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GRAFTING OF ACRYLAMIDE ON 1,1,2,2-TETRACHLOROETHANE PRESWELLED POLY(ETHYLENE TEREPHTHALATE) FILMS USING AZOBISISOBUTYRONITRILE INITIATOR

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Key Words: Graft Copolymerization, Poly(ethylene Terephthalate) Film, Acrylamide, Swelling Assisted Polymerization

ABSTRACT

Graft polymerization of acrylamide (AAm) on 1,1,2,2 tetrachloroethane (TCE) preswelled poly(ethylene terephthalate) (PET) films were performed with chemical initiation method using asobisisobutyronitrile (AIBN) initiator. Temperature was found to have a greater effect on the swelling then the swelling time. Variation of the graft yield with polymerization temperature, time, AIBN concentration, AAm concentration, AIBN and AAm inclusion times were investigated. The optimum temperature for grafting was found to be 70°C. The graft yield was observed to increase with polymerization time, AAm concentration, initiator and monomer diffusion time up to a saturation graft yield and then leveled off. An increase in AIBN concentration first enhanced the percent grafting then showed a decrease. The addition of some salts (Ni^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}) on the rate of grafting was also investigated. From the temperature dependence of the initial rate of grafting, the overall activation energy was found to be 4.1 kcal/mol and relevant rate equation have been derived. The effect of grafting on film properties, such as water absorption capacity, intrinsic viscosity were determined. Grafted films were characterized by FTIR spectroscopy and scanning electron microscopy (SEM).

INTRODUCTION

PET is a commercial synthetic polymer widely used in industry as fiber, plastic and film because of its outstanding stability and bulk properties. However, it has drawbacks such as high hydrophobicity, poor adhesion, and high static electrification. The generation of electrostatic charges on polymers has been mostly a nuisance in many fields associated with polymer. In addition to discomfort from static cling or static discharge, it often causes serious damage in semiconductor manufacture and sometimes to human life through fire or explosion. Therefore, it would be of great value to devise a simple method for eliminating static generation during the manufacturing process or to develop a new polymer that prevents charge generation.

Many efforts have been made to minimize electrostatic charging, mostly by rendering polymeric surfaces with hydrophilic or electroconductive groups. One way to introduce hydrophilic group to the polymeric material without deteriorating the bulk properties is graft copolymerization.

Graft copolymerization of vinyl monomers onto PET is considered a very fascinating field for research with unlimited future possibilities for eliminating or at least reducing one or more of the handicaps of PET.

There are extensive studies, either patented or published, concerning the grafting of vinyl monomers on PET fibers and fabrics [1–20] in the literature. However, studies on the graft polymerization of vinyl monomers on PET films are limited [4, 21–31]. Graft copolymerization of vinyl monomers onto PET films is generally considered to involve the generation of reactive sites on the polymer. This has been achieved either by radiation or by chemical means. The radiation initiation method [21–27] has the disadvantage in the degradation of the parent polymer and in the cost of radiation equipment.

Studies concerning the chemical initiation method are very limited [28–31]. The chemical nature of PET does not allow formation of its macrochains on an appreciable quantity of radicals that can initiate the grafting and the high extent of crystallization and ordering of the amorphous regions retard monomer and initiator diffusion. One way of facilitating diffusion is to open up the physical structure of the polymer by swelling to allow the monomer and initiator to enter in sufficient quantities.

Osipenko *et al.* [4] reported that previous swelling of the PET film in dichloroethane changed its sorption diffusional properties and increased the degree of grafting. Hsieh and coworkers [23] used dimethylformamide (DMF), pyridine (py), and dimethylsulphoxide (DMSO) as swelling agents to facilitate monomer incorporation in the post polymerization of acrylic acid on PET film. Hsieh and colleagues [27] used DMF, γ–butyrolactone, py, tetrachloroethane as swelling agents in the graft copolymerization of acrylic acid (AA) to PET films by glow discharge. Xue and Wilkie [28] studied the graft polymerization of methacrylic acid onto PET by pretreating the PET films with TCE. Sanli *et al.* used [10] DMF, morpholine, acetic acid, n-butanol, 1,2 dichloroethane (DCE) as swelling agent in graft polymerization of AAm on PET fibers using cerium ammonium nitrate initiator and DMSO was found to be the most suitable swelling agent among the solvents studied. Ünal *et al.* pretreated the PET films with DMSO before the graft copolymerization of n-vinyl-2-pyrrolidone [30] and 4-vinyl pyridine [31] onto PET films.

There are only a few studies concerning the grafting of AAm which was chosen as the monomer in this study, onto PET fibers [8–10] and films [29, 32–34] in the literature. Uchida and colleagues [32] studied graft copolymerizaton of AAm onto the surface of PET film with simultaneous UV radiation method without photosensitizer and without degassing. Sanli and Pulat [29] reported grafting of AAm onto PET films using benzoyl peroxide, (Bz_2O_2), initiator after swelling the film in DMSO, py, DCE, DCE/H_2O (20/80 v/v). As part of a broader study on the grafting of AAm onto PET films, the present paper deals with a view of studying the different parameters which affect grafting of TCE preswelled PET films with AAm using azobisisobutyronitrile initiator to discover the optimal graft copolymerization conditions.

