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Effect of Layer Age and Interfacial Relaxations on the Self-Exchange Kinetics of Poly(ethylene oxide) Adsorbed on Silica

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ABSTRACT: The interfacial states in adsorbed PEO layers on silica were probed through the self-exchange of coumarin-tagged chains and native analogues. New evidence for nonequilibrium interfacial behavior is presented, though prior studies supported local equilibrium for adsorbed PEO. Results suggest that entanglements or high numbers of segment−surface contacts can be as important as a high bulk T_g in leading to trapped interfacial chains. Interfacial "glasses" can occur for systems where bulk (solution or melt) states are not glassy. For the specific PEO−water−silica system, measurable relaxations persisted for the first 10 h of layer incubation in pure solvent. Additional relaxations may have occurred beyond this time; however, such additional interfacial evolution was not detectable by self-exchange. Self-exchange was generally incomplete, often revealing a population of chains whose attachment to the surface appeared irreversible and suggesting that various interfacial states, differing in their extent of surface attachment, are long-lived.

Introduction

The technologically important phenomenon of polymer adsorption from solution onto solid surfaces is governed by segment−surface attractions and entropic losses. While much attention has been paid to the equilibrium aspects of polymer adsorption,[1−3] the fact is that most adsorbed layers are not expected to fully equilibrate on experimental time scales.[4−7] Kinetically trapped metastable states occur when high molecular weight polymers experience 50−100 segment−surface contacts per chain, each contributing an energy on the order of a kT. Therefore, after the initial chain attachment, the adsorbed layer relaxes toward equilibrium.

A general understanding of interfacial relaxations has yet to be achieved. In particular, it is desirable to relate relaxation rates to chemical and physical features of the interphase, such as the solvent quality, adsorption energy, polymer chain length, backbone stiffness, and segmental mobility. Also to be examined are the specific roles of interfacial entanglements and cooperative motions. Another issue, still to be addressed, is the extent to which interfacial relaxations influence the various macroscopically observable features of the layer and which of these are relevant to specific technological applications.

Direct measures of interfacial properties, such as the adsorbed amount from ellipsometry or the interfacial concentration profile from neutron reflectivity, may not provide evidence for interfacial relaxations, which often occur at constant interfacial mass. Tracking the evolution of the number of segment−surface contacts may also be a difficult means of measuring relaxations because their number could be fixed overall. Since relaxations are a dynamic feature of an adsorbed layer, it turns out that measuring other layer dynamics provides insight into the relaxation rates. While adsorption is generally fast, desorption into the adsorption solvent is tediously slow. The displacement of adsorbed chains by an appropriate low molecular weight species may occur on a tractable time scale[8] but often cannot distinguish between different states of previously adsorbed chains. The self-exchange of adsorbed polymers with like chains in free solution, however, has been shown to be sensitive to features of the adsorbed layer,[8] including interfacial relaxations.

In an attempt to determine the mean time spent by a macromolecule in an adsorbed layer, Varoqui and co-workers measured the displacement kinetics of radio-labeled high molecular weight polymers by their native (non-radio-labeled) analogues. For polyacrylamide (PAAm)[9] and polystyrene (PS)[10] adsorbing on a silica glass bead surface, they observed very slow exchange rates which became even slower as the adsorbed layers matured at constant interfacial mass. This was firm evidence that slow interfacial relaxations increased the tightness of binding in a system already possessing slow interfacial dynamics. More recently, Granick and co-workers[11−13] found a significant influence of adsorbed layer age (up to 24 h beyond the time needed to reach the steady-state mass coverage) on the displacement kinetics of protio-PS by deuterio-PS.

The PAAm samples of Varoqui presumably had relatively strong segment−surface attractions while the PS chains employed by both groups were somewhat stiff and, in the bulk melt, have a high T_g. Both these factors could be expected to contribute to slow interfacial dynamics and metastable interfacial states;[14−16] however, it is unclear the extent to which slow interfacial dynamics might be expected for polymer chains that are highly flexible and have only moderate segment−surface attractions. This question motivates studies of polymer systems, such as poly(ethylene oxide) (PEO), with greater backbone flexibility.

For PEO adsorbing onto silica from aqueous solution, it has been established by Dijt[14] and us[17] that molecular-weight-driven exchange kinetics are transport-controlled for chains of 30K molecular weight or less and interfacial layer ages on the order of a few minutes. Therefore, the interfacial motions for PEO at these conditions are relatively rapid. This conclusion is also consistent with the observation of transport-limited adsorption kinetics up to coverages within a few percent

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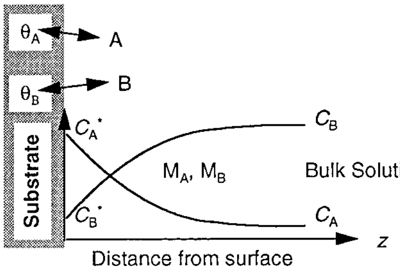

Figure 1. Illustration of bulk mass-transport and surface exchange processes between two species, A and B, in bulk solution, near the surface, and on the surface.

of saturation:[18] Preadsorbed chains can rapidly adjust their conformations to make room for additional ones. In contrast, low molecular weight PS adsorbing on silica from decalin shows signs of deviation from local equilibrium.[14] Under some conditions, adsorbed PEO can also exhibit sluggish dynamics: We observed surface-influenced exchange kinetics and history dependence when presadsorbed PEO layers on the order of 100K were challenged by chains of higher molecular weight.[19]

These preliminary observations motivated a further exploration of the aging process for PEO adsorbed onto silica (after the mass saturation the a surface), via the measurement of self-exchange kinetics. In the work presented here, we employed a fluorescent tag on one end of each PEO chain to distinguish preadsorbed and late arriving PEO populations at an interface. We demonstrate that this fluorescent method, with a coumarin tag, is less invasive than deuterio-labeling. The observed self-exchange kinetics are benchmarked against transport limitations, a simple Langmuir surface exchange model, and single and stretched exponential behavior, none of which were, by themselves, entirely adequate to describe the observations. Self-exchange showed a strong dependence on molecular weight, with layers approaching maturation and possibly equilibrium on the time scale of tens of hours. The results suggest that the final layer state may consist of loosely and tightly bound populations.

A Simple Kinetic Model for Self-Exchange

This section presents a simple treatment of self-exchange, motivating a mathematical form used to fit experimental data. This simple model presumes that the state of the layer is fixed during a self-exchange test, which is short relative to the overall layer relaxation process. The treatment also presumes that self-exchange does not alter the state of the layer.

