

Notes

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

The readily available peroxydisulfate is an excellent and versatile oxidant for a variety of organic and inorganic compounds. It has been used lately to bring about the oxidation of organic compounds, and the kinetics of these processes have been studied by different workers. Work on the oxidation of a variety of organic and inorganic substrates by peroxydisulfate upto 1962 was reviewed by House¹ and Wilmarth and Haim.² That peroxydisulfate ion could initiate polymerization of certain vinyl monomers was reported by Bacon³ as early as 1946. Peroxydisulfate ion when coupled with monovalent silver ion acts as better initiator, since Ag^{2+} which is produced during the reaction, is a more powerful initiator than peroxydisulfate. Morgan⁴ reported the polymerization of acrylonitrile initiated by peroxydisulfate with silver nitrate, sodium thiosulfate, and ferrous ammonium sulfate as reductant. Kern and co-workers⁵ and Whitby et al.⁶ reported the kinetics of the polymerization of acrolein initiated by the peroxydisulfate— Ag^+ redox system. Recently Kagiya and co-workers⁷ reported the kinetic features of the redox polymerization of acrolein with the potassium persulfate—silver nitrate redox system. Arai and co-workers⁸⁻¹² have studied the graft copolymerization of vinyl monomers onto wool and silk fibers using the peroxydisulfate—lithium bromide redox system. Nayak et al.¹³⁻²² have studied the graft copolymerization of methyl methacrylate onto natural and synthetic fibers using a multitude of metal and nonmetal ions.

This note presents the graft copolymerization of methyl methacrylate onto nylon-6 using the potassium peroxydisulfate—silver redox system.

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 persulfate (AR) and silver nitrate (AR) were used as such. The grafting reactions were carried out according to our previous procedure.¹³

RESULTS AND DISCUSSION

The use of the peroxydisulfate— Ag^+ redox system as initiator for graft copolymerization of methyl methacrylate onto nylon-6 fibers was studied at various concentrations of monomer, initiator, and acid, Ag^+ , and temperature. The grafting-on percentage was found to increase progressively with increasing time (Fig. 1).

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentrations within the range, 0.281–0.8449M at different peroxydisulfate concentrations (2.5×10^{-3} – $7.5 \times 10^{-3}M$). The perusal of the result indicates that with increasing peroxydisulfate concentrations the graft yield increases (Fig. 2). The plots of R_p vs. [MMA] were found to be linear (Fig. 3).

Effect of Initiator Concentration

The effect of peroxydisulfate concentration on the rate of grafting is shown in Figure 4. The graft yield increases with increasing the peroxydisulfate concentration up to $7.5 \times 10^{-3}M$, and thereafter the graft yield decreases.

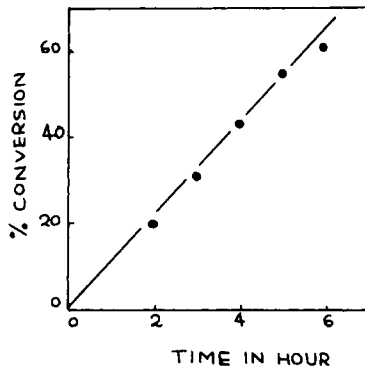


Fig. 1. % conversion: $[AgNO_3] = 25 \times 10^{-3}M$; $[peroxydisulfate] = 7.5 \times 10^{-3}M$; $[MMA] = 0.4694M$; temp = $70^\circ C$; time = 6 h; M:L = 1:100.

Effect of Silver Nitrate Concentration

Figure 5 shows the effect of silver nitrate concentration ($5 \times 10^{-3}M$ – $50 \times 10^{-3}M$) on grafting. It is observed that the graft-on percentage increases up to $25 \times 10^{-3}M$ and thereafter it decreases.

