Graft Copolymerization of 2-Methyl-5-vinylpyridine onto Poly(ethylene Terephthalate) Fibers

Previous reports have shown that certain properties of poly(ethylene terephthalate) fibers (PET) such as dyeability and antistatic properties can be improved via chemical modification through the polycondensation process[1,2] or by graft copolymerization reaction with different vinyl monomers.[3–8] However, vinyl graft copolymerization was mostly initiated by irradiation methods, e.g., 2- and 4-vinylpyridine.[3–6] This type of monomer improves the dyeability of PET toward acid dyes. To the authors' knowledge, no work has yet been published on graft copolymerization of vinylpyridines using the chemical methods of initiation. In the present communication, some experimental results of the graft copolymerization reaction of 2-methyl-5-vinylpyridine (MVP) with PET using benzoyl peroxide (Bz_2O_2) as initiator are given.

The effect of Bz_2O_2 concentration on the graft yield of poly(2-methyl-5-vinylpyridine) (PMVP) onto PET is illustrated in Figure 1. Obviously, the graft yield increases by increasing the concentration of Bz_2O_2 up to a concentration of 0.8–1.0%. Thereafter, any increase in the initiator concentration leads to a decrease in the graft yield. This result could be ascribed to a faster rate of termination at higher initiator concentration.

Figure 2 shows the graft yield as a function of reaction time at three different concentrations of Bz_2O_2. In all cases, the graft yield increases as the reaction time increases, then levels off to give maximum grafting. The time required to attain maximum grafting depends on the initiator concentration, being shorter at higher Bz_2O_2 concentration. On the other hand, the efficiency of grafting at a concentration of 0.4% Bz_2O_2 increases by increasing the reaction time (Table I). At higher concentration of Bz_2O_2 (0.6–1.0%), a remarkable maximum in the graft efficiency is obtained within 60 and 30 min, respectively. This means that the lower the concentration of Bz_2O_2, the longer the time needed for the termination reaction to take place.

The effect of temperature on the graft yield is shown in Figures 3 and 4. The data indicate that the graft yield increases with increasing reaction temperature and reaches its maximum at 85°C. Further increase in the reaction temperature leads to a decrease in the graft yield (Fig. 3).

Grafting of MVP onto PET has been carried out at four different temperatures, viz., 65°, 75°, 85°, and 95° (Fig. 4). Under these conditions, increasing the reaction time at 65°, 75°, and 85° causes proportional increase in graft yield without leveling off till 120 min, whereas at 95°, the time required to attain maximum grafting is about 45 min. This suggests that at temperatures higher than 85°, a faster rate of termination of the grafted chains as well as of the primary free radicals occurs.

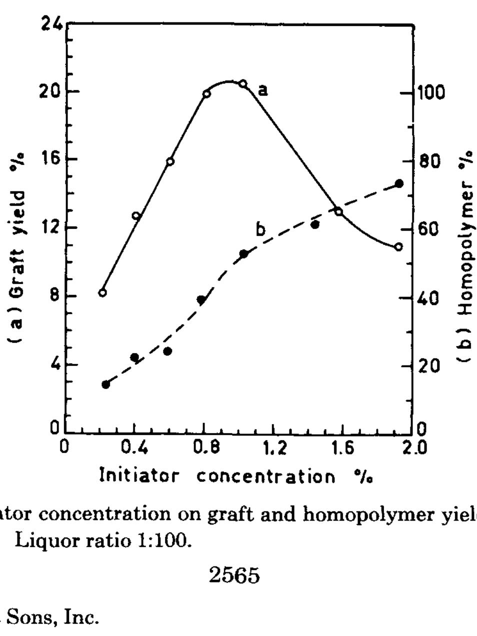

Fig. 1. Effect of initiator concentration on graft and homopolymer yields using 5 ml/50 ml solution at 85° for 60 min. Liquor ratio 1:100.

TABLE I
Relation Between Efficiency of Grafting and Duration of Reaction at Different Concentrations of Initiator

Concn. of Bz_2O_2, %	Efficiency of grafting at different reaction times, %				
	15 min	30 min	45 min	60 min	120 min
0.41	nil	0.9	2.9	5.4	5.9
0.62	nil	3.1	4.4	6.2	3.8
1.03	1.9	5.6	4.7	3.8	3.0

Figure 5 shows the effect of monomer concentration on the graft yield. Increasing the monomer concentration from 1 to 5 ml/50 ml solution brings about a significant increase in the graft yield.

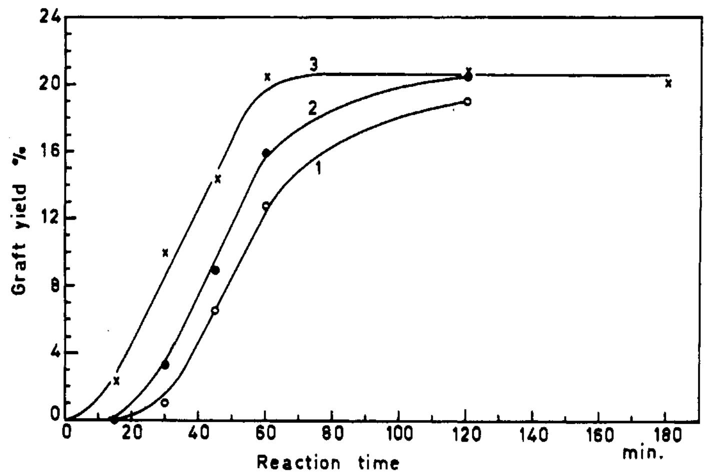

Fig. 2. Effect of reaction time on graft yield using 5 ml MVP/50 ml solution at 85°. Liquor ratio 1:100: (1) in presence of 0.41% Bz_2O_2; (2) in presence of 0.62% Bz_2O_2; (3) in presence of 1.03% Bz_2O_2.

