

## Liquid-Induced Crystallization of Poly(ethylene Terephthalate)

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### Synopsis

Amorphous unoriented poly(ethylene terephthalate) was crystallized at 25°C by various organic liquids. The crystallinity induced in the amorphous polymer was measured by differential scanning calorimetry and infrared spectroscopy. The ability of liquids to interact with and induce crystallinity in the amorphous polymer was classified on the basis of their solubility parameters. Measurements of the density of liquid-crystallized 0.8-mil films of poly(ethylene terephthalate) indicated the presence of extensive internal voids in the semicrystalline polymer matrix. Comparison of differential scanning calorimetric thermograms and infrared spectra of heat-crystallized and liquid-crystallized polymer indicated significant differences in the polymer morphologies induced by the two crystallization processes.

### Introduction

Amorphous poly(ethylene terephthalate) polymer (PET) is readily crystallized by immersion in numerous liquids at room temperature. The diffusion of liquid into the amorphous polymer apparently secures a freedom of movement for chain segments and allows suitable juxtaposition of chain segments for crystallization to occur. Sheldon<sup>1,2</sup> has measured the rate of benzene-induced crystallization of amorphous PET and deduced that localized crystallization occurs along the front accompanying diffusion of liquid into the polymer. The rate of heat-induced crystallization of amorphous PET has been reported to be adequately described by the Avrami treatment.<sup>3,4</sup>

A number of isolated experimental observations have been reported which reflect apparent differences in the morphologies of heat- and liquid-crystallized PET. The solubilities of liquids in the liquid-crystallized polymer are reported to be higher than in the heat-crystallized polymer;<sup>5,6</sup> microscopic voids have been observed in the liquid-crystallized polymer,<sup>7</sup> and mechanical properties of the liquid-crystallized polymer are reported to differ from those of heat-crystallized polymer.<sup>6,8</sup>

### Experimental

The poly(ethylene terephthalate) polymer (PET) was a melt-cast 0.8-mil film which had an intrinsic viscosity in tetrachloroethane-phenol at 30°C of

0.56, a diethylene glycol content of 1.44 mole-%, and a ratio of weight-average to number-average molecular weight of 1.6–1.7. Density, infrared, and x-ray diffraction measurements indicated that the film was amorphous and unoriented. The liquids used in the study were reagent grade.

Unrestrained samples (0.1 g) were crystallized by immersion in liquid (25 ml) at 25°C for 48 hr. Preliminary measurements indicated that a 48-hr immersion period was sufficient time for a steady-state crystallinity to be induced by the liquids studied. This was followed by extraction of imbibed liquid in ethanol at 25°C and drying under vacuum at room temperature. The drying procedure was carefully monitored by calorimetric and gravimetric means to insure complete removal of imbibed liquids. Ethanol does not induce crystallinity in the amorphous polymer at 25°C. Annealing treatments were carried out in a forced-convection oven controlled to  $\pm 1.0^\circ\text{C}$ .

Infrared spectra were determined on a Perkin-Elmer Spectrophotometer Model 337. Densities were measured by flotation in a *n*-heptane–carbon tetrachloride density gradient column at 25°C. Some of the density measurements were reproduced by using the titration-flotation method of Moore and Sheldon.<sup>9</sup> The x-ray measurements were made by the method of Dumbleton and Bowles.<sup>10</sup> Thermograms of samples were determined on a Perkin-Elmer differential scanning calorimeter, Model 1B, at a heating rate of 40°C/min. A rapid heating rate was employed to minimize possible annealing of crystalline structures in the polymer while it is being heated in the calorimeter. Quantitative fusion data were obtained in the following way. Tangents to the baseline were drawn on both sides of the transition. A straight line was used to connect the two sides at the points where the baseline departed from the tangent. The area enclosed by this straight line and the curve outlining the transition peak was measured with a planimeter. The calorimeter was calibrated with indium, tin, and lead standards.

