Toughening Poly(L-lactide) Blends: Effectiveness of Sequence-Controlled Six-Arm Star-Branched Block Copolymers of Poly(L-lactide) and Poly(ε-caprolactone)

Megha D. Deokar, Baijayantimala Garnaik, and Swaminathan Sivaram*

ABSTRACT: Well-defined six-arm star-branched bio-degradable block copolymers of L-lactide and ε-caprolactone were prepared using controlled ring-opening polymerization and a sequential monomer addition method using dipentaerythritol as the initiator core and organocatalysts at low temperatures in solution. Sequence of enchainment was changed by reversing the order of monomer addition giving, either, a crystalline PLA block or an amorphous PCL block as the outer segment. Well-defined six-arm poly(ε-caprolactone-b-L-lactide), 6s-PCL-b-PLA block copolymers were obtained with a range of segment molecular weights. However, in the case of six-arm poly(L-lactide-b-ε-caprolactone), 6s-PLA-b-PCL), disruption of the block structure was observed on account of competing transesterification reactions accompanying a chain-growth reaction. Such sequence-controlled block copolymers showed interesting phase morphologies, as evidenced by differential scanning calorimetry (DSC) studies. 6s-PCL-b-PLA showed two glass-transition temperatures and two melting temperatures characteristic of the amorphous and crystalline blocks. 6s-PCL-b-PLA and 6s-PLA-b-PCL with different segment chain lengths were solution blended (10 wt %) with a commercially sourced PLA. All the blends were highly transparent. The structure and properties of the blend were examined by DSC, measurement of mechanical properties, and scanning electron microscopy. The results show that a phase-separated 6s-PCL-b-PLA copolymer results in two- to three-fold improvement in tensile toughness without the loss of modulus. A possible hypothesis for the mechanism of tensile toughness in the blend has been proposed.

1. INTRODUCTION

Poly(L-lactide) (PLA) is a well-known, bio-resourced, and bio-degradable (compostable) polymer derived from corn starch and sugar. As of now, PLA is the most promising bio-degradable polymer with many consumer applications. However, as a thermoplastic, PLA suffers from several property deficits. These are, inter alia (a) slow crystallization rates ($t_{1/2}$: ~30 min at 90–120 °C), resulting in poor mechanical properties for injection molded parts, (b) low glass-transition temperature ($T_g$) and poor heat distortion temperature (55 °C) which limits the use of PLA in applications above 45 to 50 °C, (c) low degrees of chain entanglement resulting in poor melt strength causing problems during processing of PLA in the form of extruded sheets, films, and foams, (d) poor ductility and impact strength, and (e) poor moisture and oxygen barrier properties. These deficiencies have restricted the volume growth of PLA in many applications.

Intense efforts have been devoted to improving the balance of physical properties of PLA with a view to make this polymer useful for a broader range of applications. To accomplish this goal, many strategies have been suggested with varying degrees of success. Recent literature indicates that property enhance-
such as poly(ε-caprolactone) (PCL)\textsuperscript{11,17,22–24} poly(butylene succinate) (PBS)\textsuperscript{25} poly(butylene adipate terephthalate) (PBAT)\textsuperscript{26–28} and polyhydroxyalkanoates\textsuperscript{29} (c) blending PLA with random and block copolymers of lactide with ε-caprolactone or δ-valerolactone\textsuperscript{30–33} or ethylene-2,5-furane dicarboxylate\textsuperscript{33a} and (d) blending with lactide copolymers with novel macromolecular architectures such as multiam star-branched random and block copolymers.\textsuperscript{33b,33c,40,41}

Of the above, strategy (a) is the least desirable because it compromises two key desirable properties of PLA, namely, biodegradability and transparency. Superior toughening of PLA has been achieved using a reactive extrusion process by blending PLA with PBS and PBAT using a peroxide to cross-link the blend components.\textsuperscript{3} The resulting blend showed an impact strength >530 J/m and a good stiffness–toughness balance. Controlling the morphology and viscosity of PBAT components during reactive extrusion contributes to the desirable mechanical properties of the PLA/PBS/PBAT blends.

However, of greater interest are strategies (c) and (d), which use bio-degradable lactide copolymers with different chemical compositions and molecular architectures. The relevant literature on the use of strategies (c) and (d) for improving the toughness of PLA is summarized in Table S1.\textsuperscript{23,24,30} In general, random copolymers of ε-caprolactone with δ-valerolactone or δL-lactide, which exhibit low $T_g$ and $T_m$ act as a plasticizer and improve the tensile toughness at the cost of modulus. When linear block copolymers were used as additives, some degree of phase separation with one of the segments having compatibility with PLA appears to yield a better balance of toughness and modulus. The ability of the PLA matrix in the blend to crystallize upon annealing or by addition of nucleating agents has been reported to influence the toughening of PLA. This has been attributed to the formation of ductile fibrils through the deformation of spherulite under stress.

Improving the toughness of PLA has been generally achieved by the addition of non-biodegradable petroleum-based polymers (≥20 wt %), which has a negative influence on the biodegradability and compostability of PLA. The improvement in toughness is invariably accompanied by the loss of modulus and tensile strength. The used well-defined block copolymers comprising a semi-crystalline (PLA) and a rubbery (PCL) segment are easily synthesized by sequential ROP and may offer a better balance of mechanical, optical, and biodegradable properties by virtue of enhanced intermolecular interactions between the block copolymer segments and the PLA matrix. Balancing these often opposing physical and chemical properties of PLA remains a continuing scientific challenge.\textsuperscript{16b}

In our earlier work, several multiam star-branched random and block copolymers of l-lactide and ε-caprolactone were studied as an additive for improving the tensile toughness of PLA.\textsuperscript{33a} Star-branched copolymers showed a larger improvement of % elongation at break compared to linear polymers. Six-arm star-branched random and block copolymers, for example, 6s-ε-lactide-co-ε-CL ($T_g$ \textgreater \textasciitilde 0.2 °C) and 6s-l-lactide-b-ε-CL ($T_g$ \textasciitilde 11 °C) having a similar comonomer composition and $M_w$ \textasciitilde 30,000 were equally effective in improving the tensile toughness of the blend. The larger the number of branches, the better the property improvement.\textsuperscript{12a,13} However, in this study, $M_0$ of the block copolymer having a composition of 70:30 mol % LA/CL was restricted to less than 30,000 g/mol.

An optimum toughening effect of a block copolymer additive is likely to depend on factors such as the route used for the synthesis of block copolymers (ROP in the melt phase at high temperatures or in solution at low temperatures) as well as the molecular weight of the individual block segments.\textsuperscript{16b} These factors, in turn, will influence properties, such as, the particle size of the dispersed phase, nature of intermolecular interactions, (affinity) between the additive and the matrix, extent of interchain entanglement, and the ultimate morphological features of the blend. The chemical composition of the block segments, the sequence of enchainment of the monomer, and the molecular architecture are likely to play an important role in determining the nature of intermolecular interactions.\textsuperscript{33a}

In continuation of our earlier work, we have examined systematically the influence of segment molecular weight on the structure, property, and morphology of the PLA blends. For this purpose, we prepared well-defined six-arm poly(ε-caprolactone-b-l-lactide) and six-arm poly(l-lactide-b-ε-caprolactone) block copolymers with $M_n$ of 30,000, 50,000, and 70,000 g/mol using sequential ring-opening polymerization of ε-caprolactone and l-lactide. Herein, we used organo-catalyzed ROP in solution under mild conditions in an attempt to avoid or minimize inter- and intramolecular ester–ester exchange reactions, which could lead to the loss of fidelity of the block structure and segment composition. Our earlier studies were performed using block copolymers prepared via the melt phase ROP at 130 °C using tin(II) octoate as the catalyst. Access to block copolymers with larger $M_n$ from this study has enabled a better understanding of the crystallization behavior of the prepared block copolymers. In addition, the tensile fracture morphology of the blend has been examined to understand the reasons behind the observed property improvement. Furthermore, to minimize complications arising out of inadvertent polymer degradation or ester interchange reactions between the block copolymer additive matrix polymer during melt blending, we resorted to the use of a milder solution blending technique in this study.

