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COMMUNICATION

Topological Behavior Mimicking Ethylene-Hexene Copolymers Using Branched Lactones and Macrolactones

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A new approach towards polyolefin-like copolyesters is introduced based on a single set of reaction conditions. The delicate balance between steric hindrance and monomer reactivity determines whether random or block copolymers are formed.

Polyolefins are of paramount importance in the world of polymers due to their technological and economic potential.¹ However, their nonpolar character significantly restricts the compatibility and adhesion properties, which consequently limits their versatility. Moreover, an intensified demand for materials from renewable resources can also become a problematic venture for the current polyolefin industry.² Although Braskem and DOW presented an innovative and economically viable approach towards biomass-based ethylene produced via dehydration of bio-ethanol prepared from sugar cane, the relatively low scale of the process does by far not cover the worldwide demand for this monomer.³ Therefore, one of the interesting additions to petrochemical polyolefins are polymers with polyolefin-like properties based on renewable monomers. Two types of renewable polymers have been reported to have polyolefin-like properties viz. polyhydroxybutyrate (PHB) resembling those of isotactic polypropylene and linear fatty acid-based polyesters, which have been reported to resemble high density polyethylene.⁴ It is well-known that these polyesters can be produced via enzymatic⁵ or catalytic⁶ ring-opening polymerization (ROP) of the cyclic esters. This concept can be successfully extended to a large variety of functionalized or branched lactones. For example, it is anticipated that copolymerization of macrolactones with branched lactones produces linear low-density polyethylene (LLDPE)-like materials. Although enzymes are highly active and selective, the enzymatic ROP, leads to products with limited control over the copolymers' microstructure.⁷ Alternatively, various organic or metal-based ROP catalysts are known to provide excellent control over the polymers molecular weight, stereo-regularity, copolymer-microstructure and properties of ring-strained lactones.⁸ Hitherto, there are only few catalytic systems known that are capable of polymerizing macrolactones to high molecular weight products in a controlled way.^{6a,9} In search for highly efficient living or immortal catalysts, a Zn complex containing a tridentate phenoxy-imine ligand was selected (Figure 1). This type of catalyst revealed excellent

performance, demonstrating quasi-living behavior, in ROP of *e.g.* cyclic carbonates and lactide,¹⁰ and was therefore expected to be a suitable candidate for forming high molecular weight homo- and copolymers of all types of cyclic monomers including macrolactones.

Herein, we report the synthesis and in-depth characterization of copolyesters obtained via catalytic ROP of pentadecalactone (PDL) and ϵ -decylactone (eDL), using **1** as catalyst and benzyl alcohol as an initiator (Figure 1). ϵ -Caprolactone (eCL) was used alongside eDL to distinguish the effect of branching versus the increased density of ester functionalities in the polymers. The irregularity, resulting from the presence of polar units and branches distributed along the polymers backbone, was assumed to significantly affect their structure and dynamics. This complex correlation was elucidated using advanced solid-state NMR and wide angle X-ray diffraction (WAXD) techniques.¹¹

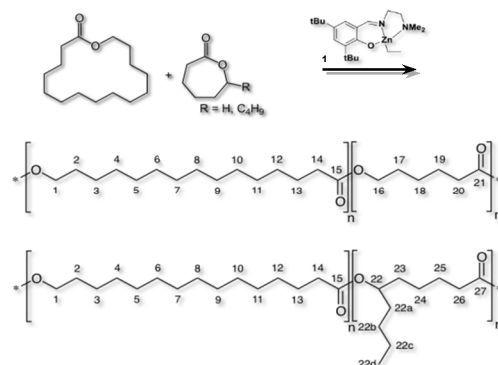


Figure 1. Polyesters synthesized by ROP of PDL + eCL and PDL + eDL catalyzed by **1** with benzyl alcohol as initiator.

Initially, homopolymerizations of each of the monomers (PDL, eCL, eDL) were performed using **1** as catalyst precursor and benzyl alcohol as the initiator. The catalyst showed good activity and produced high molecular weight PPDL ($M_n = 73$ kg/mol, PDI = 2.3) and PeCL ($M_n = 41.3$ kg/mol, PDI = 1.8). Although conversion of eDL was 100% within 3 h, the obtained molecular weight of PeDL was considerably lower (14 kg/mol, PDI = 2.3). Subsequently, PDL

Table 1. Polymerization conditions and properties of the synthesized homopolymer and block copolymers.

