Forced Rayleigh Scattering Study of Diffusion of Block Copolymers. 2. Self-Diffusion of Block Copolymer Chains in Lamellar Microdomains and Disordered Melts

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ABSTRACT: Forced Rayleigh scattering (FRS) has been used to measure the diffusion coefficients D of a dye-labeled lamella polystyrene (PS)–polyisoprene (PI) block copolymer ($M_n = 2.1 \times 10^4$, PS content 42 wt %) in the bulk state. The FRS measurements lead to double-exponential signal decays, the decay constants being grossly proportional to the square of the fringe spacing. We suggest interpreting the signals as originating from a Rouse-like diffusion parallel to the lamella interfaces in lamellae tilted at different angles against the measuring direction. Over the temperature range covered ($90 < T < 208$ °C), no drastic change in the behavior of the diffusion coefficient could be observed on crossing the order–disorder transition (ODT) temperature at about 190 °C.

I. Introduction

The development of new methods for measuring especially slow diffusion coefficients mainly during the past decade was followed by a large improvement of our understanding of translatory transport processes in polymer solutions and melts. These methods include fluorescence recovery after pattern photobleaching (FRAPP),[1] forced Rayleigh scattering (FRS),[2] elastic recoil detection (ERD), and forward recoil spectrometry (FRES).[3] More recently, such methods have begun to be applied to the study of mobilities in block copolymer systems whose rich structural variability should be reflected in an interesting transport behavior. This is because classical transport mechanisms of the polymer melt[4] such as reptation or Rouse motion are getting confronted with the topological constraints of the ordered block copolymer microdomain structure. Theoretical work on the diffusion in block copolymer systems[5] is still scarce and of limited applicability.

Some valuable information has already been obtained about the diffusion of homopolymers inside[6,7] or into[8] block copolymer structures and about the diffusion of block copolymers forming spherical micelles in solution.[9,10] Least explored is the diffusion of the block copolymer molecules themselves in the microdomain structures in the bulk. The first information concerning the self-diffusion of a bulk lamellar block copolymer has been reported by Shull et al.[11] using the FRES technique on a partially deuterated poly(ethylenepropylene-*block*-ethylethylene) (PEP–PEE) film diffusing into the identical protonated polymer.

In this study we investigate the diffusion of almost symmetrical dye-labeled polystyrene–polyisoprene (PS–PI) block copolymers diluted with some identical unlabeled block copolymers using the FRS technique.

II. Experimental Section

A. Material. The PS–PI block copolymer was prepared by sequential living anionic polymerization using *sec*-butyllithium as initiator and methylcyclohexane as solvent, thus leading to the microstructure of polyisoprene composed mostly of 1,4-linkage. A part of the polystyrene precursor was separated from the solution containing living polystyryl anions and terminated with methanol for molecular weight determination prior to adding the isoprene. The living block copolymer solution was divided into two halves, one being terminated with methanol and the other one with an excess of α,α'-dichloroxylene dissolved in dried and degassed tetrahydrofuran to yield a terminal functionalization with an active chloro group. The functionalized block copolymer was reacted in dried *N,N*-dimethylformamide with the cesium salt of 2-nitro-4-carboxy-4′-(dimethylamino)stilbene (ONS-Cs salt) as a photosensitive dye for forced Rayleigh scattering. The details of functional termination and FRS labeling with ONS have been described elsewhere.[12,13]

This ONS dye is used frequently for FRS measurements and is well known[13] to have an irreversible photochemistry. This means no back-reaction after bleaching is possible. The thermal oxidation step mentioned in ref 13 is avoided by application of nitrogen as an inert gas. This is easily seen as the samples do not turn blue after bleaching; thus no isatogene is formed, and the immediate photoproduct, dihydroisatogene, is the end product in our case.

As the functional termination leads to a varying amount of bimolecular coupling of AB block copolymers to symmetric ABA block copolymers of just double molecular weight, this component was eliminated by preparative GPC fractionation to yield the pure AB block copolymer.

The number-average molecular weight M_n of the polystyrene precursor ($M_n = 9.0 \times 10^3$) was determined by GPC, the absolute molecular weight of the block copolymer was obtained by membrane osmometry in toluene ($M_n = 2.12 \times 10^4$), and $M_w/M_n = 1.07$ from GPC, thus leading to a polystyrene content of 42 wt %. Using the UV–vis absorption of the ONS dye, the labeling efficiency was determined to 60%. The glass transition temperature of the polystyrene microdomain in the block copolymer was determined to be 78 °C by DSC with a heating rate of 20 K/min.

B. Small-Angle X-ray Scattering (SAXS) and TEM. SAXS measurements were performed using a Rigaku rotating-anode X-ray generator (Cu Kα line, 0.154-nm wavelength), graphite monochromator, slit collimation, and a one-dimensional position-sensitive proportional counter as a detector. All measurements were corrected for detector sensitivity, air scattering, and background scattering and were normalized on sample thickness.

