

# Solvent-Assisted Graft Copolymerization of Acrylamide on Poly(ethylene terephthalate) Films Using Benzoyl Peroxide Initiator

OYA ŞANLI<sup>1,\*</sup> and EMSAL PULAT<sup>2</sup>

<sup>1</sup>Gazi Üniversitesi Fen-Edebiyat Fakültesi Kimya Bölümü, 06500, Teknikokullar, Ankara, Turkey; <sup>2</sup>Ankara Üniversitesi Fen Fakültesi Kimya Bölümü, 06100, Beşevler, Ankara, Turkey

## SYNOPSIS

Graft-copolymerization of acrylamide (AAm) on poly(ethylene terephthalate) (PET) films using benzoyl peroxide ( $Bz_2O_2$ ) initiator has been studied. Four organic solvents, namely, pyridine (Py), 1,2-dichloroethane (DCE), DCE/H<sub>2</sub>O (20/80, v/v), and dimethyl sulfoxide (DMSO), were used as swelling agents. DMSO was found to be the most suitable swelling agent. Solvent inclusion in the films increased with increased length of solvent treatment time and temperature. Elevated temperatures had a greater effect on the inclusion of swelling agents than did the length of swelling. Variation of graft yield with the type of solvent, initiator concentration, monomer concentration, temperature, and polymerization time were also investigated. The graft yield increased in the order of toluene, benzene, DMSO. The optimum temperature for grafting was found to be 70°C. The graft yield was observed to increase with monomer concentration and polymerization time, then reached a plateau. The graft yield increased up to a certain  $Bz_2O_2$  concentration, then decreased. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

PET has proved to have the most excellent mechanical properties among the commodity polymers, especially when utilized as a film and fiber. However, some problems have been pointed out to exist with regard to the surface properties, mostly originating from its low on water wettability and poor antistatic properties. Grafting of hydrophilic monomers on PET films and fibers improve their color absorption, adhesion, hydrophilicity, or antistatic properties.

There are many studies on the grafting of vinyl monomers on to PET fibers and fabrics in the literature. The grafting of styrene,<sup>1-4</sup> acrylic acid (AA) and methacrylic acid,<sup>5-9</sup> vinyl acetate,<sup>10</sup> acrylonitril,<sup>5</sup> bromostyrene,<sup>11</sup> acrylamide,<sup>12</sup> and methyl methacrylate<sup>7-13</sup> onto PET fibers and fabrics have been reported.

However, studies concerning the graft polymerization of vinyl monomers on PET films are limited;

of those, graft polymerization of AA has been extensively used for the modification of PET films.<sup>14-21</sup>

There are serious difficulties in grafting monomers onto PET. The chemical nature of PET does not allow formation of its macrochains of an appreciable quantity of radicals that can initiate the grafting, and the high extent of the crystallization and ordering of the amorphous regions retard monomer diffusion. To overcome these difficulties, Kochkodan and Bryk<sup>18</sup> thermally activated PET films at 353 K for 1800 s to prepare suitable ultrafiltration membranes by grafting PET films with AA. Stolarewicz and Kurzeja<sup>17</sup> reported that the degree of grafting of AA on the activated surface of film depended on the activation method and decreased in the series of UV light, hot air (65–100°C), irradiation, and  $Bz_2O_2$  treatment.

In a heterogeneous polymer–monomer reaction system, diffusion controls chain growth and chain termination in the internal structures of the polymer. One way of facilitating diffusion is to open up the physical structure of the polymer by swelling to allow the monomer to enter in sufficient quantities. Preferential interaction solvents whose solubility

\* To whom correspondence should be addressed.

