

## Preparation and solution properties of a novel cationic hydrophobically modified polyacrylamide for enhanced oil recovery

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Keywords:	hydrophobically modified polyacrylamide, temperature tolerance, salt resistance, enhanced oil recovery, hydrophobic association
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## Preparation and solution properties of a novel cationic hydrophobically modified polyacrylamide for enhanced oil recovery

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### ABSTRACT

A novel cationic water-soluble monomer allyldimethylisooctylammonium bromide (ADIAB) containing a short-chain alkane was synthesized successfully. This monomer was copolymerized with acrylamide and sodium acrylate to produce hydrophobically modified polyacrylamide (HMPAM) using solution polymerization without surfactants. The structures of monomer ADIAB and HMPAM were characterized with infrared spectroscopy and nuclear magnetic resonance spectroscopy. Influence of preparation condition on viscosities of products was studied. The aqueous solution viscosity of the terpolymer was also investigated as functions of concentration, temperature and salinity. The results showed that when the temperature exceeds the 60°C and NaCl concentration exceeds about 2000mg/L, the temperature and salt tolerance characters of terpolymer were demonstrated. The enhanced oil recovery tests were initially carried out using homogeneous sandpack models.

### KEYWORDS

hydrophobically modified polyacrylamide; temperature tolerance; salt resistance; enhanced oil recovery; hydrophobic association

### 1. Introduction

The partially hydrolyzed polyacrylamide (HPAM) and hydrophobically modified

polyacrylamide (HMPAM) have been widely used in the field of enhanced oil recovery (EOR).<sup>[1-6]</sup> HPAM is a salt sensitive conventional polymer, and it is easy to be mechanically degraded.<sup>[7-8]</sup> The HMPAM is synthesized by introducing a very small amount of hydrophobic groups (normally less than 2 mol%) into the polyacrylamide backbone.<sup>[9-10]</sup> In aqueous solution, the hydrophobic groups have a tendency to associate with each other, and thus result significantly increased water viscosity. In addition to tackifying, the temperature and salt tolerance of hydrophobically modified polyacrylamide is believed to be better than that of conventional polymers for example HPAM.<sup>[11-16]</sup> Therefore, HMPAM is considered as a good substitute to replace HPAM under harsh reservoir condition, such as high temperature and high salinity environment.

However, the introduction of hydrophobic groups inevitably reduces the water solubility of HMPAM.<sup>[17]</sup> Sometimes phase separation or precipitation may occur for HMPAM.<sup>[18]</sup> What's more, micellar copolymerization is commonly used to produce the HMPAM.<sup>[19]</sup> In micellar copolymerization, surfactants are used to solubilize hydrophobic monomers.<sup>[20-21]</sup> While the added surfactant may have negative impact on the properties of HMPAM, and what's more it is difficult to remove the surfactant after the copolymerization.

Therefore, it is essential to focus on preparing HMPAM with good water solubility without adding surfactants. In this paper, a cationic water-soluble monomer containing a short-chain alkane was synthesized. And then, this monomer was copolymerized with acrylamide and sodium acrylate to produce HMPAM using solution polymerization without surfactants. The structures of monomer and HMPAM were characterized. The solution properties of HMPAM including the salt tolerance and temperature resistance were investigated later. The effectiveness of HMPAM on EOR was illustrated by core flooding test in sandpack samples.

## 2. Experimental

### 2.1 Materials and polymerization

The acrylamide (AM), acrylic acid (AA), N,N-dimethylallylamine (DMAA), 2-ethylhexyl bromide (EHB), 2,2'-azobis(2-methylpropionamide)dihydrochloride

(AIBA) and other reagents are analytical reagent and are used without further purification.