EXPERIMENTAL

Materials

PET films (Hoksp) with a thickness of 50-125 μm were used for grafting. They were purified by soxhlet extraction with methanol for 24 hours before use. AAm (BDH) was used as supplied. AIBN (Merck) was recrystallized twice from methanol and dried in vacuum oven for 48 hours. Other reagents were Merck products and used as supplied.

Swelling Procedure

PET films were cut to dimensions about 20 X 30 mm and had a weight of approximately 0.05 g. Before the grafting reaction was carried out, they were preswelled in TCE, in 100 mL Pyrex tubes placed in a temperature controlled oil bath. After treatment, solvent on the film was removed by blotting between a filter paper and percentage increase in weight was determined.

Polymerization Procedure

Pretreated PET film of a known mass was dipped into a 100 mL polymerization tube containing 8 mL of an aqueous solution of AAm at a known concentration and nitrogen gas was allowed to pass through the solution for 45 minutes. The required amount of AIBN (dissolved in 2 mL acetone) was added and polymerization was carried out for a predetermined period of time under nitrogen atmosphere in a thermostated water bath. At the end of polymerization time, the film was removed from the polymerization tube and the residual solvent, monomer and homopoly(AAm) were removed by washing with hot water for 5 hours till the vacuum dried films reached a constant weight. In this period, washing water was replaced at least five times. The grafted film was then vacuum dried at 50°C for 72 hours and weighed. The graft yield (%) was calculated from the weight increase of film:

$$\text{Grafting Yield (\%)} = [(w_g - w_i)/w_i] \times 100 \qquad (1)$$

where w_i and w_g denotes the weights of the original and grafted PET films respectively.

Homopoly(AAm) formed in the grafting medium was precipitated by the addition of excess non-solvent. The grafting efficiency and rate of grafting were calculated as follows:

$$\text{Grafting efficiency} = \frac{(w_g - w_i)}{(w_g - w_i) + w_h} \times 100 \qquad (2)$$

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

where w_h, M_w, t, V are the weight of homopolymer, molecular weight of monomer, polymerization time (s) and volume of reaction medium (mL), respectively.

Determination of Water Absorption Capacity

Grafted PET films were immersed in thermostated distilled water at 20°C± 0.1°C for 48 hours, then removed and blotted between filter papers and weighed.

They were then vacuum dried at 50°C for 96 hours and weighed again. Water absorption capacity of films was determined from the weight increase of the films.

Determination of Intrinsic Viscosity

Viscosity measurements of the original and AAm grafted PET films were carried out in phenol/TCE (1:1) solvent system using a Ubbelohde capillary flow viscometer mounted in a water bath thermostated at 25 °C ± 0.1°C.

Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of PET films were recorded using a Mattson model 1000 FTIR spectrometer. Samples were analyzed as films cast from phenol/TCE (1:1) onto sodium chloride plates.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) studies of the original and AAm grafted PET films coated with gold were performed using a JEOL model JEM-100 CX II microscope.

RESULTS AND DISCUSSION

Effect of Solvent Inclusion

Preferential interaction of solvents whose solubility parameters (δ) are close to those of PET, are thought to provide the necessary chemical energy to disrupt intermolecular cohesive forces between the polymer chains and permit chain mobility. A study of longitudinal shrinkage and volume swelling of PET in various solvents suggested that PET may be considered as an $(AB)_x$ alternating copolymer with δ value of 9.8 and 12.1 [35]. TCE is a solvent with a solubility parameter of 9.85 which is close to the solubility parameter of one of the segments of PET. For this reason, it was selected to open up the physical structure of PET.

PET films were swelled in TCE for 15 minutes at temperatures ranging from 50–130°C. Results were presented in Figure 1. As seen from the figure, uptake of solvent increases as the temperature increases. Higher temperatures do have a greater effect on the incorporation of the solvent in films.

At low temperatures, only small crystallites formed, and upon removal of the solvent, the swollen structure was not supported by the small crystallites and collapsed. At high temperatures, larger and more stable crystallites were formed and were capable of supporting the swollen structure upon removal of the solvent. The structural modification was attributed to the solvent induced crystallization,

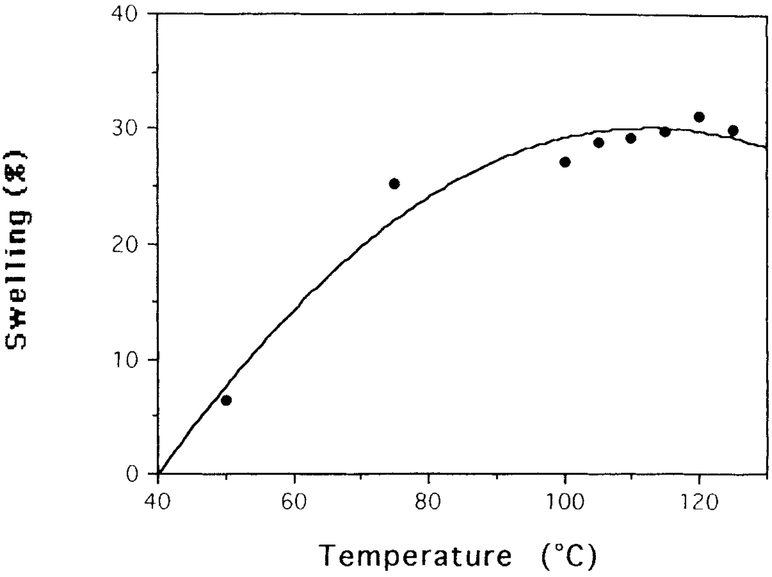

Figure 1. The effect of temperature on swelling. t = 15 minutes, λ = 50 μm.

while PET structure was swollen [36]. However, TCE was found to induce longitudinal shrinkage of PET at temperatures higher than 120°C, so this was selected as the swelling temperature in the rest of the study.

