Macromolecules **1991,** *24,* 1179–1184

Time Regimes in Polymer Interdiffusion Determined by Marker Movement

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Received May 1, 1990; Revised Manuscript Received August 7, 1990

ABSTRACT: We have investigated interdiffusion of two thin polystyrene films by X-ray reflectometry. For two films of different molecular weight a net matter flux across the interface is predicted. Putting gold particles at the position of the interface, one can follow the displacement of these markers with time. Using the high-resolution of X-ray reflectometry, we have been able to detect a delay in the onset of bulk flow, which depends on molecular weight. There is a strong indication for a correlation between this induction time and the reptation or disengagement time. We assume that in this time regime the displacement of segments does not lead to a difference in polymer flux across the interface and thus no movement of markers is observed. The rearrangement of distorted molecules at the interface between the two films is also a possible reason for a delayed onset of bulk flow. The marker velocity at times shorter than the disengagement time of the long molecules is not influenced by the long molecules. It is determined by the diffusion coefficient of the small molecules only.

Introduction

Over the last years many experiments were performed in order to answer the question of how polymers of different molecular weight interdiffuse into each other.[1-4] There are also several theoretical approaches describing polymer interdiffusion.[1,5,6] Although different in their basic assumptions, all theories come to the results that the different mobilities of long and small molecules cause a bulk flow of matter.[7] These theories are dealing with center of mass diffusion of the whole molecules. Therefore, at present no theoretical description for the interdiffusion of two different polymers at very early times is available.

According to the reptation model proposed by de Gennes[8] and the theoretical treatment of Doi and Edwards,[9] the diffusion process is dominated by the motion of segments at times shorter than the characteristic disengagement time. Two constraints are imposed upon the segments. First, they cannot move independently because they are connected to other segments. Second, they are forced to move along the primitive path[8,9] because they cannot cross or cut neighboring molecules. These effects have to be considered when polymer diffusion at short times is investigated.

On the basis of the experiments of Kramer and Green et al.[1,2] using Rutherford backscattering spectrometry, we take the advantage of the high depth resolution of X-ray reflectometry to investigate the effect of bulk flow at short times. In this context bulk flow means the shift of the interface between two polymer films of different molecular weight. It is caused by different fluxes across the interface. The shift will be toward the lower molecular weight side. The effect of bulk flow can be compared to the swelling of a high molecular weight polymer matrix by small molecules. The sensitivity of our method enables us to measure bulk flow with angstrom resolution. Therefore, we can get information about early stages of diffusion.

Experimental Section

Sample Preparation. For our investigations we use polystyrenes of different molecular weight characterized by GPC. Numbers are given in Table I. Thin films of these polymers are prepared by dissolving them in toluene at a concentration of approximately 10 g/L and subsequent spin coating on float glass (70 × 30 × 10 mm^3). The films are analyzed by X-ray reflectometry,[10] and the results are given in Table II. For our experiments it is essential to have extremely flat and well-characterized films. We want to measure subnanometer variations, and therefore the roughness of our films has to be as small as possible. We describe the rough interfaces by an error function profile with the characteristic parameter σ. While the roughness of the film–glass interface is mainly determined by the surface of the substrate, the roughness of the air–film interface depends mostly on the spin-coating process. It is also important to know thickness and density of the single films to be able to follow possible changes during the preparation of the four-layer sample and during the experiment. Our films have a density comparable to the bulk polymer; therefore, no shrinkage durinig annealing is expected.

After characterization by X-ray reflectometry, samples 1–3 are covered by evaporation with a thin gold layer. The evaporated amount of gold is equivalent to a homogeneous layer with the bulk density for gold of approximately 2 nm. As shown by Green et al.[2] and checked by electron microscopy in our laboratory, gold forms small particles on the polymer surface. The samples are annealed under vacuum for 2 h at 160 °C. As examined by electron microscopy and X-ray reflectometry, the size of the particles gets larger, reducing the percentage of the polymer surface covered by gold. By X-ray reflectometry, one averages laterally over areas of approximately 1 μm^2 and does not see the particle structure. Therefore, the gold layer seems to be a homogeneous medium for the X-ray beam.

