

## Kinetics of swelling assisted grafting of 4-vinyl pyridine onto poly(ethylene terephthalate) fibers using a benzoyl peroxide initiator

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### Summary

Poly(ethylene terephthalate) (PET) fibers were grafted with 4-vinyl pyridine (4-VP) using benzoyl peroxide (Bz<sub>2</sub>O<sub>2</sub>) as initiator. Fibers were swelled in dichloroethane (DCE) for 2 h at 90°C to promote the incorporation and the subsequent polymerization of 4-VP onto PET fibers. Variations of graft yield with time, temperature, initiator and monomer concentrations were investigated. Percent grafting was enhanced significantly by increasing Bz<sub>2</sub>O<sub>2</sub> concentration up to 2x10<sup>-3</sup> mol/L and then decreased upon further increase in initiator concentration. Increasing the 4-VP concentration up to 0.6 mol/L improves the graft yield significantly. The optimum temperature and polymerization time was found to be 50°C and 2 h respectively. Further changes in properties of grafted PET fibers such as moisture absorption capacity and intrinsic viscosity were determined. Grafted PET fibers were characterized by thermogravimetric analysis and scanning electron microscopy (SEM). Molar mass of the grafted chains was also determined.

### Introduction

PET fiber is one of the most important synthetic fibers used in the textile industry. However, it is hydrophobic in nature and do not contain chemically reactive groups. For these reasons this material cannot combine with the either dye cations and anions. Certain desirable properties such as improved dyeability, water absorbancy, as well as antistatic, mechanical and thermal properties can be imparted to PET fiber by grafting with different vinyl monomers.

This is indeed a very fascinating field for research, with unlimited future possibilities for improving the properties of the product. Out of several methods available for grafting, the chemical initiation method has been found to be best fitting for the purpose owing to the low degradation of the base polymer. There are extensive studies, either patented or published concerning the grafting of vinyl monomers onto PET fibers in the literature [1-12,17,18,23,24,27]. However, there are serious difficulties in grafting vinyl monomers onto PET. The chemical nature of PET does not allow formation of its macrochains of an appreciable quantity of radicals, which can initiate the grafting, and the high extent of crystallization and ordering of amorphous regions retard monomer diffusion inside the material.

One way to overcome this difficulty is pretreatment of PET samples, with swelling solvents before the grafting procedure, to open up the physical structure of the polymer, allowing the monomer and initiator to enter in sufficient quantities [7,14-17]. Osipenko and Martinovic [8] swelled PET films and fibers by treatment with dichloroethane (DCE) and reported that preswelling leads to an increase in the degree

of grafting of acrylic acid (AA). Şanlı et al. used [17] dimethyl formamide, morpholine, acetic acid, n-butanol, DCE and dimethyl sulfoxide (DMSO) as swelling agents in the graft polymerization of acrylamide (AAM) onto PET fibers using cerium ammonium nitrate as initiator. Ünal and Şanlı [16] pretreated the PET films with DMSO before the graft copolymerization of 4-vinyl pyridine onto PET films. Şanlı and Pulat [18] reported grafting of AAM onto PET films using benzoyl peroxide ( $Bz_2O_2$ ) initiator after swelling the films in DMSO, pyridine, DCE, DCE/H<sub>2</sub>O (20/80 v/v). Ünal et al. [19] studied graft copolymerization of AAM onto 1,1,2,2-tetrachloroethane (TCE) preswelled PET films.

There are only a few studies in the literature concerning the grafting of vinyl pyridines onto PET, which are stimulating materials for the preparation of water-attractive films and fibers. Shalaby and colleagues [20-21], Hebeish and coworkers [9,21,26] were grafted 2-methyl-5-vinyl pyridine using  $\gamma$ -rays or peroxides onto PET fibers and analyzed the moisture gain and dyeability of fibers. Ünal and Şanlı [16] studied the grafting of 4-vinyl pyridine on PET films after swelling of the films in DMSO for 1 h at 140°C and reported significant enhancement in percent grafting due to the use of swelling agent.

