A New Tricrystalline Triblock Terpolymer by Combining Polyhomologation and Ring-Opening Polymerization. Synthesis and Thermal Properties

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ABSTRACT: New tricrystalline triblock terpolymers, polyethylene-*block*-poly(ε-caprolactone)-*block*-poly(*L*-lactide) (PE-*b*-PCL-*b*-PLLA), were synthesized by ROP of ε-caprolactone (CL) and *L*-lactide (LLA) from linear ω-hydroxyl polyethylene (PE-OH) macroinitiators. The linear PE-OH macroinitiators were prepared by C1 polymerization of methylsulfoxonium methylide (polyhomologation). Tin(II) 2-ethylhexanoate was used as the catalyst for the sequential ROP of CL and LLA in one-pot polymerization at 85 °C in toluene (PE-OH macroinitiators are soluble in toluene at 80 °C). ^{1}H NMR spectra confirmed the formation of PE-*b*-PCL-*b*-PLLA triblock terpolymers through the appearance of the characteristic proton peaks of each block. GPC traces showed the increase in the number average molecular weight from PE-OH macroinitiator to PE-*b*-PCL, and PE-*b*-PCL-*b*-PLLA corroborating the successful synthesis. The existence of three crystalline blocks was proved by DSC and XRD spectroscopy. © 2019 The Authors. *Journal of Polymer Science Part A: Polymer Chemistry* published by Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: crystalline polymer; metal catalyst; polyhomologation; ring-opening polymerization; triblock terpolymer

INTRODUCTION Crystalline block co/terpolymers composed of two or three crystallizable blocks have attracted enormous attention in polymer science.[1] This is because of the combination of two or three crystalline blocks that have different chemical nature in one polymeric chain giving rise to some remarkable properties.[2,3] Moreover, recent advances in synthetic polymer chemistry unlock the opportunity to tune the thermomechanical, morphologies, biocompatibility, biodegradability, and optoelectronic properties of the crystalline polymeric materials.[4–8]

There are many reports on double-crystalline diblock copolymers, for example, poly(ε-caprolactone)-*block*-poly(*L*-lactide) (PCL-*b*-PLLA), poly(ethylene oxide)-*block*-poly(ε-caprolactone) (PEO-*b*-PCL), poly(small lactones)-*block*-poly(macrolactones) (PSLs-*b*-PMLs), poly(ethylene oxide)-*block*-poly(*L*-lactide) (PEO-*b*-PLLA), and poly(*p*-dioxanone)-*block*-poly(ethylene oxide) (PPDX-*b*-PCL).[9–19] Those copolymers are intensively studied for biomedical applications.[20–22] On the other hand, double-crystalline diblock copolymers composed of PE segments such as polyethylene-*block*-poly(ε-caprolactone)(PE-*b*-PCL), polyethylene-*block*-poly(*L*-lactide) (PE-*b*-PLLA), and polyethylene-*block*-poly(ethylene oxide) (PE-*b*-PEO) are commonly used as compatibilizers in PE-based polymer blends.[23–29]

In contrast to diblock copolymer, triblock terpolymers consisting of three crystalline segments are less explored, owing to the challenging synthetic procedure. Only two types of tricrystalline triblock terpolymer are reported until now. The first type is poly(ethylene oxide)-*block*-poly(ε-caprolactone)-*block*-poly(*L*-lactide) (PEO-*b*-PCL-*b*-PLLA) triblock terpolymer, which was prepared by ROP of ε-caprolactone (CL) and *L*-lactide (LLA) from PEO macroinitiator in one-pot using metal or organic catalysts.[30–32]

The second type is polyethylene-*block*-poly(ethylene oxide)-*block*-poly(ε-caprolactone) (PE-*b*-PEO-*b*-PCL), which was reported by Abetz and his coworker in 2006.[33] To the best of our knowledge, this is the only example of tricrystalline triblock terpolymer containing PE block in the chain due to the challenging polymerization steps. The PE-*b*-PEO-*b*-PCL was prepared in three consecutive steps. First, poly(butadiene)-*block*-poly(ethylene oxide) (PB-*b*-PEO) precursor was

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synthesized in one-pot by anionic polymerization of 1,3-butadiene followed by ROP of EO in the presence of strong phosphazene base *t*-BuP$_4$. Second, the PB-*b*-PEO was purified and dried by three freeze-drying cycles and used as the macroinitiator for the ROP of CL at 180 °C without any catalyst (thermally activated ROP). Third, the PB segment in PB-*b*-PEO-*b*-PCL was hydrogenated using Wilkinson catalyst to afford PE-*b*-PEO-*b*-PCL. Due to the high temperature during the ROP of CL, PEO block degraded through random chain scission that leads to the formation of undesired PEO-*b*-PCL diblock copolymer. Furthermore, the PE prepared by anionic polymerization of 1,3-butadiene and subsequent hydrogenation contains at least 4% ethyl side groups.

