Supporting Information for

Lanthanum complexes stabilized by a pentadentate schiff-base ligand: synthesis, characterization, and reactivity in statistical copolymerization of ε-caprolactone and L-lactide

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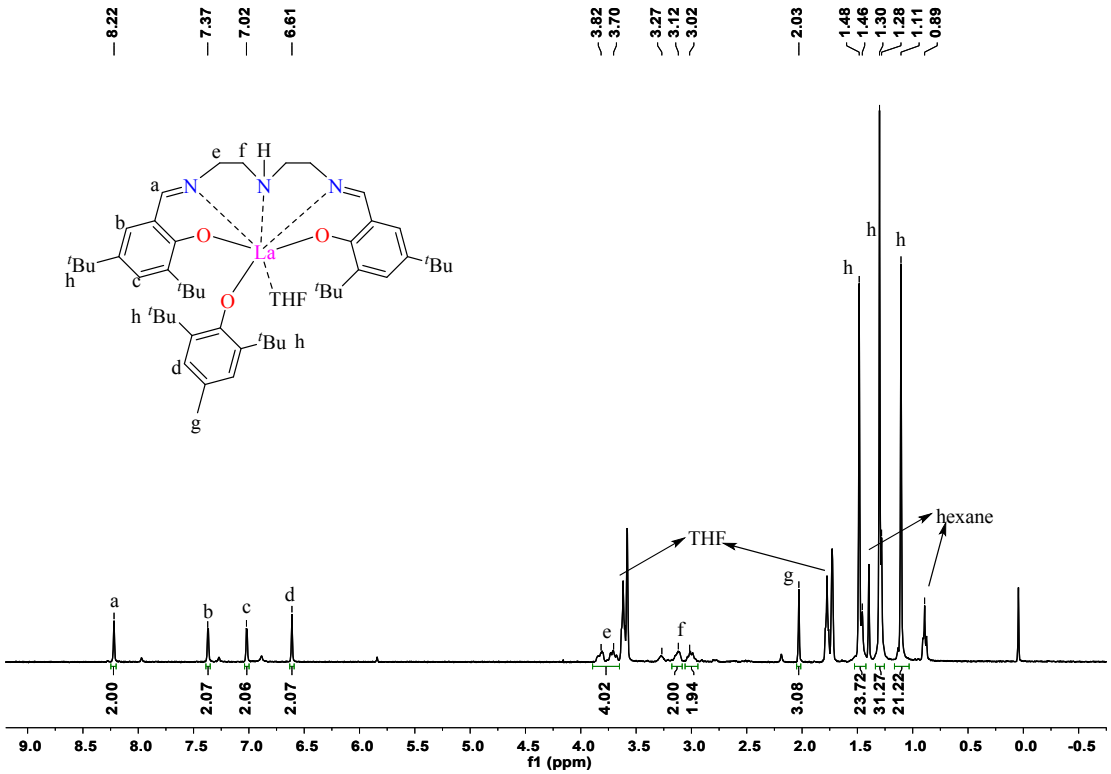

