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ORIGINAL PAPER

Synthesis and solution properties of novel comb-shaped acrylamide copolymers

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Abstract An amphiphilic macro-monomer of allyl polyoxyethylene-12 ether with butyl-end group ($AE_{12}B$) was synthesized, and its chemical structure was characterized. $AE_{12}B$ and the other two macro-monomers with different hydrophobic and hydrophilic groups were copolymerized with acrylamide to prepare the novel comb-shaped acrylamide copolymer (CPAM) through aqueous free radical polymerization. The solution properties of CPAM with different side-chain lengths were studied and compared with those of partially hydrolyzed polyacrylamide (HPAM). The experimental results show that the obtained CPAM, compared to HPAM, exhibited a dramatic enhancement in the heat- and salt-resistant properties. In addition, the increase of the side-chain length and the amount of hydrophobic groups in the side-chain improved the thickening properties of CPAM solution under high temperature and high mineralization conditions. Among the investigated macro-monomers, $AE_{12}B$ was optimized for the enhanced thickening properties of the CPAM solution.

Keywords Acrylamide copolymer · Comb-shaped polymer · Solution properties · Heat- and salt-resistance

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Introduction

Partially hydrolyzed polyacrylamide (HPAM) has been one of the most widely used polymers in polymer flooding, and its application in oil fields has become an important technology for enhanced oil recovery [1–3]. However, there are many drawbacks in the practical use of HPAM including poor heat- and salt-resistant properties, which limit their applications in high temperature and high mineralization oil fields [4]. For the past several decades, a large number of researches have been done in order to overcome these shortcomings. Luo et al. [5, 6] reported a novel polymer-thickening agent made up of comb-shaped acrylamide copolymers (CPAM) and discovered that its thickening ability is 50% greater than that of HPAM in salt solution, which was attributed to the more perfect net microstructure of CPAM. Moreover, the CPAM also possessed excellent salt-resistant and oil displacement efficiency. Hence, CPAM became a high-efficiency polymer flooding agent for the enhanced oil recovery.

Comb-shaped polyacrylamide is a kind of polymer with lipophilic and hydrophilic groups at the same side-chain [7, 8]. The amphiphilic chain comprising the lipophilic group of polyoxyethylene (POE) and the hydrophilic group of alkyl has been widely investigated because of their unique and facilely adjustable molecular structure [9, 10]. In this article, an amphiphilic macro-monomer of allyl POE ether with alkyl-end group (AE_nA, as shown in Scheme 1) was synthesized with allyl polyoxyethylene ether and chloralkane. The obtained macro-monomer was characterized by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) techniques. Three macro-monomers AE_nA with different hydrophobic or hydrophilic groups were then copolymerized with acrylamide to prepare a series of novel CPAMs with different side-chain lengths using the free radical polymerization. The chemical structure of CPAM prepared was characterized, and their solution properties were studied and compared with those of HPAM. The objective of this study was to develop a novel comb-shaped polyacrylamide containing the lipophilic and hydrophilic groups in the same side-chain for potential enhanced oil recovery application in oil reservoirs with the high temperature and high mineralization.

Experimental

Materials

Raw materials including chloralkane, toluene, sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium hydrogen sulfite ($NaHSO_3$), potassium

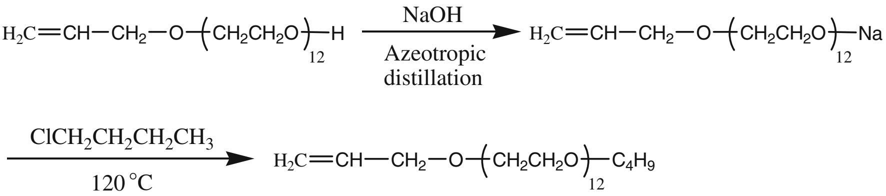
$$H_2C{=}CH{-}CH_2{-}O{-}\left(CH_2CH_2O\right)_n{-}R$$

Scheme 1 Chemical structure of macro-monomer allyl polyoxyethylene ether with alkyl-end group (AE_nA)

peroxydisulfate ($K_2S_2O_8$), anhydrous calcium chloride ($CaCl_2$), and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acrylamide (AM) was purchased from Sigma-Aldrich Co. Ltd (St. Louis, MO, USA). The above chemicals were used as received. Allyl polyoxyethylene-12 ether (AE_{12}, molecular weight (M_W) = 586), Allyl polyoxyethylene-12 ether with methyl-end group ($AE_{12}M$, $M_W = 600$), and Allyl polyoxyethylene-8 ether with methyl-end group (AE_8M, $M_W = 424$) were obtained from Yangzhou Chenhua Group Co., Ltd (Jiangsu, China). These macro-monomers were purified with magnesium silicate adsorbent and then were distilled to eliminate water. The water for all experiments was distilled water.

