Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201908688
Angew. Chem. 10.1002/ange.201908688

Link to VoR: http://dx.doi.org/10.1002/anie.201908688
http://dx.doi.org/10.1002/ange.201908688
Tetracrystalline Tetrablock Quarterpolymers: Four Different Crystallites under the Same Roof

Viko Ladelta,[a] George Zapsas,[a] Edy Abou-hamad,[b] Yves Gnanou,[c] and Nikos Hadjichristidis*[a]

Abstract: Multicrystalline block copolymers having three or more crystalline segments are essential materials for the advancement of physics in the field of crystallinity. Due to the challenging synthesis of multicrystalline polymers only a limited number of tricrystalline terpolymers are reported until now. We report, for the first time, the synthesis of poly(ethylene)-b-poly(ethylene oxide)-b-poly(ε-caprolactone)-b-poly(L-Lactide) (PE-b-PEO-b-PCL-b-PLLA) tetracrystalline tetrablock quarterpolymer, by combining polyhomologation, ring-opening polymerization, and an organic/inorganic "catalyst switch" strategy. 1H NMR spectroscopy and gel-permeation chromatography confirm the formation of the tetrablock quarterpolymer, while differential scanning calorimetry, X-ray diffraction, and wide-line separation solid-state NMR spectroscopy reveal the existence of four different crystalline domains.

Introduction

Crystalline polymers are important materials with myriad applications.[1] For example, high density polyethylene (HDPE), the most widely used crystalline polymer,[2] is applied in packaging, plumbing, electrical, automotive industry, among others. Other well-known crystalline polymers such as poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG), poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLLA) are generally used for biomedical applications thanks to their biodegradability and biocompatibility.[3] Moreover, combining two or more crystalline blocks in one polymeric chain will result in a new material with remarkable properties.[4]

Double-crystalline diblock copolymers containing PCL and/or PLLA block are usually prepared by ring-opening polymerization (ROP) of ε-caprolactone (CL) and L-Lactide (LLA) in one-pot with primary alcohol as (macro)initiator and Sn(II) 2-ethylhexanoate [Sn(Oct)]2 as catalyst.[4] Sn(Oct)2 is cheap and commercially available, highly active at a temperature range of 60 – 180 °C, and has good solubility in many organic solvents.[5] Moreover, Sn(Oct)2 has been approved as a food additive by the United States Food and Drug Administration.[6]

Several examples of the double-crystalline diblock copolymers containing PCL and/or PLLA block are PCL-b-PLLA[6] PEG-b-PCL[7] and PEG-b-PLLA.[8] For the synthesis of PCL-b-PLLA[9] and PEG-b-PLLA[10] two approaches have been reported. In the first approach an ω-hydroxy 1,4-polybutadiene (PB-OH) was prepared by anionic polymerization of 1,3-butadiene, followed by chain-end functionalization with ethylene oxide (EO).[11] ROP of CL or LLA was carried out from PB-OH macriniitator catalyzed by Sn(Oct)2. Then, the PB block was hydrogenated to obtain PEG-b-PLLA[12, 13] or PE-b-PLLA.[13a, 13b] In the second approach, an ω-hydroxy polyethylene (PE-OH) was synthesized by the polymerization of ethylene using metallocenes as a catalyst.[9, 10] Subsequently, PE-OH was used to initiate the ROP of lactones to achieve PE-b-PCL or PE-b-PLLA.[9d, 10d] Nevertheless, the PE prepared by the first approach is not fully hydrogenated and contain some 1,2 isomer whereas the PE prepared by metallocenes catalyst is not perfectly linear.

