Benzoyl-Peroxide-Initiated Graft Copolymerization of Poly(ethylene terephthalate) Fibers with Acrylic Acid

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SYNOPSIS

The grafting of acrylic acid onto poly(ethylene terephthalate) fibers subjected to a no-swelling treatment using benzoyl peroxide was investigated. The temperature was found to increase the graft yield. The grafting yield increased up to a benzoyl peroxide concentration of 4.0×10^{-3} M and slightly decreased at higher initiator concentrations. The effects of solvents such as dimethylformamide, dimethylsulfoxide, pyridine, and some alcohols upon the grafting were examined by carrying out the graft copolymerization at various water/solvent ratios. Pyridine was found to inhibit the grafting totally. The properties of the grafted fibers such as density, diameter, dyeability, and moisture regain were also investigated. It was concluded due to the observations made in these properties that the grafting took place mainly in the subsurface regions of the fibers and there occurred a diffusion barrier after the grafting value of 8–9%. The overall activation energy for grafting was calculated to be 9.9 kcal/mol. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There are extensive studies, either patented or published, concerning the grafting of various vinyl monomers onto poly(ethylene terephthalate) (PET) fibers. The general purpose of grafting studies is the investigation of the graft copolymerization conditions and/or the properties of grafted fibers. There are various monomers grafted onto PET fibers such as styrene,[1-3] methacrylic acid,[4,5] methyl methacrylate,[6,7] p-bromostyrene,[8] acrylonitrile,[9] and acrylamide.[10-12] As it very well known that PET fibers show undesirable features such as poor dyeability, low moisture regain, and poor antistatic properties, the purpose of grafting is to improve these poor properties of the fibers and/or furnish them with new properties.

Acrylic acid has also been used as a monomer in the grafting studies onto PET fibers by various workers. The PET fibers in these studies have been either subjected to preswelling treatment or grafted with the presence of a swelling solvent. The solvents used in the swelling treatment of the PET fibers were methylene chloride,[1] 1,2-dichloroethane/wa-ter,[9,13,14] and 1,1,2,2-tetrachloromethane/water[9,14] mixtures. Acrylic acid itself also acted as a swelling agent.[15] It is clear that some physical and surface properties of PET fibers subjected to a swelling treatment will change as a result of swelling. Due to these changes, the determined features of acrylic acid-grafted PET fibers such as density, diameter, dyeability, and moisture regain will not exactly reflect the effect of grafting onto original PET fiber features.

In our study, the PET fibers used in the experiments have not been subjected to any preswelling procedure and there was no swelling solvent used in the polymerization medium. The changes of graft yield with the temperature, time, monomer, and initiator concentration were investigated. The effects of various solvents and alcohols onto graft yield were also examined. The density, moisture regain, diameter, and dyeability of the grafted PET fibers were determined.

EXPERIMENTAL

Materials

The PET fibers (multifilament) used in this study were provided by SASA Co. (Adana, Turkey). The

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fiber samples were prepared as small hanks (0.30 ± 0.01 g), Soxhlet-extracted for 6 h with acetone, and dried at ambient temperature. Benzoyl peroxide (Bz_2O_2) was recrystallized twice from the methanol–chloroform mixture and dried in vacuum. Acrylic acid (AA) was vacuum-distilled over a column filled with copper wires at 30°C. AA, freshly distilled throughout the study, was kept in the dark. All other chemicals were chemically pure grade.

Polymerization Procedure

The graft copolymerizations were carried out in 100 mL Pyrex tubes. The mixture containing the fiber sample, monomer, and Bz_2O_2 at the required concentration in 5 mL acetone was made up to 50 mL with deionized water. The polymerization mixture was immediately placed into the water bath (Lauda D 40 S, Germany) adjusted to the grafting temperature. The fiber sample taken from the system after the polymerization procedure was roughly washed with water. Then, it was washed in boiling water for 4 h by changing the washing water at least three times. It was finally Soxhlet-extracted with methanol for 8 h. The fiber sample thus freed from poly(acrylic acid) (PAA) was dried and brought to constant weight. The graft yield was calculated from the weight increase observed in the grafted fibers.

Dyeing Procedure

The grafted and original fiber samples were dyed with methylene blue (2 g/L) for 2 h at boiling temperature. The fiber/liquor ratio was 0.6/100. The dye uptake values of the fiber samples were calculated from the amount of the dye remaining in the dye bath and the predetermined calibration curve. The measurements were made at a wavelength of 663 nm by a Shimadzu 160 A Model UV spectrophotometer.

