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Solution Characterization of Poly(isobornyl Methacrylate) in Tetrahydrofuran

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SYNOPSIS

Thermodynamic and hydrodynamic properties of dilute solutions of poly(isobornyl methacrylate) (PIMA) in tetrahydrofuran (THF) were characterized by using viscosity, static, and dynamic light scattering measurements. PIMA samples with different molecular weight were obtained by fractional precipitation of PIMA solution. Chain dimension parameters (R_g and R_H), together with second virial coefficient A_2 and intrinsic viscosity $[\eta]$, were used to calculate various solution parameters characterizing polymer chains in polymer solutions. The experimental results are compared with calculation, indicating that PIMA behaves as a flexible coil in THF. © 1994 John Wiley & Sons, Inc.

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INTRODUCTION

Amorphous atactic poly(methyl methacrylate) (PMMA) is currently used for fiber optics applications, due to its transparency in the visible region. Because of its glass transition temperature of ca. 100°C, PMMA's fiber optics applications are limited to about 80°C. However, by replacing methyl in the ester group with isobornyl, one obtains poly(isobornyl methacrylate) (PIMA), which has a considerably higher T_g ($\approx$ 150°C). PIMA is heat resistive and also exhibits superior optical transparency. It presents an alternative choice for a variety of fiber optics applications. We have in recent years carried out extensive investigations of optical and mechanical properties of PIMA and of PIMA/PMMA copolymers. Results of this research will be published elsewhere. In this communication we present solution characterization data of PIMA by static and dynamic light scattering, and by viscometry and size exclusion chromatography (SEC).

EXPERIMENTAL

Poly(isobornyl methacrylate) was prepared by a standard free radical polymerization procedure. Pure IMA monomer was provided by Rohm & Hass Co. It was purified by vacuum distillation to remove inhibitor. An equal amount of purified IMA was placed in each of several test tubes; with 0.2 wt % of benzoyl peroxide initiator added to each tube. Test tubes containing monomers and initiator were flame sealed and placed in an oven for controlled polymerization by a gradual temperature increase of 10°C every 24 h, raising from 40° to 160°C. Transparent rods free from the presence of monomer were obtained after 12 days of polymerization. After completion of the polymerization process, narrow molecular weight distribution fractions of the polymer ($\bar{M}_w/\bar{M}_n < 1.13$) were obtained by fractional precipitation from tetrahydrofuran–water (THF-H_2O) mixtures at 25°C. Here $\bar{M}_w$ and $\bar{M}_n$ are weight- and number-average molecular weights, respectively. Several synthesized PIMA rods were dissolved in THF in a vessel to yield a solution containing about 3 wt % of PIMA. The PIMA/THF solution was subject to vigorous agitation in a constant temperature bath kept at 22°C. Nonsolvent (water) was then slowly added in a dropwise manner to the solution until the solution began to turn milky. A specified amount of water was then added to precipitate the fraction of PIMA with the highest molecular weight. To collect the PIMA precipitate, we stopped the agitation and keep the milky solution for several hours until the clear solution is separated from the precipitate. The precipitated PIMA was first separated by si-

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phoning off the clear solution and appeared as slurry after most of the clear solution was siphoned off. THF was then added to dissolve the PIMA slurry before a large amount of nonsolvent (H_2O) was finally added to precipitate most of the PIMA polymer which appears as solid powder. The powder was collected on a glass filter and dried at 50°C in vacuum.

To obtain the next weight fraction, the supernatant liquid was treated with another specified amount of nonsolvent; the procedure described above was repeated to obtain the next highest molecular weight fraction of PIMA polymer. Several weight fractions of PIMA were obtained, we ended up with a large amount of supernatant liquid containing PIMA with small molecular weight fraction. The solution was then concentrated to a convenient volume under reduced pressure. The final fraction was obtained by evaporating the supernatant liquid to dryness. The SEC measurements were used to determine the polydispersity index ($\bar{M}_w/\bar{M}_n$) of each weight fraction obtained above. For this a total of 0.5 μL of each sample at a concentration of approximately 0.1% by weight of PIMA was injected onto a single silica gel column (Waters Co.) using THF (at 25°C) as the mobile phase and a differential refractometer as the concentration detector. The flow rate was 0.5 ml/min. Waters μ-Bondagel column was used. The optimum molecular weight range for this column is from 2,000 to 2×10^6. The column was calibrated with a series of narrow distribution polystyrene standards. Calculations of average molecular weights and polydispersity were carried out by using a program provided by Waters Co. (Waters 730 data processor). While the value of molecular weight obtained from SEC may be affected by the polymer standards used, the polydispersity index will be only slightly affected by the standards.

