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A Novel Branched Polymer Gel System with Delayed Gelation Property for Conformance Control

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Summary

Excessive water production from oil reservoirs not only affects the economical production of oil, but it also results in serious environmental concerns. Polymer gels have been widely applied to decrease water production and thus improve oil production. However, traditional polymer gels such as partially hydrolyzed polyacrylamide (HPAM)/chromium (III) gel systems usually have a short gelation time and cannot meet the requirement of some conformance control projects. This paper introduces a novel polymer gel system of which crosslinking time can be significantly delayed. A branched polymer grafted from arginine by the surface initiation method is synthesized as the backbone, chromium acetate is used as the crosslinker, and no additional additives are used for the gel system. The results show that the gelation time of this system can be delayed to 61 days at 45°C and 20 days at 65°C because of the rigid structure of the branched polymer and the excellent chromium (III) chelating ability of arginine. The polymer gels have been stable for more than 150 days at 45 and 65°C. Coreflooding and rheology tests have demonstrated that this branched polymer has good injectivity and shear resistance in high-permeability rocks.

Introduction

Early water breakthrough and excessive water production have become a major problem in the oil industry that has resulted in leaving a considerable amount of unrecoverable hydrocarbon in reservoirs. It was reported that in the USA, more than 910×10^9 gallons of wastewater are produced each year from oil fields with an average of approximately 10 barrels of water being produced for each barrel of oil production (Veil 2015). Such a huge amount of wastewater not only increases the treatment cost, but it also poses a significant threat to the environment. Polymer gel treatment has been widely applied to control the excessive water production problem.

The gel system composed of HPAM and chromium (III) has been most commonly applied for conformance control because of its relatively low cost and good plugging performance (Bai et al. 2015; Zhang et al. 2020). However, the gelation time of the HPAM-based gel system is usually short, up to only a few hours when no additional additives are used (Cordova et al. 2008). The short crosslinking time does not influence the gel propagation through the preferential fluid flow path when the conformance control problem is caused by fractures inside a reservoir (Seright 1988, 1995; Liang et al. 1993). The gelation systems with delayed gelation time have still drawn some interest by some companies such as ConocoPhillips, Marathon Oil, Halliburton, and Saudi Aramco because it is believed that they can be used in specific circumstances (Sydansk 1989; Vasquez 2005; Huili et al. 2020; Wang et al. 2020). Currently, the delayed gelation of the HPAM/chromium (III) system can be achieved by the following three commonly used technologies. First, the gelation time can be extended by adding organic ligands such as acetic acid, propionic acid, lactic acid, and amino acid into HPAM and chromium (III) hybrid solutions also termed as gelant solutions. The gelation mechanism is attributed to the interaction between chromium (III) ions and carboxylate groups on the polymer chains, or in other words, the crosslinking reaction is a ligand-exchanging process (Sydansk 1988; Lockhart and Burrafato 1992; Albonico et al. 1993; Lockhart and Albonico 1994). Therefore, extra organic ligands can delay the reaction rate between the chromium (III) ions and HPAM by temporarily sequestering the chromium (III) ions. Lockhart and Burrafato (1992) reported that the gelation time at 60°C could be extended to 16 days by using serine as the ligand with a ligand to chromium molar ratio of 25. Albonico et al. (1993) reported that the gelation time could be extended to 66 days by using lactate as the ligand with a ligand to chromium molar ratio of 50. However, gels tend to become relatively weak when the ligand to chromium (III) molar ratio exceeds 3.9:1 (Sydansk 1990). The second method is chromium (III) encapsulation technology (Cordova et al. 2008; Huili et al. 2020). For example, the self-assembled polyelectrolyte complex nanoparticles formed by polyethylenimine and dextran sulfate were deployed to entrap chromium ions, and the gelation time at 40°C was extended to 4.5 days (Cordova et al. 2008). However, it is very difficult to ensure that the chromium (III) ions are released simultaneously and homogeneously in the gelant, so partial overcrosslinking problems might not be avoided. The third method is to use polyacrylamide with ultralow molecular weight and hydrolysis degree. It is well acknowledged that the gelation time has a close relationship to HPAM properties and increases with hydrolysis degree, molecular weight, and polymer chain flexibility (Gales et al. 1994; Karimi et al. 2016). For instance, Sydansk (1993) extended the gelation time to 25 days at 60°C by using nonhydrolyzed polyacrylamide with a molecular weight of 270 000 g/mol. Compared with a commonly used high-molecular-weight gelant system, a high concentration of polymer and crosslinker solution is required to formulate acceptable gel strength (Sydansk 1993). This is because the degree of physical entanglement decreases with molecular weight, and thus more polymer molecules and chemical crosslinking points are needed to form a 3D network (Norioka et al. 2021).

To overcome some drawbacks of current gelation-delayed gel systems, we developed a novel gel system with a relatively long gelation time. Branched polyacrylamide (BPA) with less chain flexibility was synthesized by the one-step surface initiation method. Ceric ammonium nitrate, which can form a very effective redox system with the presence of amines and alcohols, was used to trigger the polymerization (Mino and Kaizerman 1958; Pei et al. 2008). Polymer chains are grafted from the core, and we selected arginine as the core because it has good metal ion chelating ability, which can delay the gelation time by temporarily chelating the chromium (III) ions (Ashmead et al. 1989; Zheng et al. 2015; Koilraj et al. 2019).

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In this paper, we studied the effect of branched polymer structure on the gelation time. We evaluated the factors that affect the gelation time, including arginine, polymer, chromium acetate concentrations, temperature, and pH. We also studied the long-term thermal stability of the polymer gels by monitoring the volume and phase changes during the testing process. In addition, we tested the injectivity of this novel gel system by injecting gelant through a high-permeability core. The pressure gradient and resistance factor along different sections of the core were calculated to evaluate the injectivity.

