Adsorption of a Radiolabeled Random Hydrophilic/Hydrophobic Copolymer at the Liquid/Liquid Interface: Kinetics, Isotherms, and Self-Exchange

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ABSTRACT: The synthesis and labeling (with ^{35}S) of a water-soluble random copolymer of styrenesulfonate and *tert*-butylstyrene (20 mol %) is described. Adsorption of this copolymer to the toluene/water interface is followed *in situ* using a proximity radiometric detection scheme, where the organic phase also serves as a scintillator. Adsorption isotherms, determined with the aqueous phase either salt-free or containing 1 M NaCl, are of the high-affinity type, with respective pseudolimiting adsorbed amounts of 0.24 and 1.4 mg m^{-2}. Adsorption is fairly rapid, occurring with a time constant of a few minutes. Self-exchange of radiolabeled polymer at the interface, performed with a solution excess of unlabeled polymer, is complete within a few hours, providing evidence that the surface excess is under thermodynamic, rather than kinetic, control. Preliminary comparisons of the liquid/liquid interface and a chemically similar polystyrene/water interface reveal that the adsorption isotherms are similar despite the additional mobility afforded to adsorbed segments at the fluid interface. The free energy of adsorption for *tert*-butylstyrene units is estimated to be ca. 13 kT from solubility and partitioning measurements of the corresponding monomer.

Introduction

The adsorption of polymers at liquid/liquid interfaces is key to their application as emulsifiers, surfactants, and stabilizers.[1−3] However, the study of polymer adsorption at the liquid/liquid interface has been eclipsed by extensive research on adsorption at the solid/liquid interface,[4] primarily due to the limited experimental accessibility of the "buried" interface in the former system. Experimental techniques for liquid/liquid interfaces that have met, nevertheless, with some success include ellipsometry[5] and surface pressure measurements.[6−8] In addition, the interfacial reflection of neutrons[9,10] or X-rays[11] yields concentration profiles at the air/liquid and liquid/liquid interface. A number of promising new optical methods have appeared recently, including second harmonic generation, where the interface induces a noncentrosymmetic distribution of chromophores required for macroscopic second-order nonlinearity.[12,13] We describe here a radiochemical assay of interfacial polymer concentration that is an extension of our use of solid scintillating materials to study the adsorption of polyelectrolytes.[14,15] The radiochemical method is based on the proximity detection of labeled molecules which accumulate at an interface.[16,17] Radiotracers have been employed for evaluating *in situ* the adsorption of proteins at the air/liquid and liquid/liquid interface.[18,19]

Theory has been applied to both random and block copolymers at liquid/liquid interfaces.[20−26] Since most theoretical predictions are made assuming equilibrium conditions, the use of liquid/liquid interfaces may be beneficial in ensuring that the interface is under thermodynamic (reversible), rather than kinetic, control. At a liquid/liquid boundary, polymer segments move more freely in two dimensions, whereas adsorption at a solid/liquid interface may lead to nonequilibrium surface conformations that are dictated by adsorption kinetics, particularly for strong adsorbers. With the increasing interest in, and availability of, new polymer architectures for adsorption, there is good reason to expect renewed experimental attention to the liquid/liquid interface. In this paper we describe initial studies on the adsorption at the toluene/water interface of a poly(styrenesulfonate)/poly(*tert*-butylstyrene) random copolymer bearing the ^{35}S label. This polymer has hydrophobic and hydrophilic segments that exhibit strongly negative free energies of solvation for their respective solvents (toluene and water).

Experimental Section

Copolymer was prepared by free radical polymerization of styrene (Aldrich) and *tert*-butylstyrene (Dajac Laboratories) in benzene using AIBN as initiator. For example, 3.04 g of styrene, 1.30 g of *tert*-butylstyrene, and 3.4 mg of AIBN were added to benzene in a 50 mL polymerization tube. The mixture was degassed with several freeze−pump−thaw cycles, sealed, and placed in an oil bath at 60 °C for 16 h. The product was recovered by precipitation in methanol, washed with copious quantities of methanol, and dried. The composition, determined by ^1H NMR ($CDCl_3$, Gemini 300 MHz) was 18.8 mol % (26.3 wt %) *tert*-butylstyrene and 81.2 mol % (73.7 wt %) styrene. Molecular weight (gel permeation chromatography with polystyrene standards): M_w = 186 000, M_w/M_n = 1.72. Several other (nonradiolabeled) compositions were prepared and sulfonated as below, but the 19 mol % *tert*-butylstyrene copolymer was selected for labeling and interfacial adsorption experiments.

