

# Graft Copolymerization of *n*-Vinyl-2-pyrrolidone on Dimethyl Sulfoxide Pretreated Poly(ethylene terephthalate) Films Using Azobisisobutyronitrile Initiator

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Received 8 May 1996; accepted 19 November 1996

**ABSTRACT:** Poly(ethylene terephthalate) (PET) films were grafted with *n*-vinyl-2-pyrrolidone (*n*-VP) using an azobisisobutyronitrile (AIBN) initiator. Films were pretreated in dimethyl sulfoxide (DMSO) for 1 h at 140°C before the polymerization reaction was carried out. Variations of graft yield with time, temperature, initiator, and monomer concentrations were investigated. The optimum temperature and polymerization time was found to be 70°C and 4 h, respectively. Increasing monomer concentration from 0.28 to 1.22M and initiator concentration from  $1.77 \times 10^{-3}$  to  $4.20 \times 10^{-3}$ M enhanced the percent grafting. The effects of monomer and initiator diffusion on PET films were also studied. The overall activation energy for grafting was calculated as 11.5 kcal/mol. Further changes in properties of PET films such as water-absorption capacity and intrinsic viscosity were determined. The grafted films were characterized with FTIR and scanning electron microscopy (SEM). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1437–1444, 1997

**Key words:** graft copolymerization; poly(ethylene terephthalate) film; *n*-vinyl-2-pyrrolidone polymerization; swelling-assisted polymerization

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is most widely used in industry as fiber, film, and plastic resins because of its outstanding stabilities and bulk properties. It makes an excellent film but a few disadvantages exist in respect to the surface properties, mostly originating from its low wettability, high static electrification, and poor adhesion.

One of the most common ways resorted to to improve the poor features of PET is grafting hydrophilic monomers onto it by graft copolymerization. Grafting on PET film can be achieved either

by radiation<sup>1–7</sup> or chemical means.<sup>8–12</sup> Radiation-induced graft copolymerization of monomers on PET has been the subject of several studies. But grafting by chemical methods is often limited. However, PET is one of the most difficult polymers on which to graft. This is particularly true with PET films. The reasons for the difficulty in grafting are essentially twofold: (1) In the case of radiation grafting, the yield of free radicals on radiolysis is unusually low and (2) the drawn film absorbs very little of most organics and the rates of diffusion into the films are extremely low.

Previous works have shown, however, that the grafting yield is improved by judicious use of suitable swelling agents.<sup>9–12</sup> In our previous study, we studied the effect of pyridine, dichloroethane (DCE), DCE/H<sub>2</sub>O (20/80 v/v), and DMSO as swelling agents in the graft copolymerization of

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Contract grant sponsor: Gazi University Research Fund.

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acrylamide on PET films using a benzoyl peroxide ( $Bz_2O_2$ ) initiator and reported that pretreatment of the films in DMSO for 1 h at  $140^\circ C$  is the best condition.<sup>10</sup> We also used this condition in the graft copolymerization of 4-vinylpyridine on PET film using a  $Bz_2O_2$  initiator.<sup>12</sup> In the present study, we aimed to graft copolymerize *n*-vinyl-2-pyrrolidone (*n*-VP), which improves the flexibility of substrates to which it is cured,<sup>13</sup> on PET films using the previously determined swelling condition.

## EXPERIMENTAL

### Materials

PET films (Hoksp) of a thickness of 50–125  $\mu m$  were used for grafting. *n*-VP (Merck) was purified by vacuum distillation at 2 mmHg at  $65^\circ C$ . AIBN (Merck) was recrystallized twice from methanol and dried in a vacuum oven for 48 h. Other reagents were Merck products and used as supplied.

### Polymerization Procedure

PET films were cut to dimensions of about  $25 \times 30$  mm and had a weight of approximately 0.06 g. Before the grafting reaction was carried out, they were preswelled in DMSO for 1 h at  $140^\circ C$  in a temperature-controlled oil bath.<sup>10</sup> After treatment, solvent on the films was removed by blotting between a filter paper and then placed into the polymerization medium.

