

Osmotic and Viscometric Studies of Poly(methyl Methacrylate) in Butanone

Viscosity-molecular weight relationships of atactic poly(methyl methacrylate) (PMMA) have been studied by many workers in different solvents and at different temperatures. The results have been summarized and tabulated.¹ Reported dilute solution properties of PMMA in butanone, however, have been studied mostly by light scattering methods.²⁻⁶ In the present study, the number-average molecular weight \bar{M}_n and the intrinsic viscosity $[\eta]$ have been determined for several "ordinary" fractionated¹ PMMA. The viscosity-molecular weight relationships of PMMA in butanone at 25°C have been established, and the osmotic second virial coefficients A_2 have been calculated.

Elvacite 2021 and 2008 were obtained from the du Pont Company. High molecular weight PMMA, Esschem 12, was obtained from the Esschem Company, Essington, Pennsylvania. Elvacite 2021 and 2008 and Esschem 12 were each fractionated into three or four fractions by a fractional precipitation method.⁷ For both Elvacite 2021 and 2008, the low molecular weight fraction F_3 was discarded and the high molecular weight fractions F_1 and F_2 were used. For Esschem 12, the high and low molecular weight fractions F_1 and F_4 were discarded and the middle fractions F_2 and F_3 were used.

A Wescan Model 231 Recording Osmometer was used to measure osmotic pressure π on butanone solutions of polymers at 25°C. Three separate polymer solutions with concentrations between 2 and 8 g/l. were used for each polymer sample. The results of osmotic pressure measurements are shown in Figure 1. Solution viscosities of the butanone solvent and PMMA solutions were measured at 25°C by means of an Ubbelohde viscometer. The capillary size was so chosen that kinetic energy corrections were negligible. A Water Associates Model 202 gel permeation chromatograph was used to estimate the dispersity \bar{M}_w/\bar{M}_n of the polymer samples. The dispersity of the polymers are shown in Table I. Since calibration of the GPC column was made with polystyrene standards in tetrahy-

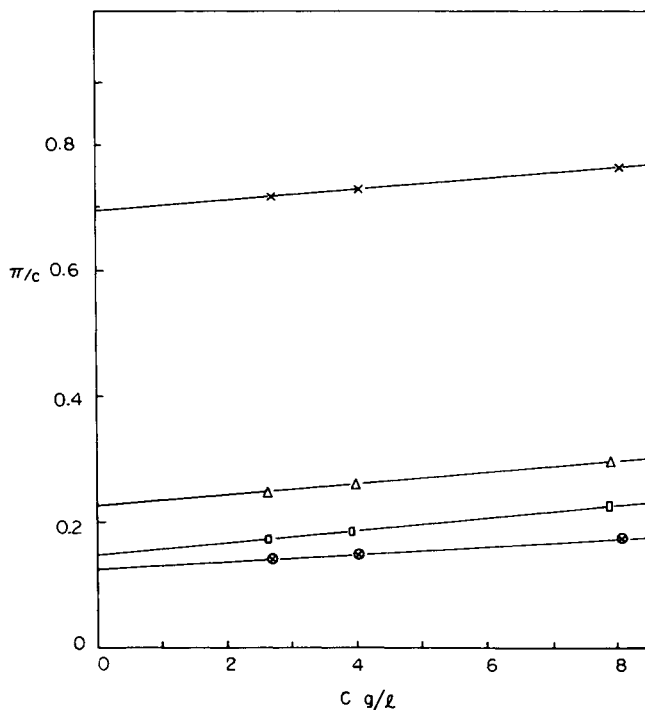


Fig. 1. Plot of π/c (π in cm butanone, C in g/l.) vs. C : (X) Elvacite 2008 F_1 ; (Δ) Elvacite 2021 F_2 ; (\square) Elvacite 2021 F_1 ; (\otimes) Esschem 12 F_3 .

TABLE I
Characterization of Poly(methyl Methacrylate)

Polymer	$[\eta]$, dl/g	$\bar{M}_n \times 10^{-5}$	$A_2 \times 10^4$, (cm ³ mole)/g ²	Dispersity \bar{M}_w/\bar{M}_n
Elvacite 2008F ₂		0.31	3.59	1.4
Elvacite 2008F ₁	0.18	0.45	2.66	1.4
Elvacite 2021F ₂	0.41	1.39	2.76	1.2
Elvacite 2021F ₁	0.54	1.97	2.64	1.4
Esschem 12F ₃	0.67	2.58	1.98	1.5
Esschem 12F ₂	1.12			1.5

drofuran at 25°C, the listed dispersity values may be in error. However, no attempt was made to calibrate the GPC column with poly(methyl methacrylate) standards.

The results of the present study are shown in Table I and Figures 1 and 2. In Figure 1, π/C is plotted as a function of concentration C . The number-average molecular weight \bar{M}_n was obtained by linear extrapolation of the π/C -versus- C plot to zero concentration. The osmotic second virial coefficient A_2 was obtained from the slope of the plot. The values of A_2 were found to show the expected decrease with increase in molecular weight, and they are in good agreement with the values determined by light scattering methods.^{3,4,6}

Intrinsic viscosities $[\eta]$ were obtained by extrapolation of both η_{sp}/C and $\ln(\eta_{rel})/C$ to infinite dilution. Figure 2 shows the plot of $\log [\eta]$ as a function of $\log \bar{M}_n$.

A least-squares analysis of the linear plot gave the following viscosity-molecular weight relationship:

$$[\eta] = 5.89 \times 10^{-5} \bar{M}_n^{0.75}$$

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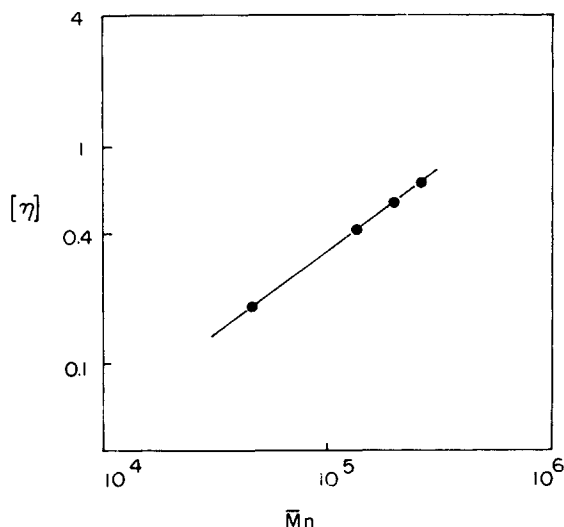


Fig. 2. Plot of $\log [\eta]$ vs. $\log \bar{M}_n$.

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