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B. N. Misra<sup>a</sup>; D. S. Sood<sup>a</sup>; I. K. Mehta<sup>a</sup>

<sup>a</sup> Department of Chemistry, Himachal Pradesh University, Simla, India

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## Grafting onto Wool. XIX. Graft Copolymerization of Mixed Vinyl Monomers by Use of Ceric Ammonium Nitrate as Redox Initiator\*

B. N. MISRA, D. S. SOOD, and I. K. MEHTA

Department of Chemistry  
Himachal Pradesh University  
Simla 171005, India

### ABSTRACT

In order to ascertain the effect of a donor monomer, vinyl acetate (VAc), on the graft copolymerization of an acceptor monomer, methyl acrylate (MA), grafting of mixed vinyl monomers (VAc + MA) was carried out on Himachali wool in aqueous medium using ceric ammonium nitrate (CAN) as redox initiator. Optimum conditions for maximum grafting of mixed monomer were evaluated by conducting graft copolymerization reactions as functions of 1) concentration of mixed vinyl monomers (VAc + MA), 2) concentration of CAN, 3) concentration of  $\text{HNO}_3$ , 4) temperature, and 5) reaction time. Maximum grafting of 90.0% of mixed vinyl monomers occurred at 45°. Nitric acid was found to catalyze the graft copolymerization. VAc, the donor monomer, was found to decrease percent grafting of MA onto wool. An explanation based on the relative reactivities of MA and VAc toward grafting is suggested.

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## INTRODUCTION

Modification of natural and synthetic polymers by the graft copolymerization technique has been extensively studied. A variety of vinyl monomers has been successfully grafted to cellulose [1, 2], starch [3, 4], rubber [5], and synthetic polymers [6] by using various types of initiators. Comparatively less attention has been paid to the modification of proteins in general and of wool fiber in particular by the graft copolymerization method. Among fibrous proteins, collagen and silk have been subjected to graft copolymerization by using different initiating systems. Nayudamma and co-workers [7] were successful in preparing the graft of collagen and poly(methyl methacrylate) (PMMA) by using ceric ammonium nitrate (CAN) as the redox initiator. Styrene (St) and acrylonitrile were grafted to silk by  $\gamma$ -irradiation, and from infrared spectra of grafted samples it was concluded that grafting of polystyrene (PS) and polyacrylonitrile (PAN) occurred on silk [8]. Kenyon and Garnett [9] were recently able to graft ethyl acrylate (EA) to wool fiber in the presence of nitric acid and a good swelling solvent. Various redox systems have been successfully utilized in effecting grafting of vinyl monomers onto wool [10, 11]. In recent years, numerous attempts have been made to effect grafting of vinyl monomers onto wool fiber by using radical initiator [12], metal chelates [13], and  $\gamma$ -irradiation [14]. It has been possible in our laboratory to effect grafting of MA [15], EA [16], MMA [17], Acrylic acid (AAc) [13], butyl acrylate (BA) [18], styrene (St) [12], and vinyl acetate (VAc) [19] onto wool fiber by using a variety of initiating systems.

Grafting of mixed vinyl monomers onto wool fiber has not been reported. However, mixed monomers have been grafted to cellulose [20] and poly(vinyl alcohol) [21]. In an attempt to study the effect of donor monomer on grafting of acceptor monomer, we have studied grafting of mixed vinyl monomers (VAc + MA) onto wool fiber by using CAN as the redox initiator. The percentage of grafting has been determined as a function of various parameters. The solubility behavior of grafted samples in different solvent systems has also been studied.

## EXPERIMENTAL

Methyl acrylate (BDH) was treated with 5% NaOH solution, washed with water, and dried over anhydrous sodium sulfate. Dried methyl acrylate was 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 was purified by passing it through a freshly prepared alkaline pyrogallol solution in order to remove any traces of oxygen.

Graft Copolymerization

Purified Himachali wool fiber (1.0 g) was dispersed in 300 mL of deaerated water in a three-necked flask. A weighed amount of CAN in  $\text{HNO}_3$  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 maintained throughout the reaction period. A calculated amount of a mixture of VAc and MA was added dropwise and the copolymerization was carried out for various reaction periods at different temperatures. At the end of the reaction the reaction mixture was filtered, and the residue was extracted with benzene for 48 h to remove the homopolymer. The grafted material was dried at  $50^\circ$  until constant weight was obtained. From the increase in weight of the original wool fiber, percent grafting and percent efficiency were calculated as follows:

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

where  $W_1$ ,  $W_2$ , and  $W_3$  denote, respectively, the weight of wool, grafted wool after benzene extraction, and weight of mixed vinyl monomer (MA + VAc) added.

