Grafting Vinyl Monomers onto Wool Fibers. VII. Graft Copolymerization of Methyl Methacrylate onto Wool Using Peroxydiphosphate-Thiourea Redox System

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ABSTRACT

Graft copolymerization of methyl methacrylate onto wool was investigated in aqueous solution using the potassium peroxydiphosphate-thiourea redox system as the initiator. The rate of grafting was determined by varying the monomer, peroxydiphosphate ion, temperature, and solvent. The graft yield increases with increasing peroxydiphosphate ion up to 80×10^{-4} mol/L, and with further increase of peroxydiphosphate ion the graft yield decreases. The graft yield increases with increasing monomer concentration. The percentage of grafting decreases with increasing thiourea concentration. The rate of grafting increases with an increase of temperature. The effect of acid and water-soluble solvent and certain salts on graft yield has been investigated and a suitable rate expression has been derived.

INTRODUCTION

The graft copolymerization of vinyl monomers onto wool fibers has attracted attention in recent years [1-4]. Various workers have

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studied the grafting of wool with a variety of initiator such as per-
sulfate, ferrous(II)-hydrogen peroxide [5], Ce(IV) [6], Mn(IV) [7],
periodate [8], Cu^{2+}-complex-trichloroacetic acid [9], azobisiso-
butyronitrile [10], and dimethyl aniline-benzyl chloride [11]. Very
recently we have reported the graft copolymerization of wool fibers
using Cr(VI) [12], V(V) [13], Mn(IV) [14], and several other initia-
tors. This communication presents the results of graft copolymeriza-
tion of methyl methacrylate onto wool using the potassium peroxy-
diphosphate-thiourea redox system.

EXPERIMENTAL

Indian Chokla wool fibers were purified by Soxhlet extraction with
acetone for about 24 h followed by cold distilled water washing and
air drying. Methyl methacrylate was washed with 5% sodium hy-
droxide solution; it was then dried with anhydrous sodium sulfate and
distilled under reduced pressure in nitrogen before use.

Peroxydiphosphate was a gift sample from FMC Corp., U.S.A.
All other reagents were of AnalaR grade. Water distilled twice over
alkaline permanganate and deionized by passing through a column of
Biodeminolit resin (Permutit Co., U.K.) was used to prepare all the
solutions. Peroxydiphosphate solution was estimated by cerimetry.

The reactions were carried out according to our previous pro-
cedure [12, 13] by using peroxydiphosphate from 50×10^{-4} to $100 \times$
10^{-4} mol/L at temperatures from 45 to 55°C in the presence of
ethylene glycol monoethyl ether which acts as a monomer solubilizer.
The graft yield was calculated as the percentage increase in weight
over the original weight of the sample.

Alkali Solubility

The alkali solubility of wool was tested in aqueous solution of 0.1 N
sodium hydroxide solution for 1 h at 65°C using a wool-liquor ratio of
1:100.

RESULTS AND DISCUSSION

Effect of [Peroxydiphosphate] on Graft Yield

Figure 1 shows the graft percentage as a function of peroxydiphos-
phate concentration when graft copolymerization of methyl methacry-
late onto wool was carried out in the presence of thiourea (0.00025
mol/L) at 50°C. As is evident, increasing the peroxydiphosphate
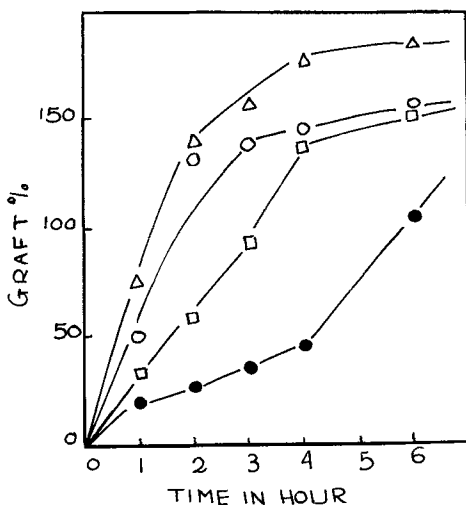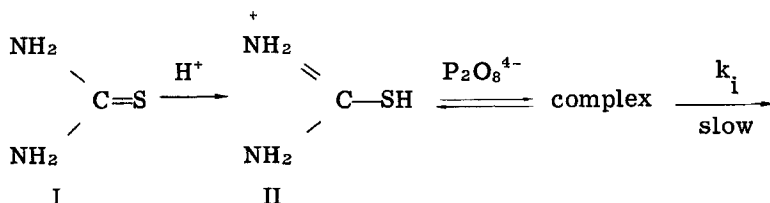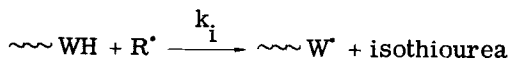concentration from 50×10^{-4} to 80×10^{-4} mol/L is accompanied by

