Wetting Behavior of Lightly Sulfonated Polystyrene Ionomers on Silica Surfaces

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Introduction

Contemporary coatings technologies require increasingly thinner polymeric films, and the ability to produce useful and uniform coatings depends on the wettability and adhesion of the polymer to the substrate. Dewetting of a coating exposes the underlying substrate and compromises the barrier properties of the coating, as well as producing surface roughness and defects that may be deleterious to the performance of the polymer film. Dewetting of polymeric films may be prevented by modifying the equilibrium polymer–surface interactions.

Controlling film stability is crucial for obtaining uniform, continuous, defect-free, and stable coatings. The polymer–substrate and polymer–air interfacial energies and kinetic barriers play important roles in determining the morphology and dynamics of thin films. Confinement influences conformation and interaction of the molecules. Structural changes induced by the interaction with a solid substrate can also affect the dynamics of polymers, as well as the adhesion and wetting characteristics.

The wetting/dewetting of polystyrene (PS) has received considerable attention. Thin PS films are metastable when the spreading coefficient, \( S \), is less than zero, where

\[
S = \Gamma - (\Gamma_s + \Gamma_p)
\]

\( \Gamma \) and \( \Gamma_p \) are the surface free energies of the substrate and polymer, respectively, and \( \Gamma_s \) is the interfacial energy between the polymer and the substrate. For glassy polymers such as PS, dewetting can be metastable below the glass transition temperature \( T_g \), but dewetting occurs above \( T_g \). The dewetting process is driven by long-range interactions and proceeds in three basic steps: rupture, expansion, and coalescence of dewetted holes to form a network, and, finally, break-up of the network system into droplets.

Strategies to stabilize thin polymer films against dewetting include chemical and physical modifications of the substrate, introduction of reactive end-groups onto the polymer, and the addition of nanoparticle or dendrimer fillers to the polymer. Previous work in our group showed that randomly sulfonated polystyrene (SPS) ionomers were much more resistant to dewetting from silica than PS with the same molecular weight. This paper addresses the effects of sulfonation level, molecular weight, the choice of the cation, and the solvent history of the SPS ionomer on its wetting and dewetting behavior on silica.

Experimental Details

Materials and Sample Preparation. Toluene (99.9%), tetrahydrofuran (THF, 99.9%) and methanol (99.9%), and 1,2-dichloroethane (reagent grade) were obtained from Fisher Scientific Co. and used as received.

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The wetting/dewetting behavior of thin films of lightly sulfonated low molecular weight polystyrene (SPS) ionomers spin-coated onto silica surfaces were studied using atomic force microscopy (AFM), contact angle measurements, and electron microscopy. The effects of the sulfonation level, the choice of the cation, the solvent used to spin-coat the films, and the molecular weight of the ionomer were investigated. Small angle X-ray scattering was used to determine the bulk microstructure of the films. The addition of the sulfonate groups suppressed the dewetting behavior of the PS above its glass transition temperature, e.g., no dewetting occurred even after 240 h of annealing at 120 °C. Increasing the sulfonation level led to more homogenous and smoother surfaces. The choice of the cation used affected the wetting properties, but not in a predictable manner. When tetrahydrofuran (THF) or a THF/methanol mixed solvent was used for spin-casting, a submicron-textured surface morphology was produced, which may be a consequence of spinodal decomposition of the film surface during casting. Upon annealing for long times, the particles coalesced into a coherent, nonwetted film.
as received. Two narrow molecular weight distribution PS precursors were obtained from Pressure Chemicals: (1) $M_w = 4.0$ kg/mol, polydispersity index (PDI) < 1.06, $T_g = 82$ °C and (2) $M_w = 13.5$ kg/mol, PDI < 1.06, $T_g = 98$ °C, denoted as PS4 and PS13.5, respectively. These molecular weights are far below the chain entanglement molecular weight ($M_e$) of PS, 16.6 kg/mol.\(^{(25)}\) The PS's were sulfonated at 50 °C in 1,2-dichloroethane using acetyl sulfate, prepared by the reaction of concentrated sulfuric acid (Fisher Scientific Co., 95%) with acetic anhydride (Aldrich Chemical Co., 95%). The sulfonation procedure randomly sulfonates the styrene ring, primarily at the para-position. The nomenclature used for the ionomers was $2.5\text{LiSPS}4$ for 2.5 mol% Li sulfonation of PS4 and $2.7\text{LiSPS}13.5$ for 2.7 mol% Li sulfonation of PS13.5. As with any radical process, the average number of sulfonate groups per chain, calculated by multiplying the sulfonation level by the degree of polymerization, $N$, the probability of a monomer being sulfonated, $p$, and the mole fraction of substituted styrene, $x$, is the sulfonation level in mol% of styrene substituted, $x/100$. \(^{(26)}\)

