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Synthesis, characterization, and performance evaluation of the AM/AMPS/DMDAAC/SSS quadripolymer as a fluid loss additive for water-based drilling fluid

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ABSTRACT: According to the molecular structure design requirements of the fluid loss additive resistant to high temperature, 2-acrylamide-2-methyl propane sulfonic acid (AMPS), acrylamide (AM), dimethyl diallyl ammonium chloride (DMDAAC) and sodium styrene sulfonate (SSS) are selected as the structure monomers. Using ammonium persulfate as initiator, a new quadripolymer is synthesized through free radical aqueous solution polymerization. According to the minimum filtration loss of the fresh water-based drilling fluid with 0.5 wt % quadripolymer, The synthesis conditions are optimized by orthogonal test: the mole ratio of AMPS/AM/DMDAAC/SSS is 5/7/2/1, the monomer concentration is 30 wt %, the initiator concentration is 0.8 wt %, the reaction temperature is 75°C and the pH is 10. The structure of the quadripolymer is characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance hydrogen spectroscopy. The results show that the quadripolymer contains all the designed functional groups. The thermal stability of the quadripolymer is tested by thermogravimetry, differential thermogravimetry, and differential scanning calorimetry. The results show that the thermal degradation of the quadripolymer is not obvious before 272.3°C. The rheological performance and filtration loss of the quadripolymer are evaluated. The results indicate that the filtration loss decreases with the increasing dosage of the quadripolymer before and after thermal aging test at 180°C for 16 h, and the filtration loss before the thermal aging test is smaller than that after the thermal aging test. The high temperature high pressure filtration loss ($FL_{(HTHP)}$) experiment results also show that the quadripolymer fluid loss additive has excellent temperature-resistant performance. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41762.

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INTRODUCTION

With the rapid development of the modern petroleum industry, the exploration of oil and gas has gradually turned to the deep formation. The formation temperatures of the deep wells may rise up to 200°C or higher, which naturally puts forward a challenge for the drilling fluid under high temperature and high pressure.[1,2] During the drilling, the drilling fluid can suspend the cuttings, cool the drill bit and control the formation pressure. So, the high temperature stability of the drilling fluid decides the success or failure of the drilling engineering, drilling speed and costs of the deep wells and ultra deep wells.[3]

For the different drilling fluid systems, the viscosity and filtration loss have different scopes. For example, the plastic viscosity (PV) of the ferrochrome lignosulfonate (FCLS) drilling fluid is from 8 mPa s to 12 mPa s at room temperature, and the FL_{API} is less than 8 mL. However, for the salt water drilling fluid, the PV is from 25 mPa s to 30 mPa s at room temperature, the FL_{API} is less than 5 mL and the FL_{HTHP} is less than 20 mL.[4,5] Fluid loss additive as one of the important treatment agent in water-based drilling fluid plays a significant role in safety, rapid and high efficient drilling. However, the high temperature of the deep well leads to the crosslinking and degradation of the conventional fluid loss additives. As a result, the rheology and filtration loss of the drilling fluid cannot be controlled. Besides, the high pressure mainly affects the density of drilling fluid. The borehole wall instability, the borehole collapsing and the drill bit burying usually happen under high pressure.[6,7]

The traditional fluid loss additives are natural polymers and their modified products, such as modified cellulose,[8,9] modified humic acid,[10–12] and modified starch products,[13–16] which are usually used when the temperature is less than 150°C. Therefore, the most important developing direction of the fluid loss additives is the synthetic polymer products.[17–27] A series of binary copolymers, terpolymers and quadripolymers, containing

2-acrylamide-2-methyl propane sulfonic acid (AMPS), have been synthesized as fluid loss additives. All these polymers indicate that the sulfonate structure may be resistant to the high temperature and the salt, and the drilling fluids containing sulfonated polymers can be used in some deep wells. However, fewer researches have been reported about the dimethyl diallyl ammonium chloride (DMDAAC) and sodium styrene sulfonate (SSS), which are used as fluid loss additives. If DMDAAC and SSS are used as monomers, according to the mechanism of the polymerization, a five carbon ring would be produced. The five carbon ring and the six benzene ring structures can improve the resistance to high temperature and the salt. So, based on the above analysis, AMPS, AM, DMDAAC and SSS as the structure monomers are selected according to the high temperature requirements. A novel quadripolymer as a kind of fluid loss additive for drilling fluid used under high temperature is synthesized. The filtration loss and the rheological properties of the drilling fluids with this quadripolymer are studied. The thermal properties of the quadripolymer in different drilling fluids are also researched.

EXPERIMENTAL

Materials

Acrylamide (AM) and DMDAAC were analytical reagent, which were, respectively, provided by Chengdu Kelong Chemical Reagent Co. (China) and Shanghai Dibo Chemical Technology Co. (China) AMPS and SSS were commercial products, which were, respectively, purchased from Shouguang Songchuan Industrial Auxiliaries Co. (China) and Shandong Ziboruihou Commercial and Trade Co. (China). The initiator was ammonium persulfate, also obtained from Chengdu Kelong Reagent Co. (China).