Experimental Procedures

Materials. Acrylamide (99%), L-arginine (Ar, 98.5%), ceric ammonium nitrate (99%), nitric acid (HNO₃, 90%), and sodium hydroxide (NaOH, 99%) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Chromium acetate (CH₃COO)₃Cr, 24% chromium (III) solid was purchased from Alfa Aesar (Haverhill, Massachusetts, USA). Sodium chloride (NaCl) was purchased from Fisher Scientific (Hampton, New Hampshire, USA). All materials were used directly without further purification.

Polymer Synthesis. A representative branched polymer was prepared by free radical polymerization as shown in Fig. 1. Under vigorous stirring, acrylamide (15.00 g, 211.27 mmol), arginine (50.00 mg, 0.29 mmol) were added into deionized water (35.00 g). HNO₃ was used to adjust the solution pH from 4 to 6. After bubbling with argon for 30 minutes at 23°C, ceric ammonium nitrate (200.00 mg, 0.36 mmol) was added to begin the polymerization. Two hours later, the three-neck flask containing the reactants was placed in an oil bath at 45°C for 4 hours. After that, the bulk gel was dried at 45°C and crushed into powder. Four BPAs with different amounts of arginine were synthesized and listed in Table 1.

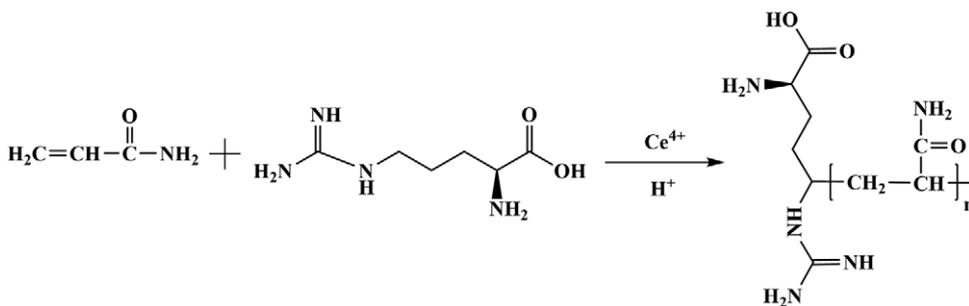


Fig. 1—General synthetic scheme of a branched polymer via surface initiation polymerization.

Number	Arginine (g)
BPA-1	0.30
BPA-2	0.20
BPA-3	0.10
BPA-4	0.05

Table 1—Preparation of the BPA (15.00 g of acrylamide, 0.20 g of ceric ammonium nitrate, 35.00 g of deionized water, pH 5.0).

Preparation of Gelants. To prepare all the gelants, 1% NaCl solution was used. A representative gelant was prepared as follows. A specified amount of chromium acetate stock solution and the polymer solution were mixed using a magnetic stir bar.

Characterization of the Branched Polymers and Gels. Fourier transform infrared spectrometry was carried out on a Nicolet iS50 spectrometer (Thermo Fisher Scientific; Waltham, Massachusetts, USA) with a resolution of 2 cm⁻¹ at room temperature. EVO LS 15 scanning electron microscope was used to characterize the gel morphology. The crosslinked gel was freeze-dried and coated before testing.

An Ubbelohde viscometer was used to test the intrinsic viscosity of the branched polymer (Kulicke et al. 1982; Fujishige 1987). The intrinsic viscosity of the branched polymer was converted to the intrinsic viscosity of the linear polymer following the method of Zimm and Kilb (1959), and the molecular weight was calculated using Eqs. 1 through 4 (Zimm and Stockmayer 1949; Kulicke et al. 1982):

$$g = \frac{2(13f^2 - 20f + 8)}{f(9f^2 - 9f + 2)}, \dots \dots \dots (1)$$

$$g' = g^{0.5}, \dots \dots \dots (2)$$

$$g' = \frac{[\eta]_b}{[\eta]_l}, \dots \dots \dots (3)$$

$$[\eta] = KM^\alpha, \dots \dots \dots (4)$$

where f is the functionality, g is the gyration radii, g' is the branching parameter, $[\eta]_b$ is the intrinsic viscosity of the branched polymer, $[\eta]_l$ is the intrinsic viscosity of the linear polymer, M is the molecular weight, and K and α are constants for a particular polymer solvent system.

Rheological and Gelation Time Tests. HAAKE MARS III rheometer (Thermo Fisher Scientific) was used to test the elastic modulus of the gel with a gap of 0.5 mm (P35 Ti L). Strain sweep experiments were conducted to determine the linear viscoelastic region. Oscillation time-dependent experiments were performed at a fixed frequency of 1 Hz and controlled strain of 1% to obtain elastic modulus (G') and viscous modulus (G'') as a function of time.

Brookfield DV3T was used to test the viscosity of the gelant during the crosslinking process, and the spindle used for the measurements was #18 with the shear rate fixed at 7.34 s^{-1} . We prepared 50 samples for each gelant composition, and argon was purged into each gelant sample for 5 minutes before sealing the tube. We took one sample out of the oven and put it directly in a preheated cylinder in which the temperature was maintained by a circulation water bath, so the result represents the temperature same as the aging temperature. In this paper, we define gelation time as the time when an abrupt increase in gelant viscosity was observed. The gelant viscosities before gelation were recorded based on the designed schedule and observation.

Thermal Stability Tests. The thermal stability test was carried out by monitoring the volume and appearance of the gels at 45, 65, and 80°C . Gel volume and phase stability changes were monitored during the aging test.

