

Grafting Vinyl Monomers onto Wool Fibers. I. Graft Copolymerization of Methyl Methacrylate onto Wool Using V^{5+} -Thiourea Redox System

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Synopsis

The graft copolymerization of methyl methacrylate in wool fibers was investigated in aqueous solution using V^{5+} -thiourea redox system. The rate of grafting was determined by varying monomer, thiourea, acidity of the medium, temperature, nature of wool, different acrylic monomers, and reaction medium. The graft yield increases significantly by increasing reaction time in the initial stages of the reaction but it does slow down on prolonging the duration of grafting. The effect of increasing monomer concentration brings about a significant enhancement in the graft yield. The graft yield increases with increasing thiourea concentration, but beyond 0.0075M, the percentage graft yield decreases. The graft yields are considerably influenced by chemical modification prior to grafting. Wool reduced with thioglycolic acid is more susceptible to grafting than untreated wool; the opposite effect is noted in the case of trinitrophenylated and esterified wools. A suitable kinetic scheme has been proposed and the rate equation has been evaluated.

INTRODUCTION

Chemical modifications have been devised to give natural macromolecules more desirable properties; application of synthetic macromolecules forms an important area of such chemical modification. In recent years, chemical modification of wool through grafting has received considerable interest,¹⁻⁵ since preformed polymers are incapable of diffusing into the internal structures of wool. The major problem during the process of grafting is the formation of homopolymer on the wool backbone which might be entangled within the wool matrix and very difficult to remove completely by the usual solvent extraction technique.

The successful grafting of vinyl monomers onto wool involves the creation of free radical on the backbone of wool. This can be achieved by several methods, i.e., high-energy radiation,^{6,7} low-energy radiation in presence and absence of sensitizers,^{8,9} and redox systems.¹⁰⁻¹⁴ The last method has attracted attention in recent years because it provides a direct experimental evidence of the existence of transient radical intermediates, generated in redox reactions.

In the recent past, thiourea and *N*-substituted thioureas have been extensively used for the polymerization of vinyl monomers in aqueous medium. Bonvicini and Caldo¹⁵ and Sugimura et al.¹⁶ have used these reducing agents with hydrogen peroxide as the oxidant for initiation of aqueous polymerization of acrylonitrile. Mukherjee et al.¹⁷ have used thiourea as reductant with a number of oxidants such as ferric chloride (Fe^{3+}), ethylene dibiguanide complex salts of tripositive

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silver (Ag^{3+}), hydrogen peroxide, etc. for initiation of aqueous polymerizations of methyl methacrylate. We have reported the aqueous polymerization of acrylonitrile using V^{5+} , Cr^{6+} , Mn^{3+} , bromate/HCl, and thiourea as the redox couple.¹⁸⁻²¹ Very recently, Hebeish and Bendak have used thiourea coupled with hydrogen peroxide,²² Fe^{3+} ,²³ di- and tert-butyl peroxide²⁴ for grafting vinyl monomers onto wool fibers.

This paper presents the results of studies of graft copolymerization of methyl methacrylate (MMA) onto wool fibers using V^{5+} -thiourea redox system.

EXPERIMENTAL

Indian Chokla wool fibres were purified by Soxhlet extraction with acetone for about 24 hr, followed by cold distilled water washing and air drying.

MMA was washed with 5% sodium hydroxide solution; it was then dried with anhydrous sodium sulphate and distilled under reduced pressure in nitrogen before use.

Ammonium metavanadate (AR), thiourea (AR,BDH), and sulphuric acid (18 M; AR,BDH) were used. Water, distilled twice over alkaline permanganate and deionized by passing it through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen used to deaerate the experimental systems was freed from oxygen by passage through five columns of Fieser's solution, a column of saturated lead acetate solution, and finally through a wash bottle containing distilled water.

A stock solution of V^{5+} ($\approx 0.4 N$ in $\approx 4 M \text{H}_2\text{SO}_4$) was prepared by suspending ammonium metavanadate (4.7 g) in distilled water (25 ml) and adding with stirring 75 ml of 10 N sulphuric acid. The concentration of V^{5+} in the experimental systems was determined by vanadometry.

