

Compatibility of Plasticizers with Poly(Vinyl Chloride)

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Synopsis

The tendency of a plasticizer to resist exudation from poly(vinyl chloride) (PVC) under compressive stress, known technologically as "compatibility," is treated in terms of a network model, the plasticized composition being thought of as a rubber crosslinked by crystallites. Compatibility is increased by increased solvency (Flory-Huggins χ) and decreased by increasing plasticizer molar volume. A large crosslink density and/or insufficient melting of crosslinks during processing (thermal history) also decreases compatibility. All commercial primary plasticizers are believed to be infinitely miscible with amorphous PVC. Phase separation which occurs is syneresis and not related to any phase diagram. Swelling tests for compatibility and swelling measurements on dilute PVC gels are described. Some general principles relating to gel formation and association in polymer solutions are also discussed.

INTRODUCTION

It was desired to establish whether the exudation of plasticizer from poly(vinyl chloride) (PVC) which occurs under compressive stress or, in the case of very poor solvency, on aging is the result of a true phase separation. By the latter term is meant equilibrium coexistence, at some temperature, of a dilute and a concentrated phase. It was also desired to investigate the equilibrium swelling of PVC compositions¹ and dilute gels in excess plasticizer as a test of compatibility and as a means, in combination with stress-strain measurements, for estimating crosslink density, as in vulcanized rubbers.² This procedure also yields values of the Flory-Huggins interaction constant χ , chemical crosslinking as used in the past³ being unnecessary. It is known⁴⁻⁷ that PVC has some crystalline content. Furthermore, it is now generally accepted that PVC compositions are crosslinked through small crystallites.⁸⁻¹¹

It was shown by Alfrey and co-workers^{8,9} (1947-1949) that plasticized PVC acts like a sluggish three-dimensional network whose crosslinks in the vicinity of room temperature are very stable. These workers suggested that the crosslinks were small crystallites. This concept was supported and extended by Walter¹¹ (1954) who investigated the temperature dependence of the elastic modulus.

The concept that the crosslinks are crystallites was reinforced by the observation that PVC forms aggregates in dilute solutions in most solvents (observed by Hengstenberg in 1940 and Doty and co-workers¹² in 1947, but not reported in detail by Hengstenberg and Schuch until 1964¹³). These

aggregates were shown by Hengstenberg¹³ and Crugnola and Danusso¹⁴ (1968) to involve on the average 11–20 molecules of polymer each, and the latter workers showed that the amount of aggregates formed correlated with the crystallinity indices of bulk polymers prepared in different ways.

We have concluded, at least in the case of commercial primary plasticizers, that exudation is a case of syneresis, the expulsion of solvent by compressing a solvent-containing network or by forming an excessive number of crosslinks by continued crystallization on standing. Progressive crystallization was also shown¹¹ by the increase of elastic modulus of di-2-ethyl hexyl phthalate (DOP) compositions with time, without exudation in this case, since this plasticizer is an excellent solvent.

Some generalizations regarding gelation in polymer solutions have also been developed as a result of this work and literature data, particularly for nonhydrogen-bonding polymers. It appears that crystallinity, rather than dipole interaction, is responsible for gelation for these materials. Also, the concept of "binding" of plasticizer to polymer via dipole inter-

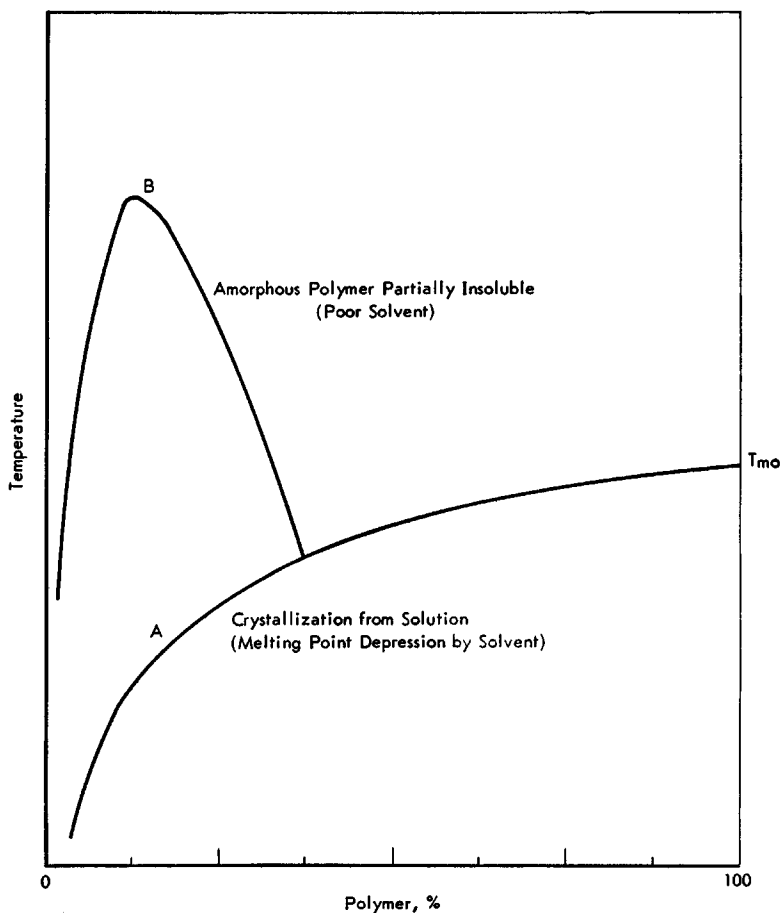


Fig. 1. Phase diagrams of crystalline polymers.

actions is believed to be incorrect, based on distribution of mixed solvents between solution and PVC gel phases.

