Supporting Information For:

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

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EXPERIMENTAL SECTION

Materials:

ε-Caprolactone (Sigma-Aldrich), and ε-decalactone (Sigma-Aldrich) were each distilled under reduced pressure over calcium hydride and passed through a column of dry activated basic alumina (Sigma-Aldrich) without exposing to air. Tin(II) 2-ethylhexanoate (Sigma-Aldrich) was distilled (3×) under reduced pressure. 1,4-Benzenedimethanol (Sigma-Aldrich) was dried under reduced pressure at room temperature for 96 h. 4, 4'-Methylenebis(phenyl isocyanate) (Sigma-Aldrich) was stored in a -4°C freezer and used as received. Toluene (Fisher), used for triblock syntheses, was purified by passing though activated alumina columns (Glass Contour, Laguna Beach, CA) prior to use. $_{D,L}$-Lactide, a kind gift from Ortec Inc (Easely, SC), was used as received. Chromium(III) acetylacetonate (Sigma-Aldrich) was purchased and used as received. All reagents mentioned were stored in a nitrogen-filled glovebox. Toluene (Fisher) used for large scale multiblock syntheses was distilled to remove the azotrope, stirred over calcium hydride for at least 24 hours, then distilled again under argon immediately prior to use. All other solvents were used as received without further purification.

Glass ampules, pressure vessels, Teflon caps, and Teflon-coated magnetic stir bars were dried in a 110 °C oven for a minimum of 6 hours prior to use. Pressure vessels, used for copolymer and block polymer syntheses, were charged and sealed in a glovebox under nitrogen then quickly removed and placed in a heating bath. Ampules, used for small-scale copolymerization reactions, were also charged in an inert atmosphere then flame sealed under vacuum.

If improperly handled some of the chemicals used in this work can be significant health hazards. Specifically, 4, 4’-methylenebis(phenyl isocyanate) is a known irritant, allergen, and sensitizer, and is also a suspected carcinogen. Chloroform, used to dilute the polymers prior to precipitation, is toxic and a carcinogen. Methanol and toluene are both flammable. All chemicals should be handled with appropriate caution in a well-ventilated area.

Nomenclature:

In this work copolymer midblocks are named using a two-letter two-number code denoting the composition of the polymer. The letter codes are C and D for ε-caprolactone, and ε-decalactone, respectively. The number code is used to indicate the mole fraction of ε-caprolactone in the polymer. The number average molar mass is enclosed in parentheses following the name, e.g. CD77 (22.6) indicates a poly(ε-caprolactone-*co*-ε-decalactone) copolymer that is 22.6 kg mol^{-1} and 77 mol% poly(ε-caprolactone) as determined by MALLS SEC and ^{1}H NMR spectroscopy, respectively. Block-statistical copolymer triblocks are named using LXX##L, where XX## is the two-letter, two-number code of the midblock used to prepare the triblock. Block-statistical copolymer multblocks blocks are named (LXX##L)$_n$, where *n* is defined as the ratio of multiblock M_n to triblock M_n (both determined from MALLS SEC). For both triblock and multiblock polymers, the total molar mass and PLA volume fraction are included parenthetically following the letter/number code. Total triblock molar mass was calculated from the molar mass of the midblock, determined using MALLS-SEC and the composition, determined using ^{1}H NMR spectroscopy.

Representative synthesis of poly(ε-caprolactone)-co-poly(ε-decalactone) statistical copolymer [PCD77 (22.6)]:

In the glovebox ε-decalactone (123 g, 0.71 moles), ε-caprolactone (185 g, 1.62 moles), $Sn(Oct)_2$ (0.9342 g, 2.306 mmol), and 1,4-benzenedimethanol (1.7513 g, 12.67 mmol) were added to a 500 mL pressure vessel equipped with a Teflon-coated magnetic stir bar. The sealed reaction vessel was placed in a 120 °C oil bath and stirred for 2 h before cooling to room temperature. A crude aliquot was taken to determine conversion, then the reaction solution was cooled to room temperature, diluted with dichloromethane, precipitated in methanol, and dried, yielding PCD77 (223.5 grams, 84% gravimetric yield).

PCD77: (22.6, 0.30) ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ 0.85-.91 (t, J=7.15, 115 H, $-C\mathbf{H_3}$) 1.19 – 1.43 (m, 494 H, $-OC{=}O-CH_2CH_2C\mathbf{H_2}CH_2CH(CH_2C\mathbf{H_2}C\mathbf{H_2}CH_3)-$ and $-OC{=}O-CH_2CH_2C\mathbf{H_2}CH_2CH_2-$) 1.46-1.70 (m, 824 H, $-OC{=}O-CH_2C\mathbf{H_2}CH_2C\mathbf{H_2}CH(C\mathbf{H_2}CH_2CH_2CH_3)-$ and $-OC{=}O-CH_2C\mathbf{H_2}CH_2C\mathbf{H_2}CH_2-$) 2.26-2.33 (m, 315 H, $-OC{=}O-C\mathbf{H_2}CH_2CH_2CH_2CH(CH_2CH_2CH_2CH_3)-$ and $-OC{=}O-C\mathbf{H_2}CH_2CH_2CH_2CH_2-$) 3.54-3.63 (m, 2.0 H, $C\mathbf{H_2}-OH$) 3.98-4.14 (m, 250H, $-OC{=}O-CH_2CH_2CH_2CH_2\mathbf{CH_2}-$) 4.79-4.91 (quin, *J*=5.8 Hz, 37 H, $-OC{=}O-CH_2CH_2CH_2CH_2C\mathbf{H}(CH_2CH_2CH_2CH_3)-$) 5.10 (s, 4 H, $C\mathbf{H_2}-O$) 7.33 (s, 4 H, Ar-**H)**

Representative synthesis of poly($_{\mathrm{D,L}}$-lactide)-*block*-poly(ε-caprolactone)-co-poly(ε-decalactone)-*block*- block-statistical copolymer [LCD77L (34.2, 0.30)]:

In a nitrogen filled glovebox a 500 ml pressure vessel equipped with a Teflon-coated magnetic stir bar was charged with PCD (110 grams), (±)-lactide (58.716 grams, 0.407 moles), Sn(oct)_2 (300 mg, 0.741 mmol), and toluene (300 ml). The vessel was capped, removed from the glovebox, and heated in an oil bath to 60 °C. When the contents were dissolved, the vessel was transferred to a 120 °C oil bath and stirred for 2 hours (until the (±)-lactide conversion reached 83 %). At this time the reaction was cooled and precipitated in cold methanol. The isolated polymer was dried in a vacuum oven to obtain LCD77L (135 grams, 85% gravimetric yield).

LCD77L (34.2, 0.30): ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ 0.85-.91 (t, J=7.15, 113 H, $\text{-C}\mathbf{H}_3$) 1.19 – 1.43 (m, 488 H, $\text{-OC=O-CH}_2\text{CH}_2\text{C}\mathbf{H_2}\text{CH}_2\text{CH(CH}_2\text{C}\mathbf{H_2}\text{C}\mathbf{H_2}\text{CH}_3\text{)-}$ and $\text{-OC=O-CH}_2\text{CH}_2\text{C}\mathbf{H_2}\text{CH}_2\text{CH}_2\text{-}$) 1.46-1.70 (m, 1346 H, $\text{-OC=O-CH}_2\text{C}\mathbf{H_2}\text{CH}_2\text{C}\mathbf{H_2}\text{CH(C}\mathbf{H_2}\text{CH}_2\text{CH}_2\text{CH}_3\text{)-}$ and $\text{-OC=O-CH}_2\text{C}\mathbf{H_2}\text{CH}_2\text{C}\mathbf{H_2}\text{CH}_2\text{-}$ and $\text{- O-C=OCHC}\mathbf{H_3}\text{-}$), 2.26-2.33 (m, 315 H, $\text{-OC=O-C}\mathbf{H_2}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{)-}$ and $\text{-OC=O-C}\mathbf{H_2}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$) 3.98-4.14 (m, 245 H, $\text{-OC=O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\mathbf{CH_2}\text{-}$) 4.33-4.38 (m, 2.0 H, $\text{-C}\mathbf{H}\text{-CH3-OH}$) 4.79-4.91 (quin, *J*=5.8 Hz, 37 H, $\text{-OC=O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\mathbf{H}\text{(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{)-}$), 5.10 (s, 5.0 H, $\text{Ar-C}\mathbf{H_2}\text{-O-}$) 5.11 - 5.26 (m, 145 H, $\text{- OC=O-C}\mathbf{H}\text{(CH}_3\text{)-O-}$) 7.33-7.35 (s, 4 H, Ar–**H** initiator)

Poly($_{\mathrm{D,L}}$-lactide)-*block*-poly(ε-caprolactone)-co-poly(ε-decalactone)-*block*-poly($_{\mathrm{D,L}}$-lactide) multiblock statistical copolymer [$\text{(PCD77)}_{2.0}$ (34.2, 0.30)]:

To a 1 liter 3-necked round bottom flask was added 57.0 grams LCDL triblock polymer, the flask and its contents were dried in a vacuum oven overnight and then fitted with an overhead stir assembly, gas inlet, bubbler, and septum. The reaction was purged with argon for one hour then freshly distilled toluene (250 ml) was added to dissolve the block polymer. The reaction was heated to 110 °C in an oil bath and stirred while purging with argon for 1 hour, at this time $Sn(oct)_2$ (200 mg, 0.494 mmol) was injected. Following the introduction of the catalyst, the reaction was purged an additional 10 minutes then 4,4’-methylene bis(phenyl isocyante) (0.4050 grams, 1.6184 mmol) was added under a vigorous argon flow. The reaction was stirred at 110 °C for 1 hour then cooled, precipitated in cold methanol, and dried to give $(LCD77L)_{2.0}$ (53 grams, 91% yield).

Poly(ε-caprolactone)-co-poly(ε-decalactone) Semibatch polymerization:

To a flame dried 100 milliter 2-necked round bottom flask equipped with septum, gas inlet, and magnetic stirrer was added 1,4 benzene dimethanol. This was dried under vacuum overnight then backfilled with argon. An argon atmosphere was maintained using a bubbler and a mixture of ε-decalactone and ε-decalactone were injected. Sn(oct)2 were then injected and the reaction stirred (1000 rpm) at 120 °C as ε-decalactone was injected to the flask under constant argon flow using a syringe pump. The addition rate (r), addition start time (t_a), initial feed composition ($f_{C(0)}$), and total reaction time were adjusted to randomize the copolymer structure. The results of several different trials are given in Table S13.

1**H NMR Spectroscopy:**

^{1}H NMR spectra were collected from $CDCl_3$ solution on a Varian INOVA-500 spectrometer operating at 500 MHz. Chemical shifts are referenced to the protic solvent peaks at 7.26 ppm. ^{1}H NMR spectra are reported as the average of at least 24 scans and were acquired using a 5 second acquisition time and a 10 second delay. Overlays of representative ^{1}H NMR and ^{13}C NMR spectra are shown in Figure S2 and Figure S3 respectively.

Poly(ε-caprolactone-*co*-ε-decalactone) copolymer composition and molar mass were estimated using the following method: The singlet corresponding to the initiator methine (5.10 ppm) protons was used as an internal standard. The degree of polymerization of the PDL component, $N_{N(D)}$, was found using the integral of the peak corresponding to the PDL methine resonances in the region of 4.90–4.78 ppm ($-OC{=}OCH_2CH_2CH_2CH_2\mathbf{CH}(CH_2CH_2CH_2CH_3)O-$). The degree of polymerization of the PCL component, $N_{N(C)}$, was calculated from one half the integral of the peak in the region of 4.0–4.11 ppm ($-OC{=}OCH_2CH_2CH_2CH_2\mathbf{CH_2}O-$. Component molar masses found using the degree of polymerization times the mass of the respective repeat unit. Number average molar mass was taken to be the sum of the two component molar masses.

Block-statistical copolymers composition and molar mass were estimated using the following method: The singlet representative of the initiator aromatic protons (7.34 ppm) was used as an internal standard. The degree of polymerization of the PLA block, $N_{N(LA)}$ was calculated using the integral of PLA methine protons in the region of 5.12 –5.35 ppm ($-C\mathbf{H}(CH_3)OC{=}O-$). The midblock composition was estimated using the method outlined above. Number average molar mass was taken to be the sum of the component molar masses. The poly(lactide) volume fraction (f_{PLA}) was calculated from the composition using 1.248 g cm^{-3} and 1.02 g cm^{-3} for the midblock and PLA blocks, respectively. Total triblock molar mass was determined by using the number average mass of the midblock (determined using MALLS-SEC) and composition (determined by ^{1}HMR spectroscopy) to calculate end block molar mass.

