

Swelling-Assisted Graft Copolymerization of 4-Vinyl Pyridine on Poly(ethylene terephthalate) Films Using a Benzoyl Peroxide Initiator

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SYNOPSIS

Graft copolymerization of 4-vinyl pyridine (4-VP) on poly(ethylene terephthalate) (PET) films using a benzoyl peroxide (Bz_2O_2) initiator was investigated under different conditions including polymerization time, temperature, monomer concentration, and initiator concentration. Dimethyl sulfoxide (DMSO) was used as swelling agent to promote the incorporation and the subsequent polymerization of 4-VP to PET films. Maximum percent grafting was obtained when the polymerization was carried for a period of two hours at 65°C. Increasing the monomer concentration from 0.2M to 0.8M and Bz_2O_2 concentration from $1.0 \times 10^{-3}M$ to $2.5 \times 10^{-3}M$ was accompanied by a significant enhancement in percent grafting. Monomer diffusion on PET films and its effect on the grafting yield were studied and intrinsic viscosities of grafted films were also measured. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that both textile and nontextile materials based on poly(ethylene terephthalate) (PET) are used in a series of processes. Introduction of hydrophilic groups by vinyl grafting broadens their use as membranes in separation technology (ultrafiltration, reverse osmosis, and pervaporization). Certain desirable properties such as improved dyeability, thermal and mechanical properties, and increase in moisture regain as well as antistatic properties can be imparted to PET by graft copolymerization.

Grafting of vinyl monomer onto PET can be accomplished either by radiation¹⁻⁸ or chemical means.⁸⁻¹⁹ The chemical initiation method has been found best fitting for this purpose owing to the low degradation of the base polymer.

Vinyl pyridines are stimulating materials for the preparation of water-attractive films or fibers. Shalaby and colleagues,⁸⁻⁹ and Hebeish and coworkers¹⁰ grafted 2-methyl-5-vinyl pyridine using γ -rays and peroxides onto PET fibers and analyzed the moisture gain and dyeability of fibers.

The aim of the present investigation was to study the graft copolymerization of 4-vinyl pyridine (4-VP) onto PET films using a benzoyl peroxide (Bz_2O_2) initiator. However, the grafting of vinyl monomers onto PET meets with some difficulties. First, the chemical structure of PET hinders considerable amounts of radicals for initiating grafting.¹¹ Second, high crystallinity of industrial PET samples and highly ordered macromolecules in amorphous regions hinder monomer diffusion inside the material and limit the grafting zone to subsurface regions; also, homopolymerization inhibits effective grafting.

A factor that may affect the grafting reaction is pretreatment of fibers or films, primarily with swelling solvents, before the grafting procedure. A pre-swelled polymer was more easily grafted than one that had not been swelled due to the opening up of the physical structure of the polymer, allowing the monomer and initiator to enter in sufficient quantities. Osipenko and Martinoviez¹³ swelled the PET films and fibers by treatment with dichloroethane (DCE) and reported that pre-swelling leads to changes in their sorption-diffusion properties and favors an increase in the degree of grafting of acrylic acid (AA). Hsieh and colleagues¹⁴ used dimethyl formamide, γ -butyrolactone, pyridine, and chloroethane as swelling agents to promote the incorporation of AA to PET films by glow discharge. Xue

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and Wilkie¹⁵ pretreated the PET films with 1,1,2,2-tetrachloro ethane before the graft copolymerization of the methacrylic acid onto PET using hydrogen peroxide as initiator, and reported that the amount of add-on increased as the swelling level increased. Şanlı and Pulat¹⁶ also studied the effect of organic solvents, namely pyridine, DCE, DCE/H₂O (20/80 vol/vol) and dimethyl sulfoxide (DMSO) as swelling agents in the graft copolymerization of acrylamide on PET films using Bz₂O₂ initiator, and found that solvent inclusion in the films increased with the increased length of solvent treatment time and temperature. Elevated temperatures were found to have greater effect than the length of swelling time on the inclusion of swelling agents into PET films.¹⁶ For the pretreatment of the films in DMSO, 1 h and 140°C were reported as the best conditions.¹⁶ For this reason, in the present work we have pretreated PET films in DMSO at these conditions before the graft copolymerization was carried out.

