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Temperature Dependence of the Interaction Parameter of Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: The Flory–Huggins interaction parameter, χ, has been determined for polystyrene, PS, and poly(methyl methacrylate), PMMA, by measuring the small-angle neutron scattering, SANS, from P(S-*b*-MMA), symmetric, diblock copolymers above the microphase separation temperature. The SANS profile can be well described by the correlation hole scattering from which χ is easily obtained. Measurements as a function of temperature yield $\chi = (0.028 \pm 0.002) + (3.9 \pm 0.06)/T$ where T is the absolute temperature. These results show that the entropic contribution of χ is much greater than the enthalpic contribution and that the temperature dependence of χ is weak.

Introduction

The Flory–Huggins interaction parameter between poly(styrene), PS, and poly(methyl methacrylate), PMMA, has been the subject of several studies over the last 4 decades.[1–7] Surprisingly or not, the reported values of the interaction parameter vary from 0.0044[5] up to 0.032[3] as measured by a wide variety of techniques. For most purposes, this wide range of the interaction parameter is not of critical importance since for most mixtures of high molecular weight PS and PMMA these values of the interaction parameter are sufficiently large and positive to make the two incompatible. Recently, the interfacial characteristics of these two polymers have been the focus of attention,[8–10] and such a broad range in the values of the interaction parameter is unacceptable because determination of the width of the interface between domains of homopolymers or microdomains in block copolymers depends strongly on the interaction parameter. According to Helfand and co-workers,[11–13] the interfacial width a_I between immiscible homopolymers or block copolymer microdomains in the strong segregation limit is given in terms of the interaction parameter, χ, and the statistical segment lengths of the two components, b_1 and b_2, with monomer number densities, ρ_{01} and ρ_{02}, respectively, by

$$a_I = 2\left(\frac{\rho_{01}b_1 + \rho_{02}b_2}{12\chi\rho_0}\right)^2 \qquad (1)$$

where ρ_0 is the average monomer number density. Consequently, with the range in published χ values of a_I can vary by as much as 40% and a critical comparison between experimental results and theoretical predictions cannot be made. It is also evident that with the recent developments in neutron reflectivity[8–10,14] quantitative measurements of the interface in both magnitude and functional form can be made. Therefore, provided reliable values of χ exist, the opportunity now presents itself to make significant strides in understanding the interfacial behavior of polymers.

Focusing on the polymers of interest in this study, namely, PS and PMMA, measurements of the interfacial width for the homopolymers and copolymers have been reported. Fernandez et al.[8] and Anastasiadis et al.,[10] in a recent neutron reflectivity studies, have found that the interface between homopolymers of PS and PMMA is 50 ± 5 Å.[15] X-ray scattering[15,16] and neutron reflectivity studies,[9,10] of Russell and co-workers on block copolymers have also shown that the interface between the lamellar microdomains is ca. 50 Å, identical with that for the homopolymers and well within the broad range of predicted values. In both cases, a heavy weighting is placed on χ, and given the wide range of published values of χ it is difficult to draw any conclusions.

It is the intent of this paper to address specifically the interaction parameter between PS and PMMA in the solid state. Since PS and PMMA homopolymers are immiscible, it is impossible to use scattering techniques to obtain χ except in dilute mixtures of one homopolymer in the other. Independent studies on the surface behavior of PS/PMMA copolymers[9,10,18] gave strong evidence that PS/PMMA copolymers, where the molecular weight of each block is ca. 15 000 or less, are phase mixed or, in other words, above the microphase separation temperature, MST. This finding led to the small-angle neutron scattering, SANS, studies reported herein where χ was measured as a function of temperature using the well-known correlation hole scattering effect. It is found that χ varies linearly with reciprocal temperature but only weakly. In fact, the entropic contributions to χ are found to be dominant and the enthalpic portion of χ is quite small. This result is much different from that reported for numerous other diblock copolymers.