Selective sulfonation of styrene units was performed by following the method of Valint and Bock[27] and Guenoun et al.,[28,29] who used a sulfur trioxide−triethyl phosphate (SO_3·TEP) complex as a mild sulfonating

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agent[30,31] for block copolymers of styrene and *tert*-butylstyrene. Liquid SO_3 was distilled from 20% fuming sulfuric acid and dissolved in 1,2-dichloroethane (DCE) to make a 0.8−1.0 M solution, which was standardized against a NaOH reference solution just prior to use. Unlabeled polymer was prepared by mixing 2.81 mL of 0.824 M SO_3 in DCE with 0.166 mL of TEP in a 10 mL flask. The mixture was stirred at −20 °C for 30 min to form the SO_3·TEP complex and 83 mg of copolymer (19 mol % *tert*-butylstyrene), dissolved in 2.04 mL of DCE was added. After 30 min the temperature was raised to 0 °C and the reaction was allowed to continue for another 30 min, the sulfonated polymer precipitating from solution, before the reaction mixture was added to hexane. The product was washed with hexane and then dissolved in 5 mL of distilled water. The fully soluble product was dialyzed extensively against distilled water (with 12 000−14 000 molecular-weight-cutoff dialysis tubing) to remove small molecules and impurities. The dried product contained 14.31 wt % sulfur (elemental analysis). Elemental analysis, wt %: C, 52.5; H, 5.33; S, 14.31. Calc for $[(C_{12}H_{16})_{0.19}(C_8H_8SO_3)_{0.81}]_n$: C, 58.6; H, 5.3; S, 14.4.

To prepare ^{35}S-labeled copolymer, 2.24 mL of 1.045 M SO_3 in DCE was added to a sealed 10 mL flask containing 5 mCi (ca. 5−6 μL) of $H_2{}^{35}SO_4$ (^{35}S, β-emitter E_{max} = 0.167 MeV, half-life = 87.4 days, ICN Radiopharmaceuticals). (*Caution*: radioactive materials must be handled in accordance with regulations and with attention to good laboratory practice, which includes the wearing of protective gloves, handling in properly ventilated enclosures, and storage and disposal in approved containers.) The solution was then stirred for 3 h to allow exchange of ^{35}S with the unlabeled sulfur in the SO_3·TEP complex. After the solution was cooled to −20 °C, 0.166 mL TEP and 83 mg of copolymer were then added and the procedure for making the unlabeled polymer was followed. Radiolabeled polymer was stored as a 1.99×10^{-2} M aqueous stock solution. Specific activity was approximately 1 Ci mol^{-1} at the time of synthesis.

Scintillating organic phases were made by dissolving *p*-terphenyl, PTP (1 wt %), and 1,4-bis(2-methylstyryl)-benzene, bis-MSB, (0.1 wt %), both from National Diagnostics (Atlanta, GA), in HPLC grade toluene (Fisher Scientific). Since impurities tend to collect at interfaces, this scintillation cocktail was shaken with an equal volume of water and the organic layer was separated for use in further experiments. The solid scintillator was a blue-fluorescing polystyrene-based plastic[15,32] cut from sheets 3 mm thick (SCSN 81, Kuraray Inc.). An area for adsorption was defined by affixing a 25 mm i.d. glass tubing to one side of the plastic scintillator with silicone rubber.

Counting measurements were acquired in a dark box equipped with an RCA 8850 end-on photomultiplier tube biased to 2200 V with a Bertan 313B high-voltage supply. Scintillation pulses were counted with a Philips PM 6654C frequency meter interfaced to a computer. The pulse height threshold was set to 20 mV, and counts were collected with a 30 s gate time. Consecutive data points could be coadded at a later time for better signal/noise. The instrumental background count rate under our conditions was 1−2 cps.

Liquid/liquid adsorption experiments were performed in 20 mL glass scintillation vials. The interface was formed by carefully placing the organic layer on top of the aqueous one. The area of the interface was calculated from the meniscus height and the diameter of the scintillation vial, under the assumtion that the interface was elliptical in cross-section. The polymer concentration in the aqueous phase was increased by adding small aliquots from concentrated stock solutions with a 100 μL syringe. After each addition the vial was placed in the dark box underneath the PMT and the adsorbed amount was allowed to equilibrate for 1−2 h under gentle stirring with a micro stir bar. Adsorption kinetics were determined *in situ* by injecting polymer into the aqueous phase with a remotely operated syringe. A standard (for converting count rate to adsorbed amount) was made by depositing a known mass of polymer onto a glass microscope cover slide and suspending it near the interface in the organic phase. Adsorption at the solid/liquid interface was performed in a similar manner, except that the solution was stirred from the top and the PMT was placed beneath the scintillator. The standard for this interface was made by allowing an aliquot of polymer solution to dry on the plastic scintillator. Small corrections for differences in reflection losses between air/plastic and water/plastic phase boundaries were applied.

