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Incorporation of Isosorbide into Poly(butylene terephthalate) via Solid-State Polymerization

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The biomass-based monomer isosorbide was incorporated into poly(butylene terephthalate) (PBT) by solid-state polymerization (SSP) using the macrodiol monomer BTITB-(OH)₂, which consists of isosorbide (I), terephthalic acid (T), and 1,4-butanediol (B) residues. This macromonomer can be synthesized by a simple one-pot, two-step reaction. Polymers with number-average molecular weights up to 100 000 g·mol⁻¹ were readily synthesized from various ratios of PBT/BTITB-(OH)₂. Their molecular weights, thermal properties, and colors were compared with corresponding copolyesters that were obtained by melt polycondensation. We found that *T*_m, *T*_g, and especially *T*_g were superior for materials that were obtained by SSP. This is ascribed to differences in the microstructures of both types of copolyesters; the SSP products exhibit a more blocky structure than do the more random melt-polymerized counterparts. The SSP method resulted in much higher molecular weights and much less colored polymers, and it seems to be the preferred route for incorporating biobased monomers that exhibit limited thermal stability into engineering plastics.

Introduction

Poly(butylene terephthalate) (PBT) is a semicrystalline aromatic polyester that is used in a wide range of engineering applications. A high crystallization rate combined with good thermal and mechanical properties makes PBT very suitable for injection molding applications.¹ However, PBT possesses a low glass-transition temperature (*T*_g ≈ 45 °C), which makes it without glass fibers or other fillers less suitable for applications at elevated temperatures because of a loss of dimensional stability. The mechanical properties of PBT can be modified by the introduction of fillers during compounding,² blending, or copolymerization.

The introduction of biomass-based 1,4:3,6-dianhydro-D-glucitol (isosorbide, Scheme 1), a dianhydrohexitol that is prepared on the industrial scale from starch, into polycondensates has received a significant deal of attention in literature.³ In particular, the incorporation of isosorbide into terephthalate polyesters such as poly(ethylene terephthalate) and PBT afforded polymers with increased *T*_g and thermal stability.^{4–8} The polymers of highest molecular weight were obtained via polycondensation in solution from terephthaloyl chloride and the corresponding diols, whereas the transesterification reaction in bulk with dimethylterephthalate (DMT) turned out to be tedious because of the lack of control of the reaction stoichiometry and the temperature limits in view of degradation reactions that occur during melt polymerization.⁷ In fact, even in the absence of isosorbide, PBT with a molecular weight of >25 000 g·mol⁻¹ is relatively difficult to obtain by melt polycondensation.⁹ High molecular weight can only be reached

through polymerization in the solid state at temperatures that are 10–40 °C below the melting temperature of PBT in the presence of a nitrogen flow or vacuum.¹⁰ During the solid-state polymerization (SSP) of PBT below the melting point of the crystals but relatively far above the glass-transition temperature of the amorphous part, the polymer chains in the amorphous phase are sufficiently mobile to undergo transesterification reactions with a non-volatile diol to be incorporated into the main chain, whereas the volatile products (1,4-butanediol, water) diffuse out of the PBT particles and leave the reactor with the help of an inert gas stream or vacuum. Whereas various copolymers were already obtained via this process from semicrystalline, oligomeric blends of polycondensates,¹¹ the incorporation of monomers has been limited so far.^{12,13}

In this work, we investigated the incorporation of isosorbide into PBT via SSP. For that purpose, we synthesized in good yield a non-volatile macrodiol monomer that is based on isosorbide, butanediol, and terephthalate moieties. Various mixtures of BTITB-(OH)₂/PBT were then subjected to SSP, during which 1,4-butanediol moieties were replaced by the macrodiol residues. The resulting polymers were analyzed and compared with analogues with similar chemical compositions that were obtained via melt polycondensation.

Experimental Section

Materials. Isosorbide (gifts from Agrotechnology and Food Innovations and Roquette Frères), poly(butylene terephthalate) (GE plastics), titanium isopropoxide, triethylamine (Fluka), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) ethanol and diethyl ether (Biosolve) were used as received. Tetrahydrofuran (THF), dichloromethane, and toluene (Biosolve) were dried over an alumina column, degassed, and stored on molecular sieves. Pyridine (Merck) was dried over potassium hydroxide prior to distillation and was stored over molecular sieves. DMT (Merck) was recrystallized from ethanol, terephthaloyl chloride (Aldrich) was

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Scheme 1. Synthesis of the Macromonomer BTITB-(OH)₂

purified by sublimation, and 1,4-butanediol (Acros) was distilled and stored over molecular sieves.

