Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Tripodal hydrogen bond donor binding with sulfonic acid enables ring-opening polymerization

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Content

Experimental Section

Materials

Thiophosphoric triamide were prepared following Shea's method[1] and stored under argon. L-Lactide was purified by recrystallizations in toluene and stored under argon. Methanesulfonic acid (99.5%, Aldrich) was bubbled for some hours with argon, prior to use, then stored in a flask under this gas. TMC (99%, Sinopharm Chemical Reagent) were recrystallized with benzene–*n*-hexane three times and further dried under vacuum for 24 h before use. *ε*-Caprolactone and δ-valerolactone (99%, Sinopharm Chemical Reagent) were refluxed over CaH_2 for 12 h and distilled under reduced pressure. Dichloromethane (>99.5%; water content, <0.001%, Sinopharm Chemical Reagent) was distilled over CaH_2 under an argon atmosphere. Benzyl alcohol (99%, Acros) was refluxed over CaH_2 for 48 h before its distillation.

Characterization

^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker ARX-400 spectrometer at 400 MHz at room temperature. The size exclusion chromatography (SEC) was performed using an Agilent 1200 system (Agilent 1200 series degasser, isocratic pump, auto sampler and column heater) equipped with STYRAGEL columns (HR2, 500–20000 g mol^{-1}, 7.8 × 300 mm columns), Wyatt ViscoStar viscometry (VISC) detector, Wyatt DAWN EOS multi-angle light scattering (MALS) detector (GaAs 30 mW laser at λ = 658 nm) and Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. The column temperature and the detectors temperature were 25 °C using THF as the eluent at the flow rate of 0.7 mL min^{-1}. Polymer molecular weight (Mw) and molecular weight distribution (M_w/M_n) were obtained by conventional SEC analysis with a calibration curve. The calibration curve was constructed with polystyrene standards (M_n = 500 g mol^{-1}–20 kg mol^{-1}, Polymer Laboratories, Inc.) by using Astra's column calibration template. These SEC values were corrected using the correction coefficients * determined by Guillaune[2].

X = 0.57 for M_n (SEC raw data) < 5000 g mol^{-1}

X = 0.88 for M_n (SEC raw data) > 10,000 g mol^{-1}

X = 0.73 for 5000 g mol^{-1} < M_n (SEC raw data) < 10,000 g mol^{-1}, an average value between these two data was applied.

dn/dc Measurement. The refractive index increment (dn/dc) of the synthesized polymers was measured using Wyatt's rEX DRI detector and Astra software dn/dc template. Polymers were dissolved in THF, and the solutions with different and precise concentrations of polymer were sequentially injected into the DRI detector. The measured refractive index values were plotted versus concentration. The slope from a linear fitting of the data is the dn/dc of the polymer. The dn/dc of poly(δ-valerolactone), poly(ε-caprolactone), poly(trimethylene carbonates) and poly(L-lactide) were determined as 0.086, 0.071, 0.043 and 0.050 $mL \cdot g^{-1}$ respectively.

Matrix assisted laser desorption/ionization time-of-fight mass spectra (MALDI-ToF MS) were recorded on a mass spectrometer (Ultra extreme; Bruker Co.) with a Smartbeam/-Smartbeam II modified Nd: YAG laser. Mass spectra of 500 shots were accumulated for the spectra at a 25 kV acceleration voltage. The polymer samples were dissolved in $CHCl_3$ at a concentration of 5 mg mL^{-1}, while the matrix 2,5-DHB (2,5-dihydroxybenzoic acid) was dissolved in a solution of trifluoroacetic acid and acetonitrile with a volume ratio of 70 : 30 in 10 mL water (1%). Samples for the MALDI-ToF MS were prepared by mixing the matrix and polymer solutions with the volume ratio of 1:1. The MALDI target was spotted with 1.0 mL of solution and allowed to air-dry.

Polymerization of L-lactide by the combination of thiophosphoric triamide and methanesulfonic acid

In a glove box, LA (0.288 g, 2.0 mmol, 30 equiv.) was dissolved in dichloromethane (2.0 mL, $[LA]_0$ 1.0 mol L^{-1}, Benzyl alcohol (6.7 μL, 0.067 mmol, 1.0 equiv.) as the initiator, the combination of TPTA (0.050 g, 0.067 mmol, 1.0 equiv.) with MSA (4.3 μL, 0.067 mmol, 1.0 equiv.) as the catalysts, were successively added. The reaction mixture was stirred for 45 h at room temperature under an argon atmosphere. Triethylamine was

added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion *via* ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 96%; yield: 70%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 7.26−7.47 (m, 5 H, aromatic), 5.13−5.20 (m, 2 H, ArCH_2 and 2H × (n−1) + 1H, CH(CH_3)$_2$), 4.34 (q, 1 H, HOC$H$$CH_3$), 1.48−1.59 (m, 3 H, HOCHCH_3 and 6H × (n−1) + 3H, CH(CH_3)$_2$), SEC (THF): M_n = 4,120, M_w/M_n = 1.21.

Polymerization of ε-caprolactone (ε-CL) by the combination of methanesulfonic acid and thiophosphoric triamide

In a glove box, ε-CL (0.228 g, 2.0 mmol, 30 equiv) was dissolved in dichloromethane (2.0 mL, $[\varepsilon\text{-CL}]_0$ 1.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1 equiv.) as the initiator for the polymerization, the combination of MSA (4.3 μL, 0.067 mmol, 1 equiv.) and thiophosphoric triamide (0.050 g, 0.067 mmol, 1 equiv.) as the catalyst were successively added. The reaction mixture was stirred for 1.5 h at room temperature under an argon atmosphere. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion via the ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 95%; yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$): 1.38 (m, 2H × n, (–$CH_2CH_2CH_2CH_2CH_2$–)$_n$), 1.64 (m, 2H × n, (–$CH_2CH_2CH_2O$–)$_n$), 1.68 (m, 2H × n, (–$COCH_2CH_2CH_2$–)$_n$), 2.33 (t, 2H × n, J = 7.3 Hz, (–$OCOCH_2CH_2$–)$_n$), 3.65 (t, 2H, J = 6.6Hz, –CH_2CH_2OH), 4.06 (t, 2H × n, J = 6.6 Hz, (–CH_2CH_2O–)$_n$), 5.12 (s, 2H, ArCH_2O), 7.34 (m, 5H, aromatic); SEC (THF): M_n= 3,300 g mol^{-1}, M_w/M_n = 1.12.

Polymerization of δ-valerolactone (δ-VL) by the combination of methanesulfonic acid and thiophosphoric triamide

In a glove box, δ-VL (0.81 g, 8.0 mmol, 30 equiv.) was dissolved in dichloromethane (2.0 mL, $[\delta\text{-VL}]_0$ 4.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1 equiv.) as the initiator for the polymerization, the combination of MSA (4.3 μL, 0.067 mmol, 1 equiv.) and thiophosphoric triamide (0.050 g, 0.067 mmol, 1 equiv.) as the catalyst were successively added. The reaction mixture was stirred for 20 min at room temperature under an argon atmosphere. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion via the ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 91%; yield: 65%. ^{1}H NMR ($CDCl_3$), δ (ppm), 1.68 (m, 2H × n, (–CH2C*H2*CH2O–)n), 1.70 (m, 2H × n, (–COCH2C*H2*CH2–)n), 2.34 (t, 2H × n, J = 6.6 Hz, (–OCOC*H2*CH2–)n), 3.65 (t, 2H, J = 6.1Hz, –CH2C*H2*OH), 4.08 (t, 2H × n, J = 5.6 Hz, (–CH2C*H2*O-)n), 5.12 (s, 2H, ArC*H2*O), 7.34(m, 5H, aromatic); SEC (THF): M_n= 2,840 g mol^{-1}, M_w/M_n = 1.16.

Polymerization of Trimethylene Carbonates (TMC) by the combination of methanesulfonic acid and thiophosphoric triamide

In a glove box, TMC (0.204 g, 2.0 mmol, 30 equiv.) was dissolved in dichloromethane (2.0 mL, $[TMC]_0$ 1.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1 equiv.) as the initiator for the polymerization, the combination of MSA (4.3 μL, 0.067 mmol, 1 equiv.) and thiophosphoric triamide (0.050 g, 0.067 mmol, 1 equiv.) as the catalyst were successively added. The reaction mixture was stirred for 3 h at room temperature under an argon atmosphere. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine

the monomer conversion via the ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 96%; yield: 75%. ^{1}H NMR (CDCl3) δ (ppm), 1.94 (q, 2H, J = 6.1 Hz, -CH2C*H2*OH), 1.99–2.07 (2H × n, (-OC*H2*CH2-)n), 3.75 (t, 2H, J = 6.0 Hz, -C*H2*OH), 4.20–4.30 (m, 4H × n, (-OC*H2*CH2C*H2*O-)n; m, 2H, -CH2CH2C*H2*OH), 5.14 (s, 2H, ArC*H2*O), 7.26–7.35 (m, 5H, aromatic); SEC (THF): M_n= 3,040 g mol^{-1}, M_w/M_n = 1.15.

Block Copolymerization of L-lactide and trimethylene carbonates by the combination of thiophosphoric triamide and methanesulfonic acid

In a glove box, LA (0.288 g, 2.0 mmol, 30 equiv.) was dissolved in dichloromethane (2.0 mL, $[LA]_0$ 1.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1.0 equiv.) as the initiator, the combination of TPTA (0.050 g, 0.067 mmol, 1.0 equiv.) with MSA (4.3 μL, 0.067 mmol, 1.0 equiv.) as the catalysts, were successively added. The reaction mixture was stirred for 45 h at room temperature under an argon atmosphere. Then, 30 equiv. of TMC (0.204 g, 2.0 mmol) was added to start the block copolymerization for another 20 h. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion *via* ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 96%; yield: 73%. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ*(ppm) 7.26–7.35 (m, 5 H, aromatic), 5.13−5.20 (m, 2 H, ArCH_2 and 2H × m, O$CH(CH_3)_2$), 4.22−4.37 (m, 4H × k + 2H, O$CH_2CH_2CH_2$O), 3.89 (m, 2 H, $OCH_2CH_2CH_2$OH), 2.01−2.09 (m, 2H × k + 2H, $OCH_2CH_2CH_2$O), 1.48−1.59 (m, 6H × m, $CH(CH_3)_2$), SEC (THF): M_n = 7,410, M_w/M_n = 1.19.

