



**HAL**  
open science

## Synthesis and properties of poly(1,4-cyclohexanedimethylene-co-isosorbide terephthalate), a biobased copolyester with high performances

Nicolas Jacquél, H  l  ne Amedro, Ren   Saint-Loup, Jean-Pierre Pascault, Alain  
Rousseau, Fran  oise Fenouillot

### ► To cite this version:

Nicolas Jacqu  l, H  l  ne Amedro, Ren   Saint-Loup, Jean-Pierre Pascault, Alain Rousseau, et al.. Synthesis and properties of poly(1,4-cyclohexanedimethylene-co-isosorbide terephthalate), a biobased copolyester with high performances. *European Polymer Journal*, 2019, 115, pp.22-29. <10.1016/j.eurpolymj.2019.03.018>. <hal-03032949>

**HAL Id: hal-03032949**

**<https://hal.science/hal-03032949v1>**

Submitted on 22 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destin  e au d  p  t et    la diffusion de documents scientifiques de niveau recherche, publi  s ou non,   manant des   tablissements d'enseignement et de recherche fran  ais ou   trangers, des laboratoires publics ou priv  s.



Distributed under a Creative Commons CC BY-NC 4.0 - Attribution - Non-commercial use - International License

## Synthesis and properties of poly(1,4-cyclohexanedimethylene-*co*-isosorbide terephthalate), a biobased copolyester with high performances

Sylvain LEGRAND<sup>1,2,3</sup>, Nicolas JACQUEL<sup>3</sup>, H el ene AMEDRO<sup>3</sup>, Ren e SAINT-LOUP<sup>3</sup>, Jean-Pierre PASCAULT<sup>1,2</sup>, Alain ROUSSEAU<sup>1,2,\*</sup>, Fran oise FENOUILLOT<sup>1,2</sup>.

<sup>1</sup> Universit e de Lyon, F-69003, France.

<sup>2</sup> INSA Lyon, Ing enierie des Mat eriaux Polym eres, IMP, CNRS UMR5223, 17 Avenue Jean Capelle, 69621, Villeurbanne, France

<sup>3</sup> Roquette Fr eres, F-62136, Lestrem, France.

\*Correspondence to: A. Rousseau (E-mail: [alain.rousseau@insa-lyon.fr](mailto:alain.rousseau@insa-lyon.fr))

**Abstract:** In this paper, the synthesis and properties of poly(1,4-cyclohexanedimethylene-*co*-isosorbide terephthalate) (PCIT) with isosorbide (IS) content ranging from 16 to 61 mol% relative to the total diols amount were investigated. Amorphous polymers were successfully synthesized without isosorbide ring hydration. Glass transition temperature ( $T_g$ ) linearly increased of 1.1  C for each molar percent of isosorbide included in the polyester, meanwhile melting temperature ( $T_m$ ) linearly decreased of 2.1  C for semi-crystalline samples (up to 25 mol% of isosorbide). Molar masses of semi-crystalline samples were easily increased using high temperature solid-state polymerization (SSP) and reduced viscosity ( $\eta_{red}$ ) higher than 70 mL.g<sup>-1</sup> were obtained. Semi-crystalline samples exhibit outstanding impact resistance compared with commercial high performance copolyester, whereas amorphous copolyesters exhibit acceptable mechanical properties coupled with high thermal resistance. Results confirmed the promising association between isosorbide and 1,4-cyclohexanedimethanol to reach tunable thermal and mechanical properties, depending on the targeted applications.

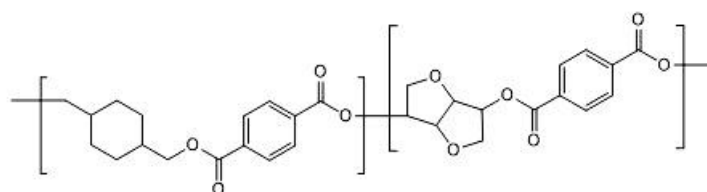
**Keywords:** Isosorbide, 1,4-cyclohexadimethanol, biobased polyester

# 1. Introduction

In recent years, the interest in renewable polymers has been growing due to concerns for the environment and the depletion of petroleum resources. Isosorbide (IS) is a 1,4:3,6-dianhydrohexitol industrially produced from glucose. It is a renewable bifunctional diol with a V-shaped backbone composed of two tetrahydrofuran rings<sup>1</sup>. This rigid skeleton is responsible for the increase of glass transition temperature ( $T_g$ ) of macromolecules in which isosorbide is included<sup>2-4</sup>. Isosorbide is also known to give excellent optical properties to polymers, by increasing the transmittance and reducing the haze<sup>5</sup>. With such characteristics, isosorbide has been used for the production of polyesters<sup>6-7</sup>, polycarbonates<sup>8-9</sup> and polyamides<sup>10</sup> with enhanced properties.

1,4-cyclohexanedimethanol (CHDM) is a cyclic diol. CHDM increases the mechanical properties and is available in many commercial polymers<sup>11-13</sup>. The ring structure of CHDM flips from the e,e-trans cyclohexylene ring to form an a,a-trans cyclohexylene ring via a twisted-boat structure<sup>14</sup>. This phenomenon allows a better relaxation from its conformational transition, resulting in better chain mobility of the macromolecules in which CHDM is included. CHDM is also known to give high melting temperature ( $T_m$ ). For instance, homopolymer from purified terephthalic acid (PTA) and CHDM, namely poly(1,4-cyclohexanedimethylene terephthalate) (PCT) has melting temperature ranging from 250 to 310 °C, depending on the cis/trans ratio of CHDM<sup>15</sup>. Processing can be troublesome as for other high performance polyesters<sup>16</sup>.

Thus, isosorbide and CHDM can be associated with PTA to optimize their thermal and mechanical properties. Koo *et al.*<sup>17</sup> described this association with content of isosorbide ranging from 5 to 25 mol% in the copolyester from 1,4-cyclohexanedimethanol and terephthalic acid (PCIT, see Figure 1). They reported molar mass between 41 700 and 48 200 g.mol<sup>-1</sup> for the different polymers. As expected, they found a  $T_g$  increase and a  $T_m$  decrease by incorporating isosorbide within PCT backbone.



**Figure 1. Structure of poly(1,4-cyclohexanedimethylene-co-isosorbide terephthalate) (PCIT).**

Khan *et al.*<sup>18</sup> used this new copolyester to produce fibers by electrospinning. Phan *et al.*<sup>19</sup> also worked on PCIT fibers and noted the enhanced properties of PCIT fibers, especially regarding tensile properties and thermal stability. Kasmi *et al.*<sup>20</sup> synthesized poly(1,4-cyclohexanedimethanol-co-isosorbide 2,5-furandicarboxylate) (PCIF) copolyesters, with isosorbide content ranging from 0 to 35 mol% (diol part) and they highlighted the enhanced thermal properties of this new biobased copolyester. Therefore, this promising association between CHDM and isosorbide makes it possible to obtain materials with improved mechanical properties and tunable  $T_g$  and  $T_m$  values.

