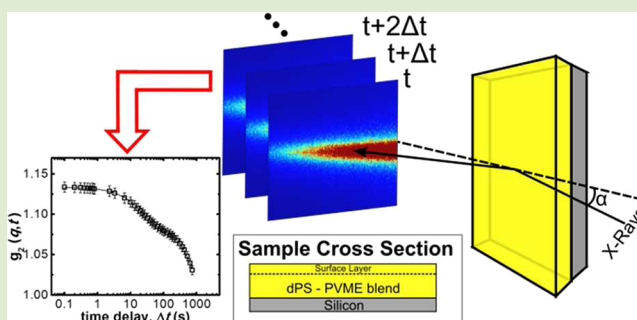


## Surface Layer Dynamics in Miscible Polymer Blends

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## Supporting Information

**ABSTRACT:** In thin film A/B polymer/polymer mixtures, the formation of a layer at the free surface, with average composition that differs from the bulk, due to the preferential segregation of the lower cohesive energy density component, is well understood. While much is also understood about this surface layer formation and growth to date, virtually nothing is known about the surface dynamics of the chains in such mixtures. Questions about the surface chain dynamics in relation to the bulk have remained unanswered. With the use of X-ray photon correlation spectroscopy (XPCS) we show that the dynamics of poly(vinyl methyl ether) (PVME) chains at the free surface of polystyrene (PS)/PVME thin film mixtures can be orders of magnitude larger than the PVME chains in the bulk. These dynamics manifest from differences between the local compositions of the blend at the free surface and the bulk, as well as film thickness constraints.



In A/B polymer/polymer mixtures, the free surface composition is, in the absence of unusual entropic effects, dominated by the lower cohesive energy density component; this contributes to decreasing the overall free energy of the system.<sup>1,2</sup> Much is understood about the phase behavior of these systems, including phenomena such as surface directed spinodal decomposition, dating back nearly 20 years.<sup>3–7</sup> The preferential interfacial segregation by one component can change the shape of the coexistence curve; thus, the phase and wetting transition temperatures also become dependent on film thickness. Near the phase boundary a wetting transition would occur, wherein the wetting layer becomes very large.<sup>8–10</sup> In this paper we are particularly interested in the surface dynamics of compatible A/B polymer/polymer mixtures at temperatures far from the phase boundaries. Indeed, apart from open scientific questions related to dynamic phenomena at surfaces, this topic is of particular interest because most polymeric systems of practical interest are mixtures. The design of smart coatings and surfaces, used for different practical applications, from medicine and biology to microelectronics and sensors, would benefit from further insight into the structure and dynamics at interfaces.

There are quantitative differences between the chain dynamics at free surfaces and the bulk. For single component, linear chain, homopolymer systems, the glass transition temperature,  $T_g$ <sup>11–14</sup> at the free surface is lower than the bulk; the surface dynamics<sup>15–17</sup> are fast compared to the bulk. Moreover, the effective chain entanglements, in highly entangled melts, are lower at the free surface, further contributing to enhancements of the free surface translational dynamics. A long chain in a highly entangled polymer melt

undergoes slithering motions within the confines of a virtual tube, defined by its intersections with neighboring chains.<sup>18–20</sup> The longest relaxation time,  $\tau_{\text{Rep}}$ , of the dynamics of a polymer chain of degree of polymerization  $N$  in this highly entangled melt is dictated by a molecular friction factor,  $\zeta$ , manifesting the “drag” that the chain experiences due to local inter- and intramolecular interactions:  $\tau_{\text{Rep}} \propto (\zeta/T)N_e^{-2}N^3$ ;  $N_e$  is the average degree of polymerization between entanglements and  $T$  is the absolute temperature.<sup>18</sup> When the chains are short and unentangled, the relaxation time of a chain is  $\tau_{\text{Ro}} \propto \zeta N/T$ .

