

# ***Grafting Vinyl Monomers onto Polyester Fibers. II. Graft Copolymerization of Methyl Methacrylate onto Poly(ethylene Terephthalate) Fibers Using a Pentavalent Vanadium Ion***

## **INTRODUCTION**

Poly(ethylene terephthalate) (PET) fibers are hydrophobic in nature and do not contain chemically reactive groups. Therefore, these fibers are not easily penetrated by dyes of large molecular dimensions and can not combine with dye anions or cations. Certain desirable properties, i.e., dyeability with basic, direct, and other classes of dyes; improvement in antistatic properties; increase in moisture regain, etc., could be imparted to PET fibers by grafting with a number of different hydrophilic and other vinyl monomers.

Graft copolymerization of a monomer to a polyester fiber can be accomplished either by radiation or by chemical initiation. Ionizing radiation like  $\gamma$  rays from a Co-60 source or high-energy electrons from accelerators interact with the polyester fiber and produce radicals, one of which was identified by electron spin resonance<sup>1</sup> as  $-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2-$ . These radical sites initiate grafting by interaction with monomer molecules.

In the chemical initiation method, the active site can be created by oxidizing the polymer hydroperoxide<sup>2-6</sup> at several points along the chain in a random manner and allowing it to decompose into the active form in the presence of the monomer either by heat or via a redox system.

Suzuki and co-workers<sup>7</sup> carried out the grafting of vinyl monomers onto PET fibers using a ceric ion as the initiator. Stannett and co-workers<sup>8-11</sup> studied various aspects of radiation grafting on polymers. Sakurada et al.<sup>12</sup> studied poly(ethylene terephthalate) styrene copolymerization and from the chemical structure found a low degree of grafting of styrene which was attributed to the low sensitivity of polyester to irradiation.

Nyak et al.<sup>13-16</sup> have reported graft copolymerization onto wool, silk, and cellulose using the pentavalent vanadium ion as the initiator.

In this note the authors wish to present the results of graft copolymerization of methyl methacrylate onto PET fibers using a pentavalent vanadium ion as the initiator.

## **EXPERIMENTAL**

Ammonium metavanadate (AR) and sulphuric acid (ca. 18M, AR, BDH) were used. Water distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen used to deaerate the experimental systems was freed from oxygen by passing through five columns of Fieser's solution, a column of saturated lead acetate solution, and finally through a wash bottle containing distilled water.

A stock solution of  $\text{V}^{5+}$  (ca. 0.4N in ca. 4M  $\text{H}_2\text{SO}_4$ ) was prepared by suspending 4.7 g of ammonium metavanadate in 25 ml of distilled water and adding with stirring 75 ml of 10(N) sulphuric acid. The concentration of  $\text{V}^{5+}$  in the experimental systems was determined by vanadometry.

The reaction was carried out in a nitrogen atmosphere in Pyrex flasks equipped with gas inlet and outlet tubes. Dried and purified PET fibers were immersed in a solution of  $\text{V}^{5+}$  ( $1 \times 10^{-3}$ – $15 \times 10^{-3}M$ ) in  $\text{H}_2\text{SO}_4$  ( $1.5 \times 10^{-1}$ – $9.0 \times 10^{-1}M$ ) at temperatures from 50 to 65°C. The required amount of monomer was added to the reaction mixture. After the desired reaction time the PET fibers were taken out and washed thoroughly with water and acetone. Finally, the fibers were Soxhlet extracted with benzene or acetone until the homopolymer was completely removed. They were then dried in an oven, cooled to room temperature, and weighed. The amount grafted was calculated as the percentage increase in weight over the original weight of the sample.

