

Enthalpic Effects in Competitive Polymer Adsorption: Adsorption Isotope Effect and Chain End Effect

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ABSTRACT: Competitive adsorption was studied of deuteriopolystyrene (PS), protio PS, and carboxylic acid terminated PS, from cyclohexane solutions (0.05 or 0.1 mg mL⁻¹) onto a single surface of silicon oxide at 30.0 °C. Surface excess mass of the polymer was measured by infrared spectroscopy in the mode of attenuated total reflection. In competitive adsorption using a family of polymer fractions, preferential adsorption was observed of the deuterio (versus protio) isotopes and of the carboxylic acid terminated (versus hydrogen-terminated) chains. From considerations of relative enthalpic and entropic tendencies toward adsorption, it was concluded that (a) the magnitude of the differential sticking enthalpy (deuterio versus protio isotope) was ≈ 80 J mol⁻¹ (0.03 kT) per polystyrene repeat unit and (b) the magnitude of the differential sticking enthalpy (carboxylic acid terminated versus hydrogen-terminated chain) was $\approx 1.6 \times 10^4$ J mol⁻¹ (6.4 kT) per carboxylic acid end group. The implications of these findings for competitive adsorption when samples contain traces of polar impurities (for example, of oxidation impurities) are discussed quantitatively.

Introduction

The reliable prediction of which chemical species in a mixture will segregate to a surface is not yet possible.¹ There are equilibrium and nonequilibrium effects to contend with. In other studies we have addressed history-dependent nonequilibrium states of mixtures of flexible chains in solution.^{2-4,35} Here we consider competitive enthalpic effects.

It is customary to consider the entropic aspects of competitive adsorption. When homopolymers with the same chemical structure adsorb competitively from solution, at equilibrium the molecules of larger molecular weight adsorb at the expense of smaller ones (note however that at earlier times, differences may result from differences in the rate of adsorption). The equilibrium conclusion is clear when one considers that the adsorbed mass to saturate a surface is limited, only 1–10 mg m⁻², and therefore that the mass of polymer available in even a dilute solution far exceeds the mass required to saturate a single surface. The driving force for competitive adsorption is the net entropic advantage gained in returning more smaller molecules to solution than are lost by adsorbing an equivalent surface coverage (but smaller number) of larger molecules. Roe⁵ and Scheutjens and Fleer⁶ have given quantitative predictions. When molecules differ by a factor of 2 in molecular weight and are sufficiently large, the lower molecular weight species should be essentially excluded from a surface at equilibrium.⁶ Silberberg has emphasized the generality of this conclusion: the entropy tendency to adsorb the larger molecules holds whether the molecule is linear or branched, flexible or compact in shape, depending essentially on the relative sizes of the molecules.⁷

Qualitatively, this phenomenon is well-known on the experimental side. When polymer samples of broad molecular weight distribution are employed, the high molecular weight species adsorb selectively.¹ Kolthoff and Gutmacher⁸ were perhaps the first to report this observation. In studying the adsorption of rubber fractions onto carbon blacks, they observed that when a low molecular weight polymer fraction was adsorbed first and a higher molecular weight fraction was added later, the intrinsic viscosity of the solution decreased slowly with time, suggesting that exchange occurred between molecules

in the adsorbed state and free solution. Also noted at an early stage is that if the substrate is porous, the opposite rule holds: smaller molecules adsorb selectively,⁹ presumably because a larger surface area is accessible to them.

Also in studies in which sharp polymer fractions were employed, these qualitative conclusions are evident. Grant et al.¹⁰ studied radioactively labeled polystyrenes adsorbed from cyclohexane to chrome surfaces at the θ temperature, T_θ , and showed that a fraction of a fraction of $M_w = 1 \times 10^6$ adsorbed exclusively during competitive adsorption with a fraction of $M_w = 1 \times 10^5$. Howard and Woods¹¹ studied adsorption of a 1:1 mixture by weight of moderately polydisperse polystyrenes, differing in M_w by a factor of 7, onto silica particles from cyclohexane at 35 °C. For adsorption from solution of concentration sufficiently high that the amount adsorbed was nearly independent of solution concentration (the "plateau region" of the isotherm), the species of lower molecular weight was indeed excluded entirely from the particles at steady state. But from solutions of lesser concentration, the lower molecular weight fraction constituted one-fifth of the total amount adsorbed even at steady state.

Detailed investigations, again for polystyrene adsorbed from cyclohexane at T_θ to colloidal particles of silica, were also made by Furusawa and co-workers.^{12,13} The surface population was inferred by gel permeation chromatography of the supernatant. Early in the experiments, the surface population appeared to reflect the rate of access to the surface. For example, when the surface coverage was low, the quantities adsorbed were in fact the same for a 1:1 mixture of fractions with $M_w = 775\,000$ and 186 000. With further elapsed time the lower molecular weight fraction actually overshot its ultimate level of surface excess. Displacement of the lower molecular weight fraction was not complete even after 24 h. Also using gel permeation chromatography, Vander Linden and Van Leemput obtained qualitatively similar results.¹⁴ Using ellipsometry, Kawaguchi et al. studied the thickness as well as the absorbance in competitive adsorption of polystyrene fractions adsorbed from cyclohexane¹⁵ and *trans*-decalin¹⁶ at T_θ .