EXPERIMENTAL

Materials

PET films (Hoksp) of 50- μ m thickness were used for grafting. 4-VP was purified by vacuum distillation at 2 mmHg at 65°C. Bz₂O₂ was twice precipitated from chloroform in methanol and dried in a vacuum oven for 2 days. Other reagents were used as supplied. All reagents were Merck products.

Swelling Procedure

A temperature-controlled oil bath was used for heating. Films were dipped into DMSO for 1 h at

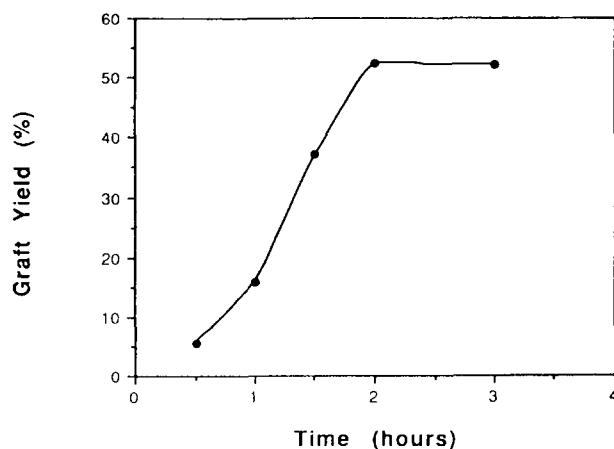


Figure 1 Variation of graft yield with polymerization time: [4-VP] = 0.8 M, [Bz₂O₂] = 3.0 × 10⁻³ M, T = 85°C.

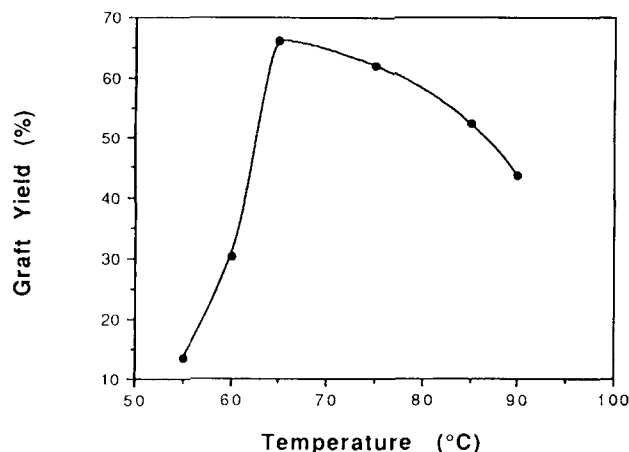


Figure 2 Variation of graft yield with temperature: [4-VP] = 0.8 M, [Bz₂O₂] = 3.0 × 10⁻³ M, t = 2 h.

140°C.¹⁶ After treatment, solvent on the films was removed by blotting between filter paper and put into the polymerization medium.

Polymerization Procedure

PET films were cut to dimensions of about 30 × 44 mm and had a weight of about 0.07 g. Polymerization was carried out in a thermostatted 100 mL tube under reflux. Solvent-treated film of known mass was introduced into a tube containing an aqueous solution of 4-VP at known concentration and brought to the polymerization temperature. Bz₂O₂ at predetermined concentration in DMSO was added and polymerization was allowed to proceed for a specified period of time. At the end of the predetermined polymerization time, films were removed from the polymerization medium and residual solvent; monomer and homopoly(4-VP) were removed by washing the

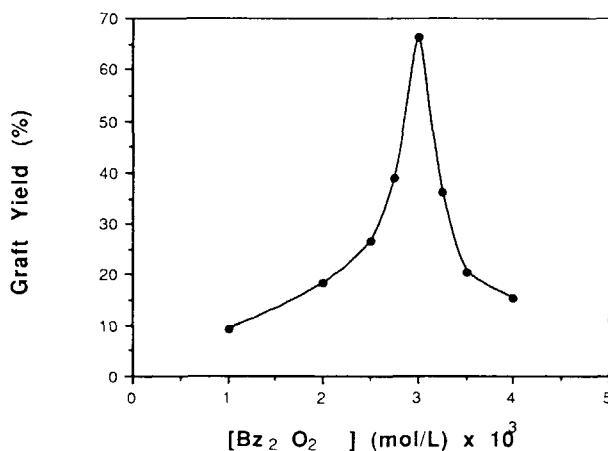


Figure 3 Dependence of initiator concentration on graft yield: [4-VP] = 0.8 M, t = 2 h, T = 65°C.

