Macromolecules **1998,** *31,* 8436−8438

Comparison of Inter- and Intramolecular Correlations of Polystyrene in Poor and Θ Solvents via Small-Angle Neutron Scattering

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Received August 6, 1998

At sufficiently low or high temperatures polymer solutions demix, separating into two coexisting phases. The neighborhood of the upper critical solution (UCS) and lower critical solution (LCS) phase boundaries on the phase diagram of the polymer−solvent system is traditionally associated with the poor solvent domain.[1] Along the UCS boundary, the solvent quality can be improved by increasing the temperature (T) or changing the pressure (P) (usually, but not always, by increasing P),[2] to move the solution away from the phase boundary and allow larger molecular weight (M_w) molecules to be dissolved. The improvement of solvent quality thus obtained depends on the ability of the solvent molecules to better screen attractive intrachain interactions at the new temperature and pressure. At the phenomenological level, organic solvents for polymers may be divided into three groups: poor (non-Θ) solvents, Θ-solvents, and good solvents. In poor solvents, the solution is believed to be incapable of reaching the Θ-condition (i.e. the point at which the attractive monomer−monomer interactions are annulled by excluded volume effects, and the conformation of the polymer coils is described by Gaussian statistics). For Θ-solvents, this condition can be reached at some accessible T and P. In good solvents, polymer coils swell with T and P and the solution eventually reaches the athermal solvent domain[3] where the conformation of the polymer becomes independent of the temperature and pressure.

The structural changes in the polymer coils and solutions that accompany the shift from poor, through Θ, to the good solvent regime are not completely understood. In previous papers we have studied the temperature dependence of the radius of gyration, R_g, and the intermolecular correlation length, ξ, in semidilute solutions of polystyrene (PS) in the Θ-solvent cyclohexane-d_{12} (CH-d) at ambient pressure using small angle neutron scattering (SANS).[4] We found that the R_g of PS chains remains constant and equal to the unperturbed dimension predicted by the Gaussian model over the whole poor solvent domain, $T_c \le T \le \Theta$. In addition, the osmotic compressibility of the solutions experienced a sharp and nonmonotonic crossover when passing from the critical fluctuation regime near T_c to mean field behavior around $T = \Theta$.[5] The crossover occurred when $\xi \sim R_g$ indicating once again that the thermodynamic and structural properties of the polymer solutions are strongly interrelated. In the present communication we compare the temperature and pressure dependences of R_g and ξ of PS in the poor solvent acetone-d_6 (AC-d) with those in the Θ-solvent CH-d.

To obtain R_g and ξ we make use of the SANS high concentration isotope labeling method,[6−8] which allows the determination of both parameters for semidilute polymer solutions in the poor solvent domain which lies between the Θ-condition ($\xi < R_g$) and the critical point (T_c, P_c) ($\xi \gg R_g$). The coherent scattering intensity, I, from an incompressible mixture of identical protonated and deuterated polymer chains dissolved in a solvent is[9]

$$I(Q,x) = I_s(Q,x) + I_t(Q,x) \qquad (1)$$

$$I_s(Q,x) + KnN^2S_s(Q) \qquad (2)$$

$$I_t(Q,x) = LnN^2S_t(Q) \qquad (3)$$

Subscripts “s” and “t” correspond to scattering from a single chain and total scattering, respectively and thus $S_s(Q)$ is the single-chain structure factor which contains information on the intramolecular correlations. Similarly, the total scattering structure factor, $S_t(Q)$ embodies information on the total (both intra- and intermolecular) correlations between monomer units and is related to the correlation length of the concentration fluctuations, ξ. The structure factors are normalized so that $S_s(Q = 0) = 1$ and $S_t = S_s$ at infinite dilution. The scattering vector is given by $Q = 4\pi\lambda^{-1} \sin \theta$, where 2θ is the scattering angle and λ is the neutron wavelength. Also, x is the mole fraction of protonated chains in the solvent, and n and N are the number density of the polymer molecules and the degree of polymerization, respectively. The prefactors K and L are

$$K \equiv (b_H - b_D)^2x(1 - x); \quad L \equiv [b_Hx + (1 - x)b_D - b_s']^2 \qquad (4)$$

where b_H and b_D are the scattering lengths of the protonated and deuterated monomers and b_s' is the normalized scattering length of a solvent molecule.