A new route to prepare well-defined and perfectly linear polyethylene is the polyhomologation or C1 polymerization. This (alkyl)borane initiated polymerization of ylides was discovered by Shea et al., and proved to be a powerful methodology to synthesize well-defined PE-based materials.[13] The polymerization is performed in two consecutive steps: (i) formation of an “ate” complex between the ylide (monomer) and the alkylborane (initiator), followed by (ii) intramolecular 1,2-migration of the methylene groups from the ylide into the three alkyl branches of borane with the simultaneous elimination of dimethyl sulfoxide. After quantitative consumption of the ylide, a boron-linked PE 3-arm star is generated, giving three linear PE-OH chains by oxidation/hydrolysis. This methodology enables the synthesis of perfectly linear PE-OH with controlled microstructure.[13] The PE-OH can be used as a macroinitiator to prepare various complex macromolecular architectures in combination with other living/controlled polymerization techniques.[13]

A limited number of reports are available in the literature on tricrystalline triblock terpolymers. Abetz et al. reported the synthesis of PB-b-PEO from PB-OH macriniitator. PB-b-PEO was used as the macriniitator for the non-catalyzed thermal ROP of CL to afford PB-b-PEO-b-PCL.[14] Then, hydrogenation of PB block was performed by Wilkinson catalyst to yield PE-b-PEO-b-PCL triblock terpolymers. Side reactions have detected that lead to the formation of undesired PCL-b-PEO diblock copolymer, which was removed by several purification steps. Kuo et al. recently reported the synthesis of PEG-b-PCL-b-PLLA by a two-pots ROP of CL and LLA from PEG macriniitator catalyzed by Sn(Oct)2.[15] Coulombier et al. reported a one-pot two-step process for the synthesis of PEG-b-

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Supporting information for this article is given via a link at the end of the document.
Our group have reported the synthesis of PEO-b-PCL-b-PLLA by ROP of EO, CL and LLA in one-pot catalyzed by phosphazene superbase (PSB) 1-tert-butyl-2,2,4,4,4-pentakis(dimethylamino)-2,4,4-tris(dimethyloxide)-2,2-bis(tris(dimethylamino)phosphoranylid-ename)-2λ,4λ-catenadi(phosphazene) (t-BuP_5, _pK_acn = 33.5). The complex interplay and isothermal crystallization behavior of the terpolymer were also studied extensively. We also developed an organic/organic catalyst switch strategy from PSB 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis(tris(dimethylamino)phosphoranylid-ename)-2λ,4λ-catenadi(phosphazene) (t-BuP_5, _pK_acn = 42.7 ) to an organic acid (diphenyl phosphate [DPP], _pK_dms = 3.88), or t-BuP_2. First, an alcohol initiator was activated by t-BuP_5 (suitable for polymerizing epoxides [EXs] and macro lactones [MLs]) and promoted the ROP of EXs or MLs to high conversion. Afterward, two strategies were performed. The first strategy was the addition of an excess of DPP to neutralize t-BuP_5 and polymerizing small lactones (SLs) or trimethylene carbonate (TMC) from PEXs macroinitiators catalyzed by the excess of DPP to afford PEXs-b-PSLs and PEXs-b-PPL. The second strategy was the addition of a weaker PSB, t-BuP_2, that can act as a catalyst for the ROP of LLA from PEXs macroinitiators towards PEX-b-PPL or small lactones (SLs) from PMLs macroinitiators towards PMLs-b-PSLs. To the best of our knowledge, there is no report on one-pot synthesis and properties of tetracrystalline tetrablock terpolymer. The absence of the report might be attributed to the challenging synthetic methodology in combining two or more different polymerizations in one-pot.

The interplay between crystallization and phase separation is a complex and fundamental problem in the physics of block copolymers. As the number of crystallizable block increases, their interactions regarding nucleation, crystallization, and morphology becomes very complex and at the same time fascinating. As we reported for the first time in our recent papers,[18] PCL-b-PEO-b-PCL-b-PLLA triblock terpolymers crystallized from a melt/mixed melt forming tricrystalline spherulites and axialites, where three different types of lamellae (i.e., PCL, PEO, and PLLA) co-exist in a single superstructure. The addition of a fourth crystallizable block and formation of a tetrablock terpolymer increases the complexity even more.

In this article, we report for the first time, the synthesis of a tetracrystalline PE-b-PEO-b-PCL-b-PLLA terpolymer, by combining polyhomologation (PE) with sequential block copolymerization (PE-b-PEO) and a new organic/metal catalyst-switch (t-BuP_5/DPP/SnOct_3) strategy. The molecular structure of the tetrablock terpolymer was confirmed by one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy (in liquid and solid-state), as well as by gel-permeation chromatography (GPC). The preliminary results on differential scanning calorimetry (DSC) and X-ray diffraction spectroscopy (XRD) confirms the existence of four crystallites. An in-depth study on the phase structure, crystallization and morphology is being performed and will be reported in the near future.

