

Adsorption of Acrylic Acid Copolymers with Hydrophobic Chain Substituents on Polystyrene Latex

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Synopsis

Adsorption of three copolymers of acrylic acid with *N*-1-naphthylacrylamide on monodisperse polystyrene latex was studied as a function of pH, ionic strength, and latex concentration. A comparison of the observed adsorptive capacities with predictions based on a model in which the adsorbed polymers retain their shape in solution showed that this model leads to an increasing underestimate as the density of the hydrophobic groups on the polymer is increased and as the pH is reduced.

INTRODUCTION

The adsorption of flexible chain polymers on surfaces has been a subject of much theoretical and experimental study.¹ Since the polymer which is sorbed at saturation greatly exceeds the amount which can be accommodated in a unimolecular layer, it is generally concluded that only a fraction of the monomer residues of the chain molecules are in contact with the sorbent, while the rest of the chains extend into the solution. In the theories of Silberberg² and Hoeve et al.³ trains of monomer residues attached to the surface were assumed to alternate with loops extending into the solution. Predictions of these theories concerning the number of chain segments in contact with the surface may be compared with experimental data obtained by IR spectroscopy^{4,5} or calorimetry⁶ while the thickness of the adsorbed polymer layer has been studied by ellipsometry⁶ and the flow rate through capillaries⁷ or through sintered glass disks.⁸ Yet, a comparison of experimental data with theory is complicated by various factors. For instance, the film thickness varies with the surface coverage and the solution concentration,^{6,7} the fraction of adsorbed segments varies also with the surface coverage,⁶ and flow rate data may reflect hydrodynamic interactions with the adsorbed polymer film which extend beyond the space occupied by the surface-bound chain molecules.⁷

In most previous studies, the adsorption of homopolymers was investigated so that all segments of the macromolecules had the same affinity for the surface. However, Howard and his collaborators have shown that although polystyrene is not adsorbed from a trichloroethylene solution on carbon or silica, the incorporation of even small fractions of methyl methacrylate,^{8,9} vinylpyridine,¹⁰ or acrylonitrile¹¹ residues leads to styrene copolymers which are strongly sorbed. Similarly, although the highly hydrophobic poly(vinyl alcohol) would not be expected to be adsorbed from an aqueous medium on polystyrene latex particles,

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6–13 mol % of vinyl acetate residues are sufficient to hold the polymer to the hydrophobic polystyrene surface.¹²

In the present investigation, we studied the adsorption of acrylic acid copolymers with a comonomer carrying a hydrophobic residue on monodisperse latex particles. This system has the advantage that the surface area of the adsorbent is well defined and that a change of pH— or the ionic strength— can alter profoundly the interaction of the acrylic acid residues with the aqueous medium while the forces binding the hydrophobic anchor points to the polystyrene surface are independent of these variables.

There were two other reasons why such a system was of interest to us. (i) It has been demonstrated that a suspension may be stabilized by polymer adsorption^{10–16} and such a stabilization, similar to that produced by adsorbed detergents,¹⁷ is of much interest to polymer latex technology. Since this stabilization is believed to be due to the resistance of the adsorbed polymer chains against interpenetration¹⁸ this effect should be particularly pronounced if the adsorbed chains carry ionized groups. (ii) Ever since polystyrene latex on which γ -globulin has been adsorbed has been shown to be coagulated by rheumatoid arthritis serum^{19,20} a variety of applications of polystyrene latex for serological tests have been described.^{21–25} Our study of polymer adsorption on polystyrene latex was then partly motivated by a desire to obtain background information for future studies in which the adsorbed polymer would carry hapten substituents so that latex agglutination would provide a sensitive test for the antihapten antibody.

EXPERIMENTAL

Monodisperse emulsifier-free polystyrene latex was prepared as described by Kotera et al.²⁶ The particle diameter, $0.54 \pm 0.01 \mu\text{m}$, was determined by electron microscopy. To obtain the charge density on the particle surface, due to sulfate groups derived from the persulfate initiator, the latex was first dialyzed against 0.01N HCl and then against water until the dialyzate gave no test for chloride. Conductometric titration with 0.01N NaOH revealed 0.14 anionic charges per square nm of the latex surface.

