

Factors Affecting Polymerization of 2-Methyl-5-vinylpyridine in Poly(ethylene Terephthalate) Fibers Using Benzoyl Peroxide as Initiator

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Synopsis

Polymerization of 2-methyl-5-vinylpyridine (MVP) in the presence of poly(ethylene terephthalate) fibers (PET) using benzoyl peroxide (BP) as initiator caused a substantial increase in the weight of fibers. The mechanism of this polymerization is believed to be grafting by vinyl addition to PET radical formed under the influence of BP. Increasing the BP concentration up to 4.26×10^{-3} mole/l. causes a significant enhancement in grafting, while further increase brings about a marked fall in the graft yield. Increasing the MVP concentration up to 10% also improves significantly the graft yield, but the latter, particularly in the later stages of the reaction, shows lower values at higher MVP concentrations. Raising the reaction temperature from 65° to 95°C causes a significant enhancement in the rate of grafting, though the maximum graft yield obtained at 95°C is much lower than at 85°C. Incorporation of Cu^{2+} ion in the polymerization system enhances the graft yield outstandingly. The same holds true for Fe^{3+} and Li ions, but the enhancement is much less than that for Cu^{2+} ion. Addition of acetic or oxalic acid to the reaction decreases the magnitude of grafting. The same situation is encountered when a water/solvent mixture is used as reaction medium. Solvents employed were methanol, ethanol, propanol, and butanol. Also studied was the polymerization reaction with respect to homopolymer, total conversion, and graft efficiency.

INTRODUCTION

Chemical modification of poly(ethylene terephthalate) fibers (PET) via grafting with vinyl monomers has gained considerable attention during the last decade. This is indeed a very fascinating field for research, with unlimited future possibilities for improving the properties of the product.

Besides this highly crystalline nature and hydrophobic character, PET fibers do not contain chemical reactive groups. For these reasons, this material is not easily penetrated by dyes of large molecular dimensions and cannot combine with dye anions or cations. Certain desirable properties such as improvement in dyeability and antistatic properties; increase in moisture regain; increase in soil, weather, and alkali resistance; and improved mechanical as well as thermal properties can be imparted to PET fibers by grafting PET with styrene,¹⁻⁶ 4-vinylpyridine,^{7,8} acrylonitrile,⁹⁻¹² acrylate esters,¹³⁻¹⁸ acrylamide,¹⁹⁻²⁴ acrylic and methacrylic acids,²⁵⁻³⁹ vinyl acetate,⁴⁰ and N-vinyl-3-morpholinone.⁴¹

Grafting of these monomers could be achieved either by radiation or chemical means. Ionizing radiation such as γ -rays from a ^{60}Co source,^{3,4,7,10,12,17,19,20,24,26,28,31-34,36,37,38,41,45} x-rays,⁴⁶ or high-energy electrons from accelerators^{17,29,40} interact with the polymer fiber (PET) and produce

radicals one of which was identified by ESR⁴⁷ as $-\text{CO}-\text{C}_6\text{H}_4-\text{COO}-\dot{\text{C}}\text{HCH}_2-$. These radical sites permit the attachment of monomer molecules which may grow into short chains. Similar PET macroradicals could be obtained under the action of high temperature in the presence of oxygen,^{2,15,16,22,35} benzoyl peroxide,^{5,30} hydrogen peroxide,⁶ ammonium or potassium persulfate,^{6,11} ceric ion,^{38,48} or azobisisobutyronitrile.^{1,6}

In this paper, polymerization of 2-methyl-5-vinylpyridine (MVP) in the presence of PET fibers using benzoyl peroxide (BP) as an initiator was carried out with a view of studying the conditions which affect the extent and rate of polymerization. In addition, the effect of incorporation of metallic ions, acids, and solvents in the polymerization system on the graft yield, homopolymer, and total conversion was investigated.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) fibers (PET-Trevira, Hoechst-1,2 den/40 mm, cotton type) were purified through a mild cleaning treatment with sulfonated fatty alcohol (2 g/l.) for 30 min at 65°C, rinsed with hot and cold water, dried at room temperature, and finally extracted with alcohol for 24 hr.

2-Methyl-5-vinylpyridine (MVP) was freshly distilled (75°C/13 mm Hg).

