Topological behavior mimicking ethylene-hexene copolymers using branched lactones and macrolactones


Published in:
Polymer Chemistry

DOI:
DOI:10.1039/c3py01754k
10.1039/c3py01754k

Published: 01/01/2014

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 07. Dec. 2018
Topological behavior mimicking ethylene–hexene copolymers using branched lactones and macro lactones†

Lidia Jasinska-Walc,*abc Michael Ryan Hansen,de Dmytro Dudenko,df Artur Rozanski,g Miloud Bouyahyi,c Manfred Wagner,d Robert Graf and Robbert Duchateau*ac

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. 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. 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 by far does not cover the worldwide demand for this monomer. Therefore, one class of interesting additions to petrochemical polyolefins is 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. It is well-known that these polyesters can be produced via enzymatic or catalytic ring-opening polymerization (ROP) of 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 macro lactones 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. Alternatively, various organic or metal-based ROP catalysts are known to provide excellent control over the polymer molecular weight, stereo-regularity, copolymer-microstructure and properties of ring-strained lactones. Hitherto, there are only a few catalytic systems known that are capable of polymerizing macro lactones to high molecular weight products in a controlled way. In search for highly efficient living or immortal catalysts, a Zn complex containing a tridentate phenoxy-imine ligand was selected (Fig. 1). This type of catalyst showed excellent performance, demonstrating quasi-living behavior, in ROP of e.g. cyclic carbonates and lactide, and was therefore expected to be a suitable candidate for forming high molecular weight homo- and co-polymers of all types of cyclic monomers including macro lactones.

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

† Electronic supplementary information (ESI) available: Experimental part and the characterization techniques. See DOI: 10.1039/c3py01754k
Herein, we report the synthesis and in-depth characterization of copolysters obtained via catalytic ROP of pentadecalactone (PDL) and ε-decalactone (εDL), using 1 as the catalyst and benzyl alcohol as an initiator (Fig. 1). ε-Caprolactone (εCL) was used alongside εDL 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 polymer 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.43

Initially, homopolymerization of each of the monomers (PDL, εCL and εDL) was performed using 1 as the catalyst precursor and benzyl alcohol as the initiator. The catalyst showed good activity and produced high molecular weight PPDL (Mn = 73 kg mol⁻¹, PDI = 2.3) and PeCL (Mn = 41.3 kg mol⁻¹, PDI = 1.8). Although conversion of εDL was 100% within 3 h, the obtained molecular weight of PeDL was considerably lower (14 kg mol⁻¹, PDI = 2.3). Subsequently, PDL was copolymerized with εCL and εDL, respectively. As evidenced by liquid-state ¹³C NMR analysis, the copolymerization of PDL with εCL leads to random copolymers, which crystallize over the whole range of comonomer composition.44 Sequential addition of PDL followed by εCL affords a pure block copolymer (Tm(PPCL block) = 55 °C, Tm(PeCL block) = 90 °C; Fig. 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 (Table 1).

The copolymerization of PDL with εDL gave a rather unexpected result. Although the single-feed copolymerization was expected to produce a random copolymer, similar to the one produced for copolymerization of PDL with εCL, it was found that instead a perfect block copolymer was formed (Fig. S2 and S2a†). As demonstrated by liquid-state ¹H NMR analysis (Fig. S3†), the rapid disappearance of the εDL α-CH signals at 4.22–4.28 ppm in comparison to the α-CH₂ resonance of PDL (at 4.12 ppm) indicates that as long as unreacted εDL 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 εDL strongly prefers incorporation of another equivalent of the ring-strained εDL rather than a large and unstrained PDL monomer, despite the (assumed) higher steric hindrance at the active site during coordination and insertion of εDL.

To obtain more insight into the reason why εCL + εDL and εCL + PDL copolymerization reactions result in random copolymers whilst εDL + PDL copolymerization affords a block copolymer, a computational study was performed using DFT-D (B97-D with the energy dispersion correction scheme of Grimme45). Since coordination of the monomer is the first step in the catalytic ROP, we first identified adducts (C1) between the monomers (εCL, εDL and PDL) and the catalyst 1 (see ESI, Fig. S4†). In all species, the monomers tend to coordinate to the metal center through the exocyclic oxygen atom of the carbonyl group [Zn···O=C is 2.236/2.241, 2.234/2.237 and 2.319/2.315 Å for n-propyloxy/i-pentyloxy for εCL, εDL, and PDL, respectively]. Unexpectedly, even though an isopentyl group was used to include the effect of the branch in the growing chain during polymerization, the Zn···O distances for coordinated εCL and εDL are very similar which shows that the pentyl branch does not affect the coordination of the monomer. Only for coordinated PDL, the Zn···O distance is slightly elongated. For catalyst 1, ΔE of complexation for all monomers (formation of adduct C1) is ~5 kcal mol⁻¹, indicating a moderately strong Zn···O non-covalent interaction, which is noticeably stronger than for other zinc-based catalysts discussed elsewhere.46 The next step, being the insertion of the monomer, (C1 → INT1, Fig. 2) starts with the nucleophilic attack of the zinc-bonded alkoxy groups (n-propyloxy and i-pentyloxy) at the activated sp² carbon of the corresponding lactone (eDL) and benzyl alcohol as an initiator (Fig. 1). ε-Caprolactone (εCL) was used alongside εDL 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 polymer 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.43