The effect of solvent inclusion time upon the graft yield and percentage swelling is illustrated in Table 1. It is clear that the effect of swelling time on percentage swelling was not as large as that of temperature. Similar results were obtained in the graft copolymerization of AAm onto DMSO pretreated PET films [29] and DMSO, morpholine, acetic acid, n-butanol, and 1,2 dichloromethane pretreated PET fibers [10].

Effect of Polymerization Temperature and Time

Graft polymerization of AAm onto PET film was studied by varying the temperature from 60–80°C for a period of time ranging from 10–90 minutes (Figure 2). The results show that graft yield progressively increases with temperature up to 70°C, then decreases. Generally a rise in temperature (1) improves the swelling capacity of the films, (2) leads an increase in the mobility of the monomer and initiator molecules, (3) increases the diffusion rate of monomer and initiator from the solution phase to the PET backbone, (4) accelerates the decomposition rate of initiator molecules, hence increases the number of free radicals in the reaction

TABLE 1. Change of Grafting Yield with Swelling Time and Swelling Percent [AAm] = 1.5 M, [AIBN] = 6.0 X 10^{-3} M, time = 1 hour, T = 70°C, $\lambda = 50\ \mu m$

Swelling Time (min.)	Swelling (%)	Grafting Yield (%)
5	25.3	1.80
10	31.1	3.10
15	31.6	3.70
20	31.8	4.40
30	31.1	3.00

medium. PET chains around glass transition temperature, T_g, (65°C) also become more reactive and give easy radicalic reactions [37]. The decrease of the graft yield after 70°C may be attributed to the favored chain termination reactions, increase in the formation of homopolymer, which plays a more important role than does the graft polymerization at elevated temperatures, and decrease in the half life of AIBN molecules [40]. Similar results were observed in the Bz_2O_2 initiated graft polymerization of AAm [29] and 4-vinyl pyridine onto PET films [31], and AAm grafting onto PET fibers [10]; whereas, graft yield increased steadily with the rise in temperature in the polymerization of acrylic acid-styrene mixture and methyl methacrylate onto PET fibers using tetravalent cerium and H_2O_2 initiators [38, 39].

On the other hand, as it is reflected from Figure 2, the grafting is characterized by an initial fast rate, followed by a slower one and then leveled off (after 60 minutes). This may be attributed to the formation of a diffusion barrier, an increase in the medium viscosity due to the homopoly(AAm) formed in the polymerization medium. Similar results were observed in the graft polymerization of AAm on PET fibers [10], and methacrylic acid on PET films [28].

Effect of Initiator and Monomer Concentration

The effect of AIBN concentration on percent grafting was studied at different initiator concentrations and the results obtained were shown in Figure 3. It is seen that increasing AIBN concentration up to 6.0 X 10^{-3} M is accompanied by a significant enhancement in the percent grafting. Further increase in AIBN concentration decreases the grafting.

It is known that AIBN molecules dissociate with the influence of temperature to give isobutyronitrile radicals. These free radicals increase the

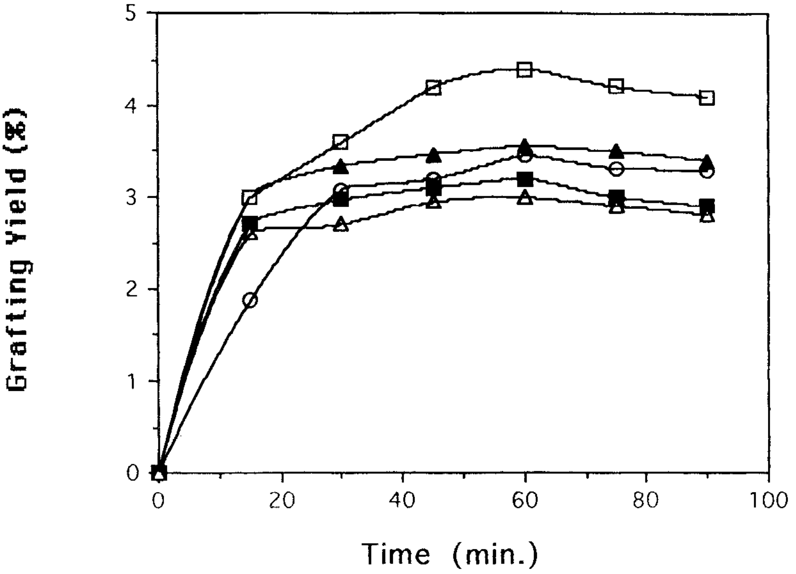

Figure 2. The effects of temperature and time on percentage grafting [AAm] = 1.5 M, [AIBN]= 6.0 X 10^{-3} M, λ = 50 μm
(O) 60°C, (▲) 65°C, (□) 70°C, (■) 75°C, (△) 80°C.

