Semi-aromatic polyesters based on a carbohydrate-derived rigid diol for engineering plastics

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New carbohydrate-based polyesters were prepared from isoidide-2,5-dimethanol (extended isoidide, XII) through melt polymerization with dimethyl esters of terephthalic acid (TA) and furan-2,5-dicarboxylic acid (FDCA), yielding semi-crystalline pre-polymers. Subsequent solid-state post-condensation (SSPC) gave high molecular weight \( (M_n = 30 \text{ kg mol}^{-1}) \) for FDCA materials, the first examples of high \( M_n \) semi-aromatic homopolymers containing isohexide derivatives obtained via industrially relevant procedures. NMR spectroscopy showed that the stereo-configuration of XII was preserved under the applied conditions. The polyesters are thermally stable up to 380 °C. The TA- and FDCA-based polyesters have high \( T_g \) (105 °C and 94 °C, resp.) and \( T_m \) (284 °C and 250 °C, resp.) values. Its reactivity, stability, and ability to afford high \( T_g \) and \( T_m \) polyesters make XII a promising diol for the synthesis of engineering polymers.

Synthetic semi-aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are widely applied engineering thermoplastics that have high heat distortion temperatures, good mechanical properties, and excellent chemical resistance and electrical insulation properties.[1] In particular, the combination of a relatively high glass transition temperature \( (T_g) \) and a high melting temperature \( (T_m) \) facilitates that these engineering plastics maintain their shape and strength at elevated temperatures, which renders them useful in a wide range of automotive, electronics, and packaging applications.

In recent years, concerns regarding fossil feedstock availability and related price increases have sparked research efforts into alternatives for petrochemicals.

Carbohydrates are increasingly investigated as a renewable source of raw materials for the production of chemicals, adding value to agricultural products and residues. However, most currently available biobased monomers are aliphatic, flexible molecules. In addition, the synthesis of high-molecular-weight polymers through step-growth polymerization requires monomers with high purity and is typically performed at high temperatures, while many biobased monomers lack the required thermal stability. As a result, the preparation of high-molecular-weight, semi-crystalline polymers with both high \( T_g \) and high \( T_m \) from renewable resources remains challenging. Still, some biobased monomers seem suitable to replace conventional monomers while obtaining comparable polymer properties. For example, carbohydrate-derived furan-2,5-dicarboxylic acid (FDCA) is a rigid monomer that is advocated as an alternative for the petrochemical-based terephthalic acid (TA).[2] Potentially, new polymers based on FDCA, such as poly(ethylene furanoate) (PEF), could provide the desired performance.[3] Alternatively, biobased monomers can be introduced into existing petrochemical-derived polymers to improve their properties. For such an approach, isohexides or 1,4,3,6-dianhydrohexitols are of interest. Isohexides are a group of rigid secondary diols derived from C₆-sugar alcohols, and are found in three major isomeric forms: isosorbide (1,4,3,6-dianhydro-δ-sorbitol, IS), isoidide (1,4,3,6-dianhydro-δ-iditol, II), and isomannide (1,4,3,6-dianhydro-δ-mannitol, IM) (Figure 1).[4,5] By introducing isosorbide into PET, the \( T_g \) values of the resulting poly(ethylene-co-isosorbide terephthalate) (PEIT) copolyesters were enhanced from 80 °C (0 % IS) to as high as 200 °C (100 % IS).[5] The application window of PET can thereby be significantly broadened for high-temperature applications. Similar effects have also been demonstrated in the case of PBT.[6] A wide variety of isohexide-based polymers have thus far been investigated, including polyesters, polycarbonates, polyurethanes, polyamides, as well as others.[5,7] Despite the apparent advantages of incorporating rigid diols such as isohexides into polymers, the low reactivity of the sec-
ondary hydroxyl groups is a major drawback, resulting in relatively low molecular weights ($M_n = 2000–5000 \, \text{g mol}^{-1}$) and discolored products after melt polycondensation at high temperatures (> 230°C).\(^\text{[8]}\) In addition, the asymmetrical isosorbide is known to significantly reduce the crystallinity and melting temperatures of terephthalate-based polyesters due to stereo-irregularity. Hence, there is a need for a more reactive, and more thermally stable, rigid biobased symmetrical primary diol, which allows for milder melt polymerization conditions and which would yield semi-crystalline polymers, facilitating the subsequent application of solid-state post-condensation (SSPC), a synthetic method in which a semi-crystalline polymer is allowed to polymerize at a temperature just below its $T_m$ but well above its $T_g$ leading to condensation reactions taking place exclusively in the mobile amorphous phase.\(^\text{[9]}\) Recently, bicyclic acetalized C$_6$ alditols and methyl aldarates were studied as rigid, biobased monomers for polyester synthesis. Although most of these (co-)polymers are semi-crystalline materials, their melting temperatures are typically lower than those of for example, PET and PBT.\(^\text{[10]}\)

