Mechanism of Polyacrylamide Hydrogel Instability on High-Temperature Conditions

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ABSTRACT: A gel system composed of acrylamide (AM), N,N′-methylenebisAM (BIS), and ammonium persulfate ((NH4)2S2O8) was developed and applied extensively in reservoirs to reduce water cut and increase oil production in mature fields. However, this gel system suffers from thermal stability loss and syneresis at high temperatures that reduces its ability to control water flow. It has been widely accepted that the loss of gel thermal stability can be explained via three aspects: the rupture of polymer chains, the breakage of cross-linker chains, and hydrolysis of polymer. The mechanism of hydrogel syneresis through polymer hydrolysis has been investigated extensively in other publications. However, research on the other two mechanisms is quite limited. In this article, we conduct a series of experiments to demonstrate how the rupture of polymer and cross-linker chains leads to the hydrogel instability at high temperatures. Viscosity and energy-dispersive system measurements suggested that polyAM chains were disrupted by the oxidation reactions involving free radicals. The method to measure the cross-linking degree was established and in combination with X-ray photoelectron spectroscopy measurements, the results showed that cross-linker chains were broken as a result of weaker C−N bond resulting from positively charged mesomethylene carbon and hydrolysis of amide groups on the cross-linker. Because of the application of deionized water in the experiments, nuclear magnetic resonance and FTIR measurements showed that the hydrolysis degree of polymer was weak. Hence, our results verified that breakage of polymer and cross-linker chains led to the rupture of the gel network at high temperature. Besides, cross-linker chains may play a more important role in the thermal stability of the gel, which explains some work into high-temperature-resistant gels.

INTRODUCTION

Because of the oil-field development in China, many mature oil fields have entered into the high water-cut stage. Because of the formation of heterogeneity, injected waters will break along the highly permeable channels and reduce oil recovery efficiency. It is reported that the water content can reach up to 90% of the fluid brought to the surface for production in mature oil fields.1,2 Excess water content has made the water flooding measurements uneconomical and has increased the cost related to water/oil separation, scale, corrosion, and well shut-in.3,4 Thus, the control of unwanted water production has been a huge challenge for oil-field operators.5

Recently, polymer gels have been developed to modify the water injection profile and enhance oil recovery.6–8 Polymer gels possess a uniform three-dimensional network structure and are formed by cross-linking the polymer molecules with a cross-linker. The most commonly used polymers are polyacrylamide (PAM), partially hydrolyzed polyAM (HPAM), and AM copolymers such as N-vinyl pyrrolidone, 2-acrylamido-2-methyl-propanesulfonate, and N-vinyl acetamide.9–12 Cross-linking agents used in polymer gels are mainly organic cross-linkers and metallic cross-linkers such as Cr3+, Al3+, and Zr4+.13–15 Besides, a novel nanocomposite hydrogel consisting of layered double hydroxide has been developed by Chen.16–18 These hydrogels have ultrahigh tensility and hierarchical porous structure and can overcome the mechanical weakness and brittleness or poor deformability of general gel system. When the gelant solution was injected into the reservoirs, the fluids tend to preferentially enter into high-permeability zones and form effective plugging for large pore throats. Therefore, the subsequent injected water will be diverted into the low-permeability zones and displace the remaining oil. This improves the sweep efficiency and oil recovery.

However, the gel used for profile modification suffers syneresis problems with strength degradation at high temperatures.19,20 Gel syneresis will cause plugging failure in high permeability zones and reduce the impact of the gel on water cut-in.3,4 Thus, the control of unwanted water production has been a huge challenge for oil-field operators.5

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production. The environmental factors affecting gel syneresis include formation temperature, divalent metal-ion concentration, and pH of the formation aqueous solution. Therefore, gel syneresis has been the main factor that limits the applications of hydrogels under this high temperature.

Recently, a novel gel system composed of AM, N,N’-methylenebisAM (BIS), and ammonium persulfate ((NH4)2S2O8) has been applied to the water shut-off treatment. However, this gel system loses thermal stability through gel syneresis in high-temperature reservoirs. To improve the thermal stability of the gel system, the syneresis mechanism must be understood for the gel system. Some studies on the syneresis mechanism have been conducted for a HPAM/Cr3+ gel system. Experimental analysis on inorganic salts affects the hydrolysis degree and suggests that the gel syneresis is the result of a decrease in hydrogel hydrophilicity. Such hydrophilicity changes can be explained by complexation of the carboxylate group with Ca2+ and over cross-linking at elevated temperatures and salinities.