The exchange of preadsorbed molecules with those free in solution, illustrated in Figure 1, is treated as a surface reaction in series with a bulk mass-transfer process, in our case, corresponding to shearing flow. Generalizing the self-exchange as exchange between preadsorbed species A and displacer B, the surface reaction proceeds according to

$$\theta_A + B \underset{k'_{ex}}{\overset{k_{ex}}{\rightleftarrows}} A + \theta_B \tag{1}$$

where A and B represent each species free in solution, and θ_A and θ_B represent the adsorbed molecules. The forward and reverse exchange rate constants, k_{ex} and k'_{ex}, are, in principle, a function of the instantaneous interfacial state, including surface coverage. In the self-exchange studies presented here, the surface is saturated by the layer of preadsorbed A, incubated in solvent, and later challenged by a solution of B. Also, B is essentially identical to A, a fact which will be taken into account later. Because of the similarity between A and B and the presaturation of the surface with A, no evolution in the total surface mass occurs during self-exchange:

$$\Gamma_A + \Gamma_B = \text{constant} \tag{2}$$

Here, Γ_A and Γ_B are the adsorbed amounts of A and B. Also, to the extent that A and B are identical (except for a label), the exchange process itself should not alter the state of the layer. Therefore, without evolution of fundamental layer properties (total adsorbed amount and chemical makeup of the layer) during self-exchange, k_{ex} and k'_{ex} can be presumed constant. One then defines the equilibrium constant for the exchange reaction between A and B as

$$K_{B-A} = \frac{k_{ex}}{k'_{ex}} = \left[\frac{\Gamma_B C_A}{\Gamma_A C_B}\right]_{\text{equilibrium}} \tag{3}$$

Note that to the extent that aging decreases the self-exchange rate, k_{ex} and k'_{ex} will decrease with age but should still remain constant during the relatively short time of a single self-exchange experiment. One also expects that, to the extent that aging does not shift the equilibrium between A and B, the ratio of k_{ex} and k'_{ex} would be fixed, independent of layer age. For the PEO system studied here, we confirmed that this is indeed the case.

The kinetics of the self-exchange reaction at the interface follow from eq 1:

$$\frac{d\Gamma_B}{dt} = -\frac{d\Gamma_A}{dt} = k_{ex}\Gamma_A C^*_B - k'_{ex}\Gamma_B C^*_A \tag{4}$$

Here, C_A* and C_B* are the local concentrations of A and B in the fluid layer nearest the surface, while C_A and C_B without the asterisk denote their bulk solution concentrations. The fluxes, J_A and J_B, of A and B toward the surface depend on the mass-transfer coefficients M_A and M_B according to

$$J_A = M_A(C_A - C^*_A) \tag{5a}$$

$$J_B = M_B(C_B - C^*_B) \tag{5b}$$

For shearing flow through a slit cell, M_i, the mass-transfer coefficient of species i is given by $0.538(\gamma/L)^{1/3}D_i^{2/3}$,[18] where γ is the wall shear rate, L is the distance from the flow cell entrance to the point of observation, and D_i is the diffusion coefficient of species i. We have confirmed that this expression accurately describes the diffusion of polymer chains to the interface in our flow cell.[18] Since the fluxes must be equal to the exchange rates, $J_B = -J_A = d\Gamma_B/dt = -d\Gamma_A/dt$. Equations 3−5 were therefore combined to eliminate the unknown C_i* terms, yielding

$$\frac{d\Gamma_B}{dt} = \frac{M_B(\Gamma_A C_B - \Gamma_B C_A/K_{B-A})}{M_B/k_{ex} + \Gamma_A + (M_B/M_A)\Gamma_B/K_{B-A}} \tag{6}$$

During our self-exchange experiments, the gently flowing bulk solution contains only *B*, and *A* and *B* are physically identical. Therefore, eq 6 should be integrated with $C_A = 0$, C_B constant, and $M_A = M_B = M$ (a result of self-exchange, with $D_A = D_B$). The result yields time as a function of surface composition: the desired inverse function, surface composition as a function of time, is obtained implicitly. It is most convenient to represent the evolution of surface composition in terms of the fractional coverage of A, $F_A = \Gamma_A/(\Gamma_A + \Gamma_B)$, and the same variable at time zero, $F_A{}^0$. (In our experiments $F_A{}^0$ is unity.) The result is

$$\tau = -\left(\frac{1}{\lambda} + \frac{1}{K_{B-A}}\right)\ln\left(\frac{F_A}{F_A{}^0}\right) + \left(1 - \frac{1}{K_{B-A}}\right)(F_A{}^0 - F_A) \quad (7)$$

where τ, the normalized time, has been defined:

$$\tau = \frac{M_B C_B}{\Gamma_A + \Gamma_B}t \quad (8)$$

It is worth noting that the time in eq 8 starts at the beginning of the exchange experiment, even though significant time may have elapsed since the original layer deposition prior to the initiation of exchange. Also, in eq 7, the dimensionless number λ represents the relative speeds of the fundamental surface exchange and bulk mass transport rates:

$$\lambda = \frac{k_{ex}(\Gamma_A + \Gamma_B)}{M} \quad (9)$$

As λ approaches ∞, the fundamental surface rate exceeds the diffusion of chains between the bulk solution and the interface, and the macroscopic exchange process becomes transport limited.

The principle of self-exchange requires that A and B are identical, giving $k_{ex} = k'_{ex}$, and $K_{B-A} = 1$. We find, however, that fluorescent tagging, though less invasive than other tracer methods, still gives a slight surface selectivity for the labeled (as opposed to the unlabeled) chains. By allowing K_{B-A} to take on values other than unity, this perturbation of the equilibrium can be taken into account directly and provides insight into the shapes of our exchange curves.

Equation 7 was compared with experimental observation by first measuring K_{B-A} for competitive adsorption between labeled and unlabeled chains at long times (independent of kinetics) and then using λ as the sole fitting parameter and measure of exchange kinetics.

