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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Sood, D. S. , Kishore, J. and Misra, B. N.(1985) 'Grafting onto Wool. XXVII. Graft Copolymerization of Mixed Vinyl Monomers by Use of Ceric Ammonium Nitrate as Redox Initiator', *Journal of Macromolecular Science, Part A*, 22: 3, 263 – 278

To link to this Article: DOI: 10.1080/00222338508056602

URL: <http://dx.doi.org/10.1080/00222338508056602>

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Grafting onto Wool. XXVII. Graft Copolymerization of Mixed Vinyl Monomers by Use of Ceric Ammonium Nitrate as Redox Initiator

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ABSTRACT

In order to ascertain the effect of a donor monomer, vinyl acetate (VAc), on the graft copolymerization of acceptor monomers, ethyl acrylate (EA) and butyl acrylate (BA), grafting of mixed vinyl monomers (EA + VAc) and (BA + VAc) was carried out on Himachali wool in aqueous medium using ceric ammonium nitrate (CAN) as a redox initiator. Graft copolymerization was carried out at different temperatures for various reaction periods. Percent grafting and percent efficiency were determined as functions of 1) concentration of mixed vinyl monomers, 2) concentration of CAN, 3) concentration of HNO_3 , 4) temperature, and 5) reaction time. VAc, the donor monomer, was found to decrease percent grafting of EA and BA onto wool.

INTRODUCTION

Following the discovery of Mino and Kaizerman [1] that ceric ion is capable of forming a redox system with alcohol, a number of polyhydroxy compounds such as starch [2] and cellulose [3] 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 a redox reaction with ceric ion. It is therefore natural that vinyl monomers in the presence of ceric ion may be graft copolymerized onto wool. Nayudamma and co-workers [4] were successful in preparing the graft of collagen and poly(methyl methacrylate) (poly(MMA)) by using ceric ammonium nitrate (CAN) as redox initiator. In recent years, numerous attempts have been made to effect grafting of vinyl monomers onto wool fiber by using radical initiator [5] and metal chelates [6, 7]. It has been possible in our laboratory to effect grafting of methyl acrylate [8], ethyl acrylate [9], methyl methacrylate [10], acrylic acid [6], butyl acrylate [7], and vinyl acetate [11] onto wool by using a variety of initiating systems.

Grafting of mixed vinyl monomers onto wool has not been reported. However, mixed vinyl monomers have been grafted to cellulose [12] and poly(vinyl alcohol) [13]. In continuation of our previous study [14], we report here the grafting of mixed vinyl monomers (EA + VAc) and (BA + VAc) onto wool fiber by using CAN as the redox initiator.

EXPERIMENTAL

Ethyl acrylate (BDH) and butyl acrylate (BDH) were washed with 5% NaOH solution, water, and dried over anhydrous sodium sulfate. Dried monomers were distilled and the middle fraction was used. Vinyl acetate (SISCO) was freshly distilled. Ceric ammonium nitrate (BDH) was used as received. Nitric acid of known strength was used in all experiments.

Nitrogen gas was purified by passing it through alkaline pyrogallol solution in order to remove any traces of oxygen.

Graft Copolymerization

Purified Himachali wool (1 g) was dispersed in 200 mL of deaerated water in a three-necked flask. A weighed amount of CAN in HNO_3 of known strength was added to the reaction flask. Prior to the addition of vinyl monomers, the reaction mixture was flushed with purified nitrogen for 30 min and then a continuous supply of nitrogen was main-

tained throughout the reaction period. A calculated amount of a mixture of EA or BA and VAc was added dropwise and copolymerization was carried out for various reaction periods at different temperatures. At the end of reaction the reaction mixture was filtered and the residue was extracted with benzene for 48 h to remove homopolymer. The grafted material was dried until constant weight was obtained. From the increase in weight of the original wool fiber, percent grafting and percent efficiency were calculated as follows:

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

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

where W_1 , W_2 , and W_3 denote the weight of the wool, grafted wool after solvent extraction, and weight of mixed vinyl monomer (EA or BA + VAc) added, respectively.