Evidence of Grafting

A. The infrared spectrum of wool-g-poly(MA + VAc) showed strong absorption at  $1725 \text{ cm}^{-1}$ , attributed to  $\text{C}=\text{O}$  of poly(MA + VAc). No such absorption band was present in the IR spectrum of wool.

B. Wool-g-poly(MA + VAc) was hydrolyzed with 6 N HCl for 24 h. All the wool fiber goes into solution, leaving behind a resinous material. IR spectrum of this resinous material showed absorption at  $1725 \text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of poly(MA + VAc).

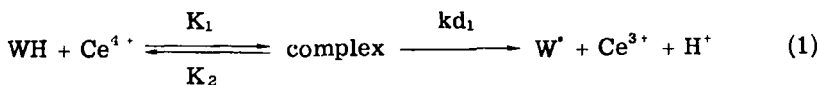
C. Comparison of scanning electron micrographs of wool and wool-g-poly(MA + VAc) indicated considerable deposition of polymer on the wool surface.

## RESULTS AND DISCUSSION

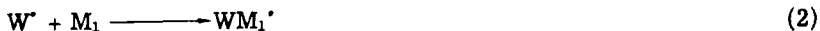
Ceric ion is known to form complexes with  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ , and imino groups. Wool (WH) contains numerous functional groups such as  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$ ,  $-\text{SS}-$ ,  $-\text{COOH}$ , and imino group. All these functional groups of wool are capable of forming

complexes with ceric ion. The complexes can subsequently decompose to generate macro radical ( $W^{\cdot}$ ) on wool backbone where appropriate vinyl monomer could be grafted. By following this method it has been possible to graft a number of vinyl monomers onto wool fiber. Misra et al. have reported grafting of MA [15] and VAc [19] onto wool in the presence of CAN as redox initiator. It was observed that under optimum conditions MA could be grafted to the extent of 271% and VAc to the extent of 39.5% only.

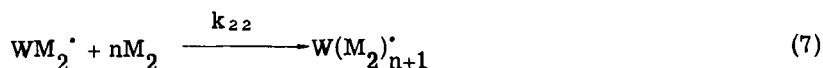
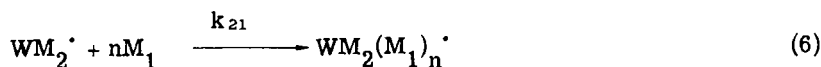
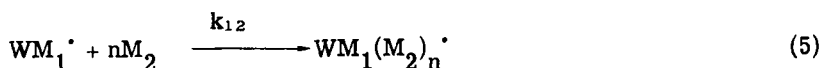
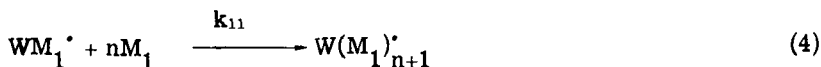
Table 1 shows that mixed vinyl monomers (MA + VAc) under optimum conditions afforded less grafting than MA alone. This indicates that in the presence of VAc, grafting of MA is suppressed. In analogy with the mechanism of ceric ion initiated grafting of single monomer onto wool, the following mechanism (Eqs. 1-9) is suggested for grafting of mixed monomers (MA + VAc) onto wool fiber.



#### Initiation



#### Propagation



#### Termination

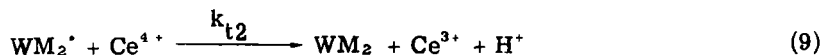
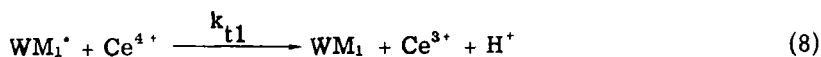


TABLE 1. Effect of Concentration of Mixed Monomers (MA + VAc) on Percent Grafting of Mixed Monomers onto Wool<sup>a</sup>

