Aggregation Behavior of and Surface Tension Reduction by Comblike Amphiphilic Polymers

C. Maltesh, Qun Xu, and P. Somasundaran*

Langmuir Center for Colloids and Interfaces, School of Engineering and Applied Science, Columbia University, New York, New York 10027

W. J. Benton and Hung Nguyen

BP Research, BP America Inc., Warrensville Research Center, 4440 Warrensville Center Road, Cleveland, Ohio 44128

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The solution behavior of a comblike polymer with hydrophobic and hydrophilic chains (DAPRAL GE 202) was studied using fluorescence spectroscopy, light scattering, and surface tension. Results suggest that the segments of the polymer aggregate at very low concentrations to form hydrophobic domains. The surface tensions of aqueous solutions were also reduced drastically comparable to those obtained by using surfactants. Surface tension and light scattering results suggest no clear critical aggregation concentration in solutions of low ionic strength, but high concentration of electrolyte favored the formation of monodisperse aggregates. Surprisingly, polymer aggregates formed in the presence of high salt concentration were more hydrophilic than those formed in the absence of any salt as indicated by pyrene fluorescence measurements.

Introduction

Modification of polymers by the introduction of hydrophobic groups on the backbone of the macromolecular chain is fast gaining popularity because of the advantages of such polymers in applications like detergency and enhanced oil recovery. Hydrophobically modified polymers form association complexes which can be used to increase the viscosity and the elasticity of polymer solutions. The molecular weights of such polymers are low, and the advantage they have over ultrahigh molecular weight polymers is that the associated structures are resistant to permanent shear degradation.[1,2] Such polymers are also effective in reducing the surface tension and are comparable to low molecular weight surfactants in this regard.[3] In this paper we present some preliminary results obtained with a comblike polymer (DAPRAL GE 202) using fluorescence spectroscopy, light scattering, and surface tension.

Experimental Section

The polymer studied here was DAPRAL GE 202, a maleic anhydride α-olefin copolymer, having a comblike structure with both hydrophobic and hydrophilic side chains. The polymer was supplied by Akzo Chemie America and had a number average molecular weight of 20 000. The structure of the polymer is shown in Figure 1. Reagent grade sodium chloride, hydrochloric acid, and sodium hydroxide from Fisher Scientific Co. were used. Pyrene obtained from Aldrich Chemicals was recrystallized from ethanol.

Surface tension was determined at 23 ± 2 °C using a Fisher du Nuoy ring tensiometer with a platinum–iridium ring. Fluorescence spectra were recorded on a Photon Technology International PTI-LS 100 spectrometer. The excitation wavelength was 320 nm and appropriate correction was applied to avoid interference from the lamp. The intensities of pyrene emission peaks at 373 and 383 nm were recorded. A Nikon 200 fixed angle laser light scattering setup was used for determining the size of the aggregates in solution. The temperature for this measurement was 30 ± 1 °C.

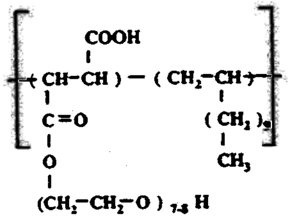

Figure 1. Molecular structure of DAPRAL GE 202 (determined by BP America).

Results and Discussion

In this investigation, fluorescence spectroscopy was used as a probing technique to determine the aggregation characteristics of DAPRAL. The fluorophore used was pyrene, primarily because its emission characteristics depend upon the nature of the solvent. The ratio of relative intensities of the I (373 nm) and III (383 nm) peaks (I_{III}/I_I) on a pyrene emission spectrum shows the greatest solvent dependency.[4] Qualitatively, this ratio decreases as the polarity increases (e.g. ~1.65 for hexane and ~0.6 for water) and can be used to estimate the solvent polarity of an unknown environment. Since this ratio is sensitive to the polarity of the medium in which the pyrene probe resides, it will be termed here the *polarity parameter*. An important application of this parameter is in the determination of surfactant micellization and/or aggregation. Owing to their hydrophobic nature, these probes are incorporated exclusively within the micelle or a hydrocarbon environment during their excited lifetimes.

Effect of pH on the aggregation behavior of the polymer was determined and is reported in Figure 2. The aggregation behavior of DAPRAL is identical at the two values of pH studied. At low polymer concentrations, the value of the I_{III}/I_I ratio corresponds to that of water (~0.6). At a DAPRAL concentration of 10 ppm there is an increase in the value of the polarity parameter (I_{III}/I_I) indicating

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* To whom correspondence should be addressed.