Equipments

Fourier transform infrared spectrometer (NICOLET 6700) was produced by American Thermo Scientific Co.. Thermal analyzer (type: DSC823 TGA/SDTA85/e) was provided by Switzerland Mettler Toledo Co. (Switzerland) Nuclear magnetic resonance hydrogen spectroscopy (Angilent 400) was obtained from Agilent Co. (America) Mud medium pressure filtration apparatus (type: SD3), high temperature and high pressure filtration apparatus (type: GGS42-2), frequency conversion rolling oven (type: GW300), and six-speed rotational viscometer (type: ZNN-D6B) were produced by Qingdao Tongchun Petroleum Instrument Co. (China).

Synthesis of AMPS/AM/DMDAAC/SSS Quadripolymer

The quadripolymer of AM, AMPS, DMDAAC and SSS was synthesized by free radical aqueous solution polymerization. The orthogonal test was used to optimize the synthesis conditions. The optimized conditions can be obtained according to the minimum value of $FL_{(API)}$ of the fresh water-based drilling fluid with the quadripolymer (0.5 wt %) after aging test at 180°C for 16 h. Five main factors were considered, including the mole ratio of AMPS/AM/DMDAAC/SSS, monomer concentration, reaction temperature, initiator concentration, and pH value.

According to the orthogonal test conditions, at first, a certain amount of AMPS was dissolved in distilled water, and equimolar sodium hydroxide was mixed with the former solution in ice-bath. Then, the mixture monomers of AM/DMDAAC/SSS were dissolved in the solution according to the molar ratio of the orthogonal test. The pH was adjusted to the corresponding value with sodium hydroxide. The solution was deoxygenated with nitrogen gas. The aqueous solution of ammonium persulfate was dropped gradually, and keeping the reaction system at a set temperature (65°C, 70°C, 75°C, or 80°C, according to the orthogonal test) for 6 h with constantly stirring. After the reaction, the product was extracted with anhydrous ethanol for three times, and then it was immersed in acetone for 24 h. Soxhlet extraction method was used to eliminate the residual monomers and initiator. At last, the product was dried under vacuum at 50°C.

Characterization of the Quadripolymer

Fourier transform infrared spectrometer was used to characterize the molecular structures and the chemical compositions of the quadripolymer through the infrared absorption peaks of the functional groups. Before the test, the quadripolymer was grinded together with the potassium bromide, and the mixture powder was transferred into the mold to form a circular sheet. The quadripolymer was tested with Fourier transform infrared spectrometer (NICOLET 6700).

Nuclear magnetic resonance (NMR) was used to analyze the chemical structure. 10 mg pure sample was dissolved in 0.65 mL D_2O, and then, the solution was transferred to the nuclear magnetic sample tube. Nuclear magnetic resonance (Angilent 400) was used to record the proton absorption peaks of the quadripolymer.

The thermal stability of the quadripolymer was tested with the thermal analyzer (DSC823 TGA/SDTA85/e) in the nitrogen atmosphere. The heating rate was 10°C/min, and the temperature was from 50°C to 650°C.

Preparation of the Drilling Fluid

The fresh water-based drilling fluid was composed of 500 mL running water, 20.0 g bentonites (4.0 wt %) and 1.0 g anhydrous sodium carbonate, which are mixed together under high speed stirring for 20 minutes. The system was stable for 24 h at room temperature, and then, the base mud was prepared. A certain amount of AMPS/AM/DMDAAC/SSS quadripolymer was added into the base mud before the system was tested. The other two kinds of drilling fluids, the same procedures as the previous, containing 4.0% of NaCl or saturated brine were also prepared.

Performance Evaluation of the Drilling Fluid

The drilling fluid was evaluated according to American Petroleum Institute (API) test programs. At first, the API filtration loss (FL_{API}) of the mud was evaluated through the mud medium pressure filtration apparatus (SD3). The aging tests was carried out by the frequency conversion rolling oven (type: GW300) through hot rolling at different temperatures (120°C, 150°C, 180°C, and 200°C) for 16 h. Then the high temperature and high pressure filtration loss (FL_{HTHP}) was tested with the high temperature and high pressure filtration apparatus (GGS42-2). During the filtration loss test, filter cake was formed

Table I. Factors and Levels of the Synthetic Experiment

	Parameters				
Level	Mole ratio of AMPS/AM/DMDAAC/SSS [A]	*T* (°C) [B]	Monomer concentration (wt %) [C][a]	Initiator Concentration (wt %) [D][b]	pH [E]
1	3/9/2/1	65	15	0.4	4
2	4/8/2/1	70	20	0.6	7
3	5/7/2/1	75	25	0.8	10
4	6/6/2/1	80	30	1.0	13

