Grafting Vinyl Monomers onto Wool Fibers. X. Graft Copolymerization of Methyl Methacrylate onto Wool Using Acetylacetonato Complex of Manganese(lII)

P. L. Nayak[a]; G. Sahu[a]; S. Samal[b]

[a] Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India [b] Department of Chemistry, Bhadrak College, Bhadrak, Orissa, India

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PADMA L. NAYAK and GANGADHAR SAHU

Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

SASHADHAR SAMAL

Department of Chemistry
Bhadrak College
Bhadrak, Orissa, India

ABSTRACT

The graft copolymerization of methyl methacrylate onto wool fibers was investigated in aqueous solution using the acetylacetonato complex of manganese(III). The rate of grafting was determined by varying the monomer, the complex, the temperature, the acidity of the medium, the nature of the wool, and the reaction medium. The graft yield increases with increasing monomer and complex concentrations. The graft yield also increases with increasing temperature. The grafting is considerably influenced by chemical modification of wool prior to grafting. A suitable mechanism has been proposed and a rate equation has been derived.

INTRODUCTION

Grafting vinyl monomers onto the backbone of synthetic and natural polymers considerably modifies the properties of the base polymer. This field has been the subject of investigation by various workers [1-3] using chemical and radiation methods. Redox polymerization of methyl methacrylate using various metal chelates, such as Mn(acac)₃ and Co(acac)₃, has been investigated by Bamford and Lind [4]. However, no attention has been paid toward grafting of vinyl monomers onto natural polymers using these chelate complexes. In the present investigation a chelate complex, namely acetylacetonato manganese-(III) [Mn(acac)₃], has been used for grafting MMA onto wool fibers.

EXPERIMENTAL

The purification of wool fibers, monomer, and solvents, the method of rate measurement, and the calculation of percentage of graft yield were reported in previous communications [5, 6].

RESULTS AND DISCUSSION

Effect of Mn(acac)₃ Concentration

The rate of grafting has been investigated by changing the Mn(acac)₃ concentration within the range 0.003 to 0.01 M. The data indicate that in this range the graft yield increases with an increase of chelate concentration (Fig. 1).

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

The formation of an acetylacetone free radical is assisted by the solvent which presumably weakens the Mn—O bond by H-bonding with the oxygen atom [4, 7].

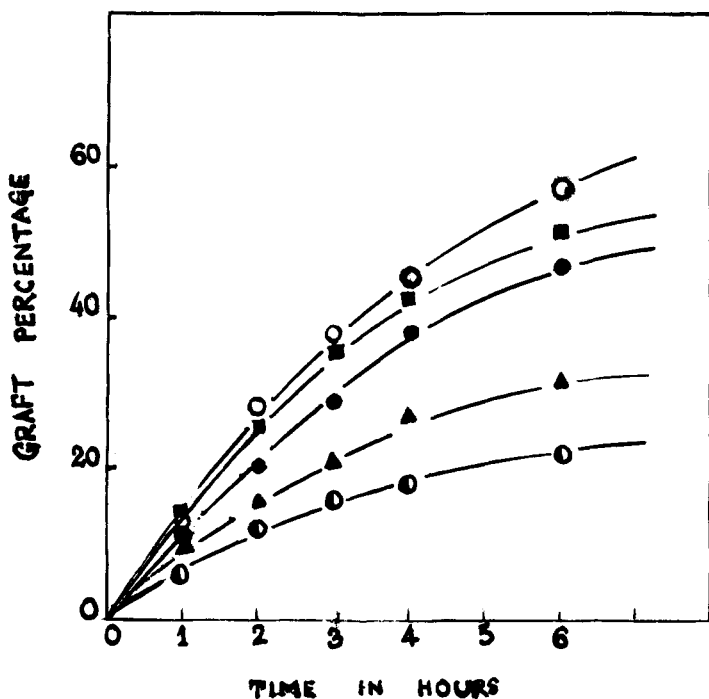The mechanism for the formation of free radical is

FIG. 1. Effect of $[Mn(acac)_3]$ on graft yield: $[MMA]$ = 0.4694 mL^{-1}; $[HClO_4]$ = 5 × 10^{-3} mL^{-1}; M:L = 1:100; temperature = 50°C. ($\circ$): $[Mn(acac)_3]$ = 10 × 10^{-3} mL^{-1}. ($\blacksquare$) $[Mn(acac)_3]$ = 8 × 10^{-3} mL^{-1}. ($\bullet$): $[Mn(acac)_3]$ = 6 × 10^{-3} mL^{-1}. ($\blacktriangle$): $[Mn(acac)_3]$ = 5 × 10^{-3} mL^{-1}. ($\ominus$): $[Mn(acac)_3]$ = 3 × 10^{-3} mL^{-1}.