In such studies one presumes that each of the repeat segments of the competing molecules has the same segment-surface enthalpic interaction with the substrate

surface. But there are also possible enthalpic considerations of competitive adsorption. A small mismatch in polymer-surface interaction on a segmental basis amounts to a large effect on a molecular basis, as Roe has emphasized.⁵ An early study along these lines by Thies concerned the competitive adsorption of incompatible polymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA).¹⁷ One might have expected to find a high activation energy and, consequently, little (or slow) displacement, when a polymer of one kind penetrated into the adsorbed layer of a polymer with which it is not compatible, but this was not observed. With PS-PMMA mixtures adsorbed onto silica from trichloroethylene, PS did not adsorb at all unless the available PMMA was insufficient to saturate the surface. When PS was allowed to adsorb first and excess PMMA then added, complete PS displacement occurred over the same time scale (2-4 h) as for PMMA adsorption onto a bare surface. Recent systematic studies with modern polymer samples confirm these early findings.¹⁸

Subsequently, it has emerged that even a single polar functionality on a chain end can result in strong selective adsorption when nonpolar polymers adsorb from a nonpolar solvent. The adsorption of polystyrene terminated by a zwitterionic end group to mica from toluene solution under conditions where PS homopolymer did not adsorb was considered to be so strong as to be effectively irreversible.¹⁹ A polar chain end functionality can result in enhanced surface coverage even if the other repeat segments of the molecule do adsorb.²⁰ It has even proved possible to separate unfunctionalized from hydroxyl and carboxylic acid terminated polystyrenes by taking advantage of the large number of separation plates provided by thin-layer chromatography (TLC).²¹

These experiments show that seemingly small differences in chemical structure can result in a tendency toward selective adsorption that outweighs entropic considerations based on relative chain size. This is a worrisome observation when one considers that it is a fact of life that polymer samples are not absolutely pure. Indeed, it has been suggested on the basis of TLC observations that trace oxidation impurities may cause a significant amount of selective adsorption.²²

Upon surveying all of the experimental results described above, it must be acknowledged that they are qualitative and indicative of general trends but not quantitative. This circumstance probably stems from several causes, not only from questions of sample purity. Second, there is uncertainty regarding the achievement of equilibrium, especially when the experiments have concerned polymer fractions of high molecular weight. And third, there is uncertainty regarding the validity of comparing theories developed for planar surfaces to results of experiments with the tiny colloidal particles employed, in many of these studies, as the solid substrates. Indeed, often the dimensions of the colloidal particles employed as substrates have actually approached the dimensions of the polymer coils in solution, so that the adsorbed layer around a single particle was presumably comprised of only one or a few polymer molecules. In recent years the theoretical problem of the influence of roughness and surface curvature on polymer adsorption has begun to be addressed explicitly.²³

The purpose of the studies undertaken by us was to provide quantitative analysis of competitive enthalpic effects, using samples from several provenances studied at a single substrate surface. Preliminary reports of these results have appeared previously.^{24,25}

Table I
Characterization of the ProtioPolystyrenes^a

M_w^a	M_w/M_n	source
5 100	1.04	PL ^b
6 000	1.04	UM ^d
9 600	1.02	TS ^c
12 000	1.04	UM ^d
43 900	1.01	TS
115 000	1.04	PL
465 000	1.04	PL
575 000	1.06	PC ^e
1080 000	1.05	PL
1260 000	1.05	TS

^a Suppliers' data. ^b Polymer Laboratories. ^c Toyo Soda. ^d University of Massachusetts. ^e Pressure Chemical.

Table II
Characterization of the DeuterioPolystyrenes^a

M_w^a	M_w/M_n	source
4 500	1.03	PL ^b
6 000	1.04	UM ^c
6 900	1.03	PL
12 500	1.03	UM
87 000	1.05	PL
520 000	1.15	PC ^d
550 000	1.05	PL

^a Suppliers' data. ^b Polymer Laboratories. ^c University of Massachusetts. ^d Pressure Chemical.

Table III
Characterization of the Functionalized Polystyrenes^a

M_w^a	M_w/M_n	code
6 000	1.06	PS- <i>d</i> -COOH
7 000	1.07	PS- <i>h</i> -COOH
12 500	1.06	PS- <i>d</i> -COOH
13 500	1.08	PS- <i>h</i> -COOH

^a Donated and characterized by T. McCarthy and D. R. Iyengar (University of Massachusetts).

Experimental Section

General Methods. The experimental protocol was close to that described in our earlier FTIR-ATR study of poly(methyl methacrylate) adsorption.⁴ Infrared spectra were collected by using a Nicolet IR/30 Fourier transform infrared spectrometer (FTIR) equipped with a mercury-cadmium-telluride detector. The attenuated total reflection optics (Circle Cell) were purchased from Spectra Tech, Inc. The infrared beam sustained roughly seven internal reflections as it travelled the length of a cylindrical prism with an angle of incidence of 45°. The prism was mounted inside a thermostated steel jacket.

Anionically polymerized atactic polystyrene (PS) and protio (PS-*h*) and deuterio (PS-*d*) standards of various degrees of polymerization were obtained from several sources and were used as received. Their characteristics are listed in Tables I and II, respectively. In addition, carboxylic acid terminated (PS-COOH) protio and deuterio species were generously donated by Prof. T. McCarthy of the University of Massachusetts. The characteristics of these samples are listed in Table III.

Because the nominal molecular weights of the deuterio samples were based on gel permeation chromatography calibrated by using protio standards, those molecular weights are protio equivalent. To calculate the degree of polymerization of the deuterio samples, one therefore divides the nominal molecular weight by the segmental molecular weight of protio polystyrene.

The solution concentration of PS in the experiments reported below was 0.1 or 0.05 mg/mL. The experiments were thermostated at 30.0 °C, which is the θ temperature, T_θ , for PS-*d* in cyclohexane.²⁶ For PS-*h* in cyclohexane, $T_\theta = 34.5$ °C,²⁶ so that PS-*d* at the temperature of the experiment found itself in a slightly better solvent than did PS-*h*.