Experimental Section

A diblock copolymer comprised of a perdeuterated PS block and a normal PMMA block, with total molecular weight of 27 660 and a polydispersity of 1.084, was purchased from Polymer Laboratories. The weight-average molecular weight, M_w, of the PS block was 13 280 with a polydispersity of 1.058 as determined from size-exclusion chromatography. The molecular weight of the PMMA block, determined from the difference in the peak positions of the chromatogram, was 15 100. The total fraction of PS in the block copolymer, f, was 0.44. The copolymer was used as received without further purification. Specimens for the SANS experiments were prepared by compression molding a powder of the copolymer into 1.4-cm diameter disks with 1

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mm thickness at 80 °C. The disks were then heated to 140 °C under vacuum for several days. Independent small-angle X-ray scattering measurements on the specimens showed that the void content was minimal. The specimens were placed between aluminum windows separated by a 1-mm retaining ring. The entire assembly was placed in a hot stage designed for the neutron spectrometer. Prior to each measurement the sample was allowed 30 min to achieve thermal equilibrium. The temperature was monitored and controlled by a thermocouple located in close proximity to the specimen. The temperature control was to within ±1.5 °C at each temperature.

SANS measurements were performed on the low Q diffractometer, LQD, at the Manuel P. Lujan, Jr. Neutron Scattering Center, LANSCE, at the Los Alamos National Laboratory. Specific details of the instrument and data reduction have been discussed previously.[19-21] The LQD, calibrated against a series of secondary standards, measures the entire SANS profile over a range of momentum transfer, q, from 0.003 to 0.23 Å^{-1}. Here, q is defined as $(4\pi/\lambda)\sin\theta$, where λ is the incident neutron wavelength and 2θ is the scattering angle. The measured scattered intensity was reduced as described elsewhere.[19-21] The diffractometer equipped with a two-dimensional array detector uses time-of-flight to measure the incident neutron momentum and, hence, λ of the pulses of neutron scattered by the specimen yielding $t[(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q)]$ which is the scattering probability as a function of q, where t is the sample thickness and $[(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q)]$ is the absolute scattering cross section per unit volume. Dividing by the known sample thickness gives $[(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q)]$ in units of cm^{-1}. For a time of flight instrument such as the LQD it is important to note that the transmission of a specimen is wavelength-dependent. Separate examination of the transmission as a function of wavelength permitted the selection of the appropriate time slices (i.e., wavelengths) of the spectrum where the transmission was always greater than 60% in order to avoid complications from multiple scattering. Comparisons were made for different wavelength selections to ensure that any effects of instrument nonidealities and multiple scattering were minimal.

The scattering observed for the P(d-S-*b*-MMA) copolymer in the phase mixed state was much less intense than that observed for copolymers of slightly higher molecular weight in the microphase separated state. Despite this and the fact that 55% of the specimen was comprised of normal PMMA, i.e., protonated PMMA, the incoherent scattering was an insignificant fraction of the observed scattering. Since the incoherent scattering could not be measured precisely, several different estimates were used on the basis of the calculated ratio of the incoherent to coherent scattering at large scattering vectors. This ratio was varied by 50% to establish a reasonable range of confidence. However, regardless of the value of the incoherent scattering used, the effect on the coherent scattering was small over the scattering vector range studied.

Results and Discussion

The SANS profiles for the P(d-S-*b*-MMA) diblock copolymer obtained at three temperatures are shown in Figure 1. All the scattering profiles exhibit a single, broad reflection with a peak position centered near $q_{\max}$ of 0.044 Å. No evidence was found for higher order reflections. At most, there is only a 2% shift in the $q_{\max}$ (0.043–0.044) as the temperature was increased over the range indicated. As the temperature was raised, the absolute intensity of the reflection decreased and the profile broadened. Both are consistent with the copolymer being in a phase-mixed state.