In this article, we report the synthesis of a new tricrystalline triblock terpolymer polyethylene-*block*-poly(*ε*-caprolactone)-*block*-poly(*L*-lactide) (PE-*b*-PCL-*b*-PLLA). Linear PE-OH with 100% functionality[34] macroinitiator obtained from polyhomologation of methylsulfoxonium methylide was used to initiate the ROP of CL and LLA using tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) as the catalyst. The molecular structure of the triblock terpolymer was characterized by ^{1}H NMR spectroscopy and GPC. Differential scanning calorimetry (DSC) and x-ray diffraction (XRD) spectroscopy reveal the existence of three crystalline blocks in the polymer.

EXPERIMENTAL

Materials

Methanol (MeOH), THF, dichloromethane (DCM), and ethyl acetate (EtOAc) were purchased from VWR Chemicals (HiPerSolv Chromanorm, United Kingdom). 1,2,4-trichlorobenzene (TCB; ≥99%, anhydrous), 1,4-dioxane (anhydrous, >99.9%), benzoic acid (99.5%), calcium hydride (CaH$_2$, 95%), trimethylsulfoxonium iodide (≥98%), benzyltributylammonium chloride (98%), triethylborane (TEB) in hexane (1 M), trimethylamine-*N*-oxide dihydrate (TAO.2H$_2$O; ≥99%), and sodium hydride (NaH) were purchased from Sigma-Aldrich (United States) and used as received. Toluene was dried by distillation over CaH$_2$ and polystyrilithium. THF was refluxed over sodium/benzophenone before used. CL (99%) from Sigma-Aldrich was distilled twice over CaH$_2$ under dynamic vacuum. LLA (Sigma-Aldrich, 99%) was recrystallized from EtOAc three times and dissolved in anhydrous 1,4-dioxane, cryo-evaporating the 1,4-dioxane, followed by drying under vacuum overnight. Sn(Oct)$_2$, (95%, Sigma-Aldrich) was distilled twice over anhydrous MgSO$_4$ and activated 4 Å molecular sieves followed by azeotropic distillation with dry toluene. All monomers, solvents, and catalysts for polymerizations were stored under argon (Ar) in a glove box (LABmaster$^{\text{pro}}$SP, MBraun, Germany).

Instrumentation

^{1}H NMR measurements were performed using a Bruker AVANCE III spectrometers operating at 400 or 600 MHz; toluene-d_8 or CDCl$_3$ were used as the solvents. ^{1}H NMR spectra were used to calculate the number average molecular weight (M_n) of each block by using the integrals of the characteristic signals from the end groups of each block and methylene protons of PE, PCL, as well as methine proton of PLLA. High-temperature GPC (HT-GPC) measurements were performed with a Viscotek High-Temperature Chromatograph (Malvern) with 2 x PLgel 10 μm MIXED-B, 300 x 7.5 mm columns. TCB was used as eluent at a flow rate of 1.0 mL min^{-1} and temperature 150 °C. The instrument was calibrated with PS standards. DSC measurements were performed with a Mettler Toledo DSC1/TC100 under nitrogen (N$_2$), calibrated with indium (purity > 99.999%). The samples were first heated from 25 °C to 200 °C at a heating rate of 5 °C min^{-1} to erase the thermal history and then cooled to −20 °C at a cooling rate of 1 °C min^{-1}. This cycle was repeated two times while melting and crystallization temperatures (T_m and T_c) were recorded. X-ray diffractograms were obtained from XRD Bruker D2 Phaser using Cu Kα radiation. The sample for XRD measurements was deposited on a glass substrate with an approximate size 1.5 cm × 1 cm, preannealed at 180 °C for 5 min, and cooled down to room temperature (rt) with a cooling rate ~2 °C min^{-1}.