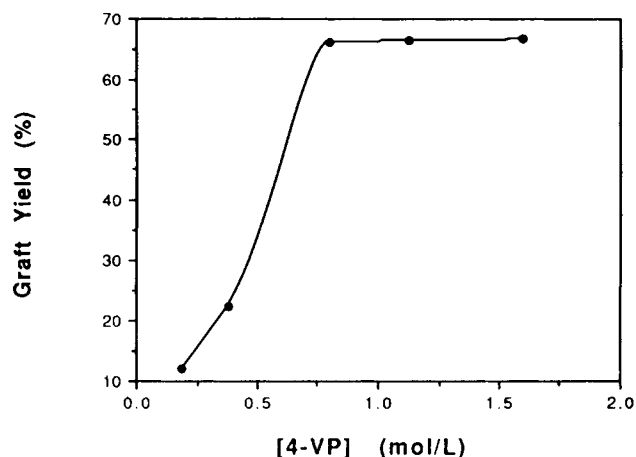


Figure 4 Effect of monomer concentration on graft yield: $[Bz_2O_2] = 3.0 \times 10^{-3} M$, $t = 2$ h, $T = 65^\circ C$.

films in methanol for 2 h. The grafted films were then vacuum-dried at $50^\circ C$ for 72 h and weighed. The graft yield was calculated from the weight increase in grafted films as follows:

$$\text{Graft Yield (\%)} = [(w_g - w_i)/w_i] \times 100$$

where w_i and w_g denote the weights of the original (ungrafted) and grafted PET films, respectively.

Determination of Intrinsic Viscosity

Intrinsic viscosity measurements of the original and grafted PET films were determined in phenol/tetrachloroethane (1 : 1) solvent system using an Ubbelohde capillary viscometer mounted in a water bath at $25^\circ C \pm 0.1^\circ C$.

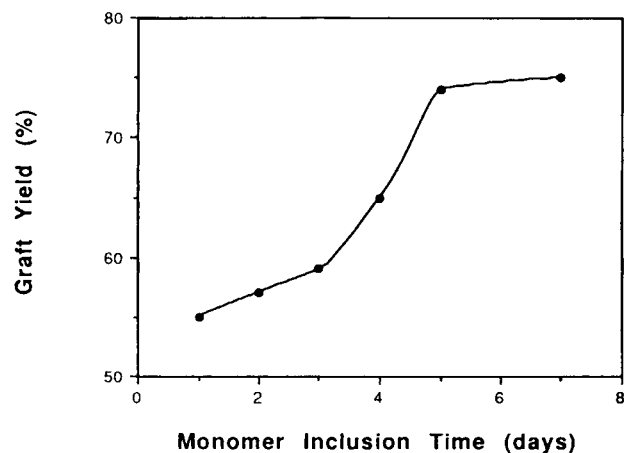


Figure 5 Effect of monomer inclusion time on graft yield: $[4-VP] = 0.8 M$, $[Bz_2O_2] = 3.0 \times 10^{-3} M$, $t = 2$ h, $T = 65^\circ C$.

Table I Intrinsic Viscosity Data for Grafted PET Films

Graft Yield (%)	Intrinsic Viscosity (dL/g)
Ungrafted	0.095
16.5	0.268
22.7	0.504
56.0	0.563
65.0	0.833

Determination of Water Absorption Capacity

PET films were immersed in distilled water at $20^\circ C$ for 48 h, blotted between filter paper, and weighed. They were then vacuum-dried at $50^\circ C$ for 72 h and weighed again. Water absorption capacity was determined from the weight increase of the films.

FTIR Spectrum

Fourier transform infrared (FTIR) spectra of 4-VP-grafted PET films were recorded using a Mattson model 1000 FTIR spectrophotometer. Samples were analyzed as films cast from phenol/tetrachloroethane (1 : 1) (AR) onto sodium chloride plates.

