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Deposition of Block Copolymer Thin Films onto Polymeric Substrates by Adsorption from Supercritical Carbon Dioxide

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ABSTRACT: A novel method for the deposition of monolayer and submonolayer films of block copolymers onto polymeric substrates is described. We show that poly(styrene-*b*-dimethylsiloxane) films form spontaneously on polystyrene substrates by simply placing a sample of the block copolymer and the substrate into a pressure vessel that is charged with supercritical carbon dioxide. The modified polystyrene substrates are characterized by water contact angle and angle-dependent X-ray photoelectron spectroscopy (ADXPS) measurements performed after depressurization. Water contact angles indicate that a continuous PDMS surface layer forms when the pressure is 15 MPa or greater at 50 °C, illustrating that the block copolymer self-assembles as a bilayer structure at the surface under these conditions. ADXPS measurements confirm that monolayer to submonolayer coverage is produced as the PDMS layer thickness increases from ca. 0.8 nm at 15 MPa to a maximum of ca. 1.5 nm for pressures of 30 MPa and higher. The thickness data indicate that the PDMS layer forms a wet brush wherein PDMS chains adopt nearly unperturbed dimensions. The atomic concentration of silicon in the bulk, associated with PDMS from copolymer impregnated into the bulk phase, is negligible for pressures below about 30 MPa and rises to about 2% for pressures of 40 Pa and higher. Pressures in the range of 20−30 MPa produce a surface film of maximum thickness with little block copolymer dissolved in the bulk of the substrate, and are therefore optimal conditions for monolayer film fabrication by adsorption from supercritical carbon dioxide.

Introduction

The ability of block copolymers to lower the surface tension of a polymeric substrate is well-known.[1] The copolymers employed in these applications comprise a low surface tension sequence, such as poly(dimethylsiloxane) (PDMS) or a fluorinated polymer, and a second sequence that is generally identical to the polymeric substrate. Relatively small amounts of block copolymer are required because the block copolymer segregates strongly to the air−polymer interface to lower the surface free energy. The second sequence provides a mechanical anchor by virtue of entanglements with the polymer chains of the substrate. In most cases, surface-active block copolymers are used to create a low-energy release surface; however, incorporation of a functional terminus on the surface-active block can impart selective adhesion properties to the surface.[2] The equilibrium[3,4] and dynamic[5−7] aspects of block copolymer surface segregation have been studied extensively and are relatively well understood.

Block copolymer surface modification is not used extensively in industry, however, due to limitations of current thin film fabrication technologies. If segregation is designed to occur from the bulk phase, for example, the block copolymer must first be dispersed within the polymer matrix. Because the viscosity of block copolymers is generally higher than that of the matrix, block copolymer phases are difficult to break up, even with intensive shear mixing. In addition, the inherent incompatibility between the surface-active and anchor blocks often leads to micelle formation. Thermal annealing above the melting points and/or glass transitions of both polymers may also be required to give the block copolymer chains sufficient mobility to self-organize at the surface. Finally, the rate of diffusion of block copolymers to the surface is slow,[7] requiring annealing times that are too long to be commercially viable.

Thin block copolymer films on polymeric substrates may also be formed by solvent-based methods[8,9] such as spin coating. The primary shortcoming of solution coating methods is that a solvent is required. Residual solvent is often difficult to remove after coating, and solvent toxicity may lead to environmental or safety issues. In addition, spin coating is incapable of forming coatings on objects of arbitrary shape. Block copolymer coatings can also be made by melt processing; however, it is nearly impossible to achieve monolayer thickness by these methods, and again coatings are usually possible only for flat substrates.

In this paper, we describe a new and simple method that is capable of producing monolayer or submonolayer films of block copolymers on polymeric substrates. The new method is also environmentally friendly as it is based upon adsorption from supercritical carbon dioxide ($scCO_2$). $scCO_2$ is an excellent alternative to conven-

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tional organic solvents because it is inexpensive, nonflammable, and nontoxic and can be completely removed by simply lowering the pressure of the system. An added benefit of the $scCO_2$ process is that excess block copolymer can be easily recycled without complex recovery steps. $scCO_2$ is a natural choice for surface modification applications because the required surface-active low surface tension polymers necessarily have low solubility parameters that render them soluble in $scCO_2$. PDMS[10-12] and several other low surface tension polymers[13-18] are known to dissolve in $scCO_2$ under relatively mild conditions, and therefore can be used as the surface-active block copolymer sequence required for surface modification applications.

Polymers of higher solubility parameter do not dissolve in the $scCO_2$, but instead exhibit swelling due to the sorption of carbon dioxide. Supercritical CO_2 is know to swell poly(styrene) (PS)[19] and can depress the glass transition temperature by as much as 50 °C[20] within the pressure range of 10−100 MPa. Polymer substrates swollen with $scCO_2$ often exhibit a foamlike structure after depressurization. Scanning electron microscopy results[21] illustrated that the size of holes on the surface of a $scCO_2$-swollen PS substrate measured after depressurization increased with both swelling temperature and depressurization time.

