Block Copolymers of Macrolactones/Small Lactones by a “Catalyst-Switch” Organocatalytic Strategy. Thermal Properties and Phase Behavior

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Supporting Information

ABSTRACT: Poly(macrolactones) (PMLs) can be considered as biodegradable alternatives of polyethylene; however, controlling the ring-opening polymerization (ROP) of macrolactone (ML) monomers remains a challenge due to their low ring strain. To overcome this problem, phosphazene (*t*-BuP₄), a strong superbases, has to be used as catalyst. Unfortunately, the one-pot sequential block copolymerization of MLs with small lactones (SLs) is impossible since the high basicity of *t*-BuP₄ promotes both intra- and intermolecular transesterification reactions, thus leading to random copolymers. By using ROP and the “catalyst-switch” strategy [benzyl alcohol, *t*-BuP₄/neutralization with diphenyl phosphate/(*t*-BuP₂)], we were able to synthesize different well-defined PML-*b*-PSL block copolymers (MLs: dodecalactone, ω -pentadecalactone, and ω -hexadecalactone; SLs: δ -valerolactone and ϵ -caprolactone). The thermal properties and the phase behavior of these block copolymers were studied by differential scanning calorimetry and X-ray diffraction spectroscopy. This study shows that the thermal properties and phase behavior of PMLs-*b*-PSLs are largely influenced by the PMLs block if PMLs components constitute the majority of the block copolymers.

INTRODUCTION

Aliphatic polyesters are important materials with a wide range of properties and applications.^{1–5} In particular, aliphatic polyesters derived from lactones have tunable mechanical and thermal properties, crystallinity, and are biocompatible/biodegradable materials.^{6,7} Lactones can be prepared from cheap and renewable bio-based materials such as fatty acids.^{8,9} In addition, the current development of synthetic methodologies allows the synthesis of new copolymers of lactones with lactides, cyclic carbonates, and epoxides to afford novel biocompatible/biodegradable polymeric materials with diverse properties.¹⁰

The ring-opening polymerization (ROP) of lactones is a versatile method to synthesize (co)polymers with controlled molecular parameters.¹¹ ROP of small lactones (SLs ≤ 8 membered rings) such as δ -valerolactone (VL) and ϵ -caprolactone (CL) has been well studied, and ways have been developed leading to control polymerization.^{10,12,13} In contrast, for medium lactones and macrolactones (MLs) (ring size >8), it is more difficult to find the appropriate conditions for controlled ROP due to their low ring strain. Only a limited number of enzymes^{14–16} and catalysts, metal based^{14–17} or organocatalysts,^{18–21} are capable of promoting ROP of MLs to high conversion. In addition, attempts to prepare block copolymers of poly(macrolactones) and poly(small lactones) (PMLs-*b*-PSLs) with these catalysts have been unsuccessful.

The ROP of ω -pentadecalactone (PDL) with enzyme *Candida antarctica* lipase-B (CAL-B) resulted in high conversion but broad molecular weight distributions ($\bar{M}_w$).²² The copolymerization of PDL with CL, by sequential monomer addition, catalyzed by the same enzyme, produced random structure instead of block due to rapid interchain transesterification.²³ The aluminum–salen complex, known to be very active for the ROP of MLs, also produced random instead of block copolymers by sequential addition of MLs and SLs.²⁴ Dove et al. reported the copolymerization of PDL with CL, VL, and η -caprylolactone using Mg(BHT)₂(THF)₂ as catalyst, but no block copolymerization was described.²⁵ Recently, a combination of *N*-heterocyclic olefin/metal halide Lewis pair as dual catalysts system showed a rapid ROP of PDL.²⁶ This system also was used to sequentially copolymerize PDL with CL, VL, and γ -butyrolactone, which again led to the formation of random copolymers. A bicyclic guanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), was reported as the first organic catalyst capable of promoting ROP of PDL.¹⁸ Attempts to prepare block copolymer by sequential addition of PDL and CL with the benzyl alcohol (BnOH)/TBD initiating system were unsuccessful.

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To the best of our knowledge, only zinc- and calcium-based complexes bearing ancillary ligands, reported by Duchateau et al., are capable of promoting the homopolymerization of PDL to high conversion and the subsequent copolymerization with CL to form semicrystalline PPDL-*b*-PCL (only one sample was reported, and the actual length of each block was not clarified).¹⁴ The structure of PPDL-*b*-PCL was confirmed by ¹H and ¹³C NMR spectroscopies, and thermal properties were analyzed by differential scanning calorimetry (DSC). Moreover, block copolymers of PDL with ϵ -decalactone (ϵ DL) were also prepared to study the effect of the amorphous ϵ PDL block (branch lactone) on the crystallization of the PPDL block.²⁷ Nevertheless, block copolymers comprising both ML and SL blocks and prepared by an organic catalyst in one pot are still absent in the literature.

