Grafting Vinyl Monomers onto Nylon-6. X. Graft Copolymerization of Methyl Methacrylate onto Nylon-6 Using Peroxydiphosphate as Initiator

Recently Nayak and co-workers have used peroxydiphosphate ion as the initiator for grafting vinyl monomers onto wool,[1–5] silk,[6,7] and cellulose[8] fibers. We have reported the graft copolymerization of vinyl monomers onto nylon-6 using a multitude of metal and nonmetal ions.[9–12] This note presents the results of grafting methyl methacrylate onto nylon-6 fibers using peroxydiphosphate (PP) as the initiator.

EXPERIMENTAL

Potassium peroxydiphosphate ($K_4P_2O_8$) was a gift sample from F. M. C. Corporation, U.S.A. Nylon-6 fibers were kindly supplied by J. K. Synthetics, Kota, Rajsthan, India. The graft copolymerization was carried out according to our previous methods.[2–6]

RESULTS AND DISCUSSION

The effect of monomer concentration on the polymerization reaction was evaluated by changing the monomer concentrations within the range of $27.98–122.00 \times 10^{-2}M$. The graft-on percentage increases up to $103.27 \times 10^{-2}M$, and thereafter it decreases (Fig. 1). The effect of the initiator concentration on the graft yield was investigated by changing the initiator concentration from 50×10^{-4} to $140 \times 10^{-4}M$. The graft yield increases progressively with increasing initiator concentration (Fig. 2). The effect of acid concentration has been studied by changing sulphuric acid concentration within the range of $0.021–0.248M$. The graft-on percentage decreases with increasing acid concentration. The effect of raising the temperature from 65°C to 75°C is to bring about significant enhancement in the rate of grafting. From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy (E_a) and the activation energy of initiation (E_d) were computed to be 11.5 kcal/mol and 14.0 kcal/mol, respectively (Fig. 3). The reaction was investigated by adding some neutral salts like $LiNO_3$, NaF, $MnSO_4$, etc. The graft yield follows the order

$$LiNO_3 > NaF > MnSO_4$$

depending on the ability of these salts to catalyze the propagation step. When the reaction was carried out in presence of $CuSO_4$, the percentage of grafting increses in the initial stages, and thereafter it decreases with increasing the salt concentration. The reaction medium plays an im-
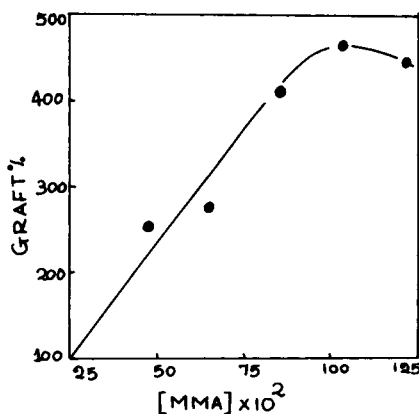

Fig. 1. Effect of [MMA] on graft yield: [PP] = $140 \times 10^{-4}M$; [H^+] = $0.021M$; temp = 70°C; time = 6 h; M:L = 1:100.
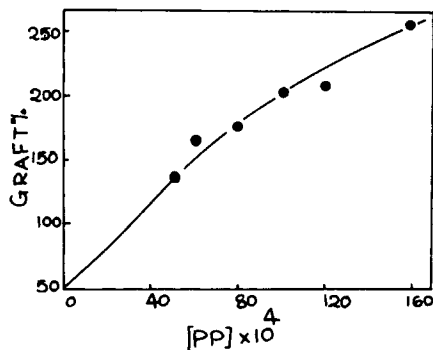
Fig. 2. Effect of [PP] on graft yield: [MMA] = $0.4694M$; [H$^+$] = $0.021M$; temp = 70°C; time = 6 h; M:L = 1:100.

portant role on grafting vinyl monomers onto nylon-6. The graft yield follows the order: methanol > ethanol > propanol > butanol > pentanol. The decrease in graft yield from methanol to pentanol is due to the decrease in the ability of swelling of polyamide and the difference in capability of these solvents as the terminator for the nylon-6 macroradical.

Mechanism

Assuming initiation by radicals of the type H_2PO_4·, HO·, and HPO_4·$^-$, formed by the decomposition of peroxydiphosphate, the following reaction scheme is suggested for the graft copolymerization of MMA onto nylon-6 using PP as the initiator:
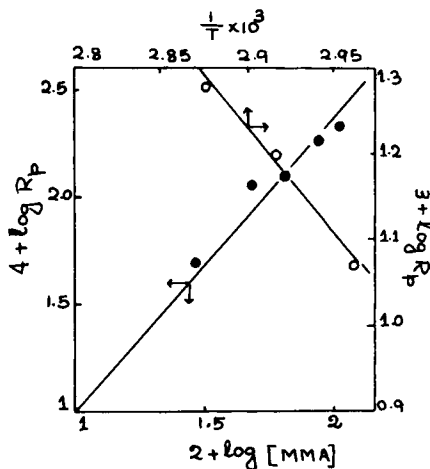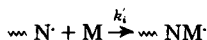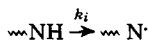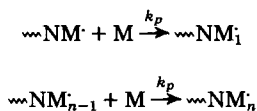Initiation:

$$\text{wwNH} \xrightarrow{k_i} \text{ww N·}$$

$$\text{ww N· + M} \xrightarrow{k_i'} \text{ww NM·}$$

Fig. 3. Arrhenius plot of log R_p vs. $1/T$ and plot of log R_p vs. log [MMA]

Propagation:

$$\text{\tiny ww}NM\cdot + M \xrightarrow{k_p} \text{\tiny ww}NM_1^{\cdot}$$

$$\text{\tiny ww}NM_{n-1}^{\cdot} + M \xrightarrow{k_p} \text{\tiny ww}NM_n^{\cdot}$$

Termination:

$$\text{\tiny ww}NM_n^{\cdot} + \text{\tiny ww}NM_m^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$
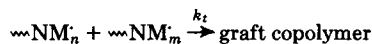
Considering steady state principle for the radicals, the rate of polymerization, R_p, has been derived to be

$$R_p = k_p \left(\frac{k_i}{k_t}\right)^{1/2} [\text{NH}]^{1/2} [\text{M}]$$

The plot of log R_p vs. log [M] (Fig. 3) is linear, indicating the validity of the above reaction scheme. The percentage of moisture regain of the grafted sample has been studied. The percentage of moisture regain of the grafted samples increases with increasing the graft-on percentage.

References

1. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem., C* **14(2),** 193 (1976).
2. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.,* **25,** 63 (1980).
3. P. L. Nayak, S. Lenka, and M. K. Mishra, *Macromol. Sci. Chem.,* **16** (4), (1981), to appear.
4. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.,* **26,** 733 (1981).
5. P. L. Nayak, S. Lenka, and M. K. Mishra, *Angew. Makromol. Chem.,* **90,** 155 (1980).
6. P. L. Nayak, S. Lenka, and M. K. Mishra, *Angew. Makromol. Chem.,* **84,** 183 (1980).
7. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Polym. Sci.,* **18** (7), (1980), to appear.
8. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.,* **25,** 1323 (1980).
9. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem., C* **17** (2), 267 (1979).
10. P. L. Nayak, R. K. Samal, and M. C. Nayak, *Angew. Makromol. Chem.,* **80,** 95 (1979).
11. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.,* **26,** (1981), to appear.
12. P. L. Nayak, N. C. Pati, and A. K. Pradhan, *J. Polym. Sci., Polym. Chem. Ed.,* **19,** 831 (1981).

SUBASINI LENKA

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College, Cuttack-753003,
Orissa, India