The glass transition temperatures ($T_g$) of the polymers were determined with a differential scanning calorimeter (DSC, TA2920, TA Instruments, using a heating rate of 20 °C/min. The dielectric constants, $\delta$, of toluene, THF, and methanol (9/1, v/v) and (4) a mixture of THF and toluene/methanol (9/1, v/v). The solubility parameters, $\delta$, are summarized in Table 1. The column labeled $\delta_{ave}$ corresponds to the average number of sulfonate groups per chain, calculated by multiplying the solubility parameter of the solvent mixtures, also obtained using a volume average of the solubility parameters of the individual components, and the mole fraction of substituted styrene, $x$. The latter is the probability of a monomer being sulfonated (see eq 1). Note that $p = x$ mol% sulfonation divided by 100.

$$P(x) = \frac{N!}{(N-x)!}p^x(1-p)^{(N-x)}$$

Figure 1 shows the distribution function $P(x)$ for the four ionomers studied. Although the average number of sulfonate groups per chain varied from 1 to 4 for the various ionomers produced (see Table 1), the distributions show that each sample will also have a finite number of chains with no sulfonation and with more sulfonate groups than the average. The latter is particularly important with regard to the experimental results that are discussed below, in that the samples with an average of

<table>
<thead>
<tr>
<th>sample</th>
<th>sulfonation level (mol %)$^a$</th>
<th>cation</th>
<th>$M_w$ (PS) (kg/mol)</th>
<th>$N$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5LiSPS4</td>
<td>2.5</td>
<td>Li</td>
<td>4.0</td>
<td>39</td>
<td>1.0</td>
</tr>
<tr>
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<td>6.5</td>
<td>Li</td>
<td>4.0</td>
<td>39</td>
<td>2.5</td>
</tr>
<tr>
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<td>2.5</td>
<td>Na</td>
<td>4.0</td>
<td>39</td>
<td>1.0</td>
</tr>
<tr>
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<td>2.5</td>
<td>K</td>
<td>4.0</td>
<td>39</td>
<td>1.0</td>
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<tr>
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<td>2.5</td>
<td>Rb</td>
<td>4.0</td>
<td>39</td>
<td>1.0</td>
</tr>
<tr>
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<td>2.5</td>
<td>Cs</td>
<td>4.0</td>
<td>39</td>
<td>1.0</td>
</tr>
<tr>
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<td>0.76</td>
<td>Li</td>
<td>13.5</td>
<td>130</td>
<td>1.0</td>
</tr>
<tr>
<td>2.7LiSPS13.5</td>
<td>2.7</td>
<td>Li</td>
<td>13.5</td>
<td>130</td>
<td>3.5</td>
</tr>
</tbody>
</table>

$^a$ $p =$ sulfonation level/100. $^b$ $N =$ degree of polymerization. $x_{ave} = p \cdot N.$

Table 1. Sulfonated PS Ionomers (SPS) Used in This Study
one sulfonate group per chain ($x = 1$) will also have a finite concentration of multiple substituted chains. For simple ion–dipole associations, one would expect that chains with one or two sulfonate groups ($x = 1$ and $x = 2$) only produce chain extension of the oligomers (see Figure 2a,b). When $x > 2$, network formation is possible. According to the distributions $P(x)$ for the different ionomers, one might reasonably expect that network formation is possible in all of the samples studied here, since all should contain some chains with $x > 2$ (see Figure 2c). If ionic aggregation occurs, as SAXS data discussed later in this paper indicates, more complicated structures are possible, including networks with micelle-like structures, as shown in Figure 2d.

