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Notes

Adsorption Phenomenon of Lightly Sulfonated Polymers on a Solid Substrate Surface

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Introduction

The incorporation of relatively low levels of ionic groups onto the backbone structure of a polymer chain profoundly changes the physical properties of these materials as compared to its unmodified counterparts.[1-11] These changes to a large extent are caused by the formation of ionic cross-links arising from mutual association of the ionic groups. However, for such polymers in polar solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF),[12] classic polyelectrolyte behavior occurs. The effect is so pronounced that sulfonated polystyrene itself is soluble in DMSO, but its nonfunctionalized counterpart is not. To a first approximation, polyelectrolyte behavior and ion-pair association are both dependent on the dielectric properties of the solvent and the specific interaction energy between the solvent and the sulfonate group. Since ionically modified and unmodified polymer chains can have very different bulk solution properties, it is of interest to examine their behavior at a solid/solid interface, i.e., whether the chains form an adsorption or depletion layer at an interface. This is important since it is well-known that the interfacial properties of polymers can markedly influence the properties of a large number of systems. For example, stability of colloidal dispersions[13] and adhesion and wetting properties on substrates are improved. An understanding of the interfacial properties on a molecular level is of substantial scientific and technological importance.

A recent report[14] shows that a phase-modulated evanescent-wave ellipsometry technique similar to the one used in this study has sufficient sensitivity to probe polymer adsorption or depletion at liquid/solid interface. Those initial measurements are in good agreement with previous results obtained with other techniques. Our present effort focuses on the measurements of a series of lightly sulfonated monodisperse polystyrenes in DMSO (i.e., high dielectric constant solvent) absorbed or depleted in the vicinity of a chemically modified hydrophilic and hydrophobic substrate surface.

Experimental Section

The glass (prism) surface was modified chemically by grafting a monolayer of trichlorooctadecylsilane (OTS) using a procedure described by Sagiv.[15] After the hydrophobic monolayer is grafted onto the glass surface, the wettability of the OTS-coated glass surface was checked to ensure the hydrophobicity of the surface. The wettability of the surface after immersion in the polymer solution also was used as an indicator to qualitatively determine whether the polymer adsorbs on the surface; i.e., does the surface become hydrophilic upon adsorption or remain hydrophobic without adsorption? For the preparation of a hydrophilic surface, the glass prism was soaked in no-chromix sulfuric acid and washed with plenty of distilled water and subsequently with DMSO.

The experimental arrangement and the procedure of polymer sulfonation were described in detail in a previous publication.[14] The polymers used in this experiment are listed in Table I. The first polymer is an 8.3 mol % manganese (Mn^{2+}) neutralized sulfonated polystyrene. The second material contains a similar amount of sulfonated polystyrene but with a sodium counterion. The third and fourth polymers have 5.1% and 3.05% sulfonate levels, respectively, with Na^+ as the counterion. The ionic groups (sulfonated polystyrene) are distributed randomly along the polystyrene backbone.

The phase difference in reflection of ordinary and extraordinary beams at the critical angle $\Delta\Phi(\theta_t)$ depends on the excess in the optical dielectric constant in the interfacial region due to either polymer depletion or adsorption. Letting the optical dielectric constant at a distance z from the interface be $\epsilon(z)$, which is linearly dependent on the polymer concentration profile $c(z)$ at z, then

$$\epsilon(z) = \epsilon_{\rm solv} + \frac{c(z)}{c_{\rm b}}\Delta\epsilon_{\rm ss} \qquad (1)$$

where $c_{\rm b}$ is the polymer concentration in the bulk solution and $\Delta\epsilon_{\rm ss}$ is the difference between the dielectric constants of the solvent and solution ($\Delta\epsilon_{\rm ss} = \epsilon_{\rm solutn} - \epsilon_{\rm solv}$). Following the derivation of Drude,[16] we find that for $d/\lambda \ll 1$ and to the first order in $\Delta\epsilon_{\rm ss}$, the total polymer excess in the interfacial region due to absorption or depletion is

$$\Gamma = \int_0^\infty (c(z) - c_{\rm b})\, {\rm d}z = \Delta\Phi(\theta_t)\frac{c_{\rm b}\epsilon_{\rm solv}}{2k_0\Delta\epsilon_{\rm ss}\Delta\epsilon_{\rm ps}{}^{1/2}} \qquad (2)$$

