Hexavalent-Chromium-Initiated Graft Copolymerization of Methyl Methacrylate onto Cellulose

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) onto cotton–cellulose has been carried out using hexavalent chromium Cr(VI) as initiator. Aqueous-methanolic solution of perchloric acid has been chosen as the reaction medium. The effect of monomer, initiator, acid, reaction medium, and temperature on the graft percentage has been found out. The reactions have also been carried out in the presence of polymerization, inhibitors, and retarders, such as hydroquinone and transition metal salts like $CuSO_4$, $FeCl_3$, etc. The grafted samples, after exhaustive separation of homopolymers and purification, were subjected to various chemical, mechanical, and thermal testings. The results of various analyses have been compared with the reference, and the improvement in the graft has been evaluated. A suitable mechanism for the grafting processes has been suggested, in accordance with the experimental results.

INTRODUCTION

Modification of the properties of natural and synthetic macromolecules, through chemical modification, leading to attachment or binding of synthetic polymer onto the backbone of the base polymer, is a restricted case of graft copolymerization. The modification of the properties of cellulose, by chemical and macromolecular modifications to increase their usefulness, is of special interest. Celluloses with high molecular weights are the most abundant renewable agricultural raw material which is transferred into multifarious products, and are useful in clothing, housing, and industrial products, affecting every phase of our daily life. Grafting reaction onto cellulose and its derivatives began in early 1950s. There has been intense research and development activity in the field since those early days, and many hundreds of papers and patents have been published. Conscious grafting onto cellulose was first reported[1] in 1953, although relevant and some what earlier work in the USSR[2] and in England[3] certainly preceded it. This work was variously described as copolymerization actually accompanied by extensive crosslinking,[2] and as polymer deposit.[3] Both chemical and macromolecular modification of cellulose and its derivatives, involving various initiators and methods to increase their usefulness in application in films, binders, and plastics, have been reported.[4–17] Sakadura et al.[12] have carried out radiation-induced grafting of styrene, methyl methacrylate, and other vinyl monomers onto cellulose and observed various improved properties of the grafted fibers. The present report includes the graft copolymerization of methyl

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methacrylate onto cotton–cellulose, initiated by hexavalent chromium, an initiator, which produces less quantity of homopolymers, a major problem in graft copolymerization. The grafted samples after the separation of the homopolymers are subjected to chemical, mechanical, and thermal analysis, and the improvement in properties is determined. In all such analysis, a comparison is made with the reference.

EXPERIMENTAL

Cotton–cellulose fibers were purified by extraction with hot ethanol, followed by boiling with dilute sodium hydroxide solution avoiding air oxidation. Sodium hydroxide was removed by washing with distilled water, followed by souring with dilute acetic acid, neutralizing with dilute ammonia and finally with water. Methyl methacrylate was purified by washing with 5% sodium hydroxide followed by distilled water and finally dried over anhydrous calcium chloride.

Water used for the preparation of solutions was obtained by redistilling distilled water over alkaline permanganate and passing through "Biodeminrolit" (Permutit Co., U.K.) mixed-bed ion-exchange resin for removal of ion if any.

Chromic acid solution (0.1M) was prepared by dissolving chromiumtrioxide (B.D.H., analytical reagent) in water. The strength of the stock solution was determined either by cerimetry or spectrophotometry after the addition of o-phenanthroline and measuring the optical density of ferrous-o-phenanthroline complex at 510 nm with reference to a previously calibrated plot of optical density vs. Fe(II).

Nitrogen used for the deaeration of the experimental system was purified by passing, through Fieser's solution, a column of saturated lead acetate solution and finally a wash bottle containing distilled water. All other reagents were of B.D.H. quality and were used as such.

Graft copolymerization was carried out as reported earlier,[18] by two methods. In one, the cellulose fibers are immersed in the reaction mixture at the desired temperatures, and, after the system attains thermal equilibrium, the required amount of the initiator is added. In the second, the pretreated, cellulose fibers with chromic acid are then immersed in the reaction mixture containing the initiator. The grafted samples were subjected to exhaustive homopolymer extraction with acetone, dried, and finally subjected to various analyses as mentioned earlier.