2. RESULTS AND DISCUSSION

2.1. Synthesis of 6s-PCL-b-PLA and 6s-PLA-b-PCL Block Copolymers. Most studies in the literature use tin(II) octoate as a catalyst for ring-opening polymerization of cyclic esters. Such reactions are generally conducted in the melt at 150–160 °C for an extended period of time. We had also used this method for the preparation of block copolymers of l-lactide and ε-caprolactone in our previous study.\textsuperscript{31} However, there are possibilities of inter- and intramolecular ester–ester exchange reactions in high-temperature ROP reactions, which could compromise the fidelity of the block structure and segment composition. To avoid this complication, in this study, we resorted to the use organocatalysts at temperatures below 40 °C in solution for the synthesis of block copolymers.\textsuperscript{43} Organocatalysts have been well described for the ROP of cyclic esters.\textsuperscript{33a,34} Block copolymers of ω-pentadecalactone and l-lactide have been prepared using DBU as the organocatalyst using a sequential monomer addition method.\textsuperscript{35a} The authors reported that at a long reaction time (24 h at 25 °C) employed for the formation of the second block revealed the occurrence of some transesterification. Sequential block copolymerization of l-lactide and δ-valerolactone using DBU and DPP as catalysts has also been described in literature studies.\textsuperscript{34} We used a similar approach
for the synthesis of a block copolymer of \( l \)-lactide and \( \varepsilon \)-
caprolactone using DBU and DPP as catalysts.\(^{44}\) We resorted
to the use of DBU for ROP of \( l \)-lactide\(^{46}\) and DPP for \( \varepsilon \)-
caprolactone.\(^{47a}\)

6s-PCL-\( b \)-PLA and 6s-PLA-\( b \)-PCL block copolymers with
targeted nominal \( M_n \) of 30,000, 50,000, and 70,000 g/mol were
synthesized using sequential ring-opening polymerization of \( \varepsilon \)-
CL and \( l \)-lactide (Schemes 1 and 2). A macroinitiator of one of
the monomers was first prepared, isolated, and was used for
initiating the ROP of the other monomer. Dipentaerythritol
(DPE) was used as the hexafunctional initiator. Diphenyl-
phosphate was used as the organocatalyst for the ROP of \( \varepsilon \)-CL
and DBU for the ROP of \( l \)-lactide. For the synthesis of 6s-
PCL-\( b \)-PLA, ROP of \( l \)-lactide was initiated by a six-armed star
(6s-PCL) macroinitiator-bearing terminal primary hydroxyl
groups. For the synthesis of 6s-PLA-\( b \)-PCL block copolymer,
ROP of \( \varepsilon \)-CL was initiated by a six-arm star (6s-PLA)
macroinitiator containing terminal secondary hydroxyl groups.
The chemical structure and comonomer composition of 6s-
PCL-\( b \)-PLA and 6s-PLA-\( b \)-PCL block copolymers were
determined by \(^1\)H NMR spectroscopy.

\(^1\)H NMR spectra of 6s-PCL macroinitiators are shown in
Figures S1–S3 and 6s-PLA-\( b \)-PLA copolymers are shown in
Figures S7–S9. \(^1\)C NMR spectra of 6s-PCL-\( b \)-PLA copoly-
mers are shown in Figures S13–S15. The absence of the signal
due to the terminal \(-\text{CH}_2\text{OH}\) group of the macroinitiator in
the \(^1\)H NMR spectra of 6s-PCL-\( b \)-PLA indicate that the
initiation of the PLA chain has occurred from the PCL
Table 1. Synthesis of 6s-PCL and 6s-PLA Macroinitiators

| Sample designation | M/I | Conversion (%) | M<sub>theory</sub> (g/mol) | M<sub>6s-PCL</sub> (g/mol) | M<sub>6s-PLA</sub> (g/mol) | D | I<sub>eff</sub> |
|--------------------|-----|----------------|-----------------------------|---------------------------|---------------------------|---|-----------|
| 6s-PCL             | a   | 80:1           | 92                          | 9,000                     | 15,000                    | 1.20 | 0.93     |
|                    | b   | 132:1          | 90                          | 15,000                    | 24,650                    | 1.26 | 0.92     |
|                    | c   | 184:1          | 96                          | 21,000                    | 35,000                    | 1.30 | 0.95     |
| 6s-PLA             | d   | 146:1          | 94                          | 21,000                    | 34,300                    | 1.25 | 0.95     |
|                    | e   | 243:1          | 93                          | 35,000                    | 55,850                    | 1.30 | 0.93     |
|                    | f   | 340:1          | 98                          | 49,000                    | 79,850                    | 1.35 | 0.94     |

<sup>a</sup>I = Initiator in mol; M = γ-lactide; ε-caprolactone in mol. <sup>b</sup>Determined by GPC using polystyrene standards in CHCl<sub>3</sub>. M<sub>6s-PCL</sub> (column 6) = M<sub>0</sub> (column 5) × 0.56; M<sub>6s-PLA</sub> (column 6) = M<sub>0</sub> (column 5) × 0.38. <sup>c</sup>I<sub>eff</sub> = M<sub>experiment</sub>/M<sub>theory</sub>.

Table 2. Composition and Molecular Properties of 6s-PCL-b-PLA and 6s-PLA-b-PCL Block Copolymers

| Sample designation | M/I | LA/CL (mol %) in feed | LA/CL (mol %) in polymer | Conversion (%) | M<sub>theory</sub> (g/mol) | M<sub>b</sub> (g/mol) | D | I<sub>eff</sub> |
|--------------------|-----|-----------------------|--------------------------|----------------|---------------------------|-------------------|---|-----------|
| 6s-PCL-b-PLA (1)   | 1a  | 146:1                 | 70:30                    | 71:29          | 91                         | 30,000            | 1.25 | 0.91     |
|                    | 1b  | 243:1                 | 70:30                    | 71:29          | 93                         | 50,000            | 1.30 | 0.96     |
|                    | 1c  | 340:1                 | 70:30                    | 72:28          | 94                         | 70,000            | 1.36 | 0.94     |
| 6s-PLA-b-PCL (2)   | 2a  | 80:1                  | 70:30                    | 71:29          | 91                         | 30,000            | 1.27 | 0.93     |
|                    | 2b  | 132:1                 | 70:30                    | 72:28          | 88                         | 50,000            | 1.32 | 0.95     |
|                    | 2c  | 184:1                 | 70:30                    | 72:28          | 94                         | 70,000            | 1.35 | 0.95     |

<sup>a</sup>I = Initiator in mol; M = γ-lactide; ε-caprolactone in mol; M<sub>theory</sub> was calculated by taking the ratio and multiplying it with conversion. <sup>b</sup>Determined from 1H NMR. Determined by GPC using the polystyrene standard in CHCl<sub>3</sub>. In view of the branched structure of the block copolymers, the M<sub>b</sub> values must be considered as apparent. <sup>c</sup>I<sub>eff</sub> = M<sub>experiment</sub>/M<sub>theory</sub>.