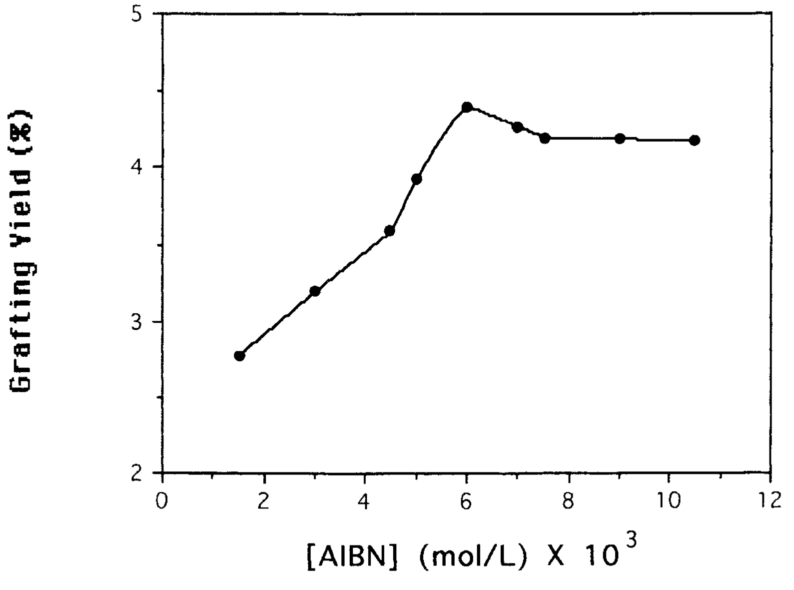

Figure 3. The effect of initiator concentration on grafting yield. [AAm]= 1.5 M, T = 70°C, t = 1 hour, λ = 50 μm.

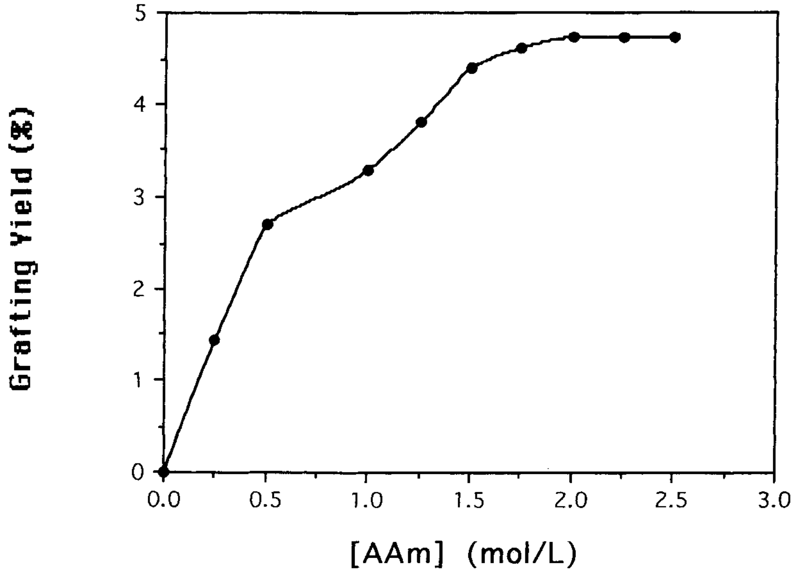

Figure 4. The effect of monomer concentration on grafting yield [AIBN]= 6.0 X 10^{-3} M, T = 70°C, t = 1 hour, λ = 50 µm.

number of active homopoly(AAm) chains which give chain transfer reactions with PET macroradicals to form PET macroradicals capable of initiating grafting. On the other hand, initiator free radicals also abstract hydrogen atoms from PET macroradicals to form suitable radicalic active sites for grafting. These effects cause an increase on the grafting yield as the AIBN concentration increases. At high AIBN concentrations abundance of initiator radicals is expected. As a result, participation of the initiator radicals in the termination process with growing polymer chains, and PET macroradicals as well as self–reaction (combination) would be favored over the graft initiation, thereby decreases the grafting. Similar trends were reported in the grafting of vinyl monomers on PET fibers [1,8–10, 20], and films [28–31] in the literature.

The effect of monomer concentration on the grafting yield was shown in Figure 4. As is evident, the percent grafting increases with increasing the AAm concentration up to 1.5 M. Thereafter, no significant improvement in the percent grafting is observed. This may be attributed to the spontaneous increase of homopoly(AAm) in the reaction medium, as the monomer concentration was increased, which acts as a barrier on the film surface. Besides, the diffusion of the