(A$^\cdot$)
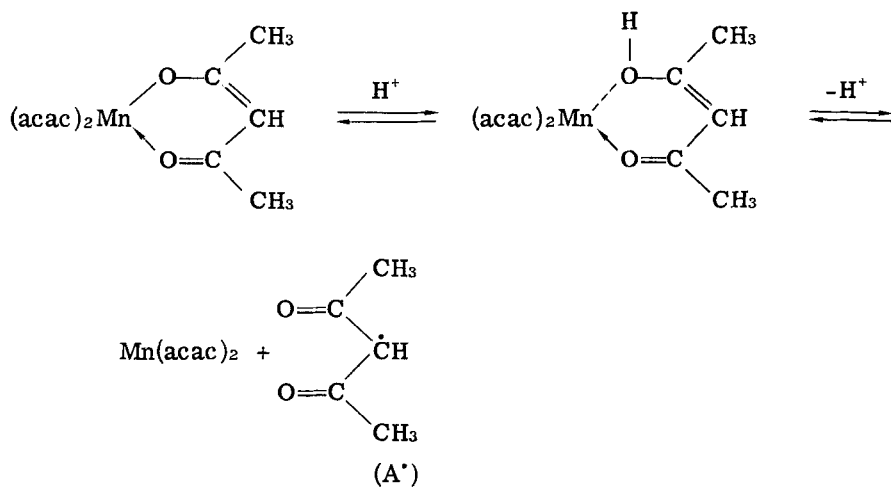
Production of free radical on wool backbone:

$$WH + A^{\bullet} \xrightarrow{\quad k \quad} W^{\bullet} + AH$$

Initiation:

$$W^{\bullet} + M \xrightarrow{\quad k_i \quad} WM^{\bullet}$$

Propagation:

$$WM^{\bullet} + M \xrightarrow{\quad k_p \quad} WM_2^{\bullet}$$

$$WM_{n-1}^{\bullet} + M \xrightarrow{\quad k_p \quad} WM_n^{\bullet}$$

Termination:

$$WM_n^{\bullet} + WM_n^{\bullet} \xrightarrow{\quad k_t \quad} \text{graft polymer}$$
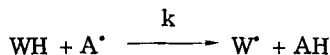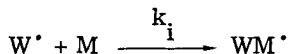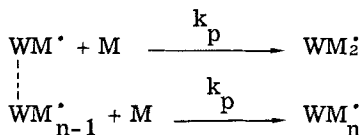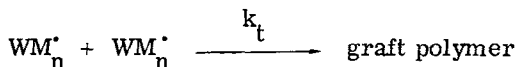
where WH is wool, M is the monomer, and $W^{\bullet}$ and $WM^{\bullet}$ are the corresponding radicals. Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

