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Synthesis and application of starch-graft-poly(AM-co-AMPS) by using a complex initiation system of CS-APS

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Abstract

A graft copolymer was synthesized by graft copolymerization of starch with acrylamide (AM) and 2-acrylamido-2-methylpropanesulfoacid (AMPS). The copolymerization was carried out by using a complex initiation system of cerium sulfate (CS) and ammonium persulfate (APS). The effects of reaction conditions on graft copolymerization and the use of the copolymer as the flooding agent in enhanced oil recovery were investigated. Experiments showed that a graft copolymer with higher grafting level, higher intrinsic viscosity and higher anionic degree could be obtained by changing the method of monomer addition and by controlling the ratio of AMPS–AM. When using 0.2% of the grafted starch [S-g-P(AM-co-AMPS)] as the flooding agent, a higher enhanced oil recovery rate was obtained than with hydrolytic polyacrylamide (HPAM), which showed that the novel graft polymer had much better resistance to temperature and shear rate than HPAM, and had potential application in enhanced oil recovery.

Keywords: Starch; Acrylamide; 2-Acrylamido-2-methylpropanesulfoacid; Complex initiation system; Graft copolymerization

1. Introduction

Anionic polymers of acrylamide and other vinyl monomers are currently commercialized and widely applied in numerous fields such as the petroleum industry and environmental protection. Kurenkoy, Verihznikova, and Myagchenkov (1984) reported the preparation of copolymers of acrylamide with sodium acrylate in inverse emulsion; Kathmann, White, and Mccormick (1996) studied synthesis and characterization of *N*-vinylformamide with sodium 3-acrylamido-3-methylbutanoate, sodium 2-acrylamido-2-methylpropanesulfonate, and sodium acrylate; Liu, Han, and Jin (2000) investigated synthesis of APAM by inverse suspension and adding alkali for hydrolysis polymerization; Luo, Pu, and Wang (2002) studied performance properties of salt tolerant polymer KYPAM for EOR. However, drawbacks of these products are a high cost and poor dissolution properties.

Starch is a naturally abundant polysaccharide and a low cost material. In recent years, particular attention has been attached to synthesis of starch graft copolymer due to an increasing interest in the synthesis of new cost-effective polymer. Gao, Yu, and Wang (1998) studied the graft copolymerization of starch and acrylonitrile initiated by potassium permanganate; Tai and Liu (2004) reported that synthesis and flocculation properties of starch-graft-acrylamide; Cao, Yang, and Liu (2004) investigated the graft copolymerization onto starch with acrylamide and acrylic acid in inverse emulsion.

Choice of initiator is also of great importance in the graft copolymerization reaction. Ceric ions can form particularly efficient redox systems in the presence of organic reductants. Many research groups have studied the graft copolymerization of starch with ethylene monomers initiated by ceric salts. Liu, Cheng, and Wu (1993) studied the

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graft copolymerization of methyl acrylate onto potato starch initiated by ceric ammonium nitrate; Song and Ma, 2003 investigated synthesis of strong anionic flocculant by grafting starch with acrylonitrile by ceric salt as the initiator. However, the high price of ceric salts confines the wide use of this initiator.

In this paper, synthesis of starch-graft-poly(acrylamide-co-2-acrylamido-2- methylpropanesulfoacid) [S-g-P(AM-co-AMPS)] is studied by using a new complex initiation system of cerium sulfate (CS) and ammonium persulfate (APS). Not only does the article discuss the preparation method and effect of reaction conditions on properties of the product, but it also compares the complex initiation system with systems using either Ce(IV) ion or persulfate. In addition, the application of the graft copolymer as the flooding agent in enhanced oil recovery is investigated.

2. Experimental

2.1. Materials and instruments

The materials used in this study were purchased from the following suppliers: 2-acrylamido-2-methylpropanesulfoacid (AMPS) from Dandong Shengli Chemical Plant (Dandong, China); acrylamide (AM) from Nanchang Changjiu Chemical Co., Ltd. (Nanchang, China); corn starch from Changchun Huanglong food Co., Ltd. (Changchun, China); cerium sulfate and ammonium persulfate from Shanghai Chemical Reagent Corporation (Shanghai, China); and hydrolytic polyacrylamide (HPAM) from Dalian Guanghui Chemical Co., Ltd. (Dalian, China).