We recently reported a fast and living organocatalytic ROP of PDL and ω -hexadecalactone (HDL) to high conversion catalyzed by a phosphazene superbase (PSB) 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (*t*-BuP₄, $pK_{a,ACN} = 42.7$).²¹ The ROP proceeds to high conversion under a wide range of conditions. Our group had also reported the controlled and living ROP of SLs promoted by a weaker PSB 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (*t*-BuP₂, $pK_{a,ACN} = 33.5$) with different initiators.¹² A one-pot sequential block copolymerization of epoxides and CL was successfully performed by a catalyst-switch strategy from *t*-BuP₄ to an organic acid (diphenyl phosphate [DPP], $pK_{a,DMSO} = 3.88$) or *t*-BuP₂.^{28–32} An alcohol initiator, activated by *t*-BuP₄ (suitable for polymerizing epoxides but not SLs), was used to promote the ROP of epoxides, followed by neutralization of the superbase with DPP. Subsequently, a weaker PSB, *t*-BuP₂ (suitable for polymerizing SLs but not epoxides), was added to promote ROP of SLs leading to well-defined polyepoxide–polyester block copolymers. These findings motivated us to employ similar catalyst-switch methodology to prepare PMLs-*b*-PSLs.

Herein, we report the ROP of MLs (dodecanolactone [DDL], PDL, and HDL) to high conversion with *t*-BuP₄ as catalyst, the neutralization of *t*-BuP₄ with DPP, and the subsequent addition of *t*-BuP₂ as second catalyst for the growth of the PSLs (VL and CL) block from the PMLs macroinitiator in one-pot. The formation of PMLs-*b*-PSLs was evidenced by ¹³C NMR, ¹H NMR, and high-temperature gel permeation chromatography (HT-GPC). Their thermal properties and phase behavior were analyzed using DSC, and the crystal structure was determined by X-ray diffraction (XRD) spectroscopy.

EXPERIMENTAL SECTION

Materials. Toluene (AnalaR NORMAPUR ACS, VWR International Chemicals) was dried first over calcium hydride (CaH₂, 95%, Sigma-Aldrich), then over polystyryllithium and distilled before use. DDL (98%), PDL (>98%), HDL (>98%), CL (99%), and VL (99%) from Sigma-Aldrich were distilled twice over CaH₂ under dynamic vacuum. *t*-BuP₄ (0.8 M solution in hexane), *t*-BuP₂ (2 M solution in THF), and benzoic acid (99.5%) were purchased from Sigma-Aldrich and used as received. DPP (99%, Sigma-Aldrich) was purified by dissolving it in benzene (anhydrous, 99.8%, Sigma-Aldrich), followed by cryo-evaporation of benzene and drying under vacuum overnight. BnOH (99.8%, Sigma-Aldrich) was distilled twice over CaH₂ under vacuum. BnOH, lactone monomers, DPP, and PSBs were stored under argon (Ar) in a glovebox (LABmaster^{pro}SP, MBraun, Germany). Methanol (HiPerSolv CHROMANORM, VWR International Chem-

icals) and 1,2,4-trichlorobenzene (TCB; $\geq 99\%$, anhydrous, Sigma-Aldrich) were used as received.

Instrumentation. NMR measurements were performed at room temperature (rt) using a Bruker AVANCEIII spectrometer operating at 500 or 950 MHz in CDCl₃. ¹H NMR spectra were used to calculate the number-average molecular weight ($M_{n,NMR}$) of the polyesters by using the integrals of the characteristic signals from the end group and ω -methylene protons of PMLs-PSLs. HT-GPC measurements were performed with a PL-GPC 220 high temperature chromatograph (Agilent Technologies) with one PLgel 5 μ m MIXED-C column. The column has a linear molecular weight operating range from 200 to 2 000 000 g mol⁻¹ and high resolution. TCB was used as eluent at a flow rate of 1.0 mL min⁻¹ at 150 °C. The instrument was calibrated with polystyrene (PS) standards. DSC measurements were performed with a Mettler Toledo DSC1/TC100 under air. The samples were first heated from rt to 120 °C in order to erase the thermal history, then cooled to -20 °C, and finally heated again to 120 °C at a heating/cooling rate of 10 °C min⁻¹. This cycle was repeated until constant melting and cooling temperatures (T_m and T_c) were recorded. XRD spectra were obtained from XRD Bruker D8 Advance using Cu K α radiation. The sample for XRD measurements was deposited on a glass plate with an approximate size 1.5 cm $\times$ 1 cm, preannealed at 120 °C for 10 min, and cooled down to rt with a cooling rate 10 °C min⁻¹.