Benzoyl peroxide (BP) was freshly prepared according to Vanino and Herzer.⁴⁹

Polymerization Procedure

The polymerization reaction was carried out in a 50-ml stoppered conical flask. PET fiber (0.5 g) was introduced into a 50-ml aqueous solution containing the monomer and 2 ml emulsifying agent (Emulsogen DG-Hoechst). The flask was immediately stoppered and placed in a thermostated water bath for a certain period until the required temperature was reached, and the initiator was then added. The contents were stirred occasionally during polymerization. After the desired reaction time, the contents were filtered on a sintered glass crucible, washed with water, dried in an oven at 105°C for 5 hr, cooled to room temperature, and weighed. The sample was then Soxhlet extracted with methyl alcohol, dried as already indicated, and weighed. The increase in weight of the sample due to incorporation of poly-MVP divided by the original dry weight of the sample and multiplied by 100 will be referred to as per cent of graft yield.

$$\% \text{ graft yield} = \frac{\text{dry wt grafted sample} - \text{dry wt original sample}}{\text{dry wt original sample}} \times 100$$

The percentages of homopolymer, total conversion, and graft efficiency were calculated as follows:

$$\% \text{ homopolymer} = \frac{\text{dry wt homopolymer}}{\text{wt monomer used}} \times 100$$

$$\% \text{ total conversion} = \frac{\text{wt grafted polymer} + \text{wt homopolymer}}{\text{wt monomer used}} \times 100$$

$$\% \text{ graft efficiency} = \frac{\text{wt grafted polymer}}{\text{wt grafted polymer} + \text{wt homopolymer}} \times 100$$

The term polymer yield, which is shown in some of the figures, is used in this paper to refer to either the graft yield, homopolymer, or total conversion.

RESULTS AND DISCUSSION

Polymerization of MVP initiated by BP in the presence of PET fibers was found to bring about an increase in the weight of these fibers even after extracting the latter several times with methanol, which is a solvent for poly-MVP. The increase in weight is unequivocally due to incorporation of the vinyl polymer within the PET fibers. The mechanism of such incorporation is not yet established. However, the mechanism of polymerization onto the fibers is believed to be grafting by vinyl addition to PET radicals formed under the influence of BP. Hence, the term grafting will be used for simplicity. Presented below are the different parameters that affect the polymer yield.

Initiator Concentration

The effect of BP concentration on the graft yield obtained upon polymerization of MVP in the presence of PET fibers is shown in Figure 1. As is evident, grafting, though very little, does occur even in the absence of BP, indicating formation of PET macroradicals capable of initiating grafting. These PET macroradicals may be generated via thermal oxidation of PET.⁵⁰ A significant increase in the graft yield could be achieved when BP was included in the system. For instance, a graft yield of 20% was obtained at a BP concentration of 3.26×10^{-3} mole/l. This contrasts with a graft yield of 3% in the absence of BP.

Increase the BP concentration up to 3.26×10^{-3} mole/l. is accompanied by a substantial increase in the graft yield. A concentration range of 3.26×10^{-3} mole/l. brings about comparable, if not identical, graft yield. Using concentrations larger than 4.26×10^{-3} mole/l. lowers grafting to a considerable degree.

The above findings can be explained as follows: BP decomposes to yield primary free-radical species ($C_6H_5COO\cdot$) and/or secondary free-radical species

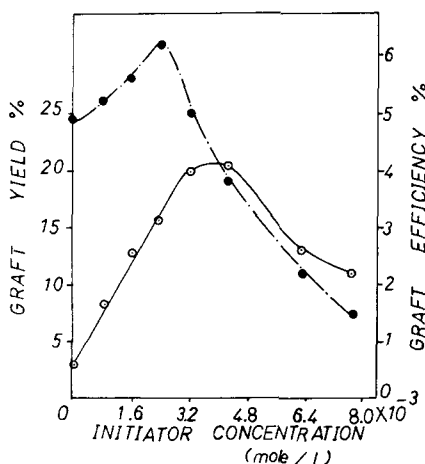


Fig. 1. Influence of initiator concentration on graft yield and graft efficiency: (O) % graft yield; (●) % graft efficiency; [MVP], 0.81 mole/l.; 1 hr; temperature, 85°C; material:liquor ratio, 1:100.

(C_6H_5). These free radicals may participate in (a) direct abstraction of hydrogen atom from the polyester backbone to yield a polyester macroradical capable of initiating grafting; (b) the termination process with the growing polymer chains; (c) the combination of the free-radical species, in particular, the secondary free-radical species; and (d) the termination process with the polyester macroradicals. At lower BP concentration, the effect of (a) seems to prevail over the combined effect of (b), (c), and (d), thereby increasing the graft yield. The opposite holds true at higher BP concentration.

Unlike the graft yield, homopolymer and total conversion increase significantly as the BP concentration increases within the range studied (Fig. 2). Differences in the ability of BP in initiating and terminating the graft and homopolymer would account for this. Since the total conversion is the sum of monomer converted to graft and homopolymer, the present data indicate that homopolymerization is more favored than grafting, particularly at higher initiator concentrations. Indeed, this is substantiated by the significant reduction in graft efficiency at higher initiator concentrations (Fig. 1).

Kinetic investigation (Fig. 3) of the effect of BP on rate of total conversion (R_p) and rate of grafting (R'_p) at constant MVP concentration revealed that they are proportional to the 0.96 and 1.1 power of the BP concentration, respectively. It should be pointed out that these values are derived after the rates of grafting and total conversion in the absence of BP were calculated and subtracted from the rates obtained at each BP concentration within a range of 1.65×10^{-3} to 4.13×10^{-3} mole/l. (Table I).