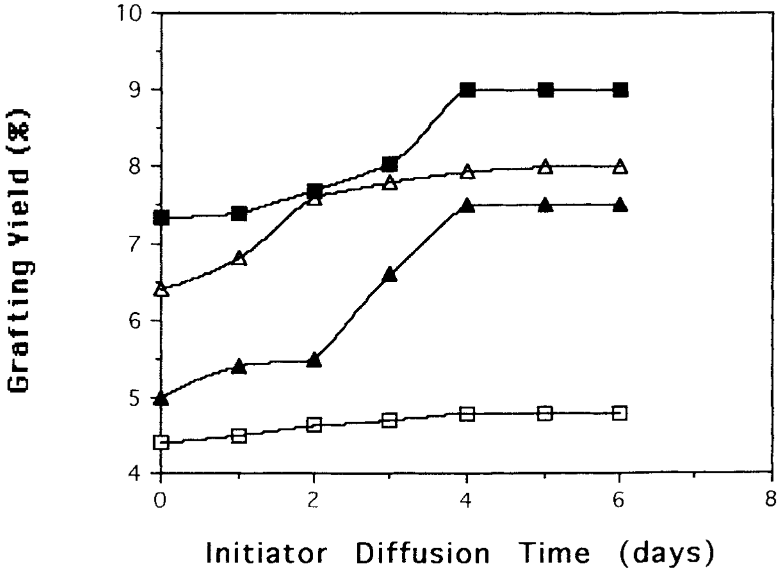

Figure 5. The change of grafting yield with initiator diffusion. [AAm]= 1.5 M, [AIBN]= 6.0 X 10^{-3} M, T = 70°C, t = 1 hour λ = (□) 50 μm, (▲) 75 μm, (△) 100 μm, (■) 125 μm.

monomer becomes difficult due to the increase in the medium viscosity. Similar results were reported in the literature [8, 20, 29–31].

Effect of Initiator and Monomer Diffusion on Grafting Yield

TCE preswelled PET films of various thicknesses (λ = 50–125 μm) were dipped into a 6.0 X 10^{-3} M AIBN and 1.5 M AAm solutions for 1–6 days at 20°C (Figures 5, 6) before the polymerization procedure took place. As seen from Figure 5, the grafting yield was increased with increasing initiator inclusion time up to 4 days, irrespective of the film thickness, then leveled off. A similar trend was observed in our previous studies [30, 31]. This may be attributed to the saturation of PET back-bone due to the initiator diffusion and decrease in the number of radicals formed from AIBN molecules, which has a half life of approximately 6400 hours at 20°C [40].

The effect of inclusion of AAm on the grafting yield is shown in Figure 6. As reflected from the figure a saturation grafting value was reached in 5 days. Results are in consistent with the previous studies on the graft copolymerization of vinyl monomers onto PET films [30, 31].

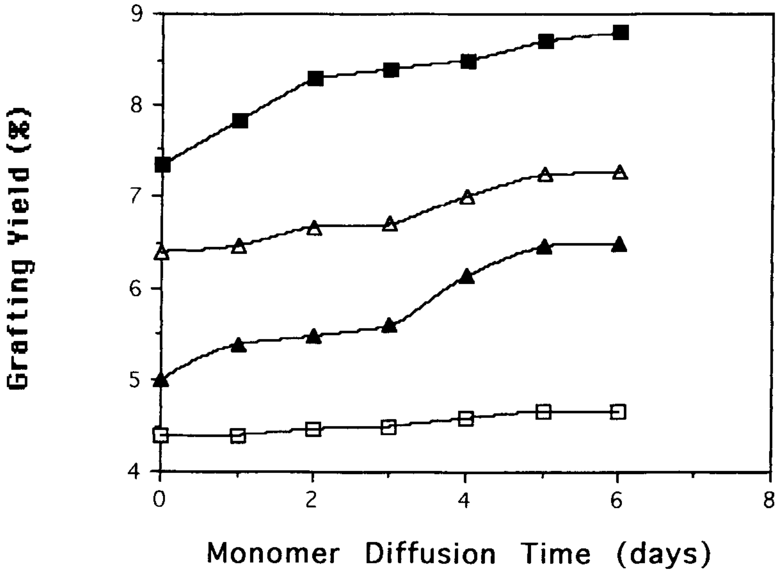

Figure 6. The change of grafting yield with monomer diffusion.
[AAm]= 1.5 M, [AIBN]= 6.0 X 10^{-3} M, T = 70°C, t = 1 hour
λ = (□) 50 μm, (▲) 75 μm, (△) 100 μm, (■) 125 μm

Kinetics of Grafting

Interest in studies of kinetics of grafting has been low, perhaps because of the complexities of such systems. However, some researchers have been investigated the kinetics of grafting of various vinyl monomers onto PET fibers and films, using different initiators [10–12, 30, 41–43], assuming a normal kinetic scheme. Examination of their results from the given references show that, the dependence of rate of grafting on monomer and initiator concentrations varies with the types of initiator and monomer grafted onto the PET back bone.

The initial rate of grafting for the system undertaken was determined changing the [AAm] between 0.25–1.75 M, by keeping the other variables constant and the results were presented in Figure 7. The slope of the logR_g vs. log[AAm] graph reflects that the rate of grafting is proportional to 0.56 power of [AAm].