FIG. 1. Effect of [peroxydiphosphate] on graft yield. [H₂SO₄] = 0.15 mol/L, [TU] = 0.00025 mol/L, [MMA] = 0.4694 mol/L, temperature = 50°C, M:L = 1:100. (□) [peroxydiphosphate] = 50 × 10⁻⁴ mol/L, (○) [peroxydiphosphate] = 60 × 10⁻⁴ mol/L, (△) [peroxydiphosphate] = 80 ×10⁻⁴ mol/L, (●) [peroxydiphosphate] = 100 × 10⁻⁴ mol/L.

a significant increase in the graft yield. Thereafter, grafting decreases as the peroxydiphosphate concentration increases.

These findings could be explained as follows.

(1) In the presence of thiourea, peroxydiphosphate decomposes to yield HPO_4^{2-} and isothiocarbamido(III) radicals as shown below. These free radicals may participate in (a) direct abstraction of a hydrogen atom from the wool backbone to bring about wool macroradicals capable of initiating grafting, (b) the termination process with the growing polymer chains, and (c) the termination process with wool macroradicals. At lower peroxydiphosphate concentrations the effect of (a) seems to prevail over the combined effect of (b) and (c), thereby increasing grafting. The opposite holds true at higher peroxydiphosphate concentrations where the combined effect of (b) and (c) is more pronounced than (a). As a result, lower grafting occurred.

$$\overset{+}{N}H_2$$
$$\diagdown$$
$$\qquad C-S^{\cdot} + HPO_4^{-2}$$
$$\diagup$$
$$NH_2 \qquad (R^{\cdot})$$
$$\qquad III$$

$$\text{\textasciitilde\textasciitilde} WH + R^{\cdot} \xrightarrow{k_i} \text{\textasciitilde\textasciitilde} W^{\cdot} + \text{isothiourea}$$
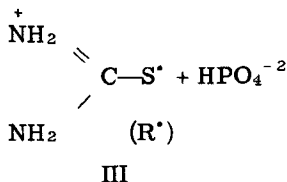
(2) The second possibility is that $H_2\overset{\cdot}{P}O_4$, $\overset{\cdot}{O}H$, and $HPO_4^{-\cdot}$, which are produced during the reaction as shown below, interact with the groups present in the wool backbone to produce wool macroradicals which initiates grafting. The reaction scheme is

$$H_2P_2O_8^{2-} + H^+ \underset{}{\overset{K}{\rightleftharpoons}} H_3P_2O_8^{-}$$

$$H_3\overset{-}{P}_2O_8^{-} \xrightarrow{\text{slow}} H_2PO_4^{\cdot} + HPO_4^{\cdot-}$$

$$H_2PO_4^{\cdot} + H_2O \rightleftharpoons H_3PO_4 + OH^{\cdot}$$
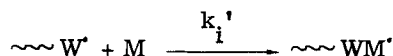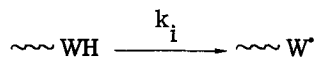
$$HPO_4^{\cdot-} + H_2O \rightleftharpoons H_2PO_4^{-} + OH^{\cdot}$$

(i) Initiation:

$$\text{\textasciitilde\textasciitilde} WH \xrightarrow{k_i} \text{\textasciitilde\textasciitilde} W^{\cdot}$$

$$\text{\textasciitilde\textasciitilde} W^{\cdot} + M \xrightarrow{k_i'} \text{\textasciitilde\textasciitilde} WM^{\cdot}$$
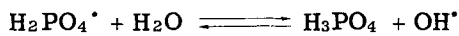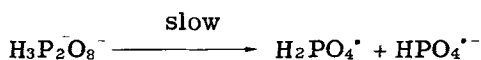
Where $\text{\textasciitilde\textasciitilde} WH$ represents the reactive group in the wool backbone, M is the monomer, and $\text{\textasciitilde\textasciitilde} W^{\cdot}$ and $\text{\textasciitilde\textasciitilde} M^{\cdot}$ the corresponding radicals.

