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J. S. Shukla^a; G. K. Sharma^a; R. K. Tewari^a; S. K. Shukla^a

^a Department of Chemistry, University of Lucknow, Lucknow, India

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Graft Copolymerization of Poly(methyl Methacrylate) onto Wool by the Potassium Persulfate-Thiomalic Acid Redox Couple in the Presence of Atmospheric Oxygen. Part I

J. S. SHUKLA, G. K. SHARMA, R. K. TEWARI, and S. K. SHUKLA

Department of Chemistry
University of Lucknow
Lucknow, India

ABSTRACT

The graft copolymerization of poly(methyl methacrylate) [PMMA] onto wool initiated by the potassium persulfate-thiomalic acid (TMA) redox couple has been investigated in the presence of atmospheric oxygen. The percentage of grafting efficiency and polymerization as a function of initiator, activator, monomer, temperature, time, and wool was estimated. Evidence of grafting was confirmed by IR spectroscopy. It was observed that the grafting ranged from 25 to 70% depending upon the concentration of the redox system, the time, and the temperature.

INTRODUCTION

In recent years, chemical modification of wool by graft copolymerization has received considerable attention [1-6].

Wool is a natural polypeptide that contains a number of functional groups like -OH, -SH, -NH₂, -COOH, etc. They provide active sites

for graft copolymerization. The free radical technique is a powerful medium for the creation of active sites on the polymer backbone. The technique of free radical aqueous polymerization of vinyl monomers in the presence of air by a redox pair has been known for years [7-10]. In the present communication we report the graft copolymerization of vinyl monomers onto wool, and the results of a study of graft copolymerization of methyl methacrylate (MMA) by the potassium persulfate-thiomalic acid (TMA) redox couple in the presence of air are described.

EXPERIMENTAL

Wool obtained from U.P. was purified by the usual method [11] and monomer was washed by a standard method [12]. All the other chemicals were of analytical grade.

Purified wool (0.5 g) was dispersed in 100 mL of water in a flask. A calculated amount of TMA followed by the initiator $K_2S_2O_8$ were placed in the reaction flask and kept in a thermostat at $45 \pm 0.2^\circ C$ (when otherwise not mentioned). A calculated amount of the monomer MMA was introduced dropwise to the reaction flask.

At the end of the desired interval, the reaction was quenched by adding an excess of methanol. The colloidal phase was broken by adding $MgSO_4$. The grafted material with homopolymer was filtered. The residue was extracted with benzene in a Soxhlet for complete removal of homopolymer. The extracted polymer was dried overnight to constant weight.

Percentage of grafting, efficiency, and polymerization were determined as follows:

$$\% \text{ Grafting} = \frac{w_2 - w_1}{w_1} \times 100$$

$$\% \text{ Efficiency} = \frac{w_2 - w_1}{w_3} \times 100$$

$$\% \text{ Polymerization} = \frac{w_4}{w_3} \times 100$$

Where w_1 , w_2 , w_3 , and w_4 are the weight of the wool, the weight of the grafted wool, the weight of the monomer, and the total increase in the weight including homopolymer and grafted polymer.

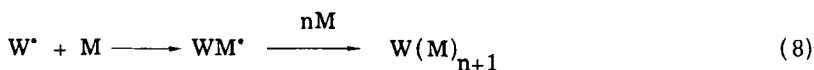
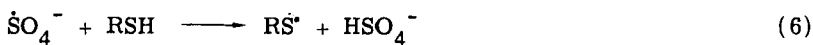
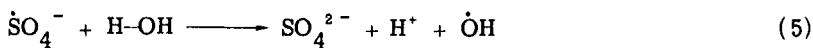
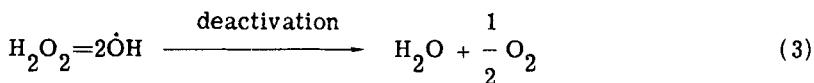
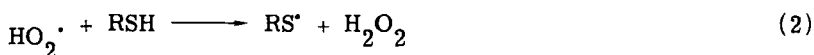
RESULTS AND DISCUSSION

