Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Grafting onto Wool. XV. Graft Copolymerization of MA and MM A by Use of Mn(acac)$_3$ as Initiator

B. N. Misra[a]; R. K. Sharma[a]; I. K. Mehta[a]
[a] Department of Chemistry, Himachal Pradesh University, Simla, India

To cite this Article Misra, B. N. , Sharma, R. K. and Mehta, I. K.(1982) 'Grafting onto Wool. XV. Graft Copolymerization of MA and MM A by Use of Mn(acac)$_3$ as Initiator', Journal of Macromolecular Science, Part A, 17: 3, 489 — 500
To link to this Article: DOI: 10.1080/00222338208056486
URL: http://dx.doi.org/10.1080/00222338208056486

J. MACROMOL. SCI.–CHEM., A17(3), pp. 489-500 (1982)

Grafting onto Wool. XV. Graft Copolymerization of MA and MMA by Use of $Mn(acac)_3$ as Initiator

B. N. MISRA, R. K. SHARMA, and I. K. MEHTA

Department of Chemistry
Himachal Pradesh University
Simla 171005, India

ABSTRACT

Graft copolymerization of acceptor monomers MA and MMA onto Himachali wool fiber in an aqueous medium was studied by using $Mn(acac)_3$ as initiator. Nitric acid was found to catalyze the graft copolymerization. Percentage of grafting and percent efficiency have been determined as functions of the concentration of chelate, nitric acid, monomer, time, and temperature. Under optimum conditions, MMA produced a maximum grafting of 82.5% while MA afforded maximum grafting to the extent of 27.5%. Relative reactivities of MA and MMA toward grafting have been compared with those of EA, BA, and VAc reported earlier from this laboratory. Different vinyl monomers were found to follow the following reactivity order toward grafting onto wool fiber in the presence of $Mn(acac)_3$: MMA > EA > BA > MA > VAc. An attempt has been made to explain the observed reactivity pattern shown by different vinyl monomers in graft copolymerization reactions.

INTRODUCTION

In recent years many attempts have been made to modify wool fibers by a graft copolymerization technique. One of the major problems in wool grafting is the formation of large amount of homopolymer which presents considerable difficulty in the purification of of the graft. Apart from this, formation of homopolymer leads to the waste of expensive monomers. In order to overcome these difficulties, attempts have been made to search for new initiating systems that would selectively afford graft or at least minimize the formation of homopolymer. For effecting grafting onto wool fiber [1-3], a variety of initiating systems have been tried with varying degrees of success. A comprehensive research program on grafting onto wool fiber has been initiated in our laboratory, and it has been possible to effect grafting of a variety of vinyl monomers by using ceric ion [4-6], ceric-amine system [7-9], Fenton's reagent [10], KPS-FAS system [11], and BPO [12] in the presence of suitable pH modifiers as initiators. Use of metal chelates as graft initiators has not been extensively investigated. Metal chelates are reported [13] to produce free radical species upon heating. It has also been reported that certain metal chelates can initiate polymerization of styrene [13]. Kastning et al. [14] have reported that of the simple acetylacetonates, those of Mn^{III} and Co^{III} are the most active initiators. Indicator and Linder [15] reported that Co^{II}, Co^{III}, Cr^{III}, and Fe^{III} acetyl acetonates in the presence of TBHP can be used as initiators for the polymerization of styrene. Bamford and co-workers [16] have made extensive studies on the polymerization of AN, MMA, St, and VAc by using a variety of metal chelates as initiators. Nandi et al. [17] have reported on the polymerization of MMA in the presence of Fe^{III} acetyl acetonate. Relatively less attention has been paid to the utilization of metal chelates as graft initiators. Recently Misra et al. [18] have been able to effect grafting of MMA, VAc, and AAc onto Himachali wool fiber by using $VO(acac)_2$ as initiator. Nayak and co-workers [19] observed that MMA could be grafted to wool fiber in the presence of hexavalent chromium. In a previous paper [20] we reported studies on the suitability of $Mn(acac)_3$ as the initiator for grafting EA, BA, and VAc onto wool fiber. It was observed that not all vinyl monomers are equally reactive toward graft copolymerization in the presence of $Mn(acac)_3$. This study indicated that vinyl monomers show selectivity in $Mn(acac)_3$-initiated grafting. This effect was particularly pronounced when grafting was carried out in the presence of electron donor additives. As an extension of this work, in the present article we report studies on grafting of acceptor monomers, e.g., MMA and MA, onto wool by using $Mn(acac)_3$ as initiator with the objective of comparing relative reactivities of different vinyl monomers toward grafting onto wool fiber. Several grafting experiments were carried out in the presence of $ZnCl_2$ as additive. Grafting of MMA was enhanced in the presence of $ZnCl_2$.