Sample	Mol ratio [M]/[Cat]/[ROH]	monomers mol ratio [PDL]/[eCL]/[eDL]	reaction time [h]	conversion ^a [PDL]/[eCL]/[eDL], [%]	M_n^b [kg/mol]	PDI ^b	T_m^c [°C]
PPDL	500/1/0.5	1/0/0	5	54/-/-	73.0	2.3	93
PeCL- <i>block</i> -PPDL	230/1/1	1/1.3/0	4	90/50/-	41.3	1.8	90, 55
PeDL- <i>block</i> -PPDL	500/1/0.5	1/0/1	24	64/-/100	21.8	2.3	81

^a determined from ¹H NMR spectra, ^b determined by HT-SEC in TCB against PE standards, ^c melting point (T_m)

was copolymerized with eCL and eDL, respectively. As evidenced by liquid-state ¹³C NMR analysis, the copolymerization of PDL with eCL leads to random copolymers, which crystallize over the whole range of comonomer composition.^{6b} Sequential addition of PDL followed by eCL affords a pure block copolymer ($T_{m(\text{PeCL block})} = 55$ °C, $T_{m(\text{PPDL block})} = 90$ °C; Figure S1). At first sight this might seem foreseeable. However, the reactivity of the ester functionality in the more or less ring strain-free PDL is likely to be very similar to that of the ester groups in the corresponding copolymer. Nevertheless, even after prolonged heating (16 h, 100 °C) no transesterification was observed. Hence, **1** shows remarkable selectivity for ring-opening of macrolactones versus transesterification of the corresponding copolymer.

The copolymerization of PDL with eDL gave a rather unexpected result. Although the single-feed copolymerization was expected to produce a random copolymer, similar as for copolymerization of PDL with eCL, it was found that instead a perfect block copolymer was formed (Figure S2, S2a). As demonstrated by liquid-state ¹H NMR analysis (Figure S3), the rapid disappearance of the eDL α -CH signals at 4.22-4.28 ppm in comparison to the α -CH₂ resonances of PDL (at 4.12 ppm) indicates that as long as unreacted eDL is present no PDL is incorporated. As a consequence, the polymerization of a mixture of the monomers leads to block copolymers rather than the initially expected random copolymers. Apparently, the secondary alkoxy group attached to zinc formed upon insertion of eDL strongly prefers incorporation of another equivalent of the ring-strained eDL rather than a large and unstrained PDL monomer, despite the (assumed) higher steric hindrance at the active site during coordination and insertion of eDL.

To obtain more insight into the reason why eCL+ eDL and eCL + PDL copolymerization results in random copolymers whilst eDL + PDL copolymerization affords a block copolymer, a computational study was performed using DFT-D (B97-D with energy dispersion correction scheme of Grimme¹²). Since coordination of the monomer is the first step in the catalytic ROP, we first identified adducts (C1) between the monomers (eCL, eDL, PDL) and the catalyst **1** (see supporting information Figure S4). In all species, the monomers tend to coordinate to the metal center through the exocyclic oxygen atom of the carboxyl group ($Zn \cdots O=C$ is 2.236/2.241, 2.234/2.237 and 2.319/2.315 Å for *n*-propyloxy/*i*-pentyloxy for eCL, eDL, and PDL, respectively). Unexpectedly, even though an isopentyloxy group was used to include the effect of the branch in the growing chain during polymerization, the $Zn \cdots O$ distances for coordinated eCL and eDL are very similar which shows that the pentyl branch does not affect the coordination of the monomer. Only for the coordinated PDL, the $Zn \cdots O$ distance is slightly elongated. For catalyst **1**, the ΔE of complexation for all monomers (formation of adduct C1) is ~5 kcal/mol, indicating a moderately strong $Zn \cdots O$ non-covalent interaction, which is noticeably stronger than for other zinc-based catalysts discussed elsewhere.¹³ The next step, being the insertion of the monomer, (C1 \rightarrow INT1, Figure 2) starts with the nucleophilic attack of the zinc-bonded alkoxy groups (*n*-propyloxy and *i*-pentyloxy) at the activated sp^2 carbonyl group of the coordinated