EXUDATION AND PHASE SEPARATION IN PVC-LIQUID SYSTEMS

Figure 1 shows typical phase diagrams for semicrystalline polymers.¹⁵ Curve A represents phase separation of the material in the form of microcrystals over the whole range of concentration. Curve B represents phase separation from a poor solvent, where at temperatures above curve A an amorphous polymer precipitates out. On reaching the temperature given by curve A, this material then starts to crystallize. In this case, the phase diagram contains both these curves; where the amorphous polymer is infinitely miscible with solvent, only curve A is observed.

The temperature of first detectable turbidity on slow cooling (cloud point) was measured in two artificially poor solvents; 30% by weight decalin in 1-chloronaphthalene and 25% by volume Shell 371 oil in dibutyl sebacate

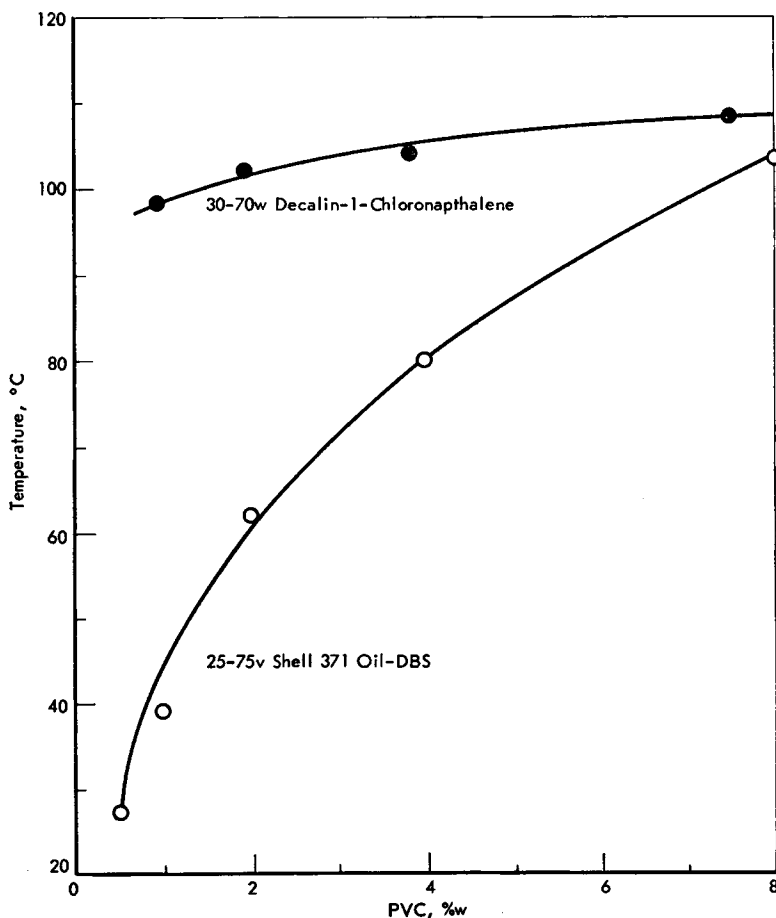


Fig. 2. Phase diagrams for poly(vinyl chloride).

(DBS). Results are shown in Figure 2. These phase diagrams (for Geon 101F-4 PVC) are typical of those for polymer crystallizing from solution. In fact, formation of PVC single crystals is claimed in the literature from very dilute solutions.¹⁶ However, in these solvents, above about 8% by weight PVC, the solution sets to a clear gel before any turbidity develops, and the subsequent development of turbidity is slow, nonreproducible, and absent at even higher concentrations of polymer, although the clear gels exude solvent copiously. In contrast, materials such as polyethylene and polypropylene always turn turbid at high polymer concentrations, solvent also being exuded.

The phase diagram B (Fig. 1) also exists in PVC solutions. In 30% by volume mixtures of Shell 371 oil in DBS, a viscous concentrated phase separated at high temperatures at 5% by weight PVC, and the dilute phase clouded at 120°C on further cooling. Thus, we have a superposition of phase separation given in Figure 1 by A and B. The high temperature phase separation¹ which occurs in sufficiently poor solvents is that of amorphous PVC. In 20% by volume mixtures of Shell 371 oil in DBS, no separation of any kind occurred even at room temperature.

It was next desired to determine the nature of the phase separation in a commercial plasticizer of borderline compatibility. Ditridecyl phthalate (DTDP) was selected for this purpose since it exudes in a bent loop test.¹⁷ Solutions of 1% and 2% by weight PVC in this material were transparent and homogeneous at room temperature. The 1% solution remained fluid indefinitely; the 2% solution set rapidly to a clear gel, with no exudation of liquid. A 10% solution set rapidly to a very slightly turbid gel which was dry and leathery to the touch; it exuded no liquid on standing six months. (This poly(vinyl chloride) contained a very slight residual turbidity which according to Kratochvil and co-workers¹⁸ is probably highly syndiotactic material.) On cooling the 1% solution to -70°C, it became glassy with no sign of turbidity. The 2% solution on very rapid cooling to -70°C from the still liquid state became turbid somewhere around -30°C. This temperature could only be estimated. The material also became glassy. Thus, even for a borderline plasticizer, the true phase separation (crystallization) curve lies well below room temperature in this concentration range; by analogy with the chloronaphthalene and DBS mixtures, at high polymer concentrations no macroscopic phase separation would be expected, merely exudation, if any. We tentatively conclude, therefore, that most, if not all, commercial primary plasticizers are *infinitely miscible with amorphous PVC*, at use temperatures.

It is also concluded that only in relatively dilute solutions is there sufficient mobility for small crystallites to form and separate. In more concentrated solutions, the material becomes crosslinked before phase separation can occur; in effect, a dispersion of crystallites is "solubilized" by the atactic chain sequences, in contrast to the Ziegler polyethylene situation where all of the molecule is crystallizable. In the more dilute region, the situation is analogous to the covalent gelation of a multifunctional polymer,

where at sufficiently low concentrations a macroscopic gel will not form, only crosslinked aggregates.