Percent grafting and percent efficiency were determined as functions of various reaction parameters, and the results are presented in Tables 1 and 2. The percentage of grafting and percent efficiency were determined in the following manner:

TABLE 1a. Effect of Temperature on Percent Grafting of MMA[a]

No.	Temperature (°C)	% Grafting	% Efficiency
1	50	10.0	2.12
2	65	27.0	5.74
3	75	26.0	5.53
4	85	20.0	4.25

[a] Wool = 1 g [$Mn(acac)_3$] = 17.4×10^{-3} mol/L; [MMA] = 23.5×10^{-2} mol/L; water = 200 mL; [HNO_3] = 24×10^{-2} mol/L; time = 180 min.

TABLE 1b. Effect of Concentration of $Mn(acac)_3$ on Percent Grafting of MMA[a]

No.	[$Mn(acac)_3$] (mol/L)	% Grafting	% Efficiency
1	6.3×10^{-3}	9.5	2.02
2	11.6×10^{-3}	21.5	4.5
3	17.4×10^{-3}	46.0	9.78
4	20.5×10^{-3}	34.0	7.23
5	21.6×10^{-3}	39.5	8.40

[a] Wool = 1 g; temperature = 65°C; [MMA] = 23.5×10^{-2} mol/L; water = 200 mL; time = 180 min; [HNO_3] = 24.0×10^{-2} mol/L.

TABLE 1c. Effect of Concentration of HNO_3 on Percent Grafting of MMA[a]

No.	[HNO_3] (mol/L)	% Grafting	% Efficiency
1	24×10^{-2}	46.0	9.78
2	32×10^{-2}	41.0	8.72
3	16×10^{-2}	5.5	1.12

[a] Wool = 1 g; temperature = 65°C; [MMA] = 23.5×10^{-2} mol/L; water = 200 mL; time = 180 min; [$Mn(acac)_3$] = 17.4×10^{-3} mol/L.

TABLE 1d. Effect of Time on Percent Grafting of MMA[a]

No.	Time (min)	% Grafting	% Efficiency
1	90	7.0	1.48
2	120	7.5	1.38
3	150	15.5	3.29
4	180	46.0	9.78

[a] Wool = 1 g [Mn(acac)$_3$] = 17.4 × 10^{-3} mol/L; [MMA] = 23.5 × 10^{-2} mol/L; water = 200 mL; [HNO_3] = 24 × 10^{-2} mol/L; temperature = 65°C.

TABLE 1e. Effect of Concentration of MMA on Percent Grafting[a]

No.	[MMA] (mol/L	% Grafting	% Efficiency
1.	23.5 × 10^{-2}	46.0	9.78
2	32.9 × 10^{-2}	47.0	7.14
3	42.3 ×10^{-2}	82.5	9.75
4	51.7 × 10^{-2}	43.5	4.20

[a] Wool = 1 g; temperature = 65°C; [HNO_3] = 24 × 10^{-2} mol/L; water = 200 mL; time = 180 min; [Mn(acac)$_3$] = 17.4 × 10^{-3} mol/L.

TABLE 2a. Effect of Concentration of MA on Percent Grafting[a]

No.	[MA] (mol/L)	% Grafting	% Efficiency
1	27.6 × 10^{-2}	2.5	0.5
2	38.0 × 10^{-2}	1.0	0.1
3	16.5 × 10^{-2}	1.5	0.5

[a] Wool = 1 g; temperature = 65°C; [HNO_3] = 24 × 10^{-2} mol/L; water = 200 mL; time = 180 min; [Mn(acac)$_3$] = 8.8 × 10^{-3} mol/L.

