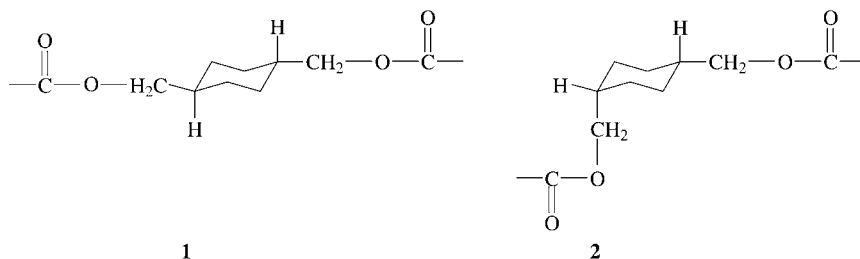


## CYCLOHEXANEDIMETHANOL POLYESTERS

### Introduction

1,4-Cyclohexanedimethanol (CHDM) is an important commercial cycloaliphatic diol that is used in a variety of important commercial polyesters. It is produced by the catalytic hydrogenation of dimethyl terephthalate (DMT) (1). CHDM can exist as the cis or trans isomer; however, most commercial high volume production CHDM is a mixture of isomers with an approximately 70/30 trans/cis ratio. This isomer ratio plays an important role in determining the final properties of polyesters containing CHDM by influencing the ability of chains to pack efficiently. Structure **1**, trans (axial, axial) enchainment, and structure **2**, cis enchainment, schematically illustrate the differences in these structures. Most CHDM containing polyesters are based on the 70/30 (trans/cis) mixture and the stereochemistry of CHDM is maintained during the polycondensation.



The amount of CHDM incorporation as a comonomer also has a large effect on the crystalline nature of the backbone since it is so dissimilar in size and shape to other common diols (2). Poly(ethylene terephthalate) (PET) containing low levels of CHDM (less than 5 mol%) has enjoyed widespread use in stretch blow molded carbonated soft drink containers, where the CHDM modifies strain hardening during stretching, which therefore serves to widen the processing window. When incorporated into a terephthalic acid (TPA) based polyester at higher levels, the absolute level of CHDM can regulate whether the polyester is a high melting crystalline material or a tough clear amorphous composition. In general, when CHDM is copolymerized with other aliphatic diols with common diacids such as TPA, it increases the  $T_g$  of the backbone as well as rendering the backbone more resistant to hydrolysis. The flexible character of the CHDM unit is also known to impart enhanced impact and toughness to polyesters. The origin of these effects has been studied and a recent report correlates these properties to secondary relaxation modes arising from the CHDM structure (3).

The most important commercial polyesters containing CHDM are based on TPA and ethylene glycol (EG). Isophthalic acid (IPA) can also be used as a comonomer with TPA. The polyester of CHDM with TPA is poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), which melts at 300°C. When this structure is modified with an acid such as IPA, the abbreviation PCTA (acid-modified PCT) is used. PCT polyesters with glycol modification of up to 50 mol% EG are abbreviated as PCTGs. Likewise, PET polyesters with up to 50% CHDM content are called PETGs. The abbreviations of PETG, PCTG, and PCTA are generally reserved for compositions that contain enough of the comonomer to render the backbone slow to crystallize or amorphous. This article discusses the chemical characteristics and properties of the important commercial crystalline and amorphous examples of polyesters based on CHDM.

### Crystalline Polymers Based on CHDM

The primary crystalline polymer based on CHDM is the terephthalate, PCT. PCT was originally developed for fiber applications but has since found wider utility as a reinforced polymer for injection molding and (when copolymerized with a small amount of IPA) as a material for crystallized food packaging trays. The key property of PCT, which sets it apart from other thermoplastic polyesters in these latter applications, is melting point.

When made with the normal 70/30 trans/cis CHDM isomer ratio, the melting point of PCT is about 290°C. The melting point varies substantially with isomer ratio, however, as shown in Table 1 (4).

**Table 1. Effect of trans/cis Isomer Ratio on Melting Point of PCT**

% trans	$T_m, ^\circ\text{C}$
100	315
70	290
50	275
0	250

For comparison, the melting point of poly(butylene terephthalate) (PBT) is 225°C and that of PET is in the range of 250–260°C.

Crystallization of PCT is relatively rapid, but because of its higher  $T_g$  (90°C) the maximum rate of crystallization occurs at a higher temperature than is typical of other crystalline polymers such as PET ( $T_g$  about 70°C) or PBT ( $T_g$  about 35°C).

