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Associative Properties of Amphiphilic Statistical Polymers in Aqueous Media

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A novel series of comb-like amphiphilic statistical copolymers were synthesized by polymerization of an amphiphilic macromonomer, 2-(acrylamido)-dodecanesulfonic acid ($AMC_{12}S$), with 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS). The association behaviors of the polymers in NaCl aqueous solution were investigated by steady-state fluorescence measurements with pyrene as a polarity probe, quasielastic light scattering techniques (QELS), and a transmission electron micrograph (TEM). It was found that the series of polymers shows a strong tendency for interpolymer association, leading to the formation of multimolecular aggregates. The critical aggregation concentration (CAC) and the micropolarity of the polymer aggregates strongly depend on $AMC_{12}S$ mole fraction (X). An interesting feature of the polymers is that hydrodynamic sizes of the aggregates (R_h) continuously decrease with increasing X, and the increase extent of R_h with increasing polymer concentration (C) inclines to be smaller for higher X, suggesting that the polymer aggregates become a closed type progressively with increasing X.

Introduction

Amphiphilic polymers have been studied extensively over the past decades because of their relevance to biological macromolecular systems and the potential in industrial applications such as mineral separation, enhanced oil recovery, water treatment, detergency, cosmetics, and foodstuff.[1−6] Amphiphilic polymers can be divided into two categories: block and statistical polymers. The aggregation properties (critical micelle concentration, micellar and core sizes, the aggregation number, etc.) of block polymers in aqueous media have been a target of extensive studies recently.[7−10] However, the aggregation behaviors of statistical polymers are less clear because of the complexity of inter- or intramicellar electrostatic and hydrophobic interactions along the polymer chains.[11]

So far, it has been well-established by a number of research groups that some architectural factors, such as the types of hydrophobic and ionic monomers,[12−17] polymer composition,[15−21] the degree of polymerization of polymer chains,[22] and the spacer between hydrophobe and polymer backbone,[17,23−27] are important to determine the characteristics of molecular interaction of statistical polymers, namely, intra- or interpolymer association. Intrapolymer association leads to the formation of polymer aggregates made up with a single molecule independent of polymer concentration, yielding comparatively low viscosity of aqueous solution even at very high polymer concentrations. In contrast, interpolymer association results in a rapid increase in solution viscosity with increasing polymer concentration, even followed by the formation of gelation. In other words, the number of polymer molecules that can associate to form an aggregate is unlimited. A typical example of that is a class of polymers known as "associative thickeners", which can construct extensive hydrophobic "cross-links", leading to dramatic increase of solution viscosity. Actually, we have made a novel series of associative thickeners with the amphilphilic monomer as the uniform side chains in our lab,[28,29] which shows an excellent solution viscosity enhancing performance.

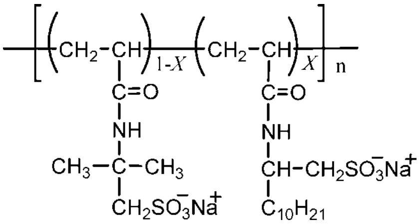

Figure 1. Chemical structure of the polymers studied. $X = 0.1$, 0.3, and 0.5.

Several studies have yet been reported investigating association properties and conformations of amphiphilic statistical polymers in salt solution; however, few of these ever concern polymers comprising high content of the amphiphilic monomer. In the present work, we synthesized for the first time the series of comb-like amphiphilic statistical copolymers (Figure 1) with the amphiphilic units of 2-(acrylamido)-dodecanesulfonic acid ($AMC_{12}S$) as the side chains and 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) as the ionic moieties, in which the mole fractions of $AMC_{12}S$ (X) range from 0.1 to 0.5. Our aim was to gain insight into the association properties of the polymers, exploring the effect of X on the association performance.

Experimental Section

Materials. Sodium chloride, ammonium persulfate, ammonium iron [II] sulfate hexahydrate, acrylonitrile, and sulfuric acid fuming were purchased from Beijing Chemical Co., analytical reagent grade. Dodecene was obtained from Fluka with the purity of above 99 %. Pyrene purchased from Aldrich was recrystallized from ethanol. Distilled water was used for all of the experiments.