Coreflooding Experiments. The injectivity of this novel branched polymer was evaluated by calculating the resistance factors along the core. The set of coreflooding experiments and core parameters were shown in Fig. 2. The salinity of the injected brine was 1 wt% NaCl. Pre-waterflooding was performed to calculate the rock permeability. Then a gelant solution composed of 0.3 wt% polymer and 0.05 wt% chromium acetate, was injected at different flow rates, and the stable pressures were recorded. The resistance factor (F_r) can be calculated using Eq. 5, where ΔP_{gelant} and ΔP_{water} are gelant and water injection pressure gradients, respectively, measured at the same injection rate.

$$F_r = \frac{\Delta P_{\text{gelant}}}{\Delta P_{\text{water}}} \dots \dots \dots (5)$$

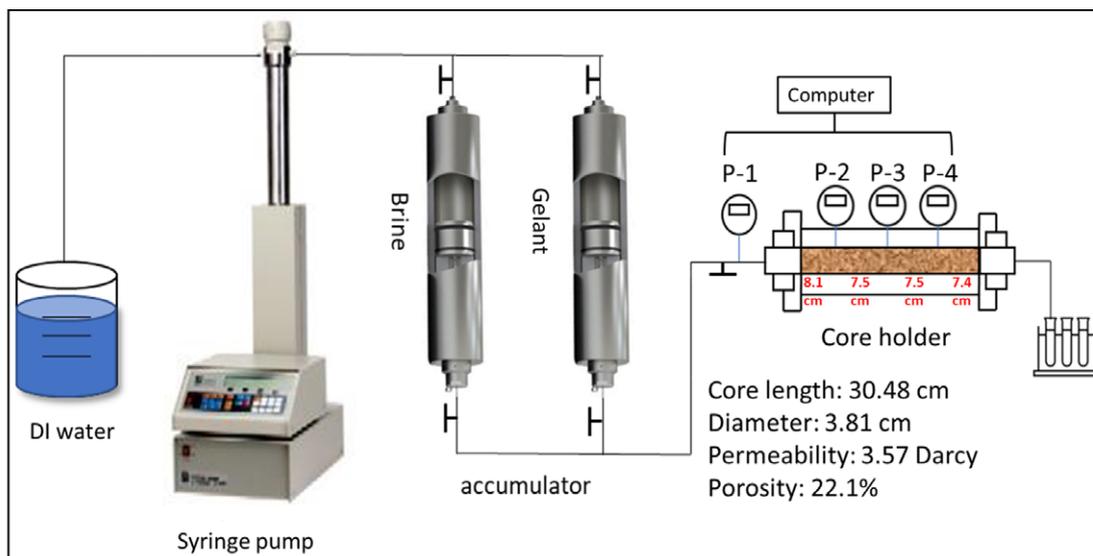


Fig. 2—Schematic of coreflooding setup. DI = deionized.

The effluent viscosities at different injection rates were also measured, and the viscosity retention ratio (μ_r) was calculated using Eq. 6, where μ_{eff} and μ_{ini} are the viscosities of effluent and initial gelant solution, respectively.

$$\mu_r = \frac{\mu_{\text{eff}}}{\mu_{\text{ini}}} \dots \dots \dots (6)$$

We tested the shear resistance of the gelant using a Haake MARS III rheometer equipped with concentric cylinder geometry cup DG-41 and rotor DG-41. The shear rate was increased from 10 to $2,000 \text{ s}^{-1}$, and after that, the shear rate was decreased from 2,000 to 10 s^{-1} . The measurement was repeated for three cycles.

Results and Discussion

Characterization of the Branched Polymers and Gels. Fig. 3 shows the Fourier transform infrared spectrum of the branched polymer. The broadband between 3647 and 2979 cm^{-1} was mainly caused by O-H stretching of COOH, crystallization of water, N-H stretching of C-NH_2 and -NH_3^+ , and C-H stretching of CH_2 and CH. The band at 1665 cm^{-1} was attributed to the stretching vibration of C=N and C=O bonds. The absorption intensities from BPA-1 to BPA-4 gradually decreased, which was consistent with the gradual decrease of the arginine concentration. Fig. 4 shows the morphology of BPA-1 gel, and the gelant was composed of 0.3 wt% polymer and 0.1 wt% chromium acetate. The crosslinked polymer gel has a dense network structure with pore size ranges from 10 to $30 \mu\text{m}$.

Effect of Arginine Concentration on the Gelant Viscosity. Fig. 5 shows the molecular weight and viscosity of gelants BPA-1 to -4 composed of 0.3 wt% polymer and 0.05 wt% chromium acetate. Both the viscosity and molecular weight decreased with the increase of arginine concentration. This is because arginine is a part of the initiator, and the kinetic chain length decreases with the increase of initiator concentration. Therefore, polymers with short branched chains, such as BPA-1, are more rigid and less entangled than those with long branched chains, like BPA-4.

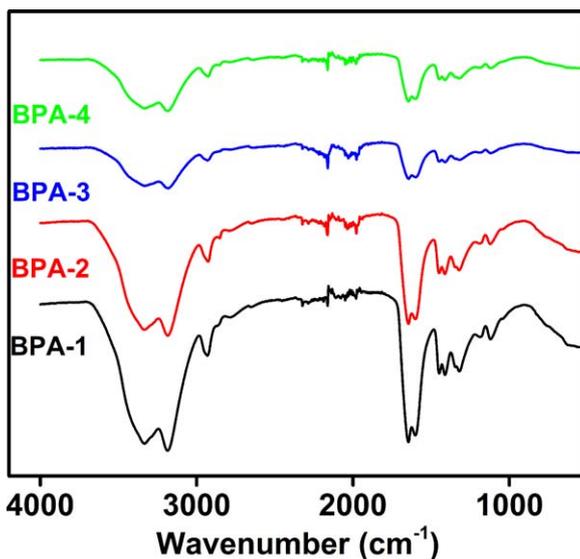


Fig. 3—Fourier transform infrared spectrometry of BPA.

