

Dynamics in adsorbed homopolymer layers: Understanding complexity from simple starting points

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Abstract

Now more than ever, smart material interfaces in a variety of applications demand control over complex interfacial processes, often involving adsorbed polymers. To this end, this opinion article addresses the dynamic complexity in homopolymer layers adsorbed at liquid–solid interfaces, summarizing some of the simplest examples and examining the potential impact of specific complicating mechanisms: The distinction between diffusion limited (in free solution) and surface-controlled chain release is made, and then for the latter, several different cases of single-exponential desorption, self-exchange, and displacement are compared: Though the systems present great chemical variety, they have either a limited number of or a weak energy of segment–surface contacts. Increasing the strength and/or numbers of these contacts complicates dynamics, as does increasing molecular weight which can introduce chain pinning.

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1. Introduction

Traditional engineering applications of polymers, that is, strong adhesives, robust composites, and effective coatings have typically demanded permanent interfaces. As a result, an entire field of synthetic chemistry has been devoted to the development of covalent chemistries between unlike materials. By contrast, the new revolution in smart materials targets responsiveness, implicitly requiring systems that reversibly undergo stimulated bulk restructuring and interfacial re-organization. New technologies exploiting “smart” interfaces include reversibly adherent polymer melts such as those used for photolithography, removable inks, healable surfaces and interfaces, and contact adhesives. At liquid–solid interfaces, lab on chip technologies, biomaterials, and sensors require tunable interfacial dynamics.

Dynamic interfacial response (on a desired timescale) can be assigned to materials through precisely tuned physical bonds on their surfaces (and at internal interfaces such as micellar junctions). These include van der Waals, hydro-

phobic, electrostatic, and polar interactions. Interaction strength is governed by the density of interactive groups, controlled through chemistry, along with solution phase parameters such as pH, ionic strength, and dielectric constant. Polymeric systems are dynamically complicated by their chain architecture which, through entanglements and cooperative motions, imparts memory and viscoelasticity, and broad dynamic spectra.

Historically, the scientific focus on polymer liquid–solid interfaces has grown out of the colloid community, where adsorbed polymer layers presented a means to manipulate colloidal stability. Technologists in the fields of paints, inks, coatings, and other complex fluids benefited from an understanding of interfacial structure (and the related thermodynamic implications for colloidal stability), developed mostly in the late 70s and early 80s [1,2], yet it was appreciated that well-accepted treatments for equilibrium properties often fell short of predicting processing behaviors. Most notable of these was the general acceptance that some phenomena, such as bridging flocculation, were inherently kinetic (and technologically important) [3]. Hence, a modest but significant effort to understand relaxations in adsorbed layers emerged in the literature of the early 90s. This perspective benchmarks recent works

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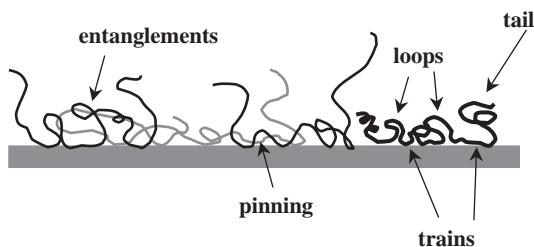


Fig. 1. Adsorbed layer of tails, loops, and trains. The highlighted chain is both pinned and tangled with neighbors. (Pinning is defined to be trapping of a train by loops or other trains. More classical, entanglements are tapping of loops by other loops.)

against the classical dynamic literature which, itself, is relatively new.

The recent technological thrusts of targeted delivery, selective adhesion, and processing at small lengthscales (i.e., Lab-on-chip applications) have rejuvenated interest in polymeric liquid–solid interfaces with new emphasis on pattern recognition [4], interfacial heterogeneity [5], polyelectrolytes [6], bioactivity [7], and charged biomolecules [8]. In this current surge, scientific advances in equilibrium and static aspects of polymeric interfaces again lead the development of dynamic principles, despite the practical importance of the latter.