Effect of Temperature

The graft copolymerization was carried out at three different temperatures ranging from $50^\circ C$ to $75^\circ C$, keeping the concentrations of all other reagents constant (Fig. 6). The perusal of the results indicate that with increasing temperature the graft-on percentage increases. The enhancement

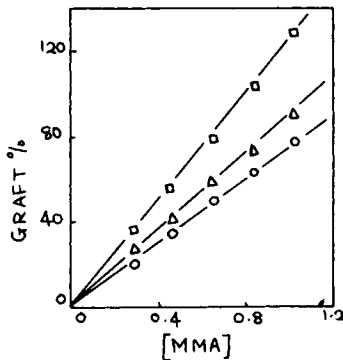


Fig. 2. Effect of monomer: $[AgNO_3] = 25 \times 10^{-3}M$; temp = $70^\circ C$; time = 6 h; M:L = 1:100. [Peroxydisulfate]: (O) $2.5 \times 10^{-3}M$; (Δ) $5.0 \times 10^{-3}M$; (\square) $7.5 \times 10^{-3}M$.

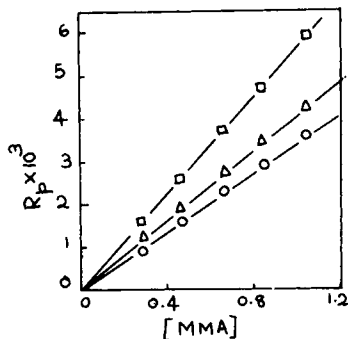


Fig. 3. Plots of R_p vs. $[MMA]$. [Peroxydisulfate]: (O) $2.5 \times 10^{-3}M$; (Δ) $5.0 \times 10^{-3}M$; (\square) $7.5 \times 10^{-3}M$.

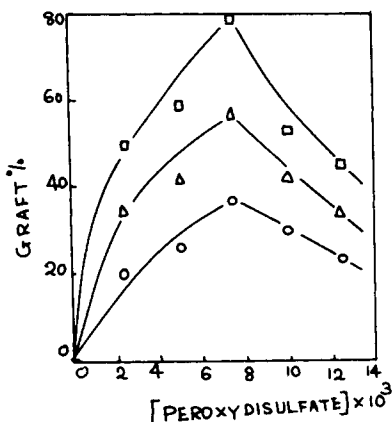


Fig. 4. Effect of [peroxydisulfate]: $[AgNO_3] = 25 \times 10^{-3}M$; temp = $70^\circ C$; time = 6 h; M:L = 1:100. [MMA]: (O) 0.281M; (Δ) 0.4694M; (\square) 0.657M.

of graft yield with increasing temperature could be ascribed to the greater activation energy, the swellability of fiber, the solubility of monomer, and its rate of diffusion to the fiber matrix. From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy was computed to be 1.2 kcal/mol (Fig. 7).

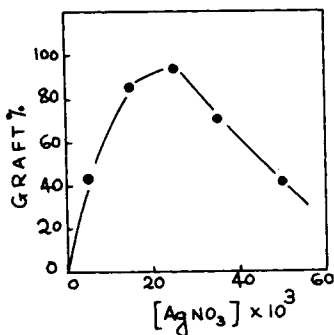


Fig. 5. Effect of $[AgNO_3]$: [MMA] = 0.4694M; [peroxydisulfate] = $7.5 \times 10^{-3}M$; temp = $70^\circ C$; time = 6 h; M:L = 1:100.

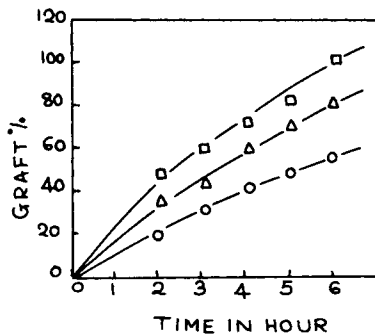
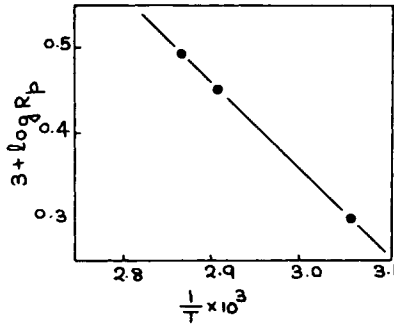
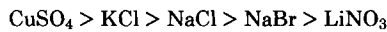


Fig. 6. Effect of temperature: $[AgNO_3] = 25 \times 10^{-3}M$; [peroxydisulfate] = $5.0 \times 10^{-3}M$; [MMA] = 0.4694M; M:L = 1:100. Temp: (O) $50^\circ C$; (Δ) $70^\circ C$; (\square) $75^\circ C$.