[a] Based on the mass fraction of the solution.
[b] Based on the total mass of AMPS, AM, DMDAAC, and SSS.

on the filter paper, which can contribute to reduce the filtration loss. Apparently, if the filtration loss is small, the drilling fluid would have better performance. Finally, the rheological parameters of the drilling fluid were measured with the six-speed rotational viscometer (ZNN-D6B) at room temperature. Apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were evaluated through the numerical values when the rotational speed was 600 rpm and 300 rpm. Φ600 represents the numerical value shown on the indicator dial of the six-speed rotational viscometer when it was rotated with 600 rpm. Φ300 represents the numerical value shown on the indicator dial of the six-speed rotational viscometer when it was rotated with 300 rpm. The computation formulas were as follows:[28]

$$\mathrm{AV} = \frac{1}{2}\Phi 600 \ (\mathrm{mPa\ s})$$

$$\mathrm{PV} = \Phi 600 - \Phi 600 \ (\mathrm{mPa\ s})$$

$$\mathrm{YP} = \frac{1}{2}(\Phi 300 - \mathrm{PV}) \ (\mathrm{Pa})$$

RESULTS AND DISCUSSION

Synthesis Conditions Optimizing of the Quadripolymer

The orthogonal $L_{16}(4^5)$ experiments are designed to optimize the synthesis conditions. The five main factors, including mole ratio of AMPS/AM/DMDAAC/SSS, monomer concentration, reaction temperature, initiator concentration and the pH are selected to research the synthesis conditions as listed in Table I.

Table II. L_{16} (4^5) Orthogonal Experimental Results

Sample	A	B	C	D	E	$FL_{(API)}$ (mL)[a]
1	1	1	1	1	1	29.2
2	1	2	2	2	2	31.6
3	1	3	3	3	3	25.4
4	1	4	4	4	4	26.4
5	2	1	2	3	4	29.0
6	2	2	1	4	3	26.8
7	2	3	4	1	2	29.6
8	2	4	3	2	1	32.0
9	3	1	3	4	2	28.0
10	3	2	4	3	1	23.8
11	3	3	1	2	4	30.8
12	3	4	2	1	3	28.8
13	4	1	4	2	3	30.0
14	4	2	3	1	4	34.4
15	4	3	2	4	1	29.6
16	4	4	1	3	2	30.6
k_1	28.150	29.050	29.350	30.500	28.650	
k_2	29.350	29.150	29.750	31.100	29.950	
k_3	27.850	28.850	29.950	27.200	27.750	
k_4	31.150	29.450	27.450	27.700	30.150	
R	3.300	0.600	2.500	4.900	2.400	

[a] $FL_{(API)}$ test condition: 25°C, 0.69 MPa.

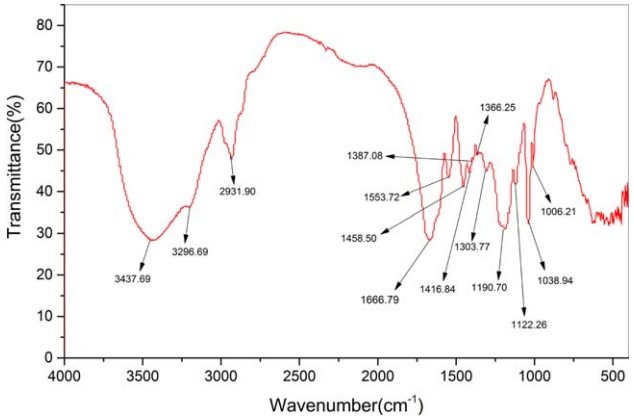

Figure 1. FTIR of AMPS/AM/DMDAAC/SSS quadripolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

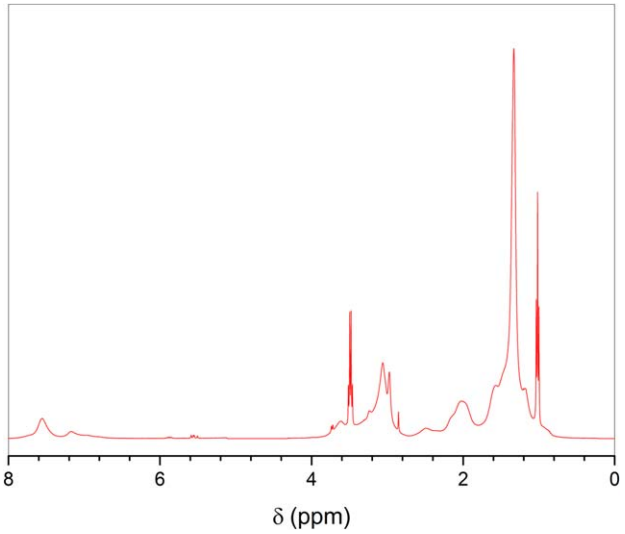

Figure 2. H^1-NMR of AMPS/AM/DMDAAC/SSS quadripolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The optimized conditions can be obtained according to the minimum value of the filtration loss of the fresh water-based drilling fluid with the quadripolymer (0.5 wt %) after aging tests at 180°C for 16 h. Table II shows the results of the orthogonal tests.