Block copolymerization of L-lactide and ε-caprolactone by the combination of thiophosphoric triamide and methanesulfonic acid

In a glove box, LA (0.288 g, 2.0 mmol, 30 equiv.) was dissolved in dichloromethane

(2.0 mL, $[LA]_0$ 1.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1.0 equiv.) as the initiator, the combination of TPTA (0.050 g, 0.067 mmol, 1.0 equiv.) with MSA (4.3 μL, 0.067 mmol, 1.0 equiv.) as the catalysts, were successively added. The reaction mixture was stirred for 45 h at room temperature under an argon atmosphere. Then, 30 equiv. of ε-CL (0.228 g, 2.0 mmol) was added to start the block copolymerization for another 20 h. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion *via* ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 95%; yield: 76%. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ*(ppm) 7.26−7.35 (m, 5 H, aromatic), 5.13−5.20 (m, 2 H, ArCH_2 and 2H × m, O$CH(CH_3)_2$), 4.01−4.30 (m, 2H × k, $CH_2CH_2CH_2CH_2CH_2$), 3.80 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2OH$), 2.22−2.26 (m, 2H × k + 2H, $CH_2CH_2CH_2CH_2CH_2$), 1.50−1.62 (m, 6H × m, $CH(CH_3)_2$ and 4H × k + 4H, $CH_2CH_2CH_2CH_2CH_2$), 1.27−1.35 (m, 2H × k + 2H, $CH_2CH_2CH_2CH_2CH_2$), SEC (THF): M_n = 7,820, M_w/M_n = 1.18.

Polymerization of L-lactide by methanesulfonic acid

In a glove box, LA (0.288 g, 2.0 mmol, 30 equiv.) was dissolved in dichloromethane (2.0 mL, $[LA]_0$ 1.0 mol L^{-1}). Benzyl alcohol (6.7 μL, 0.067 mmol, 1.0 equiv.) as the initiator and MSA (4.3 μL, 0.067 mmol, 1.0 equiv.) as the catalyst were successively added. The reaction mixture was stirred for 75 h at room temperature under an argon atmosphere. Triethylamine was added to quench the polymerization, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion *via* ^{1}H NMR measurement. The precipitate was filtered and dried under vacuum.

Conversion: 96%; yield: 70%. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ*(ppm) 7.26−7.47 (*m*, 5 H, aromatic), 5.13−5.20 (*m*, 2 H, ArCH_2 and 2H × (n−1) + 1H, C$H(CH_3)_2$), 4.34 (*q*, 1 H,

HOC*H*CH_3), 1.48−1.59 (*m*, 3 H, HOCHC*H*$_3$ and 6H × (n−1) + 3H, CH(C*H*$_3$)$_2$), SEC (THF): M_n = 4,120, M_w/M_n = 1.21.

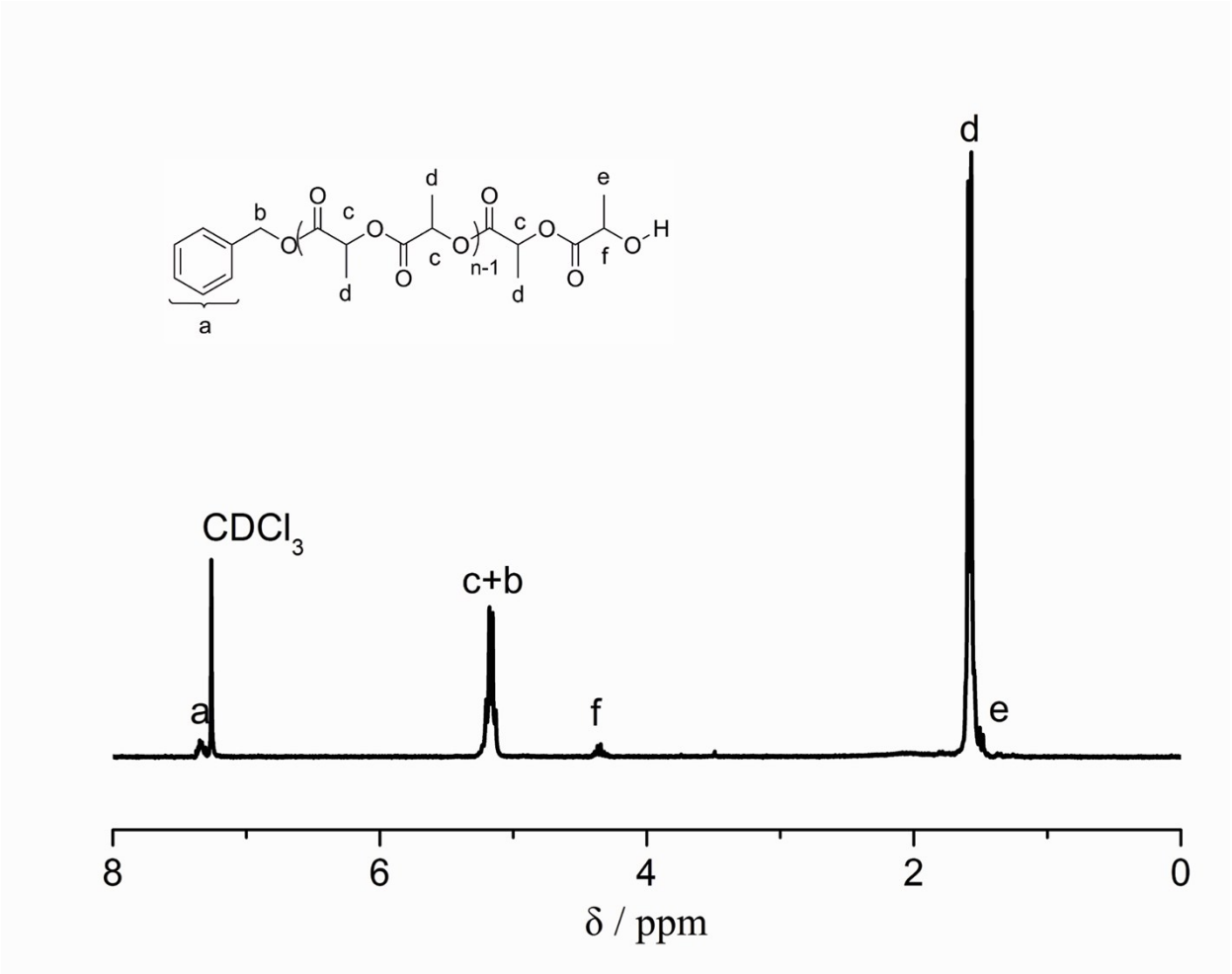
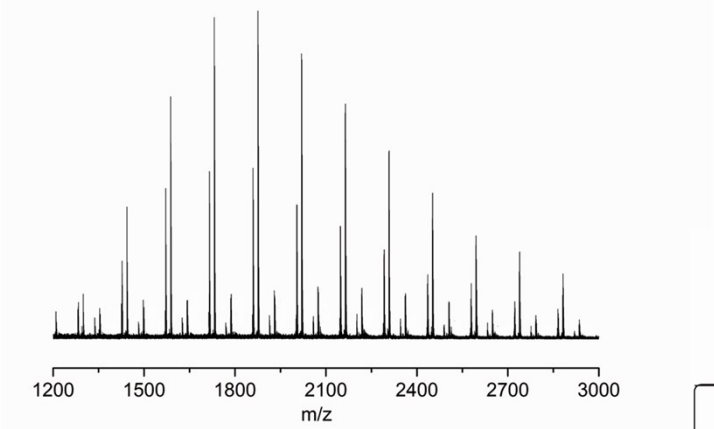
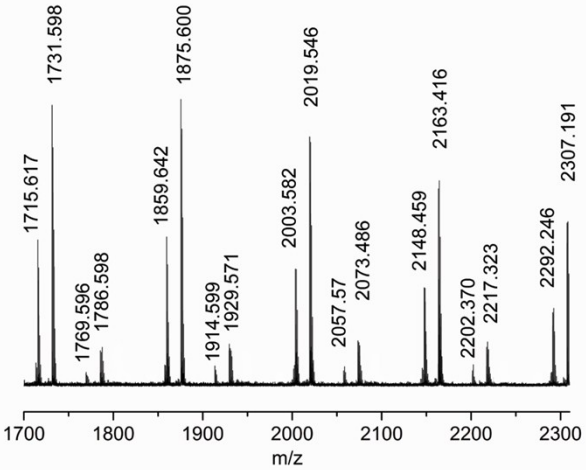
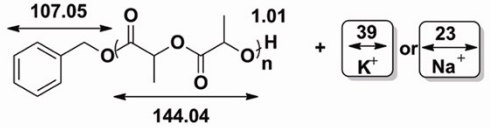


Figure S1: ^{1}H NMR spectra of the obtained PLA







		theoretial values(n)				
	cationizing agent	11	12	13	14	15
PLA initiated by BnOH	K^+	1731.50	1875.54	2019.58	2163.62	2307.66
	Na^+	1715.50	1859.54	2003.58	2147.62	2291.66
PLA initiated by H_2O	K^+		1785.49	1929.53	2073.57	2217.61
	Na^+		1769.49	1913.53	2057.57	2201.61

Figure S2: MALDI-ToF MS spectra of the obtained PLA ($[LA]_0/[BnOH]_0/[MSA/TPTA]$ = 20/1/1/1, dichloromethane, 25 °C, conversion = 95%, $M_{n,\,NMR}$ = 2,980 g mol^{-1}, M_w/M_n = 1.23)

