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Grafting Vinyl Monomers onto Nylon 6. VIM. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using Peroxydiphosphate-Fe(II) and Mn(II) Redox Systems

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Grafting Vinyl Monomers onto Nylon 6. VIII. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using Peroxydiphosphate-Fe(II) and Mn(II) Redox Systems

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ABSTRACT

The graft copolymerization of methyl methacrylate onto nylon 6 initiated by peroxydiphosphate coupled with bivalent metals like Fe(II) and Mn(II) is studied. The rate of grafting increases progressively with increasing the peroxydiphosphate, monomer, and acid concentrations. The graft yield also increases with increasing the concentrations of Fe(II) and Mn(II) from 5.0×10^{-4} to 60×10^{-4} M. The effect of the addition of some solvents and temperature on graft yield is also studied. Both systems were investigated at identical conditions. A larger percentage of grafting is observed for Mn(II) than for Fe(II). A suitable kinetic scheme is developed and rate equations are derived.

INTRODUCTION

Literature abounds with examples of the successful formation of graft copolymers of some natural as well as synthetic fibers [1-6],

but graft copolymerization onto nylon has not been studied in detail. Varma et al. [7-9] and Nayak et al. [10-15] reported the use of Fe^{3+} , Mn^{3+} , Ce^{4+} , and V^{5+} ions alone or coupled with thiourea as initiators for graft copolymerization onto nylon 6, but very little work has been reported using peroxydiphosphate as initiator for graft copolymerization [16-21].

Earlier we reported graft copolymerization onto wool and silk fibers using a number of metal and nonmetal ions [15-21]. This paper presents the results of graft copolymerization of methyl methacrylate onto nylon 6 using peroxydiphosphate- $\text{Fe}(\text{II})$ and peroxydiphosphate- $\text{Mn}(\text{II})$ redox systems as initiators.

EXPERIMENTAL

Nylon 6 was supplied by J. K. Synthetics Kota, Rajasthan, India, as a gift sample. It was swollen in 2% phenol solution for 48 h and then washed with water and dried in air before use. Potassium peroxydiphosphate (a gift sample from FMC Corporation, U.S.A.), H_2SO_4 (A.R. ~ 18 M), manganese chloride (A.R., BDH), and ferrous ammonium sulfate, (A.R., BDH) were used. The grafting reaction was carried out according to our previous communication [12]. The molecular weight of the grafted polymer was determined using the equation

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

The moisture regain percentage was calculated according to

$$\% \text{ of moisture regain} = \frac{\text{difference in wt}}{\text{wt of the dry sample}} \times 100$$

DISCUSSION

There is a progressive enhancement in the percentage of grafting with increasing monomer concentration from 9.38 to 70.41×10^{-2} M (Fig. 1) in the case of both systems. This might be due to the following factors: 1) The gel effect [22], i.e., the solubility of PMMA in its own monomer. Owing to 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 nylon, thus assisting the diffusion of monomer to the growing grafted chains and active sites on the nylon backbone, thereby enhancing grafting, 2) The monomer molecules might form some type of charge transfer complex

