Influence of Molecular Weight and Layer Age on Self-Exchange Kinetics for Saturated Layers of PEO in a Good Solvent

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ABSTRACT: The dynamics in adsorbed homopolymer layers were probed using self-exchange studies with the model system poly(ethylene oxide), PEO, adsorbed on silica from aqueous solution. The latter constitutes a good solvent for PEO. The influence of layer age and molecular weight was investigated. The self-exchange traces themselves were bimodal, fitting a simple noncooperative exchange model at short times and then switching over to stretched exponential behavior. In mature PEO layers (where no further influence of aging was found), higher molecular weight layers were less mobile than lower molecular weight layers, with a linear influence of molecular weight on the stretched exponential time constant and on the time constant describing the initial stages of exchange. The stretching exponent was 0.34 ± 0.04, independent of molecular weight. Also, the approach of newly formed layers to the mature state followed a single exponential, with faster maturation of layers of longer chains.

Introduction

Understanding the dynamic behavior of adsorbed polymers is important because the complexities that arise in the simplest systems, for instance a homopolymer layer adsorbed onto a stable colloid or a planar solid in solution, dominate many important technologies. These include the processing of complex fluids in paints, coatings, and ceramics, the behavior of adhesives, and the performance of new biological technologies. The dynamics of adsorbed polymers also pose an interesting physical problem, one for which no predictive framework exists. Ultimately, the issue to be addressed is one of polymer chain dynamics in a constrained geometry, where the energetics and dynamics of segment−surface, segment−segment, and segment−solvent interactions must be considered.

Homopolymer chains adsorbed on a solid surface from a polymer solution provide a point of departure to examine these issues. It is known, for instance, that most adsorbed homopolymer layers set up quickly on a surface after chains diffuse to the interface from the bulk solution.[1−3] After the initial mass accumulation, continued interfacial rearrangements cause the layer to become more tightly bound to the surface.[4−6] Evidence for slow interfacial relaxations is provided primarily by the observation that polymers in solution readily displace chains in newly adsorbed layers but are slower to displace chains in mature layers. When the challenging chains are identical to the adsorbed chains with the exception of a chemical or physical label, "self-exchange" is said to occur. Self-exchange studies are significant because they potentially capture the dynamic equilibrium between adsorbed and solution phases.

Self-exchange studies also provide insight into the mechanism of chain motion through the layer: Since self-exchange always proceeds more quickly than desorption into pure solvent,[5,7,8] it follows that kinetic barriers, such as the breaking of physical segment−surface bonds, are smaller during self-exchange.[4] Indeed, it is generally accepted that desorption is relatively slow because all segment−surface bonds must be disrupted at once for a chain to escape the interface into pure solvent. In the case of self-exchange, the invading chain may trade places with the preadsorbed chain a few segments at a time, contributing a lower energetic cost.[4]

The current study examines the influence of molecular weight on the aging and self-exchange dynamics of poly(ethylene oxide) (PEO) layers adsorbed onto silica from aqueous solution, a moderate or good solvent. Though the exchange traces for PEO roughly resemble prior findings, both qualitative and quantitative differences were found. The most comprehensive prior reports for the influence of molecular weight on self-exchange kinetics were given for polystyrene (PS) on silica in a Θ-solvent.[8,9] Prior to the current work, less was known about exchange in a good solvent: Slow dynamics and incomplete exchange confounded quantitative reports of the molecular weight influence for PS or poly(methyl methacrylate) (PMMA) in a good solvent.[10,11] Another complicating factor with PS in a good solvent was that the molecular weights of the adsorbed and challenging chains were not always matched, and both influenced the kinetics.[10] The current study adheres to the strict definition of self-exchange, with the identical lengths of the adsorbed and challenging chains, so that the influence of molecular weight is clearly defined. The influence of molecular weight differences (adsorbed vs challenging) on exchange, including the entropic driving force, has already been documented for PEO.[12,13]

Some important properties of PEO and the PEO/silica/water system are summarized in Table 1. PEO is known to adsorb onto silica at the transport limited rate up to full coverage.[1,2] It also undergoes transport-limited molecular weight-driven exchange during coadsorption from bimodal or polydisperse samples.[12,13] These observations suggest chains within the adsorbed layer are highly mobile and that the first chains to adhere to the surface readily reconfigure to make way for late arrivers. Despite this interfacial mobility, which may result from the modest $1kT$ segment−surface interaction between PEO backbone ethers and nonionized surface silanols,[15] adsorbed PEO layers are resistant to removal in solvent, with no desorption observed on reasonable

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Table 1. Properties of the PEO−Silica Water System

T_g, PEO melt	−41 °C
χ (refs 32, 14)	0.40, 0.45
χ_s (ref 15)	$-1kT$
M_e, entanglement mol wt in a melt (ref 16)	2000
M_c critical mol wt in a melt (ref 17) where viscosity scales as $M^{3.4}$	3500

Table 2. Properties of the PEO Samples in This Work.

mol wt	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 2)	5.4×10^{-5}	3.4×10^{-5}	2.3×10^{-5}	1.4×10^{-5}

experimental time scales.[2] Also, adsorbed PEO layers reconfigure at time scales much longer than that for initial adsorption. Such layer relaxations make the PEO chains increasingly resistant to displacement by polymers in solution.[5]

The current work examines the influence of molecular weight on the self-exchange dynamics and the aging kinetics for PEO on silica in a good solvent. The individual traces are interpreted in the context of a simple model which captures the essence of a noncooperative exchange process and a stretched exponential form which describes cooperative processes such as glassy relaxations[18] and has previously been employed to interpret exchange behavior in adsorbed layers.[19,20] The evolution and crossover of adsorbed layers from noncooperative behavior to more complex dynamics motivates a discussion of the potential rate-limiting factors for the exchange process, in a good solvent as opposed to Θ-conditions.

Experimental Section

Molecular weight standard PEO was purchased from Polymer Laboratories, with sample properties summarized in Table 2. Each chain is terminated by a hydroxyl group at one end and by a butyl group at the other. To facilitate self-exchange studies, a fluorescent tracer strategy was employed to distinguish various populations. A coumarin derivative (7-(diethylamino)coumarin-3-carbonyl azide, Molecular Probes, Inc.) was chosen as the fluorescent tag because of its low molecular weight (<300), and neutral charge near pH 7, which avoids electrostatic interactions between the dye and the negatively charged silica surface. Labeled chains are denoted CPEO. Labeled and unlabeled versions of a particular sample were essentially the same molecular weight, with no influence of labeling on the free solution diffusivity.

