Grafting Vinyl Monomers onto Polyester Fibers. VI. Graft Copolymerization of Methyl Methacrylate onto PET Fibers Using Tetravalent Cerium as Initiator

ADWAIT K. PRADHAN, NRUSINGHA C. PATI, and PADMA L. NAYAK, *Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India*

Synopsis

The graft copolymerization of methyl methacrylate onto polyester fibers (PET) was investigated using tetravalent cerium as the initiator. The rate of grafting was found to increase progressively with the initiator and monomer concentrations up to $2.5 \times 10^{-2}M$ and $70.41 \times 10^{-2}M$, respectively. The reaction was found to be catalysed by acid up to $15.0 \times 10^{-2}M$. The graft yield increased by increasing temperature. The effect of addition of some solvents and thiourea on the rate of grafting was also investigated. A suitable kinetic scheme has been pictured, and rate equations have been derived.

INTRODUCTION

During the last decade much interest has been focussed on the modification of the properties of natural and synthetic fibers through graft copolymerization.[1–5] Out of several methods available for grafting the chemical initiation method has been found befitting for the purpose owing to the low degradation of the base polymer. Graft copolymerization onto polyester fibers (PET) has been accomplished either by radiation[6–16] or chemical initiation methods.[17–21] But since polyester fiber (PET) is a hard substrate containing no chemically reactive groups, very low graft yield has been obtained[22] in comparison with other fibers.

Tetravalent cerium (Ce^{4+}), a versatile oxidizing agent capable of reacting with almost all types of functional groups, has been extensively used for polymerization of a large number of vinyl monomers.[23–32] On account of its high grafting efficiency compared to other known redox systems, this system has gained considerable importance in grafting vinyl monomers onto cotton and cellulose,[33–42] wool,[43–44] silk,[45] collagen,[46,47] and nylon-6.[48–50]

Very recently, Nayak and co-workers have reported graft copolymerization of methyl methacrylate onto polyester fibers (PET) using some metal ions.[20,21,51,52] This paper presents the results of graft copolymerization of methyl methacrylate onto PET fibers using tetravalent cerium as the initiator.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET) fibers were supplied by J.K. Synthetics, Kota, Rajsthan, India, as a gift sample. Ceric ammonium nitrate (AR,BDH), H_2SO_4 (AR, $\sim 18M$, BDH) and thiourea (AR, BHD) were used. Purification

Journal of Applied Polymer Science, Vol. 27, 1873–1881 (1982)
 CCC 0021-8995/82/061873-09$01.90

of monomer, the method of graft copolymerization reaction, and the calculation of moisture regain percentage were carried out according to our previous paper.[20]

RESULTS AND DISCUSSION

The effect of the variation of monomer concentration on the graft yield was evaluated keeping the concentration of all other reagents constant. As evident from Figure 1, the graft yield increases progressively with increase of monomer concentration from 4.694 to 70.41 × $10^{-2}M$. Many factors attribute to this variation of graft yield with monomer concentration: (i) The gel effect, i.e., the increase of the viscosity of the medium due to the solubility of poly(methyl methacrylate) in its own monomer. Hence, besides hindering the termination of growing polymer chain radicals by coupling, the gel effect also causes swelling of the polyester fiber, thus assisting diffusion of monomer to the growing grafted chains and active sites on the polyester backbone, thereby enhancing grafting. (ii) The monomer molecules might form some types of charge-transfer complex with the polyester fibers which is favored only at high monomer concentration, thus activating the monomer molecules. This enhanced monomer reactivity also causes an increase in the graft yield.

Effect of Initiator Concentration

Figure 2 represents the effect of different concentrations of ceric ion on graft yield. From the figure it is evident that there is a progressive enhancement of the graft yield with increasing ceric ion concentration from 0.5 to 2.5 × $10^{-2}M$.

