Graft Copolymerization of Methyl Methacrylate onto Wool Using Thallium(III) Ions as Initiator

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Synopsis

The graft copolymerization of methyl methacrylate onto wool initiated by thallium(III) perchlorate was investigated in aqueous perchloric acid medium. The rate of grafting was evaluated varying the concentrations of the monomer, initiator, acid, and temperature. The rate of grafting was found to increase with the increase of the monomer and the initiator concentration. The graft yield was found to decrease upon increasing the acid concentration. Increase of temperature was accompanied with the increase of the graft yield. From the Arrhenius plot the overall activation energy was calculated to be 4.7 kcal/mol. The effect of inhibitors, various solvents, cationic and anionic surfactants, and different inorganic salts on the graft yield was studied. The grafting was considerably influenced by chemical modification of wool prior to grafting. A suitable kinetic scheme has been proposed, and a rate equation has been derived.

INTRODUCTION

Grafting vinyl monomers onto natural and synthetic fibers modifies various properties of the fiber such as stereoregularity, hygroscopicity, and thermal stability. Several reviews are available on this general subject.[1–6] Chemical modification of wool through graft copolymerization has been studied by many authors.[7–11] The successful grafting of vinyl monomers onto wool involves the formation of free radicals on the backbone of wool. This can be achieved using chemical[12–17] and radiation methods. Both transition and non-transition metal ions in their higher valence states have been used as chemical initiators for homopolymerization of vinyl monomers.[18–21] Recently we have used thallium(III) perchlorate as an initiator for homopolymerization of vinyl monomers. So far no studies have been made on grafting vinyl monomers onto wool using thallium(III) ions as initiator. This communication presents the results of studies on grafting methyl methacrylate onto wool using thallium(III) ions as initiator.

EXPERIMENTAL

Indian Chokla wool fibers were purified by Soxhlet extraction with acetone for about 24 h followed by washing with cold distilled water and air drying. Reduced wool was prepared by thioglycolic acid (TGA) treatment of wool (0.2 mol/L TGA, 25°C, 16 h). Oxidized wool was prepared by treatment with a 3% solution of hydrogen peroxide at 50°C for 3 h at pH 4, followed by thorough washing with cold water and drying. Trinitrophenylated (TNP) wool was prepared by its treatment with 1-chloro-2,4,6-trinitrobenzene in ethanolic solution for several days at room temperature.[22] Crosslinked wool was prepared by

treatment of the wool with a 6% solution of formaldehyde at 50°C and at pH 6.5 for 48 h followed by washing with distilled water and subsequent drying.

Identical procedures as described in our previous communication[23] were followed for the preparation and estimation of thallium(III) perchlorate solution, purification of the monomer and other chemicals, and for graft copolymerization reactions.

RESULTS AND DISCUSSION

The factors affecting the graft copolymerization of methyl methacrylate onto wool initiated by thallium(III) perchlorate were investigated varying monomer concentration, initiator concentration, acid concentration, and temperature. The effect of various solvents, inorganic salts, surfactants, and inhibitors on graft yield was studied. It was observed that the graft yield was considerably influenced by chemical modification of wool prior to grafting.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration in the range 28.16–103.26 × 10^{-2} mol/L at fixed concentrations of all other reagents. The rate of grafting was found to increase with increase of monomer concentration (Fig. 1). Several explanations can be offered to account for the higher rate of grafting observed upon increasing the monomer concentration. First, complexation of wool with monomer, which is required for enhancing monomer activity, would be favored at higher monomer concentrations. Secondly, the gel effect,[24] i.e., increase in viscosity due to solubility of polymethyl methacrylate in its own monomer, would be more pronounced at higher monomer concentration. This causes hindrance in termi-
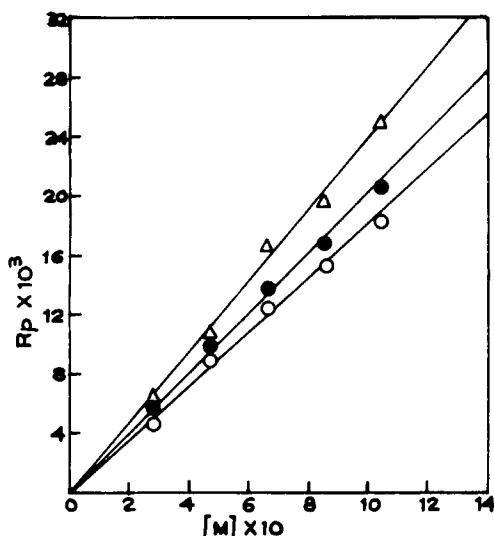

Fig. 1. Effect of monomer concentration on rate of grafting: [HClO$_4$] = 4.75 × 10^{-1} mol/L; [ether] = 2.425 × 10^{-1} mol/L; time = 6 h; temp = 70°C; M:L = 1:100; (O) [Tl^{3+}] = 4.08 × 10^{-3} mol/L; (●) [Tl^{3+}] = 8.16 × 10^{-3} mol/L; (△) [Tl^{3+}] = 12.24 × 10^{-3} mol/L.

nation particularly by coupling of the growing polymer chains. Besides, this gel effect also causes swelling of wool thus facilitating diffusion of monomer to growing chains and active sites on the wool backbone, thereby enhancing grafting. Third, some species which are either present or generated during the polymerization reaction act as an efficient radical scavenger. Competition between this and the monomer in capturing the free wool radical play the key role in the amount of graft formation. It is likely that capture of wool radical by monomer predominates at higher monomer concentration.

