ELECTRONIC SUPPLEMENTARY INFORMATION

Exploitation of dinuclear salan aluminum complexes for versatile copolymerization of ε-caprolactone and *L*-lactide

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5. Representative ^{1}H NMR, ^{13}C NMR spectra and DSC curves of *ε*-CL/*L*-LA copolymers

1. Experimental

1.1 General procedure.

The synthesis of aluminum complexes and polymerization reactions were performed under an atmosphere of dry argon using standard Schlenk techniques or in a glove-box. Toluene and hexane were freshly distilled from sodium benzophenone ketyl immediately prior to use. *rac*-Lactide and *L*-lactide (Aldrich) were recrystallized with dry toluene and then sublimated twice under vacuum at 80 ºC. ε-Caprolactone was distilled over CaH_2 under reduced pressure prior to use. 2-Propanol, BnOH and ^{t}BuOH were dried over CaH_2 prior to distillation. 2-(Bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol was synthesized according to the literature.[1] NMR spectra were recorded on a Bruker Avance-400 spectrometer at ambient temperature. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Elemental analyses were performed on an EA-1106 instrument. Spectroscopic analyses of polymers were performed in $CDCl_3$. Gel permeation chromatography (GPC) analyses were carried out on a Waters 1515 Breeze instrument in THF at 25 °C, at a flow rate of 1 mL/min. Narrowly distributed polystyrenes covering a broad range of molecular weights ($10^3 < M < 2 \times 10^6$ g mol^{-1}) were used as standards.

1.2 Synthesis and characterization of proligands.

2-(Bromomethyl)-4,6-dibromophenol. 2,4-Dibromophenol (25.0 g, 0.100 mmol), paraformaldehyde (3.6 g, 0.12 mol) were added to a solution of 30% hydrogen bromide in acetic acid (30 mL), and the reaction mixture was stirred at 70 °C for 12 h. After being cooled to 0 °C, water and ice were added, and the white precipitate that formed was filtered and collected to give the product. Yield: 17.1 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 2.0 Hz, 1H, Ar*H*), 7.41 (d, J = 2.0 Hz, 1H, Ar*H*), 5.82 (s, 1H, O*H*), 4.50 (s, 2H, ArCH_2).

2-(Bromomethyl)-4,6-dicumylphenol. 2,4-Dicumylphenol (33.0 g, 0.100 mol), paraformaldehyde (3.6 g, 0.12 mol) were added to a solution of 30% hydrogen bromide in acetic acid (30 mL), and the reaction mixture was stirred at 70 °C for 12 h. After being cooled to 0 °C, water and ice were added, and the organic lay was extracted with petroleum ether (50 mL× 2). The solvent was removed under vacuum to give sticky dark brown oil. The crude product was used without further purification. Yield: 24.5 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.11 (m, 12H, Ar*H*), 4.41 (s, 2H, ArCH_2), 1.71 (s,

6H, C(CH_3)$_2$Ph), 1.59 (s, 6H, C(CH_3)$_2$Ph).

2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)]-bis(4,6-dibromophenol) **(1).** Under an argon atmosphere, a solution of 2-(bromomethyl)-4,6-dibromophenol (6.84 g, 20.0 mmol) in dry THF (20 mL) was added to a stirred solution of *N*,*N*′-dimethyl-1,3-propanediamine (1.02 g, 10.0 mmol) in dry THF (10 mL). A solution of triethylamine (4 mL) in dry THF (5 mL) was added dropwise and a precipitate formed. The reaction mixture was stirred for 2 h in dark. After filtration, the solvent of the brown filtrate was removed under vacuum to give a sticky brown solid. The crude product was purified by flash chromatography on Silica gel with a mixture of petroleum ether: ethyl acetate in gradient polarity as eluent. The pure product was obtained as an off-white solid. Yield: 3.63 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H, Ar*H*), 7.04 (s, 2H, Ar*H*), 3.68 (s, 4H, ArCH_2), 2.53 (t, *J* = 7.2 Hz, 4H, CH_2CH$_2$CH_2), 2.29 (s, 6H, NCH_3), 1.83 (p, *J* = 7.2 Hz, 2H, CH$_2$CH_2CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.04 (Ar(*C*)-O), 134.09, 130.07, 124.00, 110.86, 110.55 (Ar-*C*), 60.82 (Ar*C*H$_2$), 54.53 (*C*H$_2$CH$_2$*C*H$_2$), 41.15 (N*C*H$_3$), 24.41 (CH$_2$*C*H$_2$CH$_2$). Anal. Calcd. for $C_{19}H_{22}Br_4N_2O_2$: C, 36.22; H, 3.52; N, 4.45. Found: C, 36.22; H, 3.53; N, 4.37%.

2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)]-bis(4,6-di-tert-butylphenol) **(2).** This compound was prepared in an analogous manner to that described for **1**. Off-white solid was isolated (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 2H, Ar*H*), 6.81 (s, 2H, Ar*H*), 3.65 (s, 4H, ArCH_2), 2.46 (t, *J* = 7.2 Hz, 4H, CH_2CH$_2$CH_2), 2.27 (s, 6H, NCH_3), 1.79 (p, *J* = 7.2 Hz, 2H, CH$_2$CH_2CH$_2$), 1.41 (s, 18H, C(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.26 (Ar(*C*)-O), 140.42, 135.46, 123.23, 122.79, 121.18 (Ar-*C*), 62.33 (Ar*C*H$_2$), 54.46 (*C*H$_2$CH$_2$*C*H$_2$), 41.25 (N*C*H$_3$), 34.82 (*C*(CH$_3$)$_3$), 34.10 (*C*(CH$_3$)$_3$), 31.70 (C(*C*H$_3$)$_3$), 29.62 (C(*C*H$_3$)$_3$), 24.55 (CH$_2$*C*H$_2$CH$_2$). Anal. Calcd. for $C_{35}H_{58}N_2O_2$: C, 78.01; H, 10.85; N, 5.20. Found: C, 78.17; H, 10.77; N, 5.19%.

2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)]-bis(4,6-dicumylphenol) **(3).** This compound was prepared in an analogous manner to that described for **1**. Off-white solid was isolated (41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 8H, Ar*H*), 7.25-7.15 (m, 12H, Ar*H*), 7.08 (t, *J* = 6.4 Hz, 2H, Ar*H*), 6.70 (s, 2H, Ar*H*), 3.47 (s, 4H, ArCH_2), 2.13 (t, *J* = 7.3 Hz, 4H, CH_2CH$_2$CH_2), 2.06 (s, 6H, NCH_3), 1.71 (s, 12H, C(CH_3)$_2$Ph), 1.66 (s, 12H, C(CH_3)$_2$Ph), 1.42 (p, *J* = 7.3 Hz, 2H, CH$_2$CH_2CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.75 (Ar(*C*)-O), 151.46, 151.33, 139.73, 134.85, 127.81, 127.58, 126.69, 125.44, 125.34, 125.24, 124.81, 124.76, 121.31 (Ar-*C*), 61.75 (Ar*C*H$_2$), 53.87 (*C*H$_2$CH$_2$*C*H$_2$), 42.38 (*C*(CH$_3$)$_2$Ph), 41.96 (*C*(CH$_3$)$_2$Ph), 41.02 (N*C*H$_3$), 31.06 (C(*C*H$_3$)$_2$Ph), 29.50 (C(*C*H$_3$)$_2$Ph), 23.84

($CH_2CH_2CH_2$). Anal. Calcd. for $C_{55}H_{66}N_2O_2$: C, 83.92; H, 8.45; N, 3.56. Found: C, 83.85; H, 8.63; N, 3.34%.

