Kinetics of Adsorption and Desorption of Polystyrene on Silica from Decalin

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Received November 22, 1993; Revised Manuscript Received February 28, 1994®

ABSTRACT: Measurements are made of the rate of adsorption and desorption of polystyrene (PS) from decalin onto silica. The adsorbed mass as a function of time is monitored by means of optical reflectometry, and mass transfer through the solution is controlled by means of an impinging jet geometry. It is found that the initial rate of adsorption is entirely controlled by mass transfer, attachment being a fast step on the time scale of the experiment. This result agrees with previous findings for the system poly(ethylene oxide)/water/silica. However, at higher coverage the rate of adsorption slows down gradually and for long chains becomes quite slow. By varying the concentration in solution, it could be shown that the rate of adsorption in this regime remains proportional to the bulk concentration. This can be understood in terms of a first-order attachment step; the corresponding rate coefficient is given as a function of coverage. For comparison, we include a few data for PS with a strongly adsorbing imine end group. These polymers initially adsorb very much like their unfunctionalized counterparts but at higher coverage show a slow continuous rise to considerably higher coverages than ordinary PS, which must be due to formation of a dense brush. As with PS, the overall kinetics is proportional to the bulk concentration which again points toward a rate-limiting attachment step. By means of variations in the chain length, in the segmental adsorption energy, and in the polymer/solvent interaction, it could be shown that the rate of attachment is not simply related to the coverage but rather to the amount of anchoring energy that an incoming chain can gain in its first encounter with the surface, i.e., to the degree of undersaturation. Deviations from fast equilibration were also observed for desorption of short PS chains into pure decalin.

Introduction

The rate at which an adsorbed polymer layer forms from dilute solution is controlled by at least three processes: (i) transport through the solution (by diffusion and convection), (ii) attachment, and (iii) equilibration toward the equilibrium configuration of the chains. In principle, each of these processes could be rate determining. Studies on the rate of adsorption[1] and desorption[2] of poly(ethylene oxide) (PEO) have emphasized the importance of the mass transfer between the bulk solution and surface. In that case, processes ii and iii were presumably fast. Only for a high molar mass polymer ($M \approx 1000$K, where 1 K ≡ 1 kg/mol) near saturation was a clear decrease of the adsorption rate due to the buildup of the adsorbed layer observed.

In this paper we examine the question whether fast equilibration is a general characteristic of the adsorption of uncharged homopolymers. A reason for the rapid adaptation of adsorbed PEO could be the large dynamic flexibility of its chain, which enables fast reconformation during the adsorption process. In view of this argument we chose for the present study polystyrene (PS), which is much less flexible than PEO due to its bulky phenyl side groups. Polystyrene is available in fractions with a narrow molecular weight distribution, like PEO, and therefore we expect little or no effect of polydispersity on the adsorption kinetics.

In the past 25 years various authors have reported kinetic curves for the adsorption of PS[3-14] but in none of these studies were the adsorption kinetics investigated systematically under well-controlled conditions. For all these experiments the mass-transfer conditions were poorly defined, so that it is often difficult to distinguish between transport and surface processes. We shall first briefly review the main results.

Grant et al.[15] studied the adsorption of PS ($M \approx 10^3$K) from dilute cyclohexane solutions at 36 °C and found a remarkable influence of the substrate: on mercury the adsorption was completed within 1 h, whereas it took about 72 h on a chrome surface. Kawaguchi and co-workers[7,10] have studied the adsorption on chrome from solutions of high molar mass PS ($10^2 < M < 10^4$K). As solvents they used cyclohexane[10] and carbon tetrachloride,[7] both at 35 °C, at which temperature the former is a Θ-solvent and the latter a good solvent. The shape of the adsorption curves and the time needed to attain a stable adsorbed amount (2-4 h) were found to be about the same for both solvents and for all molecular weights studied. The final adsorbed amount was much higher in cyclohexane than in carbon tetrachloride, as expected (the amounts were found to be 5 and 1 mg/m^2, respectively, in these solvents).

For the adsorption of PS from cyclohexane solutions onto silica good agreement exists between the results of Vander Linden[11] and those of Frantz et al.[12] Both groups find that the time to obtain a stable adsorbed amount increases with chain length: from less than 10 min for $M \approx 100$K up to several hours for $M \approx 2000$K. All results cited above are obtained for concentrations of 100 g/m^3 or higher. If mass transfer had been rate limiting, the saturated adsorbed amount would probably have been reached in a few minutes or less. The observed times are much longer, though. This indicates that the behavior of PS differs from that of PEO. Furthermore, some of these results indicate that the adsorption kinetics depend on the chain length and substrate used.

We decided to investigate the adsorption kinetics of polystyrene more systematically by using well-defined mass-transfer conditions and by varying the concentration, the chain length, the solvent quality, and the adsorption energy of the polymer. Obviously, the concentration and chain length of PS can easily be varied. The solvent quality and adsorption energy cannot be directly changed, and therefore we discuss below the possibilities of influencing

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® Abstract published in *Advance ACS Abstracts,* April 15, 1994.

0024-9297/94/2227-3207$04.50/0

Table 1. Polymer Samples of Polystyrene

code	M, kg/mol	M_w/M_n	code	M, kg/mol	M_w/M_n
1K	1.32	1.09	1030K	1030	1.05
3K	3.25	1.04	3040K	3040	1.04
9K	9.2	1.03	6500K	6500	1.12
66K	66	1.03	20000K	20000	1.3
514K	514	1.05			

these parameters.

The solvent quality for a polymer can be changed by variation of the temperature or the composition of the solvent. With temperature variation the composition of the solution remains constant, which is an advantage over a change in the solvent composition. However, temperature is also directly related to molecular motions, and these may well affect the adsorption kinetics. For this reason we chose to vary the solvent composition rather than temperature. For the reflectometric technique that we use in this study, working at room temperature is also easier. We decreased the solvent quality by addition of small amounts of a nonsolvent. We have to bear in mind that such a nonsolvent could also change the effective adsorption energy of the polymer. We therefore decided to use a nonsolvent which is not expected to interact specifically with the surface, so that it has little or no influence on the adsorption energy.

Cohen Stuart and Van der Beek[16-19] showed that the effective segmental adsorption energy of a polymer can be varied in a quantitative manner by using mixtures of two solvents, one of which is a displacer of the polymer. We chose a rather strong displacer, so that the amounts needed are relatively small. Therefore, we expect little effect of the displacer on the solvent quality. Moreover, the concomitant changes in the hydrodynamic and optical conditions will be small.

For comparison, we also consider the adsorption kinetics of a low-molar-mass polystyrene (M = 17K), that carries at one end a polar, strongly adsorbing iminium ion group. Due to this end group, the adsorption is strongly enhanced. With such an end-capped polymer we can investigate the adsorption kinetics of a short chain at high coverage.

Experimental Section

Materials. Polystyrene samples of narrow molar mass distribution were purchased from Polymer Laboratories and were used without further purification. Their molar masses and degrees of polydispersity are listed in Table 1. According to the manufacturer the three lowest molecular weights have a "vinylhexane" end group. Polystyrene with an iminium ion end group and the corresponding homopolymer with a styrene end group were kindly provided by Dr. Furusawa, Tsukuba University, Japan. Both were made by anionic polymerization and have a molecular weight of 17K.

The solvent decalin was obtained from Merck (for synthesis quality). From an analysis with gas chromatography we found that it is a 30/70 mixture of the cis and trans forms, respectively. Before use the decalin was led over a column of zeolite and stored in bottles containing anhydrous $CaCl_2$. From experiments we concluded that this treatment removes low concentrations of impurities (possibly alcohols) from the decalin which act as displacers of PS.

In some experiments the solvent decalin was mixed with n-hexadecane (Merck; for synthesis quality) or ethyl acetate (Merck, p.a.), which are a nonsolvent and a displacer of PS, respectively. Before mixing both additives were purified by the same method as used for decalin.

Table 2. Sensitivity Calculations for Adsorption of Polystyrene from Decalin Solution onto Silica

Optical Parameters		
silicon	$n = 3.80$	
silica layer	$n = 1.46$	$d = 105$ nm
adsorbed PS layer (1 mg/m^2)	$n = 1.497$	$d = 5$ nm
decalin solution	$n = 1.473$	
angle of incidence (deg)	59.35	
wavelength (nm)	632.8	
refractive index increment PS/decalin (cm^3/g)[21]	0.120	
Results		
R_p/R_s without adsorbed polymer	0.0562582	
sensitivity factor A_s (m^2/mg)	0.0174	

As the substrate for adsorption, strips cut from an oxidized silicon wafer were used. These were cleaned by red-glowing in a natural-gas flame for about 5 s. After cooling down in ambient air, they were directly used. The silica film thickness was determined by means of reflectometry[20] and found to be about 105 nm for all strips used. Because of the small surface area involved, small amounts of impurities are detrimental to the results. Therefore, all glassware had to be rigorously cleaned. Two methods were applied. In the first, the glassware was first immersed into sulfochromic acid for 24 h and then another 24 h into 2 N nitric acid, finally rinsed with deionized water, and dried at 100 °C. The second method consists of a single cleaning step with a solution of 10 g/L of $(NH_4)_2S_2O_8$ in concentrated H_2SO_4, followed by rinsing with water and drying.

