

Baroplastic Effect of Aliphatic Polyester Block Copolymers for Degradation-Free Multicycle Processing of Poly(L-lactide)

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ABSTRACT: Advancing sustainable plastics is crucial to achieving a circular plastic economy. Baroplastics, block copolymers exhibiting order–disorder transitions under pressure, allow polymer processing at ambient temperatures, reducing energy use and avoiding thermal degradation. Their application, however, has been limited by structural constraints. This study introduces poly(ϵ -caprolactone-random-5-ethyleneketal ϵ -caprolactone)-block-poly(L-lactide) (PmCL-*b*-PLLA) as a “baroplasticizer” for nonbaroplastic PLLA. Blending with the block polymers lowered PLLA’s flow temperature by up to 100 °C (160 to 60 °C at 50 MPa) while preserving molecular weight after repeated pressure cycles, ensuring recyclability. The improved formability would arise from a pressure-induced ordered (solid)-to-disordered (melt/solid) phase transition. This work eliminates structural constraints in baroplastics, enabling broader low-temperature processing applications and advancing sustainable polymer technologies.



EXPERIMENTAL SECTION

Processing of Block Copolymers and Their Blends. PmCL-*b*-PLLAs were subjected to pressure-processing at 50 MPa on a Shimadzu CFT-500 capillary rheometer (Kyoto, Japan). Approximately 1.0 g of polymer specimen was placed into the rheometer’s sample chamber and subjected to 50 MPa pressure using a piston (ID: 1.0 cm) from above, extruding the material through the lower die upon heating. The rheological parameters, including shear rate ($\dot{\gamma}$) and viscosity (η), were calculated using the following equations (eqs 1 and 2), where D , P , L , and Q represent the die orifice diameter (1.0 mm), test pressure (Pa), die length (1.0 mm), and flow rate (= piston area $\times$ piston travel distance $\times 10^{-1} \Delta t^{-1}$ (cm³·s⁻¹)), respectively.

$$\dot{\gamma} = 32Q \cdot \pi^{-1} \cdot D^{-3} \times 10^3 \text{ (s}^{-1}\text{)} \quad (1)$$

$$\eta = \pi D^4 P \cdot 128^{-1} \cdot L^{-1} \cdot Q^{-1} \times 10^{-3} \text{ (Pa} \cdot \text{s)} \quad (2)$$

Measurements. SAXS analysis was conducted on a NANOPIX3.5 instrument with a Cu K α X-ray source ($\lambda = 1.54 \text{ \AA}$) equipped with a HyPix-6000 detector (Rigaku, Tokyo, Japan). The camera length and exposure time were set to 1400 mm and 4 min, respectively. A custom-made pressure cell (Syn Corp. Kyoto, Japan) was used for the under pressure measurements, and nitrogen gas was used as the pressure media. The two-dimensional SAXS pattern was processed using 2DP software and converted to one-dimensional data via a SAXS 1D viewer. Each sample was scanned under ambient conditions. The average structural length (Λ_{ave}) was calculated by using eq 3.

$$\Lambda_{\text{ave}} = 2\pi/q_{\text{max}} \quad (3)$$

DSC measurements were performed using a Shimadzu DSC-60 equipped with a thermal analyzer (TA-60 WS) and a TA Instruments 2920 modulated DSC (MDSC). The second heating profiles, following quenching, were recorded at a heating rate of 5 °C min⁻¹. The X_c was calculated using eq 4.

$$X_c = (\Delta H_c + \Delta H_m)/\Delta H_{m,100} \times 100 \text{ (\%)} \quad (4)$$

where ΔH_m and ΔH_c represent the enthalpy of fusion and crystallization of PLLA crystal, respectively. $\Delta H_{m,100}$ denotes the enthalpy of fusion for fully crystalline PLLA, with a value of 135 J·g⁻¹.²⁷

