in a correspondingly modified manner.

Technical Performance

Technically, the process is being exploited in discontinuously operating units of stainless steel (similar to type 316) which are constructed in two ways. In one method, an esterification vessel is combined with a Raschig column, a heat exchanger to preheat the alcohol recycled for esterification by the vapors emerging from the column, and an air cooler. In a second type of esterification unit partial condensation of the water from the vapors is carried out. Contrary to the former process, neither an esterification column, nor a heat exchanger, nor an equipment for a subsequent separation of the reaction water, nor a reflux pump is needed.

The disadvantages of a discontinuous process are reduced to a minimum by automating both methods. At the end of each step (feeding, heating, esterification, and topping) the next step is started.

Feeding is carried out independent of time by quantity only; the following steps are conducted according to a timer.

The progress of the various steps (the temperature increase under constant pressure during the heating phase, or the pressure decrease at a constant temperature during the esterification and the topping period) is checked at specific times in order to ascertain the development up to that point.

If the standard and actual values differ, the operating staff is asked to intervene. In practice this does not happen, however, and hence, it is possible to limit the supervision to testing a sample after the process has been concluded. After the esterification phase, which proceeds to a conversion of 99.5%, the excess alcohol is topped under a pressure of 2 mm. as a final step. The crude ester received, having an acid number of about 0.1, is freed from the remaining acid in an agitated vessel. Here, copper plated steel has proved its worth as a construction material. A 25% solution of caustic soda is added, and then the product is dried under vacuum and, if necessary, brightened with small quantities of activated carbon. A high quality product will be obtained after filtering the solids in an automatically functioning settling filter with photometric quality control.

Intentions

In order to meet the requirements, a further unit is being prepared at present. This is intended to esterify alcohols C_4–C_6 which have comparatively low boiling points, under high pressure, and, which under normal pressure, would not allow the esterification temperature to rise to the point required.

Hüls Plasticizers

In Table II the technical effectiveness of the esterification process is demonstrated by specifying typical quality data for the most important Hüls plasticizers

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Table II. Quality Values of Hüls Plasticizers

	Butyl-stearate	*Dibutyl-phthalate*	*Dihexyl-phthalate*	*Hexyl-stearate*	*Dioctyl-phthalate*	*Octyl-stearate*	*Dinonyl-phthalate*	*Dicy-clohexyl-phthalate*
Acid value mg. KOH/g.	0.0	0.0	0.02	0.04	0.01	0.02	0.02	0.04
Hydroxylic value mg. KOH/g.	0.04	0.01	0.16	0.32	0.48	0.15	0.12	0.03
Boiling range 20 mm. °C	229.0–248.3	211.1–213.2	246.4–250.8	246.9–264.1	262.5–266.5	256.2–278.4	279.2–286.0	231.3–233.1
Analysis by Ester value %	100.0	99.9	99.7	99.0	99.8	99.1	99.1	99.7
Color value APHA	35	10	35	50	20	35	25	20
Volume-restivity 20°C	—	—	—	—	2.7	110	5.0	—
10^{11} ohm-cm. 50°C	—	—	—	—	0.6	40	0.6	—

and extenders as far as they pertain to our considerations. In all cases there are undistilled products. The high quality for the manufacture of electric insulations, especially for the standard plasticizers, can be seen from the data in the last five lines.

When using high purity ester alcohols, of a quality offered everywhere today, the favorable influence of our catalyst in achieving good plasticizer qualities is not so important as when recycle alcohols are used for the esterifications.

During the main manufacturing process it is possible, by using aluminum and sodium compounds, to feed the recycle alcohol more than 1000 times without risking an intolerable deterioration of the color number.

Alcohol Standards. The alcohols chiefly used are the acetylene derivates 1-butanol, 2-ethylbutanol, 1-hexanol, 2-ethylhexanol, and isononyl alcohol produced from octene by the oxo synthesis.

Table III gives a survey of the essential characteristics of the alcohols. It is remarkable that, despite the poor color value of the sulfuric acid test, esters can be obtained from the two hexanols with color values falling within the range of the platinum cobalt scale from 35 to 50.

Table III. Quality Values of Alcohols to be Esterified

	1-Butanol	*2-ethyl butanol*	*1-Hexanol*	*2-ethyl hexanol*	*Isononyl alcohol*
Acid value, mg KOH/g.	0.005	0.005	0.005	0.02	0.01
Ester value, mg KOH/g.	0.17	0.38	0.33	0.13	0.88
Analysis by hydroxylic value weight %	100.0	99.5	99.8	99.8	100.0
Carbonyl value, mg. KOH	0.07	0.43	0.43	0.04	0.03
Bromine value, g. Br/100 g.	0.01	0.01	0.02	0.01	0.02
H_2SO_4—Test Lovibond 6" Küvette					
yellow	0.2	4.9	9.0	0.4	0.8
red	0.0	0.6	1.7	0.1	0.1
Boiling range 760 mm. °C.	117.3–117.7	143.8–146.1	153.0–154.8	184.84–185.09	199.0–203.3

When the plasticizer plant was constructed, the extremely limited space forced the planners to utilize it most economically. According to the experience gained so far, it would be possible to build up a production of 6000 tons/month on an area of 2.300 sq. meters. This capacity limitation is due to the outside measure-

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ment of a central building which houses the agitated vessels with the respective filters, as well as the control room and the electric switch room.

The profitability of the process can be seen from the following figures which hold good for a plant producing 150 million pounds/year and referring to 1000 pounds.

Raw Materials

Phthalic Anhydride	392 lbs.
2-Ethylhexanol	685 lbs.
Catalyst and Chemicals	$1.98

Utilities

Power	13.6 kwh.
Cooling Water	1 300 gal.
Steam 285 p.s.i.g.	1 380 lbs.
Steam 50 p.s.i.g.	80 lbs.
Nitrogen 50 p.s.i.g.	40 cu. ft. (NTP)

Operating Expenses

Labor	0.5 hour
Maintenance	2.25% per year of total investment cost

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Polymeric Plasticizers

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Polymeric plasticizers can be made by: (1) Internal plasticization whereby a monomer is copolymerized with one which tends to yield soft polymers by itself; (2) Mechanical mixing of a polymerizable monomer with a polymer, followed by polymerization; (3) Mechanical blending of two compatible polymers. In many cases it is necessary to combine the polymeric plasticizer with a liquid plasticizer because the compatibility of polymers with each other is generally limited. From the industrial polymeric plasticizers, especially polyesters of low degree of polymerization and several copolymers of butadiene with acrylonitrile, acrylic acid esters and fumaric acid esters were studied. These polymeric plasticizers are characterized by good compatibility and improved cold resistance of the final product.

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The properties demanded from a plasticizer are extremely complex. For each application of a plasticized polymer, one or the other of the properties has special importance. Practically, the following properties must be considered:

1. High plasticizing effect in as low as concentration as possible.
2. Low volatility and high binding fastness without decreasing the mechanical properties.
3. Good fastness to light, solvents, and low temperatures.

Plasticizers should be nontoxic, free from odors, and compatible with pigments and dyestuffs. In addition they should have good electrical properties, high insulation resistance, low dielectrical losses, and resistance to high temperatures.

With these many requirements, it is obvious that each group of polymers has its own plasticizers, although some types of plasticizers have been developed which are suitable for several plastics. They belong to the groups of esters, ketones, ethers, acetals, epoxides, and nitrogen containing compounds like the sulfonamides.

Not one known plasticizer can fulfill all of these requirements for practical applications. Liquid plasticizers with good general properties and low viscosity are likely to show bad aging properties owing to volatility on storage for long periods. This is one reason why the plastics industry is interested in polymeric plasticizers. They can be applied by the following methods:

1. By internal plasticizing, using products with long unpolar side groups, or by copolymerization with components of low polarity.
2. By mechanically mixing the polymer with a polymerizable monomer and subsequent polymerization.
3. By mechanically mixing the polymer with another compatible polymer, eventually in combination with liquid plasticizers.

It was obvious to turn at first to the oligomers of the polymer, because these were expected to have good compatibility, low volatility, and light fastness. Of course, the molecular weight of polymeric plasticizers must range within strict limits that is, between 1000 and 30,000—but molecular weights from 1000 to about 8000 give the best effects. According to Jones (*4*), the efficiency of a plasticizing substance decreases with increasing molecular weight. Therefore, it is often necessary to combine high molecular plasticizers with low molecular weight plasticizers. The second-order transition point, which is decreased by the plasticizer, can be used as a measure of the efficiency of a plasticizer.

The principal polymeric plasticizers are the polymer hydrocarbons and the polyesters. The condensation products of diols and dicarboxylic acids, belonging to the polyester group, are most important. Higher functional compounds, like triols and tricarboxylic acids, are less important as are polyethers, polyacetals, and polymeric acids.

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Internal Plasticization

Polymerization products with internal plasticization have the advantage that there is no migration or efflorescence of the plasticizer on storage. On the other hand, the mechanical properties—above all, flexibility at low temperatures—are decreased in comparison with the products with low molecular plasticizers. This is because mobility in the solvatized molecules is diminished. The same refers to tensile strength, which is often decreased with internally plasticized polymers. In this respect they are inferior to externally plasticized products, which also have an advantage in that type and quantity of plasticizer can be varied widely. Internally plasticized products must have a definite ratio of components. These are reasons why combinations of both types of plasticizers are preferred.

Internal plasticizing demands a chemical relationship between the components which constitute the product. Therefore, good effects can be expected from copolymers of styrene and isobutylene, ethylene, or diolefins like butadiene or isoprene. Internal plasticizing of PVC can be effected by copolymerizing vinyl chloride with acrylates of higher alcohols or maleates and fumarates. The important ABS products are internal copolymers of butadiene, styrene, and acrylonitrile. The hardness of the unipolymers of styrene and acrylonitrile can be modified by butadiene which, as a unipolymer, gives soft, rubberlike products. As the copolymerization parameters of most monomers are known, it is relatively easy to choose the most suitable partner for the copolymerization. When the product of the r—values is 1, there is an ideal copolymerization, because the relative reactivity of both monomers toward the radicals is the same. Styrene/butadiene, styrene/vinyl thiophene, and methyl methacrylate/2.5-dichlorostyrene show similar behavior in copolymerizations.

Combination of a Polymer with Another Polymerizable Monomer

The application of polymeric plasticizers can be effected by mixing a preformed polymer mechanically with a polymerizable monomer containing the catalyst and subsequent polymerization. But side reactions, like grafting, must be expected. Generally, this method has not found wide application because the resulting products are likely to show poor mechanical properties. Besides, mixing the monomer on the rolls or in the extruder leads to losses by evaporation and causes unpleasant odors. Furthermore, some of the more important monomers, like the acrylates, show poor compatibility with many polymers. For instance, PVC is not sufficiently plasticizable with acrylates.

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Combination of Polymers with Other Compatible Soft Polymers

This type of plasticization is important and several groups of polymers have been suggested for this method: polymer hydrocarbons; polymer halogen-containing hydrocarbons; polymers containing ester groups; polyvinyl ethers and acetals, and some other polymers of different constitution.

Among the aliphatic polyhydrocarbons, polyisobutylene with a molecular weight between 1000 and 30,000 was suggested for hard polymers like chlorinated rubber, polystyrene, and PVC by I.G. Farbenindustrie in 1932.

Standard Oil Co. claims the use of polyisobutylene as a plasticizer for polyvinyl acetate. Copolymers of isobutylene with vinyl ethers and other monomers are mentioned in several patents. For synthetic rubbers, oligomers of butadiene are claimed. Rubberlike polyolefins (10 to 50% is sufficient) are used extensively for plasticizing phenolic resins to increase impact strength.

If the polymers and the polymeric plasticizers are prepared by emulsion polymerization, incorporating the plasticizer can be simplified if the mixture of both emulsions is coagulated and processed further.

In line with the importance of plasticized PVC, the polymeric plasticizers are important for this field. Standard Oil Co. has patented a copolymer of 50 to 90% butadiene and 50 to 10% acrylonitrile, prepared in emulsion in the presence of octyl mercaptan as chainstopper regulator. The copolymer is a viscous oil (molecular weight of 13,000), which can be mixed with PVC in a ratio of 20 to 40%. According to another patent (*3*), the molecular weight of such plasticizers should not exceed 80,000. This can be controlled by using larger amounts of chain stoppers, higher polymerization temperatures, or with low conversion rates. The commercial Geons are latices of this type.

To control compatibility and other properties of butadiene/acrylonitrile copolymers with PVC, there is an optimum acrylonitrile content of 37%. For practical handling, the nitrile rubber is treated on rolls at normal temperatures, and afterwards the mixture is rolled with PVC at elevated temperatures. The reverse process—plasticizing PVC first and mixing with nitrile rubber afterwards—is not so favorable because discoloring and decomposition may occur. This can be avoided by simultaneously applying the liquid plasticizers. Nitrile content influences the tensile strength of PVC films with nitrile rubber. For example, tensile strength of 200 kg./sq. cm. is produced by the following mixtures:

PVC, %	+	Copolymers, %,	+	Acrylonitrile, %
90		10		11.7
85		15		19.6
80		20		28.0
70		30		37.0
50		50		49.8

Copolymers with less than 49.8% acrylonitrile have poor tensile strength. The acrylonitrile is obviously responsible for the interaction between the paraffinic butadiene and the polar PVC.

Similarly acrylonitrile content influences elongation; 400% elongation is obtained with the following mixtures:

PVC, %	+	Copolymer, %	+	Acrylonitrile, %
19		81		11.7
25		75		19.6
30		70		28.0
35		65		37.0

Retention of elongation reaches a maximum at 35 to 50% copolymer content. Higher butadiene content in the copolymer gives increased softness and elasticity. According to experimental data, the copolymer with 37% acrylonitrile has optimal efficiency in handling, homogeneity, and mechanical properties. This composition corresponds to a molar ratio of 1.5 mole of butadiene to 1 mole of acrylonitrile.

Similar results are obtained with copolymers of vinyl acetate, acrylates, and maleates. The addition of small amounts of liquid plasticizers improves the surface gloss and smoothness of the films. The brittle point is excellent, and it is possible to get values down to −62°C. with 40 to 45% of the plasticizer combination.

Another advantage of nitrile rubbers that contain PVC combinations is that they are nontoxic and not influenced by mineral oils. Water vapor permeability is also good.

In practice, most PVC combinations are made with equal amounts of nitrile rubber and dioctyl phthalate. These combinations show good aging properties and cold resistance, but light fastness cannot be improved because of the oxidation of the double bonds contained in the diolefins.

Other copolymers that are used instead of nitrile rubber are, for instance, chlorinated polyethylene which, in combination with PVC, gives the commercial product, Hostalit Z, of Farbwerke Hoechst.

In contrast to the polymers and copolymers of butadiene, the oligomers of aromatic olefins, like styrene, are not compatible with PVC. Oligomers of alkylated polystyrenes are a little better, especially in combination with other liquid plasticizers. Copolymers of styrene and isobutylene are not suitable for use with PVC.

Efforts have been made to use the low molecular weight PVC obtained by polymerization in solution, but the results were disappointing. On the other hand, according to a publication (*1*), copolymers of vinyl chloride and allyl chloride are suitable. These copolymers can be prepared with low molecular weights (up to 1000) and can be combined with vinyl chloride to give oils with good properties.

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Furthermore, oligomers of vinyl chloride/vinyl acetate copolymers with molecular weights between 8000 and 15,000 have been suggested for PVC. Also copolymers of vinyl chloride with styrene, combined with dioctyl phthalate (DOP), are reported to have good properties. Another liquid polymer of allyl chloride and allyl acetate with a molecular weight of 470 shows good compatibility with PVC and gives films with good mechanical properties. Polyfluorolefin oligomers of monochlorotrifluoroethylene with a polymerization degree of 4 to 16 have been recommended as well.

Among the polymeric plasticizers, those with ester groups have the greatest importance. They have generally good compatibility and stability. Low molecular weight polymers of vinyl acetate have been used for plasticizing cellulose esters. Polyallyl acetate can also be used as a plasticizer for PVC. Higher molecular weight polyallyl esters from polyallyl butyrate to allyl laurate have been recommended for cellulose esters. Copolymers of ethylene and vinyl acetate with molecular weights of 350 to 1200 have been suggested for PVC; good cold resistance is mentioned for these combinations.

For cellulose nitrate, polyacrylates of higher alcohols have proved to give very smooth and transparent films. Good results are obtained with polybutyl acrylate and polyethylhexyl acrylate. The polyacrylates of higher alcohols can be used as plasticizers for rubber. Oligomers of acrylates can not be used in combination with PVC, because they give only hard films.

Among the polyesters that are used for PVC, the copolymers of butadiene with ethyl fumarates and ethyl acrylates deserve mention. They have been produced by Badische Anilin-und Sodafabrik (BASF) under the commercial name Palamoll. Palamoll I consists of 75% diethyl fumarate and 25% butadiene; Palamoll II contains equal parts of butadiene and ethyl acrylate. In combination with the same amount of liquid plasticizers (such as DOP), films with cold resistance down to −60°C. can be produced. These products are especially important for cable insulation because of their good dielectric properties. The Palamoll products are produced by emulsion polymerization and can be directly combined with emulsions of PVC.

Copolymers of itaconic esters with butadiene have not yet been used technically. On the other hand, acrylonitrile containing copolymers with other components have been studied from several points of view. Standard Oil Co. has claimed a terpolymer of isobutylene, butadiene, and acrylonitrile, and BASF a similar product of butadiene, acrylonitrile, and styrene. The films from these combinations are said to have high flexibility and cold resistance. However, all butadiene containing copolymers are not light fast. Copolymers of butadiene, acrylonitrile, and unsaturated dicarboxylic esters are suggested for plasticizing PVC, but they must be thermally degraded before they are combined with the polymer.

The good solubility of the polyvinyl ethers in polar and nonpclar solvents was useful for the combination with nitrocellulose, whereby the water solubility of the polyvinylmethyl ether has no influence. Polyvinyl ethers have low compatibility with many polymers and therefore are mostly combined with other compatible plasticizers. As they are nontoxic they can be used in food packaging.

Other ethers suggested as plasticizers are the oligomers of epoxides—for instance, the polymers of glycerol allyl ethers and the polymers of 1,3-dioxolane. These products do not seem to have practical importance.

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Heat-setting resins cannot be plasticized by low molecular weight plasticizers. Polyvinyl acetals have been claimed for these products. American Cyanamid Co. has suggested polyvinyl acetals or butyrals in an amount of 10 to 25% of the resin for urea and melamine resins. For varnishes and adhesives, combinations of phenolic resins and polyvinyl formal are recommended. Polyvinyl acetals with higher alkyl radicals are suitable for cellulose esters and improve elasticity as well as resistance against water.

A Du Pont patent (*2*) describes a colorless, viscous polyacetal from the divinyl ether of 1, 5-pentanediol and subsequent acetalization. This product can be used for cross-linking polyvinyl alcohol films.

Polyesters

A variety of polyesters can be prepared from dicarboxylic acids and glycols, of course, although compatibility with polymers decreases with increasing molecular weight.

The esters of polyglycols with higher fatty acids are suitable for plasticizing cellulose esters. Polyethylene glycol dilaurate with a molecular weight of about 900 has been claimed for copolymers of vinyl chloride with vinyl acetate, whereby films with good tensile strength and a brittle point of −42°C. can be obtained. The esters of pentaerythritol with higher fatty acids can be used for plasticizing vinyl polymers. The acid esters of polyols with dicarboxylic acids can be esterified with a monovalent alcohol to give neutral products with improved properties. For instance glycerol sebacate, which is esterified with octanol, has proved to be a good plasticizer for PVC.

Recently, polymer esters derived from azelaic esters and glycols were introduced by Unilever-Emery; these show better compatibility and resistance to saponification compared with the polymer adipic esters.

The typical polyesters from dicarboxylic acids and polyalcohols, especially glycols, which have no tendency to crystallize, are suitable as plasticizers for PVC. The well known polyesters of the alkyd type obtained from glycerol or glycol with phthalic acid have been recommended for PVC by I.G. Farben but have not found practical application.

Polyesters from propylene glycol and dicarboxylic acids, especially adipic and sebacic acid, are commercial products suggested for PVC as well as for cellulose esters. The well known Paraplex resins of Rohm & Haas, which are compatible with nitrile and GRS rubber, belong to this group. Other products are the Ultramolls of Farbenfabriken Bayer. Some polyesters of this type have a tendency to exude on storage, especially if esterification is not complete.

Sebacic acid is important as a component for compatible polyesters, especially in combination with higher glycols like 1,3- or 1,4-butanediol. Secondary OH-groups in the ortho position of the glycol decrease compatibility.

The gel time for PVC varies within wide limits, depending on the structure of the ester (Table I).

The different polyesters derived from sebacic acid show widely different viscosities which have no great influence on the yield curve. Therefore, the general opinion that the efficiency of a plasticizer depends only on its viscosity is not justified. The polyesters derived from sebacic acid do not have the same good behavior in cold as the corresponding esters have with monovalent alcohols. This is due to their tendency to crystallize. For instance, the brittle point of PVC with 35% dibutyl sebacate is −70°C., whereas polypropylene glycol sebacate with molecular weights of 7000 has a brittle point of only −19°C., and this can reach −37°C. with higher amounts (50%). The polyester plasticizers are better than the usual phthalates for light stability. They are also more stable against solvents and oils. Stability against fuels and mineral oils varies with the nature of the polyester. The glycol adipate with molecular weights of 2000, for instance, can be extracted to 7% with normal fuel.

Table I. Gel Time (GT) and Gel Temperature (Gt) for Mixtures of PVC and Polyesters

Composition of mixture	*GT, sec.*	*Gt, °C.*
50 Paraplex G50 (Ethylhexyl adipinate)	283	138
50 Adipinate	106	126
50 Phthalate	71	118
60 Paraplex G50	274	126
60 Adipinate	—	—
60 Phthalate	92	121
25 Phthalate + 10 adipinate + 15 Paraplex G50	85	126
25 Phthalate + 10 trikresyl phosphate + 15 methylacetyl ricinoleate	55	115
15 Phthalate + 10 adipinate + 10 Paraplex G50 + 15 alkylacryl phosphate	54	115

A polyester of adipic acid and a mixture of isomer polyethylene glycols shows good compatibility with cellulose esters, chlorinated rubber, and PVC.

Polyesters from γ, γ-dibutyric acid and 1,3-butylene glycol (Plastomoll TB of BASF) is in practical use for PVC and gives combinations with low brittle points. From sulfonyl dibutyric acids and glycols, BASF has developed a liquid polyester (molecular weight about 1000), which is compatible with several polymers. Many other combinations are possible—for instance, use of the oxethylated products of carboxylic acids and polyalcohols, which have not yet been fully investigated.

Polyesters which can be cross linked can be made from maleic acid with unsaturated alcohols. They can be incorporated as sirupy prepolymers and transformed into the insoluble elastic end product by heating. For plastisols, Monsanto has developed Santoset I, which has little odor and good storage properties. Rohm & Haas, Borden Chemical Co., and Santomer Resins have introduced polymethacrylates of polyols as cross linking plasticizers. X970 of Rohm & Haas is 1,3-butanediol dimethacrylate, SR350 of Santomer Resins is trimethylolpropane trimethacrylate, and the Borden product is tetraethyleneglycol dimethacrylate. In our own laboratory, we studied the allylesters of polycarboxylic acids—that is, of butene–1,2,3,4–tetracarboxylic acid. The results were not very promising.

The products of amino alcohols and polycarboxylic acids contain an ester and an acid amide group.

Finally, the water-soluble polyesters of phosphoric or boric acid with glycols or glycerol should be mentioned. They can be used in combination with water-soluble polymers like polyvinyl alcohol, polyacrylamide, and polyvinyl pyrrolidone.

It is obvious that the field of polymer plasticizers still offers many possibilities that can lead to interesting and valuable results, but it seems certain that they will not attain the same importance as have the low molecular weight products.

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Plasticizer Analysis Using Chromatographic Methods

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Plasticizer analysis is indispensable in establishing the purity of technical plasticizers and determining the chemical nature of plasticizers in finished and semi-finished articles. When plastics are used for food packaging and similar purposes, only certain nontoxic substances are acceptable as plasticizers, and this is why health authorities take an active interest in plasticizer analysis. Requirements such as these have promoted the development of analytical methods that are as simple and as time-saving as possible. This article deals with the present art of plasticizer analysis—its methods and problems—based on the literature as well as on the results of the author's own investigations.

Among the numerous auxiliaries used in converting high polymers, plasticizers, on a percentage basis, rate high, because many polymers become technically high grade substances only when plasticizers are added to them. For this reason, chemists have searched for suitable agents that efficiently combine plasticizing action with other requirements. In the past few years, thousands of substances, including many types of chemicals, have been recommended as plasticizers, and plasticizer analysis has become a complicated problem. Fortunately for the analyst, only about 300 of these plasticizing substances are produced on an industrial scale, and of these 300, only 100 are important in converting high polymers; the others are specialized products.

Plasticizer production figures indicate the relative value of different groups of these materials and point up some substances that may rate special attention. Table I gives plasticizer production in the U. S. in 1960. Although all production figures since then show considerable growth, the relationships between groups remain fairly constant. The figures show that nearly all plasticizers chemically are esters: esters of phthalic acid account for 57% of total plasticizer production in 1960; esters of phosphoric acid account for 11%; and esters of five aliphatic mono-

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and dicarboxylic acids for 10%; the remaining 22% represents a wide range of monomeric and polymeric compositions with plasticizing capacity. Most of these also belong to the ester group. Thus, plasticizer analysis consists primarily of describing the characteristics of esters and determining their acid and alcohol components.

Table I. U. S. Production of Plasticizers—1960

	Tons Produced	*Total*
Cyclic Plasticizers		
Phosphoric acid esters		24,891
Tricresyl phosphate	14,748	
Phthalic acid esters		156,512
Dibutyl phthalate	8,601	
Diethyl phthalate	7,612	
Diisodecyl phthalate	16,134	
Dioctyl phthalates, total	77,280	
All other cyclic plasticizers		20,511
Total		201,914
Acyclic Plasticizers		
Adipic acid esters	10,050	
Azelaic acid esters	3,312	
Oleic acid esters	2,823	
Phosphoric acid esters	4,308	
Sebacic acid esters	6,257	
Stearic acid esters	5,579	
All other	39,126	
Total		71,455

Plasticizer analysis requires use of both physical and chemical methods. Prior to analysis, mixtures must be separated. But plasticizers often have such low vapor pressures and high boiling points that standard separations—distillation and crystallization—are not adequate, and the analyst must use chromatographic separations. Currently, the most popular of these methods are:

1. Column chromatography
2. Paper chromatography
3. Thin layer chromatography
4. Gas chromatography

Some plasticizer mixes require pretreatment, such as saponification, but in most instances chromatographic separations can be accomplished with the mix. In addition to the usual identification of substances by organochemical analysis, other methods now being used include color tests, physical tests (determinations of boiling point and refractive index), and infrared and ultraviolet spectroscopy.

Chromatographic Methods for Separating Plasticizers

All chromatographic methods are based on a two-phase partition of the substances or mixtures to be separated. Hence these separating methods utilize differences in physical properties of the components. Liquid adsorption chromatography (now referred to as column chromatography) uses silicious gel or aluminum oxide as the solid phase. Paper chromatography is essentially a liquid-liquid partition; one phase, in most cases, is represented by water adhering to paper, while the eluent represents the second phase. Gas chromatography, as gas adsorption chromatography, adsorbs gaseous substances on solids, mostly inorganic materials such as diatomaceous earth. However, as gas partition chromatography, it fixes the liquid phase to a solid substrate by impregnation; organic substances with high boiling points are best suited for the liquid phase. Thin layer chromatography is not easily classified. However, it works more like partition chomatography than like pure adsorption chromatography.

Column Chromatography. Among chromatographic methods, adsorption to solid adsorbents (almost exclusively carried out in columns) has been popular because it can be used on a laboratory scale in connection with syntheses. It is, therefore, also used extensively for separating and purifying mixtures. But the technique is not effective for separating the diverse chemical components that are found in plasticizers. Nevertheless, some results of adsorption chromatography studies are included here because the method is related to thin layer chromatography, which has become an important development in plasticizer analysis. Sease (*22*) has adsorbed dimethyl and dibutyl phthalate in a silica gel column on a milligram scale with a zinc sulfide—zinc silicate fluorescence indicator. The different zones of the column material were eluted with diethyl ether.

Cachia and his team (*9*) describe the column chromatographic separation of polyvinyl chloride plasticizers. The plasticization agent in the eluate was identified by infrared spectroscopy. These authors expressly state that chromatography is useful for separations only; it is not intended to identify substances. However, they mention that spectroscopy, in the future, may be replaced by combining refractive index data with color tests.

Their investigation showed that carbon tetrachloride and isopropyl ether can be used as eluents in separating various types of plasticizing agents. The column used was 30 cm. long and 1 cm. in diameter. It was filled with 5 grams of silica gel 200/300 and Celite 545 in equal portions. Two drops of the plasticizer mixture, dissolved in 1 ml. of carbon tetrachloride, were then added to the top of the column for the separation. Some further tests (*4*), aimed at adapting these methods to the analysis of larger quantities—for example 100 mg. Under similar conditions, with methylene chloride as eluent, dimethyl and dinonyl phthalates have been adsorbed in a silica gel column (Merck). However, the technique is not really suitable for separating unknown substances when there are a large number of possible components. These tests do prove that, in principle, inorganic adsorbents can be used to separate components, provided that sharpness of separation is improved and that simpler identification methods are developed for the separated substances.

Thin layer chromatography, as a kind of chromatography in open columns, has been upgraded to a simple technique in the last few years. But column chromatography obviously does not deserve this much attention in connection with plasticizer analysis.

Paper Chromatography. For some time, paper chromatography has provided an analytical method for identifying organic substances, and the technique is still significant. But the literature includes only two reports that deal with the separation of polyvinyl chloride (PVC) plasticizers. The reason for this lack of interest may be that it is often difficult to recognize plasticizer spots on the chromatographic paper after migration.

Burns (*8*) has succeeded in chromatographically fixing a large number of plasticizers on a paper impregnated with 14% PVC and in identifying them by their

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R_F values. Chromatography without pretreated paper, however, has not given satisfactory results.

Chromatography has been carried out ascendingly with a mixture of pyridine, ammonia, isopropyl alcohol, and water as eluent. At the starting point, 0.001 ml. of the plasticizer mixture was applied, and the chromatography was completed within eight hours. The paper subsequently was dried in hot air at 85° C. and then, at room temperature, was gradually treated with Universal indicator solution (British Drug House).

An exact analysis of plasticizers according to this method involves fluctuations in the R_F values, characterized by the authors as "daily deviations." To eliminate these fluctuations the authors related their R_F values to tricresyl phosphate (of high meta content) with a mean R_F value equated to 0.66.

Figure 1 gives the corrected R_F values for a number of plasticizers and a chart showing location of the spots. The data prove that in certain cases separations have been achieved which entirely meet the analytical purposes. However, the important groups of the phosphates, phthalates, and some of the sebacates and adipates have not been sharply separated. Binary mixtures of phosphates are not at all separatable according to this method, and the degree of separation observed with other

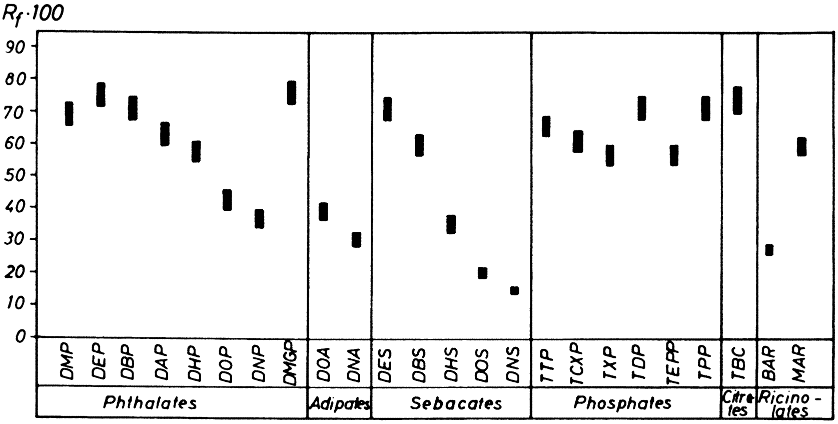

Figure 1. Paper chromatography of plasticizers (8)

DMP = Dimethyl phthalate
DEP = Diethyl phthalate
DBP = Dibutyl phthalate
DAP = Diamyl phthalate
DHP = Dihexyl phthalate
DOP = Dioctyl phthalate
DNP = Dinonyl phthalate
DMGP = Dimethylglycol phthalate

DOA = Dioctyl adipate
DNA = Dinonyl adipate

DES = Diethyl sebacate
DBS = Dibutyl sebacate
DHS = Dihexyl sebacate
DOS = Dioctyl sebacate
DNS = Dinonyl sebacate

TTP = Tritolyl phosphate
TCXP = Tritolyl(xylenyl) phosphate
TXP = Trixylenyl phosphate
TDP = Tolyl diphenyl phosphate
TEPP = Tri(ethylphenyl) phosphate
TPP = Triphenyl phosphate
TBC = Tributyl citrate
BAR = Butyl acetyl ricinoleate
MAR = Methyl acetyl ricinoleate

mixtures remains below the differences between the R_F values of the respective pure substances. With ternary mixtures the results are even more uncertain. And the method has one great disadvantage—the technique is too complicated. Apart from the comparatively long chromatographic propagation period, the preparation of the paper itself is difficult. Further, thin layer chromatography can be performed in a much shorter period and the results are at least as satisfactory as those furnished by paper chromatography.

Gude (*13*) has developed a method for plasticizer separation which resembles the one developed by Burns (*8*). With an eluent mixture from acetone and water, the spots show even less tail formation; Gude argues that acetone makes the PVC swell on the paper; hence, the PVC acts as a stationary phase while the acetone-water mixture represents the mobile phase.

Chromatography can be carried out either ascendingly or descendingly. After a period of two to four hours the solvent front has migrated 20 to 23 cm. The paper is dried in a drying cabinet at 100°C., and the spots are made visible either by dipping into iodine vapor or, better, by spraying the paper with a solution of 0.2% N,N,N',N'-tetramethyl–4,4'-diaminodiphenyl methane in methanol and subsequent drying at 100° C. The paper then is iodized in iodine vapor, and the plasticizer spots appear white to blue on a slightly gray-bluish background. The R_F values fluctuate within 10%. With oval-shaped spots, a second chromatogram can be obtained in a direction vertical to the first one; uniform substances migrate in parallel to the second baseline, while substances that differ from each other are recognized by different migration rates at both ends of the oval-shaped spots. With two-dimensional chromatography, however, the spots can only be made visible by dipping the paper into iodine vapor. The contours of the spots are outlined carefully with a pencil, and the iodine is removed by exposure to air before the second elution chromatography begins.

