Lateral Mobility of Single Chains at a Liquid Polymer Interface

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The chain dynamics of polymers at surfaces and interfaces has been a very interesting research topic because it will help us to understand the physical picture of fluids, rheology and tribology, at microscopic scale. Because of spatial confinement, this chain dynamics is different from that in the bulk system. One of the interesting issues is about the dynamics of molecules at the interface between two immiscible liquids. The understanding of this question is highly related to the principle of rheological properties of multiphase systems, such emulsions, polymer blends, etc.

It is believed that the rheological properties at the interface of two immiscible polymers differ drastically to the bulk that construct the interface.[1−8] Such a difference has been considered to be the reason for multiple phenomena of mixed polymer liquids, such as the abnormal viscosity of polymer mixture and the slip motion at interfaces of polymer blends under shear.[9] Direct studies on rheological properties of the polymer−polymer interface, for example, the interfacial viscosity, have been mainly by theoretical methods such as computer simulations.[7,8] It was only until recently that there has been direct experimental measurement of the interfacial viscosity. By examining the interfacial relaxation time, the interfacial viscosity of polystyrene (PS) layers has been found to be 2% of the bulk PS polymer.[10]

The reduced interfacial viscosity originates from the structure of the interface, for example, the distribution of different chain segments because of the interaction strength between the two polymers. By theoretical investigations, de Gennes and his coworkers discovered that the interface was constructed mainly by chain loops and predicted that the interfacial width is largely dependent on the interaction parameters of the two polymers. Another important prediction of his is that the interfacial viscosity is not dependent on the molecular weight of the polymers.[1−4] A similar discovery has also been verified by computer simulation, which shows that the interfacial viscosity has minimal dependence on the molecular weight of the two polymers when the repulsion between them is high enough.[8]

On the basis of these microscopic pictures of the interfacial viscosity, any experimental study on the chain dynamics at the liquid polymer interfaces is very important, as it can verify theoretical models and furthermore reveal more information to the fundamental understanding of the problem. Here, we report our study of the interfacial chain motion by a sensitive technique at the single molecular level: fluorescence correlation spectroscopy.[11−13] The lateral diffusion of single diblock copolymer chain, polystyrene-*b*-polyisoprene (PS-*b*-PI), at the interfaces of a liquid polymer, polyisoprene (PI), with its nonsolvent, *N,N*-dimethylformamide (DMF), was studied, and emphasis was placed on the variation of the diffusion rate when the molecular weight of PI was changed.

Poly(1,4-isoprene) was chosen as the model system (details of the samples are listed in Table 1). The probe polymer was a diblock copolymer, polystyrene-*b*-polyisoprene (PS-*b*-PI, $M_n = 23 \times 10^3 - 37.5 \times 10^3$ g mol^{-1}, $M_w/M_n = 1.06$), purchased from Polymer Source, Quebec, Canada. The copolymer was functionalized at its chain end at the polyisoprene side, through which a bright and stable fluorescent dye molecule was attached chemically. In the study, different fluorescent dye molecules were adopted, such as Rhodamine 6G and Bodipy FL (Invitrogen). The fluorescence-labeled samples were purified from residual free fluorescent dyes by size-exclusion chromatography for multiple times, and the purity was verified by gel permeation chromatography measurement.

The interface under investigation was between PI polymer and DMF. The latter is a nonsolvent of PI but a good solvent of PS. The construction of the interface was by the application of DMF onto a thin film of PI spin-coated on a silica substrate. In order to stabilize the PI thin films under polar DMF, silica substrates were precoated with a self-assembled monolayer of octadecyltriethylsilane (OTE) following a protocol already published.[15] To prepare the PI thin film on the substrates, PI was first dissolved in anhydrous *n*-hexane with the presence of 0.1 wt % antioxidant (2,6-di-*tert*-butyl-*p*-cresol, Fluka).[16] After spin-coating, the samples were immediately annealed under vacuum at room temperature for 24 h to remove all of the residual solvent.

The probe diblock copolymer was allowed to absorb onto the interface from its DMF solution of a concentration of 10^{-9} M. About 4 h was allowed to let PS-*b*-PI chains absorb onto the interface and equilibrate. Such low solution concentration resulted in very low interfacial concentration of the adsorbed probe chain. Afterward, the sample was rinsed copiously with pure DMF to remove possible residual PS-*b*-PI in the liquid phase. Because of the good solubility of each block of PS-*b*-PI in DMF and PI, the probe diblock copolymer resided at the interface only, and this was verified by the detection of the fluorescence only when focus was adjusted at the interface. The lateral diffusion coefficient of the probe chain was measured by a home-built setup of fluorescence correlation spectroscopy (FCS). A detailed description of the setup can be found in a previous publication.[17] In the present study, the excitation laser was 488 or 514 nm output of an ion laser. An oil-immersion objective lens (Plan Apochromat 60×, numerical aperture = 1.4) was used to guarantee high excitation and fluorescence collecting efficiency. Extreme attention was paid to keep the purity of the sample in order to suppress the background fluorescence. The excitation light was introduced from the DMF side of the interface (please refer to the inset of Figure 1 for the experimental configuration).