However, associating two monomers generally leads to decreasing crystallization ability with increasing minor comonomer part. As a result, copolymers with equal part of each monomer are often amorphous, despite the fact that homopolymers present good crystallization ability. For instance, copolymers from terephthalic acid (PTA), CHDM and ethylene glycol (EG), namely poly(ethylene-*co*-1,4-cyclohexanedimethylene terephthalate) (PECT) present an amorphous window between 20 and 40 mol% of CHDM relative to the total diol amount<sup>15,21-23</sup>, whereas PET and PCT are known to have good crystallization ability.

Koo *et al.*<sup>17</sup> also studied the crystallization behavior of their PCIT and concluded to an alteration of crystalline structure due to V-shaped isosorbide. It lowered the crystallinity and melting temperature of PCIT. For higher isosorbide incorporation, this leads to exclusion of isosorbide from the crystalline region. Samples with isosorbide between 5.8 and 16.7 mol% (diol part) are semi-crystalline whereas sample with 25.4 mol% isosorbide (diol part) is found to be amorphous. For PCIF polymers, Kasmi *et al.*<sup>20</sup> found a semi-crystalline domain up to 25 mol% isosorbide (diol part) as well.

It is of interest to study PCIT having more than 25 mol% isosorbide. It is anticipated that these polymers are amorphous and have increased glass transition temperature and optical properties. But authors report that breakage of the isosorbide ring by hydration occurs above 40 mol% isosorbide, forming a branched structure and leading to polymers having high molar mass dispersity<sup>17,24</sup>.

As can be seen, limited studies were published concerning this new copolyester family. In this paper, the effect of increasing isosorbide content on the PCIT synthesis is studied by varying its content from 16 to 61 mol%. Thermal properties of semi-crystalline and amorphous polymers are also investigated. Molar masses of semi-crystalline polyesters were increased with solid-state polymerization. Finally, a special emphasis is given to the mechanical properties of the polymers obtained and they are compared with commercial high performance polyesters.

## 2. Experimental

### 2.1. Materials

Purified terephthalic acid (PTA) (99.9%) was supplied by Thermofisher Acros Organics. 1,4-cyclohexanedimethanol (CHDM) (99.8%) with 70 mol% of the trans-isomer, dimethyltin oxide (DMTO) and germanium dioxide (99.9%) were supplied by Sigma Aldrich. Isosorbide (99.8%) commercialized under the trade name Polysorb P was kindly supplied by Roquette Frères. Calcium phosphonate (Irgamod 195 from BASF) was used as antioxidant. All these chemicals were used as received without further purification.

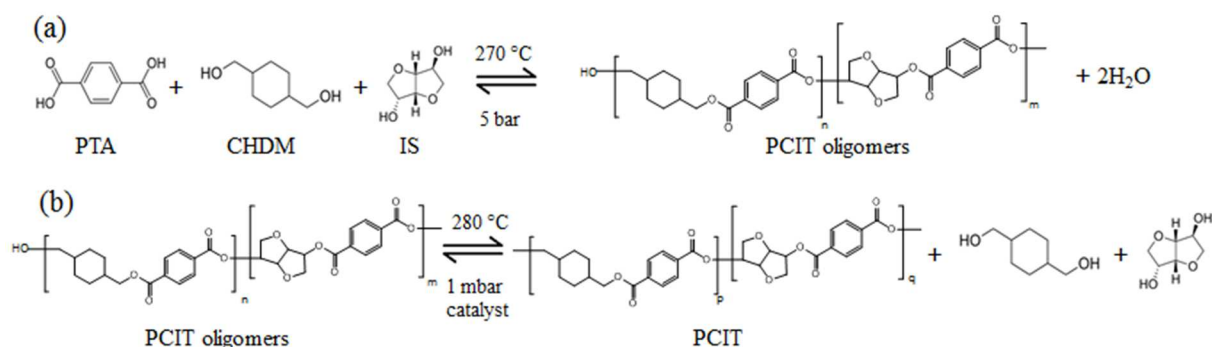
### 2.2. Polyester synthesis

Polymer samples were synthesized via a two-step, melt polycondensation reaction (esterification and transesterification, see Figure 2) in a 100 L stainless-steel batch reactor equipped with a heating system, a mechanical stirrer with torque measurement, a distillation column, a vacuum line and a nitrogen-gas inlet.

In the first step, PTA (21.05 kg, 126.7 moles), CHDM and isosorbide were added in a 1/1.1 (acid/alcohol) molar ratio. Additionally, dimethyltin oxide and germanium dioxide were added as catalyst. Quantities were adjusted, depending on the feed compositions. Finally, 500 ppm of antioxidant relative to the weight of monomers was added to the mixture. Then, the system was inerted via 4 cycles of vacuum/nitrogen gas between 60 and 80 °C. The reaction medium was then heated to 270 °C under 5 bar of pressure and constant stirring. The rate of esterification was estimated by the quantity of distillate collected.

In the second step, the pressure was reduced to 1 mbar in 60 minutes and the temperature was raised to 280 °C to initiate the transesterification. Low-pressure conditions were maintained until the desired torque, as measured by the stirrer, was reached.

A polymer strand was then withdrawn from the bottom drain valve of the reactor and quenched in a water bath. PCIT pellets were obtained after granulation. Using such a procedure avoids contact of the warm polymer with oxygen, thus reducing coloration and thermo-oxidative degradation.



**Figure 2. General scheme of PCIT synthesis from PTA, IS and CHDM (a) esterification, (b) transesterification.**

A solid-state polymerization (SSP) stage was applied to the semi-crystalline copolyesters that have been synthesized. Prior to SSP, they were crystallized at 170 °C under nitrogen flow during 4 hours. Then SSP was run under nitrogen flow in an oil bath with temperatures ranging from 230 to 240 °C.

### 2.3. Characterization

The polymer molar mass was assessed by size exclusion chromatography (SEC) in a mixture of chloroform: 1,1,1,3,3,3 hexafluoro-2-propanol (95/5 v/v). Samples of 1 g.L<sup>-1</sup> were eluted at a flow rate of 0.75 mL.min<sup>-1</sup>. The signals were then detected with a RI detector (Viscotek VE-3580). The average molar masses ( $M_n$  and  $M_w$ ) were determined with a calibration method using poly(methylmethacrylate) (PMMA) standards.

The reduced viscosity ( $\eta_{red}$ ) of the polymers was determined (according to ISO 1628) with an automated Ubbelohde capillary at 25.0 ± 0.1 °C. Polymer samples were dissolved at 80 °C in dichloroacetic acid at a concentration of 1 g.L<sup>-1</sup>.

The thermal properties of the PCIT were measured on a TA Instrument Q20 Differential Scanning Calorimeter (DSC) under a nitrogen atmosphere (50 mL.min<sup>-1</sup>). The polymer sample was first heated from 10 to 300 °C at a rate of 10 °C.min<sup>-1</sup>. Then, the sample was cooled to 10 °C at a rate of 10 °C.min<sup>-1</sup>. Finally, the sample was heated again to 300 °C at a rate of 10 °C.min<sup>-1</sup>. The crystallization temperature (T<sub>c</sub>) was taken at peak maximum during the cooling scan and the crystallization enthalpy (ΔH<sub>c</sub>) was determined with the integration of the peak. The glass transition temperature (T<sub>g</sub>) of the polymer was taken at midpoint during the second heating scan. The cold crystallization temperature (T<sub>cc</sub>) was taken at peak maximum during the second heating scan and the cold crystallization enthalpy (ΔH<sub>cc</sub>) was determined with the integration of the peak. The melting temperature (T<sub>m</sub>) was taken at maximum peak during the second heating and the melting enthalpy (ΔH<sub>m</sub>) was determined with the integration of the peak.