Techniques. We performed all manipulations under an inert atmosphere (argon or nitrogen) by using glovebox (Braun MB-150GI or LM-130) and Schlenk techniques. ¹H and ¹³C{¹H} NMR spectra were recorded at 400 and 100.6 MHz, respectively, on a Varian Mercury Vx spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to the residual deuterated solvent signal. Size exclusion chromatography (SEC) spectra were recorded on a Waters GPC instrument equipped with a Shimadzu LC-10AD pump, a WATERS 2414 differential refractive index detector (at 35 °C), and a MIDAS autoinjector (50 μ L injection volume). HFIP was used as the eluent at a flow rate of 1.0 mL $\cdot$ min⁻¹. PSS (2 $\times$ PFG-lin-XL, 7 μ m, 8 $\times$ 300 mm², 40 °C) columns were used. Molecular weights and molecular weight distributions were calculated relative to PMMA standards. Data acquisition and processing were performed by the use of Viscotek OmniSec 4.0 and Waters Empower 2.0 software. The thermal stabilities of the polymer samples were determined by the use of a Perkin-Elmer Pyris 6TGA apparatus. Polymer (~10 mg) was heated from 40 to 700 °C at a heating rate of 10 °C $\cdot$ min⁻¹ under a N₂ flow of 20 mL $\cdot$ min⁻¹. Results were analyzed by the use of Pyris 4.01 software. Thermal analyses were carried out with a differential scanning calorimeter (DSC Q1000 from TA Instruments). Polymer (~4 mg) was placed in an aluminum pan. Each sample was heated from -25 to 250 °C at 10 °C $\cdot$ min⁻¹, was held at 250 °C for 2 min, and was then cooled to -25 °C at 10 °C $\cdot$ min⁻¹. After 2 min at this temperature, the sample was heated again to 250 °C at 10 °C $\cdot$ min⁻¹. MALDI-TOF measurements were performed on a Voyager DE-STR apparatus from Applied Biosystems. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]-malononitrile) was used as the matrix. Potassium trifluoroacetate (Aldrich, >99%) was added to the polymer samples as a cationization agent. The matrix was dissolved in THF at a concentration of 40 mg $\cdot$ L⁻¹. Potassium trifluoroacetate was added to THF at a typical concentration of 1 mg $\cdot$ mL⁻¹. In a typical MALDI-TOFMS analysis, the matrix, potassium trifluoroacetate, and the polymer solution were premixed in a weight ratio of 10:1:5. The premixed solutions were hand-spotted on the target well and were left to dry. Spectra were recorded in reflector mode at positive polarity.

Isosorbide 2,5-Bis[4-(hydroxybutyl)terephthalate] (BTITB-(OH)₂). Isosorbide (15 g, 0.10 mol) was added in portions to molten terephthaloyl dichloride (205 g, 1.01 mol) at 180 °C during ca. 15 min. The excess terephthaloyl dichloride was removed by distillation in vacuo. The pale-green residue was then dissolved in dichloromethane (500 mL) in the presence of pyridine (50 mL, 0.62 mol) at 0 °C. After the rapid addition of 1,4-butanediol (100 mL, 1.05 mol), the mixture was allowed to warm to room temperature and was stirred for 4 h, after which water (500 mL) was added. The organic phase was separated by decantation and was washed with brine (300 mL) and water (500 mL). After drying over magnesium sulfate for 12 h, the volatiles were removed in vacuo, affording an orange oil that was dissolved in ethyl acetate (200 mL) and refluxed. The cooling of the mixture to room

temperature gave white crystals (15.3 g), which were washed with diethyl ether (2 $\times$ 100 mL). The cooling of the mother liquor to -16 °C and the further concentration yielded two other crops of white crystals (18.3 and 11.1 g, respectively, 85%).

