Small-Angle Neutron Scattering from Bimodal Melts of Polystyrene[†]

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Received February 5, 1990; Revised Manuscript Received April 30, 1990

ABSTRACT: Small-angle neutron-scattering measurements of deuterated polystyrene in a series of undeuterated polystyrene solvents that vary in molecular weight are reported. The second virial coefficients decrease with increasing molecular weight of the solvent as is expected, but the functional dependence of this decrease is not in accord with Flory-Huggins theory or simple modifications of it. The results are qualitatively similar to earlier work of Kirste and Lehnen on the poly(dimethylsiloxane) system.

Introduction

The global conformation of a polymer molecule in bulk is the same as that of a polymer molecule in a Θ solvent.[1] If the polymer molecule is dissolved in a monomer or monomeric analogue, the polymer coil is expanded, and, in general, the monomer is a good solvent for the polymer. If the solvent is a low molecular weight polymer, the solvent power is intermediate; successive increases in molecular weight of the polymer used as solvent correspond to lesser degrees of molecular swelling and reduced second virial coefficients. There has been only one systematic investigation of the influence of solvent size on solvent power in a polymeric system,[2] and here we provide a few new results for further consideration.

The analysis of the experiment uses, as a starting point, the random-phase approximation described by Jannink and de Gennes[3] and by Benoit and Benmouna,[4] which yields a result identical with the single contact approximation of Zimm.[5] The coherent neutron-scattering intensity, $I(q,c)$, corrected for background, incoherent scattering, and absorption is given by

$$I(q,c) = KM_wcS_s(q)/(1 + 2A_2M_wcS_s(q)) \qquad (1)$$

where $S_s(q)$ is the single-chain scattering function, M_w is the weight-average molecular weight of the polymer, c is concentration, A_2 is the second virial coefficient, and K is a contrast factor multiplied by instrumental constants. q is the magnitude of the wave vector equal to $(4\pi/\lambda)\sin(\theta/2)$ where λ is the neutron wavelength and θ is the scattering angle.

The polymer chosen for these experiments is polystyrene in the deuterated form (PSD); the solvents are protonated polystyrene (PSH) of lower molecular weight. In order to provide an adequate difference between the PSD polymer and the PSH solvents, the molecular weight of the PSD was relatively high. In our experiment, this meant that the molecular radius of gyration, R_g, was so large that experimental values of $S_s(q)$ could not be obtained at low enough values of qR_g to map out $S_s(q)$ over a sufficiently broad range. Instead, as an approximation, a Gaussian model was assumed whereby

$$S_s(q) = 2(x - 1 + e^{-x})/x^2 \qquad (2)$$

where $x = q^2R_g^2$. It has been shown in earlier studies of polystyrene solutions that this approximation is very good[6] in good solvents, and, indeed, theoretical support for the Gaussian approximation for $S_s(q)$ has been offered by Witten and Schaefer[7] and also by Ohta, Oono, and Freed.[8]

The experimental procedure reduces to a least-squares analysis of eq 1 with eq 2 substituted for $S_s(q)$. There are three parameters, K, R_g, and A_2, to be fitted, and these are obtained from experimental results over a q range of $0.008 \leq q \leq 0.07$ Å^{-1}.

