How Does Monomer Structure Affect the Interfacial Dynamics of Supported Ultrathin Polymer Films?

Amber N. Storey,* Wengang Zhang,*§ Jack F. Douglas,* and Francis W. Starr*

ABSTRACT: We utilize recently introduced chemically specific but coarse-grained models of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) to explore the influence of monomer architecture on the dynamics of supported thin polymer films based on molecular dynamics simulations. In particular, we contrast differences in the molecular packing and mobility gradients in these materials near the substrate and “free” interface regions. As expected, relaxation is generally enhanced in the free surface region relative to the film interior (and bulk), and the degree of enhancement is similar for both PEO and PMMA. However, the dynamical changes near the substrate are more sensitive to monomer structure, and are enhanced with increasing polymer–substrate interaction strength, $\varepsilon$. PMMA is relatively stiff compared to PEO and has a side group of appreciable size, and we find that the dynamics of PMMA near the substrate are slowed significantly more in comparison to PEO for the same substrate. Substrate interactions lead to a notable difference of local fragility near the substrate that appears to arise from a higher cohesive interaction strength of the PMMA chains in this region. Our data also reveal the inadequacy of the these coarse-grained polymer models to reproduce the experimentally known differences in the fragility of these materials. However, this technical shortcoming is not expected to alter our qualitative conclusions regarding the comparative effect of substrate interactions on relatively flexible polymers such as PEO versus a relatively stiff polymer such as PMMA.

INTRODUCTION

It is generally appreciated that the molecular mobility of thin polymer films near interfaces can be significantly modified from the bulk.1–7 Both experimental and computational studies have sought to quantify the effect of the interfacial mobility gradient near the interfaces through estimates of the local glass transition temperature $T_g$ in the interfacial region,8–10 the film (shear) viscosity $\eta_s$,11,12 segmental relaxation time $\tau_s$,13–24 of the entire film, and average molecular diffusion coefficient in thin films.25–27 Theoretical studies28–33 have also shed light on the molecular origin of these changes in dynamics near interfaces. There is a general consensus that linear polymers near their “free” interfaces exhibit an enhanced mobility in the this interfacial region,12,16,34–39 while the molecular mobility near the substrate can be either enhanced or diminished, depending on the interaction between supporting substrate and polymer.34,40–44 The highly mobile layer at the polymer–air interface can be “liquid-like” in terms of mobility even when the temperature $T$ is below the $T_g$ of polymer film as a whole,44 while the mobility near a highly attractive substrate is normally diminished near the supporting substrate. As a result, the overall properties of the supported polymer film reflect the competition between the dynamics of the free and supporting substrate.40,46–48 On the other hand, since polymers can be built from a myriad of monomer types, sequences of different monomers, and topologies (e.g., linear, ring, star, or comb), we expect the resulting interfacial mobility to depend on the details of the specific polymer monomer structure and topology, as well as the structure, surface energy, and stiffness of the substrate.49–53 Recent molecular dynamics studies have shown that the glass-formation can be significantly altered in ring54 and star polymers,55 and there are ongoing measurements by many groups showing that polymer topology (rings, stars, bottlebrush polymers)56 greatly affects the $T_g$ of thin films, even changing the sign of $T_g$ deviation relative to their bulk values with confinement.

Motivated by these considerations and observations, we consider the role of monomer structure in altering the interfacial mobility gradients in glass-forming ultrathin polymer films. We examine the degree to which a monomer structure alters dynamics near interfaces (free interface or substrate). Understanding how monomer structure affects the structure and dynamics in thin films should enhance the tailoring of their use in particular applications. Furthermore, to efficiently design polymer materials for applications, a fundamental understanding of the structure–property relationships is required.

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From a technical prospective, the supporting substrate can alter the molecular packing and mobility near the substrate surface due to the variations of the interactions between different chemical groups in the polymer chain and the substrate. However, the precise influence of the boundary interaction on the interfacial dynamics when the monomer structure is also varied is not well-understood. On the other hand, there has been considerable progress investigating the effects of polymer chemical structure on the dynamics of bulk polymers. Studies on bulk polymers have shown that the stiffness of the backbone of a polymer chain, and the size, length, and stiffness of the side chain play important roles. For example, changing the relative rigidity of the side chains of polymers in comparison to the backbone is known to alter the fragility of glass-formation—a measure of the steepness of the temperature variation of relaxation time of the glass-forming material. In general, either a high backbone stiffness or high stiffness of the backbone relative to the side groups leads to an increase in $T_g$ and fragility, if the cohesive interaction is fixed. This general trend has been established by theoretical and experimental studies on bulk polymers by Dudowicz et al., Stukalin et al., and Kunal et al. Of course, polymer molecular mass and topology (ring, star, bottlebrush, and structures, etc.) are also important, as these molecular parameters can also alter molecular packing efficiency.

