Adsorption Behavior of Polymers with Ionic End Groups: Mono- and Difunctional Polystyrenes in Toluene

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Received September 21, 1994; Revised Manuscript Received June 27, 1995[⊗]

ABSTRACT: The adsorption behavior of mono- and difunctional telechelic polymers, ω- and α,ω-sulfonato polystyrenes, from dilute toluene solution on the surface of a silicon wafer is investigated by ellipsometry. Polystyrene without ionic end groups does not adsorb, and the attachment of molecules to the silicon dioxide surface proceeds via the functional ionic ends. Already a single ionic group promotes adsorption, and adsorption kinetics at small times is found to be diffusion limited. The approach of an equilibrium adsorbed amount at later times is controlled by the hindered diffusion of chains through the already existing layer. With monofunctional chains a thin stable monolayer at the surface is formed. With difunctional chains there is strong indication for coupling of ionic ends and the formation of additional layers. It is caused by the interaction of dangling ends, when only one end of the chains is adsorbed at the surface. The molecular weight dependence of the grafting density is consistent with scaling predictions, and differences in the adsorbed amount of telechelics with different counterions are explained on the basis of different valencies.

Introduction

For the past two decades, intense research work has focused on the structure and properties of ionomers, i.e., hydrocarbon polymer chains bearing less than 15 mol % of ionic groups. The unique mechanical, rheological, and transport properties of ionomers result from the intermolecular interactions of the ionic moieties. It is now generally accepted that ion pairs aggregate into small ionic domains, called multiplets, which act as thermoreversible physical cross-links and are responsible for the original properties of these materials.[1-4] Most ionomers, however, result from random copolymerization or postpolymerization reactions. Therefore, the ionic groups are distributed at random along the hydrocarbon chains, and the molecular parameters of ionomers are often ill-defined. This problem has been obviated by the synthesis of model compounds, i.e., halato-telechelic polymers (HTP's), which are linear chains or star-shaped polymers selectively capped by an ionic group at each end.[5-12] Their very well-controlled molecular characteristics and clean architecture have improved the understanding of the structure–property relationships that prevail in ionomers. Recently, halato-semitelechelic polymers (HSTP's), which are linear chains bearing a single ionic group at one end, have been proposed as the simplest model compounds for the study of ionic interactions in ionomers.[13-16] Light scattering investigations on dilute HSTP solutions allowed a precise determination of the average aggregation number in these compounds.[15,16]

Although ionomers have been used in adhesives, lubricants, and antistatics,[1-3] the surface and interfacial behaviors of ion-containing polymers have been the subject of very little attention. The technological importance of adsorbing polymers, however, does not need to be demonstrated. They can be used for the stabilization or flocculation of colloidal dispersions, for the dispersion of fillers, or to attain adhesive properties.[17,18] Polymer thin films are an integral part of a wide range of applications such as microelectronics and optoelectronics.[19] In some applications, ultrathin films and monolayers are desirable. Nevertheless, recent theoretical and experimental investigations have shown that, below a critical thickness, polymer films may be inherently unstable[20,21] and spontaneously dewet the substrate when brought close to their glass transition temperature. Tethering the polymer chains to the surface by means of specific interactions could prevent thin-film dewetting. This approach has recently been reported by Klein,[22] who has used end-carboxylated polymer chains to stabilize ultrathin polymer films.

Tethered chains have been the subject of several theoretical treatments (for a recent review, see, e.g., ref 23), and at high surface coverage a brushlike chain conformation is predicted. In particular, monofunctional polymers with a polar head are believed to form such a brushy layer[24] when the main chain does not adsorb on the substrate. Polymers with two sticky ends, on the other hand, may behave quite differently[25] and relatively complex structures may be formed at the substrate. This is understood by the influence of two effects not present with monofunctional materials. First chains may form loops on the surface, giving rise to an increase of the density in the vicinity of the surface, if the number of chains would be the same as in the case of monofunctional materials. Because of repulsion of neighboring chains, the adsorbed amount thus is expected to decrease. Second, however, chains may form bridges to other chains via one of their sticky ends, while the other end is attached to the surface. This could result in multilayer formation, thus increasing the adsorbed amount.

In a recent study on polystyrene, lightly sulfonated statistically along the chain, Kim *et al.*[26] have shown that both the ionic content and the nature of the ion pair can deeply influence the adsorption behavior at the solid/liquid interface. At present, however, the key

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

0024-9297/95/2228-6986$09.00/0

parameters controlling the adsorption of ion-containing polymers at solid interfaces are hardly known. For this reason, the present paper reports on systematic investigations of metal sulfonato halato-(semi)telechelic polystyrenes adsorption from toluene solutions.

Experimental Section

Sample Preparation. ω- and α,ω-sulfonato polystyrenes were synthesized by living anionic polymerization of styrene followed by deactivation with 1,3-propanesultone, as reported elsewhere.[13] The functionality was systematically better than 90%, as checked by potentiometric titration of the acid end groups with a standard solution of tetramethylammonium hydroxide in a toluene/methanol (9/1 v/v) mixture. Molecular weight and molecular weight distribution were measured by size exclusion chromatography of a polymer sample picked out before the functionalization step.