Infrared spectrum (IR) was carried out on a Spectrum One-B infrared spectrometer (Perkin-Elmer Company of USA); nuclear magnetic resonance spectrum (NMR) was tested by an INOVA400 nuclear magnetic resonance spectrometer (Varian Company of USA).

2.2. Preparation of the graft copolymer

The reaction was carried out in a four-necked round-bottom flask equipped with stirrer, thermometer, nitrogen gas inlet and condenser. The flask was heated in a thermostatic water bath. 0.25 mol AGU/L of starch slurry was metered into the flask and preheated for 30 min at 80 °C. After starch had been gelatinized (starch slurry turned to a transparent solution), the flask contents were cooled to 30 °C. AM, AMPS, CS and APS were added and the mixture was allowed to react for 4 h at 50 °C.

2.3. Analysis of the graft copolymer

The solution with prepared S-g-P(AM-co-AMPS) was precipitated with ethanol, and the precipitated S-g-P(AM-co-AMPS) was washed with acetone, thus removing the unreacted monomer. The product was dried at 40 °C.

The homopolymers and the AM–AMPS copolymer were removed from the precipitated graft copolymer by soxhlet extraction with a 60:40 (v/v) mixture of ethylene glycol and acetic acid according to the method of Cao, Yang, and Liu (2003). The graft copolymer was then washed with ethanol, and was dried in a vacuum oven at 40 °C to constant weight. The product was analyzed by IR spectrophotometer as KBr pellet and by ^{1}H-NMR spectrophotometer with the deuteroxide as the solvent.

2.4. The graft level of the graft copolymer

The purified sample (0.5 g) was hydrolyzed in 100 mL 1 M HCl solution under reflux for 3 h at 70 °C. The solution was neutralized with 1 M NaOH and the copolymer side chains were precipitated with cold ethanol. The product was then dried in a vacuum oven at 40 °C to constant weight. The percentage of grafting (PG), the grafting efficiency (GE) and the conversion of the monomer (C) were calculated by the following equations (Gao et al., 1998):

$$\mathrm{PG} = \frac{\text{weight of grafted P(AM-co-AMPS)}}{\text{weight of starch}} \times 100\%$$

$$\mathrm{GE} = \frac{\text{weight of grafted chains}}{\text{weight of reacted monomers}} \times 100\%$$

$$C = \frac{\text{weight of grafted chains} + \text{weight of homopolymers}}{\text{weight of monomers}} \times 100\%$$

2.5. The intrinsic viscosity of the graft copolymer

The intrinsic viscosity of the graft copolymer was determined with an Ubbelohde viscometer at 30 ± 0.1 °C in a 1 M aqueous $NaNO_3$ solution. A series of η_{sp} of the copolymer with different concentrations were measured. The data were processed and the regression equation was established. The intrinsic viscosity $[\eta]$ was calculated from the equation reported by Qian and Du (1988).

2.6. Anionic degree of the graft copolymer

Measurements of anionic degree: a dry product sample (0.03–0.05 g) was dissolved in distilled water and titrated with a standardized solution of sodium hydroxide (0.01 mol/L). The endpoint of titration was determined conductometrically. The following formula was used to calculate the anionic degree of the product:

$$\text{Anionic degree(wt\%)} = \frac{207\ C\ V}{1000\ W} \times 100\%$$

where C (mol/L) is the molar concentration of sodium hydroxide, V (mL) is the volume of the consumed sodium hydroxide for the sample, W(g) is the weight of the sample, and 207 is the molecular weight of AMPS.

2.7. The enhanced oil recovery experiment

The enhanced oil recovery experiment was performed on the rock core with oil reserves according to the method of Liu, Liu, and Yang (2006). The water flooding was carried out, and the oil recovery rate E_1 was obtained. When the polymer concentration was 0.2%, the polymer flooding continued and the total oil recovery rate E_2 could be obtained. Finally, the oil recovery rate was calculated from the following expression:

$$E_1 = \frac{V_1}{V} \times 100\%$$

$$E_2 = \frac{V_2}{V} \times 100\%$$

where E_1 (%) is the oil recovery rate by water flooding, E_2 (%) is the total oil recovery rate by polymer flooding, V (cm^3) is oil reserves in rock core, V_1 (cm^3) is the oil volume flooded by water flooding, and V_2 (cm^3) is the total oil volume flooded by polymer flooding.

