

# The Effects of Selected Organic Solvents on the Polymerization of Acrylic Acid to Poly(ethylene Terephthalate) by Glow Discharge

YOU-LO HSIEH, COLLEEN PUGH,\* and M.S. ELLISON,† *Division of Textiles and Clothing, University of California, Davis, California 95616*

## Synopsis

Six organic solvents with solubility parameters close to those of poly(ethylene terephthalate) (PET), namely, dimethyl sulfoxide,  $\gamma$ -butyrolactone, dimethyl formamide, pyridine, tetrachlorethane, and chlorobenzene, were selected as swelling agents to promote the incorporation and the subsequent polymerization of acrylic acid to PET films. Variables studied included time of swelling, temperature of swelling, and length of glow discharge treatment. Elevated temperature had greater effects on the inclusion of the swelling agents and acrylic acid than did the length of swelling. Polymerization was generally increased with longer glow discharge treatment time. Surface wettability as well as the moisture regain values of PET films were greatly improved by both the solvent and the glow discharge treatments. The solvent-assisted glow discharge polymerization process was found to impose modification of PET films not restricted to the surface. Morphological modification of the treated PET was confirmed by DSC data.

## INTRODUCTION

High energy radiation and chemical and thermal energy have been well studied for inducing polymerization of various monomers to polyester. With high-energy radiation, it is generally known that the bulk properties of the host polymer are affected as a result of degradation and/or crosslinking reactions. Effective polymerization has usually been achieved under elevated temperature for extended reaction time, and generally a small amount of stable polymer is formed.<sup>1</sup> Other energy sources which impose minimal changes on the physical integrity of the polymer substrate and yet are still effective in initiating polymerization are, therefore, of particular interest.

Glow discharge, as a less ionizing "cold plasma" energy source, has the capability of producing sufficiently energetic species to cause the rupture of molecular bonds at ambient temperature.<sup>2</sup> The distinguishing characteristic of the glow discharge is that chemical reactions induced by partially ionized gas and/or gases are limited only to the surface. The depth of penetration, a few hundred angströms, is much smaller than that of high-energy radiations.<sup>3</sup> These characteristics of glow discharge have enabled applications in both surface modification and in *in situ* polymer synthesis.<sup>3-6</sup>

Surface modification of polymers are usually introduced by glow discharge of non-polymer-forming gases, such as oxygen, nitrogen, inert gases,

\* Current address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44118.

† Current address: School of Textiles, Clemson University, SC 29631.

and reactive gases.<sup>7-9</sup> Changes on the polymer surfaces were found to be highly dependent upon the types of gases and the conditions of plasma generation.<sup>10,11</sup> Monomers with desirable functional groups have also been polymerized to the polymer to improve wetting characteristics<sup>9,12</sup> and biocompatibility.<sup>13</sup>

Substantial polymerization can be easily achieved by glow discharge. However, most of the polymers formed were merely deposited on the surface and could be removed by extraction.<sup>14</sup> Little attempt has been made to enhance the stability of the newly formed polymer on the substrate. In addition, limited research has been done in using glow discharge to induce polymerization on PET.

In a heterogeneous polymer-monomer reaction system, diffusion controls chain growth and chain termination in the internal structures of the polymer. One way of facilitating diffusion is to open up the physical structure of the polymer by swelling to allow the monomer to enter in sufficient quantities. Radiation and chemical induced polymerization of some vinyl monomers in PET has been promoted in the presence of organic solvents, such as DMF,<sup>15</sup> DMSO, and pyridine,<sup>1,15</sup> methanol, and 1,2-dichloroethane.<sup>16,17</sup>

Many solvents have been recommended as separate swelling agents for radiation graft polymerization onto PET, among them methanol<sup>18</sup> and various chlorinated hydrocarbons, such as ethylene dichloride,<sup>19-22</sup> 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane.<sup>20-23</sup> Aqueous solutions have also been recommended. They include DMSO and water mixtures for grafting styrene to PET, and water mixtures of dichloroethane and tetrachloroethane for grafting vinyl monomers to PET.<sup>20</sup>

