Solubility Characteristics of Polyvinyl Chloride

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PART I. INTRODUCTION

Although poly(vinyl chloride) (PVC) is known to dissolve in a variety of liquids, there are some anomalies which need explanation. Using a microtechnique, Anagnostopoulos et al.[1] found elevated minimum solution temperatures for PVC in a number of liquids. Two of these, however, nitrobenzene and ethylene dichloride, have been used as solvents for determining intrinsic viscosities of PVC at room temperatures. Values for the interaction constant χ as determined by Doty and Zable[2] indicate that several of the liquids should be good solvents for PVC at room temperatures, having χ values below 0.5–0.6 as required by the Flory-Huggins theory.

Also, in an unpublished report Doty and Zimm[3] gave limiting concentrations for solutions of PVC, above which gelation took place at room temperature.   A selection of these results is included in Table I and compared with the observations of Anagnostopoulos et al.[1]

TABLE I

Solvent	χ, 20°C	α	β	Limiting conc. at $R.T.$[3]	Minimum solution temp[1]
Tributyl phosphate	−0.85	−1030	0.96	5%	64–65°
Dibutyl phthalate	−0.12	−260	0.44	3%	90–94°
Di(ethylhexyl) phthalate	−0.03	−170	0.22	2%	116–118°
Nitrobenzene	0.29	0	0.29	8%	41–43°
Ethylene dichloride	0.52	+130	0.06	2%	52–57°

In this table the χ values of Doty and Zable[2] reported at 63°C and 76°C have been extrapolated to 20°C by the formula

$$\chi = (\beta + \alpha)/R.T. \tag{1}$$

where $R.T.$ is room temperature.   Anagnostopoulos et al.[1] define χ by the equation $\chi = BV/R.T.$, ignoring the entropy contribution. This is surprising, as Doty and Zable point out that in the range 0.2 to 0.4 χ is almost independent of temperature; it is evident also that Anagnostopoulos et al., when converting χ values to different temperatures, applied eq. (1). The model for χ as expressed by eq. (1) was originally put forward by Hug-

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gins[15] and has since been confirmed on theoretical consideration by Guggen-
heim[16] and others.

It is possible of course that in certain cases β may be zero, but examina-
tion of the values for χ quoted by Doty and Zable[2] show that β is usually
positive and contributes substantially to the total.   This agrees with the
findings of Moore and Hutchinson[5] for χ values for PVC and a number of
solvents as determined by a different method.   Also with systems of
cellulose derivatives and numerous liquids, eq. (1) has been shown to apply
with positive values for β.   Exceptionally β appears to be negative in a few
cases where the χ values are around 1.75.   Reliance should not of course
be placed on the accuracy of values of β and α calculated from the data of
Doty and Zable for χ at only two temperatures, but it may be significant to
recall that Huggins[4] found negative values for β by analyzing the results of

TABLE II
Solution of PVC

Solvent	Temp, °C	Time to dissolve, days					
		Vinnol Y100/60	Breon 121	Breon 111EP	Bakelite VY19	Bake-lite VY11	Hostalit C70
Tributyl phosphate (4 g PVC: 100 ml)	ca15°	25	≩ 20	—	>20	≩ 20	—
	35°	2	16	—	—	—	>16
	45°	0.35	0.6	4	0.75	3	3.5
	55°	—	—	0.2	—	—	0.23
	65°	—	—	—	—	—	0.1
Dibutyl phthalate (1 g PVC: 100 ml)	65°	2	—	—	3	—	—
	75°	0.2	>10	10	0.2	—	—
	85°	—	—	3.5	—	—	—
	95°	—	0.6	1.0	—	—	—
	105°	—	—	0.05	—	—	—
Di(ethylhexyl) phthalate (1 g PVC: 100 ml)	85°	>19	—	—	—	—	—
	95°	1.1	—	—	—	—	—
	105°	0.4	—	—	—	—	—
	115°	—	2	3	—	—	—
	125°	—	0.1	0.15	—	—	—
Ethylene dichloride (1 g PVC: 100 ml)	35°	2.7	—	—	—	—	—
	45°	0.23	—	—	—	—	—
Nitrobenzene[a] (5 g PVC: 100 ml)	ca15°	4	10	8	—	—	—
	30°	—	2	2	—	—	—

> Mostly dissolved, some gels left.
≩ Gelled and partly dissolved.
[a] Nitrobenzene is anomalous in that solution takes place rapidly at first, but some gels
remain undispersed.   Times given are when appearance of solution does not change
appreciably on further standing.