The bulky in-chain CHDM moiety results in several other important differences between PCT and crystallizable polyesters such as PET. The amorphous density is significantly lower, 1.195 g/cm<sup>3</sup> for PCT compared to 1.334 g/cm<sup>3</sup> for PET. PCT also exhibits a strong sub- $T_g$  molecular relaxation, which results in a relatively low modulus at room temperature (155 MPa vs 240 MPa for PET) and improved toughness in the amorphous state. As an example of the latter phenomenon, the notched Izod impact strength of amorphous PCT is greater than 1000 J/m, while that of amorphous PET is less than 100 J/m.

The CHDM isomer ratio also has an effect on gas barrier properties, with better barrier properties resulting from higher cis levels. Because of the higher local free volume contributed by the CHDM structure, the diffusivity through PCT is generally higher than that through denser structures like PET (5). However, the magnitude of this effect is strongly dependent on the isomer ratio, as shown in Table 2. A recent patent (6) discloses that PCT with a 93/7 cis/trans ratio containing 50% 2,6-naphthalene dicarboxylic acid has a permeability of 2.68 (cm<sup>3</sup>·mil)/(100 in.<sup>2</sup> · 24 h · atm).

Preparation of PCT is best accomplished from DMT using standard transesterification catalysts such as titanium compounds. Because of the high melting point of the polymer, final polyesterification temperatures must be high (greater than 300°C at typical commercial trans/cis ratios) (7). PCT prepared in the melt phase can be crystallized and then solid phase polymerized to obtain even higher molecular weights.

If PCT is modified with relatively high levels of comonomer, substantially amorphous materials result (as described later). However, it is possible to maintain crystallinity at lower levels of modification. For example, replacing up to about 10 mol% of the terephthalate units with isophthalate results in a polymer with reasonable crystallization rates and ultimate degrees of crystallinity.

One might expect that replacing the terephthalate unit in PCT with naphthalene dicarboxylate would make an interesting high temperature polymer. This polymer cannot be successfully prepared, however, because its melting point is above its degradation temperature. Reduction of the melting point by

**Table 2. Effect of cis Isomer Content on Gas Barrier Properties of PCT**

% cis CHDM	Oxygen permeability, nmol/(m·s·GPa) <sup>a</sup>
93	30
46	62
26	80

<sup>a</sup>To convert nmol/(m·s·GPa) to (cm<sup>3</sup>·mil)/(100 in.<sup>2</sup>·24 h·atm), divide by 2.

copolymerization (for example either with terephthalic acid or isophthalic acid) eliminates this problem (8).

Crystalline polyesters from CHDM and aliphatic diacids are possible, but generally are of little interest because of low melting points and low glass-transition temperatures. Cyclic aliphatic diacids offer some potentially attractive possibilities since the melting points are not so depressed. For example, the polyester of CHDM with the high trans isomer of 1,4-cyclohexane dicarboxylic acid has a melting point similar to that of PBT (7).

**Processing of Crystalline PCT-Based Polymers.** Melt processing of the high-melting PCT-type polymers must be done carefully, owing to a relatively small window between the melting point and the temperature at which degradation rates become significant. The degradation is both thermal and hydrolytic in nature. While it may be argued that the PCT structure is inherently more hydrolytically stable than other polyesters such as PET, the higher processing temperature compensates by accelerating the rate. Thus drying of the polymer or formulation before processing is recommended. Dessicant drying at temperatures up to about 125°C is commonly used.

Degradation results in color formation, loss of molecular weight, and deterioration of critical mechanical properties such as toughness.

**Injection Molding Applications.** PCT forms the basis of a family of reinforced, crystalline plastics for injection molding. As mentioned previously, the high melting point of the polymer is a key property, as this results in high heat-deflection temperatures (HDT) in glass-fiber-reinforced formulations. Good toughness, flow into the mold, and rapid crystallization are also important attributes in these applications.

Formulations for injection molding typically contain 30–40 wt% glass fiber or a mixture of glass fiber and mineral filler. Stabilization packages to improve processing stability and additives to enhance crystallization rate are also incorporated. These products may or may not be flame-retarded, depending on the application area, with HDTs ranging from about 250°C to about 260°C. This level of heat resistance makes PCT-based plastics suitable for high temperature applications such as electronic connectors, where high soldering temperatures are encountered. Typical competitive materials in this market include poly(phenylene sulfide), with an HDT of about 260°C, and high temperature polyamides, with HDTs in the range of 270–280°C. Other properties of a typical 30% glass-reinforced, flame-retarded grade of PCT are shown in Table 3.