Table 3. T<sub>g</sub> and T<sub>m</sub> of Macroinitiators and Block Copolymers

| Sample designation | M (g/mol) | T<sub>g</sub> (°C) | T<sub>m</sub> (°C) | ΔH<sub>m</sub> (J/g) |
|--------------------|-----------|----------------|----------------|-------------------|
| a                  | 8,400     | −57.8          | 54.0           | 70.2              |
| b                  | 13,800    | −55.6          | 54.6           | 67.8              |
| c                  | 19,600    | −57.7          | 56.8           | 72.6              |
| d                  | 19,900    | −54.7          | 144.3          | 32.0              |
| e                  | 32,400    | −56.9          | 163.4          | 38.6              |
| f                  | 46,300    | −57.2          | 165.0          | 37.2              |
| 1a                 | 27,300 (<i>M</i><sub>b</sub><sub>PCL</sub> = 8,400; <i>M</i><sub>b</sub><sub>PLA</sub> = 18,900 g/mol) | 26.4            | 146.3          | 22.5              |
| 1b                 | 47,850 (<i>M</i><sub>b</sub><sub>PCL</sub> = 13,800; <i>M</i><sub>b</sub><sub>PLA</sub> = 34,050 g/mol) | −55.9          | 45.2           | 1.8               |
| 1c                 | 66,100 (<i>M</i><sub>b</sub><sub>PCL</sub> = 19,600; <i>M</i><sub>b</sub><sub>PLA</sub> = 46,500 g/mol) | 33.9            | 142.9          | 41.9              |
| 2a                 | 27,750 (<i>M</i><sub>b</sub><sub>PLA</sub> = 19,900; <i>M</i><sub>b</sub><sub>PCL</sub> = 7,850 g/mol) | 35.5            | 149.6          | 43.0              |
| 2b                 | 46,500 (<i>M</i><sub>b</sub><sub>PLA</sub> = 32,400; <i>M</i><sub>b</sub><sub>PCL</sub> = 14,100 g/mol) | 30.5            | 118.2          | 10.5              |
| 2c                 | 66,350 (<i>M</i><sub>b</sub><sub>PLA</sub> = 46,300; <i>M</i><sub>b</sub><sub>PCL</sub> = 20,050 g/mol) | 36.0            | 120.0          | 7.0               |

segment. The copolymer compositions determined by <sup>1</sup>H NMR were close to the feed composition indicating near quantitative conversion of both the monomers.

The structure of the 6s-PCL-b-PLA copolymers was examined by <sup>13</sup>C NMR using the expanded carbonyl carbon (C=O) region from δ = 168–175 ppm. 6s-PCL-b-PLA shows two distinct peaks at 173.61 and 169.55 ppm corresponding to the carbonyl resonances of the PCL and PLA segments. The manner of preparing the block copolymer using an isolated macroinitiator of 6s-PCL and the observation in <sup>1</sup>H NMR of the disappearance of the resonance at 3.61–3.68 ppm (d’) due to the −CH(CH<sub>3</sub>)OH end group of the 6s-PCL macroinitiator along with the presence of two single peaks for the carbonyl group in <sup>13</sup>C NMR leads us to conclude that the synthesized polymer has a block structure. A similar conclusion was drawn in the case of poly(<i>a</i>-pentadecalactone)-<i>b</i>-poly(<i>l</i>-lactide) block copolymers based on the carbonyl resonances in <sup>13</sup>C NMR. Furthermore, the absence of additional responses in the region of carbonyl resonances indicates the absence of transesterification reaction.<sup>1</sup>H NMR spectra of 6s-PLA macroinitiators are shown in Figures S4–S6 and that of 6s-PCL-b-PLA are shown in Figures S10–S12. The absence of the signal due to the terminal −CH(CH<sub>3</sub>)OH group of the macroinitiator in the <sup>1</sup>H NMR spectra of 6s-PLA-b-PCL indicates that the initiation of the PCL chain has occurred from the PLA segment. The copolymer compositions determined by <sup>1</sup>H NMR were close to the feed composition, indicating a near quantitative conversion of both the monomers.

<sup>1</sup>C NMR spectra of 6s-PLA-b-PCL copolymers are shown in Figures S16–S18. The structure of the copolymers was determined using the expanded carbonyl carbon (C=O)
The results confirm that all polymerization reactions were well controlled with \( D \) values in the range of 1.20 to 1.35. \( T_g \) was generally between 0.90 and 0.95.

2.2. Melting and Glass Transition of 6s-PCL-b-PLA and 6s-PLA-b-PCL Block Copolymers. \( T_g \) and \( T_m \) values of six-arm macroinitiators and six-arm block copolymers are shown in Table 3. \( T_g \) and \( T_m \) of 6s-PLA increases with increasing \( M_n \) of the star-branched polymer, whereas that of 6s-PCL did not show significant changes in the range of \( M_n \) studied. In the case of PLA, branched polymers have been reported to exhibit lower \( T_g \) and \( T_m \). A four-arm star-branched PLA (\( M_n: 20,000 \text{ g/mol and } D: 2.0 \)) prepared using Sn (Oct)$_2$ at 130 °C showed a \( T_m \) of 179 °C and \( T_g \) of 60 °C compared to the corresponding values of 182.5 and 63.2 °C for a linear polymer of the same \( M_n \). A six-arm star-branched PLA [\( M_n: 75,600 \text{ g/mol prepared using Sn (Oct)$_2$} \) at 130 °C] showed a \( T_m \) of 175 °C, which was about 5 °C lower than their linear analogue of similar molecular weight. \( T_m \) was found to increase with an increase in \( M_n \) of the star-branched polymer. In comparison, the six-arm star-branched PLA prepared using an organocatalyst at lower temperatures showed \( T_m \) of 165 and 163.4 °C and \( T_g \) of 57.2 and 56.9 °C (\( M_n: 46,300 \) and 32,400 g/mol, respectively).

\( T_g \) values of six-arm star-branched PCL prepared using Sn (Oct)$_2$ has also been reported in the literature.\(^{48}\) For polymers having \( M_n \) of 6,400 g/mol (\( D: 1.5 \)) and 13, 410 g/mol (\( D: 1.15 \)), reported \( T_g \) were 51.2 and 55.7 °C, respectively. This should be compared with the values reported herein for a six-arm star-branched polymer of \( \varepsilon \)-caprolactone, \( T_m \): 54.0 °C for a polymer having \( M_n: 8,400 \text{ g/mol (} D: 1.2 \) ) and \( T_m \): 54.6 °C for a polymer having a \( M_n: 13,800 \text{ g/mol.} \)

The observed lower melting and glass transition of star-branched polymers of PLA has been attributed to its higher chain mobility due to greater free volumes.\(^{48}\) Star-branched polymers are also likely to possess a poor folding property, which may inhibit crystallization. Star-branched polymers also...
may have greater crystalline defects due to a larger number of end groups and branch points, an effect more pronounced in lower molecular weight polymers.