(ii) Propagation:
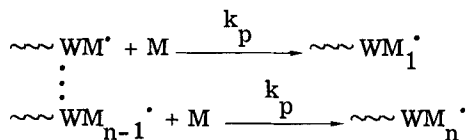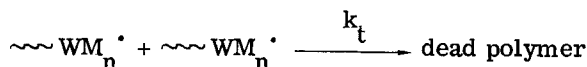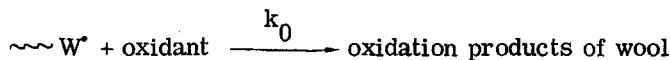
$$\text{\textasciitilde\textasciitilde} WM^{\cdot} + M \xrightarrow{k_p} \text{\textasciitilde\textasciitilde} WM_1^{\cdot}$$
$$\vdots$$
$$\text{\textasciitilde\textasciitilde} WM_{n-1}^{\cdot} + M \xrightarrow{k_p} \text{\textasciitilde\textasciitilde} WM_n^{\cdot}$$

(iii) Termination:

$$\text{\textasciitilde\textasciitilde} WM_n^{\cdot} + \text{\textasciitilde\textasciitilde} WM_n^{\cdot} \xrightarrow{k_t} \text{dead polymer}$$

(iv) Oxidation:

$$\sim\sim W^{\bullet} + \text{oxidant} \xrightarrow{\quad k_0 \quad} \text{oxidation products of wool}$$

Now

$$\frac{d[W^{\bullet}]}{dt} = k_i[WH] - k_i'[W^{\bullet}][M] = 0$$

$$k_i[WH] = k_i'[W^{\bullet}][M]$$

$$[W^{\bullet}] = \left(\frac{k_i}{k_i'}\right)\frac{[WH]}{[M]}$$

Again,

$$\frac{d[WM^{\bullet}]}{dt} = k_i'[W^{\bullet}][M] - k_t[WM_n^{\bullet}]^2 = 0$$

$$[WM_n^{\bullet}]^2 = \frac{k_i'}{k_t}\frac{k_i}{k_i'}\frac{[WH[M]]}{[M]} = \frac{k_i}{k_t}[WH]$$

$$[WM_n^{\bullet}] = \left\{\frac{k_i}{k_t}[WH]\right\}^{1/2}$$

The rate of polymerization is

$$R_p = k_p[WM_n^{\bullet}][M] = k_p\frac{k_i^{1/2}}{k_t^{1/2}}[WH]^{1/2}(M)$$

Thus the plot of log R_p vs log $[M]$ should be linear, passing through the origin (Fig. 2) and indicating that the rate is first order with respect to monomer concentration.

With increasing peroxydiphosphate concentration, a large number of $H_2PO_4^{\bullet}$, $OH^{\bullet}$, and $HPO_4^{\bullet-}$ radicals are produced which interact with the wool backbone, giving rise to free radicals at several sites on the
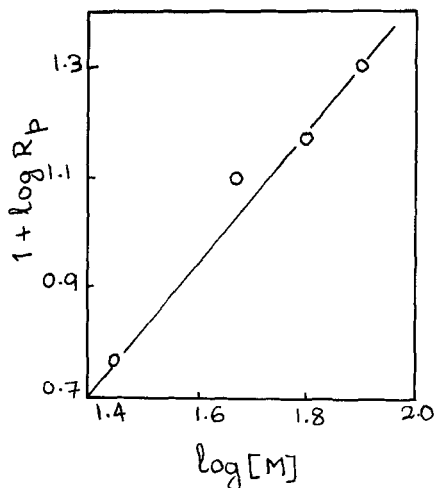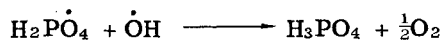
FIG. 2. Plot of log [M] vs log R_p.

wool backbone which initiate grafting, thereby increasing the graft yield. The fall in graft yield with increasing peroxydiphosphate concentration could be explained as follows.

(a) The oxidant could react with the growing free radicals to give rise to oxidation products.
(b) At higher concentrations of oxidant there is a possibility of formation of homopolymer.