3. Results and discussion

3.1. Characterization of grafting

In Fig. 1, the IR spectrum shows that the characteristic absorption peak at 1018.18 cm^{-1} is attributed to C–O stretching vibration of starch, that the characteristic absorption peak at 1655.44 cm^{-1} results from C=O stretching vibration of the $-\mathrm{CONH}_2$ group, and that the characteristic absorption peak at 1038.72 cm^{-1} is due to S=O stretching vibration of $-\mathrm{SO}_3^-$ in AMPS. These results prove that starch has grafted with AM and AMPS.

In Fig. 2, the resonances at 3.62 and 2.28 ppm are attributed respectively to the protons of methylene group and methyl group of $-\mathrm{C(CH_3)_2CH_2SO_3^-}$ in the AMPS

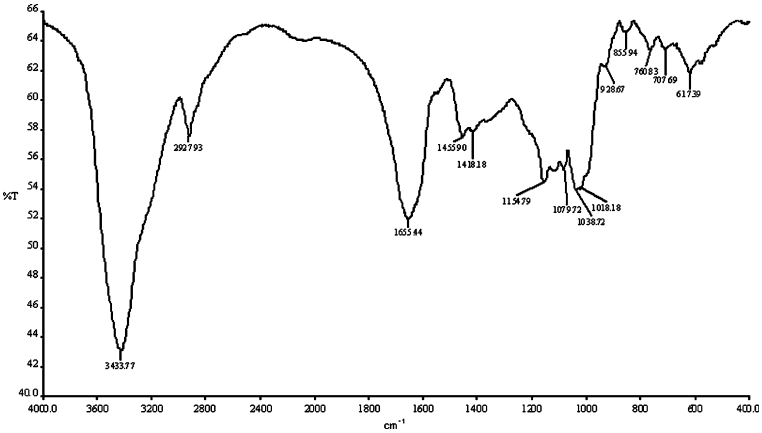

Fig. 1. IR spectrum of S-g-P(AM-co-AMPS).

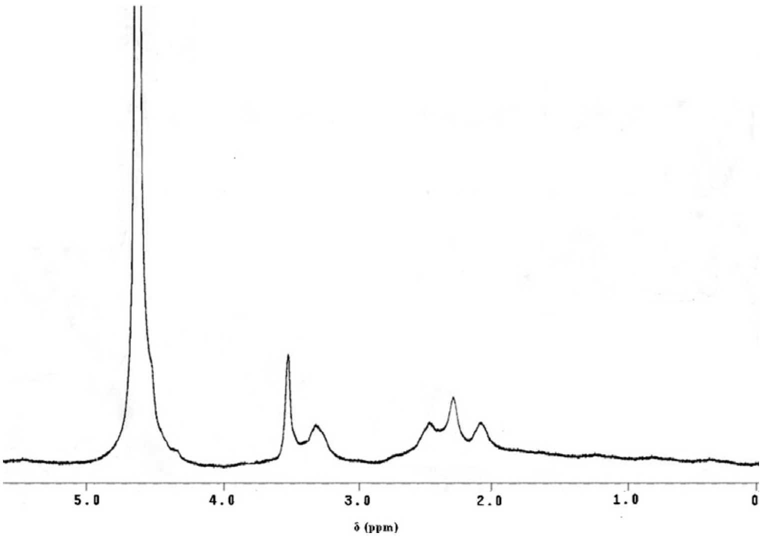

Fig. 2. ^{1}H-NMR spectrum of S-g-P(AM-co-AMPS).

molecule. The results prove that AMPS is found in the product.

3.2. Effect of the addition method

In graft copolymerization of starch with AMPS and AM, using a batch process may lead to a high ratio of AM–AMPS in the copolymer chains in the initial stages. The composition drift is severe, and the uneven charge distribution in the copolymer can adversely affect its applications. Consequently, the graft copolymer is synthesized in a modified batch process. First, all AMPS and part of AM are added, and then remainder of AM is dropped into the system at a speed of 1.0 mL/min after the reaction is initiated. Experiments show that this method is feasible; e.g. anionic monomer is consumed successively with prolongation of reaction time, the graft copolymer has a higher intrinsic viscosity and the charge of the polymer is well-distributed. The more AM is dropped into the solution, the higher the intrinsic viscosity is (Table 1). The ground for the improvement in product properties is as follows: when the acrylamide monomer of high activity is continuously added, the graft copolymerization is carried out more easily, and therefore, the amount of acrylamide homopolymers may decrease. And by controlling the addition rate of acrylamide, a constant composition of the chains of starch-graft-poly(AM-co-AMPS) could be obtained.