Silicon ATR prisms were employed. As purchased, the surfaces had been polished with 1/4- μ m diamond paste. Energy transfer in the attenuated total reflection mode is more efficient for silicon

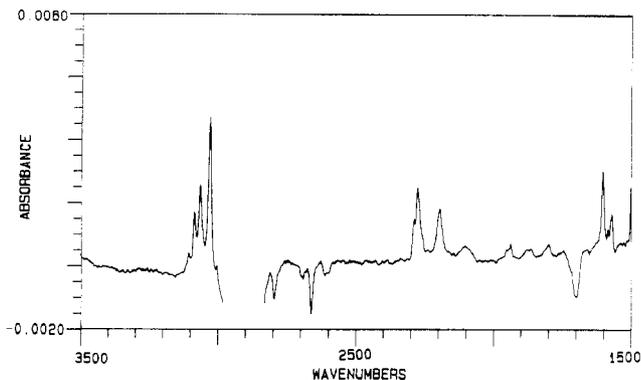


Figure 1. Infrared spectrum, measured in attenuated total reflection, of PS-*d* and PS-*h* jointly adsorbed onto silicon oxide from a cyclohexane solution of concentration 0.1 mg/mL. Absorbance is plotted against wavenumbers. The negative peaks correspond to cyclohexane displaced by adsorbed polymer. Note regions of polystyrene C-H ring vibrations (3000–3150 cm^{-1}) and of C-D vibrations (2000–2300 cm^{-1}) plotted in succeeding figures.

than for the germanium prism we used previously,² thus enhancing experimental sensitivity. Reproducibility of the experiment was better than using the Amtir alloy prism that we also used previously.³ Before each experiment the thermostat cell for the infrared prism was disassembled and cleaned (soaked in nitric acid, rinsed in water and acetone, and dried under nitrogen).

The surface preparation method was modified once during the collection of the data presented here. Initially, for the experiments to determine the adsorption isotope effect, the prism was prepared before each experiment by the following protocol: ultrasound in ethyl acetate for 10 min, reflux for several hours in ethyl acetate, ultrasound in ethyl acetate for another 10 min, and treatment in oxygen-purged argon-ion plasma for 1 min. This method was revised when the effects of chain end functionality were undertaken, by including a rinse, preceding the refluxing step, in a 49% aqueous solution of hydrofluoric acid. This change in procedure produced a second surface on which the mass adsorbed was uniformly higher by $\sim 10\%$, yet control experiments showed that the differential sticking energies were unchanged.

Immediately after the properly prepared prism had been installed in the steel cell, a spectrum was collected. A second spectrum was then collected of the cell filled with freshly distilled cyclohexane that had been dried over type 4A molecular sieves. Polymer solution was not added until 30–60 min after the cell had been filled with cyclohexane; this improved baseline stability, perhaps reflecting desorption of adsorbed gases. Under ambient conditions such as were used, it is well-known that silicon is covered by a native oxide layer.²⁷

The index of refraction of Si is 3.42, and that of cyclohexane is 1.42. In these experiments with dilute cyclohexane solution, the penetration depth was $d = 0.27 \mu\text{m}$ at the largest carbon-hydrogen stretch of 3050 cm^{-1} . At every wavelength, the penetration depth was far larger than the characteristic thickness of the adsorbed polymer layer (ca. the radius of gyration). Therefore the measured polymer peak intensities did not contain information about segment distribution as a function of depth but represented the surface excess of adsorbed polymer in toto.

The spectra were observed at each stage of the experiments for infrared absorption bands indicating the presence of contaminating surface species, and the experiment was aborted if contamination was encountered. Measurements reported here employed the Happ-Genzel apodization. They are based on the collection of 800 interferograms with a spectral resolution of 8 cm^{-1} and a time average of 3 min.

Representative Spectra. Figure 1 shows an ATR spectrum of PS-*h* and PS-*d* adsorbed jointly. Absorbance is plotted against wavenumbers. Protio PS-*h* shows a series of carbon-hydrogen vibrations in the region 3000–3150 cm^{-1} , and PS-*d* shows a series of carbon-deuteron vibrations in the region 2000–2300 cm^{-1} . The negative peaks may be attributed to the depletion of cyclohexane from the surface, and the peaks in the region 1800–2000 cm^{-1} are common to both PS species.

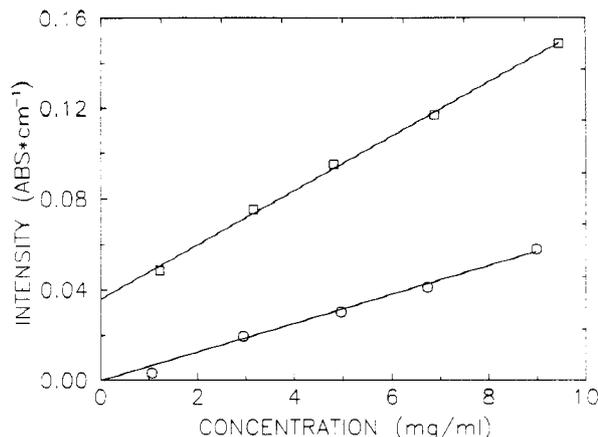


Figure 2. Integrated peak intensities plotted against concentration of polystyrene in cyclohexane solution: squares, PS-*d* ($M_w = 6900$); circles, PS-*h* ($M_w = 5100$). Experiments with PS-*h* extrapolate to the origin because in that experiment the surface was nonadsorbing. As explained in the text, the data in this figure enable separation of the surface excess from infrared signal owing to polymer in bulk solution and also enable calibration of the surface excess mass per unit area.

The infrared peaks (3000–3150 cm^{-1} for PS-*h* and 2000–2300 cm^{-1} for PS-*d*) were integrated for purposes of tracking the surface excess. By Beer's law, both peak height and integrated peak intensity would be proportional to polymer concentration. However, the latter measure is more reliable in the context of the present experiment, where oscillator line shapes may be broadened by local changes in environment during the course of adsorption.

Data Analysis. Beer's law works well in these films, which are much thinner than the penetration depth of the radiation and which have low energy loss as a result of the adsorbed layer. The usefulness of ATR for quantitative work generally depends on using films much thinner than the penetration depth of the radiation and on having low energy loss as a result of the adsorbed layer. The conditions for Beer's law to hold to a good approximation have been discussed by Harrick.²⁸ When they are not satisfied, the ATR signal is not necessarily linear in concentration because the reflectivity of the interface is not linear in solution concentration. The absorption bands in ATR may be shifted or distorted in frequency or line shape because the reflectivity, which depends on the refractive index of the sample, changes abruptly at frequencies near the sample's absorption peak. However absorption losses were low for the present adsorbed PS layers, as is illustrated in Figure 1.

