## Determination of the Hydrodynamic Radii of Poly(p-isopropyl α-Methylstyrene) by Photon Correlation Spectroscopy

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## ABSTRACT

The mean hydrodynamic radius of poly(p-isopropyl $\alpha$-methylstyrene) in toluene has been determined at 21.5°C as a function of weight-average molecular weight $\overline{M}_w$ from 18,000 to 625,000 dalton. The measurements of hydrodynamic radii were made using photon correlation spectroscopy with a convenient specially designed filtering system to remove dust from the samples. The coefficients in the relationship $D = CM^{-a}$ have been determined for our polydisperse samples. Although the polydispersity severly affects the determination of C, we have determined a = 0.57 ± 0.03 in agreement with theories for linear chains in good solvent. We also report the first determinations of the Huggins coefficients for poly(p-isopropyl $\alpha$-methylstyrene).

## INTRODUCTION

The relationship between diffusion constant and molecular weight is of interest in the theory of dilute solutions as well as being of practical importance in the determination of molecular weight and the molecular weight distributions of unknown samples. If the coefficients in the relationship $D = CM^{-a}$ are known for a particular

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polymer, then a determination of D for any sample can be used to determine the $\overline{M}_w$ and molecular weight distribution [1] of that sample.

Previous work in determining C has focused on measurements on monodisperse polystyrene [2, 3] and, recently, monodisperse poly-($\alpha$-methylstyrene) [4]. The requirement for monodisperse samples places severe restrictions on the polymers that can be analyzed. In this paper we report the determination of the diffusion constant and hydrodynamic radius of samples of poly(p-isopropyl $\alpha$-methylstyrene) in toluene at 21.5°C by heterodyne photon correlation spectroscopy. The samples, obtained from Malhotra et al. [5], had molecular weights ranging from 18,000 to 625,000 dalton [1]. The molecular weight distributions of these samples have been analyzed by GPC [6] and have no irregular features.

In order to make these measurements it was necessary to use a flow-through cell with a filtering system to eliminate dust. Heterodyne, rather than homodyne, spectroscopy was used because this allowed measurements at substantially lower concentrations of polymer in solvent. At these low concentrations the effect on D of interactions between molecules can be neglected.

The cell, filtering system, and spectrometer are described in the next section. The results are analyzed and discussed in the following section, and our conclusions are presented in the final section.


## SCATTERING CELL AND SPECTROMETER


The optics of the spectrometer was of a conventional design. Approximately 100 mW of light from a Spectra Physics model 165 Ar$^+$ laser operating at 514.5 nm was focused with a 61-cm focal length lens into a rectangular cell containing the sample. The scattered light from a single coherence area was collected by a cooled RCA model C31034-RF photomultiplier operating in the photon-counting mode. A single-clipped digital autocorrelator was used to determine the autocorrelation function.

The light scattering-cell was 3.5 cm long with a 1-cm square cross section. The scattering angle was 20.23°, corrected for refraction, and stray light from the cell walls acted as the local oscillator for heterodyning.

The filtering system depicted in Fig. 1 was connected to the flow-through quartz scattering cell. Prior to recording the spectrum, each sample was filtered for 20 min through a 0.2-$\mu$m fluoropore filter. After filtering for 15 min the scattered light intensity was constant, indicating that the dust had been removed. The autocorrelation function did not change with subsequent filtering, indicating that filtering for these short periods of time did not seriously damage the polymer.
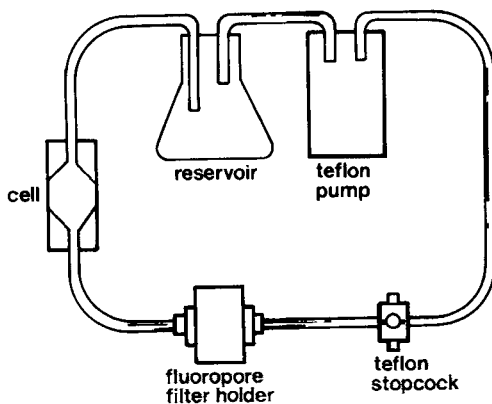
FIG. 1. Light-scattering cell and filtering system used to remove dust from the samples.
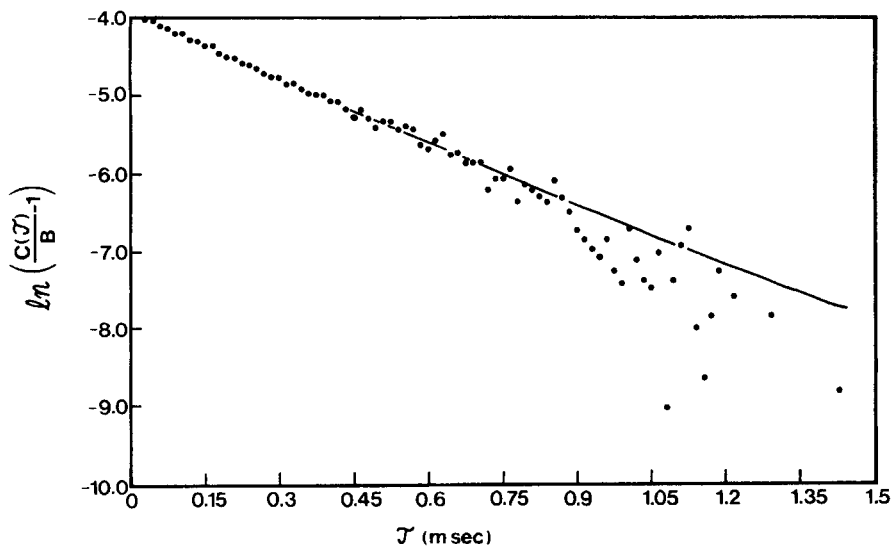