No.	[MA] × 10 <sup>2</sup> mol/L	[VAc] × 10 <sup>2</sup> mol/L	% Grafting	% Efficiency
1	18.4	0.0	166.5	35.05
2	14.7	3.6	28.0	5.91
3	11.0	7.2	22.0	4.67
4	7.3	10.8	15.5	3.19
5	3.6	14.4	14.5	3.10
6	0.0	18.0	11.0	2.38
7	11.0	0.0	64.5	22.63
8	7.3	3.6	14.0	4.94
9	3.6	7.2	7.0	2.49
10	0.0	10.8	8.0	2.86
11	25.7	0.0	271.0	40.75
12	22.0	3.6	62.0	9.35
13	18.4	7.2	90.0	13.60
14	14.7	10.8	63.5	9.63
15	11.0	14.4	55.5	8.44
16	7.3	18.0	47.0	7.17
17	3.6	21.6	44.0	6.73
18	0.0	25.2	39.5	6.06

<sup>a</sup>Wool = 1 g; temperature = 45°C; [CAN] =  $8.97 \times 10^{-3}$  mol/L; water = 300 mL; time = 180 min; [HNO<sub>3</sub>] =  $16.0 \times 10^{-2}$  mol/L.

In addition to termination steps (8) and (9), termination can also occur by involving a combination of different growing polymeric radicals.

#### Effect of Composition of Monomer Mixture

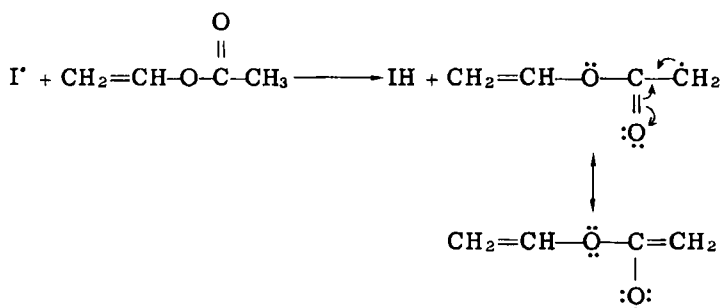
In accordance with the above-postulated mechanism, percent grafting should increase with an increase in the concentration of mixed vinyl monomers (MA + VAc). It is observed from Table 1 that percent grafting of (MA + VAc) increases with increasing concentration

TABLE 2. Effect of Concentration of Ceric Ammonium Nitrate on Percent Grafting of Mixed Monomers onto Wool<sup>a</sup>

No.	[CAN] × 10 <sup>3</sup> mol/L	% Grafting	% Efficiency
1	5.37	14.5	2.19
2	7.17	25.5	3.85
3	8.97	90.0	13.60
4	10.7	15.0	2.26

<sup>a</sup>Wool = 1 g; temperature = 45°C; [MA] = 18.4 × 10<sup>-2</sup> mol/L; [VAc] = 7.2 × 10<sup>-2</sup> mol/L; water = 300 mL; time = 180 min; [HNO<sub>3</sub>] = 16.0 × 10<sup>-2</sup> mol/L.

of mixed vinyl monomers and reaches the maximum value (90.0%) at a mixed monomer concentration of 25.6 × 10<sup>-2</sup> mol/L. However, it is also observed that maximum grafting of mixed vinyl monomers is much less than that given by MA alone. Under optimum conditions, MA affords maximum grafting of 271.0%. It can also be seen from TABLE 1 that VAc alone under optimum conditions affords maximum grafting to the extent of 39.5%. This clearly indicates that in the presence of VAc, grafting of MA is suppressed. Earlier work [19] from this laboratory has indicated that VAc is a poor monomer for graft copolymerization. The poor reactivity of VAc is attributed to the high tendency of VAc to undergo monomer transfer reactions, leading to wastage of VAc in side reactions in the following manner:



No such monomer transfer reactions are possible with MA, since the radical arising from the abstraction of hydrogen atom from the monomer (MA) is not resonance stabilized. Thus VAc would be expected to decrease percent grafting. It is important to note that MA with  $r_1 = 9.0$  and VAc with  $r_2 = 0.1$  are not an ideal monomer pair

TABLE 3. Effect of Concentration of Nitric Acid on the Percent Grafting of Mixed Monomers onto Wool<sup>a</sup>

No.	[HNO <sub>3</sub> ] × 10 <sup>2</sup> mol/L	% Grafting	% Efficiency
1	10.6	32.0	4.84
2	13.3	63.0	9.53
3	16.0	90.0	13.60
4	18.6	11.0	1.73

<sup>a</sup>Wool = 1 g; temperature = 45°C; [MA] =  $18.4 \times 10^{-2}$  mol/L; [VAc] =  $7.2 \times 10^{-2}$  mol/L; water = 300 mL; time = 180 min; [CAN] =  $8.97 \times 10^{-3}$  mol/L.

for copolymerization [22]. Thus the graft copolymer mainly consists of PMA chain along with a few PVAc chains. During grafting of MA alone it was observed that the grafted wool fiber was sticky; this was due to the extensive cross-linking tendency of MA. The graft copolymer obtained with mixed vinyl monomers (MA + VAc) was soft. Grafting of mixed vinyl monomers (MA + VAc) affords grafted material with superior luster.