Experimental Conditions

Four mixtures were studied. The deuterated polystyrene (PSD) had a molecular weight 228 400. The solvent chains were protonated polystyrene, with M_w equal to 580, 3600, 9100, and 19 800. The weight-average molecular weights and M_w/M_n ratios are given in Table I. For each solvent, three PSD concentrations were used, 1%, 3%, and 5%. For all mixtures except those containing PSH580, the samples were prepared by freeze-drying a mixture from a 6% benzene solution. PSH580 is a viscous liquid at room temperature. For these samples the high M_w PSD was dissolved in the PSH at 50 °C. Originally, it was intended to prepare samples by hot pressing under vacuum, but samples 3600 and 9100 cracked in the mold upon cooling below this glass transition temperature, T_g. It was decided to maintain the samples at a fixed temperature of 120 °C, above T_g. To do this, a set of milled flat brass cells was constructed in halves, which when screwed together contained the molten sample sandwiched between nearly transparent windows. An annular brass spacer and high-temperature O-ring confined the molten material and defined a fixed sample thickness of 0.13 cm. The cell fitted tightly into a milled furnace, which could be heated to a controlled temperature and mounted, through insulators, directly on the sample stage of the spectrometer. Figure 1 gives an exploded view of a cell and furnace. The unobstructed window diameter is 2.0 cm, but the neutron beam was defined by a fixed cadmium aperture of 1.0-cm diameter, mounted $^1/_2$ cm ahead of the furnace source face.

The initial cell design called for two single-crystal silicon windows of diameter $1^1/_2$ in. and thickness $^1/_8$ in. The neutron transmission for an empty silicon sandwich was measured at λ = 1.6 Å to be above 0.985 and was expected to behave similarly at λ = 4.75 Å. However, much difficulty was encountered in guaranteeing sample filling without bubble inclusions, and therefore one window was replaced with quartz to provide visibility

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[*] Author to whom correspondence is addressed.

[†] Work supported by NSF Grants DMR-79-26254 and DMR 88-11066.

[‡] Sponsored by Comissao Nacional de Energia Nuclear/Brazil.

[§] Operated by Martin Marietta Energy Systems, Inc., under Contract DE-AC05-48OR21400 for the U.S. Department of Energy.

0024-9297/90/2223-5266$02.50/0

Table I
Molecular Weight and Molecular Weight Distribution of Samples

polymer	M_w	M_w/M_n	polymer	M_w	M_w/M_n
PSD (solute)	2.28×10^5	1.06	PSH9100	9100	1.06
PSH580	580	1.14	PSH19800	19800	1.06
PSH3600	3600	1.06			

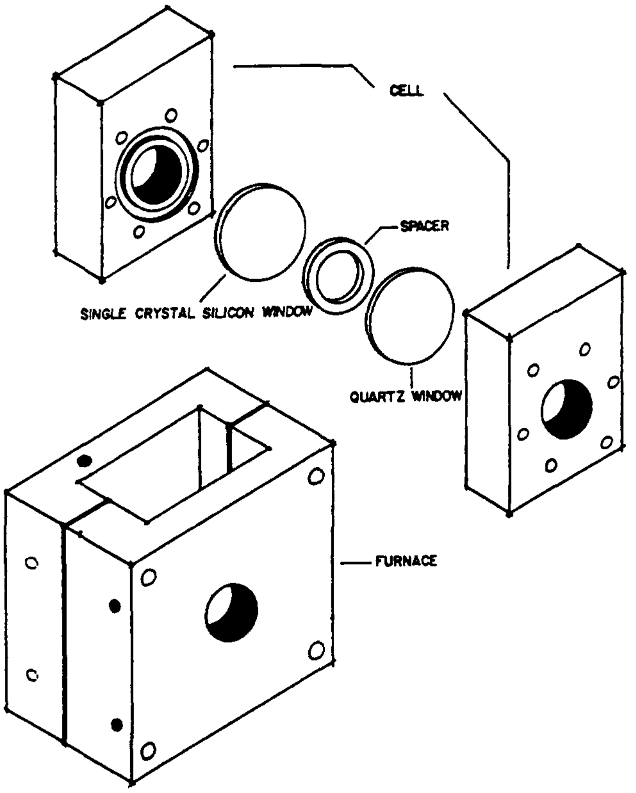

Figure 1. Exploded view of the cell and furnace used to mount molten polymer specimens on the spectrometer sample stage.