¹H NMR (CDCl₃, δ): 1.71 and 1.86 (m, CH₂CH₂ 4-hydroxybutyl), 1.92 (s br, CH₂CH₂ B), 3.34 (s br, OH), 3.70 (t, ³J(H⁴H³) = 6.4 Hz, CH₂OH 4-hydroxybutyl), 3.71 (t, ³J(H⁴H³) = 6.4 Hz, CH₂OH 4-hydroxybutyl), 4.05 (d, J(H^{6a,b}H⁵) = 5.1 Hz, H^{6a,b}), 4.08 (s br, H^{1a,b}), 4.34 (t, ³J(H¹H²) = 6.2 Hz, CH₂OC(O) 4-hydroxybutyl), 4.35 (t, ²J(H¹H²) = 6.6 Hz, CH₂OC(O) 4-hydroxybutyl), 4.40 (s br, CH₂OC(O) B), 4.68 (d, ³J(H³H⁴) = 4.8 Hz, H³), 5.06 (dd, ³J(H⁴H³) = 4.8 and ³J(H⁴H⁵) = 5.1 Hz, H⁴), 5.42 (dt, ³J(H⁵H⁴) = 5.5, ³J(H⁵H^{6a,b}) = 5.1 Hz, H⁵), 5.4 (s, br, H²), 8.00–8.13 (m, H aryl), 8.08–8.15 (m, H aryl). ¹³C{¹H} NMR (CDCl₃, δ): 25.2 (CH₂CH₂OH 4-hydroxybutyl), 25.4 (CH₂CH₂ B), 29.0 (CH₂CH₂OC(O) 4-hydroxybutyl), 62.2 (CH₂OC(O) 4-hydroxybutyl), 64.9 (CH₂C(O) B), 65.0 and 65.3 (CH₂OH 4-hydroxybutyl), 70.8 (C⁶), 73.3 (C¹), 74.9 (C⁵), 78.8 (C²), 81.1 (C⁴), 86.1 (C³), 129.3 and 129.6 (CH aryl, I side), 129.7 and 129.7 (CH aryl, 4-hydroxybutyl side), 129.9 and 130.0 (CH aryl, 4-hydroxybutyl and B side), 133.1, 133.1, 133.2, 133.3 and 133.5 (C_{quat} aryl, I side), 134.4 and 134.5 (C_{quat}, B side), 164.7, 164.8, and 165.1 (C=O T, I side), 165.7 and 165.7 (C=O T, 4-hydroxybutyl and B side). MALDI-TOFMS (fraction b, cationization ion: K⁺): 811.1 (4%, [T₃BI₂ + K]⁺, cyclic), 845.21 (13%, [T₃B₃I + K]⁺), 867.1 (11%, [T₃I₃ + K]⁺, cyclic), 901.2 (6%, [T₃B₂I₂ + K]⁺), 1049.2 (8%), 1077.2 (8%), 1087.2 (22%, [T₄BI₃ + K]⁺, cyclic), 1121.3 (100%, [T₃B₃I₂ + K]⁺), 1215.7 (7%), 1341.3 (17%, [T₅B₄I₂ + K]⁺), 1363.2 (6%), 1397.3 (43%, [T₅B₃I₃ + K]⁺), 1617.4 (27%, [T₆B₄I₃ + K]⁺), 1673.3 (9%, [T₆B₃I₄ + K]⁺), 1894.4 (9%, [T₇B₄I₄ + K]⁺).

Preparation of PBT–Macrodiol Mixtures for SSP. As an example, PBT (15.4 g, 0.070 mol) and the macrodiol (15.0 g) were dissolved in HFIP (120 mL) at 55 °C. After complete dissolution, HFIP was first distilled off under atmospheric pressure and was then briefly distilled off in vacuo. The residual wet lump was powdered after being treated with liquid nitrogen, was meshed, and was sieved through a 30 mesh sieve (0.60 mm) and was dried in a vacuum oven at 60 °C.

Solid-State Copolymerizations. SSP reactions were performed in similar set ups, as previously described, that consist of a glass reactor (inner diameter of either 2.4 or 4.5 cm) with a glass frit at the bottom.¹² A flow of argon was passed through the reactor via a glass tube entering the latter below the glass frit. Various PBT/(macro)diol mixtures (2–30 g) were placed on the frit, were covered by glass beads (diameter = 2 mm, 6–20 g), and were subjected at 180–195 °C (which is roughly 30 °C below the *T*_m of the PBT crystals) to an argon flow of 2.5 L $\cdot$ min⁻¹. Samples of the reaction mixtures were collected at different time intervals and were analyzed by ¹H NMR and SEC in HFIP. The resulting SSP copolymers were separated from the glass pearls on a 12 mesh sieve (1.70 mm). The copolymers that were obtained by SSP are abbreviated P(B_xI_yT)_{ssp}, where B_x and I_y are the mol percentages (mol %) of butanediol and isosorbide, respectively.

Figure 1. ^1H NMR spectrum of macromonomer BTITB-(OH) $_2$ in CDCl_3 (* represents butanediol diester signals).

