Macromolecular Aggregation of Aqueous Polyacrylic Acid in the Presence of Surfactants Revealed by Resonance Rayleigh Scattering

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ABSTRACT: On the basis of the relationship between macromolecular aggregate and resonance Rayleigh scattering (RRS) intensity, RRS spectra were utilized to monitor macromolecular aggregating process in poly(acrylic acid) (PAA). No probe and labeling were incorporated; RRS can reveal the macromolecule extension or contraction under external stimuli such as the changes in pH and ionic strength, as well as the addition of surfactant. Results indicated that the addition of base, acid and NaCl altered macromolecular phase behavior of PAA in aqueous solution due to electrostatic effect. Besides, sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) interacted with PAA in solution to form polymer-surfactants complexes, inducing macromolecular chain aggregate. On the basis of the analysis of the results, two models were proposed in this work to explain the observed phenomena. RRS is a sensitive method to characterize the macromolecular aggregate.

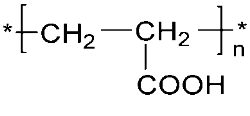
Introduction

Polymer−surfactant solutions have come under intense study because their self-assembling property leads to a wealth of fascinating behavior. Therefore, the mixtures of polymers and surfactants have received extensive attention throughout the last decades.[1–4] In particular, complexes between polycarboxylic acids (such as polyacrylic and polymethacrylic acids (PAA and PMAA)) and ionic surfactants in aqueous solution were widely investigated.[5–7] Furthermore, PAA and PMAA can be used as models for natural macromolecules, such as humic and fulvic acids (naturally occurring macromolecules, like humic substances, often strongly bind most metal cations).[8] The addition of a surfactant is expected to lead to instant aggregation in solution of polyelectrolytes such as PAA and PMAA for electrostatic and hydrophobic interactions.[9–11] Schematic representation of the chemical structure of PAA molecules is shown in Scheme 1. Some studies on polymer-surfactant systems dealt with the adsorption of surfactants on polycarboxylic acids in aqueous solution using viscosity and surface tension measurements.[5,6,11,12] Other works on polycarboxylic acids/surfactants interactions have been carried on through fluorescence probe techniques aiming to investigate the micellar formation and stability[10,13,14] and light scattering focusing on studing the mechanism of interaction of polycarboxylic acids/surfactants[7] in dilute solution.

The fluorescence method is widely applied to investigate polymer micromorphology in solution with probe and labeling, although this method can obtain lots of useful information of polymer micromorphology and microstructure, the labeling procedure is often tedious. In addition, in most of the fluorimetric studies of polymer, the fluorescent probe (for example, pyrene) was covalently attached to one of the polymers, which in fact changed the microenvironment of macromolecules and made the macromolecules more hydrophobic, thus enhancing their complexation ability. The conventional light scattering technique should lie on the expensive equipment and complicated process. Besides, it is limited in studying within the absorption wavelength region. In recent years, resonance Rayleigh scattering (RRS) has received much attention to determination of biological macromolecules,[16–18] trace amounts of inorganic ions[19] and complex formation[20–22] in analytical field for its simplicity, rapidity and sensitivity. In particular, RRS maintains some advantages of conventional light scattering and fluorescent spectroscopy, while overcomes the disadvantage of them mentioned above. RRS is a special elastic scattering which might emerge when the wavelength of Rayleigh scattering is located at or close to the molecular absorption band. In this case, the frequency of the electromagnetic wave absorbed by the electron is close to its scattering frequency which leads to intensively absorption and rescattering.[23,24]

In general, this method which has received extensive attention in analytical field could be implemented by means of the fluorescence experiment, i.e., fluorescence synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e., $\Delta\lambda = 0$ nm).[23–26] Typically, to carry on study utilized RRS, one of the partners is labeled with a suitable chromophore.[25,27] Because the labeling procedure is often tedious, RRS has not become very popular for the study of common polymers. Recently, Dai et al. had studied various well-known surfactant systems displaying significantly enhanced RRS signals to detect anionic biopolymer based on their bindings with cationic surfactant.[22] This indicated that the probing and labeling are not necessary to study molecular aggregation or complex of polymer solution by RRS, consequently, this will further extend the application range of RRS method, especially for most polymers which do not possess the chromophores. RRS

Scheme 1. Schematic Representation of the Chemical Structure of PAA Molecules



$*\!-\![CH_2-CH_2(COOH)]_n\!-\!*$

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can characterize the aggregation in polymer solution by one parameter: the I_{RRS} (RRS intensity), which can be considered as an index of the degree of PAA aggregates. If PAA is in different surroundings, the RRS intensity will promptly indicate the information of the change of macromolecular phase behavior.

In order to investigate further the macromolecular aggregate of PAA solution without chromophore as the probe, the present work extends the RRS technique to approach polymer solution and macromolecular complexes and reports on the aggregate of the macromolecular chains, such as the aggregation process in response to the application of external stimuli (changes in pH, ionic strength, addition of surfactants, etc.). The results were compared with those obtained from the literatures.[10,14,28] On the basis of the experimental results, we have proposed two models to explain the macromolecular aggregation process in the process of polymer association with surfactants.

Theoretical Background

When the incident light passes through a solution containing aggregates, the intensity of light scattering can enhance because of the absorbing and rescattering, and this scattering (RRS) intensity can usually be characterized by turbidity.[29] The turbidity of an absorbing system (τ_c) was given by Miller based on the fluctuation theory of Einstein and absorbing theory of Mie according to the relation[29]

$$\tau_c = \frac{32\pi^3 n^2}{3\lambda_0^{\,4} N_A}\left[\left(\frac{\delta n}{\delta M}\right)^2 + \left(\frac{\delta k}{\delta M}\right)^2\right]1000M \tag{1}$$

where λ_0 is the wavelength of the incident radiation in vacuum, N_A is the Avogadro number, n is the refractive index of solvent, k is the absorption coefficient, and M is the molarity of the absorbing solute. If the solute forms aggregates or clusters in solution, then the turbidity given by eq 1 must be multiplied (the molarity remains based on the molecular weight of the monomer).