For the semi-crystalline polymers, a solid-state polymerization (SSP) step was carried out. Samples of polymers were withdrawn during the SSP to assess the evolution of reduced viscosity and mechanical properties as a function of the SSP time.

The <sup>1</sup>H-NMR analysis of PCIT was performed using a 400 MHz Bruker liquid-state NMR spectrometer equipped with a QNP probe. 10 mg of each sample was dissolved in 0.6 mL of deuterated tetrachloroethane (TCE-d<sub>2</sub>). Tetramethylsilane (TMS) was used as internal standard. NMR measurements were recorded at 25 °C.

The theoretical value of isosorbide loss during the synthesis is calculated according to equation (1)

$$\text{Isosorbide loss (\%)} = 100 - \frac{[100 - (100-x)xe]}{x} \times 100 \quad \text{eq. (1)}$$

where x is the isosorbide content used in feed (mol%) and e the alcohol/acid molar ratio

The glass transition temperature, T<sub>g</sub>, for copolymers or polymers blends can be estimated with equation (2):

$$1/T_g = \omega_1/T_{g1} + \omega_2/T_{g2} \quad \text{eq. (2)}$$

where ω<sub>1</sub> and ω<sub>2</sub> are the weight fractions of the comonomers and T<sub>g1</sub> and T<sub>g2</sub> the glass transition temperatures of the respective homopolymers in °C.

Prior to injection molding, samples were carefully dried during 6 hours at temperatures ranging between 120 and 150 °C. Before injection molding, samples moisture was controlled using an Aquatrac-3E machine (Brabender Messtechnik).

Injection molding of the specimens was done at temperatures between 270 and 290 °C using a Engel Victory 80 injection molding machine. Mould temperature was kept at 50 °C.

The measurement of mechanical properties such as tensile modulus, flexural modulus, tensile stress at break and elongation at break were carried out by using a Instron 5 966 machine and following ISO 178 (bars dimensions: 80×10×4 mm) and ISO 527 (dumbbell type: 5A).

Charpy impact resistance was determined with a Ceast 9050 device (Instron). Trials were run according to ISO 179-1eU first. If the result was higher than 125 kJ.m<sup>-2</sup>, notched trial at 23 °C was performed following ISO-179/ 1eA.

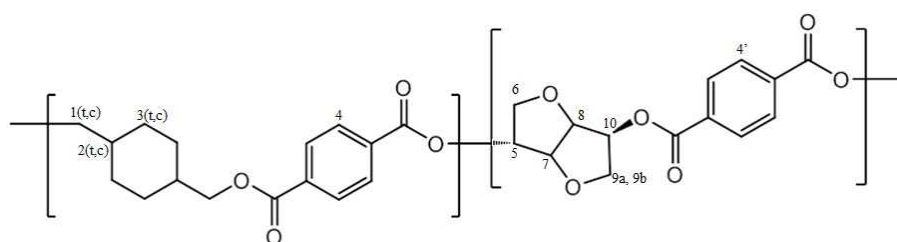
Heat Deflection Temperature (HDT) was determined under a load of 0.455 MPa and the temperature was raised at 2 °C.min<sup>-1</sup> until a deflection of 0.34 mm (ISO75).

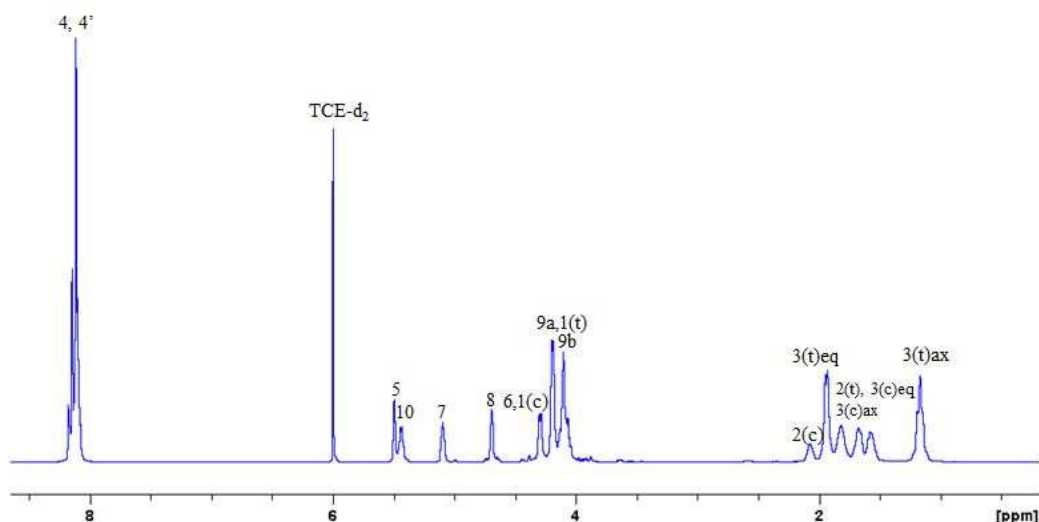
### 3. Results and discussion

#### 3.1. Synthesis of PCIT polyesters

The different polyesters were synthesized using a classical two-step, melt polycondensation reaction, as depicted in Figure 2. Esterification and polycondensation between PTA, CHDM and isosorbide were carried out at 270 and 280 °C, respectively. Dimethyltin oxide (DMTO) and germanium dioxide (GeO<sub>2</sub>) were used as catalysts. Quantities were calculated as the weight of metallic element to the theoretical polymer quantity. These catalysts were described to be efficient for polyester synthesis with isosorbide<sup>17,24,25</sup>. Quantity of each catalyst was changed depending on isosorbide molar content (see Table 1). The aims were to reach acceptable molar masses for all the PCIT samples and to study if degradation occurs.

Polyesters with isosorbide content ranging from 16 to 61 mol% relative to the total amount of diols were successfully synthesized. The CHDM used in this study was composed from 70/30 mol% of trans/cis isomers. <sup>1</sup>H-NMR spectrum for PCIT<sub>40</sub>T is given in Figure 3 as example. Peaks for CHDM are at δ = 1.17 ppm (2H<sub>3(trans)</sub> ax), δ = 1.59 ppm (2H<sub>3(cis)</sub> ax), δ = 1.68 ppm (2H<sub>3(cis)</sub> eq), δ = 1.83 ppm (1H<sub>2(trans)</sub>), δ = 1.95 ppm (2H<sub>3(trans)</sub> eq), δ = 2.08 ppm (1H<sub>2(cis)</sub>), δ = 4.20 ppm (2H<sub>1(trans)</sub>), and δ = 4.31 ppm (2H<sub>1(cis)</sub>). Peaks for isosorbide are at δ = 4.10 ppm (1H<sub>9a</sub>), δ = 4.20 ppm (1H<sub>9b</sub>), δ = 4.31 ppm (1H<sub>6</sub>), δ = 4.71 ppm (1H<sub>8</sub>), δ = 5.10 ppm (1H<sub>7</sub>) and δ = 5,51 ppm (1H<sub>5</sub> and 1H<sub>10</sub>). With oxymethylene protons of IS and CHDM from <sup>1</sup>H-NMR spectrum, the composition ratio can be determined for the different samples. Ratio of trans/cis isomers of CHDM in the polymers was found to be equal to feed ratio.