Melt Polycondensation. In a typical example, isosorbide (8.15 g, 0.056 mol), DMT (39.24 g, 0.202 mol), 1,4-butanediol (15.8 mL, 0.167 mol), and the antioxidant Irganox HP2921 (0.3 g) were placed under an argon atmosphere in a 250 mL three-necked round-bottomed flask equipped with a Vigreux column, a Dean–Stark condenser to collect the condensation products, and a mechanical stirrer. The mixture was then heated to 180 °C by the use of a heating mantle before the addition of a toluene solution of $\text{Ti}(\text{O}-i\text{-Pr})_4$ (40 μL , 4×10^{-5} mol), and the temperature was gradually further raised to 220 °C and was stirred for 6 h. Toluene (10 mL) was added from time to time to prevent the formation of sublimed DMT on the wall of the reactor. A continuous flow of argon was then applied for 2 h to remove unreacted monomers and residual methanol while the mixture was heated to 230–240 °C. Subsequently, vacuum was applied to the system, and the pressure was slowly reduced to ~ 1 mbar. After 16 h, the brown melt was removed from the reactor and was left to cool and solidify (41.4 g, 90%). The copolymer (38 g) was dissolved in CHCl_3 (800 mL), precipitated in ethanol (1000 mL), filtered, washed with diethyl ether (2×200 mL), and dried in vacuo. The copolymers that were obtained by melt polymerization are abbreviated $\text{P}(\text{B}_x\text{I}_y\text{T})_{\text{melt}}$, where B_x and I_y are the mol percentages (mol %) of butanediol and isosorbide, respectively.

Results and Discussion

PET-containing isosorbide polyesters have already been synthesized by SSP.^{14,15} However, they were prepared from the corresponding copolymers obtained by melt polycondensation that were submitted to SSP in a later stage. To our knowledge, the direct incorporation of isosorbide or other dianhydrohexitol-based monomers into a semicrystalline polycondensate via SSP has not yet been reported. This is probably due to their tendency to evaporate at SSP temperatures (typically from 180 to 210 °C for PBT) and the limited reactivity of secondary diols under these conditions. This is fully in line with the results of our own experiments with pure isosorbide and isoidide. An SSP experiment on a mixture of, for example, 15 wt % isosorbide and PBT resulted in no incorporation of isosorbide into the amorphous PBT chain parts. These results prompted us to modify the diol to perform the SSP with a monomer that was more reactive and less volatile than pure isosorbide and isoidide. The macrodiol monomer isosorbide 2,5-bis[4-(hydroxybutyl)-terephthalate (BTITB-(OH) $_2$) that is derived from isosorbide, terephthalate, and 1,4-butanediol units appeared to be an appropriate candidate for that purpose.

Synthesis of Macrodiol Monomer. BTITB-(OH) $_2$ was prepared in a one-pot, two-step synthesis according to Scheme 1. First, bis[4-chlorocarbonyl]benzoate-1,4:3,6-dianhydro-D-glucitol (TIT-Cl $_2$) was formed in situ by treatment of isosorbide

with a 10-fold excess of terephthaloyl chloride (T-Cl $_2$) in the melt. After the removal of the excess terephthaloyl chloride by distillation, the residue was dissolved in methylene chloride and was treated with excess 1,4-butanediol in the presence of pyridine. BTITB-(OH) $_2$ was purified by a washing with water and recrystallization from ethyl acetate, and it was isolated in good yield as three crops of crystals.

The nature of the macromonomer was confirmed by ^1H NMR spectroscopy. Isosorbide-based compounds, which are asymmetric by definition, always possess eight nonequivalent protons and six nonequivalent carbons. The resonances are often well separated from each other, and their chemical shifts are very sensitive to the substituents on the two and five positions of the two rings. In this way, by comparison with data (chemical shift, coupling constants/patterns) from the literature related to isosorbide,^{6,16–18} ^1H (Figure 1) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure 2) are in agreement with the structure of BTITB-(OH) $_2$ because no CHOH end-group signal from isosorbide was detected. Consequently, the ^1H NMR spectrum shows, besides the resonances that correspond to terephthaloyl and 2,5-diester isosorbide units, two multiplets at 1.71 and 1.86 ppm and four triplets at 3.70, 3.71, 4.34, and 4.35 ppm, which is characteristic of 4-hydroxybutyl groups.

