Structures of Thin Ionomer Films in Solvent Mixtures

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Received December 11, 2000. In Final Form: August 6, 2001

We have used neutron reflectivity to measure the concentration profiles of polystyrenesulfonated acid (PSSAₙ) films with three different degrees of sulfonation (x = 3.4%, 12.8%, and 27.0%) in water, CCl₄, and a mixture of the two solvents. The data show that, except for the x = 3.4% films where CCl₄ 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 CCl₄ concentration. The results showed that CCl₄ 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. In particular, thin films of these polymers have been used as coatings to control the adhesion of cells or in producing electronic devices. In all these cases the polyelectrolyte copolymers have been shown to have numerous applications as biomimetic or electronic materials. In practical applications random copolymers where the film is 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.

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In this paper we have chosen to present a comprehensive study of the conformation in different solvents of the random polyelectrolyte copolymer, sulfonated polystyrene (PSSA), 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 solvents and water, which we show to produce the largest 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 (Mn/Mw < 1.07) random polystyrenesulfonated acid ((C8H8)n—(C8H7SO3—H)m) or (C6D6)n—(C6D6SO3—H)m copolymer, designated as PSSA, of Mn = 150–200 g mol−1 with degree of sulfonation, χ, (m(n− m)) ranging from 3.4 to 27 mol %, were synthesized using the procedures described in ref 11. Both hydrogenated (hPSSA) and deuterated (dPSSA) forms of PSSA, 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. 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 < 10−6 mbar at 175 °C,12 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.13

The thickness was usually about 90–140 Å, which is approximately 1Rq of the Mn = 160 × 103 PSSA. The thickness of each layer was measured before and after each neutron experiment to check whether any polymer loss had occurred during the experimental procedure.

The solvents studied were analytical grade CCl4, 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 were used. First, to determine the structure of polymers in the mixed solvents, the water was contrast matched to CCl4 (SLDh,0 = 2.80 × 106 Å−2). This was accomplished by mixing H2O (SLDh,0 = −0.56 × 106 Å−2) and D2O (SLDD2O = 6.35 × 106 Å−2) where the average scattering length density, (SLDh,0), of the contrast matched water is given by

\[ \langle SLD_{h,0} \rangle = \phi_{H_2O}SLD_{H_2O} + (1 - \phi_{H_2O})SLD_{D_2O} \]  

where \( \phi_{H_2O} \) is the volume fraction of H2O in the mixture. In this case, the contrast between CCl4 and the contrast matched water is isoslated, and the scattering intensity is the interference of the solvent mixture (SLD = 2.80 × 106 Å−2) and dPSSA, (−5.70−6.12) × 106 Å−2) and the Si substrate (SLD_{SiO_{2}} = 2.96 × 106 Å−2) and dPSSA. To profile the CCl4 concentration in the mixed solvent sample, a mixture of H2O and D2O was prepared to match the scattering contrast of hPSSA, (−1.41 × 106 Å−2). In this case, the CCl4 profile near the hPSSA, layer can be obtained since CCl4 becomes the highest SLD component in the system.

### Table 1. Characterization of PSSA, Used in This Study

<table>
<thead>
<tr>
<th>designation</th>
<th>x [mol %]</th>
<th>M_w [g/mol]</th>
<th>d_{air} [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPSSA27.0%</td>
<td>27.0</td>
<td>150K</td>
<td>120</td>
</tr>
<tr>
<td>hPSSA23.0%</td>
<td>23.0</td>
<td>200K</td>
<td>170</td>
</tr>
<tr>
<td>hPSSA12.8%</td>
<td>12.8</td>
<td>169K</td>
<td>200</td>
</tr>
<tr>
<td>dPSSA12.8%</td>
<td>12.8</td>
<td>169K</td>
<td>100</td>
</tr>
<tr>
<td>dPSSA3.4%</td>
<td>3.4</td>
<td>169K</td>
<td>126</td>
</tr>
</tbody>
</table>


(13) The strong adsorption was observed only after the annealing procedure.
were modeled using SCF theory.16a The only parameter introdu-
tions of the random copolymer brush in pure and mixed solvents
where \( n \) of monomer the three unit blocks while keeping the total polymerization index
of sulfonation was varied by choosing different combinations of
interaction parameter between \( SA \) developed by Gersappe et al.16b Each monomer has a finite
fractions of sulfonated segments: 25.6, 12.0, and 3.8 mol %. The
sulfonation level and performed calculations for three different
monomers. We first examined the structure as a function of the
denote two monomer species, in this case styrene and sulfonated
PS substrate, solvents, \( \text{PS} \), \( \text{PS} \text{SA} \), or \( \text{PS} \text{SA} \text{SA} \) site. Thus, the model
introduced randomness, where the ensemble of sequence distri-
butions in the system is allowed to fluctuate. The random
copolymer was designed by a combination of three different
structures of unit blocks: \( \text{PS} \text{SA} \), \( \text{PS} \text{SA} \text{SA} \), and \( \text{PS} \text{SA} \text{SA} \),
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 \( \gamma_{\text{SA-SiO}} \) was fixed at \( \gamma_{\text{SA-SiO}} = -20 \) in all calculations.17

For pure solvents (designated \( 1 \) for organic and \( 2 \) for aqueous)—

\[
\nu_0 = 1 - 7.475 \times 10^{-6}, \quad n_{\text{CCl}_4} = 1 - 10.09 \times 10^{-6}, \quad \text{and} \quad n_{\text{H}_2\text{O}} = 1 + 2.019 \times 10^{-6}, \quad \text{respectively. The} \ \delta \text{is given linearly in terms of}
\text{the SLD by} \ \delta = \chi^2 \text{SLD} / 2\pi, \ \text{where} \ \chi \ \text{is the wavelength of neutron}
\text{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 \( \chi \) until \( \chi \) was