Lithium sulfonate terminated polymers were purified by a twofold precipitation in methanol. For other cations, the lithium sulfonate terminated polymers were converted into the sulfonic acid counterparts by a twice repeated precipitation in methanol containing at least 20 equiv of perchloric acid and a final reprecipitation in pure methanol. (Semi)telechelics were kept in the acid form in a toluene/methanol solution. The sulfonic acid end groups were neutralized by 1.05 equiv of the required metal acetate. Methanol and acetic acid were removed by the azeotropic distillation of the solvent (regularly replaced by dry toluene) until no polar compounds could be detected in the distillate by gas chromatography and/or potentiometric titration. The solvent was finally removed by distillation. All the samples were dried at 160 °C, under vacuum, for 16 h.

Solutions were prepared by dissolving a weighed amount of polymer in a precise amount of toluene (analytical grade) previously distilled over sodium metal. After stirring for at least 1 h at 25 °C, the solutions were filtered on a Millipore filter (0.2 μm). The samples are labeled as follows: functionality of the chains (either 1 or 2), molecular weight in thousands, and cation (Li, Na, or Ba).

Silicon wafers (p-type boron doping, conductivity 1–10 Ω cm, Cz(100) polished surfaces) kindly supplied by Wacker Chemitronix, Burghausen, were used as substrates. They were polished to a surface roughness of typically 1 nm as measured by phase measurement interference microscopy or X-ray reflectometry. The surface of the wafers was chemically oxidized and consisted of an oxide layer of approximately 150 nm. The exact oxide film thickness differed slightly for each piece of the wafer and was measured for each sample by ellipsometry before adsorption was started. A careful cleaning procedure as described earlier[27] was applied prior to each experiment, which ensured reproducible results. Wafers were cleaned in an ultrasonic bath with chloroform and acetone, oxidized in a 1:1 mixture of NH_3 and H_2O_2 and rinsed several times with distilled water.

Adsorption Experiments. Null ellipsometry was used to measure the adsorbed amount of polymer as a function of time during the adsorption process. A detailed description of the apparatus and the data analysis procedure can be found elsewhere[27] and will be only briefly exposed here.

The sample cell was trapezoidal (Hellma) and had entrance and exit windows fixed at 70.0°. A clean silicon wafer (1 × 1 cm^2) was placed in the cell, which was then filled with 60 mL of freshly distilled and filtered toluene. All runs were performed at a temperature of (20.0 ± 0.1) °C. After stabilization of the baseline signal, 0.5 mL of polymer solution was injected into the cell and the ellipsometric angles were monitored with time, with a 25 s interval between two successive measurements. For a better distribution of chains after the injection, the solution was stirred for 1 min, while already the first data points were taken. Control experiments with toluene and unfunctionalized polystyrene showed no evidence of adsorption.

Table 1. Molecular Parameters of the Series of ω- and α,ω-Metal Sulfonato Polystyrenes Reported in This Paper

code	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	cation	fty[a]
1PS7KLi	7000	7700	1.1	Li^+	0.99
1PS8KNa	8300	8900	1.07	Na^+	0.95
1PS8KBa	8300	8900	1.07	Ba^{2+}	0.95
1PS18KLi	18400	19800	1.08	Li^+	0.92
1PS18KBa	18400	19800	1.08	Ba^{2+}	0.92
1PS30KBa	30000	30600	1.02	Ba^{2+}	0.96
1PS49KLi	49000	49500	1.01	Li^+	0.93
2PS14KBa	14000	16500	1.18	Ba^{2+}	1.90
2PS30KBa	29500	32500	1.1	Ba^{2+}	1.93
2PS102KBa	102000	109000	1.07	Ba^{2+}	1.86

[a] Average number of ionic end groups per chain.

The technique of null ellipsometry uses a motorized linear polarizer (P_1) and a compensator to generate a state of elliptical polarization, which, when reflected, becomes linear polarized light. A second motorized linear polarizer (P_2) is used to extinguish the reflected light. The intensity of light passing through the second polarizer is monitored using a photodiode, and the computer control of the polarizers allows for an automated search for the null settings. When total extinction is reached, the ellipsometric angles Ψ and Δ are given by the position of the polarizers: $\Psi = P_2$ and $\Delta = 2P_1 + 90°$. These angles contain information about the relative attenuation and phase shift of the component waves perpendicular (s-wave) and parallel (p-wave) to the plane of incidence.[28] Assuming a multilayer model with the polymer film being a homogeneous layer, the unknown film thickness, d_1, and refractive index, n_1, can be calculated using eq 1:

$$e^{i\Delta}\tan\Psi = R_p/R_s = F(n_k,d_k) \qquad (1)$$

where n_k and d_k refer to the index of refraction and the thickness of each layer present in the system, denoted by subscript k (i.e., solution, polymer, silicon dioxide, and silicon). R_p and R_s represent the overall reflection coefficients for the component p- and s-waves. Since Ψ and Δ are measured and n_k and d_k are known except for the polymer layer thickness, d_1, and refractive index, n_1, eq 1 can be solved. In the present study, the measured refractive indices were $n_{Si} = 3.882 + 0.018i$, $n_{SiO_2} = 1.4620$, $n_{toluene} = 1.4940$, and $n_{PS} = 1.59$. The small differences due to end groups are neglected. The amount of adsorbed polymer, A (mg m^{-2}), can then be calculated using eq 2:

$$A = d_1c_1 = d_1(n_1 - n_0)/(dn/dc)_0 \qquad (2)$$

where n_0 is the refractive index of the polymer solution and $(dn/dc)_0$ is the refractive index increment of the polymer in the solution. $(dn/dc)_0 = 0.1070$ mL/g was measured for 1PS19KBa, which does not differ significantly from the value of pure PS in toluene. The small difference in refractive index between the polymer and the solution makes a separate determination of d_1 and n_1 difficult. The product n_1d_1, however, is essentially independent of the adopted layer model and concentration profile near the wall,[27] and the discussion will therefore focus on the adsorbed amount of polymer, A. The grafting density, σ (nm^{-2}), is calculated from eq 3:

$$\sigma = \frac{A\ (\mathrm{mg/m^2})}{\bar{M}_w\ (\mathrm{mg/mol})} N_a\ (\mathrm{mol^{-1}}) \times 10^{-18}\ (\mathrm{nm^{-2}}) \qquad (3)$$

where N_a is Avogadro's number. σ is the inverse of the average area per adsorbed chain. Accordingly, the mean interchain spacing between adsorbed chains, D_{inter}, can be calculated from

$$D_{inter} = (1/\sigma)^{1/2} \qquad (4)$$

The experimentally determined value of D_{inter} will be compared with the interchain spacing of unperturbed chains D_{over} as will be discussed later.

Results and Discussion

A series of ω- and α,ω-metal sulfonato polystyrenes were synthesized, and their molecular characteristics are summarized in Table 1. Molecular weight distribu-

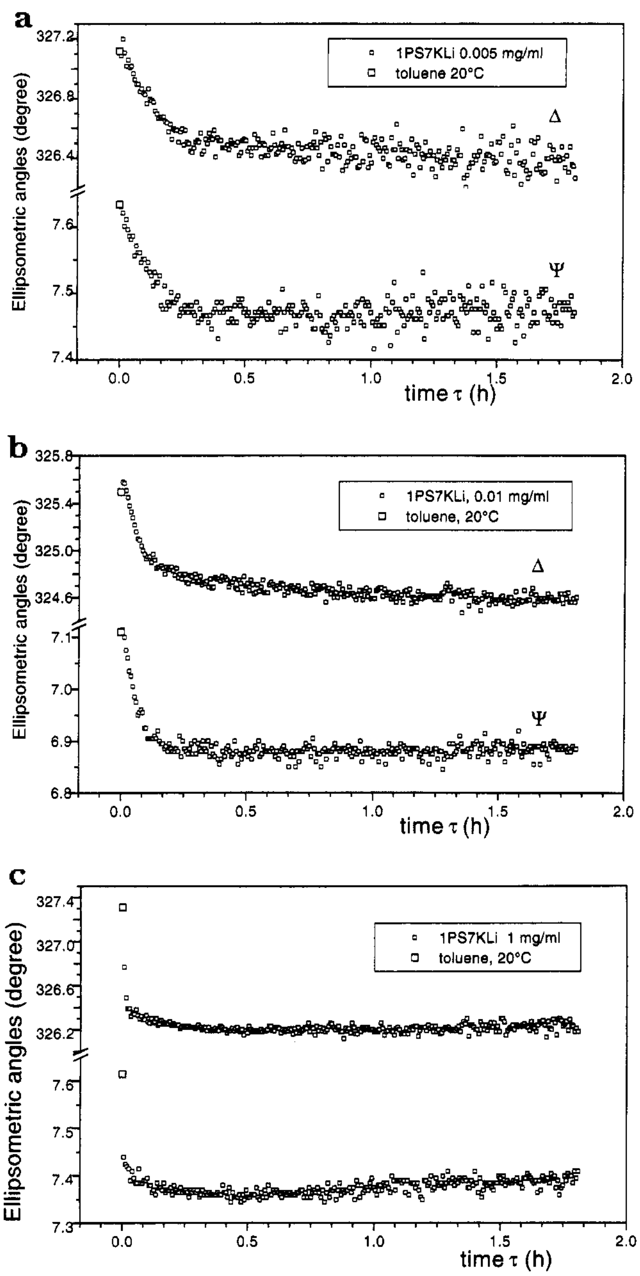

Figure 1. Change of ellipsometric angles during adsorption runs at different concentrations as a function of reduced time. $\tau = 0$ corresponds to the injection time of the polymer solution. Materials and concentrations are indicated in the plots. The first (larger) point corresponds to the measurement of the wafer in pure toluene prior to the adsorption experiment.

tions are very narrow, as usual for anionic synthesis, and functionality is systematically better than 90% for monofunctional samples and 185% for difunctional samples. Values of 100 and 200% would correspond to complete functionalization of mono- and difunctional samples, respectively.