Polymerization was carried out in a 100 mL tube under a nitrogen atmosphere. Pretreated PET films of known mass were put into the polymerization tube containing 8 mL of an aqueous solution of *n*-VP at a known concentration and nitrogen gas was allowed to pass through the solution for 45 min. Then, the polymerization tube was placed into a thermostatted water bath. After thermal equilibrium was reached, the required amount of AIBN (dissolved in 2 mL acetone) was added. Polymerization was allowed to proceed for a specified period of time under a nitrogen atmosphere. At the end of the predetermined polymerization time, films were removed from the polymerization medium and residual solvent, monomer, and homopoly(*n*-VP) were removed by washing in water for 2 h. The washing water was changed at least four times. 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:

$$\text{Graft yield (\%)} = [(w_g - w_i)/w_i] \times 100 \quad (1)$$

where  $w_i$  and  $w_g$  denote the weights of the ungrafted and grafted PET films, respectively.

At the end of the grafting procedure, homopoly(*n*-VP) formed in the grafting medium was precipitated by addition of excess acetone. The grafting efficiency was calculated as follows:

Grafting efficiency

$$= \frac{\text{weight of graft}}{\text{weight of graft} + \text{weight of homopolymer}} \times 100 \quad (2)$$

The rate of grafting ( $R_g$ ) was found by using the formula<sup>14</sup>

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

where  $M_w$  is the molecular weight of the monomer;  $t$ , the polymerization time (s); and  $V$ , the volume (mL) of the overall reaction medium.

### Determination of Intrinsic Viscosity

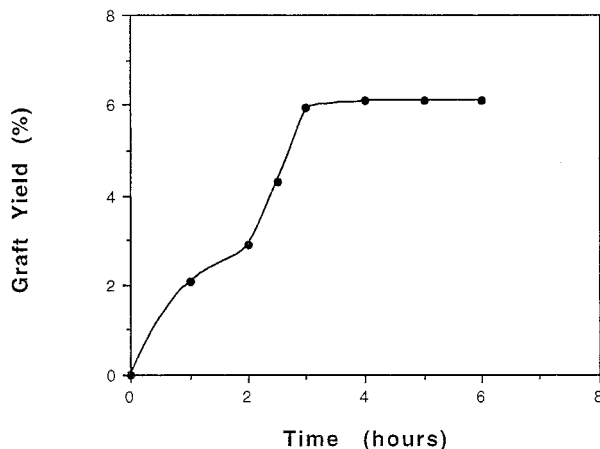
Intrinsic viscosity measurements were made in a phenol/tetrachloroethane (1 : 1) solvent system using an Ubbelohde capillary flow viscometer mounted in a water bath maintained at  $25.0 \pm 0.1^\circ C$ .

### Determination of Water Absorption Capacity

PET films were immersed in thermostatted distilled water at  $20 \pm 0.1^\circ C$  for 48 h, blotted between a filter paper, and weighed. Films were then vacuum-dried at  $50^\circ C$  for 96 h and brought to a constant weight and weighed again. Water-absorption capacity was determined from the weight increase of the films.

### Infrared Spectroscopy

An FTIR spectrum was recorded using a Mattson Model 1000 FTIR spectrophotometer. Samples were analyzed as films cast from phenol/tetrachloroethane (1 : 1) onto sodium chloride plates.



**Figure 1** Variation of graft yield with polymerization time.  $[n\text{-VP}] = 0.47M$ ,  $[\text{AIBN}] = 4.20 \times 10^{-3}M$ ,  $T = 70^\circ\text{C}$ , film thickness:  $50 \mu\text{m}$ .

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) studies of the films coated with gold were performed using a JEOL Model JEM-100 CX II microscope.

## RESULTS AND DISCUSSION

### Effect of Polymerization Time

Grafting of PET films was carried out at various polymerization times, keeping the monomer and initiator concentrations and temperature constant. As shown in Figure 1, graft yield was first increased with increase in polymerization time, then leveled off after 4 h, reaching a 6% saturation grafting value. The leveling off of grafting may be attributed to the saturation of the active PET backbone by poly(*n*-VP). Similar results were obtained from the graft copolymerization of acrylamide<sup>10</sup> and 4-vinylpyridine<sup>12</sup> on PET films.