Films 4–6 are floated off onto a clean water surface and are transferred on samples 1–3, respectively. These double layers with gold in the middle are dried at 60 °C for several hours under vacuum to remove residual water and air between the two layers. Finally, a second gold layer is evaporated on top of the outer polystyrene film. A schematic drawing of our samples is given in Figure 1.

We prepared three different samples having the same polymer in the top layer (M_w = 660 000 g/mol) but different polymers in the bottom layers (sample PS660-660, M_w = 660 000 g/mol; sample PS660-198, M_w = 198 000 g/mol; sample PS660-117, M_w = 117 000 g/mol).

X-ray Measurements. In Figure 2 we show reflectivity curves for the different stages of sample preparation. Curve a was measured after a thin gold layer was deposited on a PS film. One can see two periodic features representing two thicknesses of our system. The long-range oscillation comes from the thin gold layer, and the superposed small and more often oscillating structure

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Table I
Characterization of the Polymers Used in This Work

polymer	M_w, g/mol	M_w/M_n	obtained from
PS117	117 000	1.03	Polymer Laboratories, Ltd., U.K.
PS198	198 000	1.04	PSS, FRG
PS660	660 000	1.11	PSS, FRG

Table II
Characterization of Polystyrene Films by X-ray Reflectometry

sample no.	thickness, nm	density, g/cm^3	σ,[a] nm	
			air–polymer	polymer–glass
1	74.2	1.05	0.9	0.6
2	112.6	1.05	1.2	0.5
3	78.2	1.05	1.0	0.8
4	62.1	1.04	0.8	0.4
5	67.0	1.06	0.9	0.6
6	69.1	1.05	0.9	0.5

[a] σ is the parameter of the error function used to describe the interfaces.

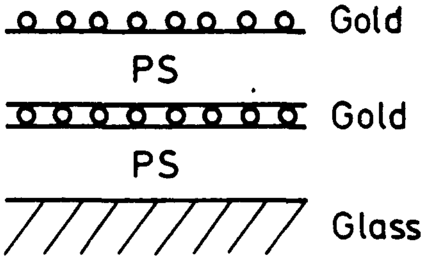

Figure 1. Schematic drawing of the four-layer samples used in the experiments.

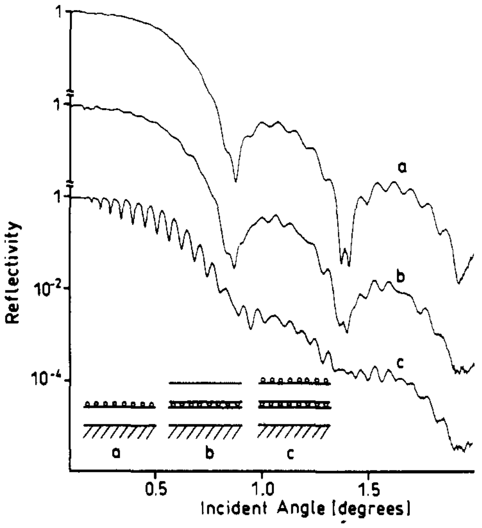

Figure 2. Measured reflectivity versus incident angle for three different stages of sample preparation: (a) a single polystyrene film on glass covered with a thin gold layer, (b) an additional polystyrene film put on top of the polystyrene–gold sample, (c) the three-layer sample covered with a second gold layer. The wavelength of X-rays is 0.154 nm.

is determined by the thickness of the PS film. The most reflecting interfaces are determined by the gold layers. Therefore, the interference structure of the reflectivity curve is dominated by the beams reflected at the different gold interfaces. This explains why nearly no changes can be detected in the reflectivity curve if a second PS film is added (curve b compared to curve a). Such a three-layer system cannot be used for the investigation of polymer diffusion. Therefore, we deposited a second thin gold layer on this system. The effect on the reflectivity curve is seen in Figure 2c. There is an oscillating structure below the critical angle for total reflection[11] of gold ($\theta_{cr,gold} = 0.57°$). Because of the small thickness of the top gold layer, the evanescent wave is only partially attenuated by this layer and can propagate into the adjacent polystyrene film. Eventually it is reflected at the second gold layer. The two beams reflected at the two gold layers interfere, and the period of the oscillations is correlated with the distance between the gold layers. Figure 2 demonstrates the changes in the reflectivity curve at different stages of preparation and the necessity of this rather complicated four-layer system for the aim of our experiment. The oscillations below $\theta_{cr,gold}$ representing the thickness of the top polymer film are only seen after evaporation of the second gold layer.

