*Macromolecules* 1994, *27*, 3219–3228

# Competitive Adsorption Kinetics of Polymers Differing in Length Only

**J. C. Dijt, M. A. Cohen Stuart,* and G. J. Fleer**

*Laboratory for Physical and Colloid Chemistry, Wageningen Agricultural University, P.O. Box 8038, 6700 EK Wageningen, The Netherlands*

*Received November 22, 1993; Revised Manuscript Received February 28, 1994*[⊗]

ABSTRACT: We have investigated competitive adsorption between homopolymer chains of different lengths. Optical reflectometry was used to monitor adsorbed amounts as a function of time, and an impinging jet flow cell was used to control mass-transfer rates between the solution and the adsorbing surface. For poly(ethylene oxide) (PEO) adsorbing from water onto silica we found that exchange of short adsorbed polymers against longer ones in solution takes place *at constant coverage*, the total adsorbed amount being equal to the saturated level of the short component. This result agrees fully with predictions for an adsorbed layer of mixed composition which is in full equilibrium with its immediate surroundings. We infer from this that relaxation times of adsorbed layers of PEO are shorter than the time scale of the experiment (seconds). For polystyrene (PS) adsorbing from decalin onto silica we also observed exchange, but for this case the total adsorbed amount *increased* during exchange, indicating incomplete relaxation of the polymer layer. It was found that the excess adsorbed amount with respect to equilibrium depends on the history of the adsorbed layer and on the rate of arrival at the surface of displacing long chains. Moreover, desorption of this excess adsorbed amount could actually be observed when the supply of polymer from solution was interrupted. From the latter type of experiments we determined a relaxation time of 45 s for pure decalin, but faster relaxation occurred in toluene/decaline mixtures and in tetrachloromethane. We forward arguments to show that the relaxation in these mixed layers is due to *spreading* of the adsorbed long chains from a highly coiled to a flat conformation.

## Introduction

Polymer adsorption rates are determined to a large extent by transport through solution and attachment to the interface.[1] Reorganizations in the adsorbed polymer layer only play a role when saturation is approached, and studies of *ad*sorption kinetics do not easily give information on these. During polymer *exchange* there is not only adsorption but also desorption. The desorption is the result of a competition between chains in the adsorbed layer and can therefore possibly be used as a probe of the dynamics of the adsorbed polymer layer.

For polymers, the adsorption energy per molecule is usually very high due to the great number of segment–surface contacts. It is therefore extremely unlikely that desorption proceeds by simultaneous release of all anchored segments. More probable is a segment-by-segment displacement process. The competition at a segmental level might be seen as an elementary step in the exchange process. We expect that the rate of this step depends on the interactions between polymer, surface, and solvent. This displacement rate might also depend on the rate of conformational changes in the adsorbed layer and thus on the dynamic stiffness of the polymer chain.

The rate of conformational changes could also be reduced by topological constraints. Examples of such constraints are the intertwining of chains or the pinning of a molecule to the surface by loops of another chain. Disentanglement and, hence, desorption proceeds by slow diffusional motions of the adsorbed chain. Probably, the formation of entanglements proceeds also slowly. One may therefore expect that the number of entanglements increases with time, so that the desorption rate of a polymer decreases with the residence time on the surface. Granick and co-workers have obtained some evidence that such processes indeed play a role.[2,3] The effect of topological constraints on the exchange kinetics was shown to depend strongly on the chain length of the polymer.

In this study, we are concerned with exchange between free and adsorbed polymers, in the case where these polymers are chemically identical. The exchange of polymers of a different chemical nature is discussed elsewhere.[4]

The driving force for the exchange between chemically identical polymers from dilute solutions is the (small) increase in translational entropy in solution when short adsorbed chains are replaced by longer ones. At equilibrium, longer chains are therefore preferentially adsorbed over shorter ones. According to the results of the Scheutjens–Fleer theory complete preferential adsorption occurs as soon as the chains differ in length by a factor of about 2 or more.[5]

Experimentally, the exchange rate between chemically identical polymers is difficult to assess. Exchange between chains of equal length does not lead to any change at all in the adsorbed layer or solution. Here, the only method seems to use labeled polymers. Care should be taken, however, to ensure that the label itself does not influence the adsorption. Exchange between polymers of different length leads to a shift in adsorbed mass that might be measurable without using labeled material. For example, the adsorbed amount $\Gamma$ may increase if a layer of short chains is completely displaced by longer ones.

As yet, there are only a few experimental studies on polymer exchange kinetics. Pefferkorn et al. used radioactively labeled polymers to study the exchange between chains of equal length.[6,7] For polyacrylamide ($M$ = 1200K; K stands for kg/mol) it was found that the exchange is very slow indeed and still incomplete after 15 h.[6] Also for polystyrene ($M$ = 360K) adsorbed on silica from a carbon tetrachloride solution a slow exchange was observed.[7]

Granick and co-workers[3,8,9] have studied the exchange between protonated and deuterated samples of one and the same polymer. These could be distinguished by their infrared absorption spectra. Exchange of poly(methyl

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[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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methacrylate) ($M$ = 60K) was found to proceed extremely slowly, at a rate of about 1% of the mass adsorbed per hour.[8] For polystyrene ($M$ = 550K) adsorbed on silica from cyclohexane[3] and carbon tetrachloride,[9] it was found that the age of the preadsorbed polystyrene layer strongly affects the exchange kinetics. Effects of aging times up to tens of hours were observed. This is an indication that after the initial adsorption process slow rearrangements take place, possibly leading to entanglements.

Kawaguchi et al. studied displacement of adsorbed polystyrene of low molar mass (102K and 422K) by longer chains (775K) by means of ellipsometry.[10] After adding the higher molecular weight, the adsorbed amount first increased rapidly but attained a final level (after 50 h) well below that for individual adsorption of $M$ = 775K. In view of the small chain-length difference, this may reflect an equilibrium situation of incomplete exchange. However, a kinetic barrier could also explain the result.

The data in the literature suggest that exchange between chemically identical polymers is often a slow process. Some results indicate the formation of entanglements on the time scale of hours. However, the exchange mechanism and factors influencing it are so far at best only partly understood.

We decided to focus on the displacement of low ($\approx$10K) by high molecular weight samples (>100K) and to rely mainly on a reflectometric technique that has proven to be most appropriate for adsorption studies[1,11] As polymers we chose poly(ethylene oxide) (PEO) and polystyrene (PS), for which polymers we also have studied the adsorption kinetics.[1,12] Due to the large chain-length difference, the adsorbed amount $\Gamma$ increases considerably upon exchange, and reflectometry measurements can monitor the exchange accurately. The experimental results will be compared to a theoretical prediction which is based on the assumption that the adsorption rate is limited by mass transfer and that near the surface a (local) equilibrium exists between free and adsorbed chains.

## Exchange According to Local Equilibrium

Recently, Dijt et al. introduced the concept of local equilibrium in order to predict polymer adsorption and desorption rates in cases where the equilibration of the adsorbed polymer layer is faster than the mass transfer through solution. The central idea is that polymer on the surface is continuously in equilibrium with free polymer of concentration $c_s$ in the immediate vicinity of the surface and that the mass transfer between the bulk solution and the surface region is the rate-controlling step in the adsorption or desorption process.[13]

In the present section we apply this concept to the exchange of polymers. In order to be able to do this, we must first discuss equilibrium adsorption for the case of a bimodal mixture of chain lengths. Let us denote the shorter and longer chains in the mixture by 1 and 2 and their lengths by $r_1$ and $r_2$, respectively. A theoretical adsorption isotherm for the case $r_1$ = 100 and $r_2$ = 1000 is given in Figure 1. The total adsorbed amount $\Gamma_t$ (full curve), and the contributions of 1 (dotted) and 2 (dashed) to $\Gamma_t$ are given as a function of the concentration $c_2$, for a fixed value of $c_1$ equal to 1 ppm. Note the logarithmic scaling of the abscissa. The isotherm was calculated with the theory of Scheutjens and Fleer,[14] extended to polymer mixtures.

