A novel hydrophobically associating polyampholytes of poly(AM/AA/AMQC12): preparation, characterization, and solution properties

Huiyong An · Cuige Lu · Pixin Wang · Wenbo Li · Ying Tan · Kun Xu · Chang Liu

Abstract A novel hydrophobically associating polyampholytes of poly(AM/AA/AMQC12) were synthesized by the free radical copolymerization of acrylamide (AM), acrylic acid (AA), and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (AMQC12) in water without any surfactants (named AAQ series). The structures of polymers were confirmed by ^{1}H NMR and ^{13}C NMR. The molecular weight and polydispersity were obtained using gel permeation chromatography (GPC). The hydrophobically associated properties of polymer solution were characterized by rheology, steady-state fluorescence probe, and ^{1}H NMR relaxation time (T_2). Isoelectric points (IEPs) of polymer solution were determined by the effect of pH on viscosity below critical association concentrations (cac), and the reduced viscosities of samples at IEPs were increased in the presence of NaCl. Moreover, the steady-shear viscosity of sample at IEP was also greatly enhanced in NaCl solutions when the polymer concentration is above the cac. Meantime, the storage modulus and the loss modulus of copolymers showed that the sample behaved as gel in salt media.

Keywords Water-soluble polymers · Hydrophobic association · Polyampholyte · Stimuli-sensitive polymers · Rheology

H. An · C. Lu · P. Wang (✉) · W. Li · Y. Tan · K. Xu · C. Liu
Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
e-mail: pxwang@ciac.jl.cn

H. An
Liaoning SHIHUA University, Fushun 113001, People's Republic of China

H. An · C. Lu · W. Li
Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Introduction

Hydrophobically associating water-soluble polymers (HAWPs) have attracted increasing interests over the past decades due to its ability in viscosity enhancement [1–4]. Micellar free radical polymerization is one of the most popular method to synthesize HAWPs for the poor solubility of hydrophobic monomers [5, 6]. However, this method needs large amounts of surfactants and causes some problems, such as chain transfer effects and difficulties in purification of products [7, 8].

Recently, ionic surfmer [9] (surfactant monomer) [10], composing both amphiphilic structure and ionic groups, has been used as comonomer to synthesize the HAWPs. The incorporation of ionic surfmer into such system can sustain the homogeneous phase copolymerization without any surfactants, and the obtained polymers retain high dissolubility [9, 11–13].

Hydrophobically associating polyampholyte (HAPA) is the most special HAWP bearing both anionic and cationic groups along the polymer backbone [14–19]. Electrostatic interaction between opposite charges influences hydrophobically associating interaction by the alteration of chain conformation, that is the collapsed coils prefer to intramolecular hydrophobic association when polymer concentration is extremely low and extending chains shielding by added electrolytes promote the intermolecular hydrophobic association when polymer concentration is high. Thus, HAPA has particular solution properties resulting from interactions between electrostatic force and hydrophobic association [14, 19]. It is noted that the HAPA behavior is intensively affected by charge density and distribution of charges along the polymer chain [18]. However, unlike the common polyampholyte, HAPAs are difficult to improve the ratio of ionic surfmer in polymer backbone due to its poor solubility [15, 16]. Therefore, designing an ionic surfmer with appropriate hydrophilic–hydrophobic balance is crucial to modulate the charge density and distribution of HAPA when the ionic surfmer is used as comonomer.

In this paper, dimethyldodecyl(2-acry1amidoethyl)ammonium bromide (AMQC12) was used as the ionic surfmer. A series of novel HAPAs were synthesized using acrylamide (AM), acrylic acid (AA), and AMQC12 by the free radical polymerization in aqueous solution and named as AAQ series. AAQ series had sophisticated structure, the anionic groups located on the hydrophilic and short side chains, whereas the cationic groups located on the hydrophobic and long side chain. Moreover, the effects of NaCl concentration and pH on the polymer solution properties are also investigated in detail to gain better insight into the synergy between electrostatic interaction and hydrophobic association of HAPAs.

Experimental

Materials

N,N-dimethylethylenediamine (Aladdin, 98%) and 1-bromododecane (Aladdin, 99%) were used as received. Acrylamide (Shandong Shouguang Fine Chemicals

Co., Ltd.) was twice recrystallized from acetone and vacuum dried at 30 °C. Acrylic acid (Beihua Fine Chemicals Co., Ltd.) and acryloyl chloride (Shanghai RC Chemicals Co., Ltd.) were vacuum distilled to remove inhibitor. 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, from Wako Pure Chemicals, Japan) was used as the initiator without further purification. Pyrene (from Alfa Aesar) was recrystallized twice from ethanol. Phenothiazine (Huzhou Biochemicals Plant) and other reagents were used as received. Water was purified with a Millipore Milli-Q system.
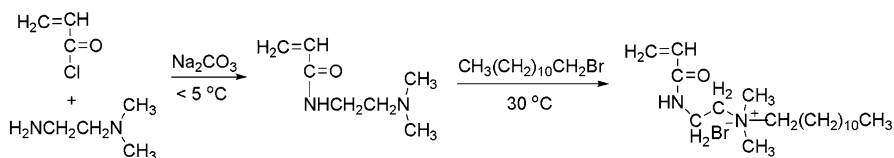
Synthesis

Synthesis of AMQC12

Synthesis route of dimethyldodecyl(2-acry1amidoethyl) ammonium bromide (AMQC12) is illustrated as Scheme 1.

A 250-mL three-necked round-bottom flask fitted with a dropping funnel and a reflux condenser was charged with N,N-dimethylethylenediamine (8.82 g, 0.1 mol) in methylene chloride (120 mL) and Na_2CO_3 (11.66 g, 0.11 mol). The mixing solution was agitated and placed in an ice bath under nitrogen atmosphere. Acryloyl chloride (9.96 g, 0.11 mol) was resolved in anhydrous methylene chloride (80 mL) and slowly added into the flask at a rate of 2–3 drops per minute when the temperature dropped to 5 °C or less. After complete addition, the reaction was continued for several hours at 30 °C. The mixture was filtrated and brown liquid was obtained. The organic layer was washed twice with concentrated Na_2CO_3 solution. The combined water layers were saturated with NaCl and extracted three times with CH_2Cl_2. All collected organic layers were dried with anhydrous $MgSO_4$ for night. After evaporation of the solvent, brown oil (12.67 g, yield 89%) was obtained. The crude product was purified by vacuum distillation in the presence of a small amount of phenothiazine as an inhibitor. A slightly yellow oily liquid (8.87 g, yield 62.3%) was collected at 116–118 °C under vacuum of 3 mmHg. ^1H NMR ($CDCl_3$): δ 2.05(s, 6H), 2.32–2.35(t, 2H), 3.20–3.22(t, 2H), 5.57–5.59(m, 1H), 6.00–6.09(m, 2H).

