NOTE

Grafting Vinyl Monomers onto Nylon 6. IX. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using Peroxydiphosphate–Cu(II) Redox System

INTRODUCTION

Modification of the properties of synthetic fibers like nylon 6 has received considerable interest in recent years.[1–9] But the use of peroxydiphosphate as the initiator of graft copolymerization onto nylon 6 has not been studied in detail. Nayak and co-workers, for the first time, have reported the graft copolymerization of methyl methacrylate onto wool, silk, and nylon 6 fibers using peroxydiphosphate ion as the initiator.[10–16] This communication presents the results of the graft copolymerization of methyl methacrylate onto nylon 6 using the peroxydiphosphate–Cu(II) redox system as the initiator.

EXPERIMENTAL

Nylon 6 was supplied by J. K. Synthetics, Kota, Rajsthan (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. Copper sulphate (BDH) and sulphuric acid ($\sim 18M$, BDH) were used. The graft copolymerization was carried out according to our previous procedure.[9]

RESULTS AND DISCUSSION

The use of the peroxydiphosphate–Cu(II) redox system as initiator for graft copolymerization of methyl methacrylate onto nylon 6 fibers was studied at various concentrations of monomer, initiator, acid, Cu(II), and temperature. The rate of grafting was found to be increased progressively with the monomer concentration from 9.38×10^{-2} to $70.41 \times 10^{-2}M$ (Fig. 1). The above observation could be attributed to the following reasons: (i) increasing the monomer concentration, the swellability of the fiber increases, thus facilitating the penetration of the monomer and initiator into the active sites of the fiber; (ii) the gel effect,[17] which hinders the mutual termination of growing chains; and (iii) complexation of the fiber with monomer.

The graft yield was found to be increased with increasing Cu^{2+} concentration from 5×10^{-4} to $30 \times 10^{-4}M$ after which a decreasing trend was noticed (Fig. 2). This might be due to the fact that, at lower concentrations, Cu^{2+} ions facilitate the formation of free radical species by reacting with peroxydiphosphate ions, thus enhancing the graft yield. Similar observation has been noted by
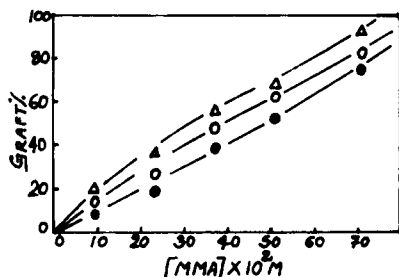

Fig. 1. Effect of [MMA] on graft yield: $[Cu(II)] = 5.0 \times 10^{-3}M$; $[H^+] = 9.0 \times 10^{-2}M$; time = 6 h; temp = 60°C; M:L = 1:100; (●) [PP] = $2.5 \times 10^{-3}M$; (○) [PP] = $5.0 \times 10^{-3}M$; (△) [PP] = $7.5 \times 10^{-3}M$.
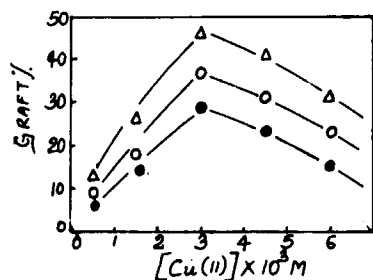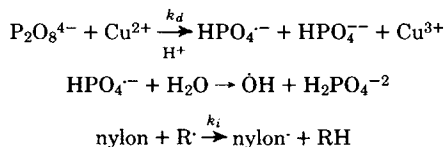
Fig. 2. Effect of [Cu(II)] on graft yield: [PP] = $7.5 \times 10^{-3}M$; [H$_2$SO$_4$] = $6.0 \times 10^{-2}M$; time = 6 h; temp = 60°C; M:L = 1:100; ($\bullet$) [MMA] = $23.47 \times 10^{-2}M$; (O) [MMA] = $46.94 \times 10^{-2}M$; ($\triangle$) [MMA] = $70.41 \times 10^{-2}M$.

Galiba et al.[18] in case of the reaction of the sister ion peroxydisulphate with Cu^{2+} ions. The drop in graft yield at higher Cu^{2+} concentrations might be due to the participation of Cu^{2+} ions in termination reaction. The graft yield was also found to be increased with increasing the sulphuric acid concentration from 1.5×10^{-2} to $18.0 \times 10^{-2}M$. As peroxydiphosphate is an oxyanion derivative and is acid catalyzed, with the increase of acid concentration, more active species like H$_3$P$_2$O$_8^-$ and H$_4$P$_2$O$_8$ are formed. These are responsible for producing a large number of free radicals on the backbone of nylon thus facilitating the graft yield.