**Dewetting of PS from Silica.** The dewetting behavior of PS from silica has been studied extensively by a number of authors and is only discussed briefly here. Figure 3 shows optical micrographs of spin-coated PS films with $M_w = 4.0$ kg/mol and 13.5 kg/mol annealed above $T_g$ at 120°C for 20 h. The dewetting process for both PS films followed the typical pattern described by Reiter, which involves the following steps: (1) The initially flat film ruptures spontaneously, resulting in the formation of holes at random sites; (2) The holes then grow laterally and coalesce, resulting in a polygon pattern of holes with polymer ridges; (3) The polymer ridges finally break up into spherical droplets. The dewetting kinetics of the higher molecular weight PS film (Figure 3b) was slower than that of the lower molecular weight PS film (Figure 3a). After 20 h of annealing, the lower molecular weight film had completely broken up into droplets, while the higher molecular weight film still exhibited only dewetted holes typical of early stage dewetting, i.e., after 20 h. The slower dynamics of the dewetting process for the higher molecular weight PS is a consequence of decreased molecular mobility due to the higher viscosity of the polymer melt.

**Effect of Sulfonation Level.** Figure 4 shows AFM topographical images of 2.5LiSPS4 (Figure 4a–d) and 6.5LiSPS4 (Figure 4e–h) films spin-coated onto silica from toluene (Figure 4a,b,e,f) and THF (Figure 4c,d,g,h) and annealed under vacuum at 120°C for 0 h (a,c,e,g) and 240 h (b,d,f,h). Scan size $50 \times 50 \mu m^2$ (a,b,e,f,g,h) and $20 \times 20 \mu m^2$ (c,d).
~37% of the chains in the 2.5LiSPS4 were unsulfonated and the molecular weight was sufficiently low that the chains should not be entangled. Figure 1 also indicates that ~10% of the chains have three or more sulfonate groups, which can produce network formation (see Figure 2c). Interactions of the sulfonate groups with the silica surface, e.g., ion–dipole interactions, should improve wetting, and the network formation should suppress the kinetics of dewetting. However, it is puzzling that unentangled, unsulfonated chains, if present at the concentrations shown by Figure 1, would not dewet sufficiently to be apparent in the morphology shown in Figure 4.

The 2.5LiSPS4 spin-coated from THF (Figure 4c) and a solvent of (9/1 v/v) THF/methanol exhibited an unusual morphology (see Figure 5) that was not caused by dewetting. This morphology of well-wetted, submicron particles is believed to involve a spinodal decomposition of the surface.27 When annealed at elevated temperature, that morphology coalesced into a rough, but wetted film (Figure 4d).

Increasing the ionic concentration of the SPS produced a higher effective density of physical cross-links, which increased $T_g$ and the melt viscosity. The 6.5LiSPS4 films spin-coated from toluene (Figure 4e,f) and THF (Figure 4g,h) were featureless (i.e., smoother and more homogeneous than the 2.5LiSPS4 films), even after annealing 240 h at 120 °C. Figure 1 predicts that the unsulfonated chain concentration in the 6.5LiSPS4 is only ~8%, and the concentration of chains with $x \geq 3$ is ~50%. Thus, the probability that a single chain has a functional group that can complex with the silica is greater than that for the lower sulfonated ionomer, and the higher physical cross-link density provides a much higher viscosity that help suppress dewetting of these films above $T_g$.

**Effect of Solvent.** The ionic groups of SPS ionomers tend to aggregate in relatively nonpolar solvents due to the incompatibility of the polar sulfonated groups with the solvent. The ion aggregation influences the properties and conformation of the ionomer molecules in solutions.28 Therefore, the nature of the solvent used in the spin-coating process was expected to affect the conformation and size of the polymer coils in solution and the location of the sulfonate groups and the polymer conformation of the cast films, since the solvent is removed very rapidly during spin-coating. On the basis of the differences in the dielectric constants (2.4 and 5.5) and solubility parameters (18.2 and 19.6 $1^{1/2}$/cm$^3$), toluene was judged to be less polar than THF and probably a poorer solvent for the sulfonate groups.

