

Effect of Recrystallization on the Solubility of Poly(vinylidene Chloride)

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Synopsis

A study of the crystallization of poly(vinylidene chloride) from dilute solution in various solvents was carried out. The temperature at which the polymer dissolved was dependent on crystallization history. The minimum solution temperature obtained by recrystallization at high undercooling and redissolving is the preferred parameter for characterizing solvents for poly(vinylidene chloride).

INTRODUCTION

This paper describes a further study of the effect of crystallization temperature of poly(vinylidene chloride) on its solubility. Earlier work in this area was concentrated primarily on characterizing the solubility of "as polymerized" PVDC.¹⁻³ Only a limited amount was done on recrystallization and annealing and their effect on solution temperature. We observed that samples crystallized under quenching conditions would dissolve at a lower temperature than "as polymerized" PVDC; annealed samples dissolved at higher temperatures.

Changes in apparent solubility with crystallization history have been observed with most crystalline polymers.⁴⁻¹⁴ The effect of crystallization temperature T_c on solution temperature T_M in the same solvent is the phenomenon most commonly studied. Above some minimum temperature, T_M increases linearly with T_c . This result has been ascribed to changes in the thickness of the lamellar polymer crystals that grow in dilute solution. PVDC is known to crystallize in a lamellar habit from solvents like tetramethylene sulfide and bromobenzene. The linear dependence of T_M on T_c has been observed in the former. It seems likely, therefore, that the explanation described above also applies to PVDC.

As noted earlier, a comparison of 1% solution temperatures is useful for characterizing the effectiveness of solvents for PVDC. But the absolute values obtained depend on the polymer history. It was proposed that the equilibrium solution temperature obtained by extrapolation of T_M -versus- T_c data would be a better measure since it is independent of simple history. The present study was undertaken to see if this were the case.

EXPERIMENTAL

The polymers used in this study have been described previously. The solvents were reagent grade or were distilled before use.

Solution temperatures were observed usually by heating a rapidly stirred mixture at $\sim 10^\circ\text{C}/\text{min}$ until it cleared. In most of this work, the solutions were prepared from 0.25 g polymer and 15 ml solvent.

For recrystallization studies, the solutions were prepared as above. After ensuring that the polymer was completely dissolved, the solution was quenched to the desired crystallization temperature and allowed to crystallize without agitation until no further changes could be observed. PVDC solutions in this concentration range crystallize slowly enough to allow thermal equilibration to occur before crystallization starts.

Single growth experiments were carried out at much lower concentrations but over the same temperature range. In this case, however, the solutions were prepared by transferring 2 cc of a hot concentrated stock solution to 18 cc of solvent maintained at the desired temperature.

Crystal lamellar thicknesses were measured from micrographs taken with an Hitachi HU-11A electron microscope. Care was taken during specimen preparation and observation to keep the crystals below the crystallization temperature to prevent annealing and thickening of the platelets. The crystal suspensions were kept in the freezing compartment of a refrigerator at -20°C until they were transferred to carbon-coated copper grids which had been cooled to the same temperature. After transfer and drying of the crystals on the grids at -20°C , the specimens were placed in a vacuum evaporator on a magnesium block cooled by liquid nitrogen and were shadowed with 80/20 Pt/Pd at $\arctan 0.5$. Finally, the replicas were viewed cold in the electron microscope by means of a specimen holder cooled by liquid nitrogen. The electron acceleration potential was 75 kV. No evidence (torn, moving, or bubbling replicas, etc.) was seen to indicate heating of the samples in the electron beam, although it probably occurred. In any event, it is believed that the shadows cast during replication had valid dimensions, and these were used for the thickness measurements.

RESULTS

The effect of crystallization temperature on solution temperature in a variety of solvents was studied. The range of solvents included tetramethylene sulfoxide, which is one of the best solvents for PVDC, and tetrahydronaphthalene, a relatively poor solvent, as well as various solvents of intermediate activity. The solution temperatures of "as polymerized" PVDC in these solvents can be used to compare their relative effectiveness.¹ These data are listed in Table I.