Careful measurements were taken to determine the dimension of the excitation spot inside the sample because FCS measurement of diffusion coefficient is highly dependent on the dimension of the excitation volume. This was accomplished by measuring the diffusion coefficient of standard samples, fluorescence-labeled monodispersed PS ($M_n = 32\,000$ g mol^{-1}, $M_n/M_w = 1.04$). Its diffusion coefficient in DMF was measured to be 55.8 μm^2/s by dynamic light scattering below the semidilute concentration. The data were adopted for the calibration of FCS

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Table 1. Polyisoprene Samples Used in This Study[a]

M_n ($\times10^3$ g mol^{-1})	M_w/M_n	η (Pa s)[b]
1.2	1.11	0.8
3.2	1.06	2.2
10.5	1.04	7.6
34.5	1.04	4.16×10^2
138.0	1.06	9.77×10^4

[a] Poly(1,4-isoprene) samples were purchased from Polymer Source, Quebéc, Canada. [b] Data of viscosity taken from ref 14.

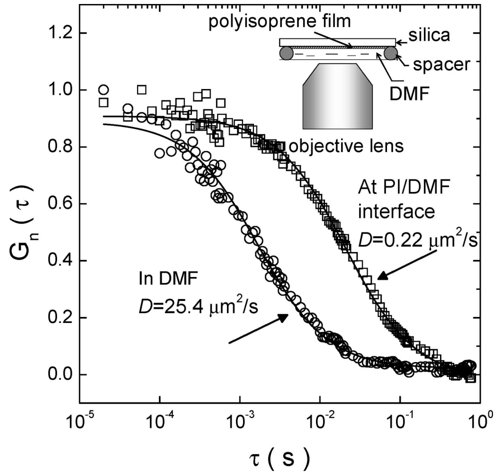

Figure 1. Normalized autocorrelation function of fluorescence-labeled PS-*b*-PI diffusing in DMF and at the interface of PI/DMF. *D* denotes diffusion coefficient. Inset: schematic illustration of the experiment configuration.

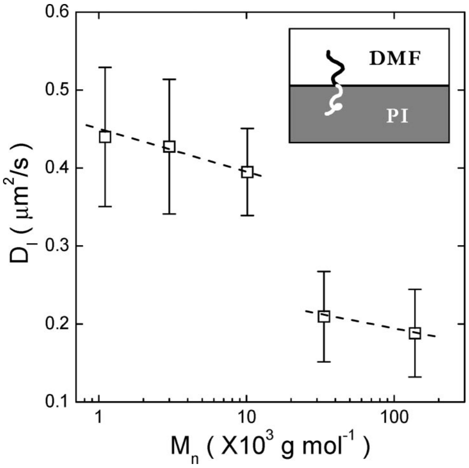

Figure 2. Interfacial diffusion coefficient of single PS-*b*-PI chain as a function of the molecular weight of bulk PI. The dashed line is for the guide of eye. Inset: illustration of the sample geometry.

excitation volume, whose lateral radius in DMF was determined to be 0.30 μm.

To measure the lateral interfacial diffusion of single PS-*b*-PI chain, the focus of the microscope was adjusted to travel in the direction perpendicular to the interface, and a maximum fluorescence photon count was recorded when the focus was positioned at the interface. FCS measurements were conducted at different locations across the interface for every sample, and more than 10 measurements were performed for each sample. Figure 1 shows the normalized autocorrelation function of PS-*b*-PI diffusing at the interface between DMF and PI (M_n = 34 500 g mol^{-1}). For comparison, the diffusion data of PS-*b*-PI in DMF are also shown. By fitting the data with theoretical models for three-dimensional and two-dimensional Brownian motion, the diffusion coefficient was determined. The diffusion coefficient of PS-*b*-PI in DMF is 25.4 μm^2/s, and that at the interface is 0.21 μm^2/s.[18] The diffusion rate in DMF shows the existence of micelles or aggregates of the block copolymer. A calculation shows a hydrodynamics radius of 10 nm, similar to the published data of micelle formed by the same polymer in a different solvent.[19]