The polarity of the SPS ionomer surface did depend upon the solvent used to spin-coat the films. Contact angle data for 2.5LiSPS4 films spin-coated from toluene and THF solution and 6.5LiSPS spin-coated from toluene are shown in Figure 6. For the 2.5LiSPS4, the as-cast toluene solutions were more hydrophobic, as judged by the higher water–air contact angle. This result suggests that the THF evaporation during spin-coating promotes the location of the sulfonate groups to the air–polymer surface, at least to a greater extent than does toluene. Both solvents are good solvents for PS, but the THF is probably a better solvent for the polar, sulfonate groups. That is, in solution, one might expect that the sulfonate groups are more likely to bury themselves inside the polymer coil to avoid contact with the toluene solvent than THF. That hypothesis is supported by the intrinsic viscosity data for toluene and THF solutions given in Table 2. The higher intrinsic viscosity for the THF solution indicates a more expanded ionomer coil, which is expected if THF is more favorable to the sulfonic groups than is toluene. The hydrophilic nature of the films cast from toluene did, however, increase when the sulfonation level of the ionomer increased (see Figure 6). In this case, one might expect that the higher sulfonate group concentration and restrictions of the chain conformation of the polymer film as it dries traps some sulfonate groups at the air–film interface.

The 2.5LiSPS4 samples spin-coated from either toluene or THF became more hydrophobic, i.e., the contact angle of water increased, when annealed above the $T_g$ of the ionomer. The toluene–cast films, however, remained more hydrophobic than the THF–cast films for a fixed annealing time. The increase in the hydrophobicity with time may be explained by the lower energy hydrocarbon part of the polymer displacing the more polar sulfonate groups at the surface.29 Surprisingly, the higher sulfonated, 6.5LiSPS4 sample spin-coated from toluene exhibited...

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the opposite behavior. The as-cast sample had a water contact angle similar to that of the 2.5LiSPS4 cast from toluene, but decreased, i.e., the sample became more hydrophilic, upon annealing at 120 °C (see Figure 6).

The differences in the contact angles for the 2.5LiSPS4 samples spin-coated from the two different solvents may also be due to the differences in the film morphology, as shown in Figure 4. The films spin-coated from toluene (Figure 4a) were relatively smooth and covered the silica, while those cast from THF exhibited a submicron particle morphology (see Figures 4c and 5). Upon annealing, both films formed coherent films that covered the silica, but were rougher than the toluene as-cast film. The 6.5Li-SPS4 spin-coated from either toluene or THF appeared to be similar to the 2.5Li-SPS4 samples spin-coated from toluene, but the annealed films were much smoother. Those morphologies, however, do not appear to explain the increase in the hydrophilicity of the 6.5Li-SPS4 film when annealed at 120 °C.

The addition of methanol to either toluene or THF increases the average polarity of the solvent, and mixed polar–nonpolar solvents can have a dramatic effect on the ionic aggregation and chain conformation of ionomers in solution. The intrinsic viscosity data in Table 2 show that the addition of methanol expands the chain conformation of the Li-SPS4 ionomers, especially in the case of the 6.5Li-SPS4 in a 9/1 (v/v) THF/methanol solution. Previous solution viscosity studies by Lundberg and co-workers indicate that the methanol preferentially solvates the ionic associations in toluene/methanol and THF/methanol solutions.

Whereas the surface of the 2.5LiSPS4 spin-coated from toluene was smooth and homogeneous (Figure 4a), the addition of methanol to the solvent produced films with a small amount of discrete particles on the surface of the film (Figure 7a). The addition of methanol to the THF produced a wetted, submicron discrete particles on the surface of the film (Figure 7a). The particles were not well resolved in the micrographs (c.f. Figures 4c and 8c), even smoother than the films spin-coated from the toluene solutions.

