

# Structures of Thin Ionomer Films in Solvent Mixtures

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We have used neutron reflectivity to measure the concentration profiles of polystyrenesulfonated acid (PSSA<sub>x</sub>) films with three different degrees of sulfonation ( $x = 3.4\%$ ,  $12.8\%$ , and  $27.0\%$ ) in water,  $\text{CCl}_4$ , and a mixture of the two solvents. The data show that, except for the  $x = 3.4\%$  films where  $\text{CCl}_4$  is a good solvent, the largest degree of swelling occurred in the mixed solvent. Contrast matching the water to the polymer layer enabled us to profile the  $\text{CCl}_4$  concentration. The results showed that  $\text{CCl}_4$  and water were mixed within the polymer film in a ratio of 1:2 and 1:4 for 12.8 mol % and 27.0 mol % PSSA, respectively. Self-consistent-field calculations indicated that the number of adsorbed sulfonated blocks scales linearly with the degree of sulfonation. Using the interaction parameters between the PS and SA blocks obtained by fitting to the data in pure solvents, excellent agreement is obtained for the profiles of the polymer and the solvent mixtures for all values of  $x$ .

## Introduction

There has recently been much interest in polyelectrolyte copolymers since they have been shown to have numerous applications as biomimetic or electronic materials.<sup>1,2</sup> In particular, thin films of these polymers have been used as coatings to control the adhesion of cells<sup>3a</sup> or in producing electronic devices.<sup>3b</sup> In all these cases the polyelectrolyte coatings were used in solvents or their mixtures under

conditions of varying pH or dielectric properties. To know the function of these polyelectrolyte components, it is important to first understand their interactions with the solvent media.<sup>4</sup> Most theoretical studies to date have concentrated on the conformation of polyelectrolyte brushes.<sup>5–7</sup> Since these brushes are very difficult to synthesize,<sup>8</sup> only limited experimental results<sup>9,10</sup> have been reported. In addition, the films most relevant for practical applications have been random copolymers where even less is known about the conformation in thin films in contact with one or more solvents.

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**Table 1. Characterization of PSSA<sub>x</sub> Used in This Study**

designation	<i>x</i> [mol %]	<i>M<sub>w</sub></i> [g/mol]	<i>d</i> <sub>0</sub> (air) [Å]
dPSSA <sub>27.0%</sub>	27.0	150K	120
hPSSA <sub>23.0%</sub>	23.0	200K	170
hPSSA <sub>12.0%</sub>	12.0	169K	220
dPSSA <sub>12.8%</sub>	12.8	169K	100
dPSSA <sub>3.4%</sub>	3.4	169K	126

In this paper we therefore have chosen to present a comprehensive study of the conformation in different solvents of the random polyelectrolyte copolymer, sulfonated polystyrene (PSSA<sub>*x*</sub>) where *x* is the degree of sulfonation. We are able to show that with a simple annealing procedure irreversible adsorption to silicon substrates can be achieved. This method eliminates the need for complicated chemical procedures involved in grafting brushes to the surface and makes it practical to perform large-scale studies.

We first present the results where the films are swollen in good solvents, and from their thickness we use self-consistent-field theory (SCF) to extract the number of segments adsorbed irreversibly to the substrate as a function of degree of sulfonation. We then determine the profiles in water as a function of pH and obtain the solubility parameters for various degrees of sulfonation. Finally, we measure the profiles in mixtures of organic solvents and water, which we show to produce the largest amount of swelling. In contrast to theoretical predictions for fully charged brushes, no segregation of the solvents to interfaces is observed. The results are therefore interpreted as being due to the polymer acting as an effective surfactant inducing miscibility of the solvents.

### Experimental Section

Monodisperse (*M<sub>w</sub>/M<sub>n</sub>* < 1.07) random polystyrenesulfonated acid ((C<sub>8</sub>H<sub>8</sub>)<sub>*n*</sub>-(C<sub>8</sub>H<sub>7</sub>-SO<sub>3</sub>-H<sup>+</sup>)<sub>*m*</sub> or (C<sub>8</sub>D<sub>8</sub>)<sub>*n*</sub>-(C<sub>8</sub>D<sub>7</sub>-SO<sub>3</sub>-H<sup>+</sup>)<sub>*m*</sub>) copolymer, designated as PSSA<sub>*x*</sub>, of *M<sub>w</sub>* = 150–200K g/mol with degree of sulfonation, *x* (~*m*/(*n* + *m*)), ranging from 3.4 to 27 mol %, were synthesized using the procedures described in ref 11. Both hydrogenated (hPSSA<sub>*x*</sub>) and deuterated (dPSSA<sub>*x*</sub>) forms of PSSA<sub>*x*</sub> were synthesized in order to have the option of contrast matching in the neutron studies. The characteristics of the polymers used are summarized in Table 1. The sulfur content was determined by Dietert sulfur analysis.

Si wafers (3 in. diameter) were cleaned in saturated chromium trioxide (CrO<sub>3</sub>) in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and reoxidized to produce a hydrophilic surface using a modified Shiraki technique.<sup>12</sup> The samples were prepared by dissolving the ionomers into dimethylformamide (DMF) at a concentration of 1% (w/v) polymer and spun-cast at 2500 rpm onto the silicon wafers. The initial film thickness, ca. 200 Å, was monitored by ellipsometry (AutoEL-II). The samples were annealed for 24 h in a vacuum of *P* ~ 10<sup>-6</sup> mbar at 175 °C,<sup>13</sup> well above the glass transition temperature of polystyrene. The samples were rinsed in toluene after annealing, and a layer was found to be irreversibly adsorbed.<sup>13</sup> The thickness was usually about 90–140 Å, which is approximately 1*R<sub>g</sub>* of the *M<sub>w</sub>* = 160 × 10<sup>3</sup> PSSA<sub>*x*</sub>. The thickness of each layer was measured before and after each NR experiment to check whether any polymer loss had occurred during the experimental procedure.

