

Graft Copolymerization of 2-Methyl-5-Vinyl Pyridine to Poly(Ethylene Terephthalate) Fibres using a Post-Radiation Technique

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Synopsis

Radiation-induced grafting of 2-methyl-5-vinyl pyridine (MVP) to poly(ethylene terephthalate) fibers (PET) was investigated under a variety of conditions employing a post-radiation technique. Over a range of a total dose of 1–10 Mrad, increasing the total dose from 1 up to 3 Mrad was accompanied by a significant enhancement in the extent and rate of grafting. Further increase in the total dose caused a decrease. The same situation was encountered with respect to MVP concentration (5%–10%) and polymerization temperature (75°–90°C). A MVP concentration of 8% and a temperature of 85°C constituted the optimal. Addition of copper sulfate at a concentration of 0.05 mmole/l. offset grafting. The effect of the said parameters on homopolymerization occurring during grafting was also investigated.

INTRODUCTION

Radiation-induced graft copolymerization of various vinyl monomers on poly(ethylene terephthalate) fibers (PET) has been extensively studied. The monomers used were styrene,^{1–3} 4-vinyl pyridine,^{4,5} acrylonitrile,^{6,7} acrylic and methacrylic acids,^{8–12} vinyl acetate,¹³ *N*-vinyl morpholinone,¹⁴ and 2-methyl-5-vinyl pyridine.^{12,15,16} To our knowledge, however, not much work has yet been published on post-irradiation graft polymerization of 2-methyl-5-vinyl pyridine on PET.

The present work was undertaken with a view to studying (a) factors affecting graft copolymerization of 2-methyl-5-vinyl pyridine on PET using a post radiation technique, (b) general kinetics of the copolymerization process, and (c) influence of incorporating copper sulfate in the polymerization system on grafting and homopolymerization.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) fibers (PET) (Trivira, 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 Soxhlet extracted with methanol for 24 hr to remove any material adhering to the surface. 2-methyl-5-vinyl pyridine (MVP) was freshly distilled (75°C/13 Torr); emulsifying agent (Emulsogen DG-Hoechst). Copper sulphate (CuSO₄·5H₂O) was of analytical grade chemicals. High-energy γ rays were provided by the 8000 Ci Co-60 radiation source of the Middle Eastern Regional Radioisotope Center. The dose rate of this source is 0.36 Mrad/hr.

Irradiation Technique and Grafting Procedure

The PET fiber (0.5 g) was irradiated in air to the required dose by γ rays. The graft copolymerization was carried out in a 100 ml stoppered flask. The irradiated sample was introduced into a 50 ml aqueous solution containing the monomer and 2 ml of emulsifying agent. The flask was thermostatically heated until the required temperature before adding the irradiated sample. The reaction was allowed to proceed for different periods of time. The product was washed with distilled water and Soxhlet extracted with methanol and dried. Extraction with alcohol and drying were repeated until a constant weight was attained.

To investigate the effect of copper sulfate on polymerization, copper sulfate solution was added to the polymerization system before adding the irradiated samples.

Percentages of graft yield and homopolymer, were calculated as follows:

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

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

RESULTS AND DISCUSSION

Effect of Dose

Figure 1 shows the effect of variation of total dose given to the PET on grafting of the latter with MVP. As can be seen, increasing the total dose from 1 up to 3 Mrad is accompanied by a significant enhancement in the extent and rate of grafting, indicating an increase in the concentration of peroxidic and free radical groups formed by increasing doses of radiation within this range. Further increase in the total dose does not cause any increase; on the contrary, the extent and rate of grafting decrease. For instance, the extent and rate of grafting obtained at a dose of 10 Mrad are much lower than those obtained at a dose of 3 Mrad. This implies that a dose of 3 Mrad constitutes the optimum dose for graft copolymerization of MVP on PET by the post radiation technique, and an upper

