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Energy Barrier to Self-Exchange between PEO Adsorbed on Silica and in Solution

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ABSTRACT: This investigation sought to reveal the dynamic mechanism for self-exchange between an adsorbed homopolymer layer and chains in free solution, employing poly(ethylene oxide) (PEO) adsorbed on silica from aqueous solution as a model system. Fluorescence tracer studies of individual populations within a saturated adsorbed layer revealed no dynamic distinctions between those chains which reached the interface early or late during the initial layer preparation. This observation ruled out the explanation of trapped and mobile subpopulations for bimodally shaped self-exchange kinetic traces. Studies focusing on chains aged in unsaturated or starved layers revealed faster self-exchange rates compared with chains aged in saturated layers. Surface coverage was found to be more important than molecular weight in controlling the exchange rate. Taken together, these results ruled out the number and strength of segment−surface contacts per chains as the determining kinetic factor in exchange dynamics. Interactions between neighboring chains were shown to be extremely important; however, if classical melt-type entanglements played a role, they did so only at extremely high molecular weights, above 112K. The osmotic barrier posed by loops and tails of the existing layer (present only at moderate and high surfaces coverages) to approaching chains from solution was thought to provide a substantial kinetic barrier to the approach chains from solution.

Introduction

Adsorbed polymers play critical roles as colloidal stabilizers in paints and coatings, as flocculants for wastewater treatment and papermaking, or as lubricants and surface modifiers. Much attention has been paid to the relationship between molecular architecture and interfacial structure to develop polymers of appropriate composition for particular applications. The equilibrium concentration profile of a homopolymer layer, with loops and tails extending into solution and trains near the surface, is understood to be an exponential decay according to mean field theory[1] or a power-law decay with an exponent of $-^4/_3$ from scaling theory.[2] The structure of adsorbed or grafted brushes is equally well understood.[3] Little is known, however, about the interfacial dynamics of polymer layers, even for the least chemically complex situation of adsorbed homopolymers.

It is generally accepted that, after a layer's mass is established in the initial stages of adsorption, chains within a layer relax in ways that make them more difficult to remove from the surface.[4] Experiments have also revealed extremely slow dynamics when homopolymer layers are exposed to stimuli, such as changes in the bulk solution composition.[5] Long chains are more sluggish than short chains, as expected.[6] The mechanistic details involved in layer relaxation are, however, poorly understood since the exact structural changes occurring in a relaxing layer have not been quantified. Without an understanding of the mechanism, it is impossible to identify a rate-limiting step for a layer's relaxation or response to stimuli and therefore impossible to develop predictive treatments for kinetics of chains in layers. The current work therefore aims to identify the rate-limiting step for one type of layer dynamic: the exchange of chains between an adsorbed layer and free solution.

In self-exchange experiments, a tracer (deuteration or a fluorescent label) distinguishes initially adsorbed chains from those free in solution. Time-resolved measurements of the adsorbed labeled population elucidate the exchange between the surface and chains in free solution. Such tracer studies with poly(styrene) adsorbing on silica from a Θ solvent revealed characteristic times that were exponential in molecular weight.[6,7] This result was interpreted to suggest that the rate-limiting step for exchange was the breaking of segment−surface contacts as invading chains replaced those originally on the surface.[6,7] Specifically, the energy barrier to exchange was anticipated to be proportional to the number and strength of such contacts.[7] Self-exchange for polystyrene in a good solvent was observed to be so much slower than that at Θ conditions that quantitative forms for the kinetics were unclear.[8] One possible reason, in our view, for slower exchange in a good solvent is the osmotic barrier posed by loops and tails of the initially adsorbed layer to incoming chains. Finally, bimodally shaped exchange kinetics have caused speculation by different groups that distinct interfacial populations exist in kinetically trapped layers, giving rise to unusual exchange kinetics.[7−10] Spectroscopic evidence for long-lived interfacial populations was recently found for poly(methyl methacrylate) adsorbed onto silica from carbon tetrachloride,[11] but the observation has not been directly linked to bimodal kinetics.

Our lab is interested in identifying factors that dominate the interfacial dynamics of adsorbed homopolymers. Therefore, we wish to determine the extent to which the kinetic forms and molecular weight dependences reported for polystyrene in organic solvents[6,7] are universal for other polymer/solvent/substrate combinations. A lack of universality would suggest that different rate-limiting steps lead to different kinetic behaviors, depending on the chemical details. Also of

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Table 1. Properties of PEO

molecular weight	10K	32K	112K	460K
polydispersity	1.03	1.02	1.02	1.06
Γ_{sat}, mg/m^2	0.35	0.40	0.47	0.62
D, cm^2/s	7.0×10^{-7}	3.5×10^{-7}	1.9×10^{-7}	9.4×10^{-8}
M, cm/s (ref 15)	5.4×10^{-5}	3.4×10^{-5}	2.3×10^{-5}	1.4×10^{-5}

interest is the extent to which relaxation functions measured indirectly in colloidal systems[5] accurately represent the fundamental dynamics of a polymer at a single interface. Our studies therefore directly probe an adsorbed layer and carefully control the adsorption history, particularly the rate of chain arrival to a single interface during adsorption and exchange.

Our model polymer, poly(ethylene oxide) (PEO), derives industrial and biomedical utility from its water solubility and the hydrogen bonds it forms with solid substrates such as silica. Its adsorption strength per segment, χ_s, is about 1 kT on silica.[12] Water is a moderately good solvent for PEO with χ in the range 0.45−0.48.[13,14] The binding isotherm for aqueous PEO on silica is flat with coverage independent of concentration.[15] This is expected for homopolymer adsorption[16] and consistent with the observation of minimal desorption of PEO chains into water at long times.[17] PEO adsorption is sufficiently strong to appear irreversible, similar to the behavior of PS on silica in organic solvents, where χ_s is about 2 kT in cyclohexane and 1 kT in carbon tetrachloride.[7,8] Both PEO and PS are known to be reversibly bound on silica because exchange is observed between the adsorbed layer and chains in free solution.[6,7,18]

Unlike PS, PEO self-exchange kinetics were found to be linear,[19] not exponential in molecular weight. After initial adsorption, PEO layers approached their mature (fully relaxed or kinetically jammed) states in the form of exponentially decaying kinetics, but the time constant for higher molecular weights was shorter such that longer chains appeared to age the most quickly. More precisely, long chains more quickly reached an immobilized state, which was not likely to have been equilibrated, since the final state itself was highly immobile. In contrast, mature layers of low molecular weight chains were mobile and therefore more likely to have reached full equilibrium.[19]

The current paper follows a communication concerning self-exchange in PEO layers, where certain populations had been aged at coverages less than the equilibrium coverage.[20] The prior results suggested that coverage, not molecular weight up to 112 000, was the sole parameter influencing the characteristic exchange time. The present work more closely investigates this observation, expanding the molecular weight range to assess the different potential mechanisms for interfacial motion and the role of kinetically trapped populations, which may have been set up during the initial deposition of the layer.

