

# Synthesis and characterization of well-defined random and block copolymers of $\epsilon$ -caprolactone with L-lactide as an additive for toughening polylactide: Influence of the molecular architecture

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**ABSTRACT:** Well-defined multiarmed star random and block copolymers of  $\epsilon$ -caprolactone with L-lactide with controlled molecular weights, low polydispersities, and precise numbers of arms were synthesized by the ring-opening polymerization of respective cyclic ester monomers. The polymers were characterized by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  to determine their chemical composition, molecular structure, degree of randomness, and proof of block copolymer formation. Gel permeation chromatography was used to establish the degree of branching. Star-branched random copolymers exhibited lower glass-transition temperatures ( $T_g$ 's) compared to a linear random copolymer. When the star random copolymers were melt-blended with poly(L-lactic acid) (PLA), we observed that the elongation of the blend increased with the number of arms of the copolymer. Six-armed block copolymers, which exhibited higher  $T_g$ 's, caused the maximum improvement in elongation. In all cases, improvements in the elongation were achieved with no loss of stiffness in the PLA blends. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43267.

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## INTRODUCTION

Poly(L-lactic acid) (PLA) is the quintessential bioderived, biorenewable, biodegradable, and biocompatible polymer with a unique set of properties unmatched by any other polymer in its class. It is, therefore, not surprising that it has elicited widespread attention from researchers in academia and industry.<sup>1,2</sup> Derived from the simplest of self-polymerizable AB monomers, PLA possesses attractive physical properties, including a high melting temperature ( $T_m$ ), high strength, high modulus, and good optical clarity. However, the polymer is also beset by several drawbacks, namely, poor impact properties, a low elongation at break, a poor melt viscosity, a low heat deflection temperature, and slow rates of crystallization. These drawbacks limit the range of applications accessible to PLA. Consequently, substantial research efforts have been made to devise methods to improve these properties.

Several methods for toughening PLAs have been reported recently in the literature.<sup>3,4</sup> The toughening of glassy and semi-crystalline polymers by melt blending with elastomers has been the most frequently used method for improving the impact properties of brittle polymers. Elastomeric ethylene–butyl acry-

late–glycidyl methacrylate terpolymers,<sup>5</sup> poly(*n*-butyl acrylate)-*g*-PLA,<sup>6</sup> core–shell nanoparticles consisting of Polyhedral oligomeric silsesquioxane–PLA-*b*-Poly(D-lactide),<sup>7</sup> and PLA-grafted elastomer<sup>8</sup> have been reported to improve the toughness of PLA. The majority of these efforts have been made toward the melt blending of PLA with low-glass-transition-temperature ( $T_g$ ) polymers or copolymers derived from monomers such as  $\epsilon$ -caprolactone ( $\epsilon$ -CL), trimethylene carbonate, and  $\delta$ -valerolactone or polymers such as poly(butylene succinate), polyhydroxybutyrate, and linear low-density polyethylene. Although some of these polymers caused improvements in elongation, invariably, this was accompanied by a loss of the modulus of rigidity.<sup>4</sup>

More recently, Odent and coworkers<sup>9,10</sup> examined the toughening ability of random copolymers of  $\epsilon$ -CL with  $\delta$ -valerolactone and with lactic acid. Both these polymers are also biodegradable. A random copolymer of  $\epsilon$ -CL (45 mol %) with  $\delta$ -valerolactone [55 mol %; number-average molecular weight ( $M_n$ ) = 60,000 g/mol] was melt-blended with PLA ( $M_n$  = 95,000 g/mol, 10 wt %). The resulting blend showed a 300% improvement in the impact strength. The random copolymer was an amorphous rubbery

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polymer with a  $T_g$  of  $-80^\circ\text{C}$ . The domain size of the rubber phase in PLA was in the region 400–800 nm. The loss of transparency in the blend was not very significant. In a subsequent study, the same authors demonstrated a similar effect with a random copolymer of  $\epsilon$ -CL with D,L-lactide.<sup>10</sup> A 72:28 mol % poly( $\epsilon$ -caprolactone-*co*-D,L-lactide) copolymer caused a 400% increase in the impact strength. The copolymer had a  $M_n$  of 34,000 g/mol and a  $T_g$  of  $-37^\circ\text{C}$ . The copolymers had a polydispersity of about 2. In both cases, the formation of well-dispersed rubbery microdomains within the PLA matrix was considered to be the cause of the reduced brittleness of PLA.

Recently, the synthesis of well-defined multiarmed star-branched polymers and copolymers of L-lactide (L-LA),  $\epsilon$ -CL, and other cyclic ester monomers have attracted considerable attention.<sup>11–18</sup> In several reviews, researchers have comprehensively surveyed the literature in this area.<sup>19,20</sup> Star-shaped polymers are characterized by a low melt viscosity and a lower  $T_g$  and are less crystalline and more compact in size compared to linear polymers of similar molecular weights. They have found wide applications as rheology modifiers, compatibilizers, macromolecular surfactants, and drug carriers with improved degradation properties under physiological conditions.

We, therefore, reasoned that multiarmed star-branched random and block copolymers of  $\epsilon$ -CL with L-LA would offer some unique advantages as additives in enhancing the toughness of PLAs; these advantages would include an improved segmental miscibility and a better trade-off between the toughness and modulus. So, we synthesized a series of well-defined star-branched random and block copolymers of  $\epsilon$ -CL with L-LA with controlled molecular weights, narrow molecular weight distributions, and well-defined numbers of arms and explored their utility as additives for improving the toughness of PLAs. To the best of our knowledge, there has been only one report in the literature on the use of a multiarmed star-branched polymers of L-LA and  $\epsilon$ -CL as toughening additives for PLA.<sup>21</sup> However, the properties of the poly( $\epsilon$ -caprolactone-*co*-L-lactide) used were poorly characterized.

## EXPERIMENTAL

### Materials

L-LA (Purac, Singapore) was purified by recrystallization from dry ethyl acetate; it was then sublimated under reduced pressure and stored in a glovebox. Tin-2-ethyl hexanoate ( $\text{SnOct}_2$ ; Sigma-Aldrich) was used as received.  $\epsilon$ -CL (Sigma-Aldrich) was dried over calcium hydride for 24 h and vacuum-distilled before use. D-Sorbitol (DS) was purified by recrystallization from aqueous ethanol; it was then dried over vapors of acetone in a Soxhlet apparatus. Dipentaerythritol (DPE), pentaerythritol (PE), trimethylol propane (TMP), and 1-pyrene butanol (1-PB; all from Sigma-Aldrich) were dried at  $30^\circ\text{C}$  *in vacuo* (1 mm of Hg) for 5 h before use. Other reagents and solvents were laboratory-grade products and were used without further purification. Commercially available injection-molding-grade PLA (Ingeo 3052D) from NatureWorks was used as received.

### Preparation of the Six-Armed Star Poly(L-lactide-*co*- $\epsilon$ -caprolactone) Random Copolymer (6s-DS-LA-*co*-CL) with DS as the Initiator

Poly(L-lactide-*co*- $\epsilon$ -caprolactone) random copolymer with six arms was synthesized by the melt-phase ring-opening polymerization of a mixture of L-LA (70 mol %) and  $\epsilon$ -CL (30 mol %) with DS as the initiator in the presence of a catalytic amount of  $\text{SnOct}_2$ . The reaction was carried out in a sealed glass ampule at  $150^\circ\text{C}$  for 12 h. The copolymer obtained was dissolved in dichloromethane containing a small amount of dilute HCl and precipitated with cold methanol. The precipitated copolymer was washed repeatedly with methanol, filtered, and dried in a vacuum oven under reduced pressure at  $30^\circ\text{C}$  until a constant weight was reached.