With respect to surface composition, the isotherm can be roughly divided into three regions: 1 only ($c_2 < 10^{-50}$ ppm), 1 and 2 ($10^{-50} < c_2 < 10^{-30}$ ppm), and exclusively 2 ($c_2 > 10^{-30}$ ppm). The region of mixed surface composition is situated at extraordinarily low values of $c_2$. This reflects the strong preferential adsorption of longer chains. In practice, the preference is so high that mixed layers can only exist as long as there are not enough long chains to fill the surface, e.g., because they have not (yet) been supplied.

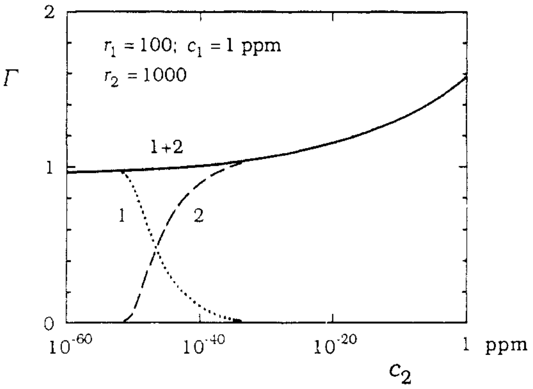

**Figure 1.** Theoretical adsorption isotherm from a solution containing a bimodal mixture of chain lengths. The chain lengths $r_1$ and $r_2$ are indicated and the concentration of 1 has a fixed value of 1 ppm. The isotherm was calculated with the theory of Scheutjens and Fleer. The adsorbed amount $\Gamma$ is given in equivalent monolayers. The bulk volume fraction as given by the theoretical model was converted to ppm (=g/m$^3$) using a specific volume of $10^{-6}$ m$^3$/g. Segmental adsorption energy $\chi_s$ = 1.0, solvency parameter $\chi$ = 0.5, cubic lattice.

The region of mixed surface composition has another important characteristic. The total adsorbed amount $\Gamma_t$ is approximately constant and about equal to $\Gamma_1$ in the absence of 2 ($c_2 < 10^{-50}$ ppm). In other words, adsorption of a certain amount (mass) of 2 is accompanied by desorption of an equal amount of 1.

In order to arrive at a kinetic picture, we now consider the mass transfer during exchange. The steady-state flux $J$ of polymer is proportional to the concentration difference $c^b - c^s$, where $c^b$ and $c^s$ are the polymer concentrations in the bulk solution and surface region, respectively:[13]

$$J = k(c^b - c^s) \tag{1}$$

In this equation, $k$ is a transport coefficient that depends on the hydrodynamics of the flow system and on the diffusion coefficient of the polymer.[15] By way of illustration we discuss the exchange kinetics according to the adsorption isotherm in Figure 1. Imagine the following experiment. First an adsorbed layer of 1 is equilibrated with a solution of concentration $c_1$ = 1 ppm ($c_2 < 10^{-50}$ ppm in Figure 1). Since $c_1$ is uniform throughout the solution, we have $c_1^b = c_1^s = c_1$. Next, a solution of a mixture of 1 + 2 is injected, where the value of $c_1^b$ is the same as before (i.e., 1 ppm) in order to avoid desorption of 1 by dilution. For the solution concentration $c_2^b$ we choose also 1 ppm, which is the highest value in the isotherm of Figure 1.

According to eq 1 the adsorption rate of 2 equals $k$ ($c_2^b - c_2^s$). The value of $c_2^b$ remains constant at 1 ppm during the experiment, since continuously fresh solution is injected. We now assume that during adsorption of 2 the concentration $c_2^s$ is determined by a local equilibrium near the surface between free and adsorbed molecules, which is described by the adsorption isotherm of the polymer. Hence, $c_2^s$ equals $c_2$ according to the isotherm of Figure 1. Inspection of Figure 1 shows that $c_2^s \ll c_2^b$ for $\Gamma$ nearly up to its final value for $c_2^s$ = 1 ppm, at which value of $c_2^s$ there is full equilibrium between the adsorbed layer

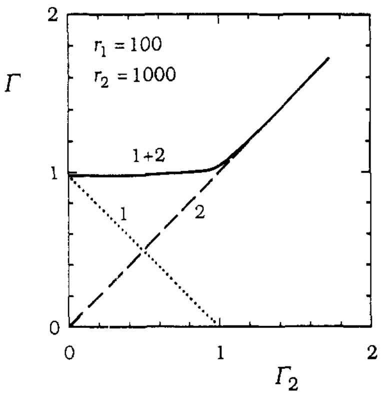

**Figure 2.** Equilibrium composition of mixed adsorbed layers and exchange kinetics according to the local equilibrium concept. The adsorbed amounts $\Gamma_1$, $\Gamma_2$, and $\Gamma_t = \Gamma_1 + \Gamma_2$ are plotted as a function of $\Gamma_2$ according to the isotherm of Figure 1. For an explanation, see the text.

and the bulk solution. Hence, we can ignore $c_2^s$ during adsorption and obtain directly $J \approx d\Gamma_2/dt \approx kc_2^b$. The adsorption rate of 2 is constant nearly up to saturation, and it equals the *maximum* mass-transfer rate from the solution. The adsorption rate of 2 is not influenced by the adsorption of 1.

The scenario is shown in a different way in Figure 2. In this figure the isotherm values $\Gamma_1$, $\Gamma_2$, and $\Gamma_1 + \Gamma_2$ of Figure 1 are replotted but now as a function of $\Gamma_2$ instead of $c_2$. The graph can be interpreted both in terms of equilibrium and in terms of kinetics. According to the equilibrium picture, it shows the equilibrium surface composition of 1 and 2. In the range of mixed composition, the total adsorbed amount is constant (full curve).

The kinetic representation is as follows. According to the mass-transfer limit, we have $d\Gamma_2/dt = kc_2^b$. Since this adsorption rate is constant nearly up to saturation, integration immediately yields $\Gamma_2 = kc_2^bt$. Thus, replacing $\Gamma_2$ by $kc_2^bt$ transforms the abscissa into a (scaled) time axis. The full curve then represents the total adsorbed amount during exchange of 1 by 2, which is constant in time. The dotted and dashed curves give the adsorbed amounts of 1 (nearly linearly decreasing in time) and 2 (linearly increasing), respectively. Diagrams like Figure 2 will be used for the interpretation of experimental results.

## Experimental Section

**Materials and Methods.** Monodisperse samples of PS (9K and 3040K) and PEO (7K, 105K, 400K, and 847K) were purchased from Polymer Laboratories and used without further purification. PEO was dissolved in deionized water. PS was dissolved in decalin (Merck; for synthesis, with a cis/trans ratio of 30/70), that had been dried over a zeolite column, and stored over anhydrous $CaCl_2$. Toluene (Baker analyzed) and carbon tetrachloride (Merck p.a.) were used without further purification.

Adsorbed amounts as a function of time were determined with a specially designed reflectometer, equipped with an impinging jet flow cell.[1] As the substrate we used strips of silicon wafers which had been oxidized in order to produce a thin dielectric film of $SiO_2$. This film not only serves as the adsorbent but also is an essential optical element that determines the sensitivity and linearity of the measured signal with respect to the adsorbed amount.[11] For all solvents, the sensitivity was calibrated as described earlier.[11] For PS in decalin and decalin/toluene mixtures, the sensitivity was found to be 0.0174 m$^2$/mg; for $CCl_4$ we obtained 0.0217 m$^2$/mg;[12] the angle of incidence was 60° in these solvents. For PEO solutions in water we calculated $A_s$ = 0.0232 m$^2$/mg at an angle of incidence of 70°.