**Table I Solvent Inclusion (Weight Gain %)**

Solvent	Swelling Time (h)	Temperature (°C)	Weight Gain (%)
Py	1.0	82	4.95
	2.0	82	7.11
	3.0	82	7.41
DCE	3.0	82	7.14
20% DCE + 80% H <sub>2</sub> O	24 at RT + 3.0	82	9.20
	3.0	82	9.30
DMSO	0.5	82	9.30
	1.0	82	9.63
	3.0	82	10.23
	0.5	140	12.60
	1.0	140	12.70
	2.0	140	13.00
	3.0	140	13.95

parameters ( $\delta$ ) are close to those of PET are thought to provide the necessary chemical energy to disrupt intermolecular cohesive forces between polymer chains and permit chain mobility.<sup>21,22</sup> It has been shown that organic solvents with  $\delta$  near the estimated  $\delta$  of amorphous PET ( $\delta = 10.7$ ) induce appreciable crystallinity in the polymer.<sup>23,24</sup> However, it was thought that the use of this solubility parameter may not provide a sufficient indication of the solvent's capability to interact with PET. A study of longitudinal shrinkage and volume swelling of PET in various solvents further suggested that PET may be considered as an (AB)<sub>x</sub> alternating copolymer, where A is the semirigid aromatic segment  $-\text{CO}-\text{C}_6\text{H}_4-$  with a  $\delta$  value of 9.8 and B is a flexible aliphatic ester  $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$  with a  $\delta$  value of 12.1. Results from a study in which organic solvents were found to induce crystallization in unoriented amorphous PET, with maximum density changes in solvents,  $\delta$  around 9.5 and 12.0, confirmed these statements.<sup>22</sup>

Hsieh et al.<sup>25</sup> studied the effects of various swelling solvents on the polymerization of AA to PET films by glow discharge. Uchida et al.<sup>26</sup> performed graft polymerization of AAm by UV radiation. They have pretreated the PET film with benzyl alcohol for enhancement of the graft polymerization.

The present study investigated the use of some selected organic solvents (DMSO,  $\delta$ : 12.93; Py,  $\delta$ : 10.61; DCE,  $\delta$ : 9.0, whose solubility parameters are close to those of PET ( $\delta$ : 9.5 and 12.0), as swelling agents to promote the diffusion and incorporation of the monomer and subsequent polymerization of AAm with the help of the Bz<sub>2</sub>O<sub>2</sub> initiator. The en-

hancing effects of swelling solvents, temperature, reaction time, monomer concentration, and initiator concentration were evaluated.

## EXPERIMENTAL

### Materials

PET films (Hoksp) of thickness 50  $\mu\text{m}$  were cut to strips of  $2 \times 3 \text{ cm}^2$  and then subjected to Soxhlet extraction with methanol for 1 day before use. AAm monomer was purified by recrystallization from aqueous solution. Bz<sub>2</sub>O<sub>2</sub> was twice precipitated from chloroform solution in methanol and dried in a vacuum oven for 2 days. Benzene was crystallized by cooling in the refrigerator. All reagents were Merck products.

**Table II Variation of Graft Yield with the Type of Solvent: temp 92°C; Polymerization Time 3 h; [AAm] 5%; [Bz<sub>2</sub>O<sub>2</sub>] = 0.159/50 mL**

Solvents	Temp (°C)	Graft Yield (%)
20% DCE + 80% H <sub>2</sub> O	92	—
Toluene	92	1.0
Benzene	80	4.40
DMSO	92	16.22

**Table III Effect of Monomer and Initiator****Inclusion: [AAM] 5%; [Bz<sub>2</sub>O<sub>2</sub>] 1.8%;****Polymerization Time 3h; Temp 92°C**

Reagent	Time (day)	Graft Yield (%)
Bz <sub>2</sub> O <sub>2</sub>	5	43.75
	6	45.10
AAM	5	55.44
	6	57.02

### Swelling Procedure

A temperature-controlled oil bath was employed for heating. Films were dipped into the selected organic solvents for predetermined times at the desired temperatures. After treatment, only solvent on the film was removed by blotting between filter paper and percentage increase in weight was determined.

### Polymerization Procedure

Solvent-treated specimens were placed in a 100 mL polymerization tube containing the monomer at known concentration and the tube is placed in an oil bath adjusted to the polymerization temperature; Bz<sub>2</sub>O<sub>2</sub> solution in the desired concentration was added and the reaction was carried out under N<sub>2</sub> atmosphere.