Brönsted for critical solution temperatures of polystyrene in a series of alkyl laurates that were evidently also very poor solvents.

In regard to the anomalies as shown in Table I it was decided to see whether PVC would not dissolve at lower temperatures than those found by Anagnostopoulos et al.[1] For this purpose a number of samples of PVC available commercially were suspended in some of the liquids in question and left either at room temperature in the range 15–20°C or at a controlled
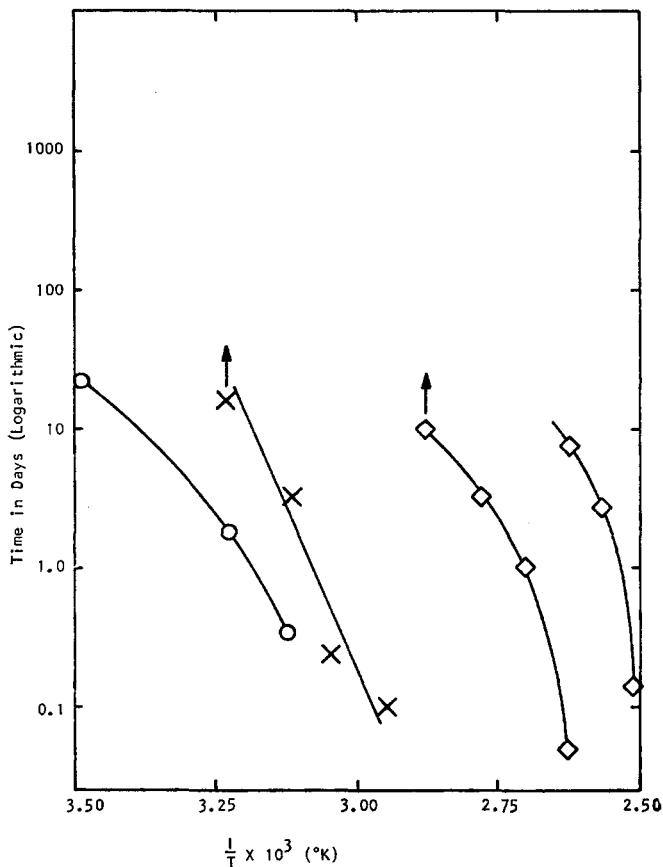

Fig. 1. Solution times of PVC: (O) Vinnol Y100/60; (X) Hostalit C70; (◇) Breon 111EP.

temperature and shaken at irregular intervals. Tributyl phosphate was chosen at first because of its exceptionally favorable R value. Results are shown in Table II, from which it will be seen that, given sufficient time, PVC will dissolve at considerably lower temperatures than those reported in ref. 1. The effect of temperature on the time for PVC to dissolve is however very great, and this is illustrated in Figure 1. Ref. 1 reported no difference in solution temperatures by changing the rate of heating, but it

will be seen from Table II and Figure 1 that to make any appreciable difference the time scale would have to be changed by a factor of at least 10.

Results in Table II are necessarily rather inexact, but the trend is quite clear. The three main types of PVC are represented and Vinnol Y100/60 (made by bulk polymerization) is the most easily soluble. Next is the emulsion polymer Breon 121. Suspension-type polymers, for example Hostalit C or Breon 111, are the most difficult to dissolve. Opalon 300 as used in ref. 1 is no longer available but is a very similar type to Breon 111. If the trend shown in Figure 1 can be relied on, Breon 111, for example, would require 200–300 days to dissolve in tributyl phosphate at room temperature.

