

Viscometric and Osmometric Determination of Molecular Masses of Fractionated Poly(methyl Acrylate)

INTRODUCTION

The relationship between the limiting viscosity number $[\eta]$ and the molecular mass M of a polymer is given by the Mark¹ equation

$$[\eta] = KM^\alpha. \quad (1)$$

Constants K and α apply to either a number- or a mass-average molecular mass, depending on whether they were evaluated from osmometry or light scattering measurements.

Sen, Chatterjee, and Palit² determined the number-average molecular masses of poly-(methyl acrylate) samples and found K and α to be 1.282×10^{-4} and 0.7143, respectively, in benzene solution at 35°C, while Matsuda, Yamano, and Inagaki³ found values of 4.5×10^{-6} and 0.79, respectively, at 30°C. However, Sen et al. determined their constants for unfractionated polymer samples with a wide molecular mass distribution, whereas Matsuda et al. used fractionated samples. Since we were interested in the values of the constants at 35°C for fractionated samples of poly(methyl acrylate), we decided to redetermine the constants.

EXPERIMENTAL

Polymerization and Fractionation

BDH laboratory reagent-grade methyl acrylate was distilled to remove the inhibitor and polymerized in methanol solution at 30°C in the presence of tertiary butyl perbenzoate as activator according to the method of Noro.⁴ On completion of the polymerization, the mixture was washed with methanol to remove unreacted monomer and the initiator, and the product was dried by pumping for 48 hr. Yields of about 95% were obtained after reaction periods of 4.5 hr.

Eleven fractions of approximately equal mass were precipitated from a 1% solution in acetone at 25°C by the dropwise addition of distilled water. After the formation of each fraction, the solution was heated to 45°C with constant stirring and held there for 1 hr until all the polymer had redissolved. The stirrer was then turned off and the solution allowed to cool in the thermostat overnight to 25°C, during which time reprecipitation of the fraction occurred. This procedure⁵ was followed to avoid the inclusion in any fraction of low molecular mass material precipitated owing to the high local concentration of nonsolvent during the addition of water. The polymer settled to the bottom of the flask and was easily separated from the solution. Fractions were dried by pumping for 48 hr, after which time no further loss in mass occurred.

Viscosity Measurements

Viscosities were measured in benzene solution at 35°C \pm 0.01°C using an Ostwald viscometer with a flow time for benzene of 199.3 sec. No corrections were made for the rate of shear.

Osmotic Pressure Measurements

Osmotic pressures were measured at 35°C in benzene solution using a Hewlett Packard Model 501 membrane osmometer. The instrument allows osmotic pressure to be read on a digital scale to 0.01 cm of solvent head, with a reproducibility of better than 0.05 cm between successive tests on the same sample. H.P. membrane 08 suitable for use with organic solvents was supplied packed in 50% isopropanol-50% water solution. The membrane was treated for successive 4-hr periods in 50% acetone-50% water, 100%

acetone, 50% acetone–50% toluene, 100% toluene, and 50% toluene–50% benzene and was finally conditioned in pure benzene for 24 hr prior to its use in the osmometer.

RESULTS AND DISCUSSION

Limiting viscosity numbers were calculated from plots of both the Huggins⁶ and Kraemer⁷ equations:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad (2)$$

$$\frac{\ln \eta_r}{c} = [\eta] - k''[\eta]^2c \quad (3)$$

Straight-line plots were obtained in either case, giving closely similar values of $[\eta]$, and the means of these values were used for each fraction. The slopes and intercepts of these and all other plots referred to were computed by the method of least-squares deviation to obtain the best fit to the experimental results. Number-average molecular masses were calculated from the well-known osmotic pressure–concentration relationship which yielded straight-line plots that could be accurately extrapolated to zero concentration for each fraction. The results are given in Table I, and constants K and α were eval-

TABLE I
Limiting Viscosity Numbers and Number-Average Molecular
Masses of Polymer Fractions

Fraction	$[\eta]$, dl/g	\bar{M}_n
2	0.840	3.731×10^6
3	0.532	1.659×10^6
4	0.404	9.747×10^4
5	0.337	7.674×10^4
7	0.216	4.307×10^4
8	0.171	2.982×10^4

uated from the plot of $\log [\eta]$ versus $\log \bar{M}_n$ shown in Figure 1.

