

# Polymerization of Glycidyl Methacrylate with Poly(ethylene Terephthalate) Fibers Using $\text{Fe}^{+2}\text{-H}_2\text{O}_2$ Redox System

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## Synopsis

$\text{Fe}^{+2}\text{-H}_2\text{O}_2$  redox system initiated polymerization reactions of glycidyl methacrylate (GMA) from aqueous solution with poly(ethylene terephthalate) fibers (PET) were investigated. The polymer add-on is greatly influenced by  $\text{H}_2\text{O}_2$  concentration, GMA concentration, as well as reaction time and temperature. Polymer add-on was directly related to  $\text{H}_2\text{O}_2$  concentration up to 30 meq/L and GMA concentration up to 4%. Further increase in concentrations of  $\text{H}_2\text{O}_2$  and GMA resulted in lower polymer add-on. Raising the reaction temperature from 65°C to 95°C caused a significant enhancement in the rate of polymerization, the latter follows the order 95 > 85 > 75 > 65°C. However, at 65°C, the polymerization reaction showed an induction period of about 120 min, in contrast with reactions at 75°C, 85°C, and 95°C, where no induction period was observed though the polymer add-on was quite low at 75°C during the initial stages of the reaction. Using dimethylformamide (DMF) alone or mixed with water as polymerization medium offset the polymerization reaction. Incorporation of thioureadioxide in the polymerization system decreased the polymer add-on significantly.

## INTRODUCTION

Polymerization of various vinyl monomers with poly(ethylene terephthalate) fibers (PET) has been the subject of a number of publications.<sup>1-11</sup> The polymerization can be accomplished either by radiation<sup>3,6,8,12</sup> or chemical means.<sup>1,4,5,13,14</sup> 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 polymerizing PET with styrene,<sup>1</sup> 4-vinylpyridine,<sup>3</sup> 2-methyl-5-vinylpyridine,<sup>4,5</sup> acrylonitrile,<sup>6</sup> acrylate esters,<sup>7,14</sup> acrylamide,<sup>8</sup> acrylic,<sup>13</sup> and methacrylic acids.<sup>9</sup>

Incorporation of a monomer such as glycidyl methacrylate in synthetic fibers such as polyester or polyacrylonitrile fibers via graft polymerization initiated by radical initiators (radiation or ozone) has been reported to improve their dyeability due to presence of the glycidyl group.<sup>15</sup>

The present work deals with polymerization of glycidyl methacrylate (GMA) with PET fibers using  $\text{Fe}^{+2}\text{-H}_2\text{O}_2$  redox under different conditions.

## EXPERIMENTAL

### Materials

Poly(ethylene terephthalate) fibers (PET-Tergal, Hoechst-1.2 den/40 mm, cotton type) were purified through a mild cleaning treatment with sulphonated

fatty alcohol (2 g/L) for 30 min at 65°C, rinsed with hot and cold water, dried at room temperature, and finally Soxhlet-extracted with methanol for 24 h to remove any material adhering to the surface.

Glycidyl methacrylate obtained from a commercial source was freed from the inhibitor by vacuum distillation before use.

Hydrogen peroxide (MERCK), ferrous ammonium sulphate [ $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ] and thioureadioxide were of analytical grade chemicals. Dimethylformamide (MERCK) was laboratory grade.

### Polymerization Procedure

Unless otherwise indicated, the polymerization reaction was carried out as follows:

PET fibers (0.5 g) was impregnated in an aqueous solution containing 0.1% freshly prepared ferrous ammonium sulphate for 1 h at room temperature. The sample was then squeezed till almost dryness. The  $\text{Fe}^{+2}$ -treated PET was introduced in a 50-mL stoppered conical flask containing an aqueous solution of glycidyl methacrylate at a certain temperature followed by addition of  $\text{H}_2\text{O}_2$ . The contents of the flask were stirred occasionally during polymerization. After the desired reaction time, the contents were filtered on a sintered glass crucible and thoroughly washed with water. The sample was then Soxhlet-extracted with methyl ethyl ketone (MEK) for 48 h and dried in an oven at 85°C for 2 h, followed by cooling over  $\text{P}_2\text{O}_5$ , and weighed. The increase in weight of the extracted sample, as compared with that of untreated PET sample, was recorded as polymer add-on.