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Monomers. $AMC_{12}S$ was synthesized by using dodecene, acrylonitrile, and sulfuric acid fuming in a manner analogous to the synthesis of 2-(acrylamido)-tetradecane sulfonate ($NaAMC_{14}S$) as reported elsewhere.[30] ^1H NMR (400 MHz, D_2O) δ: 0.83 to 0.87 (t, 3H), 1.25 to 1.30 (m, 16H), 1.53 to 1.58 (m, 1H), 1.72 to 1.77 (m, 1H), 3.09 (d, 2H), 4.31 to 4.34 (m, 1H), 5.73 to 5.76 (d, 1H), and 6.15 to 6.28 (m, 2H).

AMPS with a purity above 99.4 % was purchased from Shouguang City Yuyuan Chemistry Co., Ltd., and used without further purification.

Polymers. The copolymers were prepared by free radical polymerization of AMPS with $AMC_{12}S$ in aqueous media, taking advantage of the solubility in water of both monomers. A representative procedure for the polymerization is as follows: 0.025 mol of AMPS and $AMC_{12}S$ were dissolved in water in a 50 mL jar with the solid content of 25 %, and the mole fractions of $AMC_{12}S$ were 0.1 to 0.5. Nitrogen feeding was continued for 10 min at room temperature for deoxygenation, followed by the addition of 0.0007 mol of ammonium persulfate and 0.0003 mol of ammonium iron [II] sulfate hexahydrate to the solution to initiate the polymerization, causing the system temperature to increase to about 50 °C. After the system was cooled to the ambient temperature, the product was dissolved in dilute aqueous NaOH, and the pH was adjusted to 7. The aqueous solution was dialyzed against water for a week with a cellulose tube (Wise & Well Co., flat width: 34 mm, corresponding to a molecular weight cutoff of 3500), and the polymer was finally recovered by a freeze-drying technique. The compositions of the polymers were determined from the nitrogen to carbon ratios from elemental analysis, which shows that the copolymerization of AMPS and $AMC_{12}S$ is nearly an “ideal polymerization”, leading to polymer compositions equal to monomer feed compositions. We attempted to estimate the apparent molecular weights for all of the polymers in aqueous solution by gel permeation chromatography but failed to get credible results probably because the hydrophobic interactions are too intensive to let the polymers exist as single molecules.

Measurements. a. Preparation of Sample Solutions. Sample solutions for fluorescence, quasielastic light scattering techniques (QELS), and transmission electron micrograph (TEM) measurements were prepared as follows: Solid polymer samples were dissolved in pure water, and the solutions were heated to about 90 °C, followed by the addition of a predetermined amount of NaCl aqueous solution to adjust the ionic strength of the solutions to $0.05\ \text{mol}\cdot\text{L}^{-1}$. The solutions were continually stirred for another 15 min. The chain entanglement of the polymers in the process of freeze-drying could be eliminated in this way because it can no longer exist in the high temperature and the intense stir, and thus, the polymers could form unimolecular or multimolecular aggregates as their intrinsic nature.[31] All sample solutions were filtered with 0.45 μm membrane filters and stirred for 12 h at room temperature prior to measurements. The uncertainties on polymer concentrations (C) are estimated to be less than or equal to $\pm\ (5\cdot10^{-4})\ \text{g}\cdot\text{L}^{-1}$.

b. Steady-State Fluorescence Measurement. Steady-state fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorometer equipped with a thermostatted water-circulating bath at (25.0 ± 0.1) °C. Emission spectra of pyrene were measured with excitation at 335 nm, and excitation spectra were monitored at 372 nm. The slit widths for both the excitation and the emission sides were kept at 2.5 nm during measurements. A predetermined amount of $0.1\cdot10^{-3}\ \text{mol}\cdot\text{L}^{-1}$ pyrene ethanol solution was input to sample vials, and then ethanol was evaporated, followed by the addition of polymer salt solutions at various C. The concentration of pyrene in each sample solution was maintained to be $0.1\cdot10^{-6}\ \text{mol}\cdot\text{L}^{-1}$. The aqueous solutions were stirred overnight for equilibration prior to measurements.

c. Quasielastic Light Scattering (QELS). The apparent hydrodynamic radius (R_h) and the distribution of the relaxation times were obtained at various scattering angles (30° to 90°) at 25 °C with a spectrometer of standard design (ALV-5000/E/WIN multiple tau digital correlator) and a Spectra-Physics 2017 200 mW He−Ne laser (632.8 nm wavelength).