Determination of reactivity ratios:

ε-Caprolactone and ε-Decalactone reactivity ratios were determined using catalytic $Sn(Oct)_2$ at 180 °C. Bulk polymerizations were run in 1ml prescored glass ampoules equipped with magnetic stirbars. To ensure that the sample was heated uniformly the total reaction volume was less than 100 ml. Ampules were submerged in a 180 °C oil bath then removed, broken, and the sample diluted with cholorform. ^{1}H NMR spectroscopy was used to determine the ε-CL composition of the feed and polymer, f_{CL} and F_{CL}, respectively. Polymerization times were adjusted such that the total monomer conversion was less than 10%. The dependence of polymer composition on feed composition was used to determine reactivity ratios, r_C and r_D, using non-linear fit to the copolymer equation:

$$F_C = \frac{r_C f_C^2 + f_C f_D}{r_C f_C^2 + 2 f_C f_D + r_D f_D^2} \qquad (1)$$

In this equation *F* and *f* are the composition of the polymer and feedstock, respectively. The reactivity ratios, r_C and r_D, are defined as the ratio of the rate constants for homopolymer propagation divided by cross propagation:

$$r_C = \frac{k_{CC}}{k_{CD}} \text{ and } r_D = \frac{k_{DD}}{k_{DC}} \qquad (2)$$

^{13}C NMR Spectroscopy:

^{13}C NMR spectra were collected from $CDCl_3$ solution on a Varian INOVA-500 spectrometer operating at 126 MHz. Chemical shifts are referenced to the middle solvent peak at 77.36 ppm, respectively. The ^{13}C NMR spectra show signals in the region of 169-170 ppm and 68.6-69.3 ppm consistent with carbonyl and methine resonances of poly(lactide) segments, respectively. This is shown in Figure S2 and Figure S3.

For each of the poly(lactide) containing triblock polymers, the resonances in the methine region can be assigned to isi and iiisi, isiii, iii, isisi, iiisi, and isiii sterosequences, indicating minimal transesterification within the poly(lactide) block.[1] PCL-*block*-PDL-*block*-PCL, used as a reference spectrum, was synthesized using the procedure described in the methods section of this work except the chain extension was conducted with ε-caprolactone rather than (±)-lactide. The spectrum of PCL-PDL-PCL exhibits resonances consistent with poly(ε-decalactone) and poly(ε-caprolactone) homopolymers but not poly(ε-decalactone-*co*-ε-caprolactone). Because no interblock transesterification is observed in this model system it seems likely that transesterication is minimal within the poly(CL-co-DL) copolymer midblocks.

An absence of signals from 172 to 172.5 ppm in the ^{13}C NMR spectrum of PLA-*block*-PCD-*block*-PLA suggest that interblock transesterification is suppressed.[2] The other poly(lactide)-containing polymers also show no evidence of significant transesterification between poly(lactide) endblocks and the homopolymer or copolymer midblock. The spectrum of PLA-*block*-PCL-*block*-PLA also indicates interblock transesterification is absent in these materials.[3,4,5] Taken together these results suggest the absence of transesterifiaction and sucessfull preservation of the desired triblock block architecture.

Determination of copolymer sequence lengths:

Sequence Length distributions of poly(ε-caprolactone-*co*-ε-decalactone) were determined by ^{13}C NMR Spectroscopy using the instrument and parameters described previously. Samples were prepared by dissolving ≈ 100 mg of copolymer in a 1-2 ml of $CDCl_3$. Once samples had been inserted into NMR tubes, they were injected with 100 µL of a 3.7 mM Chromium(III) acetylacetonate solution and mixed. Integral identities were determined by adding 10 weight % homopolymer to a 50 mol % copolymer.[6] In samples where homopolymer had been added, peaks with obvious increases in intensity were assigned as having resulted from caprolactone-caprolactone (CC) or decalactone-decalactone (DD) sequences. Caprolactone-decalactone (CD) and decalactone-caprolactone (DC) peaks were determined on the basis of proximity to the respective homopolymer peaks. Relevant regions of a ^{13}C spectrum of a representative PCD copolymer are shown in Figure S4, and corresponding peak assignments are given in Table S9. Microstructures were analyzed using the method outlined by Qiu *et al.*[7]

Using this method the probability of addition values was determined for several different compositions of copolymers.

$$P_{CC} = \frac{[CC]}{[CC]+[CD]} \tag{3}$$

$$P_{CD} = \frac{[CD]}{[CC]+[CD]} \tag{4}$$

$$P_{DC} = \frac{[DC]}{[DC]+[DD]} \tag{5}$$

$$P_{DD} = \frac{[DD]}{[DC]+[DD]} \tag{6}$$

From these results the average sequence lengths were estimated:

$$\bar{\nu} = \frac{1}{P_{CD}} \tag{7}$$

$$\bar{\mu} = \frac{1}{P_{DC}} \tag{8}$$

Here $\bar{\nu}$ and $\bar{\mu}$ represent the average PCL and PDL sequence lengths, respectively, in a poly(ε-caprolactone-*co*-ε-decalactone) copolymer.

These results were compared to those predicted using the known composition and experimentally determined reactivity ratios (r_C and r_D).

$$\bar{\nu} = 1 + r_C \frac{[C]}{[D]} \tag{9}$$

$$\bar{\mu} = 1 + r_D \frac{[C]}{[D]} \tag{10}$$

The probability of addition values were also calculated:

$$P_{CC} = \frac{[C]\ r_C}{[C]\, r_C + \ [D]} \tag{11}$$

$$P_{CD} = \frac{[D]}{[C]\, r_C + \ [D]} \tag{12}$$

$$P_{DD} = \frac{[D]\ r_D}{[D]\, r_D + \ [C]} \tag{13}$$

$$P_{DC} = \frac{[C]}{[D]\, r_D + \ [C]} \tag{14}$$

The calculated probability and sequence lengths are compared to the experimentally observed values for a number of compositions in Table S7.

Although the calculated average CL sequence length, $\bar{\nu}$, is correctly anticipated to increase as f_C approaches 1.0, the reactivity ratios consistently overestimate this value compared to the results observed using ^{13}C NMR spectroscopy. Although more work is necessary to explain this difference, the moderately high dispersities of the polymers used for sequence length analysis could indicate some randomization of the polymer microstructure by intermolecular transesterification. Additionally, as shown in Table S8, there are slight differences in the compositions determined using ^{13}C NMR spectroscopy and the compositions determined using ^{1}H NMR spectroscopy, this may indicate some error in the model we used to analyze polymer microstructure.

Differential Scanning Calorimetry:

Differential scanning calorimetry was conducted on a TA Instruments Q-1000 DSC. Samples were analyzed in hermetically sealed aluminum pans. The samples were equilibrated at -80 °C, heated to 100 at 10 °C min^{-1}, cooled to -80 at 5 °C min^{-1}, then reheated to 100 °C at the same rate. To ensure consistent thermal history, glass transitions and melting endotherms are reported upon the second heating cycle. For this work we used ΔH_f^0 = 139.5 J g^{-1}, the enthalpy of fusion for fully crystalline poly(ε-caprolactone), as a reference value to calculate copolymer crystallinity.[8] For the triblock copolymers studied in this work, the T_g values of the highest molar mass PLA blocks were close to the values anticipated for PLA homopolymer. A significant deviation from Flory-Fox behavior was observed at lower molar masses; this is shown Figure S21.[9] It is likely that this difference is likely due to partial mixing of the copolymer and PLA domains.

Size exclusion chromatography:

Dispersity and mass-average molar mass were determined using a size exclusion chromatography instrument with THF as the mobile phase at 25 °C and a flow rate of 1 mL min^{-1}. Size exclusion was performed with three successive Phenomenex Phenogel-5 columns. The mass average molar mass and dispersity were found using the known concentration of the sample in THF and the assumption of 100% mass recovery to calculate d*n*/d*c* from the RI signal.

Small Angle X-ray Scattering:

SAXS analysis was performed at the Advanced Photon Source (APS) at Argonne National Laboratory in beamline Sector12-ID-B. Samples were cut from plaques compression molded at temperatures above the poly(lactide) glass transition and were annealed at 120 °C for 12 hours and 60 °C for 8 hours prior to cooling to room temperature. Experiments were conducted using a sample to detector distance of 360 cm and energy of 13.9984 keV. Scattering intensities were monitored using a silicon pixel Pilatus detector. Additional SAXS experiments were performed at the DuPont-Northewstern Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center located at Sector 5 of the APS. For these experiments the energy was 16.4000 keV, and scattering intensities were monitored using a CCD area detector at a sample to detector distance of 850 cm. To obtain 1-D spectra the 2-D scattering patterns were azimuthally integrated to give the scattering intensity with respect to the scattering vector (*q*).

Dynamic Mechanical Analysis:

The order–disorder transition temperatures were determined by dynamic mechanical analysis using a TAInstruments DHR-3 instrument equipped with electrically heated 25 mm plates and a nitrogen-purged sample chamber. All temperature ramps were conducted at an angular frequency of 1 rad s^{-1} unless otherwise noted. To minimize thermal degradation triblock and multiblock samples were not heated above 200 °C and 150 °C, respectively. Dynamic strain sweeps were conducted at temperatures near the T_{ODT} to ensure the measurements were in the linear regime. Isothermal frequency sweeps were also conducted near the T_{ODT} to corroborate the temperature ramp data. Dynamic mechanical analysis of PCD and P6MCL samples was conducted on a TA Instruments ARES-G2 rheometer using 8 mm plates. The sample temperature was controlled using an oven cooled with liquid nitrogen.

Determination of the molar mass between entanglements (M_e) for PCD:

Using dynamic mechanical analysis of a high molar mass PCD63 sample (100 kg mol^{-1}) was used to estimate the molar mass between entanglements for PCD63. Small amplitude oscillatory shear frequency sweeps were conducted at multiple temperatures. Using time-temperature-superposition a master curve was generated at a reference temperature of 25 °C. A master curve was created using horizontal shifts to tan δ; the shift facters thus obtained were applied to G’ and G’’. No vertical shifts were applied to G’, G’’, or tan δ. The plateau modulus ($G_N°$) at frequency corresponding to the minimum in tan δ was used to calculate the molar mass between entanglements, M_e.

$$M_e = \frac{\rho RT}{G_N^{\circ}} \tag{15}$$

In this equation ρ, R, and T are the density, gas constant, and temperature, respectively. For this sample, the experimentally determined value of the midblock copolymer density ($\rho_{CD70} =$ 1.01±0.05 g cm^{-3}) was used. Using the plateau modulus taken at the minimum of tan δ, the molar mass between entanglements was estimated to be 3.9 kg mol^{-1}. The master curve for this sample is provided Figure S14.

The shift factors used to make the PCD63 master cruve were fit to a linear version of the Williams-Landel-Ferry equation.

$$-\frac{1}{\log(a_T)} = \frac{C_2}{C_1}\frac{1}{(T - T_r)} + \frac{1}{C_1} \tag{16}$$

This linearized fit and the teperature dependence of the sift factors are shown in Figure S15 and Figure S16. A similar analysis was conducted on a P6MCL sample, the results are shown in Figure S17, Figure S18, and Figure S19.

Uniaxial Extension Tests:

Samples for mechanical tests were prepared by compression molding the polymer between two Teflon sheets at 120 °C to form a plaque of uniform thickness (~0.5 mm). After cooling and ageing for a 24-hour period the plaques were cut with a dog-bone-shaped die to prepare test specimens with dimensions that were 3.0 mm (width) 10.0 mm (gauge length). Tensile measurements were performed on a Shimadzu Autograph AGS-

X Series tensile tester (Columbia, MD). All samples were elongated at constant crosshead velocity of 50 mm min^{-1} until failure.

Hysteresis:

Hysteresis tests were conducted in triplicate using a Shimadzu Autograph AGS-X Series tensile tester. Samples were elongated at a crosshead velocity of 110 mm min^{-1} to 67% strain and relaxed at the same rate. For all samples 67% strain is less than half of the elongation at break. Energy loss and recovery data are reported in Table S12 as the range obtained for the three specimens tested.