RESULTS AND DISCUSSION

Effect of Polymerization Time

The effect of polymerization time on the graft yield (%) with constant initiator concentration, monomer concentration, and reaction temperature was studied. Results are presented in Figure 1. As seen from

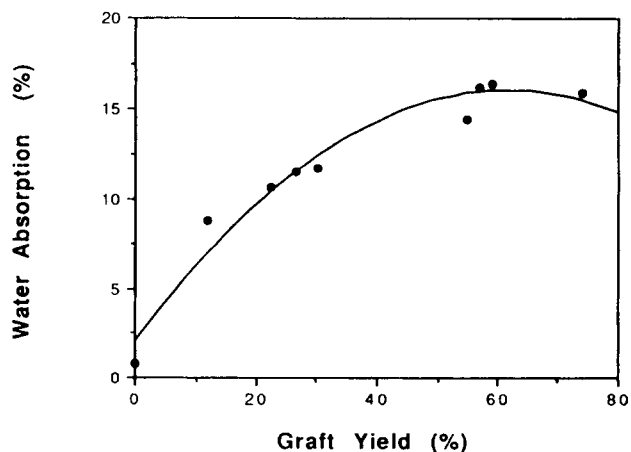


Figure 6 Change of water absorption capacity with graft yield.

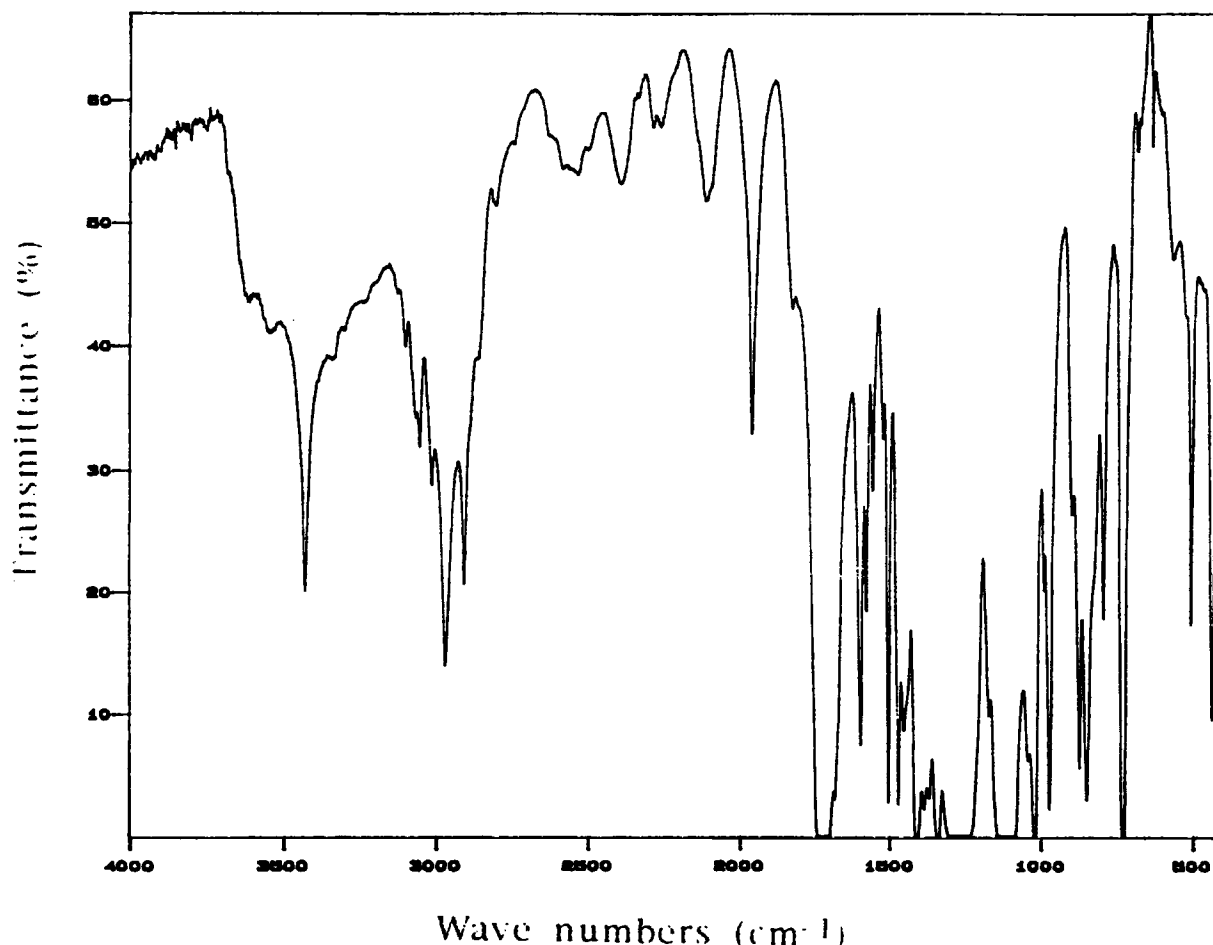


Figure 7 FTIR spectrum of 4-VP grafted PET film.

the figure, the saturation grafting value of 55% was reached after 2 h of polymerization time. A similar trend was observed in the graft copolymerization of 2-methyl-5-vinyl pyridine,^{8,10} methacrylic acid,¹⁵ and acrylamide¹⁶ grafting onto PET films.

