Polystyrene/Poly(methyl methacrylate) Blends in the Presence of Cyclohexane: Selective Solvent Washing or Equilibrium Adsorption?

Shane E. Harton,†⊥ Jan Lünning,† Heike Betz,§⊥ and Harald Ade*,§⊥

Department of Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina 27695; Stanford Synchrotron Radiation Laboratory, Stanford, California 94309; Department of Chemical Engineering, The Pennsylvania State University, State College, Pennsylvania 16802; and Department of Physics, North Carolina State University, Raleigh, North Carolina 27695

Received June 22, 2006; Revised Manuscript Received August 16, 2006

Abstract: Cyclohexane has been frequently used as a selective solvent to remove PS layers or domains from polystyrene-poly(methyl methacrylate) (PS:PMMA) blends and for reorganization or self-assembly of polymer brushes and block copolymers. We have found that cyclohexane is not efficient at PS removal, observing significant residual PS at PMMA surfaces. In contrast, 1-chloropentane was found to be a far greater selective solvent (i.e., residual PS was essentially nonexistent). These results were compared to PMMA surfaces after PS was allowed to adsorb to the surface from a dilute theta solution in cyclohexane. Using near-edge X-ray absorption fine structure spectroscopy and inverse gas chromatography, coupled with self-consistent mean-field theory calculations, we have demonstrated that selectively washing a polymer from a polymer blend is nearly identical to adsorption of a polymer to a "soft" surface from a dilute solution. Improved knowledge about the effects of selective solvents will improve experimental analysis of washed systems as well as manipulation of block copolymers and polymer brushes for reorganization or self-assembly.

Introduction

Macromolecular adsorption from a solution to an impenetrable surface has been the subject of numerous investigations in recent years.1–3 Unlike simple Langmuirian adsorption of small molecule liquids or gases,4 these systems are quite complicated due to the strong conformational limitations created by chain connectivity.1 Common model systems employed in such investigations have included polystyrene–cyclohexane (PS:CH), poly(methyl methacrylate)–carbon tetrachloride (PMMA:CCl4), and PS:CCl4 adsorbing to a silicon oxide (SiO2) substrate.5–8 Because of technologically relevant applications, such as protein adsorption and DNA separation,9,10 more recent investigations have also focused on adsorption at so-called “soft” surfaces, where the substrate is an organic material such as a polymer or lipid membrane.11–13 Unlike the above-mentioned model systems, these systems often involve complex thermodynamic interactions between the substrate and adsorbate (adsorbing polymer) as well as between the adsorbate and solvent and the substrate and solvent.14

Selective solvents have been employed for reversible self-assembly or reorganization of block copolymers15,16 and polymer brushes17–19 as well as to remove polymer layers or domains for experimental characterization using techniques such as scanning force microscopy (SFM), scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), and forward recoil spectrometry (FRES). For analysis using SFM and SEM, selectively washing away domains of one polymer, while leaving another polymer domain intact, provides topographical contrast for investigations such as morphological development during physical or reactive blending.20–22 For a depth profiling technique such as SIMS or FRES, selective washing can remove excess layers, allowing for further sample preparation and processing or providing improved depth resolution.23,24 Although the use of selective washing is a well-established and seemingly trivial experimental aid, the optimal conditions, relevant parameters, and detailed outcome have not been fully investigated. Furthermore, increased understanding of selective washing and adsorption at “soft” surfaces will provide improved knowledge of adsorption and self-assembly mechanisms as well as improved experimental characterization using techniques such as SFM, SEM, SIMS, and FRES.

Here, we demonstrate that selective solvent washing is physically quite similar to equilibrium adsorption from dilute polymer:solvent solutions and optimal preferential solvents are required for “true” selective washing.1–3 Using the self-consistent mean-field theory (SCF) of Scheutjens and Fleer3 coupled with experimental characterization using near-edge X-ray absorption fine structure spectroscopy (NEXAFS),25 selective washing of PS from PMMA surfaces and adsorption of PS to PMMA surfaces have been systematically investigated for two solvents. NEXAFS results show that significant residual PS remains after washing PS:PMMA bilayers using CH as a selective solvent and that PS adsorbs to PMMA from dilute PS:CH solutions. Alternatively, 1-chloropentane (1CP) is shown to be far more efficient at PS removal from PS:PMMA bilayers (i.e., residual PS was essentially nonexistent), which implies that it provides a weaker driving force than CH for adsorption of PS to PMMA. SCF along with polymer:solvent Flory–Huggins parameters (χ) measured using inverse gas chromatography (IGC)26 is used to interpret these observations.
Table 1. Polymers Used in This Investigation