Reported measurements are average values from three or more replicate samples. The infrared relative intensities were reproducible to  $\pm 2\%$ ; densities, to  $\pm 0.1\%$ ; thermal transitions, to  $\pm 3\%$ . The peak maxima of thermal transitions were reproducible to  $\pm 1^\circ\text{C}$ .

## Results

This investigation extends the number of liquids which have previously been reported to induce crystallinity in PET and compares the degree of crystallinity induced in the polymer as measured by infrared spectroscopy, calorimetry, and density. The intensity of the 973  $\text{cm}^{-1}$  infrared absorption band (a C-O stretching mode of the ethylenedioxy linkage in the *trans* conformation) relative to the intensity of the 795  $\text{cm}^{-1}$  absorption band (a normal mode of the *p*-benzenoid linkage, used to correct for thickness

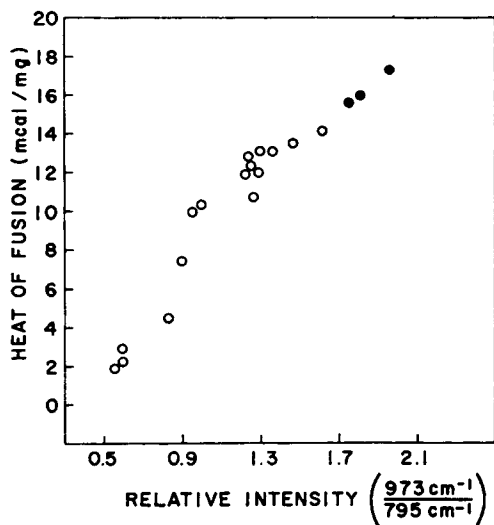


Fig. 1. Relationship between heat of fusion and intensity of  $973 \text{ cm}^{-1}$  infrared band relative to  $795 \text{ cm}^{-1}$  band; O, liquid-crystallized; ●, liquid-crystallized and subsequently heat-treated.

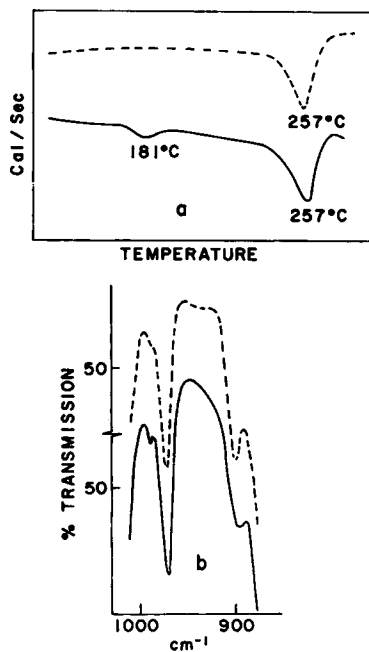


Fig. 2. Comparison of PET crystallized by heat and acetone to 30% degree of crystallinity: (a) thermograms; (b) infrared spectra of (—) heat-crystallized and (---) acetone-crystallized material.

TABLE I  
Intensity of 973  $\text{cm}^{-1}$  Absorption Band in PET Relative to  
Intensity of 795  $\text{cm}^{-1}$  Band after Liquid Interaction

