

Polymer-Diluent Interactions. I. A New Micromethod for Determining Polyvinyl Chloride-Diluent Interactions*

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INTRODUCTION

The determination of polymer-diluent interactions is a problem of considerable theoretical as well as practical interest, in that knowledge of these interactions is a key to understanding the properties of polymer solutions and gels, including plasticized polymer systems. Much effort therefore has been directed toward the development of methods for determining the type and degree of these interactions.¹⁻²⁵ Thus far, however, the majority of the methods reported are either too empirical or they require rather tedious and exact measurements. Furthermore, many are based on the solubility of the polymer in the diluent and therefore are not applicable to nonsolvents. This is a serious limitation, especially in the study of plasticizers, many of which are nonsolvents. The purpose of this paper is to present a fast and simple method for determining the degree of interaction in polyvinyl chloride-diluent systems based on Flory's statistical thermodynamic treatment of the effect of diluent on the melting temperature of crystalline polymers.²⁶ Polyvinyl chloride was chosen because of our interest in the plasticization of the polymer and because Flory's treatment has not been previously applied to this polymer.

The method herein reported involves the micro-determination of a temperature at which a single polyvinyl chloride particle, in the presence of excess diluent, undergoes a characteristic change that can be best described as a transformation from the gel to the sol state. This temperature was found to be characteristic for each polyvinyl chloride-diluent pair and quite reproducible. We have considered the possibility of this being a depressed melting temperature for polyvinyl chloride in the presence of diluent and have used it as

TABLE I

Effect of Diluents and Diluent Content on Apparent Melting Temperature t_m of Polyvinyl Chloride

Diluent	t_m , °C.	Volume fraction v_1 of diluent at t_m	Parameter χ (Doty and Zable ⁴), extrapolated to t_m
Nitrobenzene	41-43	0.95	0.29
Mesityl oxide	41-46	0.87	0.42
Ethylene dichloride	52-57	0.92	0.45
Methyl <i>n</i> -amyl ketone	60-63	0.95	0.18
γ -Valerolactone	61-63	0.95	0.31
Tri- <i>n</i> -butyl phosphate	64-65	0.99	-0.59
Triethyl phosphate	67-70	0.96	0.15
Nitropropane	70-76	0.96	0.42
1-Bromonaphthalene	76-78	0.92	0.38
Chlorobenzene	73-80	0.95	0.48
Anisole	79-84	0.95	0.50
<i>n</i> -Butyl acetate	90-91	0.96	0.42
Di- <i>n</i> -butyl phthalate ^a	90-94	0.93	0.02
Ethyl acetoacetate	101-103	0.93	0.46
Diethyl phthalate	98-104	0.94	0.38
Dimethyl sebacate	104-108	0.86	0.34
Di- <i>n</i> -hexyl phthalate	106-108	0.94	-0.04
Diethyl sebacate	106-109	0.92	0.19
Dimethyl phthalate	109-112	0.90	0.49
Dioctyl phthalate ^b	116-118	0.97	0.06
Dihexyl adipate ^c	124-125	0.93	0.30
Dibutyl Cellosolve phthalate ^d	125-128	0.90	0.39
Dibenzyl sebacate ^e	132-137	0.88	0.42
Di- <i>n</i> -octyl succinate	141-143	0.86	0.39
Methyl acetyl ricinoleate ^f	145-147	0.83	0.56
Dioctyl sebacate ^g	151-152	0.85	0.53
Butyl acetyl ricinoleate ^h	156-157	0.88	0.73

^a Dibutyl phthalate plasticizer, Monsanto Chemical Co.

^b DOP plasticizer, Monsanto Chemical Co.

^c Harflex 260, Harchem Div., Wallace and Tiernan.

^d Kronisol, Ohio-Apex Div., Food Machinery and Chemical.

^e Morflex 250, Morton-Withers Chemical.

^f Flexricin P-4, Baker Castor Oil.

^g Monoplex DOS, Rohm and Haas.

^h Flexricin P-6, Baker Castor Oil.

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such in applying Flory's treatment. Whether it is a true first-order transition or some other form of order-disorder transition cannot be known for certain until more direct evidence has been obtained. The fact, however, remains that it is a rate-independent transition and one to which Flory's treatment can be successfully applied for the determination of the polymer-diluent interaction parameter χ .

EXPERIMENTAL

Materials

The polyvinyl chloride used in this work was commercial grade Opalon 300 (Monsanto Chemical Company) and Geon 101 (B. F. Goodrich Chemical Company). Several experimental high molecular weight vinyl chloride homopolymers were also used to check the general applicability of our techniques. No special treatment of the polymers was found necessary, except for repeated screening to remove all fine particles below 0.2 mm. in diameter. All data reported here were obtained on material from a single container of Opalon 300. However, no significant differences in results were obtained with different batches of this polymer or with various batches of Geon 101.

The diluents tested were commercial products. The solvents were of the highest purity commercially available. The source of each of the various plasticizers is specified in Table I.

Equipment

The equipment consisted of a conventional microscope capable of $\times 100$ magnification, equipped with a Kofler micro hot stage (30–340°C., A. H. Thomas Co.). The illuminator was a filament lamp designed to operate at 6 v. and 18 amp. (Bausch and Lomb Illuminator PR-27). A suitably mounted 35 mm. camera or a Polaroid Land Camera was used for photographic recording of the microscope field images. Calibration of the hot stage was not found necessary as long as the rate of heating was kept constant for all runs and set at approximately 0.5°C./min.

Procedures

A drop of the solvent or plasticizer to be tested was placed on a microslide and a few granules of polyvinyl chloride sprinkled on the surface and thoroughly mixed with a micro spatula. The preparation was then covered with a cover glass and inspected to assure that enough liquid was present to occupy all the space between slide and