The solvents studied were analytical grade CCl<sub>4</sub>, which is a good solvent for PS, and distilled and deionized water of pH = 2, 4, and 7. The pH was varied by the addition of hydrochloric acid (HCl). In the case of solvent mixtures, contrast-matching

techniques<sup>14</sup> were used. First, to determine the structure of polymers in the mixed solvents, the water was contrast matched to CCl<sub>4</sub> (SLD<sub>H<sub>2</sub>O</sub> = 2.80 × 10<sup>6</sup> Å<sup>-2</sup>). This was accomplished by mixing H<sub>2</sub>O (SLD<sub>H<sub>2</sub>O</sub> = -0.56 × 10<sup>6</sup> Å<sup>-2</sup>) and D<sub>2</sub>O (SLD<sub>D<sub>2</sub>O</sub> = 6.35 × 10<sup>6</sup> Å<sup>-2</sup>) where the average scattering length density, ⟨SLD<sub>H<sub>2</sub>O/D<sub>2</sub>O</sub>⟩, of the contrast matched water is given by<sup>14a</sup>

$$\langle \text{SLD}_{\text{H}_2\text{O}/\text{D}_2\text{O}} \rangle = \phi_{\text{H}_2\text{O}} \text{SLD}_{\text{H}_2\text{O}} + (1 - \phi_{\text{H}_2\text{O}}) \text{SLD}_{\text{D}_2\text{O}} \quad (1)$$

where  $\phi_{\text{H}_2\text{O}}$  is the volume fraction of H<sub>2</sub>O in the mixture. In this case, the contrast between CCl<sub>4</sub> and the contrast matched water is eliminated, and the scattering intensity is due to the interfaces of the solvent mixture (SLD = 2.80 × 10<sup>6</sup> Å<sup>-2</sup>) and dPSSA<sub>*x*</sub> (~(5.70–6.12) × 10<sup>6</sup> Å<sup>-2</sup>) and the Si substrate (SLD<sub>SiO</sub> = 2.96 × 10<sup>6</sup> Å<sup>-2</sup>) and hPSSA<sub>*x*</sub>. To profile the CCl<sub>4</sub> concentration in the mixed solvent sample, a mixture of H<sub>2</sub>O and D<sub>2</sub>O was prepared to match the scattering contrast of hPSSA<sub>*x*</sub> (~1.41 × 10<sup>6</sup> Å<sup>-2</sup>). In this case, the CCl<sub>4</sub> profile near the hPSSA<sub>*x*</sub> layer can be obtained since CCl<sub>4</sub> becomes the highest SLD component in the system.

Specular neutron reflectivity was performed with the fixed wavelength (λ = 4.76 Å) reflectometer, NG7 at the National Institute of Standards and Technology (Gaithersburg, MD) and on the H-9A reflectometer (λ = 4.16 Å) at the Brookhaven National Laboratory (Upton, NY) High Flux Beam Reactor. The slit settings were adjusted to fix the resolution at a constant value of *dq/q* = 0.03 and 0.02 for NG7 and H-9A, respectively. Details of the NR experimental setup and data acquisition procedures are described elsewhere.<sup>15</sup> The specular reflectivity was measured as a function of scattering wave-vector transfer *q<sub>z</sub>* = 4π/λ sin(θ), where θ is the incident angle. The incident beam entered and reflected through the silicon substrate.

The thickness of the film was first measured by reflectivity in air before the immersion. The liquid cell used consisted of spherical Teflon block with a 1 mm groove machined for the solvent. The groove gives an 8.3 cm<sup>3</sup> volume space for a solvent reservoir. The cell was sealed by pressing the sample side of 1/2 in. thick Si slab against the groove. The solvent was then injected into the groove through one port while another port allowed trapped air to be removed. To check whether air bubbles are trapped in the cell during the injection, many test runs using a transparent glass cover instead of the silicon slab were performed.

The scattering geometry used is shown in Figure 1, where the neutron beam is incident on the polymer interface through the Si wafer and the momentum transfer vector is positive. For the mixed solvent case care was taken that the organic solvent, which is a good solvent for major segments of the ionomer, not be adjacent to the polymer surface unless it was preferentially adsorbed there. Since the specific gravity of the organic solvent was greater than 1 (*d*<sub>CCl<sub>4</sub></sub><sup>25°C</sup> > *d*<sub>H<sub>2</sub>O</sub><sup>25°C</sup>), only an aqueous layer can directly contact the sample surface in the geometry shown in Figure 1.

To explain the general behavior depending on the film thickness *d* and the roughnesses (*σ*), the Born approximation can be used.<sup>15</sup> The reflectivity *R<sub>F</sub>*(*q<sub>z</sub>*) is given by

$$R(q_z) \propto R_F \left| \int \frac{d\text{SLD}(z)}{dz} \exp(-iq_z z) dz \right|^2 \quad (2)$$

where *R<sub>F</sub>* is the Fresnel reflectivity at an infinitely sharp interface, which can be approximated by (*q<sub>z</sub>*/*q<sub>z</sub>*)<sup>4</sup> at high *q<sub>z</sub>* region. *d*SLD(*z*)/*d**z* is the gradient of SLD of the sample along the surface normal. The sharp interfaces are smeared by rms roughness, *σ*, which is given by convoluting the infinitely sharp profile with a Gaussian smoothing function. The indices of refraction of "deuterated" PSSA are quite different from those of Si substrate or solvent media. For example, neglecting absorption, the calculated indices of refraction *n* = 1 - δ with dispersion δ of dPSSA<sub>3.4%</sub>, Si, CCl<sub>4</sub>, and H<sub>2</sub>O are *n*<sub>dPSSA3.4%</sub> = 1 - 22.07 × 10<sup>-6</sup>,

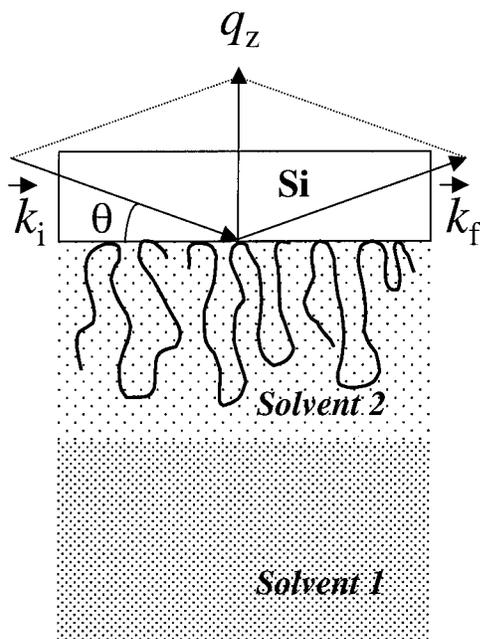
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**Figure 1.** Scattering geometry of specular NR. The momentum vector transfer is defined by  $q_z = k_r - k_i$ , where  $k_i$  and  $k_r$  are the incident and exit wave vectors. In the case of a solvent mixture (in text solvent **1** =  $\text{CCl}_4$ , solvent **2** = water), the lower density medium (i.e., water) is always contacting with the polymer layer.