The films were taken from the polymerization tube after a specified polymerization period and residual solvent, monomer, unstably bonded oligomers, and polyacrylamide were removed from the film substrates by washing the films in boiling water

for 1.5 h. Washing water was changed at least four times. Washing was continued to constant weight. The films were then dried and weighed. The graft yield (%) value was based on weight.

### FTIR Spectrum

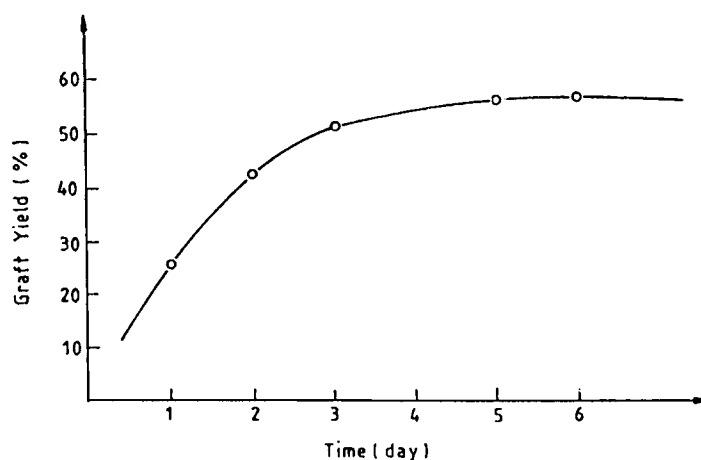
The FTIR spectrum was recorded by using Perkin-Elmer Model 1700 spectrophotometer.

## RESULTS AND DISCUSSION

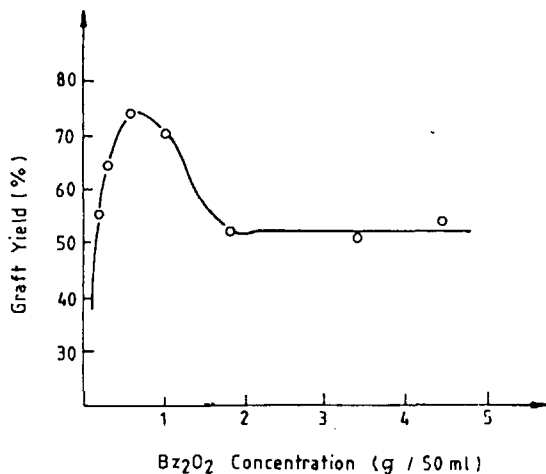
### Solvent Inclusion

Py, DCE/H<sub>2</sub>O (20/80, v/v), and DMSO were used as swelling agents. The uptake of solvents (Table I) was calculated from the specimen weight changes after the solvent treatment. As seen from the table, solvent inclusion in the films increased with increased length of solvent treatment time and temperature. Solvent inclusion was found to increase in the order of Py, DCE, DCE/H<sub>2</sub>O (20/80), DMSO at 82°C, and DMSO is selected as the most suitable swelling agent.

Solvent inclusion in the films were considerably higher at 140°C than at 82°C for DMSO. High temperature had a greater effect on the incorporation of solvent in films. However, the effect of solvent treatment time was not as great as the temperature. In the rest of the study, films were pretreated with DMSO for 1 h at 140°C, before the polymerization procedure.



**Figure 1** Variation of the graft yield with monomer inclusion time: [AAM], [15%]; [Bz<sub>2</sub>O<sub>2</sub>], 1.8%; time, 3 h; temp, 92°C.



**Figure 2** Variation of graft yield with initiator concentration. [AAM], 15%; time, 3 h; temp, 92°C.

### Effect of Solvent

The variation of graft yield with the type of solvent used in the polymerization was investigated by carrying out the polymerization at four different solvents (Table II). The graft yield increased in the order of toluene ( $\delta$ : 8.9), benzene ( $\delta$ : 9.5), DMSO ( $\delta$ : 12.93). In the rest of the study, DMSO was used as the solvent.

