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GRAFT COPOLYMERIZATIONS OF MODIFIED CELLULOSE: GRAFTING OF METHYL ACRYLATE, ETHYL ACRYLATE AND ETHYL METHACRYLATE ON CARBOXY METHYL CELLULOSE

F. E. OKIEIMEN and D. E. OGBEIFUN
University of Benin, Department of Chemistry, Benin City, Nigeria

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Abstract—Graft copolymers of methyl acrylate, ethyl acrylate and ethyl methacrylate on carboxy methyl cellulose (d.S 0.4–0.5) were obtained by the use of ceric ion in aqueous media at 35°C. The extent of graft polymer formation was measured in terms of graft level, molecular weight of the grafted polymer chains, and frequency of grafting. It was found that, although the reaction conditions were similar, the frequencies of grafting of the monomers were not of the same order of magnitude. It was suggested that graft polymer formation may not be due mainly to propagation by radicals formed on the backbone polymer by interaction with ceric ions.

INTRODUCTION

The use of ceric ions to initiate graft copolymerization of vinyl monomers on synthetic and natural polymers has been reported by many workers [1–20]. Graft polymer formation is often considered to result from propagation by radicals formed on the backbone polymer by interaction with ceric ions. Consequently, the loci of initiation of graft polymer formation on cellulosic backbone polymer are radicals formed by oxidative 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 carboxyl groups in the cellulosic backbone polymer [23]. However, the low efficiency and frequency of grafting associated with ceric ion-initiated graft copolymerization are inconsistent with the idea of graft polymer formation resulting mainly from propagation by radicals formed on the cellulosic backbone polymer. Consequently, Gaylord and co-workers [24–26] 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 ion complex and uncomplexed monomer. It would seem that, 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 mechanism of graft polymer formation. For instance, would graft polymer formation result from the reactions of growing homopolymer chains with radicals formed on the backbone polymer? The enhanced frequency of grafting reported for methyl methacrylate on plantain pulp in the presence of isopropanol was explained in terms of the participation of isopropanoyl radicals formed by interaction of isopropanol with ceric ions in the initiation of poly(methyl methacylate) chains which combined with radicals on the cellulosic backbone polymer [27]. It is thought that, if graft polymer formation was by way of propagation by radicals formed on the backbone polymer, then for comparable reaction conditions, the frequency of grafting vinyl monomers should be about the same order of magnitude. In a previous report we examined the grafting characteristics of acrylonitrile, methyl methacrylate and their mixtures on carboxy methyl cellulose [28]. The results of that study suggest that the radicals formed by the oxidative interactions of ceric ions with the backbone polymer are not reactive in graft polymer formation. In this report we examine the grafting characteristics of methyl acrylate, ethyl acrylate and ethyl methacrylate on carboxy methyl cellulose.

EXPERIMENTAL PROCEDURES

Materials

Methyl acrylate, ethyl acrylate and ethyl methacrylate monomers were purified by extraction with aqueous sodium chloride–sodium hydroxide solution and dried over sodium sulphate. The stabilizer-free monomers were distilled under reduced pressure and the middle fractions were collected as pure monomers. Ceric ammonium nitrate and carboxy methyl cellulose (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 [29]. 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 and a known amount of the monomer was added with stirring. Polymerization was allowed to proceed for 15 min and the reaction was stopped by the addition of 2 ml of 5% (w/v) quinone solution. The reaction mixture was poured into a large excess of a non-solvent