<table>
<thead>
<tr>
<th>polymer</th>
<th>supplier</th>
<th>$M_w$/kDa</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-8</td>
<td>SPP</td>
<td>8.0</td>
<td>1.05</td>
</tr>
<tr>
<td>PS-10</td>
<td>PL</td>
<td>10.1</td>
<td>1.02</td>
</tr>
<tr>
<td>PS-12</td>
<td>SPP</td>
<td>12.4</td>
<td>1.06</td>
</tr>
<tr>
<td>PS-18</td>
<td>SPP</td>
<td>18.1</td>
<td>1.07</td>
</tr>
<tr>
<td>PS-29</td>
<td>SPP</td>
<td>29.1</td>
<td>1.09</td>
</tr>
<tr>
<td>PS-107</td>
<td>SPP</td>
<td>107</td>
<td>1.08</td>
</tr>
<tr>
<td>PMMA-92</td>
<td>SPP</td>
<td>92.5</td>
<td>1.09</td>
</tr>
<tr>
<td>PMMA-808</td>
<td>SPP</td>
<td>808</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Experimental Section

For this investigation, we selected PS and PMMA, as they are a highly investigated polymer pair\(^{15-19,21}\) and are completely immiscible for all molecular weights used here.\(^{22,27}\) Monodisperse atactic PS ($T_g \approx 100 \, ^\circ C$) and syndiotactic PMMA ($T_g \approx 130 \, ^\circ C$) spanning a range of molecular weights were purchased from Scientific Polymer Products (SPP) or Polymer Laboratories (PL), and their properties are summarized in Table 1. Silicon (100) wafers were cut into 2.5 cm x 2.5 cm squares and cleaned following established procedures.\(^{28}\) First, they were soaked in a solution of sulfuric acid/hydrogen peroxide for 30 min at \(\sim 100 \, ^\circ C\) to remove surface contaminants. Next, they were rinsed with deionized (DI) water. To remove the \(~2\) nm oxide layer (SiO\(_x\)) created during this process, the substrates were soaked in hydrofluoric acid (10% v/v) for 1 min and again rinsed with DI water to leave a hydrogen-passivated surface (SiH). Cyclohexane (Acros) was distilled over calcium hydride immediately prior to use, 1-chloropentane (Aldrich) was used as received. PMMA-92 and PMMA-808 were each dissolved in chlorobenzene and subsequently filtered (Sigma-Aldrich) was used as received. PMMA-92 and PMMA-808 substrates were immediately rinsed with anhydrous cyclohexane to remove any unadsorbed PS chains, blown dry with N\(_2\), and subsequently placed under vacuum at 25 \(^\circ C\) for 1 h. Table 2 summarizes these sample preparation steps.

Table 2. Systems and Preparation Methods

<table>
<thead>
<tr>
<th>sample</th>
<th>PMMA</th>
<th>PS</th>
<th>process 1</th>
<th>process 2</th>
<th>process 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PMMA-92</td>
<td>PS-10</td>
<td>spin cast (CIP)</td>
<td>anneal (150 (^\circ C))</td>
<td>CIP rinse</td>
</tr>
<tr>
<td>B</td>
<td>PMMA-92</td>
<td>PS-107</td>
<td>spin cast (CIP)</td>
<td>anneal (150 (^\circ C))</td>
<td>CIP rinse</td>
</tr>
<tr>
<td>C</td>
<td>PMMA-92</td>
<td>PS-10</td>
<td>spin cast (CIP)</td>
<td>anneal (150 (^\circ C))</td>
<td>CH rinse</td>
</tr>
<tr>
<td>D</td>
<td>PMMA-92</td>
<td>PS-107</td>
<td>spin cast (CIP)</td>
<td>anneal (150 (^\circ C))</td>
<td>CH rinse</td>
</tr>
<tr>
<td>E</td>
<td>PMMA-92</td>
<td>PS-18</td>
<td>spin cast (CH)</td>
<td>CH soak</td>
<td>CH rinse</td>
</tr>
<tr>
<td>F</td>
<td>PMMA-92</td>
<td>PS-18</td>
<td>spin cast (CH)</td>
<td>CH soak</td>
<td>CH rinse</td>
</tr>
<tr>
<td>G</td>
<td>PMMA-808</td>
<td>PS-8</td>
<td>adsorb (CH)</td>
<td>CH rinse</td>
<td>CH rinse</td>
</tr>
<tr>
<td>H</td>
<td>PMMA-808</td>
<td>PS-12</td>
<td>adsorb (CH)</td>
<td>CH rinse</td>
<td>CH rinse</td>
</tr>
<tr>
<td>I</td>
<td>PMMA-808</td>
<td>PS-18</td>
<td>adsorb (CH)</td>
<td>CH rinse</td>
<td>CH rinse</td>
</tr>
<tr>
<td>J</td>
<td>PMMA-808</td>
<td>PS-29</td>
<td>adsorb (CH)</td>
<td>CH rinse</td>
<td>CH rinse</td>
</tr>
</tbody>
</table>

