Synthesis of Starch-g-Poly(Acrylamide-co-Sodium Allylsulfonate) and Its Application of Flocculation to Kaolin Suspension

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SYNOPSIS

Studies were conducted on grafting of acrylamide (AM) and sodium allylsulfonate (SAS) onto cornstarch utilizing Ce(IV) as initiator. The influence of synthetic variables on percent grafting and grafting efficiency have been discussed. The starch-g-poly(AM-co-SAS) samples prepared by this method were characterized by IR spectroscopy, scanning electron micrograph, and elemental analysis. These graft copolymers may induce the flocculation of Kaolin suspension and showed excellent ability in both the rates of sedimentation and the clearing of supernatant liquid in the presence of NaCl.

INTRODUCTION

The Ce(IV)-induced graft copolymerization of vinyl monomers onto polysacharide substrates is a widely used process for property modification of naturally occurring polymers.[1-7] However, very few studies can be found on grafting of mixed acrylamide and sulfonate-containing monomers onto polysachride.[4] In this work, the results of the grafting of mixed acrylamide and sodium allylsulfonate onto cornstarch in aqueous medium using Ce(IV) as the redox initiator will be reported, and the starch-grafted copolymer used as flocculant for Kaolin suspension will be discussed. This is an extension of our recent work[8,9] on flocculant. Water-soluble polymeric flocculants are of considerable importance in colloidal science and in various industrial solid–liquid separation operations such as drilling fluid, water treatment, mineral processing, and papermaking.

EXPERIMENTAL

Materials

Commercial cornstarch was purified in hot methanol, followed by hot filtering the solution. Sodium allylsulfonate (SAS), commencial grade, was purified by recrystallization from 90% ethanol twice. Acrylamide (AM) was recrystallized once from benzene and vacuum dried to constant weight. Ceric ammonium nitrate (CAN, analatically pure) and Kaolin clay (chemically pure) were purchased and used without further purification.

Grafting Procdure

A definite amount of starch was dissolved in distilled water, and nitrogen was bubbled through while stirring, heated at 85–90°C for 30 min and cooled, then, initiator (CAN as a known molar solution in $1M$ HNO$_3$) was added. After 15 min AM and SAS were added. Graft copolymerization was conducted at 30°C for the desired time. At the end of the reaction, the resulting product was precipitated by pouring the reaction mixture solution into ethanol, washed, and dried under reduced pressure to constant weight. The grafted product was extracted with ethylene glycol–acetic acid mixture. Percent grafting, percent efficiency, and percent conversion were calculated in the following manner:

$$\%\text{Grafting, }(G\%) = \frac{W_2 - W_0}{W_0} \times 100$$

$$\%\text{Efficiency, }(E\%) = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

$$\%\text{Conversion, (wt \%)} = \frac{W_2 - W_0}{W_3} \times 100$$

where W_0, W_1, W_2, and W_3 denote the weight of starch, weight of graft copolymerization product, weight of graft copolymer, and weight of total monomers, respectively.

Isolation of Side Chain

A portion of starch-g-poly(AM-co-SAS) was treated by the acid hydrolysis. The graft copolymer in $0.5M$ HCl was heated under reflux condition for 2 h. All the starch went into solution, leaving behind a resinous material.

Characterization

The IR spectra was recorded on a NICOLET FT-20 SX spectrometer using KBr discs.

