Grafting onto Wool. VII. Ceric Ion-Initiated Graft Copolymerization of Vinyl Monomers. Comparison of Monomer Reactivities

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Synopsis

In an attempt to compare relative reactivities of vinyl monomers toward grafting, methyl methacrylate (MMA) and acrylic acid (AAc) were grafted separately to Himachali wool in aqueous medium by using ceric ammonium nitrate (CAN) as redox initiator. Nitric acid was found to catalyze the reaction. Percent grafting was determined as a function of concentration of nitric acid, concentration of CAN, concentration of monomer, time, and temperature. Optimum conditions for maximum grafting were evaluated for each monomer and were found to depend upon the nature of the monomer. Reactivities of MMA and AAc toward grafting were compared with those of methyl acrylate (MA), ethyl acrylate (EA), and vinyl acetate (VAc) reported earlier from this laboratory and were found to follow the order MA > EA > MMA > VAc > AAc. An explanation for the observed order of reactivity of different vinyl monomers is presented.

INTRODUCTION

Following the discovery of Mino and Kaizermann[1] that ceric ion is capable of forming redox system with alcohol, a number of polyhydroxy compounds such as starch,[2,3] cellulose,[4] and poly(vinyl alcohol) have been graft copolymerized with a number of vinyl monomers by employing the ceric ion technique. Wool (WH) is a natural polypeptide and contains a number of functional groups such as hydroxyl, amino, imino, sulfhydryl, and disulfide linkages. All these functional groups have been reported to enter into redox reaction with ceric ion. It is therefore natural that vinyl monomers in the presence of ceric ion may be graft-copolymerized onto wool. Graft copolymerization of vinyl monomers onto wool has not been studied extensively. However, in recent years attempts are being made to modify wool fibers by grafting various vinyl monomers in the presence of a variety of initiating systems. As early as 1949, Lipson[5] studied polymerization of methacrylic acid in the presence of untreated and reduced wool and concluded that thiol groups of wool provide the active site for grafting. Among various redox initiators that have been studied, persulfates[6] and Fenton's reagent[7,8] were found effective in producing grafts of methacrylic acid, styrene, and acrylonitrile onto wool. Recently, Misra and co-workers[9] have reported on grafting of poly(vinyl acetate) onto Himachali wool by use of Fenton's reagent as redox initiator and observed that the molar ratio of $[H_2O_2]/[Fe^{2+}]$ plays an important role in grafting. Japanese workers[10] have been able to graft MMA to wool by using a novel initiator system comprising $LiBr-S_2O_8^{2-}$ without homopolymer formation. Other redox systems have also been tried with varying degrees of success. Ceric ion has been found extremely suitable for effecting grafting of a number of vinyl monomers onto cellulose and starch. But its use

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in effecting grafting of vinyl monomers onto proteins in general and wool in particular has received comparatively less attention.   Nayudamma and co-workers[11] were able to graft PMMA onto collagen by using ceric ammonium nitrate as redox initiator.   Imai et al.[12] have successfully prepared ovalbumin graft copolymer using the ceric ion technique.   Kantouch and co-workers[13] attempted grafting of MMA onto wool in the presence of ceric sulfate and observed that wool promoted polymerization of MMA.   Verma et al.[14,15] reported that relative reactivities of vinyl monomers toward grafting onto wool varied with the nature of monomer.   No attempts, however, seem to have been made to compare reactivities of donor and acceptor monomers toward grafting onto wool. A comprehensive study on grafting of a variety of vinyl monomers onto Himachali wool by the ceric ion method has been initiated in our laboratory, and it has been possible to graft MA,[16] EA,[17] and VAc[18] onto wool by using ceric ammonium nitrate as redox initiator.   In this paper, we report on grafting of MMA and AAc onto wool as a function of various reaction parameters.   Percent grafting and efficiency of grafting have been expressed as functions of concentration of nitric acid, concentration of CAN, concentration of monomer, time, and temperature. An attempt has been made to compare the relative reactivities of MMA and AAc toward grafting with those of MA, EA, and VAc reported earlier from this laboratory.