Owing to the large penetration depth of the evanescent wave, the measurements included contributions from oscillators in the isotropic polymer solutions in addition to those within the adsorbed polymer layers. Accounting for this solution contribution was straightforward. First PS was adsorbed until the mass adsorbed had reached a plateau, and then PS solutions of a range of concentrations were added in rapid succession. Since the mass adsorbed is insensitive to solution concentration over this range of dilute solution concentrations,¹ the intercept at $c = 0$ represented signal from the adsorbed layer. The additional signal at finite concentrations was the contribution from PS in solution.

Calibration of the Surface Excess Mass per Unit Area. In Figure 2, the integrated intensities of C-H vibrations measured by ATR are plotted, for PS-*h*, as a function of solution concentration. The relationship is linear up to the highest concentration investigated. From this slope, it was straightforward to calculate the solution contribution that corresponded to a given solution concentration. For the PS data reported below, this calibrated solution contribution was subtracted from the raw values of integrated peak intensity.

This calibration of the solution signal also allows one to calibrate the absolute level of PS adsorbed. The integral of the exponentially decaying electric field, integrated from the surface to deep into the solution, is easily shown to be proportional to cd_p (the bulk solution concentration is c ; the penetration depth

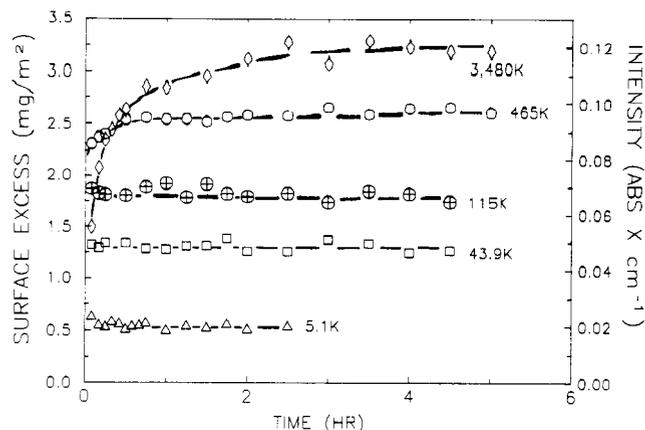


Figure 3. Surface excess (mass per unit area) of protiopolystyrenes plotted against time during adsorption from cyclohexane solution onto an initially bare surface at 30.0 °C. Equivalent infrared peak intensity (units: absorbance units times wave-numbers) is shown on the right-hand ordinate. Molecular weights of the polystyrene samples (in kilodaltons) are noted in the figure. The line through the points is an empirical fit to a power law, $\Gamma = KM^{0.33}$.

is d_p). Because the PS layer thickness is small compared to d_p ,¹ the evanescent wave decays to a negligible extent as it samples the adsorbed layer. It follows that an integrated peak intensity (the 3000–3150-cm⁻¹ region) of 0.05 absorbance units cm⁻¹ corresponds to a surface excess of 1.4 mg m⁻². In the data reported below the data for PS-*d* have been scaled by the calibrated fraction from transmission experiments, 0.834, so that PS-*h* and PS-*d* infrared intensities are proportional by the same constant to the surface excess.

Uncertainty in the levels of surface excess was ± 0.1 mg m⁻².

Results

Effects of Molecular Weight and of Isotopic Labeling on the Surface Excess. First, noncompetitive adsorption onto initially bare surfaces was considered.

Examples of the adsorption kinetics are shown in Figure 3. For fractions with $M < 115\,000$ g mol⁻¹, the mass adsorbed reached steady state rapidly, a plateau being attained within the first 10 min of the experiment. For larger molecular weight fractions, equilibration required up to 2 h. These slower kinetics may be attributed in part to the lower solution concentration of these samples on a molar basis.

The surface excess of the deuterio samples was systematically larger than that of protio samples of similar molecular weight by a small amount, on the order of 0.2 mg m⁻². This is close to the uncertainty of the measurements, but the differences are consistent with the higher segment-surface enthalpy of adsorption that we infer below.

In Figure 4, the equilibrated surface excess is plotted linearly against molecular weight. The surface excess grew monotonically with molecular weight, increasing by a factor of 7 from $M = 5 \times 10^3$ to $M = 1 \times 10^6$. When discussing the molecular weight dependence of the surface excess, it has been customary to employ the plateau levels from the adsorption isotherms as a function of solution concentration. In view of the striking result obtained, it is interesting to further consider the present findings obtained at a single solution concentration.

Figure 5 shows the molecular weight dependence of the surface excess plotted on log-log scales. A plateau in the surface excess was observed for the two samples with molecular weight larger than 1×10^6 , consistent with earlier experiments.¹ For the samples of lesser molecular weight the molecular weight dependence of the surface excess

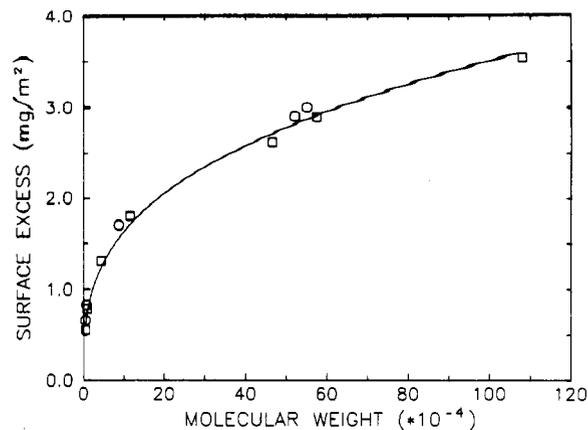


Figure 4. Surface excess (mass per unit area) of polystyrenes plotted against linear weight-average molecular weight when adsorbed from dilute cyclohexane solution at 30.0 °C: squares, PS-*h*; circles, PS-*d*. The line through the points is an empirical fit to a power law, $\Gamma = KM^{0.33}$.