Preferential interaction solvents whose solubility parameters ( $\delta$ ) are close to those of PET are thought to provide the necessary chemical energy to disrupt intermolecular cohesive forces between the polymer chains and to permit chain mobility.<sup>18,24</sup> It has been shown that organic solvents with  $\delta$  near the estimated  $\delta$  of amorphous PET ( $\delta = 10.7$ ) induce appreciable crystallinity in the polymer.<sup>22,25</sup> However, it was thought that the use of this solubility parameter may not provide a sufficient indication of the solvent's capability to interact with PET. A study of the longitudinal shrinkage and volume swelling of PET in various solvents further suggested that PET may be considered as a  $(AB)_x$  alternating copolymer, where A is a semirigid aromatic segment  $-\text{CO}-\text{C}_6\text{H}_4-$  with a  $\delta$  value of 9.8 and B is a flexible aliphatic ester  $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$  with a  $\delta$  value of 12.1.<sup>24</sup> Results from a study in which organic solvents were found to induce crystallization in unoriented amorphous PET, with maximum density changes in solvents with  $\delta$  around 9.5 and 12.0, confirmed these statements.<sup>24</sup>

Certain strongly interacting solvents such as DMF, tetrachloroethane, and  $\gamma$ -butyrolactone were found to induce irreversible modifications of PET at elevated temperature.<sup>26</sup> At low temperature, only small crystallites were formed, and, upon removal of the solvent, the swollen structure was not supported by the small crystallites and collapsed. At high temperature, 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 while the PET structure was swollen.<sup>14</sup> The formation of pores and voids in the PET

structure was hypothesized, and significant increases in dye uptake and diffusion rate was observed.<sup>26-28</sup>

The present study investigates the use of selected organic solvents as swelling agents to promote the diffusion and incorporation of the monomer and the subsequent polymerization of acrylic acid by nitrogen glow discharge. The enhancing effects of these solvents on the durability of the glow discharge induced polymerization to the PET substrates are evaluated. The hygroscopic characteristics of the modified PET are also studied.

## EXPERIMENTAL

Poly(ethylene terephthalate) (PET) materials used in this study were Mylar films (DuPont). Six solvents with solubility values ( $\delta$ ) close to those of PET (9.5 and 12.0) and to the total solubility values of PET (10.5) were all reagent grade (Table I).

PET films (1.5 cm  $\times$  4.0 cm) were cleaned and degreased by rinsing in trichloro-trifluoro-ethane (CFC1<sub>2</sub>-CC1F<sub>2</sub>). The initial sample weight ( $W_i$ ) was obtained after drying the cleaned film under vacuum at 105°C for 4 h. Variables in swelling conditions included two elevated temperatures, 100°C and 140°C, and three swelling times, 10, 30, and 60 min. A temperature-controlled silicone oil bath was employed for heating. It has been reported that complete removal of the swelling agent decreased the monomer uptake in PET.<sup>12</sup> Therefore, only solvent on the film surface was removed by blotting between filter paper.

Sensitizer in acrylic acid was removed by passing through neutral activated alumina. The solvent treated specimens were then exchanged with acrylic acid for six days. A high monomer to polymer ratio of 100 mL acrylic acid to 1 g PET was selected to provide sufficient monomer for exchange with solvents. The specimens were then blotted with filter paper to remove extra monomer, and the weights of the monomer exchanged films obtained.

Polymerization of acrylic acid incorporated in the PET substrates was induced by glow discharge using a radio frequency plasma reactor<sup>29</sup> with a continuous flow of nitrogen at 0.2 torr. The lengths of glow discharge treatment ranged from 0.5 to 10 min. And the power level was maintained at 30 W.

