Surface Dynamics of Miscible Polymer Blend Nanocomposites

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ABSTRACT
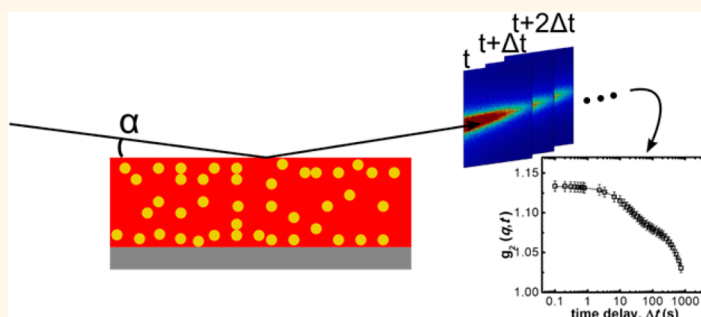
Diverse processes that include energy conversion, wettability, lubrication, adhesion, and surface-directed phase separation in mixtures fundamentally depend on the structure and dynamics of materials' surfaces and interfaces. We report an unusual phenomenon wherein the surface viscosity of polymer nanocomposites of polystyrene (PS), polyvinyl methyl ether (PVME), and PS-coated gold nanoparticles (PS/PVME/PS-Au) is over an order of magnitude smaller than that of the neat miscible PS/PVME blend. Our X-ray photon correlation spectroscopy studies of the surface dynamics also reveal that the polymer chains manifest dynamics associated with two separate average compositional environments: a PVME-rich region, significantly in excess of its bulk concentration, and a separate PS-rich environment, where the dynamics are approximately 2 orders of magnitude slower. The unusually rapid surface dynamics in the PS/PVME/PS-Au nanocomposite are due largely to the excess PVME chains and the polymer/brush-coated nanoparticle interactions at the free surface.

KEYWORDS: surface dynamics · nanocomposites · blends · XPCS · viscosity

The design and function of polymer surfaces have significant scientific and practical implications in diverse areas, from medicine and biology to microelectronics energy conversion and storage. Fundamental questions regarding connections between the structure and dynamics of macromolecules at interfaces are of interest to various interdisciplinary research communities. The local structure, organization of segments, of polymeric molecules in the vicinity of an interface, free surface, or otherwise differs from the bulk, due largely to local competing entropic and enthalpic interactions. The consequences of such interactions can be significant, as they are often responsible for changes in average physical materials properties such as glass transition temperatures,[1,2] adhesion,[3] and various transport properties, from segmental dynamics[4] to electronic carrier transport,[5] measured by different techniques. Polymer nanocomposites (PNCs) represent an important class of materials in which polymer/nanoparticle interfacial interactions play an important role toward dictating the overall phase behavior and physical properties.[6,7] In PNCs, the properties of the polymer host are modified appreciably with the addition of small quantities, even less than a few percent, of nanoparticles (*e.g.*, quantum dots, fullerenes, metallic nanoparticles, *etc.*). Based on the functionality of the nanoparticle and that of the polymer, diverse physical properties may be achieved.

The dynamics of polymer chains in bulk PNCs have been investigated by a number of authors, and a reasonable understanding

exists. For example, it has been shown that the addition of polystyrene (PS) nanoparticles to a PS host has the effect of reducing the viscosity of the polymer by approximately a factor of 2.[8] On the other hand, the addition of silica and other inorganic nanoparticles to polymers has the effect of increasing the viscosity of melts and enhancing the mechanical properties of the material in the solid state.[7] The addition of fullerenes, C_{60}, to polymethyl methacrylate (PMMA) has been shown, through a series of rheological measurements, to increase the longest relaxation time or, equivalently, the viscosity of the PMMA chains.[9] Quasi-elastic neutron scattering (QENS) studies revealed that the effect of the C_{60} nanoparticles on the dynamics occurred on a local scale; at short nanosecond time scales, an increase of the local friction factor of the chain was due to intermittent attractive polymer segment/nanoparticle interactions.[10] Hence the longest relaxation time of the polymer, τ_R, and therefore the viscosity increased. More recently, we demonstrated that the PS chain relaxations could be influenced significantly with the addition of polystyrene brush-coated nanoparticles to PS polymer hosts.[11] Control of the volume fraction of NPs, the brush length of the grafted PS chains relative to the host chain length, enabled the relaxation times to increase, or decrease, by up to an order of magnitude.