$n_{\text{Si}} = 1 - 7.475 \times 10^{-6}$ ,  $n_{\text{CCl}_4} = 1 - 10.09 \times 10^{-6}$ , and  $n_{\text{H}_2\text{O}} = 1 + 2.019 \times 10^{-6}$ , respectively. The  $\delta$  is given linearly in terms of the SLD by  $\delta = \lambda^2 \text{SLD} / 2\pi$ , where  $\lambda$  is the wavelength of neutron beam. Therefore, the reflected intensity at the interfaces is sensitive to the SLD. In this study, NR shows enough resolution to determine the changes of structures of the PSSA ionomer layer within a few angstroms. The goodness of fits was evaluated by a least-squares algorithm. We systematically varied and then optimized fitting parameters SLD,  $d$ , and  $\chi^2$  until  $\chi^2$  was minimized.

**Self-Consistent-Field Calculation (SCF).** The configurations of the random copolymer brush in pure and mixed solvents were modeled using SCF theory.<sup>16a</sup> The only parameter introduced was the Flory–Huggins parameters ( $\chi$ ) between the substrate, solvents, **PS**, and **SA** segments, where **PS** and **SA** denote two monomer species, in this case styrene and sulfonated monomers. We first examined the structure as a function of the sulfonation level and performed calculations for three different fractions of sulfonated segments: 25.6, 12.0, and 3.8 mol %. The effect of randomness was incorporated into the SCF model developed by Gersappe et al.<sup>16b</sup> Each monomer has a finite probability of being either a **PS** or **SA** site. Thus, the model introduces randomness, where the ensemble of sequence distributions in the system is allowed to fluctuate. The random copolymer was designed by a combination of three different structures of unit blocks:  $[\text{PS}_3\text{SA}_1]_n$ ,  $[\text{PS}_8\text{SA}_1]_n$ , and  $[\text{PS}_{33}\text{SA}_1]_n$ , where  $n$  is the number of repeating units. Therefore, the degree of sulfonation was varied by choosing different combinations of the three unit blocks while keeping the total polymerization index of the three copolymers constant. To model the greater affinity of monomer **SA** to the surface of the substrate, the Flory–Huggins interaction parameter between **SA** and the oxide covered substrate ( $\chi_{\text{SA-SiO}}$ ) was fixed at  $\chi_{\text{SA-SiO}} = -20$  in all calculations.<sup>17</sup> For pure solvents (designated **1** for organic and **2** for aqueous)—

monomer (**PS** or **SA**) interaction,  $\chi_{1\text{PS}}$  (or  $\chi_{2\text{PS}}$ ) and  $\chi_{1\text{SA}}$  (or  $\chi_{2\text{SA}}$ ) are considered. In the case of a mixed solvent, solvent components **1** and **2** are introduced simultaneously. We set the Flory–Huggins parameter between **1** and **2**,  $\chi_{12} = 3.5$ , to ensure the immiscibility of the two solvents.<sup>6</sup> To ensure that we are studying chains irreversibly stuck to the surface, one segment of monomer **SA** has been permanently fixed to the substrate.

The composition of **1** and **2** has been characterized by the amount of solvent **1**,  $\theta_1$ , which is given by  $\theta_1 = \int_0^L \phi_1(z) dz$ .  $\phi_1(z)$  is the volume fraction of solvent **1** in the system, and  $L$  is the size of the system in the direction perpendicular to the wall. In our system,  $\theta_1$  was varied from 0.1 to 9 to fit the experimental results, while the size was set at  $L = 50$ . The details of the modeling theory are described in other articles.<sup>6,16b</sup>

## Results and Discussion

**Neutron Reflectivity.** Parts a, b, and c of Figure 2 show the reflectivity data of the dPSSA<sub>3.4%</sub>, dPSSA<sub>12.8%</sub>, and dPSSA<sub>27.0%</sub>, respectively, in air (open circles) and three kinds of solvents (solid circles, water; open squares,  $\text{CCl}_4$ ; solid squares, water/ $\text{CCl}_4$  mixed solvents). The solid lines together with the symbols are the fits obtained by the corresponding volume fraction profiles, which are shown in Figure 2a', b', c'. The Fresnel reflectivities,  $R_F$ , at various media with an infinitely sharp interface were simulated, and the measured reflectivities,  $R$ , and fits were then normalized by the respective  $R_F$ . Therefore, the each data set in Figure 2 shows unique interference fringes, which contain only the damping factors due to the surface roughnesses and an oscillating term due to the film thickness without  $q^{-4}$  decay in eq 2.

First we discuss the layer structures of dPSSA<sub>3.4%</sub>. From the NR spectra in Figure 2a, one can see that only the profiles in air and water have well-defined Kiessig fringes. The solid line in Figure 2a' is the concentration profile of the adsorbed layer in air. After exposure to a solvent, we dry the sample at  $T = 90^\circ\text{C}$  for 3 h and then remeasured the thickness in air before immersion it in next solvent. The thickness of the layer, 126 Å or approximately  $1 R_g$ , remained unchanged. This implies that at least one segment has been irreversibly fixed to the substrate, and no chain loss occurred during the exposure to solvents. We believe this behavior is in analogy to the adsorption process by carboxyl acid in ref 18a. This irreversibly adsorbed layer was found only in samples that were sulfonated.<sup>18b</sup> Hence, the sulfonated group acts like a sticker where bonding occurs. The long dashed line corresponds to the concentration profile of dPSSA<sub>3.4%</sub> in water of pH = 4. One can see that the film thickens by 6 Å or less than 5%. Changing pH to either 2 or 7 does not affect significantly the thickness of the film as shown in Table 2. This is consistent with water being a poor solvent for this relatively low sulfonation polymer.