**Figure 3.**  $^1\text{H-NMR}$  spectrum of  $\text{PCI}_{40}\text{T}$  with peak assignments ( $\text{C}_2\text{D}_2\text{Cl}_4$  at  $25^\circ\text{C}$ ,  $400\text{MHz}$ ).

The characteristics of the PCIT polyesters are summarized in Table 1. During polycondensation, the torque measured from the stirrer reflects the evolution of the melt viscosity for one copolymer composition. It is related to the increase in molar mass. Reactions were stopped when the targeted torque was reached.

All the PCIT polymers have satisfactory molar masses, even with different catalysts composition. The amorphous polyesters do not suffer from ring hydration of isosorbide which leads to increase molar mass dispersity ( $\text{Đ}$ ). Therefore, our synthesis process is well adapted for this polyester, whatever isosorbide molar content and catalysts composition.

**Table 1.** Characteristics of PCIT synthesized with various molar fraction of isosorbide relative to the diols.

Sample code <sup>a</sup>	Feed ratio IS/CHDM	Composition ratio <sup>b</sup> IS/CHDM	Catalysts (ppm) <sup>c</sup>	IS loss (%) <sup>d</sup>	$M_n^e$ (g.mol <sup>-1</sup> )	$\text{Đ}^e$	$\eta_{\text{red}}^f$ (mL.g <sup>-1</sup> )	$t_{\text{pc}}^g$ (min)
$\text{PCI}_{16}\text{T}$	21.8/78.2	15.7/84.3	Sn (250)	28.0	14 400	2.1	61.1	158
$\text{PCI}_{20}\text{T}$	26.6/73.4	21.3/78.7	Sn (200) Ge (200)	19.9	12 640	2.2	56.0	337
$\text{PCI}_{25}\text{T}$	31.4/68.6	24.7/75.3	Sn (250)	21.3	12 350	2.2	56.5	199
$\text{PCI}_{39}\text{T}$	45.9/55.1	39.2/60.8	Sn (350)	14.6	16 250	2.1	57.7	311
$\text{PCI}_{61}\text{T}$	65.1/34.9	60.8/39.2	Sn (350)	6.6	10 000	2.8	53.5	280

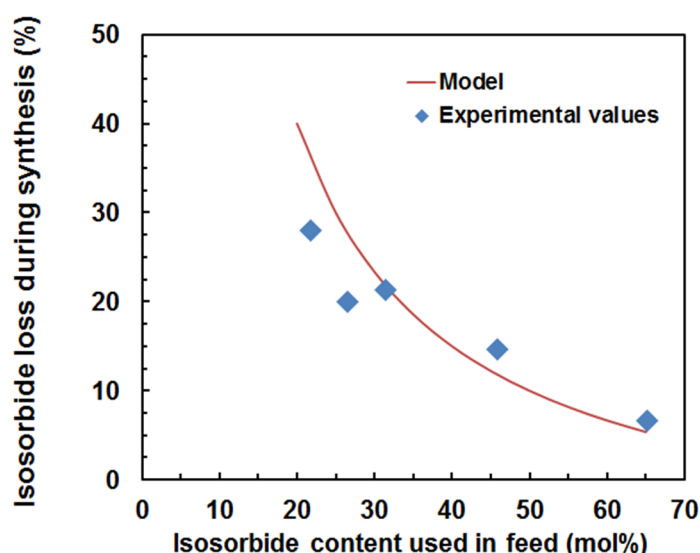
<sup>a</sup> The sample codes denote the proportion of IS in the copolyester relative to the total diol. <sup>b</sup> Determined by  $^1\text{H-NMR}$  spectroscopy at  $25^\circ\text{C}$  using deuterated tetrachloroethane as solvent. <sup>c</sup> The sample codes denote the weight of metal relative to theoretical polymer weight. <sup>d</sup> Defined with the rate between composition ratio and feed ratio. <sup>e</sup> Determined by SEC using PMMA standards. <sup>f</sup> Determined at  $25^\circ\text{C}$  using dichloroacetic acid as solvent. <sup>g</sup> Total polycondensation time.

As can be seen in Table 1, polycondensation time increases with increasing isosorbide molar content. It is remarkable that association between tin and germanium were not as efficient as expected by increasing polycondensation time to 337 minutes for  $\text{PCI}_{20}\text{T}$ , whereas  $\text{PCI}_{25}\text{T}$  only requires 199 minutes to reach similar properties. Thus, for higher isosorbide molar content, tin catalyst content was increased and germanium was removed. Tin (IV) catalysts are well-known to be very efficient as polycondensation catalysts. However, even with higher

content of catalyst, polycondensation time was increased. For  $\text{PCI}_{61}\text{T}$ , polycondensation was stopped earlier because of torque stagnation. This increasing time of polycondensation has to be related with secondary hydroxyl groups of isosorbide compared to primary hydroxyl groups of CHDM.

Furthermore, isosorbide hydroxyl groups are majority of oligomers end-groups (more than 80% calculated by  $^1\text{H-NMR}$ ) and most of them are *endo* groups (around 2/3). This effect is due to the steric hindrance of the *endo* group. It explains why the polycondensation is more difficult resulting in higher polycondensation times.

The amount of isosorbide actually inserted in polymer chains is not 100% (Table 1). A fraction of isosorbide does not react fast enough and remains as free isosorbide. Then, this part is removed during the polycondensation under vacuum. It is remarkable that this difference is lower for composition with higher isosorbide molar content (see Figure 4). This phenomenon was also observed by Quintana *et al.*<sup>3</sup> for the poly(ethylene-*co*-isosorbide terephthalate) (PEIT) synthesis and by Lavilla *et al.*<sup>25</sup> for the poly(butylene-*co*-isosorbide terephthalate) (PBIT) synthesis but to a lesser extent.



**Figure 4.** Isosorbide loss during the PCIT synthesis at 280 °C with various molar fraction of isosorbide (relative to the diols) in the polymers (blue symbols) and comparison with mathematic model (red curve).

Yoon *et al.*<sup>14</sup> and Kim *et al.*<sup>26</sup> carried out terpolyesters synthesis where CHDM, isosorbide and ethylene glycol were involved. Kim *et al.* found that CHDM has the best reactivity, despite its bulky structure. They also noted EG is most of the time at the end of oligomers, improving the transesterification rate. EG is also easier to be removed than CHDM during polycondensation under vacuum, because of lower boiling point. Beside, Yoon *et al.* considered EG as an effective chain linker for PEICT synthesis. Park *et al.* also found higher CHDM content in the product than in the feed, while EG showed the opposite trend.

In the case of PCIT, this trend is amplified because of the much lower reactivity of IS compared to CHDM. CHDM reacts first with PTA and isosorbide is incorporated later. Then,

CHDM is fully incorporated, even its excess. A fraction of remaining isosorbide part does not react and is removed during polycondensation.