Miscible A/B polymer/polymer blends are compositionally heterogeneous due to effects associated with self-concentrations, due to monomer connectivity and to thermally induced composition fluctuations. The A- and B-type chains each experience a different local composition. Moreover, they each experience a distinct local T_g and temperature-dependent dynamics that are similar to their pure components, as revealed by broad-band dielectric spectroscopy[12,13] and molecular tracer diffusion measurements.[14] While these techniques provide information about the dynamics of individual components, techniques such as rheology[14,15] and X-ray photon correlation spectroscopy (XPCS)[16] provide information about relaxations that enable determination of the viscosity of blends.

Of particular interest in the paper is the manner in which nanoparticles influence the surface dynamics, or surface viscosity, of a polymer nanocomposite composed of a miscible polymer/polymer blend and brush-coated nanoparticles. By way of context, we note that in miscible A/B polymer/polymer systems the free surface composition is generally dominated by the lower cohesive energy density component, in comparison to its bulk concentration; this reduces the overall free energy of the system.[17,18] While, notably, much is understood about surface-directed spinodal decomposition and wetting transitions in miscible blends, dating back nearly 20 years, only very recently were reliable and direct measurements of the free surface dynamics of polymer mixtures achieved.[16] X-ray photon correlation spectroscopy was used to show that, in a

miscible blend of PS and poly(vinyl methyl ether) (PVME),[16] the surface relaxations of the blends were characterized by two separate time scales: a rapid process associated with a PVME-rich environment, and a second dynamic process, 2 orders of magnitude slower, associated with polymer chains in a local compositional environment appreciably richer in PS. In this paper, we report the effect of PS-brush-coated gold nanoparticles on the surface dynamics of the PVME chains in a PS/PVME/PS-Au nanocomposite measured by XPCS. Our primary finding is that, in the nanocomposite, the dynamics are shown, remarkably, to be nearly an order magnitude faster than those of the neat PS/PVME blend, suggesting that the surface properties of the nanocomposite remain significantly more fluid than the neat blend. The dynamics of the surface are otherwise similar to those in the neat blend; the polymer chain relaxations manifest the influence of two significantly different average compositional environments.

RESULTS AND DISCUSSION

In this study, we investigated the surface dynamics of supported thin films consisting of a miscible blend of 75% deuterated PS (dPS) and 25% PVME containing 4 wt % Au nanoparticles (NPs) of different sizes (2 and 5 nm diameter). The XPCS measurements of the dynamics of the dPS/PVME/brush-coated gold NP polymer nanocomposites reveal the existence of two distinct relaxations. Details of the XPCS experiment are described elsewhere as well as in the Experimental Section.[19] Plotted in Figure 1a, for various q-vectors, are the intermediate scattering functions, $f(q,t)$, determined from the intensity autocorrelation functions, $g_2(q,t)$:

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

for experiments performed at 90 °C.[20] In this equation, A represents the speckle contrast, and the intermediate scattering function is

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

where r is the fraction of the contribution to the exponential decay from the shorter relaxation, and τ_1 and τ_2 are the shorter and longer relaxation times, respectively.

As discussed in our previous publication, these two relaxation processes represent the dynamics of chains undergoing translational motion in one environment with a high PVME concentration and the other exhibiting significantly slower chain relaxations in a different environment, with a higher PS concentration. This point is further illustrated in Figure 1b where the relaxation time is plotted as a function of q-vector; a 2 order of magnitude difference between the two relaxation processes is evident.