The development of sustainable plastics is fundamental to establishing a sustainable circular plastic economy.¹ A diverse array of initiatives are currently underway, including polymer synthesis from biobased monomers derived from renewable feedstocks,² depolymerization reactions,³ molecular switches to trigger degradation on demand,⁴ efficient chemical and materials recycling of end-of-life polymers,⁵ and the development of degradable polymers to mitigate adverse environmental impacts.⁶ Polymers that undergo an order–disorder transition (ODT) and flow upon compression, known as baroplastics, are unique among sustainable plastics in that they address sustainability challenges from a polymer processing perspective.⁷

In conventional polymer processing, thermoplastics are shaped by melt molding, which entails energy-intensive resin heating and mold cooling processes.^{8–10} In stark contrast, baroplastics can be processed at ambient temperatures through the application of pressure.^{7,11} Because high-pressure generation for baroplastic processing demands minimal energy,^{11,12} low-temperature processing reduces energy consumption and CO₂ emissions associated with polymer processing. Another crucial aspect of low-temperature processing is the avoidance of thermal degradation of polymers during the process. A previous study demonstrated that the mechanical properties of baroplastics were preserved even after ten processing cycles.⁷ The preservation of

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mechanical properties significantly prolongs the polymer's lifespan in material recycling.^{13,14}

Baroplastic behavior is generally observed in block copolymers comprising a soft and hard segment. The soft segment, possessing a low glass transition temperature (T_g), exists in a rubbery state at ambient temperatures, whereas the hard segment, with a high T_g , remains in a glassy state at ambient temperature. The compressibility mismatch between the two segments plays a pivotal role in the emergence of the pressure-responsive ODT.^{15–17} Baroplastic block copolymers reported to date include poly(2-ethylhexyl acrylate)-*b*-polystyrene, poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS),⁷ poly(*n*-pentyl acrylate)-*b*-polystyrene,¹⁸ poly(ϵ -caprolactone-*r*-5-ethylene ketal ϵ -caprolactone)-*b*-poly(L-lactide) (PmCL-*b*-PLLA),¹⁹ poly(2-isopropoxy-2-oxo-1,3,2-dioxaphospholane)-*b*-PLLA,²⁰ and poly(trimethylene carbonate)-*b*-PLLA.²¹ To further harness the potential and benefits of low-temperature processing, it is desirable to eliminate the molecular structural constraints of baroplastics. One possible solution is to impart low-temperature formability or *baroplasticity* to nonbaroplastic polymers by using baroplastics as an additive. This additive, used as a plasticizer, was termed a “*baroplasticizer*” due to its baroplastic nature.

Polyesters, such as PLLA, derive significant advantages from low-temperature processing since they are particularly susceptible to thermal degradation.^{22,23} This paper demonstrates that the baroplastic PmCL-*b*-PLLA serves as a “*baroplasticizer*” for nonbaroplastic PLLA. Through the incorporation of PmCL-*b*-PLLA, we achieved a reduction in the flow temperature of PLLA at 50 MPa from 160 to 60 °C, while enhancing the recyclability of PLLA. The low-temperature formability is explained by the pressure-induced flow resulting from a phase transition from the ordered (solid) state to the disordered (melt/solid) state under pressure. This study represents the first endeavor to eliminate the molecular structural constraints of baroplastics. Our findings represent a potential breakthrough in applying low-temperature processing to a broad spectrum of polymers.

Baroplastic block copolymers, PmCL-*b*-PLLA, were synthesized via a two-step ring-opening polymerization (ROP) of the corresponding lactones followed by L-lactide, utilizing tin(II) 2-ethylhexanoate (SnOct₂) as a catalyst (Figure 1). The soft segment comprised ϵ -

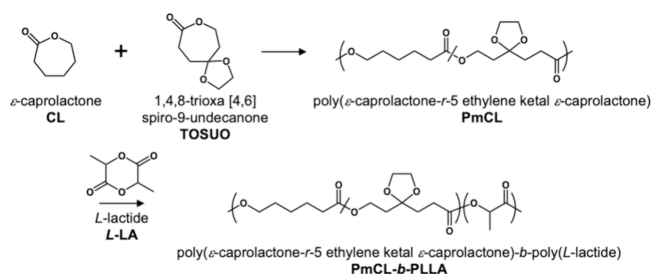


Figure 1. Synthetic scheme of PmCL-*b*-PLLAs by two-step ring-opening polymerization.