6s-PCL-b-PLA block copolymer showed two distinct \( T_\text{m} \)'s and \( T_\text{g} \)'s, characteristic of each of the two segments (Figure S21). This is indicative of the heterophase nature of this copolymer. It is observed that an outer block consisting of more crystallizable PLA segments depress the \( T_\text{m} \) of the inner PCL block by about 5 °C. However, the inner PCL block inhibits the crystallization of the outer PCL block more strongly with a depression of \( T_\text{m} \) by about 15–20 °C, especially, for copolymers having a higher PLA block segment length (1b and 1c). 6s-PCL-b-PCL copolymers show a significantly lower \( T_\text{m} \) for the PLA segment compared to the corresponding \( T_\text{m} \)'s of 6s-PLA of comparable \( M_n \) (Figure S22). The segmental mobility of the inner PLA block appears to be significantly enhanced by the presence of the more amorphous and flexible outer PCL segment. The lower the \( M_n \) of the inner PLA segment, the higher is the segmental mobility of PLA (lower \( T_\text{g} \)). Whereas 2a did not show any melting transition, 2b and 2c showed only a single melting peak corresponding to the PLA segment. No crystallization peak due to the PCL segment was observed. The crystallization of the inner PLA segment was strongly inhibited in 6s-PLA-b-PCL, depressing the \( T_\text{m} \) of the PLA segment by about 45 °C. Crystallization of the PLA segment in the vicinity of the core of the branched molecule strongly inhibited the crystallization of the outer PCL segment. Further studies will be needed to understand the influence of monomer sequences in multi-arm star-branched block copolymers on the crystallization behavior of individual segments.

The above observations cannot be merely attributed to the nature of molecular architecture; six-arm branching did not substantially influence the \( T_\text{g} \) and \( T_\text{m} \) of homopolymers of similar \( M_n \). Consequently, the observed changes must be ascribed to some unique properties of the block copolymer, its secondary structure, as well as the sequence of monomer enchainment. An outer PCL block substantially changes the crystallization behavior and segmental mobility of the inner PLA block. This could be a result of the less constrained (far from the core) and more flexible PCL block, plasticizing the inner PLA block. The more constrained inner PCL block (attached to the initiator core) is unable to significantly influence the segmental mobility or the crystallization behavior of the outer PLA block.

Blending 10 wt % of 6s-PCL-b-PLA (1a–1c) and 6s-PLA-b-PCL (2a–2c) in PLA resulted in a 4–5 °C reduction in the \( T_\text{m} \) of the blend (Figure 1). However, \( T_\text{g} \) was lower for the blends 1a–c and 2a, and the heat of fusion showed a significant increase for all the blends (Table 4). The low heat of fusion of PLA (\( \Delta H_\text{m} \); 29.1 J/g) indicates that the polymer is largely amorphous when it was cooled from the melt. The increase in the \( \Delta H_\text{m} \) exhibited by the blends indicates that the block copolymer additives enhance the crystallization behavior of the blend with \( \Delta (T_\text{m} - T_\text{g}) \) values for 1b and 1c lower by about 4 °C than that of the PLA matrix polymer. This indicates that some of the block polymers can influence the crystallization rate of the blend.

\( T_\text{g} \) was depressed by about 6–7 °C with the addition of the block copolymers to PLA (Table 4). Lowering of \( T_\text{g} \) of the blends indicates a mild plasticization of the matrix PLA, on account of significant miscibility in the matrix PLA.

In summary, differential scanning calorimetry (DSC) provides evidence for both plasticization and enhanced rate of crystallization by some of the six-arm star-branched block copolymer additives with PLA. Multi-arm star-branched PLAs have been reported to accelerate the nucleation rate and early spherulite growth of PLA by a heterogeneous nucleation mechanism.51,52

### 2.3. Effect of Six-Arm Star-Branched Poly(<i>ε</i>-caprolactone-<i>b</i>-lactide) (6s-PCL-b-PLA) and Poly(<i>ε</i>-lactide-<i>b</i>-<i>ε</i>-caprolactone) (6s-PLA-b-PCL) Copolymers on the Mechanical Properties of the PLA Blend

Six-arm star-branched block copolymers, 6s-PCL-b-PLA and 6s-PLA-b-PCL, were solution blended with an injection molding grade PLA (10:90 wt %). Clear transparent films were obtained (Figure S23). In all cases, the l-lactide to e-caprolactone composition ratio was maintained at 70:30 mol %.

### Table 4. Thermal Properties of PLA/6s-PCL-b-PLA and PLA/6s-PLA-b-PCL Blends

| entry | sample designation | \( M_n \) (g/mol) | PLAs/blend component | \( T_\text{m} \) (°C) | \( \Delta H_\text{m} \) (J/g) | \( \Delta H_\text{f} \) (J/g) | crystallinity (%) |
|-------|-------------------|-----------------|----------------------|---------------------|-----------------|-----------------|----------------|
| 1     | 1a                | 27,300          | 90/10                | 104.2 (101.1)       | 29.6            | 35.6            | 39.1           |
| 2     | 1b                | 47,850          | 90/10                | 100.7 (100.5)       | 33.3            | 156.2           | 40.3           |
| 3     | 1c                | 66,100          | 90/10                | 99.6 (99.3)         | 32.6            | 156.1           | 40.6           |
| 4     | 2a                | 27,750          | 90/10                | 103.7 (101.4)       | 36.1            | 155.2           | 41.2           |
| 5     | 2b                | 46,500          | 90/10                | 117.0 (100.1)       | 40.1            | 154.5           | 40.2           |
| 6     | 2c                | 66,350          | 90/10                | 119.1 (101.4)       | 26.0            | 155.3           | 35.4           |

*Numbers in parenthesis indicate data from the first heating cycle.

### Table 5. Mechanical Properties of PLA/6s-PCL-b-PLA and PLA/6s-PLA-b-PCL Blends

| entry | blend designation | \( M_n \) (g/mol) | PLAs/blend component | modulus (MPa) | yield stress (MPa) | yield strain (%) | elongation (%) | domain size (microns) |
|-------|-------------------|-----------------|----------------------|---------------|-------------------|-----------------|---------------|----------------------|
| 1     | PLA (A)           | 95,000          | 100/00               | 25.8 ± 1.5    | 49.4 ± 1.1        | 2.7 ± 0.1       | 9.1 ± 0.5     | 0.7 ± 0.2            |
| 2     | PLA + 1a (B)      | 27,300          | 90/10                | 23.5 ± 0.5    | 56.6 ± 0.2        | 3.5 ± 0.3       | 19.9 ± 0.4    | 2.6 ± 0.8            |
| 3     | PLA + 1b (C)      | 47,850          | 90/10                | 23.7 ± 0.7    | 54.1 ± 0.6        | 3.8 ± 0.3       | 23.8 ± 0.4    | 1.5 ± 0.4            |
| 4     | PLA + 1c (D)      | 66,100          | 90/10                | 26.0 ± 1.2    | 57.2 ± 0.8        | 3.6 ± 0.3       | 17.3 ± 0.3    | 1.5 ± 0.4            |
| 5     | PLA + 2a (E)      | 27,750          | 90/10                | 24.5 ± 1.3    | 58.6 ± 0.6        | 3.6 ± 0.4       | 16.9 ± 0.2    | 0.6 ± 0.2            |
| 6     | PLA + 2b (F)      | 46,500          | 90/10                | 25.5 ± 1.2    | 55.5 ± 0.8        | 3.7 ± 0.3       | 18.8 ± 0.7    | 1.1 ± 0.4            |
| 7     | PLA + 2c (G)      | 66,350          | 90/10                | 25.4 ± 0.6    | 64.2 ± 0.7        | 4.0 ± 0.2       | 14.6 ± 0.5    | 0.5 ± 0.1            |
The results of the mechanical properties of the blends are shown in Table 5 and schematically presented in Figure 2. The following observations can be made from an examination of Table 5.

