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FUNCTIONALIZATION OF POLY(ETHYLENE TEREPHTHALATE) BY MEANS OF GLOW-DISCHARGE-INITIATED POLYMERIZATION OF ACRYLIC ACID

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ABSTRACT

Glow-discharge-initiated polymerization of acrylic acid incorporated in poly(ethylene terephthalate) (PET) films was investigated. An increase in polymerization yield with plasma treatment duration and power was found. Polymerization was not confined to the film surface. At high power and long treatment time, polymerization in the bulk of the PET also took place. Water regain and contact angle of the PET-treated films were affected by the presence of poly(acrylic acid) (PAA). The carboxyl groups of the PAA chains incorporated in the PET matrix were utilized for further chemical modification of the PET film. Poly(ethylene glycol) (PEG) was grafted onto PAA by esterification. DSC studies showed the presence of both PAA and PEG in the PET matrix and shed light on the morphology of the multicomponent polymeric system. Free isocyanate groups were introduced into the PET matrix by reacting PAA carboxyl groups with hexamethylene diisocyanate.

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INTRODUCTION

Incorporation of poly(acrylic acid) (PAA) into poly(ethylene terephthalate) (PET) and its subsequent polymerization may lead to physical and chemical changes in bulk and surface properties of PET films and yarns. The presence of PAA in the PET matrix should decrease its hydrophobicity. Wettability and water regain of the PET are expected to increase as a result of the presence of PAA.

PET is a polymer hard to functionalize because the ester group, which is the only active site in the polymer chain, exhibits only limited reactivity. Furthermore, functionalization of PET by reaction with this group will result in chain scission. Only when the extent of the reaction with the ester group and its location in the PET matrix can be controlled, can successful functionalization be carried out [1].

Generating a PET/PAA interpenetrating polymer network should allow the easy introduction of new functional groups into the system. Also, further derivatization of the matrix via the reactive carboxyl groups of PAA should be significantly more effective than direct functionalization of the polyester backbone. A variety of condensation reactions can be performed at the pendent carboxylic groups of PAA, leading to significant changes in the chemical properties of the system without chemical modification of the PET chains.

Incorporation of PAA into PET films and yarns by different polymerization techniques has been reported in the literature. Polymerization of acrylic acid (AA) in a PET matrix was initiated by conventional chemical initiators such as benzoyl peroxide [2, 3]. Most of the reported work made use of a variety of irradiation techniques. Polymerizations by γ-irradiation [2-5], electron beam irradiation [6], and glow discharge [7-11] have been studied.

Surface modification of PET films and fibers by polymerization of acrylic acid can be achieved by glow discharge pretreatment of the substrate, followed by exposure to acrylic acid. Such surface modifications of PET, due to graft polymerization of acrylic acid [7] and other vinyl monomers [8], have been reported. A similar surface modification was obtained when polyethylene was activated by helium plasma and exposed to acrylic acid [9].

Incorporation of PAA into a PET matrix can also be achieved when acrylic acid is swollen into the substrate prior to plasma treatment. Such glow-discharge-initiated polymerization of acrylic acid and other vinyl monomers has been reported in the literature [10, 11].

Although glow-discharge effects are limited to the film surface, *in situ* polymerization of acrylic acid has been obtained [10]. At short plasma treatment time, only surface modification occurred, while longer treatments resulted in bulk modification as well. It was shown by selective staining of the

PAA present in PET that polymerization was initiated at the film surface and gradually advanced toward the film center. This glow-discharge-initiated polymerization of acrylic acid absorbed in PET film was carried out under nitrogen flow, using platinum electrodes at 50 Hz. Preswelling of the PET matrix with strongly interacting solvents such as dimethylformamide (DMF) [10] and others [11] was found to be essential for successful diffusion of the penetrating monomer and its *in situ* polymerization [10].

The present paper is an account of the glow-discharge-initiated polymerization of acrylic acid incorporated in PET matrices as a function of plasma duration and power. Also, the plasma-induced polymerization of acrylic acid in a PET substrate was compared with processes redox initiated by benzoyl peroxide or the initiating species present in solution outside the PET films. The carboxyl groups of PAA can be utilized for the introduction of isocyanate groups by reaction with polyfunctional isocyanates, such as hexamethylene diisocyanate (HDI). The chemically active carboxyl moieties present in the PET matrix can be used not only for the introduction of other functional groups but also for graft polymers. The present work also reports on the practicality of these chemical modifications of PAA in PET matrices.

