

Random copolymerization of trimethylene carbonate with L-lactide initiated by amine-bridged bis(phenolate) neodymium alkoxides

^a Guojun Hu, ^a Yanwei Wang, ^a Yaorong Wang, ^a Xuehua Zhu, ^b Dan Yuan,^{*,a} and Yingming

Yao^{*,a,c}

^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China. E-mail: yuandan@suda.edu.cn; yaoym@suda.edu.cn.

^b School of Chemistry and Life Science, Suzhou University of Science and Technology, Suzhou 215009, People's Republic of China.

^c Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Engineering Laboratory of Novel Functional Polymeric Materials, Soochow University, Suzhou, 215123, People's Republic of China.

Contents

1. General considerations.....	S2
2. Synthesis of ligand H ₂ L.....	S3
3. Synthesis of complexes 1 and 2.....	S5
4. X-ray single crystal diffraction analysis of complexes 1 and 2.....	S6
5. Ring-opening polymerization of _L -LA/TMC initiated by complexes 1 and 2.....	S8
6. Reactivity ratio calculation for copolymerization of _L -LA and TMC.....	S9
7. Characterization of the polymer.....	S10
8. References.....	S23

1. General considerations

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques or in a purified argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. 1,1,1,3,3,3-hexafluoroisopropanol and 2,2,2-trifluoroethanol were degassed and distilled from sodium under argon atmosphere prior to use. L -LA and TMC were recrystallized from toluene three times and dried. $(C_5H_5)_3RE(THF)$ and the ligand H_2L [$L = (CH_3)_2NCH_2CH_2N[CH_2-(2-OH-3-tBu-5-OMe-C_6H_2)]_2$] were prepared according to the previously reported methods in the literature.^{1,2}

Samples of rare-earth-metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (1H , ^{13}C) spectra of rare-earth-metal complexes were recorded on a Bruker Ascend 500 spectrometer at 25 °C and referenced internally to residual solvent resonance (C_6D_6 7.16 ppm). NMR spectra of polymers were recorded on a Bruker Ascend 500 spectrometer. Hydrogen, carbon and nitrogen analyses were performed by direct combustion on an Elementar Vario EL III analyzer. The molecular weight (M_n) and molecular weight distribution (D) of the polymers were determined using a TOSOH HLC 8320 GPC instrument with a THF (HPLC grade) flow rate of 0.35 mL/min at 40 °C. DSC was calculated on a DSC Q200V24.9 Build 121 instrument. Samples were heated rapidly to 180 °C and maintained for 5 min to remove thermal history, then cooled to -50 °C at a rate of 5 °C min⁻¹ and finally reheated to 180 °C at the same rate under a nitrogen flow. X-ray crystallographic data were collected using an Agilent Gemini Atlas or a Bruker D8 QUEST CCD X-ray diffractometer or Bruker D8 Venture Metal Jet. Data reduction was accomplished by the Bruker APEX program. Structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using the OLEX2 program. All of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically.

The sequence lengths of L -LA and TMC were calculated according to equations 1, 2³:

$$L_{LA} = \frac{I_{5.17ppm}}{I_{5.00PPM}} + 1 \quad (1), \quad L_{TMC} = \frac{I_{154.3ppm}}{I_{154.0PPM}} + 1 \quad (2)$$

2. Synthesis of ligand precursor H₂L

3-*tert*-Butyl-2-hydroxyanisole (16.22 g, 90.0 mmol), *N,N*-dimethylethylenediamine (2.73 g, 30.0 mmol) and paraformaldehyde (1.80 g, 60.0 mmol) were placed in a flask and reacted for 3 days at 80 °C. After cooling, methanol was added and sonicated to yield a large amount of pale yellow powder, which was filtered under reduced pressure to give a white powder (12.30 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ 9.41 (s, 1H, OH), 6.79 (d, *J* = 2.4 Hz, 2H, ArH), 6.47 (d, *J* = 2.4 Hz, 2H, ArH), 3.73 (d, 6H, OCH₃), 3.57 (s, 4H, ArCH₂N), 2.55 (m, 4H, NCH₂CH₂N), 2.27 (s, 6H, NCH₃), 1.37 (s, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, C₆D₆): δ 152.1, 149.6, 138.1, 127.4, 123.1, 113.1 (ArC), 55.9 (ArCH₂N), 54.9 (N(CH₂)₂N), 48.7 (N(CH₂)₂N), 44.1 (N(CH₃)₂), 35.0 (OCH₃), 29.5 (C(CH₃)₃).

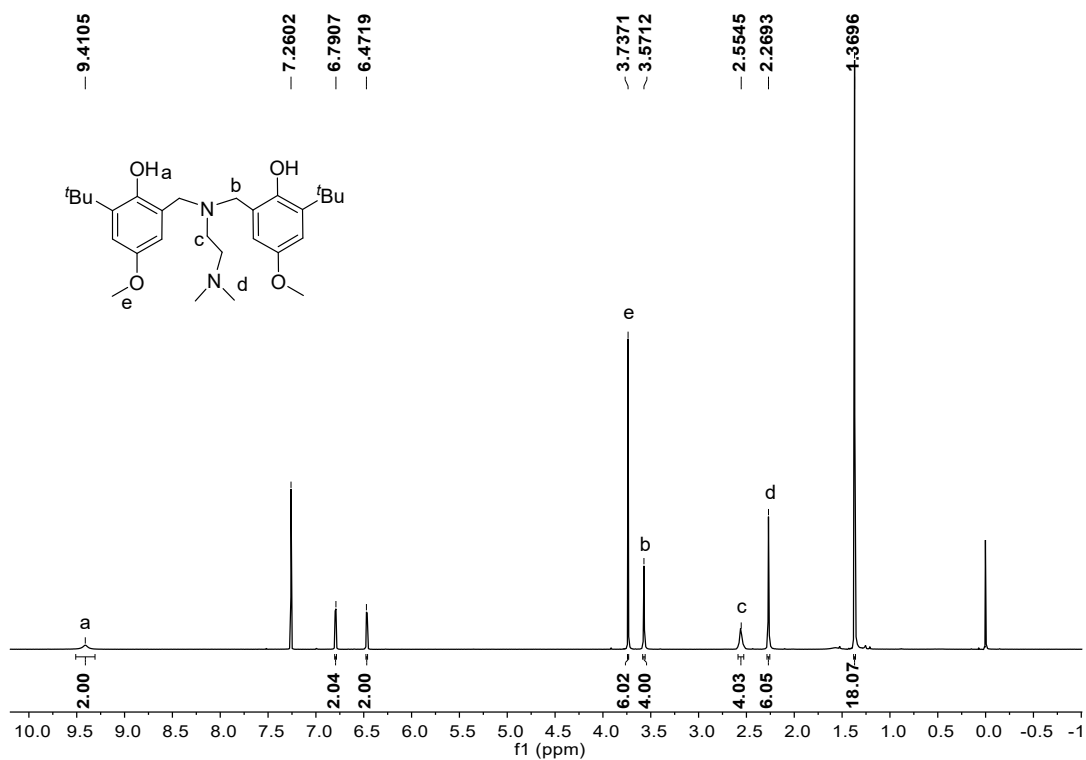


Figure S1. ¹H NMR spectrum of H₂L (400 MHz, CDCl₃, 25 °C)

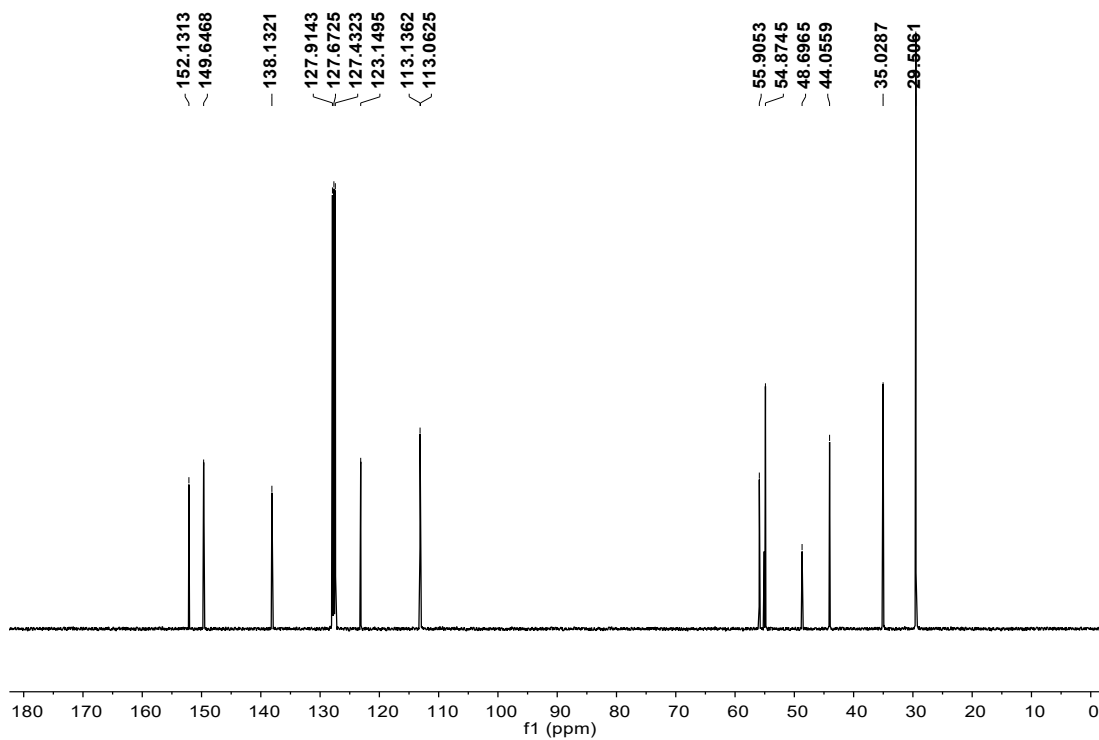


Figure S2. ¹³C NMR spectrum of H₂L (101 MHz, C₆D₆, 25 °C)

