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Chain confinement effects on interdiffusion in polymer multilayers

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We have measured interdiffusion in polystyrene on length scales approaching and below the overall dimensions of the polymer molecules, by using neutron reflectometry to follow the relaxation of the composition modulation in an isotopic polymer multilayer. After an initial transient, relaxation of the composition modulation is diffusive, even for times less than the reptation time. The diffusion coefficient decreases with increasing wave vector, in qualitative, but not quantitative, accord with theory. [S1063-651X(99)11801-4]

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When two identical polymers are put together and annealed above their glass transition temperature, the initially sharp interface is broadened by the diffusion of chains across that interface. It is this process of interfacial healing that leads to the development of interfacial strength, so it is of practical importance in a wide variety of industrial applications, including polymer welding, the healing of weld lines in injection molding, and the formation of films from latex suspensions. For times such that the interface has become broad compared to the overall chain dimensions, broadening is controlled by a process of mutual diffusion, which is now reasonably well understood [1], at least for pairs of polymers with comparable mobility properties. However, recent experiments making a direct correlation between the toughness of an interface and its width [2] reveal that an interface achieves essentially bulk toughness by the time its width has reached 100–200 Å, comparable to overall chain dimensions. Thus the regime of greatest interest for understanding the development of interfacial strength corresponds to the broadening of an interface on length scales less than the overall chain dimensions, which we cannot expect to be controlled by simple center-of-mass diffusion. In effect, because of perturbations to the thermodynamics of mixing when steep concentration gradients are involved, and because broadening of the interface can be achieved without whole chain motion, one must expect the diffusion coefficient to have a dependence on length scale that will become important for broadening on length scales less than overall chain dimensions. In this paper, we report measurements of this dependence.

Deviations from simple diffusive behavior at polymer/polymer interfaces at early diffusion times have previously been directly measured using neutron reflectivity [3–7]. These experiments showed that at early times the interfacial width does not grow with the square root of time, as it would for a simple diffusive process. Instead, an early abrupt increase in the interfacial width is followed by an interval in which the interfacial width has a weaker than square root dependence on time, recovering simple diffusive behavior only when the interfacial width is comparable to overall chain dimensions. Interpretations of these experiments initially were framed in terms of the dynamics of a single polymer chain; the theory of reptation predicts a hierarchy of power laws for the time dependence of the mean squared segment displacement for times less than the reptation time τ_d, after which conventional diffusive dynamics are recovered [8]. However, interfacial broadening is fundamentally a collective, many-chain effect, and while the single chain dynamics are undoubtedly important it may be useful to relate interfacial broadening to a more explicitly collective property. We report here experiments in which we directly measure the collective diffusion coefficient $D(k)$ as a function of the wave vector **k** characterizing the concentration modulation that is relaxing. This gives us a straightforward way to characterize the effect of length scale on diffusion over distances smaller than overall chain dimensions.

The experiment is essentially a polymer realization of the classical experiment of Cook and Hilliard [9], in which gradient effects on interdiffusion between gold and silver were studied. In our experiment, we created a multilayer stack of alternating layers of polystyrene (PS) and its deuterated analogue (dPS). For Fickian diffusion (by which we mean here diffusion characterized by a diffusion coefficient independent of concentration and time, though possibly dependent on wave vector) the evolution of an arbitrary concentration profile is given by

$$\phi(z,t)=\sum_{n=1}[A_n \cos(nkz)+B_n \sin(nkz)]\left[\exp\left(-\frac{t}{\tau_k}\right)\right], \tag{1}$$

where $\tau_k^{-1}=D(k)n^2k^2$, $k=2\pi/\lambda$ and λ is a characteristic length scale. In our case the initial conditions are found as a Fourier transform of the initial concentration profile. If our multilayer has enough layers it is well approximated by an infinite square wave in composition; for alternating layers of thickness *l*, the fundamental wavelength of a cosinusoidal composition fluctuation that contributes to the square wave

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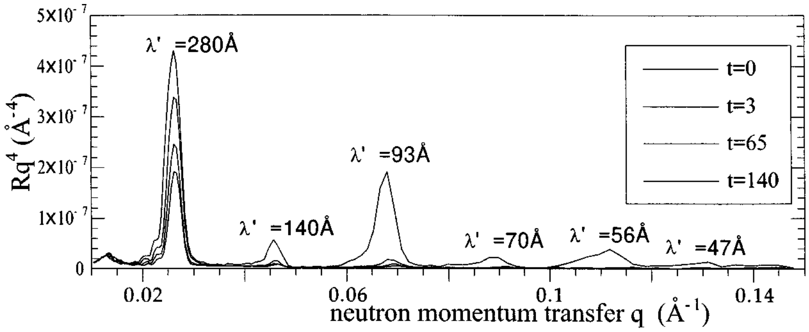

