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Grafting Vinyl Monomers onto Cellulose. VI. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using Potassium Permanganate as the Initiator

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A B S T R A C T

The graft copolymerization of methyl methacrylate onto cellulose using tetravalent manganese as the initiator has been studied. An increase in initiator concentration up to 1.0×10^{-2} M increases the graft yield. With a further increase, the graft yield decreases. The graft yield also increases with an increase of monomer concentration and temperature. There is an initial increase in graft yield with acid concentration up to 4.5×10^{-2} M after which the graft yield decreases. The effect of addition of solvents, CuSO_4 concentration, and redox system on the rate of grafting has been studied and a suitable kinetic scheme has been pictured.

I N T R O D U C T I O N

Graft copolymerization of vinyl monomers onto cellulosic materials has received considerable interest in recent years [1] since grafted celluloses are now finding various applications such as ion-exchange

resins, rot- and mildew-resistant materials, and soil-resistant garments. Out of various methods used for grafting, the redox systems have attracted attention in recent years [2-6]. Some of the redox systems which have been studied for the graft copolymerization of vinyl monomers onto cellulose include ceric salts [7-18], ferrous salt-hydrogen peroxide [19], sodium thiosulfate-potassium persulfate [20], sodium periodate [21], and manganic sulfate-sulfuric acid [22].

Nayak and co-workers [23-26] have reported the use of V^{5+} , Cr^{6+} , peroxydiphosphate, and acetylacetonato Mn(III) for graft copolymerization onto cellulose. This communication presents the results of graft copolymerization of methyl methacrylate onto cellulose using potassium permanganate as the initiator.

EXPERIMENTAL

Egyptian cotton slivers were purified by a mild alkaline scouring (2% Na_2CO_3 , 1.0% Na_3PO_4 , and 0.2% wetting agent on weight of the material) for 5 h at 110°C.

Methyl methacrylate was washed with 5% NaOH solution, dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Potassium permanganate (AR), H_2SO_4 (~18 M, AR, BDH), and oxalic acid (AR) were used. Water, distilled twice over alkaline permanganate and deionized by passing through a column of Bio-deminrolit resin (Permutit Co.), was used to prepare all solutions. A stock solution of permanganate (0.1 M in distilled water) was used throughout the experiment.

The reaction was carried out according to our previous methods [23].

RESULTS AND DISCUSSION

The effect of different concentrations of monomer (methyl methacrylate) on the rate of grafting was investigated at a fixed concentration of oxidant, acid, and temperature. The rate of grafting increases steadily with the increase of monomer concentration from 4.694×10^{-2} to 70.41×10^{-2} M (Fig. 1), which could be ascribed to the following reasons: (1) the cellulose molecule might complex with monomer (which is favored at high monomer concentration) as a result of which graft yield increases; (2) gel effect [27], i.e., increase in the viscosity of the medium due to the solubility of poly(methyl methacrylate) in its own monomer, which would be more pronounced at high monomer concentration. This causes hindrance in termination, particularly by coupling of growing polymer chains. The gel effect also causes swelling of cellulose, thus facilitating the diffusion of monomer to growing chains and active sites of the fiber, thereby enhancing

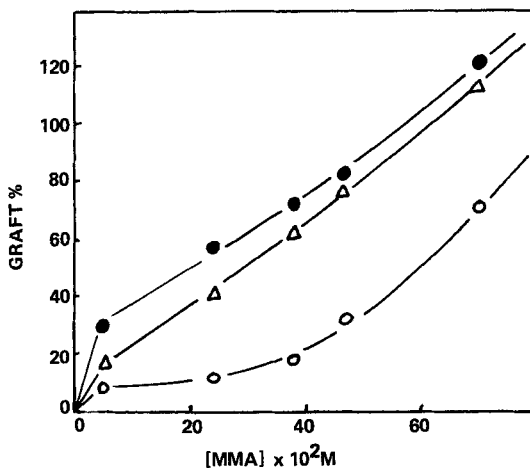


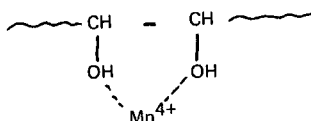
FIG. 1. Effect of $[MMA]$ on graft yield. $[H] = 7.5 \times 10^{-2} M$. Time = 4 h. (○): $[KMnO_4] = 0.5 \times 10^{-2} M$. (●): $[KMnO_4] = 1.5 \times 10^{-2} M$. (△): $[KMnO_4] = 2.5 \times 10^{-2} M$.

grafting. Similar results have been reported by Nayak and co-workers [23] in the case of grafting MMA onto cellulose using quinquevalent vanadium ion.