As is shown in Table II, the orthogonal test and the range analysis are used to study the influence of the synthesis conditions on the filtration loss. The results show that the mole ratio of AMPS/AM/DMDAAC/SSS and the initiator concentration play an important role in the reduction of the filtration loss than other factors. The dosage of the initiator has the greatest influence on the free radical polymerization because of the induced decomposition and the cage effect. Less initiator leads to low efficiency and slow polymerization rate. At the same time, due to the negatively charged clay surface, the cationic quaternary ammonium group () adsorbs on the surface of the clay particle through strong electrostatic interaction. The nonionic amide (≡$CONH_2$) adsorbs on clay surface through hydrogen bonding. The cationic quaternary ammonium group transforms the clay electric double layer structure and the zeta potential of the clay,[29] which improve the dispersion of the clay particles in the drilling fluid. And then, a low permeability filter cake is formed. The particles of the drilling fluid originate from the clay. The aggregation and dispersion of the clay particles in the drilling fluid make the sizes of the particles have a suitable scope.[30,31] Wu[22] found that the average particle size of the fresh water-based mud is 501.6 nm, while the average particle size of the polymer fresh water-based mud is 307.2 nm. So the particle size distribution of the drilling fluid is also an important factor to control the filtration loss. Besides, sulfonic group ($-SO_3^-$) as hydration group is advantageous to the polymer dispersion.

The optimized synthesis conditions are as follows: mole ratio of AMPS/AM/DMDAAC/SSS is 5/7/2/1, the monomer concentration is 30 wt %, the initiator concentration is 0.8 wt %, the reaction temperature is 75°C and the pH is 10. The order of the influence on the filtration loss is D > A > C > E > B. The $FL_{(API)}$ of the quadripolymer drilling fluid is 21.8 mL when the quadripolymer is synthesized under the optimized synthesis conditions.

FTIR Analysis of the Quadripolymer

The spectrum shows the infrared characteristic absorption peaks of the quadripolymer, which are shown in Figure 1.

The absorption peak at 3437.69 cm^{-1} (N–H stretching band, primary amide group) corresponds to the AM. The absorption peak at 3196.69 cm^{-1} (N–H stretching band, second amide group) corresponds to the AMPS. The absorption peak at 1666.79 cm^{-1} (C═O stretching band) corresponds to the AM and AMPS. The absorption peaks at 1553.72 cm^{-1} and 1458.50 cm^{-1} (benzene stretching band) correspond to SSS. The absorption peaks at 1416.84 cm^{-1} and 1416.84 cm^{-1} (C–N stretching and bending vibration band) correspond to the DMDAAC. The absorption peaks at 1190.70 cm^{-1}, 1122.26 cm^{-1}, 1038.94 cm^{-1}, and 1006.21 cm^{-1} (stretching SO_3, S═O) correspond to the sulfonic group.

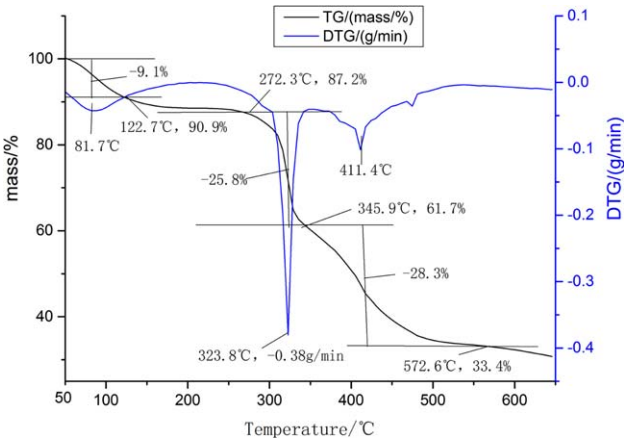

Figure 3. TG and DTC of AMPS/AM/DMDAAC/SSS quadripolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

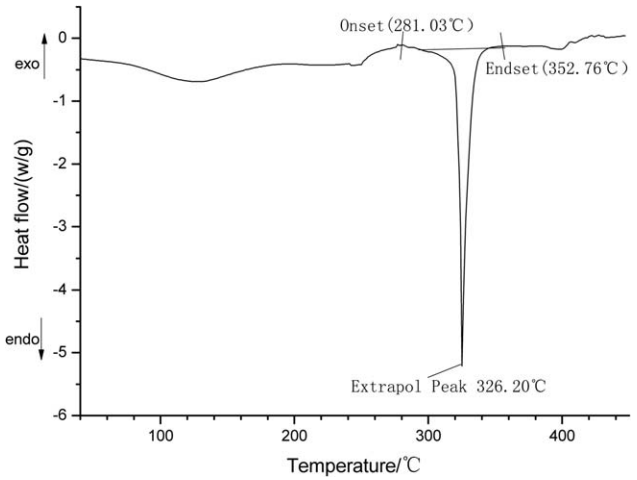

Figure 4. DSC of AMPS/AM/DMDAAC/SSS quadripolymer.

