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SHORT COMMUNICATION

Synthesis and characterization of a series of modified polyacrylamide

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Abstract We present the synthesis and the characterization of a new class of modified polyacrylamides (MPAM) with the unusual trait of strong emulsification ability, viscosity enhancement capacity, and significant salt tolerance. Besides, the synthesized polymers have the peculiar aggregation behaviors in aqueous solution. The synthesis was carried out by polymerizing the monomers such as acrylamide (AM), acrylic acid (AA), unsaturated amphiphilic functional moieties, and high steric hindrance functional units. Their aggregation behaviors were investigated by using a scanning electron microscope (SEM). The emulsion, formed by 10 ml of MPAM (with the polymer concentration of 1,000 mg/L) and the 10 ml of crude oil, was very stable, which indicates that the synthesized polymers have unique emulsification properties. The strong hydrophobic interaction between molecules and the three-dimensional network formed in aqueous solution were exhibited by the experimental results of steady fluorescence and SEM experiments. It could be concluded that the performance of polymers for enhanced oil recovery (EOR) can be remarkably enhanced by introducing functional monomers to polymer backbone, which allows the new class of modified polymers to have more promising application in enhanced oil recovery.

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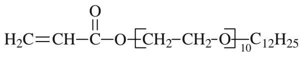
Introduction

After conventional water-flooding processes, the residual oil in the reservoir remains as a discontinuous phase in the form of oil drops trapped by capillary forces and is likely to be around 70% of the original oil left in place. Chemical flooding has proved to be an effective method to improve the oil recovery. PAM is one of the most widely used polymers in chemical flooding. However, there are many defects in its practical application, such as low temperature resistance, poor salt tolerance, and easy oxidative degradation. As there is no lipophilic groups that exist in the molecule structure, PAM cannot emulsify the oil–water system, which limits its oil recovery capability. In order to reduce the oil–water interfacial tension and enhance the emulsification to improve the displacement efficiency, the binary flooding systems of PAM-surfactant or PAM-surfactant-alkali tertiary combination were developed [1–3]. However, for these combined systems, the use of a large amount of surfactant leads to a high cost, and the presence of alkali causes problems such as the separation of oil from water and waste water treatment [4]. To overcome these difficulties, the modified polymer system that can increase the interface activity, improve the emulsification ability, and enhance the viscosity without the addition of surfactant and alkali is suggested.

In this work, a series of MPAMs were synthesized by polymerizing the acrylamide, acrylic acid, unsaturated amphiphilic functional moieties, and high steric hindrance functional monomers. The amphiphilic functional monomers were able to greatly enhance the emulsification ability,

Fig. 1 Structure of monomer A



$$\mathrm{H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}\!\left[CH_2{-}CH_2{-}O\right]_{10}C_{12}H_{25}}$$

decrease interfacial tension, and increase the viscosity of the solution and hence allowing a greater recovery efficiency. The monomers with the steric hindrance would reduce the curliness of molecular chains and, consequently, enhance the temperature resistance and improve the salt tolerance. Such advantages provide the modified PAM with great potential in EOR field.

Experimental section

Materials

The MPAMs used in this experiment were denoted as I, II, III, and IV, respectively .All polymer samples and monomers were synthesized in our laboratory and purified by film filtration. The structures and nomenclature of the monomer A, B, and polymers were shown in Figs. 1, 2, and 3. Polyacrylamide (PAM), with the average molecular weight of 1.2×10^6, was also made and purified in our laboratory. Other chemicals used (analytical grade) were obtained from local sources. All the solutions were made with simulate-brine, the component of simulated-brine is listed in Table 1.

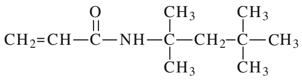
Synthesis of MPAMs by micellar copolymerization

The aqueous solution containing AM, AA, and two other functional monomers was prepared in a round bottom flask equipped with a mechanical stirrer, a thermometer, and an inlet of N_2. The temperature was increased up to 45°C, the initiator $K_2S_2O_8/NaHSO_3$ was added, and the ratio between $K_2S_2O_8/NaHSO_3$ is 2:1. The reaction was carried out at a temperature of 60°C under stirring and protection of N_2, for 3 h. With the variation of the ratio of two functional monomers, the polymers with different compositions and properties were obtained. The product was precipitated in ethanol three times to remove the residual monomers and finally dried under vacuum.

