

Synthesis and Solution Properties of Hydrophobically Associative Polyacrylamides by Microemulsion Polymerization

Tao Wan · Chuzhang Zou · Liyi Chen · Zhiling Zhou ·
Min Xu · Wenzhong Cheng · Ruixiang Li

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Abstract A series of hydrophobic associative copolymers using acrylamide (AM), sodium 4-styrenesulfonate (SSS) and hydrophobic stearyl methacrylate (SMA) as comonomers were prepared by microemulsion polymerization. Factors affecting the rheological properties of the aqueous copolymer solutions, such as the content of hydrophobic monomer, amount of SSS, amount of initiator, amount of sodium dodecyl sulfate, the copolymer concentration and the addition of salt, were investigated. The hydrophobic associative copolymers show good temperature-, shear-, and salt-resistance with the critical aggregation concentration of the copolymers being around $0.4 \text{ g}\cdot\text{dL}^{-1}$. The apparent viscosities of hydrophobic associative copolymer solutions increase as SMA content is increased from 8 to 12 %. The apparent viscosity and temperature resistance of the hydrophobic associative copolymers are enhanced by incorporation of a suitable amount of SSS segments into the polymeric chains. In addition, the apparent viscosities of hydrophobic associative copolymer solutions are increased by the addition of a small amount of NaCl and CaCl_2 . Both the storage modulus and loss modulus of the hydrophobic associative copolymers increase with angular frequency ω and were well fitted by the Maxwell model in the low-frequency region. FTIR and ^1H NMR spectra indicate the structure of hydrophobic associative copolymers. AFM indicated that some aggregates and small network connections between polymeric chains were present.

T. Wan (✉) · L. Chen (✉)

State Key Lab of Geohazard Prevention & Geoenvironment Protection, Chengdu University of Technology, Chengdu 610059, China
e-mail: wantaos@126.com

L. Chen
e-mail: cly@cdut.edu.cn

T. Wan
State Key Lab of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China

T. Wan · C. Zou · Z. Zhou · M. Xu · W. Cheng · R. Li
Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu University of Technology, Chengdu 610059, China

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1 Introduction

Hydrophobically associating water-soluble polymers are hydrophilic polymers modified with a small number of hydrophobic groups, i.e., 8–18 carbon atom moieties [1–4], distributed along the main backbone [5]. They have become of great interest in the past two decades due to their unique rheological behavior resulting from the reversible association/dissociation process of their hydrophobic moieties. In particular, hydrophobically associating polyacrylamide (HAPAM), in which a relatively small amount (generally less than 2 mol%) of hydrophobic groups is incorporated onto the acrylamide (AM) backbone [6, 7], has received increasing attention in oil recovery, drilling fluids, and so on [8–12]. The role of the HAPAM in oil recovery is to increase the viscosity of the aqueous phase, thus improving sweep efficiency during enhanced oil recovery (EOR) processes. The physical links between the associated molecules break under increased shear. Consequently, irreversible mechanical degradation characteristic of high molecular weight polymers in high shear applications can be avoided [13]. This shear thinning behavior is desired for drilling fluids, which can suspend drilling cuttings at low shear rates but offer little resistance to flow at high shear rates [14, 15].

There are different ways to prepare such associating polymers, such as micellar [16, 17], homogeneous [18, 19] and heterogeneous [16] copolymerization. Among these different methods, micellar copolymerization is the most commonly used method [8, 10]. This method is extremely attractive since it allows the preparation of polymers with a hydrophobic microblock structure in which the hydrophobic blocks are of tunable length and number, according to the experimental conditions [9, 15]. As a result, the polymers exhibit higher thickening abilities than those with randomly distributed structures of similar molar mass. However, the initial concentration of the reaction mixture is relatively low and the water solubility of the HAPAM is often poor [12, 20], causing difficulties in practical applications.

Microemulsion polymerization can be used to obtain HAPAM with higher solid content and better water solubility and thus can overcome the problems mentioned above. Lu [21–23] found that HAPAM prepared by inverse microemulsion polymerization had a homogeneous composition and exhibited hydrophobic association interaction in porous media under flowing condition and different retention behavior due to the existence of the hydrophobic association group in the HAPAM molecular frame. Gao [24] prepared three series of hydrophobic block copolymers using AM and styrene (St) as hydrophobic comonomers, SDS as surfactant, and potassium persulfate as the initiator in microemulsion media. The effects of the microstructure of the amphiphilic block copolymers PAM-*b*-PSt on their aqueous solution properties were investigated by the fluorescence probe technique and surface tension measurement.