At higher concentrations of peroxydiphosphate the following reactions might take place:

$$HPO_4^{\cdot-} + \overset{\cdot}{O}H \longrightarrow H_2PO^{4-} + \tfrac{1}{2}O_2$$

$$H_2\overset{\cdot}{P}O_4 + \overset{\cdot}{O}H \longrightarrow H_3PO_4 + \tfrac{1}{2}O_2$$
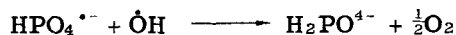
The oxygen formed might act as an inhibitor, thereby decreasing the rate of grafting.

Effect of [Thiourea] on Graft Yield

Figure 3 shows the variation of graft uptake with a changing concentration of thiourea. It is clear that considerable grafting does occur even in the absence of thiourea, indicating the formation of wool

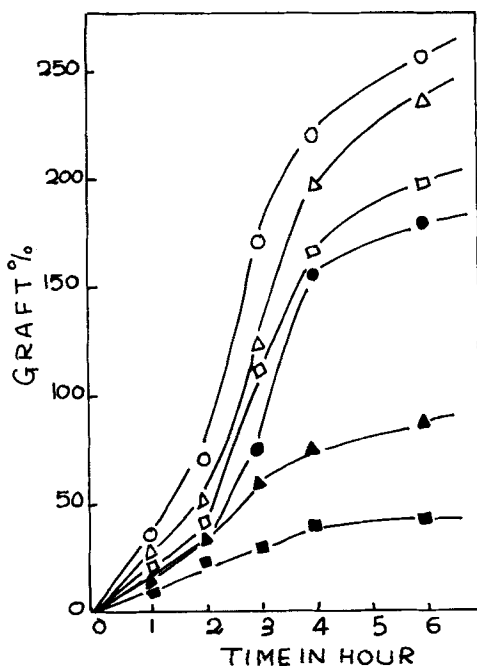FIG. 3. Effect of [TU] on graft yield. [Peroxydiphosphate] = 80 × 10⁻⁴ mol/L, [H₂SO₄] = 0.15 mol/L, [MMA] = 0.4694 mol/L, M:L = 1:100, temperature = 50°C. (○) [TU] = 0.00025 mol/L, (△) [TU] = 0.000375 mol/L, (□) [TU] = 0.001 mol/L, (●) [TU] = 0.0035 mol/L, (▲) [TU] = 0.005 mol/L, (■) [TU] = 0.0075 mol/L.

macroradicals capable of graft initiation. These wool macroradicals may be generated via the decomposition of peroxydiphosphate.

The effect of thiourea concentration on graft yield has been investigated by varying thiourea over a wide range of concentration. It is observed that with increasing thiourea concentration the graft yield decreases considerably. Several reasons might be responsible for the decrease of the graft uptake with increasing thiourea concentration.

1. Peroxydiphosphate interacts with thiourea to produce isothiourea radicals. There will be abundance of this free radical species in the polymerization medium with increasing thiourea concentration which might terminate the growing polymer chain, thus reducing the percentage of grafting.

2. It is also possible that at higher concentrations of thiourea the latter might act as a radical scavenger, thereby decreasing grafting.
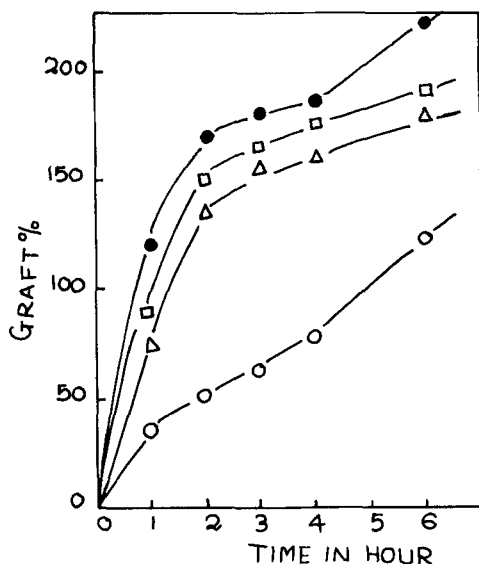
FIG. 4. Effect of [MMA] on graft yield. [Peroxydiphosphate] = 80 × 10^{-4} mol/L, [H$_2$SO$_4$] = 0.15 mol/L, [TU] = 0.00025 mol/L, temperature = 50°C, M:L = 1:100. (○) [MMA] = 27.98 × 10^{-2} mol/L, (△) [MMA] = 46.94 × 10^{-2} mol/L, (□) [MMA] = 65.72 × 10^{-2} mol/L, (●) [MMA] = 84.50 × 10^{-2} mol/L.