Experimental Section

We employed silica glass microscope slides as the adsorption substrate, which constituted one wall of a thin rectangular flow channel with dimensions of 0.13 by 1.0 by 4.0 cm. Before the adsorption experiments, the glass substrate was treated by concentrated sulfuric acid for 15 h followed by flushing DI (deionized) water and pH 7 phosphate buffer to neutralize the surface. Analysis via XPS revealed that, after this treatment, the glass surface composition was primarily SiO_2.[20] Adsorption experiments were carried out by pumping polymer solution through the flow cell, and kinetics at the center of the surface were monitored by near-Brewster optical reflectometry and total internal reflectance fluorescence. A dilute phosphate buffer (1 mM phosphate composed of KH_2PO_4 and Na_2HPO_4 in a 1:4 molar ratio) was used as the solvent to stabilize the pH at 7.1. Wall shear rates in the range of 2.3−11.5 s^{-1} were used in the adsorption and exchange runs. (This gentle wall shear rate mediates the rate of chain arrival from the bulk solution to the interface but is too weak to alter the fundamental adsorption kinetics.[18]) Details of the flow cell assembly, cleaning, and experimental procedures have been described previously.[18]

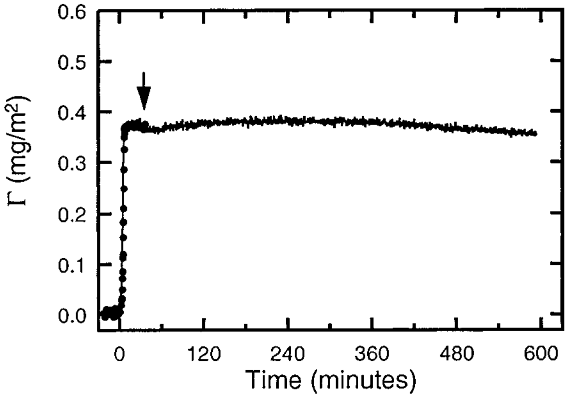

Figure 2. TIRF (line) and reflectivity (symbols) traces of 33K C-PEO adsorption from a 5 ppm solution and at a wall shear rate of 7.2 s^{-1}. The arrow indicates the time when the bulk solution was switched to buffer.

We employed a coumarin dye (7-(diethylamino)coumarin-3-carbonyl azide, purchased from Molecular Probes, Inc.) on one end of each labeled PEO chain to distinguish different interfacial populations. Details of the labeling reaction and sample purification procedures have been described before.[19] Coumarin was chosen because of its relatively low molecular weight (less than 300) and inclusion of some polar groups, which tend to reduce its hydrophobicity compared with other labels such as pyrene or anthracene. Also, the coumarin dye is neutral under the pH conditions we used,[19] thereby avoiding electrostatic interactions near the silica surface. The 33K and 120K molecular weight PEO was purchased from Polymer Laboratories with polydispersities of 1.02 and 1.03, respectively. The molecular weight distribution of each coumarin-labeled PEO (C-PEO) sample was compared with that of the corresponding native sample using gel permeation chromatography, and no significant change was detected.[19] The C-PEO 33K MW and 120K MW samples used in this study had labeling densities of 95% and 93%, respectively.

In the self-exchange kinetics studies, the evolution of the adsorbed C-PEO was tracked by TIRF, while the total surface mass was measured by reflectivity. Instrumental and calibration details for TIRF[20−22] and reflectivity[18] have been described previously. Figure 2 shows an adsorption and aging kinetic trace of 33K molecular weight C-PEO. Initially, 5 ppm polymer solution was flowed, and the adsorption rapidly reached its steady-state value. Then the adsorbed polymer layer was aged against pure flowing buffer for 10 h. During the aging process, the TIRF trace shows stable fluorescence signal from the layer, with only ~5% variation from instrumental drift. The stable TIRF signal indicates that there was no desorption or photobleaching of the labels during the long aging process. The reflectivity-based measurement of surface excess during the initial adsorption is also shown in Figure 2 and matches the TIRF adsorption curve exactly. Other reflectivity data, not shown here, confirmed identical adsorption kinetics and ultimate coverage levels for PEO and C-PEO.

To measure the binary adsorption isotherms from C-PEO/PEO mixtures (for the determination of K_{B-A} in eq 3), solutions with different relative amounts of C-PEO and PEO, and a total concentration of 5 ppm, were flowed through a clean adsorption cell. The adsorption of C-PEO was measured by TIRF, and the total adsorbed amount was measured by reflectivity. While it took less than 10 min for the initial fast adsorption of C-PEO to occur and for the total adsorbed amount to reach its plateau, the bulk solutions were flowed continuously up to 2 h to more nearly equilibrate. Reflectivity measurements showed no affect of bulk solution composition on the adsorption kinetics and the total adsorbed amount. The total surface excess on silica glass was found to be 0.37 ± 0.04 mg/m² for 33K PEO and 0.46 ± 0.05 mg/m² for 120K PEO. The bulk concentration of 5

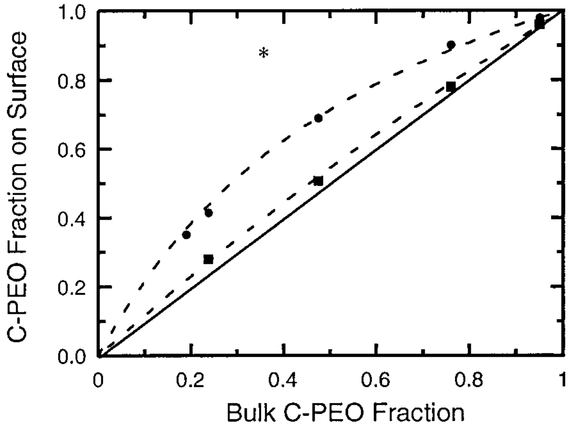

Figure 3. Binary adsorption isotherms from a 5 ppm mixed solution of C-PEO and PEO: (●) 33K and (■) 120K molecular weight. The star shows a data point from the deuterio- and protiopolystyrene (of ~550K molecular weight) binary adsorption system.[12] Dashed lines are eq 3 for $K_{\mathrm{C-PEO-PEO}}$ values of 2.5 and 1.2 for 33K and 120K molecular weights.

ppm was sufficiently high to be well on the plateau of the single species adsorption isotherm.[18]

Results

Binary Adsorption Isotherms. Figure 3 presents the equilibrium fraction of C-PEO on the surface as a function of the bulk solution composition, for a total bulk solution concentration of 5 ppm. While the total surface coverage was independent of the bulk solution composition, the surface fraction of C-PEO was always greater than that in the bulk solution, an effect that was more pronounced in the lower molecular weight sample.

The surface preference for PEO chains with a terminal coumarin tag represents a very slight difference in the adsorption free energy of the labeled and unlabeled chains, which can be quantified. Fitting eq 3 to the data reveals $K_{\mathrm{C-PEO-PEO}}$ values of 2.5 for the 33K molecular weight chains and 1.2 for 120K molecular weight chains. Using the definition of the equilibrium constant in terms of the Gibbs free energy of reaction (in this case the reaction of self-exchange), $\ln K_{\mathrm{C-PEO-PEO}} = -\Delta G_{\mathrm{C-PEO-PEO}}/RT$, one finds a difference in free energy (favoring labeled chain adsorption) of $0.9kT$ and $0.18kT$ per chain for chains of 33K and 120K, respectively. Figure 3 reinforces the remarkable fact that such small differences in adsorption energies can, with careful measurements, be detected experimentally. In Figure 3, the influence of chain length is in accord with expectations. With polymers adsorbing by their main backbone, the number of segment surface contacts per chain increases with molecular weight, reducing the relative contributions of the chain ends.