This paper addresses dynamics in homopolymer layers physically adsorbed at liquid–solid interfaces, as a model system that can inform the design of solution–solid and melt–solid polymer interfaces through the identification of the core dynamic principles. Engineering smart, responsive polymer interfaces requires control of dynamics including chain release and constrained diffusion that affect adhesion, lubrication, and interfacial mechanics. While various kinetic forms have been reported in the literature of the past 15 years for different polymer chemistries, architectures, and interfacial scenarios, no unifying understanding has prevailed. In a recent review, Granick summarizes factors (entanglements, friction, incomplete equilibration) that contribute to complex layer dynamics [9].

The current perspective tackles complexity by starting with simplicity: First identified are specific cases and well-defined experiments where mechanisms are clear. Extrapolations, upheld by concrete experimental evidence, are then presented that argue for specific mechanisms of complexity. Since, in some cases, experimental design may give the appearance of complexity, these pitfalls are also pointed out. Among the dynamically simple cases identified from recent literature, transport-limited desorption, and surface-controlled activated desorption, self-exchange, and displacement that appear to be governed by single energy barriers follow single exponential kinetics. Complexities such as entanglements or interfacial competition between like species produce crossovers to stretched exponential behavior or alterations in the overall timescale.

2. Background on layer structure

Since the dynamic complexity of adsorbed homopolymers follows from their structure, a discussion must begin with layer structure. Adsorbing homopolymers adopt sequences of tails, loops, and trains, highlighted in Fig. 1 for a single chain, along with potential topological relationships to neighboring chains. Relevant to dynamics, removal of a chain from this interface requires disruption of the trains, (overcoming an enthalpic barrier), and disentanglement from neighboring chains (a diffusive process). Motions involving subchains obey the same processes.

The train fraction (the fraction of the backbone contacting the surface) decays monotonically with increasing molecular weight, from unity for an adsorbed monomer [2^{**}]. Typically, the train fraction approaches 0.5 for chains of modest length (75–100+ statistical segments) and adsorption energies near 1 kT [10]. Higher molecular weight nonionics exhibit train fractions as low as 20% [2^{**},11]. More recently it was found that weak polyelectrolytes on oppositely charged surfaces generally acquire dense charge and higher train fractions (with fewer loops and tails) [12] than their nonionic analogs [13,14], suggesting that adsorbed polyelectrolytes might display more sluggish dynamics than nonionics. In nonionic systems of moderate (order 1 kT) binding energy, the enthalpy of adsorption per chain (proportional to the train fraction times the molecular weight) scales as (distinctly) less than a power unity in molecular weight [2^{**},15], implying a particular molecular weight dependence (not yet observed) for desorption if train release controls the process.

Important to dynamics is the possibility of nonequilibrium chain conformations: Using spectroscopic methods, the Granick lab finds differences in the train fraction of early- and late-adsorbing chains with (Poly(methyl methacrylate) [16] and Poly(dimethylsiloxane) [17]), though connections to the dynamic behavior of these populations relies on theory [18^{**},19^{**}] and is very recent. Other systems (Polyethylene oxide (PEO)–water–silica [20^{**}], Polydimethylamino-ethylmethacrylic acid–water–silica [21,22]) were found to exhibit no influence of early-versus late-adsorbing populations on exchange or desorption dynamics, suggesting near-equilibration. Since the ability of early and late adsorbing chains to equilibrate and reach a uniform distribution of train fractions should depend on train motions, it is interesting to note new NMR data on ethylene oxide surfactants indicating what seems like relative immobility of trains, with interfacial residence times of several seconds [23]. The observation of dynamic equilibration (minutes or hours) between early and late adsorbing populations of higher molecular weight PEO [20^{**}] chains suggests that relative to other systems, these NMR-measured processes are still rapid compared with potential train motions of more strongly adsorbing systems.

Also influencing interfacial dynamics are the loops and tails, which, at equilibrium, have been described by

extensive theory [22,24–27] and classic experiments [28–30]. While part of the discussion below addresses dynamic interfacial control by the trains, there are instances where loops dominate through interfacial pinning [31], entanglements [32], and osmotic [20] or electroosmotic [22] barriers to the approach of chains to an existing layer. It is therefore important to appreciate that in most cases, the loop and tail layer is diffuse, with 90% of the adsorbed mass within the first few nanometers of the surface [2]. Indeed, the classic $z^{-4/3}$ scaling of the interfacial concentration (z is distance from the surface) is reconfirmed by new experiments exploiting sophisticated contrast measurements [33]. The interfacial gradient in loop properties complicates quantitative interpretation of experiments: Different dynamic processes, for instance one dominated by pinning and another osmotically controlled, will be sensitive to different parts of the loop size distribution or interfacial concentration gradient.