SWELLING OF POLY(VINYL CHLORIDE) COMPOSITIONS IN EXCESS PLASTICIZER

This work was undertaken for two reasons: (1) to determine whether concentrated PVC compositions were mechanical mixtures in equilibrium with free plasticizer in microdroplet form; in this case such materials would not swell in excess plasticizer; (2) as a measure of compatibility; the greater the swelling under standard conditions, the greater the compatibility of the plasticizer. Later in this report, a quantitative theory of swelling and exudation under mechanical constraint will be developed.

It was found that PVC specimens reached an equilibrium degree of swelling (at room temperature) and did not dissolve; after this work was done, a previous paper¹ was found on similar measurements on many plasticizers, with essentially the same conclusions. Swelling was measured on slush-molded films 0.001 in. to 0.004 in. thick, by observing a characteristic dimension in the Nikon Shadowgraph.¹⁹ The cube of this dimension, assuming isotropy, is proportional to specimen volume. Films were colorless between crossed polaroids. Data on a number of plasticizers are shown in Table I.

Thus, plasticizer is always initially present at less than unit activity, since the film takes up more plasticizer. However, a very interesting situation is present here. After swelling, the plasticizer in the film must be at unit activity at some concentration greater than its initial one. If a film is pressed directly from a slurry of this altered concentration, we then have two specimens of identical composition, in one of which the plasticizer is at unit activity, in the other of which it is at less than unit activity. Then, even such films swollen in very "compatible" plasticizers will exude under compressive stress and appear to be "incompatible." This, of course, is

TABLE I
Effect of Plasticizer Type on Swelling of 101F-4 PVC^a
2 phr Thermolite 35 Stabilizer, Pressed at 200°C

Plasticizer	V_f/V_i	V_f/V_i at 60% PVC	Aging time
	(final/initial volume) at 50% PVC		
Neodol 45 phthalate ^b	1.07		24 hr
Hercoflex 600	1.07	1.10	16 days
Di-tridecyl phthalate	1.48	1.45	36 hr
Tri-2-ethyl hexyl trimellitate	1.68	1.66	14 days
Dibutyl sebacate	2.25	—	1 hr
Di-2-ethyl hexyl phthalate	2.47	2.57	21 hr

^a Swelling at 23°C except for Neodol, 52°C (solid at 23°C). Aging time refers to time elapsed between pressing of film and start of swelling.

^b Registered trademark, Shell Chemical Company.

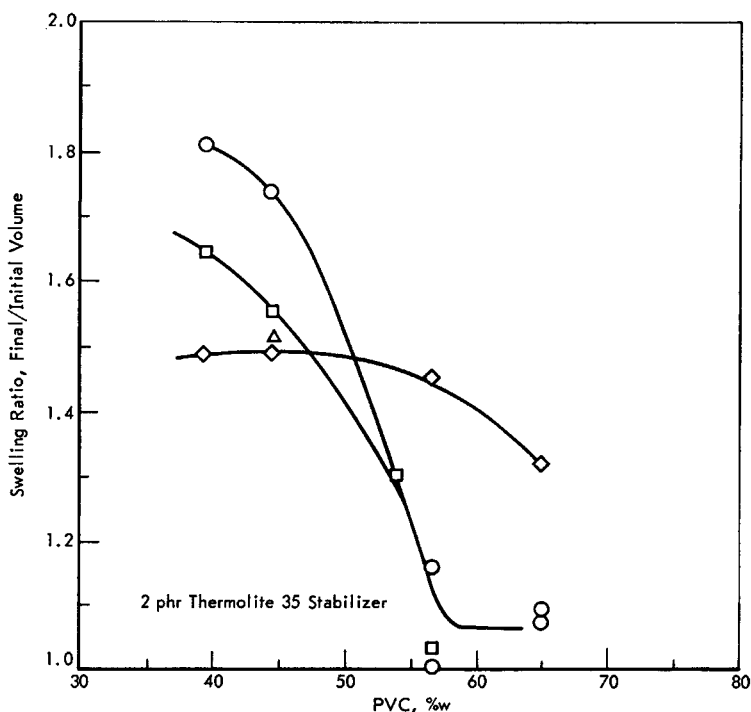


Fig. 3. Slush molding of PVC-di-tridecyl phthalate compositions: (O) pressed at 160°C, 10 minutes; 1 hour aging 23°C: (□) pressed at 180°C, 3 minutes; 1 hour aging: (◇) pressed at 200°C, 30 seconds, 36 hours aging: (△) pressed at 160° or 180°, 8 days aging.

the difference between saturating an existing network and forming a network at this concentration in the relaxed state (equilibrium extension of polymer molecules).

This fact has application to the processing temperature of PVC-plasticizer compositions. If most crystallites are not melted out during processing, the plasticizer swells an existing network, and the resulting material should exude readily or swell less. Poorer solvents should require higher processing temperatures, a fact which has sometimes been neglected in the past, as has been recently pointed out.²⁰ This idea led to experiments on slush-molding slurries of PVC in DTDP at various temperatures. Results are shown in Figure 3. As expected, pressing temperatures of 160° and 180°C led to compositions which swelled little or not at all at high PVC contents. The upturn in swelling at the lower PVC concentrations is believed to be caused by (1) melting out of the more imperfect crystallites at the higher solvent content because of melting point depression, (2) higher swelling of freshly pressed film (modulus increased rapidly immediately after molding),¹¹ and (3) experimental irreproducibility. Note that after eight days' aging, the 160° and 180°C compositions approached the 200°C compositions at 45% polymer in swelling. The 200°C compositions might have swelled more at the lower polymer concentrations had their pressing time been longer, but dehydrochlorination at this temperature occurs at a significant rate.