1.3 Synthesis and characterization of dinuclear salan aluminum complexes.

***2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)-bis(4,6-dibromophenolate)] dialuminum tetramethyl* (4).** To a stirred solution of proligand **1** (1.252 g, 2.000 mmol) in toluene (20 mL) was added $AlMe_3$ (2.00 mL of 2.0 M solution in toluene, 4.00 mmol). The reaction mixture was stirred at 110 °C overnight. The solvent was removed under vacuum. Colorless crystals formed after recrystallization from hot toluene. Yield: 1.31 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 1.9 Hz, 2H, Ar*H*), 7.02 (d, *J* = 1.9 Hz, 2H, Ar*H*), 3.97 (d, *J* = 13.3 Hz, 1H, ArCH_2), 3.95 (d, *J* = 13.3 Hz, 1H, ArCH_2), 3.54 (d, *J* = 13.3 Hz, 1H, ArCH_2), 3.51 (d, *J* = 13.3 Hz, 1H, ArCH_2), 2.88-2.74 (m, 2H, CH_2CH$_2$CH_2), 2.53-2.41 (m, 2H, CH_2CH$_2$CH_2), 2.40 (s, 6H, NCH_3), 2.13-1.97 (m, 2H, CH$_2$CH_2CH$_2$), –0.70 (s, 3H, AlCH_3), –0.71 (s, 6H, AlCH_3), –0.75 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.51, 155.43 (Ar(*C*)-O), 136.13, 136.11, 131.14, 130.99, 122.03, 115.08, 114.99, 108.44, 108.28 (Ar-*C*), 60.85 (Ar*C*H$_2$), 60.24 (Ar*C*H$_2$), 55.29 (*C*H$_2$CH$_2$*C*H$_2$), 54.93 (*C*H$_2$CH$_2$*C*H$_2$), 41.07 (N*C*H$_3$), 41.03 (N*C*H$_3$), 19.35 (CH$_2$*C*H$_2$CH$_2$), 18.02 (CH$_2$*C*H$_2$CH$_2$), –10.20 (Al*C*H$_3$), –10.35 (Al*C*H$_3$), –11.00 (Al*C*H$_3$), –11.10 (Al*C*H$_3$). Anal. Calcd. for $C_{23}H_{32}Al_2Br_4N_2O_2$: C, 37.23; H, 4.35; N, 3.77. Found: C, 37.33; H, 4.26; N, 3.81%.

***2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)-bis(4,6-di-tert-butylphenolate)] dialuminum tetramethyl* (5).** A similar method was employed as that described for **4**. Colorless crystals were obtained after recrystallization from a mixture of toluene and hexane at room temperature (74% yield). ^{1}H NMR (400 MHz , $CDCl_3$): δ 7.29 (d, *J* = 2.2 Hz, 1H, Ar*H*), 7.28 (d, *J* = 2.2 Hz, 1H, Ar*H*), 6.81 (d, *J* = 2.2 Hz, 1H, Ar*H*), 6.78 (d, *J* = 2.2 Hz, 1H, Ar*H*), 4.07 (d, *J* = 13.2 Hz, 1H, ArCH_2), 3.96 (d, *J* = 13.2 Hz, 1H, ArCH_2), 3.55 (d, *J* = 13.2 Hz, 1H, ArCH_2), 3.45 (d, *J* = 13.2 Hz, 1H, ArCH_2), 2.85-2.74 (m, 2H, CH_2CH$_2$CH_2), 2.49-2.37 (m, 2H, CH_2CH$_2$CH_2), 2.36 (s, 3H, NCH_3), 2.34 (s, 3H, NCH_3), 2.14-1.99 (m, 2H, CH$_2$CH_2CH$_2$), 1.39 (s, 18H, C(CH_3)$_3$), 1.27 (s, 18H, C(CH_3)$_3$), –0.75 (s, 3H, AlCH_3), –0.76 (s, 3H, AlCH_3), –0.77 (s, 3H, AlCH_3), –0.79 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.12, 156.02 (Ar(*C*)-O), 138.85, 138.73, 137.95, 124.87, 124.77, 124.10, 123.97, 119.37, 119.29 (Ar-*C*), 62.56 (Ar*C*H$_2$), 61.62 (Ar*C*H$_2$), 55.68 (*C*H$_2$CH$_2$*C*H$_2$), 54.80 (*C*H$_2$CH$_2$*C*H$_2$), 40.82 (N*C*H$_3$), 40.70 (N*C*H$_3$), 35.01 (*C*(CH$_3$)$_3$), 34.05 (*C*(CH$_3$)$_3$), 31.75 (C(*C*H$_3$)$_3$), 29.50 (C(*C*H$_3$)$_3$), 19.94

($CH_2CH_2CH_2$), 17.89 ($CH_2CH_2CH_2$), −10.21 ($AlCH_3$), −10.36 ($AlCH_3$), −10.81 ($AlCH_3$), −11.04 ($AlCH_3$). Anal. Calcd. for $C_{39}H_{68}Al_2N_2O_2$: C, 71.96; H, 10.53; N, 4.30. Found: C, 72.08; H, 10.58; N, 4.20%.