The relation of the RRS intensity and solution were further declared by Pasternack et al. in detail as follows. The scattering cross section of the system, C_{sca}, the ratio of the rate of energy scattering out of the incident beam (in all directions) to the intensity of the incident beam, can be expressed as[23]

$$C_{sca} = \frac{(2\pi/\lambda_m)^4}{6\pi}|a|^2 = \frac{(2\pi)^4}{6\pi\lambda_m}(a_r^{\,2} + a_i^{\,2}) \tag{2}$$

The absorption cross section of the system, C_{abs}, the ratio of the rate of energy absorption from the incident beam to the intensity of the incident beam, depends on α_i only[23]

$$C_{abs} = \frac{2\pi}{\lambda_m}a_i \tag{3}$$

where α_r and α_i are the real and imaginary parts of the polarizability of the aggregates and λ_m is the wavelength of incident light in the solvent.

In addition, the absorbance A of a sample of thickness L is[23]

$$A = 2.3^{-1}(N/V)C_{abs}L \tag{4}$$

where N/V is the number of aggregates per unit volume. From eq 3, the absorption is proportional to the volume of the aggregate.[30] Thus, a solution with a fixed concentration of the aggregating component will exhibit little change in A, even as slight aggregation occurs if N/V and α_i stay constant. However, the intensity of scattering depends on the square of the volume of the aggregate, and thus it greatly increases as a result of aggregation.[23] Therefore, it indicates that resonance Rayleigh scattering is, extremely sensitive to the aggregation of macromolecular chain even at very low concentrations in solution.

In this study, we will further propose a simple formula to express the relationship between two extremes: the scattering intensity of RRS and the radius of hydromechanics of macromolecules (R_H). Provided in a fixed concentration of polymer solution, the diffusion theory is valid for polymer chains, then, according to the Stokes−Einstein equation[23]

$$R_H = \frac{k_B T}{6\pi\eta D} \tag{5}$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium, and D is the diffusion coefficient. The relaxation time is[23]

$$\tau = (2Dq^2)^{-1} \tag{6}$$

where $q = 4\pi[\sin(\theta/2)]/\lambda_m$ and θ is the scattering angle.

In addition, for the scattering by particles or impurities, the relaxation time τ is related to the scattering cross section as[31]

$$\tau = \frac{1}{cvC_{sca}} \tag{7}$$

where c denotes the concentration and v is the velocity. Therefore, $C_{sca} = 2Dq^2/cv$.

In order to easily deal with these different scatterings, the intensity of rescattering is converted to the intensity of common scattering. The turbidity of a polymer solution (τ_c) can be proposed as follows:[32]

$$\begin{aligned}\tau_c &= N'C \\ &= N'\sqrt{1 + k^2(r)}C_{sca} \\ &= N'\sqrt{1 + k^2(r)}(2q^2)D/cv \\ &= \frac{N'\sqrt{1 + k^2(r)}(2q^2)k_B T}{6\pi c\eta v R_H} \\ &= \frac{K\sqrt{1 + k^2(r)}}{R_H}\end{aligned} \tag{8}$$

Here C denotes the scattering cross section and rescattering cross section because of the absorption, $K = N'(2q^2)k_B T/6\pi c\eta v$, and $k(r)$ is the ratio of rescattering cross section to the scattering cross section.[23,29,30]

It can be found that R_H can indicate the macromolecular chain extension when the intensity of RRS decreases and it is noted that R_H shows the macromolecular chain contraction as the intensity increases. Therefore, RRS can be used to monitor the change of geometric sizes of macromolecules chains from the RRS intensity variances as the macromolecules extend or contract.

Experimental Section

Materials and Samples Preparation. Polyacrylic acid with viscosity-average molecular weight (M_W) of 240 000 was purchased from Acros Organic Co., Ltd., which was an aqueous solution of 25% (wt). All other chemical reagents including sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), sodium chloride, hydrochloric acid and sodium hydroxide were obtained from Tianjin City Damao Chemical Reagent Co., Ltd. (China). Reagent-grade chemicals were used in all experiments.

Aqueous stock solution of polymers (4.0 g/L) was prepared in a standardized way[33] in water at room temperature and by magnetic stirring for 24 h. Then, the standard solutions of polymer were obtained in series by dissolving definite quantity of stock solution in 50 mL volumetric flask filled with doubly distilled water. The

