

# Grafting Vinyl Monomers onto Polyester Fibers. I. Graft Copolymerization of Methyl Methacrylate onto PET Using Hexavalent Chromium

## INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers do not contain chemically reactive groups. Hence, this material cannot combine with dye cations and anions. Certain desirable properties (e.g., improved dyeability, antistatic properties, improved water absorbancy) can be imparted to PET fibers by grafting with vinyl monomers.

Literature study reveals that Sakurada and Kawahara<sup>1</sup> investigated the radiation-induced grafting of styrene onto PET. Suzuki et al.<sup>2</sup> carried out the grafting of vinyl monomers onto PET by ceric sulfate in nitrogen atmosphere. Nayak et al.<sup>3-5</sup> studied the redox polymerization of hexavalent chromium and graft copolymerization of methyl methacrylate onto wool<sup>6</sup> and silk<sup>7</sup> using  $\text{Cr}^{6+}$  as the initiator.

The present note represents the study of the graft copolymerization of methyl methacrylate onto PET using hexavalent chromium ion.

## EXPERIMENTAL

PET was supplied by J. K. Synthetics, Kota, India, as a gift sample. Potassium dichromate (AR Sarabhai M. Chemicals), perchloric acid (GR E. Merck 60%), and methyl methacrylate (Lab. Chem. Co., India) were used. The graft copolymerization was carried out according to our previous procedure.<sup>7</sup> The graft yield was calculated as the percent increase in weight over the original weight of the fiber.

## RESULTS AND DISCUSSION

The effect of perchloric acid concentration on grafting was investigated by varying the concentrations from  $9.33 \times 10^{-2}$  mole/l. to  $69.97 \times 10^{-2}$  mole/l. It was observed that the percent of grafting increases with increasing acid concentration up to  $23.32 \times 10^{-2}$  mole/l. and that it decreases thereafter. A similar observation was made by Nayak et al.<sup>7</sup> while grafting MMA onto silk. With increasing monomer concentration, from  $27.98 \times 10^{-2}$  mole/l. to  $103.27 \times 10^{-2}$  mole/l., the graft yield increases. The effect of  $\text{Cr}^{6+}$  concentration from  $8.33 \times 10^{-4}$  –  $58.31 \times 10^{-4}$  mole was also studied: With increase in  $\text{Cr}^{6+}$  concentration, the rate of grafting increases. This finding could be explained

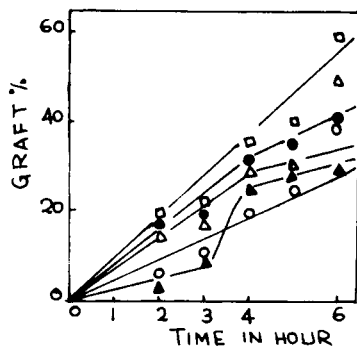


Fig. 1. Effect of [TU] on graft yield:  $[\text{Cr}^{6+}] = 58.31 \times 10^{-4}$  mole/l.;  $[\text{HClO}_4] = 23.32 \times 10^{-2}$  mole/l.  $[\text{MMA}] = 46.94 \times 10^{-2}$  mole/l.; temp. =  $60^\circ\text{C}$ ;  $M:L = 1:100$ ; (O)  $[\text{TU}] = 5 \times 10^{-4}$  mole/l.; ( $\Delta$ )  $[\text{TU}] = 15 \times 10^{-4}$  mole/l.; ( $\square$ )  $[\text{TU}] = 25 \times 10^{-4}$  mole/l.; ( $\bullet$ )  $[\text{TU}] = 35.0 \times 10^{-4}$  mole/l.; ( $\blacktriangle$ )  $[\text{TU}] = 50 \times 10^{-4}$  mole/l.