The much slower diffusion of the probe at the interface is because PI is much more viscous than DMF (a difference of 6 orders of magnitude for this molecular weight). More importantly, this diffusion rate at the interface is about 2 orders of magnitude higher than in the bulk polymer of the same molecular weight (~0.003 μm^2/s).[20] This indicates a much lower interfacial viscosity compared with that in the bulk, and it is in good agreement with the previous theoretical prediction[7,8] and also consistent with the result of low interfacial viscosity reported by other experimental studies.[10] A rough estimate shows that the results of diffusion rate agree with theoretical analysis.[8] Considering the simple case of the unentangled system, Rouse theory shows that the bulk viscosity (η_B) of the polymer can be written as $\eta_B = \zeta b^2 N/v_0$, where ζ denotes monomer friction coefficient, b the segment length, N the degree of polymerization, and v_0 the monomer volume.[8,21] As for the interfacial viscosity (η_I), de Gennes' theory shows that it has the form of $\eta_I = \zeta b^2 s^*/v_0 = \zeta b^2/v_0\chi$, where χ is the Flory–Huggins interaction parameter.[1-4,8] Therefore, the ratio of bulk viscosity and interfacial viscosity (η_B/η_I) can be scaled as $N\chi$. By taking the typical value of PI used in this study (M_c ~ 13 000 g mol^{-1} and χ ~ 0.5–1 for nonsolvent[22]), the estimated ratio is at the order of 10^2, which agrees with the ratio of the bulk and interfacial diffusion rate.[23]

The influence of photobleaching of the fluorescence dye molecule, which often exists in fluorescence techniques, was evaluated by changing the excitation laser power. With a 10 times change of laser power, no noticeable change of diffusion coefficient was observed, excluding the possible effect of photobleaching on the preciseness of diffusion coefficient determination.

The following experiments investigate the variation of the lateral interfacial mobility of the probe chain when the molecular weight of bulk PI was changed (data shown in Figure 2). When the molecular weight was changed for more than 2 orders of magnitude, the interfacial diffusion coefficient changed only by a factor of 2, from 0.4 to 0.2 μm^2/s. Such a small change is really striking considering the fact that the viscosity of bulk PI changes more than 5 orders of magnitude during the molecular weight variation, from 0.8 to 9.77×10^4 Pa s.[14]

The location of the probe diblock copolymer chain is believed at the interfacial region between these two liquids. With DMF and PI serving as good solvent for PS and PI block, respectively, the highest probability of finding the probe chain is in the middle of the interfacial region. A control experiment showed that polystyrene alone did not adsorb onto the interface from DMF. So, due to the overwhelming value of PI's viscosity compared with that of DMF, the viscous drag force experienced by the probe is dominantly from the PI side of the interface. Therefore, the data demonstrate that the viscosity of PI at the interface is hardly changing despite the huge increase of the viscosity in the bulk polymers. This result verified the prediction by de Gennes' model that the interfacial viscosity is not dependent on the molecular weight of the bulk polymers.[1-4,8]

Although the reduced interfacial viscosity may have a possible contribution from the fact that PI may be slightly swollen by DMF, it is not considered to be a major effect here. This is because the viscosity of the swollen PI should have its strong molecular weight dependence, which is not observed here.

On the other hand, the data do show a slight decrease of interfacial diffusion coefficient (D_I) with the increase of the molecular weight of PI, from 0.4 to 0.2 $\mu m^2/s$. Especially, there exists a much faster drop around the molecular weight of (1−3) $\times 10^4$ g mol^{-1}. The slight decrease of D_I is attributed to the effect of graduate narrowing the interface. It is known that the interfacial tension of polymer systems is molecular weight dependent: the increase of molecular weight elevates the interfacial tension and as a result reduces width of the interface.[24,25] This leads to the situation that some segments near the chain end of the probe PS-*b*-PI begins to experience or "feel" the viscous drag force from the much more viscous bulk polymer outside the interfacial region. Interestingly, the molecular weight range of the faster drop of D_I coincides with the critical molecular weight for chain entanglement of PI ($\sim 1.3 \times 10^4$ g mol^{-1}),[14] and this feature gives an implication that the interfacial structure and dynamics is different for the cases with and without chain entanglement.[26−28] The PI block is big enough to probe possible entanglement. Its molecular weight is 37 500 g mol^{-1}, corresponding to an end-to-end distance (R_e) of 14 nm, which is much bigger than the entanglement length of PI, ~6 nm, for M_e of 6500 g mol^{-1}. From this point, we also envision that different shape of data may be obtained when using probe polymer of different molecular weight, and further work is in process. The entanglement of polymer chains at interfaces has been an interesting topic, and the situation of entanglement at interfaces compared with the bulk polymers is still not clear. The above results show a correlation of the change in interfacial chain mobility with the critical molecular weight for chain entanglements, indicating a considerable change of the interfacial structure when the molecular weight is lower and higher than the critical value for entanglements. Further investigations are needed to provide a clear physical picture.

In summary, the lateral diffusion of single diblock copolymer chain at the interface of PI and DMF demonstrates a much less viscous state of the interface than that in the bulk polymer, and a very weak dependence of the interfacial diffusion rate on the molecular weight of the bulk PI polymer was discovered. Such a finding agrees with de Gennes' prediction that the interfacial viscosity of polymers is independent of the molecular weight. The weak molecular weight dependence of interfacial diffusivity exhibits a faster change near the critical molecular weight of entanglement, implying an effect of chain entanglement of the bulk polymer to the chain mobility at the interface.

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