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Synthesis and application of cationic starch graft polymer by using the complex initiation system

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ABSTRACT

A graft copolymer was synthesized by graft copolymerization of starch with acrylamide (AM) and acrylacyloxyethyltrimethyl ammonium chloride (AAC). The copolymerization was carried out by using a complex initiation system of urea [$CO(NH_2)_2$] and ammonium persulfate [$(NH_4)_2S_2O_8$]. The effect of reaction conditions on graft copolymerization and the application of the polymer as the flocculant were investigated. Experiments showed that a graft copolymer with higher grafting level and higher intrinsic viscosity could be obtained by changing the method of monomer addition and by controlling the ratio of AAC to AM. The application test showed that the results of treatment of two kinds of industrial waste water by the grafted starch [S-g-P(AM-co-AAC)] were better than those treated with cationic polyacrylamide (CPAM).

1. Introduction

Cationic polymers of acrylamide and other vinyl monomers are currently commercialized and widely applied in numerous fields such as the petroleum industry and environmental protection. Hunkeler and Hamielec (1991) investigated synthesis, kinetics and modeling of inverse microsuspension polymerization of acrylamide with quaternary ammonium cationic monomers; Hou and Ha (1995) studied synthesis and kinetics of diallydimethyl ammonium chloride with acrylamide in inverse emulsion. However drawbacks of these products are poor dissolution properties and a high cost.

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. Ma, Cao, and Cui (1998) reported synthesis of SCAM and application in petroliferous water treatment; Tai and Ma (2002) investigated synthesis of the graft copolymerization onto starch with acrylamide and diallydimethyl ammonium chloride as strong cationic flocculant; Cao, Yang, and Liu (2003) studied synthesis of graft copolymer of AM-DM on starch in inverse emulsion; Tai and Liu (2004) investigated synthesis and flocculation properties of starch-graft-acrylamide.

In this paper, synthesis of starch-graft-poly(acrylamide-co-acrylacyloxyethyl trimethyl ammonium chloride) [S-g-P(AM-co-AAC)] is studied by using a complex initiation system of urea [$CO(NH_2)_2$] and ammonium persulfate [$(NH_4)_2S_2O_8$]. The article discusses the preparation method and effect of reaction conditions on properties of the product. In addition, the application of the graft copolymer as a flocculant is investigated.

2. Experimental

2.1. Materials and instruments

The materials used in this study were purchased from the following suppliers: acrylacyloxyethyltrimethyl ammonium chloride (AAC) from Yantai Xinghuo Chemical Plant (Yantai, China); acrylamide (AM) from Nanchang Changjiu Chemical Co., Ltd. (Nanchang, China); corn starch from Changchun Huanglong Food Co., Ltd. (Changchun, China); ammonium persulfate and urea from Shanghai Chemical Reagent Corporation (Shanghai, China); and cationic polyacrylamide (CPAM) 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).

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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. 0.3 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. Then AM, AAC, ammonium persulfate and urea were added and the mixture was allowed to react for 4 h at 45 °C.

2.3. Analysis of the graft copolymer

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

The homopolymers and the AM-AAC 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 et al. (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), and the grafting efficiency (GE) were calculated by the following equations (Gao, Yu, & Wang, 1998):

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

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

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. Cationic degree of the graft copolymer

Measurements of cationic degree: a dry product sample (0.2 g) was dissolved in distilled water, and 1 mL of an aqueous potassium chromate solution was added. The solution was titrated with a silver nitrate solution (0.05 mol/L). The endpoint of titration was determined until the color of the solution turned to brick red. The following formula was used to calculate the cationic degree of the product:

$$\text{Cationic degree } (\%,\ \text{w/w}) = 193.5 \times 0.05 \times \frac{V - V_0}{1000W} \times 100\%$$

where V (mL) and V_0 (mL) are the volumes of the consumed silver nitrate solution for titration of the sample and the blank, respectively, W (g) is the weight of the sample, and 193.5 is the molecular weight of AAC.

3. Results and discussion

3.1. Characterization of grafting

In Fig. 1, the IR spectrum shows that the characteristic absorption peaks at 1129.23 cm^{-1}, 2924.21 cm^{-1}, and 3433.07 cm^{-1} are, respectively, attributed to C–O, C–H, and O–H stretching vibration of starch. The characteristic absorption peak at 1631.22 cm^{-1} results from C=O stretching vibration of the $-CONH_2$ group. The characteristic absorption peak at 956.15 cm^{-1} is due to $-N^+(CH_3)_3$ stretching vibration in AAC. These results prove that starch has grafted with AM and AAC.