RESULTS AND DISCUSSION

Hexavalent chromium itself is incapable of initiating vinyl polymerization, but when coupled with easily oxidizable organic compounds such as alcohols, aldehydes, ketones, mercaptans, etc. smoothly initiates vinyl polymerization.[19–22] Facile oxidation of alcohols and diols, via free-radical path involving the formation of intermediate chromium ester,[23] led the author to exploit the possible interaction of the hydroxyl groups of glucose units in the cellulose molecules to create free radicals on the backbone, which readily attack the vinyl monomer in the immediate vicinity to initiate chain propagation.

Effect of Monomer Concentration. The grafting reactions were studied at various concentrations of the monomer (0.04694–0.9388M), keeping the concentration of other reagents constant. The graft percentage increases, by

TABLE I
Graft Percentage at Various Concentrations of the Monomer (MMA)[a]

Time (h)	Graft percentage ([MMA])						
	$0.04694M$	$0.09388M$	$0.28164M$	$0.56328M$	$0.65716M$	$0.75104M$	$0.9388M$
1	4.51	7.61	12.22	16.15	20.56	17.12	13.19
2	9.85	13.80	16.19	19.80	31.73	22.15	17.22
4	13.67	17.67	19.89	28.98	40.62	30.13	22.59
6	14.12	20.52	26.67	35.41	48.92	35.55	29.89
8	16.19	22.12	31.92	41.61	54.78	42.61	38.86
10	18.20	29.56	38.29	49.62	60.80	48.59	42.19

[a] $[Cr(VI)] = 6.66 \times 10^{-3}M$; $[H^+] = 0.7052M$; $u = 0.8M$; temp = 50°C.
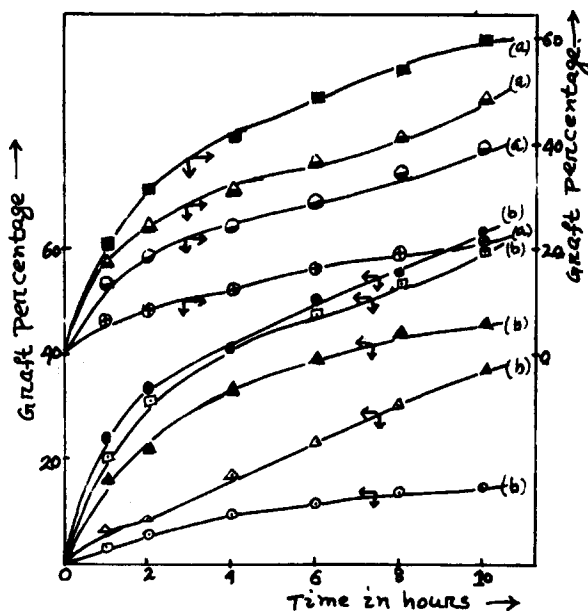
Fig. 1. (a) Variation of graft percentage with time: effect of Cr(VI) concentration. [MMA] = 0.65716M; [H$^+$] = 0.7052M; u = 0.8M; solvent = 30%; temp = 50°C. Plots: ($\oplus$) [Cr(VI)] = 2.06 $\times$ 10^{-3}M; ($\triangle$) [Cr(VI)] = 5.0 $\times$ 10^{-3}M; ($\blacksquare$) [Cr(VI)] = 6.6 $\times$ 10^{-3}M; ($\ominus$) [Cr(VI)] = 10 $\times$ 10^{-3}M. (b) Variation of graft percentage with time: effect of H$^+$ ion concentration. [Cr(VI)] = 6.66 $\times$ 10^{-3}M; [MMA] = 0.65716M; solvent = 30%; temp = 50°C. Plots: ($\odot$) [H$^+$] = 0.13M; ($\triangle$) [H$^+$] = 0.325M; ($\square$) [H$^+$] = 0.7052M; ($\bullet$) [H$^+$] = 1.905M; ($\blacktriangle$) [H$^+$] = 3.9M.
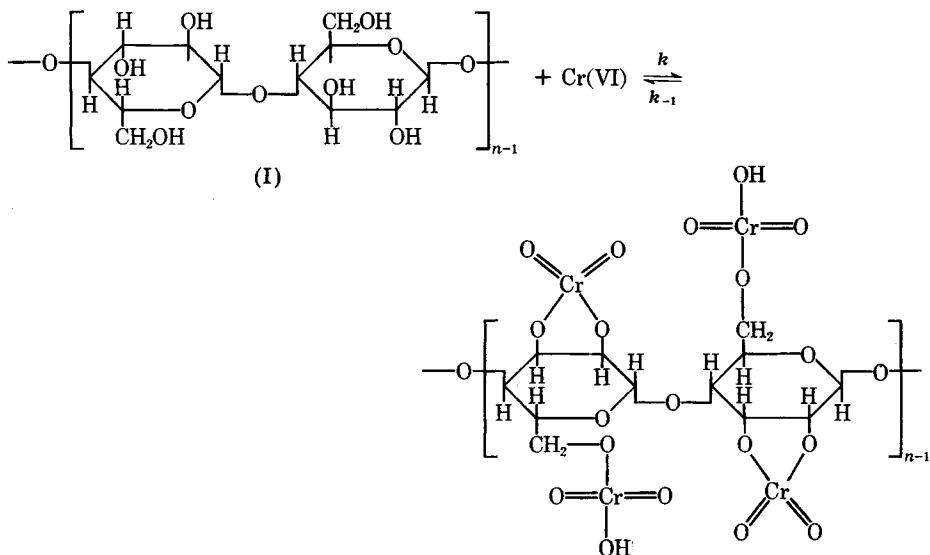
increasing the concentration of MMA from 0.04694M to 0.65716M, following which it decreases. The results are recorded in Table I. The enhancement of the graft percentage between 0.04694M and 0.65716M of the monomer might be due to (i) increase in the monomer concentration at the reaction site, (ii) swelling of the fibers, which knocks out the interior hydroxyl groups to be coordinated with Cr(VI) ion, and (iii) complexation of cellulose with MMA, which enhances the reactivity of MMA, owing to formation of a donor–acceptor complex in which the uncomplexed MMA, though initially an electron acceptor, behaves as donor, relative to the complexed MMA, which is converted to a strong acceptor. Similar explanations for enhancement in grafting with increasing monomer concentration have been suggested by Gaylord[24] and Hebeish et al.[25] The decrease in graft percentage at higher monomer concentration might be due to solubility of grafted PMMA chain in their own monomer.

