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HYDROPHOBICALLY ASSOCIATING POLYACRYLAMIDES MODIFIED BY A NOVEL SELF-ASSOCIATIVE CATIONIC MONOMER

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Abstract A series of hydrophobically associating polyacrylamides modified by small amounts (< 3 mol%) of a self-associative cationic monomer 4-(2-(acryloyloxy) ethoxy) benzyl tri-ethyl ammonium bromide (AEBA) as hydrophobe were synthesized by radical copolymerization in aqueous solutions without external surfactants. The resulting copolymers containing a multiblock structure exhibited a high tendency for hydrophobic association and a high thickening capacity. Solution properties and aggregation structures were investigated by viscometry and fluorescence technique. The high viscosity enhancement was found as the polymer concentration beyond a critical value c^* and strongly depended on the copolymer microstructures. The number and length of hydrophobic microblocks within the copolymer backbones could be controlled by changing the AEBA concentration in copolymerization system. Addition of salt induced more hydrophobic association and viscosity enhancement. The synthesis method used was simple and environmentally friendly without any external surfactant contamination in comparison with the conventional micellar copolymerization.

Keywords: Self-associative monomer; Hydrophobically associating copolymer; Aggregation behavior and structure; Viscosity enhancement.

INTRODUCTION

Water-soluble associating polymers have been extensively studied for both academic and industrial purposes[1–3]. Hydrophobically associating polyacrylamides containing small amounts of hydrophobic groups have received an increasing amount of attention due to their unique rheological characteristics and application in oil recovery, drilling fluids, coatings *etc*[4–7]. These polymers exhibit a high tendency to self-associate in aqueous solutions in order to minimize water-hydrophobe contacts. A major difficulty in synthesizing hydrophobically associating polyacrylamides is that hydrophobes are insoluble in water. The current solution is to adapt the micellar copolymerization technique and prepare the hydrophobically associating polyacrylamides using external conventional surfactants. In this system, hydrophobic monomers are solubilized within the micelles and copolymerized with acrylamide in the aqueous solution resulting in copolymers with a microblocky structure. A lot of work has focused on polymer structures, solution behaviors and thickening properties of hydrophobically associating polyacrylamides[8–14]. Hydrophobic microblock structures within copolymer backbones significantly reinforce hydrophobic associative interactions which promote intermolecular association and induce viscosifying behavior. The number and length of hydrophobic units within the polymer backbone play an important role in determining the polymer conformation and its rheological properties in aqueous solutions[8, 9, 15–17]. Conventional micellar copolymerization systems require external surfactants which usually negatively affect the polymer properties such as low molecular weight caused by a surfactant chain transfer effect and surfactant impurities. Complicated post treatment processes are also necessary to remove the surfactants[18, 19].

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This results in potential difficulties for conventional micellar copolymerization in commercial applications. In terms of environmental protection and economy, new routes for the preparation of hydrophobically associating polyacrylamides need to be found.

Recently, monomers composed of hydrophobic tail groups and hydrophilic head groups as well as a polymerizable group have been investigated[20–27]. Their special molecular architecture gives them unique physicochemical properties, such as their surface activity and they can be initiated to polymerize. These surface active monomers (surfmers) self-organize into an aggregate conformation above the critical association concentration (CAC). By using the surface active monomers instead of the commonly used hydrophobic monomers, the copolymerization with acrylamide (AM) can readily be carried out in aqueous solutions. This is a simple and promising approach to overcome the drawbacks of external surfactants. This copolymerization system results in copolymers with a microblocky structure as the concentration of surfmers is above the CAC. When surfmers have concentrations below the CAC, the resulting copolymers have hydrophobes with a random sequence. The hydrophobic block sequences can, thus, be controlled under selected conditions. This is quite attractive as it offers real versatility in tuning some characteristic parameters of the resulting copolymers and therefore enables the design of tailored materials with excellent performance properties. However introduction of ionic groups contained in surfmer into polymer chains will improve the water solubility accompanying with perturbance of the hydrophobic association resulting in lowering the thickening effect. Therefore, it usually requires addition of another hydrophobic monomer as third component or the present of added salt in order to manifest increased interchain association[15, 28]. Through adequate choice of the ionic and hydrophobic contents, it is possible to obtain a synergistic enhancement of the thickening efficiency.