3. The isothiocarbamido radical produced in the system might react with the monomer to give rise to the homopolymer. There will be competition between homopolymerization and grafting. The homopolymerization reaction exceeds grafting at higher concentrations of thiourea.

4. Increasing in concentration of thiourea might increase the viscosity of the medium, thereby inhibiting the combination of the growing polymer chain.

Effect of [MMA] on Graft Yield

The effect of MMA concentration on the extent of grafting is illustrated in Fig. 4 where monomer concentration ranging from 27.98 × 10^{-2} to 84.50 × 10^{-2} mol/L is plotted against graft uptake. The data indicate that there is a significant enhancement in the graft yield with an increase in monomer concentration.

The higher rate of grafting upon an increase in monomer concentration in this system could be interpreted as follows: (1) Complexation of the wool with the monomer enhances its reactivity, thereby
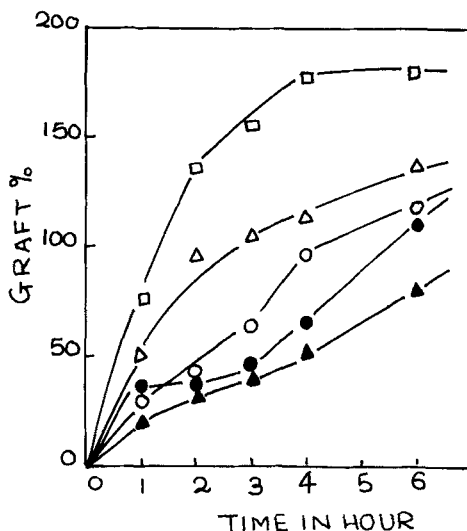
FIG. 5. Effect of $[H_2SO_4]$ on graft yield. [Peroxydiphosphate] = 80×10^{-4} mol/L, $[TU]$ = 0.00025 mol/L, $[MMA]$ = 0.4694 mol/L, temperature = 50°C, M:L = 1:100. (o) H_2SO_4 = 0.048 mol/L, (△) H_2SO_4 = 0.098 mol/L, (□) H_2SO_4 = 0.148 mol/L, (●) H_2SO_4 = 0.248 mol/L, (▲) H_2SO_4 = 0.498 mol/L.

increasing the graft percentage. (2) The monomer molecule might form some type of charge transfer complex with the oxidant at higher monomer concentrations which might favor the percentage of graft-ing. (3) The third reason might be the gel effect [15], i.e., an in-crease in viscosity of the medium due to solubility of poly(methyl methacrylate) in its own monomer would be more pronounced in higher monomer concentrations. This causes hindrance in termina-tion, particularly by coupling of the growing polymer chains. Besides this, the gel effect also causes swelling of wool, thus facilitating dif-fusion of monomer to the growing chain and active sites on the wool backbone, thereby enhancing grafting. (4) The fourth reason might be that some species which are either present or generated during the copolymerization reaction act as efficient radical scavengers. Com-petition between this and the monomer in capturing the free wool radical would play the key role in the amount of graft formation. It is likely that the capturing of wool radicals by monomer predominates at higher monomer concentrations.

Effect of $[H_2SO_4]$ on Graft Yield

To investigate the effect of acid concentration, the graft copolym-erization of methyl methacrylate onto wool was carried out at acid

concentrations ranging from 0.048 to 0.498 mol/L. It is seen in Fig. 5 that increasing the acid concentration up to 0.148 mol/L brings about a significant enhancement in the graft yield. Beyond this concentration the graft yield drops sharply. In other words, an acid concentration of 0.148 mol/L constitutes the optimal concentration of grafting under the condition studied.