Because the scattering signal of polymer thin films from XPCS measurements conducted below the critical angle of external reflection are dominated by the relaxation modes of thermally induced surface capillary waves, the viscosity of the surface layer may be extracted based
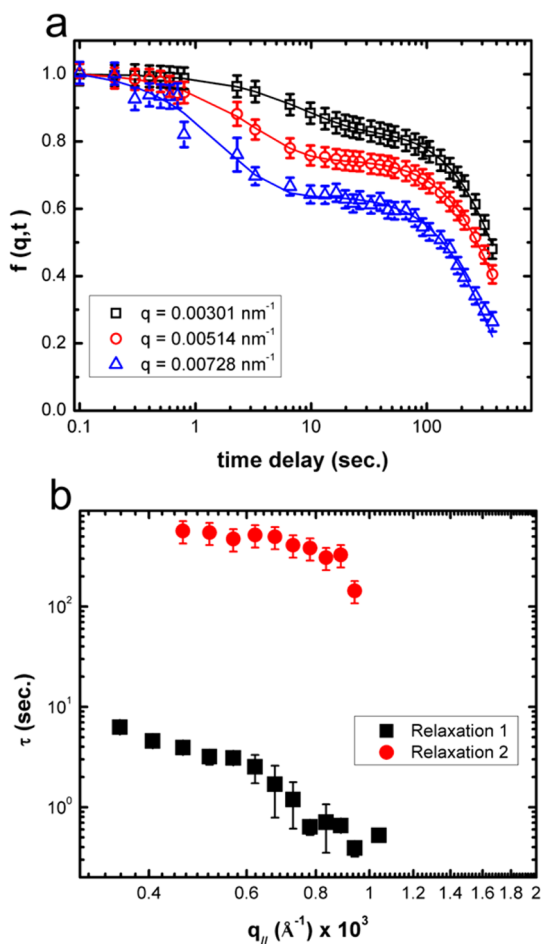
Figure 1. (a) Measured intermediate scattering function f(q,t) of dPS11k/PVME with 4 wt % 2 nm Au NPs for three different q-vectors at T = 90 °C. Solid lines are the fittings to a simple exponential, assuming that two relaxations (τ_1 and τ_2) exist (eq 2 in the main text). (b) Relaxation time (τ) as a function of q-vector ($q_{//}$) at T = 90 °C. The black squares represent the relaxation time of the faster relaxation and the red circles the slower relaxation.

on the following. According to hydrodynamic theory, the ratio τ/d is proportional to η/γ, where η is the viscosity γ is the surface tension, such that

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

This equation has been successfully applied to homopolymer films, from which the viscosity was extracted.[19] Under these conditions, the relaxations throughout the film are manifested in the relaxation spectrum measured using XPCS in the off-specular mode. Hence the viscosity measured using this technique is indicative of a viscosity of the entire film of thickness, d, as opposed to a surface viscosity. We employ this analysis for the PS/PVME blend system. However, in our case, the effective film thickness, d, is the thickness of the surface interfacial layer.[16] In the neat blend, this layer possesses an average composition that is rich in PVME, 70%, compared to the bulk, which is 25%, as discussed previously. Due to the high PVME

concentration in this layer, the surface viscosity is orders of magnitude smaller than that of the remainder of the film. Hence one may consider the surface layer to relax in a manner, with nonslip boundary conditions,[21] independent of the remainder of the film. In other words, we use the approximation that the relaxation spectrum is representative of the surface layer dynamics, not that of the remainder of the film.

The composition of the free surface region of a thin film nanocomposite blend is readily examined using variable-angle spectroscopic ellipsometry (VASE). Moreover, the thickness of the wetting layer, d, may be extracted. We determined that $d = 7.0 \pm 1.0$ nm in the nanocomposite containing the 2 nm Au nanoparticles and $d = 8.1 \pm 1.0$ nm in the other nanocomposite containing the 5 nm Au nanoparticles. We also learned that the effective concentration of PVME in the wetting layer was 80 ± 15 vol % in both nanocomposites, compared to 70 ± 15 vol % in the neat blend. These results are consistent with dynamic secondary ion mass spectroscopy (dSIMS) measurements, as discussed later.

The data shown in Figure 2, plotted as the ratio of τ/d versus $q_{//}d$, clearly illustrate that η/γ is proportional to τ/d.[19,22] These XPCS measurements were off-specular measurements, conducted below the critical angle ($\theta_c \approx 0.16°$) for the neat dPS11k/PVME blends (squares) at a temperature of T = 80 °C. The faster relaxations represent the center of mass diffusive motions of the PVME chains in a PVME-rich 70% environment at the free surface, compared to 25% in the bulk, as has been previously discussed.[16] The second, slower relaxation is of course associated with the dynamics of PVME chains in an environment containing a higher local concentration of PS and associated with a higher local T_g.

The important observation is that the relaxation times of the polymer chains at the free surface in the nanocomposite are appreciably more rapid than those in the pure polymer/polymer blend, as shown in Figure 2. The second relaxations in the nanocomposites are also more rapid than those of the polymer/polymer blend. The enhanced dynamics would be consistent with the apparently enhanced fraction of PVME at the free surface in the PNC, compared with the neat blend. It is important to note moreover that there is a particle size dependence on the dynamics at the free surface, which will be discussed later.

