Surface Exchange Kinetics of Chemically Different Polymers

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ABSTRACT: The kinetics of exchange between an adsorbed polymer and a chemically different, more strongly adsorbing polymeric displacer was investigated by means of an optical reflectometry technique, using an impinging jet flow cell. Three polymer/displacer pairs were studied: polystyrene (PS)/poly(tetrahydrofuran) (PTHF), poly(butyl methacrylate) (PBMA)/PTHF, and PS/PBMA, all in decalin solutions. We find that both PS and freshly adsorbed PBMA are displaced by PTHF at a rate which is entirely determined by the supply of displacer through the solution. The surface processes in these cases are thus so rapid that they do not affect the overall exchange kinetics. A PBMA adsorbed layer which has been aged for 20 h is displaced slightly more slowly by PTHF than a fresh one, but the aging effect is minor. In contrast with the above, the displacement of PS by PBMA is much slower and to a large extent determined by surface processes. The exchange of low molar mass adsorbed PS (M = 9 kg/mol) by PBMA in pure decalin proceeds in two steps which are separated by a distinct break in the kinetic curve: a rapid initial desorption of PS upon attachment of PBMA, followed by a much slower desorption of PS at constant PBMA coverage. For high molar mass PS the displacement by PBMA in pure decalin was too slow to be measurable. However, upon addition of low molar mass displacers like toluene or ethyl acetate, the displacement of PS becomes considerably faster. The kinetic curves have again two distinct parts, related to fast desorption and slow rearrangements within the adsorbed layer, respectively. The second step (rearrangement process) could be shown to be a true surface process, that did not respond to changes in the free polymer concentration. We argue on the basis of these data that the segmental adsorption energy plays an important role in the kinetics but also that this factor cannot explain the large difference between PBMA and PTHF as displacers. We suggest that dynamic chain flexibility is another important factor.

Introduction

Chemically different polymers usually have a different affinity for the surface, which leads to preferential adsorption of the polymer with the highest (segmental) adsorption energy. Under most conditions the preference on the basis of a different segmental adsorption energy is much stronger than that due to the chain-length difference, so that the adsorption preference is determined by the type of polymer, irrespective of its chain length. A long polymer is easily displaced by a shorter one if the latter has a higher adsorption energy.[1]

Displacement of a polymer molecule by simultaneous desorption of all segments of the chain is very unlikely due to the high adsorption energy per molecule. Therefore, a segment-by-segment process is more likely. If the adsorbing and desorbing segment are chemically the same, the adsorption energy remains constant upon exchange. Hence, in this case there is no driving force at the segmental level for exchange. This case was studied in a previous paper.[2] For chemically different polymers the (anchoring) energy decreases upon exchange, which constitutes a driving force at the segmental level. We might therefore expect faster exchange kinetics for chemically different polymers as compared to chains that differ in length only. In addition to differences in the adsorption energy, differences in solvency may play a role.

The exchange kinetics between chemically different polymers has hardly been investigated. The displacement of polystyrene (PS) adsorbed on silica by poly(methyl methacrylate) (PMMA) in a dilute solution of trichloroethylene was studied as early as 1966 by Thies.[3] Much later, in 1992, Johnson and Granick[4] investigated the same combination of polymers adsorbing on an oxidized silicon surface from the solvent carbon tetrachloride. In both studies it was found that, after addition of PMMA, PS desorbed rather slowly, over a time scale of hours. A similar slow-exchange kinetics was observed by Van der Beek et al.[5] for displacement of adsorbed poly(butyl methacrylate) (PBMA) by poly(tetrahydrofuran) (PTHF) in a carbon tetrachloride solution. These results indicate that slow-exchange processes occur in the adsorbed layer. However, as yet no general conclusions on the nature of these processes can be drawn.

We take here an experimental approach using a technique that has been used successfully before.[2] Polymer is adsorbed from a stagnation point flow onto the surface of an oxidized silicon wafer. Exchange starts when a second polymer is injected into the cell. The adsorption process is monitored by reflectometry. The exchange kinetics of three polymers were investigated: polystyrene (PS), poly(butyl methacrylate) (PBMA), and poly(tetrahydrofuran) (PTHF). In all cases the solvent was decalin. Van der Beek et al.[6] determined for these polymers the segmental adsorption energy parameter χ_s for adsorption from cyclohexane onto silica and found values of 2, 3.8, and 4.8 for PS, PBMA, and PTHF, respectively. Since cyclohexane and decalin are chemically very similar, we expect that in decalin the values of χ_s are approximately the same as those in cyclohexane. Accordingly, in decalin PBMA is expected to displace adsorbed PS, and PTHF should displace both PS and PBMA.

By reflectometry one cannot distinguish directly between different polymers on the surface because the reflectometric signal contains contributions of all adsorbed species. However, for the polymers chosen in this study meaningful data can be obtained because the sensitivity of the method is quite different for PS, PBMA, and PTHF. This is due to the fact that the refractive index increments dn/dc of PBMA and PTHF are very small, whereas that of PS in decalin is considerable. As a result, the reflectometric signal changes strongly if an adsorbed layer of PS is displaced by PBMA or PTHF. In addition, the refractive index increments of PBMA and PTHF differ

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Table 1. Polymer Samples

sample	M, kg/mol	M_w/M_n
PS(9K)	9.2	1.03
PS(1030K)	1030	1.05
PS(3040K)	3040	1.04
PS(20000K)	20000	1.3
PTHF(4K)	4	1.12
PTHF(690K)	690	1.25
PBMA	240 ($=M_w$)	2.5

in sign. This makes it possible to study displacement of PBMA by PTHF, be it with less sensitivity.

In order to study the effect of the adsorption energy of the polymers on the exchange kinetics, we examine in this paper for one of the polymer pairs (PS/PBMA) the effect of two displacers of low molar mass. By addition of a low molar mass displacer the effective segmental adsorption energy of the polymers decreases, the effect being relatively stronger for the displaced component (PS) than for the polymeric displacer (PBMA). Generally, we would expect that a decrease of the adsorption energy leads to an increase of the mobility of the adsorbed polymers, possibly resulting in faster exchange kinetics. In addition to the adsorption energy a low molar mass displacer will usually also influence the solvency of the polymers, which also might have an effect on the exchange kinetics.

The two low molar mass displacers chosen for this study are ethyl acetate and toluene, which are solvents for both PS and PBMA.[7] Ethyl acetate is a strong displacer, and toluene a weak one. For the critical ethyl acetate weight fraction $w_{\mathrm{eth}}^{\mathrm{cr}}$ for adsorption of PS from decalin on silica we have found $w_{\mathrm{eth}}^{\mathrm{cr}} \approx 0.11$.[8] For PBMA the value of $w_{\mathrm{eth}}^{\mathrm{cr}}$ is probably considerably higher. Van der Beek et al.[9] concluded that for displacement of PS the critical volume fraction of toluene in cyclohexane equals 0.80. In decalin this value is expected to be about the same. Toluene cannot completely displace PBMA adsorbed on silica.[6]

Experimental Section

Materials. Polystyrene and poly(tetrahydrofuran) samples of narrow molar mass distribution were purchased from Polymer Laboratories. Analytical-grade, rather polydisperse poly(butyl methacrylate) was obtained from Aldrich Chemical Co. All samples were used without further purification. Their molar masses and degrees of polydispersity are listed in Table 1. For PBMA, the molar mass distribution as determined by gel permeation chromatography is given by Van der Beek et al.[5] The solvents decalin (Merck; for synthesis quality), ethyl acetate (Merck, p.a.), and toluene (Baker analyzed) were purified before use by drying over zeolite and anhydrous $CaCl_2$.[8]

As the substrate for adsorption, strips cut from an oxidized silicon wafer were used. These were cleaned in a gas flame.[8] The silica film thickness was about 105 nm for all strips used.

