The Initiation of in situ Polymerization of Vinyl Monomers in Polyester by Glow Discharge*

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Synopsis

Glow discharge initiation of in situ polymerization of acrylic acid and other vinyl monomers incorporated in PET films was investigated. The influence of glow discharge conditions such as the gas used, plasma power, discharge current, and plasma treatment time on polymerization yield was determined. Though glow discharge effects are limited to the film surface, in situ polymerization of the vinyl monomers took place and the vinyl polymer could be found all through the film cross section. At short plasma treatment time only surface modification took place, while at longer treatment time bulk modification occurred, too. Good polymerization yields were obtained. Gel effect behavior was observed. Mechanical properties of the modified PET film were not changed, while the contact angle with water improved when polar vinyl monomers were used.

INTRODUCTION

Chemical modifications of polyester (PET) by in situ bulk polymerization or graft polymerization of vinyl monomers are potentially useful tools for improving chemical and physical properties of this polymer. Practically all known conventional chemical and irradiation polymerization techniques were already applied for this purpose. It was recently shown[1] that when in situ polymerization of vinyl monomers in PET yarns was initiated by the use of a free-radical initiator or γ irradiation, in a system in which a constant supply of free radicals was available from the outside of the PET fiber, relatively low initiator concentration and low γ irradiation dose were necessary for obtaining good conversion.

In such systems good polymerization yields were obtained under free-radical initiation conditions which most probably did not lead to the formation of free radicals on the PET itself. Initiation of polymerization was carried out after the monomer had been incorporated into the PET fiber. It was shown that in situ polymerization started at the surface of the PET fiber and later advanced and reached the fiber core. This behavior was attributed to a lower efficiency of initiation inside the PET fiber caused by mobility restrictions in the polymeric media. When such in situ polymerization takes place, it is expected that these restrictions will eventually lead to the well-known gel effect.

Since in situ polymerization of vinyl monomers in PET could be initiated just by free radicals formed outside the hose polymer, it was interesting to find out whether polymerization initiation techniques in which location of free-radical formation is limited to the PET film or filament surface can be applied for such purpose. Plasma created by electric glow discharge is an example of such a technique.

* This work is part of a Ph.D. thesis to be submitted to the Senate of the Hebrew University of Jerusalem.

Glow discharge treatment is of very limited penetration ability, of the order of 10 μ,[2-5] and its effects are practically localized and limited to the film surface. It is generally accepted that such plasma-initiated graft polymerization of vinyl monomers yields surface grafting in a more strict sense compared to those obtained by a more penetrating radiation.[6]

Recently, it was reported[7,8] that ionized plasma can be used to initiate conventional free-radical polymerization and copolymerization of methyl methacrylate and other vinyl monomers in either bulk liquid state or in solution. If polymerization of a monomer already present in a PET film can be initiated by glow discharge plasma, such treatment can be used for in situ polymerization of vinyl monomers in PET. It will be of interest to find out whether location of the vinyl polymer formed during plasma treatment can be controlled, under what conditions surface modification takes place, and when bulk modification occurs. If bulk modification of PET can be achieved by glow discharge-initiated in situ polymerization of vinyl monomers, chemical modifications of this polymer can be carried out under relatively mild conditions. In this case glow discharge treatment can be used also when bulk modifications are preferred, as was suggested for flame retardance of PET.[9]

Plasma treatment may form free radicals at the PET film surface, derived from the host polymer. These free radicals may initiate true graft polymerization. No effort was made at this stage to distinguish between grafted vinyl polymer and entrapped homopolymer. Our main goal was to find out whether and under what conditions glow discharge can initiate in situ polymerization of vinyl monomers in PET, how location of the vinyl polymer can be controlled, and what the factors influencing such polymerization are. For this purpose a relatively thick PET film (350 μm wide) was used. In such film glow discharge effects are practically limited to the film surface, and any in situ polymerization which takes place should be initiated only by the glow discharge at the film surface.