Evidence of Grafting

- A. The infrared spectrum of wool-g-poly(EA + VAc) and poly(BA + VAc) showed strong absorption at 1730 and 1735 cm^{-1} , respectively, whereas ungrafted wool showed a (-CONH-) band at 1650 cm^{-1} .
- B. Wool-g-poly(EA + VAc) and poly(BA + VAc) were hydrolyzed with 6 N HCl for 24 h. All the wool went into solution, leaving behind a resinous material. IR spectra of this resinous material showed absorption at 1730 and 1735 cm^{-1} due to C=O of poly(EA + VAc) and poly(BA + VAc).
- C. Comparison of scanning electron micrographs of wool, wool-g-poly(MA + VAc) [12], wool-g-poly(EA + VAc) and wool-g-poly(BA + VAc) indicated that a considerable amount of polymer was deposited on the surface of the wool fiber (Figs. 1-3).

RESULTS AND DISCUSSION

Grafting of vinyl monomers onto cellulose by the ceric ion method has been explained by assuming a prior complex formation between ceric ion and polyhydric alcohol in the following manner:

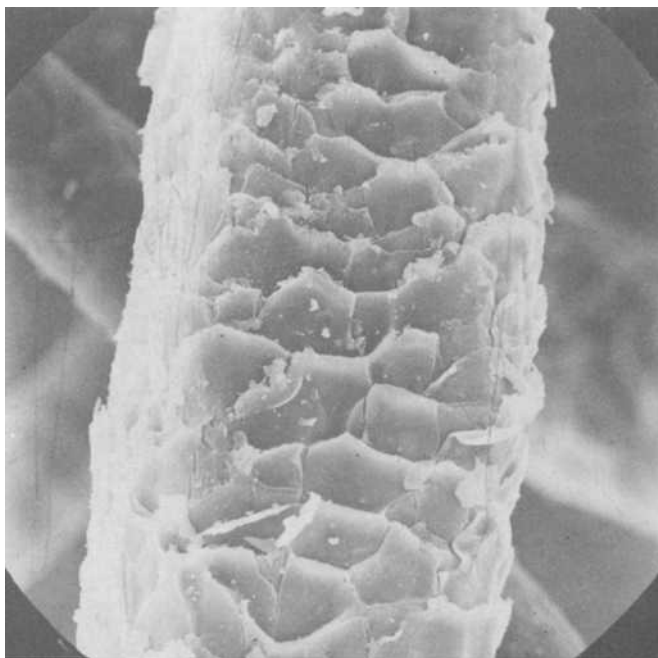


FIG. 1. Scanning electron micrograph of wool-g-poly(MA + VAc) (600 \times).

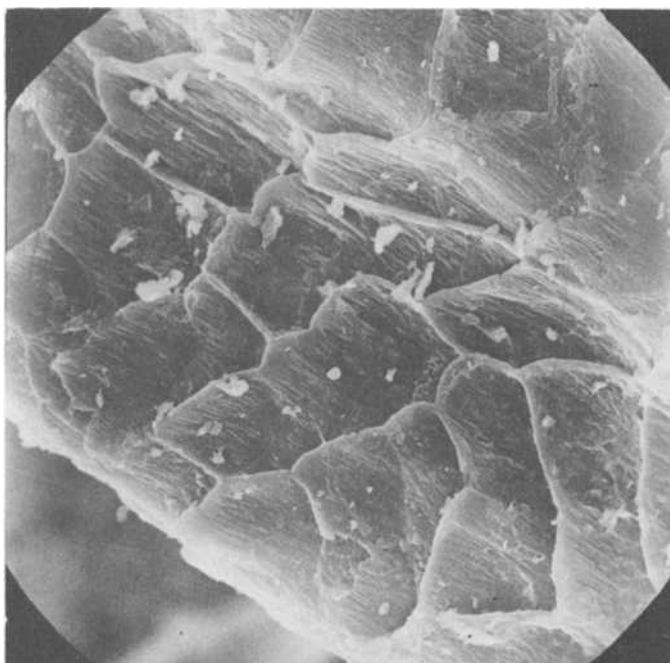


FIG. 2. Scanning electron micrograph of wool-g-poly(EA + VAc) (1300 \times).