The extension of these relationships to thin polymer films and polymer nanocomposites where there are large gradients in mobility can exist is not obvious. Recently, Hsu et al. investigated the influence of confinement on supported films of two commonly studied polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS) molecules by molecular dynamics simulation. This is a particularly interesting comparison, as these polymers have similar fragilities and glass transition temperatures in the bulk, yet the glass transition temperature $T_g$ of these polymers is known to exhibit a different sensitivity to confinement. The simulations of Hsu et al. suggested that the difference in the finite size effects of these polymer films was due to the inherently different stiffnesses of the side groups of PMMA and PS—the PMMA side group having larger amplitude of fluctuations than that of PS.

The present work uses molecular dynamics simulations of coarse-grained poly(ethylene oxide) (PEO) and PMMA models developed in previous literatures to investigate the effect of monomer structure on the structure and dynamics of thin films near both free interface and substrate. The film–substrate interactions mimic those of a silicon substrate; we also consider a case where we artificially double the interaction strength with the substrate to compare the sensitivity of polymers with different monomer structure to the substrate interactions. In experiments, PEO and PMMA have rather different $T_g$ values and fragilities in the bulk, namely, PEO has a considerably lower $T_g$ and fragility than PMMA, and PEO is susceptible to crystallization. In the classification scheme of Dudowicz et al., PMMA corresponds to a polymer having a relative stiff backbone and flexible side groups (SF model), while PEO has relative flexible backbone and no side groups, which can be categorized into a class of polymers with flexible backbones and flexible side groups (FF model). The packing of the flexible polymers is, in most cases, relatively efficient compared to polymers with stiff backbone as noted before. By the same argument, the effect of the substrate interaction strength on $T_g$ and the dynamics of thin films of flexible polymers such as PEO could be weaker than in relatively stiff polymers (such as PMMA), and our simulations results are also consistent with experiment. We emphasize that the presence of boundaries changes packing locally and gives rise to gradients in mobility and associated gradients in fragility, so we need to be careful in applying trends found for bulk materials to the properties of thin films, especially in the case of highly attractive substrates where the mobility gradients can be expected to be large. We will see that the fragility changes near the substrate are influenced by substrate interaction strength and monomer structure, and they are not accounted for by correlations between packing and fragility in the bulk material, so that fragility trends in thin polymer films are more subtle than those in bulk materials. Moreover, this effect should be distinguished from the “confinement effect” describing the difference in the properties of thin film and its bulk counterpart. Specifically, previous experimental work and simulations have indicated a stronger confinement effects for polymers with more flexible backbone, when comparing free-standing thin films to the bulk material.

Based on these observations, we find that there is indeed a significant difference in the molecular packing of PMMA and PEO films. Despite the differences in the packing, and the distinct monomer structures of PEO and PMMA, we find that the overall average relaxation dynamics of both of these polymer films to be only weakly impacted when the polymer–substrate interactions are only moderately attractive. Given the experimentally known differences in fragility of PEO (relatively strong) and PMMA (relatively fragile), one may expect a larger difference in the dynamics on of these films confinement; however, the models used to simulate PEO and PMMA materials have nearly the same fragility in the bulk, an unfortunate shortcoming of the models that we did not anticipate. Although the quantitative comparison between PEO and PMMA then has limited value from the experimental standpoint of these particular materials, the comparison of the effect of side groups remains of interest in relation to how boundary interaction and monomer structure influence polymer properties near solid substrates. An examination of the dynamics in three different regions of the film (near the substrate, near the free interface, and in the interior) is instructive. As expected, the interior of the film dynamics is rather similar to the bulk material, while the free interface region has enhanced dynamics, and the substrate layer has greatly diminished dynamics relative to the film interior when the boundary interaction is highly attractive. Despite the difference in molecular architecture and chain rigidity, the dynamics near the free interface of both materials is rather similar, suggesting that the enhancement at the free surface is only weakly dependent on chain structure. On the other hand, the relaxation near the film–substrate is significantly slower for the PMMA film. This effect can be amplified by increasing the polymer–substrate interaction strength, which shows that the relaxation of PMMA near the substrate is much more strongly affected than that for PEO. In other words, the temperature dependence of relaxation near the solid substrate of the PMMA film is more sensitive to the substrate due to the molecular packing associated with its side group and relative chain rigidity. Our findings suggest that changes to dynamics near the free interface is relatively insensitive to monomer structure, while confinement by a strongly interacting substrate magnifies the polymer-specific properties in the substrate interfacial region. Of course, the study of further polymers will...
be necessary to confirm our present findings for other polymers.