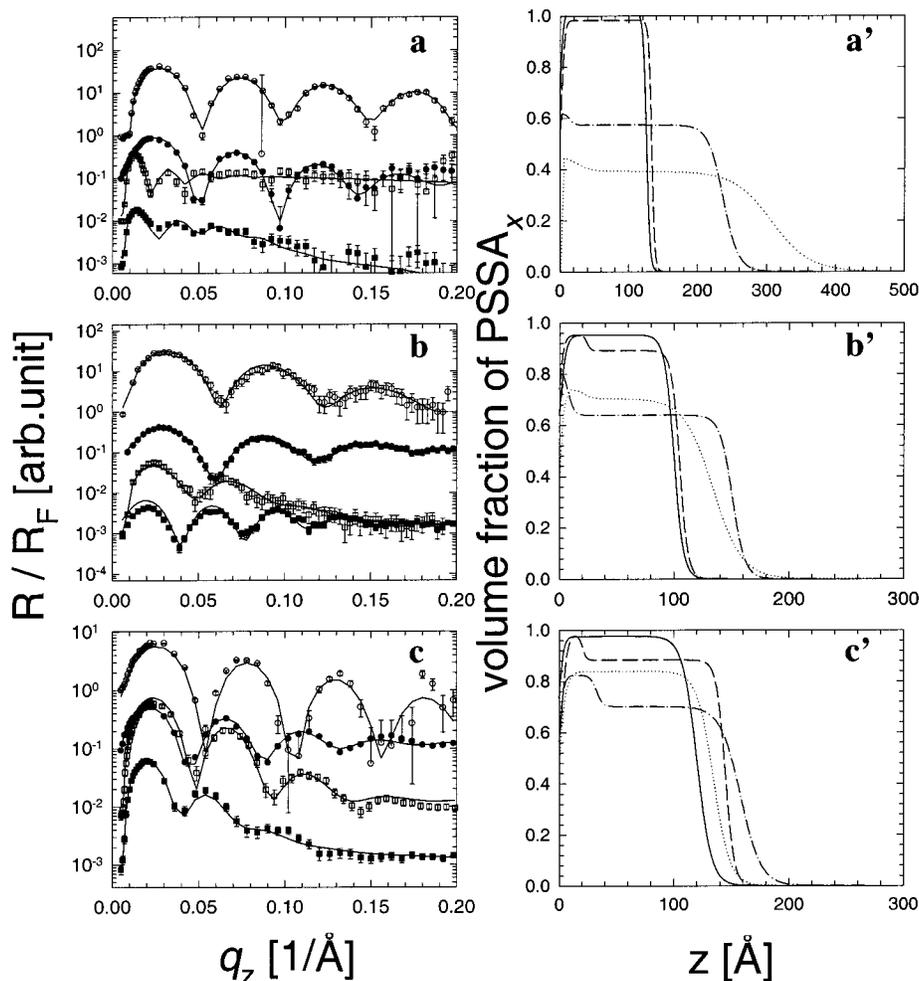
In contrast, the Kiessig fringes disappear in the reflectivity profile when  $\text{CCl}_4$  is introduced, indicating that the interfacial width has broadened. The dotted line in Figure 2a' is the model profile in  $\text{CCl}_4$ . For this low level of sulfonation,  $\text{CCl}_4$  is still a good solvent for this polymer. The thickness of the film is seen to swell to ca. 300 Å, and the profile has a parabolic-like form. This shape is qualitatively consistent with the Guiselin model<sup>19</sup> except that in this case not all monomers have equal probability

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(17) To describe the irreversible adsorption between the substrate and the sticky segments regardless of polymer–solvent interactions ( $\chi = 0.0$  and 3.0 for a good and poor solvent, respectively), we fix  $\chi_{\text{SA-SiO}} = -20$ . This value is larger than any other favorable parameter in the system.

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**Figure 2.** Neutron reflectivity data of (a) dPSSA<sub>3.4%</sub>, (b) dPSSA<sub>12.0%</sub>, and (c) dPSSA<sub>27.0%</sub> in air (○), water (●), CCl<sub>4</sub> (□), and a contrast matched water/CCl<sub>4</sub> mixture (■). The solid lines through the data are the best fits. The curves are shifted arbitrarily for clarity. (a', b', c') The corresponding concentration profiles are obtained from the fits of (a), (b), and (c), respectively. The *x*-axis *z* is taken from the substrate. The solvents are denoted as follows: (---) air, (—) water, (···) CCl<sub>4</sub>, (-·-·) water/CCl<sub>4</sub> mixture.

**Table 2. NR Fitting Parameters of DPSSA<sub>3.4%</sub> in Different pH Solutions**

pH	SLD ( $\times 10^{-6}$ )/ $\text{\AA}^{-2}$	$\sigma_1$ ( $\text{\AA}$ ) <sup>a</sup>	$d_1$ ( $\text{\AA}$ ) <sup>b</sup> $\pm$ 2
Aqueous			
2	6.11	8	127
4	5.92	10	130
7	6.07	11	129
Mixed with CCl <sub>4</sub>			
4	4.18	108	228
7	4.25	43	234

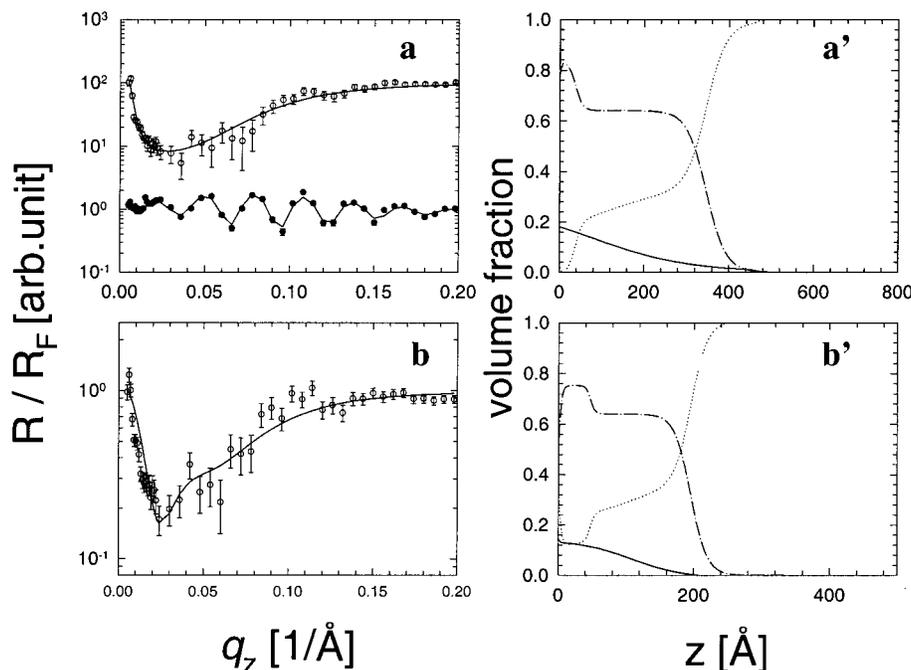
<sup>a</sup> Rms roughness at the solution/polymer interface. <sup>b</sup> The film thickness was  $d_0 = 126 \text{ \AA}$  before the immersion.

of being adsorbed; rather, only some of the sulfonated groups are irreversibly attached.<sup>18</sup> The exact profile, as well as the number of adsorbed sulfonated groups, will be discussed later.