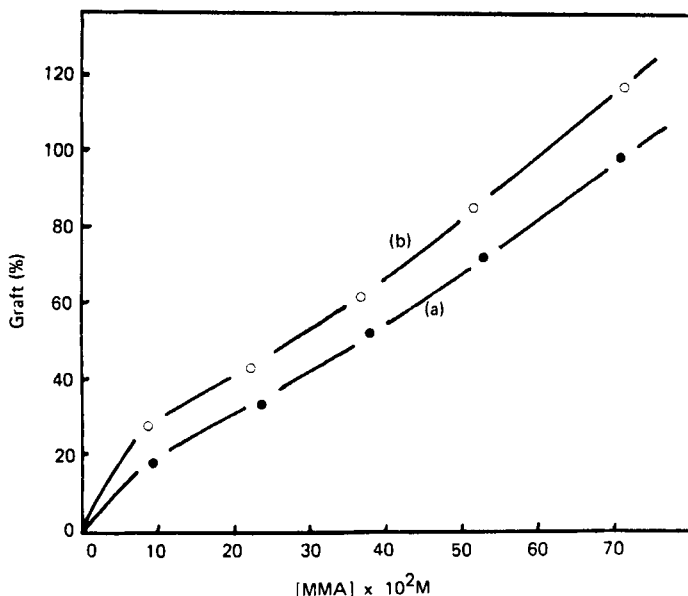


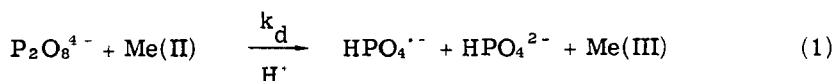
FIG. 1. Effect of [MMA] on graft yield. (a) [PP] = 5.0×10^{-3} M, [Fe(II)] = 5.0×10^{-3} M, [H₂SO₄] = 9.0×10^{-2} M, 6 h, 50°C, M:L = 1:100. (b) [PP] = 5.0×10^{-3} M, [Mn(II)] = 5.0×10^{-3} M, [H₂SO₄] = 9.0×10^{-2} M, 6 h, 50°C, M:L = 1:100.

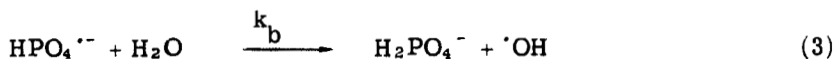
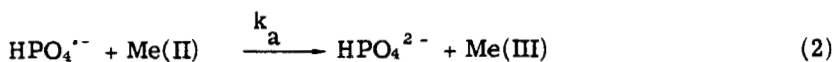
[14] with the nylon which is only favored at high monomer concentrations. This complexation of monomer with nylon enhances the reactivity of the former, as a result of which the graft yield increases.

Effect of Initiator Concentration

Figure 2 depicts the results of initiator concentration on the graft copolymerization reaction. The concentration of peroxydiphosphate was varied from 2.5×10^{-3} to 12.5×10^{-3} M for both systems at fixed concentrations of all other reagents. It is evident from the results that the percentage of grafting increases steadily with the increase of peroxydiphosphate concentration. A probable explanation to the above observations might be the following.

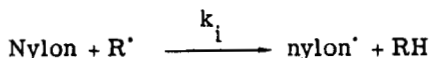
In a system consisting of peroxydiphosphate ion, monomer, acid, and a bivalent metal ion like Fe(II) or Mn(II), the free radicals are formed in the following manner:





where $\text{Me(II)} = \text{Fe(II)}$ or Mn(II) .

The free radicals ($\text{HPO}_4^{\cdot-}$ or $\cdot\text{OH} = \text{R}'$) might interact with the nylon matrix to produce nylon macroradicals which propagate at a faster rate, resulting in grafting:



Initiation:

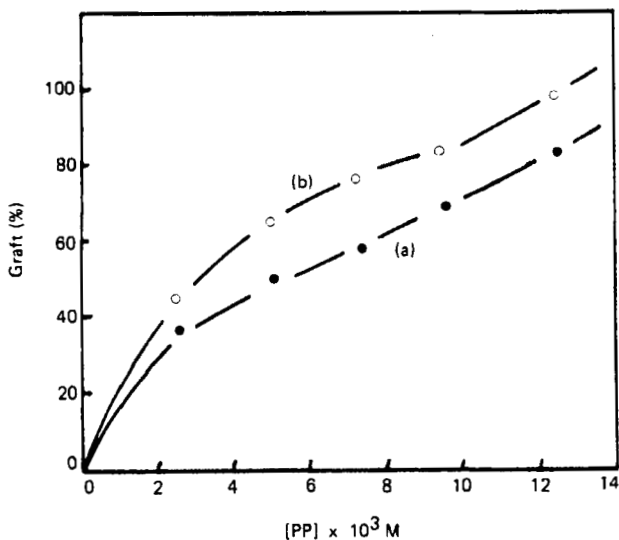
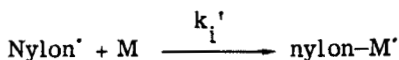
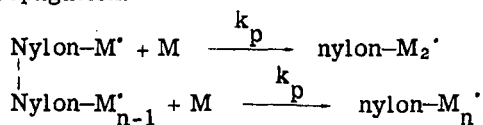
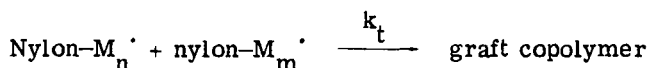


