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Photograft Copolymerization of Methyl Methacrylate on Wool Using Ce^{4+}-Oxalic Acid Redox Initiator in a Limited Aqueous System

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ABSTRACT

Photograft copolymerization of methyl methacrylate on reduced wool (reduction done by treatment with thioglycollic acid, TGA) was studied at nearly 30°C using a Ce^{4+}-oxalic acid redox initiator system in a limited aqueous system (2.7 mL water for 0.15 g wool). Reduction of wool for 16 h with 15% TGA solution produced optimum grafting effects. Percent grafting and grafting efficiency under different sets of conditions were studied and compared, and the mechanism of grafting discussed. Generation of grafting sites (radical centers) on reduced wool was more effective in the presence of light than in the dark. Percent grafting of 250-350% and grafting efficiency of 65-80% over a conversion range of 60-90% in 3-5 h were easily obtained.

INTRODUCTION

Grafting of vinyl polymers on wool has drawn the attention of some investigators in the last few decades [1-11]. Different methods of modification of wool have also been studied, a majority of which were aimed at finding suitable systems and conditions for improved vinyl

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grafting. Modification of wool by treatment with thioglycollic acid (TGA) resulting in transformation of the –S–S– bond of cystine present in wool to the –SH (thiol) group [12] is reported to be one such method for producing improved results. In the present investigations we studied several reagents likely to form redox combinations with the thiol groups in TGA-modified wool and examine their suitabilities in bringing about improved vinyl grafting using methyl methacrylate monomer in limited aqueous systems. Extended studies of the grafting reactions were done only with the Ce^{4+}-oxalic acid redox initiator system and under conditions which produced the best grafting effects. Related results are reported in this paper.

EXPERIMENTAL

Wool Fiber

Raw (untreated) wool, obtained from a local shredder, was pale yellow in color. It was extracted for 24 h with diethyl ether to remove the greasy matter. Subsequently, the wool fiber was extracted for 24 h with acetone. The fiber was finally washed with water and alcohol and dried in air at room temperature. This wool sample is termed "unmodified wool."

Reduction of Wool with TGA

This was carried out at 30-35°C for 16 h using an aqueous solution of TGA at pH5, a dilute solution of NaOH being used to adjust the pH. Different extents of reduction were effected by varying the concentration of TGA. The liquor ratio maintained was 1:20 (w/v). After reduction, the wool sample was profusely washed with water. The reduced or modified wool was then used in grafting experiments as soon as possible after pressing it dry with filter paper.

Other Materials

Monomer methyl methacrylate (MMA) obtained from the local market was purified by standard procedures. All other chemicals and solvents were of reagent grade and were used without any treatment.

Graft Copolymerization

The procedure for photograft copolymerization is similar to that described before [13]. After polymerization the overall product containing the gross polymer system (mixture of unreacted wool, if any, wool-PMMA graft copolymer, and free PMMA) was profusely washed with water, then with a water-alcohol mixture, and finally with alcohol. The free PMMA portion was extracted from the gross polymer with benzene. Isolation, drying, and weighing of the free PMMA and the apparent graft copolymer (the residue after benzene extraction) were done following a procedure given before [13]. The percent grafting, grafting efficiency (with respect to PMMA formed), E_M (%), and total conversion (%) were then calculated for each experiment [13].

RESULTS AND DISCUSSION

Results of preliminary studies of the suitability of a number of initiating systems for inducing graft copolymerization of MMA on wool (particularly on reduced wool) are shown in Table 1. It is clear from the table that the Ce^{4+}-oxalic acid combination produced the best grafting effects when done in light at 32°C with reduced wool as the base polymer. All subsequent grafting experiments were therefore made using the Ce^{4+}-oxalic acid initiator system and reduced wool in visible light at 32 ± 1°C.

Photografting on Reduced Wool Using Ce^{4+}-Oxalic Acid Initiator System

Results of photograft copolymerization of MMA on reduced wool showing the effects of variation of extent of reduction (expressed in terms of variation of % TGA used for reduction), time, [Ce^{4+}], [oxalic acid], and [MMA] are shown in Figs. 1-5.