However, hydrophobic associative copolymers of AM, sodium 4-styrenesulfonate (SSS) and stearyl methacrylate (SMA), by microemulsion polymerization, have not yet been reported. On the basis of our previous research on microemulsion polymerization [25–34], a novel hydrophobic associative copolymer (HPASS), with a relatively high amount of hydrophobic groups (>2 mol%), was prepared by microemulsion polymerization, using

AM, SSS and hydrophobic SMA as co-monomers. Rheological behavior, temperature-, shear-, and salt-resistance of the hydrophobic associative copolymer were investigated in detail. FTIR, ^1H NMR and AFM were used to characterize the structure of the hydrophobic associative copolymers.

2 Experimental

2.1 Materials

Analytical grade AM, purchased from Chengdu Kelong Chemical Co., Ltd. (China), was recrystallized twice with chloroform. Chemical grade SMA, purchased from the Juhua Group Corporation (China), was washed with 20 wt% NaOH solution and then by water three times. Chemical grade SSS, purchased from Zibo Xingzhilian Chemical Co., Ltd. (China), was purified by recrystallization from a 9:1 (v/v) mixture of methanol and water at 60 °C and then dried under vacuum. Analytical grade sodium dodecyl sulfate (SDS) and azobisisbutyronitrile (AIBN), purchased from Chengdu Kelong Chemical Co., Ltd. (China), were used without further purification.

2.2 Preparation of AM-SSS-SMA Hydrophobic Associative Copolymers by Microemulsion Polymerization

A typical synthesis of AM-SSS-SMA hydrophobic associative copolymers (HPASS) by microemulsion polymerization is as follows: 13 g SDS is dissolved in 100 g aqueous AM solution in which the concentration of AM is 10 wt%. Then, 1.5 g SSS and 1.2 g SMA are added and the system stirred at room temperature for 30 min and heated slowly to 70 °C under a nitrogen atmosphere, followed by addition of 35 mg AIBN to the above microemulsion. After 5 h of reaction, the resulting product is washed several times with ethanol to thoroughly remove any trace of surfactant. The polymers obtained are dipped into toluene for 24 h to extract the homopolymer polystyryl methylacrylate, then dried at 60 °C to constant weight and conserved in a desiccator. The weight average molecular weight of the hydrophobic associative copolymers determined with an Ubbelohde capillary viscometer [35] is $1.8 \times 10^6 \text{ g}\cdot\text{mol}^{-1}$.

2.3 Rheological Measurements

The viscosities were measured at temperatures from room temperature to 80 °C and shear rate of 3–80 s^{-1} in deionized water and salt solution, using a NXS-11B rotary rheometer (Chengdu Instrument Factory [China]). Before measurements, polymer solutions were left without agitation for at least 1 day to reach equilibrium.

2.4 FTIR and ^1H NMR Characterization

FTIR spectra were measured on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The dried samples were crushed with KBr to prepare pellets. ^1H NMR experiments were performed in D_2O on a Bruker DRX 600 spectrometer operating at 600 MHz.

2.5 Atomic Force Microscopy

Atomic force microscopy (AFM) images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA, operating in the tapping mode at 0.5–1.5 Hz with a coefficient of elasticity of $40 \text{ N}\cdot\text{m}^{-1}$. Samples were prepared by spin coating $10 \mu\text{L}$ of polymer solutions at a concentration of $0.01 \text{ mg}\cdot\text{mL}^{-1}$ onto mica.

3 Results and Discussion

3.1 FTIR and ^1H NMR Spectra of the AM-SSS-SMA Hydrophobic Associative Copolymer

AM is a highly used hydrophilic monomer and is suitable for the preparation of water-soluble polymers with high molecular weight. SSS, having a strongly hydrophilic and sulfonate charged group, can improve the water solubility of hydrophobic associative copolymers. SMA has a long hydrophobic chain and can form intermolecular interactions. Therefore AM, SSS and SMA were selected as comonomers to synthesize hydrophobic associative copolymers. The mechanism of AM-SSS-SMA microemulsion polymerization first involves the SMA homopolymerization initiated by the oil-soluble initiator within the micelles. Secondly, hydrophobic macroradicals can initiate AM and SSS residing at the oil/water interface and water phase to form AM-SSS-SMA hydrophobic associative copolymers. FTIR and ^1H NMR were used to confirm the chemical structure of the AM-SSS-SMA hydrophobic associative copolymer.