FIG. 2. Effect of $[\text{PP}]$ on graft yield. (a) $[\text{Fe(II)}] = 5.0 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 7.5 \times 10^{-2} \text{ M}$, $[\text{MMA}] = 46.94 \times 10^{-2} \text{ M}$, 6 h, 50°C , M:L = 1:100. (b) $[\text{Mn(II)}] = 5.0 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 7.5 \times 10^{-2} \text{ M}$, $[\text{MMA}] = 46.94 \times 10^{-2} \text{ M}$, 6 h, 50°C , M:L = 1:100.

Propagation:



Termination:



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

$$\frac{-d[\text{R}']}{dt} = k_d[\text{P}_2\text{O}_8^{4-}][\text{Me}(\text{II})] - k_i[\text{R}'][\text{nylon}] = 0$$

Therefore

$$[\text{R}'] = \frac{k_d[\text{P}_2\text{O}_8^{4-}][\text{Me}(\text{II})]}{k_i[\text{nylon}]}$$

$$\frac{-d[\text{nylon-M}'_n]}{dt} = k_i'[\text{M}][\text{nylon}'] - k_t[\text{nylon-M}'_n]^2 = 0$$

Therefore

$$[\text{Nylon-M}'_n] = \left(\frac{k_i'}{k_t} \right)^{1/2} [\text{M}]^{1/2} [\text{nylon}']^{1/2}$$

$$\frac{-d[\text{nylon}']}{dt} = k_i[\text{nylon}][\text{R}'] - k_i'[\text{nylon}'][\text{M}] = 0$$

Therefore

$$[\text{Nylon}'] = \frac{k_i[\text{nylon}][\text{R}']}{k_i'[\text{M}]} = \frac{k_d[\text{P}_2\text{O}_8^{4-}][\text{Me}(\text{II})]}{k_i'[\text{M}]}$$

Therefore

$$[\text{Nylon-M}_n^{\cdot}] = \left(\frac{k_d [\text{P}_2\text{O}_8^{4-}] [\text{Me(II)}]}{k_t} \right)^{1/2}$$

$$R_p = k_p [\text{nylon-M}_n^{\cdot}] [M] = k_p \left(\frac{k_d}{k_t} \right)^{1/2} [\text{P}_2\text{O}_8^{4-}]^{1/2} [\text{Me(II)}]^{1/2} [M]$$

Thus plots of R_p versus $[M]$ (Fig. 3) and $[\text{P}_2\text{O}_8]^{1/2}$ (Fig. 4) are linear and pass through the origin, 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 5.0×10^{-4} to 60×10^{-4} M (Fig. 5). The result indicates that the graft yield increases progressively with an increase in the concentration of the reducing agent. This might be due to the fact that the

