JOURNAL OF Applied Polymer SCIENCE

New Insights into Phenol–Formaldehyde-Based Gel Systems with Ammonium Salt for Low-Temperature Reservoirs

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ABSTRACT: Polymer gels are effective tools that are still widely used in mature oilfield development to stop unwanted fluid production from oil and gas wells, but conventional gelant formulations have become increasingly difficult to apply at low and ultralow temperatures. Because of this situation, the gelation performance of phenol–formaldehyde-based gel systems at a low temperature of 25°C is discussed in this article. The results show that the gelation time and strength of the gel systems can be perfectly controlled by the adjustment of the polymer concentration, the molecular weight, the crosslinking agent concentration, the ammonium salt concentration, and the composition. The polymer concentration and molecular weight can affect not only the gelation time and the gel strength but also its stability. The ammonium salt concentration affected not only the gelation time but also its viscosity before a detectable gel formed. Among them, the polymer concentration was the most important factor affecting the gel stability. For low-temperature reservoirs, the phenol–formaldehyde-based gel system achieved a much longer gelation time. Polymer gels formulated with a combination of 0.2–0.4 wt % polymer, 0.5–1.0 wt % formaldehyde or phenol–formaldehyde, and 0.1–0.6 wt % ammonium salt, and we added 0.02–0.03 wt % resorcinol to provide a gelation time between 2 h and 2 days. The maximum gel strength reached code I. The results of this study suggest that the formaldehyde-based gel system could be used effectively in low-temperature reservoirs. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40657.

KEYWORDS: kinetics; oil & gas; thermal properties; viscosity and viscoelasticity

Received 7 January 2014; accepted 25 February 2014
DOI: 10.1002/app.40657

INTRODUCTION

Water production during oil and gas recovery is a longstanding problem, which is becoming critical with maturing fields worldwide.[1] Excessive water production will lead to a rapid decline in oil production. The lifting and separation of large amounts of water also greatly increases the operating costs. It may also induce other problems, such as a higher pipeline corrosion rate, reservoir emulsion blockage, or scaling.[2]

Currently, polyacrylamide- or acrylamide-based copolymers are the most commonly used base polymers.[3–6] They can be crosslinked either organically or inorganically.

Inorganically, crosslinkers such as Cr^{3+}, Al^{3+}, and Zr^{3+} can crosslink hydrolyzed polyacrylamide (HPAM).[1,7,8] However, it is very difficult to control or delay the gel time with aluminum ions. For instance, the gel time of the commonly used chromium(III) acetate/partially hydrolyzed polyacrylamide (PHPAM) gel system is only about 5 h at 40°C; this is too short to apply for in-depth placement into reservoir formation.[9,10] The use of stronger ligands, such as glycolate and malonate, is a possible way to delay the crosslinking time. However, dehydration synthesis can also occur when binding with Cr^{3+} gets too strong.[10,11] In addition, the stability of the gel decreases in higher temperature reservoirs because of the weakening of the ionic bonds.

The gelation mechanism between the polymer and the organic crosslinker is covalent bonding, which is much more stable than ionic bonds. Furthermore, organic crosslinkers have been introduced to obtain gels that can remain stable over a wide temperature range.[12–14] Nowadays, the most commonly used organic crosslinkers are phenol–formaldehyde and poly(ethylene imine) (PEI).

Recently, the PEI crosslinking of copolymers of acrylamide and *tert*-butyl acrylate (PAtBA) as water shutoff gels has been widely reported. PEI-based gel systems can be used for either high-

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Table I. Gelation Performance of the HPAM/Formaldehyde/NH_4Cl Gel System

Composition					Viscosity (mPa.s) or strength code of the gel															
HPAM M_w (kDa)	HPAM concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	Initial	2 h	6 h	10 h	12 h	15 h	1 day	2 days	3 days	4 days	5 days	7 days	15 days	30 days	60 days	90 days
8,000	0.2	0.5	0.02	0	23.0	24.7	48.2	B	B	B	B	B	B	B	B	B	B	B	B	B
				0.2	13.9	12.5	9.3	<1	21.5	B	C	D	D	E	E	E	—	—	—	—
				0.4	10.2	8.8	7.5	<1	14.6	15.7	A	C	D	D	D	D	—	—	—	—
				0.6	7.5	6.6	3.7	<1	9.8	10.9	A	B	C	C	D	D	—	—	—	—
	0.3			0	52.9	55.8	58.9	B	B	B	C	C	C	C	C	C	C	C	C	C
				0.2	20.8	20.0	13.9	8.9	32.8	B	C	D	E	E	E	E	—	—	—	—
				0.4	17.2	16.9	12.3	4.3	19.0	23.3	B	C	D	E	E	E	—	—	—	—
				0.6	15.9	14.9	11.8	2.7	15.7	16.3	B	B	D	D	D	D	—	—	—	—
16,000	0.2			0	159.6	159.6	A	A	B	B	C	C	C	C	C	C	C	C	C	C
				0.2	76.6	61.6	50.0	A	C	D	D	F	F	G	G	G	H	H	H	H
				0.4	43.4	42.3	27.5	34.8	46.0	A	C	E	F	F	F	F	G	G	G	G
				0.6	31.6	30.5	16.9	29.1	38.0	A	A	D	E	E	E	F	F	—	—	—
	0.3			0	342.8	319.8	A	A	B	B	C	C	C	C	C	C	C	C	C	C
				0.2	126.4	81.6	69.6	A	C	D	D	F	G	G	G	G	H	I	I	I
				0.4	103.9	81.4	68.3	77.5	A	A	C	E	F	G	G	G	H	H	H	H
				0.6	92.7	58.4	49.3	59.8	A	A	C	D	E	F	F	F	G	G	—	—