Figure 1 illustrates the typical variation of the ellipsometric angles, Ψ and Δ, after injection of the polymer solution ($\tau = 0$), for different concentrations. Obviously, end-functionalized polystyrene adsorption occurs on a time sacle which increases when the polymer concentration is decreased. Thus the equilibrium values of Ψ and Δ are reached after approximately 30, 15, and within 5 min at concentrations of 0.005, 0.01, and 1 mg/mL, respectively (Figure 1a–c). Thus even at low concentrations the adsorption kinetics remains relatively fast, and a precise measurement of the time dependence of adsorption in particular at higher concentrations is difficult, taking the time resolution of the experiment into account. Time resolution is determined by the measurement time for a set of the ellipsometric angles (25 s) as well as the injection and stirring period (25–75 s). Thus the starting point $\tau = 0$, where a homogeneous concentration in solution is reached and adsorption starts, is difficult to determine on a smaller time scale. When after a few minutes the equilibrium value of the angles Ψ and Δ is reached, no further evolution can be detected, even after several hours. Since control experiments with unfunctionalized polystyrene solutions showed no evidence for polymer adsorption, adsorption of the metal sulfonato (semi)telechelic polystyrenes is due to the presence of the ionic SO_3 end groups. In the case of HSTP's, the introduction of a *single* ionic group at the end of the polymer chain is enough to change deeply the interfacial behavior of the polymer. For monofunctional samples, only the end groups adsorb, leaving the polystyrene chains dangling in solution. For difunctional samples, the situation is more complex, as will be discussed hereafter. HTP and HSTP adsorption, moreover, is irreversible against replacement by toluene, since, even after several days, no change in the ellipsometric angles can be detected when the polymer solution is replaced by pure toluene.

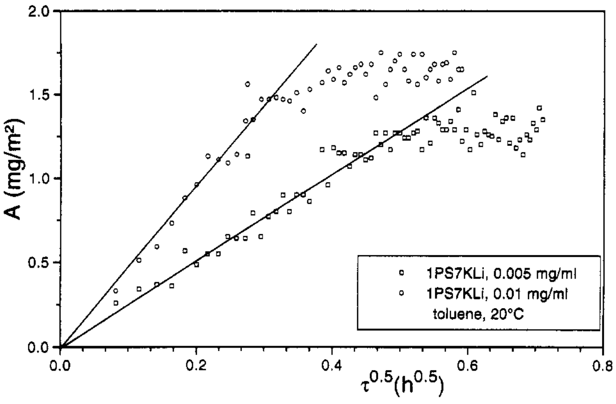

Figure 2. Time dependence of adsorbed amount A at different concentrations for initial stages of adsorption. The straight lines indicate model fits assuming diffusion-limited adsorption with diffusion coefficients as indicated in the text.

The short-time adsorption kinetics is exemplified in Figure 2. Clearly, the adsorbed amount of polymer, A, increases linearly with the square root of time, which is indicative of a transport-limited regime, where simple Fickian diffusion to the surface is the rate-limiting step. Assuming appropriate boundary conditions, i.e., a well-defined starting point, an initially homogeneous chain concentration in solution and a "sink" for adsorption at the surface, the diffusion equation can be solved[27] to yield eq 5:

$$A(t) = \frac{2c}{\pi^{1/2}}(D_{AB}t)^{1/2} \qquad (5)$$

where D_{AB} is the diffusion coefficient of the polymer in solution and c is the uniform bulk concentration of the solution. Provided the diffusion coefficient is known, eq 5 has no adjustable parameters. Alternatively, D_{AB} may be determined from the measured time dependence of A.

As already discussed, the starting point of adsorption is difficult to specify and at the low concentrations, which are necessary to resolve the time dependence with the given experimental resolution, also the exact values of the concentrations are difficult to determine. Thus the absolute values of the diffusion coefficients obtained on the basis of eq 5 can only be taken as an estimate. From the slope of the straight lines in Figure 2 one obtains for instance diffusion coefficients of 5.9×10^{-7} and 4.8×10^{-7} cm^2 s^{-1} for the concentrations of 0.005 and 0.01 mg/mL of 1PS7KLi in toluene, respectively. Diffusion coefficients of other materials are of the same order of magnitude ($(4-14) \times 10^{-7}$ cm^2 s^{-1}).

Previous light scattering measurements on toluene solutions of HSTP's have shown that HSTP's aggregate into micelles at high concentrations and that the association–dissociation equilibrium is strongly displaced in favor of the free chains at concentrations below 1 mg/mL. Therefore, the diffusion rate of HSTP's is expected to be similar to that of unfunctionalized polystyrene chains of comparable molecular weight. The diffusion coefficients obtained from Figure 2 are well in the range of values reported for diffusion coefficients of polystyrene in toluene solution.[29] This agreement between experimentally determined values with those obtained for polystyrene of comparable molecular weight is evidence for the assumption that the diffusion of single chains in solution determines HSTP adsorption from toluene in the early stage.

At later stages we observe deviations from the $t^{1/2}$ behavior. This can be assumed to be due to the hindered diffusion of chains through the already adsorbed layer. In this stage adjacent adsorbed chains have already started to touch, leaving no space for newly arriving chains to adsorb. Those chains have to diffuse through the layer, pushing the already adsorbed chains aside, which causes an entropic contribution to the free energy due to the deformation and stretching of chain conformations. We will discuss the balance between this entropic contribution and the enthalpic gain due to adsorption at the surface in detail below.