Other copolymers with three- and four-armed star-shaped random copolymers of L-LA with  $\epsilon$ -CL were synthesized in a similar fashion, but with TMP and PE as initiators. A six-armed star-shaped random copolymer of L-LA with  $\epsilon$ -CL was also synthesized with DPE as the initiator. A linear random copolymer of L-LA and  $\epsilon$ -CL was prepared with 1-PB as the initiator. The details of the copolymer synthesis are shown in Tables I and II.

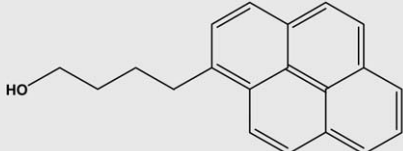
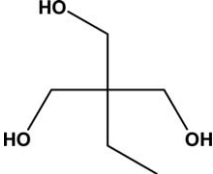
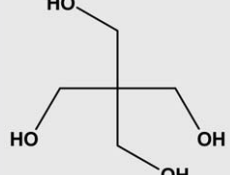
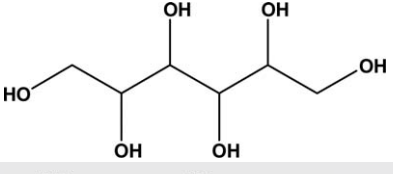
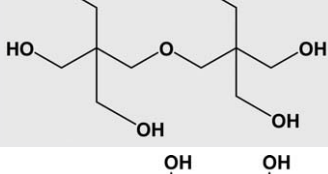
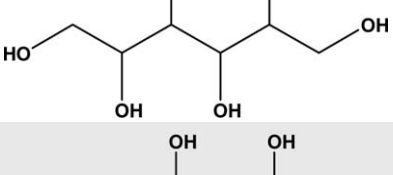
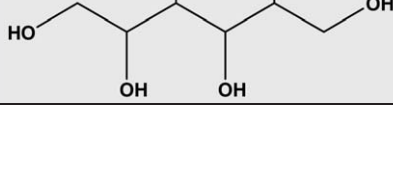
### Preparation of the Six-Armed Star Poly(L-lactide-*block*- $\epsilon$ -caprolactone) Block Copolymer with DS as the Initiator

The synthesis of the poly(LA-*b*-CL) block copolymer was carried out in two steps by sequential addition of monomers. In the first step, star poly(L-lactide) with six arms (6s-DS-PLA) was synthesized by the ring-opening polymerization of L-LA (4 g, 0.028 mol) with DS (35 mg, 0.192 mmol) as the initiator in the presence of a catalytic amount of  $\text{SnOct}_2$ . Polymerization was carried out at  $180^\circ\text{C}$  for 1 h. The polymer obtained was dissolved in dichloromethane and precipitated in cold methanol, filtered, and dried in a vacuum oven under reduced pressure at  $30^\circ\text{C}$  until a constant weight was reached. The purified 6s-DS-PLA was then used as a macroinitiator for the synthesis of the second block. 6s-DS-PLA (2.8 g, 0.13 mmol),  $\epsilon$ -CL (1.2 g, 0.0105 mol), and  $\text{SnOct}_2$  were placed in a glass ampule and held *in vacuo* for 4 h at  $30^\circ\text{C}$ . The glass ampule was sealed *in vacuo* and heated at  $150^\circ\text{C}$  for 12 h. The resulting product was dissolved in dichloromethane, precipitated in cold methanol, and washed with methanol. The polymer was separated by filtration and dried in a vacuum oven under reduced pressure at  $30^\circ\text{C}$  until a constant weight was reached.

### Preparation of the Six-Armed Star Poly( $\epsilon$ -caprolactone-*block*-L-lactide) Block Copolymer with DS as the Initiator

The synthesis of the poly(CL-*b*-LA) block copolymer was carried out in two steps by the sequential addition of monomers. In first step, star poly( $\epsilon$ -caprolactone) with six arms (6s-DS-PCL) was synthesized by the ring-opening polymerization of  $\epsilon$ -CL (4 g, 0.035 mol) with DS (80 mg, 0.44 mmol) as the initiator in the presence of a catalytic amount of  $\text{SnOct}_2$ . The reaction was carried out in a sealed glass ampule at  $150^\circ\text{C}$  for 10 h. The polymer obtained was dissolved in dichloromethane and precipitated in cold methanol, filtered, and dried in a vacuum oven under reduced pressure at  $30^\circ\text{C}$  until a constant weight was reached. The purified 6s-DS-PCL was used as a macroinitiator for the synthesis of the second block. 6s-DS-PCL (1.2 g, 0.13 mmol), L-LA (2.8 g, 0.019 mol), and  $\text{SnOct}_2$  were placed in a glass ampule

**Table I.** Polymers Synthesized in This Study

Entry	Sample code	Initiator	Number of arms	Copolymer sequence
1	LA-co-CL		Linear	Random
2	3s-LA-co-CL		3	Random
3	4s-LA-co-CL		4	Random
4	6s-DS-LA-co-CL		6	Random
5	6s-DPE-LA-co-CL		6	Random
6	6s-DS-LA-b-CL		6	Block
7	6s-DS-CL-b-LA		6	Block

and held *in vacuo* for 4 h at 30°C. The glass ampule was sealed *in vacuo* and heated at 150°C for 12 h. The resulting product was dissolved in dichloromethane, precipitated in cold methanol, and washed with methanol. The polymer was separated by filtration and dried in a vacuum oven under reduced pressure at 30°C until a constant weight was reached.

#### Melt Blending of PLA with Multiarmed Star Random and Block Copolymers

PLA (Ingeo 3052D) pellets were dried for a 12 h at 45°C in a vacuum oven under reduced pressure. Just before melt blending,

PLA pellets were fluidized in a glass tube under a flow of dry nitrogen (dynamic drying) for 3 h at 45°C. The resulting PLA pellets were melt-blended with 10 wt % vacuum oven-dried random and block copolymers with a DSM Micro 5 twin-screw microcompounder at 180°C for 5 min at a screw speed of 100 rpm. The melt-blended extrudate was cut into small pieces and compression-molded in a hot press (Technosearch Instrument, model PF 15) at 180°C under pressure of 50 kg/cm<sup>2</sup> for 5 min. The samples were cooled to 30°C. The thicknesses of the films were uniformly maintained between 0.11 and 0.12 mm. This was ensured with a Teflon mold 100 mm in diameter and

