Graft Copolymerization of Acrylamide onto Polyethylene Terephthalate (PET) with Potassium Permanganate as Initiator

Grafting of vinyl monomers onto natural and synthetic macromolecules has attracted the attention of several groups of investigators in recent years.[1-4] Literature study reveals that different initiating systems have been tried with varying degrees of success. Suzuki et al.[5] have reported the grafting of vinyl monomers onto polyester by ceric sulfate in nitrogen atmosphere. We[6,7] have also reported the grafting of vinyl monomers onto PET using Cr^{6+} and V^{5+} as initiators, respectively. A few studies have shown the ability of potassium permanganate to induce graft copolymerization onto textile fibers.[8-10] In this article we report studies on grafting of acrylamide onto polyester using potassium permanganate as the initiator in aqueous solution. The percentage of grafting has been determined as functions of various reaction variables, and the results are reported in Table I.

TABLE I
Effect of Variables on Potassium Permanganate Initiated Grafting onto Polyethylene Terephthalate[a]

Sample no.	Concn of Mn^{4+} (mol/L) $\times 10^4$	Concn of monomer (mol/L)	Concn of H_2SO_4 (mol/L)	Temp (°C)	Time (h)	Grafting (%)
1	3.4	1.0	0.6	50	6	4.6
2	5.1	1.0	0.6	50	6	14.8
3	6.8	1.0	0.6	50	6	8.3
4	8.5	1.0	0.6	50	6	5.0
5	13.6	1.0	0.6	50	6	3.55
6	5.1	1.0	0.3	50	6	5.2
7	5.1	1.0	0.45	50	6	7.6
8	5.1	1.0	0.75	50	6	10.8
9	5.1	1.0	0.9	50	6	6.3
10	5.1	0.25	0.6	50	6	5.6
11	5.1	0.5	0.6	50	6	12.6
12	5.1	0.63	0.6	50	6	16.5
13	5.1	0.75	0.6	50	6	18.6
14	5.1	1.25	0.6	50	6	12.6
15	5.1	0.75	0.6	45	3	5.2
16	5.1	0.75	0.6	45	4	8.8
17	5.1	0.75	0.6	45	5	12.1
18	5.1	0.75	0.6	45	6	16.1
19	5.1	0.75	0.6	50	3	6.3
20	5.1	0.75	0.6	50	4	10.8
21	5.1	0.75	0.6	50	5	14.3
22	5.1	0.75	0.6	55	3	4.1
23	5.1	0.75	0.6	55	4	6.2
24	5.1	0.75	0.6	55	5	9.3
25	5.1	0.75	0.6	55	6	13.2

[a] Reaction condition: Total volume including water = 20 cm³; PET = 0.2 (g); dioxane = 0.5 cc.

MATERIALS AND METHODS

PET fibers were treated with methanol and acetone and dried over vacuum to constant weight before use. Potassium permanganate (AR), H_2SO_4 (18 M, AR, BDH), and acrylamide (Am), BDH grade, were used.

GRAFT COPOLYMERIZATION

Polyester samples (0.2 g) were steeped in 20 mL of a solution containing known concentration of Mn^{4+}, Am, and H_2SO_4 in Pyrex flasks equipped with gas inlet and outlet tubes under nitrogen atmosphere at a particular temperature. After the desired reaction time, the contents of the flask were filtered on a sintered glass exucible and repeatedly washed with water, dried in an oven, cooled to room temperature, and weighed. The percentage of grafting was calculated in the following manner:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 denote, respectively, the weight of the fiber and the grafted fiber.
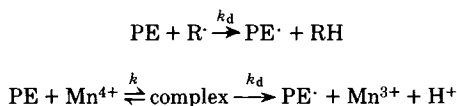
RESULTS AND DISCUSSION

Table I shows that, with an increase in concentration of monomer, the percentage of grafting increases rapidly and a maximum percentage of grafting was obtained at a monomer concentration of 0.75 mol/L. Beyond this concentration, homopolymerization occurs preferentially, and the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed which grows rapidly as the monomer concentration increases. Haworth and Holker[11] have reported similar observations. The percentage of grafting also increases up to a certain acid concentration (0.6 mol/L) and beyond this decreases. At higher acid concentration, MnO_2 might react with acid producing oxygen, which might inhibit the grafting process:

$$MnO_2 + 2H^+ \rightarrow Mn^{2+} + H_2O + O$$
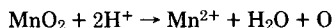
The effect of initiator concentration on graft yield was investigated by varying the permanganate concentration within the range 3.4–13.6×10^{-4} m/L. The maximum percentage of grafting was obtained at a concentration of 6.8×10^{-4} mol/L. In this system, the mechanism for free radical formation, initiation, and termination may be represented as follows:
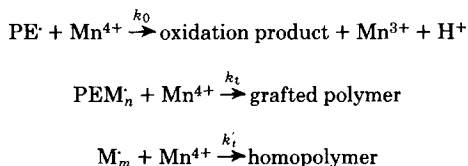
$$Mn^{4+} + H_2SO_4 \rightarrow Mn^{3+} + H^+ + HSO_4^-; \quad Mn^{4+} + H_2O \rightarrow Mn^{3+} + H^+ + O \cdot H$$

These free radicals (HSO_4^- or $O \cdot H = R \cdot$) might attack fibers, giving rise to fiber macroradical or in this system an intermediate complex of Mn^{4+} and fiber might be formed with dissociates, giving rise to free radicals on the backbone of the fiber:

$$PE + R \cdot \xrightarrow{k_d} PE \cdot + RH$$

$$PE + Mn^{4+} \underset{}{\overset{k}{\rightleftharpoons}} complex \xrightarrow{k_d} PE \cdot + Mn^{3+} + H^+$$

where $PE \cdot$ is the polyester macroradical which reacts with monomer to propagate the chain subsequently.

At a higher concentration of Mn^{4+}, the free radicals produced on the backbone of the polyester might be oxidized to give rise to oxidation products or the termination of most of the formed reactive sites by the exceedingly formed free radicals at higher Mn^{4+} concentration, which results in a marked fall in the graft yield. Secondly, at higher Mn^{4+} concentration, the metal ions might interact with the monomer to give rise to a higher amount of homopolymer thereby decreasing grafting:

$$PE \cdot + Mn^{4+} \xrightarrow{k_0} \text{oxidation product} + Mn^{3+} + H^+$$

$$PEM_n^{\cdot} + Mn^{4+} \xrightarrow{k_t} \text{grafted polymer}$$

$$M_m^{\cdot} + Mn^{4+} \xrightarrow{k_i'} \text{homopolymer}$$

The optimum temperature for maximum grafting was 50°C. A further increase in temperature reduces the percentage of grafting. This is expected because at higher temperatures chain transfer reactions with higher activation energy are favored and some of the chain transfer steps are wasteful reactions and contribute nothing to grafting.

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