Effect of Initiator Concentration

Figure 2 represents the results of the effect of initiator (potassium permanganate) concentration on the rate of grafting. The grafting reaction was investigated by changing the initiator concentration from 0.5×10^{-2} to $1.5 \times 10^{-2} M$. The rate of grafting has been found to increase with the initiator concentration from 0.5×10^{-2} to $1.0 \times 10^{-2} M$ and thereafter it decreased. An explanation for this observation might be as follows.

First, Mn^{4+} might complex with 1,2-glycol units of cellulose [23], as represented below, and break in an unimolecular fashion to produce a free radical $\sim CH_2-\dot{C}H-CH-O$ on the backbone of the cellulose.



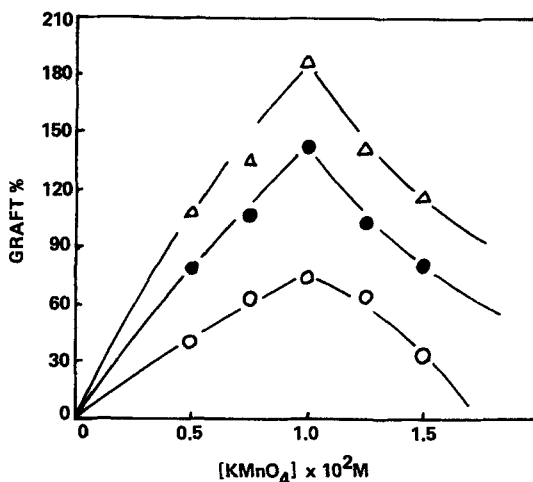
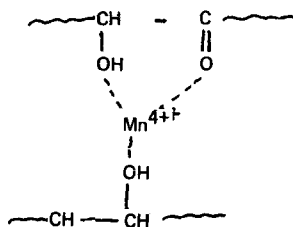


FIG. 2. Effect of $[KMnO_4]$ on graft yield. $[H] = 7.5 \times 10^{-2} M$. Time = 4 h. (○): $[MMA] = 46.94 \times 10^{-2} M$. (●): $[MMA] = 70.41 \times 10^{-2} M$. (△): $[MMA] = 93.88 \times 10^{-2} M$.

With an increase of initiator concentration, a large number of such radicals are produced, resulting in an increase in graft yield. Second, when the complex breaks, Mn^{3+} is produced which in turn might initiate polymerization. But when the concentration of permanganate increases beyond $1.0 \times 10^{-2} M$, it oxidizes the free radical to form keto alcohol, thereby reducing its population on the backbone of cellulose. Therefore the rate of grafting decreases. Further, this keto alcohol might complex with initiator with a neighboring $-OH$ group as presented below:



This phenomenon might block some of the $-OH$ groups so that the free radicals are not formed at these centers, thereby reducing grafting.

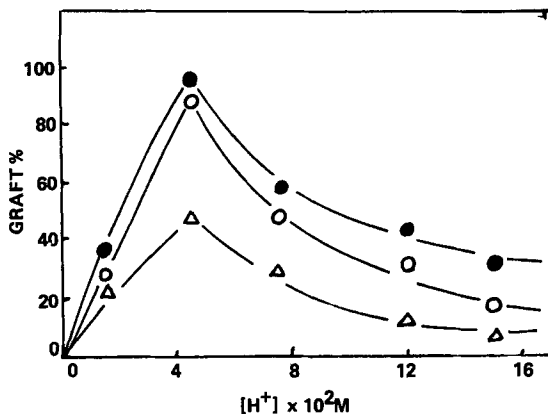
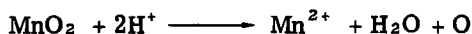


FIG. 3. Effect of $[H^+]$ on graft yield. $[MMA] = 46.94 \times 10^{-2} \text{ M}$. Time = 4 h. (○): $[KMnO_4] = 0.75 \times 10^{-2} \text{ M}$. (●): $[KMnO_4] = 1.75 \times 10^{-2} \text{ M}$. (△): $[KMnO_4] = 2.75 \times 10^{-2} \text{ M}$.