Consider for instance a molar feed ratio of 45.9/55.1 (IS/CHDM) and an 1.1 diols excess. If the CHDM is fully incorporated, the copolyester contains 60.6 mol% (= 55.1×1.1) of CHDM and 39.4 mol% of isosorbide. This allows to predict a final isosorbide incorporation of 85.8% (= (39.4/45.9)×100) and then an isosorbide loss of 14.2% (= 100-85.8). Experiment has given an isosorbide loss of 14.6%.

~~By following the same scientific reasoning, equation 1 can be obtained to calculate the theoretical value of isosorbide loss:~~

~~$$\text{Isosorbide loss (\%)} = 100 \left[ \frac{100 - (100 - x) \times e}{x} \right] \times 100 \quad (1)$$~~

~~where x is the isosorbide content used in feed (mol%) and e the alcohol/acid molar ratio.~~

Theoretical values can be calculated for all isosorbide molar content from equation (1) with e = 1.1 (see Exp. Part). Experimental results fit well with theoretical values (see Figure 4) for isosorbide molar content between 20 and 65%. However, such phenomenon was not reported by Koo and co-workers<sup>17</sup> for the poly(1,4-cyclohexanedimethylene-co-isosorbide terephthalate) (PCIT) synthesis. They found for some composition a higher composition ratio of isosorbide in the polymer than in the feed ratio.

### 3.2. Thermal properties

Thermal properties of PCIT synthesized are summarized in Table 2. Data for PCT are coming from the study of Turner<sup>23</sup> and glass transition temperature for high molar mass PIT is coming from the study of Storbeck *et al.*<sup>2</sup>. They are given for comparison purpose.

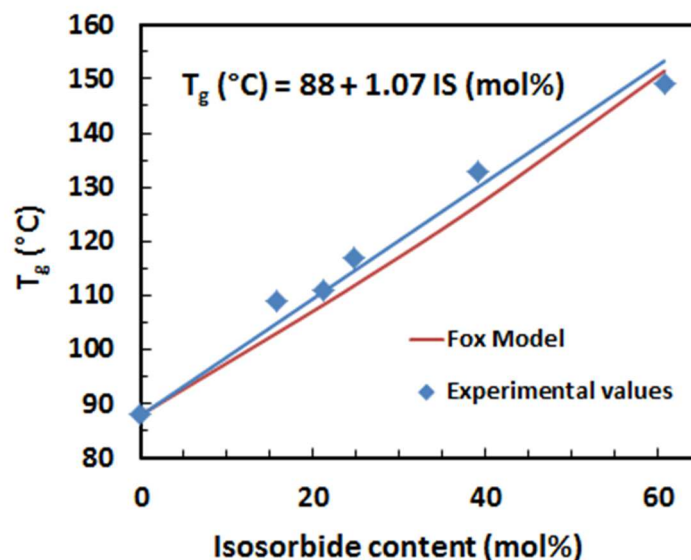
**Table 2. Thermal properties of PCIT synthesized with various molar fraction of isosorbide (relative to the diols) in the polymers.**

Sample code <sup>a</sup>	Nature	First heating scan <sup>b</sup>					Cooling scan <sup>b</sup>			Second heating scan <sup>b</sup>			
		T <sub>g</sub> <sup>c</sup> (°C)	T <sub>cc</sub> <sup>d</sup> (°C)	ΔH <sub>cc</sub> (J.g <sup>-1</sup> )	T <sub>m</sub> <sup>d</sup> (°C)	ΔH <sub>m</sub> (J.g <sup>-1</sup> )	T <sub>c</sub> <sup>d</sup> (°C)	ΔH <sub>c</sub> (J.g <sup>-1</sup> )	T <sub>g</sub> <sup>c</sup> (°C)	T <sub>cc</sub> <sup>d</sup> (°C)	ΔH <sub>cc</sub> (J.g <sup>-1</sup> )	T <sub>m</sub> <sup>d</sup> (°C)	ΔH <sub>m</sub> (J.g <sup>-1</sup> )
PCT		88 <sup>e</sup>	-	-	300 <sup>e</sup>	-	-	88 <sup>e</sup>	-	-	300 <sup>e</sup>	-	
PCI <sub>16</sub> T	Semi-crystalline	105	184	28	266	30	175	11	109	184	18	263	33
PCI <sub>20</sub> T		108	178	25	260	27	ND	ND	111	187	25	256	24
PCI <sub>25</sub> T		114	188	2	253	3	ND	ND	117	186	2	250	3
PCI <sub>39</sub> T		132	-	-	-	-	-	-	133	-	-	-	-
PCI <sub>61</sub> T	Amorphous	149	-	-	-	-	-	-	149	-	-	-	-
PIT		205 <sup>f</sup>	-	-	-	-	-	-	205 <sup>f</sup>	-	-	-	-

<sup>a</sup> The sample codes denote the proportion of IS in the copolyester relative to the total diol. <sup>b</sup> 10 °C.min<sup>-1</sup>. <sup>c</sup>Midpoint. <sup>d</sup> Peak maximum. <sup>e</sup> From reference 23. <sup>f</sup> From reference 2. ND = Not Detected.

The glass transition temperature (T<sub>g</sub>) of the PCIT copolyester increased almost linearly with isosorbide content (Figure 5). For each molar percent of isosorbide included in the polyester, the glass transition temperature increases of 1.07 °C. Results are very close to those found by

Quintana *et al.*<sup>3</sup> for poly(ethylene-co-cyclohexanedimethylene-co-isosorbide terephthalate) (PEICT) synthesis (1.12 °C/mol% of isosorbide). Results fit well with theoretical values from Fox model<sup>27</sup> eq.2 (see Exp. Part) with  $T_{g1}$  and  $T_{g2}$  the glass transition temperatures of the homopolymers: 88°C for PCT and 205°C for PIT respectively.



**Figure 5. Glass transition temperature ( $T_g$ ) of PCIT with various molar fraction of isosorbide (relative to the diols) in the polymers and comparison with Fox model (eq.2).**

As the isosorbide content increases from 0 to 25 mol% in the PCIT, the melting temperature linearly decreases from 300 to 250°C, meanwhile the glass transition temperature increases from 88 to 117°C (Table 2). These polymers are still semi-crystalline even with 25 mol% of isosorbide. This feature is relevant for solid-state polymerization and will be discussed later.

The value of melting enthalpy of  $PCI_{25}T$  is very low, indicating a lower crystallinity than  $PCI_{16}T$  and  $PCI_{20}T$ . Meanwhile, the value of cold crystallization enthalpy is rather low, indicating a weaker ability to crystallize at  $10^{\circ}C.min^{-1}$ . This has to be related with the increasing comonomer part, which alters the chain regularity resulting in lower crystallization ability and linear melting temperature decrease (see Figure 6). Moreover, CHDM has potential to be aligned with PTA thanks to its different conformation, explaining the good crystallization ability for  $PCI_{16}T$ .