Monomer Concentration

Figure 4 shows the effect of MVP concentration on the rate of grafting. It can be seen that the rate of grafting increases significantly as the concentration of MVP increases from 6% to 10%. Further increases in MVP concentration does not enhance grafting: the extent of grafting obtained during the later stages of the reaction is lower at 12% than at 10% MVP concentration. This suggests that there is an optimal concentration of MVP for maximum grafting. Beyond this

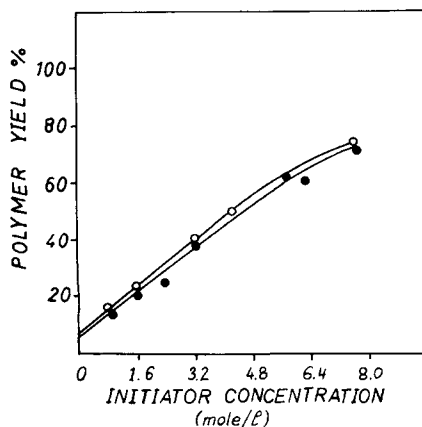


Fig. 2. Influence of initiator concentration on homopolymer and total conversion: (●) % homopolymer; (○) % total conversion; [MVP], 0.81 mole/l.; 1 hr; temperature, 85°C; material:liquor ratio, 1:100.

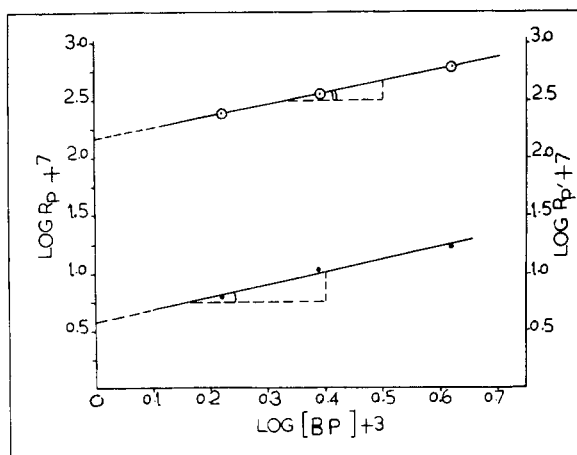


Fig. 3. Rates of grafting reactions, R'_p , and total conversion, R_p vs initiator concentration: (○) R_p ; (●) R'_p ; [MVP], 0.81 mole/l.; temperature, 85°C; material:liquor ratio, 1:100.

concentration, much of the monomer seems to be physically adsorbed on the PET fibers and impedes diffusion of the initiator inside the fibers, thereby lowering the graft yield.

Figure 5 illustrates the effect of MVP concentration on the rate of homopolymerization. Unlike grafting, the rate of homopolymerization increases as the MVP concentration increases from 6% to 12%. This, indeed, substantiates the assumption that at higher MVP concentration (i.e., 12%), there is a diffusion barrier for the initiator caused by adsorption of the monomer on the fiber. With homopolymerization, the situation is different since initiation and propagation of polymer can proceed independently of this. Similar to homopolymerization, the total conversion increases as the monomer concentration increases (Fig. 6).

From the kinetic point of view, it is clear from Fig. 7 that no grafting occurred within a range of MVP concentration of 0–0.4 mole/l. To compensate for this, the line representing the relation between R'_p and the MVP, was extrapolated and the value of R'_p at this range of MVP concentration was subtracted from the value of R'_p at MVP ranging from 0.49 to 0.81 mole/l. (Table II). After subtraction, $\log R'_p$ was plotted versus $\log [\text{MVP}]$ in Fig. 8, from which it can be seen that R'_p is proportional to the 1.02 power of MVP concentration. Figure 8 also shows the plot of R_p (rate of total conversion) versus [MVP]. As is evident, the rate of total conversion, R_p , is proportional to the 0.68 power of MVP concentration.

With respect to BP and MVP concentrations, kinetic measurements of R_p and R'_p can now be formulated as follows:

$$R_p = K[\text{BP}]^{0.96}[\text{MVP}]^{0.68}$$

$$R'_p = K[\text{BP}]^{1.1}[\text{MVP}]^{1.02}$$

TABLE I
Dependence of Rate of Total Conversion (R_p) and Rate of Grafting (R'_p) on BP Concentration^a

BP Concentration, mole/l.	$\log [\text{BP}] + 3$	R_p , mole l. ⁻¹ sec ⁻¹	$\log R_p + 7$	R'_p , mole l. ⁻¹ sec ⁻¹	$\log R'_p + 7$
0		6.5×10^{-5}		3.35×10^{-6}	
1.65×10^{-3}	0.2182	9.0×10^{-5}	-4.6021	2.3979	-6.1871
2.48×10^{-3}	0.3943	10.0×10^{-5}	-4.4559	2.5441	-5.9393
4.13×10^{-3}	0.6162	12.6×10^{-5}	-4.2147	2.7853	-5.7825