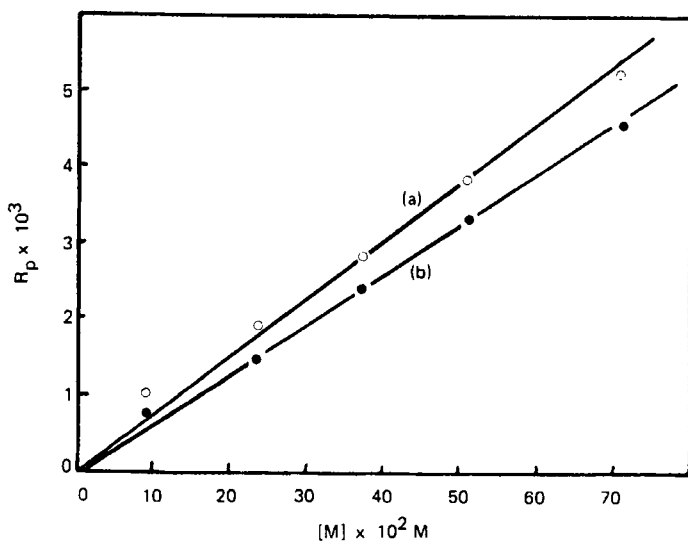


FIG. 3. Plot of R_p vs $[M]$. (a) For PP-Mn(II) redox system. (b) For PP-Fe(II) redox system.

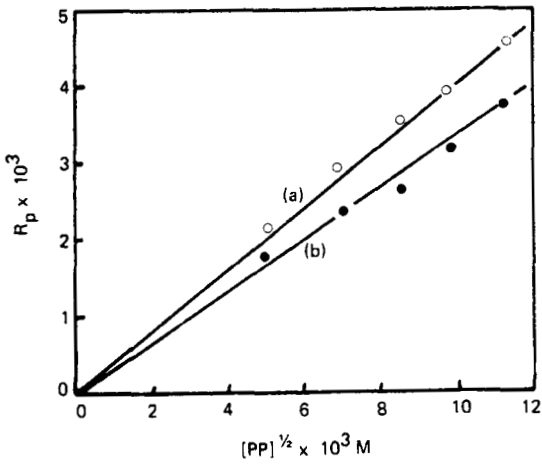


FIG. 4. Plot of R_p vs $[PP]^{1/2}$. (a) For PP-Mn(II) redox system. (b) For PP-Fe(II) redox system.

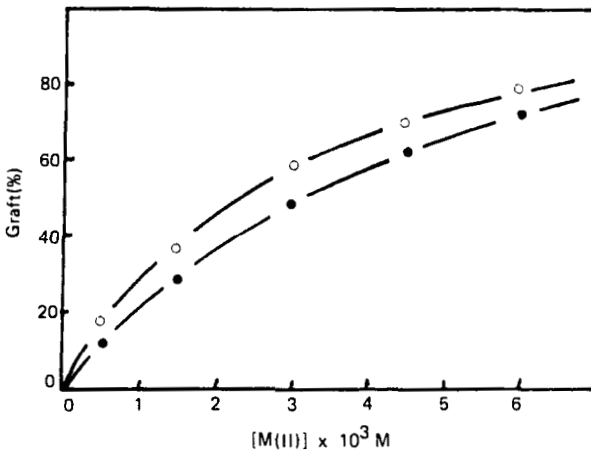


FIG. 5. Effect of reducing agent on graft yield. $[PP] = 7.5 \times 10^{-3}$ M, $[H_2SO_4] = 6.0 \times 10^{-2}$ M, $[MMA] = 23.47 \times 10^{-2}$ M, 6 h, 50°C, $\bar{M}:L = 1:100$. (●) Fe(II). (○) Mn(II).

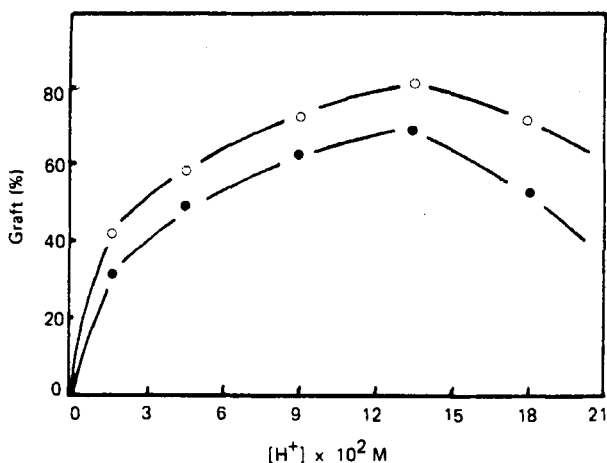


FIG. 6. Effect of $[H_2SO_4]$ on graft yield. $[PP] = 5.0 \times 10^{-3} \text{ M}$, $[MMA] = 46.94 \times 10^{-2} \text{ M}$, 6 h, 50°C , M:L = 1:100. (●) $[Fe(II)] = 2.5 \times 10^{-3} \text{ M}$. (○) $[Mn(II)] = 2.5 \times 10^{-3} \text{ M}$.