Plots of T_M versus R_c are shown in Figure 1. We were unable to get data in TMSO because of the very slow recrystallization of PVDC from this solvent. A precipitate that crystallized over a period of weeks at

TABLE I
Analysis of T_M -versus- T_c Plots

Solvent	T_M , ^a °C	T_M (min), °C	Estimated T_M (eq), °C	Slope
Tetramethylene sulfoxide (TMSO)	34	—	—	—
N-Methylpyrrolidone (NMP)	42	—	102	—
Tetramethylene sulfide (TMS) ^a	87	73	115	0.42
Cycloheptanone (CHO)	96	80	122	0.44
Cyclopentanone (CPO)	106	101	132	—
Bromobenzene (BB)	129	124	152	—
Tetrahydronaphthalene (THN)	142	140	160	—

^a From reference 1.

25°C dissolved at 60°C. A reluctance to recrystallize is characteristic of solutions of PVDC in good solvents. The process is somewhat faster in NMP. Unfortunately, the plot of T_M versus T_c (Fig. 1) was nonlinear over the range in which crystallization would occur in this solvent, making it difficult to analyze the data.

The results in the other solvents are more typical of what was reported before for PVDC in tetramethylene sulfide.¹ Below a certain crystalliza-

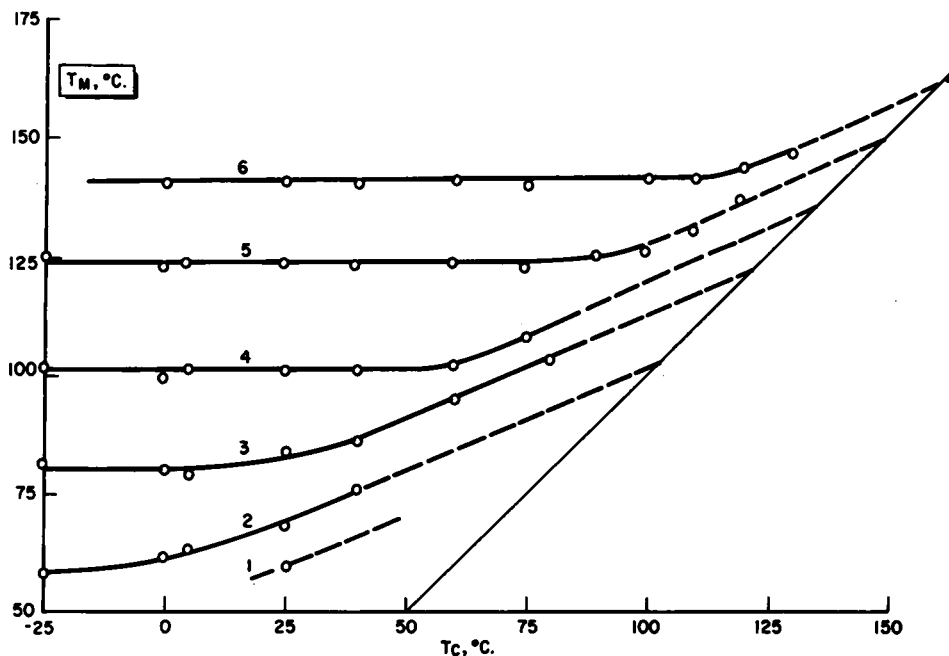


Fig. 1. Effect of recrystallization on 1% solution temperature in various solvents; (1) tetramethylene sulfoxide; (2) N-methylpyrrolidone; (3) cycloheptanone; (4) cyclopentanone; (5) bromobenzene; (6) tetrahydronaphthalene.

tion temperature, T_M reaches a minimum value, but at higher temperatures it increases with increasing T_c . The data should extrapolate to the equilibrium solution temperature (the point where the experimental curve intersects the $T_M = T_c$ curve). Sufficient data to make a good extrapolation were obtained only in cycloheptanone. The slope is close to that found in tetrahydrothiophene. The other extrapolations were made by assuming that this slope is invariant to solvent and temperature. This can be justified only in that it appears to reasonably fit the available data.

A measure of how much recrystallization affects solution temperatures is the difference $T_M(\text{eq}) - T_M(\text{min})$. When PVDC is crystallized from increasingly poorer solvents, this difference becomes smaller. This is shown in Figure 2. In very poor solvents, therefore, all samples would show the same solution temperature regardless of sample history. In strong solvents, however, the solution temperature is very sensitive to such differences.