The infrared spectrum of the AM-SSS-SMA hydrophobic associative copolymer synthesized with mass ratios $m(\text{AM}):m(\text{SSS}):m(\text{SMA}) = 10:1.5:1.2$ is displayed in Fig. 1. It can be seen that there are characteristic absorptions of amide groups, including the bands at about $3,451$, $1,668$, and $1,406 \text{ cm}^{-1}$, whereas the bands at $2,921$ and $2,851 \text{ cm}^{-1}$ are ascribed to asymmetrical stretching vibration absorptions of C–H asymmetric and symmetric stretching peaks. The bands at $1,720$ and $1,081 \text{ cm}^{-1}$ are attributed to the

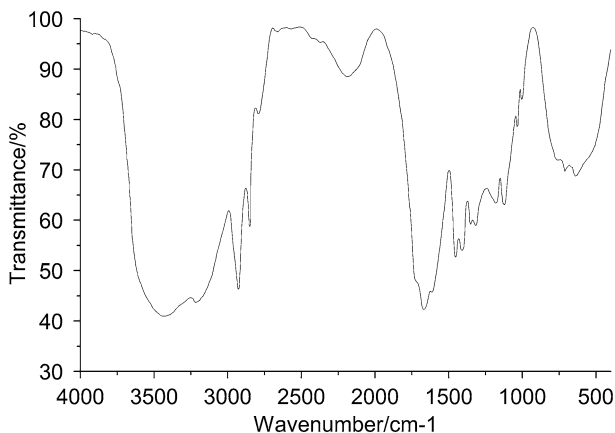


Fig. 1 FTIR spectrum of the AM-SMA hydrophobic associative copolymers; $m(\text{AM}):m(\text{SSS}):m(\text{SMA}) = 10:1.5:1.2$

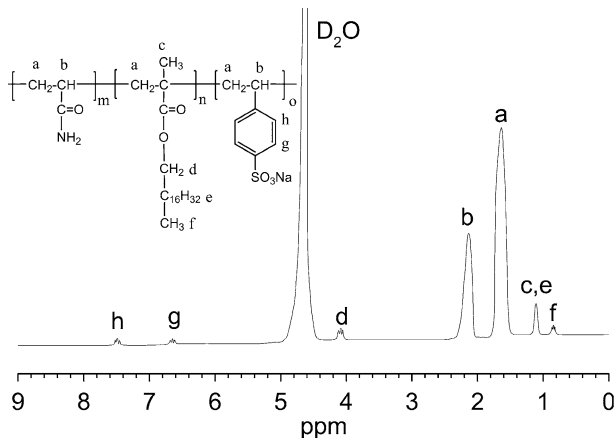


Fig. 2 ^1H NMR spectrum of the AM/SMA/SSS hydrophobic associative copolymers; m(AM): m(SSS): m(SMA) = 10:1.5:1.2

characteristic absorptions of C=O and C–O groups of the SMA unit, respectively. The band at $1,456\text{ cm}^{-1}$ is attributed to the benzene skeleton vibration, and the bands at $1,035$ and $1,009\text{ cm}^{-1}$ are ascribed to the $-\text{SO}_3^-$ group. The appearance of the above characteristic absorptions indicates the formation of an AM-SSS-SMA hydrophobic associative copolymer that was prepared by microemulsion polymerization.

A typical ^1H NMR spectrum of the AM-SSS-SMA hydrophobic associative copolymer ($M_w = 1.8 \times 10^6\text{ g}\cdot\text{mol}^{-1}$), synthesized with m(AM): m(SSS): m(SMA) = 10:1.5:1.2, is shown in Fig. 2. The spectrum displays the expected resonances for the strong methylene protons (a, $\delta = 1.51\text{--}1.77\text{ ppm}$) and methenyl protons (b, $\delta \sim 2.15\text{ ppm}$) on the polymeric main chains, methylene protons (d, $\delta \sim 4.05\text{ ppm}$) adjacent to the ester bond, methylene protons of stearyl groups ($-(\text{CH}_2)_{16}-$), α -methyl proton (c and e, $\delta = 1.08\text{--}1.15\text{ ppm}$), methyl proton (f, $\delta = 0.84\text{--}0.88\text{ ppm}$) and benzene protons (g, $\delta \sim 6.68\text{ ppm}$; h, $\delta \sim 7.49\text{ ppm}$). This confirms the presence of the AM-SSS-SMA copolymer structure.