TABLE 2b. Effect of Temperature on Percent Grafting of MA[a]

No.	Temperature (°C)	% Grafting	% Efficiency
1	45	0	0
2	50	2.5	0.5
3	65	27.5	5.6
4	70	16.0	3.3

[a] Wool = 1 g; time = 180 min; [HNO_3] = 24×10^{-2} mol/L; water = 200 mL; [MA] = 27.6×10^{-2} mol/L; [$Mn(acac)_3$] = 8.8×10^{-3} mol/L.

TABLE 2c. Effect of Concentration of $Mn(acac)_3$ on Percent Grafting of MA[a]

No.	[$Mn(acac)_3$] (mol/L)	% Grafting	% Efficiency
1	8.8×10^{-3}	27.5	5.6
2	6.3×10^{-3}	5.5	1.1
3	11.6×10^{-3}	5.4	1.1
4	17.4×10^{-3}	5.5	1.1

[a] Wool = 1 g; time = 180 min; [HNO_3] = 24×10^{-2} mol/L; water = 200 mL; [MA] = 27.6×10^{-2} mol/L; temperature = 65°C.

TABLE 2d. Effect of Concentration of HNO_3 on Percent Grafting of MA[a]

No.	[HNO_3] (mol/L)	% Grafting	% Efficiency
1	16.0×10^{-2}	1.2	0.2
2	24.0×10^{-2}	27.5	5.6
3	32.0×10^{-2}	17.0	3.5

[a] Wool = 1 g; temperature = 65°C; [MA] = 27.6×10^{-2} mol/L; water = 200 mL; [$Mn(acac)_3$] = 8.8×10^{-3} mol/L; time = 180 min.

TABLE 2e. Effect of Time on Percent Grafting of MA[a]

No.	Time (min)	% Grafting	% Efficiency
1	120	4.0	0.8
2	150	16.0	3.3
3	180	27.5	5.6
4	210	18.0	3.7

[a] Wool = 1 g; temperature = 65°C; [HNO_3] = 24×10^{-2} mol/L; water = 200 mL; [MA] = 27.6×10^{-2} mol/L; [$Mn(acac)_3$] = 8.8×10^{-3} mol/L.

$$\%G = \frac{W_2 - W_1}{W_1} \times 100; \qquad \%E = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2, and W_3 are the weights of wool, grafted wool after benzene extraction, and the monomer added, respectively.

EXPERIMENTAL

Preparation of Manganese Acetyl Acetonate

The chelate was prepared by the method reported in Inorganic Synthesis [21] and characterized by IR spectroscopy and decomposition temperature. The chelate decomposes at 151°C (literature value 152°C). The IR spectrum shows a strong band at 1600 cm^{-1} assigned to C=O of chelate.

Materials and Methods

Methyl methacrylate and methyl acrylate were washed with 5% NaOH and dried over anhydrous sodium sulfate. Dried MMA and MA were then distilled and the middle fraction was used. Nitric acid (BDH) of known strength was used. Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Himachali wool was purified by the method described earlier [4].

Graft Copolymerization

One gram of purified wool was dispersed in 200 mL of deareated water in a three-necked flask. A known quantity of metal chelate was added. Prior to the addition of the monomer, nitrogen was passed through the reaction flask for about 30 min and then a continuous supply of nitrogen was maintained throughout the reaction period. Vinyl monomer was added dropwise to the reaction flask. Copolymerization reaction was carried out under stirring at different temperatures for various reaction periods.

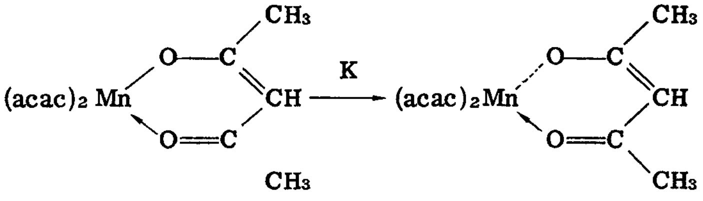
After the reaction was over, the reaction mixture was filtered and the residue was extracted with benzene for removal of PMMA and PMA.