The intensity autocorrelation function $g^{(2)}(t)$ is related to the normalized electric field autocorrelation function $g^{(1)}(t)$, described as

$$g^{(2)}(t) = B[1 + \beta|g^{(1)}(t)|^2] \tag{1}$$

where β is a constant parameter for an optical system and B is a baseline term. The inverse Laplace transform (ILT) analysis is performed using the algorithm REPES[32] to obtain the relaxation time distribution $\tau A(\tau)$, according to

$$g^{(2)}(t) = \int \tau A(\tau) \exp(-t/\tau)\, \mathrm{d}(\ln \tau) \tag{2}$$

where τ is the relaxation time. Diffusion coefficients D are calculated from the ILT moments as

$$\mathrm{D} = (\Gamma/q^2)_{q\to 0} \tag{3}$$

where Γ is the relaxation rate and q represents the magnitude of scattering vector expressed as

$$q = (4\pi n/\lambda) \sin(\theta/2) \tag{4}$$

where θ is the scattering angle and n is the refractive index of the solvent. R_h values are calculated using the Stokes−Einstein equation

$$R_h = k_B T/(6\pi\eta D) \tag{5}$$

where k_B is Boltzmann’s constant, T is the absolute temperature, and η is the solvent viscosity.

d. Transmission Electron Micrograph (TEM). Electron micrographs were taken with a Hitachi H800 transmission electron microscope. A negative staining technique with uranyl acetate was used for TEM sample preparation. An aqueous polymer salt solution ($C = 1\ \text{g}\cdot\text{L}^{-1}$) was applied to a brass sample holder followed by air-drying. The cast film was stained by applying a drop of 1 % mass fraction uranyl acetate aqueous solution. The specimen thus prepared was observed at a direct magnification of $(1\text{ to }8)\cdot10^4$.

Results and Discussion

Molecular pyrene is often used as a fluorescence probe for the characterization of molecular aggregates of numerous surfactants and associating polymers.[33−36] It is well-known that the steady-state fluorescence spectra reflects the partition of pyrene molecules between aqueous bulk and polymer aggregates as well as the micropolarity of polymer aggregates.[35,36]

As is known, the 0−0 absorption maximum of pyrene shifts toward longer wavelengths when pyrene is solubilized in hydrophobic aggregates.[33,37] We can conclude from the excitation spectra (Figure 2) that the pyrene 0−0 absorption bands of all of the polymers stay at 336 nm when C values are relatively low and shift to 339 nm as C are increased, indicating that an increasing number of pyrene probes are solubilized in the hydrophobic aggregates with increasing C. Figure 3 shows I_{339}/I_{336} ratios of pyrene probes dissolved in salt solution in the presence of the polymers with different X at various C. The

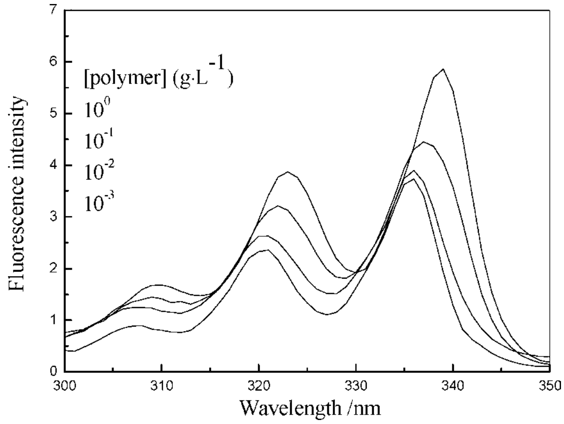

Figure 2. Steady-state fluorescence excitation spectra for pyrene at varying polymer concentrations with $X = 0.5$ in 0.05 mol·L^{-1} NaCl aqueous solution.

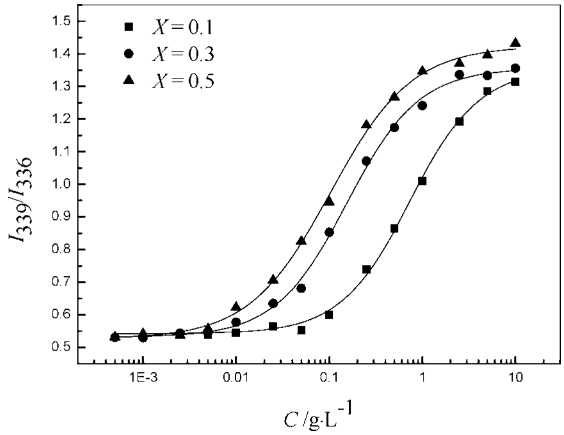

Figure 3. Relationship between I_{339}/I_{336} ratios and C for the polymers with $X = 0.1$ (■), 0.3 (●), and 0.5 (▲) in 0.05 mol·L^{-1} NaCl aqueous solution.

