Langmuir **2002,** *18,* 5921−5926

Intramolecular Association of Poly(maleic acid/octyl vinyl ether) in Aqueous Solution

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Received December 20, 2001. In Final Form: May 14, 2002

The properties of aqueous solutions of poly(maleic acid/octyl vinyl ether), PMAOVE, were studied by pyrene solubilization and fluorescence, solution viscosity, and phase separation induced by inorganic salts. The results indicate the existence of hydrophobic intramolecular microdomains formed by the octyl side groups. Pyrene solubilization and intramolecular alkyl chain association diminish sharply as the polymer is neutralized and unfolds with increasing ionization. The saturation solubilization of pyrene by PMAOVE corresponds to a ratio of 35 octyl side chains per pyrene at higher polymer concentrations for the unneutralized polymer, and 42 at constant pH 4.0. Some hydrophobic solubilization averaging one pyrene per polymer molecule persists up to complete neutralization. Besides pH, the polymer conformation is also sensitive to solution ionic strength. A compact conformation is induced by the addition of 0.01 M NaCl, as indicated by the low reduced viscosity at low pH. Further increase to about 0.1 M leads to the precipitation of PMAOVE at concentrations of 500 ppm and above. Precipitation or phase separation of PMAOVE solutions at pH 4 by bivalent cations occurs at much lower salt concentrations than with single-valent cations. With barium in particular, the phase separation is not a simple precipitation. A very weak gel phase separates from the solution. Only minor differences are detected with a range of anions of sodium salts in precipitating PMAOVE at pH 11. In contrast to PMAOVE, the less hydrophobic lower homologue poly(maleic acid/methyl vinyl ether), PMAMVE, shows no hydrophobic solubilization of pyrene and is not precipitated by addition of NaCl up to saturation of the salt.

Introduction

Hydrophobically modified (HM) homopolymers, also called polysoaps or polymeric surfactants, are water-soluble polymers with hydrophobic side groups. Interest in this class of macromolecules has grown since their conception about 50 years ago,[1] largely due to their unique associative behavior and their potential for applications in detergency, mineral separation, pharmaceuticals, rheology control, enhanced oil recovery, paints and coatings, etc. The performance of these polymers is determined primarily by the polymer conformation and the corresponding hydrophobic associations.

In aqueous solutions, HM polymer molecules with sufficient hydrophobicity can assume hypercoiled conformations with the formation of intramolecular clusters or micelles. However, unlike ordinary surfactant micelles, which are intermolecular aggregates, intramolecular micellization occurs at all polymer concentrations, with no critical micelle concentration of polymer observed.[2] Polysoap conformation in solution may be studied by fluorescence techniques applied to fluorescers hydrophobically solubilized by the polymers.[3,4] In particular, pyrene fluorescence has been widely used to monitor the microenvironments in aqueous solutions. Many studies have employed the hydrolyzed form of the regularly alternating copolymers of maleic anhydride and alkyl vinyl ethers.[1,2,5−10] Of special interest are the members of this family with alkyl groups containing four to 10 carbon atoms. They form intramolecular micelles at low pH, but the extent of micellization diminishes with increasing pH as a result of the repulsion between the ionized carboxylate groups.[11,12] Fluorescence quenching studies revealed that these polysoap molecules contain a large number of relatively small micelles[6,7] with aggregation numbers ranging from 25 to 140.[8−10] As a consequence of the aggregation, HM polymers generally show much lower reduced viscosity than the corresponding unmodified entities. However, upon shearing or uncoiling, for example by increasing the charge density, the molecules may form a network-like structure and thereby increase the solution viscosity.[11] The presence of hydrophobic microdomains in aqueous solutions also enables the HM polymers to remove organics from water, and in the case of aromatic hydrocarbons, their solubilization can even enhance the intramolecular hydrophobic association of the polymer.[12] Since most polysoaps are sensitive to pH and ionic strength,[13] regulation of these variables can also be used to manipulate conformation and solution rheology.[14]

To extend understanding of the determining factors for HM polymer conformation, an intermediate modified poly(maleic acid/alkyl vinyl ether) homologue, namely, poly-

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10.1021/la0118356 CCC: $22.00

(maleic acid/octyl vinyl ether) (PMAOVE), was studied by pyrene solubility, fluorescence methods, viscosity, and salt-induced precipitation. The results are compared with those for a less hydrophobic homologue, poly(maleic acid/methyl vinyl ether) (PMAMVE), to elucidate the effect of hydrophobic substitution.