Coumarin was attached to PEO chain ends via its reactive carboxylate group which converts to an isocyanate group upon heating (above 80 °C) in organic solvents.[5] PEO and coumarin were combined at a molar ratio of 1/2.5 polymer chains/dye. The reactants were dissolved in toluene and maintained near 90 °C for 24 h. Samples were purified by subsequent dissolution in warm acetone and, except for the 10K sample, precipitation in cold acetone (−15 °C), until the supernatant showed negligible traces of fluorescence. The 10K sample was precipitated with pentane, because it remained soluble in cold acetone. Since coumarin is only sparingly soluble in pentane, the precipitation step had to be repeated many times. The extent of labeling, found to be near 100%, was determined by the absorbance at 405 nm.

Because this labeling chemistry resulted in a number-wise addition of tags to PEO, the labeling density was inversely proportional to the chain length within a particular sample. As a result, the fluorescence signal was extremely weak for the highest molecular weight sample, 460K. In fact, we had insufficient signal from coumarin tagging of this sample and switched to a fluorescein label (with a greater absorbance and quantum yield) to increase the signal. Fluorescein labeling was conducted using procedures already described,[21] achieving a labeling density of 60%. In the mathematical treatment of the Results section, the subscript CPEO refers to any labeled PEO sample, even with the fluorescein tag.

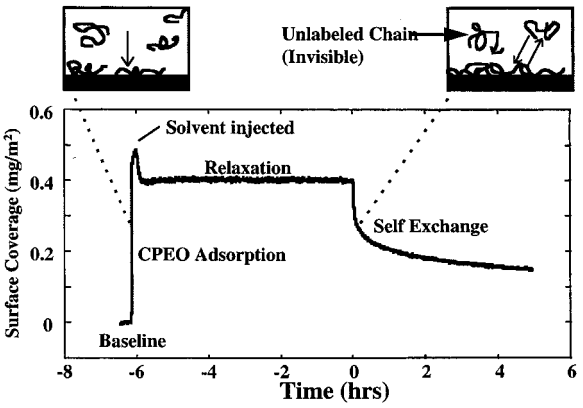

Figure 1. Typical self-exchange history, measured by TIRF, for 32K PEO. C-PEO concentration during adsorption is 100 ppm, the PEO concentration during exchange is 100 ppm, and the wall shear rate is 5 s^{-1}.

The evolving adsorbed amounts of CPEO during adsorption and self-exchange were determined using total internal reflectance fluorescence, TIRF, in a modified SPEX Fluorolog II, as detailed previously.[22] Coumarin was excited at 405 nm, with fluorescence measured at 500 nm, while fluorescein was excited at 488 nm and fluorescence collected at 510 nm. TIRF experiments were conducted in a slit-shear flow cell, following the design of Lenhoff.[2,5,23] Here a microscope slide, which served as the adsorption substrate, formed one wall of the flow chamber, with the rest machined out of Teflon. Continuous gentle shearing flow, 5 s^{-1}, over the surface maintained a well-characterized flux of polymer molecules to the surface, as described by the Leveque solution to the convection−diffusion equation.[24] This shear rate is too weak to perturb polymer coils. Prior work in our lab established the steady-state mass transfer coefficients for the shear cell,[2] which depended on the diffusivity of the adsorbing species and which are summarized in Table 2.

The silica substrate was generated by treatment of soda lime glass microscope slides (Fisher Finest) with concentrated sulfuric acid for 15 h in the assembled flow chamber. The acid was then flushed out with deionized (DI) water and then pH 7.4 phosphate buffer prior to the start of experiments. The influence of this treatment on the glass surface was documented previously.[2] All experiments were conducted at a polymer concentration of 100 ppm unless otherwise stated. This concentration is higher than in our previous studies[5] and results in a larger rate of chain arrival to the interface from the bulk solution. As made clear in the simple model below, this increased rate of chain to the interface facilitates greater resolution in measuring surface rates compared with our prior studies which employed more dilute solutions.[5] Since it had already been established that the PEO isotherm on silica was relatively independent of bulk solution concentration,[2] the primary effect of the higher bulk solution concentration in the current study was to increase the interfacial transport.

Also, as previously documented, molecular weight has a substantial influence on the apparent equilibrium adsorbed amount.[2] These coverages, which correspond to surface saturation, were found to be insensitive to bulk solution concentration and to experimental history. The saturated adsorbed amounts are summarized in Table 2.

Results

Experimental History. A typical self-exchange experimental history is illustrated in Figure 1, as measured with TIRF. Upon establishing a baseline with flowing buffer and 6 h in advance of exchange, a

buffered C-PEO solution is introduced and adsorption occurs. Shortly after surface saturation, flowing buffer is reintroduced, and the layer is aged in the absence of free chains. The signal drop upon buffer reintroduction results from the loss of free chains near the surface whose labels are excited by the evanescent wave. In the example, the sample relaxes for 6 h, and then self-exchange is initiated at time zero with the introduction of unlabeled PEO, at a concentration of 100 ppm. As the PEO chains displace the C-PEO chains, the fluorescence signal drops. Separate optical reflectivity runs[2,25,26] (not shown here), on a number of different histories with the various molecular weight samples in this paper, detected no change in interfacial mass over the full course of self-exchange, consistent with the intended experimental design.

The lack of desorption during aging in flowing buffer, in Figure 1, was typical of all our experimental runs. It emphasizes the fact that though the segmental energy of adsorption for PEO on silica is small, on the order of $1kT$,[15] the overall physisorption energy per chain is substantial, so that adsorption appears irreversible on reasonable experimental time scales. Only in the presence of challenging chains (unlabeled ones, in Figure 1) are the originally adsorbed chains displaced.

Aging in pure solvent is crucial because even in samples with a narrow molecular weight distributions, there exist significant populations of short and long chains. The long chains slowly displace the short ones if the interface is aged in polymer solution rather than pure solvent.[5,27] The resulting "relaxed" layer is then higher in average molecular weight than the polymer solution at the start of the exchange process, and the exchange kinetics are artificially retarded.