(for this sandwich, the transmission dropped to 0.94). A technique was developed for cell filling and maintenance at elevated temperature for all samples except those with a matrix of M_w = 580, as follows: the mixed powder was melted in the lower half of the horizontal cell, fitted with a temporary filling annulus, in an evacuated oven at T = 120 °C. When the sample was completely melted and free of bubbles, the upper half of the cell was mounted, in the oven, tightened, and brought to the vertical position. The cell temperature was maintained at 120 ± 10 °C throughout the scattering experiment by rapid transfers to and from the heated target stage. Each sample was inspected for bubble inclusion before and after the scattering experiment.

The same cell and furnace system was used for the samples of M_w = 580, but the temperature was maintained at 35 °C both before and during the experiment. To determine any observable change due to the temperature difference, a second, later scattering experiment was performed at 120 ± 10 °C. No changes in scattering with temperature were detected.

The scattering experiments were performed on the 30-m small-angle camera designed and operated at the National Center of Small Angle Scattering Research at ORNL.[9] The spectrometer conditions used were chosen to reach the lowest regime of q consistent with adequate counting statistics. The source and sample apertures were 2.0 and 1.0 cm in diameter, respectively; the source to sample and sample to detector path lengths were 7.5 and 7.0 m, respectively. The direct beam was limited by a 4.0-cm-diameter beam stop. The neutron wavelength was 4.75 Å. Running times were 8 h for 1% samples, 6 h for 3% samples, and 4 h for 5% samples.

Results

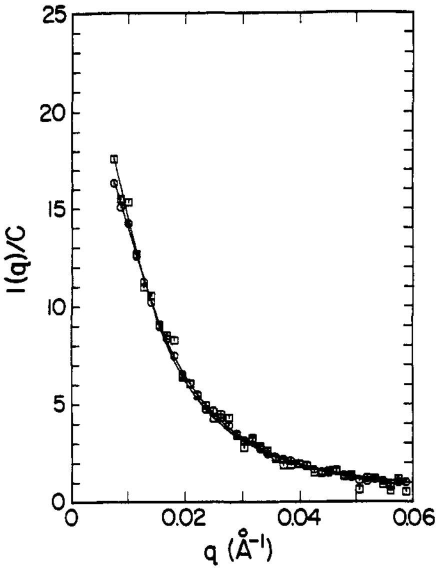

Figure 2. $I(q,c)/c$ for PSD in PSH19800: □, c = 0.0113 g/mL; ○, c = 0.0338 g/mL. T = 120 ± 10 °C.

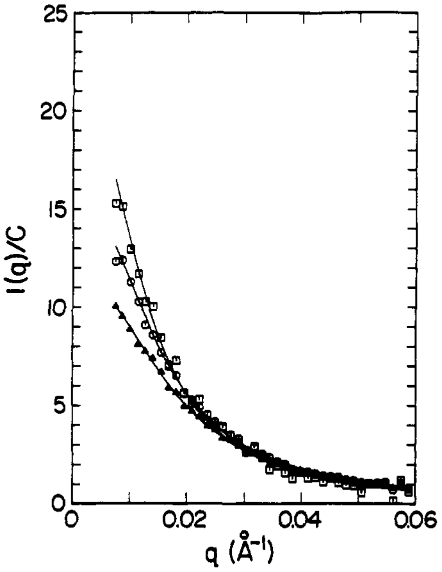

Figure 3. $I(q,c)/c$ for PSD in PSH9100: □, c = 0.0113 g/mL; ○, c = 0.0338 g/mL; Δ, c = 0.0563 g/mL. T = 120 ± 10 °C.

The measured intensity for each sample is corrected first for detector sensitivity, beam-blocked background, transmission, and then empty-cell background. This result is further treated for incoherent scattering by using the intensity from a blank sample filled with PSH. The total incoherent scattering was set equal to I_0, the incident neutron intensity, multiplied by $1 - T$ where T is transmission. $I_0(1 - T)/(4\pi)$ is the approximate incoherent scattering per unit solid angle, and this is the factor used to correct the scattering from PSD solutions for incoherent background. This result depends on assumptions about multiple incoherent scattering. The corrections are done cell by cell.