FIG. 2. Heterodyne spectrum for poly(p-isopropyl $\alpha$-methyl-styrene) dissolved in toluene. ● : Data points for sample with $\overline{M}_w$ = 40,000. Curve fit to the data with a two-term cumulant expansion.

TABLE 1.[a]  Hydrodynamic Radius $r_h$ from Photon Correlation Spectra Compared to Data from Ref. 5

| Sample | Conc. (mg/mL) | Ve (5 mL counts) | $[\eta]$ dl/g | $k_H$ | $\overline{M}_w \times 10^{-5}$ g | $\overline{M}_n \times 10^{-5}$ g | $K^{SZ}$ | $K^{LN}$ | $\langle S^2 \rangle^{1/2}_z$ (Å) | $r_h$ (Å) | $\dfrac{r_h}{\langle S^2 \rangle^{1/2}_z}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S-20 | 0.3 | 25.9 | 0.120 | - | 0.18 | 0.156 | .98 | .98 | - | 28 | - |
| S-23 | 0.3 | 25.0 | 0.165 | 0.52 | - | 0.288 | .97 | .96 | - | 46 | - |
| S-5 | 0.3 | 24.7 | 0.178 | 0.36 | 0.40 | 0.204 | .94 | .92 | - | 52.5 | - |
| S-17 | 0.2 | 24.5 | 0.255 | 0.30 | 0.75 | 0.348 | .94 | .91 | - | 63 | - |
| S-15 | 0.1 | 23.6 | 0.440 | 0.42 | 2.40 | 0.682 | .92 | .86 | 272 | 150 | .55 |
| S-25 | 0.01 | 23.6 | 0.600 | 0.33 | 4.15 | 1.314 | .92 | .87 | 336 | 191 | .57 |

[a] $\overline{M}_W$ and $\langle S^2 \rangle^{1/2}_z$ are the molecular weight and radius of gyration obtained from conventional light–scattering measurements, and $\overline{M}_N$ was obtained by osmometry.  Ve and $[\eta]$ represent the GPC elution volumes and intrinsic viscosities of the samples.  Also shown are the concentrations of the samples used in the PCS measurements. $k_H$ is the Huggins coefficient.  Huggins coefficient for branched samples of poly(p-isopropyl $\alpha$-methylstyrene) ($\overline{M}_W = 0.66 \times 10^5$ to $1.7 \times 10^6$ series F in Ref. 3) ranged between 0.47 to 0.71, the value being higher in THF as compared to that in toluene.
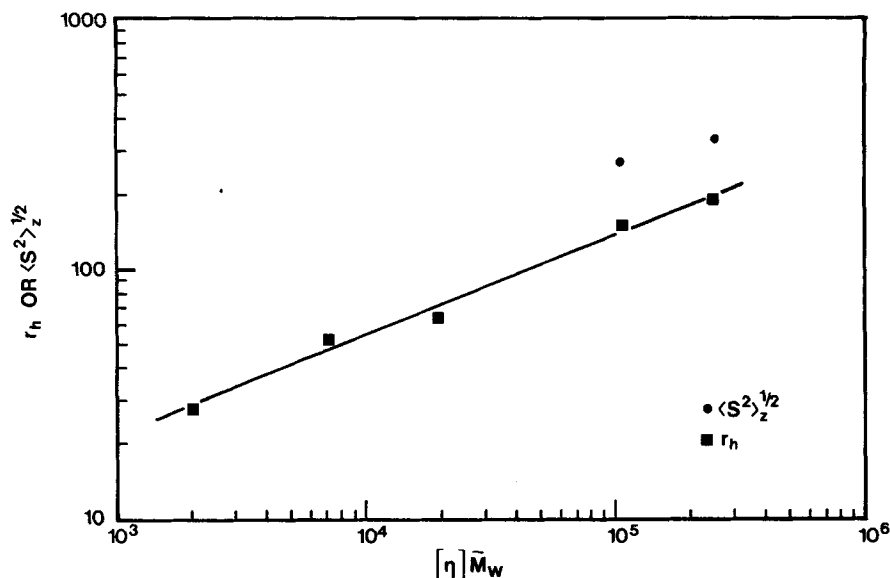
FIG. 3. Plot of $r_h$ and $\langle S^2 \rangle_z^{1/2}$ versus elution volume for poly(p-isopropyl α-methylstyrene).

