Parallel and Perpendicular Chain Diffusion in a Lamellar Block Copolymer

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Relatively little is known about chain dynamics in microstructured block copolymers. Ultimately, the kinetics of structure formation and dissolution, the rheological properties and processability of the microstructured materials, and the stability of a given morphology must all reflect the dynamics of the individual chains. A fundamental quantity, therefore, is the translational diffusivity, D, of the block copolymer molecules. The diffusivity in microstructured systems is inherently interesting, for two additional reasons: within a given morphology, the free energy density varies spatially, which can lead to confinement of individual molecules, and the lamellar and cylindrical morphologies are anisotropic. In the strong segregation limit, one expects the chains to be severely confined, leading to an overall decrease in D. Chain motions that require passage of an A-block through a B-rich microdomain will be suppressed, possibly favoring diffusion along the cylinder axes or in the lamellar planes, respectively.

In this report we describe measurements of D in a lamellar block copolymer and, in particular, measurements resolved along the directions perpendicular (D_{perp}) and parallel (D_{par}) to the lamellar planes. The sample in question is a poly(ethylenepropylene)-poly(ethylethylene) diblock copolymer designated PEP-PEE-2. The molecular weight is 5×10^4, the composition is 55% PEP, and the order-disorder transition (ODT) occurs at 96 ± 1 °C.[1] Diffusion measurements were made at 25.0, 70.0, 80.0, and 94.0 (±0.2) °C and thus fall in the weak segregation regime. Forced Rayleigh scattering (FRS) was used to determine D. With a dynamic range of $10^{-5} \geq D \geq 10^{-16}$ cm^2/s, a typical precision of ±20-30%, and the ability to determine a uniaxial diffusion coefficient, FRS is ideally suited to this problem.[2] An Ar$^+$ laser operating at 488 nm was used both to create the grating and to probe its decay, the intensity being attenuated by a factor of 10^4 in the latter case. This corresponds to the amplitude grating mode; i.e., the signal results from spatial modulation of the extinction coefficient in the sample.

To follow polymer diffusion by FRS, it is necessary to attach the dye to the chain. For PEP-PEE-2, this was achieved via bromination of the few (ca. 1%) double bonds that survived the earlier hydrogenation step, followed by an elimination reaction with the cesium salt of the dye. The dye, 4′-(*N*,*N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid, was synthesized by an established three-step procedure.[3] Size-exclusion chromatography confirmed that the polymer underwent no degradation during the labeling, and the extent of reaction was estimated to be ca. 1 label/chain, by UV-visible spectroscopy. The labeled sample was mixed in the ratio 1:20 with the unlabeled precursor for the FRS measurements.

When a block copolymer sample is quenched below the ODT, the resulting morphology is generally "polycrystalline", i.e., there are coherent grains of local lamellar order, but macroscopically the sample is isotropic. However, it has been amply demonstrated that shear flows can be used to generate macroscopically-oriented "single crystal" samples.[4-6] Accordingly, three PEP-PEE-2 specimens were prepared. Specimen I was examined "as-cast" and is presumably polycrystalline, although the average grain size is not known. Specimen II was subjected to an oscillatory shear in the x direction, with z the gradient direction, at a frequency of 0.001 43 Hz and a strain amplitude of 100%, for 18 h at 83 °C; specimen III was sheared at 0.166 Hz under otherwise identical conditions. As has been previously established, these shear histories generate highly-oriented lamellar samples,[5] as illustrated schematically in Figure 1. Thus, specimen II has the lamellar planes parallel to the shear (x-y) planes, whereas for specimen III the lamellae are "flipped" parallel to the x-z plane. Specimens II and III were 0.6 mm thick in the z direction and approximately 0.5 cm^2 in area; the laser beams were oriented so as to determine D along the y-axis.

FRS data from specimen I are displayed in Figure 2. The diffracted intensity exhibits an excellent signal-to-noise ratio and is very well described by a single-exponential decay; both features are common to the measurements on all three specimens. The decay time, τ, depends linearly on the square of the grating spacing, d, with zero intercept, as shown in the inset to the figure. This confirms the diffusive origin of the decay. For specimen III, measurements were repeated at various angles of rotation, ϕ, about the z axis; $\phi = 0°$ thus corresponds to a measurement of D_{perp} and $\phi = 90°$ to a measurement of D_{par} (see Figure 1). However, for these measurements it would be prohibitively time-consuming to examine the grating spacing dependence, so a single value of d was used for each temperature.