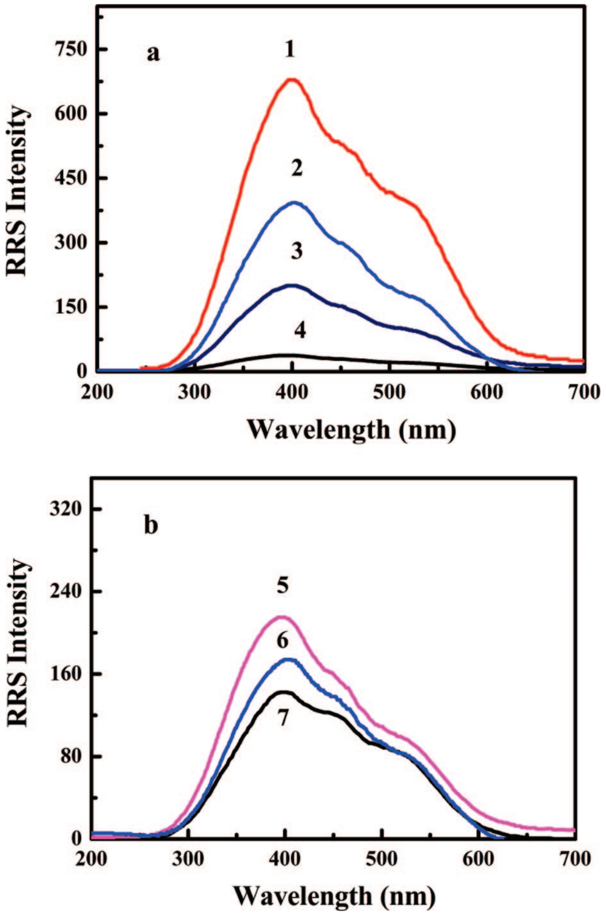

Figure 1. RRS spectra of aqueous polymer solutions: (a) (1) pH = 4.5, 0.1 mol/L NaCl, 6.0 × 10^{-3} mol/L SDS; (2) pH = 3.0, 6.0 × 10^{-3} mol/L SDS; (3) pH = 4.5, 0.1 mol/L NaCl; (4) pH = 4.5; (b) (5) pH = 3.0; (6) pH = 4.5, 6.0 × 10^{-3} mol/L SDS; (7) pH = 4.5, 6.0 × 10^{-3} mol/L CTAB. Curves 1−6 are the spectra of 0.4 g/L PAA solution; curve 7 is the spectrum of 0.05 g/L aqueous PAA (extremely dilute) solution.

pH value was adjusted with minute amounts of aqueous HCl (0.1 mol/L) or NaOH (0.1 mol/L) solutions. The polymer concentration was kept constant at 0.4 g/L in all the measurements except for PAA/CTAB system, which was kept constant at 0.05 g/L.

The stock solution of SDS (or CTAB) was obtained by dissolving the solid powder of SDS (or CTAB) in doubly distilled water at a concentration of 1.0 × 10^{-3} mol/L. The polymer−surfactant complexes were prepared by mixing the stock solutions of polymers and SDS or CTAB in some desired ratios to obtain its dilute or extremely dilute solution. The mixtures were stirred for enough time to ensure the homogeneity of the solution. All aqueous solutions were prepared with doubly distilled, deionized water.

Apparatus. The RRS measurement was performed at room temperature on a RF-5000 Spectrofluorophotometer (Shimadzu Corporation, Japan) equipped with a 150 W xenon lamp, a recorder and dual monochromators. The slit (ex/em) width was 3.0 nm/1.5 nm. The sensitivities of the equipment under all detecting conditions were high except investigating PAA/CTAB system, which was low. The excitation and emission spectra were recorded in range of 200−700 nm with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e., $\Delta\lambda = 0$ nm) according to the literatures.[24,34]

A UV-3150 spectrophotometer (Shimadzu Corporation, Japan) was used to record the absorption spectrum. pH-values were measured by using a PHS-2C digital pH meter (Shanghai Weiye Instruments Plant, China).

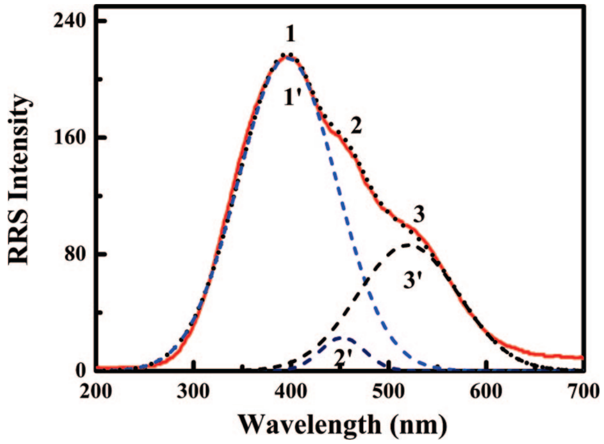

Figure 2. RRS spectra of 0.4 g/L aqueous solution of PAA (solid line), the fitting curve (dotted line), and the single peak curve (dash line).

Results and Discussion

RRS and Absorption Spectra of PAA in Aqueous Solution. The RRS intensity can promptly indicate the information of the aggregate of PAA, because RRS is extremely sensitive and selective in probing the aggregation of the molecular chains. RRS spectra of PAA are shown in Figure 1a,b in aqueous solution at various pH values, ionic strengths and in the presence of SDS or CTAB. The spectral characteristics of all solution systems are similar. Their maximum scattering wavelengths, λ_{max}, are at 401 nm, and two smaller scattering peaks appear at 471 and 536 nm, respectively. The I_{RRS} undergoes significant changes, as illustrated in Figure 1a,b in the case of PAA solutions at low and neutral pH in the absence and presence of salt. The increase of I_{RRS} indicates that both surfactants interact strongly with PAA. In order to eliminate the interference of adjacent peaks and obtain the accurate value of RRS intensity, the decomposition treatment of these peaks is necessary and accomplished by fitting with Ganssian distribution reported in the literature.[35] Results from RRS measurements for the most part will be presented as the scattering intensity ratio, which corresponds to the ratio of areas of the different bands. These three fitted peaks of RRS spectrum are shown in Figure 2 in detail for the sample PAA aqueous solution. Considering the sensitivity of detection, the maximum scattering wavelength was selected for further work.