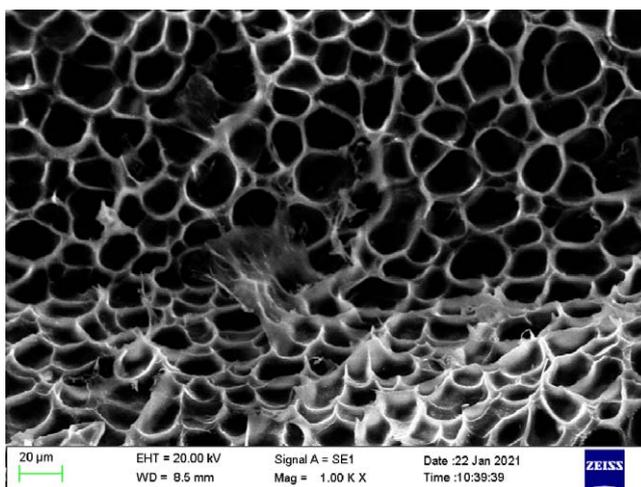


Fig. 4—Scanning electron microscope photograph of the crosslinked polymer gel. EHT = electron high tension; WD = working distance; Mag = magnification.

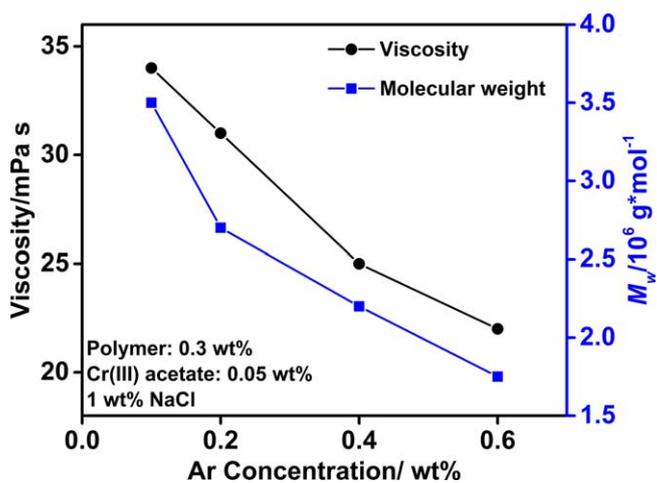


Fig. 5—Viscosity and M_w as a function of arginine concentration.

Factors Affecting Gelation Time. The effects of arginine, polymer, and chromium acetate concentration on the gelation time were investigated using the bottle-testing method.

Effect of Arginine Concentration. To test the effect of arginine concentration on the gelation time, we fixed the gelant formation as follows: 0.3 wt% polymer and 0.05 wt% chromium acetate with a testing temperature of 65°C. Fig. 6 shows the viscosity changes of different gelants during the gelation process. The gelation time increased with arginine concentration, and the gelation time of BPA-1, BPA-2, BPA-3, and BPA-4 were 10, 5, 3, and 1.5 days, respectively.

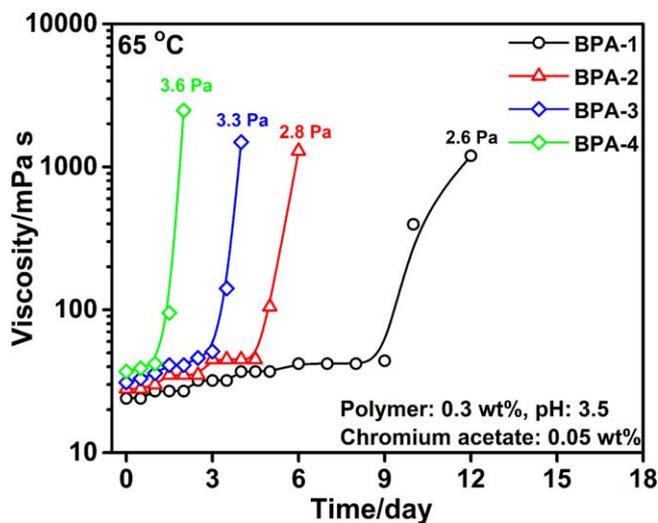


Fig. 6—Gelation process at 65°C.

In general, gelation time has a close relationship to the polymer properties (Sydansk 1993; Zhang et al. 2015). Gelation reaction can be divided into two steps: uptake and intermolecular crosslinking. The uptake reaction can also be termed as intramolecular crosslinking, where only one polymer chain takes part in the ligand-exchanging reaction. The uptake reaction plays a significant role in the whole gelation process because it is the rate-determining process (Jain et al. 2005). Next, the intermolecular crosslinking is the reason for the formation of a 3D network (Gales et al. 1994). As shown in Fig. 6, the viscosities of all the samples slowly increased at the beginning and then increased sharply when the gel point was reached.

BPA gels have a relatively long gelation time. Taking the example of BPA-1, the gelant viscosity did not change significantly after 9 days; however, the gelant viscosity increased to more than 300 mPa·s on the 10th day. Different from the conventional HPAM/chromium (III) systems, which have a relatively fast uptake reaction and intermolecular crosslinking rate, the intermolecular crosslinking of the BPA gel system is greatly hindered because of the branched structure and the lack of chain flexibility. In addition, arginine has strong chelating efficiency to metal ions, so fewer chromium (III) ions are available to the crosslinking reaction with the increase of arginine concentration. Therefore, BPA-1 with the highest arginine concentration has the longest gelation time among the four samples. However, as shown in Fig. 6, BPA-1 was the weakest gel among the four samples, with a G' of 2.6 Pa, and the gel strength decreased with the increase of arginine concentration. This is because arginine has a negative effect on molecular weight and chain flexibility. In general, for a given polymer and crosslinker concentration, the strength of the crosslinked gel decreases as polymer molecular weight decreases (Sydansk 1993). Therefore, BPA-1, with the longest gelation time, has the weakest gel strength among all the samples. This result is also consistent with the previous rheology test results, in which the viscosity decreased with the increase of arginine concentration.

