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Poly(lactide)-*block*-poly(ε-caprolactone-*co*-ε-decalactone)-*block*-poly(lactide) copolymer elastomers†

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Batch ring opening transesterification copolymerization of ε-caprolactone and ε-decalactone was used to generate statistical copolymers over a wide range of compositions and molar masses. Reactivity ratios determined for this monomer pair, r_{CL} = 5.9 and r_{DL} = 0.03, reveal ε-caprolactone is added preferentially regardless of the propagating chain end. Relative to poly(ε-caprolactone) the crystallinity and melting point of these statistical copolymers were depressed by the addition of ε-decalactone; copolymers containing greater than 31 mol% (46 wt%) ε-decalactone were amorphous. Poly(lactide)-*block*-poly(ε-caprolactone-*co*-ε-decalactone)-*block*-poly(lactide) triblock polymers were also prepared and used to explore the influence of midblock composition on the temperature dependent Flory-Huggins interaction parameter (χ). In addition, uniaxial extension tests were used to determine the effects of midblock composition, poly(lactide) content, and molar mass on the mechanical properties of these new elastomeric triblocks.

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†Electronic supplementary information (ESI) available: Additional Information including materials and methods, detailed synthetic procedures are provided. ^{1}H NMR Spectra, ^{13}C NMR Spectra, DMA Data, DSC Data, Hysteresis Data and SAXS spectra are also provided in Tables S1–S12 and Fig. S1–S25. See DOI: 10.1039/c5py00202h

Introduction

Whereas the range of thermal and mechanical properties that may be accessed by a homopolymer is largely dictated by molar mass, architecture, and processing conditions, an expanded range of property profiles can be obtained through the incorporation of one or more comonomers. The physical characteristics of the resulting copolymer may be influenced greatly by the specific choice of monomers used, the composition, and the distribution of comonomers along the polymer backbone. In the case of a block polymer different comonomers are partitioned into distinct segments that can microphase separate to form ordered nanoscopic morphologies.[1,2] Microphase separated block polymers have been utilized for a number of innovative applications including gene and drug delivery,[3,4] energy capture and storage,[5–7] lithography,[8,9] and filtration membranes.[10,11] Despite remarkable advances in each of these areas, ABA styrenic block polymers elastomers—first commercialized over half a century ago—remain the cheapest, highest volume, commercial examples to date.

We and others have previously shown that a low glass transition temperature (T_g) midblock in combination with glassy poly((±)-lactide) (PLA) or semicrystalline poly((−)-lactide) (PLLA) endblocks can be used to prepare materials with mechanical properties similar to styrenic block polymers.[12–20] A number of previous studies have focused on developing sustainable poly(lactide) containing elastomers that are renewable[21,22] and degradable.[23–26] Polyester midblocks are particularly attractive for reasons of synthetic ease; triblock polymers can be synthesized by sequential monomer addition in a one pot approach.[18,19] The choice of a particular midblock may not only influence the rheological, mechanical, and degradation behavior of the block polymer but also define processing and service temperatures.[20,27,28] To strategically tune the properties of a block polymer it is desirable to select a midblock with a given combination of characteristics, *e.g.* melting point (T_m),[29,30] entanglement molar mass (M_e),[27] and glass transition temperature.[31] Because there are synthetic challenges associated with the efficient large-scale production of new monomers, the number of viable and practical homopolymer midblocks is limited.
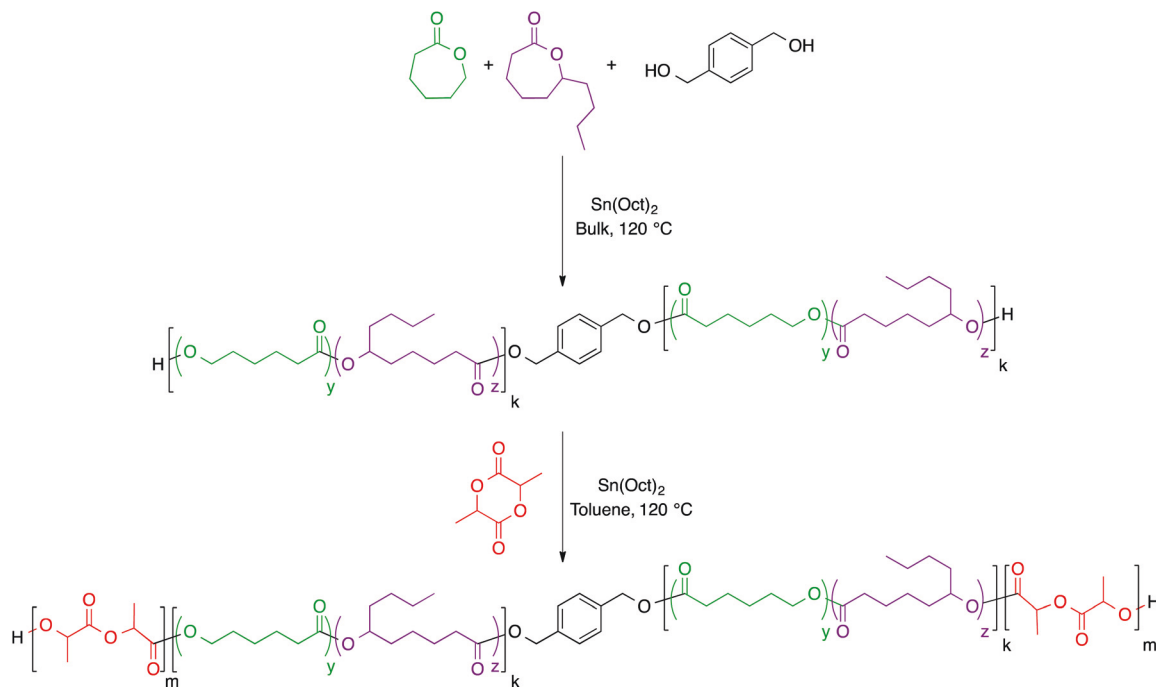
Others have previously studied block and multiblock polymers where at least one of the segments is a statistical copolymer.[29,32–41] In 2007 Staudinger *et al.* demonstrated using poly(styrene)-*block*-poly(styrene-*co*-butadiene)-*block*-poly(styrene) triblock polymers that the midblock composition