Results and Discussion

Carbon K-edge NEXAFS spectra of samples A–D are plotted in Figure 1. Also shown in the figure inset are the reference spectra of PMMA and PS. The obvious difference between these two spectra is that the PS spectrum exhibits a sharp C 1s \(\rightarrow \pi^\ast_{\text{C=C}}\) resonance at 285.18 eV (transition of the C=C double bond) while the strongest resonance of the PMMA spectrum is located at 288.52 eV and is a C 1s \(\rightarrow \pi^\ast_{\text{C-O}}\) resonance transition to the lowest unoccupied molecular orbital of the ester group.\(^{38}\) Comparison of these reference spectra to the NEXAFS spectra of samples A–D shows that the concentration of residual PS at the PMMA surface is a strong function of the PS molecular weight and the solvent type used for washing. For example,
for sample D (PS-107 washed with CH), there is complete saturation of the PMMA-92 surface with PS.

To be able to explain this observation, the phase behavior of the various polymer:solvent combinations (PS:CH, PS:CIP, PMMA:CH, and PMMA:CIP) must be known. Previous investigations using IGC have measured the phase behavior, in the limit of pure polymer (PS:CH and PMMA:CH), and PMMA:ClP (150–180 °C) and (---) PMA:CH (90–110 °C). Lines are linear fits to the experimental data. Results for PMA:CH were extrapolated to a temperature range of ≈150–180 °C for comparison to the other polymer:solvent systems.

Figure 2. IGC measurements of χ∞ for (○) PS:CIP and (△) PMMA:CIP (150–170 °C), along with previously reported results (ref 40) for (●) PS:CH (160–180 °C) and (---) PMA:CH (90–110 °C). Lines are linear fits to the experimental data. Results for PMA:CH were extrapolated to a temperature range of ≈150–180 °C for comparison to the other polymer:solvent systems.

Adsorption of PS to a PMMA substrate,5,6 as CH provides a stronger driving force for adsorption than CIP.

Samples E, F, and I were used to test this hypothesis regarding the underlying mechanism, and their carbon K-edge NEXAFS spectra are shown in Figure 3. The amount of adsorbed PS is almost identical for both adsorption of PS to PMMA from CH and washing a PS:PMMA bilayer using CH after an equilibrium interface has formed (see samples F and I). The equilibrium interfacial overlap (interfacial roughness measured from scattering) is ~2 nm15,27,45 for the PS:PMMA interfaces of samples F and I, although CH has been shown previously not to penetrate the PMMA layer.15 The adsorption also requires a finite residence time for equilibrium arrangement of the chains (i.e., chain conformations) at the interface,46–48 which is observed in Figure 3. Sample E (PS/PMMA bilayer immediately washed with CH after spin-casting the PS layer) shows significantly less adsorbed PS than samples F (PS/PMMA bilayer annealed and then washed with PS) and I (PS adsorption to PMMA from CH solution). However, adsorption equilibrium appears to occur extremely fast for sample F, as observed from a comparison of samples F and I (see Figure 3). This is somewhat surprising, as an equilibrium melt interface, within the limit of mean-field theory,49,50 and an equilibrium adsorption interface formed with a net attractive surface (χ2 > 0, see eq 1)49,50 have significantly different equilibrium chain conformations (see Figure 4). At a strongly segregated (mean-field) melt interface, the chains will maintain weakly perturbed Gaussian conformations,49,50 with a characteristic length scale of the perturbation ~Rg. In contrast to this, chains adsorbed at a net attractive surface tend to be

\[ \chi_s \approx \tilde{\lambda}_1 \left( \chi_{1,3} - \chi_{2,3} \right) \]  

where \( \chi_s \) is an adsorption strength parameter, \( \tilde{\lambda}_1 \) is a lattice weighting factor (1/4 for hexagonal), \( \chi_{1,3} \) is the interaction between the solvent and the substrate polymer, and \( \chi_{2,3} \) is the interaction between the two polymers, the results shown in Figure 1 are similar to what would be expected with equilibrium adsorption of PS to a PMMA substrate,5,6 as CH provides a greater driving force for adsorption than CIP.
incident photons (X-rays) penetrate much deeper than \( z \) generated using the SCF model of Scheutjens and Fleer \(^3\) is belonging to free chain ends \(^{48,52}\).

