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

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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:CCl_4), and PS:CCl_4 adsorbing to a silicon oxide (SiO_x) 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 copolymers[15,16] and polymer brushes[17−19] 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 Fleer[3] 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 (ClP) 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.

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Table 1. Polymers Used in This Investigation

polymer	supplier	M_n/kDa	M_w/M_n
PS-8	SPP	8.0	1.05
PS-10	PL	10.1	1.02
PS-12	SPP	12.4	1.06
PS-18	SPP	18.1	1.07
PS-29	SPP	29.1	1.09
PS-107	SPP	107	1.08
PMMA-92	SPP	92.5	1.09
PMMA-808	SPP	808	1.04

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.[27,28] Monodisperse atactic PS ($T_g \approx 100$ °C) and syndiotactic PMMA ($T_g \approx 130$ °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 × 2.5 cm squares and cleaned following established procedures.[29] First, they were soaked in a solution of sulfuric acid/hydrogen peroxide for 30 min at ∼100 °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 stored over 4 Å molecular sieves (Acros), and chlorobenzene (Sigma-Aldrich) was used as received. PMMA-92 and PMMA-808 were each dissolved in chlorobenzene and subsequently filtered with 0.45 μm PTFE syringe filters. They were then cast onto the SiH surfaces to a thickness of ∼150 nm and annealed at 165 °C for 12 h to provide smooth, uniform PMMA substrates.

For the investigation of selective washing of PS from PMMA, PS-10 and PS-107 were cast from ClP (thickness ∼ 100 nm) onto PMMA-92 and annealed at 150 °C for 1 h. The bilayer assemblies were washed with ClP (samples A and B) or CH (samples C and D) at room temperature (25 °C). Washing involves immersing the sample into pure solvent (CH or ClP), manually agitating the solution with the immersed sample, and then drying with an N_2 jet. This process is repeated 4−5 times for each sample (samples A−D). Similarly, PS-18 was cast onto PMMA-808 from CH (thickness ∼ 200 nm) and either immediately soaked in pure anhydrous CH for 5 min followed by a CH rinse (sample E) or annealed for 12 h at 120 °C to form an equilibrium interface[30,31] and then soaked in pure anhydrous CH for 5 min followed by a CH rinse (sample F). The diffusion constant (D) for 130 kDa PS in dilute CH solutions at 34.5 °C has been reported to be $\sim 3 \times 10^{-7}$ cm^2/s,[32] which would provide $D \approx 8 \times 10^{-7}$ cm^2/s for PS-18 in solution ($D \sim M_w^{-1/2}$ for a dilute theta solution[32,33]). Therefore, a 5 min immersion time will allow the unadsorbed PS-18 chains to move $\sim (2Dt)^{1/2} \sim 600R_g$ (radii of gyration) from the surface (considering the diffusive flux only), while the adsorbed chains will remain at the surface.[34,35]

For the investigation of PS adsorption to PMMA, PS powder was placed in 120 mL amber jars and annealed under vacuum at 120 °C for 12 h to remove any residual solvents that may interfere with the adsorption process (e.g., methanol is often used to precipitate PS after polymerization). The PS used here (see Table 1) had been synthesized using living anionic polymerization[36] and had no functional groups added along the chains or chain ends. Anhydrous CH was added to the annealed PS powder to create 0.1% (v/v) solutions of PS-8 (sample G), PS-12 (sample H), PS-18 (sample I), or PS-29 (sample J). PMMA-808 substrates were immersed completely in the solution, and the amber jars were closed and sealed with Teflon tape. The jars were placed in an ethylene glycol bath maintained at 34.5 ± 0.5 °C (theta temperature for PS/CH)[37] for 24 h. Upon removal from the adsorption solutions, the 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 °C for 1 h. Table 2 summarizes these sample preparation steps.