Flocculation Tests

To demonstrate the flocculating ability of the graft copolymer of this invention, a series of 4% dispersions of Kaolin clay in salt-free aqueous solution and in aqueous solution containing added salt were prepared. To each of these was added various concentration of flocculant solution. This specified amount of flocculant was added to the dispersion in
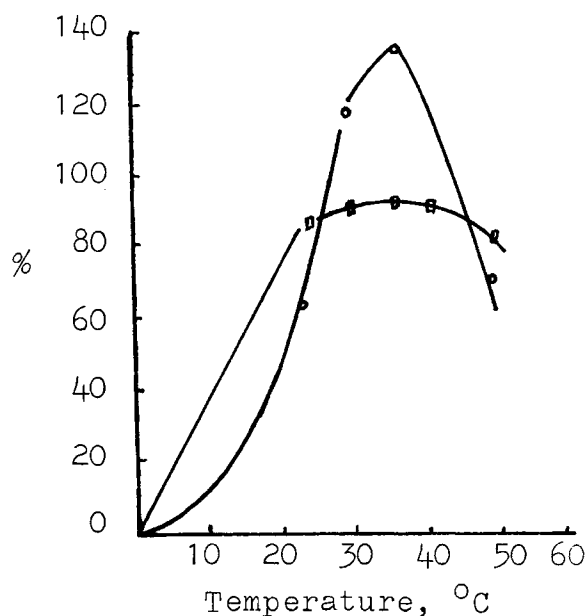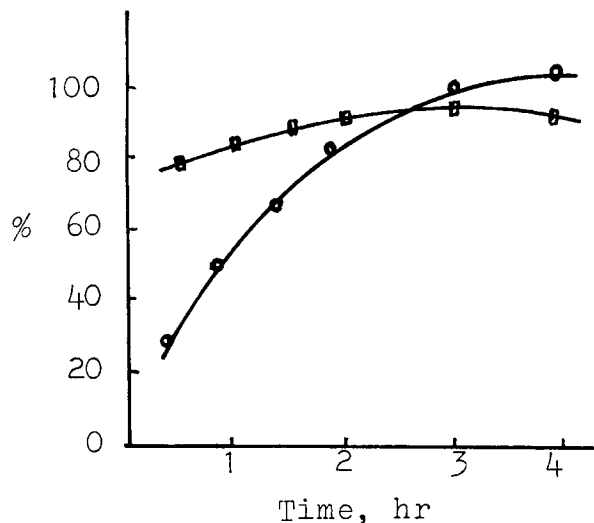

Figure 2 Effect of reaction time on $G\%$ and $E\%$. Starch = $0.25M$, AM = $0.96M$, SAS = $0.04M$; CAN = 2.5 $\times 10^{-3}M$, reaction temperature 30°C, (O) $G\%$, (□) $E\%$.

a 100-mL graduated cylinder. The mass was throughly mixed, allowed to stand, and the height of interface between the supernatant and the flocculated settling solids is recorded periodically. The logarithm of the time is plotted against the height of the interface. From the curve drawn, the time to obtain 50 mL of settling is determined and reported as $t_{\frac{1}{2}}$.[10] In addition, the optical absorbance of supernatant layer was also determined and compared with that of a blank to which no flocculant was added. The observed reports as relative absorbance (A_r)[11,12] are

A_r
= absorbance of test sample/absorbance of blank

Thus a relative absorbance of 1.0 indicates that the added reagent did not affect the stability of the suspension, whereas strong flocculation is indicated by a low value of A_r, approaching zero, because flocs have formed and settled out.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Grafting

Reaction Temperature

As Figure 1 shows, the reaction temperature influenced the percent grafting more than the efficiency. At a temperature 30–40°C higher, percent grafting is achievable. Both the lower and the higher temperature poor grafting yield was obtained, while a large amount of copolymer of AM and SAS was found, which can be extracted by ethylene glycol-acetic acid mixture.
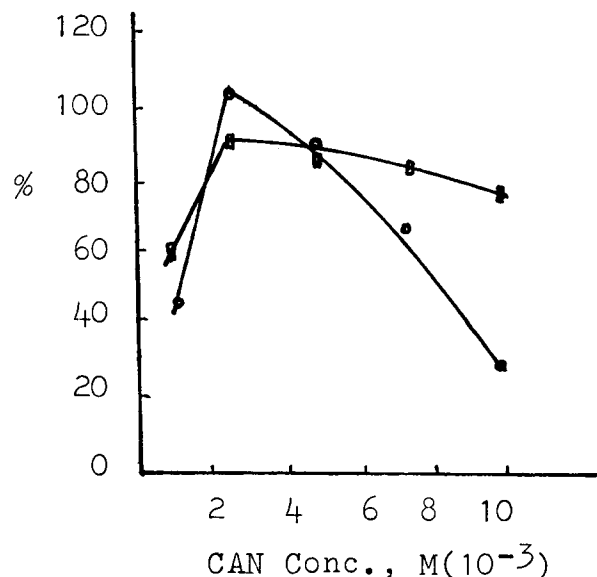

Figure 1 Effect of reaction temperature on $G\%$ and $E\%$. Starch = $0.25M$(AUG), AM = $0.96M$, SAS = $0.04M$; CAN = 2.5 $\times$ 10^{-3} M, reaction time 6 h, (O) $G\%$, (□) $E\%$.