The more extended parallel to the surface, which can be quantified through the amount of trains (segments in contact with the surface), loops (segments between trains), and tails (segments belonging to free chain ends) \(^{38,52}\).

In Figure 5 an example of a simulated adsorption profile generated using the SCF model of Scheutjens and Fleer \(^1\) is shown (\( \chi = 0.5, \chi_s = 0.5, \) and \( N = 200 \)), with the inset showing the fraction of the segments in the adsorbed chains belonging to trains \( (f_{\text{train}}) \), tails \( (f_{\text{tail}}) \), and loops \( (f_{\text{loop}}) \).

The NEXAFS measurements can be further quantified by considering the relationship between the C 1s \( \pi^* \rightarrow \sigma_{\text{cc}} \) intensity \( (I_{\pi^*}) \) at 285.18 eV \(^{38}\) normalized to the intensity for the pure PS reference \( (I_\text{ref}) \), and the effective PS adsorbed dry-layer thickness \( (h^*) \), which is given by \(^{39}\)

\[
\frac{I_{\pi^*}}{I_{\text{ref}}} = \frac{\int_0^{h^*} \exp\left(\frac{-z}{\lambda_0}\right) dz}{\int_0^{h} \exp\left(\frac{-z}{\lambda_0}\right) dz} = 1 - \exp\left(-\frac{h^*}{\lambda_0}\right)
\]

where \( z \) is the functional depth. Equation 2 is valid when the incident photons (X-rays) penetrate much deeper than \( \lambda_0 \), which is the case here, and the resolved peak of interest is in the top layer. The results for samples E–J are shown in Figure 6. Also shown in Figure 6 is a linear fit of \( h^*/\lambda_0 \) vs \( \log(N) \), where \( N \) is the number of segments in a polymer chain, for samples G–J. It has been shown previously that the equilibrium adsorption amount (i.e., dry layer thickness) of a polymer to a substrate from a dilute theta solution will have a logarithmic dependency on polymer molecular weight (i.e., \( N \)). \(^{53}\) This is also theoretically demonstrated in Figure 7 using the SCF model of Scheutjens and Fleer \(^3\). Although a small molecular weight range is shown in Figure 6, with sizable error bars due to the exponential functionality of eq 2, this linear trend is still qualitatively obeyed, thereby further demonstrating the equivalence between selective solvent washing and equilibrium adsorption.

**Conclusions**

Using NEXAFS and inverse gas chromatography, coupled with SCF calculations, we have demonstrated that selectively washing a polymer from a polymer blend is nearly identical to adsorption of a polymer to a “soft” surface from a dilute solution. After washing polystyrene–poly(methyl methacrylate) (PS/PMMA) bilayers with cyclohexane (CH) or 1-chloropentane (ClP), considerable residual PS was found with the CH wash but was essentially nonexistent with the CIP wash (see Figure 1). This can be explained in terms of the Flory–Huggins parameter (\( \chi \)) for PMMA:solvent and PS:PMMA (see Figure 2), with CIP providing a better, albeit still poor, solvent for PMMA. The use of CIP therefore creates a weaker driving force for PS adsorption than does CH (see eq 1). Furthermore, these results were also compared to PMMA surfaces after PS was allowed to adsorb to the surface from a dilute theta solution (\( \chi = 0.5 \)) of PS:CH (see Figures 3 and 6), and experimental results were found to be comparable to theoretical results of a polymer adsorbing to a solid substrate from a theta solution (see Figure 7). Because selective solvents are frequently used for sample preparation or sample processing, improved knowledge of this behavior will greatly improve experimental analysis as well as improve processes such as block copolymer and polymer brush reorganization or self-assembly.
Acknowledgment. This work was supported by the U.S. Department of Energy (DE-FG02-98ER45737). The authors gratefully acknowledge invaluable discussions with Prof. M. Rubinstein (University of North Carolina) and Prof. R. P. Danner (The Pennsylvania State University). The IGC experiments were carried out at the Center for the Study of Polymer-Solvent Systems, Department of Chemical Engineering, The Pennsylvania State University, State College, PA. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

References and Notes


PS:PMMA Blends in Presence of Cyclohexane 7733