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Equilibration in Glassy Polymer Blends: Effects on Interaction Parameters Measured by Small-Angle Neutron Scattering

Edward J. Kramer*

Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, New York 14853

Hans Sillescu

Institut für Physikalische Chemie, Johannes-Gutenberg Universität, D-6500 Mainz, FRG.
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ABSTRACT: Small-angle neutron scattering (SANS) measurements of the Flory–Huggins interaction parameter χ in glassy polymer blends are shown to be subject to large systematic errors due to the fact that the composition fluctuations in the melt may fall out of equilibrium at widely differing temperatures T_e depending on cooling rate and molecular weight. As a concrete example we compute T_e for the system dilute deuteriated polystyrene (d-PS) in polyxylenyl ether (PXE) using measured diffusion coefficients of d-PS and show that, even at slow cooling rates, the resulting increase in T_e with d-PS molecular weight leads to decreasing negative values of χ that are in quantitative agreement with those measured in the same system by Jelenic et al.[1]

Introduction

One of the most promising applications of small-angle neutron scattering (SANS) in polymer research is its use for determining the Flory–Huggins segment–segment interaction parameter χ for miscible polymer blends.[1-14] While some of the measurements have been made as a function of temperature by using special specimen holders that permit the sample to be held at a given temperature during the SANS measurement, many of the measurements on blends that are glasses at room temperature have been made by the following method: The sample is homogenized by heating to temperatures well above the glass transition temperature T_g and then cooled to room temperature where the SANS measurements are made. Because the cooling is usually reasonably slow, it is assumed that the sample falls out of equilibrium at T_g so that the χ thus determined corresponds to χ at this temperature. While this method is popular because it simplifies the SANS measurements, the results on some systems are rather disappointing. For example in the system deuteriated polystyrene (d-PS)–poly(2,6-dimethyl-1,4-phenylene oxide) [or polyxylenyl ether (PXE)] the results from different investigators using SANS to determine the χ for blends of dilute d-PS in PXE vary from almost −0.04 to 0.00, well outside what should be the experimental error of the technique.[1-5] Even more disturbing are the careful measurements of Jelenic et al.[1] which appear to show that the magnitude of χ depends strongly on the molecular weight M of d-PS, decreasing monotonically from −0.0124 for M = 24 000 to −0.0006 for M = 465 000. The entire concept of a segment–segment interaction parameter seems meaningless if it depends this strongly on M.

In a following paper we examine the crucial assumption of this procedure, i.e. that the sample falls out of equilibrium only at T_g, and show that because of the very slow mutual diffusion in the molten state of many polymer blends, this assumption is not even approximately correct. Depending on the magnitude of the mutual diffusion coefficient D and the cooling rate, the sample can fall out of equilibrium at a temperature as much as 60 K above T_g. If the Flory–Huggins parameter depends strongly on temperature, the χ's measured by investigators using different cooling rates during sample preparation certainly will not be the same. Moreover if the molecular weight of the component polymers are changed as in the Jelenic et al. experiment,[1] that must change the temperature at which the sample falls our of equilibrium and hence the measured χ, since D decreases with increasing molecular weight.

While one might imagine special cases where this problem in achieving equilibrium would produce negligible error in the measured χ, it seems worthwhile to check whether it might be the reason for the scatter in the data for d-PS:PXE expecially since independent determinations of both D and $\chi(T)$ have been possible recently from measurements of tracer diffusion and mutual diffusion in this system. Using these values of D and $\chi(T)$ we show that the equilibration temperatures in d-PS:PXE do in fact lie well above T_g for reasonable cooling rates and moreover that the dependence of D on molecular weight M of d-PS can account for some of the apparent M dependence of χ measured by Jelenic et al.