N,N-[(dimethylamino)ethyl]acrylamide(7.14 g, 0.05 mol) was treated with dodecyl bromide (15.0 g, 0.06 mol) in two-necked round-bottom flask equipped with reflux condenser. The reaction was under nitrogen at 30 °C for 72 h. Excess dodecyl bromide was decanted and a white solid was formed by freezing for night. The crude product was washed with ether and extracted three times with water. The aqueous solution was lyophilized and a white powder (AMQC12, 17.67 g, yield

Scheme 1 Synthesis route of AMQC12

90%) was obtained. ^{1}H NMR (DO$_2$): δ 0.82–0.84(t, 3H), 1.24–1.29(br m, 18H), 1.71(t, 2H), 3.15(s, 6H), 3.36–3.39 (t, 2H), 3.50–3.52 (t, 2H), 3.71(t, 2H), 5.56–5.58(m, 1H), 6.19–6.31(m, 2H).

Solution copolymerization of AM/AA/AMQC12

A 100-mL four-necked round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet, and a thermometer was charged into AM and AA. Dimethyldodecyl(2-acry1amidoethyl) ammonium bromide (AMQC12) was dissolved completely in deionized water by agitating and then was poured into the round-bottom flask. The quantities of AM, AA, and AMQC12 were in the desired ratio and total monomer concentration was 5%. The mixture was stirred, and the flask was put into a 30 °C water bath. The nitrogen streamed into system at least 30 min, and then VA-044 (1 wt%) was added with a syringe. Polymerization was conducted continuously at 30 °C for 24 h. After the reaction, the polymer solution was precipitated by a large quantity of acetone. The precipitate was washed by acetone three times and immersed in acetone for 12 h to remove all traces of water, initiator, and residual monomers. Then the white precipitate was sliced and dried under vacuum at 50 °C for 24 h. At last, the slices were shattered, and the white powder was obtained.

Characterization

Structure determination

^{1}H and ^{13}C NMR spectra were obtained by a Bruker AV 600 NMR spectrometer (Bruker Group Company, Germany). Monomer structure was characterized by ^{1}H NMR in deuterochloroform (CDCl$_3$) or deuterium oxide (D$_2$O). Copolymer composition was determined by ^{1}H and ^{13}C NMR in deuterium oxide (D$_2$O).

Intrinsic viscosity

Intrinsic viscosity of polymer solution was determined using a dilution-type Ubbelohde viscometer with 1.0 mol/L NaCl as solvent and the concentration of the polymer was 0.05 g/dL. The measurement was kept at 30.0 ± 0.1 °C. The relation of reduced viscosity and polymer concentration was extrapolated to c_0 and intrinsic viscosity and Huggins constant were obtained by intercept and slope. The reduced viscosity was calculated by dividing flow time of polymer solution by flow time of solvent obtained by the dilution method.

Molecular weight and molecular weight distribution

The molecular weights and molecular weight distributions of the polymers were determined with a gel permeation chromatography (GPC) instrument (Waters Co., USA). GPC analysis was performed with a Waters 515 HPLC pump equipped with a Waters 2414 refractive index detector and two columns (Ultrahydrogel 2000 and Ultrahydrogel 1000) using 0.1 M NaNO$_3$ aqueous solutions as the eluent at a flow

rate of 0.5 mL/min. All the analysis was conducted at 30 °C. The volume of injection was 100 μL. Molecular weights of the copolymer were calibrated with sodium polyacrylate standard samples (M_p: 900–11,00,000 Da).

Solution properties measurements

Stock solutions were prepared by the dissolution of a measured amount of the polymer in water or NaCl solutions. Effect of pH on solution properties was measured in a 0.01 mol/L phosphate buffer, of which the ionic strength is 0.05 mol/L by NaCl addition. Subsequent dilute solutions were made from the stock solutions. The range of concentrations of the polymer solutions was 0.005–2 wt%. All the polymer solutions were agitated gently for 24 h. The solutions were centrifuged at 3500 rpm for 30 min to eliminate the bubbles. Polymer solutions were allowed to stand for 24 h before measurement. All solution properties were measured at 30 °C and the value of pH were at 7.1 unless otherwise stated.

Rheological study

Apparent viscosities of dilute solutions were performed by a Brookfield DV III Ultra rheometer (Brookfield Engineering Laboratories, Lnc., USA) equipped with ultra-low viscosity taker and ULA spindle. These measurements were at a temperature of 30 °C with a temperature-control water bath.

Reduced viscosity was measured in various polymer solutions to eliminate the influence of the solvent on the viscosity. Reduced viscosity of dilute solution was calculated by Eq. 1, which was determined using an Ubbelohde viscometer at 30 ± 0.1 °C. All flow time was above 110 s.

$$\eta_{red} = \frac{t_p - t_0}{t_0} \times \frac{1}{c_p} = \frac{(t_p - t_0)}{t_0 \cdot c_p} \tag{1}$$

where t_p (s) was flow time of polymer solution, t_0 (s) was flow time of pure solvent, c_p (g/dL) was the concentration of polymer solution.

Rheology measurements on semi-dilute solutions were carried out using a Physica MCR300 controlled stress rheometer (Physica, co., Germany) equipped with concentric cylinder geometry (CC17: cup radius 9.33 mm, bob radius 8.33 mm). The temperature was controlled with a TEZ180-C cylinder system and was set to 30 °C. Apparent viscosities were measured with Rotation Mode by increasing the shear rate from 0.05 to 50 s^{-1} by logarithmic steps and waiting for 30 s at each step for equilibrium. Linear viscoelasticity experiments were performed on the samples with Oscillatory Mode under strain that led to a linear response and in the range of angular frequencies of 0.01–50 rad/s.

Steady-state fluorescence analyse

Steady-state pyrene fluorescence probe measurements were performed on a Hitachi F-2500 fluorescence spectrometer (Hitachi, Ltd., Japan) using a 10 mm path length

quartz cuvette. All measurements were performed at ambient temperature. The slit width of excitation and emission were kept at 2.5 nm. The excitation wavelength was set at 337 nm. The ratio of the intensities of the first vibronic peak (I_1, 373 nm) to that of the third vibronic peak (I_3, 384 nm) of pyrene probe fluorescence spectrum was used as an estimate of polarity of microenvironment [20]. A required volume of stock solution of pyrene in ether (1×10^{-5} mol/L) was pipetted into a standard flask and a thin film of pyrene was deposited on the bottom and sides of the flask, through evaporation of solvent by bubbling N_2 gas. Then polymer solution was put inside the flask. The effective concentration of pyrene was maintained at 1×10^{-6} mol/L in all the solutions. The concentrations of the polymers were in the range of 0.005–1 g/dL.