However, the presence of two additional singlets of lower intensities, at 1.92 and 4.40 ppm, that are attributed to $(\text{CH}_2)_2$ and $\text{CH}_2\text{O}-$ of 1,4-butanediol moieties esterified on both ends (* in Figure 1) suggests the presence of minor amounts of higher oligomer side products. Such compounds have been previously observed during the synthesis of macromonomers via the coupling of monomers by condensation reactions.¹⁹

It has been demonstrated that ^{13}C NMR chemical shifts of the terephthalate carbonyl²⁰ and quaternary carbon atoms C_{quat} from terephthalate-based (poly)esters²¹ depend on the adjacent group. Therefore, besides the signals that are assigned to the isosorbide (71–86 ppm), 4-hydroxybutyl and the minor butanediol diester units (25–29 and 62–65 ppm, see the Experimental Section), the main feature of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum consists of the splitting of the signals into four peaks as a result of the carbonyls and the quaternary carbons (around 165 and 133 ppm, respectively), which results from the nonequivalence of the C–O bonds at $\text{C}_{2\text{exo}}$ and $\text{C}_{5\text{endo}}$ of isosorbide (Figure 2).

Because only one peak, which belonged to BTITB-(OH) $_2$, was observed in the LC-MS diagram of BTITB-(OH) $_2$ (b), more information about the different minor side products was collected from MALDI-TOFMS measurements. The MALDI spectrum that corresponds to the 800–2000 $\text{g}\cdot\text{mol}^{-1}$ mass

Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of macromonomer BTITB-(OH) $_2$ (b) in CDCl_3 (* represents butanediol diester signals).

Figure 3. MALDI-TOFMS of BTITB-(OH) $_2$ (b) (cationization ion: K^+) side products.

region is shown in Figure 3. The predominant mass series corresponds to linear oligomer $\text{La}_{x,y}$ of the general formula $\text{BT}(\text{BT})_x(\text{IT})_y\text{B}-(\text{OH})_2$ ($x = 1$ to 2 and $y = 1$ to 4) with two 4-hydroxybutyl end groups and internal butanediol diester unit(s). These linear oligomers were generated by a reaction of both hydroxyls of a butanediol molecule with a terephthaloyl chloride molecule, followed by the monoesterification of butanediol to obtain the 4-hydroxybutyl ends. Other linear chains were present as well, but the intensity of their corresponding peaks in the MALDI spectrum was much lower, and although MALDI-TOFMS is only a qualitative technique, these peaks are considered to be minor products: Lb_y , with no internal butanediol diester fragment, $\text{B}(\text{TIT})_y\text{B}-(\text{OH})_2$ ($y = 1$ to 2), and $\text{Lc}_{x,y}$, oligomers terminated by one hydroxyl and one carboxyl group (resulting from the hydrolysis of a $-\text{COCl}$ end group), $\text{HOBT}(\text{BT})_x(\text{IT})_y\text{O}_2\text{H}$ ($x = 1$ to 2 , $y = 2$ to 4). Two families of cyclic oligoesters²³ were also visible in small amounts: $\text{Ca}_{1,y}$, $(\text{BT})(\text{IT})_y$ ($y = 2$ to 3), and Cb_y , $(\text{IT})_y$ ($y = 3$ to 4), the latter being generated before the addition of butanediol.

Synthesis and Characterization of PBIT Copolymers.
Solid-State Polymerization. We incorporated isosorbide into PBT by subjecting various BTITB-(OH) $_2$ /PBT mixtures to SSP at

temperatures that varied from 185 to 195 $^\circ\text{C}$ under a 2.5 $\text{L}\cdot\text{min}^{-1}$ flow of nitrogen. The B/I ratios of the feed varied from $86/14$ to $72/28$. The reactions were monitored by SEC, and the resulting polymers were analyzed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and DSC. Data related to these polymers are collected in Table 1.

Synthesis of $P(\text{B}_x\text{I}_y\text{T})$ Copolyesters in the Melt. As a comparison with the materials obtained by SSP, a series of poly(butylene isosorbide terephthalate) copolyesters was synthesized by the melt polycondensation of isosorbide, 1,4-butanediol, and DMT (Scheme 2). The reactions were carried out in bulk at 220 – 230 $^\circ\text{C}$ with different isosorbide/butanediol feed ratios in the presence of titanium tetraisopropoxide as a catalyst. The results of the polycondensations are summarized in Table 2. Because esterification and transesterification reactions continuously occur throughout the entire melt-copolymerization process in which the entire material participates, this technique will furnish a more random copolymer microstructure than will SSP, where the crystalline segments of the PBT are excluded from the transesterification process.^{12,13}

The copolyesters that were produced by SSP all exhibited high number-average molecular weights (M_n), viz., between