3. Experimental measures of interfacial dynamics

The most incisive experiments probing interfacial dynamics attempt to target specific processes. For instance, establishing an adsorbed layer on a bare surface involves the concomitant, but fundamentally independent, processes of *bulk diffusion* (relatively fast), *segmental adhesion* (very fast), and interfacial chain *relaxation and entanglement* (slower and of varied timescales). Decoupling these can be challenging.

Another process is *desorption* of adsorbed chains into pure solvent, which potentially affects more competitive processes involving exchange and adhesion. Often sluggish, desorption is attributed to non-equilibrium kinetic-trapping of chains which could include pinning; [34,35–37] however, this complicated mechanism is unnecessary. Two simpler explanations exist: Since adsorbing polymers typically make ~ 100 segment–surface contacts, each with energy of $\sim kT$, the effective equilibrium partition constant between adsorbed and free chains can be immense (exceeding 10^{50} M [38]). As a result, even the most dilute solution contacting an adsorbed layer will tend to prevent desorption, producing sluggish chain release kinetics. Therefore, desorption studies MUST continually replenish the fresh solvent, and preferably via a well-defined mass-transport coefficient between the surface and bulk solution. Even for transport-limited desorption (the fastest observable) into continually replenished solvent, the large adsorption equilibrium constant leads to very slow desorption [39]. However, without resistance from interference by transport, the disruption of the large number of segment–surface contacts contributes a high energy barrier against desorption [40]. Therefore both transport-limited [39] and kinetic (activated process) [40] arguments predict extremely slow desorption kinetics without invoking non-equilibrium chain conformations or entanglements as an additional complex-

ities. Indeed, the fundamentally slow nature of desorption makes probing entanglements even more difficult.

Self exchange, where chains from solution, identical to those on the surface with the exception of a tracer, displace those in the layer, often turns out to be mechanistically distinct from desorption. Self exchange has been used to characterize layer dynamics, with young layers typically more mobile than mature ones [41–43]. Meaningful experiments must satisfy the same bulk replenishing and mass transfer requirements of desorption studies, and also ensure that adsorbed and free chains are identical. This requires a minimally-invasive label; however, there are other potential differences between adsorbed and free chains, for instance those arising from slight polydispersity (even 1.05). In polydisperse samples, long chains adsorb preferentially to short ones [44], and as the layer develops, originally adsorbed short chains are displaced [38,45,46]. The molecular weight of the resulting layer is substantially greater than the free solution, and subsequent “self-exchange” is sluggish [47]. The layer *appears* trapped because the higher molecular weight adsorbed chains have become thermodynamically resistant to displacement by chains from solution of lower (albeit the nominal) molecular weight. It is for this reason that self-exchange studies in the Santore lab incubate layers in solvent rather than polymer solution: Aging in solvent prevents the exchange-driven upward drift in layer molecular weight [47].

Displacement studies, more complex than self-exchange, employ one polymer to displace another previously adsorbed polymer, where the two are chemically different. Though the driving forces for displacement are rarely quantified, data provide qualitative perspective on interfacial mechanisms, for instance the formation of an overlayer of challenging chains on top of the original layer, which may limit the escape of original chains via pinning or chemical incompatibility between original and challenging chains. Indeed, these more complicated mechanisms are often accompanied by overshoots in adsorbed mass [48,49], absent from true self-exchange studies which proceed at constant interfacial mass [20–22,41,42].

3.1. Case 1: simple single-activation for chain removal/escape

A simple case study which serves as a departure point for more complex interfacial scenarios is one with complete domination of interfacial dynamics by adsorbed trains. In the well-defined system, pDMAEMA (polydimethylaminoethyl methacrylate, a weak polyelectrolyte) adsorbing onto silica from high pH (9.6), the silica carries a dense negative charge and the polymer is extremely weakly charged (3–4 charges in a chain of molecular weight 31,300) [50,51]. Adsorption occurs exclusively through electrostatic attractions [52]. In Fig. 2, [21] self-exchange and desorption are single exponential and quantitatively

identical, with an ionic strength-dependent time constant (in Fig. 3). Kinetics are bulk transport-independent, dominated by the release of trains of the originally adsorbed chains, whether they escape into solution (desorption) or are replaced by free chains (self-exchange).