Firstly, the allyldimethylisooctylammonium bromide (ADIAB) was synthesized following these steps as shown in Figure 1A. The DMAA and EHB were allowed to react with a molar ratio of 1 : 1.1 (DMAA:EHB) in acetone at 65°C under the continuous magnetic stirring and reflux condenser. After 30 hours of reaction, the reaction mixture was cooled down to fully crystallize the product. Secondly, the solid-liquid mixture was negative-pressure filtered and washed with acetone in order to remove the non-reacted reactants. The product, ADIAB, was dried under vacuum at 45°C until constant weight. And secondly, the cationic hydrophobically modified polyacrylamide (AM/AA/ADIAB copolymer) was prepared according to the following procedure as shown in Figure 1B. The AA was neutralized to sodium acrylic acid (NaAA) using NaOH solution. A certain mass of AM, NaAA, ADIAB and deionized water were added into the beaker. Then, the dissolved oxygen in solution was removed by bubbling nitrogen for 1 hour. Thirdly, a certain amount of AIBA as initiator was added to the mixture and the temperature was increased to the present value for 6 h. The obtained gel was sheared, washed with ethanol and dried for 24 hours. And at last the obtained xerogel is pulverized by a pulverizer.

## 2.2 Characterization

<sup>1</sup>H-NMR spectra of ADIAB and AM/AA/ADIAB copolymer were measured on a VarianGemini-500 NMR spectrometer with D<sub>2</sub>O as the solvent. A Bruker IFS 66 v/s IR spectrometer was used for FTIR spectroscopy analysis of ADIAB. Solution viscosities of polymer solution were determined with Brookfield DV-II viscometer (rotor No.:S63; rotor speed: 200 revolutions/min).

## 2.3 Tertiary coreflooding test

The brine (2.31 wt% NaCl and 0.32 wt% CaCl<sub>2</sub>) was continuously injected into the well-packed sandpack (Φ2.5×20cm) until a stable pressure was established to determine the permeability. Next, the packed sandpack was saturated by the oil sample (asphaltenes 7.8%, resins 33.9%, oily constituents 58.3%) until no further water production. The packed sandpack was aged at 70°C for 3 days. Thereafter,

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brine was continued injected until the water cut reaches 98%, and the secondary oil recovery of brine flooding could be estimated. The tertiary processes were performed after secondary brine injection; this is accomplished by 0.3 Pore Volume (PV) of AM/AA or AM/AA/ADIAB copolymer solution slug injection (3000 mg/L), and then followed by brine injected until the water cut reaches 98%. The final oil recovery and tertiary recovery can be calculated. It has also to be noted that all the coreflooding test was carried out at 70°C.

### 3. Results and discussion

#### 3.1 Characterization of monomer ADIAB and AM/AA/ADIAB copolymer

The infrared spectrum of the synthesized monomer ADIAB is shown in Figure 2. The pronounced peaks at 2950 and 2868  $\text{cm}^{-1}$  are assigned to the stretching of C-H bonds from compound. The absorption peak shown around 1634  $\text{cm}^{-1}$  is mainly attributed to the stretching vibration of C=C bonds. The peak at 1471  $\text{cm}^{-1}$  is characteristic of bending vibration from C-H bond. Besides, there is a characteristic peak at 954  $\text{cm}^{-1}$  due to C-H out-of-plane bending vibration from the R-CH=C group. The complete  $^1\text{H-NMR}$  spectrum of ADIAB is presented in Figure 3. It clearly shows each characteristic signal of hydrogen atoms in different positions from monomer ADIAB. The synthesized cationic hydrophobically modified polyacrylamide, AM/AA/ADIAB copolymer is also characterized by  $^1\text{H-NMR}$  spectroscopy as shown in Figure 4. The area with the largest peak from 4.36 to 5.47 ppm is the solvent peak. The peak at 1.78–2.42 ppm is the characteristic signal of methine protons from copolymer chains. The signal from 0.83–1.78 ppm is assigned to methylene protons copolymer backbone. Compared with Figure 3, some proton peaks of the monomer ADIAB appear in the red circle position of Figure 4 including 0.78, 2.93 and 3.85 ppm. However, the characteristic signal of protons from double bonds at 5.62 and 5.98 ppm in Figure 3 almost disappears in Figure 4. It means that the double bonds of the ADIAB are opened during the copolymerization. That is, the monomer ADIAB participates in the copolymerization reaction.