Dilute solution viscosities were measured with a Cannon Ubbelohde viscometer equipped with a timer. The flow times were chosen in such a way that the kinetic energy corrections were negligible. The intrinsic viscosity, $[\eta]$, of PIMA in THF was determined by extrapolation of the reduced specific viscosity η_{sp}/c, to zero polymer concentration according to the Huggins equation:

$$\eta_{sp}/c = (\eta_{rel} - 1)/c = [\eta] + k[\eta]^2c + \cdots \quad (1)$$

where $\eta_{rel} = \eta/\eta_0$ with η and η_0 being the viscosities of the solution and solvent (THF), respectively. Shown in Figure 1 are plots of the reduced viscosity η_{sp}/c as a function of polymer concentration c (in g/ml) for each fraction of PIMA. The value of $[\eta]$ for each PIMA fraction was obtained by extrapolating the reduced viscosity to infinite dilution. The values of $[\eta]$ at 25°C are listed in Table I.

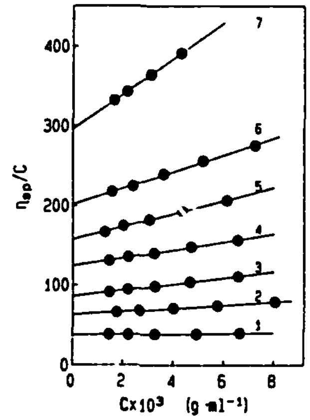

Figure 1. Reduced viscosity plotted versus concentration of PIMA in THF for each PIMA sample fractionally precipitated from THF-H_2O mixture at 25°C.

The glass transition temperature T_g were measured with differential scanning calorimetry (DSC) (Perkin Elmer Delta-7 series); the heating rate was 10°C/min. The T_g values obtained are also given in Table I. For the T_g determination, we have calibrated the instrument with three standards indium (melting temperature T_m = 156.60°C) C_{36} (T_m = 73.84°C) and Zn (T_m = 419.47°C). At $\bar{M}_w = 2.15 \times 10^5$ g/mol, T_g is about 150.4°C, and it increases slightly with $\bar{M}_w$ and reaches the asymptotic value of 165°C at high $\bar{M}_w$. Our result for T_g is in agreement with Tatsukami et al.,[1] but is considerably higher than the value of 110°C given in polymer Handbook.[2]

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The static and dynamic light scattering measurements were carried out with a Brookhaven Model BI-200 SM goniometer equipped with a BI-2030 correlator. A Spectra-Physics Model 125 He-Ne laser at λ = 632.8 nm and at the power of 15 mW was the light source. Decalin was used as a refractive index matching liquid. The sample temperature was controlled at 25 ± 0.1°C for all experiments. The differential refractive index increments at 632.8 nm for PIMA in THF were determined to be: $dn/dc = 0.108$ cm³/g, using a Chromatic KMX-16 differential refractometer. The refractive index of the polymer solution was measured with an Abbe refractometer (Reichert Mark II model). The light scattering spectrometer was calibrated with benzene for which the Rayleigh ratio at λ = 632.8 nm is 12.6

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Table I. Thermodynamic and Hydrodynamic Parameters of PIMA in THF at 25°C

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$\bar{M}_w \times 10^{-4}$, g/mol	[η], cm³/g	$D_0 \times 10^7$, cm²/s	R_h (nm)	Rg (nm)	$A_2 \times 10^4$, mol · ml/g² Experimental	$A_2 \times 10^4$, mol · ml/g² Theoretical	Tg (°C)
2.15	37.3	5.98	10.1	13.8	2.06	2.27	150
4.45	63.8	3.78	16.0	21.7	1.79	2.09	153
7.10	88.5	2.83	21.4	29.0	1.59	1.96	161
10.7	124	2.21	27.4	36.7	1.43	1.78	162
14.7	156	1.90	31.8	43.3	1.26	1.48	162
22.4	201	1.50	40.3	55.2	1.16	1.31	163
32.7	296	1.18	51.0	71.3	1.14	1.24	165

