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Grafting Vinyl Monomers onto Chemically Modified Wool Fibers: Graft Copolymerization of Methyl Methacrylate onto Reduced Wool Fibers Using Acetylacetonate Complex of Manganese(III)

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ABSTRACT

The graft copolymerization of methyl methacrylate (MMA) onto reduced Indian Chokla wool fibers was studied in aqueous solution using the acetylacetonato complex of Mn(III) as the initiator. Perchloric acid was found to catalyze the reaction. The rate of grafting was investigated by varying the concentration of the monomer and the complex, acidity of the medium, the temperature, and the reaction medium. It is observed that the graft yield increases with increasing concentration of the chelate and acid and with increasing temperature. There is an increase in graft yield within a certain concentration range of the monomer, after which it falls. The grafting is considerably influenced by changing the solvent composition of the reaction medium. A comparative study reveals that oxidized

and reduced wools are better substrates than untreated and other chemically modified wools. The effect of various monomers on graft yield is investigated. MMA is found to be a most active monomer compared to other vinyl monomers like methyl acrylate, ethyl acrylate, n-butyl acrylate, and acrylic acid. A suitable reaction scheme for grafting of MMA on reduced wool has been proposed and activation energy calculated from the Arrhenius plot.

INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic fibers has invoked considerable interest in recent years. Extensive work has been done in the field, and several reviews are presently available [1-4]. Arnett and Mendelson [5] observed that metal chelates, upon heating, decompose to generate free radical species. This is essentially the scission of the M-O bond with the reduction of the metal to a lower valency state. Consequently, metal chelates can be employed for vinyl polymerization. Bamford and Lind [6] have made extensive studies on the polymerization of a number of monomers using $Mn(acac)_3$ and $Co(acac)_3$ as initiators. Following this finding, many workers reported grafting of vinyl monomers onto wool [7, 8], silk [9], nylon [10], and cellulose [11, 12] using simple metal acetylacetonates as initiators. Recently Niezette and co-workers [13] reported graft copolymerization of MMA onto chemically modified wool using the $LiBr-K_2S_2O_8$ redox system. In an attempt to determine the role of -SH groups, Mishra and co-workers [14] investigated grafting of poly(vinyl acetate) and poly(methyl methacrylate) on reduced wool in the presence of $K_2S_2O_8$ -ferrous ammonium sulfate as the redox initiator. Hebeish and co-workers [15] investigated the graft copolymerization of methyl methacrylate (MMA) and acrylonitrile (AN) on cotton treated with cross-linking agents.

The present work describes the graft copolymerization of MMA onto reduced Indian Chokla wool using $Mn(acac)_3$ as the initiator. The observations with reduced wool are compared with native wool and other chemically modified substrates such as oxidized, cross-linked, and trinitrophenylated wool.

Extensive study of grafting onto chemically treated wool using various other chelates such as $Co(acac)_3$, $VO(acac)_2$, and $Fe(acac)_3$ are being undertaken in this laboratory at present. Grafted samples are being characterized by spectral measurements (UV, IR, PMR spectroscopy), scanning electron microscopy, and x-ray studies which will be reported in our subsequent communications.

EXPERIMENTAL

Purification of wool, monomers, and solvents, method of rate measurement, and calculation of percentage of graft yield have been re-

ported in our previous communications [16]. In order to prepare reduced wool, the native wool is treated for 18 h at 35°C with a solution of 0.5 M TGA, the material-to-liquor ratio being 1:100. It was washed with running water for 24 h, treated with 0.1 M HCl for 12 h, washed with distilled water, and air dried. Wool was oxidized by 3% H₂O₂ solution at 50°C for 3 h (M:L = 1:100), washed with distilled water repeatedly, and air dried. Cross-linked wool was prepared by treating wool with a 6% HCHO solution for 48 h at 50°C (M:L = 1:100), washed with distilled water, and air dried. Wool was trinitrophenylated by treating 1 g of wool with a solution of water (25 mL) and ethanol (50 mL) containing 1 g of picryl chloride and 1 g of NaHCO₃ for 24 h at 35°C, washed with running water overnight, followed by repeated washing with distilled water, and air dried.

