Grafting Vinyl Monomers onto Polyester Fibers. III. Graft Copolymerization of Methyl Methacrylate onto Poly(ethylene Terephthalate) Using Potassium Permanganate–Oxalic Acid Redox System

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Synopsis

The use of the KMnO$_4$—oxalic acid redox system to initiate graft copolymerization of methyl methacrylate (MMA) onto poly(ethylene terephthalate) (PET) fiber has been investigated. The rate of grafting was determined by varying the concentrations of monomer, KMnO$_4$, oxalic acid, acidity of the medium, and temperature. The graft yield increases steadily with increasing KMnO$_4$ concentration. The graft yield is influenced by oxalic acid concentration: it decreases with increasing oxalic acid concentration. The graft yield increases steadily with sulphuric acid concentration. The graft yield is also influenced with temperature. The effect of certain solvents on the rate of grafting has been investigated, and a suitable reaction mechanism has been proposed.

INTRODUCTION

Literature survey reveals that poly(ethylene terephthalate) (PET) fibers are difficult to graft vinyl monomers. However, graft copolymerization reactions onto PET have been carried out either by radiation[1-5] or chemical initiation[6-10] method. Arai et al.[11] have identified the radical to be —CO—C$_6$H$_4$—CO—O—ĊH—CH$_2$— produced by the interaction of γ-rays from a CO-60 source or high energy electron from accelerators by ESR technique. This radical when it reacts with vinyl monomers produces a graft copolymer. Sakurada[12] and co-workers, from the low degree of grafting obtained from styrene polyester copolymers, suggested the low sensitivity of polyester to irradiation.

Permanganate ion coupled with simple water-soluble organic substrates can produce radicals which can initiate vinyl polymerization. Palit and Konar[13-15] and Mishra et al.[16-19] have used a large number of redox systems involving permanganate ion as the initiator. Of all the redox systems, permanganate–oxalic acid was proved to be one of the best initiating system for the polymerization of vinyl monomers.

Nayak and co-workers[20,21] have reported the use of permanganate–oxalic acid redox system for graft copolymerization of methyl methacrylate onto wool and silk fibers. They have also reported graft copolymerization of vinyl monomers onto several other fibers like nylon,[22-24] cellulose,[25-27] and PET,[9,10] using some metal ions. This communication presents the results of the graft copolymer-
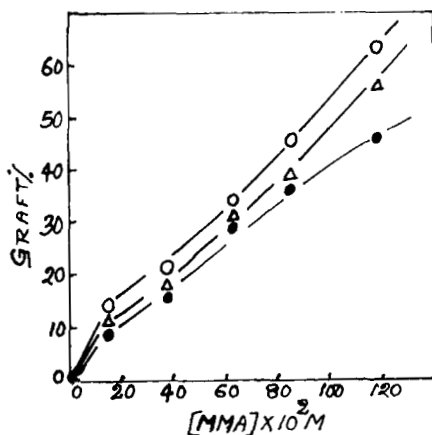
Fig. 1. Effect of [MMA] on graft yield: $[H^+] = 1.5 \times 10^{-1}M$; $[OA] = 2.5 \times 10^{-3}M$; temperature $= 70°C$; time $= 6$ h; M:L $= 1:100$. ($\bullet$) $[KMnO_4] = 5.0 \times 10^{-3}M$; ($\triangle$) $[KMnO_4] = 10.0 \times 10^{-3}M$; ($\bigcirc$) $[KMnO_4] = 15.0 \times 10^{-3}M$.