Since the oxidation potential of ceric ion is very high and the polyester fiber has no pendant groups to be easily oxidized, it is probable that the free radicals on the polyester fibers are created as a result of interaction of the metal ion with the fiber matrix. Hence it is possible to suggest the following reaction mechanism

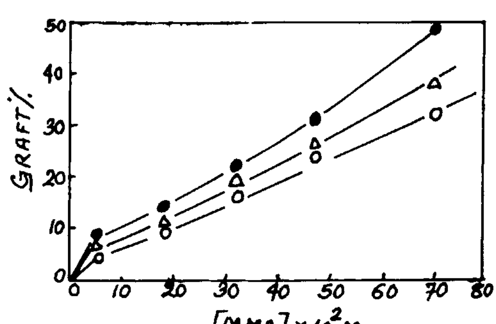


Fig. 1. Effect of [monomer] on graft yield: $[H^+] = 7.5 \times 10^{-2}M$; time = 6 h; temperature = 70°C; material:liquor = 1:100; (○) $[Ce^{4+}] = 0.5 \times 10^{-2}M$; (△) $[Ce^{4+}] = 1.5 \times 10^{-2}M$; (●) $[Ce^{4+}] = 2.5 \times 10^{-2}M$.

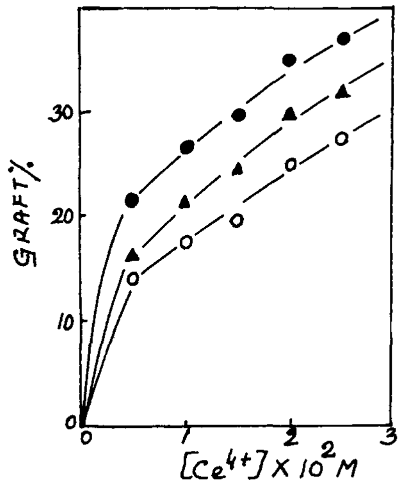


Fig. 2. Effect of $[Ce^{4+}]$ on graft yield: $[H^+] = 7.5 \times 10^{-2}M$; time = 6 h; temperature = 70°C; material:liquor = 1:100; (○) [MMA] = $23.47 \times 10^{-2}M$; (▲) [MMA] = $46.94 \times 10^{-2}M$; (●) [MMA] = $70.41 \times 10^{-2}M$.

for graft copolymerization of methyl methacrylate onto polyester fibers, using Ce^{4+} as the initiator:

$$\mathrm{PET} + \mathrm{Ce}^{+4} \xrightarrow{k_d} \mathrm{PET}^{\cdot} + \mathrm{Ce}^{3+} + \mathrm{H}^+$$

Initiation:

$$\mathrm{PET}^{\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{PET{-}M}^{\cdot}$$

(where PET = polyester fiber, M = monomer)

Propagation:

$$\mathrm{PET{-}M}^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{PET{-}M}_2^{\cdot}$$

$$\mathrm{PET{-}M}_{n-1}^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{PET{-}M}_n^{\cdot}$$

Termination:

$$\mathrm{PET{-}M}_n^{\cdot} + \mathrm{PET{-}M}_m^{\cdot} \xrightarrow{k_t} \mathrm{polymer}$$

Applying the steady state assumption both for $[\mathrm{PET}^{\cdot}]$ and $[\mathrm{PETM}_n^{\cdot}]$, the rate expression may be derived as follows:

$$\frac{d[\mathrm{PET}^{\cdot}]}{dt} = k_d[\mathrm{Ce}^{4+}]\,[\mathrm{PET}] - k_i[\mathrm{PET}^{\cdot}]\,[\mathrm{M}] = 0$$

$$[\mathrm{PET}^{\cdot}] = \frac{k_d[\mathrm{Ce}^{4+}][\mathrm{PET}]}{k_i[\mathrm{M}]}$$

$$\frac{d[\mathrm{PET{-}M}_n^{\cdot}]}{dt} = k_i[\mathrm{PET}^{\cdot}]\,[\mathrm{M}] - k_t[\mathrm{PET{-}M}_n^{\cdot}]^2 = 0$$