Block copolymers generally form micelles in supercritical solvents, because only one block copolymer sequence will normally be soluble in $scCO_2$. Micelle formation of block copolymers in $scCO_2$ has been characterized by a variety of techniques including small-angle neutron scattering (SANS),[22-24] small-angle X-ray scattering (SAXS),[23,25,26] dynamic light scattering (DLS),[26-28] and nuclear magnetic resonance (NMR) spectroscopy.[29,30]

Block copolymers have been employed to reduce the interfacial tension between polymeric particulates and $scCO_2$,[31] but there has been no report to date of the use of $scCO_2$ to modify polymer surface properties. In this paper, we demonstrate that PS substrates may be simply and efficiently modified with poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS)] block copolymers by adsorption from $scCO_2$. The nature of the surface films produced is characterized by contact angle and angle-dependent X-ray photoelectron spectroscopy (ADXPS) measurements.

Experimental Section

Materials. Carbon dioxide was purchased from CT Airgas (minimum purity of 99.998%). Oxygen in the carbon dioxide was removed by an oxygen trap connected between the CO_2 tank and the syringe pump (ISCO, model 260D). The polymeric substrate, PS (M_n = 152000 g/mol, M_w/M_n = 1.06, Pressure Chemicals) was spin-coated onto silicon wafer specimens. The P(S-*b*-DMS) copolymer was synthesized by standard anionic polymerization methods. The number-average molar mass (M_n) of the PS block in the copolymer was determined by gel permeation chromatography (GPC) to be 2700 g/mol. M_n of the entire P(S-*b*-DMS) copolymer was measured by GPC after addition of the dimethylsiloxane block and estimated to be 6340 g/mol with a polydispersity index of 1.15. In the GPC characterizations, PS standards with known MW were used for calibration and tetrahydrofuran was used as the mobile phase. The hydrodynamic volume of the PDMS block thus corresponded to that of a PS polymer with M_n = 3640 g/mol. The molar mass of the PDMS block is an overestimate because PS has a smaller hydrodynamic volume than PDMS for the same molar mass.[32] To estimate M_n of the PDMS block more accurately, solutions of the block copolymer in tetrahydrofuran were characterized by fluorescence spectroscopy. Since PS is fluorescent while PDMS and tetrahydrofuran are not, the characteristic intensity ($\lambda_{em,max}$ = 334 nm with λ_{ex} = 260 nm) from the block copolymer solution was used to estimate the mass fraction of PS in the copolymer by comparison to the fluorescence of standard PS solutions. M_n of the PDMS block calculated from the fluorescent intensity measurements was 2800 g/mol, 32% lower than the result obtained by GPC. In view of these results, the copolymer studied will be referred to as P(S2.7-*b*-DMS2.8), where the numbers indicate the molecular mass in kilodaltons of each block.

Au: Please check the use of molecular weight and molar mass throughout. Molecular weight is unitless, and molar mass has units of grams per mole.

Apparatus and Procedure. A schematic diagram of the high-pressure system used for the adsorption measurements is shown in Figure 1. Silicon wafers were cut into proper sizes and washed with tetrahydrofuran, piranha solution (50:50 mixture of H_2O_2 and H_2SO_4), deionized water, and acetone. PS was spin-coated onto the wafers, and the thickness of the PS layer was measured by variable-angle spectroscopic ellipsometry (VASE; J. A. Woolam Co., Inc., WVASE32). The thickness of the PS layer was approximately 130−170 nm. The PS-coated specimens were then placed in the high-pressure vessel with a certain amount of block copolymer and a magnetic stir bar. The block copolymer and the stir bar were placed at the bottom of the vessel, and the specimens were stacked on a shelf made of a Teflon sheet. To prevent the deposition of the block copolymer on the PS surface by gravity, the specimens were faced downward. After the samples were loaded, the vessel and the valve system were flushed with carbon dioxide several times. Once the temperature of the oven reached a set temperature, carbon dioxide was charged into the pressure vessel and the contents were stirred. The vessel was depressurized in a controlled fashion after prescribed adsorption times by adjusting a bleed valve to vent solvent as shown in Figure 1. The depressurization period (DP) is simply defined as the time required to bleed pressure off of the system.

