

Graft Polymerization of Methyl Methacrylate on Poly(ethylene Terephthalate) Fibers Using H₂O₂ as Initiator

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Synopsis

The presence of poly(ethylene terephthalate) (PET) fibers during polymerization of methyl methacrylate (MMA) using H₂O₂ as initiator resulted in a substantial, constant increase in the weight of the fibers after repeated extraction with acetone. Fractional precipitation curves of the extracted PET-MMA polymerization product and a physical mixture of PET and PMMA were different, indicating that the interaction of MMA with PET involved grafting. The magnitude of the latter enhanced considerably by increasing H₂O₂ concentration up to 30 mequiv/L, then decreased by further increasing H₂O₂ concentration. There was also an optimal temperature (80°C) for grafting; below or above this temperature, lower grafting was obtained. Similarly, carrying out the polymerization reaction at different pH values revealed that pH 7 constituted the optimal. On the other hand, grafting increased upon increase of the methyl methacrylate concentration within the range studied (8–20%). Incorporation of Cu²⁺ or Fe³⁺ ions in the polymerization medium caused a decrement in grafting, irrespective of the metallic ion concentrations. Using methylene chloride as a swelling agent for the fibers failed to enhance the susceptibility of the latter toward grafting. On the contrary, tetrachloroethane was quite promising in this regard. The homopolymer formed during grafting was also reported.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are highly crystalline and hydrophobic in nature. They do not contain chemical reactive groups. For these reasons, PET fibers are not easily penetrated by dyes of large molecular dimensions and cannot combine with dye anions or cations. Furthermore, they suffer from a number of drawbacks, the most significant of which are static build-up and low moisture regain. Graft polymerization of vinyl monomers onto PET fibers is considered as a very fascinating field for research with unlimited future possibilities for eliminating or at least reducing one or more of these handicaps.

Although PET is one of the most difficult polymer to be grafted,¹ its chemical modification via vinyl graft polymerization has evoked considerable interest during the last decade.² Previous reports have dealt with grafting of PET with styrene,^{3–8} 4-vinylpyridine,^{9,10} acrylonitrile,^{11–14} acrylate esters,^{15–20} acrylamide,^{21–26} acrylic and methacrylic acids,^{27–41} vinyl acetate,⁴² *N*-vinyl-3-morpholinone,⁴³ and 2-methyl-5-vinylpyridine.^{48–50} Grafting of these monomers could be achieved either by radiation or chemical means. Ionizing radiation such as γ -rays from a ⁶⁰Co source,^{5,6,9,12,14,19,21,22,26,28,30,33–36,39,40,43,44,49} x-rays,⁴⁵ or high-energy electron beams from accelerators^{19,31,42} interact with the polymer fiber (PET) and produce radicals one of which was identified by ESR⁴⁶ as —CO—C₆H₄—COO— \dot{C} H CH₂—. These radical sites permit the attachment of

monomer molecules which may grow into short chains. Similar PET macroradicals can be formed under the influence of free radical initiators such as benzoyl peroxide,^{7,32,48} hydrogen peroxide,^{8,50} ammonium or potassium persulfate,^{40,47} or azobisisobutyronitrile.^{3,8}

The present work was undertaken with a view of studying the different parameters which affect grafting of PET fibers with methyl methacrylate using H₂O₂ as initiator to discover the optimal graft polymerization conditions.

EXPERIMENTAL

Materials

PET fibers (Tergal, 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 methyl alcohol for 24 h.

Methyl methacrylate (MMA) was shaken with 10% sodium hydroxide solution, washed with distilled water, and dried over calcium sulfate and distilled before use.

Hydrogen peroxide (Merck), copper sulfate (CuSO₄·5H₂O), and ferrous ammonium sulfate (FeSO₄·(NH₄)₂SO₄·6H₂O) were analytical-grade chemicals.

1,1,2,2-Tetrachloroethane (GDR, DDA, RDA) and methylene chloride (Cambrian Chemicals) were pure-grade chemicals.

Polymerization Procedure

Unless otherwise indicated, 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. 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 h, cooled to room temperature, and weighed. The sample was then Soxhlet extracted with acetone, dried as already indicated, and weighed. The increase in weight of the sample due to incorporation of poly(MMA) divided by the original weight of the sample and multiplied by 100 will be referred to as the percent of graft yield, thus:

% graft yield

$$= \frac{(\text{dry weight of grafted sample}) - (\text{dry weight of original sample})}{\text{dry weight of original sample}} \times 100$$

The percentage of homopolymer was calculated as follows:

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

RESULTS AND DISCUSSION

H_2O_2 -Induced polymerization of MMA in the presence of PET fibers was investigated under a variety of conditions. It was observed that there was a substantial increase in the weight of PET fibers after polymerization even after several extractions of the PET fibers with acetone which is solvent for poly(MMA). The increase in weight is unequivocally due to inclusion of the poly(MMA) within the PET fibers. Whether the poly(MMA) is chemically bonded to PET fibers (i.e., grafted) or intimately associated with the fibers as a result of "in situ" polymerization is still uncertain. Nevertheless, the mechanism of polymerization onto the fibers is believed to be grafting by vinyl addition to PET radicals formed under the influence of H_2O_2 . Furthermore, it will be shown later that with the PET-MMA polymerization product, a more or less continuous precipitation curve is obtained, whereas with the physical mixture of PET and PMMA, the curve shows a sharp difference in the solubility behavior of the two homopolymers, i.e., PET and PMMA, indicating grafting. Given below are the different factors that affect the graft add-on as well as homopolymer formed during polymerization.