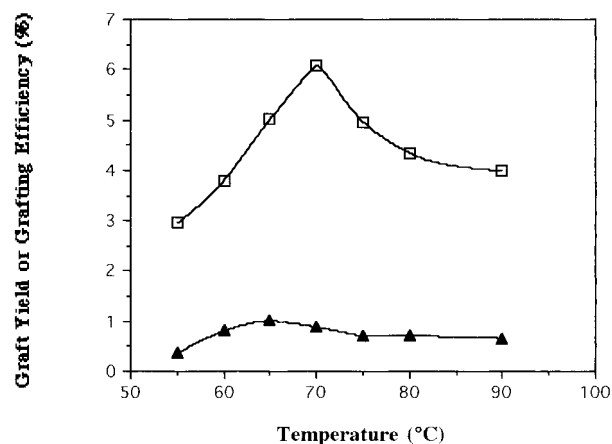
### Effect of Temperature

The effect of temperature on the graft copolymerization of *n*-VP on PET films was studied within the range of  $55\text{--}90^\circ\text{C}$  (Fig. 2). As the temperature was increased from  $55$  to  $70^\circ\text{C}$ , a sharp increase in the graft yield was observed. The graft yield value reached a maximum at  $70^\circ\text{C}$  and then a gradual decrease was observed with further increase in temperature. The increase in the graft yield with increasing temperature may be attributed to following reasons: (1) The swellability of PET films increases with increasing temperature.

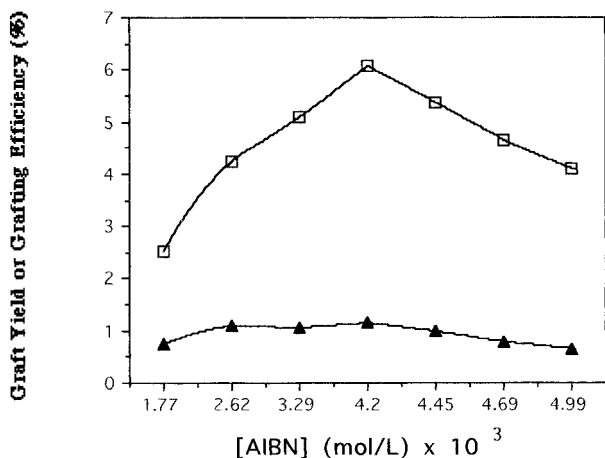
(2) Around the glass transition temperature ( $65^\circ\text{C}$ ), PET chains become more reactive and give easy radicalic reactions.<sup>15</sup> (3) The mobility of the monomer and initiator molecules increases. (4) The diffusion rate of the monomer and initiator molecules from the solution phase to the PET backbone also increases. In the graft-copolymerization system, the monomer is competitive both in grafting and homopolymerization. The decrease of the graft yield after  $70^\circ\text{C}$  was due to the favored chain-termination reactions and increase in the formation of homopoly(*n*-VP), as reflected from the grafting efficiency curve in Figure 2, which plays a more important role than does graft copolymerization at elevated temperatures.<sup>16,17</sup> Similar results were also reported in the  $\text{Bz}_2\text{O}_2$ -initiated graft copolymerization of acrylamide<sup>10</sup> and 4-vinylpyridine<sup>12</sup> on PET films.

### Effect of Initiator Concentration

Keeping the monomer concentration, time, and temperature constant as  $0.47M$ , 4 h, and  $70^\circ\text{C}$ , respectively, the effect of initiator concentration on the graft yield was studied within the range of  $1.77 \times 10^{-3}$  to  $4.69 \times 10^{-3}M$ . Graft yield was increased up to  $4.20 \times 10^{-3}M$  AIBN concentration, reached a maximum, then showed a gradual decrease with further increase in the initiator concentrations (Fig. 3). Dissociation of AIBN molecules form free radicals in the polymerization medium. These free radicals abstract hydrogen atoms from the PET backbone and form active sites for the grafting reactions to take place. Increase in AIBN concentration promotes the num-



**Figure 2** Effect of temperature on grafting: ( $\square$ ) graft yield; ( $\blacktriangle$ ) grafting efficiency.  $[n\text{-VP}] = 0.47M$ ,  $[\text{AIBN}] = 4.20 \times 10^{-3}M$ ,  $t = 4$  h, film thickness:  $50 \mu\text{m}$ .