EXPERIMENTAL

Materials

PET (Mylar) films, 90 μm, supplied by Du Pont were used. Acrylic acid and thionyl chloride (Fluka) were redistilled before use. Poly(ethylene glycol) 1500 (PEG), 1,1,1,3,3,3-hexafluor-2-propanol, pyridine, dibutyltin dilaurate (Fluka), DMF, benzoyl peroxide (BDH), ammonium persulfate (Mallinkrodt), sodium bisulfite (Riedel-DeHaen), and hexamethylene diisocyanate (Merck) were used. THF (Frutarom) was dried by distillation from sodium benzophenone solution.

DMF Treatment of the Mylar Film

Mylar films (0.5 g) were immersed in DMF at 140°C for 10 min. Excess DMF was removed by blotting with filter paper.

Acrylic Acid Incorporation

DMF-treated films (0.5 g) were kept in acrylic acid (AA) aqueous solutions (50 mL) for 48 h. Excess monomer was removed by blotting with filter paper. The AA content of the PET films was determined by weighing.

Glow-Discharge Polymerization

The plasma experiments were conducted in a Pyrex cylindrical reaction chamber (70 cm long, 10 cm i.d.), capacitatively coupled by two external electrodes to a 13.56-MHz HFS-501s RF generator (Plasma-Therm, RF Plasma Products). The samples were placed in the reaction vessel, the system was then evacuated to approximately 0.05 torr, and finally, nitrogen was allowed to flow into the chamber until 0.30 torr pressure was obtained. RF power up to 120 W was applied to the system through a matching network (MN 500, Plasma-Therm) for various durations.

Initiation of AA Polymerization by Benzoyl Peroxide and Redox System

DMF-treated PET films containing AA were immersed in 50% AA solution (30 mL). Benzoyl peroxide was added, and the reaction mixture was kept at 55°C for 48 h under constant shaking. The film was removed, washed with water, and Soxhlet extracted with methanol for 48 h. The extent of PAA incorporation was determined from the weight increase after drying the film in vacuum for 48 h.

Polymerization reactions initiated by the ammonium persulfate/sodium bisulfide redox system were carried out similarly in a 50% AA solution at room temperature.

Graft Polymerization of Polyethylene Glycol

PET films containing 7.7% PAA (0.2 g) were immersed in pyridine (20 mL) for 1 h and then transferred to thionyl chloride (10 mL). The reaction mixture was kept at 90°C for 2 h. The treated films were removed, blotted with filter paper, and transferred to PEG (15 g) and pyridine (3 mL). The reaction was conducted at 40°C overnight. The films were washed and then extracted for 72 h in a Soxhlet apparatus in order to remove ungrafted PEG chains. After drying, the films exhibited an average 14% weight increase.

Reaction with HDI

Mylar films (0.4 g) with 7.0% PAA content were left in HDI (25 mL) overnight in the presence of dibutyltin dilaurate (0.2 mL) at room temperature. The films were washed with dry THF, and their isocyanate content was determined by titration with *n*-butylamine according to a known procedure [13].

Staining the PET Film with Methylene Blue

Staining PAA-containing PET films with methylene blue was carried out as previously described [10].

Determination of the Free Carboxyl Content of the Graft Polymer

Free carboxyl content was determined by titration with 0.1 *N* sodium hydroxide with hexafluoroisopropanol as solvent. Bromophenol blue was used as indicator.

Differential Scanning Calorimeter (DSC)

A Mettler TA3000 thermoanalyzer was used for the thermal analysis of polymers. The thermograms covered the -120 to 300°C temperature range at a 10°C/min heating rate under nitrogen. The crystallinity is directly proportional to the heat of fusion, ΔH. The relative crystallinity of the polymeric systems was assessed by integrating the normalized area of the melting endotherms, determining the heat of fusion, and relating it to that of the respective homopolymer [14, 15]. This relative degree of crystallinity will be denoted by C_r.

Contact Angle Measurements

An optical-bench goniometer was used for the measurement of the contact angle of distilled water in air, each reported value being the average of at least six measurements.

Water Regain

Water regain was determined at 21°C and 70% relative humidity.