Angle-Dependent X-ray Photoelectron Spectroscopy. In ADXPS experiments, photoelectrons emitted from the substrate are detected at several different takeoff angles, θ, with respect to the surface normal. The kinetic energy of the escaping electrons is related to their binding energy and is thus specific for a particular atom and core level. If the concentration depth profile for a particular atom, i, is $f_i(x)$, the angle-dependent photoelectron intensity, $I_i(\theta)$, can be expressed as

$$I_i(\theta) \propto \int_0^{\infty} f_i(x)\, e^{-(x/\lambda_i)(\sin\theta)}\, dx \tag{1}$$

where x is the depth from the surface and λ_i is the mean free path of electrons in the matrix. ADXPS data are normally reported as an integral-average atomic concentration, $N_i(\theta)$, defined as

$$N_i(\theta) = 100(I_i(\theta)/S_i)/\sum_k (I_k(\theta)/S_k) \tag{2}$$

where S_i are sensitivity factors. Because ADXPS does not directly furnish the actual atomic concentration depth profile represented by $f_i(x)$, a model for $f_i(x)$ must be developed and inserted into (1) and (2) to obtain model values for $N_i(\theta)$. The model values are then compared to the experimental $N_i(\theta)$ values to optimize parameters used in $f_i(x)$. The sampling depth of ADXPS, approximated as $3\lambda_i \cos\theta$, is typically in the range of 1−10 nm.

Results and Discussion

The procedure for forming thin block copolymer films is very simple: the substrate (PS) and a small amount of P(S-*b*-DMS) block copolymer are placed in a pressure vessel, the vessel is charged with supercritical carbon dioxide, and the copolymer film forms spontaneously on

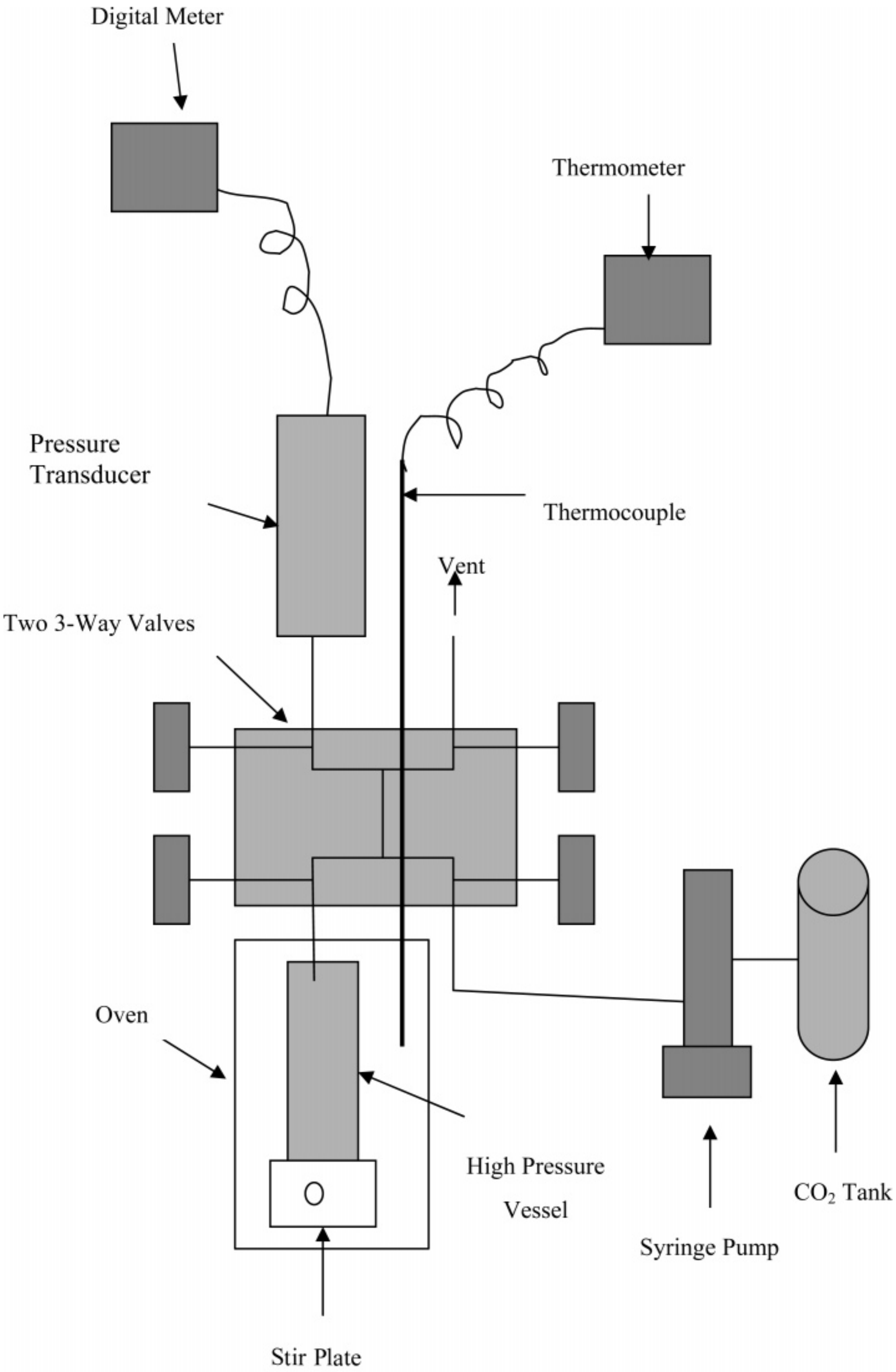

Figure 1. Schematic diagram of the adsorption experiment setup.