Effect of Initiator Concentration

The effect of thallium(III) concentration on grafting was investigated by changing the thallium(III) concentration within the range $4.08-20.40 \times 10^{-3}$ mol/L at fixed concentrations of all other reagents. The data indicate that increase of thallium(III) concentration is accompanied by a significant increase in the rate of grafting (Fig. 2). Similar results were reported by Bendak and co-workers[11] in case of cerium(IV) initiated graft copolymerization of MMA onto wool fibers. A possible explanation for these observations might be as follows: As the concentration of the initiator goes on increasing, more and more, free radicals are formed on the wool backbone, thus increasing the rate of grafting.

Effect of Acid Concentration

The graft copolymerization reaction was carried out in aqueous perchloric acid medium. The acid concentration was varied from 0.19 to 0.59 mol/L at fixed concentrations of all other reagents. The graft yield was found to decrease with increase of the acid concentration (Fig. 3). The decrease in the percentage of grafting at high acid concentration might be due to the recombination and dis-
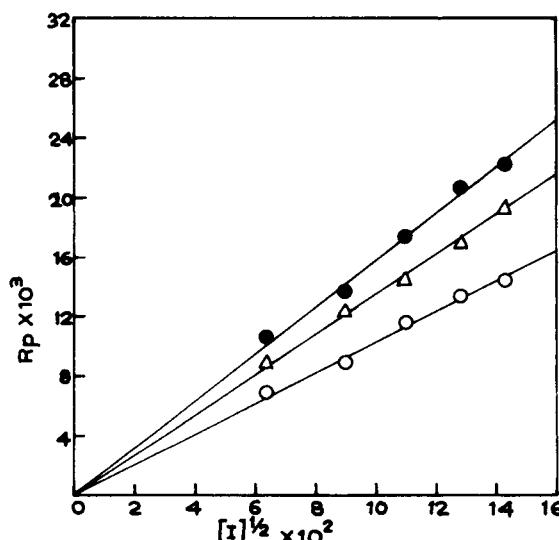

Fig. 2. Effect of initiator concentration on rate of grafting: $[HClO_4]$ = 1.2 mol/L; [ether] = 2.425 $\times 10^{-1}$ mol/L; time = 6 h; temp = 70°C; M:L = 1:100; (O) [MMA] = 4.694×10^{-1} mol/L; (△) [MMA] = 7.041×10^{-1} mol/L; (●) [MMA] = 9.388×10^{-1} mol/L.
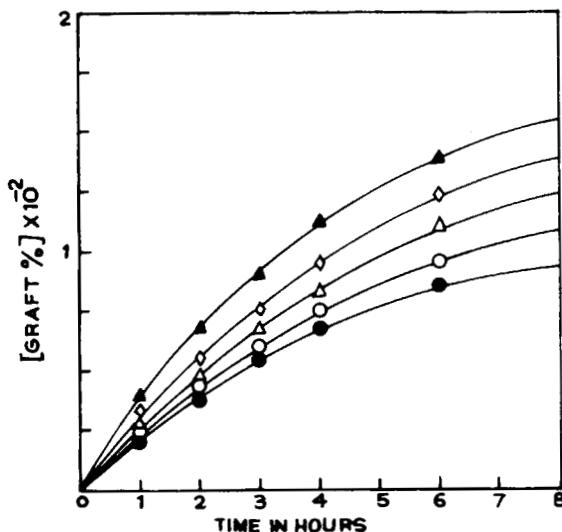
Fig. 3. Effect of acid concentration on graft yield: $[MMA] = 4.694 \times 10^{-1}$ mol/L; $[Tl^{3+}] = 3.26 \times 10^{-3}$ mol/L; [ether] $= 2.425 \times 10^{-1}$ mol/L; temp $= 70°C$; M:L $= 1:100$; (▲) $[HClO_4] = 1.90 \times 10^{-1}$ mol/L; (◊) $[HClO_4] = 2.90 \times 10^{-1}$ mol/L; (△) $[HClO_4] = 3.90 \times 10^{-1}$ mol/L; (O) $[HClO_4] = 4.90 \times 10^{-1}$ mol/L; (●) $[HClO_4] = 5.90 \times 10^{-1}$ mol/L.

proportionation of the graft macroradicals and also might be due to the decrease in complexation efficiency of the wool fibers at high acid concentrations.