Scheme 1 Synthesis of a PCD statistical copolymer midblock and subsequent chain extension to prepare the corresponding LCDL block–statistical copolymers.

could be used to tune the miscibility of the copolymer midblock and polystyrene endblock segments. At fixed molar mass, changes in midblock composition dramatically impacted both the phase behavior and mechanical properties of the material.[38] More recently, Widjaja et al. investigated poly((−)-lactide)-block-poly(caprolactone-co-trimethylene carbonate)-block-poly((−)-lactide) triblock polymers. In this system the soft segment composition dramatically impacted the thermal and mechanical properties of the material; triblocks with amorphous middle segments were less tough but exhibited better elasticity than those with semicrystalline midblocks containing a majority of poly(ε-caprolactone) (PCL).[29]

We recently reported the synthesis and properties of amorphous poly((±)-lactide)-block-poly(ε-decalactone)-block-poly((±)-lactide) (LDL) triblock and (LDL)$_n$ multiblock elastomers.[20] Although ε-decalactone block and statistical copolymers containing pentadecalactone[42,43] and (−)-lactide[13,15,16] have also been reported, work on poly(ε-caprolactone-co-ε-decalactone) (PCD) statistical copolymers has been limited. Pitt and coworkers examined the impact of composition on the biodegradation of two semicrystalline PCD copolymers ($F_{CL} = 0.87$ $F_{CL} = 0.92$).[28] Glavas et al. prepared block polymers micelles comprised of poly(ethylene oxide) (PEO) in combination with PLA, PCL, or PCD ($F_{CL} = 0.5$).[44] They demonstrated that it was possible to tune the critical micelle concentration and micelle size by changing the composition of the polyester block. We posited that amorphous PCD copolymers could be used to prepare poly((±)-lactide)-block-poly(ε-caprolactone-co-ε-decalactone)-block-poly((±)-lactide) (LCDL) elastomers and that the ε-caprolactone content could be used to tune the miscibility of

the midblock and endblock segments. We also predicted that the entanglement molar mass of the copolymer midblock would decrease with the addition of ε-caprolactone, which would lead to a substantial improvement in the mechanical performance of LCDL compared to LDL.[20,27,45]

In this work we utilize the Sn(Oct)$_2$ catalyzed batch ring opening transesterification polymerization (ROTEP) of ε-caprolactone and ε-decalactone to generate statistical copolymers that could be chain extended with lactide to prepare LCDL triblock polymers. We compare these LCDL block polymers to LDL and poly((±)-lactide)-block-poly(ε-caprolactone-block-poly((±)-lactide) (LCL) to determine the effects of midblock composition on segment–segment miscibility. Additionally, the mechanical properties of LCDL triblocks were evaluated using uniaxial extension and compared to chemically similar polyester block polymers, poly((±)-lactide)-poly(menthide)-poly((±)-lactide) (LML),[18] poly((±)-lactide)-block-poly(6-methyl-ε-caprolactone)-block-poly((±)-lactide) (L6MCL),[16] and poly((±)-lactide)-block-poly(ε-decalactone)-block-poly((±)-lactide).[20] The general synthetic strategy used for this work is summarized in Scheme 1.

Results and discussion

We synthesized statistical copolymers using the bulk batch copolymerization of ε-caprolactone and ε-decalactone with catalytic Sn(Oct)$_2$ at 120 °C. 1,4 Benzene dimethanol (BDM) was added as an initiator to control the molar mass and end functionality. Typical of Sn(Oct)$_2$ catalyzed ROTEP, both PCD co-

Table 1 Composition and thermal characteristics of telechelic PCL and PCD copolymers

| Sample	M_n (NMR)[a] (kg mol^{-1})	F_{CL}[b]	M_n (SEC)[c] (kg mol^{-1})	$Đ$[c]	T_g[d] (°C)	T_m[d] (°C)	X[d] (%)
PCD66 (9.2)	8.2	0.66	9.2	1.10	−60		
PCD66 (10.2)	9.7	0.66	10.2	1.20	−63		
PCD65 (15.5)	14.2	0.65	15.5	1.10	−61		
PCD63 (18.3)	18.3	0.63	18.3	1.13	−62		
PCD69 (19.4)	19.6	0.69	19.4	1.05	−62		
PCD69 (83.4)	96.0	0.69	83.4	1.16	−62		
PCD78 (10.6)	9.4	0.78	10.6	1.08	−64	20	19
PCD77 (12.5)	11.4	0.77	12.5	1.05	−64	16	16
PCD76 (13.1)	13.8	0.76	13.1	1.12	−63	18	12
PCD76 (17.0)	15.0	0.76	17.0	1.08	−65	16	15
PCD77 (22.6)	20.5	0.77	22.6	1.04	−64	18	15
PCL (10.8)	11.1	1.0	10.8	1.06	−62	55	52
PCL(12.2)	12.2	1.0	12.2	1.13	−62	55	34
PCL (11.6)	10.1	1.0	11.6	1.06	−60	54	50
PCL (14.5)	16.2	1.0	14.5	1.06	−62	55	49
PCL (15.7)	16.0	1.0	15.7	1.13	−64	55	59
PCL (18.9)	16.9	1.0	18.9	1.15	−63	56	62
PCL (18.1)	18.8	1.0	18.1	1.18	−62	55	53
PCL (22.1)	18.9	1.0	22.1	1.16	−63	55	50