It is necessary to note that every labeling method has some degree of invasive effect on the polymer systems whose adsorption is being studied. As a point of comparison, in Figure 3 we include a datum from Granick's work[12] where protio- and deuterio-PS chains of 500K molecular weight underwent competitive adsorption on silica from CCl_4. The surface selectivity for deuterio-PS chains over protio-PS chains is greater than its preference for C-PEO over PEO. Fitting eq 3 through the single data point for the PSH/PSD pair reveals a $K_{\mathrm{PSD-PSH}}$ value of 17 and a $\Delta G_{\mathrm{PSD-PSH}}$ of $2.8kT$ per chain. In the PSH/PSD system, this energy difference is distributed among all the backbone segments while with coumarin-tagged PEO, the free energy difference results from one end group per chain.

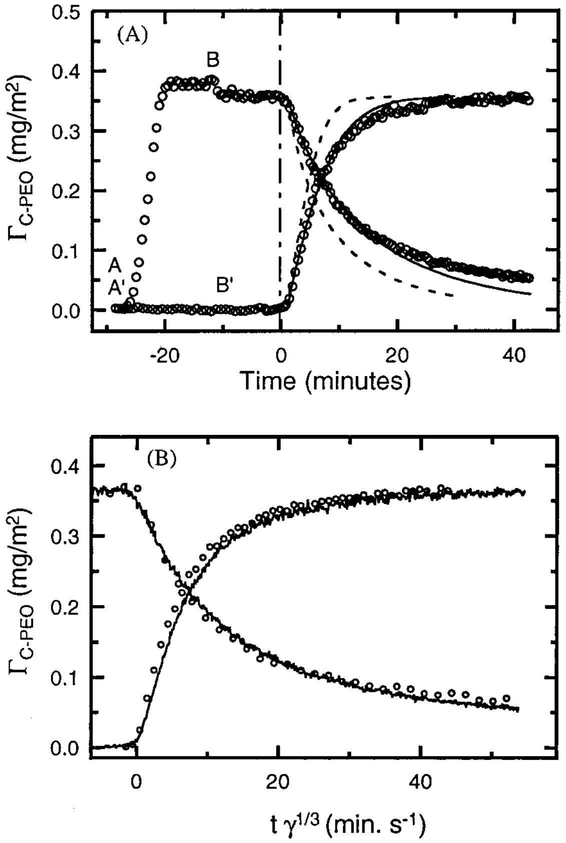

Figure 4. (A) TIRF kinetic traces (symbols) of C-PEO surface excess during the adsorption and self-exchange of 33K C-PEO and PEO chains from a 5 ppm bulk solution at a wall shear rate of 2.3 s^{-1}. In one sequence, C-PEO was preadsorbed between A and B, buffer was flushed after B, and PEO solution was flowed after time 0. In the other sequence, PEO was preadsorbed between A′ and B′, then buffer was flowed, and C-PEO solution was flowed after time 0. Dashed lines: kinetics predicted from eq 7 assuming bulk mass-transport control. Solid lines: kinetics predicted from eq 7 for surface exchange rate constants: $k_{\mathrm{ex}} = 1500$ cm^3 g^{-1} s^{-1} (for replacement of PEO by C-PEO) and $k'_{\mathrm{ex}} = 600$ cm^3 g^{-1} s^{-1} (for replacement of C-PEO by PEO). **(B)** Wall shear rate (γ) dependence of the exchange kinetics for the 33K C-PEO/PEO pair. Line, $\gamma = 2.3$ s^{-1}; ○, $\gamma = 11.5$ s^{-1}.

Self-Exchange in Relatively Young Adsorbed Layers. Figure 4 shows two types of exchange runs with 33K molecular weight PEO and C-PEO samples. In the first sequence, C-PEO was preadsorbed from a 5 ppm bulk solution and cultivated for 10 min against the same solution before a short rinse with buffer. Next, a 5 ppm PEO solution was pumped continuously through the flow cell and the displacement of the C-PEO monitored. In the other sequence, PEO was preadsorbed and rinsed according to the same procedure and later challenged by a 5 ppm C-PEO solution, whose incorporation into the adsorbed layer was monitored. In either sequence, only the behavior of the C-PEO is visible in Figure 4; however, reflectivity measurements (not shown here) confirmed negligible changes in the interfacial mass during both exchange sequences. In Figure 4B, both sequences are run at two different volumetric flow rates corresponding to wall shear rates of 2.3 and 11.5 s^{-1}. The time axis is scaled as $t\gamma^{1/3}$, which collapses the runs and argues that bulk mass transport is a major factor in determining the overall kinetics.[18,23,24]

In Figure 4A, the same data from the runs at 2.3 s^{-1} are compared with calculations. The dashed lines show the predictions of eq 7 with $\lambda = \infty$ and $K_{C-PEO-PEO} = 2.5$, representing the transport-limited case for this particular system. Notably, the observed self-exchange processes are slower than the transport limited rate (though we have independently confirmed that these same mass-transport-limited parameters accurately describe the adsorption behavior[18]). Also borne out by the explicit presentation of the transport-limited kinetic predictions is the skewed shape for the combined presentation of the forward and backward exchange reactions: The rate of C-PEO incorporation into a preadsorbed layer of PEO is expected, at the transport-limited rate, to exceed the displacement of C-PEO by PEO as a result of the surface selectivity for CPEO. The nonunity $K_{C-PEO-PEO}$ value of 2.5 for 33K molecular weight chains essentially says that the driving force for replacement of PEO by C-PEO is greater than that for the replacement of C-PEO by PEO. The kinetics for the former process are therefore faster than those for the latter. The experimental data show the same extent of skew as the transport-limited predictions in the first $^1/_2$ h of exchange. It is also worth noting that the transport-limited exchange rate is significantly slower and rounder in shape than the kinetics of the original adsorption, another result of the finite K values for exchange between C-PEO and PEO. To obtain exchange kinetics as rapid as those for the original adsorption, one requires $K = \infty$, a strong preference for the challenging chains.

Thus far, it is established that exchange occurs somewhat slower than the transport-limited maximum rate but still with significant influence of the mass transport rate. The kinetics can be quantified by fitting the initial part of the exchange traces to eq 7 for finite values of λ. The best fits corresponding to $\lambda = 2.3$ (and a $K_{C-PEO-PEO}$ value of 2.5) are shown as solid lines in Figure 4A. With $M = 2.4 \times 10^{-5}$ cm/s, this corresponds to $k_{ex} = 1500$ cm^3 g^{-1} s^{-1} (for replacement of PEO by C−PEO) and $k'_{ex} = 600$ cm^3 g^{-1} s^{-1} (for replacement by C-PEO by native PEO). The simple model gives an adequate fit to the data for the first 20 min of exchange, corresponding to about 80% of the original surface mass. The last chains to exchange out of the original layer do so at a rate that is slower than this first-order treatment, demonstrating the limits of analyzing complex systems with a model as simple as this one. Ultimately more complex models involving polymer physics must be developed.