$\times 10^{-6}$ cm^{-1}.[3] *To ascertain the light scattering result* of $\bar{M}_w$, we also carried out static light scattering experiments of PIMA in cyclohexane (CH). Our molecular weight result of PIMA in CH is consistent with that previously obtained by Hadjichristidis.[4]

RESULTS AND DISCUSSION

Static light scattering from polymer solutions is interpreted according to the relation[6]

$$\frac{Kc}{R_\theta} = (1/\bar{M}_w + 2A_2c + \cdots) \times (1 + q^2R_g^2/3 + \cdots) \quad (2)$$

where the optical constant $K = \dfrac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4}$, and the amplitude of the scattering vector $q = (4\pi n/\lambda)\sin(\theta/2)$. Here R_θ is the Rayleigh factor at scattering angle θ (the solvent contribution is subtracted out); $\bar{M}_w$ is the weight-average molecular weight, A_2 is the z-average second viral coefficient, c is the concentration in g/mL, n_0 and n are the refractive indices of the solvent and solution, respectively. N_A is Avogadro's constant, and λ is the wavelength of the incident light in vacuum, R_g is the z-average radius of gyration.

Systematic measurements of the intensity of the scattered light at various scattering angles and polymer concentrations were carried out. The results obtained for one molecular weight fraction are shown in Figure 2 as the Zimm plot.[6] From eq. (2) we obtain the values of $\bar{M}_w$, A_2, and R_g by simultaneous extrapolation of Kc/R_θ to zero scattering angle and to infinite dilution in the Zimm plot. The results are listed in Table I for the PIMA samples with different molecular weights. The intensity data are reproducible to within 5%; we expect the $\bar{M}_w$, *A_2 and R_g values to be accurate to* within 10%. Over the molecular weight range, R_g (in cm) varies with molecular weight $\bar{M}_w$ (in g/mol) according to (Fig. 3)

$$R_g = 9.51 \times 10^{-10} \bar{M}_w^{0.59} \quad (3)$$

Shown in Figure 4 is the logarithmic plot of the second virial coefficient A_2 with respect to the molecular weight $\bar{M}_w$. Over the molecular weight range studied, A_2 decreases with increasing molecular weight, given by the power law relation:

$$A_2 = 3.66 \times 10^{-3} \bar{M}_w^{-0.23} \text{ (mol. ml/g}^2) \quad (4)$$

The Mark-Houwink-Sakurada plot for PIMA in THF is presented in Figure 5. The power law relationship for [η] versus $\bar{M}_w$ is

$$[\eta] = 3.80 \times 10^{-3} \bar{M}_w^{0.748} \text{ (cm}^3\text{/g)} \quad (5)$$

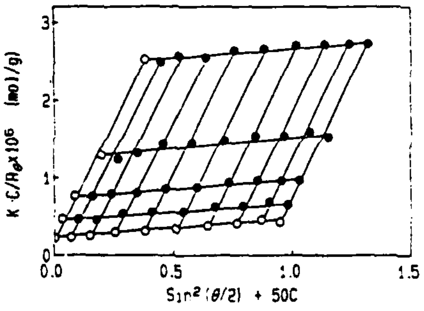

Figure 2. Zimm plot of the light scattering intensity of a PIMA fraction in THF at 25°C. Solid circles are experimental data and empty circles values obtained by extrapolation to zero angle and zero concentration.

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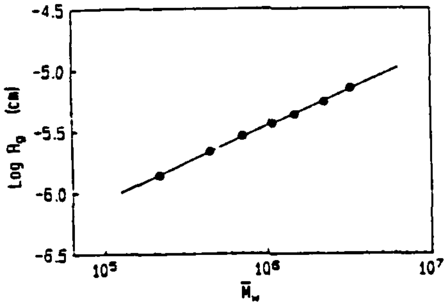

Figure 3. Root mean square radius of gyration R_g from light scattering versus molecular weight $\bar{M}_w$ power law plot for PIMA in THF.