Evidence of Grafting

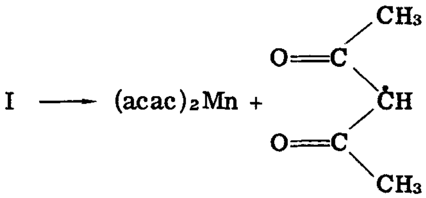
Wool-g-P(MA) and wool-g-P(MMA) were hydrolyzed with 6 N HCl at 115°C for 24 h. After all the wool had gone into solution, the resinous masses obtained were characterized by IR spectroscopy as P(MA) and P(MMA), respectively. The physical mixtures of wool and benzene solution of PMMA and PMA were prepared by stirring 1.0 g of wool fiber in benzene solutions of PMMA and PMA for 24 h. The wool fiber was separated by filtration and then subjected to extraction by benzene for 24 h and dried. Recovery of 0.99 g of wool fiber indicated that the homopolymer is quantitatively separated by benzene extraction from the mixtures. After extraction, the recovered wool fiber was refluxed with 6 N HCl at 135°C for 48 h. No residue was left behind, indicating that PMMA and PMA were completely removed by solvent extraction. Isolation of PMMA and PMA from the grafted material after treatment with 6 N HCl constituted evidence for grafting.

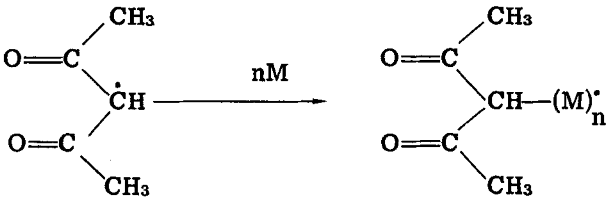
RESULTS AND DISCUSSION

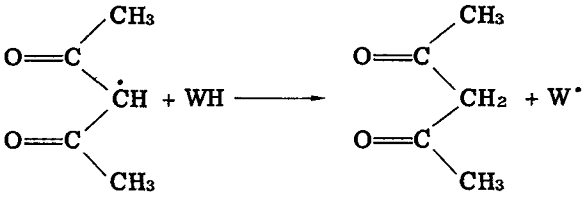
It was observed by Arnett and Mendelsohn [13] that metal chelates decompose upon heating to generate free radical species by electron transfer. As a consequence of this electron transfer, initiation of vinyl polymerization may occur. Following this discovery, Bamford et al. [16] used a variety of metal chelates as initiators for the polymerization of AN, MMA, St, and VAc. The structure of the ligand and the nature of central metal atom were found to play major roles in vinyl polymerization. When vinyl polymerization is carried out in the presence of a backbone polymer (WH), grafting may occur. The mechanism of Eqs. (1)-(7) is suggested to explain grafting of MA and MMA in $Mn(acac)_3$-initiated grafting onto wool fiber:

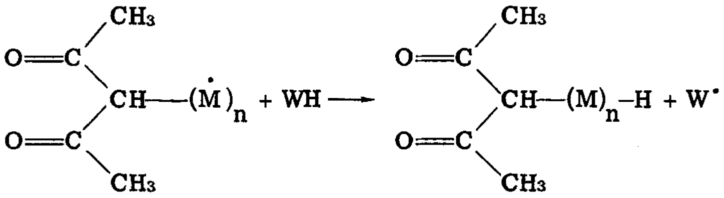

(I)

(1)

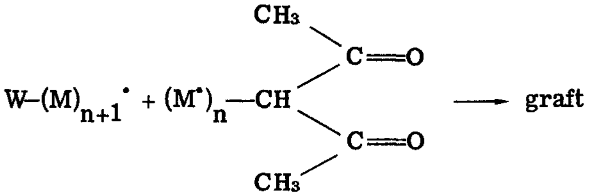

(2)


(3)


(4)



