Grafting onto Wool. XVIII. Graft Copolymerization of Methyl Methacrylate onto Wool Fiber in the Presence of Tertiary Butyl Hydroperoxide-Mineral Acid as Initiator

R. K. Sharma[a]; B. N. Misra[a]

[a] Department of Chemistry, Himachal Pradesh University, Simla, India

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R. K. SHARMA and B. N. MISRA

Department of Chemistry
Himachal Pradesh University
Simla 171005, India

ABSTRACT

Graft copolymerization of methyl methacrylate onto Himachali wool fiber has been studied in aqueous medium using tertiary butyl hydroperoxide (TBHP) in the presence of H_2SO_4, HNO_3, and $HClO_4$. The percentage of grafting and percent efficiency have been determined as functions of concentrations of TBHP, acid, monomer, time, and temperature. TBHP alone did not produce any graft within the temperature range 60 to 75°C. In the presence of mineral acids, graft copolymerization of MMA occurred readily, indicating that acids play an important role in the production of graft copolymer of MMA onto wool. A free radical mechanism for the initiation of grafting has been suggested. The mineral acids were found to vary in their abilities to produce graft copolymer, and the following order of reactivity of different acids was observed: $H_2SO_4 > HClO_4 > HNO_3$.

INTRODUCTION

In recent years, graft copolymerization has attracted attention as a convenient technique for modification of fibrous proteins. In our laboratory it has been possible to successfully graft a number of vinyl monomers onto wool fiber by chemical and radiation methods [1-5]. Grafting by a chemical method [6-8] is a simpler process and often can be carried out in aqueous medium by a radical method. Chemically induced grafting by free radicals, however, suffers from a serious limitation in that the grafting is often accompanied by the formation of a large amount of homopolymer, the separation of which from the graft involves the use of a large amount of expensive solvent. Apart from this, during chemically induced grafting a considerable amount of expensive vinyl monomer is wasted in side reactions. In order to circumvent these difficulties, attempts are being made to select newer initiating systems that would selectively cause grafting. Recently, we have been successful in grafting a number of donor and acceptor vinyl monomers onto Himachali wool [9, 10] by using different metal chelates as initiators of graft copolymerization.

Few studies have been reported on the use of tertiary butyl hydroperoxide (TBHP) as an initiator of graft copolymerization. This is because TBHP is known to decompose into free radicals only at higher temperature, and various chain transfer reactions are accelerated at such temperature.

Recently, Rizzardo et al. [11] reported that mineral acids are capable of decomposing TBHP at lower temperature into free radical species which initiate polymerization of methyl methacrylate. This finding of Rizzardo et al. has prompted us to investigate graft copolymerization of MMA onto Himachali wool in the presence of the TBHP-mineral acid system. In the present article we report grafting of MMA onto wool fiber by using TBHP-H_2SO_4, TBHP-HNO_3, and TBHP-$HClO_4$ acid systems as initiators. The percentage of grafting and the percent efficiency are expressed as functions of various reaction parameters. A plausible mechanism for initiation of grafting is suggested.

EXPERIMENTAL

Materials and Methods

Methyl methacrylate (MMA) (BDH) was washed several times with a 5% NaOH solution followed by washing with water and dried over anhydrous sodium sulfate. The dried monomer was distilled and the middle fraction was used. HNO_3 (BDH), perchloric acid (E. Merck, GR 70%), and H_2SO_4 (E. Merck, GR) of known strength were used. Tertiary butyl hydroperoxide (Koch Light, U.S.A.) was used as such.

Nitrogen was purified by passing through alkaline pyrogallol solution. Himachali wool was purified by the method described earlier [12].