ization of methyl methacrylate onto PET fibers using the potassium permanganate–oxalic acid redox system.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET) fibers were supplied by J. K. Synthetics, Kota, Rajsthan, India, as a gift sample. Potassium permanganate (AR, Sarabhai Chemicals), H_2SO_4 (AR, $\sim 18M$, BDH), and oxalic acid were used. Purification of methyl methacrylate, the method of graft copolymerization reaction and the calculation of moisture regain percentage etc. were carried out according to our previous communications.[20,24]
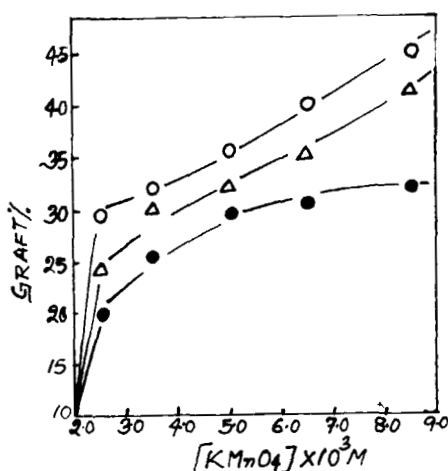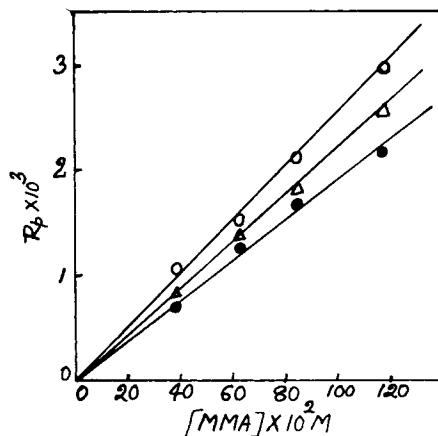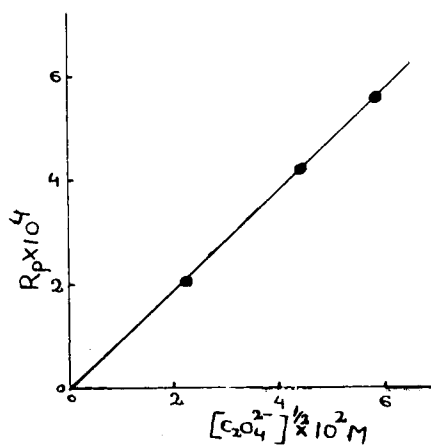

Fig. 2. Effect of [oxidant] on graft yield: $[H^+] = 1.5 \times 10^{-1}M$; $[OA] = 2.5 \times 10^{-3}M$; temperature $= 70°C$; time $= 6$ h; M:L $= 1:100$. ($\bullet$) $[MMA] = 46.94 \times 10^{-2}M$; ($\triangle$) $[MMA] = 70.41 \times 10^{-2}M$; ($\bigcirc$) $[MMA] = 93.88 \times 10^{-2}M$.

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

RESULTS AND DISCUSSION

The graft copolymerization of methyl methacrylate onto PET fibers was carried out at different concentrations of monomer and at three fixed concentrations of initiator, keeping all other reagents constant. The graft on percent was found to increase steadily with the monomer concentration from $14.08 \times 10^{-2}M$ to $117.35 \times 10^{-2}M$ (Fig. 1). The higher rate of grafting observed upon increasing the monomer concentration could be attributed to the following reasons: (a) complexation of PET fibers with monomer (which is favored at higher monomer concentration) and (b) the gel effect,[28] i.e., the increase in the viscosity of the medium due to the solubility of poly(methyl methacrylate) in its own monomer. This causes hinderance in termination particularly by coupling of growing polymer chains. Similar results have been reported by Nayak and co-workers[29] in case of grafting MMA onto silk fiber using quinquevalent vanadium ion.
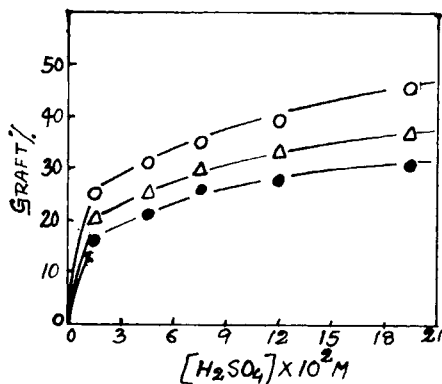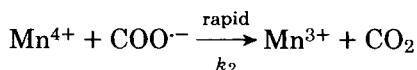

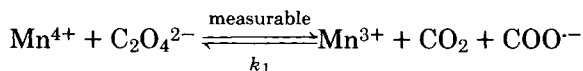Fig. 4. Plot of R_p vs. $[C_2O_4^{--}]^{1/2}$.

Fig. 5. Effect of [H$^+$] on graft yield: [KMnO$_4$] = 5.0 × 10^{-3}M; [OA] = 2.5 × 10^{-3}M; temperature = 70°C; time = 6 h; M:L = 1:100. (●) [MMA] = 46.94 × 10^{-2}M; (△) [MMA] = 70.31 × 10^{-2}M; (○) [MMA] = 93.88 × 10^{-2}M.