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

$$[W^{\bullet}] = \frac{k[WH][\text{complex}]}{k_i[M]}$$

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

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

Then, putting the value of $[W^{\bullet}]$ in the above equation,

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

Then

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

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

Effect of Monomer Concentration

The effect of monomer on graft yield has been studied in the range of 0.1878 to 0.7512 M MMA concentration. It has been found that in this range the graft yield increases with an increase in monomer concentration (Fig. 4). This can be attributed to various factors:
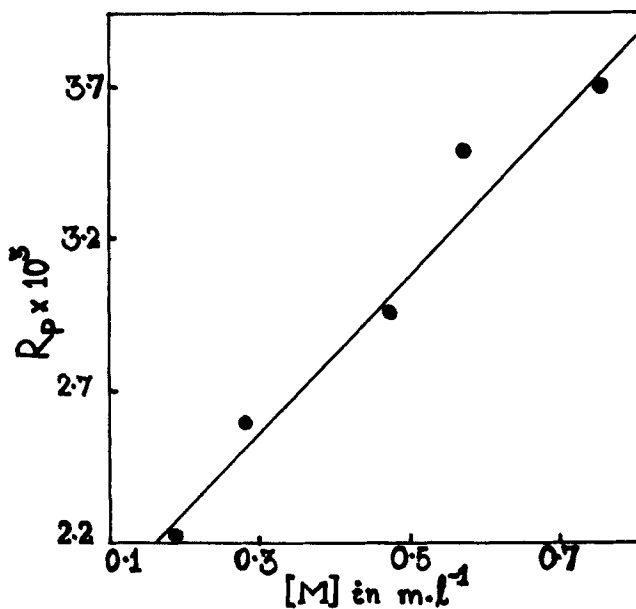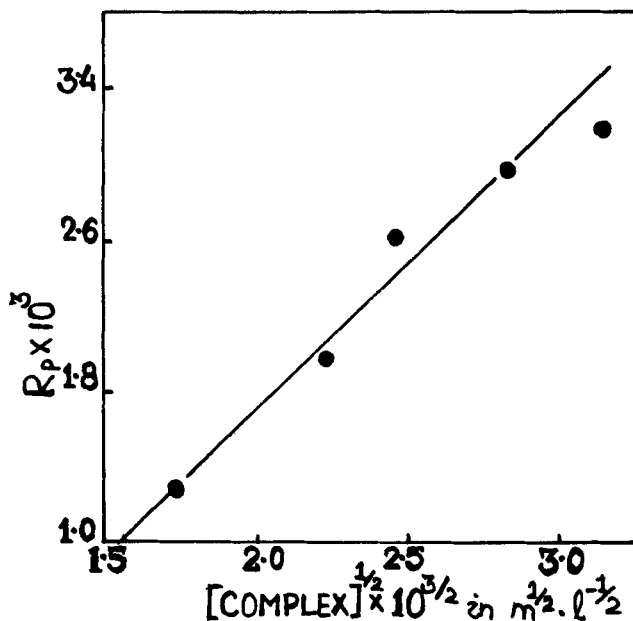

FIG. 2. Plot of R_p versus $[M]$.

FIG. 3.   Plot of R_p versus $[complex]^{1/2}$.

(1) complexation of the wool with the monomer which enhances the
monomer activity at higher monomer concentrations. (2) Due to the
gel effect [8], i.e., increased solubility of polymethyl methacrylate
(PMMA) in its own monomer, which causes hindrance in termination,
particularly by coupling of the growing polymer chains. This gel
effect also causes swelling of wool, thus facilitating diffusion of mono-
mer to the growing chains and active sites on the wool backbone,
thereby enhancing grafting. (3) Some species which are either present
or generated during the polymerization reaction act as efficient radi-
cal scavengers. Competition between these and the monomer in cap-
turing 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 Temperature

   Graft copolymerization was carried out at four different tempera-
tures ranging from 40 to 55°C while keeping the concentrations of all
other reagents constant (Fig. 5). A perusal of the results indicates
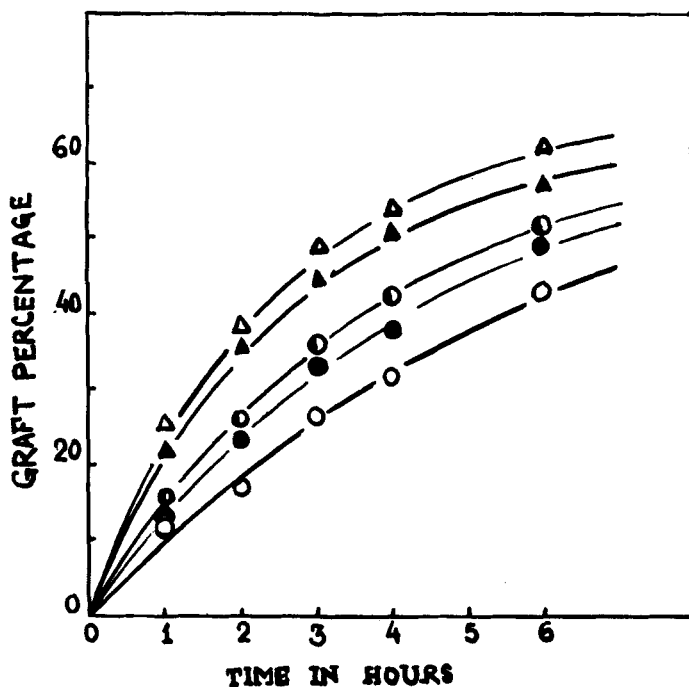that with increasing temperature, the percentage of grafting increases.