monomer. For the intermediate products, the Zn-O bond has become covalent and consequently shortened to 1.970, 1.948, and 1.960 Å for eCL, eDL, and PDL, respectively, while both C-O bonds have elongated. This bond elongation reflects the rehybridization of the former carbonyl atom from sp^2 to sp^3 . In INT1, the acceptor orbital at the activated carbonyl group is oriented in the direction of the alkoxy group, bridging the metal center and the activated former (now sp^3) carbonyl carbon atom. The energy loss for eCL, eDL and PDL were found to be 12.3/14.0, 9.0/10.6, 12.5/15.5 kcal/mol for *n*-propyloxy/*i*-pentyloxy substituents, respectively (Figure 2). Thus, the loss in energy was found to be the lowest for eDL. This is rather unexpected since the steric hindrance of the branch in eDL was expected to hamper the insertion process. Conversely, during the insertion of PDL into the branched *i*-pentyloxy substituent, the steric hindrance becomes decisive and dramatically hampers the reaction of PDL. The high-energy barrier for insertion of PDL into a branched alkoxy (9 kcal/mol and 13 kcal/mol higher than for eCL and eDL insertion, respectively) can be attributed to the different conformation the reacting PDL molecule adopts. This conformation strongly hampers the branched alkoxy-group at zinc to approach the accepting orbital of the exocyclic activated carbonyl carbon atom of PDL. The outcome of the DFT calculations indeed confirms that the eCL + eDL and eCL + PDL copolymerization should result in pure random copolymers. Furthermore, the significant difference in ΔE for eDL and PDL insertion into a branched alkoxy group is also in line with the observation that copolymerization of eDL and PDL yields PeDL-*block*-PPDL copolymers rather than random copolymers.

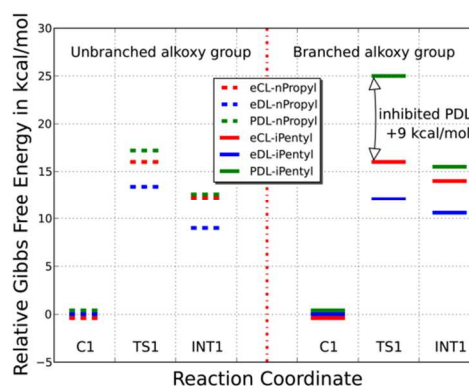


Figure 2. Energy diagram of the ROP for all three compounds (C1, TS1, INT1) with a linear (left) and branched (right) alkoxy-group at zinc. In the figure C1=monomer adduct, TS1=transition stage, INT1=insertion product.

Another interesting feature is that a sample taken from the reaction mixture at >90% eDL conversion shows a monodisperse PeDL homopolymer ($M_n = 13$ kg/mol, PDI = 1.08). The corresponding PeDL-*block*-PPDL copolymer ($M_n = 21.8$ kg/mol), obtained after consumption of PDL, shows a considerably broader PDI of 2.3, which indicates that transesterification is taking place. It is assumed that the transesterification takes place mainly in the

PPDL block. This is supported by MALDI-ToF-MS spectrum of the homo- and copolymer (Figure S5, S6), which mainly shows cyclic PPDL, some cyclic poly(eDL-co-PDL) from the tapered transition section of the polymer, but no cyclic PeDL. Note that the cyclic structures are over-represented in the recorded m/z region since MALDI-ToF-MS is restricted to the low molecular weight fraction of the polymer. Since the unbranched PeCL-*block*-PPDL copolymer did not show any randomization either, it is assumed that backbiting is the dominant transesterification mechanism active in these systems (compared to intermolecular transesterification). By applying 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) as transesterification catalyst, the PeCL-*block*-PPDL and PeDL-*block*-PPDL can easily be randomized, as evidenced by the appearance of dyad signals in the ^{13}C NMR spectrum corresponding to the different $\alpha\text{-CH}_2$ and $\alpha\text{-CH}$ resonances around 64 ppm and 74 ppm,¹⁴ (Figures S2c, S7), corresponding to random poly(eCL-co-PDL) and poly(eDL-co-PDL), respectively. The latter resembles our initially targeted LLDPE.

To assess the influence on the thermal properties of the polymers of both the butyl branches and the distance between ester groups along the polymer backbone, DSC analysis was performed (Figure S1). The PeCL-*block*-PPDL copolymer displays two well-resolved melting points at 55 °C and at 90 °C, respectively, corresponding to the crystalline PeCL and PPDL domains. The PeDL-*block*-PPDL shows a remarkable drop of the PPDL-block melting temperature ($T_m=81$ °C) and enthalpy of the transition. Interestingly, although the butyl branches are clustered in a PeDL block within the block copolymer, they still significantly perturb the ordered structure of PPDL, as was also deduced from the solid-state NMR and WAXD experiments discussed below. An even more pronounced effect of the presence of eCL and eDL units in the polymer backbone was found for random poly(eCL-co-PDL) and poly(eDL-co-PDL) copolymers, where the eCL-based copolymer revealed a single melting transition ($T_m=74$ °C), whilst the latter one proved to be an amorphous material.