^a Reaction conditions: [MVP], 0.81 mole/l.; temperature, 85°C; material:liquor ratio, 1:100

TABLE II
Dependence of the Rate of Total Conversion (R_p) and Rate of Grafting (R'_p) on MVP Concentration^a

MVP Concentration, mole/l.	$\log [\text{MVP}] + 1$	R_p , mole l. ⁻¹ sec ⁻¹	$\log R_p + 6$	R'_p , mole l. ⁻¹ sec ⁻¹	$\log [R'_p - R'_{p0}] + 6$
0		0			
0.49	-0.31	7.35×10^{-6}	-5.13	0.83×10^{-6}	-5.28
0.65	-0.19	9.34×10^{-6}	-5.03	2.23×10^{-6}	-5.14
0.81	-0.09	10.5×10^{-6}	-4.98	4.50×10^{-6}	-5.05
0.97	-0.01	11.67×10^{-6}	-4.93	1.07	—

^a Reaction conditions: [BP], 2.48×10^{-3} mole/l.; temperature, 85°C; material:liquor ratio, 1:100; R'_{p0} = rate of grafting at [MVP] ranging from 0 to 0.4 mole/l.

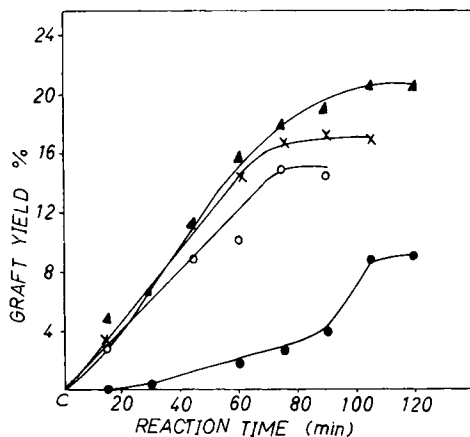


Fig. 4. Rate of grafting of MVP onto PET at different concentrations of MVP; [MVP], mole/l.: (●) 0.49; (○) 0.64; (▲) 0.81; (×) 0.97; [BP], 2.48×10^{-3} , mole/l.; temperature, 85°C; material:liquor ratio, 1:100.

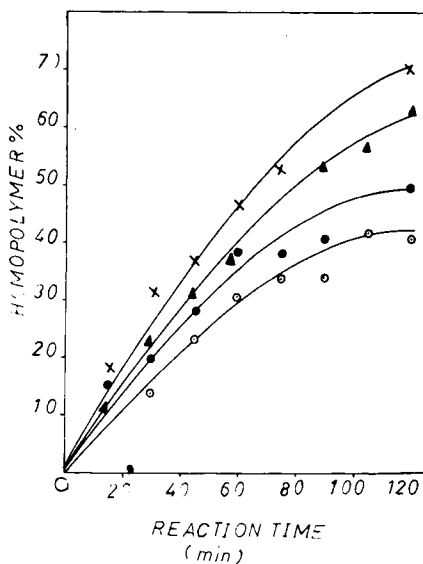


Fig. 5. Rate of homopolymerization at different concentrations of MVP: [MVP], mole/l.: (○) 0.49; (●) 0.65; (▲) 0.81; (×) 0.97; [BP], 2.48×10^{-3} mole/l.; temperature, 85°C; material:liquor ratio, 1:100.

Reaction Temperature

The effect of raising the polymerization temperature up to 85°C is to bring about a significant acceleration in the rate of grafting (Fig. 9). At 95°C, on the other hand, though the initial rate of grafting is exceedingly higher than that at 85°C, yet the maximum graft yield obtained at 95°C is much lower than at 85°C.

The favorable effect of temperature on grafting could probably be associated with (a) a faster rate of BP decomposition, giving rise to more free radicals; (b) enhancement in PET fibers swellability; (c) increased mobility of the monomer molecules; (d) higher rate of monomer diffusion from the reaction medium to the PET fibers; (e) possible reaction between the growing homopolymer chain

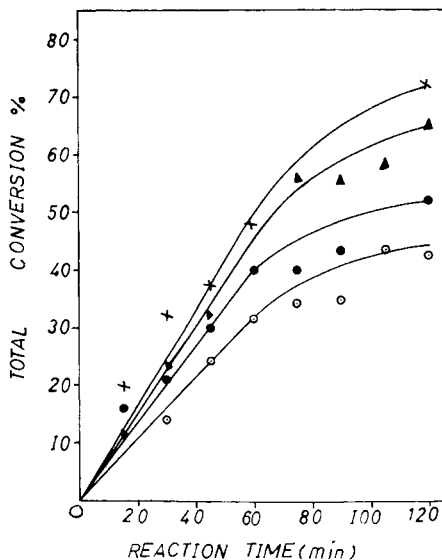


Fig. 6. Rate of total conversion of MVP in the presence of PET at different concentrations of MVP; [MVP], mole/l.: (○) 0.49; (●) 0.65; (▲) 0.81; (×) 0.97; [BP], 2.48×10^{-3} mole/l.; temperature, 85°C ; material:liquor ratio, 1:100.