For transmission electron microscopy (TEM), ultrathin sections were stained with osmium tetraoxide (OsO_4) according to standard procedures.

C. Forced Rayleigh Scattering (FRS). Diffusion measurements were performed with a newly constructed FRS setup using an NEC argon ion laser as a light source for bleaching and reading (488 nm, single-mode operation). The equipment resembles other present FRS setups.[14] Daylight was shielded from the detector by using interference filters. Incident beam intensity was monitored and used to normalize the FRS signal. For data acquisition and operation of shutters and attenuator, an NEC 9801 computer was used with self-made programs and interfacial hardware. According to the conventional method,[15] the decay of FRS signal intensity I with time t was fitted to a single- or double-exponential function (the latter being necessary in most of the cases) by using a nonlinear least-squares fitting

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program:

$$I = [A \exp(-t/\tau) + B]^2 + C \qquad (1)$$

or

$$I = [A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)]^2 + C \qquad (2)$$

In these equations A, A_1, and A_2 are amplitudes and τ, τ_1, and τ_2 are relaxation times of the signal decay, while B and C are constant background values[16] which may contribute coherently (B) or incoherently (C) to the signal. The coherent background B given in eq 1 was neglected in eq 2, because B was found to be negligible by measuring the light intensity scattered from the specimens before bleaching (C) and after diffusion had ceased ($B^2 + C$).

The relative uncertainties in determination of the parameters τ_1 and τ_2 based on eq 2 are less than about 20%. Here we would like to emphasize that the fitting of the decay curves with the two-exponential decay functions does not mean at all that there are two physically distinct decay processes but rather that there is a distribution of decay times which is just narrow enough to be fitted to the double-exponential function. For this reason we shall not present tables containing all five fitting parameters for each of the decay curves.

All measurements were carried out by shielding specimens in vacuum or under an inert gas atmosphere to suppress the thermal oxidation step of the ONS dye photoproduct. FRS samples were prepared starting from a powdery precipitate of the block copolymer which was first cold pressed between metal plates and then hot pressed (at about 150 °C in the ordered state) between two plates. The sample thus formed has a 1-cm diameter, and the film thickness is adjusted to about 50 μm by use of Teflon spacers. The biaxial flow occurring during the hot-pressing step leads to a strong preferential orientation of the lamellae with their interfaces parallel to the film surface.[17]

Temperature was kept constant with an accuracy of 0.25 °C and was usually constant after 30 min. However, 3-4 h (sometimes more) was necessary to let flow processes relax, which are visible as a downward bending in the time variation of FRS signal decays with time. As block copolymers are only in metastable equilibrium, as long as grains of finite size persist, some continual slow reordering may be expected to take place above the glass transition temperature.

III. Results and Discussion

A. SAXS Measurements. Figure 1 shows the static SAXS structure factors of the PS-PI block copolymer as obtained in situ at different temperatures. 2θ is the scattering angle and q is the magnitude of the scattering vector defined by $q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength of the X-ray beam used. The position q_m of the scattering maximum which can be seen up to the third order at lower temperatures is in agreement with the electron microscopy results in Figure 2, confirming a lamellar type domain. The domain spacing $2\pi/q_m$ changes from 18.8 to 16.2 nm as the temperature is elevated from 30 to 250 °C, and the shrinking of the domain spacing or the wavelength of the dominant mode of the concentration fluctuations is continuous across the order-disorder transition temperature T_{ODT} without showing a significant change in slope. In this work T_{ODT} was determined using different methods, as will be presented elsewhere.[18] Measurement of the absolute scattering intensity in the disordered state well above 200 °C was difficult because of the onset of thermal degradation. Thus a true linear region for the reciprocal scattering intensity I_m^{-1} at a fixed q near the first-order maximum (q_m) plotted against reciprocal temperature could not be observed. However, a drastic change in the scattering profile is observed in the change in the line shape of the first-order scattering maximum as measured by the half-width at half-maximum intensity $W_{1/2}$. According to Leibler's theory,[19] $W_{1/2}$ is proportional to $(1/T - 1/T_c)^{1/2}$, where T_c is the mean-field spinodal temperature. In Figure 3, $[W_{1/2}]^2$ is plotted as a function of $1/T$. The temperature dependence of $W_{1/2}$ changes at 190 °C: above 190 °C, $[W_{1/2}]^2$ increases linearly with $1/T$ but below 190 °C it stays nearly constant with $1/T$. $W_{1/2}$ seems in this case to be a more reliable measure to determine the ODT, leading to have a value of 190 ± 5 °C.[18]