Graft Copolymerization

Purified Himachali wool fiber (1.0 g) was dispersed in 200 mL of deaerated water in a three-necked flask. To this aqueous dispersion a known quantity of H_2SO_4 was added. A stream of purified nitrogen was passed through the reaction flask for 30 min. A definite quantity of a mixture of TBHP and MMA of known composition was added drop-wise to the reaction mixture. The graft copolymerization reaction was carried out under stirring at different temperatures for various reaction periods in a controlled thermostatic water bath ($\pm 0.5°C$). A continuous supply of nitrogen was maintained throughout the reaction period. After the reaction was over, the reaction mixture was filtered and the residue extracted with acetone and benzene separately for 48 h for the complete removal of homopolymer. The percent grafting and percent efficiency were calculated from the increase in weight of the wool fiber in the following manner:

$$\% \text{ Grafting } = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \text{ Efficiency } = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0, W_1, and W_2 denote the weights of wool fiber, grafted wool fiber after extraction, and monomer added, respectively. Graft copolymerization using TBHP-HNO_3 and TBHP-$HClO_4$ was carried out by the same method.

Evidence of Grafting

i) A physical mixture of wool and benzene solution of poly(methylmethacrylate) (PMMA) was prepared by stirring 1.0 g of wool in 100 mL of benzene solution of PMMA for 24 h. The wool fiber was separated by filtration. The residue was subjected to extraction by benzene for 24 h and dried to constant weight. No change in the weight of the wool was observed. This indicates that homopolymer is quantitatively removed by solvent extraction. Hence, any increase in weight of wool fiber after grafting is not due to blending of PMMA with wool fiber.

ii) Grafted wool samples were hydrolyzed by a 1:1 mixture of benzene-5% KOH for 12 h. Grafted wool formed an opaque emulsion. The emulsion was acidified with concentrated HCl. The benzene layer was

separated and the polymer was precipitated with petroleum ether. Iso-
lation of polymer from the graft by alkaline hydrolysis constitutes
evidence for grafting. The infrared spectra of wool-g-PMMA showed
an absorption band at 1730 cm^{-1} which was not present in the ungrafted
wool fiber.

iii) Ninhydrin test for residual amino acids. The grafted polymer
obtained from alkaline hydrolysis of the graft copolymer was thorough-
ly washed with water and dried. The dried polymer was dissolved in
acetone, and a drop of ninhydrin in acetone solution was added to it.
There was no violet coloration as such. However, violet color was
developed on a filter paper soaked in above solution and dried at 90°C.
The positive ninhydrin test indicates the presence of residual amino
acid groups in the PMMA isolated from the graft.

RESULTS AND DISCUSSION

Organic hydroperoxides are known [13] to decompose at higher
temperatures into free radical species. Mineral acids, however, are
capable of inducing decomposition of TBHP at a lower temperature.
Acid-induced decomposition of TBHP is known to follow heterolytic
pathways [14, 15]. Recently, Rizzardo et al. [11] were able to poly-
merize MMA in the presence of the TBHP-H$_2$SO$_4$ system and they
claimed that H$_2$SO$_4$ induced decomposition of TBHP partially by
radical pathway. If free radical species are generated by the inter-
action of mineral acids with TBHP, then it is expected that MMA,
which is known to polymerize by a free radical mechanism, would be
graft copolymerized onto wool fiber in the presence of a TBHP-min-
eral acid system. It is observed from Tables 1, 2, and 3 that a con-
siderable amount of graft copolymer of wool was obtained when graft-
ing was carried out in the presence of a TBHP-mineral acid system
at a temperature much below the decomposition temperature of TBHP.
It is also observed that TBHP alone is not capable of producing graft
copolymer below 100°C. This indicates that mineral acid plays a sig-
nificant role in inducing decomposition of TBHP at a lower tempera-
ture. The following free radical mechanism is suggested to explain
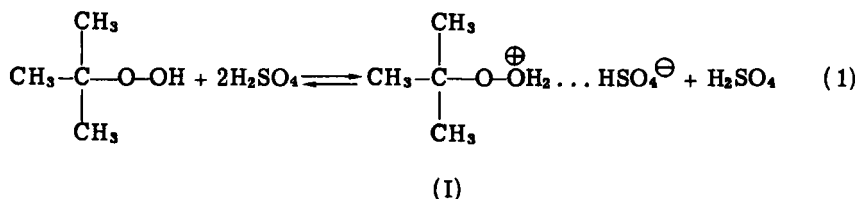grafting of MMA onto Himachali wool fiber in an aqueous medium:

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O-OH + 2H_2SO_4 \rightleftharpoons CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O-\overset{\oplus}{O}H_2 \ldots HSO_4^{\ominus} + H_2SO_4 \qquad (1)$$

(I)

TABLE 1. Effect of Concentration of MMA, TBHP, H_2SO_4, Time, and Temperature on Percent Grafting of MMA onto Wool Fiber[a]

Sample	MMA + TBHP		$[H_2SO_4] \times 10^2$ mol/L	Temperature (°C)	Time (min)	% G	% E
	$[MMA] \times 10^2$ mol/L	$[TBHP] \times 10^2$ mol/L					
1	23.5	4.9	2.8	50	180	5.0	1.06
2	"	"	"	60	"	32.0	6.80
3	"	"	"	65	"	84.0	17.87
4	"	"	"	70	"	132.0	28.08
5	"	"	"	75	"	139.0	29.57
6	"	2.4	"	"	"	169.0	35.95
7	"	7.4	"	"	"	62.5	13.29
8	"	9.9	"	"	"	160.0	34.04
9	"	2.4	9.3	"	"	184.0	39.14
10	"	"	18.6	"	"	159.2	33.87
11	"	"	37.3	"	"	162.5	34.57
12	"	"	4.6	"	"	146.5	31.17
13	"	"	9.3	"	120	110.5	23.51
14	"	"	"	"	150	150.0	31.91
15	"	"	"	"	210	147.0	31.27
16	14.1	"	"	"	180	110.0	39.00
17	32.9	"	"	"	"	143.0	21.73

[a]Wool = 1 g, water = 200 mL.

TABLE 2. Effect of Concentration of MMA, TBHP, HNO₃, Time, and Temperature on Percent Grafting of MMA onto Wool Fiber[a]

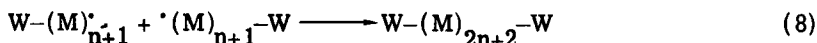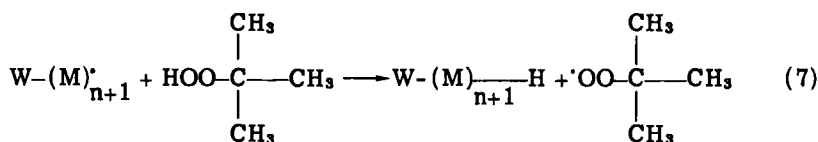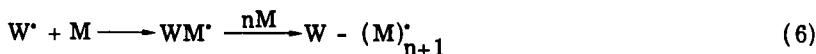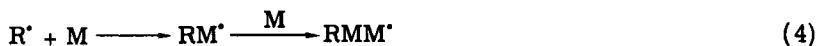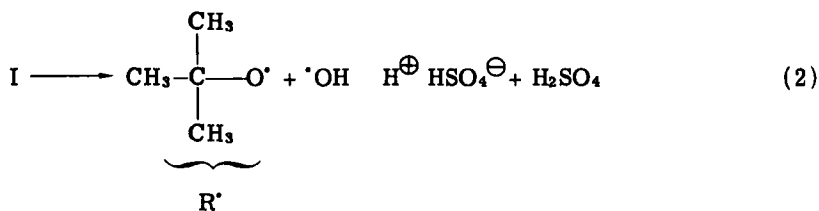| Sample	MMA + TBHP		$[HNO_3] \times 10^2$ mol/L	Temperature (°C)	Time (min)	% G	% E
	$[MMA] \times 10^2$ mol/L	$[TBHP] \times 10^2$ mol/L					
1	23.5	4.9	24.0	50	180	1.5	0.31
2	"	"	"	60	"	51.2	10.89
3	"	"	"	65	"	100.5	21.38
4	"	"	"	70	"	116.5	24.78
5	"	"	"	75	"	139.0	29.57
6	"	"	"	"	"	90.0	19.14
7	"	2.4	"	"	"	85.0	18.08
8	"	7.4	"	"	"	96.0	20.42
9	"	4.9	32.0	"	"	93.0	19.78
10	"	"	16.0	"	"	114.0	24.25
11	"	"	12.0	"	"	117.0	24.89
12	14.1	"	24.0	"	"	25.0	8.86
13	18.8	"	"	"	"	97.0	25.79
14	32.9	"	"	"	"	85.5	12.99
15	23.5	"	"	"	120	41.0	8.72
16	"	"	"	"	190	86.5	18.40

[a]Wool = 1 g, water = 200 mL.