The surface exchange rate constants from fitting the simple model to the data in Figure 4 can be compared with that obtained by Varoqui in self-exchange experiments of 360K molecular weight PS and radio-labeled PS, adsorbing on silica glass from carbon tetrachloride.[9] They obtained an exchange rate constant of 5 cm^3 g^{-1} s^{-1}, which is considerably slower than our values. This difference is likely a result of the differences in the ages of the adsorbed layers and polymers studied. The PS was of higher molecular weight and greater backbone stiffness than our PEO.

As an aside, it is worth pointing out that, in most tracer studies similar to those in Figure 4, other investigators typically run the exchange only in one direction (A replaced by B, but not vice versa). With such unidirectional experiments, it is easy to mistake the gradual displacement of a preadsorbed species, relative to its rapid initial adsorption kinetics, as the result of slow surface processes. Running the experiments forward and reverse and explicitly accounting for nonunity values of K (surface selectivity) ensures proper interpretation of the data. In our case this analysis provided hard proof that the surface rates for the young 33K PEO layers, while finite, are similar in magnitude to those of interfacial transport, and therefore the decay shapes are influenced by the surface selectivity. Also worth noting is that in quiescent test apparatuses running experiments in forward and reverse can be quite difficult, because the final surface composition will be a function of the ultimate bulk solution composition, which changes as the experiment progresses and is influenced by the ratio of available surface area to solution volume. There is, therefore, a distinct advantage to running kinetic tracer studies in a flow apparatus where the bulk solution composition is specified by the user and maintained at that level by continuous flow.

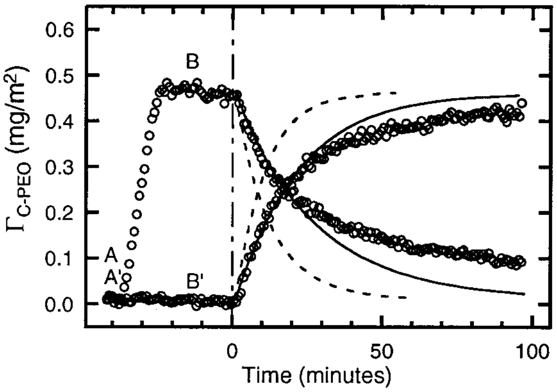

Figure 5. TIRF kinetic traces (symbols) of C-PEO adsorption and C-PEO behavior during self-exchange of 120K C-PEO and PEO chains from 2.5 ppm bulk solution at a wall shear rate of 7.2 s^{-1}. In one sequence, C-PEO was preadsorbed between A and B, buffer was flushed after B, and PEO solution was flowed after time 0. In the other sequence, PEO was preadsorbed between A′ and B′, then buffer was flowed, and C-PEO solution was flowed after time 0. Dashed lines: kinetics predicted from eq 7 assuming bulk mass-transport control. Solid lines: kinetics predicted from eq 7 for surface exchange rate constants: $k_{ex} = 600$ cm^3 g^{-1} s^{-1} (for replacement of PEO by C-PEO) and $k'_{ex} = 500$ cm^3 g^{-1} s^{-1} (for replacement of C-PEO by PEO).

Figure 5 illustrates self-exchange experiments similar to those in Figure 4A, but now focusing on PEO of molecular weight 120K. The observed self-exchange rates with 120K PEO are significantly slower than the predicted transport-limited behavior from eq 7, with $K_{C-PEO-PEO} = 1.2$ and $\lambda = \infty$. An important observation, however, is that at this higher molecular weight, with the K value closer to unity, both the predicted and observed exchange curves are less skewed than the results in for lower molecular weight PEO in Figure 4.

In Figure 5 the kinetic parameters giving the best fits to the self-exchange curves (with $K_{C-PEO-PEO}$ equal to 1.2) include an independently measured mass transport coefficient[18] of $M = 2.91 \times 10^{-5}$ cm/s, $k_{ex} = 600$ cm^3 g^{-1} s^{-1} (for replacement of PEO by C-PEO), and $k'_{ex} = 500$ cm^3 g^{-1} s^{-1}(for replacement of C-PEO by PEO). These rate constants are still more rapid than Varoqui's value for PS. Further, eq 7 applies only to the first 50% of the mass being exchanged. Beyond this time more detailed polymer physics are needed to explain the observed exchange kinetics, possibly including aging of (relaxations within) the adsorbed layer during the course of the exchange experiment.

Two conclusions are supported by the self-exchange studies in Figures 4 and 5. First, for young (10−15 min old) layers of PEO chains of moderate molecular weight, the interfacial chain dynamics are rapid but of finite time scale that can be distinguished from the transport-limited kinetics. Second, for PEO layers in this range of molecular weights and ages, though local equilibrium is not achieved, it is approached experimentally, as evidenced by the influence of the surface selectivity on the extent to which the forward and reverse kinetics appear skewed. The data in Figures 4 and 5 also suggest that some populations of adsorbed chains may be extremely tightly bound and resist exchange. These findings motivate a closer scrutinization of the influence of layer age on the interfacial dynamics and extent to which preadsorbed chains can be displaced by like chains.

Influence of Interfacial Age. In runs focusing on the aging of adsorbed layers, a self-exchange procedure similar to that for the young layers was employed. PEO chains were preadsorbed until the steady-state coverage was achieved, and the layer was cultivated in the same polymer solution for another 10−15 min. After that, pure solvent (buffer) was gently flowed over the layer (at a wall shear rate of 7.2 s^{-1}) as the layer was further aged, prior to being challenged with labeled chains. The incubation time in pure solvent was systematically varied, and both forward and reverse exchange experiments were run.

Aging in pure solvent rather than continued cultivation in the original polymer solution eliminates two concerns: (1) Prolonged contact of the surface with continuously flowing polymer solution will lead to significant molecular weight-driven exchange[19] which would significantly increase the *average* molecular weight of the adsorbed chains above those in the solution. Even with the narrow molecular weight samples employed here, the samples may contain some chains that are more than a factor of 2 longer than others. Though the continuous adsorption of this high molecular weight population will be slow because of its low concentration, at long cultivation times it has the potential to dominate the surface. Since, in other systems, chain length was an important factor contributing to interfacial relaxation rates,[10−13] and since the amount of longer chains transported to the surface will vary with the extent of aging, care must be taken to avoid artifacts when attempting to determine the interfacial relaxation rate and the influence of molecular weight on interfacial dynamics. (2) Continued exchange between the bulk solution and the surface will lead to layers with significantly different average chain residence times (and therefore different extents of relaxation) than those aged in solvent.