FIG. 4. Effect of $[MMA]$ on graft yield: $[Mn(acac)_3] = 8 \times 10^{-3}$ mL^{-1}; $[HClO_4] = 5 \times 10^{-3}$ mL^{-1}; M:L = 1:100; temperature = 50°C. ($\circ$): $[MMA] = 0.1878$ mL^{-1}. ($\bullet$): $[MMA] = 0.2817$ mL^{-1}. ($\ominus$): $[MMA] = 0.5634$ mL^{-1}. ($\blacktriangle$): $[MMA] = 0.4694$ mL^{-1}. ($\triangle$): $[MMA]$ $= 0.7512$ mL^{-1}.

This can be ascribed to the greater ease of acetylacetone free radical formation for which the graft yield increases. The swellability of wool, solubility of monomer, and its diffusion rates are enhanced by increasing the reaction temperature. The Arrhenius plot (Fig. 6) of $\log R_p$ versus $1/T$ is linear, and the activation energy was computed to be 8.1 kcal/mol.

Effect of Acid Concentration

The effect of perchloric acid concentration has been investigated in the range 2.5×10^{-3} to 1.0×10^{-2} $\underline{M}$ (Fig. 7). It has been observed that the yield increases from 2.5×10^{-3} to 5×10^{-3} $\underline{M}$, and thereafter it decreases.