The bottom reflectivity spectrum (solid squares) in Figure 2a corresponds to the in situ profile in mixed solvents, where water at pH = 4 and CCl<sub>4</sub> have been mixed at a ratio of 1:1 (v:v). From the data one can see that the interface is broad, indicating that the layer is still swollen. This profile differs slightly from that in CCl<sub>4</sub> in that the oscillation at low  $q$  is somewhat better defined. The model used for the fitting is shown as a dash-dot line in Figure 2a'. From the model we can see that even though the water is in contact with the polymer layer in this geometry, the layer remains swollen, indicating that CCl<sub>4</sub> may exist

within it. The main differences between this profile and the one in pure CCl<sub>4</sub> are that the thickness of the layer is somewhat smaller and the interfacial width is sharper than that of the layer in CCl<sub>4</sub> only.

In Figure 2b we show the reflectivity profiles obtained from the dPSSA layer with 12.8 mol % sulfonation. Comparing the spectra in air with that in water of pH = 4, we find that the oscillations decay more rapidly, and the Kiessig fringes have shifted to higher frequency. The model used to fit the data is shown in Figure 2b'. The overall layer thickness has now increased from 100 to 106  $\text{\AA}$ . It should be noted that the frequency of the oscillation is not uniform, and a two-layer model where a denser polymer layer exists near the SiO surface is needed to fit the data.<sup>20</sup> This type of model is similar to the one used by Tran et al.<sup>9</sup> and Perahia et al.<sup>21</sup> This extra layer was explained as being due to additional interactions between the PS monomers and the Si substrate, which became more probable as the "sticky" sections increased and the PS loops became smaller. The oscillation again disappears for the profile in CCl<sub>4</sub>, indicating that the layer is swollen and CCl<sub>4</sub> is still a good solvent at this sulfonation level. The bottom curve (solid squares) shows the in situ reflectivity curve in the mixed solvents. In comparison with the data of pure CCl<sub>4</sub> we see the interface with the solvent phase is much sharper and the frequency of the oscillations is higher, indicating that the layer is signifi-



**Figure 3.** (a) Neutron reflectivity data of hPSSA<sub>12.8%</sub> in a mixture of CCl<sub>4</sub> and the contrast matched water (SLD<sub>water</sub> = SLD<sub>hPSS12.8%</sub>) (○) and in D<sub>2</sub>O (●). The solid lines are the fits. The curves are shifted by  $1 \times 10^{-1}$  of  $R/R_F$  for clarity. (a') The concentration profile shows the proposed volume profiles of components from the fits. The profiles are denoted as follows: (---) CCl<sub>4</sub>, (···) water, (— · —) the proposed polymer profile, which is rescaled from the concentration profile of a 320 Å thick dPSSA<sub>12.8%</sub> in mixed solvents (dash-dot line in Figure 2b'). (b) NR data of hPSSA<sub>23.0%</sub> in a mixture of CCl<sub>4</sub> and the contrast matched water (SLD<sub>water</sub> = SLD<sub>hPSS23.0%</sub>) (○). The solid lines are the fits. (b') The proposed concentration profiles of components (---, CCl<sub>4</sub>; ···, water; — · —, polymer) from the fits.

cantly thicker. In addition, the denser layer near the interface is more pronounced in the mixed solvent.

Figure 2c shows the reflectivity data for the polymer layer with 27.0 mol % sulfonation. From the figure we can see that the data for pure CCl<sub>4</sub> and water are comparable. The Kiessig fringes disappear only in the CCl<sub>4</sub>/water mixture, indicating that the largest swelling and interfacial width now occurs in the mixed solvent. The models used to fit these data are shown in Figure 2c'. From the figure we can see that the initial profile is swollen by 18% in water (long dashed line), consistent with the expectation that water becomes a better solvent with increasing sulfonation. We can also see that the adsorbed layer near the Si substrate has also increased as the number of sulfonated groups increases. The dot-dashed line is the profile in the mixed solvent. From the profiles we can see that a large amount of swelling has occurred. In contrast to the data for the lower sulfonation PSSA, the interface with the solvent is now broader in the mixed than in the pure solvents.

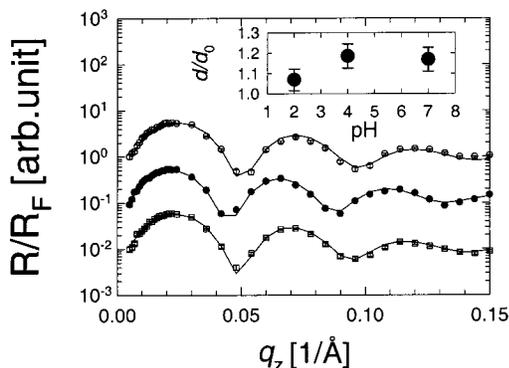
To determine the distribution of the solvent in the brush, we mixed D<sub>2</sub>O and H<sub>2</sub>O for the water medium in a ratio of 0.284 to 0.716. This resulted in a SLD of  $1.41 \times 10^{-6}$  Å<sup>-2</sup>, which was contrast matched for the SLD of hydrogenated 12.8 mol % sulfonated polymer as shown in eq 1. The first curve (open circles) in Figure 3a is the reflectivity profile of a film of hPSSA<sub>12.8%</sub> in contrast matched water of pH = 4 and CCl<sub>4</sub>. Therefore, the reflectivity contrast observed is now purely from the CCl<sub>4</sub>. The fitted model (solid line) to the data is shown in Figure 3a'. The thickness of the polymer layer ( $d = 320$  Å) was measured from the profile in deuterated water and is shown in Figure 3a (solid circles). The shape of the polymer profile was then obtained by normalizing for thickness effects with the profile measured from the deuterated polymer and shown in Figure 3a'. The normalized polymer profiles are shown by dashed lines in Figure 3a'. The water profile was then

obtained from the difference between the polymer and CCl<sub>4</sub> profiles and shown as dots in the figure. From the profile we can see that water is completely excluded from the dense layer near the Si substrate. In the center of the brush, water and CCl<sub>4</sub> are intimately mixed with an average ratio of 1:2. An interfacial region is then observed where the volume fraction of water in the solution increases as the water bulk phase is approached. These data show that the sulfonated polymer layer, regardless of the low degree of sulfonation, acts as an effective surfactant, enabling mixing of the two solvents.