Effect of Cr(VI) Concentration. Graft percentage was found to increase with increasing concentration of Cr(VI) (2.06 $\times$ 10^{-3}–6.66 $\times$ 10^{-3}M), and then to decrease [Fig. 1(a)]. The probable explanation for this behavior can be obtained by considering the following reaction mechanism, for the grafting process.
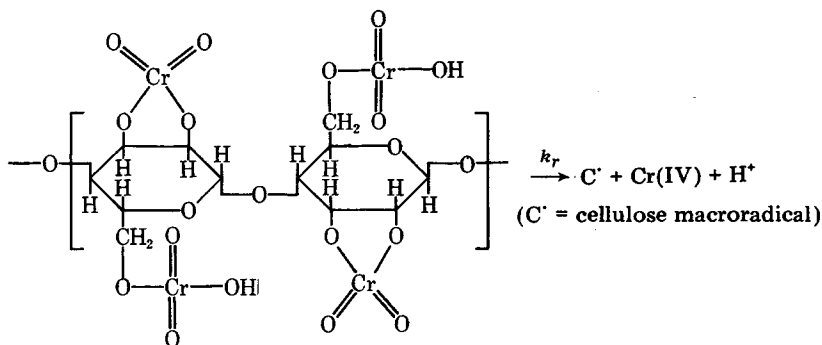
The cellulose molecule is a linear polymer containing β-glucose units linked to each other, through the 1 and 4 positions (I), where each glucose unit contains three free hydroxyl groups, one primary and two secondary. The secondary hydroxyl groups are vicinal. Chromic acid alone is found to be not effective as

initiator of vinyl polymerization.   Preliminary experiments carried out with
chromic acid and methyl methacrylate in perchloric acid medium showed no
polymerization and there was a decrease in [Cr(VI)].   Of the various possible
schemes examined, that involve the formation of intermediate chromate ester
by the interaction of Cr(VI) with hydroxyl groups to produce free radicals on
the backbone of cellulose molecules, which attack the monomer molecules at the
immediate vicinity, resulting in chain propagation and termination by Cr(VI)
ion satisfies the experimental results.   Intermediate formation of simple[23] and
cyclic esters, between the Cr(VI) ion and primary hydroxyl and glycollic systems,
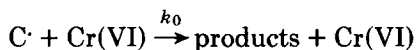has been suggested by Chang and Westheimer[26] in the oxidation of pinacols.
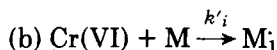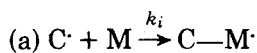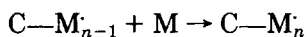
1(a).   Ester formation:

(I)

(b) Generation of Macroradical:

$$\xrightarrow{k_r} C^{\cdot} + Cr(IV) + H^+$$

($C^{\cdot}$ = cellulose macroradical)

2.   Oxidation:

$$C^{\cdot} + Cr(VI) \xrightarrow{k_0} products + Cr(VI)$$

3. Initiation:

$$\text{(a) } C^{\cdot} + M \xrightarrow{k_i} C\text{---}M^{\cdot}$$

$$\text{(b) } Cr(VI) + M \xrightarrow{k'_i} M_1^{\cdot}$$

4. Propagation:

$$\text{(a) } C\text{---}M^{\cdot} + M \xrightarrow{k_p} C\text{---}M_2^{\cdot}$$

$$C\text{---}M_{n-1}^{\cdot} + M \rightarrow C\text{---}M_n^{\cdot}$$

$$\text{(b) } M_1^{\cdot} + M \xrightarrow{k'_p} M_2^{\cdot}$$

$$M_{n-1}^{\cdot} + M \rightarrow M_n^{\cdot}$$

5. Termination:

$$\text{(a) } C\text{---}M_n^{\cdot} + Cr(VI) \xrightarrow{k_t} \text{graft copolymer}$$

$$\text{(b) } M_n^{\cdot} + Cr(VI) \xrightarrow{k'_t} \text{homopolymers}$$
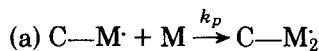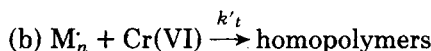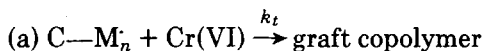
Applying the steady state condition and assuming the simple graft copolymerization, the overall rate of polymerization has been found to be
6.

$$R_p = \frac{Kk_p k_i k_r [M]^2 [C]}{k_t (k_i [M] + k_0 [Cr(VI)])}$$

Equation 6 requires that increase in Cr(VI) ion concentration increases the magnitude of the denominator, which results in decreasing value of the rate. A maximum value of the graft percentage is obtained in an optimum concentration of the Cr(VI) ion beyond which the graft percentage decreases. Similar results have been noticed by us in the case of grafting of acrylomide onto nylon 6[27] and silk fibers.[28]

Effect of Acid Concentration. Increase in the concentration of $HClO_4$ from $0.13M$ to $1.905M$, increases graft percentage, after which the rate falls [Fig. 1 (b)]. Further the graft percentage were highest in perchloric acid medium and decreased in the order $HClO_4 > HNO_3 > H_2SO_4$. The observed trend is due to, probably, change of the oxidation potential of Cr(VI) in different acids. The oxidation potential of Cr(VI) is greater in $HClO_4$ than in HNO_3 and H_2SO_4.

Effect of Temperature. The graft percentage was found to increase with increase of temperature from 35°C to 50°C and then decrease (Fig. 2). These results are in good agreement with the Arrhenius theory that increase of temperature increases the value of the activation energy, leading to high percentage graft. Beyond 50°C, the decrease in the rate might be due to (i) vaporization of the monomer and (ii) the greater rate of linear termination of the growing grafted chains by Cr(VI) ions.
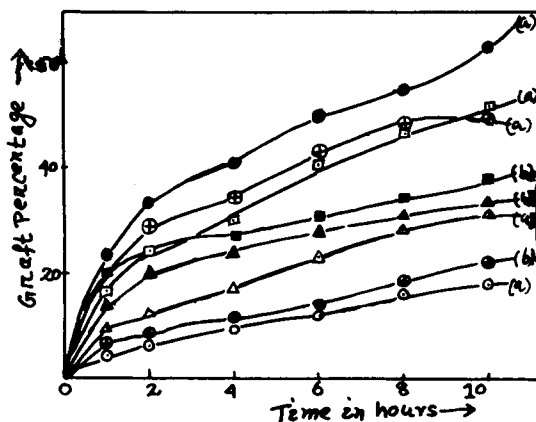
Fig. 2. (a) Variation of graft percentage with time: effect of temperature. [Cr(VI) = 6.66 × 10^{-3}M; [H$^+$] = 1.905M; [MMA] = 0.65716M; solvent = 30%. Plots: (○) temp = 35°C; (▲) temp = 40°C; (□) temp = 45°C; (●) temp = 50°C; (⊕) temp = 55°C. (b) Variation of graft percentage with time: effect of polymerization inhibitors and retarders. [Cr(VI)] = 6.66 × 10^{-3}M; [H$^+$] = 1.905M; [MMA] = 0.6576M; solvent = 30%; temp = 50°C. Plots: (●) control; (▲) [CuSO$_4$] = 0.02M; (■) [FeCl$_3$] = 0.02M; (⊕) [HQ] = 0.01M.