Figure 3 Effect of CAN concentration on $G\%$ and $E\%$. Starch = $0.25M$, AM = $0.96M$, SAS = $0.04M$; reaction temperature 30°C, for 6 h, (O) $G\%$, (□) $E\%$.

Reaction Time

Figure 2 presents the relationship between reaction time and the grafting. As the reaction time became longer, the percent grafting increased initially, but after about 3–4 h it reached 100% or more. The efficiency also increased with increasing grafting time up to 80% within 1 h and then increased slowly.

Initiator Concentration

Varing the concentration of CAN affects the grafting as shown in Figure 3. The falling off of $G\%$ and $E\%$

at higher CAN concentration is a well-known phenomenna[3] and ascribed to the increasing participation of the ceric ion in the termination of growing grafted chains by the following reaction:

$$StM \cdot + Ce(IV) \rightarrow StM + Ce(III) + H^+$$

The percent grafting and the efficiency reached maxima at $2.5 \times 10^{-3}M$ of the initiator concentration.

Nitric Acid Concentration

It has been found that maximum grafting occurs at $HNO_3 = 1.25 \times 10^{-2}M$. The percent grafting decreases with further increase in acid concentration.

Composition of AM, SAS, and Starch in Feed

Table I illustrates the dependence of the grafting on AM, SAS, and starch content. The conversion and efficiency percents decreased with increasing SAS constant and increased as the concentration of AM was reached. The conversion percent and the grafting efficiency ($E\%$) all increased with increasing starch content.

Proof of Grafting

IR absorption bands of grafted starch appeared at 1665 cm^{-1} (—CONH$_2$), 1040—1156 cm^{-1} (S=O), and 860 and 760 cm^{-1} (characteristic absorption of starch α glucoside). Characteristic band of α glucoside is not present in the spectrum of the pure side chain, which isolated from starch-g-poly(AM-

Table I   Effect of Composition of AM, SAS, and Starch on Grafting[a]

No.	AM (M)	SAS (M)	Starch (AUG) (M)	Analysis (wt %) C	Analysis (wt %) H	Analysis (wt %) N	$E\%$	Conversion (wt %)	η_a^b (cp)
1	1.92	0.04	0.25	44.34	6.76	12.78	98.8	94.2	40
2	1.92	0.08	0.25	43.47	6.72	11.38	95.4	83.1	25
3	1.92	0.12	0.25	43.40	6.52	12.28	96.0	78.3	24
4	1.92	0.16	0.25	43.28	6.38	11.68	95.1	59.4	20
5	1.92	0.20	0.25	43.38	6.60	11.25	93.6	55.0	15
6	0.60	0.04	0.25				85.0	63.1	
7	0.96	0.04	0.25				96.5	82.4	
8	1.40	0.04	0.25				96.1	89.3	
9	1.92	0.04	0.25				95.4	92.9	
10	1.96	0.04	0.25				94.5	94.3	
11	1.92	0.08	0.125				96.1	74.7	
12	1.92	0.08	0.25				96.5	86.5	
13	1.92	0.08	0.50				97.5	93.1	

[a] Reaction condition: Reaction time 6 h; temperature 30°C; Ce(IV) conc. 2.5×10^{-3} M; nitric acid conc. 1.25×10^{-2} M.
[b] 30°C, 2% aq. at 532 s^{-1} (shear rate) by NDJ-79 Model Rotary Viscometer.
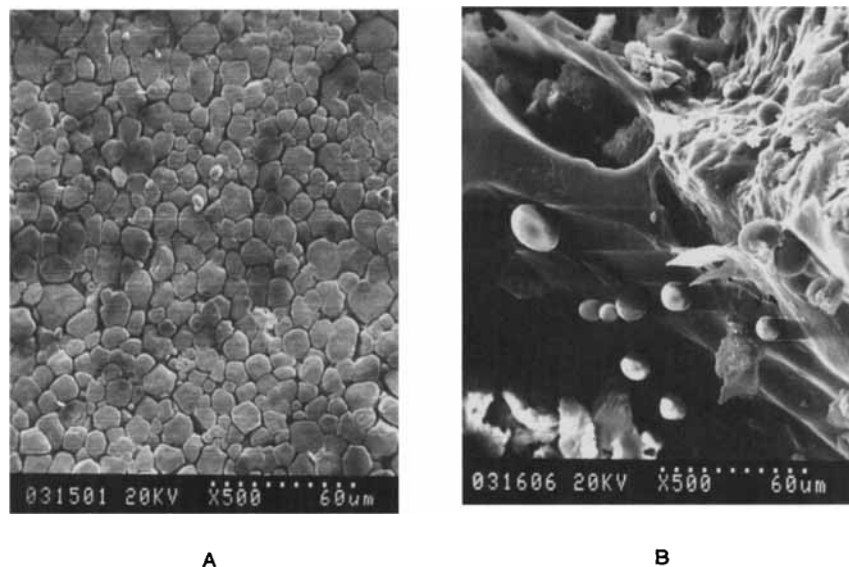
A