EXPERIMENTAL

Materials. Polyester film Mylar A (du Pont) 350 μm wide was used. Acrylic acid, 2-dimethylaminoethyl methacrylate, styrene, methyl methacrylate, 4-vinylpyridine (Fluka), and 2-hydroxyethyl methacrylate (Eastman Kodak Co.) were used. All monomers were redistilled in vacuum before use. The following gases were used: argon, nitrogen, ammonia and acetylene (Matheson Gas Products Company).

DMF Treatment of the PET Film. PET film (0.22 g) was exposed to DMF at 140°C for 15 min. Excess DMF was removed by pressing the PET film with filter papers. Weight increase of 12.5% (1.93 mole/kg) due to DMF incorporation was found. When necessary, the DMF was extracted with boiling methanol for 4 hr, followed by drying under vacuum at 70°C.

Monomer Incorporation. DMF treated PET film (0.22 g) was exposed to monomer (50 ml) for six days. Excess monomer was removed by pressing the PET film with filter paper.

Glow Discharge. Schematic presentation of the electric system used for the electric glow discharge is given in Figure 1. Glow discharge was carried out at 50 Hz, using a high-voltage transformer. Discharge current was regulated by the use of a Variac variable autotransformer. Discharge current was measured
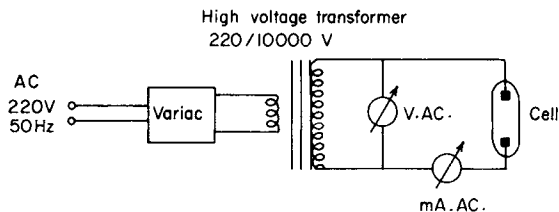
Fig. 1. Schematic representation of the electric system used for the glow discharge.

by an ac milliammeter, and discharge voltage was measured by an ac voltmeter. Glow discharge was carried out in a flow system. The glow discharge apparatus is described in Figure 2. The discharge cell consisted of a glass tube 3 cm I.D. and 50 cm long, which was cooled by a water jacket. Two cylindrical platinum electrodes (1.5 cm O.D., 2.5 cm long) located inside the cell 40 cm apart were used. Gas openings were situated between the two electrodes, 7 cm each. The cell was kept horizontal during the glow discharge experiment. The gas to be used in the glow discharge experiment was first introduced into container A (7.8 l.) under 25 psi pressure at 20°C. PET film samples (3 × 1.5 cm) were introduced into the reaction cell and were positioned halfway between the electrodes. The film was kept always parallel to the discharge current. A new sample was used for each experiment. Prior to the glow discharge the reaction cell was evacuated to 10^{-3} torr and was swept for 10 min with the gas to be used in the experiment. Gas flow rate was adjusted in all experiments to 0.21 mmole/min at 20°C at 0.25 torr. Gas flow rate was determined from the pressure drop in container A, as measured by test gauge C, during the electrical glow discharge. Pressure in the system was determined by the use of a mercury manometer. When argon and nitrogen were used, no change in pressure was observed. Glow discharge in ammonia led to an increase in pressure in the reaction cell from 0.25 to 0.50 torr. Glow discharge in acetylene caused a decrease in pressure from 0.25 to 0.10 torr.
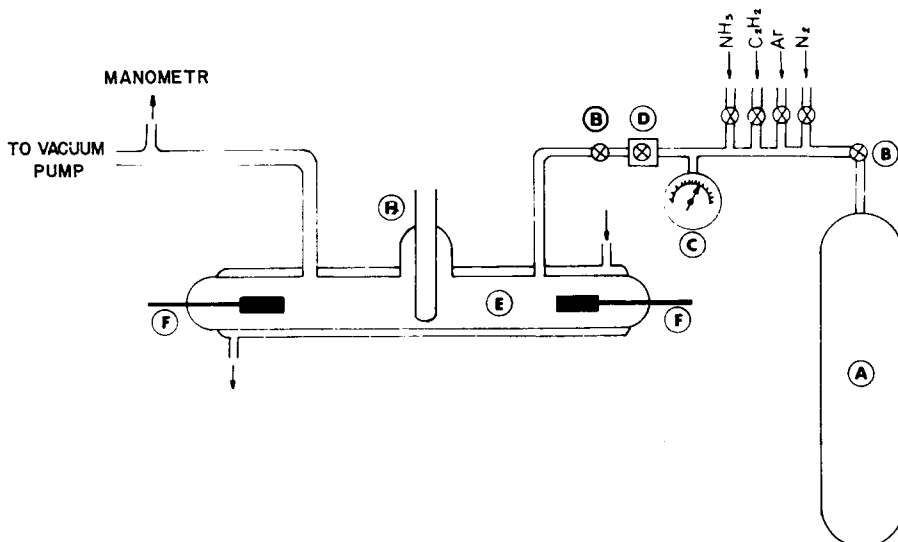