In the A/B polymer/polymer mixtures, virtually nothing is understood about the dynamics of chains at the free surface in relation to the bulk. This kind of information may uniquely be extracted from X-ray photon correlation spectroscopy (XPCS) measurements. Herein, XPCS is used to examine the surface dynamics of a miscible blend of deuterated polystyrene (dPS) and poly(vinyl methyl ether) (PVME). The dynamics of capillary waves are probed at the free surface of PS/PVME blends of varying thickness. These dynamics manifest the behavior of PVME chains in different environments in the mixture. We show that the PVME chains exist in in two local environments of distinct composition: a rapid process associated with a PVME-rich environment at the free surface, and a second slower dynamic process, 2 orders of magnitude slower, associated with the other population of PVME in the bulk, composed of a higher PS composition. The dynamics of

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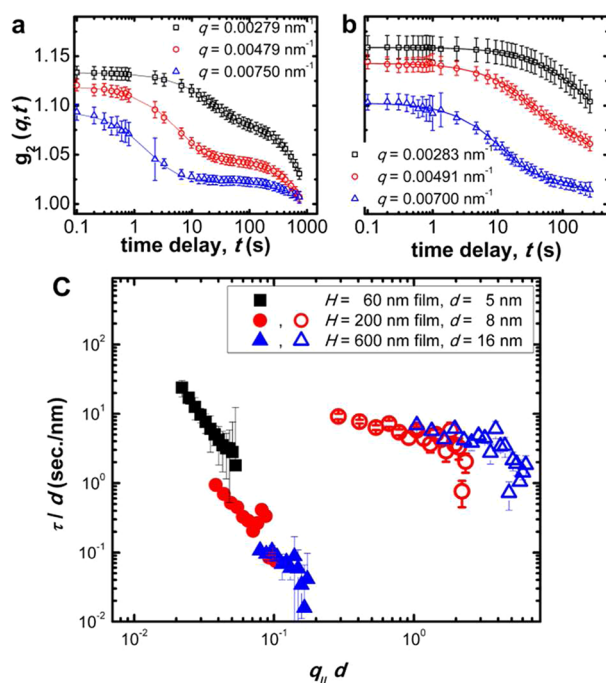
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these chains in the bulk and at the free surface manifest from the influence of film thickness constraints.

In this study we investigated blends of dPS,  $M_n = 10900$  g/mol ( $M_w/M_n = 1.05$ ) and PVME,  $M_n = 24400$  g/mol ( $M_w/M_n = 1.08$ ) purchased from Polymer Source, Inc. Thin films of thickness,  $H$ , ranging from 30 to 600 nm of the polymer blends (75% dPS, 25% PVME) were prepared by spin-coating from a toluene solution onto precleaned silicon substrates with a native oxide layer of approximately 1.5 nm. Further details describing sample preparation and experimental techniques are described in the Supporting Information.

The free surface dynamics of supported polymer films were investigated using XPCS through monitoring the scattering of X-rays from surface capillary waves. The XPCS experiments were performed at beamline 8-ID-I at the Advanced Photon Source (APS) at Argonne National Lab. Details of the XPCS experiment are described elsewhere.<sup>21</sup> The XPCS measurements of the dynamics of the dPS/PVME polymer blends reveal the existence of two distinct relaxations. Plotted in Figure



**Figure 1.** Measured autocorrelation function,  $g_2(q,t)$ , of dPS/PVME film at three different  $q$  vectors at  $T = 90$  °C for (a) 200 and (b) 60 nm films. Solid lines are the fittings to the KWW equation, assuming that two relaxations ( $\tau_1$  and  $\tau_2$ ) exist (eq 2 in the main text). (c) Relaxation time/surface segregated layer thickness as a function of  $q$ -vector  $\times$  surface segregated layer thickness at the free surface of dPS/PVME blend films for  $\tau_1$  (closed symbols) and  $\tau_2$  (open symbols) for various film thicknesses.

1A, for various  $q$ -vectors, are the intensity autocorrelation functions,  $g_2(q,t)$ :

$$g_2(q, t) = 1 + A |f(q, t)|^2 \quad (1)$$

for two temperatures, 80 and 90 °C.<sup>22</sup> In this equation  $A$  represents the speckle contrast; the intermediate scattering function is