Spin–spin relaxation time determination

^{1}H NMR spin–spin relaxation times were measured in D_2O or NaCl D_2O solution by the Bruke MiniSPCT mq20 NMR Analyzer (Bruker Group Company, Germany). The T_2 of the polymer solution was determined by the Carr–Purcell–Meiboom–Gill (CPMG) method using a $\{90^\circ_x \tau(180^\circ_y 2\tau)_n\}$ pulse sequence. The value of τ was set at 1 ms. The number of scan times was 256. The number of dummy shots was 70. Recycle delay time was 12 s. The number of data points was 7500. Diexponential fitting method was adopted in data processing.

Results and discussion

Polymer synthesis and characterization

AM, AA, and AMQC12 were copolymerized successfully in water. The synthesis route and the structure of the AAQ series are shown in Scheme 2.

Table 1 shows the reaction parameters for AAQ series. Sample code is made of AAQ and two numbers which represent the feed ratio of AA and AMQC12, respectively. The yields of the samples are all above 95% by weighing method.

The ^{1}H NMR spectrum and ^{13}C NMR spectrum of AAQ-3-3 and adscription of the characteristic peak are shown in Fig. 1 a and b, respectively. The amounts of AA and
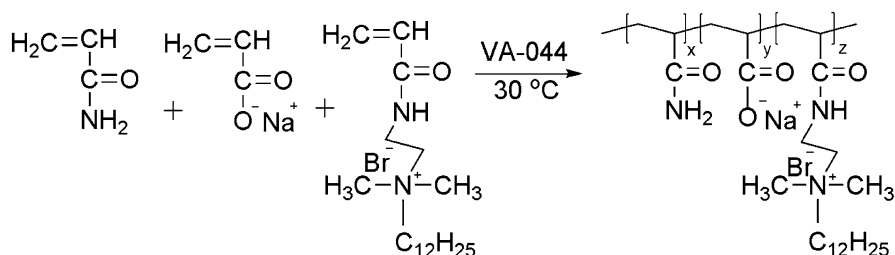
Scheme 2 Copolymerization of AM, AA, and AMQC12

Table 1 Reaction parameters for the hydrophobically associating polyampholytes(AAQ series)

Sample code	Feed composition (mol%)			Polymer composition (mol%)			$[\eta]^c$ (mL g^{-1})	k_H^c	$10^{-5} \times \overline{M}_w{}^d$	PDI^d
	AM	AA	AMQC12	AM^a	AA^a	AMQC12^b				
AAQ-3-1	96	3	1	96.3	2.8	0.9	501.6	0.51	4.15	1.84
AAQ-3-2	95	3	2	95.5	2.7	1.8	498.9	0.61	4.41	1.51
AAQ-3-3	94	3	3	94.8	2.6	2.6	457.3	0.74	3.92	2.11
AAQ-0-3	97	0	3	96.9	0	3.1	487.6	0.78	4.21	1.78
AAQ-3-0	97	3	0	97.4	2.6	0	554.9	0.35	4.53	1.42

^{a} Calculated from the integral area of ^{13}C NMR

^{b} Calculated from the integral area of ^{1}H NMR

^{c} Extrapolated from reduced viscosity and calculating by Huggins equation
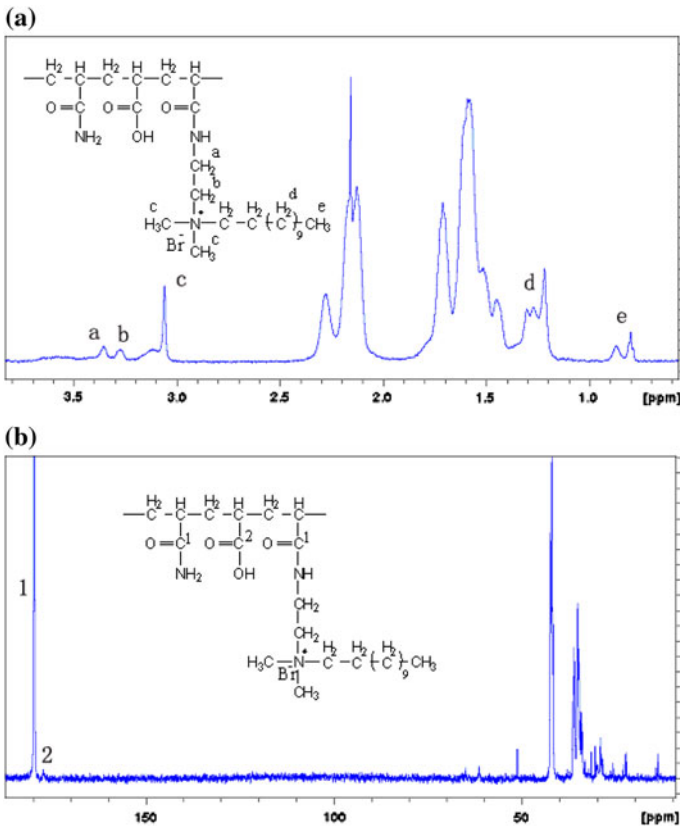
^{d} Obtained from GPC

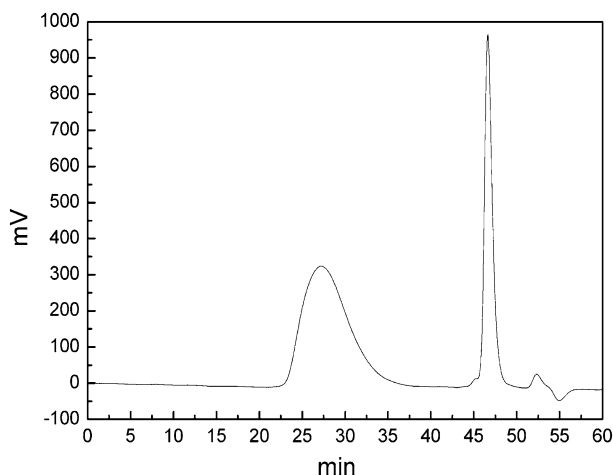**Fig. 1** NMR spectra of AAQ-3-3. **a** ^{1}H NMR, **b** ^{13}C NMR

Fig. 2 GPC curve of AAQ-3-3

AM in polymer were obtained by ^{13}C NMR (–COO–: 177.4 ppm and –CONH–: 179.8 ppm) and that of AMQC12 was determined by ^{1}H NMR (–CH$_2$–: 1.22–1.31 ppm) and polymer composition (shown in Table 1) corresponds to feed ratio.