### Effect of Monomer and Initiator Inclusion

Pretreated (DMSO) PET films were dipped into AAm (5% wt) and Bz<sub>2</sub>O<sub>2</sub> (1.8%) (w/v) solutions

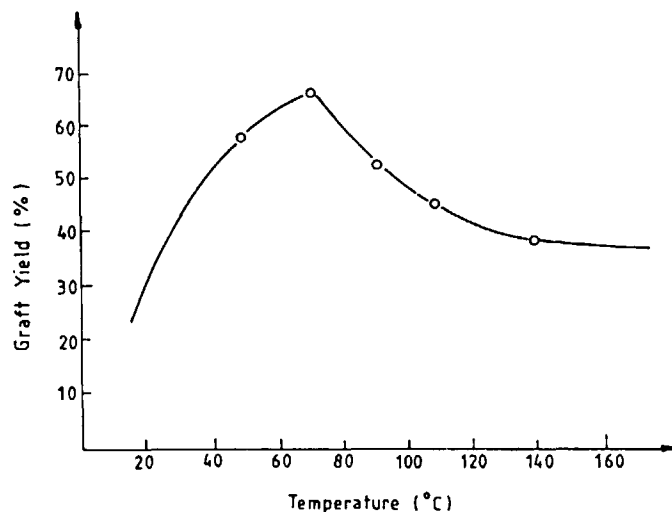
for 5 and 6 days before the polymerization was carried out. As seen from Table III, diffusion and incorporation of the monomer is higher than the initiator, leading to a higher graft yield. This may be attributed to the molecular size of the monomer compared to the initiator. Figure 1 shows that 5 days of treatment with AA is sufficient to reach maximum graft yield.

### Effect of Initiator Concentration

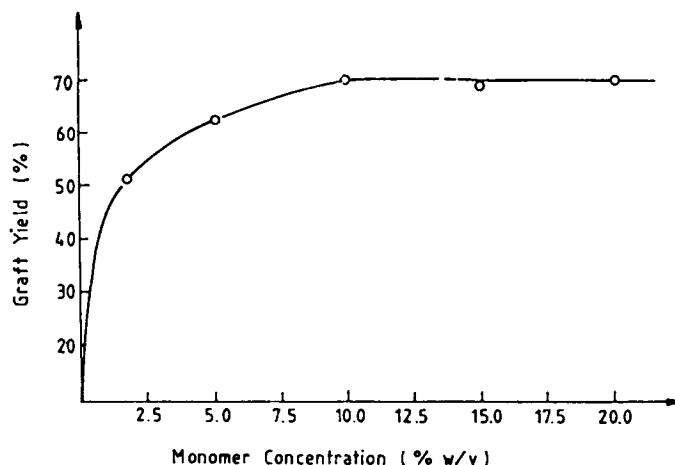
Figure 2 represents the effect of Bz<sub>2</sub>O<sub>2</sub> concentration on percent grafting. Evidently, the percent grafting increased significantly as the Bz<sub>2</sub>O<sub>2</sub> concentration increased from 0.1650 to 0.500 g/50 mL. A further increase in Bz<sub>2</sub>O<sub>2</sub> concentration decreased the percent grafting.

The enhancement of grafting by increasing the Bz<sub>2</sub>O<sub>2</sub> concentration to a certain limit implies that the primary free radical species (C<sub>6</sub>H<sub>5</sub>COO<sup>•</sup>) and/or the secondary free radical species (C<sub>6</sub>H<sub>5</sub><sup>•</sup>) formed by the dissociation of Bz<sub>2</sub>O<sub>2</sub> in the polymerization system participate essentially in the initiation of grafting. Above this limit, the abundance of these radicals leads to participation of them in the termination of the growing polymer (grafted chains and PET macroradicals) as well as to the combination of phenoxo and phenyl radicals, thereby giving rise to decreased grafting.

Similar results were obtained in the H<sub>2</sub>O<sub>2</sub>-induced graft polymerization of AA/styrene mixtures<sup>13</sup> and Bz<sub>2</sub>O<sub>2</sub>-induced polymerization of AA<sup>12</sup> on PET fibers.