Our work advances the understanding of monomer structure on the interfacial structure and dynamics of thin polymer films and should be useful in developing a general understanding of the design and engineering of thin polymer films with specific properties related to glass-formation, i.e., fragility, glass transition temperature, etc. and our work is also complementary to the contribution of Hsu et al.68

## MODELING AND SIMULATION

Our findings are based on molecular dynamics (MD) simulations using previously introduced coarse-grained models of atactic PMMA70 and PEO.69 The primary difference between these polymers is the presence of a single side group bead in PMMA, as illustrated in Figure 1; this figure also provides a “cartoon” image of the coarse-graining of the atomically described monomers. We choose to use this coarse-grained representation to allow us to more readily simulate the large time scales associated with the approach to the glass transition. The physically appropriateness of these models must be assessed after the results they produce and we discuss the limitations of these models in the Conclusions. PEO has a must be assessed after the results they produce and we discuss the computational definition of $T_g$ later in the manuscript. The persistence length, characterized by the bond orientation correlation functions, of PMMA is larger than that of PEO. Specifically, the persistence length is approximately 7.7 Å for PMMA and 5.4 Å for PEO in the bulk, and these values depend weakly on temperature. In other words, the model PMMA is substantially stiffer than PEO. We describe the quantification of the persistence length of our model polymers in the Supporting Information. The flexibility of PEO plays an important role in differences with PMMA.

For supported films, we use an explicit supporting substrate, rather than a smooth wall. We choose parameters for the substrate to mimic that of a (111) face of a FCC silicon lattice. Beads of the substrate are tethered by a spring force to the ideal locations of a (111) face with spring constant $k = 16.7$ kcal-mol⁻¹ Å⁻², keeping the particles near their equilibrium position. The initial values for interaction strengths between the polymer beads and the substrate are estimated from the components of the surface tension and the work of adhesion for a silicon substrate and polymer film.80–82 We provide a detailed description of these interfacial interaction strengths in the Supporting Information. The resulting interfacial interaction strength ratio $\varepsilon \equiv \epsilon_{ss}/\epsilon_{ps} \approx 1$, which corresponds to a neutral substrate since the substrate–polymer interaction is similar to the polymer–polymer interaction strength. To investigate the dependence of the structure and dynamics of the film on the substrate interaction strength, we also consider a strongly attractive substrate interaction strength $\varepsilon \equiv \epsilon_{ss}/\epsilon_{ps} \approx 2.0$, where we double the nonbonded interaction strength between each polymer and the substrate. Specifically, the Lennard-Jones interaction strength parameters between the polymer beads and the substrate particle $\epsilon_{ps}$ for both substrates are tabulated in Table 1. In the case of PMMA, we double the interaction strength between each type of bead and the substrate bead; the resulting substrate effect may differ if the backbone and side group interactions did not scale in direct proportion. We use the term “neutral” to describe the substrate.

### Table 1. Lennard-Jones Parameters for PMMA, PEO, and Substrates

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interaction strength for the case when the nonbonded substrate interaction strength is within 25% of the nonbonded interaction strength of backbones, and “strong” when the substrate interaction strengths are more than 25% greater. For the clarity of the paper, we refer to substrate parametrized by the experimental properties of silicon as the natural substrate, and the artificially enhanced attractive substrate as the enhanced interaction substrate. The strongly attractive interface corresponds to an atomically smooth interface having an adhesion energy about 100 mJ/m².⁵¹