Synthesis of macro-monomer

The macro-monomer, allyl polyoxyethylene-12 ether with butyl-end group ($AE_{12}B$), was synthesized according to the procedure described in the previous report [11]. A typical procedure for synthesizing $AE_{12}B$ with allyl polyoxyethylene-12 ether and 1-chrolobutane is depicted in Scheme 2. 0.1 mol of allyl polyoxyethylene-12 ether and 200 mL toluene were placed in a 500-mL reaction vessel and the mixture was dehydrated by azeotroping. 0.15 mol pulverized potassium hydroxide was added and the temperature was raised to reflux. Water was removed by the azeotropic distillation. The reaction mixture was cooled to 60 °C and 0.2 mol of 1-chrolobutane was added carefully. The mixture was then heated to 120 °C for 4 h. The mixture was finally transferred to a rotary evaporator where the toluene was removed under a 760-mm vacuum at 110 °C temperature. Once the toluene was removed, the finished product was filtrated and left to cool. The liquid allyl polyoxyethylene ether with butyl-end group ($AE_{12}B$) was obtained. The crude product was purified with magnesium silicate adsorbent and then was distilled to eliminate water. The yield of $AE_{12}B$ was 72.3 wt%. The hydroxyl value (HV) of AE_{12} and $AE_{12}B$ was determined by the phthalic anhydride method for non-ionic surface active agents based on Chinese National Standard GB/T 7383-1997. The hydroxyl value for AE_{12} and $AE_{12}B$ was 96.7 and 5.4 KOH mg g^{-1}, respectively. Thus, the closed-end rate of macro-monomer $AE_{12}B$ was 94.4%.



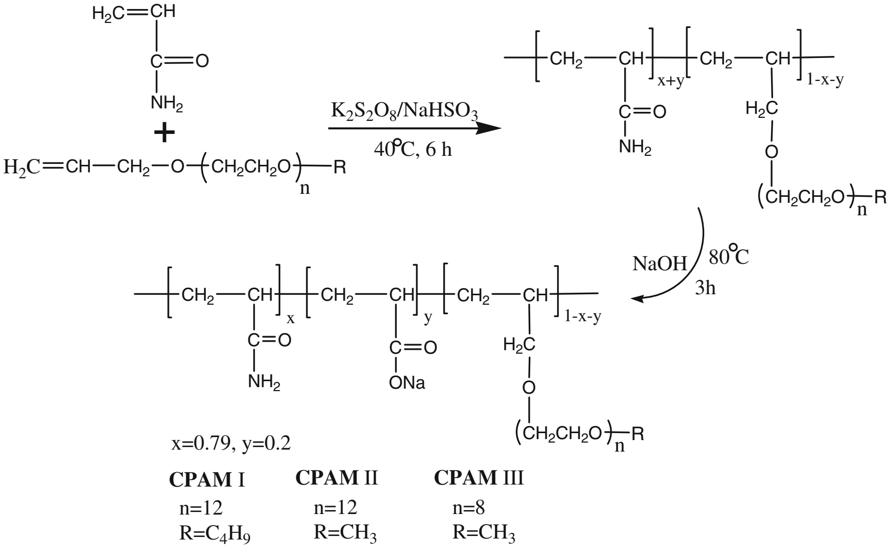
Scheme 2 Synthesis of macro-monomer allyl polyoxyethylene-12 ether with butyl-end group ($AE_{12}B$)

Preparation of comb-shaped acrylamide copolymer (CPAM)

