Dilute Solution Properties of Low-temperature Polymerized Polyvinyl Chloride. I. Effects of Dissolution Temperature and Time

By Takashi KOBAYASHI

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Asahina and his coworkers have reported[1-3] that the physical properties of the solid state of polyvinyl chloride depend upon the temperature at which the sample is polymerized. The purpose of the study presented in this paper is to examine if there is any difference in the dilute solution properties of polyvinyl chloride polymerized at different temperatures. Our preliminary experiment had indicated that the samples polymerized at low-temperatures were more difficult to dissolve in tetrahydrofuran than commercially available materials usually polymerized at 50~60°C. In this study we measured the viscosity, osmotic pressure and light scattering of tetrahydrofuran solutions of polyvinyl chlorides polymerized at three different temperatures and the changes with time of these properties when left standing; we aimed at establishing the conditions required for the preparation of a solution of this polymer stable enough to use for the evaluation of its physical behavior.

Experimental

Materials.—Three samples of polyvinyl chloride were studied. They were obtained in the following manner:

S-796—A whole polymer suspension polymerized at 58°C. The 43 wt. % lower molecular weight portion was removed, and the remaining portion was designated as S-796-M.

S0968—This was a whole polymer suspension polymerized at 48°C.

F-5-M—The 3 wt. % higher molecular weight portion and the 29 wt. % lower molecular weight portion of a polymer bulk polymerized at −15°C were removed by fractional precipitation, and the remaining portion was designated as F-5-M.

The solvent used was tetrahydrofuran. After the material purchased in a 20 l. can had been dried for about one week over sodium hydroxide pellets, it was distilled, and the fractions between 65.8~66.2°C were collected.

Preparation of Solutions.—An accurately weighed sample was mixed in an ampoule with the required amount of solvent; after the air in it had been replaced by nitrogen, the ampoule was sealed and heated and occasionaly shaken in an oil bath for two hours at the desired temperature. Then it was transferred into a thermostat regulated at 30°C and kept for fifteen minutes. The ampoul was then cut off, and the solution was ready to use.

The concentration of the solution so obtained was calculated from the amounts of polymer and solvent weighed before mixing for the purpose of plotting viscosity and osmotic pressure data. For the light-scattering study it was determined gravimetrically by drying up an aliquot of the solution.

Viscosity Measurements.—Capillary viscometers of the Ostwald type were used throughout the present study. For example, one of them had the following characteristics: bore diameter=0.037 cm., capillary length=10.4 cm., volume of the upper bulb=1.99 cc., and efflux time for tetrahydrofuran of 30°C=167.7 sec. The kinetic energy correction was applied to all flow times measured. Flow times were determined at four concentrations between 3×10^{-3} and 8×10^{-3} g./ml., and the limiting viscosity number was estimated by graphical extrapolation of the plots for viscosity number against concentration (in g./ml.).

Osmotic Pressure Measurements. — A modified Zimm-Meyerson osmometer fitted with gelcellophane was used. The measurements were made at 30°C using the dynamic method. Data were taken at four concentrations between 3×10^{-3} and 8×10^{-3} g./ml.

Light Scattering Measurements. — Use was made of a photometer of the Brice type manufactured by Shimadzu Seisakusho, Kyoto. The calibration was made by referring to the literatures value[4] for the Rayleigh ration, R_{90}, of pure benzene. Measurements were made in a cylindrical cell over the range of scattered angle from 40 to 140° and at three polymer concentrations, using both unpolarized blue light, $\lambda=4360\,\text{Å}$, and green light, $\lambda=5460\,\text{Å}$, emitted from a mercury lamp. The depolarization correction was not applied. Dust was removed from the given solution by centrifuging it at 2×10^{4} times gravity for one and a half hours immediately before use. All measurements were performed at room temperature, without any specific temperature-controlling device fixed to the instrument. No marked temperature variation occurred during any series of measurements.

The refractive index increment of this system of polymer and solvent was measured by means of a differential refractometer of the Debye type manufactured by Shimadzu Seisakusho, Kyoto. The values obtained were 0.115 and 0.110 for the lights

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[1] M. Asahina et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1011 (1960).