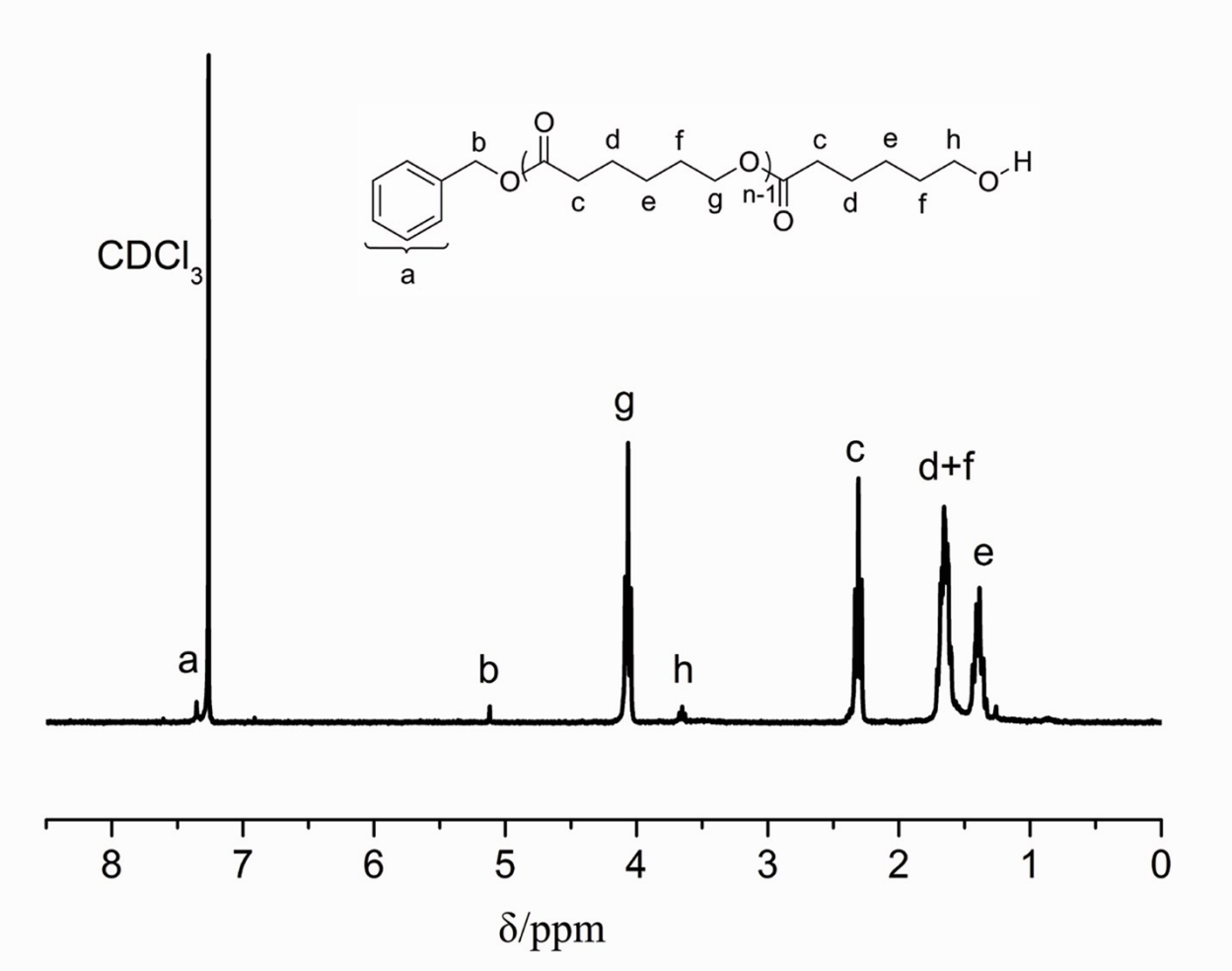
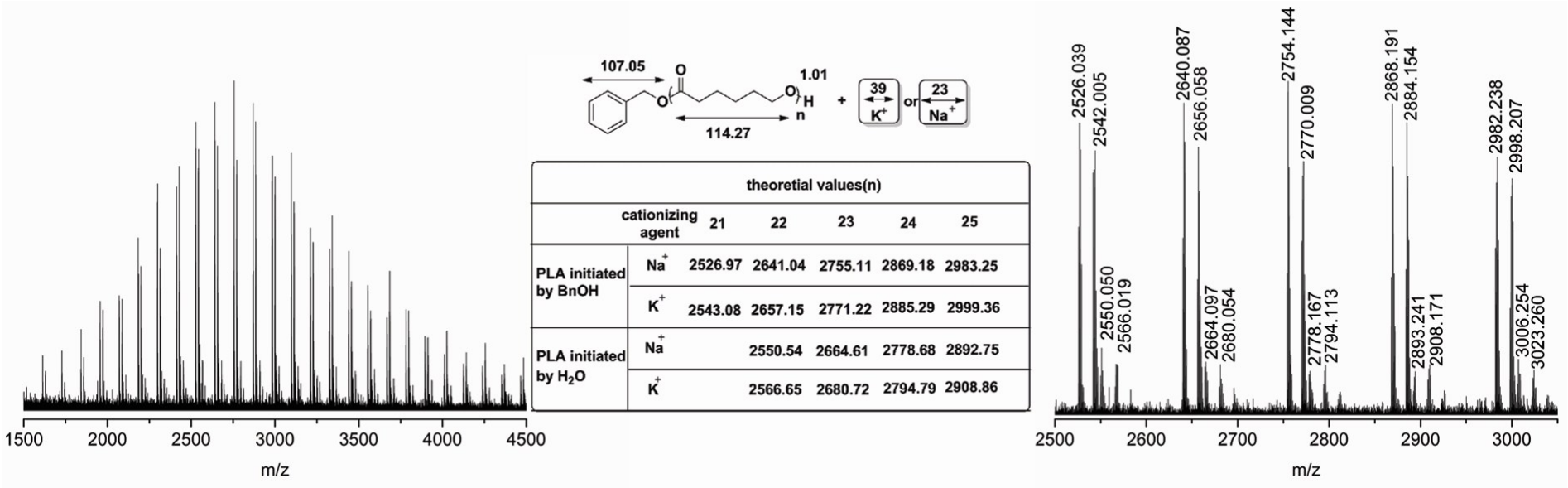


Figure S3*:* ^{1}H NMR spectra of the obtained PCL



		theoretial values(n)				
cationizing agent		21	22	23	24	25
PLA initiated by BnOH	Na^+	2526.97	2641.04	2755.11	2869.18	2983.25
	K^+	2543.08	2657.15	2771.22	2885.29	2999.36
PLA initiated by H_2O	Na^+		2550.54	2664.61	2778.68	2892.75
	K^+		2566.65	2680.72	2794.79	2908.86

Figure S4: MALDI-TOF MS spectra of the obtained PCL $(\varepsilon\text{-CL})_0/[BnOH]_0/[MSA/TPTA]$ = 30/1/1/1, dichloromethane, 25 °C, conversion = 95%, $M_{n,\,NMR}$ = 3,360 g mol^{-1}, M_w/M_n = 1.11.

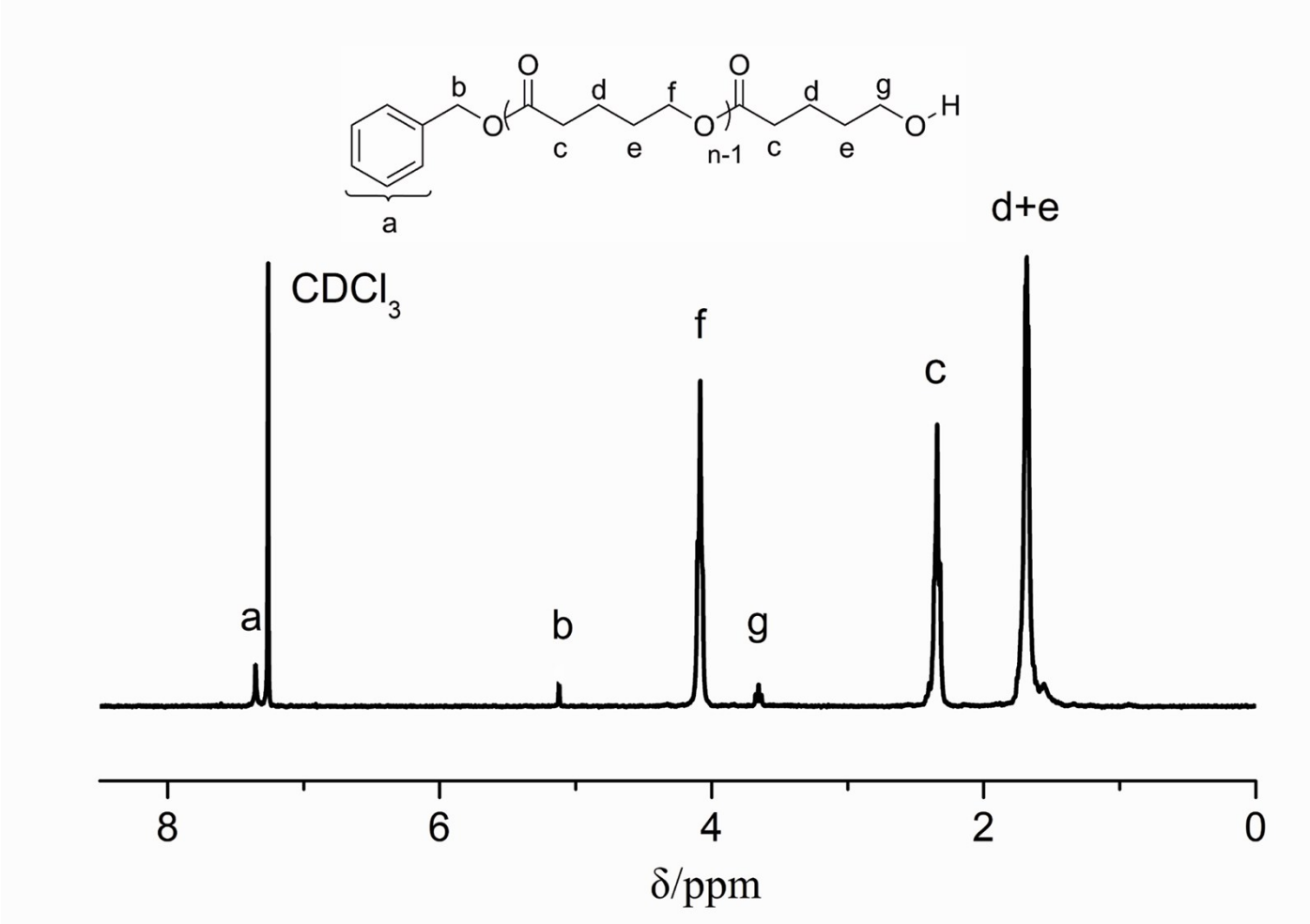
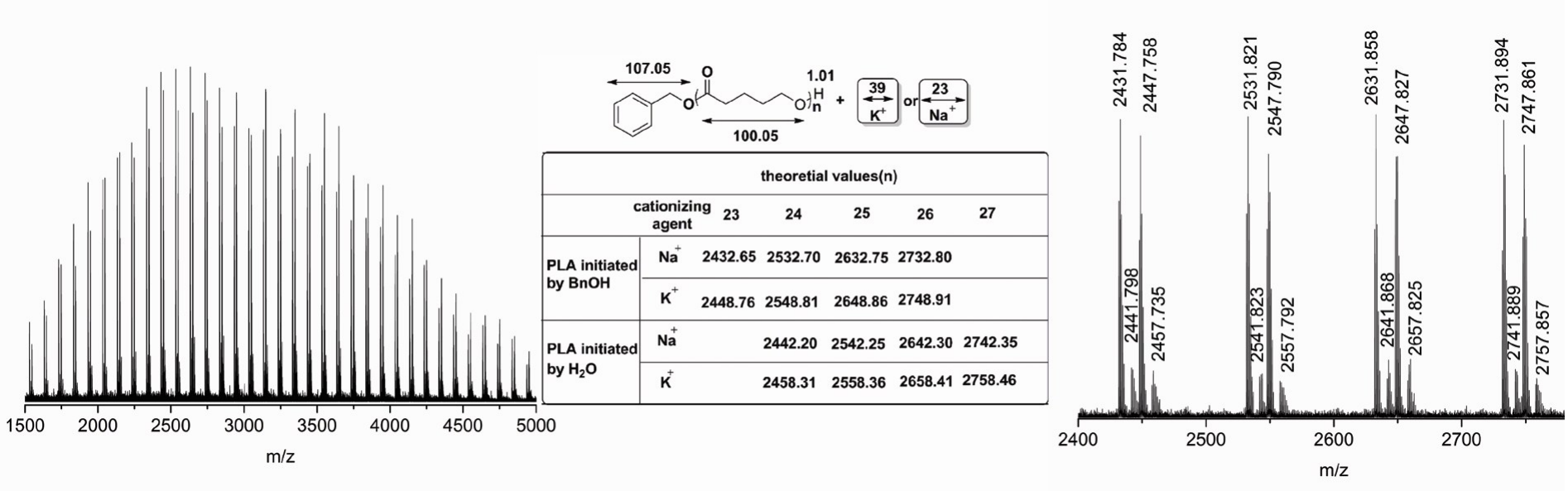