RESULTS AND DISCUSSION

PET films were pretreated with DMF at 140°C before acrylic acid incorporation. This first step is essential since it leads to swelling and concomitant solvent-induced crystallization of the PET, allowing the later diffusion of considerable amounts of AA into the PET matrix. Acrylic acid was incorporated into the substrate from aqueous solution by solvent exchange with DMF already present in the pretreated PET. The results reported in Table 1 clearly

TABLE 1. Incorporation of Acrylic Acid into PET Films

Acrylic acid in water, %	Acrylic acid content, %	
	DMF pretreated	Untreated
10	7.4	0.0
20	7.9	0.0
30	8.8	0.0
50	10.0	0.9
100	11.0	1.5

show that a relatively high acrylic acid content can be reached even with a 10% AA solution. Since a 50% aqueous solution was almost as effective as pure acrylic acid, incorporation of AA was carried out by solvent exchange with such a solution.

Table 2 shows that attempts to initiate the polymerization reaction by a redox system showed very limited success, not exceeding 30% yield after 72 h. Significant polymerization yields with benzoyl peroxide could be reached only after 48 h and at high initiator concentrations.

The location of PAA in the substrate film was determined by selectively staining it with methylene blue and observing the stained cross section under a microscope. Our findings indicate that both initiation systems resulted not only in surface modification of the PET film but also in the polymerization of AA in the bulk of the PET sample. When the redox system was used, even though bulk polymerization did take place, it did not reach the film core. With benzoyl peroxide at high polymerization yields, PAA was present all through the film cross section. It seems reasonable to assume that the initiation of acrylic acid polymerization by the redox system, and most probably by benzoyl peroxide as well, is confined to the aqueous solution; the diffusion of the two salts in the external aqueous medium into the PET matrix should be minimal if it occurred at all. Therefore, initiation of the polymerization of AA present in the bulk of the PET matrix should start at the film should start at the film surface. It is surmised that, as polymerization proceeds, the termination rate decreases due to the lack of mobility of the growing chains, and the polymerization advances into the bulk of the PET substrate.

TABLE 2. Redox and Benzoyl-Peroxide-Initiated Polymerization of Acrylic Acid in PET

Acrylic acid in PET, %	Initiating system	Polymerization time, h	PAA in PET, %	Polymerization yield, %
9.3	$(NH_4)_2S_2O_8$ (0.4%, 35 mL) $Na_2S_2O_5$ (2%, 25 mL)	72	2.5	26
9.1	$(NH_4)_2S_2O_8$ $Na_2S_2O_5$ (0.1%, 1 mL)	72	2.9	30
9.1	$K_2S_2O_8$ $Na_2S_2O_5$ (2%, 25 mL)	72	2.2	22
8.7	0.1[a]	48	3.5	38
9.1	0.5[a]	48	6.1	65
9.1	1.0[a]	48	7.2	86

[a] Wt% benzoyl peroxide.

1. Acrylic Acid Glow-Discharge-Initiated Polymerization

PET films containing acrylic acid were subjected to a nitrogen glos discharge plasma. Unpolymerized AA and free PAA were removed by extraction with methanol. The polymerization yield was determined from the weight increase of the PET film after extraction. Since there is some AA evaporation during the plasma treatment, which was conducted at low pressure (0.3 torr), the polymerization yield was corrected for this weight loss. The correction factor was determined by a separate experiment in which the film was placed in the reaction vessel and exposed to the same experimental conditions (pressure and time) but without the RF field. After polymerization, the PET sample was thoroughly washed with water and methanol to ensure full removal of unpolymerized AA and free PAA. A "pseudo-interpenetrating polymeric network" was obtained [16] in which the *in situ* polymerized PAA was entrapped in the PET matrix, the mutual entanglement of the chains stabilizing the system and preventing PAA from leaching out. The influence of treatment duration and glow discharge power on the reaction yield, as well as the location of the PAA formed in the PET film, were determined.