Relatively little research has been performed to demonstrate the effect of the structural changes in polymers or cross-linker chains on the gel syneresis. In addition, the HPAM/Cr3+ gel system is formed via an ionic bond, whereas the AM/BIS gel system is polymerized through the covalent double bond. Thus, the cross-linking mechanism between the two gel systems is different, and this may lead to different syneresis mechanisms for the two gel systems. Although the effect of inorganic salts on polymer hydrolysis and gelation has been discussed in previous publications, it is important to study the effect of structural change on polymer and cross-linker chains for gel syneresis at high temperatures. In this study, we investigated the instability mechanism of the AM/BIS gel system. The data provide a theoretical explanation for the gel syneresis, and this will be used to optimize the gel system in profile modification treatments.

**RESULTS AND DISCUSSION**

**Rupture of Linear PAM Chains.** The viscosity of the polymer solution was highly correlated with the molecular weight of the polymer. This can be expressed via the following eq 1. Therefore, to investigate the effect of aging time on molecular weight, the viscosity of the polymer as a function of aging time was measured at different temperatures (Figure 1). The results showed that the viscosity of the linear PAM solution decreases over time, and the elevated temperature sharply decreases viscosity. Equation 1 implied that there was a positive correlation between the viscosity and molecular weight. Because PAM prepared by AM and (NH4)2S2O8 was linear, the molecular weight was positively relative to the length of polymer chain. Thus, viscosity degradation meant the reduction of molecular weight, which result from breakage of the molecular chain of the polymer at high temperatures.

\[
M = 802 \times \eta^{1.25}
\] (1)

In the equation, \(M\) is the molecular weight of the polymer and \(\eta\) is the intrinsic viscosity number.

To study the mechanism of the chain scission, the energy-dispersive system (EDS) spectrum of linear PAM was examined after aging for 12 h at 150 °C (Figure 2). From Figure 2a, it can be seen that the surface of the sample was flat and smooth after syneresis, which suggests that the gel samples dehydrate uniformly in the drying process. The energy-disperse spectrum of C, O, and N elements was exhibited in Figure 2b.

The results gave a percentage of C (50.69%), O (22.50%), N (19.71%), and H (7.09%) in the PAM before hydrolysis and [C (50.00%), O (44.40%), and H (5.59%)] after complete hydrolysis. The contents of each element in the partially hydrolyzed PAM can be calculated based on the percentage of reference element N obtained from EDS. The content of each element obtained via EDS and theoretical calculation are listed in Table 1. The carbon content obtained from both methods is close, whereas the oxygen content obtained from EDS was much higher than theory. We proposed that the dissolved oxygen was involved in the reaction of the PAM backbone.
rupture suggesting that the polymer degradation and viscosity loss might be because of oxidation at high temperatures.

The rupture mechanism of the PAM backbone was proposed and shown in Figure 3. The oxidation process can be divided into three phases. The first phase is radical initiation. The initiator ((NH₄)₂S₂O₈) reacts with dissolved oxygen to generate peroxyl radicals. The oxidation reaction was then initiated by the peroxyl radicals, which captures the active α-H on the carbon next to the amide or carboxyl group. This led to the formation of radicals on the polymer backbone (Figure 3a). The second phase (Figure 3b) is propagation. The polymer radicals reacted with oxygen and formed a peroxyl radical on the polymer backbone, which propagated the chain reaction (Figure 3c). The hydroperoxyl on the backbone weakened the C–C bond and broke the polymer backbone producing short polymer chains (Figure 3d). At higher temperature, the chain reaction was accelerated, and the rupture rates of the polymer chain were enhanced. This result corresponds to the viscosity decline of the polymer solution (as shown in Figure 1). Chain oxidation reaction will cease when the radical completed the coupling reaction and the disproportionation reaction.

Table 1. Element Contents of Linear PAM via EDS and Theory

| element | EDS percentage (%) | theoretical percentage (N as the reference element) (%) |
|---------|-------------------|-------------------------------------------------------|
| C       | 49.23             | 50.44                                                 |
| N       | 12.69             | 12.69                                                 |
| O       | 32.01             | 30.16                                                 |

Hydrolysis of a Linear PAM Polymer. Oilfield brines usually contain divalent cations such as Ca²⁺ and Mg²⁺. It has been widely accepted that the divalent metal cations would bind to the carboxylic groups and decrease the viscosity and hydrophilicity of the polymer and even lead to polymer precipitation. Thus, some experiments were conducted to investigate the hydrolysis mechanism of linear PAM.

