

Grafting Vinyl Monomers Onto Wool Fibers. VIII. Graft Copolymerization of Methyl Methacrylate onto Wool Using Peroxydiphosphate–Fructose Redox System

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Synopsis

The graft copolymerization of methyl methacrylate onto wool fibers was investigated in aqueous solution using the peroxydiphosphate–fructose redox system. The rate of grafting was determined by varying monomer, acidity of the medium, temperature, nature of wool, and reaction medium. The graft yield increases with increase in peroxydiphosphate concentration. With increase in concentration of fructose up to 7.5×10^{-4} mole/l., there is a significant increase in graft yield; and with further increase in concentration of fructose the graft yield decreases. The graft yield increases with increase in monomer concentration up to 65.72×10^{-2} mole/l. and decreases thereafter. The grafting is considerably influenced by chemical modification prior to grafting. The effect of acid, temperature, and solvent on the rate of grafting has been investigated and a suitable rate expression has been derived.

INTRODUCTION

The modification of the properties of natural and synthetic fibers through graft copolymerization has attracted attention in recent years.¹⁻³ During the last two decades, peroxydisulfate has been used extensively for grafting vinyl monomers onto these fibers. Peroxydiphosphate, which is isoelectronic and isostructural with peroxydisulfate, has not been used as an initiator for graft copolymerization studies.^{4,5} Recently, Hariharan and Meenakshi⁶ and Nayak et al.^{7,8} have reported the polymerization of acrylonitrile and methyl methacrylate using this ion as the initiator. Marvel et al.⁹ reported the emulsion copolymerization of butadiene and styrene using peroxide and fructose as redox couple. Recently, Nayak et al.¹⁰ reported aqueous polymerization of methyl methacrylate using Mn^{3+} –fructose redox system and predicted that fructose is a very good reducing agent for producing free radical in solution. This communication presents the results of graft copolymerization of MMA onto wool using peroxydiphosphate–fructose as cocatalyst.

EXPERIMENTAL

The purification of wool fibers and preparation of modified such as oxidized, reduced, crosslinked, etc., wool were carried out according to literature procedure.^{3,11}

The reactions were carried out according to our previous procedure¹²⁻¹⁴ by

using peroxydiphosphate from 50×10^{-4} to 120×10^{-4} mole/l. at temperatures of 45–55°C. The graft yield was calculated as the percentage increase in weight over the original weight of the sample.

RESULTS AND DISCUSSION

Effect of MMA Concentration on Graft Yield

The graft copolymerization of methyl methacrylate onto wool was investigated by varying the monomer concentrations from 27.98×10^{-2} mole/l. to 103.27×10^{-2} mole/l., keeping the concentration of all other reagents constant. A perusal of the results indicates that the percentage of grafting increases with increasing monomer concentration up to 65.72×10^{-2} mole/l. and thereafter decreases with further increase in monomer concentration (Fig. 1).

The initial increase in the percentage of grafting with increase in the monomer concentration might be due to gel effect,¹⁵ i.e., increase in viscosity of the medium due to solubility of poly(methyl methacrylate) in its own monomer, which would be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of growing polymer chains. Besides, this gel effect also causes swelling of wool thus facilitating diffusion of monomer to growing chains and active sites on wool backbone, thereby enhancing grafting.

The decrease of the rate of grafting beyond 65.72×10^{-2} mole/l. of monomer concentration may be explained considering the fact that as the concentration of PMMA macroradicals increases, the rate of their combination and disproportionation increases than their combination with wool molecules. On the other hand, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which increases rapidly at higher monomer concentration.

Effect of Peroxydiphosphate Concentration on Graft Yield

Figure 2 shows the dependence of the graft percentage on the concentration of peroxydiphosphate. With increasing the concentration of peroxydiphosphate from 50×10^{-4} mole/l. to 120×10^{-4} mole/l., the graft-on percentage increases.

