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Synthesis, Characterisation and Flocculation Properties of Carboxymethyl Cellulose-g Acrylamide

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Abstract

Graft copolymers of acrylamide on carboxymethyl cellulose (d.s 0.4-0.5) were prepared by the use of ceric ion, ceric ion/reductant molecule initiator systems in aqueous medium. The graft copolymers were characterized by IR spectroscopy. The extent of graft copolymerisation was measured in terms of grafted chains as a function of both ceric ion and ceric ion/reductant molecule concentrations. It was found that introduction of reductant molecule resulted in up to 13 fold increase in percent graft levels. Flocculation of the copolymer samples and ungrafted carboxymethyl cellulose were studied using synthetic effluent of Kaolin (0.25%) in distilled water. The flocculation capacity measured in terms of reduction in the turbidity was found to be highest for carboxymethyl cellulose-g acrylamide and was dependent on the number and molecular size of the grafted polyacrylamide.

Keywords: Flocculation; Carboxymethyl cellulose; Acrylamide

Introduction

The use of ceric ion to initiate graft copolymerisation of vinyl monomers on synthetic and natural polymers has been reported by several workers [1-10].

Graft copolymerisation of vinyl monomers onto cellulose in the presence of ceric ions is generally presumed to result from propagation from radical sites generated on the backbone polymer. Thus the progress of graft copolymerisation is considered to result from propagation of radical formed on the cellulose backbone polymer as a result of oxidation reactions between ceric ions and cellulose chain ends containing hemiacetal linkages [11], glycol linkages leading to C─C bond cleavage (C_2 and C_3) [12] and/or with carbonyl groups on the cellulose substrate [13]. However, the low efficiency and frequency of grafting associated with ceric ion initiated graft copolymerisation are in consistent with the graft polymer levels obtained from propagation by radicals formed on the backbone polymer. Consequently, Gaylord and co-workers [14,15] proposed a mechanism in which the formation of graft polymer is considered to result from a donor-acceptor type of interaction between cellulose-water-monomer-ceric complex and the uncomplex monomer. It would seem therefore that although the use of ceric ions to initiate graft copolymerisation of vinyl monomers onto cellulose has been extensively reported, a gap exists in the present knowledge of the mechanism of graft polymer formation. For instance would graft polymer formation result from the reactions of growing homopolymer chains with radicals formed in the backbone polymer? In previous reports, we examined the grafting characteristics of methyl acrylate, ethylacrylate, and ethyl methylacrylate, methyl methylacrylate, acrylonitrile and their mixtures on

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carboxyl methyl cellulose [16-18]. The results of this study suggest that the radicals formed by the backbone polymer are non reactive in graft polymer formation. In this report, we examine the grafting characteristics of acrylamide on carboxymethyl cellulose using ceric ion and ceric ion/thiourea redox systems and tested the flocculation property of the grafted copolymers.

Experimental Procedures

Material

Acrylamide (Aldrich) was recrystallized twice from methanol followed by drying in vacuum over silica gel. Ceric ammonium sulphate, thiourea and carboxy methyl cellulose (ds 0.4-0.5) were from BDH and were used without further purification.

Grafting Procedure

The graft copolymerisation procedure was based on the method described by Rout and co-workers [19]. In a typical experiment, 0.5 g of CMC was stirred into 100 ml of deionised and doubly distilled water in a beaker overnight, and a known amount of ceric ion on ceric ion-thiourea was added. The initiator was allowed to interact with the substrate for 30 min at and a known amount of the monomer was added with stirring. Polymerisation was allowed to proceed for 150 min at 23°C and the reaction was stopped by adding 2 ml of 5% (w/v) quinone solution. The reaction mixture was poured into a large excess of isopropanol, filtered and the residue dried in vacuum and weighed. The ungrafted homopolymer was extracted with morpholine. The CMC graft polymer was then again dried in vacuum and weighed. The percent graft level, P_g, is reported as the weight of the grafted polymer divided by the weight of CMC used multiplied by 100. The percent grafting efficiency, P_e, is reported as the weight of the grafted polymer divided by the weight of the total polymer formed, multiplied by 100.