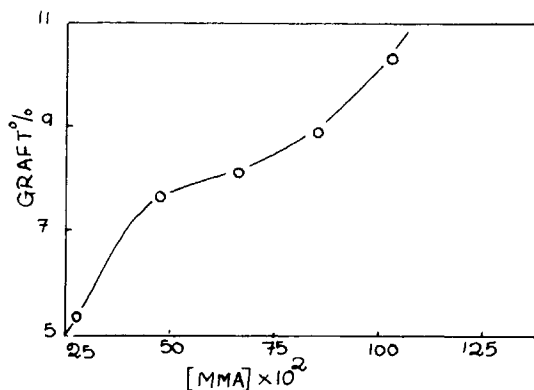


Fig. 1. Effect of monomer concentration of graf yield:  $[V^{5+}] = 5 \times 10^{-3}$ ,  $[H^+] = 0.45$  mol/l;  $T = 60^\circ\text{C}$ ; time = 6 h; M:L = 1:100.

## RESULTS AND DISCUSSION

### Effect of Monomer Concentration

The effect of monomer was studied by varying the concentration from  $27.98 \times 10^{-2}$  to  $103.27 \times 10^{-2}M$  (Fig. 1). The graft yield increased progressively with increasing monomer concentration. The higher rate of grafting observed upon increasing the monomer concentration could be attributed to the following: First, the complexation of PET with monomer required for enhancing monomer activity would be favored at higher monomer concentration; a second factor might be the gel effect.<sup>17</sup>

### Effect of Initiator Concentration

The rate of grafting was investigated by changing  $[V^{5+}]$  within the range  $1 \times 10^{-3}$ – $15 \times 10^{-3}M$  (Fig. 2). The data indicate that with increasing  $[V^{5+}]$  up to  $5 \times 10^{-3}M$ , the percent grafted increases; further increase causes a marked fall in grafting. A possible explanation for these observations might be as follows: At higher concentration of  $V^{5+}$ , the free radical produced on the backbone of the PET fiber might be oxidized to give rise to the oxidation products; hence the graft percentage decreases. Further graft formation and homopolymerization depend on the direct attack of the  $V^{5+}$  ion on PET and monomer. At higher concentrations of  $V^{5+}$ , the metal ions might interact with the monomer

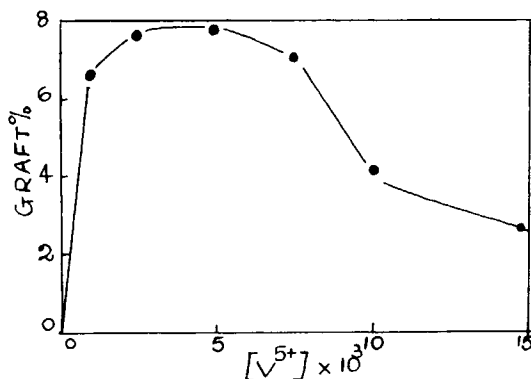


Fig. 2. Effect of vanadium concentration on graft yield:  $[MMA] = 46.94 \times 10^{-2}$ ,  $[H^+] = 0.45$  mol/l;  $T = 60^\circ\text{C}$ ; time = 6 h; M:L = 1:100.

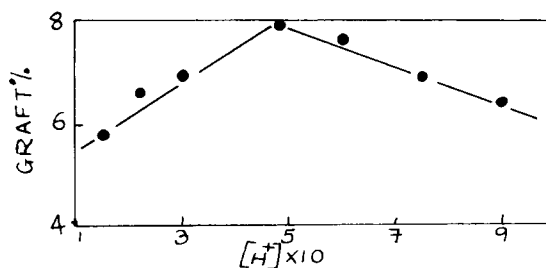
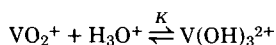


Fig. 3. Effect of acid concentration on graft yield:  $[V^{5+}] = 5 \times 10^{-3}$ ,  $[MMA] = 46.94 \times 10^{-2}$  mol/l;  $T = 60^\circ\text{C}$ ; time = 6 h; M:L = 1:100.

to give rise to a higher amount of homopolymer, thereby decreasing grafting. Similar observations have been reported by Bendak et al.<sup>18</sup> in the case of Ce(IV)-initiated graft polymerization of MMA onto wool fibers.