Effect of Counterion. The effect of the cation on the morphology of the SPS ionomers, 2.5MSPS4 (where M represents an alkali metal cation: Li, Na, K, Rb or Cs) is shown in Figures 7 and 8 for samples spin-coated onto silica from 9/1 (v/v) toluene/methanol and THF/methanol solutions, respectively. Changing the cation changes the strength of the ion-pair, which affects the ion–dipole associations in the ionomer and with a solid surface. The strength of the ion-pair scales as the Coulomb energy, which for a fixed anion (i.e., for the sulfonate, charge = 1), is $q/a$, where $q$ is the charge of the ion and $a$ is the ionic radius. The values of $q/a$ for the alkali metal salts are given in Table 3. For the alkali metal salts, the strength of the ion-pair decreases with increasing ionic radius. The distribution of particle sizes for the spin-coated samples of the Li, Na, and Rb salts are shown in Figure 9. The particles were not well resolved in the micrographs for the K and Cs salts. In general, there does not appear to be any trend in the data with respect to the strength of the ion-pair. The average size, $D_m$, of the particles is also shown in Figure 8. These values are similar for each salt.

![Figure 7. AFM topographical images of 2.5MSPS4 on silica, spin-coated from toluene/methanol and annealed at 120 °C for 0 h (a,c,e,g,i) and 240 h (b,d,f,h,j). M is the alkali cation: Li (a,b), Na (c,d), K (e,f), Rb (g,h) and Cs (i,j). Scan size is 50 × 50 μm².](image)

The morphology of the as-cast samples for all of the salts was similar to the results described above for 2.5LiSPS4. Coherent, but rough films with some holes were produced from the toluene/methanol solutions. Annealing the toluene/methanol films roughened the surface, but no dewetting was observed for any of the salts (see Figure 7). The submicron particles produced from THF/methanol casting became larger and anisotropic in shape upon annealing. After 240 h at 120 °C, coherent films were formed, although the surfaces were rough, with the notable exception of the 2.5LiSPS4 sample (Figure 8). None of the salts, however, exhibited any dewetting after 240 h of annealing.

The transition kinetics of the particle morphology was affected by the choice of the cation (see Figure 8), but the quantitative nature of the results was not easily correlated to $qa$. In all cases, the particles coalesced and flowed into a film, but the process generally took at least 20 h or more. The Cs salt, which has the weakest ion-pair, appeared to lose the particle morphology the quickest and formed a rough film after 20 h of annealing at 120 °C. The Li salt, which has the strongest ion-pair, formed the most homogeneous and smoothest surface after 240 h. A variety of morphologies were displayed by the different salts, although, for the most part, annealing produced very rough films, and it was clear that the origin of the film formation began with coalescence and growth of the particles.

The addition of methanol to toluene or THF preferentially solvates the ion–dipole interactions, which expands the polymer coils. As a result, $[\eta]$ increased upon the addition of methanol for any of the alkali metal salts (see Table 2). However, one might expect that $[\eta]$ should decrease with increasing strength and concentration of the ion-pairs, i.e., increasing $qa$ and the number of interacting groups per chain, since the interacting ion-pairs in those cases should be less amenable to solvation by the methanol cosolvent. The data in Table 2 show that, for the...
2.5SPS4 ionomers, [η] of the Li salt in the mixed solvents was relatively low, as expected since that salt is expected to have the strongest ion-pair. [η] increased for the Na salt, which again is consistent with the idea that the methanol is able to more efficiently solvate the weaker Na=sulfonate interactions. However, as q/a decreased more, the [η] appeared to pass through a maximum, for the K salt in toluene/MeOH and the Na salt in THF/methanol solutions. Lower [η]'s were observed for the Rb and Cs salts, even though those salts had the weakest ion-pairs. While inconsistent with the idea that methanol can more easily solvate lower salts with lower q/a, the decrease in the intrinsic viscosity of the Rb and Cs salts compared with the Li, Na, and K salts in the mixed solvents are consistent with the solubility of the different salts in THF and toluene. The stronger ion-pairs (Li, Na, and K salts) dissolved, but the weaker ion-pairs (Rb and Cs) did not (see Table 2). The reason for the unexpected cation effect is not yet known, but it would seem apparent that there is some specific unfavorable interaction of the larger cations with the nonpolar solvent that has an opposite effect on solubility than the ion group solvation by the methanol. In that case, the lowering of the [η] when methanol was added to the Rb and Cs salts (and K salt for the toluene/methanol solutions) may be more related to unfavorable interactions of the methanol with the PS backbone than favorable interactions with the sulfonate groups. These complicated mixed solvent effects deserve more scrutiny than was possible in this study.