Liquid	Relative intensity $\left(\frac{973 \text{ cm}^{-1}}{795 \text{ cm}^{-1}}\right)$
A. Nonpolar liquids; $8.5 < \delta < 10.0$ ; $0 < p < 0.16$	
1,4-Dioxane	1.85
Dichloromethane	1.79
1,2-Dibromoethane	1.67
Methyl acrylate	1.53
Toluene	1.51
Benzene	1.47
Monochlorobenzene	1.39
Ethyl formate	1.32
Isopropylbenzene	1.30
Ethyl acetate	1.30
Dimethyl <i>o</i> -phthalate	1.27
1,2,4-Trichlorobenzene	1.26
<i>m</i> -Xylene	1.24
<i>o</i> -Xylene	1.23
Amyl acetate	1.17
Butyl acetate	1.15
Carbon disulfide	1.13
<i>p</i> -Xylene	1.05
Ethyl benzene	1.03
Diethyl <i>o</i> -phthalate	0.83
B. Polar liquids; $9.0 < \delta < 13.5$ ; $0.25 < p < 0.85$	
Benzyl formate	1.80
Acetophenone	1.75
Nitrobenzene	1.71
Anisaldehyde	1.68
Benzaldehyde	1.66
<i>N,N</i> -Dimethylaniline	1.63
<i>N,N</i> -Dimethylformamide	1.62
<i>o</i> -Nitrotoluene	1.60
Pyridine	1.57
Methyl benzoate	1.54
Nitroethane	1.41
<i>p</i> -Methylacetophenone	1.40
Methyl ethyl ketone	1.38
Acrylic acid	1.37
Dimethyl sulfoxide	1.36
Nitromethane	1.35
Acetaldehyde	1.35
Acetone	1.27
Acrylonitrile	1.26
Cyclohexanone	1.25
2-Nitropropane	1.24
Acetonitrile	1.23
Isobutyraldehyde	1.21
Acetic acid	1.20
Formic acid	1.20

TABLE I (continued)

Liquid	Relative intensity $\left(\frac{973 \text{ cm}^{-1}}{795 \text{ cm}^{-1}}\right)$
C. Hydrogen-bonded liquids; $\delta > 10$ ; $p > 0.05$	
Benzyl alcohol	1.27
Isobutanol	0.73
Ethylene glycol	0.73
Formaldehyde (36%)	0.72
Isodecanol	0.71
Isopropanol	0.68
1-Hexanol	0.65
Thiodiethyleneglycol	0.64
2-Ethyl-1-hexanol	0.64
Cyclohexanol	0.57
1-Pentanol	0.57
Methanol	0.57
Ethanol	0.56
1-Butanol	0.55
1,4-Butanediol	0.54
2-Butanol	0.54
Water	0.54
Isopentanol	0.54
D. Liquids having low solubility parameters; $\delta < 9$ ; $p < 0.10$	
<i>n</i> -Heptane	0.72
Decahydronaphthalene	0.68
1-Amino-2-ethylhexane	0.64
<i>n</i> -Hexane	0.62
Cyclohexane	0.62
Triethylamine	0.62
Tetralin	0.61
Carbon tetrachloride	0.60
Diethyl ether	0.60
<i>n</i> -Octane	0.60

variations) is a convenient measure of degree of crystallinity in thin films of PET.<sup>3,11</sup>

In Figure 1, the heats of fusion of PET films crystallized by immersion in liquids for 48 hr are plotted as a function of the relative intensity of the 973  $\text{cm}^{-1}$  absorption band. Specimens possessing a degree of crystallinity less than 25% undergo a "cold crystallization" exotherm during the calorimeter run. The melting endotherm therefore measures this crystallinity as well as that induced by treatment with organic liquid. The enthalpy change corresponding to fusion of crystallinity induced in the polymer by organic liquid was estimated by subtracting the enthalpy change associated with the cold crystallization exotherm from that of the fusion endotherm. It should also be pointed out that the thermograms of the liquid-crystallized specimens exhibited a single melting endotherm, while the thermograms of

the liquid-crystallized and subsequently heat-treated specimens exhibited double endotherms (Fig. 2a). The heats of fusion in Figure 1 of the liquid-crystallized and subsequently heat-treated specimens are the sums of the enthalpy changes of the two endotherms.

The intensity of the  $973\text{ cm}^{-1}$  absorption band appears to measure approximately the same crystalline population as the heat of fusion. Relative intensities of the  $845\text{ cm}^{-1}$  absorption band,<sup>11</sup> which is also characteristic of the crystalline phase of the polymer, and of the  $898\text{ cm}^{-1}$  band,<sup>11</sup> which is characteristic of the amorphous phase, gave results in agreement with those of the  $973\text{ cm}^{-1}$  band.