To elucidate their crystallization behavior the PDL homo- and copolymers have been analyzed by WAXD (Figure S8). The diffraction profile of PPDL, showing three characteristic signals that corresponds to the 001, 110 and 200 crystallographic planes (Table S1), indicates that the material crystallizes into an orthorhombic form, similar to HDPE.¹⁵ The degree of crystallinity of 47 % (42 % from DSC measurements) was estimated according to the ratio between the surfaces of peaks and amorphous halo, corresponding to crystalline and amorphous components.¹⁵ The PeCL-*block*-PPDL copolymer crystallizes in a crystallographic structure analogous to PPDL with a notably higher degree of crystallinity (55 %). The increase in crystallinity compared to the PPDL homopolymer was also described for random poly(eCL-co-PDL) copolymers with relatively low content of eCL units.¹⁵ The PeDL-*block*-PPDL copolymer displays a significantly less ordered structure. Markedly weaker signals are observed for the crystallographic planes 110 and 200 in relation to the amorphous phase background, which is indicative for a lower degree of crystallinity of the material (21 %). Hence, the presence of the PeDL block induces a considerable reduction of the overall degree of crystallinity of the copolymer, which is not unexpected since the eDL homopolymer is completely amorphous. The observed reduction of the intensity of the signal that corresponds to the crystallographic 001 plane in the PeDL-*block*-PPDL copolymer is also assumed to be caused by a decrease of the degree of crystallinity rather than by loss of crystallographic regularity along the chain. It is assumed that the PeDL chain fragments are "pushed out" of the crystalline domains and localized preferentially in the amorphous phase area. The location of the signals that arise from the crystallographic planes 001, 110, 200 in

the PeDL-*block*-PPDL copolymer has not changed in relation to the location of the analogous signals in the corresponding PPDL (Table S1).

For characterizing the polymer chain conformations and their dynamics in the synthesized polyesters we have employed solid-state magic-angle spinning (MAS) NMR. This technique offers access to these molecular scale properties via the proton (^1H) and carbon (^{13}C) chemical shifts as reflected in their isotropic chemical shift and resonance line widths.¹⁶ Here, we further exploit the different T_2 -relaxation properties of the crystalline and amorphous regions of the polymers by applying the refocused $^{13}\text{C}\{^1\text{H}\}$ Inertive Nuclei Enhanced by Polarization Transfer (INEPT) sequence¹⁷ in parallel with solid-state $^{13}\text{C}\{^1\text{H}\}$ cross-polarization CP/MAS experiments. Thereby, the ^1H magnetization is transferred via the one-bond J -coupling (without homonuclear ^1H - ^1H decoupling)¹⁸ or the through space dipole-dipole coupling, respectively, allowing us to differentiate between rigid and flexible regions of the polyesters. Figures 3a-c summarize these results using the assignment given in Figure 1. For PeCL-*block*-PPDL, the main signal of the rigid methylene segments is centered at ~ 33 ppm, whereas those next to the ester group (1, 14, 16, and 20) appear at higher frequencies (Figure 3a). The carbonyl groups are of low intensity and display a sharp signal at ~ 174 ppm along with a broad underlying component, manifesting the semi-crystalline nature of the sample (*cf.* Figure S8).

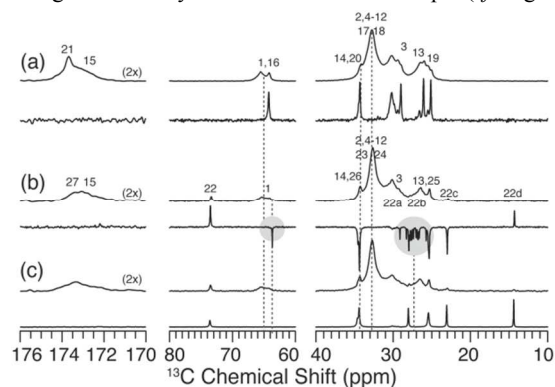


Figure 3. Solid-state ^{13}C MAS NMR spectra of (a) PeCL-*block*-PPDL, (b) PeDL-*block*-PPDL, and (c) PeDL-*block*-PPDL after preparative GPC purification. Each part include (top) a $^{13}\text{C}\{^1\text{H}\}$ CP/MAS NMR and (bottom) a $^{13}\text{C}\{^1\text{H}\}$ INEPT MAS NMR spectrum. Note the $^{13}\text{C}\{^1\text{H}\}$ INEPT MAS NMR spectrum in (b) displays CH_2 groups as negative and CH/CH_3 groups as positive signals, whereas (a,c) show all signals as positive.