The data in Figure 3a,b reveal that the viscosities extracted from the XPCS data are independent of film thickness. This is not unexpected because the surface layer thickness is comparable in these films. Additionally, the surface region relaxes, approximately, independently of the remainder of the film because of the significant differences between the PVME composition at the free surface and in the bulk.

The viscosities extracted from these data are plotted in Figure 4. Notably, the viscosity of the neat blend is approximately equal to the zero-shear viscosity measured by rheology, as has previously been demonstrated.[16]
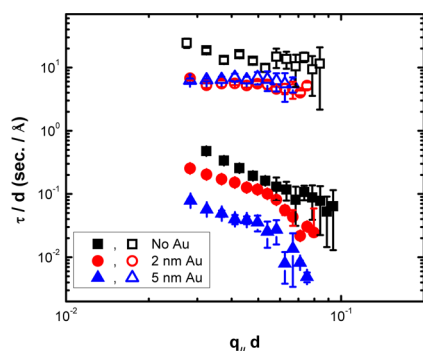
Figure 2. Relaxation time normalized by the surface layer thickness d, τ/d, is plotted as a function of $q_{||}d$ for measurements of the PNC blends at $T = 80$ °C. The closed symbols represent the first relaxation, and the open symbols represent the second relaxation process.

Similar observations have been documented for homopolymers, where the viscosity extracted from the XPCS data is equal to the zero-shear viscosity measured using rheology.[19,23] This follows from the fact that the surface relaxation spectrum manifests the influence of the relaxations throughout the entire homopolymer film for homopolymer films that are not too thin.[19]

It is clear from the foregoing that the viscosities for the nanocomposite systems are more than an order of magnitude smaller than those of the neat blend. Moreover, the viscosities of the PNC containing the 5 nm particles are a factor of 5 smaller than those containing the 2 nm particles. To understand these results, it is important to understand the following about the dynamics of miscible polymer blends. 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, monomer−monomer mixing of the dissimilar A/B segments is not random, due to the connectivity between monomers that constitute each chain.[24,25] 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.[26,27] So spatially the local composition will vary from φ_{self} to an effective composition φ_{eff}, due to the effect of the self-concentration and of concentration fluctuations. Natural consequences of the chain connectivity and local concentration fluctuations are that the A- and B-type chains experience different, and distinct, local compositions and a distinct local glass transition temperatures T_g^{eff}. Consequently, the relaxation rates of the individual components are significantly different, particularly when there is a significant difference in the T_g values of the pure components. The longest relaxation time, τ_L, of the dynamics of a polymer chain in a melt is dictated by a molecular friction factor, ζ, manifesting the "frictional drag" that the chain experiences due to local inter- and intramolecular interactions. In other
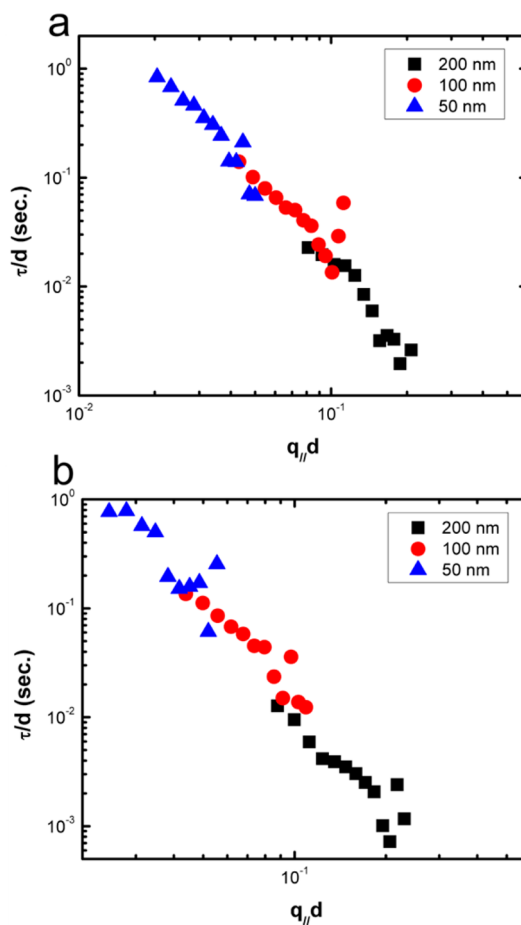

Figure 3. Plot of τ/d as a function of $q_{||}d$ for three different film thicknesses: 200 nm (black squares), 100 nm (red circles), and 50 nm (blue triangles) at $T = 80$ °C for Au/dPS/PVME blends containing (a) 2 nm Au NPs and (b) 5 nm Au NPs.