Our group recently exploited a novel cationic monomer, 4-(2-(acryloyloxy) ethoxy) benzyl tri-ethyl ammonium bromide (AEBA) and studied its fundamental characteristics, which exhibited high tendency for self-association. Here, we extend our work by utilizing AEBA as a self-associative monomer to copolymerize with AM in aqueous solutions without external surfactants. The solution behaviors and association structure of copolymers are studied by viscometry and fluorescence technique. The associative behavior of AEBA affects the eventual chain structure and hydrophobic properties of the resultant copolymers greatly. The effects of microblock structure, molecular weight and salt addition are discussed.

EXPERIMENTAL

Materials

Acrylamide (AM) was obtained from Jiangxi Changjiu Biochemical Engineering Corporation. AEBA was synthesized in our laboratory. 2,2′-Azo-bi-(2-amidino-propane) dichloride (AIBA) was used as an initiator.

Synthesis of Copolymers P(AM/AEBA)

An aqueous solution of monomer AM and AEBA was prepared according to a given molar ratio in a 50 mL tube. The total concentration of the two monomers was 0.7 mol/L. To exclude air, the solution was purged with nitrogen gas for 20 min and then the initiator AIBA was added. The tube was then put into a thermostat water bath at 45°C. The reaction was carried out for 10–12 h, and then the copolymer product was dissolved in water and reprecipitated from acetone twice. Finally, the copolymer was dried under vacuum. By varying the feed ratio of the two monomers resulting copolymers with different microstructures were obtained, and they are referred to as the NS series in this report.

Characterization

Intrinsic viscosities of copolymers

The viscosities of the copolymers were measured in 0.5 mol/L NaCl aqueous solutions at a constant temperature of (25.0 ± 0.1)°C with an Ubbelohde viscometer. The value of intrinsic viscosities ([η]) were calculated with the dilution extrapolation method. The molecular weights of copolymers were expressed relatively with the intrinsic viscosities.

Molar content of AEBA monomer in copolymers

The UV spectra of copolymers were examined from 200 nm to 300 nm on a JASCO-530 UV-Spectrometer. The AEBA molar content in copolymers was calculated from maxima absorbance of copolymer at 275 nm, according to Eqs. (1) and (2)[29].

$$W\% = \frac{A_0}{\varepsilon}\frac{M_2}{y} \times 100 \tag{1}$$

$$\text{mol}\% = \frac{(W/M_2)}{\left[(W/M_2)+\left((100-W)/M_1\right)\right]} \times 100 \tag{2}$$

where y is the concentration of copolymer in g/L and ε is 465.8 ($\text{mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{L}$), the value of the molar absorption coefficient determined from the corresponding homopolymer P(AEBA), A_0 is the maxima absorbance of copolymer samples at 275 nm. The values M_1 and M_2 are the molecular weights of acrylamide and comonomer AEBA, respectively. The values of AEBA content for various copolymer samples have been calculated and are listed in Table 1.

Apparent viscosity of the aqueous copolymer solution

Copolymer samples were dissolved in distilled water for 24–48 h so that the copolymers were dissolved entirely and then diluted to the required concentration. The apparent viscosities (η_{app}) of copolymers in aqueous solutions at different concentrations were determined at a constant temperature of (25.0 ± 0.1)°C using a Brookfield DV-III rotary viscometer and at a shear rate of 6 s^{-1}.

Fluorescence spectra

Steady-state fluorescence spectra were taken at room temperature on a Hitachi F-4500 spectrofluorometer. The fluorescence excitation spectra of copolymer samples at different concentrations were determined in a scanning range of 200–295 nm and detected at 300 nm.

The Aggregation number (N_{agg})

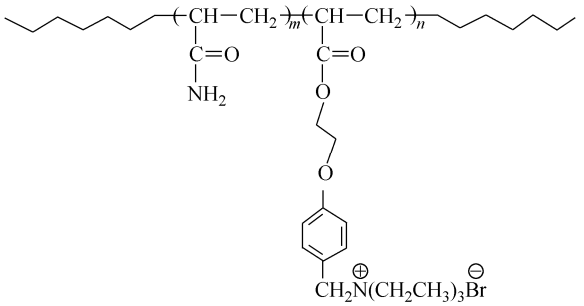
Aggregation numbers of the copolymers were obtained by fluorescence quenching experiments[30, 31] carried out at room temperature using pyrene and benzophenone as a luminescence probe-quencher pair. The corresponding equations and experimental details were given elsewhere[32].