Measurement of Density and Diameter

The density gradient column used for the density measurements (with diameter of 5 cm and height of 45 cm) was prepared from xylene and carbon tetrachloride. The calibration of the column was made by the marker floats (made by Davenport Ltd.), whose densities at 23°C were known within an accuracy of 1/10,000. The levels of the marker floats and the fiber samples were determined using a cathetometer having a sensitivity of ±0.01 mm. The measurements of the fiber diameters and the examination of the dyed fiber cross section were made

using a Nikon Type 104 microscope. The fiber diameters were determined by the measurements made at least from five different regions for each sample at a magnification of ×600.

Determination of Moisture Regain

The fiber samples dried over P_2O_5 were conditioned in a medium at 20°C with a relative humidity of 65% for 24 h. The moisture regain values were determined from the dried and conditioned fiber weights.

FTIR Spectrum

The FTIR spectra of ungrafted and AA-grafted PET fiber were recorded using a Perkin-Elmer Model 1710 spectrophotometer with a KBr disc.

RESULTS AND DISCUSSION

In grafting systems like the one in this study, it is inevitable that the homopolymer of the grafted monomer forms in the graft copolymerization medium. The homopolymer is generally removed from the grafted fiber by extraction using the appropriate solvent and/or solvents. This is a long time- and solvent-consuming process. However, it is easily applicable. The solvents used in the extraction of homoPAA from the grafted fibers are generally water[13,15,16] or methanol.[17,18] In this study, both these solvents were sequentially employed for this purpose. Although prolonged extraction times are used, it is not clear that the increase observed in the weight of the grafted fibers is due to grafting and/or in situ polymerization. There is no method available that shows the binding points of the side PAA chains to the PET main chains. In spite of this, these polymerization reactions are believed to be grafting reactions. That is why we took the increase in weight in the original fibers after the grafting procedure as the graft yield. The results obtained from the experimental studies are discussed below.

Effect of Temperature and Time

Some preexperiments were made to determine whether any thermal grafting is present. The fiber was kept at 90°C in the polymerization medium containing only water and monomer for 5 h, then washed and weighed. The samples were found to show no increase in their original weights after a number of such trials. Depending upon these results,

it was assumed that there was no question of thermal grafting.

Figure 1 shows the relation between graft yield and temperature. The graft yield was examined as a function of time at seven different temperatures ranging from 60 to 90°C. The increase of the temperature progressively increased the saturation graft yield with the grafting rate. The saturation graft yield of 2.5% at 65°C was found to increase approximately 13.1% at 90°C. Also, there were induction periods for 60°C (45 min) and 65°C (15 min).

The increase in temperature increases the initiation and propagation rates of the graft copolymerization, together with the decomposition rate of the initiator. It also causes the mobilities of the monomer molecules and other reactive species (such as radicals from initiator and active PAA chains) to increase. The swellability of the PET fibers also increases with increasing temperature. The effects of these last two factors shows itself as an increase in the rate of diffusion to the fiber phase. This diffusion becomes much easier at temperatures around and above the glass transition temperatures of PET ($\approx$ 80°C) since both the mobilities and activities of PET segments increase above this temperature.[19] All these effects cause the increase in the grafting rate and graft yield by the increase in temperature as reported by the other workers.[7,20]
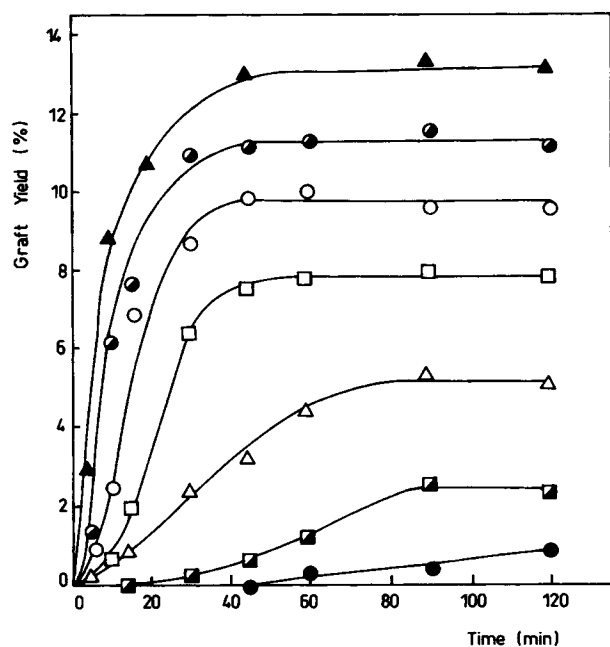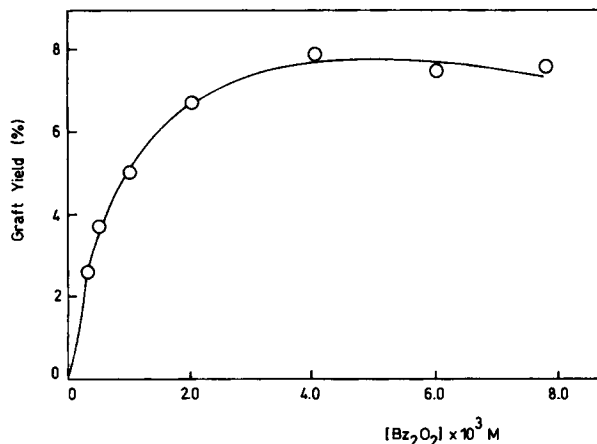