**Table 3. Properties of 30% Glass-Reinforced Flame-Retarded PCT**

Specific gravity	1.63
Tensile strength, MPa <sup>a</sup>	120
Tensile elongation, %	2
Flexural modulus, MPa <sup>a</sup>	9600
Notched Izod impact, J/m <sup>b</sup>	90
HDT, 1.82 MPa, °C	255
UL Subject 94 flammability	V0

<sup>a</sup>To convert MPa to psi, multiply by 145.

<sup>b</sup>To convert J/m to ft-lbf/in., divide by 53.38.

Flame-retarded grades are widely used for various computer connectors and circuit board components. Representative applications are edge card connectors, grid arrays, and memory modules. Non-flame-retarded grades find use in automotive (under the hood) applications, typically connectors and related parts. As higher temperature soldering techniques become more common in the automotive industry, the use of high temperature plastics such as PCT is expected to increase.

It is also possible to formulate unreinforced PCT with crystallization aids and tougheners to provide a material similar in some respects to supertough nylon. PCT provides advantages in dimensional stability and lower moisture sensitivity compared to the polyamide-based products.

**Extrusion Applications.** A well-established application for extruded unreinforced PCT (copolymerized with isophthalate) is in the preparation of crystallized, thermoformed trays for foods. Crystallized PET is widely used for this application, but where higher temperature performance is needed the PCT-based polymer may be chosen. Such trays are formed from extruded sheet, using a hot mold to promote crystallization. Isophthalate-modified PCT polymers are approved by the Food and Drug Administration for high temperature food contact use.

The good hydrolytic stability of PCT-based polymers leads to applications for monofilament in paper machine belts. Monofilament is extruded from high molecular weight polymer, drawn, and crystallized, then woven into a screen. Such belts are found in the drying section of paper machines, where there is a combination of high moisture and high temperature. Because of their hydrolytic stability, PCT-based polymers provide much longer service life in this application than PET-based.

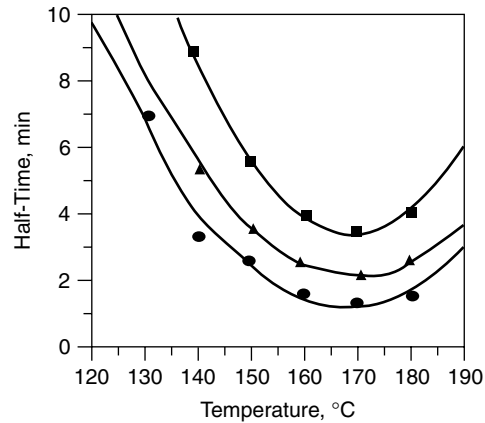
### Amorphous Polyesters, CHDM-Modified PET and PCT

The size and shape of CHDM render it as an effective diol for modifying crystallinity in polyesters. The decrease in crystallization rates for low levels of CHDM incorporation into PET is shown in Figure 1, where the half-times (measured by dsc) for crystallization vs temperature in the melt are plotted. When copolymerized with EG and TPA, the middle composition ranges, from approximately 70/30 CHDM/EG to 20/80 CHDM/EG, have very slow crystallization rates and do not show crystallization peaks when scanned by dsc at 20°C/min and thus are amorphous polyesters. These compositions can be processed into clear, transparent sheets and molded articles.

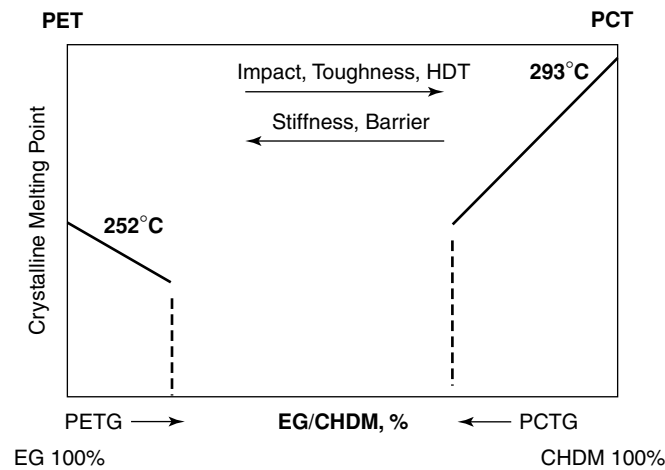
As the composition is varied from a PETG composition to a PCTG composition, several general property trends are noted. These are illustrated in the schematic in Figure 2.

Increasing CHDM level leads to an increase in toughness, as measured by impact and increasing elongation-to-break values, a decrease in tensile modulus, and increases in  $T_g$  and HDT. A comparison of the physical and mechanical properties for a PETG composition of approximately 70 EG/30 CHDM and a PCTG composition of approximately 60 CHDM/40 EG is shown in Table 4.