For the following discussion we will use the equilibrium adsorbed amount reached after 5–30 min depending on concentration (Figure 1). For all the samples investigated, the equilibrium adsorbed amount was found to increase with concentration until a plateau value is reached, which depends on the metallic counterion associated to the sulfonate end group. An example of this adsorption is shown in Figure 3a for monofunctional samples of comparable molecular weights. Plateau values with increasing concentration are reached at concentrations as low as 0.1 mg/mL. For monofunctional samples, barium sulfonate end groups are slightly, but significantly, less efficient in promoting adsorption onto the silicon oxide surface compared to the other ion pairs. In fact, the adsorbed amount for the barium-neutralized sample (1.6 mg/m^2) is approximately 20% less than for the lithium- and sodium-neutralized samples (1.8–2 mg/m^2). Such differences might arise from the higher valency of the barium cation (+2) compared to both lithium and sodium (+1). In toluene, indeed, ions are associated into contact ion pairs, and isolated ions are not likely to exist, due to the very small dielectric constant of this solvent. Therefore, the divalent barium ions must be surrounded by two poly(styrenesulfonate) chain ends, which is expected to increase steric hindrance around the ionic dipoles. Moreover, in the $-SO_3-Ba-O_3S-$ ion triplet, two ionic dipoles are directly opposed, which undoubtedly reduces the overall dipolar interactions of barium sulfonate end groups. Electrostatic interactions of barium sulfonate end groups are thus expected to be weaker compared to monovalent metal sulfonates such as lithium or sodium. This behavior is observed for all investigated molecular weights, since the adsorbed amount for a given counterion does not significantly depend on molecular weight (Figure 3b and Table 2). Clearly, the adsorbed amount of polymer is lower for barium than for lithium counterion, regardless of the molecular weight of the chains. The singularity of barium-neutralized end-sulfonated polystyrene chains in toluene has also been observed by static light scattering measurements, where the weight-average aggregation number of the reverse micelles formed at higher concentration has been found to be significantly smaller for barium counterion compared to other mono- and divalent ions.[16] Thus, the electrostatic interactions occurring in barium-neutralized end-sulfonated polystyrene solutions in toluene are reduced compared to other ion pairs, probably due to the symmetry of the contact ion triplets formed in this apolar solvent.

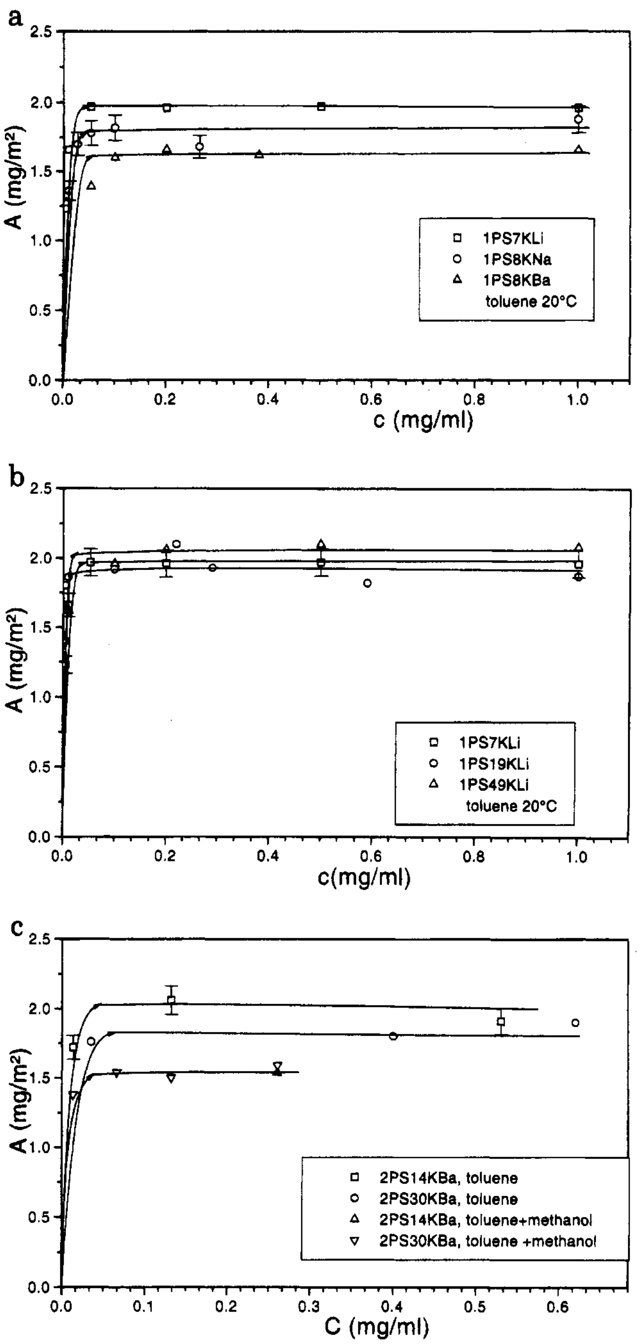

Figure 3. Adsorption isotherms of mono- and difunctional ionomers. The solid lines are guides for the eye.