Other suspension-type polymers behave similarly, except for Bakelite VY19, a low molecular weight polymer, which is close to Vinnol in its solubility characteristics.

In dibutyl phthalate a similar effect was observed although rates of solution are lower; and if the trend indicated by Table II and Figure 1 is maintained, it would take about three years to dissolve Vinnol to a 1% solution and about 15 years for Breon 111, at room temperature. Solution in di(ethylhexyl) phthalate is slower still, but the general tendency is similar. With these liquids the temperature at which solution is rapid, i.e., about 1 hr, agrees fairly well with the observations in ref. 1. A few results for solution in nitrobenzene and in ethylene dichloride are included in Table II.

These observations were made on samples of commercial PVC without any pretreatment. Extraction of the emulsion polymer with alcohol followed by drying at a low temperature removed soaps, but no difference in solubility characteristics was found; similarly with Hostalit C70, where however only a trace of material was removed by alcohol extraction. In the form of film cast from solution, there was a substantial difference. Films were cast by dissolving the polymer in a mixture of tetrahydrofurane and acetone and the film was air dried. At this stage it retains up to 10% of solvent which was difficult to remove entirely. In tributyl phosphate, film from all three types of polymer dissolved in less than one day at room temperature, compared with at least 25 days for the original powder. If the film is dried further at a temperature of 100° to constant weight, almost all the retained solvent is lost and the film is then much more difficult to dissolve, resembling the original powder. On the other hand, addition of 1% tetrahydrofurane to tributyl phosphate, which represents a far greater proportion than that retained in an air-dried film, was without apparent effect on the solvent power.

It was further observed that if PVC is first wetted with acetone, which is a nonsolvent at room temperature, it dissolves more readily in tributyl phosphate, in the case of Vinnol in three days instead of 25 days. Also, a film from Vinnol which had been thoroughly dried and which then took 25 days to dissolve was wetted with acetone after which it dissolved in less than a day.

The explanation suggested for these phenomena is that a liquid such as tributyl phosphate, although a good solvent for PVC thermodynamically, is a very poor solvent kinetically. Dissolution of a polymer such as PVC in a liquid takes place first of all by inhibition and swelling and the polymer may have to absorb many times its weight of liquid before it forms a gel sufficiently dilute to disperse in the remainder of the liquid. Rate of diffusion of the liquid into the polymer particle is the governing factor in the solution process. Diffusion constant is related exponentially to temperature, i.e.:

$$\log D = \frac{k}{T} + k_2. \tag{2}$$

This relationship has been confirmed in many experiments both for diffusion of gases and liquids, for example, toluene or amyl acetate in polystyrene by Asmussen & Überreiter.[6] Time for liquid to diffuse through a particle of radius r is given by the formula

$$t \alpha r^2/D \text{ or } \log t = 2 \log r - \log D + k_3. \tag{3}$$

Combining eqs. (2) and (3) gives

$$\log t = 2 \log r - \frac{k_2}{T} \tag{4}$$

so that for particles of a given size the logarithmic time to dissolve would be expected to be proportional to the reciprocal of absolute temperature.

Comparison of different liquids shows that molecular volume is an important factor, the largest molecule having the slowest diffusion rate. Small molecules such as acetone, even if nonsolvents, can penetrate PVC particles and assist the penetration of the larger solvent molecules. Instances of this effect have already been mentioned; but in another experiment, a mixture of dibutyl phthalate and acetone in the volume ratio 60:40 dissolved PVC (Vinnol) in two days at 45°C whereas dibutyl phthalate alone would take an estimated 40 days. Even with more active solvents there is a marked difference in rate of solution which can be explained by the effect of molecular volume. Thus cyclohexanone (mol vol 103) took 48 hours to dissolve 1% of PVC (Hostalit C70) at room temperature, whereas tetrahydrofurane (mol vol 81) took only seven hours. The respective interaction constants as determined by Moore and Hutchinson[5] are 0.18 and 0.21.