TABLE II
Effect of Specimen Aging (Pressed at 200°C) on Swelling

Initial PVC, wt-%	V/V ₀	
	Swelling after 36 hr	Swelling after 32.5 days
	Di-Tridecyl Phthalate	
44.6	1.49	1.25
49.5	1.48	1.20
56.7	1.45	1.22
	Tri-2-Ethyl Hexyl Trimellitate	
	14 days	34 days
50.0	1.67	1.61
55.0	1.67	1.64
60.0	1.66	1.64
	Hercoflex 600	
	6 hr	62 days
35.0	1.20	1.00
	DOP	
	21 hr	84 days
60.0	2.57	2.47

The effect on swelling of aging time after film pressing is shown in Table II. A figure of 1.00 means, of course, no swelling. Good solvent plasticizers give compositions which show less effect of aging, since the rate of crystallization should be lowered because of greater melting point depression. Specimens were always cut from the same film sample. However, the melting point depression for plasticizers of large molar volume is small. This quantity, as well as the Flory-Huggins χ , which is a measure of free energy of dilution, also affects compatibility via the effective crosslink density of the material and also, as will be seen later, directly in its resistance to exudation. For the melting point depression of a crystalline polymer¹⁵ by a solvent, we have (where T_m and T_{m0} do not differ too much)

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} \left[v_1 - \chi v_1^2 - \frac{\ln(1-v_1)}{x} \right], \quad (1)$$

where T_{m0} = melting point of pure polymer, in °K; T_m = melting point at volume fraction v_1 of solvent; V_u = molar volume of repeating unit; V_1 = molar volume of solvent; ΔH_u = heat of fusion per repeating unit; and x = number of repeating units in polymer molecule. For PVC, $\Delta H_u = 2.7$ kcal/monomer.²¹ Thus, a PVC crystallite melting at 212°C in the absence of diluent will melt at 194°C if $V_1 = 400$, $\chi = 0$, and $x = 1000$, at $v_2 = 1 - v_1$ of only 10^{-10} . The stability of PVC gels at moderate temperatures is thus easily understood. Of course, many crystallites have melting points well below 212°C; a distribution in T_m must exist. Also, in order to melt a gel, only enough linkages must be broken to satisfy the gel point²² criterion. The resulting solution is still very highly associated. Equation (1)

represents curve A of Figure 2 near T_{m0} for highly crystalline materials. This is not an accessible region in the case of PVC because of the long annealing necessary to develop enough crystallinity to observe T_m .¹⁵

In this connection, it is interesting that a 4% solution of PVC in methyl ethyl ketone, whose viscosity increased slowly on standing at room temperature, gelled on cooling to -70°C and did not melt on rewarming to room temperature on standing over a year, even in contact with excess solvent or with the original solution. During this time, a glass bead sank 5 mm into the gel.

SWELLING OF DILUTE PVC GELS

At high PVC contents, the 10-sec modulus of elasticity of plasticized materials (always assumed above T_g in this discussion) has a large enthalpic component.¹¹ However, in gels up to about 20% by weight, the modulus is proportional to T , and little delayed elasticity is present.¹¹ This prompted a study of swelling and elastic behavior of dilute PVC gels, from which, if ideal rubber elasticity theory is obeyed, the values of χ and the number ν of elasticity active chains per milliliter can be obtained. Gels were aged 30 days or more before measurement.¹¹ The effect of molecular structure on χ was of particular interest (χ can, of course, also be concentration dependent). Gels were prepared according to Walter's¹¹ method. Stress-strain curves were measured using a modified balance, as previously described.¹¹ A micrometer screw compressed the cylindrical specimen in an upward direction between Teflon surfaces, and the force was measured by the weight required to maintain balance. The distance between the Teflon faces at balance at zero micrometer reading was known. The initial length of the sample at zero force was obtained from this, and the micrometer reading was extrapolated, by the polynomial of best fit, to zero force. Affine deformation was assured by lubricating the Teflon surfaces with a small amount of silicone oil. The relation

$$\tau = RT\nu'[\lambda - (1/\lambda^2)] \quad (2)$$

was closely obeyed, where τ = stress based on original cross section, and λ = compression ratio l/l_0 , referred to initial specimen dimensions. For unconstrained equilibrium swelling of such gels, subject to limitations described below,

$$0 = \ln(1 - v_f) + v_f + \chi v_f^2 + V_1\nu' \left(\left(\frac{v_f}{v_0} \right)^{1/2} - \frac{2}{f} \frac{v_f}{v_0\lambda_0^2} \right) \quad (3)$$

where χ is the interaction constant; v_f is the volume fraction of polymer at swelling equilibrium; v_0 is the volume fraction of network (excluding soluble polymer, which is considered as a diluent) before swelling in excess solvent; f is the functionality of crosslinks; λ_0 is a parameter which expresses the departure of end-to-end chain vectors from their equilibrium (relaxed) value; ν' is an *apparent* crosslink density; and V_1 is the solvent molar volume.

Equations (2) and (3) are written in this form since ν' is directly obtainable from stress-strain measurements, using eq. (2). In fact,

$$\nu' = \nu\lambda_0^2v_0 \quad (4)$$

where ν is the number of active chains based on 1 ml of neat PVC, or alternatively

$$\nu' = \nu^*/\lambda_0 \quad (5)$$

where ν^* is the number of active chains in 1 ml of *relaxed* state, including solvent. (For example, if a cube of plasticized material containing 1 ml solid PVC network, neat polymer, has dimensions l in the *relaxed* state, it will have dimension $l\lambda_0$ in the real *initial* state, prior to swelling. These definitions involve changes in plasticizer content.)