Residual solvent, monomer, and unstably bonded oligomers and polyacrylic acid were removed from the film substrates by hot methanol extraction for 4 h. The films were dried in air and then under vacuum at 105°C for 4 h again. Sample weight after each treatment during the entire process, i.e., solvent treatment ( $W_{\text{solv}}$ ), monomer exchange ( $W_{\text{aa}}$ ), glow dis-

TABLE I  
Organic Swelling Agent

Swelling agents	Solubility parameter ( $\delta$ )	Boiling point (°C)
Dimethyl sulfoxide (DMSO)	12.93	189
$\gamma$ -Butyrolactone	12.78	206
Dimethyl formamide (DMF)	12.14	153
Pyridine	10.61	115
Tetrachloroethane	9.85	147
Chlorobenzene	9.57	131

charge ( $W_{gd}$ ), and extraction/drying ( $W_{ext/dry}$ ) was monitored so that the effects of all treatments could be analyzed.

Surface wettability of the films was determined by water contact angle measurement with a goniometer. Ten measurements, each with 0.5  $\mu\text{L}$  droplet of triply deionized distilled water, were made for each specimen. The conditioned weights ( $W_{cond}$ ) of films were obtained after conditioning at 21°C and 65% RH for 48 h.

Differential scanning calorimetry (DSC) was performed using a Mettler TA2000 on the untreated PET and the modified films. The modified films were solvent treated at 100°C for 30 min and glow discharged for 10 min. A heating rate of 10°C/min and small samples of approximately 1.8 mg were used to determine the melting temperature ( $T_m$ ), heat of fusion ( $\Delta H$ ), and the decomposition temperature ( $T_{decomp}$ ). Samples of 1 magnitude larger were used at a heating rate of 5°C/min in determining the glass transition temperature ( $T_g$ ) and the heat capacity ( $\Delta C_p$ ) of the materials. Samples used for  $T_g$  and  $\Delta C_p$  were first heated to 325°C and rapidly cooled to room temperature under nitrogen prior to thermal analysis.

## RESULTS AND DISCUSSION

### Solvent and Monomer Inclusion

The uptake of solvents and of acrylic acid in PET (Table II) was calculated from the specimen weight changes after the solvent treatment and monomer exchange processes as

$$\text{solvent inclusion, } \delta W_{\text{solv}}, \% = (W_{\text{solv}} - W_i) / W_i \times 100 \quad (1)$$

$$\text{acrylic acid inclusion, } \delta W_{\text{aa}}, \% = (W_{\text{aa}} - W_i) / W_i \times 100 \quad (2)$$

At 100°C, both the solvent inclusion and monomer incorporation in the films increased with increased lengths of solvent treatment time with all solvents but pyridine. The increases with DMF were not as drastic as other solvents. Specimen weights were further increased after exchange with acrylic acid for each solvent treatment. This was observed at all three temperatures. However, it was more obvious at 20°C, as compared to the elevated temperatures. Exceptions could be found with tetrachloroethane and pyridine at 100°C. At this condition, monomer inclusion was several times higher than the solvent inclusion for pyridine whereas monomer inclusion was considerably less than solvent inclusion for tetrachloroethane. At 100°C, monomer inclusion was found to increase in the order pyridine, tetrachloroethane, DMF, chlorobenzene,  $\gamma$ -butyrolactone, and MSO.

Since the boiling points of pyridine, tetrachloroethane, and chlorobenzene are below 140°C, treatments in these three solvents were not performed at 140°C. Both solvent and monomer inclusion in the films were considerably higher at 140°C than at 100°C for DMSO,  $\gamma$ -butyrolactone, and DMF. Higher temperature does have a greater effect on the incorporation of solvent and monomer in films. However, neither solvent nor monomer incorporation was found to be dependent on the solvent treatment time at 140°C. Treat-

TABLE II  
Solvent and Acrylic Acid Inclusion (Weight Gain, %)