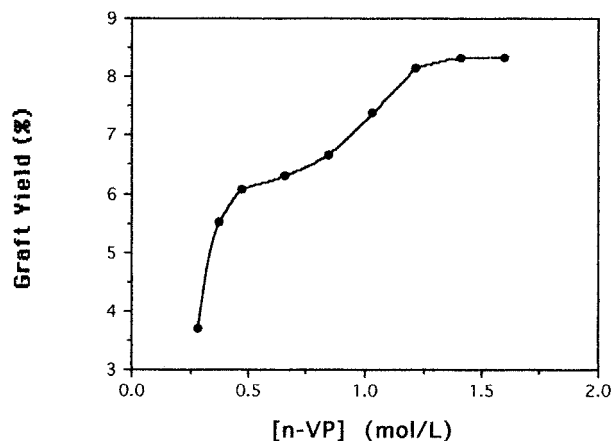


**Figure 3** Effect of initiator concentration on grafting: (□) graft yield; (▲) grafting efficiency.  $[n\text{-VP}] = 0.47\text{M}$ ,  $T = 70^\circ\text{C}$ ,  $t = 4\text{ h}$ , film thickness:  $50\ \mu\text{m}$ .

ber of active poly( $n\text{-VP}$ ) chains. These active poly( $n\text{-VP}$ ) chains undergo chain-transfer reactions with PET macromolecules. These chain-transfer reactions and hydrogen abstraction result with increased graft yield. As the initiator concentration further increased, (1) more active macromolecular chains form and combine with each other to give a termination reaction, (2) termination reactions between initiator radicals predominate to the propagation reactions, and (3) increase in the formation of homopoly( $n\text{-VP}$ ) leads to decreased graft yield and grafting efficiency (Fig. 3).

#### Effect of Monomer Concentration

The effect of monomer concentration on graft yield was investigated at  $4.20 \times 10^{-3}\text{M}$  [AIBN], 4 h, and  $70^\circ\text{C}$ . The change of graft yield with monomer concentration is presented in Figure 4. Graft yield increased up to  $1.22\text{M}$  [ $n\text{-VP}$ ] and remained constant with further increase in the monomer concentration. As the monomer concentration increases, the diffusion of monomer molecules into the PET structure increases, leading to a higher graft yield. The leveling off of the grafting, after saturation graft yield, could be associated with depletion in available  $n\text{-VP}$  concentration as well as with reduction in active sites on the PET backbone as the graft copolymerization proceeds. In addition, the homopoly( $n\text{-VP}$ ) accumulated in the reaction medium increases the medium viscosity and the monomer diffusion into the PET structure becomes more difficult.

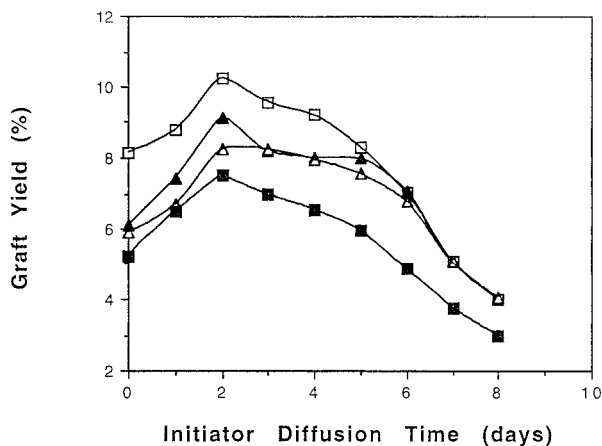


**Figure 4** Dependence of graft yield on monomer concentration.  $[\text{AIBN}] = 4.20 \times 10^{-3}\text{M}$ ,  $T = 70^\circ\text{C}$ ,  $t = 4\text{ h}$ , film thickness:  $50\ \mu\text{m}$ .