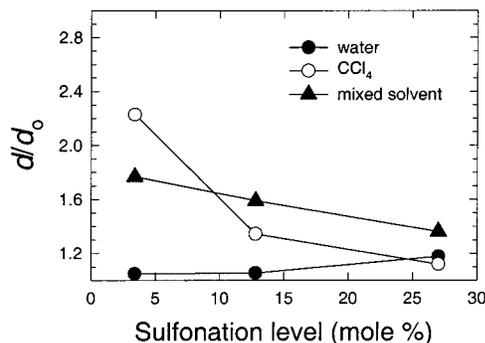
hPSSA with 23.0 mol % sulfonated groups was also imaged as described for hPSSA<sub>12.8%</sub> in solutions of contrast matched water and CCl<sub>4</sub>. The profiles, which are similar to hPSSA of 12.8 mol %, are shown in Figure 3b. The thickness of the hydrogenated polymer layer was obtained from the reflectivity data in air. The profiles of all three components in the mixed solvents are shown in Figure 3b'. As addressed above, the polymer profile in the inset (dash-dot) is scaled from the one measured from the deuterated polymer and the water profile to the difference between solvent and hydrogenated polymer. From the figure we can see that the CCl<sub>4</sub> profile follows that of the brush profile, and as observed previously, water and CCl<sub>4</sub> are mixed at a comparable level initially and water increases at higher  $z$ . In comparison with the data of the hPSSA<sub>12.8%</sub> in Figure 3b', we see a very thin water layer near the Si substrate.

Furthermore, as shown in Figure 4 where we plot the reflectivity data of dPSSA<sub>27.0%</sub> in water of different pH, we can see that the swelling ratio ( $d/d_0$ , where  $d$  and  $d_0$  are the heights in a solution and air, respectively) is decreased in water of pH = 2 where dissociation of the ion groups is blocked by the increasing acidity. Little change is observed between pH = 4 and pH = 7.

The experimental results are summarized in Figure 5, where we plot the ratio of the swelling vs degree of



**Figure 4.** (a) Neutron reflectivity scans of dPSSA<sub>27.0%</sub> in various pH controlled water. The curves are shifted by  $1 \times 10^{-1}$  of  $R/R_F$  for clarity. The solid lines are the best fits. The inset displays the swelling ratio ( $d/d_0$ ) vs the degree of pH.

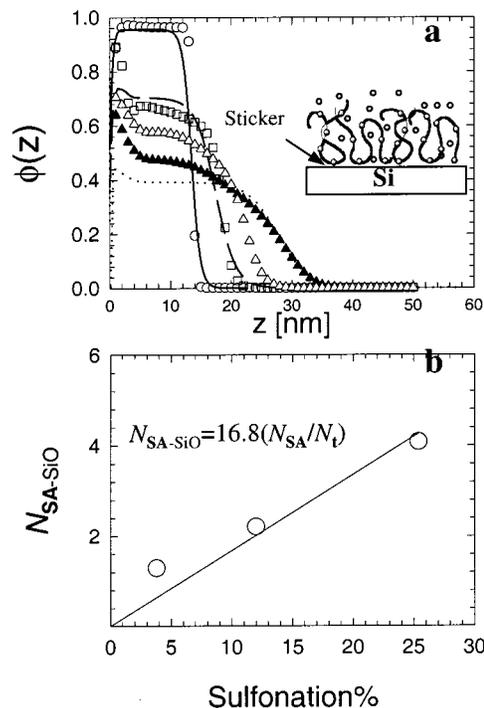


**Figure 5.** Swelling ratio ( $d/d_0$ ) plotted as a function of sulfonation level. The error of the thickness  $d$  is 2–3 Å, and the error bars are smaller than symbol sizes.

sulfonation level in pure water (pH = 4), pure CCl<sub>4</sub>, and mixed solvents. From the figure we can see that for  $x < 10$  mol % more swelling occurs in CCl<sub>4</sub> than water, and hence CCl<sub>4</sub> is the better solvent. For  $x \sim 10$  mol %, the swelling in the two solvents becomes comparable. For  $x > 10$  mol %, we see that the largest swelling occurs in the mixed solvents.

**SCF Calculation.** The SCF calculations were conducted by modeling the polymer as an alternating block with [PS<sub>3</sub>SA<sub>1</sub>], [PS<sub>8</sub>SA<sub>1</sub>], and [PS<sub>33</sub>SA<sub>1</sub>]. Note that PS refers to a styrene segment while SA refers to a sulfonated polystyrene segment in this text. This method of modeling random copolymers has been used before,<sup>16b</sup> and it has been shown that the results are insensitive to the arrangements of the monomers on the block. One permanently fixed segment at the wall to every polymer single chain has been introduced at the start of the calculation.

To calculate the number of sulfonated groups irreversibly attached to the substrate, we modeled a polymer layer in a solvent, which is good for block PS and poor for block SA ( $\chi_{1SA} = 3$ ). The interaction with the substrate is neutral for block PS and strong ( $\chi_{SA-SiO} = -3$ ) for block SA, so block SA becomes an “irreversibly adsorbed segment”. The number of irreversibly adsorbed segments for a given fraction of block SA was determined by fitting the Flory–Huggins interaction parameters,  $\chi$ , to obtain the thicknesses determined experimentally in the CCl<sub>4</sub> solvent. The fits to all three degrees of sulfonation were done simultaneously so that a single value of the interaction parameter between solvent 1 and PS,  $\chi_{1PS}$ , could be obtained for all the spectra. The calculated profiles are shown in Figure 6 for 3.8, 12.0, and 25.7% of block SA or irreversibly adsorbed segments. All lines are the profiles deduced from the NR data. From the figure we see that



**Figure 6.** (a) Density profiles from SCF calculation vs NR results in CCl<sub>4</sub>. Simulated density profiles of alternating copolymers, [PS<sub>3</sub>SA<sub>1</sub>]<sub>26</sub> ( $\Delta$ ), [PS<sub>8</sub>SA<sub>1</sub>]<sub>12</sub> ( $\square$ ), and [PS<sub>33</sub>SA<sub>1</sub>]<sub>3</sub> ( $\circ$ ) in solvent 1 when  $N_t = 100$  and  $\chi_{1PS} = 0.7$ . In the case of [PS<sub>33</sub>SA<sub>1</sub>]<sub>3</sub>, note that the simulation and experimental data are matched better when  $\chi_{1PS} = 0.3$  ( $\blacktriangle$ ). The solid line, long dashes, and dots correspond to the concentration profiles of dPSS<sub>27.0%</sub>, dPSS<sub>12.0%</sub>, and dPSS<sub>3.4%</sub> in CCl<sub>4</sub> respectively shown in Figure 2, a', b', and c'. (inset) Schematic picture of a polymer brush having randomly distributed stickers in a pure solvent. (b) The number of stickers at polymer/substrate interface ( $N_{SA-SiO}$ ) in a PSSA chain as a function of sulfonation level (mol %).  $N_{SA-SiO}/N_t$  represents the sulfonation level, where  $N_{SA}$  is the total number of stickers out of the total number of monomers in a single chain,  $N_t$ .