The corrected intensities divided by PSD concentrations are shown plotted against q in Figures 2–5. Two samples are not included because the sample appearances were suspicious. It is clear that beginning with Figure 2, where the 1% and 3% data are virtually coincident, there is a progressive separation between I/c profiles for different concentrations as the matrix molecular weight grows smaller. That is, there is a growing dependence of the reduced scattering on c as the solvent M_w is reduced.

For each matrix the data from each sample of different concentration were fitted to eq 1 in the region $1 < qR_g <$

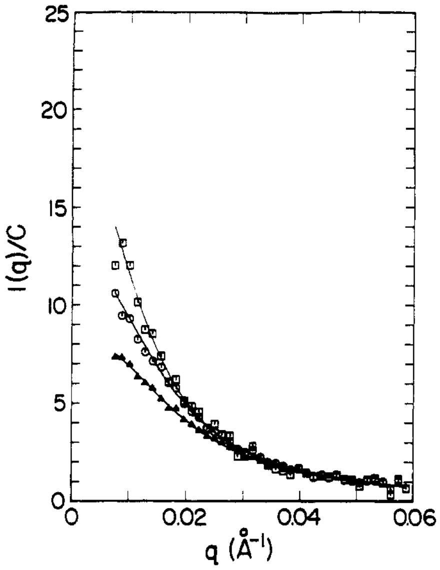

Figure 4. $I(q,c)/c$ for PSD in PSH3600: □, c = 0.0112 g/mL; ○, c = 0.0335 g/mL; △, c = 0.0557 g/mL. T = 120 ± 10 °C.

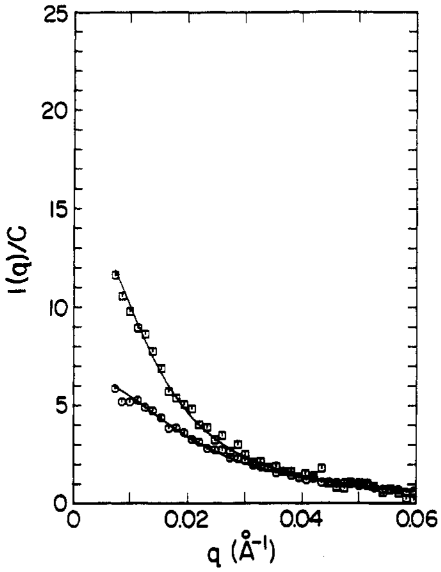

Figure 5. $I(q,c)$ for PSD in PSH580: □, c = 0.0110 g/mL; ○, c = 0.0328 g/mL. T = 35 ± 2 °C.

Table II
Measured Values of R_g and A_2

solvent	M_w	R_g, Å	$A_2 \times 10^4$ [a]	$R_g/R_g(\theta)$ [b]
PSH	580	150, c = 0.0113 g/mL	3.24	1.18
		138, c = 0.0338 g/mL		1.08
PSH	3600	145.5	2.16	1.14
PSH	9100	145.5	1.78	1.14
PSH	19800	130.5	0.92	1.02

[a] A_2 is expressed in mL mol/g^2. [b] $R_g(\theta) = 0.267M_w^{1/2}$. Tangari, C.; King, J. S.; Summerfield, G. C. *Macromolecules* 1982, *15*, 132.

4, by a least-squares routine in which the fitting parameters are R_g, A_2, and a normalization constant. In each case, except for the matrix M_w = 580, the values of R_g and A_2 were found to be the same for all the concentrations in one matrix. For the matrix M_w = 580, the value of R_g for the 3% concentration is 8% lower than the value at 1%, although the magnitudes for A_2 are in close agreement.