Both bulk systems and supported ultrathin films are simulated for comparison purposes. Simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics package. For bulk systems, periodic boundary conditions are used in all directions. The system size is N = 6000 coarse-grained beads for PEO and N = 10000 beads for PMMA (5000 backbone beads and 5000 side group beads). Our bulk polymer is prepared by the following protocols: (1) Starting from a high temperature, we cool the bulk system at a rate of 10⁻⁴ K/fs using the NPT ensemble with $\langle P \rangle = 0$, and then heat at the same rate. (2) We take the configurations from the heating run at $T$ above the temperature where there is a kink in the potential energy (indicating that the system should be in equilibrium for this cooling/heating rate). We then simulate isothermally in the NPT ensemble with $\langle P \rangle = 0$ for 200 ns to determine the mean box size. (3) We adjust the box size to the mean value just determined and briefly equilibrate in the NVT ensemble for 1 ns to relax any effects from the small adjustment of box dimensions. We then collect configurations for 200 ns in the NVT ensemble for our data analysis. For films, periodic boundaries are employed for the directions parallel to the film interface. To obtain the initial configurations for isothermal data collection of our thin films supported by the natural substrate, we first perform cooling and reheating simulations of films using a cooling/heating rate of 10 K/ns. To obtain the initial configuration for the isothermal data collection simulations, we take a configuration from the heating run at the desired $T$ (above the rate-dependent $T_c$ defined from the kink in potential energy), and then perform a very short additional equilibration of this configuration for 1 ns prior to the data collection. For PMMA, the duration of data collection is 100 ns for $T \geq 410$ K, 200 ns for $T = 400$ K, 400 ns for $T = 390$ K, 1000 ns for $T = 380$ K, and 1400 ns for $T = 370$ K. For PEO, the duration of the data collection run is 200 ns for all $T$. For the substrate with the enhanced interaction strength, we use the configurations from the weaker attractive strength as initial configurations, which we then equilibrate for an additional 100 ns for PEO, and an additional 300 ns for PMMA (longer than PEO because, as we shall see, the substrate relaxation of PMMA is dramatically slowed). Following this preparation equilibration, we then conduct data collection for another 100 ns. We provide additional simulation details on the bulk polymers and thin films in the Supporting Information.

## RESULTS AND DISCUSSIONS

Before we contrast the dynamical behavior of these polymer films, it is a useful reference point for our discussion to characterize differences in the density profiles of these two films. The density profile is helpful to understand any differences that might be attributable to variations in the local density of these materials. Accordingly, we show the density profile $\rho(z)$ in Figure 2 as a function of the distance $z$ from the film–substrate. For the case of PMMA, we separate the contributions to $\rho(z)$ into the backbone and side group bead. The most notable difference between the films is that the peak in density near the substrate is considerably more pronounced for PEO ($\rho = 4.5$ g/cm³) than for PMMA (peak $\rho = 3.7$ g/cm³). Additionally, the primary peak for PMMA is split, with a weak prepeak that occurs at $z = 3.4$ Å and a larger main peak at $z = 7.5$ Å. Further inspection of $\rho(z)$ for PMMA shows that the first peak is associated with the side group beads, and the second is from the larger backbone beads. In the case of PEO, a stronger substrate interaction strength results in an increase of the density in the layer closest to the substrate in Figure 2b as expected. In contrast, for PMMA, increasing the substrate interaction leads to a small decrease in the magnitude of the first peak from the density profile and an increase in the second peak of the density profile in Figure 2a. This unexpected behavior is a result of the relative backbone/side group–substrate interaction strengths and the differential masses of backbone and side group beads. Specifically, for the strongly interacting substrate, the interaction strength between the side group bead of PMMA and substrate bead $\varepsilon_{\text{sub–sg}} = 2.77$ kcal/mol is significantly stronger than the polymer–polymer interaction ($\varepsilon_{\text{sg–sg}} = 1.5$ kcal/mol, $\varepsilon_{\text{bb–bb}} = 0.5$ kcal/mol), where sg stands for side group and bb stands for backbone. As a result, the side group adheres to the substrate better than the backbone beads. We observe this effect as the increase of side group density near the substrate for the enhanced substrate interaction strength as shown in Figure 2a. However, the effect on the total density profile is more nuanced. Since the side group is directly connected to the backbone bead within the same monomer, the backbone beads that connect to the side group near the substrate contribute to the significant increase of the backbone density around $z \approx 7$.
monomers move only a fraction of a diameter over the total number of monomers. We evaluate vector from the value, $1/N$, as the time when $F_{s}(q_{0}, t)$ reaches the fixed value, $1/e$ (i.e., $F_{s}(q_{0}, t) = 1/e$). Alternatively, $\tau$ can also be evaluated by fitting the scattering function to a stretched exponential, which results in nearly the same value. To extract the position dependence of $\tau$, we evaluate $F_{s}(q_{0}, t)$ conditioned on monomer position at the time origin ($t = 0$); since monomers move only a fraction of a diameter over the relaxation time, our data do not qualitatively differ if we condition the position based on the position at time $t = 0$ or $t = \tau$. Representative data for $F_{s}(q_{0}, t, z)$ are shown in Figure S5 in the Supporting Information. We also show the relaxation profile of backbone and side group separately in Figure S6 in the Supporting Information.