Methods. All adsorption and desorption measurements were carried out using a reflectometer with a stagnation point flow cell as described elsewhere.[1] From reflectivity calculations we derived the relation between the reflectometric signal S (which is proportional to the reflectivity ratio R_p/R_s between the parallel (p) and perpendicular (s) components of the polarization, respectively) and the adsorbed amount Γ (mass/unit area); these calculations are described *in extenso* in ref 20. They show that, for the conditions chosen here, the signal S does *not* depend on the shape of the concentration profile of the adsorbed layer but only on the total adsorption Γ. Moreover, the increment ΔS due to polymer adsorption is to a very good approximation proportional to Γ. In order to calculate the proportionality constant A_s ($=\Delta S/S_0\Gamma$), the adsorbate was modeled as a homogeneous layer for which the thickness was *arbitrarily* chosen to be 5 nm, after which the refractive index was derived using the refractive index increment dn/dc in solution. These numbers are given in Table 2, together with all other relevant optical parameters. The result, $A_s = 0.0174$ m^2/mg, is also obtained for other combinations of the polymer layer thickness and refractive index that give the same Γ. For reflectometry to give a sensitive adsorption measurement, it is important to have a significant dn/dc. As explained in ref 20, it is also important to choose appropriate values for the angle of incidence and for the thickness of the silica film. The fact that the silica is nearly index-matched with the solvent does not adversely affect the sensitivity.

For experiments with organic solvents an impinging jet flow cell and flow system were constructed in which solutions come into contact with glass and Teflon only. Essentially the new cell is the same as in ref 1, but now the cell is made of Teflon and the two prisms by which the laser beam enters and leaves the cell are replaced by one, through which a cylindrical channel (as inlet for the polymer solution) is drilled from top to base. Teflon valves and tubing were used throughout. The flow of solvent or solution was maintained by hydrostatic pressure. An experiment starts by turning a valve, whereby the solvent that is initially flowing through the cell (base line) is abruptly replaced by polymer solution. As soon as the solution impinges on the substrate, adsorption starts.

Mass transfer in the impinging jet (stagnation point) flow has been described in a previous paper.[1] For the experiments in decalin we determined the distance h between the collector surface and the inlet tube (1.3 mm) and the radius R of the inlet tube (0.75 mm). Hence, h/R equals 1.7. The flow rate was determined from the weight of solution that passed through the flow system in 3 min. Using a density of decalin of 0.88 g/cm^3, we find that the volume flow rate is 1.31 mL/min. The corresponding Reynolds number is 3.28. We estimate from these data with the help of the plots shown in ref 1 that the flow intensity parameter $\bar{\alpha}$ equals 2.13.

We can now calculate the flux J of polymer between the bulk solution and stagnation point in terms of the mean fluid velocity

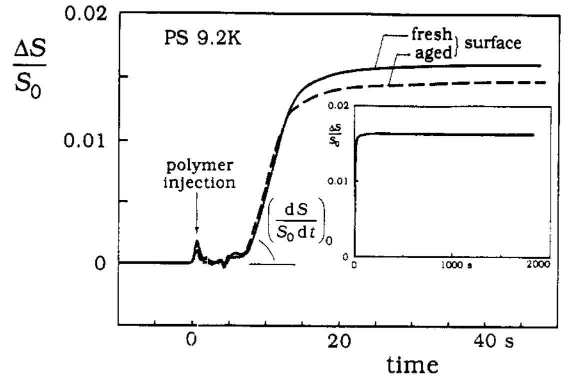

Figure 1. Example of the adsorption kinetics of low molar mass PS. The full and dashed curves represent experiments with 3 and 40 min of solvent injection for $t < 0$, respectively. The inset shows $\Delta S/S_0$ during prolonged polymer injection. Concentration 50 g/m^3; A_s = 0.0174 m^2/mg.

v_m, at the end of the inlet tube, of the diffusion constant D of the polymer, and the concentration difference $c_b - c_s$, where c_b and c_s are the polymer concentrations in the bulk solution and (sub)-surface region, respectively. This flux is given by

$$J = k(c_b - c_s) \qquad \text{(1a)}$$

where the transport coefficient k is given by

$$k = 0.776(D^2\bar{\alpha}v_m/R^2)^{1/3} \qquad \text{(1b)}$$

The concentration c_b is equal to that of the polymer solution which is injected (for injection of pure solvent, $c_b = 0$). Usually, the (sub)surface concentration c_s is not known beforehand. It is the concentration of nonadsorbed molecules near the surface that can freely take part in diffusion and convection. The often used "perfect sink" boundary condition amounts to the assumption that c_s equals zero. However, also other boundary conditions can be applied. For the sake of generality, we here retain eq 1.

In order to examine the effect of the addition of the nonsolvent n-hexadecane on the solvent quality, the cloud point of the PS solutions was measured. To this end, a tube containing about 5 mL of a solution of concentration 500 g/m^3 was placed in a thermostatic bath. The temperature was decreased in small steps (1 °C), and the cloud point was determined visually.

Results

Adsorption and Desorption in Pure Decalin. Introductory experiments showed that the reliability and reproducibility of the results are strongly dependent on the degree of purification of solutions and glassware. For example, if an adsorbed polymer is exposed to a nonpurified solution, the adsorbed amount of polymer may decrease considerably due to displacement by the pollutant. The sensitivity for contamination of this method originates from the high volume-to-surface area ratio: impurities are continuously being supplied to the surface by the flowing solution. We give one example to illustrate that by our cleaning methods the contamination of solutions has been reduced to an acceptable level. For this the adsorption of a low molecular weight PS (9K) is chosen, since adsorption of short chains appeared to be most sensitive to contamination. In Figure 1 the results of two experiments are given. Before $t = 0$ only solvent flows through the cell. At $t = 0$ the valve is switched and the injection of polymer solution starts. After about 7 s, which is the time needed to refresh the volume between the valve and cell, the signal starts to rise due to adsorption of the polymer. The initial slope of the signal $[\mathrm{d}S/(S_0\,\mathrm{d}t)]_0$ which is proportional to the adsorption rate $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ is indicated. After some 20–30 s the surface is saturated and no further adsorption takes place. The saturated level corresponds to an adsorbed amount of about 1 mg/m^2. The difference between both experiments is the time of solvent injection before $t = 0$: 3 and 40 min for the full and dashed curves, respectively. The saturated adsorbed amount is about 8% lower for the experiment with the longer time of solvent injection. If, instead of purified solvent (as in Figure 1), untreated decalin is used, there is almost no adsorption of polymer left after 40 min of solvent injection. This is clearly due to adsorption of contaminants.

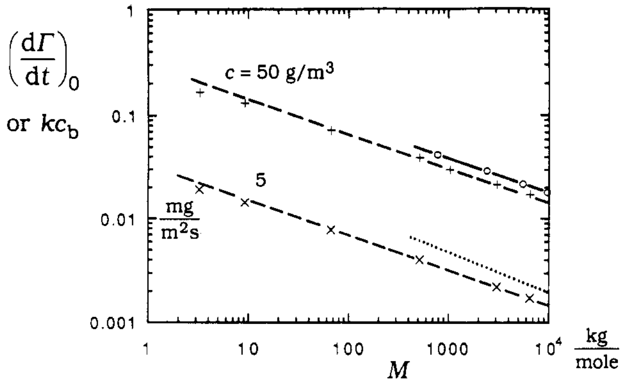

Figure 2. Effect of molar mass on the initial adsorption rate for two concentrations. Crosses and pluses refer to c = 5 and 50 g/m^3, respectively. The dashed and dotted lines are drawn with a slope according to the scaling theory for Θ-solvents and athermal solvents, respectively. Circles represent a calculation of the mass-transfer rate kc_b for c_b = 50 g/m^3; see text.

The inset of Figure 1 shows $\Delta S/S_0$ during prolonged injection of polymer solution for the experiment with the short solvent pretreatment. After rapid initial adsorption, the signal remains stable up to about 30 min. If untreated decalin is used instead, the signal decreases strongly due to displacement by contaminants, becoming nearly zero after ≈2500 s. We conclude that our cleaning method effectively removed adsorbing contaminants and that experimental results are hardly affected by contaminants for a period of at least 30 min.

1. Initial Adsorption Rate. It has been found that for PEO the initial adsorption rate is completely determined by mass transfer from the bulk solution.[1] In order to check whether this is also the case for adsorption of PS from decalin solutions, we varied the mass-transfer conditions by means of the concentration and the chain length of the polymer and compared the observed initial adsorption rates to the predicted mass-transfer rates (eq 1).