Density Determination:

Sample densities were measured using a temperature regulated density gradient column prepared from isopropanol and diethylene glycol and were taken as the average of a minimum of 6 trials. The column was calibrated using floats of known density and the temperature was regulated at 23 °C using a water bath. Small, bubble-free spheres of polymer were introduced to the column and allowed to equilibrate for 1 h. The height of each sample was recorded and the density was calculated based on calibration standards. The density of P6MCL was determined to be 0.97 g cm^{-3}. The densitity value of semicrystalline poly(ε-caprolactone) was taken as the value previously measured by otheres (1.15 g cm^{-3} for PCL).[10,11] The amorphous density of PCL was taken as the theoretical value, 1.02 g cm^{-3}.[12] Because poly(ε-caprolactone) and poly(ε-decalactone) have only negligable differences in density we used the a constant value (1.02 g cm^{-3}) to calculate midblock volume fraction regardless of compostion.[13] Based on the thermal expansion coeffecients for PLA and PCL, we estimate that for symetric ($f_{LA} \approx 0.5$) block polymers the use of these room temperature density values leads to errors of $\leq 5\%$ in volume fraction at higher temperatures; this error is predicted to be more significant in samples containing a majority PLA.[14,15]

Solubility Parameter Estimates of χ

In Table S5 we provide solubility parameter estimates for χ of poly(lactide) with a number of different poly(esters) at 140 °C. For these estimates the solubility parameter was found using group contributions, and is the square root of the cohesive energy density.

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i}\right)^{1/2} \tag{17}$$

Specifically, the energy of vaporization of the polymer was calculated using the energy of vaporization contribution, (Δe_j) of each group (*j)* and number (*n)* of groups of type *j* in the repeat unit. V_i, the molar volume of the species *i*, was calculated in a similar manner.

$$\Delta E_i^v = \sum_j n_j \Delta e_j \tag{18}$$

$$V_i = \sum_j n_j V_j \tag{19}$$

Solubility parameters for a CD66 copolymer was calculated as a volume average of the respective homopolymers using room temperature amorphous densities of 1.02 g cm^{-3} and 0.97 g cm^{-3} for ε-caprolactone and ε-decalactone, respectively.

$$\delta_{copolymer} = \sum_i \delta_i \Phi_i \tag{20}$$

For block-random copolymers if regular mixing is obeyed the effective interaction parameter between the blocks can be varied continuously with the composition of the random copolymer block. Others have demonstrated that this is applies in the case of polystyrene-poly(ethylene-alt-propylene) block–random copolymers but fails for unknown reasons in ternary systems containing a poly(ethylene) block.[16,17] It is worth noting that in LCDL triblocks the midblock is a gradient rather than a truly random copolymer. Because the DL units are enriched near the junction of the PLA and copolymer blocks it is possible that at a given midblock composition the interaction parameter with lactide is lower than would be predicted for a truly random copolymer.[18]

Using the solubility parameters thus estimated we calculated χ for a number of polymer pairs using the difference in the solubility parameters.

$$\chi_{A-B} = \frac{V_{ref}\,(\delta_A - \delta_B)^2}{RT} \qquad (21)$$

In this work all interaction parameter estimates were calculated using a reference volume of 118 Å^3. For the polymers shown in Table S5, the component values of energy of vaporization and group molar volume used to calculate solubility parameters were taken from Fedors.[19] For comparison, the interaction parameter for poly(caprolactone)-poly(lactide) and poly(valerolactone)-poly(lactide) were also estimated using group contribution method with the parameters reported by Van Krevelen.[20,21] The estimates differed depending on whether the component values were taken Fedors or Van Krevelen; however, in both cases poly(lactide) is predicted to be more miscible with poly(valerolactone) than with poly(caprolactone).

The interaction parameter for poly(caprolactone) and poly(lactide) was also calculated from Hansen solubility parameters experimentally determined by Bordes[22]and Schenderlein [23] using swelling tests as well as Bordes[19] and Schively[24] using turbidity experiments. For the poly(lactide)-block-polyester systems analyzed in this work and the works of Martello, the group contribution methods consistently overestimates the incompatibility of the component blocks compared to mean field estimates taken from the T_{ODT} values of compositionally symmetric block polymers. [25,26] For poly(caprolactone)-poly(lactide), the mean field estimate of χ was much closer to the value calculated using experimentally determined Hansen solubility paramters than to the value calcualted using group contributions.

Table S1. Telechelic PCL polymer midblocks used for this work.

Midblock	$^{a}M_n^{NMR}$ (kg mol^{-1})	$^{b}M_n^{SEC}$ (kg mol^{-1})	$^{b}Đ$	$^{c}T_g$ (°C)	$^{c}T_m$ (°C)	^{c}X (%)
PCL (10.8)	11.1	10.8	1.06	-61.5	54.5	51.7
PCL(12.2)	12.2	12.2	1.13	-61.7	54.7	34.0
PCL (11.6)	10.1	11.6	1.06	-60.3	54.3	50.2
PCL (14.5)	16.2	14.5	1.06	-61.5	55.2	49.4
PCL (15.7)	16.0	15.7	1.13	-64.1	55.1	59.0
PCL (18.9)	16.9	18.9	1.15	-63.4	55.5	62.1
PCL (18.1)	18.8	18.1	1.18	-62.3	54.6	53.2
PCL (22.1)	18.9	22.1	1.16	-63.2	55.4	50.8

[a] Number average molar mass determined using ^{1}HNMR spectroscopy. Calculated using initiator methylene protons as an internal standard. [b] Number average molar mass and dispersity determined using MALLS-SEC; d*n*d*c* was found from the RI signal using the known concentration and the assumption of 100% mass recovery. [c] Glass transition temperature values and melting point values were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. Crystallinity was calculated using a reference enthalpy of fusion of 139.5 J g^{-1} for fully crystalline PCL.

Table S2. Telechelic PCD polymer midblocks used for this work.

Midblock	$^{a}M_n^{nmr}$ (kg mol^{-1})	$^{b}F_{CL}$	$^{c}M_n^{SEC}$ (kg mol^{-1})	$^{c}Đ$	$^{d}T_g$ (°C)	$^{d}T_m$ (°C)	^{d}X (%)
CD66 (9.2)	8.2	0.66	9.2	1.10	-60.0		
CD66 (10.2)	9.7	0.66	10.2	1.20	-62.5		
CD65 (15.5)	14.2	0.65	15.5	1.10	-61.0		
CD63 (18.3)	18.3	0.63	18.3	1.13	-62.3		
CD78 (10.6)	9.40	0.78	10.6	1.08	-63.6	19.7	18.9
CD77 (12.5)	11.37	0.77	12.5	1.05	-63.6	16.4	16.8
CD76 (13.1)	13.8	0.76	13.1	1.12	-63.3	18.1	12.3
CD76 (19.0)	15.0	0.76	17.0	1.08	-64.5	15.9	14.8
CD77 (22.6)	20.5	0.77	22.6	1.04	-64	18.2	15.3
CD69 (19.4)	19.61	0.69	19.4	1.05	-62.0		
CD68 (42.5)	41.5	0.68	42.5	1.10	-62.6		
CD67 (48.5)	45.1	0.67	48.5	1.30	-61.3		
CD68 (50.1)	54.5	0.68	50.1	1.41	-61.4		
CD69 (83.4)	95.8	0.69	83.4	1.16	-61.6		
CD68 (86.5)	104.5	0.68	86.5	1.44	-61.1		

[a]Number average molar mass determined using ^{1}HNMR 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; d*n*d*c* was found 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}. Cystallinity was calculated using a reference enthalpy of fusion of 139.5 J g^{-1} for fully crystalline PCL

Table S3. Telechelic LCL polymer triblocks used for this work.

Triblock	Block M_n (kg mol^{-1})		$^cM_n^{SEC}$ (kg mol^{-1})	$^c Đ$	$^dN_{tot}$	$^e f_{PLA}$	^fD (nm)	^gT_g (°C)	^gT_m (°C)	^gX %	$^hT_{ODT}$ (°C)
	^{a}PLA	^{b}PCL									
LCL (23.6, 0.44)	5.7	12.2	27.8	1.06	300	0.45	17	-64.5	53.5	33.0	<60
LCL (19.6, 0.50)	4.4	10.8	23.8	1.05	250	0.50	17	-63.2	50.0	30.1	75
LCL (24.2, 0.48)	9.1	16.0	35.0	1.08	425	0.48	19	-62.1	54.3	36.1	112
LCL (35.1, 0.53)	10.3	14.5	33.6	1.03	430	0.53	19	-63.1	49.3	32.5	118
LCL (34.3, 0.46)	8.7	16.9	29.7	1.09	430	0.46	21	-64.0	53.7	35.1	119
LCL (40.1, 0.48)	10.6	18.9	40.7	1.11	500	0.48	23	-63.0	54.0	42.0	146
LCL (43.1, 0.53)	12.5	18.1	40.8	1.04	530	0.53	20	-62.0	51.2	34.7	174

[a]Molar mass reported for PLA block, or ½ the total molar mass of PLA per triblock chain. This value was calculated from the molar mass of the midblock, determined using MALLS-SEC and the composition, determined using ^{1}HNMR spectroscopy. [b] Midblock molar mass determined using MALLS-SEC. [c]Determined using MALLS-SEC. [d]Calculated from total molar mass (sum of block molar masses) using a reference volume of 118 Å and room temperature densities of 1.248 g cm^3 and 1.02 g cm^{-3} g cm^{-3} for PLA and PCL midblock, respectively. [e]Volume fraction of poly(lactide) in the statistical block polymer determined using ^{1}H NMR spectroscopy. [f]Principal domain spacing of the bulk sample determined by SAXS at room temperature. [g]Glass transition temperatures and melting point values were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. [h]Order to disorder transition temperatures were determined using DMA. Values are reported for an isochronal (1 rad s^{-1}) temperature ramps at a rate of 1 °C and a constant strain of (1%).

Table S4. Telechelic LCDL polymer triblocks used for this work.

Triblock	**Block M_n (kg mol^{-1})**		**$^{c}M_n^{SEC}$ (kg mol^{-1})**	**^{c}Đ**	**$^{d}N_{tot}$**	**$^{e}f_{PLA}$**	**^{f}D (nm)**	**$^{g}T_g$ (°C)**	**$^{g}T_g$ (°C)**	**$^{h}T_{ODT}$ (°C)**
	^{a}PLA	^{b}PCD								
LCD65L (20.0, 0.49)	5.4	9.2	18.1	1.12	250	0.49	15	-54.2	25.9	65
LCD66L (22.2, 0.49)	6.0	10.2	17.1	1.25	280	0.49	17	-56.0	31.4	92
LCD67L (43.7, 0.49)	9.1	15.5	31.9	1.18	420	0.49	20	-57.1	37.3	126
LCD63L (40.7, 0.5)	11.2	18.3	32.8	1.04	510	0.50	24	-59.3	48.8	170
LCD78L (22.8, 0.48)	6.1	10.6	19.1	1.05	280	0.48	17	-58.1	28.5	70
LCD77L (27.1, 0.49)	7.3	12.5	25.2	1.07	340	0.49	18	-58.0	35.1	100
LCD76L (28.7, 0.49)	7.8	13.1	24.8	1.10	360	0.49	20	-56.0	41.4	130
LCD76L (39.4, 0.49)	11.2	17.0	33.1	1.15	520	0.49	22	-55.4	39.0	150
LCD69L (104, 0.17)	10.5	83.4	82 (103)	1.26	1270	0.17	44	-60.0	46.7	>200
LCD69L (113, 0.21)	14.6	83.4	92 (117)	1.27	1320	0.21	34	-60.4	50.2	>200
LCD69L (131, 0.32)	24.0	83.4	100 (125)	1.25	1420	0.32	60	-59.4	52.9	>200

[a]Molar mass reported for PLA block, or ½ the total molar mass of PLA per triblock chain. This value was calculated from the molar mass of the midblock, determined using MALLS-SEC and the composition, determined using ^{1}HNMR spectroscopy. [b]Number average molar mass of the midblock determined using MALLS-SEC [c]Determined using MALLS-SEC.[d]Calculated from total molar mass (sum of block molar masses) using a reference volume of 118 Å and room temperature densities of 1.248 g cm^3 and 1.02 g cm^{-3} g cm^{-3} for PLA and copolymer midblock, respectively. [e]Volume fraction of poly(lactide) in the statistical block polymer determined using ^{1}H NMR spectroscopy. [f]Principal domain spacing of the bulk sample determined by SAXS at room temperature. [g]Glass transition temperatures and melting point values were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. Crystallinity was estimated using a reference enthalpy of fusion of 139.5 J g^{-1}. [h]Order to disorder transition temperatures were determined using DMA. Values are reported for an isochronal (1 rad s^{-1}) temperature ramps at a rate of 1 °C and a constant strain of (1%).