[2] M. Aahina et al., *Chem. High Polymers* (*Kōbunshi Kagaku*), **17**, 612 (1960).

[3] M. Asahina et al., ibid., **17**, 325 (1960).

[4] S. H. Maron et al., *J. Polymer Sci.*, **14**, 273 (1954).

of λ=4360 Å and λ=5460 Å respectively, in good agreement with the literature's, value[5].

The procedure developed by Zimm[6] was followed to evaluate results from these light-scattering experiments.

Results and Discussion

Effect of Dissolution Temperature. — It is generally accepted that polyvinyl chloride samples polymerized at low-temperatures are less soluble than those prepared at higher temperatures. In order to examine this point in a qualitative manner, we measured viscosities, osmotic pressures, and turbidities of solutions of S–796 and of F–5–M prepared at different temperatures. Table I gives viscosity data for S–796 dissolved in tetrahydrofuran at 60, 100 and 140°C. It can be seen that the viscosity values of sample S–796 in tetrahydrofuran are practically independent of the dissolution temperature in the range above 60°C; this is in accordance with Kuroiwa's results[7]. Similar conclusions were derived also from osmotic pressure and turbidity measurements on this sample.

TABLE I. VISCOSITY DATA ON SOLUTIONS OF S–796 PREPARED AT DIFFERENT TEMPERATURES

Concn. g./ml. $\times 10^3$	η_{sp}/c of solution prepared at, 60°C ml./g.	100°C ml./g.	140°C ml./g.
3.000	110	110	110
4.000	113	114	112
6.000	120	120	120
8.000	128	127	127
[η] ml./g.	99.0	99.0	99.0
k' *	0.36	0.36	0.35

* k' : Huggins' constant

Figure 1 shows η_{sp}/c (viscosity number) for sample F–5–M in tetrahydrofuran as a function of the temperature at which the solution was made. As has been mentioned above, the polymer was dissolved in the solvent by heating at a given temperature for two hours. It was found that a more prolonged heating did not give rise to any detectable change in the viscosity values. Thus, the results shown in Fig. 1 should be free from the effects of the time used to dissolve the sample polymer. The data for osmotic pressure and for light scattering corresponding to Fig. 1 are given in Figs. 2 and 3 respectively. These figures indicate that, contrary to the case of sample S–796, the viscosity, osmotic pressure and light-scattering

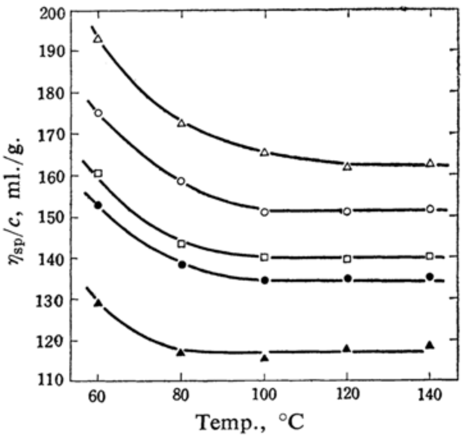

Fig. 1. Viscosity of F–5–M solutions prepared at different temperatures. △ 8.0 $\times 10^{-3}$ g./ml.; ○ 6.0$\times 10^{-3}$ g./ml.; □ 4.0 $\times 10^{-3}$ g./ml.; ● 3.0$\times 10^{-3}$ g./ml.; ▲ Limiting viscosity number.

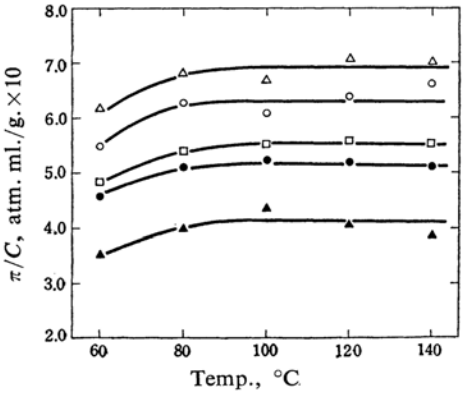

Fig. 2. Osmotic pressure of F–5–M solutions prepared at different temperatures. △ 8.0$\times 10^{-3}$ g./ml.; ○ 6.0$\times 10^{-3}$ g./ml.; □ 4.0$\times 10^{-3}$ g./ml.; ● 3.0$\times 10^{-3}$ g./ml.; ▲ $(\pi/C)_{C\to 0}$.