3. Synthesis of complexes 1 and 2

Synthesis of complex **1**. A THF solution (5 mL) of $(C_5H_5)_3Nd(THF)$ (0.66 g, 1.5 mmol) was added to a THF solution (6 mL) of H_2L (0.71 g, 1.50 mmol), and the reaction mixture was heated at 60 °C for 12 h. Then, a THF solution of 1,1,1,3,3,3-hexafluoroisopropanol (1.5 mL, 1.0 mol/L) was added via a syringe, and the mixture was left at 60 °C for 12 h. The volatiles were removed under reduced pressure, and the residue was recrystallized with a mixture of THF (1 mL) and hexane (1 mL). Blue crystals were obtained at room temperature after several days (0.70 g, 0.83 mmol, 55%). IR (KBr pellet, cm^{-1}): 2946 (s), 2904 (s), 2829 (s), 1117 (m), 1064 (m), 998 (s), 950 (s), 772 (s), 702 (s), 683 (s). Anal. calcd for: $C_{35}H_{51}F_6N_2NdO_6$: C, 49.22; H, 6.02; N, 3.28. Found: C, 49.32; H, 6.28; N, 3.32.

Synthesis of complex **2**. A THF solution (5 mL) of $Nd[N(SiMe_3)_2]_3$ (0.93 g, 1.5 mmol) was added to a THF solution (6 mL) of H_2L (0.71 g, 1.50 mmol), and the reaction mixture was heated at 60 °C for 12 h. Then, a THF solution of 2,2,2-trifluoroethanol (1.5 mL, 1.0 mol/L) was added via a syringe, and the mixture was left at 60 °C for 12 h. The volatiles were removed under reduced pressure, and the residue was recrystallized with a mixture of THF (1 mL) and hexane (1 mL). White crystals were obtained at room temperature after several days (0.65 g, 0.77 mmol, 51%). IR (KBr pellet, cm^{-1}): 2955 (s), 2870 (s), 2834 (s), 1605 (s), 1162 (s), 1134 (m), 1043 (m), 861 (s), 811 (s), 771 (s), 689 (s), 669 (s). Anal. calcd for: $C_{42}H_{68}F_3N_2NdO_8$: C, 54.32; H, 7.37; N, 3.01. Found: C, 54.67; H, 7.44; N, 3.18.

4. X-ray single crystal diffraction analysis of complexes 1 and 2

Table S1. Crystallographic data for complexes 1 and 2

complex	1	2·THF
Empirical formula	C ₃₅ H ₅₁ F ₆ N ₂ NdO ₆	C ₄₂ H ₆₈ F ₃ N ₂ NdO ₈
Formula weight	854.01	930.22
Temperature/K	273.15	120.0
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
a/Å	54.57(5)	11.4516(6)
b/Å	10.212(9)	17.9776(10)
c/Å	37.13(4)	21.6593(12)
α/°	90	99.326(3)
β/°	132.65(5)	92.638(3)
γ/°	90	90.353(3)
Volume/Å ³	15217(26)	4395.0(4)
Z	16	4
ρ _{calc} g/cm ³	1.491	1.406
μ/mm ⁻¹	1.438	6.423
F(000)	6992.0	1940.0
Crystal size/mm ³	0.3 × 0.2 × 0.2	0.2 × 0.15 × 0.1
2θ range for data collection/°	4.116 to 55.014	5.166 to 105.956
Reflections collected	75717	101115
Independent reflections	17391 [R _{int} = 0.1034]	15529 [R _{int} = 0.116]
Data/restraints/parameters	17391/822/1043	15529/1063/1312
Goodness-of-fit on F ²	1.064	1.063
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0516, wR ₂ = 0.1180	R ₁ = 0.0639, wR ₂ = 0.1587
Final R indexes [all data]	R ₁ = 0.0976, wR ₂ = 0.1482	R ₁ = 0.1016, wR ₂ = 0.1774
Largest diff. peak/hole / e Å ⁻³	1.61/-1.54	1.43/-2.23

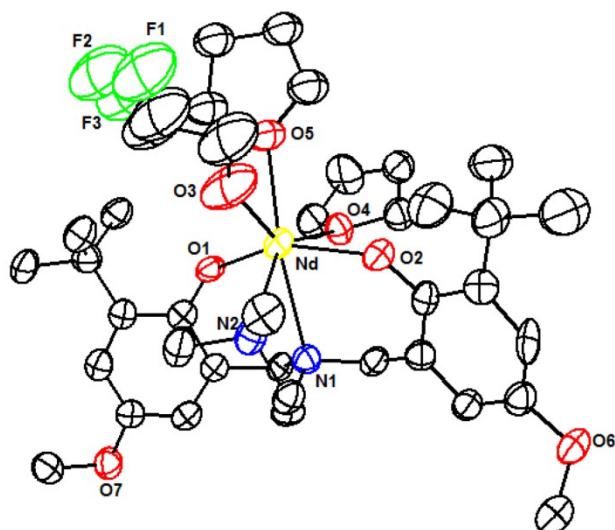


Figure S3. ORTEP view of complex **2** with ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity

5. Ring-opening polymerization of _L-LA/TMC initiated by complexes **1** and **2**

Table S2. ROP of _L-LA/TMC initiated by complexes **1** and **2**^a

Entry	Monomer	Cat.	[M] ₀ /[I] ₀	t/min	Yield ^b /%	<i>M</i> _c ^c (kg/mol)	<i>M</i> _n (kg/mol)	<i>D</i> ^d
1	_L -LA	1	1000 : 1	30	38	54.77	47.67	1.3
2	_L -LA	2	1000 : 1	30	89	128.28	106.93	1.5
3	TMC	1	1000 : 1	5	55	56.12	59.72	1.5
4	TMC	1	1000 : 1	10	99	101.01	119.44	1.6
5	TMC	2	1000 : 1	5	99	101.01	113.24	1.7

^a Polymerization conditions: [Monomer] = 1 mol/L, in THF, T = 30 °C. ^b Yield: (weight of polymer obtained)/(weight of monomer used). ^c *M*_c = 144.13 × [_L-LA]₀: [I]₀ × yield(%) or *M*_c = 102.03 × [TMC]₀: [I]₀ × yield(%). ^d Measured by GPC calibrated with standard polystyrene samples.

6. Reactivity ratio calculation for copolymerization of L-LA and TMC

Table S3. Reactivity ratio calculation for copolymerization of L-LA and TMC

Entry	$f_{[LA]}^a$	$f_{[TMC]}^a$	Conv. LA	Conv. TMC	F_{LA}^b	F_{TMC}^b	x	y	F	G
1	0.30	0.70	0.041	0.064	0.360	0.640	0.429	0.563	0.326	-0.332
2	0.50	0.50	0.092	0.061	0.590	0.410	1.000	1.439	0.695	0.305
3	0.60	0.40	0.087	0.050	0.660	0.340	1.500	1.941	1.159	0.727
4	0.70	0.30	0.095	0.035	0.740	0.260	2.333	2.846	1.913	1.513
5	0.80	0.20	0.089	0.024	0.830	0.170	4.000	4.882	3.277	3.181

^a f_1 and f_2 are defined as mole fractions of monomers LA and TMC in the feed and $f_1 = 1 - f_2$. ^b F_1 and F_2 represents the mole fraction of each monomer in the copolymer and $F_1 = 1 - F_2$.