Synthetic Procedure. Synthesis of PPDL-*r*-PCL by a One-Shot Monomer Addition (Table 1, Entry 2). In a glovebox under Ar atmosphere, 2.3 μ L of BnOH (23 μ mol), 28 μ L (23 μ mol) of *t*-BuP₄ solution, and 3 mL of dry toluene were charged into a round-bottom flask. The flask was quickly sealed by a Rotaflo stopcock, removed from the glovebox, and stirred for 10 min in a preheated oil bath at 80 °C. Then, a mixture of 0.54 g of PDL (2.3 mmol) and 0.25 mL of CL (2.3 mmol) in 2 mL of dry toluene was added to the initiator solution. The copolymerization of PDL and CL was performed for 3 h, and monomer conversion was monitored by ¹H NMR analysis. After PDL and CL reached high conversion, the reaction was quenched by adding benzoic acid/CHCl₃ (10 vol %) and cooled to rt. One drop of crude product was withdrawn and dissolved in CDCl₃ to check the monomer conversion by ¹H NMR. The rest of the reaction mixture was precipitated in 500 mL of methanol, filtered by glass filter, and dried *in vacuo* at 45 °C for 12 h. ¹H NMR (950 MHz, CDCl₃, 298 K) δ /ppm = 7.30–7.37 (aromatic protons on the end group) δ 5.11 (s, 2H; C=OCH₂Ar), 4.05 (m, CH₂OC=O, 4H; for PPDL and PCL), 2.29 (t, J = 7.6 Hz, -CH₂C=OO (PCL)), 2.27 (t, J = 7.5 Hz, -CH₂C=OO (PPDL)), 1.64 (m, CH₂CH₂OC=O PCL), 1.60 (m, CH₂CH₂OC=O PPDL), 1.22–1.40 ppm (all remaining hydrogens). $M_{n,NMR} = 22.2$ kg mol⁻¹ (PPDL); $M_{n,NMR} = 11.9$ kg mol⁻¹ (PCL).

Typical Polymerization Procedure for the Synthesis of PMLs-*b*-PSLs (Table 2, Entry 1). In a glovebox under Ar atmosphere, 4.6 μ L of BnOH (45 μ mol), 56 μ L (45 μ mol) of *t*-BuP₄ solution, and 2.5 mL of dry toluene were charged into a round-bottom flask. The flask was quickly sealed by a Rotaflo stopcock, removed from the glovebox, and stirred for 10 min in a preheated oil bath at 80 °C. Then, 1.1 g of PDL (4.5 mmol) in 2 mL of dry toluene was added to the initiator solution. The homopolymerization of PDL was performed for 2 h, and conversion was monitored by ¹H NMR analysis. The reaction mixture was neutralized by the addition of 113 μ L of DPP (45 μ mol) at 80 °C and kept stirring for 30 min. 118 μ L (225 μ mol) of *t*-BuP₂ solution was added. After 30 min, 0.49 mL (4.5 mmol) of CL was added to the polymerization mixture. After CL reached high conversion, the reaction was quenched by adding benzoic acid/CHCl₃ (10 vol %) and cooled to rt. For all polymerization reactions, one drop of crude product was withdrawn and dissolved in CDCl₃ to check the monomer conversion by ¹H NMR. The rest of the reaction mixture was precipitated in 500 mL of methanol, filtered by a glass filter, and dried *in vacuo* at 45 °C for 12 h. ¹H NMR (950 MHz, CDCl₃, 298 K) δ /ppm = 7.34 (aromatic protons on the end group) δ 5.10 (s, 2H; C=OCH₂Ar), 4.05 (m, CH₂OC=O, 4H; for PPDL and PCL), 2.30 (t, J = 7.6 Hz, -CH₂C=OO (PCL)), 2.28 (t, J = 7.6 Hz, -CH₂C=OO (PPDL)), 1.64 (m, CH₂CH₂OC=O PCL), 1.60 (m, CH₂CH₂OC=O PPDL), 1.22–1.40 ppm (all remaining hydrogens). $M_{n,NMR} = 35.5$ kg mol⁻¹ (PPDL); $M_{n,NMR} = 15.9$ kg mol⁻¹ (PCL).

Figure 1. ^{13}C NMR spectra of copolymerization products of PDL and CL: sequential monomer addition (left), one-shot monomer addition (middle), and catalyst-switch strategy (right) (CDCl_3 , rt).

Table 1. RO Copolymerization of PDL and CL Catalyzed by PSBs with Different Method in Toluene at $80\text{ }^\circ\text{C}$ ^a

entry	method	$[\text{PDL}]_0/[\text{CL}]_0/[\text{I}]_0/[\text{P}_4]/[\text{P}_2]$	time (h)	conv ^c (%)		dyads sequence distribution ^d (%)			
				PDL	CL	CL*-CL	CL*-PDL	PDL*-PDL	PDL*-CL
1	sequential	100/100/1/1/-	2	96	100	26.2	24.0	24.4	25.4
2	one-shot ^b	100/100/1/1/-	3	98	100	27.8	24.1	22.8	25.3
3	catalyst-switch	100/100/1/1/5	50	99	92	49.1	0	50.9	0

^aPolymerizations were performed under Ar, $[\text{M}]_0 = 1\text{ M}$. ^bTotal initial monomer concentration = 2 M . ^cConversions of PDL and CL were determined by $950\text{ MHz } ^1\text{H}$ NMR spectra of crude product from the integral of ω -methylene protons of PDL, CL, and copolymers in CDCl_3 .

