Grafting Vinyl Monomers onto Wool Fibers: Graft Copolymerization of Methyl Methacrylate onto Wool Fibers Using Vanadyl Acetyl Acetonate Complex

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Synopsis

The graft copolymerization of methyl methacrylate (MMA) onto native and reduced Indian Chokla wool fibers was studied in aqueous solution using the acetylacetonate oxovanadium (IV) complex. The rate of grafting was investigated by varying the concentration of the monomer and the complex, acidity of the medium, and the solvent composition of the reaction medium. The graft yield increases with increasing concentration of the initiator up to 8.75×10^{-5} mol/L, of the monomer up to 0.5634 mol/L, and thereafter it decreases. MMA was found to be the most active monomer when compared to other vinyl monomers. Grafting increases with increasing concentration of $HClO_4$ and with increasing temperature. Reduced and oxidized wools were found to be better substrates than untreated, esterified, crosslinked, and trinitrophenylated wools. The extent of grafting was mostly dependent upon the concentration of —SH groups in case of reduced wool. A suitable reaction scheme has been proposed and the activation energy was calculated from Arrhenius plot.

INTRODUCTION

The use of chelate complexes for initiating vinyl polymerization has attracted attention in recent year.[1–7] Arnett and Mendelson[3] observed that metal chelates, upon heating, decompose to generate free radical species by homolysis of M—O bond with the reduction of the metal to a lower valency state. Kasting et al.[1,8] reported that the acetylacetonates of Mn(III) and Co(III) are most active initiators. Bamford and Lind[2] reported the polymerization of vinyl monomers using such complexes. Otsu et al.[5,7] have studied the polymerization of vinyl monomers using a large number of metal acetylacetonates. Many other workers reported grafting of vinyl monomers onto wool,[9] silk,[10] nylon,[11] and cellulose[12,13] using simple acetylacetonates. Recently we reported the graft copolymerization of MMA onto wool using $Mn(acac)_3$ as initiator.[14]

Niezette and co-workers[15] reported graft copolymerization of MMA onto chemically modified wool using $LiBr$–$K_2S_2O_8$ redox system. In an attempt to determine the role of —SH groups, Mishra and co-workers[16] investigated grafting of poly(vinyl acetate) and poly(methyl methacrylate) onto reduced wool in presence of $K_2S_2O_8$-ferrous ammonium sulfate as redox initiator. Hebeish and co-workers[17] investigated graft copolymerization of MMA and acrylonitrile on cotton treated with crosslinking agents.

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This communication presents the kinetics and mechanism of graft copoly-
merization of MMA onto native wool and modified wool fibers using VO(acac)$_2$
complex. Spectral studies, thermogravimetric analysis, and SEM studies of the
grafted samples will be reported in our subsequent communications.

EXPERIMENTAL

Purification of wool, monomers, solvents, method of rate measurement, and
calculation of percentage of graft yield has been reported in our previous com-
munications.[18] Wool was chemically modified following a standard procedure.[19]
Grafted poly(methyl methacrylate) (PMMA) was regenerated by HCl-digestion
technique, and the average molecular weight ($\overline{M}$) was determined viscometri-
cally.

DISCUSSION

Nature of the Substrate. The effect of the changes in physical and chemical
structure of wool brought about by reduction, oxidation, esterification, cross-
linking, and trinitrophenylation on grafting has been investigated. The order
of reactivity is: reduced > oxidized > native > esterified > crosslinked > trin-
itrophenylated (Fig. 1).

When wool is subjected to formylation, active radical sites are blocked by
crosslinking. Acetylation and trinitrophenylation also blocks such reaction sites.
Free radicals cannot be created on the wool backbone by the interaction with
the initiating radicals. The other reasons might be (1) lowering of swellability
of the fiber leading to suppressed adsorption of VO(acac)$_2$ and MMA and (2)
repulsion of MMA molecules by the negatively charged substituted nitro
groups.