Differences in rates of solution of various types of PVC are probably due to crystallinity, tacticity, and particle size.

PART II. MELTING POINT AND HEAT FUSION OF PVC

The apparent solution temperatures recorded by Anagnostopoulos et al.[1] were used in conjunction with the thermodynamic equation of Flory for the effect of diluents on melting temperatures

$$\frac{1}{T} - \frac{1}{T^\circ} = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} (V_1 - \chi V_1^2) \qquad (5)$$

to estimate melting point (T°) and heat of fusion (ΔH_u), but as some of the values of T used were shown in part I not to represent an equilibrium state, the value of T° arrived at would be expected to be subject to error.
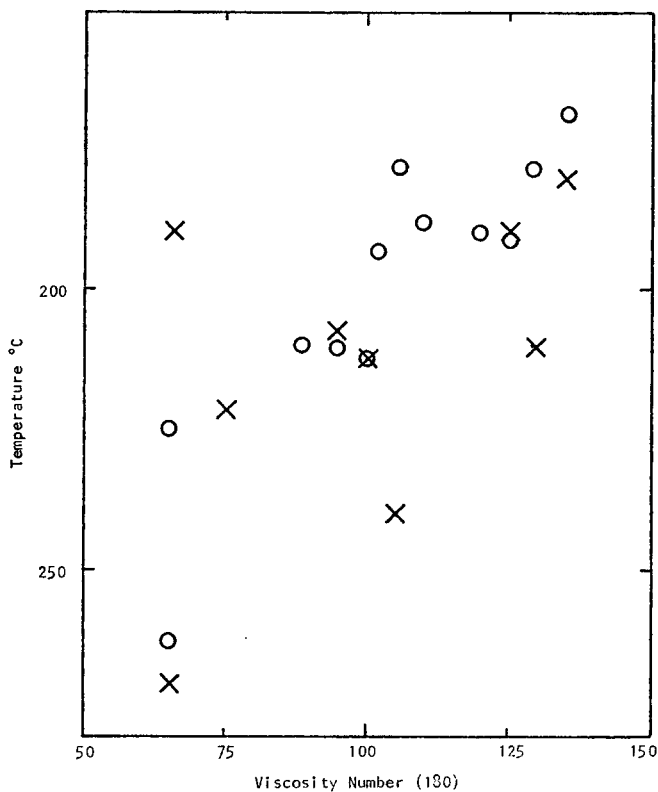

Fig. 2. Melting temperature and heat of fusion of PVC: ($\bigcirc$) melting temp; ($\times$) heat of fusion.

Values on record for the melting point and heat of fusion of PVC show a wide disparity.   Reding, Walter, and Welch[9] found, by a method involving a short extrapolation, melting points of 155°, 220°, and 265°C for laboratory preparations made by polymerizing vinyl chloride at temperatures 155°, 40°, and −10°C, respectively.   Kochott[10] reported 220° for a laboratory specimen with crystalline content of 25% and further estimated that fully syndiotactic PVC would melt at 273° with a heat of fusion of 2700 cal per unit.

Against this, Nakojuna et al.,[8] by extrapolation from solution temperatures in high dilution, estimated melting points using eq. (5) of 285° and 310°C for laboratory samples made by polymerization at −75° and −15°C,

TABLE III
Melting Point and Heat of Fusion of PVC

Type of polymer	Viscosity number, ISO	Melting point, °C	Heat of fusion, cal
Bakelite VY19	65	174°	1100
VY16	77	190°	770
VY18	102	207°	—
VY11	105	221°	600
Hostalite C70	125	208°	1100
Breon 111EP	130	222°	900
112EP	120	210°	—
115	100	188°	880
113	110	212°	—
Vinnol Y60	95	191°	950
Breon 121	135	232°	1200

respectively, with a value for heat of fusion in each case of only 785 cal. Apart from the estimate in ref. 1 of mp 174°C and ΔH 659 for Opalon 300, the only other commercial sample noted is QY3 (Union Carbide) for which Clark[11] found by direct thermogravimetric method a melting point of 225°C.