Table S5. Estimated values of χ at 140 °C for poly(lactide) and various poly(esters)

Second block	[a]Solubility parameter Estimate	[f]Mean field Estimate	Reference:
poly(δ-valerolactone)	0.037, [b]0.042	-	-
poly(ε-caprolactone)	0.077, [b]0.064 [c,d]0.035, [c,e]0.027	0.039	This work
poly(δ-methyl-δ-valerolactone)	0.118	-	-
poly(CD66)	0.147	0.041	This work
poly(ε-methyl-ε-caprolactone)	0.158	0.048	22
poly(ε-decalactone)	0.249	0.095	23

[a]Calculated from solubility parameters estimated by group contribution method using the parameters reported by Fedors.[16] [b]Calculated using solubility parameters estimated by group contribution method with the parameters reported by Van Krevelen[17,18] [c]Calculated from experimentally determined Hansen solubility parameters reported by [d]Bordes[19] and Schenderlein[20] (swelling tests) as well as [e]Bordes[19] and Schively[21] (turbidity experiments). [f]This estimate is from the temperature dependence of the interaction parameter reported by the indicated refernce.

Table S6. Thermal Characteristics of representative poly(ε-caprolactone-*co*- ε-decalactone) statistical copolymers

${}^{a}F_{CL}$	${}^{a}M_{N}$	${}^{b}T_{M}$ (°C)	${}^{b}T_{g}$ (° C)	${}^{c}X$ (%)
1.00	22.1	56.8	-61.5	49.2
0.96	21.6	48.5	-62.0	39.0
0.94	24.8	52.5	-61.0	44.9
0.92	22.3	49.9	-62.0	38.6
0.91	21.5	44.8	-61.8	39.0
0.89	15.5	44.6	-62.1	34.0
0.88	20.2	39.2	-62.5	29.3
0.85	21.2	40.8	-61.0	26.5
0.77	20.5	18.2	-64.0	16.0
0.74	16.1	21.3	-63.6	18.6
0.73	17.9	19.5	-62.8	1.2
0.71	16.0	18.7	-61.5	5.5
0.69	19.4	-	-62.0	-
0.63	18.3	-	-62.3	-
0.60	17.7	-	-60.1	-

[a] Copolymer compositions and number average molar masses were determined using ^{1}H NMR spectroscopy. [b] Thermal characteristics were determined using DSC and are reported for the second heating (5 °C min^{-1}). [c] X was found using the reference heat of fusion (139.5 J g^{-1}) for fully crystalline poly(caprolactone).

Table S7. Sequence length analyses for representative poly(ε-caprolactone-*co*- ε-decalactone) statistical copolymers

[a]F_C	[b]P_{CC}	[b]P_{CD}	[b]P_{DC}	[b]P_{DD}	[c]$\bar{\nu}$	[d]$\bar{\mu}$
0.592	0.643 *(0.895)*	0.357 *(0.105)*	0.576 *(0.980)*	0.424 *(0.020)*	2.80 *(9.52)*	1.74 *(1.02)*
0.785	0.807 *(0.956)*	0.193 *(0.044)*	0.843 *(0.992)*	0.157 *(0.008)*	5.18 *(22.70)*	1.19 *(1.01)*
0.874	0.887 *(0.975)*	0.112 *(0.024)*	0.927 *(0.996)*	0.072 *(0.004)*	8.93 *(41.40)*	1.08 *(1.00)*

[a]Compositions were determined using ^{13}C NMR spectroscopy. Values indicated in parentheses are theoretical compositions used to calculate sequence lengths and probability of addition. [b]Probability of addition values determined using ^{13}C NMR spectroscopy. Values indicated in parentheses were calculated from composition and experimentally determined reactivity ratios. [c]Average CL sequence length calculated from probability of addition determined using ^{13}C NMR spectroscopy. Values indicated in parentheses were calculated from composition and experimentally determined reactivity ratios. [d]Average DL sequence length calculated from probability of addition determined using ^{13}C NMR spectroscopy. Values indicated in parentheses were calculated from the feed composition using experimentally determined reactivity ratios.

Table S8. Molecular characteristics of poly(ε-caprolactone-*co*- ε-decalactone) statistical copolymers detailed in Table S7.

Sample ID	**[a]Target M_n (kg mol^{-1})**	**[b]F_C**	**[c]F_C**	**[d]Reaction Time (min)**	**[e]M_n (kg mol^{-1})**	**[e]Đ**
1	16	0.711	0.592	40	25.5	1.89
2	16	0.809	0.785	40	33.8	1.66
3	15.5	0.894	0.874	40	35.1	1.68

[a]Target molar mass calculated from mole ratio of monomer to initiator. [b]Mole percent calculated by ^{1}H NMR spectroscopy. [c]Mole fraction ε-caprolactone in polymer determined using ^{13}C NMR spectroscopy. [d]Reactions carried out in 180˚C oil baths. [e]Measured via SEC with poly(styrene) standards. The molar mass using this method is about double the expected molar mass due to the difference in hydrodynamic volume of PDL and PS.[23]

Table S9. Correlation of peak numbers (Figure S4) to sequence assignments

Peak Numbers	0	1	2+4+5	3	6+8	7	9+11	10	12	13	14	15	16
Assignment	DC	CC	DC	DD	CD	DD	DC	CC	DD	CD	DC	CC	CD+DD

Peak Numbers	17	18	19	20	21	22	23+24+25+26	27	28	29	30
Assignment	CD	DD	CD+CC	DC+DD	DC	CC	2DD+ 2DC	DC	CC	DD+DC	DD+DC

[a] Correlation of peak numbers to sequence assignments for PCD copolymers ^{13}C NMR assignments are shown in **Figure S4**.

Table S10. Telechelic LCDL triblocks and (LCDL)$_n$ multiblocks used for this work.

Sample ID	Block M_n (kg mol^{-1})		[c]M_n^{SEC} (kg mol^{-1})	[c]Đ	[d]N_{tot}	[e]<n>	[f]f_{PLA}	[g]D (nm)	[h]T_g (°C)	[h]T_g (°C)	[i]T_{ODT} (°C)
	[a]PLA	[b]PCD									
LCD69L (24.2, 0.17)	2.5	19.4	26.5	1.04	320	-	0.17	17	-51.8	18.0	nd
LCD69L$_{3.46}$ (24.2,0.17)	2.5	19.4	91.8	1.41	1120	3.46	0.17	17	-52.3	30.0	nd
LCD69L (31.4, 0.33)	6.0	19.4	23.2	1.08	400	-	0.33	26	-59.4	29.5	95
LCD69L$_{2.0}$ (31.4, 0.33)	6.0	19.4	47.9	1.41	810	2.0	0.33	28	-58.0	41.2	112
LCD77L (34.2, 0.30)	5.8	22.6	27.5	1.04	440	-	0.30	20	-56.8	42.6	106
LCD77L$_{2.0}$ (34.2, 0.30)	5.8	22.6	54.7	1.33	890	2.0	0.30	20	-55.7	46.9	120
LCD69L (43.2, 0.5)	11.9	19.4	19.4	1.06	540	-	0.50	22	-51.3	38.2	190
LCD69L$_{1.9}$ (43.2, 0.5)	11.9	19.4	36.0	1.42	1020	1.91	0.50	22	-53.0	44.0	>200

[a]Molar mass reported for PLA block, or ½ the total molar mass of PLA per triblock chain. This value was calculated from the molar mass of the midblock, determined using MALLS-SEC and the composition, determined using ^{1}HNMR spectroscopy. [b]Number average molar mass of the midblock determined using MALLS-SEC [c]Determined using MALLS-SEC.[d]Calculated from total molar mass (sum of block molar masses) using a reference volume of 118 Å and room temperature densities of 1.248 g cm^3 and 1.02 g cm^{-3} g cm^{-3} for PLA and copolymer midblock, respectively. [e] The average number of triblocks per multiblock chain, taken from the ratio of multiblock number average molar mass and triblock number average molar mass, determined using MALLS-SEC. [f]Volume fraction of poly(lactide) in the statistical block polymer determined using ^{1}H NMR spectroscopy. . [g]Principal domain spacing of the bulk sample determined by SAXS at room temperature. [h]Glass transition temperatures were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}.[i]Order to disorder transition temperatures were determined using DMA. Values for triblocks are reported for an isochronal (1 rad s^{-1}) temperature ramp at a rate of 1 °C and a constant strain of (1%). Values for multiblocks are reported for an isochronal (0.1 rad s^{-1}) temperature ramp at a rate of 0.2 °C and a constant strain of (1%).

Table S11. Room temperature tensile properties of poly(lactide) block–statistical triblock and multiblock polymers

[a]Sample	E_Y (MPa)	σ_{300} (MPa)	σ_b (%)	ε_b (%)
LCD69L (31.4, 0.33)	1.07 ± 0.13	0.57 ± 0.06	0.93 ± 0.13	609 ± 22
LCD77L (34.2, 0.30)	7.12 ± 1.28	1.60 ± 0.05	1.67 ± 0.19	580 ± 64
LCD69L (43.2, 0.50)	46.5± 16.0		2.91 ± 0.53	90.8 ± 30
$(LCD69L)_{2.0}$ (31.4, 0.33)	1.37 ± 0.42	1.61 ± 0.09	6.36 ± 0.23	1651 ± 97
$(LCD77L)_{2.0}$ (34.2, 0.30)	2.33 ± 0.38	1.86 ± 0.06	9.04 ± 0.31	1950 ± 73
$(LCD69L)_{2.1}$ (43.2, 0.50)	32.05 ±4.2	6.64 ± 0.60	8.53 ± 0.59	860 ± 60

Room temperature tensile properties of multiblock samples. [a]All samples were prepared by compression molding and tested at room temperature with a constant crosshead velocity of 50 mm min^{-1}. The data are the average and standard deviation for a minimum of 5 samples.

Table S12 Hysteresis of block-statistical copolymer triblock and multiblock samples

Sample	[a]Cyle1 (%)	[b]Cycle2 (%)
LCD69L (104, 0.17)	26-28	15-17
LCD69L (113, 0.21)	24-27	11-14
LCD69L (131, 0.32)	34-37	19-20
LCD77L (34.2, 0.30)	55-57	36-38
$(\mathrm{LCD77L})_{2.0}$ (34.2, 0.30)	29-32	18-22

[a] Hysteresis tests were conducted at a constant crosshead velocity of 110 mm min^{-1} and strain of 67%. The data is reported is the energy loss (%) on relaxation for the indicated cycle and is given as the measured range of three specimens.

Table S13 Semibatch polymerization of PCD

Sample ID	[a]F_{CL}	[bc]X (%)	[c]T_m (°C)	[d]Mw kg mol^{-1}	[d]Đ	[e]$f_{c(0)}$	[f]r ml hr^{-1}	[g]t_a (hr)	[h]t_f (hr)
PCL	1.00	40.3	55.9	30.6	1.29	1.0	-	-	3
PCL-Batch1	0.92	31.9	53.9	29.3	1.32	0.9	-	-	12
PCL-Semibatch1	0.90	32.4	48.8	26.1	1.23	0.0	1.5	0	16
PCL-Semibatch2	0.92	36.6	53.4	23.8	1.19	0.0	2.9	0	12
PCL-Semibatch3	0.90	32.0	47.9	15.9	1.18	0.21	2.9	0.5	16
PCL-Semibatch4	0.91	29.6	45.8	28.8	1.29	0.21	2.9	0	12

[a] Determined from ^{1}H NMR of precipitated polymers. [b] Crystallinity was calculated using a reference enthalpy of fusion of ΔH=139.5 J/g for 100 % crystalline P(εCL). [c] Maximum peak melting temperature and ΔH were obtained from DSC second heating at a ramp rate of 5 °C/min. [d] Obtained using MALLS-SEC, with THF eluent. Dispersity is determined from LS-SEC using the assumption of 100% mass recovery to determine dn/dc of the copolymer. [e] Inital feed composition prior to CL addition. [f] Rate of CL addition. [g] Start time of CL addition, t = 0 is defined as the start of polymerization, i.e. when the catalyst was added to the CD monomer solution. [h] Total reaction time.

