

## Differential Thermal Analysis of High Polymers. IV. Saturated Linear Polyesters\*

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### Introduction

In the approximate order of increasing temperature, four transitions may take place in saturated linear polyesters: glass transition, "cold" crystallization, premelt crystallization, and melting. Glass transition, which involves the onset of motion of short segments of chains in the amorphous region of the polymer, has been studied by dilatometry,<sup>1</sup> nuclear magnetic resonance,<sup>2</sup> dynamic mechanical measurements,<sup>3</sup> and calorimetry.<sup>4</sup> In cold crystallization, segments of neighboring chains in the amorphous portion crystallize above the glass-transition temperature but far below the melting temperature; this phenomenon has been observed in density measurements,<sup>1</sup> infrared spectrophotometry,<sup>5</sup> and calorimetry.<sup>4</sup> Premelt crystallization occurs at temperatures near but below the melting point. Melting is a first-order crystalline-amorphous transition; the transition temperature and the accompanying heat effect define the chemical composition and crystallinity of the polyester.

Because most transitions occurring in polyesters, like those in other semicrystalline polymers,<sup>6,7</sup> are accompanied by a heat effect, they should be amenable to study by differential thermal analysis. Recent notes<sup>8-10</sup> have indicated this possibility, but comprehensive studies have not been reported.

Polyethylene terephthalate—the commonest and most important commercial polyester—and several modifications of it have now been systematically investigated by differential thermal analysis. The influence of chemical structure on physical properties was studied by using structurally modified polyesters containing different acid and glycol monomers. Thermally and mechanically treated

polyesters were studied to determine the effects of such treatments on the transition.

### Experimental

Polyethylene terephthalate and other polyesters were prepared by transesterification between the respective methyl esters and glycols. Quenched samples were obtained by extruding the polymer melt into cold water. The polyethylene terephthalate sample had an intrinsic viscosity of 0.53 in a 2:3 trichloroethane:phenol mixture at 25°C., corresponding to a number-average molecular weight of 12,000.<sup>11</sup> Other polyesters studied had similar molecular weights. One copolymer, polyethylene/diethylene terephthalate, contained ether linkages resulting from dehydration between the ethylene glycol molecules. Four copolymers contained either a second acid or a second alcohol as comonomer (Table I).

TABLE I

| Acid 1                   | Acid 2                  | Alcohol 1       | Alcohol 2                    |
|--------------------------|-------------------------|-----------------|------------------------------|
| Terephthalic             | —                       | Ethylene glycol | 1,3-Cyclohexylene dimethanol |
| Terephthalic             | —                       | Ethylene glycol | 1,4-Cyclohexylene dimethanol |
| Terephthalic (90 mole-%) | Isophthalic (10 mole-%) | Ethylene glycol | —                            |
| Terephthalic (60 mole-%) | Isophthalic (40 mole-%) | Ethylene glycol | —                            |

Commercial polyethylene terephthalate, in monofilament form represented by Dacron and in film form represented by Mylar, was studied to determine the effects of thermal and mechanical treatments they received during fabrication. The Mylar film was 0.005 in. thick and had been biaxially stretched. In the newly commercialized

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polyester (Eastman Kodol) besides being a melt-spun fiber, the ethylene glycol has been replaced by 1,4-cyclohexylene dimethanol.

The thermograms for the quenched materials were measured on 0.2 g. powdered samples placed in glass cells heated in a metal block.<sup>7</sup> The Mylar film was cut into strips 1 in. wide and wrapped around the thermocouple. All thermograms were obtained at a heating rate of 2°C./min. Annealed samples were obtained by heating the quenched material directly in the cell 10-20°C. above the melting point and then cooling at 0.5°C./min. The thermograms for the annealed materials were then obtained simply by reheating through a second cycle.

### Effects of Composition

Transitions that quenched and annealed polyethylene terephthalate undergo are shown in Figure 1. The differences in the thermograms reflect different changes in crystallinity of the quenched and annealed materials as temperature is raised.

In the thermogram for the quenched material, the deflection near 70°C. represents glass transition. Cold crystallization starts at 100°C., the minimum crystallization temperature. Crystallization rate reaches a maximum at the peak temperature of 125°C. Premelt crystallization gives a peak at 220°C. The thermogram shows that melting begins at slightly above 250°C. The temperature of the melting peak is usually taken as the melting point of the polymer; the indicated 265°C. is identical with the literature value.<sup>12</sup> Transition temperatures and the development of crystallinity in polyethylene terephthalate with temperature

have recently been studied by x-ray diffraction;<sup>13</sup> the results agree well with those estimated from the present thermogram.