As shown in Table 3, very high AA polymerization yield were obtained in as little as 75 min. Evidently, the plasma-induced polymerization of AA is strikingly more effective compared to the conventionally initiated reactions (see Table 2). This phenomenon is most probably due to the high rate of initiation resulting from the extremely high dose rates characteristic of plasma processes [17]. Staining the treated PET films showed that polymerization was initiated at the film surface and gradually penetrated the PET sample with increasing treatment time. The color intensity in the stained areas also increased with time, suggesting that the penetration of the reaction front is accompanied by a concomitant increase in the extent of polymerization in the regions behind the advancing front. After 90 min the presence of PAA could be clearly identified throughout the film cross section. The dependence of the polymerization yield on the glow discharge power is reported in Fig. 1. It is apparent that the efficiency of the process increases with the discharge power, as evidenced by the higher polymerization yields obtained. This behavior prevails until a plateau level is reached. Both surface and bulk polymerization took place. Higher discharge power resulted in deeper PAA penetration into the film, full penetration being observed at 120 W.

The presence of PAA at the surface of the PET film should affect its surface free energy, a decrease in the water contact angle (θ) being expected due to the hydrophilicity of PAA. The water contact angle dependence on the polymerization time reported in Fig. 2 clearly shows a gradual decrease in θ as the plasma duration increases.

TABLE 3. Glow-Discharge-Initiated Polymerization of Acrylic Acid in PET

Acrylic acid in PET, %	Glow discharge treatment time,[a] min	PAA in PET, %	Polymerization yield, %	
			Uncorrected	Corrected[b]
10.7	10	4.2	36.8	37.0
11.1	30	4.0	33.5	46.0
10.7	60	7.1	64.0	78.0
12.0	75	9.1	78.4	95.0
9.9	90	7.8	78.0	96.4
10.7	150	8.7	77.0	100.0

[a] Glow discharge conditions: pressure, 0.400 mbar; power, 120 W.
[b] Corrected for loss due to monomer evaporation.

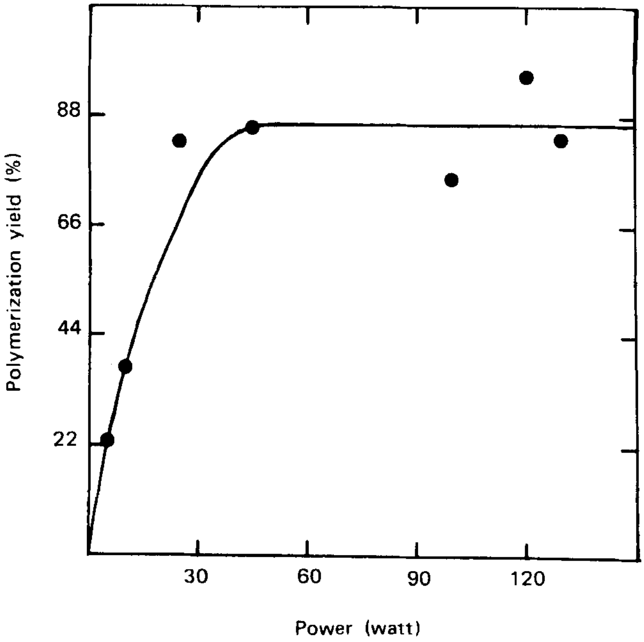

FIG. 1. Polymerization yield as a function of glow discharge power. Plasma conditions: pressure, 0.4 mbar; duration, 90 min.