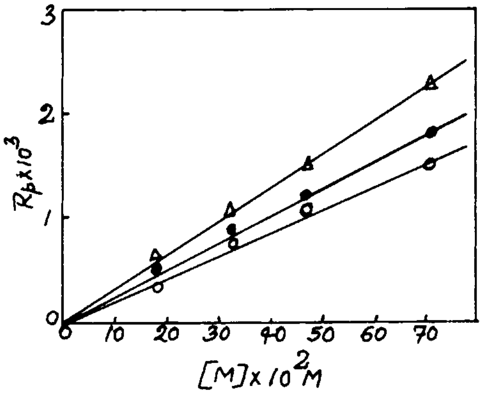


Fig. 3. Plot of R_p vs. [M].

or

$$[\text{PET—M}_n^{\cdot}] = \left(\frac{k_i}{k_t}[\text{PET}\cdot][\text{M}]\right)^{1/2} = \left(\frac{k_d}{k_t}[\text{Ce}^{4+}][\text{PET}]\right)^{1/2}$$

$$R_p = k_p[\text{PET—M}_n^{\cdot}][\text{M}]$$

or

$$R_p = k_p\left(\frac{k_d}{k_t}\right)^{1/2}[\text{Ce}^{4+}]^{1/2}[\text{PET}]^{1/2}[\text{M}]$$

Hence the fact that the plot of R_p vs. [M] (Fig. 3) and R_p vs. $[Ce^{4+}]^{1/2}$ (Fig. 4) are linear supports the above reaction scheme.

Effect of Acid Concentration on Grafting

The effect of acid concentration on the graft copolymerization reaction was studied by changing the concentration of sulphuric acid from 1.5 to 15.0 × $10^{-2}M$. The result shows that the graft yield increases with the acid concentration (Fig. 5). Since the oxidizing ability of ceric ion is largely affected by the acid concentration, it is probable that at higher acid concentration a large number of free radicals are produced which increase the percentage of grafting.

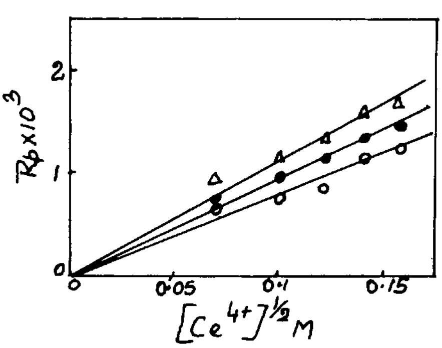


Fig. 4. Plot of R_p vs. $[Ce^{4+}]^{1/2}$.

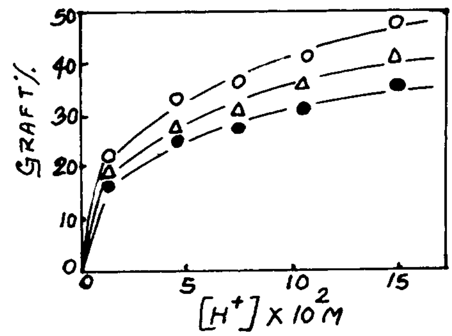


Fig. 5. Effect of $[H_2SO_4]$ on graft yield: [MMA] = $46.94 \times 10^{-2}M$; time = 6 h; temperature = 70°C; material:liquor = 1:100; (●) $[Ce^{4+}] = 2.0 \times 10^{-2}M$; (△) $[Ce^{4+}] = 2.5 \times 10^{-2}M$; (○) $[Ce^{4+}] = 3.0 \times 10^{-2}M$.

Effect of Temperature

The graft copolymerization of methyl methacrylate onto polyester fibers was studied by varying the temperature from 50°C to 70°C. The data indicate that the graft yield progressively increases with the temperature (Fig. 6). This may be attributed to the following factors: (i) enhancement of the swellability of the fiber, (ii) increase in the mobility of the monomer and initiator, (iii) higher rate of diffusion of monomer and initiator from the solution phase to the fiber phase, and (iv) higher rate of initiation and propagation of the graft. All the above factors specially (i), (ii), and (iii) in a cumulative way affects the enhancement of the graft yield.