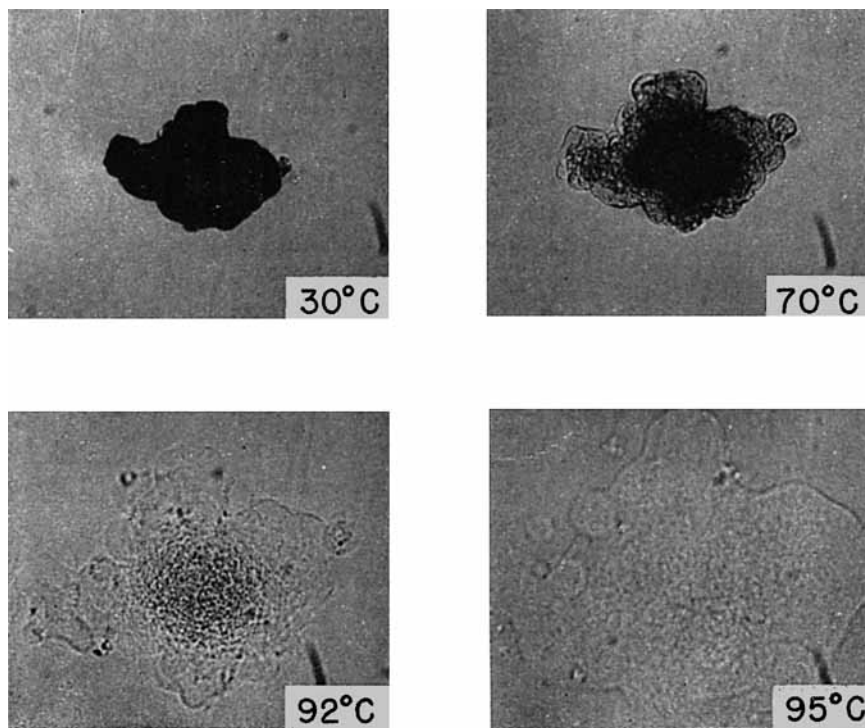


Fig. 1. Photomicrograph showing the effect of heating a single polyvinyl chloride particle in *n*-butyl phthalate.

cover glass, so that the cover glass rested on a cushion of liquid rather than on the particles. At this point the preparation was surveyed under magnification in search for the right particle. In general, two types of polyvinyl chloride particles

were distinguishable—those which appear translucent and those which appear black. The reasons for this difference are not quite clear. Nevertheless, black particles were chosen for further observations, although the other kind exhibited the

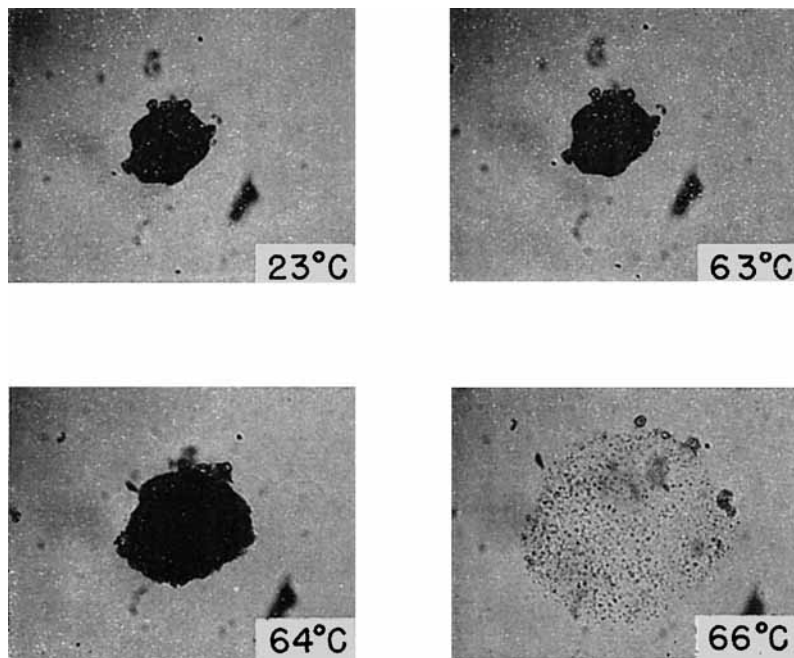


Fig. 2. Photomicrograph showing the effect of heating a single polyvinyl chloride particle in tri-*n*-butyl phosphate.

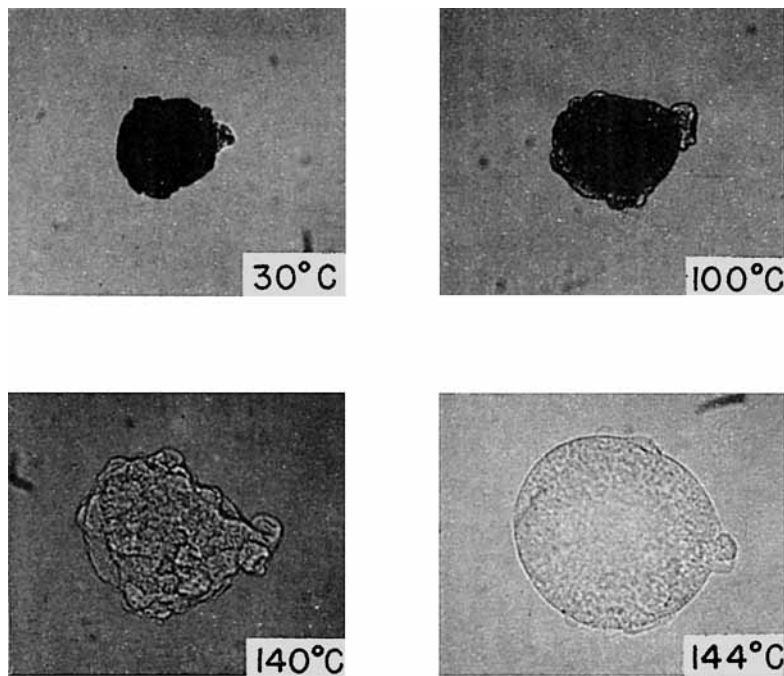


Fig. 3. Photomicrograph showing the effect of heating a single polyvinyl chloride particle in di-*n*-octyl succinate.

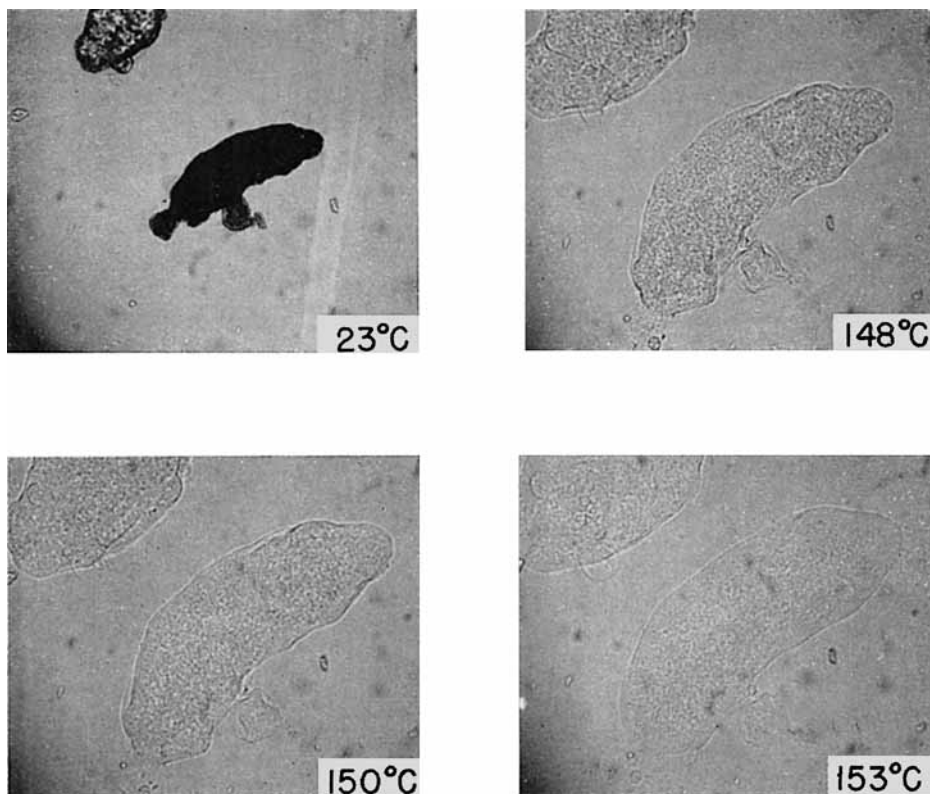


Fig. 4. Photomicrograph showing the effect of heating a single polyvinyl chloride particle in dioctyl sebacate.