DISCUSSION

Nature of the Substrate

The various chemically modified wool fibers graft copolymerized by MMA follow this order of reactivity: reduced > oxidized > native > cross-linked > trinitrophenylated (Fig. 1).

The increase in graft percentage in the case of reduced wool may be explained by the larger number of thiol groups that are formed by the reduction of the cystine disulfide bond. The -SH groups are known as active grafting sites [17, 18], and it seems easier to abstract hydrogen from thiol groups by initiating radicals than from other groups existing on the wool backbone. Further, reduced wool exhibits greater swelling and this enhances grafting.

Graft yield increases with increasing concentration of the reducing agent (TGA). However, it is observed that with such reduced substrates there is a considerable loss in fiber character which might be due to degradation of the base polymer during chemical treatment. Similar observations are reported by Sudhir and co-workers [19]. From x-ray diffraction data, SEM, and thermogravimetric studies, these authors concluded that treatment of Chokla wool with TGA, H₂O₂, and peracetic acid resulted in considerable chemical damage to the base polymer, leading to decreased fiber strength.

Oxidation of wool with H₂O₂ also enhances grafting, but the graft percentage is lower than that with reduced wool. Oxidation most probably converts cystine to cystic acid, and creation of a free radical is comparatively more difficult on cystic acid than on the -SH group.

When wool is subjected to formylation, active radical sites are blocked by cross-linking. Trinitrophenylation also blocks such reaction sites. Free radicals cannot be created on the wool backbone by interaction with the initiating radicals. The other reasons might be 1) lowering of the swellability of the fiber leading to suppressed absorption of Mn(acac)₃ and MMA, and 2) repulsion of MMA molecules by the negatively charged substituted nitro groups.

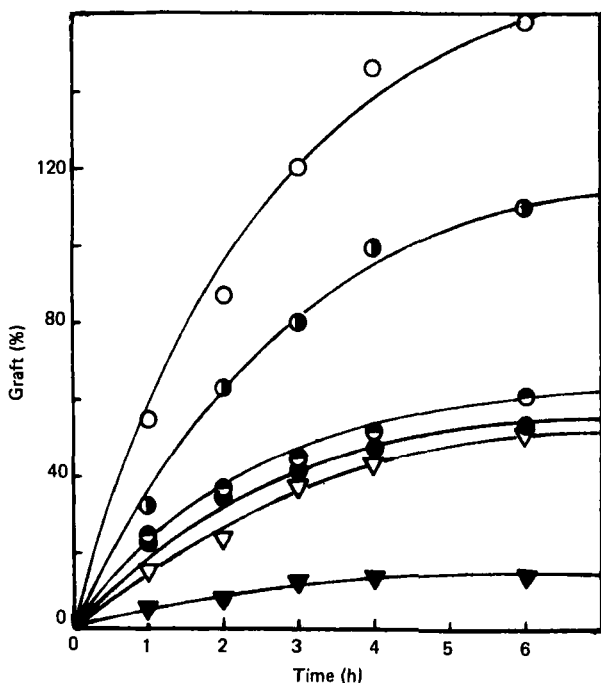


FIG. 1. Effect of modified wool on graft yield: $[\text{Mn}(\text{acac})_3] = 8 \times 10^{-3}$ mol/L, $[\text{MMA}] = 0.4694$ mol/L, $[\text{HClO}_4] = 5 \times 10^{-3}$ mol/L, M:L = 1:100, 50°C . (○) Reduced wool (0.5 M TGA), (◐) reduced wool (0.3 M TGA), (◑) reduced wool (0.1 M TGA), (●) oxidized wool, (▽) native wool, (▼) cross-linked wool.

Effect of Initiator Concentration

The rate of grafting was investigated by changing the $\text{Mn}(\text{acac})_3$ concentration within the range 0.003 to 0.009 mol/L (Fig. 2). The data indicate that within this range, the graft yield increases with increasing chelate concentration.

In the initial stages a charge transfer complex is probably formed between the pendant groups on the wool backbone with the chelate and the monomer. Hence, the concentrations of the chelate and the monomer are increased in the vicinity of the wool matrix. This assists in the breakage of the acetylacetonate linkage, and a free radical is formed on the methylene carbon atom. This free radical interacts with the active free radical sites on the wool backbone, thus forming a wool macro-radical which reacts with the vinyl monomers, resulting in the formation of graft copolymer.