reducing agent facilitates the formation of peroxydiphosphate ion radicals, 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

The graft yield was found to increase with the sulfuric acid concentration from 1.5×10^{-2} to $13.5 \times 10^{-2} \text{ M}$, after which it decreased with a further increase of sulfuric acid concentration in the case of both systems (Fig. 6).

It is a known fact that oxyanion reactions are acid catalyzed [23, 25]. Similarly, the reactions of peroxides are also subject 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 such species as $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^-$, $H_4P_2O_8$, $H_5P_2O_8^+$, and $H_6P_2O_8^{2+}$. Santappa and co-workers [26, 27] have reported that the reaction rate as well as the concentrations of $H_3P_2O_8^-$ and $H_4P_2O_8$ increase with increasing acid concentration. In the concentration range from 1.5×10^{-2} to $13.5 \times 10^{-2} \text{ M}$, 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.

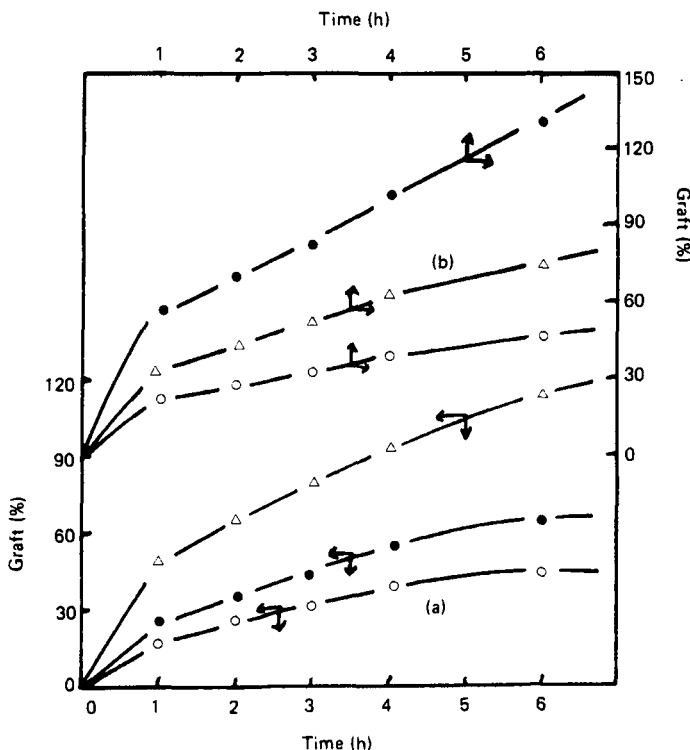


FIG. 7. Effect of temperature on graft yield. $[PP] = 1.0 \times 10^{-2} M$, $[H^+] = 7.5 \times 10^{-2} M$, $[MMA] = 46.94 \times 10^{-2} M$, $M:L = 1:100$. (a) $[Fe(II)] = 5.0 \times 10^{-3} M$, (\circ) $50^\circ C$, (\bullet) $60^\circ C$, (Δ) $70^\circ C$. (b) $[Mn(II)] = 5.0 \times 10^{-3} M$, (\circ) $50^\circ C$, (Δ) $60^\circ C$, (\bullet) $70^\circ C$.

Effect of Temperature

Since in thermal reactions the temperature plays a vital role, it is essential to study the effect of different temperatures on graft copolymerization. As is evident from Fig. 7, the graft yield increases sharply with the increase of temperature from 50 to $70^\circ C$ in both initiating systems. This might be due to the increase in the activation energy. Again, with increasing temperature the rate of diffusion of monomer and initiator into the active sites and growing chains of the nylon matrix increases, thus enhancing the rate of grafting.