The absorption spectra of PAA and its mixture systems are presented in Figure 3. It can be seen from Figure 3 (curve 1) that PAA has absorption band at below 240 nm, whereas the absorbance approaches zero in the range over 240 nm. After adding the surfactants, the new absorption peaks appeared (curve 2 and 3), this indicated that complexes of polymer/surfactants may form. By comparing Figure 2 and Figure 3, we can see that the maximum light scattering intensity of the studied system appeared at about 401 nm, which located at the red side of the absorption band of polymer solution. In general, the light scattering experiments typically involved measurements away from absorption bands, whereas the wavelengths within the absorption band envelope can be extremely informative if the solute absorption is not too great and the aggregate is of sufficient size. The main reason is that the instrumental conditions are of importance to decide the spectral characteristics.[36]

RRS of PAA at Various pH and Salt Concentrations. Figure 4 presents the RRS intensities of PAA dilute aqueous solution as a function of pH values. The polymer concentration was fixed at 0.4 g/L. A sharp drop in the I_{RRS} is observed in the pH range from 3.6 to 4.5 as pH value of the solution

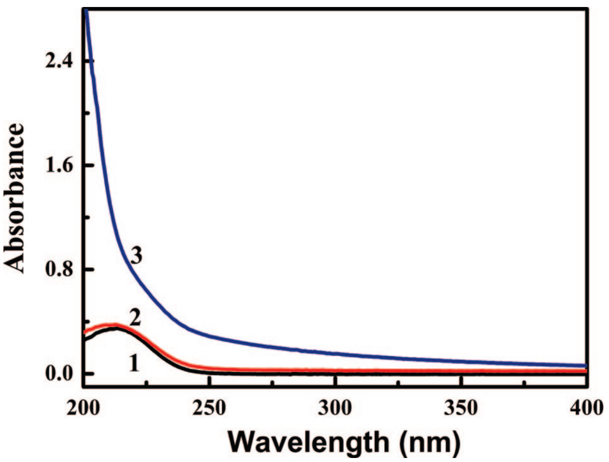

Figure 3. Absorption spectra of PAA and its mixture: (1) PAA; (2) PAA-SDS; (3) PAA-CTAB (the same concentration of PAA: 0.4 g/L, SDS: 4.0×10^{-3} mol/L, CTAB: 2.0×10^{-4} mol/L).

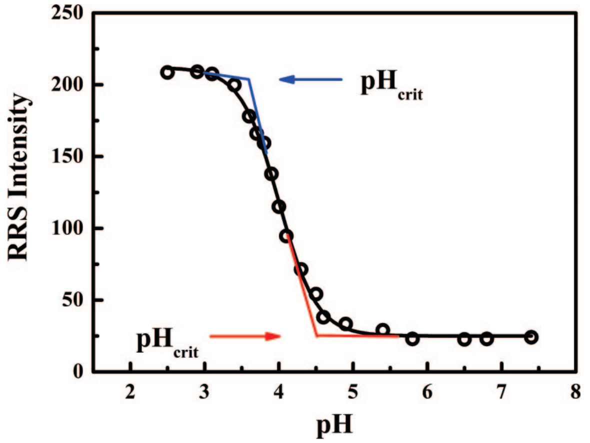

Figure 4. RRS intensity of 0.4 g/L PAA aqueous solutions as a function of pH value (pH_{crit} values shown by arrows).

increases. According to the sigmoidal Boltzmann-like equation of the formula in the literature,[37] we can deduce the dependence of the I_{RRS} on the pH values:

$$I_{RRS}(\lambda_{max}) = I_0 + \frac{I_1 - I_0}{1 + e^{(pH - pK_a)/dpH}} \quad (2 < pH < 7.5) \tag{9}$$

where I_0 is the lowest scattering intensity and I_1 is the highest scattering intensity (shown in Figure 4), I_0 and I_1 can be considered as constants. This curve shows a clear inflection from which the pK_a could be estimated to be 4.0.[37] The I_{RRS} does not change significantly below pH 3.6 and above pH 4.5. According to the literature,[15] both pH 3.6 and pH 4.5 values are equal to pH_{crit}. The pH_{crit} value was defined as the crossing point of two lines that come through the experimental points before and after a significant decrease (bend) in RRS (shown by arrows). According to eq 8, the RRS measurements could indicate that the decrease (or increase) in I_{RRS} with increasing of pH values reflects macromolecular chain expansion (or contraction) in polymer conformation. At pH 3.0, the PAA is practically uncharged with a dissociation degree $\alpha = 0$, whereas at pH 7.0, 55% of the carboxylic acid groups are deprotonated, and the PAA is a strong polyelectrolyte (for unmodified PAA, $\alpha = 0.26$ at pH 4.5 and $\alpha = 0.9$ at pH 7.0 calculated according to the Henderson–Hasselbalch equation).[10,38,39] The macromolecular chains adopt a coil conformation at low pH and undergo an even ionization-induced chain expansion by increasing pH.[14,37] The structure of PAA molecules in electrolyte solutions reported by Adamczyk[40] conformed to the present results of RRS.

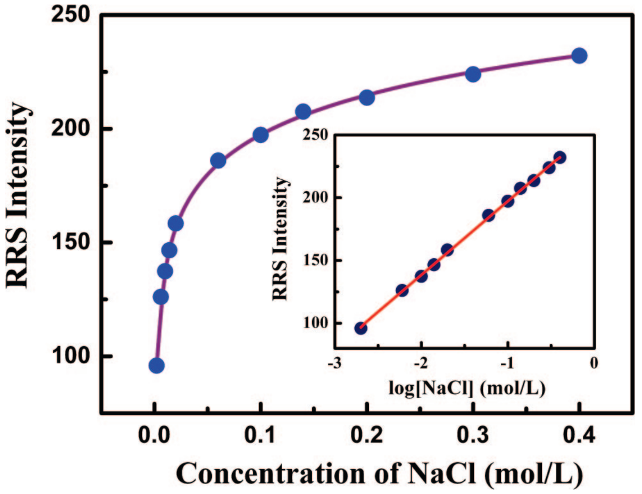

Figure 5. RRS intensity of 0.4 g/L PAA aqueous solutions as a function of NaCl concentration.