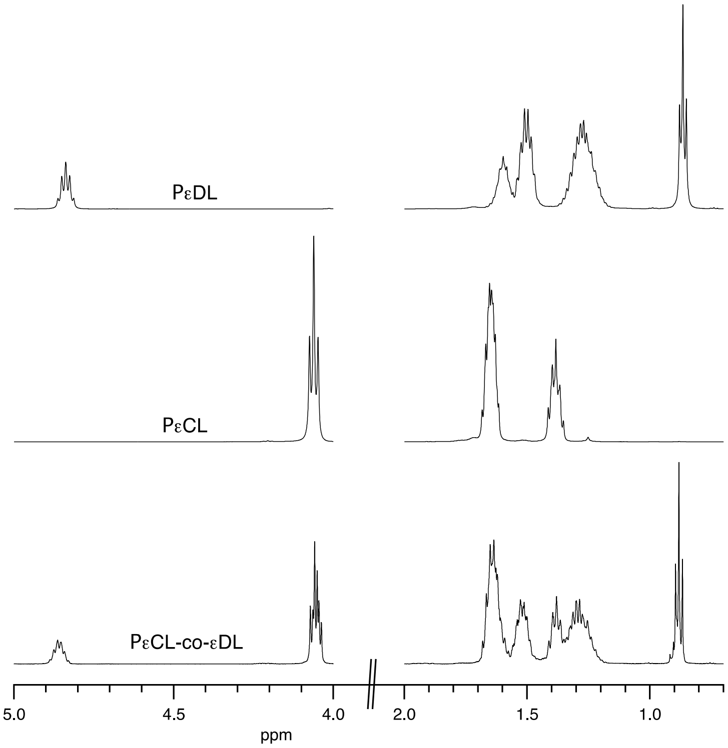


Figure S1. ^{1}H NMR spectra of poly(ε-decalactone), poly(ε-caprolactone), and poly(ε-decalactone-*co*-caprolactone) showing the resonances used to determine copolymer composition.

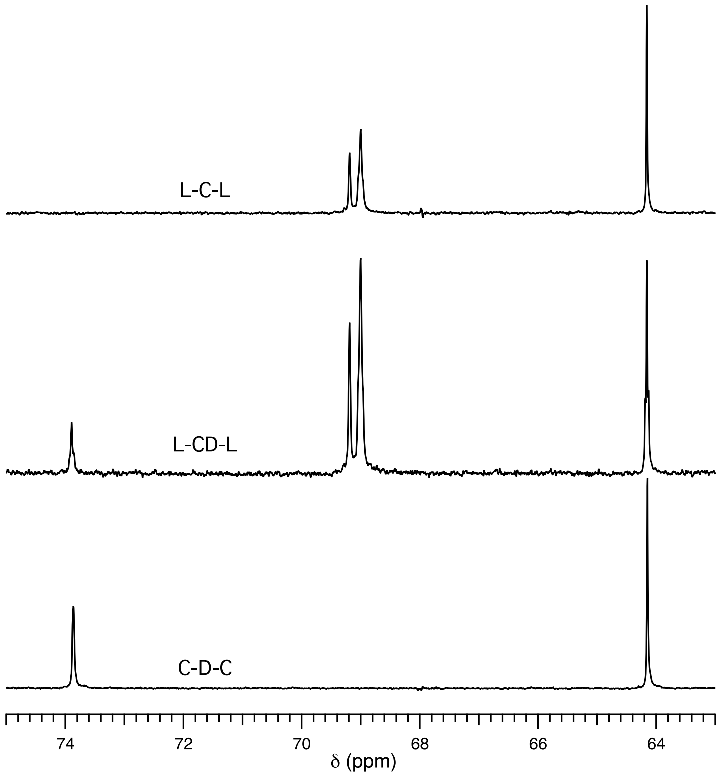


Figure S2. ^{13}C NMR spectra of representative triblock polymers showing resonances in the region characteristic of polyester methine or methylene carbons adjacent to the oxygen.

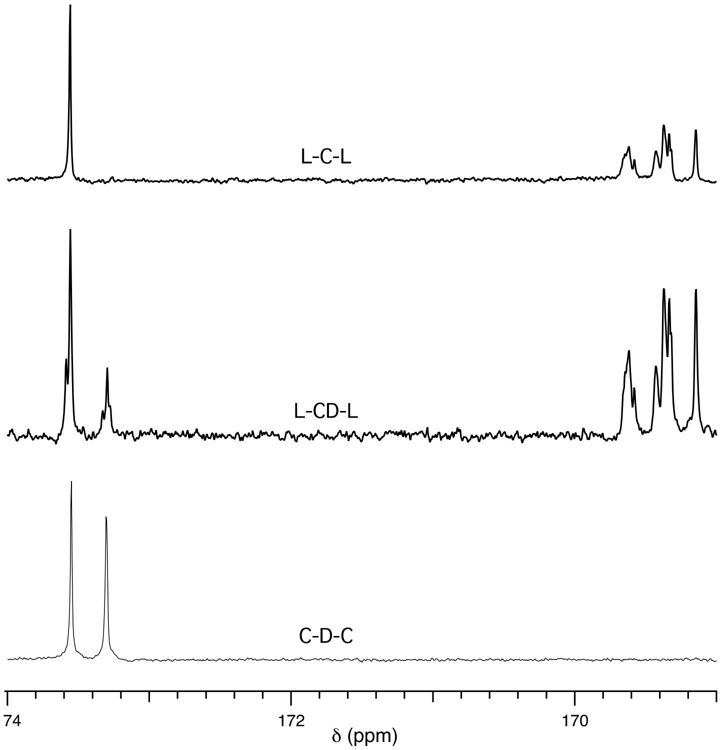
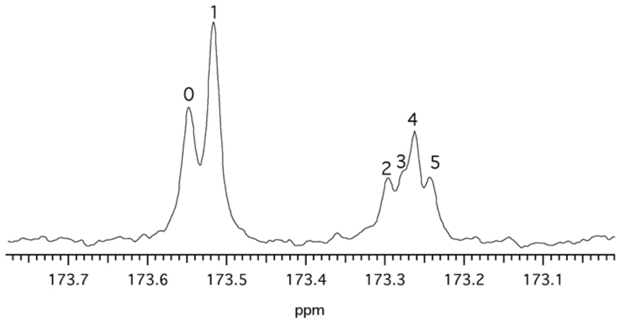


Figure S3. ^{13}C NMR spectra of representative triblock polymers showing resonances in the region (169–174 ppm) characteristic of the carbonyl carbons.

(a)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173.3
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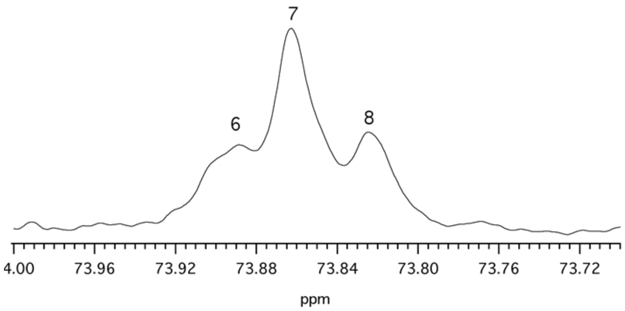
ppm

(b)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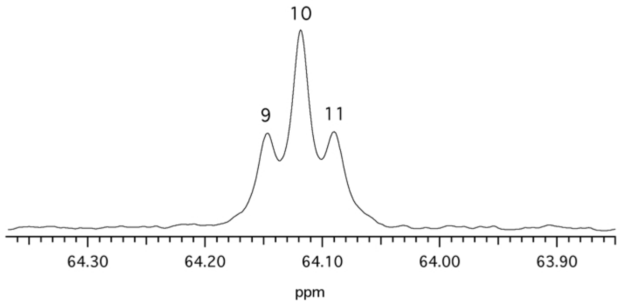
(c)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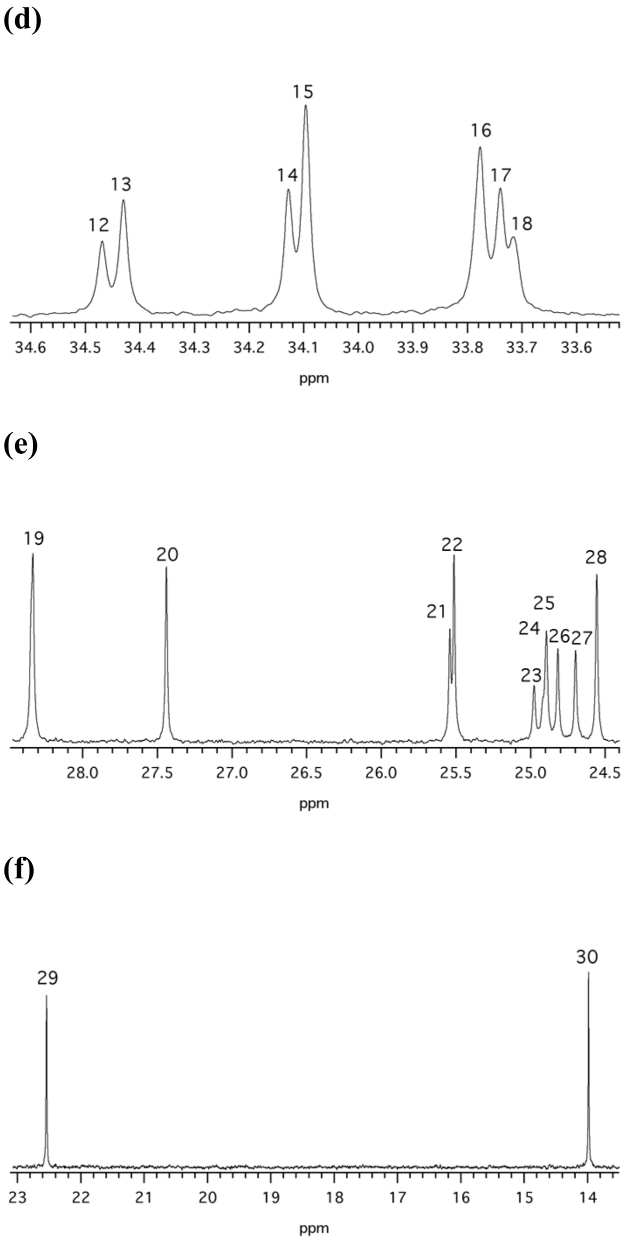

Figure S4a-4f. Relevant regions of a ^{13}C NMR spectrum of a representative a poly(ε-caprolactone-*co*-ε-decalactone) copolymer showing CC, DD, DC, and CD resonances. Assignments are given in Table S9.

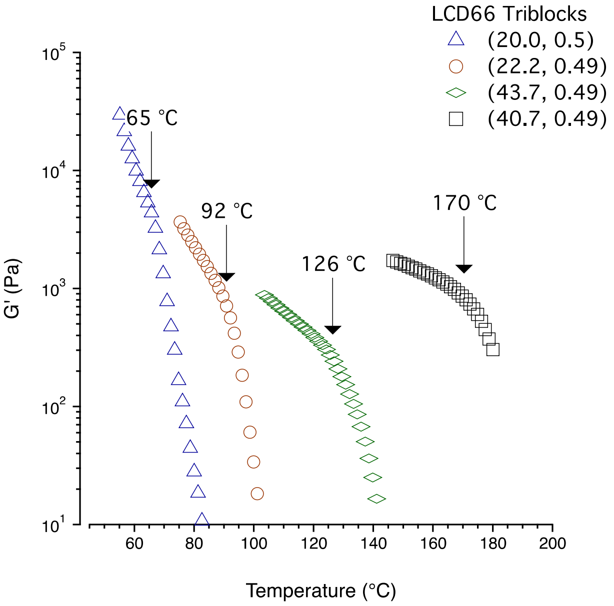

Figure S5. Isochronal temperature ramp data on heating (1 rad s^{-1}, 1°C min^{-1}, 1% strain) or LCDL triblock copolymers LCD65L (20.0, 0.50), LCD66L (22.2, 0.5), LCD67L (43.7, 0.49), LCD63L (40.7, 0.49).