Table II. Gelation Performance of the HPAM/Formaldehyde/NH_4HCO_3 Gel System

Composition					Viscosity (mPa.s) or strength code of gel															
HPAM M_w (kDa)	HPAM concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4HCO_3 concentration (wt %)	Initial	2 h	6 h	10 h	12 h	15 h	1 day	2 days	3 days	4 days	5 days	7 days	15 days	30 days	60 days	90 days
8,000	0.2	0.5	0.02	0.2	16.6	33.7 C	C	C	C	D	D	D	D	D	D	D	D	D	D	D
				0.4	13.5	30.5 C	C	C	C	D	D	D	D	D	D	D	D	D	D	D
				0.6	11.6	25.9 C	C	C	C	D	D	D	D	D	D	D	D	D	D	D
	0.3			0.2	37.2	18.8 C	C	D	E	E	E	E	E	E	F	F	F	F	F	F
				0.4	30.1	14.9 C	C	C	D	E	E	E	E	E	F	F	F	F	F	F
				0.6	24.9	14.2 C	C	C	C	C	D	D	D	D	D	D	D	D	D	D
16,000	0.2			0.2	94.3	99.1 C	C	D	E	E	F	F	F	F	F	F	F	F	F	F
				0.4	75.5	86.9 C	C	D	E	E	F	F	F	F	F	F	F	F	F	F
				0.6	62.7	81.4 C	C	D	D	D	D	D	D	E	E	E	E	E	E	E
	0.3			0.2	216.4	B	D	E	E	E	F	F	F	F	F	F	F	F	F	F
				0.4	175.7	B	D	D	E	E	F	F	F	F	F	F	F	F	F	F
				0.6	152.6	B	D	D	E	E	E	E	E	E	E	E	E	E	E	E

temperature reservoirs or low-temperature reservoirs.[2,15–19] However, the dosages of the polymer and crosslinker are still large, and the initial viscosity is high; this cannot guarantee good injectivity. The objective of this study was to improve the current acrylamide- and amine-based polymer formations through a significant reduction in the polymer concentration with retention of the gel performance.[17] In addition, a reduction in the viscosity of the gel systems before a detectable gel forms is important, too.

Compared with other HPAM gel systems, phenol–formaldehyde-based gel systems have many merits: (1) the gelation time is appropriate, (2) the final gel strength is high, (3) the thermal stability is very excellent, and (4) the systems can adapt to a wider range of salinity. However, phenol–formaldehyde-based gel systems, whose activation temperatures are above 70–80°C, are often used in high-temperature reservoirs.[20,21] The reaction and gel strength development rates are very low at low temperatures which will result in longer gel times and weaker gels. Thus, no systematic study has been done for the gelation performance of phenol–formaldehyde-based gel systems at low temperatures, and also, no guidelines have been recommended for its application in low-temperature reservoirs. Research is needed on the gelation performance of the phenol–formaldehyde-based gel systems at relatively low concentrations in low-temperature reservoirs.

In this study, a large number of experiments were conducted, and the purpose of this study included the following: (1) understanding the gelation performance of phenol–formaldehyde-based gel systems with ammonium salt at room temperature; (2) determining the effects of the polymer concentration, molecular weight, crosslinker concentration, ammonium salt concentration, ammonium salt composition, and salt content on the gelation performance; and (3) examining the thermal stability. To achieve these objectives, in this experimental study, we combined a Brookfield viscometer DV-III and gel bottle tests.

EXPERIMENTAL

Determination of the Gelation Time

The *gelation time* is defined as the time needed to reach the inflection point on the viscosity versus time curve. This method has been widely used.[1,2,17,22,23] Before gel formation, the viscosity of the gelant solutions is relatively low, so it can be measured accurately. However, after gel formation, it will be very hard to obtain the exact viscosity value.

A gel strength code presented by Sydansk and Argabright[24] was assigned to the bottle testing methods. It has been considered a convenient and inexpensive method to study gelation kinetics. The gel strength during development of gelation kinetics was expressed as an alphabetic code with letters A–J. When there is no detectable gel formation, and the gel has the same viscosity as the initial solution, the strength is coded as A. Likewise, code J indicates that there is a tuning, forklike mechanical vibration that can be felt when the bottle is tapped.

The gelation time of the water shutoff gel is usually considered as the period of time when the gelant solutions in the code A

Table III. Gelation Performance of the HPAM/Phenol–Formaldehyde/NH_4HCO_3 Gel System

Composition					Viscosity (mPa.s) or strength code of the gel												
HPAM M_w (kDa)	HPAM concentration (wt %)	Phenol–formaldehyde concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	Initial	2 h	18 h	1 day	2 days	3 days	4 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
8,000	0.2	0.5	0.02	0	43.9	55.7	A⁻	A⁻	A	A	B	B	B	B	B	B	B	B
				0.2	12.9	16.6	E	E	E	F	F	F	F	G	—	—	—	—
				0.4	7.5	10.2	A	C	C	D	E	E	F	—	—	—	—	—
				0.6	5.8	8.0	A	A	A	B	C	C	C	—	—	—	—	—
	0.3			0	51.4	48.7	A⁻	A	B	B	B	B	C	C	C	C	C	C
				0.2	35.3	31.6	E	E	F	G	G	G	G	H	H	H	H	H
				0.4	21.4	17.7	A	C	D	E	E	F	E	—	—	—	—	—
				0.6	16.1	13.4	A	B	C	C	D	D	E	—	—	—	—	—
16,000	0.2			0	182.6	153.2	B	B	B	C	E	E	E	E	E	E	E	E
				0.2	77.1	52.0	E	F	F	G	G	G	H	H	H	H	H	H
				0.4	51.4	40.7	A	D	E	F	G	G	G	H	H	H	H	H
	0.3			0.6	48.2	35.9	A	B	C	D	E	E	F	F	G	—	—	—
				0	356.2	320.8	B	B	B	D	E	E	E	E	E	E	E	E
				0.2	129.6	99.6	E	F	F	G	G	H	H	H	H	I	I	I
				0.4	108.7	96.9	A	D	E	F	G	G	G	H	H	I	I	I
				0.6	88.4	76.6	A	C	C	D	F	F	G	H	H	H	H	H

Table IV. Effect of the Ammonium Salt Concentration on the Gelation Performance

Composition					Gel strength code									
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	12 h	1 day	2 days	3 days	4 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.02	0.5	A^-	B	D	D	F	F	C	—	—	—	—	—
				0.8	A^-	A^-	A^-	C	D	D	C	—	—	—	—	—
				1.0	A^-	A^-	A^-	A	B	C	C	—	—	—	—	—
				0.4	A^-	C	E	F	F	F	F	F	G	G	G	G
				0.5	A^-	B	C	D	E	E	F	F	G	—	—	—
				0.8	A^-	A^-	A^-	C	C	C	D	E	—	—	—	—
				1.0	A^-	A^-	A^-	A	B	C	C	—	—	—	—	—

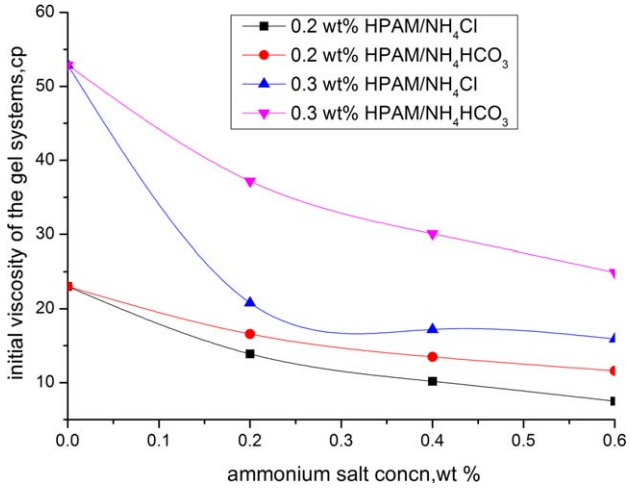

Figure 1. Effect of ammonium salt concentration on the initial viscosity of the gel systems (polymer $M_w = 8000$ kDa). The second crosslinker was formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

state turns to a flowing gel with code C; this can also be called the *initial gelation strength* (or the *gel point*). The strength code and apparent viscosity measurement methods were all used in this study to obtain the accurate gelation time and gel strength, respectively. The gel viscosity was measured through a Brookfield DV-III viscometer. The strength code method is used to monitor the dynamic gel strength.