### Determination of the Epoxide Content

For estimation of free epoxy rings in poly(GMA)-containing PET, the following procedure was adopted, which, in essence, is based on methods described elsewhere<sup>16,17</sup>: Fiber sample (ca. 1 g) was immersed in concd. HCl:dioxane mixture (3:1) at room temperature for 2 h using a material-to-liquor ratio of 1:10. The sample was then thoroughly washed with distilled water to avoid any traces of the acid. Accurate weight of the acid-free sample (20–25 mg) was combusted in an Erlenmeyer flask containing 5 mL of 5% KOH, 15 mL 6%  $\text{H}_2\text{O}_2$ , and filled with  $\text{O}_2$ . The flask was then allowed to cool at room temperature under shaking. After washing the glass stopper and the platinum wire with the least amount of bidistilled water, the solution was boiled for 5 min to decompose excess  $\text{H}_2\text{O}_2$ . The solution was then allowed to cool and 80 mL ethanol was added, 5 drops of alcoholic bromophenol blue solution (0.05%) were added, and the whole solution neutralized with 0.5N  $\text{HNO}_3$  till the end point of the indicator. One mL of 0.5N  $\text{HNO}_3$  was also added to bring the pH to a value of about 3.5. At this end, 15 drops of alcoholic diphenylcarbazone (0.5%) were added then titrated against 0.01N  $\text{Hg}(\text{NO}_3)_2$  till the end point (from faint yellow to cherry red). The percent polymer add-on of poly(glycidyl methacrylate) was calculated as follows:

$$\text{polymer add-on \%} = \frac{(V - V_1)N \cdot 0.1785}{G} \times 100$$

where  $V$  and  $V_1$  = volume (mL) of 0.01N  $\text{Hg}(\text{NO}_3)_2$  of solution and blank, respectively,  $N$  = Normality of  $\text{Hg}(\text{NO}_3)_2$  used, and  $G$  = weight of sample (g).

### Moisture Regain Determination

The dry samples were conditioned at 65% relative humidity, at 25°C and weighed. They were then oven-dried at 105°C for 4 h and weighed again:

$$\text{moisture regain \%} = \frac{\text{wt conditioned sample} - \text{wt dry sample}}{\text{wt dry sample}} \times 100.$$

## RESULTS AND DISCUSSION

### Hydrogen Peroxide Concentration

The effect of  $\text{H}_2\text{O}_2$  concentration on  $\text{Fe}^{+2}$ - $\text{H}_2\text{O}_2$  redox system initiated polymerization of GMA from aqueous solution with PET fibers is shown in Figure 1. PET fibers were immersed for 1 hr in freshly prepared 100 mL aqueous solution of 0.1% ferrous ammonium sulphate at room temperature, blotted between filter papers till they become almost dry, and then introduced into an aqueous solution of GMA (4%).  $\text{H}_2\text{O}_2$  at different concentrations (5–200 meq/L) was added and the reaction was allowed to proceed at 85°C for 4 h.

It is seen (Fig. 1) that increasing the  $\text{H}_2\text{O}_2$  concentration up to 30 meq/L is accompanied by a substantial increase in the polymer add-on. Further increase in  $\text{H}_2\text{O}_2$  concentration causes a marked fall in the polymer add-on. A similar trend was reported for grafting 2-methyl-5-vinylpyridine<sup>5</sup> and acrylic acid<sup>13</sup> to PET fibers.

