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Grafting Vinyl Monomers onto Cellulose. IX. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using Peroxydiphosphate-Fe(II) and Mn(II) Redox Systems

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ABSTRACT

The application of peroxydiphosphate coupled with bivalent metal ions like Fe(II) and Mn(II) to induce graft copolymerization of methyl methacrylate onto cellulose fibers by varying the concentrations of monomer, initiator, acid, reducing agent, solvents, and temperature has been studied. The rate of grafting increases progressively with increasing monomer and reducing agent concentrations. The rate of grafting also increases with peroxydiphosphate concentration up to 10.0×10^{-3} $\underline{M}$ and with sulfuric acid concentration up to 9.0×10^{-2} $\underline{M}$ after which it decreases. The effects of addition of some solvents and temperature on graft yield were also studied. The effect of modified cellulose on the rate of grafting was also studied. Both systems have been investigated under identical conditions. A larger percentage of grafting was observed in the case of Mn(II) than of Fe(II). A suitable kinetic scheme has been developed, and rate equations have been derived.

INTRODUCTION

In recent years graft copolymerization onto synthetic as well as natural fibers using peroxydiphosphate ion as the initiator has received much attention since very little homopolymers and high grafting efficiency are obtained in this method. Though successful graft copolymerization onto cellulosic materials has occurred using a large number of metal ions, nonmetal ions, and redox systems [1-23], there are few studies involving peroxydiphosphate as the initiator. Nayak and co-workers have reported graft copolymerization onto wool, silk, and nylon [24-29] using peroxydiphosphate ion alone or coupled with some other metal ions as the initiator.

This article presents the results of graft copolymerization of methyl methacrylate onto cellulose using peroxydiphosphate-Fe(II) and peroxydiphosphate-Mn(II) redox systems as initiators.

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 weight of material) for 5 h at 110°C and 10-15 psi in a laboratory kier with a liquor ratio of 10. Potassium peroxydiphosphate (a gift sample from FMC Corp., U.S.A.), H_2SO_4 (AR, ~ 18 M), ferrous ammonium sulfate (AR, BDH), and manganese sulfate (AR, BDH) were used.

The modified cellulose was prepared using a standard procedure [34], and reaction was carried out according to our previous method [23]. The percentage of moisture regain (M.R.) was determined by using

$$\% \text{ of M.R.} = \frac{\text{difference in weight}}{\text{weight of the dry sample}} \times 100$$

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of variation of methyl methacrylate concentration on the rate of grafting was studied at a fixed concentration of all other reagents. From Fig. 1 (a and b) it is evident that there is progressive enhancement in the percentage of grafting with increasing monomer concentration from 9.38×10^{-2} to 70.41×10^{-2} M in the case of both systems. This might be due to: 1) gel effect, [30], i.e., the solubility of PMMA in its own monomer. Owing to

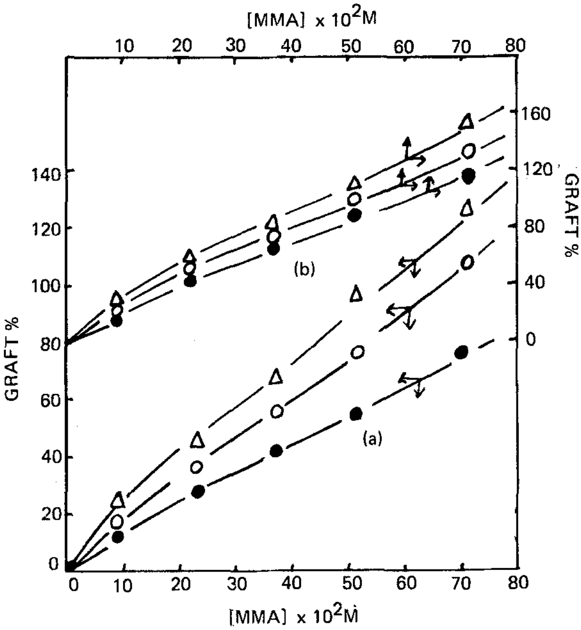

FIG. 1. Effect of [MMA] on graft yield. [H_2SO_4] = 4.5 × 10^{-2} M, time = 6 h, temperature = 50°C, M:L = 1:100. (a) [Fe(II)] = 5.0 × 10^{-3} M: (●) [PP] = 2.5 × 10^{-3} M, (○) [PP] = 5.0 × 10^{-3} M, (△) [PP] = 7.5 × 10^{-3} M. (b) [Mn(II)] = 5.0 × 10^{-3} M: (●) [PP] = 2.5 × 10^{-3} M, (○) [PP] = 5.0 × 10^{-3} M, (△) [PP] = 7.5 × 10^{-3} M.