In Table I are listed the relative intensities of the  $973\text{ cm}^{-1}$  absorption band of PET after crystallization by liquids. The liquids are classified on the basis of their solubility parameter  $\delta$  and fractional polarity  $p$ .

$$\delta^2 = (\Delta H - RT)/V$$

where  $\Delta H$  is the molar heat of vaporization and  $V$  is the molar volume of the liquid, both at temperature  $T$  ( $298^\circ\text{K}$ ); and  $R$  is the ideal gas constant. The fractional polarity  $p$  approximates the fraction of the total cohesive energy density of the liquid which is due to dipole-dipole interactions; the remainder of the cohesive energy density is assumed to be due to dispersion and induction forces. Properties of liquids were taken from the literature.<sup>12</sup> The solubility parameter of the amorphous polymer is reported to be 10.7.<sup>13</sup>

A crystallinity index may be calculated for each value of relative intensity in the way previously described.<sup>14</sup> Thus a relative intensity value of 0.56 corresponds to a crystallinity index of 0.00, while a value of 2.00 corresponds to a crystallinity index of 0.61. However, as will be discussed below, the densities of liquid-crystallized films show no systematic dependence on degree of crystallinity and therefore could not be used to establish the validity of the calculated index. Nevertheless the data of Figure 1 suggest that relative intensity constitutes a measure of the degree of crystallinity.

The densities of liquid-crystallized thin films of PET were found not to be necessarily related to the degree of crystallinity of the polymer. Acetone is an example of a group of liquids which produced semicrystalline polymer with abnormally low densities. Densities were determined in a liquid medium of *n*-heptane and carbon tetrachloride, a relatively nonpenetrating medium that is capable of showing the presence of voids in the polymer. In Table II, the densities of films crystallized in acetone and subsequently heat-treated are compared with degrees of crystallinity measured by x-ray diffraction and infrared spectroscopy. The acetone-crystallized film was highly crystalline but had a density below that of the amorphous polymer. It was established gravimetrically and calorimetrically that imbibed acetone had been removed from the film. It was also found that crystallization in liquids with a density greater than  $1.5\text{ g/cm}^3$  resulted in semicrystalline polymer with abnormally low densities; thus the lowering of density cannot be accounted for by the presence of imbibed liquid in the film. Apparently,

TABLE II  
Properties of Acetone-Crystallized PET

Treatment	Crystallinity index		Density, g/cm <sup>3</sup> (C <sub>7</sub> H <sub>10</sub> -CCl <sub>4</sub> med.)	Optical density to white light	$\Delta H_m^2$ , mcal/mg	$T_m^2$ , °C	$\Delta H_m^1$ , mcal/ mg	$T_m^1$ , °C
	X-Ray	Infrared						
Amorphous	0.00	0.00	1.335	0.04	None	None	— <sup>a</sup>	257
Acetone-crystallized	0.33	0.30	1.290	0.48	None	None	10.8	257
Acetone-crystallized and heat-treated at 195°C, 12 hr	0.54	0.53	1.324	0.50	2.0	208	10.7	257
Acetone-crystallized and heat-treated at 195°C, 48 hr	—	0.53	1.329	0.50	7.9	232	8.1	257
Acetone-crystallized and heat-treated at 235°C, 2 hr	0.58	0.59	1.423	0.18	17.3	249,257 <sup>b</sup>	—	—

<sup>a</sup> The amorphous film had a cold crystallization exotherm at 156°C amounting to 8.3 mcal/mg and a melting endotherm at 257°C amounting to 10.2 mcal/mg.<sup>14</sup>

<sup>b</sup> Fusion endotherm composed of two distinct peaks.

extensive voids may be formed when thin polymer film is crystallized by liquids.