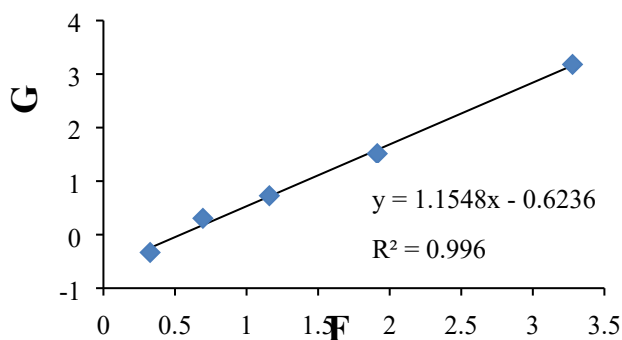


Figure S4. Linear relationship of F and G

$$r_{LA} = \frac{k_{LALA}}{k_{LATMC}}$$

$$r_{TMC} = \frac{k_{TMC}TMC}{k_{TMC}LA}$$

$$\frac{d[LA]}{d[TMC]} = \frac{[LA] r_{LA}[LA] + [TMC]}{[TMC]r_{TMC}[TMC] + [LA]} \quad (1)$$

$$r_{TMC} = \frac{[LA] \frac{d[TMC]}{d[LA]} (1 + \frac{r_{LA}[LA]}{[TMC]}) - 1}{\frac{d[LA]}{d[TMC]}} \quad (2)$$

$$y = \frac{F_{LA}}{F_{TMC}} = \frac{d[LA]}{d[TMC]}$$

$$x = [LA]/[TMC] \quad (3)$$

$$y = \frac{xr_{LA} + 1}{xr_{TMC} + x} \quad (4)$$

$$x - \frac{x}{y} = r_{LA} \frac{x^2}{y} - r_{TMC} \quad (5)$$

$$G = x - \frac{x}{y} \quad F = \frac{x^2}{y} \quad (6)$$

7. Characterization of the polymer

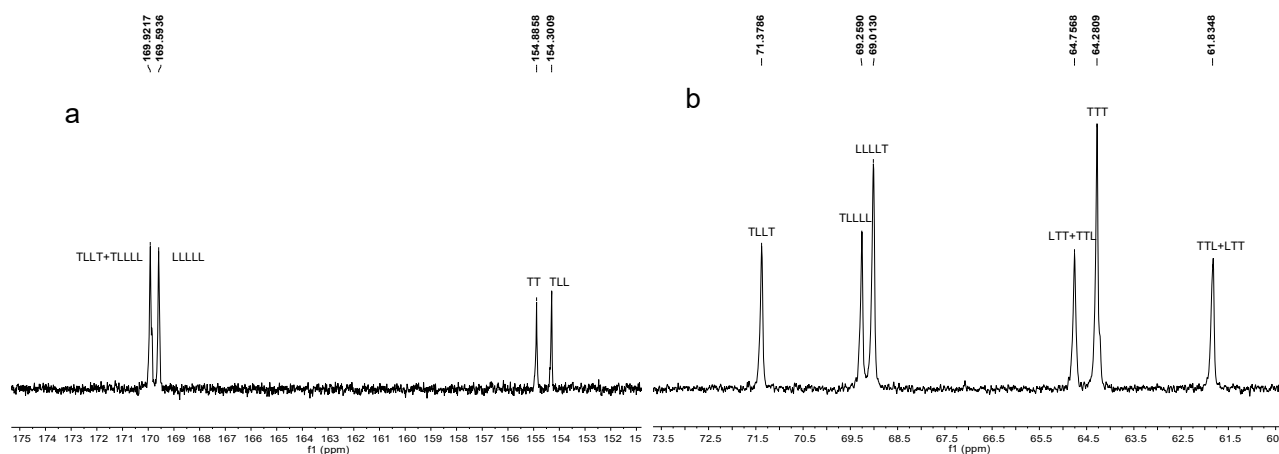


Figure S5. ^{13}C NMR spectrum of P(TMC-co-LLA) (CDCl_3 , 100 MHz)

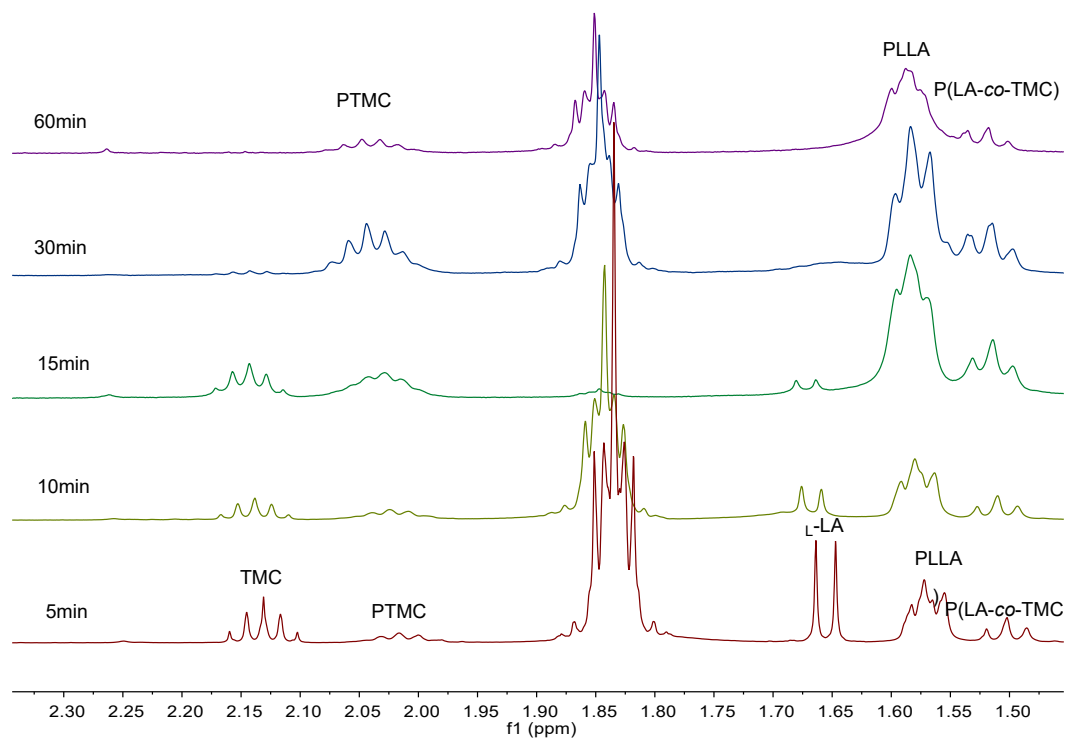


Figure S6. ^1H NMR monitoring of copolymerization using complex 2 (CDCl_3 , 400 MHz)

Table S4. Monitoring of the copolymerization of TMC and _L-LA initiated by complex **2**^a

t	C _{LA} , C _{TMC} ^b %	TMC/LA ^c %	LA-TMC/LA-LA
1 min	15, 10	34 : 66	19 : 81
5 min	63, 38	37 : 63	23 : 77
10 min	74, 53	40 : 60	25 : 75
15 min	92, 68	43 : 57	31 : 69
30 min	99, 84	47 : 53	32 : 68
60 min	99, 99	50 : 50	33 : 67

^a Polymerization conditions: [TMC] = [_L-LA] = 1 mol/L, [TMC]₀: [_L-LA]₀: [**2**]₀ = 200: 200: 1, in THF. ^b Monomer conversion was determined by ¹H NMR spectroscopy. ^c TMC/LA molar ratio in the copolymer.

Table S5. Copolymerization of TMC and _L-LA with different feed ratios initiated by complex **2**^a

Entry	[TMC] ₀ : [_L -LA] ₀ : [2] ₀	C _{LA} , C _{TMC} ^b %	TMC/LA ^c %	LA-TMC /LA-LA%	M _c ^d (kg/mol)	M _n (kg/mol)	D ^e	T _g ^f (°C)
1	360 : 40 : 1	99 : 69	92 : 8	49 : 51	31.05	106.40	1.6	-10.88
2	320 : 80 : 1	99 : 86	79 : 21	44 : 56	39.49	38.67	1.6	-4.18
3	280 : 120 : 1	99 : 90	70 : 30	39 : 61	42.83	74.43	1.7	3.57
4	240 : 160 : 1	99 : 93	64 : 36	35 : 65	45.60	34.64	1.8	9.93
5	200 : 200 : 1	99 : 99	50 : 50	33 : 67	48.74	75.30	1.8	21.97
6	160 : 240 : 1	99 : 95	39 : 61	26 : 74	49.75	72.01	1.6	24.43
7	120 : 280 : 1	99 : 96	30 : 70	20 : 80	51.71	77.95	1.7	28.61
8	80 : 320 : 1	99 : 91	19 : 81	17 : 83	53.09	79.99	1.5	43.82
9	40 : 360 : 1	99 : 92	10 : 90	9 : 91	55.12	61.36	1.4	50.89

^a General polymerization conditions: [TMC] + [_L-LA] = 2 mol/L, ([TMC]₀ + [_L-LA]₀): [I]₀ = 400: 1, THF as the solvent, at 30 °C, t = 1h; ^b Determined by ¹H NMR spectroscopy. ^c TMC/LA mole ratio in the copolymer. ^d M_c = (102.03 × [TMC]₀: [I]₀ × C_{TMC} %) + (144.13 × [_L-LA]₀: [I]₀ × C_{LA} %). ^e Measured by GPC calibrated with standard polystyrene samples. ^f Determined from DSC. All T_g values were obtained from the second heating scan; the heating rate and the cooling rate were 5 °C/min.

