Electric Supporting Information

A Strategy to Enhance Recyclability of Degradable Block Copolymers from Renewables by Introducing Low-Temperature Formability

Ikuo Taniguchi,* Thao Thi Thu Nguyen, Kae Kinugasa, and Kazunari Masutani

In this Supporting Information, we provide a phase diagram prediction by the Compressible Regular Solution (CRS) model, details of experimental procedures, and the following supporting display items (figures, tables, and a movie).

Fig. S1 ^{1}H and ^{13}C NMR spectra of various copolymers prepared from TMC and LAs.

Fig. S2 DSC thermographs of various copolymers prepared from TMC and LAs.

Fig. S3 GPC profiles of PTMC-*b*-PLLA(48) before and after pressure-processing.

Table S1. EOS parameters of components for phase diagram calculation.

Table S2. Thermal properties of various block copolymers.

Table S3. Block copolymers prepared by 2-step ROP of TMC and LAs.

Movie S1. Extrusion of PTMC-*b*-PLLA(48) under 49.5 MPa at 50 °C.

Phase diagram prediction

The CRS model for a binary system (Fig. 1) allows to predict the phase behavior of more than 30 weakly interacting polymer pairs.[11-14] The second derivative with respect to composition yields the spinodal criterion (Equation 2), which shows a mixed-state stability of the polymer pair using only pure component properties as input. To calculate the spinodal curve, the relevant equation of state (EOS) parameters should be obtained, such as the thermal expansion coefficient α_i, and hard-core density ρ_i^* or volume v_i^* (0 K).[12,14] The density dependence on temperature $\rho_i(T)$ is described by Equation S1.

$$\rho_i(T) = \rho_i^* e^{-\alpha_i T} \tag{S1}$$

The α_i was obtained from the Sanchez-Lacombe lattice fluid equation of state,[S1] and the ρ_i^* was taken to be the extrapolation to 0 K.[13] The cohesive energy or solubility parameter at 298 K was first calculated by group contribution methods,[S2] and then the parameter for a given temperature was determined by the following equation (Equation S2).[12,14]

$$\delta_i^2(T) = \delta_i^2(298)(\frac{\tilde{\rho}_i(T)}{\tilde{\rho}_i(298)}) \tag{S2}$$

The EOS parameters used in this study were listed in Table S1. The CRS free energy stability criterion was evaluated as a function of temperature and composition with the component properties as parameters to produce Figure 1a. Here, the CRS model is derived for polymer blend, block copolymer phase behavior can be approximated by using a bcp-to-blend degree of polymerization (N) equivalence of 5.25 ($N_{i,blend} = N_{i,bcp} 5.25^{-1}$).[S3]

Experimental details

Materials: TMC was purchased from Tokyo Chemical Industry and purified by recrystallization from anhydrous ethyl acetate under cooling immediately before use. *L*-lactide (*L*-LA) was obtained from Sigma-Aldrich and *D*-lactide (*D*-LA) was kindly gifted by Prof. Emer. Yoshiharu Kimura of Kyoto Institute of Technology. Lactides were also purified by recrystallization from anhydrous toluene twice immediately before use. Ethanol, Tin(II) 2-ethylhexanoate (SnOct$_2$), and diphenyl ether were from Wako, and ethanol (99.9+ %, Wako) was dried over 3A molecular sieves (Nacalai tesque). Other organic and inorganic compounds were of regent grade and used without further purification.