The present paper deals with a view of studying factors affecting the graft copolymerization of 4-VP onto PET fibers, for the purpose of preparing suitable grafted PET fibers for the use of adsorption of heavy metal ions from industrial waste water.

## Experimental

### Materials

The PET fibers (126 denier, 28 filaments) used in these experiments were provided by SASA Co. (Adana, Turkey). The fiber samples were Soxhlet-extracted for 6 h with acetone and dried in a vacuum oven at ambient temperature. 4-VP was purified by vacuum distillation at 2 mmHg and 65°C.  $Bz_2O_2$  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. The fiber samples were dipped into DCE for 2 h at 90°C. After treatment, solvent on the fibers was removed by blotting between a filter paper and put into the polymerization medium.

### Polymerization Procedure

Polymerization was carried out in a thermostated 100 mL tubes under reflux. The mixture containing the PET fiber sample ( $0.3 \pm 0.01$ g), monomer and  $Bz_2O_2$  at required concentration in 2 mL acetone was made up to 20 mL with deionized water. The mixture was immediately placed into the water bath adjusted to the polymerization temperature. At the end of the predetermined polymerization time, fibers were removed from the polymerization medium and residual solvent, monomer and homopoly (4-VP) were removed by Soxhlet-extracting the PET fibers in methanol for 96 h. The grafted fibers were then vacuum-dried at 50°C for 72 h and weighed. The graft yield (G Y) was calculated from the weight increase in grafted fibers as follows :

$$G Y (\%) = [(w_g - w_i) / w_i] \times 100 \quad (1)$$

Where  $w_i$  and  $w_g$  denote the weights of the original (ungrafted) and grafted PET fibers, respectively.

Homopoly(4-VP) formed in the grafting medium was determined from the grafting efficiency (G E) according to the following equation:

$$G E (\%) = [(w_g - w_i) / (w_g - w_i) + w_h] \times 100 \quad (2)$$

Where  $w_h$  is the weight of homopolymer.

The rate of grafting ( $R_g$ ) was calculated by using the formula as follows :

$$R_g = [(w_g - w_i) \times 1000] / [M \times t \times V] \quad (3)$$

Where M is the molar mass of the monomer ; t is the polymerization time (s); and V is the volume (mL) of the overall reaction medium.

#### *Determination of Intrinsic Viscosity*

Intrinsic viscosity measurements were carried out for both 4-VP grafted PET fibers and homopoly(4-VP) (formed in the grafting medium) in m-cresol and in ethanol, respectively, using a Ubbelohde capillary flow viscometer at  $25.0 \pm 0.1^\circ\text{C}$ .

#### *Determination of Water Absorption Capacity*

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

#### *FTIR Spectrum*

Fourier transform infrared (FTIR) spectra of 4-VP grafted PET fibers were recorded using a Mattson model 1000 FTIR spectrophotometer with KBr discs.

#### *Differential Scanning Calorimetry*

Thermal analyses were performed with General V4.1C Dupont 2000 Differential Scanning Calorimeter (DSC). Sample weights ranged from 3.0 to 9.0 mg. The samples were heated from  $30^\circ\text{C}$  to  $300^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The intercept points of slopes were taken as glass transition temperatures ( $T_g$ ).

#### *Scanning Electron Microscopy*

SEM studies of the original and 4-(VP) grafted PET fibers, coated with gold, were performed using a JEOL Model JSM 5600 microscope.

## **Result and Discussion**

### *Effect of Polymerization Time*

Grafting of PET fibers was carried out at various polymerization times. As it is reflected from Fig.1, graft yield progressively increases with the increase in polymerization time up to 2 h then levels off reaching a 55% saturation grafting value. This may be attributed to the formation of a diffusion barrier, an increase in the medium viscosity due to the homopoly(4-VP) formed in the polymerization medium, as reflected from the grafting efficiency curve in Fig. 1. Similar results observed in the graft copolymerization of AAm [12,17,18], methyl methacrylate [23], glycidyl methacrylate [24] on PET fibers and n-vinyl-2-pyrrolidone (n-VP) [25], and AAm (19), 4-VP [16] on PET films.