Fig. 2. Schematic representation of the glow discharge apparatus: A, gas container; B, needle valve; C, vacuum test gauge; D, pressure transducer; E, reaction cell; F, electrodes; G, quartz cell.

TABLE I
Monomer Uptake by PET[a]

Monomer	Sol. Parameter δ, $(cal/cm^3)^{1/2}$	Monomer uptake	
		DMF-treated, mole/kg	DMF-treated monomer exchanged, mole/kg
Methyl methacrylate	8.8	0.19	1.18
Styrene	9.3	0.02	1.22
4-Vinylpyridine	10.1	0.30	1.81
2-Hydroxyethyl methacrylate	11.0	0.00	1.07
2-Dimethylaminoethyl methacrylate	—	0.01	0.78
Acrylic acid	12.0	0.20	2.37

[a] PET film was treated in DMF for 15 min at 140°C.

Initiation of Free-Radical Polymerization by UV Emission Accompanied Glow Discharge. DMF-treated PET film (3 × 1.5 cm) containing 12.7% acrylic acid was kept in a quartz cell (1.1 cm O.D., 1.0 cm I.D.) parallel to the discharge current. The quartz cell was exposed for 30 min to the UV emission accompanying the nitrogen glow discharge. The quartz cell was kept at 10^{-3} torr during exposure. The flowing glow discharge conditions were used: nitrogen pressure 0.25 torr, discharge current 30 mA, discharge power 15 watts, gas flow 0.21 mmole/min.

TABLE II
Glow Discharge Initiated Polymerization of Acrylic Acid in PET[a]

Gas	Glow discharge conditions[b]			Weight loss during glow discharge		Extent of Polymerization	
	Current, mA	Power, W	Treatment time, min	PET film,[c] %	Monomer,[d] %	Film weight increase,[e] %	Polymerization yield, %
Argon	30	11.2	30	1.3	9.2	1.8	11.4
	30	11.2	5	1.8	12.7	0.0	0.0
	10	3.7	30	1.7	12.1	0.0	0.0
	10	3.7	5	2.3	15.9	0.0	0.0
Nitrogen	30	15.0	30	2.4	16.4	10.1	70.1
	30	15.0	5	1.7	12.2	1.1	7.1
	10	5.0	30	2.2	15.6	3.5	21.9
	10	5.0	5	1.8	13.2	0.0	0.0
Ammonia	30	15.0	30	2.6	18.1	0.0	0.0
	30	15.0	5	2.5	17.1	0.0	0.0
	10	5.0	30	2.9	17.7	0.0	0.0
Acetylene	30	22.5	30	2.9	17.7	0.3	1.7
	30	22.5	5	—	—	0.0	0.0
	10	7.5	30	—	—	0.0	0.0

[a] DMF-treated PET was solvent exchanged with acrylic acid. Films with 14.6 ± 0.3% weight increase were used.