Because the area under a thermogram peak is directly proportional to the amount of heat accompanying the transition, the heats of transition can be estimated by straightforward calibration with a reference material.<sup>6</sup> Such heats of transition are for cold crystallization, 7.9 cal./g.; for pre-melt crystallization, 6.4 cal./g.; for fusion, 14.0 cal./g. Because the sum of the heats of the two crystallizations almost equals the heat of fusion, the original material can be judged as totally amorphous.

In the thermogram for the annealed material, the glass transition near 70°C. is barely perceptible, and both crystallization peaks are missing. The flattening of the glass-transition deflection is expected, because the crystalline portion would impose strain on the amorphous segments. The annealed polymer displays a sharper melting peak and shows a larger heat of fusion, 16.7 cal./g., corresponding to a greater amount of crystallinity developed during annealing. A measured density of 1.41 g./cc. corresponds to 60% crystallinity.<sup>5</sup> The calculated true heat of fusion is therefore 16.7/0.60 or 27.8 cal./g.

Incorporation of a longer glycol unit into the chain of polyethylene/diethylene terephthalate markedly changes the thermogram. Thermograms for the quenched and annealed polyethylene/diethylene terephthalate are shown in Figure 2. The deflection corresponding to glass transition is much greater than that for the totally amorphous homopolymer and occurs at a slightly lower tem-

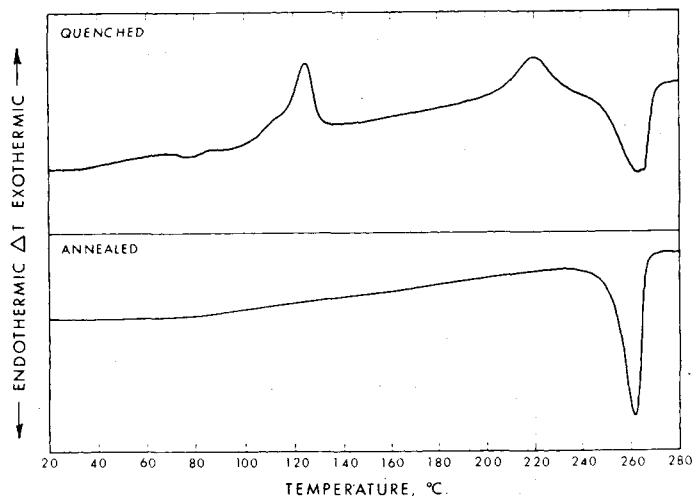


Fig. 1. Thermograms of polyethylene terephthalate

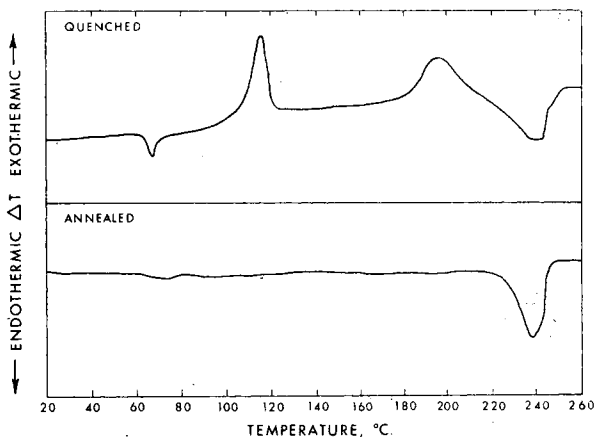


Fig. 2. Thermograms of polyethylene/diethylene terephthalate.