Previously, we reported the development of a new family of 1-carbon-extended isohexides, and their application in the synthesis of various aliphatic polyesters.\(^\text{[11]}\) Comparison of the new 1-carbon-extended diol isoidide-2,5-dimethanol (extended isoidide, XII, Scheme 1) with the parent isohexides in the polymerization with isoidide dicarboxylic acid and adipic acid showed that, while the observed $T_g$ values were higher for the parent isohexides, XII yielded higher molecular weights and semi-crystalline polymers. This prompted us to investigate the potential of XII as rigid biobased diol in industrially-relevant semi-aromatic polyesters. The focus of this study is to evaluate the effect of XII incorporation on polyester synthesis (reactivity, molecular weight build-up, color formation, polydispersity) and polymer properties ($T_g$ crystallinity, $T_m$ thermal stability). The development of more efficient, environmentally benign and industrially viable methods to produce XII are beyond the scope of the present study.

Hence, herein we describe the synthesis and molecular characterization of new XII-based, semi-aromatic polyesters. The thermal properties of these polyesters are discussed and compared to those of relevant reference polyesters.

Due to the relatively low reactivity of the isoxides, the few reported high-molecular-weight isoxide-based, semi-aromatic polyesters are almost exclusively prepared by solution polymerization with acid chlorides.\(^\text{[8b, c, 12]}\) Our aim was to investigate the feasibility of synthesizing XII-based, semi-aromatic polyesters by more industrially relevant methods, that is, melt polymerization and SSPC (Scheme 2). The aromatic monomers included in this study are the dimethyl esters of terephthalic acid (TPA) and furan-2,5-dicarboxylic acid (FDCA).

Poly(isosidiole-2,5-bismethylene terephthalate) (PXIIIT) and poly(isoside-2,5-bismethylene furan-2,5-dicarboxylate) (PXIIIF) prepolymer were synthesized by melt polymerization (MP). During the prepolymer synthesis, both polyesters crystallized from the melt after polymerization at 180°C for about 1 h. The PXIIIT and PXIIIF prepolymer are white solids with moderate number-average molecular weights ($M_n = 2300 \, \text{g mol}^{-1}$ and 6900 g mol$^{-1}$, respectively, Table 1). Still, compared to similar polymerizations of isosorbide with TPA and FDCA, the molecular weight values of XII-based polyesters after the rather short melt polymerization time of 1 h are remarkable and indicate that XII is significantly more reactive than the parent isohexides. Furthermore, the PXIIIT and PXIIIF prepolymer showed rather high melting temperatures (approx. 278–282°C and 246–250°C respectively, as determined by melting point testing), which confirms the crystallizability of these polyesters, allowing for post-condensation in the solid state between $T_g$ and $T_m$. In the case of PXIIIF, increasing the polymerization temperature to 260°C to maintain a polymer melt causes discoloration and thermal degradation of the prepolymer, evidenced by an increase of the polydispersity ($M_w = 13400 \, \text{g mol}^{-1}$, PDI = 2.9). Therefore, to obtain PXIIIT and PXIIIF with high molecular weights, narrow molecular weight distributions, and limited discoloration, SSPC was applied to the prepolymer.

SSPC of PXIIIT was performed at two temperatures: 200 and 240°C. As shown in Figure 2A, the polymerization temperature strongly influences the SSPC reaction rate: after 23 h at 200°C a product with an $M_n$ of 4700 g mol$^{-1}$ is obtained. When SSPC
Table 1. Molecular and thermal properties of XII-based polyesters.

| Sample | Mₐ after Mp (g mol⁻¹) | Mₙ after SSPC (g mol⁻¹) | PDI | Mₘ after SSPC (g mol⁻¹) | Mₚ after SSPC (g mol⁻¹) | PDI | T_g (°C) | T_m (°C) | T_c (°C) | T_d (°C) | ΔH_c (kJ mol⁻¹) |
|--------|------------------------|------------------------|-----|------------------------|------------------------|-----|---------|---------|---------|---------|-------------|-----------------|
| PXIIIT | 2300                   | 3900                   | 1.7 | 7700                   | 17700                  | 2.3 | 385     | 417     | 266     | 50.6    | 10590       | 284             |
| PXIIIF | 6900                   | 15200                  | 2.2 | 30300                  | 60600                  | 2.0 | 376     | 411     | 193     | 26.8    | 94250       | 250             |