Synthesis of copolymers: The degradable block copolymers were prepared by two-step ROP of TMC and then *L*-LA or *D*-LA to provide PTMC-*b*-PLLAs or PTMC-*b*-PDLAs. A typical block copolymer synthesis was described as follows. A 5.0 g of TMC (49.0 mmol) was placed into a 100 mL flame-dried round bottom flask equipped with a magnetic stir bar, and the flask was evacuated for at least 6 h at ambient temperature. To the flask were added 32.4 µL of SnOct$_2$ (100 µmol), 5.8 µL of ethanol (100 µmol), and 10 mL of diphenyl ether as a reaction solvent under Ar atmosphere in a Miwa 1ADB-3KSO glove box. The TMC polymerization was conducted at 100 °C under stirring for 24 h to complete the monomer conversion. Then, 5.0 g of *L*-LA (34.7 mmol) was added to the reaction flask anhydrously in the glove box, and the second block propagation was continued for another 24 h at 100 °C under stirring. The obtained copolymer was recovered and purified by reprecipitation in methanol twice with yield and recovery of 9.7 g and 97 %, respectively. The PLLA weight fraction was 51 wt% determined by ^{1}H NMR. On the other hand, a random copolymer of TMC and *L*-LA, PTMC-r-PLLA, was synthesized as follows. A 2.5 g of TMC (24.5 mmol) and a 2.5 g of *L*-LA (17.4

3

mmol) were placed into a 50 mL flame-dried round bottom flask equipped with a magnetic stir bar followed by the same drying processes. A 16.2 µL of SnOct$_2$ (50.0 µmol), 2.9 µL of ethanol (50.0 µmol), and 5.0 mL of diphenyl ether under Ar atmosphere in the glove box. The polymerization was conducted at 100°C under stirring for 24 h. The copolymer recovery procedures were the same as described above. The PLLA fraction, yield, and recovery were 52 wt%, 4.8 g and 96 %, respectively.

Chemical structure, composition of the soft and hard segment, and monomer sequence along the polymer backbone were analyzed by ^{1}H NMR and ^{13}C NMR measurements. The composition was determined from the integral values of the peaks at 5.17 ppm (2H of TMC) and 2.05 (1H of LA). The block sequence was examined from the peaks in the carbonyl region from 150 to 175 ppm, where homosequences of TMC and LA gave a peak at 154 ppm and 169 ppm, respectively.

^{1}H NMR (600 MHz, CDCl$_3$, δ): 5.17 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 4.24 (t, 4H, C*H*$_2$CH$_2$C*H*$_2$), 2.05 (m, 1H, CH), 1.60 (d, 3H, CH$_3$). ^{13}C NMR (150 MHz, CDCl$_3$, δ): 169 (1C, C=O of LA), 154 (1C, C=O of TMC), 69.0 (1C, CH), 64.2 (2C, C*H*$_2$CH$_2$C*H*$_2$), 28.0 (1C, CH$_2$C*H*$_2$CH$_2$), 16.6 (1C, CH$_3$).

Pressure-processability: Rheological properties of the copolymers were studied on a Shimadzu CFT-500EX capillary rheometer under various pressurized conditions. Melt flow rate MFR at 70 °C under 49 MPa, flow rate Q, apparent shear rate γ, and apparent viscosity η were given by the following equations (**Equation (S3) to Equation (S6)**),

$$MFR = 600A(S_2\text{-}S_1)\rho\,\Delta t^{-1} = 600m\,\Delta t^{-1} \text{ (g 10-min}^{-1}) \tag{S3}$$

$$Q = A(S_2\text{-}S_1)\,10^{-1}\,\Delta t^{-1} \text{ (cm}^3\text{ s}^{-1}) \tag{S4}$$

$$\eta = \pi D^4 P\,128^{-1}\,L^{-1}\,Q^{-1}\,10^{-3} \text{ (Pa s)} \tag{S5}$$

$\gamma = 32Q\,\pi^{-1}\,D^{-3}\,10^3\,(\text{s}^{-1})$ (S6)

where A, S_1, S_2, Δt, D, P, L were piston area (1.0 cm^2), calculation start point (mm), calculation end point (mm), piston travel time from S_1 to S_2 (s), die orifice diameter (1.0 mm), test pressure (Pa), and die length (1.0 mm), respectively. Polymeric density at 70 °C ρ is amount of charged polymer m (g) divided by initial chamber volume $A(S_2\text{-}S_1)$ (cm^3).