FIG. 1. Selection of reflectivity data for a multilayer sample with a layer thickness of 140 Å, depicting decay of Bragg peaks for times greater than $t=0$ minutes. The corresponding wavelengths for all the visible Bragg satellites are denoted.

will be $\lambda \equiv 2l$. Subsequent composition contributions arise from odd harmonic cosinusoidal fluctuations, i.e., from wavelengths of $\lambda/3$, $\lambda/5$, etc. Each Fourier component will give rise to a Bragg peak in a scattering experiment; on annealling each Bragg peak will decay in intensity exponentially, from which decay the characteristic time τ_k and the diffusion coefficient $D(k)$ for the corresponding wave vector can be determined. By creating dPS PS multilayers of a selected fundamental wave vector and observing the decay of the corresponding Bragg peaks we can thus observe the relaxation of concentration fluctuations at any given length scale.

We have made multilayers from PS and dPS with molecular weights (M_w) of 629 000 and 641 000, respectively. The polymers were bought from Polymer Laboratories; they were synthesised by anionic polymerization and have polydispersity indices of less than 1.1. We needed to use large molecules (in this case, the radius of gyration is about 220 Å), so that the natural length scale set by the overall chain dimensions was as large as possible. However the molecular weight was not high enough that the unfavorable thermodynamic interaction between dPS and PS becomes significant [10], leading to thermodynamic slowing down of diffusion. A layer of dPS was spun cast onto a silicon disk, from a toluene solution. Subsequent layers of alternating PS and dPS layers were then spuncast onto microscope glass and floated onto water before being deposited onto the substrate. Each sample had a total of 16 polymer layers; every attempt was made to match the thicknesses of the dPS and the PS layers in each sample. In the event the layers were found, using spectroscopic light ellipsometry, to differ by 10 Å. Five samples were used, with mean layer thicknesses varying from 80 to 186 Å. Neutron reflectivity measurements were carried out on the reflectometer CRISP at the Rutherford Appleton Laboratory. Because of the rapidity of diffusion in these very thin layers it proved necessary to anneal the sample *in situ*, using a Linkam microscope hot stage, iteratively measuring the reflectivity and annealing until the Bragg peak of interest had decayed to insignificant levels. The lowest annealing temperature used (as measured at the surface of the sample) was 133 °C, allowing us to investigate some of the early time behavior of the mixing experiment. In some cases the same samples were later annealed at a temperature of 146 °C in order to gain information over the latter stages of the peak decay. Other samples were annealed at an intermediate temperature of 139 °C.

We also measured the small wave vector limit of the interdiffusion coefficient, $D(0)$, for our samples by measuring the broadening of an interface in a bilayer sample of the same polymers with nuclear reaction analysis [11]. Samples, made from a thick (1–2 μm) PS and a thin(1200 Å) dPS layer on a silicon substrate, were annealed for a range of times above τ_d at 133 °C and subsequently analyzed using NRA (at the University of Surrey, U.K.). The concentration/depth profiles obtained from NRA were fit using a standard error function solution to the diffusion equation to calculate the diffusion coefficient. $D(0)$ was found to be 9.14×10^{-18} cm^2/sec$\pm 2 \times 10^{-18}$ at 133 °C. This value compared favorably with reported values in the literature [3,4,6], after suitable corrections for molecular weight [8], temperature (using the Williams-Landel-Ferry expression [12]), and isotopic effects [10].

If the neutron reflectivity data was in a range of momentum transfer in which the Born approximation was valid, we would have been able to extract the diffusion coefficient directly from the decay of the Bragg peaks. However, as the Born approximation becomes less accurate as one approaches the critical condition for total reflection, we instead obtained free-form fits to the real space composition profile using the maximum entropy method [13]. The resulting composition profiles were fast Fourier transformed (FFT) back into scattering space. The resulting power spectrum can then be considered to be equivalent to the intensities that would be obtained in an ideal scattering experiment. If the decay of the concentration profiles is diffusive we can extract $D(k)$ from the slope with which these ideal intensities decay with time [14]:

$$D(k) = -\frac{1}{2k^2} \frac{d \ln[I(k)/I_0(k)]}{dt}. \tag{2}$$

A representative set of raw data for one of the multilayer samples before and after annealing is shown in Fig. 1. The Bragg peaks are labeled with their corresponding composition fluctuation wavelengths. We have been able to produce high quality multilayer samples, as reflected by the number and clarity of higher order Bragg peaks evident in the data for the unannealed sample. A limiting factor to the quality of data in the high q range is the times required to achieve sufficiently good statistics. In this range the Bragg peaks are in the positions predicted by the kinematic (first Born) approximation. This is less true as the peaks approach the critical edge ($q = 0.013$ Å^{-1}). Furthermore the data has even harmonics of the fundamental composition fluctuation