The formation of acetylacetonate free radical is assisted by solvent

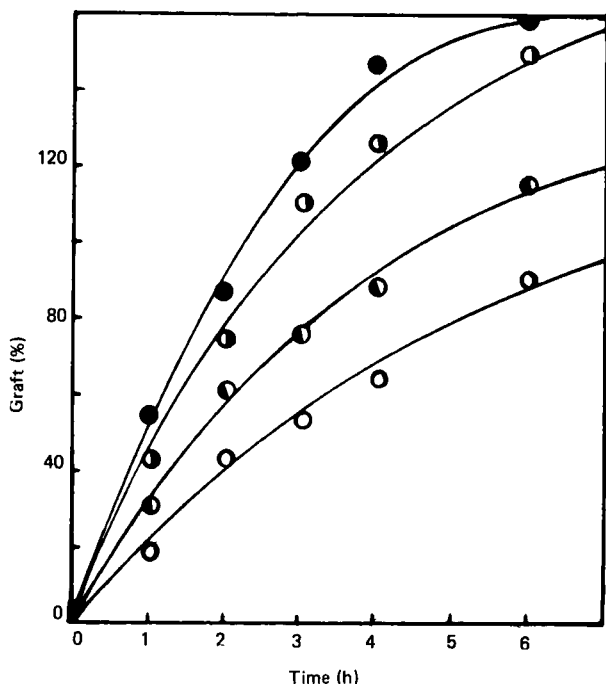
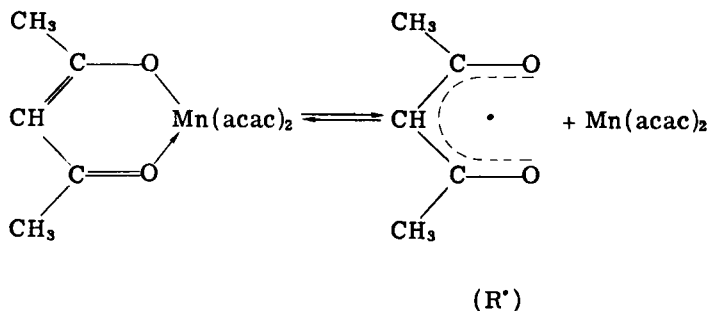
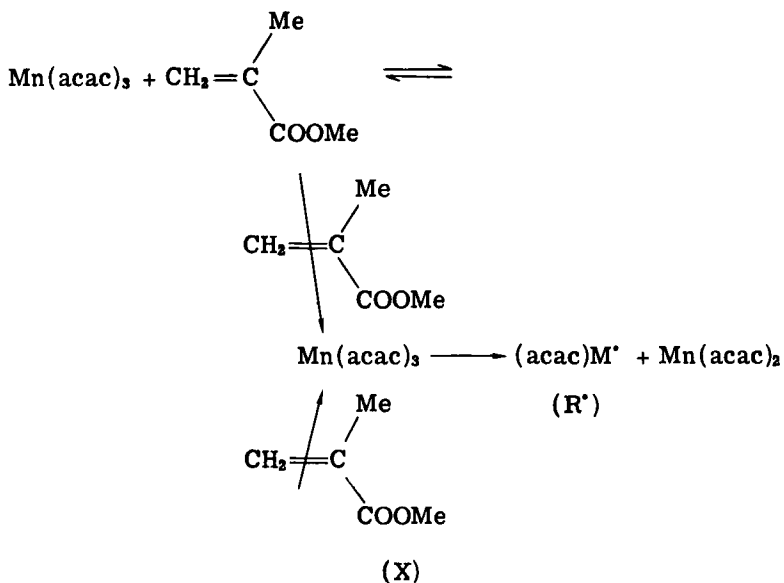


FIG. 2. Effect of $[\text{Mn}(\text{acac})_3]$ on graft yield. $[\text{MMA}] = 0.4694 \text{ mol/L}$, $[\text{HClO}_4] = 5 \times 10^{-3} \text{ mol/L}$, $\text{M:L} = 1:100$, 50°C . $[\text{Mn}(\text{acac})_3]$ values (in mol/L): (o) 3×10^{-3} , (◐) 5×10^{-3} , (◑) 7×10^{-3} , (●) 9×10^{-3} .