The above findings can be explained as follows:  $\text{H}_2\text{O}_2$  decomposes in the presence of  $\text{Fe}^{+2}$  ions to yield hydroxyl radicals ( $\dot{\text{O}}\text{H}$ ) as suggested by reaction (1). The hydroxyl radicals may be terminated by  $\text{Fe}^{+2}$  ions (reaction 2) or further decompose  $\text{H}_2\text{O}_2$  to yield  $\text{HO}_2$  radicals (reaction 3). Reaction of the  $\text{HO}_2$

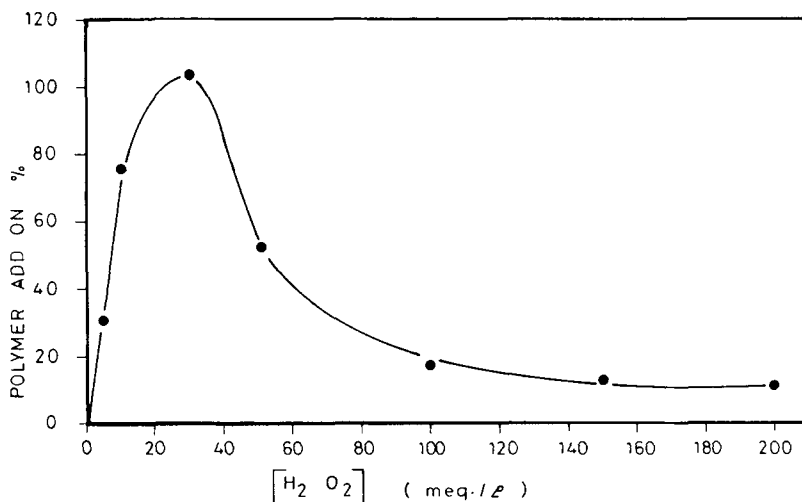
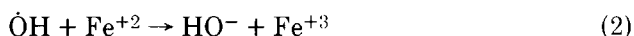
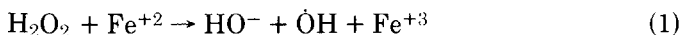
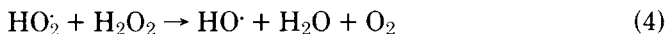
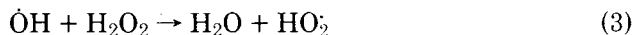


Fig. 1. Variation of polymer add-on with  $\text{H}_2\text{O}_2$  concentration. PET fibers pretreated with 0.1% ferrous ammonium sulphate, [GMA], 4%; reaction time = 4 h; temperature = 85°C; material:liquor ratio 1:100.



radical with  $\text{H}_2\text{O}_2$  lead to hydroxyl radicals (reaction 4).



Thus in a system containing PET, GMA,  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{+2}$ , and water, the following processes are likely to occur: (a) direct abstraction of hydrogen atom from the PET backbone by  $\text{HO} \cdot$  and  $\text{HO}_2$  radicals to yield PET macroradical capable of initiating reaction with GMA; (b) direct attack on GMA by these radicals leading to growing poly(GMA) chains; (c) termination of the latter by PET via chain transfer would lead to similar PET macroradical chains; (d) termination of free radical species by coupling; and (e) termination of PET macroradical and growing poly(GMA) by the  $\text{HO} \cdot$  and  $\text{HO}_2$  radicals. The ultimate effects of all these processes determine the magnitude of polymer add-on. Current work suggests that the effects of (a), (b), and (c) prevail over those of (d) and (e) provided that  $\text{H}_2\text{O}_2$  concentration does not exceed 30 meq/L, and, as a result, higher polymer add-on was achieved. Above this concentration, the situation is reversed most probably due to abundance of free radicals which favors the termination processes, thereby giving rise to lower polymer add-on.

### Monomer Concentration

The effect of GMA concentration on polymer add-on is shown in Figure 2. It is clear that the polymer add-on is directly related to GMA concentration up to 4%. As the monomer concentration increases above this value, there is a substantial reduction in polymer add-on. That is, concentration of 4% constitutes the optimal concentration for achieving maximum polymer add-on.