Experimental Section

The properties of the narrow molecular weight standard PEO, from Polymer Laboratories, are summarized in Table 1. Attachment of a coumarin tag (7-(diethylamino)coumarin-3-carbonyl azide, Molecular Probes) to the single hydroxyl terminus of each chain, per established procedures,[18,20] facilitated fluorescent tagging for tracer studies. Because the fluorescent yield of coumarin is only moderate and because fewer chain ends were available on long chains (per unit mass of polymer), a brighter label, fluorescein, was employed for the highest molecular weight sample, 460K. Labeled PEO is denoted CPEO regardless of its label. We have shown that both labels are minimally invasive, contributing only 0.9 kT of adsorption energy per chain for the 10K sample and having no measurable affect for the 460K sample.[19] With the lower molecular weight samples, the increased adsorption energy from the label causes the surface to be selective for labeled chains; however, there is no effect of the labeling on the adsorbed amount or the intrinsic kinetics.[18,19]

The evolution of the total surface excess was measured using near-Brewster optical reflectometry,[15] while the adsorbed amounts of labeled chains were measured with total internal reflectance fluorescence (TIRF).[18,21] Both techniques have been described previously. Adsorption onto the silica surface of an acid-etched microscope slide was measured from gently flowing pH 7 phosphate buffer in a slit shear cell. Control of the pH near 7 maintained a constant density of nondissociated surface silanols, to which the ether oxygens of the PEO backbone hydrogen bond, facilitating adsorption. The wall shear rates were sufficiently gentle (5 s^{-1}) to set up a well-defined concentration gradient near the interface, mediating the rate of chain arrival without perturbing or stretching the adsorbing polymers. The flow chamber,[15,21] the acid treatment of microscope slides,[15] fluorescent labeling,[18,21] and quantification of the influence of the fluorescent label[18,19] have been documented.

Results

Interfacial Populations. Population studies were conducted to determine whether chains arriving early to a surface during adsorption are dynamically different from those incorporated later. Figure 1A shows the experimental scheme for the 10K molecular weight sample, with the kinetics in run 1 for a fully saturated layer. Adsorption begins at time zero, shortly after a valve turnover which switches the flow cell contents from flowing buffer to flowing buffered PEO solution at a concentration of 1 ppm and a wall shear rate of 5 s^{-1}. The adsorption rate is constant up to saturation,[15] conforming to the Leveque solution for transport limited adsorption from laminar flow through a slit-shear flow cell.[22] These dilute conditions were employed to accomplish slow layer deposition so that the composition of the interface could be carefully controlled by the timing of valve turnovers.

Run 2 in Figure 1A shows the procedure for depositing a layer where the first 28% of the adsorbed chains are labeled and the last 72% are unlabeled. Run 2 begins like run 1, with introduction of a buffered CPEO into the flow cell. After 400 s the bulk solution is switched to unlabeled PEO, which continues to adsorb, making up the remainder of the layer. The addition of the unlabeled chains to the interface is not seen in run 2 because, with TIRF, the unlabeled chains are invisible. Hence, beyond 400 s, the signal is flat even though the unlabeled chains continue to adsorb. In run 2, at 1400 s when the surface should be saturated (based on the kinetics observed in run 1), the flow is switched to pure buffer. This prevents any displacement of adsorbed PEO or CPEO by self-exchange. If we had continued to flow the PEO solution beyond 1400 s, then the CPEO would begin to be displaced and the fluorescence signal would decay.

Run 3 in Figure 1A shows the procedure for depositing a layer where the first 72% of the adsorbed chains are unlabeled, and the last 28% are labeled. Here, at time zero, a flowing solution of PEO is introduced. No change in signal results because unlabeled chains do not affect the TIRF signal. At 1000 s, the flow is switched to CPEO, which is allowed to adsorb for 400 s, giving a completely saturated surface, based on the full kinetics