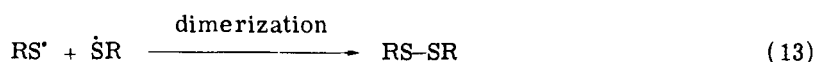
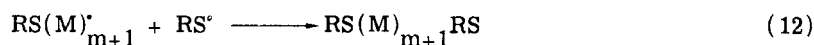
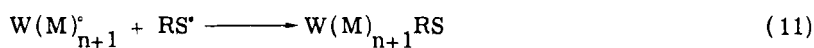
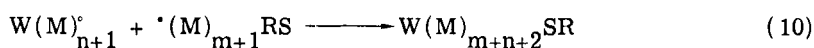
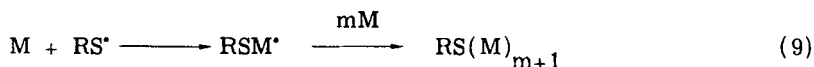
Evidence of Grafting

The grafted sample was hydrolyzed by 8 *N* sulfuric acid at 135°C for 48 h. All wool went into solution, leaving a resinous mass which was identified as poly(MMA) by IR spectroscopy. The IR spectrum of grafted poly(MMA) showed a band at 1725 cm⁻¹, attributed to the C=O bond of grafted polymer. The isolation of poly(MMA) from the grafted sample after hydrolysis indicated that poly(MMA) was covalently bonded to the wool backbone [5].

Mechanism

On the basis of the mechanism given by Ghatge et al. [13] and Shukla et al. [7] for the addition polymerization of MMA by K₂S₂O₈-ascorbic acid in the presence of air, we propose the following mechanism for the graft copolymerization of MMA by K₂S₂O₈-TMA in the presence of air. The grafting is initiated when the free radical (W') generated from wool attacks the monomer molecule. Wool is represented as WH.





In Steps (10) and (11), grafted polymer is formed, and in Step (12), homopolymer is formed.

Effect of Variation in Initiator Concentration

The effect of variation in initiator concentration on the percentage of grafting efficiency and polymerization has been studied over a wide range of initiator concentrations (7.5 to 40 mmol/L) at fixed concentrations of activator and monomer and fixed values of temperature and wool for a definite period of 3 h. The results are shown in Fig. 1.

It was observed that the percentage of grafting and efficiency increased up to 20 mmol/L concentration of initiator and thereafter decreased. These results are in line with the observation recorded by Toda [14], Mukherjee and Sanyal [15], and Ogiwara et al. [16].

Effect of Variation in Activator Concentration

Under otherwise constant conditions, variation in activator (TMA) concentration is shown in Fig. 2. It was observed that an increase in activator concentration up to 20 mmol/L gave a corresponding increase in percentage of grafting and efficiency and thereafter both decreased although gradually. Similar results have been recorded by Toda [14] and Ogiwara [16]. This could be due to mutual termination taking place at higher activator concentrations with the result that the percentages of grafting and efficiency both decrease.

Effect of Variation in Monomer (MMA) Concentration

At a fixed concentration of activator, initiator, and wool, the effect of variation in monomer MMA concentration is as in Fig. 3.

