



Enhanced Dynamics of Confined Polymers near the Immiscible Polymer–Polymer Interface: Neutron Reflectivity Studies

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differ from the bulk because of significant contributions from the polymer–polymer interface. Herein, we investigated the diffusion dynamics of entangled polymer thin films confined between different polymers in a direction perpendicular to the surface using neutron reflectivity. We found that a bilayer of poly(methyl methacrylate) (PMMA) and deuterated PMMA (*dPMMA*) sandwiched between polystyrene (PS) layers exhibited significant increase in mobility near the polymer–polymer interface with decreasing PMMA thickness. This indicates that the contribution of repulsive interactions at the immiscible polymer–polymer interface becomes more significant as the film thickness decreases. We also found that the interfacial roughness between PMMA and PS (28 Å at equilibrium) and soft confinement of PS layers did not significantly affect the change in the diffusion dynamics of the adjacent PMMA. This was



evidenced by comparison with the diffusion results of multilayers with a flat interface (8 Å at equilibrium) between PMMA and hard PS by UV cross-linking.

he confinement of polymers to nanoscale dimensions leads to complex physical properties with regard to their structure and dynamics. For example, polymer thin films on solid substrates exhibit enhanced or reduced mobility near solid supports depending on the polymer-substrate interaction, while the region near the free surface is highly mobile, like a liquid-like layer.¹⁻³ The overall dynamics of polymers are usually determined by the interplay of substrate and free surface effects. Computer simulation studies have shown that there is a mobile surface layer with fast dynamics for unentangled linear chain polymers near a free surface.^{1,4,5} Similarly, for free-standing films without solid supports, the glass transition temperature (T_g) decreases with decreasing film thickness, d ($d \approx$ tens of nanometers).⁶ With regard to experimental studies, the situation remains complicated for asymmetric confinement (air/polymer/solid substrate), where the polymer thin film is confined between an upper airpolymer interface and lower polymer-solid interface. In this case, because the polymer-substrate interactions influence the overall polymer dynamics more than the air-polymer interface, a strong attractive interaction increases $T_{\rm g}$, whereas a weak interaction causes the average T_g to be comparable to or lower than that of the bulk.⁷⁻¹⁰

In addition to polymer–solid and polymer–air interfaces, studies have recently focused on polymer structure and properties, such as T_g and dynamics of nanoconfined polymers, near polymer–polymer interfaces.^{11–19} The contribution of the region near the polymer–polymer interface in polymer blend systems is not ignorable if the domain size is sub-100 nm, and the interface predominantly influences the overall

blend structure and properties.^{20,21} In this respect, understanding the local dynamics is clearly necessary. We have previously investigated the diffusion dynamics of PMMA/ *d*PMMA confined between graphene oxide (GO) sheets (GO/ PMMA/*d*PMMA/GO) using the neutron reflectivity (NR) technique.³¹ In that case, because of the attractive interaction between PMMA and GO, the diffusion coefficients of PMMA are reduced by more than 30 times as the thickness of PMMA/ *d*PMMA decreased. However, in this study, we obtained the enhanced diffusion of PS/PMMA/*d*PMMA/PS as the confinement increases. This difference reflects that the type and strength of interactions between the polymer and the confining surface significantly affect the polymer mobility.

The importance of this research topic for practical applications has resulted in numerous theoretical and experimental studies of changes in the structure, dynamics, and $T_{\rm g}$ of thin polymer films on various polymer surfaces with different interfacial structures, mechanical softness, and interfacial energies.^{11,15–19,22} Lang et al. also perfomed molecular dynamics (MD) simulation study regarding the effects of polymer–polymer interaction energy and hardness of confining polymer on change in $T_{\rm g}$ of confined polymers.¹⁵