Fig. S**1** ^{1}H NMR spectrum of complex **1** in THF-d_8

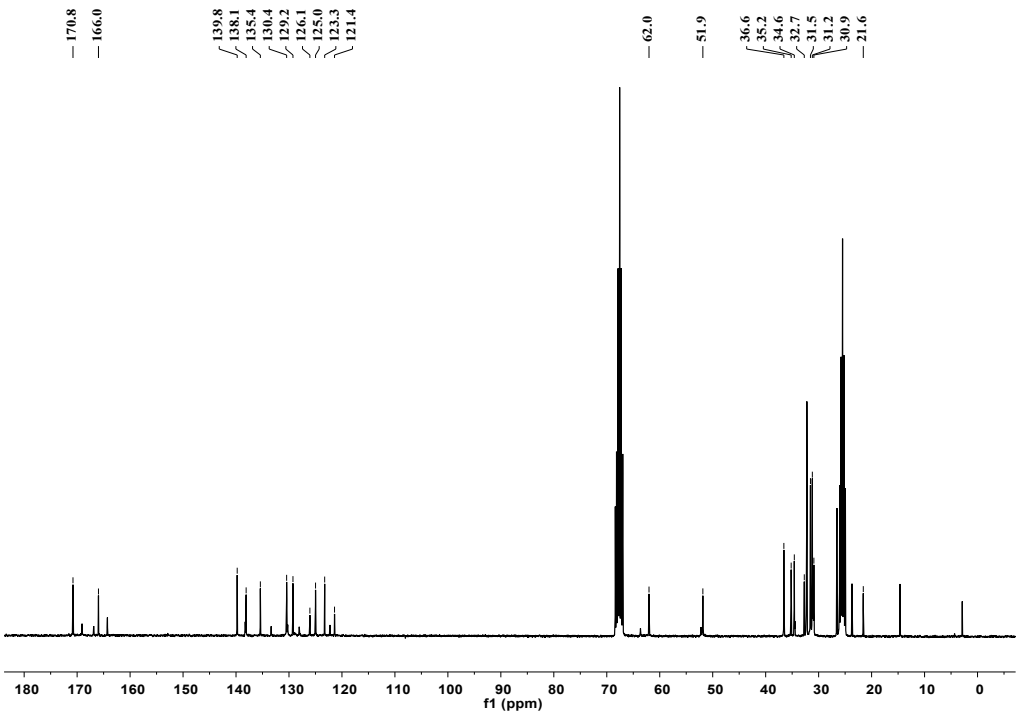

Fig. S**2**. ^{13}C NMR spectrum of complex **1** in THF-d_8