With increasing acid concentrations the chelate probably breaks
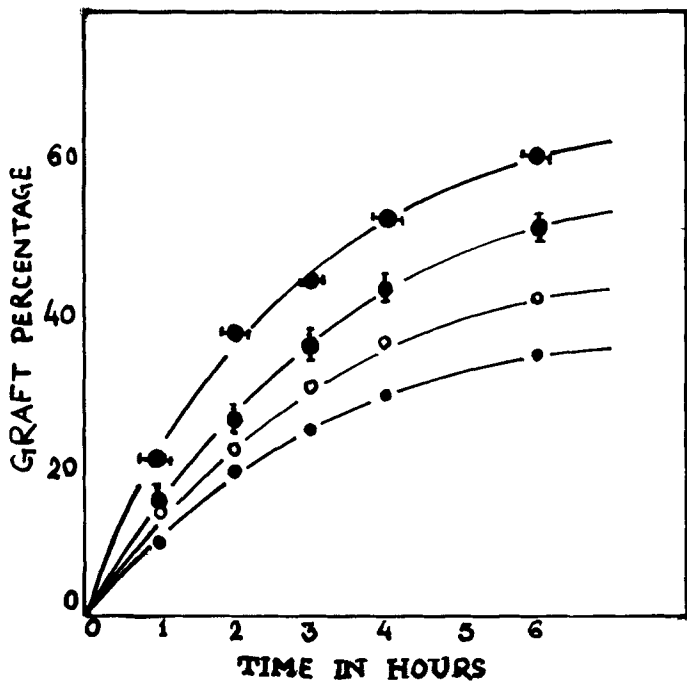
FIG. 5. Effect of temperature on graft yield: $[Mn(acac)_3] = 8 \times 10^{-3}$ mL^{-1}; $[HClO_4] = 5 \times 10^{-3}$ mL^{-1}; $[MMA] = 0.4694$ mL^{-1}; M:L = 1:100. Temperatures: (•) 40°C, (○) 45°C, (⊕) 50°C, (⊢•⊣) 55°C.
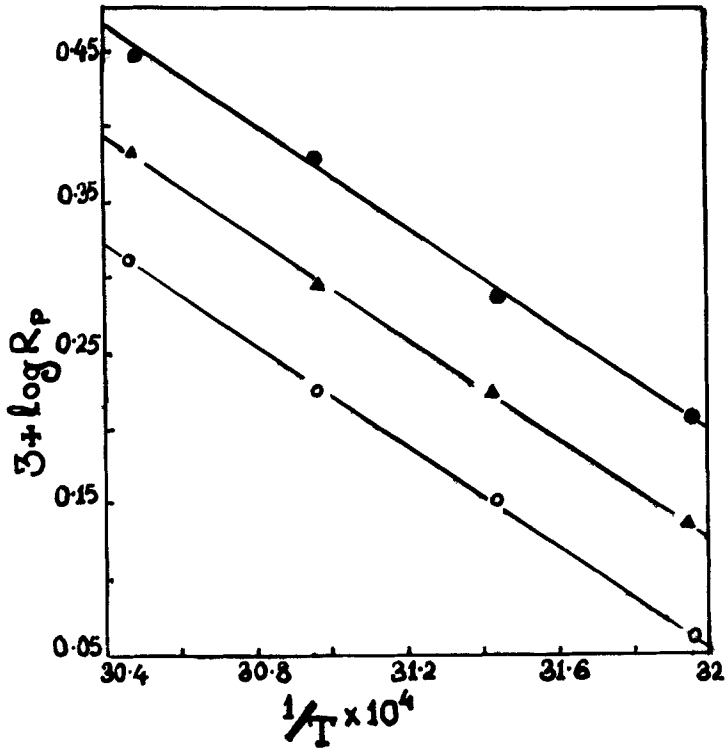
FIG. 6. Arrhenius plot of log R_p versus $1/T$: (●) 6 h, (▲) 4 h, (○) 3 h.
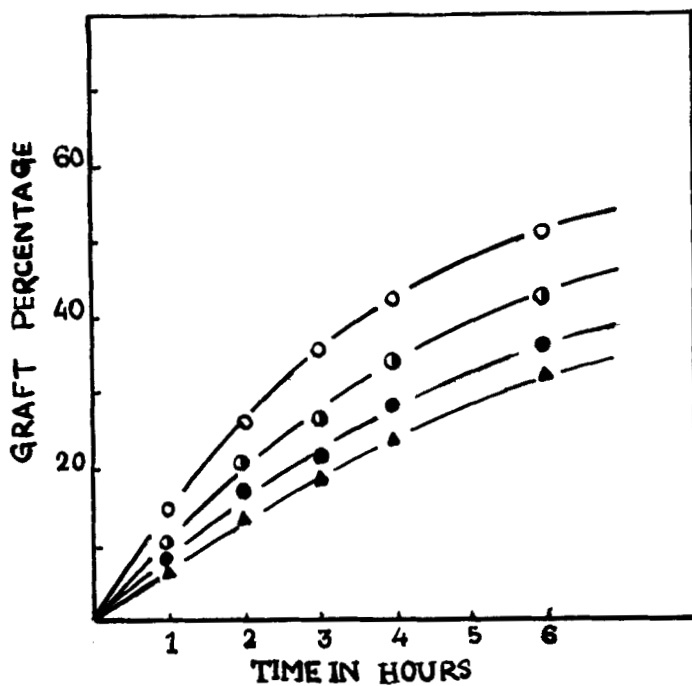
FIG. 7.   Effect of $[HClO_4]$ on graft yield: $[Mn(acac)_3] = 8 \times 10^{-3}$ mL^{-1}; $[MMA] = 0.4694$ mL^{-1}; m:L = 1:100; temperature = 50°C. (◑): $[HClO_4] = 2.5 \times 10^{-3}$ mL^{-1}. (●): $[HClO_4] = 7.5 \times 10^{-3}$ mL^{-1}. (○): $[HClO_4] = 5 \times 10^{-3}$ mL^{-1}. (▲): $[HClO_4] = 10 \times 10^{-3}$ mL^{-1}.
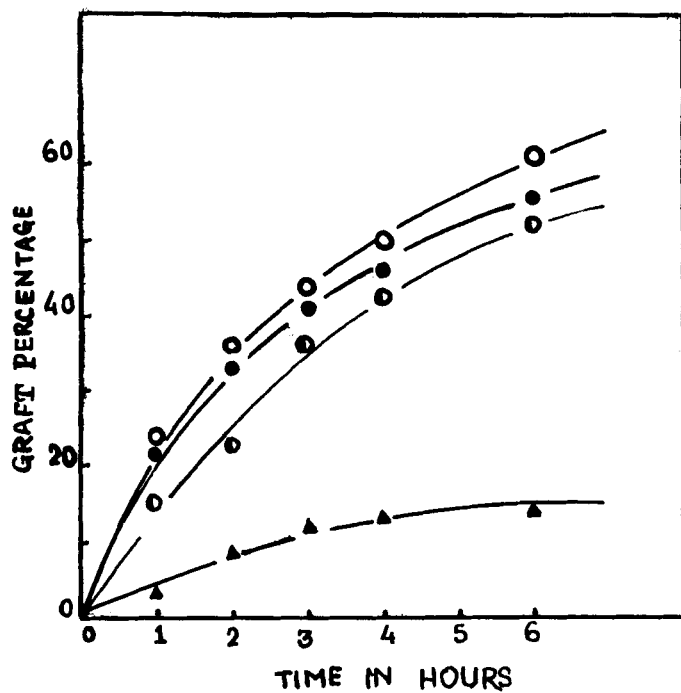
FIG. 8. Effect of modified wool on graft yield: $[Mn(acac)_3]$ = 8×10^{-3} mL^{-1}; $[MMA]$ = 0.4694 mL^{-1}; $[HClO_4]$ = 5×10^{-3} mL^{-1}; M:L = 1:100; temperature = 50°C. (o) Oxidized wool. (▲) Cross-linked wool. (•) Reduced wool. (◐) Native wool.