Reduced wool is found to be a better substrate than native wool. The reaction
proceeds to completion within 3–4 h without considerable induction period (Fig.
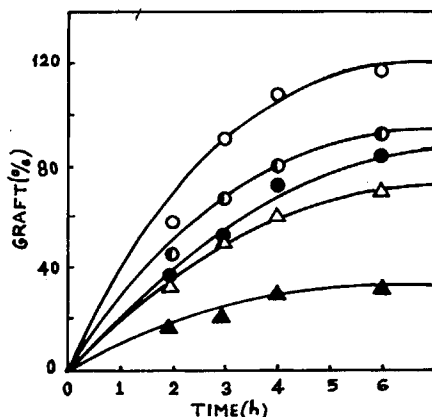2). The —SH groups formed by the homolytic cleavage of the cystine disulfide

Fig. 1. Effect of modified wool on graft yield: [VO(acac)$_2$] = 7.5 × 10^{-5} mol/L; [MMA] = 0.3756
mol/L; [HClO$_4$] = 0.005 mol/L; [EtOH] = 1.3 mol/L; M:L = 1:100; temp = 50°C; (O) reduced (0.5M
TGA); (◉) reduced (0.3M TGA); (●); oxidized; (△) native; (▲) crosslinked.
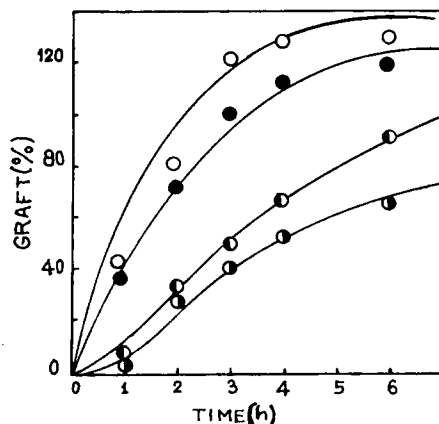
Fig. 2. Effect of [VO(acac)$_2$] on graft yield (time conversion): [MMA] = 0.4694 mol/L; [HClO$_4$] = 0.005 mol/L; [EtOH] = 1.3 mol/L; M:L = 1:100; temp = 50°C. Native wool: (◐) [complex] = 6.25 × 10^{-5} mol/L; (◑) [complex] = 8.75 × 10^{-5} mol/L. Reduced wool: (●) [complex] = 6.25 × 10^{-5} mol/L; (○) [complex] = 8.75 × 10^{-5} mol/L

linkage are known as active grafting sites[20] and the abstraction of hydrogen from —SH group by initiating radicals seems to proceed much more easily than from other existing groups on the wool backbone. Further, treatment of wool with thioglycollic acid (TGA) might increase its accessibility or swelling and hence enhance grafting.[21] In order to ascertain the role of —SH groups, reduced wool was further acetylated, and such acetyl derivatives showed a remarkable decrease in graft yield.

Graft yield increases with increasing concentration of the reducing agent (TGA). But it is observed that, with such reduced substrates, there is a considerable loss in fiber character which might be due to the degradation of the base polymer caused during chemical treatment.[19] Similar observations are reported by Sudhir and co-workers.[22] From X-ray diffraction data, SEM, and thermogravimetric studies, these authors concluded that treatment of Chokla wool with TGA, H$_2$O$_2$, and peracetic acid resulted in a considerable chemical damage to the base polymer, leading to decreased fiber strength.

Oxidation of wool with H$_2$O$_2$ also enhances grafting. But graft percentage is lower than that with reduced wool. Oxidation most probably converts cystine to cysteic acid and creation of a free radical is comparatively more difficult on cysteic acid than on —SH group.

Effect of Initiator Concentration. The rate of grafting was investigated by varying the VO(acac)$_2$ concentration within the range 3.75–18.75 × 10^{-5} mol/L (Fig. 3). The data indicate that within the range, the graft yield increases up to 8.75 × 10^{-5} mol/L, decreasing thereafter.