Figure S5*:* ^{1}H NMR spectra of the obtained PVL



theoretial values(n)						
cationizing agent		23	24	25	26	27
PLA initiated by BnOH	Na^+	2432.65	2532.70	2632.75	2732.80	
	K^+	2448.76	2548.81	2648.86	2748.91	
PLA initiated by H_2O	Na^+		2442.20	2542.25	2642.30	2742.35
	K^+		2458.31	2558.36	2658.41	2758.46

Figure S6: MALDI-TOF MS spectra of the obtained PVL (δ-VL)$_0$/[BnOH]$_0$/[MSA/TPTA] = 30/1/1/1, dichloromethane, 25 °C, conversion = 95%, $M_{n,\ NMR}$ = 3,360 g mol^{-1}.

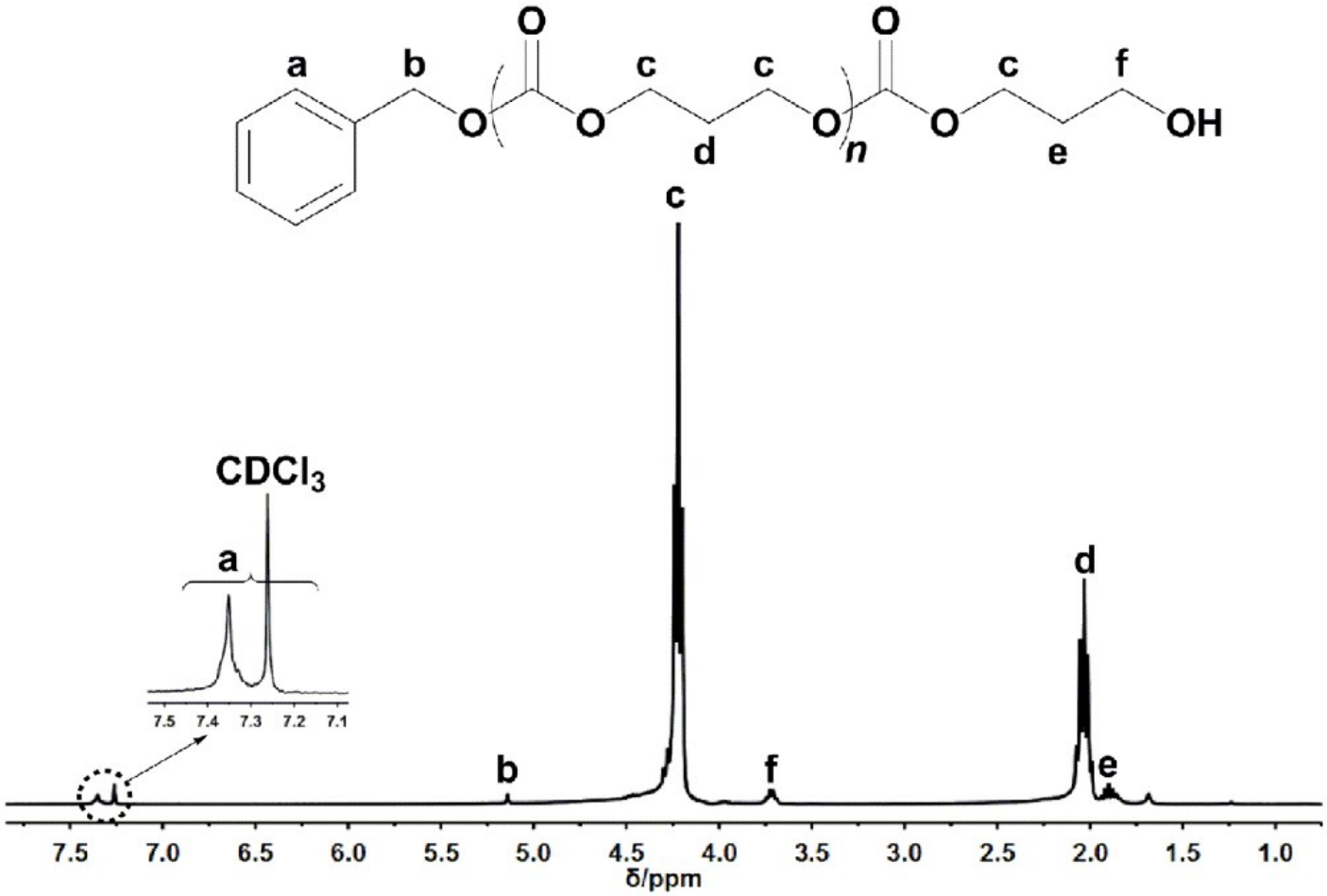
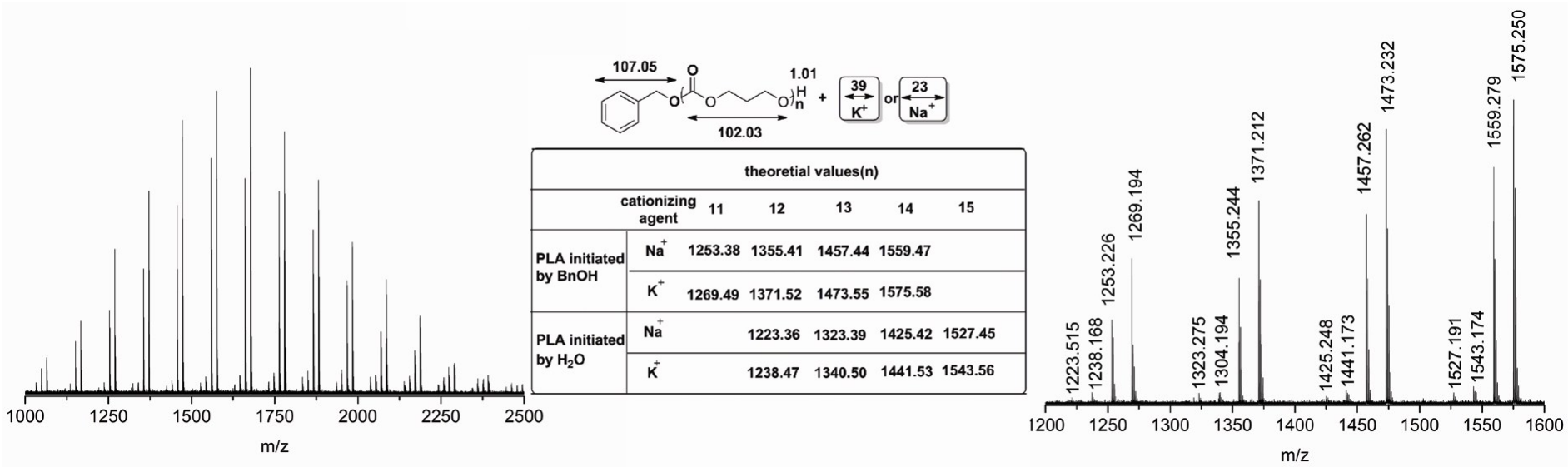


Figure S7: ^{1}H NMR spectra of the obtained PTMC



theoretial values(n)						
	cationizing agent	11	12	13	14	15
PLA initiated by BnOH	Na^+	1253.38	1355.41	1457.44	1559.47	
	K^+	1269.49	1371.52	1473.55	1575.58	
PLA initiated by H_2O	Na^+		1223.36	1323.39	1425.42	1527.45
	K^+		1238.47	1340.50	1441.53	1543.56

Figure S8: MALDI-TOF MS spectra of the obtained PTMC $(TMC]_0/[BnOH]_0/[MSA/TPTA]$ = 20/1/1/1, dichloromethane, 25 °C, conversion = 95%, $M_{n,\ NMR}$ = 1,960 g mol^{-1}.