Acrylic acid was copolymerized with *N*-1-naphthylacrylamide (NA) (Polysciences, Inc.) recrystallized from ethanol-water (melting point 139–140°C) in methanol solution at 65°C using AIBN (4 mmole/mole monomer) as initiator. The conversion was kept to 15–25%. The NA content of the copolymers was determined by ultraviolet spectroscopy, assuming that the extinction coefficient of the NA residues in aqueous copolymer solutions at the absorption maximum of 282 nm was the same ($5200M^{-1} \text{ cm}^{-1}$) as for the monomer in chloroform at the absorption maximum of 290 nm. From three copolymerizations in which the monomer mixture contained 5, 10, and 15 mol % NA, the reactivity ratio of acrylic acid was estimated as 0.46. Intrinsic viscosities were determined in aqueous buffer solutions of ionic strength 0.04. Molecular weights of polymers in methanol solution were determined by light scattering in a KMX-6 instrument of the Chromatix Co. which uses light from a He-Ne laser, permitting measurements at scattering angles as low as 2°. The characterizations of the polymers used are listed in Table I.

Unless stated otherwise, a latex concentration of 0.76 g/100 ml was used in

TABLE I
 Characterization of Polymers

Polymer designation	mol % NA	$10^{-4} \bar{M}_w$	$[\eta]$ (dl/g)		
			pH 4.9	pH 6.7	pH 8.8
P-1	9.4	5.7	1.7	1.9	2.58
P-2	19.5	3.7	0.32	0.32	1.02
P-3	27.6	6.2	a	0.52	0.74

^a Insoluble.

determinations of adsorption isotherms. Samples of the latex containing added acrylic acid-naphthylacrylamide copolymer and buffer were shaken for 20–24 hr at 25°C and centrifuged for 20 min at approximately 27,000 g. The copolymer concentration in the supernatant c_f (ppm) was then determined by UV absorption. The amount of polymer sorbed S expressed in mg per gram of latex, was obtained from the materials balance. Acetate buffer was used for pH 4.9, phosphate buffers for the pH range 5.9–7.5 and borate buffer for pH 8.8. Unless specified otherwise, the ionic strength was kept at 0.04. If desired, the ionic strength was increased by addition of NaCl. In a series of experiments in which the contact time of the latex with polymer was varied it was shown that 18 hr was sufficient for attaining equilibrium.

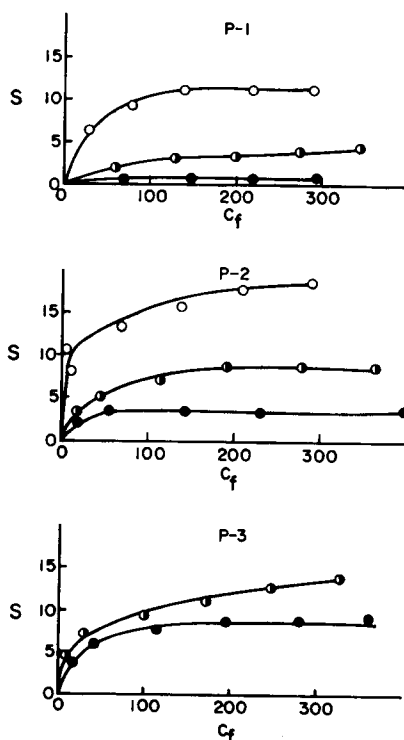


Fig. 1. Adsorption isotherms at pH 4.9 (○), 6.7 (◐), and 8.8 (●).

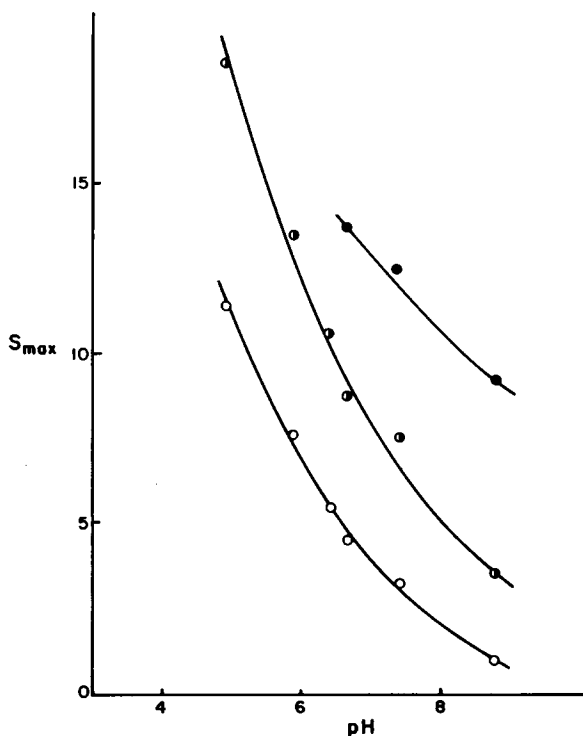


Fig. 2. Dependence of adsorptive capacity on pH for copolymers P-1 (○), P-2 (◐), and P-3 (●).