The results are presented in Figure 2 in a double-logarithmic plot of the initial adsorption rate $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ against molecular weight M, for concentrations of 5 and 50 g/m^3, respectively. From the graph one finds easily that $(\mathrm{d}\Gamma/\mathrm{d}t)_0 \propto c$. This is in agreement with eq 1, as long as the (sub)surface concentration c_s is negligibly small as compared to the concentration c_b in the bulk. This is very likely the case for adsorption on a bare surface.[1]

The initial adsorption rate is proportional to $D^{2/3}$ and hence decreases with M due to the slower diffusion of longer chains. Polymer solution theory states that the diffusion constant of a polymer scales as $D \propto M^{-\gamma}$. Under Θ-conditions, where Gaussian statistics apply, $\gamma = 0.5$ for every M. In a good solvent a transition occurs from $\gamma = 0.5$ for low M to 0.588 for high M, due to the swelling of long chains by excluded volume. The transition between these regimes is rather broad and extends over about 2 decades in M.[22] In Figure 2 the slopes of the dashed and dotted lines are drawn according to γ = 0.5 and 0.588, respectively. For $M >$ 10K there is excellent agreement between the experiment and the scaling theory for

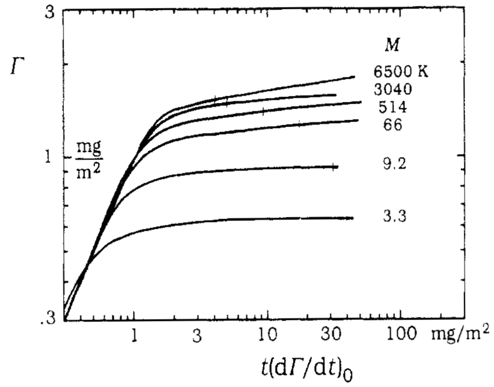

Figure 3. Comparison of the adsorption kinetics for different molar masses. The initial slope is normalized to unity. Note the double-logarithmic scaling. Vertical ticks along the curves indicate $t = 4$ min of polymer injection. Concentration 50 g/m^3.

Θ-solvents. Only for extremely short chains ($M < 10$K), which actually consist of less than 100 monomeric units, the experiments deviate slightly from scaling theory.

From the agreement between experiment and the theory for polymer diffusion constants in solution we conclude that the measured dependence of $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ on M reflects the molecular weight dependence of the diffusion constant in solution and is thus in agreement with mass-transfer-controlled adsorption. Moreover, from the slope of the curve at high values of M it follows that at ≈22 °C decalin is (nearly) a Θ-solvent for PS. From measuring D by dynamic light scattering, Tsunashima et al. concluded that the Θ-temperature of PS in *trans*-decalin is 20.4 °C,[23,24] which is in good agreement with our result. We have to realize, however, that Tsunashima used pure *trans*∼decalin and that our result applies to a 70/30 mixture of the trans and cis forms. Finally, we note that the initial adsorption rate gives a remarkably accurate measurement of the chain-length dependence of the diffusion constant. With the same method we observed for aqueous solutions of PEO with increasing M a transition in D, which is characteristic of good solvents.[1]

The above considerations suggest that $(\mathrm{d}\Gamma/\mathrm{d}T)_0$ of PS from decalin solutions is entirely determined by transport through solution and thus equals the maximum mass-transfer rate kc_b ($c_\mathrm{s} = 0$ in eq 1). A further check is to compare the quantitative values of $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ and kc_b. In order to be able to calculate k, we used the values for D as given by Tsunashima et al. The calculated maximum mass-transfer rate is shown as open circles in Figure 2. The calculated value of kc_b is about 20% higher than the experimental value for $(\mathrm{d}\Gamma/\mathrm{d}t)_0$. As discussed already for the adsorption of PEO,[1] one expects on theoretical grounds that $(\mathrm{d}\Gamma/\mathrm{d}t)_0 = kc_\mathrm{b}$. The discrepancy is easily explained by errors in D and in the calibration of the signal. Therefore, it is likely that the initial adsorption rate of PS from decalin solutions is entirely determined by mass transfer from the bulk, as was found before for PEO from water.

2. Adsorption Rate at Higher Coverage. Figure 1 shows that the adsorption rate $\mathrm{d}\Gamma/\mathrm{d}t$ is constant up to about $\Delta S/S_0 = 0.01$ and then decreases gradually to zero in the plateau region. The decrease in $\mathrm{d}\Gamma/\mathrm{d}t$ is caused by the buildup of the adsorbed layer. Below, we investigate how the adsorption rate at higher coverage depends on the chain length and the concentration of the polymer.

In order to be able to examine the effect of M on the adsorption kinetics, we plotted in Figure 3 the adsorbed amount Γ as a function of $t(\mathrm{d}\Gamma/\mathrm{d}t)_0$ on a double-logarithmic scale for samples of different M. In such a plot all initial slopes are normalized to unity. Since it was concluded before that $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ is determined by mass transfer for all molar masses, the initial tangent represents mass-transfer-controlled adsorption. With increasing M the mass-transfer-limited region extends up to higher Γ. This behavior has also been found for PEO. However, for all chain lengths of PS we find a *gradual* transition from the transport-limited region to the final value, in contrast with the *sharp* transition for the low molar masses of PEO ($M < 100$K). For the two lowest molar mass samples of PS (3K and 9K) the final value corresponds to a stable, saturated level. For longer chains the final level is not completely constant, $\mathrm{d}\Gamma/\mathrm{d}t$ being finite even after long times (note the logarithmic scaling). The adsorption rate in the plateau region was found to increase considerably if less well-purified decalin was used. Therefore, for the moment we cannot exclude that the slow increase of Γ in the plateau region is an undesired side effect. However, it may also be a real effect related to polymer adsorption kinetics of long, stiff chains.

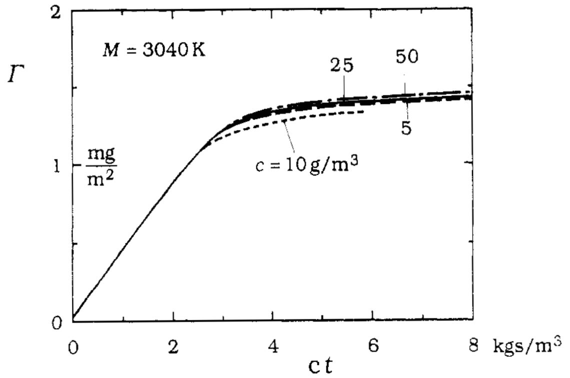

Figure 4. Effect of polymer concentration on adsorption rate. Note that Γ is plotted as a function of the product ct of concentration and time. Concentrations are as indicated.

The effect of the concentration on the adsorption kinetics of a high molar mass sample (3000K) is shown in Figure 4 for four concentrations in the range 5–50 g/m^3. The adsorbed amount Γ is plotted as a function of the product ct of concentration and time. The initial slope $[\mathrm{d}\Gamma/\mathrm{d}(ct)]_0$ is the same for each concentration studied, which again shows that initially $\mathrm{d}\Gamma/\mathrm{d}t \propto c$, in agreement with the transport equation (1). In Figure 4 the curves $\Gamma(ct)$ for different c coincide within experimental error, not only in the initial part but also at higher coverage and in the final level. This implies that $\mathrm{d}\Gamma/\mathrm{d}t$ is proportional to the solution concentration for each value of Γ. No influence of the age of the adsorbed layer on $\mathrm{d}\Gamma/\mathrm{d}t$ is observed in these experiments. Similar results are obtained for other molecular weights. Only for very short chains (M = 3K and 9K) could this result not be verified with certainty because the saturated levels for these samples are somewhat concentration dependent. It turns out that it is possible to analyze the kinetic curves $\Gamma(t)$ in terms of a two-step process: transport of free molecules from the bulk solution, followed by attachment to the interface. From this analysis a rate constant for the attachment can be extracted.

The transfer part is described by eq 1. According to this equation the polymer flux to the surface is proportional to the concentration difference $c_\mathrm{b} - c_\mathrm{s}$ between the bulk solution and surface region. For the attachment step we suppose that the adsorption rate $\mathrm{d}\Gamma/\mathrm{d}t$ is proportional to the concentration c_s of free molecules near the surface, with an attachment rate constant $K(\Gamma)$ which depends on the adsorbed amount Γ

$$\mathrm{d}\Gamma/\mathrm{d}t = K(\Gamma)\, c_s \qquad (2)$$

In a steady-state situation, the flux J (eq 1) equals the adsorption rate $\mathrm{d}\Gamma/\mathrm{d}t$ (eq 2). However, during adsorption $\mathrm{d}\Gamma/\mathrm{d}t$ usually decreases in time, so that a real steady state does not exist. Since the changes in $\mathrm{d}\Gamma/\mathrm{d}t$ are slow as compared to the rate of adjustment of the flux from solution, a quasi-steady state does exist, for which $J \approx \mathrm{d}\Gamma/\mathrm{d}t$. After elimination of c_s from eqs 1 and 2 the following expression is obtained:

$$\frac{c_b}{\mathrm{d}\Gamma/\mathrm{d}t} = \frac{1}{k} + \frac{1}{K(\Gamma)} \qquad (3)$$

If $K(\Gamma) \gg k$, this reduces to $\mathrm{d}\Gamma/\mathrm{d}t = kc_b$ and the adsorption rate is mass transfer limited ($c_s \cong 0$). If, however, $K(\Gamma) \ll k$, then $\mathrm{d}\Gamma/\mathrm{d}t = K(\Gamma)\, c_b$ and the adsorption is entirely determined by the attachment step ($c_s \cong c_b$).

