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Grafting Vinyl Monomers onto Poly(ethylene Terephthalate) (PET). IV. Graft Copolymerization of Methyl Methacrylate onto PET Fibers Using Acetyl Acetonate Complexes of Mn(III), Co(III), and Fe(III)

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ABSTRACT

The graft copolymerization of methyl methacrylate onto poly(ethylene terephthalate) using metal complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} as initiators was studied. The rate of polymerization, R_p, increased with increasing complex concentrations. The rate of polymerization was also studied by varying monomer concentrations. Increasing monomer concentrations, the rate of polymerization increases significantly. The graft yield increases with increasing temperature within the range 60-75°C. The graft yield is medium dependent. A suitable kinetic scheme has been pictured and rate equations have been derived.

INTRODUCTION

Polyethylene terephthalate (PET) is a linear polyester consisting of the repeating ester groups, –C(=O)–O–. Besides the highly crystalline nature and hydrophobic character, PET fibers do not contain chemically reactive groups. Therefore, dyes of large molecular dimensions cannot easily penetrate this material and hence PET fibers do not combine easily with dye anions and cations.

Grafting reactions on fibers can bring about a variety of chemical property changes, depending on the nature of the monomers used for grafting. Therefore, it is necessary to modify the fiber to improve certain basic properties such as dyeability; antistatic properties; ultraviolet stabilization; increase in moisture regain; increase in soil, weather, and alkali resistance; and flame proofing. A number of workers have used radiation [1-6] and chemical [7] methods for grafting vinyl monomers onto PET fiber. A multitude of vinyl monomers such as styrene [8-10], 4-vinyl pyridine [11], acrylonitrile [13], acrylate esters [14-16], acrylamide [17-20], acrylic and methacrylic acids [21-26], vinyl acetate [27], and N-vinyl-3-morpholinone [28] have been used for grafting PET fibers. In both the radiation and chemical methods of grafting, the homopolymer of the vinyl monomer is also to be expected and often can be suppressed by suitable additives.

Recently, the use of metal chelates with O,O donor atoms in the ligand molecule has attracted attention [29] for initiating vinyl polymerization. Among the metal chelates, acetyl acetonate complexes of such transitional elements as Mn^{3+}, Co^{3+}, and Fe^{3+} are found to be most effective. Nayak and Lenka have used acetyl acetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} for grafting vinyl monomers onto nylon 6 [30]. This communication presents the results of the graft copolymerization of methyl methacrylate onto PET fibers using acetyl acetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+}.

EXPERIMENTAL

Poly(ethylene terephthalate) fibers were supplied by J. K. Synthetics, Kota, Rajsthan, India, as a gift sample. The acetyl acetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} were prepared according to the literature procedure [31, 32]. The graft copolymerization was carried out according to our previous methods [33-36].

RESULTS AND DISCUSSION

Polymerization of methyl methacrylate initiated by the acetylacetonate complexes of Mn^{3+}, Co^{3+} and Fe^{3+} was noticed to bring about an enhancement in the weight of these fibers even after extracting the fiber several times with benzene or acetone, which is a solvent for PMMA. The increase in weight is most probably due to the incorporation of the vinyl polymer into the matrix of the PET fiber. The mechanism of grafting of the methyl methacrylate onto these fibers