Effect of Reaction Medium.   Variation in solvent composition has a pronounced effect on the grafting reaction. Graft percentage increases, with increasing percentage of solvent (methanol) in the reaction medium, and a ratio of 30:70 (methanol:water) was found to constitute the most favorable medium (Fig. 3) for grafting of MMA onto cotton–cellulose. Variation of graft percentage with variation in the ratio of methanol:water could be explained by considering the following factors: (i) solubility or miscibility of the monomer, (ii) swelling of the fibers, which results in the diffusion of the monomer more toward the grafting site, (iii) formation of solvent radical and/or hydrogen or hydroxyl radicals from water under the influence of primary radical species of the initiating system, and (iv) termination of the growing grafted chains via chain transfer reactions.

The first three factors are responsible for enhancement in the graft percentage. The last factor operates at high ratio of methanol, and this also explains the depression in the rate in the cases of radical polymerization.

Effect of Polymerization Inhibitors and Retarders.   Grafting reactions were studied in the presence of free-radical terminators, such as hydroquinones and higher valency transition metal salts such as Cu(II) and Fe(III) ions. Addition of 0.02M solution of CuSO$_4$ and FeCl$_3$ and 0.01M hydroquinone leads to inhibition followed by retardation in the rate. The inhibition is more pronounced in the case of hydroquinone (Fig. 2). These observations indicate the free-radical nature of the reaction. Hydroquinone results have been attributed to its interaction with the monomer and growing polymer radicals. The reduction in the rate, in the case of CuSO$_4$ and FeCl$_3$, might be due to (i) complexation between Cu(II) and Fe(IV) ions with the free-hydroxyl groups in each glucose unit of cellulose molecule, as a result of which the intermediate chromium ester formation is greatly affected. This lowers the rate of macromolecular radical formation, the vital factor, which contributes to high graft yield, thereby retarding
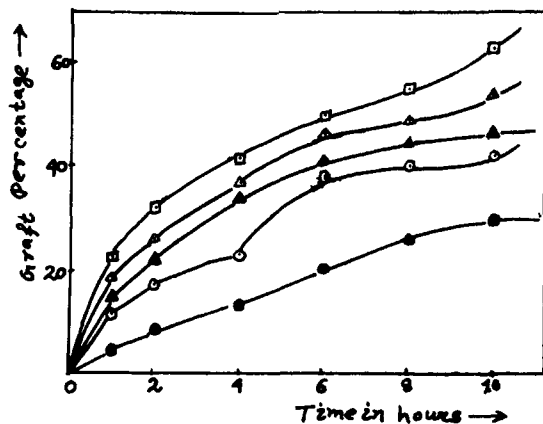
Fig. 3. Variation of graft percentage with time: effect of solvent composition: [Cr(VI)] = 6.66 × 10^{-3}M; [H$^+$] = 1.903M; [MMA] = 0.65716M; temp = 50°C. Plots: (⊙) methanol = 12%; (▲) methanol = 20%; (☐) methanol = 30%; (▲) methanol = 40%; (●) methanol = 50%.

the rate; (ii) termination of growing grafted chains by Cu(II) and Fe(III) ions. Termination of growing polymer chains in free radical polymerization by Cu(II) and Fe(III) ions is well recognized.[29,30] Apart from these, it is also clear that the retardation in graft percentage may be due to the poor oxidizing ability of Cr(VI) in the presence of Cu(II) and Fe(III) ions.

PROPERTIES OF GRAFTED FIBERS

Methyl methacrylate grafted cotton–cellulose fibers have the following properties: (i) the loss of tensile strength of the fiber is slight; (ii) thermoplasticity of the grafted sample becomes progressively pronounced, as the graft percentage increases (>45%); (iii) the absorption of water and water vapor are decreased in comparison to the base fiber and the drying rate is increased; (iv) the grafted fibers have good water repellency character; (v) the soil resistance is enhanced; (vi) degradation by bacteria is reduced; (vii) the thermal stability of the grafted fibers is remarkable. The details of such analysis will be reported in our subsequent communications.

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