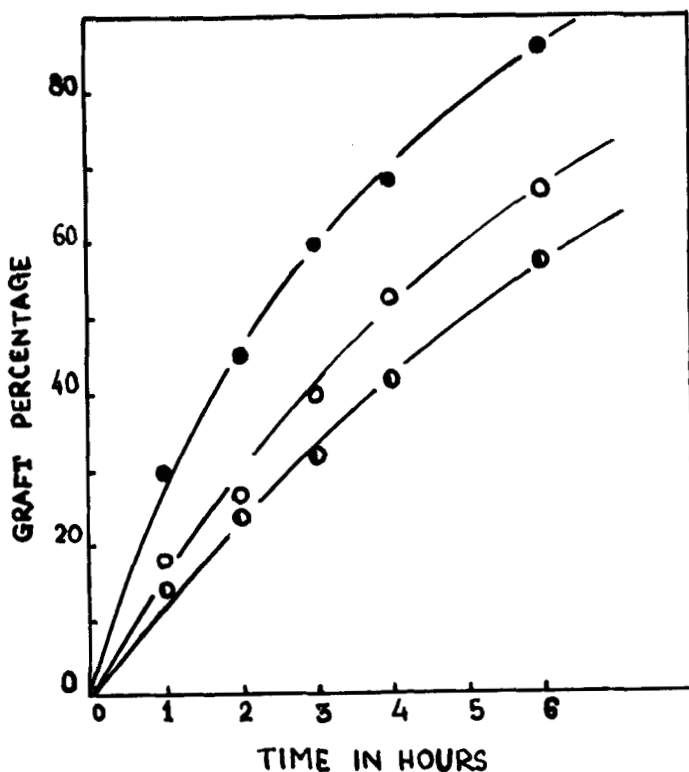FIG. 9. Effect of alcoholic solvents on graft yield: $[Mn(acac)_3]$ = 8×10^{-3} mL^{-1}; $[MMA]$ = 0.4694 mL^{-1}; $[HClO_4]$ = 5×10^{-3} mL^{-1}; M:L = 1:100; temperature = 50°C. (○) Methyl alcohol (25% v/v). (●) Ethyl alcohol (15% v/v). (◑) Amyl alcohol (5% v/v).

down at a considerable rate, thus sufficiently increasing the concentration of acetylacetone free radical which increases the percentage of grafting. But with a further increase of acid concentration the probability of homopolymer formation appreciably increases, thereby decreasing the graft yield.