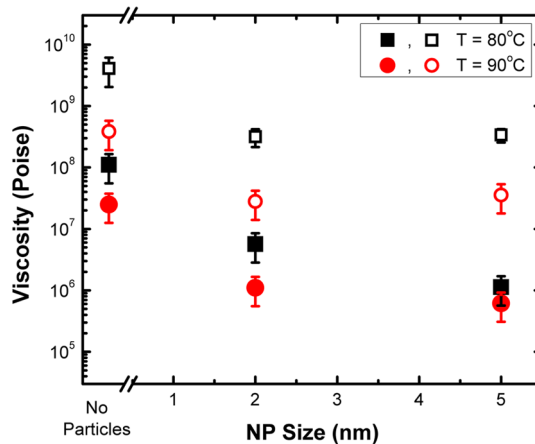**Figure 4.** Viscosity as a function of NP diameter at 80 °C (squares) and 90 °C (circles). The viscosity calculated from relaxation 1 (closed symbols) and relaxation 2 (open symbols) is shown as is viscosity of the pure polymer blend (which is indicated as no particles on the abscissa).

words, the characteristic relaxation time of a chain is sensitive to its local composition environment.

Having discussed the dynamics in miscible blends and the effect of a free surface on the dynamics of a

mixture, we now turn to the question of the surface dynamics of polymer chains in polymer nanocomposites. We have shown that these nanoparticles exhibit a tendency to preferentially migrate to free surfaces of homopolymers and polymer blends,[6,28,29] where they modify the composition of the surface region. The depth profiles (Figure 5a,b), determined using secondary ion mass spectroscopy (SIMS), indicate that the brush-coated gold nanoparticles preferentially enrich the interfaces of both nanocomposites. Because the resolution of the SIMS experiment is smaller than the thickness of the wetting layer, quantitative arguments on the size and composition of the wetting layer cannot be gleaned from these results. Nevertheless, it is evident from the H-profile in Figure 5a that there may be an excess of hydrogen at the free surface; this would be consistent with excess PVME in this region. This is consistent with the VASE data and anticipated, due to the lower surface tension of PVME.

The interfacial segregation of nanoparticles may be understood from the following. In athermal systems, nanoparticles migrate to interfaces because the host polymer chains gain conformational entropy; this entropic gain would be mitigated by the loss of translational entropy of the nanoparticles, which increases with decreasing nanoparticle size.[30] van der Waals interactions between the nanoparticles and an interface would contribute to a preferential attraction of the nanoparticles to a substrate.[31] The concentration profiles of the Au nanoparticles in SIMS spectra in Figure 5b show evidence of the preferential segregation of nanoparticles to both interfaces. The segregation of the 5 nm diameter Au nanoparticles is more significant than that of the 2 nm nanoparticles, due to the larger van der Waals forces associated with the larger nanoparticles. The free surface enrichment is also larger for the larger nanoparticle system, due to entropic effects. The lower interfacial segregation exhibited by the smaller particles is due to the fact that the host chains experience a much lower entropy gain when the nanoparticles segregate to the interfaces. Since the PVME chains possess a considerably lower surface energy than PS, they will remain at the free surface in excess of the bulk, as shown in Figure 5a.[32,33]