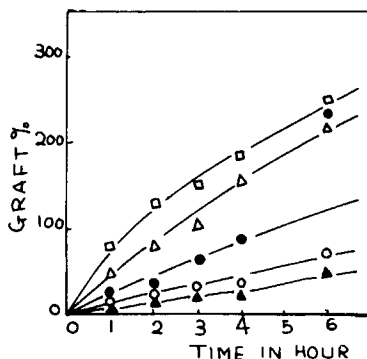


Fig. 1. Effect of MMA concentration on graft yield: $[PP] = 120 \times 10^{-4}$ mole/l.; $[H_2SO_4] = 0.5$ mole/l.; $[Fr] = 7.5 \times 10^{-4}$ mole/l.; temperature = 50°C; $M:L = 1:100$; (○) $[MMA] = 27.98 \times 10^{-2}$ mole/l.; (Δ) $[MMA] = 46.94 \times 10^{-2}$ mole/l.; (□) $[MMA] = 65.72 \times 10^{-2}$ mole/l.; (●) $[MMA] = 84.50 \times 10^{-2}$ mole/l.; (▲) $[MMA] = 103.27 \times 10^{-2}$ mole/l.

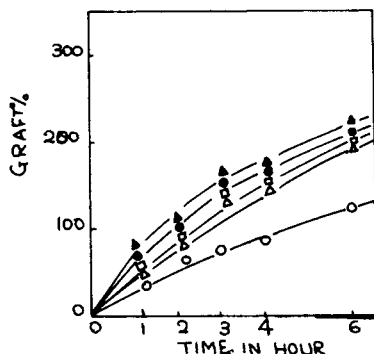
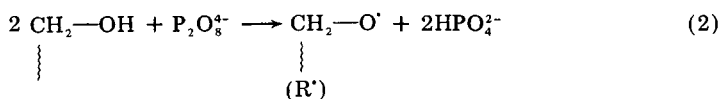
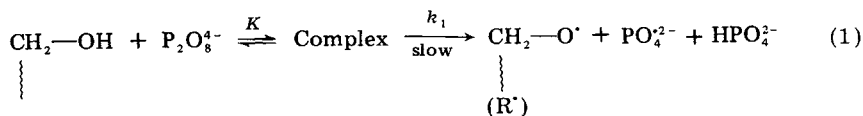
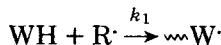


Fig. 2. Effect of peroxydiphosphate concentration on graft yield: $[Fr] = 7.5 \times 10^{-4}$ mole/l.; $[H_2SO_4] = 0.15$ mole/l.; $[MMA] = 0.4694$ mole/l.; temperature = $50^\circ C$; $M:L = 1:100$; (O) $[PP] = 50 \times 10^{-4}$ mole/l.; (Δ) $[PP] = 60 \times 10^{-4}$ mole/l.; (\square) $[PP] = 80 \times 10^{-4}$ mole/l.; (\bullet) $[PP] = 100 \times 10^{-4}$ mole/l.; (\blacktriangle) $[PP] = 120 \times 10^{-4}$ mole/l.

These observations could be explained as follows: In the presence of fructose, peroxydiphosphate decomposes to yield HPO_4^{2-} , PO_4^{2-} , and fructose radicals as shown below. These free radicals might participate in direct abstraction of hydrogen atom from wool backbone to create wool macroradicals capable of initiating grafting:

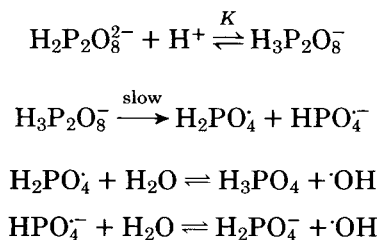


This (R') abstracts hydrogen from the amino or hydroxyl groups in wool to yield wool macroradical to initiate grafting:

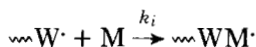
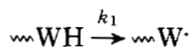


The second possibility might be that $H_2PO_4^\bullet$, $\cdot OH$, and $HPO_4^{\bullet -}$, which are produced during the reaction as shown below, interact with the groups present in wool backbone producing wool macroradicals which initiate grafting.