The reactions were carried out in Pyrex flasks equipped with gas inlet and outlet tubes in a nitrogen atmosphere. Dried and purified wool fibers were immersed in a solution of V^{5+} (0.0025–0.01 M) in H_2SO_4 (0.50–2.5 N) at temperatures from 35° to 50°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 15 to 120 min and the material to liquid ratio was 1:100. After the desired reaction time, wool fibers were taken out and washed thoroughly with water and acetone. Finally, the fibers were Soxhlet extracted with benzene or acetone until the homopolymer was completely removed. They were then dried in an oven, cooled to room temperature, and weighed. The graft on was calculated as the percentage increase in weight over the original weight of the sample.

RESULTS AND DISCUSSION

Grafting in the presence and absence of thiourea (TU): Figure 1 shows the graft yield as a function of reaction time. In presence and absence of TU a considerable amount of grafting occurred. But, for a given reaction time, the graft yield obtained in presence of TU is significantly higher than in its absence.

The effect of thiourea concentration was studied by varying thiourea concentration over the range (0.0025–0.015 M). The percentage of graft yield increases with the increase of the concentration of thiourea (Fig. 2). This corresponds to our reaction scheme as outlined in eqs. (1)–(8). But beyond 0.0075

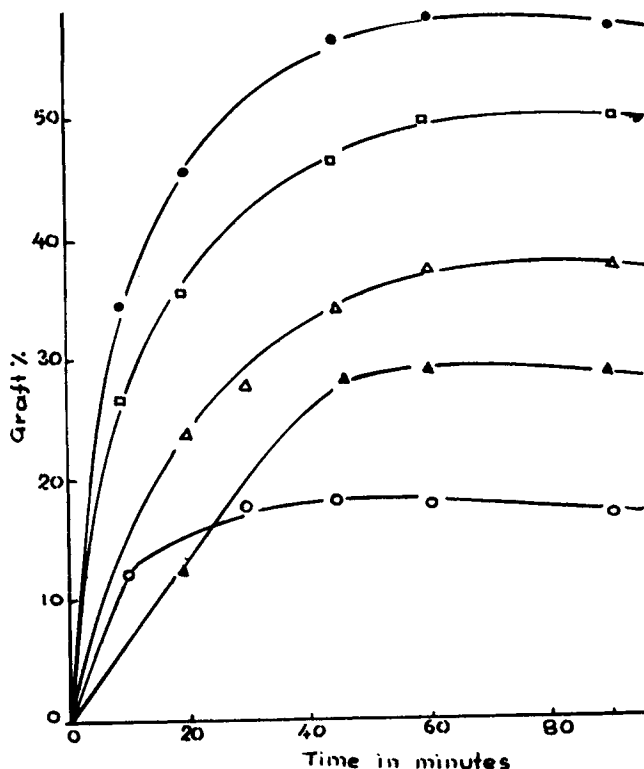


Fig. 1. Effect of monomer concentration on graft yield. $[TU] = 0.006 M$; $[V(V)] = 0.01 M$; $[H_2SO_4] = 0.3 M$; temperature = $45^\circ C$. (○): $[MMA] = 9.4 \times 10^{-2} M$; (△): $[MMA] = 14.10 \times 10^{-2} M$; (□): $[MMA] = 18.77 \times 10^{-2} M$; (●): $[MMA] = 23.47 \times 10^{-2} M$; (▲): $[MMA] = 14.10 \times 10^{-2} M$ in absence of thiourea.

M of thiourea, a considerable decrease in graft yield is observed, which might be due to the following reasons: (a) the increased amount of free radical inhibitor in thiourea, which is always present in it (a relatively pure product may contain inhibitors up to 0.48 mole %)²⁵; (b) fixed amounts of thiourea being converted to isothiurea which actually participates in producing initiating species; and (c) at a higher concentration of thiourea some species might be generating what might be acting as radical scavenger.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration and keeping the concentrations of other reagent constant (Fig. 1). The graft yield increases with increasing reaction time in the initial stages of the copolymerization reaction but it does slow down when the duration of grafting is prolonged. Further, the graft yield also increases with increase of monomer concentrations. Since the copolymerization reaction was carried out at the same temperature and at fixed concentrations of V^{5+} , thiourea, and acidity, it is possible to assume that the concentration, nature and efficiency of the free radical, and other species generated during the reaction would be the same. Hence, the higher rate of grafting observed upon increasing the monomer concentration could be attributed to a variety of reasons. First, complexation