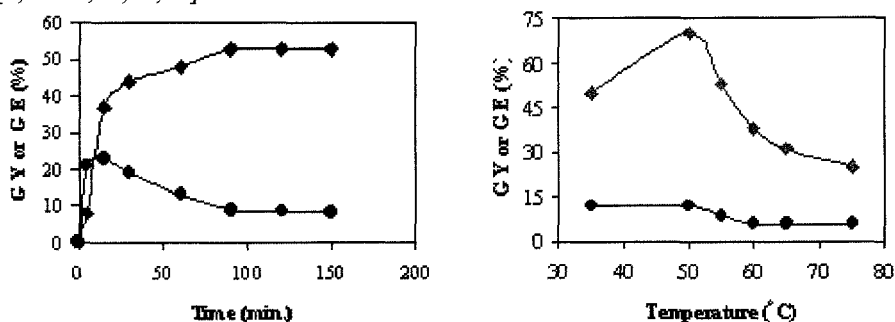
### *Effect of Temperature*

The effect of temperature on the graft copolymerization of 4-VP onto PET fibers was studied by varying temperature between  $15$ - $75^\circ\text{C}$  (Fig. 2). It is clear that the graft yield increases with increasing the temperature from  $15^\circ\text{C}$  to  $50^\circ\text{C}$ ; further increase in the temperature decreases the graft yield. The enhancement in grafting upon raising the polymerization temperature could be ascribed to higher rate of  $\text{Bz}_2\text{O}_2$  decomposition, and possible reaction between the growing homopolymer chain radical with PET. It also increases swellability of PET fiber and facilitates the diffusion of monomer into

PET matrix, thus resulting in increased rates of grafting. Whereas, lowering of grafting by raising the temperature above 50°C could be due to the favoured chain termination reactions and increase in the formation of homo(4-VP), as reflected from the grafting efficiency curve in Fig. 2. Similar results were obtained in the  $Bz_2O_2$  initiated graft copolymerization of AAm on PET fibers [18].

#### Effect of Initiator Concentration

Fig. 3 shows the effect of  $Bz_2O_2$  concentration on the rate of grafting as the  $Bz_2O_2$  concentration increased. The graft yield increases significantly by increasing the  $Bz_2O_2$  concentration up to  $2.0 \times 10^{-3}$  M, and then falls down upon further increase in initiator concentration. This is a typical behaviour reported in many other studies [3,11-13,17,23,24].



**Figure 1.** Variation of graft yield (♦) and grafting efficiency (●) with polymerization time:  $[4\text{-VP}] = 0.8$  M;  $[Bz_2O_2] = 3.0 \times 10^{-3}$  M;  $T = 55$  °C  
**Figure 2.** Variation of graft yield (♦) and grafting efficiency (●) with temperature:  $[4\text{-VP}] = 0.8$  M;  $[Bz_2O_2] = 3.0 \times 10^{-3}$  M;  $t = 2$  h.

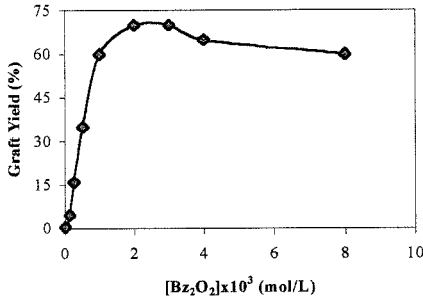
The enhancement of grafting by increasing the  $Bz_2O_2$  concentration to a certain limit implies that, primary free radical species ( $C_6H_5COO^\bullet$ ) and/or secondary free radical species ( $C_6H_5^\bullet$ ) may participate essentially in the direct abstraction of hydrogen atom from the PET backbone to yield a polyester macroradical capable of initiating the grafting. Above this limit, the termination process with the growing polymer chains, the combination of the free radical species and the termination process with the polyester macroradicals prevail over the initiation process.

