Graft Copolymerizations of Modified Cellulose, Grafting of Acrylonitrile, and Methyl Methacrylate on Carboxy Methyl Cellulose

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SYNOPSIS

Graft copolymers of acrylonitrile (ACN), methyl methacrylate (MMA), and their mixtures on carboxy methyl cellulose (d.S 0.4–0.5) were prepared by the use of ceric ion initiator in aqueous medium. The graft copolymers were characterized by IR spectroscopy. The extent of graft copolymerization of ACN and MMA was measured in terms of graft level, molecular weight of grafted polymer chains, and the frequency of grafting as functions of ceric ion concentration. It was found that at comparable reaction conditions, the molecular weight of the grafted polymer chains and the frequency of grafting were not of the same order of magnitude. For the monomer mixtures, the copolymer compositions obtained from the total nitrogen contents of the copolymer samples showed that a disproportionately low amount of ACN monomeric units were incorporated into the graft copolymer, even at high ACN content of the feed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Many workers[1-20] have reported on the modification of both synthetic and natural polymers via graft copolymerization, often using ceric ion as initiator. Graft copolymerization of vinyl monomers onto cellulose in the presence of ceric ions is generally presumed to result from propagation by radical sites generated on the backbone polymer. Thus initiation of graft copolymerization is considered to result from propagation by radicals formed on the cellulosic backbone polymer by oxidation reactions of ceric ions with cellulosic chain ends containing hemiacetal linkages,[21] glycol linkages leading to $C-C$ bond cleavage (between C_2 and C_3),[22] and/ or with carbonyl groups on the cellulosic substrate.[23] Hydrogen abstraction from a carbon-atom-carrying hydroxyl group is also considered important in the initiation of graft polymer formation.[24] However, the relatively high levels of homopolymer formation associated with grafting and the observed low frequency of grafting are inconsistent with the idea of graft polymer formation resulting mainly from radicals formed on the cellulosic substrate.

Consequently, Gaylord and Anand[25] proposed a nonradical mechanism in which the formation of graft polymer is considered to result from a donor-acceptor type of interaction between a cellulose-water–monomer–ceric ion complex and uncomplexed monomer rather than from radicals generated on the cellulosic substrate. Thus, although the use of ceric ions to initiate graft copolymerization of vinyl monomers on cellulose has been extensively reported, a gap exists in the present knowledge of the exact mechanism of graft copolymer formation. For instance, could the graft polymer chain result from the interaction of radicals formed on the substrate with the growing homopolymer chain formed in the aqueous phase? The results of our previous studies on the role of radicals formed on the backbone polymer, by interaction with ceric ions, in the initiation of graft polymer formation were inconclusive,[26,27] partly because the results were obtained for heterogeneous copolymerization systems in which the partitioning of the reactants between the polymeric substrate–aqueous phase and the transfer of the reactants across phase boundaries could affect grafting characteristics. It is thought that if graft polymer formation results mainly from propagation by radicals formed on the backbone polymer, at comparable reaction conditions the frequency of grafting vinyl monomers on cellulosic materials should be about the same order of mag-

nitude. In this communication we examine some characteristics of the homogenous graft copolymerization of acrylonitrile (ACN), methyl methacrylate (MMA), and their mixtures on carboxy methyl cellulose (CMC).

EXPERIMENTAL

Materials

ACN and MMA monomers were purified by extraction with aqueous sodium chloride–sodium hydroxide solution and dried over sodium sulfate. The stabilizer-free monomers were distilled through Vigreaux columns and the middle fractions were collected as pure monomers. Ceric ammonium nitrate and CMC (d.S 0.4–0.5) were used without further purification.