In order to calculate χ from eq. (3), we must assume values for f and λ_0 . These are taken to be 4 (because of experience with block polymers)²³ and 1, respectively. Hence, we now denote χ by χ_{app} . However, the term in which these quantities appear has relatively little influence on the results. In order to obtain more information about the quantity $f\lambda_0^2$, swelling pressure measurements²⁴ on these gels would be required, which would also yield the concentration dependence of χ , if any.

It was found that some of the solids initially present in the gel phase were extracted on swelling. This effect could be reduced in the future by pre-extracting the PVC with ethyl acetate.²⁵ Correction was made for the amount extracted, where possible. Data are presented in Table III. For solvents of low viscosity, cylindrical sections about 1.6 cm in diameter and 1 cm long will come to equilibrium swelling in about a week. In viscous plasticizers, equilibrium may take months. It is imperative to use samples as thin as possible. A gravimetric method is used, where possible, because of the difficulty of cutting thin sections of well-defined diameter from these dilute gels. Laser cutting may be possible. Thin sections of gel cut with a hot wire (rapid equilibrium) yielded the same values for ν' as thicker uncut pieces (8 months swelling).

There is also some suspicion that very dilute, and hence imperfect, networks swell less than they should with respect to the more concentrated networks (*o*-dichlorobenzene at 0.05 volume fraction). The viscosity-average molecular weight of the PVC used, according to the relation²⁵

$$[\eta] = 1.50 \times 10^{-4} M^{0.77} \quad (6)$$

in THF, is only 81,000. Note that the apparent molecular weights between crosslinks based on dry polymer (M_c) are frequently of this order of magnitude or bigger (Table III), which means that $M_c \geq M_n$, an improbable situation where crosslinks are tetrafunctional. This must mean that some linkages of effective functionality of only 2 are present, certainly containing more than two chains, but with all but two dangling free. If $\lambda_0 < 1$, this also raises the apparent M_c . Hengstenberg¹³ found, in dilute MEK solution, that the smallest associated aggregates contained eleven chains, and since the material was not a gel, the ends must have been free.

TABLE III
 Swelling of Dilute PVC Gels

Solvent	PVC initial volume fraction	Volume swelling ratio	Active chains, ^a moles/ml	Mol wt between crosslinks	PVC extracted, %	χ_{app}	χ^e
<i>o</i> -Dichlorobenzene	0.0551	1.45	5.99×10^{-7}	130,000	8.6	0.477	
<i>o</i> -Dichlorobenzene	0.0835	1.63	1.61×10^{-6}	73,600	18.9	0.454	
<i>o</i> -Dichlorobenzene	0.109	1.56	4.30×10^{-6}	35,800	11.3	0.456	
<i>m</i> -Dichlorobenzene ^b	0.0982	0.756	4.95×10^{-5}	21,200	Not meas.	0.533	
Monochlorobenzene	0.0784	1.18	1.90×10^{-6}	58,500	14.3	0.488	0.53
Di-2-ethyl hexyl sebacate	0.0691	1.08	2.33×10^{-6}	42,000	0 ^c	0.396	
Di-2-ethyl hexyl isophthalate	0.0727	1.23	2.34×10^{-6}	44,000	0 ^c	0.380	
Di-2-ethyl hexyl pythalate	0.0711	2.47	1.39×10^{-6}	72,500	0 ^d	0.149	0.01
Di-2-ethyl hexyl phthalate	0.1085	2.65	3.17×10^{-6}	48,600	0 ^d	0.113	0.01

^a Based on initial volume, v' .

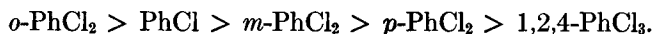
^b Synthesized spontaneously.

^c Plasticizer diluted with petroleum ether after swelling; no turbidity.

^d Plasticizer diluted with petroleum ether after swelling; turbidity, no precipitate.

^e Values of Doty and Zable,² 54°C; because of their use of an incorrect swelling relation, their χ values are in error by a maximum amount of -0.07 at $\chi = 0$ and -0.02 at $\chi = 0.5$. (Volume fraction of solvent unknown in their case.)

With respect to χ_{app} versus chemical constitution, note the great differences between the phthalate and isophthalate, which are only positional isomers. This is partly related to differences in dipole moment. Likewise except for H atoms, the sebacate is nearly isomeric with the other two. With respect to compatibility (swelling) alone, the chlorobenzenes rank in this order:



Comparisons had to be made at two temperatures to rank $p\text{-PhCl}_2$. Except for the last two members of the series, this is also in the order of the dipole moments; cohesive energy densities do not differ radically. However, V_1 is also a determining factor and the trichloro compound has $V_1 = 125$ cc, compared to 102–113 cc for the others, which is in the right direction, since a low V_1 means greater swelling.

It is possible in principle^{26–28} to correlate solubility-related properties, such as χ or solution or nonsolution under a standard condition, with three structure-dependent quantities: cohesive energy density,²⁹ dipole moment, and a hydrogen-bonding parameter obtainable from the infrared spectrum of CH_3OD in the solvent.²⁷ PVC itself would not be expected to have H-donating or H-accepting capability, but this effect enters when considering solvent-solvent interaction. In fact, surfaces have been obtained in the space of these three parameters, inside of which a given polymer dissolves at a standard temperature and concentration and outside of which it does not.²⁷ These parameters are in turn calculable from group contributions and hence can be estimated from a structural formula. In the next section, it will be shown that "compatibility" or resistance to exudation under stress depends only on a solubility parameter, χ , and the molar volume V_1 . This would be expected to be qualitatively true even under conditions where the Flory-Huggins free energy relationship and ideal rubber elasticity theory are not valid. Thus, there is a possibility of relating "compatibility," in terms of a standard swelling test, to V_1 and to the structural formula of the plasticizer. A set of surfaces of equal swelling would be obtained in 4-space or in the case of a "go-no-go" test, volumes inside of which the test is passed, outside of which it is not.