#### Effect of Monomer Concentration

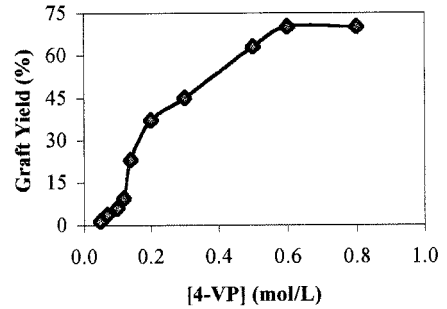
Variation of grafting yield with monomer concentration was studied in the range of 0.05-0.8 M. The percentage of grafting was found to increase steadily with the monomer concentration up to 0.6 M then levelled off (Fig.4). As the monomer concentration increases, the diffusion of monomer molecules into the PET structure increases, leading to a higher grafting yield. The levelling off of the grafting after saturation graft yield (70%) could be associated with depletion of the available 4-VP due to the simultaneous increase in the homopolymerization rate with growing 4-VP concentration in the polymerization medium. In addition, the homopoly(4-VP) accumulated in the reaction medium increases the medium viscosity and the monomer diffusion into the PET structure becomes more difficult. Similar results obtained in our previous study on the graft copolymerization of 4-VP onto PET films [16].

#### Kinetics of Grafting

It is obvious that the mechanism of the graft copolymerization is quite complex due to the propagation, termination and homopolymerization reactions. However, kinetically,



**Figure 3.** Effect of initiator concentration on graft yield :  
[4-VP] = 0.6 M; T = 50°C; t = 2 h.



**Figure 4.** Effect of monomer concentration on graft yield : [Bz<sub>2</sub>O<sub>2</sub>] = 3.0x10<sup>-3</sup> M; T = 50°C; t = 2 h.

the rate of graft copolymerization ( $R_g$ ) with respect to monomer and initiator concentrations can be written as follows [25].

$$R_g = k[4\text{-VP}]^m [\text{Bz}_2\text{O}_2]^n \quad (3)$$

where  $m$ , and  $n$  can be experimentally determined. The experimental results showing the change of the initial rate of grafting with  $\text{Bz}_2\text{O}_2$  concentration (Table 1) in the range of 0.0 to 2.0x10<sup>-3</sup> M (keeping the concentration of 4-VP constant) were related by plotting  $\text{Log}R_g$  vs.  $\text{Log}[\text{Bz}_2\text{O}_2]$ . Fig. 5 shows that the rate of grafting was proportional to 1.0 power of  $\text{Bz}_2\text{O}_2$  concentration. Similarly, at constant  $\text{Bz}_2\text{O}_2$  concentration the initial rates of grafting obtained at various 4-VP concentrations (Table 2) were related (Fig 6). Fig. 6 shows that the rate of grafting was proportional to the 1.5 power of 4-VP concentration in the range of 0.05–0.6 M 4-VP concentration. Therefore, the grafting rate of 4-VP and PET fibers using the  $\text{Bz}_2\text{O}_2$  initiator can be written as

$$R_g = k[4\text{-VP}]^{1.5} [\text{Bz}_2\text{O}_2]^{1.0} \quad (4)$$

Table 1. Kinetic data showing the change of the initial rate of grafting with  $\text{Bz}_2\text{O}_2$  concentration

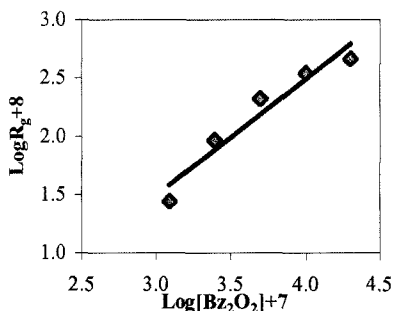
[Bz <sub>2</sub> O <sub>2</sub> ]x10 <sup>3</sup> molL <sup>-1</sup>	Grafting Yield (%)	Log[Bz <sub>2</sub> O <sub>2</sub> ]+7	R <sub>g</sub> x10 <sup>6</sup> molL <sup>-1</sup> .s <sup>-1</sup>	LogR <sub>g</sub> +8
0.125	4.8	3.097	0.275	1.439
0.25	16.0	3.398	0.917	1.962
0.5	35.0	3.699	2.078	2.318
1.0	60.0	4.000	3.437	2.536
2.0	70.0	4.301	4.590	2.662