The rate of grafting were followed for different [AIBN] ranging from 1.5 X10^{-3}–6.0 X 10^{-3} M by keeping the other experimental conditions constant ,and the plot of log R_g vs. log[AIBN] (Figure 8) were found to be straight line with a slope of 0.34. This indicates a 0.34 dependence of [AIBN] on R_g. Therefore, the rate of

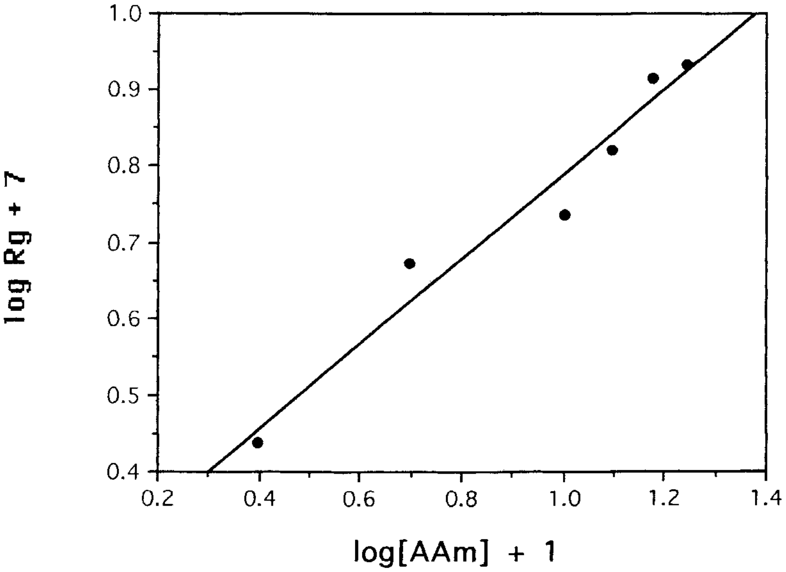

Figure 7. The change of rate of grafting with monomer concentration. [AIBN]= 6.0 X 10^{-3} M, T = 70°C, t = 1 hour, λ = 50 μm.

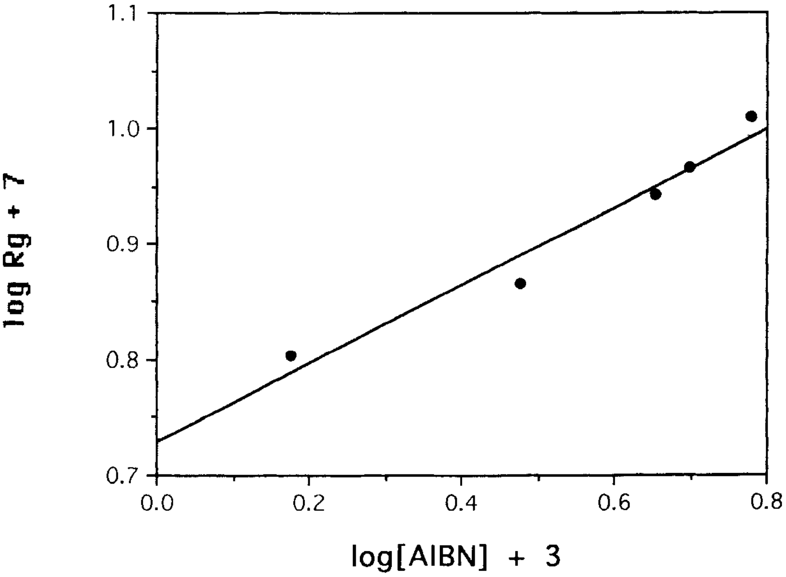

Figure 8. The change of rate of grafting with initiator concentration. [AAm]= 1.5 M, T = 70°C, t = 1 hour, λ = 50 μm.

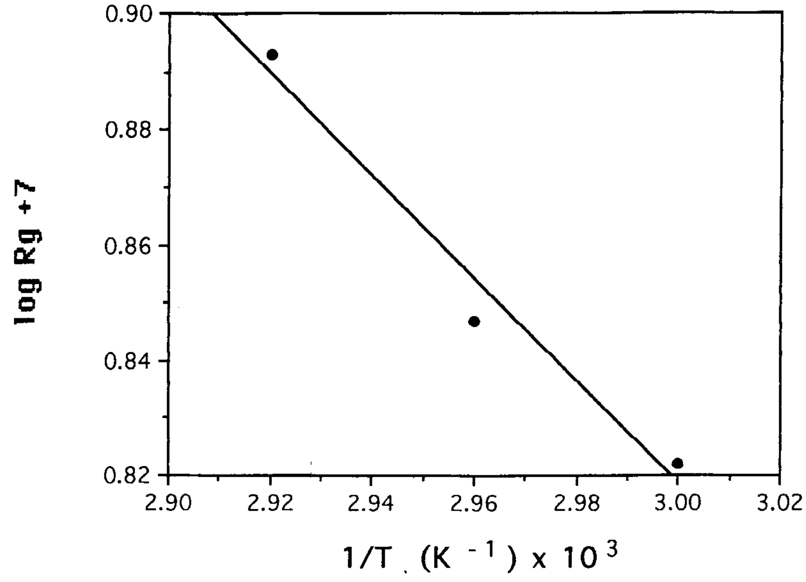

Figure 9. The change of rate of grafting with temperature.
[AAm]= 1.5 M, [AIBN]= 6.0 X 10^{-3} M, T = 70°C, t = 1 hour, λ= 50 µm.

polymerization is given by

$$R_g = k[AAm]^{0.56}[AIBN]^{0.34} \tag{4}$$

The overall activation energy for grafting of AAm onto PET film using AIBN initiator was computed to be 4.1 kcal/mol from the Arrhenius plot of logR_g vs. 1/T (Figure 9).

There are no kinetic data related to the grafting of AAm onto PET films in the literature. However, we have previously studied the grafting system of AAm onto PET fiber using a tetravalent cerium initiator, and reported the dependence of rate of grafting on monomer and initiator concentrations as 0.87 and 1.73 powers, respectively; and the activation energy as 7.25 kcal/mol [10].