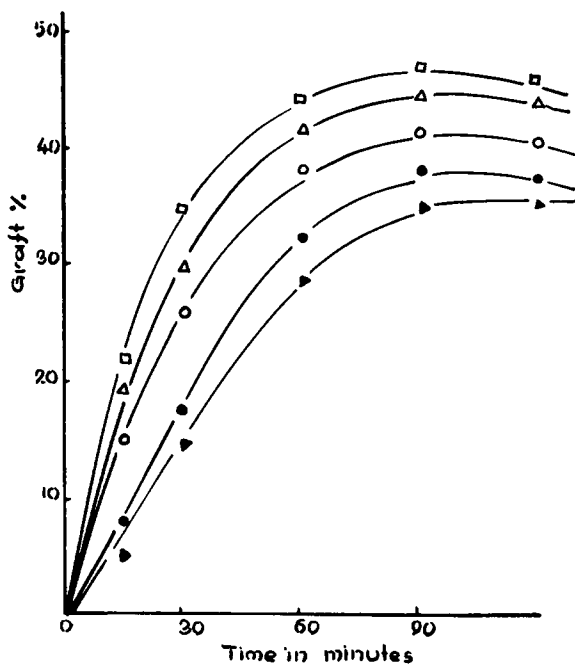


Fig. 2. Effect of thiourea concentration on graft yield. $[V(V)] = 0.01 M$, $[MMA] = 18.77 \times 10^{-2} M$, $[H_2SO_4] = 0.75 M$; temperature = $45^\circ C$. (O): $[TU] = 0.0025 M$; (Δ): $[TU] = 0.005 M$; (\square): $[TU] = 0.0075 M$; (\bullet): $[TU] = 0.015 M$; (\blacktriangle): $[TU] = \text{Nil}$ (in the absence of thiourea).

of wool with monomer, which is required for enhancing monomer activity would be favored at higher monomer concentrations. The second reason might be due to gel effect, i.e., the solubility of polymethylmethacrylate in its own monomer; this could be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of these growing polymer chains. Besides this, the gel effect also causes swelling of wool, thus facilitating diffusion of monomer to growing grafted chains and at active sites on the wool backbone, thereby enhancing grafting. The initial rates of grafting dG_0/dt were obtained for different monomer concentrations. The plot of logarithm of dG/dt vs. the logarithm of the initial monomer concentration $[M]_0$ is linear and pass through the origin (Fig. 3) showing that the rate of polymerization is proportional to $[M]$ as suggested in eq. (8). The value of $k_1 K k_p / kt$ was computed from the slope to be 1.36.

Effect of Temperature

The graft-copolymerization was carried out at four different temperatures between 30° and $50^\circ C$, keeping the concentrations of all other reagents constant. A perusal of the result (Fig. 4) indicates that the increasing temperature the percent of graft-on increases up to $45^\circ C$ and then decreases. The dependence of the rate of grafting on temperature between 30° – $45^\circ C$ could be ascribed to the greater activation energy. The swellability of wool, solubility of monomer, and its diffusion rates are enhanced by increasing the reaction temperature. But beyond $45^\circ C$, the percent graft-on decreases probably due to the fact that at higher temperature, there is a possibility of higher combination rates of monomer

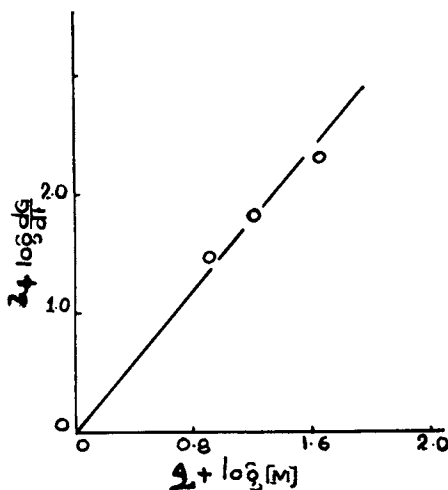


Fig. 3. Plot of logarithm of monomer concentration vs logarithm of dG/dt .