General procedure for synthesizing PLA and PTMC in control experiments:

A Schlenk flask was charged with *L*-LA (1.5 mmol), complex **2** (0.0070 mg, 0.0075 mmol) and THF (1.5 mL). After 1 h reaction at room temperature, ethanol (20 mL) was added to precipitate the polymer. The polymer precipitated was collected, and dried (0.2096 mg, 97%).

PTMC was prepared from the reaction of TMC (1.5 mmol) and complex **2** (0.0014 mg, 0.0015 mmol) at room temperature in THF (1.5 mL). After 10 min reaction, the polymerization was quenched with EtOH (20 mL). The polymer precipitated was collected, and dried (0.1527 mg, 99%).

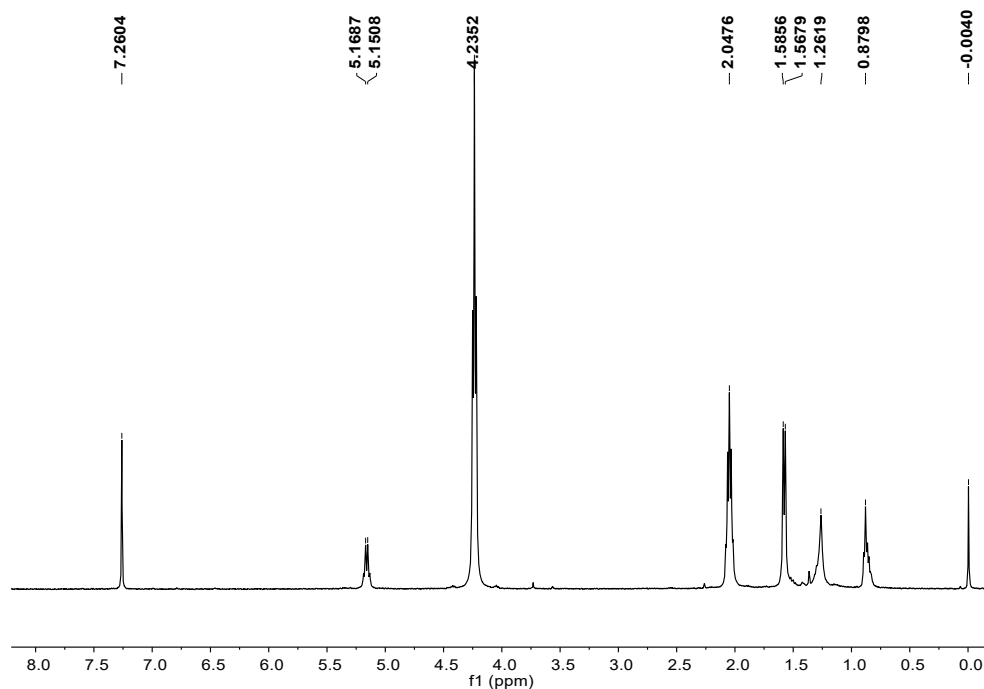


Figure S7. ^1H NMR spectrum of the mixture of PLA and PTMC (400 MHz, CDCl_3)
(result of the control reaction of PLA and TMC initiated by complex **2**)

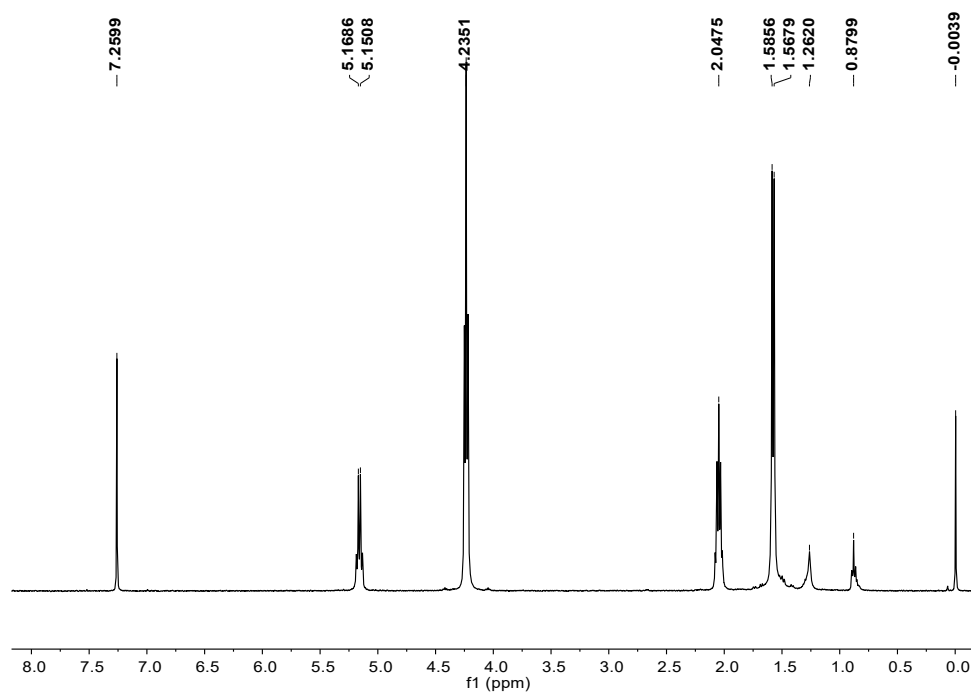


Figure S8. ^1H NMR spectrum of the mixture of PLA and PTMC (400 MHz, CDCl_3)
(result of the control reaction of PTMC and L-LA initiated by complex **2**)

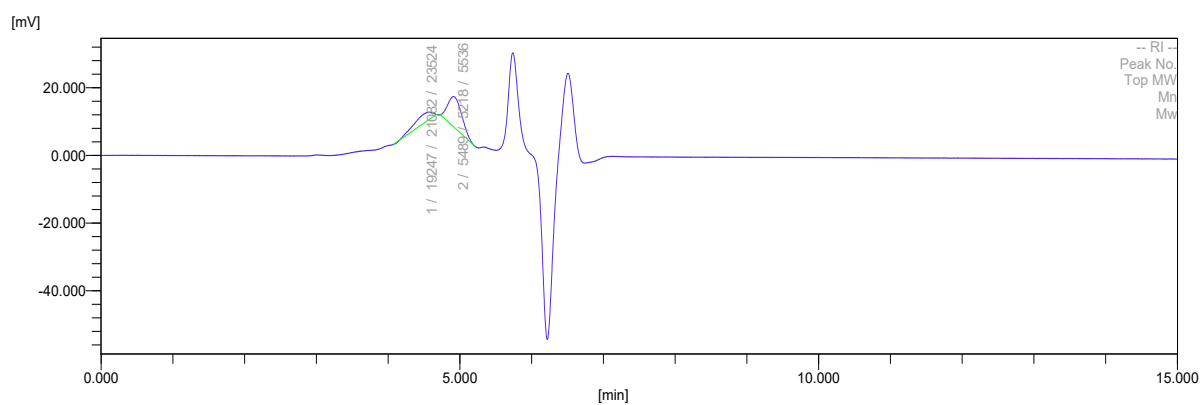


Figure. S9. GPC traces of the resulting mixture obtained by complex **2**
(result of the control reaction of PLA and TMC initiated by complex **2**)

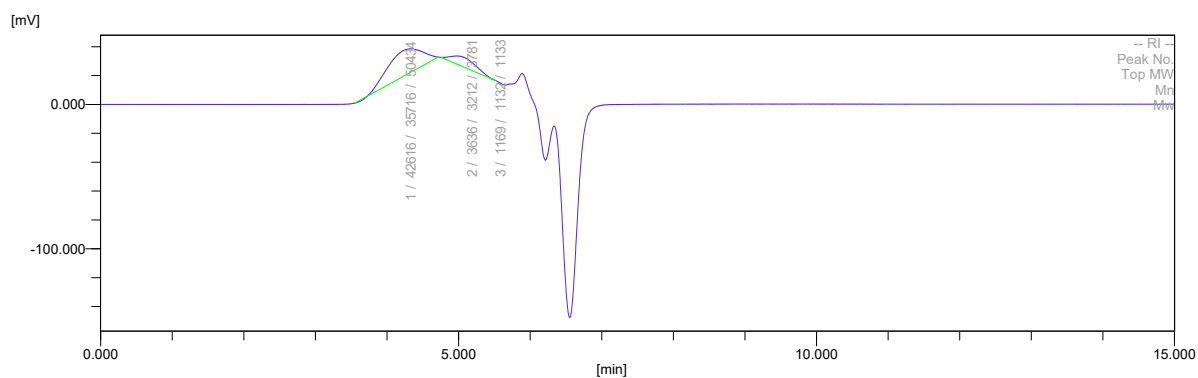


Figure S10. GPC traces of the resulting mixture obtained by complex **2** (result of the control reaction of PTMC and L -LA initiated by complex **2**)