[b] Glow discharge was carried at flow rate of 0.21 × 10^{-3} mole/min. Pressure in the reaction chamber during glow discharge in argon, nitrogen, ammonia, and acetylene was 0.25, 0.30, 0.50, and 0.10 torr, respectively.

[c] Before extraction with methanol.

[d] Calculated assuming that weight loss is due only to monomer loss.

[e] Weight increase after extraction with methanol.

Monomer Removal after Polymerization. After the glow discharge treatment the PET film was left for 4 hr in cold methanol and was then extracted with hot methanol for an additional 4 hr. The film was dried under vacuum for 4 hr at 60°. This procedure removed the untreated monomer, as was proved by a control experiment.

Staining the PET Film Cross Sections. Microtome cross sections of 0.2 mm were exposed to the staining solution. Excess of staining dye was removed by extraction. Poly(acrylic acid) in PET was stained by exposing the PET film cross section to a 0.5% Methylene Blue solution of isopropanol/water (1:1) at boiling temperature for 15 min. The film cross section was then extracted with boiling water for 30 min, followed by boiling methanol for additional 30 min. Poly(4-vinyl pyridine) was stained with bromine as previously described.[1] Staining of poly(dimethylaminoethyl methacrylate) was carried out in 0.5% acidified Congo Red solution in isopropanol/water (1:1) at reflux temperature for 15 min. The stained cross section was extracted as previously described.

Extent of Polymerization Advancement in the PET Film. Extent of polymerization advancement in the PET film was measured from photographs of the stained cross section which were taken at magnification of 42×.

Mechanical Properties Evaluation. Mechanical properties were determined according to ASTM D 882-67 using an Instron model 1114.

TABLE III
PET Film Weight Change during Plasma Treatment[a]

| Gas | Glow discharge conditions | | | Weight change, % |
	Current, mA	Power, W	Pressure, torr	
Argon	30	11.2	0.25	−0.2
Nitrogen	30	15.0	0.30	−0.3
Ammonia	30	15.0	0.50	−0.2
Acetylene	30	22.5	0.10	+0.1

[a] PET films were treated for 15 min at flow rate of 0.21×10^{-3} mole/min.

TABLE IV
Glow Discharge Initiated Polymerization of Vinyl Monomer in PET[a]

| Monomer | PET weight increase, % | Weight loss during glow discharge | | Extent of Polymerization | |
		PET film,[b] %	Monomer,[c] %	Film weight increase,[d] %	Polymerization yield, %
Acrylic acid	14.6	2.4	16.4	10.7	70.1
2-Dimethylaminoethyl methacrylate	10.9	0.7	7.0	8.6	77.3
2-Hydroxyethyl methacrylate	12.3	0.4	3.9	6.2	47.5
Methyl methacrylate	10.6	2.6	25.0	6.1	55.2
Styrene	11.6	2.1	18.2	7.6	62.5
4-Vinyl pyridine	14.9	1.7	11.5	4.2	25.1

[a] DMF-treated PET, which was monomer exchanged, was heated in nitrogen plasma (nitrogen flow rate 0.21×10^{-3} mole/min, pressure 0.25 torr, current 30 mA, power 15 W) for 30 min.

[b] Weight loss prior to extraction of the film with methanol.

[c] Calculated, assuming that weight loss is due to monomer loss.

[d] Weight increase after extraction with methanol.

Contact Angle Measurements.   Contact angle was determined 4 hr after glow discharge treatment and 1 min after the deposition of the water drop. Measurements were made on both sides of the water drop and were repeated five times.