TABLE 3. Effect of Concentration of MMA, $HClO_4$, TBHP, Time, and Temperature on Percent Grafting of MMA onto Wool Fiber[a]

Sample	MMA + TBHP		$[HClO_4] \times 10^2$ mol/L	Temperature (°C)	Time (min)	% G	% E
	$[MMA] \times 10^2$ mol/L	$[TBHP] \times 10^2$ mol/L					
1	23.5	4.9	12.91	60	180	51.7	11.0
2	"	"	"	65	"	117.0	24.89
3	"	"	"	70	"	158.0	36.61
4	"	"	"	75	"	138.0	29.36
5	"	"	2.15	70	"	101.5	21.59
6	"	"	4.30	"	"	138.5	29.46
7	"	"	17.20	"	"	130.0	27.65
8	"	2.4	12.91	"	"	131.0	27.87
9	"	7.4	"	"	"	128.0	27.23
10	"	9.9	"	"	"	107.5	22.87
11	"	4.9	"	"	120	112.5	23.93
12	"	"	"	"	150	87.0	18.51
13	"	"	"	"	210	115.0	24.46
14	14.1	"	"	"	180	61.5	21.80
15	32.9	"	"	"	"	99.2	15.07

[a]Wool = 1 g, water = 200 mL.

$$I \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^{\cdot} + {}^{\cdot}OH \quad H^{\oplus} HSO_4^{\ominus} + H_2SO_4 \qquad (2)$$

$$R^{\cdot}$$

$$R^{\cdot} + WH \longrightarrow RH + W^{\cdot} \qquad (3)$$

$$R^{\cdot} + M \longrightarrow RM^{\cdot} \xrightarrow{M} RMM^{\cdot} \qquad (4)$$

$$R-MM^{\cdot} + WH \longrightarrow RMMH + W^{\cdot} \qquad (5)$$

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

$$W-(M)^{\cdot}_{n+1} + HOO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow W-(M)_{n+1}-H + {}^{\cdot}OO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \qquad (7)$$

$$W-(M)^{\cdot}_{n+1} + {}^{\cdot}(M)_{n+1}-W \longrightarrow W-(M)_{2n+2}-W \qquad (8)$$

According to the above postulated mechanism, one molecule of acid first protonates TBHP to give a protonated complex (I) which is stabilized by the second molecule of H_2SO_4 involving hydrogen bonding in the following manner:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O \overset{\oplus}{O}H_2 \quad \overset{\ominus}{O}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \ldots \overset{H}{O}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

(I)
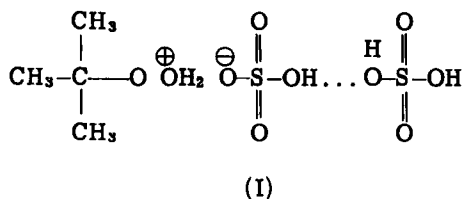
Complex (I) can also be stabilized by the water molecules of the medium. If such a complex formation occurs, then it would be expected that the free energy of activation for the homolysis of the O–O would be decreased and the decomposition of TBHP would occur at a lower temperature. The data presented in Tables 1, 2, and 3 indicate that all the mineral acids are capable of producing graft copolymers of MMA at a lower temperature.