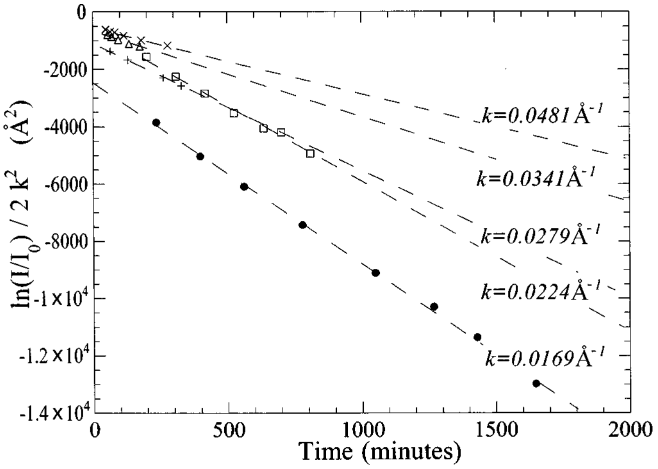

FIG. 2. The terminal decay of the first order Bragg peaks from all five multilayer samples. (●, $k=0.0169$ Å^{-1}; □, $k=0.224$ Å^{-1}; + $k=0.279$ Å^{-1}; △, $k=0.0341$ Å^{-1}; ×, $k=0.0481$ Å^{-1}). Times shown have been reduced by the WLF expression to 133 °C.

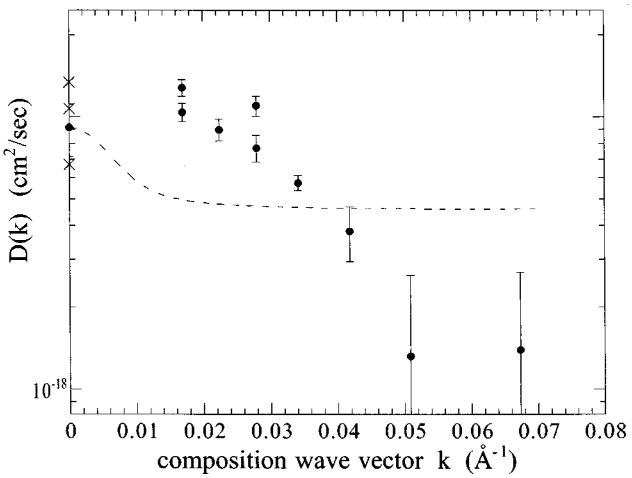

FIG. 3. $D(k)$ at 133 °C measured from bilayer [$D(k)$ for $k=0$] and multilayer [$D(k)$ for $k>0$] samples. Also included are data points ($k=0.051$, 0.067 Å^{-1}) from the terminal decay of third order Bragg peaks from two multilayers. Also shown is the Pincus prediction for $D(k)$ behavior, scaled by an approximate $D(0)$ and the literature reported values for $D(0)$. (●, experimental data; ×, literature reported values for $D(0)$; line, prediction of Eq. (3)].

present that are not predicted in the case of an ideal square wave. These peaks are thought to arise due to a systematic difference in the thickness of the deuterated and nondeuterated layers that make up the multilayer. After the initial anneal a large decrease in all Bragg peak intensities is observed. There was no clear correlation between sample thickness and this initial decay. Subsequent anneals lead invariably to a monotonic decrease in peak intensities, though at a much slower rate.

There are a number of possible reasons for the initial dramatic decrease in Bragg peak intensity. The first originates from nonequilibrated density effects as a result of the spin-casting method of the multilayer film formation. Annealing the multilayer will then lead to an initial reorganization of the polymer film. This is also seen in the small shift to higher q values of the peaks, expressing an overall contraction of the film. This initial fast relaxation of the density of a spin-cast film has been directly observed using ellipsometry [15], which shows that equilibrium density is achieved in the timescale of the thickness measurement when a thin film is heated to 115 °C. Another plausible reason arises from a description of movement of polymer chains at the interface, within a tube constraint model, so that the chains will be able to move ‘‘freely’’ at a very fast rate within a distance characterized by the tube diameter. Such a supposition also implies that composition fluctuations of wavelengths smaller than the tube diameter will necessarily disappear. An examination of Fig. 1 does indeed seem to indicate this effect with peaks corresponding to wavelength of ~60–70 Å disappearing after the first anneal. This compares favorably with the dimension of the tube constraint found using infrared dichroism of 57 Å [16].