Thin Layer Chromatography. While column chromatography is used successfully for separating larger quantities of substances, its adaption to small quantities has met with difficulties. It has been tried in a so-called "open column" method, where substrates such as silica and starch are applied to glass plates in thin layers. The substrates are pasted with water, applied to the glass plate, and subsequently dried. But poor adhesive capacity between layers and glass plates and the varying thickness of the layers, involving essential differences in migration rates, were strong handicaps. Stahl (*23*), however, has made thin layer chromatography a simple, quick, easy-to-handle procedure by developing efficient spreader equipment. Now the layers of substrate can be applied to the plates in consistent thickness—generally 250μ.

In plasticizer analysis, silica gel with gypsum added has proved to be the most recommended substrate. As to the chromatography itself, the plasticizers, to be examined in 1 to 5 % benzene or ether solution, as dots, are applied 1.5 cm. from the lower edge of the plate; in most cases 2 cu. mm. of the 5% solution serves this purpose. The solvents quickly evaporate; evaporation rate can be speeded up in a hot-air flow from blower or fan. At 10 cm. from the starting line, a boundary is marked. The eluent is allowed to migrate to this point, which is usually reached in 20 to 45 minutes. Migration distances of more than 10 cm., instead of being advantageous, may prolong the migration period.

Peereboom (*17*) and Braun (*3*) were among the first to adapt thin layer chroma-

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tography to the problems of plasticizer analysis. Peereboom examined mainly products approved by the U. S. for use in food packagings and a few other technically important plasticizing agents. In pasting the silica gel, he adds 0.005% of a water-soluble fluorescence indicator (such as Ultraphor from Badische Anilin-u. Sodafabrik; after migration the spots are identified in ultraviolet light and therefore need not be visible. Table II gives the substances examined and their R_A values, each determined with three different eluents. The so-called "R_A values" are related to dibutyl sebacate, whose value at random is assumed to be 1. Certain fluctuations, due to slight differences in the quality of the plates, thus can be eliminated. Peereboom states that the variations may be as large as 0.06, and this statement has been

Table II. Relative R_A Values;[a] of Some Plasticizers in Four Solvent Mixtures

Eluents	Parts by volume
1. Isooctane	9
Ethyl acetate	1
2. Benzene	0.5
Ethyl acetate	5
3. Dibutyl ether	4
n-Hexane	1
4. Methylene chloride	

	R_A values			
Phthalates	*Eluent 1*	*Eluent 2*	*Eluent 3*	*Eluent 4*
Dimethyl	0.30	0.65	0.36	0.98
Diethyl[b]	0.51	0.79	0.60	—
Dibutyl	0.75	1.03	0.92	1.33
Dihexyl	1.00	1.32	1.10	1.54
Dioctyl	1.14	1.47	1.22	1.65
Dinonyl	1.02	1.43	1.15	1.63
Didecyl	1.06	1.41	1.15	1.60
Di(2-ethylhexyl)	1.13	1.46	1.20	1.63
Benzyl butyl	0.72	1.05	0.87	1.21
Di(methoxyethyl)	0.053	0.13	0.07	1.73
Dicyclohexyl	0.72	1.07	0.92	1.13
Dimethylcyclohexyl	0.81	1.13	1.00	1.23
Diisodecyl	1.08	1.46	1.16	1.61
Diisononyl	1.03	1.44	1.20	1.62
Ethyl phthalyl ethyl glycolate[b]	0.22	0.66	0.30	—
Butyl phthalyl butyl glycolate[b]	0.43	0.90	0.65	—
Adipates				
Dioctyl	1.14	1.33	0.98	1.02
Di(2-ethylhexyl)	1.17	1.27	1.02	1.06
Dinonyl	1.09	1.16	1.00	1.07
Benzyl octyl	0.47	0.82	0.59	
	0.80	1.03	0.86	1.06
	1.16	1.27	1.08	
Polyadipate	0.00	0.00	0.00	0.05
Diisobutyl adipate[b]	0.83	0.86	0.85	—
Sebacates				
Dibutyl	1.00	1.00	1.00	1.00
Dioctyl	1.31	1.50	1.20	1.49
Di(2-ethylhexyl)	1.40	1.53	1.20	1.48
Polysebacate	0.00	0.00	0.00	0.05
Phosphates				
Trichlorethyl	0.04	0.08	0.03	0.255
Trioctyl	0.41	0.47	0.62	0.49
Diphenyl octyl	0.41	0.72	0.65	0.89
Triphenyl	0.29	0.75	0.58	0.99
Diphenyl cresyl	0.35	0.82	0.63	1.08
Tricresyl	0.41	0.875	0.73	1.13
2-Ethylhexyl diphenyl[b]	0.46	0.77	0.58	—

In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

Citrates				
Triethyl	0.16	0.23	0.13	0.255
Tributyl	0.37	0.45	0.39	0.30
Acetyl triethyl	0.255	0.40	0.22	0.32
Acetyl tributyl	0.60	0.91	0.61	0.50
Acetyl tri(2-ethylhexyl)	1.10	1.53	1.24	0.98
Different Plasticizers				
Butyl stearate[b]	1.61	1.23	1.28	—
Methyl acetyl ricinoleate	0.80	1.00	0.835	0.85
Butyl acetyl ricinoleate	1.02	1.23	1.104	1.03
Benzenesulfonic acid butylamide	0.22	0.575	0.39	0.83
Benzenesulfonic acid-*N*-methylamide	0.04	0.31	0.13	0.51
Di(2-ethylhexyl)thiodibutyrate	0.82	0.94	0.955	0.79
(2-Ethylhexyl)-p-hydroxybenzoate	0.36	0.45	0.84	0.34
Glyceryl triacetate	0.16	0.245	1.19	0.28

[a] R_A value = R_F value with reference to dibutyl sebacate

[b] From J. W. C. Peereboom (17).

confirmed by independent tests (*3*). Meanwhile a number of other plasticizers were examined with the same eluents (*7*); these R_A values are also shown in Table II.

According to Braun (*3*), methylene chloride is a good eluent for thin layer chromatography of plasticizers and is easier to use than mixed systems. The methylene chloride R_A values (Table II) are related to dibutyl sebacate (R_A = 1). The R_A values determined in methylene chloride are also shown in Figure 2 to furnish a clear picture of its separating possibilities. As expected, the polymeric plasticizers do not migrate. Of the usual low molecular weight plasticizers, the esters with different alcohol residues are distinguished clearly by differences in length, but isomers or similar compositions can not be separated—the R_A values of octyl- and 2-ethylhexyl-esters, for example, are practically identical. Hence in these cases other separating methods must be adopted.

Spots on thin layer chromatograms can be identified according to the method specified by Peereboom (*17*), using fluorescent substrates. However, a simpler method is based on spraying the plates with a solution of antimony pentachloride (20 vol. %) in carbon tetrachloride. After spraying, the plasticizers become visible as brown spots on the light background if the plate has been preheated to 120° C. for a short period. Some plasticizers cannot be recognized directly, but they appear if the plates are placed under ultraviolet light. Thus, antimony pentachloride is useful for identifying many plasticizers.

Another simple and useful method includes exposing the plasticizer to iodine vapor. The plates are exposed in a glass trough which contains iodine crystals. The plasticizers become visible as brown spots (*21*). After exposure to air the spots disappear. In this method, the plasticizers are identified without undergoing a chemical change. This provides an advantage if the separate substances subsequently are scratched off the plates so they may be used in further investigations. For instance, the spots can be extracted and spectroscopically examined.

Compared to other plasticizer analysis methods, thin layer chromatography is simple and quick. If used alone, it does not always lead to positive identification of every unknown plasticizing agent, but it does indicate the presence ot a plasticizer or a mixture of plasticizing substances.

Gas Chromatography. In principle, plasticizers with low volatility at processing temperatures and at the occasionally far higher conversion temperature are

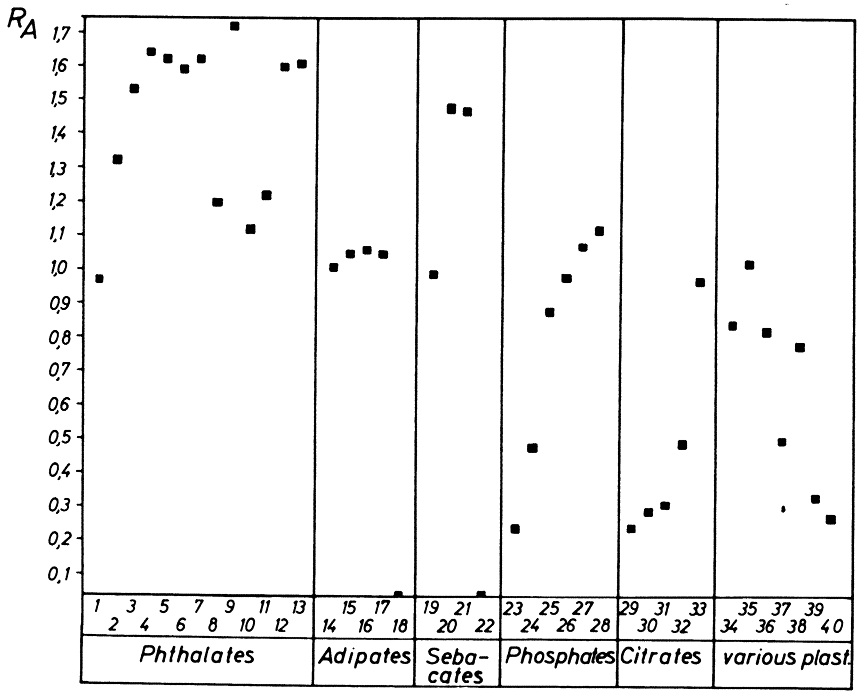

Figure 2. Thin layer chromatography of plastizicers
Eluent: methylene chloride, R_A = R_F with reference to dibutyl sebacate

1. Dimethylphthalate
2. Dibutyl phthalate
3. Dihexyl phthalate
4. Dioctyl phthalate
5. Dinonyl phthalate
6. Didecyl phthalate
7. Di-(2-ethylhexyl) phthalate
8. Benzyl phthalate
9 Di-(methoxyethyl) phthalate
10 Dicyclohexyl phthalate
11. Dimethylcyclohexyl phthalate
12. Di-isodecyl phthalate
13. Di-isononyl phthalate
14. Dioctyl adipate
15. Di-(2-ethylhexyl) adipate
16. Dinonyl adipate
17. Benzyloctyl adipate
18. Polyadipate
19. Dibutyl sebacate
20. Dioctyl sebacate
21. Di-(2-ethylhexyl)-sebacate
22. Polysebacate
23. Trichlorethyl phosphate
24. Trioctyl phosphate
25. Diphenyloctyl phosphate
26. Triphenyl phosphate
27. Diphenylcresyl phosphate
28. Tricresyl phosphate
29. Triethyl citrate
30. Tributyl citrate
31. Acetyltriethyl citrate
32. Acetyltributyl citrate
33. Acetyltri-(2-ethylhexyl) citrate
34. Methylacetyl ricinoleate
35. Butyl acetyl ricinoleate
36. Benzenesulfonic acid butylamid
37. Benzenesulfonic acid-*N*-methylamide
38. Di-(2-ethylhexyl)-thio dibutyrate
39. (2-Ethylhexyl)-*p*-hydroxybenzoate
40. Glyceryl triacetate

given preference. Most of the plasticizers, to meet this requirement, have relatively high boiling points which makes their separation by gas chromatography difficult. The gas chromatographs presently used operate at temperatures up to 400° C. Most of the organic stationary phases on inorganic substrates, however, become instable even at lower temperatures, and only a few among them (such as apiezone and certain silicones) remain stable up to 300° C. On the other hand, it is a general rule that the vapor pressure of the substance being examined must not be lower than 10 mm.

(with respect to the column temperature) or migration proceeds too slowly. Since the boiling points of most plasticizers, when exposed to pressures of 5 to 10 mm., range between 200° and 300° C., their separation by gas chromatography should be possible theoretically.

Not many gas chromatography investigations have been reported to date. Adlard and Withham (*1*) examined sebacic acid and phthalic acid esters at 255°C. in a helium flow (30 ml./min.) on columns of silicone high vacuum grease and fireclay grog; they were particularly interested in testing the purity of these substances.

Lewis and Patton (*16*) have furnished more detailed information on plasticizer analysis by gas chromatography. They analyzed a number of plasticizers of the ester type, present in technical mixtures and in plastics, using a glass column (length: 120 cm.; diameter: 0.5 cm.) heated to 283° C. by the vapor from boiling dimethyl phthalate. The column was packed with apiezone oil on Celite 545: helium flow was 50 ml./min.

Under these conditions, the elution period is a maximum of 35 minutes, and the separation results are said to be satisfactory. Although bis-2-ethylhexyl, bis-2-ethylbutyl, and dibutyl phthalates in mixtures are not distinguishable by infrared spectroscopy, these three components are separated sharply by gas chromatography, which can even provide quantitative analyses of such mixtures. Thus, gas chromatography is useful in plasticizer analysis, however, exact analyses and a detailed compilation of the retention periods still remain to be worked out.

Our tests in this direction, under similar conditions have been successful in separating plasticizers in a rather low boiling point range to a rather satisfactory sharpness. With increasing higher boiling points, the sharpness of the peaks weakens and the separation becomes more difficult. Therefore, it seems advisable to operate with temperature programming; however, presently no such experience is available. In complicated separations, preference is indicated for gas chromatography as a method of identifying the saponification products of plasticizers, since assignment of the peaks is easier.

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Chromatographic Identification of Saponification Products of Plasticization Agents

If plasticizer analysis presents difficulties by direct chromatographic methods there is always the possibility of chemically converting the plasticizers into reaction products which are easier to separate. Since, chemically, esters predominate among the technical plasticizers, analysis of their saponification products must be dealt with first.

Once the unknown sample is saponified, conditions may be chosen which will allow direct identification of the acids and alcohols formed. Sometimes it may be advantageous to re-esterify the products so that alcohols appear in the form of their 3,5-dinitrobenzoic acid esters, which lend themselves to separation by thin layer chromatography.

The literature on the identification of organic acids and alcohols is extensive. But only those methods which have been used successfully in plasticizer analysis are described here.

Identification of Acids. If plasticizers are saponified by means of alcoholic patassium hydroxide, the potassium salts of most of the carboxylic acids precipitate

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in solid phase. These can then usually be identified in terms of method applied—either directly or after conversion into free acids or other derivatives.

Clasper and Haslam (*11*) have separated mixtures from adipic acid, sebacic acid, and phthalic acid of pH 4.3 on a silica gel column by elution with butanol-carbon tetrachloride mixtures. In general, however, column chromatography is better suited for preparative purposes than for identifying unknown acids.

Carboxylic acids often have been identified by means of paper chromatography. Clarke and Bazill (*10*) have extracted plasticizers from polyvinyl chloride first with ether and then with methanol. Subsequently the extracts were saponified with alcoholic potassium hydroxide, and the precipitated potassium salts were isolated and converted into free acids. These, in alcoholic solution, were then applied to paper and chromatographed ascendingly with a mixture of butanol, pyridine, water, and ammonia; the migration period was about six hours. A number of additional color tests facilitated identification of unknown acids.

Thin layer chromatography may be simpler than paper chromatography for identifying acids. According to Braun and Geenen (*6*), aliphatic dicarboxylic acids, from oxalic acid to sebacic acid, and a few other acids that are important in plasticizer analysis, can be separated on silica gel G with a mixture of ethanol, water, and ammonia as eluent. Bromocresol green is recommended as indicator. After spraying, the acids become visible as yellow spots on a blue background. However, the spots also may be made visible by iodine vapor. In this case, the eluent mixture more preferably consists of methanol, pyridine, and ammonia. The R_F values of the more important acids are given in Table III. If made visible by iodine, light-colored spots appear on a dark background; only phthalic acid produces brown spots. After evaporation of the iodine, other color reactions can be carried out with the marked substances; tests for phthalic acid are best carried out with phenol (*5*); for adipic acid, with a color reaction of cyclopentanone as a result of pyrolysis (*19*); and for phosphoric acid, with ammonium molybdate (*14*). Spots scratched off the plates can be used for these color tests.

Table III. Thin-Layer Chromatography of Some Acids on Kieselgel G

	Parts by volume
Eluent 1:	
Ethanol (96%)	100
Water	12
Ammonia (27%)	16
Eluent 2:	
Methanol	100
Pyridine	30
Ammonia (27%)	40

	R_F value	
Acid	*Eluent 1*	*Eluent 2*
Phthalic	0.26	0.33
Adipic	0.43	0.49
Azelaic	0.56	0.62
Sebacic	0.67	0.66
Citric	0.05	0.06
Phosphoric	0.0	0.0
Acetic	—	0.70
Butyric	—	0.70
Oleic	—	0.81[a]
Tartaric	0.08	0.19
Benzoic	0.76	0.59
p-Toluenesulfonic	—	0.79

[a] Long tail

For separating higher aliphatic dicarboxylic acids, Knappe and Peteri (*15*) recommend the use of silica gel layers impregnated with polyethylene glycol with molecular weight of 1000; the differences between the R_F values of homologs, distinguished only by their CH_2 groups, are markedly better than if silica gel alone is used.

The gas chromatographic separation of acids present in plasticizers, apart from identifying volatile aliphatic carboxylic acids up to C_6, deals mainly with methyl esters. Carboxylic acids, present either as free acids or as alkali salts after saponification of the plasticizers, must be esterified. Conversion with methanol in presence of boron trifluoride (*2*) is recommended. But even better suited for plasticizer analysis is direct re-esterification of the plasticizers with methanolic hydrochloric acid (*2*).

Many substances can serve as the stationary phase for gas chromatographic separations of methyl esters; in most cases polyester, polyether, or silicone greases are used. Percival (*18*) has investigated the composition of polyesters by methanolysis with sodium methyl oxide. The dimethyl esters of the dicarboxylic acids present in the composition and free glycols are formed and subsequently are separated at temperatures between 110° and 180° C. on a column of GE silicone SF–96 and Fluoropak 80. It should be possible to adapt this method to the analysis of polyesters used as plasticizers.

Identification of Alcohols. The alcohol component of the plasticizers, after direct isolation, can be identified by gas chromatography, whereas, paper or thin layer chromatographic methods require that alcohols be converted into suitable derivatives prior to identification.

Gas chromatography of alcohols offers no particular problems, and there is much literature on separating and identifying alcohols.

We, in most cases, have used a 2-meter column of polypropylene glycol (Ucon LB–550 X) on Celite 545 at 191° C. in helium flow and have succeeded in separating the aliphatic alcohols and diols. D. F. Percival's method (*18*) for separating diols from saponified polyesters should be adaptable to plasticizer analysis.

Alcohols, prior to the separation by means of paper or thin layer chromatography, must be converted into suitable derivatives, mostly into 3,5-dinitrobenzoic acid esters or into the acid semiesters of 3-nitrophthalic acid or diphenic acid. The direct re-esterification of ester plasticizers with 3,5-dinitrobenzoic acid is applicable to plasticizer analysis (*7*).

For thin layer chromatography, 50 to 60 mg. of the formed ester is dissolved in 1 ml. of ether, and a few drops of alcohol are added; 2 microliters of this solution are applied to a silica gel G plate and chromatographed ascendingly with a mixture of 150 parts by volume of benzene and 1 part by volume of acetic acid methyl ester; a 10-cm. migration takes 25 to 30 minutes. After the plate has been dried in hot air, the substances are made visible with iodine vapor; they appear as brown spots on a light background. However, the esters cannot be distinguished from other substances present in the reaction mixture. It is therefore advisable to spray the plate with a 0.5% ethanol solution of Rhodamin B (*24*). Under normal daylight the 3,5-dinitrobenzoic acid esters appear as dark spots on a light background, and under ultraviolet light the esters are marked sharply as dark spots while all other substances are lighter in color than the red fluorescent background.

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Table IV. Thin Layer Chromatography of 3,5-Dinitrobenzoic Acid Esters on Kieselgel G

Eluent: 150 pt. by vol. of benzene; 1 pt. by vol. of methyl acetate

Ester	*R_F value*
Methyl	0.40
Ethyl	0.49
Butyl	0.65
n-Hexyl	0.73
n-Octyl	0.80
2-Ethylhexyl	0.81
n-Decyl	0.81
Cyclohexyl	0.68
Benzyl	0.63
Glycerol	0.05

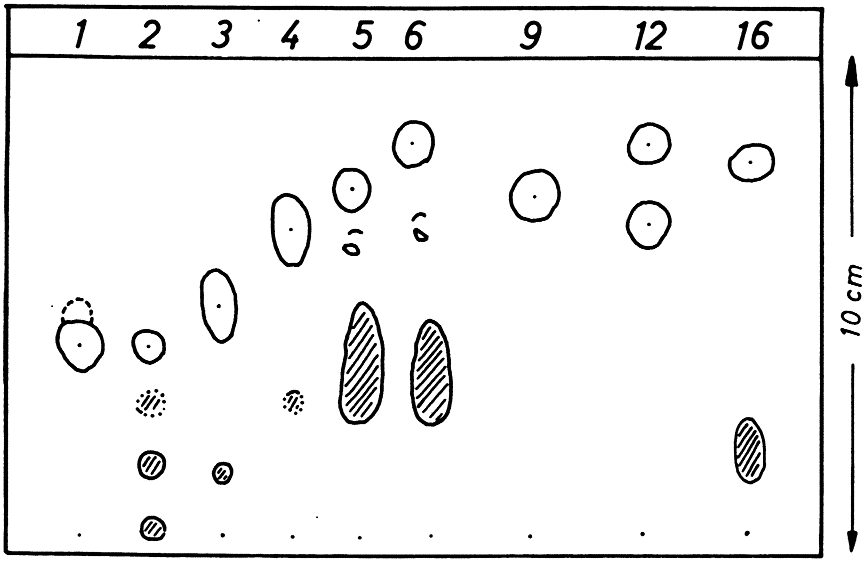

Figure 3. 3,5-Dinitrobenzoic acid esters from transesterification of some plasticizers
Kieselgel G; Eluent: benzene, methyl acetate (150:1 pt. by vol.)

1. Dimethyl phthalate
2. Methyl acetyl ricinolate
3. Triethyl citrate
4. Dibutyl phthalate
5. Dihexyl phthalate
6. Di-*n*-octyl sebacate
9. Dicyclohexyl phthalate
12. Benzyloctyl adipate
16. Diphenyloctyl phosphate

Table IV gives the R_F values determined under these conditions. Figure 3 shows the chromatograms of the reaction products of the re-esterification of a number of plasticizers. It is obvious that the method is suitable for identifying the alcohol components of all frequently used ester types. Difficulties have been met with phenolic components although they are present primarily in phosphoric acid esters. To identify these, evaporate to dryness a few drops of the reaction mixture of an alkaline saponification and mix this with a bit of the precipitated alkali salt. Add this residue to 10 to 20 drops of chloroform and gradually evaporate it; repeat this procedure three times. Then add this residue to one drop of acetic acid and mix with one or two drops of hydrazine solution, stir well, and apply to a filter paper. Without exception, the aldazines formed show yellow to orange fluorescence (*12*) under ultraviolet light. A blank test without hydrazine solution is recommended. Among others phenyl-, *p*-, and *m*-cresyl as well as *p*-oxybenzoic acid esters show positive reactions.

Several gas chromatographic separations of phenols from plasticizers have been accomplished. Dinonyl phthalate (*25*) or silicone oil (*20*) are recommended as column materials. Saponification is best carried out in glycolic potassium hydroxide, which, for example, saponifies tricresyl phosphate quantitatively.

Pattern of Plasticizer Analysis. Use of the analytical methods discussed here allows a general pattern for separating and identifying plasticizers to be designed which allows quick and simple characterization, at least for the more frequently occurring substances.

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10

Chlorinated Normal Paraffins as Polyvinyl Chloride Plasticizers

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The chlorination of high purity molecular-sieved normal paraffins yields plasticizers for polyvinyl chloride (PVC) with better properties than chlorinated waxes. The chlorinated *n*-paraffins are much lighter in color than chlorinated wax and are more thermally stable in PVC formulations. They also have better plasticizer efficiency and low temperature properties in PVC and have lower viscosity. The latter three property advantages are due to the use of lower molecular weight paraffins than those available from wax. These properties are functions of both the chlorine content and carbon chain length of the *n*-paraffins. The compatibility and volatility properties of the chlorinated *n*-paraffins in PVC are similar to those of chlorinated wax and serve to set lower limits on chlorine content and average molecular weight, respectively.

Chlorinated paraffinic hydrocarbons have been commercially available for at least 45 years (*6*). The literature on the chemistry and technology of chlorination processes of all types is rather extensive (*7*). However, the principal chlorinated paraffins or chloroalkanes of commerce today represent what can best be described as either low or high molecular weight products. This is essentially a reflection of the length of the carbon chain of the hydrocarbon used in the chlorination process. On one hand, there are the chlorinated derivatives of hydrocarbons ranging from methane to the pentanes; on the other, there are the chlorinated derivatives of petroleum wax. This wax usually consists of mixtures of paraffins with average molecular weights in the range C_{20} to C_{26}.

The uses for low molecular weight chloroparaffins are familar; they include solvents, cleaning agents, fire extinguishing agents, and chemical intermediates. Applications for the chlorinated waxes include plasticizers, cutting oils, additives for paint, rubber, printing inks, plastics, mastics, adhesives, and textiles. Often their principal function is to reduce or eliminate flammability.

An important reason for the lack of intermediate molecular weight products has been the unavailability of low cost paraffins with molecular structures suitable for these materials. Synthetic paraffins, prepared by the Fischer-Tropsch process and often known as Kogasin, have been available in this intermediate molecular weight range (*10*) and have been used in Europe to make chloroparaffins (*9*). However, these materials also are not completely satisfactory because of a combination of cost, purity, and molecular structure.

The problem of availability of suitable paraffinic feedstocks of low cost, which represent a potentially wide range of molecular weight, will soon be rectified. Linear alkanes of high purity will be available from petroleum on a large scale, as is evident from recent announcements by both chemical and petroleum companies of plans to build normal paraffin extraction plants (*2*, *3*, *8*).

The balance of this article consists of a discussion of the properties of chlorinated derivatives of these *n*-paraffins as plasticizers for polyvinyl chloride (PVC). This application of course, represents just one of many potential uses for these materials.

Experimental

All elemental and molecular weight analyses on both laboratory and commercial samples of chlorinated paraffins and the composition and purity determinations of the *n*-paraffins were carried out by the Analytical Research Division of Esso Research & Engineering Co.

***n*-Paraffins.** Single component *n*-paraffins, n-$C_{16}H_{34}$, n-$C_{18}H_{38}$, and n-$C_{22}H_{46}$ were obtained from Matheson, Coleman, and Bell Co. Gas chromatography showed that essentially only one component was present. The purity was not checked further, and they were used without further treatment.

The *n*-paraffin mixture was used as produced by the Esso molecular seive process.

Commercial Chlorinated Products. The commercial products reported herein are typical of chloroparaffins produced both in the U. S. and in Germany. They were used as received. All reported analyses and physical properties were determined in these laboratories.

Chlorinations. Photochemical chlorinations were carried out both with and without solvent (CCl_4) as is typified by the following example:

A solution of 100 grams (0.39 mole) of C_{18} average *n*-paraffin and 150 grams of carbon tetrachloride was placed in a two-necked 500-ml. round-bottomed flask equipped with a condenser, thermometer, magnetic stirrer, and a gas inlet tube that did not extend below the surface of the liquid. The flask was partially immersed in a water bath at 25°C., and the system was swept with nitrogen. Chlorine was then introduced at a measured rate of 150 cc./minute as determined by a calibrated Brooks rotameter. A 150-watt unfrosted tungsten light bulb was placed against the flask. The temperature of the solution during the course of the reaction was 35°C. The effluent gas stream was checked for unreacted chlorine by passing it through an excess of 1*N* potassium iodide solution for 0.5 hour, followed by titration with 2.00*N* sodium thiosulfate. Approximately 5 cc./minute of chlorine was not reacting, so that the actual rate of absorption was 145 cc./minute. To obtain a product that has an average structure of $C_{18}H_{33}Cl_5$ (molecular weight 427, 41.6% Cl), 1.95 moles (approximately 48 liters at 25°C.) of chlorine are required. Thus,

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the chlorination was run for 5.5 hours. The solution was then washed with aqueous sodium bicarbonate and water, followed by drying and heating to remove solvent at 0.05 mm. pressure and 100°C.

The product was characterized as follows:

Color, Gardner scale	<1
Viscosity, Brookfield, 25°C., cp.	315
Analysis, %	
C	50.27
H	42.30
Cl	7.66
Empirical formula	$C_{18}H_{32.7}Cl_{5.1}$
Molecular weight,	
Calculated	430
Found (Osmometer)	395

Thermal chlorinations were carried out similarly except that a solvent was not used. Chlorine was introduced in the dark below the surface of the rapidly stirred paraffin at 80°C. The temperature quickly rose to 120 to 125°C. for the balance of the reaction period. Chlorine was not absorbed as efficiently as it was in the photochemical chlorinations. After the reaction was complete, chloroform was added to facilitate washing of the product.

PVC Formulation and Processing. The following PVC formulation was used throughout this work: B. F. Goodrich Co., Geon 101 EP, 100 parts; Argus Chemical Co., Mark M, 2.0 parts/100 parts of resin (p.h.r.); stearic acid, 0.5 p.h.r.; total plasticizer, 50 p.h.r.

The formulation was milled for eight minutes at 154°C. on a two-roll mill. The vinyl stock was molded at 166°C. for five minutes at 1500 p.s.i.g.

Evaluation. Ultimate tensile strength, ultimate elongation, and 100% modulus were determined by using 0.075-inch samples in an Instron operating at a rate of 20 inches/minute (ASTM D-638-61T).

Oven-aging was carried out on 0.075-inch samples mounted on a rotating turntable in an air-circulating oven (port velocity 1000 ft./minute) for seven days at 100°C.

The Clash-Berg temperature (ASTM D1043-61T) is the temperature at which the torsional modulus of a 0.075-inch sample equals 135,000 p.s.i. A constant torque of 0.5 inch-pound was applied and five-second readings were taken on a Tinius-Olsen instrument.

The activated carbon volatility (ASTM D1203-61T) was determined with 0.010-inch samples placed between layers of coarse activated carbon for 24 hours at 70°C.

The compatibility was measured by estimating the amount of exudation that developed after strips of 0.075-inch vinyl were clamped into loops for 24 hours.

Heat stability was measured by determining the color that developed in 0.075-inch samples placed in an air-circulating oven at 177°C. (ASTM D-2115-62T).

Basic Plasticizer Properties

Chlorinated wax is considered a secondary plasticizer for PVC because it has limited compatibility (*11*) and low plasticizer efficiency, compared with primary plasticizers such as dioctyl phthalate. It has good permanence properties—for

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example, low volatility and resistance to extraction—and good chemical resistance. It also imparts flame resistance by replacing a portion of a flammable primary plasticizer. Chlorinated derivatives of high purity *n*-paraffins possess similar basic properties, as would be expected. However, in a number of areas the *n*-paraffin derivatives show marked improvement.

Molecular Structure of the Paraffins

An important feature of paraffins used for chlorinated plasticizers is a high degree of straight-chain character. Branched acyclic and alicyclic paraffins possess tertiary hydrogen atoms, which yield tertiary chlorine atoms during chlorination (*4*). The latter readily eliminate hydrogen chloride during thermal treatment (*5*). The facile breakdown of the branched chloroparaffin plasticizer can lead to a discolored or degraded PVC compound (*1*). In addition, the amounts of other possible impurities, such as olefinic and aromatic moieties, should be as low as possible to prevent the formation of unstable chlorinated structures that might lead to colored decomposition products.

The most common raw material used for chlorinated hydrocarbon plasticizers is a low oil content paraffinic wax with an average molecular weight of C_{20} to C_{26} (*12*). The purity of this material is dependent on the number of refining steps employed. In the current commercial process—that is, the precipitation process—the molecular weight range is limited, especially below C_{20}, by the melting point of the products. The percentage of normal alkanes is a function of the original crude oil, as well as the process, and may vary over a wide range.

The new Esso molecular sieve *n*-paraffin process does not have these limitations (*8*). The molecular weight range is dependent on the boiling range of the feedstock used. The purity of the products is very high as the percentage of normal alkanes can be greater than 99%. The data reported here were obtained by using both a *n*-paraffin mixture with an average molecular weight of C_{18} and a distribution of C_{10} to C_{24} as is shown in Figure 1, and single component *n*-paraffins. The im-

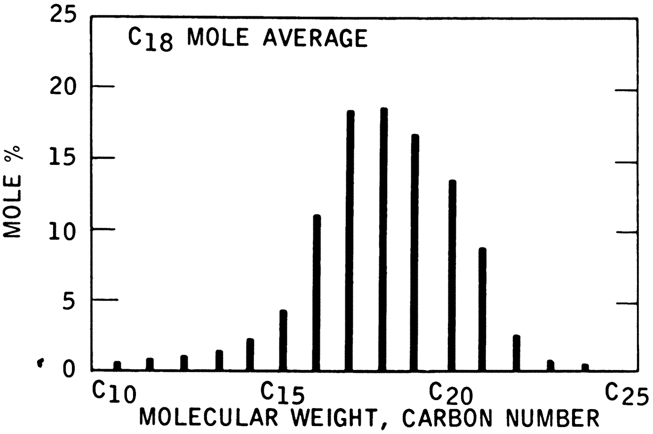

Figure 1. Distribution of n-alkanes in paraffin mixture used for chlorination

purities in the mixture consisted of <1% iso- and cycloparaffin, <100 p.p.m. aromatics, and <5 p.p.m. sulfur.

Color of Chlorinated Products

The purity and straight-chain character of the paraffins are reflected in the color of the chlorinated products. Both thermally and photochemically chlorinated derivatives of the *n*-paraffin mixture were essentially colorless. Gardner scale color values of 1 and <1, respectively, were obtained on samples chlorinated to about the same degree by thermal (44% Cl) and photochemical (42% Cl) procedures. Commercial chlorinated wax has Gardner scale color values of 2½ to 4.

Thermal chlorinations were carried out at 125°C. and photochemical chlorinations at about 35°C. No posttreatment was employed other than removal of dissolved hydrogen chloride, followed by the removal of solvents, if present, by heating under vacuum. No difference in plasticizer properties was observed for chlorinated *n*-paraffins made by the two methods.