Grafting Procedure

The graft copolymerization procedure was based on the method described by Lepoutre and Hui.[28] In a typical experiment, 0.5 g of CMC was stirred into 100 mL of distilled water overnight and a known amount of ceric ion was added. The initiator was allowed to interact with the substrate for 30 min at 25°C and a known quantity of the mechanism (constant amount of 40 mmol) was added with stirring. Polymerization was allowed to proceed for 150 min and the reaction was stopped by the addition of 2 mL of 5% (w/v) hydroquinone solution. The reaction mixture was poured into a large excess of methanol, filtered, and the residue was air dried and weighed. The graft copolymerization of the monomer mixtures was carried out as described above except that constant amounts of initiator (0.5 mmol) and monomer mixtures (50 mmol) were used at 35°C. The ungrafted homopolymers were extracted with suitable solvents, ethanol for poly(methyl methacrylate) (PMMA) and N,N-dimethyl formamide for polyacrylonitrile (PACN). The CMC graft copolymers were than air dried and weighed. The percentage graft level, P_g, is reported as the weight of the graft polymer, divided by the weight of CMC used, multiplied by 100.

Isolation and Molecular Weight Determination of Grafted Polymer Chains

The grafted polymer chains were isolated from the backbone polymer by treatment with glacial acetic acid/perchloric acid mixture.[29]

The molecular weight of the isolated polymer was

determined by viscosity measurements: PACN in dimethyl formamide (DMF) solution and PMMA in acetonitrile solution, both at 30°C using the relationships:

$$\log[\eta] = \log 2.09 \times 10^{-4} + 0.75 \log \bar{M}_v \quad (1)$$

and

$$\log[\eta] = \log 3.93 \times 10^{-6} + 0.50 \log \bar{M}_v. \quad (2)$$

Characterization

The graft copolymers were characterized by infrared (IR) spectroscopy using a Fourier transform spectrophotometer and KBr pellets in the sample preparation. The nitrogen contents of the copolymer samples (obtained from the monomer mixtures) were determined using elemental analysis.

Frequency of Grafting

The weight of the polymer grafted divided by the average molecular weight of the grafted chains ($\bar{M}_v$) gives the number of grafted chains, N_g.

RESULTS AND DISCUSSION

Characterization

The IR spectra of CMC graft copolymers of ACN, MMA, and ACN/MMA monomers (Fig. 1) showed absorption bands at 3310, 2360, 1630, and 1000–1100 cm^{-1}, characteristic of CMC, and additional bands at 1750 cm^{-1} that belong to the spectrum of PMMA at 2990 and 2240 cm^{-1} (CN stretch) that belong to the spectrum of PAN.
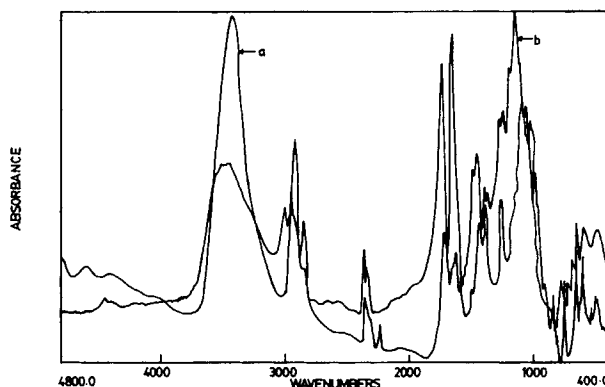

Figure 1 IR spectra of (a) CMC graft polyacrylonitrile and (b) CMC graft poly(methyl methacrylate).
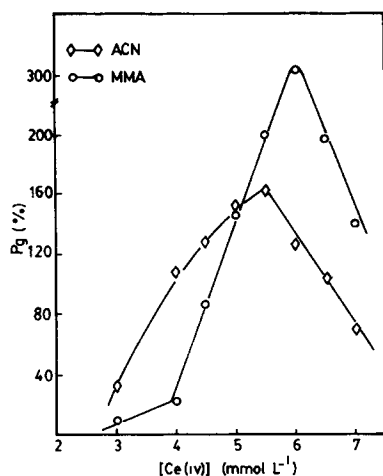
Figure 2 Graft copolymerization of acrylonitrile and methyl methacrylate on CMC at 35°C. Variation of P_g with ceric ion concentration.