In Figure 6, TIRF data illustrate the influence of aging in pure solvent on the self-exchange kinetics of 33K PEO chains. In Figure 6A, preadsorbed C-PEO is displaced by PEO, and in Figure 6B, C-PEO incorporates into a layer of preadsorbed PEO, displacing the PEO which is invisible to TIRF. (Parallel Brewster reflectivity studies confirmed that self-exchange occurred at constant total interfacial mass for all runs.) The results show that as the preadsorbed layers age, relaxations change the states of the layers, making subsequent exchange processes slower. After approximately 10 h, further aging appears to have no additional effect on the self-exchange process, though it is not clear that 10 h old layers are truly equilibrated.

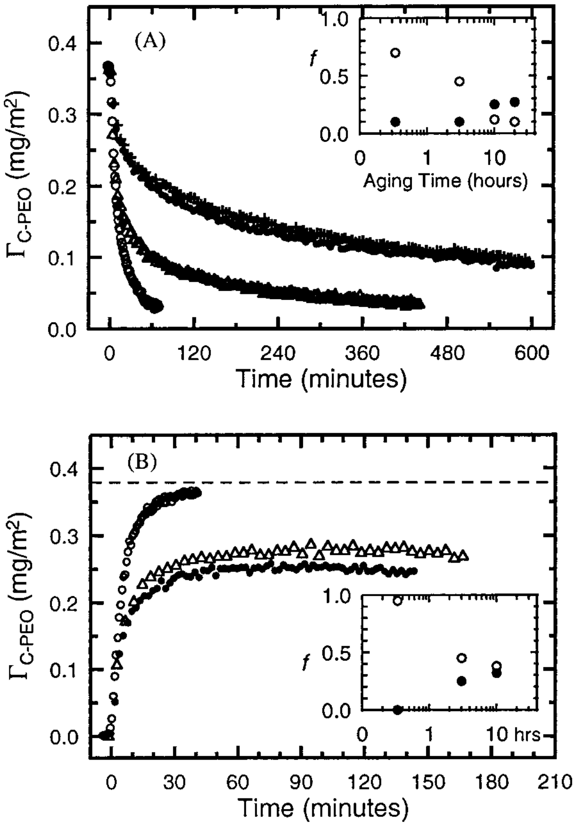

Figure 6. (A) Displacement kinetics for 33K C-PEO layers of different ages when challenged by 5 ppm of 33K PEO at a wall shear rate of 7.2 s^{-1}. Layer ages are (○) 20 min, (△) 3 h, (●) 10 h, and (+) 20 h. Inset: (●) fraction of original chains trapped on the surface after 10 h of exchange; (○) original chain fraction which followed eq 7 fit to the initial decay. **(B)** Kinetics for the incorporation of C-PEO (33K, 5 ppm, wall shear rate of 7.2 s^{-1}) into preadsorbed 33K PEO layers of different ages. Symbols for layer ages are the same as (A). Inset: (●) deviation of ultimate C-PEO coverage from pure species equilibrium coverage; (○) original chain fraction which followed eq 7 fit to the initial rise.

In Figure 6, the shapes of the individual curves suggest several stages for the kinetics of the self-exchange. Regardless of layer age, self-exchange begins with an age-independent rapid replacement of some preadsorbed C-PEO by PEO or a rapid (approaching but not quite reaching the transport-limited rate) incorporation of C-PEO into the preadsorbed PEO layer. This persists for about 10 min. The self-exchange kinetics then go through a transitional stage with a duration between 10 min and 2 h, depending on the layer age. The final stages of self-exchange are extremely age dependent: The displacement of C-PEO follows exponential decay (not shown), while the incorporation of C-PEO into a preadsorbed PEO layer is incomplete with some native PEO appearing to permanently block C-PEO incorporation. This multistage process for self-exchange suggests that adsorbed chains experience different interfacial states: some are loosely bound and others are more tightly bound. Furthermore, the dynamic equilibrium between tightly and loosely bound interfacial states is sufficiently slow that some tightly bound chains appear permanently retained.

The fraction, *f*, of preadsorbed C-PEO chains resisting displacement by native PEO after 10 h is summarized

Table 1. Summary of the Effect of Aging on Self-Exchange Kinetics[a,b]

	33K PEO				120K PEO			
aging time (h)	0.33	3	10	20	0.5	1.5	3	10, 20
k_{ex} (C-PEO replace PEO), cm^3 g^{-1} s^{-1}	600	600	600	600	500	309	50	∞
k'_{ex} (C-PEO replace PEO), cm^3 g^{-1} s^{-1}	1500	1500	1500	1500	600	371	59	∞
exponential time constant (min)	42	483	803	828	132	465	1290	∞

[a] Surface exchange rates determined from best fit of the initial decay or rise to eq 7. [b] Exponential time constant determined from best fit of exponential form to long time decay.

by the solid points in the inset of Figure 6A. Another way to interpret the self-exchange data was to fit the initial stages of the exchange to eq 7. The resulting surface exchange rate constants are summarized in Table 1. As eq 7 did not describe the entire self-exchange process, the fractional coverage that could be described by eq 7 is summarized by the hollow circles in the inset in Figure 6A. (The portion of the exchange process deviating from eq 7 is significant in that these chains may be more entangled or tightly bound.) Therefore, as the aging time increases, the immobile fraction increases, possibly as a result of greater segment−surface contacts and entanglements, and the applicability of the simple kinetic model decreases.

In Figure 6B the incorporation of C-PEO chains into a preadsorbed layer occurs at a significantly faster rate than the C-PEO displacement by PEO in Figure 6A. As already discussed for Figure 4, the difference in initial kinetics results from the difference in adsorption driving forces as a result of $K_{\text{C-PEO-PEO}} = 2.5$. Even for layers that have undergone significant relaxation, the more loosely bound exchangeable chains see this influence of the end group. It is significant that in Figure 6B the incorporation of C-PEO into the mature PEO layers is fairly incomplete and quickly reaches a finite steady-state value, in contrast to the exponentially slow displacement of C-PEO in Figure 6A which continues for long times. (The extent to which C-PEO adsorption was incomplete relative to its coverage on a bare surface is shown in the inset of Figure 6B, as a function of the age of the preadsorbed native PEO layer.) We also fit the initial data to eq 7 and summarize the exchange rate constants in Table 1. The portion of the layer not described by eq 7 is summarized in the inset in Figure 6B.