Solubility and partition coefficients of *tert*-butylstyrene were determined in order to gauge the affinity of hydrophobic segments for the interface. To measure partition coefficients, 10 wt % *tert*-butylstyrene in toluene (0.56 M) was placed in contact with pure water or 1.0 M NaCl for 1 week at room temperature. For solubility measurements, saturated solutions of *tert*-butylstyrene in water and in 1 M $NaCl_{aq}$ were made by exposing the aqueous phase for 2 weeks at room temperature (23 ± 2 °C) to vapor from a plug of glass wool soaked in monomer. Monomer content in both cases was determined using reversed-phase liquid chromatography (C_{18} column, acetonitrile/water mobile phase).

Results and Discussion

Copolymer Synthesis and Labeling. Total conversion of the monomers was kept in the range 10−15% to avoid composition drift. A 30% in-feed of *tert*-butylstyrene resulted in 19% composition in the polymer. Elemental analysis of sulfonated copolymer indicated almost complete sulfonation of styrene units, as found by Valint and Bock[27] for similar procedures on *tert*-butylstyrene/styrene diblock copolymers. Since the copolymers used in our work are random, rather than block, micelle formation[27−30] was not an issue. Indeed, we saw no evidence of phase separation over the concentration range and conditions employed.

Our labeling scheme requires exchange of SO_3 in the TEP.SO_3 complex with labeled sulfur in the H_2SO_4 added.

$$H_2{}^{35}SO_4 + SO_3\cdot TEP \rightleftharpoons H_2SO_4 + {}^{35}SO_3\cdot TEP$$

Sulfonation, following such an exchange, of polystyrene homopolymer yielded approximately 50% of the specific activity expected for full exchange. The level of labeling is not critical, as long as the count rate for adsorbed polymer is high enough to give acceptable counting statistics. Polymer made under our conditions had a specific activity of ca. 1 Ci mol^{-1}, which yields a count rate of about 40 cps mg^{-1} m^{-2}. A half-life of 87 days, however, meant that the specific activity of a batch

of copolymer dropped significantly over the course of our studies. Isotope is provided by the manufacturer as >99% $H_2{}^{35}SO_4$ in ca. 10 μL of water. Unlabeled sulfonation runs with a few microliters of water revealed no measurable difference in the level or efficiency of sulfonation.

Detection Scheme. Measurements based on radioisotopic labeling have several desirable features, such as sensitivity, low cost, and long-term stability including immunity from small temperature/refractive index fluctuations. The major disadvantages include safety concerns in the handling of radioactive materials, and the requirement that an efficient labeling protocol must be included in the synthesis.

In the analytic technique employed here, β-particles are emitted omnidirectionally from labeled polymer adsorbed at the interface.[14,15] Half of these β-particles penetrate into the organic phase, which is also a liquid scintillator, causing scintillation. The interfacial polymer causes a proportionate increase in the count rate, as detected by the photomultiplier. The choice for organic phase is dictated by the same considerations involved in selecting a solvent for a liquid scintillation cocktail. For example, aromatic units (i.e., toluene) are useful in transferring energy from β-particles to fluorescent dyes. A primary dye is present in *ca.* 1% concentration, and a much more dilute secondary dye red-shifts the energy of the emitted light to a spectral region matched to the optical response of a photomultiplier (blue). There are many possible combinations of primary and secondary fluorescent dyes (fluors). For example, the duo of PPO (2,5-diphenyloxazole) and POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene) is common, and a related oxazole has been employed by Graham and Philips in evaluating the adsorption of radiolabeled protein at interfaces.[18,19,32,33] We elected to use PTP and bis-MSB as primary and secondary fluors, respectively, to avoid the possibility that heteroatom-containing molecules may exhibit some affinity for the liquid/liquid interface. For copolymers containing strongly adsorbing (i.e., very hydrophobic) segments, such as *tert*-butylstyrene, there is little possibility that fluorescent dye would compete for the surface, but problems may be encountered for weaker interactions. The overall counting efficiency was approximately 40%.

The time resolution for this *in situ* method involves a tradeoff between precision and counting time. Error, determined by Poisson statistics, depends on the absolute number of counts.[34] Experimental count rates were in the range 1−50 cps. Thus, a rate of 20 cps accumulated over 1 min would yield 1200 counts for an error of ca. 3%. Since each data point would typically be allowed to equilibrate over 1 or 2 h, and each reading would have count rates averaged over several minutes, precision was usually better than 2% of a monolayer.