Effect of Temperature, Chromium Acetate, and Polymer Concentration. BPA-1 has the longest gelation time among all the samples, so we further evaluated the effect of temperature, chromium acetate, and polymer concentration on the gelation time of the BPA-1 gel system.

Table 2 gives the gelation testing results at 45°C. The gelation occurs only when the crosslinker concentrations were 0.05 and 0.1 wt%. The gelant composed of 0.3 wt% polymer and 0.05 wt% chromium acetate has the longest gelation time of 61 days. It is surprising that the gelants did not change to gels when chromium acetate concentration is high. Fig. 7 shows that the gelant samples composed of 0.02, 0.3, and 0.5 wt% chromium acetate still remained as transparent solution without forming any precipitations after 150 days at 45°C. It is common that HPAM/chromium (III) gel systems have a lower critical chromium (III) concentration, below which gel cannot be formed because of the limited amount of crosslinking points (Sydansk 1993; Romero-Zeron et al. 2008). However, for this branched polymer-based gel system, it has both lower and upper critical chromium concentrations. This observation is not yet fully understood. One possible reason for this phenomenon is the strong screen effect caused by chromium (III) ions. Chromium (III) is a trivalent cation with a much stronger screening effect than Ca^{2+} and Na^+ (Xin et al. 2014). Polymer chains are less stretched in a concentrated chromium acetate solution, in which the intermolecular crosslinking probability is significantly decreased. The reasons for the delayed gelation could be explained as follows. Most chromium ions are chelated by either acetate or amino acid groups, and these chromium ligand complexes have a relatively good kinetic stability at 45°C (Lockhart and Albonico 1994). In addition, more intramolecular crosslinking can be expected for the BPA-1 gel system because of the branched structures, whereas the intramolecular crosslinking in a single polymer cannot contribute to the formation of a 3D network, so the gelation time was delayed at 45°C.

Table 3 shows the gelation test results at 65°C. The gelant composed of 0.3 wt% polymer and 0.5 wt% chromium acetate has the longest gelation time of 20 days. The crosslinked polymer gels were shown in Fig. 8. As the chromium acetate concentration kept increasing, the gelation time decreased first and then increased when the chromium acetate concentration was 0.3 wt%. Two main factors might contribute to the differences in gelation time and critical chromium acetate concentrations between 45 and 65°C. First, the temperature has a negative effect on the stability of the chromium ligand complex. The conversion rate from chromium ligand complex to chromium polymer complex is greatly accelerated at high temperatures, so the gelation time decreases at high temperatures (Prud'homme 1984; Lockhart and Albonico 1994). Second, high temperature and low pH can accelerate the hydrolysis of amide groups

(O'Connor 1970). The hydrolysis rate at 65°C is hence greatly accelerated compared with that at 45°C. Polymer chains are more stretched with the increase of hydrolysis degree and chain-chain repulsion, and more carboxylate groups are available for the gelation reaction. Therefore, the lower critical chromium acetate concentration decreases due to the increase of crosslinking points and crosslinking reactivity. In a concentrated chromium acetate solution, the strong screening effect caused by the chromium (III) ions can be gradually alleviated with the increase of hydrolysis degree/chain-chain repulsion, so gels composed of 0.3 and 0.5 wt% chromium acetate can still change to gels with the extension of aging time.

Chromium Acetate (wt%)	Gelation (times/D)		
	0.3 wt% Polymer	0.5 wt% Polymer	1 wt% Polymer
0.02	No gelation	No gelation	No gelation
0.05	61	42	29
0.1	30	22	13
0.3	No gelation	No gelation	No gelation
0.5	No gelation	No gelation	No gelation

Table 2—Summary of gelation time at 45°C.



Fig. 7—Gelant samples after 150 days at 45°C (1 wt% polymer, pH 3.5).

Chromium Acetate (wt%)	Gelation (times/D)		
	0.3 wt% Polymer	0.5 wt% Polymer	1 wt% Polymer
0.02	18	14	8
0.05	10	8	6
0.1	9	6	4
0.3	15	12	5
0.5	20	15	8

Table 3—Summary of gelation time at 65°C.

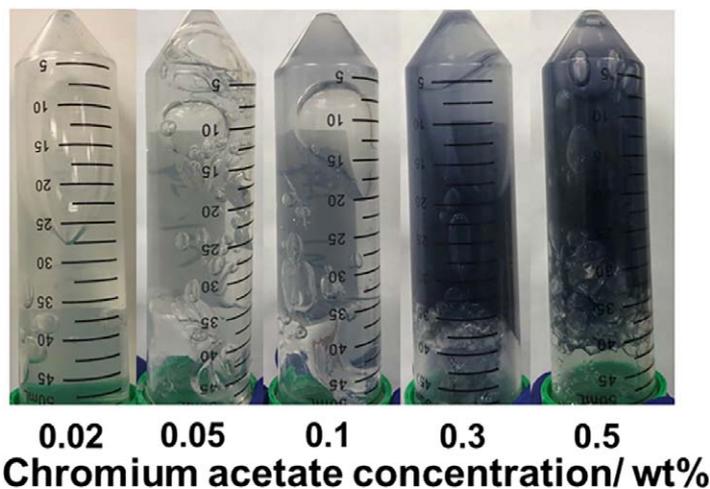


Fig. 8—Gelant samples after 150 days at 65°C (polymer 1 wt%, pH 3.5).

Table 4 shows the gelation time data at 80°C. The gelation time was significantly shortened. The branched structure has less effect on the gelation time with the increase of temperature.

Chromium Acetate (wt%)	Gelation (times/D)		
	0.3 wt% Polymer	0.5 wt% Polymer	1 wt% Polymer
0.02	2	1	0.4
0.05	1	0.8	0.3
0.1	0.8	0.6	0.2
0.3	1	0.6	0.3
0.5	1.6	1	0.5

Table 4—Summary of gelation time at 80°C.