2,2'-[1,7-(N,N'-dimethyl-2,6-diazaheptanediyl)-bis(4,6-dicumylphenolate)] dialuminum tetramethyl **(6).** A similar method was employed as that described for **4**. Colorless crystals were obtained after recrystallization from a mixture of toluene and hexane at room temperature (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 2.2 Hz, 1H, Ar*H*), 7.31 (d, J = 2.2 Hz, 1H, Ar*H*), 7.30-7.23 (m, 8H, Ar*H*), 7.20-7.05 (m, 12H, Ar*H*), 6.63-6.61 (m, 2H, Ar*H*), 3.81 (d, J = 13.2 Hz, 1H, ArCH_2), 3.74 (d, J = 13.2 Hz, 1H, ArCH_2), 3.39 (d, J = 13.2 Hz, 1H, ArCH_2), 3.34 (d, J = 13.2 Hz, 1H, ArCH_2), 2.50-2.39 (m, 2H, CH_2CH_2CH_2), 2.21-2.12 (m, 1H, CH_2CH_2CH_2), 2.07 (s, 3H, NCH_3), 2.05 (s, 3H, NCH_3), 2.00-1.95 (m, 1H, CH_2CH_2CH_2), 1.85-1.72 (m, 2H, $CH_2CH_2CH_2$), 1.68 (s, 12H, C(CH_3)$_2$Ph), 1.66 (s, 6H, C(CH_3)$_2$Ph), 1.62 (s, 3H, C(CH_3)$_2$Ph), 1.60 (s, 3H, C(CH_3)$_2$Ph), −1.13 (s, 3H, AlCH_3), −1.15 (s, 3H, AlCH_3), −1.24 (s, 3H, AlCH_3), −1.28 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.53, 154.45 (Ar(*C*)-O), 151.99, 151.95, 151.46, 151.43, 137.94, 137.81, 127.89, 127.87, 127.45, 126.70, 126.66, 126.44, 126.26, 126.04, 126.03, 125.46, 125.43, 125.40, 124.52, 119.22, 119.17 (Ar-*C*), 61.52 (ArCH_2), 60.89 (ArCH_2), 54.69 ($CH_2CH_2CH_2$), 53.92 ($CH_2CH_2CH_2$), 42.34 (*C*(CH$_3$)$_2$Ph), 42.31(*C*(CH$_3$)$_2$Ph), 42.04 (*C*(CH$_3$)$_2$Ph), 42.03 (*C*(CH$_3$)$_2$Ph), 40.18 (N*C*H$_3$), 40.11(N*C*H$_3$), 31.21 (C(*C*H$_3$)$_2$Ph), 31.17 (C(*C*H$_3$)$_2$Ph), 31.10 (C(*C*H$_3$)$_2$Ph), 31.06 (C(*C*H$_3$)$_2$Ph), 29.74 (C(*C*H$_3$)$_2$Ph), 29.45 (C(*C*H$_3$)$_2$Ph), 28.74 (C(*C*H$_3$)$_2$Ph), 28.45 (C(*C*H$_3$)$_2$Ph), 18.52 ($CH_2CH_2CH_2$), 17.17 ($CH_2CH_2CH_2$), −11.03 ($AlCH_3$), −11.06 ($AlCH_3$), −11.46 ($AlCH_3$), −11.67 ($AlCH_3$). Anal. Calcd. for $C_{59}H_{76}Al_2N_2O_2$: C, 78.81; H, 8.52; N, 3.12. Found: C, 78.81; H, 8.55; N, 3.03%.

1.4 NMR tube reaction of complex 4 with 2-propanol.

To a solution of complex **4** (22.1 mg, 0.03 mmol) in 0.4 mL $CDCl_3$ was add 2-propanol (0.1 mL, 3.6 mg, 0.06 mmol) in $CDCl_3$ (36 mg diluted in 1.0 mL $CDCl_3$) at ambient temperature. The tube was vigorously shaken. After 2 h, the reaction was checked by ^{1}H NMR. Then another 0.1 mL 2-propanol (3.6 mg, 0.06 mmol) was introduced to the NMR tube at ambient temperature, the reaction mixture was checked by ^{1}H NMR again after 2 h.

1.5 Typical polymerization procedures.

Polymerization of rac-lactide. To a solution of *rac*-lactide (0.576 g, 4.00 mmol) and dinuclear aluminum complex (0.04 mmol) in 3.2 mL toluene, a solution of 2-propanol (9.6 mg, 0.16 mmol) in 0.8 mL toluene was injected. The mixture was then immerged into an oil bath of 70 °C for polymerization. 1 mL of polymerization aliquots were withdrawn at appropriate time intervals, and quenched with cold petroleum ether. Monomer conversion was monitored by ^{1}H NMR spectroscopy after removal of all the volatiles. The crude sample was dissolved in CH_2Cl_2 and the polymer was precipitated from excess methanol. The obtained polymers were further dried in a vacuum oven at 60 °C for 24 h.

Polymerization of ε-caprolactone. To a solution of ε-caprolactone (0.456 g, 4.00 mmol) and dinuclear aluminum complex (0.01 mmol) in 3.8 mL toluene, a solution of 2-propanol (2.4 mg, 0.04 mmol) in 0.2 mL toluene was injected. The mixture was thermostatized at 25 °C for polymerization. 1 mL of polymerization aliquots were withdrawn at appropriate time intervals, and quenched with cold petroleum ether. Monomer conversion was monitored by ^{1}H NMR spectroscopy after removal of all the volatiles. The crude sample was dissolved in CH_2Cl_2 and the polymer was precipitated from excess methanol. The obtained polymers were further dried in a vacuum oven at 60 °C for 24 h.

Block copolymerization of L-lactide and ε-caprolactone. To a solution of ε-caprolactone (0.228 g, 2.00 mmol) and dinuclear aluminum complex (0.02 mmol) in 1.8 mL toluene, a solution of 2-propanol (2.4 mg, 0.040 mmol) in 0.2 mL toluene was injected. The mixture was stirred at 25 °C for 1 h, after which time *L*-lactide (0.288 g, 2.00 mmol) was added and the mixture was heated to 70 °C for polymerization. Aliquots were withdrawn for determination of the level of monomer conversion by ^{1}H NMR spectroscopy. The copolymerization was quenched with petroleum ether and the polymer was isolated by being precipitated into methanol. The precipitation was collected and dried in a vacuum oven at 60 °C for 24 h. The polymer was characterized by NMR spectroscopy, GPC and DSC analysis.

Solution random copolymerization of L-lactide and ε-caprolactone. To a solution of *L*-lactide (0.576 g, 4.00 mmol), ε-caprolactone (0.456 g, 4.00 mmol) and dinuclear aluminum complex (0.02 mmol) in 7.6 mL toluene, a solution of 2-propanol (4.8 mg, 0.080 mmol) in 0.4 mL toluene was injected. The mixture was kept at 70 °C. After appropriate time intervals, aliquots were withdrawn for determination the level of monomer conversion by ^{1}H NMR spectroscopy. The copolymerization was quenched with petroleum ether. The colorless sticky copolymer was obtained by being precipitated

into cold methanol, dried under vacuum at 60 °C for 24 h, and characterized by NMR spectroscopy, GPC and DSC analysis.

Bulk random copolymerization L-lactide and ε-caprolactone. *L*-lactide (0.576 g, 4.00 mmol), ε-caprolactone (0.456 g, 4.00 mmol) and dinuclear aluminum complex (0.02 mmol) were placed in a polymerization ampoule. To this ampoule was added 2-propanol (4.8 mg, 0.080 mmol) in 0.4 mL toluene. After certain time intervals, the copolymerization was quenched in petroleum ether. The colorless sticky copolymer was obtained by being precipitated into cold methanol, dried at 60 °C for 24 h, and characterized by NMR spectroscopy, GPC and DSC analysis.

Reference

1 W. O. Appiah, A. D. DeGreeff, G. L. Razidlo, S. J. Spessard, M. Pink, V. G. Young, Jr. and G. E. Hofmeister, *Inorg. Chem.*, 2002, **41**, 3656-3667.