Streaming potential measurements in $10^{-3}$ M NaCl were carried out on single glass capillaries into which polymer solution was injected. The setup has been described elsewhere.[3]

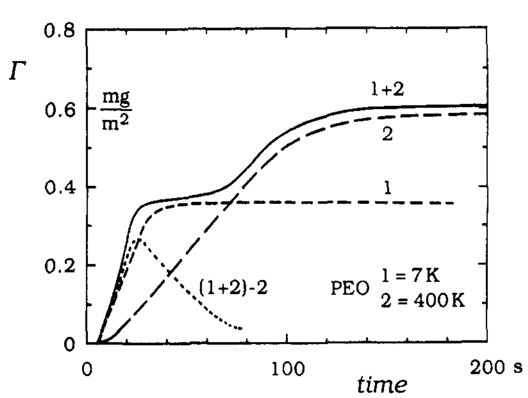

**Figure 3.** Exchange kinetics of PEO for adsorption from aqueous solution on silica. Experimental results are given for adsorption from a solution of 1 + 2 (full curve) and 1 or 2 individually (dashed). The dotted curve is the difference of the curves 1 + 2 and 2. The notation "1 + 2" is an abbreviation for "simultaneous addition of 1 and 2". Concentrations: $c_1^b$ = 5.0 g/m$^3$ and $c_2^b$ = 10 g/m$^3$.

## Results

**1. Poly(ethylene oxide).** In Figure 3 an example of the exchange kinetics of PEO is given. The adsorbed amount as a function of time is plotted for injection of a solution of pure 1 or 2 (dashed curves) and for a mixture of 1 + 2 (full curve). The molar masses of 1 and 2 were 7.1K and 400K, respectively. The difference $\Gamma_{1+2} - \Gamma_2$ is presented as the dotted curve.

At $t = 0$ the injection of polymer solution starts. The adsorbed amount remains zero for a few seconds, due to the dead volume between the valve and surface. For the individual adsorption of 1 and 2 (dashed curves) the adsorption rate is constant nearly up to saturation. It has been shown before[1,12] that this rate is entirely determined by the *maximum* mass transfer $kc_b$ from the bulk solution toward the surface.

In the curve for the mixture (1 + 2) we can distinguish three regions. In the initial part ($t < 30$ s), the overall adsorption rate $d\Gamma/dt$ for the mixture is virtually equal to the sum of the individual adsorption rates of 1 and 2. This implies that 1 and 2 adsorb independently, at a rate limited by mass transfer from the bulk solution. In the middle section ($30 < t < 70$ s), Γ remains constant at a level that corresponds to the saturated value for adsorption of 1. In the final region ($t > 70$ s), the curves $\Gamma(t)$ for injection of the mixture (1 + 2) and of pure 2 nearly coincide. From this we infer that no molecules 1 are left on the surface. Furthermore, we conclude that the adsorption of 2 from the mixture proceeds exactly like individual adsorption of 2. This means that the rate of adsorption of 2 from a mixed solution of 1 + 2 is given by the maximum mass transfer and that adsorbed 1 does not affect this rate at all.

The above analysis implies that the adsorption of 1 from the mixture is given by the difference $\Gamma_{1+2} - \Gamma_2$ (dotted curve). From Figure 3 it becomes clear that in the range $30 < t < 70$ s molecules 1 are displaced by 2 at a constant total mass adsorbed. We may compare Figure 3 for $t >$ 30 s with Figure 2 in which the expected exchange under conditions of local equilibrium is plotted. In all respects the exchange kinetics of PEO is in agreement with the theoretical prediction. The adsorption of 2 is limited by the maximum mass transfer from solution, and during exchange of 1 by 2 the total adsorbed amount $\Gamma_t$ remains constant at the level that is observed for pure component 1.

In the above experiment the molar mass of the displaced chain (1) is rather low, 7.1K. It would be interesting to

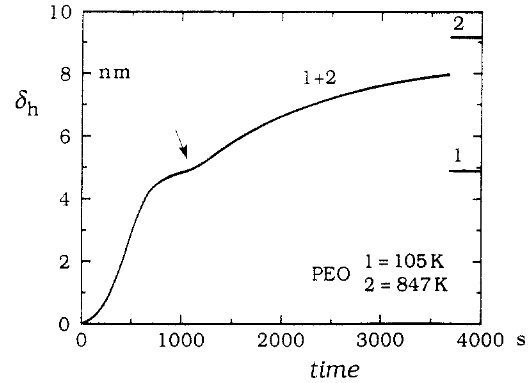

**Figure 4.** Exchange kinetics of high molar mass PEO in a streaming potential experiment. Along the ordinate the hydrodynamic thickness $\delta_h$ is plotted. To the right the saturated levels of 1 and 2 individually are indicated. Concentrations: $c_1^b = c_2^b = 0.50$ g/m$^3$.

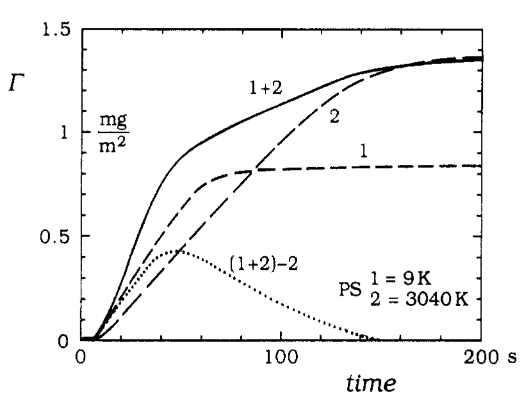

**Figure 5.** Exchange kinetics for adsorption of PS from decalin solutions on silica. The setup of the experiment is the same as in Figure 3. Concentrations: $c_1^b = 5.0$ g/m$^3$ and $c_2^b = 25$ g/m$^3$.

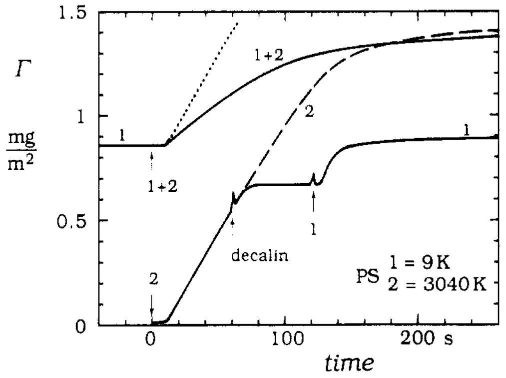

**Figure 6.** Sequential adsorption experiments with PS. The type of solution injected is indicated. The slope of the dotted line is drawn according to adsorption of 2 on a bare surface. Same molar masses and concentrations as for Figure 5. For an explanation, see the text.

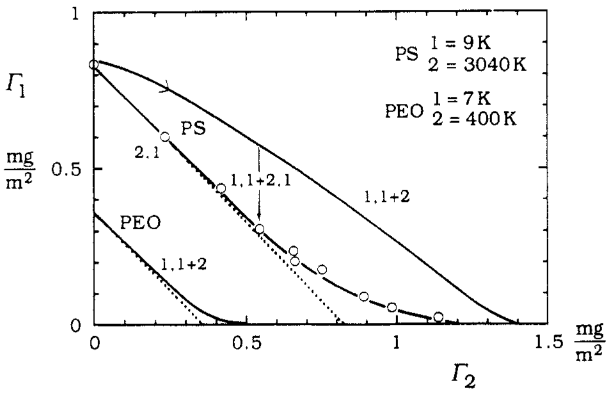

**Figure 7.** Overshoot adsorption of PS during exchange. The graph shows the composition $\Gamma_1(\Gamma_2)$ of the adsorbed layer under static (2,1) and dynamic conditions (1,1+2). Here 2,1 stands for "first 2 and then 1". The composition is derived from sequential adsorption experiments like in Figure 6. For comparison, a result for PEO in water is also included. The dotted lines are drawn according to exchange of 1 by 2 at constant total mass adsorbed. The vertical arrow represents relaxation experiments of the type 1,1+2,1 as given in Figure 8. Molar masses and concentrations of PS and PEO are the same as in Figures 5 and 3, respectively.

know whether for a longer chain the exchange kinetics is still the same. However, with increasing length of 1 the difference between the saturated values of $\Gamma_1$ and $\Gamma_2$ soon becomes too small for an accurate measurement. For long chains, the hydrodynamic thickness $\delta_h$ is a more suitable quantity, since its value at saturation strongly depends on the chain length at high molar mass.[13] For uncharged polymers like PEO $\delta_h$ can be obtained from the streaming potential.