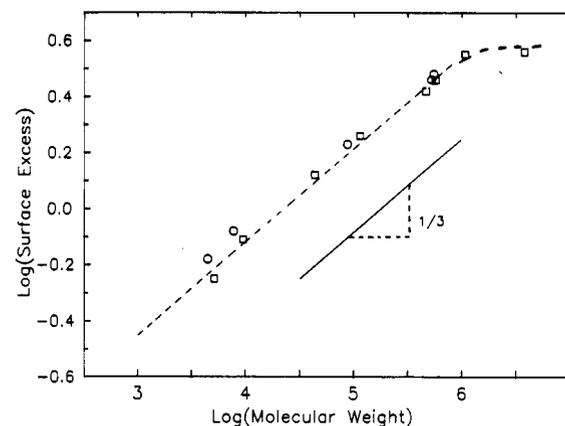


Figure 5. log-log plot of data shown in Figure 3. Symbols are the same as in Figure 6.

was well represented by a power law:

$$\Gamma \sim M^{0.33} \text{ (empirically)} \quad (1)$$

The fit is over 2.5 decades of molecular weight and over nearly 1 decade of mass adsorbed. This same relation, with the same power of molecular weight (though different prefactors) is also apparent when one surveys raw data from another study of the adsorption of sharp PS fractions onto silica from cyclohexane at 35 °C.²⁹

Observation of power-law behavior brings to mind the early view that power-law behavior of the surface excess is normal and unremarkable behavior, except for samples of very low and very high molecular weight.¹¹ In light of present understanding,¹ the earlier notion that the power in M directly reflects chain conformation at the surface¹¹ is clearly naive. Nonetheless on an empirical basis, this apparently serendipitous observation is striking.

Competitive Adsorption of Protio- and Deuterio-polystyrenes. The baseline levels of noncompetitive adsorption having been established, situations of competitive adsorption were explored. Results of a family of experiments on pairs of deuterio and protio samples are summarized in Table IV. In the graphs discussed below, circles always denote the deuterio sample and squares the protio sample.

Figure 6 shows the competitive adsorption of a 50:50 mixture by weight of protio and deuterio samples: PS-*h* ($M_w = 12\,000$) and PS-*d* ($M_w = 12\,500$). The steady-state surface excess of these same samples, when they adsorbed noncompetitively in separate experiments, is also indi-

Table IV
Adsorption Isotope Effect

M , g mol ⁻¹		Γ/Γ^0 , mg m ⁻²		Δh , J mol ⁻¹ segment ⁻¹
PS- <i>d</i>	PS- <i>h</i>	PS- <i>d</i>	PS- <i>h</i>	
6 000	12 000	0.1/1.2	0.8/1.3	50
6 900	5 100	0.6/0.8	0.1/0.6	80
	9 600	0.3/0.8	0.7/0.9	40
	43 900	0.2/0.8	1.0/1.4	220
12 500	12 000	1.1/1.3	0.1/1.3	110
	12 000	1.2/1.3	0.1/1.3	120
87 000	115 000	1.8/1.9	0.1/1.8	20
	465 000	0.6/1.9	2.0/2.6	20
	1 080 000	0.2/1.9	3.3/3.5	20
520 000	465 000	2.7/3.1	—/2.6	
	575 000	2.9/3.1	—/2.8	
550 000	575 000	3.1/3.1	—/2.8	
	1 260 000	3.1/3.1	—/3.5	

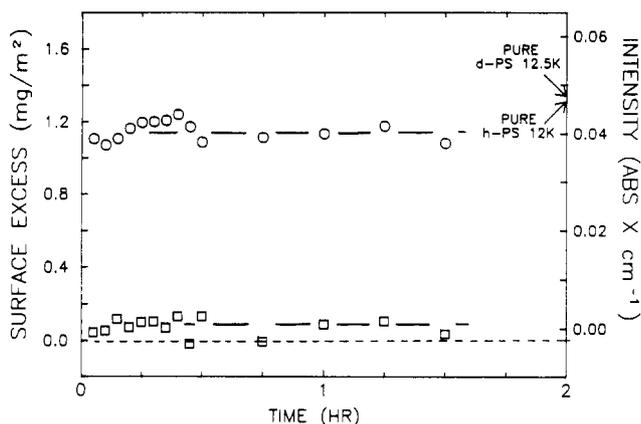


Figure 6. Surface excess (mass per unit area) of deuterio- and protio polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in a cyclohexane solution at 30.0 °C: squares, PS-*h*, $M_w = 12\ 000$; circles, PS-*d*, $M_w = 12\ 500$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

cated. Equilibration was rapid in every experiment, the surface excess stabilizing within 15 min. The surface excess of the deuterio sample was close to that measured noncompetitively, while the surface excess of the protio sample was barely detectable, an order of magnitude less.

This trend toward selective adsorption of deuterio samples, when adsorbed competitively with protio samples of similar molecular weight, was confirmed by using other pairs of deuterio and protio samples obtained from other sources. Table IV shows that for mixtures of higher molecular weight ($M \approx 550\ 000$, 550 000 (d), and 575 000 (h)), the selectivity for the deuterio sample was so pronounced that surface excess of the protio sample was not detectable at all, despite the fact that the protio samples was of slightly larger molecular weight.

However, significant adsorption of the protio sample did result if the molecular weight of the protio sample was larger than that of the deuterio sample. Figure 7 shows the competitive adsorption of a 50:50 mixture by weight of PS-*h* ($M_w = 12\ 000$) and PS-*d* ($M_w = 6000$). The selectivity was reversed with respect to the situation in Figure 6, the protio sample adsorbing preferentially.