Effect of Initiator Concentration

The rate of grafting was investigated by changing potassium permanganate concentration from 2.5 × 10^{-3}M to 8.5 × 10^{-3}M. The result shows that the graft yield progressively increases with the permanganate concentration (Fig. 2). A probable explanation for the above observation might be as follows:

In an initiating system consisting of permanganate, oxalic acid, and sulphuric acid, Mn(IV) interacts with oxalic acid producing carboxyl free radicals (COO$^{·-}$) in the following manner[30]:

$$Mn^{4+} + C_2O_4^{2-} \underset{k_1}{\overset{\text{measurable}}{\rightleftharpoons}} Mn^{3+} + CO_2 + COO^{·-}$$

$$Mn^{4+} + COO^{·-} \underset{k_2}{\overset{\text{rapid}}{\longrightarrow}} Mn^{3+} + CO_2$$

Weiss[31] has suggested that there is also the production of oxalic acid radicals (C$_2$O$_4$$^{·-}$) in such a system as shown below:
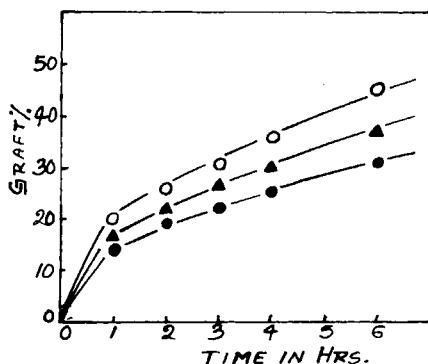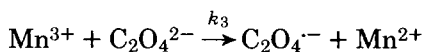
$$Mn^{3+} + C_2O_4^{2-} \overset{k_3}{\rightarrow} C_2O_4^{·-} + Mn^{2+}$$

Fig. 6. Effect of temperature on graft yield: [KMnO$_4$] = 5.0 × 10^{-3}M; [H$^+$] = 1.5 × 10^{-1}M; [OA] = 1.5 × 10^{-3}M; [MMA] = 46.94 × 10^{-2}M; M:L = 1:100; temperature (°C) (●) 50; (▲) 60; (○) 70.

Fig. 7. Arrhenius plot.

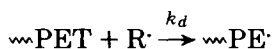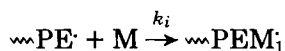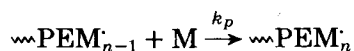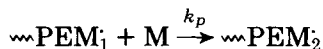The free radicals ($COO^{\cdot-}$ and $C_2O_4^{\cdot-} = R^{\cdot}$) formed by the above mechanism might attack PET fibers, giving rise to PET radicals ($PE^{\cdot}$):

$$\text{\textasciitilde PET} + R^{\cdot} \xrightarrow{k_d} \text{\textasciitilde PE}^{\cdot}$$

(i) Initiation:

$$\text{\textasciitilde PE}^{\cdot} + M \xrightarrow{k_i} \text{\textasciitilde PEM}_1^{\cdot}$$

(ii) Propagation:

$$\text{\textasciitilde PEM}_1^{\cdot} + M \xrightarrow{k_p} \text{\textasciitilde PEM}_2^{\cdot}$$

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

(iii) Termination:

$$\text{\textasciitilde PEM}_n^{\cdot} + \text{\textasciitilde PEM}_n^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$
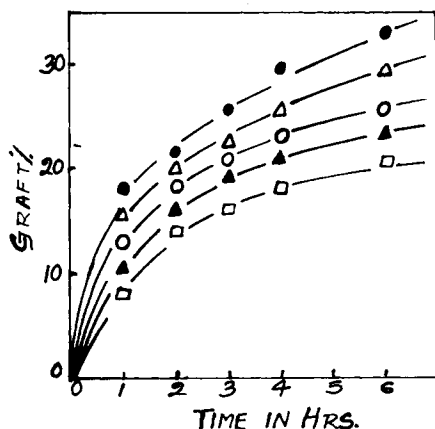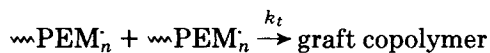

Fig. 8. Effect of solvents on graft yield: $[KMnO_4] = 5.0 \times 10^{-3}M$; $[H^+] = 1.5 \times 10^{-1}M$; [MMA] $= 46.94 \times 10^{-2}M$; [OA] $= 2.5 \times 10^{-3}M$; M:L = 1:100; temperature = 70°C. Solvent: ($\bullet$) acetic acid; ($\triangle$) methanol; ($\circ$) dimethyl formamide; ($\blacktriangle$) chloroform; ($\square$) formic acid.
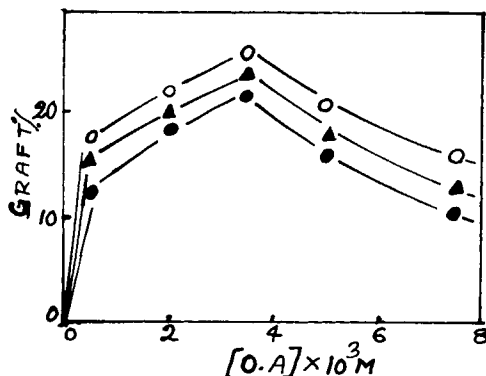
Fig. 9. Effect of [OA] on graft yield: $[KMnO_4] = 5.0 \times 10^{-3}M$; $[H^+] = 1.5 \times 10^{-1}M$; temperature $= 70°C$; M:L = 1:100; time - 6 h; (●) $[MMA] = 46.94 \times 10^{-2}M$; (▲) $[MMA] = 70.41 \times 10^{-2}M$; (○) $[MMA] = 93.88 \times 10^{-2}M$.