caprolactone (CL) and the derivative 1,4,8-trioxaspiro[4.6]undecanone (TOSUO), in a 50/50 molar ratio. Copolymerization with TOSUO inhibits the crystallization of the resulting PCL derivatives and yields soft segments with a T_g of -44 to -36 °C that flow at room temperature.¹⁹ Subsequent polymerization of L-lactide was conducted without optical inversion,¹⁹ and the formation of the block copolymers was confirmed by ¹H and ¹³C NMR in Figures S1 and S2.

The ROP process can precisely control the soft/hard segment ratio. Three PmCL-*b*-PLLAs were developed containing hard segment PLLA fractions of 38, 49, and 57 wt % (Table S1), designated PmCL-*b*-PLLA40, PmCL-*b*-PLLA50, and PmCL-*b*-PLLA60, respectively. All the block copolymers possessed a similar molecular weight of approximately 50000 and a polydispersity index ($\bar{D}$) of 1.2 (Table S1).

The rheological properties of PmCL-*b*-PLLAs of these compositions are anticipated to undergo significant alternations due to pressure-induced ODTs.¹⁹ The changes in rheological properties were investigated by heating the block copolymers under a constant pressure using a capillary rheometer. Herein, the flow temperature is defined as the temperature at which the shear rate increases abruptly or the viscosity decreases sharply. It was found that PmCL-*b*-PLLA40, PmCL-*b*-PLLA50, and PmCL-*b*-PLLA60 flowed at 2, 10, and 35 °C, respectively, under a constant pressure of 50 MPa (Figure S3). Under a pressure-induced ODT, the soft segment PmCL and the hard segment PLLA became miscible, leading to pseudodissolution of PLLA into PmCL in the melt state, thereby facilitating flow. As the weight or volume fraction of PmCL increased, the block copolymer exhibited enhanced flow at temperatures significantly lower than the T_m of the PLLA crystal (175 °C determined by differential scanning calorimetry (DSC)), down to or below ambient temperature.

The polymer blends of PLLA and the block copolymers were prepared by dissolving them in chloroform at the weight ratio of 1:9, 2:8, 3:7, 4:6, and 5:5. The polymer blends were then recovered through reprecipitation in methanol, followed by drying under reduced pressure for a minimum of 12 h. To investigate the changes in the flow properties of PLLA (M_n : 74.6; $\bar{D}$: 1.23) induced by the addition of PmCL-*b*-PLLAs, the PLLA/PmCL-*b*-PLLA blends were subjected to molding cycles. Hereafter, the polymer blend is denoted as PmCL-*b*-PLLAX(Y), where X signifies the weight fraction of the PLLA block in the block copolymer and Y denotes the weight fraction of the block copolymer in the polymer blend.

The polymer blends were subjected to a capillary rheometer to find changes in the rheological properties upon heating (5 °C min⁻¹) under a pressure of 50 MPa. With PmCL-*b*-PLLA40(40), the polymer blend flowed at 76 °C during the first molding. However, the flow temperature decreased to 69 °C when the molded sample was subjected to the second molding. After four processing cycles, no significant changes in flow temperature were observed (Figure S4), demonstrating that the polymer blend had been homogenized. Thereafter, the following are the results of the investigations used to determine the flow temperatures of the blends subjected to four subsequent extrusion molding tests.

The changes in shear rate and viscosity of the polymer blends consisting of PLLA and PmCL-*b*-PLLA40, PmCL-*b*-PLLA50, and PmCL-*b*-PLLA60 at different mixing ratios are illustrated in Figure 2. The flow temperatures of the polymer blends with different block copolymer compositions are listed in Figure 3. At 50 MPa, the flow temperature of the matrix PLLA itself exceeded 160 °C but decreased with the addition of PmCL-*b*-PLLAs.