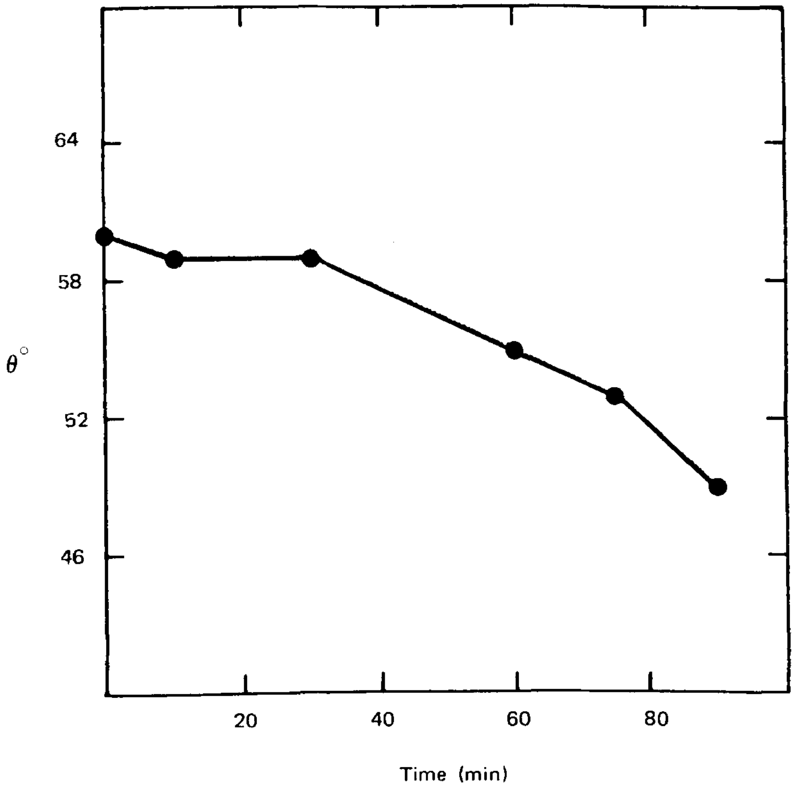

FIG. 2. Water contact angle dependence on plasma polymerization time. Plasma conditions: pressure, 0.4 mbar; power, 120 W.

The presence of PAA in the PET matrix was expected to increase its water regain. Even though the points are somewhat scattered due to difficulties in accurately measuring the low water contents of these materials, it is apparent from Fig. 3 that the very low water regain of the hydrophobic PET sample increases gradually with PAA content.

It has been reported [18] that polymerizing AA under plasma conditions may result in its decarboxylation, resulting in a rather hydrophobic material. Elemental analysis of plasma-polymerized PAA (calculated: C = 50.00, H = 5.56, O = 44.44%; observed: C = 49.62, H = 5.58, O = 44.80%) showed that no decarboxylation of acrylic acid took place under these plasma condi-

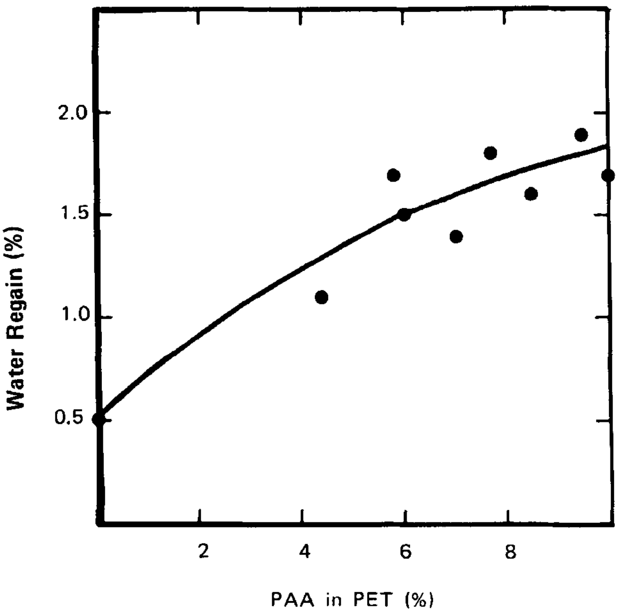

FIG. 3. Water regain of modified PET samples as a function of AA content. Plasma conditions: pressure, 0.4 mbar; power, 120 W; duration, 10 to 150 min.

tions. Furthermore, IR spectrum and DSC analysis of the plasma-polymerized PAA revealed no differences between its chemical composition and structure, and those of the polymer obtained by normal free-radical polymerization of AA. All these findings are in full agreement with the enhanced hydrophilicity of the PET sample containing PAA.

2. Graft Polymerization of Poly(Ethylene Glycol) on PAA in PET

The carboxyl functional groups now present in the PET matrix can be used as active sites for graft polymerization of a variety of molecules. Esterification of carboxyl pendent groups of PAA with PEG via its terminal hydroxyl groups should introduce PEG chains into the PET matrix. Even though the PEG is not covalently bound directly to the PET chains, the entangled PAA molecules play the bonding role. Due to the relatively high molecular weight of the PEG (1500) and its consequent slow diffusion, it is expected that esterification will be mainly confined to the film surface.