Materials

The polymer and phenol were received in solid form; the formaldehyde (effective concentration = 37–40 wt %) was received in liquid form. The commercial polymers used in the conducted experiments, including HPAM [weight-average molecular weights (M_w's) = 8000, 16,000, and 24,000 kDa]. All polymers were supplied by Hengju Chemical (Beijing, China). Other materials, such as formaldehyde, phenol, and salts, were supplied by Kelong Chemical (Chengdu, China). The crosslinker

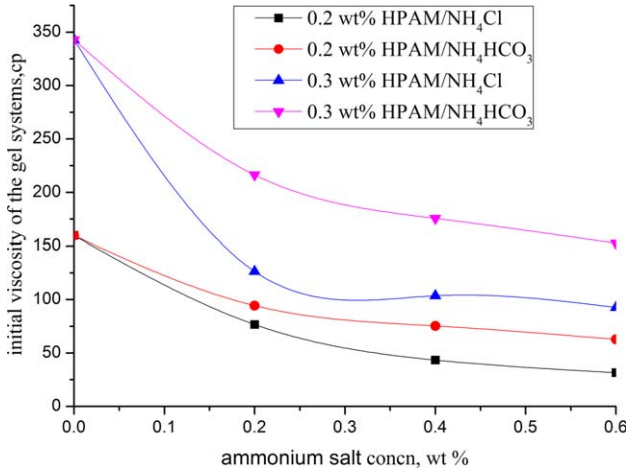

Figure 2. Effect of ammonium salt concentration on the initial viscosity of the gel systems (polymer $M_w = 16{,}000$ kDa). The second crosslinker was formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

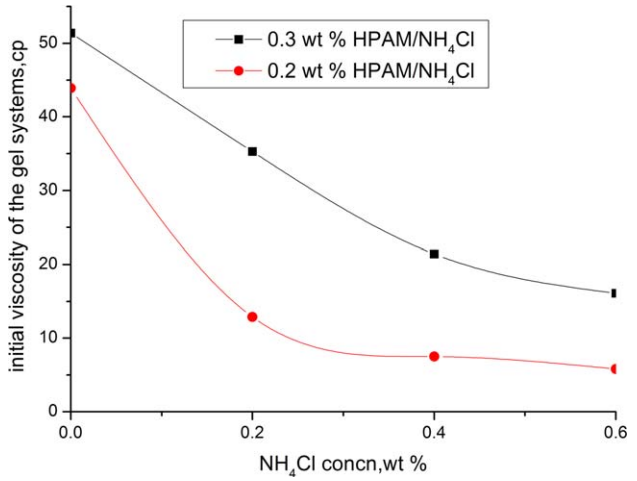

Figure 3. Effect of ammonium salt concentration on the initial viscosity of the gel systems (polymer $M_w = 8000$ kDa). The second crosslinker was phenol–formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenol–formaldehyde was made in our laboratory. In our study, a phenol–formaldehyde crosslinker was prepared by a simple method: 1 g of phenol was dissolved in 10 mL of formaldehyde to prepare this crosslinker. Resorcinol, NH_4Cl, and NH_4HCO_3 was furnished as an analytical-reagent grade reagent with a net weight of more than 99.5%. Deionized water was made in our own laboratory. The effect of ammonium salt on the gelation performance was examined by the addition of NaCl, which was analytical-reagent grade and was used as received.

Methods and Procedures

The polymer and crosslinker were dissolved in fresh water or saline solution with complete stirring to prepare a gelant solution, and the viscosity measurement was conducted to investigate the crosslinking performance at room temperature (25°C).

In this section, the crosslinking properties were studied in different formulations. A 20-mL volume of the gelant solution was

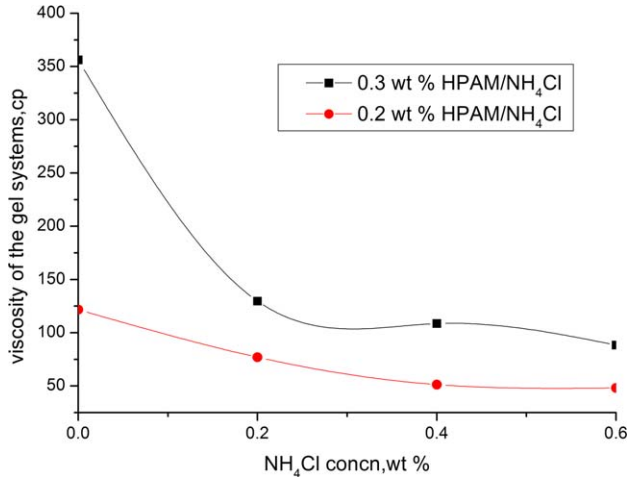

Figure 4. Effect of inorganic activators on the initial viscosity of the gel systems (polymer $M_w = 16{,}000$ kDa). The second crosslinker was formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Effect of the Ammonium Salt Concentration on the Gelation Performance

Composition					Gel strength code											
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4HCO_3 concentration (wt %)	3 h	5 h	6 h	1 day	2 days	3 days	4 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.02	0.5	B	C	C	E	E	E	E	E	E	E	E	E	E	E
				0.8	A	C	C	E	E	E	E	E	E	E	E	E	E	E
				1.0	A	B	C	D	E	E	E	E	E	E	E	E	E	E
24,000				0.4	B	D	E	F	F	F	F	F	F	F	F	F	F	F
				0.5	B	D	E	F	F	E	E	E	E	E	E	E	E	E
				0.8	B	C	E	E	E	E	E	E	E	C	C	C	C	C
				1.0	B	C	D	D	D	E	E	E	E	C	C	C	C	C