this gel effect the medium becomes viscose, and hence the termination of the growing polymer chains by coupling is hindered. The gel effect also causes swelling of cellulose, thus facilitating the diffusion of monomer to growing chains and active sites on the backbone, thereby enhancing grafting. 2) The monomer molecule might form some type of charge transfer complex with cellulose, thus favoring grafting.

Effect of Initiator Concentration

The concentration of peroxydiphosphate was varied from 2.5 × 10^{-3} to 12.5 × 10^{-3} M for both systems at a fixed concentration of all other reagents. The graft yield increases with increasing concentration of peroxydiphosphate up to 10.0 × 10^{-3} M and thereafter it decreases (Fig. 2a and b). A plausible explanation to the above observation might be as follows.

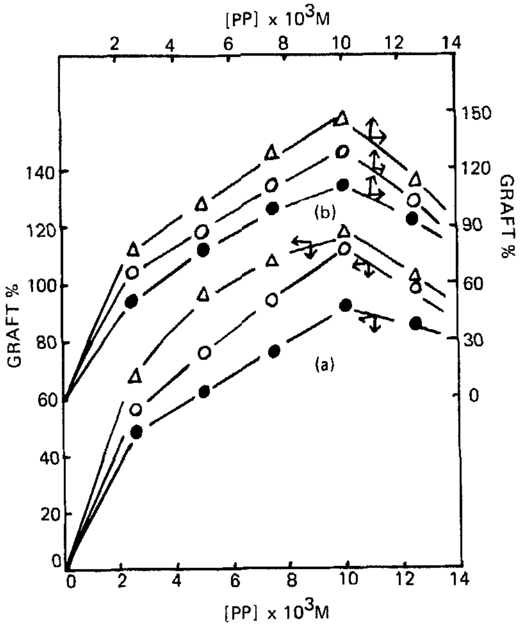

FIG. 2. Effect of [PP] on graft yield. [H_2SO_4] = 7.5 × 10^{-2} M, time = 6 h, temperature = 50°C, M:L = 1:100. (a) [Fe(II)] = 5.0 × 10^{-3} M: (●) [MMA] = 23.47 × 10^{-2} M, (○) [MMA] = 46.94 × 10^{-2} M, (△) [MMA] = 70.41 × 10^{-2} M. (b) [Mn(II)] = 5.0 × 10^{-3} M: (●) [MMA] = 23.47 × 10^{-2} M, (○) [MMA] = 46.94 × 10^{-2} M, (△) [MMA] = 70.41 × 10^{-2} M.

In a system consisting of peroxydiphosphate ion, monomer, acid, and a bivalent metal ion like Fe(II) or Mn(II), the production of free radicals takes place according to the following mechanism:

$$P_2O_8^{4-} + \text{Me(II)} \xrightarrow{k_d} HPO_4^{\bullet -} + HPO_4^{2-} + \text{Me(III)} \tag{1}$$

$$HPO_4^{\bullet -} + \text{Me(II)} \xrightarrow{k_a} HPO_4^{2-} + \text{Me(III)} \tag{2}$$

$$HPO_4^{\bullet -} + H_2O \xrightarrow{k_b} H_2PO_4^{-} + {}^{\bullet}OH \tag{3}$$

where Me(II) = Fe(II) or Mn(II)

The above free radicals ($HPO_4^{\cdot -}$ or $^{\cdot}OH = R^{\cdot}$) might interact with the groups present in the cellulose backbone to produce cellulose macroradicals. Thus, at the initial stage there is an abundance of such free radicals which interact with cellulose, giving rise to free radicals at several sites which initiate grafting. But beyond 10.0×10^{-3} M there is a marked fall in the graft yield, the reasons being: 1) with an increase of initiator concentration there will be large numbers of free radicals which might terminate the grafted chain, 2) at higher concentrations of initiator there is a possibility of formation of homopolymer, and 3) at higher concentrations of peroxydiphosphate the following reaction might take place [34]:

$$HPO_4^{\cdot -} + {}^{\cdot}OH \longrightarrow H_2PO_4^{-} + \tfrac{1}{2}O_2$$

$$H_2PO_4^{\cdot} + {}^{\cdot}OH \longrightarrow H_3PO_4 + \tfrac{1}{2}O_2$$

The formation of oxygen might affect the growth of the chain, and hence the percentage of grafting decreases.