From the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 8), the overall

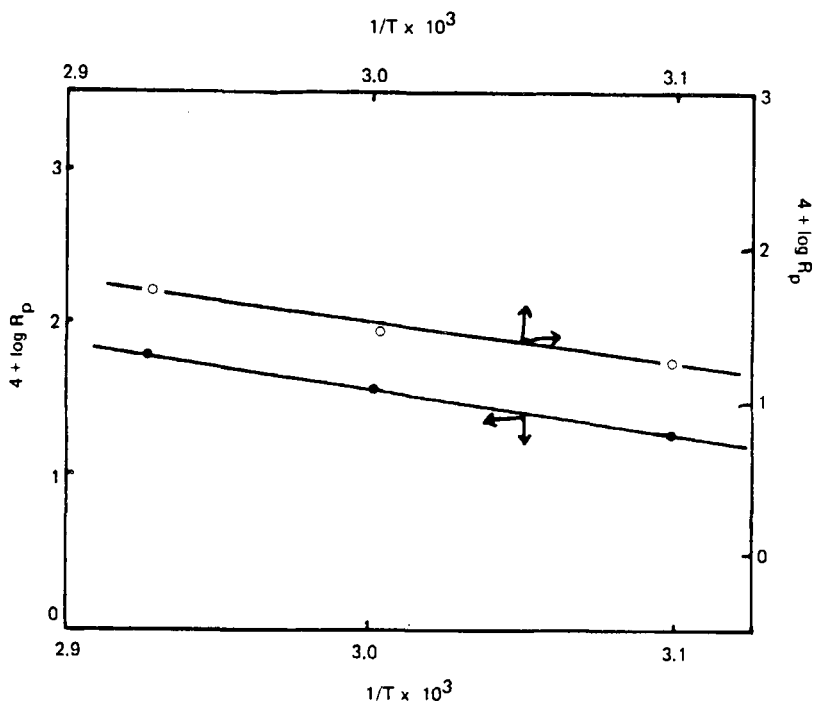


FIG. 8. Arrhenius plot. (●) PP-Mn(II). (○) PP-Fe(II).

activation energy (E_a) was found to be 13.8 and 12.6 kcal/mol for the peroxydiphosphate-Mn(II) system and the peroxydiphosphate-Fe(II) system, respectively. Using the value $E_p - \frac{1}{2}E_t = 4\sim 5$ kcal/mol obtained by Tololsky [28], where E_p and E_t are the energies of propagation and termination, respectively, the energy of initiation E_d was found by

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

where $E_d = 18.0$ kcal/mol for the PP-Mn(II) system and 16.2 kcal/mol for the PP-Fe(II) system.

Effect of Solvents

The effect of the addition of different water-miscible solvents on the rate of polymerization was studied. From the graft yield