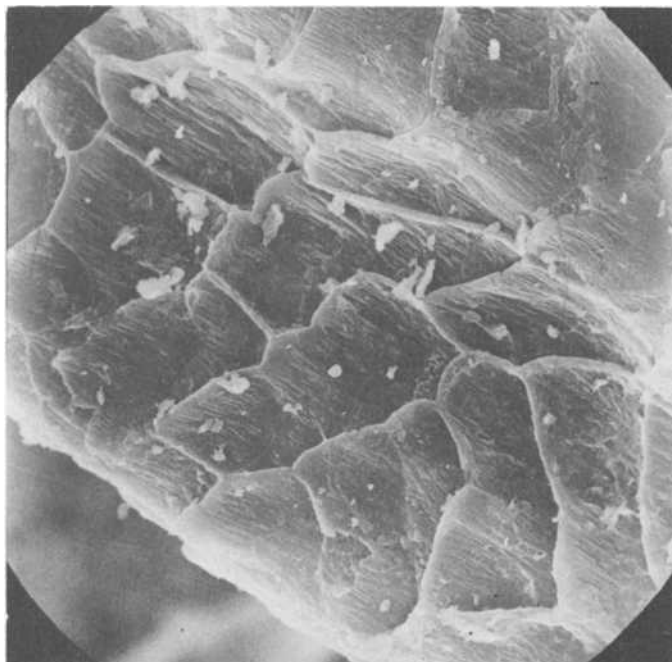
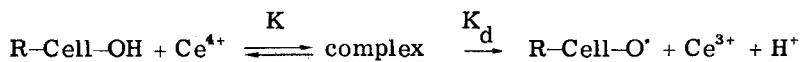
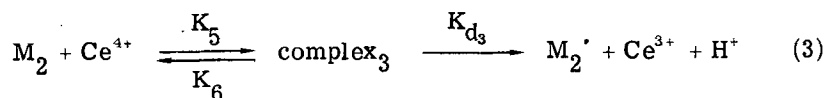
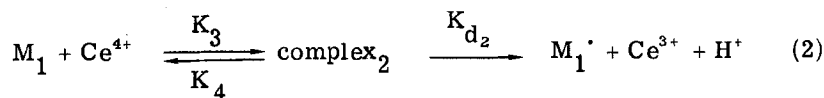
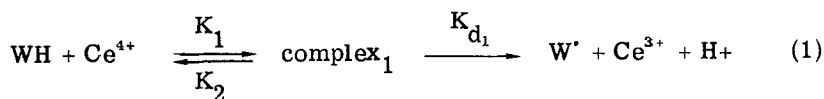


FIG. 3. Scanning electron micrograph of wool-g-poly(BA + VAc) (1300X).



This complex decomposes to generate a free radical which provides active sites for grafting of appropriate vinyl monomers. A similar mechanism was given by a number of workers to explain grafting of vinyl monomers onto starch in the presence of ceric ion. Since wool contains such functional groups as $-\text{OH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{SS}-$, and imino, it is expected that Ce^{4+} will readily form a complex with the functional groups of wool and thus promote grafting.

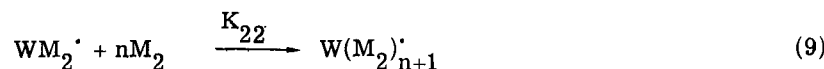
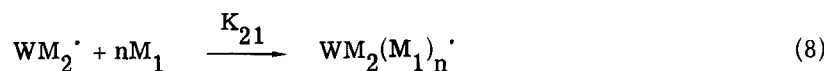
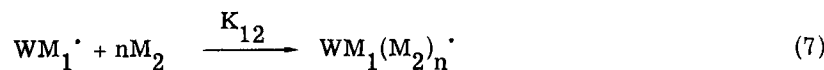
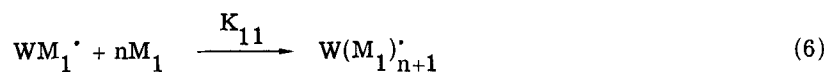
In order to ascertain the effect of a donor monomer, e.g., vinyl acetate (VAc), on the graft copolymerization of an acceptor monomer, e.g., EA and BA, grafting of mixed vinyl monomers, e.g., (EA + VAc) and (BA + VAc), was carried out in an aqueous medium using CAN as the redox initiator. The following mechanism (Eqs. 1-11) is suggested to explain the grafting of mixed vinyl monomers onto wool in the presence of ceric ion:



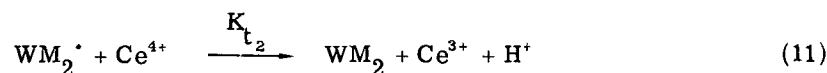
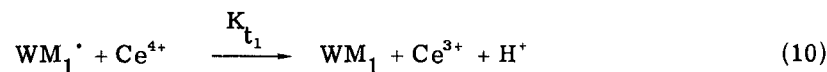
Initiation:



Propagation:



Termination:

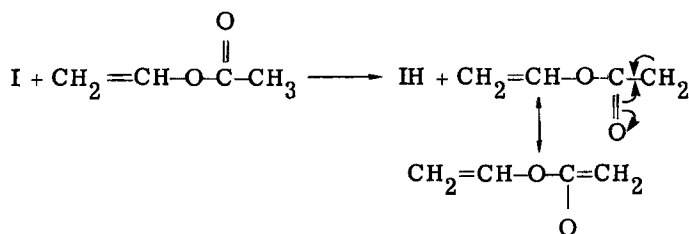


In the above postulated mechanism it is assumed that ceric ions combine with wool to form complex₁ which dissociates to give free radical sites where an appropriate monomer can be grafted. Vinyl monomers M₁ and M₂ also react with Ce⁴⁺ to give complex₂ and complex₃, respec-

tively, which favor homopolymerization. If the complex formation between monomer and Ce^{+} is favored, large amounts of homopolymer or copolymer will be obtained at the expense of the graft. The complex formation between monomer and Ce^{4+} is evident from the fact that during grafting of vinyl monomers onto wool, varying amounts of polymers of VAc + acrylates were formed. Since vinyl monomers also enter into a redox reaction with Ce^{4+} , it is expected that different monomers will show different reactivities toward grafting onto wool.

Effect of Composition of Binary Mixture of Vinyl Monomers

In accordance with the above postulated mechanism, the percent grafting should increase with an increase in the concentration of mixed vinyl monomers (EA + VAc) and (BA + VAc). It is seen from Tables 1 and 2 that the percent grafting of mixed vinyl monomers increases with an increase in the concentration of mixed vinyl monomers and reaches maximum values of 50.5 and 18.5% at mixed vinyl monomer concentrations of 33.8×10^{-2} mol/L for (EA + VAc) and 12.4×10^{-2} mol/L for (BA + VAc), respectively. However, it was observed that grafting of mixed vinyl monomers is much less than that of EA and BA alone. Under optimum conditions, EA and BA afforded maximum grafting of 121 and 71%, respectively. This clearly indicates that in the presence of VAc, grafting of acrylate monomers is suppressed. Vinyl acetate [11] is known to be a poor monomer for graft copolymerization by a radical process. The poor reactivity of VAc is attributed to the hydrogen abstraction reaction which leads to a waste of VAc in side reactions, e.g.,



EA and BA do not show such reactions since the free radical species arising from the abstraction of a hydrogen atom from these monomers are not resonance stabilized. Thus VAc is expected to decrease the percent grafting. Figures 4, 5, and 6 describe percentage of grafting and percent efficiency as functions of the mole fraction of vinyl acetate in binary mixtures of (EA + VAc) and (BA + VAc). It is seen that VAc decreases the percentage and efficiency of grafting in both cases. However, this effect is much more pronounced with MA

TABLE 1. Effect of the Concentration of a Binary Mixture of Monomers, CAN, HNO₃, Temperature, and Time on the Percent Grafting of (EA + VAc) onto Wool^a