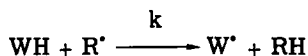
[6], acidity of the medium [6], and the monomer [20]. The solvent presumably weakens the M–O bond by H–bonding with oxygen.

The metal chelate of Mn(III) decomposes to yield the acetylacetonate free radical or a radical in combination with monomer as presented below.

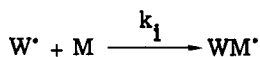




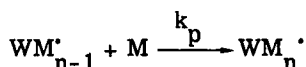
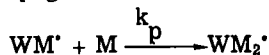
Production of free radical on wool backbone:



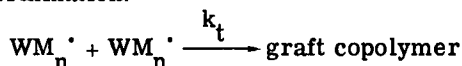
Initiation:



Propagation:



Termination:



where WH is wool, M is monomer, and W' and WM' are the corresponding radicals. Taking mutual termination into account and assuming steady state for the free radicals, the rate law has been derived as follows:

$$-\frac{d[W^*]}{dt} = k[WH][\text{complex}] - k_1[W^*][M] = 0$$

$$[W^*] = \frac{k[WH][\text{complex}]}{k_1[M]}$$

$$-\frac{d[WM_n^*]}{dt} = k_1[W^*][M] - k_t[WM_n^*]^2 = 0$$

$$[WM_n^*] = \left\{ \frac{k_1[W^*][M]}{k_t} \right\}^{1/2}$$

Then, putting the value of $[W^*]$ in the above equation:

$$[WM_n^*] = \left\{ \frac{k[WH][\text{complex}]}{k_t} \right\}^{1/2}$$

Then

$$R_p = k_p \left[\frac{k}{k_t} \right]^{1/2} [WH]^{1/2} [\text{complex}]^{1/2} [M]$$

The plots of R_p versus $[M]$ and $[\text{complex}]^{1/2}$ (Figs. 3 and 4) are linear, confirming the validity of the above reaction scheme.

Effect of Monomer Concentration

The effect of various monomers on graft yield has been studied. MMA is found to be the most active vinyl monomer, the order of reactivity being MMA > methyl acrylate > ethyl acrylate > butyl acrylate > acrylic acid.

This order of reactivity suggests that the formation of initiating radicals is monomer assisted, leading to the formation of an intermediate complex (X). The ease of formation of such a complex will be maximum with MMA because of increased π -electron density due to the +I effect of the substituted methyl group.

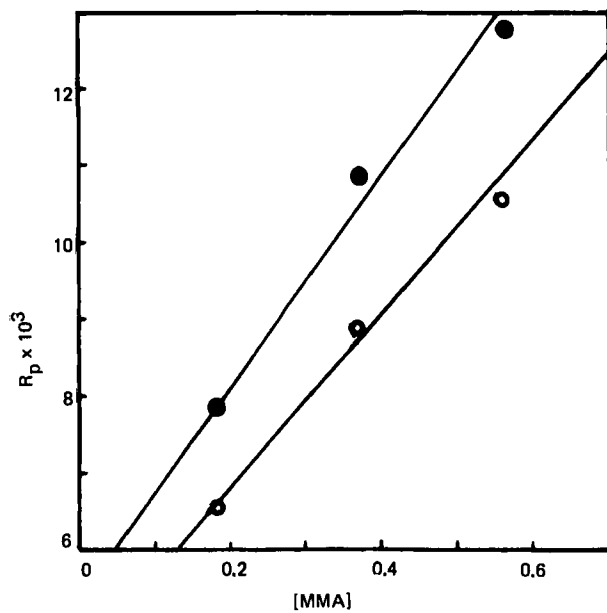


FIG. 3. Plot of R_p vs $[M]$: (●) 3 h, (○) 4 h.