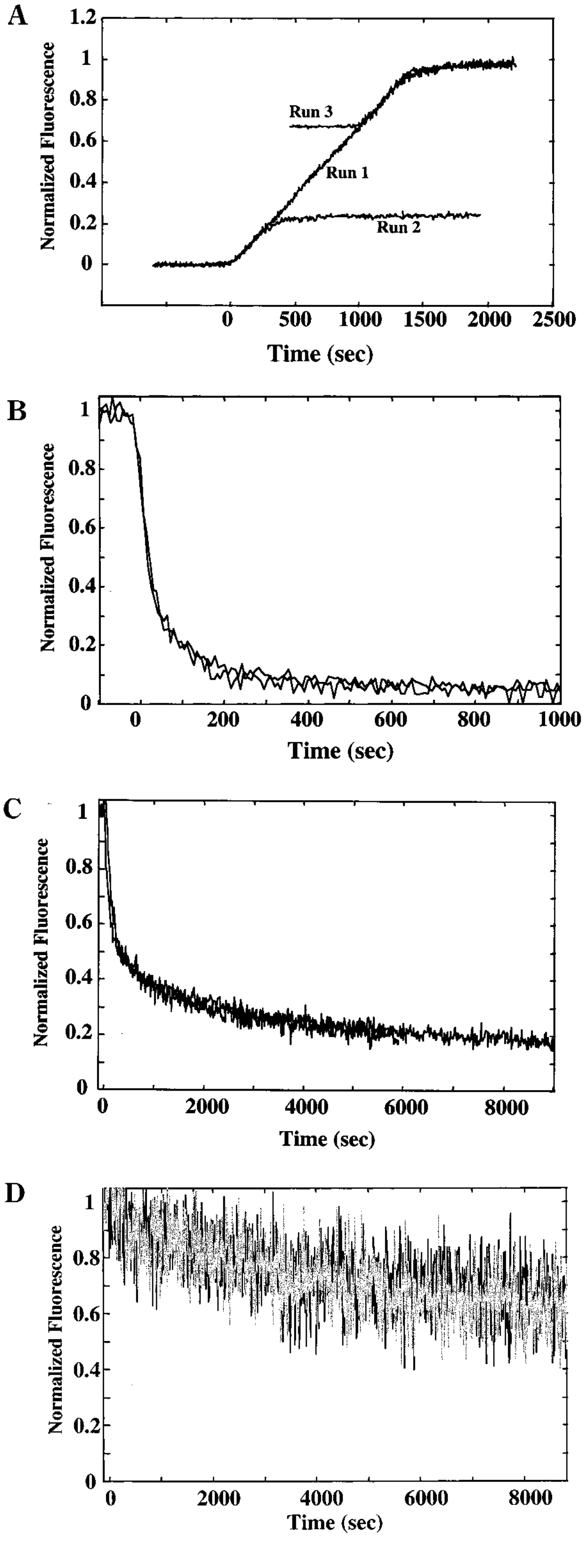

Figure 1. (A) Example adsorption history, with 10K sample, to achieve layers whose early or late arriving populations are labeled. Run 1 shows evolution of the entire layer. Runs 2 and 3 show deposition of early and late arriving labeled populations, respectively. The bulk solution concentration is 1 ppm, and the wall shear rate is 5 s^{-1}. (B) Normalized exchange traces of early and late arriving CPEO 10K populations. (C) Normalized exchange traces of early and late arriving CPEO 32K populations. (D) Normalized exchange traces of early and late arriving CPEO 112K populations.

shown in run 1. At this point the flow is switched to pure buffer to prevent displacement of preadsorbed PEO by the CPEO in bulk solution. In Figure 1A, the entire curve for run 3 is shifted up so that the CPEO adsorption kinetics during the last 28% of the layer deposition superpose with run 1, to illustrate the consistency of the adsorption procedure.

After the layers were deposited, they were exposed to gently flowing buffer for 4 h. During this time, the layers relaxed and became more tightly bound to the surface. Our previous work with PEO layers adsorbed on silica has shown that layers may relax or reconfigure for as long as 16 h following the initial deposition of interfacial mass, depending on molecular weight.[19] Therefore, the 4 h relaxation time in Figure 1A, during which the layers were exposed to flowing buffer, was generally not sufficient for complete maturing of the adsorbed layers.

After this 4 h relaxation time, the layers were exposed to a flowing 100 ppm PEO solution at a wall shear rate of 5 s^{-1}, initiating self-exchange. Figure 1B shows the self-exchange phase of the runs, comparing the fluorescent signal decays for runs 2 and 3. The two traces superpose almost exactly, demonstrating that there is no significant difference between the displacement kinetics of populations incorporated early or late during layer deposition. The same holds true for the other molecular weight samples tested, 30K and 112K in parts C and D of Figure 1, respectively. (We were unable to conduct this study with the highest molecular weight sample, 460K, because the signal was too weak to permit observations of populations within the layer.)

There is no evidence, based on the self-exchange dynamics in Figure 1, that interfacial populations develop based on the chain sequence during adsorption. This observation is particularly interesting in light of the fact that the 4 h relaxation period was insufficient for complete layer equilibration.

The equilibrium state of an adsorbed homopolymer layer should have no interfacial populations that depend on adsorption history. Rather, an equilibrium layer will contain chains in a wide variety of configurations, where the number of segment–surface contacts, loop size, and tail extension, for example, vary as described by a Boltzmann distribution. In such a layer, some chains will be more readily displaced than others during self-exchange. Even so, the resulting distribution of self-exchange probabilities should be independent of adsorption history. One might imagine then that kinetically trapped layers or those still evolving toward equilibrium might possess distinct populations, which have been locked in at the time of adsorption. For the case of PEO on silica, however, we see no such populations, even though the adsorbed layers are not completely mature. As an aside, we note that such populations may exist in younger layers and, if they exist, are short-lived. This possibility is left to future work.

The presence of distinct interfacial populations based on adsorption history has been speculated in many instances because of the observation of bimodal exchange kinetics.[7–10] Such populations have, in fact, been measured spectroscopically in one instance[11] but not linked to bimodal kinetics. The self-exchange kinetic decays in Figure 1–1D can also be classified as bimodal, with exchange at short times described by a first-order surface reaction in series with diffusion between the surface and the bulk solution.[18,19] This work illustrates, however, that the bimodal form of the observed self-exchange kinetics is not a result of different interfacial

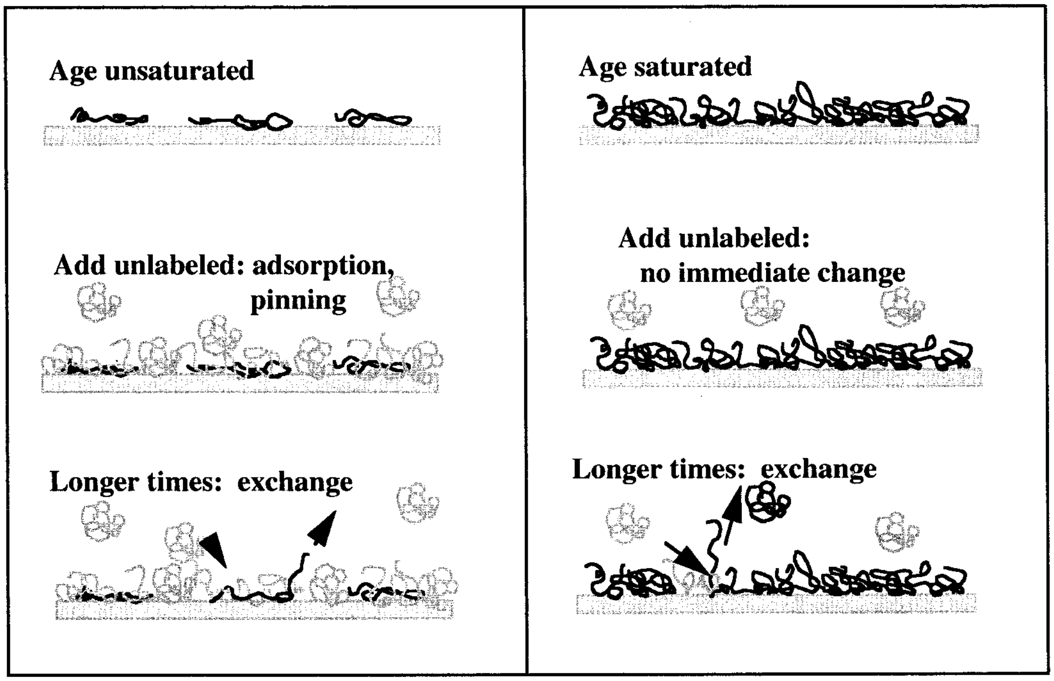

Figure 2. Schematic of potential differences between exchange of chains aged in unsaturated layers (on the left) vs saturated layers (on the right). Chains aged in the unsaturated layers become flat, with greater numbers of segment−surface contacts per chain. This increases the likelihood of pinning by an adsorbed overlayer when unlabeled chains are added, perhaps increasing the difficulty of displacing the preadsorbed chains. Saturated layers (on the right) are expected to be more entangled, but the loops and tails may osmotically repel the subsequently added labeled chains.