Materials

1. Polymers. The polymers, PMAOVE and PMAMVE, were provided by International Specialty Products, Inc. These polymers were synthesized using free-radical polymerization of a 1:1 mol ratio of maleic anhydride and vinyl ether in toluene with Vaso-69 (azo bis-valeryl nitrile) as initiator. The products were purified twice by first dissolving in acetone (~5 wt %) followed by precipitation with excess tertiary butanol (~40 times in volume). Residual solvent was removed by vacuum-drying at 50 °C to constant mass. The anhydride moiety of the polymer was then hydrolyzed in triply distilled water to make approximately ~5 wt % solution. The solution was stirred at 500 rpm at 70 °C for about 10 h, then freeze-dried. As determined by gel permeation chromatography calibrated with a polyethylene standard, the weight-average molecular weights are 180 000 for PMAOVE and 138 400 for PMAMVE, with a polydispersity of 2.6. Using GPC with a multiangle laser light scattering detector for the PMAOVE gave a weight-average molecular weight of 154 000.

2. Probes and Additives. Pyrene was purchased from Aldrich Chemical Co. and was specified to be 99+% pure. Solutions of 0.1 and 1 N NaOH were products from Fisher Scientific. The following inorganic salts were also used: NaCl, Na_2HPO_4, KCl, 99+% pure, from Amend; NaBr, 99+% pure, from Aldrich; NH_4Cl, from J.T. Baker Chem. Co; $CaCl_2$, NaF, $BaCl_2$, $MgCl_2 \cdot 6H_2O$, from Fisher Scientific; Na_2SO_4, 99+% pure, from Aldrich; all salts are of ACS grade and were used as received.

Methods

Unless otherwise stated, experiments were carried out at room temperature ($T = 22-23$ °C).

1. Viscosity. An Ubbelohde capillary viscometer from Cannon Instrument Company was used to measure the relative viscosity of aqueous polymer solutions. The body of the viscometer was immersed in a water bath maintained at 25 ± 0.03 °C. Prior to each measurement, the instrument was washed several times with acetone, then dried by blowing clean air. About 10 mL of polymer solution was needed, and 20 min was allowed for temperature equilibration. The ratio of the flow time of polymer solutions to that of pure water is referred to as relative viscosity, measured to a limit of ±0.15%

2. Pyrene Solubility. Pyrene solubility has been used to quantify the hydrophobic microdomain volume in surfactant micellar solutions.[15] The same method is used in this work to estimate the amount of hydrophobic aggregates formed by PMAOVE. Excess pyrene was added to the sample solution in a 20 mL glass vial topped with Teflon-coated caps. The vials were wrapped completely in aluminum foil and subjected to wrist-action shaking for one week at 250 rpm. After centrifugation at 4000 rpm for 1 h, the supernatant was carefully removed with a glass pipet and then filtered through a 0.2 μm Nalgene membrane. The filtrate was collected and analyzed by UV absorption at 335 nm. The validity of this method was tested using sodium dodecylsulfate (SDS) solutions, which showed very low constant pyrene solubilization below the CMC, equivalent to the pyrene solubility in water but increasing linearly with surfactant concentration above the CMC.

3. Fluorescence. The intensity ratio of the third and the first peaks, the polarity index (I_3/I_1, in the pyrene fluorescence spectrum) is sensitive to the microenvironmental polarity surrounding the pyrene molecule,[16-18] while the excimer to monomer fluorescence intensity ratio, I_e/I_m, is associated with the distribution and local concentration of the solubilized pyrene.[3,18,19] Thus, under saturated concentrations of pyrene, both the I_3/I_1 and I_e/I_m are expected to be independent of the polymer concentration if the number of pyrenes per polymer and the conformation remain constant. In this study, two sets of aqueous pyrene solutions were used: pyrene saturated in the chosen polymer solution and a solution of fixed pyrene concentration (8×10^{-6} M). To prepare the latter solution, pyrene was first dissolved in acetone at about 0.025 wt % Then an aliquot was transferred to a 20 mL glass vial and dried in a vacuum and the requisite amount of water or polymer solution added. Steady-state fluorescence spectra were obtained by exciting pyrene at 335 nm, and the intensities at 373, 382, and 480 nm recorded for the first, third, and excimer peaks, respectively.