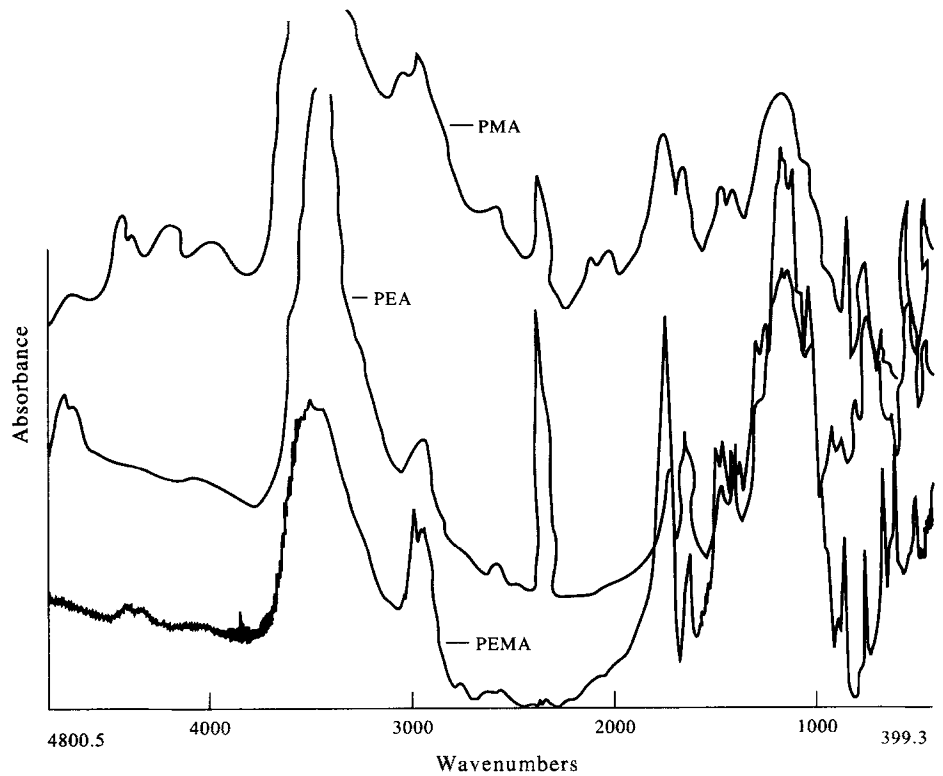

Fig. 1. Infrared spectra of CMC graft poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA) and poly(ethyl methacrylate) (PEMA).

(methanol for reaction mixtures of methyl acrylate and ethyl methacrylate and ethanol/isopropanol mixture for reaction mixture of ethyl acrylate), filtered and the residue air-dried and weighed. The ungrafted homopolymers were extracted with suitable solvents [acetone for poly(methyl acrylate), methanol for poly(ethyl acrylate), and ethanol for poly(ethyl methacrylate)]. The CMC graft polymer was then air-dried and weighed. The per cent graft level, P_g, is reported as the weight of the grafted polymer divided by the weight of CMC used, multiplied by 100. The per cent grafting efficiency, P_g, is reported as the weight of the grafted polymer divided by the weight of the total polymer formed, 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 [30]. The molecular weight of the isolated polymer was determined by viscosity measurements using the following relationships [31]:

$$\log[\eta] = \log 7.79 \times 10^{-5} + 0.069 \log \bar{M}v \tag{1}$$

$$\log[\eta] = \log 27.7 \times 10^{-3} + 0.67 \log \bar{M}v \tag{2}$$

$$\log[\eta] = \log 4.75 \times 10^{-6} + 0.50 \log \bar{M}v \tag{3}$$

for poly(methyl acrylate) in toluene at 30°C, poly(ethyl acrylate) in benzene at 30°C and poly(ethyl methacrylate) in isopropanol at 37°C, respectively.

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 moles of grafted polymer chains, N_g.

Table 1. Graft copolymerization of vinyl monomers on carboxy methyl cellulose: effect of monomer concentration on the grafting characteristics of CMC using 5 mmol l^{-1} ceric ion at 35°C

	% Graft level (P_g)			% Grafting efficiency (P_e)		
[M]	MA	EA	EMA	MA	EA	EMA
0.1	8.26	40.20	20.44	31.19	55.68	37.68
0.2	15.78	118.12	40.26	43.93	76.48	27.58
0.3	19.56	170.40	68.22	40.97	59.99	20.55
0.4	166.64	180.04	95.92	38.56	74.75	22.83
0.5	290.28	216.30	97.44	60.44	80.04	38.20
0.6	412.24	167.92	106.42	52.07	79.81	38.72
0.7	408.32	189.10	108.40	41.99	76.16	35.32

MA: Methyl acrylate; EA: ethyl acrylate; EMA: ethyl methacrylate.

Characterization

The graft copolymers were characterized by infrared spectroscopy using a Fourier Transform Spectrophotomer and KBr pellets in the sample preparation.

RESULTS AND DISCUSSION

Characterization

The i.r. spectra of CMC graft copolymers of methyl acrylate, ethyl acrylate and ethyl methacrylate (Fig. 1) showed absorption bands at 3410, 1750, 1340 and 1100 cm^{-1} characteristic of CMC, with additional absorption bands at 2950 and 1610 cm^{-1} which belong to poly(methyl acrylate), at 2950 and 1650 which belong to the spectrum of poly(ethyl acrylate), and at 3000, 2940 and 1650 cm^{-1} which belong to the spectrum of poly(ethyl methacrylate).