Figure 2   Variation of graft yield with initiator concentration. [AA], 0.875 M; temperature, 75°C; time, 1 h.

The concentrations of monomer and initiator are expected to decrease throughout the graft copolymerization reaction. They are used for grafting and homopolymerization. Also, deposition of PAA, which starts to form from the initiation of polymerization, upon the PET surface may constitute a barrier against the diffusion. If the fact that grafting starts from the fiber surface and proceeds toward the center, the grafted PAA chains appear as a barrier for grafting to proceed. The graft yield tends to remain a constant value (saturation grafting) after a certain time due to the factors mentioned above. As seen from Figure 1, the graft yield reaches a saturation value after 40–50 min at all temperatures except at 60 and 65°C and remain constant afterward.

The Effect of Initiator and Monomer Concentrations

The Bz_2O_2 concentration was changed between 0.0 and 7.7×10^{-3} M, keeping all other variables constant, in order to investigate the variation of the graft yield. The experimental results are shown in Figure 2. As was mentioned before, there is no question of any grafting whatsoever if there is no initiator used. As seen in Figure 2, the graft yield shows a rapid increase up to a Bz_2O_2 concentration of 4.0 $\times 10^{-3}$ M. It shows a slight decrease above this concentration. It is very clear that the concentrations of radicalic dissociation products of Bz_2O_2 (C_8H_5-$COO^\bullet$ and/or $C_8H_5^\bullet$) will increase with the increase in Bz_2O_2 concentration. Obviously, above a critical concentration (4.0 $\times 10^{-3}$ M), an increase in the concentration of these radicalic species slightly decreases the graft yield due to the domination of the

Figure 1   Variation of graft yield with polymerization temperature and time: [AA], 0.875M; [Bz_2O_2], 4.0 $\times 10^{-3}$ M; ($\bullet$) 60°C; (▨) 65°C; ($\triangle$) 70°C; ($\square$) 75°C; ($\bigcirc$) 80°C; (◓) 85°C; (▲) 90°C.

termination reactions with PET macroradicals, with growing active PAA chains, with grafted active side PAA chains, and with each other. At the same time, these free radicals abstract hydrogen atoms from the PET main chain and create active sites necessary for the grafting process. Active sites also form by the transfer reaction of growing PAA chains with PET macromolecules (the increase in the free-radical concentration increases the number of active PAA chains). The last two factors increase the graft yield. In our study, it can be concluded that the last two factors predominate up to a Bz_2O_2 concentration of 4.0×10^{-3} M and the termination reactions become dominant when the concentration of Bz_2O_2 exceeds this value.