In the initial stages, a charge transfer complex is probably formed between the pendant groups on the wool backbone and the chelate and monomer. Hence the concentration of the chelate and the 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 on the methylene carbon atom. This free radical interacts with the active sites on the wool backbone, forming wool macroradical which interacts with the vinyl monomer, resulting in the formation of a graft copolymer.
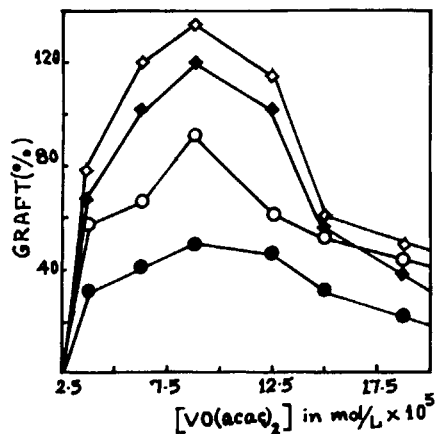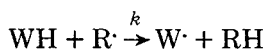
Fig. 3. Effect of [VO(acac)₂] on graft yield: [MMA] = 0.4694 mol/L; [HClO₄] = 0.005 mol/L; [EtOH] = 1.3 mol/L; M:L = 1:100; temp = 50°C. Native wool: (●) 3 h; (○) 6 h. Reduced wool: (■) 3 h; (□) 6 h.
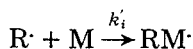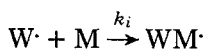
The formation of acetylacetonate free radical is assisted by the solvent,[2] the acidity of the medium[2] and the monomer.[19] The solvent presumably weakens the M—O bond by hydrogen bonding with oxygen. The chelate decomposes to yield acetylacetonate free radical or radical in combination with the monomer as presented below:
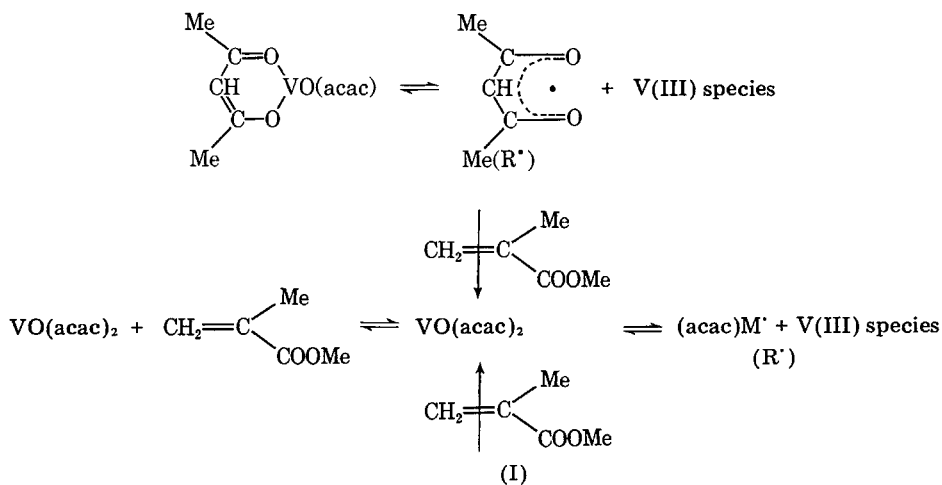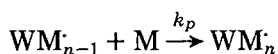

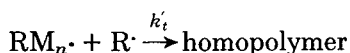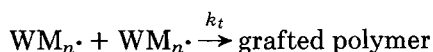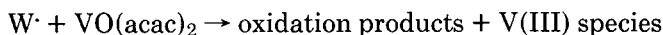*Production of free radical on wool backbone:*

$$WH + R\cdot \xrightarrow{k} W\cdot + RH$$

Initiation:

$$W\cdot + M \xrightarrow{k_i} WM\cdot$$

$$R\cdot + M \xrightarrow{k_i'} RM\cdot$$

Propagation:

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

$$RM_{n-1}^{\cdot} + M \xrightarrow{k_p'} RM_n^{\cdot}$$

Termination:

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

$$RM_n^{\cdot} + R^{\cdot} \xrightarrow{k_t'} \text{homopolymer}$$

Oxidation:

$$W^{\cdot} + VO(acac)_2 \rightarrow \text{oxidation products} + V(III) \text{ species}$$

WH is wool, M is monomer, and $W^{\cdot}$ and $M^{\cdot}$ are the corresponding radicals.

At higher concentration of the complex, the free radicals produced on wool might be ozidized, thus terminating reactive sites. In addition, the complex might interact with growing PMMA radicals, producing homopolymer.

Taking into account mutual termination and assuming steady state principle, the rate of graft copolymerization was found to be[14]

$$R_p = k_p [k/k_t]^{1/2} [WH]^{1/2} [VO(acac)_2]^{1/2} [M].$$

The plots of R_p vs. [M] (Fig. 4) and R_p vs. $[VO(acac)_2]^{1/2}$ (Fig. 5) for both native and reduced wools are linear, confirming the validity of the above reaction scheme.

Effect of Monomer Concentration: The effect of various monomers on graft yield has been investigated. MMA was found to be the most active vinyl monomer, the order of reactivity being methyl methacrylate > methyl acrylate > ethyl acrylate > n-butyl acrylate > acrylic acid.

This order of reactivity suggests that the formation of initiating radical is monomer-assisted, leading to the formation of an intermediate complex (I). The ease of formation of such a complex will be maximum with MMA because of
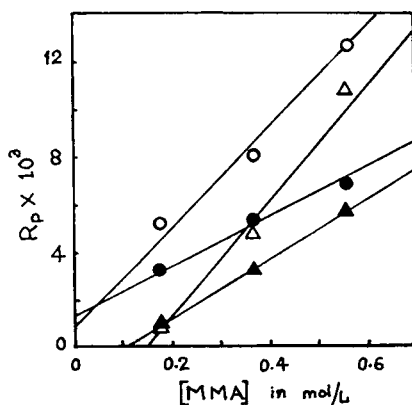

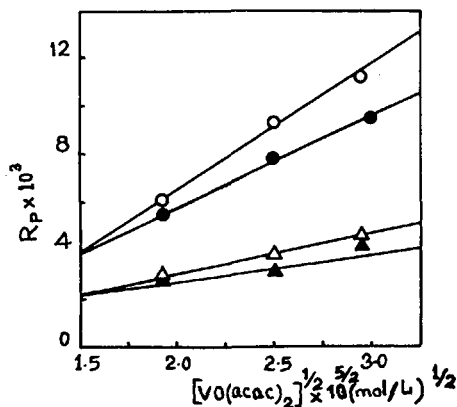Fig. 4. Plot of R_p vs. [M]. Native wool: (△) 2 h; (▲) 6 h. Reduced wool: (○) 2 h; (●) 6 h.

Fig. 5. Plot of R_p vs. $[VO(acac)_2]^{1/2}$. Native wool: (O) 3 h; (●) 4 h. Reduced wool: (△) 3 h; (▲) 6 h.

increased π-electron density due to the $+I$ effect of the substituted methyl group.