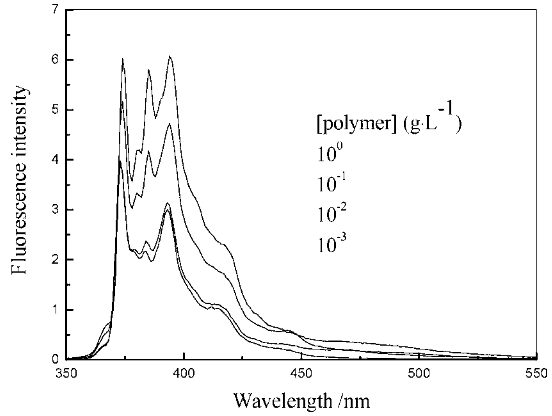

Figure 4. Steady-state fluorescence emission spectra for pyrene in 0.05 mol·L^{-1} NaCl aqueous solution in the presence of varying polymer concentrations with $X = 0.5$.

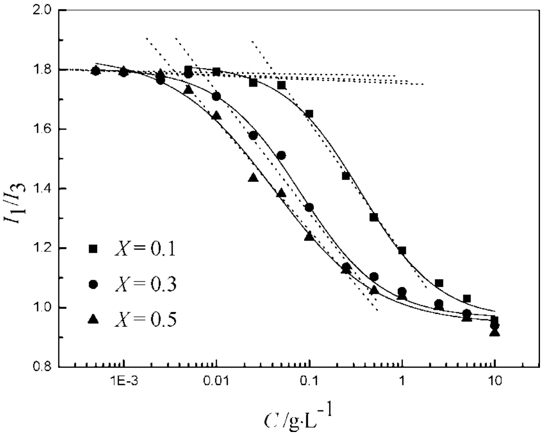

Figure 5. Plots of I_1/I_3 ratios as a function of C for the polymers with $X = 0.1$ (■), 0.3 (●), and 0.5 (▲) in 0.05 mol·L^{-1} NaCl aqueous solution.

Table 1. Values of Critical Aggregation Concentration (CAC), Diffusion Coefficient D, and Apparent Hydrodynamic Radius R_h of the Polymers with Different X at Various C

X	CAC g·L^{-1}	C g·L^{-1}	D	R_h nm
0.1	0.0467	0.2000	0.0712	34.3
		0.5000	0.0450	54.2
		1.0000	0.0353	69.1
0.3	0.0074	0.2000	0.0906	26.9
		0.5000	0.0720	33.9
		1.0000	0.0566	43.1
0.5	0.0039	0.2000	0.0916	26.6
		0.5000	0.0906	26.9
		1.0000	0.0712	34.3

ratios depend strongly on C and also on X, indicating that the pyrene probes are solubilized in the aggregates and the solubility of pyrene is increasing in proportion to the amount of polymer in the solution. Upon an increase of C, the I_{339}/I_{336} ratio for each polymer exhibits a significant increase, and the onset C of which is much lower for higher X.

The I_1/I_3 ratios of the emission spectra (Figure 4) are shown in Figure 5 for all of the polymers plotted against C, and these plots have the usual sigmoid shape. At the lowest C, the I_1/I_3 ratios are in the neighborhood of 1.8, which is practically the same as that for molecular pyrene in water. As C is increased, the I_1/I_3 ratios start to decrease significantly at certain C, indicating the solubilization of pyrene probes in hydrophobic aggregates. C for the onset of decrease of the I_1/I_3 ratios depends strongly on X, and the onset C is much lower for higher X. In the case of $X = 0.5$, the I_1/I_3 ratio begins to decrease at $C = (2.5 \text{ to } 5)\cdot 10^{-3}$ g·L^{-1}, and the onset C for $X = 0.3$ is nearly two times of that for $X = 0.5$. For the polymers with $X = 0.1$, the onset C is more than one order of magnitude higher than that for $X = 0.5$.