B

Figure 4 Scanning electron micrographs. (*a*) starch, (*b*) starch-*g*-poly(AM-co-SAS).

co-SAS) by acid hydrolysis. It has supported the incidence of the graft reaction.)

The scanning electron micrograph of grafted starch is shown in Figure 4. A considerable amount of grafted copolymer was deposited, which appears to have a different structure from the ordinary starch.

Flocculation

The following samples are used for flocculation test: No. 1, No. 3, No. 4 (listed in Table I); HPAM-1 (partial hydrolyzed polyacrylamide, $\bar{M} = 2.5 \times 10^6$, hydrolytic degree $H\% = 19.5$); HPAM-2 ($\bar{M} = 3.9 \times 10^6$, $H\% = 30.1$).
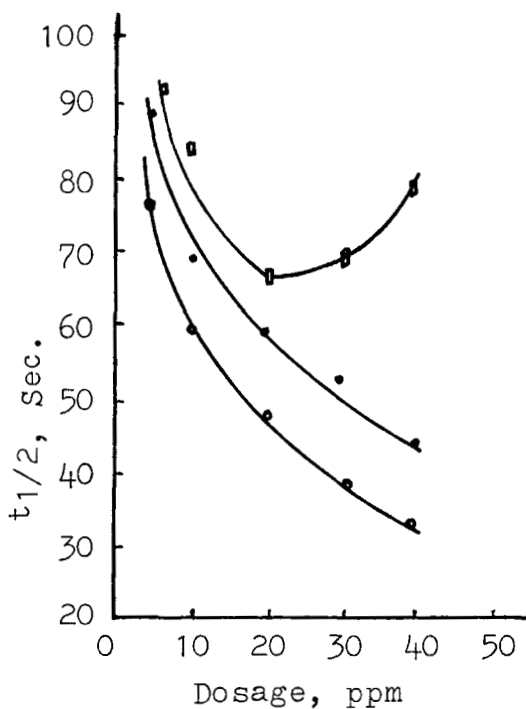
Figure 5 shows the Kaolin was flocculated by

Figure 5 Relationship between dosage of starch-*g*-poly(AM-co-SAS) and rate of sediment ($t_{\frac{1}{2}}$) in distilled water. (O) sample No. 1, (●) sample No. 3, (□) sample No. 4.
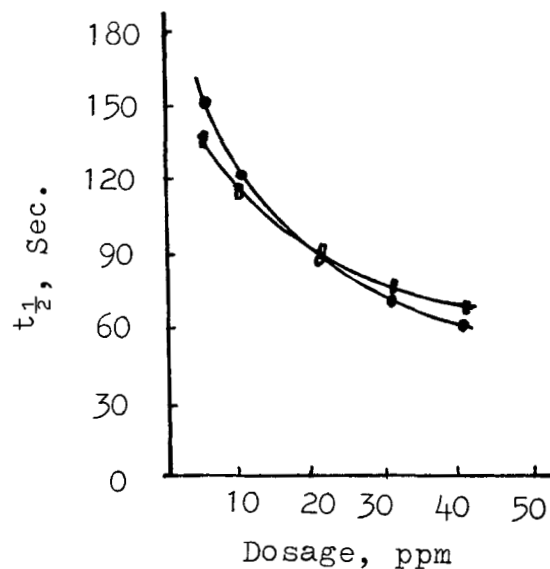