3.3. Initiation characteristics of CS–APS system and effect of the initiator concentration on grafting

Type and concentration of initiator greatly affect graft copolymerization. Table 2 compares different initiators and illustrates the changes in PG and GE in dependence on complex initiators. This shows that the grafting level of S-g-P(AM-co-AMPS) by using the complex initiation system of CS–APS is greater than that by using either CS or APS alone. Thus, it can be supposed that Ce(III) formed during the initiation reaction with Ce(IV) will react with APS to regenerate Ce(IV). The reaction mechanism is as follows:

$$Ce^{4+} + StOH \rightarrow Ce^{3+} + StO\cdot \qquad (1)$$

$$S_2O_8^{2} + 2Ce^{3+} \rightarrow 2SO_4^{2-} + 2Ce^{4+} \qquad (2)$$

where StOH denotes starch. This mechanism has also been revealed by UV spectroscopy (Li & Qiu, 1994). This shows that Ce^{3+} can be oxidized by persulfate and a new absorption at 330–400 nm is observed. The entire reaction can be demonstrated through the continuously decreased UV absorption intensity of Ce^{4+} by adding APS. Experiments indicate that the reaction is close to end after 30 min at 50 °C.

Table 1
Effect of the monomer addition method on grafting

Ratio of dropped AM to total AM (%)	PG (%)	GE (%)	$[\eta]$ (mL/g)
0	170	85	775
30	175	87	793
50	181	89	812
80	185	90	848
100	188	91	850

[Starch] = 0.25 mol AGU/L; $[Ce^{4+}] = 2.0 \times 10^{-3}$ mol/L; $[(NH_4)_2S_2O_8] = 4.0 \times 10^{-3}$ mol/L; reaction temperature = 50 °C; reaction time = 4 h; n(AM):n(AMPS) = 7:3; the total monomer concentration of AM and AMPS = 1.0 mol/L; $[\eta]$ = intrinsic viscosity.

Table 2
Initiation characteristics of CS-APS system

$[Ce^{4+}] \times 10^3$ (mol/L)	$[(NH_4)_2S_2O_8] \times 10^3$ (mol/L)	PG (%)	GE (%)
2.0	0	130	65
3.0	0	152	77
0	4.0	118	47
2.0	4.0	185	90
3.0	4.0	187	91

[Starch] = 0.25 mol AGU/L; n(AM):n(AMPS) = 7:3; the total monomer concentration of AM and AMPS = 1.0 mol/L; reaction temperature = 50 °C; reaction time = 4 h.

Table 3
Effect of the complex initiator concentration on grafting

$[Ce^{4+}] \times 10^3$ (mol/L)	$[(NH_4)_2S_2O_8] \times 10^3$ (mol/L)	PG (%)	GE (%)
1.0	2.0	62	34
1.0	3.0	96	45
1.0	4.0	134	57
1.0	5.0	122	52
2.0	4.0	185	90
3.0	4.0	187	91
4.0	4.0	181	89

[Starch] = 0.25 mol AGU/L; n(AM):n(AMPS) = 7:3; the total monomer concentration of AM and AMPS = 1.0 mol/L; reaction temperature = 50 °C; reaction time = 4 h.

In addition, Table 3 shows that when $[Ce^{4+}]$ is 1.0×10^{-3} mol/L, PG and GE both increase first, and then decrease with increase of $[S_2O_8^{2-}]$, and they reach a maximum value at 4.0×10^{-3} mol/L $[S_2O_8^{2-}]$. Keeping 4.0×10^{-3} mol/L $[S_2O_8^{2-}]$, PG and GE both increase rapidly as $[Ce^{4+}]$ varies from 1.0×10^{-3} to 2.0×10^{-3} mol/L. However, when Ce^{4+} concentration is greater than 2.0×10^{-3} mol/L, it is difficult to further increase the grafting level. Thus, at a Ce^{4+} concentration of 4.0×10^{-3} mol/L a decrease in grafting level is observed. It seems that an appropriate molar ratio of $[Ce^{4+}]$ to $[S_2O_8^{2-}]$ exists, which should be 1/2.