Table 1. P(B_xI_yT)_{ssp} Obtained from the PBT/BTITB-(OH)₂ Mixture by SSP^a

expt no.	I/B feed (mol %) ^b	I/B polym. (mol %) ^b	<i>t</i> (h)	<i>M_n</i> (g·mol ⁻¹) ^c	<i>M_w</i> (g·mol ⁻¹) ^c	<i>M_w</i> / <i>M_n</i>	<i>T_g</i> (°C)	<i>T_m</i> (°C)	<i>T_c</i> (°C)	Δ <i>H_m</i> (°C) ^d
1	0/100	0/100	48	93 300	228 900	2.4	43w	220–211	175	43.1
2	14/86	11/89	95	85 200	207 000	2.4	59w	207	163	32.9
3	20/80	17/83	116	92 700	218 400	2.4	69	199	147	27.0
4	28/72	25/75	422	142 600	373 400	2.6	78	194	138	13.8

^a *T_g*, *T_m*, and Δ*H_m* were derived from the second heating trace. For thermal transitions, peak values were taken. ^b Determined by ¹H NMR. ^c Determined by SEC in HFIP. ^d Determined by DSC measurements (heating and cooling rates of 10 °C·min⁻¹); w means weak.

Scheme 2. Synthesis of Poly(butylene isosorbide terephthalate) by Melt Polycondensation

85 000 and 140 000 g·mol⁻¹. Moreover, limited amounts of isosorbide were lost during the process. For example, the feed with an I/B ratio of 28/72 resulted in P(B₇₅I₂₅T)_{ssp} (entry 4, Table 1). This was not always the case for polycondensations performed in the melt that lead to low *M_n* values and lower stoichiometry control, which was also observed by others.⁷ In addition, the melt-polymerized samples all had a deep-brown color. Despite the relatively high incorporated amounts of isosorbide, the slightly yellow SSP copolymers crystallize from the melt in a DSC experiment without any exception. A more extensive discussion of the thermal transitions of melt- and SSP-synthesized copolyesters is presented later.

The evolution of the *M_n* of an SSP feed mixture with an I/B of 20/80 (entry 3, Table 1) is represented in Figure 4. The plot reveals a significant decrease in the *M_n* in an early stage of the SSP before the *M_n* is steadily increasing with time. This behavior has been previously observed during the incorporation of other diols into PBT by SSP.^{12,13} This initial decrease in *M_n* is attributed to the reaction of the low molar mass diols with the amorphous phase of PBT by alcoholysis, which results in the cleavage of PBT chains, the formation of hydroxybutyl chain end groups, and, as a consequence, the reduction of molecular weight. Eventually, these hydroxybutyl end groups will undergo further transesterification by alcoholysis, and 1,4-butanediol will gradually be entirely liberated from the main chain and removed from the polymer, which results in the build up of the molecular weight.

The progress of the SSP reaction over time was studied by ¹H NMR (Figure 5). The spectra reveal a decrease in hydroxybutyl at 3.9 ppm after 5 h and the presence of both 2-exo and 5-endo isosorbide hydroxyl end groups of similar intensities and of 20% intensity relative to the total amount of isosorbide. (See Figures 1 and 6 for assignments.)

Between 28 and 44 h, all OH end groups disappeared. It is reasonable that the first stage of the reaction involves a self-condensation of BTITB-(OH)₂ because the latter, upon heating even at a relatively low temperature of 160–170 °C, yielded some low molecular weight PBIT that was end-capped with exo- and endo-OH isosorbide and hydroxybutyl groups. This self-condensation has already been proposed to be the first step

in the incorporation of bis(2-hydroxyethyl)terephthalate into PBT.¹³ The following step involves the transesterification reaction of these oligomers via their end groups with ester groups in the amorphous PBT phase, which leads first to shorter PBT chains and then to molecular weight build up via alcoholysis and butanediol release (and, to a lesser extent, isosorbide).

¹³C NMR spectroscopy is generally a useful tool for analyzing the sequences within copolyesters that contain terephthalate units because the chemical shifts of the quaternary aromatic carbon²¹ and the ester carbonyl carbon²² are sensitive to the adjacent fragment. When two different but symmetrical diols comprise the terephthalate polyester, each carbonyl or quaternary carbon atom should split into four different signals. However, because isosorbide is asymmetric and contains endo- and exo-orientated hydroxyl groups, nine different resonances are theoretically possible.