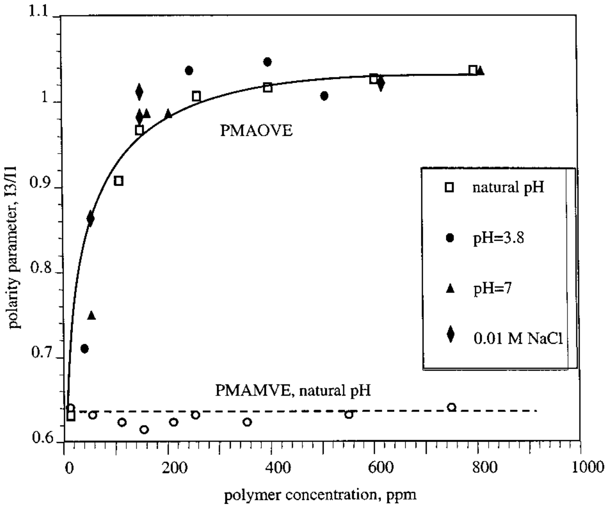
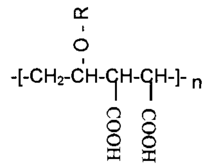


Figure 1. Polarity parameter (I_3/I_1) for pyrene (8×10^{-6} M) fluorescence in aqueous solutions of PMAOVE and PMAMVE.

4. Definition of Degree of Neutralization. The degree of neutralization (α) of the polymer is expressed as the mole ratio of added NaOH to the total polymer carboxylic acid groups present in the solution.

Results and Discussion

The structural formula for the repeating subunits of PMAOVE is



$$-[-CH_2-\underset{}{\overset{O-R}{CH}}-\underset{COOH}{CH}-\underset{COOH}{CH}-]-_n$$

where R = CH_3 for PMAMVE and n-C_8H_{17} for PAMOVE.

A computer simulation minimizing the structural energy in vacuo indicates a helical structure of 30 subunits per turn for PMAOVE. The helix is tape-like with the octyl chains oriented within the spiral and the carboxyl groups to the outside. The octyl side group is large compared to the monomer backbone and is expected to play a significant role in determining the interaction of the polymer with water with consequent modification of the helical structure.

1. Pyrene Fluorescence. Pyrene fluorescence at constant concentration (8×10^{-6} M) was measured in unneutralized aqueous solutions of both PMAOVE and PMAMVE. The results are given in Figure 1. As expected, even at high polymer concentrations the polarity parameter I_3/I_1 for pyrene in aqueous PMAMVE solutions is close

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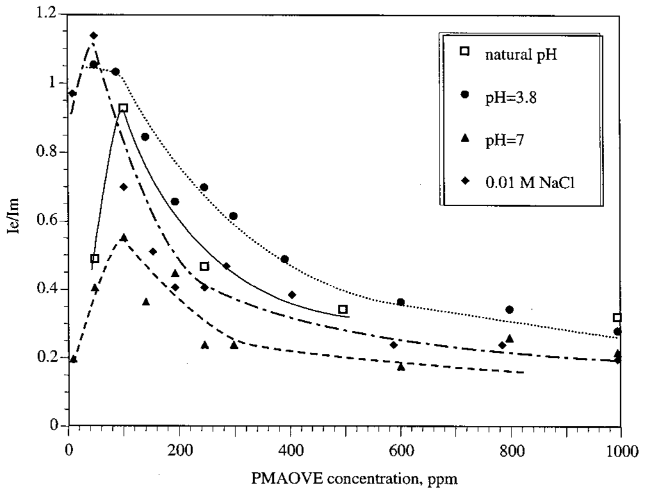

Figure 2. Excimer/monomer band ratio of pyrene (8×10^{-6} M) fluorescence in aqueous PMAOVE solutions under various conditions.

to 0.63, the characteristic value for pyrene in water.[18] No excimer fluorescence was observed in this case. In contrast, a microenvironment that is substantially hydrophobic was detected in aqueous PMAOVE solutions throughout the concentration range studied. The micropolarity parameter increases initially with polymer concentration, rising to a plateau at around 100 ppm. No further variation was detected at higher concentrations. The initial increase in I_3/I_1 with un-neutralized polymer concentration cannot be explained by the concomitant decrease in pH caused by the dissociation of the carboxylic acids of the polymer since a similar pattern was also observed at fixed pH. At sufficiently low PMAOVE concentrations the amount of pyrene in the polymer hydrophobic microenvironment will be comparable to that remaining in the water (8×10^{-6} M in the absence of polymer), and the micropolarity parameter observed will be an average for the two environments. As the polymer concentration is increased, the pyrene is more partitioned into the hydrophobic microdomains until the free pyrene concentration in the water becomes negligible and the polarity parameter reaches a constant plateau value. Similar partition of pyrene has been reported by others.[20−22]