Since the initial adsorption rate of PS is completely determined by mass transfer (see Initial Adsorption Rate), the transport coefficient k equals $(\mathrm{d}\Gamma/\mathrm{d}t)_0/c_b$. Hence, the attachment rate constant $1/K(\Gamma)$ can be extracted from the data by

$$\frac{1}{K(\Gamma)} = c_b\left(\frac{1}{\mathrm{d}\Gamma/\mathrm{d}t} - \frac{1}{(\mathrm{d}\Gamma/\mathrm{d}t)_0}\right) \qquad (4)$$

By way of example we analyzed one of the curves in Figure 4 (c = 50 g/m^3) and plotted in Figure 5 $K(\Gamma)$ as a function of the adsorbed amount Γ (full curve) and compared it to k (horizontal dashed line). For Γ up to about 0.5 mg/m^2 the deviation of $\mathrm{d}\Gamma/\mathrm{d}t$ from $(\mathrm{d}\Gamma/\mathrm{d}t)_0$ is so small that $K(\Gamma)$ cannot be determined. At the point where the curves cross ($k = K(\Gamma)$) the adsorption rate is half of its initial value. With increasing the adsorbed amount $K(\Gamma)$ decreases sharply (note the logarithmic scaling). This means that due to the buildup of the adsorbed layer the attachment of the surface becomes more and more difficult.

As is clear from Figure 4, $\mathrm{d}\Gamma/\mathrm{d}t \propto c_b$ at any coverage, so that the value of the left-hand side of eq 3 is independent of $\mathrm{d}\Gamma/\mathrm{d}t$ or c_b. Consequently, the same applies to $K(\Gamma)$. This means that for polystyrene $K(\Gamma)$ is independent of the mass-transfer conditions. It is a rate constant which is entirely determined by the attachment step to the surface (see also Discussion). Since we are not able to give a quantitative interpretation to $K(\Gamma)$, we decided to present and compare the experimental results in their original form. Note, however, that from each curve $\Gamma(t)$ we could extract $K(\Gamma)$ and that we could thus compare and discuss results in terms of $K(\Gamma)$.

3. Final Adsorbed Amount. In order to examine the effect of the chain length on the final adsorbed amount Γ_f, we plotted in Figure 6 $\Gamma_f(M)$ for a polymer concentration of 50 (open circles) and 500 g/m^3 (open squares). At the lower concentration Γ_f is the value of Γ at $t(\mathrm{d}\Gamma/\mathrm{d}t)_0$ = 30 mg/m^2 (Figure 3). At the higher concentration Γ_f is the adsorbed amount at $t \approx$ 25 min. For comparison, results of Van der Linden and Van Leemput[25] for the adsorption of PS from cyclohexane on silica dispersions at 35 °C and c = 2000 g/m^3 are given in open triangles. The meaning of the filled symbols will be discussed later in this paper (Effect of a Nonsolvent).

First we discuss the effect of the concentration on the curve of Γ_f as a function of M. For M up to ≈20K the values for Γ_f can be determined unambiguously, since the adsorbed amount attained a constant stable level for those chains lengths (Figure 3). Moreover, the adsorption is reversible with respect to concentration changes between 5 and 500 g/m^3, as will be shown in the next section. Therefore, we conclude that the final adsorbed amounts Γ_f for $M <$ 20K represent equilibrium values. For $M >$ 20K the adsorption rate at the end of the experiment was not yet zero, and thus Γ_f does not correspond to equilibrium. The higher value of Γ_f at c = 500 as compared to 50 g/m^3 can be explained from the proportionality between $\mathrm{d}\Gamma/\mathrm{d}t$ and c. In terms of Figure 4, the product ct is much higher for c = 500 than 50 g/m^3, and thus Γ_f for the higher concentration is nearer to equilibrium than that for the lower concentration.

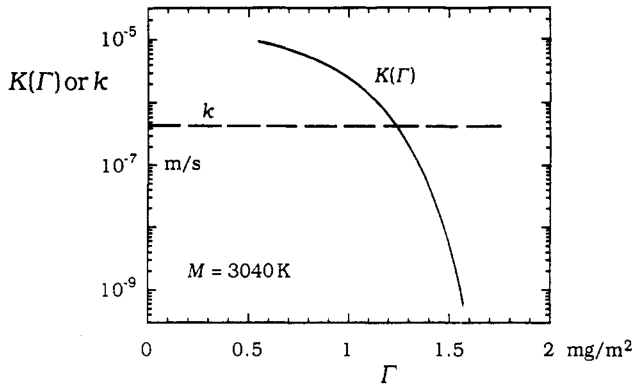

Figure 5. Attachment rate constant $K(\Gamma)$ and transport coefficient k as a function of the adsorbed amount Γ. Polymer concentration 50 g/m^3.

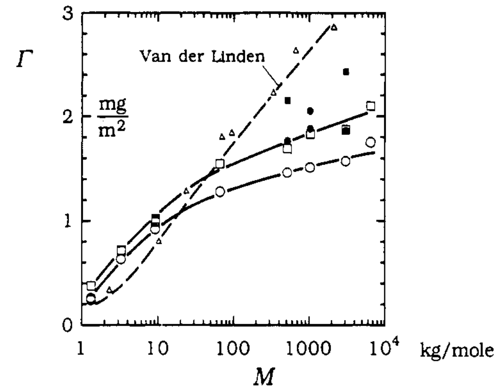

Figure 6. Effect of molar mass on the final adsorbed amount in decalin solutions (open symbols) and 96.5/3.5 (w/w) mixtures of decalin and n-hexadecane (filled symbols). Circles and squares refer c = 50 and 500 g/m^3, respectively. For comparison, the results of Van der Linden for PS absorbing from cyclohexane (34 °C) on silica are included (triangles).

The fact that the rate of attachment is proportional to the solution concentration implies that equilibrium is attained at a certain value of the *product ct*. Thus the time needed to establish equilibrium is inversely proportional to the solution concentration. This could well be the reason for the often encountered strong decrease in Γ_f at low concentrations in experimentally determined adsorption isotherms. For example, Van der Linden[11] determined an adsorption isotherm of monodisperse PS (M = 300K) from cyclohexane at 35 °C on silica dispersions after stirring for 2 h. For $c >$ 500 g/m^3 the isotherm showed a plateau value of 2 mg/m^2. For $c <$ 500 g/m^3 the adsorption gradually decreased, and at 20 g/m^3 only 0.95 mg/m^2 was adsorbed. For an equilibrium adsorption isotherm we would not expect such a strong concentration dependence. However, for c = 20 g/m^3 the value of ct was only 4% of that for c = 500 g/m^3, and it was possibly insufficient to reach equilibrium.

Comparison in Figure 6 of our results with those of Van der Linden and Van Leemput shows the following trends.

For low molar mass, Γ_f in decalin is somewhat higher than that in cyclohexane. According to the Scheutjens–Fleer theory, curves of Γ vs log M shift to the left with increasing adsorption energy per segment. The difference at low M may thus be an indication that the adsorption energy in decalin is somewhat higher than that in cyclohexane. At high M the value of Γ_f in decalin is lower than that in cyclohexane. Presumably, Γ_f in decalin is still below the equilibrium value. In addition, the solvent quality for PS in decalin could be slightly better than that in cyclohexane, which would correspond to lower adsorption levels. The second argument is supported by the results of Chin and Hoagland.[26] These authors reported that for high M adsorbed amounts in decalin at 22 °C were about half the value of those in cyclohexane at 35 °C. For both solvents, the adsorbed amounts were about twice as high as the values given here. This may be a result of the different substrate used: Chin and Hoagland used chrome. (Another possibility is that the molar volume of the solvent has a direct effect on adsorbed amounts; this effect has been discussed recently by Ploehn.[27])

4. **Desorption.** In a recent paper, we proposed a model for the rate of polymer desorption into pure solvent which was based on mass transfer and a local equilibrium argument.[2] For PEO, this model seemed to be adequate. Here, we want to investigate whether the desorption rate of PS is also limited only by mass transfer away from the surface or whether detachment plays a role. As explained in ref 2, the adsorbed amount Γ at any time t after the start of solvent injection on a polymer layer initially in equilibrium at an adsorbed amount Γ_0 and concentration c_0 is given by

$$\Gamma = \Gamma_0 - p \log(1 + t/\tau) \qquad (5)$$

where p is the slope $\mathrm{d}\Gamma/\mathrm{d} \log c$ of the adsorption isotherm and the time constant τ is given by $0.43p/kc_0$. For $t \gg \tau$ a simple correlation between the desorption rate and adsorption isotherm exists: $\mathrm{d}\Gamma/\mathrm{d} \log t = -\mathrm{d}\Gamma/\mathrm{d} \log c$. The desorption process was studied as a function of the chain length. For $M > 100\mathrm{K}$ no detectable desorption of PS into a flow of pure solvent could be detected over a period of ≈30 min. According to the Scheutjens–Fleer theory the slope p of the adsorption isotherm decreases with increasing M. For long chains p/Γ_0 is on the order of 1% or less. Due to this low value of p, desorption of long chains is expected to be very small indeed, unless t is very long, much longer than the time scale of a typical desorption experiment in our setup. Thus, the lack of a measurable desorption is consistent with the model based on mass-transfer and local equilibrium but gives, of course, no proof for this model.