populations locked in at the time of initial adsorption, as previously anticipated.

An interesting question, left to future work, is why polymers such as PMMA do become trapped in distinct populations based on adsorption history,[11] while PEO does not. At least for PEO, there is no spectroscopic or dynamic evidence for such populations. The segmental adsorption energy for PMMA is roughly double that for PEO (2 kT vs 1 kT), which is one potential source for the kinetic trapping of the former. A second possible reason is the local cooperativity, which is thought to be needed for the motion of isolated PMMA chains.[23] No such constraints have been described for PEO motion, to our knowledge.

Influence of Surface Coverage. Self-exchange of chains aged in unsaturated layers was compared with that for chains aged in saturated layers to probe potential mechanisms for chain displacement and the nature of chain reconformation during aging. The schematic in Figure 2 highlights some possible distinctions between aging of saturated and unsaturated layers. In unsaturated layers, interactions between neighboring chains are reduced; however, there are increased segment−surface contacts per chain. Indeed it is well-established that at low coverages adsorbed layers are made primarily of trains, with all segments lying close to the surface.[24] This train-dominated regime need *not* be extremely dilute, for instance, the gaslike monolayer regime for molecules at an air−liquid interface.

Particularly relevant to the current work, the bound fraction in PEO layers adsorbed on silica from aqueous solution was probed in the Cosgrove lab using solvent relaxation NMR.[25] The train fraction was observed to be near unity at PEO coverages below and near 0.2 mg/m^2. At higher coverages, the bound fraction was inversely proportional to the incrementally adsorbed mass, in agreement with expectations.[24] The interpretation is, then, that at low coverages up to 0.2 mg/m^2 PEO adsorbs exclusively in trains with a large number of segment−surface contacts. Additional surface mass above 0.2 mg/m^2 contributes to loops and tails, reducing the bound fraction per chains.

Figure 2 illustrates the possibility that, with preadsorbed chains lying flat during aging at low coverages, the increased number of segment−surface contacts per chain may pose an enthalpic resistance to subsequent displacement by incoming chains. Additionally, with the preadsorbed chains in a flat conformation, there is greater likelihood that they would be pinned by an overlayer formed by incoming chains at the start of self-exchange, preventing their escape from the interface.

In contrast, the saturated layers in Figure 2 are made up of tails, loops, and trains, where the former extend into solution and may present an osmotic barrier to the approach of incoming chains. Additionally, at the crowded interface there is the possibility that lateral entanglements between neighboring chains might hinder self-exchange. These entanglements might resemble those in a concentrated polymer solution, or there may be a different type of entanglement, where a combination of segment−surface contacts and pinning of small loops or trains of neighboring chains occurs. Such interfacial entanglements that might occur in a saturated layer would involve local pinning, but not the formation of the distinct overlayer, speculated to trap preadsorbed chains in the dilute layer of the previous paragraph.

Figure 3 shows the mass evolution measured by reflectometry during two example runs with the 112K sample, illustrating the history for adsorption, aging, and self-exchange in saturated vs unsaturated layers. Initially, pH 7 buffer flows through the adsorption cell. Following a valve turnover, CPEO solution is introduced and begins to adsorb at time zero. In run 1, adsorption

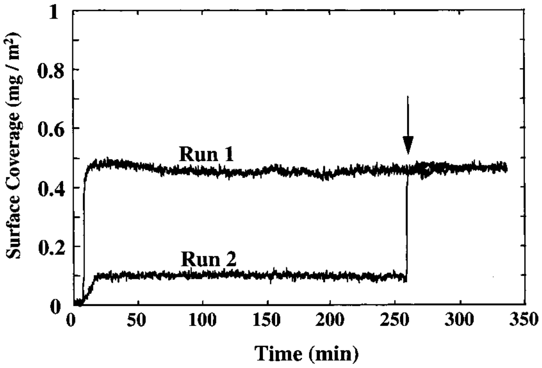

Figure 3. Uninterrupted adsorption of CPEO 112K on silica monitored by reflectivity (upper curve). Prematurely terminated adsorption of CPEO on silica (lower curve). At the point marked by an arrow, both layers were exposed to a solution of unlabeled PEO, initiating the exchange process.

is allowed to go to completion, giving a coverage near 0.46 mg/m^2. Shortly after saturation, the flow is switched back to buffer. In run 2, the adsorption is prematurely interrupted at a coverage near 0.10 mg/m^2 by the introduction of flowing buffer. (In run 2, a more dilute polymer concentration of 3 ppm was employed for the initial adsorption, just for this particular run. This resulted in slower adsorption kinetics, allowing us to more precisely control the exact unsaturated coverage levels we wished to study.) After the initial deposition, both layers were aged for 4 h in gently flowing buffer solution. Then following a valve turnover, unlabeled PEO was introduced at a concentration of 100 ppm to initiate self-exchange. For the saturated polymer layer, no change in interfacial mass is seen during self-exchange, a desirable feature of a self-exchange study. When the unsaturated layer is exposed to the same PEO solution, the coverage rapidly increases, at the transport-limited rate, to the saturation coverage. We find that this increase in coverage precedes displacement of labeled chains by self-exchange, though the actual self-exchange process is not apparent in Figure 3. Figure 3 tracks only the interfacial mass and not the behavior of labeled populations.