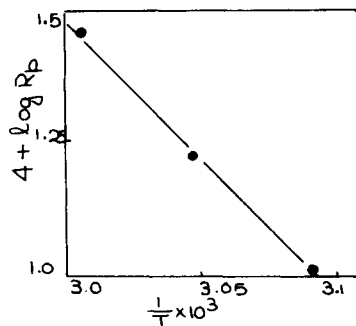
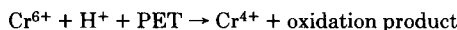


Fig. 2. Arrhenius plot of  $\log R_p$  vs.  $1/T$ :  $[\text{Cr}^{6+}] = 58.31 \times 10^{-4}$  mole/l.;  $[\text{HClO}_4] = 23.32 \times 10^{-2}$  mole/l.  $[\text{MMA}] = 46.94 \times 10^{-2}$  mole/l.; time = 2 hr;  $M:L = 1:100$ .

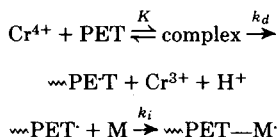
by the fact that with increasing  $\text{Cr}^{6+}$  concentration, more PET macroradicals are formed and hence the rate of grafting increases.

The graft copolymerization was also studied using the  $\text{Cr}^{6+}$ -thiourea redox system (Fig. 1). Thiourea concentration was varied from  $5 \times 10^{-4}M$  to  $50 \times 10^{-4}M$ . With increase of thiourea concentration graft yield increases up to  $25.0 \times 10^{-4}M$  and thereafter it decreases. The grafting reaction was carried out at four different temperatures ranging from  $50$ – $65^\circ\text{C}$ . The graft yield increases with increasing temperature. Similar observations have been reported by Nayak et al.<sup>7</sup> From the Arrhenius plot of  $\log R_p$  vs.  $1/T$  (Fig. 2) the overall activation energy was found to be  $24.50$  kcal/mole.

### MECHANISM



Initiation:



Propagation:

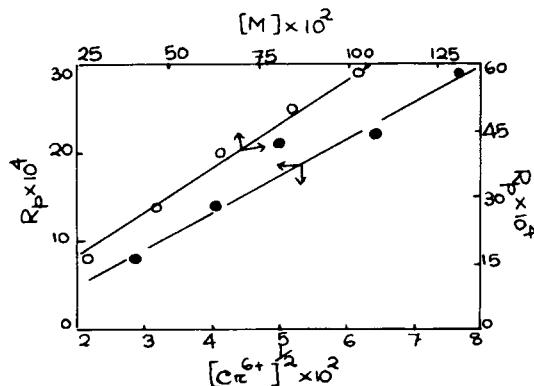
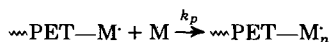
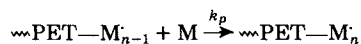
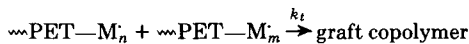


Fig. 3. Lower line: plot of  $R_p$  vs.  $[\text{Cr}^{6+}]^{1/2}$ ;  $[\text{HClO}_4] = 23.32 \times 10^{-2}$  mole/l.;  $[\text{MMA}] = 46.94 \times 10^{-2}$  mole/l.; temp. =  $60^\circ\text{C}$ ; time = 2 hr;  $M:L = 1:100$ . Upper line: plot of  $R_p$  vs.  $[\text{MMA}]$ ;  $[\text{Cr}^{6+}] = 58.31 \times 10^{-4}$  mole/l.;  $[\text{HClO}_4] = 23.32 \times 10^{-2}$  mole/l.; temp. =  $60^\circ\text{C}$ ; time = 2 hr;  $M:L = 1:100$ .



Termination:



Considering the steady-state principle, the rate of polymerization was found to be

$$R_p = \frac{k_p K^{1/2} k_t^{1/2}}{k_t^{1/2}} [\text{Cr}^{6+}]^{1/2} [\text{M}] [\text{PET}]$$

The plots of  $R_p$  vs.  $[\text{Cr}^{6+}]^{1/2}$  and  $R_p$  vs.  $[\text{M}]$  (Fig. 3) are linear, supporting the above scheme.

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