The generality of this response to mismatch of molecular weight was confirmed by using other pairs of deuterio and protio samples. Figure 8 illustrates the competitive adsorption of a 50:50 mixture by weight of PS-*h* ($M_w = 465\ 000$) and PS-*d* ($M_w = 87\ 000$). The equilibration time was considerably longer, on the order of 2 h, than when using samples of lower molecular weight. At the earliest measurement times the surface excess of both polymer

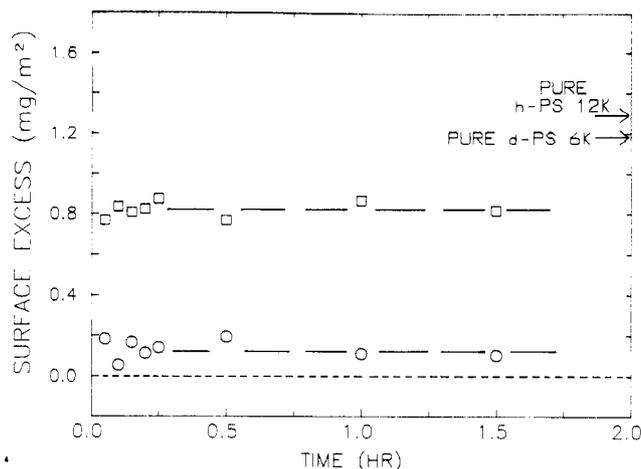


Figure 7. Surface excess (mass per unit area) of deuterio and protio unfunctionalized polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in cyclohexane solution at 30.0 °C: squares, PS-*h*, $M_w = 12\ 000$; circles, PS-*d*, $M_w = 6000$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

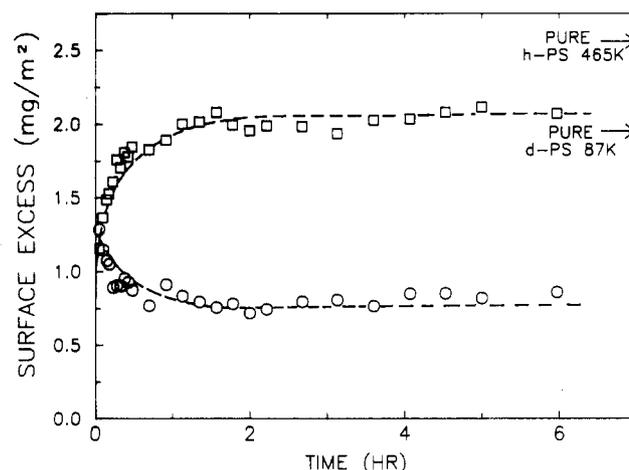


Figure 8. Surface excess (mass per unit area) of deuterio and protio unfunctionalized polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in cyclohexane solution at 30.0 °C: squares, PS-*h*, $M_w = 465\ 000$; circles, PS-*d*, $M_w = 87\ 000$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

fractions was nearly the same. The trend of the data was that, at still earlier times, the species of lower molecular weight appeared to occupy the surface preferentially. This would be expected in view of its higher diffusion coefficient and therefore more rapid access to the surface. But with increasing equilibration time the surface excess of this species lessened and that of the higher molecular weight species grew. After 2 h of elapsed time the surface excess of the sample of higher molecular weight was more than twice that of the deuterio sample of lower molecular weight.

Effect of Temperature. The generality of these findings was tested in an experiment performed under conditions of better solvent quality. The same experiment depicted in Figure 6 was repeated at 50 °C. The result was that whereas the surface excess was 20% lower, the inferred adsorption isotope effect (discussed below) was 100 J mol⁻¹ segment⁻¹, quantitatively consistent with the result at 30 °C.

Competitive Adsorption of Hydrogen-Terminated and Carboxylic Acid Terminated Polystyrenes. The effect of polar chain end functionality was also explored.

Table V
Carboxylic Acid Chain End Effect

$M, \text{g mol}^{-1}$		$\Gamma/\Gamma^{\circ}, \text{mg m}^{-2}$		$10^{-4}h, \text{J mol}^{-1}$ end group ⁻¹
PS-d	PS-h	PS-d	PS-h	
6 000 ^a	7 000 ^b	0.1/1.2	1.3/1.3	1.9
6 000 ^c	12 000 ^d	1.2/1.5	0.1/1.3	1.5
12 000 ^a	7 000 ^b	0.2/1.3	0.9/1.3	1.9
12 000 ^c	13 500 ^b	0.2/1.3	0.8/1.5	1.4
12 000 ^a	13 500 ^b	0.3/1.3	1.1/1.5	1.5
12 500 ^c	12 000 ^d	1.6/1.7	<0.05/1.3	1.4
550 000 ^a	7 000 ^b	2.5/2.8	0.3/1.3	2.9

^a PS-d. ^b PS-h-COOH. ^c PS-d-COOH. ^d PS-h.

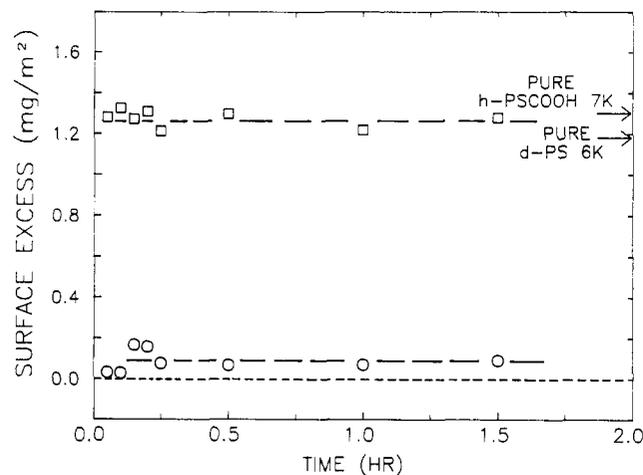


Figure 9. Surface excess (mass per unit area) of deuterio- and protio polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in cyclohexane solution at 30.0 °C: squares, PS-h-COOH, $M_w = 7000$; circles, PS-d, $M_w = 6000$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

In noncompetitive adsorption, the levels of surface excess of these samples were 15–20% larger than for the hydrogen-terminated polymers of corresponding molecular weight. These levels of surface excess are included in Table V.

Figure 9 shows the competitive adsorption of a 50:50 mixture by weight of PS-h-COOH ($M_w = 7000$) and PS-d ($M_w = 6000$). Unlike the selective adsorption of the deuterio sample observed for unfunctionalized samples of matched molecular weight, the protio but carboxylic acid terminated sample segregated to the surface nearly completely.