RESULTS AND DISCUSSION

Successful incorporation and polymerization of vinyl monomer in PET can be accomplished only if the host polymer is in a swollen state.[1,9] Pretreatment of PET with strong interacting solvent such as DMF at high temperatures, in which the PET swollen structure is stabilized by solvent-induced secondary crystallization, was already used successfully for such purpose[1] and therefore
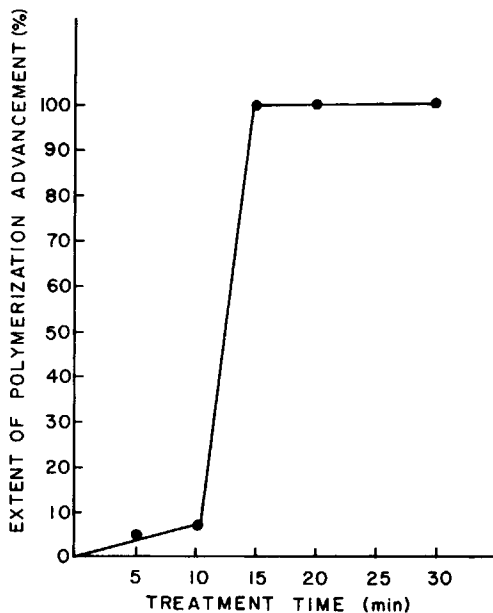

Fig. 3. Extent of acrylic acid polymerization advancement in the PET film as function of plasma treatment time. Plasma conditions: pressure 0.25 torr, nitrogen gas flow 0.21 mmole/min, discharge current 30 mA, discharge voltage 500 volts.

TABLE V
Nitrogen Glow Discharge-Initiated Polymerization of Acrylic Acid in PET[a]

Glow discharge conditions				Extent of Polymerization	
Pressure, torr	Voltage, V	Power, W	Flow rate, mole/min	Film weight increase,[b] %	Polymerization yield[c]
0.25	500	15.0	0.21	10.7	70.1
0.50	500	15.0	0.42	9.3	64.0
1.00	750	22.5	0.94	10.9	75.9
1.50	1000	30.0	1.42	9.8	67.5

 [a] PET was treated in DMF for 15 min at 140°C and was solvent exchanged with acrylic acid. Glow discharge treatment was carried for 30 min using current of 30 mA.
 [b] After extraction with methanol.
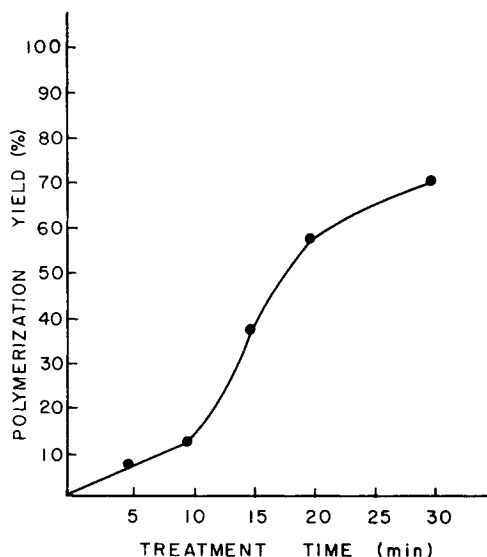 [c] Based on monomer present in PET before plasma treatment.

Fig. 4. Acrylic acid polymerization yield as function of plasma treatment time. Plasma conditions, see Fig. 3.

was adapted in this work, too. PET films were treated in DMF for 15 min at 140°C. Monomer was incorporated either by solvent exchange with the DMF in the film immediately after the pretretment or by exposing the film to the monomer after the DMF had been removed by extraction with methanol and dried. Monomer incorporation is reported in Table I. No monomer uptake was found when the PET was not treated with DMF. The DMF pretreatment of the PET film is essential for monomer incorporation. When the DMF was removed from the PET film prior to monomer incorporation, lower monomer uptake was found. Monomer uptake varied with its solubility parameter. Better results were obtained with those monomers whose solubility parameters are close to those reported for PET[10,11] (δ = 9.8, 12.1). When solvent exchange technique is used for monomer incorporation, minimal collapse of the PET-swollen structure takes place and higher monomer uptake is found. When this technique was used even those monomers whose solubility parameters deviated from those of the PET were incorporated in reasonable amounts. The solvent exchange technique was used for monomer incorporation during this work.