Equilibration in Polymer Blends

The Flory–Huggins parameter can be determined by small-angle neutron scattering from blends of deuteriated and hydrogenated polymers because such scattering is sensitive to composition fluctuations in the blend, composition fluctuations which increase as χ becomes less negative and the spinodal is approached. The scattering at a wave vectors $\mathbf{q}$ ($q = (4\pi/\lambda) \sin(\theta/2)$ where θ and λ are the scattering angle and the wave length of the neutrons, respectively), corresponding to composition fluctuations with wave lengths $\sim q^{-1}$, is proportional to the

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structure factor of the blend $S(q)$. The equilibrium value of the structure factor is given in the random phase approximation by[15]

$$\frac{1}{S_e(q)} = \frac{1}{N_A\varphi_A g_D(R_{g,A},q)} + \frac{1}{N_B\varphi_B g_D(R_{g,B},q)} - 2\chi \quad (1)$$

where φ_A, N_A, $R_{g,A}$ and φ_B, N_B, $R_{g,B}$ are the volume fraction, degree of polymerization, and radius of gyration, respectively, of the two components A and B, respectively, in the blend and where g_D, the Debye function, is given by

$$g_D(R_g,q) = 2[(qR_g)^2 + e^{-(qR_g)^2} - 1]/(qR_g)^4 \quad (2)$$

The equilibrium structure factor $S_e(q)$ depends of temperature primarily through the temperature dependence of χ.

The structure factor measured by SANS may not be the equilibrium one, however. In this regard it is useful to examine the evolution of the structure factor after a quench from T_0 to T_1. Binder[15] has shown that this structure factor is given by

$$S(q,t) = S_e(q,T_1) + [S_e(q,T_0) - S_e(q,T_1)]e^{-2q^2D(T_1)t} \quad (3)$$

where $D(T_1)$ is the mutual, or interdiffusion, coefficient at T_1. The structure factor at a wave vector q only relaxes to its new equilibrium value when mutual diffusion has occurred over a length scale larger than wavelength q^{-1} of the corresponding composition fluctuation.

To determine the structure factor of a blend after cooling at a constant rate from a temperature T_0, far above, to a temperature T_f, far below, the glass transition temperature T_g, we need only imagine that the continuous cooling curve, starting from a time $t' = 0$, is made up of a large number of step quenches, whose effect we can compute via eq 3. The sample is quenched from T_0 to T_1, held at T_1 where the mutual diffusion coefficient is D_1 for a time t_1, then quenched to a temperature T_2, where the diffusion coefficient is D_2 and held for a time t_2, and so on. The resulting $S(q,t)$ will be given by

$$S(q,t) = S_e(q,T_f) + \{...[(S_0 - S_1)\exp(-2q^2D_1t_1) + (S_1 - S_2)]\exp(-2q^2D_2t_2) + ...\} \quad (4)$$

Here S_0, S_1, and S_2 are the $S_e(q)$'s at T_0, T_1, and T_2, respectively and T_f is the final temperature. Thus in the series that results, the magnitude of each of the S jumps, e.g. $(S_0 - S_1)$, is multiplied by a exponential of a sum of products of diffusion coefficients and times, e.g., $\exp(-2q^2\sum D_it_i)$, which represent the decay of this S jump over the entire cooling history.

The sums in eq 4 are readily transformed to integrals by passing to the limit where the steps are infinitesmal. From the cooling rate r we find the temperature T at a time t', $T_0 - rt'$, and the values of the mutual diffusion coefficient $D(t')$, the equilibrium structure factor $S_e(t')$ and its time derivative $S'_e(t')$. The actual structure factor at time t is thus given by

$$S(q,t) = S_e(q,t) + \int_{-\infty}^{t} dt' \left[S'_e(q,t') \exp\left(-2q^2 \int_{t'}^{t} d\xi\, D(\xi)\right)\right] \quad (5)$$

The most temperature dependent quantity in eq 4 or 5 is the mutual diffusion coefficient of the blend which, in the small q limit, is given by

$$D = 2\varphi_A\varphi_B D_T(\chi_s - \chi) \quad (6)$$

where χ_s is the value of χ at the spinodal given by

$$\chi_s = 0.5[(1/\varphi_A N_A) + (1/\varphi_B N_B)]$$

and D_T is an Onsager transport coefficient given by[16-23]

$$D_T = \varphi_B N_A D^*_A + \varphi_A N_B D^*_B \quad (7)$$

and where the D^*'s are the tracer diffusion coefficients of the respective polymer species.