Since β-particles have a finite range in water, most labeled polymer in the bulk of the aqueous solution is not detected. However, the observed count rate contains a contribution from labeled material in a thin layer of liquid adjacent to the interface. This "background" contribution is present in all samples and is directly proportional to the solution concentration of labeled polymer. The effective thickness of polymer solution that contributes to the background is about 30 μm.[35] For an experiment where concentration is a variable (i.e., for an adsorption isotherm), one may project the following scenarios, summarized in Figure 1: (1) No adsorption to the interface occurs, the count rate comes only from the solution background, which is proportional to the solution concentration of polymer (curve A). (2) High affinity adsorption occurs with a constant surface excess over all measured concentrations, the count rate has a constant contribution from the adsorbed polymer on a rising background, and the *y*-intercept yields the adsorbed amount (curve B). (3) Increasing adsorption with concentration occurs, the count rate rises, and eventually the surface excess reaches a (pseudo) constant value (curve C). In all cases, background (curve A) contributes to the observed count rate and must be removed to yield the true surface excess.

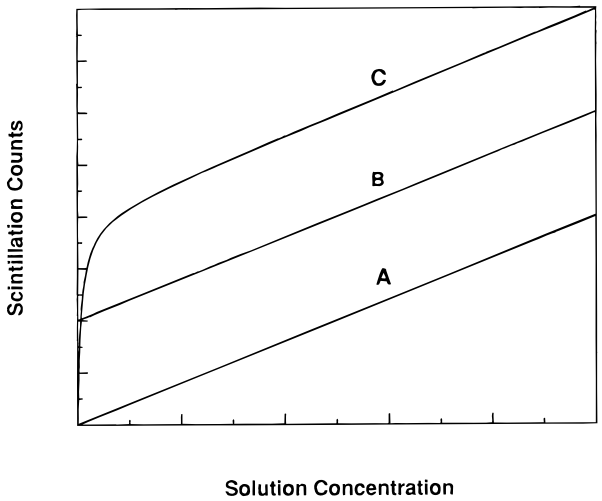
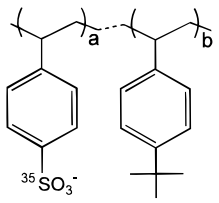


Figure 1. Generalized response at an aqueous/organic scintillator interface for the adsorption of radiolabeled polymer. Curve A represents no adsorption of polymer, with signal from solution only. Curve B is expected for high-affinity adsorption with a constant surface excess. Curve C is for increasing adsorbance with concentration, with a pseudoconstant adsorbance at higher solution concentrations.

The possibility of dissolution of polymer in the bulk organic phase was probed by withdrawing aliquots of scintillator following adsorption experiments and counting these aliquots separately. No evidence (counts above background) for solubility of copolymer in toluene was found.

Copolymer Adsorption. Figure 2 depicts room-temperature adsorption isotherms for 19% *tert*-butylstyrene random copolymer (PSS-*co*-PBS) adsorbing at



PSS-co-PBS
random
a/b = 4
M_w = 290,000
M_w/M_n=1.72

a water/toluene interface from pure water and from 1 M $NaCl_{aq}$. In solution, salt ions shield the charges along the polymer backbone, which leads to a more compact conformation.[36] The densification of polymer at the surface is expected from the same mechanism. Thus, more polymer is localized at the interface for the higher salt concentration, as is generally observed for polyelectrolyte adsorption.[37] Data for both salt-free and salt-containing systems approach a linear dependence on polymer concentration. The slope of this line is the solution background (curve A Figure 1), which when subtracted, yields the experimental isotherms depicted

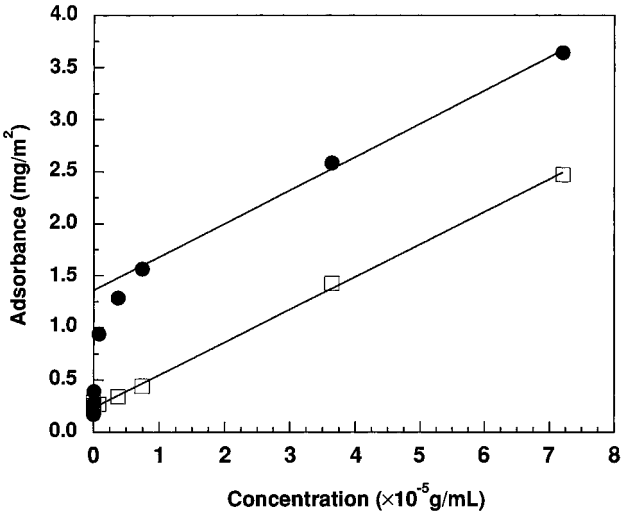


Figure 2. Apparent adsorption of copolymer at the aqueous/toluene interface as a function of concentration in water (squares) and 1 M NaCl (circles). Uncorrected for solution background.