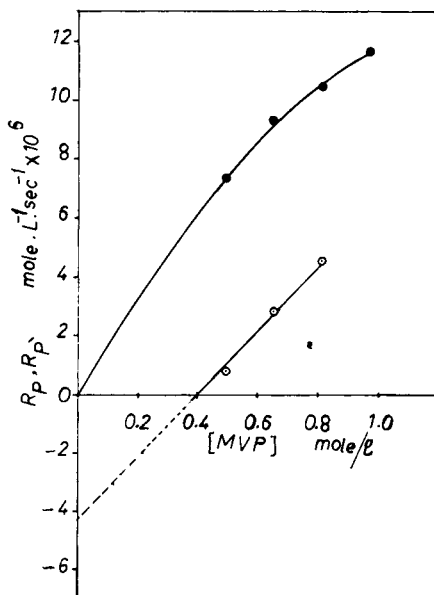


Fig. 7. Rates of grafting (R'_p) and total conversion (R_p) vs [MVP]: (●) R_p ; (○) R'_p ; [BP], 2.48×10^{-3} mole/l.; temperature, 85°C ; material:liquor ratio, 1:100.

with PET and/or the PET macroradicals; and (f) enhancement in the rate of initiation and propagation of grafts. The net effect of these factors would be expected to lead to higher grafting. That a lower maximum graft yield is obtained at 95°C than at 85°C could be interpreted in terms of a faster rate of termination at 95°C .

The apparent activation energy for grafting was calculated from the Arrhenius plot of R'_p versus $1/T$ (Fig. 10); it amounts to 20.0 kcal/mole. Hence, the total

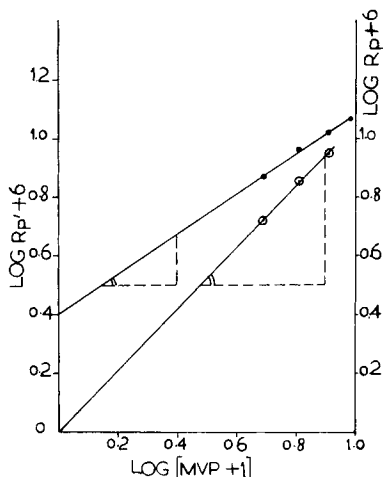


Fig. 8. Rates of grafting (R'_p) and total conversion (R_p) vs [MVP]: (●) R_p ; (○) R'_p ; [BP], 2.48×10^{-3} mole/l.; temperature, 85°C ; material:liquor ratio, 1:100.

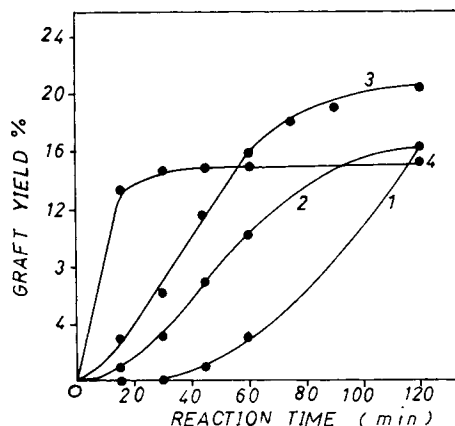


Fig. 9. Effect of temperature on the rate of grafting: (1) 65°C ; (2) 75°C ; (3) 85°C ; (4) 95°C ; [MVP], 0.81 mole/l.; [BP], 2.48×10^{-3} mole/l.; material:liquor ratio, 1:100.

energy of activation approximates to 35.0 kcal/mole, because 30/2 kcal/mole required for BP decomposition must be added.

Metallic Ions

Previous reports have disclosed that the presence of metallic ions such as Cu^{2+} and Fe^{3+} ions during free-radical graft polymerization of vinyl monomers onto cellulose,⁵¹⁻⁵³ wool,⁵⁴ and nylon⁵⁵ enhances grafting significantly. It appears, therefore, of interest to establish the influence of such ions on grafting of PET fibers with MVP under the initiating action of BP.