Mechanism

Initiation:

$$\sim\!\sim \text{Cell–OH} + R^{\cdot} \xrightarrow{k_i} \sim\!\sim \text{Cell–O}^{\cdot}$$

$$\sim\!\sim \text{Cell–O}^{\cdot} + M \xrightarrow{k_i'} \sim\!\sim \text{Cell–OM}^{\cdot}$$

Propagation:

$$\sim\!\sim \text{Cell–OM}^{\cdot} + M \xrightarrow{k_p} \sim\!\sim \text{Cell–OM}_1^{\cdot}$$

$$\vdots$$

$$\sim\!\sim \text{Cell–OM}^{\cdot}_{n-1} + M \xrightarrow{k_p} \sim\!\sim \text{Cell–OM}_n^{\cdot}$$

Termination:

$$\sim\!\sim \text{Cell–OM}_n^{\cdot} + \sim\!\sim \text{Cell–OM}_m^{\cdot} \xrightarrow{k_t} \text{polymer}$$

Considering the first equation of free radical formation and applying steady-state assumptions to the growing radicals, we have,

$$\frac{-d[R^{\cdot}]}{dt} = k_d[P_2O_8^{4-}][\text{Me(II)}] - k_i[R^{\cdot}][\text{Cell-OH}] = 0$$

Therefore,

$$[\mathrm{R}^\bullet] = \frac{k_d[\mathrm{P_2O_8}^{4-}][\mathrm{Me(II)}]}{k_i[\mathrm{Cell{-}OH}]}$$

$$\frac{-[\mathrm{Cell{-}OM_n}^\bullet]}{dt} = k_i'[\mathrm{M}][\mathrm{Cell{-}O}^\bullet] - k_t[\mathrm{Cell{-}OM_n}^\bullet]^2 = 0$$

Therefore,

$$[\mathrm{Cell{-}OM_n}^\bullet] = \left(\frac{k_i'}{k_t}\right)^{1/2} [\mathrm{M}]^{1/2}[\mathrm{Cell{-}O}^\bullet]^{1/2}$$

$$\frac{-d[\mathrm{Cell{-}O}^\bullet]}{dt} = k_i[\mathrm{Cell{-}OH}][\mathrm{R}^\bullet] - k_i'[\mathrm{Cell{-}O}^\bullet][\mathrm{M}] = 0$$

Therefore,

$$[\mathrm{Cell{-}O}^\bullet] = \frac{k_i[\mathrm{Cell{-}OH}][\mathrm{R}^\bullet]}{k_i'[\mathrm{M}]}$$

$$= \frac{k_d[\mathrm{P_2O_8}^{4-}][\mathrm{Me(II)}]}{k_i'[\mathrm{M}]}$$

Therefore,

$$[\mathrm{Cell{-}OM_n}^\bullet] = \left(\frac{k_d[\mathrm{P_2O_8}^{4-}][\mathrm{Me(II)}]}{k_t}\right)^{1/2}$$

$$R_p = k_p[\mathrm{Cell{-}OM_n}^\bullet][\mathrm{M}]$$

$$= k_p(k_d/k_t)^{1/2}[\mathrm{P_2O_8}^{4-}]^{1/2}[\mathrm{Me(II)}]^{1/2}[\mathrm{M}]$$

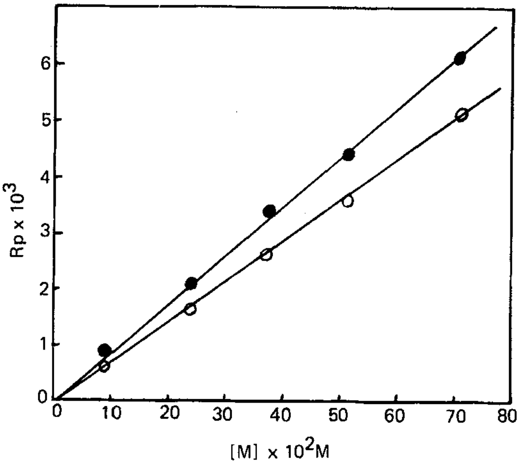

FIG. 3. Plot of R_p versus [M]: (●) for PP-Mn(II), (○) for PP-Fe(II).