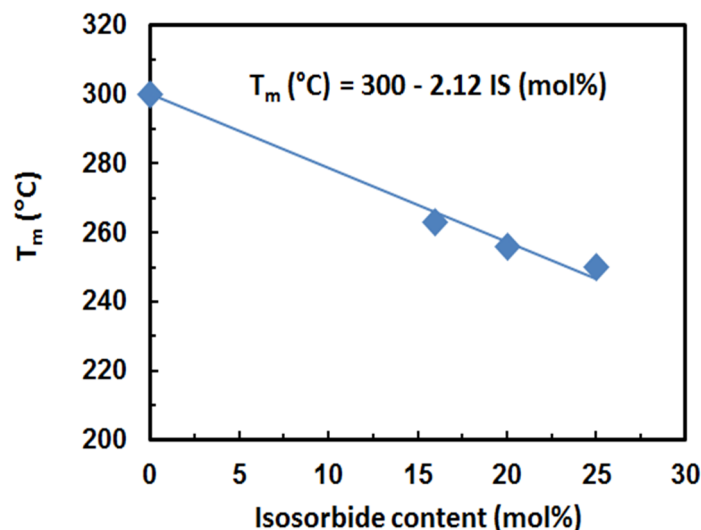


Figure 6. Melting temperature ( $T_m$ ) of semi-crystalline PCIT with various molar fraction of isosorbide (relative to the diols) in the polymers.

### 3.3. Solid-state polymerization

The high melting temperatures of semi-crystalline PCIT are of interest for solid-state polymerization (SSP). High temperatures ( $\geq 230$  °C) can be used, reducing the solid-state polymerization time and high viscosities of semi-crystalline materials may be reached faster. SSP temperature was defined as  $T_m - 20$  °C for semi-crystalline samples.

To assess evolution of molar masses with SSP time, polymers samples were carefully removed from the flask at different time intervals. They were characterized by their reduced viscosity. Results are plotted in Figure 7 and summarized in S1 (see ESI, S1).

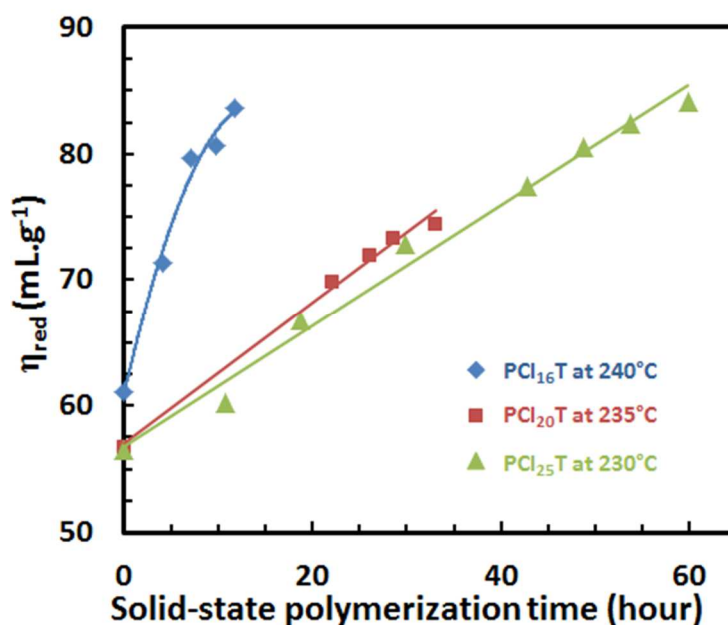


Figure 7. Evolution of the reduced viscosity ( $\text{mL}\cdot\text{g}^{-1}$ ) of PCI<sub>16</sub>T, PCI<sub>20</sub>T and PCI<sub>25</sub>T under nitrogen flow depending on the solid-state polymerization time at  $T = 240$  °C,  $T = 235$  °C and  $T = 230$  °C, respectively.

These results showed that high molar masses can be obtained by SSP for semi-crystalline materials. As can be seen, semi-crystalline PCITs strongly differ in their SSP kinetics. Indeed, PCI<sub>16</sub>T reduced viscosity increases very fast, by increasing from 61.1 to 85.6 mL.g<sup>-1</sup> in only 14 hours. Meanwhile, PCI<sub>20</sub>T and PCI<sub>25</sub>T present more or less the same kinetics and more time is required to achieve reduced viscosity higher than 70 mL.g<sup>-1</sup>.

This result was expected and has to be related with the lower crystallinity, the different catalytic composition for PCI<sub>20</sub>T and the lower SSP temperature. Therefore, lower crystallinity is expected for higher isosorbide content reducing the concentration of reactive functions in amorphous phase. However, for all the PCIT samples, the obtained reduced viscosity was good and enough for end-use requirements.

### 3.4. Mechanical properties

Poly(1,4-cyclohexanedimethylene terephthalate) (PCT) is known to exhibit ductile mechanical properties coupled with high glass transition temperature<sup>16</sup>. According to Chen *et al.*<sup>11</sup>, this property comes from the flexibility of CHDM cyclohexylene ring. This flexibility allows a better relaxation and finally a better chain mobility. This is one of the reasons why CHDM is widely studied and added as monomer or as comonomer into polymers to improve their mechanical resistance<sup>28-29</sup>.

The semi-crystalline samples were subjected to solid-state polymerization in order to follow the evolution of mechanical properties with increasing molar masses. The results for PCI<sub>16</sub>T are given in Table 3. As can be seen, it is noteworthy the flexural and tensile properties do not change a lot with increasing molar masses. This means the maximum value for these properties were reached earlier. However, notched impact strength was greatly improved, by increasing from 8 ± 2 kJ.m<sup>-2</sup> for sample without SSP to 107 ± 3 kJ.m<sup>-2</sup> for sample with 14 hours of SSP. Meanwhile, tensile stress and elongation at break slowly increase from 44 ± 3 to 60 ± 1 MPa and from 98 ± 14% to 122 ± 2%, respectively.

**Table 3. Evolution of mechanical properties depending on solid-state polymerization time for PCI<sub>16</sub>T**

Sample code <sup>a</sup>	$\eta_{red}^b$ (mL.g <sup>-1</sup> )	Notched impact strength at 23 °C (kJ.m <sup>-2</sup> )	Flexural modulus (MPa)	Tensile modulus (MPa)	Tensile stress at break (MPa)	Elongation at break (%)
PCI <sub>16</sub> T	61.1	8 ± 2	1 450 ± 10	1 810 ± 20	44 ± 3	98 ± 14
PCI <sub>16</sub> T SSP-4h	71.3	45 ± 25	1 430 ± 30	1 910 ± 10	52 ± 1	97 ± 4
PCI <sub>16</sub> T SSP-14h	85.6	107 ± 3	1 430 ± 10	1 730 ± 20	60 ± 1	122 ± 2

<sup>a</sup> The sample codes denote the composition ratio of Is in the copolyester (diol part) and the time (hour) of solid-state post-condensation is indicated below. <sup>b</sup> Determined at 25 °C using dichloroacetic acid as solvent.

To evaluate the mechanical properties of polymers, it is relevant to compare them with other polyesters containing CHDM and another rigid diol. Kelsey *et al.*<sup>30</sup> described copolyesters with 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) and others diols (1,3-propanediol, 1,4-butanediol and CHDM). They found CHDM and TMCD offer a good compromise between high thermal resistance and enhanced mechanical and optical properties. TMCD is a bulky rigid diol produced under very harsh operating conditions<sup>30</sup>. Afterwards, this copolyester based on CHDM and TMCD was developed by Eastman Chemical Company<sup>31</sup> and commercialized under the trade name Tritan®. This polymer has been commercialized with success as bisphenol A-polycarbonate replacement<sup>32</sup>. Thus, comparing the mechanical properties of high performance Tritan ® polymers and PCIT polymers is of interest for our study.