[a] Number average molar mass determined using ^{1}H NMR spectroscopy, calculated using initiator methylene protons as an internal standard. [b] Mole fraction of ε-caprolactone in the copolymer determined using ^{1}H NMR spectroscopy. [c] Number average molar mass and dispersity determined using MALLS-SEC; dn/dc was determined from the RI signal using the known concentration and the assumption of 100% mass recovery. [d] Glass transition temperatures and melting point values were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. T_m is taken as the peak maximum. Crystallinity was calculated using the reference enthalpy of fusion (139.5 J g^{-1}) for fully crystalline PCL.[48]

polymers and similarly prepared PCL homopolymers exhibited relatively narrow dispersities ($1.05 \leq Đ \leq 1.20$).[13,20,46,47] The number average molar masses determined using ^{1}H NMR spectroscopy were in fair agreement with both the theoretical values and those ascertained using size exclusion chromatography with a multi-angle laser light scattering detector (MALLS-SEC). Since both adventitious initiation and transesterification are minimized, low dispersity linear telechelic polymers can be synthesized with control over molar mass and functionality. The characteristics of telechelic PCD and PCL polymers used in this work are summarized in Table 1.

At high monomer conversions the compositions of PCD copolymers deviated only slightly from the feed. However, more significant differences were observed in polymerizations with lower monomer conversion. We used the dependence of instantaneous polymer composition (total monomer conversion <10%) on feed composition to determine reactivity ratios for the bulk copolymerization of ε-caprolactone and ε-decalactone. The results of this experiment are shown in Fig. 1. The relative reactivity of the two commoners tend to promote a gradient microstructure with longer initial runs of CL than DL emanating from the central difunctional initiator. Thus, the middle of midblock will be richer in CL whereas the ends of the midblock will be richer in DL.

Differential scanning calorimetry (DSC) was used to analyze the impact of composition on the thermal properties of an array of statistical copolymers prepared using batch copolymerization of DL and CL. PDL is amorphous, PCL is semicrystalline with a melting temperature near 60 °C.[13,20,49] The
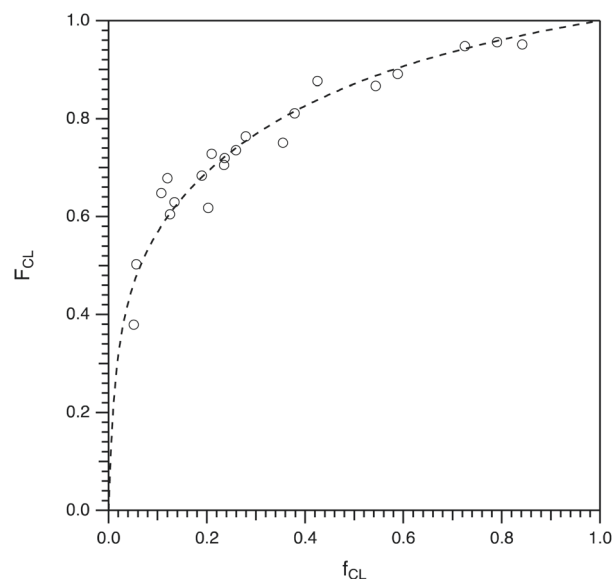
Fig. 1 Dependence of polymer composition (total monomer conversion <10%) on feed composition (○). F_{CL} and f_{CL} are the mole fraction of caprolactone in the polymer and feed, respectively. Nonlinear least-squares fit (−) to copolymer equation used to find reactivity ratios r_{CL} = 5.9 ± 0.7 and r_{DL} = 0.03 ± 0.01. The reactivity ratios and error values were determined using the assistance of Igor Pro (Wavemetrics, Lake Oswego, OR, USA) software. This software uses the Levenberg-Marquardt algorithm, an iterative, nonlinear, least squares fitting method, to find coefficient values that minimize the value of chi-square.
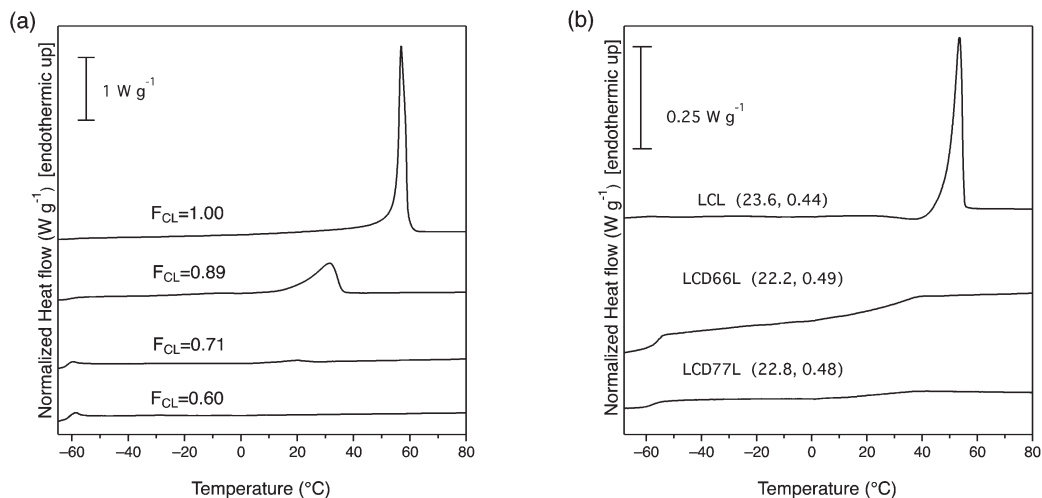
Fig. 2 (a) DSC thermograms for PCL and representative PCD copolymers. To ensure consistent thermal histories all samples were heated to 100 °C (rate of 5 °C min^{-1}) and cooled at the same rate. Data were taken from the second heating ramp (5 °C min^{-1}) and are for polymers with molar masses near 20 kg mol^{-1}. Characteristics of these and other copolymer samples are given in the ESI† (Table S6). (b) DSC thermograms for select LCL, LCD66L, and LCD77L triblock polymers described in Table 2. To ensure consistent thermal histories all samples were heated to 100 °C (rate of 5 °C min^{-1}) and cooled at the same rate. Data were taken from the second heating ramp (5 °C min^{-1}).