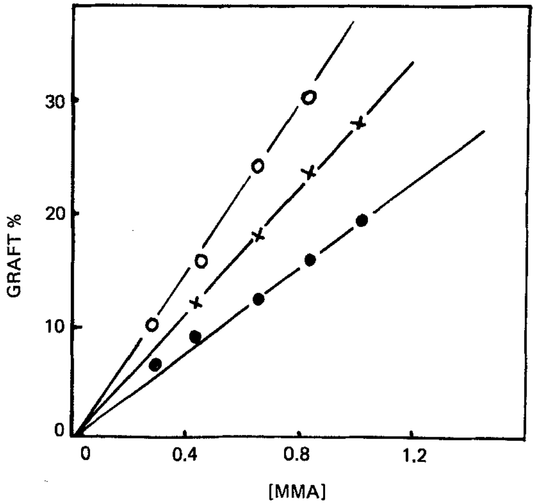


FIG. 1. Effect of [monomer]. (○) [$Mn(acac)_3$] = 7.70 × 10^{-2} M, [$HClO_4$] = 3.72 × 10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100. [$Co(acac)_3$] = 7.50 × 10^{-4} M, [H_2SO_4] = 7.50 × 10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100. (●) [$Fe(acac)_3$] = 3.75 × 10^{-4} M, [H_2SO_4] = 15.0 × 10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100.

is most probably by the vinyl addition to PET macroradical formed by the interaction of metal chelates with the fiber matrix.

Monomer Concentration

The graft copolymerization of methyl methacrylate onto polyester fibers (PET) was carried out at different concentrations of monomer and at three fixed concentrations of initiator keeping all other reagents constant (Fig. 1). It can be seen that the rate of grafting increases significantly as the concentration of methyl methacrylate increases. This, indeed, substantiates the assumption of gel effect. Besides hindering the termination of the growing polymer chain radicals by coupling, the gel effect perhaps causes swelling of poly(ethylene terephthalate) fiber, thus assisting diffusion of monomer to the growing grafted chains, and active sites on the PET backbone, thereby enhancing grafting.

In the initial stages a complex might be formed between PET and MMA molecules. The probability of the formation of this complex is favored at higher monomer concentrations. Complexation of PET with the monomer activated the latter through the formation of a donor-acceptor complex in which the uncomplexed MMA, though

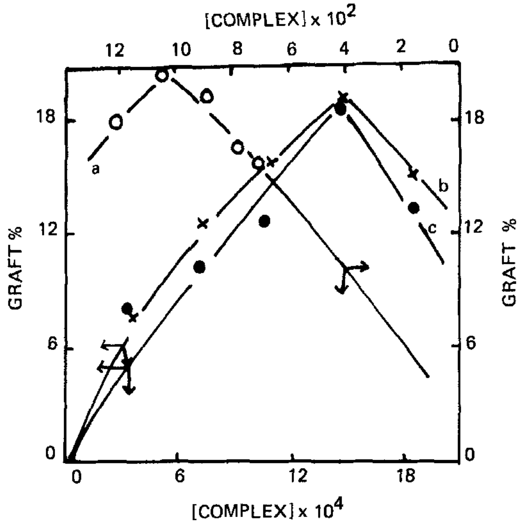


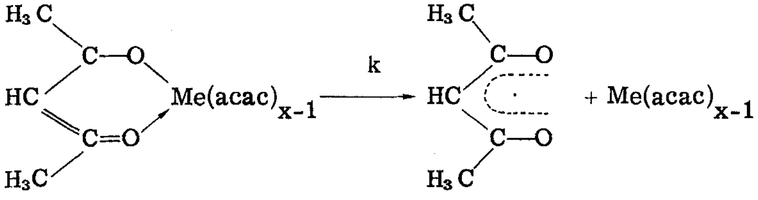
FIG. 2. Effect of [complex]. (a) [MMA] = 0.4694 M, [$HClO_4$] = 3.72×10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100, (○) [$Mn(acac)_3$]. (b) [MMA] = 0.4694 M, [H_2SO_4] = 7.50×10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100, (×) [$Co(acac)_3$]. (c) [MMA] = 0.4694 M, [H_2SO_4] = 15.00×10^{-2} M, time = 6 h, temperature = 70°C, M:L = 1:100, (●) [$Fe(acac)_3$].

normally an electron acceptor, behaves as a donor relative to the complexed MMA which has been converted to a strong acceptor. Enhancement of monomer reactivity is also apparently due to association of complexed monomer into an organized array, since nylon acts as a matrix for such alignment. Hence the effect of the enhanced monomer reactivity favors the increase of graft yield.