Figure 3 gives the relation between the graft yield and the monomer concentration. The change of graft yield for the five different AA concentrations at 75°C was investigated. When the monomer concentration was increased up to 0.875M, the grafting rate together with the graft yield also increased. The further increase in AA concentration increased the grafting rate, however, the saturation graft yield remained virtually at the same level (8.0%) obtained at the preceding monomer concentration.
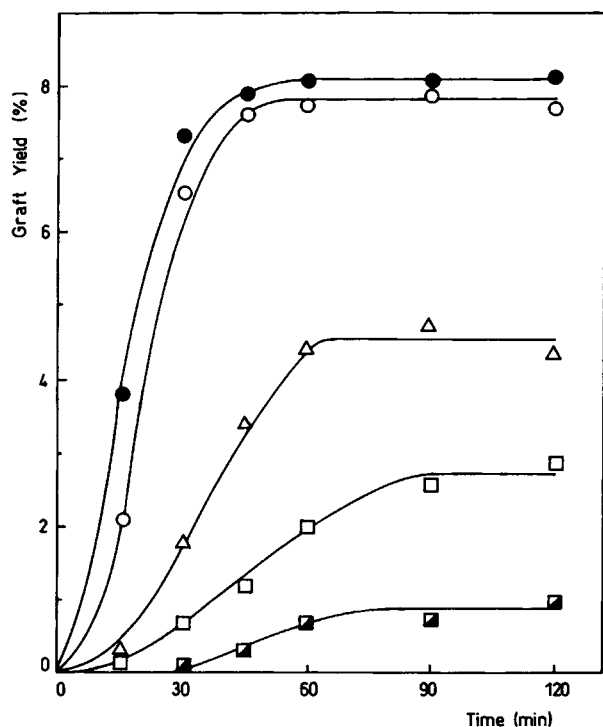

Figure 3 Variation of graft yield with AA concentration: [Bz_2O_2] 4.0 $\times$ 10^{-3} M; temperature, 75°C. [AA]: (◩) 0.146M; (□) 0.292M; (△) 0.583M; (○) 0.875M; (●) 1.167M.

The increase of the monomer concentration increases the AA concentration diffused into the fiber and remained in the other solution. This increases the change of PET macroradicals and growing PAA side chains to find monomer molecules. This shows itself as an increase in the graft yield. The fact that saturation graft yield remains constant when the monomer concentration is increased further (above 0.875M) can be attributed to the physical adsorption of monomer upon the PET fiber; the deposition of homoPAA upon the fiber surface; and the formation of a diffusion barrier by the PAA chains that are first grafted onto the subsurface regions of the fibers.

Effect of Reaction Medium

In this part of the study, the effect of some solvents upon the graft yield was investigated by adding various organic solvents to the reaction medium. The grafting was carried out at different water/solvent ratios by keeping the total volume of the reaction system at 50 mL. All the solvents tried showed an effect that decreased the graft yield (Table I). Also, if Table I is examined, it can be seen that for each solvent the increase in the amount of solvent in the mixture decreased the graft yield. Pyridine showed an absolute inhibiting effect on the grafting. Similarly, the following mixtures 60/40 (v/v) water/propanol, 70/30 (v/v) water/butanol, and 60/40 (v/v) water/dimethylformamide were found to inhibit the grafting process.

The solvents added in the grafting medium may have physical (can affect the swellability of PET and miscibility of monomer) and chemical (may take place in initiation, chain transfer, and termination reactions) effects upon the graft copolymerization system. These effects may vary according to the water/solvent ratio employed. As is clearly seen, the effect of solvents upon the graft yield is highly complicated and dependent upon many factors. For instance, it was reported that the grafting medium of 80% DMF (aq) increased the graft yield of glycidyl methacrylate onto PET fibers using Bz_2O_2,[21] while the same grafting medium decreased the graft yield of the same monomer onto PET fibers using hydrogen peroxide (only the initiator has been changed).[22]

Kinetics of Grafting

In a grafting system similar to ours, the relation of the rate of grafting (Rg) with the monomer and initiator concentrations can be written as

$$Rg = k[\text{monomer}]^m[\text{Initiator}]^n$$

Here, m and n can be experimentally determined.

Table I Effect of Some Solvents on Graft Yield[a]

Water/Solvent Ratio (v/v)	Graft Yield (%)						
	DMSO[b]	Methanol	DMF[b]	n-Buthanol	Ethanol	Pyridine	n-Propanol
100/00	7.7	7.7	7.7	7.7	7.7	7.7	7.7
90/10	4.0	4.1	3.2	2.7	3.6	0.0	2.7
80/20	1.8	2.1	0.9	0.7	1.4	0.0	0.8
70/30	0.9	1.3	0.6	0.0	0.6	0.0	0.4
60/40	0.8	0.9	0.0	0.0	0.4	0.0	0.0
50/50	0.4	0.5	0.0	0.0	0.0	0.0	0.0

[a] [AA], $0.875M$; [Bz_2O_2], 4.0×10^{-3}; time, 1 h; temperature, 75°C.
[b] DMSO, dimethylsulfoxide; DMF, dimethylformamide.