Effect of Acid Concentration

The graft copolymerization reaction has been carried out at different sulfuric acid concentrations from 1.5 to $15.5 \times 10^{-2} \text{ M}$. Initially the graft yield increases with the acid concentration up to $7.5 \times 10^{-2} \text{ M}$ and then it decreases (Fig. 3). A similar result has been reported by Pati et al. [28] in the case of graft copolymerization onto silk fibers using permanganate as the initiator.

The increase in graft yield with an increase in acid is quite evident since it catalyzes the reaction and enhances the oxidizing capacity of the initiator. But the decrease in graft yield beyond $7.5 \times 10^{-2} \text{ M}$ of acid concentration might be due to (1) the coagulation of colloidal homopolymer in solution and within fibers which increases at lower pH [29] and retards the diffusion of both monomer and initiator into the cellulose fiber for grafting to occur, (2) the production of oxygen as a result of the reaction of MnO_2 with acid, which inhibits grafting:



Effect of Temperature

The graft copolymerization reaction is greatly influenced by an increase in temperature. The graft yield steadily increases from 50 to 70°C (Fig. 4). The dependence of the rate of grafting on

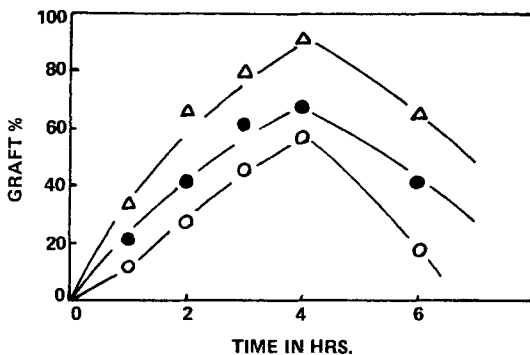


FIG. 4. Effect of temperature on graft yield. $[KMnO_4] = 1.0 \times 10^{-2}$ M. $[H] = 7.5 \times 10^{-2}$ M. $[MMA] = 46.94 \times 10^{-2}$ M. Time = 4 h. (\circ) 50°C . (\bullet) 60°C . (\triangle) 70°C .

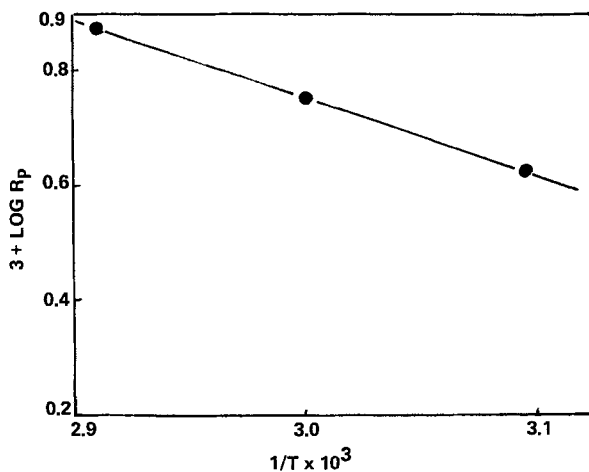


FIG. 5. Arrhenius plot.

temperature can be ascribed to the greater activation energy. Again, the swellability of cellulose, the solubility of monomer, and its diffusion rates are enhanced by increasing temperature as a result of which the graft yield increases.

From the Arrhenius plot of $\log R_p$ versus $1/T$, the overall activation energy (E_a) was found to be 6.0 kcal/mol (Fig. 5). Using the value