EXUDATION OF PLASTICIZER UNDER COMPRESSIVE STRESS

Following Treloar's treatment,³⁰ we find for a gel in equilibrium with solvent under a uniaxial deformation:

$$0 = \ln(1 - v_f) + v_f + \chi v_f^2 + V_1 v' \left(1/\lambda - \frac{2v_f}{fv_0\lambda_0^2} \right). \quad (7)$$

All symbols have been previously defined except for λ , which represents the deformation ratio l/l_0 in the direction of the applied stress with respect to actual initial specimen dimensions.

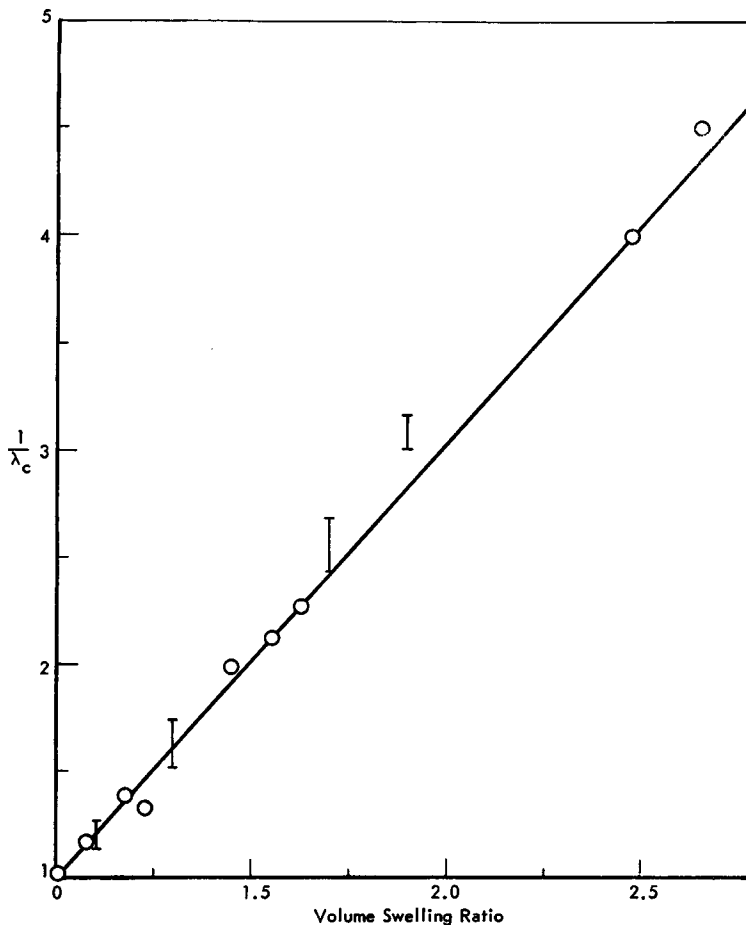


Fig. 4. Reciprocal of theoretical critical compressive deformation ratio vs. volume swelling ratio: See text for significance of vertical bars.

If we let $v_f = v_0$, there will be some value of $\lambda = \lambda_c < 1$ which satisfies eq. (7). At this point, if the compressive strain is increased by an infinitesimal amount (λ decreased), solvent will start to exude.

Using values of v_0 (corrected for solubles), ν' , and χ_{app} from Table III, these values of λ_c have been calculated for various solvents. Results are shown in Table IV and Figure 4. The relation between swelling, V_1 , χ , and compatibility, as measured by the compressive deformation required for incipient exudation, is clearly evident. Thus "compatibility" is actually a function of two variables, χ and V_1 .

However, the apparent functional relationship shown in Figure 4 must be accepted with caution. The value of λ_c is a function of χ , V_1 , and λ_0 , and so is the experimental volume swelling ratio, q ; but they are not the same functions. For example, by eliminating $\nu'V_1$ from eqs. (3) and (7), we find, where $v_f = v_0$ in eq. (7) and $q = v_0/v_f$ in eq. (3), the following:

$$1/\lambda_c = 1/(2\lambda_0^2) + \frac{[\ln(1 - v_0) + v_0 + \chi v_0^2][q^{-1/3} - (1/2q\lambda_0^2)]}{\ln[1 - (v_0/q)] + (v_0/q) + (\chi v_0^2/q^2)}. \quad (8)$$

Hence a set of samples having the same v_0 and the same swelling ratio, q , will exhibit different values of λ_c if the χ values differ. But at some constant value of q , all values of χ are not allowed, since this swelling may be unattainable at certain χ values because of a requirement for unrealistic values of V_1 and ν' . If we assume, for simplicity, that all liquid plasticizers will have $300 \leq V_1 \leq 600$ cc/mole, that χ will not be less than zero, and that ν' is inversely related to the depression of the melting point, eq. (1), then, picking one "reasonable" value of χ , the bars on Figure 4 are obtained ($\lambda_0 = 1$). In these calculations, v_0 was taken as 0.5. Thus, there will probably appear to be, technically, a one-to-one correspondence between swelling and the critical λ , should the latter be experimentally measured, although in fact "compatibility" as defined by λ_c and by q is not quite the same quantity. In practice, referring to the possibility of correlating these quantities with structural parameters,²⁶⁻²⁹ it would be desirable to establish a go-no-go criterion, perhaps presence or absence of exudation at a uniform compressive deformation ratio of 0.8, $1/\lambda = 1.25$. Tests should be carried out at a standard volume fraction of PVC, samples having a standard thermal history. Theory also predicts that values of $\lambda > 1$ lower the plasticizer activity (swelling under tension is increased), as can be seen by inspection of eq. (7).