where $k_0 = 2\pi/\lambda$, with λ denoting the laser wavelength in vacuo, and $\Delta\epsilon_{\rm ps}$ is the difference between dielectric constants of the glass prism ($\epsilon_{\rm prism}$) and the solution ($\epsilon_{\rm solutn}$). Equation 2 shows explicitly that the adsorption parameter, Γ, is linearly proportional to $\Delta\Phi(\theta_t)$. A positive or negative sign in the value of $\Delta\Phi(\theta_t)$ corresponds to adsorption or depletion at the interface, respectively, since both $\Delta\epsilon_{\rm ss}$ and $\Delta\epsilon_{\rm ps}$ are positive.

In our experiment the phase retardation for the pure solvents was first measured. It was approximately 0.1 rad, which came primarily from the inherent strain in the prism. This residual phase retardation from the pure solvent must be subtracted from the phase retardation data of the polymer solution. Extreme care is required not to alter the strain in the prism when the polymer solution was introduced. That is, the phase retardation due to replacing the solvent by the polymer solution could be minimized to less than 0.5 mrad.

Results and Discussion

As mentioned in the previous section, the sign of $\Delta\Phi(\theta_t)$ indicates, in a qualitative manner, whether the interfacial layer is best described as an adsorbed (positive) or a depleted layer (negative). $\Delta\Phi(\theta_t)$ represents the integration of the polymer concentration profile in terms of the dielectric constant through the interface. Table I shows the values of $\Delta\Phi(\theta_t)$ and Γ of these ionomer solutions at different sulfonate levels with hydrophilic and hydro-

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Table I
Lightly Sulfonated Polystyrene (M_w = 100 000) in Dimethyl Sulfoxide at a Liquid/Solid Interface

sulfonation level, mol %	counterion struct	substrate surface	$\Delta\Phi(\theta_t)$, mrad	excess amount, mg/m^2
8.2	Mn	hydrophobic	12.5	3.95
		hydrophilic	*a*	*b*
8.8	Na	hydrophobic	1.28	0.25
		hydrophilic	*a*	*b*
5.12	Na	hydrophobic	2.4	0.37
		hydrophilic	*a*	*b*
3.05	Na	hydrophobic	−0.4	−0.08
		hydrophilic	*a*	*b*

[a] The value of $\Delta\Phi(\theta_t)$ is within experimental error between −0.2 and 0.0 [b] The value of the excess amount within experimental error is between −0.04 and 0.0.

phobic substrates. For the majority of the depletion cases, $\Delta\Phi(\theta_t)$ is too small to yield a quantitative value of Γ.

These are several interesting conclusions that can be drawn from Table I. The adsorption phenomenon is strongly dependent on the nature (i.e., chemistry) of the substrate. The hydrophilic surfaces do not show an adsorption layer. Except for the lowest sulfonation level, all polystyrenes show adsorption on a hydrophobic substrate. Since the solvent is identical in these experiments, the interaction between the polymer and the substrate is the only factor responsible for the difference in polymer adsorption on these substrates. It is known that an acid-cleaned glass surface of pH = 7 is negatively charged.[17] In the same solvent, the lightly sulfonated polystyrene chains are dissociated from their counterion.[12,18] Therefore, a negative coulombic interaction between the anionically charged sulfonate moieties on the chain and the negative surface charge of the glass exists, and therefore the lightly sulfonated polystyrene is unable to form an adsorption layer on the hydrophilic surface. It would be of interest to vary the magnitude of charge on the glass surface or its sign. This would have the effect of changing the interaction between the polymer and the substrate. One could, however, also change the interaction making the glass surface hydrophobic such that the coulombic force no longer dominates the interaction between the polymer and the substrate.