Effect of Initiator Concentration on Grafting Characteristics

The variation of the graft level on ACN and PMMA on CMC with ceric ion concentration are shown in Figure 2. The results show that the levels of grafting of PMMA are much higher than for PAN. It can be seen that the initial increase in graft levels with increase in initiator concentration reached maximum levels of about 150 and 320% of PACN and PMMA, respectively, and decreased with further increase in initiator concentration. It can be seen that the ceric ion concentrations at which maximum grafting of PAN and PMMA occurred are about the same order of magnitude but somewhat higher (about 8%) for grafting PMMA. The ceric ion concentration produc-

ing maximum graft level has been shown to indicate the reduction equivalent of the backbone polymer.[23]

The molecular weight of the grafted polymer chains are shown in Table I as a function of ceric ion concentration. It can be seen that the average molecular weights of the grafted polymer chains decrease with increase in ceric ion concentration. This behavior suggests that termination of graft copolymerization may proceed by the interaction of ceric ions with growing polymer chains. A similar mechanism of termination has been reported for the grafting of acrylamide on dextrin,[30] butyl acrylate on gelation,[31] and for the grafting of ethyl acrylate on starch[32] and dextrin,[33] respectively.

The variation of the frequency of grafting PAN and PMMA on CMC with ceric ion concentration is shown in Table I. It can be seen that the values of frequency of grafting are generally low with at least 400 anhydroglucose units separating two graft polymer chains. The observed low frequency of grafting on CMC may be due to the reduced sites available for interaction with ceric ions by carboxymethylation. It has been shown from ^{13}C-NMR studies that the distribution of carboxymethyl moieties on cellulose follows the order $C_2 > C_6 > C_3$.[34] The results in Table I show that the frequency of grafting of PMMA on CMC are generally more than 10-fold lower than the values obtained for PAN, in spite of the lower P_g and $\bar{M}_v$ values reported for the latter. It has been suggested that if graft polymer formation is due to propagation by radicals generated on the backbone polymer, the frequency of grafting would be about the same order of magnitude for comparable monomer and initiator concentrations and similar reaction conditions.[11] The observed

Table I Effect of Initiator Concentration on Grafting Characteristics of Acrylonitrile (ACN) and Methyl Methacrylate (MMA) on Carboxy Methyl Cellulose (CMC)

[Ce(IV)] (mmol L^{-1})	$\bar{M}_v$ Grafted Polymer Chains		Frequency of Grafting $(10^4 N_g/100$ g CMC)	
	$10^{-5}\,\bar{M}_v$ PAN	$10^{-6}\,\bar{M}_v$ PMMA	PAN	PMMA
4.0	1.35	—	7.88; 12.7[a]	—
4.5	1.28	2.47	10.15; 16.37[a]	0.37; 0.60[a]
5.0	1.19	2.40	12.79; 20.63[a]	0.62; 1.00[a]
5.5	1.10	1.98	14.56; 23.48[a]	1.02; 1.64[a]
6.0	1.06	1.79	11.70; 18.87[a]	1.79; 2.89[a]
6.5	0.85	1.24	12.46; 20.09[a]	1.63; 2.63[a]
7.0	0.60	1.17	12.67; 20.44[a]	1.20; 1.94[a]

[a] $N_g/10^4$ anhydroglucose unit (AGU).