CPAM was prepared by an aqueous solution polymerization technique using $K_2S_2O_8$/$NaHSO_3$ redox system as initiator. The monomers containing AM and macro-monomers were dissolved in distilled water to give a 20 wt% solution in a three-neck round-bottom glass reactor. Nitrogen gas was bubbled through the reaction mixture for 30 min at 15 °C. Then 0.4 wt% $K_2S_2O_8$ and 0.8 wt% $NaHSO_3$ by monomer in solution were added dropwise to the reaction mixture. The reaction temperature was raised to 40 °C and kept at this temperature for 6 h. With the formation of the polymer, the reaction mixture became highly viscous and finally formed the gel. The polymer gel was cut into small pieces and hydrolyzed with NaOH solution for 3 h at 80 °C according to the 20 wt% of hydrolysis degree (HD). The final mixtures were precipitated in excess of acetone and washed three times by acetone to remove the residual monomers. Finally, the polymers were dried under vacuum at 50 °C for more than 24 h to a constant weight and then were milled using a high-speed grinder. The powdered samples with particle size between 80 and 120 meshes were used for the characterization and measurement. The CPAMs used in this experiment were labeled as CPAM I, CPAM II, and CPAM III, respectively, as shown in Scheme 3. For comparison, partially hydrolyzed polyacryamide was also prepared under the same experimental conditions without using the macro-monomer.

Characterizations

FTIR spectra of the macro-monomers were obtained on a Nicolet FTIR analyzer 5700 (Thermo Fisher Scientific Inc., Waltham, MA, USA) with liquid pool. FTIR



Scheme 3 Preparation, chemical structure, and nomenclature of CPAM

spectra of polymer were obtained using KBr disks. ^{1}H-NMR spectrum of macro-monomer was recorded on a Bruker AMX 400 MHz spectrometer (Bruker Optics Inc., Billerica, MA, USA) using CDCl as solvent. The intrinsic viscosities of polymer were measured by a 0.6 mm NCY automatic Ubbelohde capillary viscometer (Shanghai Sikeda scientific instruments Inc., Shanghai, China) at 30.0 ± 0.1 °C with 1 mol L^{-1} sodium chloride (NaCl) as solvent. Elemental analysis of all polymer samples was carried out with an elementary analyzer (Elementar Vario EL-III, Elementar Analysensysteme GmbH, Hanau, Germany). The HD of HPAM and CPAM were determined by titrimetric method according to the Chinese National Standard GB/T 12005.6-89 for the HD of HPAM.

Viscosity measurements

The apparent viscosities of polymer solutions were measured by a Brookfield DV-III ultra rheometer (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) with a YULA-15E spindle rotor at the shear rate of 7.34 s^{-1}. The temperature was controlled using a specially designed water bath, where the water circulated around the measuring stainless steel cup. All polymer solutions for viscosity measurement were made with simulated brine. The simulated brine consisted of 222 mg L^{-1} of $CaCl_2$ and 234 mg L^{-1} of $MgCl_2 \cdot 6H_2O$.

Results and discussion

Characterization of macro-monomer

Figure 1 shows the FTIR spectra of $AE_{12}B$ and AE_{12}. The characteristic peak at 3490 cm^{-1} for AE_{12}, assigned to the stretching vibration of –OH in the end

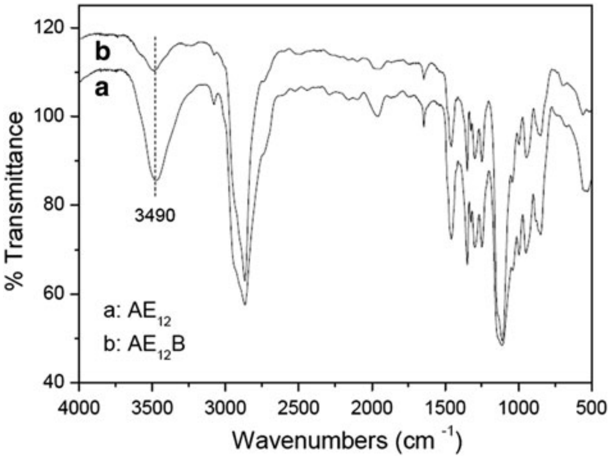


Fig. 1 FTIR spectra of AE_{12} (*a*) and $AE_{12}B$ (*b*)