Mechanical properties of the PCIT polymers are summarized in Table 4. The tests were also performed on Tritan ® TX1001 and TX2001 samples to compare the two copolyesters series using the conditions described in the experimental section.

**Table 4. Mechanical properties of the PCIT polymers and comparison with Tritan ® TX1001 and TX2001.**

Sample code <sup>a</sup>	Nature	$\eta_{red}^b$ (mL.g <sup>-1</sup> )	Impact strength (kJ.m <sup>-2</sup> )			Flexural modulus (MPa)	Tensile modulus (MPa)	Tensile stress at break (MPa)	Elongation at break (%)	HDT <sup>d</sup> (°C)
			Unnotched 23 °C	Notched 23 °C	Notched -30 °C					
PCI <sub>16</sub> T SSP-14h	Semi-crystalline	85.6	>125	107 ± 3	NM <sup>c</sup>	1 430 ± 10	1 730 ± 20	60 ± 1	122 ± 2	97
PCI <sub>20</sub> T SSP-33h		74.5	>125	99 ± 10	NM <sup>c</sup>	1 520 ± 10	1 780 ± 25	57 ± 1	109 ± 3	101
PCI <sub>25</sub> T SSP-60h		84.1	>125	95 ± 8	17 ± 1	1 540 ± 5	1 840 ± 10	57 ± 1	99 ± 3	104
PCI <sub>39</sub> T	Amorphous	57.7	>125	42 ± 10	2 ± 0.1	1 710 ± 5	2 030 ± 5	44 ± 1	37 ± 6	116
PCI <sub>61</sub> T		53.5	2 > 125 3 at 67 ± 18 5 at 28 ± 8	13 ± 2	NM <sup>c</sup>	2 180 ± 15	2 140 ± 30	50 ± 1	19 ± 3	137
Tritan ® TX1001		NM <sup>c</sup>	>125	92 ± 3	15 ± 3	1 440 ± 10	1 845 ± 5	54 ± 2	92 ± 4	96
Tritan ® TX2001	NM <sup>c</sup>	>125	NM <sup>c</sup>	NM <sup>c</sup>	1 490 ± 5	1 825 ± 30	54 ± 1	76 ± 2	104	

<sup>a</sup> The sample codes denote the composition ratio of Is in the copolyester (diol part) and the time (hour) of solid-state post-condensation is indicated below. <sup>b</sup> Determined at 25 °C using dichloroacetic acid as solvent. <sup>c</sup> Not Measured. <sup>d</sup> Heat Deflection Temperature.

Semi-crystalline PCIT polymers have outstanding mechanical properties, even with 25 mol% of isosorbide. Flexural and tensile moduli were higher than 1 400 MPa and 1700 MPa, respectively. Tensile stress at break is ranging from 57 to 60 MPa. Results were very close to those of Tritan ® TX1001 and TX2001. It is noteworthy that elongation at break slowly decreases when the amount of isosorbide increases. This may be related with a chain mobility decrease caused by rigid isosorbide or lower molar masses. However, this value remains superior or equal to 100%, even with 25 mol% of isosorbide. Moreover, the Charpy impact strength of semi-crystalline PCIT copolyesters are higher. Indeed, the values of Charpy impact strength for notched samples at 23 °C were between 95 and 107 kJ.m<sup>-2</sup>, whereas value

for Tritan ® TX1001 was  $92 \pm 3 \text{ kJ.m}^{-2}$ . It means PCIT copolyesters have enhanced impact resistance.

Amorphous PCIT could be used for applications where high thermal resistance is required. Values for elongation at break and impact strength are rather low and have to be related with lower molar masses of amorphous samples. Unnotched impact strength values for PCI<sub>61</sub>T present three families of results. This may be linked with polydispersity and molar masses, indicating they are around critical mass for entanglement for PCI<sub>61</sub>T. Therefore, molar masses still have to be increased for this polymer, by the use for example of a chain extender. Nevertheless, others properties were increased, especially tensile and flexural modulus. Mostly, these values are coupled with unique values of HDT, which clearly increases with isosorbide molar content.

PCIT polymers could be used in a wide range of temperature, demonstrating the powerful impact of isosorbide on these new copolyesters. Also, it can be easily imagined that composition of this polyester can be tuned depending on the targeted applications.

## 4. Conclusions

A biobased copolyester containing isosorbide and 1,4-cyclohexanedimethanol was successfully synthesized using two-step melt polymerization at pilot scale. By tuning the molar feed ratio of each diol, copolyesters with 16 to 61 mol% of isosorbide were synthesized, without ring hydration of isosorbide. Thermal properties ( $T_g$ ) were greatly enhanced by isosorbide, whereas CHDM increased the mechanical resistance. Thus, tunable mechanical and thermal properties were achieved. The synthesized copolyester present a semi-crystalline window until 25 mol% of IS relative to the total diol part. This means a solid-state polymerization was possible and molar masses were increased using such process. Comparison with high performance copolyester showed the outstanding properties of PCIT copolyester and it is clearly promising as a biobased BPA-polycarbonate replacement.

## Acknowledgments

The authors would like to thank the company Roquette Frères (France) and the ANRT for financial support. The authors would like to thank the NMR Polymer Center of Institut de Chimie de Lyon (FR5223) for assistance and access to the NMR facilities.

**Declaration of interest:** none

## Supporting information

**S1. Initial and final reduced viscosity ( $\eta_{\text{red}}$ ) of the PCIT polyesters depending on the molar composition, the solid-state polymerization (SSP) time (hour) under nitrogen flow and temperature ( $^{\circ}\text{C}$ ).**

Sample code <sup>a</sup>	SSP temperature ( $^{\circ}\text{C}$ )	SSP time (hour)	$\eta_{\text{red}}^{\text{b}}$ ( $\text{mL}\cdot\text{g}^{-1}$ )
PCI <sub>16</sub> T	240	0	61.1
		14	85.6
PCI <sub>20</sub> T	235	0	56.0
		33	74.5
PCI <sub>25</sub> T	230	0	56.5
		60	84.1

<sup>a</sup>The sample codes denote the proportion of IS in the copolyester relative to the total diol. <sup>b</sup>Determined at 25  $^{\circ}\text{C}$  using dichloroacetic acid as solvent.

