

Mark-Houwink-Sakurada coefficients for conventional poly(methyl methacrylate) in tetrahydrofuran

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Summary

Intrinsic viscosities $[\eta]$ in tetrahydrofuran (THF) at 30°C are reported for ten narrow molecular weight distribution poly(methyl methacrylate) (PMMA) samples covering nearly two orders of magnitude in molecular weight. By combining the viscosity results with absolute weight-average molecular weights (\bar{M}_w) determined via low-angle laser light scattering (LALLS) experiments, we have accurately determined the Mark-Houwink-Sakurada (MHS) parameters for this polymer-solvent pair ($K = 7.56 \times 10^{-5}$ and $a = 0.731$, when $[\eta]$ is in dL g⁻¹).

Introduction

Recently Wagner (1) reported MHS relationships for PMMA in various solvents. The conclusion was reached that "there appears to be little agreement and poor documentation in the accounts describing the determination of the Mark-Houwink relation for poly(methyl methacrylate) in tetrahydrofuran". Indeed, although several MHS relationships have been reported for this polymer-solvent pair (2–7), the Polymer Handbook (8) lists only the equation

$$[\eta] = 7.5 \times 10^{-5} \bar{M}_w^{0.72} \quad (1)$$

where $[\eta]$ values, in dL g⁻¹, were measured at 25°C (2). An examination of reference 2 reveals that only four polymers of unspecified polydispersities were utilized in deriving Equation 1; details of molecular weight determinations are also vague. The PMMA data of reference 2 are plotted in Figure 1. Using an unweighted linear regression analysis (corr. coeff. = 0.974) we obtain

$$[\eta] = 1.08 \times 10^{-4} \bar{M}_w^{0.702} \quad (2)$$

a result substantially different from Equation 1. The availability of reliable MHS coefficients for PMMA in THF is desirable because PMMA is one of the most widely utilized polymers. Also, THF is the most commonly employed solvent for size exclusion chromatography (SEC). Reliable MHS parameters are essential for use of universal SEC calibrations employing this polymer.

In this paper, we report $[\eta]$ and \bar{M}_w values for a series of ten narrow molecular weight distribution PMMA samples covering almost two orders of magnitude in molecular weight. These data firmly establish MHS coefficients for this polymer-solvent system.

Experimental

The PMMA samples were obtained from a variety of sources. Several samples prepared by anionic polymerization were purchased from Pressure Chemical Company and Polymer Laboratories. The lowest molecular weight specimen was prepared via anionic polymerization at the University of Athens. Other polymers were obtained by fractionation of free-radically polymerized materials, as previously described (9).

Both ¹³C-NMR and ¹H-NMR were used to probe tacticity of the polymers. All

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materials contained between 76 and 80% racemic diads ("conventional PMMA"). Polydispersities were examined in THF at 1 mL min⁻¹ using SEC with linear Ultrastaygel columns from Waters Associates. The columns were calibrated using well-defined commercial PMMA standards.

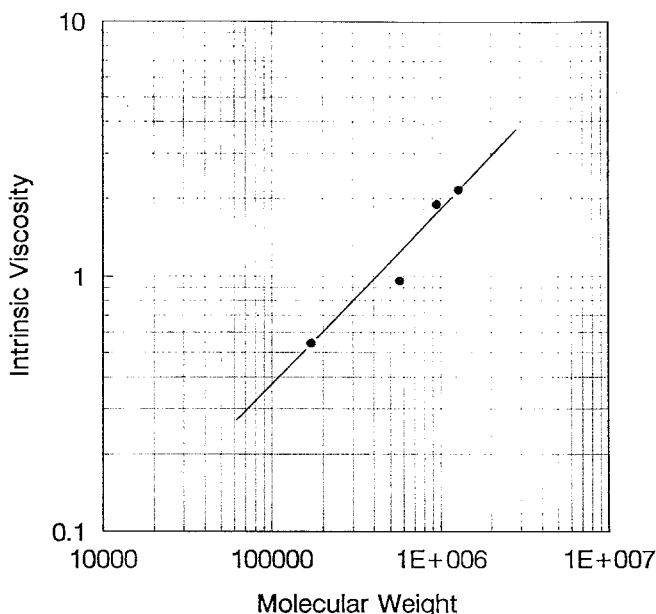


Figure 1: Double logarithmic plot of intrinsic viscosity (in dL g⁻¹) versus molecular weight for PMMA in THF at 25°C (2).