Initiator Concentration

Figure 2 shows the graft percentage as a function of complex concentration when graft copolymerization of methyl methacrylate onto PET fiber was carried out at 70°C. As is evident, increment of the complex concentration is accompanied by a significant increase in the graft yield.

The metal chelates of Mn^{3+}, Co^{3+}, and Fe^{3+} decompose to yield acetyl acetone radical or the radical ion combination with the monomer as represented below:



I

$$\mathrm{Me(acac)_x} + \mathrm{M} \rightleftharpoons [\mathrm{M} \longrightarrow \mathrm{Me(acac)_x}] \xrightarrow{k} (\mathrm{acac})\text{—}\mathrm{M}^{\bullet} + \mathrm{Me(acac)_{x-1}}$$

II

The free radicals I and II may participate in direct abstraction of hydrogen atom from the polyester backbone to yield a polyester macroradical capable of initiating grafting.

It was observed that among all the three complexes, $Mn(acac)_3$ was the most effective initiator. The order of reactivities of initiators was $Mn^{3+} > Co^{3+} > Fe^{3+}$. This order of reactivity is in agreement with the results reported by Kasting [37] and Izawa [38]. The high initiating ability of $Mn(acac)_3$ might be based on its structural strain, as is reported by Morosin and Brathorde [39]. The plots of log R_p versus log [complex] (Fig. 3) are straight lines with slopes equal to 0.55, 0.60, and 0.60 in the cases of Mn^{3+}, Co^{3+}, and Fe^{3+} complexes, respectively, indicating a 0.5 order with respect to the initiator concentrations.

Effect of Temperature

Figure 4 shows that increasing the polymerization temperature from 60 to 75°C enhances the rate of grafting significantly. Raising the polymerization temperature would be expected to cause (a) creation of more active species, i.e., free radicals, in the reaction medium due to a faster decomposition rate of the complex; (b) enhancement in the swellability of fibers; (c) increased mobility of the monomer molecules; (d) higher rate of monomer diffusion from the reaction medium to the PET medium; (e) enhancement in the rate of initiation and propagation of grafts. The net effect of all these factors could be expected to yield higher grafting.

From the Arrhenius plot (Fig. 5) of log R_p versus 1/T, the overall activation energies have been found to be 8.0, 8.7, and 9.0 kcal/mol for Mn^{3+}, Co^{3+}, and Fe^{3+}, respectively.

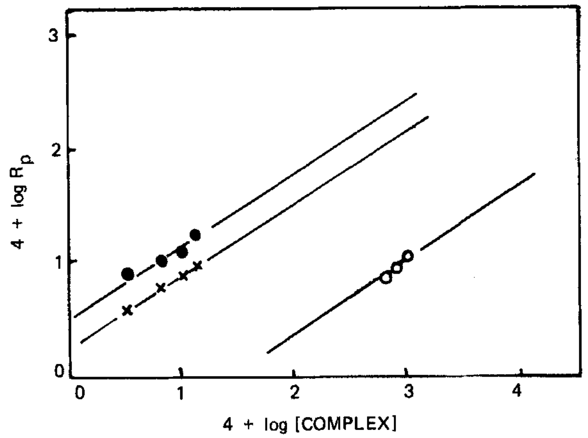


FIG. 3. Plot of log R_p vs log [complex]. (○) [$Mn(acac)_3$], (×) [$Co(acac)_3$], (●) [$Fe(acac)_3$].