^dDetermined by $950\text{ MHz } ^{13}\text{C}$ NMR spectra of the isolated polymer from the carbonyl carbon resonance.

Scheme 1. General Scheme for the Synthesis of PML-*b*-PSL by Catalyst-Switch Strategy

RESULTS AND DISCUSSION

The common method to prepare block copolymers by anionic ROP is via one-pot sequential monomer addition using a common catalyst.³³ We employed this method to prepare PPDL-*b*-PCL with $\text{BnOH}:\text{t-BuP}_4:\text{PDL}:\text{CL}$ molar ratio of 1:1:100:100 (entry 1, Table 1). BnOH was mixed with t-BuP_4 in toluene followed by the addition of PDL (dissolved in toluene) at $80\text{ }^\circ\text{C}$. The conversion of PDL reached 96% in 2 h. Subsequently, CL was added to the polymerization mixture, and the reaction was continued for 2 h. Quantitative ^{13}C NMR spectroscopy was used to monitor the progress of the reaction as well as the microstructure of the polymer formed (Figure 1, left). The ^{13}C NMR spectra shown in Figure 1 (left) were taken from the reaction mixture after addition of CL to PPDL macroinitiator with t-BuP_4 as catalyst. The ^{13}C NMR spectrum revealed that at the early stage (6 min) of the ROP of CL, the PDL*-PDL (asterisk represents the observed carbonyl

carbon) linkage at 174.1 ppm formed during the homopolymerization of PDL as the main peak and a small peak due to CL*-CL linkages (173.2 ppm). Two new peaks coming from PDL*-CL (174.0 ppm) and CL*-PDL (173.4 ppm) linkages were also observed representing the formation of a random structure. After 23 min, the incorporation of CL to the copolymer increased significantly indicating the fast ROP of CL with t-BuP_4 , but the intensity of PDL*-CL and CL*-PDL linkages also increased. After 120 min, the microstructure of the resulting polymer became fully random as shown by dyads sequence distribution of the isolated product (entry 1, Table 1). The final microstructure of the isolated polymer is similar to the copolymer prepared by one-shot addition of PDL and CL which exhibits a random distribution (Figure 1, middle, and entry 2, Table 1).

The overall observation suggests that both chain propagation and transesterification side reactions occurred during the

Figure 2. ^1H NMR spectra of PDL-CL copolymers prepared by sequential monomer addition, one-shot monomer addition, and catalyst-switch strategy (950 MHz, CDCl_3 , rt).

Table 2. Block Copolymers of MLs and SLs Prepared by Catalyst-Switch Strategy^a

entry	sample	$[\text{M}]_0/[\text{I}]_0/[\text{P}_4]/[\text{P}_2]$	time (h)	conv ^b (%)		$M_{n,\text{NMR}}^c$ (kg mol^{-1})		$\bar{D}_M^d$
				ML	SL	ML	SL	
1	PPDL- <i>b</i> -PCL	200/1/1/5	96	99	92	35.5	15.9	1.77
2	PPDL- <i>b</i> -PVL	200/1/1/5	74	99	95	27.1	8.8	1.85
3	PHDL- <i>b</i> -PCL	200/1/1/5	96	99	93	31.5	10.6	1.86
4	PHDL- <i>b</i> -PVL	200/1/1/5	74	99	96	65.9	17.4	1.92
5	PDDL- <i>b</i> -PCL	200/1/1/5	96	99	95	29.2	16.8	1.62
6	PDDL- <i>b</i> -PVL	200/1/1/5	74	99	98	39.3	19.2	1.70
7	PPDL ₅₀ - <i>b</i> -PCL ₄₀₀ ^c	230/1/1/5	96	99	85	14.7	52.3	2.20
8	PCL	100/1/0/5	48		83		10.9	1.16
9	PVL	100/1/0/5	12		96		7.9	1.19
10	PPDL	100/1/1/0	2	99		35.0		1.77
11	PHDL	100/1/1/0	2	99		42.6		1.59
12	PDDL	100/1/1/0	2	99		24.3		1.73