Effect of Temperature

The graft copolymerization reaction was carried out in the temperature range 40–70°C, at fixed concentrations of all reagents. A perusal of the results indicates that with increasing temperature the percentage of graft-on increases (Fig. 4). This might be due to several reasons. First, this might be due to the increased activity of the initiating free radical at high temperatures. Secondly, this may
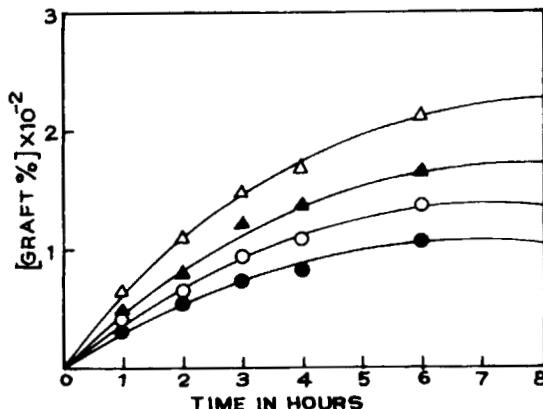

Fig. 4. Effect of temperature on graft yield: $[MMA] = 4.694 \times 10^{-1}$ mol/L; $[Tl^{3+}] = 8.16 \times 10^{-3}$ mol/L; $[HClO_4] = 4.75 \times 10^{-1}$ mol/L; [ether] $= 2.425 \times 10^{-1}$ mol/L; M:L $= 1:100$; temp: (●) 40°C; (▲) 60°C; (O) 50°C; (△) 70°C.
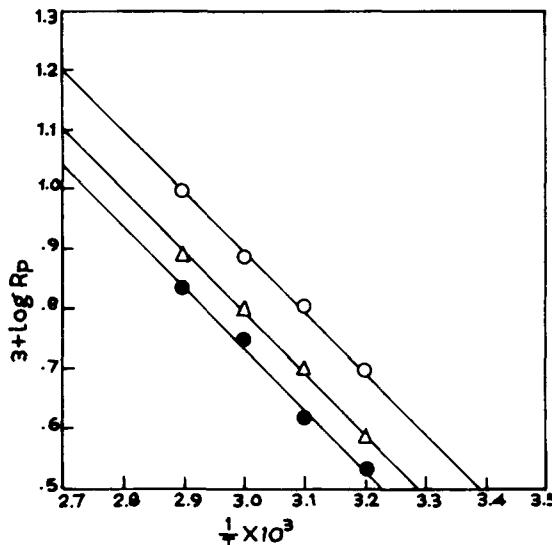
Fig. 5. Arrhenius plot of log R_p vs. $1/T$: ($\bullet$) 3 h; ($\triangle$) 4 h; ($\circ$) 6 h.

be due to the increase in activation energy at high temperatures. As a result of increase in the activation energy, the swellability of the fiber, the solubility of the monomer, and its diffusion rate from the solution phase to the fiber phase increase. Besides, the rates of initiation and propagation also increase, thus increasing the graft yield. From the Arrhenius plot of log R_p vs. $1/T$ (Fig. 5) the overall activation energy was found to be 4.7 kcal/mol. These rather small values are, however, approximate to those obtained in other polymerization systems in the presence of a macromolecule.
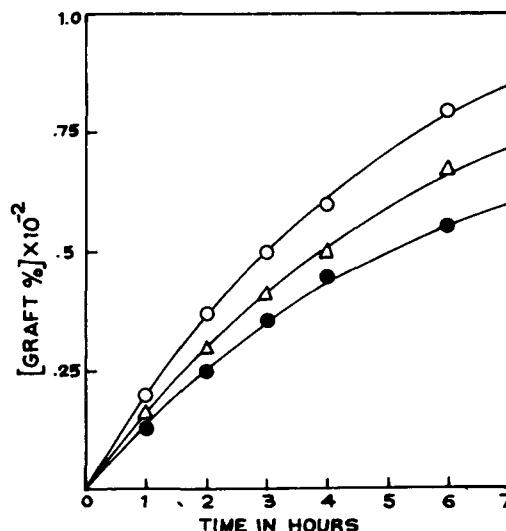