**Figure 3** Variation of graft yield with temperature: [AAM], 15%; [Bz<sub>2</sub>O<sub>2</sub>], 1.8%; time, 3 h.



**Figure 4** Variation of graft yield with monomer concentration:  $[\text{Bz}_2\text{O}_2]$ , 3.1%; time, 3 h; temp, 70°C.

### Effect of Temperature

The graft copolymerization of acrylamide onto PET films were studied by varying temperature 50–140°C. The data indicate that the graft yield increases as the temperature increases from 50 to 70°C; a further increase in temperature decreases the percent grafting (Fig. 3). With the increase in temperature, the swellability of the film and the rate of diffusion of monomer and initiator into the film matrix was increased; thus, the rate of grafting enhanced. The maximum graft yield was obtained at 70°C, which is near the glass transition temperature of PET ( $T_g = 65^\circ\text{C}$ ). The polymer chains whose activities are increased around the glass transition temperature tend to give radical reactions much more easily.<sup>2</sup> Since more and more radicals combine as the temperature is increased, they cannot take place in the initiation of graft polymerization. Furthermore, the chain termination begins to predominate due to the increase in temperature, and a lower graft yield is obtained. The similar results were obtained in the  $\text{Bz}_2\text{O}_2$ -initiated graft copolymerization of AAm on PET fibers.<sup>12</sup>

### Effect of Acrylamide Concentration

The variation of graft yield with the concentration of AAm was investigated by carrying out the polymerization at five different AAm concentrations for 3 h at 70°C (Fig. 4).

The grafting reaction takes place rapidly at first, then slows down and levels off. The fact that grafting yield remains at a certain yield can be explained by

the enhancement of homopolymer formation at high monomer concentrations. This increases the viscosity of the reaction medium retards the monomer diffusion into the film.

### Effect of Polymerization Time

The effect of polymerization time upon the graft yield is presented in Table IV. The saturation grafting value was reached for 3.5 h of polymerization time for concentrations of 15% AA and 1.8%  $\text{Bz}_2\text{O}_2$  at 92°C.

### FTIR Spectrum

Figure 5 shows the FTIR spectrum of the sample grafted with 15% AAm. The absorption at 3200–3330, 1660–1670, and 1625  $\text{cm}^{-1}$  are typical to those N—H stretching, —C=O (amide), and —C=N— resonance peaks coming from the amide group, respectively.

**Table IV** Effect of Polymerization Time upon Graft Yield (%)

Time (h)	Graft Yield (%)
0.5	45.86
1.0	42.36
2.0	42.38
3.5	53.33
4.0	53.50
6.0	53.71