From the Arrhenius plot of log R_p vs. $1/T$ (Fig. 7), the overall activation energy was computed to be 6.2 kcal/mol.

Effect of Solvents

Solvent plays a vital role during the process of grafting. The graft copolymerization was carried out in the presence of a number of water miscible organic solvents. The order of reactivity so far as the percentage of grafting concerned is as follows (Fig. 8):

acetic acid > methanol > dimethyl formamide >
chloroform > formic acid

Similar observation has been reported by Nayak and co-workers[51] in case of

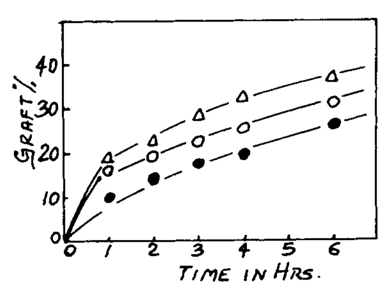


Fig. 6. Effect of temperature on graft yield: $[Ce^{4+}] = 1.5 \times 10^{-2}M$; $[H^+] = 10.5 \times 10^{-2}M$; [MMA] = $46.94 \times 10^{-2}M$; material:liquor = 1:100; temp: (●) 50°C; (○) 60°C; (△) 70°C.

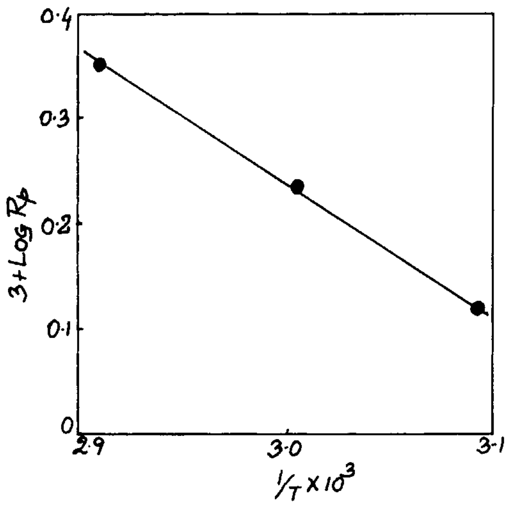


Fig. 7. Arrhenius plot.

grafting methyl methacrylate onto polyester fibers using permanganate ion as the initiator.

Effect of Redox System

The effect of redox system on the graft copolymerization was studied by changing the thiourea concentration from 0.5 to $5.0 \times 10^{-3}M$, keeping the concentration of all other reagents constant. The graft yield was found to increase with the thiourea concentration up to $2.5 \times 10^{-3}M$, after which it declines. This effect of thiourea on graft yield could be attributed to the following reasons.

Initially, at lower concentration of thiourea, some isothiocarbamido radicals ($R^{\cdot}$) are formed as a result of the interaction of Ce^{4+} with thiourea, which might participate in the initiation of graft copolymerization reaction, thus enhanc-

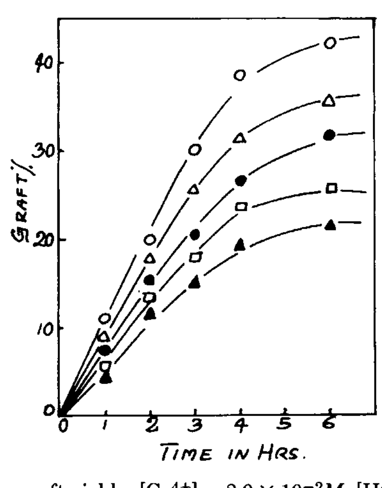
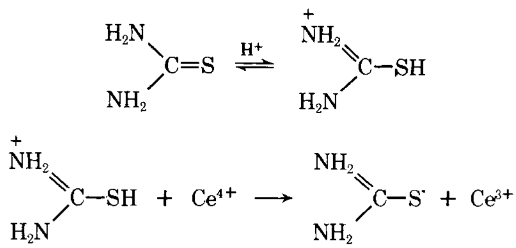