**Results and Discussion**

The general reaction for the synthesis of tetracrystalline tetrablock terpolymer is presented in Scheme 1. The first attempt was performed by combining polyhomologation (PE-OH 1 as a macroinitiator) with organic/organic catalyst-switch (t-BuP_5/DPP/t-BuP_2) strategy in toluene at 80 °C (the details are given in the Supporting Information [SI], Scheme S1, Table S1, and Figure S1 – S3). Under these conditions, t-BuP_5 promotes rapid side reactions of LLA, resulting in PE-b-PEO-b-PCL-b-PLLA-1 with amorphous PLLA block (Figure S4, SI).

In order to investigate the origin of side reactions that worsen the thermal properties of PLLA, a systematic experiment was performed. LLA was mixed with t-BuP_2 in toluene at 80 °C in the absence of primary alcohol as initiator. The progress of the reaction was followed by _¹H_ NMR and GPC (Figure S5, SI). _¹H_ NMR spectrum of an aliquot taken after 10 min of mixing shows that 91.4% of methine proton of LLA shifted downfield from 4.93 ppm to 5.18 ppm, indicating that polymerization occurred without primary alcohol. After 60 min, the conversion of PLLA reached 99%. GPC trace of the aliquot taken after 4.5 h confirms that PLLA formed in the reaction mixture but has broad _D_w (1.65). This _D_w is broader than in the case of PLLA prepared with primary alcohol (PPA) with t-BuP_2 in toluene at 80 °C ( _D_w = 1.35, Figure S6, SI).

_¹H_ NMR analysis on the reaction mixture (Figure S5a) suggested that t-BuP_2 triggered racemization through reversible deprotonation of the slightly acidic α-methine group of LLA (Scheme S2, SI). Two types of LA formed after this reaction: (i) (S,S) LLA, as a consequence of reversible deprotonation and (ii) (R,S) meso-LA as the product of tautomerization. Thus, two LA isomers existed in the polymerization mixture. At the same time, self-initiation occurred from O=C(CH_3)=O anion to another LA followed by propagation (Scheme S2, SI). This anion has a lower nucleophilicity than primary alcohol, which leads to a slow initiation as can be seen from the monomodal and broad _D_w of
Table 1. Synthesis and thermal properties of PE-b-PEO-b-PCL-b-PLLA-2 and the corresponding precursor polymers by organic-metal catalyst switch.[a]

<table>
<thead>
<tr>
<th>entry</th>
<th>sample</th>
<th>time[b] (h)</th>
<th>Conv.[c] (%)[d]</th>
<th>$M_n,NMR$[e] (kg mol$^{-1}$)[f]</th>
<th>$T_m/T_c$[g] (°C)[f]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PE-OH-2[a]</td>
<td>17</td>
<td>100</td>
<td>7.1</td>
<td>130.0/117.3</td>
</tr>
<tr>
<td>2</td>
<td>PE-b-PEO-2</td>
<td>15</td>
<td>100</td>
<td>15.1</td>
<td>76.1/63.8</td>
</tr>
<tr>
<td>3</td>
<td>PE-b-PEO-b-PCL-2</td>
<td>48</td>
<td>92</td>
<td>10.4</td>
<td>60.6/36.7/44.1</td>
</tr>
<tr>
<td>4</td>
<td>PE-b-PEO-b-PCL-b-PLLA-2</td>
<td>20</td>
<td>94</td>
<td>7.6</td>
<td>60.9/41.7/46.7/148.1/88.3</td>
</tr>
</tbody>
</table>

[a] Polymerizations were performed from PE-OH macroinitiator in toluene at 80 °C with t-BuP$_4$/DPP/Sn(Oct)$_2$ catalyst-switch.
[b] Prepared by polyhomologation of sulfoxonium methylide in toluene under Ar at 80 °C.
[c] Polymerization time of the last block.
[d] Conversion of the monomer on the last block. Determined by 600 MHz $^1$H NMR spectrometer from the polymerization mixture (toluene $d_8$, 80 °C).
[e] $M_n$ of the last block. Determined by 600 MHz $^1$H NMR spectrometer from the isolated polymer (toluene $d_8$, 80 °C).
[f] Determined by DSC (heating and cooling rates are 10 °C min$^{-1}$ except for PLLA block [cooling rate 1 °C min$^{-1}$, under N$_2$]).
[g] Split peak. The value is taken from the highest peak.