The experimental results showing the change of the rate of grafting with the concentration of Bz_2O_2 keeping the concentration of AA constant are tabulated in Table II.

The slope of the log Rg vs. log[Bz_2O_2] graph plotted from the data given in Table II showed that the rate of grafting was proportional to the 0.92 power of Bz_2O_2 concentration (Fig. 4).

Likewise, the initial rates of grafting were determined by changing the concentration of AA from 0.146 to $0.875M$ (Table III). From Figure 5, it can be seen that Rg is proportional to the 2.33 power of AA concentration. Therefore, the grafting rate of AA onto PET fibers using Bz_2O_2 can be written as

$$Rg = k[AA]^{2.33}[Bz_2O_2]^{0.92}$$

The overall activation energy for grafting was calculated to be 9.9 kcal/mol from the Arrhenius plot of log Rg vs. $1/T$ (Fig. 6).

SOME PROPERTIES OF GRAFTED FIBERS

Table IV shows the changes in densities of PET fibers depending upon the graft yield. There is very little data concerning with the densities of the

grafted PET fibers in the literature[23] and some of them reported by us previously.[4,10] In these studies, the grafted fiber densities were reported to decrease with increasing grafting. The fiber densities were observed to increase in this study. The grafted fiber density increased to 1.3861 g/cm³ of a graft yield of 13.1% from its ungrafted value of 1.3734 g/cm³. The ungrafted fiber, 6.0% grafted fiber, and 13.1% grafted fiber diameters were found to be 1.9953×10^{-2} mm, 2.0749×10^{-2} mm, and 1.9553×10^{-2} mm, respectively, after the diameter measurements (Table IV).

The increase of fiber diameter (therefore, volume) with the increase of density shows the chains inserted to the fiber structure have a much higher contribution to the fiber weight than to the fiber volume. In other words, the fiber structure becomes more densely packed with grafting. If one takes the fact that the grafting starts from the fiber surface and proceeds toward the center, it can said that this packed structure starts to form from the subsurface regions of the fibers as stated by Osipenko and Martinovicz.[24] The PAA chains could have entered the PET free volume without causing much volume increase. It is obvious that such a grafting adversely affects the diffusion into the fiber.

This barrier effect can also be seen from the moisture regain values plotted in Figure 7. The in-

Table II Dependence of Rate of Grafting on Bz_2O_2 Concentration

[Bz_2O_2] $\times 10^3$ (mol/L)	Graft Yield[a] (%)	log[Bz_2O_2] + 4	$Rg \times 10^6$ (mol/L s)	log Rg + 7
0.972	1.8	0.988	0.833	0.921
1.458	2.5	1.164	1.157	1.063
1.945	3.6	1.289	1.667	1.222
3.889	6.3	1.590	2.963	1.472

[a] Values obtained, before reaching saturation, at the 13th minute.
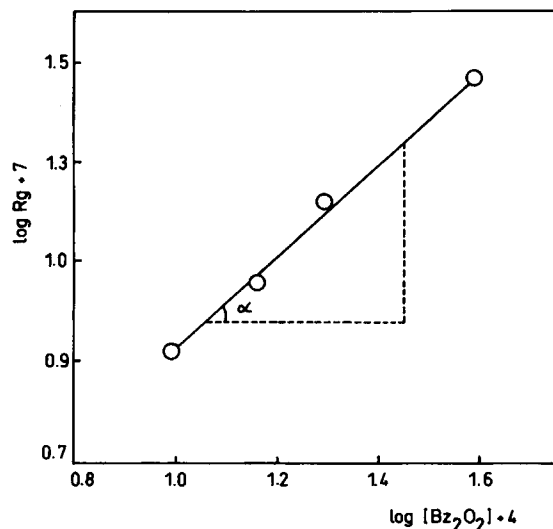
Figure 4   Plot of log Rg vs. log [Bz_2O_2].