Different samples of AAQ series have similar intrinsic viscosity and weight-average molecular weight, within the range from 450 to 550 mL/g and from 3.9×10^5 to 4.5×10^5, respectively. The GPC result of AAQ-3-3 is shown in Fig. 2. These facts proved that influence of electrostatic interaction and hydrophobic association on chain propagation is limited and samples of AAQ series were comparable. Polydispersity index (PDI) for samples of AAQ series are approximately 2.0 accounting for a relatively narrow distribution of the length of molecular chains.

The higher content of AMQC12 in the sample, the greater value of Huggins constant (k_H) is, seen from Table 1. k_H reflects the mutual effect between solute and solvent of polymer solutions. Therefore, the great value of k_H implies that there is a strong hydrophobic association [21].

Properties of polymer solution

The cac of AM/AA/AMQC12

The concentration dependence of apparent viscosity of AAQ series at shear rate of 12.23 s^{-1} is shown in Fig. 3. A linear approximation is observed for AAQ-3-0, while samples contained AMQC12 show the upturn of viscosity at different concentrations. The polymer concentration of inflexion is critical associating concentration (cac) which indicates a transformation from intramolecular hydrophobic interactions to intermolecular hydrophobic interactions. When polymer concentration is above cac, physical network is formed by intermolecular hydrophobes and the apparent viscosity increases sharply.

For AAQ series, the cac shifts toward low concentration with increment of AMQC12 content. The cacs of AAQ-3-3 and AAQ-0-3 contained the most amounts
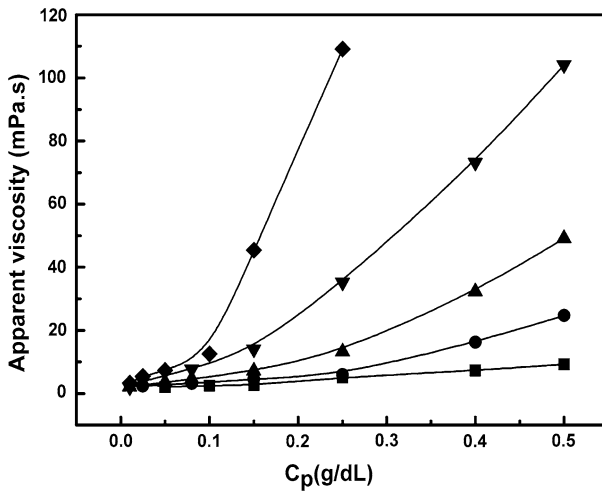
Fig. 3 Effect of polymer concentration on apparent viscosity at shear rate of 12.23 s^{-1} for AAQ series. *Filled square* AAQ-3-0, *filled circle* AAQ-3-1, *filled triangle* AAQ-3-2, *filled inverted triangle* AAQ-3-3, *filled diamond* AAQ-0-3

of hydrophobes are low, of approximately 0.15 g/dL and 0.10 g/dL, respectively (seen from the inset curves in Fig. 3). It illuminates that polymer solution forms the intermolecular hydrophobic interaction at relatively low concentration due to high hydrophobic content. Moreover, the cac of AAQ-3-2 is a little high, about 0.20 g/dL. The amount of AMQC12 is so low that the cac of AAQ-3-1 is not obvious in the range of concentration studied.

As far as AAQ-3-3 and AAQ-0-3 are concerned, the latter has higher viscosity than the former. AAQ-3-3 has similar amounts of the positive and negative charges and the electrostatic attraction collapses molecular chains, which reduces the hydrodynamics volume. At the same time, the contractive chains are difficult to form intermolecular hydrophobic domains. These two associations together result in the lower viscosity. In contrast, AAQ-0-3 possesses stronger viscosity enhancement than AAQ-3-3 because of greater hydrodynamics volume and stronger hydrophobic association. In a similar way, the cac of AAQ-0-3 is lower than that of AAQ-3-3. In other words, AAQ-3-3 needs more hydrophobic units to form intermolecular network.

Steady-state fluorescence measurements using pyrene as a probe is performed to investigate the association properties of samples. The ratio of the intensity of the first vibronic peak to that of the third vibronic peak (I_1/I_3) is sensitive to local polarity. More pyrene molecules dissolve in the lowly polar microzones formed by hydrophobic units, which provides a low value of the I_1/I_3. Figure 4 shows the effect of polymer concentration on I_1/I_3 of the AAQ series. The curves show a characteristic sigmoidal shape [22]: as polymer concentration increases, the value of I_1/I_3 decreases slowly with increasing concentration of the polymer, then reduces steeply at a certain polymer concentration and maintains a desired value finally
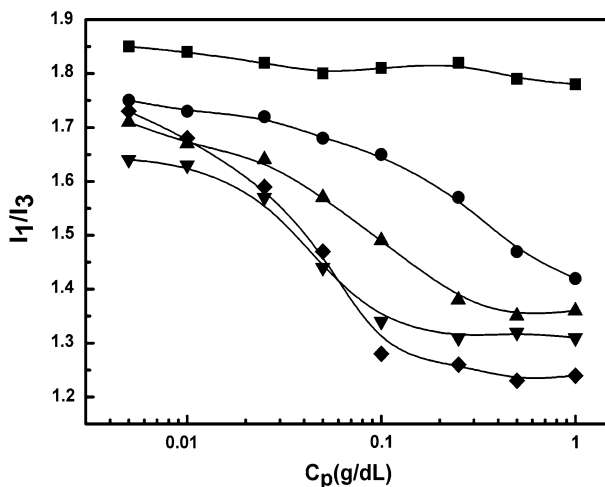
Fig. 4 Effect of polymer concentration on I_1/I_3 for AAQ series. *Filled square* AAQ-3-0, *filled circle* AAQ-3-1, *filled triangle* AAQ-3-2, *filled inverted triangle* AAQ-3-3, *filled diamond* AAQ-0-3

(except AAQ-3-1). This behavior means that strong hydrophobic association domains are formed at the high content of hydrophobic units in the polymer solutions.

It is interesting to note that the I_1/I_3 transition occurs in a broad range of concentration, which is different from Fig. 3. The broad transitional range may indicate a gradual aggregation process. The number of aggregates increases with increment of polymer concentration and hydrophobic domains are formed from intramolecular to intermolecular. The second crossover concentration is similar to cac determined from Fig. 3 and this illustrates that a large amount of hydrophobic domains are formed by intermolecular hydrophobes [22].

The curve of AAQ-0-3 declines more steeply than that of AAQ-3-3 which shows that AAQ-0-3 has stronger hydrophobic association. The same results are mentioned in Fig. 3.