Solvent	$\delta$	Swelling time (min)	100°C/24 h		140°C/24 h		20°C/24 h	
			SOLV	AA	SOLV	AA	SOLV	AA
DMSO	12.93	10	2.4	4.1	15.8	20.7	0.6	1.9
		30	4.7	6.9	15.5	13.2		
		60	6.9	8.7	12.8	12.3		
$\gamma$ -Butyrolactone	12.78	10	3.9	5.8	17.8	19.6	0.4	6.1
		30	7.6	9.1	19.5	17.7		
		60	11.3	11.9	13.4	12.7		
DMF	12.14	10	7.6	11.4	17.9	20.4	0.7	8.0
		30	8.6	11.2	12.4	17.9		
		60	9.5	12.5	10.3	15.5		
Pyridine	10.61	10	11.1	81.1	—	—	4.5	15.4
		30	10.7	88.4	—	—		
		60	11.7	86.3	—	—		
Tetrachloroethane	9.85	10	21.0	12.9	—	—	1.6	2.4
		30	28.2	14.8	—	—		
		60	41.7	19.5	—	—		
Chlorobenzene	9.57	10	5.0	7.3	—	—	5.4	12.1
		30	9.4	9.4	—	—		
		60	11.4	11.4	—	—		

ment for 10 min actually resulted in higher monomer inclusion than the longer treatment times.

### Glow Discharge Treatment

The weights of solvent treated and monomer exchanged specimens were lowered with the glow discharge treatment. The reduction in weight was due to the removal of immediate glow discharge products at the film surface by the continuous flow of nitrogen in the chamber.  $\delta W_{gd}/\delta W_{aa}$  ratios calculated according to

$$\frac{\delta W_{gd}}{\delta W_{aa}} = \frac{W_{gd} - W_i}{W_{aa} - W_i}$$

describe the fractions of acrylic acid remaining on the film after glow discharge. For each solvent system, the swelling temperatures, swelling time, and the lengths of glow discharge did not seem to affect these fractions in any specific fashion (Table III).

Differences among these six solvents were observed, however. Figure 1 shows the ratios  $\delta W_{gd}/\delta W_{aa}$  plotted against glow discharge time for films treated with these solvents at 100°C for 30 min. This seems to suggest that these solvents penetrate and/or introduce monomers into PET substrate to different degrees. Since the glow discharge reacts with only the surface

TABLE III  
 $\delta W_{gd}/\delta W_{ca}$  Fraction

Solvent	Swelling time (min)	Glow discharge time (min)											
		100°C						140°C					
		0.5	2	5	10	$\bar{X}$	(SD)	0.5	2	5	10	$\bar{X}$	(SD)
DMSO	10	0.91	0.88	0.88	0.89	0.88	(0.01)	0.78	0.73	0.64	0.73	0.72	(0.06)
	30	0.95	0.92	0.92	0.86	0.91	(0.04)	0.66	0.69	0.65	0.63	0.66	(0.03)
	60	0.92	0.88	0.84	0.84	0.87	(0.04)	0.75	0.76	0.75	0.70	0.74	(0.03)
$\gamma$ -Butyrolactone	10	0.75	0.71	0.73	0.74	0.73	(0.02)	0.68	0.72	0.70	0.69	0.70	(0.02)
	30	0.86	0.87	0.79	0.84	0.84	(0.04)	0.55	0.68	0.64	0.99	0.72	(0.19)
	60	0.78	0.85	0.75	0.67	0.76	(0.07)	0.92	0.88	0.82	0.88	0.88	(0.04)
DMF	10	0.85	0.88	0.71	0.73	0.79	(0.09)	0.67	0.68	0.58	0.65	0.65	(0.05)
	30	0.82	0.78	0.74	0.72	0.77	(0.04)	0.66	0.69	0.65	0.63	0.66	(0.03)
	60	0.79	0.77	0.71	0.68	0.74	(0.05)	0.75	0.76	0.75	0.70	0.74	(0.03)
Pyridine	10	0.95	0.95	0.93	0.91	0.94	(0.02)	—	—	—	—	—	—
	30	—	—	—	—	—	—	—	—	—	—	—	—
	60	0.94	0.91	0.88	0.85	0.90	(0.04)	—	—	—	—	—	—
Tetrachloroethane	10	0.51	0.42	0.51	0.49	0.48	(0.04)	—	—	—	—	—	—
	30	0.75	0.69	0.65	0.59	0.67	(0.07)	—	—	—	—	—	—
	60	0.38	0.34	0.31	-0.21	0.31	(0.70)	—	—	—	—	—	—
Chlorobenzene	10	0.75	0.76	0.71	0.71	0.73	(0.03)	—	—	—	—	—	—
	30	0.92	0.86	0.87	0.85	0.88	(0.03)	—	—	—	—	—	—
	60	0.82	0.80	0.79	0.70	0.78	(0.03)	—	—	—	—	—	—