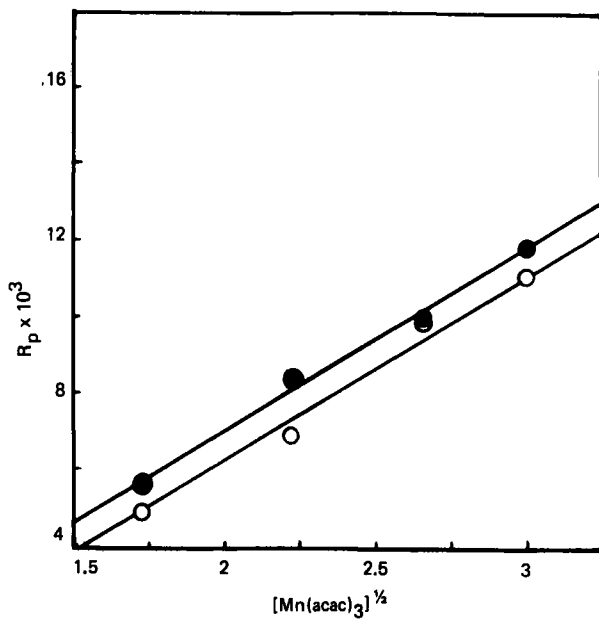


FIG. 4. Plot of R_p vs $[\text{complex}]^{1/2}$: (●) 2 h, (○) 3 h.

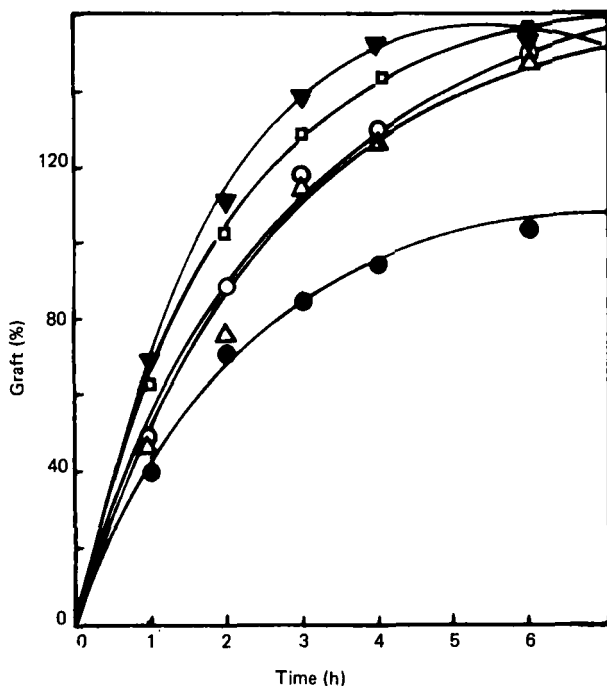


FIG. 5. Effect of [MMA] on graft yield: $[\text{Mn}(\text{acac})_3] = 7 \times 10^{-3}$ mol/L, $[\text{HClO}_4] = 5 \times 10^{-3}$ mol/L, M:L = 1:100, 50°C . [MMA] values (in mol/L): (●) 0.1878, (○) 0.3756, (▼) 0.5634, (□) 0.7512, (△) 0.9388.

The graft yield has been studied in the range 0.1878 to 0.9388 mol/L of MMA concentration. It is observed that graft yield continually increases up to 0.5634 mol/L and thereafter falls (Fig. 5). This can be ascribed to various reasons: 1) at higher concentration of the monomer, reactions that are competitive with grafting probably take place in solution, i.e., combination and disproportionation of PMMA macroradicals [21, 22]; 2) when the concentration of PMMA macroradical increases, the rate of their combination and disproportionation increases faster than the rate of their combination with wool molecules; and 3) the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which of course grows rapidly when high concentrations of monomer are used [23].

Effect of Acid Concentration

The effect of HClO_4 concentration has been investigated in the range 0.0025 to 0.01 mol/L. It is observed that the graft yield steadily in-