The increase in percentage grafting, efficiency, and extent of polymerization took place in the whole range of monomer concentration. Percentage grafting increased sharply with an increase in monomer concentration whereas the efficiency had very little effect. The percentage

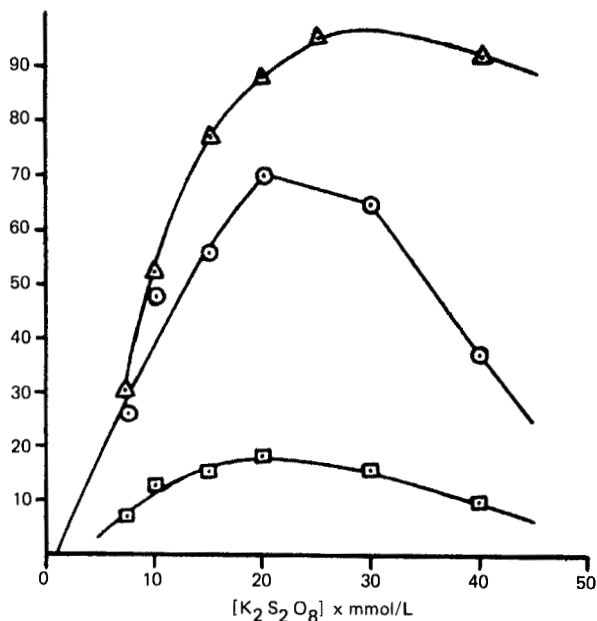


FIG. 1. Variation of % grafting (\odot), % polymerization (Δ), and % efficiency (\square) with initiator concentrations. $[MMA] = 18.512 \times 10^{-2}$ mol/L, $[TMA] = 10.0$ mmol/L, time = 180 min.

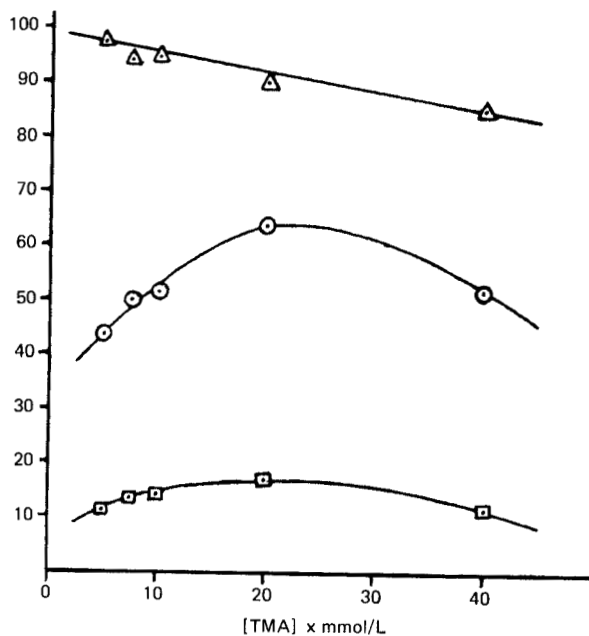


FIG. 2. Variation of % grafting (\odot), % polymerization (Δ), and % efficiency (\square) with activator concentrations. $[MMA] = 18.512 \times 10^{-2}$ mol/L, $[KS_2O_3] = 10$ mmol/L, time = 180 min.