SAXS measurement: SAXS was conducted using the synchrotron X-rays at Kyushu University Beamline (SAGA-LS/BL06). The incident X-ray wavelength was 1.3086 Å, and the camera length was 2,780 mm to a Rigaku R-AXIS VII detector, which had a 30 × 30 cm^2 imaging plate with a 100 × 100 μm^2 of actual pixel size. The 2d-SAXS pattern obtained was reduced to a one-dimensional profile by the Fit2D computer program.

References

S1   I. C. Sanchez and C. G. Panayiotou, in *Models for Thermodynamic and Phase Equilibria Calculations,* (Ed.: S. I. Sandler), Marcel Dekker, New York, USA **1993**.

S2   D. W. van Krevelen and P. J. Hoftyzer, *Properties of Polymers. Correlation with Chemical Structure*, Elsevier, New York, USA **1972**.

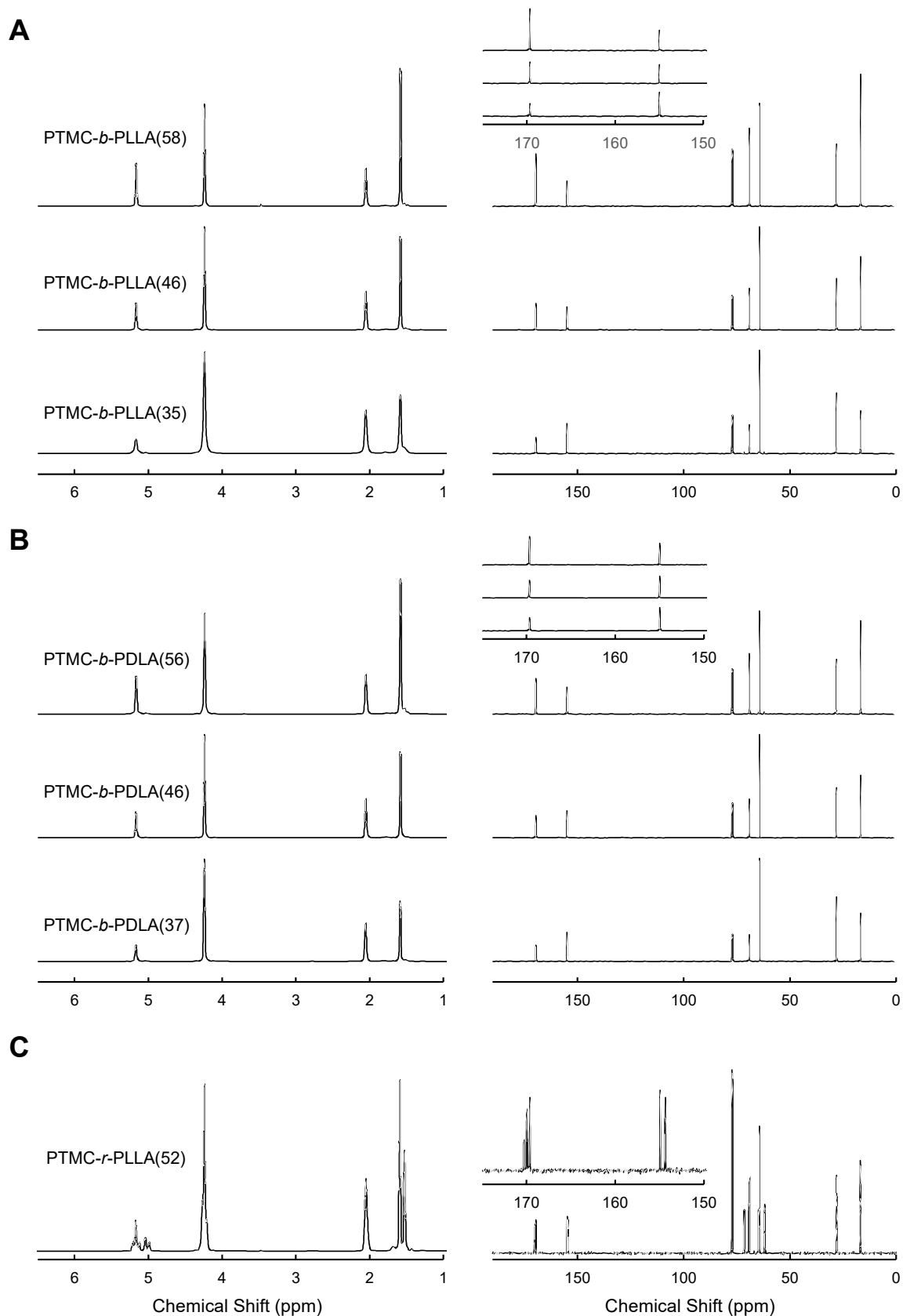S3   N. G. Lovell, Master Thesis, Massachusetts Institute of Technology, Aug. **2005**.