The results are shown in Figure 3. The solid symbols correspond to D for specimen III, as a function of ϕ. Absent any prior expectation, one might reasonably conclude from these data that $D_{\text{par}} = D_{\text{perp}}$, within the experimental uncertainty,[7] except possibly at 25 °C. Clearly, any anisotropy in D is subtle. The smooth curves represent the expression

$$D = D_{\text{par}} \sin^2 \phi + D_{\text{perp}} \cos^2 \phi \qquad (1)$$

with relative values of D_{par} and D_{perp} determined as described below. The open circles represent D_{par} obtained from specimen II, and the agreement with the data from specimen III at $\phi = 90°$ is good. The diffusivities in the unsheared sample, specimen I, are indicated as open squares in Figure 3 and designated D_{iso}.

Barrat and Fredrickson have calculated $D_{\text{perp}}/D_{\text{par}}$ for symmetric diblock copolymers in the weak segregation regime, assuming Rouse dynamics, as a function of $\alpha\chi N$;[8] here, α is the amplitude of the composition profile (assumed to be sinusoidal), χ is the Flory-Huggins interaction parameter, and N is the degree of polymerization. Results were obtained by perturbation theory for small values of α, by an activated process theory for large χN, and by computer simulation to interpolate smoothly between the two limits. Under the Rouse assumption, D_{par} is unaffected by the microstructure. From the expression for χ reported by Rosedale and Bates,[1] χN is estimated to be 11.8, 12.3, 12.6, and 14.5 at 94, 80, 70, and 25 °C, respectively. From neutron reflectivity measurements on thin films of various PEP-PEE samples, α for PEP-PEE-2 is estimated to be 0.40 ± 0.05.[9] The smooth curves in Figure 3 were generated using these parameter values and the simulation results. The vertical position of each curve was fixed at the value of D_{par} equal to the average of the results obtained from specimens II and III with $\phi = 90°$.

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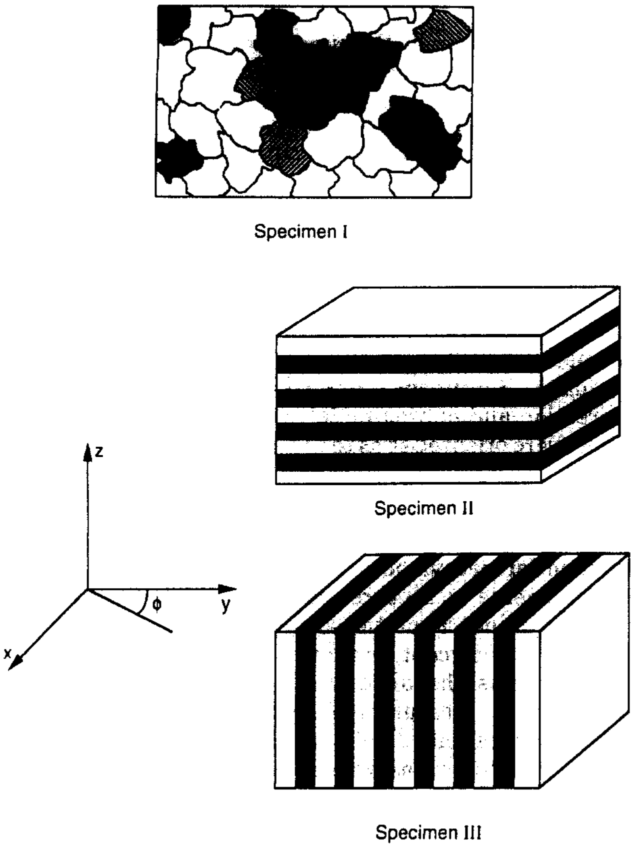

Figure 1. Schematic illustration of "as-cast" (specimen I), "parallel" (specimen II), and "perpendicular" (specimen III) lamellar samples. Note that the lamellar period is actually much less than the sample dimensions. Diffusion measurements were made along the laboratory *y*-axis, and specimen III was rotated around the *z*-axis through an angle *ϕ*.