EXPERIMENTAL

Materials

Purification and physical characterization of Himachali wool have been described earlier.[9,16]   MMA was washed with 5% sodium hydroxide solution followed by washing with distilled water and then dried over anhydrous sodium sulfate.   The monomer was distilled and the middle fraction was collected and used.   Acrylic acid (AAc) was freshly distilled under reduced pressure and the middle fraction was used.   Ceric ammonium nitrate (CAN) was of reagent grade and was dissolved in nitric acid of appropriate concentration.   Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Graft Copolymerization

Purified Himachali wool (1.0 g) was dispersed in 200 ml cold deaerated water in a three-neck flask.   A weighed amount of CAN in nitric acid of appropriate concentration was added to the reaction flask.   The reaction mixture was flushed with nitrogen for 30 min, and then a continuous supply of nitrogen was maintained throughout the entire reaction period.   Calculated amounts of monomer (MMA and AAc) were added dropwise, and the copolymerization was carried out for various reaction periods at different temperatures under nitrogen atmosphere.   At the end of the reaction, the grafted material and the homopolymer were filtered.   The residue was extracted with benzene (solvent for PMMA) and with acetone (solvent for PAAc) for 48 hr.   The grafted material was dried at 50°C in an oven until constant weight was obtained.   Percent grafting and percent efficiency were determined in the following manner:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

$$\% \text{ efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2, and W_3 denote respectively the weight of wool, grafted wool after solvent extraction, and weight of monomer added.
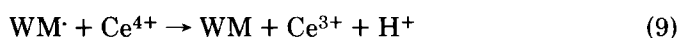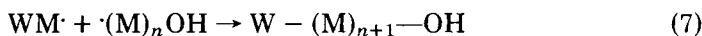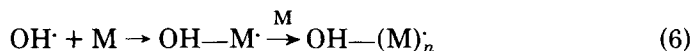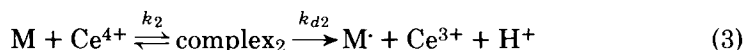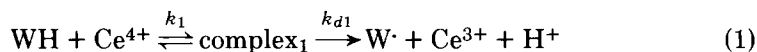
Evidence of Grafting

Wool–g–PMMA was refluxed with $6N$ HCl at 135°C for 48 hr. All wool went into solution leaving behind a resinous mass which was identified by infrared spectroscopy as PMMA.

The physical mixtures of wool and benzene solution of PMMA and acetone solution of PAAc were extracted with benzene and acetone for 24 hr. After extraction, the residue was refluxed with $6N$ HCl at 135°C for 48 hr. No residue was left behind, indicating that PMMA and PAAc were completely removed by extraction with benzene and acetone, respectively. Isolation of PMMA from the grafted material after treatment with $6N$ HCl constituted further evidence for grafting.

RESULTS AND DISCUSSION

In previous papers,[16,17] a mechanism for grafting of MA and EA onto wool was postulated by assuming a prior complex formation between wool (WH) and ceric ion. The complex then decomposes to generate the macroradical (W·) which then reacts with monomer to produce grafts. A similar mechanism with minor modification is suggested, eqs. (1)–(9), for grafting of MMA and AAc onto wool:

$$WH + Ce^{4+} \underset{k_1}{\rightleftharpoons} \text{complex}_1 \xrightarrow{k_{d1}} W\cdot + Ce^{3+} + H^+ \tag{1}$$

$$W\cdot + M \rightarrow WM\cdot \xrightarrow{M} WMM\cdot \tag{2}$$

$$M + Ce^{4+} \underset{k_2}{\rightleftharpoons} \text{complex}_2 \xrightarrow{k_{d2}} M\cdot + Ce^{3+} + H^+ \tag{3}$$

$$M\cdot + M \rightarrow MM\cdot \xrightarrow{M} M_n^\cdot \tag{4}$$

$$WM\cdot + H_2O \rightarrow WMH + OH\cdot \tag{5}$$

$$OH\cdot + M \rightarrow OH\!\!-\!\!M\cdot \xrightarrow{M} OH\!\!-\!\!(M)_n^\cdot \tag{6}$$

$$WM\cdot + \cdot(M)_n OH \rightarrow W - (M)_{n+1}\!\!-\!\!OH \tag{7}$$

$$WM\cdot + M \rightarrow WMH + M\cdot \tag{8}$$

$$WM\cdot + Ce^{4+} \rightarrow WM + Ce^{3+} + H^+ \tag{9}$$

where

$$WM = \begin{cases} W\!\!-\!\!(M)_n\!\!-\!\!CH\!\!=\!\!CHCOOH \text{ for AAC} \\[4pt] \qquad\qquad\qquad CH_3 \\[-2pt] \qquad\qquad\qquad | \\[-2pt] W - (M)_n\!\!-\!\!CH\!\!=\!\!C\!\!-\!\!COOCH_3 \text{ in case of MMA.} \end{cases}$$