^aPolymerizations were performed in toluene under Ar at 80 °C. The initial molar ratio of $[\text{ML}]_0/[\text{SL}]_0$ was 100:100. ^bConversion was determined by 500 MHz ^1H NMR spectra of crude product from the integral of ω -methylene protons of MLs, SLs, and (co)polymers in CDCl_3 . ^cDetermined by 950 MHz ^1H NMR spectra of methylene protons from BnOH and ω -methylene protons of PMLs-*b*-PSLs in CDCl_3 . ^dDetermined by HT-GPC in TCB at 150 °C (polystyrene standards). ^eThe initial molar ratio of $[\text{PDL}]_0/[\text{CL}]_0$ was 50:400.

propagation in the presence of *t*-BuP₄ as a single catalyst. Thus, synthesis of PMLs-*b*-SLs by one-pot sequential monomer addition with *t*-BuP₄ as single catalyst was not successful. The same case was also observed when $\text{Mg}(\text{BHT})_2(\text{THF})_2$,²⁵ Al-salen complex,¹⁴ enzyme CAL-B,²³ and TBD¹⁸ were used as catalysts.

In order to tackle the aforementioned challenge, we carried out sequential block copolymerization of MLs and SLs by employing catalyst-switch strategy after the ROP of MLs promoted by *t*-BuP₄. As mentioned in the Introduction, this strategy can be applied either by adding an excess of an acid (e.g., DPP) to neutralize the *t*-BuP₄ and to act as catalyst for the second, sensitive to *t*-BuP₄, SL monomer^{29–31} (e.g., CL) or by adding a stoichiometric to the superbase, acid amount, followed by addition of a more suitable catalyst (*t*-BuP₂) to promote the ROP of SLs (Scheme 1).³² We have chosen the second

methodology for the following two reasons: (a) the ROP of SLs in the presence of DPP at 80 °C, where the PML macroinitiators are soluble, was not controllable (Scheme S1 and Figure S1, Supporting Information) and (b) unlike *t*-BuP₂, DPP is not a good catalyst for the ROP of L-lactide (LLA), which is limiting the generality of our strategy.³⁰ Therefore, the catalyst-switch methodology from *t*-BuP₄ to DPP was not employed in this work.

Then, ROP of PDL was performed with BnOH:*t*-BuP₄:PDL molar ratio of 1:1:100 in toluene at 80 °C (entry 3, Table 1), followed by addition of an equivalent to *t*-BuP₄ amount of DPP and stirring. After 30 min, *t*-BuP₂ (5 mol equiv to BnOH) was added, and the solution was left under stirring was continued for 30 min to activate the PPDL chain end, followed by addition of CL. The reaction was continued for 4 days, and the progress of the reaction was monitored by ^{13}C NMR

spectroscopy (Figure 1, right). In contrast to the previous experiment with sequential addition of monomer, the ROP of CL at 80 °C proceeded without any randomization of the polymer sequencing. ^{13}C NMR spectra showed only a new linkage coming from CL^*-CL , while the linkage of PDL^*-PDL remained intact. The existence of CL^*-CL and PDL^*-PDL dyads of carbonyl carbons is a strong evidence for the formation of $\text{PPDL-}b\text{-PCL}$.¹⁴ The carbonyl carbons peaks of this $\text{PPDL-}b\text{-PCL}$ (entry 1, Table 3) are comparable to the blend of PPDL:PCL homopolymers peaks (Figure S2).

^1H NMR spectroscopy was also used to characterize the copolymers of Table 1. A full ^1H NMR spectrum of PPDL-CL copolymer as well as the characteristic peaks α and ω methylene protons of copolymers prepared by sequential (entry 1), one-shot monomer addition (entry 2), and catalyst-switch strategy (entry 3) are presented in Figure 2. As expected, no difference could be seen in shape and position among the α and ω methylene protons peaks of random and block copolymers of PPDL-PCL (entries 1–3). Multiplet peaks appear between 4.02 and 4.04 ppm coming from the overlapping of α -methylene protons of PDL and CL ($a + i$). ω -Methylene protons of PDL (b) and CL (f) appear as triplet-triplet in the chemical shift around 2.23–2.28 ppm. The rest of the CH_2 protons of PPDL and PCL appear in the range of 1.22–1.64 ppm (c, d, e, g , and h). It is worth noting that ω -methylene protons of PMLs and PCL recorded by the 500 MHz ^1H NMR spectrometer are observed as overlapped peaks, while ω -methylene protons of PMLs and PVL are well separated.²⁵ Therefore, we used the 950 MHz NMR spectrometer which has higher resolution to resolve the peaks position and allowing quantitative calculation of the block copolymer composition.

Seven block copolymers from the combination of MLs (PDL, HDL, and DDL) and SLs (VL and CL) were prepared by the catalyst-switch strategy. All PMLs- b -PSLs (runs 1–7, Table 2) as well as the corresponding PMLs and PSLs homopolymers (runs 8–12, Table 2) were prepared in toluene at 80 °C. The conversion of monomers in each block copolymerization reaches high conversion, indicating the capability of $t\text{-BuP}_4$ and $t\text{-BuP}_2$ employed in this system to promote ROP of MLs and SLs, respectively. The conversion of MLs to PMLs was determined by ^1H NMR from the integral of α -methylene protons of PMLs and those of MLs (a and a' , Figure S3). The conversion of PSLs to PMLs- b -PSLs was determined from the integral of ω -methylene protons of PSLs and those of SLs (f and f' , Figure S4).