Methods. The refractive index increment dn/dc of the polymers in decalin solutions was determined by white light interferometry at 20 °C from the difference in the refractive index of pure solvent and a polymer solution with a concentration of about 2000 g/m^3. For PS a value of +0.135 cm^3/g was found, which is in reasonably good agreement with the value of +0.12 cm^3/g measured by Appelt and Meyerhoff[10] at 20 °C and 633 nm. For PTHF and PBMA we determined values of −0.0096 and +0.0061 cm^3/g, respectively. However, for these polymers the measurement was probably rather inaccurate because of the small optical contrast, so that dn/dc may contain a large relative error.

The adsorption measurements were carried out with a reflectometer as described before.[2,8] We present the data as the relative change $\Delta S/S_0$ in the output signal S of the reflectometer rather than adsorbed amounts, for the following reason. For adsorption of a single component the adsorbed amount Γ equals $(\Delta S/S_0)/A_s$, where A_s is the sensitivity factor for adsorption.[11] Using the values of dn/dc given above, we calculated for PS, PTHF, and PBMA A_s values of +0.0196, −0.0014, and +0.00088 m^2/mg, respectively. In mixed adsorbed layers the signal $\Delta S/S_0$ contains contributions of different polymers, each with their respective sensitivities. Separation of these contributions is not possible in a direct way; therefore, the adsorbed amount cannot be calculated unambiguously. Due to the large differences in sensitivity, however, the signal is strongly dominated by the contribution of PS, so that it almost corresponds to $\Gamma_{\mathrm{PS}}(t)$.

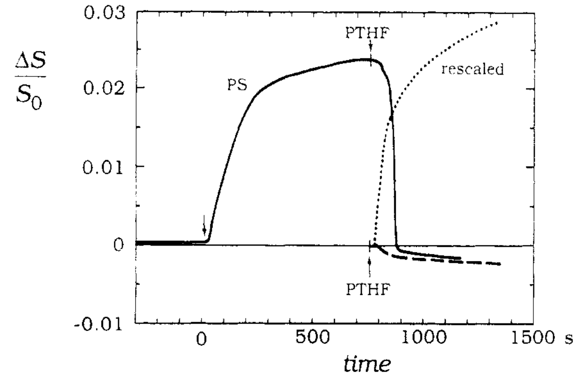

Figure 1. Example of the exchange kinetics of PS by PTHF. At $t = 0$ the injection of a solution of PS on an initially bare surface starts. Then, at $t = 750$ s the valve is switched to the injection of PTHF. For comparison, the adsorption of PTHF on a bare surface is given as $\Delta S/S_0$ (dashed) and by a dotted curve, which is corrected for the different sensitivity of the method for PS and PTHF (see text). Parameters: PS, M = 1030K, c = 10 g/m^3; PTHF, M = 690K, c = 10 g/m^3; S_0 = 0.99.

Results

Exchange of PS by PTHF. An example of the adsorption of PS and PTHF on an initially bare silica surface and of the exchange kinetics of PS by PTHF is given in Figure 1. First, we discuss the individual adsorption of PS and PTHF and then the exchange.

At $t = 0$ a solution of PS(1030K) was injected and $\Delta S/S_0$ increases due to adsorption of PS onto a bare surface. The initial adsorption rate is determined by mass transfer of PS from the bulk solution to the surface.[8] After some time (≈200 s) the adsorption rate decreases considerably due to the buildup of an adsorbed layer. We stopped the injection of PS at $t = 750$ s. The adsorbed layer is then not yet completely saturated. The final level of $\Delta S/S_0$ corresponds to an adsorbed amount Γ of 1.2 mg/m^2.

The adsorption of PTHF (690K) on silica is represented by the dashed and dotted curves. The dashed curve gives $\Delta S/S_0$ during injection of PTHF. Due to adsorption $\Delta S/S_0$ *decreases* for PTHF because A_s is negative for this polymer in decalin. In order to show more detail, we rescaled the adsorption curve of PTHF by multiplication of $\Delta S/S_0$ with $A_s(\mathrm{PS})/A_s(\mathrm{PTHF})$. The result is given as a dotted curve. Since $\Gamma(\mathrm{PTHF}) = (\Delta S/S_0)/A_s(\mathrm{PTHF})$, the adsorbed amount of PTHF can be obtained from the dotted curve by division through $A_s(\mathrm{PS})$, which is the same factor as needed to calculate Γ from the adsorption curve of PS. Consequently, equal ordinate values in Figure 1 for the adsorption curves of PS (full) and PTHF (dotted) correspond to equal adsorbed amounts.

For PTHF the shape of the adsorption curve and the amount adsorbed are roughly comparable to those of PS. The initial rapid increase of the adsorption of PTHF is presumably due to mass-transfer-limited adsorption, like for PS. Since the change in the reflectivity of the surface is very small for adsorption of PTHF, the adsorption curve for this polymer might well be strongly affected by drift of the signal caused by, e.g., temperature fluctuations. Therefore, a more detailed discussion of the adsorption curve of PTHF is not meaningful.

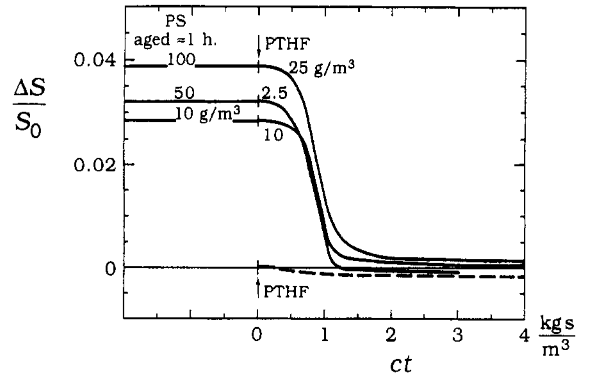

Figure 2. Effect of the concentration of PTHF on the exchange kinetics of PS by PTHF. Initially ($t < 0$), a solution of PS (M = 1030K) at a concentration as indicated was injected for about 1 h. At $t = 0$ the injection of PTHF (M = 690K, concentration as indicated) starts. The signal $\Delta S/S_0$ is plotted as a function of the product ct of the concentration and the time of injection of PTHF. For comparison, the dashed curve gives the result for adsorption of PTHF on an initially bare surface.

The exchange of PS by PTHF is represented in Figure 1 by the full curve for $t > 750$ s. At $t = 750$ s the value was switched from the injection of PS to PTHF. During injection of PTHF $\Delta S/S_0$ decreases rapidly, and around $t = 900$ s it has attained a small, negative value, closely corresponding to that for individual adsorption of PTHF. This result must imply that PS is completely desorbed and replaced by PTHF. Since the desorption of PS occurs at the same time scale as the adsorption of PTHF on a bare silica surface (dotted curve), it is likely that the mass transfer of PTHF is the rate-limiting step in the exchange process. In order to check this, we varied the adsorption rate of PTHF by adjusting its solution concentration.