The result $\delta_h(t)$ of a streaming potential experiment with a mixture of 100K and 847K is plotted in Figure 4. These chain lengths differ by factors of about 10 and 2, respectively, from those in the reflectometry experiment of Figure 3. The saturated levels of $\delta_h$ for pure 1 and 2 are indicated on the right-hand axis.

The overall shape of the curve $\delta_h(t)$ resembles that of $\Gamma(t)$ for the mixture in Figure 3. The arrow in Figure 4 points to a part of the curve where $\delta_h$ is at a nearly constant level that corresponds to saturation of 1. Probably, in this part 1 is exchanged by 2 at a constant total mass adsorbed. A complicating feature is that the rate of transport, and, hence, the surface composition in the capillary, is not uniform along its length, so that the streaming potential yields an average value of $\delta_h$. This tends to smoothen the curve, so that a clear and well-defined plateau during exchange is not observed. Since $\delta_h$ is not an additive quantity, $\delta_h(t)$ cannot be analyzed quantitatively like $\Gamma(t)$. Nevertheless, the exchange kinetics of high and low molar mass PEO can be concluded to be qualitatively similar.

**2. Polystyrene. Overshoot Adsorption.** An example of the exchange kinetics of PS is plotted in Figure 5 in the same way as in Figure 3 for PEO. The molar masses of 1 and 2 in this experiment are 9.2K and 3040K, respectively.

In the initial and final parts of Figure 5 the results for injection of 1 + 2 are similar for PS and PEO. For both polymers, the initial adsorption rate of 1 + 2 is determined by mass transfer from solution. The saturated value of $\Gamma$ for injection of 1 + 2 corresponds closely to that of component 2, suggesting that all molecules 1 that were initially adsorbed are eventually displaced by 2.

However, PS behaves remarkably differently during exchange (i.e., in the middle part, $40 < t < 140$ s). The adsorbed amount increases continuously during exchange, whereas for PEO it was found to be constant. Two explanations may be considered. One possibility is that local equilibrium is maintained during exchange of PS but that for some reason the equilibrium adsorption theory does not fit the behavior of PS. The other explanation is that the increase of $\Gamma$ during exchange of PS comes from a temporary overshoot of component 1 at the surface, i.e., desorption of 1 is a slow process.

In order to distinguish unambiguously between these two possibilities, we performed a series of experiments which are presented in Figure 6 and 7. The idea of these experiments is to determine the surface composition $\Gamma_1(\Gamma_2)$ (like the dotted line in Figure 2) under static, equilibrium conditions and under dynamic conditions, like in Figure 5. If there is local equilibrium under the dynamic conditions, the curves $\Gamma_1(\Gamma_2)$ obtained under static and dynamic circumstances should be identical.

Figure 6 shows two experiments in which the order of adsorption of 1 and 2 is reversed (full curves). The lower curve represents a sequence of injection of 2, then pure solvent, and then 1. Henceforth, this sequence is denoted as 2,1. The upper curve is the result of injection of 1 followed by 1 + 2, which will be referred to as 1,1+2. For reference, we also plotted the result for continuous injection of 2 on an initially bare surface (dashed). The slope of the dotted line corresponds to the adsorption rate of 2 on a bare surface.

We first discuss the sequence 2,1 (lower solid curve). From $t = 0$ to 60 s a solution of 2 was injected. Then, pure solvent was pumped into the cell, in order to prevent further adsorption and to obtain an undersaturated layer of 2. Due to the high adsorption energy of long chains of PS no detectable desorption occurs under these conditions. This is confirmed by control experiments in which the solvent flow was maintained over 1000 s.

At $t = 120$ s the injection of 1 started, and the adsorbed amount quickly attains a higher, stable level. Desorption of 2 during injection of 1 is improbable, since the long chains remain attached to the surface by many segments in spite of the adsorption of shorter chains. Thus the adsorbed amount of 2 during injection of 1 is constant and equals the value of $\Gamma$ ($=\Gamma_2$) during injection of solvent ($60 < t < 120$ s). The adsorbed amount of 1 is the additional adsorption upon injection of 1. For the example of Figure 6 $\Gamma_2 = 0.7$ mg/m$^2$ and $\Gamma_1 = 0.2$ mg/m$^2$.

This result gives one point for a curve of the surface composition $\Gamma_1(\Gamma_2)$, analogous to the dotted curve in the theoretical plot of Figure 2. More points were obtained by repeating the experiment with different times of injection of 2. Each point of this curve reflects a static surface composition.

Next, we consider the sequence 1,1+2 (upper full curve). For $t < 0$ the surface is saturated with 1. For $t > 0$ a solution of 1 + 2 is injected and $\Gamma$ increases due to adsorption of 2. The concentration of 1 in the mixture is the same as that injected for $t < 0$. Therefore, the chemical potential of 1 in solution is constant, and any desorption of 1 must be the result of displacement by 2. Near saturation the curves for the injection of 1 + 2 and of pure 2 coincide. We conclude that in this final stage component 1 is completely removed from the surface and that the adsorption of 2 from the mixture follows the curve for adsorption of pure 2 on a bare surface (dashed).

Just after the start of injection of 1 + 2 the observed adsorption rate (upper solid curve) is finite but lower than that of 2 only (dotted line). The difference must be due to desorption of 1. From a comparison of the adsorption rates of 1 + 2 and of 2 we determined an exchange ratio $d\Gamma_1/d\Gamma_2$ of $-0.55$. For PEO, where the adsorbed amount is constant during exchange, this ratio equals $-1$. Since for PS the rates $d\Gamma_{1+2}/dt$ (slope of the upper full curve) and $d\Gamma_2/dt$ (slope of the dashed curve) remain more or less constant almost up to saturation, the exchange ratio $d\Gamma_1/d\Gamma_2$ is also nearly constant up to saturation.

As explained before, it is a reasonable assumption that at any moment during injection of 1 + 2 the contribution of 2 to the total adsorbed amount is given by that for individual adsorption of 2 (dashed). Consequently, $\Gamma_1$ equals the difference $\Gamma_{1+2} - \Gamma_2$. Since during injection of 1 + 2 the adsorbed amount of 1 decreases from its saturated value to zero, a complete curve of the surface composition $\Gamma_1(\Gamma_2)$ can be obtained from the upper two curves in Figure 6. This result might be considered as the surface composition under dynamic conditions.

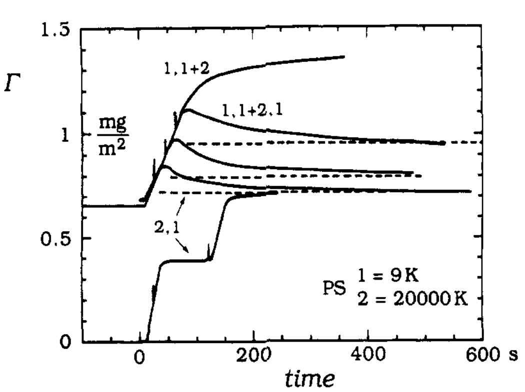

**Figure 8.** Desorption of PS by relaxation of the adsorbed layer. In these experiments the flow is switched back from the injection of 1 + 2 to 1 at the point indicated by a vertical tick. Following this, desorption of 1 occurs. The dotted horizontal lines represent the final value of experiments 2,1 with an injection time of 2 corresponding to that of 1 + 2 in the relaxation experiments 1,1+2,1. Concentrations: $c_1^b = 5.0$ g/m$^3$ and $c_2^b = 50$ g/m$^3$.

In Figure 7 we present this composition $\Gamma_1(\Gamma_2)$ under dynamic circumstances (full curve, 1,1+2) together with that under static conditions (circles, 2,1). For comparison, the result for PEO of a sequence 1,1+2 is also included. The dotted lines are drawn according to exchange of 1 by 2 at a strictly constant total adsorbed mass. These lines correspond to the theoretically predicted equilibrium composition (see also the dotted curve in Figure 2).

A mixed adsorbed layer of PS under static conditions (lower PS, curve 2,1) has a composition that is close to the theoretical prediction for equilibrium. Only for $\Gamma_2 > 0.5$ mg/m$^2$ the value of $\Gamma_1$ is slightly higher than expected on the basis of Figure 2. Hence, the equilibrium composition is approximately attained if first 2 is adsorbed followed by 1.