The particular ionic strength effect on the time constant in Fig. 3 is quantitatively consistent with the same rate limiting step for desorption and exchange: release of all contacts between an adsorbed chain and the surface [21]. In this case, this is the release of 3–4 electrostatic segmental interactions, as measured by titrations and electrophoretic mobility that measure chain protonation [51^{**}]. The small segmental number is also consistent with the vanishing train fraction at this pH [12]. The simplicity of this particular example is preserved by low pDMAEMA molecular weight (31,000), avoiding chain entanglement.

The single exponential kinetics and exclusive surface control by train release comprise the simplest case for adsorbed homopolymer dynamics: the polymeric nature of the system is lost and chains behave as single dynamic units, with an activation energy corresponding to 3–4 segment–surface contacts. Previously, single exponential kinetics from an activated desorption or exchange process were discussed as a limiting behavior [53], but their experimental

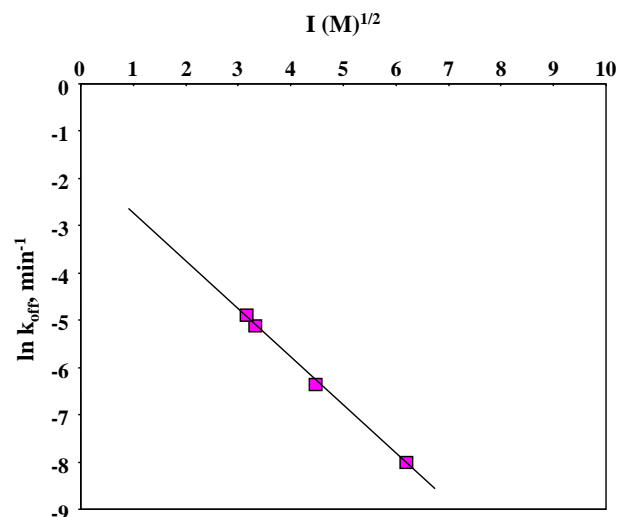


Fig. 3. Rate constants (for equivalent self-exchange and desorption) from Fig. 2, as a function of the square root of ionic strength. Reproduced with permission from Ref. [21].

confirmation was incomplete: Displacement rates [49^{**}] were independent of the challenging species; however, the comparison to pure desorption was lacking. Self exchange of pDMAEMA at pH 9.6 in Fig. 2 is kinetically identical to