Figure 3b reports a quite striking feature of the adsorption behavior of HSTP's already mentioned above. Within the experimental error, the adsorbed amount of polymer is independent of the molecular weight of the

Table 2. Experimentally Determined Parameters as Explained in the Text

polymer	N_S	A (mg/m^2)	σ(nm^{-2})	D_{inter} (nm)	R_{PS} (nm)	D_{over} (nm)	D_{inter}/D_{over}
1PS7KLi	68	1.96	0.169	2.43	23.0	4.08	0.59
1PS18KLi	180	1.94	0.063	3.98	40.9	7.25	0.55
1PS49KLi	480	2.08	0.026	6.20	73.3	12.99	0.48
1PS8KBa	78	1.60	0.125	2.83	24.4	4.32	0.65
1PS18KBa	180	1.51	0.049	4.52	40.9	7.25	0.623
1PS30KBa	294	1.49	0.030	5.77	54.7	9.70	0.59
1PS8KNa	78	1.80	1.136	2.71	24.8	4.40	0.62
2PS14KBa	139	1.98	0.085	3.43	35.0	6.20	0.55
2PS30KBa	294	1.80	0.036	5.27	54.7	9.70	0.54
2PS102KBa	1000	2.47	0.015	8.16	113.4	20.1	0.40

chains, for both lithium- and barium-neutralized samples. A better comparison with scaling theory can be made on the basis of the interchain spacing between adsorbed chains, D_{inter} (see eq 4). This quantity may be compared to the unperturbed dimensions of polystyrene chains in toluene solution, using eq 6:

$$D_{over} = \pi^{1/2} R_{PS} \tag{6}$$

where

$$R_{PS} = 1.86 N_S^{0.595} \tag{7}$$

R_{PS} is the Flory radius of polystyrene in toluene solution, N_S is the mean number degree of polymerization, and D_{over} corresponds to the distance separating two unperturbed polymer coils that come into contact. As a result, unperturbed polymer coils covering the whole surface of the substrate are expected to be separated by D_{over}. The D_{inter}/D_{over} ratio is thus a measure of the polymer conformation at the surface. It should be mentioned, however, that HSTP's in toluene solution might have a slightly different chain conformation as compared to polystyrene due to the presence of the ionic groups. Since we use the unperturbed chain conformation of polystyrene in solution for comparison, the D_{inter}/D_{over} ratio provides a measure of the chain stretching of HSTP's in relation to unperturbed polystyrene chains. Polymer chains adsorbed as unperturbed coils, indeed, are at most separated by D_{over}, and the D_{inter}/D_{over} ratio is larger than or equal to 1. A D_{inter}/D_{over} ratio larger than 1 means incomplete coverage of the surface, whereas a value of 1 means ideal coverage in the sense discussed above. Whenever the adsorption is energetically favored, the chain grafting density may be higher than the D_{over} limit, provided that the polymer chains become stretched. Increasing the chain grafting density decreases D_{inter}, and the ratio D_{inter}/D_{over} becomes smaller than 1. This situation is indicative of chain stretching: the smaller the D_{inter}/D_{over} ratio, the higher the stretching of the chains. Actually, the chain grafting density increases up to the point where the decrease in entropy due to chain stretching is just compensated by the adsorption enthalpy. Beyond this point, adsorption of additional chains is energetically demanding and not further favored. An equilibrium state is reached, which fixes the D_{inter}/D_{over} ratio.

The characteristic values for the investigated samples are reported in Table 2. In all cases, the D_{inter}/D_{over} ratios are markedly smaller than 1 and decrease with increasing molecular weight of the chains. Clearly, the bulkiest chains are more stretched than the smaller ones. It is worth pointing out that the typical values of the D_{inter}/D_{over} ratio are comprised between 0.4 and 0.65, which indicates that the chains are considerably, but not highly stretched. Adsorption thus distorts the polymer coils significantly from their unperturbed dimensions but does not give rise to a true brushlike conformation of highly extended chains. In agreement with the previous discussion, barium-neutralized HSTP's are characterized by a lower grafting density than the lithium counterparts, which in turn results in a less stretched conformation for the adsorbed chains.

Interestingly enough, the difunctional chains are adsorbed more than the monofunctional counterparts: the adsorbed amount is some 20% higher for HTP's compared to HSTP's. The adsorption isotherms of telechelics with barium cations are shown in Figure 3c and plateau values given in Table 2. Since those difunctional materials are not very soluble in toluene—much worse than the corresponding monofunctional ones—to some of the solutions also a trace amount of methanol was added. Methanol as a polar solvent is known to reduce cluster formation of ionomers[1,5] and solubility of the telechelics in toluene improves. Adsorption, on the other hand, is also affected, since the adsorbed amounts decrease by 20–30%. The influence of methanol on adsorption will be discussed in further detail below.

Based on the plateau values in pure toluene and assuming a monolayer coverage, the D_{inter} values of Table 2 have been calculated. The (apparent) D_{inter}/D_{over} ratios obtained are smaller than for the monofunctional samples, which seems to be in favor of a more stretched conformation of the chains. This behavior is, however, in sharp contrast with results reported by Dorgan *et al.*[30,31] for the adsorption behavior of PS–PEO diblock and PEO–PS–PEO triblock copolymers, where the triblock copolymers (comparable to HTP's) were found to adsorb much less than the diblock copolymers (comparable to the HSTP's). Dorgan *et al.* attributed this behavior to the ability of the triblock copolymers to form loops, which may mask part of the adsorption sites. It is similarly in contrast to recent studies of di- and triblock copolymers of styrene and butadiene, P(S-*b*-BD)u and P(BD-*b*-S-*b*-BD)u, where the butadiene block has been functionalized by urazole groups.[32] Triblock materials yield an adsorbed amount which is only about half of the adsorbed amount of comparable diblocks. Also here the lower adsorbed amount for the triblocks is attributed to loop formation.