When one of the components in the blend is dilute as in the case of the d-PS in PXE studied by Jelenic et al.,[1] the expression for D simplified greatly, with D in the limit of infinite dilution reducing to the tracer diffusion coefficient of the dilute species, i.e. $D = D^*_{d\text{-PS}}$ in the Jelenic experiments. For the purposes of illustration we henceforth confine our demonstration to this dilute case, although it should be clear that qualitatively similar behavior will be exhibited by the more concentrated blends.

To compute the structure factor after cooling at a constant rate r into the glassy state, we require the temperature dependent Flory–Huggins interaction parameter $\chi(T)$ and the tracer diffusion coefficient D^* of d-PS in PXE, both of which are available.[22,23] The tracer diffusion coefficient $D^*_{d\text{-PS}}$ is given by

$$D^*_{d\text{-PS}} = \frac{D_0}{M^2}\frac{T_{ref}}{T}a_T \quad (8)$$

where the reptation constant $D_0 = 0.022$ cm^2/s and a_T is a Vogel–Fulcher (or WLF) shift factor given by

$$\log a_T = -\frac{B}{T - T_\infty} + \frac{B}{T - T_{ref}} \quad (9)$$

where T_{ref} is a reference temperature (= 555 K in what follows), $T_\infty = T_g - 52$ K and B is a constant taken to be equal to its value 601 K found from measurements of $D^*_{d\text{-PS}}$ in a blend of 45% PXE and 55% PS.[22,23] The use of eq 8 implies that the mechanism of d-PS diffusion is reptation which will not necessarily be true for the general case. However in the case of d-PS diffusing in PXE, Composto[22] has verified that reptation holds for all molecular weights examined by Jelenic et al. Even though the highest d-PS molecular weights are more than 10 times that of the PXE matrix, the fact that the reptation constant for PXE is so much smaller than that of d-PS means that constraint release by the much slower PXE molecules makes a negligible contribution to the tracer diffusion coefficient of d-PS.

We use the values of $\chi(T)$ determined by using eq 6 and 7 from measurements of the mutual diffusion and tracer diffusion coefficients in a blend of 55:45 PS:PXE. This relation obtained from these measurements[22,23]

$$\chi(T) = 0.112 - 62/T \quad (10)$$

also produces a reasonable fit to the mutual diffusion results for d-PS:PXE blends across the entire composition range.[22,23]

Results and Discussion

For each of the d-PS molecular weights used by Jelenic et al.[1] we have performed the integrations in eq 5 numerically to obtain the $S^{-1}(q)$ versus q^2 curve for a polymer glass formed by cooling from 554 K at various rates r ranging from a moderate rate of 1 K/s to an extremely slow rate of 0.0001 K/s. The results for a d-PS of molecular weight 188 000 are displayed in Figure 1. Also shown on this figure are the equilibrium values $S_e^{-1}(q)$ corresponding to $T = 554$K (dotted line) and $T_g = 489$ K (solid line). Note that the $S^{-1}(q)$ versus q^2 curves all fall well below the $S_e^{-1}(q)$ versus q^2 curve for the blend equilibrated at T_g. At the moderate rate of 1 K/s the $S^{-1}(q)$ versus q^2 curve is much closer to the $S_e^{-1}(q)$ versus q^2 curve at the starting temperature of 554 K than to the equivalent curve at T_g and even at the extremely slow rate of 10^{-4} K/s, the $S^{-1}(q)$