(a) Addition of either of the two block copolymers improves the % elongation at break of the PLA blend with no significant loss of modulus.

(b) A block copolymer with an outer PLA segment appears superior to a block copolymer with an outer PCL segment in improving the % elongation at break;

(c) The highest improvement in % elongation at break is observed in either of the two cases with a $M_n$ of about 46,000 to 47,000 g/mol. There is a loss of elongation property when the $M_n$ of the block copolymer is increased to about 66,000 and $M_n$ of the PLA segment around 46,000 g/mol.

The fracture surface of the base PLA (A) (Figure 3) shows no distinctive features. Blends B–D, upon fracture, show surface voids, indicating that at the time of the fracture the additive block copolymer 1a–1c is being pulled out and de-bonded from the matrix. The fracture surface morphology also provides evidence of a uniform dispersion of the additive polymer in the blend. Blends E and G show a feature-less fracture surface. Blend F shows features somewhat similar to blend B–D. The increment in % elongation observed is in the order C > B > D > F > E > G. This trend appears to correlate well with the nature of the fracture surface morphology.

Improvement in % elongation at break can be understood in terms of the morphological characteristics of the blend. The brittle fracture in tensile and impact modes of inherently brittle PLA has been attributed to multiple crazing deformations. However, the semicrystalline nature of PLA can also promote failure due to the shear yielding mechanism. Improvement in elongation is predominantly caused by the shear yielding deformation of the matrix polymer caused by de-bonding of the dispersed block copolymer additive and the PLA matrix during tensile fracture. Shear yielding results in large energy absorption with the PCL phase of the block copolymer additive acting as stress concentrators and initiating crazing, de-bonding, and cavitation to halt crack propagation. Scanning electron microscopy (SEM) of fracture surfaces B, C, D, and F show evidence of de-bonding and void formation due to cavitation. The closer the dispersion of additive particles in the matrix, the larger the shear yielding region and better is the tensile toughening. Fracture surface C shows large microvoids, which are evenly distributed providing support for shear yielding as the dominant mechanism of tensile toughening. The best results are obtained with block copolymers having an $M_n$ for PCL segment $\sim$14,000 g/mol and for PLA segment.
~34,000 g/mol, suggesting the need for an optimal balance of crystalline and amorphous segments. Increasing the amorphous phase $M_n$ to 20,000 g/mol possibly contributes to some phase immiscibility, resulting in poor bonding between the phases.

Toughening of PLA by blending with a variety of polymers has been a subject of great scientific interest. PLA is an inherently semi-rigid polymer, which show poor deformation properties resulting in less than 10% elongation at break and relatively poor impact properties. Toughness is broadly understood as the ability of a material to absorb energy before failure under stress, and toughening is the ability of the material to absorb maximum external energy before its ultimate failure. Toughness is of two kinds, namely, tensile toughness, which is the ability to absorb tensile fracture energy during stretching and impact toughness, which is the ability to absorb the energy of impact. Toughness improvement by blending is dependent on a variety of factors, such as the structure of the brittle matrix polymer, the molecular structure of the additive polymers, molecular weight of the additive and the matrix polymer, extent of chain entanglement, thermodynamic miscibility at the molecular level of the matrix polymer with the additive polymer, interfacial compatibility, and phase behavior of the blend.

Addition of PLA-based copolymers have been reported to be more efficient in improving the tensile toughness of PLA. Most of the copolymers used are predominantly amorphous and ductile, for example, poly(ε-caprolactone), poly(ε-caprolactone-co-d, l-lactide), poly(ε-caprolactone-co-δ-valerolactone), and poly(lactide-b-polyethylene glycol). The ductile copolymers behave as polymeric plasticizers for PLA and improve tensile toughness. However, an improvement in tensile toughness through plasticization comes at the cost of loss of modulus (Table S1).

The use of a well-defined segmented block copolymers of PLA with PCL, such as those reported in this study, offers a balance of properties that is able to improve tensile toughness without sacrificing modulus. The presence of six-arms in the block copolymer segment provides highly interacting phases resulting in phase miscibility at the same time affording a degree of phase separation of the amorphous and crystalline phases. Star-branched polymers have higher segment density within the distance of its radius of rotation compared to their linear analogues. Higher segment density can result in enhanced molecular miscibility of the additive block copolymer with the matrix polymers through an increase in chain entanglement. The observation that 6s-PCL-b-PLA results in superior tensile toughness points out to the importance of a two-phase morphology of the additives. 6s-PCL-b-PLA exhibits two distinct $T_g$ characteristics of the crystalline PLA and amorphous PCL segments. PLA segments of the block copolymer can effectively interact with the matrix polymer through chain entanglement, weak van der Waals forces, and hydrogen-bonded interaction of the terminal hydroxyl group of the star-branched block copolymer with the matrix PLA contributing to enhanced miscibility, whereas the PCL chains present in high concentrations near the core of the initiator can act as a dispersed phase and can facilitate stress transfer. Such a hypothesis has been advanced for the ability of a multi-arm star-branched copolymer initiated using octa polyolefinic oligomeric silsesquioxane with arms comprised poly(ε-caprolactone-co-d-lactide)-b-poly(d-lactide) to improve the tensile toughness of PLA while retaining the modulus and tensile strength properties. The outer PDLA block interacted with the matrix polymer via stereocomplexation, whereas the rubbery PCL-PLA copolymer contributed to energy absorption.

On the contrary, 6s-PLA-b-PCL possesses an outer PCL segment that has limited miscibility with the matrix polymer and a PLA segment located too close to the core to afford interaction with the PLA matrix. Hence, the extent of improvement in tensile toughness is inferior.

For superior toughening of PLA, there is a need to invoke both tensile toughening and impact toughening mechanisms. This requires a combination of plasticization and shear yielding as well as multiple crazing mechanisms. The use of a nucleating agent in combination with a rubbery copolymer, poly(ε-caprolactone-co-d, l-lactide), is reported to substantially increase in toughness. Enhancing the crystallization of the matrix PLA by the use of a nucleator induces shear yielding in the crystalline zones, which promotes the dissipation of impact energy through plastic deformation. It has also been reported that in brittle polymers, when multiple crazing mechanism dominates, the size of the dispersed phase in the matrix is about 2–3 μm. It is interesting to note that the mean domain size observed in the present study for a blend showing the highest tensile toughness is about 2.5 μm (blend C, Table S1). Coupled with a preliminary observation that 6s-PCL-b-PLA acts as a mild nucleator, it is tempting to speculate that 6s-PCL-b-PLA could contribute to both the toughening mechanism. Further work will be needed to validate this hypothesis.