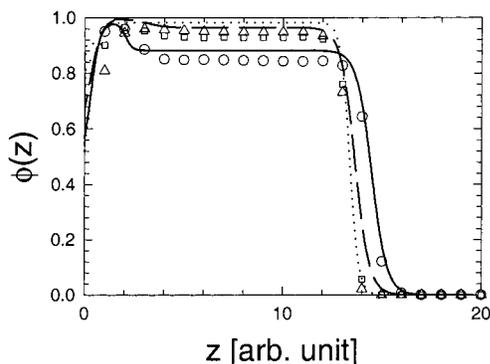
**Table 3. Number of Irreversibly Adsorbed Segments on the SiO Surface ( $N_{SA-SiO}^a$ ) Calculated by SCF Simulation**

sulfonation % ( $N_{SA}/N_t$ )	$\langle N \rangle^b$ b/w stickers	$N_{SA-SiO}$	$N_{SA-SiO}/N_{SA}$	$\langle N \rangle$ b/w adsorbed segments
25.7	4.3	4.1	0.18	20.8
12.0	11.6	2.2	0.27	39.8
3.9	36.4	1.3	0.57	58.3

<sup>a</sup> See ref 22. <sup>b</sup>  $\langle N \rangle$  = the average number of segments.

good fits with  $\chi_{1PS} = 0.7$  between experimental curves and simulations are only obtained for  $x = 12.0\%$  (open squares) and 25.7% (open circles). For the  $x = 3.8\%$  the calculated profile (solid triangles) with  $\chi_{1PS} = 0.7$  is narrower than the experimental one. Reasonable fits are only obtained if  $\chi_{1PS}$  is reduced to 0.3. This indicates that  $\chi_{1PS}$  may be concentration dependent. The values of  $\chi_{1PS}$  obtained from the fits of the PSSA<sub>x</sub> layers in the pure solvent were then used to calculate the mixed solvent profiles.

The inset to the figure is a cartoon showing the typical orientation of chains near the surface where only a fraction of the stickers are actually adjacent to the surface. This number is a balance between the gain in enthalpy by attaching the stickers and the entropic penalty of confining the chains. This effect can be seen in Table 3 where we tabulate the number of stickers at the wall, their fraction of the total, and the number of monomers between stickers. We can see that as the degree of sulfonation increases,



**Figure 7.** Normalized density profiles of alternating copolymer  $[\text{PS}_2\text{SA}_1]_{26}$  ( $\Delta$ ),  $[\text{PS}_3\text{SA}_1]_{12}$  ( $\square$ ), and  $[\text{PS}_{33}\text{SA}_1]_3$  ( $\circ$ ) in solvent **2** with  $\chi_{2\text{SA}} = -2$  and  $\chi_{2\text{PS}} = 2$ : the solid line, dashed line, and dots correspond to the NR results of dPSSA<sub>27.0%</sub>, dPSSA<sub>12.0%</sub>, and dPSSA<sub>3.4%</sub> in water respectively shown in Figure 2, a', b', and c'.

the fraction of total stickers at the wall decreases, as the entropic penalty of creating smaller loops becomes higher. In Figure 6b we plot the number of the adsorbed stickers ( $N_{\text{SA-SiO}}$ ) at the solid surface in an organic solvent as a function of the sulfonation level. Note that the initially fixed segment is not counted in  $N_{\text{SA-SiO}}$ .<sup>21</sup> From the figure we see that for the values of sulfonation used in these experiments at  $x < 30$  the relationship is linear ( $\sim 16.8 \cdot (N_{\text{SA}}/N)$ , where  $N_{\text{SA}}$  and  $N$  are the number of stickers and the total number of segments in a chain, respectively). The results, which include the calculated number of monomers in the surface loops and the number of monomers between stickers on and off the surface, are summarized in Table 3 for each PSSA<sub>x</sub> film that we studied.

Keeping the number of stickers fixed, we now model the profile of the layer in water. Since the swelling is relatively independent of charge, we ignore the polyelectrolyte nature of the polymer (i.e., we neglect charge screening and dissociation of the sulfonated groups) and just model water as a poor solvent for block **PS** ( $\chi_{2\text{PS}} = 2.0$ ) and a good solvent for block **SA** ( $\chi_{2\text{SA}} = -2.0$ ). The profiles are plotted in Figure 7. Here we see that a denser layer of the **PS** block is formed near the substrate since the interaction of **PS** with the substrate is more favorable than **PS** with the solvent. This denser **PS** layer near the wall is in good agreement with the experimental data.

From these two sets of fits we now obtain all the interaction parameters for the **PS** and **SA** blocks with both solvents and the substrate. We can now attempt to model the polymer in the mixed solvent where the only variable is the interaction between the solvents. In this case, since  $\text{CCl}_4$  (designated to **1**) and water (designated to **2**) are highly immiscible we use  $\chi_{12} = 3.5$ , which is similar to the value used by Lyatskaya and Balazs in ref 6. This value is larger than any other unfavorable parameter in the system.

The systems can be modeled by using the interaction parameter obtained from the pure systems. In Figure 8a we show the profiles calculated by this method for a film with 25.7 mol % sulfonation as a function of the amount

( $\theta_1$ ) in the system of the organic solvent (solvent **1**) within the brush. In this case we can vary the amount of solvent **1** in the system ( $\theta_1$ ) and use the interaction parameters obtained from the pure solvent systems. From the figure we can see that the swelling of the layer is determined by the amount of solvent **1**. Since we know the swelling of the layers from the NR data, we can then extract the value of  $\theta_1$  to model the profiles of all the data.

When  $\theta_1 < 5$  or less than 40% volume fraction of the polymer, the two solvent components **1** and **2** are partially mixed inside of the polymer without any preferential segregation. This is in agreement with the experimental results, and the profiles of the respective components are shown in Figure 8b. When  $\theta_1$  approaches 7, or about 50% volume fraction of the polymer volume, the polymer layer cannot adsorb all the solvent and starts to break its brushlike conformation. When  $\theta_1$  is larger than 9, the two solvents are phase-separated, and the polymer profile shows well-defined peaks.