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They found that as the polymer-polymer interfacial adhesion energy decreases, there is no difference between soft and hard confinement effect on the T_{α} changes. This indistinguishable difference was attributed to the presence of density depletion near the polymer-polymer interface for low interfacial adhesion energy. Experimental studies have also been performed using fluorescence and broadband dielectric spectroscopy to measure the local T_g and segmental dynamics of polymer thin films confined between other polymers.^{13,22} These studies commonly revealed that the interfacial energies between two polymers play an important role in both shortrange motions (corresponding to T_g) and long-range motions (such as interdiffusion dynamics). That is, strong attraction leads to an increase in T_g and a reduction in chain mobility near the polymer-polymer interface, whereas repulsive interaction induces the opposite behavior. However, few experimental measurements of local diffusion dynamics near the polymer-polymer interface have been reported, which is essential for understanding the dynamics of polymers confined at the molecular level.

In this study, we measured the diffusion dynamics of entangled polymer melts sandwiched between immiscible polymers above T_g . The effect of geometrical confinement on the mobility of the polymer thin films near the polymerpolymer interface was investigated. NRwas applied to measure the local diffusion dynamics of poly(methyl methacrylate) (PMMA) approximately one radius of gyration ($\sim 1R_{\sigma}$) away from the polystyrene (PS)/PMMA interface. The confinement effect was investigated by varying the thickness of the PMMA layer in multilayered PMMA and deuterated PMMA (dPMMA) thin films sandwiched between PS layers (denoted as PS/PMMA/dPMMA/PS) by changing the interfacial roughness of PS and PMMA and by altering the hardness of the PS layer through UV-cross-linking. In addition, we performed MD simulations with a generic, coarse-grained model for polymer chains and compared the results with the NR results.

We measure the local diffusion behavior of polymers near the polymer–polymer interface, i.e. approximately $1R_g$ from the interface. Experimental measurement of T_g for our system is very difficult. First, the problem is that we cannot tell the origin of the film thickness between the increase in free-volume increases and interdiffusion between PS and dPMMA. Second, diffusion between PMMA and dPMMA reaches a fully intermixed equilibrium at high temperatures, making it impossible to measure the thickness of each layer. Therefore, in our study, the local diffusion behavior was investigated using a specular neutron reflectivity technique instead of T_g measurement.

We prepared multilayer films of PS/PMMA/dPMMA/PS as described in Figure 1 (sample preparation details are given in the Experimental Section in the Supporting Information). These 3 in. diameter, four-layered samples were completely deposited over the entire area for NR measurements as shown in the sample photographs (Figure S1). We obtained multilayers by spin-coating with various concentrations of PS (Mw = 7100 kDa), PMMA (Mw = 92 kDa), and dPMMA (Mw = 106 kDa) solutions (see the Supporting Information for details). Both the top and bottom PS thin films were 190 \pm 6 Å thick. The molecular weight of the PS was greater than that of the PMMA to prevent dewetting of the top PS layer. Optical microscopy of these multilayers revealed no dewetting holes on the sample surface after annealing for diffusion experiments



Figure 1. Sample geometries of PS/PMMA/dPMMA/PS/Si with variable PMMA thicknesses for diffusion experiments.

(Figure S2). The thickness of the *d*PMMA thin films was fixed at 92 Å (corresponding to approximately $1R_g$), while the thicknesses of the PMMA thin films (*d*) were varied from 181 to 642 Å (corresponding to approximately $2R_g$ to $7R_g$) to investigate the confinement effects. The specular NR measurements were performed with an NG7 reflectometer at the Cold Neutron Facility of the National Institute of Standards and Technology (Gaithersburg, MD, United States) with a wavelength (λ) of 4.76 Å and $\Delta\lambda/\lambda$ of ~0.025. The analysis of NR data is described in detail in the Supporting Information.

