Graft Copolymerization of Methyl Methacrylate onto Poly(ethylene Terephthalate) Fibers Using Thallium(III) Ions as Initiator

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Synopsis

Graft copolymerization of methyl methacrylate onto poly(ethylene terephthalate) fibers was investigated in aqueous perchloric acid medium using thallium(III) ions as initiator. The rate of grafting was evaluated varying the concentrations of monomer, initiator, and acid and the temperature. The rate of grafting was found to increase with increase in monomer and initiator concentrations. The graft yield was found to increase with increase in the acid concentration up to 0.49 mL^{-1}, and beyond this concentration it was found to decrease. Increase in temperature resulted in increase in graft yield. From the Arrhenius plot the overall activation energy was found to be 3.76 kcal/mol. The effect of additives such as swelling agents, inorganic salts, different solvents, and inhibitors on graft yield was studied. A suitable kinetic scheme is proposed and a rate equation derived.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are hydrophobic in nature and do not contain chemically reactive groups. These fibers are therefore not easily penetrated by dyes of large molecular dimension and cannot combine with dye anions or cations. Certain desirable properties such as 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 onto it a number of different hydrophilic and other vinyl monomers.

Various methods are available for graft copolymerization of vinyl monomers onto PET fibers. These include activation of the fiber either through radiation or by chemical initiation. Ionizing radiations such as γ-rays from a ^{60}Co source or high-energy electrons from accelerators interact with the PET fibers and produce radicals, one of which was identified by ESR[1] to be —CO—C_6H_4—CO—O—ĊH—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[2-6] 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 by heat.

Suzuki and co-workers[7] carried out the grafting of vinyl monomers onto PET fibers by using ceric ion as the initiator. Stannet and co-workers[8-11] studied various aspects of radiation grafting on polymers. Sakurada and Kawahara[12] studied the PET–styrene copolymerization and from the chemical structure found a low degree of grafting of styrene which was attributed to low sensitivity of PET to irradiation.
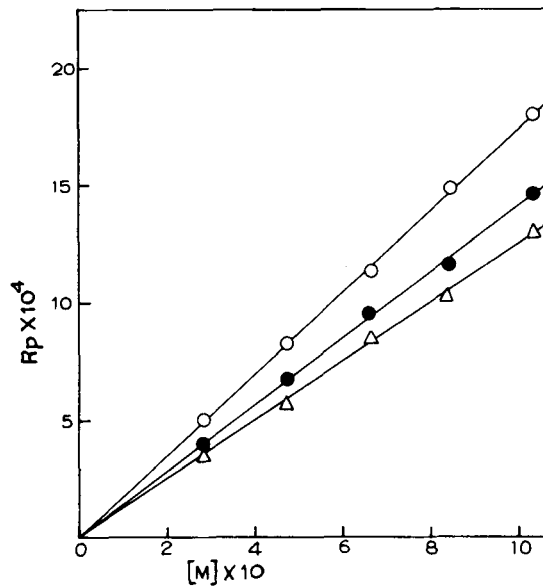
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Fig. 1. Effect of monomer concentration on rate of grafting: $[HClO_4] = 4.75 \times 10^{-1}$ mL^{-1}; [ether] = 2.5% v/v; time = 6 h; temperature = 70°C; M:L = 1:100; (△) $[Tl^{3+}] = 4.08 \times 10^{-3}$ mL^{-1}; (●) $[Tl^{3+}]$ = 8.16×10^{-3} mL^{-1}; (○) $[Tl^{3+}] = 12.24 \times 10^{-3}$ mL^{-1}.

