Grafting onto Gelatin. II. Graft Copolymerization of Ethyl Acrylate and Methyl Methacrylate onto Gelatin in the Presence of Ce4 as Redox Initiator

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ABSTRACT

In order to initiate a comprehensive study of graft copolymeri-
zation of vinyl monomers onto soluble protein-gelatin, we have
studied grafting of ethyl acrylate (EA) and methyl methacrylate
(MMA) onto gelatin using ceric ammonium nitrate (CAN) and
ceric ammonium sulfate (CAS) as the redox initiator in an aque-
ous medium. A small amount of mineral acid (HNO_3 with CAN
and H_2SO_4 with CAS) was found to catalyze the graft copolym-
erization. Graft copolymerization reactions were carried out
at different temperatures. Maximum grafting occurred at 65°C
both with EA and MMA. Percentage grafting has been determined
as function of 1) concentration of monomer (EA and MMA), 2)
concentration of initiator (CAN and CAS), 3) concentration of acid
(HNO_3 and H_2SO_4), 4) time, and 5) temperature.

INTRODUCTION

Mino and Kaizerman found that ceric ion is capable of effecting
grafting of a variety of vinyl monomers onto cellulose [1] and poly-
vinyl alcohol [2]. Ceric ion enters into complex formation with

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polyhydric alcohols, and on disproportionation the complex generates free radicals on the backbone polymer where grafting of the appropriate vinyl monomer can occur.

$$R-CH_2-OH + Ce^{4+} \rightleftharpoons B \rightleftharpoons RCH_2O^\cdot + Ce^{3+} + H^+$$
$$\text{(complex)}$$
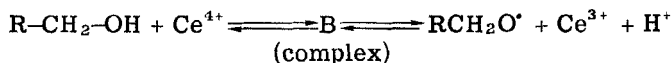
Using the ceric ion technique, a number of vinyl monomers have been successfully grafted onto starch [3, 4], cellulose [5, 6], and wool [7-10]. Relatively less attention has been paid to the modification of gelatin by graft copolymerization. It is a unique protein owing to the absence of an appreciable internal order.

Nayudamma and co-workers [11] have reported grafting of methyl acrylate onto collagen using ceric sulfate as initiator. Grafting onto gelatin has been reported by Santappa et al., and they were successful in effecting grafting of EA [12] and MA [13] using persulfate as initiator. Recently, Kuwajima and co-workers [14] have studied grafting of methyl methacrylate using potassium peroxysulfate as the initiator. Earlier we reported [15] on graft copolymerization of MA onto gelatin by using CAN as the redox initiator. As an extension of that work, we now report studies on the graft copolymerization of ethyl acrylate (EA) and methyl methacrylate (MMA) onto gelatin in the presence of ceric ion initiator in an attempt to compare the relative reactivities of different vinyl monomers toward graft copolymerization. The percentage of grafting was calculated as a function of the varous parameters, and the results are presented in the tables (1A-1E and 2A-2E).

EXPERIMENTAL

Materials and Methods

Gelatin (Oxoid, England) was in the form of granules and was used as received. The acrylate monomers (EA and MMA) were washed with 5% NaOH followed by washing with water and dried over anhydrous Na_2SO_4. The dried monomers were distilled and the middle fractions were used.

Ceric ammonium nitrate (BDH) and ceric ammonium sulfate (BDH) were used as received. Both HNO_3 and H_2SO_4 of known strength were used. Nitrogen was purified by passing it through freshly prepared pyrogallol solution for removal of traces of oxygen.

Graft Copolymerization

One gram of gelatin was dissolved in 100 mL of boiled distilled water in a two-necked flask fitted with a water condenser. The reaction

TABLE 1A. Effect of Concentration of EA on Grafting of PEA onto Gelatin

No.	[EA] $\times 10^2$ mol/L	[CAN] $\times 10^3$ mol/L	[HNO$_3$] $\times 10^2$ mol/L	Temper- ature (°C)	Time (min)	% Graft- ing	% Effi- ciency
1	36.8	10.9	4.2	65	90	289.4	78.6
2	46.0	"	"	"	"	420.6	91.4
3	55.2	"	"	"	"	386.0	69.9
4	64.4	"	"	"	"	15.8	2.6