^1H and ^{13}C NMR spectra of the isolated block copolymers (entries 1–7, Table 2) are presented in Figure S5–S18. Since the ω -methylene protons of PMLs and PSLs in the resulting block copolymers could be observed at different chemical shift by the 950 MHz NMR spectrometer, accurate determination of block length and M_n of PML- b -PSL was possible. The length of each block was determined from the integral ratio of methylene protons of initiator (BnOH) at 5.10 ppm to that of the ω -methylene protons of PMLs (~ 2.27 ppm) and PSLs (~ 2.24 ppm). ROP of MLs in the presence of $t\text{-BuP}_4$ reached high conversion in 2 h. In contrast, the ROP of SLs from PMLs macroinitiator (≥ 96 h) was slower than the homopolymerization of SLs from BnOH initiator (~ 48 h) under the same reaction conditions likely because of a retardation effect due to the organic salt (phosphazanium diphenylphosphate) generated by the neutralization of $t\text{-BuP}_4$ with DPP.^{30,34}

HT-GPC was used to monitor the molecular weight and the $\bar{M}_w$ of PPDL and $\text{PPDL-}b\text{-PCL}$ (entry 1, Table 2). The ROP of PDL catalyzed by $t\text{-BuP}_4$ gives homopolymer with monomodal distribution (blue line, Figure 3). After switching the catalyst to

Figure 3. HT-GPC traces of PPDL (blue) macroinitiator and $\text{PPDL-}b\text{-PCL}$ (red) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

$t\text{-BuP}_2$, CL monomer was added and polymerized for 4 days. The HT-GPC trace of the isolated product clearly shows the increase in molecular weight with the appearance of a monomodal peak at higher molecular weight region (red line, Figure 3), indicating that the formation of block copolymer initiated from PPDL. The monomodal and symmetrical GPC traces of $\text{PPDL-}b\text{-PCL}$ imply that minimum transesterification occurred during the chain propagation of CL from PPDL macroinitiator in the presence of $t\text{-BuP}_2$. HT-GPC traces of the rest of block copolymers (entries 2–7, Table 2), showing the increase of molecular weight from PMLs to PMLs- b -PSLs, are given in Figures S19–S24.

The relatively broad $\bar{M}_w$ of PMLs- b -PSLs (entries 1–7, Table 2) is attributed to the broad $\bar{M}_w$ of the first PML block, caused by transesterification reactions during the ROP of the ML monomer.²¹ On the contrary, intermolecular transesterification reaction is negligible for the ROP of SLs (entries 8 and 9, Table 2) with $t\text{-BuP}_2$ leading to the formation of PSLs with narrow $\bar{M}_w$.

With the literature showing a complex phase behavior for block copolymers,^{35–39} it was essential to ascertain the thermal properties to understand the phase behavior of PMLs- b -PSLs block copolymers. The T_g , T_m , and melting enthalpy (ΔH_m) of each component were determined using DSC. As seen in Figure 4 and Table 3, all block copolymers show a distinct crystallization ($62\text{ °C} < T_{c,\text{PML}} < 75\text{ °C}$) and corresponding melting peak ($85\text{ °C} < T_{m,\text{PML}} < 95\text{ °C}$) for the PML component and a smaller crystallization ($38\text{ °C} < T_{c,\text{PSL}} < 47\text{ °C}$) and corresponding melting peak ($53\text{ °C} < T_{m,\text{PSL}} < 59\text{ °C}$) for PSL, which indicates the sequential crystallization of the PML component followed by the PSL component. Despite PML constituting a majority of the block copolymer, a noticeable decrease in $T_{c,\text{PML}}$ relative to PML-homopolymer ($\Delta T_{c,\text{PML}} > 3.8\text{ °C}$) was observed. This behavior is consistent with crystallization of PML from mixed/partially mixed melt phase, expected from the chemical similarity between PMLs and PSLs. Despite a reduction in $T_{c,\text{PML}}$, little to no deviations in $T_{m,\text{PML}}$ ($\Delta T_{c,\text{PML}} < 3\text{ °C}$) was observed, indicating the

Figure 4. DSC traces of PPDL (left), PHDL (middle), and PDDL (right) based block copolymers with SLs (catalyst-switch) and the corresponding homopolymers (under air, 10 °C min⁻¹).