Other experiments with mismatch of molecular weight confirmed this picture, as summarized in Table V. Figure 10 shows the competitive adsorption of a 50:50 mixture by weight of PS-h ($M_w = 12000$) and PS-d-COOH ($M_w = 6000$). Unlike the preferential adsorption of the species of higher molecular weight observed for unfunctionalized samples of these same molecular weights (Figure 7), the carboxylic acid terminated species of lower molecular weight segregated to the surface nearly completely.

The consequence of a larger mismatch of molecular weight was also explored. Figure 11 shows the competitive adsorption of a 50:50 mixture by weight of PS-h-COOH ($M_w = 7000$) with PS-d ($M_w = 550000$). The surface excess of the sample of higher molecular weight was the same as that measured during noncompetitive adsorption, as expected from its considerably larger molecular weight. However the surface excess of the carboxylic acid terminated species was still significant, 25% of that measured during noncompetitive adsorption.

Control Experiments Using Stearic Acid. In principle, these observations might have reflected some amount

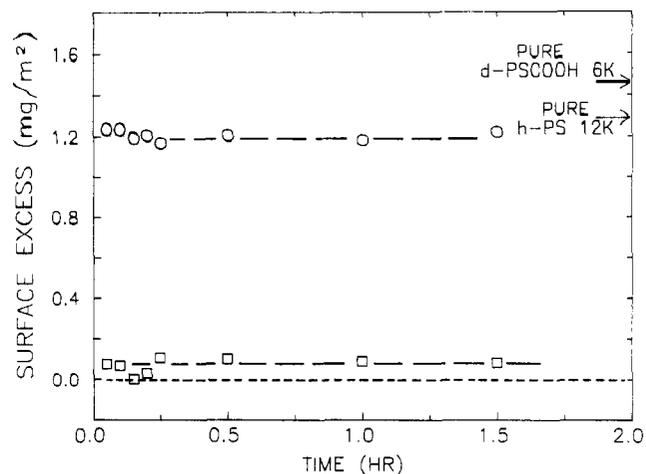


Figure 10. Surface excess (mass per unit area) of deuterio- and protio polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in cyclohexane solution at 30.0 °C: squares, PS-h, $M_w = 12000$; circles, PS-d-COOH, $M_w = 6000$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

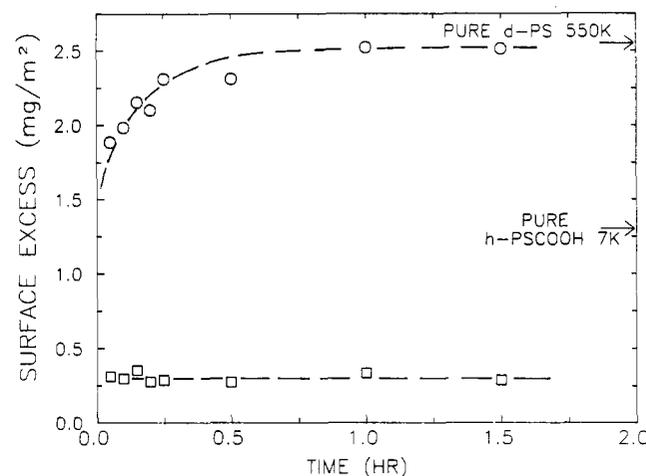


Figure 11. Surface excess (mass per unit area) of deuterio and protio unfunctionalized polystyrenes, plotted against elapsed time, when adsorbed competitively from a 50:50 mixture by weight in cyclohexane solution at 30.0 °C: squares, PS-h-COOH, $M_w = 7000$; circles, PS-d, $M_w = 550000$. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

of irreversible adsorption of the carboxylic acid terminated species. However, our previous study of the adsorption of stearic acid onto silicon oxide (from carbon tetrachloride) showed it to be reversible.⁴ The adsorption of the carboxylic acid group in the present experiment therefore appears to have been reversible, and we assume this in the following analysis.

Discussion

In general, the relevant question to ask about the consequences of different chain chemistry—be it different isotopic composition or a different chain end—is not whether consequences exist but whether they are large enough to matter. Indeed, a large family of chromatographic separation methods are based on the happy fact that even subtle chemical differences can be amplified, by the action of a large number of separation plates, to result in effective separation. The contribution of the experiments described in this report is to show that these differences can be large enough to result in surface fractionation even at a single solid surface. This is a possibly counterintuitive finding.

Semiquantitative conclusions can be drawn based on the following argument. We assume that there is equilibrium between solution and adsorbed polymer. The competitive adsorption of two polymers (A and B) from bulk solution of a given volume fraction (ϕ^b) to a surface (where it is considered to have volume fraction ϕ^s) is expressed as a Boltzmann factor in the differential molar entropy of adsorption per mole of reference (long) chains, ΔS , and the differential molar enthalpy of adsorption of these same chains, ΔH :

$$\phi_A^s/\phi_B^s = \phi_A^b/\phi_B^b \exp[(\Delta H - T\Delta S)/RT] \quad (2)$$

Note that one might be tempted to consider also the solvent. Then one would consider the absolute enthalpy of adsorption relative to that of the solvent (as is done for the well-known segment-surface interaction parameter¹). However, it is more direct to consider only the competition of the two polymers for the same surface sites. We therefore define ΔS and ΔH relative to that.

An estimate of ΔS allows an estimate of ΔH when one controls ϕ^b and measures ϕ^s . In the spirit of refs 5 and 6, the entropy of mixing upon adsorbing 1 mol of long chains (A) and concomitantly releasing c moles of shorter chains (B) to solution, is positive. It is estimated as

$$\Delta S = -R \ln [\phi_A^s/\phi_A^b] + c \ln [\phi_B^s/\phi_B^b] \quad (3)$$

Here R is the gas constant. The constant c is approximated as the ratio of the degrees of polymerization of species A and B. The volume fraction in the "adsorbed phase", ϕ^s , is approximated as Γ/Γ° , the surface excess measured in competitive adsorption (Γ) relative to that measured in noncompetitive adsorption (Γ°). Equations 2 and 3 allow one to calculate ΔH . Dividing ΔH by the degree of polymerization of species A gives an approximate estimate of Δh , the differential enthalpy of adsorption per mole of repeat segments.