It can be easily understood why plasticizer exudes only in a zone of compressive stress, e.g., in the inside of a bent loop, and never on the outside. Furthermore, disappearance of exudate from inside the bent loop on standing may result from its diffusion into the tensile zone of lowered activity on the outside of the loop. It would appear that a compatibility test in uniform compression would be preferable to the bent loop test.

These experiments are all performed on gels of low polymer concentration, which obey eq. (2), with the modulus proportional¹¹ to T . At higher polymer concentrations, Walter¹¹ reports that the modulus is no longer

TABLE IV
Calculated Critical Compression Ratios, λ_c , Final/Initial Length,
for Incipient Exudation of Solvent

Solvent	Volume swelling ratio	λ_c	χ_{app}	V_1	Order of compatibility
DOP	2.47	0.254	0.149	398	1
DOP	2.65	0.222	0.113	398	
<i>o</i> -Dichlorobenzene	1.63	0.441	0.454	113	2
<i>o</i> -Dichlorobenzene	1.56	0.472	0.456	113	
<i>o</i> -Dichlorobenzene	1.45	0.503	0.477	113	
Chlorobenzene	1.18	0.724	0.488	102	3
DO-isoP	1.23	0.755	0.380	399	4
DOS	1.08	0.908	0.396	436	5

proportional to T , and considerable amounts of delayed elastic response are present. For a composition of 40% by weight PVC, Walter's stress-strain data¹¹ in tension fit the well-known relation

$$\tau = C_1[\lambda - (1/\lambda_2)] + C_2[1 - (1/\lambda^3)] \quad (9)$$

within the experimental scatter of the points. It is doubtful whether these particular data truly represent an "equilibrium" or long-time compliance. Nevertheless, when this is the case, we may still write

$$C_1 = RT\nu' \quad (10)$$

where C_1 now should be proportional to T and C_2 may be some other function of temperature. This is true for dry or slightly swollen rubbers. Meissner and co-workers² and others have shown that ν' determined in this way gives proper values of χ in eq. (3). In this case it should be possible to predict the value of λ at which exudation occurs via eq. (7) and a measured swelling ratio for more concentrated compositions than studied here.

GELATION, COOPERATIVE, AND NONCOOPERATIVE BONDING IN POLYMERS AND POLARITY

This discussion is concerned with requirements for gelation.

By a cooperative interaction we mean a point of association between two or more molecules which requires the interaction of many monomer units at the same time; this may be a crystallite or a domain, as in thermoplastic elastomers.²³ Examples of noncooperative interactions are dipole-dipole association of two dipoles and hydrogen bonding. The essential distinguishing feature between these two types is that the number of noncooperative bonds is determined by an equilibrium relationship versus temperature and concentration involving the heat of interaction (ca. 7 kcal for hydrogen bonds). On the other hand, once a cooperative bond is formed, its lifetime is essentially infinite below some transition temperature T_m , in contrast to the very short lifetime of any one noncooperative bond. Expected properties of networks formed by these two means are shown in Table V. Examples of these different cases are presented below. PVC is type I in all properties.

Morawetz,³¹ by neutralizing a styrene-methacrylic acid copolymer, could raise the melt viscosity by many orders of magnitude, but stress relaxation and nonrecoverable flow still occurred. On the other hand, when short caprolactam chains were initiated at the acid sites (after prior amidation with ethylenediamine), the material exhibited no permanent deformation nor stress relaxation below the melting point of the nylon segments. Likewise, a mixture of copolymers containing acid and basic groups will gel, but these linkages dissociate on dilution.³² Carboxyl-terminated polymers also dissociate on dilution.³³ A gel made from $\text{Ni}(\text{OH})_2$ and carboxyl-terminated polybutadiene was rubbery, but would absorb unlimited quantities of toluene and eventually assumed the shape of the container.³⁴ Poly-

TABLE V
Properties of Gels Formed by Cooperative (Type I) Bonding
and Noncooperative (Type II) Bonding

Type I	Type II
Melts sharply at some temperature.	Melts sharply at some temperature.
Elastic modulus proportional to T in dilute systems; decreases with temperature only near melting point.	Elastic modulus always a rapid monotonically decreasing function of temperature, if gelation occurs on cooling.
Equilibrium swelling in excess solvent (except when domains are solvent sensitive). Stress will not relax to zero (after some initial relaxation due to retarded elasticity). Recoverable deformation.	Imbibes any amount excess solvent; dissolves. Stress relaxes to zero, although viscosity of system may be very high. Nonrecoverable deformation.
Not self-healing after cutting. Maintains shape.	Self-healing. Will assume shape of container if sufficient time allowed.
Frequently, x-ray powder diagram seen, unless amorphous domains present.	Amorphous.
Associated in solution; aggregation discontinuous (in PVC lowest aggregate is about a decamer). ¹³ Little if any shift in aggregate distribution, once formed, on changing solvent.	Associated in solution; continuous broad distribution of aggregates starting with dimer; rapid shifts in aggregate distribution on changing conditions.

(methacrylic acid) has a phase diagram³⁵ in which gel exists in one area; but, in contrast to PVC, when water (solvent) is added behavior is completely reversible and the gel liquefies isothermally. There are other examples in the literature.

TABLE VI
Gelation Characteristics of Various Polymers

Polymer	Polarity	Crystallinity	Gelation
PVC	+	+	+
PVC extract ^a	+	0?	0
Atactic polystyrene	0	0	0
Isotactic polystyrene	0	+	+
Atactic poly- <i>p</i> -chlorostyrene	+	0	0
Isotactic poly- <i>p</i> -chlorostyrene ³⁸	+	?	+
Atactic poly(methyl methacrylate)	+	0	0
Tactic methacrylates (mixed) ³⁹	+	+	+
Syndiotactic polypropylene ^b	0	+	+

^a Benzene extract.²⁵

^b Courtesy of J. Boor, Jr., of these laboratories.