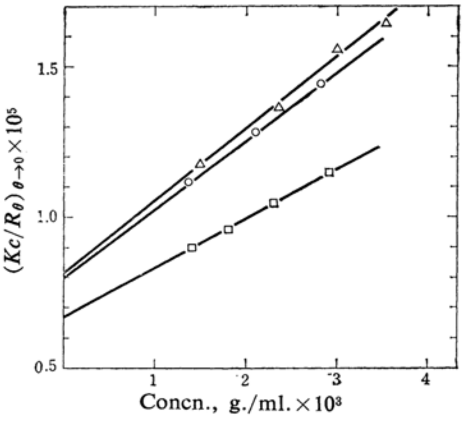

Fig. 3. Light scattering of solutions of F–5–M prepared at different temperatures. △ Solution prepared at 140°C; ○ at 100°C; □ at 80°C.

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[5] D. Laker, ibid., **25**, 122 (1957).

[6] B. H. Zimm, *J. Chem. Phys.*, **16**, 1066, 1093 (1948).

[7] T. Kuroiwa and K. Kawahara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 563 (1952).

properties of F-5-M all become practically independent of the dissolution temperature only in the region above 100°C or more. In the light-scattering plots shown in Fig. 3, there still exists a distinct, though quite small, difference between the data for 100°C and those for 140°C. One may consider this difference to be negligible or else within the limits of accuracy of the light-scattering measurements. However, since we have checked similar differences by repeated measurements, it is believed that even such a small difference is significant.

The interpretation of these differences in solution properties between S-796 and F-5-M cannot be certain, but the most obvious conclusion is that the intermolecular interaction in polyvinyl chloride becomes stronger as the polymerization temperature is lowered. In order to obtain relevant data on tetrahydrofuran solutions of a polyvinyl chloride polymerized at a temperature much lower than that used for commercially available material, the solute must be dissolved in the solvent at a temperature at least higher than 100°C and the mixture must be kept at least for two hours at that temperature. However, use should not be made of too high a dissolution temperature, since that is likely to induce thermal decomposition of the polymer.

Effect of Standing Time. — It has been reported that dilute solutions of ordinary polyvinyl chloride remain stable for several days[8]. In Table II are given viscosity data for S-796-M solutions in tetrahydrofuran as a function of the time for which the solution was allowed to stand after it had been prepared. Figure 4 shows the Zimm plots for S0968 solutions in tetrahydrofuran allowed to stand for different intervals of time. Apparently these solutions remained stable over the time intervals examined. The data for viscosity, osmotic pressure and light-scattering in tetrahydrofuran solutions of F-5-M as functions of the standing time are given in Tables III, and IV, and Fig. 5 respectively. It can be seen that the dilute solution properties of this sample, especially those at higher concentrations, chaneg to a considerable extent with time. This appears to be due to the gradual association of solute molecules taking place during the course of standing.

TABLE II. TIME EFFECT ON THE VISCOSITY OF SOLUTIONS OF S-796-M

Concn. g./ml. $\times 10^3$	η_{sp}/c, ml./g.			
	0.5* hr.	5.0* hr.	50.0* hr.	100.0* hr.
3.000	138	139	139	139
4.000	144	145	145	144
6.000	155	157	156	156
8.000	167	168	168	167
$[\eta]$ ml./g.	126	126	126	126
k' **	0.36	0.37	0.37	0.36

* Time in hour after the solution was prepared.