#### 3.2 Influence of synthesis condition on viscosity

Figure 5A shows the influence of the total monomers mass percentage on viscosity of

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3 AM/AA/ADIAB copolymer solution. As shown in this figure, the apparent viscosity  
4 initially increases with total monomer mass percentage until reaches a maximum and  
5 then decreases with total monomer mass percentage. This is because the probability of  
6 contact between monomer molecules increases with the total monomers content,  
7 which leads acceleration of polymerization, and thus improves the conversion rate. As  
8 a result, the apparent viscosity of the copolymer solution increases with increasing  
9 monomers concentration in a certain range. While it should be noted that the  
10 polymerization is exothermic reaction. As the total monomers concentration increases,  
11 the heat of polymerization also increases. If the heat would not be released in time,  
12 the local temperature will rise too fast, resulting in increasing probability of chain  
13 transfer and chain termination. Then the viscosity of copolymer solution will be  
14 reduced. As shown in the Figure 5A, the favorable mass percentage is around 42%.

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16 Viscosity of the copolymer solution is also influenced by the reaction temperature as  
17 shown in Figure 5B. The apparent viscosity first increases and then decreases with  
18 increasing reaction temperature. With a low temperature, the decomposition reaction  
19 of the initiator is inhibited to produce a small amount of free radicals. Along with the  
20 rise of temperature, the amount of free radicals produced is sufficient to promote  
21 polymerization. Along with the rise of temperature, the amount of free radicals  
22 produced is sufficient to promote polymerization, improving the molecular weight  
23 and the conversion ratio of monomers. However, if the temperature is higher than  
24 45°C, massive free radicals will be produced in a short time, resulting in chain  
25 termination thereby reducing the molecular weight.

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27 Figure 5C shows the viscosity of AM/AA/ADIAB copolymer increases first and then  
28 decreases with the increase of the initiator mass percentage. If the amount of initiator  
29 is low, the number of free radicals produced is not sufficient to initiate polymerization  
30 to produce high molecular weight polymers. However, too much free radicals also  
31 lead to chain termination before the chain grows to a sufficient length. This means  
32 that relatively high initiator mass percentage contributes to the production of low  
33 molecular weight polymers, resulting in the drop of viscosity. The optimum mass  
34 percentage of initiator is 0.02 wt%.

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3 Figure 5D shows the influence of the monomer ADIAB concentration on viscosity of  
4 AM/AA/ADIAB copolymer solution. The viscosity first increases slowly and then  
5 decreases with increasing ADIAB proportion. The steric effect of bulky side group  
6 from ADIAB may prevent the molecular chain curled to improve the extension of  
7 polymer chains which increases the viscosity. However, space hindered effect can also  
8 decrease the molecular weight of AM/AA/ADIAB copolymer. So, there is an  
9 optimum mass ratio of ADIAB concentration (0.5 mol%) with a maximum of  
10 viscosity.  
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### 18 **3.3 Temperature tolerance and salt resistance**