Applying the steady state assumption both for [PE·] ánd [PEM·$_n$], the rate expression may be derived as follows:

$$R_p = k_p[PEM_n^·][M]$$

$$= k_p \frac{k_d}{k_t} \left(\frac{k_1}{k_2} + k_3\right)^{1/2} [PE]^{1/2}[C_2O_4{}^{2-}]^{1/2}[M]$$
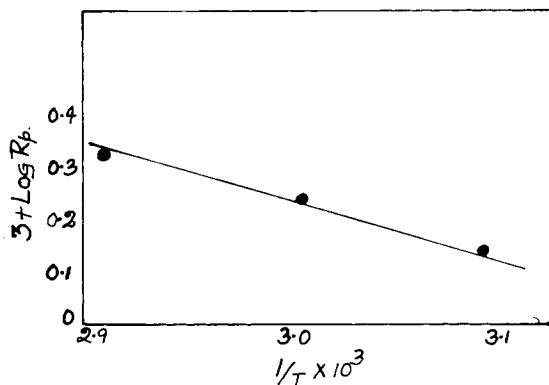
The plots of R_p vs. [M] (Fig. 3) and R_p vs. $[C_2O_4{}^{2-}]^{1/2}$ (Fig. 4) were linear supporting the above reaction mechanism.

Effect of Acid Concentration

The effect of acid concentration was studied by changing the sulphuric acid concentration from $1.5 \times 10^{-2}M$ to $19.5 \times 10^{-2}M$. The results show that the graft yield increases steadily with increasing acid concentration (Fig. 5). Since the effectiveness of permanganate ion is largely determined by the acid concentration, the increase in the concentration of acid increases the oxidizing power of permanganate ion. Hence a larger number of free radicals are produced, thus increasing the graft yield.
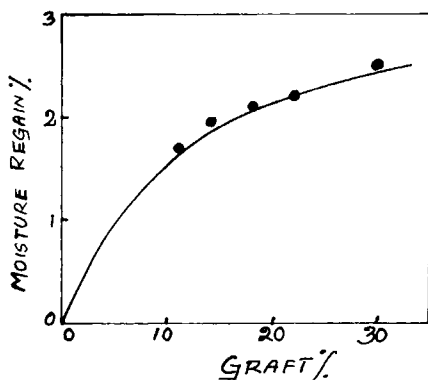

Fig. 10. Plot of graft percentage vs. moisture regain percentage.

Effect of Temperature

In thermal reaction, the temperature plays a vital role. Therefore, it is necessary to study the effect of temperature in polymerization reactions. The graft copolymerization of methyl methacrylate onto PET fibers was studied by varying the temperature from 50°C to 70°C. The result shows that the graft yield progressively increases with the temperature (Fig. 6). This may be due to the greater activation energy. Again, with increasing temperature, the swellability of the fiber and the rate of diffusion of monomer and initiator into the fiber matrix increases, thus enhancing the rate of grafting.

From the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 7), the overall activation energy was computed to be 5 kcal/mol.

Effect of Solvents

Figure 8 shows the effect of addition of different solvents on the graft copolymerization of methyl methacrylate onto PET fibers. For the solvents studied the graft yield follows the order:

<div align="center">

acetic acid > methanol > dimethyl formamide >

chloroform > formic acid

</div>

Since the solvents differ in their capability of swelling the fiber, miscibility with monomer, formation of a solvent radical from the primary radical species of the initiating system, contribution of the solvent radical in the activation of polyester fibers (PET), and termination of the graft radical and polyester macroradical via chain transfer, there is a variation in graft yield with the solvents used.[32]

Effect of Oxalic Acid Concentration

The effect of oxalic acid concentration was varied from $0.5 \times 10^{-3}M$ to $7.5 \times 10^{-3}M$. There is an increase in graft yield with the increase of oxalic acid concentration up to $3.5 \times 10^{-3}M$, and thereafter it decreases (Fig. 9). The decrease in graft yield at higher oxalic acid concentration could be due to the formation of a large amount of homopolymer.

Moisture Regain

The percent of moisture regain was found to increase with increasing the percentage of grafting (Fig. 10). This may be explained by considering the fact that introduction of the grafted chains open up the PET structure, thus offering more room for water accomodation.

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