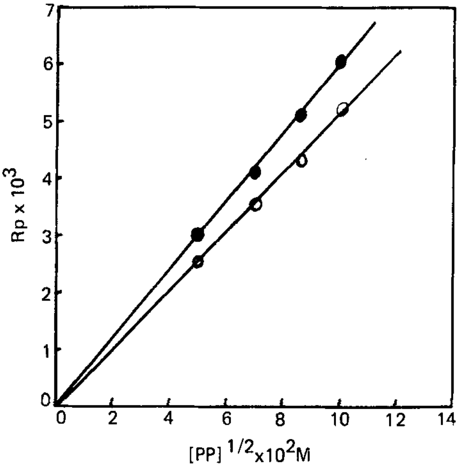

FIG. 4. Plot of R_p versus $[P_2O_8^{4-}]^{1/2}$. (●) for PP-Mn(II), (○) for PP-Fe(II).

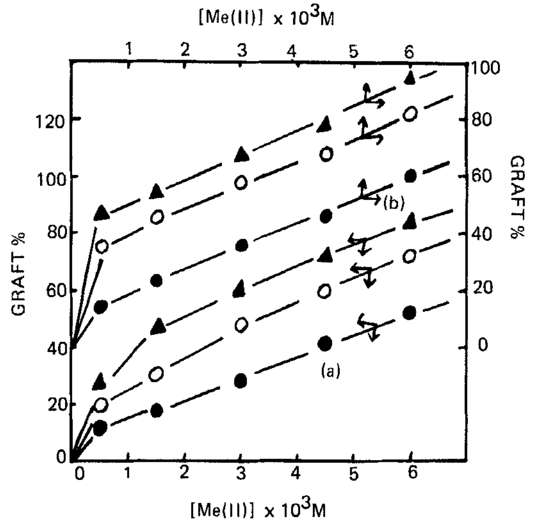

FIG. 5. Effect of [reducing agent] on graft yield. [PP] = 7.5 × 10^{-3} M, [H_2SO_4] = 6.0 × 10^{-2} M, time = 6 h, temperature = 50° C, M:L = 1:100. (a) For Fe(II): (●) [MMA] = 23.47 × 10^{-2} M, (○) [MMA] = 46.94 × 10^{-2} M, (▲) [MMA] = 70.41 × 10^{-2} M. (b) For Mn(II). (●) [MMA] = 23.47 × 10^{-2} M, (○) [MMA] = 46.94 × 10^{-2} M. (▲) [MMA] = 70.41 × 10^{-2} M.

Thus plots of R_p versus [M] (Fig. 3) and $[P_2O_8{}^{4-}]^{1/2}$ (Fig. 4) are linear, passing through the origin and thus indicating the validity of the above reaction scheme.

Effect of the Reducing Agent

The effect of the addition of the reducing agent on the graft copolymerization reaction was studied by varying the concentrations of Fe(II) and Mn(II) from 0.5 × 10^{-3} to 6.0 × 10^{-3} M (Fig. 5a and b). The result indicates that the graft yield sharply increases with increasing concentration of the reducing agent, facilitating the formation of peroxydiphosphate ion radicals and thus enhancing grafting. From the results obtained by using the two metal ions, it was observed that Mn(II) has a higher grafting order than Fe(II).