Effect of Concentration of Nitric Acid

In all of our work[16,17] involving ceric ion-initiated grafting of vinyl monomers onto wool, it was observed that small amount of nitric acid promoted grafting. Similar observations have been reported by Garnett and Kenyon[19] who observed that styrene and ethyl acrylate could be grafted to wool swollen by methanol in the presence of nitric acid. It is observed from Tables I and II that there exists a critical concentration of nitric acid which affords maximum percent grafting; this corresponds to 14.4×10^{-2} mole/l. with both MMA and AAc. Beyond this concentration, the percent grafting decreases. This is explained by the fact that ceric ion in water is believed to react in the following manner:

$$Ce^{4+} + H_2O \rightleftharpoons [Ce(OH)_3]^{3+} \tag{10}$$

$$2[Ce(OH)_3]^{3+} \rightleftharpoons [Ce\!-\!O\!-\!Ce]^{6+} + H_2O \tag{11}$$
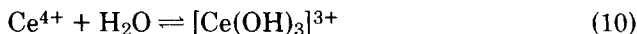
Thus, ceric ion exists as Ce^{4+}, $[Ce(OH)_3]^{3+}$, and $[Ce\!-\!O\!-\!Ce]^{6+}$ in water solution. The observed zero grafting at zero nitric acid concentration indicates the inability of $[Ce\!-\!O\!-\!Ce]^{6+}$ to form a complex with wool (WH). With increase in nitric acid concentration beyond 14.4×10^{-2} mole/l., the equilibria (10) and (11) shift toward formation of more and more Ce^{4+} and $[Ce(OH)_3]^{3+}$. These species at higher concentration affect grafting efficiency adversely.

Effect of Initiator Concentration

During grafting of MMA and AAc by the ceric ion initiation method, it was observed that varying amounts of homopolymer were formed and the amount

TABLE I
Effect of Time, Temperature, and Concentrations of CAN, HNO$_3$, and MMA on Percent Grafting[a]

Sample no.	Concn. of CAN, mole/l.	Concn. of HNO$_3$, (mole/l.) $\times 10^2$	Concn. of MMA, (mole/l.) $\times 10^2$	Time, min	Temp., °C	Grafting, %	Efficiency, %
1	0.003	14.4	23.5	180	45	1.36	0.28
2	0.003	14.4	23.5	180	55	1.54	0.32
3	0.003	14.4	23.5	180	65	10.84	2.3
4	0.0051	14.4	23.5	180	45	13.91	2.9
5	0.0051	14.4	23.5	180	55	29.14	6.2
6	0.0051	14.4	23.5	180	65	24.80	5.2
7	0.0063	14.4	23.5	180	55	27.13	5.7
8	0.0075	14.4	23.5	180	55	55.61	11.8
9	0.0081	14.4	23.5	180	55	17.08	3.6
10	0.0075	10.8	23.5	180	55	15.53	3.3
11	0.0075	18.0	23.5	180	55	38.65	8.2
12	0.0075	21.6	23.5	180	55	12.21	2.6
13	0.0075	14.4	14.1	180	55	40.40	14.3
14	0.0075	14.4	32.9	180	55	32.43	4.9

[a] Wool = 1 g; H$_2$O = 200 ml.

TABLE II
Effect of Time, Temperature, and Concentration of CAN, HNO_3, and AAc on Percent Grafting[a]

Sample no.	Concn. of CAN, mole/l.	Concn. of HNO_3, (mole/l.) $\times$ 10^2	Concn. of AAc, (mole/l.) $\times 10^2$	Time, min	Temp., °C	Grafting, %	Efficiency, %
1	0.003	14.4	36.7	180	45	0	0
2	0.003	14.4	36.7	180	55	7.06	1.3
3	0.003	14.4	36.7	180	65	5.29	1.0
4	0.00125	14.4	36.7	180	55	6.02	1.1
5	0.002	14.4	36.7	180	55	3.77	0.7
6	0.003	14.4	36.7	180	55	7.06	1.3
7	0.0039	14.4	36.7	180	55	7.16	1.3
8	0.0051	14.4	36.7	180	55	11.52	2.1
9	0.0063	14.4	36.7	180	55	5.14	0.97
10	0.0051	10.8	36.7	180	55	1.85	0.35
11	0.0051	18.0	36.7	180	55	5.03	0.95
12	0.0051	21.6	36.7	180	55	0.79	0.15
13	0.0051	14.4	22.0	180	55	0	0
14	0.0051	14.4	51.4	180	55	11.50	1.50
15	0.0051	14.4	73.5	180	55	3.98	0.37