Typical Polymerization Procedure for the Synthesis of PE-OH

PE-OH (entry 1, Table 1): PE-OH was prepared according to the procedure published in the literature.[34] In more details, 40.0 g

TABLE 1 Molecular Characterization and Thermal Properties of PE-*b*-PCL-*b*-PLLA and the Precursor Polymers[a]

						T_m[f] (°C)			T_c[f] (°C)		
Entry	sample	Time[b] (h)	Conv[c] (%)	$M_{n,\ NMR}$[d] (kg mol^{-1})	$Đ_M$[e]	PE	PCL	PLLA	PE	PCL	PLLA
1	PE-OH-1	3	100	3.3	1.21	117.3			101.2		
2	PE-*b*-PCL-1	20	87.3	3.5	1.32	111.7	55.8		98.6	40.1	
3	PE-*b*-PCL-*b*-PLLA-1	48	94.3	19.5	1.49	107.4	47.7	155.1	80.4	34.5	107.8
4	PE-OH-2	3	100	7.1	1.29	124.6			110.5		
5	PE-*b*-PCL-2	24	96.0	4.2	1.38	127.5	56.9		116.4	44.7	
6	PE-*b*-PCL-*b*-PLLA-2	48	95.9	23	1.42	126.5	54.1	154.2	100.6	45.6	119.1

[a] PE-OH was prepared by polyhomologation. PE-*b*-PCL-*b*-PLLA was prepared by sequential ROP of CL and LLA catalyzed by Sn(Oct)$_2$ at 85 °C in toluene.

[b] Polymerization time for the last block.

[c] Determined by 400-MHz ^{1}H NMR spectroscopy (CDCl$_3$, 55 °C).

[d] M_n of the last block determined by 600 MHz ^{1}H NMR spectroscopy (toluene-*d*8, 80 °C).

[e] Determined by HT-GPC in TCB at 150 °C (PS standards).

[f] Measured by DSC under N$_2$ atmosphere with heating and cooling rates 10 °C min^{-1} (cooling rate 1 °C min^{-1} for PLLA block).

of trimethylsulfoxonium iodide was added into a biphasic mixture of DCM (280 mL) and water (400 mL), followed by the addition of 61.5 g of tributylbenzylamino chloride. The mixture was kept in a dark place for 24 h. The aqueous phase was extracted and washed with DCM (70 mL × 3). After removal of water on a rotary evaporator, a white needle-like crystal was obtained. The crystal was dissolved in methanol at 50 °C and then cooled to room temperature slowly, followed by cooling to 0 °C inside a fridge overnight. A needle-like crystal product of trimethylsufoxonium chloride (19.5 g, yield: 84%) with high purity was obtained.

Next, 10.8 g (0.45 mol) of NaH was inserted into a two-necked flask connected with a reflux condenser and Ar/vacuum line. After three subsequent vacuum-Ar circles, 180 mL of freshly distilled THF was injected. It was followed with the addition of 32.0 g (0.38 mol) of dry trimethylsulfoxonium chloride. The mixture was heated and refluxed at 80 °C until the gas ceased (5–6 h). The THF was removed under low pressure and followed the transfer of 150 mL of dry toluene into the flask. After 0.5 h of stirring, the resulting turbid solution was filtered through a dry Celite 545 column. A clear and transparent solution with a light yellow color was obtained. The concentration of ylide was determined by titration with a standard hydrochloric acid aqueous solution (1.05 mmol/mL; yield 72%). The produced ylide solution was transferred into a two-neck 1000 mL flask and kept under stirring for 30 min. Then, 0.45 mL of TEB (0.40 mmol) was outright added into the flask to initiate the polymerization, and the solution was left for 30 min under stirring. After consumption of methylide, a 10 times excess (4.0 mmol, 0.45 g) TAO·$2H_2O$ was added for the oxidation/hydrolysis of tris-organoborane at 80 °C to obtain PE-OH quantitatively. After 16 h, the reaction was stopped by cooling in an ice bath. The mixture was poured into cold methanol (300 mL), and the white solids were filtered, dried under vacuum, and characterized by HT-GPC and ^{1}H NMR.

^{1}H NMR (toluene-d_8, 80 °C): δ/ppm = 3.36 (2H, $\mathit{CH}_2-\text{OH}$), 1.32 ($-\mathit{CH}_2\mathit{CH}_2-$), 0.88 (3H, CH_3); $M_{\text{n,NMR}}$ PE-OH = 7100 g mol^{-1}.