The cell was maintained at a temperature of 21.5 ± 0.3°C by a copper ballast block. At this temperature the viscosity of the toluene solvent was $0.583 \times 10^{-3}$ kg/m-s.

## ANALYSIS OF RESULTS

Each spectrum was analyzed by the method of cumulants [7]. The cumulant expansion was fit to

$$K(\tau_j) = \ln (C(\tau_j)/B - 1) \tag{1}$$

where $C(\tau_j)$ is the content of the autocorrelator in channel j and B is the baseline at long correlation times. From the first and second terms in the cumulant expansion, we determined the z-average diffusion constant $\langle D \rangle_z$ and a measure of the width of the distribution of particle sizes. Figure 2 shows a fit to a 96 channel PCS spectrum of sample S-5 having $\overline{M}_w$ = 40,000. Table 1 shows the hydrodynamic radii $r_h$ for our poly(p-isopropyl α-methylstyrene) samples, obtained from the relation
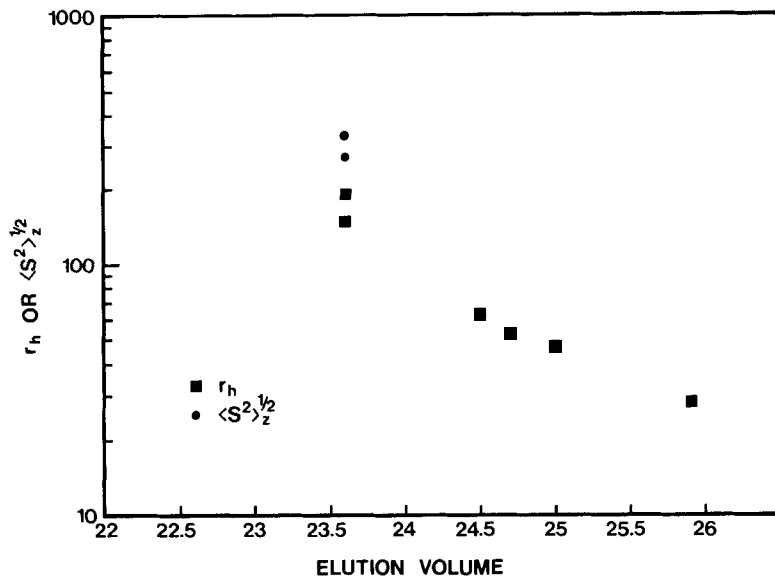
FIG. 4. Plot of hydrodynamic radius $r_h$ and radius of gyration $\langle S^2 \rangle^{1/2}$ vs $[\eta] M_w$ for poly(p-isopropyl $\alpha$-methylstyrene).

$$r_h = \frac{kT}{6\pi\eta \langle D \rangle_z} \tag{2}$$

where $\eta$ is the viscosity of the toluene solvent, T the absolute temperature, and k Boltzmann's constant. Also shown in Table 1 are the data obtained by Malhotra et al. [5] for the same samples dissolved in toluene. Table 1 also shows Huggins coefficients measured, but not reported, previously.

Figure 3 shows a plot of log $r_h$ versus elution volume Ve obtained by GPC. Figure 4 shows a log-log plot of $r_h$ versus $[\eta]\overline{M}_w$ from Malhotra's data. This curve can be used as a calibration curve for determining $\overline{M}_w$ from measurements of $[\eta]$ and $r_h$.