If the polymer flux during annealing is higher in one direction than in the opposite direction, the distance between the gold layers changes. In our samples the top film is always the one with the higher molecular weight. If many more short molecules than long ones pass through the inner gold layer, the distance between the gold films increases. Due to the preparation technique, there is a virtual shrinkage of the top film during the first few minutes of annealing, which can be correlated to the filling of voids between the inner markers with molecules of the top film. To be able to detect this kind of shrinkage, the top film has to be the one with the higher molecular weight. Otherwise, it would not be possible to differentiate between bulk flow and shrinkage. Both effects would result in a decrease of the distance between the two gold layers.

Annealing Procedure. The annealing has been done under vacuum conditions at different temperatures. Due to the thickness of our substrates, we needed approximately 10 min to reach the equilibrium temperature. The temperature was measured by a thermocouple directly mounted on the sample surface. To be able to detect even small interdiffusion effects, the annealing temperature has to be very close to the glass transition temperature of PS (103 °C). Annealing times have to be longer than at least 15 min; otherwise, the errors in determining these times become quite large. On the other side, we have to cover a significant time range. Therefore, we used different temperatures and reduced the annealing times to a single reference temperature (120 °C) by the shift factor a_T given by the WLF equation.[12]

$$\log a_T = \frac{-9.06(T-120)}{69.8+(T-120)} \qquad (1)$$

As long as the used temperatures do not differ too much, we only cause small errors by the application of the WLF equation. For a small temperature range the WLF equation approximates the actual temperature dependence of the diffusion coefficient quite well.[12]

Evaluation of Reflectivity Curves. The analysis of the reflectivity curves was done by the use of a matrix formalism.[11] Because of the high reflectance of gold as compared to the polymer films, we have very good contrast. This involves a rather large sensitivity on the detailed shape of the density profiles of the interfaces. In Figures 3 and 4 we give an example for a single gold layer on a polystyrene film on glass which was not annealed. One can see that a symmetric profile for the gold layer does not fit the data correctly. Therefore, we use a trial profile, shown in Figure 3, which is slightly asymmetric and achieved a better correspondence. The approximate shape of the profile emerges clearly from the fit, but we were not able to analyze the profile in every detail. The asymmetry can be correlated to two effects. First, the interface between gold and polymer: The gold particles penetrate the polymer film slightly. One might say that the gold particles and the polymer molecules form an intermediate layer of about 1–1.5 nm. This is proved by X-ray reflectometry. The thickness of the polymer films is reduced by 1–1.5 nm after the coverage with a thin gold layer. Second, the interface between air and gold: As gold forms particles rather than a homogeneous layer, the shape of the interface depends on the size distribution of these particles. If all particles have the same size, we would assume a cosine-squared profile. If there are some larger particles, the profile gets a tail toward air. For both interfaces the contribution of the roughness of the polymer film is superposed to the profile generated by the gold particles. Therefore, we have to use complicated density profiles for the gold layers, and this makes the evaluation of the reflectivity curves for the four-layer samples rather difficult. It causes uncertainties concerning