Fluorescence measurement

Pyrene (5×10^{-6} mol·L^{-1}) was used as the probe to investigate the micropolarity from measurement of the pyrene polarity index I_1/I_3, which is the ratio of the intensity of the first and third vibronic peaks in the fluorescence emission spectrum. The fluorescence intensities were recorded on Hitachi F-4500 spectrofluorometer. Pyrene was excited at 335 nm, and the emission was scanned from 350 to 500 nm.

Fig. 2 Structure of monomer B



$$\mathrm{CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3}$$

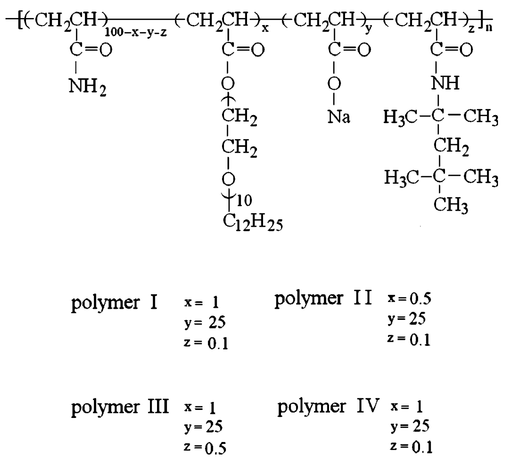


Fig. 3 Structure and nomenclature of MPAM

SEM experiment of MPAM

The samples were prepared with the vacuum sublimation freezing drying technique, and the aggregation behaviors of the polymers were investigated by using a Hitachi S-530 scanning electron microscope.

Emulsification

The emulsions samples were prepared by mixing the crude oil and polymer solution (*o*/*w* ratio 1/2, *v*/*v*) in a 50-ml scaled tube. The emulsification was carried out by shaking for 200 times. The stability of the emulsion was observed at 25±0.1°C for a period of 40 days.

Rheological text

The apparent viscosity of polymer solutions were measured using a Brookfield DVIII+ rheometer. The temperature was controlled at 45.0±0.1°C using a temperature-controlled water bath surrounding the measuring cup in addition to the standard circulating water inside the cup holder. The rheometer was calibrated with Newtonian standard fluids of appropriate viscosity.

Table 1 Component of simulated-brine

Component	Na_2SO_4	KCl	$CaCl_2$	$MgCl_2$	$NaHCO_3$	NaCl
Content (g/L)	0.1006	0.0764	0.072	0.1004	0.8974	2.92

