

Excimer Fluorescence Determination of Solid-Liquid Interfacial Pyrene-Labeled Poly(acrylic acid) Conformations

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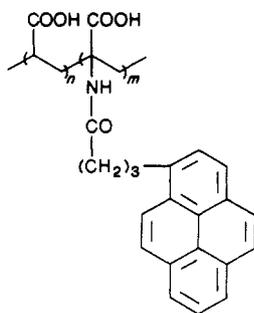
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The conformations of a pyrene-labeled poly(acrylic acid) adsorbed at the water-solid interface were studied by using fluorescence of the pyrene excimer as an indication of the presence or absence of polymer strand coiling. It is found that adsorption from aqueous solution onto positively charged alumina is rapid and that the conformation of the polymer at the surface reflects the state of the polymer in solution prior to adsorption. In the case of high pH adsorption, the extended polymer (low excimer contribution) bound to the surface is not affected by lowering the pH of the solution. In contrast, when the polymer is initially adsorbed in coiled form (low pH), raising the pH of the solution partially leads to extension of the polymer on the surface. Binding to positively charged silica leads to a more extended conformation of the polymer which is relatively unaffected by the pH of the solution; that is, adsorption at high pH followed by a decrease in pH does not change the relative amount of excimer present.

Introduction

Synthetic polyelectrolytes are widely used as simple models for biological macromolecules. In similar fashion to the behavior of biological macromolecules, polyelectrolytes can adopt secondary and tertiary structure in solution.² Fluorescence spectroscopy has been useful in the investigation of such structures.³ In a recent paper, we reported the use of the pyrene-labeled poly(acrylic acid) 1 in the investigation of conformational properties of the



1
 $n = 0.985; m = 0.015;$
 $DP = 510; MW = 40\ 000$

polymer in aqueous solution.⁴ We showed that the formation of pyrene excimers is enhanced at low pH compared to high pH solutions consistent with coiling of the polymer on protonation of the acrylate groups. At higher pH values, the polymer expands due to electrostatic repulsions as is reflected in the decreased amount of excimer formed. The ratio of monomer to excimer emission intensities, I_m/I_e , therefore serves as an indication of the structure of the polymer in solution.

In this paper, we wish to report an extension of this methodology to the study of the solid-liquid interfacial

conformations of this polyelectrolyte adsorbed on charged particulate solids. Understanding the interfacial behavior of polyelectrolytes will not only be important in the field of polymer science but will also increase our understanding of adsorption of biological macromolecules. Since the addition of a pyrene copolymer to the poly(acrylic acid) system represents a potentially significant perturbation on the native system, the results reported below may not reflect the exact properties of poly(acrylic acid) itself. However, as will be seen, this investigation allows for the determination of some adsorption properties of the model system which qualitatively, albeit not quantitatively, should be similar to those of poly(acrylic acid).

Results and Discussion

In the first set of investigations, suspensions of alumina⁵ (1 g of alumina in 9.5 mL of H₂O, 0.3 μ m, 15 m²/g) were adjusted to different pH values by using aqueous HCl or NaOH. To each suspension, a solution of the polymer 1 was added (0.5 mL of 1000 ppm polymer). The emission spectra were recorded on a Perkin-Elmer Model LS5 fluorescence spectrophotometer. In each case, less than 10% of the total pyrene remained in the supernatant, and therefore, the contribution of unbound pyrene to the total emission of the pyrene in the slurry was insignificant. As can be seen in Figure 1, the I_m/I_e ratio varies as a function of pH for adsorbed 1 on alumina in a similar fashion as was reported for 1 in solution.⁴ This suggests the adsorption model shown schematically in Figure 2. At low pH values, the adsorbed polymer coils such that more excimer formation is observed (lower I_m/I_e). Conversely, as deprotonation of the carboxylic acid moieties occurs, the polymer spreads out on the surface of the positively charged alumina. That the conformational state of the polymer is essentially the same in solution as adsorbed on the alumina suggests two possible explanations: (1) The polymer is weakly and loosely bound to the surface such that the conformation which the polymer adopts reflects the degree of carboxylic acid ionization in a manner similar to that in solution or (2) adsorption of the polymer occurs rapidly from solution to give strongly bound polymer.

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(5) Linde A grade, Union Carbide Corporation, 0.3 μ m, 15 m²/g surface area.