[a] Mₐ: number-average molecular weight, Mₚ: weight-average molecular weight, PDI: polydispersity index. Determined by HFIP-SEC against PMMA standards. [b] Measured for samples as prepared after SSPC. T_g = temperature at 5 % weight loss, T_m = temperature at maximum rate of decomposition, T_c = glass transition temperature, T_m = melting temperature, T_c = crystallization temperature, ΔH_c = enthalpy of transition. DSC data derived from the second heating and cooling runs performed at a heating/cooling rate of 10 °C min⁻¹. [c] Measured after dissolution/precipitation from TFA + CHCl₃/MeOH. [d] Measured for samples as prepared after SSPC. [e] T_d obtained by rapid quenching of the polymer melt at a cooling rate of 100 °C min⁻¹.

Figure 2. Plots of the Mₙ and PDI values vs. SSPC time: a) SSPC of PXIIIT at 200 and 240 °C; b) SSPC of PXIIIF at 200 and 230 °C. Note: trend lines are drawn to guide the eye only.

was performed at 240 °C, a comparable molecular weight (Mₙ = 5000 g mol⁻¹) was obtained after only 0.5 h. After 5 h at 240 °C, PXIIIT was obtained as a white to slightly greyish material with Mₙ = 7700 g mol⁻¹ (HFIP-SEC). Higher SSPC temperatures (> 250 °C) or prolonged reaction times (> 5 h) resulted in the formation of insoluble products, indicative of cross-linking.

The melting point of the PXIIIF prepolymer was observed at around 250 °C. It can be clearly seen from Figure 2B that the molecular weight increases rather rapidly at 230 °C: after only 30 min, the Mₙ value of PXIIIF had more than tripled to 21000 g mol⁻¹ with respect to the initial molecular weight; after 240 min, Mₙ had increased to over 30000 g mol⁻¹, with a PDI value of 2.0. When the SSPC reaction was performed at 200 °C, more than 24 h (1440 min) was required to attain an Mₙ of over 21000 g mol⁻¹. Color formation was limited during SSPC, affording slightly greyish, high-molecular-weight polyesters.

The molecular structures of the polyesters were analyzed by 1D and 2D nuclear magnetic resonance (NMR) spectroscopy, as representative shown in Figure 3 by the 2D ¹H–¹H COSY spectrum of PXIIIF. The bridge proton a appears as a singlet at 4.8 ppm. The absence of dihedral coupling with the neighboring proton b is indicative of an exo–exo configuration of the incorporated XII units, as is also the case in the XII monomer prior to polymerization. Apparently, the isoidide structure is retained under the applied reaction conditions. More details concerning the NMR spectra of these polyesters can be found in the Supporting Information.

The thermal stability of the polyesters was investigated by thermogravimetric analysis (TGA) under N₂ atmosphere. The 5 % weight loss temperatures were observed at approximately 380 °C for the two XII-based polyesters (Table 1 and Figure S2 in the Supporting Information), which are comparable to those of PET (degradation temperature T_d = 407 °C), PBT (T_d = 384 °C) and PEF (T_d = 389 °C).[13]

Differential scanning calorimetry (DSC) performed on materials obtained by SSPC confirms that PXIIIT and PXIIIF are semicrystalline materials, with melting enthalpies at 284 and 250 °C, respectively (Supporting Information, Figures S3 and S4). Wide-angle X-ray diffractograms (Figure 4) of these samples corroborate the DSC data, showing sharp crystalline diffraction signals for both XII-based polyesters (samples obtained after SSPC without further work-up). The estimated degrees of crystallinity of PXIIIT and PXIIIF, determined through peak deconvolution of the WAXD diffractograms (Figure 5), are 66 and 42 %, respectively.

The T_d values of PXIIIT and PXIIIF are 105 and 94 °C, respectively. Given the relatively low molecular weight (Mₙ = 7700 g mol⁻¹) of PXIIIT, it is probable that the ultimate value of the T_d of this polymer is even higher for high-molecular-weight samples. In addition to the observed melting transitions, PXIIIT and PXIIIF show pronounced crystallization exotherms during the DSC cooling runs (Figure S4). The crystallization tempera-
FEATURES (Tc) are 266 and 193 °C, respectively. The fact that these XII-based polyesters crystallize from the melt is remarkable, as corresponding polyesters based on the parent isohexides do not show this tendency. This phenomenon may be due to an enhanced chain flexibility of the XII-based polymers.