Effect of Variation of % TGA Used for Reduction of Wool (Fig. 1)

Unmodified wool (wool with no TGA treatment) shows low % total conversion (24%), % grafting (42%), and grafting efficiency, E_M (%), (31.5%). For reduction of wool, the TGA content was varied between 3 and 30%. While both % total conversion and % grafting follow an increasing trend with an increase in % TGA used as shown in Fig. 1, grafting efficiency (%) shoots up to about 70% even for a low extent of reduction with only 3% TGA. A further increase in TGA content does not significantly alter the grafting efficiency (%) level. Considering all the observed parameters, viz., % conversion, % grafting, and grafting efficiency (%), an optimum result is given by wool reduced with 15% TGA solution. All subsequent experiments were therefore made with this wool sample.

TABLE 1. Polymerization of MMA in the Presence of Wool Using Different Initiator Systems under Different Conditions (wool 0.15 g, MMA 1 mL, water 2.7 mL)

Base polymer	Initiator system	Initiator concentration (mol/L)	Condition of polymerization	Formation of[a]	
				Free PMMA	Grafted PMMA
Unmodified wool	Oxalic acid/ $KMnO_4$	10^{-3}	Photo, 40°C, 4 h	+	-
"	"	"	In dark, 60°C, 4 h	+	-
"	CCl_4/Br_2	10^{-2}	Photo, 30°C, 4 h	+	-
"	Ce^{4+}	"	In dark, 40°C, 4 h	+	+
"	"	"	Photo, 32°C, 4 h	+	+
Reduced wool[b]	Br_2	10^{-3}	"	+	-
"	$KMnO_4$	"	"	+	+
"	H_2O_2	"	"	+	+
"	Ce^{4+}	10^{-2}	"	+	+
"	Ce^{4+}/ oxalic acid	"	In dark, 32°C, 4 h	+	+
"	"	"	Photo, 32°C, 4 h	+	++

[a] + = reasonable to appreciable, ++ = high to very high, - = nil.

[b] Wool reduced with TGA (15%) treatment for 16 h.