Thermal Stability

The improved thermal stability of the chlorinated paraffins also reflects the purity of the *n*-alkanes. The heat stability of PVC plasticized with chlorinated *n*-paraffin at 177°C. is better than that of similar compounds using commercial chlorinated wax. This is shown in Table I by the color that developed during thermal treatment for samples in which 40% of the dioctyl phthalate was replaced by chlorinated paraffins. (In this example and those that follow, the total plasticizer concentration is constant at 33⅓%.) The color development in this test is significant as a measure of the comparative processing conditions that can be employed.

Table I. Thermal Stability at 177°C. of PVC Plasticized with Dioctyl Phthalate and Chlorinated Paraffins

Plasticizer	*Dioctyl Phthalate*	*Chlorinated n-Paraffin, 42.3% Cl, C_{18} Av.*	*Commercial Chlorinated Wax, 41.3% Cl, C_{21} Av.*
Replacement of DOP, %	—	40	40
Heat Stability[a], color after:			
15 Minutes	0	0	1
30 Minutes	0–1	1	3

[a] 0-colorless; 1-light yellow; 2-yellow; 3-orange; 4-brown.

Viscosity

The viscosity of chlorinated paraffins is a function of their molecular weight(*11*). However, the molecular weight depends on both carbon chain length and chlorine content. This relationship can be seen in Figure 2, where a wide range of viscosity is plotted against the chlorine content for chlorinated derivatives of two single component *n*-paraffins and one mixture of *n*-paraffins. It is evident that the viscosity decreases markedly as both the length of the carbon chain and the chlorine content are decreased.

At a given chlorine content the viscosity of the chlorinated *n*-paraffins decreases as the average carbon chain length decreases. For example, two materials

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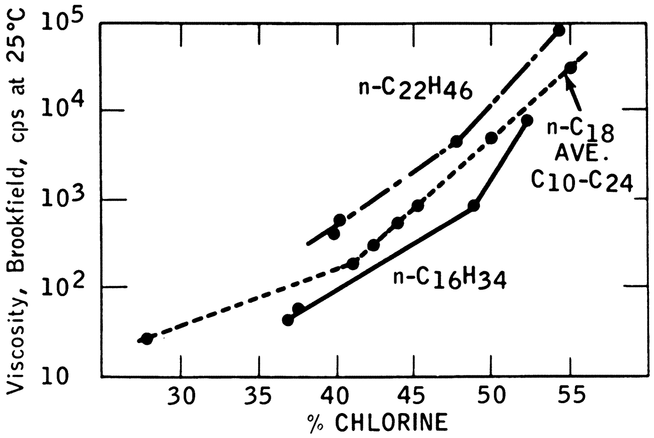

Figure 2. Viscosity of chlorinated n-paraffins

with similar levels of chlorine made from C_{21} average commercial wax (41.3% Cl) and C_{18} average *n*-paraffin (42.3% Cl) have Brookfield viscosities of 600 and 320 centipoises, respectively, at 25°C. Thus, the microstructure of the paraffins is of less importance here than it was previously, in the case of color and thermal stability properties.

The behavior of the viscosity of chlorinated paraffins emphasizes the significance of the availability of *n*-paraffins in molecular weight ranges below that of wax. Lower viscosity results in improved handling and could be an advantage in plastisol applications.

Plasticizer Efficiency

The plasticizer efficiency of chlorinated paraffins is low as compared with conventional primary plasticizers. This is shown in Figure 3, where the 100% modulus of plasticized PVC increases as dioctyl phthalate is replaced by a commercial chlorinated paraffin (C_{20} average, 46.0% Cl).

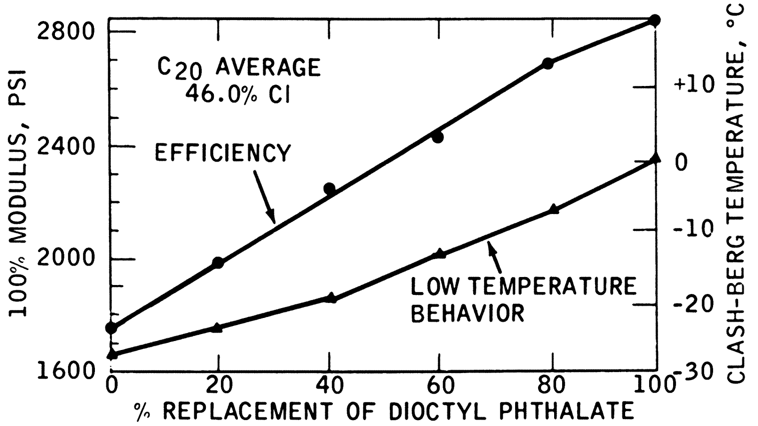

Figure 3. Efficiency and low temperature properties of a commercial chloroparaffin in PVC

However, the efficiency of chlorinated *n*-paraffins also is dependent upon both the chlorine content and carbon chain length as was the viscosity. This can be seen in Figure 4, where the 100% modulus is plotted against per cent chlorine for PVC samples plasticized by chlorinated derivatives of two single component *n*-paraffins and a mixture of *n*-paraffins, at a level of 40% replacement of dioctyl phthalate. It is evident that efficiency improves as either the chlorine content or carbon chain length is reduced. Further evidence for this point is given in Table II. Here the efficiency is compared for PVC plasticized with three chloroparaffin mixtures of approximately the same chlorine content but of increasing chain length at a concentration level of 20% replacement of dioctyl phthalate. This also emphasizes the advantage of using paraffins of lower molecular weight than wax.

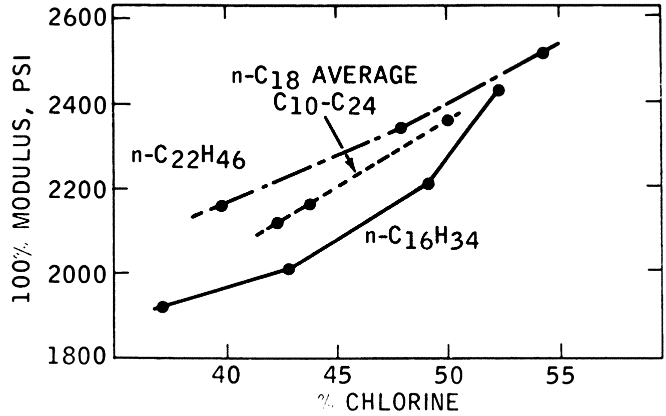

Figure 4. Efficiency of chlorinated n-paraffins in PVC at 40% replacement of dioctyl phthalate

Table II. Efficiency and Low Temperature Properties in PVC of Chloroparaffins with Similar Levels of Chlorine

		Chlorinated n-Paraffin,	*Commercial Chlorinated Wax*	
Plasticizer	*Dioctyl Phthalate*	*42.3% Cl, C_{18} Av.*	*41.3% Cl, C_{21} Av.*	*43.0% Cl, C_{26} Av.*
Replacement of DOP, %	—	20	20	20
Efficiency, 100% modulus, p.s.i.	1790	1855	1950	2025
Low temperature properties, Clash-Berg temp. °C.	−27	−29	−26	−24

Low Temperature Properties

The low temperature properties of chloroparaffinic plasticizers in PVC follow the same pattern as that presented by efficiency measurements. This is shown in Figure 3, where the Clash-Berg temperature increases as increasing amounts of dioctyl phthalate are replaced by a commercial chloroparaffin. The analogy also carries over to low temperature properties of PVC compounds as a function of chain length and chlorine content of the chloroparaffin. Figure 5 illustrates the decrease in the Clash-Berg temperature with decreasing chain length and decreasing

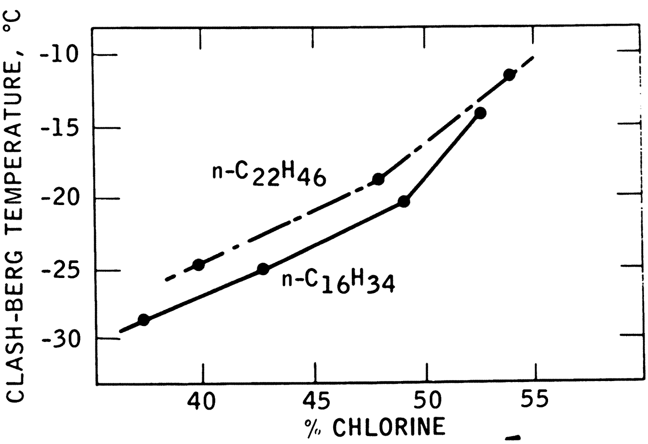

Figure 5. Low temperature properties of chlorinated n-paraffins in PVC at 40% replacement of dioctyl phthalate

chlorine content of chlorinated derivatives of two single component *n*-paraffins. The behavior at constant chlorine content and increasing chain length is shown in Table II for three chloroparaffin mixtures.

Volatility

The improvement in viscosity, efficiency, and low temperature properties of chloroparaffins as the chain length decreases suggests that even lower molecular weight material should be used. However, a limiting factor is the volatility of the plasticizer, which is a function of the average molecular weight of the relatively nonpolar chloroparaffins. For example, if the average molecular weight of the chloroparaffin is greater than that of dioctyl phthalate, the loss upon aging is less than that of the latter. Figure 6 illustrates this loss for a series of chlorinated derivatives of a single component C_{16} *n*-paraffin at a concentration level of 40% replacement of dioctyl phthalate.

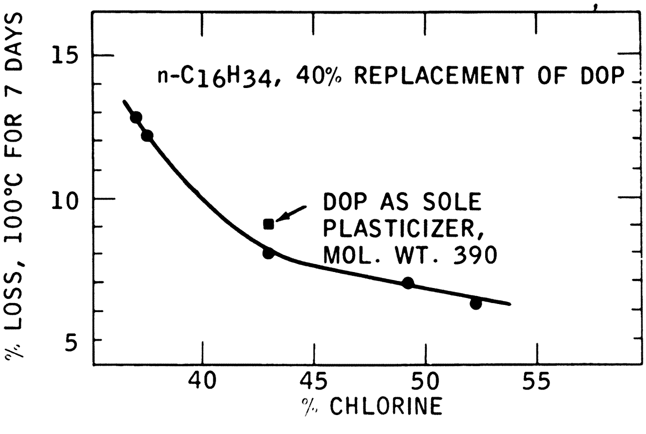

Figure 6. Loss during aging of PVC plasticized with chlorinated n-paraffin

Similarly, molecular weight range can be a factor. The example given in Table III represents a plasticizer in which the chain length of the n-paraffin is constant (C_{16}) but, of course, the number of chlorine atoms per chain can vary to give a molecular weight range. In this case the plasticizer is slightly less volatile than the dioctyl phthalate it has replaced in PVC, as is shown in the more severe test. However, a fraction of the chloroparaffin appears to be more volatile than dioctyl phthalate, as is shown in the less severe test. The same behavior was also noted for chlorinated derivatives of mixtures of n-paraffins.

Table III. Loss During Aging Under Varying Conditions of PVC Plasticized with Chlorinated *n*-Paraffin

Platicizer	*Dioctyl Phthalate, Mol. Wt. 390*	*Chlorinated n-$C_{16}H_{34}$ 42.8% Cl, Av. Mol. Wt. 390*
Replacement of DOP, %	—	40
Air volatility, % loss at 100°C. for 7 days	8.9	8.0
Activated Carbon Volatility, % loss at 70°C. for 1 day	1.2	3.5

Compatibility

Plasticizer compatibility is a second limiting property. This results from the fact the chloroparaffins containing less than approximately 40% chlorine have poor compatibility when used in conjunction with primary plasticizers (*11*). This is shown qualitatively in Table IV for a chlorinated single component n-paraffin at a level of 20% replacement of dioctyl phthalate. It is evident that the exudation first reaches its lowest value in the range 40 to 45% chlorine. This level of chlorine appears to be a minimum regardless of the length of the carbon chain of the paraffin.

Table IV. Compatibility of Chlorinated *n*-Paraffin in PVC

Plasticizer	*Dioctyl Phthalate*	*Chlorinated n-$C_{18}H_{34}$*			
		19.9% Cl	*38.4% Cl*	*47.8% Cl*	*51.3% Cl*
Replacement of DOP, %	–	20	20	20	20
Compatibility, exudation in loop test	None	Very heavy	Moderate	Slight	Slight

Conclusion

Normal paraffins offer several advantages over wax as raw materials for chlorinated paraffins. Products of improved color and thermal stability are possible because of the high purity and straight-chain character of the normal paraffins. Plasticizers with lower viscosity, higher efficiency, and better low temperature properties are possible because of the availability of lower molecular weight paraffins. Limitations on the extent of improvement in these properties are the desired plasticizer volatility and compatibility properties, which are governed by the molecular weight and chlorine content, respectively, of the chloroparaffin. In applications where chloroparaffins can be used satisfactorily chlorinated n-paraffins will show a definite advantage over chlorinated wax.

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11

Effect of Plasticization on Viscoelastic Properties of Polyvinyl Chloride

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Modulus-temperature and modulus-time curves up to high temperatures were made for polyvinyl chloride (PVC) and polyvinyl chloride plasticized with 30% dioctyl phthalate. Incorporation of stabilizer and rapid measurements minimized chemical decomposition and diluent evaporation. At temperatures above the melting point of PVC crystallites, flow regions are observed. The presence of plasticizer caused a lowering of T_m and of T_g. Below T_m both pure PVC and plasticized PVC behave like semicrystalline polymers. The presence of diluents affects the viscoelastic properties below T_m mainly by changing T_g of the amorphous regions, without very significant changes in the microcrystalline structure. Above T_m the relaxation times are difinitely shortened because of the lower value of T_g. The effect may be even greater than this because the over-all average molecular weight of polymer plus plasticizer is lower than that of polymer alone.

Polyvinyl chloride (PVC) is one of the more important of the polymers that are frequently used in the plasticized form. Its superior mechanical behavior has been the active interest of many investigations. Previous reports from this laboratory have dealt with x-ray, dilatometric, and birefringence properties of plasticized and unplasticized polyvinyl chloride (2, 25). Ferry *et al.* studied the dynamical mechanical properties of PVC gels (*5*, *10*, *11*, *12*, *20*). Creep (*1*, *9*, *17*) and elastic (*33*) behavior have also been investigated. In recent publications (*27*, *30*), we have reported time-dependent viscoelastic properties of PVC covering a range of plasticizer contents.

An important conclusion emerging from these studies is that polyvinyl chloride has a three-dimensional network structure where microcrystallites are believed to

In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

act as cross linkages (*2*, *25*). Crystallinity persists even at relatively high extents of plasticization. Consequently, more flexible polymers are obtained by plasticization without losing the resistance to flow. Recently, further x-ray studies by Natta and Corradini (*22*) revealed that radical-polymerized polyvinyl chloride possesses imperfect syndiotactic structure. Laterally ordered crystallites of the order of 50 A. were present.

Polyvinyl chloride has been known to decompose at high temperatures (>150°C.) with the evolution of hydrogen chloride (*4*, *6*, *15*). It has been suggested that abstraction of hydrogen chloride from neighboring chains may have produced chemical cross-links giving the observed high creep recovery property. However, evidence from chemical decomposition indicates that removal of hydrogen chloride occurs within the same chain (*18*). To reaffirm the hypothesis that polyvinyl chloride is semicrystalline, viscoelastic properties at high temperature were studied. Regions of rubbery flow should be observed for PVC above the melting point of its microcrystallites.

Experimental Methods

Samples were kindly supplied by Allied Chemical Corp. The unplasticized polyvinyl chloride contained 4.7 parts by weight of stabilizer and lubricant per 100 parts of PVC. The plasticized sample had 40 parts of dioctyl phthalate and 2.5 parts of stabilizer per 100 parts of polymer which is equivalent to a total plasticizer content of ~30 weight %.

Two types of measurements were made on these samples. In the region where moduli are higher than 10^9 dynes/sq. cm., a Clash-Berg torsional creep apparatus (*7*) was used. For moduli below 10^9 dynes/sq. cm., a modified Gehman apparatus (*14*) was employed. In both cases shear creep compliance, $J_c(t)$, was obtained. To convert this to relaxation modulus, $G_r(t)$, the following equation was used:

$$G_r(t) = \frac{\sin m\pi}{m\pi} \frac{1}{J_c(t)} \qquad (1)$$

where m is the slope of the double logarithmic plot of $J_c(t)$ versus t. Data were presented as $3G_r(t)$, which is approximately equal to Young's modulus. Parallel measurements were made on a stress-relaxation balance (29). Good agreement was obtained.

A Tenney environmental test chamber (Model TSU-100) was used as an air bath. Temperature can be controlled to ±0.1°C. by adapting an Aminco bimetallic thermoregulator connected to a supersensitive relay. Samples were prepared in the form of rectangular strips. First, moduli were measured as a function of temperature. At least five minutes was given to each temperature increment (~5°C.) to obtain thermal equilibrium.

A series of modulus-time curves was also made for temperatures covering the entire viscoelastic spectrum. At higher temperatures, the instrument was first allowed to reach the desired temperature and was held there for half an hour. Samples were then quickly inserted. After 10 minutes moduli were measured as a function of time up to 1000 seconds. Total measuring time for each isotherm thus was kept to less than 30 minutes to minimize chemical decomposition and plasticizer evaporation.

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Results and Discussion

In all previous work, viscoelastic measurements were performed at relatively low temperatures, below the occurrence of rubbery flow. In the work reported here viscoelastic properties of PVC were studied at temperatures higher than the melting point of the crystals. As mentioned in the previous section, precautions were taken to minimize decomposition by incorporating stabilizers and by rapid measurements. However, slight yellowing of unplasticized samples were observed after measurements, indicating some decomposition. For plasticized samples, there were minor losses of weight (~1%) by the end of experiments at high temperature, perhaps caused by evaporating plasticizer. However, the essential features of viscoelastic behavior is not believed to have been profoundly affected. Thus we feel that conclusions drawn from our experimental results can be accepted with reasonable confidence.

If indeed the degree of cross linking can be increased by heating, as suggested by Doty and Zable (*8*), modulus of polyvinyl chloride should increase directly with increasing temperature. On the other hand, should the three-dimensional network of PVC be due to the presence of microcrystallites (*2*), the rubbery flow region would commence as the temperature exceeds the melting point of crystals. Figure 1 is plot of modulus *vs.* temperature for both plasticized and unplasticized PVC. In both cases an extended decreasing rubbery plateau followed by a rubbery flow is observed. Anagnostopoulos *et al.* (*3*) estimated the melting point of PVC crystallites to be 174°C.—in good agreement with our viscoelastic data.

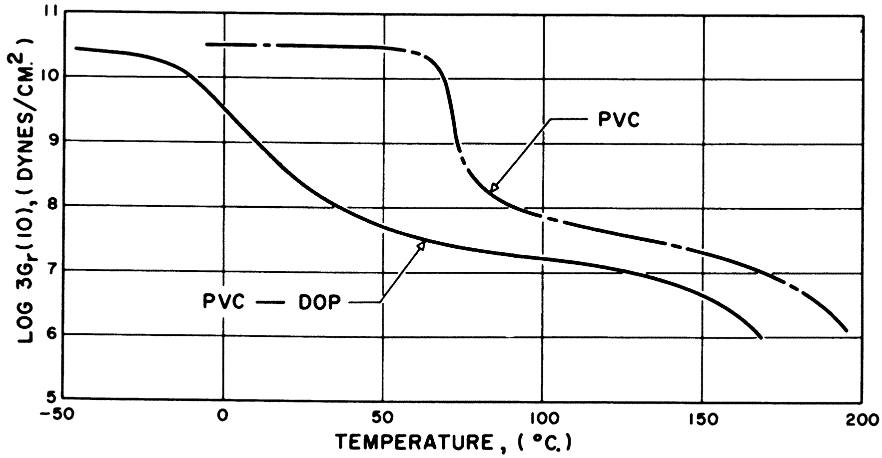

Figure 1. Modulus-temperature curves for pure and plasticized (30 wt. % dioctyl phthalate) polyvinyl chloride

Figure 1 also shows that plasticized polyvinyl chloride begins to flow at a lower temperature. This is to be expected in view of the fact that equilibrium melting temperature of polymer crystals is depressed by monomeric diluents. A statistical thermodynamic treatment by Flory (*13*), showed that this effect depends on the nature of the polymer, concentration of the diluent, and the degree of polymer-diluent interaction in the following manner:

$$\frac{1}{T_m} - \frac{1}{T_m{}^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)(v_1 - xv_1{}^2) \tag{2}$$

where $T_m{}^0$ is the melting temperature of the pure polymer; T_m is the melting temperature of the polymer incorporated with a diluent; R is the ideal gas constant; ΔH_u is the heat of fusion per "mole" of repeating unit; V_u and V_1 are the molar volumes of the polymer repeating unit and the diluent, respectively; v_1 is the volume fraction of the diluent; and x is the Flory-Huggins interaction parameter. From the data of (*3*), T_m of our PVC plasticized with 30 weight % of dioctyl phthalate is estimated to be approximately 150°C., again in the correct range of our viscoelastic data.

Table I. Viscoelastic Characteristic Parameters for PVC and PVC/30 DOP

	PVC	*PVC/30 DOP*
$3G_1$, dynes/sq. cm.	3.1×10^{10}	2.6×10^{10}
$3G_2$, dynes/sq. cm.	3.3×10^{7}	3.2×10^{7}
T_i, °C.	73	10
T_m, °C. (*3*)	174	~150
s, dynes/sq. cm./°C.	0.25	0.05
n, dynes/sq.cm./sec.	0.59	0.29

The viscoelastic characteristic parameters are summarized in Table I. Glassy modulus, $3G_1$, and rubbery modulus, $3G_2$, taken, respectively, at 50°C. below and 50°C. above the inflection temperature are effectively independent of diluent content. Inflection temperature, T_i, defined as the temperature at which $3G$ (*10*) is equal to 10^9 dynes/sq. cm., and s, the negative slope of the curve at T_i, are both depressed by the incorporation of the diluent. These data are all in good agreement with our earlier results (*27*). (T_i for pure PVC is slightly lower than the previously reported value of 77.6°C., probably because of the presence of stabilizer.) The depression of the transition temperature of polymers by plasticization is discussed in (*24*). The constancy of rubbery modulus seems to suggest that the degree of crystallinity and the volume concentration of crystallites are not altered very markedly by the incorporation of diluents beyond the obvious dilution effect. This in inferred from the kinetic theory of rubber elasticity applied to very slightly crystalline polymers (*16, 23, 28, 31*). It seems that the plasticizer swells the amorphous regions but leaves the crystallites relatively intact.

Modulus-time curves are given in Figures 2 and 3. Construction of master curves (*29*) by the time-temperature superposition principle is possible to slightly beyond the transition region. Characteristic relaxation times deduced from horizontal shifts at various temperatures followed the WLF equation (*34*). Negative slopes at the transition region, n, are given in Table I. Plasticized PVC possesses a broader transition region than the pure polymer, as noted previously (*27*).

In the lower regions of rubbery plateau, however, a good fit for the isotherms is not possible without resorting to vertical shifts as well. It is characteristic of crystalline polymers that there is not only a horizontal displacement along the log time axis due to changing rates of molecular motions with temperature but also an even more important vertical shift along the log modulus axis due to the changing structure and other factors (*32*). Takemura and coworkers (*21, 26*) atrributed this vertical shift to the changing degree of crystallinity. Recently, Matsuoka (*19*)

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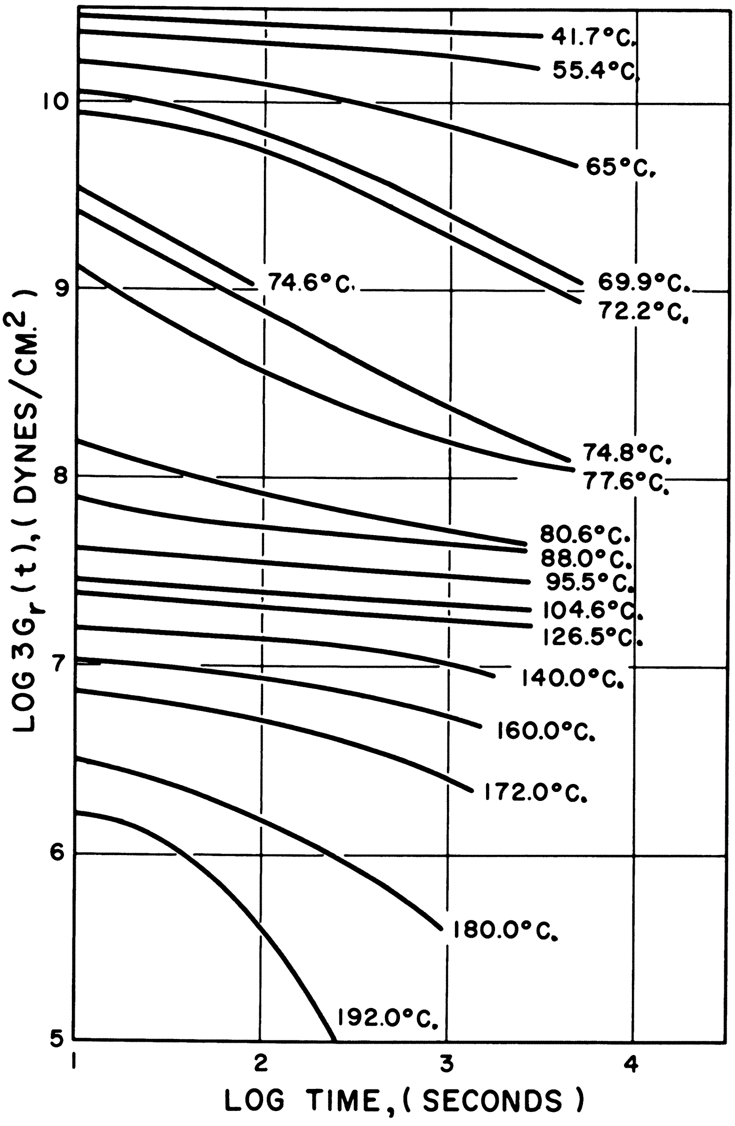

Figure 2. Isothermal modulus-time curves of pure polyvinyl chloride from 41.7° to 192.0°C.

interpreted it on the basis of "the stiffness of the crystalline regions." Thus this is a further confirmation of the semicrystalline nature of polyvinyl chloride.

Figures 1 to 3 also show that the decrease from the rubbery plateau to the rubbery flow is more rapid for plasticized PVC than for the pure polymer. This has been previously observed for polystyrene and plasticized polystyrene (*27*). Maximum relaxation times have been shown to be shorter for the plasticized sample due to the decrease in T_g as well as to a decrease in apparent average molecular weight (*27*). A similar interpretation applies in the case of plasticized polyviny. chloride.

Above the melting point, disappearance of microcrystallites destroys the network structure of PVC; consequently it behaves like a typical high molecular weight linear amorphous polymer.

In conclusion, we may state that viscoelastic data presented in this paper further reaffirm the contention that polyvinyl chloride has a network structure with microcrystallites acting as cross-links. Incorporation of plasticizer affected PVC in a way similar to amorphous polymers mainly by lowering T_g of the amorophous regions. Microcrystallites appear to be stable even in the presence of

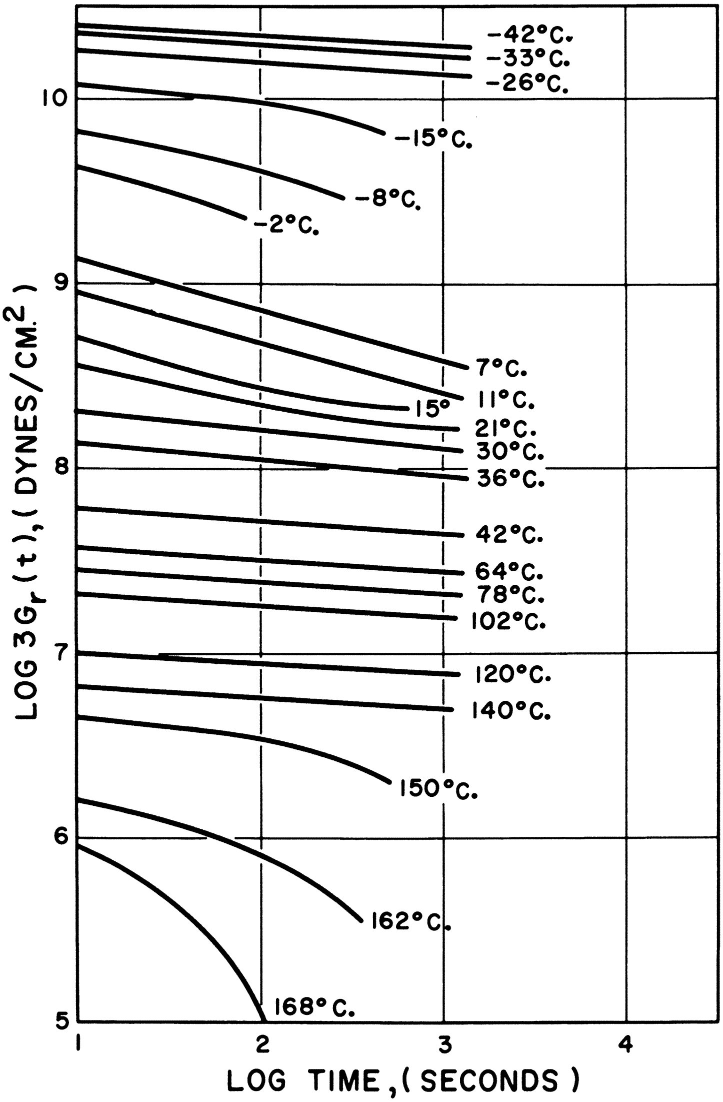

Figure 3. Isothermal modulus-time curves of plasticized polyvinyl chloride (30 wt. % dioctyl phthalate) from −42° to 168°C.

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relatively high diluent content. Below and around the glass transition temperature, PVC behaves as a typical amorphous polymer. At temperatures much higher than T_g but below T_m, it shows characteristics of a semicrystalline polymer. However, when the melting point is exceeded, polyvinyl chloride exhibits a rubbery flow region that is common among amorphous linear polymers. Thus PVC is a "borderline" polymer that possesses the viscoelastic properties of both amorphous and semicrystalline polymers.

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12

Compressibility and Volume Expansion of PVC and Solvent in the Presence of Nitrogen

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The compressibility, volume expansion, and closing pressure have been determined for a mixture of PVC, solvent, and nitrogen, the last one being dissolved in the gel-like composition at the temperature and pressure ranges investigated. The test procedure is as follows: the specimen is placed within the bore of a high pressure cylinder which is closed at both ends with movable pistons and sealed off with "Bridgman seals." A linear temperature relationship was observed for the compressibility and volume. This indicates that the system is in a state of internal equilibrium over the whole temperature and pressure range. The closing pressures are related to actual values—i.e., the degree of filling and the specific volume as a function of the temperature.

While the volume behavior of low molecular liquids and crystals under high pressure has been studied (*2*), the investigation of high molecular substances and their behavior in relation to pressure and temperature has been pursued only in recent years (*3*, *4*, *5*, *6*, *7*, *9*, *10*, *11*, *13*, *14*, *15*, *16*). It is therefore understandable that little is known about these properties for polymers.

The studies published so far have been concerned with the change in volume of pure high molecular materials. But the behavior of mixtures of polymers with solvents as well as with other components is extremely important to their use. The volume behavior of pure polymers and of polymer solvent mixtures is important for processing in injection molding machines. The solubility of gases in polymers, dependent on pressure and temperature, is significant in both of the following cases. The first case deals with polymeric seals on vacuum equipment which are subject to outgassing, particularly if the equipment was previously pressurized.

These give off significant quantities of gas when evacuated, especially if they had been exposed to excess gas pressure before evacuation. The second, technically more important case deals with high pressure processes for the manufacture of foams (*12*).

In order to be able to make products faultlessly from those kinds of mixtures, one must know the volume behavior under pressure over a wide temperature range. In making PVC foam by the high pressure process, a mixture of PVC–solvent and a blowing agent is placed in a gas-tight, high pressure mold. The mixture is heated to about 170°C. under pressure. At this temperature, the solvent rapidly penetrates the polymer, and the PVC–solvent mixture is converted to a gel. Here the PVC no longer exists in a glass state but in the state of inner equilibrium in which the diffusion and solubility processes are increased by several powers of 10 over that of the congealed state. At 170°C. the blowing agent decomposes, and much of the liberated gas remains dissolved in the gel. A smaller part of the gas expands the gel to fill the void remaining in the mold. With slow cooling of the reacted mixture one gets a foam with a uniform sealed cell structure (*12*).

The closing pressure for the mold for making uniform foams may be obtained by knowing precisely how the volume of this gel depends on temperature and pressure.

It is therefore important to determine how the volume of the mixture varies with pressure and temperature if the system exists in the gel state. Because of the low Young's modulus in rubber gels, no strongly anisotropic tension distribution can exist. The volume dependence can therefore be determined by one-sided loading and deformation, as can be applied in a hydraulic press. The compressibility can be obtained from one-sided deformation without determining the other coefficients of elasticity.

Experimental

Apparatus. The experimental arrangement is shown schematically in Figure 1. It is essentially the equipment that was used earlier for determinations on polystyrene (*4*). The specimen, *h*, is located within a high pressure cylinder, *e* (maximum internal pressure = 12,000 atm.), between two mushroom-shaped pistons, f_1 and f_2. The stems of the pistons pass through Bridgman seals (*2*), and both are held in place by supporting pistons, c_1 and c_2. The seals are copper rings with a Teflon ring between them. The stems of the pistons, f_1 and f_2, float freely in the borings of the support pistons, c_1 and c_2. This ensures that the force exerted by specimen, *h*, on the pistons, f_1 and f_2, is transmitted only through the ring-shaped surface of the seal, and that the pressure exerted on the seal is always greater than the pressure in the sample chamber. For this arrangement

$$P_D = P_p \cdot Q_p / Q_D$$

where P_p = pressure in the specimen chamber
P_D = pressure in the seal
Q_p = cross-sectional area of the specimen
Q_D = surface of the seal ring

In this apparatus the ratio of the cross-sections is 4/3.

Both the lower piston, c_2, and the cylinder, *e*, rest on a baseplate, *m*, which, for better operation, is bound by a ring, l, to the cylinder. The baseplate lies on a steel block and asbestos insulator, *o*, on a 60-ton press (Mohr and Federhaff, Mannheim, West Germany), which is fitted with a constant pressure device.