RESULTS

Adsorption isotherms of the three copolymers on the polystyrene latex at pH 4.9, 6.7, and 8.8 are represented in Figure 1. Most of the isotherms leveled off, at high c_f , to a well-defined saturation value S_{\max} . Plots of S_{\max} against pH for the three copolymers are shown in Figure 2. Adsorption increased with an increasing density of NA residues in the copolymer and with a decreasing pH. Our experimental technique was not sufficiently sensitive to determine the affinity of the copolymers for the polystyrene surface from the initial slope of the isotherm, but qualitatively the affinity exhibited a similar dependence on the NA content of the copolymer and the pH as the adsorptive capacity.

An increase in the ionic strength leads to increasing adsorption of the copolymers. This effect becomes more pronounced at high charge densities of the copolymer, i.e., at high pH. This is illustrated in Figure 3 on the pH dependence of the adsorption observed with a free polymer concentration of 300 ppm in the solution phase. On the other hand, as the concentration of the hydrophobic residues carried by the polyanion increases, the effect of ionic strength on adsorption becomes relatively less important.

A number of past investigators have encountered irreversibility in polymer adsorption.²⁷⁻³⁰ To find whether adsorption was reversible in our case, we equilibrated the latex with the polymer at pH 4.9, removed half of the supernatant after centrifugation and replaced it with a solution containing the same polymer concentration in pH 8.8 buffer. The relation between S and c_f obtained in this manner was then compared with the results obtained when the latex and

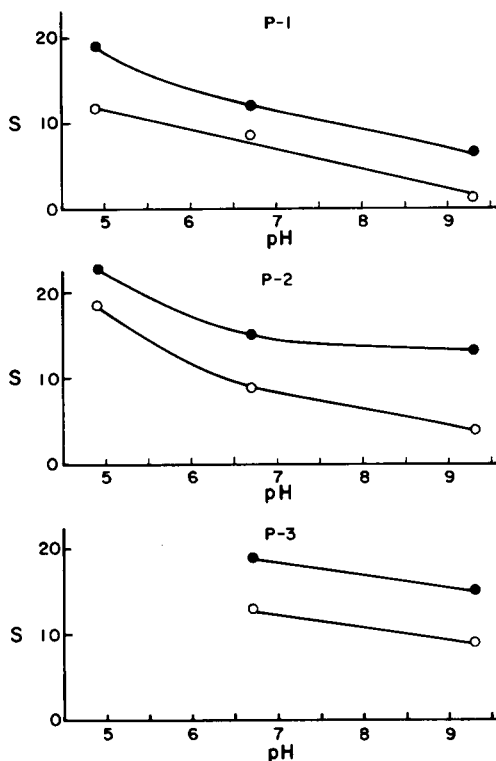


Fig. 3. Adsorption at $c_f = 300$ ppm at ionic strengths 0.04 (O) and 0.16 (●).

the polymer were directly equilibrated at the final pH of the solution. Results of these experiments are illustrated in Figure 4. They show that desorption is almost complete as long as the free polymer concentration is below 250 ppm; at higher polymer concentrations results obtained by the two procedures exhibit an increasing discrepancy.

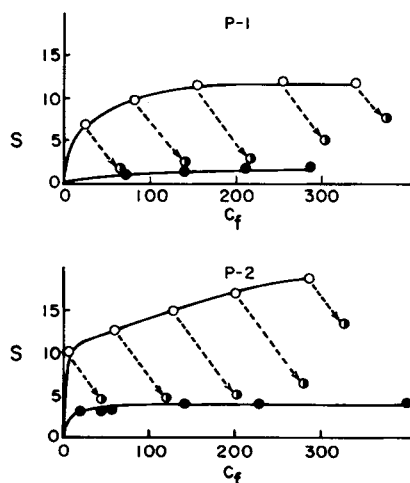


Fig. 4. Test of adsorption reversibility. Adsorption at pH 4.9 (O); desorption at pH 8.1 for P-1 and pH 8.6 for P-2 (●); adsorption at final pH (●).

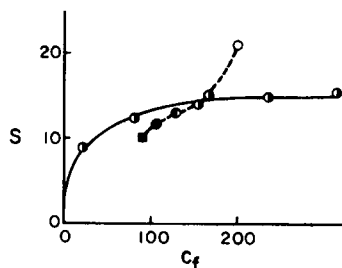


Fig. 5. Adsorption of copolymer P-2 at pH 6.7 and at latex concentrations of 0.38 (○), 0.76 (●), 1.14 (◻), 1.52 (◼), and 1.90 g/100 ml (■).