Sample	[EA] × 10 ² mol/L	[VAc] × 10 ² mol/L	[CAN] × 10 ³ mol/L	[HNO ₃] × 10 ² mol/L	Time (min)	Temperature (°C)	% G	% E
1	23.0	0.0	6.24	12.0	120	45	121.0	26.30
2	18.4	5.4	"	"	"	"	40.0	8.66
3	13.8	10.8	"	"	"	"	31.0	6.70
4	9.2	16.2	"	"	"	"	16.0	3.45
5	4.6	21.6	"	"	"	"	12.0	2.58
6	0.0	27.0	"	"	"	"	10.0	2.15
7	13.8	0.0	"	"	"	"	41.0	14.85
8	9.2	5.4	"	"	"	"	23.0	8.30
9	4.6	10.8	"	"	"	"	12.0	4.31
10	0.0	16.2	"	"	"	"	0.0	0.00

11	23.0	10.8	"	"	"	"	"	50.5	7.81
12	"	"	"	"	"	"	35	6.0	0.92
13	"	"	"	"	"	"	55	23.0	3.56
14	"	"	"	"	"	90	45	8.0	1.23
15	"	"	"	"	"	150	"	41.0	6.34
16	"	"	"	8.0	"	120	"	12.0	1.85
17	"	"	"	16.0	"	"	"	14.0	2.16
18	"	"	3.62	12.0	"	"	"	12.0	1.85
19	"	"	6.85	"	"	"	"	13.0	2.01
20	"	"	8.46	"	"	"	"	10.0	1.54

^aWool = 1 g, water = 200 mL.

TABLE 2. Effect of the Concentration of a Binary Mixture of Monomers, CAN, HNO₃, Temperature, and Time on the Percent Grafting of (BA + VAc) onto Wool^a

Sample	[BA] × 10 ² mol/L	[VAc] × 10 ² mol/L	[CAN] × 10 ³ mol/L	[HNO ₃] × 10 ³ mol/L	Time (min)	Temperature (°C)	% G	% E
1	17.5	0.0	6.14	24.0	120	45	59.0	13.11
2	14.0	5.4	"	"	"	"	14.0	3.09
3	10.5	10.8	"	"	"	"	10.0	2.19
4	7.0	16.2	"	"	"	"	2.5	0.54
5	3.5	21.6	"	"	"	"	2.0	0.43
6	0.0	27.0	"	"	"	"	1.0	0.21
7	10.5	0.0	"	"	"	"	71.0	26.29
8	7.0	5.4	"	"	"	"	18.5	6.77
9	3.5	10.8	"	"	"	"	11.0	3.98
10	0.0	16.2	"	"	"	"	3.0	1.07

11	7.0	5.4	4.95	"	"	"	8.0	2.93
12	"	"	8.18	"	"	"	5.0	1.83
13	"	"	6.14	16.0	"	"	10.0	3.66
14	"	"	"	20.0	"	"	13.0	4.76
15	"	"	"	24.0	90	"	9.0	3.29
16	"	"	"	"	150	"	11.0	4.02
17	"	"	"	"	120	35	11.0	4.02
18	"	"	"	"	"	35	17.0	6.22
19	"	"	"	"	"	65	4.5	1.64

^aWool = 1 g, water = 200 mL.