The effect of salt on PAA aqueous solutions at pH 4.5 was investigated by RRS. RRS measurements were carried out on the polymer solutions of concentration 0.4 g/L and sodium chloride concentrations ranging from 2 mmol/L to 0.4 mol/L. The I_{RRS} as a function of the salt concentration in the PAA aqueous solutions is depicted in Figure 5. As the salt concentration increases in the polymer solution, the I_{RRS} increases more than 2 times when NaCl concentration changes from 2 mmol/L to 0.4 mol/L, and the relationship between I_{RRS} and NaCl concentration can be deduced as the following:

$$I_{RRS} = a + b \log[\mathrm{NaCl}] \tag{10}$$

where a and b are the coefficients. The linear relation of I_{RRS} on log[NaCl] is shown in the inset of Figure 5. The linear part of the full graph in the inset graph corresponds the total concentration range of NaCl. The increase of I_{RRS} can reflect the contraction of the polymer chains according to eq 8. In this system, the possible reasons of the polymer chains contraction include: (1) the lowering of the entropy of the counterion distribution; (2) the screening of the electrostatic repulsion between the ionic groups by the simple salt.[10] Hence, the absorption becomes stronger and the I_{RRS} increases according to eqs 3 and 4.

RRS of PAA Dilute Aqueous Solution in the Presence of Anionic Surfactant SDS and Salt. The RRS intensity of PAA undergoes significant changes, as illustrated in Figure 6 (curves b, c, and d) in the case of PAA aqueous solutions in the presence of SDS at pH 3.0 free salt, pH 4.5 and pH 3.0 in 0.1 mol/L NaCl. Both SDS and NaCl have the similar effect on I_{RRS}; i.e., the I_{RRS} values can be remarkably enhanced by adding SDS into PAA aqueous solutions. This results can be explained by Sigmoidal shape theory of Goddard[41,42] and whose concept formalized by Jones in 1967,[43] in a system of fixed polymer concentration with increasing amounts of surfactant of two critical concentrations, namely, T_1 and T_2, of the surfactant. T_1 represents the concentration at which association between the surfactant and the polymer first occurs, which is onset of increase of I_{RRS} (critical aggregation concentration, CAC); and T_2, the concentration at which the polymer becomes saturated with surfactant, which is onset of plateau of I_{RRS}.

Addition of small amounts of SDS to PAA aqueous solutions at pH 3.0 (curve b) does not suddenly change the I_{RRS}. When [SDS] exceeds 2.0×10^{-3} mol/L, the I_{RRS} commences to increase. It can be considered as the signal for the onset of

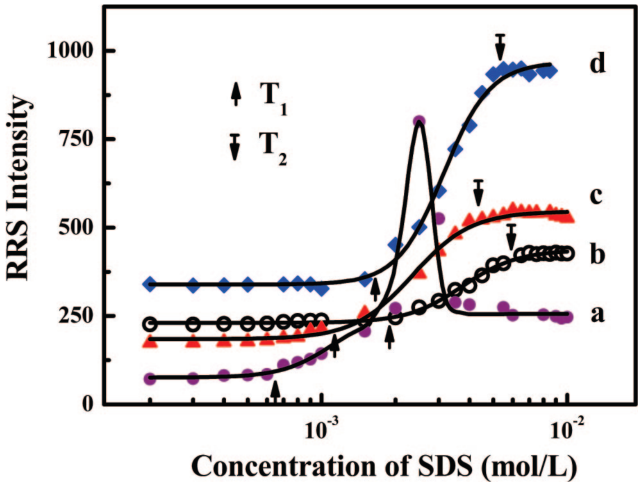

Figure 6. RRS intensity of 0.4 g/L PAA dilute aqueous solutions as a function of SDS concentration: (a) at pH 4.5; (b) at pH 3.0; (c) at pH 4.5 in the presence of 0.1 mol/L NaCl; (d) at pH 3.0 in the presence of 0.1 mol/L NaCl.

polymer/surfactant association, and then we assign this surfactant concentration as the CAC of the system similar to others.[21] The same amount of surfactants at the concentrations near their CAC could significantly increase the viscosity of the polymer-surfactant systems.[44–46] With more surfactant amount, the I_{RRS} increase steeply. By further adding surfactant, the I_{RRS} approaches a higher constant value, for [SDS] it equals 7.0 × 10^{-3} mol/L. This can be explained by the following reasons: (1) SDS molecules can form complexes with the hydrophobic zones of the CAC chains by virtue of hydrophobic interactions. (2) The different CAC chains bound together via hydrophobic interactions involving SDS molecules, upon SDS binding, the hydrophobic volume of polymer chains is expected to increase further due to the polyelectrolyte behavior.

However, in the presence of SDS, the I_{RRS} of the PAA solution in 0.1 mol/L NaCl at pH 3.0 (curve d) is higher than that without NaCl. The high I_{RRS} values in the presence of NaCl are typical for PAA as was discussed above for Figure 5 according to eqs (3, 4). The steep slope above T_1 suggests that NaCl induces a high cooperativity of surfactant association with the PAA. Another effect can be found is that NaCl reduces the T_1 as one factor comparing to the salt-free system at pH 3.0, and the recorded value of SDS concentration is 1.6 × 10^{-3} mol/L. To explain these results, it has to admit that the macromolecular chain will contract in the presence of salt for ionic interaction as above-mentioned. This would enhance the intensity of RRS in the same amounts of SDS.