Effect of monomer concentration on the grafting characteristics

The variations in the graft level and grafting efficiency of poly(methyl acrylate), poly(ethyl acrylate) and poly(ethyl methacrylate) on CMC with monomer concentration are shown in Table 1. The results show that, except for ethyl acrylate for which the initial increase in the graft level with increase in monomer concentration reached a maximum level at 0.5 M monomer and decreased with further increase in the monomer concentration, the graft levels generally increased with increase in monomer concentration. The low values of efficiency of grafting reported in this study indicate that a large proportion of the polymer formed during the grafting reaction was not grafted on to the backbone polymer. It seems from the results that the order of increasing graftability of the monomers is ethyl methacrylate < ethyl acrylate < methyl acrylate. It has been reported that the rate of polymerization of acrylate monomers decreases with increase in alkyl length [32, 33] and explanations in terms of changes in diffusion, steric hindrance, polarity and solubility with increasing monomer size were advanced. The observed variation in the values of P_g may well be due to these factors.

The effect of monomer concentration on the molecular weight of the grafted polymer chains is shown in Fig. 2. It can be seen that, whereas the molecular weights of grafted poly(methyl acrylate) and poly(ethyl acrylate) are of about the same order of magnitude and show moderate variations with increase in the monomer concentration, the values of the molecular weight of grafted poly(ethyl methacrylate) are much higher and increase (by up to 40%) with increase in the monomer concentration. The variation of the frequency of grafting with monomer concentration is shown in Fig. 3. A fixed initiator concentration was used for the graft copolymerization. Under these conditions, and assuming that graft polymer formation is by way of propagation of radicals formed on the backbone polymer (by oxidative reactions with ceric ions), the frequency of grafting would be expected to be about the same order of magnitude. The variations of the frequency of grafting with monomer concentration and type indicate that reactions other than propagation by radicals formed on the backbone polymer may lead to graft polymer formation. The free radical mechanism for graft polymer formation proposed by Gaylord and co-workers predicts that the extent of grafting would depend on the electronic charge (e-value) of the monomer, with monomers with higher e-values having higher reactivity [34] towards graft polymer formation. The approximate e-values of the monomers used in this study are methyl acrylate (0.60), ethyl acrylate (0.22) and ethyl methacrylate (< 0.22). It would seem from the results of this study that the mechanism of graft polymer formation proposed by Gaylord and co-workers is applicable to grafting methyl acrylate, ethyl acrylate

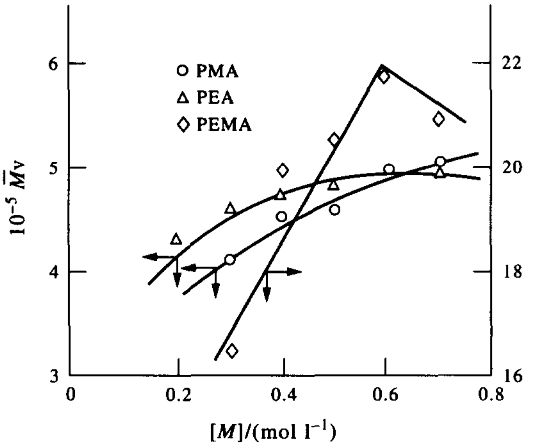

Fig. 2. Effect of monomer concentration on the molecular weight of grafted polymer chains on CMC at 35°C.

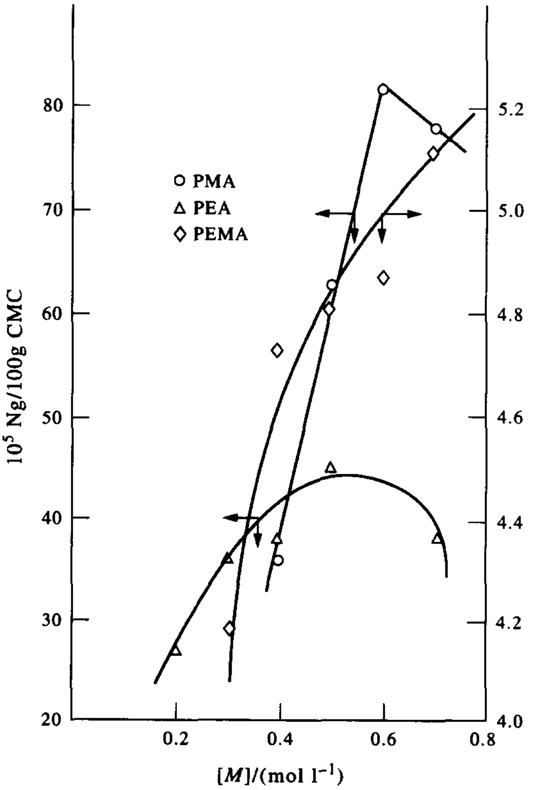

Fig. 3. Effect of monomer concentration on the frequency of grafting vinyl monomers on CMC at 35°C.