For three concentrations of PTHF in the range 2.5–25 g/m³, the exchange of PS by PTHF is given in Figure 2. The ratio $\Delta S/S_0$ is plotted as a function of the product ct of the concentration and the time of injection of PTHF. For comparison, also the result for adsorption of PTHF on a bare surface is included (dashed). For $t < 0$ a solution of PS(1030K) was injected for about 1 h with a different concentration in each experiment, as indicated. The final adsorption during injection of PS (i.e., $t < 0$ in Figure 2) increases with increasing concentration of PS. This suggests that the adsorption is strongly concentration dependent. However, it has been shown[8] that the adsorption rate of PS increases proportionally with the solution concentration, even at higher coverage where attachment to the surface is the rate-limiting step. As a result, the adsorbed amount after a *fixed* time increases with concentration. Therefore, the coverages that are shown here (fixed time 1 h) do not correspond to equilibrium but are kinetically determined.

For the three exchange experiments in Figure 2, $\Delta S/S_0$ decreases during injection of PTHF to a value close to that for adsorption of PTHF on silica, which strongly suggests that in all three cases PS is completely displaced by PTHF. The three displacement curves coincide more or less, which implies that the exchange rate is proportional to the solution concentration of PTHF and, hence, to the adsorption rate of the displacer. We conclude that the desorption rate of PS is fully determined by the adsorption rate of PTHF which, in turn, is determined by mass transfer from solution; there is no detectable barrier for PS desorption.

In the examples given above, PS was displaced by a high molar mass sample of PTHF(690K). In Figure 3 we examine the exchange kinetics of low and high molar mass PS (9K and 3040K, respectively) by short chains of PTHF (M = 4K). For comparison, the adsorption of PTHF(4K) on a bare surface is given in the same way as in Figure 1 by dashed and dotted curves. The final level of $\Delta S/S_0$ for PTHF(4K) corresponds to an adsorbed amount of only 0.25 mg/m².

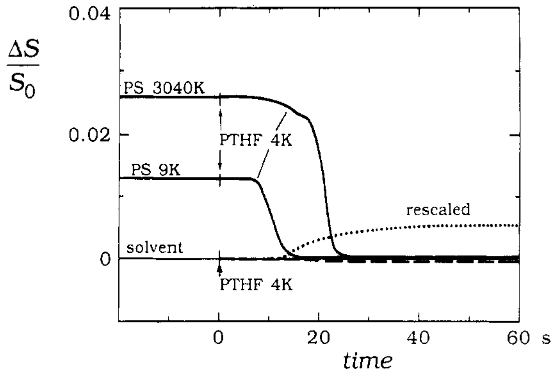

Figure 3. Effect of the chain length of PS on the kinetics of displacement by low molar mass PTHF. For comparison, we also included the result for adsorption of PTHF on an initially bare surface (dashed and dotted; the meaning of these curves is the same as that in Figure 1). Concentrations: PS(9K), 5 g/m³; PS(3040K), 50 g/m³; PTHF(4K), 10 g/m³.

The result in Figure 3 for displacement of PS by PTHF(4K) is very similar to that in Figure 1 for displacement by PTHF(690K), which implies that the displacement rate of PS by low molar mass PTHF is also mass-transfer limited. In Figure 3, the displacement of PS(3040K) lags about 10 s behind that of PS(9K), which implies that a somewhat higher coverage with PTHF(4K) is needed to displace the long chains of PS as compared to the short ones. However, both for PS(9K) and PS(3040K) the displacement is complete before the surface is saturated with PTHF(4K). The only combination of chain lengths we did not investigate was the displacement of low molar mass PS by high molar mass PTHF. We see no reason to suppose that the result would be different. We therefore generalize our previous conclusion: for *any* combination of chain lengths the exchange kinetics of PS by PTHF is determined by the mass-transfer-limited adsorption of PTHF. The surface processes are faster than the transport through solution, and therefore they have no influence on the exchange rate. Note in Figure 3 that PTHF(4K) is still preferentially adsorbed over PS(3040K), although the molar mass of PTHF is about 750 times lower than that of PS. This example clearly shows that the adsorption preference is mainly determined by a difference in the segmental adsorption energy of the polymers ($\chi_s \approx 2.0$ and 4.8 for PS and PTHF, respectively) and much less by a difference in the chain length.

Exchange of PBMA by PTHF. In this section we first discuss the adsorption of PBMA and then the exchange of PBMA by PTHF. In Figure 4 we give an example of the kinetics of adsorption of PBMA on an initially bare surface. The lower curve is for the pure solvent decalin; the upper curve is for a mixture of decalin and the displacer ethyl acetate. The effect of this displacer on the kinetics will be discussed further below. For PBMA in decalin the adsorption rate is constant up to $t = 50$ s where it abruptly falls to zero and remains so during prolonged injection of PBMA. It is very likely that the initial adsorption rate is again determined by mass transfer from the bulk solution. For the highly polydisperse sample of PBMA which was used, we did not expect such a sharp transition between initial adsorption and saturation. Since in polydisperse polymers one expects exchange of shorter by longer chains, a rounded shape of the kinetic curve

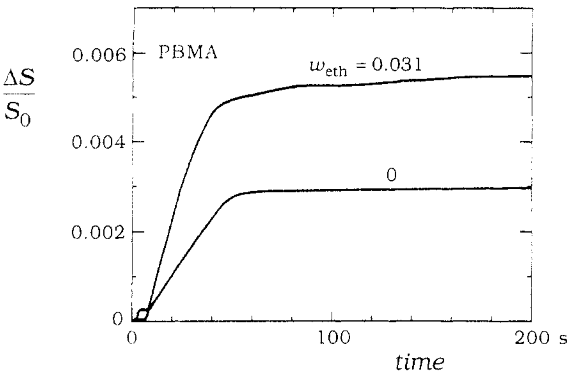

Figure 4. Adsorption kinetics of PBMA in decalin and a mixture of decalin and ethyl acetate. The weight fraction w_{eth} of ethyl acetate is indicated. The effect of ethyl acetate is to a large extent optical. Polymer concentration 25 g/m^3.

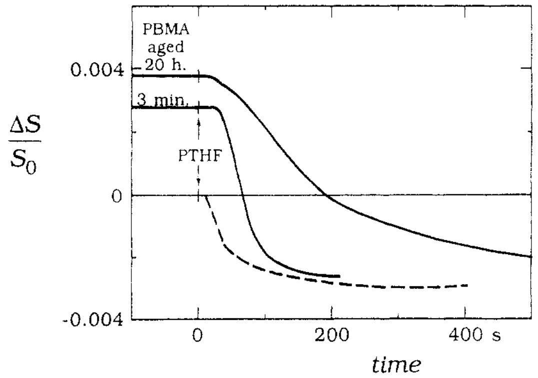

Figure 5. Kinetics of displacement of PBMA by PTHF in a decalin solution for young and strongly aged adsorbed layers of PBMA, as indicated. For comparison, the dashed curve gives $\Delta S/S_0$ for adsorption of PTHF on an initially bare surface. Concentrations: PBMA, 255 g/m^3; PTHF(690 K), 25 g/m^3.

should be observed.[12] That this is not the case may imply that there is very little exchange on the time scale of our experiment. This would mean that the exchange process between PBMA chains of different length is slow.

