

NOTE

Characterization of Poly(methyl methacrylate) Prepared by Plasma-Initiated Polymerization

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Recently, Osada *et al.*¹ found that an ultrahigh molecular weight sample of poly(methyl methacrylate)(PMMA) can be readily prepared by the plasma-initiated polymerization technique. In response to the request of the late Professor M. Shen of the University of California, Berkeley, California, we have attempted a light scattering and viscometric characterization of three PMMA samples newly prepared by this technique and put at our disposal. The main concern was to estimate the absolute molecular weights, heterogeneity, and linearity of these samples. The results obtained are described briefly in this note.

EXPERIMENTAL

Samples and Solution

The three samples were designated as 003, 178, and 194, according to the sender's indication. They were subjected to light scattering and viscosity measurements with methyl ethyl ketone (MEK) at 25°C as the solvent. Sample 194 was also examined in acetone at 25°C.

Solubility tests with acetone indicated that sample 003 contained a substantial amount of insoluble fraction. This fraction was removed by centrifugation, and the polymer was precipitated from the supernatant by the addition of methanol, freeze-dried from a benzene solution, and further dried under reduced pressure. Samples 178 and 194 were directly precipitated from acetone solutions with methanol and dried under reduced pressure.

Each of these purified samples was dissolved in

either acetone or MEK without stirring to prevent any shear degradation; the polymer-solvent mixture was left standing at room temperature for 5 to 7 days and then shaken gently for about half a day to ensure complete dissolution. The solution so prepared was diluted with the respective solvent to a desired concentration one day before each measurement. The solvents used were purified thoroughly by standard procedures.

Light-Scattering Measurement

A Fica 50 light-scattering photogoniometer was used, with vertically polarized light of 546 nm wavelength as the incident beam. Each test solution or the solvent was made optically clean by centrifuging for about 100 min at 11,000 g in a Sorvall RC2-B centrifuge and transferred directly into the light scattering cell using a pipet. Both the cell and pipet had been rinsed with acetone vapor for more than 6 h and completely dried.

Intensities of scattered light were measured at intervals of 2.5° in the range of scattering angle from 15° to 40° and at intervals of 15° in the range from 45° to 150°. No reliable data could be obtained at scattering angles below 15°. The cell constant was determined by the usual method, assuming $16.5 \times 10^{-6} \text{ cm}^{-1}$ for the Rayleigh ratio of pure benzene for unpolarized light of 546 nm and using 0.41 obtained for the depolarization ratio of benzene.

The values 0.111 and $0.1293 \text{ cm}^3 \text{ g}^{-1}$ were taken from the literature² for the specific refractive index increments of PMMA in MEK at 25°C and in

acetone at 25°C, respectively.

Viscometry

In view of the expected high molecular weights of the samples, the rotational viscometer of the Zimm-Crothers type described elsewhere³ was used, and the measurements were carried out at shear rates of about 7 s^{-1} . These shear rates were chosen on the basis of preliminary experiments indicating that the viscosities of our solutions were essentially independent of the shear rate G , if G was less than 25 s^{-1} .

RESULTS AND DISCUSSION

Light-Scattering Data

Figure 1 illustrates the angular variations of $(Kc/R_\theta)^{1/2}$ at five polymer mass concentrations c , for sample 178 in MEK at 25°C. Here, K is the familiar optical constant and R_θ is the reduced intensity of scattered light at the scattering angle θ . Similar data were obtained for samples 003 and 194 in MEK and for sample 194 in acetone. In Figure 2, the data of Figure 1 are replotted as Kc/R_θ against c for fixed values of θ . The set of data points for each θ is fitted