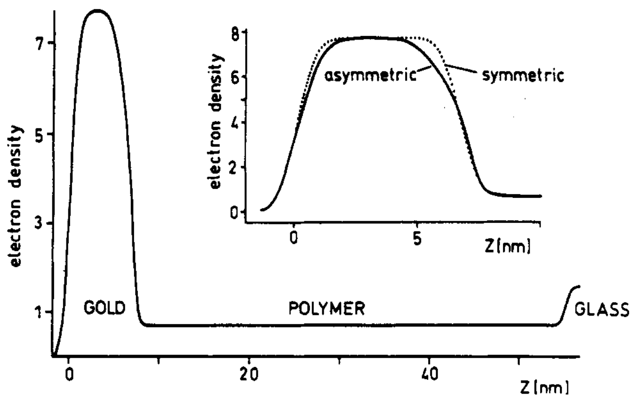

Figure 3. Model electron density versus depth for a gold–polystyrene sample as used in the analysis shown in Figure 4. The plotted values (υ) are correlated to the real part of the dielectric constant ϵ_r by $\epsilon_r = 1 - 10^{-6}\upsilon$, and υ is correlated to the electron density ρ_e by $\rho_e = 0.0778\upsilon$. In the inset the profile for the gold layer is magnified. The deviations of the asymmetric trial profile from the symmetric error function profiles can be seen.

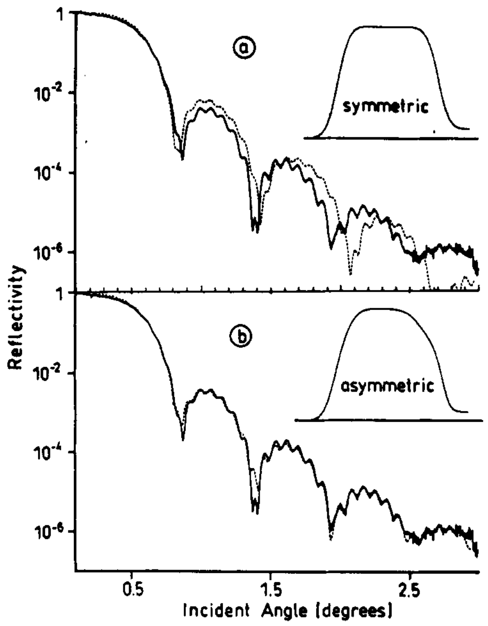

Figure 4. Comparison of the measured reflectivity curve (full line) and a simulated curve (broken line) using the model shown in Figure 3: (a) The interfaces of the gold layer are described by two error function profiles. (b) The gold layer is fitted by an asymmetric trial profile shown in Figure 3. Besides the profiles of the gold layer, nothing has been changed in the model. The correspondence between simulation and measurement is clearly better for case b.

the determination of the distance between the gold layers. Especially if the density distribution of the gold markers is changing during the experiment, one has to consider this change very carefully in the evaluation. Consequently the resolution of this method depends to some extent on the exact description of the density profile of the gold layers.

Results

The changes in the reflectivity curve caused by the annealing of sample PS660-198 are shown in Figure 5 for two typical cases. In Figure 5a nearly no changes during annealing times of 675 and 6830 s and in Figure 5b significant changes during 2.45×10^5 and 6.6×10^5 s can be seen. In Figure 6 we give the interesting part of the corresponding density profiles used for the best fit of the data. As the oscillations of the reflectivity curves shown in Figure 5 are mainly determined by the distance between the two gold layers, a change of the period of these oscillations can directly be interpreted as a change of the thickness of the top polymer film. From the long-range oscillation (not shown in Figure 5, but see Figure 2 and the explanation given in the Experimental Section) we determine the thickness of the inner gold layer. We find that throughout the whole experiment this gold layer does not change its thickness significantly. This can also be seen in Figure 6 from the peak in the density profile at about 85 nm. Only the shape of the density profile of this layer changes slightly.