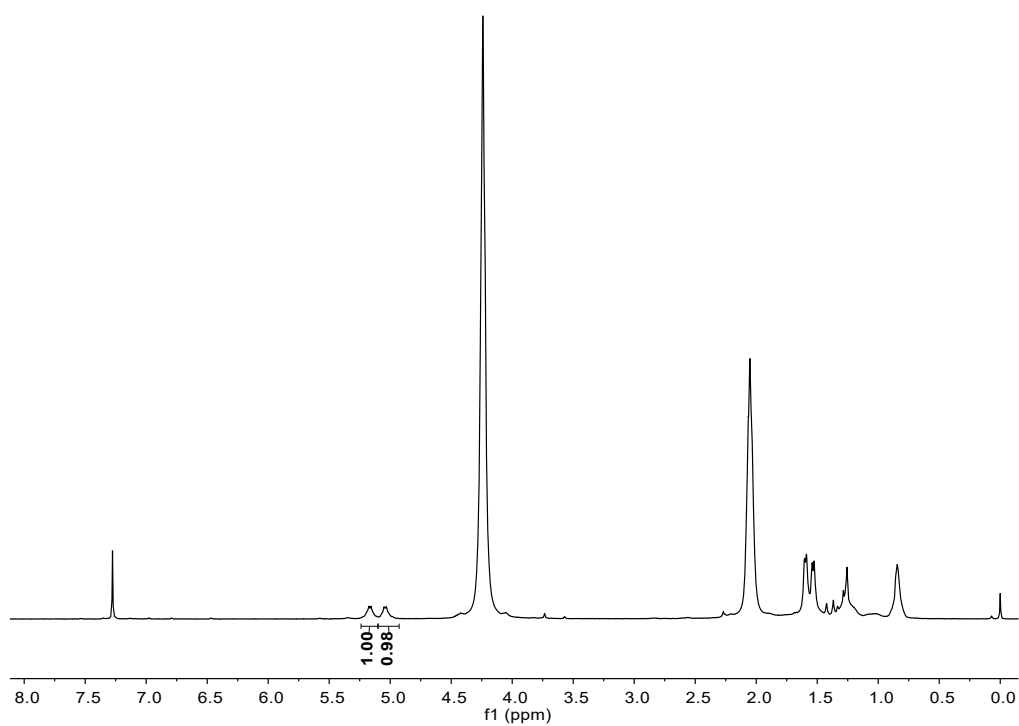


Figure S11. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 1 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

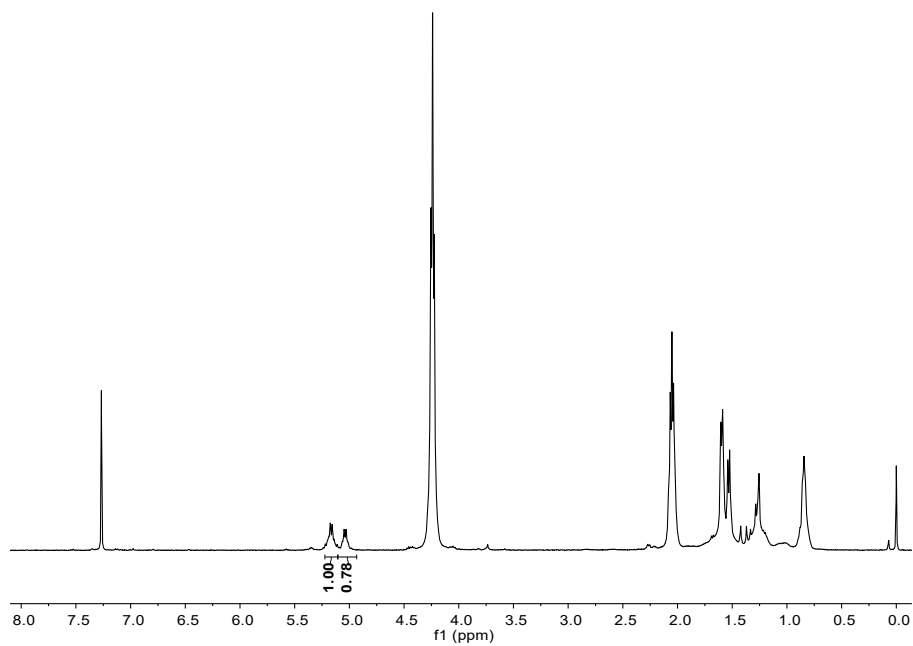


Figure S12. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 2 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

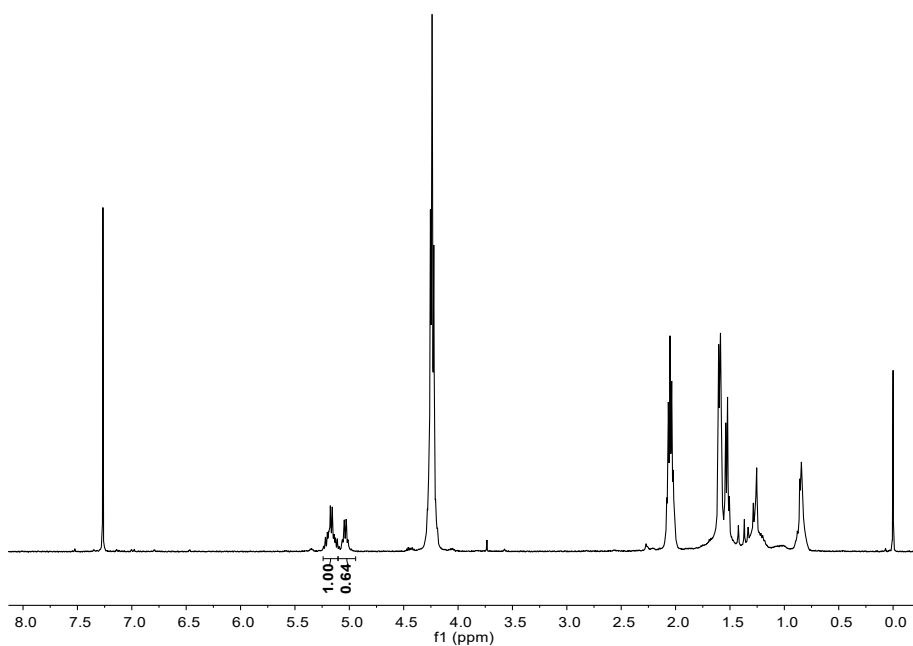


Figure S13. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 3 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

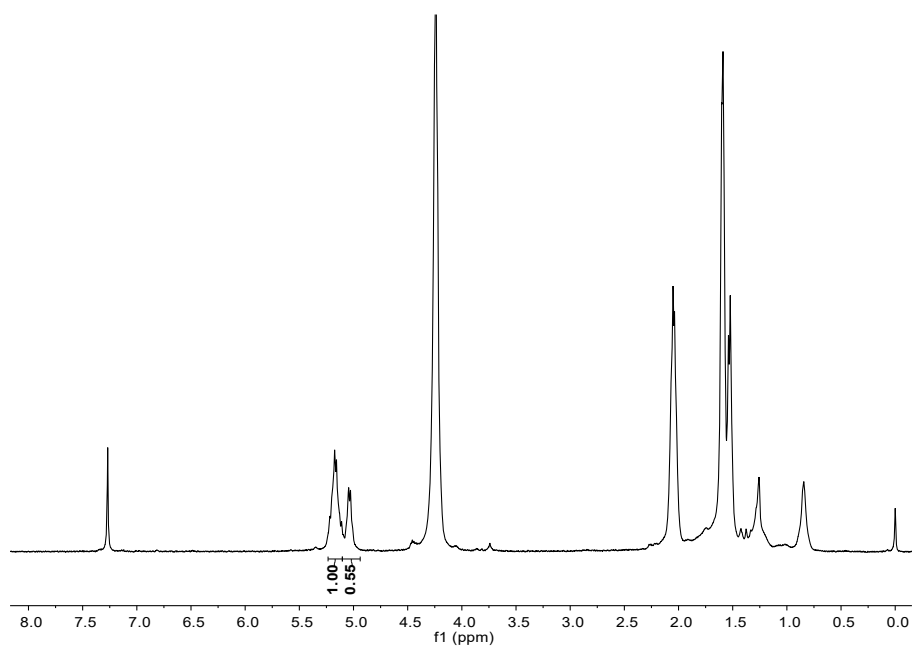


Figure S14. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 4 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