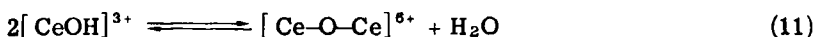
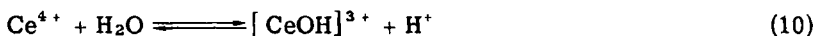
#### Effect of Concentration of Initiator (Table 2)

The maximum grafting (90%) of mixed vinyl monomer occurs at [CAN] =  $8.97 \times 10^{-3}$  mol/L. At a higher concentration, Ce<sup>4+</sup> participates in the termination of growing grafted chain. A similar behavior was observed during grafting of MA and VAc separately onto wool in the presence of CAN.

#### Effect of Nitric Acid (Table 3)

In all grafting work carried out in this laboratory using Ce<sup>4+</sup> initiator, it was observed that a small amount of HNO<sub>3</sub> promotes grafting. In the present case also, mixed monomers were found to afford maximum grafting at [HNO<sub>3</sub>] =  $16.0 \times 10^{-2}$  mol/L. Beyond this concentration, all the ceric ion exists as Ce<sup>4+</sup> which at higher concentrations is known to terminate growing polymeric chains. The observed zero grafting in the absence of HNO<sub>3</sub> can be explained by the following equilibrium reaction. Ce<sup>4+</sup> reacts with water in the following manner:





In the absence of acids,  $\text{Ce}^{4+}$  primarily exists as  $[\text{Ce-O-Ce}]^{6+}$  which, due to its large size, is incapable of entering into complex formation with functional groups of wool fiber. A similar explanation was found to hold good for grafting of both acceptor and donor monomers during ceric ion initiated grafting onto wool.

### Effect of Time and Temperature (Tables 4 and 5)

The maximum grafting of mixed vinyl monomers was found to occur at  $45^\circ$  which was also the temperature at which single monomer afforded maximum grafting. At higher temperature, various chain transfer reactions are believed to be accelerated, resulting in a decrease in percent grafting. Maximum grafting of mixed monomer was obtained within 180 min.

### Solubility Behavior in Standard Solvent System [23]

Table 6 illustrates the solubility behavior of wool, wool-g-poly(MA), wool-g-poly(VAc), and wool-g-poly(MA + VAc) in 0.1 N NaOH, 4 M HCl, oxidizing solvent (2% peracetic acid), and urea bisulfite solution. It is apparent from Table 6 that wool-g-poly(MA + VAc) closely resembles wool-g-poly(MA) toward solubility in the above-mentioned solvents. This may indicate that the graft obtained with mixed vinyl

TABLE 4. Effect of Time on Percent Grafting of Mixed Monomers onto Wool<sup>a</sup>

No.	Time (min)	% Grafting	% Efficiency
1	120	13.5	2.04
2	150	15.0	2.26
3	180	90.0	13.60
4	210	24.0	3.63

<sup>a</sup>Wool = 1 g; temperature =  $45^\circ\text{C}$ ;  $[\text{MA}] = 18.4 \times 10^{-2}$  mol/L; water = 300 mL;  $[\text{CAN}] = 8.97 \times 10^{-3}$  mol/L;  $[\text{VAc}] = 7.2 \times 10^{-2}$  mol/L;  $[\text{HNO}_3] = 16.0 \times 10^{-2}$  mol/L.

TABLE 5. Effect of Temperature on Percent Grafting of Mixed Monomers onto Wool<sup>a</sup>

No.	Temperature (°C)	% Grafting	% Efficiency
1	35	36.5	5.52
2	45	90.0	13.60
3	55	17.5	2.64
4	65	12.0	1.81

<sup>a</sup>Wool = 1 g; time = 180 min; [MA] =  $18.4 \times 10^{-2}$  mol/L; water = 300 mL; [CAN] =  $8.97 \times 10^{-3}$  mol/L; [VAc] =  $7.2 \times 10^{-2}$  mol/L; [HNO<sub>3</sub>] =  $16.0 \times 10^{-2}$  mol/L.