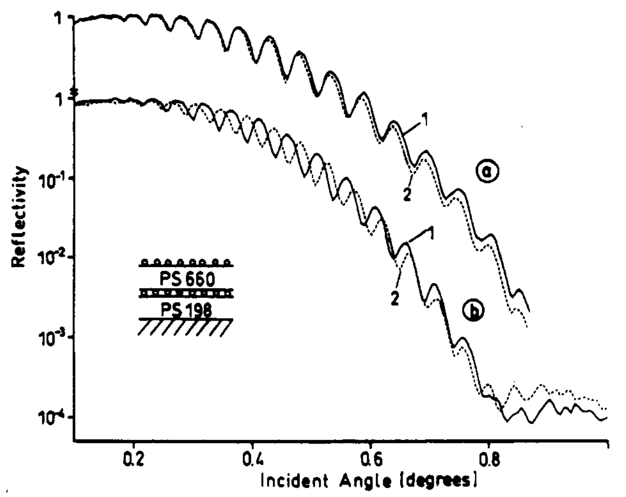

Figure 5. Comparison of measured reflectivity curves of sample PS660-198: (a) Nearly no changes can be seen after annealing for 675 s (curve 1) and 6830 s (curve 2). (b) The period of the oscillations changes significantly for annealing times of 245 400 s (curve 1) and 658 000 s (curve 2), indicating a change of the distance between the two gold layers. The analysis shows that the distance increases by 4.9 nm between curves 1 and 2.

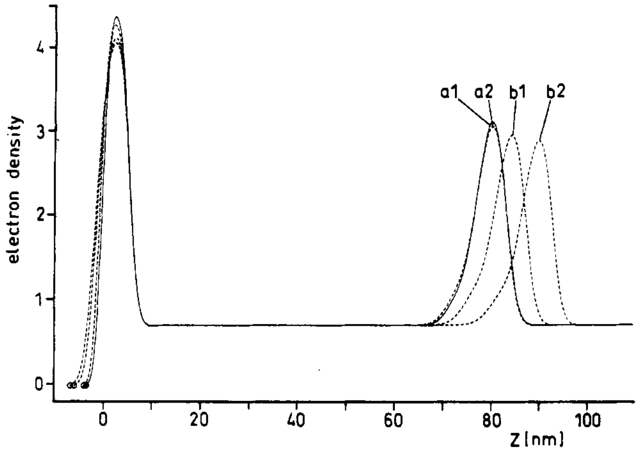

Figure 6. Part of the model electron density versus depth as used for the analysis of the reflectivity curves shown in Figure 5. The position of the top gold layer is around 3 nm. The position of the inner gold layer is shifted from about 81 nm (a1) to about 90 nm (b2). The values of the electron density have the same meaning as in Figure 3.

The analysis of the reflectivity curves shows that the electron density of the gold layers is far below its bulk value. The density profile of the gold particles between the polymer films reveals a rather asymmetric shape, having a tail toward the upper polymer film and a core region of approximately 6 nm with about 20% of the bulk electron density. This can be interpreted in two ways. Either we have small particles that are distributed according to the measured profile or we have a size distribution of particles, most of them having a diameter of approximately 6 nm. Considering the electron micro-

Table III
Results of the X-ray Measurements

(a) Sample PS660-660

actual annealing temp, °C	reduced time, s	excess thickness, nm
	0	2.4
116.5	1 197	1.0
117.5	2 884	0.6
125.5	29 412	0.0
127.5	59 400	0.0
131.0	128 400	0.0
136.0	304 800	0.0
138.0	601 300	0.0
142.5	1 210 000	0.0
145.5	3 302 000	0.2

(b) Samples PS660-198 and PS660-117

actual annealing temp, °C	reduced time, s	excess thickness	
		PS660-198 nm	PS660-117 nm
	0	2.3	2.8
114.0	675	0.0	0.0
126.0	6 830	0.0	0.7
128.5	60 350	0.4	3.8
133.0	136 800	2.2	6.8
139.5	245 400	4.1	10.8
142.0	658 000	9.0	17.6
150.5	1 553 000	14.4	28.3

graphs mentioned in the Experimental Section and the fact that the thickness of the gold layer increases during the annealing at 160 °C for 2 h (which was done prior to the addition of the second polymer layer) leads us to conclude that we have a size distribution of rather big gold particles. As a consequence almost all gold particles are not able to diffuse into the polymer films because the distance between the entanglement points is comparable to the size of the particles. However, there are certainly a few smaller particles which can diffuse into the polymer matrix, being one of the limiting factors for the resolution of this method. Especially in the case of very different polymer fluxes across the interface and long annealing times, the gold markers are affected with respect to their stability at the position of the interface. We annealed sample PS660-117 10 times longer than the maximum annealing time given in Table III. Because of diffusion paths larger than the film thickness, these data cannot be used for the measurement of bulk flow, but one can see from these data that the electron density of the polymer film slightly increases. This can be correlated to the diffusion of a few gold particles smaller than the entanglement distance into the film.