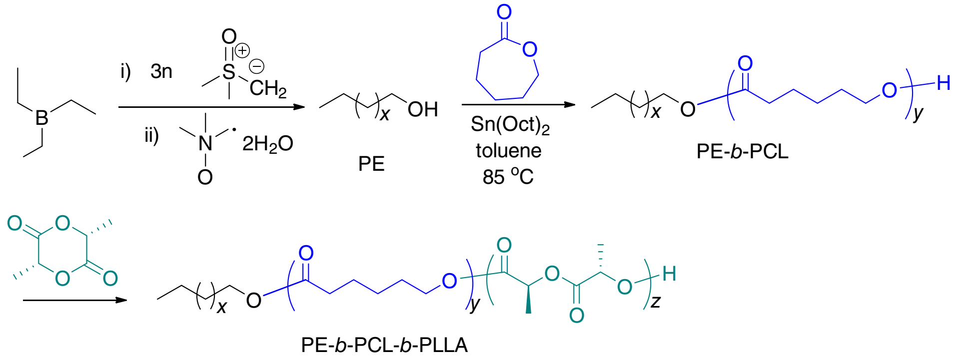
A 100-mL Schlenk flask was charged with 1 g of the isolated PE-OH and 20 mL of dry toluene. The flask was heated to dissolve PE-OH, and azeotropic distillation was performed between toluene and water three times to dry the PE-OH. The white powder was stored inside the glove box under Ar.

Typical Polymerization Procedure for the Synthesis of PE-*b*-PCL

In a glove box under Ar atmosphere, a dry polymerization flask equipped with a stirrer bar was charged with 200 mg dry PE-OH-1, 5.7 mg of Sn(Oct)_2 (0.014 mmol), 0.31 mL CL (2.8 mmol), and 7 mL dry toluene. The flask was sealed and placed in an oil bath at 85 °C outside the glove box. The ROP was monitored by ^{1}H NMR spectroscopy. After 24 h, the conversion of CL reached 96.0%, 3.5 mL of the reaction mixture was withdrawn, quenched with benzoic acid, and precipitated in cold MeOH. PE-*b*-PCL was isolated by centrifugation and dried *in vacuo* for 24 h at 40 °C. ^{1}H NMR (600 MHz, toluene-d_8, 80 °C): δ/ppm = 3.96 (PE, $[-\mathit{CH}_2\text{–O–PCL}]$), 1.32 (PE, $[-\mathit{CH}_2-]$), 3.35 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2-\text{OH}]$), 3.96 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2-]$), 2.11 (PCL, $[\text{OCO}-\mathit{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$), 1.52 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2\text{CH}_2-]$), 1.45 (PCL, $[\text{OCO}-\text{CH}_2\mathit{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$), 1.23 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\mathit{CH}_2\text{CH}_2\text{CH}_2-]$); $M_{\text{n,NMR}}$ PCL = 4200 g mol^{-1}.

Typical Polymerization Procedure for the Synthesis of PE-*b*-PCL-*b*-PLLA

The flask containing 3.5 mL (0.014 mmol OH) PE-*b*-PCL solution was transferred into the glove box. Then, 404 mg LLA (2.8 mmol) was added to the flask. The flask was transferred outside the glove box and heated in an oil bath at 85 °C for 24 h. The conversion of LLA measured by ^{1}H NMR was 95.9%. The polymerization was quenched by the addition of benzoic acid, and the polymerization mixture was precipitated in cold MeOH. The polymer was recovered by centrifugation and decantation of the solvents and dried *in vacuo* at rt for 24 h. ^{1}H NMR (600 MHz, toluene-*d*8, 80 °C): δ/ppm = 3.96 (PE, $[-\mathit{CH}_2\text{–O–PCL}]$), 1.32 (PE, $[-\mathit{CH}_2-]$), 3.35 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2-\text{OH}]$), 3.96 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2-]$), 2.11 (PCL, $[\text{OCO}-\mathit{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$), 1.52 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2\text{CH}_2-]$), 1.45 (PCL, $[\text{OCO}-\text{CH}_2\mathit{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$), 1.23 (PCL, $[\text{OCO}-\text{CH}_2\text{CH}_2\mathit{CH}_2\text{CH}_2\text{CH}_2-]$), 1.37 (PLLA, $[-\text{CH}\mathit{CH}_3]$), 5.06 (PLLA, $[\text{OCO–}\mathit{CH}\text{CH}_3\text{–}]$), 4.09 (PLLA, $[\text{OCO–}\mathit{CH}\text{CH}_3\text{–COOH}]$); $M_{\text{n,NMR}}$ PLLA = 23000 g mol^{-1}.



SCHEME 1 Synthesis of tricrystalline triblock terpolymer PE-*b*-PCL-*b*-PLLA by ROP of CL and LLA from PE-OH macroinitiator catalyzed by Sn(Oct)_2.