The excimer/monomer ratio (I_e/I_m) for pyrene at constant concentration increases to a maximum in the presence of 50−100 ppm PMAOVE, above which a continuous decrease is seen (Figure 2). The excimer/monomer ratio is considered an indication of the local concentration of pyrene in the microenvironment.[3,18,19] This implies that the polymer concentration at which the maximum ratio is reached corresponds to the polymer concentration needed to bind almost all the given amount of pyrene. Further increase in polymer concentration reduces the number of pyrene molecules per polymer molecule, leading to the local dilution of the pyrene. Following this reasoning, one pyrene molecule is bound for 40−50 octyl side groups at the maxima shown for constant pH 3.8 and 7 in Figure 2. Interestingly, this value is comparable to the ratio of 45.6 for the hexyl homologue reported by Hsu and Strauss.[8] Since two pyrene molecules are required for excimer formation, and large octyl chain clusters are sterically improbable, these ratios do not necessarily correspond to the number of octyl chains per pyrene in the local microdomains. Chain clustering may also be affected by the presence of the pyrene, and bound pyrene molecules may themselves act as preferred hydrophobic binding sites for additional pyrene.

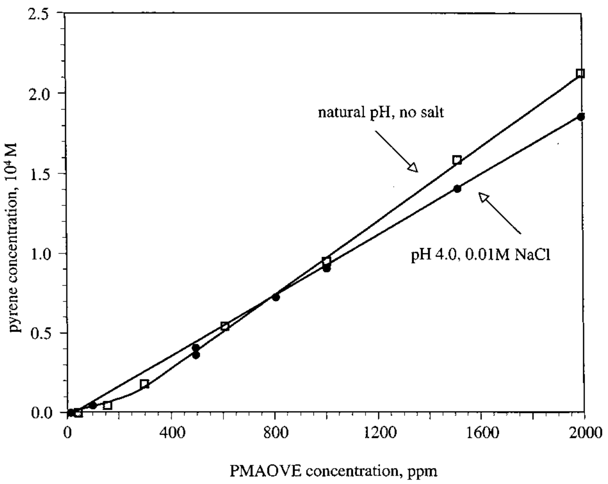

Figure 3. Pyrene solubility in aqueous PMAOVE solutions as a function of polymer concentration.

To further investigate the chain aggregation behavior of PMAOVE, pyrene solubility was determined as a function of polymer concentration at the natural pH of the polymer solution, or at pH 4.0 with addition of 0.01 M NaCl. Figure 3 shows that at the natural pH in the PMAOVE concentration range studied, pyrene solubilization per polymer molecule increases with polymer concentration up to ∼500 ppm, becoming constant at higher polymer concentrations. At constant pH 4 with 0.01 M NaCl the trend is more linear, but the experimental error is also consistent with a lower solubilization of pyrene per polymer molecule at the lower polymer concentrations. If the polymer conformation were constant as the concentration changes, pyrene solubility should increase linearly with the polymer concentration. For un-neutralized PMAOVE solutions the pH decreases monotonically with polymer concentration, reaching pH 3.48 at 600 ppm, changing little at higher concentrations. The degree of ionization therefore decreases as the polymer concentration increases, leading to greater coiling and increasing pyrene solubilization per polymer molecule, thus accounting for the observed form of pyrene solubility data. In the case of pyrene solubilization at constant pH 4, HCl is added to the solutions to achieve pH 4 at concentrations up to 600 ppm polymer, increasing the ionic strength and causing some uncoiling, consistent with the low values of I_e/I_m for saturated pyrene at low PMAOVE concentration shown in Figure 4. The effect of pH change on conformation is clearly indicated at high polymer concentrations in Figure 3, where the degree of ionization is significantly greater at pH 4.0 than at the natural pH, with consequent greater uncoiling and lower pyrene solubility. At the natural pH, pyrene binding is equivalent to 36 octyl chains/pyrene at the highest polymer concentrations shown, at which the pH falls to 3.48, compared to 42 for the less coiled polymer at constant pH 4.0.