The rates of oxyanion reactions are markedly acid dependent [16-18]. The role of protons is to labilize oxygen by converting it from the oxide ion to the hydroxide ion and on to water. The addition of a proton to an oxide ion in an oxyanion should make it easier to break the bond. In oxidations involving oxyanion, since covalent bonds to oxygen are generally broken simultaneously with electron transfer, they are found to be acid catalyzed. This acid catalysis reaction is also found in the case of peroxides. Hence it is clear that peroxydiphosphate, which is both a peroxide and oxyanion, i.e., an oxyanion derivative of H–O–H, is strongly subject to acid catalysts. Peroxydiphosphate, $P_2O_8^{4-}$, is highly protonated in acid medium due to its high negative charge. The various species present are $P_2O_8^{4-}$, $HP_2O_8^{3-}$, $H_3P_2O_8^{2-}$, $H_3P_2O_8^{-}$, and $H_4P_2O_8$, and the concentration of these species varies with a change in pH. The species involving the protonation of the peroxydic oxygen, $H_5P_2O_8^{+}$, may also be present along with the other protonated species. The population of the different species as a function of pH is given by Crutchfield [19]. It has been stated by Santappa and co-workers [20, 21] that the reaction rate as well as the concentration of $H_3P_2O_8^{-}$ and $H_4P_2O_8$ increase with an increase in [H^+]. Hence it is probable that one or both of the species are active. In the lower concentration range of the acid (that is, from 0.048 to 0.498 mol/L), the most active species, $H_3P_2O_8^{-}$, might be formed. It interacts with various other species to give rise to a multitude of free radicals which enhance grafting. When the concentration of the acid increases beyond 0.15 mol/L, the formation of less active species might be favored, thereby decreasing the percentage of grafting as has been noted in our case.

Effect of Temperature on Graft Yield

Graft copolymerization was carried out at three different temperatures ranging from 45 to 55°C, keeping the concentrations of all other reagents constant (Fig. 6). The percentage graft-on increases with an increase of temperature. In a complex system like this, several reactions might be taking place simultaneously. For example, (1) solution of the monomer in the reaction medium and its diffusion from the solution phase to the fiber phase, (2) adsorption of the monomer on the fiber and its complexation with wool molecules to enhance the availability and reactivity of the monomer, (3) formation and propagation of graft on the fiber, and (4) enhancement of activation of the monomer. The net effect of all these factors leads to higher grafting with an increase of temperature.
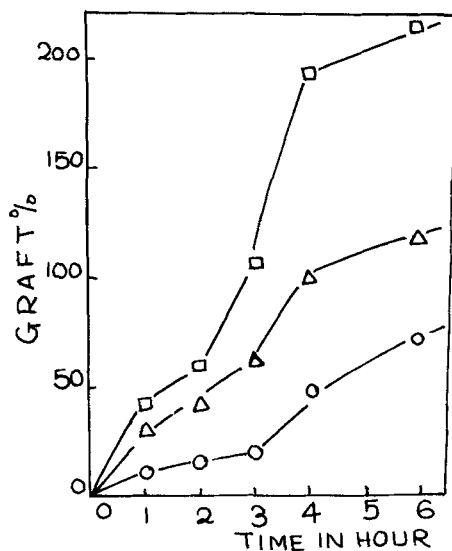
FIG. 6. Effect of temperature on graft yield. [Peroxydiphosphate] = 80 × 10⁻⁴ mol/L, [H₂SO₄] = 0.048 mol/L, [TU] = 0.00025 mol/L, [MMA] = 0.4694 mol/L, M:L = 1:100. (o) 45°C, (△) 50°C, (□) 55°C.

Nature of the Substrate

The native wool was subjected to different physical and chemical modification by reduction, oxidation, trinitrophenylation, and cross-linking (Fig. 7). The order of the percentage of graft-on is reduced wool > oxidized wool > untreated wool > cross-linked wool > tri-nitrophenylated wool.

The greater increase in the graft percentage of reduced wool may be explained on the basis that the reduction of the cystinedisulfide bond of wool with TGA increases the number of thiol groups (–SH) which act as active centers for grafting. The abstraction of hydrogen from thiol groups by initiating radicals seems to proceed much more easily than abstraction of hydrogen from amino and hydroxyl groups in the wool molecule. Further, treatment of wool with TGA might increase its accessibility or swelling and enhance grafting.