Effect of Metallic Ions

It has been reported that incorporation of certain concentration of metallic ions, such as Cu^{2+}, Fe^{2+} ions, in free radical polymerization media for grafting of vinyl monomers onto PET improves grafting significantly [4, 20]. With this in mind, we have investigated the influence of Ni^{2+}, Cr^{3+}, Co^{2+}, and Cu^{2+} ions on the

TABLE 2. Effect of Metal Salt Concentration on the Grafting Yield
[AAm] = 1.5 M, [AIBN] = 6.0 x 10^{-3} M, T = 70°C, t = 1 hour, λ = 50 µm

Type of Salt	Concentration (mmol/L)	Graft Yield (%)
$CuSO_4 . 5 H_2O$	0.00	4.40
	5.00	4.60
	10.00	4.96
	15.00	5.52
	20.00	6.10
$CrCl_3 .6 H_2O$	0.00	4.4
	5.00	4.58
	10.00	4.77
	15.00	5.09
	20.00	6.59
$CoCl_2 .6 H_2O$	0.00	4.40
	5.00	4.60
	10.00	4.78
	15.00	5.20
	20.00	5.74
$NiCl_2 . 6 H_2O$	0.00	4.40
	5.00	4.53
	10.00	4.75
	15.00	4.86
	20.00	5.47

grafting of PET film with AAm and tabulated the results in Tables 2 and 3. As seen from the tables, the addition of metal salts suppresses the homopolymerization, while increasing the grafting efficiency and the grafting yield. An increase in the salt concentration from 5 mmol/L to 20 mmol/L enhances the grafting. Cu^{2+} ions have shown the best performance among the ions tried.

Intrinsic Viscosity

Viscosity measurements of the grafted PET films (λ = 50 µm) were carried out in phenol/TCE (1:1) system at 25°C± 0.01°C in a thermostated water bath. Intrinsic viscosity data obtained from the AAm grafted PET films are tabulated in Table 4.

TABLE 3. Effect of Metal Ions on Polymer Yield
[AAm] = 1.5 M, [AIBN] = 6.0 x 10^{-3} M, [Ion] = 20 mmol/L, T = 70°C, t = 1 hour, λ = 50 μm

Type of Salt	Graft Yield (%)	Homopolymer (%)	Grafting Efficiency (%)
—	4.40	83.90	0.25
$NiCl_2.6H_2O$	5.47	80.00	0.32
$CrCl_3.6H_2O$	5.59	79.60	0.33
$CoCl_2.6H_2O$	5.74	77.50	0.37
$CuSO_4.5H_2O$	6.10	*	–

*cannot be precipitated

TABLE 4. Intrinsic Viscosities of AAm Grafted PET Films
λ= 50 μm

Grafting Yield (%)	[η] (dL/g)
0.00	0.150
1.60	0.330
2.80	0.428
3.20	0.436
4.40	0.441
4.70	0.482

As seen from the table, intrinsic viscosities of the grafted PET films were increased with increasing grafting yield. This can be thought of as evidence of grafting of AAm onto PET films. Similar results were observed in the literature [8, 10, 29–31].

Water Absorption Capacity

Water absorption capacity of AAm grafted PET films (λ = 50 μm) were determined from the weight increase and results obtained are shown in Figure 10. The water absorption capacity was found to increase as the graft yield increased (Figure 10). Water absorption capacity is mostly related to the hydrophilic nature of

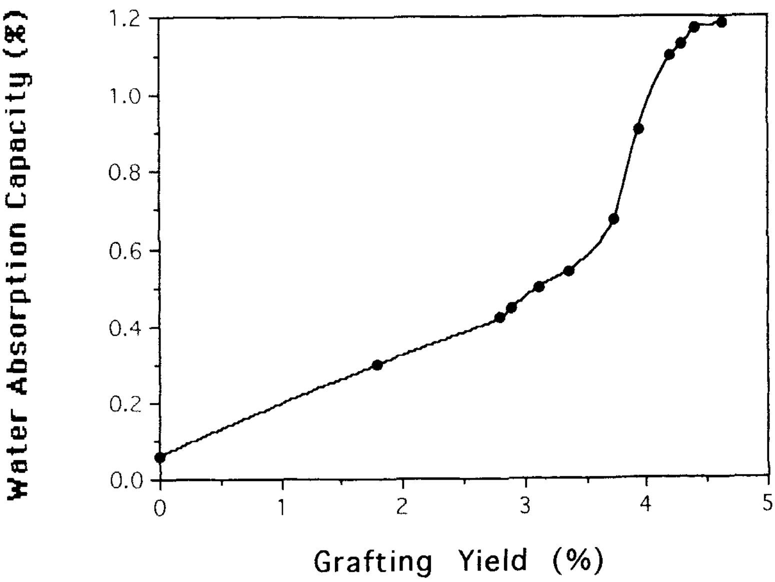

Figure 10. The change of water absorption capacity with grafting yield. λ= 50 μm.

the film gained by the grafting of AAm on the polymer matrix. Furthermore, the opening up of the PET back-bone by the grafting process also causes an increase in the water uptake of the films.