RESULTS AND DISCUSSION

The polyhomologation reaction and subsequential ROPs of CL and LLA from the PE macroinitiator with Sn(Oct)$_2$ as the catalyst are described in Scheme 1. Sn(Oct)$_2$ was selected as the catalyst instead of an organic catalyst such as phosphazene superbase to avoid the formation (*S,R*) *meso*-lactide monomeric unit during the ROP of LLA at 80 °C.[35] The presence of (*S,R*) *meso*-lactide in the PLA chain is unfavorable, because it can worsen the thermal properties of PLLA block and lead to an amorphous polymer.[35]

Two PE-OH macroinitiators having a different molecular weight (PE-OH-1 and PE-OH-2) were prepared by polyhomologation (entry 1 and entry 4, Table 1). The ROPs of CL and LLA from the macroinitiators are monitored by ^{1}H NMR spectroscopy. The conversion of CL is determined by the integral ratio of CH_2OCO protons (h) in the polymer at 4.08 ppm and monomer at 4.15 ppm (Supporting Information Fig. S1). The conversions of CL were 87.3% for PE-OH-1 (entry 2, Table 1) and 96.0% for PE-OH-2 (entry 5, Table 1). The conversion of LLA is determined by comparing the integral ratio of methine proton (k) in the polymer centered at 5.17 ppm with the methine proton in monomer centered at 5.01 ppm (Supporting Information Fig. S2). The conversion of LLA for each block is 94.3% and 95.9% (entry 3 and 6, Table 1), respectively. It is worth noting that the remaining CL was not polymerized during the ROP of LLA. Thus, the resulting third block is a pure PLLA chain.

^{1}H NMR spectra of the isolated PE-OH, PE-*b*-PCL, and PE-*b*-PCL-*b*-PLLA (entry 1–6, Table 1) are presented in Figure 1 (from PE-OH-1 macroinitiator) and Supporting Information Figure S3 (from PE-OH-2 macroinitiator). The —CH_2OH protons of PE (c) appear at 3.35 ppm, while the CH_2 protons of the main chain (b) were observed at 1.32 ppm. The integral ratio of these protons was used to calculate the M_n of PE-OH. After the copolymerization with CL, six new peaks appear in the spectrum. The peak centered at 3.96 ppm (h) is assigned as CH_2OC═O protons of PCL block and merged with the protons (i). The OCH_2 triplet protons appear at 2.11 ppm (d) while the four protons of —CH_2—CH$_2$O (g) and —CH_2—CH2—OC═O (e) appear at 1.52 and 1.45 ppm, respectively. The —CH$_2$—CH_2—CH$_2$ protons (f) arise at 1.23 ppm. Two new protons emerged after the ROP of LLA from PE-*b*-PCL macroinitiator; and methine proton (CH$_3$—CHO—CO) and methyl (—CH_3) protons of PLLA block (k and j) around 5.06