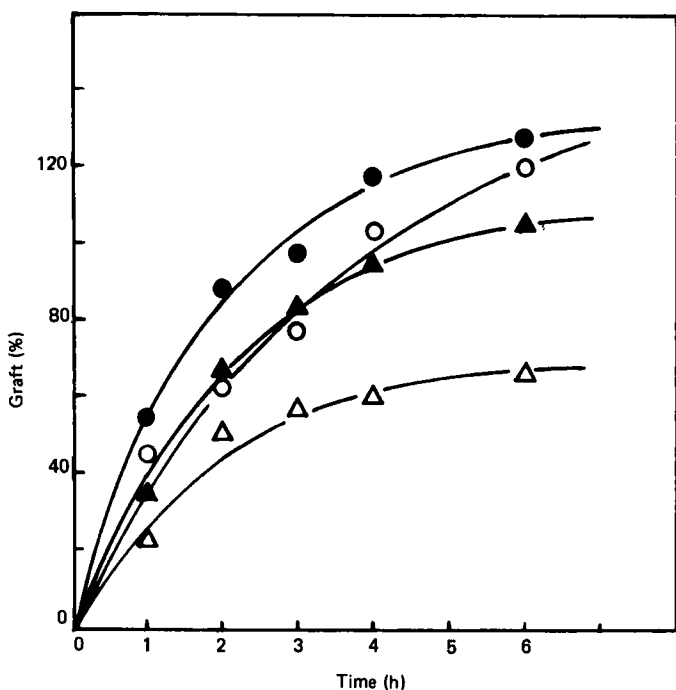


FIG. 6. Effect of $[\text{HClO}_4]$ on graft yield: $[\text{Mn}(\text{acac})_3] = 7 \times 10^{-3}$ mol/L, $[\text{MMA}] = 0.2817$ mol/L, M:L = 1:100, 50°C . $[\text{HClO}_4]$ values (in mol/L): (○) 2.5×10^{-3} , (●) 5×10^{-3} , (▲) 7.5×10^{-3} , (△) 10×10^{-3} .

creases from 0.0025 to 0.005 mol/L and thereafter decreases (Fig. 6). With increasing acid concentration the chelate probably breaks down at a considerable rate, thus increasing the concentration of acetyl-acetonato free radical which increases the percentage of grafting. But with a further increase in acid concentration, the probability of homopolymer formation appreciably increases, thereby decreasing graft yield.

Effect of Temperature

Graft copolymerization was carried out at 40, 45, 50, and 55°C , keeping the concentration of all reagents constant (Fig. 7). A perusal of the results indicates that with increasing temperature, the percentage of grafting increases. This can be ascribed to 1) the greater ease of acetyl acetone free radical formation, 2) increased solubility, and 3) enhanced diffusion rate of the monomer. The Arrhenius plot (Fig. 8) of $\log R_p$ vs $1/T$ is a straight line. From the slope of the plot, the energy of activation is computed to be 7.6 kcal/mol.