3.4. Effect of the concentration and the ratio of two monomers on grafting

The concentration and the ratio of two monomers are also the key parameters affecting both the properties of the copolymer and the economics of the process. These parameters are not only related to grafting level, but also affect the anionic degree of the copolymer. The effects are shown in Tables 4 and 5. Keeping the appropriate ratio

Table 4
Effect of the mixed monomer concentration on grafting

[AM] (mol/L)	[AMPS] (mol/L)	PG (%)	GE (%)	[η] (mL/g)
0.35	0.15	92	82	674
0.49	0.21	134	86	755
0.70	0.30	185	90	848
0.84	0.36	171	85	813
1.05	0.45	164	73	791

[Starch] = 0.25 mol AGU/L; n(AM):n(AMPS) = 7:3; reaction time = 4 h; reaction temperature = 50 °C; [CS] = 2.0×10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 4.0×10^{-3} mol/L.

Table 5
Effect of the molar ratio of two monomers on grafting

n(AM):n(AMPS)	PG (%)	GE (%)	[η] (mL/g)	Anionic degree (%)
3/7	99	54	550	42
4/6	125	67	603	40
5/5	145	75	675	37
6/4	167	85	756	35
7/3	185	90	848	30

[Starch] = 0.25 mol AGU/L; [Ce^{4+}] = 2.0×10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 4.0×10^{-3} mol/L; reaction temperature = 50 °C; reaction time = 4 h; the total monomer concentration of AM and AMPS = 1.0 mol/L.

of AM to AMPS, the grafting percentage, the grafting efficiency and the intrinsic viscosity increase with the increase in total concentration of the monomers, which changes in the range of 0.5–1.0 mol/L. When the mixed monomer concentration increases over 1.0 mol/L, the grafting percentage, the grafting efficiency and the intrinsic viscosity progressively decrease with the increase in total concentration of the monomers. This may be ascribed to the following facts.

1. Increasing the monomer concentration is beneficial to the diffusion of monomer molecules to radical site on the backbone, thus leading to an increase in PG, GE and [η].
2. The high monomer concentration favors formation of accept-donator complexes between starch and monomer, which triggers the grafting process. However, there is always a limitation for the increase in monomer concentration. Beyond the limit value, grafting is not favorable. The reasons might be that radical transfer from starch macroradicals to monomer molecules increase, that the homopolymer of monomers and the copolymer P(AM–AMPS) increase, and that the graft copolymer of starch decreases. Hence, PG, GE and [η] decrease.

Besides the effect of the mixed monomer concentration, Table 5 shows the effect of molar ratio of AM–AMPS on grafting and anionic degree. That is, the higher the content of AM, the higher the grafting level and the lower the anionic degree. When the molar ratio of AM–AMPS is 6/4–7/3 and the mixed monomer concentration is 1 mol/L, both grafting level and anionic degree are higher.

3.5. Effect of tiny copper ions

Catalytic effects of tiny metal ions on graft copolymerization have been reported by Bhattacharyya and Maldas (1984). Tiny metal ions are quite effective. In this experiment, we have found that when [$CuSO_4$] is 0.4 mmol/L, tiny copper ions greatly accelerate the polymerization of monomers by using $(NH_4)_2S_2O_8$ and CS as initiators; hence, the reaction takes only 1 h for completion and the induction period is short (Fig. 3). The percentage of grafting is higher and percentage of homopolymer formation is lower by analysis. The mechanism of such processes can be the formation of a Cu^{2+} complex with the trunk polymer along with a monomer and a water molecule, which, on subsequent rearrangement, leads to the formation of free radical sites that are responsible for bringing in grafting of the monomer (Fig. 4).

The aim of selecting an optimum condition for the preparation of a graft copolymer is to decrease the formation of homopolymer. Tiny copper ion has been found to be extremely effective in the grafting process initiated by the complex initiation system. However, Cu^{2+} may react with the growing homopolymer chains, thus resulting in termination, which can also terminate the grafting process. But the swelling of the trunk polymer has a beneficial effect on reducing the extent of termination of the graft chains. This is because the swelling can prevent the diffusion of Cu^{2+} by a viscous barrier, and as a result, such termination of the graft chain is reduced. At the same time, the formation of homopolymer is also retarded.