Recently, we have for the first time extensively studied the homopolymerization[13] and graft copolymerization[14] of vinyl monomers initiated by thallium(III) ions in aqueous perchloric acid medium. So far, no studies have been made on grafting vinyl monomers onto PET fibers using thallium(III) ions as initiator. This communication presents the results of studies on grafting methyl
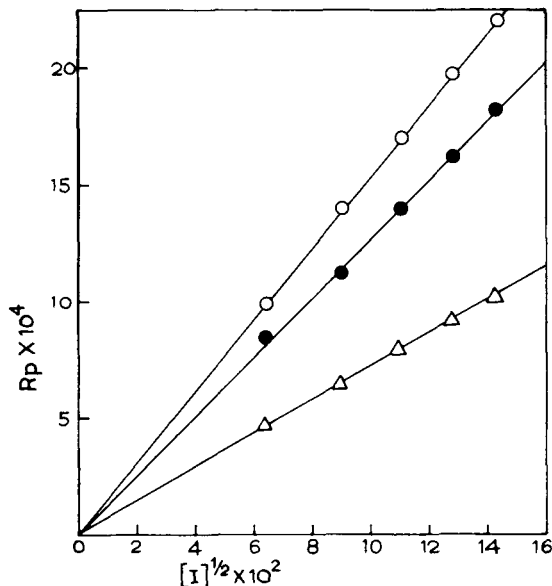

Fig. 2. Effect of initiator concentration on rate of grafting: $[HClO_4] = 1.2$ mL^{-1}; [ether] = 2.5% v/v; time = 6 h; temperature = 70°C; M:L = 1:100; (△) [MMA] = 4.694×10^{-1} mL^{-1}; (●) [MMA] = 7.041×10^{-1} mL^{-1}; (○) [MMA] = 9.388×10^{-1} mL^{-1}.

methacrylate onto poly(ethylene terephthalate) using thallium(III) ions as initiator.

EXPERIMENTAL

Identical experimental procedures as described in our earlier communication[14] were followed for purification of the fiber, for preparation and estimation of thallium(III) perchlorate solution, for purification of the monomer and other chemicals, and for graft copolymerization reactions.

RESULTS AND DISCUSSION

The factors influencing the graft copolymerization of methyl methacrylate onto PET fibers initiated by thallium(III) perchlorate were investigated. Variables studied included monomer concentrations, initiator concentrations, acid concentrations, and temperature.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration in the range $28.16-103.26 \times 10^{-2} \, mL^{-1}$. The rate of grafting was found to increase with increase of the monomer concentration