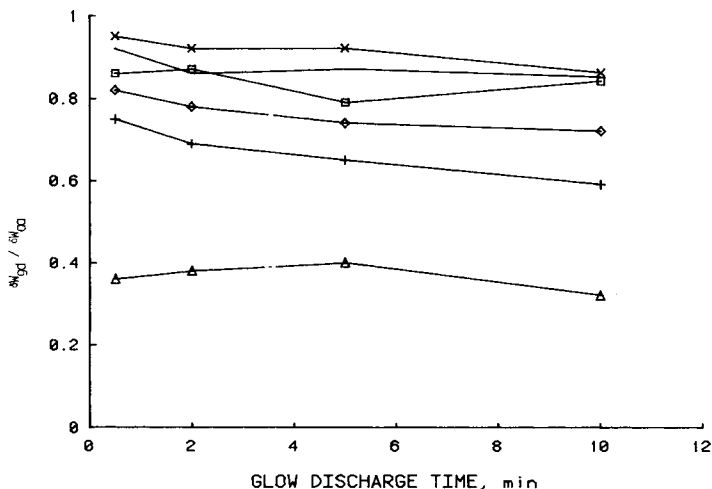


Fig. 1. Fraction of  $\delta W_{gd}/\delta W_{aa}$  of glow discharge polymerized PET films: (x) DMSO; (◇) DMF; (□)  $\gamma$ -butyrolactone; (— · —) chlorobenzene; (+) tetrachloroethane; (△) pyridine.

layer of the substrates, higher  $\delta W_{gd}/\delta W_{aa}$  values seemed to suggest more thorough penetration with solvents and/or monomer in the films.

### Polymerization Yield

The extent of polymerization was calculated as the relative weight after hot methanol extraction and drying.

$$\text{polymerization yield (\%)} = (W_{\text{ext-dry}} - W_i) / W_i \times 100 \quad (3)$$

Data calculated according to eq. (3) represent the glow-discharge-induced polymerization stably adhering to the film (Table IV). A general trend observed was that polymerization yield increased with increasing glow discharge time. This observation agrees with results from another study.<sup>12</sup> Exceptions were found, however, that the maximum polymerization yields were reached at 2-min glow discharge time for  $\gamma$ -butyrolactone and DMF treatment (10 min) and at 5-min glow discharge time for pyridine treatment (30 and 60 min). Also, the 60-min treatment with tetrachloroethane actually resulted in a monotonic decrease in weight as glow discharge time increased. Weight loss was also observed at longer solvent time and shorter glow discharge time at 140°C.

The portion of the incorporated acrylic acid that is stably polymerized onto the PET substrates could be demonstrated by the fraction  $\delta W_{\text{ext-dry}}/\delta W_{gd}$ , whereas

$$\delta W_{\text{ext-dry}} = W_{\text{ext-dry}} - W_i, \delta W_{gd} = W_{gd} - W_i$$

Figure 2 shows that the stability of polymerization was proportionally increased with the length of glow discharge treatment time. The treatments with  $\gamma$ -butyrolactone, chlorobenzene, and tetrachloroethane behaved very similarly. Pyridine leveled off after 5 min. The most drastic increases in

TABLE IV  
 Polymerization Yield (%)