With increasing peroxydiphosphate concentration, the population of $H_2PO_4^\bullet$, $\cdot OH$, and $HPO_4^{\bullet -}$ radicals increases, thereby enhancing the graft yield:

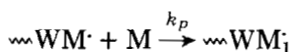


Initiation:

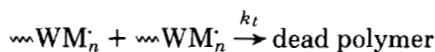


where, $\sim\text{WH}$ represents the reactive group in the wool backbone, M is the monomer, and $\sim\text{W}\cdot$ and $\sim\text{WM}\cdot$ are the corresponding radicals.

Propagation:



Termination:



Assuming steady-state principle to the initiating radicals, the expression for the rate of polymerization was derived to be

$$R_p = k_p \frac{K^{1/2} k_1^{1/2} [\text{Fr}]^{1/2} [\text{P}_2\text{O}_8^{4-}]^{1/2} [\text{M}]}{k_t^{1/2}}$$

The dependence of R_p on $[\text{M}]$, $[\text{Fr}]^{1/2}$, and $[\text{P}_2\text{O}_8^{4-}]^{1/2}$, which were experimentally observed, favors the above scheme.

Thus, the plot of $\log R_p$ vs. $\log [\text{M}]$ (Fig. 3) and $\log R_p$ vs. $\log [\text{PP}]^{1/2}$ (Fig. 4) should be linear passing through the origin, indicating that the order with respect to monomer is unity.

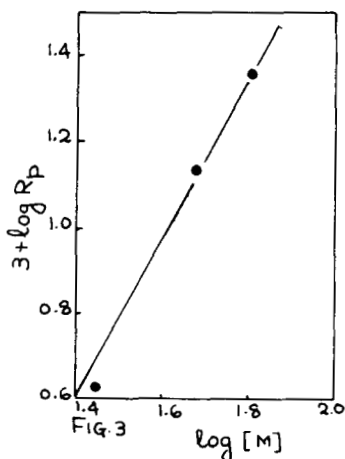


Fig. 3. Plot of $\log [\text{M}]$ vs. $\log R_p$.

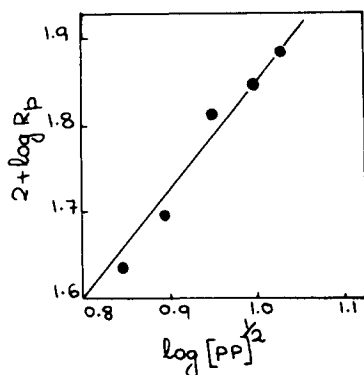


Fig. 4. Plot of $\log [PP]^{1/2}$ vs. $\log R_p$.

Effect of H_2SO_4 Concentration on Graft Yield

The effect of acid on graft copolymerization of methyl methacrylate onto wool was studied by changing the acid concentration within the range of 0.05–0.5 mole/l. The graft yield increases with increase in acid concentration, and the result is presented in Figure 5.

Edwards and co-workers^{16–18} predicted that the reactions of peroxide are subject to acid catalysis. Hence, it is assumed that the reactions of peroxydiphosphate which is both a peroxide and an oxyanion, i.e., oxyanion derivative of $H-O-O-H$, are subject to acid catalysis strongly. Peroxydiphosphate, $P_2O_8^{4-}$, is extensively protonated in acid medium because of the accumulation of high negative charge. Various species of peroxydiphosphate such as $P_2O_8^{4-}$, $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, and $H_3P_2O_8^-$ are possible in the reaction medium, and the concentration of these species differs with change in pH. The population of the different species as a function of pH is given by Crutchfield.¹⁹ Venturini et al.²⁰ suggested that in the region of $[H^+] = 0.01-0.7M$, only one kind of species, $H_3P_2O_8^-$, was responsible for the electro reduction of peroxydiphosphate, and it is likely that under the present experimental condition also, $H_3P_2O_8^-$ is the active species. With increase in acid concentration, the population of this active species increases considerably, thereby increasing the graft yield.