The final level of $\Delta S/S_0$ in decalin corresponds to an adsorbed amount Γ of 3.4 mg/m^2, which is quite high for an adsorbed layer of an uncharged homopolymer. However, this value is subject to considerable error, due to the low optical contrast between PBMA and decalin, which makes an accurate determination of dn/dc impossible.

The exchange kinetics of PBMA by high molar mass PTHF (M = 690K) is presented in Figure 5 for a young (3 min) and a strongly aged (20 h) adsorbed layer of PBMA. For the aged PBMA layer the reflectometric signal after 20 h was apparently affected by drift. We therefore used in Figure 5 rather arbitrarily the value of $\Delta S/S_0$ after a 30-min injection of PS. After 30 min the adsorption rate was zero within experimental error, so that the value of $\Delta S/S_0$ used in Figure 5 probably is a reasonable indication for the adsorption after 20 h. For comparison, $\Delta S/S_0$ for adsorption of PTHF on an initially bare surface is given by a dashed curve.

During injection of PTHF on a young layer of PBMA (lower full curve) $\Delta S/S_0$ decreases rapidly to a value characteristic for a saturated adsorbed layer of PTHF only, which indicates that PBMA is completely exchanged by PTHF. The time scale for exchange of PBMA by PTHF is the same as that for adsorption of PTHF on an initially bare surface. Hence, the exchange rate of PBMA by PTHF is again determined by the adsorption rate of the invading species, which, in turn, is controlled by mass transfer from the solution.

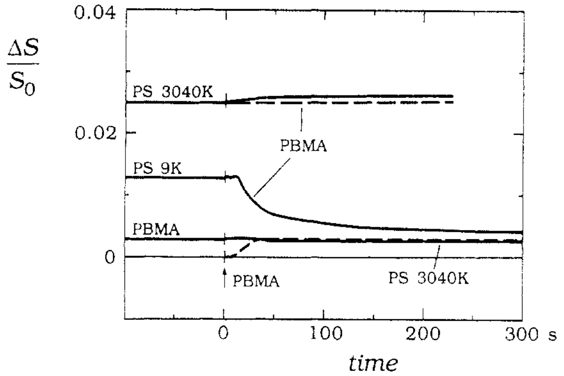

Figure 6. Kinetics of displacement of high and low molar mass PS by PBMA in decalin solutions. Initially (t < 0), a solution of PS is injected for about 2–3 min, and at t = 0 the injection of PBMA starts (upper full curves). The horizontal, dashed line at the upper curve is the value of $\Delta S/S_0$ during injection of PS. In order to check whether the adsorption preference is reversed in the case of the high molar mass PS, also the result for injection in the reverse order is included: first PBMA and then PS(3040K) (lower full curve). The dashed curve is the result for adsorption of PBMA on an initially bare surface. Concentrations: PS(9K), 5 g/m^3; PS(3040K), 50 g/m^3; PBMA, 50 g/m^3.

For the aged layer of PBMA (upper full curve) the exchange rate is slightly lower than that for the young layer, but the exchange is still relatively fast with a time constant of a few minutes. Whether for this case the exchange is complete we cannot say due to the uncertainty in the adsorption level of PBMA before exchange. Nevertheless, it seems that aging of the adsorbed PBMA layer has some but not a large effect on the exchange kinetics of PBMA by PTHF.

Exchange of PS by PBMA. Decalin Solutions. The exchange kinetics of PS by PBMA in decalin is given in Figure 6 for PS(9K) and PS(3040K) (upper full curves, as indicated). The horizontal, dashed line at the upper full curve indicates the adsorption level of PS just before injection of PBMA. In one experiment PBMA was first adsorbed, after which PS(3040K) was added; this result is given by the lower full curve. The adsorption of PBMA on an initially bare surface is represented by a dashed curve.

During exposure of an adsorbed layer of PS(9K) to PBMA, $\Delta S/S_0$ decreases and finally reaches a value close to that for adsorption of PBMA alone, suggesting that ultimately all PS(9K) is exchanged by PBMA. It is interesting to note that the kinetic curve has two distinct parts. Initially, the rate of decrease of $\Delta S/S_0$ is fast; this continues up to $t \approx 40$ s, which is approximately the time needed to form a saturated adsorbed layer of PBMA on an initially bare surface (dashed curve). In the second part, the decrease is significantly slower. Probably, the adsorption rate of PBMA in this exchange experiment is more or less equal to that on an initially bare surface so that, for t < 40 s, the decrease of $\Delta S/S_0$ in the exchange experiment is due to desorption of PS(9K) that takes place *simultaneously* with the adsorption of PBMA. For t > 40 s the adsorbed amount of PBMA remains probably nearly constant and the slower decrease of $\Delta S/S_0$ is entirely caused by desorption of PS(9K), presumably as the result of rearrangements within the adsorbed layer.

For exchange of high molar mass PS by PBMA (upper full curve) the results is dramatically different. During injection of PBMA $\Delta S/S_0$ first increases slightly (t < 40 s) and then remains constant. The small increase of $\Delta S/S_0$ for t < 40 s suggests that adsorption of PBMA does occur. However, in this case the desorption of PS is very small, if not zero. If the adsorption of PS(3040K) is

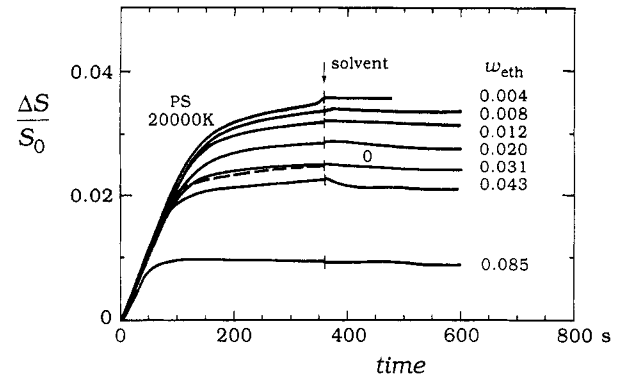

Figure 7. Adsorption of high molar mass PS in solvent mixtures of decalin and ethyl acetate. The weight fraction w_{eth} of ethyl acetate is indicated. The dashed curve gives the result for the adsorption from pure decalin.

assumed to be strictly constant for $t < 40$ s, we must conclude that the increase of $\Delta S/S_0$ corresponds to an adsorption of PBMA of about 20% of its saturated value on an initially bare surface. If, however, some desorption of PS(3040K) has occurred the adsorption of PBMA would be more than this 20%. For $t > 40$ s $\Delta S/S_0$ remains constant, which implies that there is no (measurable) desorption of PS on this time scale (about 4 min). Probably, the exchange process of PS (3040K) by PBMA is too slow to be observed in the experiment of Figure 6.