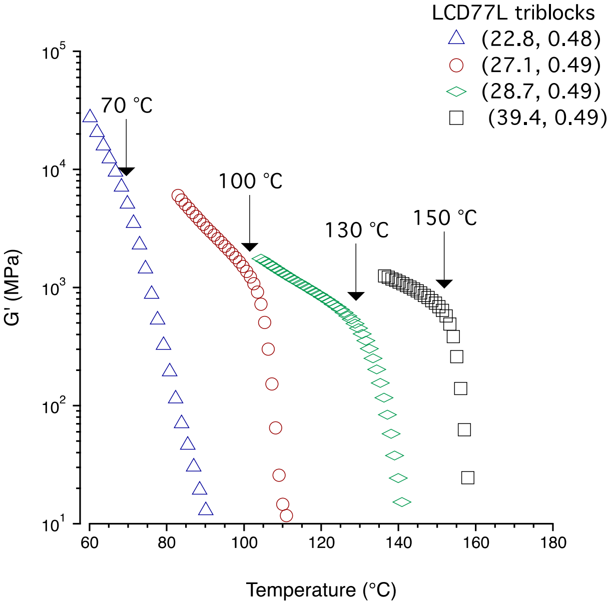

Figure S6. Isochronal temperature ramp data on heating (1 rad s^{-1}, 1°C min^{-1}, 1% strain) for LCDL triblock copolymers LCD78L (22.8, 0.48), LCD77L (27.1, 0.49), LCV76L (28.7, 0.49), LCV76L (39.4, 0.49).

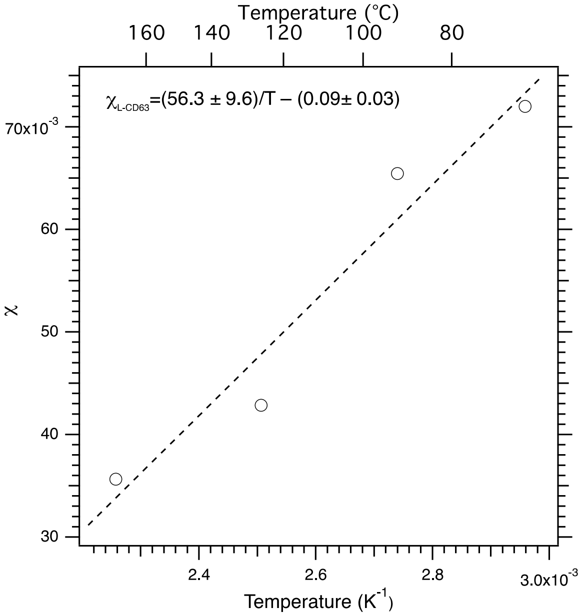

Figure S7. χ temperature dependence for LCD66L. Points shown correspond to T_{ODT} values determined using DMA, data are provided in Figure S5.

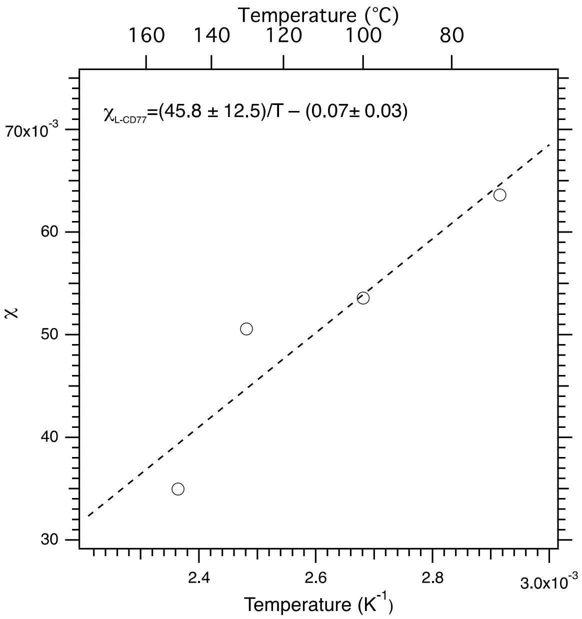

Figure S8. χ temperature dependence for LCD77L. Points shown correspond to T_{ODT} values determined using DMA, data are provided in Figure S6.

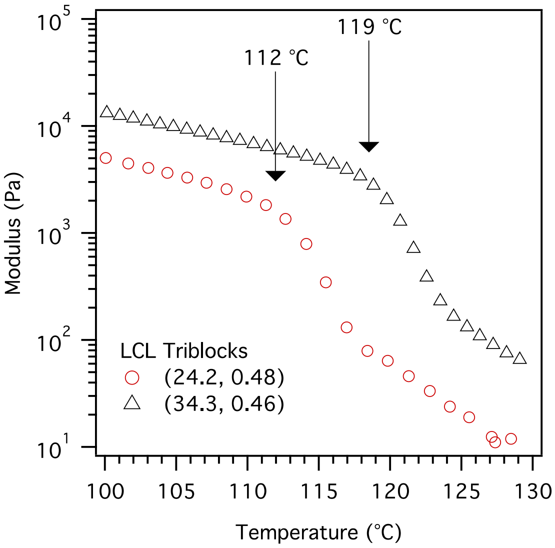

Figure S9. Isochronal temperature ramp data on heating (1 rad s^{-1}, 1°C min^{-1}, 1% strain) for LCL (24.2, 0.48) and LCL (34.3, 0.46). The data for LCL (34.3, 0.46) have been shifted vertically for clarity.

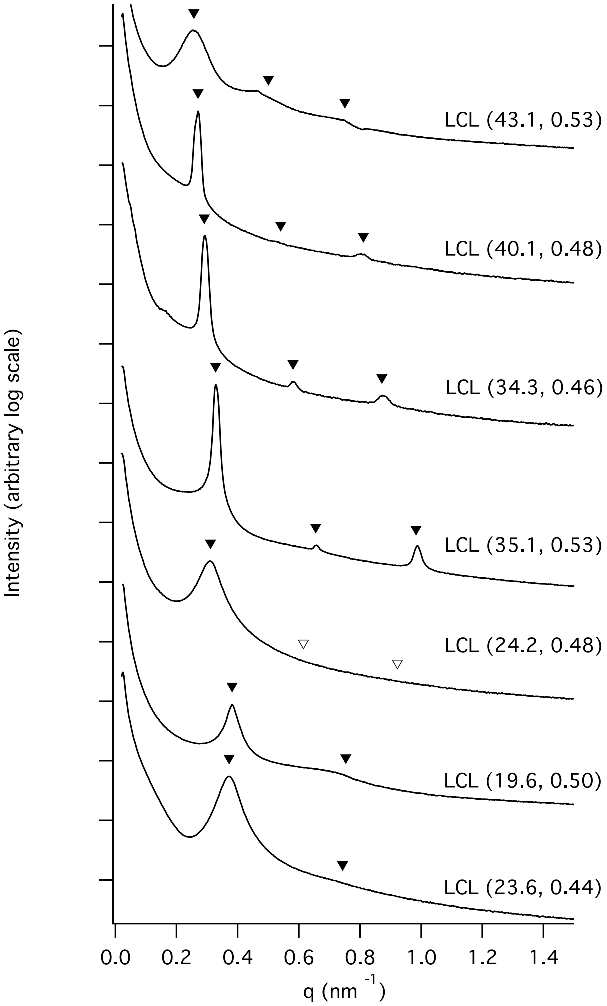

Figure S10. Room temperature SAXS data for compositionally symmetric LCL triblock samples. The principle peaks are marked with (▼). Calculated reflections for anticipated lamellar morphologies are marked with (▼) and (▽) denoting reflections that are present, and absent respectively.

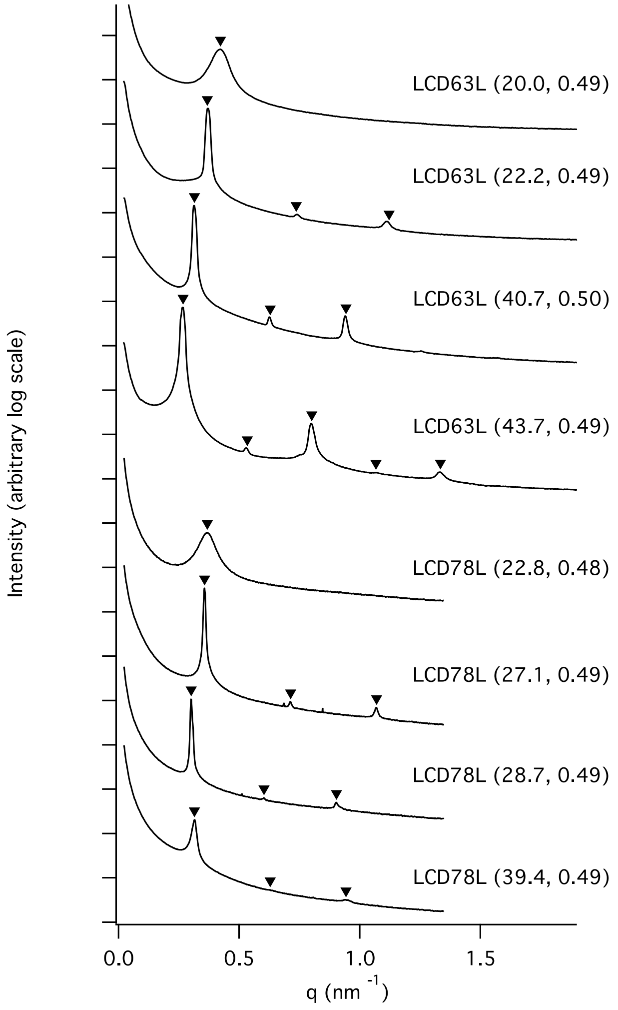

Figure S11. Room temperature SAXS data for compositionally symmetric LCDL triblock samples. The principle peaks are marked with (▼). Calculated reflections for anticipated lamellar morphologies are marked with (▼) and (▽) denoting reflections that are present, and absent respectively.

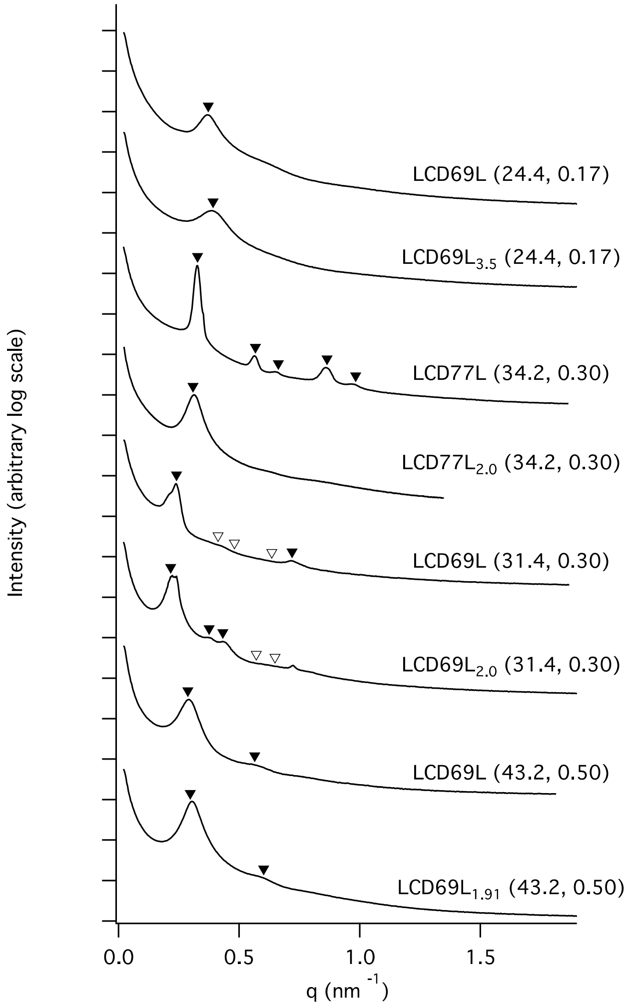

Figure S12. SAXS Data for LCDL triblocks and $(LCDL)_n$ Multiblocks. The principle peaks are marked with (▼). For $f_{LA} = 0.33$ and $f_{LA} = 0.30$ the calculated reflections for anticipated cylindrical morphologies are marked with (▼) and (▽) denoting reflections that are present, and absent respectively.