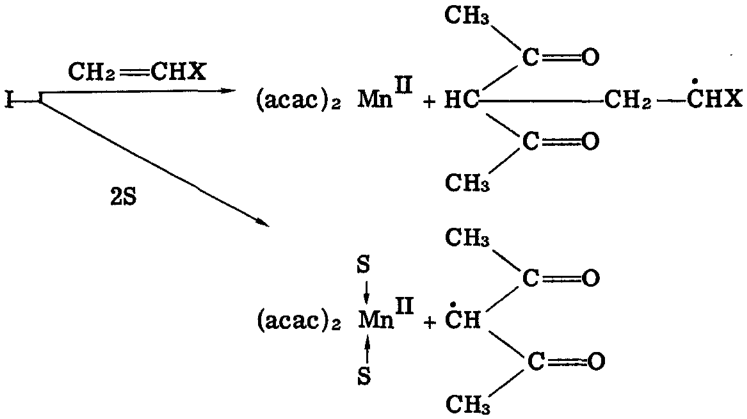
$$W^{\bullet} + M \longrightarrow WM^{\bullet} \xrightarrow{Mn} W{-}(M)_{n+1}^{\bullet} \qquad (6)$$



(7)

where WH denotes a wool backbone.

In the above mechanism it is presumed that the metal chelate, upon heating, first loosens the Mn–O bond followed by transfer of an electron to generate the free radical species. Once formation of the free radical is rationalized, the remaining processes follow in the same manner observed during grafting by free radical species involving chain transfer. According to the above postulated mechanism, active sites on wool fiber (WH) can occur by abstraction of hydrogen by the ligand radical species (Process 4) or by the growing polymeric radical (Process 5). Since the concentration of metal chelate is usually small (≈ 10^{-3} mol/L), generation of active sites by Process (4) is unlikely. Active sites are exclusively generated by Process (5). The above processes can occur at the decomposition temperature (152°) of $Mn(acac)_3$. It is, however, observed from Tables 1a and 2b that maximum grafting of both MA and MMA occurs at 65°C, much below the decomposition temperature of the chelate. EA, BA, and VAc also were found to afford [20] maximum grafting onto wool at 65°C. This tends to indicate that the chelate, instead of undergoing spontaneous decomposition, receives some assistance either from the solvent, from the monomer, or from both for facile decomposition at lower temperature. The solvent and monomer-assisted decomposition can be described as follows:



A similar mechanism involving monomer-assisted decomposition of metal chelates was proposed earlier by Misra et al. [22] for explaining grafting of VAc and MA onto cellulose.

Effect of Monomer Concentration

If the vinyl monomers do participate in the initiation process, then increasing the concentration of monomer should lead to enhancement of grafting. Tables 2a and 1e show that with increase in concentration of MA and MMA percent grafting increases and reaches maximum values at 27.6×10^{-2} mol/L for MA and 42.9×10^{-2} mol/L for MMA. Beyond these concentrations, percent grafting decreases. This indicates that at higher monomer concentrations, vinyl monomers preferentially undergo vinyl polymerization. Such behavior has been observed in all grafting reactions occurring by radical processes. Recently Garnett et al. [23] have reported that during radiation-induced grafting of PS onto PE, percent grafting increases with an increasing concentration of St up to a certain limit, then decreases. A perusal of Tables 1e and 2a shows that this effect is more pronounced with MMA than with MA. This indicates that MMA shows higher selectivity than MA toward graft copolymerization onto wool in the presence of $Mn(acac)_3$. In a recent paper, Misra et al. [20] observed similar monomer selectivity toward grafting of EA, BA, and VAc in $Mn(acac)_3$-initiated graft copolymerization onto wool..

Effect of Time and Temperature

It is observed from Tables 1d and 2e that maximum grafting of MMA and MA occurs within 180 min. Beyond this reaction period, percent grafting decreases. This indicates that when a definite amount of monomer is added to the reaction mixtures over a larger time interval, mutual annihilation of growing grafted chain assumes an importance that leads to a decrease in percent grafting. A similar finding was reported by Santappa et al. [24] during grafting of EA onto gelatin in the presence of persulfate as the radical initiator. Tables 1a and 2b show that percent grafting of both MMA and MA increases with temperature and reaches maximum values at 65°C. A further increase in temperature decreases the percent grafting, thereby indicating that termination reactions are accelerated at higher temperatures.