Since the segmental adsorption energy of PBMA is considerably higher than that of PS (χ_s = 3.8 and 2.0 for PBMA and PS, respectively), we would expect complete displacement of PS by PBMA, irrespective of the chain length of PS. In order to make sure that the adsorption preference is not reversed in the case of high molar mass PS and PBMA, we performed an exchange experiment in the reverse order: first, PBMA was adsorbed and then PS(3040K) was injected (lower full curve in Figure 6). During injection of PS(3040K) on an adsorbed layer of PBMA $\Delta S/S_0$ remains constant, which implies that there is no exchange of PBMA by PS nor any adsorption of PS. Therefore, it is very unlikely that the adsorption preference is reversed.

Effect of Low Molar Mass Displacers. In order to try to enhance the exchange rate of high molar mass PS by PBMA, we decided to decrease the adsorption energy of the polymers by addition of low molar mass displacers. We used both a strong displacer (ethyl acetate) and a weak displacer (toluene). If indeed the adsorption energy is a key factor, then the effect (in terms of adsorption energy) should be the same for both displacers.

Strong Displacer. The effect of ethyl acetate on the adsorption kinetics of PS was extensively discussed in a previous paper.[8] We recall here the main aspects. Figure 7 is a plot of the adsorption of PS(20000K) on silica from mixtures of decalin and ethyl acetate for a series of weight fractions w_{eth} of ethyl acetate, as indicated. The result for adsorption from pure decalin (i.e., $w_{eth} = 0$) is given by the dashed curve.

For all curves in Figure 7 the initial adsorption rate is practically the same because for all experiments the concentration of ethyl acetate was so low that there is hardly any effect on the mass-transfer conditions. The fact that the initial slopes coincide implies that also the optical calibration is not affected by the addition of ethyl acetate. The final level of $\Delta S/S_0$ decreases regularly with increasing concentration of ethyl acetate, as expected for a low molar mass displacer. The final level of $\Delta S/S_0$ as a function of w_{eth} is given in Figure 8 by the open circles. (The meaning of the triangles in this graph will be discussed later.) The shape of the curve in Figure 8 (open circles) is well-known for displacement of polymers by low molar mass displacers.[9,13] From the intercept with the abscissa we determined the critical weight fraction w_{eth}^{cr} of ethyl acetate needed for complete desorption of PS and found $w_{eth}^{cr} = 0.11$.

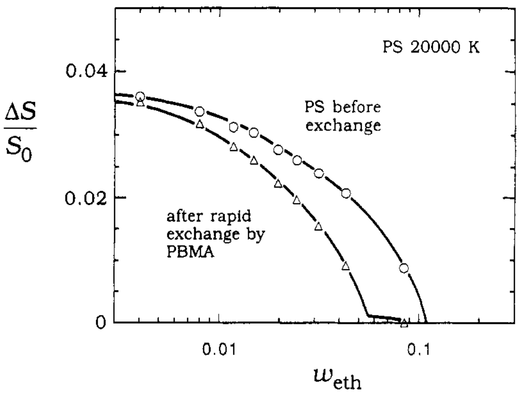

Figure 8. Effect of ethyl acetate on the final level of $\Delta S/S_0$ during injection of high molar mass PS (circles) and $\Delta S/S_0$ after rapid exchange of PS by PBMA (triangles). The circles represent $\Delta S/S_0$ at $t = 360$ s in Figure 7. The precise meaning of the triangles is given after the discussion of Figure 10.

In Figure 4 we gave the adsorption kinetics of PBMA in decalin and a mixture of ethyl acetate and decalin (w_{eth} = 0.031). Ethyl acetate appears to enhance the initial slope $d(\Delta S/S_0)/dt$ and the final level of $\Delta S/S_0$ by factors of about 2.5 and 1.9, respectively, with respect to decalin. Since for both experiments the mass-transfer conditions were nearly the same, we expect that also the initial adsorption rates were more or less equal. The influence of ethyl acetate on the initial rate $d(\Delta S/S_0)/dt$ must then be an optical effect that corresponds to an increase of A_s by a factor 2.5. Although the effect of ethyl acetate on A_s for PBMA is large in a relative sense (factor 2.5), one should realize that it is only small if absolute values of A_s are considered: A_s = +0.00088 and 0.0022 m^2/mg for w_{eth} = 0 and 0.031, respectively. Both values of A_s for PBMA are still much smaller than that of PS in decalin, for which A_s = +0.0196 m^2/mg. Possibly, the effect of ethyl acetate on A_s for PBMA is due to some association between PBMA and ethyl acetate. If the effect of ethyl acetate on the initial slope in Figure 4 is indeed entirely optical, then the final adsorbed amount of PBMA is about 25% lower for w_{eth} = 0.031 than in decalin. This seems to be consistent with a decrease of the adsorption energy and an increase of the solvency of PBMA by the addition of ethyl acetate.

An example of the exchange of high molar mass PS (M = 20000K) by PBMA in a mixture of decalin and ethyl acetate (w_{eth} = 0.031) is given in Figure 9 (full curve). For comparison, the dashed curve represents adsorption of PBMA on an initially bare surface. For $t < 0$ in the exchange experiment a sequence of a PS solution and the solvent mixture was injected, as given in Figure 7.

During injection of PBMA in the exchange experiment of Figure 9 $\Delta S/S_0$ decreases in a few minutes to a value characteristic for a saturated layer of PBMA only, indicating that PS is completely exchanged by PBMA. In a similar experiment in pure decalin (upper curve in Figure 6) no desorption of PS was observed. Thus, due to the addition of ethyl acetate the exchange rate of high molar mass PS by PBMA increases strongly. In fact, the curve for exchange of PS(20000K) by PBMA for w_{eth} = 0.031 (Figure 9) resembles that of PS(9K) by PBMA in pure decalin (Figure 6), suggesting that the exchange mechanism has again two stages. Initially, for $t < 30$ s $\Delta S/S_0$ decreases

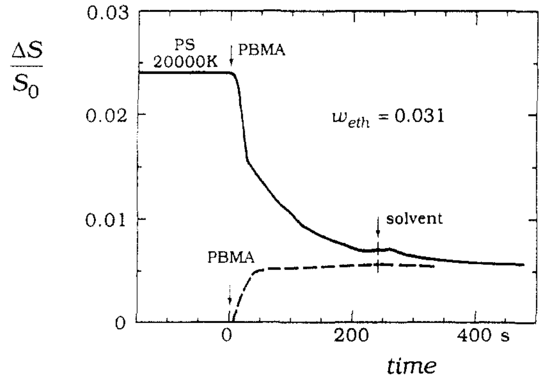

Figure 9. Kinetics of displacement of high molar mass PS by PBMA in a solvent mixture of decalin and ethyl acetate, as indicated. For $t < 0$ a sequence of PS and the solvent mixture is injected, as given in Figure 7. For comparison, the dashed curve gives the result for adsorption of PBMA on an initially bare surface. Concentration of PBMA equals 25 g/m^3.