Only six signals are observed for the ester carbonyl carbons (spectrum not shown here), whereas all four expected chemical shifts that were due to quaternary carbons of terephthalate units bearing isosorbide were split. This is shown and assigned in Figure 7 for the copolyesters that were synthesized by melt polymerization and SSP. An interesting feature is the presence (with low intensity compared with P(B₇₁I₂₉)_{melt}) of ITI dyads in the spectrum of P(B₇₅I₂₅T)_{ssp}. They are due to the alcoholysis of an ester bond by a less reactive secondary hydroxyl end group of an isosorbide fragment, which is a reaction that occurs to a lower extent at the relatively low SSP temperature that limits the release of isosorbide molecules. In addition, the analysis of the sequence distribution and the randomness of our PBIT polymers could be studied by ¹³C NMR, but much longer scanning times would be required to separate the TIT dyads from the noise. We considered this in depth analysis to be beyond the scope of this article.

Thermal Behavior of PBIT. TGA Measurements. Reported polyesters that were based on 1,4:3,6-dianhydrohexitols and terephthalic acid proved to be stable up to ≥300 °C.^{4,5} Under a nitrogen atmosphere, the P(B₇₅I₂₅T)_{ssp} synthesized in this work showed an initial weight loss at about 290 °C, which was similar to pure PBT, whereas PIT was stable up to ca. 320 °C. Our heating P(B₇₅I₂₅T)_{ssp} at this temperature under dry air for 2 min resulted in a decrease in molecular weight from 142 000 to 5000 g·mol⁻¹. The MALDI spectrum (Figure 8) showed products that were already observed during thermal degradation studies of PBT and that can be assigned to the following oligomers: (TB)_n (I_n, cyclic), HO₂(TB)_nTO₂H(K) (II_n(K), with two carboxylic acid end groups), Ol(TB)_nTO₂H(K) (III_n(K), bearing one carboxylic and one olefinic end group; Ol = 3-buten-1-yl ester (butenolate)), and Ol(TB)_nTOI (IV_n, with two butenolate end groups). In addition, three other isosorbide-containing oligomers were observed: HO(BT)_m(IT)_nBOH (A_{m,n}), Ol(TB)_m-(IT)_nTOH(K) (B_{m,n}), and Ol(TB)_m(IT)_nOl (C_{m,n}). The proposed degradation mechanism involves the formation of cyclic oli-

Table 2. P(B_xI_yT)_{melt} Obtained by Melt Polycondensation from Isosorbide, DMT, and Butanediol^a

expt no.	I/B feed (mol %)	I/B polym (mol %) ^b	M_n (g·mol ⁻¹) ^c	M_w (g·mol ⁻¹) ^c	M_w/M_n	$T_g/T_m/T_c$ (°C) ^d	ΔH_m (°C) ^d
6	19/81	15/85	11 100	22 100	2.0	58/199/157	33.6
7	25/75	17/83	11 800	44 000	3.7	59/194/143	38.8
8	25/75	22/78	8 400	16 000	1.9	64/184/125	33.4
9	35/65	29/71	8 400	22 800	2.7	63/172/126 ^e	20.8
10	50/50	36/64	11 400	29 000	2.5	78/-/-	
11	53/47	43/57	8 500	32 400	3.8	94/-/-	
12	75/25	70/30	11 400	27 300	2.4	137/-/-	
13	85/15	82/18	16 300	33 500	2.5	155/-/-	
14	100/0	100/0	>11 600	27 600	2.4	186/-/-	

^a T_g , T_m , and ΔH_m were derived from the second heating trace. For thermal transitions, peak values were taken. ^b Determined by ¹H NMR. ^c Determined by SEC in HFIP. ^d Determined by DSC measurements (heating and cooling rates of 10 °C·min⁻¹). ^e Cooling rate of 1 °C·min⁻¹.

Figure 4. Growth of M_n of 20/80 I/B SSP feed mixture (entry 3) as a function of time. **Figure 5.** ¹H NMR spectra of 20/80 I/B SSP feed mixture recorded at different reaction times (isosorbide and hydroxybutyl region, CDCl₃/CF₃CO₂D). For assignments, see Figures 1 and 6.

gomers via ester exchange reactions, followed by the thermal decomposition of both cyclics and the remaining linear chains by β -hydrogen transfer reactions, which leads to oligomers with

Figure 6. Isosorbide hydroxyl end groups for NMR assignment.

olefinic and carboxylic acid end groups (Scheme 3).^{9,24,25} Interestingly, isosorbide does not seem to take part in the degradation of PBIT because no peak series corresponds to oligomers with an isosorbide-OH or isosorbide-deoxy (unsaturated) end. These observations have been confirmed by ¹H and ¹³C{¹H} NMR studies. Therefore, the degradation of the isosorbide-based copolyesters is similar to that of pure PBT.