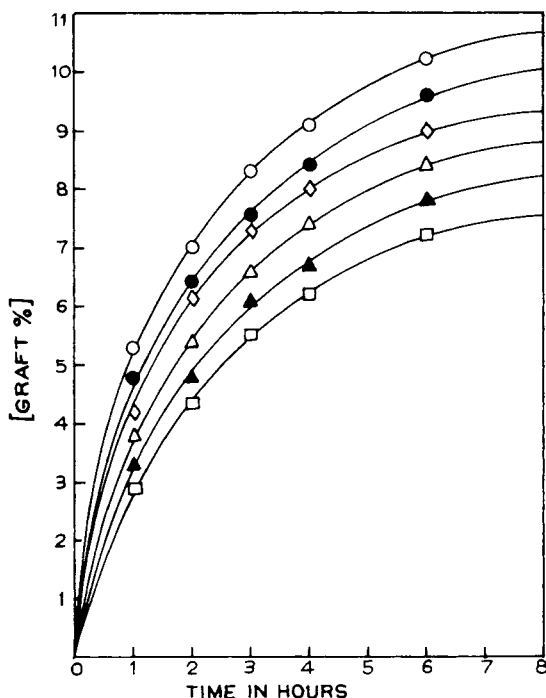Fig. 3. Effect of acid concentration on graft yield: $[MMA] = 4.694 \times 10^{-1} \, mL^{-1}$; $[Tl^{3+}] = 3.26 \times 10^{-3} \, mL^{-1}$; [ether] = 2.5% v/v; temperature = 70°C; M:L = 1:100; ($\square$) $[HClO_4] = 1.90 \times 10^{-1} \, mL^{-1}$; ($\triangle$) $[HClO_2] = 2.90 \times 10^{-1} \, mL^{-1}$; ($\bullet$) $[HClO_4] = 3.90 \times 10^{-1} \, mL^{-1}$; ($\circ$) $[HClO_4] = 4.90 \times 10^{-1} \, mL^{-1}$; ($\diamond$) $[HClO_4] = 5.90 \times 10^{-1} \, mL^{-1}$; ($\blacktriangle$) $[HClO_4] = 6.90 \times 10^{-1} \, mL^{-1}$.
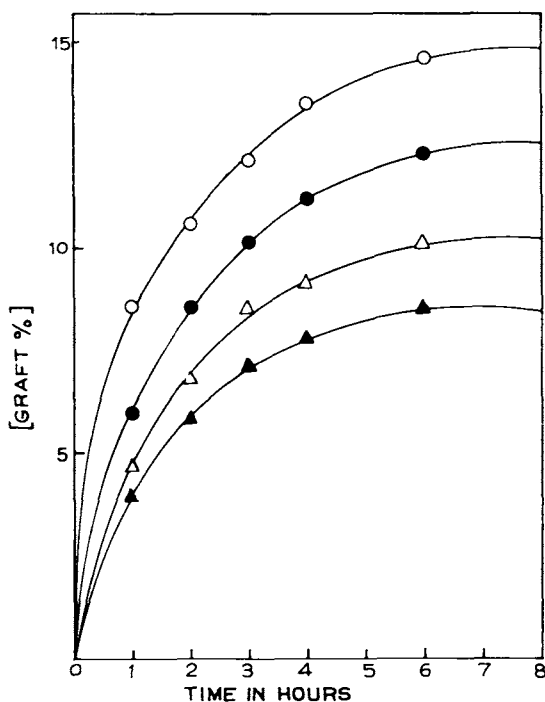
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Fig. 4. Effect of temperature on graft yield: [MMA] = 4.694 × 10^{-1} mL^{-1}; [Tl^{3+}] = 8.16 × 10^{-3} mL^{-1}; [HClO$_4$] = 4.75 × 10^{-1} mL^{-1}; [ether] = 2.5% v/v; M:L = 1:100; (▲) temperature = 40°C; (●) temperature = 60°C; (△) temperature = 50°C; (○) temperature = 70°C.

(Fig. 1). Several explanations can be offered to account for the higher rate of grafting observed upon increasing the monomer concentration. First, complexation of PET with monomer would be favored at higher monomer concentrations. Secondly, the gel effect[15] would be more pronounced at high monomer concentrations. This causes hindrance in termination, particularly by coupling of the growing polymer chains. The gel effect also causes swelling of PET, thus facilitating diffusion of the monomer to growing chains and active sites on PET skeleton, thereby enhancing grafting. Lastly, some species which are either present or generated during the polymerization reaction act as efficient radical scavenger. Competition between this and the monomer in capturing the free PET radical plays the key role in the amount of graft formation. It is likely that capture of PET radicals by monomer predominates at high monomer concentrations.

Effect of Initiator Concentration

The effect of thallium(III) concentration on grafting was investigated by changing the initiator concentration in the range 4.08–20.40 × 10^{-3} mL^{-1} at fixed concentrations of all other reagents. The data indicate that increase in initiator concentration increases the rate of grafting (Fig. 2). This is explained by assuming that more free radicals are formed at high initiator concentrations, thus increasing the rate of grafting.
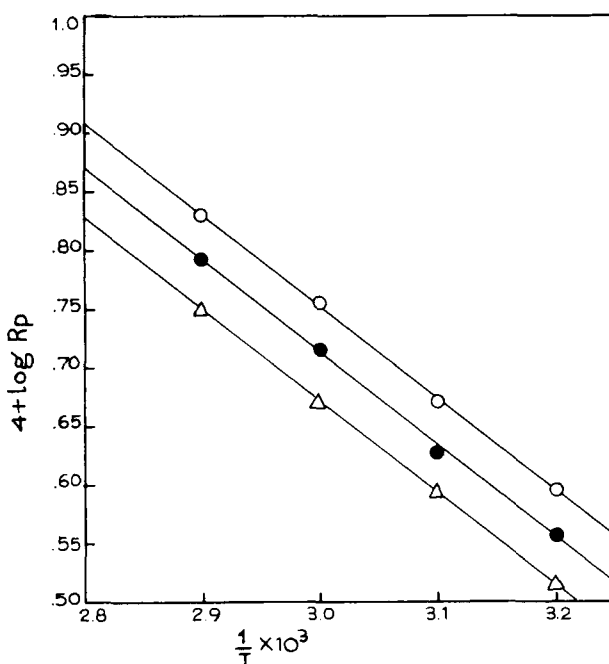
Fig. 5. Arrhenius plot of log R_p vs. $1/T$: ($\triangle$) 3 h; ($\bigcirc$) 6 h; ($\bullet$) 4 h.