Initiator Concentration

Figure 1 shows the effect of H_2O_2 concentration on the rate of grafting obtained when MMA is polymerized in the presence of PET fibers. It is seen that grafting is characterized by an initial fast rate, followed by a slower one, and then levels off. This is observed regardless of the concentration of H_2O_2 . However, for a given reaction period, the extent of grafting depends upon the H_2O_2 concentration. Maximum grafting occurs at a H_2O_2 concentration of 30 mequiv/L, whereas the maximum initial rate of grafting could be achieved upon using an H_2O_2 concentration of 40 mequiv/L. Using higher concentration of H_2O_2 (i.e., 50 mequiv/L) causes a substantial decrease in the extent and rate of grafting.

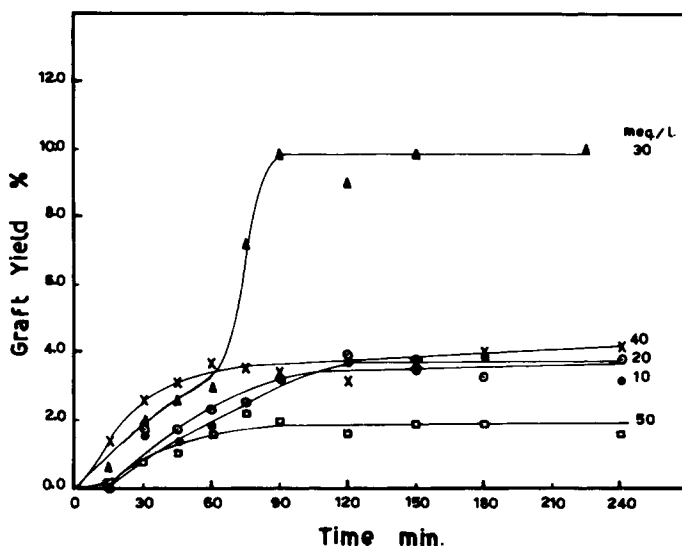
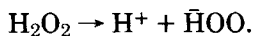


Fig. 1. Rate of grafting of MMA onto PET at different concentrations of H_2O_2 . [H_2O_2] (mequiv/L): (●) 10; (○) 20; (▲) 30; (x) 40; (□) 50. [MMA] 10% temperature 85°C; material:liquor ratio 1:100.

A more clarified picture of the effect of H_2O_2 concentration is shown in Figure 2, from which it is obvious that the graft yield increases significantly by increasing the H_2O_2 concentration up to 30 mequiv/L and then falls down sharply upon further increase in H_2O_2 concentration.

The enhancement in maximum graft yield by increasing the H_2O_2 concentration up to a certain limit (30 mequiv/L) suggests that H_2O_2 decomposes to yield perhydroxyl radical:



which may undergo further reactions to yield ultimately $\text{OH}\cdot$ radical. These free radical species, i.e., $\bar{\text{H}}\text{OO}\cdot$ and $\text{OH}\cdot$, are expected to increase by increasing the H_2O_2 concentration. Direct abstraction of hydrogen atom from the polyester backbone by these free radicals as well as formation of similar PET macroradicals via chain transfer from growing homopoly(MMA) chains seem to be in full swing at this particular concentration of H_2O_2 (i.e., 30 mequiv/L). Above this concentration, there will be abundance of free radicals which, besides contributing to the grafting, would terminate themselves by combination and/or cease the polyester macroradicals (formed via direct attack by the free radical species and via chain transfer) as well as growing grafted chain radicals thereby leading to decreased grafting. This is, indeed, the reason for the lower graft yields obtained at higher H_2O_2 concentration as well as for the induction period (Fig. 1) observed when an H_2O_2 concentration of 50 mequiv/L was used.

Figure 3 shows that the initial rate of homopolymerization formed during grafting increases by increasing the concentration of H_2O_2 up to 40 mequiv/L and then decreases upon further increase in the H_2O_2 concentration, but maximum homopolymerization occurs at a concentration of 30 mequiv/L, similar to grafting. This indicates that initiation and termination of the grafted chain as well as those of the homopolymer are similar, in contrast with other initiation systems.⁴⁸

Kinetic investigation (Fig. 4 and Table I) of the effect of H_2O_2 concentration

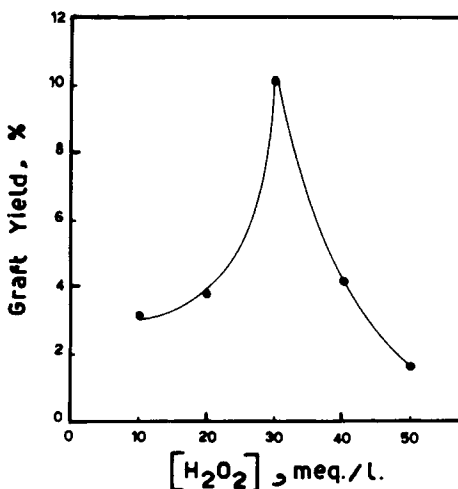


Fig. 2. Influence of initiator concentration on graft yield. [MMA] 10%; temperature 85°C; material:liquor ratio 1:100.