Glow discharge-initiated polymerization of vinyl monomers absorbed in PET film was carried out in a gas flow system using platinum electrodes and 50 Hz alternating voltage. The influence of glow discharge conditions such as the gas used, plasma power, discharge current, and treatment time on polymerization of acrylic acid and other vinyl monomers was investigated.

Glow discharge-initiated polymerization of acrylic acid in DMF-pretreated PET film was carried in plasma of argon, nitrogen, ammonia, and acetylene (Table II). Nitrogen and argon plasma are used for vinyl monomer polymerization,[12] and it was already reported that nitrogen plasma is more efficient in initiating such polymerization. Ammonia and acetylene tend to react and polymerize in the plasma.[13,14] It was of interest to find out whether they can also be used for initiation of polymerization of vinyl monomers in PET.

Extent of poly(acrylic acid) incorporation in the PET film was determined
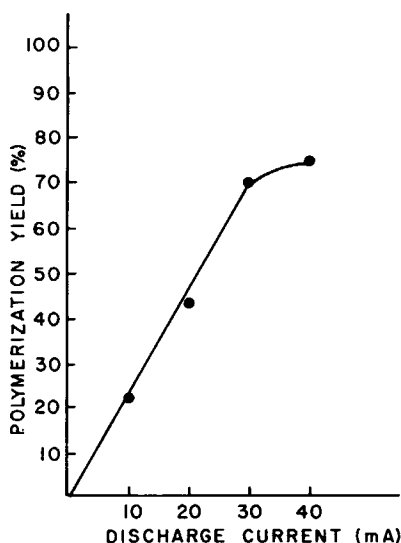
Fig. 5. Acrylic acid polymerization yield as a function of discharge current. Plasma conditions: pressure 0.25 torr, nitrogen gas flow 0.21 mmole/min, discharge voltage 500 V, treatment time 30 min.

after extraction of unreacted acrylic acid and any soluble poly(acrylic acid) with methanol. It was found that nitrogen and argon plasma initiated the polymerization of acrylic acid. Extent of polymerization initiated by nitrogen plasma was higher than that obtained with argon plasma. Ammonia and acetylene plasma failed to initiate polymerization under these experimental conditions.

Plasma treatment of PET film containing acrylic acid was accompanied by some weight loss. This weight loss may result from monomer evaporation prior and during the plasma treatment, as well as chemical degradation of the monomer and surface degradation of the PET film. It was found that surface degradation of the PET film during glow discharge is minimal (Table III). DMF-pretreated PET films were subjected to plasma treatment under the extreme conditions used in the polymerization experiments. The weight loss was much lower than that found when acrylic acid was present in the film. The small weight increase which accompanied treatment in acetylene plasma is the result of polymerization of acetylene on the film surface. The main cause for weight decrease after plasma

TABLE VI
Mechanical Properties of PET Film Containing Poly(acrylic Acid)[a]

PET film	Initial modulus, (kg/cm^2) × 10^{-3}	Yield point		Tensile strength, kg/cm^2	Break exten., %
		Stress, kg/cm^2	Exten., %		
Untreated	34.0	1020	3.0	1590	170
DMF treated	34.2	1030	3 0	1550	178
DMF treated monomer exchanged	33.3	1000	3.0	1540	175
Polyacrylic acid (8.3%)[b]	34.0	1090	3.2	1430	134

[a] Determined according to ASTM-D 882-67.

[b] Prepared by treating DMF-treated PET film containing acrylic acid for 30 min in nitrogen glow discharge at 0.25 torr, 500 V, and 30 mA.