19 The temperature tolerance and salt resistance of AM/AA/ADIAB copolymer are  
20 discussed in this section. For comparison, AM/AA copolymer without ADIAB  
21 monomer was synthesized under identical conditions. The number-averaged molecular  
22 weights of AM/AA and AM/AA/ADIAB copolymer were determined using the  
23 intrinsic viscosity measurement as described by Ye et al.<sup>[22]</sup> Effects of temperature on  
24 solution viscosity of AM/AA/ADIAB and AM/AA copolymers are shown in Figure  
25 6A. With increasing temperature, the viscosities of both kinds of copolymer reduce,  
26 but under different levels. It is noteworthy that the initial viscosity of the AM/AA  
27 copolymer is higher than that of the terpolymer. AM/AA copolymer is anionic  
28 polymer and the electrostatic repulsion between negative charges would make  
29 molecule chain stretching which then increases the viscosity. For AM/AA/ADIAB  
30 copolymer, the introduction of cationic monomer reduces the electrostatic repulsion  
31 between negative charges which reduce the expansion extent of polymer chains  
32 resulting in a decrease in viscosity. Additionally, the molecular weights of AM/AA  
33 and AM/AA/ADIAB copolymer were  $7.48 \times 10^6$  and  $1.47 \times 10^6$ , respectively. The  
34 molecular weight of the hydrophobically modified polymer is lower than that of its  
35 unmodified polymer, which is in accordance with Poh's results.<sup>[23]</sup> This is the other  
36 reason why the initial viscosity of AM/AA copolymer is higher than that of  
37 AM/AA/ADIAB copolymer. At temperatures below 60°C, the viscosity of the binary  
38 copolymer is consistently higher than that of the terpolymer. When the temperature  
39 exceeds the 60°C, the viscosity of the terpolymer begins to be higher than that of the  
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3 binary copolymer. It could be due to the effect of intermolecular association between  
4 hydrophobic groups is enhanced with increased temperatures. Because the  
5 hydrophobic association is an endothermic process accompanied by an entropy  
6 increase.<sup>[24]</sup>  
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10 The influence of NaCl concentration on viscosity of copolymers is shown in Figure  
11 6B. With increase of NaCl concentration, the viscosity of copolymers solution reduces  
12 gradually. This is probably because the electrical double layer of anions or cations  
13 from polymer chains is compressed due to the increase of ionic strength, which then  
14 weakens the electrostatic repulsive force and resulting in viscosity lose. The viscosity  
15 of the terpolymer begins to be higher than that of the binary copolymer as the NaCl  
16 concentration exceeds about 2000mg/L. The enhancement of polarity by the add salt  
17 facilitates the formation of intermolecular interaction. Also, the add salt is thought to  
18 reduce the solubility of the hydrophobic groups which enhances the degree of the  
19 hydrophobic association.<sup>[25-27]</sup> The effect of bivalent salt is also investigated, and  
20 similar results as shown in Figure 6C and Figure 6D, are observed.  
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30 The polymer concentration dependence of the viscosity is displayed in Figure 7.  
31 There is also a critical association concentration at around 3000mg/L for  
32 AM/AA/ADIAB copolymer. However, below the critical association concentration,  
33 there is no sharp increase in viscosity with increasing concentration. This  
34 phenomenon is different from hydrophobically modified polyacrylamides. This might  
35 be because the carbon chain length of hydrophobic groups is not as long as other  
36 hydrophobically modified polyacrylamides.  
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### 43 ***3.4 Tertiary enhanced oil recovery performance***

44 Two sets of enhanced oil recovery tests were carried out within homogeneous  
45 sandpack models. The permeabilities of homogeneous models are controlled at 0.5  
46  $\mu\text{m}^2$  approximately. The results of enhanced oil recovery tests are shown in Table 1. It  
47 can be seen, for the similar relative homogeneous sandpack sample, the additional  
48 recovery from tertiary injection of the AM/AA/ADIAB copolymer (15.91%) is  
49 slightly higher than that of AM/AA copolymer (12.82%). Further research on tertiary  
50 enhance oil recovery in heterogeneous sandpack models and real reservoir rock  
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3 samples with AM/AA/ADIAB copolymer will appear in our future papers.  
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#### 5 **4. Conclusions**