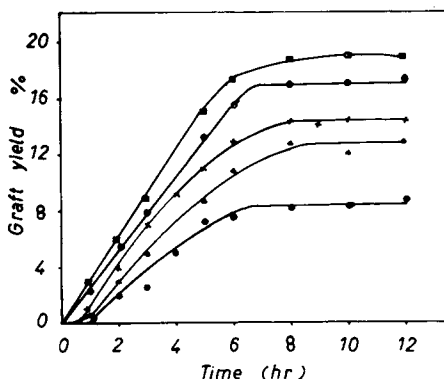


Fig. 1. Variation of the extent and rate of grafting with radiation doses: [MVP], 5%; temperature, 85°C; ●, 1 Mrad; ○, 2 Mrad; □, 3 Mrad; +, 4 Mrad; ▲, 10 Mrad.

limitation exists on the doses. Irradiation with radiation doses seems to cause crosslinking of PET chain molecules thereby lowering the susceptibility towards grafting. It should also be noted that irradiation with large doses often becomes meaningless since side reactions such as PET chain scission would occur.

Figure 2 shows variation of homopolymerization with total doses given to PET prior to polymerization. Obviously, the extent and rate of homopolymerization increases significantly as the dose increases from 1 to 3 Mrad. Therefore, the extent and rate of homopolymerization are lower if compared with those obtained using PET which has been given 2 or 3 Mrad; this is similar to grafting.

That substantial amount of homopolymer is formed during grafting suggests that the effect of γ rays on PET polymer is to bring about hydroperoxide at several points along the PET chain in a random manner. Decomposition of this peroxide leads to PET macroradical (responsible for grafting) as well as free radicals in the polymerization medium which are capable of initiating homopolymerization. Hence the lower extent and rate of homopolymerization at larger radiation doses (more than 3 Mrad) could be ascribed to faster rate of termination. At such doses, free radicals in the polymerization medium would be available in abundance.

Effect of Monomer Concentration

The effect of MVP concentration on the extent and rate of its grafting on PET at a dose of 2 Mrad is shown in Figure 3. It is clear that regardless of MVP concentration, the grafting reaction proceeds initially at a fast rate, decreases with time to a slower rate then levels off. However, the initial fast rate and the extent of grafting at the leveling off (maximum graft yield) are dependent on monomer concentration. The initial fast rate is higher at higher monomer

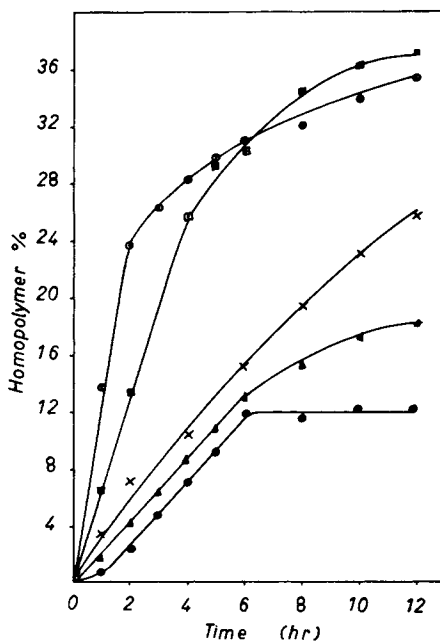


Fig. 2. Variation of extent and rate of homopolymerization with radiation doses: [MVP], 5%; temperature, 85°C; ●, 1 Mrad; ○, 2 Mrad; ◻, 3 Mrad; +, 4 Mrad; ▲, 10 Mrad.

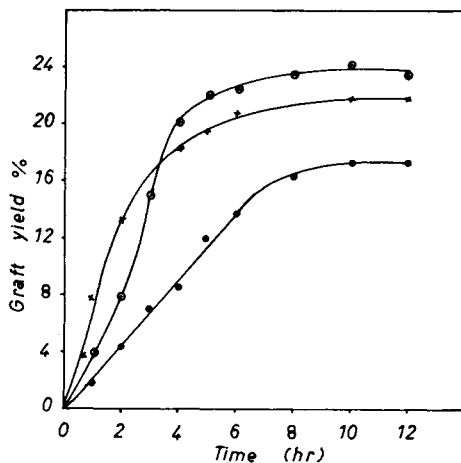


Fig. 3. Effect of monomer concentration on the extent and rate of grafting: total dose, 2 Mrad; temperature, 85°C, [MVP]: ●, 5%; ○, 8%; +, 10%.

concentrations whereas the maximum graft yield obtained at MVP concentration of 10% is higher than that of 5% concentration but lower than 8% concentration; that is, a MVP concentration of 8% constitutes the optimal monomer concentration at which the highest graft yield could be achieved.