The flow temperature of PLLA decreased monotonically with increasing PmCL-*b*-PLLA content in the polymer blends. Notably, with the addition of PmCL-*b*-PLLA40(50), the flow temperature was significantly reduced from a maximum of 160 °C to approximately 60 °C, a decrease of about 100 °C. The change in flow temperature was significantly dependent on the composition of the added block copolymers and the total amount of PLLA in the polymer blend. Specifically, for PLLA/PmCL-*b*-PLLA40 blends, as the amount of block copolymer added increased in weight fractions of 10, 20, 30, 40, and 50 wt % in the blend, which corresponds to a decrease in the total weight fraction of PLLA to 94, 88, 82, 76, and 70 wt %, the flow temperature of the mixture decreased to 136, 131, 82, 74, and 62 °C, respectively. When the block copolymers with different soft/hard segment ratios were blended with PLLA at the same weight ratio, the flow temperature of the blend decreased as the hard segment fraction in the block copolymer decreased. For PmCL-*b*-PLLA40(50) and PmCL-*b*-PLLA50(50), the polymer blends flowed at 62 and 65 °C, respectively. In contrast, PmCL-*b*-PLLA60(50) exhibited a fluidity above 117 °C under the same pressurized conditions.

These results demonstrate that the addition of block copolymers facilitated the extrusion molding of PLLA at much lower temperatures under pressurized conditions. Moreover, the consistent flow profiles observed even after repeated molding cycles indicate that the block copolymers functioned as pressure-responsive plasticizers or *baroplasticizers*.

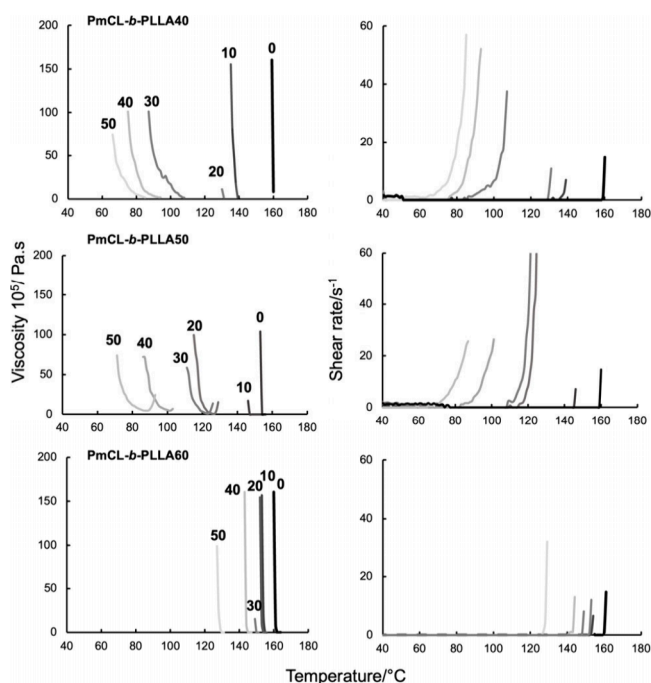


Figure 2. a) Viscosity and b) shear rate profiles of polymer blends of PmCL-*b*-PLLAs and PLLA at different mixing ratios upon heating under 50 MPa, where 0, 10, 20, 30, 40, and 50 represent the weight fraction of PmCL-*b*-PLLA in the polymer blends. The heating temperature was 5 °C min⁻¹.