6 A water-soluble cationic monomer allyldimethylisooctylammonium bromide (ADIAB)  
7 containing the short-chain alkane as hydrophobic group was synthesized successfully.  
8 ADIAB was copolymerized with acrylamide and sodium acrylate to produce  
9 hydrophobically modified polyacrylamide (AM/AA/ADIAB copolymer) using  
10 conventional solution polymerization. The structures of monomer ADIAB and  
11 AM/AA/ADIAB copolymer were characterized by FT-IR and <sup>1</sup>H-NMR. Influence of  
12 preparation condition on viscosities of products was studied, and the optimal  
13 preparation scheme was as follows. The mass percentages of the initiator and  
14 monomer were 0.4% and 42%, respectively. The mass ratio of ADIAB concentration  
15 was 0.5 mol%. The reaction temperature was 45°C. The critical association  
16 concentration of AM/AA/ADIAB copolymer was about 3000mg/L. When the  
17 temperature exceeds the 60°C and NaCl concentration exceeds about 2000mg/L, the  
18 temperature and salt tolerance characters of terpolymer were demonstrated. [The](#)  
19 [tertiary recovery of the AM/AA/ADIAB copolymer is slightly higher than that of](#)  
20 [AM/AA copolymer with application in homogeneous sandpack samples.](#)  
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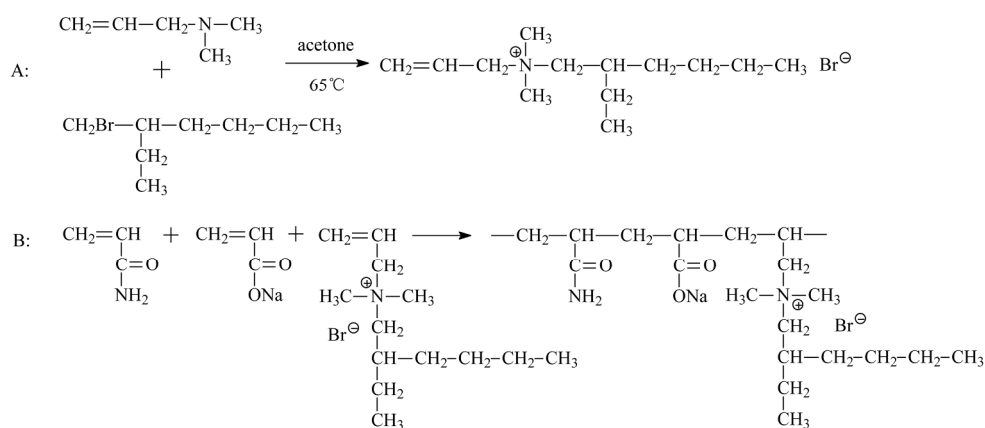


Figure 1. A: The schematic of preparing monomer ADIAB. B: The schematic of preparing AM/AA/ADIAB copolymer.

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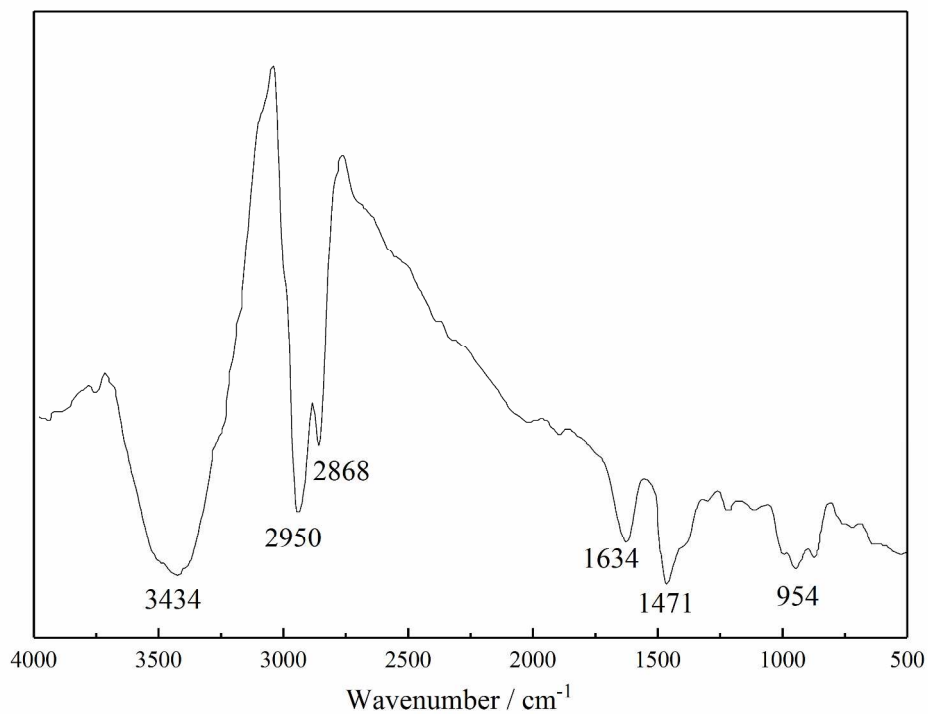


Figure 2. FT-IR spectrum of the monomer ADIAB.