#### Effect of Acid Concentration

The grafting reaction was carried out by varying  $[H_2SO_4]$  from  $1.5 \times 10^{-1}$ – $9.0 \times 10^{-1}M$  (Fig. 3). The results indicate that the graft percentage increases up to  $4.5 \times 10^{-1}M$  and decreases thereafter. In the initial stages, with the increase in the concentration of  $H_2SO_4$  the following species of  $V^{5+}$  is formed which might interact with PET, producing more free radicals on the PET backbone and hence increasing percentage grafting:



With  $H_2SO_4$  concentration increasing beyond  $4.5 \times 10^{-1}M$ , the less reactive species of  $V^{5+}$  such as  $V(OH)(H_2SO_4)$ ,  $VO.OH^{2+}$ ,  $VO_2SO_4^{3-}$ , etc. might be formed, thereby reducing the oxidizing capacity of the  $V^{5+}$ . Similar explanations have been advanced by Nayak et al.<sup>19</sup> in case of the polymerization of acrylonitrile initiated by a  $V^{5+}$ -thiourea redox system.

#### Effect of Temperature

The graft copolymerization was carried out at four different temperatures ranging from 50 to  $65^\circ\text{C}$  (Fig. 4). The graft yield increases with increase of temperature. The dependence of the rate of

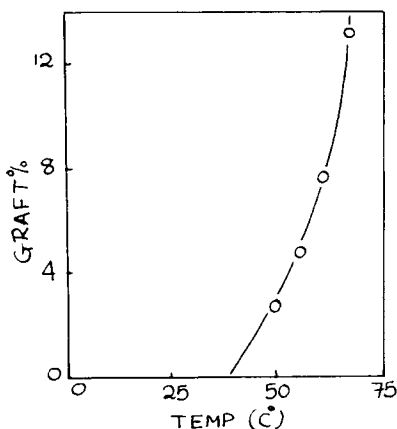


Fig. 4. Effect of temperature on graft yield:  $[V^{5+}] = 5 \times 10^{-3}$ ;  $[MMA] = 46.94 \times 10^{-2}$ ,  $[H^+] = 0.45$  mol/l; time = 6 h; M:L = 1:100.

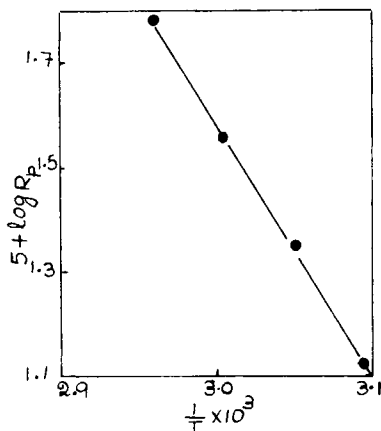


Fig. 5. Arrhenius plot of  $\log R_p$  vs  $1/T$ ;  $R_p$  is the rate of polymerization and  $T$  the absolute temperature.

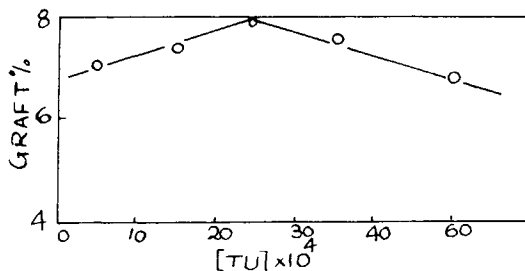


Fig. 6. Effect of thiourea on graft yield:  $[V^{5+}] = 5 \times 10^{-3}$ ,  $[MMA] = 46.94 \times 10^{-2}$ ;  $[H^+] = 0.45$  mol/l;  $T = 60^\circ\text{C}$ ; time = 6 h; M:L = 1:100.

grafting on the increase in temperature could be ascribed to greater activation energy. The swellability of PET, the solubility of monomer, and its diffusion rates are enhanced by increasing the reaction temperature. From the Arrhenius plot (Fig. 5) of  $\log R_p$  vs  $1/T$ , the overall activation energy was found to be 23.0 kcal/mol.