The fluorescence of pyrene on the polymer when the polymer solutions are saturated with pyrene is markedly different from that at a fixed low pyrene concentration. Figure 4 shows the values of I_3/I_1 and I_e/I_m with increasing polymer concentration at pyrene saturation at pH 4.0 with 0.01 M NaCl. It is observed that while the micropolarity index remains almost invariant in the concentration range studied, the excimer to monomer band ratio I_e/I_m initially increases markedly with polymer concentration until ∼600

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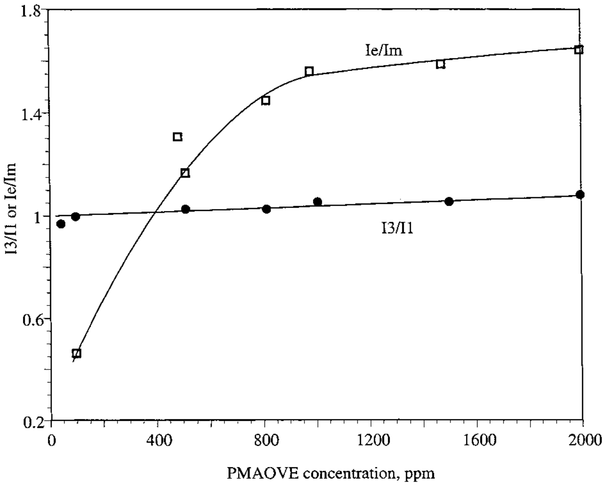

Figure 4. Pyrene fluorescence in aqueous PMAOVE solutions. Saturated pyrene, pH 4.0, 0.01 M NaCl.

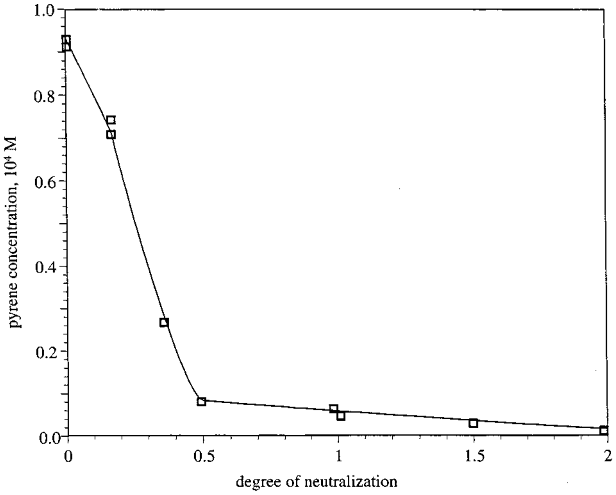

Figure 5. Pyrene solubility in PMAOVE solutions (1000 ppm) as a function of the degree of neutralization. 0.01 M NaCl.

ppm and more slowly at the higher concentrations. This change in trend corresponds with the polymer concentration below which HCl is added and above which NaOH is added to give pH 4.0, implying a change in polymer conformation as the degree of neutralization changes with PMAOVE concentration at constant pH. A conformation change, as discussed above, may also be associated with an increase of bound pyrene per polymer molecule as the polymer concentration increases at pH 4. On this interpretation, the lower I_e/I_m ratio at lower polymer concentrations is simply a reflection of the lower pyrene binding to the individual polymer molecules since the excimer formation is second-order in pyrene concentration in the hydrophobic regions along the polymer chains.

The intramolecular chain association in PMAOVE is clearly altered significantly by varying solution pH. Figure 5 shows that as the degree of neutralization of the carboxylic acid groups on the polymer increases from 0 to 0.5 (corresponding to a pH shift from 3.3 to 8.0), pyrene solubility in 1000 ppm PMAOVE solutions decreases sharply, with further decrease as alkali is added to full neutralization and beyond. Increasing the degree of ionization enhances electrostatic repulsion between adjacent segments, resulting in a more stretched conformation of the polymer and hence reduced formation of hydrophobic clusters. The residual solubility of pyrene at high values of α shows either that some microdomains persist to full neutralization or that hydrophobic clustering is induced by the presence of the pyrene. The lower pyrene solubility as neutralization increases reflects a decrease in number or size of the intramolecular hydrophobic clusters. Reduction in size is consistent with the findings of Zana et al. for the decyl homologue,[9] but not with that of Strauss et al., who concluded from their experiments with the hexyl homologue that the microdomain size is independent of α.[8] Apparently, the length of the side groups of the polymer accounts to some extent for the reported discrepancy. Interestingly, as shown in Figure 6, the hydrophobicity of the polymer microenvironment remains almost invariant in the whole range of α, but the I_e/I_m ratio decreases following a shape similar to that of the solubility curve. This ratio is still as large as 0.2 at full neutralization, showing that the few pyrene molecules bound to the polymer (equivalent to approximately one per polymer molecule on the average) tend to cluster together. This reinforces the idea that bound pyrene attracts further binding at the same site. Molecular modeling suggests that a pocket comprised of four subunits in the polymer chain is a favored configuration for the binding of two pyrenes in hydrophobic association with four octyl chains. This configuration would compete entropically with the fully stretched form of the ionized polymer, with a larger fraction of the associated pyrene singly bound to the neutralized polymer than with the un-neutralized form