Table VI. Effect of the Polymer M_w on the Gelation Performance

Composition						Gel strength code											
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NH_4HCO_3 concentration (wt %)	5 h	7 h	12 h	1 day	2 days	3 days	5 days	15 days	20 days	30 days	60 days	90 days
8,000	0.3	0.5	0.02	0.1	0	A$^-$	A	C	E	E	E	E	E	E	E	E	E
16,000						A$^-$	A	D	F	G	H	H	H	H	H	H	H
24,000						A$^-$	A	D	G	H	H	H	H	H	H	H	H
8,000				0	0.1	B	C	C	E	E	E	E	E	E	E	E	E
16,000						C	D	E	F	F	F	F	F	F	F	F	F
24,000						D	E	F	F	F	F	F	F	F	F	F	F

Table VII. Effect of the Polymer M_w on the Gelation Performance

Composition						Gel strength code											
Polymer M_w (kDa)	Polymer concentration (wt %)	Phenol–formaldehyde concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NH_4HCO_3 concentration (wt %)	5 h	12 h	1 day	2 days	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
8,000	0.3	0.5	0.02	0.1	0	A	D	E	G	G	G	G	G	G	G	G	G
16,000						B	D	F	G	H	H	H	H	H	H	H	H
24,000						B	E	F	G	H	H	H	H	H	H	H	H
8,000				0	0.1	B	D	D	E	E	E	E	E	E	E	E	E
16,000						C	E	F	F	F	F	G	G	G	G	G	G
24,000						D	F	F	F	F	G	G	G	G	G	G	G

Table VIII. Effect of the Polymer Concentration on the Gelation Performance

Composition						Gel strength code									
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	Phenol–formaldehyde concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (w t %)	1 day	2 days	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
8,000	0.2	0.5	0	0.02	0.3	A	B	D	D	E	E	—	—	—	—
	0.3					A	D	E	E	F	F	F	F	F	F
	0.4					B	E	F	F	F	F	G	G	G	G
16,000	0.2					C	D	F	F	F	F	G	G	G	G
	0.3					C	D	F	F	F	F	G	G	G	G
	0.4					C	F	F	F	F	F	G	G	G	G
24,000	0.2					C	E	F	F	F	G	G	G	G	G
	0.3					C	E	F	F	F	G	G	G	G	G
	0.4					C	F	G	G	G	H	H	H	H	H
8,000	0.2	0	0.5			C	E	E	F	F	F	—	—	—	—
	0.3					C	E	F	F	G	G	G	G	G	G
	0.4					C	F	F	F	G	G	G	G	G	G
16,000	0.2					C	E	G	G	H	H	H	H	H	H
	0.3					D	F	G	G	H	H	H	I	I	I
	0.4					D	F	G	H	H	H	H	I	I	I
24,000	0.2					D	F	G	H	H	H	H	H	H	H
	0.3					D	F	G	H	H	H	I	I	I	I
	0.4					E	F	G	H	H	H	I	I	I	I

Table IX. Effect of the First Crosslinker Concentration on the Gelation Performance

Composition					Gel strength code											
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	NH_4Cl concentration (wt %)	Resorcinol concentration (wt %)	6 h	10 h	12 h	1 day	2 days	3 days	4 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.3	0.5	0.3	0	A^-	A^-	A^-	A^-	A^-	A^-	A	A	A	A	A	A	A
				0.01	A^-	A^-	A^-	B	C	D	E	E	F	F	F	F	F
				0.03	A^-	A^-	C	F	G	G	H	H	I	I	I	I	I
				0.04	A^-	A^-	C	F	G	G	H	I	I	—	—	—	—
				0.06	B	C	D	F	G	G	H	I	I	—	—	—	—
				0.08	C	D	E	G	H	H	I	I	I	—	—	—	—
24,000				0	A^-	A^-	A^-	A^-	A^-	A^-	A	A	A	A	A	A	A
				0.01	A^-	A^-	A^-	B	C	D	E	E	F	F	F	F	F
				0.03	A^-	A	C	F	G	G	H	H	I	I	I	I	I
				0.04	A^-	A^-	C	F	G	G	H	I	I	—	—	—	—
				0.06	B	D	E	G	H	H	H	I	I	—	—	—	—
				0.08	C	E	F	G	H	H	I	I	I	—	—	—	—

Table X. Effect of the Second Crosslinker Concentration on the Gelation Performance

Composition					Gel strength code									
Polymer M_w (kDa)	Polymer concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	1 day	2 days	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.50	0.03	0.3	E	F	G	H	H	I	I	I	I	I
		0.75			D	F	F	G	G	—	—	—	—	—
		1.0			C	E	F	G	—	—	—	—	—	—
	0.3	0.50			E	G	G	H	H	I	I	I	I	I
		0.75			E	F	G	H	H	I	I	I	I	I
		1.0			E	F	F	G	G	—	—	—	—	—
24,000	0.2	0.50			E	F	G	H	H	I	I	I	I	I
		0.75			C	E	F	G	H	—	—	—	—	—
		1.0			C	D	F	G	G	—	—	—	—	—
	0.3	0.50			E	F	G	H	H	I	I	I	I	I
		0.75			D	F	G	H	H	I	I	I	I	I
		1.0			C	F	F	G	H	—	—	—	—	—

Table XI. Effect of the Second Crosslinker Concentration on the Gelation Performance

Composition					Gel strength code								
Polymer M_w (kDa)	Polymer concentration (wt %)	Phenol–formaldehyde concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	1 day	2 days	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.50	0.02	0.3	E	G	G	H	H	—	—	—	—	—
		0.75			E	G	G	H	H	—	—	—	—	—
		1.0			E	G	G	H	H	—	—	—	—	—
	0.3	0.50			E	G	H	H	—	—	—	—	—	—
		0.75			E	G	G	H	—	—	—	—	—	—
		1.0			E	G	G	H	—	—	—	—	—	—
24,000	0.2	0.50			E	G	G	H	H	—	—	—	—	—
		0.75			D	G	G	H	H	—	—	—	—	—
		1.0			D	F	F	G	H	—	—	—	—	—
	0.3	0.50			E	G	H	H	—	—	—	—	—	—
		0.75			E	G	G	H	—	—	—	—	—	—
		1.0			E	G	H	H	—	—	—	—	—	—

transferred to a 50-mL volume glass bottle, and then, the bottle was sealed before it was placed inside the oven. The effects of the polymer concentration, polymer M_w, crosslinker concentration, ammonium salt concentration, different crosslinker, and ammonium salt composition on the gelation performance were systematically studied through the bottle testing method. All of the bottle experiments were set at a temperature of 25°C.