The decrement in polymer add-on at higher GMA concentrations could be

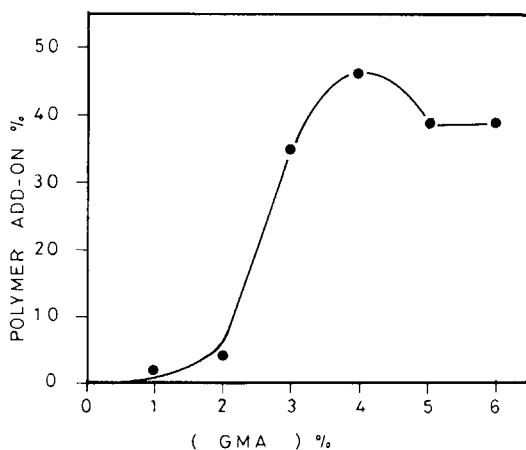


Fig. 2. Effect of glycidyl methacrylate concentration on percent polymer add-on. PET fibers pretreated with 0.1% ferrous ammonium sulphate,  $[\text{H}_2\text{O}_2]$ , 50 meq/L; reaction time = 4 h; temperature = 85°C; material:liquor ratio 1:100.

interpreted if one assumes that much of the monomer is physically adsorbed on the PET fibers and impedes diffusion of the initiator inside the fibers, thereby lowering the polymer add-on.<sup>4</sup> It is rather likely that homopolymerization prevails over polymerization with PET fibers at higher GMA concentrations, and, as a result, lower add-on is obtained. Indeed, significant amount of homopolymer formation was observed when higher GMA concentrations were used.

### Polymerization Temperature

Figure 3 shows the effect of temperature on the extent and rate of polymerization of GMA with PET fibers. Obviously, both extent and rate of polymerization increase as the reaction temperature increases from 65°C to 95°C. Nevertheless, at 65°C the polymerization reaction shows an induction period of about 120 min, in contrast with polymerization at 85°C and 95°C, at which the reaction proceeds without any induction periods. At 75°C, on the other hand, the polymerization reaction proceeds initially (during the first 90 min) very slowly then becomes faster during the later stages of the reaction.

The enhancement in polymer add-on by raising the polymerization temperature could be attributed to the favorable effect of temperature on: (a) formation of PET macroradicals through attack of H<sub>2</sub>O<sub>2</sub> decomposition product and/or thermal oxidation of PET fibers, (b) swellability of PET fibers and mobility of monomer molecules, both constitute the main controlling factors for monomer diffusion from the aqueous phase to fibre phase, (c) possible reactions between growing homopolymer chains with the substrate and/or the substrate macroradicals, and (d) rate of initiation and propagation of the polymerization of GMA with PET fibers. Besides the above parameters, PET attains its glass transition temperature ( $T_g$ ) at 80–85°C.<sup>18</sup> Since the PET segments become more mobile at  $T_g$ , reactivity of PET would increase at this temperature and above, thereby giving rise to higher polymer add-on.

Slowing down of the polymer add-on percent during the later stages of the reaction (after 150 min), in particular, at 95°C, could be associated with (a) de-