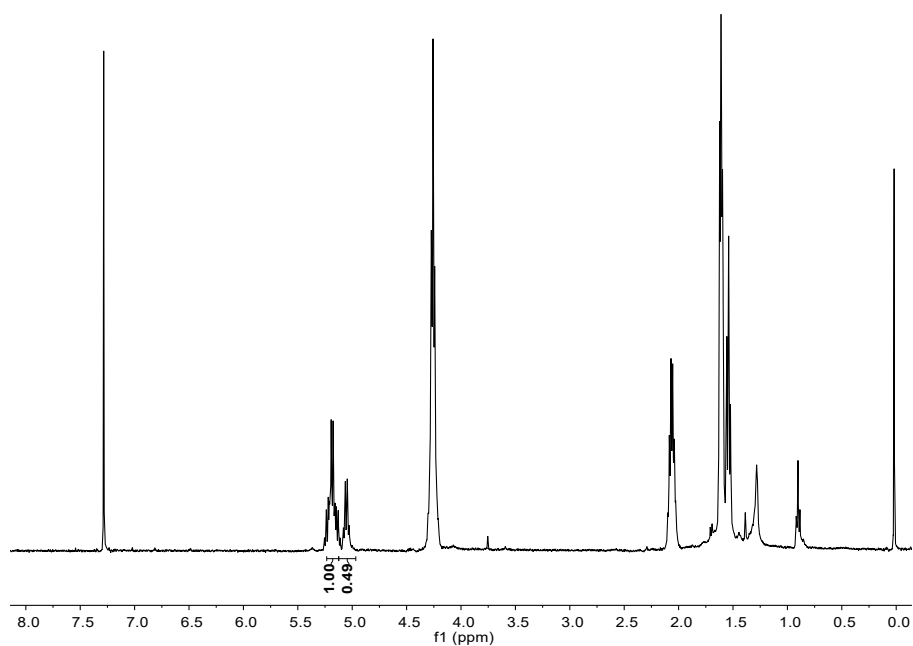


Figure S15. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 5 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

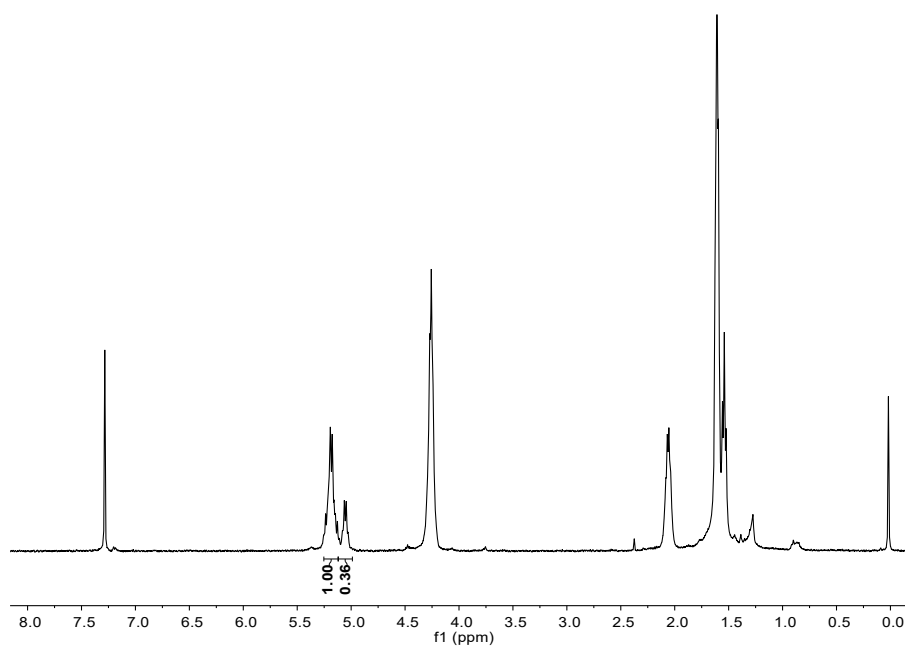


Figure S16. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 6 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

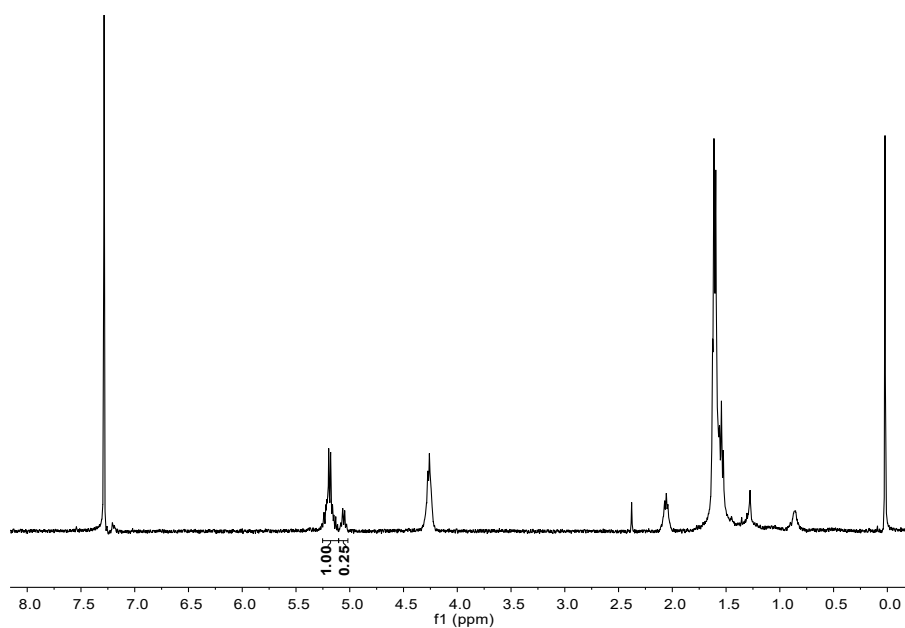


Figure S17. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 7 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

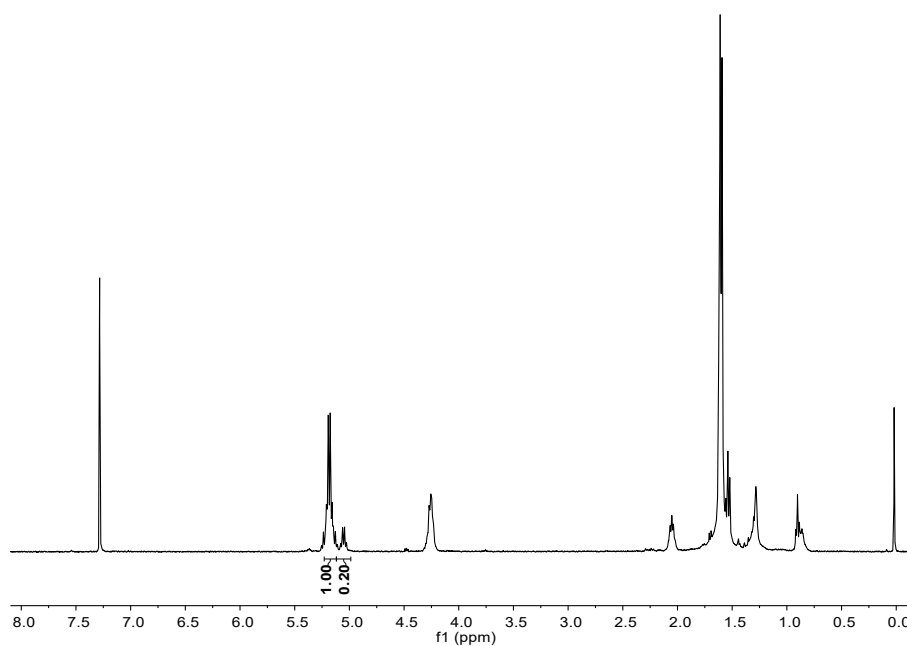


Figure S18. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 8 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

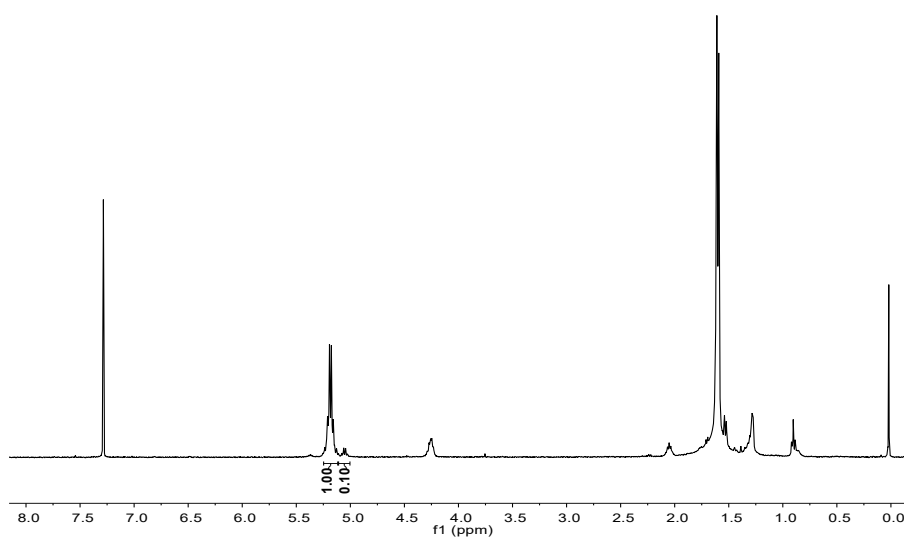


Figure S19. ^1H NMR spectrum of copolymer of L -LA and TMC. Conditions: Entry 9 in Table S5 (400 MHz, CDCl_3 , 25 $^\circ\text{C}$).