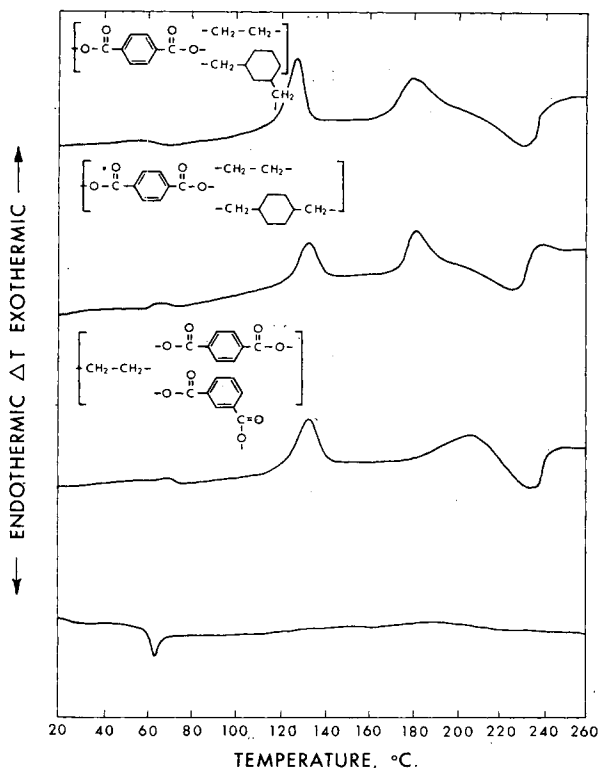


Fig. 3. Thermograms of copolyesters of polyethylene terephthalate.

perature. Cold crystallization also starts a few degrees lower; premelt crystallization starts 20°C. lower. Melting begins 40°C. lower, at 211°C., and the melting point is nearly 30°C. lower. Again, the corresponding annealed material yielded only a melting peak.

The change in both glass transition and melting behavior can be attributed to the presence of the

larger glycol molecule. The extra length and the ether linkages of diethylene glycol would, respectively, decrease the effective number of terephthalate units in the polymer molecule and make the chain more flexible. Consequently, reduced intermolecular forces lead to lower transition temperatures.

Thermograms for the quenched copolymers containing 10 mole-% of 1,3- and 1,4-cyclohexylene dimethanol and 10 and 40 mole-% isophthalic acid are shown in Figure 3. The thermograms for the first three copolymers show similar deflections near 60°C. corresponding to glass transition. The peaks for cold and premelt crystallizations are also similar, except for the copolymer containing 10 mole-% isophthalic acid, in which the melting peak almost overlaps the broad peak of premelt crystallization; both the broadness and the high temperature of this peak may be attributed to steric hindrance imposed by the asymmetric isophthalic units. With the copolymer containing 40 mole-% isophthalic acid, no crystallization or melting transition occurs above the glass-transition temperature; the large deflection due to glass transition reflects reduced chain stiffness resulting from replacing almost half of the *para* phenylene units by *meta* structures.

From the peak areas in the thermograms of the first three copolymers, the initial quenched material can again be judged to be totally amorphous. However, crystallinity was developed in these copolymers upon heating. The copolymer containing 40 mole-% isophthalic acid did not crystallize, even on very slow annealing. Isophthalate homopolymers soften at very low temperatures and do not crystallize.<sup>14</sup> It is reasonable to expect that a high isophthalate content in a polyterephthalate could make crystallization equally difficult, because greater irregularity is present in the copolymer chain.

#### Effects of Mechanical and Thermal History

The thermograms of commercial polyethylene terephthalate monofilament (Dacron) and film (Mylar) are shown in Figure 4. The monofilament has developed a high degree of crystallinity and some orientation as a result of melt spinning and drawing. Although a small deflection occurs in the 60–100°C. region, the glass transition can not be measured with certainty. The crystallization peaks are absent, and a melting peak occurs at 260°C. The thermogram of Mylar film is similar to that of Dacron. The lower base line before

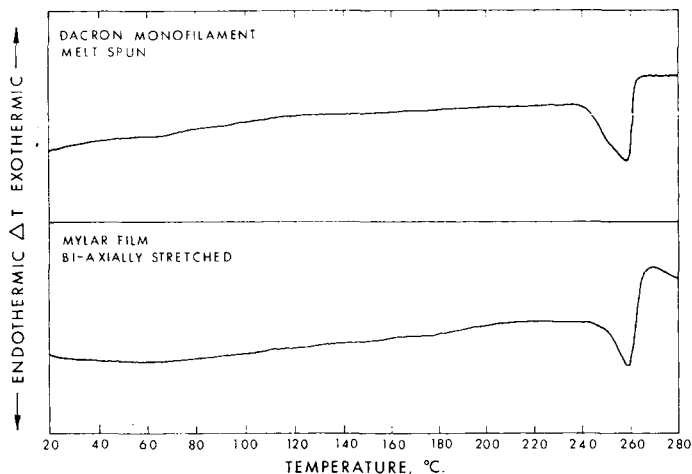


Fig. 4. Thermograms of commercial polyethylene terephthalate monofilament (Dacron) and film (Mylar).