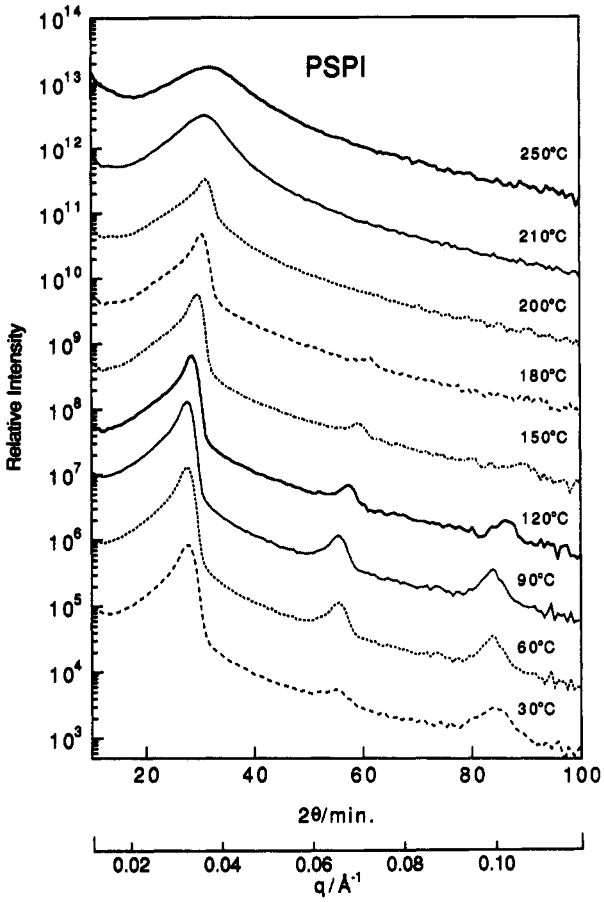

Figure 1. Small-angle X-ray scattering (SAXS) profiles of PS-PI block copolymers at various temperatures plotted as a function of the scattering angle or scattering vector q in a semilogarithmic scale. The profiles obtained at any two successive temperatures are shifted from each other by one decade.

B. FRS Measurements. In Figure 4 we show typical signal decays of the FRS intensity along with the single-exponential fit obtained by eq 1 (solid lines) at 174 and 201 °C where the block copolymer is in the ordered and disordered state, respectively. Both measurements are obtained with different fringe spacings as indicated in the figure (28.9 and 10.8 μm); thus the signal decay at the lower temperature is faster, although the diffusion in fact is slower. Furthermore, the constant background values C have not been subtracted. The high background value at 201 °C is typical for measurements with such a large fringe spacing (28.9 μm) because the position of the monitored Bragg peak is only about 1° aside of the reading beam. At larger angles the background is usually negligible if the sample is free from turbidities. In the ordered state a fit with a sum of two exponentials is generally necessary, while the tendency in the disordered state is more likely toward the single-exponential behavior.

However, a close observation indicates that even at $T > T_{ODT}$ a sum of two exponentials better describes the data. It should be noted here again that the two-exponential decays do not mean at all existence of two physically distinct relaxation processes but rather existence of a distribution in relaxation time, although the distribution seems to be much narrower in the disordered states

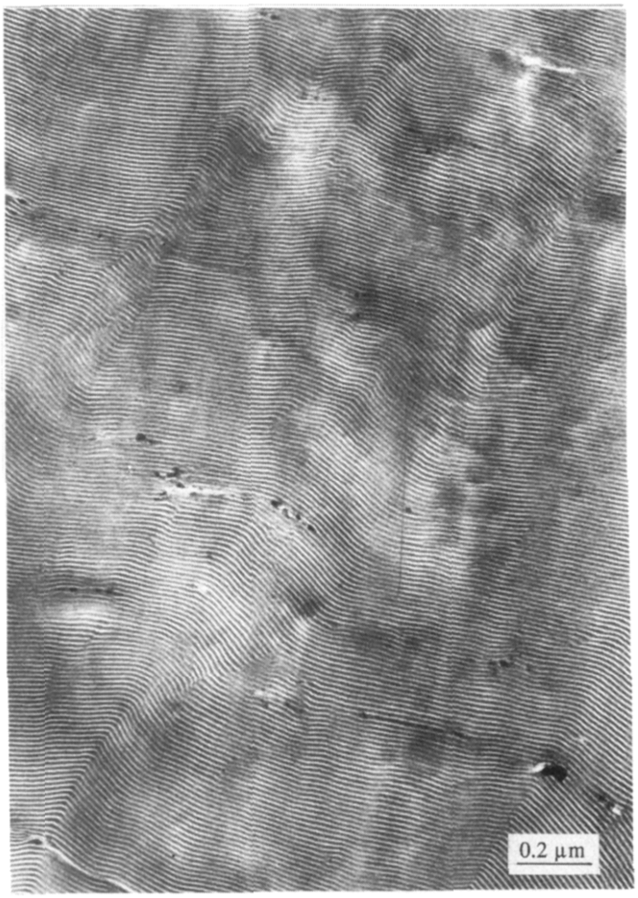

Figure 2. Transmission electron micrograph of ultrathin sections of the as-prepared SI block copolymers stained by OsO_4.