For short chains some desorption is observed in a flow of pure solvent. The results of four desorption experiments with a sample of M = 9.2K are given in Figure 7. Polymer was first deposited by injecting a polymer solution of a concentration as indicated. The adsorbed amount attains a constant saturated level, which increases with concentration. Then, at $t = 0$, the valve is switched to pure solvent or to a solution of lower concentration, as indicated. The dashed curve is the theoretical prediction based on eq 5. For all experiments, Γ decreases due to desorption. In the case of a concentration jump from c = 500 to 5 g/m^3, the desorption rate is initially the same as for a jump from c = 500 g/m^3 to pure solvent, probably because the concentration gradient between the surface and the bulk solution is almost the same. After some time the curves diverge, and the one for injection of the dilute polymer solution approaches a new, stable level. The adsorbed amount at that level corresponds to the saturation at this concentration, which is, for comparison, indicated by a dotted line. If, at t = 250 s, the solution of higher concentration is injected again, the original saturated level is quickly reestablished. This experiment shows that the adsorption is reversible with respect to changes in solution concentration. For this low M the saturated adsorbed amounts thus represent equilibrium values, and the initial values for c = 5, 50, and 500 g/m^3 give three points of the adsorption isotherm. These adsorbed amounts are nicely proportional to log c in this range; for the slope $p = \mathrm{d}\Gamma/\mathrm{d} \log c$ a value of 0.08 mg/m^2 per decade in c is found.

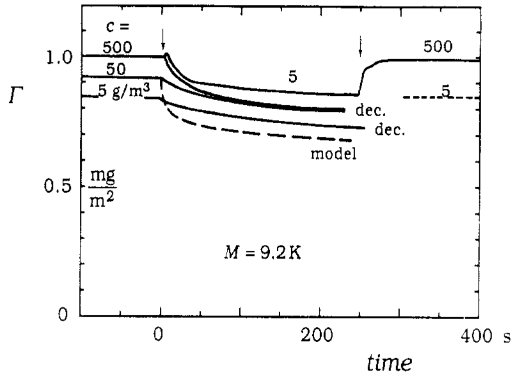

Figure 7. Desorption kinetics for M = 9.2K. Initially, for $t < 0$, polymer solution is injected, and the adsorbed layer is saturated at a concentration as indicated. At $t = 0$ the injection of pure decalin (dec) or a solution of lower concentration (c = 5 g/m^3) starts. For one of the experiments, at $t \approx 250$ s the original solution is reinjected. For comparison, the saturated level for c = 5 g/m^3 is indicated by a dotted line to the right. The dashed curve is the result of a model calculation, as discussed in the text.

With this information we can check whether during desorption the local equilibrium concept applies and whether the desorption can be described by eq 5. The transport coefficient k was determined from the initial adsorption rate for c = 5 g/m^3. From eq 1 a value of 2.86×10^{-6} m/s for k was obtained, corresponding to τ = 0.24 s. $\Gamma(t)$ during desorption was then calculated with eq 5, and the result is represented by the dashed line in Figure 7. It turns out that the experimental desorption rate is much lower than that calculated. This implies that, in contrast to what is observed for the PEO/water system, desorption of PS/decalin is not rate-limited by mass transfer only; detachment of polymer molecules must also play a role. Since we find reversibility with respect to concentration changes between 5 and 500 g/m^3 at time scales on the order of seconds to minutes, the time scale for the detachment process must be in the same range.

5. **Effect of a Nonsolvent.** In order to decrease the solvent quality we decided to add a nonsolvent to solutions of PS in decalin. For two reasons n-alkanes are suitable nonsolvents in our experiments. First, they are chemically related to decalin, and therefore perfectly miscible with this solvent. Second, they are nonpolar and hardly polarizable and therefore we do not expect a large effect on the adsorption energy of the polymer from the mixed solvent as compared to pure decalin. We chose n-hexadecane because of its low vapor pressure. In this way temperature fluctuations due to evaporation at the free solution/air interface in the flow cell are avoided.

The effect of n-hexadecane on the solvent quality can be characterized by the change of the cloud point of PS solutions. In Figure 8 the cloud point T_c of PS solutions of concentration 500 g/m^3 is plotted as a function of the weight fraction w_{hex} of n-hexadecane in mixtures with decalin. Three molecular weights were used, as indicated. For $T > T_c$ a solution is clear; for $T < T_c$ it is cloudy due

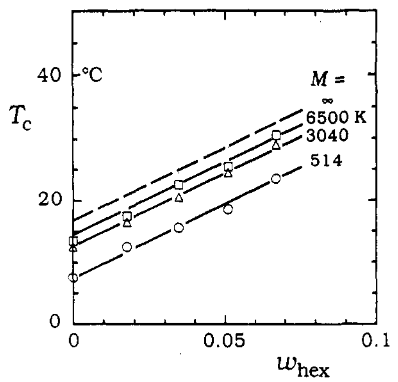

Figure 8. Cloud point T_c of PS in solvent/nonsolvent mixtures of decalin and hexadecane as a function of the weight fraction w_{hex} of hexadecane, for different molar masses, as indicated. The dashed line is an extrapolation to infinite chain length and gives thus the Θ-point. Polymer concentration 500 g/m^3.

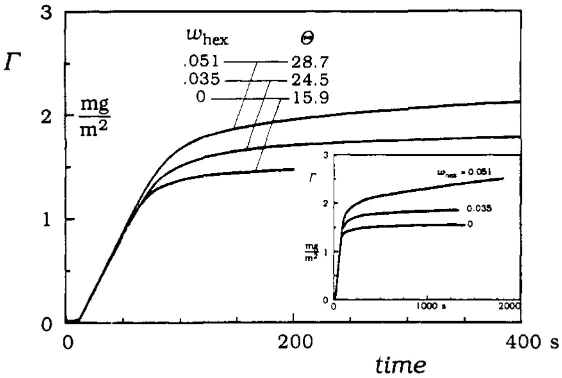

Figure 9. Adsorption kinetics of PS in different solvent/nonsolvent mixtures of decalin and hexadecane. The weight fraction w_{hex} and the corresponding Θ-point of the solution are indicated. The inset shows the same experiments on a longer time scale. M = 3040K, c = 50 g/m^3, and $T \approx 22$ °C.

to phase separation. As expected, the addition of the nonsolvent n-hexadecane to decalin solutions of PS leads to phase separation at a certain value of w_{hex}. Hence, the solvent quality is indeed decreased by n-hexadecane. According to polymer solution theory, the cloud point approaches the Θ-temperature for infinitely long chains. The extrapolation to infinite chain length should be made in a plot of $1/T_c$ as a function of $M^{-1/2}$.[28] The value of the Θ-temperature thus obtained is indicated in Figure 8 by the dashed line. In pure decalin Θ is about 16 °C (Figure 8). Our experiments were carried out at ≈22 °C, where decalin is a slightly better than Θ-solvent for PS.

The effect of n-hexadecane on the adsorption kinetics for M = 3040K is shown in Figure 9 for three values of w_{hex}, namely, 0, 0.035, and 0.051. The inset shows the same experiments on a longer time scale. The experiments were carried out at 22 °C, which is for w_{hex} = 0 about 6 °C above Θ, for w_{hex} = 0.035 about 2.5 °C below Θ, and for w_{hex} = 0.051 about 6.5 °C below Θ. For the latter experiment it was even 2 °C below the cloud point of a 10 times more concentrated solution of c = 500 g/m^3. During the experiment at w_{hex} = 0.051 the solution was clear, but 1 day later we noted a blue haze, indicating incipient phase separation.

The initial slopes in Figure 9 are the same for all three experiments. Since the hydrodynamic conditions are hardly affected by the addition of n-hexadecane, the same must apply to the optical calibration and thus dn/dc of the polymer. However, the final level in Figure 9 increases with w_{hex}. Since the optical calibration is not affected by the addition of n-hexadecane, the increase of the final level must reflect an increase of the final adsorbed amount Γ_f. The increase of Γ_f is in accordance with the expectation that n-hexadecane decreases the solvent quality. The inset shows that the two lower curves approach a constant level after some minutes, which indicates that the adsorbed layer is saturated. In contrast, the adsorbed amount for the upper curve corresponding to the unstable solution is a continuously increasing function of time. Presumably, this increase reflects incipient phase separation at the interface.

We want to stress that in Figure 9 the increase of Γ_f goes along with a more extended transport-limited region, as indicated by the longer initial straight line. This is not immediately obvious. The additional adsorption due to a decrease of the solvent quality could also have taken place at a lower rate, somewhere in the transition region toward saturation. Apparently, a decrease of the solvent quality affects mainly the *fast* part of the adsorption process.