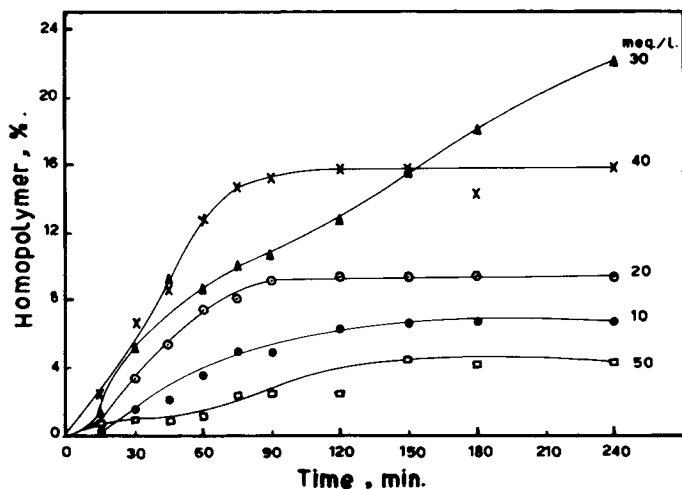


Fig. 3. Effect of H_2O_2 concentration on the extent and rate of MMA homopolymerization. $[\text{H}_2\text{O}_2]$ (mequiv/L): (●) 10; (○) 20; (▲) 30; (x) 40; (□) 50. $[\text{MMA}]$ 10%, temperature 85°C ; material:liquor ratio 1:100.

on rate of graft polymerization (R_p) revealed that the latter is proportional to the 0.193 power of the H_2O_2 concentration.

Monomer Concentration

Figure 5 shows the effect of MMA concentration on the rate of grafting. Evidently, the rate of grafting increases significantly as the MMA concentration increases. This could be associated with the gel effect^{52,54} brought about by the solubility of poly(MMA) in its own monomer. As a result, termination of the growing grafted chain radical by coupling is hindered. Besides, the gel effect

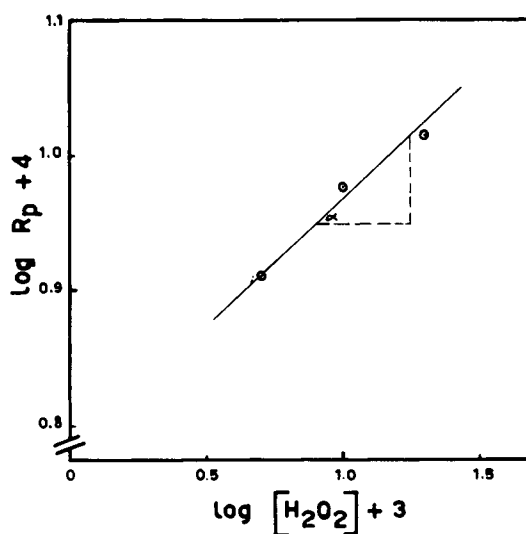


Fig. 4. Effect of H_2O_2 concentration on graft yield. $[\text{MMA}]$ 10%; temperature 85°C ; material:liquor ratio 1:100.

TABLE I
Dependence of Rate of Grafting (R_p) on Hydrogen Peroxide Concentration^a

[H ₂ O ₂], mol/L	log[H ₂ O ₂]	log[H ₂ O ₂] ^b	R_p , mol/L·s	log R_p	log R_p ^c
0.005	-2.30103	0.69897	8.1475×10^{-4}	-3.0889	0.91102
0.010	-2.00000	1.0000	9.4975×10^{-4}	-3.02239	0.97760
0.015	-1.82390	1.1761	8.6000×10^{-4}	-3.06550	0.93449
0.020	-1.69897	1.30103	1.0350×10^{-3}	-2.98506	1.01494
0.025	-1.60206	1.39794	4.6575×10^{-4}	-3.33184	0.66815

^a Reaction conditions: [MMA] 10%; temperature 85°C; material:liquor ratio 1:100.

^b See Fig. 1.

^c See Fig. 4.

perhaps causes swelling of PET fibers and facilitates diffusion of monomer to the growing grafted chains and active sites on the PET backbone thereby enhancing grafting.

It is also possible that MMA forms a complex with PET and this complex is favored at high MMA concentration. Complexation of PET with MMA would enhance reactivity of MMA owing to the formation of a donor-acceptor complex in which the uncomplexed MMA, though normally an electron acceptor, behaves as a donor relative to the complexed MMA which has been converted to a stronger acceptor.^{53,54} Naturally, increasing the MMA reactivity would give rise to increased grafting. It should be noted, however, that the PET-MMA complex has to be checked. Spectroscopic measurements may provide an answer.

Figure 6 shows the effect of MMA concentration on the rate of homopolymer formed during grafting. Like the latter, the rate of homopolymerization increases significantly as the MMA concentration increases from 8 to 20%. This could be interpreted in terms of the gel effect indicated above.

From the kinetic point of view, it is clear from Figure 7 (Table II) that the rate of graft polymerization (R_p) is proportional to the 2.13 power of the MMA con-

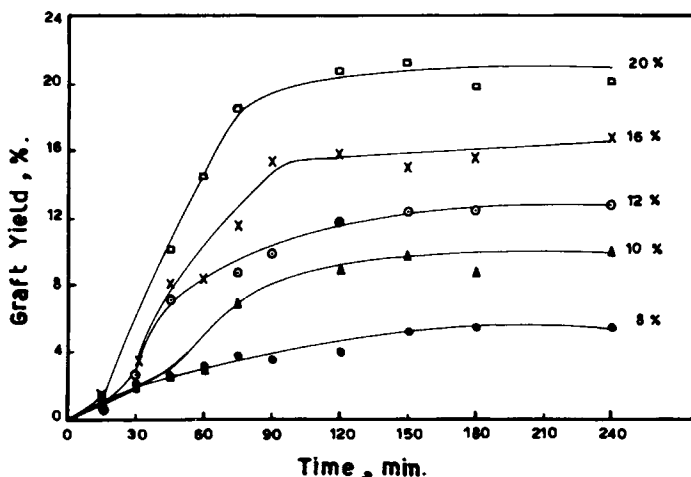


Fig. 5. Rate of grafting of MMA onto PET at different concentrations of MMA. [MMA] (%): (●) 8; (▲) 10; (○) 12; (x) 16; (□) 20. [H₂O₂] 30 mequiv/L; temperature 85°C; material:liquor ratio 1:100.