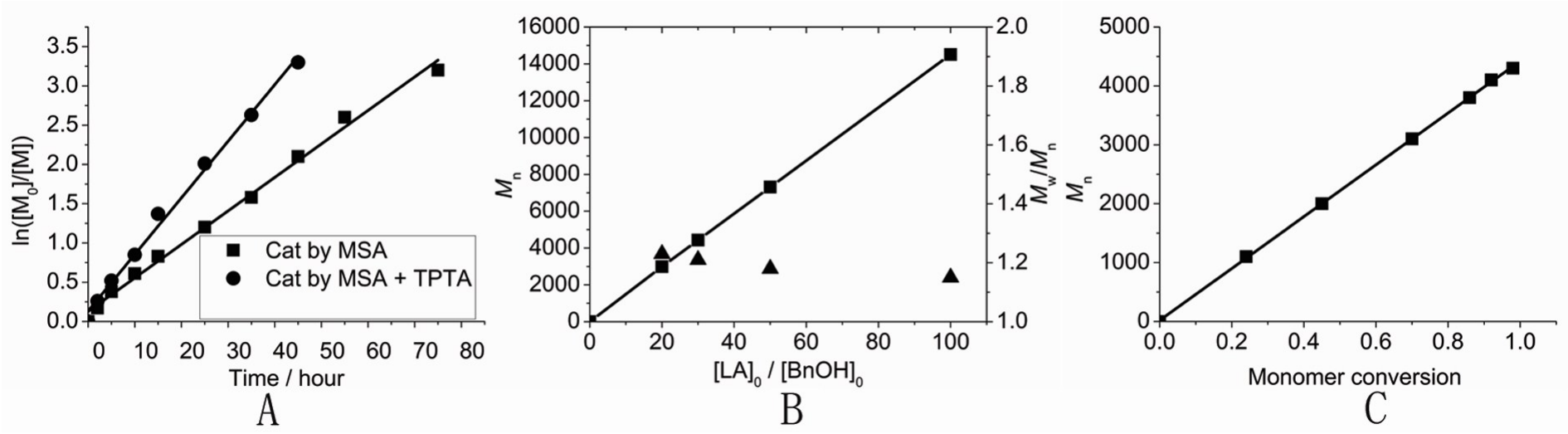


Figure S9: (A) Semilogarithmic plot of L-lactide conversion (estimated by ^{1}H NMR spectroscopy) *vs*. time in $CDCl_3$ at 25 °C ($[LA]_0$ = 1 M, $[LA]_0$/[BnOH]/[MSA] = 30/1/1, $[LA]_0$/$[BnOH]_0$/[MSA]/[TPTA] = 30/1/1/1). (B) M_n (squares) and M_w/M_n (trigons) versus the LA to initiator ratio for polymerization of LA with the combination of thiophosphoric triamide with MSA. Theoretical M_n (solid line). (C) M_n (squares) versus the monomer conversion for polymerization of L-lactide with the combination of TPTA and MSA. Theoretical M_n (solid line).

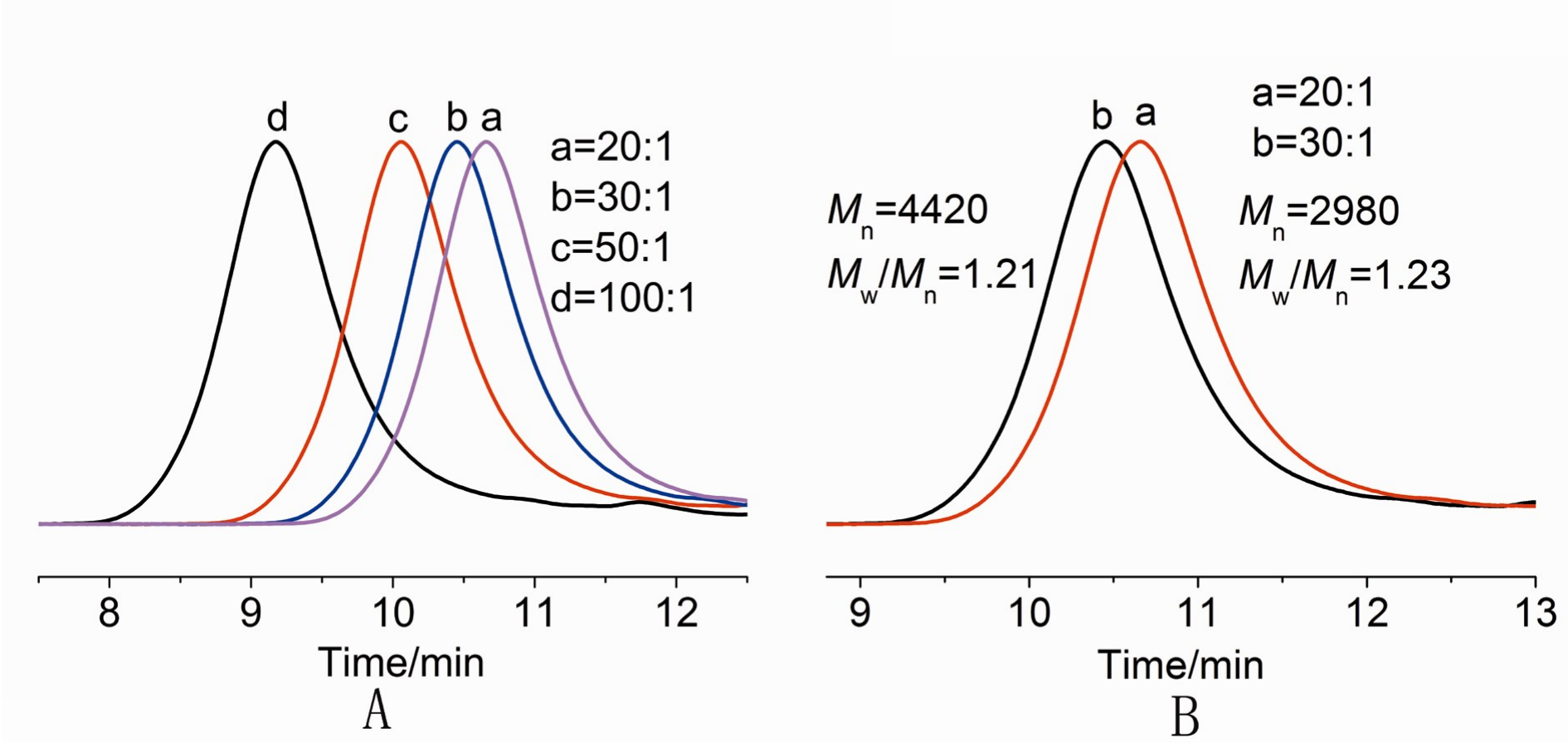


Figure S10*:* (A) SEC traces of the obtained PLAs with various monomer to initiator ratios ($[L\text{-}LA]_0/[BnOH]_0$ = (a) 20, (b) 30, (c) 50, and (d) 100) (eluent, THF; flow rate, 0.7 mL min^{-1}). (B) SEC traces of first PLA sequence (a) and second polymerization (b).

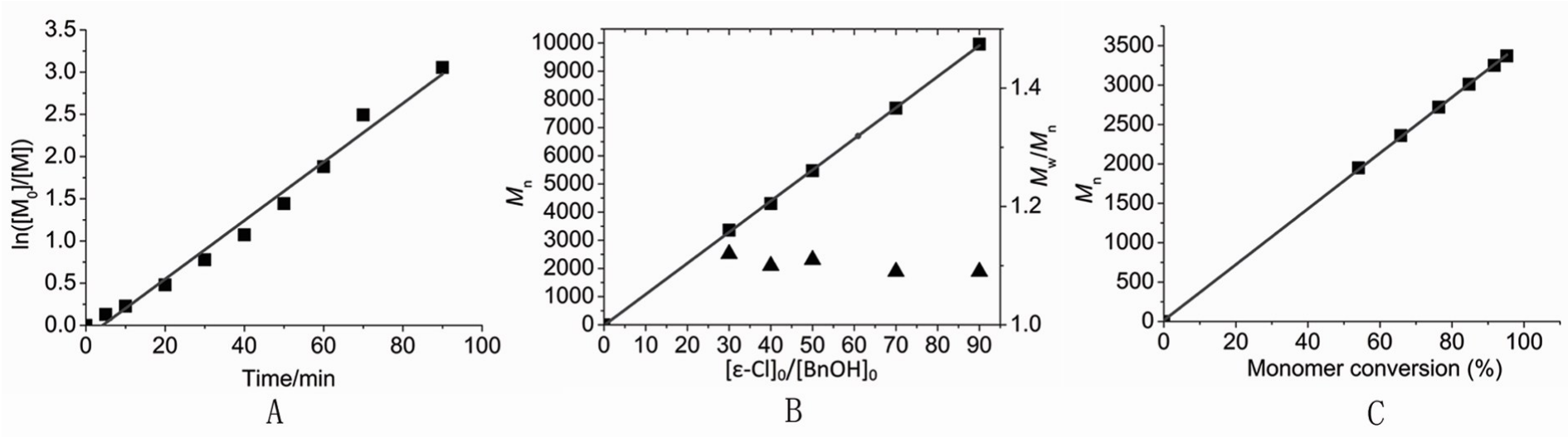


Figure S11*:* (A) Semilogarithmic plot of ε-CL conversion (estimated by ^{1}H NMR spectroscopy) vs time in $CDCl_3$ at 25 °C ($[\varepsilon\text{-CL}]_0$ = 1 M, $[\varepsilon\text{-CL}]_0/[BnOH]_0/[MSA]/[TPTA]$ = 30/1/1/1). (B) Mn (squares) and Mw/Mn (trigons) versus the ε-CL to initiator ratio for polymerization of ε-CL with the combination of MSA and thiophosphoric triamide. Theoretical Mn (solid line). (C) Mn (squares) versus the monomer conversion for polymerization of ε-CL with the combination of MSA and TPTA. Theoretical Mn (solid line).