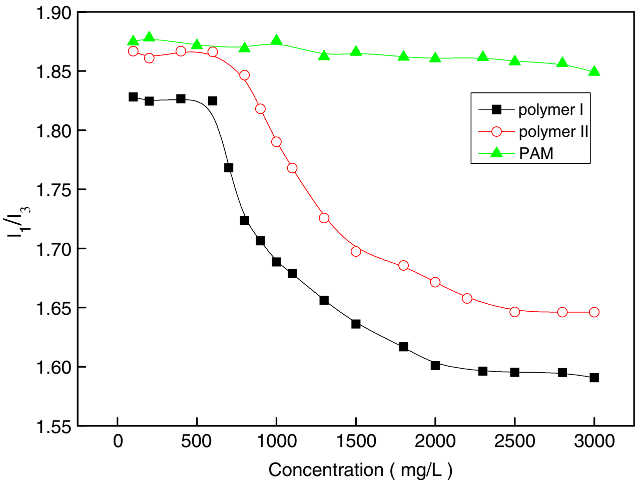


Fig. 4 Variation of the steady fluorescence intensity I_1/I_3 of polymers

Results and discussion

Hydrophobic association behaviors of MPAM

Figure 4 presents the I_1/I_3 ratios of pyrene in the solution of polymer I, polymer II, and PAM as a function of polymer concentrations. The formation of hydrophobic microdomains in aqueous media and the penetration fluorescence intensities of pyrene molecules into these domains lead to the drop of the ratios of the first and the third emission peaks (I_1/I_3) [5]. It can be found that the I_1/I_3 ratios of pyrene in the solution of all the three polymers are near 1.85 (the characteristic value for pyrene in simulate-brine) at low concentration (below 750 mg/L), whereas the I_1/I_3 ratios of pyrene in the solution of polymer I, polymer II decrease rapidly when the concentration increases. Especially in the range of higher concentrations (above 1,000 mg/L), the I_1/I_3 ratio of pyrene in the solution of functional polymer are much lower than that of PAM. This indicates that mass of the hydrophobic domains have formed in modified polymer solutions due to the hydrophobic intramolecular association at lower concentrations and intermolecularly at higher concentrations [6]. This suggests that there exist a critical association concentration (cac) around the concentration of 750 mg/L for these two polymers. It can also be found that, in the whole concentration range, the ratio I_1/I_3 of pyrene in the polymer I solution is lower than that for polymer II, and the ratio I_1/I_3 of pyrene in the polymer I solution decreases rapidly. These differences should be attributed to the fact that the content of monomer A in polymer I is twice as much as that in polymer II. After cac, interaction between the amphiphilic moieties of the polymer results in large and dense three-dimensional network structure, which causes the drop of the ratio I_1/I_3 of pyrene in the polymer solution and a rapid increases of viscosity [7–8]. For PAM system, the

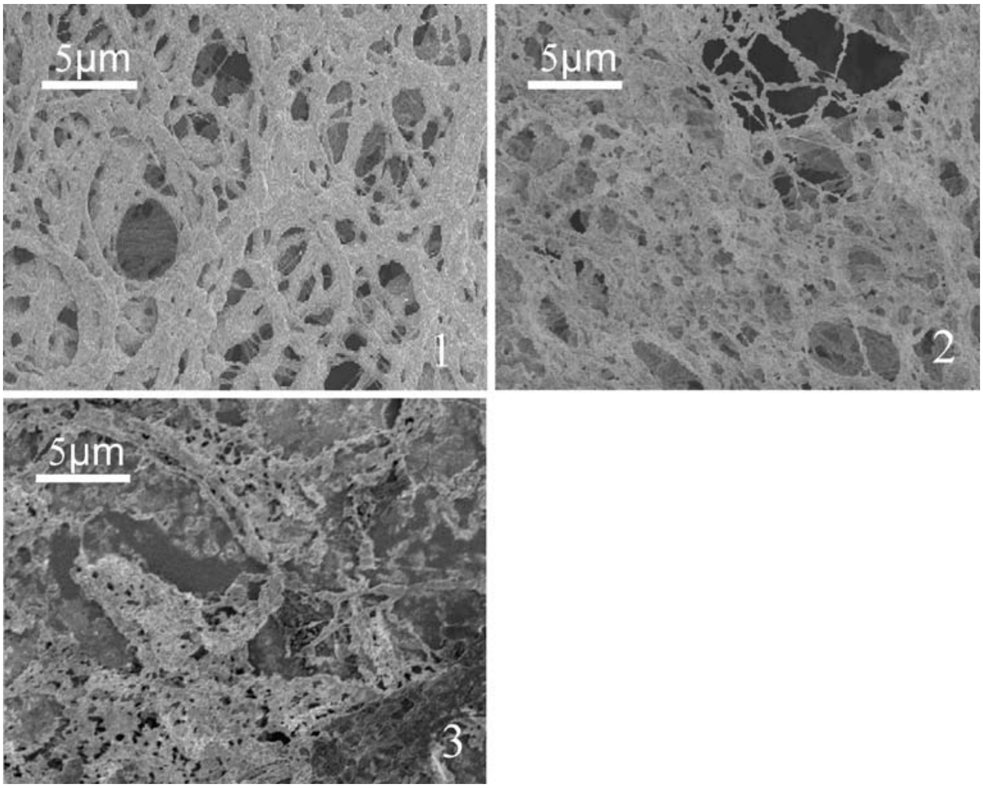


Fig. 5 SEM images for polymer systems at the concentration of 1,000 mg/L (1-polymer I; 2-polymer II; 3-PAM)

ratio I_1/I_3 of pyrene in the polymer solution remains unchanged in the whole concentration region, which evidenced the absence of hydrophobic aggregates in PAM solution.

As shown in Fig. 5, it exhibits obvious three-dimension network in polymer I and polymer II solutions. It is also shown that meshes are obviously compact and array orderly in polymer I solution, but array looser in polymer II solution. However, there is nearly no network that is observable in PAM solution. It accounts for the fact that the denseness of the network is related to the content of monomer A in the modified polymer backbone.