Fig. 6. Effect of alcoholic solvents on graft yield: [MMA] = 4.694×10^{-1} mol/L; [Tl^{3+}] = 8.16 $\times 10^{-3}$ mol/L; [HClO$_4$] = 1.2 mol/L; [ether] = 2.425×10^{-1} mol/L; [solvent] = 8.75×10^{-2} mol/L; temp = 70°C; M:L = 1:100; ($\triangle$) ethanol; ($\circ$) methanol; ($\bullet$) amyl alchol.
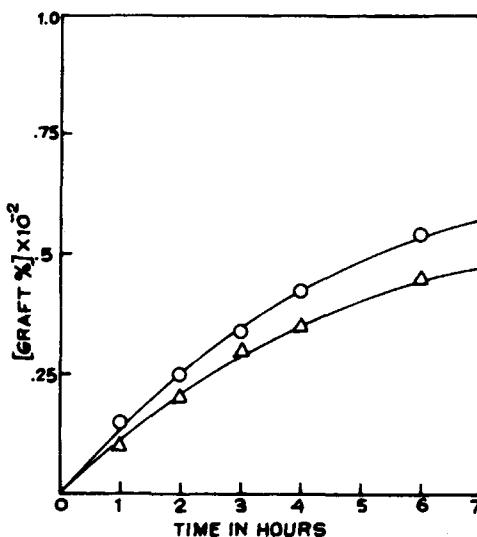
Fig. 7. Effect of chain transfer solvents on graft yield: [MMA] = 4.694 × 10^{-1} mol/L; [Tl^{3+}] = 8.16 × 10^{-3} mol/L; [HClO$_4$] = 1.2 mol/L; [ether] = 2.425 × 10^{-1} mol/L; [solvent] = 6.85 × 10^{-2} mol/L; temp = 70°C; M:L = 1:100; (O) chloroform; (△) carbon tetrachloride.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting monomers onto wool fibers.   The effect of different types of solvents (alcoholic solvents, chain transfer solvents, organic acids, and other solvents acting as solubilizer for the monomer) on graft yield has been investigated.   With different solvents the graft yield follows a definite sequence, viz., with alcoholic solvents (Figs. 6 and 15) the order of graft yield is

<center>methanol > ethanol > amyl alcohol</center>
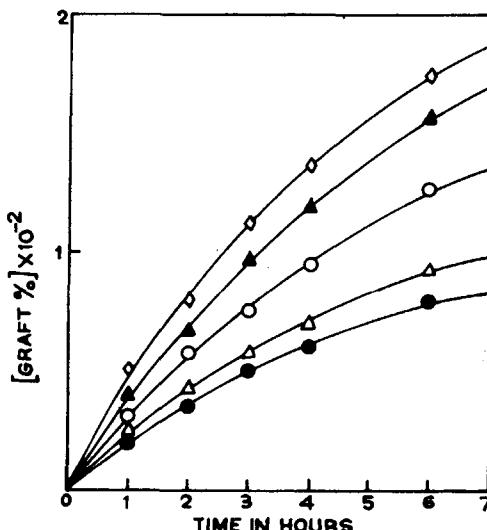
Fig. 8. Effect of various solvents on graft yield: [MMA] = 4.694 × 10^{-1} mol/L; [Tl^{3+}] = 8.16 × 10^{-3} mol/L; [HClO$_4$] = 1.2 mol/L; [ether] = 2.425 × 10^{-1} mol/L; [solvent] = 1.75 × 10^{-1} mol/L; temp = 70°C; M:L = 1:100; (◊) formic acid; (△) dioxan; (▲) acetic acid; (●) acetone; (O) dimethyl form-amide.

With chain transfer solvents (Fig. 7) the order is

<div align="center">chloroform > carbon tetrachloride</div>

With other solvents (Fig. 8 and 16) the order is

<div align="center">formic acid > acetic acid > dimethyl formamide > dioxan > acetone</div>
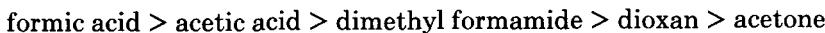
The dependence of grafting upon the nature of the solvent suggests that the solvents examined differ considerably in their (1) capability of swelling wool, (2) miscibility with monomer, (3) formation of solvent radical from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of wool, and (5) termination 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 macromolecules.

Effect of Nature of Substrate

The effect of the changes in the physical or chemical structure of wool brought about by oxidation, reduction, crosslinking, and trinitrophenylation on its behavior towards grafting has been studied (Fig. 9). The order follows:

oxidized wool > reduced wool > untreated wool

<div align="right">> crosslinked wool > trinitrophenylated wool</div>

When wool is oxidized with hydrogen peroxide solution, the interlocking bonds
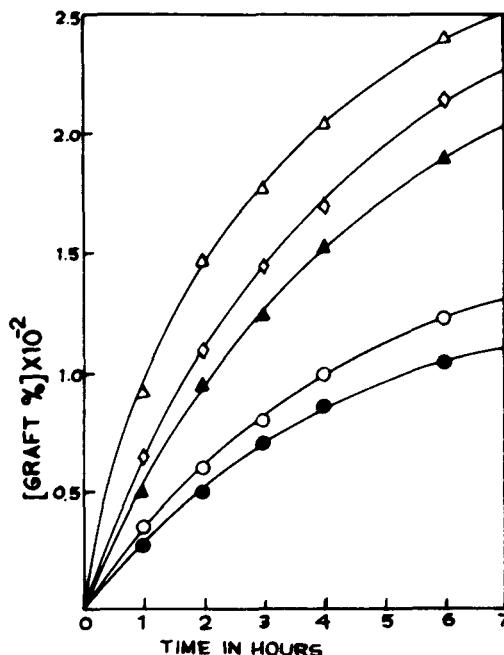