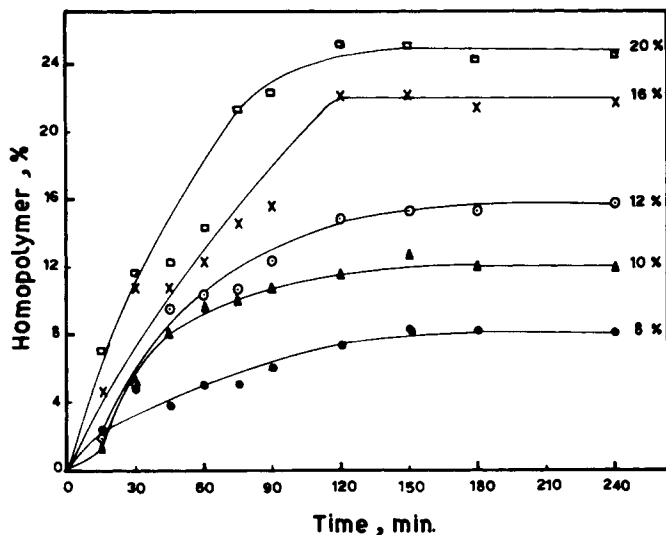


Fig. 6. Rate of homopolymerization at different concentrations of MMA. [MMA] (%): (●) 8; (▲) 10; (○) 12; (x) 16; (□) 20. [H₂O₂] 30 mequiv/L; temperature 85°C; material:liquor ratio 1:100.

centration. Thus, with respect to H₂O₂ and MMA concentrations, kinetic measurements of R_p can now be formulated as follows:

$$R_p = K[H_2O_2]^{0.193}[MMA]^{2.13}$$

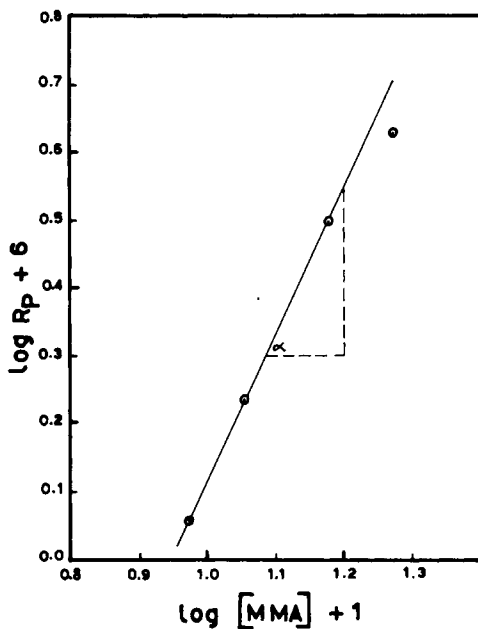


Fig. 7. Rate of grafting (R_p) vs. [MMA]. [H₂O₂] 30 mequiv/L; temperature 85°C; material: liquor ratio 1:100.

TABLE II
Dependence of Rate of Grafting on MMA Concentration^a

[MMA], mol/L	log[MMA]	log[MMA] ^b	R_p , mol/L·s	log R_p	log R_p ^c
0.752	-0.12378	0.248	1.48×10^{-6}	-5.829738	0.17026
0.940	-0.026872	0.973	1.14×10^{-6}	-5.943095	0.0569
1.128	0.052309	1.052	1.72×10^{-6}	-5.964500	0.2355
1.504	0.177248	1.177	3.16×10^{-6}	-5.500300	0.4997
1.880	0.274158	1.274	4.24×10^{-6}	-5.372600	0.6274

^a Reaction conditions: $[H_2O_2]$ 30 mequiv/L; temperature 85°C; material:liquor ratio 1:100. R_p

= Rate of grafting at [MMA] ranging 0.752–1.880 mol/L.

^b See Fig. 5.

^c See Fig. 7.

Polymerization Temperature

Figure 8 shows the effect of polymerization temperature on the rate of grafting. It is clear that graft yields at 70°C are quite low and the grafting reaction is accompanied by a long induction period which amounts to ca. 80 min. Raising the polymerization temperature results in substantial enhancement in the graft yields and the induction period falls down to ca. 30 min. Further enhancement in the graft yields and cutting down almost completely of the induction period occur upon raising the polymerization temperature to 80°C. Above this temperature, though the grafting proceeds without any induction period, yet the extent and rate of grafting decrease.

The enhancement in grafting upon raising the polymerization temperature

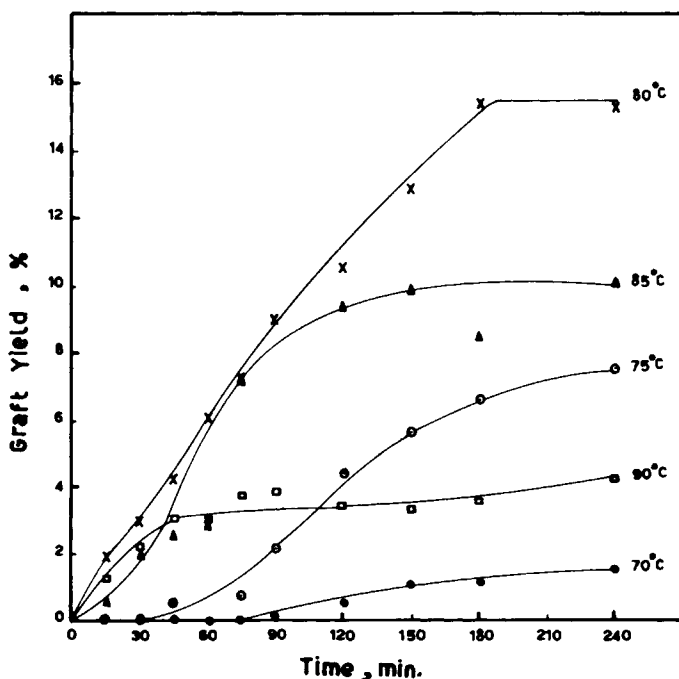


Fig. 8. Effect of temperature on rate of grafting: (●) 70°C; (○) 75°C; (x) 80°C; (▲) 85°C; (□) 90°C. [MMA] 10%; $[H_2O_2]$ 30 mequiv/L; material:liquor ratio 1:100.