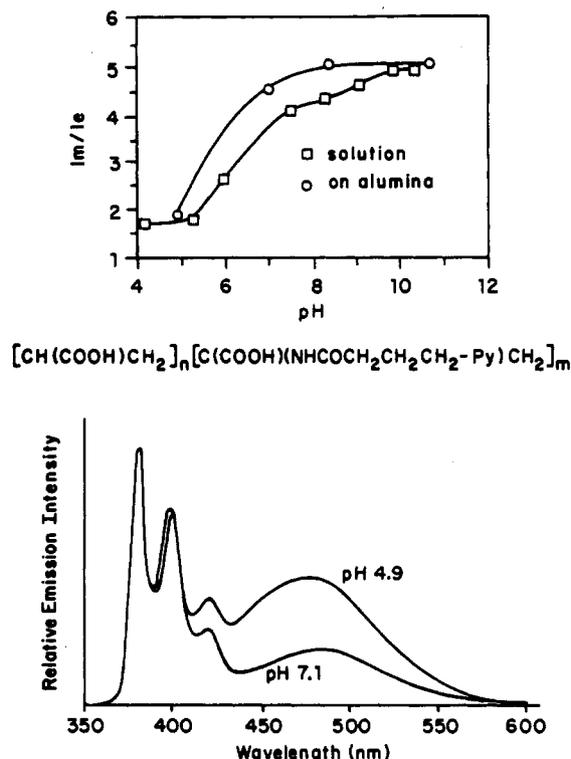


Figure 1. Emission spectra 1 in Al_2O_3 slurries and graph of monomer to excimer ratio as a function of pH for aqueous solution and adsorbed on alumina.

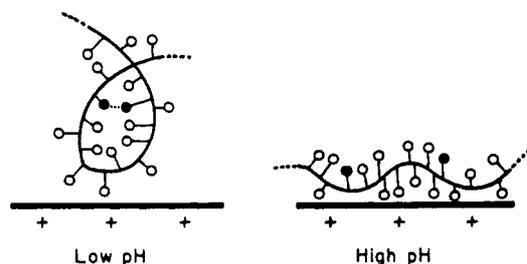


Figure 2. Schematic representation of the adsorption of polymer 1 on the alumina surface in coiled and extended form. In the coiled form, pyrene (black circles) excimer formation is promoted while in the extended form it is prevented.

Thus, the conformation of the polymer upon adsorption appears to be determined by the state of the polymer immediately before adsorption.

To distinguish between possibilities 1 and 2, the behavior of the polymer as a function of pH after adsorption was investigated. If the polymer is weakly and loosely bound, a change of pH after adsorption should result in rapid adoption of the appropriate conformation for the new pH. Conversely, if binding to the surface is strong, changes of pH after adsorption should result in no, or slow, spectral alterations. When 1 is contacted with an alumina slurry at approximately pH 8 for even just 2 min and then stirred at pH 4.8 for up to 36 h, the emission spectrum obtained is essentially the same as that for 1 at pH 8 and does not vary with time. That is, there is no evidence for polymer coiling once the polymer adsorbs in the expanded form. In solution, the coiling and expansion are rapidly reversible in that the pH changes lead to changes in I_m/I_e over a minute time scale. When 1 is adsorbed in coiled form (pH 4.7) then allowed to sit in basic solution (pH 8), the emission spectrum shows that less coiling is present than at pH 4.7, but considerably more is present than at pH 8. In this case, the initially adsorbed coiled-form polymer

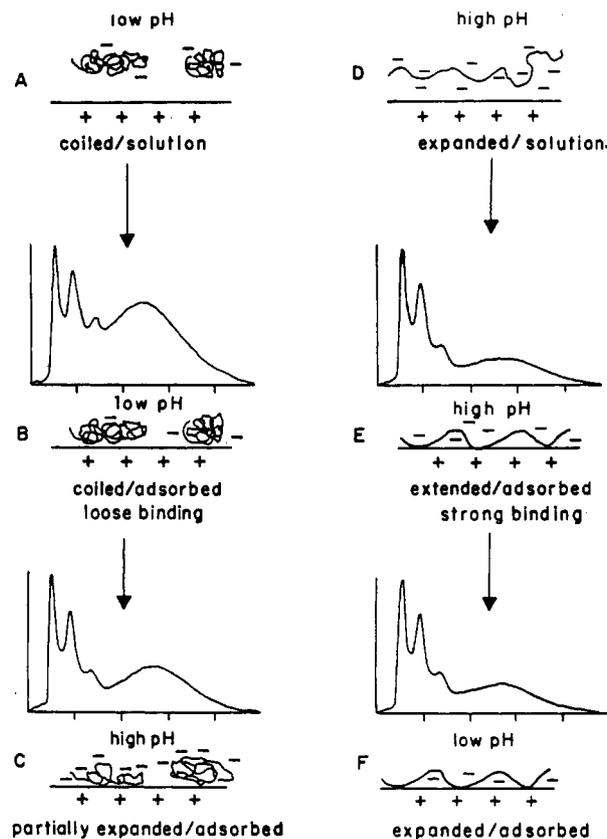


Figure 3. Schematic representation of the adsorption process of 1 on alumina. (A) At low pH the polymer is coiled in solution which leads to (B) adsorption in the coiled form. (C) Subsequent raising of the pH causes some expansion of the polymer. (D) Polymer at high pH in solution is extended and binds (E) strongly to the surface in this conformation. (F) Subsequent lowering of the pH does not allow for sufficient intrastrand interactions for coiling to occur.