Simple Kinetic Model. For the range of conditions studied, it was found that self-exchange did not conform to a single rate expression, rather that two kinetic treatments were needed to fit all the data. As opposed to a stretched exponential form which is known to capture dynamic features of cooperative processes, a simple noncooperative kinetic model turned out to more precisely describe self-exchange in young layers or layers of short chains. The significance of the simple reversible first-order treatment presented here is, then, that it demonstrates exactly when one does not need to invoke polymer physics to explain the observed kinetics. When this model does apply, the self-exchange is controlled by single bonding and disbonding events at the interface. Likewise, the point where this simple treatment breaks down highlights conditions where polymeric features such as entanglements start to become important.

The simple first-order reversible kinetic model allows labeled and unlabeled chains to trade places on the surface:

$$\text{CPEO (adsorbed)} + \text{PEO (free)} \underset{k'_{ex}}{\overset{k_{ex}}{\leftrightarrow}} \text{CPEO (free)} + \text{PEO (ads)} \quad (1)$$

The rate law corresponding to this interfacial reaction has a forward rate constant, k_{ex}, for the displacement of adsorbed labeled chains by unlabeled ones. k'_{ex} is the reverse rate constant. Equilibrium constant $K_{PEO-CPEO}$ describes the relationship between the amounts of labeled and unlabeled chains on the surface and those in free solution:

$$K_{PEO-CPEO} = \frac{\Gamma_{PEO} C_{CPEO}}{\Gamma_{CPEO} C_{PEO}} \quad (2)$$

As noted, the equilibrium constant is also the ratio of the forward and reverse rate constants. Previously,[28] we solved the interfacial rate expression from eq 1, in series with mass transfer of labeled and unlabeled chains between the interface and the surface. The resulting expression was

$$\frac{t}{\tau} = -\left(\frac{1}{\lambda} + \frac{1}{K_{PEO-CPEO}}\right) \ln\left(\frac{F_{CPEO}}{F^{o}_{CPEO}}\right) + \left(1 - \frac{1}{K_{PEO-CPEO}}\right)(F^{o}_{CPEO} - F_{CPEO}) \quad (3)$$

where $1/\tau = MC_{PEO}/(\Gamma_{CPEO} + \Gamma_{PEO})$. F_{CPEO} is the fraction of labeled chains on the surface, with F^{o}_{CPEO} equal to that at the start of exchange. Their ratio corresponds to the normalized fluorescence signal. If labeled chains are initially adsorbed, as in Figure 1, then F_{CPEO}/F^{o}_{CPEO} decays during self-exchange from unity toward zero. Values for M, the mass transfer coefficient, are summarized in Table 2 for the different molecular weight samples. M depends only on the free solution diffusivity, the flow rate, and the chamber geometry. Since labeling does not affect diffusivity, the same M values were used for labeled and unlabeled chains. λ describes the ratio between the fundamental surface exchange rate and the rate of chain arrival at the interface:

$$\lambda = \frac{k_{ex}(\Gamma_{PEO} + \Gamma_{CPEO})}{M} \quad (4)$$

In the limit of bulk solution diffusion control, λ approaches ∞. Also, when $K_{PEO-CPEO}$ approaches unity, such that the label has no influence, a single exponential form is recovered:

$$\frac{t}{\tau} = -\left(\frac{1}{\lambda} + 1\right) \ln\left(\frac{F_{CPEO}}{F^{o}_{CPEO}}\right) \quad (5)$$

Though the physical picture leading to eq 3 involved no specific polymer physics (the rate law is phenomenological), this simple expression allows one to discriminate where polymer mechanisms such as entanglements or cooperativity are needed (or not) to explain observations. For instance, if eq 3 could describe the complete exchange process, it would imply that any entanglement or cooperative effects would occur on sufficiently rapid time scales that coil exchange could be treated as a single dynamic event.

Influence of Labeling on the Driving Force for Exchange. Application of eq 3 requires knowledge of $K_{PEO-CPEO}$, the influence of the fluorescent label on the driving force for exchange. Previously, the influence of the coumarin tag on the PEO chain end was quantified by surface selectivity measurements.[5] It was shown that the asymmetry between the forward and reverse self-exchange kinetics could also be used to determine $K_{PEO-CPEO}$. Figure 2 shows the effect of molecular weight on the skewness of the forward and reverse self-exchange runs, where the originally adsorbed layers were aged in solvent 15 min prior to self-exchange. CPEO more readily displaces PEO than the reverse, because CPEO is slightly more attracted to the interface. The curves through the data represent various fits