Self-Consistent-Field Calculation (SCF). The configurations
of the random copolymer brush in pure and mixed solvents
were modeled using SCF theory.16b The only parameter intro-
duced was the Flory–Huggins parameters \( \chi \) between the
substrate, solvents, \( \text{PS} \), and \( \text{SA} \) segments, where \( \text{PS} \) and \( \text{SA} \) 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.16b Each monomer has a finite
probability of being either a \( \text{PS} \) or \( \text{SA} \) site. Thus, the model
introduced randomness, where the ensemble of sequence distri-
butions in the system is allowed to fluctuate. The random
copolymer was designed by a combination of three different
structures of unit blocks: \( \text{PS} \text{SA} \), \( \text{PS} \text{SA} \text{SA} \), and \( \text{PS} \text{SA} \text{SA} \),
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
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of monomer \( SA \) to the surface of the substrate, the Flory–Huggins
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For pure solvents (designated \( 1 \) for organic and \( 2 \) for aqueous)—

\[
(16) \text{(a) Fleer, G.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.;}
\text{Cosgrove, T.; Vincent, B. Polymers at Interfaces; Chapman and Hall:}
\text{Macromolecules. 1995, 28, 4753.}

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

Results and Discussion

Neutron Reflectivity. Parts a, b, and c of Figure 2 show the reflectivity data of the dPSSA3.4%, dPSSA12.8%,
and dPSSA27.0% 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, \( R \), at various
media with an infinitely sharp interface were simulated,
and the measured reflectivities, \( R \), and fits were then
normalized by the respective \( R \). 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 dPSSA3.4%. 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 \( R \),
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 carboxylic acid in ref 18a. This irreversibly
adsorbed layer was found only in samples that were
sulfonated.18b Hence, the sulfonated group acts like a
sticker where bonding occurs. The long dashed line

corresponds to the concentration profile of dPSSA3.4%
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
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 model19 except
that in this case not all monomers have equal probability
of being adsorbed; rather, only some of the sulfonated groups are irreversibly attached. 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 CCl₄ 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 CCl₄ 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 CCl₄ may exist within it. The main differences between this profile and the one in pure CCl₄ are that the thickness of the layer is somewhat smaller and the interfacial width is sharper than that of the layer in CCl₄ 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 Å. 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. This type of model is similar to the one used by Tran et al. and Perahia et al. 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 CCl₄, indicating that the layer is swollen and CCl₄ 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 CCl₄ 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-
The dot sulfonation. We can also see that the adsorbed layer near that water becomes a better solvent with increasing in water (long dashed line), consistent with the expectation figure we can see that the initial profile is swollen by 18%. From the profiles we can see that water is completely excluded from the dense layer near the Si substrate. In the center of the brush, water and CCl4 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 hPSSA12.8% in solutions of contrast matched water and CCl4. 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 CCl4 profile follows that of the brush profile, and as observed previously, water and CCl4 are mixed at a comparable level initially and water decreases in water of pH 7. Furthermore, as shown in Figure 4 where we plot the reflectivity data of dpSSA27.0% in water of different pH, we can see that the swelling ratio (d/d0, where d and d0 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

![Image](https://example.com/image.png)
in a solvent, which is good for blockably attached to the substrate, we modeled a polymer layer permanently fixed segment at the wall to every polymer single arrangements of the monomers on the block. One per-
been shown that the results are insensitive to the
\(\text{SA} \)
parameter between solvent
simultaneously so that a single value of the interaction
The fits to all three degrees of sulfonation were done
irreversibly adsorbed segments. All lines are the profiles obtained for all the spectra. The calculated profiles are
deduced from the NR data. From the figure we see that
dimensionless determined experimentally in the CCl\(_4\) solvent.
Huggins interaction parameters,
See ref 22. \(\langle N \rangle \) is the average number of segments.
good fits with \(\chi_{\text{PS}} = 0.7\) 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 \(\chi_{\text{PS}} = 0.7\) is narrower than the experimental one. Reasonable fits are only obtained if \(\chi_{\text{PS}}\) is reduced to 0.3. This indicates that \(\chi_{\text{PS}}\) may be concentration dependent. The values of \(\chi_{\text{PS}}\) obtained from the fits of the PSSA 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,
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_{SA-SiO}) at the solid surface in an organic solvent as a function of the sulfonation level. Note that the initially fixed segments are not counted in N_{SA-SiO}. From the figure we see that for the values of sulfonation used in these experiments at x < 30 the relationship is linear (~16.8: (N_{SA}/N_{S}), where N_{SA} and N_{S} 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 PSSAx 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 (\gamma_{PS} = 2.0) and a good solvent for block SA (\gamma_{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 CCL (designated to 1) and water (designated to 2) are highly immiscible we use \gamma_{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 \( \theta_4 \) in the Langmuir, Vol. 17, No. 21, 2001 6681 (\theta_4) in the Langmuir, Vol. 17, No. 21, 2001 6681

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 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 (PSSAx) films with three

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(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.


(22) Since the linear extrapolation begins with 0% sulfonated PS, or polystyrene, we exclude the one which was introduced initially, from N_{SA-SiO}. In this case, there should not be any permanently fixed segment present.
different degrees ($x = 3.4$, 12.8, and 27.0 mol %) of sulfonation in water, CCl$_4$, and a mixture of the two solvents. The data show that, except for the $x = 3.4\%$ films where 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 CCl$_4$ concentration. The results showed that CCl$_4$ 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 $x$.

**Acknowledgment.** This work was supported by NSF-MRSEC Program No. DMR0080604. K. Shin thanks Prof. H. White in SUNY and Prof. S. Schwarz in Queens College for helpful discussions.

LA001725j