from 70 to 80°C could probably be ascribed to (a) a higher rate of H_2O_2 decomposition, leading to more free radicals; (b) an accentuation in the swellability of PET fibers; (c) a higher rate of monomer diffusion from the polymerization medium to the PET fibers; (e) possible reaction between the growing homopolymer chain radical with PET and/or the PET macroradicals; and (f) increment in the rates of initiation and propagation of the graft. The net effect of all these factors is certainly increased grafting, whereas lowering of grafting by raising the polymerization reaction temperature above 80°C would suggest that the rate of termination prevails over the rates of initiation and propagation of the graft, similar to other initiating systems.^{48,51}

Figure 9 shows the rate of grafting R_p vs. $1/T$. From this Arrhenius plot, the apparent activation energy for grafting could be calculated; it amounts to 22.8 kcal/mol.

Figure 10 shows the effect of polymerization temperature on the rate of homopolymerization formed during grafting. It is apparent that, unlike grafting, homopolymerization proceeds without any induction period irrespective of the polymerization temperature within the range studied, though the magnitude of homopolymerization was quite low at lower temperature (70, 75°C) in the initial stages of the reaction. Increasing the polymerization temperature to 80°C is accompanied by a significant enhancement in the rate of homopolymerization, whereas increasing the polymerization temperature to 85°C reduces the rate of homopolymerization. The latter is further reduced to a significant extent by raising the polymerization temperature up to 90°C. This is rather the trend observed with grafting.

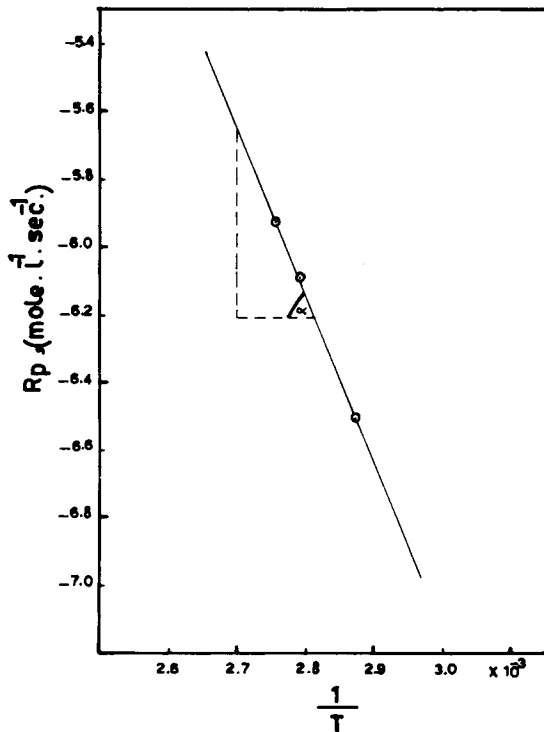


Fig. 9. Arrhenius plots for graft copolymerization of MMA in presence of PET. [MMA] 10%; $[H_2O_2]$ 30 mequiv/L; material:liquor ratio 1:100.

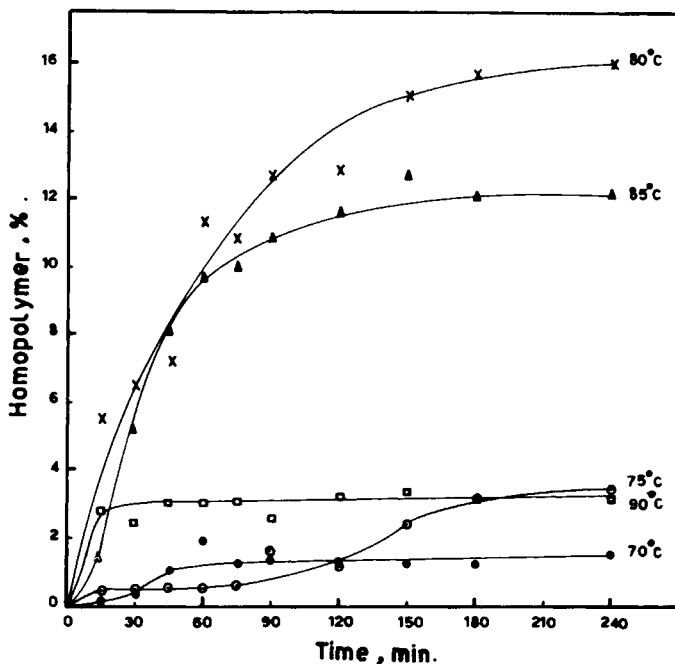


Fig. 10. Variation of extent and rate of homopolymerization with temperature in presence of PET. [MMA] 10%; [H₂O₂] 30 mequiv/L; (●) 70°C; (○) 75°C; (x) 80°C; (▲) 85°C; (□) 90°C; material:liquor ratio 1:100.

Raising the polymerization temperature to 80°C seems to favor decomposition of H₂O₂ and monomer solubility, as well as initiation and propagation of the homopolymer. As a result, homopolymerization increases. At temperature higher than 80°C, it seems that termination proceeds at a much faster rate than initiation and propagation, thereby giving rise to lower homopolymerization.