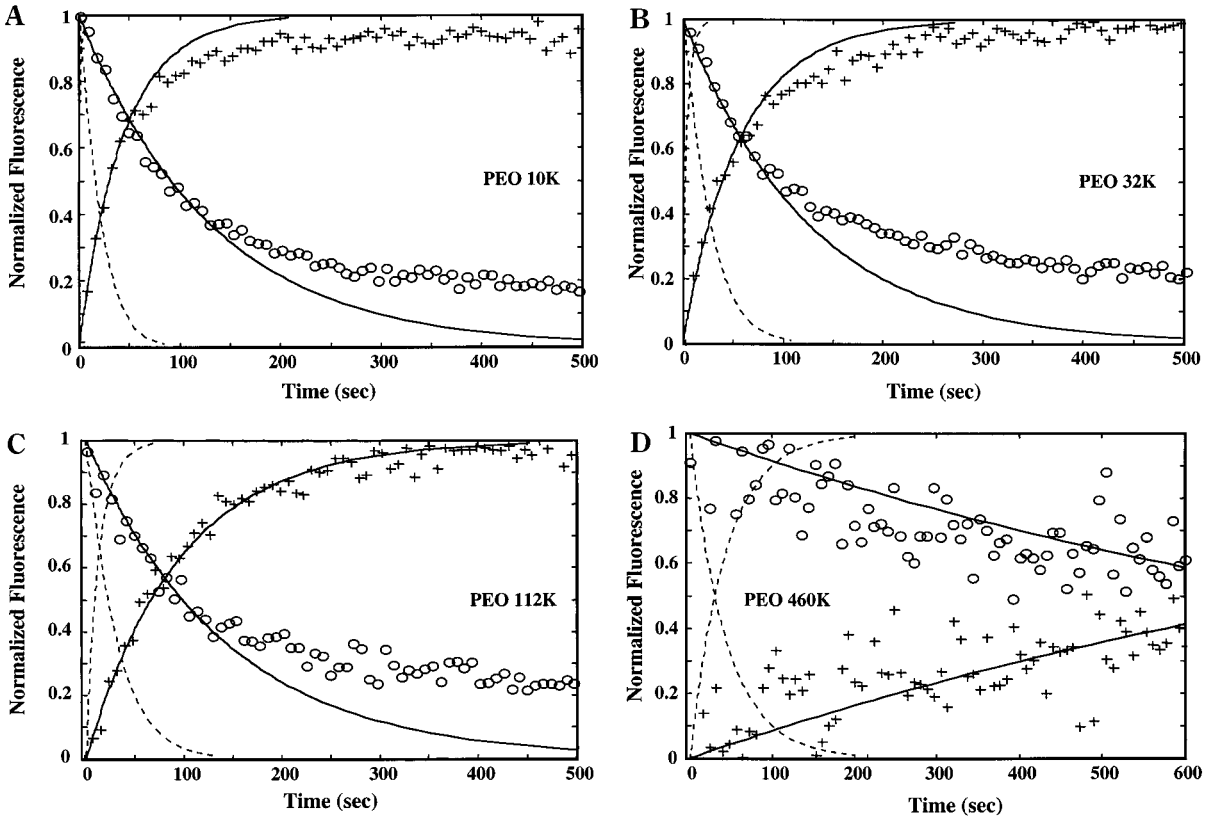

Figure 2. Forward and reverse self-exchange of PEO layers aged 15 min: (+) CPEO displacing preadsorbed PEO; (○) PEO displacing preadsorbed CPEO. Solid lines are best fit to eq 3; dashed lines are transport-limited exchange kinetics, calculated with $\lambda = \infty$ from eq 3. (A) 10K molecular weight, (B) 32K, (C) 112K, and (D) 460K.

to eq 3. The solid lines show the best fits where $K_{PEO-CPEO}$ and λ were adjusted once to give the best fit for both forward and reverse data sets. There are only two free parameters in this method, because for the reverse exchange, the equilibrium and kinetic constants are the inversion of the same constants for the forward exchange. The dashed lines are the predictions of eq 3 in the transport limit ($\lambda \sim \infty$), with the same $K_{PEO-CPEO}$ (no free parameters). In all cases, exchange was observed to occur at a rate significantly slower than the transport limit. Also, the fact that we were able to fit pairs (forward and reverse) of data sets with single $K_{PEO-CPEO}$ and λ values shows that the effect of the label is on the driving force for exchange. There is no fundamental effect of the tag on the kinetic constants.

It is reassuring that in Figure 2 the forward and reverse self-exchange studies become symmetric at the highest molecular weights. This occurs because the shortest chains contain the most label per unit mass. The influence of the label is barely noticeable for molecular weights near 100K and is quantitatively zero for the 493K sample, whose forward and reverse initial kinetics are symmetric.

Finally, as part of the discussion of Figure 2, it should be emphasized the mass was constant during all self-exchange runs examined with reflectivity. One cannot add the curves together in Figure 2 to calculate the total mass evolution. The pairs of curves represent the behavior of labeled chains only, in forward and reverse runs.

The influence of the label on the driving force for exchange is summarized in Figure 3. $K_{PEO-CPEO}$ varies from 0.4 for the 10K sample (corresponding to a free energy enhancement of $0.9kT$ for the most invasive case)

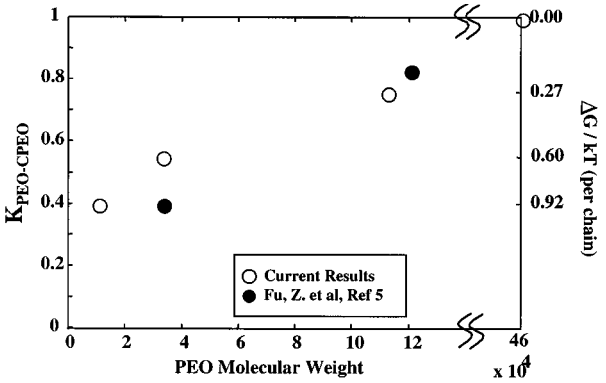

Figure 3. Dependence of the equilibrium constant on molecular weight for the PEO/CPEO system.

to 0.0 for the 460K sample, where the label did not influence adsorption at all. Though the highest molecular weight sample was actually labeled with fluorescein rather than coumarin, we would expect coumarin tagged PEO with molecular weight near 500K not to see any influence of the label, based on the small labeling effect with the 100K sample.

Influence of Layer Age on Self-Exchangeability. Figure 4 shows the influence of layer age (incubation in flowing buffer) on the self-exchange kinetics for different molecular weights. Each experiment resembled the plot in Figure 1 in its entirety, but with different solvent incubation times and exchange data collected up to 8 h. In all cases, layers newly deposited on the surface were most prone to displacement by like (but unlabeled) chains, while layers of increased age were less susceptible to exchange. Also, lower molecular weight layers were also more readily exchanged then