Solvent	Swelling time	Glow discharge time (min)											
		100°C						140°C					
		0	0.5	2	5	10	10	0	0.5	2	5	10	
DMSO	10	0.35	0.65	4.66	5.58	7.65	0.31	2.49	3.99	9.38	12.84		
	30	4.35	4.06	5.77	5.77	10.17	-1.34	-1.24	0.57	6.54	8.04		
	60	1.08	0.83	5.66	10.97	12.97	-1.29	-1.46	0.86	5.12	7.37		
$\gamma$ -Butyrolactone	10	0.40	0.24	0.32	0.55	2.04	1.06	0.94	3.57	10.30	13.10		
	30	0.87	0.73	1.02	2.17	3.97	-1.27	-1.21	0.57	8.04	9.78		
	60	1.16	1.60	7.56	3.22	1.29	-1.22	8.60	3.60	6.20	8.50		
DMF	10	3.27	2.18	9.70	2.84	4.47	-1.30	0.20	1.10	5.80	11.30		
	30	0	0	0.59	4.17	6.22	-3.78	-3.78	-3.48	-6.48	3.12		
	60	0.08	0.08	0.07	1.33	7.26	-1.96	-1.84	-0.49	4.72	7.92		
Pyridine	10	37.9	40.8	42.8	45.4	55.1							
	30	33.1	28.7	45.7	47.5	43.6							
	60	18.3	32.2	20.4	42.5	30.7							
Tetrachloroethane	10	0	0	0.09	0.92	2.21							
	30	0.16	0.48	0.19	3.17	4.98							
	60	2.59	-2.30	-2.26	-3.18	-8.92							
Chlorobenzene	10	0.72	0.56	0.82	1.50	3.67							
	30	0.92	1.57	0.80	1.67	3.69							
	60	0.94	1.00	1.28	3.29	6.96							



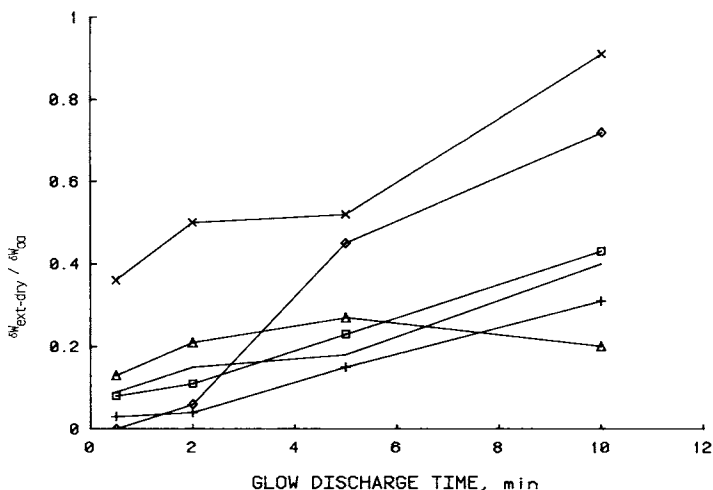


Fig. 2. Fraction of  $\delta W_{\text{ext-dry}} / \delta W_{\text{aa}}$  of glow discharge polymerized PET films: (x) DMSO; (◇) DMF; (□)  $\gamma$ -butyrolactone; (—) chlorobenzene; (+) tetrachloroethane.

polymerization with glow discharge time were found with DMF and DMSO. With the exception of  $\gamma$ -butyrolactone, the data seem to suggest that more effective polymerization was induced by solvents whose solubility parameters are close to the flexible chains of PET.

### Moisture Regain

The untreated PET film has a moisture regain value of 0.40 experimentally. Table V contains the moisture regain data of the treated films. These solvents alone had differing effects on the moisture regain of the PET substrates. The moisture regain of DMF treated films at 100°C was not affected much whereas  $\gamma$ -butyrolactone and chlorobenzene treatments resulted in a slight increase in moisture regain. DMSO and tetrachloroethane doubled the moisture regain of the PET substrates. The moisture regain of pyridine treated films was approximately eight times higher than the untreated. Elevated temperature also resulted in different effects on the moisture regain for the three solvents studied. A  $\gamma$ -butyrolactone treatment at 140°C produced a PET film with a slightly lower moisture regain. The moisture regain of DMSO treated films at 140°C remain the same as at 100°C. And, the only positive effect was with DMF of which the moisture regain increased by a factor of 2.5.