The changes induced by SDS on the I_{RRS} of PAA in 0.1 mol/L NaCl at pH 4.5 are presented in Figure 6 (curve c). Qualitatively, the I_{RRS} of this solution is lower than that of PAA solution containing 0.1 mol/L NaCl at pH 3.0 in the presence of SDS at the same concentration. The T_1 values obtained from the plot of I_{RRS} is 1.0 × 10^{-3} mol/L SDS. The I_{RRS} at pH 3.0 is higher than that at pH 4.5 in the presence of NaCl, this is due to the more contraction chains adopted by PAA at lower pH values according to eq 8 as above-mentioned. With or without addition of the surfactant, much ionization reactions of PAA occurs resulting in electrostatic intrachain repulsion which leads to an extensional chain conformation.[37] Therefore the lower I_{RRS} at pH 4.5 also demonstrates that the electrostatic repulsive forces prevent the association of anionic surfactant with the polymer according to eqs 2–4.

However, the effect of SDS on PAA solution at pH 4.5 without NaCl (Figure 6, curve a) is distinct from above three systems. Addition of small amounts of SDS to PAA solution at pH 4.5 does not suddenly change the I_{RRS}. When [SDS] exceeds 6.0 × 10^{-4} mol/L, I_{RRS} starts to increase. The same amount of surfactants at the concentrations near their CAC could significantly increase the viscosity of the polymer-surfactant systems.[44–46] Adding much more surfactant, I_{RRS} approaches the highest value at [SDS] = 2.5 × 10^{-3} mol/L. By further addition of the surfactant, I_{RRS} decreases and approaches a constant value at [SDS] 3.5 × 10^{-3} mol/L. This phenomenon has not been reported by fluorescence spectroscopy method.[14,28,36] The T_1 value of the PAA solution at pH 4.5 is the lowest (Figure 6, curve a) meanwhile the RRS intensity datum indicates that the polymer chains are in the expanded state under the conditions. To account for this, it can be suggested that there are repelling forces for electrostatic charges[11] between different macromolecular chains to form larger size aggregates which can sharply enhance the absorption of macromolecular chains according to eqs 3 and 4. Whereas the macromolecular chains will be apt to form homogeneous aggregates under the interaction of micelles with SDS precluded by electrostatic screening for a significant level of negative and positive charges (H^+, Na^+, Cl^-) in other systems. The uprush peak of I_{RRS} with SDS increasing at pH 4.5 is disappeared at pH 3.0, this is due to that there is a significant level of negative and positive charges (H^+, Cl^-) in PAA aqueous solution at pH 3.0, and the strong interaction between PAA and SDS is precluded by electrostatic screening. The macromolecular chains will be apt to form homogeneous aggregates under interaction of micelles with SDS. In addition, the uprush peak of I_{RRS} with SDS increasing is also disappearing at pH 4.5 in the presence of NaCl. The PAA aqueous solution has a significant level of negative and positive charges (Na^+, Cl^-), and the interactions between PAA and SDS are precluded by electrostatic screening; this can be explained by the same reason as mentioned above.

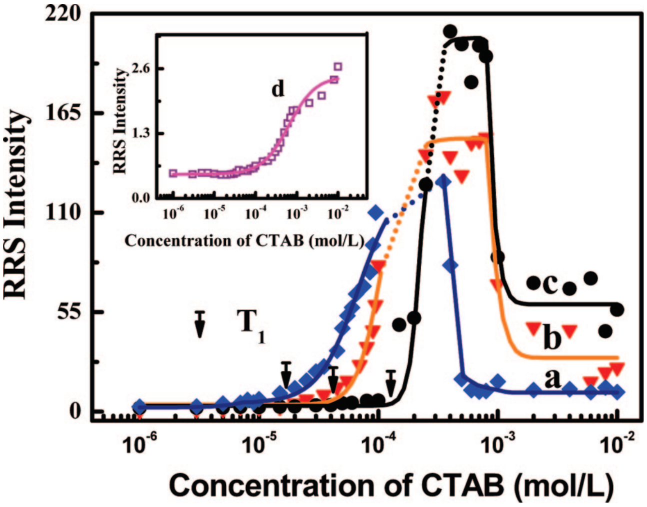

Figure 7. RRS intensity of 0.05 g/L PAA extremely dilute aqueous solutions as a function of CTAB concentration: (a) at pH 4.5 in the presence of 0.1 mol/L NaCl (dotted line denotes phase separation region); (b) at pH 7.0; (c) at pH 4.5; (d) at pH 3.0.

RRS of PAA Extremely Dilute Solution at Different pH Values in the Presence of Cationic Surfactant CTAB and Salt. In Figure 7, the I_{RRS} obtained from the RRS spectra of the PAA−surfactant systems at different pH values is presented as a function of cationic surfactant concentration. The PAA concentration was fixed at a constant of 0.05 g/L. For this extremely dilute PAA−cationic surfactant systems, since PAA−PAA interaction is weak and the interaction between cationic surfactant and PAA is strong, small amounts of CTAB cationic surfactants have no effect on the I_{RRS} until the surfactant concentration exceeds a certain value (T_1), after which I_{RRS}

increases to still a second, higher plateau. Approaching the higher plateau, the PAA−cationic surfactant mixtures pass through a narrow two-phase region, where the solutions become turbid (the phase separation region in solutions was indicated by dotted line in Figure 7). In the higher surfactant concentration range, the polymer−surfactant systems resolubilize, I_{RRS} sharply decreases with increasing surfactant concentration. The slightly change of I_{RRS} indicates that the very low concentration of surfactant less than T_1 in the polymer solutions leads to aggregation slightly.[47] However, with the addition of more surfactant, I_{RRS} increases sharply before it approach as a plateau, which implies that the size of aggregates grows up. It can extract the breakup concentrations of the CTAB as 2.3×10^{-5} mol/L (at pH 3.0), 1.6×10^{-5} mol/L (at pH 4.5), and 9.8×10^{-5} mol/L (at pH 7.0), respectively. The T_1 for PAA/CTAB system determined by the RRS intensity was found to increase with pH, similar results have been found in the literature.[48] The main reason can be deduced from that mentioned above as follows: At low pH values, the interaction was only hydrophobically driven, whereas at high pH values, a majority of the carboxylic acid groups are in their COO^- form and the polymer is negatively charged[38] so that the surfactants could bind to polymer by Coulombic forces.[14]