$$f(q, t) = r \exp[-(t/\tau_1)] + (1 - r) \exp[-(t/\tau_2)] \quad (2)$$

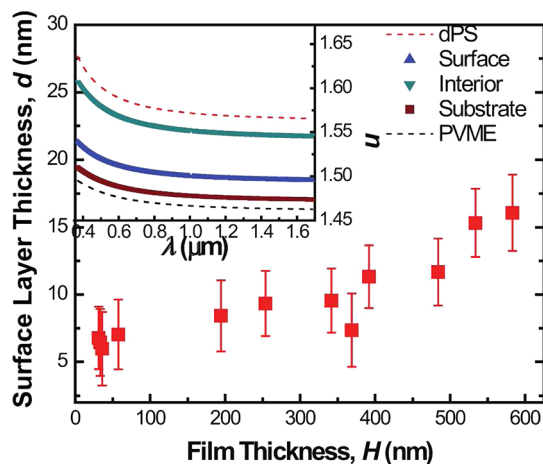
where  $r$  is the fraction of exponential decay from the shorter relaxation, and  $\tau_1$  and  $\tau_2$  are the shorter and longer relaxation times, respectively. The data in Figure 1A reveal that  $\tau_1$  is approximately 2 orders of magnitude shorter than  $\tau_2$ . Note that in single component homopolymer films, only a single dominant relaxation is observed, reflecting the dynamics of a single component.<sup>21,23</sup> If the two modes were at similar time scales, only one stretched exponential would have been observed. Therefore, the two relaxations reflect that the capillary waves at the free surface represent temperature fluctuations of two very distinct modes.

We propose that the two relaxation processes revealed by the data in Figure 1A represent the dynamics of two separate populations of chains, one undergoing translational motion in one environment and the other exhibiting ballistic, and caged, behavior of chains in a different environment. This is further demonstrated in Figure 1C where the relaxation time as a function of  $q$ -vector dependence also shows a 2 orders of magnitude increase for the second relaxation. In this plot, the relaxation time is shown as the ratio of  $\tau/d$  versus the product of  $q_{\parallel} d$ , where  $d$  is the thickness of the film. When calculating the viscosity of the free surface,  $d$  is the thickness of the surface layer (with composition different from the bulk). It has previously been demonstrated by hydrodynamic theory<sup>21,24</sup> that the ratio of  $\tau/d$  is proportional to the viscosity,  $\eta$ , over the surface tension,  $\gamma$ , as shown in eq 3:

$$\tau = \frac{2\eta(\cosh^2(q_{\parallel}d) + q_{\parallel}^2 d^2)}{\gamma q_{\parallel}(\sinh(q_{\parallel}d)\cosh(q_{\parallel}d) - q_{\parallel}d)} \quad (3)$$

The information in Figure 1 reveals the existence of two apparent relaxations, suggestive of polymer chains undergoing dynamics in two different environments. It is important to note that the PVME and PS chains are miscible at the temperatures where the experiments were conducted. For the materials used in our experiments, the lower critical solution temperature (LCST) is above 200 °C;<sup>25,26</sup> much higher than the experimental temperatures, 90 and 100 °C. Further the  $T_g$  of PVME is  $-35$  °C and that of the PS component is 91 °C measured by Differential Scanning Calorimetry (DSC). PVME possesses a much lower surface energy than PS, 22 and 32 mN/m, respectively (at 150 °C), and is well documented to reside at the free surface at concentrations in excess of its bulk.<sup>27,28</sup> Tentatively, we propose that the faster relaxation, representing a center of mass diffusive motion of the polymer chains, would be associated with the faster PVME chains in a PVME-rich environment at the free surface. The second, slower relaxation would be associated with the dynamics of bulk PVME chains in an environment containing a higher local concentration of PS and associated with a higher local  $T_g$ .

We now examine the conjecture regarding the PVME composition in the free surface region, using spectroscopic ellipsometry.<sup>29</sup> We begin with the simplest model, a three-layer model, which assumes the existence of a thin layer mixture at the free surface and at the substrate; these layers are reasonably assumed to be PVME rich in comparison to the bulk.<sup>30</sup> The optical constants of the materials were determined from ellipsometric analyses of pure 200 nm thick PS and PVME layers; these constants are distinct. The refractive indices of the pure polymers, as well as those measured for the three layers, are plotted in the inset of Figure 2 for a 200 nm blend film for different wavelengths. In the blended films, both the composition and thicknesses of the layers were modeled and



**Figure 2.** Thickness of the free surface segregated layer was measured by ellipsometry as a function of total film thickness. (Inset) The refractive index is shown as a function of wavelength for the three layers in a 200 nm film; free surface layer (blue triangles), interior (cyan inverted triangles), and substrate layers (maroon squares). The dashed lines represent the refractive index of the pure PS (red) and PVME (black) components.