The role of interfacial dynamics becomes increasingly important to the overall dynamics of ultrathin films as film thickness decreases since a greater relative fraction of the material is in the interfacial region where the density and compressibility are altered from their bulk values. Thus, we first characterize the relaxation behavior of the film as a function of distance from the substrate $z$. For this purpose, we use the self-part of the dynamic density–density correlation function (also known as the incoherent intermediate scattering function),

$$F_{s}(q, t) = \frac{1}{N} \left( \sum_{i=1}^{N} \exp[iq \cdot (\boldsymbol{r}(t) - \boldsymbol{r}(0))] \right)^{2}$$

where $\boldsymbol{r}(t)$ is the position of the $i$th particle at time $t$ and $N$ is the total number of monomers. We evaluate $F_{s}(q_{0}, t)$ at wave vector $q_{0} = 1.48 \text{ Å}^{-1}$ for PMMA and $q_{0} = 1.5 \text{ Å}^{-1}$ for PEO, corresponding to the nearest neighbor periodicity retrieved from the first peak of $S(q)$ in Figure S3 in the Supporting Information. Following common practice, we define the relaxation time $\tau$ as the time when $F_{s}(q_{0}, t)$ reaches the fixed value, $1/e$ (i.e., $F_{s}(q_{0}, t) = 1/e$). Alternatively, $\tau$ can also be evaluated by fitting the scattering function to a stretched exponential, which results in nearly the same value. To extract the position dependence of $\tau$, we evaluate $F_{s}(q_{0}, t)$ conditioned on monomer position at the time origin ($t = 0$); since monomers move only a fraction of a diameter over the relaxation time, our data do not qualitatively differ if we condition the position based on the position at time $t = 0$ or $t = \tau$. Representative data for $F_{s}(q_{0}, t, z)$ are shown in Figure S5 in the Supporting Information. We also show the resulting layer-resolved relaxation time $\tau(z)$ in Figure 3. As observed in many prior studies, $\tau$ is smallest near the free surface, while $\tau$ is largest near the solid substrate; the middle region of the film has a nearly constant value for $\tau$, which nearly coincides with $\tau$ of the bulk material. Figure 3 also reveals some differences in the relaxation profile connected to the specific molecular structures of PEO and PMMA. In particular, $\tau(z)$ increases smoothly near the substrate for PEO, but this quantity saturates for the layers nearest the substrate in PMMA. Referring back to the density profile (Figure 2), we see that the side group beads are preferentially located near the substrate, and so this behavior reflects the fact that the dynamics of the side groups dominate the behavior at the substrate. The saturation of $\tau$ thus occurs because the side group beads relax more readily than those of the backbone, owing to their smaller size and mass. Indeed, the ratio of the backbone-to-side group relaxation time essentially follows the square-root of the mass ratio, as expected. That said, the PMMA relaxation time near the substrate ($z \lesssim 2.5 \text{ nm}$) is still considerably slower than that in the film middle. The relaxation at the “free” interface does not show any particular dependence on the polymer molecular structure. We note that the saturation of $\tau$ near the substrate persists even at high $T$ when there near substrate polymer readily equilibrates fully, and thus the qualitative trend is not a result of possible nonequilibrium effects. Figure 3 also shows how the relaxation time $\tau$ behaves for two representative strengths of the substrate interaction “neutral” and “strong” (enhanced) polymer–substrate attraction, a point that we will return to below.