The effects of mild polydispersity must be considered as part of the explanation for the (premature?) leveling off of the C-PEO incorporation in Figure 6B. It is well-known that long chains are entropically favored on a surface over short chains of the same chemistry. One must also accept that, even in carefully prepared narrow molecular weight standard samples with polydispersities of 1.1 or less, there exist significant populations of chains differing by a factor of 2 in length. In the 10 h long continuous flow self-exchange experiments of Figure 6, when C-PEO challenges a PEO layer, the longest C-PEO chains may displace an equal mass of shorter C-PEO chains, reducing the overall interfacial fluorescence and causing the exchange process to appear prematurely truncated, as in Figure 6B. We have confirmed the possibility of such effects by measuring the long-time fluorescence evolution from C-PEO adsorbing on a bare surface for long periods of time. This case exhibits a gradual decrease in fluorescence over several hours. (Such a decay was not observed in Figure 2 because here solvent, not polymer solution, was flowed over the layer for several hours.) In the reverse process when native PEO chains challenge preadsorbed C-PEO chains, any replacement of short PEO chains by longer ones is not directly apparent in the fluorescence signal. Therefore, we believe the long-time shape of the decay for replacement of preadsorbed C-PEO by unlabeled PEO better represents the actual self-exchange decay. Even with narrow molecular weight samples, polydispersity effects cannot be avoided, and care must be taken not to overinterpret the long time shape of the self-exchange kinetics. More important is the influence of layer aging time on the self-exchange.

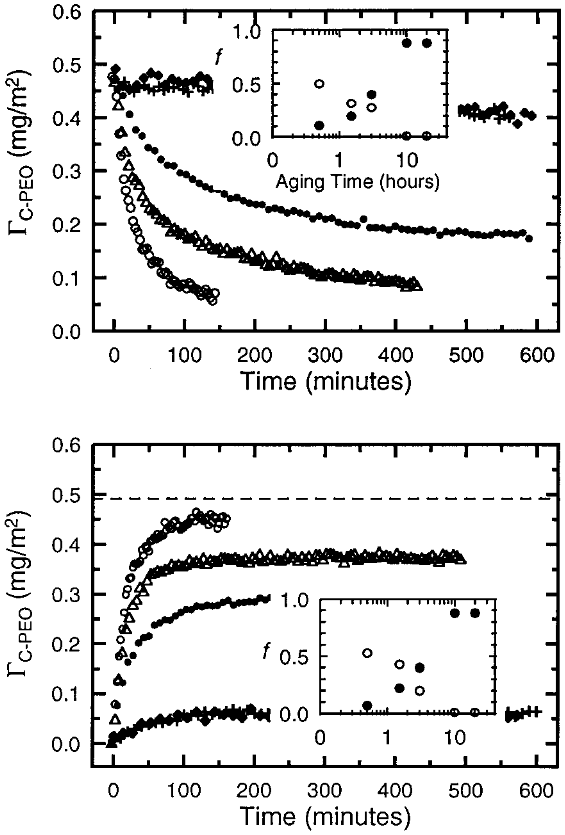

Figure 7. (A) Displacement kinetics for 120K C-PEO layers of different ages when challenged by 2.5 ppm of 120K PEO at a wall shear rate of 7.2 s^{-1}. Layer ages are (○) 30 min, (▲) 1.5 h, (●) 3 h, (+) 10 h, and (◆) 20 h. Inset: (●) fraction of original chains trapped on the surface after 10 h of exchange; (○) original chain fraction which followed eq 7 fit to the initial decay. **(**B**)** Kinetics for the incorporation of C-PEO (120K, 2.5 ppm, wall shear rate of 7.2 s^{-1}) into preadsorbed 120K PEO layers of different ages. Symbols for layer ages are the same as (A). Inset: (●) deviation of ultimate C-PEO coverage from pure species equilibrium coverage; (○) original chain fraction which followed eq 7 fit to the initial rise.

The influence of layer age on the self-exchange rate for 120K molecular weight C-PEO displaced by PEO is shown in Figure 7A. The reverse experiments are shown in Figure 7B. The insets in Figure 7A,B are similar to those in Figure 6. Like the observations for 33K PEO, it appears that the influence of interfacial relaxations on the self-exchange dynamics occurs within the first 10 h of interfacial aging, beyond which time the layers have reached a metastable if not equilibrium state. In the mature state, almost all the preadsorbed chains are extremely tightly bound and resistant to displacement by incoming PEO chains. Mature preadsorbed layers are also quite effective at preventing the adsorption of new PEO chains, as shown in Figure 7B. Note that the slight signal increase of 0.05 mg/m^2 for C-PEO incorporation into the oldest layers in Figure 7B corresponds to fluorescence background and some chains that are so loosely bound that they desorb when solvent is reintroduced. This feature is not apparent in Figure 7A because it occurred at the beginning of the aging step. The presence of these extremely loosely bound (desorbable) chains, shown in Figure 2, was seen for a variety of layer ages and molecular weights as discussed in ref 18. These desorbable chains are distinctly different from the "loosely bound" layer which self-exchanges but is resistant to desorption. The latter have greater interactions with the surface.

In Figure 7, the shapes of the individual self-exchange kinetic curves are qualitatively consistent with those in Figure 6. The initial shapes of the self-exchange curves are less skewed than in Figure 6, as is consistent with the more near-unity value of $K_{\mathrm{C-PEO-PEO}}$ at higher molecular weights. We believe the faster long-time turnover of Figure 7B relative to Figure 7A is an effect of chain length variations within the C-PEO sample, not the invasiveness of the coumarin tag. Like the lower molecular weight chains, 120K PEO appears to under go a multistep exchange process with some influence of transport in the early stages of exchange and an extremely slow exponential process at long times, ultimately revealing a population that is irreversibly bound (for as long as we were willing to wait) and exclusion of some chains from the bulk solution. The rate constants for the exponential fit to the C-PEO displacement curves in Figure 7A are tabulated in Table 1, for comparison with those of the 33K molecular weight sample.

Discussion

Table 1 summarizes the influence of molecular weight and layer age on the kinetics of self-exchange. For 33K molecular weight chains, the initial stages of self-exchange were described by rapid transport-influenced kinetics where it was difficult to distinguish any influence of layer age on the initial surface rate constant, perhaps because of loosely bound chains that were extremely mobile, independent of layer age. Beyond the initial transport-influenced exchange, the displacement of C-PEO by native PEO became increasingly slow with layer age, up to about 10−20 h. For the higher molecular weight 120K samples, the initial kinetics were also transport-limited, but any loosely bound populations were less mobile, such that there was an observable effect of layer age on the initial self-exchange kinetics. At long times, the displacement of C-PEO by native PEO was adequately described by single-exponential kinetics, with the exchange time constant, summarized in Table 1, becoming infinitely slow beyond 10 h of aging (representing layers that did not significantly self-exchange.) A stretched exponential fit was inadequate to described the overall self-exchange kinetics.