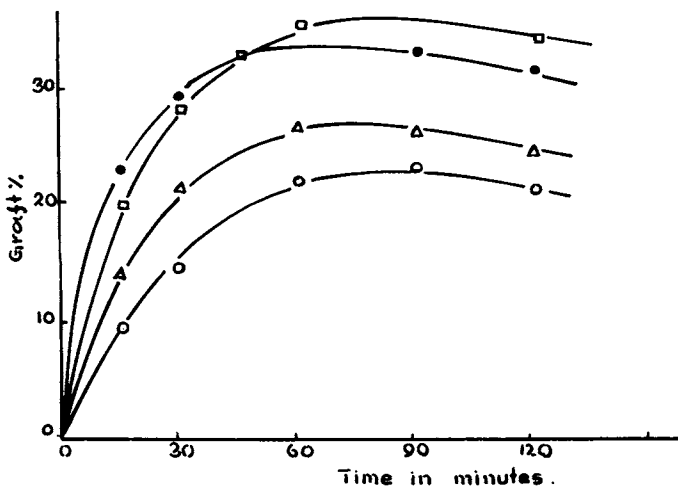
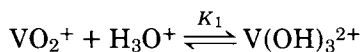


Fig. 4. Effect of temperature on graft yield. $[TU] = 0.006 M$; $[V(V)] = 0.01 M$; $[H_2SO_4] = 0.75 M$; $[MMA] = 18.77 \times 10^{-2} M$. (O): 30°C; (Δ): 40°C; (\square): 45°C; (\bullet): 50°C.

which results in a decrease in rate of grafting. Similar observations have been noted by Hebeish and Mehta,²⁶ while grafting acrylonitrile onto cellulose by ceric ion method. A probable explanation given by them was the increased rate of termination of growing polymer chains at higher temperatures.

Effect of Acid Concentration

The grafting reaction has been conducted by varying the acid concentrations (from 0.45 to 1.35 M). It is observed that the percentage graft-on increases with the increase of acid concentration in the initial stages and with further increase of acid the percentage graft-on decreases (Fig. 5). In the initial stages, with the increase in the concentration of H_2SO_4 , the following species of V^{5+} is formed which might produce more amount of free radicals and hence the percentage graft-on increases²⁷



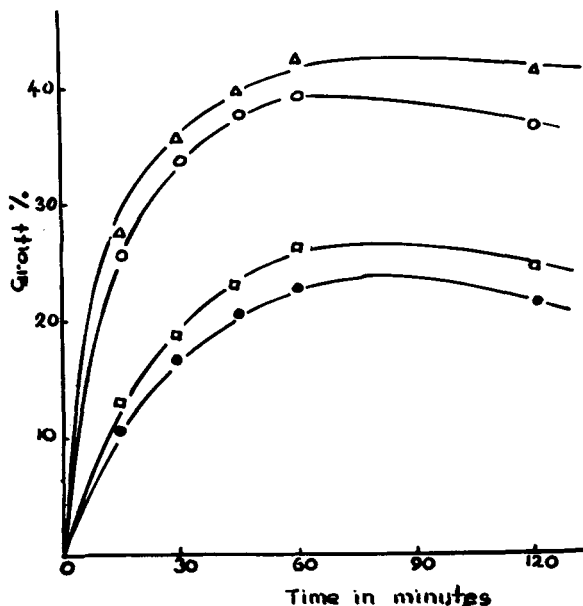


Fig. 5. Effect of acid concentration on graft yield. $[TU] = 0.006 M$; $[V(V)] = 0.01 M$; $[MMA] = 18.77 \times 10^{-2} M$; temperature = $45^\circ C$. (O): $[H^+] = 0.45 M$; (Δ): $[H^+] = 0.75 M$; (\square): $[H^+] = 1.05 M$; (\bullet): $[H^+] = 1.35 M$.