The parameter L (eq 4) is shown in Figure 1 as a function of x for isotopic PS mixtures dissolved in AC-d and CH-d. For PS in AC-d, it may be seen that $L = 0$ at $x = 0.214$, which completely eliminates the contribution of “total scattering” at that concentration [i.e. $I_t(Q, x = 0.214) = 0$], and eq 1 gives the single chain (intramolecular) scattering directly. For PS in CH-d, there is no isotopic ratio, $0 < x < 1$, which satisfies the condition $L(x) = 0$, and $I(Q,x)$ always contains a contribution from the total (intermolecular) scattering, which must be subtracted to extract R_g:[4]

$$I(Q,x) = \frac{L(x)}{(b_H - b'_s)^2}I_t(Q, x = 1) = KnN^2S_s(Q) \qquad (5)$$

If all chains are protonated ($x = 1$), the prefactor (K) = 0, and one obtains $\xi(T,P)$ directly from $I(Q, x = 1) \sim S_t(Q)$.[10]

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10.1021/ma9812480 CCC: $15.00

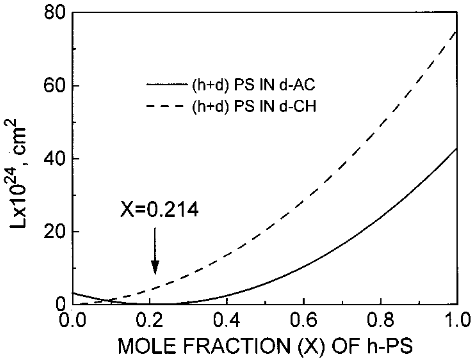

Figure 1. Variation of the parameter L in eq 3 computed as a function of x, the mole fraction of PS-*h* in solutions of (PS-*h* + PS-*d*) in AC-*d* and CH-*d* using $b_H = 2.33 \times 10^{-12}$ cm, $b_D = 10.66 \times 10^{-12}$ cm, $b_s' = 8.88 \times 10^{-12}$ cm (AC-*d*), and b_s' (CH-*d*) $= 10.99 \times 10^{-12}$ cm.[22]

Polymer samples of PS-*h* (M_w = 10 200, 11 600 and 533 000) and PS-*d* (M_w = 10 500, 11 200, and 520 000) of polydispersity $M_w/M_n \leq 1.06$ were purchased from Polymer Laboratories. Deuterated solvents AC-*d* and CH-*d* (D/(H + D) = 0.995) were purchased from Sigma Chemical and were dried over a molecular sieve prior to preparing solutions near the critical concentration C(PS/CH-*d*) = 4.4 wt %[4] and C(PS/AC-*d*) = 20.3 wt %.[11] Solutions of (h + d) PS in AC-*d* and CH-*d* were prepared at $x = 0.214$ and $x = 0.20$, respectively. The latter number provides a reasonably high signal-to-noise ratio and minimizes the contribution from the second term on the left-hand side of eq 5.

Solutions were loaded into a stainless steel cylindrical cell[12] which was fitted with optically polished sapphire windows virtually transparent to neutron radiation. The maximum area accessible to the neutron beam is ~2 cm^2 and the path length of the cell can be adjusted over the range ($0.2 < l$/cm < 2) depending on the transmission requirements. The temperature of the cell was controlled using circulating fluid (±0.1 K) and the sample pressurized using a screw-type pressure generator (HIP Model 62-6-10) which is bellows-isolated from the sample reservoir/pressure cell assembly to avoid contamination of the sample with hydraulic fluid at higher pressures. Pressure was measured using a precision digital pressure indicator (Sensotec, model AG-100).

Measurements were performed on the 30-m SANS spectrometer at the Oak Ridge National Laboratory over Q-ranges of $0.01 < Q/\text{Å}^{-1} < 0.1$ and $0.005 < Q/\text{Å}^{-1} < 0.05$ for PS solutions of $M_w \sim 10^4$ and $\sim 5 \times 10^5$, respectively. The data were radially averaged and converted to an absolute coherent cross section (in units of cm^{-1}) using procedures described elsewhere.[13] The structure factors $S_s(Q)$ and $S_t(Q)$ were obtained from eqs 1−3. $S_s(Q)$ was used to extract the (z-averaged) R_g by fitting the Debye function for Gaussian chains[14]

$$S_s^D = (2/y^2)(y - 1 + e^{-y}), \quad y = Q^2 R_g^{\,2} \qquad (6)$$

$S_t(Q)$ was used to obtain ξ by fitting the low-Q region to the Ornstein−Zernike formula

$$S_t(Q,T) = S(Q = 0)/(1 + Q^2\xi^2) \qquad (7)$$

The temperature variation of R_g in the solution of (0.214h + 0.786d)PS in AC-*d* at 0.1 MPa is shown in Figure 2. The single chain structure factor does not