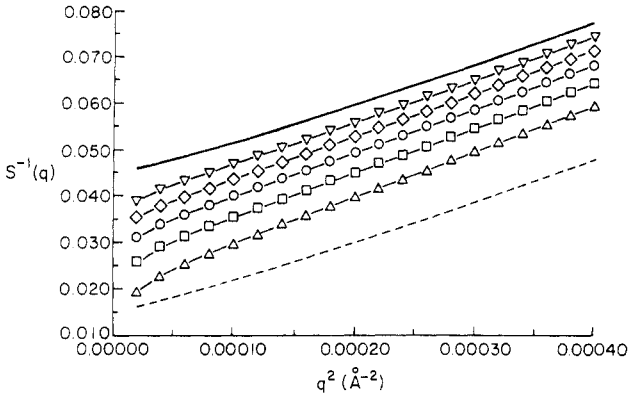

Figure 1. Reciprocal of the structure factor for a blend of 5 vol % d-PS in PXE versus the square of the scattering vector. The dotted and solid lines correspond to the equilibrium structure factors at $T = 554$ K and $T = T_g = 489$ K. The lines with symbols correspond to the computed structure factor after cooling the blend from 554 K into the glass at rates of 1 K/s (upward pointing triangles), 0.1 K/s (squares), 0.01 K/s (circles), 0.001 K/s (diamonds), and 0.0001 K/s (downward pointing triangles). The molecular weight of the d-PS is held constant at 188 000.

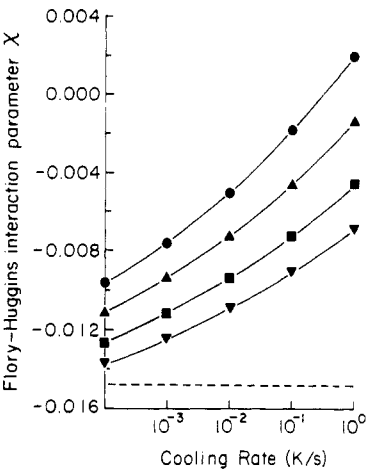

Figure 2. Flory–Huggins interaction parameter χ extracted from $S^{-1}(q)$ versus q^2 plots such as Figure 1 as a function of cooling rate for a blend of 5 vol % d-PS in PXE where the molecular weight of the d-PS is 24 000 (downward pointing triangles), 63 000 (squares), 188 000 (upward pointing triangles), and 465 000 (circles). The dotted line indicates the χ at T_g.

versus q^2 curve lies well below the equilibrium curve at T_g. To appreciate that the latter rate is really a practical lower limit for typical experiments, it is enough to realize that at this rate it requires 35 days to cool from 300 to 0 °C. A rate of 10^{-2} K/s would be more typical for "slowly cooled" samples.

Note also that the shapes of the $S^{-1}(q)$ versus q^2 curves differ markedly from the equilibrium curves, the former being concave downward while the latter are concave upward. The downward curvature of the $S^{-1}(q)$ versus q^2 curves from the glasses formed by cooling at a constant rate are a consequence of the more rapid equilibration of the composition fluctuations with larger wavevectors. At a given cooling rate these composition fluctuations do not freeze in until one reaches lower temperatures than those at which the composition flucturations with smaller wavevectors freeze in. In fact the existence of a downward curvature in the $S^{-1}(q)$ versus q^2 curve is evidence that the composition fluctuations in the blend have not been equilibrated. It is significant in this regard that the $S^{-1}(q)$ versus q^2 curves for d-PS in PXE measured by Jelenic et al. have a strong downward curvature. [Our use of the low q expression for D ignores the increase in the thermodynamic driving force for diffusion at higher q which goes as $S_e^{-1}(q)$ and an increase in D_T due to a change from a reptation mechanism to a Rouse mechanism for diffusion at the higher q's;[15] both effects, if included, would produce a faster equilibration of the $S^{-1}(q)$ at high q's and the downward curvature seen in Figure 1 would be reduced. Significant polydispersity of molecular weight also can cause even the equilibrium $S^{-1}(q)$ versus q^2 curve to show downward curvature; since the dilute d-PS in the experiments of Jelenic et al. was nearly monodisperse however, such polydispersity can not be the cause of the downward curvature they observed.]