## References

1. Fenouillot F., Rousseau A., Colomines G., Saint-Loup R., Pascault J.-P., Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Progress in Polymer Science*, 2010, 35, 578–622.
2. Storbeck R., Rehahn M., Ballauff M., Synthesis and properties of high-molecular-weight polyesters based on 1,4:3,6-dianhydrohexitols and terephthalic acid. *Makromolekulare Chemie*, 1993, 194, 53–64.
3. Quintana R., de Ilarduya A.M., Alla A., Muñoz-Guerra S., Polyterephthalates Made from Ethylene glycol, 1,4-Cyclohexanedimethanol, and Isosorbide. *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, 49, 2252–2260.
4. Thiem J., Lüders H., Synthesis of Polyterephthalates Derived from Dianhydrohexitols. *Polymer Bulletin*, 1984, 11, 365–369.
5. Zhang F., Wang Q., Wang L., Bai Y., Implementing plant-derived isosorbide and isomannide as comonomers for polyester synthesis: Effects of crystallization properties on optical properties. *Journal of Applied Polymer Science*. 2017.
6. Charbonneau L.F., Johnson R.E., Witteler H.B., Khanarian G., Polyesters including isosorbide as a comonomer and methods for making same. US5959066, 28/09/1999.
7. Bersot J.C., Jacquelin N., Saint-Loup R., Fuertes P., Rousseau A., Pascault J.-P., Spitz R., Fenouillot F., Monteil V., Efficiency increase of poly(ethylene terephthalate-co-isosorbide terephthalate) synthesis using bimetallic catalytic systems. *Macromolecular Chemistry and Physics*. 2011, 212, 2114–2120.
8. Fuji M., Akita M., Tanaka T., Polycarbonate copolymer and process for production thereof. WO 2007/148604, 27/12/2007.
9. Jansen B.J.P., Kamps J.H., Looij H., Kung E., Isosorbide-based polycarbonates, method of making, and articles formed therefrom. WO 2009/052463, 23/04/2009.
10. Caouthar A.A., Loupy A., Bortolussi M., Blais J.-C., Dubreucq L., Meddour A., Synthesis and characterization of new polyamides based on diphenylaminoisosorbide. *Journal of Polymer Science Part A: Polymer Chemistry*. 2005, 43, 2480–2491.
11. Chen L.P., Yee A.F., Goetz J.M., Schaefer J., Molecular structure effects on the secondary relaxation and impact strength of a series of polyester copolymer glasses. *Macromolecules*. 1998, 31, 5371–5382.
12. Liu J.W., Yee A.F., Enhancing plastic yielding in polyestercarbonate glasses by 1,4-cyclohexylene linkage addition. *Macromolecules*. 1998, 31, 7865–7870.
13. Cai X., Yang X., Zhang H., Wang G., Modification of biodegradable poly(butylene carbonate) with 1,4-cyclohexanedimethylene to enhance the thermal and mechanical properties. *Polymer Degradation and Stability*. 2017, 143, 35–41.
14. Yoon W.J., Hwang S.Y., Koo J.M., Lee Y.J., Lee S.U., Im S.S., Synthesis and characteristics of a biobased high  $T_g$  terpolyester of isosorbide, ethylene glycol, and 1,4-cyclohexanedimethanol: effect of ethylene glycol as a chain linker on polymerization. *Macromolecules*. 2013, 46, 7219–7231.
15. Kibler C.J., Bell A., Smith J.G., Polyesters of 1,4-cyclohexanedimethanol. *Journal of Polymer Science Part A: General Papers*. 1964, 2, 2115–2125.

16. Jeong Y.G., Jo W.H., Lee S.C., Cocrystallization of poly(1,4-cyclohexylenedimethylene terephthalate-co-hexamethylene terephthalate) copolymers. *Macromolecular Research*, 2004, 12, 459–465.
17. Koo J., Hwang S., Yoon W., Lee Y., Kim S.H., Im S.S., Structural and thermal properties of poly(1,4-cyclohexanedimethylene terephthalate) containing isosorbide. *Polymer Chemistry*, 2015, 6, 6973–6986.
18. Khan M.Q., Lee H., Khatri Z., Kharaghani D., Khatri M., Ishikawa T., Im S.-S., Kim I.S., Fabrication and characterization of nanofibers of honey/poly(1,4-cyclohexane dimethylene isosorbide terephthalate) by electrospinning. *Materials Science & Engineering*, 2017, C81, 247–251.
19. Phan D.-N., Lee H. , Choi D., Kang C.-Y., Im S.S., Kim. I.S., Fabrication of two polyester nanofiber types containing the biobased monomer isosorbide: Poly (ethylene glycol 1,4-cyclohexanedimethylene isosorbide terephthalate) and poly (1,4-cyclohexanedimethylene isosorbide terephthalate). *Nanomaterials* 2018, 8, 56.
20. Kasmi N., Majdoub M., Papageorgiou G.Z., Bikiaris D.N., Synthesis and crystallization of new fully renewable resources-based copolyesters: Poly(1,4-cyclohexanedimethanol-co-isosorbide 2,5-furandicarboxylate). *Polymer Degradation and Stability*, 2018, 152, 177–190.
21. Chen T., Jiang G., Li G., Wu Z., Zhang J., Poly(ethylene glycol-co-1,4-cyclohexanedimethanol terephthalate) random copolymers: effect of copolymer composition and microstructure on the thermal properties and crystallization behaviour. *RSC Advances*, 2015, 5, 60570–60580.
22. Yoo H.Y., Umemoto S., Kikutani T., Okui N., Co-crystallization behaviour and melting-point depression in poly(ethylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) random copolyesters. *Polymer*, 1994, 35, 1, 117–122.
23. Turner S.R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *Journal of Polymer Science: Part A: Polymer Chemistry*, 2004, 42, 5847–5852.
24. Yoon W.J., Oh K.S., Koo J.M., Kim J.R., Lee K.J., Im S.S., Advanced polymerization and properties of biobased high  $T_g$  polyester of isosorbide and 1,4-cyclohexanedicarboxylic acid through *in Situ* acetylation. *Macromolecules*, 2013, 46, 2930–2940.
25. Lavilla C., Muñoz-Guerra S., Sugar-based aromatic copolyesters: a comparative study regarding isosorbide and diacetalized alditols as sustainable comonomers. *Green Chemistry*, 2013, 15, 144–151.
26. Kim T., Koo J.M., Ryu M.H., Jeon H., Kim S.-M., Park S.-A., Oh D.X., Park J., Hwang S.Y., Sustainable terpolyester of high  $T_g$  based on bio heterocyclic monomer of dimethyl furan-2,5-dicarboxylate and isosorbide. *Polymer*, 2017, 132, 122–132.
27. Fox T.G., Influence of diluent and of copolymer composition on the glass temperature of a polymer system. *Bulletin American Physical Society*, 1956, 123–132.
28. Wang J., Liu X., Zhang Y., Liu F. , Zhu J., Modification of poly(ethylene 2,5-furandicarboxylate) with 1,4-cyclohexanedimethylene: Influence of composition on mechanical and barrier properties. *Polymer*, 2016, 103, 1–8.

29. Kasmi N., Terzopoulou Z., Papageorgiou G.Z., Bikiaris D.N., Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: Effect of different synthesis methods on molecular weight and properties. *eXPRESS Polymer Letters*, 2018, Vol.12, No.3, 227–237.
30. Kelsey D.R., Scardino B.M., Grebowicz J.S., Chuah H.H., High Impact, Amorphous terephthalate copolyesters of rigid 2,2,4,4-tetramethyl-1,3-cyclobutanediol with flexible diols. *Macromolecules*, 2000, 33, 5810–5818.
31. Barton B.J., Shackelford D.B., Process for the preparation of copolyesters based on 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 1,4-cyclohexanedimethanol. US 2007/02760665, 29/11/2007.
32. Iyer K.A., Chain mobility, secondary relaxation, and oxygen transport in terephthalate copolyesters with rigid and flexible cyclic diols. *Polymer*, 2017, 129, 117–126.

# Graphical Abstract