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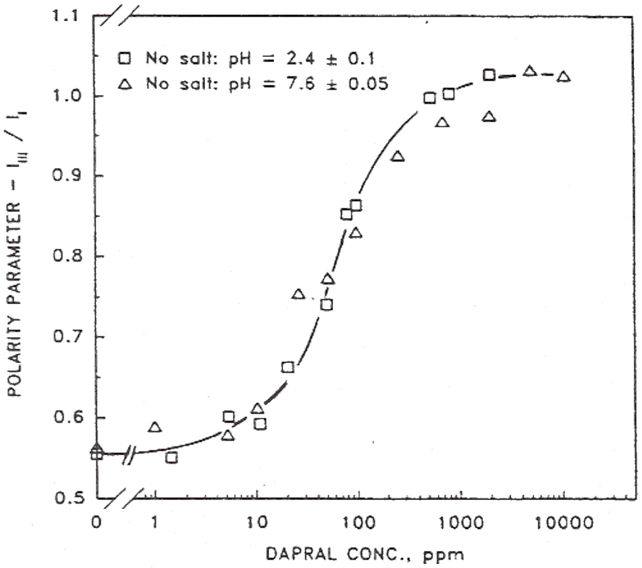

Figure 2. Effect of pH on the aggregation of DAPRAL.

the presence of hydrophobic aggregates at this concentration. In a recent study,[5] it was reported that the viscosity of aqueous solutions of a similar polymer (GE 202 Na) was low and even at 10% (100 000 ppm) dosage the apparent viscosity of the solution was ~2 cP. It was concluded that there was no entanglement even at these high polymer concentrations. From the present investigation, it is evident that there is aggregation at very low polymer concentrations. Considering that the polymer molecular weight is 20 000 and that aggregation occurs at very dilute polymer concentrations, it can be said that this aggregation is a result of intrapolymer association. It can also be speculated that at concentrations above 2000 ppm the polarity parameter remains relatively constant, and this could be the indication of the formation of micelles of the hydrophobic groups on the polymer.

There is no effect of pH on the aggregation behavior of DAPRAL. At high values of pH (above 4) the carboxylic groups along the backbone of the macromolecule will dissociate to form anionic groups. As can be seen from Figure 2, the presence of these charged groups does not impede the formation of aggregates. This could be due to the fact that the long ethoxylated chain shields the charged $-COO^-$ groups.

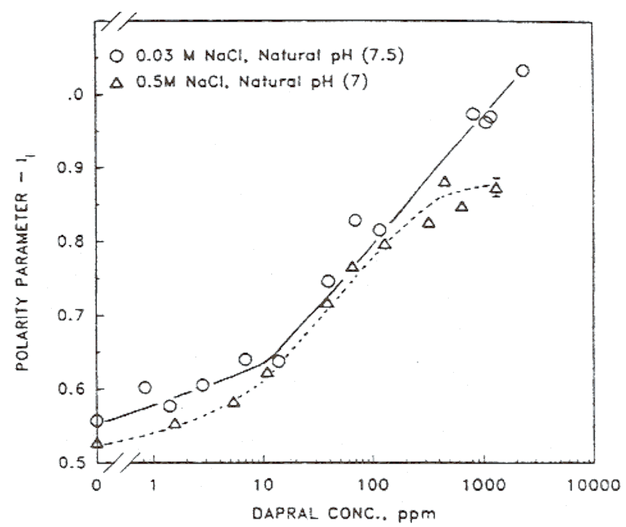

Figure 3. Aggregation behavior of DAPRAL in the presence of NaCl.

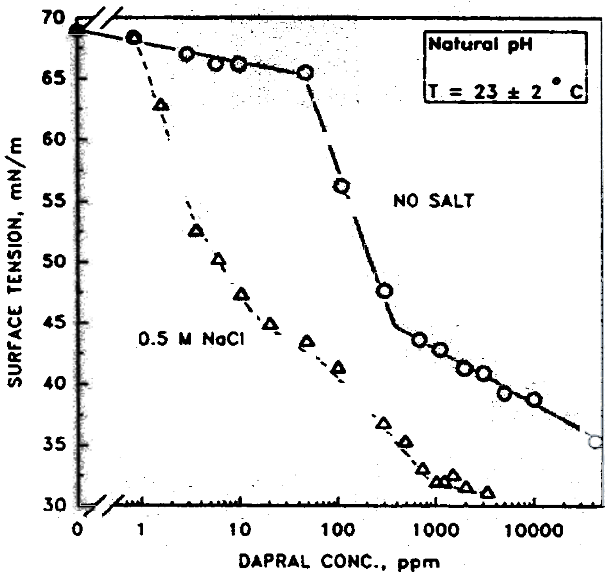

Figure 4. Surface tension of DAPRAL solutions.