Effect of Sulfuric Acid

Since peroxydiphosphate ion is catalyzed by acid, it is necessary to study the effect of acid concentration on graft yield. The acid

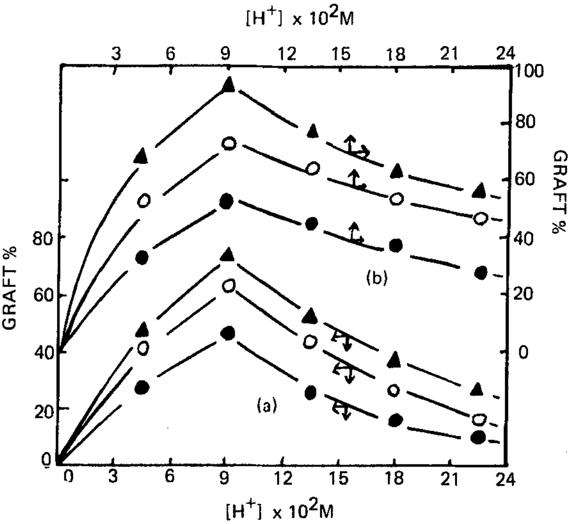

FIG. 6. Effect of [H_2SO_4] on graft yield. [PP] = 5.0 × 10^{-3} M, M:L = 1:100, time = 6 h, temperature = 50° C. (a) [Fe(II)] = 2.5 × 10^{-3} M: (●) [MMA] = 28.16 × 10^{-2} M, (○) [MMA] = 56.32 × 10^{-2} M, (▲) [MMA] = 84.49 × 10^{-2} M. (b) [Mn(II)] = 2.5 × 10^{-3} M: (●) [MMA] = 28.16 × 10^{-2} M, (○) [MMA] = 56.32 × 10^{-2} M, (▲) [MMA] = 84.49 × 10^{-2} M.

concentration was varied from 4.5 × 10^{-2} M to 22.5 × 10^{-2} M. The graft yield was found to increase with sulfuric acid concentration up to 9.0 × 10^{-2} M, after which it decreases with further increase of acid concentration in both systems (Fig. 6a and b).

It is a known fact that the oxyanion reactions are acid catalyzed. Similarly, the reactions of peroxides are also subjected to acid catalysis. Hence the reactions of peroxydiphosphate, which is both a peroxide and an oxyanion, i.e., the oxyanion derivative of H–O–O–H, are also acid catalyzed. Peroxydiphosphate is protonated due to its high negative charge, giving rise to various species like $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^-$, $H_4P_2O_8$, $H_5P_2O_8^+$, and $H_6P_2O_8^{2+}$. Santappa and co-workers [33] have reported that the reaction rate as well as the concentration of $H_3P_2O_8^-$ and $H_4P_2O_8$ increases with increasing acid concentration. In the concentration range 4.5 × 10^{-2} to 9.0 × 10^{-2} M, the most active species, $H_3P_2O_8^-$, might be formed. It interacts with various other species, giving rise to a large number of free radicals and thus enhancing the graft yield.

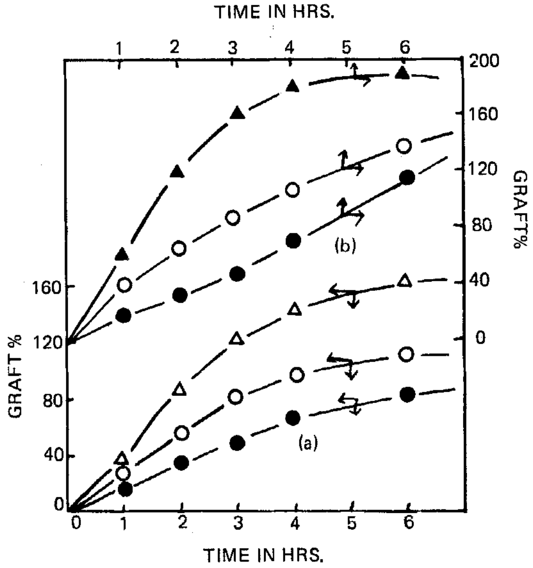

FIG. 7. Effect of temperature on graft yield. [PP] = 10.0×10^{-3} M, [H_2SO_4] = 7.5×10^{-2} M, [MMA] = 46.94×10^{-2} M, M:L = 1:100. (a) [Fe(II)] = 5.0×10^{-3} M: (●) 40°C, (○) 50°C, (▲) 60°C. (b) [Mn(II)] = 5.0×10^{-3} M: (●) 40°C, (○) 50°C, (▲) 60°C.