Control experiments for a different molecular weight (514K) showed a similar extension of the transport-limited region in the presence of n-hexadecane. Also, the coincidence of curves $\Gamma(ct)$ for different concentrations was preserved in mixtures with n-hexadecane. From this we conclude that the addition of n-hexadecane leaves the attachment process essentially the same, but its influence on the adsorption rate is shifted to somewhat higher values of the adsorbed amount.

Final adsorbed amounts for w_{hex} = 0.035 are plotted in Figure 6 as a function of M for c = 50 (filled circles) and 500 g/m^3 (filled squares). The value of w_{hex} = 0.035 closely corresponds to Θ-conditions in the experiment. The results of Van der Linden and Van Leemput for PS adsorption on silica were also obtained under Θ-conditions (cyclohexane, 35 °C) but at a higher concentration (2000 g/m^3; open triangles). For a comparison of our results on oxidized silicon with theirs on dispersed silica, we should therefore use our values at 500 g/m^3. Taking into account that Γ_f is still lower than the equilibrium level and that completely different techniques were used, the results compare quite favorably.

6. Effect of a Displacer. In order to decrease the adsorption energy of PS, we decided to use a displacer. Van der Beek et al.[16–19] showed that the effective segmental adsorption energy of a polymer can be varied in a quantitative manner by the use of mixed solvents, one of which is a displacer of the polymer. As the displacing solvent, ethyl acetate was chosen, which is a strong displacer of PS.[19] Consequently, only small amounts are needed to decrease the adsorption energy. Therefore, we do not expect a large influence of ethyl acetate on the hydrodynamic conditions and the optical calibration.

In Figure 10 the effect of the weight fraction w_{eth} of ethyl acetate in decalin solutions on the final adsorbed amount of PS is given for M = 20000K. As expected, the adsorbed amount decreases with increasing concentration of the displacer. The shape of the curve is in good agreement with the experimental results of Van der Beek[18] and with equilibrium calculations using the Scheutjens–Fleer theory.[16] An extrapolation of the experimental data to zero adsorbed amount gives the so-called critical displacer concentration w_{eth}^{cr} of ethyl acetate. We find w_{eth}^{cr} = 0.11. Unfortunately, this is not sufficient information to calculate the segmental adsorption energy χ_s (PS/decalin), since the adsorption energy of ethyl acetate from decalin and the solvency parameters are not known. Van der Beek found for χ_s (PS/cyclohexane) a value of 1.9.[18] We expect that χ_s (PS/decalin) is more or less the same, since these solvents are chemically quite similar,

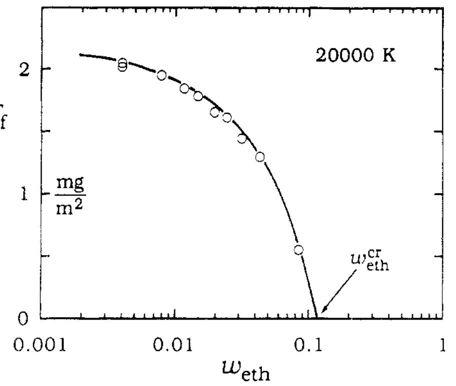

Figure 10. Final adsorbed amount of PS in solvent mixtures of decalin and ethyl acetate as a function of the weight fraction w_{eth} of ethyl acetate. From the intercept with the abscissa the critical ethyl acetate fraction w_{eth}^{cr} is determined to be 0.11. Polymer concentration 50 g/m³.

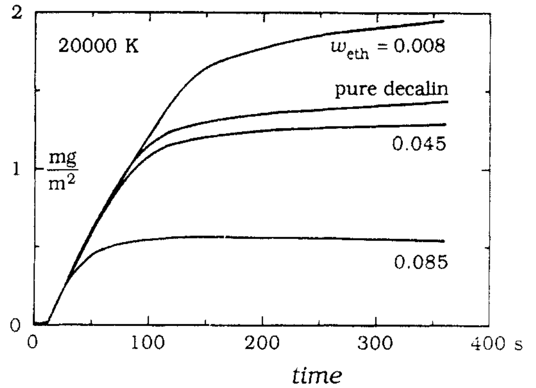

Figure 11. Effect of a low molecular weight, strong displacer on the adsorption kinetics of PS. The weight fraction w_{eth} of the displacer ethyl acetate in solvent mixtures of ethyl acetate and decalin is indicated. Polymer concentration 50 g/m³.

and the interaction with the silica surface is very weak for both. (A remarkable difference exists between w_{eth}^{cr} in decalin and that in carbon tetrachloride. We find in decalin w_{eth}^{cr} = 0.11, whereas Van der Beek et al. give for CCl_4 w_{eth}^{cr} = 0.017.[19] According to displacement theory, for not too low values of χ_s (polymer/solvent) any differences in w^{cr} between two solvents are entirely due to the solvency parameters between solvent and polymer or displacer, respectively.[16] Using this theory we calculated that approximately χ(ethyl acetate/decalin) − χ(ethyl acetate/carbon tetrachloride) $\cong$ −2. A similar effect of the solvent on w^{cr} of strong displacers was reported by Kawaguchi.[29] Kawaguchi found for w^{cr} of acetone displacing PS from silica a value of 0.11 in cyclohexane and 0.017 in carbon tetrachloride. For dioxane an even larger difference was found. We conclude that solvency effects between strong displacers and the solvent may have a large effect on the critical displacer concentration.)

Figure 11 shows the effect of ethyl acetate on the adsorption kinetics for M = 20000K for four weight fractions of ethyl acetate. Before injecting the polymer, mixed solvent was flushed through the cell. At t = 0 the injection of polymer solution starts. The initial slope is the same in all solvents, regardless of the concentration of ethyl acetate. As discussed already for n-hexadecane, this implies that the addition of ethyl acetate does not affect the optical calibration and thus dn/dc of the polymer. This, in turn, is an indication that ethyl acetate is not (strongly) associated to PS, since that would probably lead to a change in the optical properties. In the final adsorbed amount Γ_f a peculiar irregularity occurs: the first addition of ethyl acetate leads to a considerable *increase* in Γ_f as compared to pure decalin. Each further increase of w_{eth} leads to a decrease in Γ_f, which can be explained by a decrease of the adsorption energy. We suggest that the initial increase is due to a rather nonideal mixing of ethyl acetate with decalin, in combination with preferential solvation of PS by ethyl acetate, which effectively makes decalin a worse solvent for PS.

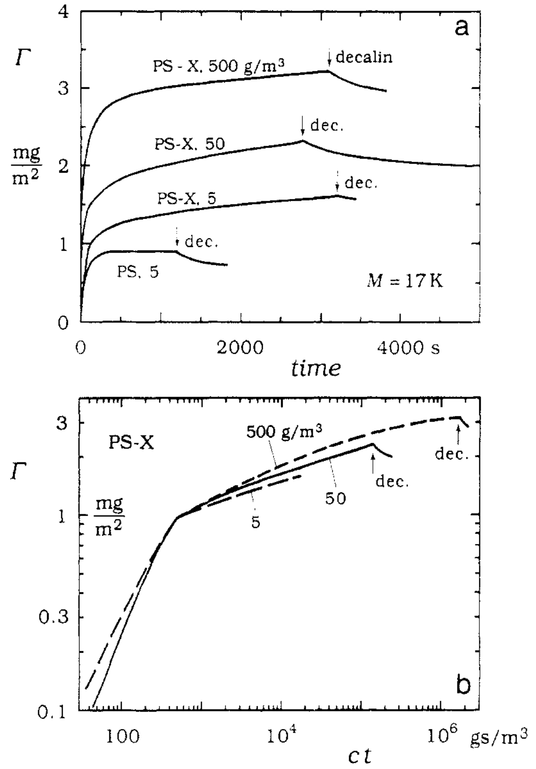

Figure 12. (a and b) Comparison of the adsorption kinetics of polystyrene with alkane and an iminium ion end group (PS, and PS-X, respectively) and the effect of the concentration c on the adsorption of PS-X. In a the experiments are given as $\Gamma(t)$, whereas in b the same curves for PS-X are replotted as $\Gamma(ct)$, now double logarithmically. The curves in a suggest that the saturated value of Γ is strongly concentration dependent. However, b shows that the adsorption proceeds in the same direction for different concentrations (see also text).

As to the kinetics, an important observation can be made. The displacer mainly affects the extension of the transport-limited region. For w_{eth} = 0.008 the adsorption rate is transport-limited up to $\Gamma \approx$ 1.5 mg/m², whereas for w_{eth} = 0.085 the adsorption rate is close to zero already at Γ = 0.5 mg/m². The region of transition from mass-transfer limitation to saturation is more or less congruent for all curves. Since attachment is rate-limiting in this part of the curve, the results suggest that the rate of the attachment step is mainly determined by the degree of undersaturation and not so much by the amount already adsorbed.