In Fig. 2, the latter stages of the decay of the first order Bragg peaks from all of the samples analyzed is shown as a function of time (reduced by the WLF expression to correspond to 133 °C [17]). There is a clearly exponential decay of the Bragg peak intensity in accordance with Eq. (2). This figure shows that there is a wave-vector dependence of the diffusion coefficient, with larger interdiffusion coefficients occurring for less confined polymer films. $D(k)$ can be calculated from the slope of the terminal decay and is shown in Fig. 3, compared with the experimental and literature cited bulk diffusion coefficients, and a theoretical prediction to be discussed below.

This decrease in the collective diffusion coefficient with decreasing length scale is reminiscent of the typical behavior in metallic multilayers, where gradient energy effects lead to an decrease in diffusion coefficient for very thin layers [9,18]. However, the origins of this decrease are quite different in the two cases. In the metallic multilayers that are usually studied the gradient coefficient is predominantly enthalpic in character, negative in sign for alloys with an ordering tendency (corresponding to a negative sign of the Flory-Huggins interaction parameter, in polymer language), and with a length scale set by interatomic distances. Gradient energy effects should also be important for polymers; however, the origin of the gradient energy is predominantly entropic [19], with a positive sign and with a larger controling length scale that is set by the overall chain dimensions of the polymer [20,21]. This is because concentration gradients that are steep compared to overall chain dimensions lead to a loss of conformational entropy and thus an increased free energy, providing an extra force for the relaxation of concentration gradients. On the other hand, because polymers are spatially extended objects which by virtue of their connectivity must have a nonlocal response to an applied field, the effective chain mobility must decrease as the wavelength of such an applied field becomes less than overall chain dimensions. Both of these effects have been incorporated into the similar theories presented by Pincus [20] and Binder [21], in which the conformational effects of confined polymer chains on interdiffusion through the static collective structure factor $s_{\mathrm{col},T}(k)$, and a k-dependent Onsager coefficient $\Lambda(k)$ is deduced by calculating the response of a polymer chain to an applied periodic longitudinal potential field. Pincus's theory [20] predicts that the time scale for relaxation of composition fluctuations is given by

$$\tau_k^{-1}=\frac{\Lambda(k)k^2}{S_{\mathrm{col},T}(k)}=D(k)k^2=D(0)k^2\,\frac{1-\dfrac{x}{2}f_d(x)}{f_d(x)},\qquad(3)$$

where $x=k^2R_g^2$, and $f_d(x)$ is the Debye single chain structure factor.

This prediction is plotted as a solid line on Fig. 3. The predicted $D(k)$ behavior agrees qualitatively with our data, and thus reflects the notion that at smaller length scales the overall rate of relaxation of the system is reduced. The quantitative agreement is much less good. A number of factors are likely to be important in explaining this discrepancy. Firstly, the conformations of the molecules in the thin films are likely to be significantly perturbed from Gaussian conformations in a way that these simple approaches based on the random phase approximation may not be able to capture. As the distance of the center of mass of a polymer chain from the interface becomes significantly less than the radius of gyration of the ''unconfined'' polymer chain R_g, the chain will align itself roughly parallel to the surface or interface. Additionally the aspect ratio of the chain conformations becomes larger as the chain is squashed up against the interface [22]. Relaxation of these potentially non-Gaussian and oriented conformations may in part account both for the initial fast relaxation apparent in Fig. 2, and for the deviations of $D(k)$ from theory. In addition to these conformational perturbations in thin polymer films, there are indications that films thinner than 400 Å or so may have significantly enhanced segmental mobility at temperatures around the glass transition temperature [23,15]. Finally, we should recognize that the simple theories contain no assumptions about internal chain dynamics, and are only really applicable for times longer than the reptation time τ_D. The reptation time for our system at 133 °C is ~850 min. In fact, the majority of data collected are for times smaller than this.

To conclude, we have studied the effect of length scale on interdiffusion in polymers for lengths comparable to and smaller than overall chain dimensions. The use of a multilayer technique familiar from the study of metallic multilayers allows us to probe the mobility of polymer chains in a way that focuses on collective motion rather than the motion of a single chain. We find a decrease in the wave vector dependent collective diffusion coefficient with increasing wave vector; this is in qualitative accord with an existing theory that proposes such a decrease due to the nonlocality of response that arises from the connectivity of the chain structure. However, the magnitude of the effect observed experimentally is greater than that predicted and a more refined theory, properly incorporating the effects of internal chain dynamics and the perturbation of chain conformation near interfaces and in thin films may be required.

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