Leveling off grafting could be associated with depletion in monomer concentration as well as reduction in active sites (free radicals) on the PET backbone as the reaction proceeds. Besides this, it is very likely that the higher amount of graft formation occurred during the initial stages of the reaction acts as a diffusion barrier for the monomer in the later stages of the reaction. Data shown in Figure 4 support this since the extent and rate of homopolymerization, which concurrently occurred with grafting, increase by increasing monomer concentration.

Effect of Temperature

Figure 5 shows the effect of raising the polymerization temperature on the extent and rate of grafting at a dose of 2 Mrad given to the PET prior to grafting. It is seen that increasing the polymerization temperature from 75° up to 85°C brings about a significant increase in the extent and rate of grafting. The latter does not increase by raising the temperature further to 90°C but rather decreases. However, at 85° and 90°C the grafting reaction proceeds without any induction period. The reverse is the case at 75° and 80°C, where an induction period of about 2 hr is observed. Consequently, it may probably be correct to say that 85°C is the optimal temperature for graft copolymerization of MVP to PET by the post irradiation technique.

That the amount of graft formation is very poor at 75°C and the observation that above this temperature the graft yield increases considerably to attain its maximum at 85°C is rather interesting. Previous reports^{17,18} have disclosed a glass transition temperature (T_g) for PET between 80° and 85°C. Since the PET chains become more mobile at T_g , reactivity of PET increases markedly at this temperature, i.e., T_g . Thus, the pronounced reactivity of the polymer at T_g is essentially responsible for the greater grafting at 85°C. Above this

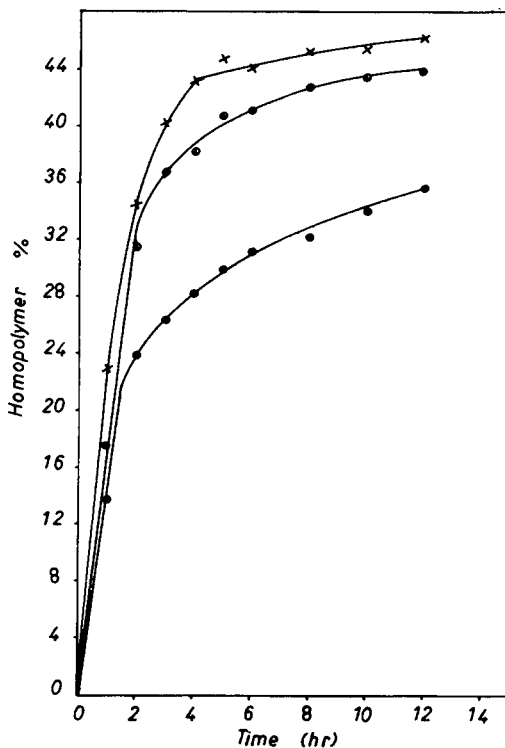


Fig. 4. Effect of monomer concentration on the extent and rate of homopolymerization: total dose, 2 Mrad; temperature, 85°C, [MVP]: ●, 5%; ○, 8%; +, 10%.

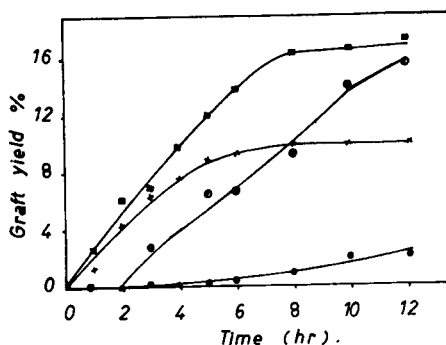


Fig. 5. Variation of extent and rate of grafting with temperature: [MVP], 5%; radiation dose, 2 Mrad; ●, 75°C; ○, 80°C; ◻, 85°C; +, 90°C.

temperature the PET passes from the glassy state into a highly viscous liquid, thereby increasing the ability to undergo radical reactions. As the temperature increases, more and more radicals combine and therefore are not capable of initiating grafting. The rate of decomposition of peroxidic groups on PET backbone to free radicals is also higher at higher temperatures and they may react so¹⁶



to give ultimately inactive products. Furthermore, chain termination may be favored due to increased diffusion rate, giving rise to lower kinetic chain length.