In Figure 6, the melting and glass transition temperatures of PXIIT and PXIIF are plotted together with those of high-molecular-weight terephthalate- and furanoate-based reference polyesters PET, PEF, PBT, poly(butylenefuranoate) (PBF), poly(1,6-hexene terephthalate) (PHT), poly(1,6-hexene furanoate) (PHF), poly(1,4-cyclohexylene dimethylene terephthalate) (PCT, commercial grade of 70% trans- and 30% cis-1,4-cyclohexylene units), and poly(2,4,3,5-di-O-methylene-D-glucitol terephthalate) (PGT). The XII-based polyesters show higher Tm and Tg values than all the reference polymers, except PGT. The Tm of PXIIT (292 °C) even exceeds that of PCT (287 °C), while the Tm of PXIIF is similar to that of PET. The Tg values of both XII-based polyesters are higher than those of PET and PBT, and are comparable to that of PCT. Compared to the terephthalate (PHT) and furanoate (PHF) polyesters based on 1,6-hexanediol, their XII-based counterparts show significantly higher Tm and Tg values although the distance between the ester linkages in the diol residues is six carbon atoms in all cases, demonstrating the rigidity of the bicyclic XII structure. Polyterephthalates based on the parent isohexides IS and II have Tg values that exceed 150 °C. Poly(isosorbide terephthalate) and poly(isoidide terephthalate) do crystallize from solution (Tm ~ 260 °C) but not from the melt.[5] As mentioned previously, increasing the molecular weights of such polymers to high values is difficult due to the limited reactivity of these secondary diols. The aforementioned alditol-based terephthalates generally also have higher Tm values than the XII-based polyesters, but are mostly amorphous, with one notable exception: poly(2,4,3,5-di-O-methylene-D-glucitol terephthalate) (PGT, included in Figure 6) was reported to have a Tg of 154 °C in combination with a high Tm of 272 °C, although this polymer did not crystallize from the melt.[10]
To conclude, we have shown that 1-carbon extension of the biobased rigid diol isosorbide results in higher reactivity during polymerization (resulting in higher molecular weights) and higher selectivity (better color, low PDI values). As a result, XII can be directly incorporated into high-molecular-weight semi-aromatic polyesters via melt polymerization. The resulting homopolymers have excellent color, display semi-crystalline behavior, and crystallization from the melt. This feature was subsequently used to further increase the molecular weights of the new polyesters by means of solid-state post-condensation (SSPC). This is the first successful application of this common industrial procedure for isoxeide-based semi-aromatic polyesters. The $T_g$ values of the polymers obtained after SSPC are in line with those of commercial benchmarks such as PET, PEF and PCT. Hence, XII can be considered as a biobased alternative to the petrochemical cyclohexanediol (CHDM). Additionally, the novel and fully biobased polyester PXXIF shows highly interesting properties, and can be prepared in high molecular weight by common industrial methods.

**Experimental Section**

**Melt polymerization:** This procedure is representative for poly(isosorbide-2,5-dimethylene terephthalate) and poly(isosorbide-2,5-dimethylene furan-2,5-dicarboxylate) (PXXIIT and PXXIF): XII (0.26 g, 1.5 mmol), which was prepared from isomannide (Sigma–Aldrich, 95%), purified by recrystallization from ethanol to achieve a final purity of 99.5 (±%), and dimethyl-2,5-furandicarboxylate (0.18 g, 1.5 mmol), which was prepared from isomannide (Sigma–Aldrich, 95 %, purified by recrystallization from ethanol to achieve a final purity of 99.5 (±%) to a powder and subsequently subjected to solid-state post-condensation between its $T_g$ and $T_m$ (vide infra) to further increase the molecular weight.

**Solid-state post-condensation (SSPC):** SSPC of the PXXIIT and PXXIF prepolymers was carried out in a glass tube reactor (2.5 cm diameter) equipped with a sintered glass plate at the bottom on which the polyester powder was deposited. Below this glass plate the SSPC reactor was fitted with an inert gas inlet through which preheated N$_2$ gas was introduced. The SSPC reactor was immersed into a salt bath preheated to the desired temperature (200–240 °C, see Supporting Information, Table S1). The reactor was heated using a salt mixture of KNO$_3$ (53 wt %), NaNO$_3$ (40 wt %), NaNO$_2$ (7 wt %). SSPC was carried out in N$_2$ atmosphere at a gas flow rate of 2.5 L min$^{-1}$. More extensive experimental information, including materials, monomer synthesis, and characterization, is provided in the Supporting Information.

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