Figure 11 shows the effect of incorporation of various concentrations of copper sulfate on graft yield. At first glance, the presence of Cu^{2+} causes an outstanding enhancement in the extent of grafting. This enhancement depends on the concentration of Cu^{2+} ion. The graft yield increases with increasing Cu^{2+} ion concentration up to 0.02 mmole/l. Thereafter, the graft yield decreases as the

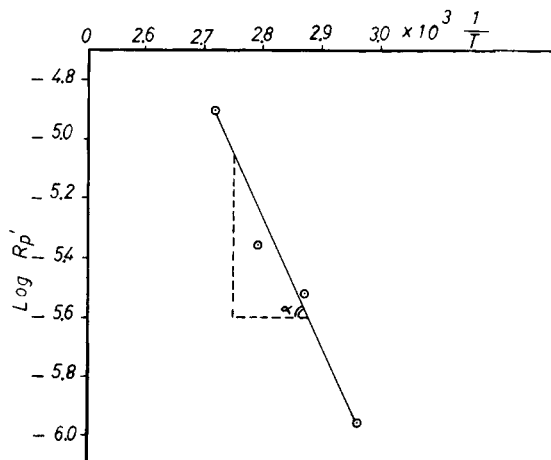


Fig. 10. Arrhenius plots for the graft copolymerization of MVP in the presence of PET: [MVP], 0.81 mole/l.; [BP], 2.48×10^{-3} mole/l.; material:liquor ratio, 1:100; R_p' , rate of graft copolymerization reaction.

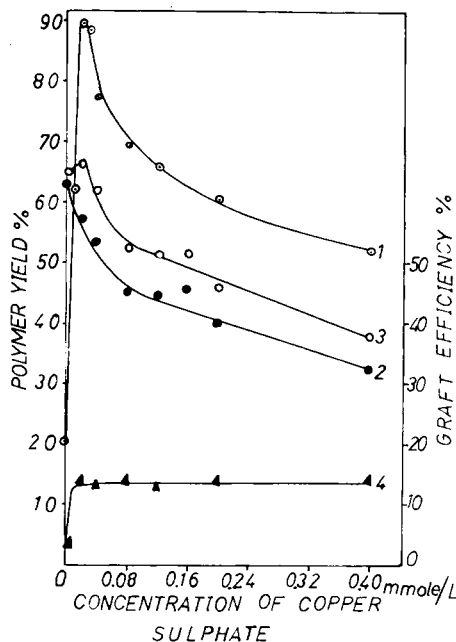


Fig. 11. Influence of Cu^{2+} ion concentration on graft yield, homopolymer, total conversion, and graft efficiency: (1) graft yield; (2) homopolymer; (3) total conversion; (4) graft efficiency; [MVP], 0.81 mole/l.; [BP], 2.48×10^{-3} mole/l.; 2 hr; temperature, 85°C ; material:liquor ratio, 1:100.

Cu^{2+} ion concentration increases. However, regardless of the Cu^{2+} ion concentration used in this work, the graft yield obtained in the presence of Cu^{2+} is much greater than in its absence.

The outstanding increase in grafting produced by the presence of Cu^{2+} ion can be ascribed to a variety of reasons. First, Cu^{2+} ion accelerates the decomposition of BP. Decomposition of peroxides by metallic ions is well established.^{56,57} Second, MVP and Cu^{2+} ion form perhaps a redox system. As a result, Cu^{2+} is converted to Cu^+ ion. Third, cuprous ion so obtained would be

oxidized back to the cupric state by atmospheric oxygen, and this conversion must presumably entail radical intermediate, as suggested by eqs. (1)–(3):^{55,58}



The HO_2 radical may be involved presumably in the initiation of grafting or can undergo a reaction leading to formation of hydrogen peroxide as well as hydroxyl radical. Moreover, the formation of both the $\text{HO}\cdot$ and HO_2 radicals in the decomposition of hydrogen peroxide by metallic ion has been reported.^{56,57}

The decrease in graft yield with higher concentrations of cupric sulfate suggests (a) that termination of free radicals in solution and/or PET backbone occurs in the presence of Cu^{2+} ions (the latter seem to act as a radical trap), and (b) that Cu^+ ions contribute to the termination of the graft, leading to lower molecular weight (Cu^+ ions are presumably formed in extensive amounts when a high concentration of copper sulfate is used). According to the data for homopolymer formation (Fig. 12), the magnitude of homopolymer decreases as the Cu^{2+} concentration in the polymerization system increases, implying the participation of copper ions in the termination process. This substantiates the above assumption.

The efficiency of grafting in the presence and absence of Cu^{2+} ion is rather interesting (Fig. 12). It is significantly higher in the presence of Cu^{2+} ion than in its absence. Furthermore, at a copper sulfate concentration of 0.02 mmole/l. the efficiency of grafting attains a value which does not change by increasing the copper sulfate concentration up to 0.4 mmole/l. This indicates that a high concentration of Cu^{2+} ion has the same effect on both the grafting and homopolymerization reactions. That is, the presence of an excess Cu^{2+} ion does not alter the magnitude of the graft/homopolymer ratio. The trend shown by the total conversion (Fig. 12) supports this.