2. Crystal data and structure refinement details

Table S1. Crystal data and structure refinement details

	5	**6**
formula	$C_{39}H_{68}Al_2N_2O_2$	$C_{59}H_{76}Al_2N_2O_2$
fw	650.91	899.18
Temp (K)	293(2)	293(2)
Crystal size (mm)	0.32 × 0.31 × 0.12	0.15 × 0.10 × 0.08
Crystal system	Monoclinic	Tetragonal
Space group	*C*2/*c*	I4(1)/*a*
a (Å)	42.154(4)	20.068(6)
b (Å)	7.8830(8)	20.068(6)
c (Å)	12.4485(12)	28.016(11)
α (deg)	90	90
β (deg)	94.660(2)	90
γ (deg)	90	90
vol (Å^3)	4123.0(7)	11282(6)
Z	4	8
D_{calc} (g cm^{-3})	1.049	1.059
Abs coeff (mm^{-1})	0.102	0.091
F (000)	1432	3888
θ range (º)	1.94 to 26.00	2.03 to 27.01
Data collected (*hkl*)	±51, –9 to 4, –14 to 15	–25 to 20, –25 to 19, ±35
Reflns collected/unique	10713/4047	27283/6131
R (int)	0.0378	0.1012
Max. and min. transmn	1.0000 and 0.6645	0.9927 and 0.9864
Data/restrains/para	4047 / 42 / 243	6131 / 0 / 301
Goodness-of-fit on F^2	1.007	0.838
Final R_1,wR_2 [I > 2σ(I)]	0.0562, 0.1342	0.0618, 0.1499
R_1, wR_2 (all data)	0.0983, 0.1573	0.1296, 0.1711
Δρmax, min/e Å-3	0.270 and –0.134	0.284 and –0.173

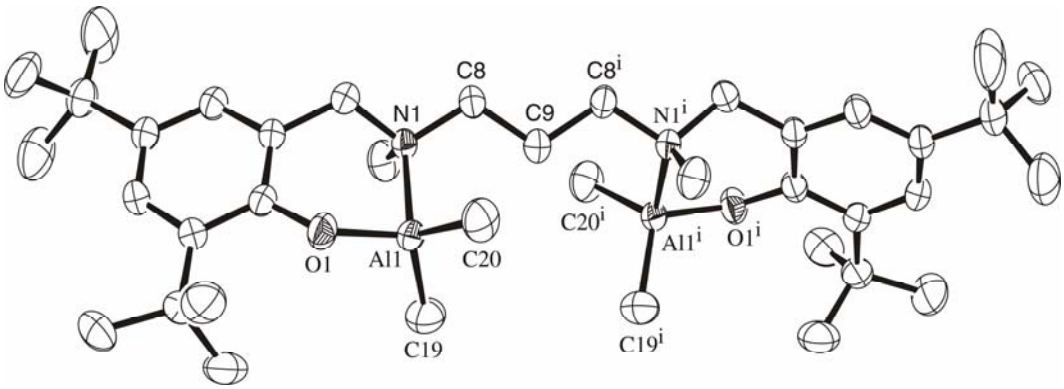

Fig. 1 Molecular structure of 5. Hydrogen atoms are omitted for clarity.

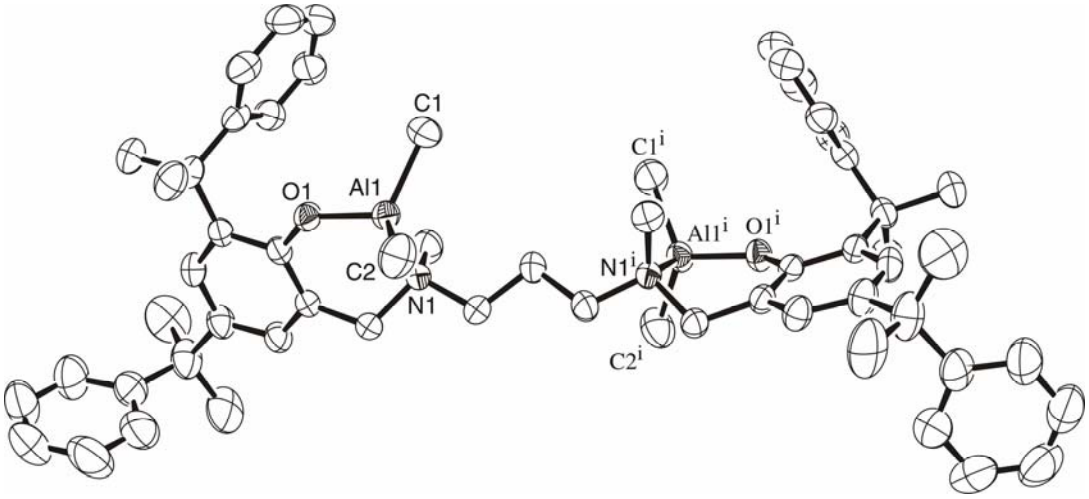

Fig. S1 Molecular structure of 6. Hydrogen atoms are omitted for clarity.

Table S2. The selected bond lengths (Å) and bond angles (deg) for complexes 5 and 6.

		5	
Al(1)–O(1)	1.7441(17)	Al(1)–C(19)	1.946(3)
Al(1)–C(20)	1.951(3)	Al(1)–N(1)	2.044(2)
O(1)–Al(1)–C(19)	114.38(12)	O(1)–Al(1)–C(20)	106.10(11)
C(19)–Al(1)–C(20)	119.31(13)	O(1)–Al(1)–N(1)	97.54(8)
C(19)–Al(1)–N(1)	107.74(11)	C(20)–Al(1)–N(1)	109.55(11)
C(8)–N(1)–C(10)	109.15(19)	C(8)–N(1)–C(7)	108.71(18)
C(10)–N(1)–C(7)	107.87(18)	C(8)–N(1)–Al(1)	112.79(14)
C(10)–N(1)–Al(1)	112.23(16)	C(7)–N(1)–Al(1)	105.87(14)
C(1)–O(1)–Al(1)	127.08(16)		
		6	
Al(1)–O(1)	1.7496(18)	Al(1)–C(2)	1.942(3)
Al(1)–C(1)	1.950(3)	Al(1)–N(1)	2.025(2)
O(1)–Al(1)–C(2)	112.94(12)	O(1)–Al(1)–C(1)	111.74(11)
C(2)–Al(1)–C(1)	117.34(15)	O(1)–Al(1)–N(1)	95.60(8)
C(2)–Al(1)–N(1)	106.32(13)	C(1)–Al(1)–N(1)	110.54(13)
C(3)–O(1)–Al(1)	132.44(15)	C(30)–N(1)–C(10)	109.7(2)
C(30)–N(1)–C(9)	109.2(2)	C(10)–N(1)–C(9)	106.21(18)
C(30)–N(1)–Al(1)	112.53(16)	C(10)–N(1)–Al(1)	113.35(16)
C(9)–N(1)–Al(1)	105.49(15)		