The profile for 25.6 mol % degrees of sulfonation in a solvent mixture when  $\theta_1 = 1.5$  is shown in Figure 8b. The symbols are then the simulation for the profiles of all the components in the 25.7% alternating polymer layer. The simulation shows that the concentration of the sticky block is very high near the wall, as expected. The concentration of block **PS** is also higher at the wall, as we observed experimentally. Both solvents are excluded from the adsorbed sections near the substrate. Solvent **1** and **2** are seen to coexist completely outside of the pinned sections. The solid line is the polymer profile deduced from the experimental data in Figure 2. From the figures we see that the experimental and the simulated profiles (i.e., the swelling ratio as well as interfacial roughness) agree well. In Figure 8c we show the simulated profiles with  $\theta_1 = 6.0$  for the 12.0 mol % film. From the figure we can see that the simulation reproduces the adsorbed layer well here, too. Comparing this profile with the one for 25.6 mol %, we see that the balance between solvent **1** (organic) and solvent **2** (aqueous) has changed. Namely, the 25.6% films contain more solvent **2** than **1** while the reverse is true for the 12% sample. The solid lines are the profiles obtained from the fits to the experimental data of dPSSA<sub>12.8%</sub> film. In this case as well, agreement between the calculated models and experiments is good everywhere except the interfacial region between the solvent layer trapped in the brush and the majority solvent. The profiles for the 3.8% film are shown in Figure 8d. Here we see that even if solvent **1** is a good solvent for the PSSA, a significant amount of solvent **2** is also present near the brush.

The slight discrepancies between the calculated and measured interfacial width may be that the hypothesis that the polymer is simply acting as a surfactant separating the oil and water phases is too simplistic and not borne out by the simulation. It is well-known that density fluctuations can exist in solvent and solvent-polymer mixtures. As yet we do not have a formalism to directly calculate this effect. But, it may be possible the swelling is purely an interfacial effect where the oil/water mixture penetrates the polymer simply to reduce the fluctuation energy, and the penetration depth will be on the order of the  $q$  vector of the fluctuations. Further experiments are in progress to study this effect in greater detail by small-angle X-ray scattering using polyelectrolyte nanoparticles with a large surface-to-volume ratio in solutions.

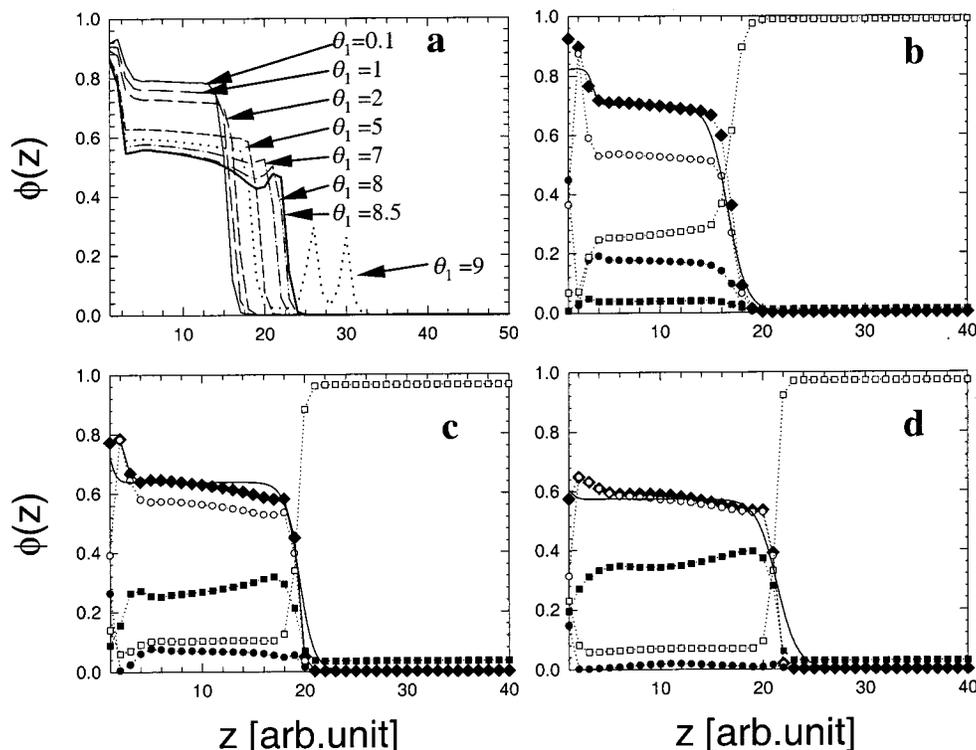
## Conclusion

We have used NR to measure the concentration profiles of polystyrenesulfonated acid (PSSA<sub>x</sub>) films with three

(20) Increasing the number of layer did not show a significant improvement in the fits. This two-layer model gave a reasonable fit to the entire reflectivity profiles.

(21) Perahia, D.; Wiesler, D. G.; Satija, S. K.; Fetters, J.; Sinha, S. K.; Milner, S. T. *Phys. Rev. Lett.* **1994**, *72*, 100.

(22) Since the linear extrapolation begins with 0% sulfonated PS, or polystyrene, we exclude the one which was introduced initially, from  $N_{\text{SA-SiO}}$ . In this case, there should not be any permanently fixed segment present.



**Figure 8.** (a) Simulated density profiles of  $[\text{PS}_3\text{SA}_1]_{26}$  when the amount of solvent 1,  $\theta_1$ , is varied. Simulated density profiles of each component of (b)  $[\text{PS}_3\text{SA}_1]_{26}$ , (c)  $[\text{PS}_8\text{SA}_1]_{12}$ , and (d)  $[\text{PS}_3\text{SA}_1]_{26}$  in a solvent mixture are seen together with solvent densities: solvent 1 (■) and 2 (□). The polymer components are denoted as follows: (○) PS, (●) SA, (···) PS + SA. The solid lines correspond to the NR results of the respective dPSSA<sub>x</sub> in the water/CCl<sub>4</sub> solvent mixture shown in Figure 2.

different degrees ( $x = 3.4, 12.8,$  and  $27.0$  mol %) of sulfonation in water, CCl<sub>4</sub>, and a mixture of the two solvents. The data show that, except for the  $x = 3.4\%$  films where CCl<sub>4</sub> is a good solvent, the largest degree of swelling occurred in the mixed solvent. Contrast matching the water to the polymer layer enabled us to profile the CCl<sub>4</sub> concentration. The results showed that CCl<sub>4</sub> and water were mixed within the polymer film in a ratio of 1:2 and 1:4 for 12.8 and 27.0 mol % PSSA, respectively. SCF calculations indicated that the number of adsorbed sulfonated blocks scaled linearly with the degree of sulfonation. Using the interaction parameters between

the PS and PSS blocks obtained by fitting to the data in pure solvents, excellent agreement was obtained for the profiles of the polymer and the solvent mixtures for all values of  $x$ .

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