3.2 AFM Image of the AM-SSS-SMA Hydrophobic Associative Copolymer

AFM was used to further demonstrate the aggregate morphology of the AM/SMA/SSS hydrophobic associative copolymer in water and the result is shown in Fig. 3. From AFM imaging of hydrophobic associative copolymer adsorbed onto the mica surface, some aggregates with size of about $100\text{--}300\text{ nm}$ were observed. Besides, there were some small network connections between them. This might be ascribed to the strong intermolecular interactions between hydrophobic groups distributed along the polymeric main backbone, thus yielding an entangled transient network structure, which is important for EOR applications.

3.3 Rheological Behavior of the HPASS Solutions

In the dilute region (at low hydrophobically associating polymer concentration) intramolecular associations dominate [5, 36], reducing the hydrodynamic volume and therefore decreasing the viscosity of the polymer solutions, whereas in the semi-dilute

Fig. 3 AFM image of the AM-SMA-SSS hydrophobic associative copolymers in water; $m(\text{AM}): m(\text{SSS}):m(\text{SMA}) = 10:1.5:1.2$

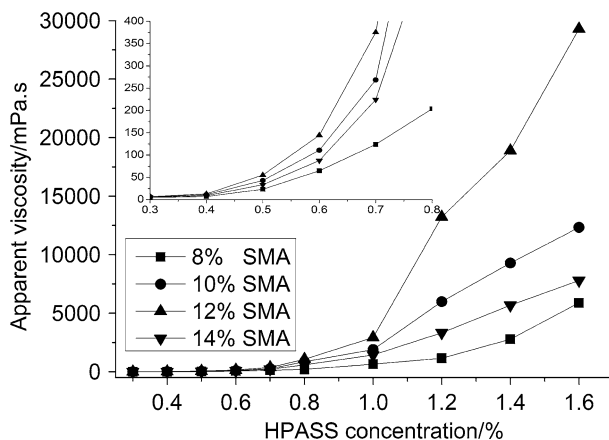
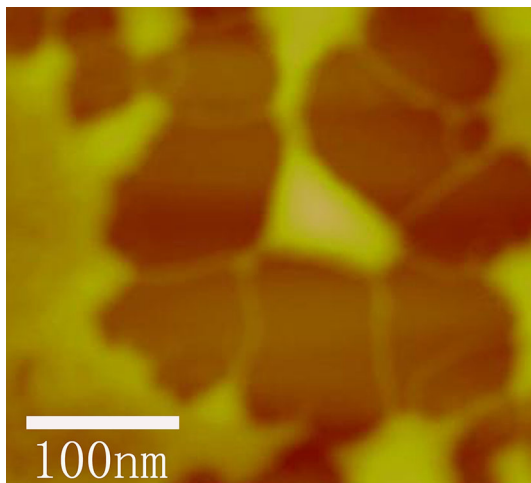


Fig. 4 Apparent viscosities of the hydrophobically associating copolymers solutions at room temperature and shear rate of 15.5 s^{-1} as a function of copolymers concentration and amount of SMA

region intermolecular associations dominate [5, 12], leading to a transient network that substantially increases the viscosity of the solutions [9, 37].

Figure 4 presents the concentration dependence of the apparent viscosities for the aqueous solutions of four hydrophobically associating copolymers synthesized with different SMA content. The apparent viscosities increase sharply as the copolymer concentration increases to approximately $0.4 \text{ g}\cdot\text{dL}^{-1}$ for the copolymers with 8, 10, 12 and 14 % SMA. This suggests that $0.4 \text{ g}\cdot\text{dL}^{-1}$ is a critical association concentration for the four hydrophobically associating copolymers, at which intramolecular association transforms into intermolecular association [8, 36]. When the copolymer concentrations increase further, the intermolecular association interaction is strengthened because of the shortening of the distance between macromolecules. This leads to an intermolecular physical network structure that contributes significantly to the thickening. Accordingly, the apparent viscosity of the HPASS solution increases rapidly.

As shown in Fig. 4, the apparent viscosities of the HPASS solutions increase rapidly as the SMA content increases from 8 to 12 %, while it decreases with further increase in the SMA content. These results are in agreement with previous trends [38–40]. In aqueous environments, the hydrophobe has a strong tendency to associate through intramolecular and intermolecular interactions. In aqueous solution (above the critical association concentration C^*), the hydrophobic units can form intermolecular hydrophobic associations, yielding an entangled transient network and resulting in a strong increase in solution viscosity [10, 12]. The copolymer with a higher hydrophobic content in the macromolecular chains will possess stronger intermolecular hydrophobic association interactions, and thus larger and denser intermolecular physical networks in the aqueous solution will be formed, resulting in an enhanced apparent viscosity of the solution. However when the SMA content exceeds 12 %, the water solubility of HPASS become poor and the hydrophobic microstructures become more compact, thus decreasing the apparent viscosities of the HPASS solutions.