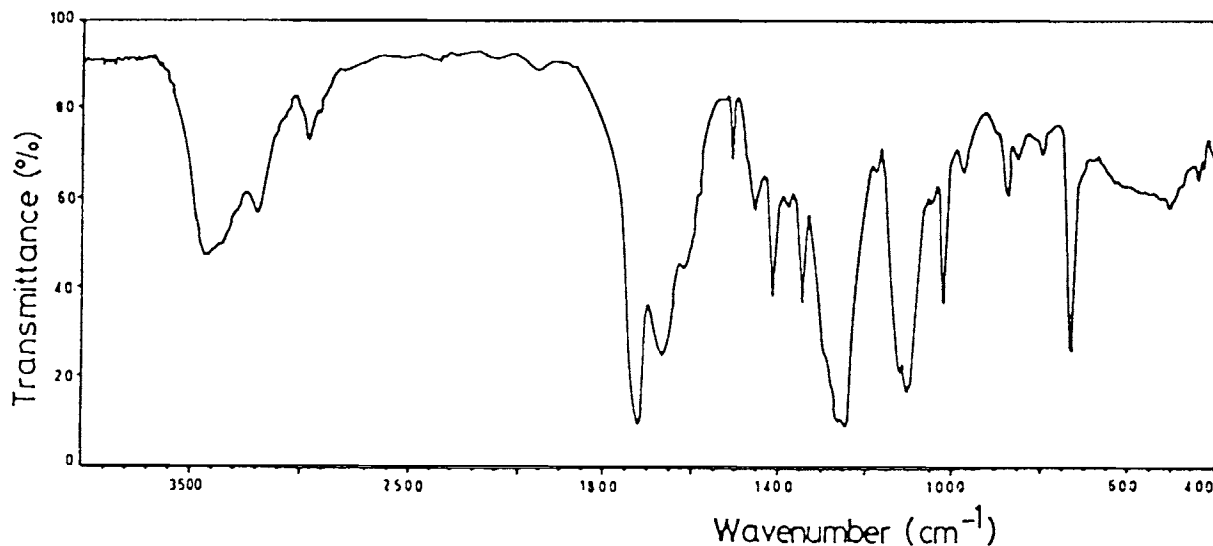


Figure 5 FTIR spectrum of AAm-grafted film.

## REFERENCES

- I. Sakurada, Y. Irada, and T. Kawahara, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 2329 (1973).
- E. Schamberg and J. Haigne, *J. Polym. Sci. Part A*, **8**, 693 (1970).
- I. Vlaqiu and V. Stannett, *J. Macromol. Sci. Chem.*, **A7**, 1677 (1973).
- T. Memetea and V. Stannett, *Polymer*, **20**, 465 (1979).
- P. D. Kale, H. T. Lokhande, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **19**, 461 (1975).
- J. C. Bonnefis and J. R. Puig, *J. Appl. Polym. Sci.*, **15**, 553 (1971).
- K. Adwait, C. N. Pradhan, and L. N. Pad, *J. Appl. Polym. Sci.*, **27**, 1873 (1982).
- K. N. Rao, M. H. Rao, P. N. Moorthy, and A. Charlesby, *J. Polym. Sci. Polym. Lett. Ed.*, **10**, 893 (1972).
- M. Okoniewski and J. Soyka-Ledakowicz, *J. Appl. Polym. Sci.*, **35**, 1241 (1988).
- S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **90**, 69 (1980).
- A. Mey-Marom, L. A. Raybenbach, and M. Levy, *J. Appl. Polym. Sci.*, **28**, 24111 (1983).
- M. Saçak and E. Pulat, *J. Appl. Polym. Sci.*, **37**, 539 (1989).
- A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *J. Appl. Polym. Sci.*, **27**, 3683 (1982).
- F. G. Hardy, Fr. Pat. 1,574,395 (1969); Chem. Abstr., **72**, 67780 j (1970).
- I. B. Gnevusheva, B. V. Sautin, L. F. Chuikova, S. Kh., Khairtadinova, A. A. Avilov, and A. V. Vlasou, *Kozh. Obuvn. Prom-st.*, **29**(9), 36 (1980).
- J. Marchand, *Rev. Gen. Caout. Plast.*, **50**(11), 929 (1983).
- A. Stolarzewicz and L. Kurzeja, *Polimery*, **19**(8), 392 (1974).
- V. M. Kochkodan and M. T. Bryk, *Geol. Khim. Biol. Nauki*, **8**, 29 (1986).
- I. F. Osipenko and V. I. Martinovich, *Ser. Khim. Novak*, **1**, 75 (1981).
- I. F. Osipenko and V. I. Martinovich, *Vysokomol. Soedin. Ser. A*, **29**(11), 2316 (1987).
- A. Ribnick, H. D. Weigman, and L. Rebenfeld, *Text. Res. J.*, **42**, 720 (1972).
- B. H. Knox, H. D. Weigman, and M. G. Scott, *Text. Res. J.*, **45**, 203 (1975).
- T. Okada, Y. Shimano, and I. Sakurada, *J.A.E.R.I.*, 35 (1973).
- W. R. Moore and R. P. Sheldon, *Polymer*, **2**, 315, (1961).
- Y. Hsieh, C. Pugh, and M. S. Ellison, *J. Appl. Polym. Sci.*, **29**, 3547 (1984).
- E. Uchida, Y. Ugama, and V. Ihada, *J. Polym. Sci. A*, **27**, 527 (1989).

Received January 13, 1992

Accepted February 14, 1992