Dilute solution properties

Effect of pH The amount of anion changes according to the pH value of the polymer solutions because the carboxyl of acrylic acid can be protonated at high pH value. Figure 5 shows the effect of pH on the reduced viscosity of AAQ series at polymer concentration of 0.03 g/dL. AAQ-3-0 absent hydrophobes is a weak anionic polyelectrolyte. As the pH reduces, negative charges decrease and the electrostatic repulsion is weaker and weaker resulting in conformation shrinkage, thus the reduced viscosity decreases. Similarly, the reduced viscosity increases as the pH increases and reaches the peak value at pH 7.1. The value of viscosity maintains high because all the carboxyl becomes anions when pH >7.1.

Being different from the carboxyl, the quaternary ammonium cation of AAQ-0-3 is unaffected by the value of pH. As a result, the high reduced viscosity of AAQ-0-3 due to the repulsion of cations is stable throughout the range of pH studied.
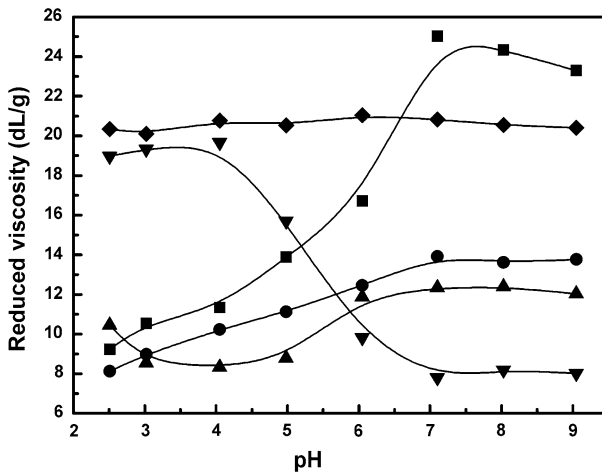
Fig. 5 Effect of pH on reduced viscosity at polymer concentration of 0.03 g/dL. *Filled square* AAQ-3-0, *filled circle* AAQ-3-1, *filled triangle* AAQ-3-2, *filled inverted triangle* AAQ-3-3, *filled diamond* AAQ-0-3

The terpolymers with net charges (AAQ-3-1 and AAQ-3-2) exhibit the similar properties to AAQ-3-0. When pH is close to isoelectric point (IEP), the viscosities are low because the contractive molecular chains reduce the hydrodynamics volume [23] and the collapsed conformations are easy to form intramolecular association. Reduced viscosities increase when the value of pH is far from IEP. Thus, IEP of AAQ-3-2 is in the range of 3–5, which is determined with the pH value of the lowest reduced viscosity from Fig. 5. IEP of AAQ-3-1 is below 2.5 because the amount of cation is too small.

In particular, the reduced viscosity of AAQ-3-3 increases with decreasing value of pH and arrives at the maximal in the range of pH <4. The reason also lies in the superposition between the electrostatic and hydrophobic interactions: as the value of pH decreases, the amount of net charges increases and the electrostatic repulsion spreads chains. The extended conformation forms less intramolecular hydrophobic association and further results in the increase of reduced viscosity.

To prove the effect of pH on the hydrophobic association, relationship between I_1/I_3 and pH of AAQ series at 0.03 g/dL is also studied. Seen from Fig. 6, the ratio of I_1 to I_3 of AAQ-3-0 is high and invariable at different pH due to the absence of hydrophobes. Low I_1/I_3 of AAQ-0-3 is steady at the low value because the strong-base cations of hydrophobic units are independent on pH.

The terpolymers have lower I_1/I_3 value at their IEPs as a result of constriction chains for the similar reason mentioned above. Moreover, the I_1/I_3 of AAQ-3-3 is lower than that of AAQ-3-2. This fact means that the association becomes strong with the increment of hydrophobe content.

Effect of NaCl concentration Effect of NaCl concentration on reduced viscosity of different samples at polymer concentration of 0.03 g/dL is shown in Fig. 7.

The reduced viscosity of AAQ-3-0 decreases dramatically with addition of NaCl because of the shrinkage of AAQ-3-0 chains due to shielding electrostatic repulsion
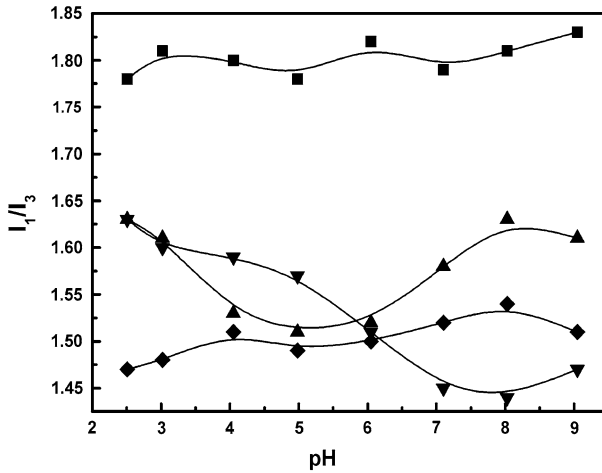
Fig. 6 Effect of pH on I_1/I_3 at polymer concentration of 0.03 g/dL. *Filled square* AAQ-3-0, *filled triangle* AAQ-3-2, *filled inverted triangle* AAQ-3-3, *filled diamond* AAQ-0-3
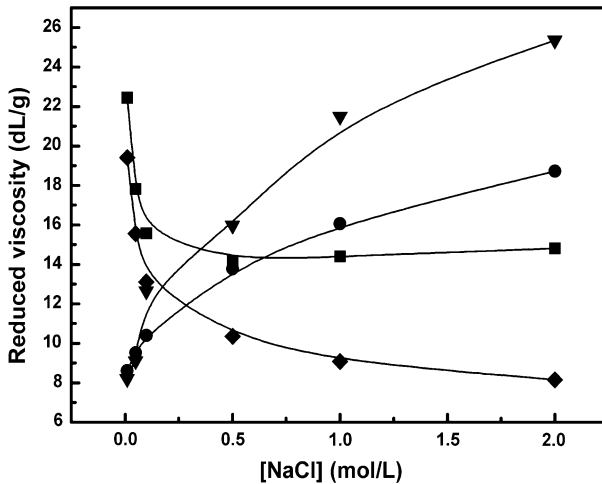

Fig. 7 Effect of [NaCl] on reduced viscosity at polymer concentration of 0.03 g/dL. *Filled square* AAQ-3-0, *filled circle* AAQ-3-1 (pH 2.51), *filled inverted triangle* AAQ-3-3, *filled diamond* AAQ-0-3

from anionic charges. The reduced viscosity maintains to a definite value when salt concentration is above 1.0 mol/L. These behaviors are typical polyelectrolyte effect.