Table 3. Physical Properties of PMLs-*b*-PSLs Prepared by Catalyst-Switch Strategy

entry	sample	<i>F</i> ^a		<i>T</i> _c ^b (°C)		<i>T</i> _m ^b (°C)		$\Delta H_{m,PML}$ ^b (J g ⁻¹)	$\Delta H_{m,PSL}$ ^b (J g ⁻¹)	<i>X</i> _c ^c (%)
		PML	PSL	PML	PSL	PML	PSL			
1	PPDL- <i>b</i> -PCL	0.69	0.31	74.2	46.9	93.3	57.9	-77.9	-9.74	55.0
2	PPDL- <i>b</i> -PVL	0.75	0.25	74.8	43.1	91.8	58.8	-96.5	-5.98	51.8
3	PHDL- <i>b</i> -PCL	0.75	0.25	74.0	38.4	93.2	53.6	-91.3	-5.20	54.7
4	PHDL- <i>b</i> -PVL	0.79	0.21	70.2	40.7	91.0	54.3	-101.3	-3.11	54.2
5	PDDL- <i>b</i> -PCL	0.63	0.37	64.3	44.7	83.1	55.0	-77.1	-8.82	48.8
6	PDDL- <i>b</i> -PVL	0.67	0.33	62.4	42.3	82.3	55.6	-82.2	-9.46	45.8
7	PPDL ₅₀ - <i>b</i> -PCL ₄₀₀	0.22	0.78	73.2	44.2	89.8	57.8	-22.9	-43.0	55.6
8	PCL		1		39.5		54.8		-77.7	62.7
9	PVL		1		39.5			57.4	-72.5	61.1
10	PPDL	1		79.0		92.9		-129.0		63.1
11	PHDL	1		77.8		91.9		-120.5		57.5
12	PDDL	1		68.6		85.3		-125.5		60.0

^aMass fraction of each block based on the molecular weight determined by 950 MHz ¹H NMR spectra from integral ratio of methylene protons BnOH and ω -methylene protons of PMLs and PSLs (CDCl₃, rt). ^bMeasured by DSC under air with heating rate 10 °C min⁻¹. ^cDetermined by XRD with formula $X_c = \text{area}_{\text{crystalline}}/\text{area}_{\text{total}}$ in XRD spectra.

presence of amorphous PSL phase only affected the kinetics of crystallization and not the size of the crystal stacks of the PML component. At temperature below $T_{c,PML}$, the crystallization of PSL is observed. Contrary to the deviations observed in $T_{c,PML}$, the crystallization of PSL shows either the same (observed for PHDL-*b*-PCL and PHDL-*b*-PVL, <1.2 °C) or an increase (observed for PPDL-*b*-PCL, PPDL-*b*-PVL, PDDL-*b*-PCL, and PDDL-*b*-PVL, >2.8 °C) in $T_{c,PSL}$ relative to the PSL homopolymer. It is evident that the PML crystals act as nucleating agents for the PSL component despite imposing spatial confinement on the PSL crystallization. $T_{m,PSL}$ shows subtle deviations from the PSL homopolymers (<3.1 °C), similar to $T_{m,PML}$, indicating the PSL crystal stack size was relatively unperturbed from the presence PML crystals.

Although DSC traces (Figure 4) show expected peaks for both PML and PSL, the ΔH_m (Table 3), normalized by the corresponding mass fraction (*F*), shows a substantial decrease in $\Delta H_{m,PSL}$ (around 60%) with a relatively unchanged $\Delta H_{m,PML}$ (reduction of roughly 10%) compared to the corresponding homopolymers. For example, in PPDL-*b*-PCL, $F_{PPDL} = 0.69$ and $F_{PCL} = 0.31$ with $\Delta H_{m,PPDL} = -77.9$ J g⁻¹ and $\Delta H_{m,PCL} = -9.74$ J g⁻¹. After normalization, the heats become $\Delta H_{m,PPDL} =$

-112.9 J g⁻¹ PPDL and $\Delta H_{m,PPDL} = -31.4$ J g⁻¹ PCL showing a 12% and 60% reduction for PML and PSL component, respectively. This surprising reduction in $\Delta H_{m,PSL}$ was observed in all block copolymer samples, which puts into question the successful synthesis of block copolymers. Double-semicrystalline random copolymers have a characteristic single-crystallization behavior, and blends with short PSL components may lead to kinetic trapping of PSL chain during the crystallization of PML, which may also exhibit a near-single-crystalline behavior.⁴⁰ Thus, additional experiments were done to eliminate the possibilities that could lead to this puzzling near-single-phase transition result to validate the successful synthesis of block copolymers. The random copolymers PPDL-*r*-PCL (Table 1, entries 1 and 2) were analyzed by DSC. The DSC traces (Figure 5) are juxtaposed with PPDL-*b*-PCL block copolymers (Table 1, entry 3). Indeed, the random copolymers show a single peak, but at temperatures much lower than that was observed for the block copolymer. Next, blends with matching composition to the *F* of each block copolymers in Table 2 were prepared (Table S1). The DSC traces of blends showed drastic differences compared to block copolymers in the number, size, shape, and position of peaks (Table S1 and

Figure 5. DSC traces of copolymers in Table 1: PPDL-*r*-PCL (one-shot, *t*-BuP₄), PPDL-*r*-PCL (sequential, *t*-BuP₄), and PPDL-*b*-PCL (catalyst-switch) (under air, 10 °C min⁻¹).