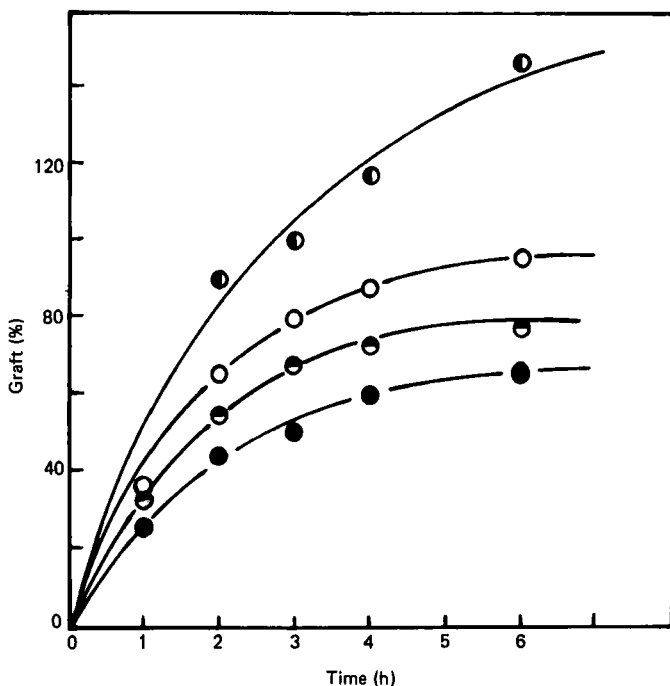


FIG. 7. Effect of temperature on graft yield: $[\text{Mn}(\text{acac})_3] = 7 \times 10^{-3}$ mol/L, $[\text{HClO}_4] = 3.5 \times 10^{-3}$ mol/L, $[\text{MMA}] = 0.2817$ mol/L, M:L = 1:100. (●) 40°C, (◐) 45°C, (○) 50°C, (◑) 55°C.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting monomers onto wool fibers. The effect of different types of alcoholic solvents, chain transfer solvents, organic acids, and other solvents acting as solubilizers for the monomer has been investigated. With alcoholic solvents the graft yield follows the order EtOH > n-Pr-OH > n-butyl-OH > amyl-OH (Fig. 9). With chain transfer solvents the order is $\text{CCl}_4 > \text{CHCl}_3 > \text{EtSH}$ (~1%) (Fig. 9), and with other solvents acting as solubilizers the order is $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{dioxane} > \text{CH}_3\text{COCH}_3 > \text{DMF}$ (Fig. 10). The dependence of grafting upon the nature of the solvents 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 solvent radical for activation of wool, 5) increase of concentration of the initiating free radical by assisting the degradation of the chelate, and 6) termination of graft

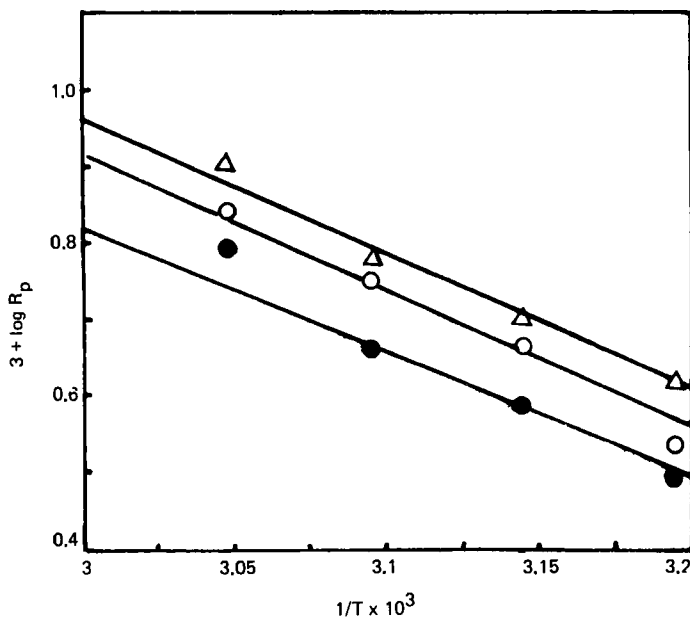


FIG. 8. Arrhenius plot of $\log R_p$ vs $1/T$. (Δ) 2 h, (\circ) 4 h, (\bullet) 6 h.

radical and wool macroradical via chain transfer. While the first five factors favor grafting by simplifying access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft [24].

The graft yield decreases with an increase in the molecular weight of the alcohol from ethanol to amyl alcohol. The lower graft yield for high molecular weight alcohols could be ascribed to 1) the adverse effect of swelling of wool by water and 2) the hydrophobic character that decreases from amyl alcohol to ethanol. These effects seriously hinder monomer access to reactive sites on wool [25].

Determination of Molecular Weight

Several samples of reduced wool were subjected to grafting under identical reaction conditions. Grafted samples were removed after regular time intervals and Soxhlet extracted. Separation and purification of grafted vinyl polymer (PMMA) from PMMA-g-reduced wool were carried out by 1) digesting in 5 M HCl, 2) extracting with 10% (v/v) diethyl ether solution in methanol, and 3) dissolving in ethyl acetate and reprecipitating by cold methanol.