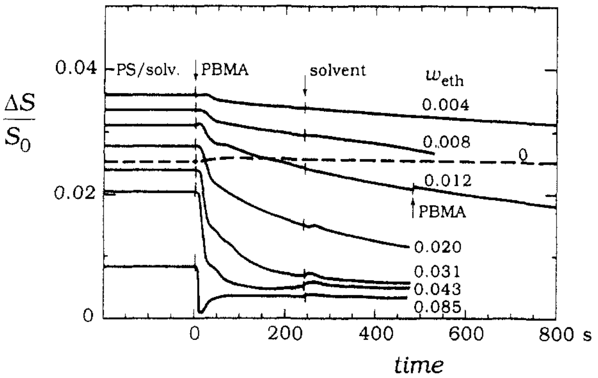

Figure 10. Effect of ethyl acetate on the exchange kinetics of high molar mass PS by PBMA in solvent mixtures of decalin and ethyl acetate. For $t < 0$ a sequence of PS and the solvent mixture is injected, as given in Figure 7. At $t = 0$ the injection of PBMA starts, followed by solvent again at $t = 240$ s. Up to the kink in the curves around $t = 30$ s PBMA adsorbs with concomitant desorption of PS. After the kink $\Delta S/S_0$ decreases due to desorption of PS by rearrangements in the adsorbed layer (see also the text). The curve for $w_{eth} = 0$ (dashed) represents continuous injection of PBMA from $t = 0$ onward. Concentration of PBMA equals 25 g/m^3.

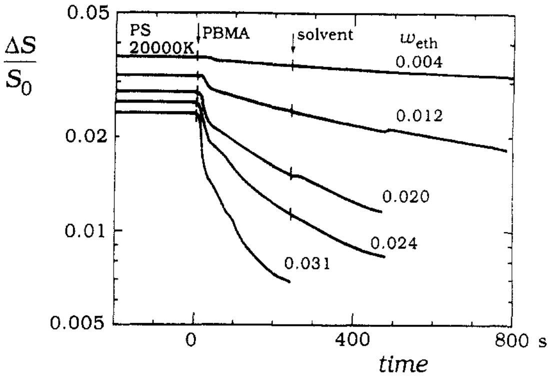

Figure 11. Check of the exponential decrease of the adsorption of PS during displacement by PBMA in solvent mixtures of decalin and ethyl acetate. Results of Figure 10 are replotted, but now on a logarithmic scale for $\Delta S/S_0$. Here, we are only interested in the part of the curves after the kink around $t \approx 30$ s, in which part the decrease of $\Delta S/S_0$ is presumably due to desorption of PS by rearrangements in the adsorbed layer.

due to desorption of PS simultaneously with (mass-transfer-limited) adsorption of PBMA. After that ($t > 30$ s) the adsorption of PBMA is probably more or less constant, and the decrease of $\Delta S/S_0$ is due only to desorption of PS, presumably as the result of slow rearrangements in the adsorbed layer.

Exchange experiments of PS(20000K) by PBMA were performed for a series of concentrations of ethyl acetate with w_{eth} increasing nearly up to the critical displacement value of 0.11, above which there is no adsorption of PS. The result is plotted in Figure 10 in the same way as the exchange in Figure 9; the curve for $w_{eth} = 0.031$ is the same in both figures. The dashed curve in Figure 10 is for displacement of PS by PBMA in decalin (i.e., $w_{eth} = 0$). For $t < 0$ a sequence of PS and the solvent mixture was injected, as shown in Figure 7.

The rate of displacement of PS(20000K) by PBMA increases gradually with increasing concentration of ethyl acetate. All curves in Figure 10 (except those for w_{eth} = 0 and 0.085) show a kink around $t = 30$ s, which is approximately the time needed to form a saturated adsorbed layer of PBMA on an initially bare surface (compare Figure 9). As before, we suggest that in the initial stage up to $t \approx 30$ s PS desorbs during mass-transfer-limited adsorption of PBMA. The decrease of $\Delta S/S_0$ in the initial stage increases with increasing concentration of ethyl acetate. Since PBMA gives only a small contribution to $\Delta S/S_0$, this means that the amount of PS desorbed in the initial stage increases with increasing the value of w_{eth}. For $w_{eth} = 0.085$, PS is presumably already completely desorbed after a small adsorption of PBMA, giving rise to the minimum in the curve at $t \approx 20$ s. After this minimum ($t > 20$ s), $\Delta S/S_0$ increases due to continuing adsorption of PBMA, and finally it reaches a stable value of about 0.004, characteristic of a saturated layer of PBMA only.

For $t > 30$ s (after the kink in the curves of Figure 10) the adsorption of PBMA is probably more or less constant and $\Delta S/S_0$ decreases due to desorption of PS. For all curves (except that for pure decalin), at $t = 240$ s we switched from the injection of PBMA to pure solvent. The rate of decrease of $\Delta S/S_0$ is hardly affected by the switch to pure solvent, which is a strong indication that for $t > 30$ s the desorption of PS is caused by a *surface process*. The desorption rate of PS for $t > 30$ s increases with increasing concentration of ethyl acetate, which implies that the surface process becomes faster with increasing the value of w_{eth}.

In order to characterize the effect of ethyl acetate more quantitatively, we analyzed the curves in Figure 10 more precisely. The effect of ethyl acetate on the initial part of the exchange is examined in Figure 8, in which we compare $\Delta S/S_0$ at two points on the exchange curves of Figure 10: at $t = 0$, just before the exchange started (circles in Figure 8) and just before the kink ($t \approx 30$ s) (triangles in Figure 8). The triangles represent the adsorption of PS which is left after exchange during adsorption of PBMA. Consequently, the vertical difference between the two curves in Figure 8 corresponds to the amount of PS which is desorbed during adsorption of PBMA. With increasing concentration of ethyl acetate an increasing amount of PS desorbs by this rapid exchange process. Probably this is due to the weaker binding of PS with increasing w_{eth}.

In order to check the effect of ethyl acetate on the surface process, we replotted the results of Figure 10 on a logarithmic scale for $\Delta S/S_0$ (Figure 11). We are only concerned with the part of the curves after the kink around $t = 30$ s. If this part is linear on the semilogarithmic scale, the adsorption of PS decays exponentially. For w_{eth} = 0.004 and 0.012 the curves are indeed nearly linear. For higher values of w_{eth} the slope of the curves decreases with time, so that the desorption is slower than exponential. We determined from the slope of the curves just after the kink (at $t = 30$ s) a time constant τ for the decrease of

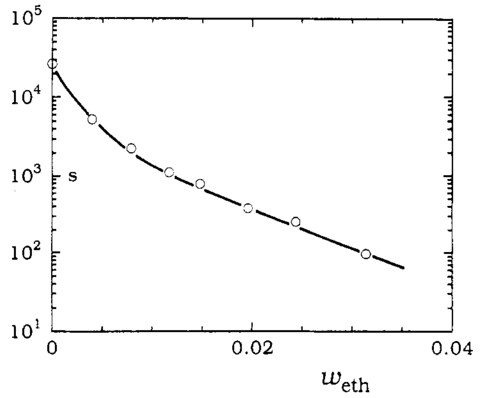

Figure 12. Effect of ethyl acetate on the time constant τ for the displacement of high molar mass PS by PBMA due to rearrangements in the adsorbed layer. The time constant τ was determined from the slope of the curves in Figure 11 just after the kink around $t \approx 30$ s.