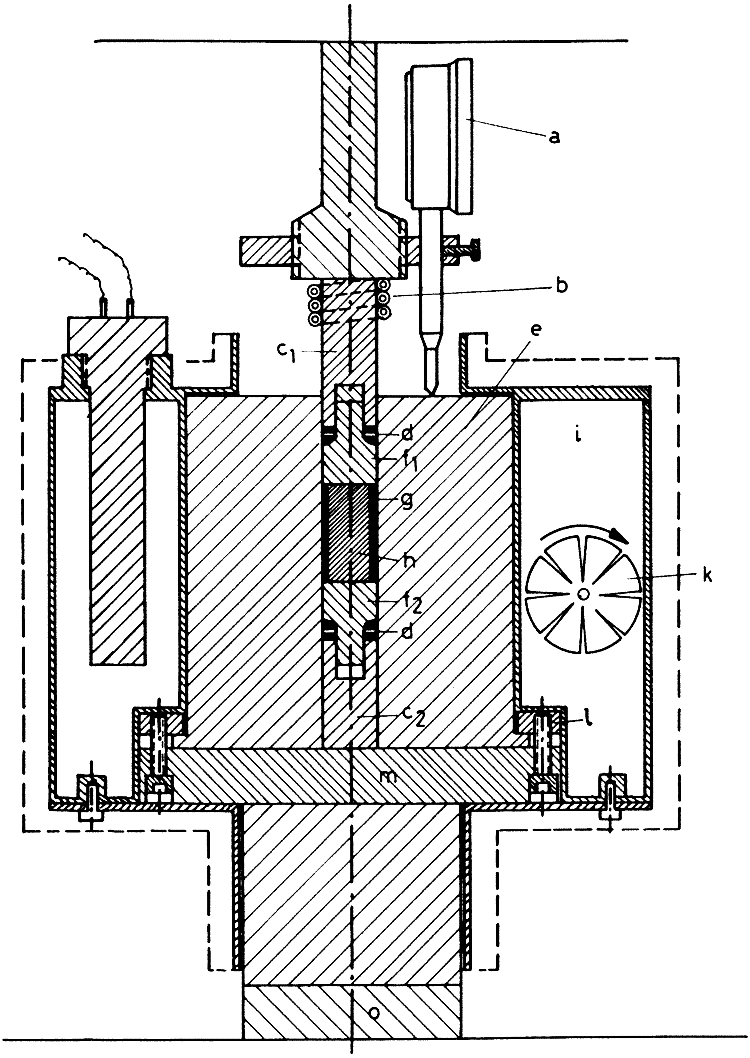

Figure 1. Diagrammatic presentation of the experimental arrangement. a, dial gage; b, water-cooling system; c_1, c_2, supporting pistons; d, seal; e, high pressure cylinder; f_1, f_2, load-applying pistons; g, steel shell; h, specimen; i. thermostat; k, stirrer, l, ring; m, baseplate; n, steel block; o, asbestos insulation, p, heating element.

The upper piston, c_1, is equipped with a water cooling system, *b*, and carries a gage in a tension ring accurate to $\pm 10^{-3}$ mm. The gage shows the position of the upper piston, c_1, relative to the cylinder, *e*; it reflects the height of the specimen and variation of the seals. The elastic and thermal behavior of the steel parts is negligible.

The temperature of the cylinder is regulated with an annular liquid thermostat, *i*. The heating medium (silicone oil) is constantly circulated to maintain temperature control. A platinum resistance thermometer which operates through a Wheatstone bridge controls the current in the heating unit with the help of a hoop-drop regulator. The temperature in the oil bath can be set between 20° and 180° C. ±0.2°.

The pressure on the specimen, *h*, is determined by the load exerted by the press and by the cross-section of the piston. Since the friction of the seal on the cylinder wall reduces the pressure rise on increasing the load, and, conversely, enhances it when the load is reduced, the true pressure is determined by averaging the values after increasing and reducing the load several times. Figure 2 shows the dependence of the piston traverse on the load. The hysteresis exhibited with high pressures has widths up to ±200 kp. (1 kp. = 2.2 lb.) at a load of 6 Mp. (1 Mp. = 2200 lb.) This corresponds to a pressure precision of ±65 atm. in 2000 atm. At lower pressures the hysteresis is narrower if the load cycle is conducted only in the low pressure region and the seals have not been made to move appreciably, as under higher pressure. In making volume measurements, the highest pressure intended to be used must be loaded on the seals at the beginning of the test in order to be sure that the seal is volumetrically reversible during actual measurement. The indicated precision of ±65 atm. applied over the entire measurement range and at 150 atm. leads to a considerable error of measurement (±20%). Bridgman seals, designed for use up to 2000 atm., are therefore not recommended for volumetric measurements at pressures below 150 atm.

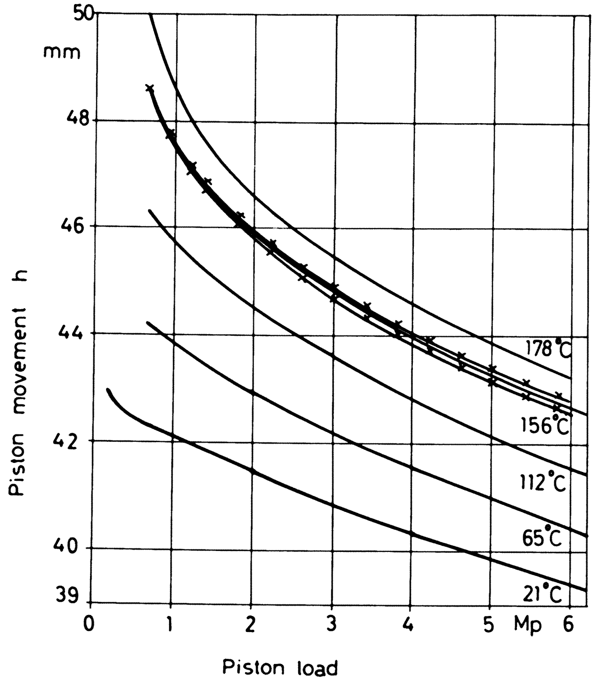

Figure 2. Relationship of the piston movement, h, to the piston load, P, at various temperatures.
The hysteresis arising from friction is shown only for 156°C.

It is then more expedient to use glass apparatus with a mercury dilatometer (*14, 15*). This method of measurement, however, leads to problems that are avoided only with difficulty, using the materials analyzed in this work.

With the method used here, the specimen is free to expand in only one direction, and this means that only a linear expansion can be determined. This is the same as volumetric expansion. If the system is above its glass temperature, T_G,

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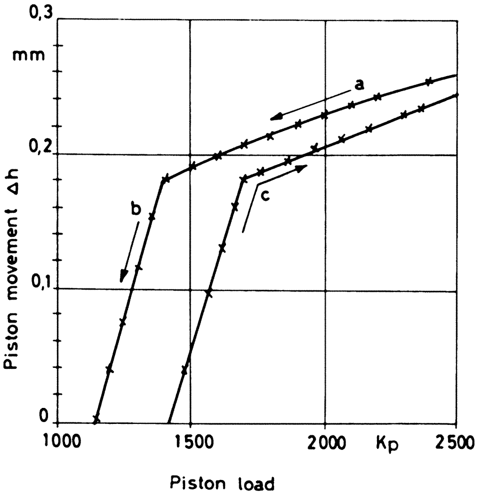

Figure 3. The change in piston movement, Δh, in relation to the load on the piston upon inserting the steel sleeve.

Above the bend, only the change in volume of the seal is recorded as the load is reduced (curve a). Below the bend, the change in volume of the specimen itself is observed (curve b). Curve c indicates the effect with increasing load.

the gel-like system behaves like a fluid, and superimposed, anisotropic stress fields can be disregarded in relation to hydrostatic pressure effects. This condition was fulfilled in all measurements.

Method. All measurements were made on a mixture of PVC and solvent in the ratio 1:1.07 by weight. Chlorinated hydrocarbons with boiling points around 60° C. were used as solvents. Nitrogen was obtained by thermal decomposition of diphenylsulfone-3,3′-disulfhydrazide. The thermal decomposition commenced at 148° C., at which temperature it yields 140 cc. of nitrogen per gram of substance at normal pressure (*8*).

To the PVC is added diphenylsulfone-3,3′-disulfhydrazide, 15 parts by weight. In order to hold the air cushion over the specimen to a minimum, the lower pistons, f_2 and c_2, and the seal are pushed high into the cylinder when inserted, so that the substance fills the cylinder up to the front side. Then the upper pistons are let down onto the specimen, and the specimen is pushed into the middle of the cylinder. By proceeding carefully, 18.6 grams of the prepared mixture could be put into the sample space. Then the pressure on the specimen was brought up to 2000 atm. and the whole system heated to 170° C. for 5 hours. Time was allowed at this temperature for the blowing agent to decompose, whereupon measurements were started. All the results reported here relate to specimens in which the blowing agent is thermally decomposed, and the gas, in this case nitrogen, is dissolved to the point of equilibrium in the PVC solvent system.

The experimental procedure described to this point does not allow measurement of the specimen to be made in a simple way at constant volume since the seal still undergoes volume change with variations in temperature and pressure, even though the gage indicator is constant. Isochore measurements at various temperatures are important for determining mold-closing pressures in making foams. By "closing pressures" is meant the least pressure that must be applied to the rigid form; with it the PVC solvent-blowing agent system does not require excess pressure to be expelled from the mold in the manufacturing process. In order to measure this closing pressure directly, a steel sleeve could be inserted in the bore of

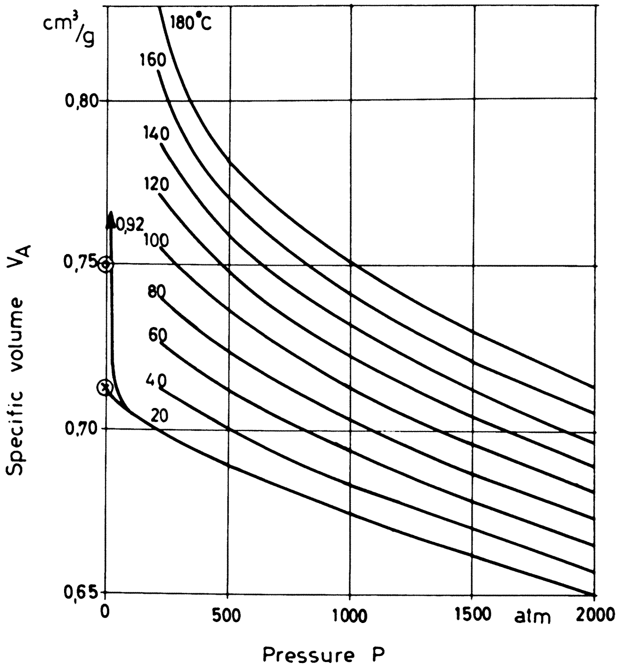

Figure 4. The mean specific volume, V_A, in relation to the pressure, P, at various temperatures

the high pressure cylinder. This sleeve is open at both ends; it is 35 mm. long and has an inside diameter of 16 mm.

This arrangement is used as follows: in the procedure described above, the force on the sample surface is always equal to that applied by the load over the entire range of pressures and temperatures used in this investigation. The volume, temperature, and pressure behavior over the entire range of temperature and pressure can be determined from the measurements made with this arrangement. With the steel sleeve, *g*, the closing pressure, P_s, can now be determined directly, as that pressure which barely suffices to relieve the force off pistons, f_1 and f_2, by sleeve, *g*.

In Figure 3 the closing pressure, P_s, is seen clearly; as long as the total pressure exerted by the press is greater than the closing pressure, P_s, the piston, f_1 or f_2, stays firmly on the sleeve, and as the pressure decreases (Curve a in Figure 3), the dial gage shows only the volume changes in the seal. However, as soon as the pressure exerted by the press becomes less than the closing pressure, the internal pressure in the specimen lifts the piston, f_1 or f_2, off the sleeve, and a sharper drop in the ordinate (Curve b in Figure 3) is seen. The extent of this drop in the ordinate is determined by the compressibility of the specimen. With increasing pressure, the process goes in the opposite direction (Curve c in Figure 3). The break in the curve occurs at a comparatively higher pressure; that is governed, as already mentioned, by the friction of the seal. The closing pressure is determined as an average of these values at various temperatures. The fact that the break in the curve occurs at different pressure values for falling and for rising load can also be explained in another way: if, starting at a pressure greater than P_s, the pressure changes, the hydrostatic pressure of the specimen acts only over a cross-sectional area which corresponds to the inner cross-section of the sleeve. As soon as the piston, f_1 or f_2, lifts off the shell, the specimen pressure acts on the entire cross-section of the piston.

Two objections can be raised against this explanation. First, the piston, f_1 or f_2, would certainly not seal the rim of the sleeve completely; and secondly, the

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break point in the curves a and b in Figure 3 should show a discontinuity in loading which corresponds to the increased load variation on the piston, f_1 or f_2, when the effective surface of the specimen under pressure suddenly changed as the shell lifted. The total cross-section of the piston is considered in calculating the closing pressure from the imposed load.

In Figure 6 the broken lines show the experimentally determined closing pressure, P_s, *vs.* temperature.

Results and Discussion

In Figure 2, the height of the specimens is plotted against the load exerted on the piston, P, in Mp, at various temperatures. To give a clearer picture, only the measurements made at one temperature (156° C.) are shown. Similarly, the hysteresis curves produced by seal friction are given only once. The mean values are given for all other temperatures.

The results of these determinations are given in Figure 4 as the specific volume, V_A, *vs.* pressure at various temperatures. In Figure 5 these same specific volumes, V_A, are plotted against temperature with pressure as a parameter. The index, A, means that the volumes are those of 1 gram of the initial mixture, the total weight of which was 18.6 grams. This definition is essential since a chemical reaction takes place in the specimen during the experiment, and the weight of the specimen can not be known exactly as the experiment proceeds. The decomposition products of the blowing agent are deposited partly as solids on the steel parts of the apparatus.

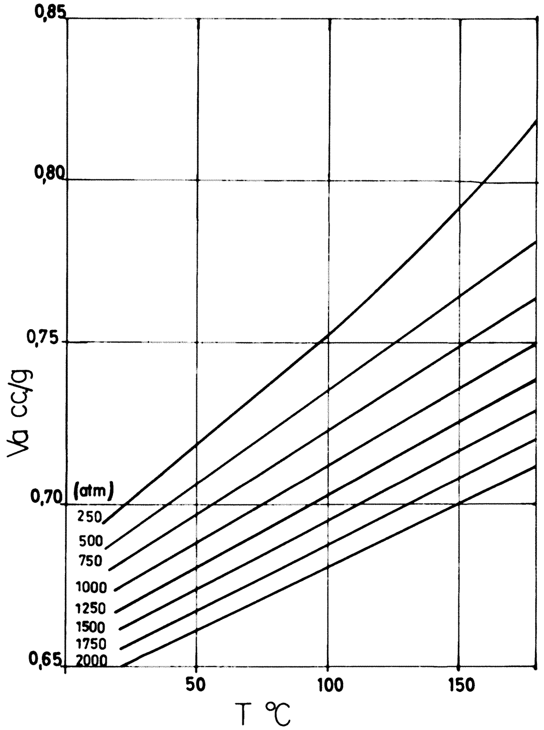

Figure 5. The mean specific volume in relation to temperature at various pressures.

If, in Figure 4, the isotherm for 20°C. is extrapolated to zero pressure, a specific volume, $V_{AO} = 0.71$ cc./gram is obtained. On the other hand, the initial weights and volumes indicate a specific volume of 0.75 cc./gram. This difference can be attributed to the inclusion of air in the paste-like mixture. At the end of the experiment the specific volume, as calculated from the weight and volume of the specimen, amounts to 0.92 cc./gram. This means that the specimen has now been expanded by the liberated gas (about 30%). From this, it follows that the specific volume of the mixture at 20° C. that was obtained by extrapolation, the value of 0.71 cc./gram, is for the completely filled test space, that is, for a test space where the filling factor is 1 (= 100% filled). Accordingly, for example, a 90% filled test space, that is, with a factor of 0.9, would correspond to a starting specific volume of $V_A = 0.71/0.9 = 0.79$ cc./gram.

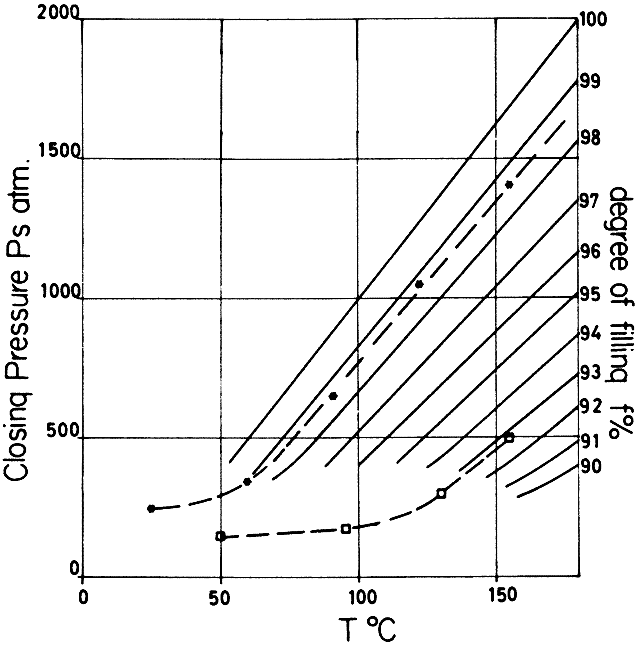

Figure 6. The relationship of the closing pressure, P_s, to the temperature for various degrees of filling, f, of the testing space.

The dashed curves show the experimental results for two specimens; they correspond to fillings of 98.6 and 92.8% respectively.

Figure 6 shows the relation of closing pressure, P_s, to temperature at various degrees of filling. The isochores are not indicated below 400 atm. since the values obtained were only poorly reproducible below this pressure. It can be seen clearly in Figure 6 that, if the test space is 90% filled at 20° C., the specimen will completely fill the space by thermal expansion by the time it reaches 160° C.

Figure 7 presents in concise form the relation between closing pressures, P_s, and three practically important parameters, the filling factor, *f*, the specific volume,

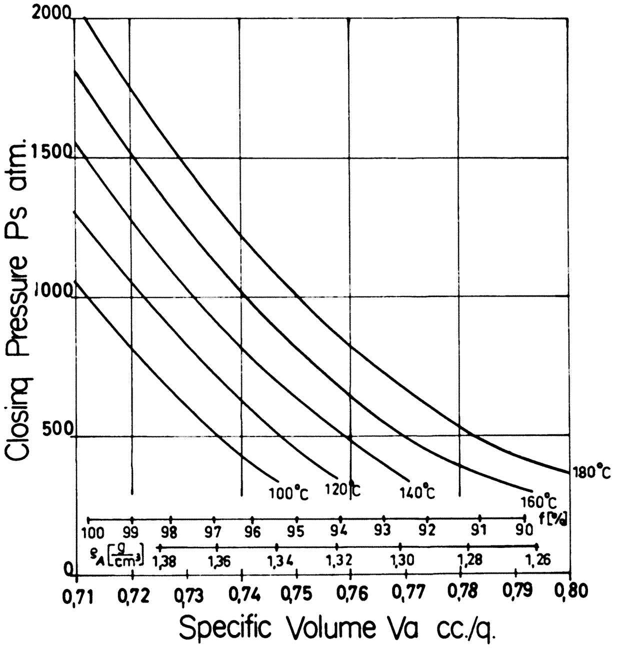

Figure 7. The relationship of the closing pressure, P_s, to the degree of filling, f, to the specific weight, ζ_A, and to the specific volume V_A at various temperatures.

Table I.

f	0.9	0.91	0.92	0.93	0.94	0.95	0.96	0.97	0.98	0.99	1.00
V_A	0.79	0.784	0.774	0.766	0.758	0.75	0.742	0.735	0.727	0.72	0.71
ζ_A	1.26	1.27	1.29	1.31	1.32	1.33	1.35	1.36	1.38	1.39	1.40

V_A, and the specific weight, ζ_A. Table I presents the specific volume, V_A, and the specific weight, ζ_A, for filling factors between 0.9 and 1.0.

It can be seen from Figure 6 and 7, that in the case of specimens that fill the test space completely, pressures up to 2000 atm. must be coped with when the mixtures are heated to 160° to 180° C. and not allowed to flow out of the mold.

The high pressures shown here are produced by thermal expansion of the specimen at constant volume. At these pressures, the generated gas is completely dissolved in the gel-like mass. The volume expansion coefficient,

$$\gamma = \frac{1}{V_A}\left(\frac{\partial V_A}{\partial T}\right)_P$$

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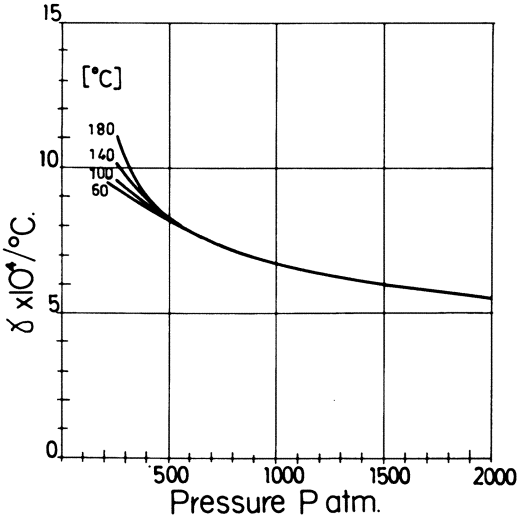

Figure 8. The pressure dependence of the coefficient of volume expansions at various temperatures.

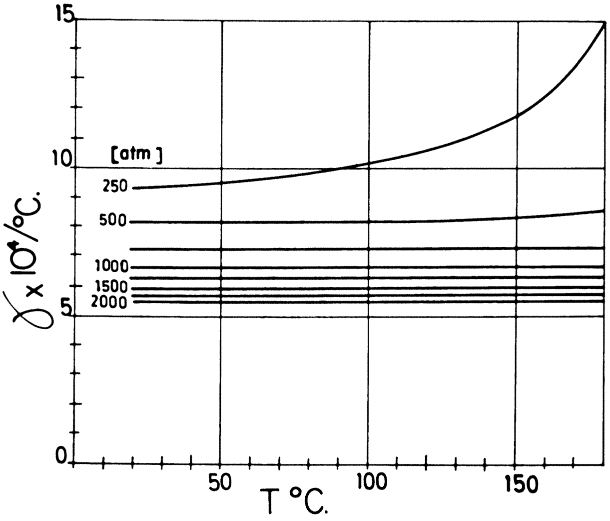

Figure 9. The temperature dependence of the coefficient of volume expansions at various pressures.

and its relation to pressure and temperature, can be obtained. This is shown in Figures 8 and 9. It can be seen clearly in Figure 8 that expansion is practically independent of temperature at pressures above 500 atm. Volume expansion occurs only at lower pressures. This behavior points to the presence of a free gas, as is obvious in Figure 9.

The compressibility

$$\kappa \equiv -\frac{1}{V_A}\left(\frac{\partial V_A}{\partial P}\right)_T$$

can be determined from Figure 4. Its dependence on pressure and temperature is shown in Figures 10 and 11. The linear relationship of compressibility to temperature, as exhibited by solids and liquids, was not observed at all over the entire range covered by the investigation (Figure 11). The curve bends clearly at a temperature of 150° C. and a pressure of 500 atm.; this great deviation of the compressibility from linear behavior is caused by a liberated gas. A separate experiment was conducted to determine whether the break in the compressibility curve could actually be caused by the solvent. These measurements over the entire range of temperature and pressure showed the usual behavior for liquids; that is, within the limits of accuracy for the dependence of volume and compressibility on temperature, compressibilities were between 11 and 14 x 10^{-5}/atm. In the temperature and pressure range concerned here, the pure solvent never reaches its boiling point.

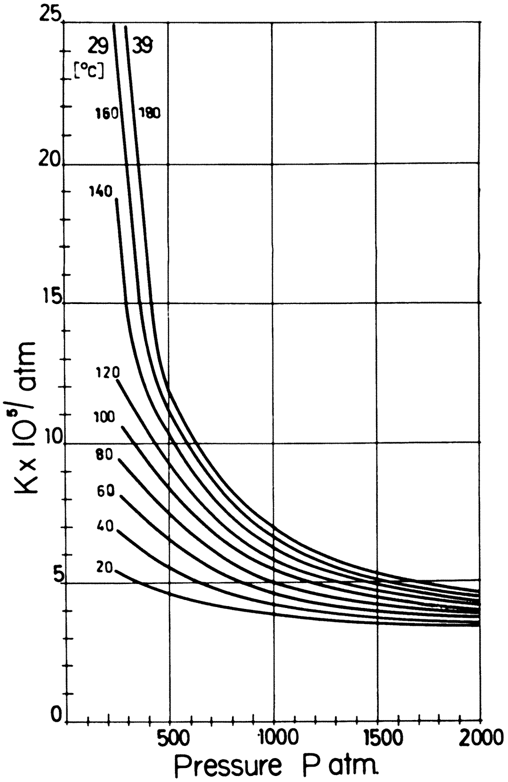

Figure 10. The pressure dependence of compressibility at various temperatures.

The closing pressure, P_s, in Figure 6 can be determined from the volume changes in Figures 4 and 5, in relation to the volume of the steel sleeve. A constant volume is obtained with the shell (thermal expansion of the steel is neglected). This shell is filled as described above, and after heating at 170° C. under a pressure of 2000 atm., the blowing reaction takes place. The load on the piston is finally reduced under isothermal conditions, and the change in height of the piston, Δh, is plotted against the load, P. (Figure 3).

The results of this kind of measurement on two specimens are shown by the dashed lines in Figure 6. They fit the group of curves well, and it can be seen that the steel shell is 98.6 to 92.8% filled. The large expansion in the specimen below 500 atm. is clearly evident from the sharp break in the curve in this pressure range.

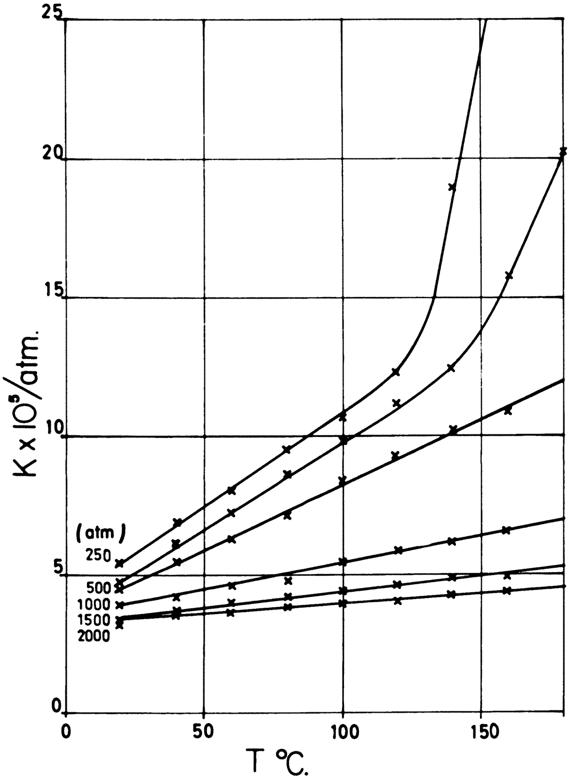

Figure 11. The temperature dependence of compressibility at various pressures.

The condition for valid results in this work is the fact that the system is in the gel-state; that is, it is in a state of inner equilibrium, and not in the glass state. Measurements of Hellwege, Knappe, and Lehmann (5) on pure PVC show the expected discontinuity in the compressibility *vs.* pressure curve at the melting point transition in the glass state. It is inferred from this study that the glass temperature for pure PVC and for the plasticized, gel-type PVC does not rise above 110° C. at pressures of 200 atm. (Figure 7). Our study showed that the system is always in a state of inner equilibrium.

As shown above, the most important quantity in making foamed plastics (*16*) is the closing pressure. In the discussion below, the pressure is understood to be that which must be applied to keep the volume of the specimen constant as the temperature is raised. In this way the closing pressure is expressed as the isochore of an equation of state.

With the compressibility

$$\kappa \equiv -\frac{1}{V_A}\left(\frac{\partial V_A}{\partial P}\right)_T$$

and the volume expansion

$$\gamma \equiv \frac{1}{V_A}\left(\frac{\partial V_A}{\partial T}\right)_P$$

the following differential expression applies:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T = \frac{dP_s}{dT} \tag{1}$$

and from it

$$\frac{dP_s}{dT} = \frac{\gamma}{\kappa} \tag{2}$$

By integration:

$$\int_{P_0}^{P_0+P_s} \kappa \cdot dP = \int_{T_0}^{T} \gamma dT \tag{3}$$

which may be approximated as

$$\int_{P_0}^{P_0+P_s} \kappa \cdot dP \approx \gamma(T - T_0) \tag{4}$$

Equation 4 shows that in order to determine the closing pressure from differential data, it is necessary to know the compressibility over the entire range of pressure and temperature.

If the system is in equilibrium, the following relation holds:

$$V_A = V_A(T, P) \tag{5}$$

$$dV_A = \left(\frac{\partial V_A}{\partial T}\right)_P \cdot dT + \left(\frac{\partial V_A}{\partial P}\right)_T \cdot dP \tag{6}$$

$$dV_A = V_A \cdot \gamma \cdot dT - V_A \cdot \gamma \cdot dP \tag{7}$$

According to Schwartz's Theorem it follows that:

$$\frac{\partial}{\partial P}(V_A \cdot \gamma)_T = -\frac{\partial}{\partial T}(V_A \cdot \kappa)_P \tag{8}$$

and from it:

$$\left(\frac{\partial \kappa}{\partial T}\right)_P = -\left(\frac{\partial \gamma}{\partial P}\right)_T \tag{9}$$

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With liquids, it is found mostly that the relationship of volume to temperature is approximately linear; that is, in the same temperature range, $\left(\frac{\partial\gamma}{\partial T}\right)_P$ = constant or

$$\gamma = \kappa(P) \tag{10}$$

On this assumption, the right side of Equation 9 will be independent of temperature $\left(= -\frac{d\gamma}{dP}\right)$ and we obtain

$$\left(\frac{\partial\kappa}{\partial T}\right)_P = a(P) \tag{11}$$

Integration with constants a and b gives

$$\kappa(T, P) = a(P)\cdot T + b(P) \tag{12}$$

From Equation 12 it is seen that, over the valid range of the approximation used, the compressibility also bears a linear relationship to the temperature, as found with the volume.

The linear relationship between compressibility and temperature is valid only when the system is in a state of inner equilibrium. If it should pass over into the glass state or if the gas dissolved in the system is liberated, a sharp deviation from the linear temperature relationship ensues (Figure 11). If the compressibility is plotted as a function of pressure, there is no simple functional relationship, and an expansion of material can not be identified with a deviation in the trends of curvature. Figure 10 illustrates an example.

Summary

The compressibility, volume expansion, and closing pressure have been determined for a mixture of PVC, solvent, and nitrogen, the latter being dissolved in the gel-like composition over the temperature and pressure ranges investigated. In these investigations, the specimen is placed within the bore of a high pressure cylinder, which is closed at both ends with movable pistons. Trouble-free seals for the pistons are guaranteed by using Bridgman seals. This procedure is useful only at pressures above 400 atm. because of the friction between the seal and the cylinder wall. Linear relationships exist between compressibility and temperature, and between specific volume and temperature when the gas is completely dissolved. This, however, assumes that the system is in a state of internal equilibrium over the whole range of temperature and pressure. In support of measurements by Hellwege, Knappe, and Lehmann (*12*), which were conducted with pure PVC, this assumption was confirmed.

The practically important closing pressure is shown for various temperatures in relation to specific volume, specific weight, and filling factor. The filling factor is the relation between the volume of the specimen and the test space.

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13

Volume Resistivity of Plasticized Polyvinyl Chloride

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Pure polyvinyl chloride alone is a rigid plastic of high volume resistivity. Addition of monomeric liquid plasticizer makes it flexible but lowers volume resistivity seriously. This loss of volume resistivity was not prevented by prepurification of commercial resin and plasticizer, though it could be worsened by addition of ionic soluble impurities. Volume resistivity was surprisingly increased by heat aging. It was not improved by use of polymeric liquid plasticizers, nor even, surprisingly, by use of nitrile rubber as plasticizer. Flexibilization without serious loss of volume resistivity was best achieved by internal plasticization by copolymerization with 2-ethylhexyl acrylate. Further studies are needed to explain these observations and to optimize the use of internal plasticization in this way.

Polyvinyl chloride alone is a rigid plastic with excellent electrical insulating properties; volume resistivity is over 10^{16} ohm-centimeters. In most of its applications, however, such as wire and cable coating, polyvinyl chloride must be flexibilized by addition of liquid plasticizers such as dioctyl phthalate. As the plasticizer concentration is increased, the plastic becomes softer and more flexible, but the volume resistivity decreases simultaneously (Table I).

This decrease has generally been accepted as an inevitable consequence of plasticization, and it is frequently explained as the migration of ionic impurities through the liquid plasticizer medium (*2*, *4*, *5*).

In order to improve the volume resistivity of plasticized polyvinyl chloride, we began by purifying both polyvinyl chloride and plasticizer. Goodrich Geon 101-EP electrical grade polyvinyl chloride was dissolved in pure tetrahydrofuran and reprecipitated by adding the solution dropwise with stirring into an excess of pure methanol, after which it was vacuum-dried overnight at 35°C. Di-2-ethylhexyl

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Table I. DOP Concentration

PVC,DOP	*Stress at 100% elongation p.s.i.*	*Shore Durometer D hardness*	*Volume resistivity, ohm-cm.*
100,0	—	75	1.5×10^{16}
100,25	3700	67	0.27×10^{16}
100,50	1600	34	0.013×10^{16}
100,75	800	18	0.0012×10^{16}
100,100	515	14	0.00018×10^{16}
0,100	—	—	0.000014×10^{16}

phthalate was vacuum-distilled before use. But neither of these treatments improved volume resistivity (Table II).

Table II. Purification of PVC and DOP

100 PVC	*100 DOP*	*Volume resistivity, ohm-cm.*
Commercial	Commercial	1.8×10^{12}
Purified	Commercial	0.50×10^{12}
Purified	Purified	0.96×10^{12}
—	Commercial	0.14×10^{12}
—	Purified	0.16×10^{12}

Thus, if there were any ionic impurities in the commercial materials, they were not removed by these purification techniques. Earlier studies also showed little or no effect unless the original polyvinyl chloride was very impure (*2*).

Experimental

Vinyl chloride/2-ethylhexyl acrylate copolymers were prepared by suspension copolymerization (1).

Polymers, plasticizers, stabilizers, and ionic impurities were blended by masticating 5 to 15 min. on a 6 inches x 12 inches two-roll differential-speed mill, adjusting the temperature between 40° and 175°C. according to the thermal plasticity requirements of the different compositions.

Milled sheets were molded into 6 inch discs 35 mils thick by preheating 1 min., pressing 1 min. at a temperature between 115° and 205°C. according to the thermal plasticity requirements of the different compositions, and cooling 1 min. under pressure before removing from the mold. Pure Hycar 1032 was too rubbery to form good moldings and was therefore cast into film from 20% solution in methyl ethyl ketone.