In spite of the thermal instability of PVC, I find that consistent melting points can be observed using the Kofler bar which has been found useful in determining melting points of cellulose derivatives.[7] In this method, a strip of solvent-cast film about 0.1 mm thick is laid on the bar, which is heated at one end and has a uniform temperature range, and after a short period of about 15 sec stripped off from the end at lower temperature. The point at which the film adheres strongly and breaks away is regarded as the melting temperature. Checks on other polymers of known melting point have shown that the method, although not very accurate, gives results within 5° of the true value.

Melting points of a number of commercial varieties of PVC are shown in Table III, which also gives estimates of heat of fusion. Heat of fusion was evaluated from the melting temperatures of a series of films of the polymer containing suitably high boiling plasticizers as diluents and using the formula

$$\frac{1}{T_m} - \frac{1}{T_m{}^\circ} = \frac{R}{\Delta H} (-\ln N_1) \qquad (6)$$

where N_1 is the molecular fraction of polymer. This formula is equivalent to eq. (5) at low concentrations of diluents but is simpler to use. Plots of $1/T$ against $\ln N_1$ or v_1 are substantially linear up to about 20% dilution and the influence of the term $\chi v_1{}^2$ in eq. (1) is only significant at higher solutions. Typical results are shown in Figure 3 in which $1/T$ is plotted against the logarithm of the molecular fraction of polymer.
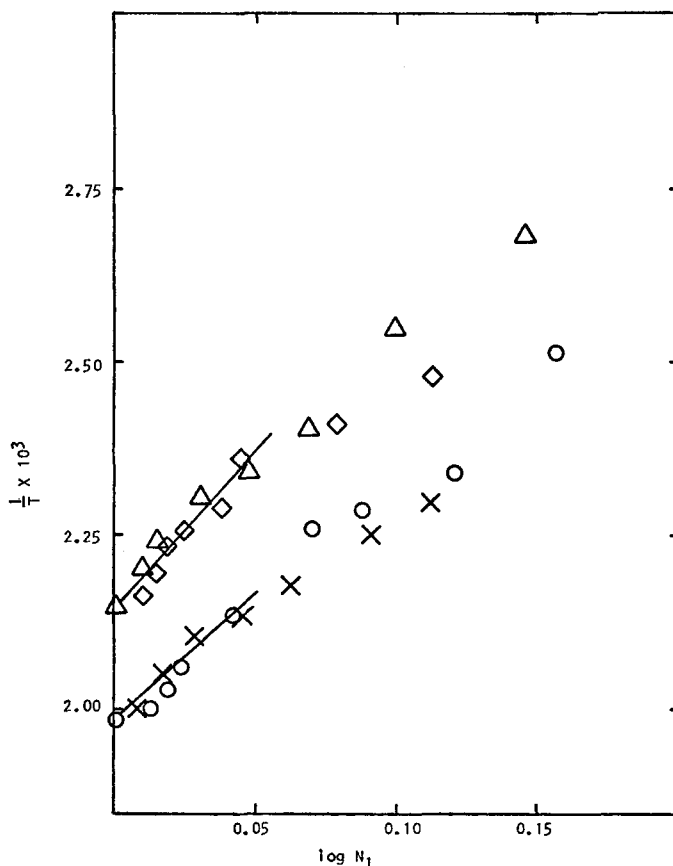
Fig. 3. Heat of fusion of PVC (EQ6): (O) Breon 121 in TBP; (X) Breon 121 in
DOP; (Δ) Vinnol Y100 in TBP; (◊) Vinnol Y100 in DOP.

When plotted against nominal viscosity numbers as in Figure 2, it will
be seen that melting point increases with intrinsic viscosity. Heats of
fusion also show a similar tendency although they appear to pass through a
minimum at about viscosity number 100.