Upon oxidation of wool with H₂O₂, the cystine content reduces slightly and the cystine most probably is converted to cystic acid. It is easier to create free radicals on the sulfur by the extraction of hydrogen from cystine than by creating a free radical in the case of cystic acid. However, the probability of creation of free radical in the case of cystic acid is more than in the case of unmodified wool where there is an –S–S– linkage.
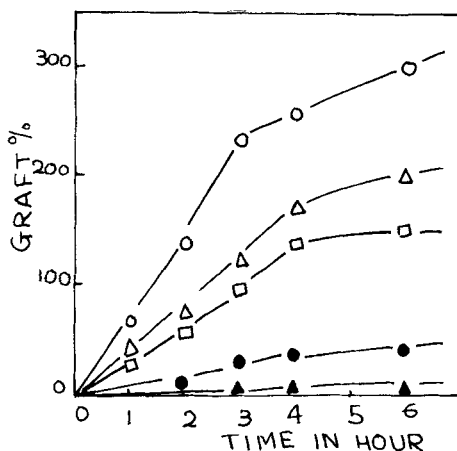
FIG. 7. Effect of nature of substrate on graft yield. [Peroxydi-
phosphate] = 50×10^{-4} mol/L, [H_2SO_4] = 0.15 mol/L, [MMA] =
0.4694 mol/L, [TU] = 0.00025 mol/L, temperature = 50°C, M:L =
1:100, (○) reduced wool, (△) oxidized wool, (□) untreated wool,
(●) cross-linked wool, (▲) phenylated wool.

Trinitrophenylation of wool significantly reduces its ability
toward grafting. When wool is subjected to trinitrophenylation, the
amino hydroxyl and thiol groups are blocked. Free radicals cannot
be created at the wool backbone by the interaction of initiating radi-
cals, as a result of which the graft yield decreases. The other reasons
for low graft yield may be (1) lowering of the swellability of wool
fibers and (2) hindrance of absorption of the 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 of
grafting.

Effect of Solvent on Graft Yield

The effect of solvent on graft copolymerization has been studied by
using various protic, dipolaraprotic, and nonpolar solvents. It is im-
portant to select the most suitable solvents for the graft copolymeri-
zation of methyl methacrylate onto wool fibers. The effect of various
solvents affecting the percentage of grafting follows the order dioxane
> acetone > methanol > hexane > chloroform.
The variation of grafting upon using different solvents could be
associated with difference in their (1) capability of swelling of wool,
(2) miscibility with the monomer, (3) formation of the solvent radical
from the primary radical species of the initiating system, (4) contri-
bution of the solvent radical in the activation of wool, and (5) termination

TABLE 1. Alkali Solubility of Grafted Wool

Graft percentage	Alkali solubility percentage
Nil	75.54
114.45	25.94
127.45	23.79
182.25	19.55
226.95	12.72
261.10	9.707

TABLE 2. Molecular Weight and Degree of Polymerization of the Grafted Wool

Graft percentage	$\overline{M} \times 10^{-5}$	$\overline{DP} \times 10^{-3}$
105.05	7.047	7.039
137.05	5.970	5.964
154.75	4.169	4.164

of the graft chain radical and wool macroradical via chain transfer. While the first four factors favor grafting by simplifying access and diffusion of the monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.

Effect of Different Acrylate Monomers on Grafting

Graft copolymerization was investigated with different acrylate monomers by keeping the concentration of all other reagents constant. The order of reactivity follows the order MA > EA > MMA > n-butyl acrylate.

Thus, as the size of the monomer is increased, diffusion of the monomer to all available sites on the fiber is not possible. As a result, the percentage of graft-on decreases in the case of bulkier monomer.

Alkali Solubility

The alkali solubility of grafted and native wool has been studied. The solubility test was performed for various time intervals following

a standard procedure. The alkali solubility measures the extent of grafting, the latter being decreased as the graft yield increases (Table 1). The reduction in alkali solubility after polymerization suggests that the synthetic polymer chains act as diffusion barriers toward alkali penetration into the wool fibers. In this way the polypeptide chains, salt linkages, and disulfide linkages in wool are protected and remain practically unimpaired.

Molecular Weight Determination

The average molecular weight, $\overline{M}$, and the degree of polymerization of the grafted poly(methyl methacrylate) were determined by the single point method using the relationship

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

Perusal of the results indicates that the average molecular weight as well as the degree of polymerization decreases with an increasing percentage of grafting (Table 2).

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