7. Polystyrene with a Polar End Group. In this section we consider the effect of a polar end group on the adsorption of a low molar mass polystyrene (M = 17K). The polymer chain contains now at one end a single iminium ion end group. Such a polymer will have a tendency to attach strongly through this end group, thereby eventually displacing adsorbed PS segments. If such displacement goes to completion, a brush results.[30]

In Figure 12a the adsorbed amount of such an end-capped polymer (PS-X) is plotted as a function of time and the results are compared with those for normal polystyrene (PS). First, we compare the adsorption of PS-X and PS for c = 5 g/m³. For PS the adsorbed amount reaches after a short time a stable saturation value of about 0.9 mg/m^2. For PS-X, the adsorbed amount at the end of the experiment is much higher, around 1.5 mg/m^2. This is not yet a saturation value, since Γ continues to increase slowly. The reason for the enhanced adsorption must be the strong binding of the iminium ion end group to the silica; i.e., a brushlike structure (with, typically, a high adsorbed amount) begins to form. The extra adsorption due to the end group proceeds at a rate which is initially mainly governed by mass transfer from the bulk solution (compare initial sections in Figure 12b) and later on by a much slower adsorption process. The effect of the iminium ion end group is, to some extent, comparable to that of an increase of the chain length (cf. Figure 3). When solvent is injected into the cell (indicated by the arrow in Figure 12a), some desorption takes place in all cases. This probably reflects that chains are not very strongly bound to the surface due to the rather low molecular weight (17K).

Two more experiments at a higher concentration are included in Figure 12a. Comparing the data, it might seem that, in the plateau region, $\mathrm{d}\Gamma/\mathrm{d}t$ is low and not so much different for the three concentrations of PS-X. From this it might be concluded erroneously that the leveling off corresponds to near-saturation and that thus the adsorption isotherm $\Gamma(c)$ strongly increases with c. This is not so. In order to see this more clearly, we replotted in Figure 12b the curves of PS-X, but now Γ is given as a function of the product ct of concentration and time, on a double-logarithmic scale. These curves for the three concentrations more or less coincide, like the curves $\Gamma(ct)$ in Figure 4 for PS of molar mass 3040K. This implies that also the adsorption rate of PS-X can be described by a combination of mass transfer and an attachment step with a rate proportional to the concentration. The results in Figure 12b suggest that the adsorption for different concentrations proceeds in the same direction almost along a kind of master curve, at a rate proportional to c. Thus, the reason why the adsorbed amounts in Figure 12a show a strong concentration dependence is only that the end points of the experiments lie far apart on the concentration–time scale of the master curve. It could well be that the equilibrium values of Γ are hardly dependent on concentration, as predicted by polymer adsorption theory, but the lower the concentration, the longer it takes to attain them. We conclude that the concentration dependence of Γ_f in Figure 12a is kinetically determined and that the observed values of Γ_f of PS-X correspond to situations away from equilibrium, especially for the two lower concentrations.

Discussion

A picture of the adsorption process should take into account the following experimental findings:

(i) The adsorption rate is proportional to the solution concentration for every Γ (Figures 4 and 12b). An effect of the age of the adsorbed layer on $\mathrm{d}\Gamma/\mathrm{d}t$ is not observed.

(ii) The extent of the initial regime, where $\mathrm{d}\Gamma/\mathrm{d}t$ is constant and equal to the maximum mass-transfer rate increases with (i) increasing chain length (Figure 3), (ii) decreasing solvent quality (Figure 9), and (iii) increasing adsorption energy (Figure 11).

(iii) The dependence of the final adsorbed amount on chain length, solvent quality, and adsorption energy is at least qualitatively in agreement with equilibrium polymer adsorption theory.

Check of Local Equilibrium. In the discussion so far, the rounded shape of the adsorption curve $\Gamma(t)$ at higher coverage has been attributed to the influence of the attachment process on the adsorption rate. However, since the final adsorbed amounts are in qualitative agreement with equilibrium and because the maximum mass transfer is to a large extent rate-limiting, the question arises whether the adsorption curves $\Gamma(t)$ can be described using the local equilibrium concept discussed in ref 2. Therefore, we first check the applicability of this concept.

According to the concept of local equilibrium, the adsorption rate is limited by mass transfer and, for a stagnation point flow, described by eq 1. The concept amounts to the assumption that in eq 1 the surface concentration c_s is determined by equilibrium between the adsorbed layer and directly adjacent solution and can thus be described by the adsorption isotherm of the polymer. The bulk concentration c_b is that of the solution which is injected, and only at saturation, when there is full equilibrium between the bulk solution and the surface, c_b equals c_s. As long as c_s is smaller than c_b there is a flux of polymer toward the surface, and the adsorption increases. Due to the high affinity of a polymer adsorption isotherm c_s is very low almost up to saturation and thus negligibly small as compared to c_b. Consequently, according to eq 1 the adsorption rate should be constant and equal to kc_b until close to saturation and then fall abruptly to zero at saturation. Polymer adsorption isotherms calculated with the theory of Scheutjens and Fleer are under nearly all conditions of the high-affinity type, except for very short chains consisting of only a few tens of segments or for χ_s very near to its critical value. Therefore, on the basis of theory we expect a *constant* adsorption rate until saturation is almost reached. This is in contrast with our experimental adsorption curves for PS, which under all conditions have a clearly rounded shape.

The existence of local equilibrium can be tested using experimental results only, by comparing adsorption isotherms obtained under static and dynamic circumstances. For the "static" isotherm we use values of Γ_f obtained at different concentrations. The "dynamic" isotherm is calculated from an adsorption curve $\Gamma(t)$, assuming local equilibrium during the adsorption process; i.e., Γ should be determined by c_s according to the isotherm of the polymer, and we call $\Gamma(c_s)$ the dynamic adsorption isotherm.

The concentration c_s during adsorption can be obtained from eq 1, which describes the flux J ($=\mathrm{d}\Gamma/\mathrm{d}t$) of polymer to the surface. The transport coefficient k in this equation can be determination from the initial adsorption rate according to $k = (\mathrm{d}\Gamma/\mathrm{d}t)_0/c_b$ (see Initial Adsorption Rate). Substituting this expression for k in eq 1, we obtain

$$c_s = c_b\left\{1 - \frac{\mathrm{d}\Gamma/\mathrm{d}t}{(\mathrm{d}\Gamma/\mathrm{d}t)_0}\right\} \qquad (6)$$

With eq 6 c_s can be determined from an adsorption curve $\Gamma(t)$ at any moment during adsorption, and from this, a dynamic adsorption isotherm $\Gamma(c_s)$ is constructed.

Static and calculated dynamic adsorption isotherms are given in Figure 13 for M = 3040K. The static isotherm $\Gamma_f(c)$ is of the high-affinity type, as expected for a high-molar-mass polymer. The dynamic isotherm $\Gamma(c_s)$ has a rounded shape and gives lower values of Γ. If there had been local equilibrium during adsorption, both isotherms should have been identical. However, this is clearly not the case, and thus local equilibrium is not strictly maintained during adsorption. This is the same conclusion that we reached before on the basis of theoretical adsorption isotherms.

Attachment of a Chain to the Surface. Since local equilibrium cannot explain the rounded shape of the curve

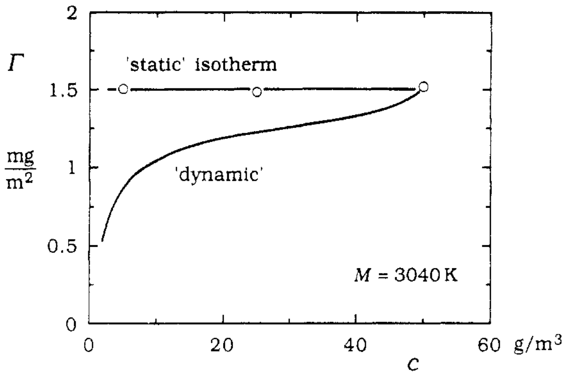

Figure 13. Experimental check of the existence of local equilibrium during adsorption of PS by comparison of static and dynamic adsorption isotherms. The static isotherm is given by the final adsorbed amount at different concentrations. The dynamic isotherm is calculated from a curve $\Gamma(t)$ under the assumption of local equilibrium. Since both isotherms do not coincide, there is no local equilibrium.

$\Gamma(t)$, we now elaborate the idea that the attachment of a chain to the surface is rate-limiting at higher coverage. According to the analysis given above (eq 4), an attachment rate constant $K(\Gamma)$ which only depends on the adsorbed amount and not on mass-transfer conditions can be extracted from the observed adsorption rate.

A strong argument in favor of the idea of an attachment step is the finding that the adsorption rate is at any Γ proportional to the solution concentration and thus to the rate at which collisions occur between free chains and the surface with an adsorbed layer. We imagine that these collisions occur by thermal motions and that they lead to adsorption with a certain probability between zero and unity, depending on the conditions. As long as successful collisions occur at a rate high enough to keep the surface concentration c_s of free molecules low as compared to the bulk concentration c_b, the mass transfer is entirely rate-limiting in the adsorption process. When successful collisions occur less frequently, $d\Gamma/dt$ decreases and a finite concentration c_s develops. The mass-transfer rate then becomes smaller as the concentration gradient between the surface and the bulk solution decreases. The question is now, by which favors is the adsorption probability during a collision determined, or, equivalently, which factors determine $K(\Gamma)$?