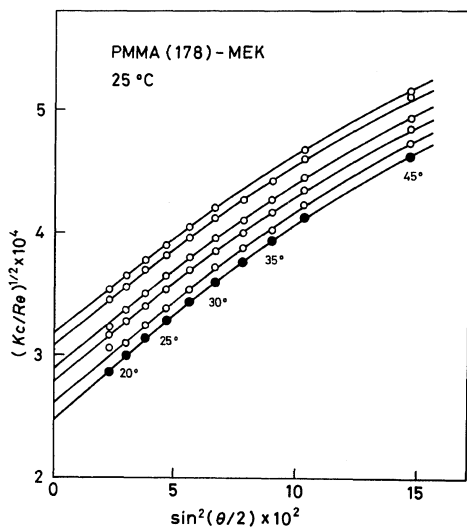


Figure 1. Angular dependence of reciprocal square-root of reduced scattering intensity for sample 178 in MEK at 25°C. Polymer concentrations are $2.08_5 \times 10^{-4}$, $1.66_5 \times 10^{-4}$, $1.23_1 \times 10^{-4}$, $0.84_2 \times 10^{-4}$, and $0.43_3 \times 10^{-4}\text{ g cm}^{-3}$ from top to bottom. Filled circles represent the values extrapolated to zero concentration.

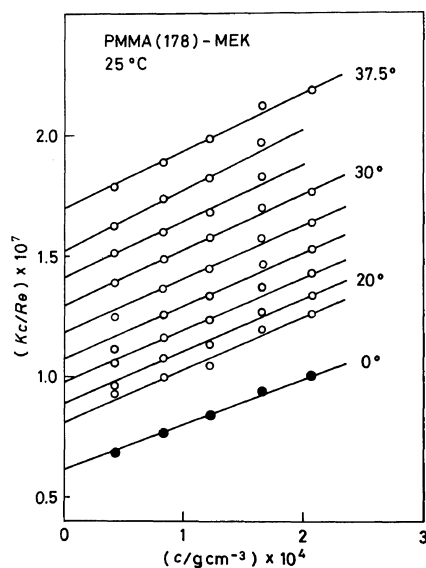


Figure 2. Reciprocal reduced scattering intensity at indicated angles as a function of polymer concentration for sample 178 in MEK at 25°C. Filled circles represent the values extrapolated to zero scattering angle.

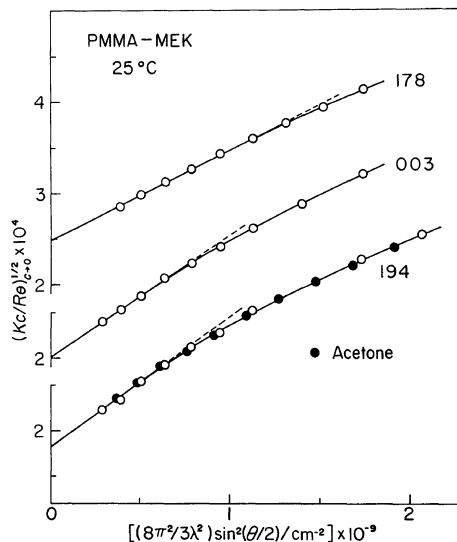
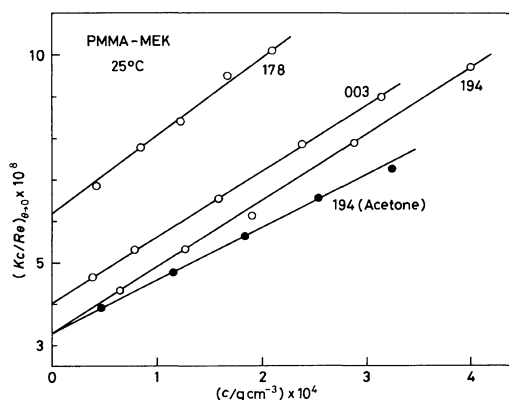


Figure 3. Reciprocal square-root of reduced scattering intensity at zero concentration as a function of scattering angle for three PMMA samples in MEK (unfilled circles) and for sample 194 in acetone (filled circles) at 25°C.