Proper interpretation of these data, however, requires independent information on the state of the copolymer; the lack of change of shape of the scattering profile and the absence of evidence of higher order reflections are not adequate proof that the copolymer is phase-mixed. For example, for these copolymers it has been shown that the interface between the PS and PMMA domains is broad, on the order of 50 Å.[9,10,16,17] Such a broad interface coupled with the fact that even order reflections are absent due to symmetry would make the observation of higher order reflections difficult. Measurements of this identical copolymer by secondary ion mass spectrocopy[22] and neutron reflectivity[9] show conclusively that over the temperature range studied, the copolymer is phase mixed.

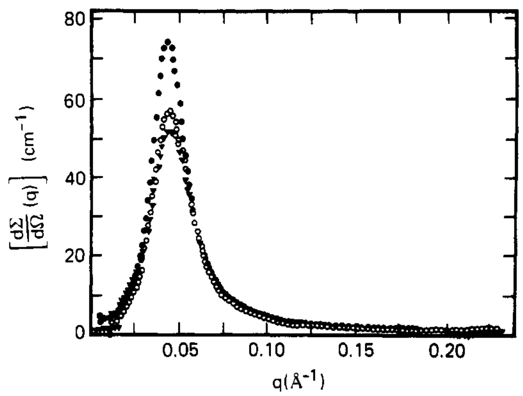

Figure 1. Small-angle neutron scattering profiles for P(d-S-*b*-MMA) symmetric, diblock copolymers (N = 262) at temperatures of 120 (●), 162 (○), and 182 °C (▼). Data are presented in absolute units as a function of the scattering vector.

The scattering from a phase-mixed, monodisperse copolymer, assuming incompressibility, has been shown by Leibler[23] to be given by

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(q)\right] = \frac{1}{V_1}\left(a_1 - \frac{\rho_2}{\rho_1}a_2\right)^2 S(q) \tag{2}$$

where a_i is the scattering length of component i with density ρ_i, V_1 is the molar volume of component 1, and $S(q)$ is defined as

$$S(q) = \frac{1}{F(q) - 2\chi} \tag{3}$$

where χ is the Flory–Huggins interaction parameter and the interference function, $F(q)$, is defined as

$$F(q) = \frac{P_{11}(q) + 2P_{12}(q) + P_{22}(q)}{P_{11}(q)P_{22}(q) - [P_{12}(q)]^2} \tag{4}$$

The functions $P_{ij}(q)$ are defined in terms of the Debye scattering functions for the individual blocks of the copolymer. The Debye scattering function is, in turn, given in terms of the radius of gyration of a Gaussian coil, $R_{g,i}^2 = N_i b_i^2/6$, where N_i is the number of statistical segment lengths, b_i, of component i. Polydispersity is known to alter the scattering profile.[24-26] The exact expressions for the scattering incorporating the effect of polydispersity, while used for the calculated profiles, are not reproduced here, and the reader is referred to the earlier literature.

For the P(d-S-*b*-MMA) diblock copolymers all the parameters for the calculation of $[(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q)]$ are known with the exception of χ. Therefore, χ was varied to produce the best fit to the scattering profiles. This worked well for the 162 and 180 °C data; however, the slight shift in the position of the scattering maximum for the data at 120 °C necessitated variation of R_g. This was done by keeping the number of statistical segments fixed and varying b, the statistical segment length, slightly. The values of b and χ used to fit the scattering profiles are shown in Table I. As can be seen, the change in b required to fit the peak position was less than 1%.

It should be noted that in the calculations an average value of the statistical segment length was used. The values of the statistical segment length for PS has been found previously to be 6.8 Å by Ballard et al.,[27] whereas

Table I
Temperature Dependence of PS/PMMA Parameters

T, °C	$q_{\max}$, Å^{-1}	b, Å	χ
120	0.0432	6.85	0.0383
162	0.0443	6.70	0.0373
180	0.0443	6.70	0.0370

that for PMMA has been reported by Kirste et al.[28,29] as being 7.4 ± 3 Å. Consequently, the statistical segment lengths of the two components are only slightly different which justifies the use of a single, averaged value. In fact, the values reported here are in good agreement with the previously reported values.