3. CONCLUSIONS

Fully biodegradable, six-arm, and star-branched block copolymers consisting of a sequence of poly(ε-caprolactone) or poly(l-lactide) chains as the outer segments were synthesized by sequential copolymerization of ε-caprolactone and l-lactide using organocatalysts under mild reaction conditions. Well-defined 6s-PCL-b-PLA block copolymers were obtained with a range of segment molecular weights. However, in the case of 6s-PLA-b-PCL disruption of the block structure was observed on account of competing transesterification reaction accompanying the chain-growth reaction. This could be due to the slower rate of initiation of the ε-caprolactone monomer by the secondary hydroxyl group of the 6s-PLA macroinitiator. Presumably, the DPP organocatalyst remains active after most of the monomers are consumed, resulting in transesterification and chain scrambling.

DSC analysis provided interesting insights into the crystallization property of the block copolymer depending on their sequence of enchainment. When the PLA was present as the outer block, the block copolymer showed two $T_g$ and $T_m$ characteristics of each segment, one crystalline and the other amorphous. This provides evidence for phase separation in six-arm star-branched 6s-PCL-b-PLA. 6s-PCL-b-PLA, upon solution blending with PLA (10 wt %), gave clear and transparent films. Tensile property measurements showed that this blend showed two to three-fold improvement in % elongation at break without a loss of modulus. Improvement in tensile toughness was attributed to favorable segmental miscibility contributed by the star-shaped branched-block copolymer and the availability of high concentrations of an amorphous segment close to the initiating core acting as a stress concentrator. The poorer property improvement shown when 6s-PLA-b-PCL was used as a component of the blend.
could be either due to the presence of an outer PCL segments, which has limited miscibility with the matrix polymer or due to some complexity arising out of the disruption of block structure due to transesterification in the case of this block copolymer additive. Further studies with structurally purer block copolymers will be necessary to better understand the morphology and tensile toughening behavior.

4. MATERIALS AND METHODS

4.1. Materials. L-lactide (Purac, Singapore) was recrystallized from dry ethyl acetate, sublimed under reduced pressure, and stored in a glovebox. ε-Caprolactone (ε-CL) (Sigma-Aldrich, USA) was dried over calcium hydride for 24 h and vacuum-distilled before use. 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) and diphenyl phosphate (DPP) (from Sigma-Aldrich, USA) were used as received. Dipentaerythritol (DPE, Sigma-Aldrich) was dried over calcium hydride for 24 h and vacuum-distilled before use. 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) and diphenyl phosphate (DPP) (from Sigma-Aldrich, USA) were used as received. Dipentaerythritol (DPE, Sigma-Aldrich) was dried at 30 °C under vacuum (1 mm of Hg) for 5 h before use. All monomers, initiators, and catalysts were stored in a glovebox (MBRAUN UNilab TM). Injection molding grade poly(L-lactide) (PLA, Ingeo 3052D, NatureWorks, USA) with n = 95,000 g/mol and D = 1.5 was used as received. The Tm of the PLA is 160 °C. Based on this, it is estimated that the enantiomeric purity of the PLA is above 95%. Other laboratory grade reagents and solvents were used as received.

4.2. Synthesis of Six-Arm Star-Branched Poly(ε-caprolactone) (6s-PCL) Polymer as the Macroinitiator (Targeted Mₙ: 21,000 g/mol). Inside the glovebox, ε-caprolactone (4 g, 0.035 mol) was placed in a 100 mL two-neck round-bottomed flask. Into this was added toluene (15 mL) followed by hexafunctional initiator DPE (48 mg, 0.19 mmol) and catalyst DPP (114 mg, 0.35 mmol, [ε-caprolactone]/[DPP] = 100). The contents of the flask were stirred under nitrogen at 40 °C for 8 h. The reaction was terminated by the addition of triethylamine (1 equiv of DPP) and precipitated in excess of methanol. The solid was filtered and dried at 45 °C in vacuum for 24 h. Conversion: 96%.

Six-arm PCL (6s-PCL) macroinitiators with targeted Mₙ of 9,000 and 15,000 g/mol were synthesized similarly.

4.3. Synthesis of Six-Arm Star-Branched Poly(ε-caprolactone-b-l-lactide) (6s-PCL-b-6s-PLA) Block Copolymer (Targeted Mₙ: 70,000 g/mol). 6s-PCL (Mₙ: 21,000 g/mol) was used as a macroinitiator for the initiating the second block. Inside a glovebox, 6s-PCL (1.2 g, 0.06 mmol), l-lactide (2.8 g, 0.019 mol), and DPU (30 μL, 0.19 mmol, [l-lactide]/[DPU] = 100) were placed in a two-neck round-bottomed flask and dissolved in 20–25 mL dichloromethane (DCM). Polymerizations were carried out at 30 °C for 2 h. The reaction was terminated by the addition of solid benzoic acid (1 equiv of DPU). The polymer was separated by precipitation in excess methanol, filtered, and dried in a vacuum oven under reduced pressure at 40 °C for 24 h. Conversion: 98%.

The six-arm PLA (6s-PLA) with target molecular weights of 21,000 and 35,000 g/mol were synthesized similarly.

4.5. Synthesis of Six-Arm Star-Branched Poly(l-lactide-b-ε-caprolactone) (6s-PLA-b-PCL) Block Copolymer (Targeted Mₙ: 70,000 g/mol). 6s-PLA (Mₙ: 49,000 g/mol) was used as a macroinitiator for initiating the second block. In a two-neck round-bottomed flask, 6s-PLA (2.8 g, 0.06 mmol), ε-caprolactone (1.2, 0.010 mol) and DPP (35 mg, 0.10 mmol, [ε-caprolactone]/[DPP] = 100) were dissolved in 20 mL of dry toluene. All manipulations were performed inside a glovebox. Polymerization was conducted under a nitrogen atmosphere at 40 °C for 8 h. The reaction was terminated by the addition of triethylamine (1 equiv of DPP). The polymer was separated by precipitation in excess methanol, filtered, and dried in vacuum at 40 °C until constant polymer weight. Conversion: 94%.

Six-arm PLA-b-PCL (6s-PLA-b-PCL) block copolymers with targeted Mₙ of 30,000 and 50,000 g/mol were synthesized similarly.

4.6. Preparation of Polymer Films. PLA (3052 D) 0.9 g and the synthesized block copolymer 0.1 g were dissolved in 5 mL of dry DCM. A clear transparent solution was obtained. Polymer films were prepared using the doctor blade technique (20 μm). The cast films were initially kept at room temperature for 24 h and then at 40 °C for 24 h. The dried films were transparent and had a thickness of 0.12 μm. Dumbbell-shaped specimens were cut using a punching apparatus. Sample dimensions were 3 x 1 cm.