dependence of the frequency of grafting on monomer type suggests that the formation of graft polymer results from propagation by radicals on the backbone polymer and/or by the interaction of growing homopolymer chains with radicals formed on the backbone polymer. Either way, the results from this study suggest that ACN monomer and/or its polymer are more reactive than MMA and/or its polymer toward radicals formed on the backbone polymer. In our previous report[13] we examined the effect of isopropanol on the grafting characteristics of MMA on modified plantain pulp using ceric ion initiator. It was found that the presence of isopropanol was associated with increased levels of grafting, reductions in the molecular weight of grafted polymer chains, and an increase in the frequency of grafting. It was suggested that the isopropanoyl radicals formed by the interaction of ceric ion with isopropanol[35]
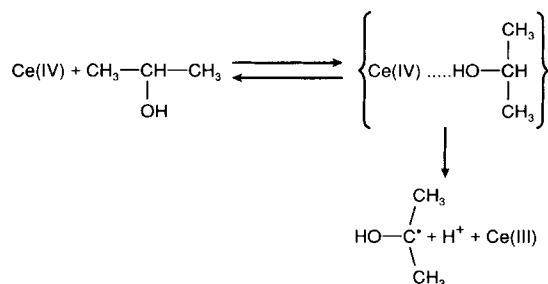
initiated polymer chains that reacted with radicals formed on the backbone polymer. The extent of grafting via the free radical mechanism depends on the electronic charge (e value) of the monomer, with monomers having higher e values having higher
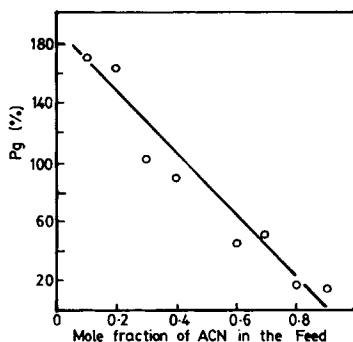
Figure 3 Graft copolymerization of binary monomer mixtures on CMC at 30°C. Variation of graft level with monomer feed composition.
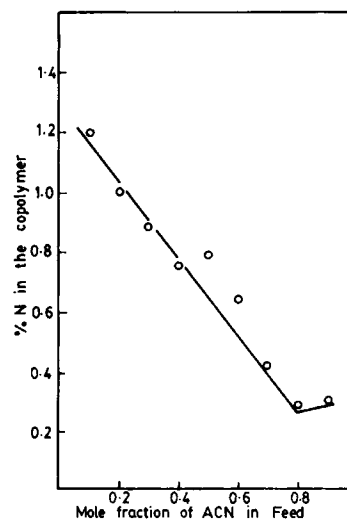
Figure 4 Graft copolymerization of binary monomer mixtures on CMC at 30°C. Variation of nitrogen content of the graft copolymer with feed composition.

reactivity.[36] The approximate e values of the monomers used in this study are 1.2 and 0.4 for ACN and MMA, respectively. These results from this study are consistent with the suggestion that graft polymer formation may result mainly by the interaction of homopolymer chains with reactive sites on the backbone polymer.

Grafting of ACN/MMA Monomer Mixtures

The grafting characteristics of ACN/MMA monomer mixtures on CMC are shown in Figures 3–5. It can be seen that the level of grafting decreased with an increase in the ACN content of the feed composition (Fig. 3). The reductions in the levels of grafting with an increase in the amount of ACN in the feed may be explained in terms of retardation by copolymerization.

The nitrogen content of the graft copolymer samples are shown in Figure 4 as a function of feed composition. There is a large deficit in the nitrogen content of the copolymer samples in comparison with the ACN content of the monomer mixture (feed) and the high levels of conversion obtained. The composition of the copolymer samples were worked out from their nitrogen contents and are shown in Figure 5 as a function of the feed composition. As with the nitrogen content of the copolymer samples, the results show that disproportionately low amounts of ACN are incorporated into the graft copolymer even at high ACN content of the feed. If the two monomeric units are built into
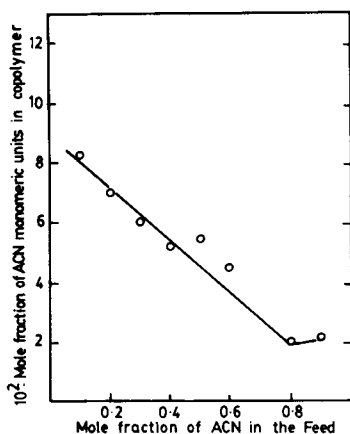
Figure 5 Graft copolymerization of binary monomer mixtures on CMC at 30°C. Variation of copolymer composition with monomer composition.

the graft copolymer chains randomly, the large deficit in the ACN content of the copolymer samples suggests that the rates of self-propagation of ACN might be low.

However, the reactivity of ratios estimated for ACN and MMA (r_1 = 1.00; r_2 = 9.00) from the copolymer composition using the Fineman and Ross method[37] do not provide adequate explanations for the low levels of ACN present in the copolymer samples. If a large proportion of ACN is grafted independently of MMA, the isolation and purification procedures adopted for the graft polymer chains may not have completely recovered the ACN-rich polymer grafts. This may explain the low levels of ACN in the copolymer samples, even for the samples obtained at high ACN content of the monomer mixtures.

The results from this study show that graft polymer formation on CMC results mainly from the interaction of growing polymer chains with radicals formed on (probably the chain ends of the backbone polymer) on the cellulosic polymer rather than by propagation by radicals formed 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 reactive radicals sites on the backbone polymer.

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