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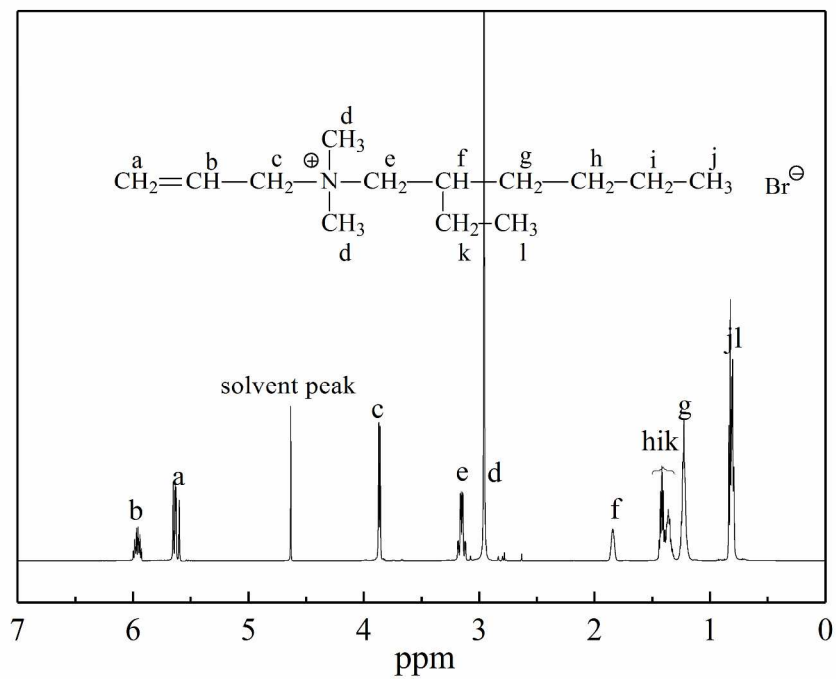


Figure 3. The  $^1\text{H}$ -NMR spectra of the monomer ADIAB using  $\text{D}_2\text{O}$  as the solvent.

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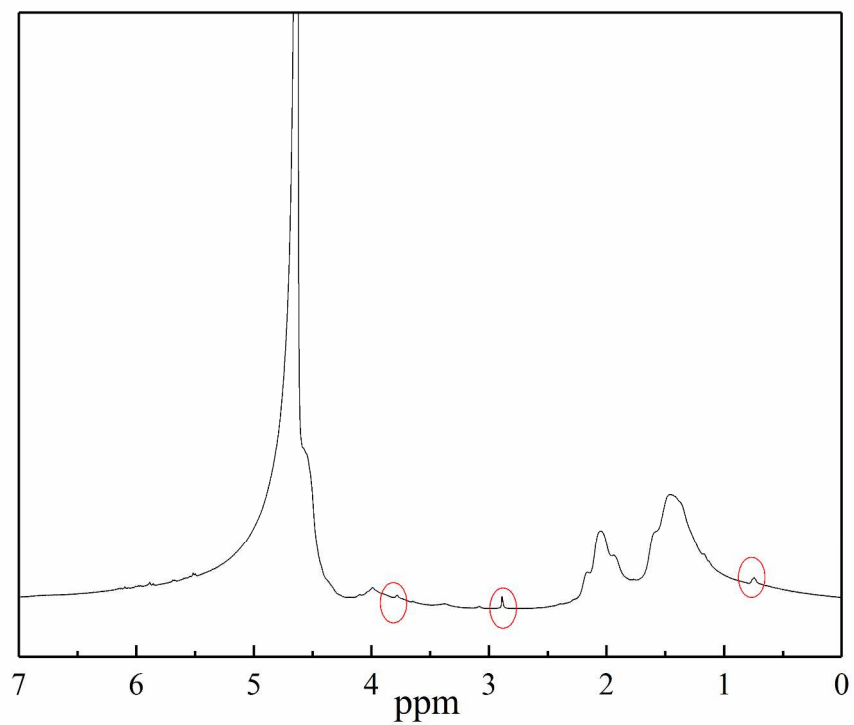


Figure 4. The  $^1\text{H}$ -NMR spectra of the AM/AA/ADIAB copolymer using  $\text{D}_2\text{O}$  as the solvent.