the polymeric substrate. The driving force for spontaneous film formation is the reduction of interfacial tension provided when the block copolymer adsorbs at the interface between the supercritical fluid and the polymeric substrate. As the PDMS block is soluble in $scCO_2$ whereas the PS block is not, it is expected that the copolymer forms a monolayer at the interface with the PS block mixing with the swollen PS substrate and the PDMS block facing the $scCO_2$ phase. When the pressure is reduced to flash off CO_2, the copolymer is expected to retain a bilayer structure at the surface of the PS substrate, presenting a surface layer of essentially pure PDMS, a structure that is well-known for PDMS copolymers adsorbed onto polymeric substrates.[33] The purpose of this study is to investigate the structure of P(S-*b*-DMS) block copolymers deposited onto PS substrates by adsorption from $scCO_2$, and how the structure depends on the pressure, the overall concentration of block copolymer charged into the pressure cell, the depressurization rate or period, and the temperature.

The actual mechanism of the adsorption process is not well understood at the present time and is beyond the scope of the present work. Initial attempts to understand the process of film formation have not been successful. For example, we have been unable to directly determine the solubility of the block copolymer in $scCO_2$ using available instrumentation. We do know that the solubility is extremely low, because we cannot detect a DLS signal using a special high-pressure cell we have developed. The copolymers are expected to form micelles[22–30] in $scCO_2$; however, since we are unable to measure a DLS signal, we cannot determine the nature of the dissolved species. Techniques such as small-angle neutron scattering or fluorescence spectroscopy on labeled copolymers might be able to determine solubility as well as the physical structure of the "dissolved copolymer", but such measurements have not yet been performed and the concentration is very low. We thus restrict the present analysis to the structure of the adsorbed layers and their dependence on processing parameters.

The first task in analyzing the structure of adsorbed block copolymer layers was to examine the morphology of the modified substrate surfaces to determine whether they were rendered rough or porous by treatment with $scCO_2$. Previous studies of $scCO_2$-treated PS substrates[21] reported the formation of micrometer-sized holes after isotropic swelling. Scanning electron micrographs of the block copolymer modified surfaces (not shown), however, were rather featureless, indicating that macroscopic pores are not present. The absence of surface pores in the block copolymer modified surfaces may be related to the thin film geometry, which constrains the swelling to be one-dimensional in character. Alternatively, the low surface tension of the block copolymers may lead to coalescence of gas bubbles in the same way that silicones are used as defoaming agents. In separate studies we have found that porous electrospun fibers of polystyrene also lose much of their porosity when treated with a surface-active block copolymer dissolved in $scCO_2$.[34] The absence of surface porosity is important because surface roughness complicates subsequent analysis of surface properties. Because the surfaces are smooth and continuous in nature, techniques such as contact angle measurements and ADXPS can be applied quantitatively to interrogate the surface.

The effects of P(S2.7-*b*-DMS2.8) adsorption on the surface tension of the modified PS substrates were characterized by water contact angle measurements under ambient conditions after depressurization. Water contact angle measurements are a convenient probe of surface tension and surface composition for this system because of the large surface tension difference between PDMS (20.4 mJ/m^2)[35] and PS (40.7mJ/m^2).[1] The contact angle of water on the virgin PS surface was determined to be 92.0 ± 0.4° at room temperature. The contact angle of water on a PDMS homopolymer of molecular weight equivalent to that of the PDMS copolymer sequence could not be directly measured because PDMS is a liquid under these conditions; however, the advancing contact angle on high molecular weight PDMS has been reported to be 112°.[36] Water contact angles were measured for modified substrates as a function of adsorption pressure, DP, adsorption temperature, overall block copolymer concentration, and residence time.

The influence of pressure on the water contact angle (i.e., adsorption isotherm) of P(S2.7-*b*-DMS2.8) is shown in Figure 2a for two different depressurization periods at an adsorption temperature of 50 °C. The contact angle increases markedly between adsorption pressures of 10 and 20 MPa, and asymptotically approaches a value of 107°. The data indicate that the surface is completely covered with an essentially pure PDMS layer at pressures above about 20MPa. The asymptotic water contact angle is slightly lower than the cited literature values because the latter are advancing contact angles and the current data are equilibrium contact angles. In a separate study,[37] we found that the solubility of PDMS homopolymers also increases sharply in the pressure region between 10 and 20 MPa, suggesting that the surface adsorption isotherm correlates strongly with the solubility of the $scCO_2$-philic block of the copolymer. The rate of depressurization reflected by the depressurization period, adsorption temperature, and residence time did not affect the adsorption behavior to any significant extent (data not shown for brevity).