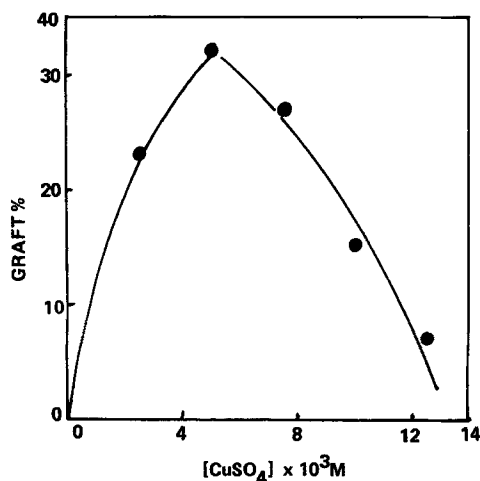


FIG. 6. Effect of $[\text{CuSO}_4]$ on graft yield. $[\text{H}^+] = 7.5 \times 10^{-2} \text{ M}$. $[\text{KMnO}_4] = 1.0 \times 10^{-2} \text{ M}$. $[\text{MMA}] = 46.94 \times 10^{-2} \text{ M}$. Time = 4 h.

of $E_p - \frac{1}{2}E_t = 4\text{--}5 \text{ kcal/mol}$ given by Tobolsky [30], the activation energy of initiation, E_d , was found to be 3.0 kcal/mol from the relationship

$$E_d = 2E_a - (2E_p - E_t)$$

where E_p and E_t are the energies of propagation and termination, respectively.

Effect of $[\text{CuSO}_4]$ on Graft Yield

Figure 6 shows the effect of the addition of different CuSO_4 concentrations on graft yield. $[\text{CuSO}_4]$ was varied from 2.5×10^{-3} to $12.5 \times 10^{-3} \text{ M}$. The result indicates that the graft yield increases up to $5.0 \times 10^{-3} \text{ M}$ and then decreases. The initial increase in graft yield might be due to the creation of a free radical species under the influence of Cu^{2+} ions, thus assisting the formation of cellulose macroradicals. The drop in graft yield beyond $5.0 \times 10^{-3} \text{ M}$ of copper sulfate concentration might be due to the fact the (1) the Cu^{2+} ions seem to act as a radical trap, resulting in the termination of free radicals in solution, on polymer and/or on cellulose; (2) a particular concentration of Cu^{2+} ions favors complexation of monomer with

cellulose, and beyond this concentration of Cu^{2+} ions, perturb such complexation.

Effect of Solvents

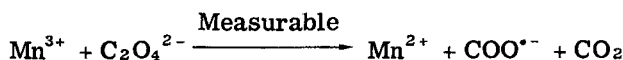
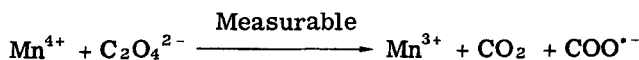
The graft copolymerization reaction was also studied in the presence of different solvents. The graft yield follows the order: dioxane > acetic acid > dimethylformamide > formic acid > methanol > chloroform > carbon tetrachloride.

The dependence of graft yield on the nature of the solvents might be due to (1) their difference in ability of swelling cellulose molecules, and (2) the difference in the capability of terminating the graft radicals as well as cellulose macroradicals via chain transfer.

Effect of Redox System

The effect of the addition of different concentrations of oxalic acid to the grafting reaction was studied at a fixed concentration of the initiator, acid, and temperature. The percentage of grafting first increases from 0.1×10^{-2} to 0.25×10^{-2} M of oxalic acid and thereafter it decreases (Fig. 7). The reasons for this behavior would be as follows.

At a lower oxalic acid concentration, it might react with Mn^{4+} in the following manner [29, 31] to produce carboxyl ion radicals ($\text{COO}^{\cdot-}$) which initiate grafting:



At higher oxalic acid concentrations, a large number of these radicals might form and interact with monomer to produce homopolymer, thereby reducing grafting.

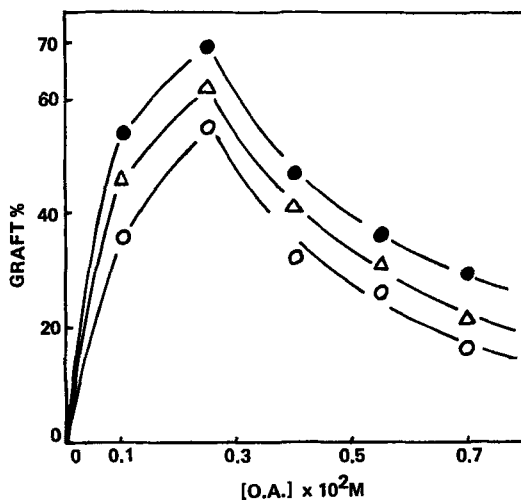
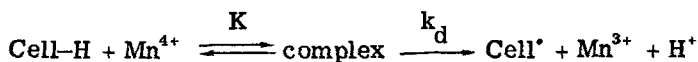