For the hydrophobic surface, the conclusion drawn from Table I is the strong sulfonate level dependence on the adsorption of the ionomers. In this case, the interaction between the polymer and solvent molecules is the key parameter governing the adsorption. With high sulfonate content, the polymer chains are stretched due to charge–charge[12,18] repulsions of the sulfonate groups on the same backbone. To significantly expand the chain dimensions, the repulsive force between the sulfonate groups needs to be larger than the attractive interaction between the individual monomer units in DMSO. Again, it is noteworthy that polystyrene is not soluble in DMSO. Because of this insolubility, i.e., "hydrophobicity", the hydrophobic substrate surface would naturally adsorb the styrene segments. In addition, the charge–charge interactions are not strong enough to stretch substantially the polymer backbone at these lower sulfonate levels. As a result, the "hydrophobic" segments could be shielded from the solvent by a corona of charged groups. Dynamic light-scattering measurements have confirmed that the chain dimension of lightly sulfonated ionomers strongly depends on the level of charged groups in highly polar organic solvents, such as DMSO.[18] Because of the formation of the corona-like styrene core possibly forming micelles, it is now mainly the charged groups that interact with the hydrophobic surface. As a consequence, the polymer chains are no longer attracted to the hydrophobic surface.

At moderately high sulfonation levels, the hydrodynamic radius of the ionomer chains is substantially increased. Therefore "hydrophobic" styrene units and the exposed styrene segments will preferentially adsorb onto the hydrophobic substrate surface. As anticipated the adsorption is enhanced with increasing sulfonate content (see Table I). However, in the limit of large anionic charge densities, i.e., water-soluble polyelectrolytes, adsorption onto a hydrophobic surface should again become strongly inhibited.[17]

Another interesting result of Table I is related to the adsorption characteristics of polystyrene at the same sulfonate level but with different counterions. Adsorption of the manganese-neutralized sulfonated polystyrene is 15 times stronger than that of sodium-neutralized sulfonated polystyrene. Since dissociation of the sulfonated units depends strongly on the valency of the counterions,[12,19] the interaction between the sulfonate groups is different for these different types of counterions. As we described earlier, the coulombic interaction shows very strong effects on the ionomer adsorption. As a consequence, the adsorption of sulfonated polystyrene strongly depends on the type of the counterions.

It is interesting to compare the amount of adsorbed polymer with that obtained at full coverage from monolayer experiments at an air/water interface. Most polymer monomer experiments[20] show that at full coverage several milligrams per square meter are required. This value is very similar to the amount of the adsorbed manganese-neutralized sulfonated polystyrene. This result strongly indicates that the sodium-neutralized sulfonated polystyrene adsorbs only partially onto the hydrophobic substrate.

Unfortunately, there is no theory to compare quantitatively the extent of the adsorbed layer as a function of the charge situated along the polymer chain backbone. However, it is known that the adsorption characteristics of polyelectrolytes are strongly dependent on the degree of ionization and the electric potential due to the local concentration of the counterion and macromolecules at the interface. In addition, the Flory–Huggins parameter (χ) of the polymer and solvent and the differential adsorption energy (χ_s) need to be taken into account.[21] The results presented here are in qualitative agreement with the numerical calculations in ref 21. The quantitative comparison between theory and experiment is difficult because the detailed parameters of the interactions and the local potential are not known.

Conclusion

The phase retardation angle, $\Delta\Phi$, was measured via evanescent-wave ellipsometry in order to study the adsorption phenomenon of ionomers in polar solvents onto hydrophobic and hydrophilic solid substrates. Several interesting results are obtained from these experiments. First, there is a strong dependence of substrate chemistry on polymer adsorption. Ionomers in a high dielectric polar solvent do not adsorb onto a hydrophilic surface. Yet, these polymers are able to adsorb onto a hydrophobic surface at higher sulfonation levels. This is due to the adsorption energy difference between the surface and the ionomer chains. Second, the adsorption of the ionomer chains onto a hydrophobic surface is very strongly dependent on the degree of the functionality of the polymer. The lowest level of charge along the ionomer chain shows a depletion layer formation rather than adsorption, which occurs at a higher level of charge. In the latter case, the ionomer adsorption interactions is a function of the adsorption energy due to not only the substrate–polymer chain interaction but also the solvent–polymer chain interaction. Third, the extent of adsorption onto a hydrophobic surface is strongly dependent on the structure of the counterion. For example, the amount of adsorption of the manganese-neutralized sulfonated polystyrene is about 15 times greater than its sodium-neutralized counterpart. This finding is related to the different dissociation constants of mono- and divalent ions in polar solvents and consequently to the marked differences in the electric potential in the vicinity of the ionomer chain. Finally, the amount of the adsorbed manganese-neutralized sulfonated polystyrene is almost the same as that of a full monolayer at an air/water interface obtained by spreading.

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