In Table II, one sees the expected qualitative behavior; both R_g and A_2 increase with decreasing molecular weight of the solvent. The R_g values are somewhat erratic; the measured A_2 is more nearly consistent. It is uncertain why this is so, but we should point out that there are no experimental data in the low q region ($qR_g < 1$), which is normally the domain from which R_g is determined. In the discussion to follow, attention is focused on the second virial coefficients, A_2. It is clear to us that the data are incomplete, and a more extensive set of experiments would be desirable.

Table III
Experimental and Calculated Second Virial Coefficients of PSD (M_w = 228 000) in PSH Solvents

solvent	M_w	$A_2 \times 10^4$ (exptl)	$A_2 \times 10^4$ (eq 7)
benzene[a]		4.68	5.2
PSH	580	3.24	3.1
PSH	3600	2.16	1.9
PSH	9100	1.78	1.8
PSH	19800	0.92	1.2

[a] Data were taken from ref 14.

Table IV
Experimental and Calculated Second Virial Coefficients of Protonated Poly(dimethylsiloxane) (M_w = 2 × 10^5) in Deuterated Poly(dimethylsiloxane) Solvents

solvent M_w	$A_2 \times 10^4$ (exptl)	$A_2 \times 10^4$ (eq 8)	solvent M_w	$A_2 \times 10^4$ (exptl)	$A_2 \times 10^4$ (eq 8)
180	4.6	5.33	9600	0.87	1.12
3000	2.8	1.84	50000	0.54	0.55

Discussion of Results

The idea that the second virial coefficient can be described by a power law of the form

$$A_2 \sim R_g^{\,3}\psi/M^2 \qquad (3)$$

where ψ is a function that describes the extent of solute overlap, is well-known.[10] When α is defined by $R_g = R_g(\theta)\ \alpha$, eq 3 becomes

$$A_2 \sim M^{-1/2}\alpha^3\psi \qquad (4)$$

Using the Flory formalism,[11] one has

$$\alpha^5 - \alpha^3 = (KM^{1/2}/V_1)(1 - \Theta/T) \qquad (5)$$

where V_1 is the molar volume of the solvent.

The dependence of A_2 on V_1 is a function of the magnitude of α. In our experiments, α is close to unity unless the solvent molecular weight is low. For large values of α (3 or greater) $\alpha \sim M^{1/2}/V_1$. For smaller values of α, the dependence of α on $M^{1/2}/V_1$ is not known but is very slight. Writing $\alpha \sim M^k/V_1^{2k}$, one has

$$A_2 \sim (M^{-0.5+3k}/V_1^{\,6k})\psi \qquad (6)$$

where k depends on $M^{1/2}/V_1$ and is substantially less than 0.1 in magnitude. Taking k as a constant, a power law

$$A_2 = 1.74 \times 10^{-3}/V_1^{\,0.272} \qquad (7)$$

was found to provide a fair fit to the experimental results in Table II. Experiments are compared with calculations from eq 7 in Table III.

The experiments of Kirste and Lehnen on poly(dimethylsiloxanes)[2] also provide values of A_2 for a polymer dissolved in solvents of the same species but different molecular weight. We decided to reanalyze their results by a power law as done for our data on polystyrene. By regression analysis, we obtained

$$A_2 = 5.25 \times 10^{-3}/V_1^{\,0.421} \qquad (8)$$

for the poly(dimethylsiloxanes). A comparison between experimental results of ref 2 and calculation from eq 8 is given in Table IV.

The present analysis is not based on a solid theoretical foundation. The fit between calculated results and experiment is fairly good, and it would be interesting to find out whether other polymers dissolved in homologous polymers as solvents yield similar results. Further experiments of this kind would be very useful.

There is a small isotope effect obtained by dissolving a deuterated polymer in a protonated polymer of the same structure. This effect, predicted by Buckingham and Hentschel[12] and demonstrated by Bates and collaborators,[13] is too small to play an important role in these experiments.

Acknowledgment. We are indebted to Z. Akcasu, B. Hammouda, and G. C. Summerfield for fruitful suggestions and incisive discussions during the course of the investigation.

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