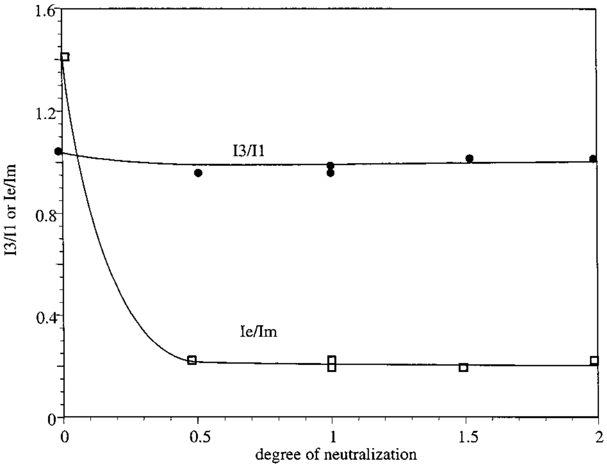

Figure 6. Pyrene fluorescence as a function of the degree of neutralization of PMAOVE (1000 ppm). Saturated pyrene, 0.01 M NaCl.

2. Solution Viscosity. As shown in Figure 7 the un-neutralized solutions of PMAOVE exhibit a much lower viscosity than PMAMVE. Since the solution pH decreases with increase in polymer concentration, a more compact configuration can be expected for the two polymers at higher concentrations. The extent of molecular coiling caused by the pH reduction, however, is different for PMAOVE and PMAMVE. The strong hydrophobic attraction between the octyl side groups of PMAOVE induces shrinking to a greater extent than for PMAMVE. To further study this phenomenon, solution viscosities were compared at fixed pH and ionic strength (Figure 8). At both pH 3.8 and 7.0 (which corresponds approximately to α = 0.4), the nonlinearity of the relative viscosity evident at the natural pH as shown in Figure 7 disappears and the relative viscosities increase rather linearly in the concentration range studied, corresponding to constant reduced viscosities as shown in Figure 8. Lowering of the pH from 7 to 3.8 causes a decrease in the reduced viscosity in the entire concentration range. This observation is in

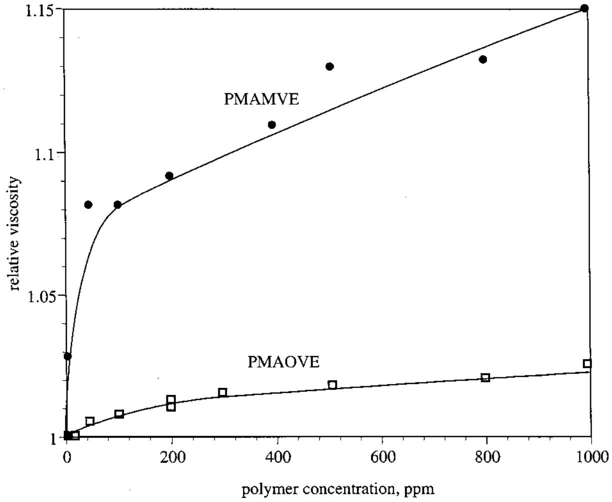

Figure 7. Solution viscosity of PMAOVE and PMAMVE as a function of concentration. $T = 25$ °C. No pH or ionic strength control.

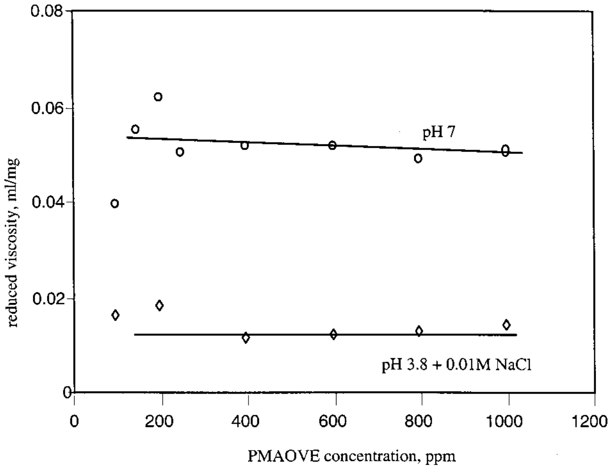

Figure 8. Effect of pH and ionic strength on the solution viscosity of PMAOVE. $T = 25$ °C.