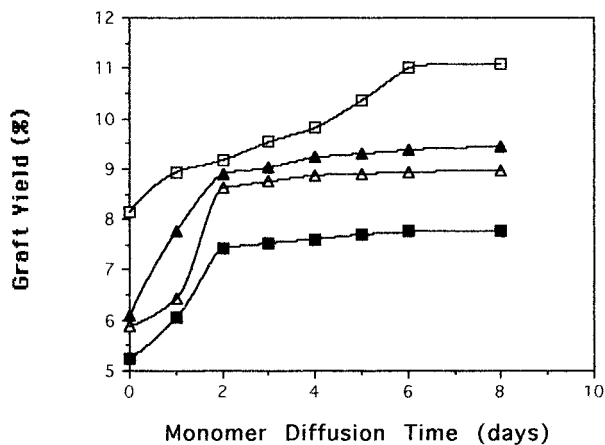
#### Effect of Initiator and Monomer Inclusion

Pretreated PET films at various thicknesses were dipped into a  $4.20 \times 10^{-3}\text{M}$  AIBN and  $1.22\text{M}$   $n\text{-VP}$  solutions for 1–8 days at  $20^\circ\text{C}$  before the graft polymerization was carried out (Figs. 5 and 6). As seen from Figure 5, graft yield increased with initiator inclusion time up to 2 days, then decreased irrespective of the film thickness. This may be attributed to the decrease in the efficiency of the initiator which has a half-life of 100 h at  $20^\circ\text{C}$ .<sup>18</sup>

The effect of diffusion and incorporation of  $n\text{-VP}$  on the graft yield of PET films is presented in Figure 6. A saturation graft yield value was reached at 6 days for  $50\ \mu\text{m}$  and at 2 days for  $75\ \mu\text{m}$ ,



**Figure 5** Effect of initiator inclusion time on graft yield.  $[\text{AIBN}] = 4.20 \times 10^{-3}\text{M}$ ,  $[n\text{-VP}] = 1.22\text{M}$ ,  $T = 70^\circ\text{C}$ ,  $t = 4\text{ h}$ . PET film thicknesses: (□)  $50\ \mu\text{m}$ ; (▲)  $75\ \mu\text{m}$ ; (△)  $100\ \mu\text{m}$ ; (■)  $125\ \mu\text{m}$ .



**Figure 6** Effect of monomer inclusion time on graft yield.  $[AIBN] = 4.20 \times 10^{-3} M$ ,  $[n\text{-VP}] = 1.22 M$ ,  $T = 70^\circ C$ ,  $t = 4$  h. Film thicknesses: ( $\square$ )  $50 \mu m$ ; ( $\blacktriangle$ )  $75 \mu m$ ; ( $\triangle$ )  $100 \mu m$ ; ( $\blacksquare$ )  $125 \mu m$ .

100, and  $125 \mu m$  of PET films. As in the case of initiator inclusion, the overall graft yield increased with increasing monomer inclusion time. These results are consistent with earlier studies of the grafting of various hydrophilic monomers on PET films.<sup>10,12</sup>

### Kinetics of Grafting

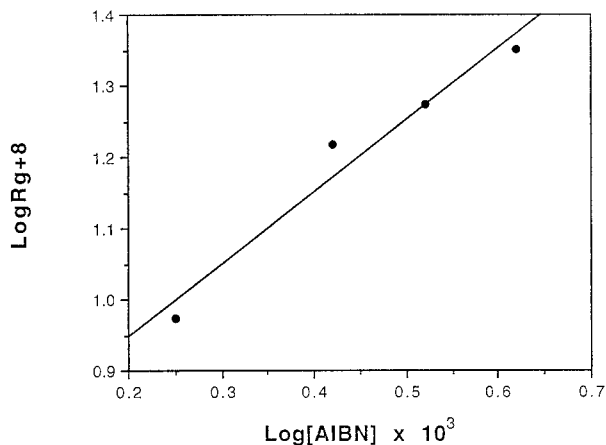
In a grafting system of *n*-VP and PET films, the relation of the rate of grafting ( $R_g$ ) with the monomer and initiator concentrations<sup>19</sup> can be written as

$$R_g = k[n\text{-VP}]^m[AIBN]^n$$

where  $m$  and  $n$  can be experimentally determined.