We now comment on the reason the surface dynamics are faster in the nanocomposite than in the neat PS/PVME blend. There would be two reasons. First, the VASE measurements indicate that PVME exists at the free surface of the nanocomposites at larger concentrations than in the neat blend. Larger PVME concentrations in the surface region would be consistent with lower surface
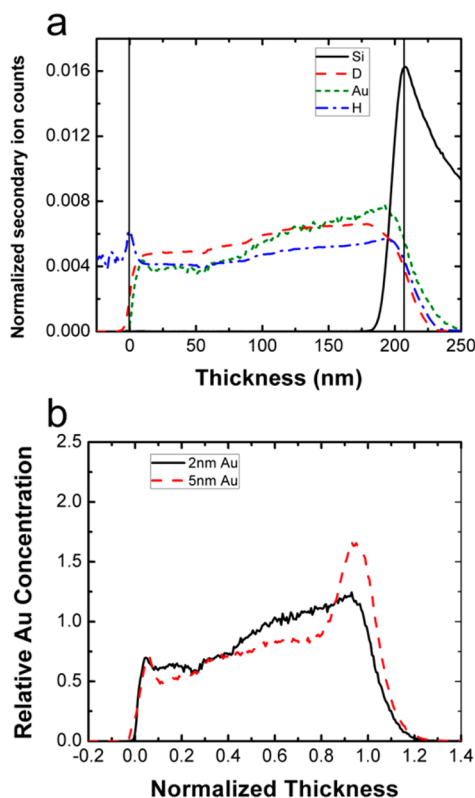

Figure 5. (a) Normalized depth profiles of the components, determined by dSIMS, of the nanocomposite containing 4 wt % of the 2 nm Au nanoparticles is shown here for silicon, deuterium, gold and hydrogen. (B) Depth profiles of Au in both nanocomposites are plotted.

viscosities. The second reason is related to polymer brush/free chain interactions. A reduction of the viscosities of blends of PS/PS-brush-coated Au nanoparticles in relation to pure PS has been reported; this is due to a reduction of the effective friction ζ (reduction in the longest relaxation times) that the flexible PS chains experience in contact with these nanoparticles.[25,26]

CONCLUSIONS

With the use of XPCS, we have measured the surface dynamics of miscible PS/PVME blends. We have shown that the surface dynamics of chain segments in a polymer nanocomposite are significantly faster than that of the neat polymer blend. In addition, the polymer blends exhibit polymer chain dynamics of two different time scales of dynamics, which are indicative of relaxations within two very different local compositional environments. These results provide a means to control the surface viscoelastic behavior of polymer systems, which would be useful in a range of applications involving thin films.

EXPERIMENTAL SECTION

Materials. In this study, we investigated blends of deuterated polystyrene (dPS), M_n = 10 900 g/mol (M_w/M_n = 1.09) and poly(vinyl methyl ether) (PVME), M_n = 24 400 g/mol (M_w/M_n = 1.08)

purchased from Polymer Source Inc. The polymers were blended in a ratio of 75 wt % dPS and 25 wt % PVME. Polystyrene-grafted gold nanoparticles were also incorporated into the polymer blends at 4 wt % Au.

Sample Preparation and Storage. Two types of thin films were prepared and examined for this study. In the first, thin films 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, measured by variable-angle spectroscopic ellipsometry (J.A. Woollam M-2000). The substrates were cleaned by washing with ethanol, acetone, and toluene and were then treated with UV-ozone. The substrates were rinsed in ethanol, acetone, and toluene prior to being UV-cleaned for 3 min. The polymer solutions were immediately spin-coated following the cleaning procedure. The samples were then immediately transferred to a vacuum oven where the samples were annealed at room temperature for 24 h under vacuum and then 18 h at 65 °C ($T_g +30$ °C). The samples were then kept in a desiccator cabinet until they were measured by XPCS or VASE. After the measurements were completed, the samples were verified to be smooth and continuous by optical microscopy and atomic force microscopy in order to confirm that the films did not dewet from the substrate. The second class of thin films was polymer nanocomposites. PNC films were prepared by adding 4 wt % (∼0.2 vol %) Au NPs to the polymer solution prior to spin-coating.

Nanoparticle Synthesis. Gold nanoparticles (Au NPs) were synthesized using the two-phase arrested precipitation method reported by Brust *et al.*[34] Thiol-terminated polystyrene molecules (PS-SH) of number-average molecular weight $M_n = 1100$ g/mol ($M_w/M_n = 1.12$), purchased from Polymer Source Inc., were then grafted onto the surfaces of the nanoparticles. We will refer to the surface-grafted chains as a brush layer throughout this article. The newly synthesized particles were cleaned at least 10 times using methanol and toluene to remove excess ligands and salts in the solution. Information from thermogravimetric analyses (TGA, TA 2960) of the samples, together with the weight fractions and densities of the gold and the ligands, was used to estimate the grafting densities, σ, of the nanoparticles.