The weight of the grafted polymer divided by its average molecular weight (m_v) gives the number of grafted polymer chains (N_g). The frequency of grafting, F_g, is expressed as the number of grafted polymer chains per anhydrous glucose unit, AGU, of the backbone polymer and is obtained from the relationship:

$$F_g\left(N_g/\mathrm{AGU}\right) = \frac{\text{wt\% of grafted polymer}}{m_\nabla \text{ of grafted polymer}} \times \frac{\text{molecular weight of AGU}}{\text{wt\% CMC in copolymer}} \qquad (1)$$

Isolation and Molecular Weight Determination of Grafted Polymer Chains

The grafted polymer chains were isolated form the backbone polymer by treatment with 70% (v/v) aqueous sulphuric acid for 36 h at room temperature. The mixture was poured into excess methanol and the polyacrylamide precipitated was redissolved in water and precipitated in methanol.

The molecular weight of the isolated polymer was determined by viscosity measurement in water at room temperature using the relationship:

$$\text{Log } [n] = \log 6.8 \times 10^{-6} + 0.66 \log m_v \qquad (2)$$

Characterisation

The graft copolymer was characterised by IR spectroscopy using a Fourier Transform Spectrophotometer and KBr pellets was used in sample preparation.

Flocculation Characteristics

The graft copolymers and the carboxy methyl cellulose were dispersed in water by adding 0.2 g of polymer to 150 ml of distilled water at 29°C. The stirred mixture was heated in a boiling water bath, cooled to room temperature and then diluted to 1 L with distilled water. Final dispersions were clear. About 400 ml portions of a 0.25% (w/v) suspension of Kaolin were placed in opened 1litre beakers and were dosed with various amounts of the flocculants solutions. Immediately after the addition of the flocculant, the suspension was stirred with a magnetic stirrer at 75 rpm for 2 min and thereafter at 20-25 rpm for 5 min. The suspension was allowed to settle for 10 min and the turbidity of aliquots of the supernatant was measured using the digital Hach 2100 AN Turbidity meter.

Results and Discussion

The IR spectra of CMC and CMC graft copolymers of acrylamide (Fig. 1) showed absorption bands at 1750, 1340 and 1100 cm^{-1} characteristic of CMC and an additional band at 1650 cm^{-1} which is characteristic of polyacrylamide. This particular absorption band is used to distinguish true polyacrylamide from the alternative polymerisation product (β-aniline) which has instead a secondary amide band at 1555 cm^{-1}.

Effect of Initiator Concentration on Grafting Characteristic

Table 1 shows the effect of ceric ion and ceric ion

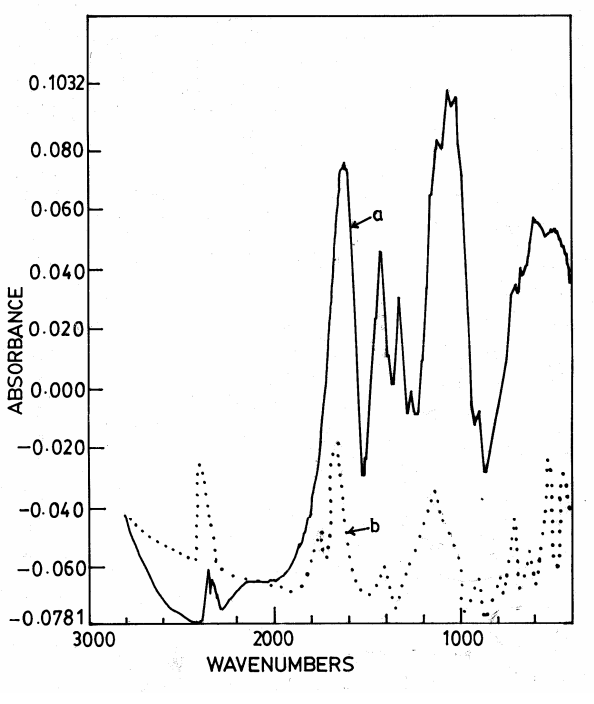
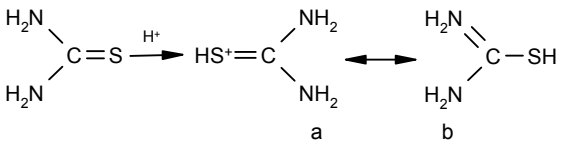