Adsorption Isotope Effect. The adsorption isotope effect calculated in this way was in the range 20–280 J mol⁻¹ segment⁻¹, as tabulated in Table IV (possible reasons for this variability are discussed below). The mean value of nine experiments was 80 J mol⁻¹ segment⁻¹. No explicit calculation was possible for the experiments using deuterio fractions of the highest molecular weights ($M > 500\,000$) because the protio fractions did not adsorb at all; this behavior would be expected from the adsorption isotope effect calculated by using the other samples. There are various refinements that might in principle improve this naive calculation, not least an allowance for the molecular weight distribution of the samples, the possible presence of trace impurities (see discussion below), and the fact that chains are expected to be bound to the surface by a fraction $p < 1$ of potential adsorption sites, where p decreases with increasing molecular weight. In the absence of direct information about these matters, we avoid these complications at this time.

The magnitude of the enthalpic effect calculated is small per repeat segment (≈ 0.03 kT) but large per chain macromolecule. The primary origin of small isotopic differences in adsorption energy has long been understood to be changes in the zero-point energy normal to the surface, the vibrational energy levels being slightly lower in the case of the deuterio isotope.³⁰ Since one expects PS to adsorb at the pendant aromatic ring, it is reasonable to expect that the magnitude of the adsorption isotope effect will be similar to that for benzene and toluene. Already a generation ago, chromatography showed that the deuterio isotopes of benzene and toluene adsorb preferentially.³⁰ The temperature dependence of retention times

in chromatography showed that the difference in enthalpy of adsorption from gas to solid is in the range 2–12 J mol⁻¹, depending on the chemistry of the solid support.³¹ This is consistent with the rough estimate given above.

An earlier paper by Cosgrove³⁴ employed the isotopic selectivity of NMR to investigate the adsorption of PS-*h* and PS-*d* at particulate surfaces.³⁴ Questions of adsorption isotope effects were not, however, addressed.

There is one other recent investigation of isotope fractionation by preferential adsorption: this involves segregation from the melt to the vacuum.³² For a melt of PS-*d* in PS-*h*, the surface energy difference between PS-*d* and PS-*h* of high molecular weight was inferred to be 0.1 mJ m⁻² at 184 °C. This is equivalent to ≈ 40 J mol⁻¹ of PS segments directly at the surface. The quantitative similarity to the estimates in Table IV is probably coincidental. Nonetheless, in view of the fact that, of course, vacuum and silicon oxide are respectively nonpolar and polar, it is interesting to note that the sign is the same, i.e., that PS-*d* segregates to both.

Chain End Effect. A similar analysis was used to estimate the differential segmental sticking energy owing to the single carboxylic acid functional group. The differential adsorption energy per molecule, ΔH , was partly the result of the adsorption isotope effect and partly the result of preferential sticking of the carboxylic acid group. In the calculations, the adsorption isotope effect was taken to be 80 J mol⁻¹ segment⁻¹.

The differential enthalpy of adsorption (carboxylic acid terminated versus hydrogen-terminated chains) is tabulated in Table V. The value was in the range 1.4×10^4 – 1.9×10^4 J mol⁻¹ of PS-COOH using samples obtained from the same source (University of Massachusetts). The mean of those six experiments was 1.6×10^4 J mol⁻¹, i.e., ≈ 6.4 kT/carboxylic acid end group.

An additional experiment using a deuterio sample obtained from a different source gave a consistent estimate, 2.9×10^4 J mol⁻¹, despite the substantial mismatch in molecular weight (a factor of 80).

Implications Regarding Effects on Adsorption of Trace Impurities. These results also permit an estimate of the effect on surface segregation of trace polar impurities. Consider that a portion of a sample becomes oxidized, say by photooxidation,³³ to give an oxidized portion (ϕ_B^b) and an intact portion (ϕ_A^b). If oxidation does not disturb the molecular weight of the chains, then $c = 1$ and eq 2 and 3 can be rearranged to give

$$\ln [\phi_A^s/\phi_B^s] = -\Delta H/2RT + \ln [\phi_A^b/\phi_B^b] \quad (4)$$

where the symbols have the same meanings as above.

For example, suppose that 0.1% of the chains were oxidized and that the enthalpic effect of oxidation were $\Delta H = 6.4RT$ (carboxylic acid functionality). One oxidation event per chain yields $\phi_A^s = 0.98$, which means that 2% of the surface would be occupied by oxidized chains. In many experiments, this effect would be inconsequential.

The effect of multiple polar impurities on the same chain would be much larger. If 0.1% of the chains were doubly oxidized ($\Delta H = 12.8RT$), one concludes that $\phi_A^s = 0.64$, which means that oxidized chains would occupy nearly 40% of the surface. This would be a large effect in nearly any experiment.

These simple calculations underscore the sensitivity of surface experiments to seemingly small amounts of polar impurities. Such impurities are to be expected unless extraordinary precautions are taken. McCarthy has cautioned that the majority of PS samples stored under ambient laboratory conditions do show signs of oxidation

by the sensitive test of thin-layer chromatography.²² This is worrisome. On the other hand, it is encouraging that we obtained consistent determinations of the adsorption isotope effect, using commercial samples obtained from a variety of sources (Table IV). The present calculations may aid in determining the degree of trace oxidation or other impurity that is acceptable in a given experiment.

Concluding Remarks

The central result of this study is to show experimentally that even slight differences in chemical structure—deuterio versus protio isotope, and hydrogen versus carboxylic acid chain end termination—can have a major influence on which polymer species in a mixture segregates to a surface. In the system we have studied, we have provided a quantitative evaluation of these effects. The consistent findings obtained by using samples obtained from several sources supports the view that our findings reflect true enthalpic effects and not the conceivable adventitious impurities in the samples. It is shown how the effects on adsorption of the presence of adventitious impurities can be estimated.

We emphasize that the habitual supposition (based on the entropy of distributing chains of different length between the adsorbed state and free solution) that large macromolecules will adsorb at the expense of short ones is not always justified. That tendency can be overwhelmed by competitive enthalpic preferences for the surface.

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