Effect of Concentration and Role of Mineral Acid

It is apparent from Tables 1, 2, and 3 that maximum grafting of MMA occurs at $[HNO_3]$ = 24.0 × 10^{-2} mol/L; $[H_2SO_4]$ = 9.3 × 10^{-2} mol/L, and $[HClO_4]$ = 12.91 × 10^{-2} mol/L. At lower acid concentrations the percentage of grafting decreases; this indicates that when the concentration of mineral acid is less than the critical concentration, protonation of TBHP is incomplete. On the contrary, when the concentration of mineral acid is higher than the critical concentration, TBHP decomposes preferentially by an ionic pathway [16]:
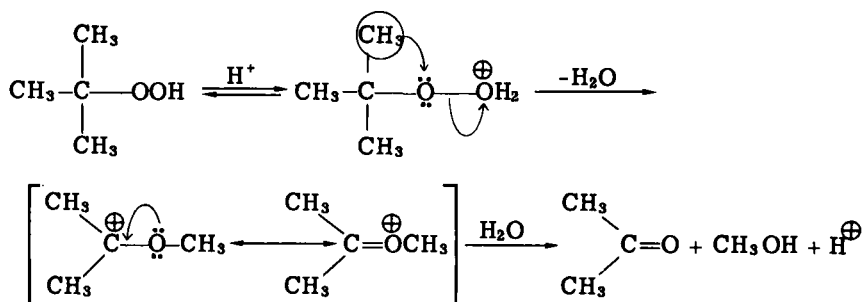
Since MMA is not susceptible to cationic polymerization, grafting of MMA by the cationic method does not occur. This would lead to a decrease in percent grafting. It is also observed from Tables 1, 2, and 3 that not all the mineral acids are equally effective in the production of the graft. Sulfuric acid is found to produce a higher percentage of grafting than HNO_3 and $HClO_4$. It appears that both HNO_3 and $HClO_4$, being strong oxidants, participate in the oxidation of vinyl monomer and lead to a decrease in percent grafting. Further, in accordance with above postulated mechanism for grafting, Complex (I) would be better stabilized by H_2SO_4 than by HNO_3 or $HClO_4$. Both these reasonings may account for the higher percentage grafting in the presence of H_2SO_4. However, it is not clear why HNO_3 and $HClO_4$ should differ in their abilities to produce grafting.

Effect of Monomer Concentration

Tables 1, 2, and 3 show that there exists an optimum monomer concentration at which the percent grafting is maximum. Beyond this concentration, percent grafting decreases. This is explained by the fact that at higher monomer concentrations, competitive homopolymerization becomes the preferred process leading to a decrease in grafting. It is observed that a fairly high percentage of grafting of MMA occurs

in the presence of a TBHP-mineral acid system. This may indicate that MMA also participates in complex formation with protonated TBHP in the following manner:
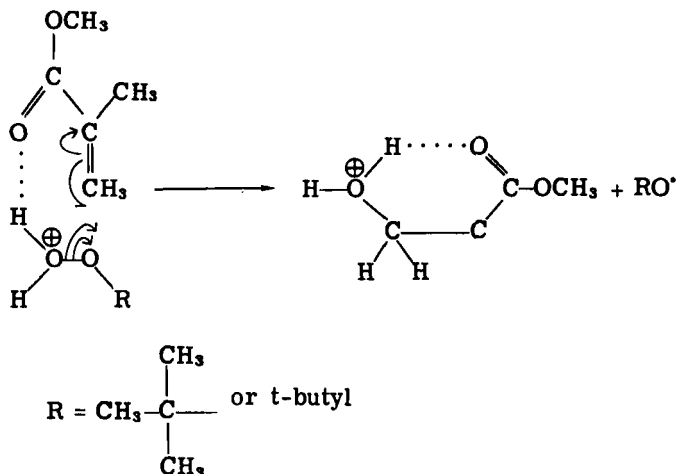
Thus it is evident from the above discussion that both acid and vinyl monomer can interact with TBHP to produce free radical species which may initiate graft copolymerization. However, it is difficult to ascertain the contribution of vinyl monomer in the production of free radicals capable of initiating grafting. This can be resolved by carrying out graft copolymerization using donor and acceptor vinyl monomers when monomer selectivity in effecting grafting is observed. Such a study is in progress.

It is, however, apparent from the foregoing discussion that a TBHP-mineral acid system is an excellent initiator for graft copolymerization of MMA onto wool and that mineral acids differ in their abilities to produce varying amounts of graft. The following reactivity order for different mineral acids toward grafting of MMA onto wool in the presence of a TBHP-mineral acid system was observed: $H_2SO_4 > HClO_4 > HNO_3$.

ACKNOWLEDGMENTS

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