**Table II.** Synthesis and Molecular Properties of the Poly(LA-co-CL) Copolymers

Entry	Sample code	Yield (%)	$[\eta]$ (dL/g) <sup>a</sup>	LA/CL (mol %) <sup>b</sup>	$M_n$ (g/mol) <sup>c</sup>	$M_w$ (g/mol)	Polydispersity index	$I_{\text{eff}}^d$	$g^e$	$g^{1/2 f}$	$g^{1/2}/g'$
1	PLA (Ingeo 3052D)	—	1.03	—	93,700	143,900	1.54	—	—	—	—
2	LA-co-CL <sup>g</sup>	90	0.55	72:28	27,100	31,700	1.17	0.90	—	—	—
3	3s-LA-co-CL <sup>g</sup>	84	0.53	71:29	27,900	32,900	1.18	0.93	0.96	0.95	0.99
4	4s-LA-co-CL <sup>g</sup>	86	0.50	73:27	27,100	31,700	1.17	0.90	0.91	0.89	0.98
5	6s-DS-LA-co-CL <sup>g</sup>	96	0.46	71:29	27,890	33,900	1.20	0.93	0.84	0.8	0.96
6	6s-DPE-LA-co-CL <sup>g</sup>	91	0.42	69:31	28,800	33,050	1.15	0.96	0.77	0.8	1.03
7	6s-DS-LA-co-CL (50:50) <sup>g</sup>	82	0.48	50:50	28,600	33,000	1.15	0.95	0.87	0.8	0.92
8	6s-DS-LA-b-CL <sup>h</sup>	72	0.46	73:27	27,750	32,800	1.18	0.72 <sup>j</sup>	0.84	0.8	0.95
9	6s-DS-CL-b-LA <sup>i</sup>	83	0.45	72:28	27,630	31,640	1.15	0.92	0.82	0.8	0.98

$M_w$ , weight-average molecular weight; CL, caprolactone,  $I_{\text{eff}}$  initiator efficiency.

<sup>a</sup> Measured with a viscosity detector in GPC (triple-detector system).

<sup>b</sup> Calculated from <sup>1</sup>H-NMR spectroscopy.

<sup>c</sup> Determined by GPC.

<sup>d</sup>  $I_{\text{eff}} = M_n^{\text{experimental}}/M_n^{\text{theoretical}}$ .

<sup>e</sup>  $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$ .  $[\eta]_{\text{star}}$ : Intrinsic viscosity of star polymer;  $[\eta]_{\text{linear}}$ : Intrinsic viscosity of linear polymer.

<sup>f</sup>  $g = 6f/(f+1)(f+2)$ , where  $f$  is the number of arms.

<sup>g</sup>  $[I]/[M] = 1:1.16$ .  $[I]$ : Initiator concentration  $[M]$ : Monomer concentration.

<sup>h</sup>  $[I]/[M] = 1:80$ .

<sup>i</sup>  $[I]/[M] = 1:208$ .

<sup>j</sup> Values corrected for conversion.

0.12 mm in thickness. Dumbbell-shaped test specimens were punched out from the compression-molded films.

### Characterization of the Multiarmed Random and Block Copolymers

Measurements of the molecular weight, molecular weight distribution, and degree of branching were performed with an advanced multidetector gel permeation chromatograph (Viscotek and Waters) consisting of a right-angle light-scattering and low-angle light-scattering detector (Viscotek, TDA max) and a concentration detector (refractive index or UV, Waters). A bridge viscometer was also used to determine the intrinsic viscosities of the polymers. The gel permeation chromatograph was equipped with three Styragel HT tetrahydrofuran column series (HT2, HT4, and HT5; molecular weight range = 2000–600,000 g/mol). Samples for gel permeation chromatography (GPC) were prepared with concentrations of 4–5 mg/ml in (High-Performance Liquid Chromatography) HPLC-grade tetrahydrofuran. Well-stirred solutions were filtered through a 0.22- $\mu\text{m}$  Millipore filter three times before injection. The injection volume was 100  $\mu\text{L}$ , and the flow rate was maintained at 1 mL/min. OmniSEC 4.7 software was used to control the sample injection sequence and solvent delivery and for acquisition and calculation of the data.

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded in CDCl<sub>3</sub> with a Bruker DRX spectrometer at a frequency of 400 or 500 MHz.

Fourier transform infrared spectroscopy was performed on a PerkinElmer spectrum GX spectrometer. The copolymer samples were dissolved in HPLC-grade CHCl<sub>3</sub> (2 mg/mL), and the spectra were recorded as a film with a NaCl cell. For the measurement of the IR transmittance, polymer films 0.11 mm in thickness were used.

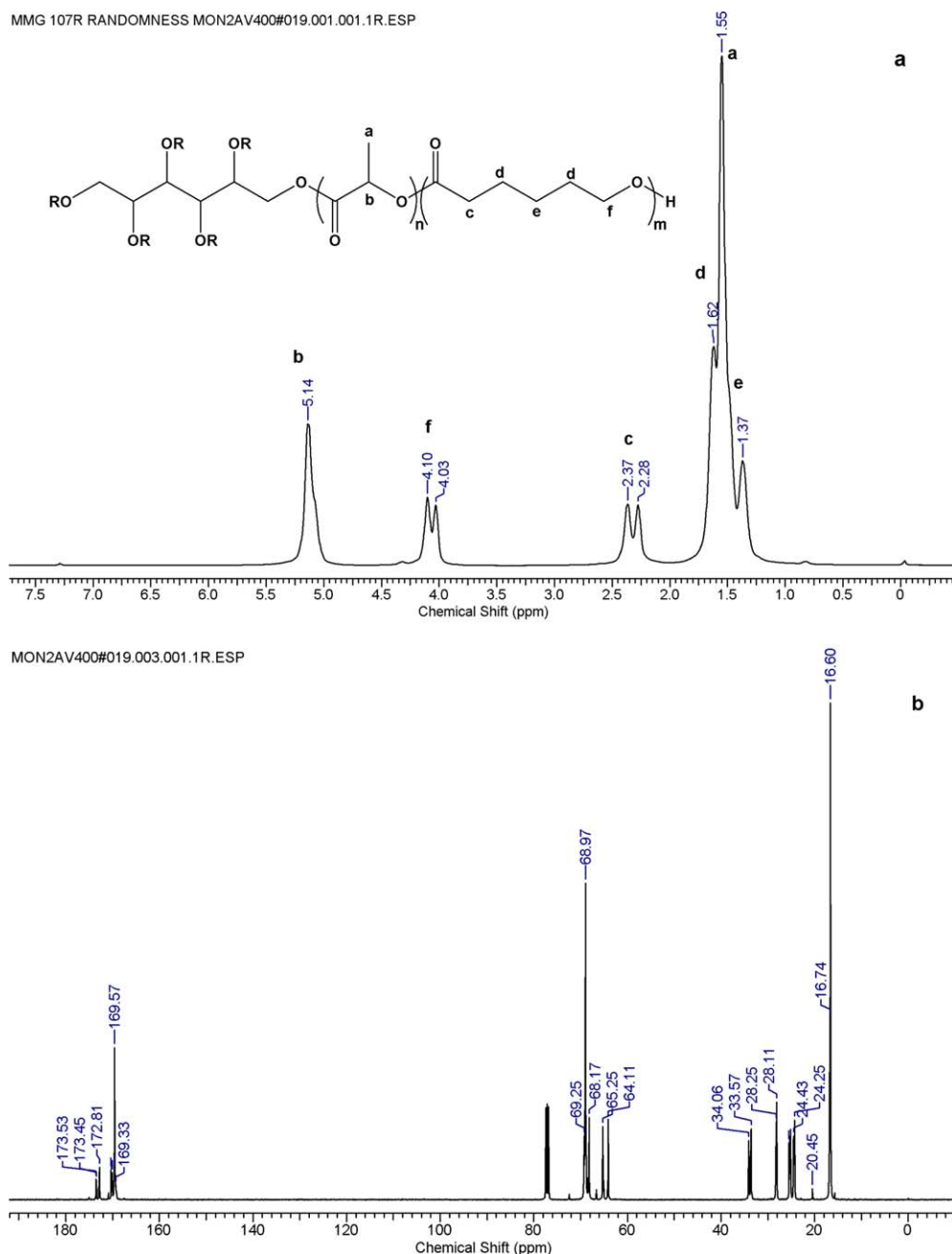
Thermal analysis was performed with a differential scanning calorimeter (DSC Q100, TA Instruments) equipped with a refrigerated cooling system. The  $T_g$ , crystallization temperature, enthalpy of crystallization,  $T_m$ , and melting enthalpy were calculated from the differential scanning calorimetry (DSC) curves. DSC measurements were carried out through the heating of the polymer samples from  $-90$  to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ ; this was followed by the cooling of the sample to  $-90^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , maintenance for 1 min at  $-90^\circ\text{C}$ , and then the repetition of the previous heating cycle. All of the measurements were carried out under a nitrogen atmosphere, and the results presented are from the second heating cycle.