Figure 3. Mechanism of polymer backbone rupture. (a) Initiation of free radicals. (b,c) Chain reaction. (d) Backbone fracture.

Linear PAM before and after hydrolysis were characterized by ¹³C nuclear magnetic resonance (NMR). The PAM showed three peaks before aging (Figure 4). After aging, two new peaks appeared at 45 and 182 ppm after the linear PAM was aged for 12 h at 150 °C. The peak at 182 ppm is assigned to the carbon in the carboxylate (COO⁻). This was formed by hydrolysis of the amides, and the peak at 45 ppm corresponds to the methine carbon (CH) attached to the carboxyl groups (−COO⁻). This suggested that the amide groups were partially hydrolyzed and form carboxylic groups. FTIR further verified the hydrolysis of PAM (Figure 5). The stretching peaks of PAM at 1630, 2854, 2925, and 3441 cm⁻¹ are assigned to O=C in −CONH₂, CH₃, CH₂, and NH₂, respectively. They remained the same before and after aging. However, after aging, a new stretching peak of PAM appeared at 1662 cm⁻¹ and it was assigned to the O==C in the −COO⁻
groups. Therefore, we confirmed that the hydrolysis reaction occurred after PAM was aged at high temperatures.

Deionized water was used to prepare the AM solution. There should be no metallic ions, and it should maintain a neutral pH. PAM hydrolysis reactions favor alkaline or acidic conditions and the presence of divalent cations such as Ca$^{2+}$ and Mg$^{2+}$. Under neutral conditions, it is difficult for amide groups to interact with water molecules and undergo hydrolysis. However, our experimental results suggest that PAM was hydrolyzed, and ammonia was generated during the reaction. According to previous reports, the additional water molecules, ammonia molecules, protonated water, and protonated ammonia could all reduce the activation energy and catalyze the amide hydrolysis reaction. This adequately explains the PAM hydrolysis under neutral conditions. The hydrolysis process of amide groups on PAM is shown in Figure 6. The positively protonated water can attack on carbonyl carbon of amide groups to initiate the hydrolysis reaction, which would produce carboxylic acid and release ammonia. The hydrolysis reaction would be retarded automatically because of the neighboring group effect. Thus, the hydrolysis rate slowed with increasing degree of hydrolysis (Figure 7). The value of the hydrolysis degree was about 5−9% at different temperatures and relatively low in the deionized water.

Rupture of Cross-linker Chains. The mobility of polymer chains mainly depends on the cross-linking degree between polymer and cross-linker. After PAM was cross-linked with different concentrations of BIS, the states of the PAM chains can be divided into two categories, that is, cross-linking chains and free chains. Protons in different kinds of chains can be distinguished via NMR measurement with $T_2$ relaxation time. This reflects the mobility of the polymer chains (Figure 8). The cross-linking density can be defined as the percentage of protons in the cross-linking chains relative to the protons in the entire system. Therefore, the cross-linking degree can be measured by solid-state NMR spectroscopy. The relaxation time of cross-linked hydrogels before and after aging is shown in Figure 9. The cross-linking density of the hydrogel before and after aging was obtained via MSE−CPMG analysis: 0.8643 and 0.5909, respectively.

The effect of BIS concentration and aging time on the cross-linking density was investigated next (Figure 10). The cross-linking density decreased with increasing aging time, which indicated that the cross-linking chain was broken and more free PAM chains were formed. We note that a high BIS concentration enhances the cross-linking degree and leads to better thermal stability. The cross-linking density of the hydrogel decreases to almost a stable level after aging for certain amounts of time, despite the BIS concentration. This observation is consistent with the hydrogel viscosity data after aging at 150 °C (Figure 11).