** Huggins' constant.

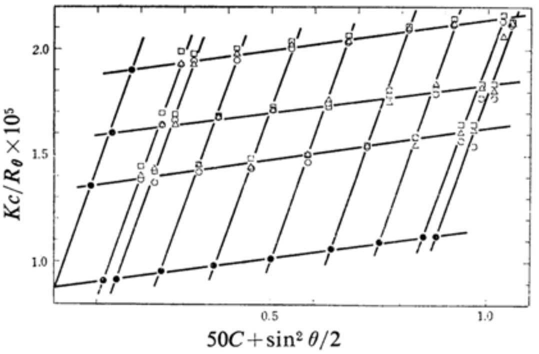

Fig. 4. Time effect on Zimm plots for light scattering of solutions of S0968. △ 5.0 hr. after the completion of heating; ○ 28 hr.; □ 76 hr.

TABLE III. TIME EFFECT ON THE VISCOSITY OF SOLUTION OF F-5-M

Concn. g./ml. $\times 10^3$	η_{sp}/c, ml./g.			
	0.5* hr.	5.0* hr.	50.0* hr.	100.0* hr.
3.000	135	136	136	137
4.000	141	142	142	142
6.000	152	154	154	155
8.000	164	166	167	169
$[\eta]$ ml./g.	118	118	118	118
k' **	0.42	0.44	0.44	0.45

* Time in hour after the solution was prepared.

** Huggins' constant.

TABLE IV. TIME EFFECT ON THE OSMOTIC PRESSURE OF SOLUTIONS OF F-5-M

Concn. g./ml. $\times 10^3$	π/C, atm. ml./g. $\times 10$			
	3.0* hr.	20.0* hr.	50.0* hr.	100.0* hr.
3.000	5.36	5.34	5.43	5.43
4.000	5.59	5.64	5.53	5.44
6.000	6.63	6.56	6.53	6.47
8.000	7.26	6.99	6.85	6.78
$(\pi/C)_{C\to 0}$	4.00	4.25	4.25	4.25
$A_2\times 10^3$	1.69	1.45	1.39	1.37

* Time in hour after the solution was prepared.

A straightforward support to this idea is the marked decrease in $Kc/R_{\theta\to 0}$ on prolonged

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[8] A. Nakajima, *Chem. High Polymers* (*Kobunshi Kagaku*), 7, 309 (1950).

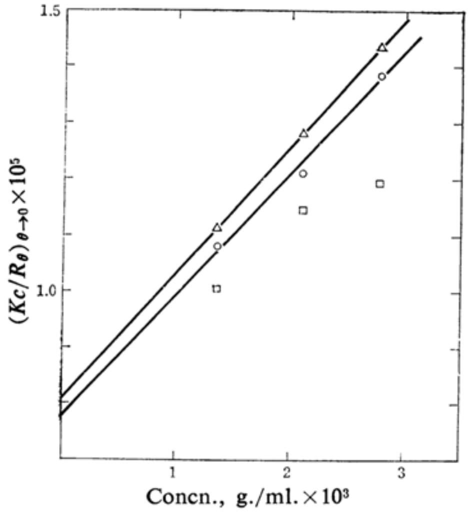

Fig. 5. The time effect on light scattering of solutions of F-5-M. △ 3.5 hr. after the completion of heating; ○ 24.5 hr.; □ 76 hr.

standing, as indicated in Fig. 5, which indicates the formation of increasingly large solute particles by association. It is worth pointing out that the association, if any, had only a minor influence on the viscosity of the solution. Doty et al.[9] have demonstrated the occurrence of the association of polyvinyl chloride molecules in relatively poor solvents. Since the time effects observed here for tetrahydrofuran solutions of F-5-M are similar to those reported by Doty et al., it appears that tetrahydrofuran, though being though of as a good solvent for ordinary polyvinyl chloride, is a relatively poor solvent for this polymer polymerized at as low a temperature as that employed for the preparation of sample F-5-M.

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Kureha Kasei Tokyo Laboratory
Shinjuku-ku, Tokyo

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[9] P. Doty et al., *J. Phys. & Colloid Chem.*, **51**, 32 (1947).