Effect of Acid Concentration

Acid is essential when thallium(III) is used as an initiator, as in the absence of the acid thallic perchlorate is hydrolyzed and subsequently converted to black thallic oxide. It is therefore interesting to study the effect of acid concentration on graft yield. The graft copolymerization reaction was carried out in aqueous perchloric acid medium, and the acid concentration was varied from 0.19 to 0.69 mL^{-1} at fixed concentrations of all other reagents. The graft yield was found to increase with increase in the acid concentration up to 0.49 mL^{-1}; and beyond this concentration of perchloric acid, the graft yield was found to decrease (Fig. 3). The enhancement of the rate of grafting observed upon increasing the acid concentration may be due to the increased activity of thallic perchlorate at high perchloric acid concentrations. Subsequent decrease in the percentage of grafting may be due to the recombination and disproportionation of the graft macroradical.

Effect of Temperature

The effect of temperature on the graft copolymerization reaction was studied in the range 40–70°C. It was observed that increase in temperature resulted in increase in graft percentage (Fig. 4). The increase in graft percentage can be ascribed to the increased activity of Tl^{3+} at high temperatures. The increase may also be due to the greater activation energy, increased swellability of the fiber, and higher rate of diffusion of the monomer.

From the Arrhenius plot of log R_p vs. $1/T$ (Fig. 5), the overall activation energy was calculated to be 3.76 kcal/mol.
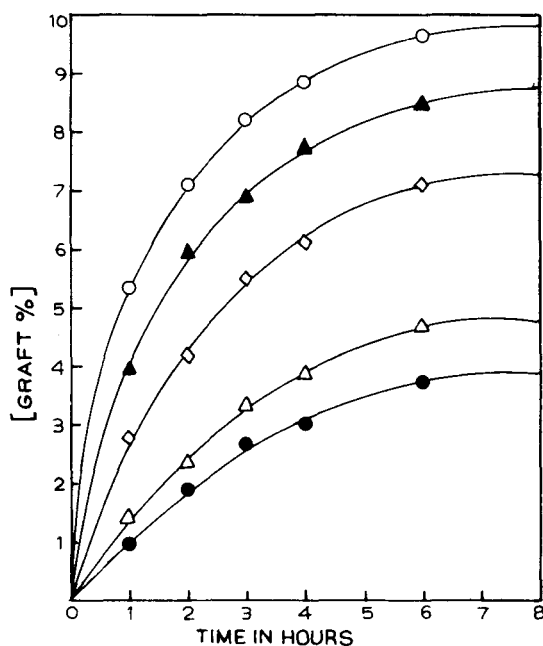
Fig. 6. Effect of solvents on graft yield: $[MMA] = 4.694 \times 10^{-1}$ mL^{-1}; $[Tl^{3+}] = 8.16 \times 10^{-3}$ mL^{-1}; $[HClO_4] = 1.2$ mL^{-1}; [ether] $= 2.5\%$ v/v; [solvent] $= 25\%$ v/v; temperature $= 70°C$; M:L $= 1:100$; (O) methanol; ($\triangle$) chloroform; ($\blacktriangle$) ethanol; ($\bullet$) carbon tetrachloride; ($\diamond$) amyl alcohol.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting vinyl monomers onto PET. The effect of different types of solvents, such as alcoholic solvents and chain transfer solvents on graft yield was investigated. With alcoholic solvents (Fig. 6), the order of graft yield is

<center>methanol > ethanol > amyl alcohol</center>

With chain transfer solvents (Fig. 6), the order is

<center>chloroform > carbon tetrachloride</center>

The dependence of graft yield on the nature of the solvents suggests that the solvents examined differ considerably in their (1) capability of swelling PET, (2) miscibility with monomer, (3) formation of solvent radicals from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of PET, and (5) termination of the graft chain radical via chain transfer. While the first four factors favor grafting, the last factor affects grafting adversely.