Different types of functional groups in the hydrogel before and after aging were characterized by X-ray photoelectron spectroscopy (XPS) to investigate the mechanism underlying the decrease in the cross-linking degree (Figure 12). The locations and contents of different groups in the XPS C 1s spectrum are listed in Table 2 for PAM before and after aging, respectively. Figure 12a showed that the XPS C 1s spectrum of the hydrogel sample before aging showed only two peaks including 284.8 eV that was assigned to $\text{−C−C−}$ and 287.7 eV assigned to $\text{−CONH}_2$. After the PAM was aged for 12 h at 150 °C, the XPS C 1s spectrum changed (Figure 12b) with two new peaks arising at 288.6 and 286 eV. These corresponded to...
COOH and C−O, respectively. The COOH groups were produced through hydrolysis of amide groups, and the other new C−O group may be from the rupture of the cross-linker chains. The two amide groups bound to the mesomethylene carbon in BIS have strong electronegativity, and thus the mesomethylene carbon is positively charged, which may result in nucleophilic attack of the protonated solvent on the mesomethylene carbon (Figure 13a). This nucleophilic attack facilitates the rupture of the cross-linker chain. In addition, according to the theoretical bond energy (Figure 14), the value of the C−N bond energy is the smallest of the molecular structures. Therefore, after the C−N bond was broken, one side produced C−OH and the other side produced C−NH2. This explains the presence of the C−O group. The second reason for the cross-linker fracture is the nucleophilic attack on the carbonyl carbon to facilitate the cross-linker hydrolysis. This hydrolysis reaction also leads to the rupture of the cross-linker (Figure 13b).

Instability Mechanism of Hydrogel. Figure 15a shows that the viscosity of the polymer declined rapidly in 10 to 20 min, and the hydrolysis reaction then proceeded slowly until...
the hydrolysis degree reached a stable value at 10 h. Because hydrolysis of amide groups was very low in deionized water and it had little effect on the polymer viscosity, the rupture of polymer chains caused most to the polymer degradation. The hydrogel still had a high viscosity even after aging for 20 min at 150 °C. This resulted from the cross-linked network. Therefore, the polymer chains were first disrupted and then the cross-linker chains began breaking at high temperatures. This suggested that the cross-linker chains might play a more important role in the thermal stability of the gel and explains some work into antihigh-temperature gels such as PEI gel and PBIS gel.

Next, the distribution of special charge was analyzed using ChemOffice to investigate the stability of the chemical bond in the hydrogel. The charge distribution of each atom and relative bond lengths were calculated under steric configuration of stable MM2 energy (Table 3). The carbon of the amide group (C18) has the highest positive charge (0.457). Thus, C18 was the easiest to attack by protonated water, which explains why the polymer was broken first. Carbon C6 (0.406) has a secondary positive charge, and thus the cross-linker hydrolysis occurs next. The C(9)−N(8) bond between methylene carbon and nitrogen has the weakest bond energy and the longest bond length (1.466 Å). Furthermore, the methylene carbon (C9) has a certain positive charge (0.098). Therefore, the methylene carbon was easily attacked by the protonated water, which was responsible for the rupture of the cross-linker chains.

These experiments show that the loss of gel stability is due to rupture of polymer chains and rupture of cross-linker chains. According to previous studies, the behavior of water including the hydrogel can be summarized into three states: nonfreezing bound water, freezable bound water, and free water. Nonfreezing bound water is strongly bound to the hydrogel network, whereas freezable bound water is weakly bound to the hydrogel network. The freezable water easily transforms into free water. The rupture of polymer and cross-linker chains can disrupt the three-dimensional network structure and cause rigidity loss. This decreases the ability of the gel to bind the aqueous molecules. The resulting freezable bound water would separate from the gel phase and become the aqueous phase (Figure 16). With increasing aging time, the volume of the gel would shrink. Finally, the gel that has shrunk would float in the aqueous phase and reduce the ability to control water.

**CONCLUSIONS**

A hydrogel system composed of AM, BIS, and ammonium persulfate was prepared. The instability mechanism of the hydrogel was studied at elevated temperatures. Although the amide groups on the polymer chains hydrolyzed at high temperatures, the degree of hydrolysis was too small to affect gel instability. The results suggested that if the gelant solutions were prepared with deionized water, then the rupture of both polymer chains and cross-linker chains were the main causes for gel instability. The polymer backbone was broken because of the oxidation reaction involving free radicals. The rupture of the cross-linker chains was due to hydrolysis of the carbonyl carbon of the amide group, followed by attack on the methylene carbon from the nucleophilic aqueous solution. The rupture of both polymer and cross-linker chains disrupts the network structure and makes the bound water separate from the gel phase. This further decreases the hydrogel function. Besides, the cross-linker chains might play an important role in the thermal stability of the gel. This explains some work in high-temperature-resistant gels. Understanding of chemical principles related to the hydrogel instability mechanism is of great significance for the optimization of the