For adsorption in the reverse order (full curves "1,1+2") the adsorbed amount of 1 is in the case of PS higher than the equilibrium value, whereas for PEO it was about equal. This implies that PS has an overshoot adsorption of component 1 during exchange. For PEO such an overshoot is not observed.

The existence of an overshoot raises the question at what time scale an adsorbed PS layer relaxes toward equilibrium. This question can be examined in an experiment in which the sequence 1,1+2 is interrupted before the surface is saturated with 2. If the injection of solution is switched back from 1 + 2 to 1, the adsorbed amount of 2 will remain constant, and the observed change in the total adsorbed amount (due to desorption of 1) reflects the relaxation process. Such an experiment is indicated in Figure 7 by the vertical arrow, and the sequence of injected solutions is referred to as 1,1+2,1. We discuss this type of experiment in the next section.

**Relaxation Experiments.** The results of three relaxation experiments are shown in Figure 8 as three curves labeled 1,1+2,1. For comparison, the result for continuous injection of 1 + 2, without interruption, is included; cf. Figure 6. The meaning of the dotted lines and the curve for injection of 2,1 will be explained later.

Before the relaxation experiments ($t < 0$) the surface is saturated with 1. Between $t = 0$ and the vertical tick indicated on the curve, a solution of 1 + 2 is injected. The three experiments shown have different times of injection of 1 + 2 and thus different amounts of 2 adsorbed. After the switch from injection of 1 + 2 to 1, the adsorbed amount continues to increase during a few seconds because there

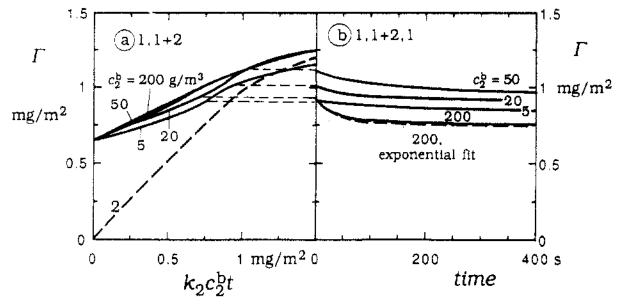

**Figure 9.** Desorption by relaxation for different concentrations of 2 (as indicated). Results are given for experiments for the type 1,1+2 (a) and 1,1+2,1 (b). In a Γ is plotted as a function of $k_2c_2^bt$ during injection of 1 + 2 on a layer which was initially saturated with 1. For comparison, also the result for adsorption of 2 only on an initially bare surface is included (dashed). Part b gives Γ($t$) during injection of 1 after a sequence 1,1+2. The concentration $c_2^b$ of 2 during injection of 1 + 2 is indicated. The horizontal dashed lines connect the curves in b to their starting points on the curves in a. Molar masses and concentration $c_1^b$ are the same as in Figure 8; $k_2$ = 3.04 × 10⁻⁷ m/s. See also the text.

are still molecules 2 coming from the dead volume between the valve and surface. As soon as the dead volume has passed, the adsorbed amount starts to decrease. After some 5–10 min a constant value is reached. The amount desorbed during injection of 1 is about 0.2 mg/m² for each experiment.

On may wonder whether the decrease in Γ is indeed due to relaxation of the adsorbed layer. We recall that desorption of 2 is very unlikely: even in pure solvent flow such a desorption is not found. For component 1, the chemical potential in solution is constant throughout the experiment, so that desorption of 1 by dilution does not occur either. The only remaining explanation is indeed that the decrease in Γ is due to desorption of 1 by relaxation of (i.e., rearrangement within) the adsorbed layer, whereby the overshoot discussed in the previous figures disappears gradually.

In order to check whether at the end of the experiments the adsorbed layer is fully relaxed, sequential adsorption experiments of the type 2,1 were performed. The injection time of 2 was chosen equal to that of 1 + 2, so that the adsorbed amount of 2 is the same for corresponding experiments 2.1 and 1,1+2,1. The total adsorbed amount after a sequence 2,1 is indicated by the horizontal dotted lines. The value of Γ at the end of the relaxation curves is in very good agreement with the equilibrium adsorbed amount obtained from a sequence 2,1. Hence, the adsorbed layer does indeed relax fully; the relaxation time is on the order of a few minutes. This result corrborates our conclusion that the decrease in Γ is due to desorption of 1 by relaxation of the adsorbed layer.

For the experiments of Figure 8 the adsorption rate of 2 is quite high as compared to the rate of desorption by relaxation. Therefore, we expect that the relaxation during injection of 1 + 2 is small. However, it is likely that the result depends on the time scale of the adsorption of 2 and thus on $d\Gamma_2/dt$. Since the adsorption rate of 2 is limited by mass transfer (i.e., $d\Gamma_2/dt = kc_2^b$), the adsorption rate of 2 can be varied by adjusting the concentration $c_2^b$ of 2 in solution. We expect that this will affect the extent of relaxation during injection of 1 + 2, so that the shape of the curve 1,1+2 will change. As a consequence, the amount desorbed during subsequent injection of 1 is also influenced.

Experimental results at four concentrations $c_2^b$ in the range 5–200 g/m³ are given in parts a and b of Figure 9 for sequential injection of 1,1+2 and 1,1+2,1, respectively. The horizontal dotted lines in Figure 9a refer to the point where the switch from injection of 1 + 2 to 1 was made in the experiments of Figure 9b. For comparison, we included in Figure 9a the adsorption of pure 2 on an initially bare surface (dashed).

Before $t$ = 0 in Figure 9a, the surface was equilibrated with 1 ($\Gamma_1 \approx 0.65$ mg/m²) and at $t$ = 0 the injection of a solution of 1 + 2 started. In order to be able to compare results, the adsorbed amount Γ is plotted as a function of $k_2c_2^bt$. Here, $k_2$ is the transport coefficient of 2, which we determined from the initial adsorption rate of pure 2. In this representation the initial slope for adsorption of 2 only is unity (dashed). Also, curves coincide as long as $d\Gamma/dt \propto c_2^b$. The results in Figure 9a are plotted in the same way as the theoretical prediction for exchange according to local equilibrium in Figure 2 (with $\Gamma_2 \approx k_2c_2^bt$).

For all four concentrations in Figure 9a the initial rate $d\Gamma_{1+2}/dt$ is lower than the adsorption rate of 2 only (dashed). This implies that during adsorption of 2 there is always some desorption of 1. Furthermore, for all curves 1,1+2 the adsorption increases initially, in contrast with the prediction of constant total adsorbed amount for exchange according to local equilibrium (solid curve in Figure 2). This means that in all cases there is an overshoot adsorption of 1 during exchange. However, for $c_2^b$ decreasing from 50 to 5 g/m³ the shape of the curves becomes gradually more convex with respect to the abscissa axis, which indicates that with decreasing value of $c_2^b$ (=decreasing adsorption rate) the overshoot of 1 during exchange decreases too. The adsorbed layer is more relaxed when the experiment is carried out at lower concentration, because more time is available for relaxation.

For $c_2^b$ equal to 50 and 200 g/m³ the curves in Figure 9a nearly coincide, which implies that the overshoot adsorption is the same for both experiments. However, at $c_2^b$ = 200 g/m³ the time available for relaxation is only 25% of that at $c_2^b$ = 50 g/m³, due to the higher adsorption rate. Probably, for both experiments the injection time of 1 + 2 is so small that relaxation during adsorption of 2 is negligible. However, there is still desorption of component 1, as we inferred above from a comparison of the initial slopes for injection of 1 + 2 and pure 2. At saturation (not shown in Figure 9a) and for $c_2^b$ in the range 20–200 g/m³, the curves Γ($t$) for injection of 1,1+2 and for pure 2 coincide, like in Figure 6 the upper solid curve 1 + 2 and the dashed curve 2. Again, we conclude from this that at saturation component 1 is completely desorbed.