The [η] data for the 6.5LiSPS4 sample are equally puzzling. For toluene and THF solutions, the [η]'s are higher than those for 2.5LiSPS4. Note that the degree of polymerization was the same for both ionomers. Then, all else equal, one would expect the two nonpolar solvents to become poorer solvents for the ionomer as the concentration of ionic groups increased. Yet, the data in Table 2 suggest otherwise. When methanol was added to the toluene solvent, the [η] of 6.5LiSPS4 did not change appreciably. Yet, the addition of methanol to THF produced a large increase in [η], indicating a more expanded chain, or more likely, a longer effective chain length due to the multiple chain associations as shown in Figure 2d. Thus, even for these low molecular weight ionomers, the intrinsic viscosity measurement is not representative of individual chains, but of soluble aggregates of multiple chains.

Initially, it was thought that the particle texture shown in Figure 5 might be related to the size of the polymer in solution. However, the data in Table 2 indicate that this is not the case, or at least it is not that simple. The particle texture occurred only when THF or THF/MeOH solutions were used for the spin-casting, but there is no consistent correlation between [η] and the occurrence of the particle texture. The solvent effect, however, can be explained if the particle texture results from a spinodal decomposition of the surface during spin-coating (see ref 28).

For the ionomers with higher sulfonation level, 6.5LiSPS4 (Figure 4e–h and Figure 10) films with smooth surfaces were formed after spin-coating, and annealing did not significantly affect the surface smoothness or texture. The films formed from THF/methanol were, however, a bit less homogeneous. In those cases, it appears that the more robust network of associations that formed at the higher sulfonation level dominated the film morphology.

SAXS characterization of the microstructure of the ionomer films is shown in Figures 11 and 12 for samples spin-coated onto silica from single-component solvents (toluene and THF) and from mixed solvents containing methanol, respectively. Ionomers generally exhibit a SAXS peak corresponding to nanophase separation of ionic aggregates with a characteristic size of d ∼ 2−5 nm and high scattering intensity at very low scattering vector, q = 4π sin 2θ/λ (where λ = the X-ray wavelength, and 2θ =
the scattering angle) that has been attributed to a heterogeneous distribution of nonaggregated ion-pairs. Both features are observed in the SAXS profiles of the 2.5MSPS ionomers shown in Figures 11 and 12. The peak is weak and diffuse, but qualitatively, it appears that the peak is better defined in the samples spin-coated from toluene and toluene/MeOH mixtures. The better developed peak from those samples is probably a consequence of the lower polarity of toluene compared to THF and, as a result, stronger aggregation of the ionic groups and better development of the nanophase separation of ion-rich aggregates. As one might expect, the intensity of the scattering for the 2.5MSPS increased as the electron density contrast increased (i.e., as the atomic number of the cation increased and as the ionic group concentration increased).

Assuming that the origin of the scattering is interparticle interference between ionic aggregates, the average distance between ionic aggregates \( (d = 2\pi/\lambda) \) was estimated from the approximate position of the maximum of the scattering peak to be 3.9–5.0 nm for the different samples. The better resolution of the peak in the samples prepared from the toluene-based solvents indicates that the particle texture formation, which occurred in samples cast from THF-based solutions, is favored by a poorer developed ionic nanostructure in these ionomers.

**Effect of Molecular Weight.** Figure 13 shows AFM topographical images of higher molecular weight LiSPS ionomers spin-coated onto silica. The average number of sulfonate groups per chain for 0.76LiSPS13.5 and 2.7LiSPS13.5 correspond to 1 and 3.5, respectively, which are comparable to the lower molecular weight ionomers 2.5LiSPS4 and 6.5LiSPS4. The \( T_g \)'s of the higher molecular weight ionomers were higher (102–104 °C), which is mainly due to the higher \( T_g \) of the parent PS. With the exception of the 0.76LiSPS13.5 sample spin-coated from THF, the spin-coated higher molecular weight ionomers were smooth and relatively featureless, and the surface morphology did not change even after annealing for 240 h at 140 °C.