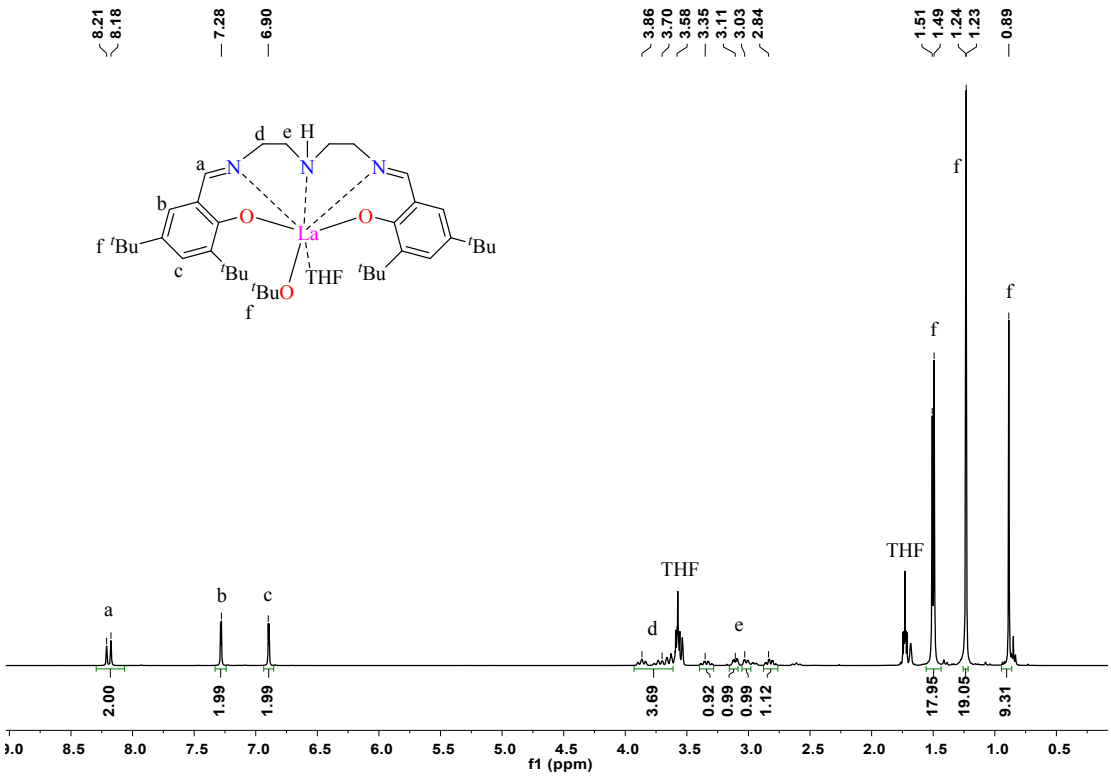

Fig. S**3**. ^{1}H NMR spectrum of complex **2** in THF-d_8

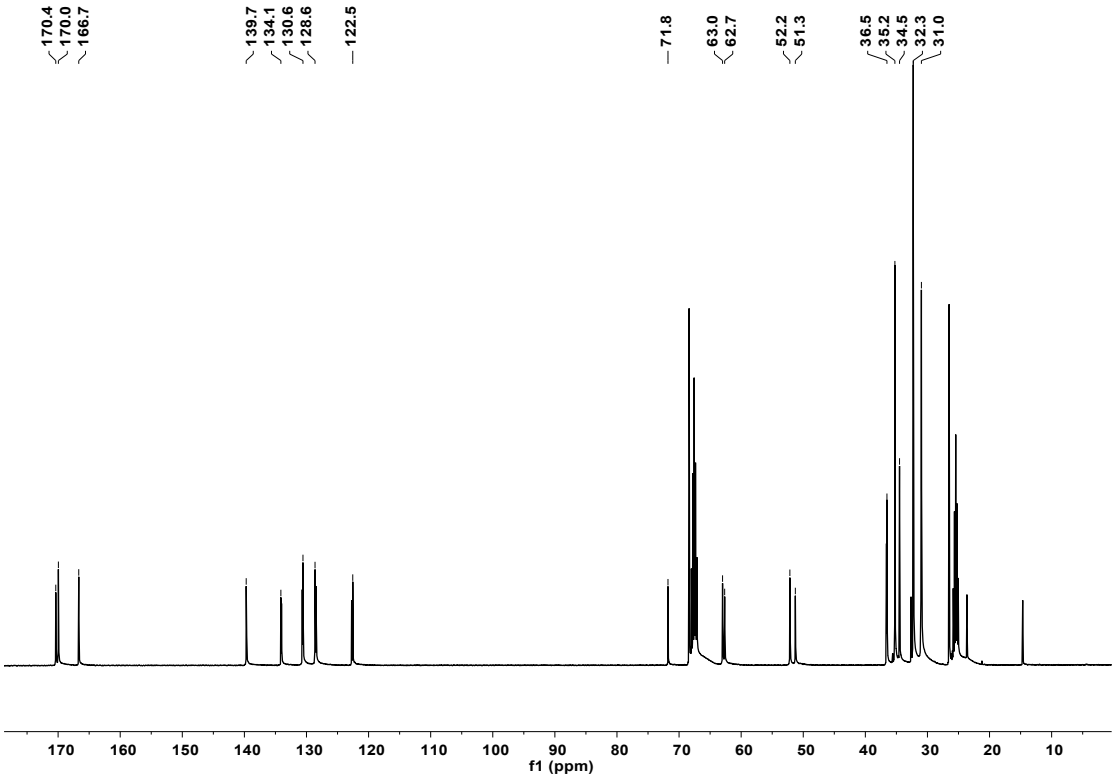

Fig. S**4**. ^{13}C NMR spectrum of complex **2** in THF-d_8