The temperature was varied from 50°C to 70°C. The graft yield increased steadily with increasing temperature. From the Arrhenius plot of log R_p vs. 1/T (Fig. 3), the overall activation energy was found to be 9.0 kcal/mol. The effect of addition of some solvents (10% v/v) on graft yield was also studied out of which HCOOH proved to be the most effective for grafting. The molecular weight of the isolated grafted samples was found to increase with increasing the percentage of grafting.

The graft yield was found to be increased upon increasing peroxydiphosphate concentration from 2.5×10^{-3} to $12.5 \times 10^{-3}M$. The presence of Cu^{2+} ions facilitates the dissociation of peroxydiphosphate to produce HPO$_4^{\cdot-}$ and $\dot{\text{O}}$H (R$\cdot$) radicals. The radicals interact with the nylon matrix, producing nylon macroradicals which initiate the grafting process as shown below:
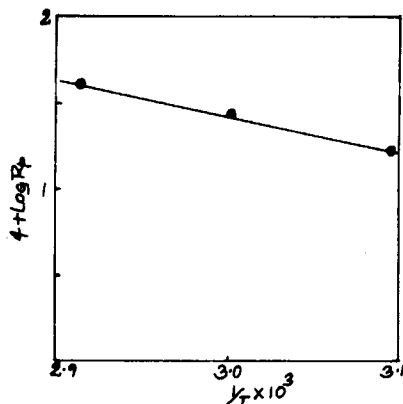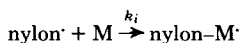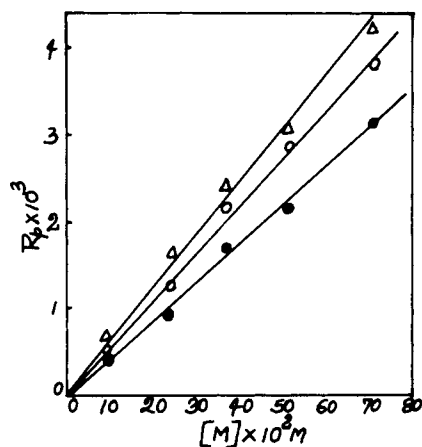
$$\text{P}_2\text{O}_8{}^{4-} + \text{Cu}^{2+} \xrightarrow[\text{H}^+]{k_d} \text{HPO}_4{}^{\cdot-} + \text{HPO}_4^{--} + \text{Cu}^{3+}$$

$$\text{HPO}_4{}^{\cdot-} + \text{H}_2\text{O} \rightarrow \dot{\text{O}}\text{H} + \text{H}_2\text{PO}_4{}^{-2}$$

$$\text{nylon} + \text{R}\cdot \xrightarrow{k_i} \text{nylon}^{\cdot} + \text{RH}$$

Initiation:

$$\text{nylon}^{\cdot} + \text{M} \xrightarrow{k_i} \text{nylon–M}^{\cdot}$$
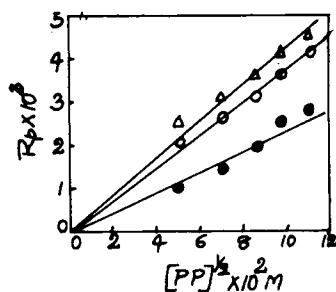

Fig. 3. Arrhenius plot.

Fig. 4. Plot of R_p vs. [M].

Fig. 5. Plot of R_p vs. $[PP]^{1/2}$.

Propagation:

$$\text{nylon–M}^{\cdot} + \text{M} \xrightarrow{k_p} \text{nylon–M}_2^{\cdot}$$

$$\text{nylon–M}_{n-1}^{\cdot} + \text{M} \xrightarrow{k_p} \text{nylon–M}_n^{\cdot}$$

Termination:

$$\text{nylon–M}_n^{\cdot} + \text{nylon–M}_m^{\cdot} \xrightarrow{k_t} \text{grafted polymer}$$
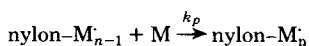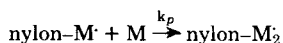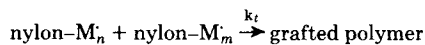
Considering the steady state principles for [R·], [nylon·] and [nylon–M$_n^{\cdot}$], the rate of polymerization was derived to be

$$R_p = k_p (k_d/k_t)^{1/2} [P_2O_8]^{1/2} [Cu^{2+}]^{1/2} [M]$$

The plot of R_p vs. [M] (Fig. 4) and $[PP]^{1/2}$ (Fig. 5) favors the above reaction scheme.

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