Another complication was revealed when we compared adsorption isotherms obtained by varying the concentration of the polymer exposed to a fixed concentration of latex or varying the latex concentration at a fixed concentration of polymer. Typical data obtained in this manner are shown in Figure 5. It may be seen that the polymer adsorption per latex particle tends to decrease for any concentration of the polymer in solution, with an increasing latex concentration. This could be attributed, in principle, to a polymer fractionation, where copolymers with a higher NA content would be preferentially sorbed. This seems unlikely, however, since the polymerizations were held to low conversion so that the drift in copolymer composition should not have been important. Alternatively, it may be assumed that at higher latex concentrations the latex particles are bridged by copolymer chains, reducing the area available for adsorption, but such bridging, if extensive, would be expected to lead to a flocculation of the latex.

DISCUSSION

Although the affinity of our copolymers for a polystyrene surface would be expected to increase with the density of hydrophobic residues carried by the polymer chain, it is far from obvious why an increasing number of naphthyl substituents should also increase the adsorption capacity. In fact, if we assume that these naphthyl residues are constrained to escape the aqueous environment by contact with the polystyrene, their increasing density should reduce the length of the poly(acrylic acid) sequences which extend into the aqueous medium, so that the adsorptive capacity would decrease. Our results show, therefore, that

TABLE II
Comparison of Experimental Adsorption Capacities with Values Calculated for Undistorted Molecular Coils

Polymer	pH	Adsorption Capacity [(g/cm ²) × 10 ⁸]	
		Found	Predicted
P-1	4.9	11	2.0
	6.7	3.8	1.9
	8.8	0.9	1.5
P-2	4.9	19	5.4
	6.7	8.7	5.4
	8.8	3.8	2.5
P-3	6.7	14	4.6
	8.8	9.2	3.7

the solvation of the polyion provides a sufficient driving force to detach a substantial fraction of the naphthyl groups from the polystyrene surface.

Our copolymers have isolated adsorptive sites and theories based on the concept of sequences of adsorbed monomer residues alternating with loops extending into solution^{2,3} should, therefore, not be applicable. It may then be of interest to compare our results with predictions based on an older model^{8,27} in which the experimentally observed adsorptive capacity is compared with the capacity corresponding to a close packing of rigid spheres with dimensions corresponding to those of the polymer coils in solution. This model receives some support from a recent careful study of the thickness of the adsorbed layer,⁷ which shows that at polymer solution concentrations exceeding 10^{-4} g/ml this thickness approaches the diameter of the dissolved polymer coil.

The latex particles, with a diameter of $0.54 \mu\text{m}$ and a density of 1.05 had a specific surface area $A_{\text{sp}} = 1.1 \times 10^5 \text{ cm}^2/\text{g}$. The radius of rigid spheres hydrodynamically equivalent to the polymer coils is $r = (30[\eta]M/\pi N_A)^{1/3}$, where $[\eta]$ is specified in dl/g, M is the molecular weight, and N_A is Avogadro's number. Thus, if the polymer coils could be represented by such rigid spheres arranged in hexagonal close packing on the surface of the adsorbent, the adsorption capacity, g/cm² would be

$$(\pi/2\sqrt{3}) (M/\pi r^2 N_A) = (1/12)^{1/2} (M/N_A)^{1/3} (\pi/30[\eta])^{2/3}$$

This is compared in Table II with the experimental values $S_{\text{max}}/1000 A_{\text{sp}}$. It may be seen that at pH 8.8, where the acrylic acid residues are almost fully ionized, the ratio of observed and predicted adsorption capacities is 0.6, 1.5, and 2.5, for P-1, P-2, and P-3, respectively, i.e., it increases with the density of hydrophobic adsorption sites on the polyanion. It also increases as the charge of the polyion is reduced at decreasing pH, from 0.6 to 5.5 for P-1 and from 1.5 to 3.5 for P-2 when the pH is changed from 8.8 to 4.9. It would appear then that the model in which the adsorbed polymer coils are assumed to retain their shape in solution gives a reasonable estimate of the adsorption capacities as long as the polymer is highly solvated and carries a low density of adsorption sites. This conclusion is similar to that arrived at by Garvey et al.³¹ concerning the adsorption of poly(vinyl alcohol) containing a small fraction of unhydrolyzed vinyl acetate residues onto polystyrene latex. With decreasing solvation and an increasing density of adsorption sites this model leads to a growing underestimation of sorption capacities.

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