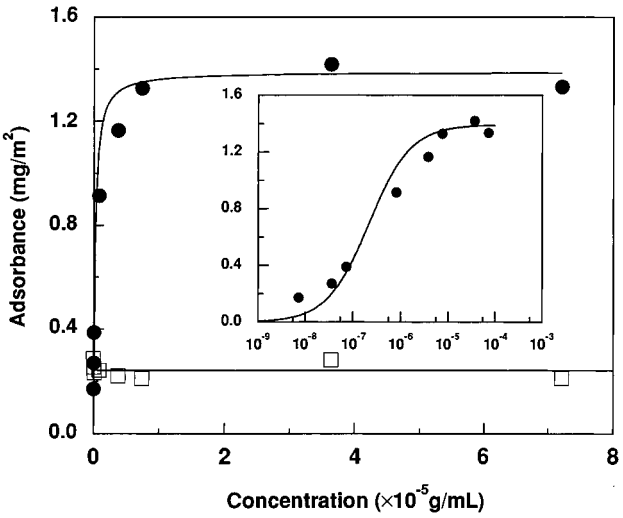


Figure 3. Room-temperature adsorption isotherms for polymer at the aqueous/toluene interface from water (squares) and 1 M NaCl (circles). Adsorbance (from Figure 2) has been corrected for solution background. The inset shows the same data as a semilog plot.

in Figure 3. At higher concentrations, the interfacial excess approaches 1.4 mg m^{-2} for 1 M NaCl and 0.24 mg m^{-2} for the salt-free solution.[38] The form of the isotherm for the salt solution is that for typical high-affinity polymer adsorption. Theoretical treatments of the solid liquid interface based on self-consistent fields (SCF) predict a sharply rising isotherm with a pseudo-plateau at high concentrations:[39,40] better solvents lead to flatter plateaus, and wider molecular weight distributions yield rounded isotherms.[41] Experiment has been compared to theory for dextran adsorbing to silver iodide[42] and poly(styrenesulfonate) adsorbing to silica,[43] among other systems.

SCF theory for copolymer adsorption has been extended to penetrable (i.e. liquid/liquid) interfaces.[44] Cosgrove et al.[44] and Phipps et al.,[10] using neutron reflection, clearly demonstrate the importance of polymer architecture on concentration profiles at liquid/liquid interfaces. A random copolymer of vinyl alcohol and vinyl acetate adsorbed as a very thin layer at the hexane/water interface, in strong contrast to a block

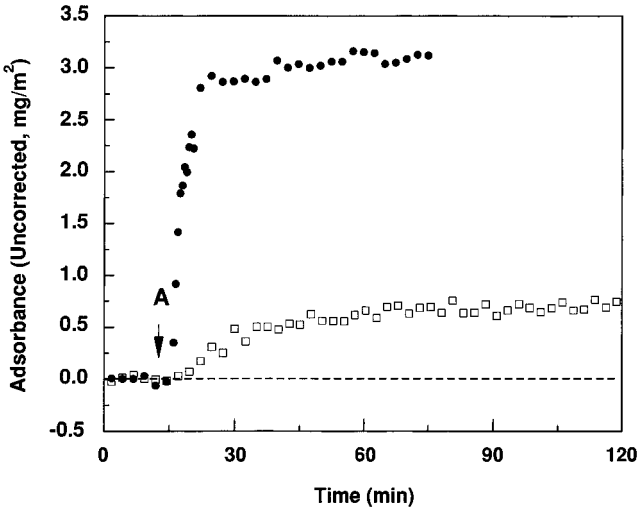


Figure 4. Adsorption kinetics: apparent surface excess as a function of time for 7.2 × 10^{-5} g/mL (circles) and 7.2 × 10^{-7} g/mL (squares) polymer in 1 M NaCl at the nascent toluene/aqueous interface. The adsorbance values, at longer times, include a ca. 60% contribution from solution background for the higher concentration sample.

hydrophobic/hydrophilic polymer.[10] Recent experiments in our laboratory on poly(vinylpyridinium-*co*-styrene) diblock polymers adsorbing to the toluene/water interface show interfacial excesses similar to the random copolymers here, but subject to kinetic limitations.[45] Experimental polymer adsorption isotherms for the liquid/liquid interface are rare. The conformation of the polymer adsorbing with the isotherm depicted in Figure 3 probably involves all the *tert*-butyl groups inserting into the toluene, while the styrenesulfonates form short loops in the water. The isotherm is also depicted on a semilogarithmic scale (inset, Figure 3): the data are presented as such to spread the concentration range out and not to imply that isotherms are of the Langmuir type. Although Langmuir behavior, $\Gamma = \Gamma_{max}(Bc/1 + Bc)$ with $\Gamma_{max} = 1.39$ mg m^{-2} and $B = 4.6 \times 10^6$ mL/g, is shown as the solid line in Figure 3, this should be considered a guide to the eye, since extensive theory on polymer adsorption[4] has shown Langmuir behavior to be an oversimplification.