In particular, many studies have reported that HAPAM usually contains a small proportion of hydrophobic groups (generally less than 2 mol%) [6, 7, 15, 41]. It is worth noting that HAPAM with a relatively high amount of hydrophobic groups (>2 mol%) can be obtained by introducing SSS segments with strong charged sulfonate groups onto the polymer backbone. This is beneficial for the HPASS used in EOR applications.

3.4 Apparent Viscosities of the HPASS Solutions Synthesized with Different Amounts of SSS

Figure 5 presents the effects of SSS content on the apparent viscosities of HPASS solutions. As indicated in Fig. 5, HPASS solutions display an increase in apparent viscosity as the content of SSS increases from 0 to 15 %. However, a further increase of the SSS content results in a decrease in the apparent viscosity. The SSS segment has a strong sulfonic anion group. With an increase in SSS segments incorporated into the HPASS polymeric chains, more sulfonic anions can ionize to increase the electrostatic repulsions

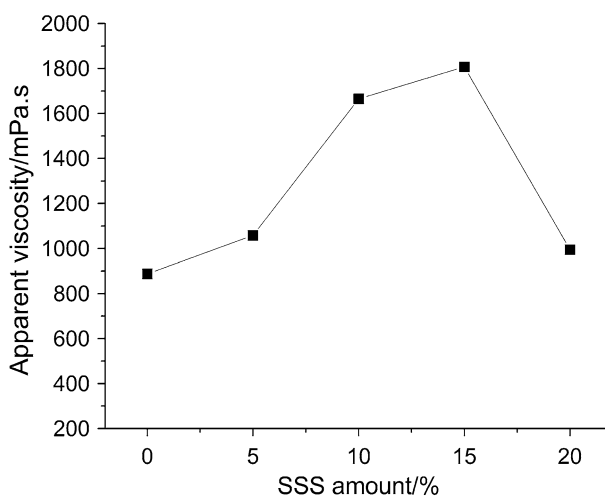


Fig. 5 Apparent viscosities of the hydrophobically associating copolymers solutions at room temperature synthesized at different SSS amount; m(AM):m(SMA) = 10:1.2

between macromolecules and therefore promote coil expansion and increase the apparent viscosity [41]. However, excess electrostatic repulsions between macromolecules do not favor intermolecular interactions. Therefore, the apparent viscosities of HPASS solutions decrease when the SSS content goes beyond 15 %.

It is well known that the limited water solubility of HAPAM impedes its popularization in EOR applications [42]. The presence of strong sulfonic charged units can not only impart better water solubility but also elongate the polymer chain to increase its hydrodynamic volume and thus solution viscosity [43], which is crucial for HAPAM in EOR applications.

3.5 Apparent Viscosity of AM-SSS-SMA Copolymer Solutions with Different Amount of SDS

The surfactant plays an important role in the microemulsion polymerization and its influence on the apparent viscosity of HPASS solutions is shown in Fig. 6. The surfactant affects the nucleation of micelles containing the oil soluble initiator and SMA, and therefore influences the microemulsion polymerization process. As can be seen from Fig. 6, the apparent viscosities of HPASS solutions increase as the SDS content increases to 12 %, but a decrease in apparent viscosity is observed at higher amounts of SDS. In principle, a decrease in surfactant concentration leads to a smaller number of micelles and therefore to a higher number of hydrophobe molecules in a micelle. As a result, one can expect larger hydrophobic lengths along the backbone, stronger intermolecular hydrophobic associations and therefore enhanced viscosification when the amount of SDS decreases from 15 to 12 %. However, when the SDS amount is below 12 %, there exist a smaller number of micelles in the microemulsion, resulting in smaller interfacial areas between the micelles and water. This might decrease the copolymerization between SMA within micelles and AM and SSS residing in aqueous phase, increasing the possibility of SMA homopolymerization, and thus decreasing the apparent viscosities of HPASS solutions.