Thus the increased radical combination, higher rate of peroxidic groups decomposition of yield inactive products, and the lower molecular weight of the grafted chains would account for the lower grafting obtained at 90°C.

Figure 6 shows the effect of variation of polymerization temperature on the extent and rate of homopolymerization occurred during grafting of MVP to PET at a dose of 2 Mrad given to the PET before commencing polymerization. It is clear that substantial amount of homopolymer formation occurs at 75°C, in

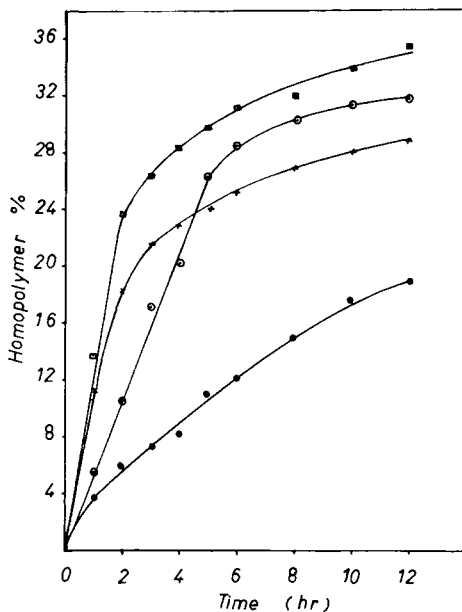


Fig. 6. Variation of extent and rate of homopolymerization with temperature: [MVP], 5%; radiation dose, 2 Mrad; ●, 75°C; ○, 80°C; ◻, 85°C; +, 90°C.

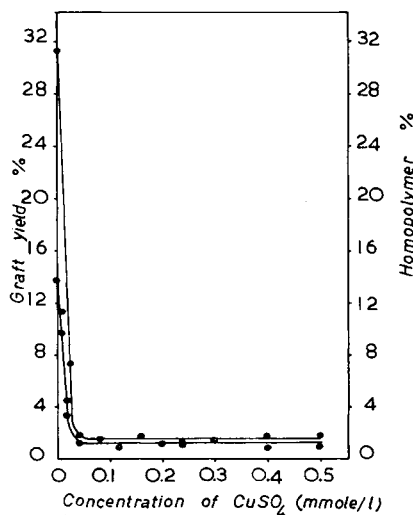


Fig. 7. Effect of copper sulphate at different concentration on the extent of grafting and homopolymerization: [MVP], 5%; radiation dose, 2 Mrad; temperature, 85°C; reaction time, 6 hr; ○, grafting; ●, homopolymerization.

contrast with grafting where virtually no significant reaction took place at this temperature. This is rather interesting since it validates the point that below T_g , reactivity of PET is quite poor. Raising the polymerization temperature up to 85°C causes a significant enhancement in the extent and rate of homopolymerization whereas further increase in temperature to 90°C results in a decrease, similar to grafting. The decrease in the extent and rate of homopolymerization at 90°C could be interpreted in terms of fast rate of termination of growing homopolymer chains.

Effect of Addition of Copper Sulfate

Presence of cupric ions in a polymerization system consisted of PET, MVP, benzoyl peroxide, and water has been reported to cause a significant increase in the graft yield.¹⁹ In order to see whether this is also the case with radiation-induced grafting, copper sulfate at different concentration was incorporated in the polymerization system. The latter consisted of PET previously given a total dose of 2 Mrad, MVP, copper sulfate, and water. Polymerization conditions were similar to those described in the experimental section. The results obtained are shown in Figure 7.

It is clear (Fig. 7) that incorporation of copper sulfate in the polymerization system causes a sharp fall in the extent of grafting and homopolymerization. A copper sulfate concentration of 0.05 mmole/l. is quite enough to offset the graft and homopolymer formation when the polymerization was induced by high-energy irradiation. This contrasts with chemical initiation using benzoyl peroxide.¹⁹ In the radiation-induced graft copolymerization of MVP to PET, the cupric ions act as a radical scavenger. They seem to contribute, to a significant extent, in termination of PET macroradicals, MVP radicals as well as poly(MVP) growing chains, if any are formed.

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