Figure 5   Plot of log Rg vs. log[AA].

crease in moisture regain value, due to hydrophilic —COOH groups entering the fiber structure as a result of AA grafting, shows a rapid increase up to graft value of 9.1%, and rate of increase slows down at higher grafting values. Similarly, the fact that graft yield remained constant above an AA concentration of $0.875M$ can be explained by the dominance of the barrier effect (Fig. 3). The dye-uptake values given in Figure 8 are of a nature that supports the above-mentioned points. Dye uptake did not show a significant increase above grafting of 9.1% but showed a slight decrease at a grafting of 13.1%, which was the highest graft yield obtained in this study. However, one expects that the dye uptake should increase due to a higher amount of —COOH groups (which can interact with dye molecules) entering the fiber structure as a result of increased grafting. The examination of the dyed fiber cross section with an optical microscope showed that dyeing did not proceed up to the fiber center. The dyeing could only extend up to one-fourth of the fiber radius.
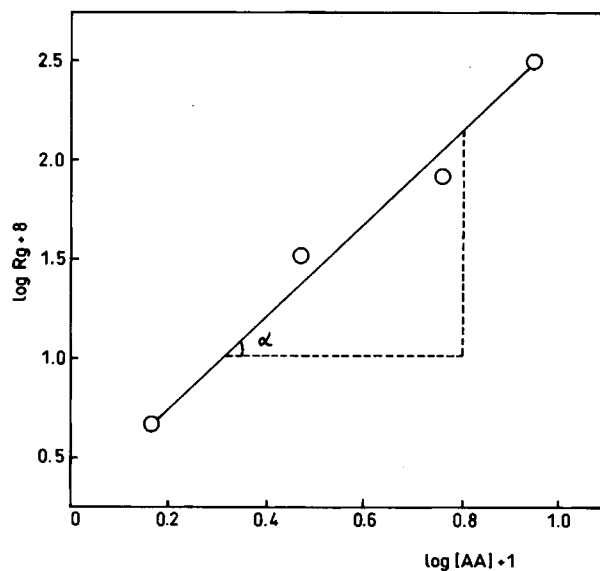
FTIR SPECTRA

Figure 9 shows the FTIR spectra of ungrafted and 13.1% AA-grafted PET fibers. When these spectra are examined, a strong band is seen due to the stretching of OH groups coming from AA at 3440 cm^{-1}. IR spectra are not sufficient to evaluate the points of the side chains binding to the main polymer backbone. However, IR spectra are given as supporting data in some grafting studies.[10,25,26]

CONCLUSION

In the studies concerning the grafting of AA onto the PET fibers using various initiators, the PET fibers have been used after being subjected to a swelling treatment. It is obvious that the surface properties and some physical features of PET fibers would change as a result of such a swelling process. Therefore, direct comparison of the properties of a

Table III   Dependence of Rate of Grafting on AA Concentration

[AA] (mol/L)	Graft Yield[a] (%)	log[AA] + 1	$Rg \times 10^7$ (mol/L s)	log Rg + 8
0.146	0.10	0.164	0.463	0.666
0.292	0.70	0.466	3.241	1.511
0.583	1.73	0.766	8.009	1.904
0.875	6.50	0.942	30.090	2.479

[a] Values obtained, before reaching saturation, at the 13th minute.

Figure 6 Plot of Rg vs. $1/T$.

Figure 7 Moisture regain values of AA-grafted PET fibers.
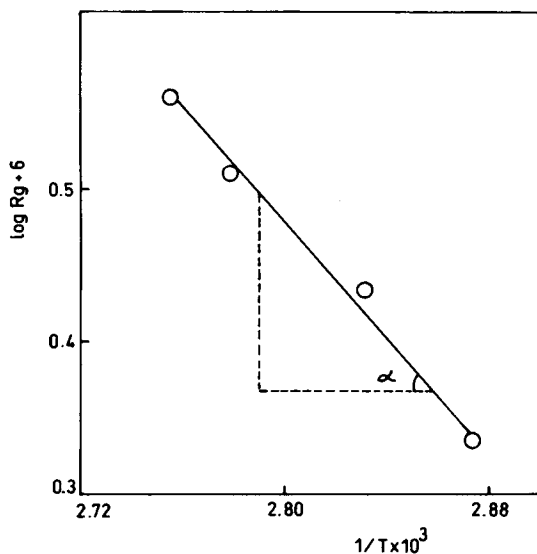
grafted fiber such as diameter, dyeability, and moisture regain with the original fiber would not reflect the real changes of these properties that occurred due to the grafting process. Here, we tried to show that AA would be grafted directly onto PET fibers not subjected to any swelling treatment in aqueous media using Bz_2O_2. Therefore, the fiber properties given in the study show the real effect of grafting of AA on the properties of original PET fibers. Similarly, the effect of some factors such as temperature, grafting time, solvent used, and monomer and initiator concentrations on graft copolymerization can be quite different in swelled and nonswelled fibers.