Samples A−J and pure reference (PS-107 and PMMA-92) films were analyzed using NEXAFS spectroscopy[25] at beamline 10-1 of the Stanford Synchrotron Radiation Laboratory (SSRL). Carbon 1s NEXAFS spectra (∼280 eV)[38] were recorded by monitoring the total electron yield (TEY), which has an effective 1/e sampling depth (λ_0) of ≈3−4 nm (i.e., ≈63% of the spectral intensity originates from the outermost 3−4 nm of the film).[39] At least three spots were analyzed on each sample, with at least two samples for each sample type. All spectra were recorded with an energy resolution of $E/\Delta E > 5000$ and in the so-called magic angle geometry, which suppresses polarization dependencies.[25]

Inverse gas chromatography[26] was used to characterize the phase behavior of 1-chloropentane with PMMA and PS, within the concentration limit of pure polymer, at temperatures of 150, 160, and 170 °C. Experiments were conducted at the Center for the Study of Polymer−Solvent Systems (The Pennsylvania State University) with a commercially available gas chromatograph using capillary columns coated with atactic PMMA ($M_w \sim 996$ kDa) (1193.7 cm × 3.0 μm × 0.053 cm i.d.) and with atactic PS ($M_w \sim 200$ kDa) (844.5 cm × 5.0 mm × 0.053 cm i.d.). 1-Chloropentane was injected as a sharp spike into the columns. The resulting elution profiles were fitted and regressed for the partition coefficient (K) using the capillary column inverse gas chromatography (CCIGC) model.[26] The Flory−Huggins interaction parameters, in the limit of pure polymer (χ_∞), were then calculated using the measured values for K.

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 → $\pi^*_{C=C}$ resonance at 285.18 eV (transition of the 1 s core level to the lowest unoccupied molecular orbital of the phenyl ring) while the strongest resonance of the PMMA spectrum is located at 288.52 eV and is a C 1s → $\pi^*_{C=O}$ 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,

Table 2. Systems and Preparation Methods

sample	PMMA	PS	process 1	process 2	process 3
A	PMMA-92	PS-10	spin cast (ClP)	anneal (150 °C)	ClP rinse
B	PMMA-92	PS-107	spin cast (ClP)	anneal (150 °C)	ClP rinse
C	PMMA-92	PS-10	spin cast (ClP)	anneal (150 °C)	CH rinse
D	PMMA-92	PS-107	spin cast (ClP)	anneal (150 °C)	CH rinse
E	PMMA-808	PS-18	spin cast (CH)	CH soak	
F	PMMA-808	PS-18	spin cast (CH)	anneal (120 °C)	CH soak
G	PMMA-808	PS-8	adsorb (CH)	CH rinse	
H	PMMA-808	PS-12	adsorb (CH)	CH rinse	
I	PMMA-808	PS-18	adsorb (CH)	CH rinse	
J	PMMA-808	PS-29	adsorb (CH)	CH rinse	

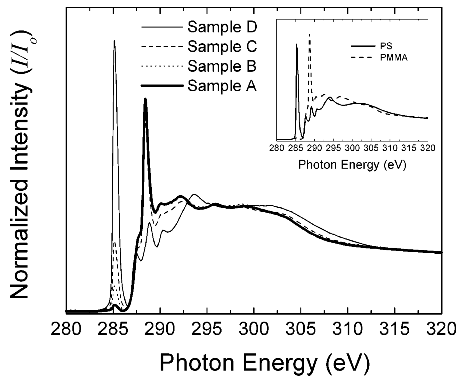

Figure 1. NEXAFS results for samples A−D. Considerable PS is observed when CH was used to wash the sample, particularly for sample D (PS-107), where complete saturation of the PMMA surface is observed.

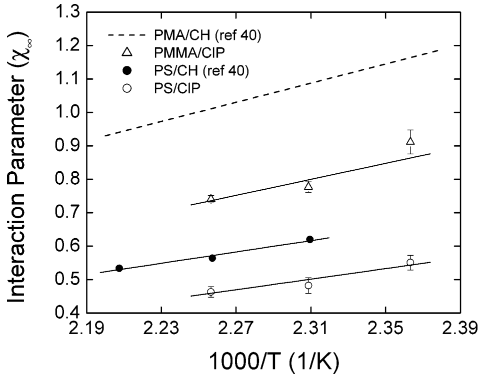

Figure 2. IGC measurements of χ_∞ for (○) PS:ClP and (Δ) PMMA: ClP (150−170 °C), along with previously reported results (ref 40) for (●) PS:CH (160−180 °C) and (- - -) PMA:CH (90−110 °C). Lines are linear fits to the experimental data. Results for PMA:CH were extrapolated to a temperature range of ≈150−180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