Fig. 9. Effect of nature of substrate on graft yield: [MMA] = 4.694×10^{-1} mol/L; [Tl^{3+}] = 8.16×10^{-3} mol/L; [$HClO_4$] = 1.2 mol/L; [ether] = 2.425×10^{-1} mol/L; temp = 70°C; M:L = 1:100; ($\triangle$) oxidized wool; ($\bigcirc$) crosslinked wool; ($\Diamond$) reduced wool; ($\bullet$) trinitrophenylated wool ($\blacktriangle$) untreated wool.

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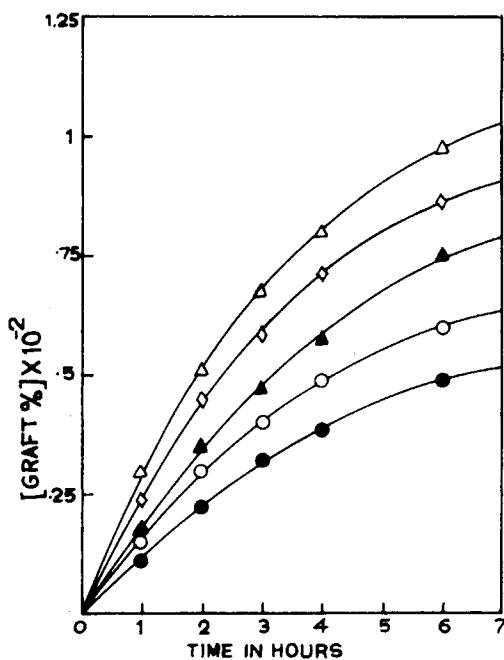
Fig. 10. Effect of inhibitor (Picrylchloride) on graft yield: [MMA] = 4.694 × 10⁻¹ mol/L; [Tl³⁺]
= 3.26 × 10⁻³ mol/L; [HClO₄] = 1.9 × 10⁻¹ mol/L; [ether] = 2.425 × 10⁻¹ mol/L; temp = 70°C; M:L
= 1:100; (△) [picryl chloride] = 5 × 10⁻⁵ mol/L; (◇) [picryl chloride] = 10 × 10⁻⁵ mol/L; (▲) [picryl
chloride] = 15 × 10⁻⁵ mol/L; (○) [picryl chloride] = 20 × 10⁻⁵ mol/L; (●) [picryl chloride] = 25 ×
10⁻⁵ mol/L.
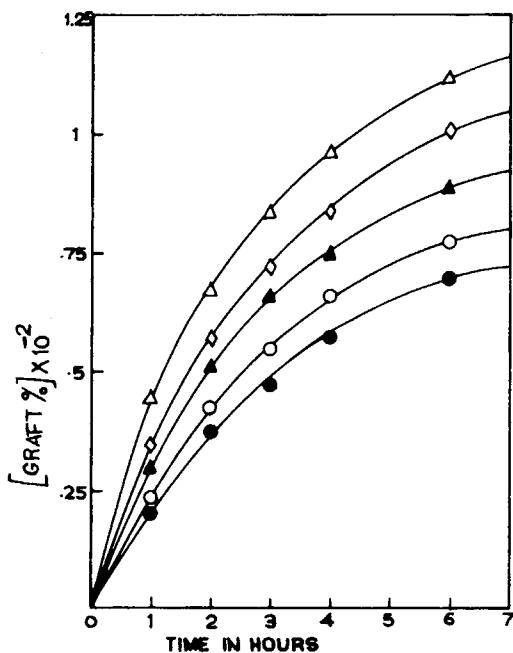
Fig. 11. Effect of inhibitor (Hydroquinone) on graft yield: [MMA] = 4.694 × 10⁻¹ mol/L; [Tl³⁺]
= 3.26 × 10⁻³ mol/L; [HClO₄] = 1.9 × 10⁻¹ mol/L; [ether] = 2.425 × 10⁻¹ mol/L; temp = 70°C; M:L
= 1:100; (△) [hydroquinone] = 5 × 10⁻⁵ mol/L; (◇) [hydroquinone] = 10 × 10⁻⁵ mol/L; (▲) [hy-
droquinone] = 15 × 10⁻⁵ mol/L; (○) [hydroquinone] = 20 × 10⁻⁵ mol/L; (●) [hydroquinone] = 25
× 10⁻⁵ mol/L.
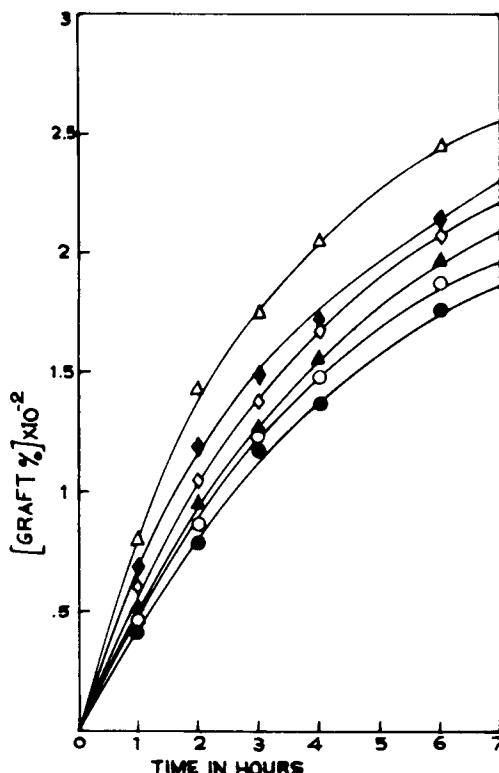
Fig. 12. Effect of inorganic salts on graft yield: [MMA] = 4.694 × 10⁻¹ mol/L; [Tl³⁺] = 8.16 × 10⁻³ mol/L; [HClO₄] = 4.75 × 10⁻¹ mol/L; [ether] = 2.425 × 10⁻¹ mol/L; [salt] = 0.01 mol/L; temp = 70°C; M:L = 1:100; (△) magnesium sulphate; (○) sodium sulphate; (◇) sodium fluoride; (●) potassium chloride; (▲) zinc sulphate; (◆) without any added salt.