The behavior, measured by TIRF, of the fluorescent populations in layers subject to similar adsorption histories is shown in Figure 4A for three example runs. Adsorption of CPEO at a concentration of 1 ppm in flowing buffer is initiated by a valve turnover at time zero. In run 1, adsorption proceeds to completion, giving a coverage of 0.40 mg/m^2. In runs 2 and 3, adsorption is interrupted prematurely by reintroduction of flowing buffer, giving coverages of 0.34 and 0.14 mg/m^2. In Figure 4A, the initial adsorption kinetics for all three runs are identical, because the same polymer concentration was used. After aging the adsorbed layers in flowing buffer for 4 h, PEO is introduced at a concentration of 100 ppm to initiate self-exchange. As unlabeled chains displace the labeled ones on the surface, the fluorescence signal decays.

For the unsaturated layers, when the PEO is introduced to initiate self-exchange, the total coverage first increases, as shown in Figure 3, before the fluorescence decays, as shown in Figure 4A. The increase is not apparent in Figure 4A, because TIRF measures the labeled chain populations, which are displaced only after the surface has saturated. (The timing of the signal increases like those in run 2 of Figure 3, relative to the fluorescent decays in Figure 4 is not shown, but determined by carefully noting exactly when the valve turnover occurred.) The displacement of preadsorbed

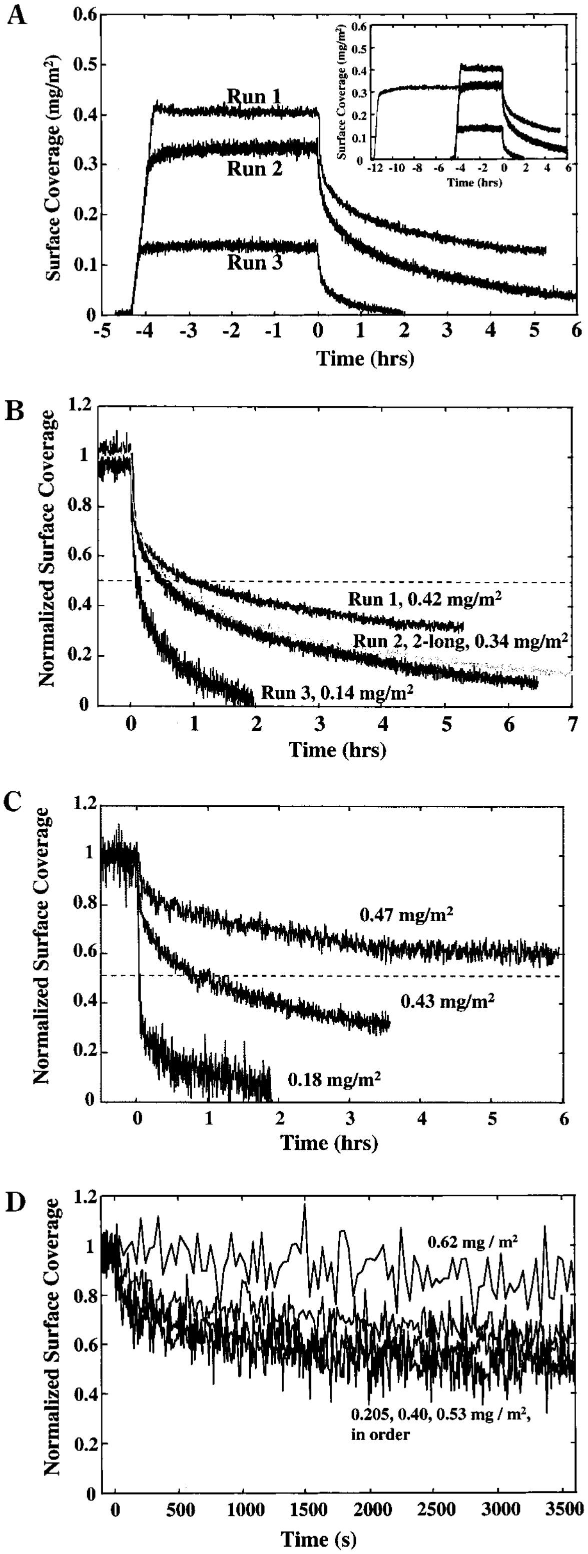

Figure 4. (A) Examples of adsorption–self-exchange histories, measured by TIRF, for the 32K sample. Run 1 adsorbs up to saturation. Runs 2 and 3 have unsaturated layers. Self-exchange was initiated at time zero by introduction of unlabeled PEO. (B) Normalized self-exchange data from (a) for the 32K sample. Runs are marked to show saturation coverages prior to self-exchange. (C) Normalized self-exchange for the 112K sample. Layer ages were 6 h prior to self-exchange. Coverages correspond to the surface loading of C-PEO prior to self-exchange. (D) Normalized self-exchange for the 460K sample.

labeled chains after saturation is consistent with prior findings that competition between different populations is significant only after the surface is nearly saturated.[26−28] For instance, in competitive coadsorption from mixtures of short and long chains, both adsorb independently when the surface is bare.[26,27] Only when the surface appears saturated to the short chains are they displaced by the longer chains, which are ultimately preferred on the surface for entropic reasons. In the current study, competition between and displacement of labeled chains by unlabeled ones occurs only after the surface mass approaches saturation.

In the main part of Figure 4A, the adsorbed layers are aged for 4 h, which was usually sufficient for them to mature completely. The inset illustrates, for an unsaturated layers with coverages near 0.35 mg/m^2, that more extensive aging of the layers, up to 12 h, has no affect on the fluorescence decay during the subsequent self-exchange.

The decay curves in Figure 4A indicate that chains aged in unsaturated layers were more readily and more completely displaced from the interface during subsequent self-exchange. Normalization of the decay portions of the traces in Figure 4B presents this observation in an even more striking fashion. The same was found for the other molecular weights studied in Figure 4C,D. These findings argue against the importance of a large number of segment−surface contacts, on a per chain basis, for hindering the release of preadsorbed chains during self-exchange. The observations also suggest that even though the interfacial mass increases to the saturated level before preadsorbed labeled chains can be displaced, the additional chains coming to the interface do not pin those that were preadsorbed, even if the preadsorbed chains lie flat in trains. In other words, we see no evidence for the formation of an overlayer at the onset of self-exchange, even when the unsaturated preadsorbed layer has relaxed for several hours before additional interfacial mass incorporates.