Approaching the higher plateau, the PAA−surfactant mixtures pass through a narrow two-phase region, and the similar phenomenon had been demonstrated by Guillemet and his colleague.[49] It is noted that the phase separation region of the polymer−surfactant systems at high pH has a broader concentration range compared with that reported by Schillén and his co-worker at low pH value.[10] This indicates that a lot of the carboxylic acid groups are associated with CTAB, therefore, an associative phase separation occurs because of the charge neutralization,[10] and the solution will contain the large multichain polymer/surfactant complexes. The turbidimetric titrations can show the same existence of multichain polymer/surfactant complexes in a Py-labeled poly(acrylamido-2-methylpropanesulfonate)/mixed cationic micellar system.[50] In the further high surfactant concentration range, I_{RRS} starts to steeply decline at [CTAB] 8.0×10^{-4} mol/L (both at pH 4.5 and pH 7.0 salt-free shown in Figure 7, curves b and c), this indicates that the polymer-surfactant systems resolubilize as above-mentioned. At this onset of steep decline, the molar ratio of [CTAB]:$[L^-]$ = 1.16:1. On the basis of these results, we can deduce that the ionic region of PAA chains is over saturated with micelles, this causes the physical network of polymer molecules to collapse initially as a result of the repulsion of same charges of micelles.[51]

On the basis of the RRS measurements on PAA/surfactant solutions at different pH values, the results can be generalized that, at low pH and low surfactant concentration, the polymer-surfactant association is driven by the hydrophobic interaction which is the same to PAA/SDS systems, whereas at high pH the association is predominantly electrostatic interaction. This similar result was also demonstrated by Schillén et al.[10]

It has qualitatively the same effect on RRS as described for salt-free solutions with addition of CTAB to a PAA solution in the presence of 0.1 mol/L NaCl and at pH 4.5. However, the I_{RRS} of this salt solution is higher than that in the absence of electrolyte with the same concentration of CTAB before the concentration of phase separation. The enhancing effect of NaCl on the RRS intensity is typical for PAA same to that the addition of salt produces a strong viscosity increase and may even induce gel formation.[52] At the same time, the slope above T_1 is very steep and the T_1 decreases at pH 4.5 compared with the salt-free system at pH 4.5. The recorded value corresponds to a CTAB concentration of 8.9×10^{-6} mol/L (shown in Figure 7, curve a). This implies a change from an open to a compact conformation of the polymer chain as the repulsion between the carboxylate groups is screened with a subsequent created in the collapsed coils.[53] Similar observations had also been carried out for PAA/CTAB system with probe.[10,38]

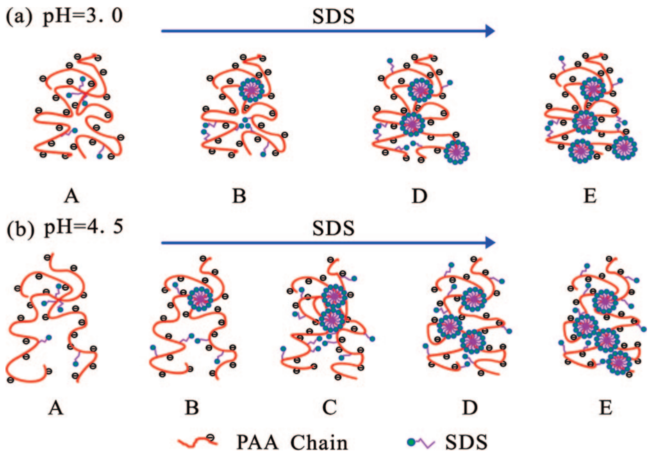

Figure 8. Schematic representation of the association process between PAA and anionic surfactant SDS at pH 3.0 (a) and pH 4.5 (b): (A) PAA solution in the presence of a low amount of surfactant, [SDS] < CAC; (B) [SDS] ≥ CAC, mixed micelles are formed initially and grow; (C) the large scale formation of aggregates; (D) the mass formation of mixed micelles; (E) the hydrophobic regions saturated completely with micelles.

Association Process of Polymer and Surfactants. The association of polymer/surfactant mixtures can be summarized by several models reported earlier for modified polyacrylic acids/surfactants systems.[14,48,54] The RRS technique can observe the association process between polymer and surfactants in the presence of NaCl at different pH values, because almost all the I_{RRS} curves of polymer/surfactants systems are of sigmoidal shape as reported in other measurements.[41] From eqs 5–8, we can find that the radius of hydromechanics of macromolecules (R_{H}) indicate that the macromolecular chain extension occurs when the intensity of RRS decreases, and the macromolecular chain contraction takes place as the intensity increases. Therefore, RRS can monitor the changing process of geometric size of macromolecules chains by RRS intensity variances as the macromolecules extend or contract.

In the view of these results and previous models, we proposed two models to explain the aggregation of PAA in the process of polymer association with adding surfactant as the following.