between two strands of wool which form a helical arrangement are broken, thus creating new reactive sites for grafting, thereby increasing the graft yield.

When wool is treated with thioglycolic acid, reduced wool is formed with more —SH groups because of the breakage of the —S—S— linkages in cystine molecules.[25] 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 radical seems to proceed much more easily than 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 enhance grafting.[26]

When wool fiber is subjected to formylation, crosslinking blocks the radical sites, thereby reducing significantly its ability towards grafting.[27,28] Trinitrophenylation of wool reduces significantly its ability towards 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 with initiating radicals, and therefore the graft yield decreases. The other reasons for low graft yield might be due to (i) lowering of the swellability of wool fibers and (ii) hindrance of adsorption of MMA molecules by the negatively charged substituted nitro group. The net effect of all these factor is the decrease of grafting.[27,28]

Effect of Inhibitors

Effect of different inhibitors such as picryl chloride and hydroquinone on the graft yield was studied at fixed concentrations of all other reagents (Figs. 10 and 11). It was observed that the graft percentage was greatly suppressed in presence of either inhibitor. The inhibiting efficiency of picryl chloride was found to be more than hydroquinone. It was also observed that the extent of inhibition increases with increase in the concentration of the inhibitor. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby reducing the molecular size of the graft and hence decreasing the graft yield.

Effect of Inorganic Salts

It has been reported by several investigators that the presence of certain cations during graft copolymerization of vinyl monomers onto wool enhances grafting significantly.[29,30] With different added inorganic salts the graft yield follows the following sequence (Figs. 12 and 13).

copper sulphate > magnesium sulphate > without any added salt
  > sodium fluoride > zinc sulphate > sodium sulphate > potassium chloride

The increase or decrease of the graft yield may be due to catalysis or inhibition, respectively, of the propagation step by the added salt.
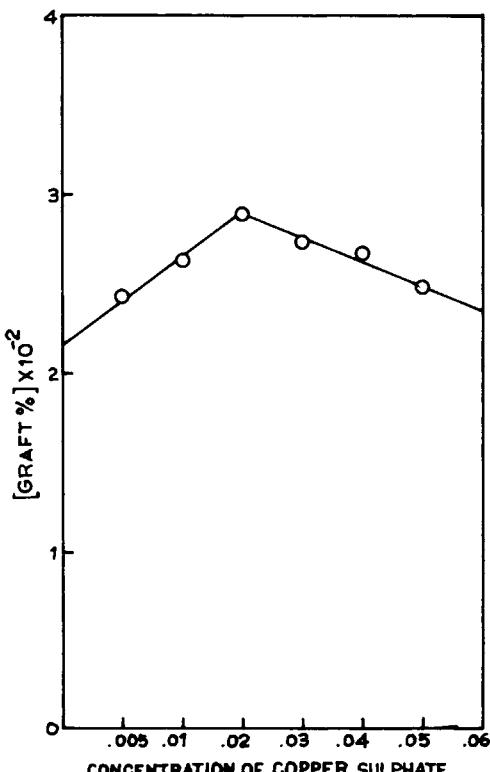