Tensile modulus was judged by measuring stress at 100% elongation according to ASTM D412 Die C. Shore Durometer D hardness was measured according to ASTM D1706. Volume resistivity was measured according to ASTM D257-61.

To learn more about the possible effects of ionic impurities on volume resistivity, we added known quantities of various impurities which are frequently present in polyvinyl chloride. Lead chloride is postulated as the end-product when lead compounds are used to stabilize polyvinyl chloride. Lauric and benzoic acids probably result from wasteful decomposition of the lauroyl and benzoyl peroxides used to initiate the polymerization reaction. Of these impurities, only benzoic acid had any noticeable effect on volume resistivity (Table III).

On the other hand addition of anionic emulsifiers, such as American Cyanamid Aerosol OT sodium dioctyl sulfosuccinate or Proctor & Gamble Ivory Soap Flakes, markedly decreased volume resistitity. Thus, it seems that an impurity will con-

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duct electricity (and lower volume resistivity) only if it is highly ionized and soluble in the liquid plasticizer. Recent studies with tetraethyl ammonium picrate demonstrate the marked increase in conductivity which results from such an ionized soluble impurity (*5*).

Table III. Addition of Impurities

100 PVC, 50 DOP, 1 impurity	*Volume resistivity, ohm-cm.*
—	1.3×10^{14}
Lead chloride	1.7×10^{14}
Lauric acid	1.2×10^{14}
Benzoic acid	0.37×10^{14}
Aerosol OT	0.041×10^{14}
Ivory Soap Flakes	0.036×10^{14}

Lead compounds are generally added to polyvinyl chloride in electrical formulations in order to stabilize them against thermal decomposition; 7 p.h.r. of National Lead Tribase XL modified tribasic lead sulfate was used throughout the present study. Since the stabilizer itself is an ionic impurity, it is remarkable to note that it actually increases volume resistivity (Table IV).

Table IV. Lead Stabilizer Concentration

Tribase XL In 100 PVC, 50 DOP	*Volume resistivity, ohm-cm.*
7	1.3×10^{14}
0.7	0.32×10^{14}
0.07	0.15×10^{14}
0	0.099×10^{14}

This effect has occasionally been explained as adsorption or neutralization of other ionic impurities (*4,5*). It is certainly remarkable enough to deserve further study.

One possible function of lead stabilizer is the removal of ionic impurities which form during thermal decomposition. To study this possibility, we aged both stabilized and unstabilized compositions in a 175°C. circulating air oven up to the point of severe darkening (Table V).

Table V. Oven Aging

Tribase XL in 100 PVC, 50 DOP	*Aging at 175°C., min.*	*Volume resistivity, ohm-cm.*
7	0	1.3×10^{14}
7	60	0.76×10^{14}
7	150	3.7×10^{14}
7	480	15×10^{14}
0	0	0.099×10^{14}
0	10	0.059×10^{14}
0	30	0.062×10^{14}
0	105	1.8×10^{14}

While initial aging did cause some loss in volume resistivity, it was no more severe in unstabilized than in stabilized compositions. The most startling effect was the marked increase in volume resistivity under severe aging conditions. This may be due to volatilization loss of DOP or cross-linking of polyvinyl chloride, both of which could reduce migration of ionic impurities, or it may involve adsorption of ionic impurities by the dark-colored, conjugated, polyene structure which forms by loss of hydrogen chloride. In any case it deserves further study.

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Migration of ions through the plasticizer is frequently considered to be a function of the mobility of the plasticizer itself (*2,5*). In many electrical applications, where fugitive monomeric plasticizers like DOP can cause damage, they can be replaced by non-fugitive polymeric plasticizers such as viscous liquid polyesters. Comparison of DOP *vs.* a typical polymeric plasticizer, Rohm & Haas Paraplex G-25 poly(propylene sebacate), showed no significant improvement in volume resistivity (Table VI), particularly when its lower plasticizing efficiency was considered. Thus plasticizer mobility alone does not help us explain volume resistivity (*5*).

Table VI. Viscous Liquid Polyester Plasticizer

PVC	*DOP*	*G-25*	*Stress at 100% elongation, p.s.i.*	*Shore Durometer D hardness*	*Volume resistivity, ohm-cm.*
100	100	. . .	515	14	1.8×10^{12}
. . .	100	. . .	. . .	. . .	0.14×10^{12}
100	. . .	100	760	20	4.0×10^{12}
. . .	. . .	100	. . .	. . .	9.9×10^{12}

Nevertheless, it would seem reasonable that, in the absence of any liquid plasticizer medium at all, mobility of ionic impurities would be reduced to such a low level that volume resistivity would remain high. For example, it is well known that polyvinyl chloride can be blended with nitrile rubber, such as Goodrich Hycar 1032 butadiene/acrylonitrile copolymer, and such "polyblends" are quite soft and flexible without the use of any liquid plasticizer at all (Table VII).

Table VII. Plasticization by Nitrile Rubber

PVC	*Hycar 1032,*	*Stress at 100% elongation p.s.i.*	*Shore Durometer D hardness*	*Volume resistivity, ohm-cm.*
100	. . .	. . .	75	1.5×10^{16}
100	25	. . .	75	0.81×10^{16}
100	50	2700	64	0.14×10^{16}
100	75	1700	44	0.030×10^{16}
100	100	1200	31	0.0087×10^{16}
. . .	100	. . .	. . .	0.000071×10^{16}

At first glance the use of solid nitrile rubber in place of liquid plasticizers would appear to improve the volume resistivity of plasticized polyvinyl chloride somewhat; but when the lower plasticizing efficiency of the nitrile rubber is considered, only little improvement remains at equal tensile modulus or hardness. This is difficult to explain in terms of the flow of ions through a liquid plasticizer medium. As we can see, the volume resistivity of nitrile rubber alone is much lower than that of polyvinyl chloride, and the volume resistivity of these blends is simply the resultant of the two components. Actually the same reasoning might well apply to conventional blends of good quality polyvinyl chlorides with good quality liquid plasticizers, in the absence of any added ionic soluble impurities, as we can see from our earlier data.

Finally, polyvinyl chloride may be "internally" plasticized by copolymerization with flexibilizing comonomers such as 2-ethylhexyl acrylate, and these internally plasticized copolymers may be quite as soft and flexible as conventional "externally" plasticized polyvinyl chloride, without the use of any added plasticizer (*3*).

The electrical properties of such internally plasticized copolymers are quite unusual (*6*), and as we can see deserve much more thorough study (Table VIII).

Table VIII. Vinyl Chloride/2-Ethylhexyl Acrylate Copolymers

VC,EHA	*Stress at 100% elongation, p.s.i.*	*Shore Durometer D hardness*	*Volume resistivity, ohm-cm.*
100,0	. . .	75	1.5×10^{16}
100,25	3920	59	0.81×10^{16}
100,50	2400	34	0.49×10^{16}
100,75	1000	22	0.21×10^{16}
100,100	445	25	0.0056×10^{16}
0,100	. . .	. . .	0.013×10^{16}

Here increasing quantities of 2-ethylhexyl acrylate produce increasing softness and flexibility, but volume resistivity remains remarkably high most of the way. When it does finally decrease, it does not have far to go, because the 100% 2-ethylhexyl acrylate component, which it is approaching, is itself quite high.

The superiority of the internally plasticized copolymer is clearly evident if we plot volume resistivity against a measure of plasticization such as tensile stress at 100% elongation (Figure 1). Here we can see that the best way to increase softness and flexibility, without loss of volume resistivity, is by copolymerization with 2-ethylhexyl acrylate. Polyblending with nitrile rubber provides only little advantage over conventional DOP, and liquid polyester plasticizer provides no advantage at all, except of course in terms of permanence. Thus, we may predict that the highest volume resistivities in plasticized polyvinyl chloride will be achieved by proper choice of internally plasticizing comonomers for copolymerization, and that such studies offer great promise for further improvement in this direction.

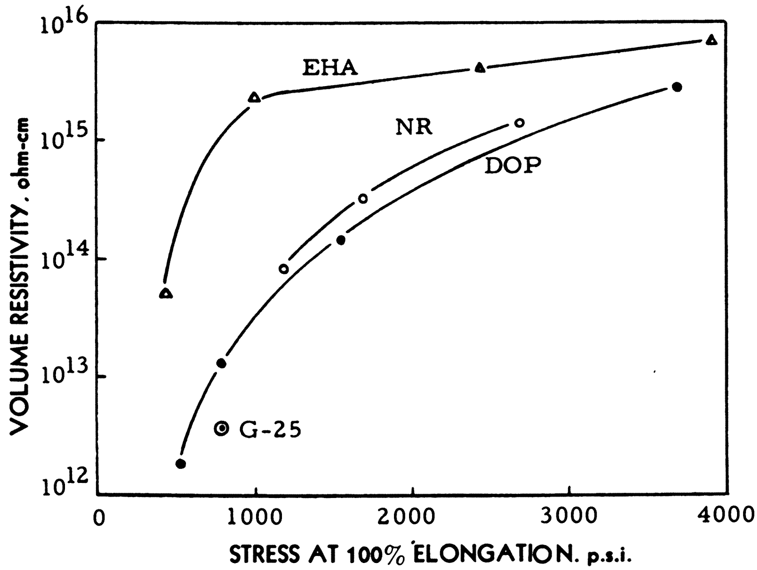

Figure 1

In summary, the volume resistivity of polyvinyl chloride plasticized by liquid or elastomeric plasticizers, or internally plasticized by copolymerization, was intermediate between the inherent volume resistivities of the pure components and combined the contributions of each of them. The presence of ionic soluble impurities in liquid plasticizers provided mobile ions which conducted electricity and thus lowered volume resistivity. Copolymerization with 2-ethylhexyl acrylate provided an excellent balance of softness and flexibility with high volume resistivity; further studies of internal plasticization by copolymerization are therefore recommended.

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14

Use of the Graded Gel Block in Evaluating PVC Plastisols

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Following a review of past work, this article describes the "Graded Gel Block," a new commercially available instrument designed to evaluate the selling characteristics of polyvinyl chloride plastisols. This instrument allows the various stages of plastisol gelation to be followed at and beyond the liquid-solid transition and facilitates the prediction of the minimum temperature necessary to attain adequate physical properties. Plasticizers studied and reported by way of examples of the types of investigation possible with the instrument include dialkyl phthalates, a triaryl phosphate and the diisooctyl esters of a series of aliphatic dicarboxylic acids.

The first commercial use of a polyvinyl chloride (PVC) plastisol in the United Kingdom was in 1941 when ICI (Hyde), Ltd. made its first sale of leather cloth to the London Passenger Transport Board for the reupholstering of London bus seats. By the end of World War II, the Distillers Co. had developed a paste grade PVC process which contributed to an agreement with B. F. Goodrich Chemical Co. and the formation in 1946 of British Geon, Ltd., whereby production of Goodrich developed suspension polymers and the Distillers' paste polymer Geon 121 was started in 1948.

It is surprising therefore that after such a lapse of time, we should consider it interesting to discuss laboratory techniques for the study of the effect of temperature on the properties of PVC plastisols.

Although this article is mainly concerned with the liquid/solid transition temperature and the effect of increasing temperature on the tensile properties of the solid state, we recognize the importance of studies on the effect of increasing temperature on the viscosity of the liquid plastisol. The latter studies, which indicate the well known initial lowering of viscosity followed by a rapid rise in viscosity, have an important bearing on the use of PVC pastes for such applications as rota-

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tional casting and the coating of heated articles by dipping. Furthermore, it is recognized that the temperature at which the viscosity/temperature curve approaches the vertical bears some relation to the liquid/solid transition temperature. Such studies have been made by Todd, Esarove, and Smith (*9*), Alter (*1*), Bauer (*2*), Newton and Cronin (*8*), and Cowperthwaite, Coe, and Frissell (*3*). Alter describes the vertical region of the viscosity/temperature curve as the "gel region," and Newton and Cronin refer to the attainment of 1000 poises, "beyond which the plastisol virtually ceases to flow," as the "setting temperature." The latter authors also studied tensile properties after heating the plastisol in a mold for a fixed time at different temperatures. The temperature at which the tensile strength reached 2000 p.s.i. was called the "gelation temperature" and where it attained a maximum, the "complete fusion temperature."

Cowperthwaite, Coe, and Frissell (*3*) in their viscosity/temperature studies have defined the temperature at which the plastisol viscosity begins to increase as the "gel temperature." These authors also studied the tensile strength of films cast on glass plates, fluxed at a series of temperatures between 300° and 425°F. They have defined the temperatures at which tensile strengths of 1000 and 1500 p.s.i. are attained as the "fluxing temperatures."

We have been concerned with the casting of a plastisol along a flat metal surface having a rising temperature gradient, which technique is by no means a new one. McKenna (*7*) cast films along such a surface and after a fixed time stripped off the film from the hot end. The temperature at the point of film rupture he called the "fusion temperature." Frissell (*4*) adopted a similar technique of hot stripping and termed the breaking point the "minimum fluxing temperature." Another method of determining plastisol fusion has been described by Graham and Darby (*5*). A small droplet of plastisol was placed between two glass plates and heated at a rate of 2°C. per minute. The temperature at which the plastisol became clear was called the "relative fusion point." Allied to this, Graham and Darby gelled thin films of plastisols at three distinct temperatures—150°, 170°, and 200°C. They found that at 150°C. only plasticizers of a high aromatic character had attained 75% of the ultimate tensile strength.

The most detailed study involving the spreading of plastisols on a metal surface having a temperature gradient has been carried out by Greenhoe (*6*). His hot bench was a modification of the incline flow plate of Castor Engineering. He cast a film of PVC paste on a strippable paper, laid the paper, film downwards, on the hot bench, and after a fixed time stripped off the paper from the hot end with the film attached. The point at which the film broke he called the "gel point." After stripping from the paper, three further so called "transition points" were assigned to the film as follows:

The temperature at which clarity begins to develop he defined as the "haze point."

A slightly higher temperature than the haze point, where there is a marked increase in strength and elongation which could readily be noticed by simple manual stressing, he defined as the "elastomeric point."

The temperature at which the film acquired resistance to disintegration by stressing in ethyl acetate and which corresponded to the attainment of maximum tensile strength he defined as the "fusion point."

As shown in Figure 1, these transition points were superimposed on the tensile strength/temperature curve, and the author suggested that they can supplant such tedious tensile strength measurements.

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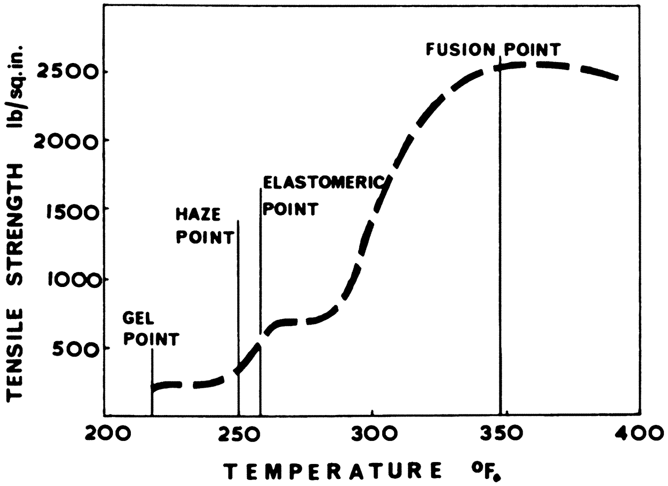

Figure 1. Tensile strength/temperature curve—DOP at 60 p.h.r. (6)

In addition to these four, Greenhoe also described two more hot bench transition points in the temperature region below the "gel point." As shown in Figure 2, these were superimposed on the well known viscosity/temperature curve. The transition points are defined as follows:

1. The temperature at which the fluid plastisol becomes dry and puttylike he defined as the hot bench "fluid point." The vertical line corresponding to this temperature cuts the viscosity/temperature curve of the plastisol at a point where the viscosity is rising rapidly.
2. The temperature where the puttylike plastisol changes to a dry crumbly solid, which is just above the temperature where the plastisol loses its identity as a fluid in the viscosity/temperature curve, he defined as the hot bench "dry point."

Six transition points in all were defined by Greenhoe which, with rising temperatures, were fluid point; dry point; gel point; haze point; elastomeric point; and fusion point.

We consider it essential in temperature gradient studies to recognize certain transition and critical points that could be useful in industrial practice, to select the important ones in this context, to keep them as few in number as possible, and to describe them with as little ambiguity as possible.

Some four years of technical service work has been carried out on the laboratory prototype of the gel block, and a preliminary report of this work has already been published by Wheeler and Clifton (*11*). Arrangements have now been made for the commercial production of the gel block (*10*). This is an improvement on the prototype in that a boost heater with automatic cut-off is incorporated to reduce the time to heat up from cold to the desired temperature gradient.

Description of the Gel Block

The gel block (Figure 3) consists of an aluminum casting 48 inches long by 4 inches wide by 1 inch deep with electrical heating elements at one end and facilities for water cooling, if required, at the other end. The block is lagged and is fitted with an insulated hinged lid. A trough 3½ inches wide by $^1/_{10}$ inch deep has been machined along the whole length of the upper surface of the block. It is in this trough that the plastisols are cast. The temperature is controlled by a thermostat mounted near the heaters. Eleven thermocouples, set 10 cm. apart, are connected to a recorder so that a permanent record may be obtained of the temperature gradient during a test. With water cooling, a temperature gradient between 40° and 200°C. can be obtained; without cooling, it is between 100° to 200°C.

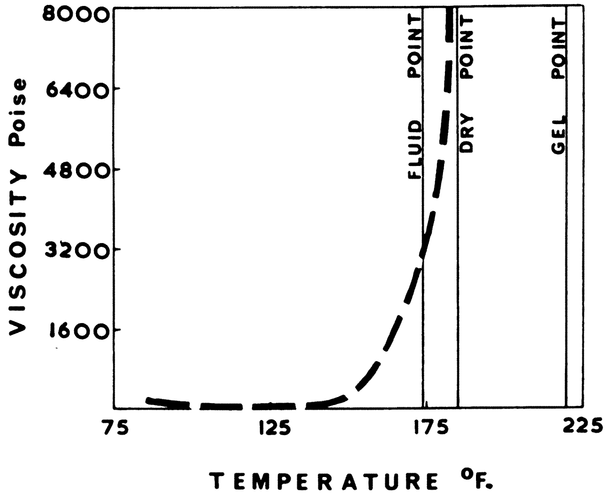

Figure 2. Viscosity/temperature curve—DOP at 60 p.h.r. (6)

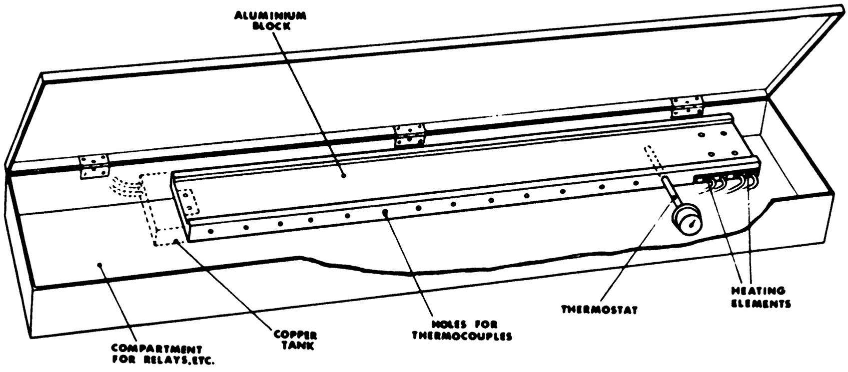

Figure 3. Diagram of graded temperature gel block

Preparation of Plastisol. In all cases the plastisols were prepared on a Winkworth-Z blade mixer and degassed before use at less than 0.1 mm. of Hg. The same order of mixing and similar mixing and degassing times were employed. A liquid cadmium-barium stabilizer was used.

Casting the Plastisol. After the gel block had attained equilibrium temperature, a thin film of silicone grease was applied to the block, and then a strip of

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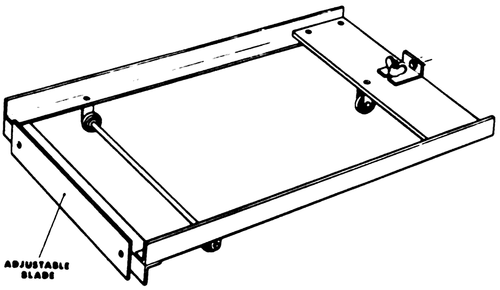

Figure 4. Diagram of doctor blade carrier

aluminum foil (3.5 inches wide and 0.001 inch thick) was laid down and the lid closed for 10 minutes. The plastisol was poured onto the cooler end of the block and spread along the surface by means of an electrically driven doctor blade mounted on three ball races (Figure 4). After a time interval the foil was removed from the block and allowed to cool for at least 30 minutes before the film was examined.

Dwell Time and Thickness of Film. After preliminary investigation into dwell time and film thickness it was found that the transition point chosen and the critical points arising from the tensile strength/temperature plot reached steady values in less than 20 minutes with thickness between 0.010 and 0.025 inch. The thickness used in practice was in the range 0.020 to 0.025 inch. The variation in thickness across the width of the film was less than 0.001 inch, and the variation along the length was never more than 0.004 inch. Along the effective length of the gelled film the variation was usually less than this.

The 20-minute dwell time used is considerably greater than that used in commercial practice. For example, in the spreading of PVC plastisols on cloth, depending on the thickness of film applied and the method of heating, such as infrared or more recently hot air jets, the dwell time can be as low as 30 seconds. The temperature attained by the plastisol in these commercial processes can be as high as 190°C. In the study reported here, however, we had to choose a dwell time which would allow the attainment of an equilibrium over the whole temperature range being studied.

Type of Polymer. Different paste grade polymers were examined and it was found that the results were dependent on the type of polymer used. In this article we report on a polymer common to both the U.S. and the U.K.—Geon 121.

Examination of Cast Film. The film can now be examined both before and after stripping from foil. A simple test was devised to determined the transition point from liquid to nonliquid state. A palette knife was drawn along the foil from the end where some of the plastisol was still liquid. Plastisol flowed easily in front of the knife until it came to a point where the plastisol was no longer spreadable. At this point, which was sharply defined, it was impossible to push the blade further. The temperature at which this occurs has been called the liquid/solid transition point (Figure 5).

Prior to the removal of the film from the gel block, samples of liquid were rapidly removed at various temperature levels and their viscosities measured on a Ferranti-Shirley cone plate viscometer at 20°C. The amount of material required for each measurement was very small and enough could be obtained by making one pass with a small spoon spatula across the width of the plastisol. At a temperature about 5°C. below the liquid/solid transition point there was a very sharp rise in the viscosity/temperature plot (Figure 5). These viscosity measurements did not correspond to the previously discussed viscosity/temperature studies since the viscosities were carried out in this case at 20°C.

As already mentioned, McKenna (*7*), Frissell (*4*) and Greenhoe (*6*) have characterized the gelation behavior of different plastisols by the temperature at which the film breaks on hot peeling from the metal surface. We found, however, that the temperature at which the film could be peeled from the foil varied depending on whether the peeling was carried out before or after the film had been allowed to cool (Figure 5). We do not consider that this type of transition point has any particular practical significance.

Dumbbell specimens 3.8 mm. wide were cut from the strip at 2° to 3°C. intervals They were tested on a Type E Tensometer, which is similar to an Instron or Scott CRE tester, at a rate of extension of 12 inches/min. Tensile strength measurements were free from scatter until the high temperature end was reached. The cause of the scatter in this region is not fully understood but was constantly present. Although it was relatively easy to estimate the maximum tensile strength within 100 p.s.i., the temperature at which the material first gave this maximum was difficult to determine. We have chosen critical temperature points corresponding to certain percentages of this estimated maximum tensile strength. The lower one (5%) corresponds approximately to a point where it is possible to handle the material without damage. Knowledge of such a temperature would be useful in pregelling operations. The upper one (90%) corresponds to a point which is just below the region where some scatter in the data begins to occur. We consider that an additional 15°C. will ensure the attainment of maximum tensile strength (Figure 5).

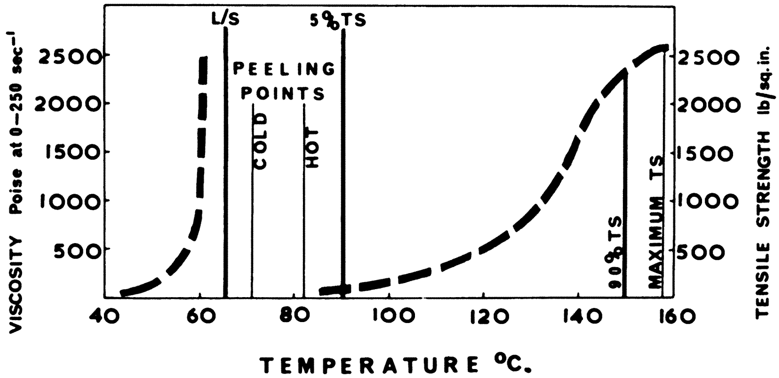

Figure 5. Viscosity/temperature and tensile strength/temperature curves

DOP at 75 p.h.r.; 20 minutes on gel block; viscosity measurements 20°C.

Transition and Critical Points. We have chosen therefore as points of particular significance:

1. The liquid/solid (L/S) transition temperature as determined by the moving blade technique.

2. The critical temperature at which 5% maximum tensile strength (5% TS) is achieved.

3. The critical temperature at which 90% maximum tensile strength (90% TS) is achieved.

Examples of Use of the Gel Block

Figure 7 (Figure 6 and Table I give explanations of Figures 7 to 12) shows the effect of increasing plasticizer content for a plastisol based on di-*n*-heptyl phthalate (D*n*HP). The transition from liquid to solid occurs at increasingly higher temperatures as the plasticizer level increases from 50 parts per hundred of resin (p.h.r.) to 130 p.h.r. Increasing the plasticizer content has little effect on the two critical temperatures with the exception of 5% TS at 130 p.h.r. which point is subject to error because of low tensile strength.

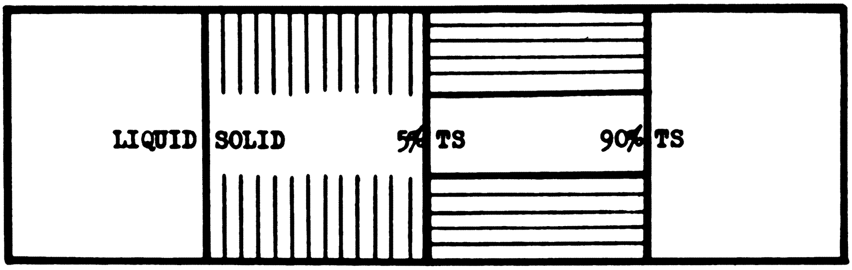

Figure 6. Key to Figures 7 to 12

Table I. Abbreviations Used in Figures 7 to 12

Phthalates	
Di-n-butyl	DnBP
Di-n-hexyl	DnHxP
Di-2-ethylbutyl	DHxP
Di-n-heptyl	DnHP
Di-Alphanol 79[a]	D79P
Di-2-ethylhexyl	DOP
Diisooctyl	DiOP
Di-n-octyl	DnOP
Di-Alfol 610[b]	D6/10P
Dinonyl[c]	DNP
Diisodecyl	DiDP
Ditridecyl	DTDP
Diisooctyl succinate	DiOSucc
Diisooctyl glutarate	DiOG
Diisooctyl adipate	DiOA
Diisooctyl azelate	DiOZ
Diisooctyl sebacate	DiOS
Trixylyl phosphate	TXP

[a] The alcohol used for this ester is known as Alphanol 79 and is produced by the Oxo process. It consists of mixed normal primary and α-methyl substituted primary aliphatic C_7, C_8, and C_9 alcohols.
[b] The straight-chain alcohol used for this ester is known commercially as Alfol 610 and is produced by the Ziegler polymerization of ethylene. The composition of the alcohol is 20% C_6, 35% C_8, and 44% C_{10}.
[c] This is essentially di-3,5,5-trimethylhexyl phthalate.

Figure 8 shows the effect of increasing molecular weight for a series of normal dialkyl phthalates at 75 p.h.r. An increase in the alkyl chain length increases the transition and critical temperatures. The examples concern a series of normal alkyl esters apart from the ditridecyl phthalate (DTDP) which is added to show the effect of high molecular weight.

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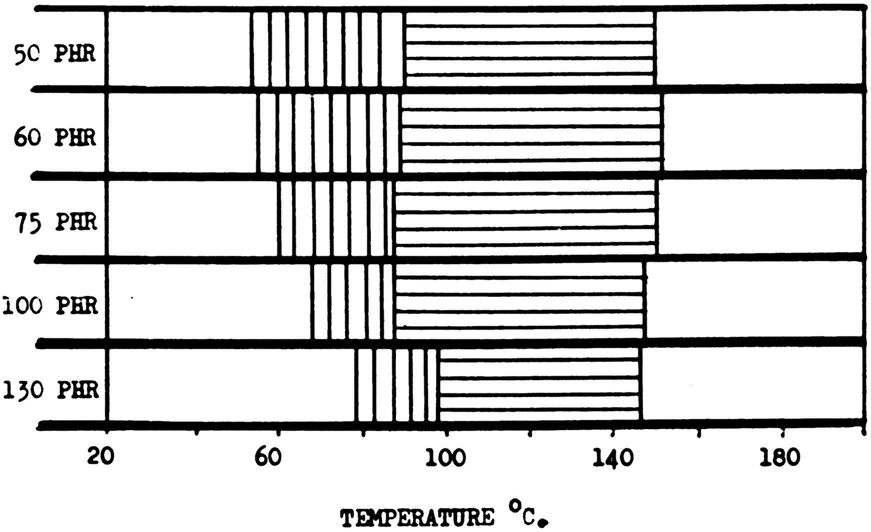

Figure 7. Effect of plasticizer concentration

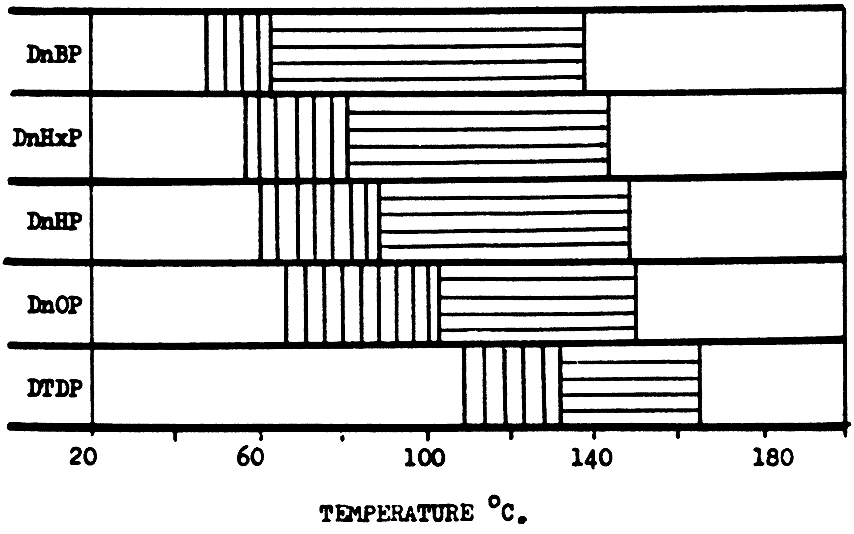

Figure 8. Effect of increasing molecular weight for a series of normal dialkyl phthalates at 75 p.h.r.

Figure 9 shows some of the more well known commercially available phthalates, also at the 75 p.h.r. level. As the molecular weight of the phthalate plasticizer increases, the general trend is toward higher transition and critical points. Individual differences in this general trend can be attributed to the alkyl groups having different degrees of branching or the alcohols used in the esterification being mixtures of different molecular weight.

Figure 10 indicates the transition points for diisooctyl esters of normal aliphatic dicarboxylic acids of increasing molecular weight. The plasticizer level

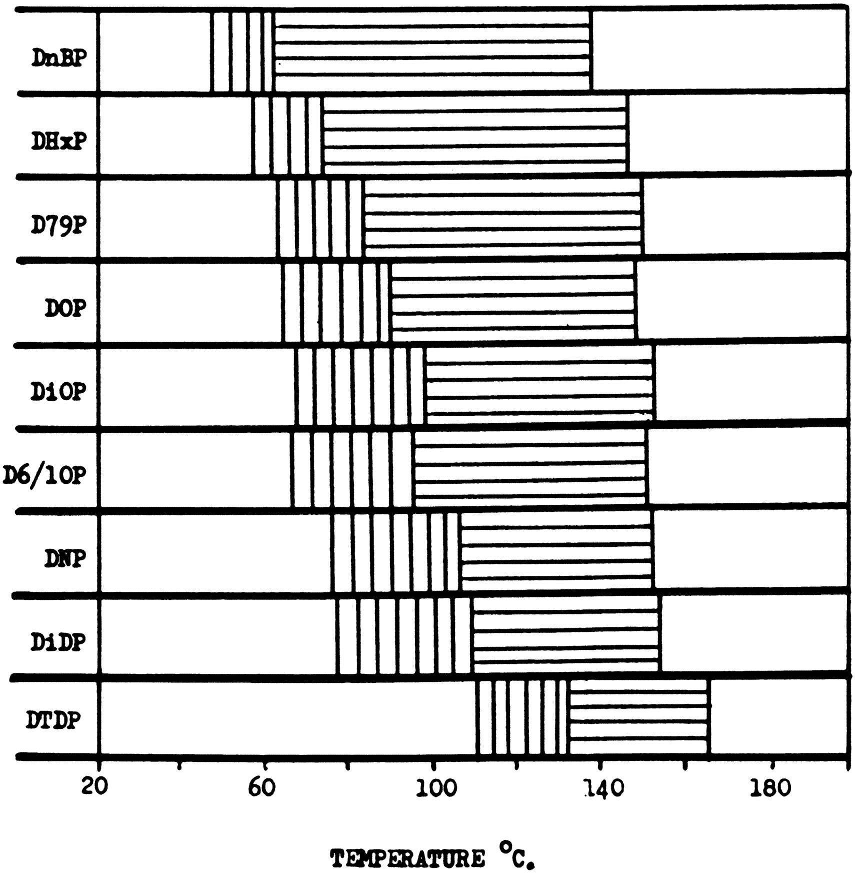

Figure 9. Comparison of commercially available phthalates at 75 p.h.r.

in this series was 50 p.h.r. These esters give low viscosity pastes and confer very good low temperature flexibility on the final product. Di-*n*-heptyl phthalate at 50 p.h.r. has been included for comparison. Although of lower molecular weight the points for the succinate are higher than for the phthalate indicating the importance of the structural difference between the two types of dicarboxylic acids. The transition and critical points within the aliphatic dibasic acid series tend to increase with increasing chain length of the dicarboxylic acid.