**Preparation of Amorphous PETGs and PCTGs.** In general, amorphous PETG and PCTG polyesters can be made by standard melt-phase polycondensation processes, starting either with DMT or TPA. One significant difference



**Fig. 1.** Plot of crystallization half-time in minutes as determined by dsc versus temperature in degree Celsius. ● PET; ▲ PET-1.5% CHDM; ■ PET-3.5% CHDM.



**Fig. 2.** Schematic showing the general properties and amorphous regions for PETG and PCTG polyesters.

in the preparation of amorphous copolyesters compared to crystalline copolyesters is the need to achieve the required degree of polymerization directly in the melt-phase process. Crystalline polyesters are readily solid-state polymerized to high degrees of polymerization, thus avoiding any problem with melt viscosity in the large-scale finishing reactors used for the melt-phase processes. However, the slow crystallization rates for amorphous copolyesters prohibit converting to a crystalline state, which is required to avoid the fusing of pellets or powders used in the solid-state processes.

**Processing and Applications of PETGs and PCTGs.** The amorphous nature of both PETG and PCTG permits them to be processed into clear transparent sheets and articles. PETG has found large volume application in extruded

**Table 4. Physical Property Comparison of Amorphous PETG, PCTG, and PCTA**

Property	PETG	PCTG	PCTA
Specific gravity	1.27	1.23	1.20
Thermal properties <sup>a</sup>			
<i>T<sub>g</sub></i> , °C	81	84	88
HDT			
0.455 MPa	70	74	75
1.82 MPa	64	65	65
Tensile properties <sup>a</sup>			
Stress @ yield, MPa	50	45	47
Stress @ break, MPa	28	52	51
Elongation @ yield, %	4.3	5	5
Elongation @ break, %	110	330	300
Flexural properties <sup>a</sup>			
Flexural modulus, MPa	2100	1900	1800
Flexural yield strength, MPa	70	66	69
Izod impact strength <sup>b,c</sup>			
Notched @ 23°C, J/m	101	NB	80
Unnotched @ 23°C, J/m	NB	NB	NB
Notched @ -40°C, J/m	37	64	40
Unnotched @ -40°C, J/m	NB	NB	NB

<sup>a</sup>To convert MPa to psi, multiply by 145.

<sup>b</sup>To convert J/m to ft·lbf/in., divide by 53.38.

<sup>c</sup>NB = no break.

heavy gauge sheet products, blister packages, etc. It offers better toughness than acrylic-based sheet products and better chemical resistance than polycarbonate products (9). The higher CHDM-containing copolyesters are often preferred for applications in medical devices where resistance to lipid solutions and property retention after gamma and ethylene oxide sterilization are important (9).

**Acid-Modified PET and PCT Amorphous Copolyesters.** Some of the performance benefits of PCT vs PET include improved toughness, hydrolysis resistance, electrical properties, color, and clarity. However, because of the high melting point of PCT (typically ~290°C), this polyester must be processed at temperatures in excess of 300°C. This results in a very narrow processing range for PCT in order to avoid degradation (10). Incorporation of relatively low levels of a modifying diacid, such as IPA, into PCT yields PCTA compositions which are less crystalline and have lower melting points but which retain the good toughness characteristics and other beneficial properties of PCT. As the isophthalate level in the PCTA is increased, the melting point decreases and the processing window increases. IPA is also used in low levels as a modifier for PET. It provides a slight improvement in barrier properties and also allows for a slightly lower processing temperature. Higher levels of IPA modification of PET can further improve the barrier properties but lead to significant loss of toughness and heat resistance of molded containers. In contrast, PCT can be modified using high levels of IPA to yield PCTA compositions with outstanding properties. Above about 20% isophthalate incorporation, the poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate) copolyesters are tough, amorphous thermoplastics, which are easy

to process. These amorphous materials can be processed at 230–280°C, much lower than the temperatures in excess of 300°C required for unmodified PCT. They can be injection molded to form tough, transparent parts and can be extruded into sheet, pipe, and profiles as well. The properties of a typical amorphous PCTA which has a composition of about 70 mol% TPA and 30 mol% IPA are shown in Table 4 and are very similar to those of amorphous PETG and PCTG. One advantage of amorphous PCTA compositions over analogous amorphous PETG and PCTG materials (with EG as the modifier) arises from the superior hydrolysis resistance of the PCTA. This manifests itself in the ability to melt process the PCTA with minimal or no drying, whereas PETG and PCTG require more extensive drying to avoid excessive loss in molecular weight during processing (11). Acids other than IPA have been investigated as modifiers for PCT and have been shown to give different performance attributes; however, no other PCTA compositions are commercially available.

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