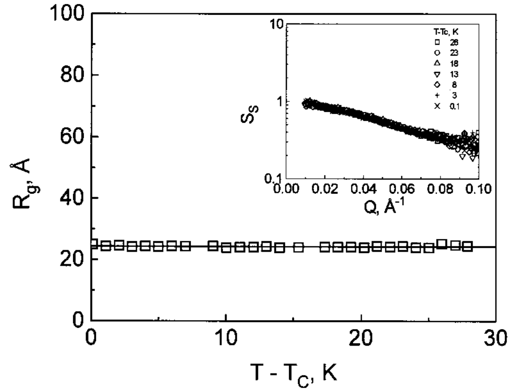

Figure 2. $R_g(T)$ of PS in the solution (0.214h + 0.786d) PS in AC-*d* at near-critical concentration of the polymer (20.3%) and P = 0.1MPa. M_w(PS-*h*) = 10 200, M_w(PS-*d*) = 10 500. For this solution T_c = 17 °C (visual observation of opacity). The inset shows the variation of the single chain structure factor S_s vs Q at different temperatures.

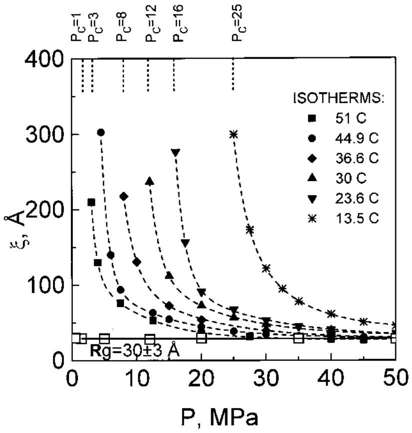

Figure 3. ξ(P) of PS-*h* (M_w = 11 600) in AC-*d* at the different temperatures shown in the inset. The lightly dotted vertical lines locate critical pressures (in MPa) for this solution for various isotherms. $R_g(P,T)$ of labeled PS-*h* chains in the solution of (h + d) PS in AC-*d* is also plotted (open squares).

vary with temperature and tends to $S_s(Q) = 1$ in the limit $Q \rightarrow 0$. Accordingly, R_g of the polymer remains constant at all temperatures down to $T_c \cong 17$ °C where the solution becomes opaque and precipitates into two liquid phases separated by a meniscus. The average $R_g = 25 \pm 3$ Å agrees within experimental error with the unperturbed dimensions for PS-*h* with M_w = 10 200 [i.e. $R_g \cong 0.27 M_w^{1/2} \cong 27$ Å].[15,16]

The effect of pressure on the thermodynamic state of PS/AC-*d* solutions is illustrated in Figure 3. Within experimental error, R_g remains independent of pressure down to the critical demixing condition (T_c,P_c). The values for R_g extracted from Debye fits to scattering data remain close to the unperturbed dimensions for Gaussian chains with M_w = 11 600 [i.e. $R_g \cong 0.27\, M_w^{1/2} \sim 29$ Å]. Conversely, the concentration fluctuations as monitored by the intermolecular correlation length, ξ, diverge as P falls to $P \sim P_c$, where the system exhibits pressure induced phase demixing. A detailed analysis of the shape of the $\xi(P,T)$ and $P_c(T)$ curves will be given in a forthcoming publication, which will also compare SANS data with dynamic light scattering measurements.[17] The main conclusion that can be drawn from the present data (Figure 3) is that for solutions of PS in a poor solvent (acetone), the magnitude of ξ is generally $\geq R_g$ and approaches or falls below the single