3. NMR tube studies

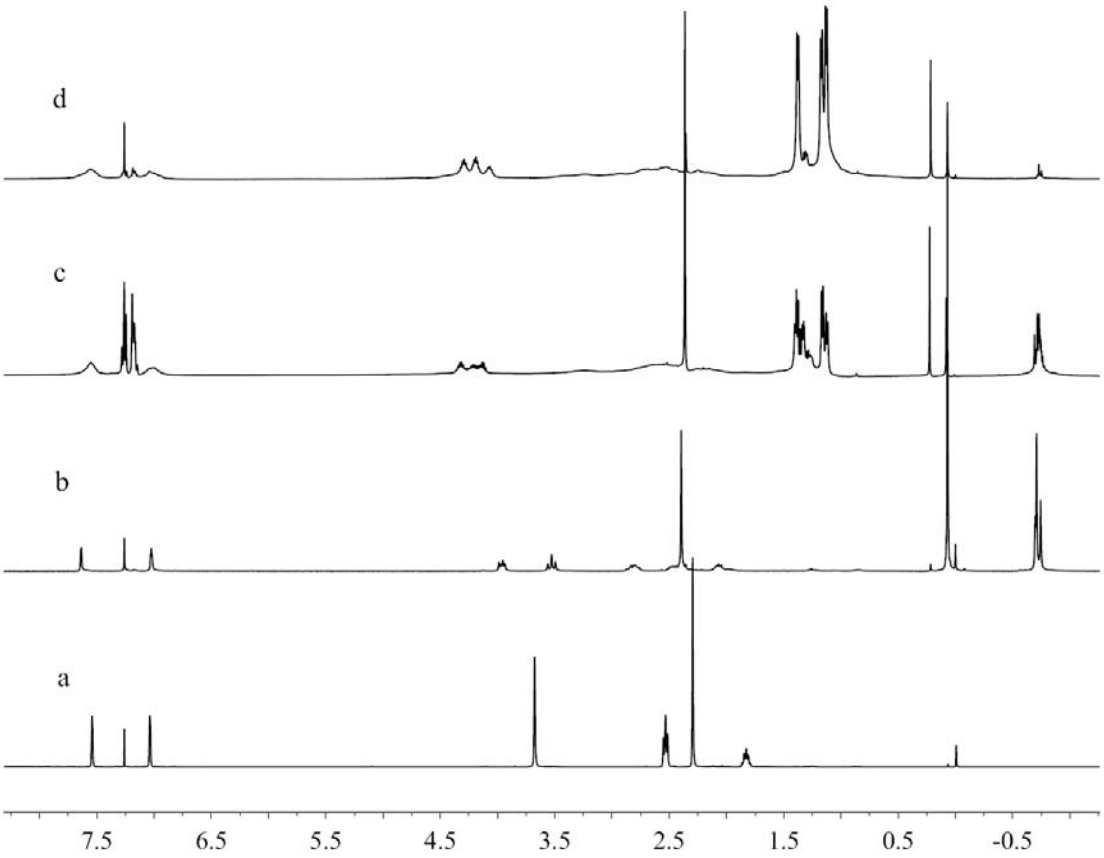

Fig. S2 ^{1}H NMR spectra of the reaction mixture of complex **4** and 2-propanol in $CDCl_3$ at room temperature. (a) proligand **1**; (b) complex **4**; (c) 2 h after the addition of 2 equiv. of 2-propanol into the solution of **4** in $CDCl_3$; (d) 2 h after the addition of another 2 equiv. of 2-propanol.

4. Copolymerization of *ε*-CL with *L*-LA

Table S3. Copolymerization of *ε*-CL with *L*-LA

Run	Cat.	Feed Ratio	Temp. (°C)	Time (h)	C_{CL}, C_{LA} [e] (%)	CL/LA [f]	M_c [g] (10^3)	M_n [h] (10^3)	M_w/M_n [h]
1	**4**	200:200:1:2	70	48	0, 70	0:100	10.1	*n.d.*	*n.d.*
2	**4**	200:200:1:4	70	20	8, 57	12:88	4.6	*n.d.*	*n.d.*
3	**4**	200:200:1:4	70	60	29, 98	23:77	8.7	9.6	1.23
4	**4**	200:200:1:4	70	144	80, 100	44:56	11.8	13.9	1.40
5	**5**	200:200:1:4	70	152	66, 94	41:59	10.5	13.1	1.20
6 [b]	**5**	200:200:1:4	70	96	61, 91	39:61	10.0	10.7	1.20
7 [c]	**5**	200:200:1:4	70	96	55, 88	39:61	9.5	10.5	1.13
8	**5**	200:200:1:4	100	12	46, 82	36:64	8.5	10.1	1.15
9 [d]	**5**	200:200:1:4	110	2	59, 73	45:55	8.6	9.7	1.23
10 [d]	**5**	150:150:1:4	110	2	69, 75	48:52	7.0	5.9	1.16
11 [d]	**5**	100:100:1:4	110	0.33	27, 25	52:48	1.7	2.4	1.14
12 [d]	**5**	100:100:1:4	110	0.67	46, 42	53:47	2.8	3.1	1.13
13 [d]	**5**	100:100:1:4	110	1	70, 64	52:48	4.3	5.2	1.08
14 [d]	**5**	150:150:1:4	140	1	95, 100	49:51	9.5	9.3	1.57
15	**6**	200:200:1:4	90	23	20, 75	21:79	6.5	7.1	1.13
16	**6**	200:200:1:4	90	47	35, 88	28:72	8.3	9.1	1.13
17	**6**	200:200:1:4	90	95	53, 98	35:65	10.1	11.0	1.12

[a] Feed Ratio = $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\text{Cat.}]_0$:$[^i\text{PrOH}]_0$, $[L\text{-LA}]_0 = [\varepsilon\text{-CL}]_0 = 1.0$ mol/L, in toluene. [b] BnOH. [c] ^{t}BuOH. [d] Melt polymerization. [e] Monomer conversion as determined by ^{1}H NMR analysis. [f] CL/LA mole ratio in the copolymer. [g] $M_c = 144.13 \times ([L\text{-LA}]_0:[\text{Cat.}]_0) \times 0.25 \times \text{conv.}\% + 114.1 \times ([\varepsilon\text{-CL}]_0:[\text{Cat.}]_0) \times 0.25 \times \text{conv.}\%$. [h] Determined by GPC in THF using polystyrene as standards.

5. Representative ^{1}H NMR, ^{13}C NMR spectra and DSC curves of *ε*-CL/*L*-LA copolymers.

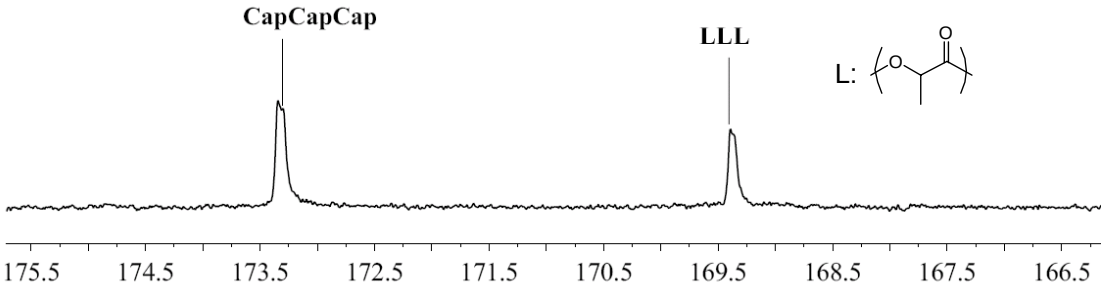

Fig. S3 ^{13}C NMR spectrum of diblock copolymer (PCL-*block*-PLA) obtained by complex **4** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{4}]_0$:$[^{i}\text{PrOH}]_0$ = 200:200:1:2).