Effect of Inorganic Salts

The graft copolymerization onto PET was carried out in the presence of different added salts, and it was observed (Fig. 7) that the graft yield followed the order

copper sulfate > magnesium sulfate > lithium nitrate
<div align="right">> sodium fluoride > manganese sulfate</div>
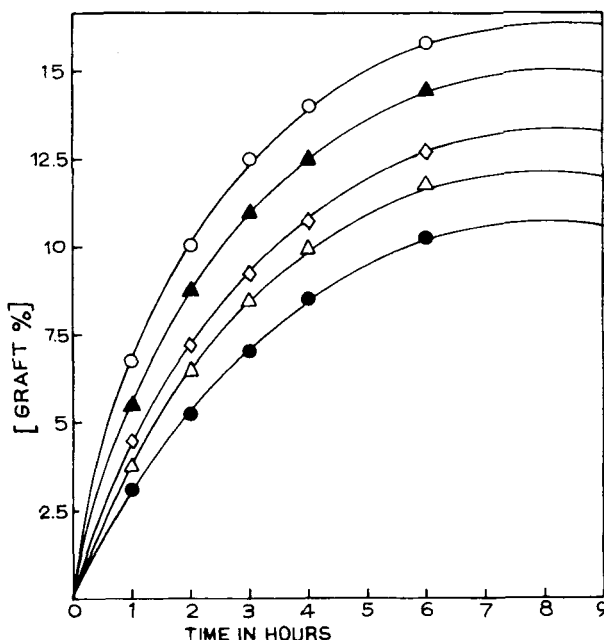
Fig. 7. Effect of inorganic salts on graft yield: $[HClO_4] = 0.525$ mL^{-1}; $[Tl^{3+}] = 8.16 \times 10^{-3}$ mL^{-1}; $[MMA] = 4.694 \times 10^{-1}$ mL^{-1}; [ether] = 2.5% v/v; [salt] = 0.1×10^{-1} mL^{-1}; temperature = 70°C; M:L = 1:100; (O) copper sulfate; ($\triangle$) sodium fluoride; ($\blacktriangle$) magnesium sulfate; ($\bullet$) manganese sulfate; ($\diamond$) lithium nitrate.

The increase or decrease of the graft yield may be due to catalysis or inhibition of the propagation step by the added salt.
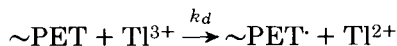
Effect of Inhibitors

Effect of different inhibitors such as picryl chloride and hydroquinone on the graft yield was studied (Fig. 8). It was observed that the graft yield was greatly suppressed in the presence of either inhibitor. The inhibiting efficiency of picryl chloride was found to be more than that of hydroquinone. It was also observed that the extent of inhibition increased with increase in the concentration of the inhibitor. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby reducing the molecular size of the graft, hence reducing the graft yield.
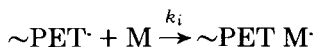
MECHANISM

The following mechanism has been suggested for the graft copolymerization of methyl methacrylate onto PET using thallium(III) as initiator:
Production of Free Radical on PET:

$$\sim PET + Tl^{3+} \xrightarrow{k_d} \sim PET^{\cdot} + Tl^{2+}$$

where PET$^{\cdot}$ is PET macroradical.
Initiation:

$$\sim PET^{\cdot} + M \xrightarrow{k_i} \sim PET\ M^{\cdot}$$
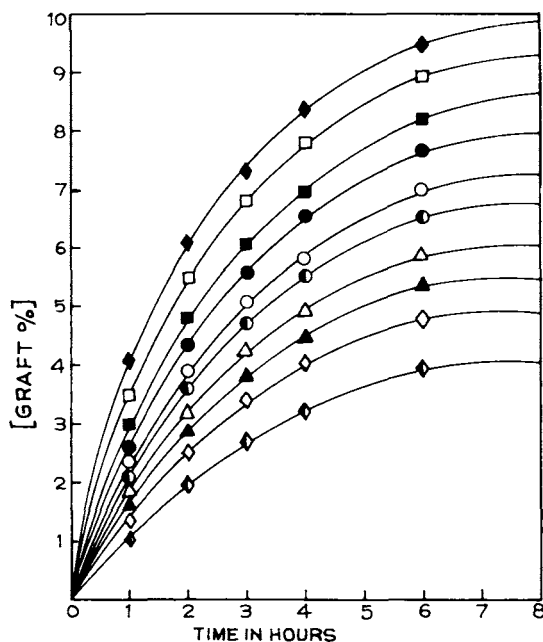
Fig. 8. Effect of inhibitors on graft yield: $[HClO_4]$ = 0.525 mL^{-1}; $[Tl^{3+}]$ = 8.16 × 10^{-3} mL^{-1}; [MMA] = 4.694 × 10^{-1} mL^{-1}; [ether] = 2.5% v/v; temperature = 70°C; M:L = 1:100; (♦) [hydroquinone] = 5 × 10^{-5} mL^{-1}; (■) [hydroquinone] = 10 × 10^{-5} mL^{-1}; (O) [hydroquinone] = 15 × 10^{-5} mL^{-1}; (△) [hydroquinone] = 20 × 10^{-5} mL^{-1}; (◊) [hydroquinone] = 25 × 10^{-5} mL^{-1}; (□) [picryl chloride] = 5 × 10^{-5} mL^{-1}; (●) [picryl chloride] = 10 × 10^{-5} mL^{-1}; (◉) [picryl chloride] = 15 × 10^{-5} mL^{-1}; (▲) [picryl chloride] = 20 × 10^{-5} mL^{-1}; (♦) [picryl chloride] = 25 × 10^{-5} mL^{-1}.

where M is monomer.

Propagation:

$$\sim\!PET\ M\!\cdot + M \xrightarrow{k_p} \sim\!PET\ M_2^{\cdot}$$

$$\sim\!PET\ M_{n-1}^{\cdot} + M \xrightarrow{k_p} \sim\!PET\ M_n^{\cdot}$$

Termination:

$$\sim\!PET\ M_n^{\cdot} + \sim\!PET\ M_n^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$
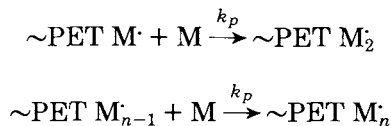
Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

$$-\frac{d[PET\!\cdot]}{dt} = k_d[Tl^{3+}][PET] - k_i[PET\!\cdot][M] = 0$$

$$[PET\!\cdot] = \frac{k_d[Tl^{3+}][PET]}{k_i[M]}$$

$$-\frac{d[PET\ M_n^{\cdot}]}{dt} = k_i[PET\!\cdot][M] - k_t[PET\ M_n^{\cdot}]^2 = 0$$

$$[PET\ M_n^{\cdot}] = \left\{\frac{k_i[PET\!\cdot][M]}{k_t}\right\}^{1/2}$$

Substituting the value of [PET·] in the above equation,

$$[\text{PET M}_n^{\cdot}] = \left\{ \frac{k_d[\text{Tl}^{3+}][\text{PET}]}{k_t} \right\}^{1/2}$$

Then

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

or

$$R_p = k_p \left[\frac{k_d}{k_t} \right]^{1/2} [\text{PET}]^{1/2}[\text{Tl}^{3+}]^{1/2}[\text{M}]$$

The plots of R_p vs. [M] (Fig. 1) and R_p vs. [initiator]$^{1/2}$ (Fig. 2) are linear passing through the origin, which confirm the validity of the above reaction scheme.

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