We also studied the effect of gelant composition on gel strength. Gelants were aged 20 days at 65°C before the strength testing. In general, the polymer and chromium acetate concentrations have a positive effect on the gel strength, but a too-high concentration of chromium acetate has a negative impact on the gel strength. **Fig. 9a** shows that the crosslinked gel has a linear viscoelastic region with shear strain ranges from 0.4 to 10%. This confirmed the chosen parameters of 1-Hz frequency at controlled strain (γ) of 1% was within the linear region. **Fig. 9b** shows the effect of chromium acetate concentration on the gel strength, with the polymer concentration fixed at 0.3 wt%. As the chromium acetate concentration kept increasing, the gel strength increased first and then decreased when the chromium acetate concentration was 0.1 wt% or higher. As discussed previously, excessive chromium (III) ions could reduce the degree of chain entanglement and hence decrease the gel strength.

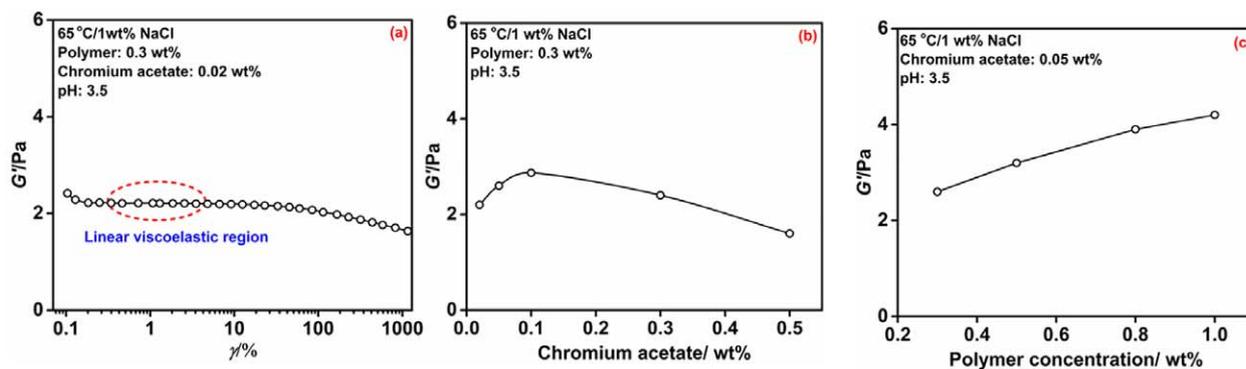


Fig. 9—(a) Oscillatory result of a crosslinked polymer gel. (b) G' responding to chromium acetate concentration. (c) G' responding to polymer concentration.

Effect of pH on the Gelation Time. It is well known that pH has a significant effect on the reaction between chromium (III) complex and carboxylate containing polymers, so we studied the effect of pH on the gelation time of the BPA-1 system at 65°C. The tested gelant was composed of 0.3 wt% polymer and 0.05 wt% chromium acetate.

Fig. 10 shows that the gelation was accelerated and the gel strength increased with pH until the pH reached 10, after which flocculent precipitate was observed. The gelant became less transparent when the solution pH was 10, which was caused by the hydrolysis of chromium (III) ions. After hydrolyzation, the concentration of unhydrolyzed chromium (III) is too low to form a 3D network, even though the polymer hydrolysis degree is high. The main reason for the accelerated gelation and enhanced gel strength at relatively high pH is the increased hydrolysis rate of amide groups. After hydrolyzation, more carboxylate groups are generated, which can decrease the gelation time and enhance the crosslinking density (O'Connor 1970; Sydansk 1993; Kurenkov et al. 2001).

Thermal Stability. We tested the thermal stability of BPA-1 polymer gels at 45, 65, and 80°C. The gelant was composed of 0.5 wt% polymer and 0.05 wt% chromium acetate. As shown in **Fig. 11**, BPA-1 had good thermal stability at 45°C, and no free water was observed after 150 days of aging. A small amount of water was observed after 80 days of aging at 65°C, and the syneresis percent after 150 days of aging was approximately 5%. The polymer gel had poor stability at 80°C, and the syneresis percent reached 70% after 70 days of aging. More work will be done in the future to find the temperature threshold for significant syneresis of this gel system.

Flory's theory (Flory 1953) can well explain the syneresis mechanism of a crosslinked gel. Based on the theory, the thermal stability of a crosslinked polymer gel has a close relationship with mixing potential and elastic potential. Therefore, the factors that affect the two potentials, such as crosslinking density, charge density, and hydrophilicity of polymer chains, also influence the gels' thermal stability. For example, polyacrylamide-based gels can absorb water and swell because of the osmotic pressure. At the same time, mixing potential decreases, and elastic potential increases. Gels further swell till the absolute value of elastic and mixing potential are the same. At 45°C, the thermal-triggered hydrolysis of amide groups and scission of polymer chains are relatively slow, so the two potentials of a crosslinked polymer gel did not change significantly (Xiong et al. 2018). However, at 65°C, with the increase of aging time, more carboxylate groups are generated after the hydrolysis of amide groups, so more crosslinking points are available to the chromium (III) ions. Polymer gels need to lose water to maintain the equilibrium state, with the increasing crosslinking density/elastic potential. Therefore, some free water can be observed on top of the gels after 90 days of aging at 65°C.