Figure 1. a, 1D $^1$H NMR spectra of PE-b-PEO-b-PCL-b-PLLA-2 and the corresponding precursor polymers (entry 1 – 4, Table 1) and b, 2D COSY spectrum of PE-b-PEO-b-PCL-b-PLLA-2 (entry 4, Table 1) prepared by organic/metal catalyst switch (toluene $d_8$, 80 °C). ° denotes the unknown impurity.

We envisaged a new strategy, namely, organic/metal catalyst-switch. The basic concept is similar to the organic/organic catalyst switch. Firstly, ROP of EO (Scheme 1) from PE-OH-2 macroinitiator (entry 1, Table 1) to afford PE-b-PEO$^+$ + [t-BuP$_4$H]$^-$. Second, neutralization of the base with the addition of an equimolar amount of organic acid (DPP). This process terminates the ROP of EO yielding a hydroxyl terminated PE-b-PEO-2 diblock copolymer (entry 2, Table 1) and residual organic salt (phosphazenium diphenyl phosphate). Subsequently, PE-b-PEO-2 was utilized as a macroinitiator for the next
polymerization because the whole system is still under inert and dry conditions. Third, the addition of Sn(OOct)2 to promote the ROP of CL (PE-b-PEO-b-PCL-2, entry 3, Table 1), and then LLA in one-pot to produce PE-b-PEO-b-PCL-b-PLLA-2 (entry 4, Table 1).

1H NMR spectra of the isolated PE-OH-2, PE-b-PEO-2, PE-b-PEO-b-PCL-2, and PE-b-PEO-b-PCL-b-PLLA-2 (entry 1 - 4, Table 1) are presented in Figure 1a. The −CH2OH protons of PE (a) appear between 3.32 – 3.41 ppm while the CH2 protons of the main chain (e) observed around 1.17 – 1.46 ppm. The integral ratio of these protons was used to calculate the Mw of PE-OH-2. For PE-b-PEO-2 diblock copolymer, a new sharp peak appears around 3.30 – 3.56 ppm (g) corresponds to (CH2)2O of PEO block. After the terpolymerization with CL, six new peaks appear in the spectrum. The peak between 3.91 – 4.01 ppm (k) is assigned as CH2OC=O protons of CL block. The OCH2 protons appear between 2.09 – 2.14 ppm (h) while the 4 protons of −CH2−CH2O (i) and −CH2−CH2−O=O (n) appear around 1.49 – 1.56 and 1.40 – 1.48 ppm, respectively. The −CH2−CH2−CH2 protons (j) arise from 1.19 – 1.26 ppm. Two new protons emerged after the ROP of LLA from PE-b-PEO-b-PCL-2 macroinitiator; methine proton (CH3−CHO−CO) and methyl (−CH3) protons of PLLA block (m and l) around 4.99 – 5.13 ppm and 1.34 – 1.49 ppm, respectively.

It is essential to assign the chemical shift of end-groups protons of each block correctly because these protons are used to determine the Mw of the block. To support the 1D 1H NMR assignment (Figure 1a), 2D 1H-13C correlation spectroscopy (COSY, Figure 1b), total correlation spectroscopy (TOCSY, Figure S7, SI), 1H-13C hetero-nuclear single-bond correlation (HSQC, Figure S8, SI), and hetero-nuclear multiple-bond correlation (HMBC, Figure S9, SI) of PE-b-PEO-b-PCL-b-PLLA-2 (entry 4, Table 1) were performed in toluene-d8 at 80 °C. The −CH2−O−(CH2)2−O protons (a) (Figure 1a and 1b) between 3.30 – 3.56 ppm is the ω-end of CH2 protons of PE (e), covalently linked to O−(CH2)2−O (g) protons of PEO as shown by HSQC (Figure S8, ESI). The −CH2−OC end groups of PEO (b), PCL (c) and PLLA (d) (Figure 1a) protons that overlap in the 1D 1H spectrum could be observed in separate positions by 2D NMR spectroscopy (Figure 1b) and Figure S7 – S9, SI assigning our assignment. Protons (b) correlated to (g) (Figure 1b) indicating that it is the CH2 end group of PEO, and in correlation with OC−CH2 (h) of PCL (Figure S7 – S9, SI). All 2D liquid NMR analyses confirm that (b) is covalently bonded to PCL and (c) is covalently bonded to PLLA block.