The curve of AAQ-0-3 has the similar shape as that of AAQ-3-0 due to net charges in copolymeric structure. However, the drop in viscosity of AAQ-0-3 is greater than that of AAQ-3-0 at the high concentration of NaCl because AAQ-0-3 is not only a cationic polyelectrolyte but also a hydrophobically associating polymer. The strong polarity from a large amount of NaCl promotes the formation of intramolecular hydrophobic association, further reduces the hydrodynamics volume.

The evolution of the relationship between reduced viscosity and NaCl concentration of AAQ-3-3 and AAQ-3-1 at IEPs is entirely opposite to those of AAQ-3-0 and AAQ-0-3. On the one hand, chain conformation extends as the salt concentration increases owing to the shielding attractive electrostatic force. On the other hand, the spreading chains build up large hydrodynamics volume and make it difficult to form the intramolecular association. As a result, reduced viscosity enhances with increment of NaCl concentration. This behavior is similar to anti-polyelectrolytes effect or polyampholyte behavior [24].

Semi-dilute solution properties

As mentioned above, intramolecular association is dominant in the hydrophobic association at low polymer concentration, especially below the cac. In the semi-dilute regime but not in entanglement regime, three-dimensional physical network is mainly caused by intermolecular association. Steady-shear flow and viscoelasticity experiments are used to illuminate that the viscosity of AAQ-3-3 is enhanced in NaCl solutions and ^{1}H NMR relaxation time (T_2) shows that the formation of hydrophobic association varies in the aqueous and NaCl solutions.

Flow curve Figure 8 obtained from shear flow experiments reveals steady-shear viscosity as a function of shear rate for AAQ series at concentration of 2 g/dL in aqueous semi-dilute solution.

The viscosity of AAQ-3-0 is low and exhibits Newtonian fluid behavior: there is no obvious variation of viscosity with shear rate. The viscosity of AAQ-0-3 is the highest and immediately deceases with increasing of shear rate. This shear-thinning phenomenon is the characteristic of three-dimensional network formed by intermolecular association [25].
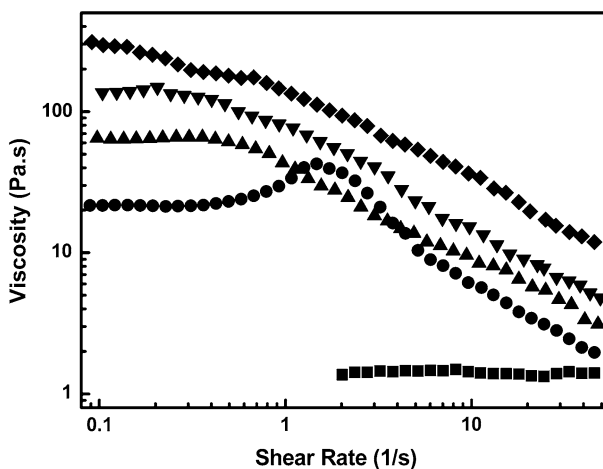

Fig. 8 Flow curves for AAQ series at 2 g/dL in aqeous solution. *Filled square* AAQ-3-0, *filled circle* AAQ-3-1, *filled triangle* AAQ-3-2, *filled inverted triangle* AAQ-3-3, *filled diamond*: AAQ-0-3

As far as the terpolymers (AAQ-3-3, AAQ-3-2, and AAQ-3-1) are concerned, the viscosities become lower as the content of the hydrophobic monomer decreases. AAQ-3-3 and AAQ-3-2 possess the shear-thinning feature similar to AAQ-0-3. Seen from Fig. 8, all the curves of samples with AMQC12 have platform at low shear rate regime following the shear-thinning. The difference lies in that the shear rate corresponding to the onset of shear-thinning is larger when the viscosity is lower. In other words, the length of platform increases as the viscosity decreases. High viscosity is caused by weak physical network, which is formed by intermolecular associations. The higher the viscosity is, the more intermolecular associations dominate, and the lower shear rate is needed to destroy the physical network [25]. The viscosity of AAQ-3-3 is higher than that of AAQ-3-1 at high shear rate because the shear rate of $50 \ s^{-1}$ is not sufficient to break the intermolecular associations [11].

It is noted that the viscosity of AAQ-3-1 increases at a definite shear rate before shear-thinning regime. This shear thickening behavior is the sign for existence of intramolecular association [19, 25]. Shearing force spreads chains and induces intermolecular association. Further shearing destroys the intermolecular association and the viscosity drops dramatically finally. AAQ-3-3 and AAQ-3-2 have no shear thickening behavior because the ratio of intramolecular association decreases as the content of AMQC12 increases.

Figure 9 shows the flow curves of AAQ-3-3 at 2 g/dL in aqueous and NaCl solutions. Before viscosity drops dramatically, there is a platform of viscosity at low shear rate. The platform is deemed to the zero-shear viscosity (η_0) [26]. The η_0 increases as the NaCl concentration increases, shown in Fig. 9. The η_0 of AAQ-3-3 in 1 mol/L NaCl solution reaches 620 Pa s, while that of AAQ-3-3 in aqueous solution is only 140 Pa s. The reason of viscosity enhancement in NaCl solution is that a large amount of NaCl screens the attractive electrostatic forces and extended
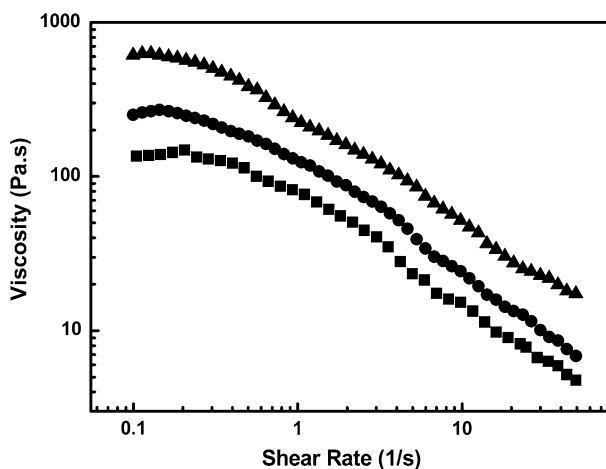