The results agree with those of Clark[11] and Reding, Walter and Welch.[9]
Heats of fusion are in the range of those of other polymers such as poly-
ethylene, polypropylene, or polyvinyl alcohol and are not inconsistent with
Kochott's estimate of 2700 cal for fully syndiotactic PVC. Commercial
PVC is considered to be about 55% to 68% syndiotactic and the degree of
syndiotacticity is probably the chief influence on melting point and heat of
fusion, although other factors such as molecular weight and branching may
also be involved.

The melting temperature of PVC is of some practical importance since it
is found in general that for development of optimum physical properties a
higher processing temperature is required. Because of thermal instability,

PVC is usually processed at or below 180°C, which is below the melting temperature of most types. However the advantage of a lower melting point may be offset by lower molecular weight.

PART III. GELATION AND SOLUTION OF PVC

Although, as pointed out by Anagnostopoulos et al.,[1] eq (5) extrapolates to a definite value of T_L at infinite dilution, this does not correspond with physical reality. In diluted systems, T_m represents the sol-gel temperature, so that the minimum concentration of solution which would gel at, say, room temperature, as noted by Doty and Zimm,[3] should also appear as a point on the curve relating T_m to dilution. In the words of Mandelkern,[14] "As a polymer system is diluted, the melting temperature is depressed and the continuity of the phase diagram is maintained to a very dilute solution."

Experimentally I have studied gelation of PVC solutions by observing changes in viscosity with time. As it has been shown by Mencik and Lanikova[12] that, to obtain a molecularly dispersed solution of PVC in cyclohexanone, heating is necessary, solutions of Breon 121 were prepared at 80°C and quickly cooled to 15°C. Viscosities were determined by the falling ball method, and there were differences in behavior according to concentration. In the range 5–12% PVC no change was observed up to 45 days. A solution of 13.6% PVC increased in viscosity steadily, log viscosity against time being linear until after 45 days viscosity became constant. A solution of 17.4% PVC increased in viscosity at a greater rate and after 36 hours gelled with the ball remaining indefinitely suspended. Thus the concentration limit for gelation at room temperature is between 13.6% and 17.4%. Doty and Zimm[3] reported a limit of over 20%, using however a copolymer VYNW.

Concentrated solutions of Breon 121 prepared by shaking with cold cyclohexanone in the range 5–10 g PVC per 100 ml were higher in viscosity than those prepared at 80°C but showed no sign of change of viscosity with time. After heating and cooling, viscosities agreed with corresponding solutions prepared first of all at 80°. It was found, however, that heating for 4 hr at 65° was adequate to complete dispersion as indicated by viscosity. The solution of 15 g PVC which had aged for more than 45 days and the 20-g solution which had gelled were heated to 80° for about 1 hr; and after cooling the viscosities reverted to the values as when freshly prepared, but again increased on standing as before.

The results are summarized in Table IV. As the cycle of viscosity changes and gelation is repeatable, it is clear that no chemical changes are involved; but to eliminate the possibility that residual surfactants or other impurities in the emulsion polymers are involved, similar experiments were carried out with a dispersion polymer Bakelite VY19. The PVC, 11 g, was mixed at room temperature (15°–20°C) with 90 ml of cyclohexanone and allowed to stand with occasional shaking until completely dissolved. This took nine days. Viscosity at 25°C was constant at 1.25 sec/cm for a $^1/_{32}$

TABLE IV
Log Viscosity at 15°C of Solutions of Breon 121 in Cyclohexanone[a]

Concentration, % PVC	Solution prepared at 80°C		Solution prepared at ca. 15°C
	original	aged	
5.0	−1.43	−1.43	−1.26
8.0	−0.74	−0.74	−0.47
9.5	−0.58	−0.58	0.26
11.2	−0.04	−0.04	—
13.6	0.34	4.0 (45 days)	—
17.4	1.00	gelled (1.5 days)	—

[a] Viscosity is expressed as time in seconds for a $^1/_{16}$-in. steel ball to fall 1 cm.

in. steel ball. After heating to 44°C for 4 hr, viscosity measured at 25°C was 0.95 sec and further heating up to 62°C brought about no further reduction in viscosity. A similar result was obtained with Vinnol Y60. It seems therefore that heating to 80°C to complete dispersion of PVC is not always necessary and the minimum temperature depends on the type of PVC and possibly on concentration.