RESULTS AND DISCUSSION

Crosslinking Performance at Room Temperature

To investigate the crosslinking properties at room temperature, two molecular weights of HPAM ($M_w = 8000$ and 16,000 kDa) were used in these experiments with concentrations varied from 0.2 to 0.3 wt %. The second crosslinker was kept at a constant concentration of 0.2 wt %. The first crosslinker (resorcinol) was kept at a constant concentration of 0.02 wt %, and the ammonium salt concentration varied from 0 to 0.6 wt %. The gelant solutions were prepared with fresh water according to the procedure outlined earlier.

It is a known fact that polymers, crosslinkers, and other additives should be dissolved in water as quickly as possible on a well site. In consideration of the dissolving time and pumping time before the first crosslinking gel enters into the formation, we chose a few times to study the viscosity of gel system at room temperature. The viscosity evolution of these solutions is shown in Tables I–IV. The effects of the ammonium salt concentration on the initial viscosity of the gel system are shown in Figures 1–4.

The results show that the gel systems with NH_4Cl and NH_4HCO_3 had shorter gelation times, stronger gel strengths, and lower viscosities before gel formation. Moreover, the viscosity decrement could be controlled by the adjustment of the polymer concentration, M_w, and ammonium salt concentrations. As shown in Figures 1–4, the ability of NH_4Cl to reduce the viscosity of the gel system was better than that of NH_4HCO_3.Thus, the time-reducing process and the gelation time were also longer. As shown in Tables II–IV, the gel strength of the gel system with NH_4Cl was stronger than that with NH_4HCO_3. In this way, the gelation time and final gel strength could be controlled by the ammonium salt composition and concentration. In addition, the initial viscosity of the gel system was very low, but the final gel strength was very high, as shown in Tables II–IV. This phenomenon showed that the performance of the formaldehyde- or phenol–formaldehyde-based gel system for low-temperature reservoir was excellent.

Effect of the Ammonium Salt Concentration on the Gelation Performance

The effects of the ammonium salt on the gelation rate are given in Tables V and VI. The polymer gel samples prepared with constant polymer and crosslinker concentrations with various ammonium salt concentrations from 0.4 to 1.0 wt % showed that the gelation time increased with increasing concentration of the ammonium salt. The increase in the ammonium salt concentration extended the time of the viscosity-reduction process before the gel formed, and this led to a longer gelation time.

Fox and Evans[25] introduced a gel system that could accelerate the gelation rate with ammonium salt at a temperature of

Table XII. Effect of the Ammonium Salt Composition on the Gelation Performance

Composition						Strength code of gel																
HPAM M_w (kDa)	HPAM concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NH_4HCO_3 concentration (wt %)	2 h	4 h	5 h	6 h	7 h	8 h	9 h	10 h	20 h	1 day	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.02	0.1	0.1	A	B	C	C	D	E	E	E	F	F	F	F	F	F	F	F	F	F
					0.2	B	C	C	D	E	E	E	E	F	F	F	F	F	F	F	F	F	F
				0.2	0.1	A	A	A	A	B	C	C	D	F	F	G	G	G	G	H	H	H	H
					0.2	A	A	A	B	C	D	D	E	F	F	G	G	G	G	G	G	G	G
				0.3	0.1	A	A	A	A	A	A	B	C	E	F	G	G	G	G	H	H	H	H
					0.2	A	A	A	A	A	A	B	C	F	G	G	G	G	G	G	H	H	H
				0.4	0.2	A	A	A	A	A	B	B	C	E	F	G	G	G	G	G	H	H	H
					0.3	A	A	A	A	A	C	C	D	E	F	F	F	F	F	F	F	F	F
24,000				0.1	0.1	A	C	D	D	E	E	F	F	G	G	G	G	G	G	G	G	G	G
					0.2	C	D	D	D	E	E	E	E	F	F	F	F	F	F	F	F	F	F
				0.2	0.1	A	A	B	B	C	C	D	E	F	F	G	G	G	G	H	H	H	H
					0.2	A	A	B	C	D	D	E	E	G	G	G	G	G	G	G	G	G	G
				0.3	0.1	A	A	A	A	A	A	B	C	E	F	G	G	G	G	H	H	H	H
					0.2	A	A	A	A	A	B	B	C	E	F	G	G	G	G	G	H	H	H
				0.4	0.2	A	A	A	A	A	B	B	C	E	F	G	G	G	G	G	H	H	H
					0.3	A	A	A	A	A	C	C	D	E	F	F	G	G	G	G	G	G	G

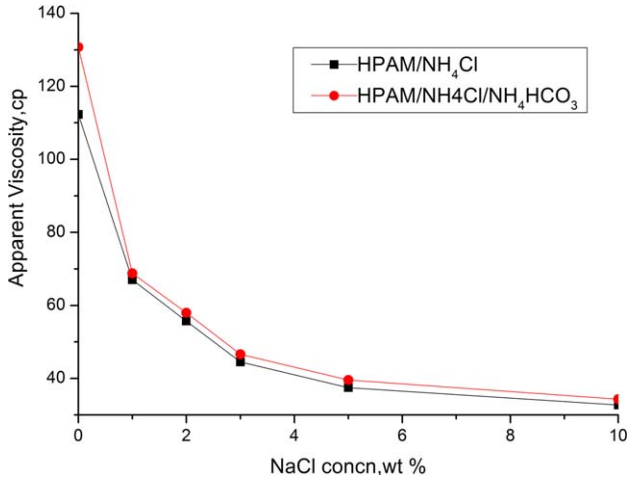

Figure 5. Viscosity as a function of the salt content of the polymer solution (polymer $M_w = 16{,}000$ kDa, active polymer concentration = 0.3 wt %). The second crosslinker was formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

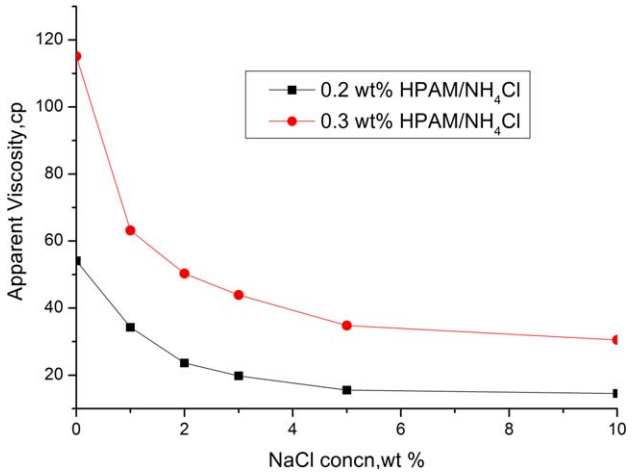

Figure 7. Viscosity as a function of the salt content of the polymer solution (polymer $M_w = 16{,}000$ kDa). The second crosslinker was phenol–formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

93.3°C. In our study, from Tables I to V, it is clearly summarized that both NH_4Cl and NH_4HCO_3 were excellent accelerators for the polymer gel at low temperatures. However, too much NH_4Cl or NH_4HCO_3 caused the degradation of the gel strength and even dehydration synthesis.