In the light of the experimental findings, the following conclusions can be drawn for the grafting of AA in aqueous media onto PET fibers not subjected to any swelling treatment using Bz_2O_2.

(a) The PAA side chains enter in the space between the PET main chains, in a way to make a

higher contribution to the fiber weight than to its volume.

(b) The grafting predominates at the subsurface regions.

(c) As a result of such grafting, the fiber structure becomes much more densely (possibly due to a partial cross-linking) packed, especially the subsurface regions.
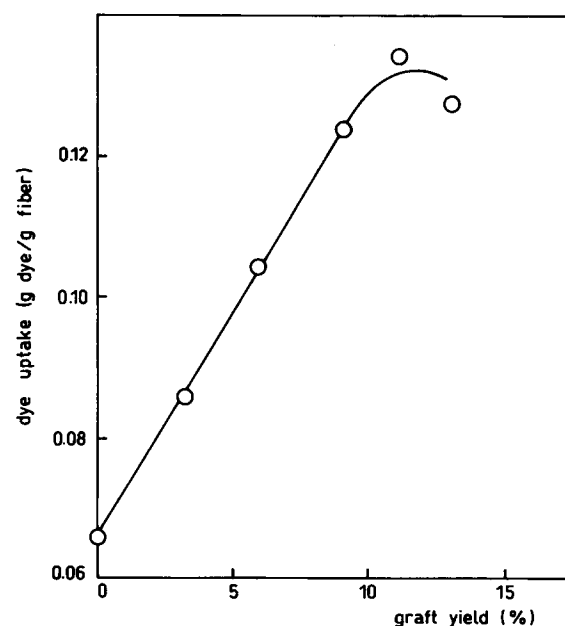
Table IV   Density and Diameter Values of AA-grafted PET Fibers

Graft Yield (%)	Density (g/cm^3)	Diameter (mm $\times$ 10^{-2})
0.0	1.3734	1.9553
2.0	1.3761	
4.1	1.3770	
6.0	1.3784	2.0749
7.2	1.3810	
9.1	1.3829	
11.2	13849	2.1753
13.1	1.3861	2.1969

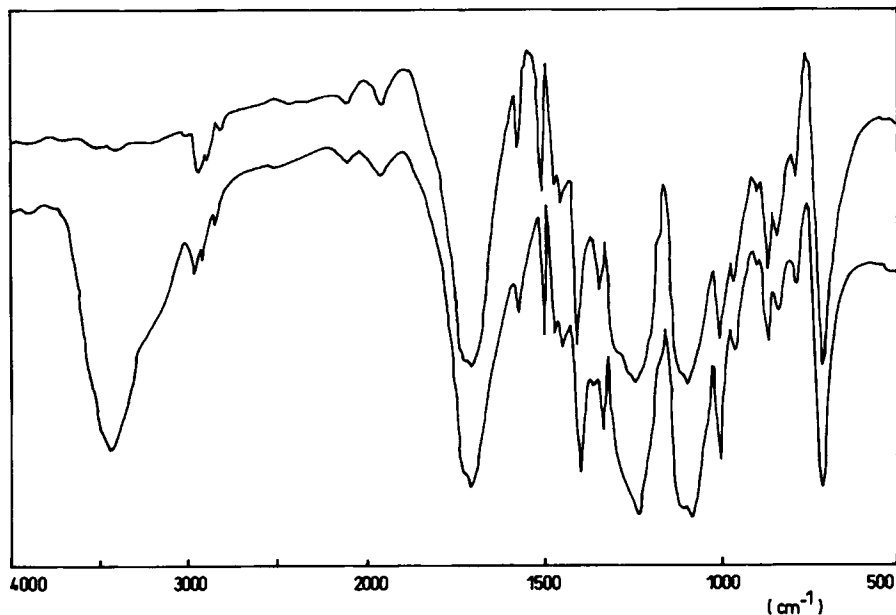**Figure 8** Dye-uptake values of AA grafted PET fibers. Dyed with methylene blue.

Figure 9   FTIR spectra of PET fibers: (top) ungrafted; (bottom) 13.1% AA-grafted.

(d) The grafting above 8–9% itself acts as a barrier that impedes diffusion into the fiber structure.

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