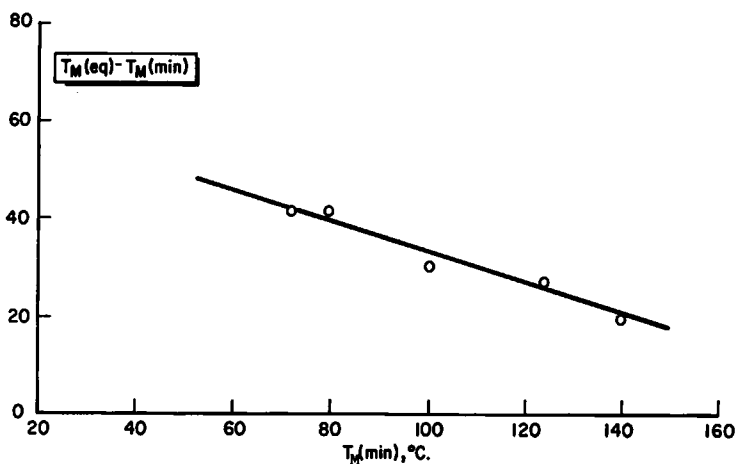


Fig. 2. Dependence of maximum T_M depression on solvent power.

Crystals for electron microscopy were grown at a polymer concentration of $\sim 0.01\%$. The best solvents did not yield lamellar crystals. Crystallization without severe degradation could not be obtained in the poorer solvents in the range where T_M was increasing. Lamellar crystals were grown successfully in the intermediate solvents. An example of crystals grown in cycloheptanone is shown in Figure 3. The ragged appearance is typical of crystals grown in polar solvents.

Thicknesses of the crystals obtained from shadow lengths are plotted against T_c in Figure 4. The thickness is constant below 20°C . The correlation between thickness and T_M is evident on comparing these results with Figure 1.

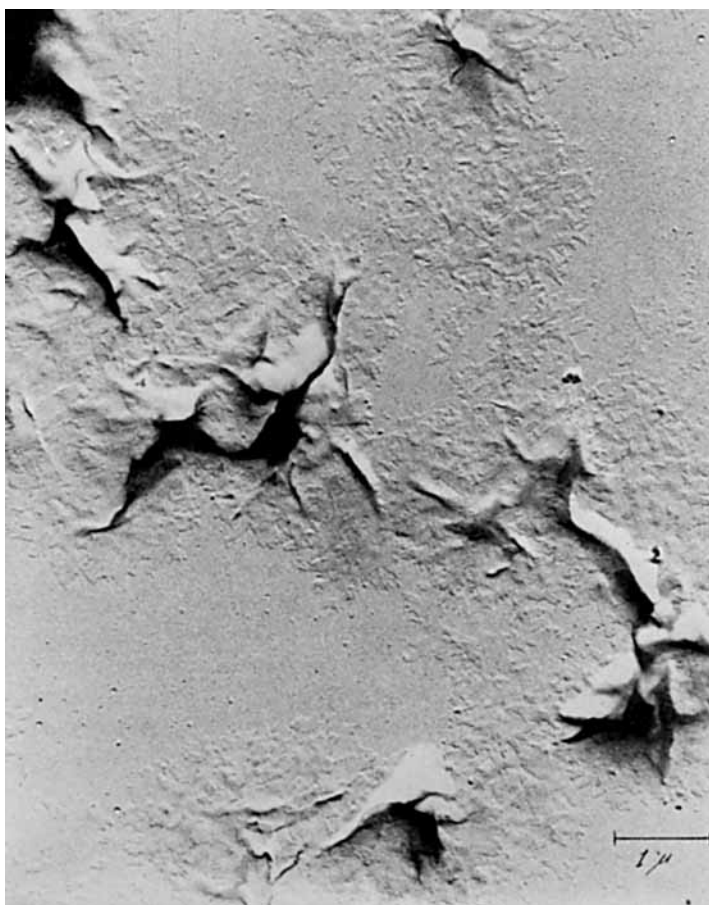


Fig. 3. Crystals of PVDC obtained from cycloheptanone solution at 35°C. Transmission electron micrograph of shadowed specimen.