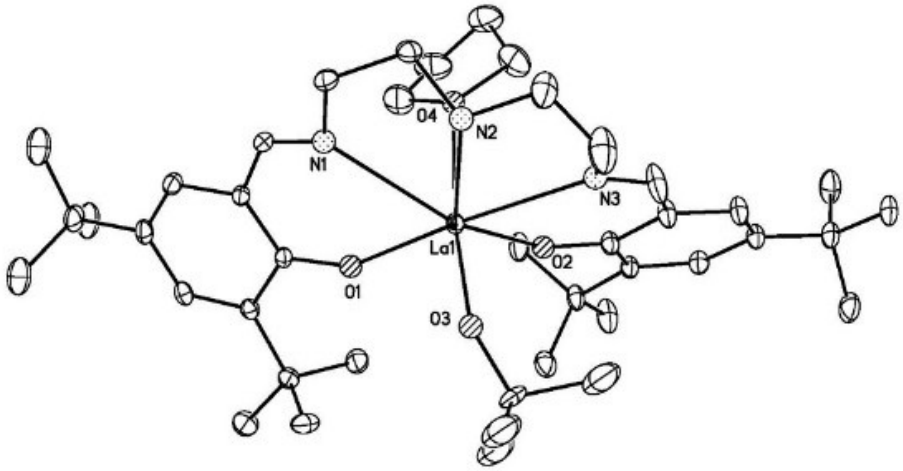

Fig. **S5.** The structure of complex **2**

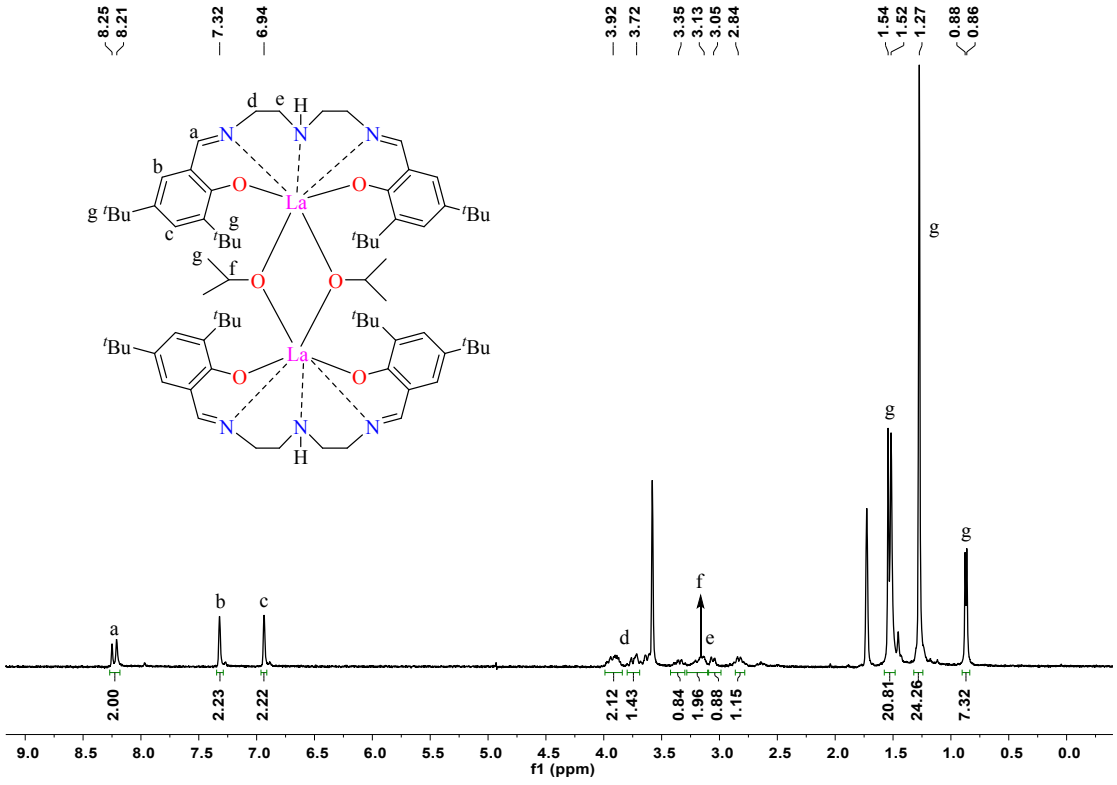