crystallinity and melting point of PCD decreases with DL content, and at approximately 31 mol% (46 wt%) DL the polymers are amorphous. Representative thermograms are shown in Fig. 2a, and data for several compositions of copolymers are summarized in the ESI† (Table S6).

It is likely that the PCD crystallization behavior is impacted by both the copolymer composition gradient and size of the DL n-butyl substituent. Based on experimentally determined reactivity ratios, the structurally similar copolymer poly-(ε-methyl-ε-caprolactone)-co-poly(ε-caprolactone) is predicted to have a much more random composition than PCD.[50] Although one would expect a random copolymer to display reduced crystallinity compared to a gradient copolymer, only PCM copolymers containing over 44 mol% (50 wt%) ε-methyl-ε-caprolactone are amorphous.[50] The probable reason for this discrepancy is that ε-methyl-ε-caprolactone is partially incorporated in the PCL crystal.[51,52] Due to the large size of the n-butyl substituent it is unlikely that PDL is included in the PCL crystal. In this way PCD copolymers are more similar to poly(γ-$tert$-butyl-ε-caprolactone)-co-poly(ε-caprolactone) copolymers.[53]

Because the glass transition temperatures of the corresponding homopolymers are similar ($T_g = -51$ and $T_g = -61$ °C for PDL and PCL, respectively), negligible variation in T_g values was observed for the copolymer samples. This is in contrast to related works where lactide is used as a comonomer, $e.g.$ poly(lactide)-co-poly(ε-decalactone),[13] and poly(lactide)-co-poly(ε-caprolactone).[41,50,54]

The difunctional α,ω-hydroxyl telechelic polymers were used as macroinitiators for chain extension with ($\pm$)-lactide. Similar conditions, 110–130 °C in toluene ([LA]$_0 \approx$ 1 M) with catalytic Sn(Oct)$_2$, were used regardless of midblock composition. As shown for representative samples in Fig. 3, the SEC
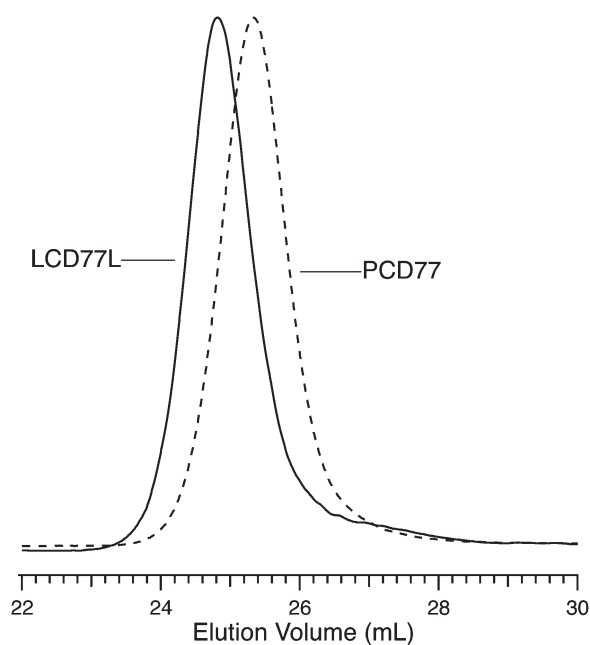
Fig. 3 A representative example of size-exclusion chromatograms for a telechelic copolymer, PCD77 (22.6 kg mol^{-1}, F_{CL} = 0.77), and the corresponding triblock, LCD77L (34.2 kg mol^{-1}, F_{LA} = 0.30). Each chromatogram is shown for the purified polymers. Additional details for these midblock and triblock polymers are given in Tables 1 and 2, respectively.