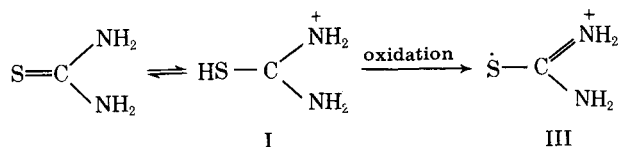
#### Effect of Thiourea Concentration

Graft copolymerization was also investigated by using a  $V^{5+}$ -thiourea redox system where the thiourea concentration was varied from  $5 \times 10^{-4}$ – $50 \times 10^{-4}M$  (Fig. 6). The graft yield increased up to  $25 \times 10^{-4}M$ , and decreased thereafter. Possible reasons for this might be as follows: (i) the increased amount of free-radical inhibitor always present in thiourea, (ii) the fixed amounts of thiourea being converted to isothiurea, which actually participates in producing initiating species, and (iii) at a higher concentration of thiourea some species might be generating and acting as radical scavengers.

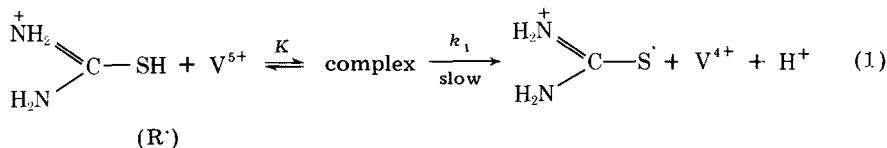
#### MECHANISM

In a system consisting of  $V^{5+}$  ion, sulphuric acid, MMA, thiourea, and PET free-radical formation on the backbone of PET might be explained as follows: In all the initiating systems containing thiourea (I) the redox component is isothiurea (II), a thiol (existing in a tautomeric equilibrium with thiourea in an aqueous solution) as the reductant. The generation of a free radical in this system takes place by the abstraction of the reactive hydrogen atom attached to the sulphur atom in iso-

thiourea generating the amidinosulphenyl free radical (III).



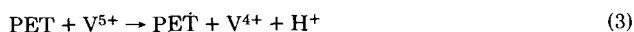
The reaction of thiourea with  $V^{5+}$  is therefore likely to be analogous to that between  $V^{5+}$  and mercaptans. It is likely that  $V^{5+}$  first forms a complex with the isothiourea moiety and that the complex breaks down, giving rise to the amidinosulphenyl free radical



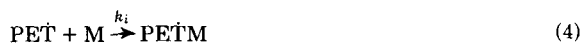
The isothiocarbamido radicals abstract hydrogen from the PET forming PET macroradicals (PET $\dot{\text{T}}$ ):



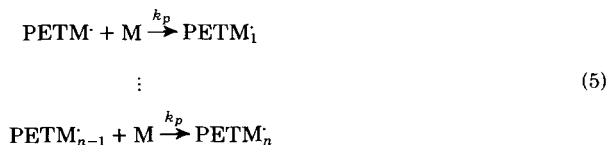
The following reaction scheme may be represented for the graft copolymerization of MMA onto PET:



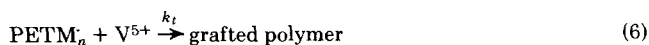
(i) *Initiation:*



(ii) *Propagation:*



(iii) *Termination:*



Here PET represents the polyester fiber; PET $\dot{\text{T}}$  a polyester macroradical; M the monomer; K the equilibrium constant, and  $k_i$ ,  $k_p$ ,  $k_t$  the rate constants.

$$\frac{d[\text{PET}\dot{\text{T}}]}{dt} = k_d[V^{5+}][\text{PET}] - k_i[\text{PET}\dot{\text{T}}][\text{M}] = 0$$