These results indicate that the micropolarity of polymer aggregates decreases along with the increase of X at any C, and the aggregate formation commences at specific C as in the case of small molecular weight surfactant micelles, and the onset

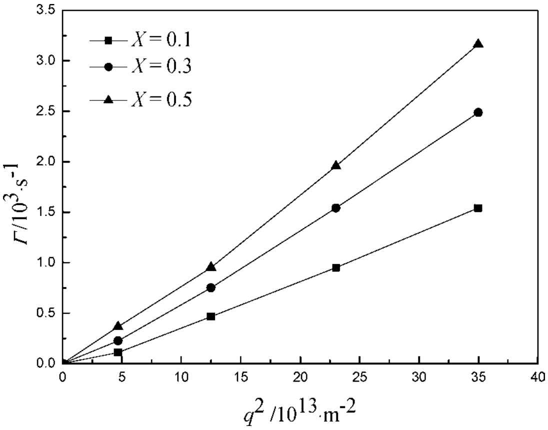

Figure 6. Plots of Γ as a function of q^2 for the polymers with $X = 0.1$ (■), 0.3 (●), and 0.5 (▲) at $C = 0.5$ g·L^{-1} in 0.05 mol·L^{-1} NaCl aqueous solution. QELS measured at $\theta = 30$, 50, 70, and 90°.

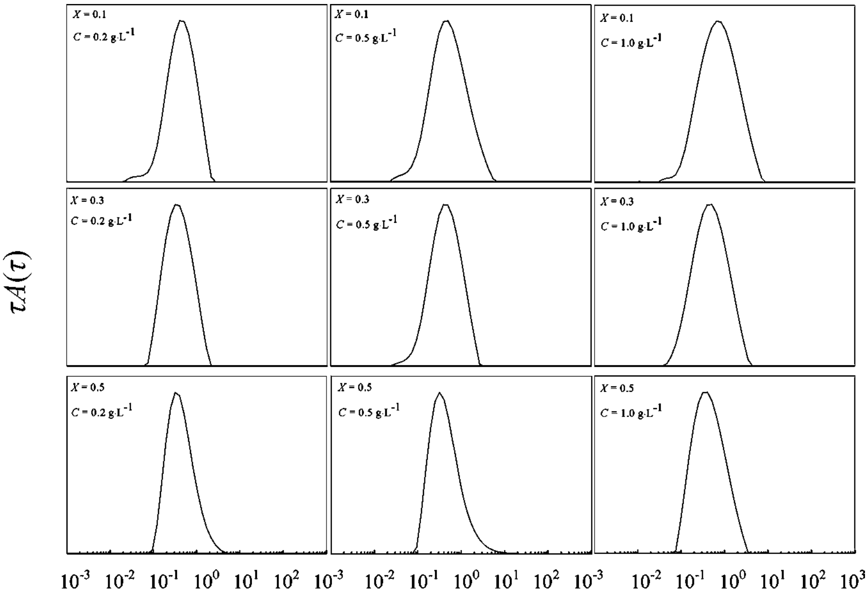

Figure 7. Distributions of relaxation time in QELS measured at $\theta = 90°$ for the polymers with $X = 0.1$, 0.3, and 0.5 at $C = 0.2$, 0.5, and 1.0 g·L^{-1} in 0.05 mol·L^{-1} NaCl aqueous solution.

C decrease significantly when X is increased. We estimated the critical aggregation concentration (CAC) for the present polymers corresponding to the point of initial sharp decrease of the I_1/I_3 curve. The CAC values could be taken as the C corresponding to the intercept between the linear extrapolations of the horizontal portion at low concentration and of the rapidly varying portion of the curve, which along with I_{339}/I_{336} values and I_1/I_3 values are given in Table 1.

In general, the relaxation rate (Γ) (i.e., the reciprocal of the relaxation time) in QELS is a function of scattering angle θ. As θ is increased, internal molecular motions would affect Γ. To examine the angular dependence of Γ for the polymers, angle-trace QELS measurements at 25 °C were performed in salt solution at various θ.

In Figure 6, the relaxation rates (Γ) for all of the polymers ($X = 0.1$, 0.3, and 0.5) at a constant $C = 0.05$ g·L^{-1} are plotted as a function of the square of scattering vector (q^2) (scattering angle $\theta = 30$, 50, 70, and 90°). Linear relationships passing through the origin observed for all of the polymers imply that the measured relaxation times are attributable to a diffusive mode, allowing us to estimate a diffusion coefficient from the slope.[38] Approximate R_h values were calculated from the estimated diffusion coefficients along with the viscosity (0.894/mPa·s) and the refractive index (1.332) of the salt solution at 25 °C using the Stokes−Einstein relation. R_h values thus calculated are indicated in Table 1.