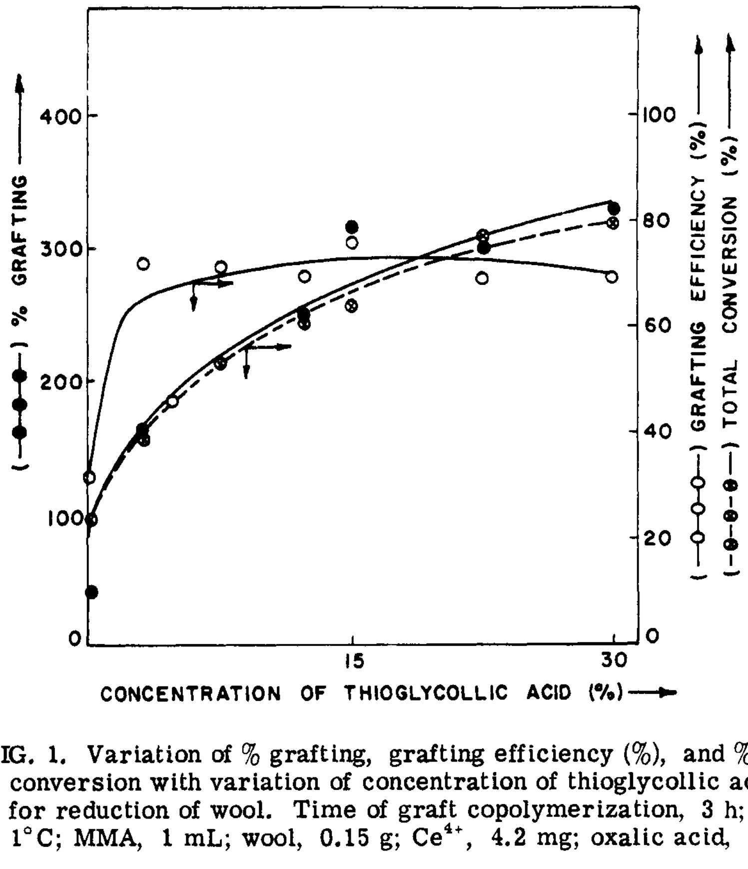

FIG. 1. Variation of % grafting, grafting efficiency (%), and % total conversion with variation of concentration of thioglycollic acid used for reduction of wool. Time of graft copolymerization, 3 h; 32 ± 1°C; MMA, 1 mL; wool, 0.15 g; Ce^{4+}, 4.2 mg; oxalic acid, 9 mg.

Effect of Variation of Time of Polymerization (Fig. 2)

Polymerization time was varied between 90 and 420 min. % Grafting, grafting efficiency (%), and % total conversion initially increase sharply with an increase in the time of polymerization up to about 180-200 min. Grafting efficiency (%) practically levels off thereafter, while % grafting and % total conversion continue to improve, although at much lower rates, and finally tend to level off as the bulk of the monomer used is consumed. 180 min appears to be the optimum time of polymerization, giving about 64% total conversion, 315% grafting, and about 76% grafting efficiency.

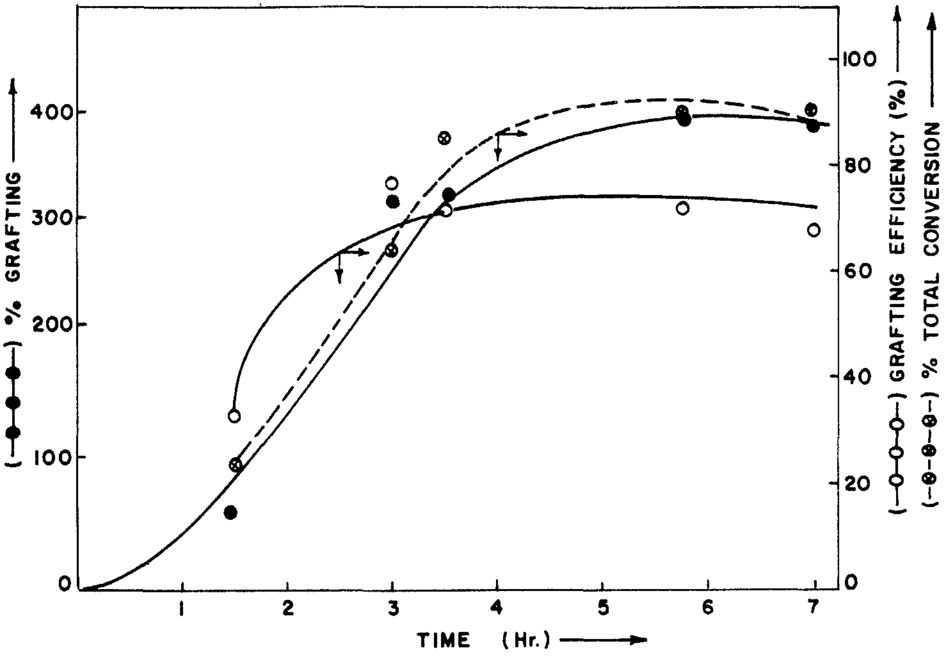

FIG. 2. Variation of % grafting, grafting efficiency (%), and % total conversion with variation of time of polymerization. Wool (reduced with 15% TGA solution), 0.15 g; 32 ± 1°C; MMA, 1 mL; Ce^{4+}, 4.2 mg; oxalic acid, 9 mg.

Effect of Variation of [Ce^{4+}] and [Oxalic Acid], (Figs. 3 and 4)

Effects of variation of the amounts of the initiator components are shown in Figs. 3 and 4. Each parameter in Fig. 3, showing the effect of Ce^{4+} variation, passes through a maximum corresponding to 2-4 mg of cerium. Studies of the effect of variation of oxalic acid content, shown in Fig. 4, points to an optimum condition close to about 8-9 mg oxalic acid. Most of the grafting experiments presented in this paper were therefore done using 4.2 mg Ce^{4+} and 9 mg oxalic acid.