Although the amorphous PET film was transparent, crystallization by various organic liquids caused the film to become opaque. Acetone crystallization in particular made the film more opaque than heat treatment alone.

The structure produced by acetone-crystallization has considerable stability since even after heat treatment at 195°C, the film continued to be quite opaque to white light, and its density remained below that of the amorphous sample (Table II). Both the voids and opaqueness of the acetone-crystallized film are eliminated by heat treatment at 235°C. At 235°C, there is sufficient gross macromolecular diffusion for a complete reorganization of the morphology induced in the film by crystallization in acetone.

When a polar flotation medium such as carbon tetrachloride-acetone, rather than a nonpolar medium such as heptane-carbon tetrachloride, was used to measure the density of acetone-crystallized films, the density of 1.39 g/cm<sup>3</sup> was obtained, confirming a high degree of crystallinity. It is apparent that the acetone-carbon tetrachloride medium penetrates much more completely into the polymer matrix than the heptane-carbon tetrachloride medium. In the polar medium, the opaque acetone-crystallized film became transparent but the opaqueness reappeared when it was removed and dried.

Densities in heptane-carbon tetrachloride of the high crystalline samples listed in Table I(A and B) also indicated the presence of internal voids in the polymer morphology.

During immersion in liquids at 25°C, the thin films of PET suffered a weight loss of 1-2% due to leaching of low molecular weight material from the polymer. This material was isolated and identified as a mixture of cyclic oligomers of the linear polymer by infrared, nuclear magnetic resonance, and elemental analysis. The leaching of this material from the polymer may account for the internal voids induced in thin films of PET during liquid-crystallization. When a thicker film was used, e.g., 4 mil film, the density of the crystallized film was normal (1.40 g/cm<sup>3</sup>), although it was quite opaque. A thin film crystallized by exposure to acetone vapor, where leaching of low molecular weight material is not possible, also had a normal density (1.39 g/cm<sup>3</sup>), but was extremely opaque.

### Discussion

Polymers spontaneously mix with those liquids whose solubility parameter, polarity, and hydrogen-bonding characteristics correspond to their own.<sup>12</sup> Although interaction of organic liquids with and their diffusion into amorphous PET have not been related quantitatively to the rate or final degree of crystallization induced in the polymer, it has been shown that liquids having solubility parameters near the estimated solubility parameter



of amorphous PET,  $10.7 \text{ (cal/cm}^3)^{1/2}$ , induce appreciable crystallinity in the polymer.<sup>9</sup>

As shown in Table I, liquids covering a wide range of solubility parameter and polarity induce crystallinity extending over rather wide limits. There is no obvious relationship between the amount of crystallinity induced, as indicated by the value of relative intensity, and solubility parameter. Those liquids which produce the highest relative intensities in the polymer have solubility parameters which fall near that of the polymer. It is somewhat surprising that the fractional polarity does not appear to be very important, at least in certain individual cases. To cite a specific case, nitrobenzene and dioxane produce large relative intensities, 1.71 and 1.85, respectively. Each liquid has a solubility parameter of 10.0, but their fractional polarities differ widely, being 0.625 for nitrobenzene and 0.006 for dioxane.<sup>12</sup> Although the polarity of the polymer is unknown, its value is probably much closer to that of dioxane than nitrobenzene.

The effectiveness of the liquids of Table IA in inducing crystallization usually decreases as the molar volume of the liquid increases. This possibly reflects a decreasing tendency of liquids to diffuse into the polymer with increasing molar volume of the liquid.<sup>9</sup> On the other hand, the liquids of Table IB with the larger molar volumes are most effective as crystallizers. The fact that these liquids contain phenyl groups suggests that the presence of a phenyl group in a compound makes it particularly effective as a crystallizer.