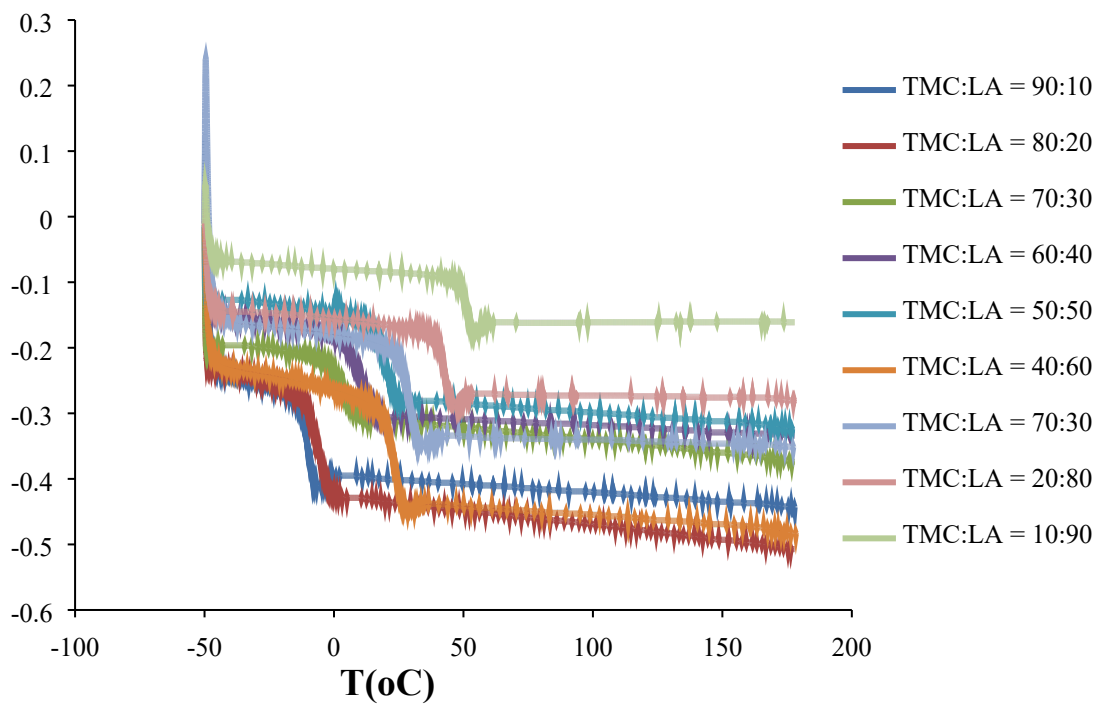


Figure S20. DSC curves of the TMC/L_L-LA copolymers listed in Table S5.

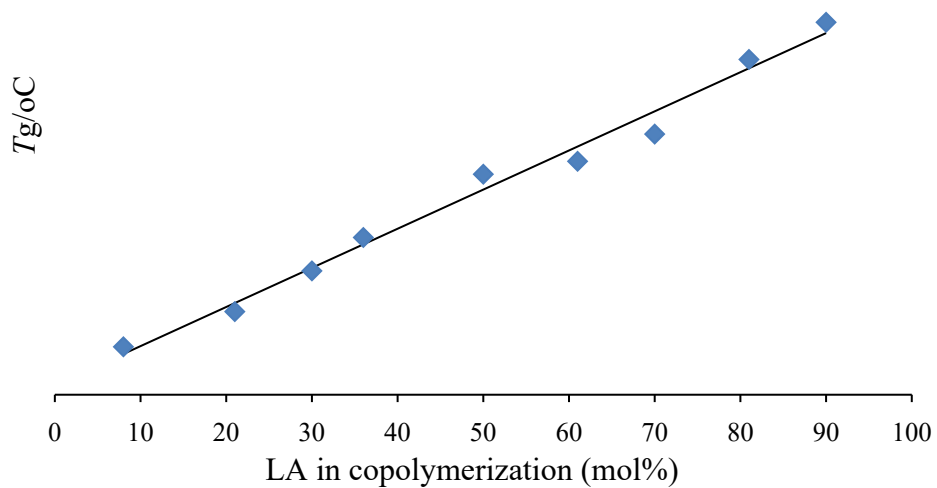


Figure 21. Plots of the dependence of T_g of the TMC/LA copolymers as a function of the molar percentage of LA in copolymers.

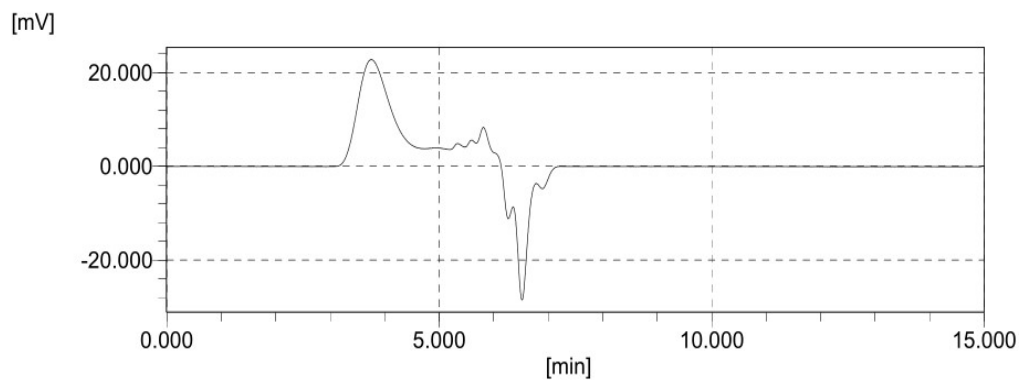


Figure S22. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 1 in Table S5.

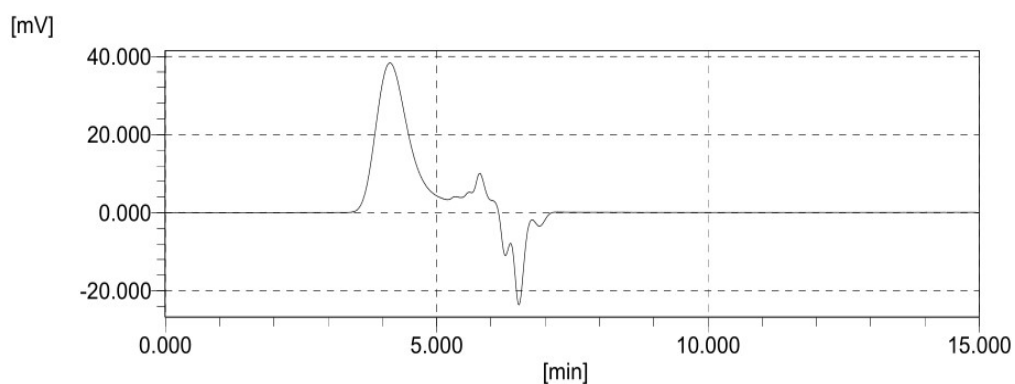


Figure S23. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 2 in Table S5.

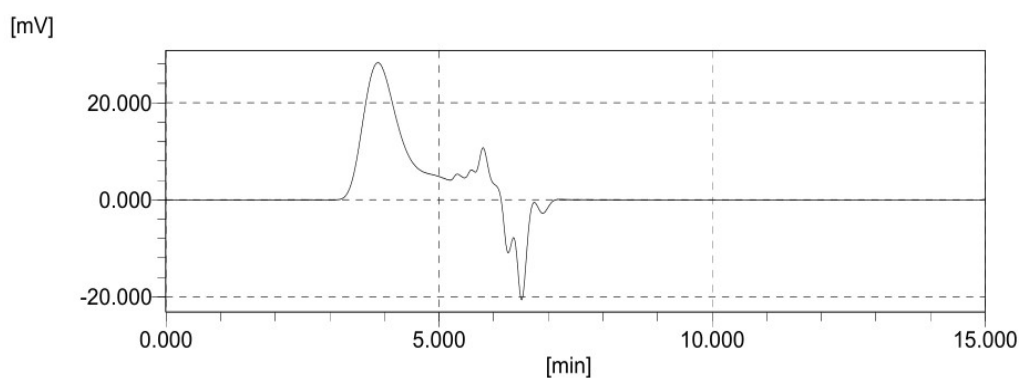


Figure S24. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 3 in Table S5.