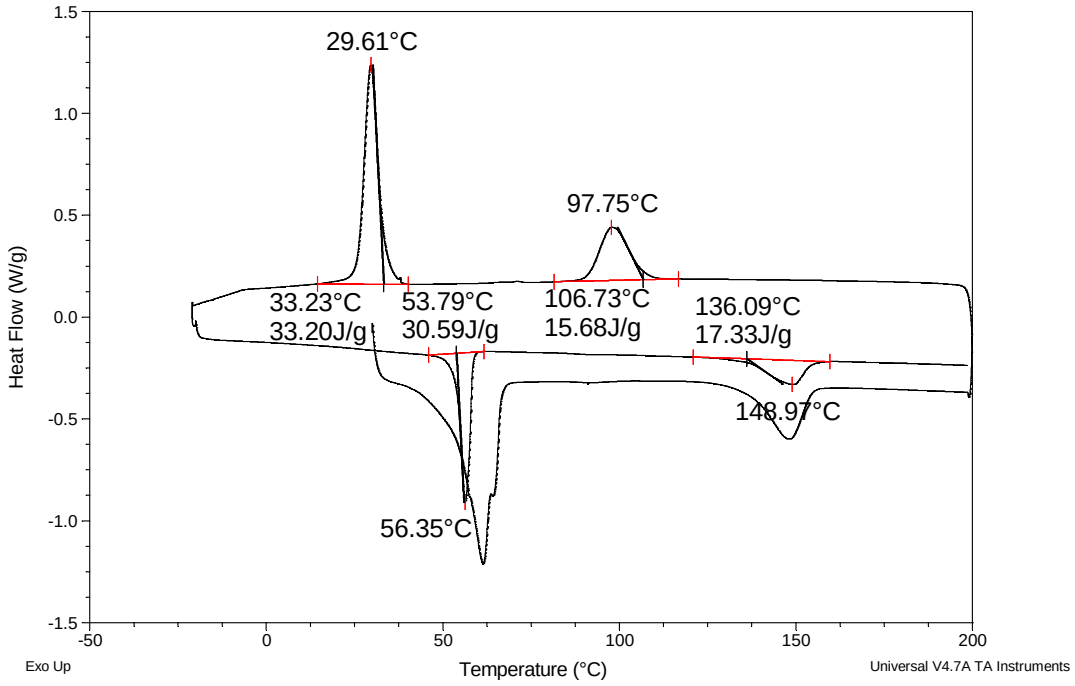

Fig. S4 DSC curves of diblock copolymer (PCL-*block*-PLA) by complex **4** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{4}]_0$:$[^{i}\text{PrOH}]_0$ = 200:200:1:2).

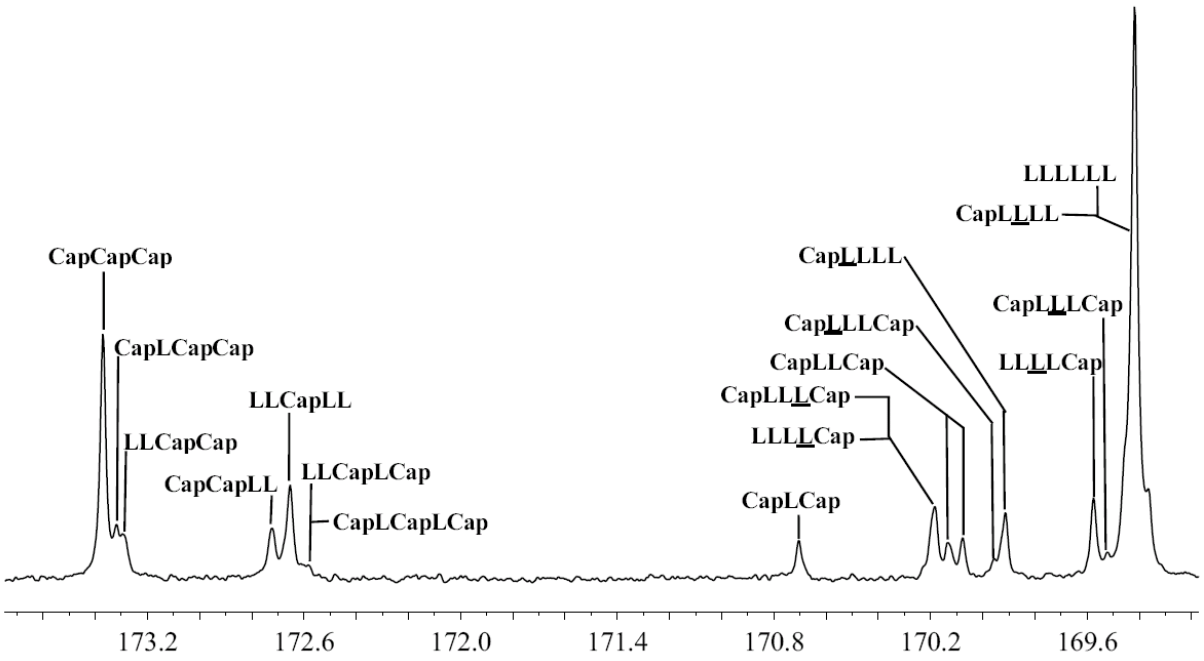

Fig. S5 ^{13}C NMR spectrum of gradient ε-CL/*L*-LA copolymer obtained by complex **4** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{4}]_0$:$[^i\text{PrOH}]_0$ = 200:200:1:4).