Although the use of radiolabeled polymer yields unambiguous values for the surface coverage, the overall accuracy is estimated to be ±15%. This is because the area of the interface is difficult to measure accurately in the scintillation vials employed (larger containers would minimize the significant curvature of the water/toluene meniscus), and the standard did not reproduce exactly the interfacial distribution of polymer. A microscopic picture of the interfacial region must include surface roughness induced by capillary waves.[46] For example, the RMS roughness of a pure water surface in air is about 3 Å.[47] Contributions to roughness will also come from the structure of adsorbed molecules.[48−50] However, the high mass and enhanced local viscosity of an adsorbed polymer would dampen thermally induced fluctuations. Enhancement of surface area over the geometric (apparent) surface area via roughness is not known for our system but is believed to be minimal.

Example kinetics of polyelectrolyte adsorption are shown in Figure 4 for two concentrations of polymer in salt. Final limiting count rates include approximately 60% contribution from solution background for the

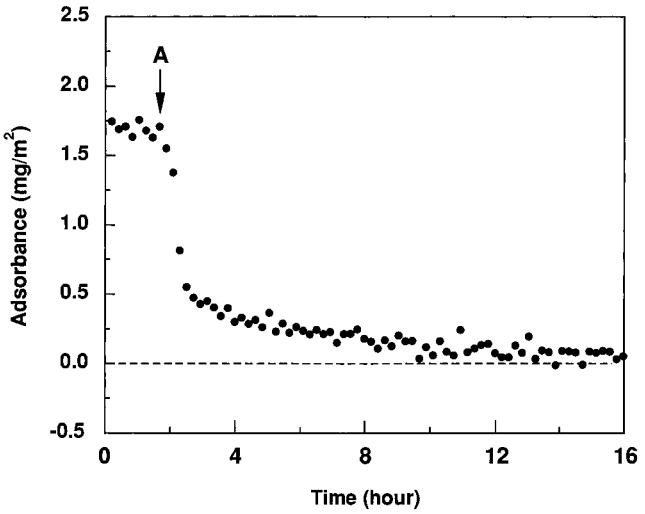


Figure 5. Self-exchange of ^{35}S-labeled polymer (solution concentration = 7.2×10^{-5} g/mL) at the toluene/1 M $NaCl_{aq}$ interface with a 10-fold excess of unlabeled polymer added at point "A". The equilibrium coverage of labeled polymer is expected to be 9% of the original amount.

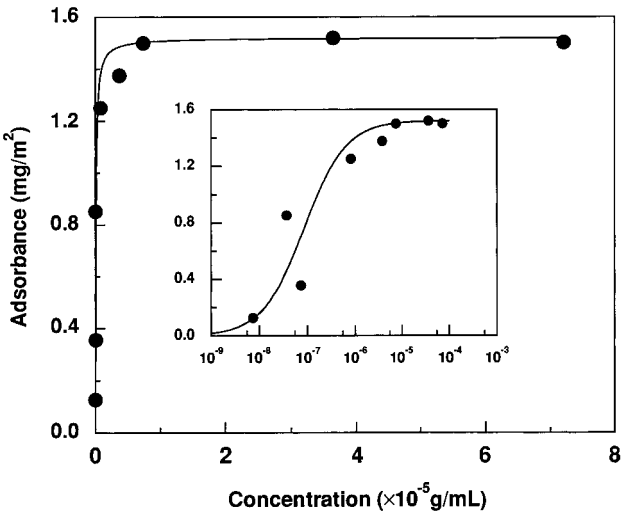


Figure 6. Room-temperature isotherm, corrected for solution background, for labeled polymer adsorbing at a plastic scintillator (2% divinylbenzene-cross-linked polystyrene) from 1 M NaCl. The inset shows the same data as a semilog plot.

higher concentration experiment, whereas the lower concentration run has negligible background. Adsorption, complete after a few minutes, is reasonably rapid. Scant evidence for a slower period of surface reorganization, after initial rapid adsorption, could be seen. This is in contrast to polyelectrolyte adsorption at a charged surface,[14] where adsorption was initially rapid, but took several hours to reach a limiting value, due presumably to slow surface rearrangements to accommodate additional polymer.[51,52] For polydisperse polymers there are entropic advantages to replacing short chains at the interface with long ones.[41,53] This may be occurring in our system on a continual basis, but if the surface excess has a weak dependence on molecular weight such a "ripening" of the interfacial composition would be difficult to observe. A slight increase in adsorption with time in Figure 4 may be evidence for this.

Since molecules at the liquid/liquid interface have mobility in two dimensions, and the surface itself has some dynamics in the form of surface capillary waves, it is probable that adsorption occurs under equilibrium conditions. A good test of whether thermodynamics or kinetics are controlling is to determine whether *self-exchange* occurs (equilibria are dynamic equilibria). If isotopic labels are employed, self-exchange is easily measured. For example, Figure 5 depicts the exchange of labeled polyelectrolyte at the liquid/liquid interface with a 10-fold excess of unlabeled polyelectrolyte (copolymer sulfonated in an identical manner with the exception of the radioisotope.) Self-exchange of most of the surface polymer is observed. The remaining polymer may be exchanged over the course of several hours. The cause of this slow portion of the exchange curve is unknown, but detailed studies on the adsorption and exchange of polystyrene and deuteriopolystyrene at silica from cyclohexane revealed displacement time constants of hours, which showed an exponential dependence on molecular weight.[54] The slow part of the exchange may thus reflect desorption of the longest chains.