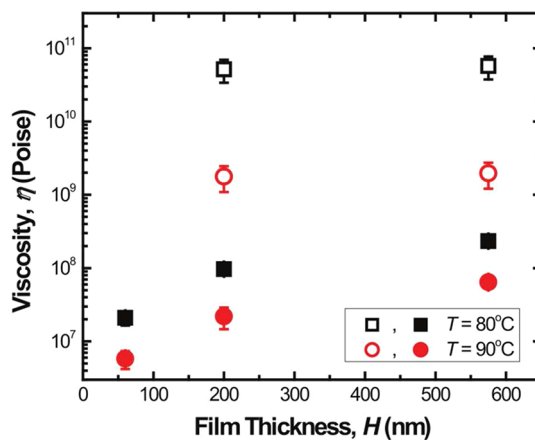
are shown in Figure 2. For thick films (films thicker than 200 nm) the composition of the free surface layer was found to be approximately 70% PVME, while the bulk is  $\sim 25\%$ ; the margin of error is approximately  $\pm 15\%$ . Such a concentration is consistent with previous studies using techniques such as X-ray photoelectron spectroscopy (XPS)<sup>27,28</sup> and variable angle spectroscopic ellipsometry (VASE).<sup>29</sup> The thickness of the surface segregated layer is found to increase as a function of total film thickness until thicknesses greater than 600 nm. This suggests that the surface segregated layer composition remains constant and increases in thickness with increasing total film thickness. Our data are consistent with those reported in the literature, the compositions at the free surface,<sup>28</sup> and the thickness dependence.<sup>31</sup>

The information provided by our ellipsometric measurements is consistent with our conjecture that the two relaxations are associated with the dynamics of PVME chains in two different environments. The first is associated with center of mass dynamics in a highly enriched PVME environment near the free surface of the film. On the other hand, the slower, caged dynamics is consistent with the behavior of the latter population of chains in a higher PS concentration with a higher local  $T_g$ . Because, the measurement temperatures are close to average  $T_g$  of this region,  $T < 1.2T_g$  ( $T_g = 41^\circ\text{C}$ ), the dynamics follow that of caged motion.<sup>32,33</sup> While at the free surface, the dynamics of the PVME chains in the nearly pure environment are expected to follow center of mass, translational diffusion, which is observed.

These observations are now discussed within the context of bulk dynamics of polymer/polymer mixtures. In a compatible A/B mixture, the A and B chains experience different average local compositional environments, which have important consequences on their dynamics. Specifically, the monomer–monomer mixing of the dissimilar A/B segments is not random due to the connectivity between monomers that constitute each chain.<sup>20,34</sup> Hence, the local environment of a monomer is characterized by a self-concentration that is different from the average macroscopic concentration of the bulk; the length scale is on the order of the Kuhn step length, at least close to the

glass transition.<sup>19,35</sup> Natural consequences of the chain connectivity and local concentration fluctuations include the fact that the dynamics of each component of blend exhibits different temperature dependences. Moreover, they each experience a different, and distinct, local glass transition  $T_g^{\text{eff}}$ . In fact, the relaxation rates of the chains in the mixtures are slower than in the pure components at the same temperature. Consequently, the relaxation rates of the individual components are significantly different, particularly when there is a significant difference in the  $T_g$ s of the pure components. In short, the effective friction factors,  $\zeta_{\text{eff}}$ , manifest, in part a unique local compositional environment, coupled with its own intramolecular contributions are distinct.

Using hydrodynamic theory (described by eq 3) and the thickness of each of the polymer layers, one can calculate the viscosity of each of the layers assuming that the faster relaxation is associated with the surface segregated layer and the latter with the polystyrene rich, interior film. In addition, the viscosities extracted from the data are plotted in Figure 3.



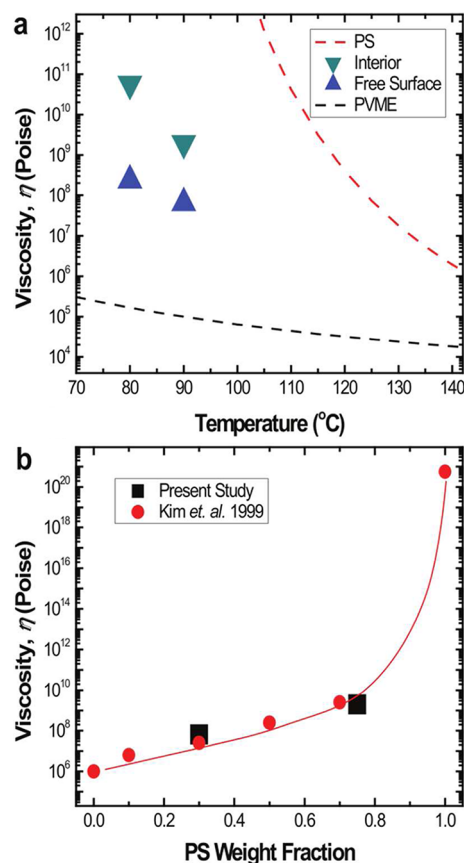
**Figure 3.** Viscosity changes as a function of total film thickness. The viscosities were measured at 80 (squares) and 90 °C (circles). The viscosity calculated from relaxation 1 is shown as the closed symbols and relaxation 2 is shown as the open symbols.