The top gold layer shows a density profile similar to the profile of the inner gold layer. Directly after evaporation, the core thickness is about 4.5 nm and there is also a small tail toward air. After the first annealing process, the core thickness increases to approximately 6 nm, the average electron density decreases, and the tail gets longer. This can be explained by a growth of the gold particles and is confirmed by electron microscopic investigations in our laboratory. During the following annealing periods the density profile of the gold layers changes slightly. Especially the gold particles of the inner layer are distorted by the moving polymers. Fortunately this distortion is rather small compared to the increase in thickness of the top polymer film (see Figure 6). Nevertheless it raises the errors of the determination of this film thickness.

The resolution of the reflectometry method itself is on the order of a few angstroms. This is verified by the measurements on sample PS660-660 where both polystyrene films have equal molecular weight and the mobility of the molecules is small compared to the other samples. In this case the accuracy of the values for the change in thickness is about 0.1–0.2 nm as can be seen in Table III. The measurements on this sample prove that even up to annealing times longer than 10^6 s the gold markers do not shift in one direction. The data show that the inner gold layer does not change its thickness or shape significantly during annealing. These measurements also prove with an angstrom resolution that the thickness of the polymer film is not changed due to the relaxation of possible internal stresses, that the coarsening of the top gold layer during annealing (the inner gold layer was annealed at an earlier stage of the preparation of the four-layer sample) does not complicate the determination of the distance between the gold layers, and finally that our annealing procedure does not produce significant temperature gradients within the sample to cause the markers to move.

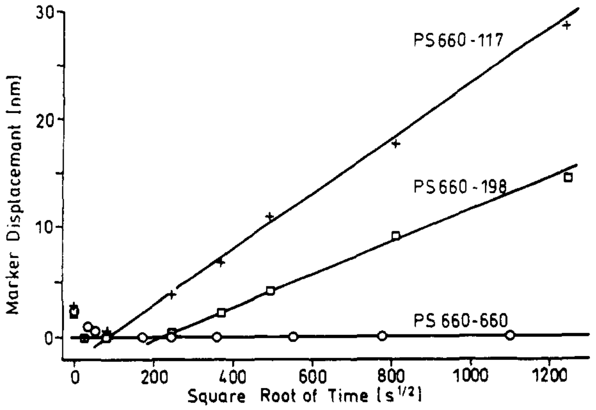

Figure 7. Displacement of the gold markers or excess thickness of the upper polystyrene film versus square root of time for three samples: (○) sample PS660-660, (□) sample PS660-198, (+) sample PS660-117.

X-ray reflectometry gives information about the gold layers and the distance between these layers. Due to the high reflectance of the gold particles, no information is available about the bottom polymer film. Reducing the evaporated amount of gold might result in a more appropriate electron density contrast to get comparable reflected beams from the gold layers and the substrate. This would enable us to determine the thicknesses of both polymer films. Such a reduction is advantageous for another reason, too. If the gold layer is rather thick and the gold particles are packed very closely together, polymer diffusion is hindered quite significantly. For a first test we evaporated a gold layer with about 70% coverage of the polymer surface. In this case the onset of the marker displacement is shifted toward higher times. A disadvantage of a light coverage is that there is a higher percentage of particles smaller than the entanglement distance. Such particles are more mobile and therefore complicate the analysis, or they make it even impossible to detect bulk flow correctly. For the present experiments we use a light gold coverage of approximately 20%. To exclude errors due to different thicknesses of the gold layers, we have covered our samples simultaneously to get identical gold layers.

In Figure 7 we have plotted the displacement of the inner gold markers versus the square root of time. The minimum distance between the two gold layers is defined as the zero position of the markers. One can see that after an initial decrease the marker position does not change for a certain period of time. In the case of different molecular weight polymers the markers then begin to move toward the lower molecular weight film. For equal polymers they do not move.