In Fig. 2, the resonances at 3.73 ppm and 2.74 ppm are attributed to the protons of methylene group and methyl group of $-COO(CH_2)_2N(CH_3)_3$ in the AAC molecule, respectively, which is an indication that AAC is found in the product.

3.2. Effect of the addition method on grafting

In graft copolymerization of starch with AM and AAC, using a batch process may lead to a high ratio of AM to AAC 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 AAC and part of AM are added, and then remainder of AM is dropped into the system at a speed of 1 mL/min after the reaction is initiated. Experiments show that this method is feasible. Cationic 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. Table 1 shows that the more AM is dropped

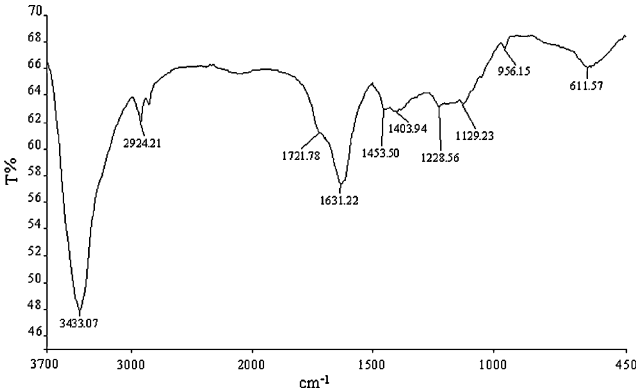

Fig. 1. IR spectrum of S-g-P(AM-co-AAC).

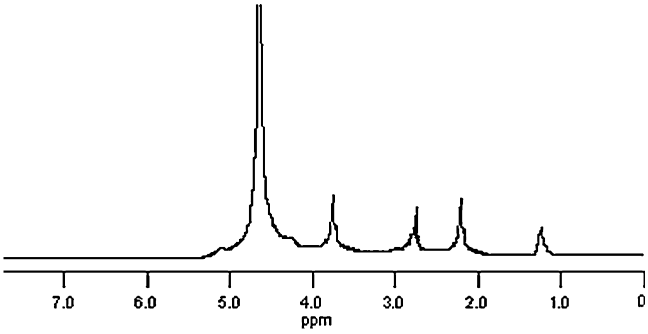

Fig. 2. ^{1}H NMR spectrum of S-g-P(AM-co-AAC).

Table 1
Effect of the monomer addition method on grafting.

Ratio of dropped AM to total AM (%)	PG (%)	GE (%)	[η] (mL/g)
0	186	82	811
30	195	86	884
50	206	90	922
80	213	92	957
100	215	93	961

[Starch] = 0.3 mol AGU/L; [$CO(NH_2)_2$] = 1.0 × 10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 3.0 × 10^{-3} mol/L; reaction temperature = 45 °C; reaction time = 4 h; m(AM):m(AAC) = 6:4; the total monomer concentration of AM and AAC = 1.2 mol/L; [η] = intrinsic viscosity.

into the solution, the higher is the intrinsic viscosity. The reason 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-AAC) could be obtained.

3.3. *Effect of the complex initiators on grafting*

The grafting level of graft polymer by using the complex initiation system of $CO(NH_2)_2$ and $(NH_4)_2S_2O_8$ is greater. It can be supposed that $CO(NH_2)_2$ would react with $(NH_4)_2S_2O_8$ to generate urea radical and initiate polymerization reaction. Concentration of initiator greatly affects graft copolymerization. Table 2 shows that when [$CO(NH_2)_2$] is 0.5 × 10^{-3} mol/L, PG and GE both increase first, and then decrease with increase of [$(NH_4)_2S_2O_8$], and they reach a maximum value at 3.0 × 10^{-3} mol/L [$(NH_4)_2S_2O_8$]. Keeping 3.0 × 10^{-3} mol/L [$(NH_4)_2S_2O_8$], PG and GE both increase rapidly as [$CO(NH_2)_2$] varies from 0.5 × 10^{-3} mol/L to 1.0 × 10^{-3} mol/L. However, when $CO(NH_2)_2$ concentration is greater than 1.0 × 10^{-3} mol/L, it is difficult to further increase the grafting level. Thus, at $CO(NH_2)_2$ concentration of 2.0 × 10^{-3} mol/L a decrease in grafting level is observed. It seems that the appropriate molar ratio of [$CO(NH_2)_2$] to [$(NH_4)_2S_2O_8$] is 1:3.

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 cationic degree of the copolymer. The effects are shown in Tables 3 and 4. Keeping the appropriate ratio of AM to AAC, the grafting percentage, the grafting efficiency and the intrinsic viscosity increase with the increase of the total monomer concentration, which changes in the range of 1.0–1.2 mol/L. When the mixed monomer concentration increases over 1.2 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.