More extended experiments were carried out with di(ethylhexyl) phthalate as solvent (DOP). For reasons discussed in part I, it is impracticable

TABLE V
Log Viscosity at 15°C of Solutions of Breon 121 in Di(ethylhexyl) Phthalate (DOP)[a]

Concentration, % PVC	Original	Aged
1.0	−0.98	−0.98 after 105 days
2.0	−0.18	1.14, constant after 75 days
2.4	0.0	2.72, constant after 15 days
2.9	0.24	gelled in 4 days
3.4	0.38	gelled in 2 days
3.9	2.5	gelled in 1 day

[a] Viscosity of all solutions in DOP expressed as time in seconds for $^1/_8$-in. steel ball to fall 1 cm.

TABLE VI
Gelation of Breon 121 Solutions in DOP

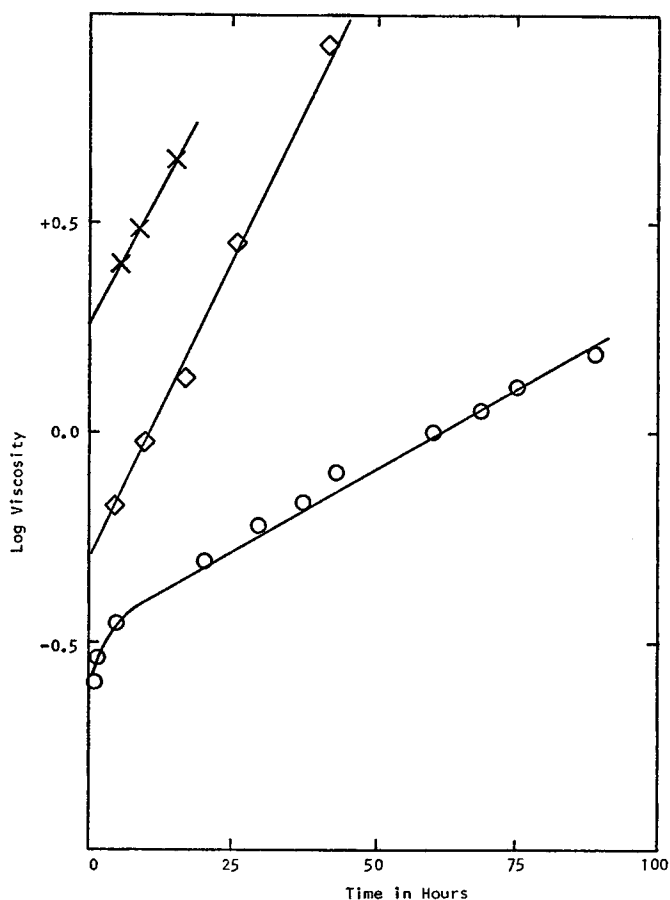| Concentration, % PVC	Gelation temp, °C	Solution temp, °C
2.9	—	69°
3.4	—	72°
3.9	—	93°
5.7	36°	108°
8.3	63°	126°
12.3	88°	—
16.2	103°	—
17.2	121°	—

Fig. 4. Gelation of PVC in DOP (Table VII): (O) 9.9% Vinnol Y100/60; (◇) 4.8% Vinnol Y100/60; (✕) 5.8% Vinnol Y100/60.

to prepare solutions in the cold and to obtain a state assumed to represent full molecular dispersion. Solutions were therefore prepared at 120°C. Results are shown in Tables V and VII; and it will be seen that the minimum concentration for gelation at room temperature is 2.5–3.0 g per 100 ml

TABLE VII
Log Viscosity at 25°C of Solutions of Vinnol Y100/60 in DOP[a]

Concentration % PVC	Original	Aged	Solution temp, °C
3.9	−0.4	gelled in 35 days	58°
4.8	−0.07	gelled in 2 days	65°
5.8	0.2	gelled in 0.8 days	75°
9.2	—	gelled at 38°C	105°