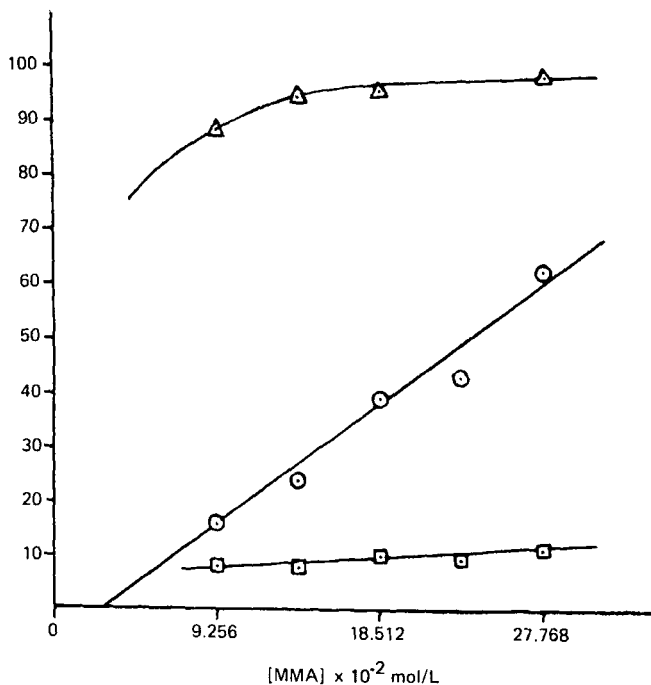


FIG. 3. Variation of % grafting (\odot), % polymerization (Δ), and % efficiency (\square) with monomer concentrations. $[KS_2O_3] = 10$ mmol/L, $[TMA] = 10$ mmol/L, time = 180 min.

conversion initially increased and finally became almost constant. The results fall in line with observations made by other workers [14, 15, 17].

Effect of Wool Concentration

The effects are shown in Fig. 4. An increase in wool concentration resulted in a corresponding decrease in the percentage polymerization as well as grafting, while the efficiency percentage increased in the whole range of wool concentration investigated. On increasing the amount of wool, the chances of the creation of more active sites increased and hence the percentage of efficiency. Since there was no increase in activator and initiator concentrations, the primary free radicals remained almost constant, resulting in a decrease of percentage grafting at higher wool concentrations.

Effect of Time and Temperature

The grafting of MMA onto wool at fixed concentrations of initiator, activator, monomer, and wool was investigated for different polymerization times. The results, presented in Fig. 5, indicate that grafting

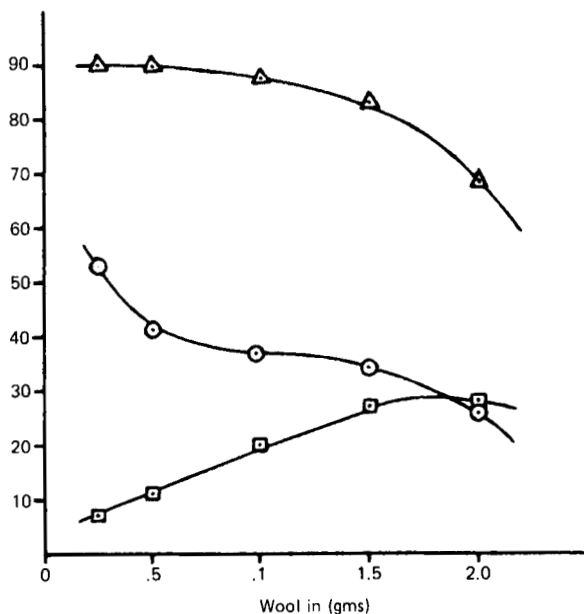


FIG. 4. Variation of % grafting (○), % polymerization (△), and % efficiency (◻) with wool. $[KS_2O_3] = 10 \text{ mmol/L}$, $[TMA] = 10 \text{ mmol/L}$, $[MMA] = 18.512 \times 10^{-2} \text{ mol/L}$, time = 180 min.