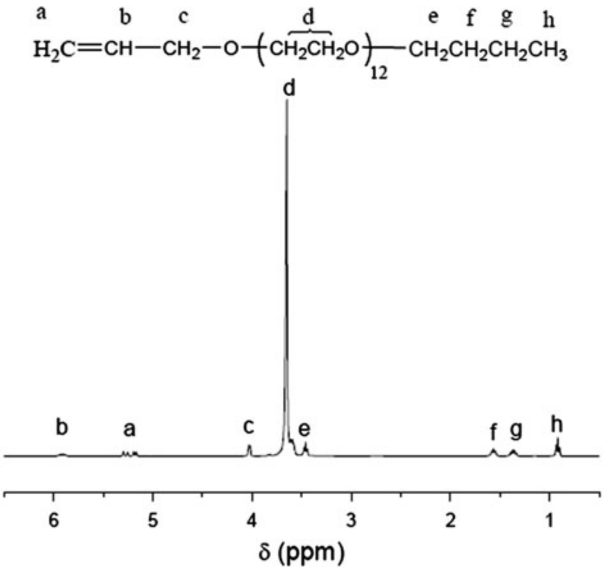


Fig. 2 ^{1}H-NMR spectrum of macro-monomer $AE_{12}B$

hydroxyl groups, significantly diminished in the $AE_{12}B$, which was in a good agreement with the closed-end rate calculated by the hydroxyl value. The result suggests that –OH group of AE_{12} likely reacted with the 1-chrolobutane, as shown in Scheme 2. Moreover, the spectra of $AE_{12}B$ displayed no distinguishable difference in the remaining band positions compared with that of AE_{12}, which indicated that the allyl and ethoxyl groups of macro-monomer were not destroyed throughout the drastic reaction. Further characterization such as ^{1}H-NMR spectra was performed to confirm such $AE_{12}B$ structure.

^{1}H-NMR spectra of $AE_{12}B$ is shown in Fig. 2. The spectrum of $AE_{12}B$ had eight characteristic peaks, which were eight kinds of hydrogen atoms attributed to different groups of $AE_{12}B$, as shown in Fig. 2. In addition, the integral area under every peak, which suggests the content of corresponding H atom, was calculated as follows: a:b:c:d:e:f:g:h = 2:0.92:2.08:50.02:2.28:2.10:2.10:2.10:3.04, which were in a good agreement with those theoretical value (a:b:c:d:e:f:g:h = 2:1:2:48:2:2:2:2:3). The results further proved the chemical structure of observed AEBE.

Characterization of CPAM

From Table 1, it can be seen that the intrinsic viscosities [η] for HPAM, CPAM I, CPAM II, and CPAM III in 1 mol L^{-1} NaCl solution at 30.0 ± 0.1 °C were 13.6, 12.7, 13.0, and 13.2 dL g^{-1}, respectively. This result suggests that the increase of polymer chain during polymerization process was hindered by the macro-monomer and its molecular weight decreased slightly with the increased side-chain length. Elementary analysis of all samples is also summarized in Table 1. The experimental

Table 1 Intrinsic viscosities, element analysis, and hydrolyzed degree of polymer

Sample	[η] (dL g^{-1})	Calculated value			Found value			HD (%)
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)	
PAM	13.6	47.62	6.08	14.81	46.89	6.43	14.94	19.6
CPAM I	12.7	48.41	6.36	13.60	47.77	6.63	13.75	19.0
CP AM II	13.0	48.21	6.32	13.67	47.72	6.55	13.84	19.1
CPAM III	13.2	45.55	6.26	13.98	45.01	6.49	14.06	19.3

values for all polymers were in a good agreement with their calculated values, indicating the macro-monomer copolymerized effectively with acrylamide and the compositions of CPAM is accordant with the description of Scheme 3. The nitrogen content of produced polymers was higher than their calculated value because of some incomplete hydrolysis of NH_2 group such as imidization [12], as shown in Table 1 about the measured results of HD. It was well known that the alkaline hydrolysis was the most frequently used approach to prepare the partially hydrolyzed polyacrylamide. However, it still is impossible to achieve 100% sodium polyacrylate by the reaction between the polyacrylamide and the added NaOH even at long reaction time [13, 14]. Hence, the measured HD of all samples only was closed to the expected HD. From the HD results, it also can be seen that HD of CPAM increases with the decreased polymer side-chain.