Fig. S1 ¹H NMR (left) and ¹³C NMR (right) spectra of various copolymers synthesized from TMC and LAs by ROP. (A) PTMC-*b*-PLLAs. (B) PTMC-*b*-PDLAs. (C) PTMC-*r*-PLLA(52). Peaks in carbonyl region are magnified in the inset of ¹³C NMR spectra.
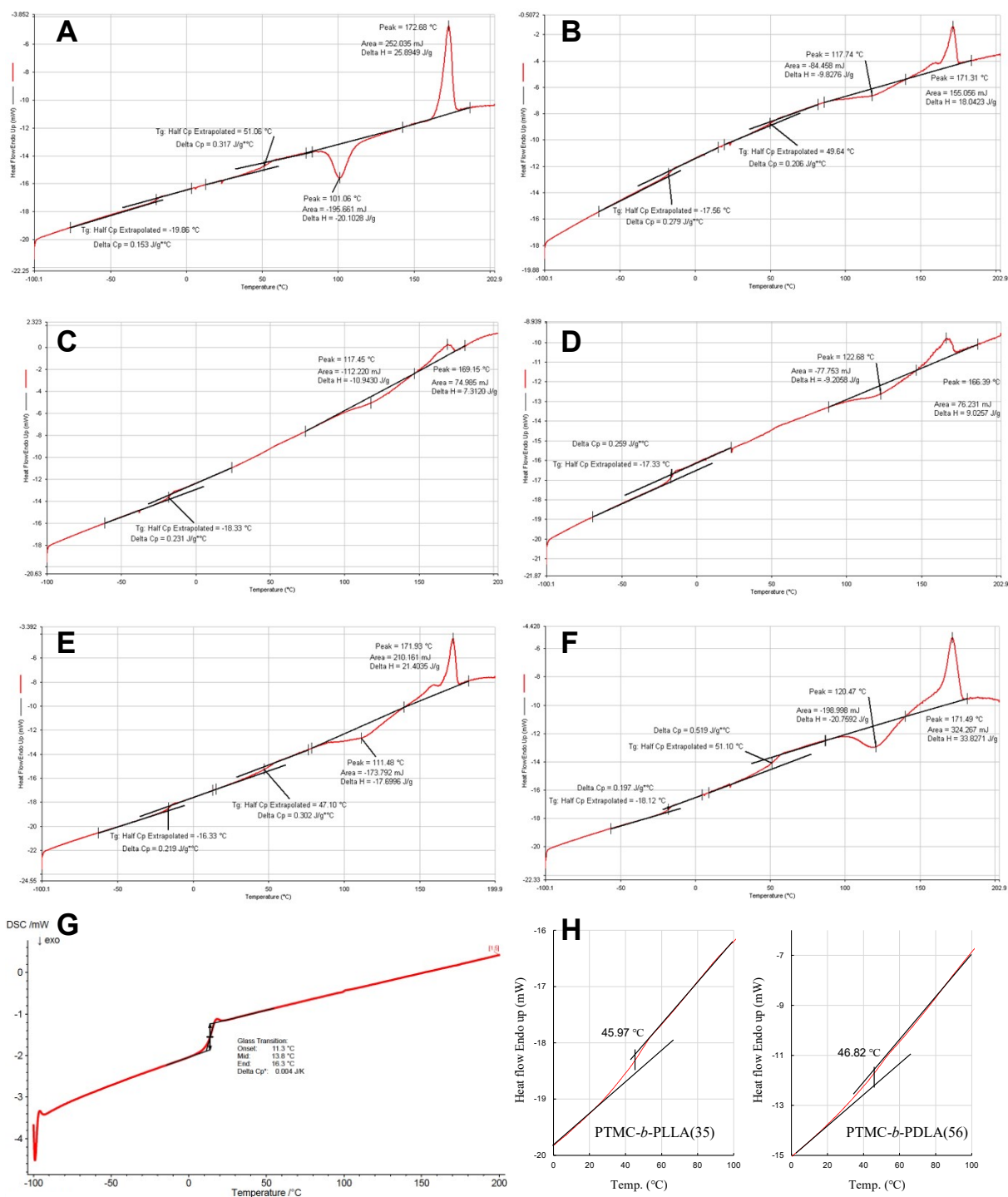
Fig. S2 DSC thermographs of various copolymers synthesized from TMC and LAs by