In the case of HTP's, loop formation is also highly probable. At low concentration, indeed, it has been shown[33] that the ion pairs of halato-telechelic polymers associate intramolecularly, giving rise to intramolecular loop formation. For barium sulfonato HTP's, this situation should be even more favored, since two sulfonate anions must surround one barium cation, as discussed previously. Therefore, most of the chains are expected to form loops already in solution (Figure 4a) and to adsorb as such. As a result, a lower grafting density is predicted for difunctional samples compared to monofunctional ones, if all the parameters are otherwise kept constant. The higher density of chains in the vicinity of the surface will result in a repulsion between neighboring chains, giving rise to a lower

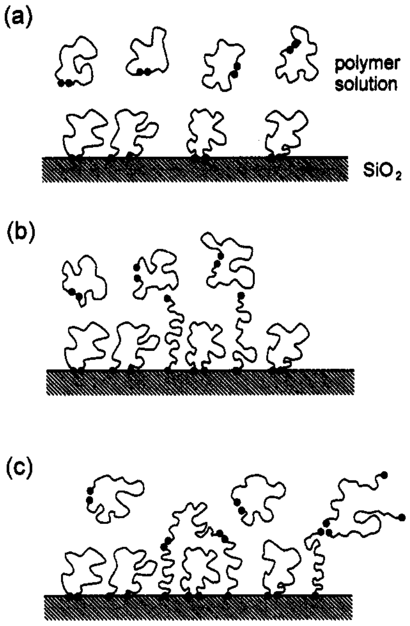

Figure 4. Schematic model for different stages of adsorption of difunctional materials and multilayer formation.

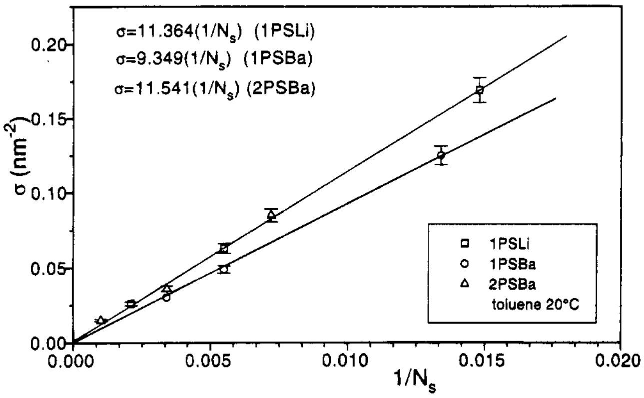

Figure 5. Scaling of grafting density σ with degree of polymerization of the nonadsorbing polystyrene chain N_S. The straight lines represent fits with parameters indicated in the plot.

surface coverage. The higher adsorption energy of two versus one adsorbing group will not be able to fully compensate the strong repulsion between chains.[24] Loop adsorption is expected to occur during the first stages of the adsorption process only (Figure 4a). Beyond a critical grafting density, the available space between adsorbed chains is too small for additional polymer loops to be inserted. Adsorption of stretched linear chains, however, is still possible (Figure 4b), and some isolated ions will adsorb with one end, provided that the adsorption process is sufficiently favored. As a result, dangling ionic groups are present on the top of the adsorbed monolayer. These ionic groups could associate with ion pairs of other chains present in solution to build up a "second layer" of adsorbed polymer (Figure 4c). Structures may be quite complex with chains bridging between several layers. The effective grafting density of HTP's in the first layer is lower than that of HSTP's due to loop formation. The presence of the (eventually very loose) second layer, however, increases the measured amount of adsorbed polymer, which leads to an apparent grafting density which can be higher than that of monofunctional chains.

For PEO−PS−PEO triblock copolymers, this problem is not relevant, since the PEO segments do not associate in dilute toluene solutions.[31] Assuming a similar probability for loop formation of the HTP's as compared to the PEO−PS−PEO triblock copolymers, one would expect a significant drop of the adsorbed amount as compared to the HSTP's (typically of the order of a factor of 2). This has to be compensated by the adsorption of HTP's in subsequent layers, which then might contain nearly as many chains as the first layer. With P(BD-*b*-S-*b*-BD)u the situation is not so clear, since at large concentrations micelles are formed in solution.[32] Adsorption experiments are, however, performed at very low concentrations, where association of molecules in solution is not pronounced.