Effect of Variation of Monomer Content (Fig. 5)

Variation of MMA content was done between 0.2 and 2.5 mL, resulting in a variation of total liquid (monomer and water) between 2.9 and 5.2 mL. Figure 5 clearly shows that optimum results are

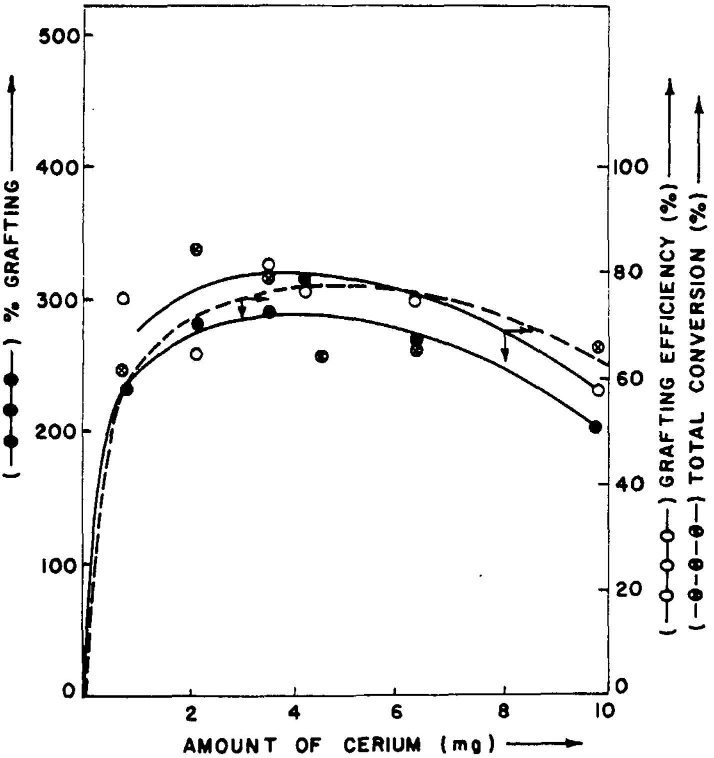

FIG. 3. Variation of % grafting, grafting efficiency (%), and % total conversion with variation of Ce^{4+} content in the polymerization system, wool (reduced with 15% TGA solution), 0.15 g; 32 ± 1°C; MMA, 1 mL; oxalic acid, 9 mg; 3 h.

obtained using only 1.0 mL MMA. Most of the grafting experiments were therefore done using 1.0 mL MMA, corresponding to a total liquid volume (monomer + water) of 3.7 mL.

Comparison of Chain Lengths of Grafted and Free PMMA

The grafted PMMA fractions from some selected experiments were isolated by destructively solubilizing the wool portions (free and grafted) with H_2SO_4 treatment according to the procedure of Negishi et al. [14]. The isolated PMMA was washed free of acid, dried, dissolved in benzene, and purified by reprecipitation. The