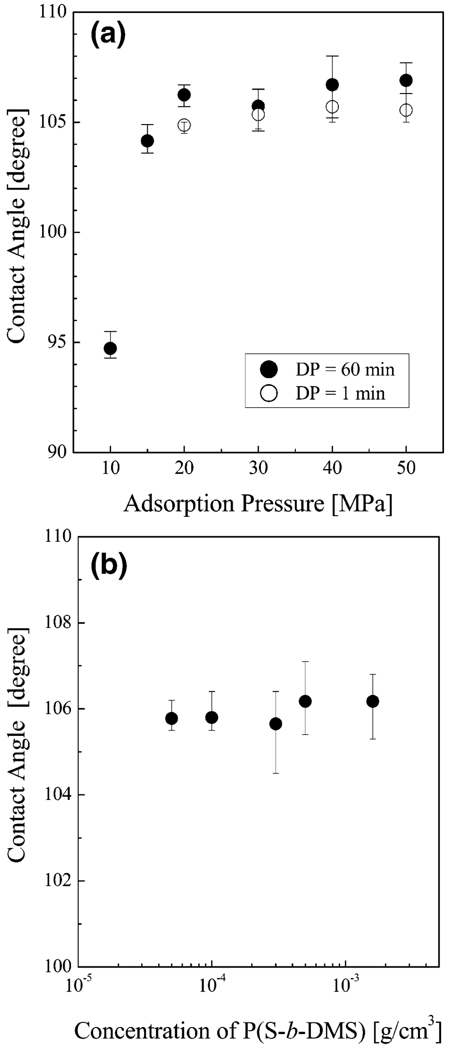

Figure 2. (a) Effect of adsorption pressure on the contact angle of a modified surface (T = 50 °C, t = 20 h, $c = 1.0 \times 10^{-4}$ g/cm^3). (b) Effect of block copolymer concentration on the contact angle of a modified surface (T = 50 °C, P = 50 MPa, DP = 60 min, t = 20 h).

The effect of the overall block copolymer concentration in the pressure chamber on the contact angle for modified surfaces is shown in Figure 2b. It should be noted that the overall concentration is not necessarily the true concentration of soluble block copolymer and that we have no independent means at present of determining the solubility of the block copolymer in $scCO_2$, in part because the solubility is very low. The data do illustrate, however, that the supercritical fluid coating method is extremely efficient, with concentrations as low as 5×10^{-4} g/cm^3 producing a continuous PDMS layer on the substrate. Experimental measurements at even lower copolymer concentrations unfortunately did not produce reliable results due to the difficulty in cleaning the pressure chamber. Even though

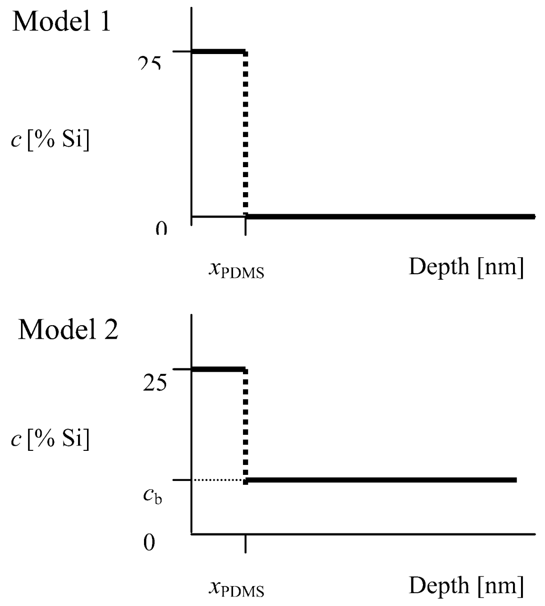

Figure 3. Concentration distribution models for ADXPS.

the high-pressure vessel and its valve system were repeatedly washed with several solvents including tetrahydrofuran, methanol, toluene, acetone, and $scCO_2$, a small amount of residual block copolymer remained on the walls of the chamber and was found to influence the adsorption behavior at the lower concentrations. The data also suggest that the solubility of block copolymer, most likely governed by the critical micelle concentration, is less than 4×10^{-4} g/cm^3 under these conditions, since higher concentrations do not increase adsorption. Saturation of block copolymer surface adsorption isotherms in this manner is usually interpreted as being associated with micelle formation.[1,38]

The previous contact angle measurements indicated that the substrate is covered by a continuous PDMS layer, but did not provide any structural information such as the thickness of the layer. ADXPS measurements were therefore used to estimate the thickness of the PDMS surface layer and the concentration of the underlying near-surface region. The concentration of the region just below the PDMS surface layer is also of interest because carbon dioxide is expected to plasticize and swell the PS substrate. It is possible that the supercritical fluid treatment causes impregnation of block copolymer within the bulk of the PS substrate, an undesirable outcome if it wastes block copolymer. A low molecular weight block copolymer was studied so that the PDMS surface layer would be thinner than the probe depth of ADXPS, allowing for subsequent quantitative determination of the composition underlying the PDMS surface layer.