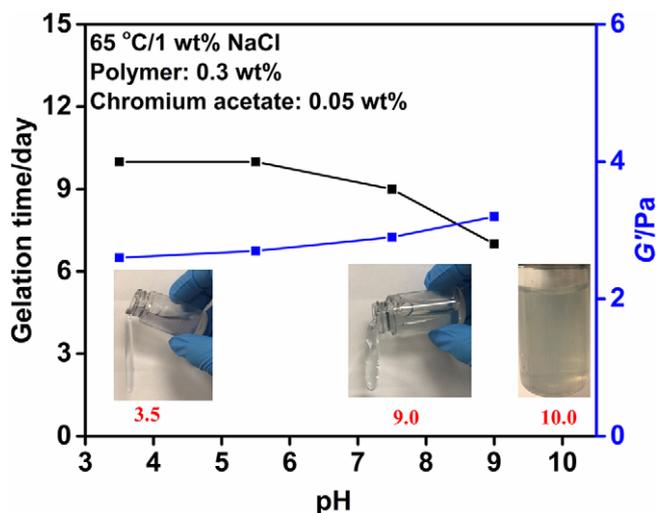


Fig. 10—Effect of pH on the gelation time and gel strength.

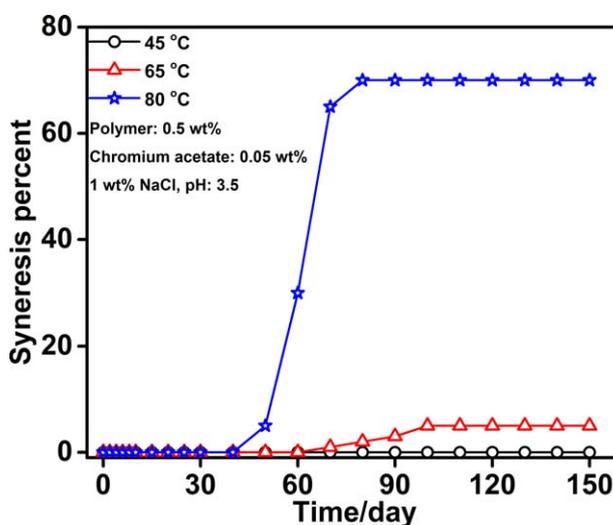


Fig. 11—Syneresis percentage of BPA-1 at 45, 65, and 80 °C.

At 80 °C, the hydrolysis of amide groups and scission of polymer backbones are significantly accelerated, so polymer gels need to keep losing water to maintain the equilibrium state with the increasing crosslinking density/elastic potential. Therefore, the crosslinked polymer gels lose integrity rapidly, and phase separation can be observed eventually.

Injectivity Test. Coreflooding and rheology tests were performed to study the injectivity and shear resistance of this branched polymer. The results of injectivity tests are shown in Fig. 12. A high-permeability rock was used to test the injectivity of this branched polymer-based gelant. Three relatively high injection rates were selected to simulate the high shearing process near the wellbore. The resistance factors increased with the injection rate. More importantly, the resistance factors of different segments are almost the same with very small fluctuation. As depicted in Fig. 12c, we did not observe any polymer cake on the rock injection surface after the injectivity test. We also measured the viscosity retention ratio using the effluent samples from the coreflooding and found the viscosity retention ratios were constant as shown in Fig. 12d. These results demonstrate that the branched polymer can flow through the core readily without severe plugging in the first segment and the surface. In addition, we tested the rheology properties of this branched polymer using a rheometer to further verify its shear resistance. As depicted in Fig. 12e, the viscosities decreased as the shear rate increases, and viscosity data during the three cycles of vigorous shearing matched quite well, which also demonstrated that the branched polymer has excellent shear resistance.

Further Discussion

In this paper, we have conducted a series of experiments to evaluate whether a branched polymer synthesized in our laboratory can be used to replace the HPAM in the HPAM/chromium acetate gel system that is commonly used in oil fields for conformance control. Our experimental results through bottle testing have indicated that the gelation time of the branched polymer and chromium acetate can be delayed up to more than 60 days at 45 °C and 20 days at 65 °C. However, more research needs to be conducted before the system can be applied in oil fields.

First, it is necessary to identify where the crosslinking delayed system can be best applied to control the conformance of a reservoir. A major concern for a gel treatment is whether the gel can only enter the preferential fluid flow paths while having no damage or very limited damage on low or nonswept zones or areas when a bullhead injection method is used to place the gel system. Seright (1988) and Liang et al. (1993) concluded through theoretical analysis that gel treatment can be successful only if a reservoir has fractures when

zones are not isolated during gel placement because productive zones may be seriously damaged if the reservoir has no fractures. Seright's research group has conducted extensive experiments to investigate whether a preformed bulk gel can transport through fractures, from which he concludes that both partially and fully crosslinked polymer gels can transport through fractures under the practical fluid flow velocity and pressure drop conditions in a reservoir, and using a crosslinking system with short gelation time rather than a delayed time can provide more opportunity to successfully treat a well in fractured reservoirs (Seright 1995, 1997; Sydansk et al. 2004, 2005). His conclusion is highly regarded in the industry and academia; however, there is still some interest in gelation-delayed gel systems for the purpose of large volume gel treatment or in-depth fluid flow diversion (Sydansk 1989; Vasquez 2005; Huili et al. 2020; Wang et al. 2020), although it is not clear where and how the system can be best applied. To our current knowledge, the delayed gelation system might provide some benefits when the gelant has a relatively low viscosity before crosslinking, and it can flow only through water flow paths under controlled injection pressure for ultrahigh-water-cut mature reservoirs. In addition, it might be possible to be used for the reservoirs that have been flooded by polymer or the tight rock reservoirs with relative fast-communication problems. For polymer flooding reservoirs with channeling problems, the gelant might only transport the same flow path as polymer solution if they have the same rheology behavior, and the injection pressure can be controlled below polymer injection pressure, from which the gelant penetration to unswept zones or areas can be minimized. For tight rock reservoirs, high-molecular-weight polymer or the branched polymer cannot penetrate in the matrix because of their ultralow permeabilities (usually less than 1 md) and surface cakes, which can prevent gelant penetration into the matrix, can form in the inlets of different zones along the wellbore and fracture surface. We guess that the surface cake formed by polymer might be much less in thickness than that formed by the preformed gel; therefore, it could provide more benefit for tight rock reservoirs, which have abundant tiny fractures and are therefore easier in injectivity maintenance and the possibility deeply delivering the gel system. Nevertheless, more research needs to be conducted to see whether our hypotheses are reasonable.