The effects of the mobility gradient in the film can be more easily understood by grouping the relaxation profile into three regions: free surface layer (top 1 nm of the film), middle layer (≈ 3 nm), and substrate layer (bottom 1 nm of the film). Figure 4 shows the time dependence of $F_{s}(q_{0}, t)$ in each of these three regions. In the case of the enhanced substrate interaction strength, the formation of the slow-moving “bound” layer near the substrate gives rise to an additional relaxation process in $F_{s}(q_{0}, t)$ described in the literature. As a result, $F_{s}(q_{0}, t)$ can be well-described by the superposition of three distinct time scales—short-time vibrational relaxation, $\alpha$ relaxation, and slow “bound” relaxation. We show in the Supporting Information that the bound relaxation time from the three-scale $\tau_{0}$ to $F_{s}(q_{0}, t)$ corresponds to the relaxation time of the substrate layer, and the $\tau$ from the $1/e$ criterion defined above is nearly the same as the $\alpha$ relaxation. Thus, the $1/e$ criterion used on $F_{s}(q_{0}, t)$ for each film region is adequate to capture the relaxation time of a particular region. As anticipated from the relaxation profile, PEO and PMMA have a similar fast relaxation behavior at the free interface (red curves) and the substrate layer relaxes the slowest. We compare the relaxation of the film interior with the bulk material (black solid and
dashed lines, respectively), and we find that their relaxation behaviors over all time scales are nearly identical.

To assess how these local differences in dynamics impact the glass-forming behavior of these materials, we evaluate the temperature dependence of α relaxation time \( \tau(T) \) in each region of the films and how these behaviors are altered by the interaction strength with the substrate in Figure 5. We first consider the behavior in the free surface layers of the films. As expected, the relaxation time near the free surface layer is significantly faster than the interior, while the relaxation time of the film interior is nearly identical with that of the bulk material, both in the case of PEO and PMMA. Moreover, \( \tau(z) \) near the middle and free interface regions is not affected by the change of substrate—polymer interaction strength in either PMMA or PEO films. Of course, if the films were thinner (\( \leq 30 \) Å), the substrate interaction strength would likely have a greater influence on these free surface layers.\(^{40,50}\)

The similar changes in the free surface layers of PEO and PMMA are contrasted by differences in the sensitivity of relaxation to the substrate interaction. Both PMMA and PEO dynamics are slowed near the substrate, as shown by the relaxation profile of Figure 3. However, the response to the increasing substrate interaction is different for these two materials. Specifically, both Figures 3 and 5 show that the strongly attractive substrate affects PMMA dynamics more significantly than those of PEO. In particular, \( \tau \) grows much more rapidly on cooling in PMMA, so that for \( T \lesssim 550 \) K, the near substrate polymer relaxation time exceeds values that are accessible to our simulations in equilibrium. In other words, the near-substrate layer of PMMA exhibits a far greater sensitivity to the boundary interaction than PEO, and it is an effect that only becomes more pronounced on further cooling toward the glass transition. Because equilibrium simulation time scales are limited to \( T \) much higher than the experimental \( T_g \), the effect of the substrate region fragility on the overall fragility of the film is not substantial; the effect would be more pronounced near the experimental \( T_g \). This effect would also probably be more pronounced in experiments, since the fragility of real PMMA in the bulk is substantially larger than PEO.\(^{96–98}\) a difference that present models do not reproduce. In spite of this quantitative limitation of the PEO model, we can still observe the impact of differences in the side groups and backbone flexibility on film dynamics and structure near the substrate. At temperatures where the near-substrate layer relaxation time exceeds our data sampling duration, the free surface layer and the middle layer results are generally still reliable, because the relaxation time in these regions is almost completely decoupled from the very slow near-substrate layer. This behavior has been observed in previous simulations of bound polymer near the film—substrate or nanoparticle (NP) interface in polymer—NP composites.\(^{52,85}\)

Since PMMA has a much higher \( T_g \) than PEO in the bulk,\(^{46}\) it is helpful to compare these systems relative to their respective \( T_g \) and bulk relaxation times. Experimentally, \( T_g \) is frequently defined at the temperature at which the relaxation time reaches 100 s (or \( \tau(T_g) = 100 \) s) in experiments. Since this time scale is inaccessible computationally, we define a computational glass transition temperature by \( \tau(T_g) = 1 \) ns in the bulk material. Based on this \( T_g \) definition, the bulk materials have \( T_g = 270 \) K for PEO, and \( T_g = 389 \) K for PMMA, qualitatively consistent with the experimental \( T_g \) trends for these polymers. In the film supported by the natural substrate, both PEO and PMMA exhibit small reductions in overall film \( T_g \) of \( \approx 5 \) K for the film thickness (\( \approx 5 \) nm) investigated here. For the enhanced substrate interaction strength, the PEO film has a 9 K increase in \( T_g \), and the PMMA film has an 8 K increase in \( T_g \) compared to their
respectively. The magnitude of the reduction is smaller than observed in the experiments due to the fact that the cooling rate in our simulations is many orders of magnitude faster than that in experiments—an inherent constraint shared by computer simulations. Figure 6 shows