The finding that the homopolymerization takes place almost without induction period at 70 and 75°C whereas grafting shows a considerable induction period is indicative that the redox system formed between the decomposition products of H₂O₂ (HO₂ and/or OH) and monomer is more efficient than its counterpart with PET fibers. That is why considerable homopolymer formation occurs during grafting under the conditions used.

pH of Polymerization

Figure 11 shows the effect of pH of the polymerization medium on the magnitude of grafting. As is evident, the graft yield increases with increasing pH of the polymerization medium, from 2 to 7. Above pH 7, lower graft yields are obtained. In other words, pH 7 constitutes the optimal pH for grafting.

The lower grafting obtained in acidic media (low pH) suggests that the hydrogen ions act as terminators for free radicals formed in the polymerization medium^{48,54} and/or termination of growing grafted chain and PET macroradicals. It is rather possible that decomposition of H₂O₂ to yield free radicals is impeded in acidic medium, thereby lowering the initiation step. Similarly, in alkaline media, decomposition of H₂O₂ to yield free radicals seems to be quite low. Furthermore, excess of hydroxyl groups in the polymerization may react with

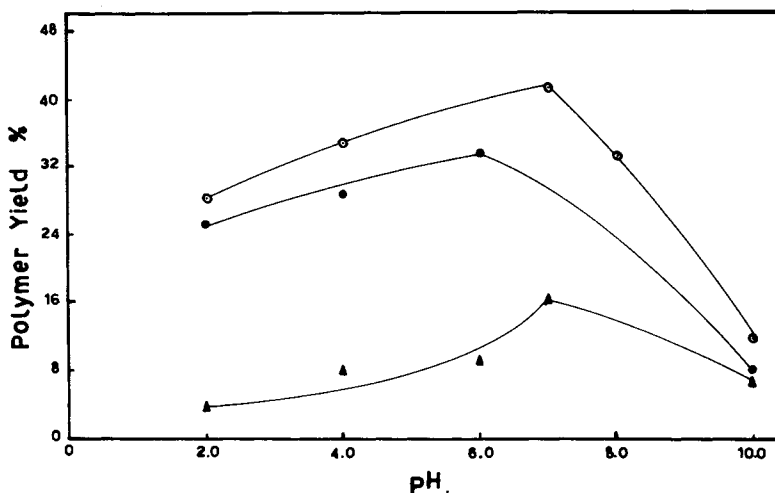


Fig. 11. The effect of pH on polymer yield: (●) graft yield; (O) homopolymer; (▲) graft efficiency. [MMA] 10%; [H₂O₂] 30 mequiv/L; reaction time 4 h; material:liquor ratio 1:100.

HO₂ and/or OH radicals to bring about oxygen which inhibit the graft polymerization reaction.

The effect of the polymerization medium on the homopolymer formed during grafting is shown in Figure 11. Similar to grafting, maximum homopolymer formation occurs at pH 7. Below or above this pH, decreased homopolymer is obtained. This again reflects the mode of the decomposition and further reactions of the decomposition products of H₂O₂ at different pH values in the presence of MMA and PET fibers.

Metallic Ions

It has been reported that incorporation of certain concentration of metallic ions such as Cu²⁺ and Fe³⁺ ions in free radical polymerization media for grafting vinyl monomers onto cellulose,^{53,55,56} wool,⁵⁷ nylon,⁵² and polyester⁴⁸ improves grafting significantly. With this in mind, trials were made in this work to find out the influence of such ions on grafting of PET fibers with MMA using H₂O₂ as initiator.

Table III shows the effect of addition of copper sulfate at various concentrations to the polymerization system on the graft yield. It is seen that the latter decreases significantly when low concentrations of copper sulfate (0.1 mmol/L) were used. However, this decrease lessens as the copper sulfate concentration increases from 0.1 to 0.8 mmol/L. Increasing the copper sulfate concentration to 1.0 mmol/L brings about a graft yield the value of which is nearly equal to that obtained in the absence of copper sulfate. Further increase in copper sulfate concentration is accompanied by a significant decrease in graft yield, the decrease being higher the higher the copper sulfate concentration.

Similar behavior is observed when ferrous ammonium sulfate is used instead of copper sulfate, except that the graft yield obtained in the presence of ferrous ammonium sulfate is substantially lower than in its absence, irrespective of the concentrations of ferrous ammonium sulfate used (Table III).

TABLE III
 Effect of Cations on Polymer Yield^a

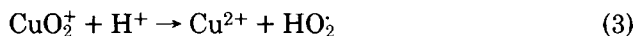
Cation concentration, mmol/L	CuSO ₄ ·5H ₂ O		FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	
	G.Y., ^b %	H., ^c %	G.Y., ^b %	H., ^c %
0.00	10.12	12.18	10.12	12.18
0.10	1.72	36.81	4.08	27.19
0.40	2.40	40.14	4.64	33.54
0.80	5.83	47.49	4.74	36.87
1.00	10.08	56.29	5.80	64.85
2.00	5.92	50.08	7.94	79.48
3.00	4.00	43.97	6.70	70.80
4.00	5.08	38.74	2.70	59.37
5.00	4.80	27.15	1.84	47.88
10.00	2.14	25.91	1.49	36.99
15.00	2.30	24.55	0.92	26.79
20.00	2.40	23.79	1.00	21.13
30.00	1.68	23.05		
50.00	1.00	21.84		

^a [H₂O₂] 30 mequiv/L; [MMA] 10%; temperature 85°C; reaction time 240 min; material:liquor ratio 1:100.

^b G.Y. = Graft yield.