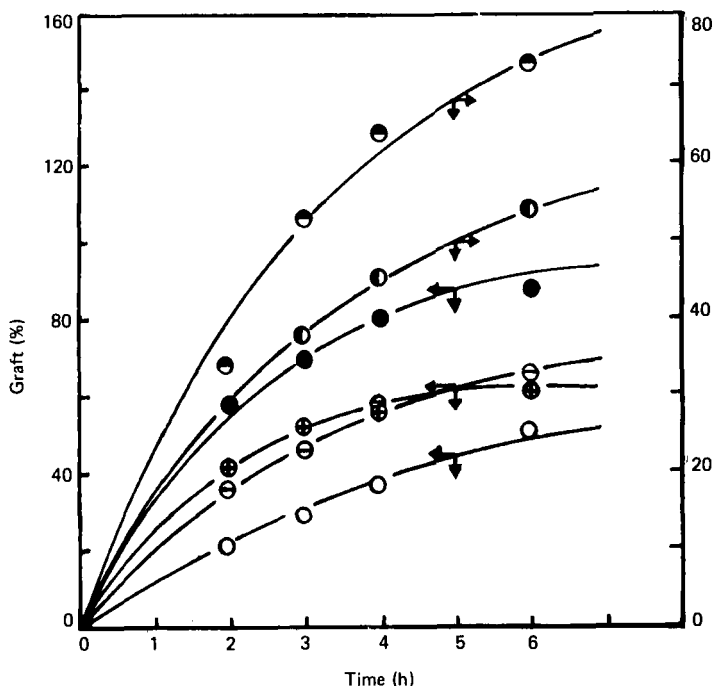


FIG. 9. Effect of alcoholic and chain transfer solvents on graft yield. $[\text{Mn}(\text{acac})_3] = 5 \times 10^{-3}$ mol/L, $[\text{MMA}] = 0.2817$ mol/L, $[\text{HClO}_4] = 3.5 \times 10^{-3}$ mol/L, [solvent] = 5% (v/v), M:L 1:100, 50°C. (●) EtOH, (⊙) n-Pr-OH, (⊖) n-butyl-OH, (⊕) CHCl_3 , (○) CCl_4 .

The average molecular weight (\bar{M}) of regenerated PMMA was determined by viscometry by employing the relationship [26, 27]

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

Study of the results suggests that the average molecular weight of the PMMA decreases with an increase in graft percentage. Since the initial concentration of MMA for each sample was the same, with an increase in graft % the concentration of monomer decreases in the vicinity of the base polymer, as a result of which the frequency of chain transfer increases. This will evidently decrease \bar{M} .

Alkali Solubility

The alkali solubility of the grafted and native wool was studied. The solubility test was performed following the procedure of Leaveau and

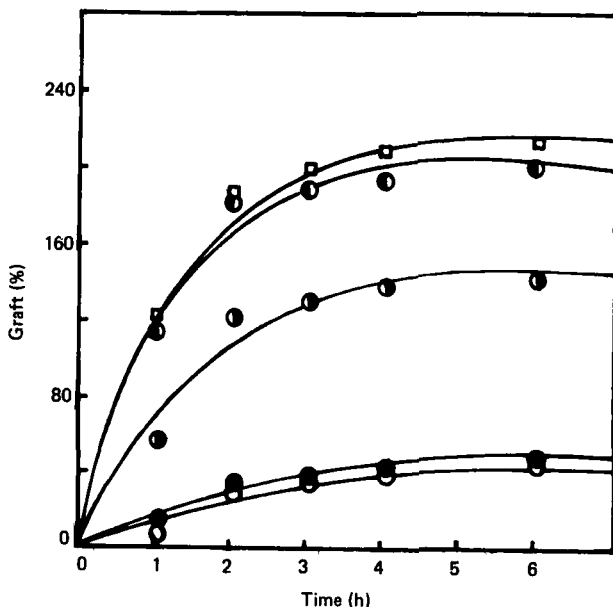


FIG. 10. Effect of solvents acting as solubilizers of the monomer on graft yield. $[\text{Mn}(\text{acac})_3] = 5 \times 10^{-3}$ mol/L, $[\text{HClO}_4] = 3.5 \times 10^{-3}$ mol/L, $[\text{MMA}] = 0.2817$ mol/L, $[\text{solvent}] = 5\%$ (v/v), M:L = 1:100, 50°C . (●) Acetone, (□) acetic acid, (○) DMF, (◐) dioxane, (◑) formic acid.

co-workers [28]. It is observed that with an increase in graft yield, the alkali solubility decreases. The reduction in alkali solubility after grafting suggests that the PMMA chains acted as diffusion barriers toward alkali penetration into the wool fibers, thus protecting the polypeptide chains, salt linkages, and disulfide bonds, if any. Similar findings have been reported by several authors [29, 30].

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