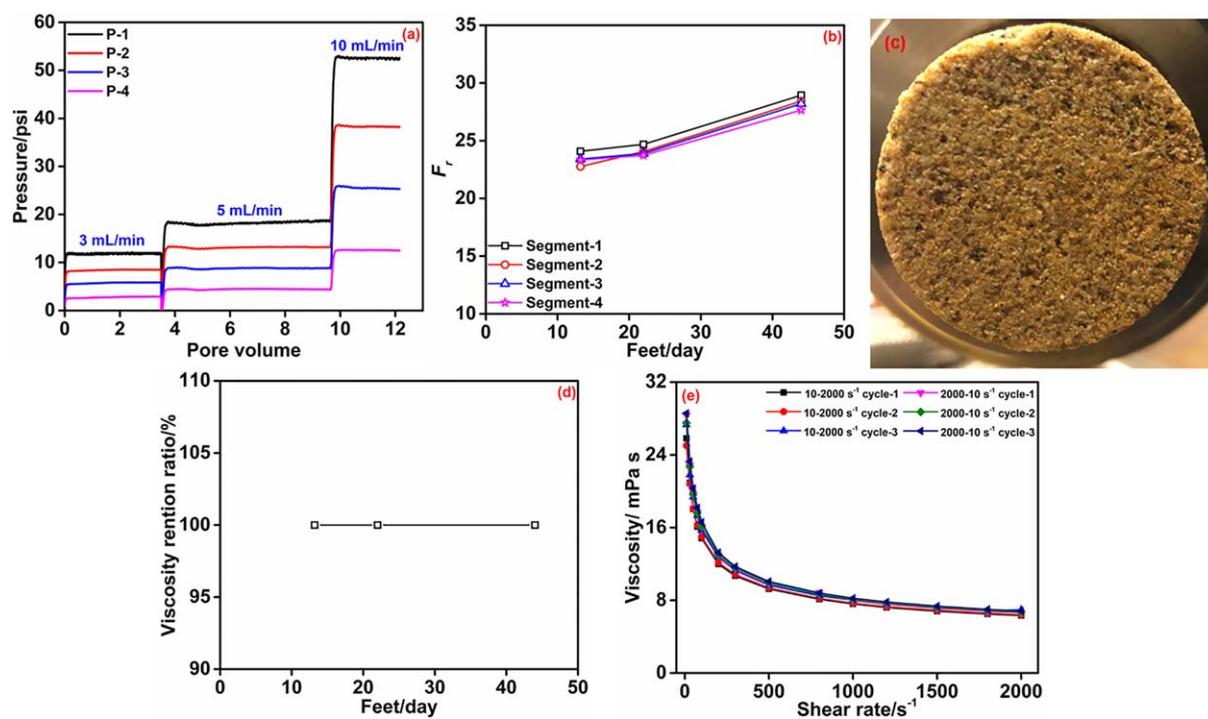


Fig. 12—Coreflooding results. (a) Injection pressure as a function of injection rate. (b) F_r along different segments. (c) Core surface after injection. (d) Effect of injection rate on the viscosity retention ratio. (e) Gelant viscosity as a function of shear rate.

Second, it is necessary to address concerns about whether the delayed gelation system can form a gel with quality as good as expected if it can be deeply delivered. Although the developed system only contains two compositions, branched polymer and crosslinker, each of them might have a different adsorption rate and equilibrium adsorption density; therefore, the chromatographic separation might not be avoided, which will result in the change of gelation time and final gel strength or even preventing the gelant from crosslinking. More research needs to be conducted to better design the compositions based on their transport behavior in porous media.

Third, reservoir environments are usually tough. The complex formation water composition and the existence of H_2S and CO_2 in a mature reservoir will also affect the gelation time and gel quality; therefore, it is necessary to conduct a series of evaluations before applying this gel system to a specific reservoir. Our research results reported in this paper only provide us the information that the branched polymer has good potential to delay the gelation time of polymer/chromium acetate without additional additive involvement.

Conclusions

We synthesized a branched polymer grafted from arginine using the surface initiation method and evaluated whether it has a delayed gelation property when crosslinked with chromium acetate and the factors impacting the gelation time. The research resulted in the following conclusions:

1. The branched polymer and chromium acetate gel systems have a relatively long gelation time, and the longest gelation times of BPA-1 polymer gels at 45 and 65°C are 61 and 20 days, respectively. The gelation time decreases with increased temperature, pH, and polymer concentration.

2. There exist both minimum and maximum crosslinker concentrations for the gel system, beyond which no crosslinking occurs at 45°C.
3. The branched polymer gels have good thermal stability at 45 and 65°C. After 150 days, for the gels composed of 0.5 wt% polymer and 0.05 wt% chromium acetate, no volume change was observed at 45°C, and the syneresis percent was lower than 5% at 65°C.
4. Coreflooding and rheology tests demonstrate that the branched polymer-based gel system has good injectivity and shear resistance in a high-permeability fluid flow channel.
5. The branched gel system has a delayed gelation property; however, more research has to be conducted to evaluate where and how it can be best used before it is applied for conformance control.

Nomenclature

- f = functionality
 F_r = resistance factor
 g = gyration radii
 g' = branching parameter
 K = constant for a particular polymer solvent system
 M = molecular weight
 α = constant for a particular polymer solvent system
 ΔP_{gelant} = gelant injection pressure gradient
 ΔP_{water} = water injection pressure gradient
 $[\eta]_b$ = intrinsic viscosity of the branched polymer
 $[\eta]_l$ = intrinsic viscosity of the linear polymer
 μ_r = viscosity retention ratio
 μ_{eff} = viscosity of effluent
 μ_{ini} = viscosity of gelant solution before injection

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