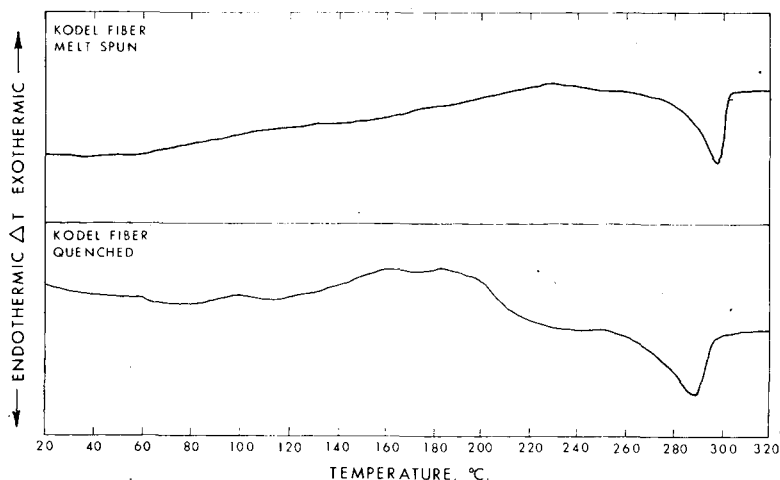


Fig. 5. Thermograms of polycyclohexylenedimethylene terephthalate (Kodel) fiber.

the melting peak may be attributed to the poorer contact likely with film wrapped around the thermocouple. Plane orientation resulting from biaxial stretching did not produce any noticeable change on the melting transition, perhaps the change is so small or so close to the melting peak that it was masked. However, in oriented nylon 66 fibers, an extra peak has been observed a few degrees below the melting point;<sup>15</sup> this was attributed to disorientation.

Thermograms of commercial poly-1,4-cyclohexylenedimethylene terephthalate (Kodel) fiber are shown in Figure 5. Kodel fiber has a thermogram with a melting peak at 299°C., which agrees with the recently reported melting point of 290–295°C.<sup>16</sup> When the Kodel melt was severely quenched at  $-80^{\circ}\text{C}.$  and reexamined, the thermo-

gram displayed two broad humps. The first region is small and spans from 90 to 110°C. This deflection may be due to glass transition or to cold crystallization. The much larger exothermic hump at 140–210°C. suggests that cold crystallization occurs with difficulty in this polyester—possibly because of chain stiffness, which has been deduced in a recent study of solution properties of these polyesters.<sup>17</sup> The quenched material melts almost 10°C. lower than the crystalline fibers.

### Conclusion

The effect of composition of polyesters can be detected from changes in the thermograms, because a composition change alters either the spatial relationship or the intermolecular forces. The thermal and/or mechanical history of a polyester

can be easily detected by differential thermal analysis, as crystallinity of a polymer is largely controlled by these treatments. The course of crystallization of a totally amorphous polyester can be followed continuously by differential thermal analysis.

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### Synopsis

Glass transition, cold crystallization, premelt crystallization, and melting in polyethylene terephthalate and copolyesters have been studied by differential thermal analysis. The transitions are affected by changing the chemical composition of the polyesters through replacing one monomer partially or completely with a different monomer. Quenching, annealing, and/or drawing, which render different degrees of crystallinity to a polyester, can also be detected directly from the thermograms.

### Résumé

On a étudié par analyse thermique différentielle la transition vitreuse, la cristallisation à froid et la cristallisation après pré-fusion, et la fusion dans le cas du téréphtalate de polyéthylène et des copolyesters. Les transitions sont affectées par un changement dans la composition chimique des polyesters lorsqu'on remplace partiellement ou complètement un monomère par un monomère différent. A partir des thermogrammes, on peut aussi détecter directement les refroidissements brutaux, les recuites, et/ou les étirements qui confèrent tous à un polyester des degrés de cristallinité différents.

### Zusammenfassung

Glasumwandlung, Kristallisation in der Kälte und unterhalb des Schmelzpunkts sowie Schmelzen wurde an Polyäthylenterephthalat und Copolyestern durch Differentialthermoanalyse untersucht. Die Umwandlungen werden durch Änderung der chemischen Zusammensetzung der Polyester durch partiellen oder vollkommenen Ersatz eines Monomeren durch ein anderes Monomeres beeinflusst. Abschrecken, Tempern und Reckung, wodurch einem Polyester verschiedene Kristallinitätsgrade verliehen werden, kann ebenfalls direkt aus den Thermogrammen erkannt werden.

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