Biobased aliphatic polyesters from a spirocyclic dicarboxylate monomer derived from levulinic acid

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Supplementary Note 1: Investigation of side reactions in the polycondensation of Monomer L and neopentyl glycol (NPG)

Scheme S1: The plausible transketalization of Monomer L with NPG to give Product A.

The $^1$H NMR investigation of the polycondensation mixture of Monomer L and NPG showed undesired signals in the spectrum, which indicated the occurrence of side reactions during the polycondensation. The transketalization of Monomer L with NPG was hypothesized due to the formation of a stable six-membered cyclic product (Scheme S1). To probe the hypothesis, the anticipated side product (Product A) was synthesized in a ketalization reaction of ethyl levulinate (EL) and NPG using a similar protocol as that used for the Monomer L synthesis (Scheme S2). However, this product was not purified further. Instead, the $^1$H NMR spectrum of the crude sample was recorded, which also displayed the signals of the starting reactants.

Scheme S2: Synthesis of Product A by a ketalization reaction of ethyl levulinate (EL) and NPG.

The $^1$H NMR spectrum of crude Product A (Figure S1 spectrum A) was compared with the spectra of polycondensation mixtures containing Monomer L and NPG in the ratios 1:3 (spectrum B) and 1:1.1 (spectrum C), respectively, to identify the side products. As can be seen, the polycondensation mixtures containing a large excess of neopentyl glycol (1:3 molar ratio of Monomer L to NPG) showed the signals (denoted as a) corresponding to the structure of transketalization product (Product A), or its structural analogue (as shown in Figure S2), in addition to the signals from the monomers and the polymer. The formation of Product A hints the presence of the monoketal ester (Product C or its analogues) in the mixture. However, signals confirming its structure were not clearly detected, probably due to overlap with other signals in the spectrum. On other hand, a number of additional isolated signals (denoted as b) were observed, which were assigned to the semi-transketalization product (Product B), or its structural analogues (Figure S2), while the rest of the corresponding signals were assumed to be merged with signals of the monomers and the polymer. The assignment of signal b was further supported by the $^1$H NMR spectrum of the polycondensation mixture employing a slight excess of NPG (1:1.1 molar ratio of Monomer L to NPG),
which mainly showed the signals assigned to Product B together with the signals from the monomers and the polymer. In contrast, the signals of Product A were observed as a trace. This observation implied that the excess amount of NPG lead to the formation of both the side products, where the semi-transketalization product B dominated compared to the cyclic transketalization product A. On other hand, the slight excess of NPG exclusively gave the semi-transketalization product B. Furthermore, the relative intensities of side product signals in both polycondensation spectra implied that the extent of side reaction was more significant when an excess of NPG was used.
**Figure S1:** Stacked $^1$H NMR spectra of condensation product of EL and NPG (A), polycondensation reaction mixtures containing 1:3 (B) and 1:1.1 (C) molar ratio of Monomer L and NPG.

**Figure S2:** The formation of transketalized (Product A), semi-transketalized (Product B) and monoketal ester (Product C) side products and their respective structural analogues produced during the polycondensation of Monomer L and NPG.
Supplementary Note 2: Optimization of polycondensation

During the polycondensation, the reversible nature of the side reaction (transketalization) was observed. Initially, both transesterification and transketalization reactions were favored until the NPG was consumed. Afterward, the equilibrium of the transketalization reaction shifted to the reactant side to give back Monomer L (or its residue in the polymer) and NPG, which subsequently underwent the desired transesterification. This critical finding allowed the optimization of polycondensation conditions. The polycondensation of Monomer L with NPG was initially attempted by conventional melt polycondensation using a 1:1.1 molar ratio of Monomer L to NPG at 130 °C (following the protocol used in melt polycondensations involving PHexL and PCycL). However, significant evaporation and sublimation of NPG led to an incomplete transesterification. In the subsequent polycondensation, an excess of NPG (1:3 molar ratio of Monomer L to NPG) was employed. Complete transesterification was achieved; however, the reversible nature of the transketalization was restricted due to the excess NPG. The polycondensation resulted in a polymer product containing a significant amount of structural residues from the side reaction. To overcome this issue, a modified melt polycondensation was investigated, where a solvent was used during transesterification to reduce the evaporation of NPG. The transesterification was carried out under continuous nitrogen flow at 130 °C using xylene (mixture of isomers) as a solvent. The subsequent polycondensation was performed using mesitylene as a solvent at an increased nitrogen flow. The 25% molar excess of NPG with regard to Monomer L was found to be an optimum in order to compensate for the loss of NPG. The progress of the polycondensation and the reversible side reaction were monitored by $^1$H NMR spectroscopy. The stacked $^1$H NMR spectra of the reaction mixture during the transesterification (after 15, 22, and 30 h) and polycondensation (after 40 h) steps are shown in Figure S3 along with the spectrum of the purified polymer (PNeoL). As can be seen, initially during the transesterification, the signals corresponding to Monomer L, NPG, the polymer product, and the semi-transketalized product (Product B) were observed, assigned as l, n, p and b, respectively (spectrum A). Afterward, the signals of the semi-transketalized product were found to be suppressed with the simultaneous increase of signals from polymer (spectrum A-C). This observation indicated the reversible transketalization to yield the starting Monomer L (or its structural residue in the polymer) and NPG, which subsequently reacted through the desired transesterification mechanism. It was concluded from the $^1$H NMR investigation that the reversible transketalization was favored after the NPG concentration in the reaction mixture was reduced to negligible. The transesterification was carried out for 30 h until the ethyl ester group signals of Monomer L disappeared. After the completion of transesterification, the signals of the side product were significant (spectrum C). Then, the polycondensation was performed for 40 h. During this period, the signals of the side product residues were considerably suppressed (spectrum D and E). However, their traces were still observed, indicating that the high viscosity reached during the polycondensation step inhibited the complete reversible transketalization and thus the formation of polymers without any structural residues from the side reaction.
**Figure S3:** Stacked $^1$H NMR spectra of the polymerization reaction mixture during transesterification (A-C), polycondensation (D) steps and the purified PNeoL (E).

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