RESULTS AND DISCUSSION

Copolymerization System

The hydrophobically associating polyacrylamide prepared by micellar copolymerization has microblocky structure; namely, the hydrophobic monomer is randomly distributed along the copolymer backbone in a microblocky manner[8, 9]. The mechanism of micellar copolymerization and characterized features of the resulting hydrophobically associating polyacrylamides were investigated in detail by several research groups. According to the nature of hydrophobic comonomer, two synthesis routes were used for the associating polymers. In the first process, the hydrophobic monomer is solubilized within micelles of external surfactants then copolymerized with acrylamide in aqueous solutions. The resulting copolymers exhibit a microblocky structure. In the second process, the comonomer itself is a water-soluble polymerizable surfactant and easily associates into micellar state in the polymerization solution. According to the micellar copolymerization mechanism, the resulting copolymers of surfmer with AM also have microblocky structure[8, 9, 14, 23–26, 33, 34]. The amphiphilic monomer AEBA similar as a surfmer exhibits high tendency for self-association into aggregates as concentration beyond a threshold value in aqueous solutions[35]. In the copolymerization system of AM/AEBA, the monomer AEBA preferentially self-associates into aggregates whereas acrylamide molecules are dissolved in the aqueous continuous medium. It is actually a microheterogeneous system in which the high local monomer concentration and the molecular arrangement of AEBA favor AEBA molecules readily to incorporate onto the

copolymer main chain with a microblocky manner. The chemical structure of the copolymer P(AM/AEBA) is illustrated in Scheme 1. The solution properties of the hydrophobic associating copolymer are dependent on their microstructure that can be manipulated by varying the experiment conditions of copolymerization. Therefore two different series of copolymers P(AM/AEBA) were synthesized. The series of copolymer NS with different AEBA contents were prepared using different monomer ratios in feed as given in Table 1. The other series NS-1(A-D) having different molecular weights were obtained by adjusting the amount of initiator as listed in Table 2.



Scheme 1 Chemical structure of copolymer P(AM/AEBA)

Table 1. NS series copolymers with different AEBA content

Copolymer sample	Monomer feed (AEBA, mol%)	Polymer composition (AEBA, mol%)[a]	Solubility[b]	[η] (mL/g)	K_H
NS-0	0.086	0.07	+	567.5	0.5565
NS-1	0.21	0.28	+	585.1	0.4766
NS-2	0.43	0.60	+	562.9	0.6494
NS-3	0.86	1.00	+	507.1	0.7043
NS-4	1.28	1.30	+	522.8	0.7757
NS-5	2.10	1.80	+	500.0	1.6676
NS-6	3.20	3.00	±	475.9	0.8625
NS-7	4.30	–	±	–	–

[a] AEBA molar content in the copolymer was calculated from its UV-absorbance at 275 nm according to reference[29];
[b] + Completely dissolved; ± Partially dissolved

Effect of Microstructure on the Hydrophobic Association Property of P(AM/AEBA) in Pure Water

Viscometry is a convenient and reliable method for determining associative properties of amphiphilic copolymers in aqueous solutions[36]. Generally, the intramolecular association results in polymer chain contraction leading to viscosity reduction. In contrast, if a rapid increasing in apparent viscosity occurs at a certain concentration, *i.e.* the critical concentration c^*, the polymer is described as intermolecular association in nature due to formation of physical network aggregates that may occupy large hydrodynamic volume.

Figure 1 presents the copolymer concentration dependence of apparent viscosity for aqueous solutions of series NS and polyacrylamide (PAM) for comparison. A more pronounced upward curvature was obtained as compared with PAM resulting from the intermolecular association. The critical concentration at which viscosity starts to significantly increase denoted as c^* can be calculated from the transition point of the plots in Fig. 1, and is around 0.006 g/mL for these copolymers of series NS. The viscosity of homopolymer PAM increases moderately with polymer concentration without any transition. The high viscosifying effect for copolymers of series NS in the semidilute solution can be explained that the major contribution is ascribed to the intermolecular hydrophobic association resulting in a formation of bulky network aggregates that have large hydrodynamic occupied volume[37, 38].