The apparent value of $\chi_s - \chi$ can be determined by finding the intercept of each of the $S^{-1}(q)$ versus q^2 curves in a manner equivalent to the treatment of the experimental SANS data. While all these curves actually extrapolate to the intercept of the $S_e^{-1}(q)$ versus q^2 curve at 554 K since it is always possible to find a q small enough (wavelength $1/q$ of composition fluctuation large enough) to make diffusion over these distances impossible during cooling, these q's are not generally accessible to the SANS experiment, since they correspond to angles that lie under the beam stop. To mimic the treatment of the experimental data, we have extrapolated the $S^{-1}(q)$ versus q^2 curves to zero q by fitting a line using the method of least squares to the first five points shown on the curve, i.e. those between $q^2 = 0.000\,02$ and $q^2 = 0.000\,10$. While this treatment of the data is necessarily arbitrary, it does simulate reasonably well the procedures used in practice to extract χ from the SANS data.

Using this procedure we have determined a value of χ for each one of the curves from the 188 000 molecular weight d-PS in Figure 1, and these results are shown as a function of cooling rate as the upward pointing triangles in Figure 2. Also shown as the dashed line is the value of χ at T_g. While the discrepancy between the two χ values increases with increasing cooling rate, it is clear that even at lowest possible cooling rates, the value of χ determined from the $S^{-1}(q)$ versus q^2 curve lies well above $\chi(T_g)$, corresponding to the fact that the composition fluctuations fall out of equilibrium during cooling at an effective equilibration temperature significantly above T_g. One may estimate this equilibration temperature from the equilibrium $\chi(T)$ relationship (eq 10), and it is plotted in Figure 3a as a function of cooling rate for the 188 000 molecular weight d-PS in PXE.

Having demonstrated that changes in the equilibration conditions can have substantial effects, even at very slow cooling rates, on the χ that would be measured in a SANS experiment on the glassy polymer blend, we turn now to the effects of increasing the molecular weight of the d-PS. Using the same procedure a value of χ was extracted from the computed $S^{-1}(q)$ versus q^2 curves for the other d-PS molecular weights, 24 000, 63 000 and 465 000, for which SANS measurements were made by Jelenic et al.[1] These values are also shown as a function of cooling rate in Figure 2. Note that while as expected the χ for even the lowest molecular weight d-PS in PXE lies above the $\chi(T_g)$, at a given cooling rate, the discrepancy between χ and $\chi(T_g)$ increases strongly with increasing molecular weight. At the highest molecular weight and the fastest cooling rate in fact the sample will yield a value of $\chi \approx 0$, corresponding to the temperature $T_0 = 554$ K from which the simulated cooling experiment was begun. Since for this sample starting the cooling at a higher temperature yields a higher value of χ, the value shown by the cross in Figure 2 corresponds to the limiting value of χ as T_0 is increased.

To show the effect of molecular weight in another way, we compute the χ values, and the equilibration tempera-