Fig. 13. Effect of copper sulphate on graft yield: $[MMA] = 4.694 \times 10^{-1}$ mol/L; $[Tl^{3+}] = 8.16 \times 10^{-3}$ mol/L; $[HClO_4] = 4.75 \times 10^{-1}$ mol/L; $[ether] = 2.425 \times 10^{-1}$ mol/L; temp = 70°C; time = 6 h; M:L = 1:100.
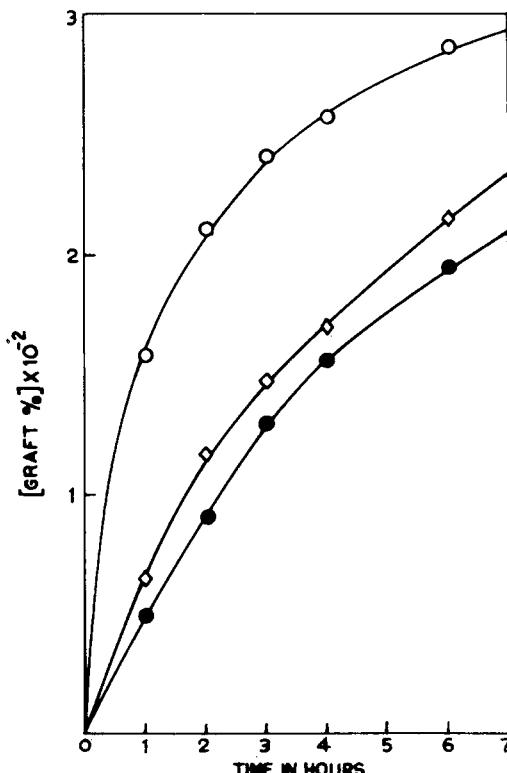
Fig. 14. Effect of surfactants on graft yield: [MMA] = 4.694 × 10⁻¹ mol/L; [Tl³⁺] = 8.16 × 10⁻³ mol/L; [HClO₄] = 4.75 × 10⁻¹ mol/L; [ether] = 2.425 × 10⁻¹ mol/L; temp = 70°C; M:L = 1:100; Surfactant at CMC: (O) sodium Lauryl sulphate ((NaLS); (●) cetyl trimethyl ammonium bromide (CTABr): (◊) control.

Effect of Copper Sulphate

The effect of copper sulphate on grafting is quite interesting (Fig. 13). It was observed that, with increase of copper sulphate concentration, the graft yield first increased up to 0.02 mol/L and beyond this concentration graft yield decreased. The initial increase in graft yield might be due to the fact that the presence of Cu^{2+} ions in the vicinity of wool favours grafting since the involvement of Cu^{2+} ion in the wool–monomer complex would be easier. Furthermore, the creation of free radical species under the influence of Cu^{2+} ions would be in the proximity of wool, thus assisting the formation of wool macroradicals. The drop in the graft yield at higher concentrations of copper sulphate can be explained by assuming radical trap on wool by Cu^{2+} ions.

Effect of Surfactants

The percentage of graft yield has also been calculated in presence of the anionic surfactant sodium lauryl sulphate (NaLS) and cationic micelles of cetyl trimethyl ammonium bromide (CTABr) at CMC. It was observed that addition of NaLS increased the graft yield whereas CTABr decreased the graft yield (Fig. 14). These observations can be explained as follows. At CMC the micelles are formed which are roughly spherical in size. In case of micelles of sodium lauryl sulphate
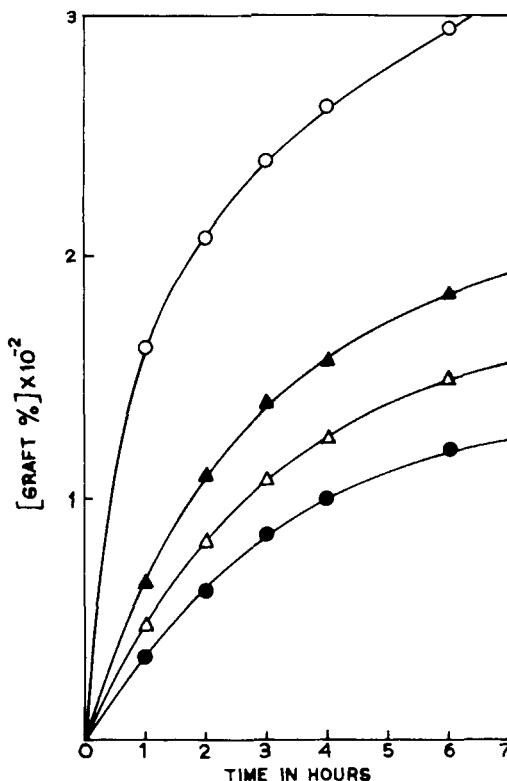
Fig. 15. Effect of alcoholic solvents on graft yield: [MMA] = 9.388×10^{-1} mol/L; [Tl^{3+}] = 8.16 $\times 10^{-3}$ mol/L; [HClO$_4$] = 1.2 mol/L; [ether] = 2.425×10^{-1} mol/L; [solvent] = 8.75×10^{-1} mol/L; temp = 70°C; M:L = 1:100; (▲) methanol; (●) amyl alcohol; (△) ethanol; (○) control.