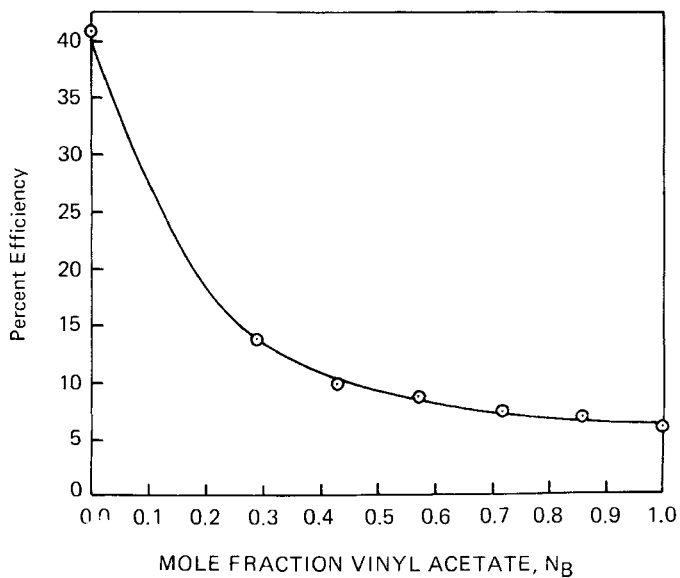
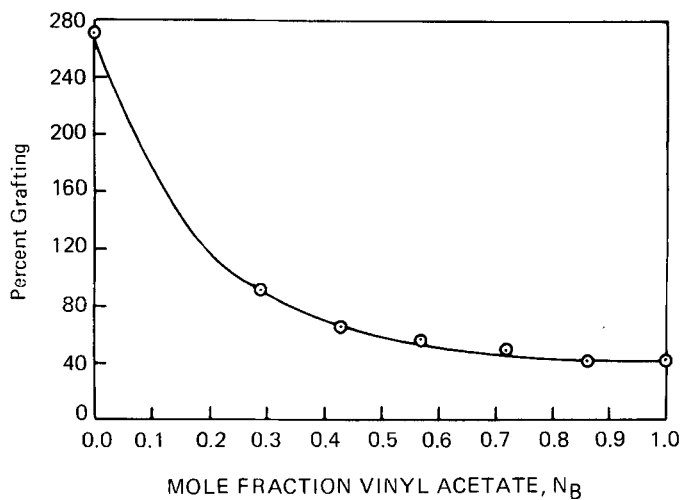


FIG. 4. Plots of percent grafting and efficiency of MA + VAc vs mole fraction of vinyl acetate in binary mixture [14].

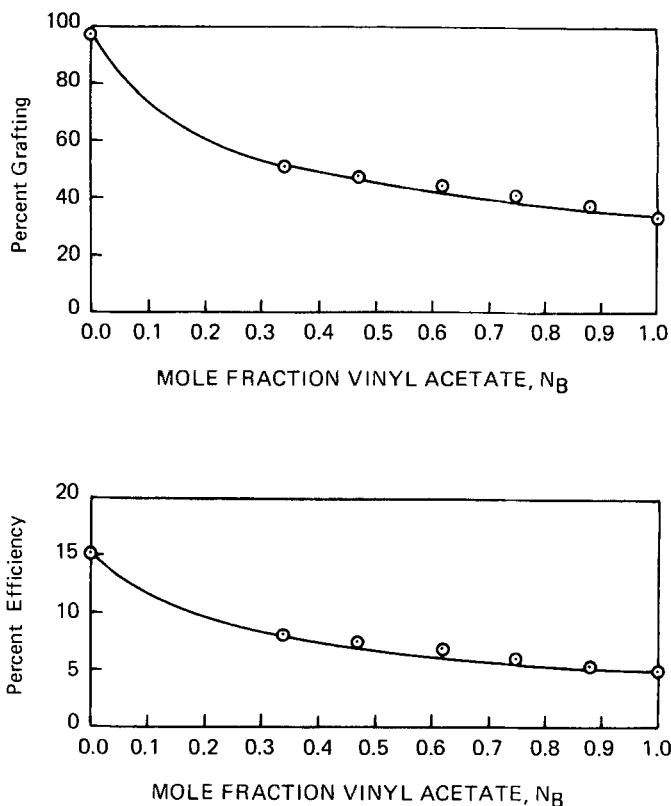


FIG. 5. Plots of percent grafting and efficiency of EA + VAc vs mole fraction of vinyl acetate in binary mixture.

[14] than with EA or BA. This may be because of the higher reactivity ratio of acrylates compared to that of VAc.