4.7. Characterization of Polymers. Measurements of the number-average-molecular weight (Mₙ), weight-average-molecular weight (Mₐ), and molecular-weight distribution were performed using a gel permeation chromatograph [Thermo Quest (TQ) spectra series AS300] with a refractive index detector. The gel permeation chromatograph was equipped with two mixed bed columns. Samples for gel permeation chromatography (GPC) were prepared with concentrations of 4–5 mg/mL in HPLC-grade chloroform (CHCl₃). Prior to sample injection, polymer solutions were filtered thrice through a Millipore filter (0.22 mm). The injection volume was 100 μL with a 1 mL/min flow rate. For calibration five different narrow molecular weight polystyrene standard samples were used (Mₙ = 9k, 33k, 96k, 105k, and 256k, all having D = 1.01).

The ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ with a Bruker DRX spectrometer at a frequency of 400 or 500 MHz. The proton decoupled ¹³C NMR spectra with NOE were recorded in CDCl₃ with a Bruker DRX spectrometer at a frequency of 125.78 MHz. The digital resolution of 32 K data points/23 Hz spectral width with a pulse angle of about 30 and relaxation delays of 2s and 10⁴ transient accumulation. The sample concentration is 100 mg/0.5 mL CDCl₃.

Thermal analysis was performed with a differential scanning calorimeter (Q100, TA Instruments) equipped with a refrigerated cooling system. The Tᵥ crystallization temperature (Tᵥ), Tᵥ enthalpy of crystallization (ΔHᵥ), and melting enthalpy (ΔHₘ) were calculated from the DSC curves. DSC measurements were carried out by heating the polymer samples from −90 to 200 °C at a rate of 10 °C/min, held
for 3 min, and cooled to −90 °C at a rate of 100 °C/min, held for 1 min at −90 °C, followed by repeating the heating cycle at a rate of 10 °C/min up to 200 °C. All measurements were performed under an atmosphere of nitrogen. DSC runs from the second heating cycle are presented.

A Linkam Scientific Instruments tensile tester (TST-350) with a 200 N load cell was used for the measurement of mechanical properties. The cross-head speed was maintained at 10 mm/s. Measurements were made on five dumbbell specimens punched out from each sample of the film. The values reported are a mean of the five measurements. The fracture surface morphology of polymer films was studied by SEM analysis. The tensile break samples were sputter-coated with gold for 4–5 min in an Emitech sputter-coating unit. Specimens were viewed in a Quanta 200 3D dual-beam field emission scanning electron microscope (FEI) at 15 kV and at different magnifications. Analysis software xT microscope control was used for the analysis of SEM images.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04486.

NMR spectra of 6s-PCL, 6s-PLA macroinitiators, 6s-PCL-b-PLA, and 6s-PLA-b-PCL block copolymers, GPC results of 6s-PCL-b-PLA and 6s-PLA-b-PCL, DSC curves of 6s-PCL-b-PLA and 6s-PLA-b-PCL, pictures demonstrating the transparency of films, and a summary of literature data on properties of blends of PLA with linear random and block copolymers and star-branched random and block copolymers (PDF)

**AUTHOR INFORMATION**

Corresponding Author
Swaminathan Sivaram — Indian Institute of Science Education and Research, Pune 411008, India; orcid.org/0000-0002-1059-6122; Email: s.sivaram@iiserpune.ac.in

Authors
Megha D. Deokar — Polymer Science and Engineering Division, Council of Scientific and Industrial Research-National Chemical Laboratory, Pune 411008, India; Academy of Scientific and Innovative Research AcSIR Headquarters, Council of Scientific and Industrial Research-Human Resource Development Centre Campus Sector 19, Ghaziabad, Uttar Pradesh 201002, India

Baijayantimala Garnaik — Polymer Science and Engineering Division, Council of Scientific and Industrial Research-National Chemical Laboratory, Pune 411008, India; Academy of Scientific and Innovative Research AcSIR Headquarters, Council of Scientific and Industrial Research-Human Resource Development Centre Campus Sector 19, Ghaziabad, Uttar Pradesh 201002, India; orcid.org/0000-0003-4264-0316

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04486

Notes
The authors declare no competing financial interest.

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**REFERENCES**

(1) Poly (lactic acid): Science and technology; Jimenez, A., Peltzer, M. A., Ruseleaeite, R. A., Eds.; Royal Society of Chemistry: London, United Kingdom, 2015.
(2) Lorenzo, D.; Laura, M. L.; Androsch, R. Synthesis, structure and properties of poly (lactic acid); Springer: Switzerland, 2018.
(3) Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. Poly (lactic acid) crystallization. Prog. Polym. Sci. 2012, 37, 1657−1677.
(4) Kulkarni, A.; Lele, A.; Sivaram, S.; Rajamohanan, P. R.; Velankar, S.; Chatterji, A. Star telechelic poly(l-lactide) ionomers. Macromol. 2015, 48, 6580−6588.
(5) Wu, F.; Misra, M.; Mohanty, A. K. Super toughened poly (lactic acid)-based ternary blends via enhancing interfacial compatibility. ACS Omega 2019, 4, 1955−1968.
(6) Auras, R.; Harte, B.; Selke, S. An overview of poly lactides as packaging materials. Macromol. Biosci. 2004, 4, 835−864.
(7) Deokar, M. D.; Kulkarni, A.; Garnaik, B.; Lele, A.; Sivaram, S. Aliphatic polyster with novel molecular architecture via ring-opening polymerization: Synthesis, properties, and applications. In Chapter 10; Macromolecular Engineering: Design, synthesis and application of polymers; Lubnin, A., Erdoci, G., Eds.; Elsevier: Cambridge, 2021.
(8) Zhao, X.; Hu, H.; Wang, X.; Yu, X.; Zhou, W.; Peng, S. Super tough poly (lactic acid) blends: a comprehensive review. RSC Adv. 2020, 10, 13316−13368.
(9) Wachirahuttapong, S.; Thongpin, C.; Sombatsompop, N. Effect of PCL and compatibility contents on the morphology, crystallization and mechanical properties of P/LA/PCL blends. Energy Procedia 2016, 89, 198−206.
(10) Likittanaprasong, N.; Seadan, M.; Suttiruengwong, S. Impact property enhancement of poly (lactic acid) with different flexible copolymers. J. Mater. Sci. Eng. 2015, 87, 012069−012075.
(11) Fortelny, I.; Ujcic, A.; Fambrì, L.; Slouf, M. Phase structure, compatibility, and toughness of PLA/PCL blends: A review. Front. Mater. 2019, 6, 206−218.
(12) Wang, M.; Wu, Y.; Li, Y.-D.; Zeng, J.-B. Progress in toughening poly (Lactic Acid ) with renewable polymers. Polym. Rev. 2017, 57, 557−593.
(13) Zhang, B.; Bian, X.; Zhou, D.; Feng, L.; Li, G.; Chen, X. Toughening modification of PLLA by combination of copolymerization and in situ reactive blending. RSC Adv. 2016, 6, 113366−113376.
(14) Yang, D.; Liu, W.; Zhu, H.-M.; Wu, G.; Chen, S.-C.; Wang, X.-L.; Wang, Y.-Z. Toward super-tough poly (L-lactide) via constructing pseudo-cross-link network in toughening phase anchored by stereocomplex crystallites at the interface. ACS Appl. Mater. Interfaces 2018, 10, 26594−26603.
(15) Caldona, E. B.; De Leon, A. C. C.; Pajarito, B. B.; Advincula, R. C. A review on rubber-enhanced polymeric materials. Polym. Rev. 2017, 57, 311−338.
(16) (a) Krishnan, S.; Pandey, P.; Mohanty, S.; Nayak, S. K. Toughening of polylactic acid: An overview of research progress. Polym.-Plast. Technol. Eng. 2016, 55, 1623−1652. (b) Liu, H.; Zhang, J. Research progress in toughening modification of poly (lactic acid). J. Polym. Sci., Part B: Polym. Phys. 2011, 49, 1051−1083.
(17) Anderson, K.; Schreck, K.; Hillmyer, M. Toughening polylactide. Polym. Rev. 2008, 48, 85−108.
(18) Hu, K.; Huang, D.; Jiang, H.; Sun, S.; Ma, Z.; Zhang, K.; Pan, L.; Li, Y. Toughening biosourced poly (lactic acid) and poly (3-hydroxybutyrate-co-4-hydroxybutyrate) blends by a renewable poly
(epichlorohydrin-co-ethylene oxide) elastomer. ACS Omega 2019, 4, 19777–19786.