Tensile property measurements were performed on a Linkam Scientific Instruments tensile tester (TST-350) with a 200-N load cell at a crosshead speed of 10  $\mu\text{m}/\text{s}$ . The reported values are an average of at least five to six measurements.

## RESULTS AND DISCUSSION

### Synthesis of the Multiarmed Star Poly(L-lactide-co- $\epsilon$ -caprolactone) Copolymers

Well-controlled linear poly(L-lactide-co- $\epsilon$ -caprolactone) copolymers and multiarmed star poly(L-lactide-co- $\epsilon$ -caprolactone) random and block copolymers with three, four, and six arms were prepared by the ring-opening polymerization of L-LA and  $\epsilon$ -CL with 1-PB, TMP, PE, and DPE as monofunctional, trifunctional, tetrafunctional, and hexafunctional initiators, respectively. Six-armed branched polymers were also prepared with DS as an initiator. Linear poly(L-lactide-co- $\epsilon$ -caprolactone) random copolymer, a four-armed star poly(L-lactide-co- $\epsilon$ -caprolactone) random copolymer (PE initiator), and a six-armed star poly( $\epsilon$ -



**Figure 1.** (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR spectra (400 MHz) of the 6s-DS-LA-co-CL in  $\text{CDCl}_3$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

caprolactone-*b*-*l*-lactide) block copolymer (DPE initiator) have been previously reported in the literature.<sup>13–15,21,22</sup>

The chemical structure of the multiarmed star copolymers was confirmed by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy. Figure 1 shows the  $^1\text{H}$ -NMR spectrum of 6s-DS-LA-co-CL; it showed peaks at 1.55 ppm, corresponding to  $-\text{CH}_3$  of LA (peak a), and 5.14 ppm, corresponding to  $-\text{CH}$  of LA (peak b). The peak due to  $-\text{CH}_2$  of  $\epsilon$ -CL (peak f) was observed at 4.03–4.10 ppm and that due to  $\text{CH}_2$  of  $\epsilon$ -CL (peak c) was observed at 2.28–2.37 ppm. The peaks corresponding to  $\text{CH}_2$  (peak d) and  $\text{CH}_2$  (peak e) of  $\epsilon$ -CL appeared at 1.61 and 1.37 ppm, respectively. The

copolymers 3s-LA-co-CL [3 star (arm) *l*-lactide-co- $\epsilon$ -caprolactone random copolymer], 4s-LA-co-CL [4 star (arm) *l*-lactide-co- $\epsilon$ -caprolactone random copolymer], and 6s-DPE-LA-co-CL [6 star (arm) *l*-lactide-co- $\epsilon$ -caprolactone random copolymer] also exhibited similar peaks in their  $^1\text{H}$ -NMR spectra (see Figure S1–S6, Supporting Information). The  $^1\text{H}$ -NMR spectrum of the linear copolymer *l*-lactide-co- $\epsilon$ -caprolactone random copolymer was in agreement with that reported in literature<sup>23</sup> (see Figure S7 and S8, Supporting Information). The comonomer composition of the copolymers were calculated from the  $^1\text{H}$ -NMR spectrum through integration of the protons because of lactide's (LA's)

**Table III.** Compositions and Sequence Distributions of the Comonomers in Multiarmed Star Copolymers of L-LA and  $\epsilon$ -CL

Entry	Sample code	LA/CL (mol % in the feed)	LA/CL (mol % in the polymer)	$L_{LA}^a$	$L_{CL}^a$	$R_H^b$	$R_C^c$
1	LA-co-CL	70:30	72:28	2.85	1.63	0.97	0.94
2	3s-LA-co-CL	70:30	71:29	3.33	1.50	0.97	0.97
3	4s-LA-co-CL	70:30	73:27	3.34	1.66	0.91	0.91
4	6s-DS-LA-co-CL	70:30	71:29	3.50	1.40	1.0	0.94
5	6s-DPE-LA-co-CL	70:30	69:31	3.26	1.50	0.97	0.93
6	6s-DS-LA-co-CL (50:50)	50:50	50:50	2.08	1.93	0.91	0.96

CL, caprolactone.

<sup>a</sup>Determined from <sup>1</sup>H-NMR spectroscopy.

<sup>b</sup>Degree of randomness calculated by <sup>1</sup>H-NMR spectroscopy.

<sup>c</sup>Degree of randomness calculated by <sup>13</sup>C-NMR spectroscopy.

methine group (peak b, Figure 1) and  $\epsilon$ -CL's methylene group (peak c, Figure 1). The comonomer composition obtained from NMR was in good agreement with the feed ratio (Table III). The number-average sequence lengths of L-LA ( $L_{LA}$ ) and  $\epsilon$ -CL ( $L_{CL}$ ) and the degree of randomness in the multiarmed star-shaped poly(L-lactide-co- $\epsilon$ -caprolactone) copolymers were determined by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR with a method reported in the literature.<sup>24–27</sup> All of the copolymers were found to be truly random (Table III, entries 1–6). The absolute molecular weights of the multiarmed star random copolymers of L-LA and  $\epsilon$ -CL were determined with a GPC multidetector. All of the copolymers were found to have a low polydispersity with an initiator efficiency of about 0.90; this indicated that the polymerization reactions were well controlled (Figure 2 and Table II, entries 2–7). The number-average branches per molecule of multiarmed star-shaped poly(L-LA-co- $\epsilon$ -CL) random copolymers were determined from Mark–Houwink plots (see Figure S9–S13 and S22, Supporting Information) of the branched copolymers and the corresponding linear copolymers with similar  $M_n$ 's (Table IV, entries 1–6). The value of  $g^{1/2}/g'$  where  $g$  is branching ratio defined as,  $g = 6f/[(f+1)(f+2)]$  and  $g^{1/2} = \{6f/[(f+1)(f+2)]\}^{1/2}$  where  $f$  is number of arms.  $g'$  = ratio of Intrinsic viscosity of star polymer,