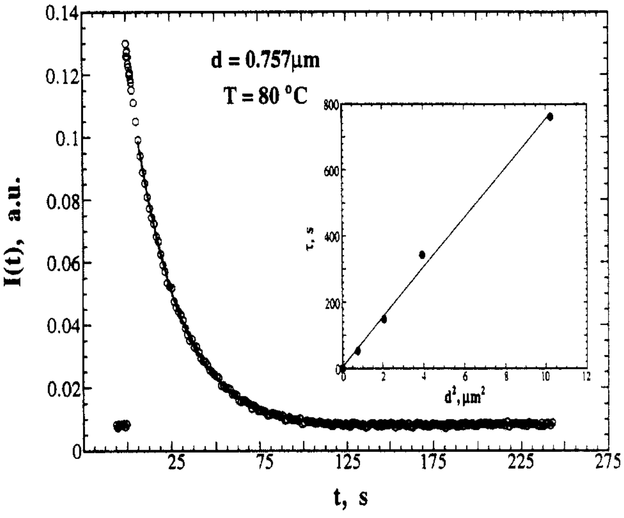

Figure 2. Forced Rayleigh scattering signal from specimen I at 80 °C (discrete points) and a single-exponential fit (smooth curve). The decay time varies linearly with the square of the grating spacing, as shown in the inset.

On the basis of the comparisons in Figure 3, we conclude that

$$(D_{\text{perp}}/D_{\text{par}})_{\text{Rouse}} \le (D_{\text{perp}}/D_{\text{par}})_{\text{measd}} \le 1 \qquad (2)$$

Two factors could contribute to the observation that the anisotropy in *D* is less than that predicted from Rouse dynamics: imperfect lamellar orientation in the specimens and entanglements. On the basis of the neutron scattering results of Koppi et al.,[5] we are confident that the degree of lamellar orientation exceeds 90%, although this could not be confirmed on the actual FRS samples, as they are not deuterium-labeled. However, specimen III exhibits a substantial uniaxial birefringence, whereas specimen II does not;[10] both observations are consistent with the assumed orientations.[11] On the basis of the rheological properties of the corresponding homopolymers,[1] PEP–PEE-2 is estimated to have about 15 entanglements/chain, and Rouse dynamics should not be expected to apply. Preliminary calculations[12] suggest that the anisotropy in *D* is *weaker* for reptating chains than for Rouse chains, because, for the former, motion in the lamellar planes will require significant excursions of the A-block into the B-rich microdomains, and vice versa. There will thus be a thermodynamic penalty for motion in any direction, in contrast to the Rouse case.

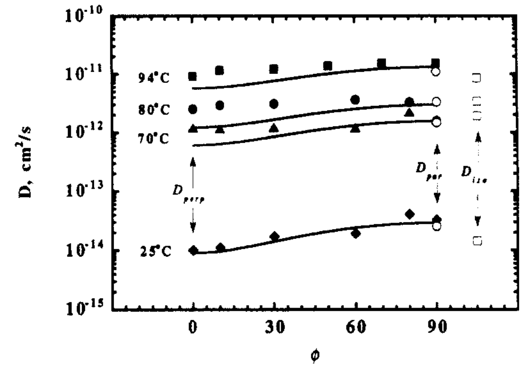

Figure 3. Measured diffusivities (filled symbols) for specimen III at the indicated temperatures, as a function of rotation angle; at $\phi = 0°$, $D = D_{\text{perp}}$, whereas at $\phi = 90°$, $D = D_{\text{par}}$. The open circles represent the data obtained from specimen II and the open squares the data from specimen I. The smooth curves correspond to eq 1, using the prediction of $D_{\text{perp}}/D_{\text{par}}$ for Rouse chains given in ref 8. The vertical position of each curve was determined by the average value of D_{par} obtained from specimens II and III.

Shull et al.[13] have reported measurements of *D* for the same PEP–PEE sample, by forward recoil spectrometry. Our results for specimen I are identical to theirs, within the combined experimental uncertainty. This agreement confirms that the presence of the dye exerts no significant effect on the chain motion, as expected. However, Shull et al. also found that, after annealing a specimen at 70 °C for 4 days, the measured *D* dropped by 2 orders of magnitude.[13] This was ascribed to the formation of a highly oriented sample such that the measured diffusivity was dominated by D_{perp}, and it was concluded that $D_{\text{perp}} \ll D_{\text{par}}$. However, on the basis of the results in Figure 3 and the theoretical calculations,[8,12] it appears that this interpretation may require some revision.

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