(19) Zhang, K.; Nagarajan, V.; Misra, M.; Mohanty, A. K. Super toughened renewable PLA reactive multiphase blends system: Phase morphology and performance. ACS Appl. Mater. Interfaces 2014, 6, 12436–12448.

(20) Oyama, H. T. Super-tough poly (lactic acid) materials: reactive blending with ethylene copolymer. Polymer 2009, 50, 747–751.

(21) Kfouri, G.; Hassouna, F.; Raquez, J.-M.; Toniazzo, V.; Ruch, D.; Dubois, P. Tunable and durable toughening of polylactide materials via reactive extrusion. Macromol. Mater. Eng. 2014, 299, 583–595.

(22) Delgado-Aguilar, M.; Puig, R.; Sazdovski, I.; Fullana-i-Palmer, P. Poly(lactide-co-caprolactone) blends: On the path to circular economy, substituting single-use commodity plastic products. Materials 2020, 13, 2655–2672.

(23) Yang, X.; Liu, S.; Yu, E.; Wei, Z. Toughening of Poly (L-Lactide) with branched polycaprolactone: Effect of chain length. ACS Omega 2020, 5, 29284–29294.

(24) Bian, X.; Zhang, B.; Sun, Z.; Xiang, S.; Li, G.; Chen, X. Synthesis of multi-arm poly (lactide) and its modification on linear polylactide. Polym. Bull. 2017, 74, 245–262.

(25) Su, S.; Kopitzky, R.; Tolga, S.; Kabasci, S. Polylactide (PLA) and its blends with poly (butylene succinate) (PBS): A brief review. Polymer 2019, 11, 1193–1213.

(26) Teaminsungvon, A.; Ruksakulpiwat, Y.; Jarukumjorn, K. Preparation and characterization of poly (lactic acid) / poly (butylene adipate-co-terephthalate) blends and their composite. Polym.-Plast. Technol. Eng. 2013, 52, 1362–1367.

(27) Deng, Y.; Yu, C.; Wongwiwattana, P.; Thomas, N. L. Optimizing ductility of Poly (Lactic Acid)/Poly (butylene adipate-co-terephthalate) blends through co-continuous phase morphology. J. Polym. Environ. 2018, 26, 3802–3816.

(28) Andrzjejski, J.; Cheng, J.; Anstey, A.; Mohanty, A. K.; Misra, M. Development of toughened blends of poly (lactic acid) and poly (butylene adipate-co-terephthalate) for 3D printing applications: compatibilization methods and material performance evaluation. ACS Sustainable Chem. Eng. 2020, 8, 6576–6589.

(29) Krishnaswamy, R. K. Toughening of polylactic acid with polyhydroxyalkanoates. AU2011256260 A1, 2011.

(30) Oyama, H. T. Super-tough poly (lactic acid) materials: reactive blending with ethylene copolymer. Polymer 2009, 50, 747–751.

(31) Suk, S.; Kopitzky, R.; Tolga, S.; Kabasci, S. Polylactide (PLA) and its blends with poly (butylene succinate) (PBS): A brief review. Polymer 2019, 11, 1193–1213.

(32) Yang, X.; Liu, S.; Yu, E.; Wei, Z. Toughening of Poly (L-Lactide) with branched polycaprolactone: Effect of chain length. ACS Omega 2020, 5, 29284–29294.

(33) Bian, X.; Zhang, B.; Sun, Z.; Xiang, S.; Li, G.; Chen, X. Synthesis of multi-arm poly (lactide) and its modification on linear polylactide. Polym. Bull. 2017, 74, 245–262.

(34) Su, S.; Kopitzky, R.; Tolga, S.; Kabasci, S. Polylactide (PLA) and its blends with poly (butylene succinate) (PBS): A brief review. Polymer 2019, 11, 1193–1213.

(35) Yang, X.; Liu, S.; Yu, E.; Wei, Z. Toughening of Poly (L-Lactide) with branched polycaprolactone: Effect of chain length. ACS Omega 2020, 5, 29284–29294.

(36) Oyama, H. T. Super-tough poly (lactic acid) materials: reactive blending with ethylene copolymer. Polymer 2009, 50, 747–751.

(37) Su, S.; Kopitzky, R.; Tolga, S.; Kabasci, S. Polylactide (PLA) and its blends with poly (butylene succinate) (PBS): A brief review. Polymer 2019, 11, 1193–1213.

(38) Yang, X.; Liu, S.; Yu, E.; Wei, Z. Toughening of Poly (L-Lactide) with branched polycaprolactone: Effect of chain length. ACS Omega 2020, 5, 29284–29294.
Sun, Z.; Xiang, S.; Li, G.; Chen, X. Synthesis of multi-arm poly (L-lactide) and its modification on linear polylactide. *Polym. Bull.* 2017, 74, 245–262.

Pannu, R. K.; Tanodekaew, S.; Li, W.; Collett, J. H.; Attwood, D.; Booth, C. A DSC study of the miscibility of poly(ethylene oxide)-block-poly(dl-lactide) copolymers with poly(dl-lactide). *Biomaterials* 1999, 20, 1381–1387.

Sun, Y.; He, C. Biodegradable “core-shell” rubber nanoparticles and their toughening of poly (lactides). *Macromolecules* 2013, 46, 9625–9633.

Odent, J.; Raquez, J.-M.; Leclère, P.; Lauro, F.; Dubois, P. Crystallization-induced toughness of rubber modified polylactide: Combined effects of biodegradable impact modifier and effective nucleating agent. *Polym. Adv. Technol.* 2015, 26, 814–822.

6s-PCL-b-PLA and 6s-PLA-b-PCL (*M_n* ~ 27,000) when added to PLA (3052D) in 10 wt % concentration reduced the crystallization half-time (*t_1/2*) from 16.2 (PLA) to 12.7 min (for blend B) and 8.2 min (for blend E). Further studies are in progress to confirm the nucleation ability of the six-arm star-branched copolymer additives in the blend. (Unpublished results).

Witzke, D. R. Introduction to Properties, Engineering and Prospects of Polylactide Polymers. Ph.D. Thesis; Michigan State University: East Lansing, MI, 1999; p 389.