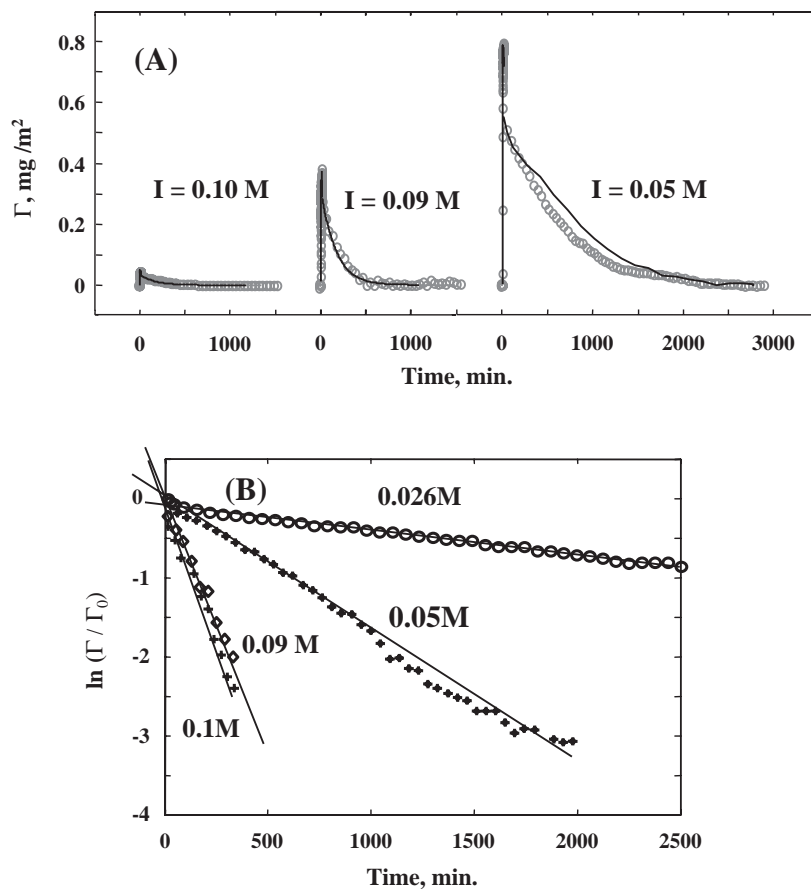


Fig. 2. (A) Comparing 3 self-exchange (o) and 3 desorption (lines) runs of pDMAEMA on silica at pH 9.6, with ionic strengths as indicated. Here the initial adsorption of polymer is shown, followed by removal of originally adsorbed chains during either desorption or self-exchange. (B) Semilog plot of self-exchange data, much of which is duplicated from (A). Reproduced with permission from Ref. [21].

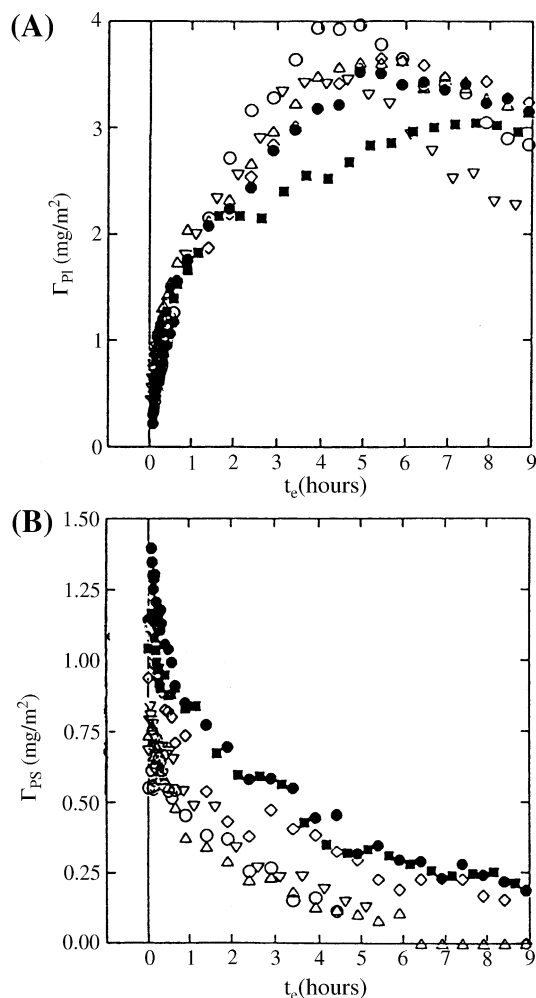


Fig. 4. Kinetic data for (A) incorporation of PI chains (150,000 molecular weight) and (B) escape of PS chains during displacement studies in which the varied PS molecular weight determines the symbols: 43,900 — open circles; 96,400 — triangles down; 355,000 — triangles up; 706,000 — diamonds; 1,260,000 — closed circles; 3,840,000 — closed squares. Reproduced with permission from Ref. [49].

desorption (a novel result), and free chains have no influence on adsorbed chain release.

The potential relationship between the adsorbed pDMAEMA structure at pH9.6 and the dynamics is interesting: With 3–4 electrostatic segment–surface contacts [52], an adsorbed chain might form a few intermediate sized, loops, or all the contacts could occur in a single train. Entropically, the latter is favored so that with a single train, the chain may act as a single dynamic unit. Further, without loops, adsorbed chains are unlikely to pin neighbors onto the surface. It would therefore be an interesting experiment to compare the results of Figs. 2 and 3 to a system containing exactly 3–4 cationic groups per chain, roughly evenly or randomly spaced. Such an experiment would introduce the possibility of pinning and interfacial entanglements and would facilitate dynamic independence of different portions of the backbone, perhaps shifting dynamics away from a single exponential.