Figure 8a,b shows the schematic representation of the association process between PAA and SDS at low and high pH in the absence of salt. There are five regions marked as regions A, B, C, D, and E, respectively. At low amount of SDS concentration (region A), [SDS] < CAC, the hydrophobic interaction between the hydrophobic regions on the PAA chains occurs with barely any influence of the surfactant. In region B, more surfactant is added, [SDS] ≥ CAC, the mixed micelles are formed initially between SDS and the hydrophobic regions of the PAA chains, and the PAA molecule chains are coiling for interaction with SDS. With uniformity in region C and further addition of the surfactant, more complexes are formed between SDS and the hydrophobic regions of PAA chains, resulting in the large scale formation of aggregates. The I_{RRS} sharply grows up mainly because of the great change in shape of complex. The higher surfactant concentrations (region D), leads to the mass formation of mixed micelles, which results in the highest value of I_{RRS}. Finally, at sufficiently high SDS concentrations (region E), the hydrophobic region of the PAA molecules is saturated completely with surfactant molecules. Consequently, the complex can not be formed and the I_{RRS} value

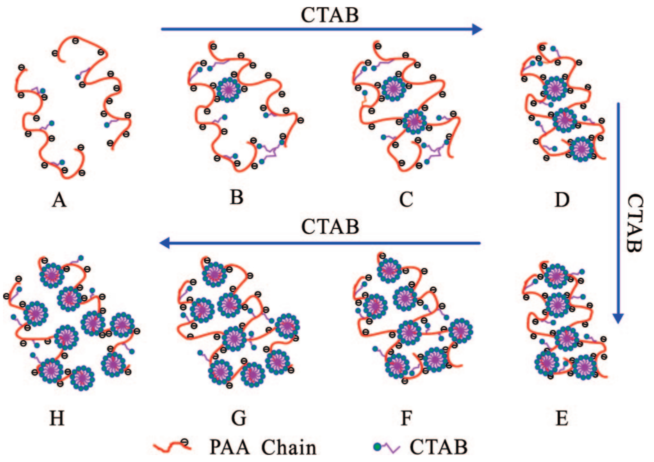

Figure 9. Schematic representation of the formation process of polymer-cationic surfactant complexes between PAA and CTAB: (A) PAA solution in the presence of a low amount of surfactant, [CTAB] < CAC; (B) [CTAB] = CAC, mixed micelles form initially; (C) mixed micelles are growing; (D) the mass formation of complex and phase separation; (E) the complex of phase separation dissolve initially; (F) the ion regions of the PAA molecules are over saturated with micelles and the physical network of polymer molecules collapses initially; (G) the physical network of polymer molecules collapses further; (H) the physical network of the PAA molecules collapses completely.

approaches a constant value.

Figure 9 is the schematic representation of the formation process of polymer/surfactant complexes between PAA and CTAB comparing with the I_{RRS} change illustrated in Figure 7. It can be divided into eight regions: A, B, C, D, E, F, G and H. At low amount of CTAB concentration (region A), [CTAB] < CAC, the CTAB has negligible effect on the performance of PAA chains. In region B, more surfactant is added, [CTAB] = CAC, the mixed micelles are formed initially between CTAB and the PAA chains. Because the positively charged endgroups of the surfactants can interact with the negatively charged groups of the polymer and the micelles formation is induced electrostatically by the charged polymer.[55] Therefore, the PAA molecular chains are distorted by absorbing of surfactants and the I_{RRS} of the polymer solution increases sharply. In region C, further addition of surfactant results in the mass formation of mixed micelles and induces the PAA molecular chains to distort further for the same reason as in region B. In region D, the addition of surfactant leads to the mass formation of complex and phase separation. The PAA molecule chains might collapse and grow into spherical aggregates, which result in phase separation region. Above the surfactant concentrations of phase separation (region E), the complexes of phase separation dissolve initially, but it results in the highest constant value of I_{RRS}. The reason is that the PAA molecule chains can not distort any longer but much more micelles can be formed. More above surfactant concentrations of phase separation (region F), the ionic regions of the PAA molecules are saturated with surfactant molecules and the physical network of polymer molecules collapses initially. The PAA molecular chains start to extend, which results in the decreasing of I_{RRS} value. At higher surfactant concentrations (region G), the ionic regions of the PAA molecules are over saturated with surfactant molecules and the physical network of polymer molecules collapses further. The PAA molecular chains will further extend and result in the steep decreasing of I_{RRS}. Finally, at much higher surfactant concentrations (region H), the ionic regions of the PAA molecules are over saturated completely with CTAB molecules and the physical network of the PAA molecules collapses completely, and the PAA molecular chains might extend freely. Consequently, the I_{RRS} reaches a lower constant value. The association process could be explained by the strong electrostatic interaction between polymer and surfactants due to the opposite charges.

Conclusion

In this work, RRS has successfully applied to investigate the conformational change and aggregation process of poly(acrylic acid) under external stimuli (including salt, SDS and CTAB) without probing and labeling. The RRS results revealed that PAA behaves from a compact, coil form to an expanded state during the process of neutralization and the contraction of the polymer coil by salt. RRS was used to study the aggregate of PAA induced by SDS because of the weak interaction between the anionic surfactant and PAA in dilute solution. RRS could monitor the aggregation process of the single PAA chain induced by CTAB without PAA−PAA interactions for the strong interaction between cationic surfactant and PAA in extremely dilute aqueous solution. Two models have been proposed to explain the macromolecular aggregation process of polymer with surfactants. RRS is a sensitive method to characterize the scale change of aggregate in polymer solutions and polymer/surfactant solutions.

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