Table I. Numerical results from light scattering measurements on PMMA in MEK and acetone at 25°C

| Sample code | Solvent | $M_w \times 10^{-7}$ | $A_2 \times 10^5$ | $\langle S^2 \rangle_z^{1/2}$ |
|-------------|---------|----------------------|-------------------------------|-------------------------------|
| | | | $\text{cm}^3 \text{mol}^{-2}$ | nm |
| 178 | MEK | 1.61 ± 0.05 | 8.6 ± 0.3 | 199 ± 5 |
| 003 | MEK | 2.45 ± 0.07 | 7.5 ± 0.3 | 257 ± 7 |
| 194 | MEK | 3.00 ± 0.1 | 7.0 ± 0.7 | 280 ± 10 |
| 194 | Acetone | 3.00 ± 0.1 | 6.0 ± 0.5 | 280 ± 10 |


Figure 4. Reciprocal reduced scattering intensity at the zero scattering angle as a function of polymer concentration for three PMMA samples in MEK (unfilled circles) and for sample 194 in acetone (filled circles) at 25°C.

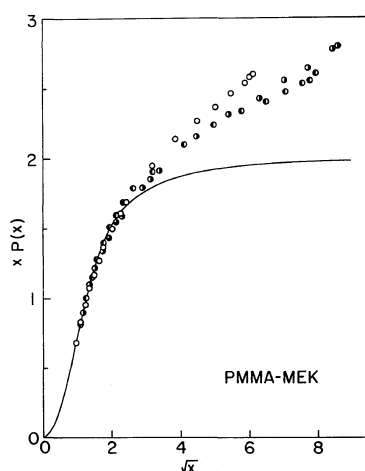
by a straight line, permitting the infinite-dilution value of Kc/R_θ to be estimated accurately. The filled circles in Figure 1 show the square-root of these infinite-dilution values as a function of $\sin^2(\theta/2)$. On the other hand, the filled circles in Figure 2 show the concentration dependence of the zero-angle values of Kc/R_θ extrapolated from the solid curves in Figure 1.

Figures 3 and 4 display the angular dependence of $(Kc/R_\theta)^{1/2}_{c=0}$ and the concentration dependence of $(Kc/R_\theta)_{\theta=0}$ for the four systems. Table I summarizes the values of the weight-average molecular weight M_w , the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$, and the second virial coefficient A_2 determined from these data. As was expected, essentially the same values were obtained for the weight-average molecular weights of sample 194 in MEK and in acetone. This agreement implies that the

polymer in these solvents is dispersed molecularly.

The feature of the plasma-initiated polymerization technique, *i.e.*, that it can yield a very high molecular weight, a property normally difficult to obtain by conventional initiation methods, is evident from the M_w values presented in Table I. Probably, the M_w value of sample 194 is the highest absolute molecular weight so far reported for PMMA.

In Figure 5 are shown the values of $xP(x)$ for the three samples in MEK as a function of $x^{1/2}$, where x is defined by $x = (4\pi/\lambda)^2 \langle S^2 \rangle^{1/2} \sin^2(\theta/2)$, with λ being the wavelength of the incident beam in the solution and $P(x)$ is the particle scattering function. The discrepancy of the plotted points from the Debye function indicated by the solid line suggests that these samples are not as homogeneous in


Figure 5. Particle scattering functions $P(\theta)$ represented as a plot of $xP(x)$ vs. $x^{1/2}$ for samples 178 (O), 003 (●), and 194 (◐) in MEK at 25°C. The solid line represents the Debye function for a monodisperse Gaussian coil.

molecular weight as expected originally.¹

Viscosity Data

Figure 6 shows the usual viscosity plots for the four systems studied. We note that these data refer essentially to the zero shear rate. Table II gives the values of intrinsic viscosity $[\eta]$ and the Huggins constant k' estimated from Figure 6. The k' values are normal, suggesting that our high-molecular-weight PMMA samples dispersed molecularly in both MEK and acetone.