relaxes partially on the surface at the higher pH values over a 24-h time scale. These results suggest that there is a significant activation barrier to coiling of the polyelectrolyte once the kinetically rapid adsorption process occurs, while expansion of coiled polymer on the surface has a significantly lower barrier. This is best explained in the following manner: At high pH values, the expanded-form polymer is mostly ionized and therefore binds strongly to the positively charged alumina surface. On lowering the pH, the stability of the carboxylate-surface binding makes protonation less favorable kinetically; i.e., the polymer is less basic since the anion is stabilized. On the other hand, when polymer is adsorbed at low pH values, the coiled-form polymer is less strongly attracted to the surface; that is, there are fewer points of attachment such that as the pH is raised, the polymer can adjust its conformational structure to allow greater contact with the alumina surface and minimize intrapolymer electrostatic repulsion. That the system does not become identical with that of the high pH adsorbed polymer probably reflects the lower flexibility of the adsorbed polymer to adopt all conformations as compared to the polymer in solution. This model behavior is shown schematically in Figure 3.

To determine the role of the solid surface charge on the conformational properties of the adsorbed polymer, 1 was adsorbed on a cationic silica gel 2, $\text{>Si}(\text{CH}_2)_3\text{NMe}_3^+$.⁶ In this case, very little excimer is observed, almost independent of pH I_m/I_e is about 5 at pH 4.3 as well as at pH

(6) From J. T. Baker Chemicals.

8.0). The lower amount of excimer formed as well as the relative independence of the I_m/I_e ratio on pH suggests that binding to the surface is stronger than in alumina. The electrostatic interactions of the carboxyl groups with the surface are greater than the hydrophobic, intrastrand interactions responsible for coiling of the polymer. The result is that even if the polymer in solution adopts a coiled conformation, on the positively charged silica surface the polymer lies flat so as to maximize polymer-surface interactions. As a control, 1 showed essentially no adsorption on a negatively charged, unfunctionalized silica gel.⁶

Conclusion

The above results demonstrate the applicability of the use of excimer fluorescence to the determination of polymer structure at the solid-liquid interface. On alumina, polymer adsorption occurs rapidly such that the degree of excimer formation depends significantly on the solution

state of the polymer immediately before adsorption occurs. With coiled-form polymer, binding to the surface is weaker (less binding sites per polymer strand) such that changes in pH allow for partial conformational adjustments to the polymer structure. Once the polymer is bound in the extended conformation, it is essentially unable to adopt the coiled conformation on the surface. In the case of the cationic silica gel 2, polymer adsorption leads to strongly bound, extended conformations independent of pH.

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Letters

Measurement of Gas Adsorption Isotherms by Continuous Adsorbate Addition

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A technique of measuring gas adsorption isotherms by continuous addition of adsorbate gas to the sample is described. Flow rates in the range of 0.01–1 mL (STP)/min can be obtained by means of orifices with diameters of 1–10 μm . The continuous-flow technique is compared with the customary incremental addition of the adsorbate gas for two sorbents, a γ -alumina and a high volatile bituminous coal.

Introduction

Gas adsorption is the standard technique for measuring the surface area of porous and finely dispersed solids. When extended to the range of capillary condensation, gas adsorption also provides information about pore size distribution for pore openings with diameters below about 20 nm.

The conventional method for obtaining a gas adsorption isotherm involves the following steps: First, the sample is outgassed under vacuum at a specified temperature. It is then isolated from the remainder of the system and cooled to the requisite temperature, which is often the normal boiling point of the adsorbate. A container of precisely known volume is filled with the adsorbate gas to the desired pressure. The container is then opened to the sample volume and, after the lapse of specified time, the pressure is recorded. The sample holder and the container are then isolated, the container is refilled, and the procedure is repeated.

The amount of gas adsorbed at each pressure level is simply the difference between the amount of gas intro-

duced into the system and the amount occupying the "dead volume" as calculated by the pressures before and after each equilibration (see ref 1). This incremental addition of gas provides a discrete set of points along the isotherm and will be referred to as the "discrete" technique. This technique of generating points along the isotherm gives good results but can be very tedious and time consuming.

An alternative to this method has been reported by Innes² and Lange.³ Both used a continuous flow of adsorbate into their systems and monitored system pressure. Innes used a mass-flow controller to admit a steady flow of gas, while Lange used a small capillary. When the ratio of upstream to downstream pressure is above its critical value, choked flow is established in the capillary, and the flow rate is independent of downstream pressure. The flow rates achieved in these two reports were limited by the capability of the mass-flow controller or the size of the capillary to a minimum of approximately 4.0 mL (STP)/min. More recently, Dollimore et al.⁴ and Bosch

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