Also shown in Fig. 4 is the radius of gyration $\langle S^2 \rangle_z^{1/2}$ versus $r_h$ for the high molecular weight samples. For low molecular weight samples, the determination of $\langle S^2 \rangle_z^{1/2}$ by conventional light-scattering is extremely difficult while the measurements of $r_h$ by PCS is still relatively straightforward. Note that the hydrodynamic radius
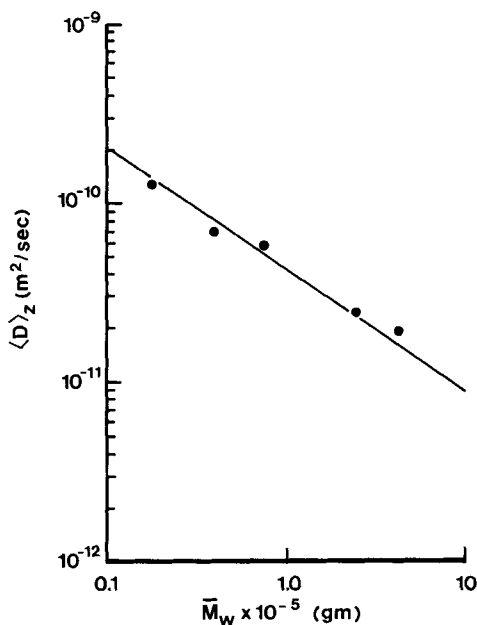
FIG. 5. Plot of diffusion constant $\langle D \rangle_z$ vs $M_w$ for poly(p-isopropyl α-methylstyrene).

is always smaller than the radius of gyration as expected, and for the two samples for which radius of gyration $\langle S^2 \rangle_z^{1/2}$ was measured, $r_h / \langle S^2 \rangle_z^{1/2}$ agrees closely with the theoretical value of 0.54 calculated by Akcasu and Han [8]. Selser [4] recently found $r_h / \langle S^2 \rangle_z^{1/2}$ = 0.54 for poly(α-methylstyrene) in good solvent.

Figure 5 shows $\overline{M}_w$ obtained by conventional light-scattering plotted against $\langle D \rangle_z$ measured for our polydisperse samples by PCS. The straight line fit to the data by linear regression gives

$$\langle D \rangle_z = (5 \pm 2) \times 10^{-8} \overline{M}_w^{-(0.61 \pm 0.04)} \qquad (3)$$

Assuming

$$D = CM^{-a} \qquad (4)$$

it can easily be shown that for a Shultz-Zimm distribution

$$\langle D \rangle_z = CK^{SZ} \overline{M}_w^{-a} \qquad (5)$$

where

$$K^{SZ} = \frac{\Gamma(2 - a + k)}{\Gamma(2 - a)(k + 1)^{-a}} \qquad (6)$$

and $k = 1/(\overline{M}_w/\overline{M}_n - 1)$. Analogous correction factors $K^{LN}$ can be determined for a log-normal distribution:

$$K^{LN} = \left( \frac{\overline{M}_w}{\overline{M}_n} \right)^{a/2(a-1)} \qquad (7)$$

$K^{LN}$ and $K^{SZ}$ are shown in Table 1 for $a = 0.6$ and the $\overline{M}_w$ and $\overline{M}_N$ determined by Malhotra et al. Using the factors $K^{LN}$, we find for a fit to the data

$$\langle D \rangle_z / K^{LN} = (4 \pm 2) \times 10^{-8} \overline{M}_w^{-(0.57 \pm 0.03)} \qquad (8)$$

Thus the errors in the determination of C are large. However, the value of a is not changed significantly by including the correction factors. The values of a in the range $a = 0.57$ to $a = 0.61$ are close to the values in the range $a = 0.59$ to $a = 0.60$ expected for linear chains in a good solvent [8-10].

CONCLUSIONS

It is possible, even with relatively polydisperse polymers, to determine the exponent in the power law relating diffusion constant to molecular weight. The constant coefficient in the relationship, however, is less precisely determined by photon correlation spectroscopy. We can conclude that poly(p-isopropyl $\alpha$-methylstyrene) is in the excluded volume regime in toluene at 21.5°C. With C and a, the measurement of diffusion constant for any unknown sample of this polymer should quickly give $\overline{M}_W$. This method of molecular weight determination is particularly useful where GPC is inconvenient or impossible.

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