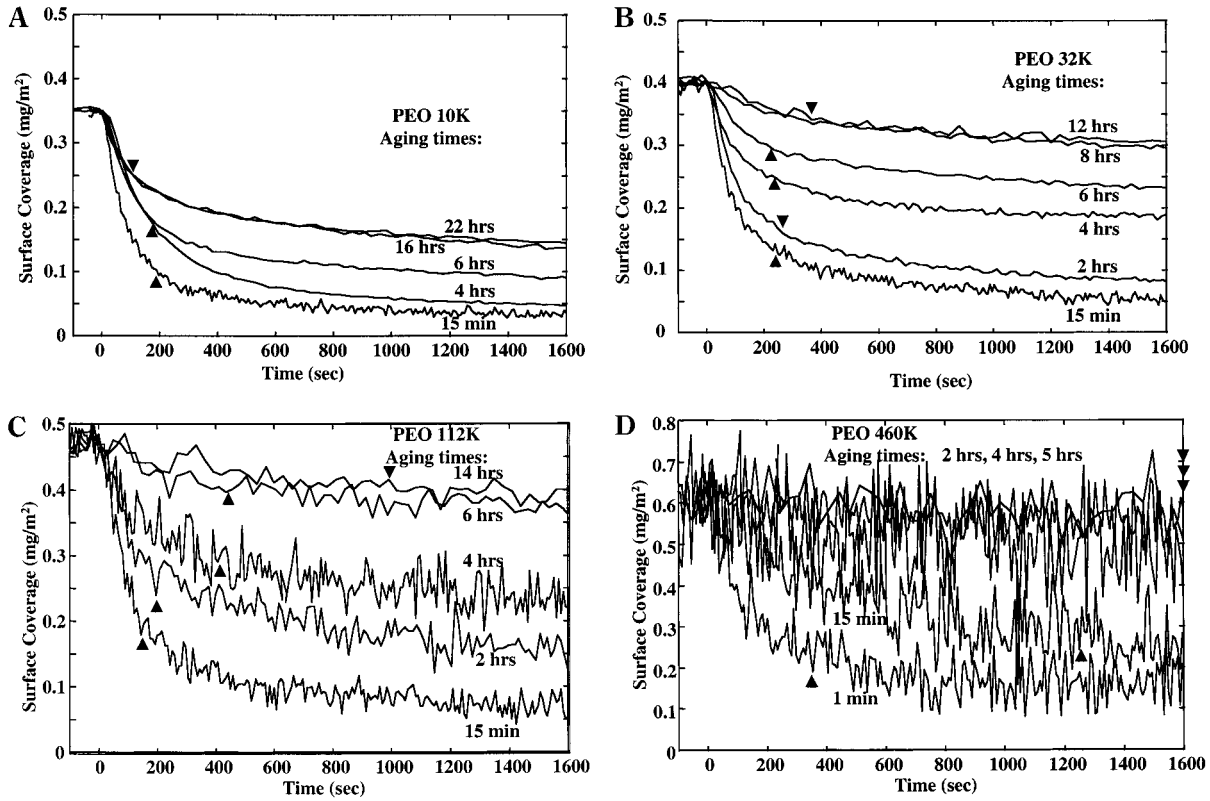

Figure 4. Effect of adsorbed layer age on self-exchange kinetics. Each layer has been aged for increasing periods prior to the onset of self-exchange. The triangles indicate the points at which eq 3 starts deviating from the data. (A) 10K sample, (B) 32K, (C) 112K, and (D) 460 K.

their higher molecular weight counterparts. For each molecular weight, aging times were increased over the series of runs, until the exchange kinetics converged to a single form, representative of the mature, and perhaps equilibrated, layer. In the case of the 10K sample, equilibration took about 16 h. For the higher molecular weights, maturation took progressively shorter times. Of note, the signal/noise ratio decreased substantially with molecular weight, and there was much noise in the runs with the 493K sample because of the scarcity of fluorescent tags. The runs, however, have been repeated several times, and the underlying kinetic shapes were reproducible.

The observed exchange kinetics had a fast initial exchange rate followed by a protracted phase lasting many hours. Figure 4 focuses on relatively short times such that differences in the initial kinetics can be readily seen. On these time scales, it is apparent that relatively loosely bound chains are readily displaced by those from free solution, though they would otherwise be retained in pure solvent. With knowledge of $K_{PEO-CPEO}$ summarized in Figure 3, eq 3 was fit to the initial kinetics to determine the initial first-order exchange rate constants, k_{ex}, summarized in Figure 5. Additionally, we noted the fraction of the initial layer which could adequately be modeled by eq 3, in Figure 6. In Figure 4, the triangles indicate where the first-order model could no longer reasonably fit the data. In many instances, the first-order model failed at very short times, on the order of a few minutes, when the entire run lasted hours. When such early breakdown of the model occurred, for instance in Figure 4A for the 10K sample, a substantial amount of the originally adsorbed mass (25−75%) was well described by the first-order kinetic form.

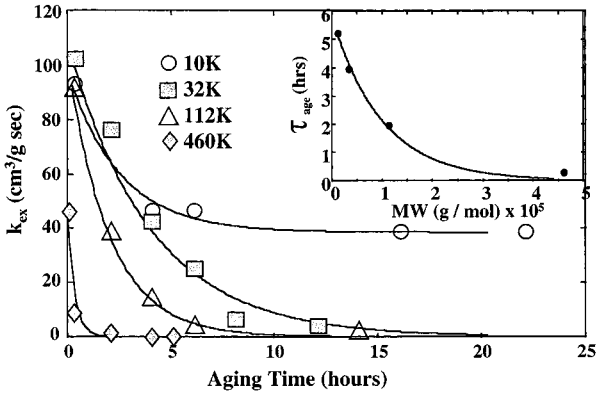

Figure 5. Values of k_{ex} obtained by fitting initial self-exchange traces to eq 3. The curve through each data set is a single exponential, $k_{ex}(\tau) = k_{ex}(0)\exp(-t/\tau_{age})$, summarizing the layer evolution for each particular molecular weight. The inset summarizes the aging time constants for the single-exponential fits in the main part of the figure. τ_{age} for the 10K sample was estimated by the rate of initial evolution rate of the 10K layer. This was necessary because the 10K layers had a different equilibrium state which would affect the interpretation of τ_{age}.

Figure 5 summarizes the evolution of k_{ex} with layer age for the different molecular weight samples. Though the first-order model only describes initial self-exchange, several profound points are borne out in the behavior of k_{ex}. First, depending on layer age and molecular weight, the rate of exchange can vary 2 orders of magnitude or more, indicating a dramatic reduction in interfacial mobility as polymer chains reconfigure at the interface or as the molecular weight of the sample is increased. Figure 5 also reemphasizes the conclusion from Figure 4 that low molecular weight chains, on the

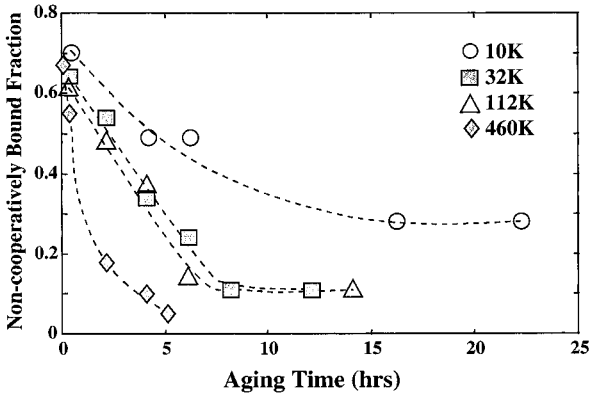

Figure 6. Fraction of adsorbed layers which could be described by the simple noncooperative model in eq 3. Dashed curves guide the eye and do not represent any particular mathematical form.