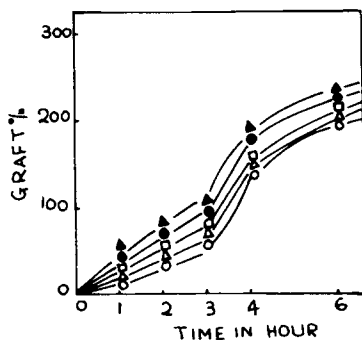


Fig. 5. Effect of H_2SO_4 concentration on graft yield: $[PP] = 120 \times 10^{-4}$ mole/l.; $[Fr] = 7.5 \times 10^{-4}$ mole/l.; $[MMA] = 0.4694$ mole/l.; temperature = $50^\circ C$; $M:L = 1:100$; (○) $[H_2SO_4] = 0.05$ mole/l.; (△) $[H_2SO_4] = 0.10$ mole/l.; (□) $[H_2SO_4] = 0.155$ mole/l.; (●) $[H_2SO_4] = 0.25$ mole/l.; (▲) $[H_2SO_4] = 0.50$ mole/l.

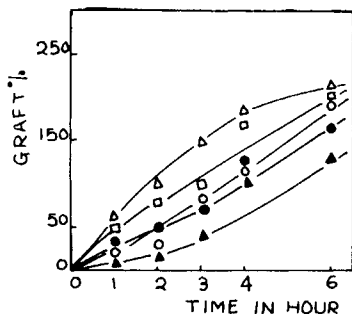


Fig. 6. Effect of fructose concentration on graft yield: $[PP] = 60 \times 10^{-4}$ mole/l.; $[H_2SO_4] = 0.15$ mole/l.; $[MMA] = 0.4694$ mole/l.; temperature = $50^\circ C$; $M:L = 1:100$; (O) $[Fr] = 5.0 \times 10^{-4}$ mole/l.; (Δ) $[Fr] = 7.5 \times 10^{-4}$ mole/l.; (\square) $[Fr] = 10 \times 10^{-4}$ mole/l.; (\bullet) $[Fr] = 25 \times 10^{-4}$ mole/l.; (\blacktriangle) $[Fr] = 50 \times 10^{-4}$ mole/l.

Effect of Fructose Concentration on Graft Yield

The effect of fructose concentration on graft yield has been investigated by varying fructose concentration from 5×10^{-4} to 50×10^{-4} mole/l. (Fig. 6). With increasing fructose concentration up to 7.5×10^{-4} mole/l., the graft percentage increases and thereafter decreases. The possible explanation might be as follows: In the initial stages, the fructose radicals produced by the interaction of fructose molecule by peroxydiphosphate ion initiate grafting. With increase in fructose concentration beyond 7.5×10^{-4} mole/l., the graft yield decreases. This might be due to (1) increase in fructose concentration, producing more fructose radicals which terminate the growing polymer chain; (2) increase in fructose concentration and the attendant increase in the viscosity of the medium, thereby inhibiting the mutual termination of the growing polymer chain; (3) increase in concentration of fructose radical could initiate the formation of homopolymer in the reaction medium, thereby decreasing grafting.

Effect of Temperature on Graft Yield

The graft copolymerization was carried out at three different temperatures ranging from 45 to $55^\circ C$ (Fig. 7). The percentage of graft-on increases with increase in temperature.

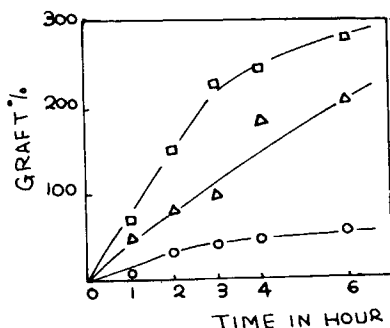


Fig. 7. Effect of temperature on graft yield: $[PP] = 120 \times 10^{-4}$ mole/l.; $[H_2SO_4] = 0.5$ mole/l.; $[Fr] = 7.5 \times 10^{-4}$ mole/l.; $[MMA] = 0.4694$ mole/l.; $M:L = 1:100$; (O) temperature = $45^\circ C$; (Δ) temperature = $50^\circ C$; (\square) temperature = $55^\circ C$.