same behavior, but in a somewhat less definite manner. The shape of the chosen particle was found to be of importance. For reasons that will become evident later, the particle chosen for observation was not perfectly spherical nor did it deviate too much from a spherical shape. Once the right particle was found the slide was covered with the cover plate of the stage and heating commenced. The changes that took place as the temperature was increased were observed under magnification with strong through illumination.

The changes that were observed can be best understood by referring to Figures 1-5. At first, as the temperature was raised, the polymer particle did not change appreciably. Then it began to imbibe the diluent without much increase in volume. This imbibition caused the particle to lose its dark appearance and become translucent. As heating continued, the particle swelled more and more, but maintained its form identity, retaining its distinct outlines and contours. Then a temperature was reached where the swollen particle began to lose its distinguishable form; within a few degrees the particle changed from a seemingly firm gel with distinct contours to a smooth-edged drop.

This distinct change took place within a range of two to four degrees. With some practice, the "endpoint" could be reproduced to within $\pm 2^\circ\text{C}$. Photographic recording of the change afforded a more accurate endpoint determination.

This apparent gel-to-sol transformation was found to be independent of the rate of heating, provided this was not too fast. In most cases a rate of $0.5^\circ\text{C}/\text{min}$. was optimum. Slower rates did not offer any advantage except in cases where the endpoint was below 80 or above 150°C .; then a rate of $1^\circ\text{C}/2-4$ min. was optimum. Faster rates caused the endpoint to be exceeded by as much as 5°C . These conditions are not unlike those recommended for the determination of melting points of monomeric crystalline compounds.

Additional evidence that these transitions were independent of the rate of heating was found in the observation that no gel-to-sol transformation occurred when a preparation was kept from three to six degrees below the transformation temperature for extended periods of time.

In addition to aiding endpoint determination, photographic recording of the changes afforded a method of measuring the volume fraction of the

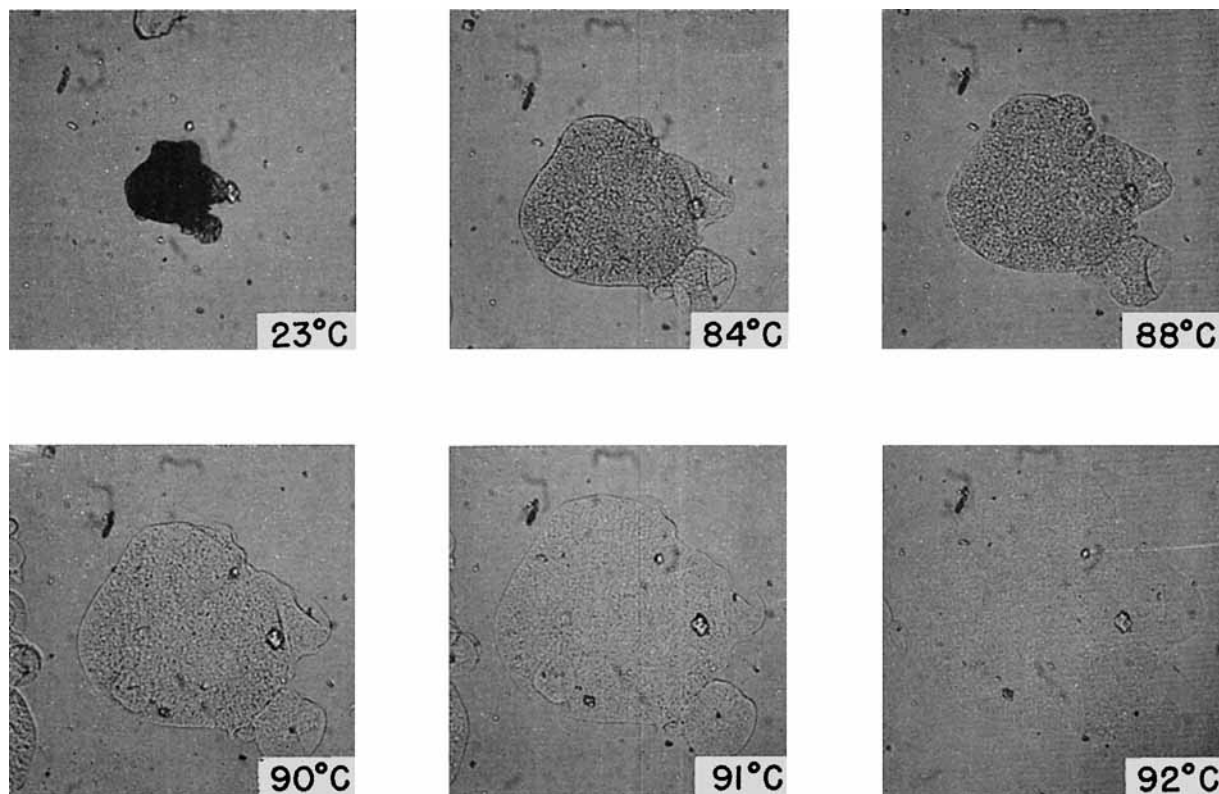


Fig. 5. Photomicrograph showing the effect of heating a single polyvinyl chloride particle in butyl acetate.

diluent at the transformation temperature. From the photographs, with the aid of a planimeter, the area of the particle image was measured at room temperature and just prior to the transformation. The volume fraction, v_1 , of the diluent was then determined from the area measurements on the basis of the assumption that the swollen particle was spherical. Observation has shown this assumption to be valid if the original polymer particle chosen for the test was nearly spherical. In addition, it was assumed that swelling was isotropic and that there was no volume change upon mixing. The validity of these assumptions has been demonstrated.⁴ The accuracy of determining volume fractions by this method is not known, although the reproducibility was found to be within 5%.