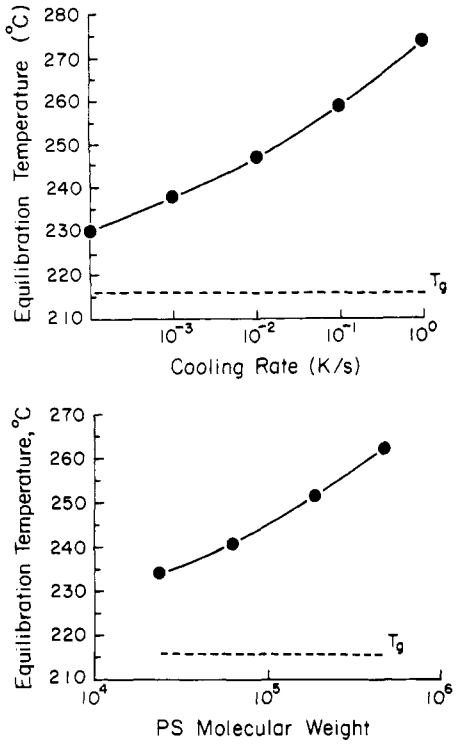

Figure 3. Equilibration temperatures of a blend of 5 vol % d-PS in PXE as a function of (a) the cooling rate for a d-PS molecular weight of 188 000 and (b) the d-PS molecular weight at a cooling rate of 2.5×10^{-2} K/s.

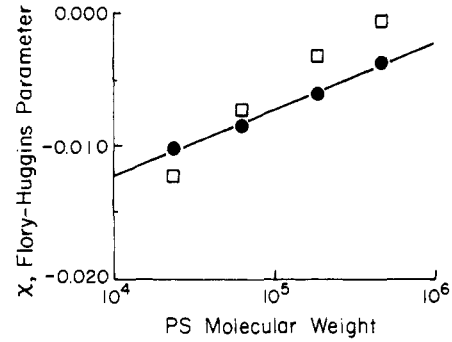

Figure 4. Flory–Huggins interaction parameter χ extracted from $S^{-1}(q)$ versus q^2 curves for a blend of d-PS in PXE as a function of the d-PS molecular weight: calculated points (solid circles); data of Jelenic et al. (open squares).

tures, that would be obtained as a function of M at a cooling rate of 1.5 K/min (0.025 K/s), which is the rate of cooling in the Jelenic experiments.[24] These results for χ are shown in Figure 4 and those for equilibration temperature in Figure 3b. The equilibration temperatures range from 230 °C for the lowest molecular weights to almost 265 °C for the highest molecular weights. The corresponding χ's range from −0.0104 at the lowest molecular weight to −0.0037 at the highest. The squares are the values measured for this system by Jelenic et al.[1] While the agreement with the computed values (solid circles) is certainly not perfect, it seems clear that a major portion of the molecular weight variation in χ as measured by SANS on the glassy d-PS:PXE blends can be accounted for by the fact that the composition fluctuations with a given q fall out of equilibrium on cooling at significantly higher temperatures for the higher molecular weight samples simply due to the mutual diffusion coefficient which decreases strongly with d-PS molecular weight in these blends.

In conclusion we have demonstrated that SANS measurements of the Flory–Huggins interaction parameter on glassy samples are rather delicate. Depending on the cooling rate or molecular weight of the sample, the composition fluctuations of a given wavelength q^{-1} will fall out of equilibrium on cooling at a temperature ranging anywhere from 10 to 100 K above T_g. The values of χ actually measured will be those corresponding to the equilibration temperatures for the smallest measurable q's so that large systematic errors in χ are possible by using this procedure. It seems possible that such errors can account for some of the scatter in the values of χ from SANS on glassy polymer blends, especially in the system PS:PXE. If χ must be measured from glassy samples, a better procedure would be to thoroughly equilibrate the sample at a temperature some 20–30 K above the glass transition temperature and then quench as rapidly as possible into the glassy state so as to prevent further diffusion and preserve the composition fluctuations which existed at the holding temperature.

From Figure 1 it also appears clear that measurements of $S^{-1}(q,t)$ in the one-phase regime hold promise for determining the mutual diffusion coefficient of polymer blends. While isothermal experiments using quasi-elastic light scattering have exploited this possibility by using low molecular weight polymer blends,[25] this method is difficult to apply to high molecular weight materials. It thus seems worthwhile to reiterate a suggestion first made by Binder[15] that D be determined from the relaxation kinetics of the $S^{-1}(q,t)$ after a temperature jump in the one phase regime. Recent experiments[26] using small-angle X-ray scattering indicate that this method is feasible.