This result is in reasonable agreement with that by Hadjichristidis et al.[13]

For dynamic light scattering the time correlation functions were collected in the homodyne mode at various scattering angles. The homodyne time correlation function $G(t)$ for the dilute PIMA/THF polymer solution is analyzed by the method of cumulants:[7]

$$\ln\left(\frac{G(t)}{A}-1\right)^{1/2} = \ln b^{1/2} - \Gamma t + \mu_2 t^2/2 + \cdots \qquad (6)$$

where A is the baseline and b is the contrast factor. The diffusion coefficient D_c at the concentration c is obtained from the first cumulant according to

$$D_c = \lim_{q\to 0} (\Gamma/q^2) \qquad (7)$$

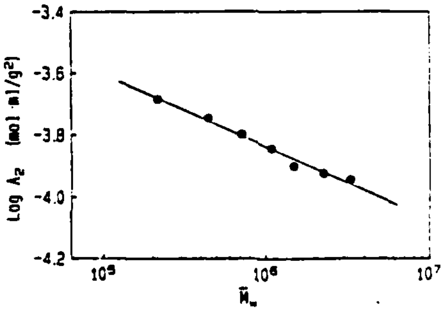

Figure 4. Second virial coefficient A_2 versus molecular weight $\bar{M}_w$ power law plot for PIMA in THF at 25°C.

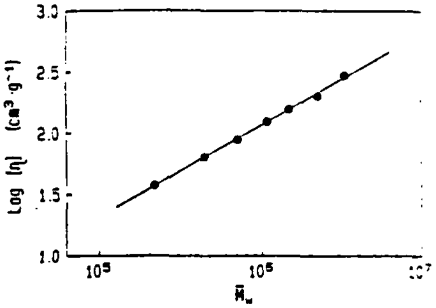

Figure 5. Mark-Houwink-Sakurada plot for PIMA in THF at 25°C.

When Γ is the decay rate constant of the time correlation function. The fractional standard deviation *is related to the first and second cumulants by* μ_2/Γ^2, which is found to be negligible for the present dilute solutions of the PIMA sample, indicating that the PIMA sample is nearly monodisperse.

To obtain the diffusion coefficient at zero polymer concentration (or self-diffusion coefficient) D_o, we express D_c as

$$D_c = D_o(1 + k_D c) \qquad (8)$$

and extrapolate the values of D_c to infinite dilution and obtain D_o and k_D values (Fig. 6). The values of

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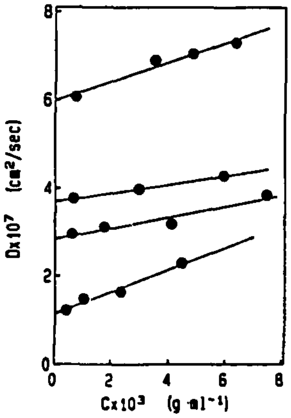

Figure 6. Concentration dependence of D obtained from extrapolation of $D(q)$ to zero angle for PIMA in THF at 25°C.

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D_o are listed in Table I for different molecular weight PIMA samples. The self-diffusion coefficient D_o decreases with increasing molecular weight. The hydrodynamic radius, R_H, can be calculated from the Stokes-Einstein equation:

$$D_o = \frac{kT}{6\pi\eta_0 R_H} \qquad (9)$$

where k is the Boltzmann constant, T is absolute temperature, η_0 is the solvent viscosity, and R_H is the hydrodynamic radius. The hydrodynamic radius, R_H, calculated for each molecular weight is also listed in Table I. Over the range of molecular weight studied, R_H (in cm) is found to vary with $\bar{M}_w$ by

$$R_H = 7.6 \times 10^{-10} \bar{M}_w^{0.59} \qquad (10)$$

Within the experimental uncertainty, the exponent is identical to that associated with R_g; however, R_H is slightly less than R_g, with $R_g/R_H = 1.36$ over the entire molecular weight range studied. This ratio is to be contrasted with the predicted value of 1.50 for monodisperse flexible coils in the limit (infinite hydrodynamic interaction).[8,9]

The concentration dependence k_D of the diffusion coefficient given in eq. (8) may be expressed in volume fraction units as