Figure 2a shows the NR profiles of the PS/PMMA/ dPMMA/PS multilayer at 145 °C, which is higher than the $T_{\rm g}$ of both PS and PMMA. The bulk $T_{\rm g}$ values are 105, 124, and 133 °C, for PS, dPMMA, and PMMA, respectively (see Figure S3). Using the specular NR technique, diffusion dynamics normal to the film surface (i.e., out-of-plate structural information along the film depth) were measured as a function annealing time. We used a sample environment equipment, i.e., a vacuum heating chamber specially designed for in situ reflectivity measurements during annealing. From the result, one can see that new fringes appear in the reflectivity profiles, indicated by red arrows, with annealing time. This indicates that a diffusion phenomenon occurs between the PMMA and dPMMA layers, and the region containing the dPMMA molecules becomes broader in the depth direction of the film. We analyzed the reflectivity profiles by fitting based on the scattering length density (SLD) profiles along the film depth. Figure 2b shows the SLD profiles corresponding to the best fit of the reflectivity profiles with annealing time, t. The SLD profiles also show that the interfacial width between PMMA and dPMMA increases with annealing time (Figure 2c). This change in interfacial width is caused by interdiffusion from dPMMA/PMMA interface to each region. It should be noted that the deuteration can also affect the interaction parameters for binary blends of amorphous polymers due to molar volume changes and reduction in combinatorial entropy.^{23,24} However, from our results, polymers at the PMMA and dPMMA interfaces continue to diffuse with annealing time until the two layers have a similar SLD. Therefore, the effect of deuteration on diffusion dynamics is expected to be small.

The change in interfacial root-mean-square (rms) roughness, $\Delta \sigma = \sqrt{\sigma^2 - \sigma_0^2}$, between PMMA and *d*PMMA is plotted over time in Figure 3a, where σ is the experimentally



Figure 2. (a) Neutron reflectivity profiles (best fit in black line) of the PS/PMMA/dPMMA/PS samples during annealing at 145 °C. The inset shows the error bars of the high q data. (b) Corresponding overall SLD profiles as a function of annealing time and (c) SLD profiles of dPMMA/PMMA.



Figure 3. (a) $\Delta\sigma$ plotted as a function of $t^{1/2}$ and (b) D plotted as a function of PMMA layer thickness, d, over R_{e} .

determined interfacial rms roughness and σ_0 is the rms roughness of the first reflectivity result obtained at 145 °C. $\Delta\sigma$ was found to linearly increase with the square root of annealing time, $t^{1/2}$. This is consistent with the Fickian relationship, $\Delta\sigma = 2(Dt)^{1/2}$,²⁵ which was used to extract the diffusion coefficient, D, from the slope of the linear fits in Figure 3a. To determine the effect of confinement on polymer diffusion, D is plotted as a function of the thicknesses of the upper PMMA layer in PS/ PMMA/dPMMA/PS in Figure 3b. The thinner the layer of PMMA in the multilayer (in other words, the geometric confinement of the PMMA between the PS walls), the faster the diffusion dynamics of the confined PMMA thin film. When the PMMA thickness is less than $4R_{g}$, D begins to increase significantly. Particularly, D reaches more than 6 times that for $2R_{g}$.

Šimilar to our study, Roth and Torkelson et al. previously investigated the distribution of T_g along film depth experimentally using the fluorescence/multilayer method.^{26,27} In that case, the local $T_{\rm g}$ of the confined thin film with the thicknesses ranged from around 10 to more than 100 nm, similar to our system. The reports disucss the polymer T_{σ} change near three types of surface or interfaces, that is, free surface, polymer-polymer interface, and polymer-solid interface. They found a reduced local T_{g} compared to bulk T_{g} near the free surface and the immiscible polymer-polymer interface. In particular, in the case of free-standing films where they have free surfaces on both sides, the thinner films exhibited significantly reduced $T_{\rm g}$ for the entire film thickness.^{6,28} These previous reports regarding the $T_{\rm g}$ changes upon confinement are consistent with our results in this study. From the results, we also found that the local diffusion behavior is faster upon approaching the polymer-polymer interface.^{13,26,27,29} The confinement also significantly affects the acceleration in polymer dynamics.