With a large number of segment−surface contacts per chain and pinning by an overlayer of late arriving chains ruled out as potential mechanisms for hindered self-exchange, we sought other origins for interfacial sluggishness. The results in Figure 4 clearly suggest that some manifestation of interfacial crowding or interchain interactions is responsible for slow self-exchange. The most obvious potential mechanism is entanglements. Classical entanglements in bulk melts exhibit a distinctive molecular weight dependence of their relaxation times. A strong but potentially different dependence on molecular weight might be expected for entanglements in adsorbed layers.

Figure 5 examines the extent to which molecular weight or surface loading is important for self-exchange. Of the many choices to describe the characteristic time for self-exchange, we chose to define τ-50, the time to displace half of the originally adsorbed chains during self-exchange. This strategy was adopted because the shapes of the individual self-exchange traces did not conform to any particular functional form. Fully mature saturated layers were well described by a stretched exponential decay.[19] The unsaturated layers, however, had a rapid initial decrease followed by slower self-exchange kinetics, where the latter were stretched exponential.

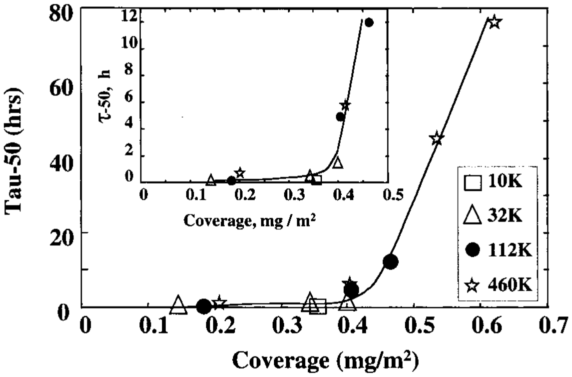

Figure 5. Dependence of self-exchange time on surface loading, for different molecular weights. All layers are fully mature.

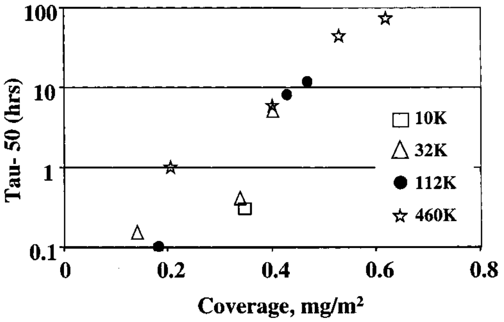

Figure 6. Data from Figure 5 on a semilog scale.

In Figure 5, the characteristic self-exchange time, τ-50, is shown as a function of surface loading. The τ-50 values covered a broad range, from 10 to 15 min to over 70 h. Therefore, the main figure shows the full time scale while the inset magnifies the behavior for runs with rapid or moderate self-exchange. The various data sets represent self-exchange runs with PEO samples of different molecular weight. We were not able to achieve the same surface coverages with all of the samples, because the saturation coverage depended on molecular weight. For instance, for the 460K sample, a saturation coverage of 0.62 mg/m^2 made it possible to prepare layers with masses from 0.2 to 0.62 mg/m^2. In contrast, the saturation coverage for the 10K sample was 0.35 mg/m^2. This low molecular sample gave extremely rapid self-exchange even for the saturated layer, such that unsaturated coverages with the 10K chains were not investigated.

When the full range of coverages was considered for all the molecular weights available, τ-50 was seen to depend strongly on the surface loading, while the influence of molecular weight was more difficult to discern. For the molecular weight range from 10K to 112K, all the data fell on a single curve in Figure 5 within experimental error. The 460K sample had slower surface dynamics than the other molecular weights, with this difference being most pronounced at the lowest coverages. The curves in Figure 5 have been drawn primarily to guide the eye; however, we note that the relaxation times are roughly exponential in coverage as shown in Figure 6.

Figure 5 illustrates that the actual molecular weight influence on self-exchange is much weaker than originally thought, by both us and other investigators.[6,7,18,19] In the prior investigations of self-exchange which focused only on saturated layers, variations in the molecular gave variations in coverage. The current work is the only one to our knowledge in which coverage and molecular weight are varied independently to decouple the two variables.

In Figure 5 we were careful to ensure the maturity of the layers undergoing self-exchange. In our prior work focusing on saturated PEO layers, it was found that high molecular weight layers more rapidly reached a "relaxed state" in which exchange dynamics were slow, while equilibration of the lower molecular weight layers took longer. Though the current work has not examined the relaxation kinetics in great detail for each molecular weight at each coverage, we did look into the question deeply enough to report some qualitative observations: For a particular molecular weight, layers at low coverages more rapidly achieved a mature state than the corresponding saturated layers. It remains undetermined, however, the extent to which the mature states were fully equilibrated or simply immobilized to a point where no further evolution could be observed on reasonable experimental time scales.

Discussion

When one imagines the process by which self-exchange might occur, several steps come to mind: diffusion of a free chain from the bulk solution to the interface, its diffusion through the loops and tails of the existing layer, the replacement of preadsorbed trains by segments of the invading chain, and disengagement of a preadsorbed chain from the interface. Disengagement may involve release of entanglements between the leaving chain and its neighbors. While the preadsorbed chain diffuses out of the layer and into the bulk solution, the newly incorporated chain must further relax, developing additional segment−surface contacts with neighboring chains within the layer. The challenge is to determine which of these steps is (are) rate-limiting and, ultimately, if the rate-limiting step varies with the nature of the chemical system. In the case of mature saturated PEO layers, we have already shown that, for substantial molecular weights, diffusion of chains between the bulk solution and the interface is not rate limiting.[19] Self-exchange is usually an interfacially controlled process.

The results in Figures 4 and 5 directly address which of the remaining steps might be rate controlling. First, the fast displacement of chains aged at subsaturated conditions demonstrates that release of segment−surface contacts occurs quickly in the presence of incoming chains. This observation refutes the hypothesis that the energy barrier of exchange is proportional to the number of segment−surface contacts per chain, at least for the current system. The findings also argue against the formation of an overlayer by the last chains to adsorb just before exchange, where the overlayer would hinder the escape of preadsorbed chains. Such overlayers may be important in sequential competitive adsorption studies described by other groups.[7,29,30] In those instances, the stronger adsorption energy of the late arriving chains (which were chemically different or deuterated) probably did cause an overlayer, as evidenced by an increase in mass at the start of exchange. In the current work, the lack of a mass overshoot is consistent with a true-self-exchange process. This subtle difference between the self-exchange nature of the current experiments and the more competitive nature of exchange processes in other labs could contribute to differences in the interfacial mechanisms and rate-controlling steps.