A physically realistic model is required for interpretation of the ADXPS results due to the integral nature of the technique as embodied in (1). The simplest surface structure possible corresponds to the case where P(S-*b*-DMS) molecules do not penetrate into the PS substrate but self-assemble to form a pure PDMS surface layer as represented in Figure 3 by model 1. Model 1 has only one parameter, x_{PDMS}, which is the outermost PDMS layer thickness. A second more complex situation, represented by model 2, arises when the concentration of block copolymer below the surface is finite due to the presence of impregnated block copolymer. In this case, an additional model parameter is required, c_b, the silicon atomic concentration in the bulk phase.

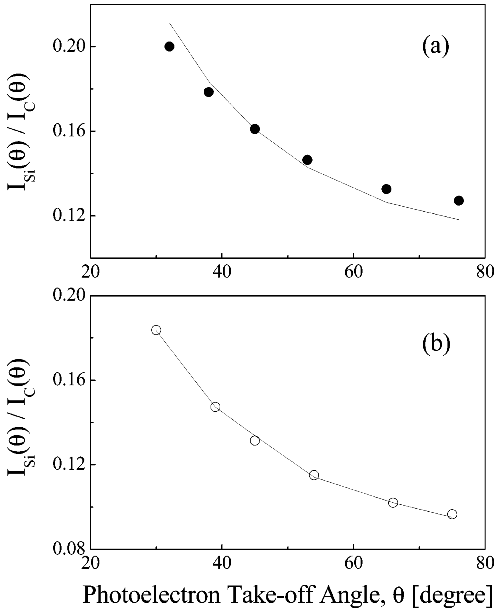

Figure 4. Typical fitting of ADXPS data by using model 1 (T = 50 °C, P = 50 MPa): (a) DP = 60 min, (b) DP = 1 min.

ADXPS experiments provide experimental measurement of the silicon 2p to carbon 1s photoelectron intensity ratios, $I_{Si}(\theta)/I_C(\theta)$, as a function of the photoelectron takeoff angle, θ; the latter is related to the integral probe depth. The intensity ratios were used to compare experimental ADXPS data to the predictions of the two models by application of (1). The model parameter(s) were adjusted until best fits were determined by using both Levenberg–Marquardt iteration and a simplex algorithm furnished by Origin software. The mean free paths for carbon 1s ($\lambda_{C1s} = 3.8$ nm) and silicon 2p ($\lambda_{Si2p} = 4.3$ nm) photoelectrons[39] were assumed constant irrespective of the substrate composition.

Model 1 provides an excellent representation of the ADXPS data for DP = 1 min for all photoelectron takeoff angles as shown in Figure 4. The model does not reproduce the data well, however, when the depressurization period is 60 min. The model with an optimized x_{PDMS} value provides reasonable agreement for photoelectron takeoff angles near 45°, but overestimates the silicon concentration near the surface and underestimates the silicon content of the bulk. Model 2 produces excellent representation of the data in all cases as shown in Figure 5, and therefore will be applied to characterize the structure of the block copolymer films.

The fit parameters obtained by applying model 2 to the ADXPS data are shown in Figures 6 and 7. The value of x_{PDMS} increases rapidly between the adsorption pressures of 15 and 20 MPa, and then approaches an asymptotic value of about 1.5 nm for higher pressures as shown in Figure 6a. This trend is consistent with the rapid increase in contact angle observed over the same pressure range. The value for x_{PDMS} (0.83 nm) at 15 MPa is probably an overestimate because the value of c_b for this fit was found to be negative, a physically unrealistic result (see Figure 7a). In this case, the value of c_b can be constrained to zero by applying model 1, which yields a more appropriate value of 0.77 nm for x_{PDMS}. For adsorption pressures above 20 MPa, x_{PDMS} approached an asymptotic value of 1.5 nm, implying saturation of

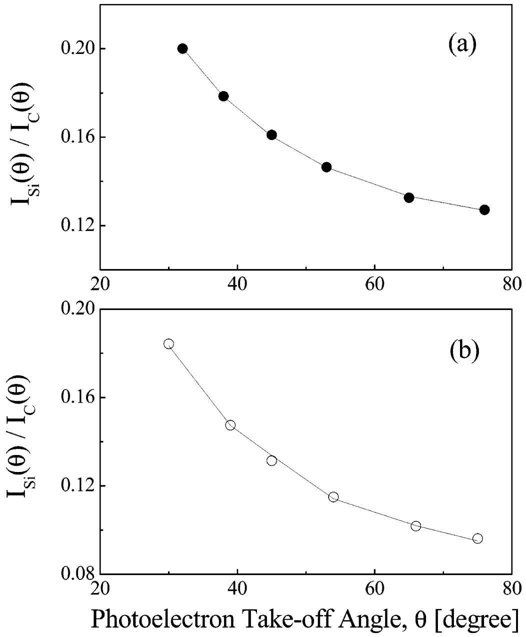

Figure 5. Typical fitting of ADXPS data by using model 2 (T = 50 °C, P = 50 MPa): (a) DP = 60 min, (b) DP = 1 min.

the adsorption isotherm. A longer depressurization period produced only slightly larger x_{PDMS} values.