In the $^{13}\text{C}\{^1\text{H}\}$ INEPT spectrum of PeCL-*block*-PPDL, the signal from the methylene segment is shifted to ~ 30 ppm. This feature demonstrates that the flexible main-chain methylene segments are predominantly in *gauche* conformation, *i.e.*, from the amorphous regions of the sample.¹⁹ The signals of the methylene groups next to the ester group do not change their position significantly. Replacing the linear eCL segments with the butyl-branched eDL gives the ^{13}C MAS NMR spectra in Figure 3b. The $^{13}\text{C}\{^1\text{H}\}$ CP/MAS spectrum shows strong similarities to that of linear PeCL-*block*-PPDL in Figure 3a. However, the ^{13}C signals appear less broad with only low intensity signals from the butyl group, which are of relative high intensity in the $^{13}\text{C}\{^1\text{H}\}$ INEPT spectrum. This indicates that the butyl-branched eDL leads to an increased chain dynamics as compared to the non-branched eCL-based polymer. Interestingly, a number well-resolved ^{13}C signals from flexible methylene segments at ~ 27 ppm (highlighted in grey) is also observed. These are completely removed after preparative recycling GPC, demonstrating that they originated from low molecular weight cyclic PPDL as evidenced by solid state NMR and MALDI-ToF (Figures S5, S9-11).

To further characterize the influence of the cyclic PPDL on PeDL-*block*-PPDL we have recorded ^1H - ^1H double quantum-single quantum (DQ-SQ) correlation spectra and relaxation-normalized ^1H - ^1H DQ build-up curves²⁰ to study the polymer chain dynamics before and after preparative GPC purification (Figure S12). In the ^1H - ^1H DQ-SQ correlation spectrum of PeDL-*block*-PPDL in Figure S12a the signals are slightly better resolved with narrower ^1H signals compared to that of the purified PeDL-*block*-PPDL in Figure S12b. This difference most likely reflects a locally increased molecular mobility in the unpurified sample. The influence of cyclic PPDL on the PeDL-*block*-PPDL chain dynamics is also visible from the ^1H - ^1H DQ build-up curves in Figure S12a, b reflecting the averaged and normalized ^1H - ^1H dipole-dipole coupling between selected ^1H sites and their ^1H neighbors caused by chain dynamics.²¹ For as-synthesized PeDL-*block*-PPDL, the DQ build-up curves show a slight spread with a noticeable decay for sites 14 and 26. Upon purification the DQ build-up curves show a more homogeneous behavior. This illustrates that the cyclic low molecular weight PPDL material mainly affects the PeDL part of the sample with PPDL being the more rigid block.

Conclusions

In summary, we described an attractive catalytic ROP route for producing high molecular weight macrolactone-based homo- and copolymers. Although it was attempted to produce copolyesters resembling LLDPE, the delicate balance between steric hindrance and monomer reactivity resulted in the formation of pure block PeDL-*block*-PPDL. The block copolymer could easily be randomized by using TBD as transesterification catalyst. Copolymerization of eCL with PDL or eDL gave the expected random poly(eCL-*co*-PDL) and poly(eCL-*co*-eDL). PeCL-*block*-PPDL can be produced by sequential feed of PDL followed by eCL. Both PeCL-*block*-PPDL and PeDL-*block*-PPDL copolymers have been analyzed by means of solid-state NMR and WAXD. The decreased crystallinity in eDL-based copolymers is not only due to the branched structure, but also as a result of the presence of low molecular weight cyclics. Solid-state NMR revealed the PPDL block in PeDL-*block*-PPDL is the most rigid part of the linear polymer.

Notes and references

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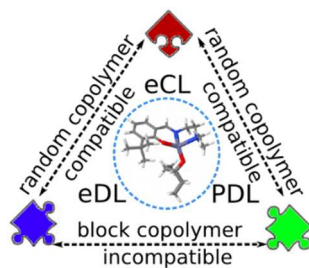
Electronic Supplementary Information (ESI) available: experimental part and the characterization techniques. See DOI: 10.1039/c000000x/. The authors declare no competing financial interests. This research was funded by SABIC, which financial support is highly appreciated.

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Topological Behavior Mimicking Ethylene-Hexene Copolymers Using Branched Lactones and Macrolactones



Block-to-block: Highly effective and facile technique for ring-opening copolymerization of lactones with macrolactone towards polyolefin-like materials is presented.