Fig. 8. Effect of solvents on graft yield: $[Ce^{4+}] = 2.0 \times 10^{-2}M$; $[H^+] = 7.5 \times 10^{-2}M$; $[MMA] = 46.94 \times 10^{-2}M$; material:liquor = 1:100; solvent = 10% v/v; temperature = 70°C; (○) solvent = acetic acid; (△) solvent = methanol; (●) solvent = dimethylformamide; (□) solvent = chloroform; (▲) solvent = formic acid.

ing graft yield as illustrated by:



(R·)

$$PET + R^{\cdot} \longrightarrow PET^{\cdot} + RH$$

$$PET^{\cdot} + M \longrightarrow PET\text{—}M^{\cdot}$$

But at higher concentration of thiourea, a large amount of isothiocarbamido radicals are formed which might participate in homopolymerization of methyl methacrylate thus decreasing the graft yield.

Effect of Different Monomers

The graft copolymerization onto polyester fibers (PET) was carried out with different monomers, out of which methyl methacrylate was proved to be the best monomer for grafting since higher percentage of grafting is obtained. The order of their reactivity, as observed from graft yield is

methyl methacrylate > methyl acrylate >
styrene > butyl acrylate > ethyl acrylate

The higher percentage of grafting obtained with methyl methacrylate than other monomers might be due to the presence of methyl group at the site of the vinyl group which stabilizes the free radicals by hyperconjugation.

Moisture Regain

The percentage of moisture regain was found to increase with the percentage of grafting. Polyester fibers are highly hydrophobic in nature and the moisture content of the fiber is low (0.45% at 20°C and 65% rh) under normal conditions of temperature and humidity. Grafting with methyl methacrylate not only brings about the opening of the structure to a certain extent but also increases hydrophilicity of the fiber as a result of the introduction of the polar groups, i.e., an ester group into the fiber matrix. This shift in the hydrophobic nature is responsible for the enhancement of the moisture regain with increasing the percentage of graft yield.

The scheme is financed by C.S.I.R., New Delhi, by Project No. 2(135)/79-EMR.II. One of the authors (A. K. P.) is thankful to C.S.I.R. for a Junior Research Fellowship.