Solid-state NMR was also used to characterize the structure of PE-b-PEO-b-PCL-b-PLLA-2 (entry 4, Table 1). 1H and 13C CP-MAS spectra (Figure S10 and S11, SI) show the −(CH2)n−protons and carbons chemical shifts of PE block (e) at 0.68 ppm and 33.75 ppm, respectively. The 2D 1H-13C short distance heteronuclear correlation (HECTOR) spectrum confirms the correlation between 1H at 0.68 ppm and 13C at 31.84 ppm (Figure 2a) in one bond. A sharp peak at 2.95 ppm is assigned as −O−(CH2)n−O− protons of PEO block (g) and pose a strong correlation with 13C at 69.17 ppm. The protons and carbons chemical shifts of PCL block are assigned as follow: −CH2−COO (k) observed at 3.46 ppm and 63.57 ppm, −CH2CO (h) at 1.67 ppm and 33.75 ppm, and three −CH2− protons (i, n, and j) merged at 0.98 ppm whereas the 13C peaks of (j) appear at 28.62 ppm and (i and n) at 25.28 ppm, respectively. The carbonyl carbon of PCL (O−C=O) at 172.9 ppm (p) reveals a strong correlation on long-distance HETCOR spectrum with methylene protons of PCL (Figure 2b). Similar long-distance correlation is also observed on the carbonyl carbon of PLLA block (170.9 ppm) with methine proton (m) of PLLA at 4.66 ppm.
A small shoulder around 169.4 ppm is probably triggered by stereoregularity of PLLA chain. The CH₃ protons of PLLA (l) merged with methylene protons of PCL at 0.98 ppm. Due to the broad ¹H peak in solid-state NMR, the end-group protons of each block are not observable.

Because PE-ÖH-2, PE-b-PEO-2, PE-b-PEO-b-PCL-2, and PE-b-PEO-b-PCL-b-ÖLLA-2 (entry 1 – 4, Table 3) are not soluble in tetrahydrofuran (THF) and partially soluble in CHCl₃, the analysis of molecular weight distribution (Đₐ) has to be performed by high-temperature GPC (HT-GPC) in 1,2,4-trichlorobenzene (TCB) at 150 °C. PE-ÖH-2 (entry 1, Table 1) exhibits a monomodal and narrow GPC trace (Đₐ = 1.21) indicating that polyhomologation of sulfoxonium methide is giving well-defined PE (Figure S12, SI). However, PE-b-PEO-2, PE-b-PEO-b-PCL-2, PE-b-PEO-b-PCL-b-ÖLLA-2 did not exhibit any peak on HT-GPC traces (Figure S12, SI). This probably due to absorption of PEO block into the columns (2× PLgel 10 μm mixed-B, 7.5 × 300 mm) since we also encountered similar circumstance on our previous work on PE containing PEO molecular co-brush. ¹H NMR analysis of PEO macroinitiator with low Mn by polyhomologation (entry 1, Table S3; SI). ¹H NMR analysis of the resulting PE-ÖH-3 gives the Mn = 800 g mol⁻¹ (Figure S16, SI). This PE-ÖH-3 is soluble in THF at 50 °C (concentration 2 mg ml⁻¹) and exhibits narrow and monomodal GPC trace (Figure 3, black). Tetrablock quarterpolymer was synthesized from PE-ÖH-3 macroinitiator via organic/metal catalyst-switch (t-BuP₄/DP/DPP/Sn[Oct]₄) strategy (entry 2 – 4, Table S3). The GPC traces of the PE-b-PEO-3 (red), PE-b-PEO-b-PCL-3 (blue) and PE-b-PEO-b-PCL-b-ÖLLA-3 (green) are monomodal with narrow Đₐ (Figure 3). The result implies that the ROPs are controlled and result in tetrablock quarterpolymer with well-defined microstructure.