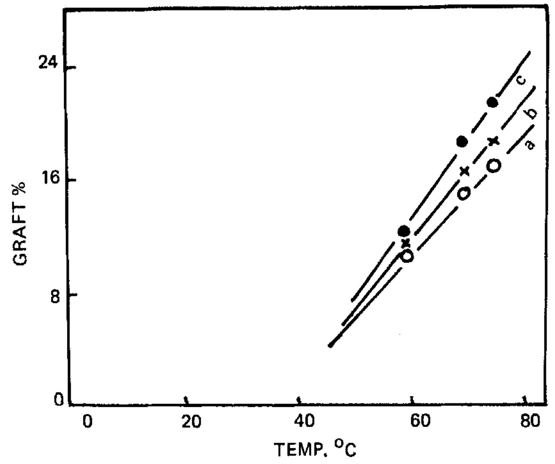


FIG. 4. Effect of temperature. (a) [$Mn(acac)_3$] = 8.80×10^{-2} M, [MMA] = 0.4694 M, [$HClO_4$] = 3.72×10^{-2} M, time = 4 h, M:L = 1:100. (b) [$Co(acac)_3$] = 16.20×10^{-4} M, [MMA] = 0.4694 M, [H_2SO_4] = 7.50×10^{-2} M, time = 4 h, M:L = 1:100. (c) [$Fe(acac)_3$] = 16.20×10^{-4} M, [MMA] = 0.4694 M, [H_2SO_4] = 15.00×10^{-2} M, time = 4 h, M:L = 1:100.

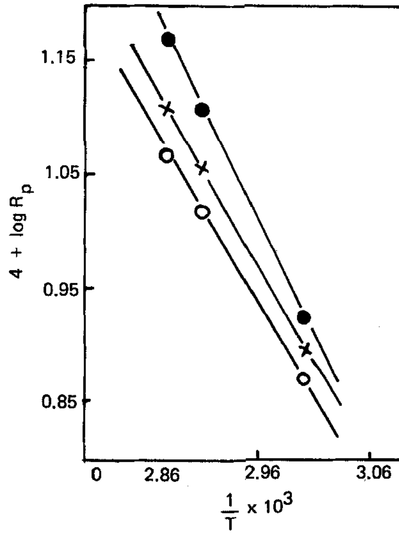


FIG. 5. Arrhenius plot of log R_p vs 1/T. (○) [$Mn(acac)_3$], (×) [$Co(acac)_3$], (●) [$Fe(acac)_3$].

Effect of Solvent

Solvent plays an important role during the process of grafting. The grafting reaction was carried out in the presence of a number of polar and dipolar aprotic solvents. The order of reactivity as far as percentage of graft yield is concerned follows the order formic acid > acetic acid > ethyl alcohol > dimethylformamide. In some solvents the graft yield was quite poor, and in some other solvents no grafting occurred at all. It was further noticed that a combination of aqueous and nonaqueous solutions provides the best media for grafting. It has been reported that swelling of nylon by solvents such as formic acid, aqueous zinc chloride, and hydrochlorid acid [40] increases the graft yield, and the grafting efficiency is related to the swelling of nylon. Since formic acid is a better swelling agent, the graft yield is higher in formic acid than with other solvents. An aqueous solution of formic acid helps in swelling the fiber to a greater extent, and the interaction of the primary radicals with the core of the fiber matrix becomes more feasible, for which the number of grafting sites increases on the fiber matrix, enhancing the graft yield.

Mechanism

From the kinetic results of polymerization and copolymerization by $Me(acac)_x$, and from the results of the polymer structure obtained, it was clear that $Me(acac)_x$ could induce the ordinary polymerization of vinyl monomers and did not give any stereospecificity of the resulting polymers.

It was suggested by Arnett and Mendelsohn [42] and by Bamford and Lind [41] that the initiation mechanism by $Me(acac)_x$ is considered to occur through the homolysis of their metal-oxygen bonds forming acetyl acetone radical or the radical in combination with the monomer [R$^\bullet$] which initiates grafting.

$$PET + R^\bullet \xrightarrow{k_i} PET + RH$$

Initiation:

$$PET^\bullet + M \xrightarrow{k_i'} PET{-}M^\bullet$$

Propagation:

$$PET{-}M^\bullet + M \xrightarrow{k_p} PET{-}M_1^\bullet$$

$$\vdots$$

$$PET{-}M_{n-1}^\bullet + M \xrightarrow{k_p} PET{-}M_n^\bullet$$

Termination:

$$PET{-}M_n^\bullet + PET{-}M_n^\bullet \xrightarrow{k_t} \text{graft copolymer}$$