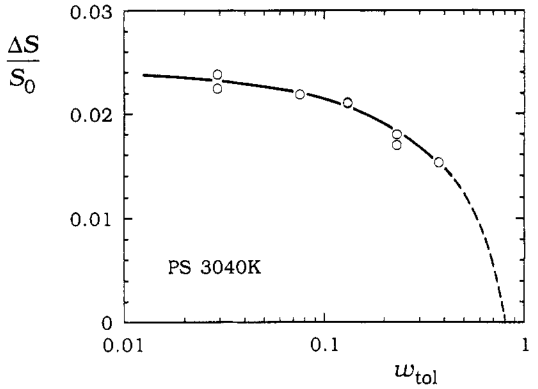

Figure 13. Effect of toluene on the final level of $\Delta S/S_0$ for adsorption of high molar mass PS in solvent mixtures of decalin and toluene. The value of $\Delta S/S_0$ after 4 min of injection of a solution of concentration 25 g/m^3 is given.

$\Delta S/S_0$ in time. This time constant is a measure of the rate of desorption of PS from a mixed adsorbed layer of PS and PBMA. Consequently, the value of τ is related to the rate of the rearrangements in such a mixed layer. In Figure 12 τ is plotted as a function of the weight fraction w_{eth} of ethyl acetate. With increasing concentration of ethyl acetate τ decreases sharply: it decreases from about 8 h in pure decalin to about 100 s for $w_{eth} = 0.031$. Probably, this decrease is due to the weaker binding of PS with increasing concentration of ethyl acetate. It would be interesting to relate w_{eth} to the (effective) segmental adsorption energy of PS. Unfortunately, this was not possible because we do not know the segmental adsorption energy and solvency parameters of ethyl acetate in this system.

Weak Displacer. Toluene is also a displacer for polystyrene but a much weaker one than ethyl acetate. We expect, therefore, that toluene has an effect comparable to that of ethyl acetate, only it should occur at a much higher concentration.

In Figure 13 we plotted the final level of $\Delta S/S_0$ for adsorption of high molar mass PS(3040K) as a function of the weight fraction w_{tol} of toluene in mixtures of toluene and decalin. These results may be compared with those for the strong displacer ethyl acetate, as given by the upper curve of Figure 8. However, there may be an important optical difference. Since in Figure 13 w_{tol} varies within a broad range (0.03–0.38), the question arises how the optical calibration depends on the solvent composition. The refractive index increments dn/dc of PS at 20 °C and 633 nm in decalin and toluene are 0.12 and 0.111 cm^3/g, respectively.[7] This difference in dn/dc in both solvents is rather small, and we expect therefore only a small effect of the solvent composition on the sensitivity factor A_s for the adsorption of PS. Consequently, the decay of $\Delta S/S_0$ in Figure 13 represents approximately the desorption of PS. The level of $\Delta S/S_0$ at low concentrations of toluene ($w_{tol} < 0.03$) corresponds to an adsorbed amount of 1.2 mg/m^2. With increasing concentration of toluene the adsorption of PS decreases, which can probably be explained by two factors: a decrease of the adsorption energy of styrene units and an increase of the solvency for PS. We extrapolated the curve in Figure 13 to zero adsorption at $w_{tol} \approx 0.8$, which is the value of the critical point found by Van der Beek et al.[9] for PS on silica from mixtures of toluene and cyclohexane. Since cyclohexane and decalin are chemically very similar, this seems a reasonable approximation. If we compare the effect of toluene (Figure 13) and ethyl acetate (circles in Figure 8) on the adsorption of PS, it is found that the shape of the curves is more or less the same and resembles the curves commonly found for displacement of polymers by low molar mass displacers.[9,13] The main difference is the shift of the desorption point toward higher weight fractions in toluene, which is related to the fact that toluene is a weaker displacer than ethyl acetate.

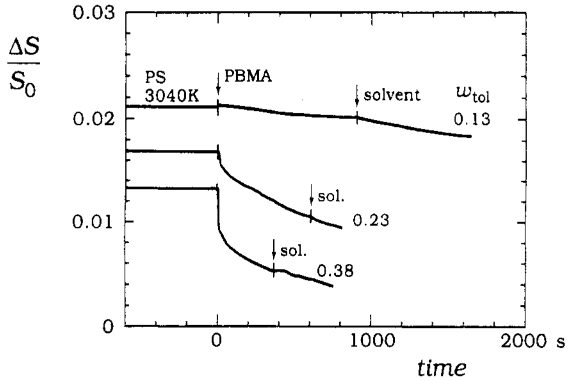

Figure 14. Effect of toluene on the exchange kinetics of high molar mass PS by PBMA in solvent mixtures of decalin and toluene, as indicated. Qualitively, the effect of toluene in Figure 14 is comparable to that of ethyl acetate in Figure 10. Concentrations: PS(3040K), 25 g/m^3; PBMA, 25 g/m^3.

The displacement kinetics of PS(3040K) by PBMA in three different mixtures of toluene and decalin is shown in Figure 14 in the same way as in Figure 13 for mixtures of ethyl acetate and decalin. Qualitatively, toluene and ethyl acetate have a similar effect on the exchange kinetics. For example, the shapes of the curves for $w_{tol} = 0.13, 0.23$, and 0.38 (Figure 14) are more or less the same as those for $w_{eth} = 0.008, 0.020$, and 0.031 (Figure 10), respectively. Again, much higher values of w_{tol} are needed to obtain the same effect on the exchange kinetics as for ethyl acetate. It seems therefore likely that the effect of toluene and ethyl acetate on the exchange kinetics is determined by their effect on the adsorption energy of PS.

Discussion

A striking result of the present study is that the kinetics of exchange of both PS and PBMA by the displacer PTHF is much faster than that of PS by the displacer PBMA. A factor that might be important is the segmental adsorption energy. For PS, PBMA, and PTHF adsorbing from decalin onto silica, χ_s is about 2.0, 3.8, and 4.8, respectively. Since displacement of one and the same polymer (PS) is sometimes slow (in case of PBMA) and sometimes rapid (for PTHF), it is unlikely that the exchange kinetics are determined by the value of χ_s of the displaced component only. The difference $\Delta\chi_s$ between the segmental adsorption energies of the polymeric displacer and the displaced component is a measure of the driving force for the exchange, and this difference could determine the exchange rate. However, this is also unlikely: for the slow displacement of PS by PBMA $\Delta\chi_s = 1.8$, and for the rapid displacements of PS and PBMA by PTHF $\Delta\chi_s = 1$ and 2.8, respectively. Another possibility would be that χ_s of the polymeric displacer is rate-determining. The relatively high value of χ_s for both displacers (3.8 for PBMA and 4.8 for PTHF) does not make this option very likely. Other effects than adsorption affinities (χ_s) must play a role.

It is also possible that the exchange rate increases with increasing dynamic flexibility of the polymer chain. The experimental results support this view: the exchange rate is higher for the rather flexible displacer PTHF than for the stiffer displacer PBMA. This effect of the chain flexibility was also suggested in a preceding study, where only chain-length differences were considered.[2] For poly(ethylene oxide) (PEO), which is very flexible and chemically resembles PTHF, a mass-transfer-limited exchange was observed. The same conclusion seems to apply for displacement by PTHF. For PS, which is less flexible than PEO, we found indeed slower exchange kinetics than for PEO, while in the present study the displacement of PS by the rather stiff PBMA was found to be relatively slow.