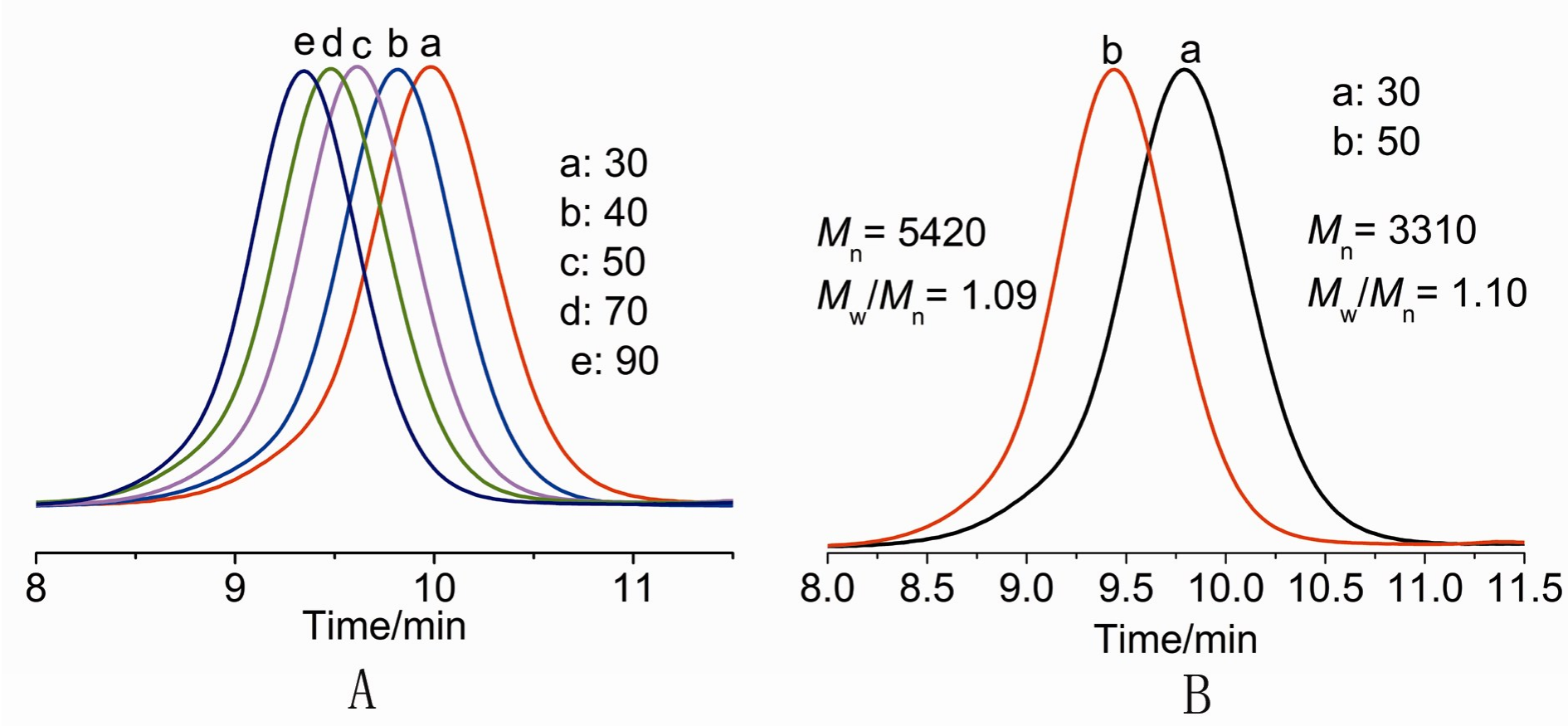


Figure S12*:* (A) SEC traces of the obtained PCLs with various monomer to initiator ratios ($[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0$ = (a) 30, (b) 40, (c) 50, (d) 70, and (e) 90 (eluent, THF; flow rate, 0.7 mL min^{-1}). (B) SEC traces of first PCL sequence (a) and second polymerization (b).

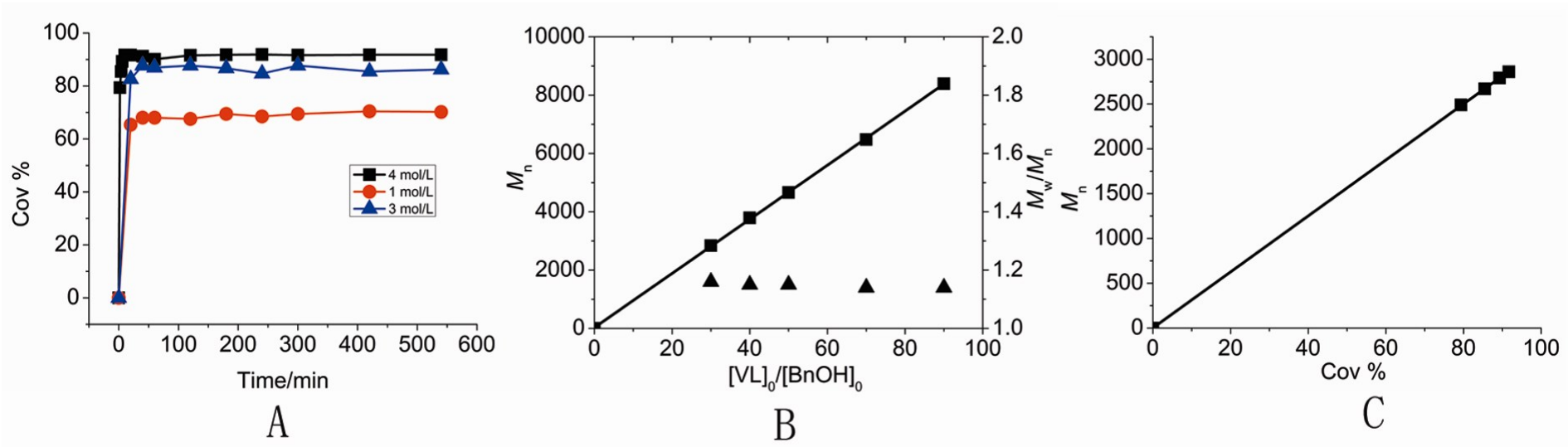


Figure S13: (A) The conversion versus time in different concentration, $[\delta\text{-VL}]_0/[\text{BnOH}]_0/[\text{MSA}]/[\text{TPTA}]$ = 30/1/1/1). (B) [M] = 4.0 mol^{-1}, Mn (squares) and Mw/Mn (trigons) versus the δ-VL to initiator ratio for polymerization of δ-VL with the combination of MSA and thiophosphoric triamide. Theoretical Mn (solid line). (C) [M] = 4.0 mol^{-1}, Mn (squares) versus the monomer conversion for polymerization of δ-VL with the combination of MSA and TPTA. Theoretical Mn (solid line).

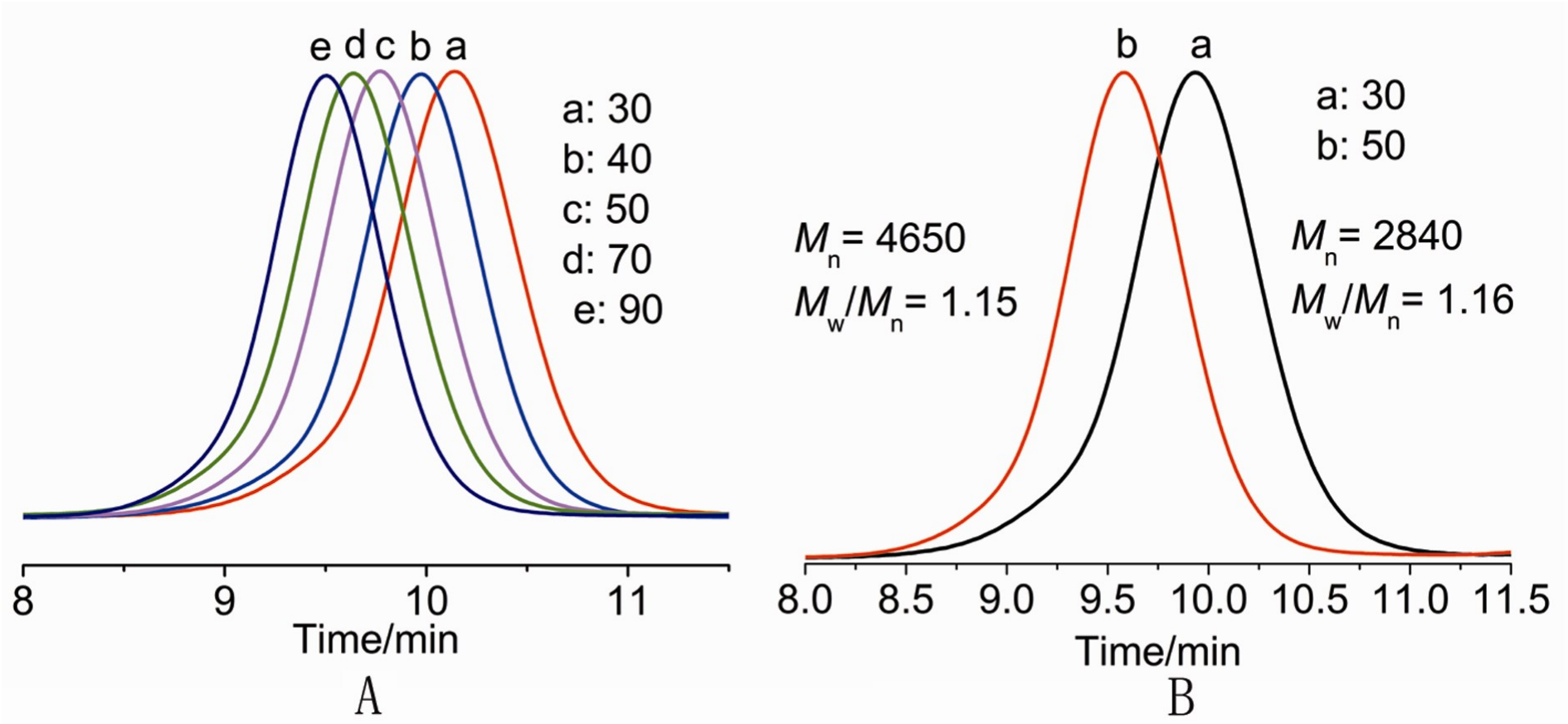


Figure S14*:* (A) SEC traces of the obtained PVLs with various monomer to initiator ratios ($[\delta\text{-VL}]_0/[\text{BnOH}]_0$ = (a) 30, (b) 40, (c) 50, (d) 70, and (e) 90 (eluent, THF; flow rate, 0.7 mL min^{-1}). (B) SEC traces of first δ-VL sequence (a) and second polymerization (b).