LALLS experiments were conducted in purified butanone (Fisher Scientific, ACS Certified, > 99.5 mole % pure) at 25°C. A Chromatix KMX-6 photometer was employed. This unit has a He-Ne laser source operating at 633 nm. Refractive index increments were measured under the same conditions with both Chromatix and Otsuka differential refractometers. The measured dn/dc values for the various samples ranged between 0.110 and 0.114 mL g⁻¹.

Intrinsic viscosities and Huggins coefficient k_H were measured in THF using Cannon-Ubbelohde dilution viscometers. At a temperature of 30.0 ± 0.02°C, solvent flow times of about 129 sec were obtained, so kinetic energy corrections could safely be ignored. Five concentrations of each polymer were used; concentrations were chosen so that relative viscosities ranged between about 1.5 and 1.1. The THF was Fisher ACS Certified grade and contained 0.025% BHT as a stabilizer.

Results and Discussion

Molecular characteristics, intrinsic viscosities and Huggins coefficients of the samples are listed in Table 1. These polymers encompass a very broad range of molecular weights and exhibit narrow, symmetrical polydispersities. The Huggins coefficients range between about 0.3 and 0.4. These are the values expected for linear flexible chains in good solvents (10), and they thus fortify the accuracy of the viscometric measurements.

The MHS plot is given in Figure 2. The data are strictly linear over the range of molecular weights studied. The following MHS equation (corr. coeff. = 0.9997) is obtained:

$$[\eta] = 7.56 \times 10^{-5} \bar{M}_w^{0.731} \quad (3)$$

This equation is similar to that cited in the Polymer Handbook (8) based on an unspecified fit to the data of reference 2, which were obtained at 25°C.

Small temperature differences should have negligible impact on $[\eta]$ values measured in thermodynamically good solvents. We therefore feel that Equation 3 should be applicable with good accuracy to data obtained at either 25 or 30°C.

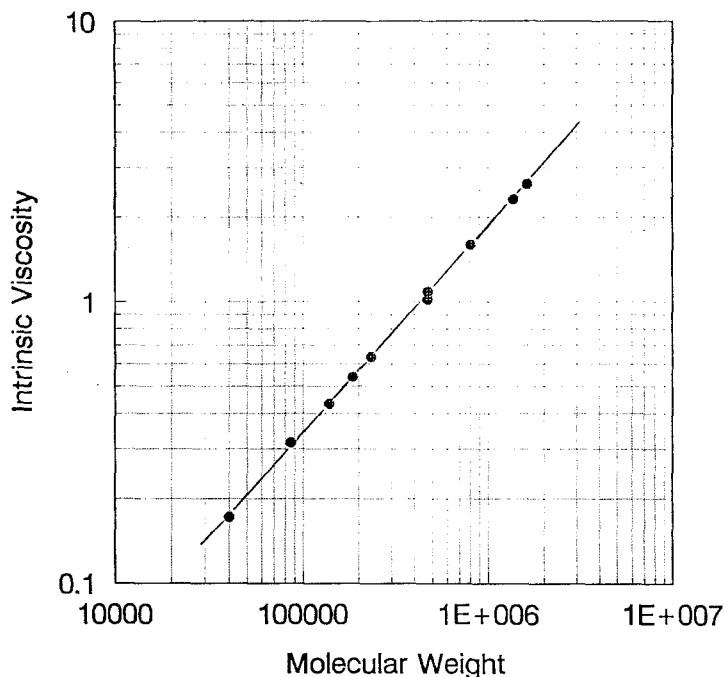


Figure 2: Double logarithmic plot of intrinsic viscosity versus molecular weight for PMMA in THF at 30°C.

Table 1: Measured Properties of Poly(methyl methacrylate) Samples

$\bar{M}_w \times 10^{-4}$ (g mol ⁻¹)	$\frac{\bar{M}_w}{\bar{M}_n}$	$\frac{\bar{M}_z}{\bar{M}_w}$	THF, 30°C	
			$[\eta]$ (dL g ⁻¹)	k_H
4.00 ^a	1.12	1.09	0.172	0.40
8.57 ^b	1.17	1.14	0.316	0.33
13.8 ^b	1.22	1.16	0.432	0.39
18.6 ^b	1.18	1.17	0.539	0.34
23.3 ^b	1.24	1.25	0.637	0.27
46.9 ^b	1.34	1.29	1.02	0.41
47.3 ^a	1.06	1.07	1.09	0.32
80.1 ^a	1.10	1.09	1.60	0.30
137 ^a	1.11	1.11	2.31	0.32
162 ^a	1.13	1.12	2.62	0.31

a) Products of anionic polymerization.

b) Products of free radical polymerization.

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