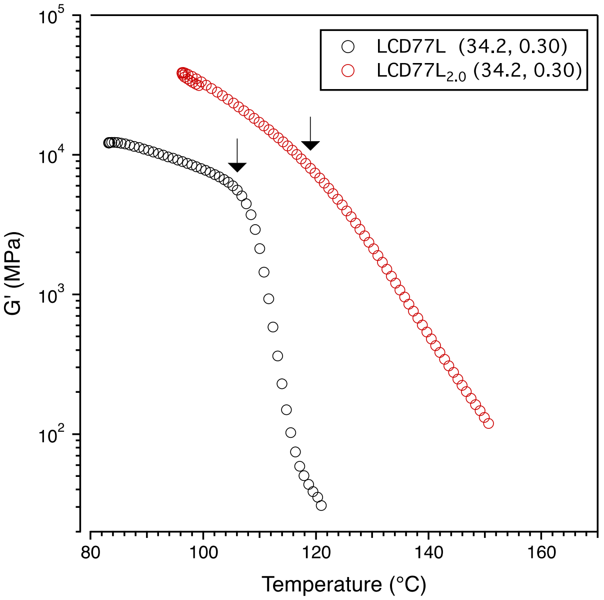

Figure S13. Isochronal temperature ramp data on heating (1 rad s^{-1}, 1°C min^{-1}, 1% strain) for LCD77L (34.2, 0.3). Isochronal temperature ramp data on heating (0.1 rad s^{-1}, 0.2°C min^{-1}, 1% strain) for multiblock $(LCD77L)_{2.0}$ (34.2, 0.3).

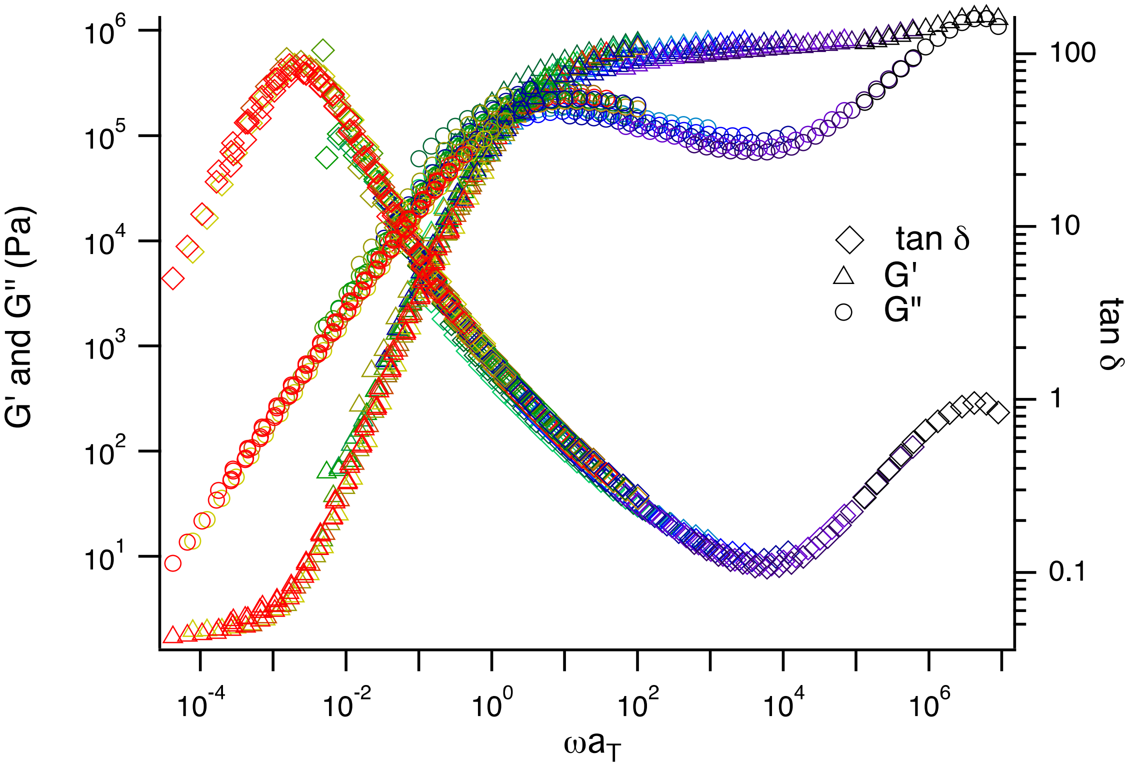

Figure S14. PCD63 Master curve created using isothermal frequency sweeps (100 to 0.1 rad sec^{-1}) data were acquired from 180 °C to -30 °C. The reference temperature used is 25 °C. The shift factors were obtained by shifting tan δ and applied to G' and G''. No vertical shifts were applied. Shift factors and fit to the WLF equation are shown in S15 and S16.

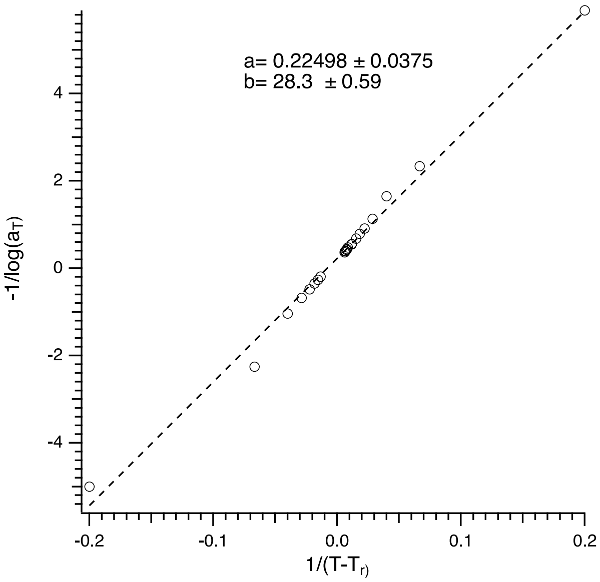

Figure S15. Linear fit (y=a+bx) to the shift factors obtained from the master curve generated for PCD63; C_1 and C_2 were calculated from this fit.

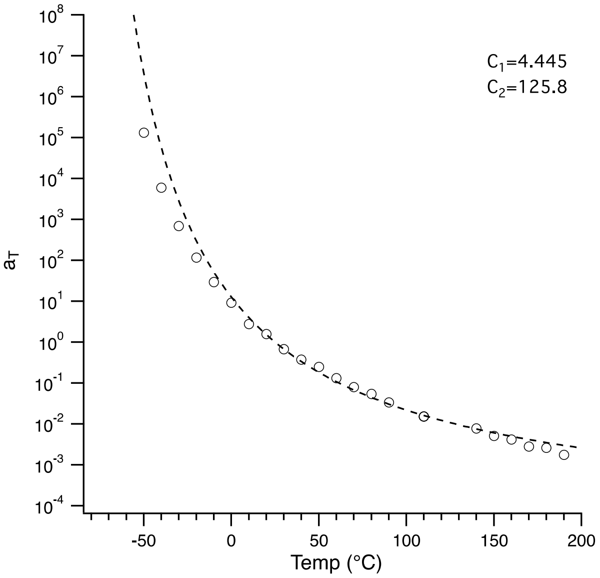

Figure S16. Temperature dependence of shift factors for PCD63.

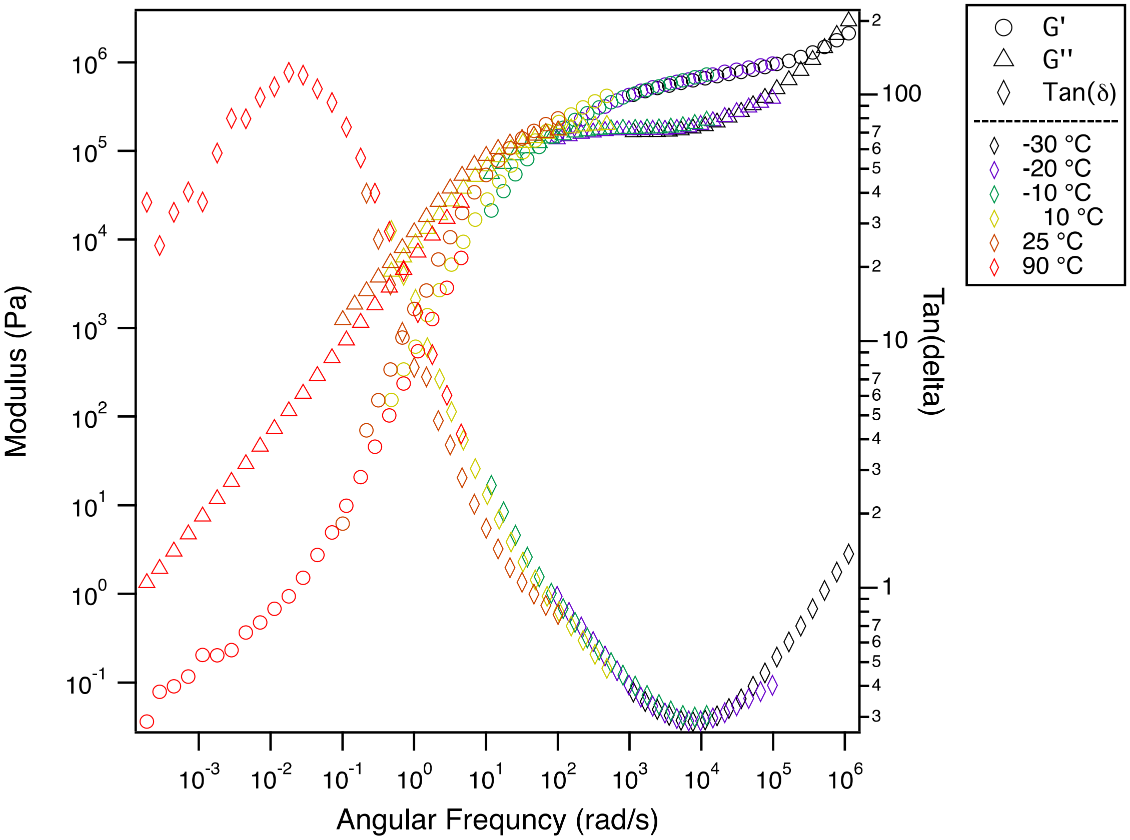

Figure S17. P6MCL Master curve created using isothermal frequency sweeps (100 to 0.1 rad sec^{-1}) data were acquired in 10 °C increments from 180 °C to -30 °C. The reference temperature used is 25 °C. The shift factors were obtained by shifting tan δ and applied to G’ and G’’. No vertical shifts were applied. Shift factors and fit to the WLF equation are shown in S18 and S19.

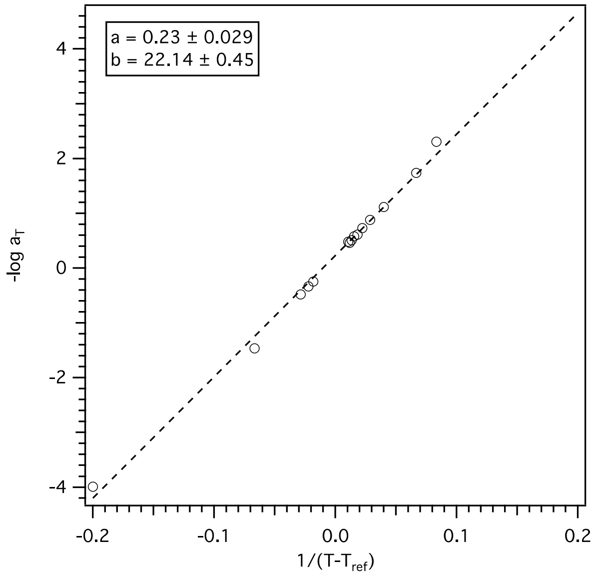

Figure S18. Linear fit (y=a+bx) to the shift factors obtained from the master curve generated for P6MCL; C_1 and C_2 were calculated from this fit.