Our values of $K = 2.55 \times 10^{-4}$ and $\alpha = 0.635$ for the fractionated polymer differ from those of Sen et al.² ($K = 1.282 \times 10^{-4}$ and $\alpha = 0.7143$) for unfractionated polymer. A particular set of constants for the Mark equation is dependent on the molecular mass distribution of the polymer samples, and the divergence between our results and those of Sen et al. is therefore not surprising.

However, there is an even larger difference between our results and those of Matsuda et al.³ ($K = 4.5 \times 10^{-5}$ and $\alpha = 0.79$), the latter determined at a slightly lower temperature. There are two possible factors that may account for these differences. Matsuda worked with polymers of a much higher number-average molecular mass than ours (150,000 to 1,500,000 compared to 30,000 to 373,000), and, while the Mark equation has been shown by many workers to be valid over a wide range of molecular masses, we find that when the results of Matsuda are plotted according to Figure 1, there is a slight curvature in the plot, tending to a reduced slope (α value) at lower molecular masses. Secondly, Matsuda et al. noted that after a year the values of $[\eta]$ of their polymer samples had changed and that \bar{M}_w had decreased by 15% to 23%, though the same $[\eta]$ – \bar{M}_w relationship still held. We encountered a similar problem after three months and found that unless the viscosity and osmometry experiments were conducted in reasonably quick succession for the same polymer fraction, the plot of the Mark equation became slightly curved and, furthermore, had a greater slope than that in Figure 1. Reproducible re-

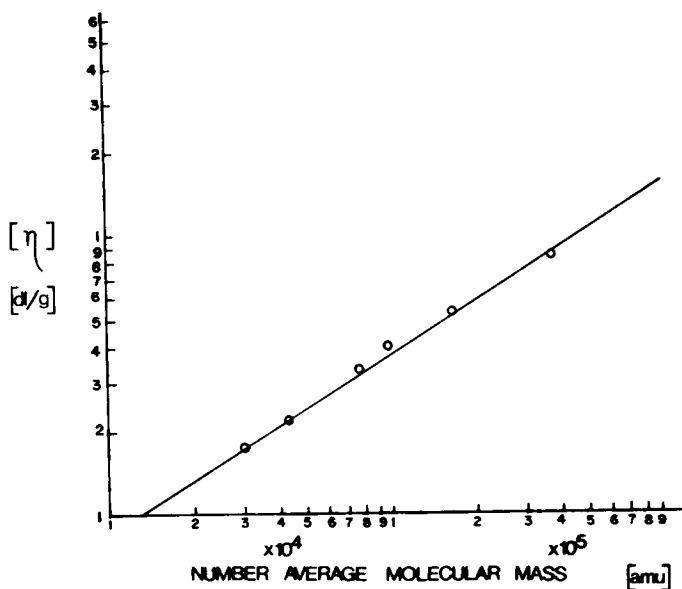


Fig. 1. Number-average molecular mass \bar{M}_n vs. limiting viscosity numbers in dl/g.

sults were possible only when all the work on a fresh preparation of polymer was completed in less than a month. When all the viscosity measurements were completed first, followed by the osmometry measurements of the same samples three months later, α was found to be approximately unity. The more concentrated solutions showed a definite yellowing on aging for a few months. We have no knowledge of the time taken by Matsuda et al. to complete their experiments.

Wunderlich⁸ has pointed out that the few values of K and α for poly(methyl acrylate) evaluated by light scattering methods reported in the literature are widely divergent. There have not, however, been similar reports of possible degradation effects.

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