The kinetics of polymer adsorption/desorption are controlled by numerous factors, such as polymer architecture, molecular weight, salt concentration (for polyelectrolytes), solvent, and surface.[55] Systems that adsorb weakly with nonspecific van der Waals type interactions, are more freely removable from the surface. For instance, polystyrene in cyclohexane at 35 °C, a Θ-solvent, adsorbs reversibly to the solid/liquid interface and may be displaced by polystyrene with higher molecular weight[56] (a phenomenon governed by entropy considerations[41,53]). Polymers with multiple strong adsorbers, such as those bearing (chemisorbing) thiol groups, stick to the surface irreversibly.[57] The range of the interaction is also important. For example, a polyelectrolyte adsorbing to an oppositely charged surface will do so irreversibly from a salt-free solution, but if the charges are screened with the addition of salt, decreasing the range of electrostatic interaction, the adsorbed polymer is (at least partially) exchangeable.[15,58,59]

Comparison with Liquid/Solid Interface. Some preliminary comparisons were made of adsorption of copolymer at the toluene/water and polystyrene/water interfaces. "Plastic scintillator"—here, polystyrene cross-linked with divinylbenzene (2%) containing <1% of fluorescent dyes—is chemically very close to toluene. Similar hydrophobic/hydrophilic driving forces and adsorption energies are expected. The *tert*-butyl segment of the adsorbing polymer may well be buried in the first couple of monolayers of plastic. The major difference is clearly the severely attenuated mobility in the plane of the interface. We thus took the opportunity to evaluate the behavior of an identical polymer on two types of interface that are effectively the same except for viscosity.

Figure 6 depicts the isotherm for adsorption of copolymer from 1 M NaCl onto a polystyrene scintillator. The form of the isotherm is similar to that obtained for the liquid/liquid interface (Figure 3). The limiting surface coverage for both types of interface is the same within experimental error. Time scales of adsorption were similar to those for the liquid/liquid interface but were not probed in detail due to limited quantities of labeled polymer. Self-exchange with unlabeled polymer was observed, as depicted in Figure 7, although the exchange was somewhat slower. Thus, the energetics for adsorption at the liquid/liquid and solid/liquid interfaces appear to be very comparable, as one would

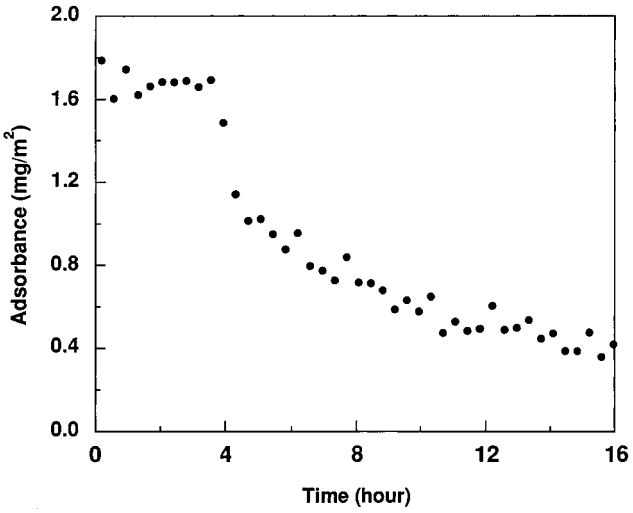


Figure 7. Self-exchange of ^{35}S-labeled polymer (solution concentration = 7.2 × 10^{-5} g/mL) at the polystyrene/1 M $NaCl_{aq}$ interface with a 10-fold excess of unlabeled polymer added at the 4-h point.

expect for a partitioning mechanism. The major difference was in the kinetics, with exchange at a solid/liquid interface occurring at roughly half the rate at the liquid/liquid system.

Adsorption Energy. Compared to common substrates for polymer adsorption, both our liquid/liquid and solid/liquid interfaces are atypical, since in both cases the substrate is chemically similar to the adsorbing polymer segment. Much attention has been directed, for example, toward polystyrene adsorbing to silica: surface silanols interact with the π-electrons of phenyls in a hydrogen-bonding fashion.[60,61] In the systems described here, hydrophobic polymer segments have the opportunity to transfer from water to a similar hydrophobic phase (toluene or polystyrene), provided the segment/surface adsorption energy is favorable enough to overcome approximately 0.2 kT (per segment) in translational entropy loss.[60,62,63] In our analysis, the hydrophobic segment is assumed to exist in the organic phase and segmental adsorption can be modeled by liquid/liquid partitioning.