H^1-NMR Analysis of the Quadripolymer

The nuclear magnetic resonance hydrogen spectrum (H^1-NMR) of the AMPS/AM/DMDAAC/SSS quadripolymer is shown in Figure 2. 7.56 ppm and 7.18 ppm correspond to the proton vibration peaks of the benzene ring of SSS. 5.85–5.92 ppm corresponds to the proton vibration peaks of the N-H primary amide group of AM. 5.51–5.59 ppm corresponds to the proton vibration peaks of the N-H second amide group of AMPS. 3.47 ppm and 3.50 ppm correspond to the proton vibration peaks of N^+–CH_3 and N^+–CH_2– of DMDAAC. Respectively, 2.86 ppm and 1.60 ppm correspond to the proton vibration peaks of –CH_2 and –CH_3 of AMPS. 2.98 ppm and 1.47 ppm correspond to the proton vibration peaks of –CH, which links with the benzene ring and the main chain, respectively. Combined with FTIR results, the quadripolymer is successfully synthesized.

Thermogravimetry and Differential Scanning Calorimetry Analysis of the Quadripolymer

The sample used to test the thermostability is synthesized under the optimized conditions as described in the orthogonal test. As is shown in Figures 3 and 4, the thermostability of AMPS/AM/DMDAAC/SSS quadripolymer is studied with thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses.

The process of the thermal decomposition of the quadripolymer includes three stages from the thermoanalysis curves shown in Figure 3. From the TG curve, it can be seen that the first stage is from 50°C to 122.7°C, and 9.1% mass losses, relatively, the loss rate is slow. The mass loss mainly appears at 81.7°C, which is mainly probably due to a small amount of adsorbed water gradually volatilized with the increasing temperature.

The second stage is from 272.3°C to 345.9°C, a dramatically decline appears in the TG curve, and a wave trough emerges at 323.8°C in the differential thermogravimetric curve. Moreover, the mass loss of the quadripolymer quickly reaches 25.8% and the maximum decomposition rate reaches 0.38 g/min.

The third stage is from 345.9°C to 572.6°C. In the TG curve of the quadripolymer, the mass loss declines constantly, 28.3% mass is left when the temperature reaches 572.6°C. A large number of mass loss is caused by the breakage of the benzene ring connected on the molecular side chain and the thermal degradation of C–C in the main chain at higher temperature. Combined the above analysis, the thermal degradation of the quadripolymer is not obvious before 272.3°C.

From Figure 4, obviously, there is a remarkable peak in the curve at 326.20°C. Combined with the TG curve, the sharp peak is an endothermic peak caused by the decomposition of the quadripolymer.

Rheological Performance of the Quadripolymer Drilling Fluid

The quadripolymer is added into fresh water drilling fluid, 4.0 wt % salt water and saturated brine-based drilling fluid with different concentrations. The rheological properties are studied before and after the thermal aging tests at 180°C for 16 h. The results, such as the apparent viscosity (AV), the plastic viscosity (PV), and the yield point (YP) are shown from Tables III to V.

Table III shows the influence of the quadripolymer concentrations on the rheological properties in fresh water-based drilling fluid. The results show that the apparent viscosity, plastic viscosity and yield point basically increase slightly with the

Table III. Rheological Behaviors of Fresh Water-Based Drilling Fluid with Different Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

	AV (mPa s)		PV (mPa s)		YP (Pa)	
Quadripolymer concentrations (wt %)	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging
0[a]	12.5	10.0	9.5	9.0	3.0	1.0
0.2	14.0	12.0	10.0	10.0	4.0	2.0
0.4	16.5	9.0	11.0	8.0	5.5	1.0
0.6	23.5	12.0	15.5	9.0	8.0	3.0
0.8	27.5	13.5	19.0	12.0	8.5	1.5
1.0	34.0	20.0	23.0	15.0	11.0	5.0
1.2	40.5	19.0	29.0	16.0	11.5	3.0

[a] Fresh water-based drilling fluid.