For more in-depth study, we analyzed the GPC traces of PEO, PCL, and PLLA prepared by ROP in toluene at 80 °C (entry 1, Table S2, SI) in both TCB and THF. PEO did not show any peak in TCB at 150 °C, which correlates to strong absorption in the column (Figure S13, SI). The same PEO exhibited a narrow and monomodal peak in THF at 35 °C (Đₐ = 1.09) (Figure S13, SI), indicating that the ROP of EO catalyzed by t-BuP₄ at 80 °C in toluene is controlled. PCL (entry 2, Table S2) also exhibited a narrow and monomodal traces in both GPCs (Figure S14, SI). PLLA shows monomodal GPC traces in both THF and TCB (Figure S15, SI). However, the Đₐ in TCB (1.54) is much broader than the Đₐ in THF (1.13). The reason behind this discrepancy is still unknown.

An ideal approach to tackle the aforementioned challenges is to prepare a PE-ÖH macroinitiator with low Mn by polyhomologation (entry 1, Table S3; SI). ¹H NMR analysis of the resulting PE-ÖH-3 gives the Mn = 800 g mol⁻¹ (Figure S16, SI). This PE-ÖH-3 is soluble in THF at 50 °C (concentration 2 mg ml⁻¹) and exhibits narrow and monomodal GPC trace (Figure 3, black). Tetrablock quarterpolymer was synthesized from PE-ÖH-3 macroinitiator via organic/metal catalyst-switch (t-BuP₄/DP/DPP/Sn[Oct]₄) strategy (entry 2 – 4, Table S3). The GPC traces of the PE-b-PEO-3 (red), PE-b-PEO-b-PCL-3 (blue) and PE-b-PEO-b-PCL-b-ÖLLA-3 (green) are monomodal with narrow Đₐ (Figure 3). The result implies that the ROPs are controlled and result in tetrablock quarterpolymer with well-defined microstructure.

DSC analysis was performed to evaluate the thermal properties (Figure 4) of PE-ÖH-2 (black), PE-b-PEO-2 (red), and PE-b-PEO-2 (blue), and PE-b-PEO-b-PCL-b-ÖLLA-2 (green). A noticeable decrease of the Tm of PE (Figure 4a, black) observed from 130.0 °C to 120.3 °C in the PE-b-PEO-2 (Figure 4a, red). The decrease of Tm might be attributed to the fact that PEO block, covalently linked to PE-ÖH-2, has a much larger Mn and melted earlier than PE-ÖH-2 block. The Tm on PE-b-PEO-b-PCL-2 and PE-b-PEO-b-PCL-b-ÖLLA-2 (Figure 4a, blue and green) is relatively unchanged (~120 °C). Little to no deviations were observed on the melting behavior of PEO block (60.6 °C < Tm < 63.8 °C) and PCL block (60.6 °C < Tm < 60.9 °C). The endothermic peaks of PCL and PEO observed as a merged peak due to the close Tm of the two blocks. The Tm on PE-b-PEO-b-PCL-b-ÖLLA-2 (green) observed at 148.0 °C indicating the formation of crystalline PLLA block.
After melting and annealing of the polymers for 3 min, crystallization behavior was observed by applying a cooling scan (1 °C min$^{-1}$) to the samples deposited on top of a glass substrate and heated up to 180 °C, annealed for 10 min, and cooled down to rt at a roughly 2 °C min$^{-1}$ rate. PE-PEO-PCL-PLLA-2 shows peaks in the range of 2θ = 15° – 26°. The peaks at 2θ = 24.0° and 21.7° correspond to diffraction from (200) and (110) crystallographic planes of PE and PCL blocks. These two blocks are known to form crystalline domain as a majority over the amorphous domain. The WISE contour of PE-PEO-PCL-PLLA-2 and PE-PEO-PCL-PLLA-2 (green) confirm the successful synthesis of tetracrystalline PE-PEO-PCL-PLLA-2. The crystal structures of PE-PEO-PCL-PLLA-2 (green) were analyzed using XRD (Figure 6) at room temperature (rt). Samples were deposited on top of a glass substrate and heated up to 180 °C, annealed for 10 min, and cooled down to rt at a roughly 2 °C min$^{-1}$ rate. PE-PEO-PCL-PLLA-2 shows peaks in the range of 2θ = 15° – 26°. The peaks at 2θ = 24.0° and 21.7° correspond to diffraction from (200) and (110) crystallographic planes of PE and PCL blocks. These two blocks are known to form the orthorhombic crystal structure. The
peak at 2θ = 19.5° denotes the diffraction from (203) PLLA overlapped with (120) PEO crystallographic planes. Two peaks at 2θ = 15.2° and 16.9° are the diffractions from (010) and (200/110) crystallographic planes of PLLA. Due to the overlap of some of the reflections, it is not easy to distinguish the separate contribution of each crystalline block in the x-ray diffractograms shown in Figure 6. Measurements as a function of temperature could easily solve this problem, and they will be reported in our next contribution. Moreover, an in-depth study of the phase segregation, crystallization, and morphology of these remarkable tetracrystalline tetrablock quarterpolymers will be presented.