data of the triblock polymers indicated a clear increase in molar mass compared to the corresponding midblock. Additionally, there was minimal evidence of PLA homopolymer or residual macroinitiator. The ^{13}C NMR spectra of triblocks samples revealed no significant transesterification between the

Table 2 Compositions and thermal characteristics of LCL and LCDL

Triblock	Block M_n (kg mol⁻¹)		N_{tot} [c]	f_{PLA} [d]	T_g [e] (°C)	T_g [e] (°C)	T_m [e,f] (°C)	X [f] (%)	T_{ODT} [g] (°C)
	PLA [a]	PC(D) [b]							
LCD65L (20.0, 0.49)	5.4	9.2	250	0.49	−5	26			65
LCD66L (22.2, 0.49)	6.0	10.2	280	0.49	−56	31			92
LCD67L (43.7, 0.49)	9.1	15.5	420	0.49	−57	37			126
LCD63L (40.7, 0.5)	11.2	18.3	510	0.50	−59	49			170
LCD69L (24.2, 0.17)	2.5	19.4	320	0.17	−52	18			nd[h]
LCD69L (31.4, 0.33)	6.0	19.4	400	0.33	−59	30			95
LCD69L (104, 0.17)	10.5	83.4	1270	0.17	−60	47			>200
LCD69L (113, 0.21)	14.6	83.4	1320	0.21	−60	50			>200
LCD69L (131, 0.32)	24.0	83.4	1420	0.32	−59	53			>200
LCD77L (22.8, 0.48)	6.1	10.6	280	0.48	−58	29			70
LCD77L (27.1, 0.49)	7.3	12.5	340	0.49	−58	35			100
LCD76L (28.7, 0.49)	7.8	13.1	360	0.49	−56	41			130
LCD76L (39.4, 0.49)	11.2	17.0	520	0.49	−55	39			150
LCD77L (34.2, 0.30)	5.8	22.6	440	0.30	−57	43			106
LCL (23.6, 0.44)	5.7	12.2	300	0.45	−65		54	33	<60
LCL 19.6, 0.50)	4.4	10.8	250	0.50	−63		50	30	75
LCL (24.2, 0.48)	9.1	15.7	420	0.48	−62		54	36	112
LCL (35.1, 0.53)	10.3	14.5	430	0.53	−63		49	33	118
LCL (34.3, 0.46)	8.7	16.9	430	0.46	−64		54	35	119
LCL (40.1, 0.48)	10.6	18.9	500	0.48	−63		54	42	146
LCL (43.1, 0.53)	12.5	18.1	530	0.53	−62		51	35	174

[a] Molar mass reported of PLA block. This value was calculated using the triblock composition and midblock molar mass. [b] Number average molar mass of the midblock determined using MALLS-SEC. Copolymer dn/dc was determined form the RI signal using the known concentration with the assumption of 100% mass recovery. [c] Calculated from total molar mass (sum of block molar masses) using a reference volume of 118 Å³ and room temperature densities of 1.248 g cm⁻³ and 1.02 g cm⁻³ for PLA and PCL or PCD, respectively.[56] [d] Volume fraction of poly(lactide) in the block polymer was calculated from the composition, determined using ¹H NMR spectroscopy. [e] Determined by DSC. To ensure consistent thermal histories all samples were heated to 100 °C (rate of 5 °C min⁻¹) and cooled at the same rate. Data reported were taken from the second heating ramp at 5 °C min⁻¹. [f] T_m is defined as the endotherm peak maximum. Crystallinity was calculated using a reference enthalpy of fusion of 139.5 J g⁻¹.[48] [g] Determined using DMA. [h] The T_{ODT} could not be accurately identified using DMA.

midblock and poly(lactide) domains (Fig. S2 and S3†). Together, these observations are consistent with the successful syntheses of the desired triblock polymers.

The thermal characteristics of the triblock polymer samples depended on composition. In the LCD77L triblock samples, crystallinity was suppressed at the molar masses and compositions investigated in this work. LCL samples exhibited significantly reduced crystallinity compared to parent macroinitiators, possibly the result of reduced chain mobility due to confinement.[55] As expected triblocks prepared using PCD69 macroinitiatiors were amorphous. In general, the LCDL triblocks exhibited two glass transition temperatures, one below −51 °C the other above 18 °C (more typically above 35 °C), consistent with microphase separation into PCD and PLA-rich domains, respectively. The thermograms of representative triblocks are shown in Fig. 2b, compositions and thermal characteristics of several triblock samples are included Table 2.

Block polymer microphase separation is influenced by architecture, the volume fraction (f) of each component, and the segregation strength—a product of the segment–segment interaction parameter (χ) and the overall (reference volume averaged) degree of polymerization (N). By utilizing controlled polymerization strategies the majority of these parameters can be altered synthetically; however, χ is measure of relative

incompatibility, a property inherent to any given polymer pair. On the basis of solubility parameter estimates the interaction parmeter for poly(lactide) with another polyester is expected to increase as the later becomes more aliphtic (these estimates are provided in Table S5†). In this work we assume that the temperature dependance of χ is inverse and can be described by eqn (1):

$$\chi(T) = \frac{\alpha}{T} + \beta \tag{1}$$

We used the order-to disorder transition temperatures (T_{ODT}) of several composisitionally symmetric (f_{LA} = 0.46–0.53) ABA triblocks and the mean field theoretical segregation strength (χN = 17.996) at the lameller to disorder phase boundry to estimate the temperature dependence of $\chi_{PLA-PCL}$.[1] The T_{ODT} values were determined using dynamic mechanical analysis (DMA),[57] and N was calculated from the overall molar mass using a reference volume of 118 Å³. This is shown for LCL in Fig. 4a and b. The interaction parameter of this system is compared to structurally similar polyester block polymers in Table 3.[16,20] Our estimate of $\chi_{PLA-PCL}$ is consistent with prior reports regarding phase behavior of doubly crystalline poly((−)-lactide-*block*-poly(ε-caprolactone) (PLLA-PCL) block polymer samples;[58–64] and is also consistent with the observed behavior of poly((±)-lactide/poly(ε-caprolactone) blends.[65]