Figure 11 indicates the differences between three different chemical types of plasticizers. A comparison has been made between a commercial trixylyl phosphate (TXP), diisooctyl phthalate (DiOP) and diisooctyl sebacate (DiOS). It is apparent that all three points increase from TXP to DiOP to DiOS. The DiOS is at 50 p.h.r. since at 75 p.h.r. the film would be very low in tensile strength.

Figure 12 shows the effect of mixing plasticizers at a total plasticizer level of 75 p.h.r. Qualitatively the results are as expected in that the transition and critical points for the blends lie between those for the individual components.

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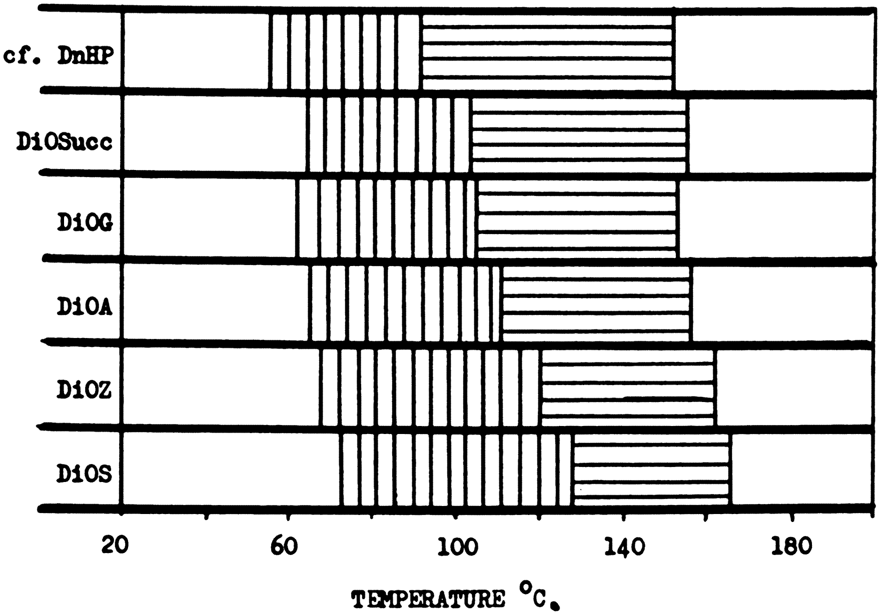

Figure 10. Comparison of diisooctyl esters of normal aliphatic dicarboxylic acids of increasing molecular weight at 50 p.h.r.

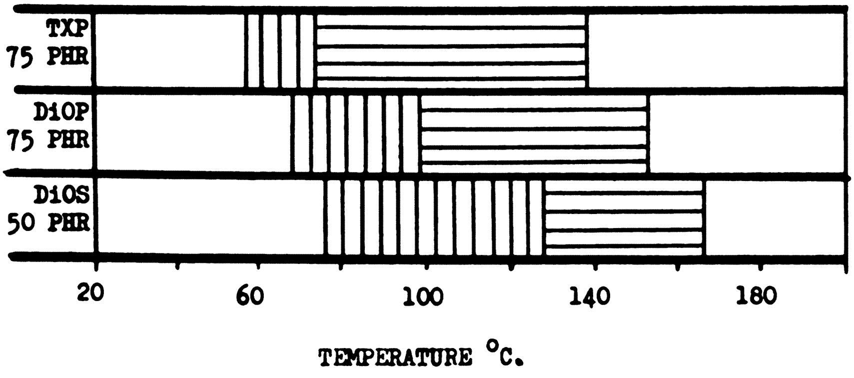

Figure 11. Comparison of different chemical types of plasticizers

Although we have used the selected transition and critical points to illustrate the gelling properties of different plasticizers, the two critical points were obtained from the full tensile strength temperature curve carried out for each plastisol. Since the shape of the tensile strength curve varies according to the plasticizer type and the concentration of the plasticizer, we have included some selected examples of such curves.

Figure 13 shows the differences between three phthalates of different molecular weight, and Figure 14 indicates the differences between three chemically different plasticizers.

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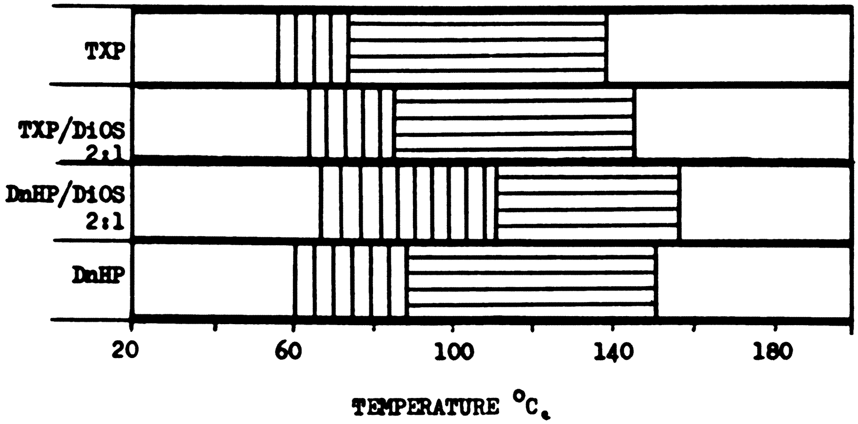

Figure 12. Effect of plasticizer mixtures at 75 p.h.r.

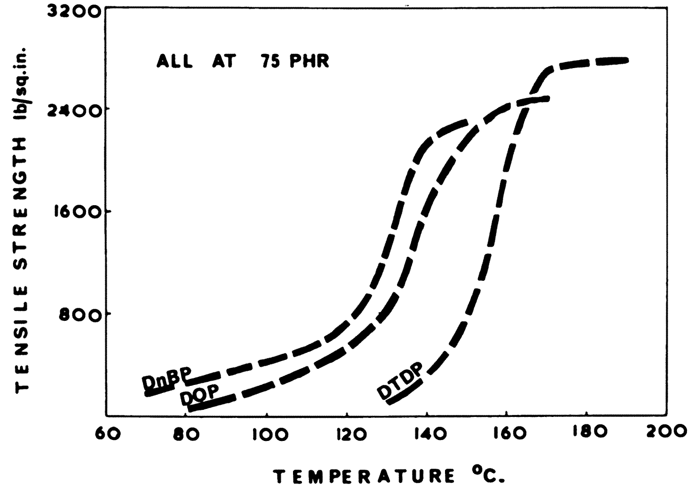

Figure 13. Tensile strength/temperature curves for phthalate plasticizers of different molecular weight

Other Uses of the Gel Block

The gel block is obviously an ideal instrument for studying stabilizers and the heat stability of other additives such as colors.

Figure 15 illustrates the effect of a 45-minute dwell time on two plastisols containing 75 p.h.r. of DOP with different stabilizer systems. The upper example is a liquid cadmium–barium system and the lower a thiotin–dibutyltin maleate system. The organotin system is obviously the more effective. The leading yellow zone, which is followed by a dark zone, may indicate two different breakdown mechanisms.

Future Work

The work reported here includes examples of th types of investigation possible with the graded gel block. As already stated, a dwell time of 20 minutes was chosen to allow attainment of an equilibrium over the whole temperature range being studied. Desirable future investigations, therefore, would include the study of dwell times of much shorter duration to correlate with commercial practice, for example between one half and two minutes Such work would be carried out without watercooling of the gel block giving a temperature range between 100° and 200°C. along the casting surface, with the possiblity of casting only over the top half of the casting

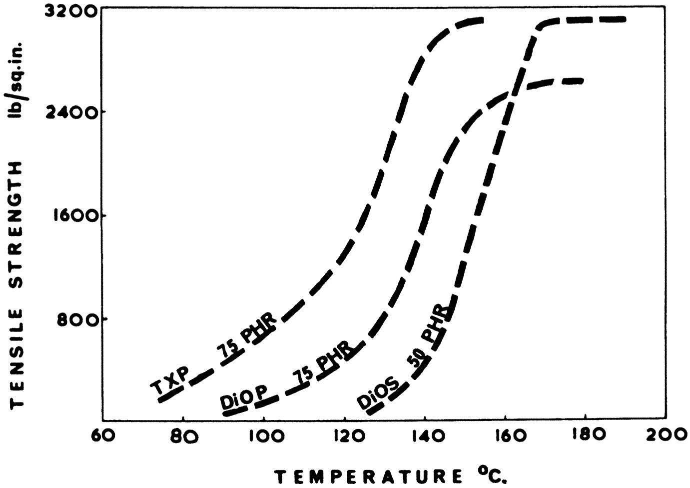

Figure 14. Tensile strength/temperature curves for different chemical types of plasticizers

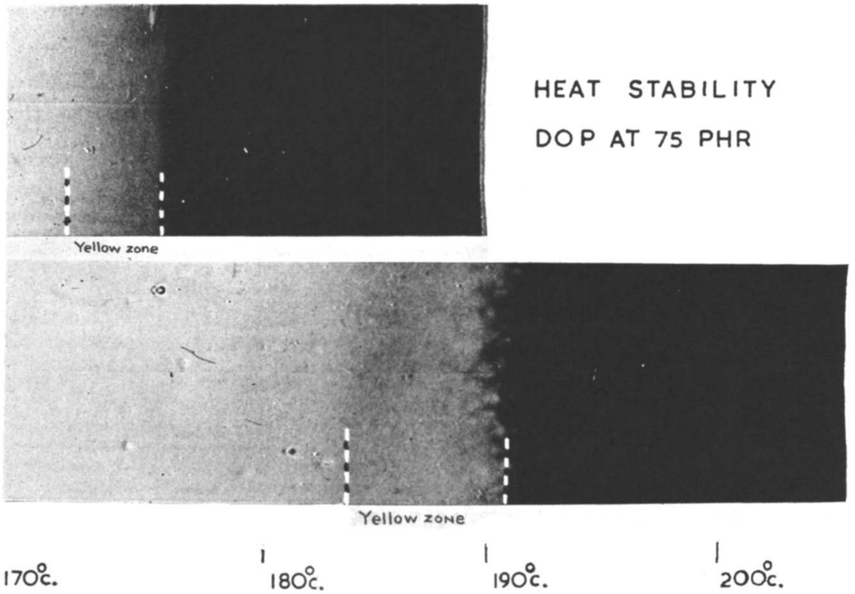

Figure 15. Effect of 45-minute dwell time on plastisols containing different stabilizer systems

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block—namely, from about 150° to 200°C. Using a mechanical drive to draw the spreading knife, it should be possible, after the desired time interval from the commencement of casting, to commence stripping the aluminum foil from the initial casting point using the same mechanical drive. This will allow investigation of the gelation at dwell times and temperatures of the same order as those used in commercial practice.

Only a brief examination was made of stabilizer systems, and future work should undoubtedly include a much more extensive examination on this subject. The examination of the effect of different types of PVC polymers is also an obvious choice for future studies.

Summary

The gel block has been found useful for organized investigations of the type discussed here and for technical service work or works study on fixed formulations chosen for their ultimate properties—for example, low temperature flexibility and extraction resistance.

In considering true transition points we have considered only one, the liquid/solid point, to be of practical significance. The other two points considered to be of practical importance—namely, the attainment of 5% and 90% maximum tensile strength—we have called critical points as opposed to transition points. We have not been able, as yet, to find simple reliable tests to replace tensile measurements.

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15

Compatibility and Plasticization of Poly-B-Vinylnaphthalene with Polyethylene Oxide

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Poly-β-vinylnaphthalene and polyethylene oxide can form homogeneous blends or graft copolymers. In polyblends microphase separation takes place upon heating, a process which becomes irreversible above 120° C. The modulus for blends having more than 46 wt. % polyether increases with temperature between 60° and 120° C. because colloidal poly-β-vinylnaphthalene particles are formed which reinforce the system. The behavior of graft copolymers is markedly modified because microphase separation is hindered. Thus, a copolymer (46% polyether) was rubbery at room temperature, and in contrast to blends did not exhibit the glass transition of poly-β-vinylnaphthalene (138° C.). Also, the behavior of the copolymer was reversible over the temperature range investigated (−30° to 200° C.). The temperature dependence of the micromorphology of these systems, as revealed by phase contrast microscopy, agreed with the above conclusions.

Polystyrene and its higher vinylaromatic homologues form thermoplastic polymers which have their glass transition temperature T_g above 100°C. (*1*). The addition of polyethylene oxide (PEO), a highly flexible polymer having T_g at −65°C. could be expected to have a plasticizing effect. But this effect usually is not observed because, in general, PEO is incompatible with vinylaromatic polymers. We have found, however, that poly-β-vinylnaphthalene (PVN), and PEO form compatible blends when prepared under conditions favoring coacervation of the two components (*3*). When PEO is grafted onto the PVN (*10*), homogeneous, rubbery copolymers are formed which exhibit a T_g intermediate to those of the two homopolymers. The properties of graft copolymers remain unchanged upon heat treatment, whereas in blends, irreversible changes take place when heated above 120°C. The striking differences in the behavior of the blends and grafts are paralleled by differences in morphology at various temperatures as revealed by phase contrast microscopy. With polystyrene, polyvinylbiphenyl, and polyacenaphthylene, PEO formed heterogeneous blends.

Experimental

Two batches of PVN, prepared by emulsion polymerization, had molecular weights of 510,000 and 720,000 and were used for the blends and grafts, respectively. Both polystyrene (PS, $\overline{M}_w$ = 150,000) and poly-4-vinylbiphenyl (PVB, $\overline{M}_w$ = 450,000) were prepared by anionic polymerization. A low molecular weight (Polyglycol E4000, Dow Chemical Co.) and a high molecular weight PEO (WSR-35, Union Carbide Chemicals Co.) were used as received.

Polyblends were prepared by dissolving both polymers in benzene, followed either by precipitating with hexane, or by freeze drying. The concentration of the solutions was about 2g./dl. The resulting powder was then dried under vacuum at 40°–50°C.

Graft copolymers were prepared by polymerizing ethylene oxide onto the PVN polyradical anion (*10*). The latter was obtained by reaction of PVN with cesium in tetrahydrofuran solution. The copolymers were extracted with water to remove the PEO homopolymer which was formed as a byproduct. Experimental details and evidence for bond formation between ethylene oxide and the aromatic moiety were presented elsewhere (*11*).

Young's modulus was determined with a torsional apparatus constructed according to ASTM standards (D 1053–61). A torsional pendulum, constructed according to a previously reported design (*7*), was used to obtain the damping constant given in log decrement. Test specimens (2 x ¼-inches and 0.05 to 0.08 inches thick) were prepared by compression molding at 1000 to 4000 psi. The molding temperature was 55°C. for the polyblends, and 40°C. for the graft copolymers.

The specific volume *vs.* temperature data were obtained by using capillary dilatometers. Specific volumes at 25°C., determined in a pycnometer, were used as reference.

Phase contrast photomicrographs were obtained using a Zeiss research microscope equipped with a built-in 35 mm. camera. For temperature control, a hot stage was constructed by fastening nichrome heating wire to a microscope slide with glass tape. Specimens approximately 1000 A. thick were cut from a polymer block using an LKB Produktor Ultrotome, and placed in Schillaber's immersion oil between two round microscope cover glasses. This sandwich assembly was taped to the hot stage situated on the microscope. All photographs employed the same exposure time and constant light source. The negatives and positives were processed identically.

Results

The modulus curves of three blends of PEO E4000 (75, 50, and 25 wt. %) with PVN are shown in Figure 1 along with that for pure PVN. The 25% PEO blend

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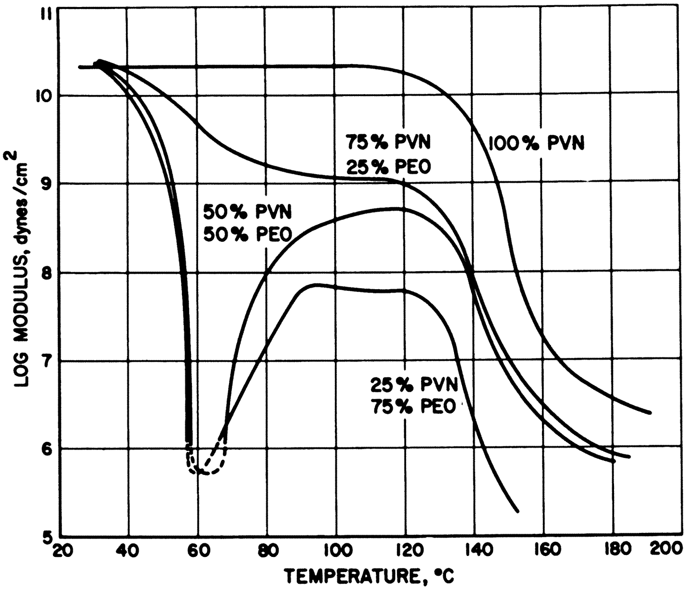

Figure 1. Log modulus vs. temperature for blends of PVN and PEO

shows a gradual decrease in modulus to about 100°C., follows a plateau to about 120°C., and then undergoes a transition similar to that of PVN. For the other two blends the modulus drops sharply at 58°C., but rises with a further temperature increase, and goes through a maximum at about 120°C. The modulus at the base of the "well" was outside the range of the torsional wire used, and is indicated with a dotted line; these lines must be nearly correct since the rubbery modulus for PEO is 10^5—10^6 dynes/sq. cm. The behavior difference between a blend and a graft polymer having 46% PEO is illustrated in Figure 2. This blend exhibited only a shallow "well."

Results for two 50-50 PVN blends (Figure 3), one with PEO E4000 and the other with WSR–35 (high molecular weight PEO), demonstrate that the increase in

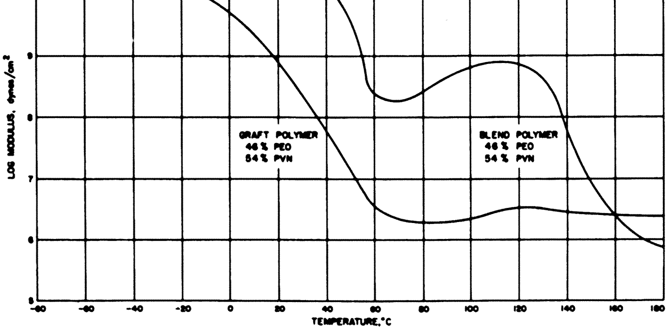

Figure 2. Log modulus vs. temperature for a polyblend and graft copolymer

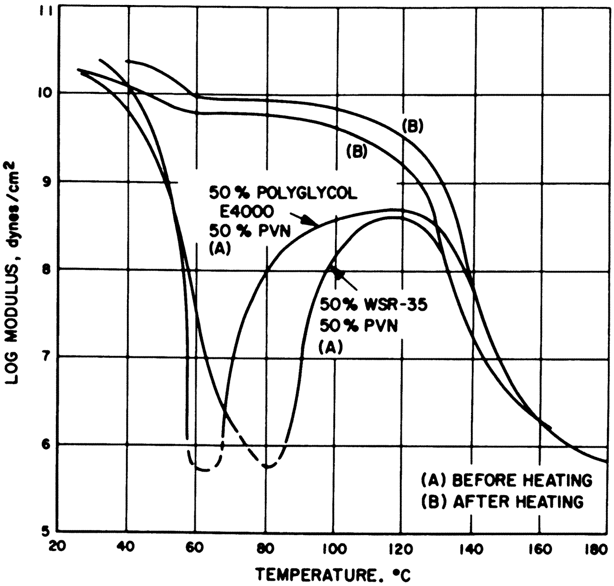

Figure 3. Log modulus vs. temperature for two 50–50 blends PVN with PEO of different molecular weights

molecular weight of PEO did not modify the characteristic features of the curve, excepting a 20°C. shift for the minimum of the "well." The "well" behavior for the blends was reversible as long as the temperature of about 120°C. was not exceeded, but once exceeded, the "well" behavior could not be reproduced, as illustrated by the two upper curves in Figure 3.

Figure 4 shows the modulus curves for two blends of PEO E4000 (75 and 50%) with poly-4-vinylbiphenyl and one blend of 50% PEO E4000 with polystyrene. None of these blends exhibited a "well," and at high temperatures the samples became friable and broke.

The damping constant was determined from dynamic measurements, and the results for the 50% (PEO E4000) blend are shown in Figure 5. The transition at 54°C. is caused by crystalline melting of PEO. The broad shoulder between 85° and 120°C. corresponds to the region of slowly increasing Young's modulus (Figures 1, 3), whereas the peak at 138°C. coincides with the dilatometric T_g for PVN. After it was heated above 120°C. the damping constant continually and gradually increased from about 40°C. until the peak at 138°C. was reproduced. The loss component of the dynamic modulus, which can be calculated from dynamic data, may resolve the shoulder for the initial sample into a separate peak, as can be seen from the shape of the Young's modulus curve (Figures 1, 3). Additional results are needed to resolve this point. For the "heated" specimen, however, the loss component should have the same appearance as the damping curve.

The specific volumes at 25°C. for the 75, 50, and 25% blends of PEO E4000 with PVN were 0.857, 0.886, and 0.891 cc./gm., respectively, and 0.888 cc./gm. for PVN. The crystalline specific volume of PEO E4000 was 0.828 cc./gm., agreeing with reported values (*8*, *13*), whereas the amorphous volume was 0.893 cc./gm. The latter value was estimated by linear extrapolation to 25°C. of the specific volume temperature line for molten PEO (Figure 6). It agrees with the published value of 0.895 cc./gm. (*8*). The relative amounts of crystalline and amorphous PEO in the blends were calculated by assuming additivity of the volumes (*6*).

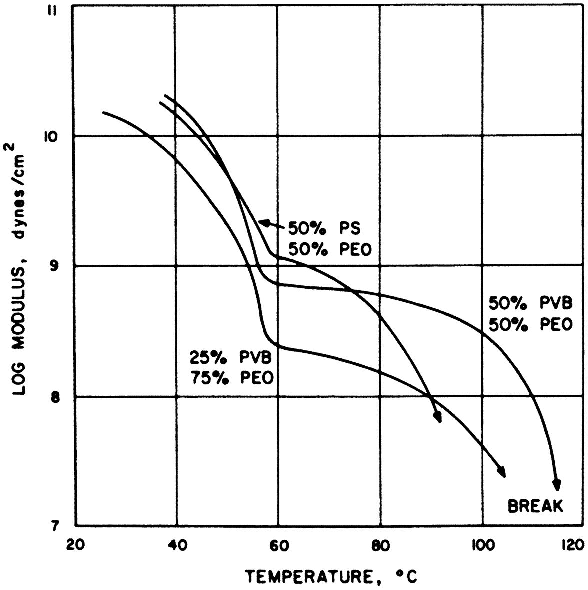

Figure 4. Log modulus vs. temperature for blends of PVB and PS with PEO

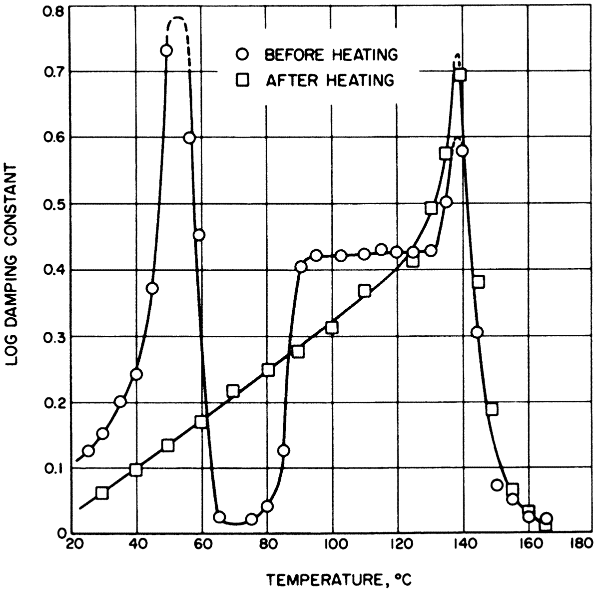

Figure 5. Log damping constant vs. temperature for a 50–50 blend of PVN and PEO

Phase contrast photomicrographs for a 50% polyblend are shown in Figure 7. The granular structure and the changes with temperature in the relative content of light *vs.* dark regions are noticeable. Also, note that the specimen heated above 120°C. retained its appearance when cooled to room temperature (Figure 8).

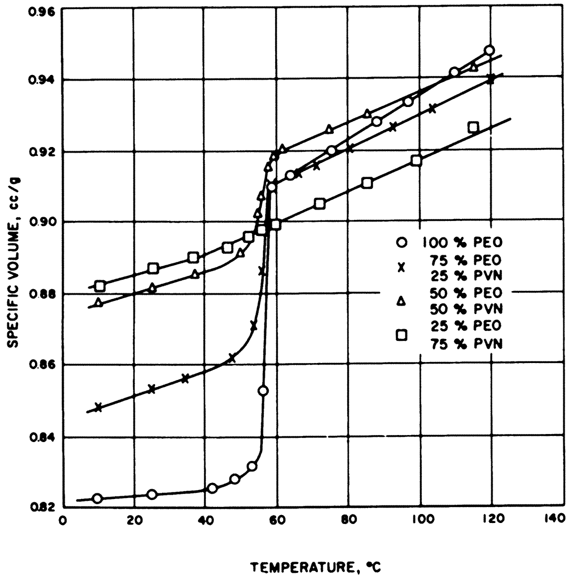

Figure 6. Dilatometric curves for blends of PVN and PEO

Three graft copolymers containing 20, 46, and 67% PEO, respectively, were examined. Although the molecular weight of the side chains could not be determined directly, it was estimated as 1,000 to 2,000. The 20% copolymer exhibited no "well" and showed no evidence of crystallinity either by x-rays or dilatometry. The 67% copolymer exhibited a "well," and x-ray and dilatometry showed that it contained both crystalline and amorphous PEO.

For the 46% copolymer both Young's modulus and damping constant curves are shown in Figure 9. During the first heating cycle (dashed lines) the sharp drop in modulus between 40° and 54°C. coincided with the peak for the damping constant, the transition being caused by crystalline melting. For several subsequent heating cycles the upper modulus curve was followed on heating and the lower on cooling. The damping constant peaks for both heating and cooling are displaced to a lower temperature, the heating curve exhibiting a shoulder. Undoubtedly, these curves are also caused by crystalline melting, their shapes depending on distribution of crystallite size. In either case, note the absence of a transition corresponding to T_g of PVN (138°C.). The dilatometer data (Figure 10) parallel the dynamic measurements: following a slightly different path on initial heating (dashed line), a reproducible hysteresis loop in the melting range was followed on subsequent heating cycles. The specific volume at 25°C. was 0.864 to

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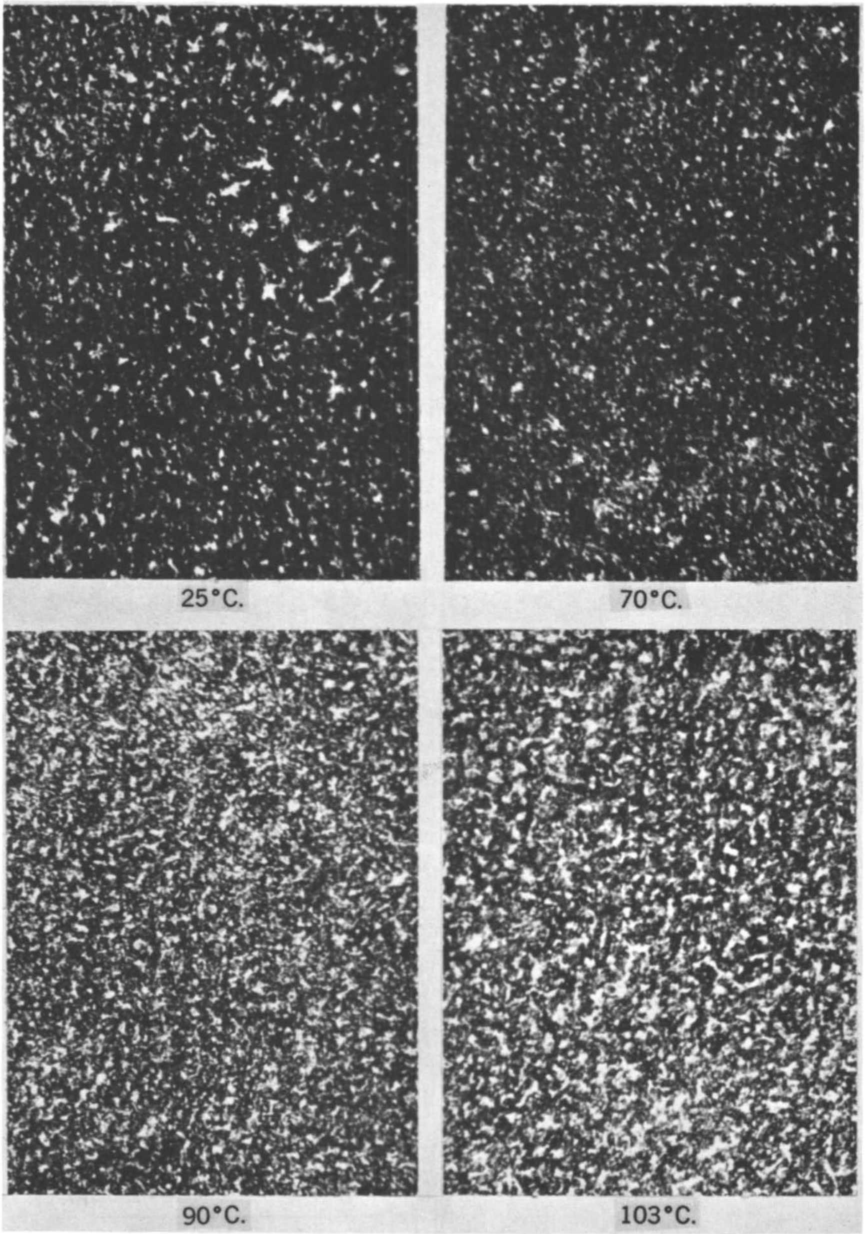

Figure 7. Phase contrast photomicrographs of a 50–50 blend of PVN and PEO at different temperatures; × 560

0.869 cc./gm. The presence of crystallinity at 43°–54°C. was corroborated by x-ray measurements. Again, the transition at 138°C. is absent.

Phase contrast micrographs show that initially the graft copolymer exhibited layers (Figure 11) perpendicular to the direction at which pressure was applied in

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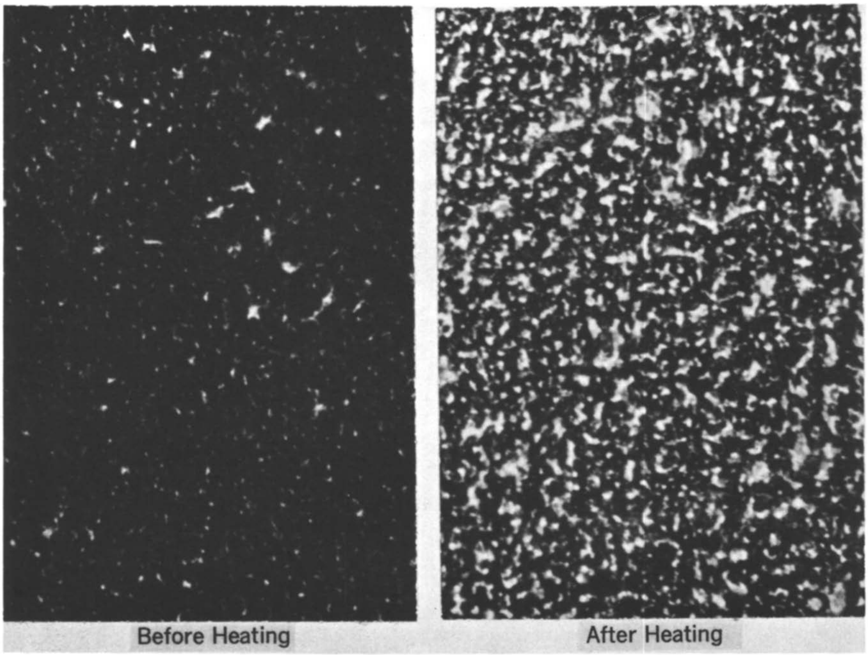

Before Heating

After Heating

Figure 8. Phase contrast photomicrographs of a 50–50 blend of PVN and PEO at 25°C. showing the effect of heating to 150°C.

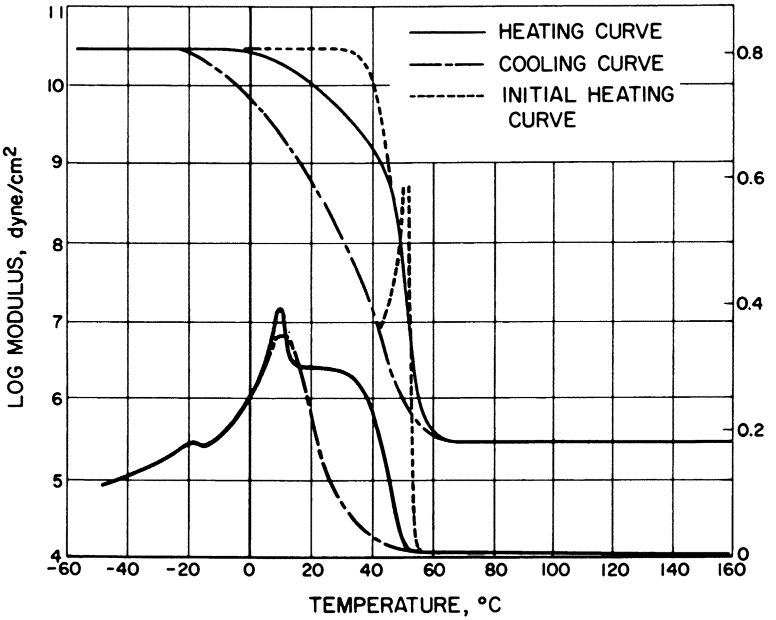

Figure 9. Log modulus and log damping constant vs. temperature for a graft copolymer of PVN and PEO

In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

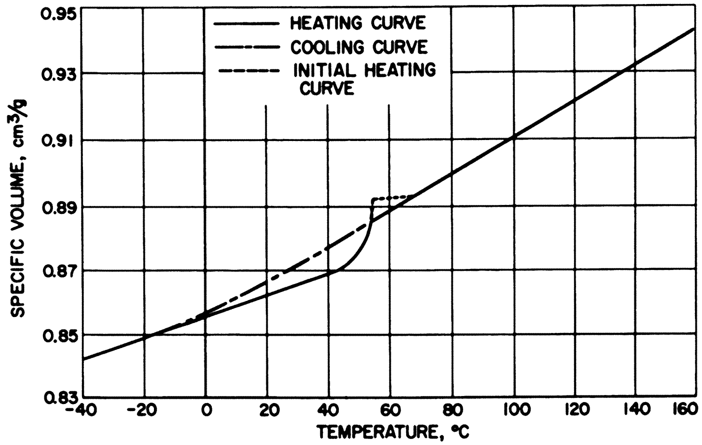

Figure 10. Dilatometric curve for a graft copolymer of PVN and PEO

forming the specimen. The layered structure disappeared above the melting temperature of PEO. After cooling below −13°C. the structure shown in Figure 11 (lower right) was formed. This structure remained unchanged upon subsequent heating and cooling (cf. dilatometric curve).