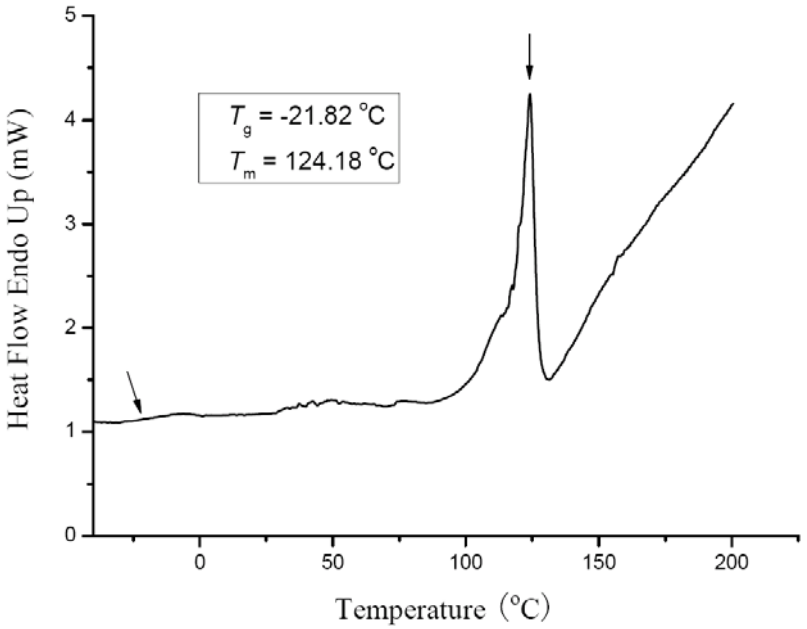

Fig. S6 DSC curves of gradient ε-CL/*L*-LA copolymer by complex **4** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{4}]_0$:$[^i\text{PrOH}]_0$ = 200:200:1:4).

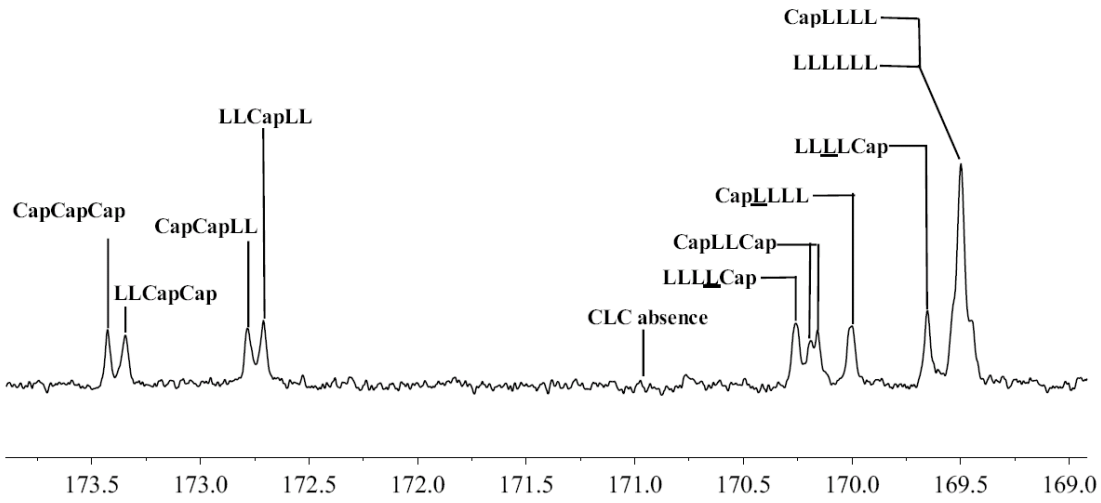

Fig. S7 ^{13}C NMR spectrum of tapered ε-CL/*L*-LA copolymer obtained by complex **5** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{5}]_0$:$[^i\text{PrOH}]_0$ = 200:200:1:4).

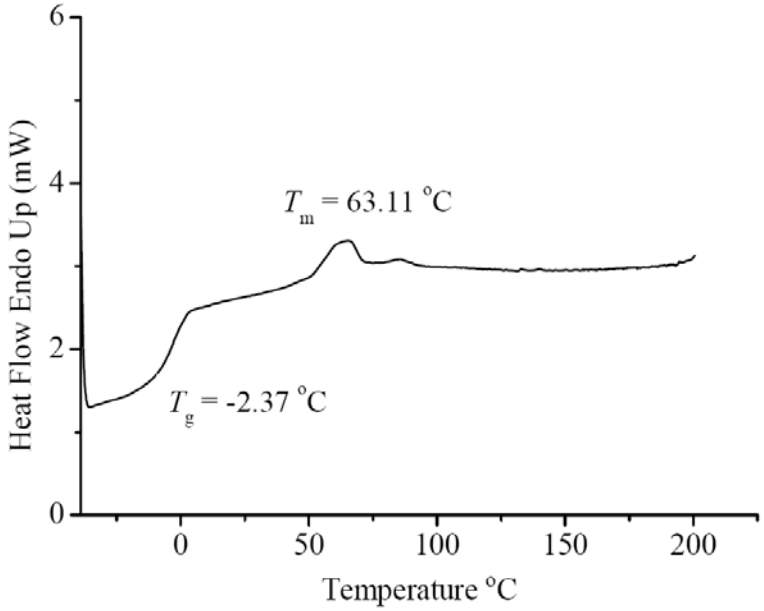

Fig. S8 DSC curves of tapered ε-CL/*L*-LA copolymer by complex **5** (70 °C, toluene, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{5}]_0$:$[^i\text{PrOH}]_0$ = 200:200:1:4).

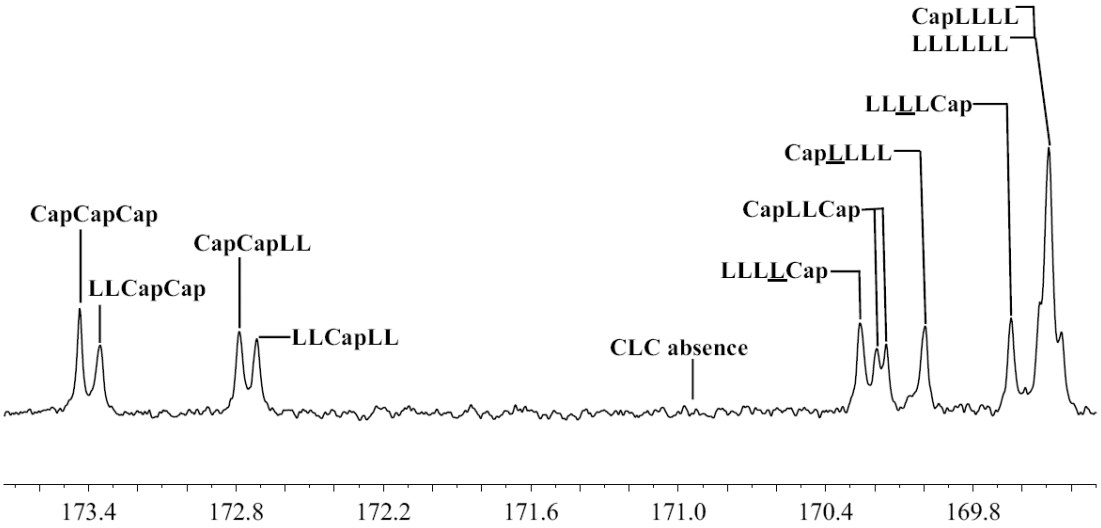

Fig. S9 ^{13}C NMR spectrum of random *ε*-CL/*L*-LA copolymer obtained by complex **5** (110 °C, [*L*-LA]$_0$:[*ε*-CL]$_0$:[**5**]$_0$:[^{i}PrOH]$_0$ = 150:150:1:4).