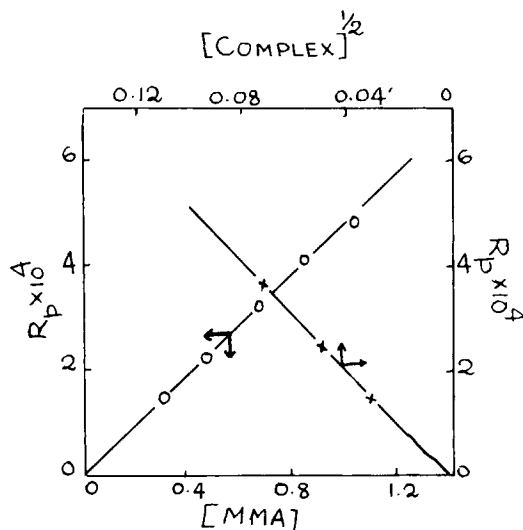
or

$$[\text{PET}\dot{\text{T}}] = \frac{k_d[V^{5+}][\text{PET}]}{k_i[\text{M}]}$$

$$\frac{d[\text{PETM}_n]}{dt} = k_i[\text{PET}\dot{\text{T}}][\text{M}] - k_t[\text{PETM}_n]^2 = 0$$

or

$$\begin{aligned}
 [\text{PETM}_n] &= ((k_i/k_t)[\text{PET}\dot{\text{T}}][\text{M}])^{1/2} \\
 R_p &= k_p[\text{M}][\text{PETM}_n]
 \end{aligned}$$

Fig. 7. Plot of  $R_p$  vs  $[M]$  and  $[V^{5+}]^{1/2}$ .

Substituting the value of  $[PETM_n]$  into the above equation,

$$R_p = k_p (k_d/k_t)^{1/2} [V^{5+}]^{1/2} [PET]^{1/2} [M]$$

Hence the plots of  $R_p$  vs  $[M]$  and  $R_p$  vs  $[V^{5+}]^{1/2}$  were linear (Fig. 7), supporting the above reaction scheme.

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### References

1. D. Campbell, K. Arai, and D. T. Turner, *J. Polym. Sci.*, **A4**, 2597 (1966).
2. V. V. Korshak, K. K. Mozgova, M. A. Shkolina, B. N. Kaorostylev, O. Ya. Lipovetskaya, and A. P. Zasechkina, *Vysokomol. Soedin.*, **4**, 1469 (1962); *Chem. Abstr.*, **59**, 4104 (1963).
3. V. V. Korshak, K. K. Mozgova, and S. P. Krukovskii, *Plast. Massy*, **6**, 9 (1963); *Chem. Abstr.*, **54**, 14755 (1960).
4. V. V. Korshak, K. K. Mozgova, and M. A. Shkolina, *Vysokomol. Soedin.*, **1**, 1604 (1959); *Chem. Abstr.*, **54**, 14755 (1960).
5. P. V. Kozlov, M. M. Iovleva, and N. A. Plate, *Vysokomol. Soedin.*, **1**, 1100 (1959).
6. P. V. Kozlova, M. M. Iovleva, A. Kh. Khakimova, and A. Zenin, *Vysokomol. Soedin.*, **2**, 1575 (1960); *Chem. Abstr.*, **55**, 19323 (1961).
7. K. Suzuki, I. Kido, and N. Tanabe, *Seni Gakkaishi*, **28**, 343 (1972); *Chem. Abstr.*, **77**, 165878 (1972).
8. V. T. Stannett, J. L. Williams, and G. S. P. Verma, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **12**, 504 (1971).
9. K. Ishigure, K. Yoshida, and V. T. Stannett, *J. Macromol. Sci. Chem.*, **7**, 813 (1973).
10. V. Stannett, D. K. Woods, L. G. Roldon, S. B. Sello, and C. V. Stevens, *Text. Res. J.*, **43**, 205 (1973).
11. I. Vlagiu and V. Stannett, *Rev. Roum. Chim.*, **17**, 379 (1972).
12. I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci. A-1*, **11**, 2329 (1973).
13. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **71**, 189 (1978).
14. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **68**, 117 (1978).
15. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Appl. Polym. Sci.*, **22**, 3301 (1978).
16. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, **25**, 1323 (1980).
17. S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phovoc, *J. Polym. Sci.*, **C37**, 57 (1972).

18. A. Kantouch, A. Hebeish, and A. Bendak, *Eur. Polym. J.*, **7**, 153 (1971).
19. B. C. Singh, T. R. Mohanty, and P. L. Nayak, *Eur. Polym. J.*, **12**, 371 (1976).

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