TABLE VII
Contact Angle of Modified PET Films

PET film	Vinyl polymer present	Contact angle	
		%	Deg.
Untreated	—	0.0	63
Ammonia plasma treated[a]	—	0.0	53
Argon plasma treated[b]	—	0.0	62
Nitrogen plasma treated[c]	—	0.0	57
Nitrogen plasma treated[c]	poly(acrylic acid)[d]	10.7	42
Nitrogen plasma treated[c]	poly(2-dimethylaminoethyl methacrylate)[d]	8.6	46
Nitrogen plasma treated[c]	poly(2-hydroxyethyl methacrylate)[d]	6.2	48
Nitrogen plasma treated[c]	poly(methyl methacrylate)[d]	6.1	55
Nitrogen plasma treated[c]	polystyrene	7.6	59

[a] Glow discharge experimental conditions: pressure 0.50 torr, current 30 mA, voltage 500 V, flow rate 0.21×10^{-3} mole/min, treatment time 30 min.

[b] Glow discharge experimental conditions: pressure 0.25 torr, current 30 mA, voltage 375 V, flow rate 0.21×10^{-3} mole/min, treatment time 30 min.

[c] Glow discharge experimental conditions: pressure 0.30 torr, current 30 mA, voltage 500 V, flow rate 0.21×10^{-3} mole/min, treatment time 30 min.

[d] Polymerization conditions: pressure 0.25 torr, current 30 mA, voltage 500 V, treatment time 30 min.

treatment is monomer loss, mainly by evaporation. When PET film containing acrylic acid was left under the vacuum used for the plasma treatment, about 1% weight loss was found. Since degradation of the PET itself during plasma is negligible, it was neglected when the extent of polymerization was calculated from weight increase of the PET film after extraction of unreacted monomer and any soluble vinyl polymer.

Nitrogen plasma-initiated polymerization of several vinyl monomers in PET is reported in Table IV. Unreacted monomer was removed by extraction with methanol. Except for polystyrene and poly(methyl methacrylate), extraction removed also any soluble vinyl polymer present. Film weight increase after extraction corresponds to vinyl polymer incorporation. Good polymerization yields were generally obtained.

Plasma created by electric glow discharge contains a variety of chemically and energetically active species, such as electrons, ions, excited molecules, and free radicals. Electric glow discharge is always accompanied by UV emission. It was suggested that the UV emission may be the primary cause of free-radical formation in polymer subjected to plasma treatment. When vinyl monomer is present initiation of homo and graft polymerization takes place.[6,15,16] Treating of a PET film containing vinyl monomer by electric glow discharge will lead to the formation of free radicals which will initiate free-radical polymerization of the monomer present in the PET. Since UV emission is considered[6] to be the main cause for free-radical formation and vinyl monomer polymerization, it was interesting to try to polymerize the vinyl monomer present in the PET film just by the UV emission without exposing the PET film to other highly chemically and energetically active species present in the plasma.

PET film containing acrylic acid was kept in an isolated quartz cell which was evacuated (10^{-3} torr) and exposed to the UV emission accompanying nitrogen glow discharge. Polymerization of the acrylic acid took place. Film weight increase of 4% corresponding to 26% polymerization yield was found after ex-

traction with methanol. This polymerization yield of acrylic acid which was initiated only by the UV emission is lower than that obtained (Table IV) when PET film containing acrylic acid was treated under the same experimental conditions in nitrogen plasma.

It is not clear at this stage whether the decrease in polymerization yield is due to the absence of other highly active species present in the plasma, capable of initiating polymerization of vinyl monomers, or just due to the reduction of both intensity and energy of the UV radiation which is available to irradiate the sample.

Interaction of polymer with reactive species present in the electric glow discharge, including the UV radiation, is practically limited to the depth of about 10 μm.[2-5] When film of 350 μm width is used, interaction between the film and the plasma can be considered practically limited to the film surface. Initiation of free-radical polymerization of the vinyl monomer present in this film should be restricted only to that region. It is expected that polymerization of the vinyl monomer will occur at the film surface, where interaction between the PET and the plasma takes place. It was interesting to find out whether the glow discharge-induced polymerization can proceed all through the film cross section and thus lead to bulk modification of the PET.