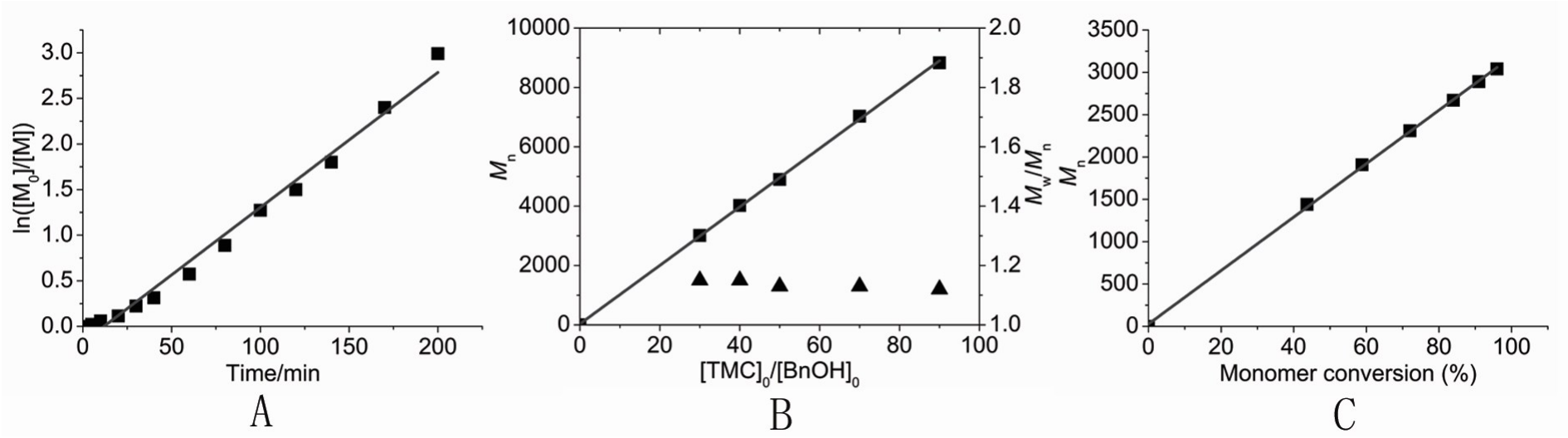


Figure S15*:* (A) Semilogarithmic plot of TMC conversion (estimated by ^{1}H NMR spectroscopy) vs time in $CDCl_3$ at 25 °C ($[\varepsilon\text{-CL}]_0$ = 1 M, $[TMC]_0/[BnOH]_0/[MSA]/[TPTA]$ = 30/1/1/1). (B) Mn (squares) and Mw/Mn (trigons) versus the TMC to initiator ratio for polymerization of TMC with the combination of MSA and thiophosphoric triamide. Theoretical Mn (solid line). (C) Mn (squares) versus the monomer conversion for polymerization of TMC with the combination of MSA and TPTA. Theoretical Mn (solid line).

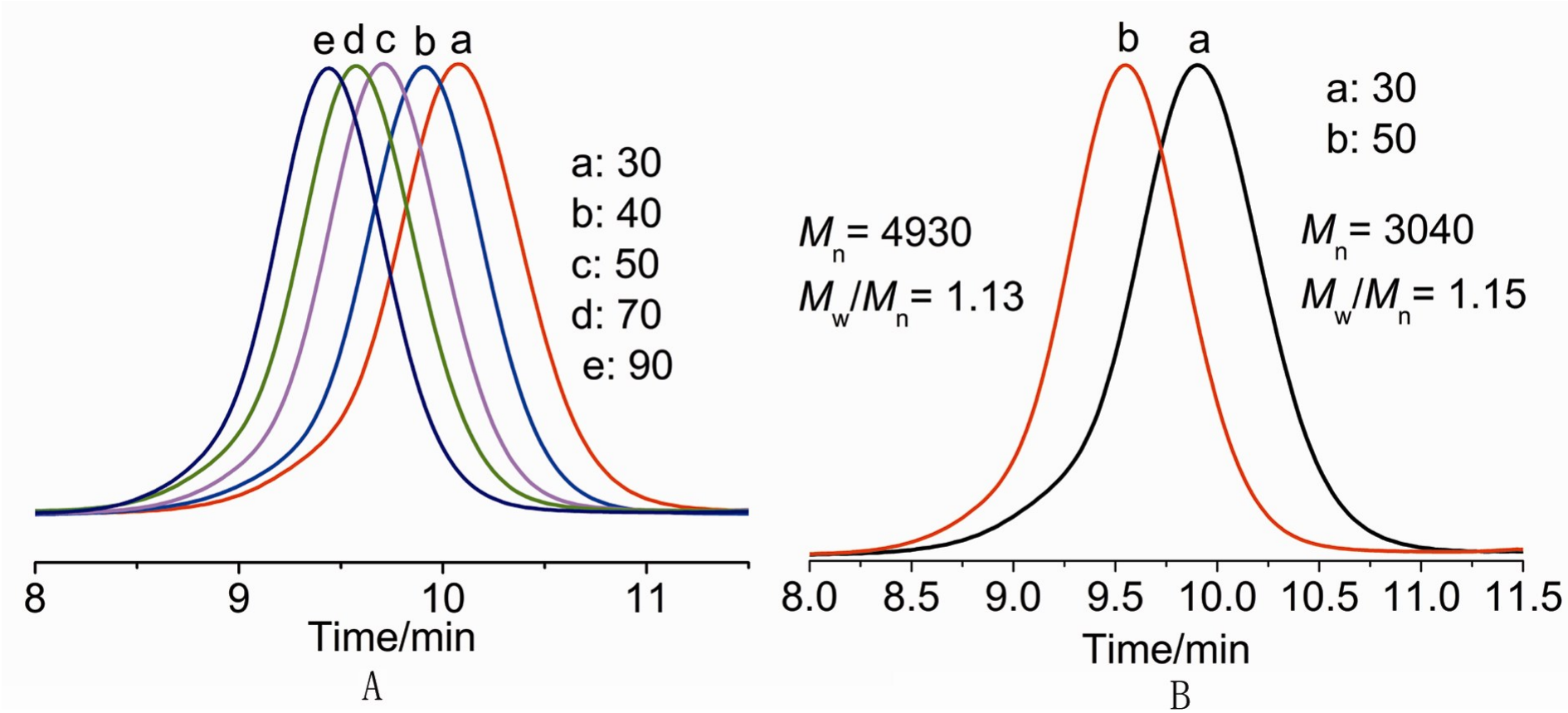


Figure S16*:* (A) SEC traces of the obtained PTMCs with various monomer to initiator ratios ($[TMC]_0/[BnOH]_0$ = (a) 30, (b) 40, (c) 50, (d) 70, and (e) 90 (eluent, THF; flow rate, 0.7 mL min^{-1}). (B) SEC traces of first TMC sequence (a) and second polymerization (b).

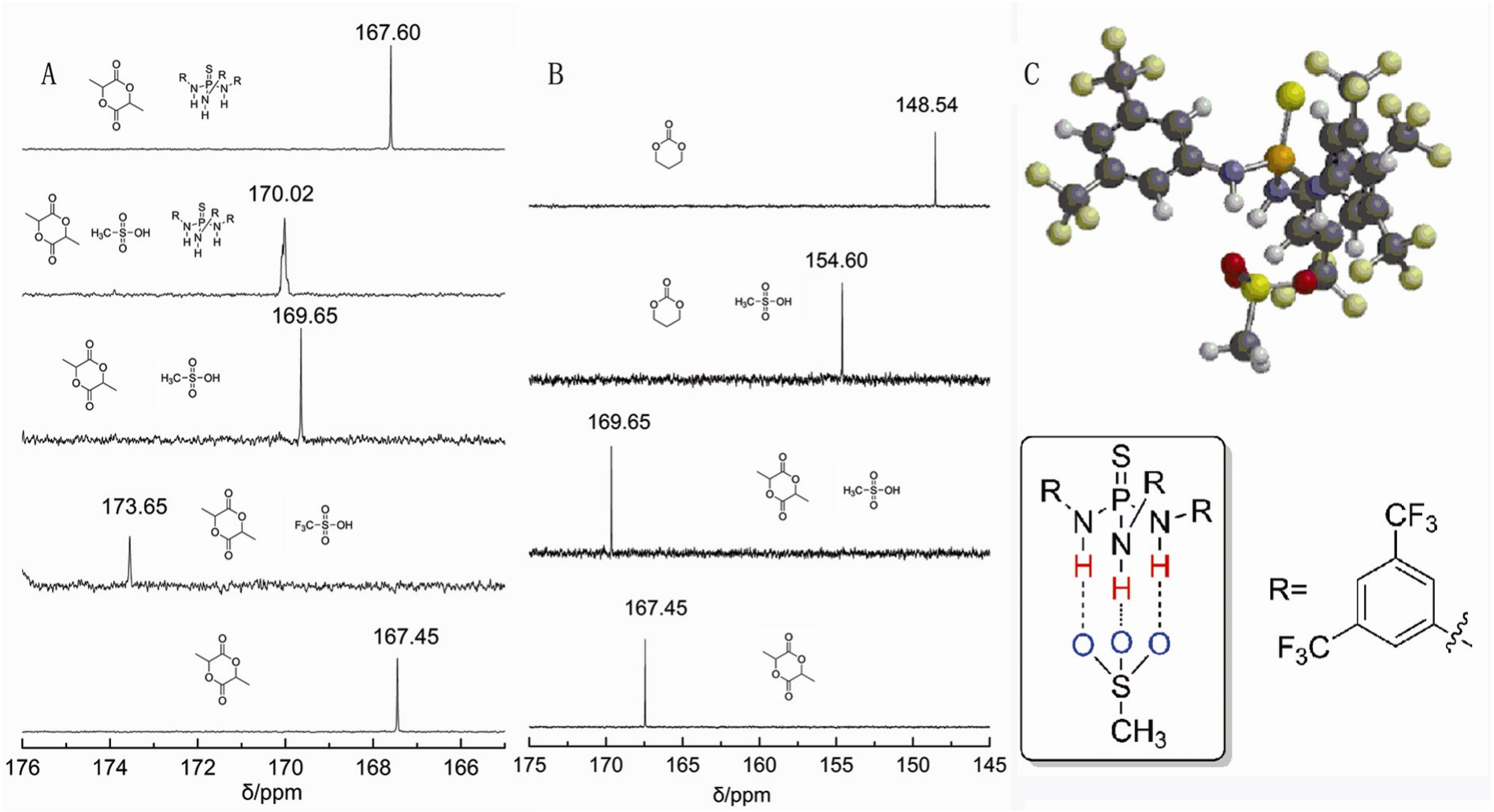

A
167.60
170.02
169.65
173.65
167.45
176
174
172
170
168
166
δ/ppm
B
148.54
154.60
169.65
167.45
175
170
165
160
155
150
145
δ/ppm
C
R=