Comparisons between the experimental and calculated profiles for the 120 and 180 °C are shown in Figures 2 and 3, respectively. It can be seen that the agreement between theory and experiment is quite good over the entire scattering vector range. Both the shape and position of the experimental profiles are well reproduced by the calculated profiles with the exception of the data at very low q. For $q \lesssim 0.025$ Å the experimental data are slightly, but consistently, higher than the calculations. This cannot be attributed to polydispersity effects or improper subtraction of the incoherent scattering. It may, in fact, be a result of the incompressibility assumption in the theory,[30] which forces the theoretical profiles to zero at $q = 0$. While small, the compressibility of the molten copolymer is not zero.

The shape of the calculated scattering profile is quite sensitive to the value of χ. Variation of χ by more than 0.001, i.e., ca. ± 3%, produced unacceptable fits to the scattering profiles. Consequently, error limits of at most 0.001 can be placed on the χ values reported. From Table I it is seen that χ decreases with increasing temperature as would be expected. The temperature dependence of χ, however, is quite weak. In Figure 4, χ is plotted as a function of $1/T$, and, as can be seen, a linear dependence is observed. The linear least-squares fit to the data in Figure 4 yield

$$\chi = (0.028 \pm 0.002) + \frac{(3.9 \pm 0.6)}{T} \tag{5}$$

Representing χ in terms of entropic, χ_s, and enthalpic, χ_H, contributions, one can write

$$\chi = \chi_s + \chi_H/T \tag{6}$$

Comparison of eq 5 and 6 show that the entropic contribution to χ, (0.028 ± 0.002), is much greater than the enthalpic contribution, (3.9 ± 0.6)/T. This is rather unusual for block copolymers since, for most systems reported in the literature, the reverse is true; i.e., the enthalpic term dominates. The dominance of χ_s leads to a weak temperature dependence of χ.

From eq 5 χ can be extrapolated to any temperature. For a symmetric diblock copolymer where $f = 0.5$, the copolymer will microphase separate when $\chi N > 10.5$. In particular for the copolymer studied here ($N = 262$), the microphase separation transition temperature is calculated as being ca. 60 °C. Consequently, the order–disorder transition occurs below the glass transition temperature of the polymer and, therefore, is not observable under equilibrium conditions. The weak temperature dependence of χ leads to an interesting result. If a temperature of 210 °C is assumed to be an upper limit where this copolymer can be studied without significant degradation, then a value of $N = 288$ is found to correspond to the condition for a microphase separation. Thus, by increasing the total number of segments in the PS/PMMA chain by only 10%, the microphase separation transition temperature has increased by 150 °C. More importantly, this small change in the number of segments has brought the microphase separation transition temperature from below the glass transition temperature to above the decomposition temperature. Therefore, the molecular weight window where the order–disorder transition can be observed is quite small.

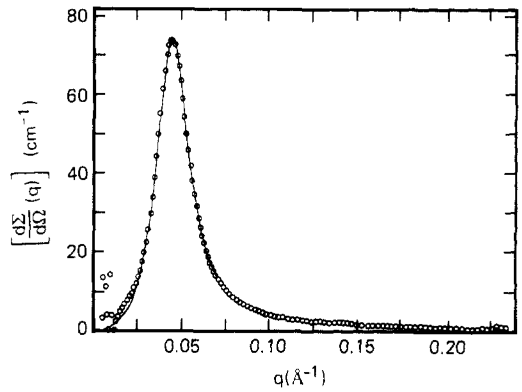

Figure 2. Comparison of the calculated and experimental neutron scattering profiles at T = 135 °C where χ = 0.0383 was used in the calculation.