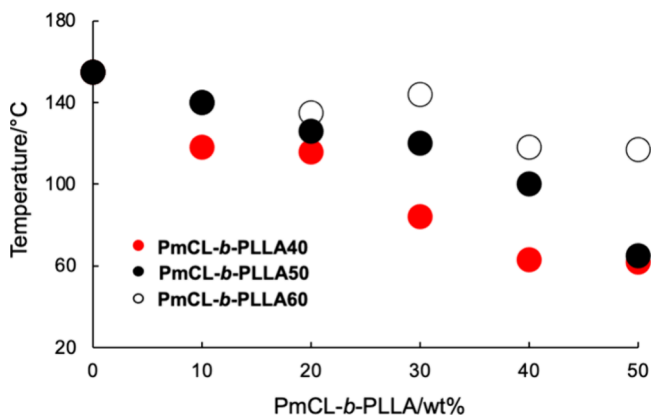


Figure 3. Changes in flow temperature of polymer blends of PmCL-*b*-PLLAs and PLLA at various mixing ratios processed at 50 MPa upon heating with a heating rate of 5 °C min⁻¹.

According to previous studies, block copolymers with higher soft-segment content generally exhibit lower flow temperatures and require lower pressures for molding due to the enhanced chain flexibility provided by the soft segment. This trend is consistent with earlier findings, which have also emphasized the critical role of the soft/hard segment ratio and segmental compatibility in determining the baroplastic behavior of copolymer systems.^{11,19,24}

The low-temperature formability under pressure was then examined from the perspective of thermal properties using differential scanning calorimetry (DSC) (Table S2). PmCL-*b*-PLLAs exhibited two phase transition points around -44 to -36 °C and 57 to 62 °C, corresponding to the T_g s of PmCL and PLLA, respectively, which suggested the formation of PmCL-rich and PLLA-rich domains upon phase separation at ambient conditions.

For PmCL-*b*-PLLAs, the T_m and the crystallinity ($X_{c, PLLA}$) of the PLLA segment increased from 144 to 163 °C and from 11.0 to 23.0%, respectively, as the PLLA composition in the block copolymer

increased from 40 to 60 wt %. The PmCL-*b*-PLLA/PLLA blends exhibited T_m s around 173 °C irrespective of the mixing ratios of PmCL-*b*-PLLA, whereas the T_m of the PLLA matrix was 175 °C. The DSC results suggest that the hard segments of the block copolymer were incorporated into the PLLA matrix to form a PLLA-rich domain, without suppressing the crystallization of PLLA. The decreased T_g of the hard segments will be attributed to the localization of the block copolymers in the amorphous regions of the PLLA matrix. Under pressure, the soft segment PmCL perturbed not only the hard segments of the block copolymers but also the PLLA homopolymer chains of the matrix. Consequently, the enhanced chain flexibility enables low-temperature processing.

DSC measurements also demonstrate that the pressure-induced phase transition is reversible. The T_m and X_c of PLLA remained essentially unchanged after a PmCL-*b*-PLLA/PLLA blend was subjected to multiple cycles of pressure processing. In addition, no changes in molecular weight and $\bar{D}$ (M_w/M_n) were observed for the polymer blend in size exclusion chromatography (SEC) analyses. In contrast, the molecular weight of the PLLA matrix itself changed after four pressure-processing cycles at the flow temperature (>160 °C), with the molecular weight decreasing from 74,600 to 41,500 as shown in Figure 4.