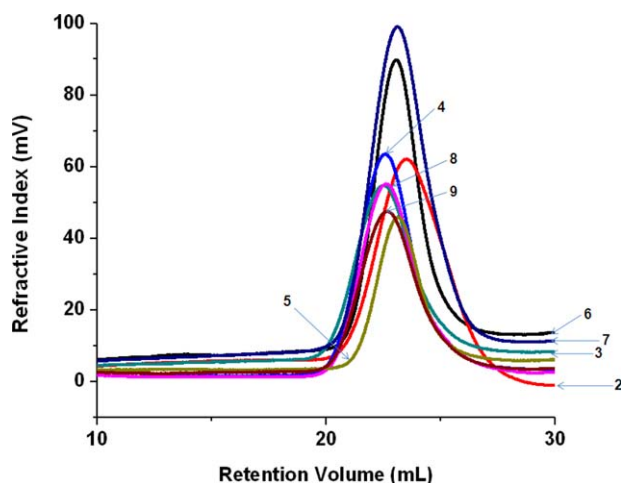
$[\eta]_{star}/$ intrinsic viscosity of linear polymer,  $[\eta]_{linear}$  (Table II, entries 3–7) was determined according to methods reported in the literature.<sup>16</sup>

#### Synthesis of the Six-Armed Star Poly(CL-*b*-LA) and Poly(LA-*block*-CL) Block Copolymers with DS as the Initiator

The 6s-DS-CL-*b*-LA 6 star (arm)  $\epsilon$ -caprolactone-block-L-lactide block copolymer was synthesized through adoption of a procedure reported in the literature and through the replacement of DPE with DS as the initiator.<sup>13–15</sup> The reaction was well controlled, as evidenced by the low polydispersity index of 1.15 and the initiator efficiency of 0.92. The chemical structure and comonomer composition were determined by <sup>1</sup>H-NMR with the spectral assignments reported in the literature.<sup>13–15</sup>

During the synthesis of 6s-DS-CL-*b*-LA, L-LA polymerization was initiated by a six-armed star macroinitiator bearing terminal primary hydroxyl groups. Primary hydroxyl groups are known to be reactive initiators for the ring-opening polymerization of L-LA. Surprisingly, we could also synthesize a six-armed star block copolymer with a reverse block sequence, namely, 6s-DS-LA-*b*-CL, where the macroinitiator possessed secondary hydroxyl groups. Secondary hydroxyl groups are believed to be less reactive as initiators. This led to the slow polymerization of  $\epsilon$ -CL (lower yields, lower initiator efficiency). However, the polydispersity values were low (1.18). A block copolymer with such a sequence has not been reported so far in the literature.

The chemical structure and comonomer compositions of the 6s-DS-CL-*b*-LA and 6s-DS-LA-*b*-CL copolymers were determined by <sup>1</sup>H-NMR analysis. The spectra of the 6s-DS-PCL macroinitiator and 6s-DS-CL-*b*-PLA were essentially similar to that reported earlier for a six-armed star poly(CL-*b*-LA) prepared with DPE as the initiator<sup>13–15</sup> (see Figure S14–S17, Supporting Information). The  $M_n$  of the PCL block was 8980 g/mol, and that of the PLA block was 18,650 g/mol (see Table S1 and Figure S19, Supporting Information). The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the 6s-DS-PLA macroinitiator are shown in Figures 3(a) and 4(a), respectively. The signal due to the methylene proton [peak e, Figure 3(a)] of the DS initiator was detected at 4.06–4.07 ppm. The large peaks at 1.57 ppm and 5.13–5.19 ppm were attributed to the methyl [–CH<sub>3</sub>, peak a, Figure 3(a)] and –CH protons of PLA, respectively, whereas the two small peaks at 1.30 ppm and



**Figure 2.** GPC of multiarmed star random and block copolymers of L-LA and  $\epsilon$ -CL (numbers 2–9 refer to the polymers in entries 2–9 in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table IV.** Determination of the Branching Parameters of the Random and Block Copolymers

Entry	Sample code	Average number of branches per molecule	Branching frequency	$R_h$ (nm) <sup>a</sup>	$R_g$ (nm) <sup>b</sup>	$\alpha^c$	Log K
1	LA-co-CL	—	—	7.2	9.4	0.66	-3.1
2	3s-LA-co-CL	2.8	1.4	6.5	8.5	0.74	-3.6
3	4s-LA-co-CL	3.8	1.5	6.2	8.1	0.68	-3.3
4	6s-DS-LA-co-CL	5.8	2.1	6.0	7.9	0.58	-2.9
5	6s-DPE-LA-co-CL	5.7	2.4	5.9	7.7	0.70	-3.6
6	6s-DS-LA-co-CL (50:50)	5.5	4.2	6.3	8.3	0.63	-3.2
7	6s-DS-LA-b-CL	5.8	2.2	6.0	7.9	0.56	-2.8
8	6s-DS-CL-b-LA	5.6	2.4	5.9	7.8	0.65	-3.3

K is Mark-Houwink constant for respective polymer determined by GPC.

<sup>a</sup>Hydrodynamic radius of the copolymer determined by GPC (triple detector).

<sup>b</sup>Radius of the gyration of the copolymer determined by GPC.

<sup>c</sup>Mark-Houwink constant determined by GPC.

the quartet at 4.32–4.37 ppm were due to the terminal methyl [—CH<sub>3</sub>, peak c, Figure 3(a)] and —CH—OH [peak d, Figure 3(a)] protons of PLA, respectively. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectrum of the 6s-DS-LA-b-CL copolymer is shown in Figures 3(b) and 4(b), respectively. We observed that the proton signals due to terminal methyl (—CH<sub>3</sub>, peak c, Figure 3(a)) and —CH—OH [peak d, Figure 3(a)] protons of the macroinitiator 6s-DS-PLA disappeared, and instead, four new peaks assigned to different —CH<sub>2</sub> protons of the PCL block [peaks c–f, Figure 3(a)] appeared. This confirmed that the PCL blocks were able to grow from the secondary hydroxyl bearing the 6s-DS-PLA macroinitiator. There was a weak singlet at 4.30 ppm; this was due to either the end group protons of  $\epsilon$ -CL or the secondary alcohol group of the unreacted macroinitiator.

The  $M_n$  of the PLA block was 19,900 g/mol, and that of the PCL block was 7900 g/mol (see Table S1 and Figure S18, Supporting Information). The number-average degree of branching of both six-armed star-shaped 6s-DS-CL-b-LA and 6s-DS-LA-b-CL block copolymers were determined as before from the Mark–Houwink plots of the branched copolymers and the similar  $M_n$  of the corresponding linear copolymer (see Figure S20–S22, Supporting Information). The results are shown in Table IV (entry 7, 8). The value of  $g^{1/2}/g'$  given in Table II (entry 8, 9) was determined according to the methods reported in the literature.<sup>16</sup>