Figure 9b shows Γ($t$) during injection of 1 after an initial sequence 1,1+2. The value of $c_2^b$ during injection of 1 + 2 is indicated. The injection time of 1 + 2 was not varied systematically, so that the amount of 2 adsorbed is different for each experiment. The time along the abscissa axis is corrected for the effect of dead volume between the valve and surface.

As before, the observed decrease in Γ is due to desorption of 1 by relaxation of the adsorbed layer. The desorption rate and the total desorbed amount during injection of 1 both decrease with decreasing value of $c_2^b$. This is due to the longer time available for relaxation during the preceding injection of 1 + 2. The decrease in the desorption rate is most conspicuous for $c_2^b$ = 5 and 20 g/m³. This is in agreement with the results in Figure 9a, which show for these concentrations a more pronounced change in the

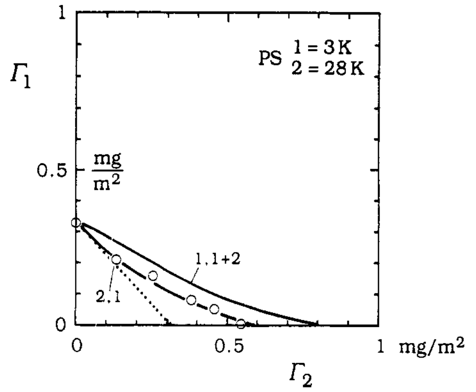

**Figure 10.** Exchange of low molar mass PS. The results are plotted in the same way as in Figure 7. Concentrations: $c_1^b = c_2^b = 10$ g/m$^3$.

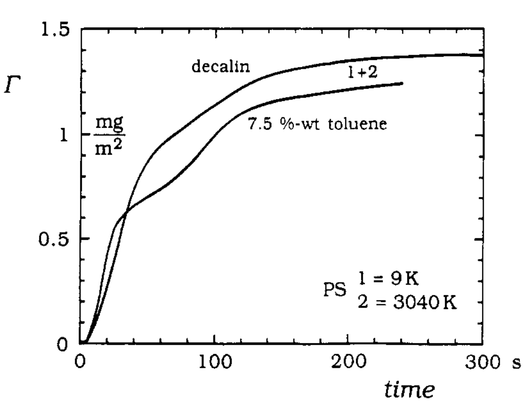

**Figure 11.** Effect of toluene on the exchange kinetics of PS. Concentrations: $c_1^b = 5.0$ g/m$^3$ and $c_2^b = 25$ g/m$^3$.

shape of the curve, indicative of a more relaxed adsorbed layer.

In order to obtain a quantitative characterization of the relaxation process, a single-exponential function was fitted to the relaxation curve for $c_2^b = 200$ g/m$^3$. This experiment was chosen for the fit because the adsorption of 2 was fastest. We therefore expect that all molecules 2 are more or less in the same, initial state of relaxation. The fit provided a time constant of 45 s and is given in Figure 9b by the dashed curve. The experimentally observed desorption appears to be slightly different from the single-exponential function. This is not surprising, however, because we do not have any *a priori* reason or model to expect an exponential behavior.

In our opinion the results in Figure 9a,b may be interpreted in terms of two different time scales for the exchange: (i) fast desorption of 1 during *attachment* of 2 and (ii) slow desorption of 1 due to *relaxation* of adsorbed chains 2. During injection of 1 + 2 and at a high adsorption rate of 2 ($c_2^b > 50$ g/m$^3$ in Figure 9a), the desorption of 1 and the overshoot adsorption are entirely determined by the fast process (i). In that case a variation of the adsorption rate by changing $c_2^b$ has no influence on the overshoot adsorption (the curves for 50 and 200 g/m$^3$ in Figure 9a coincide), since the desorption rate of 1 according to process i is proportional to the adsorption rate of 2. As noted in the discussion of Figure 9a, at high concentration $c_2^b$ complete desorption of 1 is possible during adsorption of 2. This implies that all molecules 1 can leave the surface by the fast process (i).

At lower adsorption rates (for $c_2^b < 50$ g/m$^3$) there is also desorption by the (slow) relaxation process ii. This leads to a smaller overshoot adsorption during injection of 1 + 2 (in Figure 9a the curves for 5 and 20 g/m$^3$ have a more convex shape toward the abscissa axis than at higher concentration). The desorption observed in Figure 9b reflects this slow relaxation process (ii).

**Effect of Chain Length.** In Figure 10 the exchange of PS of molar mass 3K by 28K is plotted in the same way as we did for the exchange of 9K by 3040K in Figure 7. In both figures we compare the composition $\Gamma_1(\Gamma_2)$ of an adsorbed PS layer under static and under dynamic conditions (open circles, 2,1; full curve, 1,1+2). The dotted line is drawn according to exchange at constant total mass adsorbed.

For the sequential adsorption 28K,3K the total adsorbed amount is constant for $\Gamma_2 < 0.2$ mg/m$^2$, and it gradually increases for higher values of $\Gamma_2$. As explained in the discussion of Figure 7 this type of sequential experiment is supposed to give a static, equilibrium composition $\Gamma_1(\Gamma_2)$. However, the theoretical calculations in section 2 showed that in equilibrium the value of $\Gamma_t$ should remain constant even though the composition of a mixed adsorbed layer changes (solid curve, Figure 2). The discrepancy between experiment (increase of $\Gamma_t$) and theory ($\Gamma_t$ constant) is probably a consequence of the low molecular weight of the samples. Theoretical calculations for short chains confirm this conclusion.

The adsorbed amount obtained for adsorption under dynamic conditions (upper curve 1,1+2 in Figure 10) is everywhere somewhat higher than that under static circumstances (2,1). This implies that under dynamic conditions there is again a small overshoot of 3K on the surface. Qualitatively, there is the same result as for displacement of 9K by 3040K (Figure 7); quantitatively the difference between the curves is less.

**Effect of Solvent.** The dynamics of an adsorbed polystyrene layer may depend on the interactions between the polymer, the solvent, and the surface and thus on the type of solvent. Below we compare the exchange kinetics in decalin to that in two other solvents: a mixture of toluene and decalin, and carbon tetrachloride ($CCl_4$). These solvents were chosen because they have an effect on the solvency and on the adsorption energy of the polymer.

Decalin at 16 °C is a Θ-solvent for PS,[16] whereas toluene and $CCl_4$ are good solvents. The segmental adsorption energy of PS on silica in decalin is about 2 $kT$ and in carbon tetrachloride around 1 $kT$.[17] Toluene is a weak displacer for PS on silica.[17] Qualitatively, the poor solvent quality and high adsorption energy in decalin can be explained from the fact that decalin is apolar and hardly polarizable and, consequently, has only weak interaction with PS and the surface. As a result, the effective intramolecular interaction in PS and the effective binding of the polymer to the surface are relatively strong.

In Figure 11 the adsorption of 1 + 2 from decalin is compared to that from a 92.5/7.5 (w/w) mixture of decalin and toluene. We discuss three effects of the addition of toluene. First, the initial adsorption rate increases slightly upon the addition of toluene. This increase in mass-transfer rate reflects a reduction of the viscosity due to toluene which causes an increase of the flow rate. The diffusion coefficient of the polymer might also be affected, but presumably this is a smaller effect.