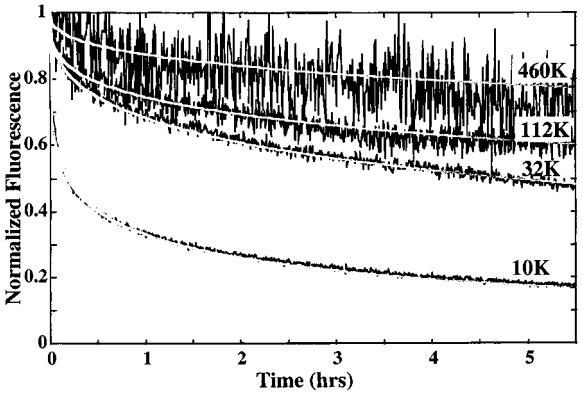

Figure 7. Self-exchange traces for mature layers of different molecular weights. Stretched exponential fits are shown in gray.

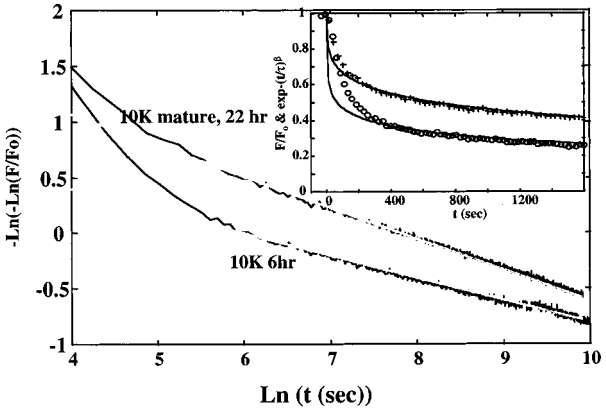

Figure 8. Test of stretched exponential fits to self-exchange data for the 10K sample from Figure 4A. The inset shows the deviation in real time. For the 6 h old layer, $\beta = 0.20$, while for the mature 22 h old layer, $\beta = 0.28$.

order of 10K, can never be completely immobilized at the interface. Finally, the evolution of the layers toward the mature immobilized states can be approximated by single exponentials for the range of molecular weights studied. The aging time constants are shown, as a function of molecular weight, in the inset and exhibit an exponential dependence on molecular weight according to τ_{age} (h) $\sim 5.9 \exp(1 \times 10^{-5}\text{MW})$.

Figure 6 summarizes the effect of aging in solvent on the fraction of the initial layers whose exchange dynamics could be described by eq 3. A substantial fraction of the lowest molecular weight layers could always be described by the noncooperative treatment regardless of layer age, while the highest molecular weights rapidly reached a state where the simple kinetics describing the initial stages of the process broke down quickly. Figure 6 essentially demonstrates that the simple treatment describes the self-exchange to a greater extent in young layers or those of low molecular weights. Further, in these young or low molecular weight layers, the simple first-order noncooperative model fit a greater fraction of the data than did the stretched exponential form, suggesting that the simple treatment is, in some cases, more appropriate than a more complex cooperative model. A nonpolymeric picture of exchange is appropriate for low molecular weight chains or chains aged in solvent for only a short time. At long times and for high molecular weights, more complicated physics such as topological constraints or cooperative motion must be invoked to describe the behavior of a greater fraction of the adsorbed layer.

It is striking in Figures 5 and 6 that for higher molecular weights the k_{ex} values and the noncooperatively released fraction more rapidly approach the mature state than for lower molecular weights. The characteristic evolution time for the 500K sample is less than an hour, while for the shortest chains, equilibrium is reached only after 16 h of incubation on the surface. This would appear to suggest that higher molecular weight samples are more mobile than the lower molecular weight samples during the course of aging. The explanation of this apparent paradox lies in the potential differences between the mature or fully aged states for the different samples. The mature state for the 10K sample is rather mobile, though its dynamics are slower than a young layer. In contrast, the mature states for the higher molecular weight samples are quite immobile from the perspective of chain displacement. It may be that, for the highest molecular weight samples, less adjustment of the originally adsorbed layer is needed to accomplish such immobilization, and as a result, the time needed to reach the immobilized state is shorter. As a caveat, it would appear that the mature states for the intermediate and high molecular weight samples may not yet be equilibrated, but more of an interfacial glass, where slow interfacial changes are not accessible on experimental time scales.

Self-Exchange Dynamics in Mature Layers. Figure 7 summarizes the self-exchange kinetics for mature layers of different molecular weights over a substantial time frame. The kinetic traces are difficult to describe by a single mathematical form: A stretched exponential fit in gray adequately describes the self-exchange 460K chains; however, for the lower molecular weights, the stretched exponential form worked well only beyond the first 10−15 min. A worst case example of the failure of a stretched exponential to fit the initial kinetics of the 10K sample is included in Figure 8 for a mature layer (22 h) and one that is 6 h old. Despite this shortcoming of the stretched exponential for the early exchange of intermediate (33K, 120K) and low (10K) molecular weights, it does a better job than the first-order model to describe the majority of chains displaced from a mature layer. Equation 3 applies only to the first 5−10 mass % for mature layers from 33K to 460K.