3.6. Application tests

Hydrolytic polyacrylamide (HPAM) is one of the flooding agents in common use in enhanced oil recovery. But the

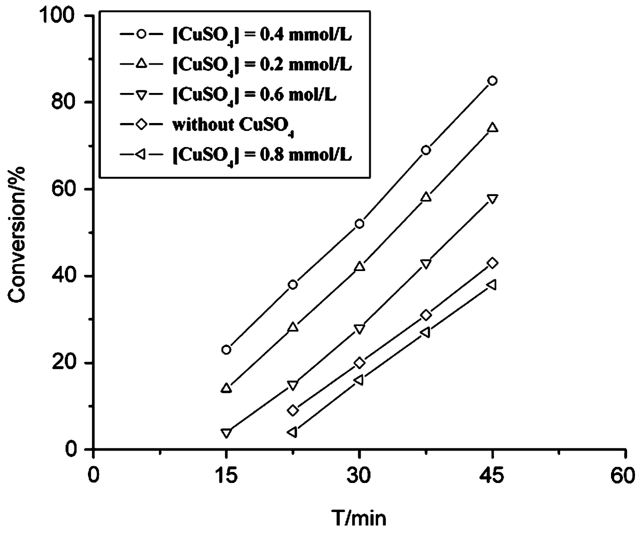

Fig. 3. Effect of tiny copper sulfate on grafting ([CS] = 2.0×10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 4.0×10^{-3} mol/L; reaction temperature, 50 °C; reaction time, 4 h).

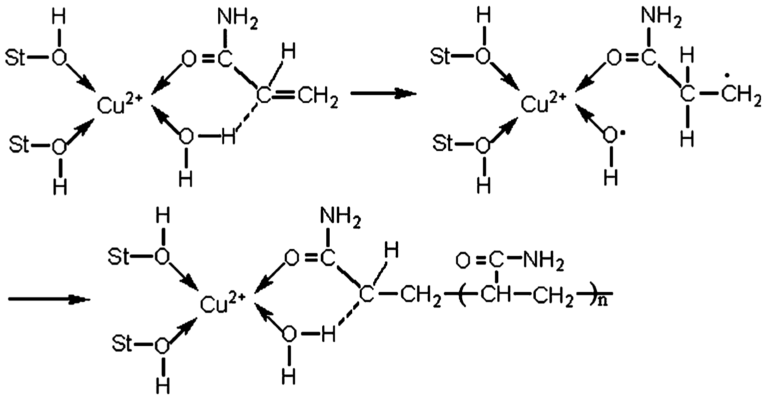

Fig. 4. Cu^{2+} complex with the trunk polymer along with monomer and water molecule.

Table 6
The result of the enhanced oil recovery experiment of the graft polymer flooding agent

	V (cm^3)	V_1 (cm^3)	V_2 (cm^3)	E_1 (%)	E_2 (%)	Enhanced oil recovery rate by polymer flooding $E_2 - E_1$ (%)
HPAM	1.40	0.48	0.79	34.29	56.15	21.86
S-g-P(AM-co-AMPS)	3.25	1.32	2.75	40.62	84.39	43.77

Polymer concentration 0.2%; V, oil reserves in rock core; V_1, the oil volume flooded by water flooding; V_2, the total oil volume flooded by polymer flooding; E_1, the oil recovery rate by water flooding; E_2, the total oil recovery rate by polymer flooding.

drawbacks of this product are the high temperature sensitivity and the poor shear stability. The graft copolymer S-g-P(AM-co-AMPS) synthesized by copolymerization of starch with acrylamide and 2-acrylamido-2-methylpropanesulfoacid contains merits of both starch and P(AM-co-AMPS). S-g-P(AM-co-AMPS) exhibits better tolerance to temperature and shear forces when it is used as the flooding agent. The results of enhanced oil recovery experiment of the polymer flooding agent (Table 6) show that the prepared new polymer flooding agent which can remarkably enhance the oil recovery rate certainly has potential application in enhanced oil recovery.