Figure S17: A) Chemical shifts of carbonyl carbon of L-lactide in different combinations observed by ^{13}C NMR spectra in $CDCl_3$, [L-lactide] / [TfOH] = 1 / 1, [L-lactide] / [MSA] = 1 / 1, [L-lactide] / [TPTA] = 1 / 1, [L-lactide] / [TSA] / [TPTA] = 1 / 1 / 1); B) Chemical shifts of carbonyl carbon of L-lactide or TMC in different combinations observed by ^{13}C NMR spectra in $CDCl_3$, [TMC] / [MSA] = 1 / 1, [L-lactide] / [MSA] = 1 / 1; C) Complex of TPTA **2** and mesylate anion (DFT, B3LYP, equilibrium geometry of the ground state in toluene, 6-31+G*).

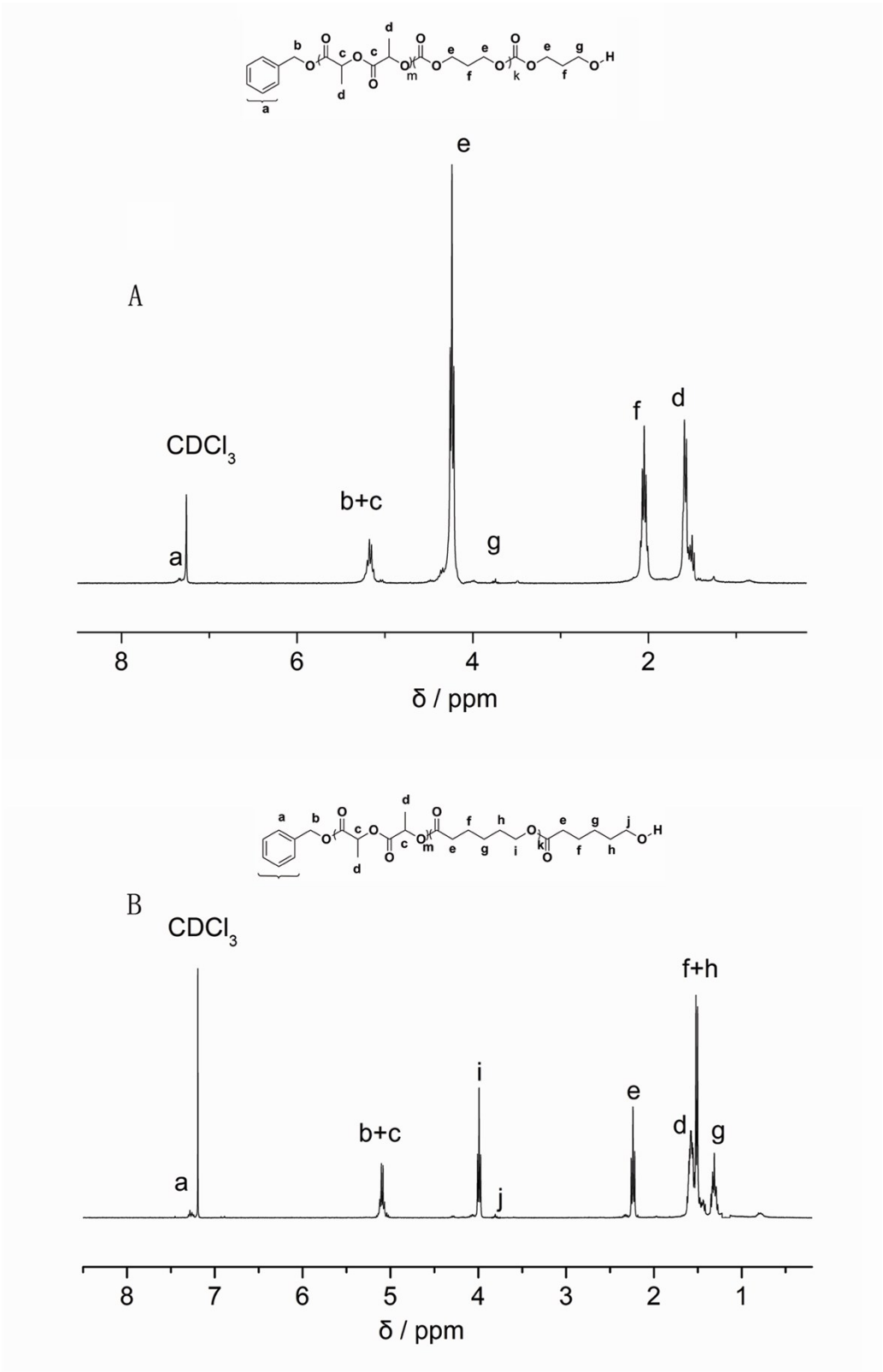


Figure S18: ^{1}H NMR spectra of the obtained (A) PLA-*b*-PTMC and (B) PLA-*b*-PLC

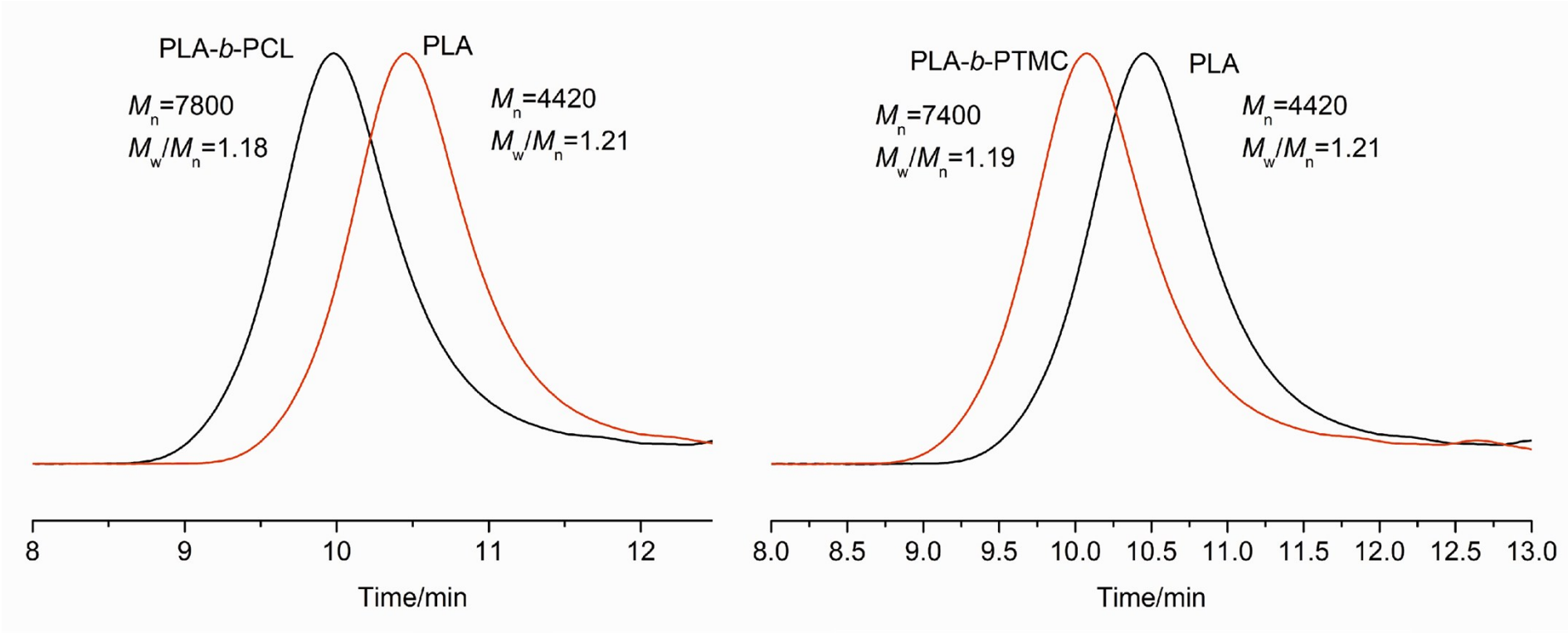


Figure S19: (a) SEC traces of first PLA sequence and PLA-*b*-PCL and (b) SEC traces of first PLA sequence and PLA-*b*-PTMC (eluent, THF; flow rate, 0.7 mL min^{-1}).

References

[1] A. A. Rodriguez, H. Yoo, J. W. Ziller, K. J. Shea, *Tetrahedron Lett.* **2009**, *50*, 6830-6833.

[2] a) I. Palard, M. Schappacher, B. Belloncle, A. Soum, S. M. Guillaume, *Chem. Eur. J.* **2007**, *13*, 1511-1521; b) D. Delcroix, B. Martin-Vaca, D. Bourissou, C. Navarro, *Macromolecules* **2010**, *43*, 8828-8835.