Discussion

The first experiments with gold markers between two polymers of different molecular weight were done by Kramer and Green et al.[1,2] The purpose was to show that there is a net matter flux (bulk flow) if interdiffusion between two polymer films of different molecular weight takes place as stated by their theoretical considerations. The assumption is that the polymers move via reptation into vacancies that are due to thermal fluctuations continuously created and destroyed. According to the higher mobility of the smaller molecules compared to the longer ones, these are more likely to diffuse into the vacancies. Consequently different polymer fluxes are crossing the interface. This is accompanied by a flux of vacancies and leads to a shift of the position of the interface.

Another theoretical approach based on the reptation model[8] and proposed by Brochard et al.[5] also finds a shift of the position of the interface. For entangled polymer systems of unequal molecular weight due to the different mobilities of the long and the small molecules, a pressure gradient would occur, which is removed by a shift of the whole polymer matrix. The main difference between these two treatments of polymer interdiffusion is the possibility of vacancy creation and destruction introduced by Kramer and Green et al.[1,2] whereas the other theory[5] assumes constant polymer density and accounts for the different mobilities of the molecules by the possibility of the environment (=the "tube") to move. In both cases this leads to different amounts of mass crossing the interface between the two polymer films. To compensate for this net flux, the interface is shifted toward the side of the smaller molecules. One might compare this process to swelling of polymers. In the limit of nearly infinite molecular weight polymers on one side (e.g., cross-linked rubber) and molecules just above the entanglement limit or even smaller on the other side, it seems quite obvious that swelling should happen if the two interdiffuse into each other.

The experiments[1-4] show that the interdiffusion process is dominated by the faster moving species. Our aim is to investigate the early stages of interdiffusion between different molecular weight polymers and to analyze in more detail the behavior of the gold markers during annealing.

The results, shown in Figure 7, demonstrate that bulk flow does not start at time zero. There is an induction time, which is different for the two samples with polymer films of unequal molecular weight, indicating a dependence of this time on molecular weight. This time cannot be caused by the gold markers because we covered all samples with equal gold layers and therefore do not expect different influence of the gold markers on the bulk flow in our samples. Only part of the delay can come from a hindrance of polymer movement by the markers.

According to the reptation model,[8] the reptation or disengagement time τ_d is given by

$$\tau_d = Nb^2/3\pi^2 D^* \tag{2}$$

where N is the degree of polymerization, b is the statistical segment length, and D^* is the self-diffusion coefficient for the center of mass.[9]

Taking the value $D^* = 5.45 \times 10^{-18}$ cm^2/s for M_w = 233 000 g/mol at 120 °C as measured by forward recoil spectrometry[14] and 6.7 Å for b,[15] one can calculate τ_d for different molecular weights by using the N^{-2} dependence of the diffusion coefficient.

For a temperature of 120 °C we get τ_d = 7900 s for M_w = 117 000 g/mol and τ_d = 38 300 s for M_w = 198 000 g/mol.

A double-logarithmic plot of marker displacement versus time (from the actual annealing time τ_d is subtracted) shows a slope of 0.5 ± 0.08. Therefore, we plotted our data versus the square root of time.

From Figure 7 one can find three straight lines. For the samples PS660-117 and PS660-198 these lines intersect the time axis for zero marker displacement at 69 ± 14 and 207 ± 21 s$^{1/2}$, respectively. For equal molecular weights we have no displacement of the gold markers apart from initial changes caused by the preparation of our samples. This proves that our technique only measures differences between the polymer fluxes.

The induction times we found are not so much different from the disengagement times for the lower molecular weight polymers of our samples. The disengagement time depends on molecular weight by an exponent of 3. The ratio of the molecular weights for our shorter molecules is 1.7. The ratio of the corresponding reptation times is therefore approximately 5, and the ratio of the induction times is 9. Within experimental error these two ratios correspond quite well.

de Gennes pointed out[16] that at the beginning only those molecules that have an end at the interface ($\sim 2/N$) can diffuse across this interface. Only after the reptation time all molecules have the possibility to cross the interface. This might explain why we do not see a net mass transport across the interface at very short times.