A graph showing the change of the rate of grafting with  $\log[AIBN]$ , keeping the *n*-VP concentration constant, is given in Figure 7. The rate of grafting obtained from the slope of the  $\log R_g$  vs.  $\log[AIBN]$  was proportional to the first power of  $[AIBN]$  in the range of  $1.77$  to  $4.20 \times 10^{-3}$  mol/L AIBN concentration.

Data obtained from the change of the rate of grafting with the  $\log[n\text{-VP}]$  at constant AIBN concentration are drawn in Figure 8. From the slope of  $\log R_g$  vs.  $\log[n\text{-VP}]$ , it was found that the rate of grafting was proportional to the 0.46 power of  $[n\text{-VP}]$  in the range of  $0.282$ – $1.408$  mol/L *n*-VP concentration. Therefore, the grafting rate of *n*-VP and PET films using an AIBN initiator can be written as

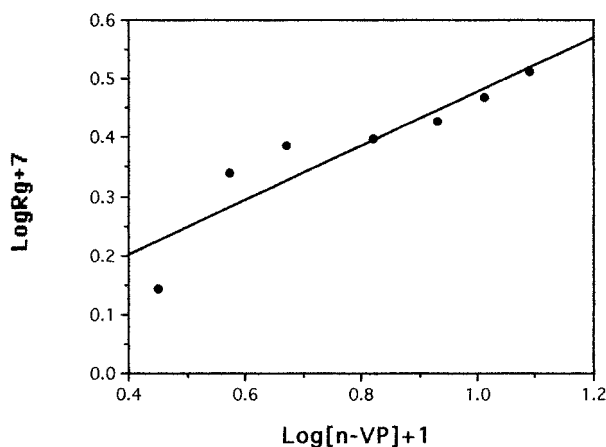


**Figure 7** Rates of grafting ( $R_g$ ) vs.  $[AIBN]$ .  $[AIBN] = 1.77 \times 10^{-3}$  to  $4.20 \times 10^{-3} M$ ,  $[n\text{-VP}] = 0.47 M$ ,  $T = 70^\circ C$ ,  $t = 4$  h, film thickness:  $50 \mu m$ .

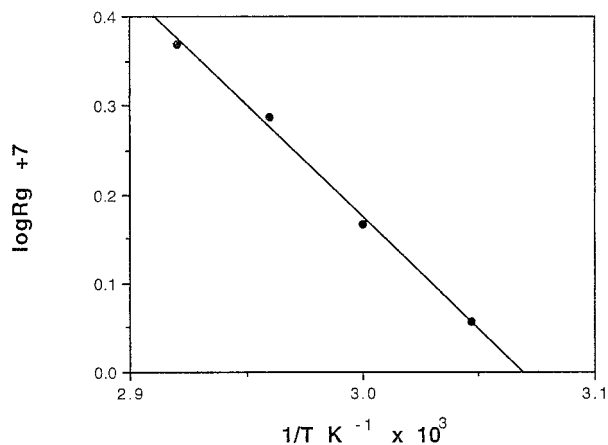
$$R_g = k[n\text{-VP}]^{0.46}[AIBN]^{1.00}$$

The overall activation energy for grafting was calculated to be  $11.5$  kcal/mol from the Arrhenius plot of  $\log R_g$  vs.  $1/T$  (Fig. 9).

There are no kinetic data concerned with the grafting of *n*-VP using AIBN in the literature. However, many researchers have investigated the kinetics of the grafting of various vinyl monomers onto PET fibers using different initiators. For instance, in the grafting of 2-methyl-5-vinyl pyridine onto PET fibers using a  $Bz_2O_2$  initiator, Shalaby et al.<sup>20</sup> reported that the grafting rate was proportional to the 1.1 and 1.02 powers of monomer and initiator concentrations, respectively. In the graft-



**Figure 8** Rates of grafting ( $R_g$ ) vs.  $[n\text{-VP}]$ .  $[n\text{-VP}] = 0.282$ – $1.408 M$ ,  $[AIBN] = 4.20 \times 10^{-3} M$ ,  $T = 70^\circ C$ ,  $t = 4$  h, film thickness:  $50 \mu m$ .