With further increase of the concentration of H_2SO_4 , less powerful species of V^{5+} , such as $V(OH)_3$ (HSO_4) $^+$, $VO-OH^{2+}$, $VO_2SO_4^{3-}$, etc., might be forming, thereby reducing the oxidizing capacity of quinquevalent vanadium ion. Similar explanation has been advanced by us in the case of polymerization of acrylonitrile initiated by the V^{5+} -thiourea redox system.¹⁸

Nature of the Substrates

The effect of the changes in the physical or chemical structure of wool brought about by reduction, esterification, or trinitrophenylation on its behavior towards grafting has been studied. The order follows: reduced wool > unmodified wool > esterified wool > trinitrophenylated wool.

When wool is treated with thioglycolic acid, reduced wool is formed with more $-SH$ groups owing to the breakage of the $-S-S-$ linkages in the cystine molecule. The higher graft yield obtained with reduced wool is due to the availability of more $-SH$ groups. It is known that the abstraction of hydrogen from thiol groups by initiating radicals seems to proceed much more easily than the abstraction of hydrogen from amino and hydroxyl groups in the wool molecule. Further, treatment of wool with thioglycolic acid might increase its accessibility or swelling and hence enhancing grafting²⁷ (Fig. 6).

Acetylation and trinitrophenylation of wool significantly reduces its ability towards grafting. When wool is subjected to acetylation or trinitrophenylation, the amino hydroxyl and thiol groups are blocked. Free radicals cannot be created at the wool backbone by the interaction of initiating radicals resulting in the decrease of the graft yield. The other reasons for low graft yield might be due to (i) lowering of the swellability of wool fibers, (ii) hindrance of adsorption of MMA owing to low fiber swellability, and (iii) repulsion of MMA molecule by

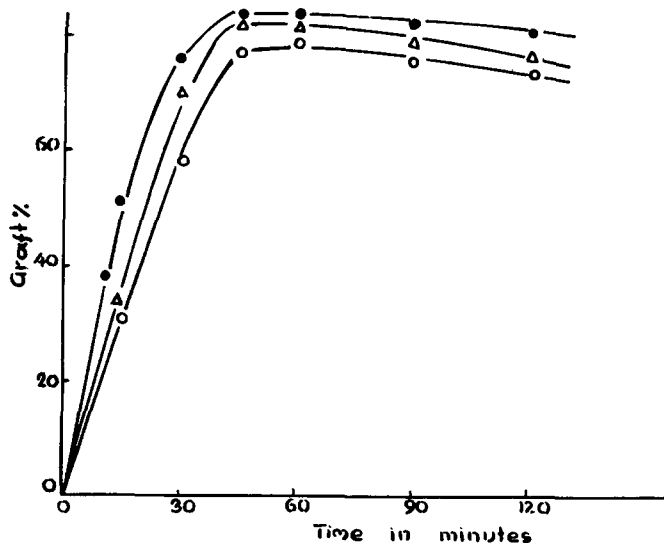


Fig. 6. Rate of grafting at varying extent of reduction of wool fibers. $[TU] = 0.006 M$; $[V(V)] = 0.01 M$; $[H_2SO_4] = 0.3 M$; $[MMA] = 23.50 \times 10^{-2} M$; temperature = $45^\circ C$. (O): $[TGA] = 0.025 (N)$; (Δ): $[TGA] = 0.05 (N)$; (\bullet): $[TGA] = 0.1 (N)$.

the negatively charged substituted nitro group in the case of TNP wool. The net effect of all these factors is the decrease of grafting.

Grafting of Different Monomers onto Wool

Graft copolymerization was investigated with different acrylate monomers (methyl, ethyl, *N*-butyl acrylate, and methylmethacrylate) keeping the concentration of other reagents constant. The order of reactivities as far as graft-on percent is concerned is as follows:

methyl acrylate > ethyl acrylate >

methylmethacrylate > *n*-butyl acrylate

Thus, as the size of the monomer is increased, the diffusion of monomer to all available sites on the fiber is not possible resulting in the decrease of the percentage of graft-on in the case of bulkier monomers.