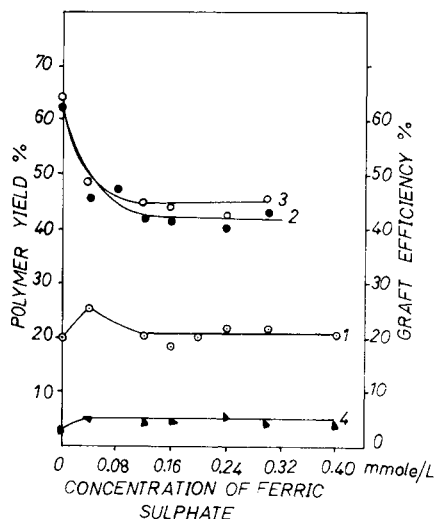


Fig. 12. Influence of Fe^{3+} ion concentration on graft yield, homopolymer, total conversion, and graft efficiency: (1) graft yield; (2) homopolymer; (3) total conversion; (4) graft efficiency; [MVP], 0.81 mole/l.; [BP], 2.48×10^{-3} mole/l.; 2 hr; temperature, 85°C ; material:liquor ratio, 1:100.

Similar to Cu^{2+} ion, the presence of Fe^{3+} and Li^+ ions in the polymerization system seems to increase the free-radical species. This is evidenced by the higher graft yields obtained in their presence than in their absence (Fig. 13). With Fe^{3+} and Li^+ ions, there are also optimal concentrations at which maximum grafting occurs. The differences between the effects of Cu^{2+} ion and both Fe^{3+} and Li^+ ions on the polymerization reaction consist of (a) maximum grafting obtained with Cu^{2+} ion is much greater; (b) the optimal concentration of Cu^{2+} ion is much lower; (c) while the graft yield shows a continuous decrease upon increasing the Cu^{2+} ion concentration beyond the optimal concentration, it reaches a constant value upon increasing either the Fe^{3+} or Li^+ concentration; (d) the graft yield in the presence of Cu^{2+} ion even at the highest concentration used within the range studied is higher than the corresponding yield in its absence, a point which contrasts with the graft yields obtained with Fe^{3+} and Li^+ ions where at higher concentrations the graft yield reaches a value which is practically equal to that obtained in their absence; (e) at certain Fe^{3+} and Li^+ ion concentrations, the homopolymer and total conversion fall to attain a constant value, unlike the Cu^{2+} ion, where a continuous decrease in homopolymer and total conversion was observed upon increasing the Cu^{2+} ion concentration.

The greater efficiency of Cu^{2+} ions in producing higher graft yields than both Fe^{3+} and Li^+ ions could be associated with differences in mode of absorption on PET fibers. Attachment of Cu^{2+} ions to PET fibers seems to involve an ionic bond which can be easily broken to allow the Cu^{2+} ions to take part in the reactions already indicated, whereas with Fe^{3+} ions, the attachment seems to entail ionic bonding and chelate bonding. Hence, it may probably be correct to say that the concentration of Fe^{3+} in the grafting reaction would be partly inhibited by the strong association of Fe^{3+} with PET through chelate bonding. Strong association of Li^+ ion with PET can also be presumed. The fact that no decrease in grafting was observed at neither higher ferric sulfate nor higher lithium chloride concentration substantiates this. In addition, previous reports on the adsorption reaction of several metallic ions with silk, wool, cellulose, and poly-

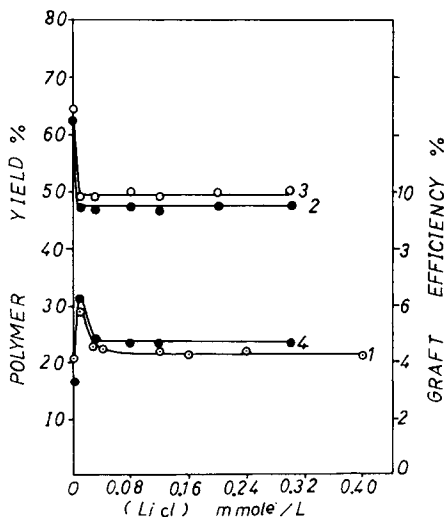


Fig. 13. Influence of Li^+ ion concentration on graft yield, homopolymer, total conversion, and graft efficiency: (1) graft yield; (2) homopolymer; (3) total conversion; (4) graft efficiency; [MVP], 0.81 mole/l.; [BP], 2.48×10^{-3} mole/l.; 2 hr; temperature, 85°C ; material:liquor ratio, 1:100.

(vinyl chloride) have shown ionic and chelate bond formation, depending upon the kind of metallic ion used.⁵⁸⁻⁶¹

Addition of Acids

Previous studies⁶²⁻⁶⁴ have shown that the copolymerization reactions are significantly influenced by the presence of acid; the influence depends upon the kind and the concentration of the acid used. In this work, the effect of acetic and oxalic acids on graft copolymerization of MVP onto PET fibers using BP as initiator was investigated. The results obtained are shown in Table III. The data indicate that addition of either of the said acids to the polymerization system causes a considerable decrease in grafting and homopolymer formation which is, in turn, reflected in the total conversion. However, the efficiency of grafting is higher in the presence of the acid, in particular acetic acid, than in its absence. This implies that the adverse effect of the acid on the homopolymerization reaction exceeds the corresponding effect on the grafting reaction.