Second, we infer from the results a decrease of the saturated adsorbed amount of 1 and 2 when toluene is added. As discussed before, the value of Γ at the first kink in the curve closely corresponds to saturation of 1. In the solvent mixture the kink occurs at a significantly lower value of Γ than in decalin (≈0.6 and ≈0.9 mg/m$^2$, respectively). The adsorbed amount at the end of the experiment corresponds to saturation of 2. This value is

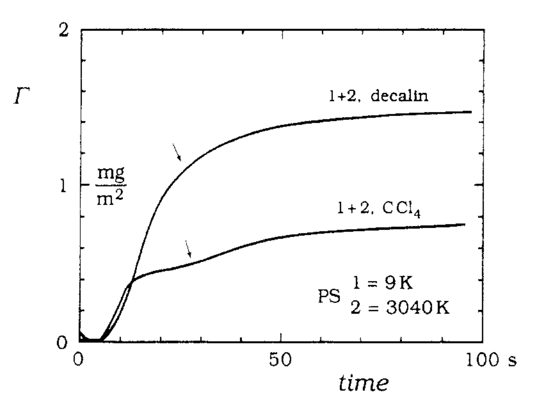

**Figure 12.** Comparison of the exchange kinetics of PS from decalin and carbon tetrachloride ($CCl_4$) solutions. In decalin $c_1^b = 20$ g/m$^3$ and $c_2^b = 100$ g/m$^3$. In carbon tetrachloride $c_1^b = 5.0$ g/m$^3$ and $c_2^b = 20$ g/m$^3$.

only slightly lower in the toluene/decalin mixture than in decalin (≈1.25 mg/m$^2$ as compared to 1.4 mg/m$^2$). We ascribe the influence of toluene on the saturated adsorbed amount of 1 and 2 by a decrease of the adsorption energy and an increase of the solvency. Both effects are known to lead to lower adsorption levels.[15]

Third, toluene addition has an effect on the exchange kinetics. During exchange in decalin ($50 < t < 140$ s) the adsorbed amount increases linearly with time, whereas during exchange in the toluene/decalin mixture ($30 < t < 120$ s) the curve $\Gamma(t)$ has a convex shape with respect to the abscissa axis. The change in the shape of the curve indicates that the overshoot adsorption in the toluene/decalin mixture is smaller than that in decalin. This must reflect a more rapid relaxation of the adsorbed layer.

The exchange kinetics in carbon tetrachloride and decalin are compared in Figure 12. The graph shows $\Gamma(t)$ during injection of a solution of 1 + 2. In order to obtain a comparable mass transfer rate in both solvents, differences in hydrodynamic conditions and in diffusion coefficients were compensated by adjusting the polymer concentrations (for values of $c$, see the figure caption).

Along the same lines as in the discussion of Figure 11, we infer from the results in Figure 12 that the saturated adsorbed amounts of 1 and 2 in carbon tetrachloride are considerably lower than those in decalin. The most likely explanation is again the lower segmental adsorption energy and the better solvency in $CCl_4$ as compared to decalin.

During exchange (indicated by an arrow) the shape of the curve is convex with respect to the abscissa axis for $CCl_4$ and slightly concave for decalin. Again, this indicates that the overshoot adsorption is less in $CCl_4$ than in decalin.

The above examples show an interesting parallel. An increase of the solvency and a decrease of the adsorption energy are in both examples accompanied by a decrease of the overshoot adsorption during exchange. This suggests strongly that the dynamics of an adsorbed layer depend on the interactions between polymer, solvent, and surface: the better the solvent and the weaker the polymer/surface affinity, the faster the relaxation.

## Discussion

Several exchange experiments with PS demonstrate that *desorption* is at least partly a slow process, even though the desorbing chains are rather short. For example, an overshoot adsorption with respect to full equilibrium occurs when the surface is first saturated with the shorter chains that are subsequently displaced by longer ones (Figure 7). Moreover, this overshoot relaxes only slowly (Figure 8).

One reason for slow desorption could be that the displaced chain carries a strongly adsorbing end group. However, according to the manufacturer the polystyrene used had a vinylhexane end group, and it is very unlikely that such a group adsorbs more strongly than the styrene segments. Slow desorption could also be explained if there were topological constraints within the adsorbed layer (e.g., entangled chains or molecules pinned to the surface by loops of other chains). Polymer molecules can only escape from such constraints (and thus desorb) by slow diffusional motions out of the adsorbed layer.[2] However, in the discussion of Figure 9a,b we pointed out that at a high adsorption rate of the long chains *rapid* and *complete* desorption of the short chains occurs. In our opinion such rapid and complete desorption would not be possible if the short chains were trapped by topological constraints. Therefore, topological constraints provide also an unsatisfactory explanation for the observed slow relaxation of the adsorbed layer.

Another mechanism explaining slow relaxation would be that the spreading of an adsorbed chain is a slow process. Suppose that the exchange is a two-step process: upon attachment of a long chain some short molecules are first quickly desorbed, but further desorption occurs by spreading of the long chain. This could be much slower because reconformation of an already adsorbed chain toward a relatively flat equilibrium structure may be slow. Various factors may influence the spreading rate; we mention four.

First, the rate of reconformations at the surface may be related to that in solution, and thus it would depend on the flexibility of the polymer. Possibly, this could explain the different behavior of PEO and PS. Since PEO is much more flexible than PS due to the presence of bulky side groups in the latter polymer, conformational changes are much faster for PEO than for PS. This would explain that adsorbed PEO layers are essentially fully relaxed during exchange (Figure 3), whereas for PS on a similar time scale and with comparable chain lengths an overshoot adsorption occurs (Figure 5), indicative of slow relaxation of the adsorbed layer.

A second factor could be intramolecular interaction, which stabilizes the chain conformation. For PS, $\pi$-orbital overlap between styrene units of different segments may play a role; similar interactions affect the luminescence of polythiophenes. These interactions depend on the solvent present and are partly reflected in the solvent quality parameter $\chi$. Third, reconformation processes are very likely slowed down by the binding of the chain to the surface. The strength of the bond is characterized by the value of the segmental adsorption energy parameter $\chi_s$. A fourth factor is the presence of surrounding adsorbed chains.

Hence, one should expect the rate of reconformation of adsorbed polymers to depend on $\chi$ and on $\chi_s$. Both these parameters depend on the nature of the solvent and so does the exchange kinetics.

As shown, such an influence of the solvent on the overshoot adsorption during exchange is found experimentally for PS (Figures 11 and 12): the relaxation is slower in decalin than in a mixture of decalin and toluene or in pure carbon tetrachloride. PS has a higher adsorption energy and a poorer solvent quality in decalin. Both factors favor a stable conformation of the adsorbed chain in decalin and thus a slow relaxation in this solvent, in agreement with the experiment.

A molecular picture which describes the main results is presented in Figure 13. The upper graph gives schematic