[a] Wool = 1 g; H_2O = 200 ml.

of homopolymer formed was dependent upon the nature of vinyl monomer. It is apparent from Tables I and II that MMA under optimum conditions gave 55.61% grafting whereas AAc gave rise to only 11.52% grafting. This indicates that during ceric ion initiation both grafting and homopolymerization are occurring. In accordance with the above postulated mechanism, homopolymer may form by processes (4) and (6). Homopolymer formation by process (4) requires that monomers react with ceric ion to give a complex by process (3). No homopolymer, however, could be isolated when polymerization was carried out under conditions of grafting in the absence of wool. This indicates that homopolymer during grafting must be formed by some other process. Since wool (WH) was found to accelerate homopolymer formation, it is concluded that the macroradical (W·) reacts with water to produce OH·, which is responsible for the formation of homopolymer by process (6).

Thus, it appears that the amount of graft produced by process (2) is in competition with homopolymer formation by processes (4) and (6). It is observed from Tables I and II that with increase in ceric ion concentration the percent grafting increases with both MMA and AAc and reaches a maximum value at $[Ce^{4+}] = 7.5 \times 10^{-2}$ mole/l. for MMA and at $[Ce^{4+}] = 5.1 \times 10^{-2}$ mole/l. for AAc. With further increase in $[Ce^{4+}]$, the percent grafting decreases. This would be expected since at higher concentration $[Ce^{4+}]$ is known to affect grafting by termination of growing grafted chains.

Effect of Monomer Concentration

It is observed from Tables I and II that with increase in monomer concentration the percent grafting increases with both MMA and AAc to give a maximum grafting of 55.61% in case of MMA and 11.52% in case of AAc. Further increase
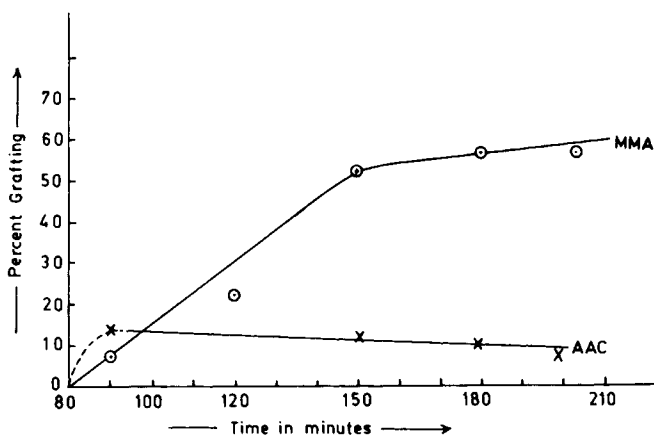
Fig. 1. Plot of time vs. percent grafting.

in monomer concentration leads to considerable decrease in percent grafting with MMA, while with AAc the percent grafting essentially remains constant.

Effect of Time and Temperature

Figure 1 shows that with MMA, the percent grafting increases with time and then levels off. With AAc, an increase in the time period has no significant effect upon the percent grafting. Grafting of MMA and AAc was carried out at 45, 55, and 65°C. It is apparent from Tables I and II that both MMA and AAc afforded maximum grafting at 55°C. Further increase in temperature decreased the percent grafting. This indicates that at higher temperature, homopolymer formation becomes predominant by process (6). At higher temperature, termination of grafted chain growth by process (9) may also be responsible for the decrease in percent grafting.

Percent grafting of MA,[16] EA,[17] and VAc[18] onto wool in aqueous medium by the ceric ion initiation method under optimum condition has been found to be 270, 77.87, and 32.26, respectively. MMA and AAc under optimum conditions produced maximum grafting to the extent of 55.61% and 11.52%, respectively. Thus, it appears that in ceric ion-initiated grafting onto wool, the reactivity of the vinyl monomers studied followed the order MA > EA > MMA > VAc > AAc. The reactivity of the first three monomers is explained by steric considerations. MMA, being a highly crowded monomer, forms a complex with Ce^{4+} less readily and thus affords minimum percent grafting. VAc, which is susceptible to monomer transfer reactions, easily terminates the growing grafted chain by process (8); this is why the percent grafting with VAc is much lower than that with acrylates. AAc has a lower steric requirement than MMA, and yet it gives a minimum percent grafting. The anomalous reactivity of AAc can be explained by the fact that AAc as well as its polymer are soluble in water medium, and as such, homopolymerization wins in the competition resulting in a decrease in percent grafting.

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