The adverse effect of the acid on the polymerization reaction suggests that the acid dissociates to yield hydrogen ions. Such ions would act as terminators for free radicals formed in the reaction medium^{65,66} and/or for termination of graft as well as homopolymer growing chains. It is rather possible that presence of the acid impedes decomposition of BP, thus lowering the initiation step.

Reaction Medium

Polymerization of MVP in the presence of PET fibers using BP as initiator was studied in water/solvent mixtures. The solvents used were methanol, ethanol, *n*-propanol, and *n*-butanol. The results obtained are given in Table IV. It is clear that there is a decrease in the graft yield regardless of the water/solvent mixture employed. Furthermore, increasing the solvent ratio in the water/solvent mixture is accompanied by a significant decrease in the graft yield. The same situation is encountered with respect to homopolymer formation, total conversion, and graft efficiency. However, this decrease depends on the nature of the solvent. The polymer yield per cent (i.e., % graft, % homopolymer, % total conversion) follows the order methanol > ethanol > *n*-propanol > *n*-butanol.

TABLE III
Effect of Addition of Acids on Percent Graft Yield, Homopolymer, Total Conversion, and Graft Efficiency^a

Concentration of acid, mmole/l.	Acetic acid				Oxalic acid			
	G.Y.	H	T.C.	G.E.	G.Y.	H	T.C.	G.E.
0	20.5	62.6	64.7	3.3	20.5	62.6	64.7	3.3
10	21.3	44.9	47.1	4.7	13.5	42.1	43.5	3.2
20	14.4	44.7	46.2	3.2	10.3	38.7	39.7	2.7
30	15.6	52.8	54.4	2.9	13.3	40.1	41.5	3.3
50	13.0	49.9	51.2	2.4	9.4	33.1	34.1	2.9
70	8.7	43.0	44.0	2.1	14.3	44.9	46.4	3.2
80	6.2	46.9	50.9	1.5	11.6	40.7	41.9	2.9

^a [BP], 2.48×10^{-3} mole/l., [MVP], 0.81 mole/l.; time, 2 hr; temperature, 85°C; *M/L* ratio, 1:100; G.Y., graft yield; H, homopolymer; T.C., total conversion; G.E., graft efficiency.

TABLE IV
Effect of Solvents on Polymer Yield and Graft Efficiency^a

Solvent ratio, %	Methanol			Ethanol			n-Propanol			n-Butanol		
	G.Y.	H	T.C.	G.E.	G.Y.	H	T.C.	G.E.	G.Y.	H	T.C.	G.E.
0	20.5	62.6	64.7	3.3	20.5	62.6	64.7	3.3	20.5	62.6	64.7	3.7
10	20.1	57.8	59.9	3.5	17.7	52.6	54.4	3.4	7.7	43.6	44.4	1.8
20	8.8	45.7	46.6	1.9	5.1	39.1	39.7	1.3	2.1	25.0	25.2	0.9
30	3.7	24.6	25.0	1.5	3.1	21.5	21.8	1.5	0.9	18.5	18.6	0.5
40	1.7	20.7	20.9	0.8	1.1	16.7	16.8	0.6	0.5	13.1	13.1	0.4
50	0.8	8.5	8.5	0.9	0.6	7.9	7.9	0.7	0.3	7.7	7.7	0.4

^a [BZ₂O₂], 2.56×10^{-4} mole/l.; [MVP], 0.81 mole/l.; time, 2 hr; temperature, 85°C; material:liquor ratio, 1:100; G.Y., graft yield; H, homopolymer; T.C., total conversion; G.E., graft efficiency.

The decrease of grafting by including solvents in the reaction medium implies that the swelling of PET fibers by water is hindered by the presence of the solvents in question. In addition, these solvents are very likely to participate in termination of the growing polymer chain of the graft. Indeed, the decrease in homopolymer upon inclusion of the solvent in the reaction mixture substantiates this.

Variation of grafting upon using different solvents could be associated with differences in their (a) adverse effect on the swelling PET fibers by water, (b) the hydrophobic character which decreases from butanol to methanol, and (c) termination of the graft chain radical and PET macroradical via chain transfer. It is to be expected that, in combination, effects (a) and (b) seriously hinder the monomer to reactive sites on PET, whereas the effect of (c) is to lower the molecular weight and initiation of the graft, thereby leading to decreased grafting. However, differences in molecular size of the solvents and the effect of each solvent on the rate of decomposition of BP, if any, cannot be ruled out.

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