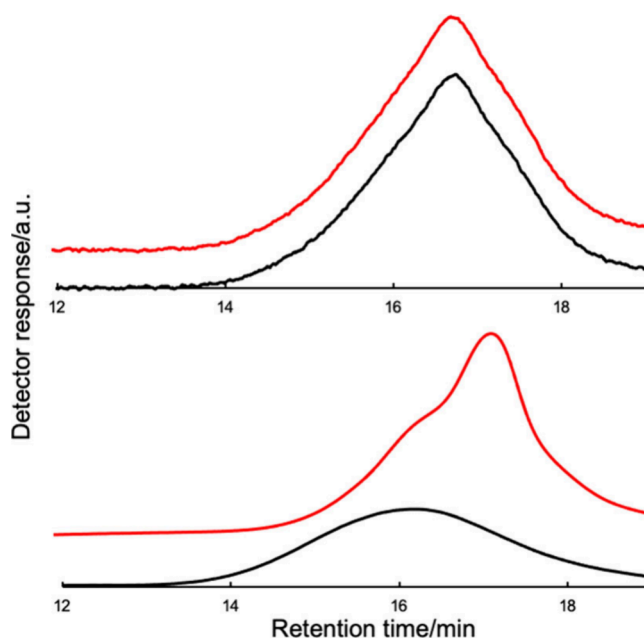


Figure 4. SEC profiles of the polymeric blend of (top) PmCL-*b*-PLLA60 and PLLA (PmCL-*b*-PLLA60(40)) and (bottom) PLLA matrix before (black line) and after (red line) four pressure-processing cycles.

One approach to understanding the mechanism and tracing the pressure-induced phase transitions is to study the nanoscale structural changes in the polymer blends by small-angle X-ray scattering (SAXS). At ambient temperature and pressure, while PmCL-*b*-PLLA50 alone exhibits a peak derived from a periodic structure, Λ_{ave} (eq 3), with a spacing of 20.9 nm upon microphase separation, no peaks associated with the formation of periodic structures were found in the PmCL-*b*-PLLA50(50) polymer blend as shown in Figure 5a. However, the formation of the PmCL-rich and PLLA-rich phases upon microphase separation was confirmed at ambient pressure as the two glass transition temperatures corresponding to these polymer blocks were found by DSC (Figure S5).

Kim et al. reported that in a polymer blend of PS and PBA-*b*-PS macrophase separation was observed when the molecular weight of PS was higher than that of PBA-*b*-PS. However, no periodic structure was observed in their system.²⁵ They also described that when a copolymer blend was thermally annealed the peaks in SAXS became

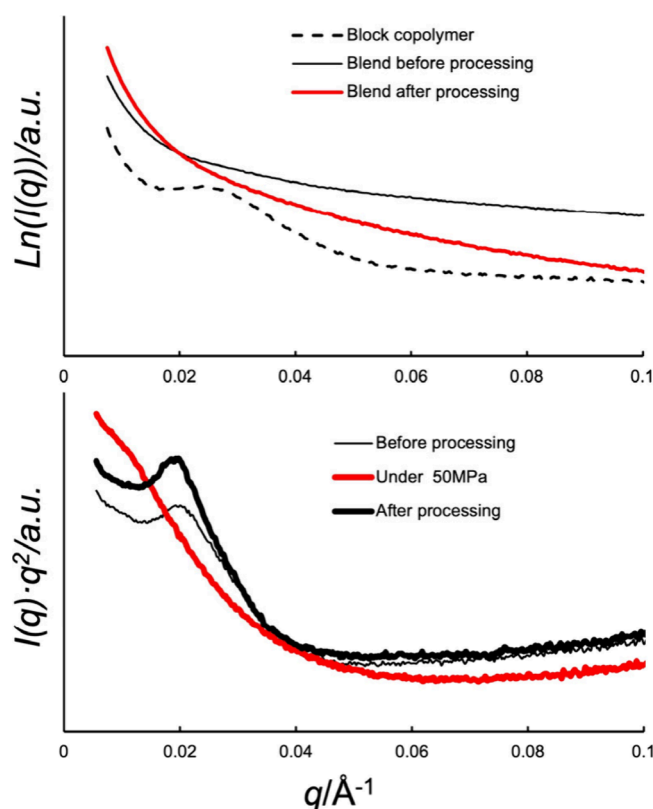


Figure 5. (top) SAXS profiles of PmCL-*b*-PLLA50 and a polymer blend of PmCL-*b*-PLLA50 and PLLA (PmCL-*b*-PLLA50(50)) before and after four cycles of pressure processing; (bottom) SAXS profile of the same blend at 100 °C at ambient pressure, at 50 MPa, and then after releasing the pressure and measured at 100 °C.