Native and reduced wools were graft copolymerized within the range 0.1878–0.9388 mol/L of MMA concentration. It is observed that graft yield increases up to 0.5634 mol/L and decreases therafter (Fig. 6). The initial increasing trend could be ascribed to (1) complexation of wool with monomer, (2) the ease of formation of complex I, and (3) gel effect. At higher concentration of the monomer, the rate of combination and disproportionation of PMMA macroradicals is increased faster than the rate of their combination with wool.[23] Besides, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, and this is more pronounced at higher concentration of the monomer.[24]

Effect of Temperature. The graft copolymerization was carried out at 40°C, 45°C, 50°C, and 55°C, keeping the concentration of all other reagents constant. The results indicate that with increasing temperature, the graft yield increases. This can be ascribed to (1) greater ease of acetylacetonate free radical formation, (2) increased solubility, and (3) enhanced diffusion rate of the monomer.
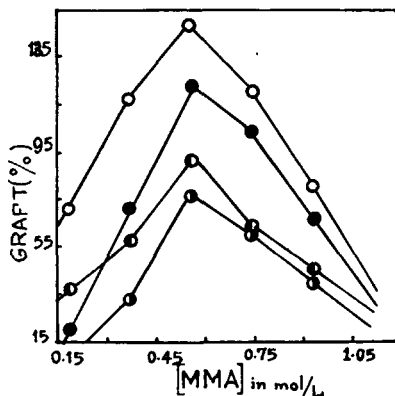

Fig. 6. Effect of [MMA] on graft yield: $[VO(acac)_2] = 7.5 \times 10^{-5}$ mol/L; $[HClO_4] = 0.005$ mol/L; [EtOH] = 1.3 mol/L; M:L = 1:100; temp = 50°C. Native wool: (◐) 2 h; (●) 6 h. Reduced wool: (◖) 2 h; (O) 6 h.
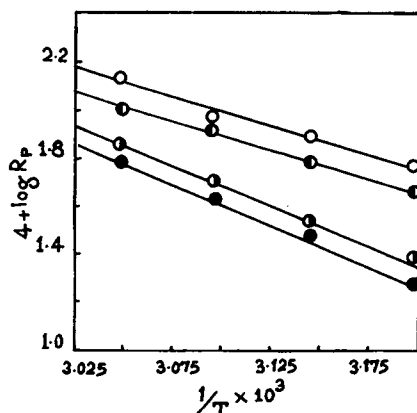
Fig. 7. Arrhenius plot of log R_p vs. 1/T. Native wool: (◖) 2 h; (●) 6 h. Reduced wool: (○) 2 h; (◓) 4 h.

The Arrhenius plot of log R_p vs. 1/T is a straight line (Fig. 7). From the slope of the plots, the overall energy of activation was found to be 66.1 kJ/mol for native wool and 47.2 kJ/mol for reduced wool. The overall activation energy (E_a) accounts for (1) energy of activation for the decomposition of the catalyst (E_d), (2) energy of activation for the growing radical to chain transfer with the backbone to form wool macroradical (E_{tr}), (3) activation energy of propagation (E_p), and (4) activation energy for termination process (E_t). These terms are related to E_a by the equation

$$E_a = E_d/2 + E_{tr}/2 + [E_p - E_t/2]$$

Using the value of $E_p - E_t/2 = 18.9$ kJ/mol given by Tobolsky,[25] the sum ½ (E_d + E_{tr}) for native wool is computed to be 47.2 kJ/mol and that for reduced wool to be 23.3 kJ/mol. Since E_d would be same for both the substrates, the lower value for reduced wool is attributed to lower energy of activation in the chain transfer process (E_{tr}), in which free radicals are created on —SH groups.

Effect of Acid Concentration and Polymerization Medium. The graft copolymerization was studied within the range of 3–12.5 × 10^{-3} mol/L of HClO$_4$ concentration. The percentage of graft yield increases with increasing acid concentration (Fig. 8). Acid presumably assists the decomposition of the complex and at higher acid concentration, more number of initiating free radicals are formed.