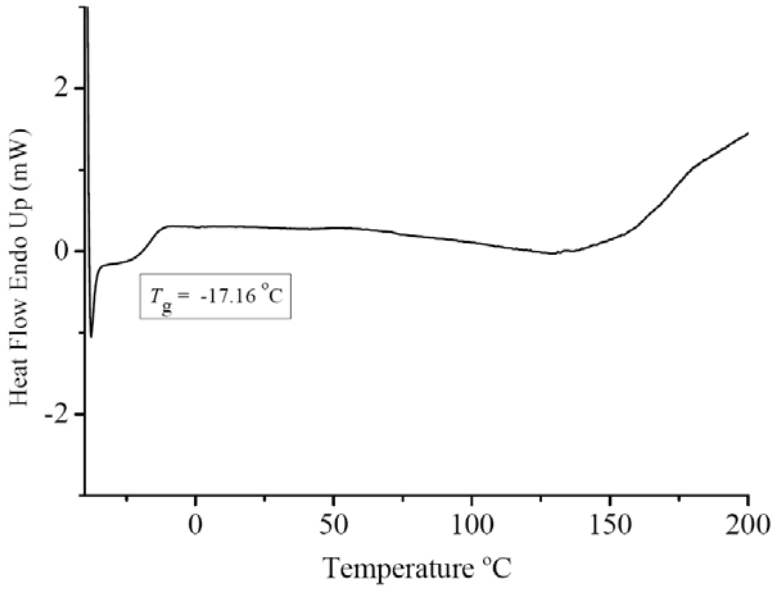

Fig. S10 DSC curves of random *ε*-CL/*L*-LA copolymer by complex **5**. (110 °C, [*L*-LA]$_0$:[*ε*-CL]$_0$:[**5**]$_0$:[^{i}PrOH]$_0$ = 150:150:1:4).

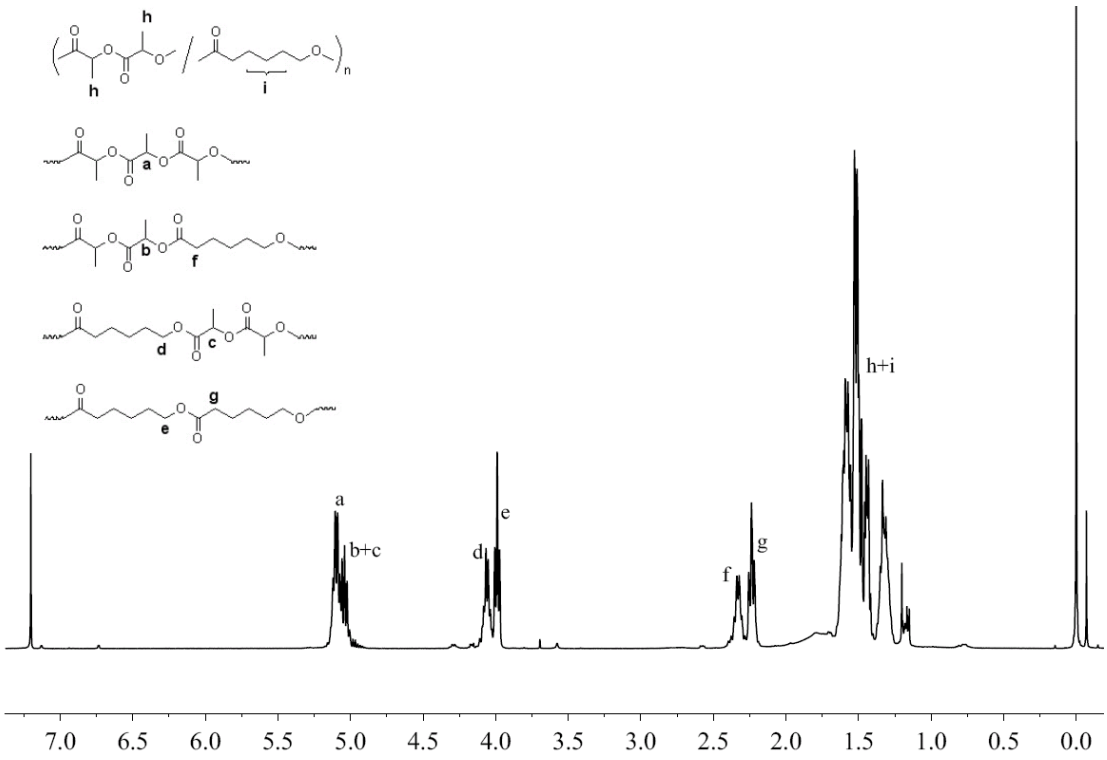

Fig. S11 ^{1}H NMR spectrum of random *ε*-CL/*L*-LA copolymer obtained by complex **5** (110 °C, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{5}]_0$:$[^{i}\text{PrOH}]_0$ = 150:150:1:4).

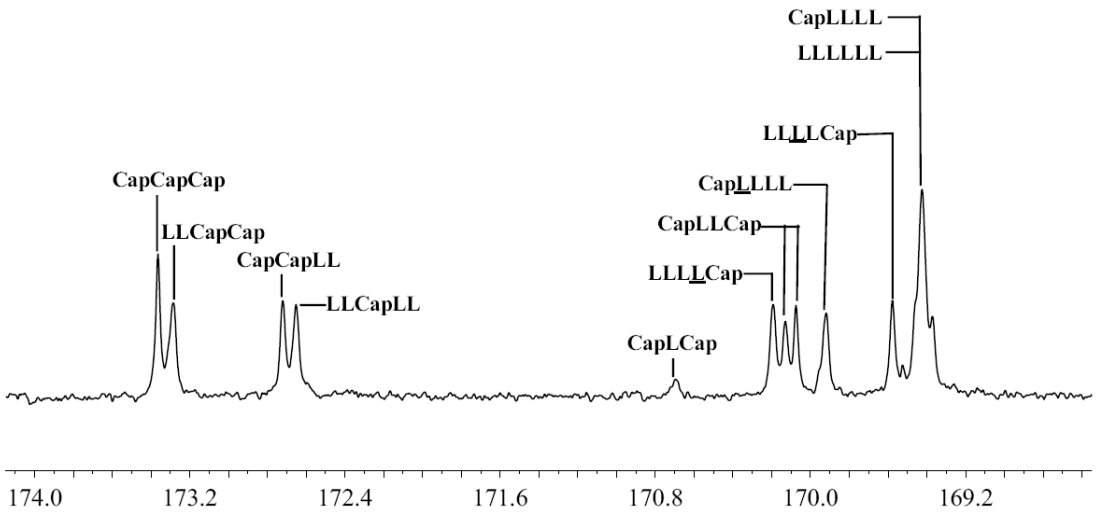

Fig. S12 ^{13}C NMR spectrum of random *ε*-CL/*L*-LA copolymer obtained by complex **5** (140 °C, $[L\text{-LA}]_0$:$[\varepsilon\text{-CL}]_0$:$[\mathbf{5}]_0$:$[^{i}\text{PrOH}]_0$ = 150:150:1:4).