Fig. 9 Flow curve of AAQ-3-3 at polymer concentration of 2 g/dL in water and NaCl solutions. *Filled square* in water, *filled circle* in 0.1 M NaCl, *filled triangle* in 1 M NaCl
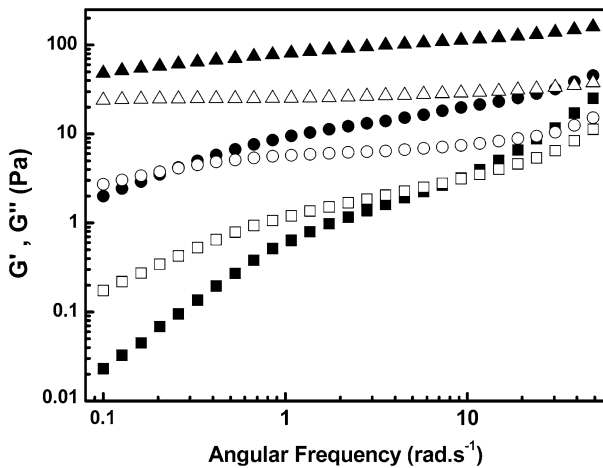
Fig. 10 Storage modulus and loss modulus at a shear stress of 1 Pa of AAQ-3-3 at polymer concentration of 2 g/dL in water and NaCl solutions. *Filled square G′* in water, *open square G″* in water, *filled circle G′* in 0.1 M NaCl, *open circle G″* in 0.1 M NaCl, *filled triangle G′* in 1 M NaCl, *open triangle G″* in 1 M NaCl

chains not only augment the hydrodynamic volume but also promote a large amount of intermolecular hydrophobic interactions. Meantime, the high ionic strength reduces the solubility of the hydrophobic units and enhances the tendency of hydrophobic association [27]. In addition, the greater the zero-shear viscosity, the higher shear rate of the transition is. The same results were mentioned above.

Viscoelasticity Dependences of storage modulus ($G′$) and loss modulus ($G″$) on angular frequency are used to characterize the viscoelastic behavior of semi-dilute polymer solutions, where $G′$ and $G″$ reflect the elastic and viscous behavior of the polymer solution, respectively. Storage modulus ($G′$) and loss modulus ($G″$) on angular frequency of AAQ-3-3 in different solutions at 2 g/dL are measured at a shear stress of 1 Pa and shown in Fig. 10.

For the 1 mol/L NaCl solution of AAQ-3-3, the value of $G′$ is higher than that of $G″$ over the entire angular frequency range studied and both of them are virtually independent of angular frequency. These indicate that AAQ-3-3 in 1 mol/L NaCl solution at 2 g/dL behaves as gel [28, 29]. $G′$ and $G″$ all decrease in water and become more frequently dependent and those value in 0.1 mol/L NaCl solution are between the values in aqueous solution and in 1 mol/L NaCl solution. The elastic response is more dominated in 1 mol/L NaCl solution than that in aqueous solution and in 0.1 mol/L NaCl solution. That is, the higher the polarity of polymer solution is the more strongly the hydrophobic domains forms.

There are crossover points of $G′$ and $G″$ curves in aqueous solution and 0.1 mol/L NaCl solution. Above the angular frequency of crossover, the value of $G′$ is higher than that of $G″$. The angular frequency corresponding to crossover in 0.1 mol/L NaCl solution is lower than that in water and no crossover of curve in 1 mol/L NaCl solutions occurs in the range of angular frequency studied. The fact once again proves that AAQ-3-3 in NaCl solution behaves like a highly elastic gel [30].

Sample solution	T_2 (ms)	
	Component(1)	Component(2)
In water	80 ± 1	4707 ± 5
In 0.1 M NaCl	46 ± 3	4745 ± 7
In 1 M NaCl	34 ± 3	4761 ± 8

Table 2 ^{1}H NMR relaxation time of AAQ-3-3 in water and NaCl solutions

Polymer concentration is 1 g/dL

Relaxation time ^{1}H NMR techniques provide a useful tool to investigate local motions of polymer chains. The spin–spin relaxation times (T_2) offer available information about the association phenomena of HAWPs. The spin–spin relaxation times (T_2) decreases as the molecular motion decreases, thus it can offer available information about the association phenomena of HAWPs.

^{1}H NMR relaxation times of AAQ-3-3 at 1 g/dL (above cac) in different solutions are shown in Table 2. The long spin–spin relaxation time (T_2) of second component belongs to protons in the main chains because of the flexibility of backbone and the short T_2 of first component comes from the protons of the long alkyl chains [31].

The short T_2 is 80 ms in aqueous solution and reduces to 46 ms and 34 ms in 0.1 M and 1 M NaCl solution, respectively. The shorter T_2 in more strongly polar medium indicates that molecular motion is restricted by hydrophobic domains, which is formed by the pendent alkyl groups of the AMQC12 unit in open chain conformations.

It is notable that the proton content obtained by measurement corresponding to short T_2 is about 17.0%. According to this, the short T_2 belongs to the protons in the $-C_{12}H_{25}$ carbon chain of AMQC12 because the protons of $-C_{12}H_{25}$ carbon chain are 18.52% of all protons in AAQ-3-3, which is similar to 17.0%.

Conclusions

A series of hydrophobically associating polyampholytes with acrylamide, acrylic acid, and dimethyldodecyl(2-acry1amidoethyl)ammonium bromide have been prepared by the free radical polymerization in aqueous solution. Polymer composition studied by ^{1}H NMR and ^{13}C NMR is in agreement with the feed ratio. Intrinsic viscosity and molecular weight determinations indicate that the samples of AAQ series are comparable with solution properties.

The relationship between apparent viscosity and polymer concentration was investigated to determine the critical association concentrations (cacs) of AAQ series. The higher the content of hydrophobic units, the lower the cac is. AAQ-3-3 has greater cac than AAQ-0-3 because of the collapsed chain conformation as a result of electrostatic attraction among the molecular chains.

The apparent viscosities and the formation of hydrophobic domains of AAQ series below cacs are seriously affected by the chains conformations, which are

changed by the variation of pH and [NaCl]. The terpolymers of AAQ series (especially AAQ-3-3) at isoelectric points (IEPs) exhibit constrictive chain conformation, which results in the strong tendency of intramolecular associating and the low hydrodynamic volume. The viscosities of these polymer solutions increase with addition of NaCl, so-called anti-polyelectrolyte effect, because of shielding the electrostatic attraction and weakening intramolecular association. Effect of pH on hydrophobic association is also proved by pyrene fluorescence probe technique.

Steady-shear flow curves of AAQ series above cacs show that the zero-shear viscosities increase with increasing content of hydrophobes. It is attributed to the stronger physical network formed by intermolecular hydrophobic association arisen from the higher hydrophobic units. The steady-shear viscosities and storage modulus and loss modulus of AAQ-3-3 in different solutions show that the AAQ-3-3 in salt media possesses very high viscosity and behaves as gel. Viscosity enhancement in salt media of AAQ-3-3, which has same amount of opposite charges in water, is due to the large hydrodynamic volume and strong intermolecular association. The formation of hydrophobic domains is also validated by the ^{1}H NMR relaxation time.