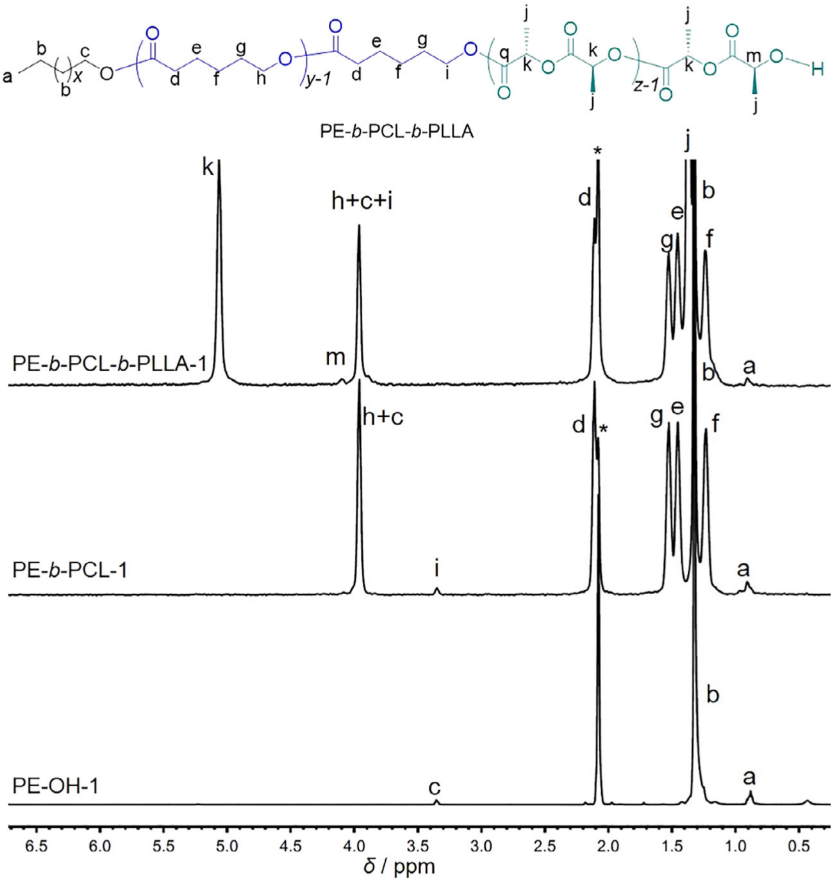


FIGURE 1 ^{1}H NMR spectra of PE-OH-1, PE-*b*-PCL-1, and PE-*b*-PCL-*b*-PLLA-1 prepared by ROP of CL and LLA from PE-OH-1 macroinitiator (entries 1–3, Table 1) with Sn(Oct)$_2$ as the catalyst (toluene-d_8, 80 °C. The mark * denotes the methyl protons signal from toluene).

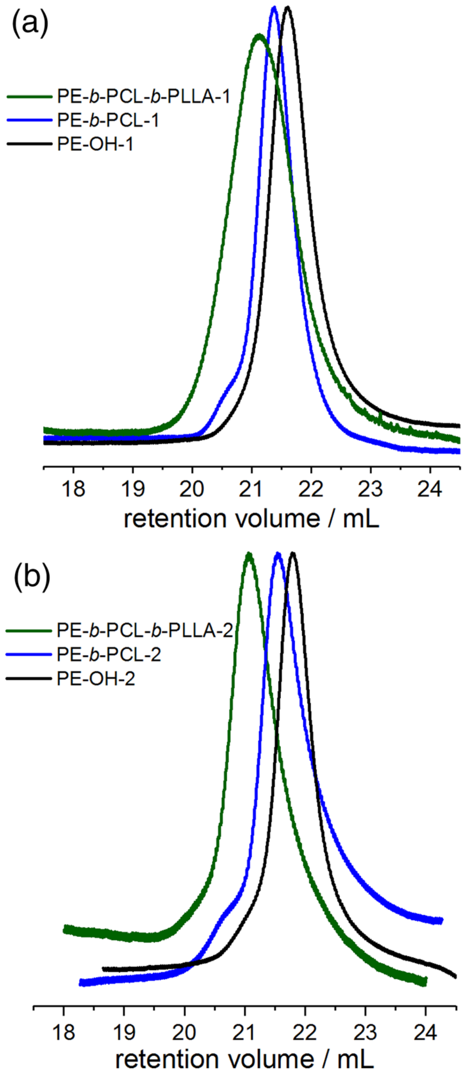


FIGURE 2 HT-GPC traces of PE-OH (black), PE-*b*-PCL (blue), and PE-*b*-PCL-*b*-PLLA (green) in TCB (150 °C, PS standards). (a) From PE-OH-1 and (b) from PE-OH-2 macroinitiators

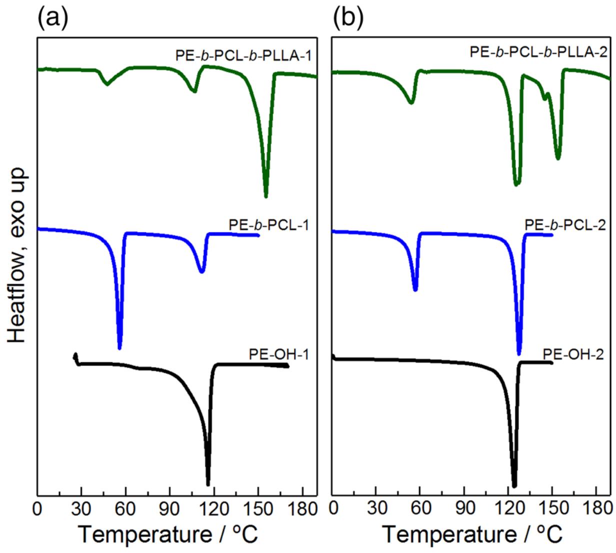


FIGURE 3 Endothermic DSC thermograms of triblock terpolymers (entries 1–6, Table 1) prepared by ROPs of CL and LLA from PE-OH macroinitiators; (a) PE-OH-1 and (b) PE-OH-2, with $Sn(Oct)_2$ as catalyst (heating rate is 10 °C min^{-1}, under N_2).

and 1.37 ppm, respectively. The end-group protons of PLLA (m) are detected at 4.09 ppm, corroborating that PLLA block is covalently linked to PCL block.