Effect of the Polymer M_w Value on the Gelation Performance

The effect of polymer M_w on the gelation time is significant, as shown in Tables VI and VII. The gelation time decreased, and the gel strength was enhanced for a higher M_w HPAM when HPAM and the second crosslinker concentrations were 0.3 and 0.5 wt %, respectively.

There is no doubt that a high-M_w polymer usually contains more carbonyl carbons attached to the amide group and will generate more crosslinking sites in amide groups, which can be easily attacked by the first crosslinker. As a result, the nucleophilic substitution reaction rate increased; this led to a high gelation rate for high-M_w polymers. Furthermore, for a series of polymers, the higher the M_w, the larger the molecular coil size. Thus, the crosslinked structure gel will have a stronger three-dimensional structure, and the gel strength becomes higher. By contrast, for a high-M_w polymer, the effective hydrodynamic volume became larger when the molecular chains rolled at a certain TDS, and the gel strength became rather stronger. This obviously performed in this experiment. For polymers with M_w from 8,000 to 24,000 kDa crosslinked with formaldehyde, in latter observations, the final gel strengths reached codes E, H, and H, respectively.

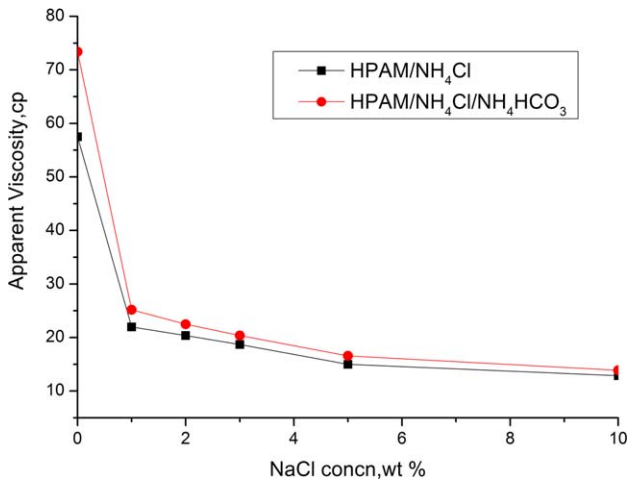

Figure 6. Viscosity as a function of the salt content of the polymer solution (polymer $M_w = 16{,}000$ kDa, active polymer concentration = 0.2 wt %). The second crosslinker was formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of the Polymer Concentration on the Gelation Performance

In this study, all of the polymer solutions were prepared with fresh water, and the concentrations of polymers with two molecular weights were varied from 0.2 to 0.4 wt % with the second crosslinker kept at a constant concentration of 0.5 wt %. Then, the gel strength code methods were used to examine the gelation performance of the gel systems.

The polymer concentration is a critical effect factor for the structure and properties of the gel polymer network. The effect of the polymer concentration on the gelation time was significant, as shown in Table VIII. Gels having a low polymer concentration were formed in much more time compared to those having lower concentrations and had lower gel strengths. Furthermore, we concluded from the study involving the effect of the polymer concentration that the gelation time was reduced with increasing polymer concentration. When the polymer concentration increased, it brought more crosslinking sites, and the crosslinking reaction chance increased.[2,15] Thus, the gel formation rate increased, and this led to a decrease in the gelation time. As a result, the time required to obtain a nonflowing polymer gel with a tolerable strength decreased along with increasing polymer dosage.

Table XIII. Effect of the Aqueous-Phase Salinity on the Gelation Performance

Composition						Strength code of the gel														
HPAM M_w (kDa)	HPAM concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NaCl concentration (wt %)	Initial	4 h	12 h	14 h	1 day	2 days	3 days	4 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.03	0.3	0	57.5	A⁻	C	C	F	G	H	H	H	H	I	I	I	I	I
					1	20.4	A⁻	A	A	C	E	E	—	—	—	—	—	—	—	—
					2	22.0	A⁻	A	A	C	E	E	—	—	—	—	—	—	—	—
					3	18.7	A⁻	A	A	C	E	E	E	—	—	—	—	—	—	—
					5	15.0	A⁻	A	A	B	D	E	D	—	—	—	—	—	—	—
					10	12.9	A⁻	A	A	B	D	E	D	—	—	—	—	—	—	—
	0.3				0	130.7	A⁻	C	D	F	G	H	H	H	I	I	I	I	I	I
					1	68.8	A⁻	C	C	E	F	G	H	H	H	I	I	I	I	I
					2	58.0	A⁻	C	C	D	F	G	H	H	H	H	I	I	I	I
					3	46.6	A⁻	B	C	C	F	G	G	G	H	H	I	I	I	I
					5	39.6	A⁻	B	B	C	E	F	F	F	G	G	G	G	G	G
					10	34.3	A⁻	A	B	C	E	F	F	F	G	G	G	G	G	G

Table XIV. Effect of the Aqueous-Phase Salinity on the Gelation Performance

Composition							Strength code of the gel														
HPAM M_w (kDa)	HPAM concentration (wt %)	HCHO concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NH_4HCO_3 concentration (wt %)	NaCl concentration (wt %)	Initial	4 h	12 h	14 h	1 day	2 days	3 days	4 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.03	0.2	0.1	0	73.4	C	F	F	F	G	G	G	G	G	G	G	G	G	G	G
						1	25.2	B	E	E	F	F	G	G	G	G	G	G	G	G	G	G
						2	22.5	B	D	D	E	F	F	F	F	F	F	F	F	F	F	F
						3	20.4	A	C	C	D	E	E	E	E	F	F	F	F	F	F
						5	16.6	A	C	C	D	E	E	E	E	E	E	F	F	F	F
						10	13.9	A	C	C	C	D	E	E	E	E	E	E	E	E	E
	0.3					0	130.7	C	F	G	G	G	H	H	H	H	H	H	H	H	H	H
						1	68.8	B	E	F	F	G	G	H	H	H	H	H	H	H	H	H
						2	58.4	B	D	E	F	G	G	G	G	G	G	G	G	G	G	G
						3	46.6	B	D	D	E	F	F	F	F	F	F	F	F	F	F	F
						5	39.6	A	C	C	D	F	F	F	F	F	F	F	F	F	F	F
						10	34.3	A	C	C	C	E	E	E	E	E	E	E	E	E	E	E