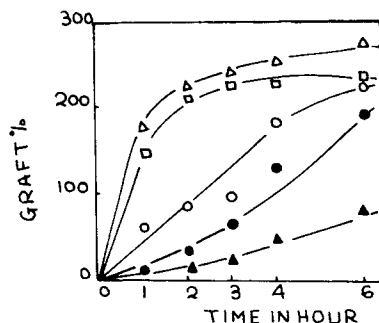


Fig. 8. Effect of nature of substrate on graft yield: $[PP] = 120 \times 10^{-4}$ mole/l.; $[Fr] = 7.5 \times 10^{-4}$ mole/l.; $[H_2SO_4] = 0.5$ mole/l.; $[MMA] = 0.4694$ mole/l.; temperature = $50^\circ C$; $M:L = 1:100$; (○) native wool; (Δ) reduced wool; (□) oxidized wool; (●) crosslinked wool; (▲) trinitrophenylated wool.

As the temperature increases, the solubility of monomer in the reaction medium, its diffusion from solution phase to the fiber phase, and the swellability of the fiber are greatly enhanced. Hence, the complexation of monomer with wool and its activity is increased as a result of which the graft-on increases.

Effect of Reaction Medium on Graft Yield

The reaction medium plays an important role in graft copolymerization reaction. Water-soluble organic solvents might affect the swelling properties of wool. Any change in wool swellability would be reflected on the behavior of wool toward grafting, since diffusion of monomer and initiation, availability of functional groups (sites of grafting), propagation, and termination of the graft, etc., would depend to a considerable extent on the swelling properties of wool. The results of various solvents affecting the percentage of grafting follow the order dioxan > formic acid > propanol > acetic acid > ethanol > methanol.

Nature of Substrate on Graft Yield

The native wool was subjected to different physical and chemical modification by reduction, oxidation, trinitrophenylation, and crosslinking (Fig. 8). The order of the percentage of graft-on follows: reduced wool > oxidized wool > untreated wool > crosslinked wool > trinitrophenylated wool.

The increase in graft percentage of reduced wool over the other modified wool may be explained on the basis that the reduction of the cystine-disulfide bond of wool with thioglycolic acid increases the number of thiol groups ($-SH$) which act as the active centers of grafting. Moreover, the initiation of grafting might involve not only abstraction of the hydrogen atom of the cystine $-SH$, but also the tyrosine $-OH$ groups on the polypeptide chains.

TABLE I
Molecular Weight and Degree of Polymerization of the Grafted Wool

Graft %	$\bar{M} \times 10^{-5}$	$\bar{DP} \times 10^{-3}$
159.45	6.998	6.998
184.4	6.823	6.823
233.6	2.443	2.443

On oxidation of wool with H_2O_2 , the cystine is most probably converted to cystic acid. The formation of free radical on the sulfur by the extraction of hydrogen from cystine is easier than creating a free radical in case of cystic acid. However, the probability of creation of free radical in case of cystic acid is more than in case of untreated wool where there is —S—S— linkage.

When wool is subjected to trinitrophenylation, the amino, hydroxyl, and thiol groups are blocked, as a result of which free radicals cannot be created at the wool backbone by the interaction of initiating radicals for which the graft yield decreases. The other reasons for low graft yield might be due to (1) lowering of swellability of wool fibers, and (2) hindrance of adsorption of methyl methacrylate molecule by the negatively charged substituted nitro group in the case of TNP wool. The net effect of all these factors is a decrease in grafting.

Molecular Weight Determination

The intrinsic viscosity was calculated by using the single point method for poly(methyl methacrylate) of Valles et al.²¹ The molecular weight was obtained from the equation²²

$$[\eta] = 9.6 \times 10^{-5} \bar{M}^{0.69}$$

The result indicates that the average molecular weight and the degree of polymerization decrease with increasing percentage of grafting (Table I).

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