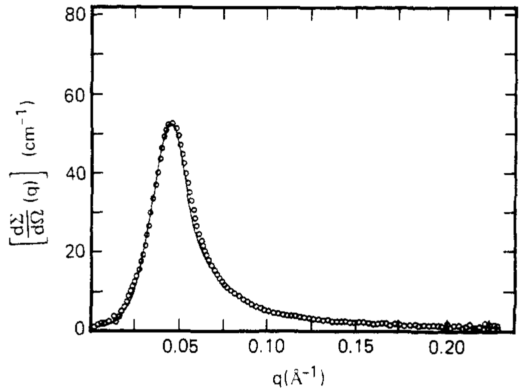

Figure 3. Comparison of the calculated and experimental neutron scattering profiles at T = 182 °C where χ = 0.037 was used in the calculation.

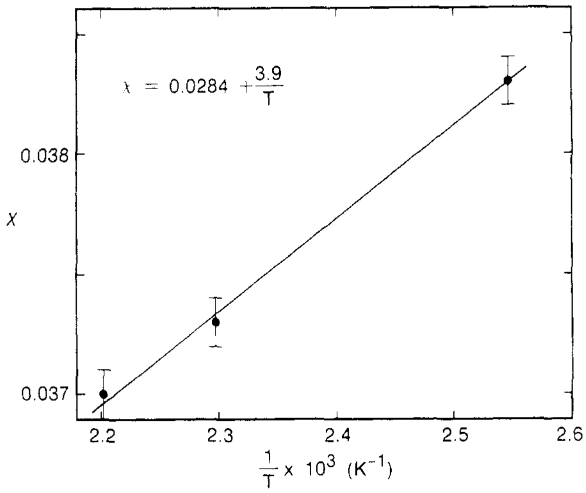

Figure 4. The interaction parameter, χ, as a function of the reciprocal temperature for P(d-S-*b*-MMA) symmetric, diblock copolymers.

Throughout this study, the effects of composition fluctuations have not been taken into account. It has been shown by Fredrickson et al.[31-33] that, close to the MST, composition fluctuations can contribute significantly to the observed scattering and can introduce substantial errors into the value of χ estimated by simple mean field arguments. For infinitely large molecular weights fluctuation effects vanish, whereas for finite molecular weights, as is the case presented here, fluctuation effects can be large. However, for the P(d-S-MMA) studied here, the measurements were performed at temperatures well above the MST where such effects would be minimized. It is clear that the simple mean field arguments used in this study may lead to errors in the prediction of the precise location of the MST; however, the values of χ reported herein should not contain marked errors. It should also be noted that independent studies on a P(S-*b*-MMA) diblock copolymer with a different molecular weight yielded an experimental MST of 179 °C that agreed well with the value of 165 °C predicted from the simple mean field arguments.[34] This may be suggesting that the fluctuation effects are not as marked in these block copolymers which may be a result of the weak temperature dependence of χ.

Using eq 5 to obtain χ and the reported values of the statistical segment lengths, eq 1 can be used to calculate the width of the interface, a_I, between the PS and PMMA domains. Assuming a temperature of 150 °C, $\chi = 0.0376$ and $a_I = 29$ Å. This result is lower than the value reported by Fernandez et al.[8,15] for the interface between PS and PMMA homopolymers and that reported by Russell et al.[9,10,16,17] for the interface in P(S-*b*-MMA) diblock copolymers, regardless of the measurement technique. The theoretical arguments relating to the interfacial width are valid in the strong segregation limit and for infinite molecular weight. However, even for high molecular weight copolymers which are in the strong segregation limit, X-ray scattering and neutron reflectivity studies on the P(S-*b*-MMA) copolymers show an interfacial width of 50 Å, nearly doubled the theoretical prediction.

Broseta et al.[35,36] have recently taken into account the effect of the finite molecular weights of polymers on the interfacial width. In this treatment an analytic expression for the interface is given as

$$a_I = (a_I)_H\left(1 + \ln 2\left(\frac{1}{\chi Z_A} + \frac{1}{\chi Z_B}\right)\right) \quad (7)$$

where Z_i is the degree of polymerization of component i and $(a_I)_H$ is the width of the interface defined in eq 1. Calculation of a_I from eq 7 yields a value of 37 which is more in line with the results presented here but is still nearly 25% too low. The difference between the experimentally observed and theoretically calculated interfacial width is quite large and points to shortcomings of theoretical treatments.