Fig. S**6**. ^{1}H NMR spectrum of complex **3** in THF-d_8

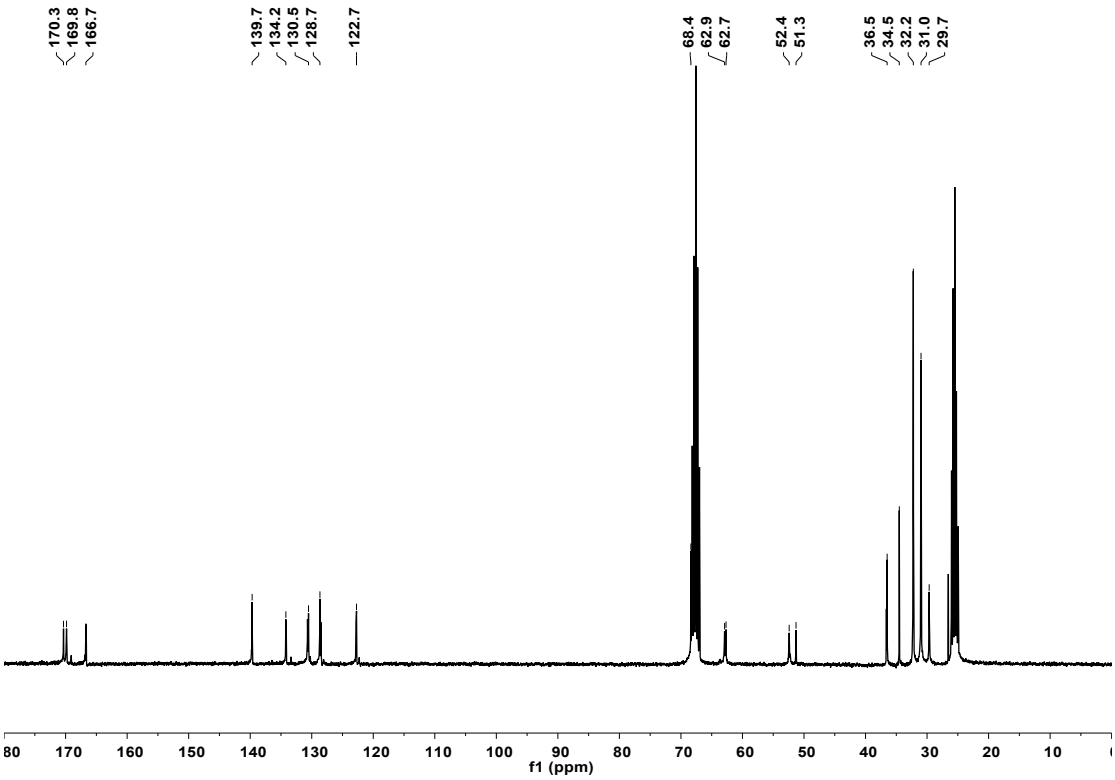

Fig. S**7**. ^{13}C NMR spectrum of complex **3** in THF-d_8

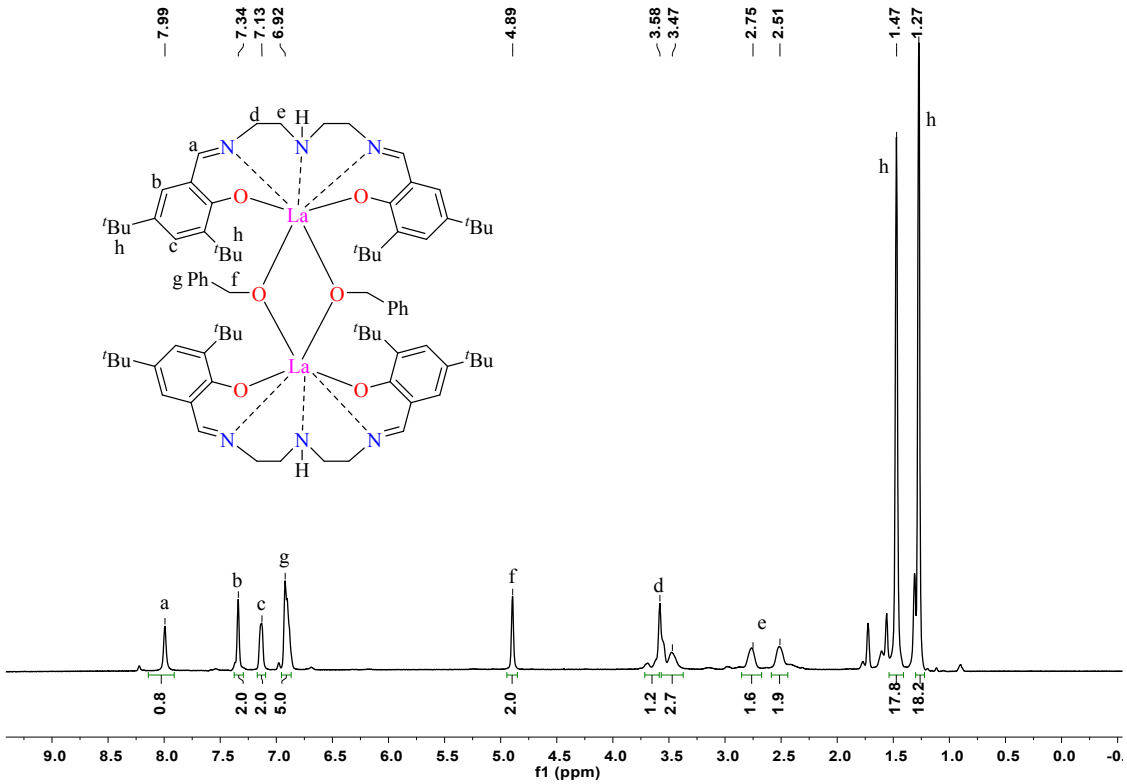