Figure 6. XRD diffractograms of PE-OH-2 (black), PE-b-PEO-2 (red), PE-b-PEO-b-PEO-b-PLLA (blue) and PE-b-PEO-b-PCL-b-PLLA (green) (entry 1–4, Table 2).

Conclusion

For the first time, tetracrystalline tetrablock quarterpolymer PE-b-PEO-b-PCL-b-PLLA was synthesized by combining polyhomologation (PE-OH macroinitiator) with a new organic/metal catalyst-switch (t-BuP/DPD/SnOct3) strategy. The use of Sn(Oct)3 instead of t-BuP2 in this strategy could overcome the side reactions occurred during the ROMP of LLA at 80 °C. The micro structure of PE-b-PEO-b-PCL-b-PLLA was fully characterized by liquid and solid-state NMR as well as GPC, DSC, WISE NMR, and XRD spectroscopies confirm the formation of four crystallites in solid-state. This new strategy opens a broader horizon on the synthesis of complex macromolecular architecture based crystalline polymers in one-pot. Moreover, the tetracrystalline tetrablock quarterpolymer will serve polymer physics in the advancement of crystallinity field.

Experimental Section

**PE-b-PEO-2** (entry 2, Table 1). In a glove box under Ar atmosphere, 400 mg PE-OH-2 (0.07 mmol), 44 μL (35 μmol) t-BuP solution and 14 mL dry toluene were charged into a round bottom flask. The flask was quickly sealed by a rotatio stopcock, removed from the glove box and evacuated through vacuum line for 10 min. Then, 0.69 mL of pre-dried EO (14 mmol) was condensed to the reaction solution at −78 °C under vacuum. The temperature was slowly increased to 80 °C, and the ROP of EO was performed for 15 h. The conversion of EO was calculated from the yield of 3 mL polymerization mixture quenched with benzoic acid and precipitated in MeOH/EtO (1:1 v/v) mixture. PE-b-PEO-2 was isolated by centrifugation and dried under vacuum for 24 h at 40 °C. The rest of the polymerization mixture was neutralized by the addition of 65 μL DPP (0.0325 mmol) at 80 °C and kept stirring. After 30 min, the reaction mixture was stored inside a glove box under Ar. 1H NMR (600 MHz, toluene-d8, 80 °C) with three drops of TFAA; δ ppm = 3.32 – 3.41 (PE, [−CH2−O−PEO]), 1.17 – 1.46 (PE, [−CH2−]), 0.83 – 1.01 (PE, [−CH3]), 3.30 – 3.56 (PEO [O−CH2−CH2−O−]), 3.99 – 4.02 (PEO, [PEO−CH2−CH2−−O−]), M_w,PEO = 15150 g mol⁻¹.