![Figure 6](image-url)

Figure 6. Normalized relaxation time of (a) PMMA and (b) PEO of the film as a whole (gray) and in the film regions for the natural interaction substrate: the air–polymer interfacial region (red), the interior (black), and the substrate interfacial region (blue). Symbols represent the substrate interfacial regions with the enhanced interaction strength. We only show curves for the substrate region in the case of the strong interaction substrate for the clarity of the figure since the interior and free surface regions have nearly identical relaxation time to that of the natural substrate.


dynamics. For example, experimental work by Vogt and co-workers reported a reduction of \( T_g \) for flexible polymers for thinner films, while the stiff polymer has little change of properties on confinement. Simulation work by Shavit and Riggleman\(^{74}\) and Simmons and co-workers\(^{75}\) found that the bulk fragility decreases for stiffer polymers, and free-standing films of stiffer polymer have a reduced confinement compared to that of flexible polymers. We also note that the interaction energy between these polymers and the enhanced substrate is approximately 2.3 times that with the natural substrate for both polymers (see details in the Supporting Information). The fact that both systems show the same increase of interaction energy suggests that this thermodynamic quantity alone is insufficient to understand the differences in the changes of dynamics.

### CONCLUSIONS

As anticipated from many earlier works, the relaxation of supported polymer films on solid substrates exhibit common trends, such as the slowing of relaxation near a solid supporting substrate with sufficiently large attractive interactions. That said, the intensities of these confinement effects, which normally have opposing contributions on the average relaxation time and the kinetic glass transition temperature \( T_g \) of the film as a whole, are system dependent.\(^{40}\) Work by Torkelson and co-workers\(^{89}\) has suggested that confinement effects on film dynamics depend strongly on the fragility of glass-formation, a result that is plausible from the interpretation of fragility variations observed in the bulk associated with variations of packing frustration with monomer structure under the constraint of fixed or slowly varying cohesive interaction strength.\(^{90}\) In particular, polymers exhibiting strong glass-formation are then naturally expected to have a weaker confinement effect than fragile glass-formers, since strong glass-formers tend to exhibit less packing frustration.\(^{62,64}\) Our original intent was to test this scenario by using polymers with significantly different fragilities. However, because the simulation model for PEO and PMMA unexpectedly had nearly identical fragility, we are limited to contrast the role the side group complexity plays. The anticipated relation between fragility and confinement effects, which might hold reasonably well for free-standing films, negates the fact that having a strongly interacting boundary means that the cohesive interaction strength can no longer be considered fixed in the film. This boundary interaction effect, which is not considered in the arguments of Torkelson and co-workers, appears to be crucial in our present study.

To contrast the difference in dynamics of these two materials, we compared their relaxation times, normalized by their respective glass transition temperatures and relaxation times in bulk. The dynamical property changes for the film as a whole are similar in both the PEO and PMMA films, despite their differing monomer architecture and the resulting differences in molecular packing near interfaces, in the case where the polymer–substrate interaction strength is nearly “neutral”, i.e., attractive polymer–substrate interactions compensate the repulsive hard core repulsions analogously to the \( \Theta \) solvent conditions of polymers solutions where polymer–polymer attractions compensate the hard-core polymer–polymer repulsions, indicates that simulated molecular architecture only has a modest effect on the relaxation of the polymer film. We further examine the dynamics in three different regions of the film—near the substrate, near the free interface, and in the interior—to determine the impact of the
interfacing on the overall film. For a weakly attractive substrate, the faster dynamics near the free interface are almost completely compensated by the slow-moving substrate region of the film in both materials, resulting in overall film dynamics that are similar to that of the film interior and thus the bulk material. This is another sense in which the boundary interaction can be considered to be nearly “neutral”. More importantly, the relaxation behavior of PMMA near the substrate is far more sensitive to substrate interactions. In particular, we find that the relaxation time of PMMA near the strongly attractive substrate has a more substantial increase than that of the PEO, this effect being so large that the substrate region is out-of-equilibrium on the computationally accessible time scales of our simulations. The large changes in the local dynamics (and associated changes in fragility) likely derive from alterations in the barriers for activated transport associated with changes in the molecular cohesive interaction strength in the interfacial region. Interestingly, the enhanced packing near the boundary that might be expected to reduce fragility based on recognized trends in the bulk material, but instead it has the opposite effect in the solid substrate region. These results indicate that we must be careful in extending trends in fragility with molecular structure in the bulk to thin films, and the same caution must extend to polymer nanocomposites where strong interactions can be expected to influence the intrinsic cohesive interaction strength of the fluid for reasons having nothing to do with cooperative dynamics in the material.