(a)

(b)
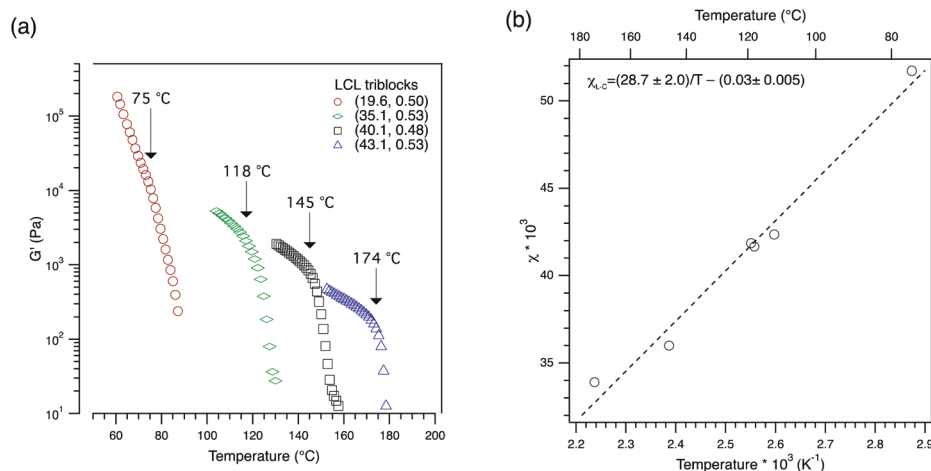
Fig. 4 (a) Isochronal temperature ramp data on heating (1 rad s^{-1}, 1 °C min^{-1}, 1% strain) for LCL triblock polymers LCL (19.6, 0.50) (○), LCL (35.1, 0.53) (◇), LCL (40.1, 0.48) (□), and LCL (43.1, 0.53) (△). (b) Inverse temperature dependence of $\chi_{PLA-PCL}$ and fit to eqn (1). Two additional triblocks, LCL (24.2, 0.48) and LCL (34.3, 0.46) were excluded from (a) for clarity but are included in the fit shown in (b). The DMA data for these samples are shown in the ESI† (Fig. S9).

Table 3 Comparison of $\chi(T)$ for poly(lactide) block polymers

	α	β	χ (140 °C)	Ref.
PDL-PLA	69.1 ± 9.2	−0.07 ± 0.03	0.1	20
P6MCL-PLA	61.2	−0.1	0.05	16
PCD66-PLA	56.3 ± 9.6	−0.09 ± 0.03	0.05	This work
PCD77-PLA	45.8 ± 12.5	−0.07 ± 0.03	0.04	This work
PCL-PLA	28.7 ± 2.0	−0.03 ± 0.005	0.04	This work

However, to our knowledge this is the first estimate of $\chi_{PLA-PCL}$ determined using experimentally measured T_{ODT} values.

To determine the effect of midblock composition on the interaction parameter for block-statistical polymers containing PLA, we explored triblock polymers prepared from PCD66, and PCD77 midblocks. The results of this analysis are summarized in Table 3, corresponding DMA and linear fit data are shown in the ESI† (Fig. S5–S8). The reactivity ratios of DL and CL favor a gradient composition; therefore in LCDL triblocks the DL units are enriched near the junction of the PLA and CD copolymer blocks. The strength of this gradient depends details of the PCD synthesis, namely the initial feed composition and final conversion of each monomer. Theoretically a strong gradient could cause the measured value of $\chi_{PLA-PCD}$. to differ from that of polymer with a truly random PCD midblock. Although we believe this may be partially responsible for scatter in the data shown in Fig. S23,† additional experiments are required for a thorough examination of this phenomenon.

Beacause the entropic terms are modest and because the enthalpic term is larger for $\chi_{PLA-PCD}$ than $\chi_{PLA-PCL}$, the segregation strength of LCL at high temperatures ($T \geq 180$ °C) is predicted to be *higher* than LCDL block statistical polymers of the same overall degree of polymerization.

Small-angle X-ray scattering (SAXS) was used to study the effects of midblock composition and crystallinity on the microphase separation of triblock samples. The SAXS data for lower molar mass samples at room temperature (20 °C), LCL (23.6, 0.44), LCD77L (22.8, 0.48), and LCD65L (20.0, 0.49), exhibited strong primary reflections but no distinct higher order reflections. These data are consistent with low segregation strength, microphase-separated materials that lack long-range order.[18,38,66,67] As shown for representative samples in Fig. 5, compositionally symmetric LCDL and LCL triblocks with higher molar mass midblocks exhibit reflections indicative of the expected lamellar morphologies. Although the latter are semicrystalline, the T_{ODT} values are higher than the crystallization temperature. When annealed above 60 °C then cooled the microstructure of the sample is preserved.