Values for the molar volume V_1 of each diluent were calculated from density measurements at the gel-to-sol transformation temperatures. Where the volatility of the diluent at this temperature was high, values for V_1 were obtained by extrapolation. A value of 44.6 was used for V_u , the molar volume of the polymer repeating unit. Changes due to thermal expansion of the polymer were disregarded because of the low expansion coefficient of polyvinyl chloride compared to that of the diluent.

INTERPRETATION OF EXPERIMENTAL OBSERVATIONS

The behavior of polyvinyl chloride particles heated in the presence of excess diluent suggests the existence of a stable polymer network system. The idea of such a network system in polyvinyl chloride gels and plasticized compositions has found support in a number of investigations. Crystallites have been identified by x-ray methods and proposed as junction points for the network.²⁷⁻³⁰ Many of the mechanical properties of polyvinyl chloride gels have been studied and explained on the basis of a three-dimensional network.¹⁵ Investigation of the time dependence of stress and birefringence as a function of temperature have supported the idea of a network of chains,²⁹ and the response of plasticized polyvinyl chloride to stress and recovery has been shown to be typically viscoelastic in nature.³¹⁻³³

On the basis of this evidence, it is reasonable to expect the following set of events to take place when a polyvinyl chloride particle is heated in the presence of large amounts of diluent. First, the particle will swell by imbibing diluent. The degree of swelling will depend on the mutual affinity between polymer and diluent. At this stage, the

diluent molecules will have occupied the voids in the polymer network and also solvated the macromolecules of the amorphous regions. Further heating of the polyvinyl chloride gel should cause no change until a temperature is reached when the crystallites begin to melt. At this point the network will begin to collapse. As more and more crystallites melt, the three-dimensional character of the network will be gradually destroyed, and the particle transformed from the gel to the sol state. The temperature interval over which this transformation occurs might be associated with a diffuse first-order transition. There is no proof, however, that this temperature range would include the true melting temperature of the polymer. It is more likely that the true melting temperature would lie above this range, since the thermodynamically significant melting temperature is the temperature at which the most perfect crystallite melts.²⁶

That polyvinyl chloride particles, when immersed in diluents and heated, do indeed undergo such changes has been demonstrated in the Experimental Section. At present there is no proof that the temperature at which this apparent gel-to-sol transformation occurs is a true first-order transition. However, it will be treated as such in the discussion to follow and will be referred to hereafter as the "apparent melting temperature" and designated as t_m .

THEORETICAL

Flory²⁶ has shown that the equilibrium melting temperature of a crystalline polymer may be depressed by a monomeric diluent incorporated in the polymer. His statistical-thermodynamic treatment of this effect has revealed that the size of the depression depends not only on the nature of the polymer and the concentration of the diluent, but also on the degree of polymer-diluent interaction. Therefore, by studying the crystal melting temperatures of mixtures of polymers and diluents one may obtain information about this interaction.

According to Flory's theory,

$$1/T_m - 1/T_m^\circ = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi v_1^2) \quad (1)$$

where T_m° is the melting point of the pure polymer, T_m is the depressed melting temperature, R is the gas constant, ΔH_u is the heat of fusion per "mole" of repeating polymer 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 χ is the Flory-Huggins interaction parameter.

The theory requires the parameter χ to have definite physical significance. It has been shown both theoretically^{26,34,35} and experimentally⁴ that a χ value of about 0.55 is the dividing line between poor solvents and nonsolvents. The region of poor solvency extends from about 0.31 to 0.55. Values of χ less than about 0.30 indicate good solvents. In general, the smaller the χ , the stronger the polymer-diluent interaction and consequently the better the solvent. By definition, χ is equal to BV_1/RT , where V_1 is the molar volume of the solvent and B represents the standard-state free energy of mixing per unit volume.^{26,35} According to the theory, the value of B could also be used as a measure of the extent of polymer-diluent interaction. Positive values for the free energy of mixing parameter B would indicate a poor solvent, while negative values would indicate preferred polymer-diluent interaction resulting in good solvent action. Actually, values of B calculated from eq. (1) may not represent solely the heat of mixing, for it is possible that they include entropy contributions.⁶ Studies on dilute polymer solutions suggest that this discrepancy probably does not exceed about 1 cal./cc. This would mean that the B values obtained exceed the true heat of mixing by as much as 1 cal. Thus, the dividing value between good and indifferent diluents is closer to one than zero. In any event, the empirical classification of solvents according to their B values remains valid.

Flory's treatment²⁶ has been successfully applied to the study of a number of polymer-diluent systems.^{6-8,10,14,22} In all cases the crystallinity of the polymer was such as to permit melting temperature determinations by the conventional methods of dilatometry, visual detection of the disappearance of last traces of crystallinity, and other such methods.

None of these methods has been successful in the detection of a first-order (melting) transition in polyvinyl chloride, in spite of the fact that in a number of instances crystallinity has been established by x-ray methods.^{27,28,41} Flory's treatment, therefore, has not been applied to polyvinyl chloride.

A method that proved quite successful in the study of polyvinyl chloride-diluent systems has been reported by Doty and Zable.⁴ It is based on the Flory-Rehner theory of swelling which relates the amount of swelling of a slightly crosslinked polymer in a liquid to the parameter χ .³⁶ Unlike the determination of χ from osmotic pressure data, this method is not an absolute method, and consequently there may be some question as to the abso-

lute accuracy of the χ values obtained. In addition, certain limitations inherent in this method may result in a probable error of ± 0.03 units. In spite of these uncertainties, Doty and Zable have demonstrated that χ obtained by this method is a satisfactory criterion for solvent quality and plasticizer compatibility.

RESULTS

Results from our microdetermination of the apparent melting temperature of polyvinyl chloride with twenty-seven diluents are shown in Table I. A range is reported rather than a single temperature. The magnitude of the range is indicative of the uncertainty in detecting t_m . A range of 2–4°C. is usual. Where the range is over 5°C., a highly diffuse gel-to-sol transformation was observed. This transformation was sharper with some diluents than with others. In general, diluents which were good solvents gave a somewhat diffuse transformation due to the simultaneous dissolution of the polymer particle. With poor solvents of high molecular weight, the resulting gel was quite hard and therefore resistant to sharp dimensional changes. Since the present method relies on sudden dimensional changes of the gelled particle, the resistance of hard gels to undergo these changes within a narrow temperature range results in diffuse transformation. Slower heating rates can remedy this situation.

In a few cases determination of t_m was extremely difficult due to the fact that differences in refractive index between swollen polymer and solvent were too small to allow detection of the boundaries of the swollen polymer particle. Highly volatile diluents also presented considerable difficulty. Excessive evaporation from the slide caused fogging and loss of diluent. Repeated additions of diluent interfered with the accurate determination of t_m . Attempts to observe the changes in a sealed system were quite successful. In these cases the polymer particles and the diluent were sealed in a flattened glass tube.