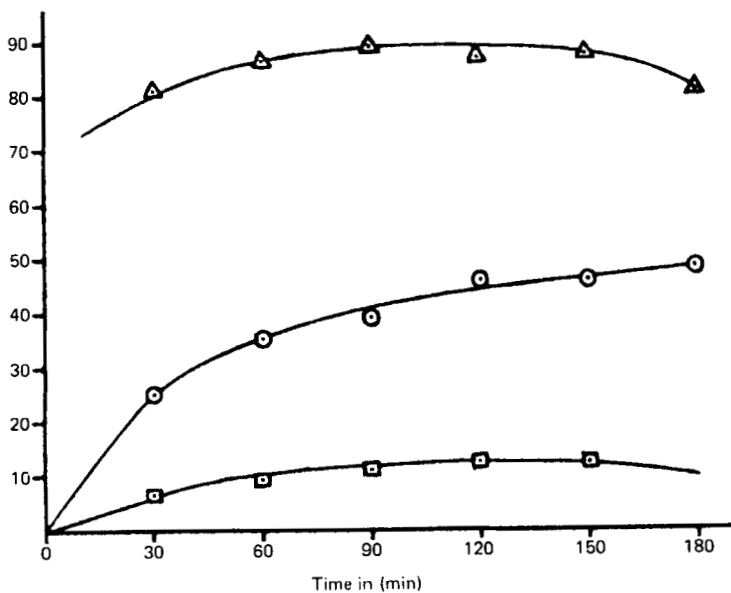


FIG. 5. Variation of % grafting (○), % polymerization (△), and % efficiency (◻) with time. $[KS_2O_3] = 10 \text{ mmol/L}$, $[TMA] = 10 \text{ mmol/L}$, $[MMA] = 18.512 \times 10^{-2} \text{ mol/L}$.

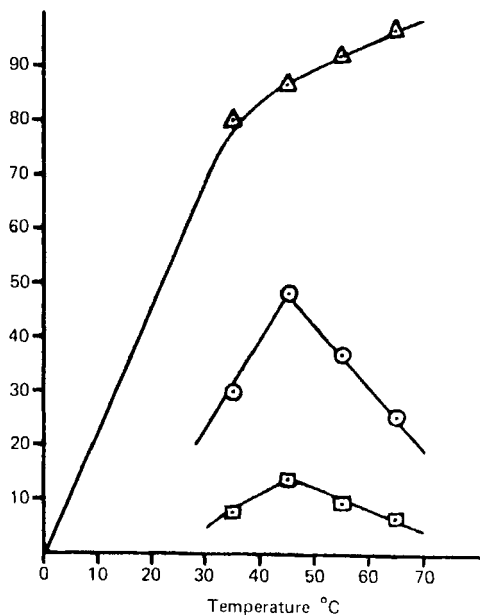


FIG. 6. Variation of % grafting (○), % polymerization (△), and % efficiency (□) with temperature. $[KS_2O_3] = 10 \text{ mmol/L}$, $[TMA] = 10 \text{ mmol/L}$, $[MMA] = 18.512 \times 10^{-2} \text{ mol/L}$, time = 180 min.

and efficiency reached their maxima in 3 h and thereafter decreased. The extent of polymerization remained almost constant for 1 to 2 $\frac{1}{2}$ h.

The fall in grafting and efficiency may be attributed to the formation of homopolymer which may in turn affect the accessibility of the monomer to the grafting sites, thus reducing the efficiency [15]. Thampy et al. [19] have also observed that with long polymerization time the branches may be shortened by the reaction with initiator, and the fragmented poly(MMA) radicals can become attached to new polymer sites in the polymer chain. A chain transfer reaction involving polymer may also be the cause of such a decrease [18].

The effect of temperature on grafting was observed and the results are plotted in Fig. 6. Four different temperatures (35, 45, 55, and 60°C) were chosen for study. It is clear from the observations that both the percentage grafting and percentage efficiency increased up to 45°C, and at higher temperature both experienced a fall. The extent of polymerization increased in the whole range of temperature. It is assumed that at higher temperature, homopolymer formation becomes predominant over graft polymerization, and termination of grafted chain free radical may also be responsible for the decrease in percent grafting [6].

Physical Properties of Graft Copolymer

It is clear from Table 1 that the solubility of grafted wool decreased in acids and alkalies, and that there was a slight increase in solubility in urea bisulfite solution.

TABLE 1. Solubility Behavior of Grafted and Ungrafted Wool at Concentrations of HCl 6.0 N, NaOH 0.1 N, urea 50%, sodium metabisulfite 3%, pH = 7.0, 65°C, 60 min

Solvent	% Loss in weight	
	Ungrafted wool	Grafted wool
HCl	15.09	8.9
NaOH	12.0	10.9
Urea-bisulfite	10.04	12.57

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