Figure 6 Relationship between dosage of flocculant and relative optical absorbance (A_r) in 400 ppm NaCl solution. (O) sample No. 1, (□) HPAM-1.
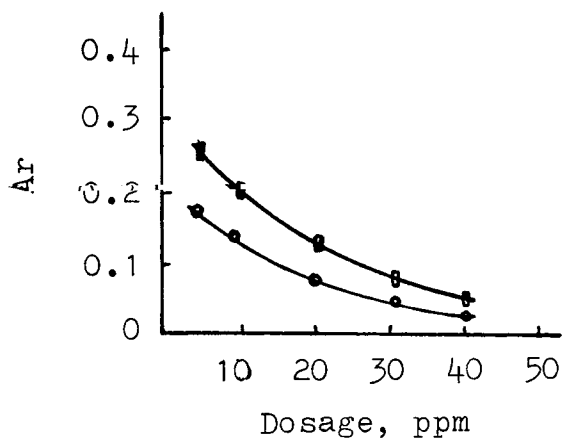
Figure 7 Relationship between dosage of flocculant and rate of sediment ($t_{\frac{1}{2}}$) in 400 ppm NaCl solution. (O) sample No. 1, (□) HPAM-1.

Figure 9 Relative between dosage of flocculant and rate of sediment in 10,000 ppm NaCl solution. (O) sample No. 1, (□) HPAM-1, (●) HPAM-2.

grafted starch, whereas No. 1 is more effective. As shown in Figures 6 and 7 and 8 and 9, it was also observed that the grafted starch (No. 1) is excellent in salt solution, and the ability of flocculation is better than HPAM-1 and HPAM-2.

CONCLUSIONS

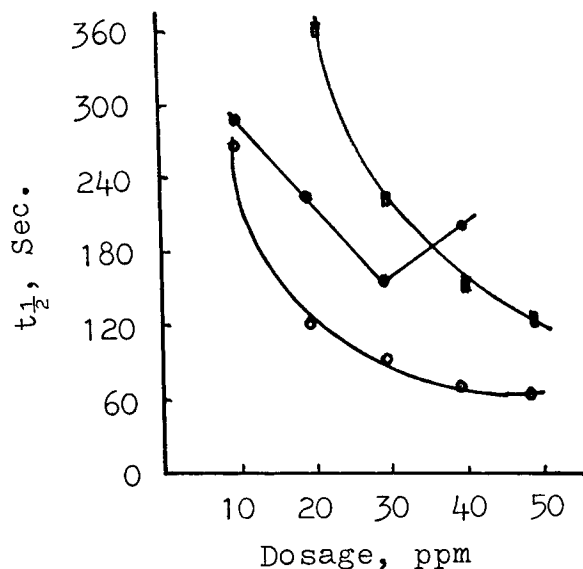Mixed AM and SAS can be graft-copolymerized onto starch efficiently in aqueous solution by using

Ce(IV)-induced initiation. Starch-*g*-poly(AM-co-SAS) was synthesized from this method and was ascertained by infrared spectroscopy. On the other hand, in the presence of NaCl, grafted starch is a more potent flocculant for Kaolin suspension and bears comparison with HPAM.

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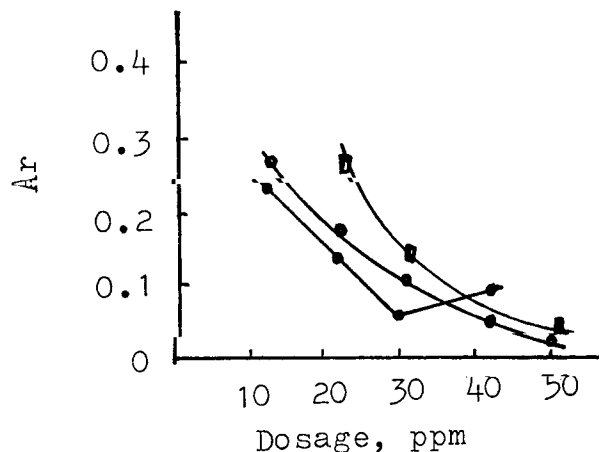**Figure 8** Relationship between dosage of flocculant and relative optical absorbance (A_r) in 10,000 ppm NaCl solution. (O) sample No. 1, (□) HPAM-1, (●) HPAM-2.