TABLE 1B. Effect of Concentration of CAN on Grafting of PEA onto Gelatin

No.	[CAN] $\times 10^3$ mol/L	[EA] $\times 10^2$ mol/L	[HNO$_3$] $\times 10^2$ mol/L	Temper- ature (°C)	Time (min)	% Graft- ing	% Effi- ciency
1	5.5	46.0	4.2	65	120	5.0	1.1
2	7.3	"	"	"	"	334.7	72.8
3	9.1	"	"	"	"	348.1	75.7
4	10.9	"	"	"	"	408.8	88.9
5	12.8	"	"	"	"	365.6	79.5

TABLE 1C. Effect of Concentration of HNO$_3$ on Grafting of PEA onto Gelatin

No.	[HNO$_3$] $\times 10^2$ mol/L	[CAN] $\times 10^3$ mol/L	[EA] $\times 10^2$ mol/L	Temper- ature (°C)	Time (min)	% Graft- ing	% Effi- ciency
1	3.4	10.9	46.0	65	120	250.7	54.5
2	4.2	'	'	"	"	408.8	88.9
3	5.6	"	"	"	"	2.6	0.6
4	8.4	"	"	"	"	1.5	0.3

TABLE 1D. Effect of Temperature on Grafting of PEA onto Gelatin

No.	Temperature (°C)	$[CAN] \times 10^3$ mol/L	$[HNO_3] \times 10^2$ mol/L	$[EA] \times 10^2$ mol/L	Time (min)	% Grafting	% Efficiency
1	45	9.1	4.2	46.0	120	32.6	7.1
2	55	"	"	"	"	115.0	25.2
3	65	"	"	"	"	348.1	75.7
4	75	"	"	"	"	338.1	73.7
5	80	"	"	"	"	232.0	50.4

TABLE 1E. Effect of Time on Grafting of PEA onto Gelatin

No.	Time (min)	$[CAN] \times 10^3$ mol/L	$[HNO_3] \times 10^2$ mol/L	$[EA] \times 10^2$ mol/L	Temperature (°C)	% Grafting	% Efficiency
1	60	10.9	4.2	46.0	65	365.7	79.5
2	90	"	"	"	"	420.6	91.4
3	120	"	"	"	"	408.8	88.9
4	150	"	"	"	"	401.5	87.3
5	180	"	"	"	"	387.6	84.3

TABLE 2A. Effect of Concentration of MMA on Grafting of PMMA onto Gelatin

No.	$[MMA] \times 10^2$ mol/L	$[CAS] \times 10^3$ mol/L	$[H_2SO_4] \times 10^2$ mol/L	Time (min)	Temperature (°C)	% Grafting	% Efficiency
1	28.2	10.3	25.5	120	55	121.0	42.9
2	47.0	"	"	"	"	408.5	86.9
3	65.8	"	"	"	"	588.0	89.3
4	84.6	"	"	"	"	782.0	94.8

TABLE 2B. Effect of Concentration of CAS on Grafting of PMMA onto Gelatin

No.	[CAS] $\times 10^3$ mol/L	[H_2SO_4] $\times 10^2$ mol/L	[MMA] $\times 10^2$ mol/L	Time (min)	Temperature (°C)	% Grafting	% Efficiency
1	6.3	25.5	47.0	120	55	11.5	2.4
2	8.2	"	"	"	"	60.5	12.9
3	10.3	"	"	"	"	408.5	86.9
4	12.2	"	"	"	"	407.0	86.7
5	13.4	"	"	"	"	382.0	81.3

TABLE 2C. Effect of Concentration of H_2SO_4 on Grafting of PMMA onto Gelatin

No.	[H_2SO_4] $\times 10^2$ mol/L	[CAS] $\times 10^3$ mol/L	[MMA] $\times 10^2$ mol/L	Time (min)	Temperature (°C)	% Grafting	% Efficiency
1	17.0	10.3	47.0	120	55	177.5	37.8
2	25.5	"	"	"	"	408.5	86.8
3	34.0	"	"	"	"	102.0	21.7
4	42.5	"	"	"	"	353.0	75.1

TABLE 2D. Effect of Temperature on Grafting of PMMA onto Gelatin

No.	Temperature (°C)	[CAS] $\times 10^3$ mol/L	[H_2SO_4] $\times 10^2$ mol/L	[MMA] $\times 10^2$ mol/L	Time (min)	% Grafting	% Efficiency
1	45	10.3	25.5	47.0	120	105.0	22.3
2	55	"	"	"	"	408.5	86.9
3	65	"	"	"	"	430.0	91.9