In order to investigate the interdiffusion of polymer chains at a molecular level, we also performed a series of molecular dynamics simulations. We prepared sandwiched polymer films to mimic the experiments. Details on the simulations are provided in the Supporting Information. In our simulations, we estimated the interdiffusion coefficient (D_{inter}) of monomers near the interface. We found that D_{inter} increased with a decrease in the thickness of confined polymer layers. However, the increase in D_{inter} in our simulations was not significant compared to that in the experiment, which could be attributed to the relatively high temperature and relatively short polymer chains employed in our simulations. Note that the T_{σ} of the polymer model used in this study is about 0.4348, but the simulation temperature of T = 1 (in reduced units) was used. The degree of polymerization in our simulation was 128, which is long enough to entangle polymers in simulations but is still much shorter in comparison to polymers in experiments. Molecular simulations near the glass transition are usually computationally extensive because the dynamics of chains becomes extremely slow. In order to see the effect of temperature on D_{inter}, we performed molecular dynamics simulations at a lower temperature of T = 0.8 and found that the increase in D_{inter} was enhanced compared to T = 1. We expect, therefore, that the increase in $D_{\rm inter}$ for thinner films would be enhanced near the glass transition. However, T = 0.8is still greater than $T_{\rm g}$ such that a systematic future simulation study would be necessary (Figure S6c).

Recently, in addition to interactions and spatial confinement between polymers and substrates, attempts have been made to theoretically and experimentally interpret the dynamics of



Figure 4. (a) NR profiles (best fit in black line) of PMMA/*d*PMMA/*cr*PS samples after annealing at 145 °C and (b) corresponding SLD profiles of interface of *d*PMMA/PS and *d*PMMA/*cr*PS.

polymers depending on their substrate roughness and mechanical hardness.^{1,11,12,15,30} Previous theoretical studies have reported that the polymer–substrate interaction and interfacial roughness affect the polymer dynamics and T_g . Hanakata et al.¹ and Douglas³⁰ reported that polymers have less of an interaction with a smooth surface compared with a rough surface because their interaction hardly overcomes the loss of configurational entropy caused by confinement. Furthermore, when there is repulsion between the polymer and substrate, this phenomenon is predicted to be more significant.³⁰

Therefore, we manipulated the interfacial roughness between PS and PMMA in the multilayers through crosslinking of PS and checked whether the diffusion dynamics of the polymer near the interface changed. The PMMA and dPMMA layers with corresponding thicknesses (i.e., d values of the PMMA layers are 493 and 761 Å while that of dPMMA is equally maintained at 92 \pm 10 Å) were deposited on UVirradiated PS thin films by using a floating technique (sample preparation is described in the Experimental Section in the Supporting Information). PMMA/dPMMA/crPS multilayer films without a top crPS layer were prepared in this study because of the difficulty of applying the floating technique for the crPS layer. However, the thickness of the top PMMA thin film was $5.3R_{o}$ or more to minimize the influence of the top free surface. From the NR results, we found that the interfacial roughness between *cr*PS/*d*PMMA ($\sigma = 8$ Å) by UV irradiation differed from that of PS/dPMMA ($\sigma = 28$ Å) in equilibrium after annealing at 145 °C for 10 h (Figure 4b). The interfacial roughness between dPMMA and crPS exhibited almost no change before and after thermal annealing because of the crosslinking of the PS.