Figure 2 displays the HT-GPC traces of the terpolymers and their corresponding precursors. The GPC traces show the increase of molecular weight from PE-OH macroinitiators (black) to PE-*b*-PCLs (blue) and PE-*b*-PCL-*b*-PLLAs (green), as indicated by the shifting of the elusion traces to lower elution volume. PE-OH-1 and PE-OH-2 prepared by polyhomologation exhibit narrow molecular weight distribution ($Đ_{\mathrm{M}}$) and monomodal traces (Fig. 2, black line). PE-*b*-PCL-1 and PE-*b*-PCL-2 (blue) traces are slightly broadened (Table 1), implying that transesterification side reactions occurred during the ROP of CL at 80 °C. Further broadening is observed on PE-*b*-PCL-*b*-PLLA-1 and PE-*b*-PCL-*b*-PLLA-2 (green) traces. It should be noted that PLLA homopolymer tends to exhibit broader elution traces in TCB at 150 °C than in THF at 35 °C.[35] This explains why the apparent $Đ_{\mathrm{M}}$ of triblock terpolymers is broader than the $Đ_{\mathrm{M}}$ of PE-OH macroinitiators. Nevertheless, all GPC traces are monomodal, indicating that only the initiation from hydroxyl end-group takes place.

DSC analysis was performed in order to evaluate the thermal properties (Fig. 3) of PE-OHs (black), PE-*b*-PCLs (blue), and PE-*b*-PCL-*b*-PLLAs (green). The T_{m} of PE-OH-2 (124.6 °C) is higher than that of PE-OH-1 (117.3 °C) due to the higher molecular weight of PE-OH-2. The T_{m} of PE-OH-1 decreases to 111.7 °C in PE-*b*-PCL-1 and 107.4 °C on PE-*b*-PCL-*b*-PLLA-1, which is attributed to the presence of PCL block that melted earlier than PE block. On the contrary, the T_{m} of PE-OH-2 increases to 127.5 °C in PE-*b*-PCL-2 and 126.5 °C in PE-PCL-PLLA-2. The reason behind this phenomenon is still under investigation. The T_{m} of PCL is observed at 55.8 °C for PE-PCL-1 and 56.9 °C for PE-*b*-PCL-2, which further decrease to 47.7 °C (PE-*b*-PCL-*b*-PLLA-1) and 54.1 °C (PE-*b*-PCL-*b*-PLLA-2). The T_{m} of PLLA is observed at 155.1 °C (PE-*b*-PCL-*b*-PLLA-1) and 154.2 °C (PE-*b*-CL-*b*-PLLA-2), indicating the formation of crystalline PLLA block.

After melting and annealing of the polymers for 3 min, crystallization behavior of the triblock terpolymers and its precursors was evaluated by applying a cooling scan 10 °C min^{-1} (Fig. 4) for PE-OHs (black), PE-*b*-PCLs (blue), and 1 °C min^{-1} for PE-*b*-PCL-*b*-PLLAs (green). A slow cooling scan (1 °C min^{-1}) must be applied to facilitate the crystallization of PLLA block.[1]

The T_{c} of PE-OH-2 decreases from 110.5 °C to 100.6 °C in PE-*b*-PCL-*b*-PLLA-2. This could be due to the presence of PLLA block that crystallizes earlier than the PE block, forcing the

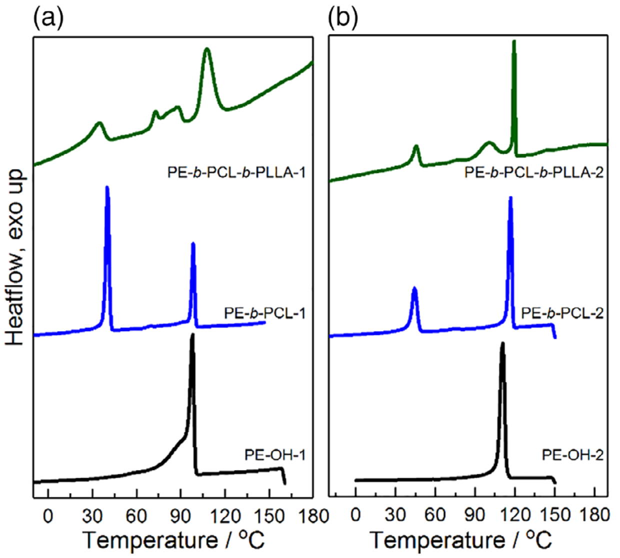


FIGURE 4 Exothermic DSC thermograms of triblock terpolymers (entries 1–6, Table 1) prepared by ROPs of CL and LLA from PE-OH macroinitiators; (a) PE-OH-1 and (b) PE-OH-2, with $Sn(Oct)_2$ as catalyst (cooling rate is 10 °C min^{-1}, under N_2).