ROP. (A) PTMC-*b*-PLLA(58). (B) PTMC-*b*-PLLA(46). (C) PTMC-*b*-PLLA(35). D) PTMC-*b*-PDLA(56). (E) PTMC-*b*-PDLA(46). (F) PTMC-*b*-PDLA(37). (G) PTMC-*r*-PLLA(52). (H) PTMC-*b*-PLLA(35) (left) and PTMC-*b*-PDLA(56) (right) enlarged.
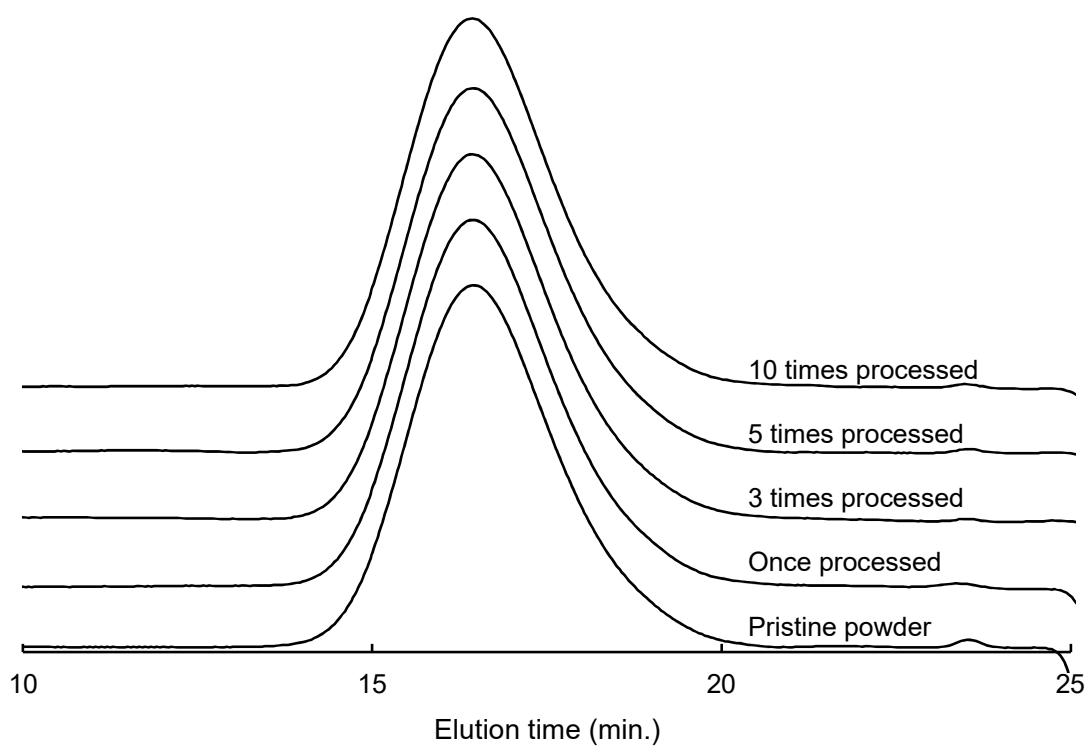
Fig. S3 GPC profiles of PTMC-*b*-PLLA(48) (M_w 45 kDa) before and after pressure-processing.