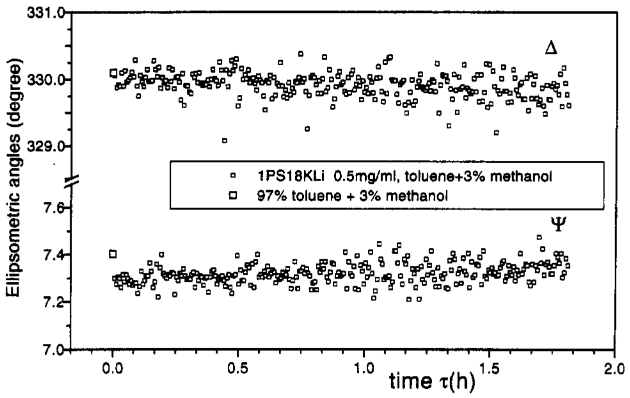

Figure 6. Change of ellipsometric angles with time for an adsorption experiment in a mixed solvent of toluene with methanol. No adsorption is detected within experimental resolution.

In all cases, the grafting density, σ, is expected to be limited essentially by the size of the nonadsorbing polymer chains, and the relatively small adsorbing groups are assumed not to significantly interact at the surface with each other. The gain in enthalpy due to adsorption is compensated by the entropic contribution caused by the distortion of the conformations of the dangling chains. In such a case one expects[30] that the grafting density scales approximately proportional to the inverse of the degree of polymerization of polystyrene, N_S. This is actually the observed behavior for both mono- and difunctional chains. Figure 5 clearly shows the influence of molecular weight, counterion, and functionality on the adsorption behavior. Barium-neutralized monofunctional samples are less adsorbed than the lithium counterparts, and the difunctional barium-neutralized chains are apparently more adsorbed than the monofunctional ones. The superimposition of the curves for monofunctional lithium and difunctional barium samples is more than likely accidental. In all cases, however, a linear dependence of σ with $1/N_S$ is observed.

Since the bulk and solution properties of ionomers are known to be deeply affected by small amounts of polar solvents,[1,5] adsorption experiments were conducted in the presence of methanol. As can be seen from Figure 6, the addition of 3 vol % methanol to a HSTP solution completely prevents any adsorption onto the silicon oxide surface. This behavior is in agreement with recent light scattering[16] and NMR[34] measurements of ion pair aggregation at higher concentration, which are in favor of a progressive solvation of the metal sulfonate ion pairs upon increasing the methanol concentration. Actually, the inhibition of the adsorption in the presence of methanol means that the metal sulfonate/silicon dioxide interactions are much weaker than those between metal sulfonate ion pairs and methanol. Other polar substances, like ethanol or water, should induce similar effects. Multilayer formation may also be the reason for the very high value of the adsorbed amount of 2PS102KBa, since also this value decreases from 2.5 to 1.5 mg m^{-2} by the addition of a trace amount of methanol.

The surface activity of HTP's and HSTP's could be used for several applications of technological importance. Adsorption of HTP's and HSTP's onto polar surfaces might be used, for example, for colloidal particle dispersion stabilization. In bulk, indeed, the adsorbed polymer brush might act as an anchoring layer, provided that the adsorbed chains are long enough. The ionic polymers would ensure good interfacial adhesion, which might considerably improve the mechanical properties of the resulting composite materials. In solution, steric repulsion between the adsorbed polymer brushes might prevent the aggregation of the colloidal particles and help to stabilize the dispersions. Another potential application might be the prevention of thin polymer film dewetting, as has been exemplified recently.[22] Although this approach deserves more attention, special care should be taken, however, on the influence of polar substances like alcohols or water on the surface properties of ionic polymer chains.

Conclusions

Adsorption of ω- and α,ω-metal sulfonato polystyrene on silicon dioxide from dilute toluene solutions has been measured by null ellipsometry. Whereas nonfunctionalized polystyrene chains do not adsorb, the presence of a single ionic end group is sufficient to promote rapid adsorption of the ionic polymer chains onto the surface. The adsorption kinetics at small times is in favor of a simple Fickian diffusion limited adsorption process. After a few minutes, the surface is completely covered, and the adsorbed amount of polymer reaches a plateau value. The adsorbed chains are significantly stretched and form a structure which is reminiscent of a polymer brush. The grafting density of this brush is higher for lithium and sodium sulfonate ion pairs than for barium sulfonate ion pairs, which could be related to the different valencies of these two cations.

In contrast to block copolymers, chains bearing stickers at both ends adsorb more than the monofunctional counterparts. This behavior has been rationalized in terms of multilayer formation via electrostatic interactions, which are not present in the case of some investigated block copolymers. For both mono- and difunctional chains, the grafting density scales with the inverse of the polymer chain length, indicating that the surface coverage is limited by the repulsion between neighboring chains. Finally, a polar cosolvent, methanol, has been shown to interact strongly enough with the ion pairs to reduce the adsorbed amount when added in trace amounts but to completely inhibit polymer adsorption when added in a few percent to the solution.

Adhesion properties of halato-telechelic polymers could be used to stabilize colloidal particle dispersions in various media or to improve the thermal stability of thin films. The potentialities of this approach, however, deserve more attention.

Acknowledgment. We gratefully acknowledge many helpful discussions and the support during ellipsometric experiments by Dr. D. Siqueira and V. Erb (Mainz). T.P. thanks the German Academic Exchange Service (DAAD) for a grant, which made her stay at the Max-Planck-Institut für Polymerforschung in Mainz possible. We are very much indebted to the Service de la Programmation de la Politique Scientifique (Brussels) for support. P.V. thanks the Belgian Fonds National de la Recherche Scientifique for a research fellowship.

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MA946381G