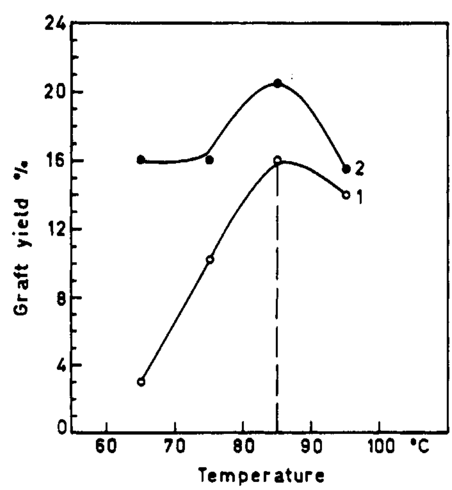

Fig. 3. Effect of temperature on graft yield using 5 ml MVP/50 ml solution and 0.6% Bz_2O_2. Liquor ratio 1:100: (1) reaction time 60 min; (2) reaction time 120 min.

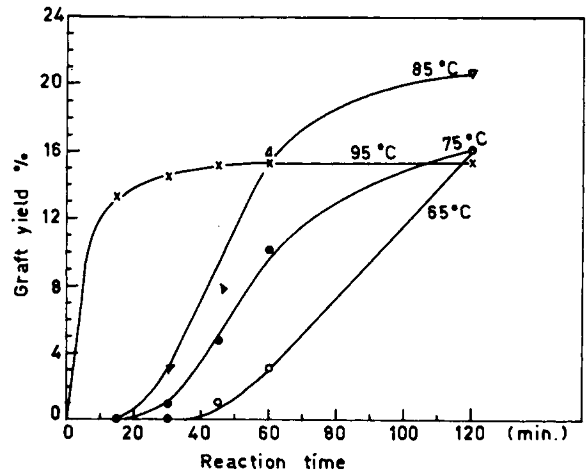

Fig. 4. Relation between graft yield and reaction time at different temperatures using 5 ml MVP/50 ml solution and 0.6% Bz_2O_2. Liquor ratio 1:100.

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°, rinsed with hot and cold water, dried at room temperature, and finally extracted with methyl alcohol for about 24 hr.

2-Methyl-5-vinylpyridine (MVP) was freshly distilled (75°/13 mm Hg). Benzoyl peroxide was freshly prepared according to Vanino and Herzer.[9]

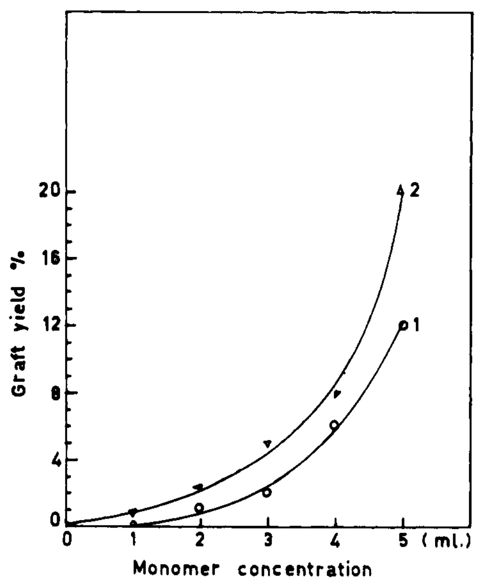

Fig. 5. Effect of monomer concentration on graft yield at 85° for 60 min. Liquor ratio 1:100: (1) in presence of 0.02 g Bz_2O_2/50 ml solution; (2) in presence of 0.04 g Bz_2O_2/50 ml solution.

Grafting Procedure

Graft copolymerization was carried out in a 100-ml stoppered conical flask. The PET sample (0.5 g) was introduced into a 50-ml aqueous solution containing the monomer and 2 ml of emulsifying agent (Emulsogen DG-Hoechst). The flask was immediately stoppered and placed in a thermostated water bath for a certain period till the required temperature was reached, and the initiator was then added. The reaction was allowed to proceed for different periods of time. The product was washed with distilled water and Soxhlet extracted with methyl alcohol and dried. Extraction with alcohol and drying were repeated until a constant weight was attained.

The graft yield was calculated on the base of constant dry weight, determined by storing the substrate over P_2O_5 at room temperature:

$$\%\ \text{graft yield} = \frac{\begin{bmatrix}\text{dry weight of}\\ \text{grafted PET}\end{bmatrix} - \begin{bmatrix}\text{dry weight of}\\ \text{original PET}\end{bmatrix}}{\text{dry weight of original PET}} \times 100.$$

The per cent conversion of monomer to homopolymer and the efficiency of grafting (E) were calculated as follows:

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

$$\%\ E = \frac{\text{dry weight of grafted polymer}}{\begin{bmatrix}\text{dry weight of}\\ \text{grafted polymer}\end{bmatrix} + \begin{bmatrix}\text{dry weight of}\\ \text{homopolymer}\end{bmatrix}} \times 100.$$

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