3.2. Case 2: displacement via single exponential kinetics

A more complex case exhibiting single exponential kinetics is the displacement of polystyrene (PS, of molecular weight near or below 96,000), adsorbed on silica from CCl_4 , by polyisoprene (PI, of molecular weight 150,000) at 50 °C [49]. Here, unlike the pure pDMAEMA self-exchange in Fig. 2, upon PI solution introduction, the interfacial mass increases (from 1 mg/m^2 PS to 3 mg/m^2 mixed PS–PI layer in Fig. 4a) and overshoots. PI chains continue to incorporate as PS leaves the interface, suggesting that the PI forms an overlayer on the originally adsorbed PS chains. Even so, in Fig. 4b, the escape of PS obeys single exponential kinetics.

The single time constants indicated by Fig. 5 come as a surprise, given the complexity of the PS–PI mixed interface, and our expectations from the pDMAEMA pH 9.6 case study (above). The original PS layer is likely to have many segment–surface contacts, multiple loops, and train fractions from 20–50% (depending on molecular weight, for $\chi_s=1$ and $0 < \chi < 0.5$, for a good solvent) [2]. Indeed, the PS–silica– CCl_4 system was characterized thoroughly at room temperature where the segmental adsorption energy was 1.3 kT and desorption into pure solvent could not be detected [54]. The presence of a substantial PI overlayer, developed during displacement, could provide topographical constraints to PS release, which is surprisingly not apparent in dynamics at 50 °C. Increasing the original PS molecular weight above 100 K, however, leads to stretched exponential PS escape upon PI introduction, suggesting the growing importance of pinning. Below 100 K molecular weight PS, however, the original PS layer is likely to be relatively unentangled. The single exponential behavior observed for PS displacement by PI at elevated temperatures may also be preserved by compatibility between the two species at this temperature: Single exponential behavior was also observed in PEO displacement studies in which

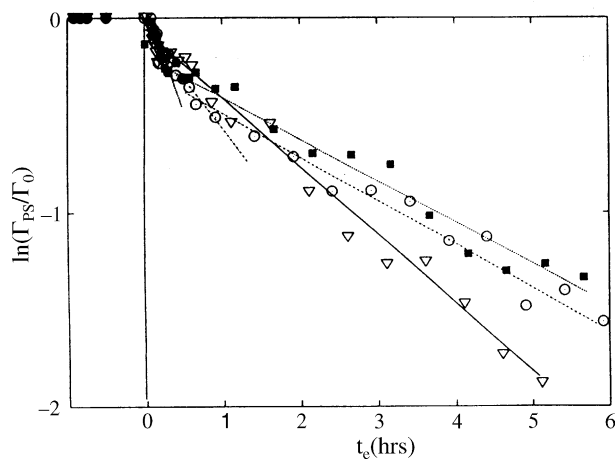


Fig. 5. Semilog plot data from Fig. 4b, demonstrating single exponential nature of the PS escape molecular weights below 100,000. Reproduced from Ref. [49].

moderate molecular weight chains in a relatively young layer were replaced by longer ones [45].

In the PS–silica–CCl₄ system, departure from the single exponential kinetics is observed at room temperature: both self-exchange [54] and displacement [48**] become stretched exponential even for the lower molecular weight PS. Therefore, the primary effect of the lower temperature is likely to be in the strength and number of segment–surface contacts. While this should impact pinning and interfacial entanglements, the dramatic crossover in both displacement and self-exchange dynamics seems to be rooted in the strength of segment–surface interactions.

3.3. Case 3: multiple train runs: still single exponential

A third interesting case, exhibiting single exponential kinetics is aqueous pDMAEMA self-exchange on silica at pHs below 9.6, where the chains are more highly charged and likely experience a greater number of segment–surface contacts than at pH 9.6. When the pH is decreased slightly so that the number of segment–surface contacts increase (at fixed ionic strength, which roughly fixes the segmental binding energy), the kinetics slow down but remain roughly single exponential, per Fig. 6 [22]. This reduction in exchange dynamics is expected with greater chain adhesion energy (per the activation energy term in an activated process); however, one also observes a departure between desorption into solvent and self-exchange. Desorption becomes slow relative to self-exchange with increased segment–surface contacts. (Recall that with 3–4 charges per chain, likely all in one train, desorption and self-exchange were identical in Fig. 2.) This divergence suggests a crossover in the dynamic mechanism of interfacial chain dynamics: In the limit of a few segment–surface contacts and perhaps one train, the release of an adsorbed chain, acting as a single dynamic unit, was uninfluenced by chains