Table XV. Effect of the Aqueous-Phase Salinity on the Gelation Performance

Composition						Strength code of gel										
HPAM M_w (kDa)	HPAM concentration (wt %)	Phenol–formaldehyde concentration (wt %)	Resorcinol concentration (wt %)	NH_4Cl concentration (wt %)	NaCl concentration (wt %)	Initial	4 h	12 h	14 h	1 day	3 days	5 days	7 days	10 days	15 days	30 days	60 days	90 days
16,000	0.2	0.5	0.03	0.3	0	54.1	A⁻	B	B	F	H	H	H	I	I	I	I	I
					1	34.3	A⁻	A	B	E	G	H	H	H	H	H	H	H
					2	23.6	A⁻	A	B	D	G	G	H	H	H	H	H	H
					3	19.8	A⁻	A	B	C	F	G	G	G	G	G	G	G
					5	15.5	A⁻	A	B	C	E	E	F	F	F	F	F	F
					10	14.5	A⁻	A	B	C	E	E	F	F	F	F	F	F
	0.3				0	115.2	A⁻	B	D	F	H	I	I	I	I	I	I	I
					1	63.2	A⁻	B	C	E	H	H	I	I	I	I	I	I
					2	50.3	A⁻	B	B	E	G	H	H	I	I	I	I	I
					3	43.9	A⁻	B	B	E	G	G	H	H	I	I	I	I
					5	34.8	A⁻	B	B	D	F	G	G	H	I	I	I	I
					10	30.5	A⁻	B	B	D	F	G	G	H	H	H	H	H

Effect of the First Crosslinker Concentration on the Gelation Performance

In the previous section, the polymer, second crosslinker, and ammonium salt concentrations were 0.3, 0.5, and 0.3 wt %, respectively, whereas the first crosslinker concentration was varied from 0 to 0.08 wt %.

Table IX shows that the gel system without resorcinol could not form a detectable gel. Furthermore, the gelation time decreased, and the final gel strength of the samples increased with increasing concentration of resorcinol. Apparently, resorcinol performed in the role of accelerator. For fractured reservoirs and these secondary crosslinking gel systems of low HPAM concentration, the relatively high final gel strength was more welcome.[26] However, when the resorcinol dosage was too small (<0.01 wt %), the final gel strength reached only code F, whereas when the resorcinol dosage was too large (>0.04 wt %), the dehydration synthesis was obvious. Thus, the optimal concentration of resorcinol was 0.02–0.03 wt %. For example, the gelation time was about 12 h, and the final gel strength was code I when the concentration of resorcinol was 0.03 wt %. In addition, the initial viscosity of the gel system was very low at room temperature. Thus, it was beneficial for gel pumping.

Effect of the Second Crosslinker Concentration on the Gelation Performance

In this study, the second crosslinker concentrations varied from 0.5 to 1.0 wt %. As shown in Tables X and XI, the gelation time increased, and the initial gelation strength decreased with increasing concentration of the second crosslinkers. This result was opposite to the effect of crosslinker on the other gel systems, such as PEI/PAtBA or PEI/HPAM gel systems[2,15,22,27] and formaldehyde/HPAM or phenol–formaldehyde/HPAM gel systems, at high or low temperatures.[26] The reasons may be as follows: (1) too much of the second crosslinker may shield the catalysis of ammonium salt, and (2) with the help of ammonium salt, reactions between the second crosslinker and resorcinol may occur even at low temperature when the second crosslinker dosage is too large.

Effect of the Ammonium Salt Composition on the Gelation Performance

In this section, the effect of the ammonium salt composition on the gelation performance was investigated through changes in the concentrations of NH_4Cl and NH_4HCO_3. As shown in Table XII, the gelation time decreased with increasing proportion of NH_4HCO_3 in a complex ammonium salt accelerator. Furthermore, the gels had good stability, even at a high ammonium salt concentration. However, the gel strength was a little weaker.

Effect of the Aqueous-Phase Salinity on the Gelation Performance

In this part of the study, fresh water and saline water were chosen to investigate the effect of total dissolved solids (TDS) on the gelation performance at a temperature of 25°C. The TDS of the prepared saline water increased from 10 to 100 g/L with increasing concentration of NaCl.

Figures 5–7 present the effects of the salinity of the polymer solution on the viscosity. The viscosity of the freshly prepared

Table XVI. Effect of the Temperature on the Gelation Performance.

Number	Composition	Temperature (°C)	Strength code of the gel										
			2 h	4 h	6 h	8 h	12 h	1 day	3 days	5 days	7 days	10 days	15 days
I	0.3 wt % HPAM (M_w = 16,000 kDa) + 0.03 wt % resorcinol + 0.3 wt % NH_4Cl + 0.5 wt % phenol-formaldehyde	25	A⁻	A	B	B	D	F	H	I	I	I	I
		45	A⁻	C	F	H	H	I	I	I	I	I	I
		60	A	C	H	H	I	I	I	I	I	I	I
		90	F	G	H	I	I	I	I	I	I	I	I
II	0.3 wt % HPAM (M_w = 16,000 kDa) + 0.03 wt % resorcinol + 0.2 wt % NH_4Cl + 0.5 wt % phenol-formaldehyde + 0.1 wt % NH_4HCO_3	25	A⁻	B	C	D	E	G	H	I	I	I	I
		45	A	F	H	H	H	I	I	I	I	I	I
		60	B	F	H	H	H	I	I	I	I	I	I
		90	F	H	H	H	H	I	I	I	I	I	I
III	0.3 wt % HPAM (M_w = 16,000 kDa) + 0.03 wt % resorcinol + 0.3 wt % NH_4Cl + 0.5 wt % formaldehyde	25	A	A	A	B	C	F	G	H	I	I	I
		45	A⁻	C	G	H	H	H	I	I	I	I	I
		60	B	C	G	H	H	H	I	I	I	I	I
		90	F	G	H	H	H	I	I	I	I	I	I
IV	0.3 wt % HPAM (M_w = 16,000 kDa) + 0.03 wt % resorcinol + 0.2 wt % NH_4Cl + 0.5 wt % formaldehyde + 0.1 wt % NH_4HCO_3	25	A	B	B	B	C	G	G	H	H	H	H
		45	A	F	F	H	H	H	I	I	I	I	I
		60	B	F	G	H	H	H	I	I	I	I	I
		90	F	H	H	H	H	H	I	I	I	I	I