The exchange mechanism of adsorbed low molar mass PS(9K) is qualitatively the same for the displacers PBMA (Figure 6) and high molar mass PS (20000K).[2] In both cases we first observe rapid partial desorption of PS(9K) during adsorption of the polymeric displacer and then slower desorption due to rearrangements within the adsorber layer. Even the time constant for the rearrangement process is about the same for both systems (on the order of one or a few minutes). Thus, high molar mass PS and PBMA, as polymeric displacers for PS(9K), behave in more or less the same way.

When PS is displaced by PBMA in decalin, the desorption rate of PS decreases strongly with increasing chain length: for PS(9K) the time constant is on the order of minutes (Figure 6), whereas it is about 8 h for PS-(20000K) ($w_{\mathrm{eth}} = 0$ in Figure 12). A strong effect of the chain length might be an indication that entanglements play a role. However, displacement of long chains of PS occurs much faster by PTHF (time scale of seconds) than by PBMA (hours). If entanglements play a role in both cases, it is remarkable that the rate of disentanglement—and thus desorption—should depend so strongly on the type of the displacing polymer, suggesting that the mobilities of the "matrices" (formed by the displacing polymer) through which the escaping chain must diffuse differ equally strongly.

Another reason why the exchange of PS(20000K) by PBMA is slow may be that the chain length of the displaced PS ($M = 20000$K) is much higher than that of the displacer PBMA ($M \approx 240$K). We could imagine that an adsorbed molecule of PS surrounded by a number of chains of PBMA does not desorb even when the chains of PBMA are completely unfolded, because PBMA molecules are not long enough to reach to the center of the adsorbed PS chain. In order to come to a more detailed explanation, a systematic investigation of the effect of the chain length on the exchange kinetics would clearly be needed. For displacement of PS by deuterated PS and PMMA by deuterated PMMA, evidence in favor of a rate-determining process diffusive in nature was obtained by others.[4]

The exchange rate of high molar mass PS by PBMA in decalin strongly increases with increasing concentration of a low molar mass displacer (ethyl acetate, Figure 10, or toluene, Figure 14). Probably, this is due to the weaker binding of the polymers to the surface. We imagine that the decrease of the adsorption energy leads to a higher mobility of the adsorbed polymers, resulting in a faster exchange.

For the displacement of PBMA by PTHF in a decalin solution, we find rapid exchange which is completed in a few minutes and which is to a large extent limited by the mass transfer of the polymeric displacer PTHF (Figure 5). In contrast with this result, Van der Beek et al.,[5] using the same polymers also adsorbing on oxidized silicon but from a carbon tetrachloride solution, found much slower exchange which was incomplete, even after many hours. We see no physical reason why the exchange would be so much slower in a carbon tetrachloride solution than in decalin. Possibly, undesired effects due to differences in experimental setup or protocol play a role. For example, the experiments of Van der Beek et al. were performed in a stagnant solution, which might give rise to effects of slow diffusion, while in our setup the adsorption takes place from a flowing solution. Also, different procedures were used in the preparation of the oxidized silicon surface. We cleaned the surface in a gas flame, whereas Van der Beek et al. used a "wet" method involving treatment with hydrogen peroxide and ammonia. According to Frantz and Granick,[14] the surface preparation of silicon may indeed greatly influence the exchange kinetics. These authors observed rapid exchange between protonated PS and deuterated PS if the surface was cleaned with an oxygen plasma, whereas extremely slow exchange kinetics was found after wet cleaning with a mixture of sulfuric acid and hydrogen peroxide. It thus seems that "dry" methods (gas flame, oxygen plasma) produce a surface on which the exchange is rapid and that wet preparations give slow exchange kinetics. We conclude that the different results of Van der Beek et al. as compared to ours are likely to be explained by the different surface preparations and different mass-transfer conditions.

Conclusions

We have studied the exchange kinetics at a silica/decalin interface using three chemically different polymers: PS, PBMA, and PTHF. Due to the widely different values of the refractive index increment dn/dc for these polymers in a decalin solution, the sensitivity of the reflectometric method is strongly different for adsorption of PS, PBMA, and PTHF, respectively. This feature enables study of the exchange kinetics of these polymers.

The displacement rate of adsorbed PS by PTHF is entirely determined by the adsorption rate of PTHF. The latter is limited by mass transfer from the solution. This conclusion applies to any combination of chain lengths of PS and PTHF.

Displacement of adsorbed PBMA by the displacer PTHF is also determined by the mass-transfer-limited adsorption rate of the displacer. The displacement rate of PBMA is slightly affected by aging of the adsorbed PBMA layer for about 20 h.

The kinetics of exchange of PS by PBMA is determined by mass transfer through solution as well as by surface processes, and it was found to depend on the chain length of PS and the solvent composition. Under all conditions the adsorption rate of PBMA on a surface with an adsorbed PS layer is initially limited by mass transfer from the solution. For low molar mass PS (M = 9K) in decalin, part of the adsorbed layer of PS desorbs during adsorption of PBMA, followed by a slower desorption of PS (over a time scale of minutes) due to rearrangements (surface processes) in the adsorbed layer. For high molar mass PS in decalin, no desorption of PS occurs in the first stage, and slow desorption is found in the second process. The time constant for desorption in this second (rearrangement) stage was estimated to be about 8 h for M = 20000K.

With increasing concentration of a low molar mass displacer (ethyl acetate or toluene) the exchange kinetics of high molar mass PS by PBMA gradually becomes faster, resembling the exchange kinetics of low molar mass PS by PBMA in pure decalin. For the displacer ethyl acetate, the time constant for desorption of PS (M = 20000K) due to surface processes decreases from about 8 h in pure decalin to less than 1 min near the critical displacer concentration for adsorption of PS. The addition of a low molar mass displacer causes a decrease of the segmental adsorption energy of the polymers, resulting in a higher mobility of the adsorbed chains and thus a higher rate of the displacement process in the adsorbed layer.

The exchange kinetics of PS by PBMA is much slower than that of PS by PTHF under comparable conditions. We suggest that the different exchange kinetics can be explained in terms of the dynamic flexibility of the chains, which is higher for PTHF than for PBMA.

References and Notes

(1) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993; p 216.

(2) Dijt, J. C.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3219–3228.

(3) Thies, C. *J. Phys. Chem.* **1966**, *70*, 3783.

(4) Johnson, H. E.; Granick, S. *Science* **1992**, *255*, 966.

(5) Van der Beek, G. P.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1991**, *24*, 3553.

(6) Van der Beek, G. P.; Cohen Stuart, M. A.; Fleer, G. J.; Hofman, J. E. *Macromolecules* **1991**, *24*, 6600.

(7) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989.

(8) Dijt, J. C.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3207–3218.

(9) Van der Beek, G. P.; Cohen Stuart, M. A.; Fleer, G. J.; Hofman, J. E. *Langmuir* **1989**, *5*, 1180.

(10) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.

(11) Dijt, J. C.; Cohen Stuart, M. A.; Fleer, G. J., accepted for publication in *Adv. Colloid Interface Sci.*

(12) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993; p 292.

(13) Cohen Stuart, M. A.; Fleer, G. J.; Scheutjens, J. M. H. M. *J. Colloid Interface Sci.* **1984**, *97*, 515.

(14) Frantz, P.; Granick, S. *Langmuir* **1992**, *8*, 1176.