The thickness of the PDMS layer obtained by ADXPS analysis can be compared to that obtained by theoretical treatments of block copolymer brushes to ascertain the configuration of copolymer chains in the PDMS layer. A theoretical treatment examining the thickness of block copolymer layers at the interface between incompatible homopolymers was presented by Leibler.[4] The thickness of a saturated brush for the dry brush case was predicted to be

$$L_i/a \cong N_i^{2/3}(\gamma_o a^2/3kT)^{1/3} \tag{3}$$

where L_i is the brush thickness, a is the statistical segment length of a block, N_i is the degree of polymerization of the block, γ_o $(=(kT/a^2)(\chi/6)^{1/2})$ is the interfacial tension between the immiscible homopolymers, k is the Boltzmann constant, and T is temperature (K). The values for a and γ_o were calculated as 1.7 nm[40] and 0.3 mN/m,[41] respectively. The thickness of the dry brush at a PS−PDMS interface is predicted to be 7.6 nm from this formula. Adsorption of block copolymer micelles from a selective solvent onto a solid plane produces a brush thickness given by[6]

$$L_{\mathrm{B}} = N_{\mathrm{B}}^{3/5} a N_{\mathrm{A}}^{4/25} (\gamma_{\mathrm{AS}} a^2/kT)^{6/25} \tag{4}$$

where γ_{AS} is the interfacial tension between the anchoring block and solvent. If γ_{AS} is assumed to be 1−2.5 mN/m,[31] the PDMS brush thickness is estimated to be 4−5 nm. Finally, the theoretical maximum thickness is comparable to that of fully extended PDMS, 5.0 nm, with a 6_1 2-fold helical conformation.[42,43] The various estimates above demonstrate that the block copolymer layer produced by supercritical fluid deposition does not behave as a dry brush. The PDMS chains do not appear to be stretched to any extent as the equilibrium PDMS layer thickness of 1.5 nm is much smaller than that predicted by dry brush theories and is similar in magnitude to the unperturbed radius of gyration of the PDMS block, estimated to be 1.7 nm. The copolymer brushes produced by adsorption from $scCO_2$ therefore behave as wet brushes with chains assuming nearly unperturbed dimensions.

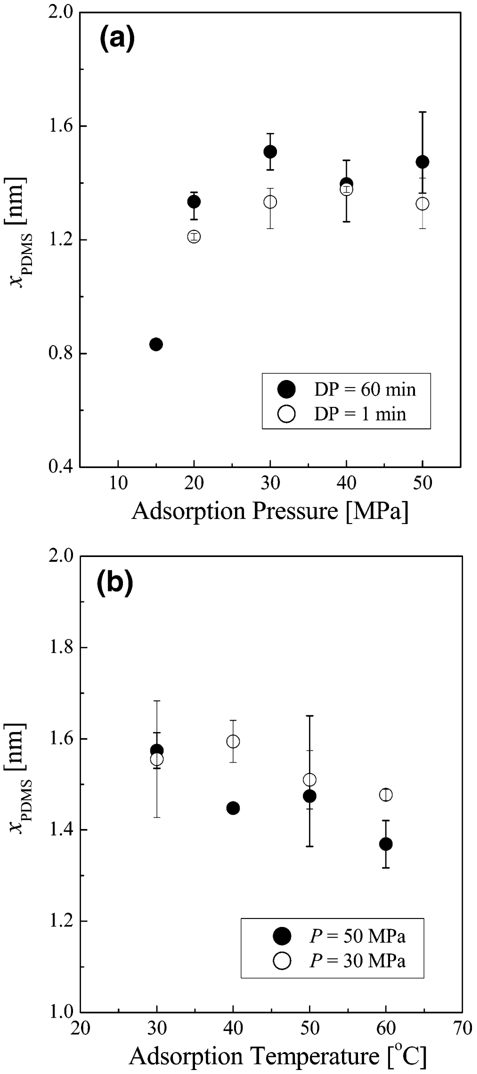

Figure 6. (a) Effect of adsorption pressure on x_{PDMS} (T = 50 °C, model 2). (b) Effect of adsorption temperature on x_{PDMS} (DP = 60 min, model 2).

The adsorption temperature had a small effect on formation of the surface PDMS layer as shown in Figure 6b. The magnitude of x_{PDMS} decreased slightly as the adsorption temperature increased at constant pressures. Increasing the pressure from 30 to 50 MPa did not change x_{PDMS} as these pressures are already in the region where asymptotic behavior is observed.