Initially, homopolymerization of each of the monomers (PDL, εCL and εDL) was performed using 1 as the catalyst precursor and benzyl alcohol as the initiator. The catalyst showed good activity and produced high molecular weight PPDL (Mn = 73 kg mol⁻¹, PDI = 2.3) and PeCL (Mn = 41.3 kg mol⁻¹, PDI = 1.8). Although conversion of εDL was 100% within 3 h, the obtained molecular weight of PeDL was considerably lower (14 kg mol⁻¹, PDI = 2.3). Subsequently, PDL was copolymerized with εCL and εDL, respectively. As evidenced by liquid-state ¹³C NMR analysis, the copolymerization of PDL with εCL leads to random copolymers, which crystallize over the whole range of comonomer composition.44 Sequential addition of PDL followed by εCL affords a pure block copolymer (Tm(PPCL block) = 55 °C, Tm(PeCL block) = 90 °C; Fig. 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 (Table 1).

The copolymerization of PDL with εDL gave a rather unexpected result. Although the single-feed copolymerization was expected to produce a random copolymer, similar to the one produced for copolymerization of PDL with εCL, it was found that instead a perfect block copolymer was formed (Fig. S2 and S2a†). As demonstrated by liquid-state ¹H NMR analysis (Fig. S3†), the rapid disappearance of the εDL α-CH signals at 4.22–4.28 ppm in comparison to the α-CH₂ resonance of PDL (at 4.12 ppm) indicates that as long as unreacted εDL 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 εDL strongly prefers incorporation of another equivalent of the ring-strained εDL rather than a large and unstrained PDL monomer, despite the (assumed) higher steric hindrance at the active site during coordination and insertion of εDL.

To obtain more insight into the reason why εCL + εDL and εCL + PDL copolymerization reactions result in random copolymers whilst εDL + PDL copolymerization affords a block copolymer, a computational study was performed using DFT-D (B97-D with the energy dispersion correction scheme of Grimme45). Since coordination of the monomer is the first step in the catalytic ROP, we first identified adducts (C1) between the monomers (εCL, εDL and PDL) and the catalyst 1 (see ESI, Fig. S4†). In all species, the monomers tend to coordinate to the metal center through the exocyclic oxygen atom of the carbonyl group [Zn···O=C is 2.236/2.241, 2.234/2.237 and 2.319/2.315 Å for n-propyloxy/i-pentyloxy for εCL, εDL, and PDL, respectively]. Unexpectedly, even though an isopentyl group was used to include the effect of the branch in the growing chain during polymerization, the Zn···O distances for coordinated εCL and εDL are very similar which shows that the pentyl branch does not affect the coordination of the monomer. Only for coordinated PDL, the Zn···O distance is slightly elongated. For catalyst 1, ΔE of complexation for all monomers (formation of adduct C1) is ~5 kcal mol⁻¹, indicating a moderately strong Zn···O non-covalent interaction, which is noticeably stronger than for other zinc-based catalysts discussed elsewhere.46 The next step, being the insertion of the monomer, (C1 → INT1, Fig. 2) starts with the nucleophilic attack of the zinc-bonded alkoxy groups (n-propyloxy and i-pentyloxy) at the activated sp² carbon.

![Fig. 2 Energy diagram of the ROP for all three compounds (C1, TSI and INT1) with a linear (left) and branched (right) alkoxy-group at zinc.](Image)

In the figure C1 = monomer adduct, TSI = transition stage and INT1 = insertion product.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Polymerization conditions and properties of the synthesized homopolymer and block copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Mol ratio [MJ]/[Cat]/[ROH]</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>PPDL</td>
<td>500/1/0.5</td>
</tr>
<tr>
<td>PeCL-block-PPDL</td>
<td>230/1/1</td>
</tr>
<tr>
<td>PeDL-block-PPDL</td>
<td>500/1/0.5</td>
</tr>
</tbody>
</table>

* Determined from ¹H NMR spectra. b Determined by HT-SEC in TCB against PE standards. c Melting point (T<sub>m</sub>).
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 sp² to sp³. 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 sp³) carbonyl carbon atom. The energy losses for eCL, eDL and PDL were found to be 12.3/14.0, 9.0/10.6 and 12.5/15.5 kcal mol⁻¹ for n-propyloxy-i-penthyloxy substituents, respectively (Fig. 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-penthyloxy substituent, the steric hindrance becomes decisive and dramatically hampers the reaction of PDL. The high-energy barrier for insertion of PDL into a branched alkoxide (9 kcal mol⁻¹ and 13 kcal mol⁻¹ higher than for eCL and eDL insertion, respectively) can be attributed to the different conformations the reacting PDL molecule adopts. These conformations strongly hamper 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 eCL + eDL and eCL + PDL copolymerization should result in pure random copolymers. Furthermore, the significant difference in ∆E for eDL and PDL insertion into a branched alkoxide group is also in line with the observation that copolymerization of eDL and PDL yields PeDL-block-PPDL copolymers rather than random copolymers.