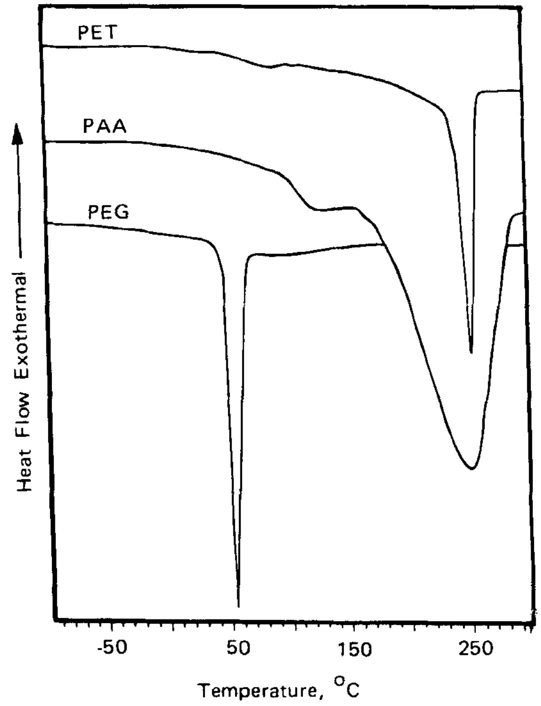

FIG. 4. DSC thermograms of PET, PAA, and PEG 1500. Heating rate: 10°C/min; nitrogen flow.

Prior to the reaction with PEG, PAA in PET was converted to its acid chloride analog by reaction with thionyl chloride in pyridine. For example, 35% of the 1.07 mmol/g carboxylic groups present in a PET sample, corresponding to 7.7% PAA in PET, were converted to the acid chloride as determined from chlorine analysis (0.37 mmol Cl/g). The modified film was allowed to react, in turn, with PEG 1500 in the presence of pyridine. After removal of unreacted PEG by water extraction, a 14% weight increase was measured, indicating that 25% of the acid chloride groups were converted to the corresponding ester.

Figure 4 presents the DSC thermograms of the three basic components of the composite polymeric system. Clearly, two different kinds of materials are shown: PET and PEG are crystalline polymers exhibiting sharp melting endotherms at 253 and 53°C, respectively, whereas PAA is an amorphous

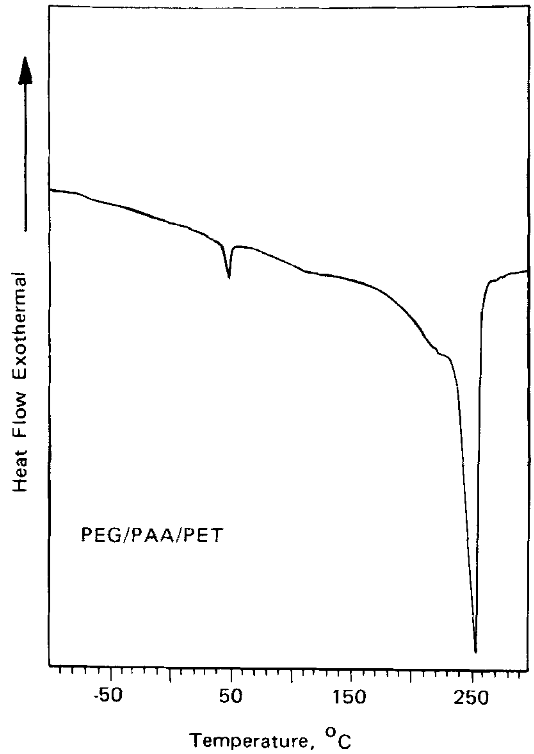

FIG. 5. DSC thermogram of a PET/PAA/PET 1500 grafted system. Heating rate: 10°C/min; nitrogen flow.

polymer with T_g at 107°C. The PAA associated broad endotherm at around 240°C is due to thermal degradation of the polymer. Figure 5 shows the thermogram of a PAA-containing PET sample (7.7 wt% PAA) which has undergone grafting of PEG 1500 chains via PAA carboxyl groups (13.9 wt% PEG). In addition to the sharp endotherm at 252°C due to the fusion of PET crystallites, two features are apparent: the glass transition temperature of PAA at around 90°C and, more clearly, the sharp melting peak at 49°C demonstrate the presence of PEG chains. The melting endotherm of PEG-grafted chains is shifted to lower temperature, from 53 (see Fig. 4) to 49°C, due to the mechanical constraints imposed on them by the surrounding stiff matrix. Furthermore, the PEG heat of fusion sharply decreased from 183.8 J/g for free PEG 1500 to 11.3 J/g for the grafted chains.