the sulphate ions form the Gouy–Chapman double layer.[31] The enhancement of the graft yield at CMC by NaLS may be due to the entanglement of the micelles with the wool fibers, as a result of which the Tl^{3+} ions are electrostatically attracted towards the wool matrix. The concentration of Tl^{3+} ions will be nearer the vicinity of the fiber which will enhance free radical formation on the wool backbone resulting in an increase of the graft yield. In case of micelles of CTABr the ammonium ions form the Gouy–Chapman double layer. Thus the entanglement of these micelles with wool fiber would result in electrostatic repulsion towards Tl^{3+} ions. As a result, free radical formation on wool backbone would be suppressed, thereby decreasing the graft yield.

MECHANISM

The following mechanism has been suggested for the graft copolymerization of methyl methacrylate onto wool fibers using thallic ion as initiator:

(i) Production of free radical on wool backbone:

$$\sim W + Tl^{3+} \xrightarrow{k_d} \sim W\cdot + Tl^{2+}$$
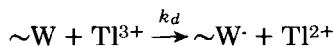
(where W = wool, and W$\cdot$ = wool macroradical)
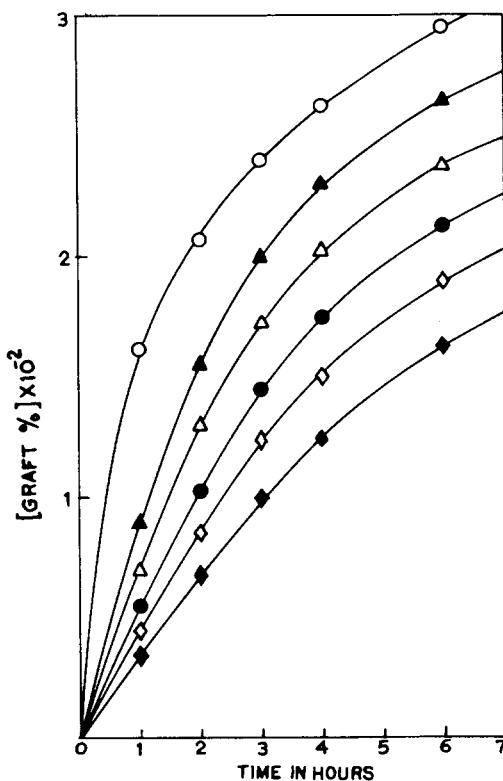
Fig. 16. Effect of various solvents on graft yield: [MMA] = 9.388 × 10⁻¹ mol/L; [Tl³⁺] = 8.16 × 10⁻³ mol/L; [HClO₄] = 1.2 mol/L; [ether] = 2.425 × 10⁻¹ mol/L; [solvent] = 1.75 × 10⁻¹ mol/L; temp = 70°C; M:L = 1:100; (▲) formic acid; (◊) dioxan; (△) acetic acid; (♦) acetone; (●) dimethyl formamide; (○) control.

(ii) Initiation: $\sim W\cdot + M \xrightarrow{k_i} \sim WM$

(where M = monomer)

(iii) Propagation: $\sim WM\cdot + M \xrightarrow{k_p} \sim WM_2^{\cdot}$

$\sim WM_{n-1}^{\cdot} + M \xrightarrow{k_p} \sim WM_n^{\cdot}$

(iv) Termination: $\sim WM_n^{\cdot} + \sim WM_n^{\cdot} \xrightarrow{k_t}$ graft copolymer
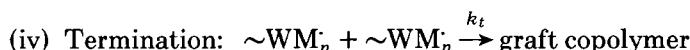
Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

$$-\frac{d[W\cdot]}{dt} = k_d \, [Tl^{3+}][W] - k_i [W\cdot][M] = 0$$

$$[W\cdot] = \frac{k_d \, [Tl^{3+}][W]}{k_i \, [M]}$$

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

$$[WM_n^{\cdot}] = \left\{ \frac{k_i \ [W^{\cdot}][M]}{k_t} \right\}^{1/2}$$

Substituting the value of [W·] in the above equation,

$$[WM_n^{\cdot}] = \left\{ \frac{k_d \ [T]^{3+}][W]}{k_t} \right\}^{1/2}$$

Then

$$R_p = k_p \ [M][WM_n^{\cdot}]$$

or

$$R_p = k_p \left[\frac{k_d}{k_t}\right]^{1/2} [W]^{1/2} \ [T]^{3+}]^{1/2} \ [M]$$

The plots of R_p vs. [M] (Fig. 1) and R_p vs. [initiator]$^{1/2}$ (Fig. 2) are linear passing through the origin, which confirm the validity of the above reaction scheme.

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