We employed two, closely related, approaches to estimating the free energy of partitioning of a *tert*-butylstyrene repeat unit into toluene from water. First, we determined the solubility of *tert*-butylstyrene (*t*BS) in water and 1 M $NaCl_{aq}$. The respective solubilities were (1.3 ± 0.1) × 10^{-5} and (0.59 ± 0.04) × 10^{-5} M. If the partition coefficient, K, is given by $K = [t\mathrm{BS}]_{org}/[t\mathrm{BS}]_{aq}$, then K = 5.5/solubility, where 5.5 is the molar concentration of pure *t*BS. Using $G_{ads} = -RT \ln K$, we obtain a free energy of partitioning of −32 kJ mol^{-1} (13.0 kT) and −34 kJ mol^{-1} (13.8 kT) for ad(b)sorption from water and 1 M NaCl, respectively. Second, we determined directly the equilibrium concentration of *t*BS in the aqueous phase in contact with 10 wt % *t*BS in toluene. For such systems, the concentrations of *t*BS in pure water and 1 M salt were 1.0 × 10^{-6} and 0.40 × 10^{-6} M, respectively, which yielded G_{ads} of 33 kJ mol^{-1} (13.3 kT) and 35 kJ mol^{-1} (14.1 kT). These two approaches yielded similar values, as expected for a system such as *t*BS/toluene, which would follow Raoult's law quite well.

These partitioning free energies, when used as a rough estimate for χ_s, Silberberg's polymer/surface adsorption energy,[64] require some refinement. The values are probably a little high, since a monomer unit transferring between two liquid phases does not experience as much entropy change as a polymer segment being immobilized at a surface (interface). In addition, the environment of a polymer segment includes, for a pendent functional group such as *tert*-butylstyrene, a lattice site that is occupied by the nonpolar polymer backbone, which would decrease the enthalpy change for segment transfer from water to organic solvent (substrate). However, this effect is compensated by the fact that segment adsorption replaces a water/interface contact. Recognizing that a 0.2 kT translational entropy correction would be much smaller than our experimental error, we estimate values for χ_s of 13 and 14 kT. Such values for χ_s are unusually high. Typical magnitudes for χ_s fall in the range of 1−4 kT. For example, polystyrene adsorbing to silica from cyclohexane has χ_s = 2 kT,[60,61] and poly(vinylpyrrolidone) adsorbing to silica from water has χ_s = 4 kT.[63] However, the forces driving adsorption of the copolymer here involve very strong hydrophobic interactions. Interestingly, the results here are a clear indication that strong polymer/interface interactions do not preclude thermodynamic reversibility. The *range* of the interaction, which is very short for solvophobic effects, is probably more important. Polyelectrolytes, for example, exhibit irreversible or very slow desorption kinetics,[4] but they have long-range Coulombic interactions.[4]

Self-exchange is considerably slower than adsorption to a "clean" interface. A molecular-level picture of polymer exchange requires the diffusion of solution polyelectrolyte to the interface followed by sequential replacement of each hydrophobic segment buried in the organic layer. Since *tert*-butyl groups are dilute and numerous, it is unlikely that all of them on a polymer chain will be desorbed simultaneously in advance of replacement by solution polymer. A kinetic model for polymer desorption presented by Douglas *et al.*[65] treats two limiting regimes: at high temperatures equilibrium parameters dominate and the rate depends on molecular weight, M, in the fashion $t_{off} \sim \exp(\alpha M)$ where t_{off} is the desorption time constant and α is a parameter that scales with the polymer−surface interaction. At low temperatures desorption is governed by diffusive flux from the surface and the coverage shows a $t^{1/2}$ dependence, with $t_{off} \sim D^{-1}$, where D is a diffusion coefficient. (D refers to diffusion through the incoming (displacing) polymer, not diffusion in free solution.) Similar kinetics of self-exchange on solid and solution interfaces are expected if the process is limited by diffusion.

In conclusion, the adsorption mechanism of *tert*-butylstyrene segments on liquid or solid aromatic substrates appears to be the same and is presumably some form of partitioning. Although adsorption energies are high, self-exchange is taken to be evidence for thermodynamic reversibility in these systems. Higher salt concentrations enhance adsorption. Since 4.2 M $NaCl_{aq}$ is a Θ solvent for poly(styrenesulfonate),[66] in 1 M NaCl the tBS/PSS copolymer is probably behaving like a neutral polymer near the Θ point. Salt-induced enhancement of surface coverage may provide for enhanced stability of dispersed systems in water: self-regulation of colloidal stability occurs because a higher salt concentration, though destabilizing from screening of surface charge, causes more polymer to adsorb (a stabilizing effect).

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