^c H. = homopolymer.

The significant decrease in grafting upon using lower and higher concentrations of copper sulfate may be explained if one assumes that at lower concentration, the Cu²⁺ ions are preferably adsorbed on the PET backbone. These adsorbed Cu²⁺ ions act as a radical trap. They participate mainly in termination of PET macroradicals, thereby decreasing grafting. Lessening of this decrease by increasing the Cu²⁺ ion concentration up to 0.8 mmol/L suggests that the Cu²⁺ ions accelerate the decomposition of H₂O₂; decomposition of peroxides by metallic ions is well established.^{58,59} Moreover, MMA and Cu²⁺ form perhaps a redox system. As a result, Cu²⁺ ion is converted to Cu⁺ ion. The latter would be oxidized back to the cupric state by atmospheric oxygen, and this conversion must presumably involve radical intermediate as suggested below:⁵²⁻⁶⁰



The HO₂ radicals are involved presumably in the initiation of grafting or can undergo a reaction leading to formation of hydrogen peroxide as well as hydroxyl radicals.⁴⁸ Initiation of grafting by this means would partially compensate for the significant decrease in grafting caused by the adsorbed Cu²⁺ ion, thereby lessening the decrease in grafting. This state of affairs seems to be valid up to a certain concentration of Cu²⁺ (0.1 mmol/L), where the onset of termination is probably counterbalanced by graft initiation caused by extra HO₂ radicals [eq. (3)] as well as by other free radical species resulted therefrom. As a consequence, no significant change in the graft yield is observed. Further increase in Cu²⁺ ion concentration would lead to an abundance of free radicals, which seem to accelerate termination in preference to grafting. This would account for the

outstanding decrease in graft yield at higher Cu^{2+} ion concentration. The behavior observed with Fe^{3+} ions can be explained on a similar basis, though the graft yield at any Fe^{3+} ion concentration is lower than in its absence.

The effect of incorporation of Cu^{2+} and Fe^{3+} ions at different concentrations in the polymerization system on the magnitude of homopolymer formed during grafting is shown in Table III. Unlike grafting, the magnitude of homopolymer increases significantly as the concentration of both said metallic ions increases from 0.1 to 2.0 mmol/L. Thereafter, the magnitude of homopolymer decreased upon further increase in the metallic ions concentration.

The enhancement in homopolymer formation by increasing metallic ions concentration up to a certain limit could be associated with the catalytic influence of these ions on the decomposition of H_2O_2 as already indicated. On the other hand, the decrement in homopolymerization with higher concentrations of Cu^{2+} or Fe^{3+} ions could be traced back to an abundance of free radicals which speed up the termination of growing polymer chains and/or self-coupling.

That homopolymerization increases in the presence of metallic ions over a wide range of concentration while grafting generally decreases implies that the presence of these metallic ions does alter the magnitude of the graft/homopolymer ratio. It further substantiates the assumption that certain amounts of the metallic ions are preferably adsorbed on PET backbone and act as a radical traps.

Swelling Agents

1,1,2,2-Tetrachloroethane^{61,62} and methylene chloride¹ have been reported as good swelling agents for PET fibers. It appears, therefore, of interest to establish the influence of these swelling agents on grafting of PET fibers with MMA under the initiation of H_2O_2 .

To start with, different concentrations of methylene chloride (2–40%) were added to a polymerization system consisting of PET, MMA (10%), and H_2O_2 (2 mequiv/L). A material-to-liquor ratio of 1:100 was used. Since the boiling point of methylene chloride is low (42°C), the polymerization reaction was carried out under reflux for 120 min. Results of these experiments reveal that at a concentration of methylene chloride of 2%, the graft yield and homopolymer amount to 3.4 and 18.76%, respectively. This compares with a graft yield of 2.96% and a homopolymer of 7.33% obtained under similar conditions in the absence of methylene chloride. Increasing the concentration of the latter was found to decrease grafting as well as homopolymerization. At methylene chloride concentration of 20%, neither grafting nor homopolymerization occur.

In another series of experiments, samples of fibers (0.5 g each) were placed in glass ampoules containing a mixture of MMA and methylene chloride at a ratio of 1:1. To this, H_2O_2 at different concentrations (2–100 mequiv/L) was added and the ampoules were evacuated and sealed. The weight ratio of the mixture (MMA/methylene chloride) to PET fibers was 15.6:1. The ampoules were kept in a thermostat at 85°C for 4 h. Similar experiments were carried out without evacuation. After repeated extraction with acetone and drying, it was found that maximum grafting (4.6) occurs under vacuum at an H_2O_2 concentration of 30 mequiv/L.

In a third series of experiments, samples of PET fibers were immersed at 25°C

in methylene chloride for different periods of time (5–20 min). Excess solvent was then removed by blotting between filter papers (pickup 62.4%). At this end, the samples were introduced in the polymerization solution. The latter consisted of MMA (10%) and H_2O_2 (2 mequiv/L). A material-to-liquor ratio of 1:100 was used. The reaction was then allowed to proceed for 120 min at 85°C. Here, too, the results revealed that no improvement in the graft yield could be achieved by preswelling of the PET fibers in methylene chloride regardless of the swelling time. On the contrary, the graft yield decreased from 2.9% in the absence of methylene chloride to 1.8% in its presence.

It can be concluded that the presence of methylene chloride during grafting of MMA onto PET fibers using H_2O_2 as initiator has little or no favorable effect on the graft yield. This is observed regardless of the techniques used in this work.