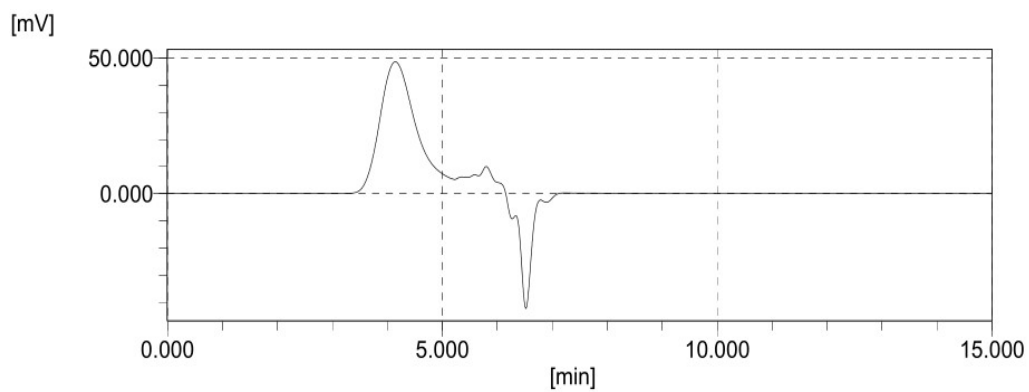


Figure S25. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 4 in Table S5.

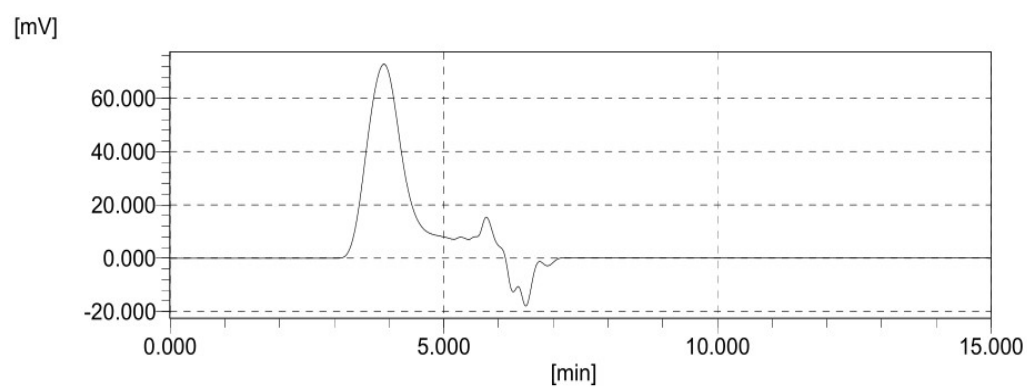


Figure S26. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 5 in Table S5.

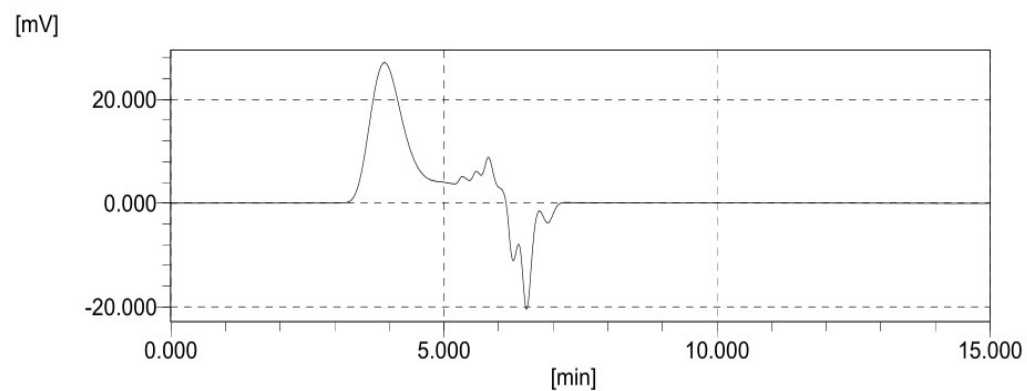


Figure S27. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 6 in Table S5.

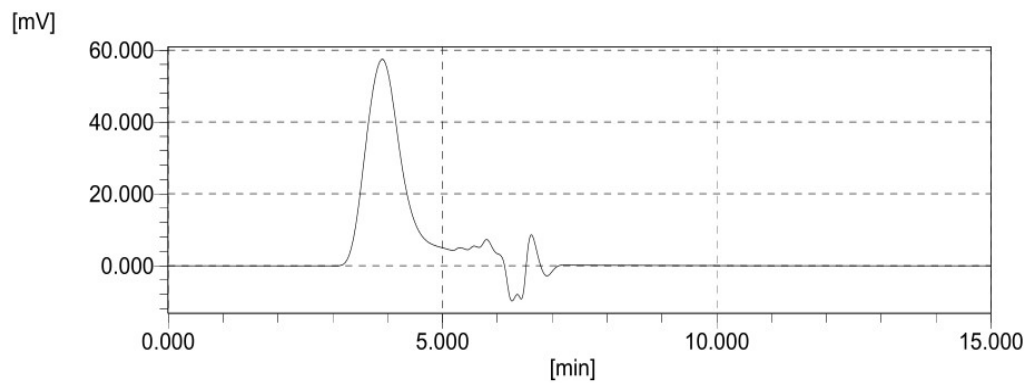


Figure S28. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 7 in Table S5.

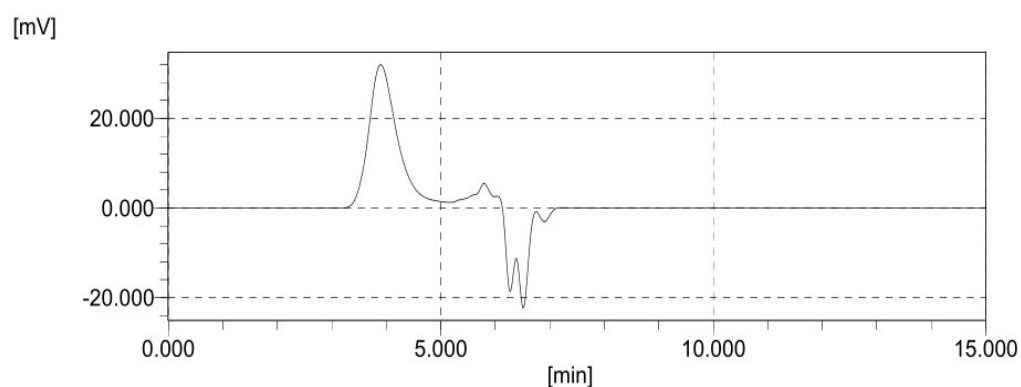


Figure S29. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 8 in Table S5.

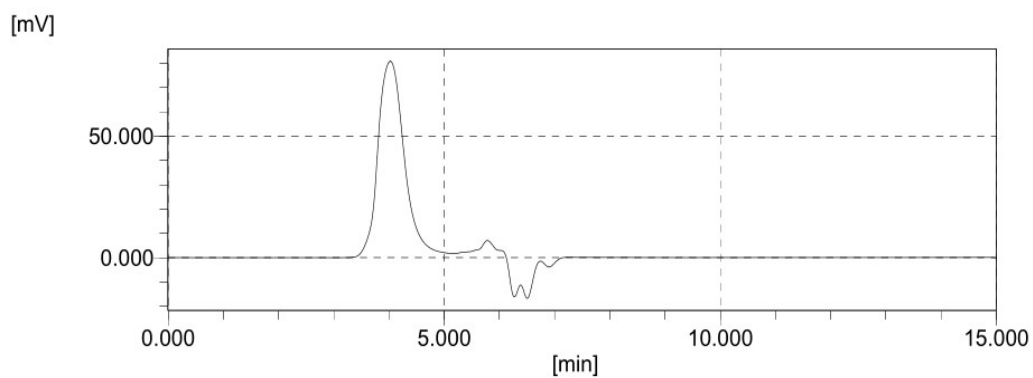


Figure S30. GPC trace of copolymer obtained by complex **2**. Conditions: Entry 9 in Table S5.

8. References

1. J. M. Switzer, P. D. Pletcher, D. K. Steelman, J. Kim, G. A. Medvedev, M. M. Abu-Omar, J. M. Caruthers and W. N. Delgass, *ACS Catal.*, 2018, **8**, 10407-10418.
2. K. Nie, L. Fang, Y. M. Yao, Y. Zhang, Q. Shen and Y. R. Wang, *Inorg. Chem.*, 2012, **51**, 11133-11143.
3. X. L. Liu, X. F. Hua and D. M. Cui, *Macromolecules*, 2018, **51**, 930-937.