Our results show that the self-exchange process between adsorbed and free chains becomes slower with increased layer incubation in *solvent*. This is most likely due to an increase in the number of segment−surface contacts as a result of interfacial relaxations and may also involve the development of interfacial entanglements. Other investigators studying chain mobility have raised the issues of trapping of one population of chains by another, especially when the incoming chains are more strongly adsorbing than those within a preadsorbed layer. In such instances, overshoots in the total interfacial mass sometimes occur:[11,25] The invading chains attach to the interface, rapidly achieving their steady-state coverage, and the preadsorbed chains must find their way out of the layer. The case of PEO self-exchange shows no evidence (overshoot) for trapping of preadsorbed chains by incoming chains. Indeed, all the self-exchange processes presented here proceeded at fixed interfacial mass, such that incoming and desorbing chains traded places.

Our results, especially those with the 33K chains, suggested that at an interface there exist distinct populations of chains with different extents of entanglements or binding energies with the surface. While this is to be expected, one might also expect that the chains sampling various interfacial states would change from one state to another on a relatively rapid time scale. In contrast, our findings suggest that tightly and loosely bound interfacial populations are distinct and long-lived: When loosely bound labeled chains are replaced by native PEO, the local equilibrium at the interface does not rapidly shift to generate more loosely bound labeled chains at the expense of those that are tightly bound (and the simultaneous tightening of the newly incorporated unlabeled chains may not to occur completely.) Instead, the tightly bound labeled chains are the last to self-exchange off the surface, regardless of any self-exchange between loosely bound chains and the bulk solution. Such a scenario was also found for cationic polyacrylamides adsorbing on polystyrene latex,[26] and recently Granick's polarized IR studies of PMMA[27] argue in favor of persistent tightly bound interfacial states.

Some interesting contrasts become apparent when the PEO self-exchange data are compared with Granick's results.[11−13] This comparison must be made with caution, because the experimental protocols were slightly different: Our PEO layers were aged in pure solvent while Granick's layers were incubated in their respective adsorbate solutions. The latter provided greater opportunity for selective adsorption of the longest chains, a significant effect even with narrow molecular weight standard samples. Our exchange process proceeded in continued flow, maintaining a zero bulk solution concentration of the desorbing species but allowing the effects of mild polydispersity to alter the shapes of decay curves. Granick's self-exchange process employed a bulk reservoir in which the desorbing chains accumulated.[11−13,15,25] Though their concentration was extremely low, Fleer has predicted that important competitive effects may occur with extremely dilute free solution concentrations of some polymeric species.[14]

Most remarkable, we see that, over the 10−20 h aging period of PEO layers, the interfacial mobility of PEO undergoes a very dramatic change: from the extremely mobile condition where young layers self-exchange near their transport-limited rate to the extremely immobile condition where hardly any exchange is observed. In contrast, Granick's self-exchange studies[11,13] with PS from cyclohexane on silica revealed that young layers were moderately mobile with strongly surface-influenced kinetics, while older layers were almost completely immobile. We both agree that molecular weight has a profound influence on the kinetics of self-exchange; however, Granick found that the interfacial relaxation rate was strongly dependent on molecular weight. Though our studies are not as extensive, we see that both 33K and 120K chains are completely relaxed (within our ability to detect such relaxations) within 10−20 h of contact with pure solvent. Finally, while Granick was usually able to fit exchange data with exponential[11,13] or stretched exponential forms,[15,28] such simple treatments are inadequate for our data: We find that a model which includes bulk transport is required to describe the short-time exchange data. Further, we are slightly cautious about fitting the long-time exchange decays to single-exponential forms because of the potential for the influence of chain length effects.

The method of self-exchange as a means to probe the dynamic spectra of adsorbed layers and interfacial populations is not a perfect approach and brings several complexities, relevant to our work and to that of other groups using the method. Ideally, a self-exchange experiment should be short compared with the evolution time of the layer, such that the exchange experiment presents a snapshot of the dynamic state of the layer at a particular age. If the exchange experiment itself is long-lived compared with the rate of layer aging, the assumption of k_{ex} and k'_{ex} being constant breaks down. More complex still is the issue of whether the self-exchange process perturbs the state of the layer. For instance, a layer maturing in pure solvent without significant amounts of chains in bulk solution would be expected to have an increasing number of segment−surface contacts and entanglements as its age increased. Exposing an old layer to a solution of new chains for the purpose of self-exchange may replace the old chains, with many segment−surface contacts, by newer chains with fewer segment surface contacts, thereby rejuvenating the layer. In the work presented here, our protocol has been to age preadsorbed saturated layers in pure solvent, to minimize the potentially rejuvenating effects of self-exchange during layer maturation. Studies of layers aged in polymer solutions of varying concentrations are forthcoming. Because of the complexity of the issues of rejuvenation and continued aging during self-exchange, the model presented here is intended as a means of benchmarking the observed processes against simple transport limitations and a crude kinetic model for the surface. The initial kinetics for a self-exchange process are expected to be free of both potential problems and provide some indication of the layer state at the start of self-exchange. To our knowledge, other investigators using self-exchange have not addressed the issue of rejuvenation or continued aging during self-exchange.

Conclusions

This work probed the interfacial states in adsorbed PEO layers on silica through the self-exchange of coumarin tagged and native analogues. It was demonstrated that this method for self-exchange is less invasive than more conventional deuteration techniques. New evidence for nonequilibrium interfacial behavior was presented, when all prior studies (to our knowledge) supported local equilibrium for adsorbed PEO. Though it had been previously argued that PEO should maintain local interfacial equilibrium due to its great backbone flexibility and low T_g, we find that entanglements or high numbers of segment−surface contacts can be equally important in trapping chains on surfaces. Interfacial “glasses” can occur for systems where bulk (solution or melt) states are not glassy.

For the specific chemical system of PEO adsorbing on silica from aqueous solution, we find that interfacial relaxations occur within the first 10 h of adsorbed layer incubation in pure solvent. Additional relaxations may occur beyond this time; however, such additional interfacial evolution is not detectable by self-exchange on a reasonable experimental time scale. Self-exchange in aging and mature PEO layers appears to occur in two stages: a fast stage that is slightly slower than the transport limit and a slow stage whose kinetics approach an exponential form. Self-exchange was generally incomplete, often revealing a population of chains whose attachment to the surface appeared irreversible. These features of the self-exchange kinetics support a picture of the interface that contains loosely bound chains that cannot desorb in pure solvent but are in dynamic equilibrium with like molecules. Additionally, chains exist that undergo slow exchange with the bulk solution. And finally, some chains appear not be removed from the surface. The transition of individual chains from one population to another must be fairly slow, because these populations can be distinguished during self-exchange experiments which are themselves quite long.

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