Discussion

For the PVN-PEO polyblends, volume changes at melting temperature (Figure 6) as well as x-ray data at room temperature (*2*) show that the 25% (PEO) blend is completely amorphous, and that the 50 and 75% blends contain significant amounts of amorphous PEO. Calculations based on specific volume data indicate that the crystalline part of both the 50 and 75% blends consists of PEO, whereas the amorphous part contains 46% PEO and 54% PVN. Another important result is that the unusual phenomenon of a "well" in the modulus temperature curves (Figure 1) was observed only for the blends which exhibit crystallinity. Based on these observations, the behavior of blends could be interpreted by postulating that the amorphous PEO forms a "complex" phase with PVN in the ratio of 3 to 1 monomer units (i.e., 46 wt. % PEO to 54 wt. % PVN), respectively.

The modulus curve for the blend having the composition of the "complex" exhibits a shallow "well." This shows indeed that a change in the composition from 50% (Figure 1) to 46% (Figure 2) leads to a drastic change in behavior. Above 60°C., droplets of liquid PEO began to appear on the surface of the test specimen, leaving behind a core of increasing PVN content which causes a slight rise in the modulus. The sweating out of the PEO is caused by the gradual dissociation of the "complex" with increasing temperature. This is consistent with our observation that PVN exhibits a negative temperature coefficient for its solubility in ether like solvents. The dissociation of the "complex" is akin to the solvent-solute dissociations described by Doolittle (*4*).

The large drop in modulus for the blends containing more than 46% PEO occurs when the crystalline PEO melts, and the specimens are then composed of

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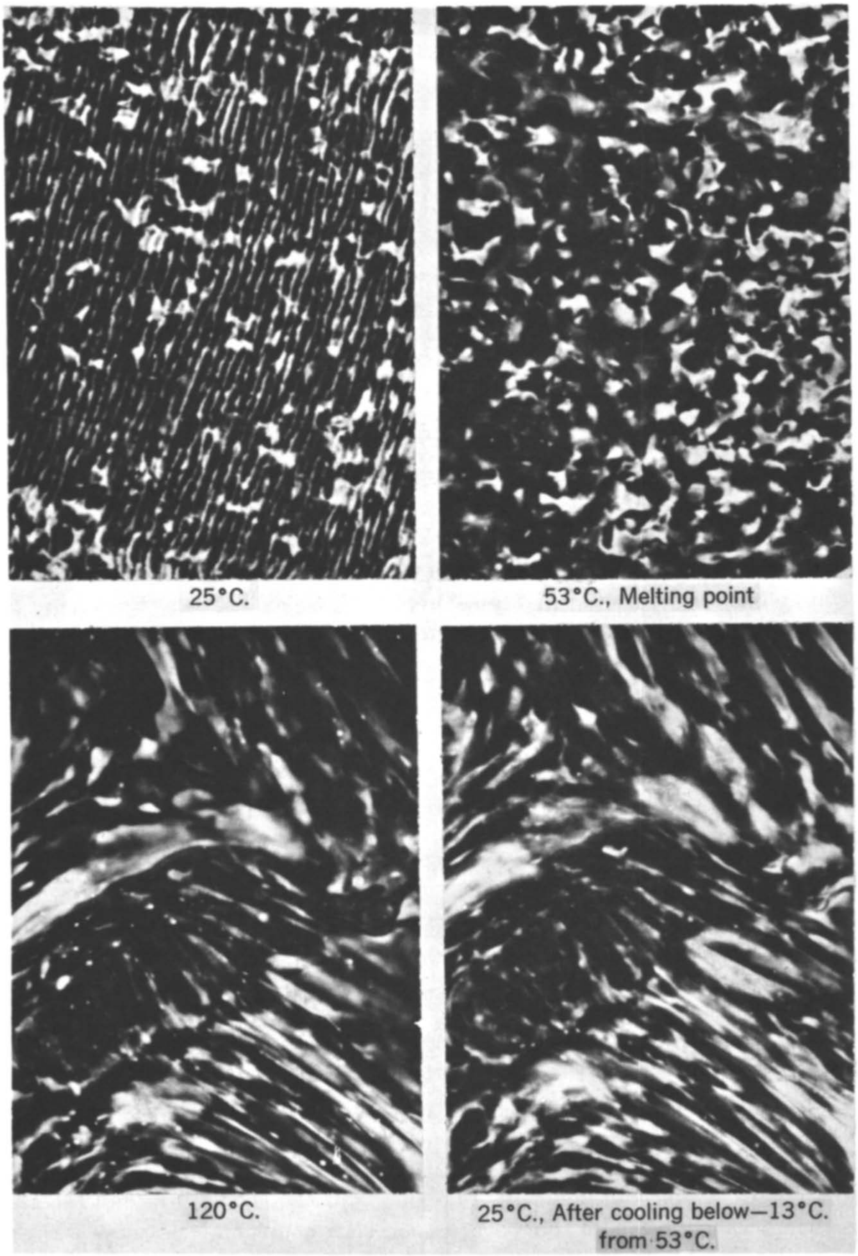

25°C.

53°C., Melting point

120°C.

25°C., After cooling below—13°C. from 53°C.

Figure 11. Phase contrast photomicrographs of a graft copolymer of 54 wt. % PVN and 46 wt. % PEO; × *560*

liquid PEO and the leathery "complex." With increasing temperature, the modulus rises because the "complex" dissociates, and PVN forms colloidal particles which reinforce the system.

The broad shoulder for the damping constant (Figure 5) is consistent with the idea of phase changes occurring over the temperature range of the "well," until T_g of PVN (138°C.) is reached, and irreversible microphase separation has taken place. The gradual rise in the damping constant with increasing temperature for the reheated polymer may be caused by localized changes occurring at the microphase boundaries.

The phase contrast photomicrographs (Figure 7) illustrate the marked morphological changes which take place on heating. Inasmuch as the dark and light regions are due to different refractive indices they reflect the presence of different microphases. Thus, the predominantly dark appearance at 25°C. is consistent with the presence of the homogeneous "complex" and a small amount of excess crystalline PEO. The gradual increase in the amount of the light regions with increasing temperature reflects the dissociation of the "complex." Again, agreeing with the observed irreversible changes in mechanical properties at elevated temperatures, the appearance of the specimen at 150°C. remained unchanged upon cooling back to 25°C. (Figure 8).

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Since one has to start with a solution in order to prepare the "complex," this suggests that a molecular dispersion is necessary to allow contacts between segments of the two polymers. In benzene, a good solvent for both components, there must be considerable overlap of the swollen polymer coils for the concentrations which were used (total of 2g./dl for 50:50 blend). For these concentrations PVN alone would have filled completely the solution volume since 1 g./dl PVN $\geq 1/[\eta]$ (*5, 12*). The optimum conditions for precipitating with hexane have not been well defined, but freeze drying always led to forming the "complex." It is necessary to start with an adequately interdispersed polymer. This was demonstrated by the fact that the complex could not be obtained from dimethoxyethane, a poor solvent for both components; the resulting blend gave a modulus curve resembling (B) in Figure 3. In dimethoxyethane the concentration was insufficient for the solution volume to be filled completely since in this case 1 g./dl PVN $< 1/[\eta] \approx 2$.

A different situation should exist for the graft copolymers in which one end of the PEO chain is attached to the PVN backbone. The modulus curve for the 20% PEO copolymer was depressed relative to pure PVN. The 67% copolymer exhibited a shallow "well" which was not reproduced once the copolymer was heated beyond 120°C. The graft copolymer having the composition of the "complex" (46% PEO, Figure 2) was transparent, rubbery, and had a glass transition temperature below −20°C. Furthermore, it retained its rubbery properties after being heated beyond 120°C. An interesting additional property is a plateau extending from about 60° to 180°C., characteristic of a crosslinked or very high molecular weight polymer (*14*). Yet this material is readily soluble in most aromatic and ether type solvents. This behavior may originate from entanglement of the PEO side chains of adjacent molecules.

Another graft copolymer having the same composition, but presumably a somewhat greater density of PEO side chains, had the same transparent appearance and low T_g. Modulus as well as dilatometric data exhibited a hysteresis loop between −20° and 60°C. These results along with x-ray measurements indicate presence of some crystallinity in contrast to the first completely amorphous copolymer. For given composition the relation between the size and distribution of the side chains, and their ability to crystallize is not yet clear.

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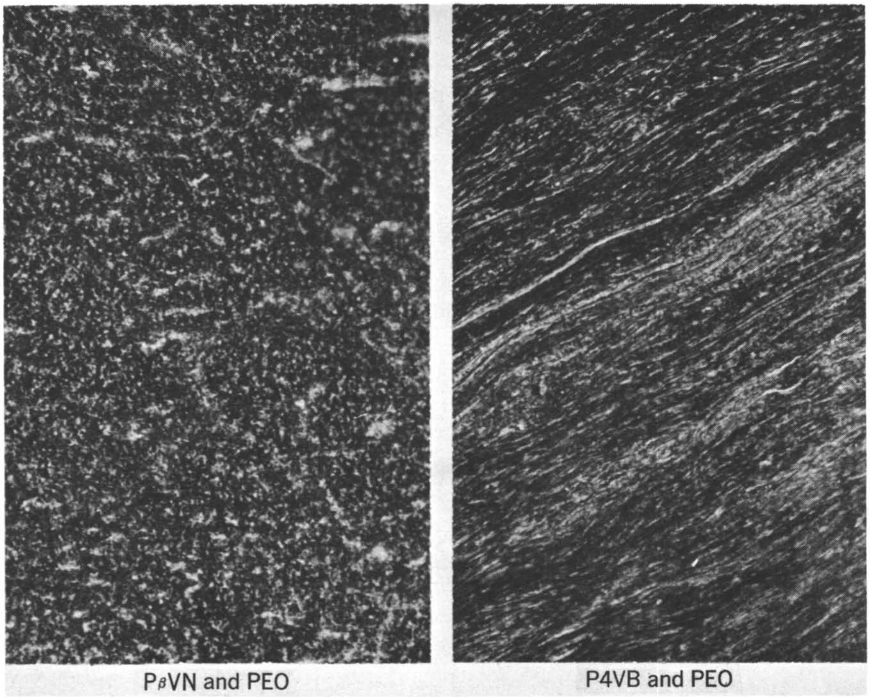

PβVN and PEO P4VB and PEO

Figure 12. Phase contrast photomicrographs of two 50–50 blends at 25°C.; × 265

The position of the damping maxima shows that the melting temperature of the PEO crystallites was depressed. It is interesting to note that the "heating" curves were followed only if the specimen was first cooled below −20°C.; otherwise the cooling curve was followed for both descending and ascending temperatures, irrespective of rate (the slowest rate was $\frac{1}{4}$°C. per minute). Doubtless this behavior is due to a large increase in the nucleation rate below a critical temperature which seems necessary to complete the crystallization process. Curiously enough, this temperature of −20°C. coincides with the secondary peaks in the damping constant, suggesting a change in the nucleation mechanism associated with a polymer transition. This transition may be due to freezing in of the side chains since it is known that T_g for PEO of molecular weight 1,000 to 10,000 is approximately −20°C. (*9*).

The observation that T_g for PVN has disappeared, as shown by examining both the damping constant and the dilatometric curve, unequivocally shows that PVN has lost its identity and that the whole copolymer behaves as an entity. The specific volume for temperatures in the amorphous region (above 60°C.) show that volume additivity for the two components is not followed, but that a contraction of about 2% has taken place. Examining the molecular models shows that one can readily entwine PEO and PVN chains. Optimum spacing is obtained with 3 ethylene oxide:1 naphthalene moiety—the "complex" composition! Thus here, as with polyblends, the importance of conformation coupled with favorable but probably weak interactions is evident.

The photomicrographs show that the characteristic granular structure of polyblends is absent for copolymers. Moreover, the rather uniform appearance achieved once the graft has been heated, remains unchanged upon further temperature cycling. This offers additional evidence that microphase separation cannot take place at higher temperatures.

Evidently, the homogeneous "complex" phase is an equilibrium property for copolymers. Any effects resulting from the history of specimen preparation (cf., photomicrographs and dashed lines in Figures 9 and 10) are eliminated by annealing. In contrast, for polyblends the compatible phase is a metastable state.

The rather unexpected properties described above seem to be peculiar to PVN, for none of the blends with polystyrene, poly-4-vinylbiphenyl, and polyacenaphthylene contained significant amounts of amorphous PEO. The modulus curves for these systems are characteristic of blends of incompatible polymers. The photomicrograph in Figure 12 illustrates the different morphologies of PVB and PEO blends. The reason for the apparently different behavior for these polymers as compared with PVN is not yet understood. But there is strong evidence from dilute solution-studies that the conformational properties for these polymers differ markedly.

In summary, our studies have shown that graft copolymers of PVN with PEO form homogeneous, rubbery materials. The properties of copolymers having low PEO content remain to be investigated to evaluate the use of PEO as an internal plasticizer. Also, the effect of the size of side chains will have to be considered.

Acknowledgment

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Plasticization of Bisphenol A Polycarbonate

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Plasticization of polycarbonate with tricresyl phosphate increases its crystallizability. Unplasticized polycarbonate crystallizes slowly after heating for 24 hours at 190°; with the addition of only 2.9% plasticizer, this time is reduced to three hours. Solvent-cast films are more crystalline than melt-pressed ones. The lowering of the glass transition temperature by tricresyl phosphate follows the equation of Gordon and Taylor, assuming for the constant, *k*, a value of 4 for cast and 3 for pressed films. A heat of fusion of 3400 cal./mole and an entropy of fusion of 6.3 cal./mole °C. are determined from the crystalline melting point depression caused by the plasticizer. The higher crystallinity of plasticized polycarbonate results in higher moduli of elasticity, higher stiffness, and higher heat distortion temperatures, compared to pure polycarbonate.

Much research has been done on the properties and applications of polybisphenol carbonates since the publication of Schnell's article in 1956 (*15*). An extensive account of this work is given in the recently published book by Christopher and Fox (*2*). Practical application of polycarbonate is based almost exclusively on the properties of this polymer in the amorphous state.

In the early literature it is suggested that polycarbonates can be easily plasticized with common plasticizers. Plasticization of polycarbonate has been investigated by Kozlov *et al.* (12). These authors described the influence of plasticization on softening points and mechanical properties of bisphenol A polycarbonates. They conclude that the behavior of plasticized polycarbonate is similar to that encountered for most amorphous polymers. The influence of crystallization effects promoted by the plasticizer was not taken into account.

The object of this study was to investigate more closely the influence of a plasticizer on the crystallization behavior of bisphenol A polycarbonate and to deduce some fundamental thermodynamic properties of the polymer.

In Plasticization and Plasticizer Processes; Platzer, N.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1965.

From a practical point of view the purpose of this study was to increase the crystallizability of the polycarbonate by incorporating in it well-defined amounts of plasticizer. With this modification, crystalline polycarbonate films could be made with a higher modulus of elasticity, and these would extend the usefulness of the polymers as photographic film bases. When this study was completed an article was published by Sears and Darby (*16*), who made an extensive study of the plasticization of polycarbonate using 50 plasticizers of widely differing types. The crystallization tendency in the presence of plasticizers was recognized by these authors as a problem and was circumvented by quench cooling.

In our study all experiments were performed using one single type of plasticizer —tricresyl phosphate. This product is compatible in all proportions with the polymer. By spot check experiments it was found, however, that similar results were also obtained with other types of plasticizers.

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Crystallization Phenomena

The crystallization tendency of polycarbonates in the pure state is limited. Kämpf (*10*) found that the first spherulites appear only after heating at 180°C. for eight days; more pronounced crystallization occurs only after heating at 190°C. for the same period of time. Orientation of films or fibers does not cause any crystallization, and relatively small improvement of elastic properties is noted.

Crystallizable polymers are characterised in most cases by easy crystallization when they are slowly cooled from the melt. After quenching a molten polymer to the amorphous state, rapid crystallization can be induced by heating for a short time above the glass transition temperature (T_g). Compared to poly(ethylene terephthalate) and poly(hexamethylene adipamide), which are highly crystalline polymers with melting point (T_m) of 264°C. compared to 267°C., the melting point of polycarbonate (*2*), the latter has a very high glass transition temperature (149°C. *vs.* 81°C. and 47°C., respectively) (*1, 11*).

The poor crystallization of polycarbonate is, apart from structural characteristics, caused by too small a temperature interval between the glass transition temperature and the crystalline melting point. The rate of crystallization of polymers shows a pronounced maximum at some temperature between T_g and T_m. This phenomenon results from two kinetic effects: First, the rate of formation and growth of the crystallites increases rapidly with temperature, the rate of crystallization being zero at T_g; and second, the rate of disappearance or melting of the crystallites increases rapidly when T_m is approached. In bisphenol A polycarbonate the rate of crystallization is small, because of a high chain rigidity that results from the accumulation of aromatic chain segments (*8*). The chain mobility required for rapid crystallization would be possible only in a temperature region close to the melting point where the rate of melting already is appreciable. Moreover, as is shown by the x-ray diagrams, the crystallites are small and imperfect; this factor contributes to melting at temperatures markedly below the melting point of the ideal crystal structure.

The crystallization tendency of polycarbonate is enhanced by the action of solvents. For example, crystallization may be accomplished by slow evaporation of solvent from cast film (*14, 17*) or by treatment with swelling agents such as ethyl acetate or acetone.

In this study the influence of plasticizer content on the rate of crystallization was briefly investigated. The time needed for the first spherulites to appear on heating the plasticized polymer at 190°C. was used as a rough indication of the crystallization tendency.

The results (Table I) show that at a given temperature the polymers crystallize faster with increasing amounts of plasticizer.

Table I. Influence of Plasticizer Content on Rate of Crystallization

Weight Fraction of Plasticizer, w_1	*Time for First Spherulites to Appear (190°C.), Min.*
0	1440
0.029	180
0.048	40
0.090	20
0.130	15
0.167	5
0.231	5
0.286	Immediately

For instance, a film containing 28.6% of plasticizer is completely opaque when cast from a methylene chloride solution. The x-ray diffraction pattern of this film shows that this is due to crystallinity.

The film used for this experiment was made amorphous by heating at 290°C. followed by quench cooling. After this treatment the x-ray photogram showed only two broad diffuse rings typical for amorphous polycarbonate (Figure 1*A*.) This same film was thermally crystallized for 60 hours at 145°C. The x-ray photogram (Figure 1*B*) is typical of a crystallized polycarbonate. The number and distance of the rings are identical with those of pure polycarbonate (*14*).

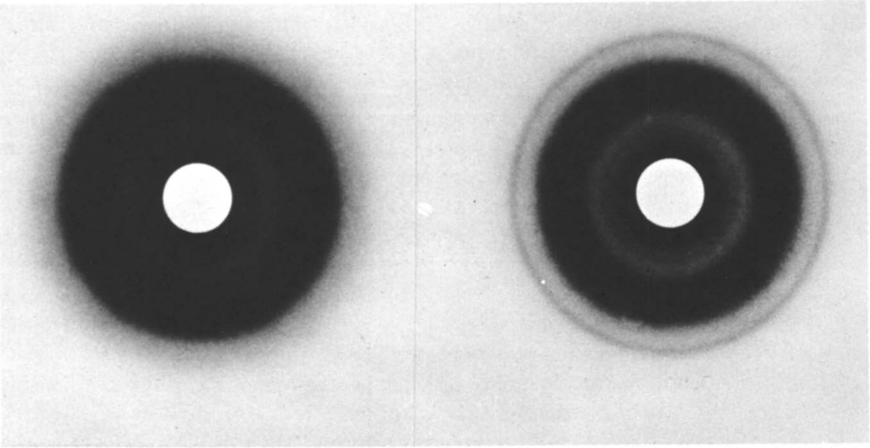

Figure 1. X-ray photograms of polycarbonate containing 28.6% of tricresyl phosphate

Glass Transition Temperatures (T_g)

The glass transition temperatures of the plasticized polycarbonates have been determined by measuring the refractive index of properly compounded films as a function of temperature. The glass transition temperatures are those temperatures

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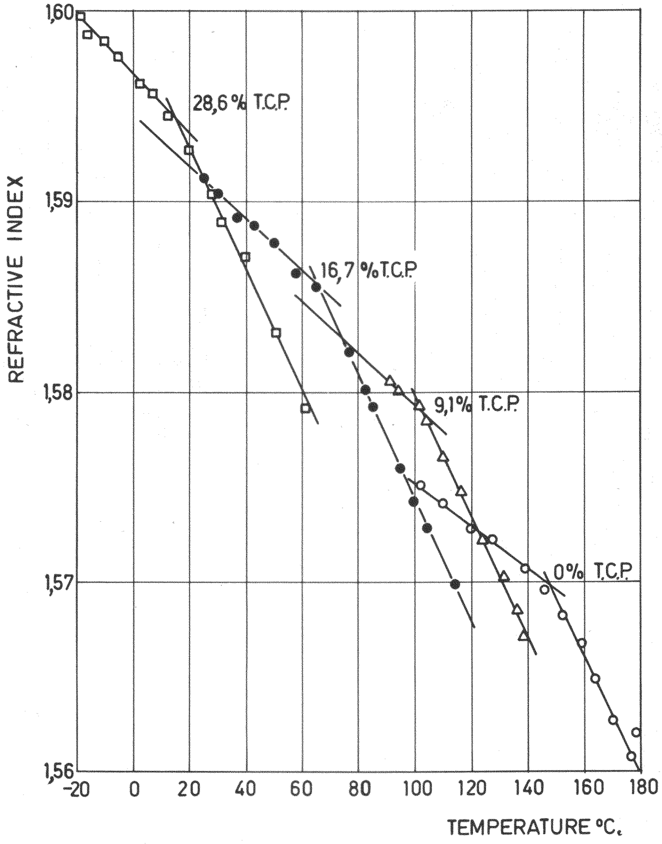

Figure 2. Refractive index of mixtures of polycarbonate and tricresyl phosphate as a function of temperature

where an abrupt change in the temperature coefficient (du/dT) of the refractive index occurs. Some of these curves are presented in Figure 2.

It is known that crystallinity has an influence on the position of the glass transition temperature. For instance, amorphous poly(ethylene terephthalate) has a T_g of 67°C. This increases to 81°C. for the crystallized polymer (*11*). This is explained by the fact that the rotation of the chain segments, which is made possible at the glass transition, is hindered by the presence of the crystallites.

The same effect is borne out by our experiments. The T_g's of solvent-cast films were higher than those determined on pressed films made from the same polymer plasticizer mixtures.

The films prepared by melt pressing are very rapidly cooled to room temperature. Under these conditions no detectable crystallization in the polymer can develop, as is proved by x-ray examination. On the other hand, in the solvent-cast films chain mobility of the polycarbonate is enhanced by the presence of solvent and crystallinity can occur. In some extreme cases the solvent cast films are turbid, and the crystallinity can be clearly demonstrated by x-ray photograms which show x-ray patterns characteristic of crystallized polycarbonate. It is assumed that

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the higher glass transition temperatures of even the clear transparent solvent cast films are due to crystallinity or at least to some form of tridimensional order which may be a precursor of x-ray crystallinity.

The lowering of T_g by plasticizers follows the same type of relationship as the equations established for copolymers. The plasticizer takes the place of the component with the lower T_g.

The most generally accepted relationship was deduced by Gordon and Taylor (*6*):

$$T_g = \frac{k\,w_1\,T_{g1} + w_2\,T_{g2}}{k\,w_1 + w_2} \tag{1}$$

wherein T_g represents the glass transition temperature of the mixture; T_{g1} and T_{g2}

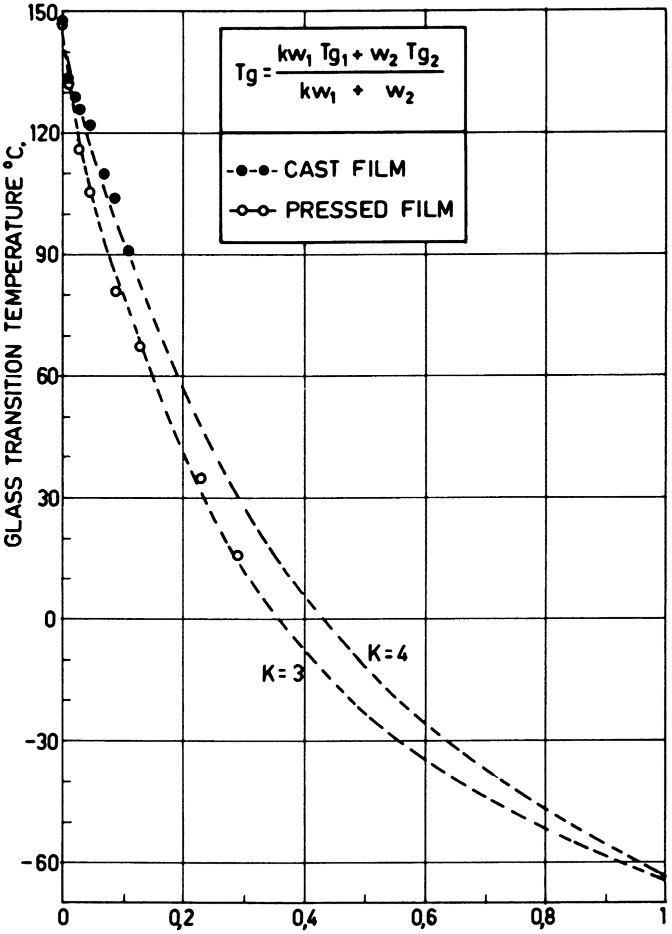

Figure 3. Glass transition temperatures for cast and pressed films of plasticized polycarbonate as a function of the weight fraction of plasticizer

those of the plasticizer and the polymer, respectively; and w_1 and w_2, the weight fractions of plasticizer and polymer units. For tricresyl phosphate a $T_0$of -64.5°C. was assumed (*9*).

The experimental results for cast and for pressed films are plotted in Figure 3. The dotted lines were calculated from Equation 1, assuming for constant k a value of 4 for cast and 3 for pressed films, respectively. The cast films do show a higher degree of crystallinity than the pressed films which are essentially amorphous.

The experimentally determined glass transition temperatures fit well with the calculated curves.

According to Gordon and Taylor constant k would be given by the relationship:

$$k = \frac{\Delta\beta_2}{\Delta\beta_1} \qquad (2)$$

wherein $\Delta\beta$ stands for the difference in expansion coefficients of the pure components in the glassy and in the molten state. (Subscript 1 refers to the plasticizer and subscript 2 to the polymer units.)

In our case this relationship could not be checked as the necessary data were lacking. It is evident, however, that $\Delta\beta$ should be higher for a crystallized sample than for an amorphous one. This postulates a higher value of k.

Crystalline Melting Points

Crystalline melting points of crystallized film samples containing known amounts of plasticizer were determined.

As expected, crystalline melting points decrease with increasing amount of plasticizer. However, the depression of the melting point for a given content of plasticizer is smaller than the decrease in glass transition temperature for the same mixture (Figure 4). Thus, the temperature interval between first- and second-order transition temperature is gradually broadened with increasing amounts of plasticizer. It is this effect that kinetically favors the crystallization phenomenon.

The heat of fusion, ΔH_u, and the entropy of fusion, ΔS_u can be determined from the crystalline melting point depression caused by solvents, using the equations given by Flory (*5*):

$$\frac{1/T_m - 1/T_m{}^\circ}{v_1} = \frac{R}{\Delta H_u} \times \frac{V_2}{V_1}\left(1 - B\,\frac{V_1V_1}{RT_m}\right) \qquad (3)$$

$$\text{and } \Delta S_u = \frac{\Delta H_u}{T_m{}^\circ} \qquad (4)$$

$T_m{}^\circ$ represents the melting point in °K. of the pure polycarbonate; T_m the melting point of the mixture; v_1 is the volume fraction of plasticizer; R the gas constant per mole; B the constant of interaction between polymer and plasticizer; and V_2 and V_1 the molar volumes of the polymer repeating unit and of the plasticizer, respectively. In Equation 3, $\frac{1/T_m - 1/T_m{}^\circ}{v_1}$ is related linearly to v_1/T_m as is illustrated in Figure 5. By applying this equation, the limit for $\frac{1/T_m - 1/T_m{}^c}{v_1}$, as v_1/T_m approaches zero, can be used to calculate the heat of fusion, ΔH_u. Using Equation 4, the entropy of fusion ΔS_u can be calculated.

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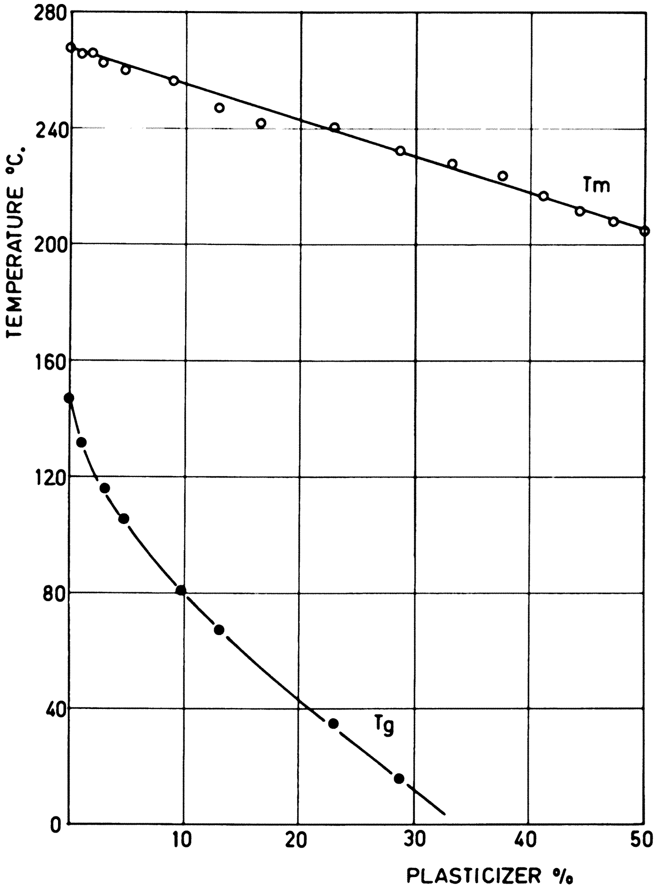

Figure 4. Crystalline melting points (T_m) and glass transition temperatures (T_g) of plasticized polycarbonate as a function of plasticizer content

In this manner, a heat of fusion of 3400 cal./mole has been calculated for bisphenol A polycarbonate. The entropy of fusion is 6.3 cal./mole °C. per repeating unit.

Table II gives heats and entropies of fusion for selected aromatic polycondensates.

The low entropy of fusion of the polycarbonate molecule can be explained by the

Table II. Heats and Entropies of Fusion of Aromatic Polycondensates

Polymer	*M.p., °C.*	ΔH_u, *Cal./Mole*	ΔS_u *Cal./Mole °C.*
Poly(bisphenol A carbonate)	268	3400	6.3
Poly(ethylene terephthalate) (*13*)	267	5820	10.8
Poly(tetramethylene terephthalate) (*3*)	232	7600	15.1
Poly(tetramethylene isophthalate) (*3*)	152	10000	23.7

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rigidity of the chains, which gain less configurational freedom on melting than the polyterephthalates. Lengthening the aliphatic part of the repeating unit or incorporating a more asymmetric group, such as isophthalic ester, lowers the melting point and increases further the entropy of fusion.

Properties of Plasticized Polycarbonate Films

The mechanical properties and the tensile heat distortion temperatures (softening temperatures) of cast and pressed polycarbonate films containing differing amounts of plasticizer have been measured (Table III and IV).

Table III. Mechanical and Thermal Properties of Cast Plasticized Polycarbonate Films

Wt. Fraction Plasticizer, w_1	*Tm,°C.*	*Tg,°C.*	*S.P.,°C.*	*E, kg./sq. mm.*	*Y, kg./sq. mm.*	*T, kg./sq. mm.*	*Elongation at Break* (ϵ), %
0	268	148	140	229	4.2	5.6	21
0.010	266	134	135	247	7.0	6.5	18
0.020	266	129	132	262	7.4	6.9	5.8
0.029	263	126	117	267	7.2	6.7	24
0.048	261	122	117	283	7.3	7.0	5.0
0.070	—	110	105	286	7.1	6.8	16
0.090	257	104	102	304	7.5	7.0	8.3
0.111	—	91	90	298	7.2	6.3	20
0.130	247	[a]					

Y = yield strength T = tensile strength

[a] Additional amounts of plasticizer produced opaque and brittle films.

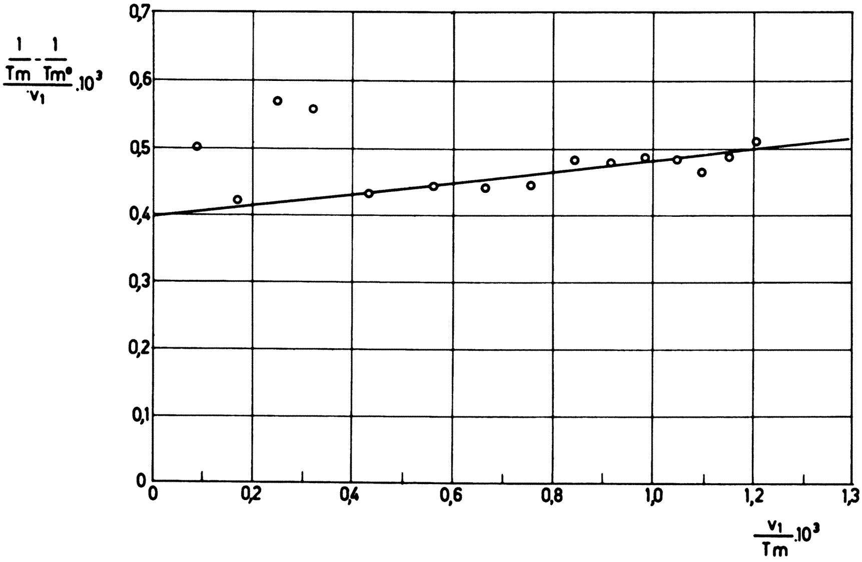

Figure 5. $(1/T_m—1/T_m°)/v_1$ *plotted against* v_1/T_m *for mixtures of polycarbonate with tricresyl phosphate*

Usually the presence of a plasticizer in a polymer film results in a lowering of its mechanical properties, especially its modulus of elasticity (*E*). The modulus of

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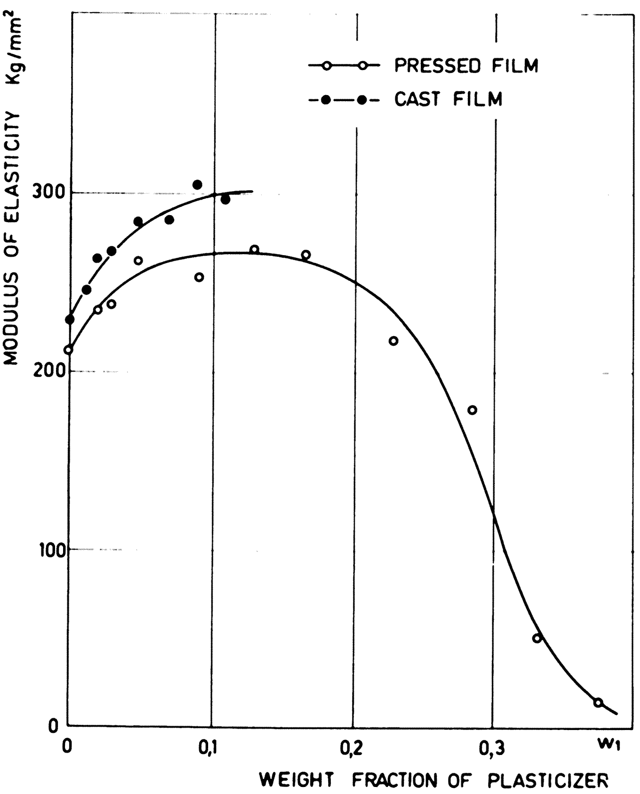


Figure 6. Modulus of elasticity for cast and pressed films of plasticized polycarbonate as a function of the weight fraction of plasticizer

elasticity is higher than that observed for the pure polymer up to about 15% of plasticizer. (Figure 6). With larger amounts of plasticizer, the usual phenomenon of decrease in elastic properties is observed.