Figure 9 summarizes the effect of molecular weight on the self-exchange kinetics by several different measures. If one considers the initial exchange kinetics in Figure 9A, an inverse linear dependence on molecular

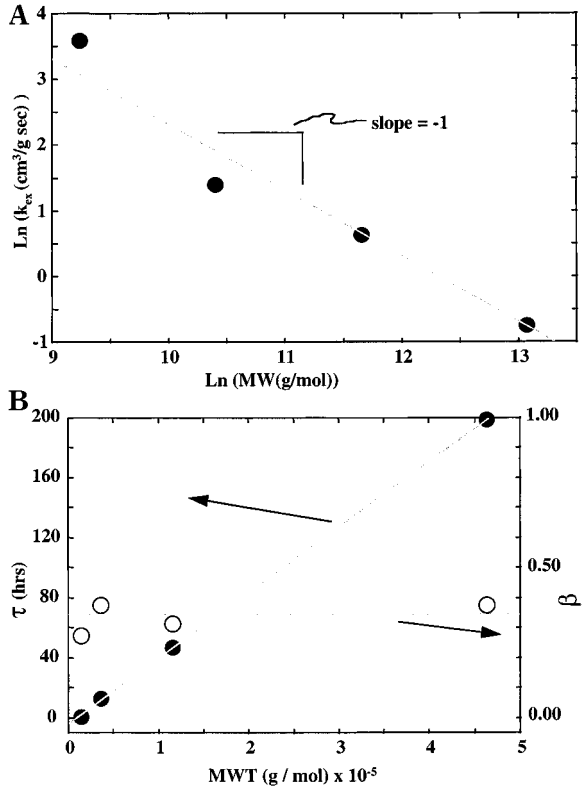

Figure 9. (A**)** Influence of molecular weight on the initial exchange kinetic constant, k_{ex}, for mature layers. (B) Summary of stretched exponential time constants, τ, and stretching exponents, β, for mature PEO layers of different molecular weights. τ is linear in molecular weight with a proportionality constant of 1.5 mol s/g or 4.4×10^{-4} mol h/g and an intercept of -4 h.

weight is observed. [If one examines the fraction of the initial layer that can be described with the simple nonpolymeric model, a mathematical form is not forthcoming: Mature layers of low molecular weight (10K sample) have a finite amount of noncooperative influence, while those of moderate and high molecular weight ultimately reach a state where the simple model does not apply and a more polymeric scenario is needed.] Figure 9B summarizes the stretched exponential parameters for mature layers of different molecular weights from Figure 7. A stretching exponent near 0.34 ± 0.04 was found for all the layers, with a time constant that varies linearly in molecular weight, according to t (h) $= 4.4 \times 10^{-4}$MW $- 4$ h.

Discussion

Studies probing the influence of layer age on the self-exchange process examine two different time scales: (1) the intrinsic dynamics revealed by the self-exchange of a particular layer at a particular age and (2) the time scale associated with the evolution of the layer from its state shortly after initial adsorption to apparent maturity. As pointed out previously,[8] the latter could potentially depend on the conditions during adsorption and aging and might not be universal. In contrast, one might have greater expectations that the dynamics intrinsic to mature layers be universal; however, it is equally possible that the final state could be kinetically trapped and therefore history dependent.

The Self-Exchange Traces Themselves. *Shapes of Individual Traces: Multiple Populations?* Using the self-exchange traces as measures of interfacial dynamics, the current work upholds previously observed general trends that younger layers are more mobile than older ones and that short chains are more interfacially mobile than longer ones.[5,7−11] Also, as seen previously,[5,8,9] the mathematical form of individual exchange traces was found to be complicated: Often one mathematical form described behavior at short times while a second fit the long time data. Our work upholds prior studies in this regard, though quantitative differences in the exchange traces may be attributed to differences in experimental design, for instance, flow vs quiescent conditions.

In the current work, the early stages of self-exchange were interpreted in the context of a simple model characterized by a single kinetic disbonding event with no cooperativity or polymeric features. This treatment described substantial portions, up to 75−80%, of runs with short chains or relatively young layers. One interpretation of the breakdown of the simple model in the middle or late stages of self-exchange is that it does not describe the portion of the layer that has become entangled or exhibits some other polymeric behavior. The two-stage exchange kinetics may also result from the fact that the layer is aging during the self-exchange process and may experience reconfigurations from the incorporation of new chains which could not be experienced during aging in solvent. (It is worth noting, however, that two-stage kinetics persisted in other studies where layers were aged in their original polymer solutions.[8−10]) A final interpretation given to the apparent two-stage nature self-exchange traces is that different populations persist at the interface.[9]

Polarized IR spectroscopy has provided evidence, in certain systems, for distinct populations based on the adsorption history.[29] For instance, with PMMA adsorbing onto silica, the chains arriving to the surface in the early stages of the original adsorption maintained flatter configurations with a greater chain fraction in trains parallel to the surface then late arriving chains. These interfacial populations could persist over the full duration of a reasonable experiment (several hours). We note here that for PEO on silica, however, control studies revealed that chains arriving early or late in the deposition of the original layer had identical displacement kinetics during self-exchange for layers aged 4 h or more.[30] Therefore, the apparent two-stage kinetic traces are inherent to the self-exchange process and not an artifact of distinct populations developing during adsorption.

Mechanism of Exchange. If self-exchange in the train region occurs piecewise, then the groups of segment−surface bonds involved in local exchange with an invading chain would contribute a small kinetic energy barrier relative to that needed to remove a whole chain.[4] In this case, molecular weight should have a modest influence on exchange at best.[8] Conversely, an exponential dependence on molecular weight might be expected if the energy barrier were extensive in chain length (proportional to the number and strength of segment−surface contacts).[20] It is well established, however, that the train fraction within a saturated homopolymer layer decreases with the increasing molecular weight as a result of the nearly constant train mass at saturation.[31−33] Loops and tails are more sensitive to molecular weight.

Molecular weight may be important if the rate-limiting step for exchange is not the segment-scale trading places of trains but some other process. Shifting

the rate-limiting step from the train exchange to, for example, diffusion through the brush does not contradict the idea that one-step desorption of whole chains should be slower than piecewise exchange in the train layer. If piecewise exchange of trains occurs, it must be one of several steps: diffusion of invading chains from the bulk solution, passage of invaders through the layer of loops and tails, piecewise segmental exchange along with release of any entanglements and other dynamic constraints such as pinning of trains by small loops, and then the reverse process for the exiting chain. The question then becomes, which step(s) is rate limiting? The influence of molecular weight on the self-exchange traces in mature layers may provide a clue.

In the mature PEO layers, molecular weight had a linear influence on stretched exponential time constant, $\tau_{stretch}$, and on the rate constant for initial exchange. Indeed, it was striking that both treatments reveal the linear influence of molecular weight. In contrast, an exponential influence of molecular weight was seen in exchange studies of polystyrene on silica in a Θ-solvent.[9] It is not clear whether the weaker influence of molecular weight in the current study can be directly attributed to the difference in solvent quality or whether other differences between the two systems are also important.