Another interesting feature is that a sample taken from the reaction mixture at >90% eDL conversion shows a mono-disperse PeDL homopolymer (Mₙ = 13 kg mol⁻¹, PDI = 1.08). The corresponding PeDL-block-PPDL copolymer (Mₙ = 21.8 kg mol⁻¹), obtained after consumption of PDL, shows a considerably broader PDI of 2.3, which indicates that transesterification takes place. It is assumed that the transesterification takes place mainly in the PPDL block. This is supported by the MALDI-ToF-MS spectrum of the homo- and co-polymers (Fig. S5 and 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 the transesterification catalyst, PeCL-block-PPDL and PeDL-block-PPDL can easily be randomized, as evidenced by the appearance of dyad signals in the ²H NMR spectrum corresponding to the different α-CH₂ and α-CH resonances around 64 ppm and 74 ppm¹⁴ (Fig. S2c and 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 (Fig. S1†). The PeCL-block-PPDL copolymer displays two well-resolved melting points at 55 °C and 90 °C, respectively, corresponding to the crystalline PeCL and PPDL domains. The PeDL-block-PPDL copolymer shows a remarkable drop in the PPDL-block melting temperature (Tₘ = 81 °C) and the 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 on 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 (Tₘ = 74 °C), whilst the latter one proved to be an amorphous material.

To elucidate their crystallization behavior the PDL homo- and co-polymers have been analyzed by WAXD (Fig. S8†). The diffraction profile of PPDL, showing three characteristic signals that correspond to the 001, 110 and 200 crystallographic planes (Table S1†), indicates that the material crystallizes into an orthorhombic form, similar to HDPE.¹² A 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.¹³ 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 a 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 of 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 and 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 (¹³C) chemical shifts as reflected in their isotropic chemical shifts 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 $^{13}$C($^1$H) Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) sequence$^{17}$ in parallel with solid-state $^{13}$C($^1$H) cross-polarization CP/MAS experiments. Thereby, the $^1$H magnetization is transferred via the one-bond $J$-coupling (without homonuclear $^1$H–$^1$H decoupling)$^{18}$ or the through space dipole–dipole coupling, respectively, allowing us to differentiate between rigid and flexible regions of the polyesters. Fig. 3a–c summarize these results using the assignment given in Fig. 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 (Fig. 3a). The carbonyl groups are of low intensity next to the ester group (1, 14, 16, and 20) appear at higher methylene segments is centered at $/C_{24}$.

Fig. 3a displays CH$_2$ groups as negative signals and CH/CH$_3$ groups as positive signals, whereas (a) and (c) show all signals as positive.

In the $^{13}$C($^1$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 a 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 Fig. 3b. The $^{13}$C($^1$H) CP/MAS spectrum shows strong similarities to that of linear PeCL-
block-
PPDL in Fig. 3a. However, the $^{13}$C signals appear less broad with only low intensity signals from the butyl group, which are of a relatively high intensity in the $^{13}$C($^1$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 of well-resolved $^{13}$C signals from flexible methylene segments at ~27 ppm (highlighted in grey) are also observed. These are completely removed after preparative recycling GPC, demonstrating that they originated from low molecular weight cyclic PPDL as evidenced by NMR and MALDI-ToF-MS (Fig. S3, S9–S11†). To further characterize the influence of cyclic PPDL on PeDL-
block-
PPDL we have recorded $^1$H–$^1$H double quantum–single quantum (DQ–SQ) correlation spectra and relaxation-normalized $^1$H–$^1$H DQ build-up curves$^{20}$ to study the polymer chain dynamics before and after preparative GPC purification (Fig. S12†). In the $^1$H–$^1$H DQ–SQ correlation spectrum of PeDL-
block-
PPDL in Fig. S12a,† the signals are slightly better resolved with narrower $^1$H signals compared to that of purified PeDL-
block-
PPDL in Fig. 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 $^1$H–$^1$H DQ build-up curves in Fig. S12a and b† reflecting the averaged and normalized $^1$H–$^1$H dipole–dipole coupling between selected $^1$H sites and their $^1$H 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 macroactone-based homo- and co-polymers. Although it was attempted to produce copolymers 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 the trans-esterification catalyst. Copolymerization of eCL with PDL or eDL gave the expected random poly(eCL-co-PDL) and poly(eCL-co-eDL) copolymers. 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 a result of the presence of low molecular weight cycles. Solid-state NMR revealed that the PPDL block in PeDL-
block-
PPDL is the most rigid part of the linear polymer.

Conflict of interest

The authors declare no competing financial interests.

Acknowledgements

This research was founded by SABIC, whose financial support is highly appreciated.

Notes and references