Table I lists the volume fractions v_1 of the diluents just prior to the apparent gel-to-sol transformation. As has been noted above, these values are only approximate because of the inherent limitations of the method. Some of the values listed are the average of three determinations. Average deviation was ± 0.03 . Pertinent to this work is the observation that v_1 in most cases is close to unity. This is especially true for low molecular weight diluents and for diluents with low χ values. This

observation will be used later to derive a simple expression correlating χ with t_m .

The effect of the molecular weight of the polymer on the apparent gel-to-sol transformation temperature was investigated by use of a number of experimental samples of polyvinyl chloride of varying molecular weights. Also investigated was the effect of small amounts (up to a few per cent) of comonomers, such as vinyl acetate. In general, the effect of molecular weight and comonomer content on the transformation temperature was small but significant, suggesting that comparisons of the apparent melting temperatures of polyvinyl chloride with different diluents be made on the same batch of polyvinyl chloride.

DISCUSSION

Apparent Melting Temperature of Pure Polyvinyl Chloride

According to Flory's theory as expressed in eq. (1), a plot of the reciprocal of the depressed melting temperature, $1/T_m$, against the expression $(v_1 - \chi v_1^2)/V_1$ should be linear for all polyvinyl chloride-diluent systems, provided the heat of fusion, ΔH_u , has a constant value independent of the type of diluent used.

This suggested the plot of Figure 6. The reciprocal of the apparent melting temperature, $1/t_m$, was plotted against $(v_1 - \chi v_1^2)/V_1$ for the twenty-seven polyvinyl chloride-diluent systems listed in Table I. The values for t_m and v_1 were determined by our microtechnique, and the values for χ were taken from the work of Doty and Zable.⁴ However, because of the known³⁴ temperature dependence of χ , the values used in this work were obtained by extrapolating to t_m the values of χ obtained at 53 and 76°C. by Doty and Zable (Table

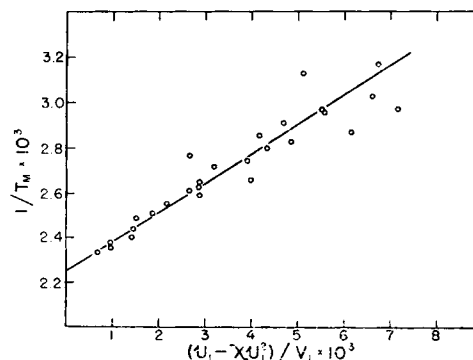


Fig. 6. A plot of $1/t_m$ against $(v_1 - \chi v_1^2)/V_1$ for the polyvinyl chloride-diluent systems listed in Table I.

TABLE II
Apparent Heats of Fusion, Interaction Parameters χ , and Energies of Interaction of Polyvinyl Chloride-Diluent Systems

Diluent	Apparent heat of fusion ΔH_u , cal./mole	Parameter χ , calculated from eq. (3)	Energy of interaction B , cal./cc.
Nitrobenzene	639	0.29	1.79
Mesityl oxide	515	0.29	1.72
Ethylene dichloride	735	0.51	4.10
Methyl <i>n</i> -amyl ketone	656	0.20	0.94
γ -Valerolactone	856	0.48	3.40
Tri- <i>n</i> -butyl phosphate	681	-0.53	-1.26
Triethyl phosphate	606	0.10	0.38
Nitropropane	870	0.56	4.19
1-Bromonaphthalene	597	0.33	1.60
Chlorobenzene	713	0.52	3.35
Anisole	676	0.51	3.11
<i>n</i> -Butyl acetate	682	0.44	2.17
Di- <i>n</i> -butyl phthalate	582	-0.05	-0.13
Ethyl acetoacetate	810	0.56	3.03
Diethyl phthalate	611	0.34	1.19
Dimethyl sebacate	542	0.24	0.72
Di- <i>n</i> -hexyl phthalate	629	-0.04	-0.09
Diethyl sebacate	608	0.16	0.41
Dimethyl phthalate	707	0.52	2.28
Dioctyl phthalate	598	-0.03	-0.06
Dihexyl adipate	592	0.23	0.50
Dibutyl Cellosolve phthalate	522	0.24	0.49
Dibenzyl sebacate	654	0.42	0.91
Di- <i>n</i> -octyl succinate	739	0.46	0.93
Methyl acetyl ricinoleate	590	0.47	0.85
Dioctyl sebacate	709	0.53	0.89
Butyl acetyl ricinoleate	674	0.66	1.20

II). Extrapolations were based on the assumption of a linear relationship between χ and the reciprocal of the melting temperature.³⁴ This assumption, of course, is not quite valid. However, the anticipated deviation from linearity should be small, considering that in most cases t_m is relatively close to the temperatures at which Doty and Zable determine their χ 's. Moreover, many diluents listed in Table I have χ values in the range of 0.2 to 0.4 where χ has been shown to be relatively insensitive to changes in temperature.⁴ The dependence of χ on polymer concentration was not taken into account because of the nonlinear dependence of χ on concentration.^{34,37,38}

The resulting plot was linear to a high degree. This is remarkable when we consider the approximations made in deriving eq. (1), the limitation of the method for determining t_m and v_1 , and the uncertainties involved in obtaining χ . The scattering

observed at high $1/t_m$ values, where points pertaining to most of the low molecular weight diluents are found, could be attributed primarily to the inherent limitations of the method, which does not permit accurate determination of t_m with diluents of high volatility. In spite of this limitation, only five of the twenty-seven points in the plot of Figure 6 are responsible for this scattering. The best straight line through all the points intersect the temperature axis at 0.002246 or at $t_m = 172^\circ\text{C}$. If the five points mentioned above are ignored, the value of t_m is slightly increased to 174°C .

According to Flory's theory²⁵ and our experimental data, the extrapolated melting point of pure polyvinyl chloride should be 174°C . We have no means of knowing how close this figure is to the true melting temperature of polyvinyl chloride. No directly measured melting temperature for this polymer has been reported. Walter,¹⁵ however, has proposed an extrapolated value of 212°C ., based on the determination of the temperatures at which cylindrically shaped samples of polyvinyl chloride gels containing various amounts of polymer flow under their own weight. The difference of 38 degrees between the two proposed melting points is too great to be attributed to the well-known fact that polymers melt over a relatively broad temperature range. Therefore, our value for the melting temperature could not represent the lower limit and Walter's value the upper limit of this range.