The effect of adsorption pressure on c_{b} is illustrated in Figure 7a. At pressures of 30 MPa and lower, the bulk concentration is effectively zero. The negative values obtained for the lowest pressure are physically unrealistic, in which case model 1 is more appropriate as discussed earlier. At higher pressures there is a jump in solubility to a value of about 2%, consistent with the expected increase in PS swelling and improvement in solvent quality for PDMS at the higher pressures. $scCO_2$ was found to act as a Θ solvent at 30 MPa and 50 °C for low molecular weight PDMS,[37] and a Θ pressure of ca. 40 MPa at 70 °C was reported for 22500 Da PDMS.[12] The sudden increase of c_{b} therefore may be related to a sudden increase in either block copolymer solubility or substrate swelling, factors which in turn would drive

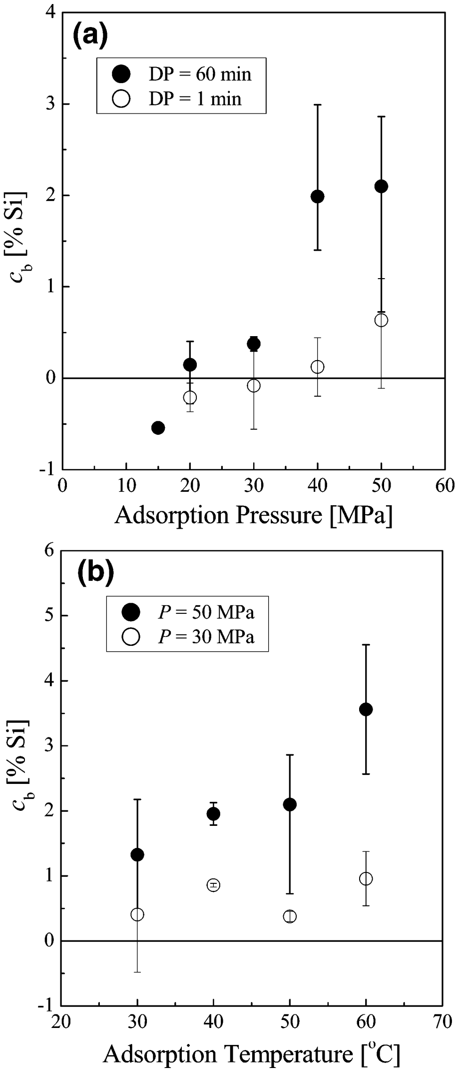

Figure 7. (a) Effect of adsorption pressure on c_b ($T = 50$ °C, model 2). (b) Effect of adsorption temperature on c_b (DP = 60 min, model 2).

additional copolymer into the swollen PS substrate. At first glance, the bulk concentration of block copolymer appears to be much smaller when a short depressurization period is employed. The error bars are large, however, and except for the data at 40MPa are not statistically different. The data therefore do not allow for any conclusions to be made regarding the influence of depressurization period on the bulk copolymer content.

The block copolymer concentration in the PS substrate increases continuously with adsorption temperature at 50 MPa, while the concentration is insensitive to temperature at 30 MPa as shown in Figure 7b. The most likely explanation for this behavior is related to solvent quality. At the lower pressure, the PDMS block is in a near-Θ state, and the solubility would be expected to be only weakly dependent on temperature. At the higher pressure, the $scCO_2$ is a better solvent and is expected to show a stronger dependence of solubility on temperature. The largest value of c_b obtained, 3.5% Si at 50 MPa and 60 °C, corresponds to an overall substrate composition of 25% PDMS and 75% PS. Since the block copolymer was approximately symmetric, this result indicates that the bulk phase contained about 50% block copolymer and 50% PS from the substrate. A high bulk concentration implies that considerable impregnation of copolymer into the bulk substrate may occur at high pressures, conditions for which swelling of the PS substrate and block copolymer solubility are highest.

Summary

Monolayer and submonolayer P(S-*b*-DMS) block copolymer films were successfully deposited onto PS substrates by adsorption from supercritical carbon dioxide. The films form spontaneously when block copolymer and the substrate are placed in a pressure vessel and the vessel is charged with $scCO_2$. Water contact angles on the modified PS substrates were 106–107° for pressures as low as 20 MPa and block copolymer concentrations as low as 5×10^{-4} g/cm^3, implying that the copolymers form a bilayer surface structure presenting a surface layer of essentially pure PDMS under these conditions. Angle-dependent XPS was used to estimate the thickness of the PDMS layer on the modified surface and the concentration of copolymer dissolved within the substrate. The saturation thickness of the PDMS layer was approximately 1.5 nm, consistent with chains that are nearly unperturbed in dimension. The concentration of block copolymer in the substrate was found to increase with adsorption pressure and temperature. These experiments illustrate that supercritical fluid deposition is a simple yet efficient process for coating monolayers of surface-active block copolymers onto polymeric substrates.

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