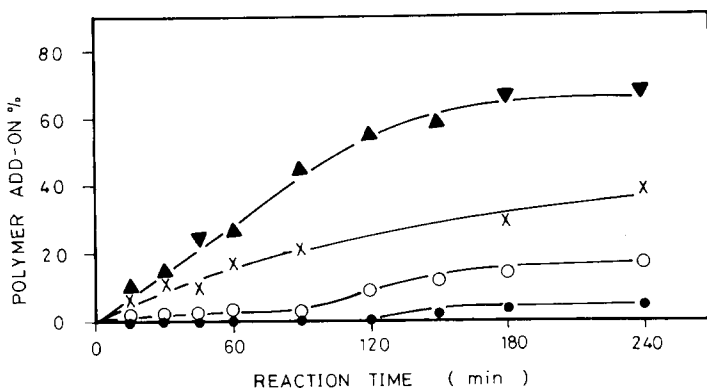


Fig. 3. Effect of temperature on the rate of polymerization. PET fibers pretreated with 0.1% ferrous ammonium sulphate: (●) 65°C; (○) 75°C; (×) 85°C; (▲) 95°C; [H<sub>2</sub>O<sub>2</sub>], 50 meq/L; [GMA], 4%; material:liquor ratio 1:100.

pletion in monomer and initiator concentration as well as decrease in the available activate sites on PET backbone, (b) fast rate of termination, and (c) prevention of monomer diffusion due to the relatively great amount of internally deposited poly GMA that has occurred during the initial stages of the polymerization.

### Reaction Time

Figure 3 shows the effect of duration of polymerization of GMA with PET fibers on polymer add-on. As is evident, the latter is related to the polymerization temperature. The significant effect of the polymerization time was only visualized when the polymerization reaction was carried out at 75°C and above. As already indicated, the polymer add-on was quite poor during the first 90 min of the reaction when the latter was formed at 75°C but became substantial upon further prolonging the duration of polymerization. At 85°C the effect of increasing the reaction time up to 240 min is to bring about significant improvement in polymer add-on. The same situation is encountered with polymerization at 95°C, but the polymer add-on does level off after 180 min reaction time.

Levelling off of the polymer add-on at 95°C could be associated with (a) depletion in monomer and initiator concentration as well as decrease in the available active sites on PET backbone as the reaction proceeds and (b) formation of relatively great amount of internally deposited poly(GMA) in PET, during the initial stages of the polymerization reaction, which would act as diffusion barrier for monomer and initiator.

### Addition of Thioureadioxide

Recent work<sup>19</sup> has disclosed that presence of thioureadioxide in the  $\text{Fe}^{+2}$ - $\text{H}_2\text{O}_2$ -GMA- $\text{H}_2\text{O}$  polymerization system is essential for initiating polymerization of GMA with cotton cellulose. The polymer add-on increased by increasing thioureadioxide concentration up to ca. 0.05% then decreases upon further increase in thioureadioxide concentration.

When thioureadioxide at different concentrations was added to the PET-GMA- $\text{H}_2\text{O}_2$ - $\text{Fe}^{+2}$ - $\text{H}_2\text{O}$  polymerization system, it was observed that the polymer add-on decreased. Moreover, the decrease was higher the higher the concentration of thioureadioxide, suggesting that thioureadioxide seems to act as radical scavenger rather than to initiate polymerization with PET irrespective of the concentration used, opposite to the cotton cellulose.<sup>19</sup>

### DMF as a Polymerization Medium

Grafting of GMA onto PET fibers using benzoyl peroxide as initiator in 80% aqueous DMF solution had been reported by Suzuki et al.<sup>20</sup> to accentuate grafting. In this work DMF/water mixtures at different ratios were used as polymerization media under conditions similar to those described in the experimental section. The results obtained indicated that presence of DMF in the polymerization system offset polymerization of GMA with PET. DMF seems to inhibit the formation of  $\text{H}_2\text{O}_2$  radicals, in contrast with benzoyl peroxide.<sup>20</sup>

TABLE I  
Stability of Epoxy Ring in PET Polymerized with Glycidyl Methacrylate

No.	Polymer add-on % based on increase in weight	Polymer add-on % based on estimated epoxy content	Moisture regain (%)
	Pure PET fibers	—	0.30
1	9.5	6.19	0.40
2	16.00	7.43	0.76
3	28.60	24.13	1.15
4	46.10	25.99	1.95
5	149.80	51.36	2.04

### Stability of the Epoxy Groups

PET fibers containing different poly(GMA) add-ons were analyzed for the epoxy content. The polymer add-ons which originally derived from the increase in weight of the PET fibers were recalculated on the basis of the free epoxy ring analysis. The results obtained are set out in Table I.