As shown in the inset of Fig. 6, higher molar mass compositionally asymmetric samples, *e.g.* LCD69L (131, 0.32), exhibited intense principle peaks indicative of microphase separation; however, the morphology of these materials could not be definitively assigned due to the absence of well-defined higher order reflections. Although it was anticipated that LCD69L (131, 0.32) would adopt a cylindrical morphology, is likely the high molar mass samples are kinetically trapped in a poorly ordered state.[18] The SAXS data for a lower molar mass sample at, LCD77L (34.2, 0.30), exhibited several higher order peaks at ($q/q^* = 3^{\frac{1}{2}}, 4^{\frac{1}{2}}, 7^{\frac{1}{2}}, 9^{\frac{1}{2}}, 12^{\frac{1}{2}}$) consistent with the hexagonally close packed cylinders anticipated for polymers of this composition.[1] The SAXS data for this triblock and other low molar mass compositionally asymmetric samples are included in the ESI† (Fig. S12).
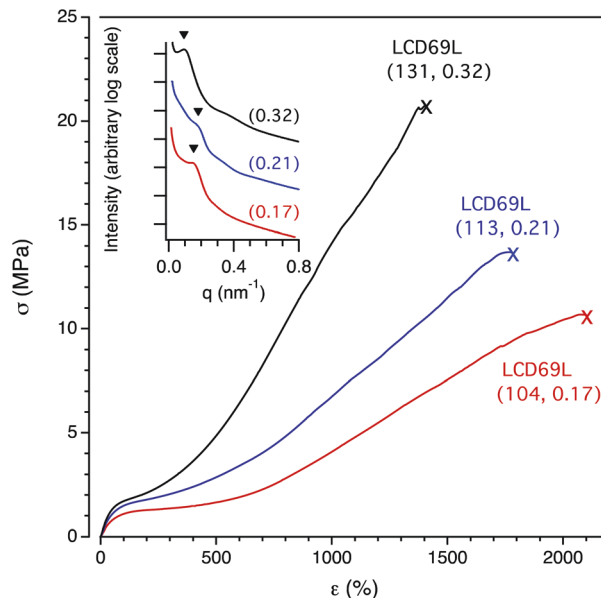
The tensile properties of LCDL triblocks, shown in Fig. 6, were found to be qualitatively similar to other PLA containing polyester triblock elastomers.[16,18–20] Over the range of compositions investigated, Young's modulus (E_y) and ultimate tensile
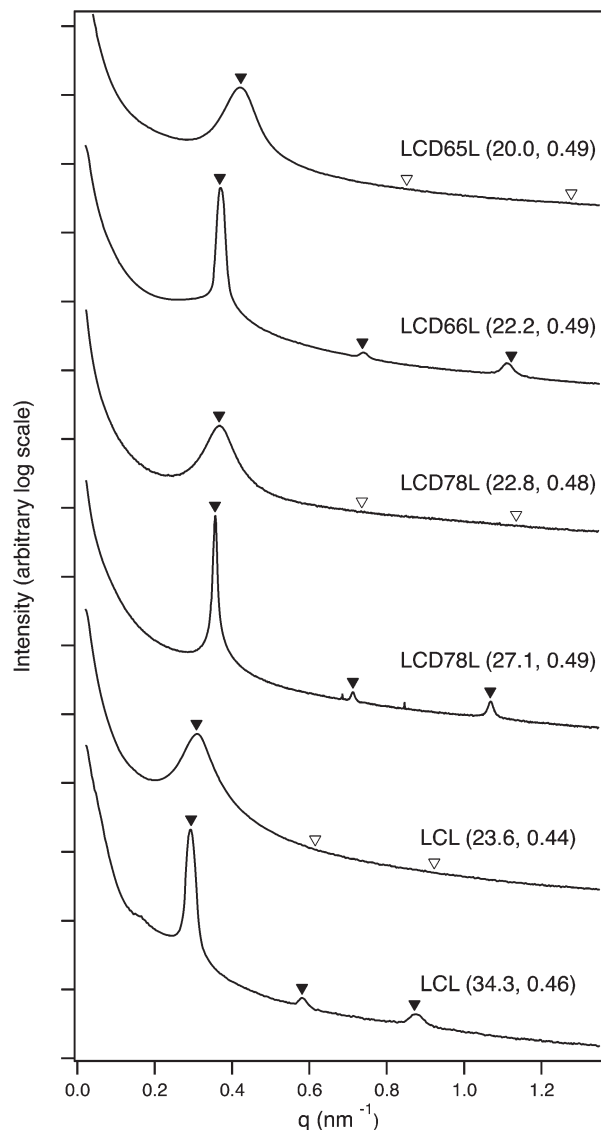
Fig. 5 Room temperature SAXS data for of representative compositionally symmetric LCL and LCDL triblock samples. The principle peaks are marked with (▼). Calculated reflections for anticipated lamellar morphologies are also marked with (▼) and (▽) denoting reflections that are present, and absent respectively.