Most of the experimental results suggest that the adsorption of PS is not too far from equilibrium. In a saturated layer the dependencies of the final adsorbed amount Γ_f on M, χ, and χ_s are in qualitative agreement with predictions of equilibrium theory, suggesting that Γ_f is determined by equilibrium, and thus by energetic and entropic factors. Moreover, the duration of the initial adsorption regime is directly affected by two energetic factors, namely, solvent quality and adsorption energy. We therefore consider it to be plausible that the adsorption probability during initial adsorption and also at higher coverage can be described using energetic and entropic arguments.

Before we do this, we first briefly recall the factors that in equilibrium contribute to the free energy of exchange of a polymer chain in solution against solvent molecules at the interface. The free energy of exchange is composed of the following terms:

(a) Adsorption energy, expressed by χ_s. Usually χ_s is on the order of one or a few kT per segment. Since long chains may be attached by hundreds or even thousands of segments, the adsorption energy per chain may be very high.

(b) Mixing energy, expressed by χ. For athermal solvents ($\chi = 0$) this term is zero. For $\chi > 0$ demixing is energetically favored.

(c) Loss of conformational entropy of the polymer chain, due to reduced orientational freedom at the surface.

(d) Mixing entropy; the demixing due to the segregation of a concentrated surface phase from a dilute, homogeneous polymer solution leads to an entropy loss. Alternatively, this can be seen as an osmotic pressure in the adsorbed layer.

Usually, polymer adsorption is favored by the energetic terms and opposed by the entropic factors. In equilibrium their sum is zero.

Now we discuss the attachment of a free chain in terms of energetic and entropic arguments. For a polymer molecule approaching a bare surface there is no barrier to actually reach the surface. The formation of new polymer–surface contacts, the unfolding of the coil, and the concomitant formation of a concentrated surface phase are practically simultaneous processes. We therefore expect that the free energy decreases continuously during adsorption on a bare surface. As a result, each collision between a free chain and a bare surface leads to adsorption, and the adsorption probability equals unity.

For adsorption on a surface covered already with a polymer layer a balance between repulsive and attractive forces during a collision determines whether or not adsorption occurs. On approach of a chain toward a surface with an adsorbed layer, a repulsive osmotic pressure builds up due to overlap and penetration by the incoming molecule. This may be accompanied by entropy loss due to chain deformation. On the other side of the balance is the gain in adsorption energy due to the formation of new polymer–surface contacts. If during the collision this gain of adsorption energy is not high enough, then the chain is quickly expelled by the force of the entropic terms. If the initial contact is successful, then the newly adsorbed chain will try to attain an equilibrium conformation with more segments adsorbed. This process involves partial displacement of surrounding adsorbed molecules. Experiments reported by Granick and co-workers have shown that displacement of normal (hydrogenated) polystyrene chains by deuterated ones is a slow process.[31] We therefore suggest that the time needed to reach conformational equilibrium in an adsorbed polystyrene layer may be rather long.

During a collision of a free chain with a surface, the gain in adsorption energy is proportional to the number of surface contacts made by the incoming chain and the adsorption energy per contact. New contacts can be made by occupying free sites or by displacing adsorbed segments of surrounding molecules. If displacement is a slow process, this displacement is less important. An increase of the segmental adsorption χ_s leads to stronger attraction and thus to a higher adsorption probability. Consequently, $d\Gamma/dt$ increases. This is consistent with the experimentally observed increased duration of the mass-transfer-limited region with increasing χ_s. We can also imagine that the gain in adsorption energy increases with chain length, since for long chains more free sites are available than for shorter ones. Consequently, the adsorption probability and $d\Gamma/dt$ increase with chain length. Again, this is consistent with the experimental results for different molar masses.

The effect of a gain in adsorption energy is opposed by the repulsive barrier formed by the adsorbed layer. This barrier mainly consists of two contributions: demixing of polymer and solvent, resulting in entropy loss and energy gain, and chain deformation, leading to entropy loss. With decreasing solvent quality, the energy gain increases, so that the barrier becomes less repulsive and an incoming chain obtains more opportunities to form surface contacts. Therefore, the adsorption probability during a collision increases with decreasing solvent quality. Accordingly, $d\Gamma/dt$ should increase. Experimentally, an increased duration of the mass-transfer-limited region is indeed observed upon a decrease of the solvent quality.

In general, we would expect that with increasing the adsorbed amount the repulsive barrier formed by the adsorbed layer increases and that the gain in adsorption energy upon initial contact decreases. As a result, the adsorption probability and thus $d\Gamma/dt$ should decrease with increasing coverage. This is indeed observed under all conditions and for all molar masses. The decrease in $d\Gamma/dt$ can be quantitatively described by the attachment rate constant $K(\Gamma)$. Figure 5 shows for M = 3040K that $K(\Gamma)$ decreases strongly from 10^{-5} m/s at low coverage (0.5 mg/m^2) to 10^{-9} m/s at 1.5 mg/m^2, which is probably close to saturation. The decrease in $K(\Gamma)$ with increasing Γ reflects the decreasing adsorption probability. Unfortunately, we are not yet able to establish a direct, quantitative relation between $K(\Gamma)$ and the adsorption probability.

Comparison with Other Results. As already pointed out in the introduction, systematic studies on the kinetics of adsorption of polystyrene have not been published before. Therefore, a comparison is hardly possible and we only discuss the results of Lee and Fuller,[32] which seem to be in agreement with the presence of an attachment step as found here.

Lee and Fuller[32] studied the effect of flow on the adsorption and desorption kinetics of polystyrene. The authors observed that for high M (>40000K) both $d\Gamma/dt$ and Γ_f decrease with increasing shear rate $\dot{\gamma}$. The inhibiting effect increases with chain length and for M = 20000K it starts at $\dot{\gamma} \approx 400$ s^{-1}. The concentration ($\approx$1000 g/m^3) was high enough to ensure that transport could nowhere be rate-limiting. These results suggest that the flow field reduces the adsorption probability during a collision with the surface. For adsorbed layers formed in rest ($\dot{\gamma}$ = 0) during 24 h, a considerable, flow-induced desorption occurred but at much higher values of $\dot{\gamma}$ (> 5000 s^{-1}) than needed for flow-inhibited adsorption. From this it was concluded that a polystyrene molecule adsorbs initially by a few segment–surface contacts and that in an equilibrated layer much more segments are adsorbed. Our view of the adsorption process goes in the same direction.

Conclusions

The kinetics of adsorption and desorption of polystyrene from decalin solutions onto silica were studied by reflectometry in a stagnation point flow. It was found that for all molar masses studied (3K < M < 20000K) the initial adsorption rate is entirely determined by mass transfer from the bulk solution. Between the initial, mass-transfer-limited part of the adsorption curve and saturation the adsorption rate $d\Gamma/dt$ decreases gradually, due to the buildup of the adsorbed layer. For the whole adsorption curve, $d\Gamma/dt$ is proportional to the solution concentration. For the initial part this reflects the mass-transfer limitation. At higher coverage, it implies that the attachment of a chain to the surface affects the adsorption rate. By an analysis of the adsorption curve we were able to extract an attachment rate constant $K(\Gamma)$, that depends only on the adsorbed amount and not on mass-transfer conditions. The chain length dependence of the final adsorbed amount indicates that decalin at 22 °C is (near to) a Θ-solvent for PS. This is confirmed by cloud-point measurements, from which we determined that $\Theta \approx 16$ °C.

The influence of the addition of *n*-hexadecane (a nonsolvent for PS) and ethyl acetate (a strong displacer of PS) on the final adsorbed amount shows that these additives decrease the solvent quality and adsorption energy, respectively.

Variation of the chain length, solvent quality, and adsorption energy mainly affects the extent of the mass-transfer-limited part of the adsorption curve; the shape and size of the transition region to saturation remain more or less the same. From this we infer that the rate of the attachment step is mainly determined by the degree of undersaturation and not so much by the value of the adsorbed amount. In our opinion these results are consistent with the following picture of the attachment process. During a collision between a free molecule and the surface with an adsorbed layer, the adsorption probability depends on a balance between the gain in adsorption energy and the repulsive interaction with the adsorbed layer. The gain in adsorption energy during a collision decreases when a displacer is added and increases with chain length since long chains can make more contacts. By a decrease of the solvent quality the repulsion by the adsorbed layer is reduced.

Desorption into a flow of pure solvent was only observed for low molar masses. The desorption rate was considerably lower than the one predicted for mass-transfer-limited desorption assuming local equilibrium near the surface. This result indicates that equilibration is slow.

It was found that a strongly adsorbing end group enhances adsorption. Most of the extra adsorption due to the end group takes place at a rate which is limited by the attachment to the surface.

Since the adsorption rate of polystyrene is proportional to solution concentration, the time needed to attain equilibrium is *inversely* proportional to concentration. For low c the equilibration time thus becomes extraordinarily long. In order to obtain an adsorption isotherm it is therefore advisable to determine the adsorbed amount at a fixed value of the product ct of concentration and time and not after a fixed time.

Acknowledgment. We thank Prof. K. Furusawa (Tsukuba, Japan) for providing us with the imine-end-capped polystyrene samples.

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