Figures S25–S31). The differences show the near single-crystalline behavior cannot be explained by random copolymerization nor the formation of blends.

Finally, we verify the possibility of the small $\Delta H_{m,PSL}$ resulting from block copolymers through prior work in the literature and additional synthesis with different *F*. Literature^{40,41} shows that for double-semicrystalline block copolymers the crystallization and melting of the lower melting component could be completely suppressed by the block copolymer arrangement at low *F*, similar molecular properties as PMLs-*b*-PSLs samples. The small $\Delta H_{m,PSL}$ result is consistent with block copolymers with a minor low melting temperature component. To further verify our claims, a block copolymer was synthesized with a major PSL and minor PML component, PPDL₅₀-*b*-PCL₄₀₀ (entry 7, Table 2). As can be seen in Figure 4 (left), two distinct crystallization and melting

peaks are observed: $\Delta H_{m,PPDL} = 22.9 \text{ J g}^{-1}$ and $\Delta H_{m,PCL} = 43.0 \text{ J g}^{-1}$ (Table 3). After normalization by the *F* value of each block, $\Delta \hat{H}_{m,PPDL} = 104.1 \text{ J g}^{-1}$ (PPDL) and $\Delta \hat{H}_{m,PCL} = 55 \text{ J g}^{-1}$ (PCL), verifying the presence of both PPDL and PCL blocks in the polymer. Thus, the DSC results (*T_c*, *T_m*, and ΔH_m) also corroborate the formation of PMLs-*b*-PSLs.

The crystal structure was analyzed using XRD. The samples were heated to 120 °C (above *T_m* of both components) and cooled to ambient condition at roughly 10 °C min⁻¹. All samples showed peaks at around $2\theta = 21.5^\circ$ and 24° (Figure 6 and Table S2), characteristic of diffraction from (110) and (200) crystallographic planes, respectively. These crystallographic planes represent orthorhombic crystal structure, consistent with prior work in PSLs and PMLs in the literature.^{14,25} Thus, the successful synthesis of PMLs and PSLs is supported by XRD results.

Slight differences in peak positions are observed due to the differences in distances in the ester group along the backbone (Figure 6 and Table S2). Most block copolymer samples resemble the diffraction pattern of the PML homopolymer, suggesting the phase behavior of the block copolymer is controlled primarily by the PML component. This behavior is expected due to the PML component (1) crystallizing first (higher *T_m* than PSL) and (2) constituting the majority of the block copolymer. PPDL-*b*-PVL and PDDL-*b*-PCL block copolymers did not show this behavior, but understanding the origin of the deviation is beyond the scope of this work and will not be discussed.

The degree of crystallinity, *X_c*, was taken to be the ratio of the area of the crystalline peaks to the amorphous halo. As can be seen in Table 3, lower *X_c* values are observed for the block copolymers ($0.46 < X_c < 0.56$) than all homopolymers ($0.58 < X_c < 0.63$), indicating that the total crystalline composition of the block copolymers is less than the homopolymers. This result is in agreement with DSC results (Figure 4 and Table 3) which showed $\Delta H_{m,PML}$ and $\Delta H_{m,PSL}$ of block copolymers having values smaller than the corresponding PML and PSL homopolymers.

CONCLUSION

Conventional block copolymerization by sequential addition of MLs and SLs with *t*-BuP₄ as catalyst produces random microstructure due to rapid transesterification side reactions.

Figure 6. XRD diffractograms of PPDL (left), PHDL (middle), and PDDL (right) based block copolymers (catalyst-switch) with PSLs and the corresponding homopolymers.

In contrast, a catalyst-switch strategy that employs two different PSBs, *t*-BuP₄ for MLs and *t*-BuP₂ for SLs, led to the successful synthesis of PMLs-*b*-PSLs. ¹³C and ¹H NMR spectroscopies as well as HT-GPC confirm the formation of block copolymers. DSC and XRD studies show that the thermal properties and phase behavior of PMLs-*b*-PSLs are largely influenced by PMLs block if PMLs components constitute the majority of the block copolymers. Since *t*-BuP₂ is also a powerful catalyst for the ROP of cyclic monomers such as lactides and cyclic carbonates, this method opens many possibilities for the synthesis of new multiblock polymers, e.g., PML-*b*-PSL-*b*-polycarbonate-*b*-poly-lactide.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00153.

Scheme S1, Figures S1–S31 (NMR, GPC, and DSC results), and Tables S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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