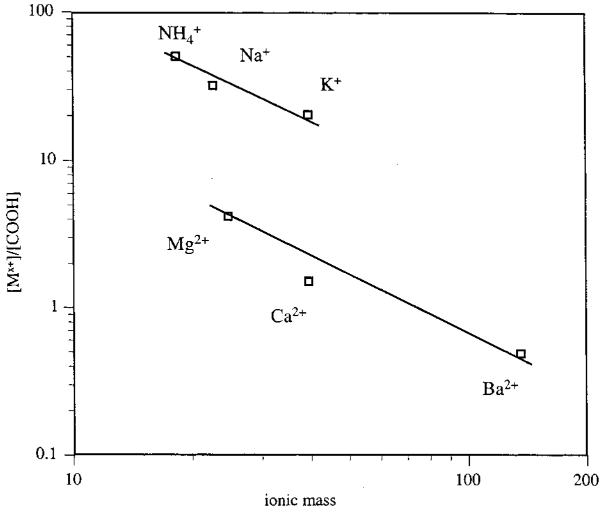

Figure 9. Ratio of total cations to carboxyls in PMAOVE solution (500 ppm) at the onset of turbidity. In all cases, the counterion is $\mathrm{Cl^-}$. M^{x+} denotes the cations.

agreement with the conformational changes of PMAOVE suggested by the pyrene solubility and fluorescence data, with increase in the pH causing the hydrophobic association to be reduced and the chain conformation to be more stretched. Counterion screening of the diffuse double layer repulsion along the chain of ionized carboxyl groups also contributes to coiling.[27] Effects similar to those described above have been reported in the study of several other poly(maleic acid/alkyl vinyl ether) homologues, the viscosities of which, under conditions of no ionic strength control, reach a maximum around $\alpha = 0.5$ and then decrease at higher values of α due to binding or screening by the counterions introduced for pH adjustment.[28] We note that the pronounced maxima in reduced viscosities found at low concentrations with salt-free fully ionized polymers[32] are unlikely with PMAOVE under the conditions of our study, in which ionization of the un-neutralized polymer is a function of concentration, and neutralization necessitates addition of cationic counterions.

3. Phase Behavior in the Presence of Inorganic Ions. The effects of added salt on the viscosity and other properties of ionizing polymers in aqueous solution are usually attributed to binding or double layer screening by the counterions. The effect of positive counterions on the carboxyl groups of PMAOVE was examined further by comparing the concentration of several salts required to precipitate the polymer, as measured by the onset of turbidity in the polymer solutions. The hydrophobic effect is associated with changes in the ordering of water around apolar solutes.[29] Salt ions modify water structure and affect the solubility of amphiphiles. In a series of experiments with sodium salts (thiocyanate, chloride, iodide, bromide, and sulfate) PMAOVE at pH 11.1 was precipitated at sodium ion concentrations within 10% of 0.125 M in each case. No sequence corresponding to the Hofmeister series[20] for these anions was observed, which is as expected for the fully neutralized anionic polymer.

Comparison of a range of chlorides showed marked cation effects with PMAOVE at pH 4.0, as given in Figure 9. Divalent cations are more efficient at inducing turbidity in the polymer solutions than univalent cations. The heavier metal cations for a given valency are more efficient, as expected for ions of larger charge/radius ratio.[30,31] The effectiveness is in the order

$$\mathrm{NH_4^+} \le \mathrm{Na^+} < \mathrm{K^+} << \mathrm{Mg^{2+}} < \mathrm{Ca^{2+}} < \mathrm{Ba^{2+}}$$

The data in Figure 9 show the turbidity threshold concentrations as ratios of the total added cations to the carboxyl groups on the PMAOVE, displayed as a function of the cation masses (daltons). Separate logarithmic linear relations are found for mono- and divalent cations.