[4-VP]=0.6 molL<sup>-1</sup>; T=50 °C; t=2 h

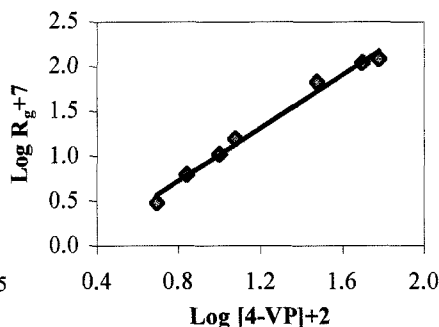
Table 2. Kinetic data showing the change of the initial rate of grafting with 4-VP concentration

[4-VP]x10 <sup>2</sup> molL <sup>-1</sup>	Grafting Yield (%)	Log[4-VP]+2	R <sub>g</sub> x10 <sup>7</sup> molL <sup>-1</sup> .s <sup>-1</sup>	LogR <sub>g</sub> +7
5	1.8	0.699	0.302	0.479
7	3.7	0.845	0.621	0.793
10	6.3	1.000	1.057	1.024
12	9.5	1.079	1.565	1.194
30	45.0	1.477	6.724	1.828
50	63.0	1.699	11.100	2.045
60	70.0	1.778	12.090	2.082

[Bz<sub>2</sub>O<sub>2</sub>]=3x10<sup>-3</sup> molL<sup>-1</sup>; T=50 °C; t=2 h



**Figure 5.** Rates of grafting ( $R_g$ ) vs.  $[Bz_2O_2]$ :  $[4-VP] = 0.6 \text{ M}$ ;  $T = 50^\circ\text{C}$ ;  $t = 2 \text{ h}$ .

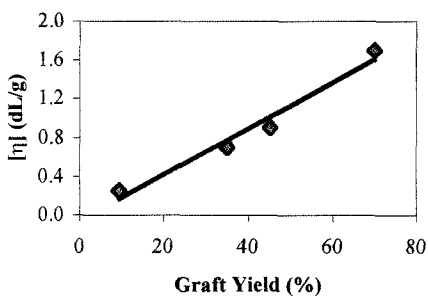


**Figure 6.** Rates of grafting ( $R_g$ ) vs.  $[4-VP]$ :  $[Bz_2O_2] = 3.0 \times 10^{-3} \text{ M}$ ;  $T = 50^\circ\text{C}$ ;  $t = 2 \text{ h}$

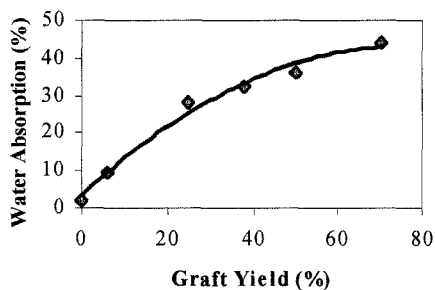
There are no kinetic data concerned with the grafting of 4-VP using  $Bz_2O_2$  in the literature. However, many researchers have investigated the kinetics of the grafting of various vinyl monomers onto PET fibers using different initiators [9,19,25-27]. As mentioned in the given references above, the dependence of the rate of grafting on initiator and monomer concentrations varies with the types of initiator and monomer grafted onto PET backbone.

#### *Intrinsic Viscosity Measurements*

Intrinsic viscosity  $[\eta]$ , data obtained from 4-VP-grafted PET fibers are plotted in Fig. 7. As reflected from the graph, intrinsic viscosity was increased with the increasing graft yields, showing an evidence of grafting. Similar results were observed during the grafting of 4-vinylpyridine [16] and n-vinyl-2-pyrrolidone onto PET films [25]. Viscosity average molar mass of the grafted homopoly(4-VP) chains were determined to be  $104,000 \text{ g/mol}$  from the Mark-Houwink equation taking  $K$  and  $\alpha$  as  $25 \times 10^{-3} \text{ mL/g}$  and  $0.68$  [29], respectively.