Fig. 7. Arrhenius plot of $\log R_p$ vs. $1/T$.

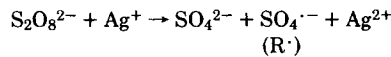
Effect of Inorganic Salts

The effect of certain neutral salts such as NaCl, KCl, NaBr, LiNO₃, and CuSO₄ has been studied. The graft-on percentage follows the order:



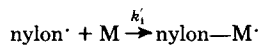
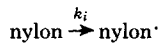
Mechanism

In a system consisting of peroxydisulfate, silver ion, MMA, and nylon, the following reaction scheme may be envisaged:

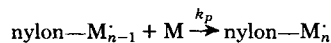
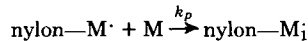


R[·] interacts with the groups present in the nylon-backbone-producing nylon macroradicals. The nylon macroradicals interact with monomer, resulting in grafting as represented below:

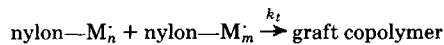
Initiation:



Propagation:



Termination:



Now,

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

$$k_i[\text{nylon}] = k_i'[\text{nylon}^{\cdot}][\text{M}]$$

or

$$[\text{nylon}^{\cdot}] = \frac{k_i}{k_i'} \frac{[\text{nylon}]}{[\text{M}]}$$

Further,

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

or

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

The rate of polymerization;

$$\begin{aligned} R_p &= k_p [\text{nylon}-M_n][M] \\ &= k_p \left(\frac{k_i}{k_t}\right)^{1/2} [\text{nylon}]^{1/2} [M] \end{aligned}$$

The plot of R_p vs. $[M]$ is linear passing through the origin (Fig. 3).

References

1. D. A. House, *Chem. Rev.*, **62**, 1855 (1962).
2. A. K. Wilmarth and A. Haim, *Mechanism of Oxidation of Peroxydisulfate Ion in Peroxide Reaction Mechanism*, J. O. Edwards, Ed., Wiley, New York, 1963, p. 175.
3. R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 169 (1946).
4. M. L. Morgan, *Trans. Faraday Soc.*, **42**, 164 (1946).
5. R. C. Schulz, H. Cherdron, and W. Karn, *Makromol. Chem.*, **24**, 141 (1957).
6. G. S. Whitby, M. D. Gross, J. R. Millen, and A. J. Costanza, *J. Polym. Sci.*, **16**, 544 (1955).
7. T. Kagiya, S. Morita, and K. Fukui, *Bull. Chem. Soc. (Jpn.)*, **42**, 2578 (1969).
8. M. Negishi, K. Arai, S. Okada, and I. Nagakura, *J. Appl. Polym. Sci.*, **9**, 3465 (1965).
9. K. Arai, M. Negishi, and T. Okabe, *J. Appl. Polym. Sci.*, **12**, 2585 (1968).
10. K. Arai and M. Negishi, *J. Polym. Sci., A-1*, **9**, 1865 (1971).
11. K. Arai, S. Komino, and M. Negishi, *J. Polym. Sci., A-1*, **8**, 917 (1970).
12. K. Arai, M. Shimizu, and M. Shimada, *J. Polym. Sci., A-1*, **11**, 3283 (1973).
13. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C14(2)**, 193 (1976).
14. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **85**, 15 (1980).
15. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **71**, 189 (1978).
16. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Polym. Sci., A-1*, **16**, 343 (1978).
17. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Appl. Polym. Sci.*, **23**, 1345 (1979).
18. S. Lenka, P. L. Nayak, and M. K. Mishra, *J. Appl. Polym. Sci.*, **25**, 1323 (1980).
19. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C17(2)**, 267 (1979).
20. P. L. Nayak, S. Lenka, M. K. Mishra, and A. K. Tripathy, *J. Appl. Polym. Sci.*, **26**, (1981), to appear.
21. P. L. Nayak, R. K. Samal, and M. C. Nayak, *Angew. Makromol. Chem.*, **80**, 95 (1979).
22. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, **26**, 2109 (1981).

SUBASINI LENKA

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

Received October 16, 1981
Accepted December 14, 1981