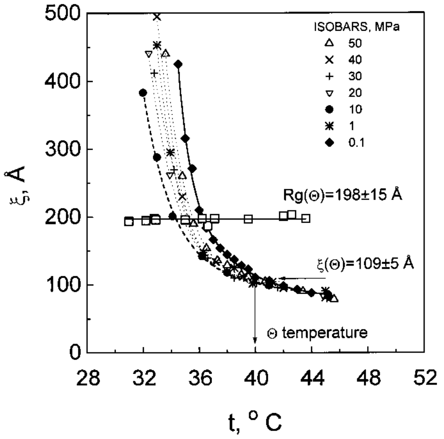

Figure 4. $\xi(T)$ for PS-*h* ($M_w = 533\,000$) in CH-*d* at different pressures. $R_g(P,T)$ of PS-*h* chains in the solution (h + d) PS in CH-*d* is also shown (open squares).

chain dimensions in the limit of the highest temperatures and pressures reached in the experiment ($T = 51$ °C, $P = 50$ MPa).

In Figure 4 we report the SANS data on the PS/cyclohexane-*d* solutions for experiments extending from well above the Θ condition to near demixing. As is seen in the figure, all isobars for $\xi(T)$ merge at or near the Θ temperature of PS-*h*/CH-*d* solutions $\Theta \cong 40$ °C[18] and the value of the average correlation length at this temperature is $\xi(\Theta) = 109 \pm 5$ Å. Assuming that the contribution of the interchain correlation is negligible at $T = \Theta$,[19] one obtains from eq 6 in the limit of small Q:[14,20]

$$S_t(Q,T) = S(Q = 0)/(1 + Q^2 R_g^{\,2}/3) \qquad (8)$$

Comparing with eq 7 yields:

$$\xi(\Theta) \cong R_g(\Theta)/3^{1/2} \qquad (9)$$

or $R_g(\Theta)/3^{1/2} \cong 114$ Å for $M_w = 533\,000$, which agrees well with the experimental value $\xi(\Theta) = 109 \pm 5$ Å.

In conclusion, in solutions of PS in the poor solvent AC-*d* intermolecular correlations dominate over the intramolecular correlations and the solution does not leave the critical region of phase demixing ($\xi \geq R_g$) even at $(T - T_c) \sim 50$ °C and $(P - P_c) \sim 50$ MPa. In the Θ solvent CH-*d*, on the other hand, the intermolecular correlations predominate only in a narrow region close to the critical line ($(T - T_c) \leq 3$ °C for PS of $M_w \sim 533\,000$, the solution studied here) and become negligible beyond the Θ point. We note that SANS measurements of the correlation length can be used to give a reasonably accurate determination of the Θ temperature using eq 9.[21] The radius of gyration of PS in both AC-*d* and CH-*d* remains unchanged and equal to the dimension of unperturbed Gaussian chains down to (T_c, P_c) which is indicative of the universality of this phenomenon for polymers in poor solvents.

Acknowledgment. Y.B.M. and G.D.W. wish to acknowledge stimulating discussions with M. Muthukumar. The research was supported by the Divisions of Advanced Energy Projects and Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-96OR-22464 (with Lockheed Martin Energy Research Corporation) and Grant No. DE-FG05-88ER-45374 (with the University of Tennessee). This research was supported in part by an appointment to the ORNL Postdoctoral Research Associates Program, administered jointly by the ORNL and the Oak Ridge Institute for Science and Education.

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(9) The inclusion of corrections for the compressibility leads to an additional cross-term in the expression for the coherent intensity of scattering.[7] In the data analysis we have included a minor correction for a small increase (≤5%) observed in $I(Q)$ for the pure d-solvents in the range ($0.1 < P$/MPa < 50). We found that eqs 1−3 yield values for $R_g(P)$ which coincide within experimental error with R_g ($P = 0.1$ MPa) and conclude that pressure corrections to eqs 1−3 are negligible in the pressure range studied in this work (due to the relatively low compressibility of both solvents and polymers).
(10) Obviously, $K = 0$ also at $x = 0$; however, this limit is not of practical interest as it corresponds to solution of a deuterated polymer in a deuterated solvent which provides no neutron contrast and thus no scattering.
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(21) Equation 9 is valid for concentrations close to the overlap concentration C^* of polymer chains, and thus includes the critical concentration of the polymer. It may be extended to arbitrary concentrations $C \geq C^*$ taking into account $\xi(C,\Theta) \sim C^{-1}$.[3]
(22) Calculated using the values of the scattering lengths for H, D, and C, tabulated in: Bacon, G. E. *Neutron Diffraction*; Claredon Press: Oxford, England, 1975.

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