Effect of sodium chloride on the aggregation behavior of DAPRAL was also studied and the results are shown in Figure 3. These experiments were conducted at natural pH. The presence of salt causes the polymer to aggregate at lower concentrations and the increase in the value of the polarity parameter commences at a polymer concentration around 2 ppm. It can also be seen that at a salt concentration of 0.5 M the maximum value of the polarity parameter is reached at a lower polymer concentration than that at 0.03 M NaCl, and also that the maximum value of the I_{III}/I_I ratio at 0.5 M NaCl is very much lower than that at 0.03 M NaCl. This indicates that the aggregates formed in the presence of 0.5 M NaCl are more hydrophilic than those formed at 0.03 M NaCl. This observation is very surprising and as of the present moment we have no satisfactory explanation for this. The concentrations studied in this experiment were those at which there was no visible precipitation of the polymer. It can be seen from Figures 2 and 3 that the behavior of DAPRAL in 0.03 M NaCl is similar to that in the absence of salt, whereas increasing the concentration to 0.5 M alters the behavior of the polymer at concentrations above 100 ppm of the polymer.

The effect of DAPRAL concentration on the surface tension is shown in Figure 4. The surface tension decreases with increasing polymer concentration and the presence of salt increases the surface activity of the polymer, particularly at low concentrations. DAPRAL is very effective in reducing the surface tension, and a 1 wt % (10000 ppm) solution can attain surface tensions as low as 30–38 mN/m depending upon the salt concentration. In the absence of salt, two transition points are observed, at about 50 and 500 ppm. Over the entire range of concentrations studied the surface tension continued to decrease. It is possible that, in the absence of the salt, the aggregates of polymer formed are polydisperse and many in number and aggregation and adsorption at the air–water interface take place simultaneously. The two transition points could correspond to changes in polymer configuration at the air–water interface. In the presence of 0.5 M NaCl, however, the surface tension shows a discontinuity at a concentration around 1000 ppm above which the surface tension remains relatively constant. The solutions above a concentration of 1000 ppm were cloudy,

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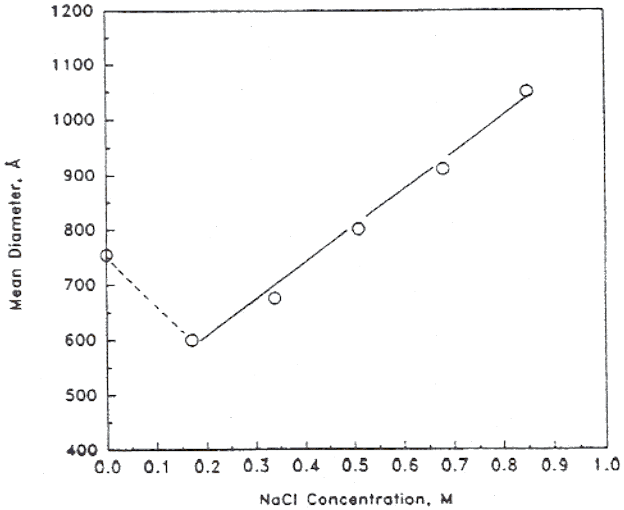

Figure 5. Light scattering of 1.0% DAPRAL solutions as a function of sodium chloride concentration.

but there was no visible precipitation. An electrolyte could promote the formation of polymer aggregates which are of uniform size and shape, and a concentration analogous to the critical micellization concentration of surfactants is proposed to be observed.

This hypothesis was tested by determining the size of the polymer aggregates in solution using fixed angle laser light scattering and the results are shown in Figure 5. In the absence of sodium chloride, the scattering intensity was very weak but addition of the salt resulted in strong scattering. Addition of sodium chloride initially causes a decrease in the size of the polymer aggregate but further increase in salt concentration results in growth of the DAPRAL aggregates. The size distribution of the aggregates was also determined and it was observed that at low salt concentrations the aggregates had a wide distribution but at higher salt concentrations the distribution was narrow.

Addition of sodium chloride would reduce electrostatic repulsion between the polymer backbone segments causing the polymer chains to contract and lead to the formation of aggregates smaller than those formed in the absence of any salt. Increase in the salt concentration would also result in a loss of hydration of the ethylene oxide groups. This would increase the driving force for the aggregation process resulting in larger polymer aggregates at high salt concentrations than those formed at low salt concentrations. Since the size distribution of the aggregates at high salt concentrations was narrower and the size larger than that formed at low salt concentrations, it does appear that the polymer aggregates combine among themselves as the salt concentration is increased.

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