The emulsification properties of MPAM

The emulsion stability data for the water-in-oil emulsions are presented in Fig. 6. It shows that the emulsion stability varies with time, and after a period of 20 days, there is no water separated from the emulsions. As known from previous investigations [9], the stability of water-in-oil emulsions depends on the structure of the molecular matrix of the interfacial active components. The size, content, and types of functional groups in the backbone of the polymer play an important role in the stability of the emulsions. It is obvious that the emulsion system in the presence of polymer I is more stable than the case of polymer II owing to the more content of monomer A in polymer I. So it is reasonable to confer that both the hydrophobic association and emulsification of MPAM are tunable through the ratio control of monomer A in the polymer backbone

Apparent viscosity characteristic of MPAM

It can be seen from Fig. 7, for HPAMs, that the viscosity increase slowly at a low polymer concentration range and increase rapidly after cac, which should be attribute to the intermolecular hydrophobic association. By comparison with polymer III, the solution viscosity of polymer IV is much smaller. This is not only owing to a weaker intermolecular association caused by a lower content of monomer B but also due to the curliness of the polymer chains. The presence of salt and high temperature (45°C) enhances the curliness of polymer chains and the loss of viscosity [10]. The great difference of viscosity between polymer III and polymer IV indicates that viscosity is affected by the high steric hindrance groups. It mainly resulted from the fact that the curliness of the polymer chain can be obviously reduced by the high steric hindrance effect of monomer B. It is worthwhile to point out that no evident viscosity increase has been observed for PAM.

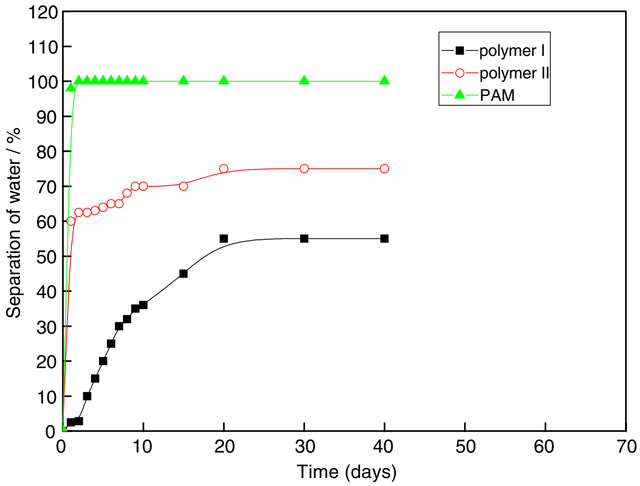


Fig. 6 Stability of the emulsion formed by crude model oil and polymer solution (with the polymer concentration of 1000 mg/L)

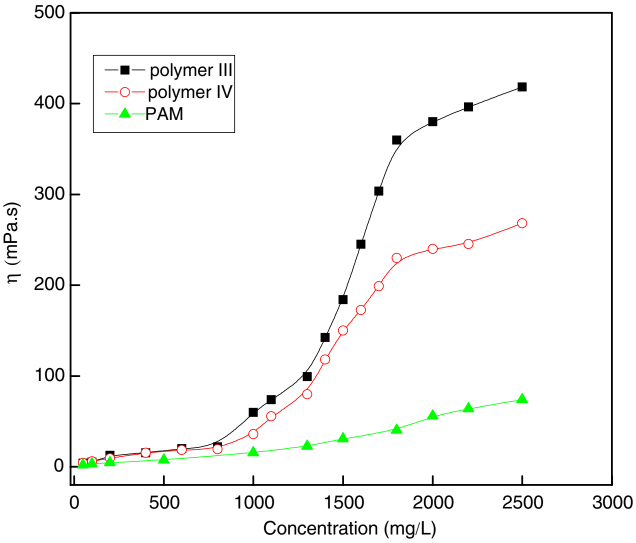


Fig. 7 Viscosity curves of polymers with different concentration

Conclusion

In this paper, the modification of PAM by inducing different functional monomers was investigated. It was shown that the induction of unsaturated amphiphilic functional moieties in MPAMs would lead to a strong intermolecular hydrophobic association in aqueous solutions, and the emulsification ability to oil–water system was remarkably enhanced. At the same time, the higher temperature resistance and stronger salt-tolerance could be attained by adjusting the content of high steric hindrance monomers.

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