Applying steady-state assumptions to the growing radicals, we have,

$$\frac{-d[R^\bullet]}{dt} = k[Me(acac)_3] - k_i[R^\bullet][PET] = 0.$$

or

$$[R^\bullet] = \frac{k[Me(acac)_3]}{k_i[PET]}$$

$$\frac{-d[RM_n^\bullet]}{dt} = k_i'[PET^\bullet][M] - k_t[PET{-}M_n^\bullet]^2 = 0$$

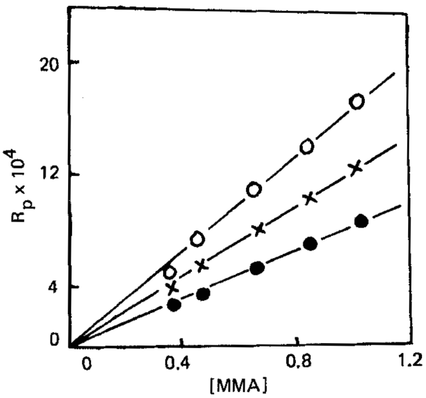


FIG. 6. Plot of log R_p vs [MMA]. (○) [Mn(acac)$_3$], (×) [Co(acac)$_3$], (●) [Fe(acac)$_3$].

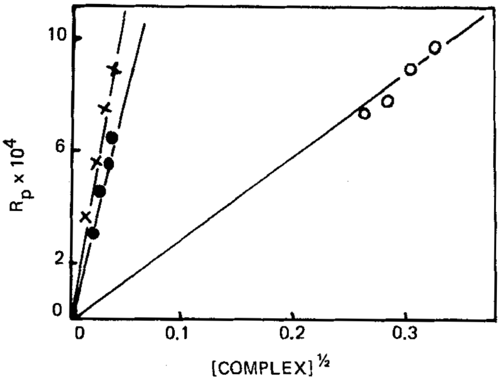


FIG. 7. Plot of log R_p vs [complex]$^{1/2}$. (○) [Mn(acac)$_3$], (×) [Co(acac)$_3$], (●) [Fe(acac)$_3$].

or

$$[\mathrm{PET{-}M_n^\bullet}]^2 = \frac{k_i'}{k_t}[\mathrm{PET^\bullet}][\mathrm{M}]$$

Putting the value of [PET•] in the above expression,

$$[\mathrm{PET{-}M_n^\bullet}] = \left(\frac{k}{k_t}\right)^{1/2}[\mathrm{Me(acac)_3}]^{1/2}$$

Further,

$$R_p = k_p[\mathrm{PET{-}M^\bullet}][\mathrm{M}]$$

Hence,

$$R_p = k_p\left(\frac{k}{k_t}\right)^{1/2}[\mathrm{Me(acac)_3}]^{1/2}[\mathrm{M}]$$

Thus the plots of R_p versus [M] (Fig. 6) and R_p versus $[\text{complex}]^{1/2}$ (Fig. 7) were linear, indicating the validity of the reaction scheme.

PET possesses low equilibrium moisture regain which makes it uncomfortable to wear. Moisture regain of the grafted fabric was determined by allowing the samples to attain equilibrium moisture

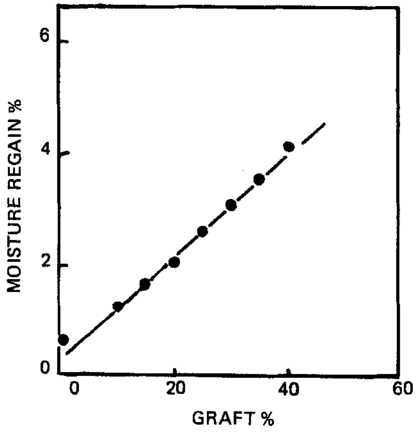


FIG. 8. Plot of moisture regain % vs graft %.

at 25°C and 65% relative humidity. The percentage of moisture regain of the grafted samples increases with increasing the graft-on percentage (Fig. 8).

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