Table IV. Rheological Behaviors of 4.0% Salt Water-Based Drilling Fluid with Different Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

	AV (mPa s)		PV (mPa s)		YP (Pa)	
Quadripolymer concentrations (wt %)	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging
0[a]	9.0	5.0	5.0	3.0	4.0	2.0
0.25	19.5	9.0	8.0	7.0	11.5	2.0
0.5	25.0	11.0	13.0	8.0	12.0	3.0
0.75	27.0	12.5	18.0	11.0	9.0	1.5
1.0	31.0	14.0	20.0	12.0	11.0	2.0
1.25	33.5	18.5	21.5	14.0	12.0	4.5
1.5	36.0	20.0	27.0	16.5	9.0	3.5

[a] 4.0% salt water-based drilling fluid.

increasing of the quadripolymer before the thermal aging test. Compared with the values before the thermal aging test, the values of these parameters are smaller after the thermal aging test. But the yield point changed little after the thermal aging test, which primarily due to the interaction between aggregation and dispersion of the clay particles under the high temperature.[32] The water-soluble quadripolymer contains cationic quaternary ammonium group ($\equiv N^+$), nonionic amide ($-CONH_2$) group and sulfonic acid group, which lead to the adsorption of the quadripolymer on the clay surface. Then, the clay is dispersed evenly and the viscosity of the drilling fluids increases.

It is found that the AV, PV, and YP of the 4.0 wt % salt water and saturated brine-based drilling fluids have similar change compared with the fresh water-based drilling fluid (Tables IV and V). The results indicate that the two salt water drilling fluids with different quadripolymer concentrations have excellent tolerance to salt.

The corresponding values of the rheological parameters of fresh water are larger than salt water drilling fluid at the same quadripolymer concentrations. The difference is mainly affected by salt screening effect.[22,33] With the addition of the salt, the electric double layer of the clay particles decreases, which adversely changes the zeta potential of the suspension and enhances the electrostatic repulsion.[29] Besides, the sulfonic group of the quadripolymer has strong salt resistance and hydration dispersion capacity.

Filtrate Properties of the Quadripolymer Drilling Fluid

The FL_{API} of the fresh water, 4.0 wt % salt water, saturated brine-based drilling fluids with different quadripolymer concentrations before and after thermal aging tests at 180°C for 16 h are evaluated. The FL_{HTHP} (150°C,3.5 MPa) of the three kinds of drilling fluids after the thermal aging tests are also accomplished. The results are shown in Figures 5–7.

As is shown in Figure 5, the results demonstrate that the filtration loss of the fresh water-based fluid decreases with the increasing of the quadripolymer concentrations. When the dosage of the quadripolymer is 1.2 wt % in the fresh water drilling fluid, the FL_{API} is 6.4 mL and 9.6 mL before and after the thermal aging test at 180°C for 16 h, and the FL_{HTHP} after the thermal aging test is controlled within 19.8 mL. It indicates that a small amount of quadripolymer can effectively reduce the filtration loss. The adsorption groups ($\equiv N^+$ and $-CONH_2$) of the

Table V. Rheological Behaviors of Saturated Brine-Based Drilling Fluid with Different Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

	AV (mPa s)		PV (mPa s)		YP (Pa)	
Quadripolymer concentrations (wt %)	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging
0[a]	10.5	5.5	5.5	4.5	5.0	1.0
0.5	18.0	15.0	12.0	12.0	6.0	3.0
1.0	29.0	19.0	17.0	16.0	12.0	3.0
1.5	33.0	24.5	22.0	20.0	11.0	4.5
2.0	35.0	31.0	25.0	24.0	10.0	7.0
2.5	37.5	40.5	26.0	32.0	11.5	8.5

[a] Saturated brine-based drilling fluid.

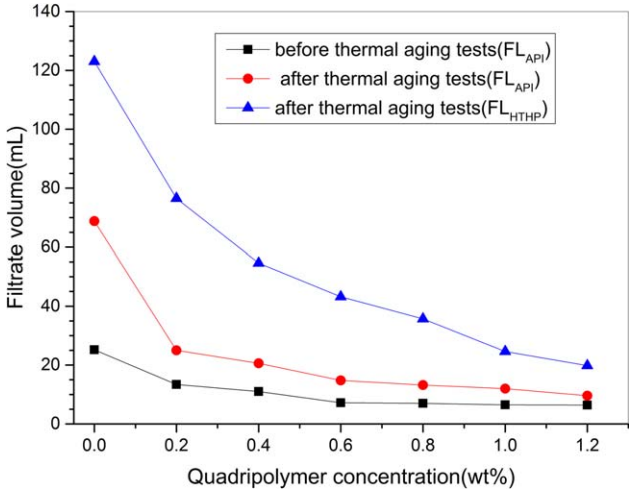

Figure 5. Influence of the quadripolymer concentrations on the filtrate volume of the fresh water-based drilling fluid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quadripolymer can adsorb on the surface of clay particles through electrostatic interaction and hydrogen band, which increases the zeta potential of the clay particles. Then, the distribution of the clay particle size is changed, and then, a thin and low permeable filter cake is formed to prevent the loss.[29,34]

Similarly, the changes of the filtration loss also present a declining trend with the increasing of the quadripolymer concentrations for the 4.0 wt % salt water- and saturated brine water-based drilling fluids (Figures 6 and 7). Apparently, the FL_{API} before and after the thermal aging test and the FL_{HTHP} after the thermal aging test in 4.0 wt % salt water- and saturated brine water-based drilling fluids are larger than that in fresh water-based drilling fluid at the same concentration of the quadripolymer. The reason is that the salt screening effect of sodium chloride in the quadripolymer-bentonite suspension makes the molecular chain of the quadripolymer twisting,[35,36] which further decreases the electric double layer of the clay particles, especially in saturated brine-based drilling fluid. But when the quadripolymer concentration increases to 2.5 wt %, the FL_{API} is less than 15 mL and the FL_{HTHP} is less than 30 mL for the saturated brine-based drilling fluid after the thermal aging at 180°C for 16 h.