The data (Table I) indicate that the polymer add-ons based on increase in weight are significantly higher than those based on estimated content. This signifies that the epoxy ring of GMA in the polymer add-on is not stable. It seems likely that ring opening occurs in part during washing via addition of H<sub>2</sub>O molecules to the free epoxy ring. Indeed, the higher moisture regain of PET fibers polymerized with GMA as compared with untreated fibers substantiates this (Table I).

### References

1. R. Tsuzuki and Maeta, Jpn. Pat. 7129, 918 (1971); *Chem. Abstr.*, **77**, 50069q (1972).
2. V. V. Korshak, K. K. Mozgova, and S. P. Krukovskii, *Vysokomol. Soedin.*, **4**, 1625 (1962); *Chem. Abstr.*, **59**, 2977f (1963).
3. M. V. Mikhailov, L. G. Tokareva, T. D. Bratchenko, V. L. Karpov, and Yu. M. Malinskii, *Tr. 2-go (Vtorogo) Vses. Soveshch. Po Radiats. Khim., Akad. Nauk SSSR, Moscow*, 589 (1960) (publ. 1962).
4. S. E. Shalaby, A. M. Bayazeed, and A. Hebeish, *J. Appl. Polym. Sci.*, **22**, 1359-1375 (1978).
5. A. Hebeish, S. E. Shalaby, and M. F. El-Shahid, *Angew. Makromol. Chemie*, **66** (966), 139 (1978).
6. E. E. Magat and D. Tanner, U.S. Pat. 3,413,378 (1968); *Chem. Abstr.*, **70**, 29994h (1969).
7. W. S. George and G. T. Teddy, U.S. Pat. 3,268,622 (1966); *Chem. Abstr.*, **66**, 11763q (1967).
8. T. Achmatowicz, A. Robalewski, and W. Zielinski, Pol. Pat. 59, (1970); *Chem. Abstr.*, **74**, 127401q (1970).
9. M. F. Blin, R. Candan, G. Gaussens, F. Lemaire, and D. Paoli, Fr. Pat. 2,045,261 (1971); *Chem. Abstr.*, **76**, 15692v (1972).
10. R. Kotake, T. Kojima, and M. Togo, Jpn. Pat., 7041, 023 (1970); *Chem. Abstr.*, **74**, 113131q (1971).
11. K. N. Rao, M. H. Rao, P. N. Moorthy, and A. Charlesby, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 893 (1972).
12. A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *J. Appl. Polym. Sci.*, **22**, 3335, (1978).
13. A. Hebeish, S. Shalaby, and A. Bayazeed, *J. Appl. Polym. Sci.*, **26**, 3245 (1981).

14. A. Hebeish, S. Shalaby, and A. Bayazeed, *J. Appl. Polym. Sci.*, **26**, 3253 (1981).
15. H. Mark, N. S. Wooding, and S. M. Atlas, *Chemical After Treatment of Textiles* Wiley-Interscience, New York, 1971, p. 244.
16. A. I. Vogel, *Elementary Practical Organic Chemistry. Part 3. Quantitative Organic Analysis*, 7th ed., Logman Group Ltd., London, 1971, p. 826.
17. F. W. Cheng, *Microchem. J.*, **3**, 537 (1959).
18. E. Schamberg and J. Hoigne, *J. Polym. Sci., A-1*, **8**, 693-698 (1970).
19. A. Waly, N. Y. Abou-Zeid, E. A. El-Alfy, and A. Hebeish, *Angew. Makromol. Chem.*, **183**, 61 (1982).
20. K. Suzuki, I. Kido, and K. Katsuki, *Sen'i Gakkaishi*, **29**(10), T428-T435 (1973); *Chem. Abstr.*, **80**, 38142n (1974).

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