When 0.8-mil amorphous PET films were immersed at 25°C, in certain chlorinated hydrocarbons and phenols, the films disintegrated into crystalline powder. Strong specific dipole-dipole forces between the polymer and liquids such as chloroform ( $\delta = 9.3$ ), tetrachloroethane ( $\delta = 10.4$ ), phenol ( $\delta = 14.5$ ), and *m*-cresol ( $\delta = 11.9$ ) account for this strong interaction. The activities of the liquid and polymer as a function of temperature are also important factors. For instance, it was observed that carbon tetrachloride induced no crystallization of the amorphous film at 25°C, but induced appreciable crystallization at 40°C.

The amorphous polymer can interact with mixtures of two noninteracting liquids. For example, neither ethanol ( $\delta = 12.7$ ) nor carbon tetrachloride ( $\delta = 8.6$ ) induces crystallinity, but a mixture of 0.64 volume fraction carbon tetrachloride and 0.36 volume fraction ethanol interacts with the amorphous film producing a crystallinity index of 0.30 as measured by infrared spectroscopy. The thermograms of the polymer treated in the pure liquids correspond to those of amorphous polymer. The thermograms of the polymer treated in the mixture correspond to that of the semicrystalline polymer with a heat of fusion of 10.0 mcal/mg.

The solubility parameter of ethanol and carbon tetrachloride mixture with  $v_1$  and  $v_2$  volume fractions was calculated as 10.1 by using the equation:<sup>12</sup>

$$\delta(\text{mixture}) = v_1\delta_1 + v_2\delta_2$$

This value is close to that of the polymer. Kashmiri and Sheldon<sup>15</sup> point out, however, that pure ethanol crystallizes the polymer at slightly elevated temperatures where its individual solubility parameter is still quite different from that of the polymer. They note that the addition of carbon tetrachloride to ethanol causes the number of single ethanol molecules to pass through a rather broad maximum, and suggest that crystallization by the mixture may involve the action of single ethanol molecules.

The liquid-crystallized and heat-crystallized polymer apparently have certain structural differences. Figure 2a shows thermograms of acetone- and heat-crystallized (150°C, 1 hr) films having crystallinity indexes of 0.33 and 0.30 respectively, as measured by x-ray diffraction. Crystallization by heat produces two endotherms,<sup>14,16,17</sup> whereas crystallization by liquids produces only one, the normal melting endotherm. The thermogram of a liquid-crystallized film also shows the lower endotherm if it is heat-treated after crystallization by liquid. It is interesting that the molecular rearrangement effected by heat treatment at 195°C was adequate to produce a second endotherm but failed to raise the density of the liquid-crystallized film above that of the amorphous film, and did not make the film less opaque (Table II). Heat treatment at 235°C, however, was sufficient to raise the density appreciably and, as mentioned earlier, to greatly reduce opaqueness. In Table II the enthalpy change and temperature at the maximum of the upper endotherm are designated, respectively,  $\Delta H_m^1$  and  $T_m^1$ . Corresponding values for the lower endotherm are designated  $\Delta H_m^2$  and  $T_m^2$ .

The liquid- and heat-crystallized films also show a difference in infrared absorption (Figure 2b). The spectra of the liquid-crystallized films listed in Table I have little or no indication of a 988  $\text{cm}^{-1}$  absorption band, whereas spectra of heat-crystallized films with degrees of crystallinity equivalent to those of the liquid-crystallized films exhibit a distinct 988  $\text{cm}^{-1}$  band. Koenig and Hannon<sup>18</sup> attribute the 988  $\text{cm}^{-1}$  band to the fold conformation of polymer chains at the surface of folded lamellae.

The appearance of the lower endotherm in the thermogram of heat-crystallized film, and of the 988  $\text{cm}^{-1}$  band in its spectrum, is evidence that the morphology of liquid-crystallized PET differs from that of heat-crystallized PET. Since liquid- and heat-crystallized polymer appear to have the same crystalline unit cell,<sup>19</sup> the observed differences in melting behavior and spectra must reflect differences in size, perfection, or internal structure of the crystallites.

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