**Figure 9** Arrhenius plot of  $\log R_g$  vs.  $1/T$ .  $T = 55\text{--}70^\circ\text{C}$ ,  $[n\text{-VP}] = 0.47\text{M}$ ,  $[\text{AIBN}] = 4.20 \times 10^{-3}\text{M}$ ,  $t = 4\text{ h}$ , film thickness:  $50\ \mu\text{m}$ .

ing of the same monomer with hydrogen peroxide, the above orders become  $-0.59$  and  $0.97$ .<sup>21</sup>

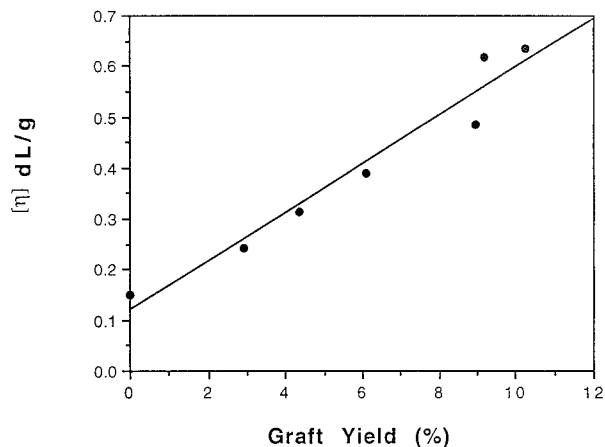
In another study, it was stated by Somanathan et al.<sup>14</sup> that the grafting rate was of 0.167 order with respect to monomer concentration and of 0.545 order with respect to initiator concentration in the grafting of methacrylic acid onto PET fibers using the  $\text{Bz}_2\text{O}_2$  initiator. It has also been stated by Saçak et al.<sup>19,22</sup> in two different studies that in the grafting of methyl methacrylate onto PET fibers using AIBN the grafting rate was 1.30 and 0.92 powers of methyl methacrylate and AIBN concentrations, respectively, and in the grafting of acrylic acid onto PET fibers using the  $\text{Bz}_2\text{O}_2$  initiator, the grafting rate was 2.33 power of acrylic acid and 0.92 power of  $\text{Bz}_2\text{O}_2$  concentrations. As seen from the given references, the dependence of the rate of grafting on initiator and monomer concentrations varies with the types of initiator and monomers grafted onto the PET backbone.

#### Intrinsic Viscosity Measurements

Intrinsic viscosity,  $[\eta]$ , data obtained from  $n$ -VP-grafted PET films are plotted in Figure 10.  $[\eta]$  increased with the increasing graft yield, showing evidence of grafting. Similar results were observed during the grafting of methyl methacrylate onto PET fibers<sup>22</sup> and 4-vinylpyridine onto PET films.<sup>12</sup>

#### Water-absorption Characteristics

The water-absorption capacity of the grafted films was first increased with increasing graft yield and