FTIR spectra of HPAM and CPAM are presented in Fig. 3. The HPAM curve had a broad band around 3450 cm^{-1} due to the stretching vibration of N–H. The characteristic peaks at 1655 and 1560 cm^{-1} were attributed to the carboxylate and

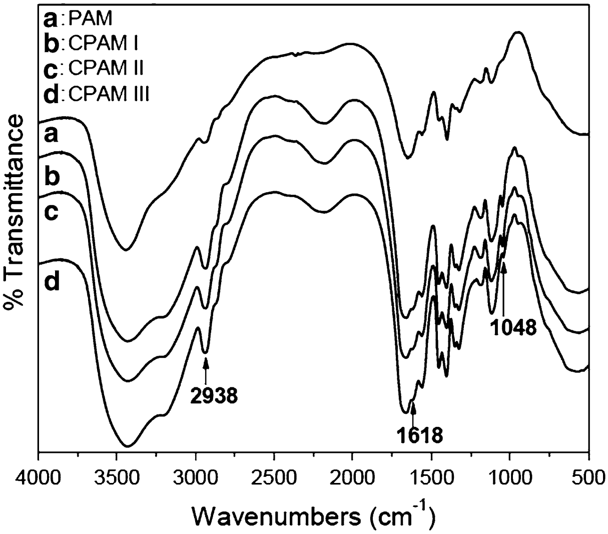


Fig. 3 FTIR spectra of HPAM (*a*), CPAM I (*b*), CPAM II (*c*), and CPAM III (*d*)

amide group [13], respectively. Compared to the spectra of HPAM, the spectrum of CPAM showed the obvious absorption peak at 2938 and 1048 cm^{-1} result from the C–O–C stretching vibration of ethoxy group. This result further confirms that macro-monomer was copolymerized with AM. In addition, the intensity of peak at 1048 cm^{-1} for CPAM improved as the length of ethoxy group in the macro-monomer increase. It can be observed that the absorption peaks at 1618 cm^{-1} (amide group) appeared in CPAM. This phenomenon was due to the macro-monomer with large size reducing the efficiency of post hydrolysis, which was proven by the hydrolyzed degree (HD) in Table 1.

Solution properties of CPAM

Figure 4 shows the variation of apparent viscosity (μ_a) for polymer brine solution with the polymer concentration at 35 °C. It can be seen from Fig. 4 that the solution viscosity of all CPAMs are much higher than that of HPAM in the 500–2500 mg L^{-1} concentration range, which can be attributed to the steric hindrance and intermolecular association of side-chains for CPAM. The μ_a of 2500 mg L^{-1} solution was 74.59, 109.39, 94.7, and 87.5 mPa s for HPAM, CPAM I, CPAM II, and CPAM III, respectively. Thus, the μ_a of CPAM I solution among all CPAM solutions at 2500 mg L^{-1} concentration was the highest and was up by 46.7% compared to that of HPAM. The difference in viscosity among CPAM I, CPAM II, and CPAM III indicates that the increase of length and hydrophobic groups in CPAM side-chain can obviously improve the viscosity of the polymer in the brine because of the longer side-chain and stronger association [15] preventing the curliness of polymer. Therefore, the above-mentioned results suggest that the amphiphilic side-chain can effectively enhance the salt-resistant properties of polymer, and the chemical structure of CPAM I was optimized among three comb-shaped acrylamide copolymers for the improved thickening properties in brine.

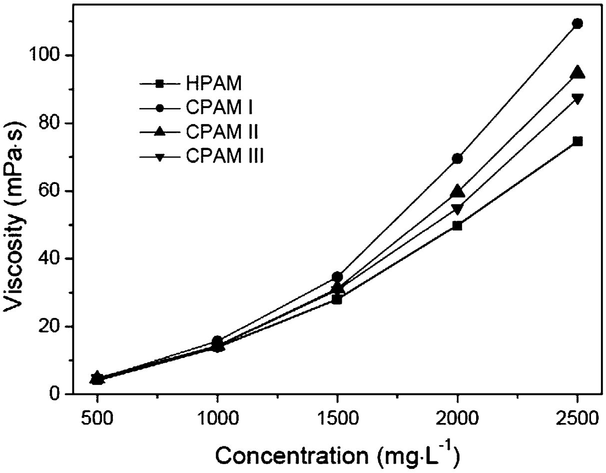


Fig. 4 Variation of the viscosity with the polymer concentration in brine at 35 °C