From previous discussion it is clear that this behavior must be ascribed to crystallization phenomena or at least to segmental motions which result in an increase of order in the polymer and hence a more efficient chain packing.

In this context an article by Gruenwald (*7*) points out that a small increase in modulus of elasticity occurs in slightly plasticized polycarbonate and polyvinyl chloride.

Why is it that the maximum modulus of elasticity of crystalline film samples of polycarbonate, even when oriented, does not increase considerably over that of amorphous samples? Van Kerpel (*19*) examined the x-ray diffraction pattern of a crystallized polycarbonate sample held under tension and showed that the crystal lattice of the polycarbonate elongates quite easily in the direction of stretch. He found that the lattice distance (d = 2.670 A.) increases to d = 2.691 A. and d = 2.714 A. when the polycarbonate film is elongated by 5 and 10%, respectively.

By following the reasoning of Dulmage and Contois (*4*), the modulus of elasticity of the crystallites can be calculated. For polycarbonate, a value between 1000

Table IV. Mechanical and Thermal Properties of Pressed Plasticized Polycarbonate Films

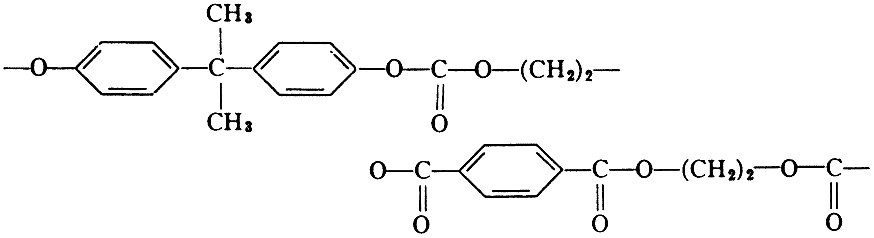
Wt. Fraction Plasticizer, w_1	*Tm,°C.*	*Tg,°C.*	*S.P.,°C.*	*E, kg./sq. mm.*	*Y, kg./sq. mm.*	*T, kg./sq. mm.*	*Elongation at Break* (ϵ),
0	268	147	140	209	5.2	5.4	80
0.010	266	132	112	245	4.9	5.2	111
0.020	266	—	100	234	5.2	5.5	110
0.029	263	116	102	237	5.6	5.4	96
0.048	261	106	90	262	6.0	5.8	28
0.090	257	81	70	252	5.9	5.1	46
0.130	247	67	57	268	5.7	4.5	16
0.167	242	—	55	266	5.5	4.6	23
0.231	240	35	35	218	4.0	3.1	7.9
0.286	233	16	45	179	3.0	2.7	44
0.333	228	—	—	51	0.67	0.94	44
0.375	223	—	—	15	0.10	0.70	160

and 2000 kg./sq.mm. is found, which is small compared to the value of 14,000 kg./sq.mm. reported for polyethylene terephthalate.

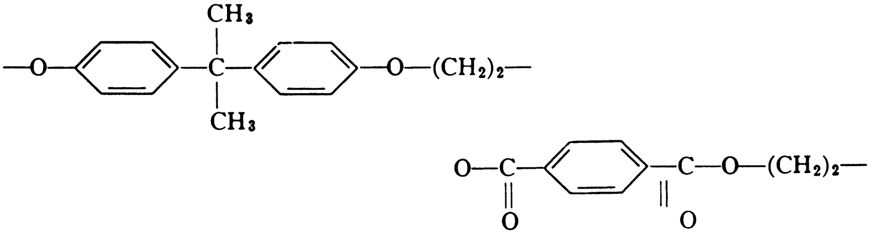
Internal Plasticization

A study parallel to the one discussed in this article focused on the problem of the internal plasticization of the polycarbonate chain by the incorporation of more flexible repeating units.

For instance bisphenol A copoly(carboxylate carbonates) have been prepared containing differing numbers of units of the following structure:



Analogously the bisphenol A polycarbonate structure has been modified by incorporating ether group-containing units of the formula:



The most striking result of this study is the observation that by incorporating even very small numbers of flexible units, the crystallizability of the polycarbonate is increased considerably.

It was also found that the tensile heat distortion temperatures of films containing only a few mole per cent of these units were considerably higher than those found for bisphenol A polycarbonate. X-ray diffraction studies made on the test samples used in the tensile heat distortion apparatus could not demonstrate an increase in crystallinity of the samples. Only a slight indication of increase of orientation was apparent. Glass transition temperatures measured by the refractometric method were considerably lower than the heat distortion temperatures.

Experimental Part

Plasticization of the Polycarbonate. "Makrolon S" of Bayer A.G. was used in the experiments. The intrinsic viscosity of this polymer is about 0.55 dl./gram.

Solvent Casting. The polymer is mixed with the plasticizer in the required proportion and dissolved in methylene chloride to form a 10% solution. Films are cast from this solution on a glass plate using a Gardner knife. The films are allowed to dry overnight at room temperature, and any residual solvent is removed by heating for 10 hours in an oven at 110°C. The thickness of the dry film should be about 100 μ.

Pressure Molding. The polymer is mixed with the plasticizer in the required proportion and dissolved in methylene chloride to form a 10% solution. This solution is poured into a tray and allowed to evaporate at room temperature. At regular intervals the content of the tray is thoroughly mixed with a spatula. The cake obtained is dried for 24 hours at 110°C.

Twenty grams of the plasticized polycarbonate are placed between two aluminum foils, separated by four 0.5-mm. metal shims. The sandwich is placed between the heating plates of a Carver laboratory press and heated without pressure to 260° to 280°C. At this temperature a pressure of 24,000 p.s.i. is gradually applied for 15 seconds. After 10 seconds more, the plates are water-cooled while still under pressure. As soon as the plates are cooled to 20° to 25°C., pressure is released and the pressed film is removed.

The correct amount of plasticizer in the cast and pressed films was checked by microanalysis of the film sample for phosphorus. The presence of residual solvent was tested by chlorine analysis and found to be negligible.

Evaluation of Thermal Properties

Glass transition temperatures were determined refractometrically, as described by Wiley (*20*), with an Abbe refractometer supplied by Bellingham and Stanley. This instrument can normally be used only at temperatures up to 70°C. The prisms of this instrument were coated with a heat resistant adhesive (epoxy-phenolic resin mixture). After this modification the refractometer can be used at temperatures up to 200°C.

The prisms are heated between 50° and 200°C. by means of thermostated silicone oil, and between −20° and 60°C. by a thermostated methanol-water mixture fed by a circulating pump.

The tested film is heated to at least 30° to 40°C. above its expected T_g. The sample should adhere firmly to the prisms. After an equilibrium temperature is reached, the refractive index is registered. The readings are repeated every 5°C.

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on cooling the sample and plotted against temperature. Different measurements showed that the results are reproducible within ± 1°C.

The crystalline melting point is determined by heating a crystallized sample on the Kofler heating stage of a polarizing microscope. The samples are crystallized by heating at 180° to 190°C. until spherulites appear.

The temperature of the hot stage is raised at a rate of 2°C./min. The crystalline melting point is determined according to Flory as the temperature where, between crossed nicols, the last trace of birefringence disappears.

The softening point (tensile heat distortion temperature) is determined as described by Van der Steen (*18*).

The elongation of film strips of fixed dimensions subjected to a constant load of 0.17 kg./sq.mm. is measured as a function of temperature. Heating rate is standardized at 10°C. per minute. The temperature range where an appreciable rise in elongation of the films is observed is taken as the softening point (S.P.)

These temperatures have only a comparative value as they are more or less dependent on the method of measurement. They are also dependent on crystallinity. When dealing with unoriented, amorphous films, the softening temperatures correspond more or less to the glass transition temperatures. When the films are crystalline, softening temperatures range from the glass transition point to the crystalline melting point of the polymers.

Conclusion

The crystallizability of bisphenol A polycarbonate is markedly increased by the addition of plasticizers, such as tricresyl phosphate.

Incorporating small amounts of plasticizer during the manufacture of solvent-cast polycarbonate films results in films with a higher modulus of elasticity, a higher stiffness, and higher heat distortion temperatures than films cast from unplasticized polymer.

The heat of melting and the entropy of melting can be calculated, from the depression of the crystalline melting point by the plasticizer. The high melting point of the polycarbonate is due essentially to a low entropy of fusion, undoubtedly caused by the high rigidity of the polycarbonate chain.

Acknowledgment

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Antiplasticizers for Bisphenol Polycarbonates

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Several classes of compounds are antiplasticizers for bisphenol polycarbonates—that is, when present in concentrations up to 30%, they increase the tensile modulus and tensile strength of films and decrease the elongation. Classes of particularly effective antiplasticizers are (1) chlorinated biphenyls and terphenyls, (2) poly(styrene glycols), and (3) abietic acid derivatives. By incorporating these materials in films of the polycarbonates studied, the tensile moduli were increased by 30 to almost 60% of the intial values.

A series of polycyclic bisphenol polycarbonates was recently developed in these laboratories (*5*). Because of the bulky, three-dimensional, polycyclic groups attached to the main molecular chains, these polymers have very high glass transition temperatures—200° to 290°C. Compared to other types of bisphenol polycarbonates, the polymers also have relatively low elongations—usually 3 to 30%. To extend the usefulness of these polymers, an effort was made to increase their flexibility and toughness by plasticization. Many compounds were tested as potential plasticizers, but none was found to be effective when present in concentrations of 20 to 30%. Instead, several classes of compounds were discovered which, in effect, acted as antiplasticizers—that is, when present in concentrations up to 30% they increased the tensile modulus and tensile strength of films and decreased the elongation. Also, the glass transition temperatures of the polymers were depressed appreciably less by these antiplasticizers than by conventional plasticizers. Since the authors were also interested in films which were suitable for applications requiring a relatively high tensile modulus (such as in photographic film and magnetic tape), the action of the antiplasticizers was studied. Results reported here were obtained with three classes of commercially available compounds which were particularly effective antiplasticizers for these polycarbonates: (1) chlorinated biphenyls and terphenyls; (2) poly(styrene glycols), formula *A*; and (3) derivatives of abietic acid, formula *B*.

Most of the experiments were carried out with two model polycarbonates

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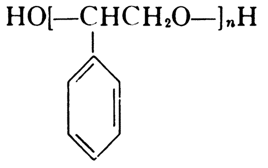
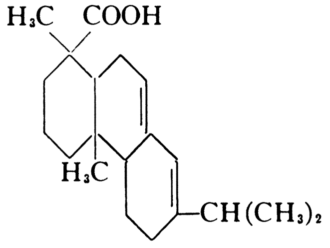
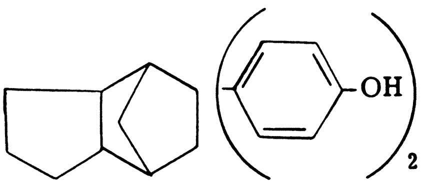


A

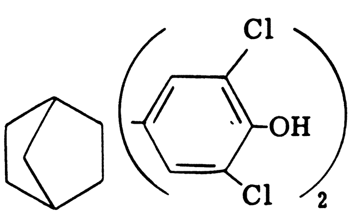


B

of polycyclic bisphenols, 4,4′-(hexahydro-4,7-methanoindan-5-ylidene)diphenol(I) and 4,4′-(2-norbornylidene) bis[2,6-dichlorophenol](II):



I



II

Since each of these polycarbonates had exceptionally high glass transition temperatures—256° and 290°C., respectively—it was possible to add appreciable amounts of antiplasticizers without depressing the glass transition temperatures to room temperature or lower. In addition, since the bisphenol II polycarbonate already had a relatively high tensile modulus (4.7×10^5 p.s.i.), it was of interest to determine how much this modulus could be increased.

To determine if the tensile properties of the commercially available polycarbonate from 4, 4′-isopropylidenediphenol were similarly affected, several of the antiplasticizers were also added to this polymer. The bisphenol itself is commonly known as bisphenol A.

Experimental

The polycarbonates which were used in these experiments had the following molecular weights (determined ebulliometrically): bisphenol I polymer, 20,700; bisphenol II polymer, 54,000; bisphenol A polymer, 28,200.

Films containing the various additives were obtained by casting from methylene chloride by conventional techniques. The films, from 1 to 3 mils in thickness, were dried at room temperature for 24 hours. Those with glass transition temperatures above 100°C. were then heated in an oven at 100° to 110°C. for 2 hours to ensure the removal of all solvent. Films with lower transition temperatures were heated under reduced pressure in an oven for 24 hours at temperatures ranging from 40° to 65°C., depending on the transition temperatures.

Tensile properties (tensile strength, elongation, modulus) were measured on an Instron tensile tester (ASTM D882-61T Method A). The tensile modulus was the slope of the initial straight portion of the stress-strain diagram. The heat-distortion

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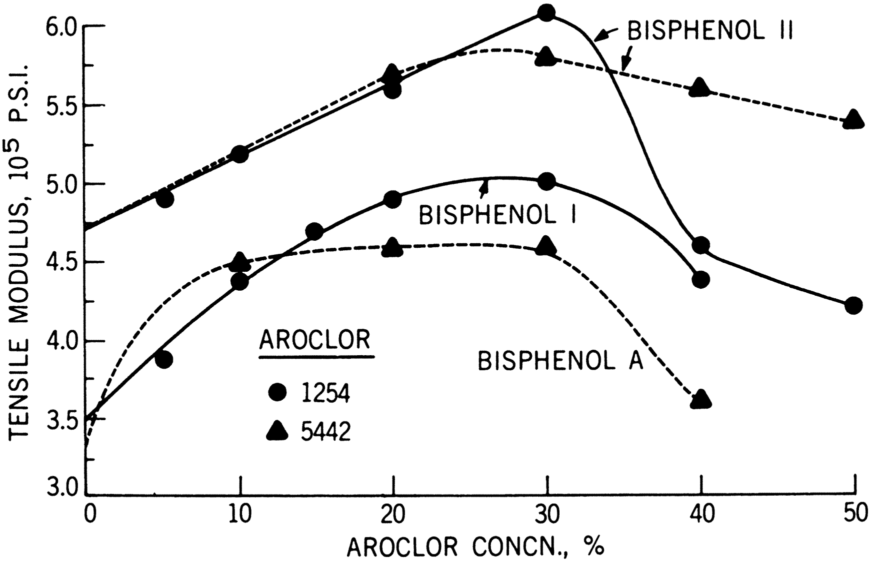

Figure 1. Effect of Aroclor concentration on tensile moduli of bisphenol polycarbonates

temperatures (2% deflection with 50-p.s.i. load) were measured in a forced-convection oven (ASTM D1637–61) (*8*). The glass transition temperature was taken as the temperature at which the film distorted 0.25% at a load of 5 p.s.i. when heated in the forced-convection oven (5).

Results

The polycarbonate films containing the additives were completely transparent, and x-ray diffractometric curves gave no indication of crystallinity. Films with a thickness of about 2 mils could be tightly creased without cracking, but 3– to 4–mil films often cracked under these conditions. Film properties of the polymers from bisphenols I and II and from bisphenol A are listed in Tables I to III, respectively. Some conventional plasticizers also are listed at the bottoms of the tables to show their effect on the film properties.

When the additive consisted of an Aroclor (a chlorinated biphenyl or terphenyl), a poly(styrene glycol), or an abietic acid derivative, the tensile moduli of the films increased as the concentration of additive was increased to about 30%. In two films (from the bisphenol I and bisphenol A polymers), the modulus increased as the concentration of a chlorinated terphenyl increased even to 40%. Instead of becoming more flexible, as would be expected, the films became stiffer. Most of these additives, incidentally, were viscous or very viscous oils. The effect of two Aroclors on the tensile moduli is shown in Figure 1.

Except for the previously mentioned two films, the moduli decreased when the antiplasticizer concentration was increased to more than 30%. The moduli were still relatively high, however, even when the concentration of the additive was 40 to 50%.

The maximum increase in tensile modulus of the bisphenol I polycarbonate was

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Table I. Effect of Additives on Film

Additive commercial name	*Composition*
—	—
Aroclor[a] 1242	Chlorinated biphenyl (42% Cl)
Aroclor 1254	Chlorinated biphenyl (54% Cl)
Aroclor 5442	Chlorinated terphenyl (42% Cl)
Aroclor 5460	Chlorinated terphenyl (60% Cl)
—	*o*-Terphenyl
Polyglycol 174–500[b]	Poly(styrene glycol), mol. wt. 500
Polyglycol 174–750[b]	Poly(styrene glycol), mol. wt. 750
Abalyn[c]	Abietic acid, methyl ester
Hercolyn[c]	Hydrogenated abietic acid, methyl ester
Staybelite Ester[c] 1	Hydrogenated abietic acid, ethylene glycol ester
Staybelite Ester 3	Hydrogenated abietic acid, triethylene glycol ester
Abitol[c]	Hydroabietyl alcohol
	Dibutyl phthalate
	Bis(2-ethylhexyl) phthalate
	Dibenzyl sebacate

[a] Monsanto Chemical Co.
[b] Dow Chemical Co.
[c] Hercules Powder Co.

from a value of 3.5×10^5 p.s.i. to 5.5×10^5 p.s.i. The maximum increase for the bisphenol II polycarbonate was from 4.7 to 6.1×10^5 p.s.i. For the bisphenol A polycarbonate, the maximum increase was from 3.3 to 4.7×10^5 p.s.i. The percentage increases in these moduli values, therefore, were very considerable—30 to 57%.

As the antiplasticizers made the films stiffer, their elongations decreased. The tensile strengths, in most cases, increased. As is shown in Table II, when the amount of additive was increased to more than 30% and the modulus decreased, the tensile strength also decreased. Tensile strengths and moduli also decreased when the additive was not an antiplasticizer.

The type of antiplasticizer had little effect on the glass transition temperatures (T_g) of antiplasticized biphenol I and II polycarbonate films. For example, as is shown in Table I, films of the bisphenol I polymer containing 20% of a chlorinated biphenyl or terphenyl (Aroclor 1242, 1254, 5442, or 5460), 20% of a poly(styrene glycol) (molecular weight 500 or 750), or 20% methyl abietate all had T_g's in the range 124° to 144°C. (seven films). Even though Aroclor 1242 has a pour point of about −20°C. and Aroclor 5442 a softening point of about 50°C., T_g's of films con-

Properties of Bisphenol I Polycarbonate

	Tensile Properties				
Concn., %	*Modulus, 10^5 p.s.i.*	*Elongation at break, %*	*Strength at break, p.s.i.*	*Glass transition temp., °C.*	*Heat Distortion temp., °C.*
0	3.5	6–20	11,200	256	266
20	4.0	3	12,000	131	133
5	3.9	4	11,300	183	—
10	4.4	4	13,000	166	—
15	4.7	4	13,500	154	159
20	4.9	4	13,600	131	133
30	5.0	3	11,400	97	94
40	4.4	4	9,900	89	69
20	4.8	4	13,800	130	133
30	5.3	3	12,500	98	94
40	5.5	3	12,700	90	79
20	4.6	3	11,800	143	155
20	3.8	6	10,300	—	—
20	4.7	3	11,300	124	—
30	4.8	3	11,500	98	88
10	4.0	5	12,800	—	—
20	5.0	3	12,500	144	148
20	4.6	4	12,700	131	128
30	4.9	3	10,800	102	—
40	3.5	3	8,200	98	—
20	4.7	3	12,000	—	—
20	4.5	3	11,400	—	—
15	4.5	3	11,100	—	—
20	4.6	3	10,300	—	—
20	3.3	4	10,000	122	114
30	2.0	15	4,700	57	—
40	0.6	121	2,600	37	—
20	2.9	6	7,700	121	—
20	3.3	5	9,700	125	—
30	2.4	5	4,800	—	—
40	1.4	112	1,300	39	—

taining 20% of these additives were 130° to 131°C. The T_g of a film containing 20% of Aroclor 5460, which softens at about 100°C., was somewhat higher (143°C.). Bisphenol A polycarbonate films containing 20% of a liquid or low melting point antiplasticizer had T_g's of 83° to 89°C. (Table III). When 20% Aroclor 1268 (m. p. ca. 150°C.) was present, T_g was about 20°C. higher (109°C.).

Figure 2 shows the effect of two Aroclors on the glass transition temperatures. A very rapid decrease in transition temperatures of the polymers from bisphenols I and II took place when as much as 5 or 10% additive was in the films. When the antiplasticizer concentration was 5 to 30% in the bisphenol I polymer and 10 to 40% in the bisphenol II polymer, there was a linear relationship between the decrease in glass transition temperature and the antiplasticizer concentration.

The heat-distortion temperatures in the tables are the temperatures at which the films distorted 2% while under a load of 50 p.s.i. Except for examples in which the antiplasticizer concentration was 40 to 50%, the heat-distortion temperatures were usually within 10°C. of the glass transition temperatures, which are the temperatures at which the films distorted 0.25% while under a load of 5 p.s.i. Distor-

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Table II. Effect of Additives on Film

Additive commercial name[a]	Concn., %	Tensile Modulus, 10^5 p.s.i.
—	0	4.7
Aroclor 1254	5	4.9
	10	5.2
	20	5.6
	30	6.1
	40	4.6
	50	4.2
Aroclor 5442	20	5.7
	30	5.8
	40	5.6
	50	5.4
Polyglycol 174–500	20	5.1
	30	5.1
Abalyn	20	5.0
	30	5.3
Dibutyl phthalate	30	1.8
	40	0.7
Dibenzyl sebacate	30	1.9
	40	0.5

[a] Sources and compositions are given in Table I.

Table III. Effect of Additives on Film

Additive commercial name[a]	Concn., %	Tensile Modulus, 10^5 p.s.i.
—	0	3.3
Aroclor 1254	20	4.4
	30	4.7
Aroclor 5442	10	4.5
	20	4.6
	30	4.6
	40	3.6
Aroclor 1268	20	4.0
	30	4.3
	40	4.4
Polyglycol 174–500	20	4.6
	30	4.5
Polyglycol 174–750	20	4.2
Abalyn	20	4.7
Dibutyl phthalate	20	3.0
	30[b]	2.5
Dibenzyl sebacate	30[b]	0.5

[a] Sources and compositions are given in Table I.
[b] According to an x-ray diffraction curve, a slight amount of crystallinity was present

tion at 50 p.s.i. was invariably caused by extension of the films, whereas at 5 p.s.i. the distortion was usually caused by shrinkage.

Discussion

It is surprising that the tensile moduli of the polycarbonate films were increased so much by the antiplasticizers, and it is even more surprising that antiplasticizer concentrations of 30% (and even 40% in two cases) could be tolerated before the

Properties of Bisphenol II Polycarbonate

Properties		*Glass transition temp., °C.*	*Heat distortion temp. °C.*
Elongation at break, %	*Strength at break, p.s.i.*		
4–6	14,000	290	300
4	13,000	242	—
3	13,700	207	—
3	13,500	174	183
3	14,000	142	144
4	11,300	108	102
4	9,100	99	86
3	13,200	169	173
3	13,500	144	—
3	12,300	101	—
3	10,700	92	79
3	12,800	171	177
3	12,700	133	—
3	11,100	157	166
3	11,000	126	—
7	5,200	84	—
171	3,300	37	—
8	4,100	96	—
177	3,000	39	—

Properties of Bisphenol A Polycarbonate

Properties		*Glass transition temp., °C.*	*Heat distortion temp. °C.*
Elongation at break, %	*Strength at break, p.s.i.*		
20–90	9,000	150	154
4	14,200	—	91
4	12,700	73	—
4	13,700	109	108
4	12,800	89	94
4	14,300	60	81
7	5,400	46	—
7	11,000	109	110
4	11,800	—	103
3	11,000	85	81
4	13,500	83	—
3	12,900	—	65
4	12,100	87	84
4	12,700	89	87
14	7,100	58	58
122	5,800	—	—
128	3,900	—	—

in the film.

moduli began to decrease. The considerable increase in the tensile strength of the bisphenol A polymer is also noteworthy.

Sears and Darby (7), in an extensive investigation of the plasticization of bisphenol A polycarbonate, reported that the tensile strength and modulus were increased somewhat and the elongation decreased when some plasticizers were present in relatively small amounts. According to a curve which showed the effect of one of these (*N*-ethyl-*o*/*p*-toluenesulfonamide) on film tensile properties, the maximum tensile strength and modulus occurred at an additive concentration

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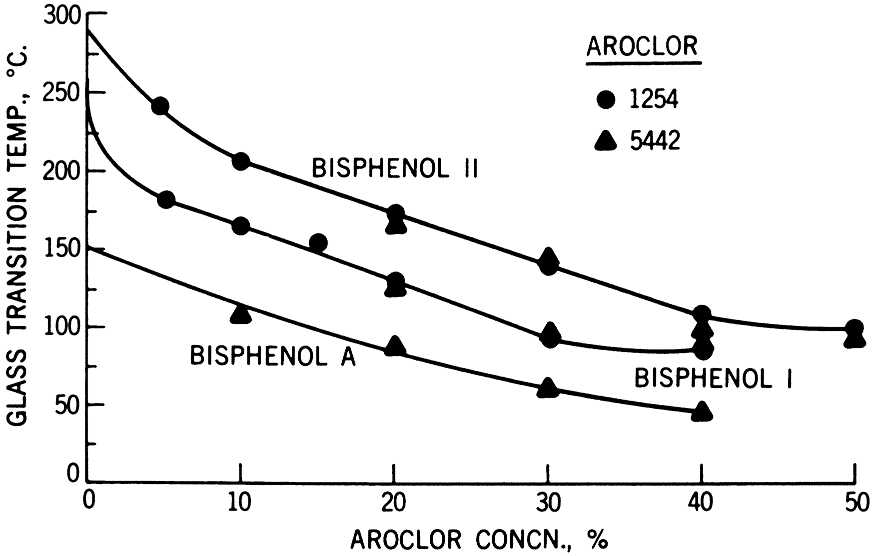

Figure 2. Effect of Aroclor concentration on glass transition temperatures of bisphenol polycarbonates

of about 15%. As the concentration was increased to 50%, the tensile strength and modulus rapidly decreased to about 1000 p.s.i. and 60,000 p.s.i., respectively, and the elongation increased to 105%. In contrast, the tensile strengths and moduli of the polymers described here were quite high when the antiplasticizer concentration was 40 to 50%, and the elongations remained low.

When poly(vinyl chloride) contains 5 to 10% of various plasticizers, a small increase in modulus and tensile strength occurs (*3*, *4*). According to Horsley (*4*), this is due to an increase in the degree of order and crystallinity of the system, and the theory is supported by x-ray diffraction patterns. According to Ghersa (*3*), a contributing factor is the steric hindrance of plasticizer molecules which, attached with polar groups to poly(vinyl chloride) chains, could act as cross links.

These two theories, proposed to explain the increase in rigidity of poly(vinyl chloride) at low plasticizer concentrations, may also be applicable, in part, to our antiplasticized polycarbonate systems. X-ray diffractometric curves gave no indication of crystallinity or order in any of the polycarbonate films containing antiplasticizers, but it is possible for a degree of order or incipient crystallization to be present which can be measured by differential thermal analysis (DTA) and not by x-ray measurements. This occurs with cellulose esters (*1*). DTA curves of films of bisphenol I polycarbonate containing 30 to 40% of an Aroclor showed a broad endotherm covering the range 50° to 200°C. and peaking at about 138°C. Similarly, DTA curves of bisphenol II and bisphenol A polycarbonate films containing Aroclors also showed broad endotherms. These endothermic peaks were not present in the Aroclor alone or in films which did not contain an additive. They also were not present in films containing dibutyl phthalate or dibenzyl sebacate.

The DTA endotherms of the antiplasticized polymers indicate the presence of forces which are broken by the input of thermal energy. Instead of a degree of order or incipient crystallization, it is possible that these forces consist of secondary bonds between the polar antiplasticizer and the polymer containing polar groups. Or perhaps both types of forces are responsible for the antiplasticizing action. In any event, since energy is required to break these forces, it would be expected that the forces limit the movement of the polymer chains. Therefore, these polymers have higher moduli, higher tensile strengths, and lower elongations than polymers which do not contain antiplasticizers.

Movement of the polymer chains would also be limited if the free volume of the polymer was reduced by the antiplasticizer—that is, if some of the "holes" between the chains were partially filled by the additive. Since movement of the polymer chains would then be more restricted, the polymer would be stiffer and the tensile modulus increased. Density measurements of several films containing Aroclors indicated that the densities were 2 to 2.5% higher than would be obtained by simple addition of the volumes of polymers and Aroclor. This increase in density is highly significant, because the free volume of the polymer alone is about 2.5% (*2*). However, the observed density was also similarly higher than calculated when dibutyl phthalate, a plasticizer, was present. Any stiffening effect caused by a reduction in the polymer free volume by a small amount of plasticizer is apparently overcome by addition of more of the flexible plasticizer molecules. The antiplasticizer molecules, on the other hand, are relatively rigid, and when more of them are added the polymer chains become stiffer because other forces apparently are involved.

Since the upper limit of the endotherms on the DTA curves was about 200°C., at this temperature the restraining forces due to the antiplasticizer were broken. It would be expected, then, that inert antiplasticizers, such as the Aroclors, would act either as plasticizers or as diluents, but not as antiplasticizers, at temperatures above 200°C. It has been observed that the glass transition temperatures of polymers are greatly depressed when true plasticization occurs and that the greatest depression is by the most efficient plasticizers (*3*, *6*). Dibutyl phthalate and dibenzyl sebacate, which are conventional plasticizers, depressed the glass transition temperatures of the polycarbonates appreciably more than antiplasticizers (Tables I to III). In view of the rapid decrease in the glass transition temperatures of the polycarbonates from bisphenols I and II when small amounts of Aroclor were present (Figure 2), it would appear that the Aroclor is functioning as a plasticizer at temperatures near and above 200°C.

Whereas Sears and Darby (*7*) found many types of compounds which would plasticize bisphenol A polycarbonate when the plasticizer concentration was 25 to 30%, the norbornane-type polycarbonates could be plasticized only with larger amounts of plasticizer. When present in concentrations of 20 to 30%, conventional plasticizers acted as diluents—that is, the tensile modulus and tensile strength were depressed, as occurs with plasticizers, but the elongation was not appreciably increased. The antiplasticizers also acted similarly and became diluents after their peak antiplasticizing action was reached.

Although bisphenol A polycarbonate is plasticized by a 30% concentration of dibutyl phthalate or dibenzyl sebacate (Table III), as has been reported (*6*, *7*), a higher concentration is required for effectively plasticizing the polycarbonates of bisphenols I and II (Tables I and II). Perhaps the reason for this is the appreciably lower mobility of polymer chains containing bulky, three-dimensional, polycyclic structures than chains of the bisphenol A polycarbonate. So even though a plasticizer may weaken the secondary attraction forces between polymer chains,

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a high degree of rigidity remains in the norbornane-type polymers because of the bulky, polycyclic structures. A plasticizer concentration of 30%, therefore, is apparently not sufficient to make these polymer chains far enough apart so that the bulky groups can pass by each other during uncoiling and slipping of the chains. The glass transition temperature also is appreciably above room temperature, whereas it is normally near or below room temperature in plasticized polymers.

In antiplasticization, on the other hand, the secondary attraction forces between polymer chains are increased and are perhaps augmented by the formation of secondary bonds between the antiplasticizer and polymer. For this phenomenon to occur to an appreciable extent, it is apparently necessary that the polymer chains be relatively rigid and that they contain polar groups to interact with the antiplasticizer molecules. This occurs with polycarbonates of bisphenols in which both phenolic groups are attached to the same carbon atom. It is also probably significant that the antiplasticizer molecules themselves are bulky, have a high degree of rigidity, and are polar compounds. *o*-Terphenyl, which is less bulky, less rigid, and less polar than chlorinated terphenyl, had very little effect on the bisphenol I polymer properties (Table I). And flexible molecules are not antiplasticizers. To obtain antiplasticizing action, therefore, it appears that the additive should be a nonvolatile compound which is: (1) compatible with the polymer, (2) polar, and (3) comparatively bulky and rigid in structure. The polymer itself should contain: (1) relatively rigid chains and (2) polar groups.

The antiplasticizing action has been described here for only three classes of commercially available antiplasticizers, but it has been observed, usually in a lesser degree, with other classes of compounds and low molecular weight polymers. These are, however, not commercially available. Bisphenol polyesters of isophthalic acid, terephthalic acid, and 1,4-cyclohexanedicarboxylic acid also have been antiplasticized; the polymer chains, as would be expected, are all relatively rigid.

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Conclusion

Antiplasticizers are of considerable value for increasing the stiffness of bisphenol polycarbonate films and thereby making them more suitable for applications requiring a high tensile modulus. Such applications include bases for photographic film and magnetic tape. Since thick films are more brittle than thin films, some applications may be restricted to films 2 mils or less in thickness. Films which combine both a very high modulus and a high glass transition temperature are obtained by antiplasticizing the polycarbonate from 4,4′-(2-norbornylidene)bis[2,6-dichlorophenol](bisphenol II).

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