On the basis of Flory's definition of the melting temperature of crystalline high polymers,²⁶ our value of 174°C . obtained by extrapolation may well be low by at least 10°C . Such a correction will place the melting of pure polyvinyl chloride at or near 185°C .—still some 25 degrees lower than the value proposed by Walter. On the other hand, Walter's value could be too high. In his study, the polyvinyl chloride gels were heated at a rate of $1^\circ\text{C}/\text{min}$. in an upright position until they began to flow. The value of 212°C . for the melting temperature of pure polymer was obtained by extrapolation from 70 to 100% polymer. In view of the polar nature of polyvinyl chloride, one would expect that at such high polymer concentrations the samples would offer viscous resistance to dimensional changes even after the crystallites have melted. This would result in abnormally high values for the melting temperatures. Moreover, the relatively fast rate of heating employed by Walter would also tend to give abnormally high values.

That excessive heating rates can give abnormally

high values for the temperature at which the gel-to-sol transformation occurs in polyvinyl chloride gels has been demonstrated in the present work. Under the conditions of our microtechnique, rates of 2°C./min. yielded an extrapolated melting temperature for pure polyvinyl chloride in excess of 200°C.

Attempts to verify our value of 174°C. for the extrapolated melting temperature of pure polyvinyl chloride by a procedure similar to that employed for the determination of the apparent melting temperature of polyvinyl chloride in diluents proved unsuccessful. The high viscosity of the polymer melt and its tendency to decompose were probably responsible. However, when polymer particles were heated in polyethylene wax, certain changes were noticed in the vicinity of 174°C. The polymer particles became translucent and began to flow slightly under the weight of the cover glass. When the temperature was raised to 215°C., no further changes were observed. The particles, of course, continue to flatten, but no other abrupt change took place. Similar behavior was observed when other nonpolar liquids were used. Moreover, under the condition of the present microtechnique, no distinct gel-to-sol transformation has been detected above 174°C.

Apparent Heat of Fusion of Polyvinyl Chloride

According to Flory's theory of melting point depression,²⁶ the heat of fusion of a crystalline polymer should have a constant value independent of the type of diluent used. Within the limits of experimental error, this has been found to be true in a number of investigations reported in the literature,^{6,7,10,14} while in some, great variations in the values for the heat of fusion were observed when the same polymer was used with different diluents.²² In the case of polyvinyl chloride no value for the heat of fusion has been reported.

Assuming once again that t_m represents a true melting temperature, we can now determine the heat of fusion of polyvinyl chloride for each of the diluents by using eq. (1) and the data of Table I. The linearity and low degree of scattering of the plot in Figure 6 indicate that the heat of fusion of polyvinyl chloride will be relatively independent of the diluent used. The actual values, calculated from eq. (1) for $t_m = 174^\circ\text{C}$. are listed in Table II. The average value for the heat of fusion of polyvinyl chloride, based on all diluents investigated, is 659 cal./mole of polymer units, with a standard deviation of 93. This corresponds to 10.5 cal./g. This value is low in comparison to the heats of

fusion reported for most polymers. However, it is not unprecedented. Polychlorotrifluoroethylene,⁸ a polymer structurally similar to polyvinyl chloride, has a reported value of 10.3 cal./g.

The corresponding average value for the entropy of fusion, $\Delta S_u = \Delta H_u/t_m^\circ$, is 1.47 ± 0.21 cal./°C./mole of structural units or 0.74 ± 0.1 cal./°C./bond, assuming two bonds per repeating unit about which rotation may occur. The entropies of fusion for most polymers reported are in the range from 1.25 to 2.0 cal./°C./bond.³⁹ The lower entropy of fusion obtained for polyvinyl chloride may be due to a number of factors: to the small size or imperfection of the crystallites, to the persistence of order after melting due to strong association forces, or to the low flexibility of the polymer chains.

Determination of the Parameter χ

What we have shown so far is that a linear relationship exists between our apparent melting temperatures and the χ values, as determined by Doty and Zable, for all of the twenty-seven polyvinyl chloride-diluent systems investigated. This relationship holds true regardless of whether the values for t_m° and ΔH_u obtained by our method represent the true melting temperature and the average heat of fusion of polyvinyl chloride. On the assumption that this relationship holds true for all polyvinyl chloride-diluent systems, a new method can now be developed for determining the parameter χ .

By introducing our extrapolated melting temperature of pure polyvinyl chloride and the average value for the heat of fusion, eq. (1) is reduced to

$$1/t_m = 0.002236 + 0.1345 (v_1 - \chi v_1^2)/V_1 \quad (2)$$

where V_1 , the molar volume of the diluent, can be readily calculated from the molecular weight and the density of each diluent. On the basis of this equation, a single microdetermination of t_m and of v_1 should yield the χ value for the diluent.

A further simplification of the procedure for determining χ is possible through the observation that under the conditions of our microtechnique the volume fraction of the diluent v_1 at the apparent melting temperature approaches unity. By equating v_1 to unity, eq. (1) assumes the simplified form

$$1/T_m - 1/T_m^\circ = (R/\Delta H_u)(V_u/V_1)(1 - \chi) \quad (3)$$

At first the approximation $v_1 = 1$ does not seem permissible because the theory on which eq. (1) is based is considered to be in error at very low polymer concentrations.²⁶ However, although eq. (3) is based on the assumption of infinite dilution, the

actual data to which eq. (3) is applied were obtained at permissible concentrations. It is reasonable to assume that Flory's theory holds as long as the gel structure in the polymer-diluent system persists.

To test the validity of eq. (3), the reciprocal of the depressed melting temperature, $1/t_m$, was plotted against the now simplified expression $(1 - \chi)/V_1$ for the same twenty-seven diluents used in the plot of Figure 6. The new plot is shown in Figure 7. Visual comparison of the two plots shows very little difference. Actually, statistical correlation shows that eq. (3) gives a better correlation between our data and those of Doty and Zable⁴

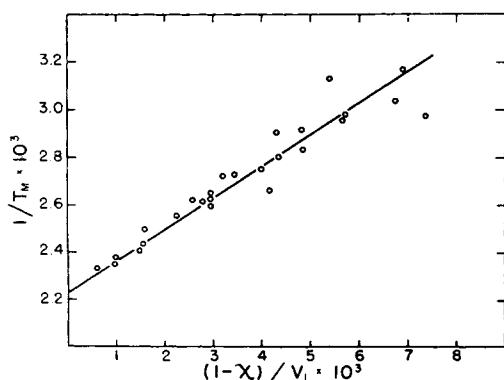


Fig. 7. A plot of $1/t_m$ against $(1 - \chi)/V_1$ for the polyvinyl chloride-diluent systems listed in Table I.

than does eq. (1). This indicates that the approximation $v_1 = 1$ describes the polymer-diluent composition at the melting temperature better than does the approximate value for the volume fraction of the diluent as determined by our microtechnique. This approximation, of course, compresses the values of χ to an upper limit of unity and thus distorts the higher values of χ . It does not, however, lessen the value of the parameter χ thus obtained as a relative measurement of polymer-diluent interaction.