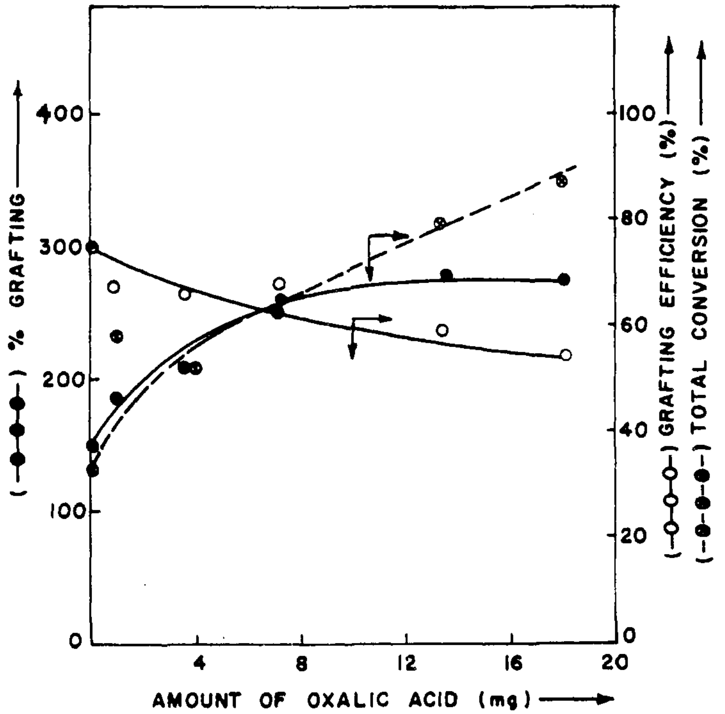

FIG. 4. Variation of % grafting, grafting efficiency (%), and % total conversion with variation of oxalic acid content in the polymerization system wool (reduced with 15% TGA solution), 0.15 g; 32 ± 1°C; MMA, 1 mL, Ce^{4+}, 4.2 mg; 3 h.

intrinsic viscosities $[\eta]$ in dL/g of the isolated grafted-on PMMA and the corresponding free PMMA samples were then determined in benzene solution at 30°C. Related results are given in Table 2. It may be clearly seen that the $[\eta]$ values and hence the average chain lengths of grafted-on PMMA chains are much higher (about double) than those of the corresponding free PMMA chains, a feature very similar to that observed in similar heterogeneous graft copolymerization of MMA on cellulose or oxycellulose [13]. Wool chain networks act as additional and more effective physical barriers for the mobility of the growing grafted-on PMMA chains in the heterogeneous system, resulting in delayed termination for them and hence giving rise to much higher molecular weights for them in comparison with the molecular weights of the corresponding free PMMA chains.

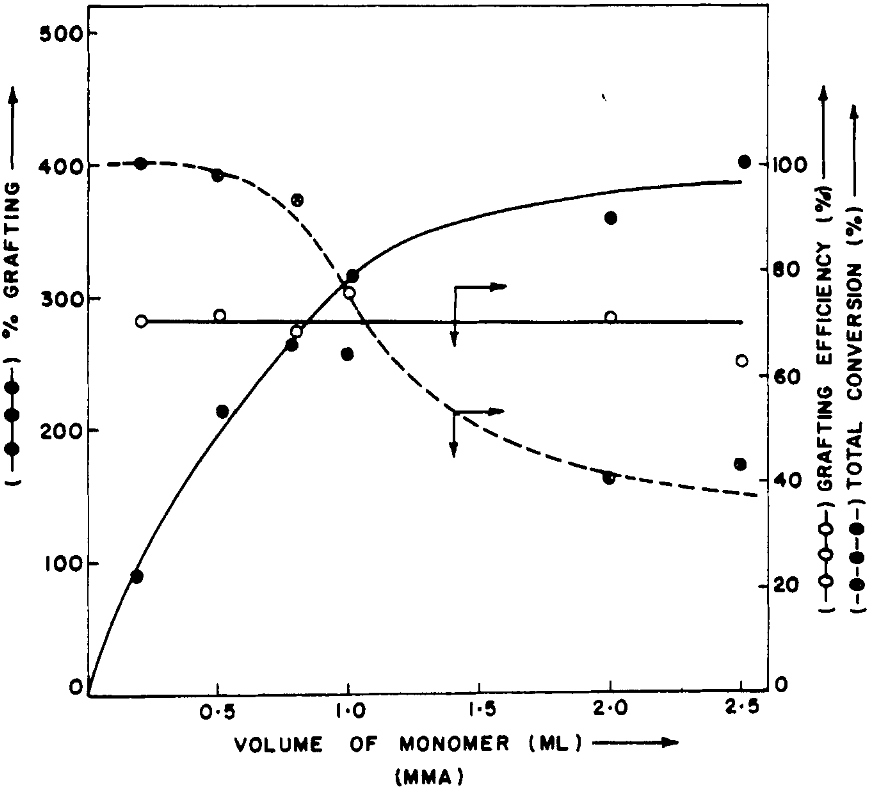

FIG. 5. Variation of % grafting, grafting efficiency (%), and % total conversion with variation of MMA content in the polymerization system wool (reduced with 15% TGA solution), 0.15 g; 32 ± 1°C; 4.2 mg; oxalic acid, 9 mg; 3 h.