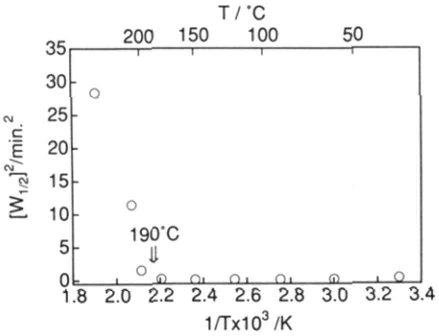

Figure 3. Square of the half-width at half-maximum for the first-order SAXS maximum plotted as a function of $1/T$.

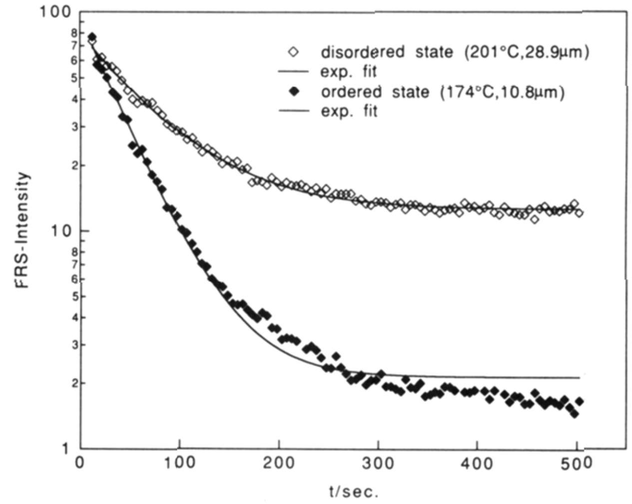

Figure 4. Time changes of FRS intensity in the disordered state (unfilled diamonds) at 201 °C and in the ordered state (filled diamonds) at 174 °C. The fringe spacings at 174 and 201 °C are 10.8 and 28.9 μm, respectively. The solid lines correspond to the results of the best fit with the single-exponential decay given by eq 1.

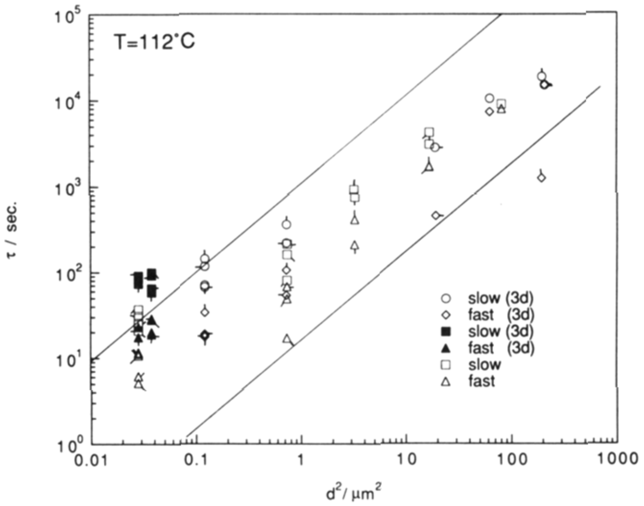

Figure 5. Relaxation time τ for the decay of the FRS signal at 112 °C plotted as a function of d^2.

than in the ordered states. Because the ODT is rather high (190 °C), the thermal instability of the polymer does not allow one to measure far above the ODT and therefore far into the disordered region where truly single-exponential decay may be expected. The origin of the distribution of the relaxation time in the disordered state is not well understood at present and will be left open for future investigation. Recent dynamic mechanical experiments[20] have shown that in the disordered region block copolymer melts are on average homogeneous but dynamically active concentration fluctuations may persist up to $T_{ODT} + 50$ K. It is tempting to tentatively relate our deviation from single-exponential FRS decay in the disordered melt to such fluctuations. The concentration fluctuations near the ODT in the disordered state are easily expected to suppress the diffusion coefficient, but they may also broaden the distribution of the relaxation time.

In Figure 5 the relaxation time τ at constant temperature $T = 112$ °C in the ordered state was measured by varying the fringe spacing d. Most of the samples were preannealed for 3 days (3d) at the measuring temperature (112 °C) prior to the first measurement. The other measurements were performed directly after reaching equilibrium (3–4 h). The FRS relaxation times τ have been plotted double logarithmically against the square of the fringe spacing to cover the large range in spacing (from 0.16 to about 20 μm). As a result of the double-exponential fits, a slow decay constant and a fast decay constant are obtained and plotted for each measurement. Corresponding pairs of the slow and fast decay times at a given spacing are shown by dashes at the same position of the symbol. All measurements below $d^2 = 0.1$ μm^2 ($d \cong 0.32$ μm) were performed in the reflection geometry,[16,21] but for those above 0.1 μm^2 ($d \cong 0.32$ μm) the transmission geometry[16,21] had to be used.