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Small-Angle Neutron Scattering from a Bisphenol A Carbonate/Dimethylsiloxane Copolymer under Uniaxial External Stretch

B. Hammouda* and W. B. Yelon

Research Reactor Facility and Department of Physics, The University of Missouri, Columbia, Missouri 65211

A. C. Lind

McDonnell Douglas Research Labs, St Louis, Missouri 63166

F. Y. Hansen

Fysisk-Kemisk Institut, The Technical University of Denmark, 206 DTH DK 2800 Lyngby, Denmark. *Received July 29, 1987; Revised Manuscript Received April 22, 1988*

ABSTRACT: There is previous evidence that random copolymers of bisphenol A carbonate (BPAC) and dimethylsiloxane (DMS) form microdomain morphology. Small-angle neutron scattering (SANS) is used to investigate this system, which shows a broad-peak spectrum. The origin of this peak is due to interference scattering between the BPAC-rich microdomain and the DMS-rich interdomain regions. SANS measurements taken from such a random copolymer (50%/50% mixture) under uniaxial external stretch show that the glassy microdomains do not follow the external drawing whereas the rubbery interdomain regions do. Two data analysis methods are used: one based on nonlinear least-squares fits of the raw data to a model consisting of two confocal ellipsoids representing the deformed microdomain morphology and the other on a two-dimensional Fourier transform of SANS data to obtain an anisotropic pair correlation function.

Introduction

Small-angle (neutron or X-ray) scattering is well suited to investigate the morphology of copolymer systems. This technique, when supplemented with some theoretical analysis, has been successfully applied to a number of copolymer systems in the solid[1-6] or melt[7-8] forms. For instance, SANS from either of these phases shows a broad-peak spectrum. The origin of this peaked behavior, however, is different. In the case of solid block copolymers, the peak is due to interference scattering between microdomain and interdomain regions (microphase segregation) while in block copolymer melts, it is due to a correlation hole[9] around single blocks, i.e., the probability of finding in the vicinity of a monomer another similar monomer belonging to a different block is decreased due to the repulsion of the polymer coils that is required to ensure the incompressibility of the system. In the Porod range, the former case shows a $1/Q^4$ decay (Q being the scattering wavenumber) while the latter case presents a $1/Q^2$ decrease characterizing correlations in Gaussian chains.

The solid randomly alternating copolymer of bisphenol A carbonate and dimethylsiloxane[10] (50%/50% random mixture of BPAC and DMS) investigated in this paper shows a broad SANS peak around $Q = 0.05$ Å^{-1} with no higher harmonic peaks. The origin of this single peak is discussed. The effect of a uniaxial external stretch on microdomain morphology is also discussed by using two methods: one based on a nonlinear least-squares fit of the two-dimensional (2D) raw data and another method based on a 2D Fourier transform of SANS data. It should be noted that the experiments reported here do not take full advantage of the SANS technique because no deuteriated samples are used. SANS can, however, be used interchangeably with SAXS on phase-segregated samples. In fact, SAXS data have been taken[11,12] on BPAC/DMS block copolymers and can be seen to qualitatively agree with SANS data. The purpose of the present investigations is to study the stretched morphology.

SANS Measurements and Data Analysis

SANS measurements are taken on a well characterized BPAC/DMS random copolymer sample unstretched and under uniaxial external stretch.

Sample Preparation and Characterization. The BPAC/DMS sample used in this study was obtained from H. A. Vaughn.[13] This sample contains 50 wt % BPAC. The block lengths are polydisperse, having a number-average degree of polymerization of about 6 for the BPAC blocks and about 20 for the DMS blocks. Additional sample characterization data have been reported previously.[14,15] For this composition and block lengths, the BPAC blocks associate into rigid domains joined together by the rubbery DMS blocks. NMR[16] results support a proposed spherical BPAC domain morphology in which the longest blocks reside at the center and the shortest blocks reside at the surface, with a gradation of block

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