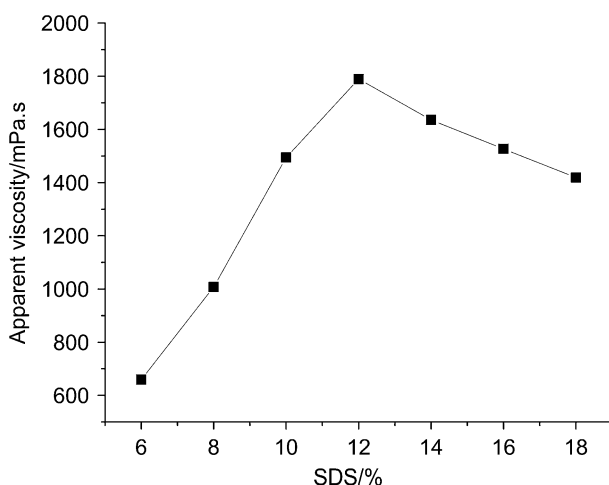


Fig. 6 Effect of the amount of SDS on the apparent viscosities of the hydrophobically associating copolymers solutions at room temperature; $m(\text{AM}):m(\text{SSS}):m(\text{SMA}) = 10:1.2:1.2$

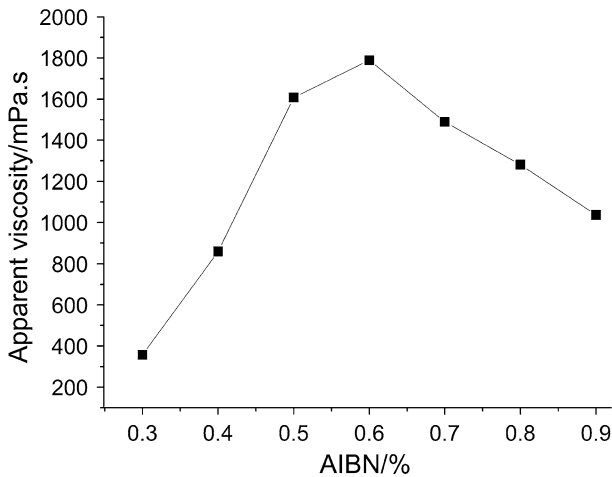


Fig. 7 Effect of the amount of AIBN on the apparent viscosities of the hydrophobically associating copolymer solutions at room temperature; m(AM):m(SSS):m(SMA) = 10:1.2:1.2

3.6 Apparent Viscosities of the AM-SSS-SMA Copolymer Solutions from Different Amounts of Initiator

The variation of the apparent viscosities of HPASS solutions with initiator concentration was investigated and the results are shown in Fig. 7. The apparent viscosities increase as the AIBN concentration increases from 0.3 to 0.6 %. However, a further increase of the AIBN concentration results in a slightly decreased apparent viscosity. Thus, the optimum AIBN concentration was found to be 0.6 %. With increasing AIBN concentration, more AIBN can penetrate into the hydrophobic micelles and initiate SMA to form SMA-based macroradicals, and then initiate AM residing at the interface of micelles, followed by the introduction of AM and SSS from the aqueous phase into the polymer backbone. Finally HPASS is formed. As a consequence, the apparent viscosity increases. However, an excessive AIBN concentration (>0.6 %) decreases the molecular weight of the copolymers and causes too rapid free radical copolymerization, which releases a large amount of heat, forming some gel-like insoluble copolymers, thereby decreasing the apparent viscosities of HPASS solutions.

3.7 Temperature Resistance of the HPASS Solutions

The temperature dependence of the solution viscosity is an interesting property of hydrophobically modified polymers for EOR applications, and the results are shown in Fig. 8. It was expected that apparent viscosities of HPASS solutions will decrease with increasing temperature, due to the decrease of the association strength of the hydrophobes [44, 45], decrease of solvent viscosity, and hence an increase in the mobility of the polymer chains. Lowering of the apparent viscosity with increasing temperature has been reported for aqueous solutions of hydrophobically associating polymers [1, 46, 47].

Besides, as shown in Fig. 8, HPASS solutions with 15 % SSS show lower temperature sensitivity in the apparent viscosity compared with HPASS solutions without SSS. It was reported that incorporating electronic charges into water-soluble polymers can control the