It is worthy to note first the origin of the "scatter" in the data in Figure 5 (and hence Figure 6). At each temperature and for a given fringe spacing d, the FRS decay was reproduced several times on different positions of the specimens. The relaxation times deduced from a single experiment on a given illuminated position of the sample are quite reproducible. Therefore the scatter in the data is not due to the uncertainty in estimating τ_1 and

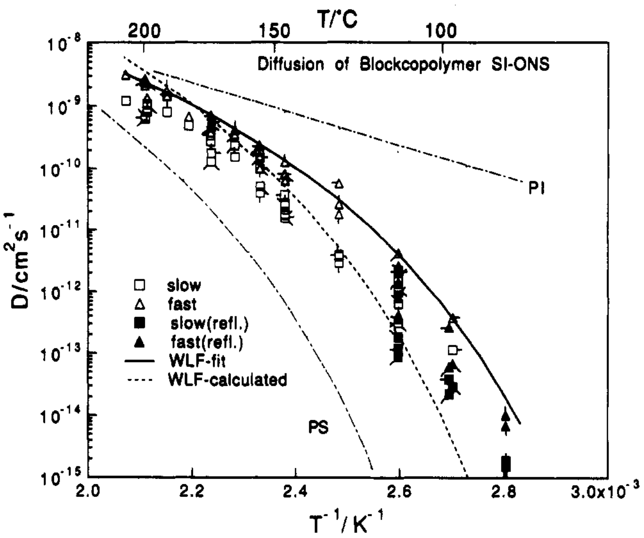

Figure 6. Temperature dependence of the tracer diffusion coefficient D.

τ_2 from the decay curve and eq 2. An effect of annealing on the change of the microdomain structure which may be encountered during the experiments with different positions of the specimens at a given T may cause a systematic change in relaxation time or diffusivity. We found this effect but this is not the main reason for the scatter in the data, because even after several days of annealing, we found a similar "scatter" in the data and because the change of the relaxation times with the sampling positions is not systematic as expected from the annealing effect but rather unsystematic. We attribute this scatter to different grain orientation distributions at different sampling positions, which makes the diffusive signal decay different and the distribution of the relaxation time different. In our system, the sampling volume is only a cylinder of about 50 μm and a tenth of a millimeter in diameter, and the grain size may be of the order of 10 μm, so that it may be quite straightforward to expect that the grains in the sampling volumes may have different orientation. Thus the "scatter" in the data is natural and to be expected.

As the decay times are increasing with the size of the spacings, they are clearly originated by a transport process. In such a plot Fickian diffusion should reveal itself by a straight line with slope equal to 1 according to

$$\log \tau = -\log (4\pi^2 D) + \log d^2 \qquad (3)$$

where D is the diffusion constant. Straight lines with slope 1 have been drawn in Figure 5 for comparison. For a multiexponential decay it is naturally somewhat ambiguous to identify a characteristic q or d dependence unless the decay cannot clearly be separated into well-defined processes. As can be seen from Figure 5, such a separation is impossible. The decay constants for the fast and slow components of the signal decay from individual measurements overlap and form a continuum. From physical reasons such a separability is also not expected to be possible. The origin of this multiexponential decay can be found to arise from the local anisotropy of diffusion due to the lamellar planes, combined with different orientations of grains relative to the measuring direction but not to arise from physically distinct diffusional processes.[21]

The gross overall behavior in Figure 5 approximately fits well to Fickian diffusion which would correspond to an interpretation of the measurements as an "intermediate-scale" experiment in the terminology of ref 21 in which we have many fringes inside each "grain" as well as many grains inside the hologram. However, as we vary the fringe spacing, also the border region to the "macroscopic-scale" experiment[21] will be covered, mainly for fringe sizes above 10 μm, because transmission electron micrographs show typical grain sizes from 1 μm to several microns. Here the criterion for the macroscopic experiment can be achieved for the systems in which the grain size is much smaller than the fringe spacing and hence the size of the hologram. The strongest deviation from d^2 behavior occurs for the spacings below 0.1 μm² ($d \simeq 0.32$ μm), corresponding to the intermediate-scale experiment,[21] and for the slower diffusion coefficients, i.e., the data points given by filled squares which are obtained after 3-day annealing. These measurements have to be performed in reflection geometry;[16,21] i.e., the measuring direction is perpendicular to the film surface. In this geometry more lamellae will be oriented with their interfaces perpendicular to the measuring direction, which should give a stronger weight to the slow diffusion coefficient perpendicular to the lamellar interface.