In conclusion, the temperature dependence of the Flory–Huggins interaction parameter for PS and PMMA has been measured by using diblock copolymers in the phase-mixed state. The temperature dependence of χ is much weaker than that seen for other block copolymers which results from a dominance of χ by χ_s, the entropic portion. Large discrepancies are found between theoretical predictions and experimentally measured values of the widths of the interfaces between block copolymer microdomains and between the corresponding homopolymers.

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References and Notes

(1) Dobry, A.; Boyer-Kawenoki, F. *J. Polym. Sci.* **1947**, *2*, 90.
(2) Stockmayer, W. H.; Stanley, H. E. *J. Chem. Phys.* **1950**, *18*, 153.
(3) Fuguta, T.; Inagaki, H. *Pure Appl. Chem.* **1983**, *55*, 1541.
(4) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548.
(5) Benoit, H.; Wu, W.; Benmouna, M.; Moser, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(6) Su, A. C.; Fried, J. R. *Macromolecules* **1986**, *19*, 1417.
(7) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.
(8) Fernandez, M. L.; Higgins, J. S.; Penfold, J.; Ward, R. C.; Schackleton, C.; Walsh, D. J. *Polymer* **1988**, *29*, 1923.
(9) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(10) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F., *J. Chem. Phys.*, submitted for publication.
(11) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers-1*; Goodman, I., Ed.; Applied Science Publishers: Essex, England, 1982; p 99.
(12) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327.
(13) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1971**, *56*, 3592.
(14) Russell, T. P.; Karim, A.; Mansour, A.; Felcher, G. P. *Macromolecules* **1988**, *21*, 1890.
(15) It should be noted that the authors in ref 8 defined the interface in terms of a Debye–Waller factor in the reflectivity equations with a value of 20 ± 5 Å. This yields an error function in real space with an efective interface width of $(2\pi)^{1/2} \times 20 \pm 5$ Å or 50 ± 12.5 Å.
(16) Russell, T. P.; Jérôme, R., unpublished results.
(17) Green, P. F.; Russell, T. P.; Jérôme, R.; Granville, M. *Macromolecules* **1988**, *21*, 3266.
(18) Russell, T. P.; Coulon, G.; Deline, V. R.; Miller, D. C. *Macromolecules*, in press.
(19) Hjelm, R. P.; Seeger, P. A.; Nutter, M. *Mol. Cryst. Liq. Cryst.* **1989**, in press.
(20) Hjelm, R. P. *J. Appl. Crystallogr.* **1988**, *21*, 618.
(21) Hjelm, R. P.; Seeger, P. A. *Conf. Phys.* **1989**, *97*, in press.
(22) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(23) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(24) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(25) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.
(26) Owens, J. N.; Grancarz, I.; Koberstein, J. T.; Russell, T. P. *Macromolecules* **1989**, *22*, 3380.
(27) Ballard, D. G. H.; Wignall, G. D.; Schelten, J. *Eur. Polym. J.* **1973**, *9*, 965.
(28) Kirste, R. G.; Kratky, O. *Z. Phy. Chem.* **1962**, *31*, 383.
(29) Kirste, R. G. *Makromol. Chem.* **1967**, *101*, 91.
(30) Freed, K., private communication.
(31) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 5306.
(32) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(33) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H.; Glinka, C. J. *Phys. Rev. Lett.* **1988**, *61*, 2229.
(34) Russell, T. P.; Anastasiadis, S. H.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.*, submitted for publication.
(35) Broseta, D.; Leibler, L.; Ouldkaddour, L.; Strazielle, C. *J. Chem. Phys.* **1987**, *87*, 7248.
(36) Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. *Macromolecules*, in press.

Registry No. (PSD)(PMMA) (block copolymer), 106911-77-7; PS, 9003-53-6; PMMA, 9011-14-7; neutron, 12586-31-1.