Comparison of Monomer Reactivity

Table 3 shows that different vinyl monomers in the presence of $Mn(acac)_3$ vary in reactivity toward graft copolymerization onto

TABLE 3. Maximum Percent Grafting of Different Vinyl Monomers in Mn(acac)^3-Initiated Grafting onto Wool

Vinyl monomer	% Grafting
MA	27.0
EA[a]	41.0
MMA	82.5
BA[a]	37.0
VAc[a]	20.0

[a] Percent grafting values refer to maximum grafting under optimum conditions and taken from Ref. 20.

wool. The following reactivity order was observed: MMA > EA > BA > MA > VAc.

ACKNOWLEDGMENTS

Financial assistance from the Department of Atomic Energy (DAE), Government of India, for this work is gratefully acknowledged. I.K.M. and R.K.S. are grateful to DAE, Government of India, for the award of Senior and Junior Research Fellowships, respectively.

REFERENCES

[1] N. Negeshi, K. Arai, S. Okada, and I. Nagakura, J. Appl. Polym. Sci., 9, 3465 (1965).
[2] K. Arai, M. Shimizu, and M. Shimada, J. Polym. Sci., Polym. Chem. Ed., 11, 3283 (1973).
[3] A. Hebeish, S. H. Abdel-Fattah, and A. Bendak, Angew. Makromol. Chem., 37, 11 (1974).
[4] B. N. Misra and P. S. Chandel, J. Polym. Sci., Polym. Chem. Ed., 15, 1545 (1977).
[5] B. N. Misra, I. K. Mehta, and R. Dogra, J. Macromol. Sci.–Chem., A12(10), 1513 (1978).
[6] B. N. Misra, I. K. Mehta, and R. Dogra, J. Appl. Polym. Sci., 25, 235 (1980).
[7] B. N. Misra, I. K. Mehta, and R. Dogra, Ibid., 24, 1595 (1979).
[8] B. N. Misra and P. S. Chandel, J. Polym. Sci., Polym. Chem. Ed., 18, 1171 (1980).

[9] B. N. Misra and I. K. Mehta, Ibid., 18, 1911 (1980).

[10] B. N. Misra, P. S. Chandel, and R. Dogra, Ibid., 16, 1801 (1978).

[11] B. N. Misra, R. Dogra, I. K. Mehta, and A. S. Singha, Angew. Makromol. Chem., 90(1393), 83-93 (1980).

[12] B. N. Misra and P. S. Chandel, J. Polym. Sci., Polym. Chem. Ed., 15, 1549 (1977).

[13] E. M. Arnett and M. A. Mendelsohn, J. Am. Chem. Soc., 84, 3821 (1967).

[14] E. G. Kastning, H. Naarmann, H. Reiss, and C. Berding, Angew. Chem., Int. Ed., 4, 322 (1965).

[15] N. Indicator and C. Linder, J. Polym. Sci., A-1, 5, 1083 (1967).

[16] C. H. Bamford and D. J. Lind, Proc. Roy. Soc. A, 302, 145 (1968).

[17] R. Prabha and U. S. Nandi, J. Polym. Sci., Polym. Lett. Ed., 14, 19 (1976).

[18] B. N. Misra, I. K. Mehta, and D. S. Sood, J. Macromol. Sci.–Chem., A14(8), 1255 (1980).

[19] P. L. Nayak, S. Lenka, and N. C. Pati, J. Polym. Sci., Polym. Chem. Ed., 17, 3425 (1979).

[20] B. N. Misra, D. S. Sood, and R. K. Sharma, J. Appl. Polym. Sci., In Press.

[21] T. Moeller (ed.), Inorganic Synthesis, Vol. VII, McGraw-Hill, New York, 1957, pp. 183.

[22] B. N. Misra, J. K. Jassal, R. Dogra, and D. S. Sood, J. Macromol. Sci.–Chem., A14(7), 1061 (1980).

[23] J. L. Garnett and N. T. Yen, J. Polym. Sci., Polym. Lett. Ed., 12, 225 (1974).

[24] M. Santappa and T. Nagabhushanam, J. Appl. Polym. Sci., 23, 1923 (1979).

Accepted by editor December 5, 1980
Received for publication January 5, 1981