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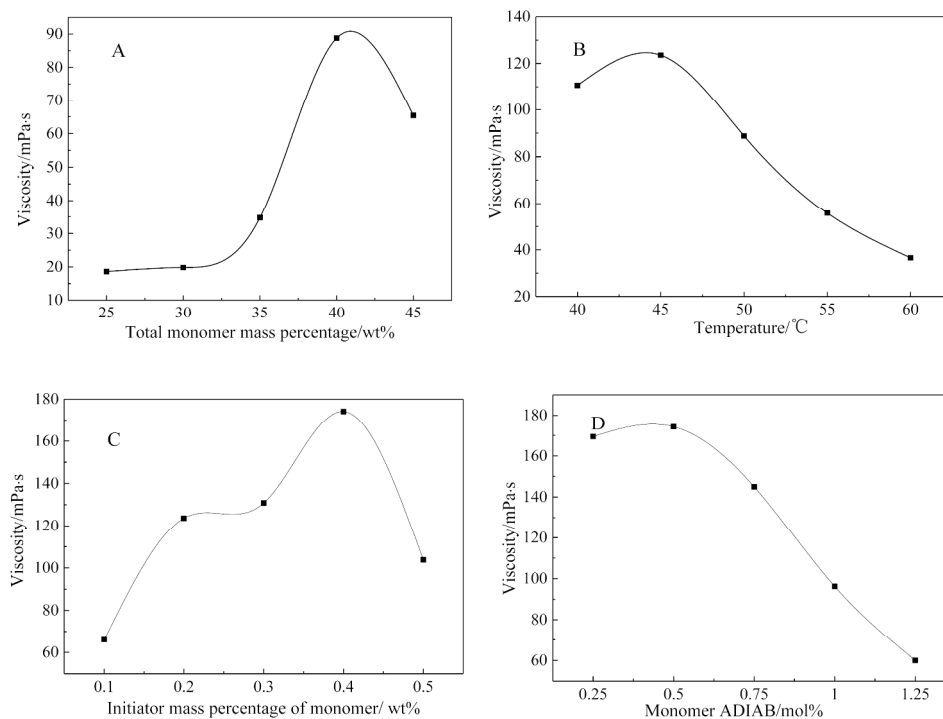


Figure 5 A: The influence of the total monomer mass percentage on viscosity of AM/AA/ADIAB copolymer solution (reaction temperature: 50°C; initiator mass percentage of monomer: 0.2%; monomers molar ratio: AM: AA: ADIAB= 74.5:25:0.5). B: The influence of the reaction temperature on viscosity of AM/AA/ADIAB copolymer solution (monomer mass percentage: 42%; initiator mass percentage of monomer: 0.2%; monomers molar ratio: AM: AA: ADIAB= 74.5:25:0.5). C: The influence of the initiator mass percentage on viscosity of AM/AA/ADIAB copolymer solution (monomer mass percentage: 42%; reaction temperature: 45°C; monomers molar ratio: AM: AA: ADIAB= 74.5:25:0.5). D: The influence of the modified monomer concentration on viscosity of AM/AA/ADIAB copolymer solution (monomer mass percentage: 42%; reaction temperature: 45°C; initiator mass percentage of monomer: 0.4%).