The extrapolated value for the melting temperature of pure polyvinyl chloride based on the simplified eq. (3) is 176°C.; this value is not significantly different from 174°C. found with eq. (1). Similarly, the corresponding values for the average heat of fusion calculated from the two equations differ by less than 1%—656 cal./mole as compared to 659 cal./mole obtained by eq. (1). Insertion of the new value for t_m and the new average value for ΔH_u in the simplified eq. (3) gives

$$1/t_m = 0.002226 + 0.1351 (1 - \chi)/V_1 \quad (4)$$

This relationship between t_m and χ permits the determination of χ for a diluent from a single determination of t_m by the microtechnique described in this work. The molar volume of the diluent can be readily determined from density measurements at t_m .

Table II lists the values of χ calculated by eq. (4) and our values for t_m and V_1 . Comparison of these values with the corresponding values for χ obtained by Doty and Zable⁴ shows the two sets of χ values to differ by ± 0.06 units on the average. Considering the approximations made in deriving eq. (4) and the accuracy of determining t_m , the agreement is quite remarkable and justifies the use of eq. (4) in determining χ values for polyvinyl chloride-diluent systems.

Determination of the Parameter B

In addition to determining χ , the present microtechnique can be used to obtain the energy of interaction parameter B . Table II lists the values of B calculated from the χ values obtained by the simplified eq. (4). According to theory, the value of B can be used as a measure of polymer-diluent interaction. However, since heretofore B has not been determined for polyvinyl chloride-diluent systems, the utility of B as a measure of plasticizer compatibility has not been ascertained. In the present work a comparison was made of the B value for each diluent listed in Table II with its known compatibility as a polyvinyl chloride plasticizer. The results indicate that the parameter B is a reliable criterion of plasticizer compatibility. Diluents with B values greater than one were incompatible with polyvinyl chloride, while those with B less than one were compatible. Borderline compatibility was observed with plasticizers having B values in the range of 0.7 to 1.0.

A comparison of the χ and B values for each diluent in Table II demonstrates that, in general, diluents with a B value less than 0.5 have a corresponding χ value of less than 0.25. Diluents of borderline compatibility, with B values between 0.5 and 1.0, have χ values ranging from 0.25 to 0.55. These results are in accord with the theoretical classification of the quality of solvents for a given polymer according to the values of χ and B .

It is of interest to note, that as the molar volumes of the diluents increase, the χ to B ratio does not remain constant but increases also. For example, while dimethyl phthalate with a molar volume of 175 has $\chi = 0.52$ and $B = 2.28$, dioctyl sebacate with a molar volume of 504 has $\chi = 0.53$ and $B =$

0.89. On the basis of χ , both diluents should have approximately the same degree of compatibility with polyvinyl chloride. On the basis of B , however, their compatibility should differ greatly. In actual practice, dioctyl sebacate is compatible, while dimethyl phthalate is not. From this and other examples it appears that, as the size of the diluent molecule increases, so does the critical value of χ that separates compatible from incompatible plasticizers. This dependence of the critical value on the size of the diluent molecule is not so pronounced in the case of the parameter B . These observations suggest that the parameter B might be a better criterion of plasticizer compatibility than χ .

CONCLUSIONS

The results of this study indicate that a transition can be detected in soft polyvinyl chloride gels which could be attributed to the melting of the polymer crystallites. The temperature at which this transition occurs is characteristic for each polyvinyl chloride-diluent system and quite reproducible.

Flory's statistical thermodynamic treatment of the effect of diluents on the melting temperature of crystalline polymers has been applied to this transition with considerable success. As a result, a simple micromethod has been developed for the determination of the polymer-diluent interaction parameter χ and the energy of interaction parameter B for polyvinyl chloride-diluent systems.

In addition, a comparison was made of the χ and B values for each of twenty-seven diluents with their known compatibility as polyvinyl chloride plasticizers. The results indicate that the parameters χ and B are reliable criteria of plasticizer compatibility.

References

1. Gee, G., *Trans. Inst. Rubber Ind.*, **18**, 266 (1943).
2. Frith, E. M., *Trans. Faraday Soc.*, **41**, 17 (1945).
3. Frith, E. M., *ibid.*, **41**, 90 (1945).
4. Doty, P., and H. S. Zable, *J. Polymer Sci.*, **1**, 90 (1946).
5. Doty, P., and E. Mishuck, *J. Am. Chem. Soc.*, **69**, 1631 (1947).
6. Flory, P. J., L. Mandelkern, and H. K. Hall, *ibid.*, **73**, 2532 (1951).
7. Mandelkern, L., and P. J. Flory, *ibid.*, **73**, 3206 (1951).
8. Bueche, A. M., *ibid.*, **74**, 65 (1952).
9. Hall, H. T., *ibid.*, **74**, 68 (1952).
10. Mandelkern, L., R. R. Garrett, and P. J. Flory, *ibid.*, **74**, 3949 (1952).
11. Wurstlin, F., and H. Klein, *Kunststoffe*, **42**, 445 (1952).

12. Duke, N. G., and W. A. Mitchell, *India Rubber World*, **128**, 485 (1953).
13. Small, P. S., *J. Appl. Chem.*, **3**, 71 (1953).
14. Flory, P. J., R. R. Garrett, S. Newman, and L. Mandelkern, *J. Polymer Sci.*, **12**, 97 (1954).
15. Walter, A. T., *ibid.*, **13**, 207 (1954).
16. Schick, M. J., P. Doty, and B. H. Zimm, *J. Am. Chem. Soc.*, **72**, 530 (1950).
17. Wurstlin, F., and H. Klein, *Makromol. Chem.*, **16**, 1 (1955).
18. Fox, T. G., Jr., and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1915 (1951).
19. Fox, T. G., Jr., P. J. Flory, and A. M. Bueche, *ibid.*, **73**, 285 (1951).
20. Wurstlin, F., and H. Klein, *Kunststoffe*, **46**, 3 (1956).
21. Fox, T. G., Jr., and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1909 (1951).
22. Witnauer, L. P., and J. G. Fee, *J. Polymer Sci.*, **26**, 141 (1957).
23. Cotten, G. R., A. F. Sirianni, and I. E. Puddington, *ibid.*, **32**, 115 (1958).
24. Kawai, T., *ibid.*, **32**, 425 (1958).
25. Valentine, L., *ibid.*, **23**, 297 (1957).
26. Flory, P. J., *J. Chem. Phys.*, **17**, 223 (1949).
27. Stein, R. S., and A. V. Tobolsky, *Textile Research J.*, **18**, 302 (1948).
28. Alfrey, T., Jr., N. Wiederhorn, R. Stein, and A. Tobolsky, *J. Colloid Sci.*, **4**, 211 (1949).
29. Alfrey, T., Jr., N. Wiederhorn, R. Stein, and A. Tobolsky, *Ind. Eng. Chem.*, **41**, 701 (1949).
30. Natta, G., and P. Corradini, *J. Polymer Sci.*, **20**, 251 (1956).
31. Leaderman, H., *Ind. Eng. Chem.*, **35**, 374 (1943).
32. Aiken, W., T. Alfrey, Jr., A. Janssen, and H. Mark, *J. Polymer Sci.*, **2**, 198 (1947).
33. Dyson, A., *ibid.*, **7**, 147 (1951).
34. Huggins, M. L., *Ann. N. Y. Acad. of Science*, **44**, 431 (1943).
35. Flory, P. J., and W. R. Krigbaum, *Ann. Rev. Phys. Chem.*, **2**, 383 (1951).
36. Flory, P. J., and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 512 (1945).
37. Bawn, C. E. H., and M. A. Wajid, *Trans. Faraday Soc.*, **52**, 1658 (1956).
38. Bawn, C. E. H., and R. D. Patel, *ibid.*, **52**, 1664 (1956).
39. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 573.