The 0.76LiSPS13.5 sample spin-coated from THF exhibited a surface morphology of densely packed nanoparticles similar to that of the 2.5LiSPS4 sample (c.f. Figures 4 and 13). When annealed for 240 h at 140 °C, the particles coalesced into a generally homogeneous film with a rough surface. There was, however, some formation of very small holes in the annealed sample (see the dark dots on the AFM photo in Figure 4a and the topographical profile in Figure 4b of the dotted line drawn in Figure 4a). These holes did not appear to grow or coalesce as would be expected if they were due to dewetting of the film, and they may have simply been imperfections arising from the coalescence of the submicron particles.

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textured surface, and the particles coalesced into a homogeneous film upon annealing. The SPS ionomers with higher molecular weight resulted in an even smoother and relatively featureless surface on the silica surface.

A remarkable result was that it was not necessary that all the chains be sulfonated to achieve the dewetting resistance. That is, the homogeneous sulfonation reaction used to prepare the sulfonate concentrations used in this study is expected to leave a high fraction of chains unsulfonated. Since the chain length of these polymers was far below the entanglement molecular weight for PS, one would have expected that the unsulfonated chains would dewet under the conditions used to anneal the samples. But, no evidence of dewetting of any part of the sample was observed in any of the experiments conducted in this study.

That observation is consistent with a study of the phase behavior of SPS polymers where it was found impossible to fractionate chains with different sulfonation concentrations, including no sulfonate groups, by cooling a solution slowly from elevated temperature. Even though the polymer samples consisted of a distribution of sulfonate groups/chains, a distinct upper critical solution temperature (UCST), which varied with the average sulfonate concentration, was observed, and at the UCST all chains, with and without sulfonate groups, precipitated. That phenomenon was attributed to aggregation of the sulfonated chains, which presumably imbibed the unsulfonated chains at about 0.5 °C above the UCST. In that study, however, all of the molecular weights used were above the entanglement molecular weight of PS, so the inclusion of the unsulfonated chains could have been the result of entanglements.

In the present study, where the molecular weight of the ionomers was below the entanglement molecular weight of PS, it is not obvious why the unsulfonated polymer does not dewet during the annealing experiments. This may, perhaps, be a consequence of miscibility of the PS with the SPS ionomer, although Beck Tan et al. reported that high molecular weight (> 10^6 g/mol) SPS and PS were immiscible because of the strong repulsive interactions between the sulfonated species and styrene. However, there is no reported data on the phase behavior of PS/SPS mixtures.

Conclusions

SPS ionomers can greatly improve the wetting behavior of PS films on a silica surface, and ionomer films showed excellent resistance to dewetting. The latter was true for unentangled ionomer chains with any alkali metal sulfonate and sulfonation levels sufficient to provide at least some chains with multiple sulfonate groups. The choice of the solvent used to prepare the films affected the surface morphology, but did not have a significant effect on dewetting. The surface was smoother and more homogeneous for higher sulfonation levels. The probability that a chain has a functional group that can complex with the silica increases with increasing the sulfonation level. Increasing the ionic concentration of the SPS also produced a higher effective density of physical cross-links which provides a much higher viscosity that also helps suppress dewetting of these films above Tg.

The effect of the cation on the morphology of the SPS ionomer films did not have a substantial effect on the surface morphology. Annealing films roughened the surface, but no dewetting was observed for any of the salts. Increasing the polarity of the solvent used for spin-coating affected the morphologies of the 2.5MSPS ionomer as-cast films from the homogeneous to a nanoparticle-

Figure 13. (a) AFM topographical images of 0.76LiSPS13.5 and 2.7LiSPS13.5 spin-coated onto silica from toluene and THF and annealed at 140 °C for 240 h. (b) Topographical profile of the white dotted line drawn on the AFM of the 0.76LiSPS13.5 sample cast from THF and annealed at 140 °C for 240 h.

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