TABLE 6. Solubility Behavior of Ungrafted, Single Monomer Grafted, and Mixed Monomer Grafted (MA + VAc) Grafted Wool in Standard Solvents

No.	Sample	% Solubility			
		0.1 N NaOH	4 M HCl	Oxidizing solvent	Urea bisulfite
1	Wool	20.6	10.7	12.5	12.9
2	W-g-poly(MA) <sup>a</sup>	19.1	18.0	8.3	9.0
3	W-g-poly(VAc) <sup>b</sup>	9.17	8.11	1.2	5.6
4	W-g-poly(MA + VAc) <sup>c</sup>	18.2	8.0	11.0	5.0

<sup>a</sup>Refers to Experiment 11 of Table 1.

<sup>b</sup>Refers to Experiment 18 of Table 1.

<sup>c</sup>Refers to Experiment 13 of Table 1.

monomers (MA + VAc) largely consists of PMA chain with few PVAc chain, which is expected from the consideration of  $r_1$  and  $r_2$  values of MA and VAc during copolymerization by radical methods.

#### ACKNOWLEDGMENT

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## REFERENCES

- [ 1 ] B. N. Misra, J. K. Jassal, and C. S. Pande, J. Polym. Sci., Polym. Chem. Ed., **16**, 295 (1976).
- [ 2 ] B. N. Misra, J. K. Jassal, and C. S. Pande, Ind. J. Chem., **16(A)**, 1033 (1978).
- [ 3 ] B. K. Srivastava, C. S. Pande, and B. N. Misra, Ibid., **14(A)**, 274 (1976).
- [ 4 ] G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, J. Appl. Polym. Sci., **15**, 1889 (1971).
- [ 5 ] J. Le Bras and P. Compagnon, C. R. Acad. Sci., **212**, 616 (1941).
- [ 6 ] I. M. Trivedi and P. C. Mehta, J. Appl. Polym. Sci., **19**, 14 (1975).
- [ 7 ] Y. Nayudamma, K. P. Rao, and K. T. Joseph, J. Polym. Sci., A-1, **9**, 3199 (1971).
- [ 8 ] S. A. Azimov, Kh. U. Osmanov, N. V. Kordub, and S. I. Sleparkova, BCIRA J., **41(1)**, 23 (1961).
- [ 9 ] R. S. Kenyon and J. L. Garnett, J. Polym. Sci., Polym. Lett. Ed., **11**, 651 (1973).
- [ 10 ] B. N. Misra, P. S. Chandel, and R. Dogra, J. Polym. Sci., Polym. Chem. Ed., **16**, 1801 (1978).
- [ 11 ] M. Negishi, K. Arai, S. Okada, and I. Nagakura, J. Appl. Polym. Sci., **9**, 3465 (1965).
- [ 12 ] P. S. Chandel and B. N. Misra, J. Polym. Sci., Polym. Chem. Ed., **15**, 1549 (1977).
- [ 13 ] B. N. Misra, I. K. Mehta, and D. S. Sood, J. Macromol. Sci.-Chem., **A14(8)**, 1255 (1980).
- [ 14 ] M. K. Horio, K. O. Gani, T. Kondo, and K. Sekimoto, Bull. Inst. Chem. Res., **41**, 10 (1963).
- [ 15 ] B. N. Misra and P. S. Chandel, J. Polym. Sci., Polym. Chem. Ed., **15**, 1545 (1977).
- [ 16 ] B. N. Misra, I. K. Mehta, and R. Dogra, J. Macromol. Sci.-Chem., **A12(10)**, 1513 (1978).
- [ 17 ] B. N. Misra and I. K. Mehta, J. Polym. Sci., Polym. Chem. Ed., **18**, 1911 (1980).
- [ 18 ] B. N. Misra, D. S. Sood, and R. K. Sharma, J. Appl. Polym. Sci., **26**, 3797 (1981).
- [ 19 ] B. N. Misra, I. K. Mehta, and R. Dogra, Ibid., **24**, 1595 (1979).
- [ 20 ] A. Hebeish and P. C. Mehta, Cellul. Chem. Technol., **3**, 469 (1969).
- [ 21 ] G. Odian and J. H. T. Kho, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., **9**, 675 (1968).
- [ 22 ] B. Vollmert, in Polymer Chemistry, Springer, New York, p. 109, 1973.
- [ 23 ] R. E. Whitfield and W. L. Wasley, in Chemical Reactions of Polymers (High Polymers, Vol. 19), Wiley-Interscience, New York, 1964, p. 439.

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