The polymer films used in this investigation are very thin. The thickness is only a few times the diameter of the molecules. Therefore, the molecules in these films are distorted, especially on the surface.[17] By putting two films together, we remove the constraint of the surface for the molecules at the interface between the two films. These molecules can relax. You can imagine that this causes a delay of the onset of bulk flow because the diffusion process is hindered by the rearrangement of the molecules at the interface. This effect is possibly superposed to the explanation mentioned above.

It is difficult to use gold markers as indicators for very small shifts of the interface because of the uncertainties produced by possible small movements of the markers themselves. Nevertheless, the error produced by such movements cannot explain the molecular weight dependent induction time we have measured.

The slope of the straight lines fitted to the data is different for samples PS660-198 and PS660-117. We get 0.0240 ± 0.0005 nm/s$^{1/2}$ for PS660-117 and 0.0141 ± 0.0004 nm/s$^{1/2}$ for PS660-198.

The following relation is given by Green et al.[2]

$$\Delta x = C(D^*_S t)^{1/2} \tag{3}$$

where Δx is the displacement of the markers, C is a constant, and D^*_S is the diffusion constant of the smaller molecules.

Using the value of D^* given by ref 14 and calculating the diffusion coefficient according the N^{-2} relation, we get C = 0.516 ± 0.010 for M_w = 117 000 g/mol and C = 0.514 ± 0.015 for M_w = 198 000 g/mol.

Green et al.[2] calculate this constant and obtain a value of 0.48 for very different molecular weight polymers. For ratios of N_S/N_L of 0.18 and 0.30 they find the value of C being 0.42 and 0.37, respectively.

Our results show that despite the difference in molecular weight there is no effect on the constant C. A possible reason for the constancy of C with molecular weight might be that our measurements are below the disengagement time for the higher molecular weight polymer $\tau_d = 1.42 \times 10^6$ s (T = 120 °C). Therefore, the unhindered center of mass diffusion of the longer molecules is not yet established. This might explain the constant C being 0.51, which would demand infinite molecular weight polymers on one side of our samples. The difference of the measured value of $C = 0.51$ to the calculated value of 0.48 can be explained by the uncertainty of the value of D^* given by ref 14. However, it is not possible to attribute the coincidence of the measured values for this constant for samples PS660-117 and PS660-198 to uncertainties of our method. The error bars for C are smaller than the difference of the values of parameter C according to the calculations in ref 2 for a concentration-dependent interdiffusion coefficient.

Conclusions

We have investigated the interdiffusion of polystyrenes of different molecular weight via the displacement of markers at the interface. The marker movement can be detected with subnanometer precision by X-ray reflectometry. For equal molecular weight materials we do not observe marker movement, while for different molecular weights of the components the marker particles at the interface move because of different fluxes of the molecules across the interface. The resulting matter flux gives rise to a shift of the location of the interface, which is called bulk flow. Our data on marker movement during polymer diffusion of chains of different molecular weight show that bulk flow does not occur at all times. It is delayed a certain time depending on molecular weight. The results suggest that this time corresponds to the disengagement time of the smaller molecules.

Within the time region of our experiments no influence of the higher molecular weight polymer on the velocity of the gold markers is observed. We did not measure at times higher than the disengagement time of the longer molecules where we expect a retardation of the marker velocity due to unhindered center of mass diffusion of the long molecules.

The resolution of our method is well below 1 nm and is mainly limited by diffusion of the markers themselves. Fortunately the gold particles are only slightly affected by the polymer diffusion, but it is very difficult to detect shifts of the markers smaller than 0.3 nm. This is necessary if we want to investigate the time behavior of interdiffusion at very short times in even more detail than is done in this work. Therefore, we are planning to perform neutron reflectometry measurements on protonated and deuterated polymers where we do not need markers and expect also subnanometer resolution.

Acknowledgment. We benefited from stimulating discussions with A. Silberberg, J. Klein, and A. Halperin. We thank G. Herrmann for the preparation of the gold layers and M. Bach for his help with technical problems. We also thank Dr. G. Lieser for the electron microscopic investigations. We acknowledge support by the BMFT.

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Registry No. PS, 9003-53-6; Au, 7440-57-5.