Annealing leads to a reduction of diffusion coefficients for both the fast process and the slow process and hence a reduction of an average diffusion coefficient, by about 1 order of magnitude after annealing 3 days. This reduction occurs independently of the measuring direction, i.e., in the direction parallel to the film surface as well as in the direction perpendicular to it. This reduction is more pronounced for the smallest fringe spacings, as indicated in the experimental results obtained for $d^2 \simeq$ 0.03 μm² ($d \simeq 0.17$ μm) and 0.8 μm² ($d \simeq 0.89$ μm) (compare the data shown by unfilled and filled triangles (the fast components) and those shown by open and filled squares (the slow components) at $d^2 = 0.03$ μm² ($d \simeq 0.17$ μm) and the data shown by triangles and diamonds (the fast components) and those shown by squares and circles (the fast components) at $d^2 = 0.8$ μm² ($d \simeq 0.89$ μm)). Thus the reduction cannot be interpreted as such a single mechanism as grain ripening in the sense of a reordering and reorientation of the lamellae. This would increase the average diffusivity measured in the direction parallel to the film surface (i.e., the diffusivity measured by transmission geometry) but decrease the diffusivity measured in the direction perpendicular to the film surface (i.e., the diffusivity measured by reflection geometry). This unexpected effect is not well understood at present but it may originate from a healing of high-mobility regions of accumulated real defects, where the lamellar domain structure has not yet been fully developed. If this is the case, this healing should be such that it reduces the diffusivities in the two directions. The clarification of this point is left for future studies.

A similar dependence of the FRS decay on the fringe spacing has been confirmed at higher temperatures, though not shown here.

Because of the gross d^2 behavior, it seems reasonable to calculate diffusion coefficients from the decay constants obtained from the double-exponential fits to the FRS decay. The temperature dependence of such diffusion coefficients is plotted in Figure 6. In this graph triangles and squares correspond to the fast and slow components of the signal decay, respectively. The filled symbols show the measurements in reflection geometry, with measuring direction perpendicular to the film surface, while the unfilled symbols show those in transmission geometry with the measuring direction being parallel to the film surface. The diffusional behaviors of a homopolystyrene (PS) and homopolyisoprene (PI) of the same molecular weight and microstructure as SI block copolymer have been included as dash-dotted lines for comparison. The diffusivity for the PI was obtained as follows: first the diffusivity was determined for a particular PI with the same microstructure as the PI in the SI block copolymer and with M_n of 3.0×10^4, and the diffusivity thus determined was extrapolated to that for the PI having the same molecular weight as the SI copolymer, using the reptation model.[12] The diffusivity for PS is obtained by extending the diffusivity measured for the PS with accurate molecular weight[22] at 185 °C to other temperatures using the WLF equation of polystyrene,[23] with a glass transition of 373 K and the WLF parameters $C_{1g} = 13.7$ and $C_{2g} = 57$. The diffusion coefficient of PI shows only a weak temperature dependence of the Arrhenius type, because the temperature investigated is far above its glass transition temperature.

We suggest interpreting the fastest diffusion coefficient thus obtained at a given temperature as the diffusion coefficient of the 2-dimensional diffusion parallel to the lamellar interfaces which are oriented along the direction of observation, i.e., the lamellar planes exactly perpendicular to the planes of the interference fringes. The slower diffusion coefficients result also from the motion along the lamellar interfaces, but in those planes which are tilted against the measuring direction. The slowest diffusion coefficient at a given temperature can only supply an upper threshold for the diffusion perpendicular to the lamellar plane. This slowest diffusion coefficient can be seen to be more than 1 order of magnitude smaller than the fastest diffusion parallel to the lamellar plane. At lower temperatures where the diffusion measurements were made possible using the reflection geometry, this difference is observed to become even larger. For example, we can show the difference by more than 2 orders of magnitude. This corresponds quite well to the experimentally obtained reduction of diffusion on annealing of about 2 orders of magnitude as reported in ref 21, which was interpreted as a reordering of lamellar grains giving dominance to the diffusion process perpendicular to the lamellar interface. However, the true diffusion coefficient perpendicular to the lamellae might be much smaller than this threshold because it is easily concealed by even slight misorientations of lamellae (of the order of a few degrees), due to bending or waviness of the lamella.

As expected, the diffusion of the block copolymer in the disordered state stays between the values for the two homopolymers but it remains there also in the ordered state. Even if T_{ODT} would be assumed to be somewhat higher than 190 °C, no step change in the diffusivity can be expected because the D value for the block copolymer at that temperature has already approached very closely the D values of the free homopolymers in unconfined three-dimensional space.

Contrary to our expectation, we can find no discontinuity or drop of diffusion coefficient at the ODT within our experimental resolution. If there were a jump in diffusivity of 1 order of magnitude or more, as found by Inoue et al.[9] on their block copolymer system having spherical micelles, we should be able to see the effect. Suppose we have an ideal "local scale" or "single-grain" experimental condition[21] in which the size of grains in the ordered state is much larger than the whole beam area, lamellar interfaces are perfectly aligned parallel to the film surfaces, and our measuring direction (indicated by an arrow) is normal to the film surface, as schematically drawn in Figure 7a. Moreover, let us consider the case where diffusivity normal to the interface $D_\perp$ is much suppressed, compared with the diffusivities parallel to the interface $D_\parallel$, and $D_\parallel$ is approximately equal to the component of the diffusivity D_z normal to the film surface in the disordered state (Figure 7b). Under this condition if the system changes from the ordered state as in Figure 7a to the disordered state as in Figure 7b, we can naturally expect a large increase in D from $D_\perp$ to D_z because $D_\perp \ll D_\parallel \simeq D_z$. Our experimental result on the change of diffusivity across the ODT is contrary to such expectation.