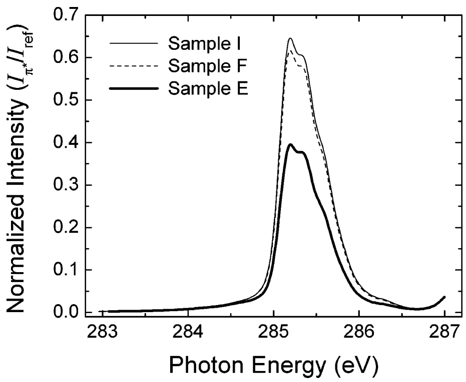

Figure 3. NEXAFS results in the π^* region (285.18 eV) for samples E, F, and I. Here, it is shown that adsorption of PS to the PMMA surface from a CH solution (sample I) is almost identical to washing a PS/PMMA bilayer with CH after an equilibrium interface has been formed by annealing at 120 °C for 12 h (sample F). However, if the PS/PMMA bilayer is washed with CH without annealing to form an equilibrium interface, much less residual PS is observed (sample E).

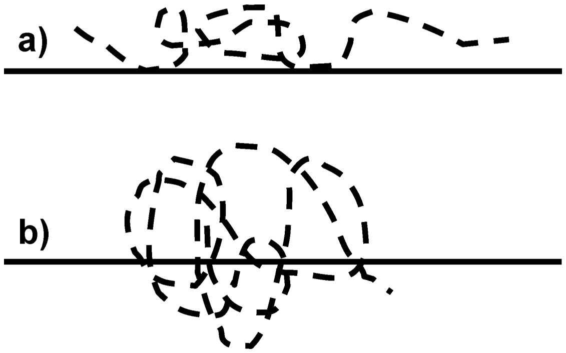

Figure 4. Equilibrium chain conformations for (a) an adsorbed chain at a net attractive surface and (b) a polymer chain at an equilibrium polymer/polymer melt interface.

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:ClP, PMMA:CH, and PMMA:ClP) must be known. Previous investigations using IGC have measured the phase behavior, in the limit of pure polymer (χ_∞), for PS:CH and poly(methyl acrylate) with CH (PMA:CH).[40] Because the values of χ_∞ have been found to be comparable for PMA-decane[40] and PMMA:decane,[41] it can be assumed that PMA:CH and PMMA:CH are reasonably close in χ_∞ values. Figure 2 shows the previously reported results for PS:CH and PMA:CH as well as our measurements for PS: ClP and PMMA:ClP χ_∞. Consistent with the results shown in Figure 2, it is also evident that χ for PMMA:CH will be higher than χ for PMMA:ClP according to the solubility parameters (δ) of CH and ClP (16.8 and 17.2 MPa$^{1/2}$, respectively, as calculated from heats of vaporization)[42,43] relative to δ for PMMA (18.6 MPa$^{1/2}$).[44] Considering that the driving force for equilibrium adsorption of a polymer to a surface is related to the difference in χ between surface−solvent and surface−polymer[3]

$$\chi_s \approx \lambda_1(\chi_{1,3} - \chi_{2,3}) \qquad (1)$$

where χ_s is an adsorption strength parameter,[3] λ_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 ClP.