TABLE 2E. Effect of Time on Grafting of PMMA onto Gelatin

No.	Time (min)	[CAS] $\times 10^3$ mol/L	[H$_2$SO$_4$] $\times 10^2$ mol/L	[MMA] $\times 10^2$ mol/L	Temperature (°C)	% Grafting	% Efficiency
1	60	10.3	25.5	47.0	55	17.0	3.6
2	120	"	"	"	"	408.5	86.9
3	180	"	"	"	"	356.0	75.7

mixture was flushed with purified N_2 gas for 20 min. A definite amount of catalyst (CAN/CAS) dissolved in a definite volume of acid (HNO_3/H_2SO_4) of known strength was added to the reaction flask. After 20 min a known weight of the vinyl monomer (EA/MMA) was added dropwise. A slow stream of nitrogen gas was passed through the reaction mixture and copolymerization was carried out under nitrogen atmosphere with constant stirring. After the reaction was over the ingredients of the flask were poured into 400 mL acetone and kept for 48 h. The grafted gelatin was filtered, washed with acetone and then with 150 mL of boiling water to remove unreacted gelatin, dried, and finally weighed. Percentage of grafting and efficiency were calculated as follows:

$$\% \; G = \frac{\text{weight of grafted material}}{\text{weight of gelatin}} \times 100$$

$$\% \; E = \frac{\text{weight of grafted material}}{\text{weight of vinyl monomer charged}} \times 100$$

Evidence of Grafting

1) Gelatin grafted with EA was hydrolyzed with 6–7.5 N HCl at its refluxing temperature for 6–8 h. All the gelatin went into solution, leaving behind a resinous mass which was identified by IR spectroscopy as poly(EA).
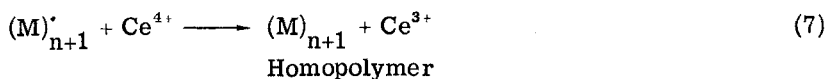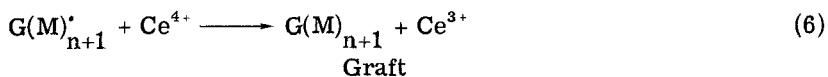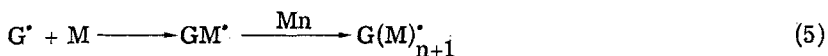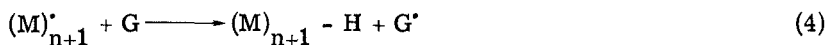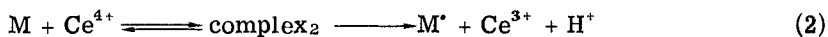
A physical mixture of gelatin (1.0 g) and poly(EA) and poly(MMA) was prepared by stirring gelatin in an acetone solution of poly(EA) and poly(MMA) for about 6 h. The mixture was filtered and the residue was extracted with acetone for 48 h, at which time all the homopolymers of PEA and PMMA were completely removed. 0.9 g of gelatin was recovered. This indicates that solvent extraction completely removes homopolymer from a physical mixture of gelatin and

PEA and PMMA. Isolation of PEA after acid hydrolysis of grafted gelatin constitutes evidence of grafting.

2) Infrared spectra of gelatin-g-PEA and gelatin-g-PMMA were determined in a Perkin-Elmer Infrachord, model 337, by swelling the graft samples in dichloromethane and then pressing the swollen material between two sodium chloride plates. IR spectra of gelatin-g-PEA and gelatin-g-PMMA showed intense absorptions at 1735 and 1730 cm^{-1}, assigned to the C=O of grafted PEA and PMMA, respectively. No such bands were observed in the IR spectrum of pure gelatin.

RESULTS AND DISCUSSION

Ceric ion is known to enter into complex formation with various functional groups such as –OH, –COOH, –NH$_2$, –CONH$_2$, –SH, and –SS. Gelatin primarily contains carboxyl, hydroxyl, and amino groups. These groups enter into complex formation with ceric ion. The complex then disproportionates via single electron transfer to generate free radical sites on gelatin where grafting of vinyl monomer occurs. In analogy with the ceric ion initiated mechanism for grafting vinyl monomers onto wool protein, the following mechanism (Eqs. 1-7) is proposed to explain the grafting of EA and MMA onto gelatin:

$$G + Ce^{4+} \rightleftharpoons complex_1 \longrightarrow G^{\bullet} + Ce^{3+} + H^+ \tag{1}$$