DISCUSSION

This study shows that 1% solution temperatures measured on "as polymerized" powders are a good measure of solvent power only in poor solvents. In strong solvents, the observed solution temperature is very sensitive to crystallization history.

The observation that crystals dissolve at temperatures much farther below the equilibrium solution temperature T_M (eq) in good solvents but not in poor solvents may be related to annealing. Assuming that annealing processes begin above the alpha transition ($\sim 80^\circ\text{C}$)¹⁵ and that this is true independent of whether or not the crystals are suspended in a solvent, then we would expect annealing only in poor solvents. This would exert a leveling effect on T_M . In good solvents, the polymer would dissolve before any changes take place.

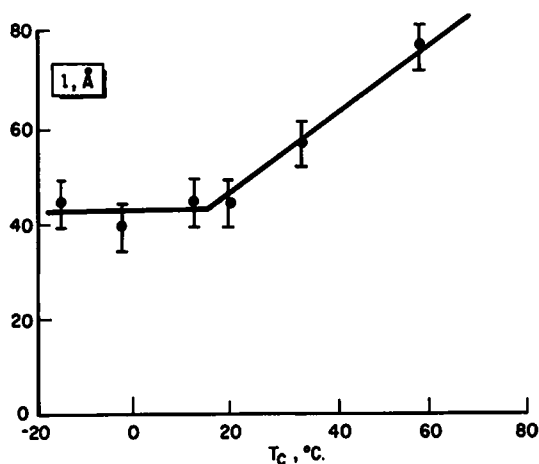


Fig. 4. Dependence of lamellar crystal thickness on crystallization temperature.

Another possible explanation is that the leveling off of the T_M -versus- T_c plot at low temperature is due to the fact that solutions cannot be quenched fast enough to attain thermal equilibrium. While this is quite true for polyethylene, in the case of PVDC, solutions in a solvent like cycloheptanone can be easily quenched and at very low temperatures may take several days to crystallize. The invariance of T_M of samples crystallized under quenching conditions must be related to other factors, such as constant lamellar thickness or defect concentration.

The equilibrium solution temperature, while of theoretical significance, is a difficult property to measure experimentally. Since our objective is to characterize solvents for crystalline polymers, it appears to be more desirable to use the minimum solution temperature as a guide. If the latter is determined by the size and perfection of the crystals formed under conditions of high undercooling, and if this in turn is fixed by ΔT_M and is not dependent on polymer-solvent interaction, then $T_M(\text{min})$ will reflect the same changes in solvent activity as $T_M(\text{eq})$. But it has the further advantage of being much more easily measured particularly for unstable polymers like PVDC.

References

1. R. A. Wessling, *J. Appl. Polym. Sci.*, **14**, 1531 (1970).
2. R. A. Wessling, *ibid.*, **14**, 2263 (1970).
3. R. A. Wessling, *ibid.*, **17**, 503 (1973).
4. D. A. Blackadder, *Rev. Macromol. Chem.*, **C1**, 297 (1967).
5. J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.*, **59**, 1906 (1963).
6. V. P. Holland, *J. Appl. Phys.*, **35**, 59 (1964).
7. R. Chiang, J. H. Rodes, and V. F. Holland, *J. Polym. Sci. A*, **3**, 479 (1965).
8. R. Chiang, *J. Polym. Sci. A*, **3**, 2019 (1965).
9. J. F. Kenny and V. F. Holland, *J. Polym. Sci. A-1*, **4**, 699 (1966).

10. H. E. Harris, J. F. Kenny, G. W. Willcockson, R. Chiang, and H. N. Friedlander, *J. Polym. Sci. A-1*, **4**, 665 (1966).
11. D. A. Blackadder and H. M. Schleinitz, *Polymer*, **7**, 603 (1968).
12. F. Danusso and G. Gianotti, *Eur. Polym. J.*, **4**, 165 (1968).
13. J. F. Jackson and L. Mandelkern, *Macromolecules*, **1**, 546 (1968).
14. R. K. Sharma and L. Mandelkern, *Macromolecules*, **3**, 758 (1970).
15. R. A. Wessling and F. G. Edwards, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Vol. 14, Wiley, New York, 1971, p. 540.

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