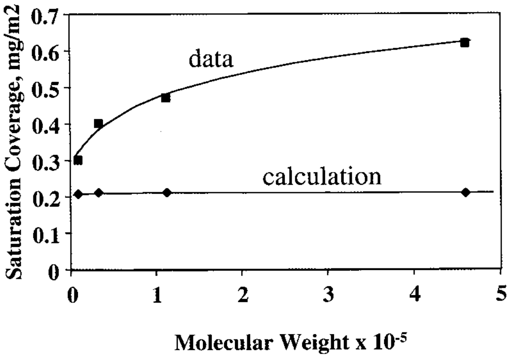

Figure 7. Experimentally measured saturation coverages, compared with saturation coverages predicted by a simple model where each coil occupies πR_g^2. Lines guide the eye.

Because Figures 4 and 5 clearly illustrate that interfacial crowding results in slow exchange, we are motivated to consider how coverage affects structural features within an adsorbed layer. As already mentioned, NMR data suggest that below coverages of about 0.2 mg/m^2 the interface is dominated by flat trains.[25] Above this coverage level, additional mass contributes to loops and tails that could provide an osmotic barrier against new chains approaching the interface. Another perspective is that above some surface loading chains will begin to encounter their neighbors, increasing the probability of entanglements.

An interesting back of the envelope calculation assumes that the footprint, πR_g^2, of each chain is dictated by its solution radius and that saturation of the surface would occur by isolated chains (to the extent that overlap does not occur). Experimentally measured saturation coverages exceeding the calculated πR_g^2 surface filling limit require overlap between neighboring chains or extension of the adsorbed chains normal to the interface. Figure 7 compares the calculation, for different molecular weights, to the saturation coverages measured experimentally. Higher molecular weights, in Figure 7, exceeded the calculated coverage by as much as a factor of 3, indicating a greater likelihood of lateral encounters or entanglements. It is interesting to note, in Figure 7, that the calculated coverage was near 0.21 mg/m^2, independent of molecular weight, a figure which is nearly identical to the maximum train mass by NMR,[25] also not a function of molecular weight.[24] There are, however, very different physics which lead to the two situations. The calculation assumes the layer thickness is roughly R_g, while the NMR data indicate that up to 0.2 mg/m^2 all segments lie flat. Regardless of the perspective, saturation of the surface by trains or filling of the surface by R_g-sized coils, it is clear that interchain interactions become important above 0.2 mg/m^2, in agreement with Figure 5. The consequences of these interactions are known to be formation of loops and tails and are likely to include intertwining of neighboring chains. Both could influence self-exchange dynamics.

For PEO in the melt state, the entanglement molecular weight from the plateau modulus, M_e, is about 2000,[31] while that from the melt viscosity, M_c, is 3500.[32] Adsorbed layers, however, are more dilute than the melts, and the entanglement molecular weight generally scales on concentration to the $-^4/_3$ power.[33] For PEO adsorbed on silica, the region nearest the surface has a local concentration of about 30 vol %, which decays to about 15 vol %, 2.5 nm from the surface.[24,34] Using this concentration as an estimate for an interfacial region where entanglements could be important, the one obtains $M_e(15\%) \sim 25\,000$ and $M_c(15\%) \sim 44\,000$. It therefore appears that entanglements could occur in adsorbed layers with several of our samples. In melts, however, the relaxation time shows a strong molecular weight dependence, which is not found in our experiments. Only the 460K sample self-exchanges more slowly than the others, with this effect being most pronounced at coverages near 0.2 mg/m^2.

While classical melt-type entanglements may indeed occur for the 460K sample, Figure 5 suggests that, if interfacial entanglements exist for the other molecular weights, they relax in ways that are relatively insensitive to molecular weight. Melts relax via reptation and constraint release. Interfacial entanglements, potentially involving intertwined neighboring chains and segment−surface contacts, could relax through the additional mechanism of segment−surface bond disruption. Because bond disruption need to not occur in a particular sequence down the chain to be effective, it could potentially involve a weaker dependence on molecular weight than reptation. It is hard, however, to imagine that molecular weight would have no effect at all. An alternate explanation is that entanglements do exist and relax on moderate experimental time scales; however, in self-exchange experiments, the rate-limiting step is of different origin and masks experimental observations of entanglement relaxation.

Another potentially rate-limiting step is penetration of the adsorbed loops and tails by invading coils. There should be a solvent-quality-dependent osmotic barrier to this process which parallels the repulsions observed in the surface forces apparatus when two PEO layers on mica are brought together.[33] Two back of the envelope methods yield estimates for the for the energy barriers associated with this process. In the first, one calculates the work to bring a coil from dilute solution into a solution whose higher concentration approaches that occurring locally in the adsorbed layer. For a 33K molecular weight coil entering an adsorbed layer with a local concentration of 15 vol % and with a second virial coefficient of 0.07 nm^3/segment,[13] one obtains a work of 10 kT. This calculation, of course, neglects the interfacial concentration gradient and the fact that the layer itself is roughly as thick as the coil, factors which will cause the calculation to overestimate the height of the energy barrier. A second estimate of the energy barrier comes from integrating the force−distance profile obtained in the surface forces apparatus and then to determine an energy per coil using the areal footprint of a single coil. In performing this integration, we numerically integrated Figure 2 of ref 35, from infinite separation to 5 nm from the surface. The latter limit on the integration corresponds to the situation where an invading coil's center of mass is R_g from the interface at closest, so that its segments just begin to access the substrate or trains. From this calculation, one determines an energy barrier exceeding 30 kT. This estimate may be too high because PEO coverages on mica were observed to be 4 mg/m^2, substantially greater than on silica in this work. Though these calculations represent rough estimates of energy barrier heights, they reinforce the notion that the osmotic barrier to approach of incoming chains can be several kT, large enough to substantially slow exchange kinetics.