Figure 7 compares relaxation time distributions in QELS for the polymers with different X at $C = 0.2$, 0.5, and 1.0 g·L^{-1} in salt solution. We could not obtain the normalized autocorrelation function for $C < 0.2$ g·L^{-1} because the scattering intensity was too weak, and the relaxation time distributions become complicated when $C > 1.0$ g·L^{-1}. The relaxation time distributions appear to be virtually unimodal in the C range of 0.2 to 1.0 g·L^{-1}, increasing with an increase of C as well as a decrease of X in a different extent.

The R_h values increase with increasing C, whereas an increase in X produces the opposite effect. We can see from the data (Table 1) that the increase extent of R_h is ($X = 0.5$) < ($X = 0.3$) < ($X = 0.1$). R_h with $X = 0.5$ does not increase significantly with increasing C, which is about 26.6 nm at $C = 0.2$ g·L^{-1} and about 34.3 nm at $C = 1.0$ g·L^{-1}. In the case of $X = 0.3$, R_h increases from 26.9 to 43.1 nm along with increasing C from 0.2 to 1.0 g·L^{-1}. When X is decreased to 0.1, the R_h values are in a range of 34.3 to 69.1 nm, showing the biggest increase extent with varying C.

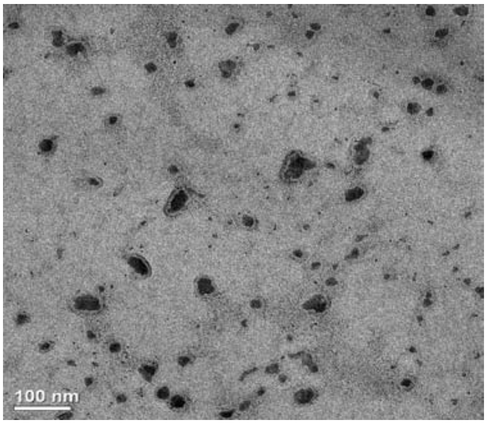

Figure 8. TEM image of the polymer with $X = 0.5$ in 0.05 mol·L^{-1} NaCl aqueous solution.

Transmission electron microscopy was performed to visualize the conformation of the polymers. Figure 8 displays the conformation of $X = 0.5$ in salt solution. The polymer aggregates appear nonspherical, exhibiting an irregular “potato-like” morphology. Several aggregates exhibit diameters of nearly 100 nm, whereas the discrete ones are about one order of magnitude smaller. This difference in size scale is in agreement with the wide relaxation time distribution obtained from QELS, and the sizes of the aggregates are also consistent with that found by QELS (average of 34.3 nm).

These observations indicate that intermolecular interaction is the main type of hydrophobe association for the series of polymers, leading to the formation of multimolecular aggregates in salt solution. It could be found from the dependent relations of R_h on C that interpolymer association occurs more favorably to form larger aggregates at higher C. The dependence of R_h on X manifests that the aggregates become a closed type progressively along with the increase of X, which could also be supported by the fact that the increase extent of R_h with higher X inclines to be smaller with increasing C.

Conclusions

The amphiphilic statistical copolymers of AMPS and $AMC_{12}S$ were synthesized by free radical polymerization with $X = 0.1$, 0.3, and 0.5, respectively. The association behaviors of the polymers in salt solution were studied by fluorescence, QELS, and TEM, focusing on the effects of X on the associative performance of these polymers. It was found that the hydrophobic aggregates begin to occur at a relatively well-defined C, which is regarded as CAC. The CAC values strongly depend on X, which were obtained as $0.0467\ g \cdot L^{-1}$ for $X = 0.1$, $0.0074\ g \cdot L^{-1}$ for $X = 0.3$, and $0.0039\ g \cdot L^{-1}$ for $X = 0.5$, respectively. It is noticeable that the polymers show a strong tendency for interpolymer association, even at low C of $0.2\ g \cdot L^{-1}$ in salt solution, forming multimolecular aggregates. The R_h values increase with increasing C, whereas an increase in X produces the opposite effect. It is reasonable to conclude that the polymer aggregates become a closed type progressively with increasing X by the dependent relation of R_h on X and the fact that the increase extent of R_h with higher X inclines to be smaller with increasing C.

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