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$$k_D^* = \frac{M_w}{N_A V_H} k_D \qquad (11)$$

where $V_H = \frac{4}{3}\pi R_H^3$. In Table II we list the k_D^* values for all PIMA samples studied. The k_D^* values range from 2.2 to 2.9, with 2.6 as the average value. This result is in reasonable agreement with the Yamakawa prediction of 2.2 in the good solvent limit.[10]

In the good solvent limit one may estimate A_2 in terms of the hard-sphere value, which is given by

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$$A_2 = \frac{4N_A}{M_w^2} V_H \qquad \bar{M}_w \qquad (12)$$

Using the R_H and M_W values we have calculated A_2. The calculated A_2 values together with the experimental ones are listed in Table I. For all samples, the hard-sphere values for A_2 are slightly higher than the measured ones, with $A_2(\text{theo.})/A_2(\text{exp.}) = 1.165$, averaging over seven samples. The result shows that thermodynamically as well as hydrodynamically PIMA in THF behaves qualitatively as a hard sphere of radius R_H; this result is also observed for polystyrene and other flexible polymers in good solvents.[10]

The various parameters obtained thus far allow the calculation of the Mandelkern-Flory-Scheraga parameter β and the ratio π

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$$\beta = \left(\frac{\bar{M}_w[\eta]}{100}\right)^{1/3} \Big/ [f] \qquad (13)$$

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$$\pi = A_2 \bar{M} / [\eta] \qquad (14)$$

where $[f] = 6\pi R_H$ is the intrinsic frictional coefficient. The results are listed in Table II. The mean experimental value for β ($= 2.17 \times 10^6$ mol$^{-1/3}$) is in better agreement with the calculation of Douglas and Freed[11] (2.16×10^6 mol$^{-1/3}$) than with that of Oono[12] or Barrett[13] (2.4×10^6 mol$^{-1/3}$). The average value of π is 1.24, which is close to the value of 1.21 obtained for polyisobutylene in cyclohexane.[12]

The Flory-Fox viscosity parameter[14] ϕ and the interpenetration function Ψ are given by[10]

$$\phi = [\eta]\bar{M}_w/(6^{3/2}R_g^3) \qquad (15)$$

Table II. Solution Parameters of PIMA in THF at 25°C

Rg

$\bar{M}_w \times 10^{-5}$, g/mol	$\beta \times 10^{-6}$ mol$^{-1/3}$	k_D^*	$\phi \times 10^{-23}$/mol	Ψ	π	R_g/R_H
2.15	2.26	2.6	2.04	0.27	1.18	1.37
4.45	2.17	2.9	1.88	0.26	1.24	1.35
7.10	2.12	2.6	1.75	0.24	1.27	1.36
10.78	2.14	2.5	1.83	0.25	1.24	1.34
14.75	2.21	2.5	1.94	0.25	1.18	1.36
22.43	2.17	2.6	1.82	0.26	1.29	1.37
32.75	2.22	2.2	1.83	0.25	1.25	1.39
Average	2.18	2.6	1.87	0.25	1.24	1.36

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and

$$\psi = \frac{A_2\bar{M}_w^2}{4\pi^{3/2}N_A R_g^3} \tag{16}$$

may also be used to assess the flexibility of the chain. Using the values given in Table I for $[\eta]A_2$, $\bar{M}_w$ and R_g, we have calculated ϕ and ψ. They are listed in Table II. The average value of ϕ parameter is 1.87×10^{23}/mol, which is smaller than the Flory viscosity constant of 2.50×10^{23}/mol with infinite hydrodynamic interaction.[10] However, the Flory viscosity constant ϕ_0 is expected for ideal chains, or flexible chains in the theta condition.[15] It has been found that in the polystyrene/cyclohexane systems, the ϕ parameter tends to decrease from the ideal value ϕ_0 with an increase in temperature from the θ point 35.4°C.[16] Our $\phi/\phi_0 = 0.75$ ratio lies between the calculation of Douglas and Freed (0.89)[11] and by Oono[12] (0.707). Thus, if the viscosity constant ϕ_0 is corrected for the good solvent condition, and R_e rather than R_g is used in the calculation of ϕ, it is expected that better agreement would be obtained between theory and experiment.

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