Similar to the previous diffusion measurements, the in situ NR profiles of the PMMA/dPMMA/crPS thin films were measured as a function of annealing time in the sample environment equipment at 145 °C under vacuum (Figure 4a). The *D* values of the PMMA near the *cr*PS surface were obtained from interfacial width results of PMMA/dPMMA for the PMMA/dPMMA/crPS thin films as a function of annealing time using NR (red symbols in Figure 3b). From the results, we found that the *D* values of PMMA at $1R_g$ from the PMMA/PS and PMMA/crPS interfaces were not significantly different with PS cross-linking. The diffusion coefficients were determined to be 14×10^{-19} and 10×10^{-19} cm²/s for PS/PMMA/dPMMA/PS and PMMA/dPMMA/crPS, respectively,

for an approximately 5.4 R_g -thick PMMA layer and $1R_g$ -thick dPMMA layer. This implies that the interfacial roughness spontaneously formed between PS and PMMA in the PS/PMMA/dPMMA/PS multilayers is not enough to induce the effects of interfacial roughness on the adjacent polymer chain mobility. Therefore, the enhanced mobility of confined PMMA in PS/PMMA/dPMMA/PS multilayers in Figure 3b is unrelated to the interfacial structure of PS/PMMA.

In addition, Baglay and Roth²² experimentally measured the T_g distribution of polymers sandwiched by different polymers along the film depth from polymer—polymer interfaces. They observed that T_g at the middle depth of the polymer thin film is as high as that of the bulk, but it dramatically decreases upon approaching the polymer—polymer interface. Previously, they also reported that the degree of T_g reduction near the interface depends on the softness of the confining polymer.¹³ Various confining polymers with different T_g values were used to change their softness. However, they did not account for changes in interfacial energy caused by using different polymers.

In this study, by UV cross-linking, we also controlled the mechanical properties of the PS layer. Note that crPS and PMMA still have immiscible properties with a nonattractive interface. To measure the mechanical properties of the PS thin films spun-cast on a Si substrate, a nanoindentation test was performed at 25 °C before and after UV irradiation. As shown in Figure S7, the hardness of the *cr*PS thin film (700 MPa) was twice that without UV irradiation (330 MPa). However, hard confinement and soft confinement effects, which have been claimed in previous reports, were not observed from our diffusion results (Figure 3b). Regardless of the hardness of the substrate, the polymer had the same diffusion coefficient near the interface. Instead, our results showed good agreement with previous simulation results reported by Lang et al.¹⁵ Using the Kremer-Grest model, they predicted no difference in confined polymers between hard and soft confinement when the two polymers had repulsive interactions. Only for attractive interaction was hard confinement reported to decrease the mobility of polymers near the interface. Experimentally, we also confirmed that hardness has no effect on the diffusion of confined polymers. This is probably due to the immiscibility of crPS and PMMA.

In summary, we used the NR technique to measure the diffusion dynamics of confined polymers next to different polymers. The mobility at the interfaces of entangled PMMA/

dPMMA bilayers sandwiched between PS walls at temperatures above T_g was quantitatively measured. By varying the PMMA layer thickness from 181 to 642 Å, we investigated the confinement effect on the diffusion dynamics of PMMA near the PS/PMMA interface. From the NR results, we found that the diffusion of PMMA in PS/PMMA/dPMMA/PS was accelerated 6-fold from 7.3 \times 10^{-19} to 4.7 \times $10^{-18}~cm^2/s$ when d decreased from approximately $7R_g$ to $2R_g$. This is because the confined polymers are more affected by the polymer-polymer interface than polymers in thick films; the repulsive interaction between PS and PMMA leads to an increase in the mobility of the confined PMMA. We also investigated the effect of the interfacial roughness between PS and PMMA layers and the hardness of the confining UVirradiated PS layer on the diffusion of PMMA near the interface. Then, we found that the effect of cross-linking was not significant. Hence, the change in dynamics of the confined PMMA in PS/PMMA/dPMMA/PS is due to the immiscibility between PS and PMMA and the geometrical confinement, rather than the soft/hard confinement effect of the confining PS layer or the interfacial roughness effects of PS/PMMA.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.9b01011.

Materials, sample preparation, neutron reflectivity techniques, and molecular dynamics simulation (PDF)

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Notes

The authors declare no competing financial interest.

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