**PE-b-PEO-b-PCL-2** (entry 3, Table 1). In a glove box under Ar atmosphere, a dry polymerization flask equipped with a stirrer bar was charged with 3 mg of Sn(Oct)3 (0.0075 mmol), 0.17 mL CL (0.75 mmol), and 1 mL dry toluene. The flask was sealed and placed in an oil bath at 80 °C inside the glove box. After 15 min, 3 mL of polymerization mixture containing PE-b-PEO-b-PCL macroinitiator was withdrawn and transferred to the flask. The ROP of CL was performed for 48 h, and the conversion was monitored by 1H NMR spectroscopy. After the conversion reached 92%, 2 mL of the reaction mixture was withdrawn, quenched with benzoic acid, and precipitated in cold MeOH/EtO mixture (7:3 v/v). PE-b-PEO-b-PCL-2 was isolated by centrifugation and dried in vacuo for 24 h at 40 °C. 1H NMR (600 MHz, toluene-d8, 80 °C): δ ppm = 3.32 – 3.41 (PE, [−CH2−O−PEO]), 1.17 – 1.46 (PE, [−CH2−]), 0.83 – 1.01 (PE, [−CH3]), 3.30 – 3.56 (PEO [O−CH2−CH2−O−]), 4.09 – 4.14 (PEO, [PEO−CH2−CH2−O−]), 4.15 (PEO, [PEO−CH2−CH2−O−]), 3.91 – 4.01 (PCL, [OOC−CH2−CH2−CH2−H]), 2.09 – 2.14 (PCL, [OOC−CH2−CH2−CH2−H]), 1.49 – 1.56 (PCL, [OOC−CH2−CH2−CH2−H]), 1.40 – 1.48 (PCL, [OOC−CH2−CH2−CH2−H]), 1.19 – 1.26 (PCL, [OOC−CH2−CH2−CH2−H]), M_w,PCL = 10400 g mol⁻¹.

**PE-b-PEO-b-PCL-b-PLLA-2** (entry 4, Table 1). The flask containing 2 mL PE-b-PEO-b-PCL-2 solution was transferred into the glove box. Then, 216 mg LLA (1.50 mmol) was added to the flask. The flask was transferred outside the glove box, heated in an oil bath at 80 °C for 24 h. The conversion of LLA measured by 1H NMR was 96%. The polymerization was quenched by the addition of benzoic acid, and the polymerization mixture was precipitated in cold MeOH/EtO (8:2 v/v). The polymer was recovered by centrifugation and decantation of the solvents and dried in vacuo at rt for 24 h. 1H NMR (600 MHz, toluene-d8, 80 °C): δ ppm = 3.32 – 3.41 (PE, [−CH2−O−PEO]), 1.17 – 1.46 (PE, [−CH2−]), 0.83 – 1.01 (PE, [−CH3]), 3.30 – 3.56 (PEO [O−CH2−CH2−O−]), 4.09 – 4.14 (PEO, [PEO−CH2−CH2−O−]), 3.91 – 4.01 (PCL, [OOC−CH2−CH2−CH2−H]), 2.09 – 2.14 (PCL, [OOC−CH2−CH2−CH2−H]), 1.49 – 1.56 (PCL, [OOC−CH2−CH2−CH2−H]), 1.40 – 1.48 (PCL, [OOC−CH2−CH2−CH2−H]), 1.19 – 1.26 (PCL, [OOC−CH2−CH2−CH2−H]), M_w,PCL,PLLA = 7600 g mol⁻¹.
The solid-state $^{1}	ext{H}-^{13}	ext{C}$ WISE 2D NMR analysis was performed according to the literature. The spectrum was acquired on Bruker AVANCE III spectrometers operating at 900 MHz resonance frequencies using a 3.2 mm MAS probe. A MAS of 5 kHz was applied in all experiments. The increment time was set to 5 µs, and the contact time was 1 ms.

**Acknowledgements**

The research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST). The authors thank Professor Alejandro J. Müller (University of the Basque Country) for the fruitful discussion on the crystallization of multicrystalline multiblock copolymers.

**Keywords:** polyhomologation • ring-opening polymerization • catalyst switch • tetrapolblock quartermers • multicrystalline polymers


Tetracrystalline tetrablock quarterpolymer, poly(ethylene)-b-poly(ethylene oxide)-b-poly(ε-caprolactone)-b-poly(L-Lactide) was synthesized by combining polyhomologation, ring-opening polymerization and an organic/metal "catalyst switch" strategy. The existence of four different crystalline domains in the polymer was confirmed by differential scanning calorimetry, X-ray diffraction, and wide-line separation solid-state NMR spectroscopy.