Table 2. Graft copolymerization of vinyl monomers on carboxy methyl cellulose: effect of ceric ion concentration on the grafting characteristics of CMC using 0.4 M monomer at 35°C

[Ce(IV)] (mmol l^{-1})	% Graft level (P_g) MA	% Graft level (P_g) EA	% Graft level (P_g) EMA	% Grafting efficiency (P_e) MA	% Grafting efficiency (P_e) EA	% Grafting efficiency (P_e) EMA
3.0	162.00	—	10.28	56.64	—	57.62
4.0	190.40	—	15.94	57.65	—	62.36
4.5	206.60	13.28	54.26	59.29	31.96	82.19
5.0	226.20	184.42	100.42	60.48	80.70	26.41
5.5	242.44	235.24	101.96	59.86	70.77	25.36
6.0	244.00	253.24	159.28	59.83	70.74	35.87
6.5	246.00	237.06	140.76	59.13	75.49	40.89
7.0	248.24	238.80	144.84	56.56	74.58	42.09

MA: Methyl acrylate; EA: ethyl acrylate; EMA: ethyl methacrylate.

Table 3. Grafting of vinyl monomers on carboxy methyl cellulose: effect of ceric ion concentration of the molecular weight (Mv) of grafted polymer chains and frequency of grafting using 0.4 M monomer at 35°C

[Ce(IV)] (mmol l^{-1})	$10^{-5}\bar{M}v$ of grafted polymer chains PMA	$10^{-5}\bar{M}v$ of grafted polymer chains PEA	$10^{-5}\bar{M}v$ of grafted polymer chains PEMA	Frequency of grafting (10^5 N_g/100 g CMC) PMA	Frequency of grafting (10^5 N_g/100 g CMC) PEA	Frequency of grafting (10^5 N_g/100 g CMC) PEMA
4.0	4.50	—	—	42.31	—	—
4.5	4.22	—	8.00	48.96	—	6.78
5.0	3.53	3.45	21.80	64.08	53.46	4.61
5.5	3.36	3.18	—	72.15	73.97	—
6.0	—	3.12	20.77	—	81.17	7.66
6.5	3.18	2.78	12.37	77.36	85.27	11.38
7.0	2.84	1.56	12.20	87.41	153.08	11.87

and ethyl methacrylate on carboxy methyl cellulose in aqueous medium.

Effect of initiator concentration on grafting characteristics

Table 2 shows the effect of ceric ion concentration on the graft level and efficiency of grafting methyl acrylate, ethyl acrylate and ethyl methacrylate on CMC at 35°C. The results show the initial increase in graft level with increase in initiator concentration levels off and decreases with further increase in initiator concentration. The reactivities of the monomers towards graft polymer formation follow the same order as observed for the dependence of graft level on monomer concentration. The values of efficiency of grafting also indicate that a large proportion of the polymer formed is not grafted on to the backbone polymer. The molecular weights of the grafted polymer chains are shown in Table 3 as functions of ceric ion concentration. It can be seen that the molecular weights of grafted poly(ethyl methacrylate) are markedly higher than those for poly(ethyl acrylate) and poly(methyl acrylate). It would seem from the dependence of the molecular weight of grafted polymer chains on ceric ion concentration that termination of graft copolymerization would proceed by the reaction of the growing graft polymer chain with ceric ions. The amounts of initiator used in this study are small compared to the monomer concentration. It is unlikely that the marked reductions in the molecular weight of the grafted polymer chains would be caused by this type of interaction.

The variation in the frequency of grafting poly (methyl acrylate), poly(ethyl acrylate) and poly(ethyl methacrylate) on CMC with ceric ion concentration is shown in Table 3. The frequency of grafting depends on the monomer type: the higher the electronic charge (e-value), the higher the reactivity of the monomer towards graft polymer formation. The frequencies of grafting reported in this study are relatively low, and indicate either that all the anhydroglucose units on the backbone polymer are not available for the reaction with ceric ions (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.

The results of this study have shown that the frequency of grafting on to CMC depends both on the monomer and ceric ion concentrations and on the e-value of the monomer. These results are consistent with the suggestion that graft polymer formation will result not from propagation by radicals formed on the backbone polymer but rather from the termination of growing homopolymer chains on the backbone polymer. The low frequencies of grafting reported in this study suggest that grafting occurred at the reducing end groups on the backbone polymer.

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