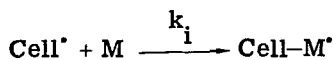
FIG. 7. Effect of [oxalic acid] on graft yield. $[H^+] = 7.5 \times 10^{-2}$ M. $[MMA] = 46.94 \times 10^{-2}$ M. Time = 4 h. (○): $[KMnO_4] = 0.5 \times 10^{-2}$ M. (●): $[KMnO_4] = 1.0 \times 10^{-2}$ M. (△): $[KMnO_4] = 1.5 \times 10^{-2}$ M.

MECHANISM

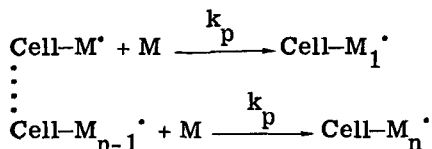
In a system consisting of permanganate, acid, and cellulose, Mn^{4+} might complex with cellulose which breaks down, giving rise to the cellulose macroradicals. These cellulose macroradicals ($Cell^{\cdot}$) propagate to give the grafted polymer.



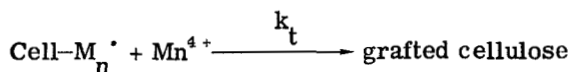
Initiation:



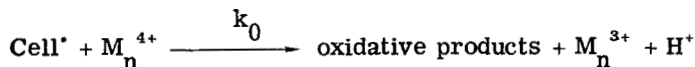
Propagation:



Termination:



Oxidation:



where Cell-H denotes a reactive group in cellulose, and M is monomer.

By applying steady-state conditions to $[\text{Cell}^*]$ and $[\text{Cell-M}^*]$, the overall rate of polymerization can be derived as follows:

$$\frac{d[\text{Cell}^*]}{dt} = Kk_d[\text{Mn}^{4+}][\text{Cell}] - k_i[\text{Cell}^*][\text{M}]$$

$$-k_0[\text{Cell}^*][\text{Mn}^{4+}] = 0$$

$$[\text{Cell}^*] = \frac{Kk_d[\text{Mn}^{4+}][\text{Cell}]}{k_i[\text{M}] + k_0[\text{Mn}^{4+}]}$$

Again

$$\frac{d[\text{Cell-M}^*]}{dt} = k_i[\text{Cell}^*][\text{M}] - k_t[\text{Cell-M}^*][\text{Mn}^{4+}] = 0$$

$$[\text{Cell-M}^*] = \frac{k_i[\text{Cell}^*][\text{M}]}{k_t[\text{Mn}^{4+}]}$$

Substituting the value of $[\text{Cell}^*]$ in the above expression we get,

$$[\text{Cell-M}^*] = \frac{Kk_d[\text{Cell-H}][\text{M}]}{k_t \left\{ [\text{M}] + \frac{k_0}{k_i}[\text{Mn}^{4+}] \right\}}$$

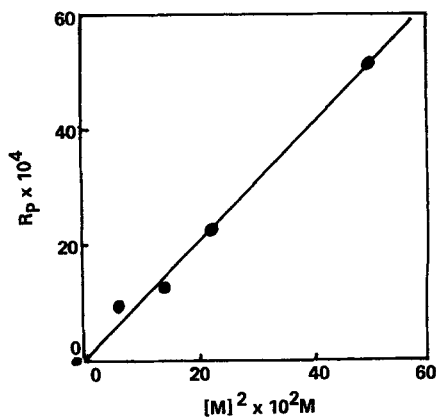


FIG. 8. Plot of R_p vs $[M]^2$.

$$\begin{aligned} \text{Hence } R_p &= k_p [\text{Cell-M}'] [M'] \\ &= \frac{k_p}{k_t} [M]^2 \left\{ \frac{Kk_d [\text{Cell-H}]}{[M] + \frac{k_0}{k_i} [\text{Mn}^{4+}]} \right\} \end{aligned}$$

Thus the plot of R_p (rate of polymerization) versus $[M]^2$ (Fig. 8) is linear, passing through the origin, which favors the above reaction scheme.

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