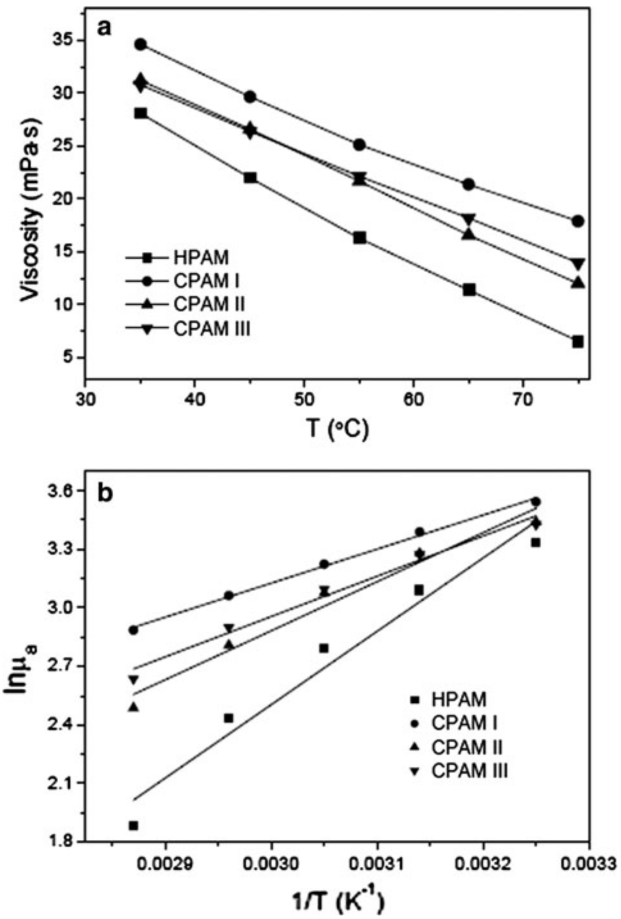


Fig. 5 **a** Variation of the viscosity for polymer brine solution with the temperature at 1500 mg L^{-1} polymer concentration. **b** Relationship between ln μ_a and 1/T

Figure 5a shows the influence of temperature on the viscosity of 1500 mg L^{-1} polymer brine solution. As shown in Fig. 5a, the viscosity of all polymer solutions decreased with the increase of temperature, which can be attributed to the weakening of intermolecular association and electrostatic repulsion with increased temperature. In order to accurately determine the heat-resistant properties of polymer, the activation energy of viscous flow was calculated by the Arrhenius equation:

$$\mu_a = A \cdot \exp(E_a/RT) \tag{1}$$

After taking the natural logarithm, Eq. 1 became:

$$\ln\mu_a = \ln A + E_a/RT \tag{2}$$

where, E_a ($J\ K^{-1}$) is the activation energy of viscous flow, μ_a (mPa s) is the apparent viscosity of polymer solution, A (mPa s) is the pre-exponential factor, R is the absolute temperature (K), and T is the gas constant ($8.314\ J\ K^{-1}\ mol^{-1}$). According to Fig. 5a and Eq. 2, the relationship chart between ln μ_a and $1/T$ is showed in Fig. 5b. It can be calculated from Fig. 5b that E_a for HPAM, CPAM I, CPAM II, and CPAM III were 31.3, 14.5, 20.9, and 17.2 kJ K^{-1}, respectively. The higher the activation energy was, the weaker the heat resistance of polymer was. Hence, the results suggest that the heat-resistant properties of CPAM were better than that of HPAM likely because of the intermolecular association of hydrophobic groups existed in CPAM. Moreover, with the decrease of hydrophobic groups or the increase of hydrophilic groups in CPAM side-chain, E_a of CPAM reduced. It indicates that the effect of intermolecular association on the solution properties of polymer is more important than that of intermolecular electrostatic repulsion in high temperature. Furthermore, the highest E_a value of CPAM I among all CPAMs suggests that it possessed the optimized thickening properties at high temperature.

Conclusions

An amphiphilic macro-monomer of allyl polyoxyethylene ether with alkyl-end group was synthesized and characterized. The chemical structure of macro-monomer was confirmed, and it copolymerized with acrylamide to form the comb-shaped acrylamide copolymer. Comb-shaped acrylamide copolymers with different side-chain lengths were successfully prepared through the free radical polymerization. The obtained CPAM, compare to HPAM, exhibited a dramatic enhancement in the heat-resistant and salt-resistant properties because of the steric hindrance and intermolecular association of side-chains. In addition, the increase of the length of side-chain and the amount of hydrophobic groups in side-chain improved the solution stability of CPAM in high temperature and high mineralization conditions. Among the investigated CPAMs, CPAM prepared from $AE_{12}B$ possesses the optimized thickening properties. In considering the excellent solution properties of novel comb-shaped acrylamide copolymer, it can be potentially used as the thickening agent for drilling fluid in addition to the oil-displacing agent.

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