Another favorable feature of the osmotic energy barrier against self-exchange is that it is not expected to have a strong dependence on molecular weight. Not only do mean field calculations and NMR data[25] substantiate the fact that the relative layer mass in loops and tails as opposed to trains is insensitive to molecular weight (depending only on total surface coverage for a particular type of polymer), scaling theory predicts a weak dependence (power 0.25) of the dynamics on molecular weight.[36]

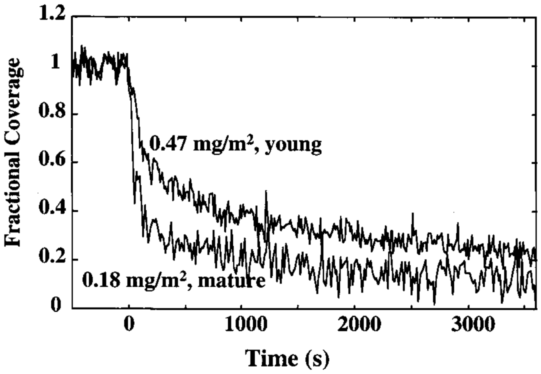

Figure 8. Faster exchange observed for mature (6 h old) layer aged with 0.18 mg/m^2, compared with young (2 h old) layer aged at saturated conditions. Both runs are with the 112K sample.

The osmotic energy barrier is an especially appealing concept because we know such osmotic repulsions must exist, and a rate-limiting self-exchange step of osmotic origin is consistent with the observed insensitivity to molecular weight. Chains aged in unsaturated layers below 0.2 mg/m^2 would themselves lack the loops and tails which contribute to the local osmotic pressure. Still, it is necessary to reconcile the observation in Figure 3: For a particular molecular weight, all self-exchange runs proceeded at the saturated surface loading which is established at the onset of exchange. This implies that, perhaps, the same osmotic barrier would oppose self-exchange in all runs with a particular sample, regardless of the initial surface loading. Application of the osmotic argument therefore requires a caveat: Perhaps the lack of loops and tails in the local vicinity of preadsorbed chains provides easy access to invaders. Perhaps the concentration profile contributed by the late arriving chains prior to self-exchange is more dilute than that occurring in an aged saturated layer (with the former contributing a weaker energy barrier to exchange.) Or perhaps the chains which make up the mass of the layer just prior to self-exchange are the ones that actually displace the preadsorbed chains, while new arrivers incorporate into the layer at a different point. The osmotic energy barrier concept is clearly appealing because it is consistent with observations of steric repulsive forces measured in the SFA, but the concept is not yet complete, based on our current observations.

One final set of observations must be resolved with any model for the rate-determining step of exchange: Chains aged in layers with high coverages were generally slower to reach the mature state than chains aged at low coverages. That is, the energy barrier to exchange was slow to develop for chains aged in layers with coverages exceeding 0.2 or 0.3 mg/m^2. Also, in young layers with high initial coverages, self-exchange was slower (and the energy barrier higher) than for chains aged to maturity in more dilute layers. Figure 8 illustrates this point by comparing the self-exchange in a young layer with 0.47 mg/m^2 of 112K chains, with that for self-exchange in a mature layer with 0.18 mg/m^2. Put another way, chains on a crowded surface have a relatively large energy barrier to exchange that grows even greater with time. Chains aged in dilute conditions initially possess a low-energy barrier which increases only modestly with layer age. One might therefore ask, what features oppose exchange in young vs mature layers, and how do these features may depend on surface coverage?

We are not currently aware of any reports where polymeric stabilizers (which adsorb onto colloidal particles) must be mixed into a dispersion for several hours before a stabilizing action is observed. This suggests that after adsorption the key features of the interfacial concentration profile are set up so that there is minimal evolution of the pairwise interaction between approaching coated particles. Extending this reasoning, we expect that the osmotic barrier to the approach of single invading chains will be set up relatively quickly (minutes, as opposed to hours). While PEO layers are known to relax on silica for hours after adsorption,[18,19] these relaxations may involve modest changes in the interfacial concentration profile (minimally affecting an osmotic barrier to incoming chains). Such relaxations might, however, involve the development of entanglements between neighboring chains.

Since entanglements take a finite time to relax, they should also take a substantial time to develop within an adsorbed layer, if the coverage and molecular weight are sufficiently high that entanglements will occur at all. In our prior studies with saturated PEO layers, we observed that the highest molecular weight samples (which also had the highest saturation coverages) took the shortest time to reach the mature immobilized state, compared with saturated layers of lower molecular weights. Since in concentrated systems, higher molecular weight chains exhibit slower dynamics and should therefore have a longer (not shorter) maturation time, it was speculated that the more rapid maturing of the higher molecular weight layers simply indicated that they more quickly reached an immobile state, which was not necessarily equilibrated. Extending this reasoning, we expect that layers with the highest molecular weights in the current study become kinetically trapped before they are fully entangled. Kinetic trapping, therefore, can potentially mask the molecular weight dependence in layers that cannot achieve their fully entangled states.

Summary

This investigation employed PEO adsorbed on silica from aqueous solution to probe the rate-limiting step for self-exchange between an adsorbed layer and chains free in solution. First, tracer studies revealed that within saturated layers up to 112K (the full molecular weight range we were able to study in this type of experiment) no dynamically distinct subpopulations, based on the initial adsorption history, exist in 4 h old layers. Aging chains in unsaturated or starved layer provided specific insight into factors affecting the exchange rate.

For all conditions and molecular weights examined, chains aged at starved or unsaturated conditions (compared with those aged in fully saturated layers) were more readily displaced from the interface by like chains from solution. The self-exchange rate decreased with increasing coverage, especially above 0.2 mg/m^2, that needed to fill the surface completely with trains. These observations demonstrated that interactions between neighboring chains contributed more to the energy barrier of self-exchange than did a large number of strong segment−surface contacts per chain.

Surface crowding was expected to result in increased entanglements among neighboring chains in addition to increased loops and tails in the layer itself. While both features of a layer should hinder exchange, the influence of molecular weight on the exchange dynamics was minimal compared with the surface coverage, arguing against classical melt-type entanglements, except in the highest molecular weight sample which exhibited sluggish dynamics at 0.2 mg/m^2, a surface coverage where the layer is dominated by trains. Simple calculations revealed that the osmotic effects should be substantial. Since the mass of loops and tails is insensitive to molecular weight, and since slow kinetics were generally observed at coverages above 0.2 mg/m^2 where loops and tails contribute substantially to a layer's mass, the osmotic barrier argument is most consistent with experimental data. The lack of a strong molecular weight dependence of the self-exchange rate could have two other origins: Interfacial entanglements might relax by a different mechanism, disruption of segment−surface bonds, reducing the molecular weight scaling. Also, because entanglements take time to relax, they must also take time to develop. If the adsorbed layers become kinetically trapped before they fully entangle, the molecular weight influence would be diminished.

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