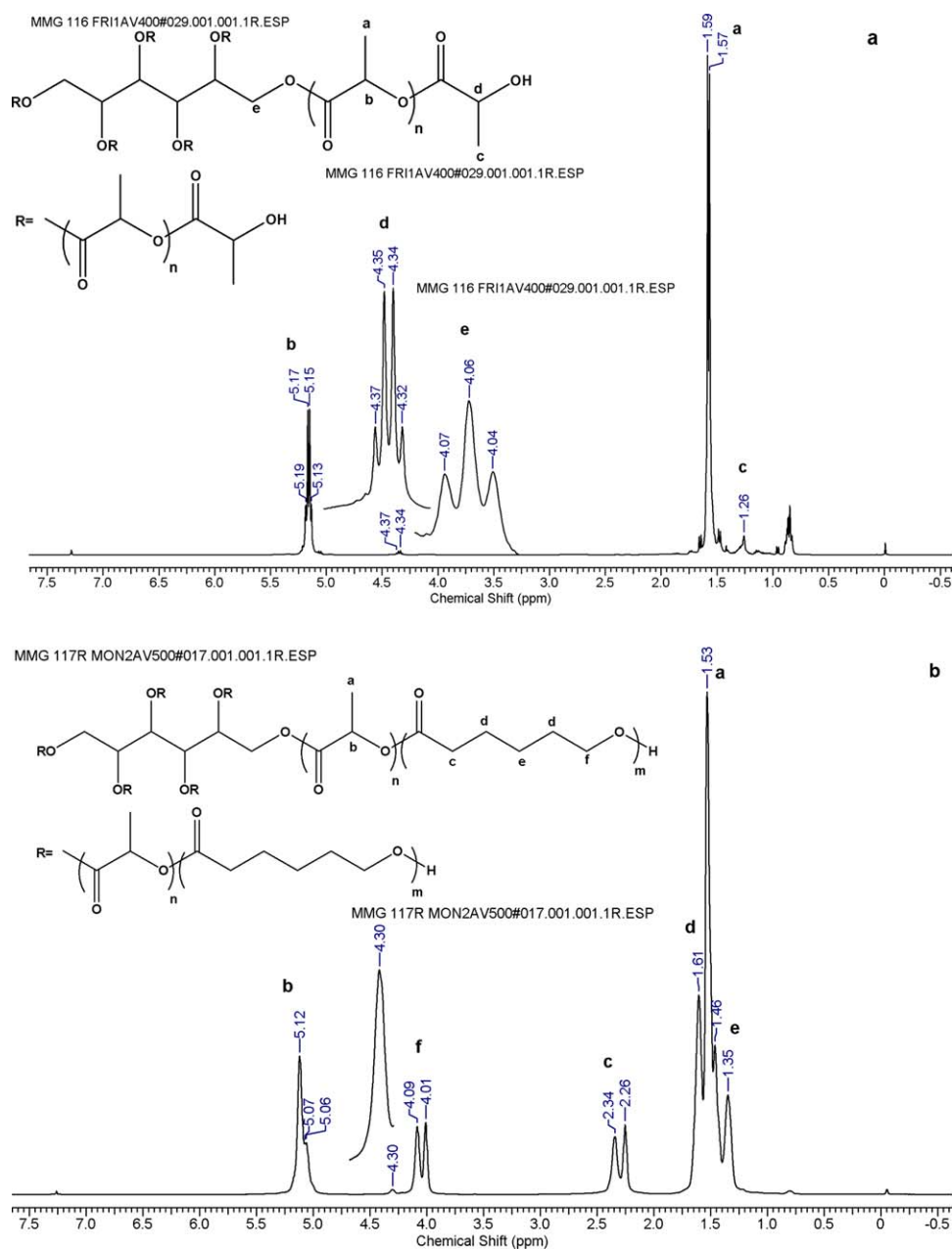
#### Thermal Properties of the Multiarmed Star Random and Block Copolymers of $\epsilon$ -CL and L-LA

The  $T_g$  values of the multiarmed star LA-co-CL random copolymers are shown in Table V and Figure 5. All of the polymers had similar  $M_n$ 's, polydispersities, and comonomer compositions (except the one polymer sample in entry 7, Table V); this made comparisons of  $T_g$  reliable. The linear random copolymer, LA-co-CL, exhibited a  $T_g$  of 25°C. This value was in agreement with what was predicted on the basis of the Flory–Fox equation (see Figure S23, Supporting Information). The  $T_g$ 's of the linear copolymers of LA-co-CL reported earlier in the literature showed deviations from the Flory–Fox equation.<sup>10</sup>  $T_g$  progressively decreased with increasing number of arms (entries 3–5, Table V).  $T_g$  of a six-armed random copolymer with DPE as the core was slightly lower than the corresponding star

polymer prepared with DS as the core; this indicated that the structure of the core had a small but perceptible effect on  $T_g$ . As expected, an increase in the content of  $\epsilon$ -CL from 30 to 50 mol % caused the  $T_g$  to decrease from 0.2 to -30°C. None of the random copolymers showed any melting or crystallization peaks; this indicated that the polymers were amorphous in nature.

The macroinitiator 6s-DS-PLA exhibited a  $T_g$  of 57°C and a  $T_m$  of 164°C. The macroinitiator 6s-DS-PCL exhibited a  $T_g$  of -58°C and a  $T_m$  of 54°C. These values were similar to those of the corresponding homopolymer. The six-armed block copolymers, namely, 6s-DS-LA-b-CL and 6s-DS-CL-b-LA, showed significantly higher  $T_g$ 's than the corresponding random copolymer. 6s-DS-LA-b-CL did not show any crystalline melting transition for either of the blocks. On the contrary, 6s-DS-CL-b-LA, where the crystallizable PLA segment was away from the core, showed a  $T_m$  for the PLA block and a  $T_m$  for the PCL block.

The crystallization behavior of the six-armed 6s PCL-b-PLA block copolymer prepared with DPE as the initiator has been previously investigated, as reported in the literature.<sup>13–15</sup> The observed changes were attributed to both the molecular architecture and the degree of polymerization in the individual block segments. Increases in the PLA block length suppressed the ability of the PCL block to crystallize. A 60:40 mol % six-armed PLA–PCL block copolymer ( $M_n$  = 63,530 g/mol, PCL block = 20,000 g/mol, PLA block = 43,530 g/mol) prepared with DPE as the initiator showed a  $T_m$  for PLA and no  $T_m$  for PCL. The copolymer did not exhibit a  $T_g$ . The longer crystallizable PLA outer segment was believed to constrain the inner PCL block from crystallizing. In the copolymers synthesized in this study with DS as the initiator, the PLA content was even higher; however,  $M_n$  of the copolymer and  $M_n$  of the individual blocks were lower ( $M_n$  = 27,000 g/mol, PCL block = 9000 g/mol, PLA block = 18,000 g/mol). When the shorter PCL segment constituted the outer segment, the copolymer did not exhibit any melting transition but only a  $T_g$  of 11°C for the PLA block. However, when the longer PLA segment constituted the outer segment, the copolymer showed weak melting transitions for PCL ( $T_m$  = 51.5°C, percentage crystallinity = 0.4) and for the PLA block ( $T_m$  = 148.6°C, percentage



**Figure 3.** <sup>1</sup>H-NMR spectra (400/500 MHz) of (a) 6s-DS-PLA and (b) 6s-DS-LA-*b*-CL in CDCl<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