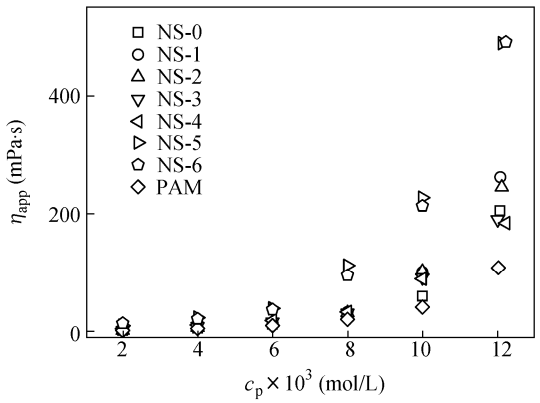


Fig. 1 Apparent viscosities of NS series copolymers as a function of copolymer concentration in salt-free aqueous solutions

Figure 2 illustrated the apparent viscosities of copolymers with different AEBA contents in 0.012 g/mL polymer solutions. It is interesting to find that there present two different regimes. At lower AEBA content levels (NS-1–NS-4) the viscosity increases moderately and nonlinearly with the hydrophobe content, and a maximum appears at 0.43 mol% of AEBA content in feed (NS-2). In the hydrophobic association system as known inter- and intra- molecular hydrophobic interactions are coexisted in the system and both enhanced with increasing hydrophobe content. The intermolecular associations results in formation of bulky network aggregates, which give rise to a significant viscosity enhancement. In contrast, intra-molecular hydrophobic interactions induce a contraction of macromolecular chains resulting in an apparent viscosity decrease. The determination role is dependent on which one is dominate in system. Owing to the competition between the inter- and intra- molecular interactions present in this system, thus a maximum apparent viscosity appears and the corresponding point is an optimal value of AEBA content in copolymers.

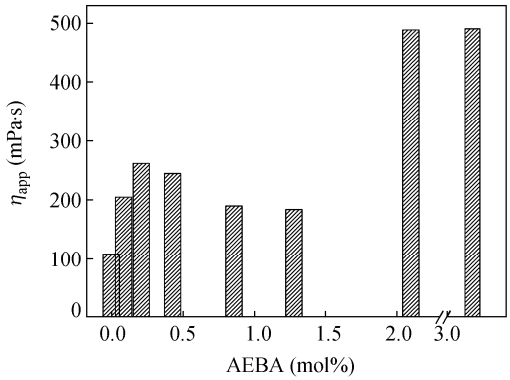


Fig. 2 Apparent viscosities of NS series copolymers as a function of AEBA content in aqueous solutions (c_p = 0.012 g/mL)

At higher AEBA content regime, a sharp viscosity rise can be found up to a new high level of 500 mPa·s for copolymers NS-5 and NS-6 which were synthesized at initial concentration of AEBA above 1.28 mol% in feed. This distinctly presented two regimes can be ascribed to the factor of hydrophobic block length which varied with the molecule number of AEBA per aggregate before copolymerization. Generally, the higher aggregation number of AEBA assembly in the system, the longer the block length in the microstructure of resulting copolymers. As similar to the micelle growth for conventional surfactants, the aggregates of AEBA monomers become enlargement as the monomer concentration exceeding 0.015 mol/L. As a result, when

copolymerization was carried out in the higher AEBA concentration range (> 0.015 mol/L) the resulting copolymers exhibit much longer hydrophobic block length as compared with those obtained at lower AEBA levels (< 0.015 mol/L), and thus display a strong viscosity enhancement in aqueous solutions. This behavior is an indication that the average length of the hydrophobic block is more effective for associating properties than their number.

Copolymers of series NS were soluble in water and each exhibited measurable fluorescence spectra from the phenyl groups in molecular structure. The molecular association process can be studied in molecular level by fluorescence spectra. For instance, the excitation spectra for sample copolymer NS-3 at different polymer concentrations are shown in Fig. 3. There are duel peaks in the excitation spectra. The small peak at 230 nm is assigned to unimolecular phenyl chromophores. The broad structureless band centered at 270 nm belongs to the aggregation structure of polymer chains in an effort to confirm the associative nature resulted from microblock distribution manner of AEBA molecules. When the copolymer concentration increases due to the formation of larger aggregates conformation *via* intermolecular association, the aggregate peak grows intensely and the monomer peak lowers. The red-shift as a result of more phenyl molecules located in the hydrophobic domains. Based on the above results, the copolymer association behavior can be described in terms of the change in relative intensities (I_{agg}/I_{mono}) as a function of polymer concentration (as given in the insert of Fig. 3). The value of I_{agg}/I_{mono} increases slowly at low level of polymer concentration, and a pronounced increase can be observed as the concentration exceeds a threshold value due to the formation of larger intermolecular aggregates. This result gives further evidence that the copolymers exhibit a microblock structure in nature which provides a better accessibility of the pendent hydrophoes association.