In general, solution properties of AAQ series are pH-responsive and salt-sensitive. More importantly, AAQ-3-3 possesses particular viscosity enhancement in salt media.

References

1. Ye L, Huang R, Wu J, Hoffmann H (2004) Synthesis and rheological behavior of poly[acrylamide–acrylic acid–N-(4-butyl)phenylacrylamide] hydrophobically modified polyelectrolytes. Colloid Polym Sci 282:305–313
2. Mylonas Y, Bokias G, Iliopoulos I, Staikos G (2006) Interpolymer association between hydrophobically modified poly(sodium acrylate) and poly(N-isopropylacrylamide) in water: the role of hydrophobic interactions and polymer structure. Eur Polym J 42:849–857
3. Peiffer DG (1990) Hydrophobically associating polymers and their interactions with rod-like micelles. Polymer 31:2353–2360
4. Camail M, Margaillan A, Martin I (2009) Copolymers of N-alkyl- and N-arylalkylacrylamides with acrylamide: influence of hydrophobic structure on associative properties. Part I: viscometric behaviour in dilute solution and drag reduction performance. Polym Int 58:149–154
5. Turner SR, Siano DB, Bock J (1985) Micellar process for the production of acrylamide-alkyl acrylamide copolymers. U.S. Patent 4 528 348
6. Lacik I, Selb J, Candau F (1995) Compositional heterogeneity effects in hydrophobically associating water-soluble polymers prepared by micellar copolymerization. Polymer 36:3197–3211
7. Hill A, Candau F, Selb J (1993) Properties of hydrophobically associating polyacrylamides: influence of the method of synthesis. Macromolecules 26:4521–4532
8. Candau F, Selb J (1999) Hydrophobically-modified polyacrylamides prepared by micellar polymerization. Adv Colloid Interface Sci 79:149–172
9. Gao BJ, Jiang LD, Kong DL (2007) Studies on rheological behaviour of hydrophobically associating polyacrylamide with strong positive salinity sensitivity. Colloid Polym Sci 285:839–846

10. Summers M, Eastoe J (2003) Applications of polymerizable surfactants. Adv Colloid Interface Sci 100–102:137–152
11. Yang QB, Chen Q, Tan Y, Song CL, Wang PX (2008) Synthesis and aqueous solution properties of hydrophobically modified anionic acrylamide copolymers. J Polym Sci B 46:2465–2474
12. Gao BJ, Jiang LD, Liu KK (2007) Microstructure and association property of hydrophobically modified polyacrylamide of a new family. Eur Polym J 43:4530–4540
13. Wu HW, Kawaguchi S, Ito K (2004) Synthesis and polymerization of tail-type cationic polymerizable surfactants and hydrophobic counter-anion induced association of polyelectrolytes. Colloid Polym Sci 282:1365–1373
14. Watterson AC, Hunter CR, Thompson AM, Salamone JC (1991) Study of hydrophobic effects in ampholytic ionomer systems. Am Chem Soc Div Polym Chem 32:126–127
15. Huang ZY, Lu HS, He Y (2006) Amphoteric hydrophobic associative polymer: I synthesis, solution properties and effect on solution properties of surfactant. Colloid Polym Sci 285:365–370
16. Umar Y, Al-Muallem HA, Abu-Sharkh BF, Ali SA (2004) Synthesis and solution properties of hydrophobically associating ionic polymers made from diallylammonium salts/sulfur dioxide cyclocopolymerization. Polymer 45:3651–3661
17. Miyazawa K, Winnik FM (2003) Solution properties of hydrophobically-modified phosphorylcholine-based polymers in water and in the presence of surfactants. J Phys Chem B 107:10677–10682
18. Santos-Rosas R, Licea-Claverie A, Arndt K (2006) Statistical copolymers of methacrylic acid derivatives with hydrophobic spacers and N,N′-dimethylaminoethylmethacrylate: new associating polyampholytes. J Mexican Chem Soc 50:164–174
19. Kujawa P, Rosiak JM, Selb J, Candau F (2001) Micellar synthesis and properties of hydrophobically associating polyampholytes. Macromol Chem Phys 202:1384–1397
20. Baskar G, Chandrasekar K, Reddy BSR (2004) Associated structures of aqueous solution of comblike polymers from 2-acrylamido-2-methyl-1-propanesulfonic acid, dodecylmethacrylate and poly(ethyleneglycol) acrylate macromonomer. Polymer 45:6507–6517
21. Ng WK, Tam KC, Jenkins RD (1999) Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions. Eur Polym J 35:1245–1252
22. Petit-Agnely F, Iliopoulos I, Zana R (2000) Hydrophobically modified sodium polyacrylates in aqueous solutions: association mechanism and characterization of the aggregates by fluorescence probing. Langmuir 16:9921–9927
23. Fevola MJ, Bridges JK, Kellum MG, Hester RD, McCormick CL (2004) pH-responsive ampholytic terpolymers of acrylamide, sodium 3-acrylamido-3-methylbutanoate, and (3-acrylamidopropyl)-trimethylammonium chloride. I. Synthesis and characterization. J Polym Sci A 42:3236–3251
24. Ezell RG, McCormick CL (2007) Electrolyte- and pH-responsive polyampholytes with potential as viscosity-control agents in enhanced petroleum recovery. J Appl Polym Sci 104:2812–2821
25. Rogalado EJ, Selb J, Candau F (1999) Viscoelastic behavior of semidilute solutions of multisticker polymer chains. Macromolecules 32:8580–8588
26. Kujawa P, Audibert-Hayet A, Selb J, Candau F (2006) Effect of ionic strength on the rheological properties of multisticker associative polyelectrolytes. Macromolecules 39:384–392
27. Volk N, Vollmer D, Schmidt M, Oppermann W, Huber K (2004) Polyelectrolytes with defined molecular architecture II; advances in polymer science, vol 166. Springer, Berlin, Heidelberg, New York, pp 29–65
28. Kujawa P, Audibert-Hayet A, Selb J, Candau F (2004) Rheological properties of multisticker associative polyelectrolytes in semidilute aqueous solutions. J Polym Sci B 42:1640–1655
29. Xue W, Hamley IW, Castelletto V, Olmsted PD (2004) Synthesis and characterization of hydrophobically modified polyacrylamides and some observations on rheological properties. Eur Polym J 40:47–56
30. Kujawa P, Audibert-Hayet A, Selb J, Candau F (2003) Compositional heterogeneity effects in multisticker associative polyelectrolytes prepared by micellar polymerization. J Polym Sci A 41:3261–3274
31. Yusa S, Sakakibara A, Yamamoto T, Morishima Y (2002) Reversible pH-induced formation and disruption of unimolecular micelles of an amphiphilic polyelectrolyte. Macromolecules 35:5243–5249