Figure 1. IR Spectra of (a) CMC and (b) CMC-g acrylamide.

thiourea concentration on the graft levels and efficiency of grafting acrylamide on CMC at room temperature. The results show that with ceric ion alone, the graft levels obtained were very low. Kantouch and coworkers [20] have also reported low graft levels in the grafting of acrylamide on native cotton. These results are consistent with the works earlier reported that ceric ion alone was not effective in the polymerisation of Acrylamide [21,22]. The results in Table 1 show that the presence of small amounts of thiourea is accompanied with marked increase in the percent graft levels.

The oxidation of thiourea by Ce^{4+} has been studied by Gomwalk and MC Auley [23] who proposed a mechanism involving the formation of free radicals which subsequently dimerize. They also suggested that in all initiating systems containing thiourea, isothiourea that exists in tautomeric equilibrium, thiourea in an aqueous solution is the reductant. In the presence of monomer and CMC, the likely reaction to bring about graft polymer formation is proposed as:



(3)

$$RSH + Ce^{4+} \xrightarrow{k} RS^{o} + Ce^{3+} + H^{+} \quad (4)$$

$$M + Ce^{4+} \xrightarrow{k_1} M^{o} + Ce^{3+} + H^{+} \quad (5)$$

$$Cel-H + Ce^{4+} \xrightleftharpoons{k_1^{i}} Complex \xrightarrow{k_d} Cel^{o} + Ce^{4+} + H^{+} \quad (6)$$

$$Cel-H + RS^{o} \xrightarrow{K_i^{ii}} Cel^{o} + RSH \quad (7)$$

In the presence of monomer

$$RS^{o} + M \xrightarrow{k_i^{iii}} RSM^{o} \quad (8)$$

Prepagation

$$RSM^{o}_{n-1} + M \xrightarrow{k_p} RSM^{o}_{n} \quad (9)$$

Termination

$$RSM^{o}_{n} + Ce^{4+} \xrightarrow{k_t} Homopolymer \quad (10)$$

$$RSM^{o}_{n} + RSM \xrightarrow{k_t^{i}} Homopolymer \quad (11)$$

$$RSM^{o}_{n} + RSM^{o}_{n} \xrightarrow{k_t^{ii}} Homopolymer \quad (12)$$

$$RSM^{o}_{n} + Cel^{o} \xrightarrow{k_t^{iii}} Graft\ polymer \quad (13)$$

The radical of CMC produced by reactions (5) and (6) would likely have equal reactivity and would therefore not explain the observed enhanced P_g in the presence of thiourea. It has been suggested that graft copolymer formation may result from the combination of homopolymer chains with radicals and therefore RS^{o} radicals are the initiators of homopolymer formation. The RS^{o} radical is considered to be more reactive than the M^{o} radical because the presence of oxygen atom in the acrylamide deactives the free radical formed.

The marked increase in P_g in the presence of thiourea can be attributed to the increase in the percent conversion of monomer to polymer. The growing polymer chains can combine with the radicals formed on the CMC backbone resulting in graft polymer.