more pronounced. The initial SAXS measurements in this study were performed at ambient temperature (Figure S6). Thus, to gain a better understanding of phase separation in polymer blends, it is very important to consider the molecular weights of the homopolymer and the corresponding block copolymer. Matsen et al. showed that the addition of a high molecular weight of homopolymer forming one of the blocks to a block copolymer inhibited the formation of a periodic structure due to microphase separation, resulting in the formation of a macrophase-separated structure.²⁶ When a high molecular weight homopolymer is added, the domain of that component swells significantly, and the other component shrinks to a smaller domain. In the current study, the matrix PLLA had a higher molecular weight than the block copolymers, so it formed the macrophase-separated structure described above, which would not have a periodic structure. This might be the reason why the peaks could not be seen in the SAXS measurements at ambient conditions, and further investigation was required to fully understand the pressure-induced flow of the polymer blends.

With PmCL-*b*-PLLA50(50), a clear peak was observed upon annealing at 100 °C in the SAXS profile (Figure 5b), indicating microphase separation with a periodic structure. Upon heating, the flexibility of the polymer chain increased, leading to homogenization of phase-separated structures with various domain sizes. The peak intensity decreased under applied pressure and recovered upon its release, providing substantial evidence of a reversible pressure-induced phase separation. This indicates that the phenomenon arises from the domain arrangement. In the polymer blend, the Λ_{ave} was found to be 31.4 nm, which was larger than that of the block copolymer itself (20.9 nm).

PmCL-rich domains would exist in a randomly dispersed state throughout the polymer blend, as hypothesized in Figure 6. In addition, the consistent rheological and thermal properties after

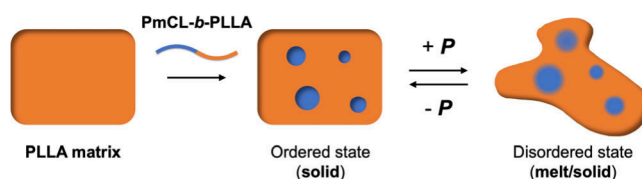


Figure 6. Schematic illustration of the mechanism of pressure-induced flow resulting from adding PmCL-*b*-PLLAs to the PLLA matrix.

multiple repeated pressure-processing cycles explain the homogenization of the microphases at the macroscopic level. On the other hand, the SAXS spectra before and after the pressure processing were almost identical, which served as conclusive evidence of a reversible pressure-induced phase transition.

In summary, we found that the addition of PmCL-*b*-PLLA to a PLLA matrix resulted in polymer blends with significantly reduced flow temperatures under pressurized conditions. In particular, the 1:1 PmCL-*b*-PLLA/PLLA blend exhibited flow at 60 °C under 50 MPa, whereas PLLA alone flowed at 160 °C. This study is the first to demonstrate that baroplastics can function as pressure-responsive plasticizers, or *baroplasticizers*, imparting low-temperature processability to nonbaroplastic polymers. To fully comprehend the pressure-induced flow, further quantitative investigations of nanostructural changes under pressure should be conducted. However, this finding has significant implications for polymer processing as it effectively mitigates polymer degradation during processing. This not only prolongs the polymer's lifespan in material recycling but also contributes to reducing energy consumption and the carbon footprint associated with polymer processing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.5c00483>.

Chemical information, experimental methods, and table and figures mentioned below: Table S1. Results of ROP of PmCL-*b*-PLLAs. Table S2. Thermal properties of PmCL-*b*-PLLAs and their blends. Figure S1. ¹H of PLLA and PmCL-*b*-PLLAs. Figure S2. ¹³C NMR of PmCL-*b*-PLLAs. Figure S3. Rheological properties of PmCL-*b*-PLLAs. Figure S4. Four cycles of PmCL-*b*-PLLAs and their blends. Figure S5. DSC thermogram of a polymer blend. Figure S6. SAXS profiles of all polymer blends (PDF)

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Author Contributions

I.T. designed the study, the main conceptual ideas, and the proof outline. N.S. collected the data and wrote the manuscript. T.K. and SD aided in interpreting the results and worked on the manuscript. All authors discussed the results, commented on the manuscript, and gave approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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