crystallization of the PE block to occur at a lower temperature than in the corresponding homopolymer. The T_c of PCL decreases from 40.1 °C (PE-*b*-PCL-1) to 34.5 °C (PE-*b*-PCL-*b*-PLLA-1). In contrast, the T_c slightly increases from 44.7 °C (PE-*b*-PCL-2) to 45.6 °C (PE-*b*-PCL-*b*-PLLA-2). The T_cs of PLLA blocks are observed at 107.8 °C and 119.1 °C for PE-*b*-PCL-*b*-PLLA-1 and PE-*b*-PCL-*b*-PLLA-2, respectively. The exothermic trace of PE in PE-*b*-PCL-*b*-PLLA-1 shows broad hump with two peaks, probably related to the formation of two different crystalline phases after cooling.

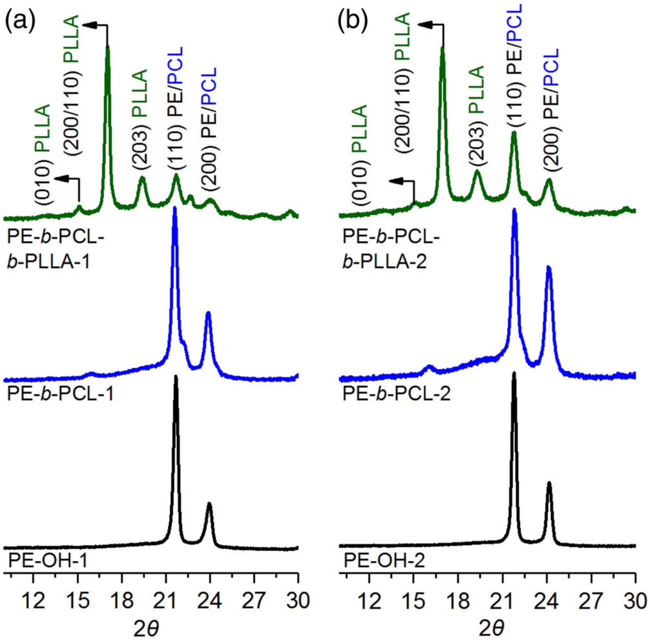


FIGURE 5 X-ray diffractograms of PE-*b*-PCL-*b*-PLLA triblock terpolymers and the corresponding precursor polymers prepared from PE-OH macroinitiators; (a) PE-OH-1 and (b) PE-OH-2 (entries 1–6, Table 1).

The crystal structures of PE-OHs (black), PE-*b*-PCLs (blue), and PE-*b*-PCL-*b*-PLLAs (green) were analyzed using XRD (Fig. 5). Samples were deposited on top of a glass substrate and heated up to 180 °C, annealed for 10 min, and cooled down to room temperature at a roughly 2 °C min^{-1}. The diffractograms show the appearance of the characteristic crystallographic planes on homo, di-, and triblock terpolymers. PE-*b*-PCL-*b*-PLLAs exhibit peaks in the range of $2\theta = 15° - 25°$. PE and PCL blocks are known to form *orthorhombic* crystal structure, thus giving an identical peak position on the diffractogram. The (200) crystallographic plane of PE and PCL is observed around $23.7° < 2\theta < 24.2°$, while the (110) crystallographic plane of PE and PCL appears around $21.5° < 2\theta < 21.9°$. Crystallographic planes of PLLA are identified with the appearance of three peaks; $19.2° < 2\theta_{(203)} < 19.4°$, $16.8° < 2\theta_{(200/110)} < 17.1°$, and $15.0° < 2\theta_{(010)} < 15.2°$, respectively. Thus, the successful synthesis of tricrystalline terpolymer is also confirmed by XRD. Slight deviations on the peak position between the two triblock terpolymers are attributed to the different molecular weights and compositions. Further details will be discussed in a separate paper.

CONCLUSIONS

Tricrystalline triblock terpolymers, PE-*b*-PCL-*b*-PLLA, were synthesized by combining polyhomologation with ROP. Polyhomologation produced perfectly linear PE-OH and used as the macroinitiator for the ROP of CL and LLA with $Sn(Oct)_2$ as the catalyst. ^1H NMR spectroscopy and GPC confirmed the molecular structure of triblock terpolymers, while DSC and XRD revealed the existence of three crystalline blocks. The synthetic approach presented in this work offers a straightforward strategy to synthesize PE-based tricrystalline triblock terpolymer with well-defined microstructure. This new PE-*b*-PCL-*b*-PLLA triblock terpolymer is essential for the advancement of polymer crystallization field.

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