Effect of Initiator Concentration

The maximum grafting of mixed vinyl monomers occurs at $[\text{CAN}]$ 5.24×10^{-3} and 6.14×10^{-3} mol/L for (EA + VAc) and (BA + VAc), respectively. At higher concentrations, Ce^{4+} participates in the termination of growing grafted chains by the following reactions:



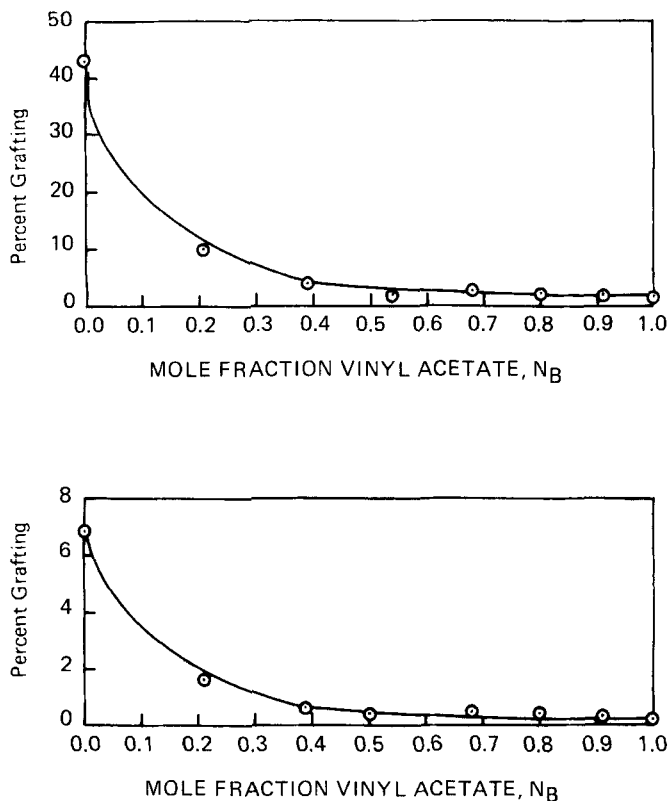
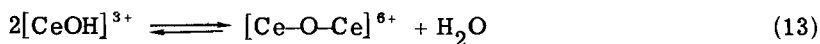
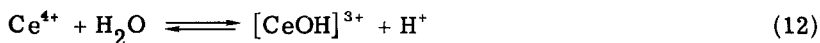


FIG. 6. Plots of percent grafting and efficiency of BA + Vac vs mole fraction of vinyl acetate in binary mixture.

A similar behavior was observed during ceric ion initiated grafting of MA, EA, and VAc individually onto wool by Misra et al. [8, 9, 11].

Effect of Nitric Acid

In the case of mixed vinyl monomers, it has been found that maximum grafting occurs at $[\text{HNO}_3] = 12.0 \times 10^{-2}$ and 24.0×10^{-2} mol/L for the (EA + VAc) and (BA + VAc) systems, respectively. Beyond these concentrations, all the ceric ions exist as Ce^{4+} which at higher concentrations is known to terminate growing polymeric chains [15]. The observed zero grafting in the absence of HNO_3 can be explained by the following equilibrium reaction in aqueous solution:



In the absence of acid, Ce^{4+} primarily exists as $[\text{Ce}]^{4+}$, $[\text{CeOH}]^{3+}$, and $[\text{Ce-O-Ce}]^{6+}$. $[\text{Ce-O-Ce}]^{6+}$, due to its large size, is incapable of entering into complex formation with the functional groups of wool fiber. Thus, with an increase in acid concentration, the equilibria (12) and (13) shift toward the formation of more $[\text{CeOH}]^{3+}$ and $[\text{Ce}]^{4+}$ which, because of their small size, can easily form complexes with the functional groups of wool, resulting in a higher percentage of grafting. When the concentration of acid is further increased, the percent grafting begins to decrease because of the formation of a large amount of $[\text{Ce}]^{4+}$ and $[\text{CeOH}]^{3+}$. At higher concentrations these species accelerate the termination of growing grafted chains, resulting in a decrease in percent grafting.

ACKNOWLEDGMENTS

D.S.S. and J.K. are thankful to CSIR, New Delhi, and the Department of Atomic Energy, Government of India, Bombay, for the award of Senior Research Fellowships.

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Accepted by editor March 26, 1984

Received for publication April 2, 1984