Mechanism

The radical generation process in the present graft copolymerization systems is complicated because of many factors controlling them include the heterogeneous nature of the systems. On addition of dilute aqueous ceric sulfate solution to TGA-reduced wool soaked in the dilute oxalic acid solution/ MMA system, the color of Ce^{4+} ion was found to fade slowly. On photoactivation, the rate of color disappearance was much faster. The most likely primary radicals to be generated are carboxyl radicals (from the Ce^{4+}-oxalic acid redox reaction) and monosulfide radicals (from the reaction between Ce^{4+} and reduced wool, W–SH):

TABLE 2. Photograft Copolymerization of MMA on Wool: Variation of Intrinsic Viscosity of PMMA Fractions with Variation of Process Conditions (wool 0.15 g, 32 ± 1°C, water 2.7 mL)

TGA solution used for reduction of wool (%)	Time of polymerization (h)	Ce^{4+} (mg)	Oxalic acid (mg)	MMA (mL)	$[\eta]$ (dL/g) Free PMMA	$[\eta]$ (dL/g) Grafted PMMA
3	3	4.2	9.0	1.0	3.40	6.50
15	3	4.2	9.0	1.0	3.00	4.80
22	3	4.2	9.0	1.0	3.00	4.50
15	7	4.2	9.0	1.0	3.80	5.00
15	3	4.2	9.0	0.5	1.40	3.00
15	3	4.2	9.0	2.5	4.50	6.50
15	3	0.70	9.0	1.0	2.80	4.60
15	3	9.8	9.0	1.0	3.50	5.10
15	3	4.2	0.90	1.0	2.00	3.50
15	3	4.2	18.0	1.0	4.50	7.00

$$\underset{\text{(wool)}}{\text{W–S–S–W}} \xrightarrow{\text{TGA}} \underset{\text{(reduced wool)}}{\text{W–SH}} \tag{1}$$

$$\text{W–SH} + Ce^{4+} \longrightarrow \text{WS}^{\cdot} + H^{+} + Ce^{3+} \tag{2}$$

$$Ce^{4+} + C_2O_4^{2-} \longrightarrow Ce^{3+} + CO_2 + {}^{\cdot}COO^{-} \tag{3}$$

During photolysis, oxalic acid may also decompose to yield $^{\cdot}C_2O_4^{-}$, $^{\cdot}COO^{-}$, and $H^{\cdot}$ radicals [13].

Reactions between Ce^{4+} and W–SH and between Ce^{4+} and oxalic acid are activated in a large measure by visible light. This explains the better grafting effects under photoconditions. The primary $^{\cdot}COO^{-}$ or $^{\cdot}C_2O_4^{-}$ radical may further react with –SH groups of reduced wool to generate more wool macroradicals:

$$\text{W–SH} + {}^{\cdot}COO^{-} \longrightarrow \text{W–S}^{\cdot} + HCOO^{-} \tag{4}$$

$$\text{W–SH} + {}^{\cdot}C_2O_4^{-} \longrightarrow \text{W–S}^{\cdot} + HCOO^{-} + CO_2 \tag{5}$$

Under photoactivation, generation of wool macroradicals through the primary redox Reaction (2) and subsequently through Reactions (4) and (5) is very likely to assume prominence. This explains the better effectiveness of photosystems over systems studied in the dark insofar as overall grafting is concerned. Grafting via wool macroradicals generated due to chain transfer involving –SH groups of reduced wool is also a distinct possibility. With the use of the Ce^{4+}-oxalic acid initiator system under photoconditions in the reduced wool/MMA system of the present kind, % grafting of 250-350% and grafting efficiency of 65-80% over a conversion range of 60-90% in 3-5 h were easily obtained.

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