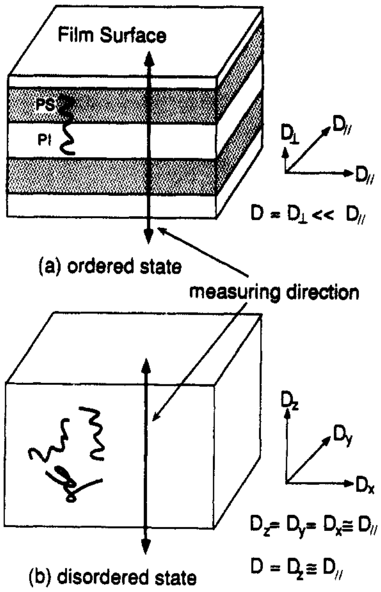

Figure 7. Schematic diagram showing a case in which a large change of diffusivity is expected to occur through a transition from the ordered state (a) to the disordered state (b).

One way to interpret our experimental fact would, of course, be to assume that on cooling below the ODT the diffusion perpendicular to the lamellar interface is still quite easily possible because the confinement of the diffusion of the chemical junctions along the lamellar interfaces increases only gradually. This, however, seems quite unphysical in regard to the experimentally proved stability and local ordering of the lamellar structure obtained from SAXS measurements; e.g., there is virtually no change in the line width of the first-order scattering maximum with increasing temperature up to T_{ODT}. Above T_{ODT}, an enormous increase of $W_{1/2}$ is observed as shown in Figure 3. It contradicts also the pronounced changes of storage and loss moduli found in low-frequency shear measurements of block copolymers on crossing the ODT.[20]

The strongest drop in diffusion coefficient on crossing the ODT (>4 orders of magnitude) has so far been reported by Inoue et al.[7,9] for an ABA block copolymer forming a regular lattice of spherical microdomains in a highly selective solvent. Can we expect such a large drop of diffusion coefficient for lamellar domains? The spherical morphology invokes a strong 3-dimensional confinement such that the interfaces along which the block copolymer molecules are transported are discontinuous in space. For a lamellar system this confinement is kept only in one dimension, i.e., along the direction normal to the interfaces, because the interfaces are continuous in the other two directions, though they may have curvature and tortuosity.[24,25] Thus the discontinuity in D across T_{ODT} is expected to be much more difficult to detect for the lamellar microdomain systems than for the spherical systems.

Another way to interpret our experimental fact would be to invoke the fact that our experiment at temperatures near the ODT is close to a "macroscopic experiment"[21] in which the grain size is smaller than the fringe spacing (10–30 μm) and hence the hologram size. Under this condition the lamellar microdomains in the ordered state are not single-crystal-like at all but have orientation distribution. Hence the measured diffusivity is the one $\bar{D}$ averaged overall orientation of lamellae

$$\begin{aligned}\bar{D} &= (D_{\parallel} - D_{\perp})\langle \sin^2 \alpha\rangle + D_{\perp} \\ &\cong D_{\parallel}\langle \sin^2 \alpha\rangle \end{aligned} \qquad (4)$$

where α is the angle between the lamellar normal and the measuring direction, and the second line of eq 4 is obtained by assuming $D_{\parallel} \gg D_{\perp}$. Note that the scatter in the data in Figures 5 and 6 discussed earlier is believed to result from variation of $\langle \sin^2 \alpha\rangle$ in different sampling spots. Note also that $\bar{D} \cong (2/3)D_{\parallel}$, if the lamellae have approximately random orientation. If the component of the diffusivity D_z in the disordered state is close to $D_{\parallel}$ in the ordered state, the measured diffusivity may change from about $(2/3)D_{\parallel}$ to $D_{\parallel}$ upon increasing temperature across the ODT. The change of diffusivity by a factor of approximately $^3/_2$ is certainly too small to be detected and buried within our experimental errors. This interpretation assumes that $D_{\parallel} \cong D_z$. A question remains whether or not this assumption is legitimate for our system. The above assumption is equivalent to stating that no significant change in diffusion mechanism is necessary for the motion parallel to the lamellar interface when the junction points between the polystyrene and polyisoprene blocks become fixed to the more or less two-dimensional interface at the ODT. For the present case this situation may be still conceivable. Because the molecular weight of the block copolymer ($M_n = 2.12 \times 10^4$) is quite small, we can try to apply Rouse motion to our system which gives $D_{\parallel} \cong D_z$.