DSC Measurements. The thermal transition temperatures of these copolyesters were determined by DSC at heating and cooling rates of 10 °C·min⁻¹. Typical heating and cooling curves for one PBIT sample, obtained by SSP, are represented in Figure 9. The data that are related to the other polymers are collected in Tables 1 and 2. The first heating runs of P(BIT)_{ssp} all exhibit a melting temperature T_m that is close to 225 °C, which corresponds to the crystalline portion of PBT that did not take part in the solid-state transesterification reaction. Accordingly, this technique renders a nonrandom, blocky structure of pure and crystallizable PBT blocks^{12,13} (the chain parts embedded in the crystals during SSP) and non-crystallizable, presumably more random copolyester blocks^{12,13} that contain B, T, and I residues. P(BIT)_{melt} with isosorbide contents of 30 mol % or less exhibits a recrystallization exotherm during the first heating because of the fast cooling at the end of the melt polycondensation, which causes an incomplete crystallization for these more random copolyesters. The cooling curves of both P(BIT)_{ssp} and P(BIT)_{melt} (the latter not shown here) showed crystallization peaks that broaden with the increasing amount of incorporated isosorbide, which is generally observed for this monomer. An explanation could lie in the good miscibility between homopolymer segments and the parts that contain isosorbide.¹³ However, the major result of this study consists of the large difference in T_g values between P(BIT)_{ssp} and P(BIT)_{melt} of similar composition as extracted from the second heating run. Therefore, beyond the increase in T_g , which is generally combined with the rise of isosorbide content, a 15 °C difference was observed between P(B₇₅I₂₅T)_{ssp} (78 °C, expt 4) and P(B₇₁I₂₉T)_{melt} (63 °C, expt 9), and a 10 °C difference was observed between P(B₈₃I₁₇T)_{ssp} (69 °C, expt 3) and P(B₈₃I₁₇T)_{ssp} (59 °C, expt 7). Possible reasons for this significant difference in T_g values include the possible presence of low molar mass, plasticizing degradation products in the melt-synthesized sample as well as the signifi-

Figure 7. $^{13}\text{C}\{^1\text{H}\}$ NMR quaternary C resonance of $\text{P}(\text{B}_{71}\text{I}_{29}\text{T})_{\text{melt}}$ and $\text{P}(\text{B}_{75}\text{I}_{25}\text{T})_{\text{ssp}}$.

Figure 8. MALDI-TOFMS spectrum of $\text{P}(\text{B}_{75}\text{I}_{25}\text{T})_{\text{ssp}}$ after being heated to 320 °C in air (cationization ion: K^+).

Scheme 3. Mechanism of the Thermal Degradation of PIBT at the Processing Temperature^{9,24,25}

cantly lower molar mass of this sample. In addition, T_m values of SSP polymers are also superior. The high molecular weight of the SSP products contributes to the improvement of the thermal properties, but the influence of the different micro-

Figure 9. DSC traces of $\text{P}(\text{B}_{83}\text{I}_{17}\text{T})_{\text{ssp}}$ (heating and cooling rates of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

structures of the SSP- and melt-synthesized copolymers on the thermal properties is probably more important.⁷

Conclusions

We successfully incorporated isosorbide into PBT by SSP via the macromonomer BTITB-(OH)₂. This macrodiol was

synthesized in a one-pot, two-step reaction from isosorbide, terephthaloyl chloride, and 1,4-butanediol. Polymers of number-average molecular weights up to $100\,000\text{ g}\cdot\text{mol}^{-1}$ were readily synthesized from various PBT/BTITB-(OH)₂ ratios. After an initial collapse of the molecular weight as a result of the transesterification of the PBT and the macrodiol BTITB-(OH)₂, the reaction proceeded to form polymers of high molecular weight. The thermal properties of the SSP copolymers showed clear differences from those of the corresponding copolymers of similar chemical composition that were obtained by melt polycondensation. Therefore, for similar B/I contents, the T_g , T_m , and T_c of the $P(B_xI_yT)_{\text{ssp}}$ polymer were significantly increased. Moreover, the milder SSP route causes less thermal degradation of the copolyesters during synthesis; accordingly, it affords less-colored materials. For the incorporation of thermally labile sugar derivatives into engineering plastics like PBT by the use of a bulk process, this SSP method looks to be more promising than melt copolymerization. Finally, because of the good thermal stability of the isosorbide-terephthalate moieties, this procedure could also be applied to polymers with higher thermal transitions, for example, PET, for which typical SSP temperature conditions are between 210 (in vacuo)²⁶ and 230 °C (under argon flow).¹¹

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