Synopsis

The changes that are observed under magnification when a single polyvinyl chloride particle is immersed in a drop of diluent and slowly heated have been explained on the basis of a three-dimensional network system in which the polymer crystallites act as junction points for the network. The existence of a temperature at which a sharp gel-to-sol transformation is observed has been attributed to the melting of the polymer crystallites. The temperature at which this transformation occurs was found to be rate-independent, reproducible, and characteristic for each polyvinyl chloride-diluent system. At this apparent melting temperature, the volume fraction of the diluent in the swollen particle was shown to approach unity. These findings made it possible, for the first time, to apply to

polyvinyl chloride-diluent systems Flory's treatment of the effect of diluents on the crystal melting temperature of semicrystalline polymers. The apparent melting temperatures of polyvinyl chloride with 27 diluents were determined by the above method. The interaction parameter χ for each of the diluents used had been previously reported by Doty and Zable. A linear relationship was obtained when the reciprocal melting temperature was plotted against $(1 - \chi)/V_1$ for all of the above polyvinyl chloride-diluent systems (V_1 is the molar volume of the diluent at the melting temperature). From this plot the values for the extrapolated melting temperature of pure polyvinyl chloride and for the average heat of fusion were calculated and found to be 176°C. and 656 cal./mole, respectively. Based on these findings a micromethod has been developed which can be used to determine the parameter χ of a diluent with polyvinyl chloride from a single determination of this apparent melting temperature. This method also yields the value for the energy of interaction parameter B .

Résumé

Les changements que l'on observe par agrandissement lorsqu'une simple particule de chlorure de polyvinyle est immergée dans une goutte de diluant et chauffée lentement ont été expliqués sur la base d'un système réticulaire tridimensionnel dans lequel les cristallites de polymère forment les points de jonction du réseau. L'existence d'une température à laquelle on observe une transformation brusque d'un gel en sol a été attribuée à la fusion des cristallites de polymère. La température à laquelle a lieu cette transformation est indépendante de la vitesse, reproductible et caractéristique pour chaque système chlorure de polyvinyle-diluant. À cette température de fusion apparente, la fraction de volume du diluant dans la particule fondue est proche de l'unité. Ces découvertes rendent possible, pour la première fois, l'application, à des systèmes chlorure de polyvinyle-diluant, du traitement de Flory sur l'effet des diluants sur la température de fusion du cristal des polymères semi-cristallins. Les températures de fusion apparentes du chlorure de polyvinyle avec vingt-sept diluants ont été déterminées par la méthode ci-dessus. Le paramètre d'interaction χ pour chacun des diluants utilisés a été antérieurement publié par Doty et Zable. On a obtenu une relation linéaire en portant l'inverse de la température de fusion en fonction de $(1 - \chi)/V_1$ pour tous les systèmes chlorure de polyvinyle-diluant ci-dessus (V_1 est le volume molaire du diluant à la température de fusion). A partir de ce diagramme, on calcule les valeurs pour la température de fusion extrapolée du chlorure de polyvinyle pur et

pour la chaleur moyenne de fusion et on trouve 176°C. et 656 cal./mole respectivement. Sur la base de ces découvertes, on a développé une microméthode qui peut être utilisée pour déterminer le paramètre χ d'un diluant avec du chlorure de polyvinyle à partir d'une simple détermination de la température de fusion apparente. Cette méthode donne également la valeur de l'énergie d'interaction du paramètre B .

Zusammenfassung

Die Veränderungen, die bei der Beobachtung eines einzelnen Polyvinylchlorid-teilchens, das in einen Flüssigkeitstropfen getaucht und langsam erhitzt wurde, unter einer gewissen Vergrößerung festgestellt wurden, können auf Grundlage eines dreidimensionalen Netzwerksystems, in welchem die Polymerkristallite als Vernetzungspunkte wirken, verständlich gemacht werden. Das Bestehen einer Temperatur, bei welcher eine scharfe Gel-Solmwandlung beobachtet wird, kann dem Schmelzen der Polymerkristallite zugeschrieben werden. Die Temperatur, bei welcher diese Umwandlung auftritt, erwies sich als unabhängig von der Geschwindigkeit, als reproduzierbar und als charakteristisch für jedes Polyvinylchlorid-Flüssigkeitssystem. Es konnte gezeigt werden, dass sich bei dieser Schmelztemperatur der Volumsbruch der Flüssigkeit im gequollenen Teilchen eins nähert. Diese Befunde machten es zum ersten Mal möglich die Flory'sche Behandlung des Einflusses von Verdünnungsmitteln auf die Kristallschmelztemperatur semikristalliner Polymerer auf Polyvinylchlorid-Flüssigkeitssysteme anzuwenden. Die scheinbaren Schmelztemperaturen von Polyvinylchlorid wurden nach der angegebenen Methode mit siebenundzwanzig Flüssigkeiten bestimmt. Der Wechselwirkungsparameter χ wurde für jede der Flüssigkeiten schon früher von Doty und Zable mitgeteilt. Für alle angeführten Polyvinylchlorid-Flüssigkeitssysteme wurde beim Auftragen der reziproken Schmelztemperatur gegen $(1 - \chi)/V_1$ eine lineare Beziehung erhalten. (V_1 ist das Molvolumen der Flüssigkeit bei der Schmelztemperatur.) Aus diesem Diagramm wurden die Werte für die extrapolierte Schmelztemperatur von reinem Polyvinylchlorid und für die mittlere Schmelzwärme berechnet; sie betragen 176°C bzw. 656 cal/Mol. Auf der Grundlage dieser Befunde wurde eine Mikromethode zur Bestimmung des Parameters χ einer Flüssigkeit mit Polyvinylchlorid aus einer einzigen Bestimmung der scheinbaren Schmelztemperatur entwickelt. Diese Methode liefert auch den Wert für den Wechselwirkungsenergie-Parameter B .

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