PET films containing acrylic acid were left in nitrogen plasma for different lengths of time, and location of the poly(acrylic acid) in the film cross section was determined. Determination was accomplished by selective staining of the poly(acrylic acid) with Methylene Blue. The cross sections were analyzed under the microscope. It was found that at short plasma treatment time polymerization was localized at the region near the film surface. When longer treatment times were allowed, in situ polymerization took place. It could be seen that polymerization started at the film surface and later advanced inside the film. Extent of polymerization advancement in the PET film cross section was determined from the stained cross section. Its dependence on plasma treatment time is described in Figure 3.

After 15 min in nitrogen plasma, polymerization reached the film core. In situ polymerization proceeded till most of the available monomer was consumed.

The presence of monomer in the PET prior to glow discharge treatment is essential for successful bulk modification of the host polymer. It was already shown[18] that fibers in PET fabrics which were exposed to low-pressure, radiofrequency glow discharge in vapors of volatile vinyl monomers were only surface modified. By the incorporation of monomer prior to plasma treatment and by controlling the glow discharge treatment time, location of the vinyl polymer can be determined. Short treatment time will lead to a conventional surface modification, while longer treatment time will initiate in situ polymerization all through the film cross section. Under such conditions glow discharge can be used for bulk modifications of PET.

Location of poly(4-vinyl pyridine) and poly(2-dimethylaminoethyl methacrylate) in the PET film cross section was determined similarly by selective staining. Poly(4-vinyl pyridine) was selectively stained by bromine vapor and poly(2-dimethylaminoethyl methacrylate) was stained by Congo Red. Analyses of the cross section under the microscope revealed that here, too, in situ polymerization took place all through the film cross section.

The influence of nitrogen glow discharge conditions on initiation of acrylic acid in situ polymerization in PET was further studied (Table V). It was found that under the experimental conditions used, good polymerization yields were obtained which were not affected by nitrogen flow rate, pressure in the reaction cell, and the discharge voltage. Polymerization yield depended on plasma treatment time (Fig. 4). An autoacceleration behavior, typical of the well-known gel effect, was observed. In situ polymerization which was initiated by glow discharge at the film surface is carried under conditions which will lead to gel effect. Under these polymerization conditions the only source of low molecular weight mobile free radicals is limited to the film surface which is exposed to the glow discharge. Termination inside the hose polymer can take place only by reaction between propagating centers of two different growing polymers. Since mobility of these polymers is restricted, gel effect will be developed. Both time dependence of polymerization advancement in the PET cross section (Fig. 3) and polymerization yield (Fig. 4) indicate the presence of such an effect.

The other factor influencing the in situ polymerization yield is the discharge current used (Fig. 5). Linear relationship was found between discharge current and polymerization yield up to 30 mA. At this discharge current most of the monomer present was polymerized.

The glow discharge initiated in situ polymerization of vinyl monomers in PET led both to surface and bulk modification of the host polymer. It was of interest to find out to what extent bulk properties such as tensile properties and surface properties such as contact angle with water were altered.

Changes in mechanical properties and water contact angle of PET film containing poly(acrylic acid) and other polymers were determined. It was found (Table VI) that at these low levels of vinyl polymer incorporation, practically no change in PET mechanical properties took place as a result of the plasma treatment and poly(acrylic acid) incorporation.

Change in water contact angle in plasma-treated PET films and vinyl polymers containing PET films is reported in Table VII. Glow discharge treatment in ammonia and nitrogen led to a small decrease in water contact angle. Argon plasma did not change the PET contact angle. The contact angle with water of vinyl polymer-modified PET films prepared in nitrogen plasma varied with the vinyl monomer used. The presence of a polar vinyl polymer at the PET film surface led to a decrease in its contact angle with water. Best results were obtained with poly(acrylic acid).

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