Movie S1. Pressure-processing of PTMC-*b*-PLLA(48) (M_w 45 kDa) under 49 MPa at 50°C

Table S1. EOS parameters of components for phase diagram calculation

Components	ρ^* (g cm^{-3})	α (10^{-4} K^{-1})	δ(298) (J$^{1/2}$ cm$^{-3/2}$)	v^* (cm^3 mol^{-1})	M_u (g mol^{-1})
PTMC	1.46	6.93	1.19	82.5	72
PLA	1.31	6.10	1.09	56.4	102

Table S2. Thermal properties of various block copolymers

Block copolymers	L-LA cont. (wt%)	T_g of PTMC (°C)	T_g of PLA (°C)	T_m of PLA (°C)
PTMC-*b*-PLLA(35)	35	-19.9	51.1	172
PTMC-*b*-PLLA(46)	46	-17.6	49.6	171
PTMC-*b*-PLLA(58)	58	-18.3	46.0	169
PTMC-*b*-PDLA(37)	37	-17.3	46.8	166
PTMC-*b*-PDLA(46)	46	-16.3	47.1	172
PTMC-*b*-PDLA(56)	56	-1.81	51.1	171
PTMC-*r*-PLLA(52)	52	n.d.	n.d.	n.d.

Table S3. Block copolymers prepared by 2-step ROP of TMC and LAs.

Copolymers	PLA fraction[a] (wt%)	M_w[b] (kDa)	PDI[b] (-)
PTMC-*b*-PLLA(23)	23	51.5	1.7
PTMC-*b*-PLLA(30)	30	31	1.7
PTMC-*b*-PLLA(33)	33	67	2.2
PTMC-*b*-PLLA(34)	34	123	1.6
PTMC-*b*-PLLA(35)	35	44	1.7
PTMC-*b*-PLLA(38)	38	89	1.6
PTMC-*b*-PLLA(40)	40	25	2.2
PTMC-*b*-PLLA(46)	46	40	1.8
		121	1.7
PTMC-*b*-PLLA(47)	47	34	1.7
PTMC-*b*-PLLA(48)	48	45	1.6
PTMC-*b*-PDLA(49)	49	92	1.7
PTMC-*b*-PLLA(51)	51	103	1.8
PTMC-*b*-PLLA(52)	52	47	1.9
PTMC-*b*-PLLA(57)	57	56	1.7
PTMC-*b*-PLLA(58)	58	85	2.1
PTMC-*b*-PLLA(59)	59	88	1.7
PTMC-*b*-PLLA(62)	62	95	1.7
PTMC-*b*-PDLA(30)	30	27	1.7
PTMC-*b*-PDLA(34)	34	85	1.7
PTMC-*b*-PDLA(37)	37	119	1.7
PTMC-*b*-PDLA(38)	38	90	1.7
PTMC-*b*-PDLA(39)	39	101	2.1
PTMC-*b*-PDLA(43)	43	23	2.0
PTMC-*b*-PDLA(44)	44	92	1.7
PTMC-*b*-PDLA(46)	46	105	2.3
PTMC-*b*-PDLA(47)	47	191	3.3
PTMC-*b*-PDLA(49)	49	100	1.7
PTMC-*b*-PDLA(56)	56	122	1.7
PTMC-*b*-PDLA(57)	57	26	2.0
PTMC-*b*-PDLA(59)	59	101	1.6
PTMC-*b*-PDLA(60)	60	109	1.7
PTMC-*r*-PLLA(52)	52	90	1.9

[a]Determined by ^{1}H-NMR, [b]determined by GPC, PDI: M_w/M_n.