The large cation/carboxyl ratios for the monovalent cations indicate that their effects are due in large measure to counterion screening, with some possible binding for potassium. For the divalent cations, the trend is clearly to direct counterion binding as the ionic mass increases, until for barium, the turbidity threshold is close to a 1:2 ratio. An interesting observation confirming this conclu-

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sion is the formation of what appears to be a very weak gel-like structure by PMAOVE in the presence of Ba^{2+}. On addition of $BaCl_2$, the solution becomes turbid during stirring, but becomes more transparent when the stirring is stopped. The solution separates into two layers. One is observed to shrink quickly downward as a whole and shows an interface with the supernatant. The shrinking takes about 5 min, giving a thin layer of viscous slightly turbid sediment. Similar observations were made with Ca^{2+} and Mg^{2+}, but in these two cases the solutions were more turbid and the shrinking of the "gel" took much longer. No such phenomenon was detected with single-valent cations, in which cases the solutions remained turbid for more than 24 h without settling. The results suggest that the divalent cations are capable of interacting with carboxylate groups on neighboring polymer chains, thus inducing the formation of a fluctuating reversible noncovalently linked polymer network. The possibility of concomitant weak intermolecular association of the octyl side chains cannot be ruled out. The density difference between the separated polymer phase and the residual solution, the former containing locally concentrated heavy metal ions, leads to the observed shrinking and settling phenomenon. The range of behavior of cations on PMAOVE solutions suggests caution in interpreting the phenomena as simple precipitation for all salts. In contrast to PMAOVE, precipitation of 500 ppm PMAMVE at pH 4.0 cannot be achieved with NaCl even when the solubility limit of the salt was reached. With $BaCl_2$ the precipitation concentration was almost 100 times higher than for PMAOVE, with no formation of a "gel". This strongly suggests that the side chains in PMAOVE are involved in the formation of the weak "gel" observed with $BaCl_2$.

Summary

The properties of hydrophobically modified polymers depend to a great extent on their conformation. This study provides insight into the governing factors for intramolecular hydrophobic association of poly(maleic acid/octyl vinyl ether) in aqueous solutions. In contrast to its less hydrophobic methyl homologue, poly(maleic acid/octyl vinyl ether) can form substantial hydrophobic microdomains in aqueous solutions. Pyrene solubility experiments indicate that the microdomains are intramolecular clusters of octyl side chains. With pyrene saturation at low pH, the number of octyl groups can be as low as about 50 per pyrene molecule, increasing sharply as the degree of neutralization is increased and the polymer coils stretch out.

The intramolecular octyl group association behavior of PMAOVE depends on the solution pH. Pyrene solubility in 1000 ppm PMAOVE solutions decreases markedly when the degree of neutralization increases from 0 to 0.5, indicating loss of hydrophobic microdomains. The polarity index for the solution, however, remained close to 1.0 in the whole range of polymer neutralization, demonstrating the existence of some hydrophobic microdomains even at very high pH. The small number of pyrenes solubilized at high degrees of neutralization (one per polymer molecule on the average for $\alpha = 1$) are not randomly distributed along the polymer chains, but tend to associate, probably in pairs in local pockets with small clusters of octyl chains co-stabilized by the pyrene, thereby allowing formation of excimer complexes on irradiation. The conformation of PMAOVE is also affected by the presence of inorganic salts. A range of sodium salts with different anions showed almost identical effects on the precipitation of PMAOVE from solution at pH 11. At pH 4 the choice of cation markedly influences the solubility of the polymer, with bivalent cations being more effective than the univalent. For the same valency cations, higher ionic mass correlates with efficiency in causing phase separation. The phase separation induced in the PMAOVE solutions by the divalent cations, notably with barium, is not a simple precipitation. A very weak gel-like structure appears, forming a distinct phase, which shrinks to a small volume. By contrast, the methyl homologue PMAMVE is not precipitated by concentrated NaCl and only at high $BaCl_2$ concentrations and without forming the weak "gel" observed with PMAOVE. These findings show that PMAOVE can reversibly cross-link at pH 4 in the presence of divalent cations, assisted by intermolecular hydrophobic side chain association.

Acknowledgment. The authors acknowledge with thanks the support of the National Science Foundation (EEC 9804618 and CTS 0089530) and of the industrial sponsors of the Center for Industrial/University Cooperation for advanced studies in novel surfactants at Columbia University. We thank Professor Nicholas Turro of Columbia University for his valued comments on this study. We also thank Dr. Ian Robb of Halliburton Inc. for his interest and helpful comments, and Dr. Larry Senak of International Specialty Products for the polymer analyses

LA0118356