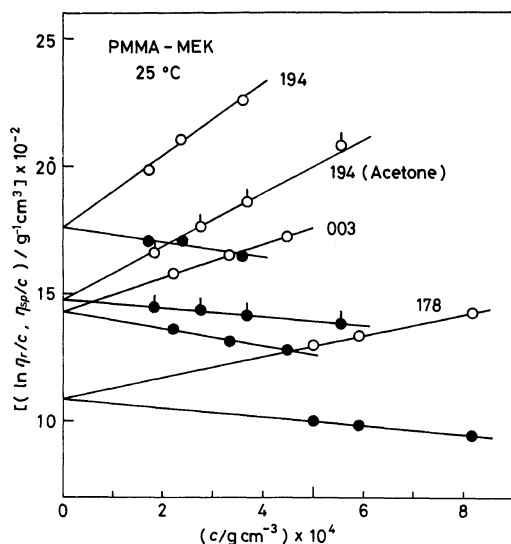


Figure 6. Concentration dependence of η_{sp}/c (unfilled circles) and $\ln \eta_r/c$ (filled circles) at the zero shear rate for three PMMA samples in MEK (without pip) and for sample 194 in acetone (with pip) at 25°C.

Table II. Numerical results from viscosity measurements on PMMA in MEK and acetone at 25°C

| Sample code | Solvent | $[\eta] \times 10^{-2}$ | k' |
|-------------|---------|-----------------------------|------|
| | | $\text{cm}^3 \text{g}^{-1}$ | |
| 178 | MEK | 10.9 ± 0.1 | 0.34 |
| 003 | MEK | 14.3 ± 0.2 | 0.33 |
| 194 | MEK | 17.6 ± 0.3 | 0.44 |
| 194 | Acetone | 14.8 ± 0.2 | 0.47 |

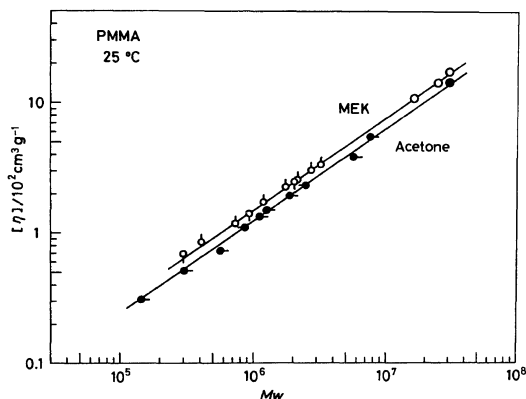


Figure 7. Molecular weight dependence of intrinsic viscosity $[\eta]$ for PMMA in MEK (unfilled circles) and in acetone (filled circles) at 25°C. Pip up, Chinai *et al.*⁴; pip down, Chinai and Bondurant;⁵ pip right, Schulz *et al.*⁶; pip left, Cohn-Ginsberg *et al.*⁷

Figure 7 shows the log-log plots of $[\eta]$ against M_w obtained from the present data and some typical literature data.⁴⁻⁷ For both MEK and acetone, the data points from the present study are consistent with the lines fitting the previous data on lower-molecular-weight samples. This fact implies that the PMMA samples from plasma-initiated polymerization are linear, thus containing neither branch nor intramolecular crosslinkage. The solid lines shown in Figure 7 are expressed by

$$[\eta] = (1.1 \pm 0.2) \times 10^{-2} M_w^{0.69 \pm 0.01} \quad (\text{MEK at } 25^\circ\text{C})$$

$$[\eta] = (5.7 \pm 0.2) \times 10^{-3} M_w^{0.70 \pm 0.01} \quad (\text{Acetone at } 25^\circ\text{C})$$

Acknowledgment. We should like to dedicate this paper to the late Professor M. Shen of the University of California, Berkeley, in the memory of his very kind friendship toward all of us. The interest of Dr. Y. Osada of Ibaraki University in this work is gratefully acknowledged.

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