In the Rouse model we can treat the polymer as an assembly of beads, each of which experiences some average friction coefficient ζ_k in the disordered state. After crossing into the ordered state microsegregation will only lead to a change in the friction coefficients. If we neglect the finite thickness of the domain boundary and assume a perfect segregation of each block chain into its respective domain, the isoprene beads will only experience the friction of the isoprene environment ζ_i and the styrene beads that of the styrene environment ζ_s, while the whole motion will be dominated by the higher friction inside the styrene microphase. The friction coefficients of the beads in the ordered state simply add up, and the diffusion coefficient of the block copolymer D_{si} is given as

$$1/D_{si} = 1/D_s + 1/D_i = (N_i\zeta_i + N_s\zeta_s)/kT \qquad (5)$$

where D_s and D_i are, respectively, the diffusion coefficients of the free homopolystyrene and homopolyisoprene having molecular weights identical to the polystyrene and polyisoprene blocks. If such an equation is accurate, the diffusion of the polystyrene block will dominate the motion of the block copolymer in the ordered state because of the higher friction coefficient in the polystyrene phase. Then we can try to estimate the temperature dependence of the diffusion coefficient D_{si}, neglecting the contribution of D_i and using the WLF equation for polystyrene with the *glass transition temperature T_g lowered to 78 °C* by the presence of the isoprene microdomains as measured by DSC

$$\log (D_s/D_g) = C_{1g}(T - T_g)/(C_{2g} + T - T_g) \qquad (6)$$

where D_g is D_s (2.27×10^{-18} cm^2/s) at T_g.

In Figure 6 we show the temperature dependence of D_{si} given by eqs 5 and 6 (broken curve) where C_{1g} and C_{2g} are set equal to 13.7 and 57. At very high temperatures this curve is meaningless because the validity of the WLF equation[23] is limited to $T < T_g + 100$ K and in the isotropic state the friction has to be calculated differently, but it appears to give reasonable diffusion coefficients around 150 °C. However, the temperature dependence is too strong and the predicted diffusion coefficients become too low, by almost an order of magnitude, compared to the experimental values as the temperature approaches 100 °C. If the above assumption of a Rouse-like motion parallel to the lamellar interface is reasonable, we may conclude from this discrepancy that the influence of the presence of the isoprene blocks on the dynamics of the block copolymer in the ordered state cannot be treated as a mere reduction of T_g of the polystyrene domains but reveals itself also in a change of the WLF parameters.

If we try to fit the WLF equation with a fixed glass transition temperature of 78 °C to the data corresponding to the quickest diffusion coefficients as mentioned before, we obtain the solid line in Figure 6, which leads to the WLF parameters $C_{1g} = 8.9$, $C_{2g} = 67$, and $\log D_g$ (cm^2/s) $= -14.38$.

The model suggested above for the diffusion in a lamellar block copolymer system is of course still very primitive. More realistically, we would have to take into account the fact that the polymer coils are stretched perpendicularly to the interface, which might change the friction coefficient compared to the homopolymer melt, and, especially, the fact that the interface is not infinitely thin. Effects of thermal concentration fluctuations and thermally activated dynamical rearrangements of the lamellar organization on the dynamics of labeled copolymers are also very important near the ODT. The latter effect of an interface of finite thickness as well as the effect of the dynamics of the lamellar organization will clearly reduce the overall friction. To some degree, this has been taken into account by using the lowered glass transition temperature for PS, but obviously this may not be sufficient to explain the dynamics. Recent dynamic ^{2}H-NMR experiments[26] to study the mobility at the interface of a PS–PI block copolymer might become helpful to estimate the friction coefficients in this region. Although the interface is supposed to sharpen on lowering the temperature because the repulsive force between the two blocks is increasing, we can expect that the accelerating effect of a finite interface on diffusion will be larger for the lower temperatures. This is just because the friction coefficients of polystyrene and polyisoprene are much more different at lower temperatures as can be seen from Figure 6; hence any mixing of the two polymers in the interphase can have a much stronger effect than at high temperatures, where the friction coefficients of PS and PI approach each other.

The assumption of a generalized 2-dimensional Rouse motion becomes questionable for higher molecular weights, but Shull et al.[11] found no significant reduction of diffusion on crossing the ODT for a block copolymer of the larger molecular weight 5.01×10^4. For even higher molecular weights, the study of diffusion below and above the ODT might turn into a new challenge or confirmation of the reptation model, as a block copolymer whose chemical junctions bound to its interface cannot be expected to be able to perform reptational translation like a linear chain, but they may rather perform the reptational translation somewhat similar to a three- or four-armed star polymer.[4,27] Perhaps it is possible to treat the interface in terms of some virtual arms, that is, to assume that the two blocks have to be retracted toward the interface to permit center of mass motion of the whole molecule along the interface. A significant reduction of the translational diffusivity due to the enhanced effect of the entanglements invoked by the diffusive motion confined to the interface may cause a more drastic, quasi-discontinuous change of the diffusivity on crossing the ODT, which deserves future studies.

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