Nanoparticle Characterization. The diameters of the NP cores, D_{core}, and the grafted brush thicknesses, h_{brush}, were determined from scanning transmission electron microscopy (STEM, JEOL 2010F), high-angle annular dark-field (HAADF) operated at 200 kV images of the samples. The average particle sizes were determined by measuring the diameters of groups more than 300 NPs in each image. Two sets of brush-coated nanoparticles were prepared: (1) Au(5)-PS is a nanoparticle of $D_{core} = 5.1 \pm 1.2$ nm, $N = 10$, $\sigma = 2.1$ chains/nm²; and (2) Au(2)-PS is a nanoparticle of $D_{core} = 2.2 \pm 0.45$ nm, $N = 10$, and $\sigma = 1.9$ chains/nm².

Nanoparticle Distribution. The film morphology and distributions of nanoparticles in these PNCs were determined using a combination of STEM and dynamic secondary ion mass spectrometry. The samples examined using STEM were prepared first by spin-coating solutions onto glass slides and then floating the film from the slide using deionized water. These films were then transferred onto Si_3N_4 grids and subsequently dried by vacuum annealing at 65 °C for 16 h. The dSIMS measurements, performed at University of California Santa Barbara by Tom Mates, using a Physical Electronics 6650 quadrupole instrument, were used to determine the depth profile of Au within the PS films.

Calorimetry Measurements. The glass transition of ∼5−10 mg of the pure polymers as well as the blend was measured by differential scanning calorimetry (DSC, TA Instruments Q200). Each sample was first heated to 150 °C at a rate of 10 °C/min to erase previous thermal history. The samples were then quenched to −100 °C at 50 °C/min using a liquid nitrogen cooling system. A second heating scan from −100 to 150 °C was then immediately carried out at 10 °C/min. The T_g was determined from the temperature corresponding to half the complete change in heat capacity on the second heating scan. All DSC measurements were completed in a nitrogen atmosphere. It is important to note that the PVME and PS chains are miscible at the temperatures (80 and 90 °C) where the experiments were conducted. For the materials used in our experiments, the lower critical solution temperature (LCST) is above 200 °C.[35,36] Further the T_g of PVME is −35 °C and that of the PS component is 91 °C. PVME possesses a much lower surface energy than PS, 32 and 22 mN/m, respectively (at 150 °C), and resides at the free surface at concentrations in excess of its bulk.[32,33]

XPCS Measurements. The free surface dynamics of supported polymer films were investigated using XPCS. The XPCS experiments were performed at beamline 8-ID-I at the Advanced Photon Source (APS) at Argonne National Laboratory. Details of the XPCS experiment are described elsewhere.[19] We used an incident angle of 0.14°, less than the critical angle of 0.16° of the PS/PVME system, which was determined by X-ray reflectivity with an incident X-ray energy of 7.5 keV. This limits the penetration of the X-ray beam to less than 10 nm from the free surface.[19] A fast X-ray reflectivity measurement was performed on the same spot as the dynamics measurement in order to ensure that the sample was not damaged during measurement by an induced surface roughness. In addition, the observed intensity did not change more than 5% during a dynamics measurement.

VASE Measurements. The same sample structure (polymer blend on precleaned silicon) was used with variable-angle spectroscopic ellipsometry (J.A. Woollam M-2000) in order to determine the wetting layer thickness. For these measurements, the ellipsometric angles Ψ and Δ are collected over the entire spectral range (375−1700 nm). The optical constants were obtained from a 200 nm film of each of the pure polymer components by fitting Ψ and Δ to a Cauchy model. For the blend films, first a Cauchy layer was used in order to obtain an estimate for the film thickness. Then, a three-layer effective medium approximation (EMA) model was then used to model the blend films, where the optical constants of PS and PVME were fixed but the weight fraction of PS in each layer and the layer thickness were allowed to vary. This allowed for obtaining a lower mean squared error (MSE) than fitting to a Cauchy layer for the entire film. The sum of all three EMA layers was verified to be approximately the same as the estimate found from the Cauchy model. Similarly, a gradient model was applied where the optical constants were allowed to follow a simple linear and exponential gradient from the interface to the interior, but the MSE was found to increase compared to the three-layer model.

Conflict of Interest: The authors declare no competing financial interest.

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