Table 2
Effect of the complex initiators concentration on grafting.

[$CO(NH_2)_2$] × 10^3 (mol/L)	[$(NH_4)_2S_2O_8$] × 10^3 (mol/L)	PG (%)	GE (%)
0.5	1.0	82	37
0.5	2.0	111	49
0.5	3.0	140	62
05	4.0	121	54
1.0	3.0	213	92
2.0	3.0	214	93
3.0	3.0	208	90

[Starch] = 0.3 mol AGU/L; m(AM):m(AAC) = 6:4; the total monomer concentration of AM and AAC = 1.2 mol/L; reaction temperature = 45 °C; reaction time = 4 h.

Table 3
Effect of the mixed monomer concentration on grafting.

[AM] (mol/L)	[AAC] (mol/L)	PG (%)	GF (%)	[η] (mL/g)
0.65	0.35	179	80	793
0.80	0.30	201	87	886
0.96	0.24	213	92	957
1.12	0.18	194	86	880
1.28	0.12	170	76	769

[Starch] = 0.3 mol AGU/L; m(AM):m(AAC) = 6:4; reaction time = 4 h; reaction temperature = 45 °C; [$CO(NH_2)_2$] = 1.0 × 10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 3.0 × 10^{-3} mol/L.

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-AAC) increase, and that the graft copolymer of starch decreases. Hence, PG, GE and [η] decrease.

Besides the effect of the mixed monomer concentration, Table 4 shows the effect of mass ratio of AM to AAC on grafting and cationic degree. That is, the higher the content of AM, the higher the grafting level and the lower cationic degree. When the mass ratio of AM to AAC is 6:4 and the mixed monomer concentration is 1.2 mol/L, both grafting level and cationic degree are higher.

3.5. *Application tests*

The graft copolymer S-g-P(AM-co-AAC) synthesized by copolymerization of starch with acrylamide and acrylacyloxyethyltrimethyl ammonium chloride contains merits of both starch and P(AM-co-AAC). S-g-P(AM-co-AAC) can be used as the flocculant and the results of disposing waste water from refineries and paper mills are shown in Table 5. It can be seen that suspended substance (SS) and chemical oxygen demand (COD) removal ratio of the waste water treated with the cationic product S-g-P(AM-co-AAC) are better than those of CPAM. The reason is that starch provides a rigid backbone as the main chain and graft copolymerized AM-co-AAC provides soft branch chains with cationic groups, so that formed big net molecular structure is favorable for flocculation. So the obtained cationic product combines many advantages. Therefore, S-g-

Table 4
Effect of the mass ratio of two monomers on grafting.

m(AM):m(AAC)	PG (%)	GE (%)	[η] (mL/g)	Cationic degree (%)
2:8	142	65	661	35
3:7	158	71	709	34
4:6	179	80	793	33
5:5	201	87	886	30
6:4	213	92	957	25

[Starch] = 0.3 mol AGU/L; [$CO(NH_2)_2$] = 1.0 × 10^{-3} mol/L; [$(NH_4)_2S_2O_8$] = 3.0 × 10^{-3} mol/L; reaction temperature = 45 °C; reaction time = 4 h; the total monomer concentration of AM and AAC = 1.2 mol/L.

Table 5
Comparison of flocculating effect of flocculants.

Sample	Flocculant	Sedimentation ration (cm/min)	SS removal ratio (%)	COD removal ratio (%)
Refinery	CPAM	7.7	82.5	87.8
Waste water	S-g-P(AM-co-AAC)	8.9	91.6	92.1
Paper mill	CPAM	4.9	74.1	86.7
Waste water	S-g-P(AM-co-AAC)	6.3	84.2	95.5

SS of the refinery and paper mill waste water is 106 mg/L and 2285 mg/L; COD of the refinery and paper mill waste water is 207 mg/L and 663 mg/L. The dosage of these agents is 5 ppm.

P(AM-co-AAC) has high molecular weight and good flocculating effect.

4. Conclusions

The graft copolymerization of starch with AM and AAC 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 to AAC. A higher intrinsic viscosity of the graft copolymer has been achieved by using this addition method. The complex initiation system consisting of urea and ammonium persulfate is used as initiation of graft copolymerization of starch with AM and AAC. This initiation system is more effective to graft copolymerized AM-co-AAC onto starch, and to obtain both higher PG and higher GE for the graft copolymer. Compared with CPAM, the graft copolymer S-g-P(AM-co-AAC) has the better treatment effect when it is used as the flocculant in industrial waste water treatment.

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