Table XVII. Effect of the Temperature on the Gelation Performance

Number	Composition	Temperature (°C)	Strength code of gel										
			2 h	4 h	6 h	8 h	12 h	1 day	3 days	5 days	7 days	10 days	15 days
1	0.2 wt % HPAM (M_w = 16,000 kDa) + 0.02 wt % resorcinol + 0.3 wt % NH_4Cl + 0.5 wt % phenol-formaldehyde	25	A−	A−	A	B	B	F	H	H	H	I	I
		45	A−	A	B	E	G	H	I	I	I	I	I
		60	A−	C	F	F	H	I	I	I	I	I	I
		90	F	G	G	H	—	—	—	—	—	—	—
2	0.2 wt % HPAM (M_w = 16,000 kDa) + 0.02 wt % resorcinol + 0.2 wt % NH_4Cl + 0.5 wt % phenol-formaldehyde + 0.1 wt % NH_4HCO_3	25	A−	B	C	D	E	F	G	G	G	G	G
		45	A	C	E	F	G	H	H	H	H	H	H
		60	A	F	F	F	G	H	H	H	H	H	H
		90	F	F	F	G	H	I	I	—	—	—	—
3	0.2 wt % HPAM (M_w = 16,000 kDa) + 0.02 wt % resorcinol + 0.3 wt % NH_4Cl + 0.5 wt % formaldehyde	25	A−	A−	A	B	C	F	H	H	H	I	I
		45	A−	A	B	E	G	H	I	I	I	I	I
		60	A−	B	F	F	H	I	I	I	I	I	I
		90	F	F	F	F	H	—	—	—	—	—	—
4	0.2 wt % HPAM (M_w = 16,000 kDa) + 0.02 wt % resorcinol + 0.2 wt % NH_4Cl + 0.5 wt % formaldehyde + 0.1 wt % NH_4HCO_3	25	A−	A	B	C	D	F	G	G	G	G	H
		45	A	C	E	F	G	H	H	H	H	H	H
		60	A	F	F	F	G	H	H	H	H	H	H
		90	F	F	F	F	G	H	H	H	—	—	—

gelant solutions at room temperature significantly decreased with the addition of NaCl. The greater the concentration of NaCl was, the lower the viscosity of the gelant solution was. The viscosity decrease was due to the charge-screening effect;[28] this had a positive effect on pumping for injection to the subterranean reservoirs. The viscosity evolution of the saline gelant solutions and the fresh solution is shown in Tables XIII–XV.

As shown in Tables XIII–XV, NaCl could be used as a retardation agent for its positive effect on the gelation time delay, as many studies have reported. This phenomenon could be explained by the fact that monovalent and divalent cations in gelant solutions could shield the negative charges available on the carboxylate groups and lead to the hydrodynamic volume of polymer chains becoming smaller. Therefore, potential crosslinking sites on the polymer chains were not as accessible to the crosslinker molecules and attached for gelation.[15] Thus, the initial gelation time was delayed. The shielding effect became stronger with increasing TDS of the gelant solutions. However, too much TDS had a negative effect on the gel strength. In Table XIII, we found that most of the samples (when the polymer concentration was 0.2 wt %, the ammonium salt was NH_4Cl only, and the second crosslinker was formaldehyde) had different degrees of syneresis. However, the gel showed better stability with complex ammonium salt (even at a low polymer concentration) or at a high polymer concentration of 0.3 wt %. When gelling solutions are prepared, this requires a reasonable water salinity. For example, in offshore oil fields, if the TDS of seawater is too high, the gelation time can be reduced with complex ammonium salt, and this changes the second crosslinker type and increases the concentration of either the polymer or the crosslinker.

Stability of the Gel System

Several variables have effects on the gel stability. Most of the experiments showed a date of 90 days of observation. Compared to other variables (crosslinker concentration, polymer M_w, polymer concentration, ammonium salt concentration, and ammonium salt accelerator composition), the polymer concentration can greatly impact the gel stability. This phenomenon was similar to that in the most commonly used gel system. However, the polymer M_w, ammonium salt concentration, ammonium salt composition, and second crosslinker type appeared to have a modest effect on the gel stability. Therefore, the gel strength and stability could be controlled by the adjustment of the polymer concentration, M_w, crosslinker concentration, ammonium salt concentration, and composition to meet the well-site requirements.

Effect of the Temperature on the Gelation Performance

It is known that temperature is a key factor affecting the gelation time of the crosslinker, and fresh water was used to prepare the gelling solution with four formulations numbered I to IV in this experiment. The test temperatures were 25, 45, 60, and 90°C, and we aimed to enlarge the usage range in different temperatures.

Tables XVI and XVII show that the gelation time of the gel system increased with increasing temperature, and the gel strength also increased. The strength code reached code G at 90°C, but the gelation time was too short. The reason was that the high temperature could accelerate the molecular motion. On the one hand, the condensation reaction for phenol–formaldehyde was accelerated. On the other hand, the chance for a crosslinker hitting amide groups increased, and the polymer obtained more crosslinking units.[26] Therefore, the gel strength became stronger, and the gelation time became shorter at high temperatures. Furthermore, no dehydrated gel was detected when the HPAM concentration was 0.3 wt %, and the gel system showed perfect thermostability even at 90°C after 15 days.

Therefore, the gel systems could be used for medium- and low-temperature reservoirs. Research on this gel system to delay crosslinking at high temperatures is worth discussing in the future.

CONCLUSIONS

A summary of the different conclusions drawn from the study are presented as follows:

1. With ammonium salt, formaldehyde and phenol–formaldehyde crosslinked HPAM at room temperature within a short time. The gel time of the gel system could be well controlled from about 2 h to 2 days at 25°C; this was longer than the commonly used chromium(III) acetate/PHPAM gel system. The final strength of this gel system reached code I and could be called a rigid gel. Various parameters could be adjusted to control the gelation time and final gel strength.
2. The ammonium salt reduced the initial viscosity of the gelant solution; the low viscosity allowed the gelant solution to be easily injected deep into a formation matrix.
3. As the concentration of polymer in the gelant solution increased, the gelation time decreased, and the final gel strength increased.
4. The increase in the crosslinkers (including the first and the second crosslinker) concentration caused a decrease in the gelation time but only up to a certain range, beyond which syneresis took place because of excessive crosslinking.
5. The gels formed with NH_4HCO_3 were more stable than those formed with NH_4Cl, whereas the final gel strength was weaker.
6. The gels formed with phenol–formaldehyde had a stronger final gel strength and better gel stability than those formed with formaldehyde.
7. When the salinity concentration increased, the gelation time increased, and the gel strength decreased.
8. The gelation time of the gel system increased with increasing temperature, and the gel strength also increased. It could be used for medium- and low-temperature reservoirs.
9. The gels formed were cost-efficient and had a high mechanical strength.

ACKNOWLEDGMENTS

This work was supported by the PetroChina Innovation Foundation (contract grant number 2013D-5006-0201), the Science & Technology Fund of Southwest Petroleum University (contract grant number 2013XJZ007), and the Special Fund of China's Central Government for the Development of Local Colleges and Universities (Project of National First-Level Discipline in Oil and Gas Engineering).

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