References

1. I. C. Watt, *J. Macomol. Sci., Rev. Macromol. Chem.*, **C5**(1), 1975 (1970).
2. K. Arai, *Block Graft Copolym.*, **1**, 193 (1973).
3. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C14**(2), 193 (1976).
4. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C17**, 267 (1979).
5. W. L. Wasley, *Block Graft Copolym.*, **1**, 311 (1973).
6. A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *J. Polym. Sci.*, **22**(11), 3335 (1978).
7. Jozefpruzinec, Stefan Verga, and G. Gaussens, *Jad. Energ.* **25**(8), 305 (1979).
8. Young Kun Kong, Lee Hoon Seum, Kwarg Chong, and Jee Lochoi, *J. Korean Nul. Soc.*, **10**(4), 195 (1978).
9. K. N. Rao, M. H. Rao, H. T. Lokhande, N. R. Mody, and A. G. Jog., *J. Appl. Polym. Sci.*, **23**(7), 2133 (1979).
10. Te-Hsiung, *Hsin Hsien Wei*, **18**(7), 4 (1976).
11. V. T. Stannett, J. L. Williams, and G. S. P. Verma, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **12**(2), 504 (1971).
12. K. Ishigure, K. Yoshida, and V. T. Stannet, *J. Macromol. Sci. Chem.*, **7**(4), 813 (1973).
13. V. Stannett, D. K. Woods, L. G. Roldon, S. B. Sello, and C. V. Stevens, *Text. Res. J.*, **43**(4), 205 (1973).
14. I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci.*, *A1*, **11**, 189 (1978).
15. A. S. Hoffman, *Large Radiation Sources for Industrial Processes*, I.A.E.A. Vienna, 1969, p. 301.
16. V. T. Stannett and A. S. Hoffman, *Am. Dyestuff, Reptr.*, **57**, 61 (1968).
17. S. E. Shalaby, A. M. Bayzeed, and A. Hebeish, *J. Appl. Polym. Sci.*, **22**(5), 1359 (1979).
18. K. Seizaki, I. Kido, and N. Tanabe, *Seni Gakkaishi*, **28**(9), 343 (1972).
19. Masakatsu Ohguchi, Kikuji Igeta, and Tomahede Yasumura, *Seni Gakkaishi*, **35**(1), 28 (1978).
20. A. K. Tripathy, P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, **26**(6), 2109 (1981).
21. P. L. Nayak, S. Lenka, M. K. Mishra, and A. K. Tripathy, *J. Appl. Polym. Sci.*, **26**, 2773 (1981).
22. I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci. A*, **11**, 2329 (1973).
23. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polym. Sci.*, **31**, 242 (1958).
24. A. A. Katai, V. K. Kulshrestha, and R. H. Maussault, *J. Polym. Sci., Part C2*, 403 (1963).
25. S. Venkatkrishnan and M. Santappa, *Makromol. Chem.*, **27**, 51 (1958).
26. J. Lalitha and M. Santappa, *Vijnana Parishad Anusandhana Patrika, Madras*, **4**, 139 (1961).
27. V. S. Ananthanarayan and M. Santappa, *Ind. J. Chem.*, **2**, 330 (1964).
28. V. S. Ananthanarayan and M. Santappa, *J. Appl. Polym. Sci.*, **9**, 2437 (1965).
29. H. Narita and S. Machida, *Makromol. Chem.*, **97**, 209 (1966).
30. H. Narita, S. Okamoto, and S. Machida, *Makromol. Chem.*, **125**, 15 (1969).
31. H. Narita, S. Okamoto, and S. Machida, *Makromol. Chem.*, **111**, 14 (1968).
32. H. Narita, S. Okamoto, and S. Machida, *Makromol Chem.*, **157**, 153 (1972).
33. A. Y. Kulkarni, A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polym. Sci.*, **7**, 1581 (1963).
34. A. Y. Kulkarni and P. C. Mehta, *J. Polym. Sci., Part B1*, 509 (1963).
35. S. Kaizerman, G. Mino, and F. Meinhold, *Text. Res. J.*, **32**, 136 (1962).
36. Y. Iwakura, T. Kurosaki, K. Uno, and Y. Imai, *J. Polym. Sci., Part C4*, 673 (1964).
37. A. Hebeish and P. C. Mehta, *Cellul. Chem. Technol.*, **8**, 469 (1969).
38. J. C. Arthur, Jr., B. J. Baugh, and O. Hinojosu, *J. Appl. Polym. Sci.*, **10**, 1951 (1966).
39. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. Part A-1*, **5**, 2791 (1967).
40. D. S. Varma and V. Narasimhan, *J. Appl. Polym. Sci.*, **16**, 3325 (1972).
41. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1625 (1968).
42. A. Hebeish and P. C. Mehta, *Text. Res. J.*, **39**, 99 (1969).
43. A. Kantouch, A. Hebeish, and A. Bendak, *Eur. Polym. J.*, **7**, 153 (1971).
44. A. Bendak, A. Kantouch, and A. Hebeish, *Kolr. Ert*, **13**, 1961 (1971).
45. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **75**, 29 (1979).
46. G. M. Braner and D. J. Termini, *J. Appl. Polym. Sci.*, **17**, 2557 (1973).
47. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *J. Polym. Sci. Part A-1*, **9**, 3199 (1971).
48. D. S. Varma and S. Radvisankar, *Angew. Makromol. Chem.*, **28**, 191 (1973).

49. D. S. Varma and N. D. Ray, *Angew. Makromol. Chem.*, **32,** 81 (1973).
50. D. S. Varma and N. D. Ray, *Angew. Makromol. Chem.*, **32,** 163 (1973).
51. A. K. Pradhan, N. C. Pati, and P. L. Nayak, *J. Appl. Polym. Sci.*, to appear.
52. S. Lenka, P. L. Nayak, and A. K. Tripathy, *Angew. Makromol. Chem.*, to appear.

Received July 6, 1981
Accepted October 26, 1981
Corrected proofs received March 23, 1982