First we will discuss the thickness dependence of the viscosity calculated from the second relaxation. The viscosity could only be calculated for the thicker films, because when the film was 60 nm thick, the relaxation time is longer than could be measured using XPCS. However, the autocorrelation functions do not exhibit plateaus at values of unity, indicating there is another slower relaxation. Such a relaxation is shown in Figure 1B. This relaxation is consistent with the results of others who have reported that in pure homopolymer systems (such as polystyrene thin films) the viscosities measured from capillary waves at the free surface using XPCS are independent of film thickness and are comparable in magnitude to the zero-shear viscosities measured using rheology.<sup>21,23</sup> Interestingly, there is significant thickness dependence of the viscosity of the surface segregated layer. For this analysis, the thickness of the film was taken to be the thickness of the surface segregated layer measured by ellipsometry. Note further that if the thickness of the entire film were to be used, there would still be a thickness-dependent viscosity.

The viscosity of the surface segregated layer decreases by almost an order of magnitude between film thicknesses of 600 and 60 nm. When the mixture is 60 nm thick, the surface segregated layer is on the order of  $R_g$  of the PVME molecules

( $R_g^{\text{PVME}} \approx 5.7 \text{ nm}$ ).<sup>36</sup> Therefore, when thickness of the surface segregated layer is comparable to the size of the polymer chain, the number of inter chain entanglements is reduced; the local friction coefficient experienced by the PVME chains is also expected to be reduced. It has also been previously demonstrated that in bilayers of polymers, the dynamics of the top layer are significantly influenced by the modulus of the bottom layer.<sup>37</sup> Therefore, when the film is thin, the interfacial segregation of PVME to the oxide substrate will influence the elastic properties of the bulk layer and therefore influence the viscosity measured at the free surface.

To understand how the viscosity of these layers compare to those measured for the bulk, the data in Figure 4 should be



**Figure 4.** (a) Viscosity as a function of temperature calculated from relaxation 1 (free surface) and relaxation 2 (interior). The temperature dependence of the viscosity for each of the pure components are reproduced from refs 38 and 39. (b) Viscosity as a function of composition for the free surface (30% PS) and interior (75% PS) as it compares to bulk viscosity values reproduced from refs 38 and 39. The size of the symbols is the same as that of the margin of error.

considered. The viscosities of the 600 nm film at the free surface (1st relaxation), for the interior (2nd relaxation), and the zero-shear viscosities of the pure PVME and PS measured by rheology are plotted.<sup>38,39</sup> It is clear that all of the measured viscosities fall between that of the pure components, demonstrating that neither the free surface or interior of the film is composed of a pure component. It is noteworthy, however, that the viscosity measured for the free surface, using XPCS, is consistent with what one would suspect from a 70% PVME material. Moreover, the viscosity we extracted for

interior is approximately what one would expect from a blend with 25% PVME; these data are plotted in Figure 4b.

With the use of XPCS, we studied the PVME chain dynamics at the surfaces of miscible thin film blends of PS and PVME of various film thicknesses. The intensity autocorrelation functions provided evidence of dynamics of PVME from two separate environments: (1) rapid center of mass dynamics of PVME chains in an environment rich in PVME at the free surface; (2) PVME chains exhibiting caged, ballistic, dynamics in an environment with a higher PS concentration and higher local  $T_g$  in the interior of the film. The latter dynamics were approximately 2 orders of magnitude slower. The viscosities extracted from the XPCS data for the two different environments are consistent with bulk viscosity values of samples of the same compositions when the film is thick. When the surface layer is on the order of  $R_g$  of the polymer chains the viscosity is depressed. These results reveal for the first time that insights into the surface viscosities of liquid/liquid mixtures strongly manifest the local composition of the mixture.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Further details of experimental procedures and additional experimental results are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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