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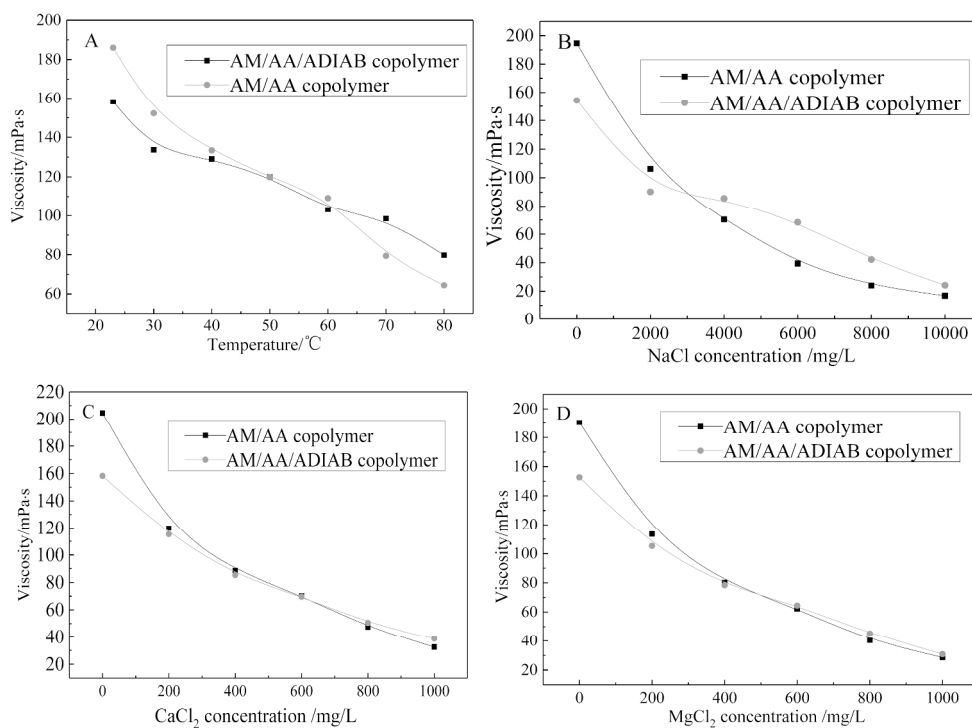


Figure 6. A: Effect of temperature on solution viscosity of polymers. B: Effect of NaCl concentration on solution viscosity of polymers. C: Effect of CaCl<sub>2</sub> concentration on solution viscosity of polymers. D: Effect of MgCl<sub>2</sub> concentration on solution viscosity of polymers.

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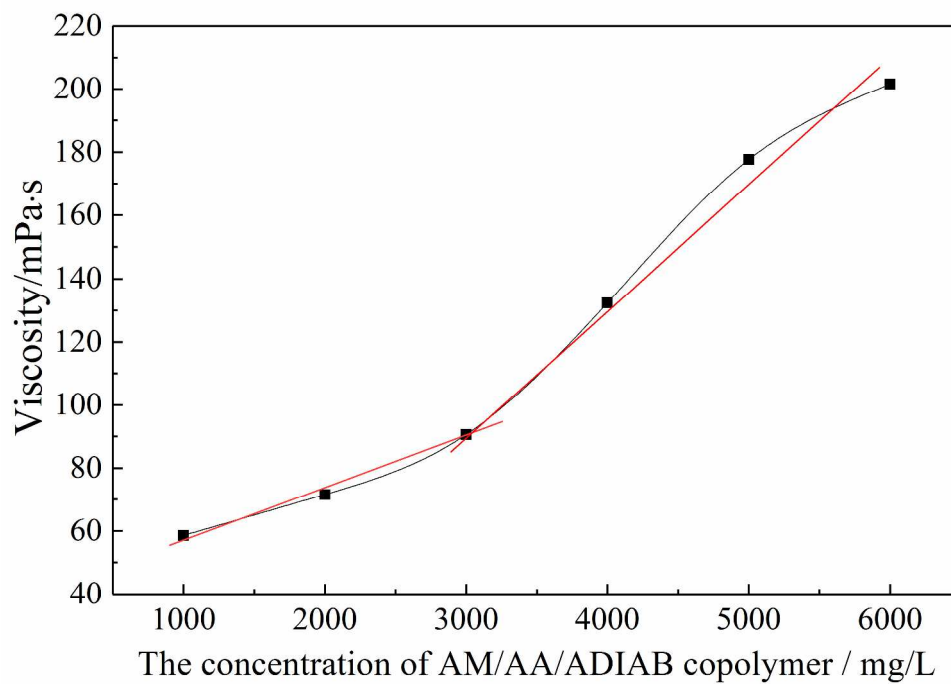


Figure 7. The influence of the concentration on viscosity of AM/AA/ADIAB copolymer solution.

296x209mm (300 x 300 DPI)

Table 1 Summary of polymer flooding tests in sandpack model (1500mg/L)

Polymer	Permeability / $\mu\text{m}^2$	Oil recovery of initial brine flooding /%	Final oil recovery /%	Tertiary recovery /%
AM/AA copolymer	0.512	45.81	58.63	12.82
AM/AA/ADIA B copolymer	0.491	44.38	60.29	15.91

For Peer Review Only