| hydrogel     | location (eV) | area (%) | bond               |
|--------------|---------------|---------|--------------------|
| before aging | 284.86        | 76.9    | C−H (C−C)          |
|              | 287.48        | 23.1    | CONH₂              |
| after aging  | 284.85        | 68      | C−H (C−C)          |
|              | 287.72        | 18.7    | CONH₂              |
|              | 288.65        | 6.2     | COOH               |
|              | 285.91        | 7.1     | C−O                |

**Figure 13.** Theoretical bond energy of BIS.

**Figure 14.** Fracture mechanism of the cross-linker chain. (a) Fracture of methylene. (b) Hydrolysis of amide groups.
polymer and the cross-linker, especially for applications of hydrogels under high-temperature reservoirs.

**EXPERIMENTAL SECTION**

**Materials.** AM was provided by JiangXi ChangJiu Biochemical Industry Co., Ltd., and BIS was used as the cross-linking agent. Ammonium persulfate ((NH₄)₂S₂O₈) was analytically pure and was purchased from Aladdin Reagent CO., Ltd. (Shanghai, China). AM (5.00 g) and 0.02 g of (NH₄)₂S₂O₈ were dissolved in 95.00 g of deionized water to prepare the linear PAM solution. If 0.02 g of (NH₄)₂S₂O₈ was added into the above solution, the hydrogel would be prepared. The cross-linking process is shown in Figure 17. The reaction was carried out at 60 °C for 1.5 h. Deionized water was used in the experiments unless otherwise mentioned.

**Measurements of Polymer Viscosity.** The resulting PAM solutions were sealed in steel cans and placed in an oven at different temperatures for different lengths of time. The viscosity of the samples after aging was measured at 25 °C with a rotation speed of 6 RPM using the NDJ-1 rotational viscometer.

**Measurements of NMR.** The solid hydrogel materials (Figure 18) were precipitated from an aqueous solution with the addition of acetone. The products were washed with methyl alcohol and dried with a vacuum drying oven for 72 h before measurement. The sample was dissolved in D₂O and 1,4-dioxane served as the reference. The molecular structure characterizations of the samples were examined with ¹³C and ¹H NMR spectra on a Bruker AV II-400 spectrometer. The cross-linking degree was measured with a VTMR20-010V-T spectrometer. The resonance frequency was 21.5556...
MHz, and the intensity of the magnets was 0.5 T. The coil diameter was 10 mm, and the temperature of the magnets was 32 °C. The A Carr−Purcell−Meiboom−Gill (CPMG) pulse sequence was used to measure the T2 spectra. The decay curve of the sample was obtained with software and the MSE-CPMG sequence. All NMR experiments were performed at room temperature. The spectra were processed and analyzed using a Bruker Topspin V2.0.

Measurements of FTIR. After the precipitated solid hydrogel materials were washed with methyl alcohol and dried in a vacuum oven for 72 h, the IR samples were prepared by mixing the hydrogel and KBr powder and pressing it into a disk. The FTIR measurements were conducted on a Nexus 670 FT-IR spectrometer, and the spectral measurements were collected from 4000 to 500 cm\(^{-1}\). All treated and untreated samples were then dried and coated with a gold coating before SEM−EDS examination.

SEM and EDS Measurements. SEM−EDS (X-Max 51-XMX0019) was used to observe the morphology and surface texture of the polymer as well as to analyze the elemental composition of the polymer. Determinations were conducted at an accelerating voltage of 25 kV and a working distance from 5 mm to 10 mm.

XPS Measurements. X-ray photoelectron spectroscopy data were obtained with a Kratos XSAM800 electron spectrometer using nonmonochromatized Al Kα (1486.6 eV) X-radiation. The operating conditions were set to 12 kV and 15 mA. High-resolution spectra of carbon were recorded. Peak positions were corrected by calibration against C 1 s occurring at 284.8 eV for this spectrometer. Curve fitting and decomposition were completed assuming Gaussian−Lorentzian fitting following a Shirley background subtraction.

Figure 17. Proposed mechanism of cross-linking AM with BIS.

Figure 18. Dry solid materials precipitated from hydrogel after aging for different times.

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Notes

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