With regard to polarity, relationships between presence of crystallinity, polarity, and gelation characteristics are shown in Table VI. It can be seen that gelation behavior in these cases (where hydrogen bonding is not a factor) seems to be determined by whether the material can crystallize, not by its polarity. Polyacrylonitrile^{36,37} may combine both type I and type II properties.

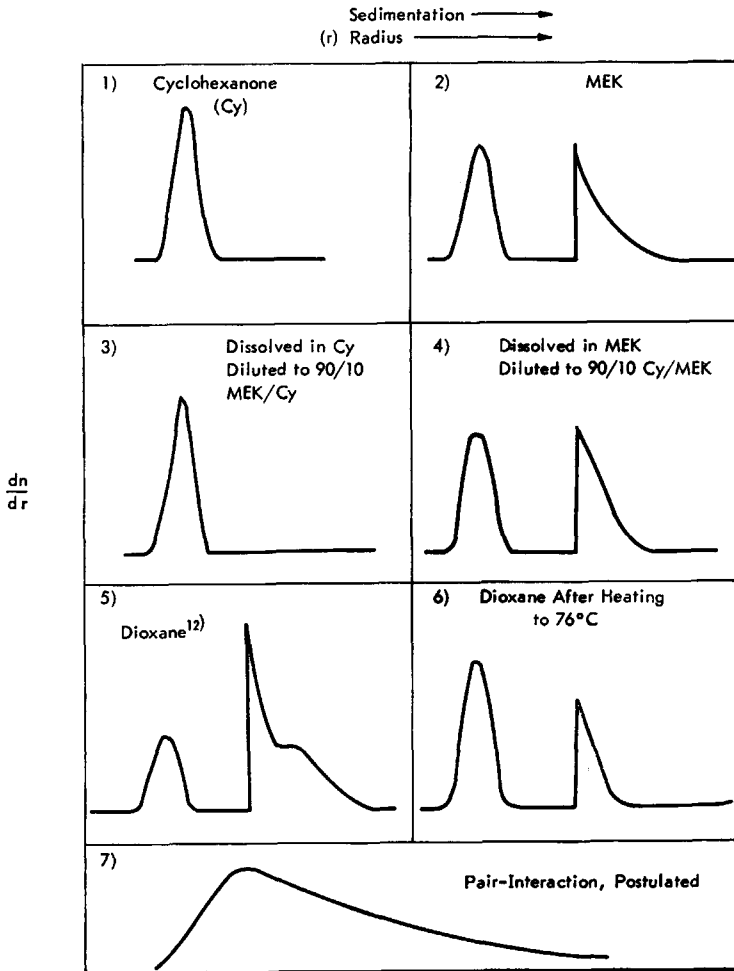


Fig. 5. Sedimentation patterns of dilute PVC solutions.

In the past, it has sometimes been assumed that plasticizers “bind” to PVC by dipole attraction. This notion is false. Propylene carbonate, with a dipole moment of 5 debyes, will solubilize PVC in toluene at 10% by weight carbonate. Neither component is a solvent for PVC. Distribution experiments on propylene carbonate inside and outside a PVC gel of initially 10% solids, at swelling equilibrium in this solvent, showed 11.6%

propylene carbonate in the liquid versus 8.3% in the gel (based on liquid content). Thus, toluene is actually slightly preferred, and no specific bonding is occurring. In fact, the cohesive energy density of toluene is considerably closer to that of PVC than is the CED of propylene carbonate.²⁹ Preference for toluene is predicted²⁷ by the solubility map for Vinylite VYHH.

CRYSTALLINITY AND ASSOCIATION IN SOLUTION

The ultracentrifuge^{12,13,14,25} is used to investigate association in dilute poly(vinyl chloride) solutions since the associated material in methyl ethyl ketone (MEK) forms a separate peak with the characteristics shown in Figure 5-2. For our purposes, the diagrams of Figure 5 may be considered to be differential MWD curves, molecular weight increasing to the right. In cyclohexanone, the material is molecularly dispersed, Figure 5-1. Figures 5-1 to 5-4 are schematics from Hengstenberg and Schuch.¹³ A narrow fraction of PVC was used. The illustrated behavior is independent of concentration from 0-0.5 g/100 ml. It has also been shown that intensity of crystalline material infrared absorption of solid PVC samples correlates with the amount of associated component in solution.¹⁴

A new interpretation of the results of Figure 5 can be given in terms of crystallite size. Note the perfectly vertical cutoff of the second peak on the low molecular weight side. This can only be caused by the fact that this represents a minimally stable aggregate (size of crystallite). It was shown that this point corresponds to about 11 primary molecules.¹³ Furthermore, no aggregates of association number 2-10 are present; if this were the case, Figure 5-7 would result. It is not possible to form indefinitely large aggregates because of the stereochemical imperfection of PVC chains. If the maximum coordination number of a segment in a PVC lattice is Z and if there are n crystallizable segments per molecule (where n may be slightly greater than unity on the average), the situation is similar to the polycondensation of an nZ -functional polymer at low conversion and high dilution. The gel point (large crystal) is not necessarily reached unless enough crystallizable segments can line up with one another. The second bump in the dioxane case (Fig. 5-5) would argue the existence of two types of crystallite, one of which is more stable at lower aggregation number than the other. This is sometimes seen in MEK also.

Finally, the behavior shown in Figure 5-4 persisted¹³ for "months," the addition of cyclohexanone not dissolving out the previously formed crystallites. It is suspected that the situation of Figure 5-4 is probably indefinitely stable. Experiments of this type could be used to distinguish between type I and type II association, as shown in Figure 5-7.

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