Effect of Reaction Medium

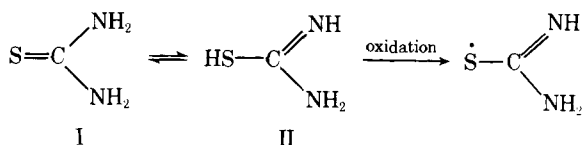
The reaction medium plays an important role in grafting vinyl monomers onto wool fibers. The reaction medium might affect on the swelling properties of wool. Any change in wool swellability would be reflected on the behavior of wool toward grafting since diffusion of monomer and initiator, availability 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 order of solvent, as far as percentage of graft yield is concerned, follows the following sequence: formic acid > acetic acid > methyl alcohol > ethyl alcohol.

Effect of Amount of Wool

The percentage of grafting increases when the amount of wool is increased from 0.1 to 0.6 g. The grafting efficiency increases as the amount of wool in the polymerizing medium increases. This suggests that polymerization of MMA onto a wool fiber initiated by thiourea- V^{5+} takes place preferentially in the wool matrix with the abundance of wool in the medium; hence the integrated surface area of the fibers greatly affects the diffusion of the monomer and free radical species as well as increasing the possibility of free-radical formation on the wool backbone.

Reaction Mechanism

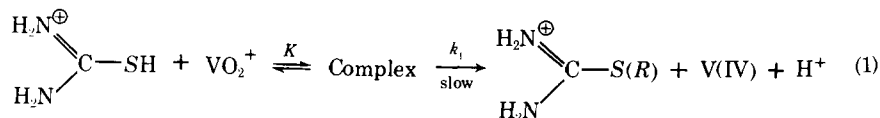
In all the initiating systems containing thiourea (I) the redox component is isothioureia¹⁸ (II), a thiol (existing in a tautomeric equilibrium with thiourea in an aqueous solution) is the reductant. The generation of a free radical in this system takes place by the abstraction of the reactive hydrogen atom attached to the sulfur atom in isothioureia generating the amidinosulfenyl radical (III)



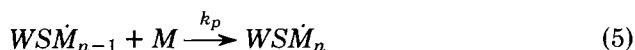
It has been observed that with all the redox systems containing thiourea, V^{5+} -thiourea redox system has the following advantages over the others. (i) The initiating efficiency is very high and the induction period is practically undetectable. (ii) Most of the water-soluble monomers could be polymerized by this system.

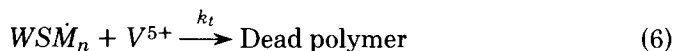
The reaction of thiourea with V^{5+} is therefore likely to be analogous to that between V^{5+} and mercaptan.²⁸ It is likely that V^{5+} first forms a complex with isothioureia moiety and the complex breaks down giving rise to the amidinosulfenyl radical as shown below. Similar complexes have been shown to occur in the oxidations of alphasmercapto acids²⁸ by V^{5+} .

Primary radical production



The isothiocarbamido radicals abstract hydrogen from thio, amino, or hydroxyl groups in wool (WH) to yield wool macroradicals (\dot{W}).





Linear termination of vinyl polymerization by metal ions is now well recognized.²⁹

Taking into account the above reaction scheme and applying steady-state assumption to both $[\dot{R}]$ and $[WS\dot{M}]$, separately, the following expressions have been derived:

$$\begin{aligned} \frac{d[\dot{R}]}{dt} &= k_1K[\text{TU}][V^{5+}] - k_2[WSH][\dot{R}] = 0 \quad (7) \\ \frac{d[WS\dot{M}]}{dt} &= k_i[WS\dot{S}][M] - k_t[WS\dot{M}][V^{5+}] = 0 \\ [WS\dot{S}] &= k_2[WSH][\dot{R}]/k_i[M] \\ [WS\dot{M}] &= k_1K[\text{TU}]/k_t \\ R_p &= k_p[WS\dot{M}][M] = (k_iKk_p/R_t)[\text{TU}][M] \quad (8) \end{aligned}$$

The dependence of R_p on $[M]$ and $[\text{TU}]$ which were experimentally observed, favored the above scheme.

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