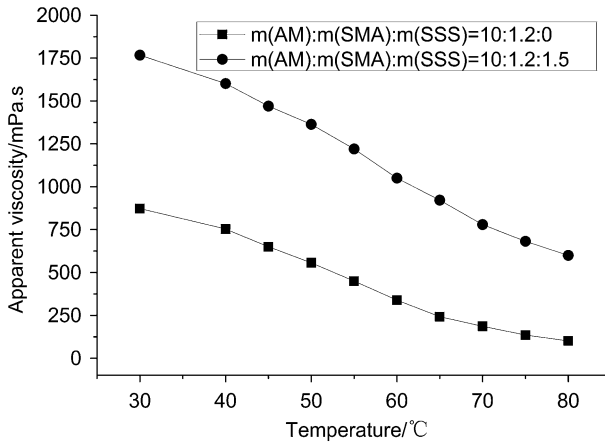
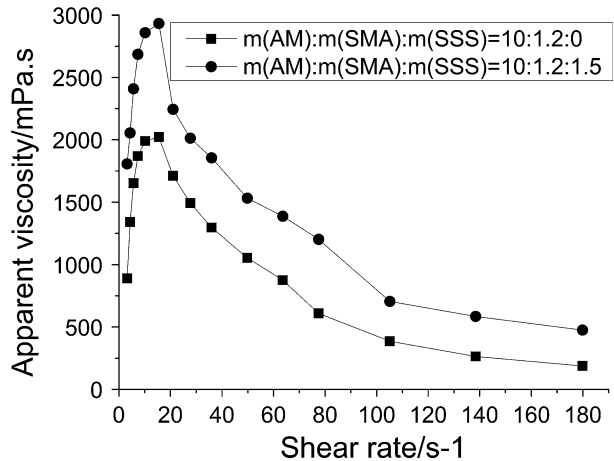


Fig. 8 Apparent viscosities of the hydrophobically associating copolymers solutions at different temperatures; $m(\text{AM}):m(\text{SSS}):m(\text{SMA}) = 10:1.5:1.2$

Fig. 9 Apparent viscosities of the hydrophobically associating copolymers solutions at room temperature and different shear rates



interaction between the polymer chains and increase their solubility in water, which makes the corresponding solutions less sensitive, in terms of viscosity, to the external temperature [15]. This is crucial and beneficial for HPASS in EOR applications.

3.8 Shear Resistance of the HPASS Solutions

Figure 9 demonstrates the apparent viscosity versus shear rate of the HPASS solutions. Both apparent viscosities of the HPASS solutions with 15 and 0 % SSS increase with increasing shear rate initially but then decrease at higher shear rate. According to several studies [48, 49], this behavior can be interpreted as a balance between intra- and intermolecular associations. Above a given shear rate the intramolecular associations are disrupted and the polymeric chains are extended, which leads to more intermolecular associations [1, 48]. However further increase in shear rate leads to the breakage of

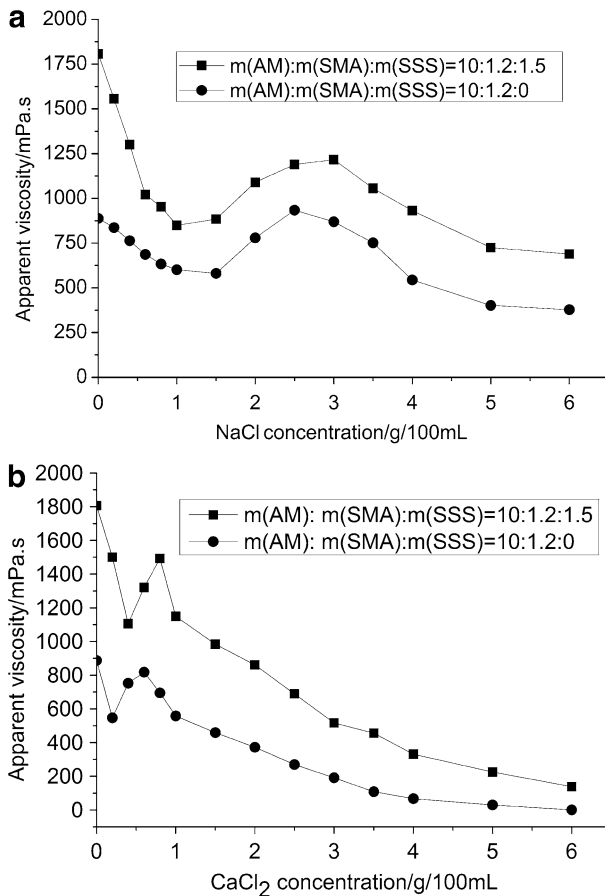


Fig. 10 Apparent viscosities of the hydrophobically associating copolymers solutions at room temperature and different NaCl (a) and CaCl₂ (b) concentrations

intermolecular associations and the copolymers exhibit shear-thinning behavior on account of the physical reversibility of the association framework [50, 51]. This shear-thinning phenomenon is a characteristic of the three-dimensional network formed by intermolecular association [52].