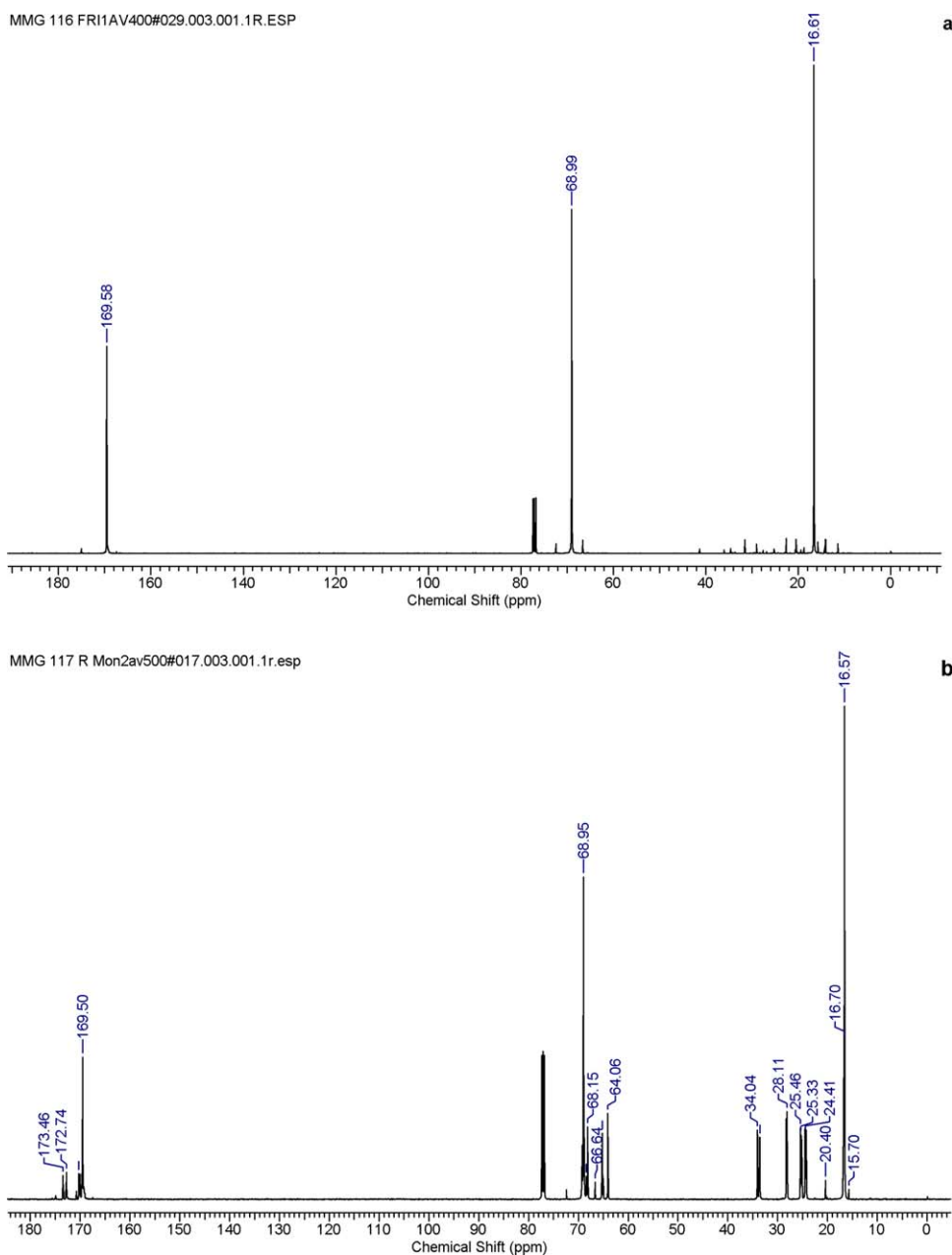
crystallinity = 20) and  $T_g$ 's of 20°C for the PLA block and -56°C for the PCL block (Figure 6). This implied that the shorter amorphous outer PCL block segment prevented the crystallization of the inner PLA segment. However, when the outer block was a crystallizable PLA segment, the inner amorphous PCL segments also underwent crystallization.

#### Influence of Melt-Blended Multiarmed Star Random and Block Copolymers of $\epsilon$ -CL and LA with PLA on the Mechanical Properties of the Blend

To examine the influence of the multiarmed star random and block copolymers of L-LA and  $\epsilon$ -CL on the mechanical properties of PLA, a commercially available injection-molding grade of

PLA (Ingeo 3052D) was melt-blended with various random and block copolymers (10 wt %). Adequate precautions were taken to dry the polymers thoroughly to prevent any hydrolytic degradation during melt blending. The absence of degradation was confirmed by the measurement of intrinsic viscosity of polymer [ $\eta$  intrinsic viscosity of polymer.] before and after the extrusion of the commercial-grade PLA (before extrusion,  $[\eta] = 1.03$  dL/g, and after extrusion,  $[\eta] = 0.99$  dL/g). All of the copolymers used for blending with PLA had similar  $M_n$ 's and comonomer compositions; this made property comparisons more reliable. The addition of random and block copolymers in the specified ratio did not affect the  $T_m$  of PLA (see Figure S24, Supporting Information).





**Figure 4.**  $^{13}\text{C}$ -NMR spectra (400 MHz) of (a) 6s-DS-PLA and (b) 6s-DS-LA-*b*-CL in  $\text{CDCl}_3$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The effects of the number of arms, comonomer composition, and sequence of enchainment of the monomers on the mechanical properties of PLA blended with the appropriate star copolymers are shown in Tables V. In all cases,  $M_n$  and the comonomer composition were held constant to enable comparison of results. As the number of arms in the star random copolymer of  $\epsilon$ -CL and L-LA increased, the elongation increased with no change in the values of the modulus. The nature of the core did not make any difference (Table V, entries 5 and 6). An increase in the content of  $\epsilon$ -CL in a six-armed star random copolymer resulted in an increase in the elongation with no change in the modulus. The six-armed block copolymers

showed a small improvement in the properties compared to random copolymers with six arms. The sequence of the comonomer in the block had a negligible effect. These results are depicted in Figure 7.

The blending of the multiarmed star random and block copolymers with PLA caused a progressive decrease in the light transmittance. An increase in the  $\epsilon$ -CL fraction in random copolymers and the placement of comonomers in a block sequence led to a greater loss of transparency (Table V, entries 7–9). Interestingly, the same copolymers also caused the largest increase in elongation. This indicated that the microphase separation of multiarmed star block copolymers had a beneficial

**Table V.** Thermal and Mechanical Properties of PLA Melt-Blended with Multiarmed Star-Shaped Random and Block Copolymers

Entry	Blend component	PLA/blend component	$T_g$ (°C) <sup>a</sup>	Modulus (MPa) <sup>b</sup>	Yield stress (MPa) <sup>b</sup>	Yield strain (%) <sup>b</sup>	Elongation (%) <sup>b</sup>	Transmittance (%; IR) <sup>c</sup>
1	— <sup>d</sup>	100:00	61.0	20.2 ± 0.8	46.6 ± 1.0	2.2 ± 0.1	6.8 ± 0.5	100
2	LA-co-CL	90:10	25.0	22.3 ± 0.7	53.5 ± 1.2	2.5 ± 0.3	9.0 ± 0.5	100
3	3s-LA-co-CL	90:10	12.5	20.7 ± 1.0	51.1 ± 1.0	2.3 ± 0.2	10.5 ± 1.0	98.5
4	4s-LA-co-CL	90:10	2.5	21.2 ± 0.9	48.0 ± 0.6	2.3 ± 0.2	11.9 ± 1.1	99.0
5	6s-DS-LA-co-CL	90:10	0.2	21.8 ± 1.0	43.9 ± 0.9	2.3 ± 0.4	12.8 ± 0.9	98.5
6	6s-DPE-LA-co-CL	90:10	-3.5	20.2 ± 0.6	41.9 ± 0.9	2.1 ± 0.4	12.6 ± 0.8	96.5
7	6s-DS-LA-co-CL (50:50)	90:10	-30.0	21.2 ± 1.0	48.1 ± 0.9	2.4 ± 0.3	14.0 ± 0.9	93.5
8	6s-DS-LA-b-CL	90:10	11.0	21.7 ± 0.8	42.9 ± 0.6	2.3 ± 0.4	14.4 ± 1.2	94.3
9	6s-DS-CL-b-LA <sup>e</sup>	90:10	20.0	22.7 ± 0.9	45.0 ± 1.1	2.1 ± 0.2	13.6 ± 0.9	94.0

<sup>a</sup>For random and block copolymers.