The effect of different type of solvents on graft yield has been investigated. Of the various alcoholic solvents studied, a mixture of solvent/water at a ratio of 5:95 constitutes the most favorable medium for n-But-OH and amyl alcohol, 10:90 for EtOH and n-Pr-OH and 20:80 for MeOH. Some of the chain transfer solvents, solvents acting as solubilizers of the monomer, and organic acids at a solvent/water ratio of 5:95, follow the order of reactivity: CHCl$_3$ > CCl$_4$ > EtSH (~1%); and HCOOH > CH$_3$COOH > dioxane > acetone > DMF. Regardless of the solvent used, an increase in the amount of solvent in the reaction mixture tends to decrease graft yield.[10,19]

Determination of Average Molecular Weight. Several samples of wool were subjected to grafting under identical reaction conditions. Grafted samples were removed after regular time intervals, and soxhlet was extracted. Separation and purification of grafted polymer were carried out by (1) digesting in 5M HCl,
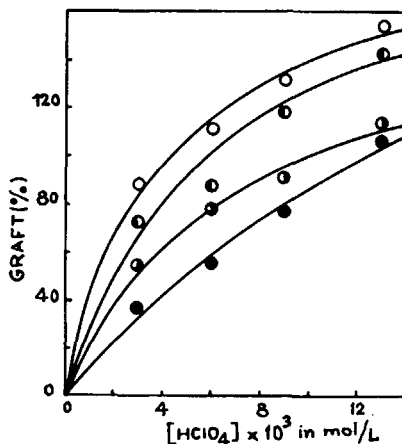
Fig. 8. Effect of [HClO₄] on graft yield: [VO(acac)₂] = 9 × 10⁻⁵ mol/L; [MMA] = 0.3756 mol/L; [EtOH] = 1.3 mol/L; M:L = 1:100; temp = 50°C. Native wool: (●) 3 h; (◐) 6 h. Reduced wool: (◑) 3 h; (○) 6 h.

(2) extracting with 0.965 mol/L diethyl ether solution in methanol, and (3) dissolving in ethyl acetate and reprecipitating by cold methanol. The average molecular weight ($\overline{M}$) of the regenerated PMMA was determined by viscometry using the relationship[26,27]

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

Study of the results suggests that, with an increase in graft percentage, $\overline{M}$ of PMMA decreases. Since the initial monomer concentration for each sample was the same, with an increase in graft percentage, the concentration of the monomer decreases at the vicinity of the base polymer as a result of which the frequency of chain transfer increases. This will evidently decrease $\overline{M}$. However, when reduced wool was graft-copolymerized by varying concentrations of the monomer, within the range 0.1878–0.5634 mol/L a linear relationship is observed between $\overline{M}$ and the initial concentration of the monomer; the plot of $1/\overline{M}$ vs. $1/[M]$ being a straight line (Fig. 9). This is expected of the observed kinetic behavior of the system.
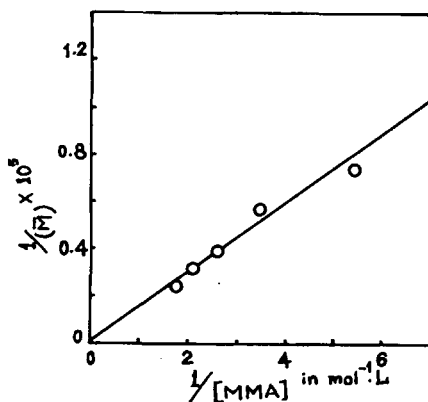

Fig. 9. Plot of $1\,\overline{M}$ vs. $1/[M]$. Substrate: reduced wool.

Alkali Solubility. The solubility test was performed following the procedure of Leaveau and co-workers.[28] It is observed that with an increase in graft yield, the alkali solubility decreases. This suggests that the PMMA chains act as diffusion barriers towards alkali penetration into wool fibers, thus protecting the polypeptide chains, salt linkages, and disulphide bonds. Similar findings have been reported by many authors.[29,30]

Spectral Study. The IR spectra of regenerated PMMA from grafted reduced wools were taken. Study of the spectra suggests that grafted PMMA chains have an atactic structure, the characteristic bands appearing at 750, 1730 and 3000 cm^{-1}. The band in the range 600–750 cm^{-1} is due to the C–S–C system and indicative of the grafting site as expected.

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