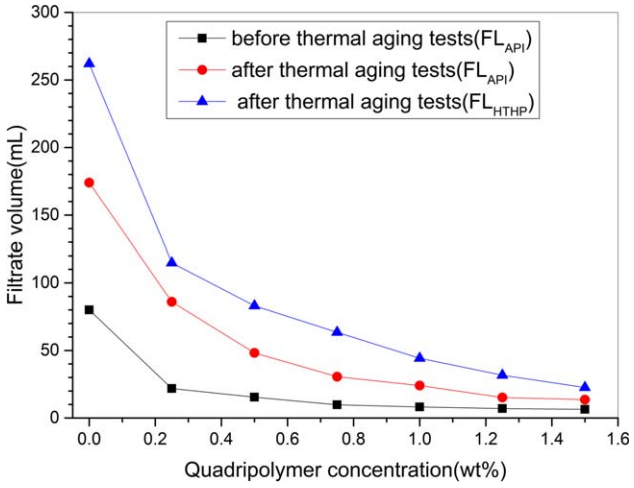

Figure 6. Influence of the quadripolymer concentrations on the filtrate volume of the 4.0 wt % salt water-based drilling fluid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

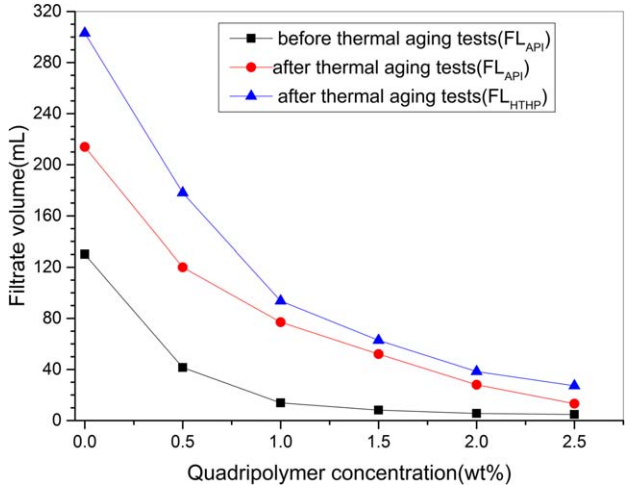

Figure 7. Influence of the quadripolymer concentrations on the filtrate volume of the saturated brine water-based drilling fluid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Temperature Resistance of the Quadripolymer Drilling Fuid

2.0 wt % quadripolymer is added into the fresh water, 4.0 wt % salt water and saturated brine water-based drilling fluids. The drilling fluids are hot rolled at different temperatures (120°C, 150°C, 180°C, and 200°C) for 16 h. The rheology and filtration loss of the three kinds of drilling fluids are evaluated after the thermal aging test. The results are shown in Table VI.

The results show that the AV, PV and YP of the three kinds of drilling fluids gradually decease with the increasing of the aging temperature from 120°C to 180°C. The declining trend becomes more remarkable when the aging temperature is changed from 180°C to 200°C. While the FL_{API} and FL_{HTHP} of the three drilling fluids with 2.0 wt % quadripolymer, respectively, appear a increasing trend when the aging temperature is from 120°C to 200°C. The adsorption and hydration abilities of the quadripolymer on the clay particles decrease with the increasing aging temperature. However, the FL_{API} and FL_{HTHP} of the drilling fluids with 2.0 wt % quadripolymer are still low after the thermal aging test at 180°C for 16 h, which is acceptable in the drilling industry.

Comparative Test Between AMPS/AM/DMDAAC/SSS Quadripolymer and Other Three Commercialized Products

AMPS/AM/NVP/SSS quadripolymer was synthesized by the method described in Tao.[37] SMP-II and PAC-42 are the commercialized products widely used in water-based drilling fluid. The four fluid loss additives are, respectively, added into the fresh water-based drilling fluid with a same concentration (2.0 wt %). The rheological properties and filtration loss of these

Table VI. The Influence of the Thermal Aging Temperature on the Rheology and Filtration Properties of the Drilling Fluids

