

Solutions of Poly(vinyl Chloride) Polymerized at Low Temperatures

In a previous work¹ the conditions for dissolution in a molecularly dispersed state of poly(vinyl chloride) (PVC) in tetrahydrofuran (THF) as required for light-scattering measurements were examined. Heat treatments at 55°C for a few hours appeared to be satisfactory when PVC samples prepared at 30°C and higher temperatures were involved. For samples polymerized at 10 and -10°C satisfactory solutions were obtained at a temperature as high as 150°C, which is considered the maximum practicable temperature, since at higher temperatures discoloration of the solutions was observed. Finally, with samples polymerized at -30 and -50°C, even prolonged heating at 150°C gave solutions in which very small amounts of polymer gels, macrogels, were discernible. Besides, on these solutions freed from the macrogels by centrifugation, very high weight-average molecular weights, \bar{M}_w , were determined. Such \bar{M}_w values were considered to be unreliable in view of the following considerations.

With the more soluble PVC samples, polymerized at higher temperatures, whenever some undissolved polymer was left in the solutions, because of a milder treatment, anomalously high \bar{M}_w values were obtained. Hence, the presence in the solutions of even very small amounts of macrogels was viewed as an index of the presence of substantial amounts of supermolecular structures, microgels, capable of significantly affecting the light-scattering measurements.

In line with this, the more reliable \bar{M}_w values for PVC (-30°C) and PVC (-50°C) were judged to be the far lower \bar{M}_w values derived from cyclohexanone (CX) solutions subjected to 150°C heat treatment, by which the PVC (-30°C) samples appeared to be completely dissolved and only trace amounts of macrogels were discernible in the case of the PVC (-50°C) samples. These findings are in agreement with the fact that CX has been recognized² on thermodynamic grounds to be a better solvent for PVC than THF.

Recently, Abdel-Alim and Hamielec³ reported that heating the PVC solutions in THF at 200°C for 2 hr could be done without danger and permitted complete dissolution even of the samples polymerized at -50°C for GPC analysis. At the same time, the treatment at 150°C was reported to be inadequate for a complete dissolution of the samples polymerized at -10°C and lower temperatures, because of the presence of highly resistant microgels, called "strong aggregates."

Therefore, it was thought a useful supplement to the previous work to carry out some additional light-scattering measurements with THF solutions of PVC subjected to a 2-hr heat treatment at 200°C.

Samples of PVC (-10°C), PVC (-30°C), and PVC (-50°C), already utilized in the previous¹ work, were examined. They were obtained by bulk radiation-induced polymerization of vinyl chloride at 2.2 rad/sec carried out up to 25-35% conversion. These conditions are the same as those utilized by other authors,³ apart from the polymerization conversion, which was from 78 to 90% for these authors.

For the sake of comparison, the \bar{M}_w determinations were repeated on the same samples in THF solutions heat treated at 150°C.

The experimental procedure for the heat treatment of the solutions and the determination of \bar{M}_w from light-scattering measurements have been described previously.¹ The results are summarized below.

With all samples investigated, the heat treatment at 150°C gave no discoloration of the THF solutions, while yellow solutions resulted from the heat treatment at 200°C. Apart from this difference, with both heat treatments the solutions appeared to be perfectly clear in the case of PVC (-10°C) and contained small amounts of macrogels when PVC (-30°C) and PVC (-50°C) were involved.

The \bar{M}_w values, obviously calculated by neglecting the small losses of polymer from the solutions on centrifugation, are collected in Table I. In the fourth column of the table there are also reported the \bar{M}_w values obtained in the previous work¹ from CX solutions subjected to heat treatment at 150°C.

The \bar{M}_w value of the PVC (-10°C) sample determined on a THF solution heat treated at 150°C can be assumed to be reliable, as supported by its agreement with the corresponding value

TABLE I
Values of \bar{M}_w of PVC Samples Determined on THF Solutions Subjected to Heat Treatment

Sample	$\bar{M}_w \times 10^{-3}$			
	150°C	200°C	Ref. 1 ^a	Ref. 3 ^b
PVC (-10°C)	765	800	760	920
PVC (-30°C)	750	880	565	941
PVC (-50°C)	1200	960	610	947

^a Determined on CX solutions.

^b By GPC analysis.

from a CX solution. Thus, with this sample it is readily understandable that the results remain practically unchanged when the THF solution with heat treatment at 200°C was used. Naturally, no occurrence of chemical modifications of the polymer should be assumed.

On the other hand, the light-scattering measurements of the THF solutions of both PVC (-30°C) and PVC (-50°C) subjected to heat treatment at 150°C should be affected by microgels. Accordingly, Table I shows that the determined \bar{M}_w values are far higher than those relative to CX solutions. At the same time the results in the case of the heat treatment at 200°C point to a similar solution behavior, despite the large differences in the \bar{M}_w values referring to the two different heat treatments. Indeed, such differences can be ascribed to a poor reproducibility in the light-scattering measurements, which are not unexpected for imperfectly dissolved polymer samples. As a conclusion of the observations gathered here, the effects on THF solutions of the heat treatment at 150°C and those at 200°C seem not to differ substantially, possibly because the microgels re-form on cooling^{4,5} rather than because the heating is insufficient to destroy them completely.

A final point worth discussing is the \bar{M}_w determination on THF solutions heat treated at 200°C, using the GPC analysis. It appears by examining the fourth and fifth columns of Table I that the \bar{M}_w values found with this technique by Abdel-Ahim et al.³ for probably identical PVC samples appear to be far higher than those from light-scattering measurements.¹ Regarding the \bar{M}_w value from light scattering of PVC (-50°C) it should be borne in mind that a more reliable value was previously¹ indicated to be the still lower value derivable by intrinsic viscosity measurements less affected by microgels.

An obvious explanation, which fits the proposed general picture, can be found in ascribing the higher \bar{M}_w values from GPC to the imperfect sample dissolution in THF. This is also suggested by the fact that these \bar{M}_w values compare better with the corresponding values from light-scattering measurements of THF solutions.

Naturally, these conclusions should be further tested by more extensive investigations.

The authors give thanks to Professor G. Talamini for his helpful criticism and to Professor G. Semerano, Director of the Laboratorio F.R.A.E., C.N.R., for his continued interest in this work.

References

1. M. Carenza, G. Palma, and M. Tavan, in *International Symposium on Macromolecules, Helsinki 1972* (*J. Polym. Sci. C*, **42**), O. Harva and C. G. Overberger, Eds., Interscience, New York, 1973, p. 1031.
2. S. H. Maron and M. S. Lee, *J. Macromol. Sci.-Phys.*, **B 7** (1) 61 (1973).
3. A. H. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **17**, 3033 (1973).
4. A. Crugnola and F. Danusso, *J. Polym. Sci. B*, **6**, 535 (1968).
5. R. Salovey and R. C. Gebauer, *J. Appl. Polym. Sci.*, **17**, 2811 (1973).

M. TAVAN

Laboratorio di Fotochimica e Radiazioni d'Alta Energia
del C.N.R. (BO),
Sezione di Legnano (Padova), Italy

Montedison S.p.A.,
Milano, Italy

G. PALMA

Centro di Studio per la Fisica delle Macromolecole del C.N.R.,
Bologna, Italy

M. CARENZA

Received November 6, 1974

Revised December 18, 1974