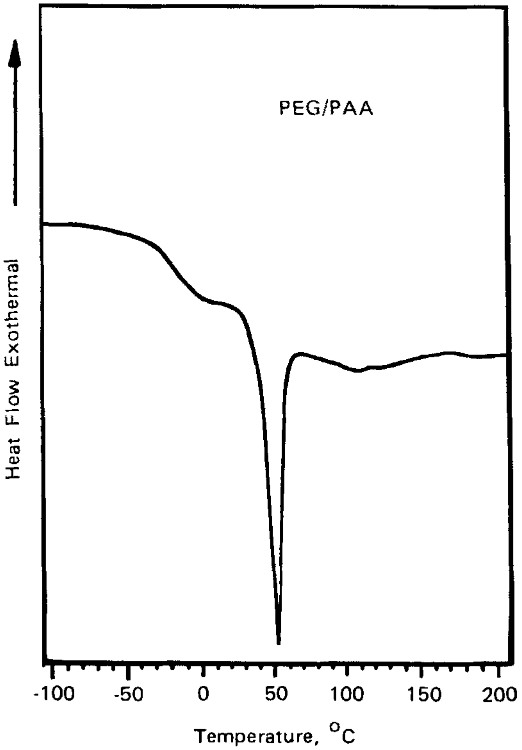

FIG. 6. DSC thermogram of PAA/PEG 1500 system. Heating rate: 10°C/min; nitrogen flow.

In an attempt to gain further insight into the system, additional experiments were conducted. DSC data of the PET/PAA "pseudo-IPN" showed no measurable shift in the PET melting point, expectedly so since, not being able to diffuse into the closely packed PET crystallites, AA will concentrate in the amorphous phase of the PET. A PAA/PEG (74/26 wt%) graft was also studied to try to isolate the effect of the different factors causing the low PEG crystallinity in the grafted system. The DSC thermogram (Fig. 6) clearly shows the PEG melting endotherm at 53°C, the PAA broad glass transition temperature at around 80-90°C, and finally its thermal decomposition at high temperatures. The shift of the PAA T_g to somewhat lower temperatures is attributed to the plasticizing effect of PEG chains, obviously molten at these temperatures. On the other hand, it is worth noting that the melting point of the PEG chains has not been shifted to lower temperatures, their degree of crystallinity being only mildly lowered (C_r 73%). Furthermore, a clear PEG-associated glass transition is apparent at -18°C. The larger magnitude of the glass transition and its pronounced shift to higher temperatures (free PEG 1500 chains show T_g at approximately -65°C) can both be explained in terms of the stiffening effect of the glassy PAA on the flexible PEG chains and its interference in the PEG crystal lattice. This is in full accordance with the somewhat lower degree of crystallinity exhibited by PEG.

These findings imply that the very large decrease in the crystallinity of PEG chains grafted to the PET/PAA system (C_r 7%) is not so much due to the very fact of grafting and covalently bonding to PAA, but mainly to mechanical constraints imposed on them by the rigid PET matrix.

3. Reaction of PAA-Containing PET with Hexamethylene Diisocyanate (HDI)

The carboxylic groups present in the modified PET film can be used as anchoring sites for the incorporation of isocyanate groups in the matrix. The high chemical reactivity of the isocyanate group can be used further to chemically modify both the surface and the bulk of PET films. PET containing 7.0% PAA (0.97 mmol COOH/g) was allowed to react with excess hexamethylene diisocyanate (HDI) in the presence of dibutyltin dilaurate catalyst. After removal of the excess unreacted HDI with dry THF, the isocyanate content was determined by titration with butylamine. The modified PET film contained 0.42 mmol NCO/g. IR analysis of the film clearly showed the isocyanate characteristic absorbance band at 2272 cm^{-1}. Assuming that HDI and the carboxylic acid groups react according to a 1:1 molar ratio, the titration data indicate that 42.9% of the carboxylic groups have reacted. In accordance with these data, titration of the free carboxyl groups showed that 62.3% of them did not react with HDI and were still present in the PET film.

CONCLUSIONS

This study has shown that PET can be effectively functionalized by glow-discharge-initiated polymerization of acrylic acid. Plasma treatments proved to be substantially more effective than conventionally initiated processes, large yields being obtained under mild conditions.

The carboxyl acid pendent groups acted as reactive anchoring sites for further derivatization of PET. This was illustrated by reaction with isocyanate groups and by esterification with the hydroxyl terminal groups of PEG chains.

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