Effect of Temperature

The grafting polymerization was carried out at six different temperatures from 55 to 90°C (Fig. 2). The degree of grafting increased with an increase in reaction temperature up to 65°C, then declined. The increase in temperature increases the rate of initiation and propagation reactions. It also increases swellability of PET film and facilitates the diffusion of monomer into PET matrix, thus resulting in increased rates of grafting. On the other hand, above the glass transition temperature, the diffusability of monomer into PET backbone was hindered by the high viscosity of the medium; termination reactions were favored which resulted in decreased rate of grafting. Similar results were obtained in the

acrylamide^{16,18} and glycidyl methacrylate¹⁷ grafting on PET film and fibers.

Effect of Initiator Concentration

As seen in Figure 3, the degree of grafting increased with the initiator concentration up to $3.0 \times 10^{-3}M$, and a further increase in Bz_2O_2 concentration decreased the percent of grafting. Similar results were reported by many researchers.¹⁶⁻¹⁹ Bz_2O_2 decomposes at a reasonable rate beginning at about 55°C to give a primary free-radical species ($C_6H_5COO\cdot$) and/or secondary free-radical species ($C_6H_5\cdot$). These free radicals can form PET macroradicals by hydrogen abstraction from the PET backbone and take a role in the grafting reactions. The created active sites and the chain transfer reactions of growing homopoly(4-VP) with PET backbone have significant effects on the degree of grafting.²⁰ However, excessive amount of Bz_2O_2 caused more active sites to form which combine with each other and give a termi-

nation reaction.^{16,18} These transfer, termination, and combination reactions reduce the degree of grafting.

Effect of Monomer Concentration

The effect of 4-VP concentration on the degree of grafting is shown in Figure 4. The increase in the concentration of 4-VP up to 0.8M results in an increase on the rate of grafting, and saturation graft yield of 65% was obtained. Further increase in 4-VP concentrations do not enhance grafting, and a levelling off of graft yield was observed. This is due to simultaneous increase in the homopolymerization rate with growing 4-VP concentration which leads to depletion of the monomer. In addition, the homopoly(4-VP) accumulated in the reaction medium increases the medium viscosity, and monomer diffusion into the PET structure becomes difficult.

Effect of Monomer Inclusion

Pretreated PET films were dipped into 0.8M 4-VP for 1 to 7 days before the polymerization was carried out. As seen in Figure 5, diffusion and incorporation of the monomer lead to a higher yield. Five days of treatment with 4-VP was found sufficient to reach maximum yield ($\geq 75\%$) and resulted in greater weight increase than all other experiments. This indicates that monomer diffusion into the PET is a rate-limiting process in the graft copolymerization process. Similar results were observed in the graft copolymerization of acrylamide¹⁶ onto PET films using Bz_2O_2 initiator.

Intrinsic Viscosity Measurements

Intrinsic viscosities of PET films were determined in phenol/tetrachloroethane (1 : 1) solvent system at 25°C. The results, tabulated in Table I, show that intrinsic viscosity of PET films increases as the graft yield increases indicating the evidence of grafting.

Water Absorption Characteristics

Water absorption capacity of the films increased from 0.8 to 16.4% as the graft percentage of 4-VP was steadily increased to 74% (Fig. 6). Grafting with 4-VP not only brings about the opening of the structure to a certain extent but also increases hydrophilicity of the film. The shift toward hydrophilic nature is responsible for the increase in water absorption percentage.

FTIR Spectrum

Figure 7 shows the FTIR spectrum of 4-VP grafted PET film. The absorptions at 1400 to 1600 cm^{-1} and 1735 cm^{-1} are typical to those aromatic C—H and C=O stretchings and the peak at 1602 cm^{-1} in the spectrum of 4-VP-grafted film is due to the resonance peak of the vinyl pyridine group.

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