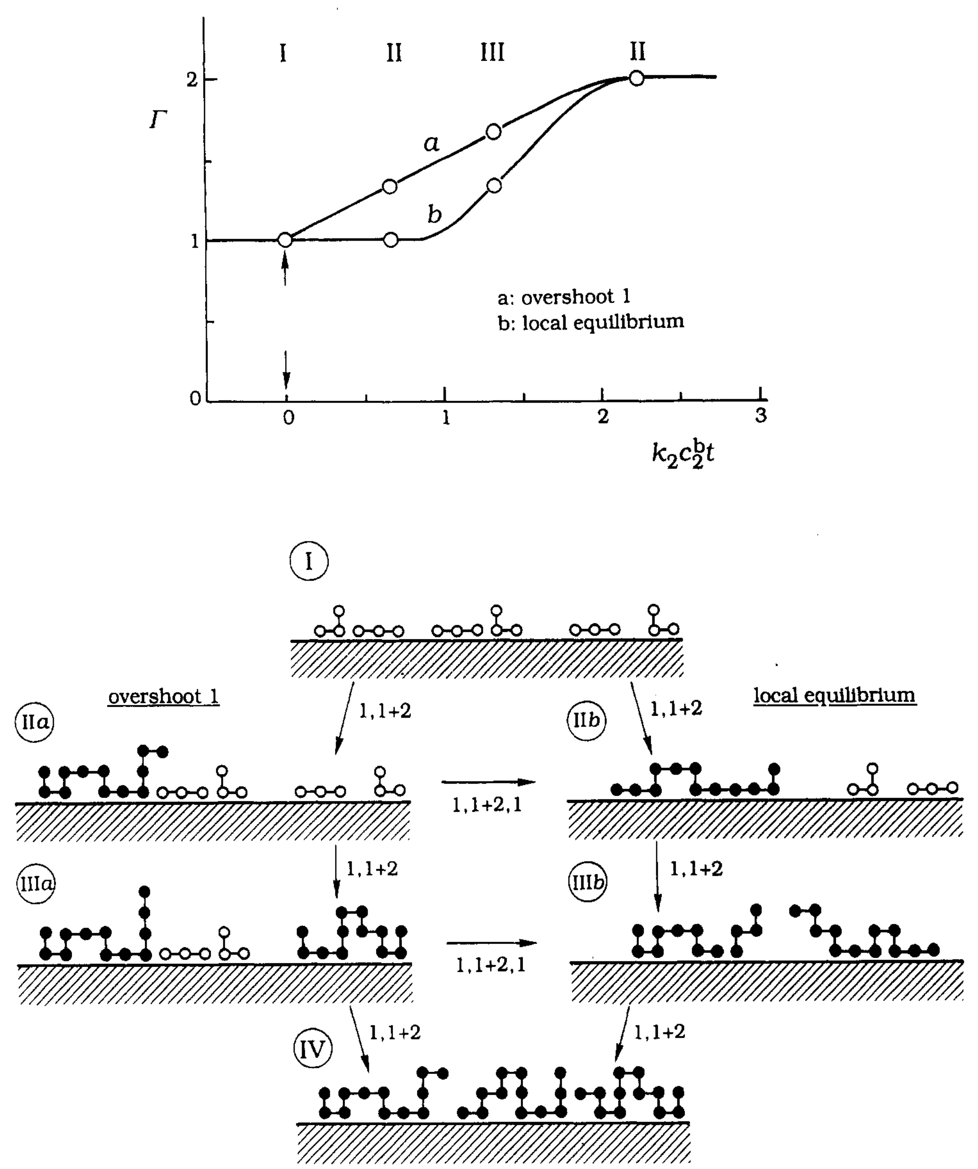

**Figure 13.** Pictorial representation of the adsorbed layer during exchange. The open circles in the upper graph (labelled I, IIa, IIb, etc.) refer to the cartoons below. Route a (top curve, left-hand-side cartoons) represents the overshoot situation and route b (bottom curve, right-hand-side cartoons) the situation according to the local equilibrium concept. For further explanation, see the text.

representations of $\Gamma(t)$ during sequential injection (1,1+2) for two limiting cases: no relaxation in the adsorbed layer during exchange (curve a) and full relaxation (curve b). Curve a corresponds to the experimental case of PS at a high adsorption rate (corresponding to $c_2^b$ = 50 or 200 g/m$^3$ in Figure 9a). Curve b represents the exchange kinetics of PEO (Figure 3) and the theoretical prediction with the local equilibrium concept (Figure 2). An intermediate position between a and b was found for PS in decalin at low adsorption rates (corresponding to $c_2^b$ = 5 or 20 g/m$^3$ in Figure 9a) or for PS in decalin/toluene mixtures and in carbon tetrachloride (Figures 11 and 12, respectively).

The open circles numbered I–IV on curves a and b refer to the pictures of the adsorbed layer below. In these "cartoons" the surface is represented one-dimensionally by a solid line and the adjacent solution by a two-dimensional square lattice. A lattice site is occupied by one segment of a polymer chain 1 or 2 (open and closed circles, respectively) or by solvent (not indicated).

Picture I shows a saturated adsorbed layer of 1 with six molecules on the surface. The relatively short chains have a rather flat conformation due to the favorable adsorption energy. In each subsequent step (I → II, etc.) one molecule 2 adsorbs. The essential difference between route a and b is the following. In a the conformation of adsorbed molecules is nearly frozen on the time scale of the experiment, whereas in b the chains are fully relaxed and in an equilibrium conformation. First, route b is discussed and then a.

In picture IIb the adsorption and complete unfolding of a molecule 2 has led to desorption of four short chains, so that the total adsorbed amount remains constant. Upon adsorption of the next two long chains (IIIb and IV), complete unfolding is no longer possible, since the surface layer is already too highly occupied. Longer loops and tails are formed by *all* molecules on the surface, including those previously adsorbed in a flat conformation.

In route a there is an overshoot adsorption of 1 during exchange. In each step one molecule 2 (12 segments) adsorbs at the expense of two molecules 1 (3 segments each), so that the total adsorbed amount increases, and an overshoot adsorption occurs in states IIa and IIIa. The exchange ratio $d\Gamma_1/d\Gamma_2$ equals −0.5, which is about the same as that in the experimental results (see the discussion of Figure 6). In route a the unfolding of an adsorbed chain of 2 is slow as compared to the rate of arrival of new ones, so that the conformation of 2 remains more or less constant up to saturation in IV. However, when in IIa or IIIa the supply of new long chains is stopped, the adsorbed layer relaxes slowly toward the equilibrium situation in IIb and IIIb, respectively. This is indicated by the horizontal arrows 1,1+2,1 and corresponds to the relaxation experiments presented in Figures 8 and 9b. Relaxation thus seems to be determined by unfolding of molecules 2.

**Comparison with Other Results.** In a previous paper[12] we reported that at higher coverage the adsorption rate of PS decreases by the buildup of an adsorbed layer. In particular, we concluded that the adsorption probability of a polystyrene chain depends on its gain in adsorption energy during collision with the surface. At high coverage, part of this gain may be due to displacement of adsorbed segments of other molecules, a process comparable to the relaxation observed in the present paper. The mere fact that at higher coverage the adsorption rate is decreased by such an attachment step is an indication that the competition between polystyrene chains is slow on a segmental level, in agreement with the slow relaxation observed here.

In the same paper,[12] it was observed that desorption of low molecular weight PS into pure solvent is much slower than expected on the basis of local equilibrium. This is another indication that adsorbed PS equilibrates slowly. For PEO this desorption follows the equilibrium picture,[13] in agreement with the absence of an overshoot that we find here.

Frantz and Granick studied the exchange kinetics of PS adsorbed from cyclohexane on silica at 30 °C.[3] They found a considerable effect of the age of the preadsorbed protonated PS layer on the displacement rate by deuterated PS of the same molar mass (550K). The displacement rate gradually decreased with aging times up to tens of hours. This was interpreted to be the result of slow reconformations in the preadsorbed layer, possibly reflecting the formation of entanglements. In comparison with their experiments our results were obtained for very young layers. Qualitatively, there is agreement on the idea of slow reconformations within an adsorbed PS layer. However, no further comparison is possible, since the design of the experiments is rather different.

## Conclusions

We have studied the exchange kinetics between polymers that differ in chain length only. A theoretical prediction of the exchange kinetics was made by using the so-called local equilibrium concept.[13] According to this concept, free and adsorbed chains are in equilibrium near the surface, and the adsorption rate is fully determined by mass transfer from the bulk solution. Using an isotherm calculated with the theory of Scheutjens and Fleer,[5] it was found that the exchange in this model takes place at a *constant* total adsorbed amount, which is approximately equal to the value for individual adsorption of the displaced chain. The rate of the exchange is limited by the adsorption rate of the displacer and is equal to the *maximum* mass-transfer rate of this component from solution. The adsorption rate of the displacer is in this picture not affected by the presence of an adsorbed layer of shorter chains.

For aqueous solutions of poly(ethylene oxide) the exchange kinetics on silica is in full agreement with these local equilibrium predictions. This was also found to be the case for the kinetics of adsorption and for desorption into pure solvent.[1,13] All our results for PEO indicate that an adsorbed layer of this polymer rapidly equilibrates with the adjacent solution.

For polystyrene adsorbed from decalin on silica the equilibration at the surface is much slower than for PEO. During exchange of PS we observed an overshoot adsorption of the displaced component. The overshoot may desorb either by rapid exchange against newly adsorbing molecules or by slow relaxation of the adsorbed layer. The time constant for the latter process is about 1 min for displacement of PS of molar mass 9.2K by a sample of 20000K. In the solvents toluene/decalin mixture and carbon tetrachloride the overshoot during exchange is smaller than that in decalin, indicating that the relaxation process is faster.

Slow reconformation (spreading) of adsorbed chains is probably the cause for the overshoot during exchange of PS. The rate of spreading depends on the type of polymer, on the intramolecular interactions and on the binding to the surface. In this picture, PEO equilibrates more rapidly than PS, since it is much more flexible. The solvent effect on the exchange kinetics of PS could be explained in terms of weaker intramolecular interaction in better solvents and weaker anchoring on the surface.

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