With the pyridine and tetrachloroethane systems, the solvents seem to be the more dominant factors than the glow discharge treatments: The moisture regains of films were affected by the solvents, but they were not further affected by the glow discharge processes. Except for the pyridine and tetrachloroethane treatments, moisture regains of the polymerized films generally increased with glow discharge time. This observation seems to suggest that moisture regain values of the treated films are related to the extend of polymerization. At the higher temperature of 140°C, the effects of the subsequent glow discharge became more prominent as the moisture regain of films increased with the increasing glow discharge time. The



improvement of moisture regains of films for the three higher boiling point solvents also seems to be greater at 140°C than at 100°C.

### Surface Wettability

Surface wettability measured by water contact angle showed a water contact angle of 71.8° for the untreated films. From Table VI, the solvent-monomer processes at both treatment temperatures apparently increased the films surface wettability. As glow discharge time increased, surface wettability of the films was further improved. The improvement in wettability was found not to be linearly related to the glow discharge time. Better wettability was found at 140°C except for the DMF-treated films glow discharged for 10 min.

### Thermal Properties

The effects of the solvent treatment and the polymerization process on the bulk properties of PET can be shown by the changes in its thermal properties. Glass transition temperature and associated heat capacity change, melting temperature and heat of fusion of melting, and the decomposition temperature of the fibers are summarized in Table VII. The lower  $T_g$  values of the modified PET films could be explained by the plasticizing effects of the trapped oligomers and the additive effects of the newly formed polymer. The lower heat capacities of the modified films reflected the lessened mobility of the polymer chains. The reduction in chain mobility could be due to the new crosslinked polymer and the possible grafting on the PET chains. The decreases of  $T_m$  could be indication for smaller crystallites, but the magnitude of temperature changes did not justify this. Lower  $\Delta H$  is usually associated with lower crystallinity. Since these solvents have shown to induce higher crystallinity in PET,<sup>14,22,25</sup> other morphological modification of the treated PET may have been induced by the heat treatment and the polymerization process.

### CONCLUSION

The swelling effects examined by the incorporation of solvent and monomer in the PET substrates are different among the six organic solvent studied. At 100°C, longer solvent treatment resulted in higher inclusion of solvents and monomer with exception of the pyridine group. Greater incorporation of solvents and acrylic acid was found for all solvents at a higher temperature of 140°C. However, time of swelling was not a dependent factor. Polymerization was proportionally higher with the increases of glow discharge treatment time. DMSO and DMF treated films had the highest rate of polymerization.

The solvent treatment itself may induce a higher moisture regain, such as DMSO at 100°C and 140°C, DMF at 140°C, and pyridine and tetrachloroethane at 100°C. The most drastic change was the increase of 0.40–3.31 by pyridine. While the extent of polymerization remained unchanged with glow discharge time for pyridine and tetrachloroethane, it increased proportionally with time for the other four solvent systems.



TABLE VII  
Thermal Properties

Solvent <sup>a</sup> treatment	$T_g$	$\Delta C_p$	$T_m$	$\Delta H$	$T_{decomp}$
Untreated	79.0	10.2	259.1	-49.4	443
DMSO	75.2	9.7	253.0	-34.1	444
$\gamma$ -Butyrolactone	72.5	8.8	254.6	-41.4	440
DMF	72.5	7.9	252.8	-37.1	437
Pyridine	71.5	7.1	256.6	-28.8	440
Tetrachloroethane	72.5	8.8	255.2	-46.9	437
Chlorobenzene	72.5	8.5	254.1	-38.2	442

<sup>a</sup> PET films were solvent treated at 100°C for 20 min and glow discharge for 10 min.

The proportional increases of polymerization and moisture regain with exposure time in glow discharge seems to suggest that these solvent-assisted polymerization processes impose modification on PET films not restricted to the surface as with normal gaseous glow discharge treatment. The lowering of glass transition temperature, heat capacity, and the heat of fusion also indicated internal morphological modification in the treated films.

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