FTIR Spectrum

FTIR spectra of both ungrafted and AAm grafted PET films were presented in Figure 11. Ungrafted PET (Figure 11a) shows absorptions at 1724 cm^{-1}, 1400–1616 cm^{-1}, 2967–2909 cm^{-1} and 3060 cm^{-1}, which are typical to those of C=O, C=C, aliphatic C–H and aromatic C–H stretchings, respectively. However, in the FTIR spectrum of AAm grafted PET film (Figure 11b), in addition to the above absorptions, more strong and broad absorptions observed at 1710 cm^{-1} were due to ester, amide carbonyls, and a doublet seen at 3400 cm^{-1} was typical to those $-NH_2$ stretchings, and peaks at 1660–1670 cm^{-1} arose from C=N resonance stretchings.

Microstructure of Grafted PET Films

Scanning electron micrographs of ungrafted and AAm grafted PET films were presented in Figure 12. It was observed from the SEM results that the ungrafted PET film surface (Figure 12a) has a smoother and more homogeneous

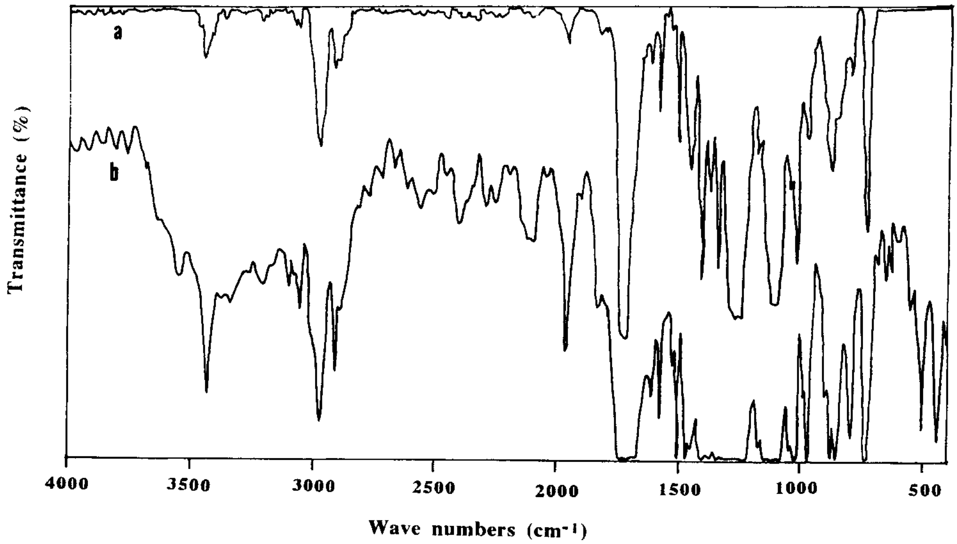

Figure 11. FTIR spectra of PET films.
(a) ungrafted, and (b) AAm grafted, $\lambda = 50$ μm.

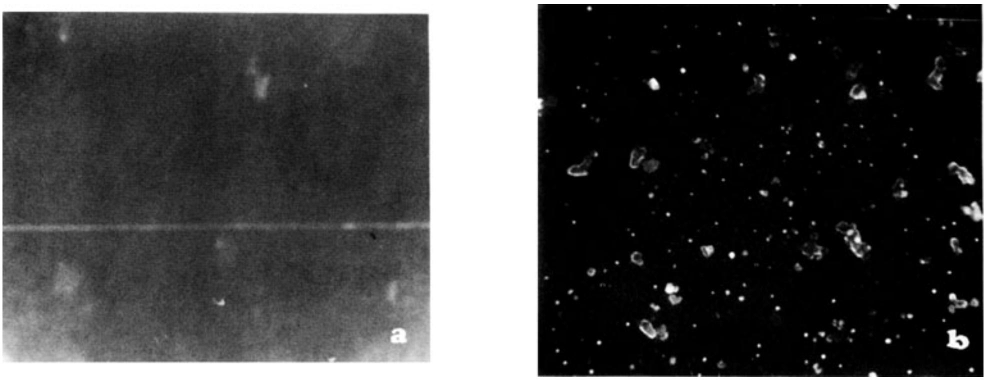

Figure 12. SEM micrographs obtained from (a) ungrafted and (b) AAm grafted PET films (1000X), $\lambda = 50$ μm.

appearance. After the grafting procedure, AAm was attached to the PET backbone as side chains, and seems to form microphases in the graft copolymer (Figure 12b). This heterogeneous appearance of the film surface shows additional evidence of grafting.

CONCLUSIONS

The present work relates to the graft polymerization of AAm onto TCE pretreated PET films using AIBN initiator. The following conclusions were drawn from the experimental results.

Swelling of the PET films in TCE at 120°C for a period of 20 minutes was found as the best condition for swelling procedure.

The optimum condition for maximum grafting were found to be 70°C polymerization temperature, 1 hour of polymerization time, 1.5 M of monomer and 6.0 X 10^{-3} M of initiator concentrations.

The inclusion of initiator or monomer before the graft polymerization enhanced the grafting.

The addition of Ni^{2+}, Cr^{3+}, Co^{2+}, and Cu^{2+} salts to the polymerization medium increased the grafting yield. Cu^{2+} was found to be more effective than the other ions tried.

The intrinsic viscosity and water absorption capacity of the films increased as the graft yield increased.

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