4. Conclusions

The graft copolymerization of starch with AM and AMPS is carried out as modified batch process. Copolymer chains with even distribution of charge densities are obtained by controlling the addition of AM and the ratio of AM–AMPS. A higher intrinsic viscosity of the graft copolymer has been achieved by using this addition method.

For initiation of graft copolymerization of starch with AM and AMPS, a new complex initiation system consisting of Ce^{4+} and ammonium persulfate is used. This is a cyclic initiation system of Ce^{4+}–Ce^{3+}–Ce^{4+}. In the system, Ce^{3+} formed from Ce^{4+} during the initiation reaction may be oxidized again by APS to regenerate Ce^{4+}. This cyclic system is more effective to graft copolymerize AM-co-AMPS onto starch, and to obtain both higher PG and higher GE for the graft copolymer. When [$CuSO_4$] is 0.4 mmol/L, tiny copper ions (Cu^{2+}) may greatly accelerate the copolymerization of monomers onto starch in the complex initiation system, and the formation of homopolymers is also retarded. Compared with hydrolytic polyacrylamide, the graft copolymer S-g-P(AM-co-AMPS) has a higher enhanced oil recovery rate when it is used as the flooding agent.

References

Bhattacharyya, S. N., & Maldas, D. (1984). Graft-copolymerization onto cellulosics. *Progress in Polymer Science, 10*, 171–270.

Cao, Y. F., Yang, J. Z., & Liu, Z. L. (2003). Study of synthesis of graft copolymer of AM-DM on starch in inverse emulsion. *Journal of Dalian University of Technology, 43*, 743–746.

Cao, Y. F., Yang, J. Z., & Liu, Z. L. (2004). Effect of oleates as emulsifiers on graft copolymerization of AM-AA on starch in inverse emulsion. *Journal of Chemical Industry and Engineering, 55*, 325–327.

Gao, J. P., Yu, J. G., & Wang, W. (1998). Graft copolymerization of starch-AN initiated by potassium permanganate. *Journal of Applied Polymer Science, 68*, 1965–1972.

Kathmann, E. E., White, L. A., & Mccormick, C. L. (1996). Polyelectrolyte of *N*-vinylformamide with sodium 3-acrylamido-3-methylbutanoate, sodium 2-acrylamido-2-methylpropanesulfonate, and sodium acrylate: synthesis and characterization. *Macromolecules, 29*, 5268–5272.

Kurenkoy, V. F., Verihznikova, A. S., & Myagchenkov, V. A. (1984). Peculiarities of the preparation of copolymers of acrylamide with sodium acrylate in inverse emulsion. *European Polymer Journal, 20*, 357–360.

Li, Z. Y., & Qiu, K. Y. (1994). Studies on the complex initiation system of ceric ion and potassium persulfate. *Acta Polymerica Sinica, 6*, 753–757.

Liu, M. Z., Cheng, R. S., & Wu, J. J. (1993). Graft copolymerization of methyl acrylate onto potato starch initiated by ceric ammonium nitrate. *Journal of Polymer Science, Part A, 31*, 3181–3186.

Liu, L. Y., Han, S. Z., & Jin, G. T. (2000). Synthesis of APAM by inverse suspension and adding alkali for hydrolysis polymerization. *Journal of Beijing University of Chemical Technology, 2*, 36–39.

Liu, Y., Liu, C. Z., & Yang, F. L. (2006). Study on improving oil recovery using high concentration polymer solution. *Oil Drilling and Production Technology, 28*, 33–35.

Luo, J. H., Pu, R. Y., & Wang, P. M. (2002). Performance properties of salt tolerant polymer KYPAM for EOR. *Oilfield Chemistry, 1*, 64–67.

Qian, J. W., & Du, Z. Q. (1988). A new one-point intrinsic viscosity equation applying to the polymer solvent systems with higher values of Huggins' constant (K'). *Acta Polymerica Sinica, 2*, 113–117.

Song, H., & Ma, X. C. (2003). Synthesis of strong anionic flocculant by grafting starch with acrylonitrile and subsequent treatments. *Speciality petrochemicals, 20*, 30–33.

Tai, Y. L., & Liu, R. W. (2004). Synthesis and flocculation properties of non-ionic inartificial high molecule. *Journal of Wenzhou Normal College, 25*, 28–31.