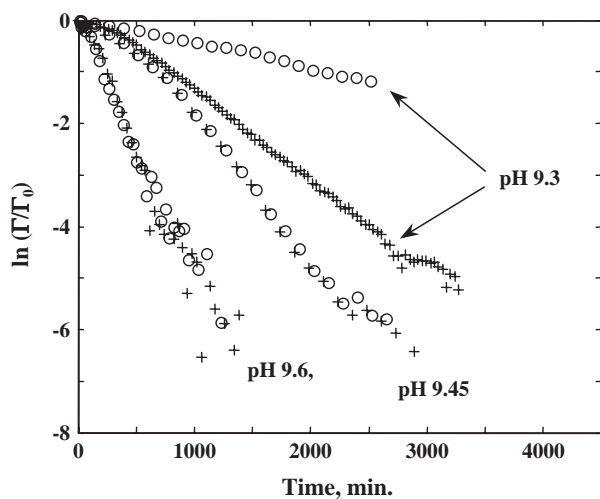


Fig. 6. Self exchange and desorption at fixed ionic strength $I=0.1$ M, and pH=9.3, 9.5, and 9.6: desorption (o), and self-exchange (+). Reproduced from Ref. [22].



Fig. 7. Dashed portions of an initially adsorbed chain (starting to desorb, on the left) and an incoming chain (just to its right) compete for the surface during self-exchange, when fully adsorbed chains have significant segment–surface contacts, as drawn on the right. This mechanism won't work if the fully adsorbed chains have very few contacts with the surface.

in free solution. With greater numbers of segment–surface contacts per chain, release of an adsorbed chain can be facilitated by an approaching chain: In Fig. 7, for instance with 2–3 trains on the originally adsorbed chain, it can release half way, and the invading chain can prevent readsorption. Without the invading chain (the desorption experiment), readsorption of the first train will slow desorption relative to self-exchange.

4. Summary and final thoughts

Dynamics in adsorbed layers tend to be complicated, even with carefully-designed experiments targeting precisely-defined processes. This opinion article synthesized a general picture of interfacial chain dynamics based on simple cases from recent literature, and examined connections to more complex dynamics through specific mechanisms. Most of the latter focused on alterations to the segmental binding energy or train fraction, or was at least driven at that level.

Arguments were first put forth that sluggish desorption could result (through 2 distinct mechanisms) from train-level physics, without invoking entanglements or non-equilibrium chain trapping. Related to this was a first case study in which chains, with just a few train segments, behaved as single dynamic activated units with equal desorption and exchange kinetics described by single exponentials. The single exponential form also appeared in a more complicated 2nd case, where adsorbed chains of one chemistry escaped the interface as those of a second chemistry adsorbed. The key to the simplicity here appeared to be compatibility between the two species and a lack of tight pinning. Temperature and molecular weight variations produced a crossover to stretched exponential kinetics, likely due to chain pinning, but also related to binding tightness in the case of temperature. To better isolate the role of structural features, in a third case, changes in the charge density of adsorbing polyelectrolyte were considered. This third case revealed crossover behavior with increased backbone charge, giving departures between self-exchange and desorption behaviors but keeping both in the single exponential regime. The single exponential behavior of this third system is consistent with the single exponential findings in the second case: It is possible to increase the number of segment surface contacts over that

needed to produce a single train and preserve single exponential dynamics. Pinning requires, in addition to multiple train runs, sufficiently high molecular weight chains.

The greatest challenges to predictive mechanistic understanding of adsorbed layers still lies ahead, but is more important than ever: New technologies employing adsorbed polymers in the biotechnical arena cannot simply rely on equilibrium layer features. Answering the dynamic questions will require incisive experiments that isolate interfacial mechanisms, and rely on well-conceived and carefully executed experiments, potentially including specially synthesized samples and surfaces that target fundamental parameters: loop size distribution, train length distribution, and segmental binding energy.

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