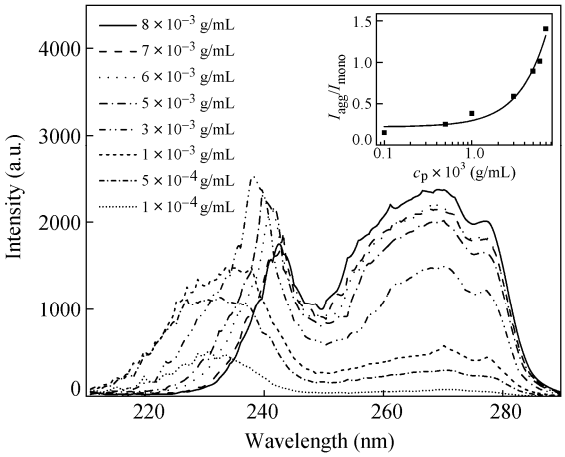


Fig. 3 Fluorescence excitation spectra for copolymer NS-3 at different polymer concentrations
The insert is the plots of I_{agg}/I_{mono} versus copolymer concentrations.

The aggregation number is an important parameter characterizing the polymer aggregation structure. Some workers have defined the aggregation number as the mean number of hydrophobes per aggregate reflecting the amount of aggregating polymer chains that participate in hydrophobic domain formation[39]. The values of N_{agg} for the hydrophobically associating NS series copolymers were determined by a steady-state fluorescence quenching technique. The method is based on the quenching of a luminescent probe by a hydrophobic quencher[40]. In the experimental system of copolymers we used pyrene as a luminescence probe and benzophenone (BP) as the luminescence quencher. Fluorescence quenching of pyrene by BP at different concentrations in aqueous solutions was monitored at 373 nm. A linear relationship between $\ln(I_0/I)$ versus concentration of quencher c_q is shown in Fig. 4. The line passes through the origin indicating that the quenching process for pyrene-benzophenone pair quite obeys the static quenching mechanism. The aggregation numbers were calculated from the slope of the line in Fig. 4 and were 4.9 for NS-3 and 9.5 for NS-5, respectively. These numbers indicate that copolymer NS-5 possesses a much larger hydrophobic domain in network aggregation structure than that of copolymer NS-3. Based on these results it is reasonable to speculate that the hydrophobic

content and microblock length in copolymer structure exhibit an important role in the determination of aggregation number N_{agg} that means the number of polymer chains participating in formation of hydrophobic domain is directly related to the size of physical cross-linking networks formed.

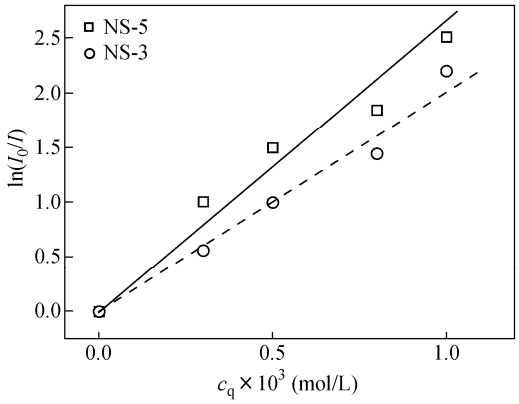


Fig. 4 Plots of $\ln(I_0/I)$ versus c_q (c_p = 0.012 g/mL)

Effect of Molecular Weight

Molecular weight is an important parameter that affects copolymer viscosity. Table 2 lists a series of NS-1 type copolymers with different molecular weights but having an identical composition of 0.21 mol% AEBA. The Huggins coefficient for each copolymer is in the range of 0.45–0.65. These values indicate good water-solubility without any association disturbance in the dilute copolymer solutions. As shown in Fig. 5 higher molecular weight copolymers have larger solution viscosities and lower critical association concentrations c^* at which the viscosities of polymer solutions start to rapidly increase. The viscosity of the high molecular weight copolymer NS-1-D rose more than two orders of magnitude from 12 mPa·s to 2500 mPa·s as the concentration increased from 0.004 g/mL to 0.012 g/mL. The viscosity thickening efficiency of these copolymers is similar to the copolymers prepared by conventional micellar copolymerization[20, 32]. The higher viscosity enhancement