[a] Viscosity of solutions in DOP expressed as time in seconds for $^1/_8$-in. steel ball to fall 1 cm.
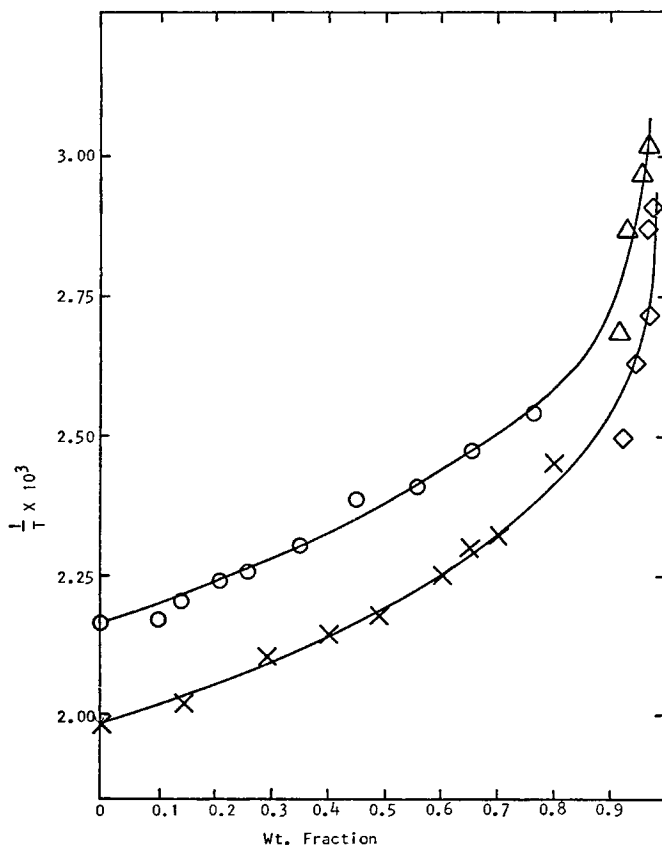
Fig. 5.   Melting temperatures in PVC–DOP system: (○) Vinnol Y60 films; (△) Vinnol
Y60 gels; (✕) Breon 121 films; (◇) Breon 121 gels.

DOP in the case of Breon 121 and around 4 g per 100 ml DOP in the case of
Vinnol Y60.   Increase of log viscosity with time is linear as with the cyclo-
hexanone solutions.   Examples are shown in Figure 4.   Gelation of solu-
tions of Vinnol Y60 in DOP was found to be similar, although the limiting
concentration for gelation was somewhat higher (Table VIII).

Temperatures at which gels reverted to solutions were determined by
heating the tubes containing gels in which the steel ball was suspended to a
fixed temperature maintained for at least 2 hr before repeating at incre-
ments of not more than 5° until a downward movement of the ball could
be detected.   Results are shown in Tables VI and VII and in Figure 5,
where they are plotted in relation to melting points found for films of
Breon 121 and Vinnol Y60 with DOP.   There is a considerable gap between
gelation and solution temperature, but it is assumed that the latter are
more representative of the true equilibrium state.

There remains some uncertainty about the requisite conditions for ob-
taining molecular dispersions of PVC.   Heating to some extent is necessary

but the minimum temperature appears to depend on the type of PVC, the nature of the solvent, and the concentration. Another uncertainty is whether there are different states of aggregation possible. From the increase in viscosity on standing, a rough calculation shows that the average state of aggregation is 2 molecules. Gelation of more concentrated solutions is thought to be due to a network formation of physically crosslinked molecules.

PVC is unusual in its solution behavior, but not unique. A similar effect of gelation on standing has been observed with solutions of cellulose derivatives. For example, a solution of cellulose triacetate (5.9%) in tri(chlorethyl) phosphate gelled on standing for five days at about 3°C but, once gelled, required reheating to 120°C to liquify. A similar effect was found with solutions of polyvinyl alcohol in glycerin.[13]

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