3.9 Salt Resistance of HPASS Solutions

Figure 10 shows the influences of NaCl and CaCl₂ concentrations on the apparent viscosities of HPASS solutions. With increasing NaCl and CaCl₂ concentrations, the apparent viscosities of the HPASS solutions decrease first, then increase, followed by a decrease in the apparent viscosity. For the HPASS having a SSS segment, the presence of salt screens the electrostatic repulsion between sulfonic acid groups, suppressing the disruption of hydrophobic associations by the charged groups, facilitating the macromolecular interpenetration, allowing the formation of a stronger network through hydrophobic associations [53, 54], and thus enhancing the solution viscosity. For the HPASS without a SSS

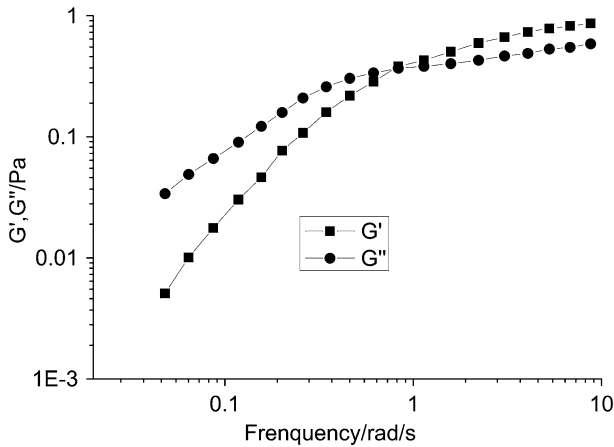


Fig. 11 Variation of the elastic modulus G' and the viscous modulus G'' with the oscillation frequency for hydrophobically associating copolymers solutions at room temperature; m(AM):m(SSS):m(SMA) = 10:1.5:1.2

segment, an increase in the apparent viscosity may be ascribed to the increase in solution polarity induced by the electrolytes, which results in reinforced intermolecular associations of the hydrophobic groups and salt-thickening behavior [55, 56]. However, with further increase in the NaCl and CaCl₂ concentrations, the solubility of the hydrophobic moieties in water decreases due to the salting-out effect [42], and the hydrophobic microstructures turn more compact, which favors intramolecular association and thus decreases the apparent viscosity of the hydrophobically associating copolymer.

3.10 Dynamic Rheology of the HPASS Solutions

At low shear frequency the rheological properties are often described by the Maxwell model. The storage modulus G' and the loss modulus G'' obey the following equations [57]:

$$G' = G_0 \omega^2 \tau^2 / (1 + \omega^2 \tau^2) \quad (1)$$

$$G'' = G_0 \omega \tau / (1 + \omega^2 \tau^2) \quad (2)$$

where ω , G_0 and τ represent angular frequency (rad·s⁻¹), high frequency plateau modulus and relaxation time, respectively. G_0 and τ can be obtained from the critical angular frequency ω^* and modulus G^* at which the curves of G' and G'' intersect according to the equations:

$$\tau = 1/\omega^* \quad (3)$$

$$G_0 = 2G^* \quad (4)$$

Rheology measurements under oscillating dynamic conditions were carried out on the HPASS solutions, and the results are shown in Fig. 11. As indicated by Fig. 11, liquid-like behavior ($G' < G''$) is observed in the low-frequency region, but both G' and G'' increase with ω , and solid-like behavior ($G' > G''$) is observed in the high-frequency region. Both

G' and G'' in the low-frequency region are well fitted by the Maxwell model, whereas they deviate from it in the high-frequency region. This is the typical viscoelastic behavior shown by hydrophobically associating polymer solutions [48, 58], which is vital for improved oil recovery in EOR applications [59, 60].

4 Conclusions

AM-SSS-SMA hydrophobic associative copolymers (HPASS), prepared by microemulsion polymerization, possess particular rheological properties which were strongly dependent on the parameters such as the content of hydrophobic monomer, amount of SSS, amount of initiator, amount of SDS, the copolymer concentration and the addition of salt. FTIR and ^1H NMR spectra confirm the structure of AM-SSS-SMA copolymers. Both the storage modulus G' and loss modulus G'' of HPASS solutions increase with angular frequency ω and are well fitted by the Maxwell model in the low-frequency region, whereas they deviate from it in the high-frequency region. AFM indicated the presence of some aggregates and small network connections between macromolecular chains. The hydrophobic associative copolymers, with the critical aggregation concentration around $0.4 \text{ g}\cdot\text{dL}^{-1}$, exhibit good temperature-resistance, salt-thickening, shear-thickening and shear-thinning behavior. Hydrophobic associative copolymers with suitable amounts of SSS segments have improved apparent viscosity and temperature-resistance. The interesting behavior of hydrophobic associative copolymers, such as shear thinning, as a function of shear rate and shear time, makes it useful in a number of applications including EOR, drilling fluids, coating or cosmetics.

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