Fig. 6 Representative examples of room temperature uniaxial extension of selected LCD69L triblock elastomers. Experiments were conducted with constant crosshead velocity of 50 mm min^{-1}. For each sample, average and standard deviation of a minimum of 5 specimens is reported in Table 4. The graph inset displays room temperature SAXS data of compression molded LCD69L elastomers prior to uniaxial extension test.

strength (σ_b) both increased with PLA content while the elongation at break (ε_b) decreased. At fixed PLA content LCD69L triblocks exhibited significant increases in stress at break compared to LDL; these data are provided in Table 4.[20] Interestingly, the elongation at break and ultimate tensile strength of high molar mass LCD69L triblocks are nearly the same as L6MCL triblocks of similar lactide content.[16] LCD69L and L6MCL, are both significantly tougher than LML of similar molar mass and composition.[68]

We believe the differences in the tensile behavior of these triblocks may be partially due to changes in the chain cross-section[70] and entanglement molar mass of the midblock.[27]

From the plateau modulus of PCD69 (Fig. S14†) we estimated the entanglement molar mass of PCD69 to be M_e = 3.9 kg mol^{-1}. Whereas the reported entanglement molar mass of PM and PDL are both relativley high, (M_e = 11–14 kg mol^{-1} and M_e = 5.9 kg mol^{-1}, respectively)[20,68] the entanglement molar mass of PCD69 is lower, closer to that of PCL (3.0 kg mol^{-1}) and P6MCL (3.0 kg mol^{-1}).[71] This is consistant with past reports regarding the relationship between composition and plateau modulus for random copolymers.[45]

At fixed composition the toughness of LCD69L triblocks decreased dramatically with molar mass. For example LCD69L (31.4, 0.33) exhibited a 95% reduction in ultimate tensile strength and a 63% decrease in elongation at break compared to LCD69L (131, 0.32). This is behavior similar to that of previously reported LDL and poly((±)-lactide)-poly(menthide)-poly-((±)-lactide) (LML) triblocks.[20,69] We recently demonstrated that melt-processable (LDL)$_n$ multiblocks can be prepared by coupling low molar mass triblocks.[20] In every case the multiblocks were considerably tougher than the parent triblock; however, because the individual domains were unentangled, the elongation and stress at break were low compared to high molar mass LDL triblocks.[20] When designing these multiblocks, the upper molar mass of the AB repeat unit is limited by the segregation strength. Because $\chi_{PLA-PCD}$ is lower than $\chi_{PLA-PDL}$ it is possible to prepare multiblocks with higher molar mass segments while retaining an accessible T_{ODT} values, this is demonstrated in the ESI† (Fig. S13 and S22).

Table 4 Tensile properties of poly(lactide) containing block polymers[a]

Sample	E_Y (MPa)	σ_{300} (MPa)	σ_b (%)	ε_b (%)
LCD69L (104, 0.17)	1.5 ± 0.3	1.3 ± 0.1	9.9 ± 0.6	2100 ± 100
LCD69L (113, 0.21)	2.0 ± 0.3	2.0 ± 1.2	13.5 ± 0.3	1690 ± 90
LCD69L (131, 0.32)	3.5 ± 0.3	2.9 ± 0.3	18 ± 4	1200 ± 100
LCD69L (31.4, 0.33)	1.1 ± 0.1	0.60 ± 0.1	0.9 ± 0.1	610 ± 20
LDL[b] (136, 0.21)	1.0 ± 0.1		4.5 ± 0.3	1600 ± 200
LDL[b] (148, 0.27)	1.1 ± 0.1		9.4 ± 0.7	1310 ± 40
LDL[b] (15.3, 0.30)	4.5 ± 0.2		0.24 ± 0.01	218 ± 9
LML[d] (122, 0.15)	0.45 ± 0.05		0.03	630 ± 60
LML[c] (48.2, 0.26)	0.8 ± 0.1		3.8 ± 0.2	872 ± 6
L6MCL[e] (122, 0.18)	1.87 ± 0.03		10.2 ± 0.8	1880 ± 70
L6MCL[e] (150, 0.31)	31 ± 9		14.0 ± 2	1400 ± 100

[a] LCD69L samples were tested at room temperature with a constant crosshead velocity of 50 mm min^{-1}. [b] Information was taken from ref. 20. [c] Information was taken from ref. 69. [d] Information for poly((±)-lactide)-poly(menthide)-poly((±)-lactide) (LML) was taken from ref. 68. Volume fractions were calculated using a room temperature of 0.975 g cm^{-3} for poly(menthide) PM.[68] [e] Information was taken from ref. 18. Volume fractions were calculated using a room temperature density of 0.97 g cm^{-3} for P6MCL.

Conclusions

We have demonstrated that the batch melt copolymerization of ε-caprolactone and ε-decalactone can be utilized to generate α,ω-hydroxy telechelic statistical copolymers with good control over composition, molecular weight and dispersity. One advantage of this particular selection of comonomers is the ability to modify the degree crystallinity and melting temperature without affecting the glass transition temperature of the material. These α,ω-hydroxy telechelic polymers were used as macroinitiatiors for the synthesis well defined telechelic triblocks. The interaction parameter for the midblock with PLA was estimated from the T_{ODT} values of microphase separated symmetric triblocks, and was found to be dependent on the composition of the midblock copolymer.

By varying midblock composition and lactide content it was possible to significantly alter the mechanical behavior of the corresponding block-statistical copolymers. At fixed midblock composition, tensile properties depended largely on molar mass and lactide content. Compared to triblock polymers with PDL midblocks, those prepared using PCD copolymers demonstrated significantly higher tensile stress at failure, an effect we attribute to the reduced entanglement molar mass relative to PDL. The facile synthesis, and tunable mechanical properties of PLA block-statistical multiblock polymers make these materials attractive new thermoplastic elastomers.

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