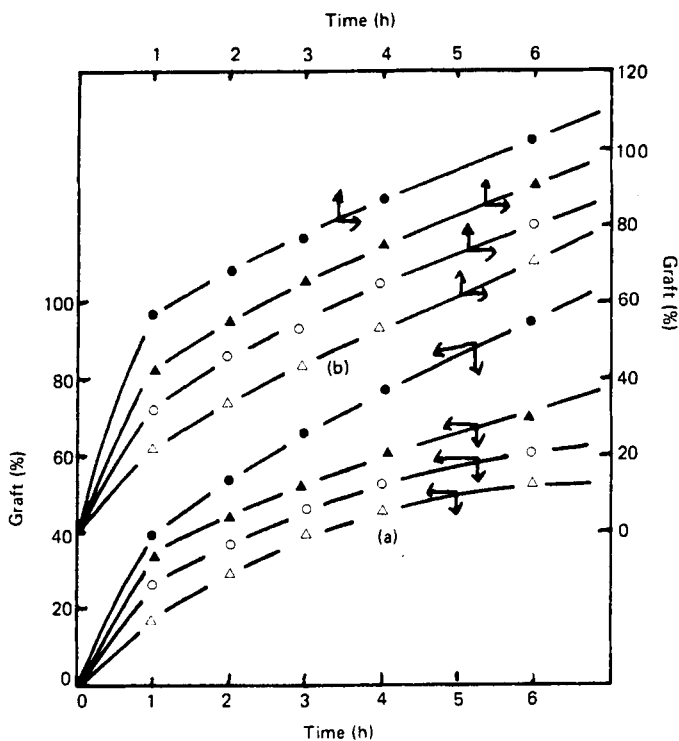


FIG. 9. Effect of solvents on graft yield. $[PP] = 1.0 \times 10^{-2} \text{ M}$, $[H^+] = 6.0 \times 10^{-2} \text{ M}$, $[MMA] = 46.94 \times 10^{-2} \text{ M}$, 6 h, solvent = 10% V/V, 50°C , M:L = 1:100. (a) $[Fe(II)] = 5.0 \times 10^{-3} \text{ M}$, (○) methanol, (●) formic acid, (△) dimethylformamide, (▲) acetic acid. (b) $[Mn(II)] = 5.0 \times 10^{-3} \text{ M}$, (○) methanol, (●) formic acid, (△) dimethyl formamide, (▲) acetic acid.

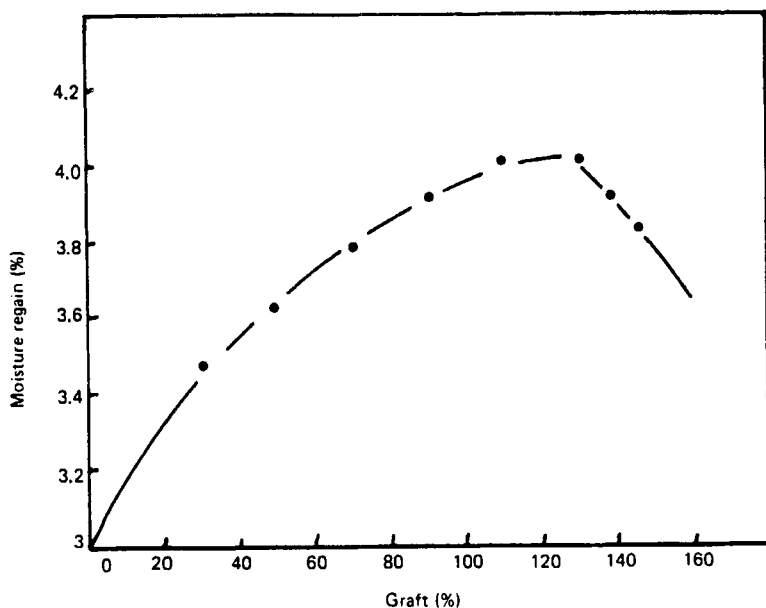


FIG. 10. Plot of moisture regain percentage versus graft percentage.

TABLE 1

Graft (%)	$\bar{M} \times 10^{-5}$	$\bar{DP} \times 10^{-3}$
16	5.823	5.823
20	5.868	5.868
30	5.932	5.932
45	6.013	6.013
60	6.312	6.312

obtained, the order of different solvents is as follows (Fig. 9): formic acid > acetic acid > methanol > dimethylformamide for both initiating systems.

The variation of the graft yield with the solvents might be due to the variation in 1) the ability to swell the fiber, 2) the miscibility with the monomer, 3) the formation of solvent radicals from the primary radical species by chain transfer, 4) the participation of the

solvent radical in the activation of nylon, and 5) the termination of the graft radical by a combination with solvent radicals. The first four factors favor grafting by simplifying access and diffusion of monomer, and the last factor adversely affects grafting by lowering the molecular size of the graft.

Moisture Regain

The percentage of moisture regain was found to increase with an increase of the percentage of grafting up to 120%. Thereafter it decreased (Fig. 10).

The molecular weights of the isolated grafted samples were found to increase with the percentage of grafting (Table 1).

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