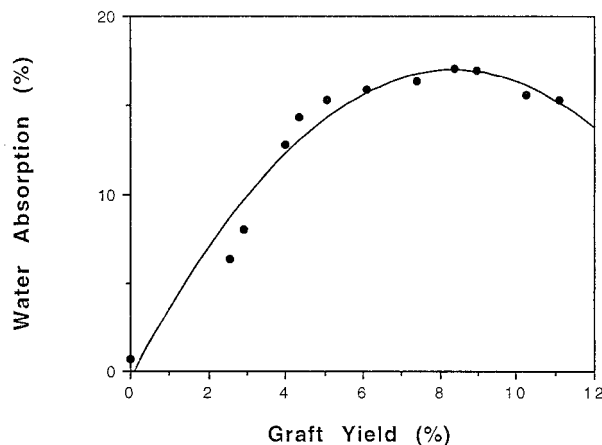


**Figure 10** Variation of intrinsic viscosity with graft yield. Film thickness:  $50\ \mu\text{m}$ .

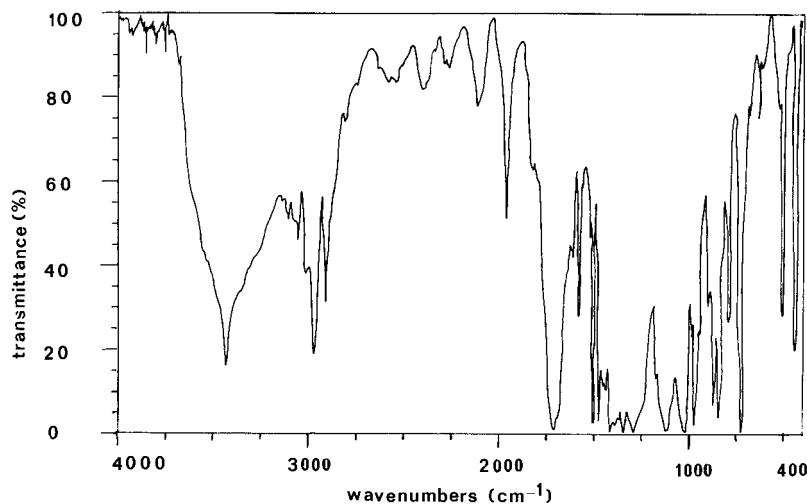
reached a maximum of 17.0% at 8.4% graft yield, then showed a slight decrease (Fig. 11). The water uptake of a film depends mainly on the number of hydrophilic groups introduced into the polymer matrix by the grafting process. Increase in the water uptake with grafting may be attributed to the hydrophilic nature of the  $n$ -VP monomer. However, a decrease after a certain graft yield is due to the densely packed structure of PET which acts as a barrier after a certain value of grafting that impedes diffusion into the polymer backbone.<sup>4,9,12,19</sup>

#### FTIR Spectrum

The FTIR spectrum of  $n$ -VP-grafted PET film is shown in Figure 12. The absorptions at  $1400\text{--}1600$  and  $1735\ \text{cm}^{-1}$  are typical to those aromatic



**Figure 11** Change of water-absorption capacity with graft yield. Film thickness:  $50\ \mu\text{m}$ .



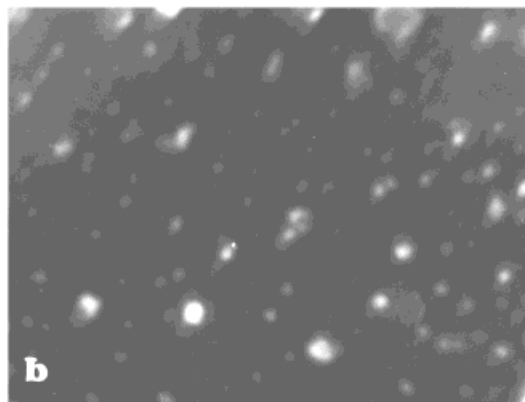
**Figure 12** FTIR spectrum of *n*-VP-grafted PET film. Film thickness: 50  $\mu\text{m}$ .

C—H and C=O stretchings. The peak at 3432  $\text{cm}^{-1}$  in the spectrum is due to the resonance peak of *n*-vinylpyrrolidone. This provides proof of grafting.



#### Microstructure of Grafted Copolymers

The scanning electron micrographs of ungrafted and *n*-VP-grafted (11.0%) PET films are shown in Figure 13. It is clear from the SEM results that the ungrafted PET film surface [Fig. 13(a)] has a smooth and relatively homogeneous appearance. The grafted side chain, *n*-VP, seems to form microphases attached to the backbone in the graft copolymer [Fig. 13(b)] and shows another proof of grafting.



**Figure 13** SEM micrographs of PET films: (a) ungrafted (1000 $\times$ ); (b) *n*-VP-grafted (1000 $\times$ ). Film thickness: 50  $\mu\text{m}$ .

Two of us are grateful to the Gazi University Research Fund for the financial support of this work.

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