The low graft levels precluded the isolation and determination of the molecular weight of grafted chains using ceric ion redox system. The frequency of grafting reported in this study is relatively low (Table 2) and indicates that either all the anhydrous glucose units on the backbone polymer are not available for reaction with the initiating system (that would lead to the formation of radical sites) or that the radicals produced on the backbone polymer are not reactive towards graft

polymer formation, graft copolymer formation may therefore be due to the termination of growing homopolymer chains on the backbone polymer. Efforts at improving on the frequency of grafting on cellulosic materials and therefore on the extent of modification of the properties of the backbone polymer must consider methods of enhancing the number of active radical sites on the backbone polymer.

Evaluation of Graft Copolymers as Flocculants

Laboratory tests were run on three graft copolymer samples with Pg 365.58, 383.76 and 423.42% to obtain estimates of their flocculation capacities. The characteristics of the copolymer samples used in the flocculation tests are given in Table 3. The flocculation characteristics of ungrafted CMC and CMC-g AAM graft copolymers are shown in Table 4. Flocculants concentrations refer to final concentration in water after addition to aqueous kaolin suspension.

Increase in flocculants dosage from 10 to 100 ppm is not accompanied with reduction in turbidity of kaolin suspension.

Marked improvement on the flocculating ability of CMC due to the incorporation of polyacrylamide grafts.

All the three copolymers showed activity, however as might be expected, effectiveness as flocculent depended on the size (molecular weight) rather than on the amount of polyacrylamide incorporated in the graft copolymers. This conforms with earlier reports [24,25].

Table 1. Graft copolymerisation of acrylamide on carboxy methyl cellulose: Effect of ceric ion, ceric ion/thiourea concentration on the grafting characteristics of CMC using 0.5 M monomer

[Ce IV] mML^{-1}	% Graft Level (P_g)	% Graft Efficiency (P_e)	[Thiourea] mML^{-1}	% Graft Level (P_g)	% Graft Efficiency (P_e)
3.0	28.40	87.43	0.10	365.58	98.16
4.0	30.04	82.89	0.10	383.76	94.01
4.5	52.00	83.60	0.10	404.78	94.33
5.0	89.32	89.57	0.10	399.96	91.73
5.5	76.10	82.45	0.10	484.22	87.97
6.0	50.24	89.01	0.10	423.42	92.41
6.5	57.72	87.57	0.10	383.86	92.41
7.0	60.42	87.74	0.10	378.84	94.23

Table 2. Effect of Ceric ion/thiourea concentration on the molecular weight and frequency of grafting of polyacrylamide on CMC

(Ce IV) mML^{-1}	(Thiourea) mML^{-1}	Molecular weight of Grafted PAAM chains 10^{-5} M_v	Frequency of grafting AAM on CMC ($Ng/10^4$)
3.0	0.10	3.27	6.02
4.0	0.10	3.70	5.20
4.5	0.10	2.7	8.01
5.0	0.10	2.88	7.03
5.5	0.10	2.59	9.04
6.0	0.10	2.07	10.23
6.5	0.10	2.00	10.25
7.0	0.10	2.00	9.04

Table 3. Characteristics of the CMC–graft copolymer sample used in flocculation tests

CMC–graft copolymer sample	Graft level (%)	Molecular weight of graft copolymer 10^{-5} M_v	Grafting frequency Fg ($Ng/10^4$ AGU)
A	365.58	3.27	6.02
B	383.76	3.70	5.20
C	423.42	2.07	10.23

Table 4. Effect of treatment with polymer solution on the turbidity of kaolin solution

Concentration	Percentage reduction in turbidity			
(ppm)	A	B	C	CMC
10	83.93	86.13	80.31	13.75
40	84.31	86.68	81.42	16.70
100	86.25	88.25	82.25	18.20

The turbidity of the 0.25% kaolin suspension was 1600 NTU.

Conclusion

This is the first reported work of using Ce4+ in grafting of acrylamide on a substrate, the graft copolymers obtained from it shows promise of being good flocculating agents.

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