$$M + Ce^{4+} \rightleftharpoons complex_2 \longrightarrow M^{\bullet} + Ce^{3+} + H^+ \tag{2}$$

$$M^{\bullet} + nM \longrightarrow (M)^{\bullet}_{n+1} \tag{3}$$

$$(M)^{\bullet}_{n+1} + G \longrightarrow (M)_{n+1} - H + G^{\bullet} \tag{4}$$

$$G^{\bullet} + M \longrightarrow GM^{\bullet} \xrightarrow{Mn} G(M)^{\bullet}_{n+1} \tag{5}$$

$$G(M)^{\bullet}_{n+1} + Ce^{4+} \longrightarrow \underset{\text{Graft}}{G(M)_{n+1}} + Ce^{3+} \tag{6}$$

$$(M)^{\bullet}_{n+1} + Ce^{4+} \longrightarrow \underset{\text{Homopolymer}}{(M)_{n+1}} + Ce^{3+} \tag{7}$$
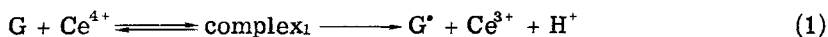
where G = gelatin and M = monomer.

From the above postulated mechanism it is observed that ceric ion enters into complex formation with both gelatin and the monomer. Thus there is competition for the formation of the graft and the homopolymer.

Effect of Monomer Concentration

Tables 1A and 2A show the effect of concentration of vinyl monomer on the percentage of grafting. It is observed that the maximum grafting of EA (420.6%) and MMA (782.0%) occurred at 65 and 55°C, respectively, at monomer concentrations of $[EA] = 46.0 \times 10^{-2}$ mol/L and $[MMA] = 84.6 \times 10^{-2}$ mol/L, respectively. With a further increase in the concentration of monomer, grafting is found to decrease. This is explained by the fact that at higher monomer concentration ceric ion preferably enters into complex formation with the monomer, leading to more homopolymer formation. Misra et al. [15] observed that methyl acrylate could be grafted onto gelatin in the presence of Ce^{4+} to the extent of 802.2% at a monomer concentration of 110.4×10^{-2} mol/L.

Effect of Concentration of Ceric Ion on Grafting

Tables 1B and 2B show the effect of concentration of catalyst, e.g., CAN and CAS, on grafting of EA and MMA, respectively. It is observed that both CAN and CAS produce almost the same amount of graft of EA and MMA when graft copolymerization is carried out using almost the same molar concentration of initiator (CAN and CAS) and monomers. This indicates that the nature of ligand attached to Ce^{4+} does not influence graft copolymerization. It is observed from Tables 1B and 2B that a further increase in the Ce^{4+} concentration leads to a decrease in the percentage of grafting of both EA and MMA. This is explained by the fact that ceric ion at higher concentration causes the termination of growing grafted polymeric chains. In all our Ce^{4+} initiated grafting work, a small amount of mineral acid was found to catalyze graft copolymerization. A similar observation is also made in the present work.

It is seen from Tables 1C and 2C that the maximum grafting of EA in the presence of CAN occurs at $[HNO_3] = 4.2 \times 10^{-2}$ mol/L, and maximum grafting of MMA in the presence of CAS occurs at $[H_2SO_4] = 25.5 \times 10^{-2}$ mol/L. This indicates that there exists an optimum concentration of acid at which grafting is maximum and beyond which grafting decreases. The role of acid in Ce^{4+}-initiated grafting of MA onto gelatin has been discussed in detail in a previous paper [15].

Effect of Temperature and Time

Graft copolymerization of EA and MMA was carried out at 45, 55, 65, and 75°C for various reaction periods. It is observed from

Tables 1D, 2D, 1E, and 2E that maximum grafting of both EA and MMA occurs at 65°C within 120 min. A further increase in temperature leads to a decrease in percentage grafting. This indicates that at higher temperatures various chain transfer reactions are accelerated that lead to a decrease in percent grafting. Beyond 120 min, percent grafting of both EA and MMA decreased, indicating that mutual annihilation of growing grafted chain occurs at a higher reaction period, leading to a decrease in graft yield. Similar behavior was observed by Santappa et al. [12] during grafting of EA onto gelatin in the presence of persulfate initiator.

From the above results it is concluded that vinyl monomers differ in reactivity toward graft copolymerization onto gelatin in the presence of Ce^{4+} initiator. The following reactivity order was observed: MA [15] > MMA > EA.

ACKNOWLEDGMENT

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