**Figure 7.** Variation of intrinsic viscosity with graft yield.



**Figure 8.** Change of water absorption capacity with graft yield.

#### *Water Absorption Capacity*

As seen from Fig. 8, water absorption capacity of 4-VP grafted PET fiber is increased with increasing grafting yield due to the introduction of hydrophilic units.

#### *Differential Scanning Calorimetry*

Thermal analysis results are given in Table 3. As seen from the table, as the amount of grafted 4-VP increases,  $T_g$  of the grafted PET fiber also increases up to 43 % grafting yield and then almost remained constant.

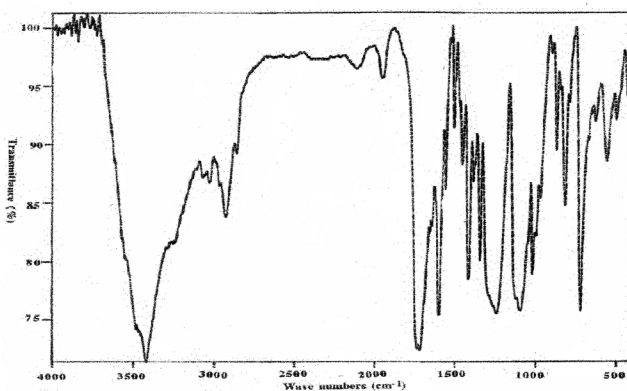
Table 3. Data obtained from DSC measurements.

% Graft Yield	$T_g$ ( $^{\circ}\text{C}$ )
Original PET	81.05
*Homopoly(4-VP)	90.63
26	141.26
43	145.07
60	146.80

\* Obtained from 35% grafting yield process.

#### FTIR Spectrum

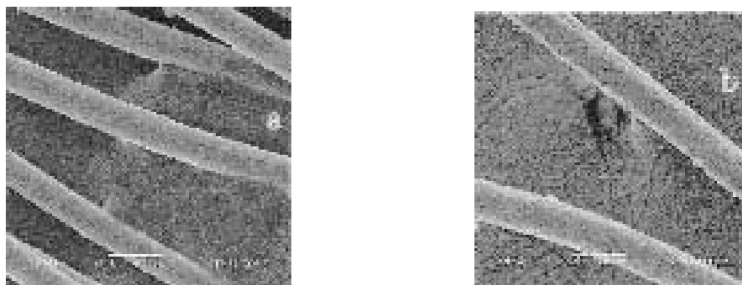
The FTIR spectrum of 4-VP-grafted PET fiber is shown in Fig. 9. The absorptions at 1400 to 1600  $\text{cm}^{-1}$  and 1735  $\text{cm}^{-1}$  are typical to those aromatic C-H and C=O stretchings and the peak at 1602  $\text{cm}^{-1}$  in the spectrum of 4-VP-grafted fibers is due to the resonance peak of the vinylpyridine group.



**Figure 9.** FTIR spectrum of 4-VP grafted PET fiber.

#### Microstructure of Grafted Copolymers

The scanning electron micrographs of ungrafted and 4-VP grafted (25%) PET fibers are shown in Figure 10. It is clear from the SEM results that, the ungrafted PET fiber surface (Fig. 10.a) has a smooth and relatively homogeneous appearance. The grafted side chain, 4-VP, seems to form microphases attached to the PET back-bone and caused a heterogeneous appearance in the graft copolymer (Fig. 10.b), and showing another proof of grafting.



**Figure 10.** SEM micrographs of (a) ungrafted (500x) and (b) 4-VP grafted (500x) PET fibers.

## Conclusions

Maximum percent grafting (70%) was obtained when the polymerization was carried at the following conditions:  $[Bz_2O_2] = 2.0 \times 10^{-3}$  M;  $[4-VP] = 0.6$  M;  $t = 2$  h and  $T = 50^\circ C$ . The rate of grafting was found to be proportional of the 1.5 and 1.0 powers of 4-VP and  $Bz_2O_2$  concentrations, respectively. It was recognized that, both water absorption capacity, intrinsic viscosity and glass transition temperature increased with the increasing graft yield.

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