Table 2. Copolymers containing 0.21 mol% AEBA with different molecular weights

Copolymer sample[a]	Solubility[b]	[η] (mL/g)	K_H
NS-1-A	+	585.1	0.4766
NS-1-B	+	789.5	0.6548
NS-1-C	+	884.8	0.6288
NS-1-D	+	1150.5	0.4826

[a] Content of monomer AEBA in each copolymer is 0.21 mol%;
[b] + Completely dissolved

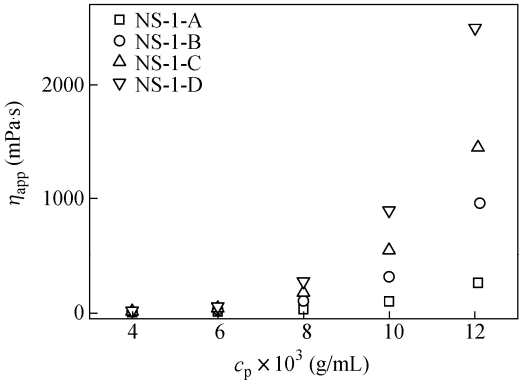


Fig. 5 Apparent viscosities of NS-1 series copolymers as a function of copolymer concentration in salt-free aqueous solutions

demonstrated that these hydrophobically associating copolymers had an important potential application as viscosifiers.

Salt Influence

P(AM/AEBA) is an ion-containing associating copolymer that has a small amount of quaternary ammonium cationic groups at the pendant end of AEBA sequences. The ionic units have opposing effects on the viscosifying properties. Intramolecular charge repulsion results in viscosity increasing due to coil expansion. Intermolecular charge repulsion lowers the degree of association and thus viscosity decreases. Due to its polyelectrolyte characteristics copolymer P(AM/AEBA) is responsive to ionic strength. Figure 6 illustrates the effect of salt on the apparent viscosity for sample NS-3 at the constant copolymer concentration 0.012 g/mL. A pronounced upward curvature was observed. This effective viscosity enhancement resulting from the salt addition is attributed to the screening of charge repulsion interactions, thus promoting the intermolecular hydrophobic association interactions, which result in forming larger physical cross-linking networks and leading to a large increase in the apparent viscosity of copolymer solutions. Besides of charge screening, the added salt will increase the polarity of the aqueous media, thus induces more hydrophobic association and viscosity enhancement, specially in the range of higher salt concentration.

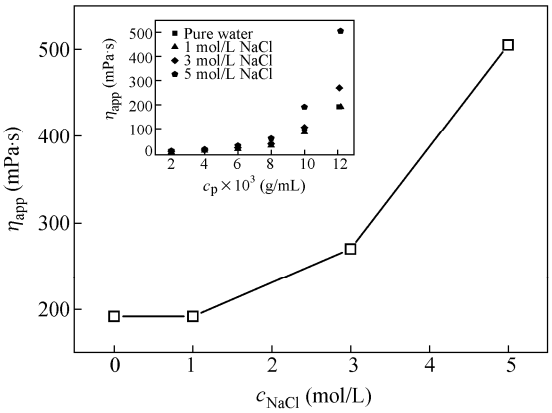


Fig. 6 Apparent viscosities of copolymer NS-3 as a function of salt concentration (c_p = 0.012 g/mL)
The insert shows apparent viscosities of copolymer NS-3 as a function of copolymer concentration in different concentrations of salt solution.

CONCLUSIONS

A series of hydrophobically associating polyacrylamide modified by a novel self-associative monomer AEBA were synthesized by radical copolymerization in aqueous solutions without external surfactant. The resulting copolymers P(AM/AEBA) containing small blocks randomly distributed along the polymer backbone have a high capacity for self-association and large viscosity enhancement. The associative behaviors and solution properties were found to be dependent on the copolymer microstructures and molecular weights. The main factors, hydrophobic content and block length which strongly affected the viscosifying ability of copolymers can be controlled by varying the concentration and associative structure of monomer AEBA in the copolymerizaton. A large viscosity enhancement was observed as concentration beyond c^* for copolymers prepared with AEBA molar content exceeding 1.28 mol%. Adding salt also induces more hydrophobic association and viscosity increase. This synthesis method is a simple and environmentally friendly process for the preparation of hydrophobically associating polymers with hydrophobic microblock structures.

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