After the failure of methylene chloride to enhance grafting, attention was directed to 1,1,2,2-tetrachloroethane. Samples of PET fibers were impregnated in 1,1,2,2-tetrachloroethane for 45 min (experimentally proved to be the most adequate time for swelling) at 25°C and then blotted with filter papers in such a way that different pickup could be obtained. After this, the samples were introduced into a polymerization solution containing MMA (10%) and H_2O_2 (30 mequiv/L). A material-to-liquor ratio of 1:100 was used. The polymerization was allowed to proceed for 240 min at 85°C. The results obtained are shown in Table IV.

It is apparent (Table IV) that a pickup by the fibers of 220% constitutes the optimal amount of tetrachloroethane to enhance the susceptibility of the fibers toward grafting. A graft yield of 48.66% could be achieved at this pickup. It seems that presence of excess tetrachloroethane within the fibers impedes diffusion of monomer and initiator by forming a barrier thereby decreasing grafting. At lower pickup, the amount of tetrachloroethane is probably not high enough to keep the PET structure swollen. However, problems associated with miscibility of the polymerization ingredients, decomposition of H_2O_2 , solubility of MMA in the polymerization solution, and solubility of poly(MMA) in its own monomer in the presence of different amounts of tetrachloroethane cannot be ruled out.

Table V shows the effect of H_2O_2 concentration on grafting when the latter was carried out in the presence of tetrachloroethane at a pickup of 220%. The conditions used were similar to those described above. Obviously, the graft yield

TABLE IV
Effect of Percent Pick-up of Swelling Agent on Graft Yield^a

Pick-up, %	Graft yield, %
418.8	1.06
235.6	22.09
220.0	48.66
196.0	5.10
173.8	3.80
146.4	3.20
57.2	0.00

^a Time of swelling 45 min; temperature 85°C; material:liquor ratio 1:100. Swelling occurred at room temperature.

TABLE V
Effect of H₂O₂ Concentration on Graft Yield^a

H ₂ O ₂ , mequiv/L	Graft yield, %
1	0.6
2	4.9
3	5.44
4	6.02
5	35.80
30	48.66

^a Preswelled PET, which has a constant percent pick-up of the swelling agent (1,1,2,2-tetrachloroethane). Swelling occurred at room temperature. Pick-up 220%; [MMA] 10%; time of swelling 45 min; reaction time 240 min; reaction temperature 85°C; material:liquor ratio 1:100.

increases slightly by increasing H₂O₂ concentration from 1 to 4 mequiv/L. Increasing H₂O₂ concentration to 5 mequiv/L is accompanied by a significant enhancement in grafting. The improvement in grafting continues with increasing H₂O₂ concentration up to 30 mequiv/L, which was the highest concentration examined. This rather agrees with the results previously discussed.

In an attempt to improve swelling of PET fibers, the latter were treated with tetrachloroethane at 85°C for 90 min, then blotted to a pickup of 220%. At this end, the fibers were introduced in a solution containing MMA (10%) and H₂O₂ (30 mequiv/L) at a material-to-liquor ratio of 1:100. The polymerization reaction was then allowed to proceed at 85°C for 4 h. Determination of the reaction product revealed 75.68, 28.50, and 21.99% for grafting, homopolymer, and graft efficiency, respectively. This reflects the improved swelling action of tetrachloroethane at higher temperatures on PET fibers.

Proof of Grafting

Polymerization of MMA in the presence of PET was carried out using H₂O₂ as initiator as described in the experimental section. After polymerization, the PET was subjected to several acetone extractions to remove the homopolymer,

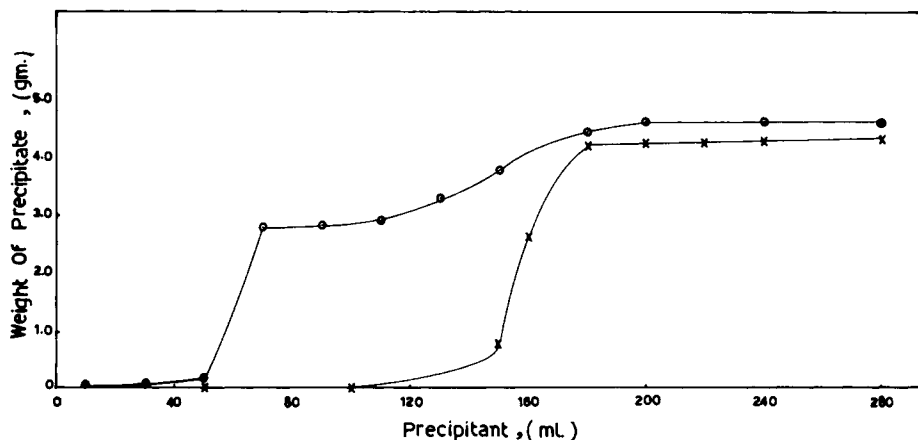


Fig. 12. Fractional precipitation curves of PET-MMA polymerization product and a physical mixture of PET and PMMA: (x) PET-MMA polymerization product; (O) physical mixture of PET-PMMA.

and the dry weights were compared with that of a blank consisting of a physical mixture of PET and homopoly(MMA). Both the extracted PET with an increase in weight of 40.45% and the blank having a similar composition were dissolved at a concentration of 1.9% in a phenol/tetrachloroethane mixture (175:125 v/v). After dissolution, a precipitant (methanol) was added gradually to the solution. At various stages, the precipitated polymer was removed, and stepwise addition of the precipitant to the remaining liquid was continued.

Figure 12 shows the weight (g) of polymer precipitate vs. the amount of precipitant added. It is clear that with the PET-MMA polymerization product, a more or less continuous precipitation curve is obtained. With the physical mixture, on the other hand, the curve shows a sharp difference in the solubility behavior of the two homopolymers, i.e., PET and PMMA. This may be taken as an indication of chemical link formation between PET and PMMA, that is, grafting.

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