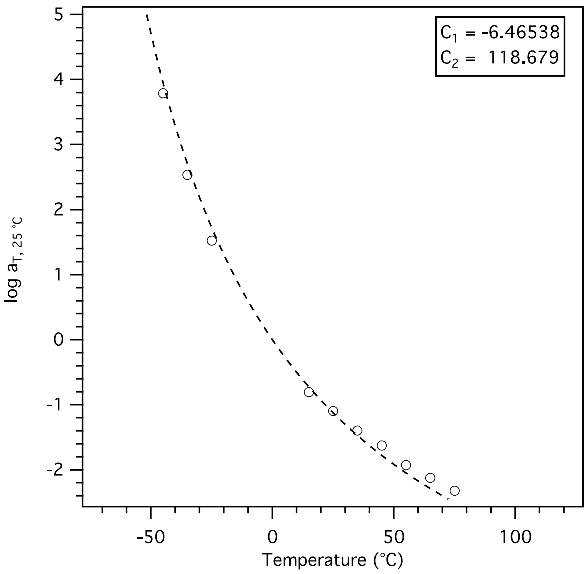

Figure S19. Temperature dependence of shift factors for P6MCL

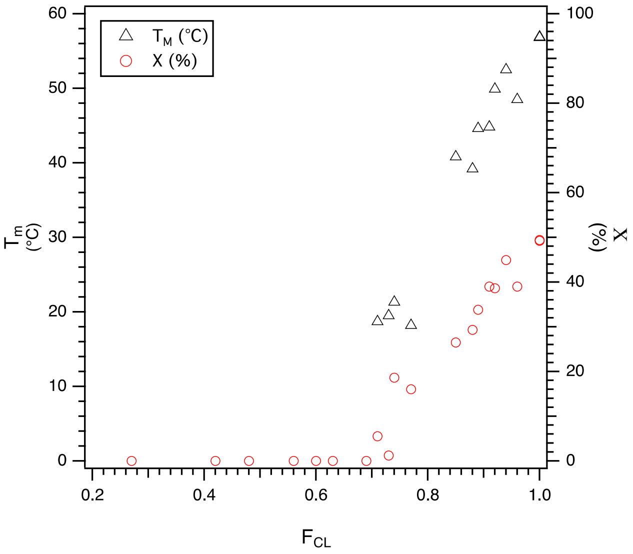

Figure S20. Dependence of T_m and X on composition for PCD copolymers. Melting point are the values of the exotherm peak maximum. T_m values were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. Crystallinity was estimated using a reference enthalpy of fusion of 139.5 J g^{-1}.

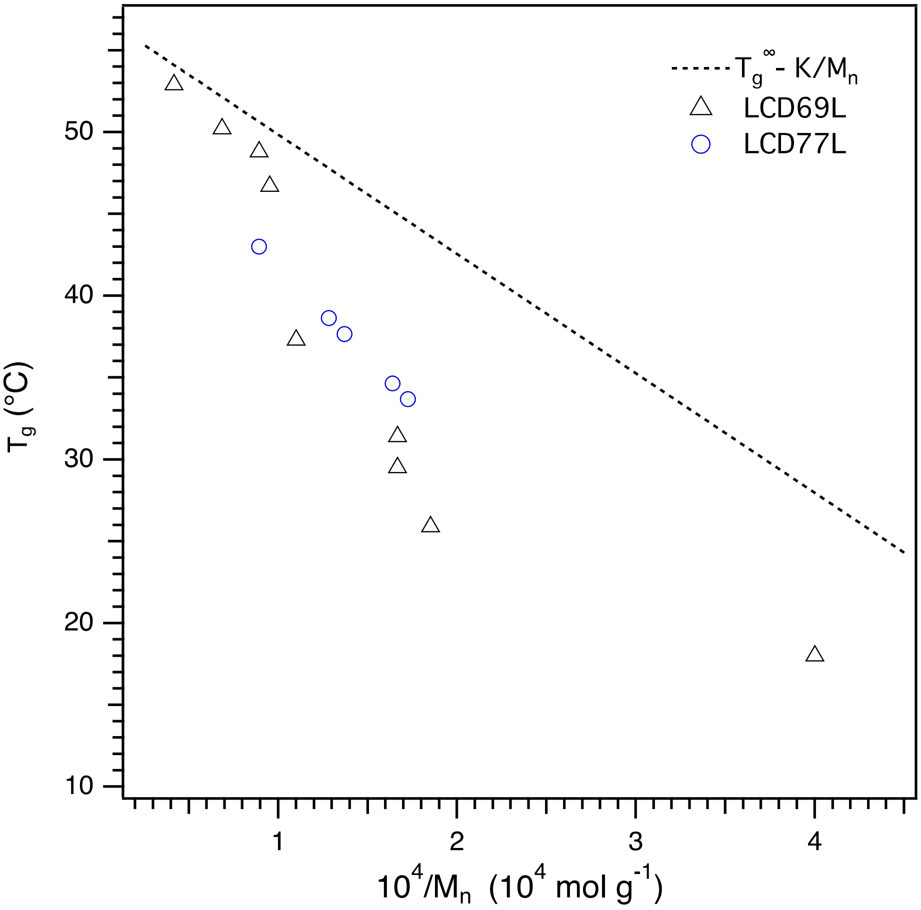

Figure S21. Molar mass dependence of the glass transition temperature of the PLA block for PLA-PCD-PLA triblocks and dependence predicted from the Flory-Fox equation.[9] Glass transition temperatures were determined by DSC on the second heating ramp with a rate of 5 °C min^{-1}. The dashed line was generated from the Flory-Fox Parameters reported by Jamshidi et al ($T_g^\infty = 57\ °C$ and $K = 7.3\ x\ 10^4$).[9]

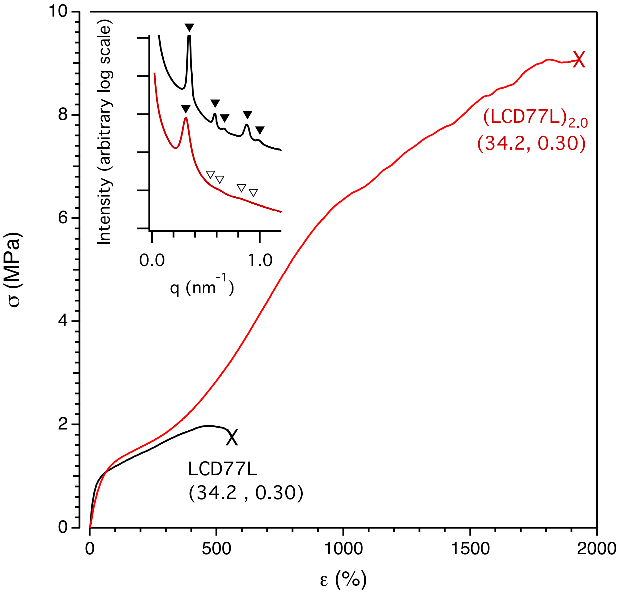

Figure S22. Representative examples of room temperature uniaxial extension of a LCD77L triblock and corresponding (LCD77L)$_n$ multiblock. Experiments were conducted with constant crosshead velocity of 50 mm min^{-1}. For each sample, average and standard deviation of a minimum of 5 specimens is reported in Table S11. The graph inset displays room temperature SAXS data of compression molded LCD69L elastomers prior to uniaxial extension test.

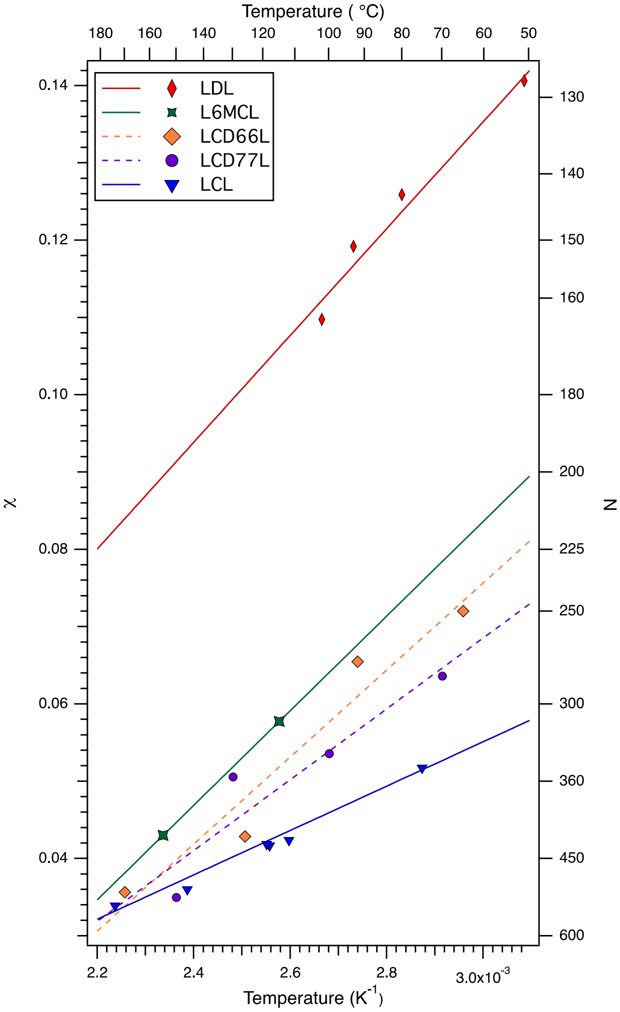

Figure S23. Dependence of interaction parameter for poly(lactide)-poly(ester) systems. The trend lines for each system are the linear best fit of the data. The data for L6MCL and LDL were taken from references 22 and 23.

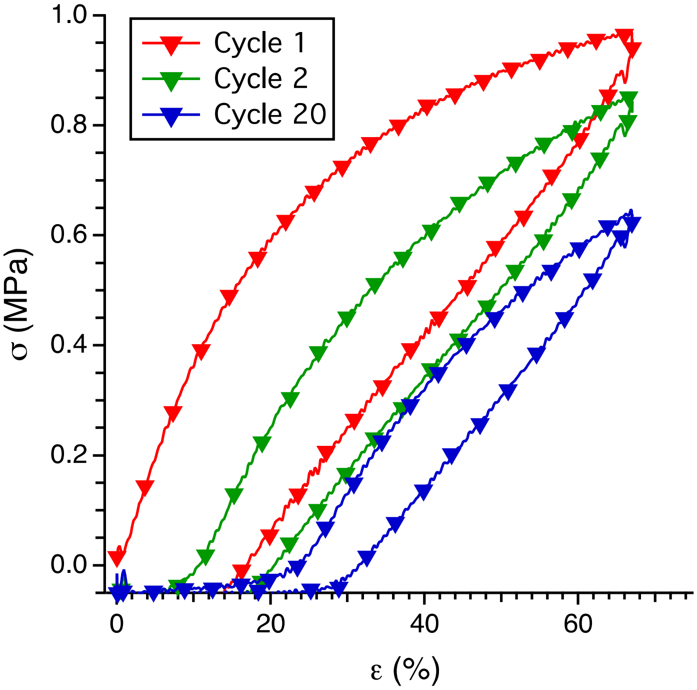

Figure S24. Hysteresis test of LCD77L (34.2, 0.30) conducted at a constant crosshead velocity of 110 mm min^{-1} and strain of 67%. The data shown are for cycles 1, 2, and 20 of a 20-cylce experiment with no recovery between cycles. The energy loss data for this test are 55% and 38% for the first and second cycle, respectively. The recovery between first and second cycle is 65%, between the first and twentieth cycle recovery is 33%.

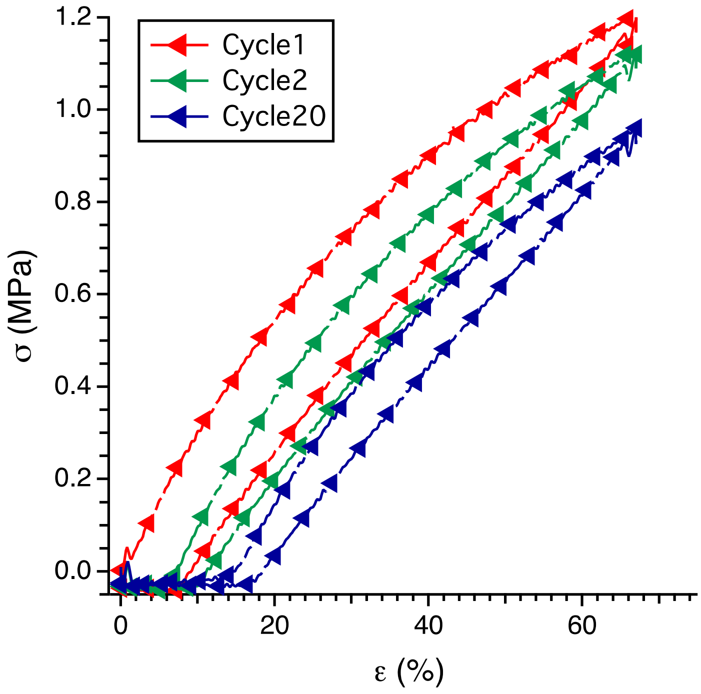

Figure S25. Hysteresis tests of $(LCD77L)_{2.0}$ (34.2, 0.30) conducted at a constant crosshead velocity of 110 mm min^{-1} and strain of 67%. The data shown are for cycles 1, 2, and 20 of a 20-cylce experiment with no recovery between cycles. The energy loss data for this test are 31% and 20% for the first and second cycle, respectively. The recovery between the first and second is 71%, between the first and twentieth cycle recovery is 60%.

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