Drilling fluid type	Aging conditions	AV (mPa s)	PV (mPa s)	YP (Pa)	$FL_{(API)}$ (mL)[a]	$FL_{(HTHP)}$ (mL)[b]
Fresh water-based drilling fluid + 2.0 wt % quadripolymer	120°C, 16 h	45.0	37.5	7.5	5.6	17.0
	150°C, 16 h	41.5	34.5	7.0	7.2	19.8
	180°C, 16 h	32.5	27.0	5.5	9.8	26.2
	200°C, 16 h	17.5	14.0	3.5	13.0	43.2
4.0 wt % salt water-based drilling fluid + 2.0 wt % quadripolymer	120°C, 16 h	41.5	33.0	8.5	6.0	17.4
	150°C, 16 h	38.5	30.5	8.0	8.6	24.6
	180°C, 16 h	23.5	18.5	5.0	11.8	41.4
	200°C, 16 h	19.5	11.0	8.5	25.2	77.8
Saturated brine-based drilling fluid + 2.0 wt % quadripolymer	120°C, 16 h	38.5	31.0	7.5	7.0	19.2
	150°C, 16 h	36.0	29.5	6.5	10.4	25.8
	180°C, 16 h	25.5	20.0	5.5	14.5	46.2
	200°C, 16 h	13.0	11.0	2.0	26.0	95.0

[a] $FL_{(API)}$ test condition: 25°C, 0.69 MPa.
[b] $FL_{(HTHP)}$ test condition: 180°C, 3.5 MPa.

products are measured before and after the thermal aging test at 180°C for 16 h. The results are listed in Table VII.

The results demonstrate that the FL_{API} and FL_{HTHP} of AMPS/AM/DMDAAC/SSS are smaller than other three products. The FL_{HTHP} can be controlled within 26.2 mL, while the FL_{HTHP} of SMP-II is 94.0 mL. The temperature has less influence on the filtration loss of the AMPS/AM/DMDAAC/SSS quadripolymer drilling fluid.

CONCLUSIONS

The AMPS/AM/DMDAAC/SSS quadripolymer is synthesized through free radical aqueous solution polymerization, and the optimal polymerization conditions are obtained: the mole ratio of AMPS/AM/DMDAAC/SSS is 5/7/2/1, the monomer concentration is 30 wt %, the initiator concentration is 0.8 wt %, the reaction temperature is 75°C and the pH is 10. The structure of the quadripolymer is characterized by FTIR and H^1-NMR. The results show that the quadripolymer contains all the designed functional groups. TG and DSC analysis prove that the thermal degradation of the quadripolymer is not obvious before 272.3°C. The performance of the quadripolymer is evaluated in the fresh water drilling fluid, 4.0 wt % salt water drilling fluid, and saturated brine water drilling fluid. The apparent viscosity, plastic viscosity and yield point regularly increase with the increasing dosage of the AMPS/AM/DMDAAC/SSS quadripolymer before and after the aging test, and these values before the aging test are larger than that after the aging test. When the

Table VII. The Rheological Properties and Filtration Loss of AMPS/AM/DMDAAC/SSS Quadripolymer, AMPS/AM/NVP/SSS Quadripolymer, SMP-II and PAC-42

Drilling fluid	Aging conditions	AV (mPa s)	PV (mPa s)	YP (Pa)	$FL_{(API)}$ mL[a]	$FL_{(HTHP)}$ (mL)[b]
Fresh water-based drilling fluid +2.0 wt % AMPS/AM/DMDAAC/SSS	Before aging	42.5	33.0	9.5	5.2	-
	After aging	32.5	27.0	5.5	9.8	26.2
Fresh water-based drilling fluid +2.0 wt % AMPS/AM/NVP/SSS	Before aging	32.0	18.5	13.5	6.2	-
	After aging	26.0	16.0	10.0	12.6	29.8
Fresh water-based drilling fluid +2.0 wt % SMP-II	Before aging	10.0	7.5	2.5	18.8	-
	After aging	8.0	7.0	1.0	28.2	94.0
Fresh water-based drilling fluid +2.0 wt % PAC-42	Before aging	83.5	65.0	18.5	6.0	-
	After aging	21.0	17.5	3.5	15.0	49.6

[a] $FL_{(API)}$ test condition: 25°C, 0.69 MPa.
[b] $FL_{(HTHP)}$ test condition: 180°C, 3.5 MPa.

dosage of the quadripolymer is 1.0 wt % in the three kinds of drilling fluids, the API filtration loss ($FL_{(API)}$), respectively, decreases 57 mL, 150 mL and 137 mL compared to the base mud after hot rolling at 180°C for 16 h. The FL_{API} and FL_{HTHP} of the three drilling fluids decrease with the increasing quadripolymer concentration. The filtration loss after the aging test is larger than that before the aging test. The high temperature high pressure fluid loss ($FL_{(HTHP)}$) experiment results also show that the quadripolymer fluid loss additive has excellent temperature-resistant performance when the temperature is less than 200°C. The temperature has less influence on the filtration loss of the AMPS/AM/DMDAAC/SSS quadripolymer drilling fluid compared with the AMPS/AM/NVP/SSS quadripolymer, SMP-II, and PAC-42.

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