<sup>b</sup>Mechanical properties of PLA melt-blended with multiarmed star random and block copolymers (10 wt %) of L-LA and ε-CL.

<sup>c</sup>The transmittance of the virgin PLA film was set to 100%, and all other samples were measured with respect to the virgin PLA film. The film thickness was 0.11 mm.

<sup>d</sup>PLA (Ingeo 3052D).

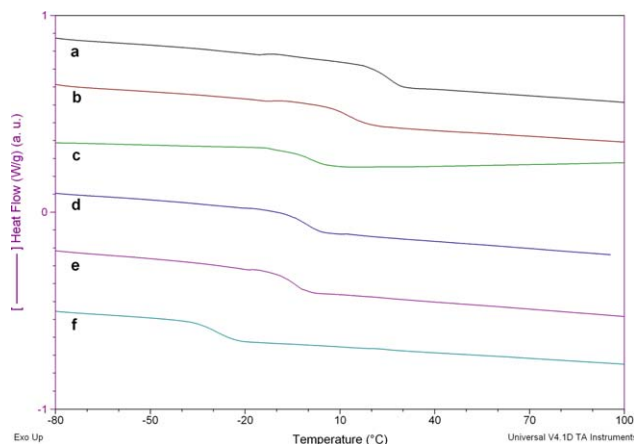
<sup>e</sup> $T_m$  for the PCL block = 51.5°C ( $\Delta H_m = 0.5$  J/g).  $T_m$  for the PLA block = 148.6°C ( $\Delta H_m = 18.9$  J/g).  $T_g$  for the PCL block = -56°C.

effect on the properties of the blends. In all cases, an increase in the elongation was observed without a loss in the rigidity. This is a desirable attribute of a useful impact modifier.

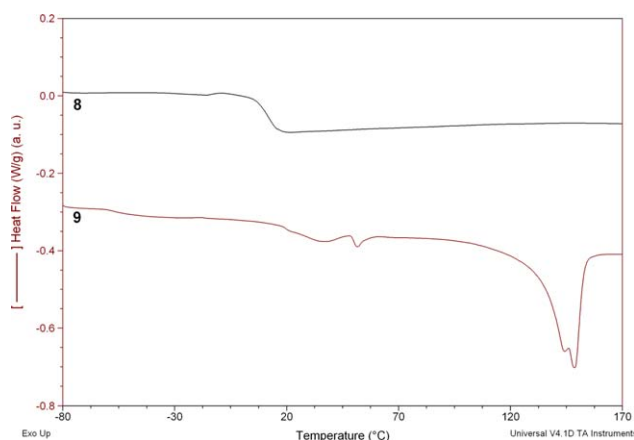
Several variables are known to influence the toughening ability of an additive.<sup>4</sup> These are, among other things,  $M_n$ ,  $T_g$ , the molar fraction of the comonomers, and the nature of copolymers (random or block). The additive must have a balance of compatibility and immiscibility for adequate phase separation to occur in the blend to confer toughening properties. In this study, we chose star random and block copolymers of relatively low  $M_n$  and polydispersity values. Star-branched polymers have lower melt viscosities and, hence, are easier to melt-blend. Furthermore, a star polymer enables one to change  $T_g$  merely by changing the number of arms without changing the composition of the comonomers. Core-shell polymers consisting of a low- $T_g$  rubbery core encapsulated by a glassy shell have been

reported as useful toughening additives for PLA.<sup>4</sup> Multiarmed star block copolymers can be considered to possess core-shell structures, where the chemical composition of the inner and outer arms determine the morphology.

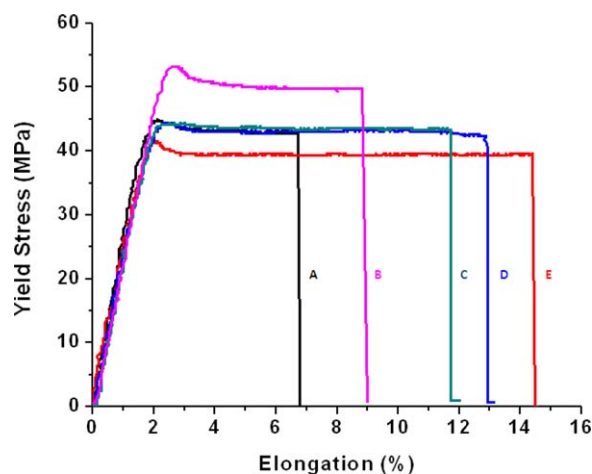
This study revealed the subtle influence of the molecular architecture on the toughening ability of star block and random copolymers of L-LA and ε-CL. Systematically lowering  $T_g$  through changes in the number of arms of a star random copolymer of similar  $M_n$  and comonomer composition improved the elongation. The L-LA content was maintained at 70 mol %; this ensured that the stiffness of the blend was not impaired. Even a star random copolymer with a  $T_g$  of -30°C, which resulted in a twofold increase in the elongation, did not cause a reduction in the modulus of the blend. This pointed out the beneficial effect of the molecular architecture in determining the mechanical properties of the blend. The use of a



**Figure 5.** DSC of the multiarmed star-shaped random copolymers of L-LA and ε-CL: (a–f) the polymers in entries 2–7, respectively, in Table V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 6.** DSC of the six-armed star block copolymers of L-LA and ε-CL: (a,b) the polymers in entries 8 and 9, respectively, in Table V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7.** Effects of the linear, random, and star-shaped six-armed random and block copolymers of L-LA and  $\epsilon$ -CL on the elongation of the PLA blends: (a) PLA, (b) PLA + LA-co-CL, (c) PLA + 6s-DS-LA-co-CL, (d) PLA + 6s-DS-CL-b-LA, and (e) PLA + 6s-DS-LA-b-CL. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

star block copolymer with significantly higher  $T_g$ 's (11 and 20°C) caused a further increase in the elongation similar to a lower  $T_g$  polymer (−30°C).

## CONCLUSIONS

A series of well-defined multiarmed star and block copolymers of L-LA and  $\epsilon$ -CL were synthesized by the controlled ring-opening polymerization of L-LA and  $\epsilon$ -CL. The copolymers were characterized to determine properties such as the molecular weight, polydispersity, comonomer composition, sequence of monomer enchainment, and degree of branching. The  $T_g$  and  $T_m$  values of the copolymers were studied by DSC. The copolymers were melt-blended with PLA, and their mechanical properties were studied. The results reveal the subtle effects of the molecular architecture on the toughening ability of the copolymer additive in the blend. A low- $T_g$  six-armed star random copolymer of L-LA and  $\epsilon$ -CL with a LA content of 50 mol % and a six-armed block copolymer of the same monomers with a much higher  $T_g$  were equally effective in improving the toughness of the blend. The sequence of comonomer placement in the block copolymer did not change the toughening ability of the additive. Limited immiscibility was found to be desirable in determining the useful properties of the copolymer additives. The desirable consequences of the molecular architecture were also evident from the fact that an improved toughness was achieved without a sacrifice of the stiffness properties of PLA.

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