Effect of Temperature

It is evident from Fig. 7 (a and b) that the graft yield increases steadily with an increase of temperature from 40 to 60°C in both initiating systems. This might be due to the increase in activation energy. Again, with increasing temperature the rate of diffusion of monomer and initiator into the active sites and growing chains of the cellulose matrix increases, thus enhancing the rate of grafting. From the Arrhenius plot of log R_p versus 1/T (Fig. 8), the overall activation energy (E_a) was computed to be 15.0 and 11.0 kcal/mol for the peroxydiphosphate-Mn(II) system and the peroxydiphosphate-Fe(II) system, respectively. Using the value $E_p - \frac{1}{2}E_t$ = 4-5 kcal/mol obtained by Tobolsky [31], where E_p and E_t are the energy of propagation and termination, respectively, the energy of initiation E_d was calculated using

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

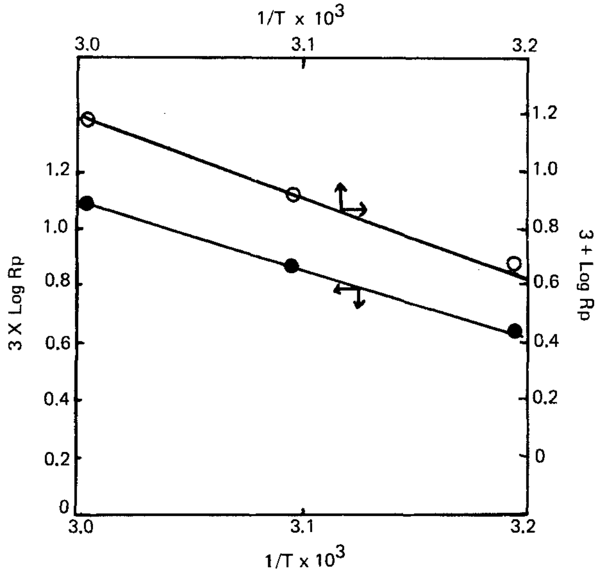

FIG. 8. Arrhenius plot: (●) for PP-Fe(II) redox system, (○) for PP-Mn(II) redox system.

where E_d = 21.0 kcal/mol for the PP-Mn(II) system and 13.0 kcal/mol for the PP-Fe(II) system.

Effect of Solvents

The graft copolymerization of MMA onto cellulose was studied in the presence of different water-miscible solvents. From the graft yield obtained, the order of different solvents is (Fig. 9a and b): Methanol > acetic acid > dimethylformamide > acetone for both initiating systems.

The variation of the graft yield with the solvents might be due to the variation in: 1) the swelling ability of the fiber, 2) miscibility with monomer, 3) formation of the solvent radicals from the primary radical species by chain transfer, 4) participation of the solvent radical in the activation of cellulose, and 5) termination of the graft radical by combination with the solvent radical. The first four factors favor grafting by simplifying access and diffusion of monomer, while the last factor adversely affects grafting by lowering of the molecular size of the graft.

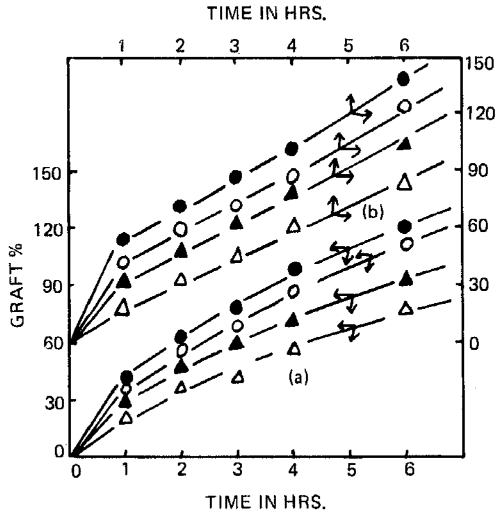

FIG. 9. Effect of solvents on graft yield. [PP] = 10.0 × 10^{-3} M, [H_2SO_4] = 7.5 × 10^{-2} M, [MMA] = 46.94 × 10^{-2} M, solvent = 10% v/v, M:L = 1:100, temperature = 50° C. (a) [Fe(II)] = 5.0 × 10^{-3} M: (○) acetic acid, (●) methanol, (▲) dimethylformamide, (△) acetone. (b) [Mn(II)] = 5.0 × 10^{-3} M: (●) methanol, (○) acetic acid, (▲) dimethylformamide, (△) acetone.

Nature of Substrate

The cellulose was subjected to different modifications prior to grafting. The percentage graft follows the sequence (Fig. 10a and b) unmodified > NaOH–Cell > $ZnCl_2$–Cell > cyanoethylated Cell > cross-linked Cell.