Nature of the Substrate

By changing the physical and chemical structure of wool, the graft percentage is remarkably affected (Fig. 8). The order of the effect is: oxidized wool > reduced wool > native wool > cross-linked wool > trinitrophenylated wool. When wool fiber is subjected to formylation, cross-linking blocks the radical sites [5, 6] and, similarly with
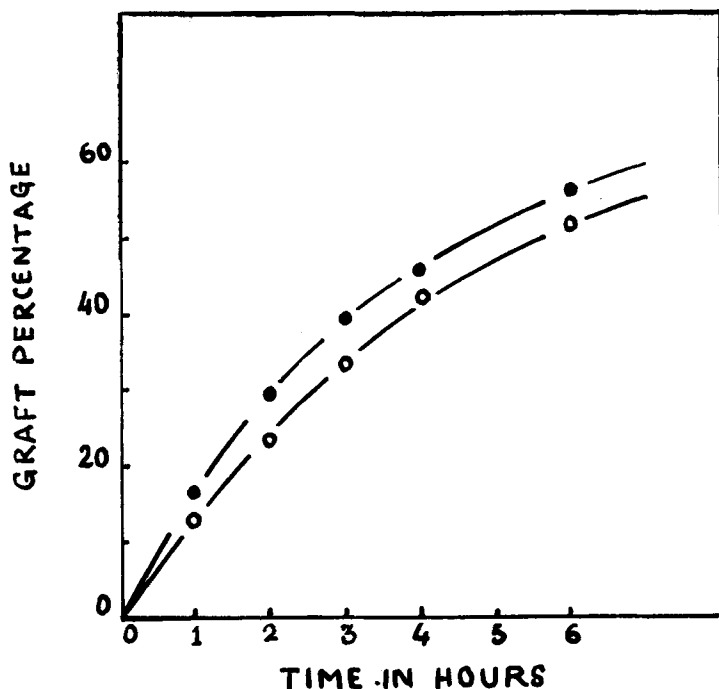
FIG. 10. Effect of chain transfer solvents on graft yield: $[Mn(acac)_3]$ = 8×10^{-3} M; $[MMA]$ = 0.4694 mL^{-1}; $[HClO_4]$ = 5×10^{-3} mL^{-1}; M:L = 1:100; temperature = 50°C. (●) Chloroform (5% v/v). (○) Carbon tetrachloride (5% v/v).

trinitrophenylation, active reaction sites are blocked. Free radicals cannot be created at the wool backbone by the interaction of the acetyl-acetone free radical. The other reasons for low graft yield might be (1) lowering of the swellability of the fiber and (2) hindrance of adsorption of $Mn(acac)_3$ and MMA owing to low fiber swellability and repulsion of MMA molecules by the negatively charged substituted nitro groups in the case of trinitrophenylated wool. The net effect of these factors is a decrease of grafting. With oxidized (by H_2O_2 solution) and reduced (by thioglycolic acid) wool, the interlocking bonds between two strands of wool which form a helical arrangement are broken, thus creating new reactive sites for grafting.

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) has been investigated. With alcoholic solvents the graft yield follows the order (Fig. 9) methanol > ethanol > amyl alcohol. With chain transfer solvents (Fig. 10) the order is CCl_4 > $CHCl_3$. With other solvents the order is formic acid > acetic acid > DMF > dioxane > acetone.

The dependence of grafting upon the nature of the solvent suggests that the solvents examined differed 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, (5) increased concentration of the initiating free radical by assisting the degradation of the chelate, and (6) termination of the graft radical and wool microradical via chain transfer. While the first five 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.

In the case of alcohols the order of graft yield suggests that with increasing molecular weight of the alcohol, graft yield decreases. The lowering of graft yield could be ascribed to the adverse effect of water on the swelling of wool. The hydrophobic character of the solvent increases from methanol to amyl alcohol by hindering monomer access to reactive sites on the wool. This is another factor for low graft yield.

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