One would expect that in a good solvent loops and tails would pose a substantial osmotic barrier to the entry of additional chains into the layer. Indeed, for PEO, this effect is well documented, as least indirectly with surface forces measurements[34,35] and observations of the stabilizing power of bound PEO layers.[36] Worth noting are predictions that chain entry into a homopolymer layer of loops and tails should have a less than linear dependence on molecular weight, with a power law exponent of 0.25, weaker than what we observe.[4,37]

Another potential source of sluggish behavior comes from crowding of trains and nearby chain segments: In the dense train layer and in the first few segment lengths near the interface, high chain concentrations may lead to entanglements or pinning of trains by very short loops, requiring a cooperative motion to release adsorbed chains. This crowded cooperative effect could result from inter- or intramolecular chain encounters, giving the appearance of glassy behavior. The crowded interfacial region should, however, fall short of being truly glassy, since the T_g of PEO is well below our experimental temperature. Still, the observed behavior parallels that of glasses, for instance the Kolrauch, Williams, Watts stretched exponential,[18] with a stretching exponent near $^1/_3$, also seen in Figure 9b.

Interfacial Evolution during Aging. In Figure 5, the initial exchange rate for young layers is very similar for all the samples. Even with the 460K sample, short aging times yielded layers that were readily displaced, at least initially. (It is not clear whether with even shorter aging times, difficult to achieve in a real experiment, the initial exchange of the 460K chains would approach that of the other samples.) It appears that, at least for samples in the 10K to 120K molecular weight range, chain length does not affect the initial displacement rate. This may result from the noncooperative (unentangled, for instance) nature of the first chains to be displaced in young layers. It also suggests that, if disruption of train−surface bonds is the rate-limiting step, then the initial number of segment−surface bonds is not influenced by molecular weight.

With incubation in pure solvent, adsorbed PEO layers became more difficult to replace by like chains. In the current study, long PEO chains more rapidly reached their mature state than short chains. This feature is distinctly different from other reports where long polystyrene chains were slower to mature at Θ-conditions.[8,9] The current work therefore demonstrates that the sign of the molecular weight influence (increased aging rate vs slower aging rate) is system-specific and may depend on solvent quality, in addition to other factors. It is not necessarily a surprise that long chains may reach immobile states more quickly than short chains, since long chains may undergo smaller reconformations to achieve immobilization. It is, however, surprising that opposing effects were found in another lab.

Differences in the apparent aging behavior of the PEO layers from that of PS in a Θ-solvent may result from different self-exchange mechanisms in the two situations (discussed above) or from different processes during aging. In a Θ-solvent with minimal lateral interactions between chains, entanglements may begin to form during aging, and short loops may pin sections of trains. Then, as aging proceeds, additional layer reconfiguring would occur by reptation in addition to breaking and re-forming of segment−surface bonds. In this case, one might expect slower maturation in layers of long chains, as seen with PS. In the case with PEO in a good solvent, segment−segment repulsions may hinder the lateral interactions of neighboring chains, retarding entanglements and pinning of trains by short loops. In this case, it may be that a finite overall relaxation of a large coil could result in a greater number of new segment−surface contacts compared with the equivalent relaxation in a small coil. This would be consistent with the current observations.

As pointed out previously,[8] one must be careful about interpreting the rate of approach to the final state, because the aging process itself could be history dependent, making comparisons between work in different labs difficult. For the current work, the adsorption of all initial layers is extremely well-defined: With gentle shearing flow over the adsorbing surface and a known bulk solution concentration during adsorption, the arrival of chains to the interface proceeded at a *constant* rate. Then, shortly after saturation, solvent prevented further exchange between the bulk solution and the interface which could alter the average molecular weight in the adsorbed layer, even for monodisperse samples. We observed no history-dependent behavior that could be attributed to the concentration from which the initial layer absorbed. (In making this statement, however, we note since layer deposition takes longer in the most dilute solutions, the average interfacial age is slightly greater, which has a slight effect.)

Conclusions

Aging and self-exchange in homopolymer layers of PEO on silica was found to resemble behavior seen in previous studies; however, the current work revealed several different features. First, like earlier studies, two-stage kinetics were seen, but no direct evidence was found for multiple populations, an issue which was taken up in detail elsewhere.[26,30] The individual exchange traces themselves could be fit to a pair of models: At short times a simple nonpolymeric first-order model adequately described chain displacement while at longer times and especially in mature layers

of high molecular weight, stretched exponential kinetics were appropriate.

Mature layers exhibited a linear influence of molecular weight on the characteristic time constant of the stretched exponential and on the characteristic time constant for the simple nonpolymeric model (inverse of the rate constant). This striking behavior was markedly different from the exponential dependence of the initial rate constant on molecular weight found for PS on silica at Θ-conditions. Solvent quality is the obvious explanation. The weaker influence of molecular weight in a good solvent is qualitatively consistent with the notion that the kinetic barrier to exchange is the osmotic force exerted on chains entering the loops and tails of a previously established layer. This effect would be much reduced or absent at Θ-conditions. The observed molecular weight effect is, however, greater than anticipated by models of chain entry into a layer of loops and tails, motivating the possible role of constrained motion closer to the surface. Also, since PEO in water and PS in cyclohexane are chemically and physically different, other explanations may be forthcoming.

The current work also quantified the influence of incubation in solvent on layer mobility. Over the entire molecular weight range, an exponential approach from the initially adsorbed state to the mature state was found. Further, initial exchange rates of the young layers were all very nearly similar, with only a slightly slower rate found for the 460K sample. This suggests that the noncooperative self-exchange mechanism depends weakly, at best, on molecular weight. The aging rate, however, was greatly dependent on molecular weight with longer chains immobilizing more quickly than short ones. This observation is in direct opposition to prior reports for PS aging at Θ-conditions. The difference has two possible sources: First, if the mechanism of self-exchange is different at Θ-solvent and good solvent conditions, then the layer evolution as measured by self-exchange could appear different. Second, differences in solvent quality and other system features may result in different modes of interfacial evolution. Clearly for PEO in water, segment−segment repulsions would hinder the development of lateral interactions and constraints from segment−segment interactions which would be less retarded at Θ-conditions.

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