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 nm[15,27,45] 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 ($\chi_s > 0$, see eq 1)[51,52] 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 $\sim R_g$. In contrast to this, chains adsorbed at a net attractive surface tend to be

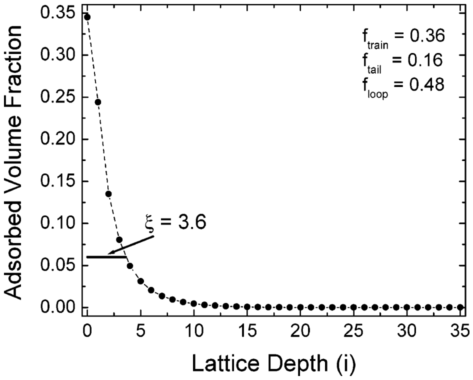

Figure 5. Results of SCF calculations for a system with $N = 200$, $\chi = 0.5$, $\chi_s = 0.5$, and a bulk solution containing 0.1% polymer (v/v). A hexagonal lattice ($z = 12$) was employed here, and the adsorbing surface is an impenetrable boundary. The model equations and numerical methods have been outlined in refs 51 and 52. Only the concentration of adsorbed chains (i.e., any chain with at least one segment in contact with the substrate) is shown in the profile. Also shown is the rms thickness of the adsorbed layer ($\xi = 3.6 \sim R_g/2$) and the fraction of segments in the adsorbed chains belonging to trains (f_{train}), tails (f_{tail}), and loops (f_{loop}).

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).[48,52]

In Figure 5 an example of a simulated adsorption profile generated using the SCF model of Scheutjens and Fleer[3] 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, tails, and loops. The equations and numerical procedures have been detailed previously.[51,52] Of course, the adsorption equilibrium of PS at this "soft" surface is somewhat of a hybrid of a melt interface and a net attractive surface (combination of Figure 4a,b), which could explain the extent of the adsorption observed in Figures 1 and 3, but this does not explain the near-immediate adsorption equilibrium formed when the quenched equilibrium melt interface is exposed to pure anhydrous CH (sample F).

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

$$\frac{I_{\pi^*}}{I_{ref}} = \frac{\int_0^{h^*} \exp\left(-\frac{z}{\lambda_0}\right) dz}{\int_0^{\infty} \exp\left(-\frac{z}{\lambda_0}\right) dz} = 1 - \exp\left(-\frac{h^*}{\lambda_0}\right) \qquad (2)$$

where z is the functional depth. Equation 2 is valid when the incident photons (X-rays) penetrate much deeper than λ_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^*/λ_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.

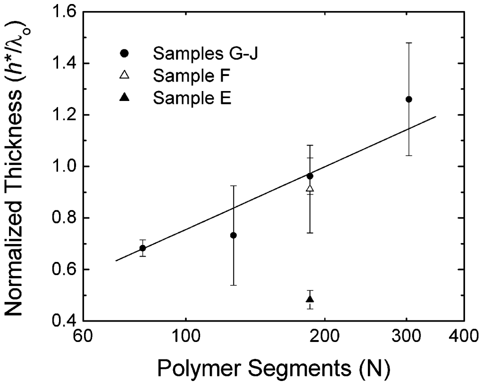

Figure 6. NEXAFS results for (▲) sample E, (△) sample F, and (●) samples G−J were converted to normalized thickness (h^*/λ_0) using eq 2. The solid line has been fit to the results for samples G−J.

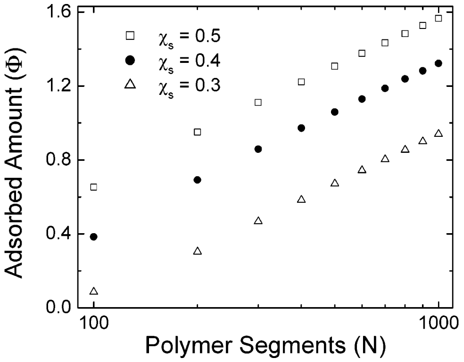

Figure 7. SCF calculations spanning a χ_s (0.3−0.5) and N (100−1000) range, with $\chi = 0.5$ (theta solution) for all calculations. The adsorbed amount (Φ) is determined from the area under the adsorption curve, which is shown in Figure 5 for $N = 200$ and $\chi_s = 0.5$. Results show a linear trend for Φ vs log(N) for each χ_s. This linear trend is qualitatively obeyed in Figure 6 with samples G−J.

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 ClP wash (see Figure 1). This can be explained in terms of the Flory−Huggins parameter (χ) for PMMA:solvent and PS/PMMA (see Figure 2), with ClP providing a better, albeit still poor, solvent for PMMA. The use of ClP 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.

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