When cellulose is treated with sodium hydroxide, the sodium salt of the cellulose (sodium cellulosate) is formed. Hence the hydroxyl group is blocked and it would be difficult to create free radicals on the cellulose backbone, thereby decreasing the extent of grafting. When cellulose is treated with zinc chloride, a chelate type of complex with the hydroxyl group of the cellulose molecule forms. The availability of the free hydroxyl group is considerably reduced by the interaction of the PP free radicals to create grafting site on the cellulose backbone and hence the graft yield decreases. Etherification and other studies have shown that the C_2 group is etherified twice as fast as C_3 group. Sonnerskog [32] reported the preferential reactivity of C_2 of the anhydroglucose unit of cellulose. Hence cyanoethylation occurs most probably through the C_2–OH groups. The presence of such groups at the C_2 position will certainly decrease the extent of

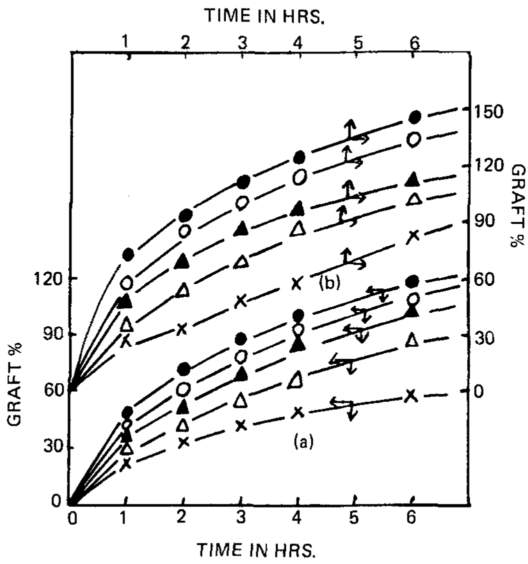

FIG. 10. Effect of nature of substrate on graft yield. [PP] = 10.0×10^{-3} M, [H_2SO_4] = 7.5×10^{-2} M, [MMA] = 46.94×10^{-2} M, M:L = 1:100; temperature = 50°C. (a) [Fe(II)] = 5.0×10^{-3} M: (●) unmodified cellulose, (○) NaOH treated cellulose, (▲) $ZnCl_2$ treated cellulose, (△) cyanoethylated cellulose, (×) cross-linked cellulose. (b) [Mn(II)] = 5.0×10^{-3} M: (●) unmodified cellulose, (○) NaOH treated cellulose, (▲) $ZnCl_2$ treated cellulose, (△) cyanoethylated cellulose, (×) cross-linked cellulose.

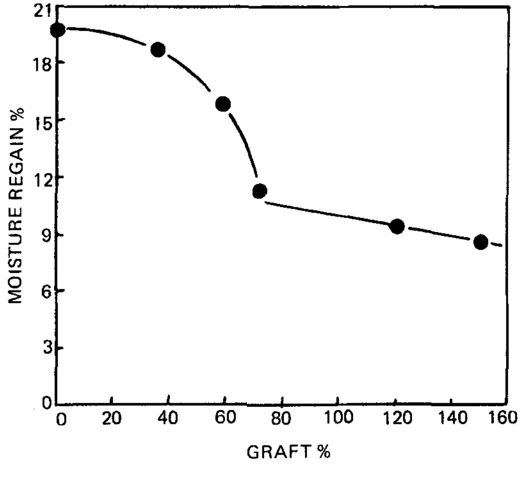

FIG. 11. Plot of moisture regain percentage versus graft percentage.

formation of free radical on the cellulose backbone, thereby inhibiting graft yield. Cross-linking cellulose by formaldehyde decreases the extent of grafting compared to the control. This is expected since the cross-linking reaction takes place in highly disordered regions. Besides blocking some of the cellulose hydroxyls, the cross-links result in a measurable reduction in fiber swellability, probably by restricting mobility of the cellulose molecule during grafting. Thus low swellability of the cross-linked cellulose could impede diffusion of monomer and initiator, therby adversely affecting the grafting reaction.

The moisture regain percentage decreases with an increase in graft percentage (Fig. 11) for both initiating systems.

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