Both coarse-grained polymer models are parametrized by matching the local structure, and the conformational properties of the atomistic system are parametrized by matching with that of a coarse-grained model. While these models seem to reproduce the qualitative differences in the glass transitions of PEO and PMMA in the bulk to a reasonable approximation, the methodology these models employed is insufficient to capture the rather different fragilities of these materials. This unanticipated shortcoming of these previously established models limits our ability to show how a difference in the fragility of glass-formation influences their sensitivity to confinement. Given the similarity of the fragility of our model polymers, it is not surprising that many of our observations are rather similar to previous comparative simulations of polystyrene (PS) and PMMA, polymers known to have similar fragilities and \( T_g \) values in the bulk. Even so, these models do capture differences in fragility near the substrate that we expect are realistic. Our results also suggest that the similar fragility found for these polymers near the free interface is likely a robust result—indeed of the molecular modeling methodology or chemical structure of the polymer. It is evident that further work is required to capture the fragility of glass-formation more faithfully in coarse-grained molecular modeling of polymers. On the basis of our findings, we suggest that the modeling of polymer side groups as individual beads, or as polymers with no side groups, as in the case of PEO, is overly simplified to capture the appreciable change in fragility with changes in monomer structure seem in real polymer materials. In the future, we suggest using the generalized entropy theory (GET) to help guide the creation of model polymers as having a variable number of side groups whose relative stiffness compared to the chain backbone can be varied as in real polymers. Recent simulations based on this type of model indicate that increasing the stiffness of the polymer side group relative to the polymer backbone has the effect of reducing the polymer density in bulk, significantly increasing fragility and \( T_g \) in a proportional fashion, and increasing the shift of \( T_g \) with confinement. These observations are all consistent with the view that fragility changes (at fixed cohesive interaction strength) are derived from packing frustration changes. We find these simulations to be highly encouraging since this approach to coarse-grained modeling offers a strategy for improving the modeling of specific polymers within a computationally tractable framework. We plan to pursue these modeling improvements ourselves in the future, as well as giving greater attention to addressing model parameters through appropriate measurement information.

As a last remark, further work is required to understand the fundamental origin of the influence of monomer architecture on the dynamics of thin polymer films. One approach would be the systematic tuning of model parameters (such as the backbone and side group stiffness and chain length) in a way not possible in experiments. Since the PEO model that we use does not formally have side groups, it is difficult to quantify the competing effect between the side group/backbone stiffness. Polymers like polycarbonate (PC), a stiff polymer with a relatively flexible side group (SF polymer), would be interesting alternative to study, since PMMA and PC both have side groups, but different degrees of backbone-to-side group stiffness ratios, leading to different experimentally measured fragilities. By conducting more controlled simulations, one may uncover further details on the effect of molecular architecture on dynamical properties in thin films. There is also a need for better quantification of packing frustration in terms of metrics that are experimentally accessible, given the significance of this property for film dynamics. Xu et al. have suggested based on recent calculations based on the generalized entropy theory, that the thermal expansion coefficient and isothermal compressibility should provide useful practical metrics for quantifying packing frustration in measurement and simulation. For example, recent findings have indicated that packing frustration can be related to the thermal expansion coefficient or the isothermal compressibility in bulk materials, and we should seek useful analogs of these properties in thin films.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c01413.

Additional modeling and simulation details, pair correlation function, structure factor, persistence length, and dynamics of backbone and side group for PMMA (PDF)

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Notes
The authors declare no competing financial interest.

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