Fig. S**8**. ^{1}H NMR spectrum of complex **4** in THF-d_8

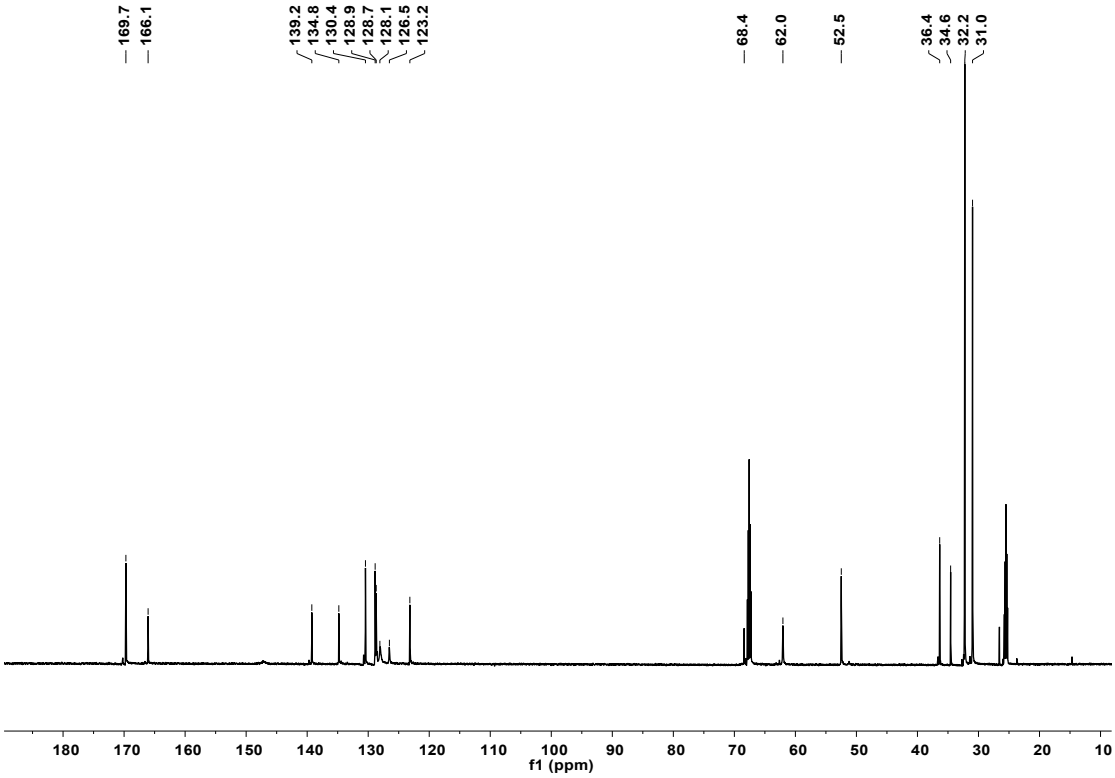

Fig.S**9**. ^{13}C NMR spectrum of complex **4** in THF-d_8

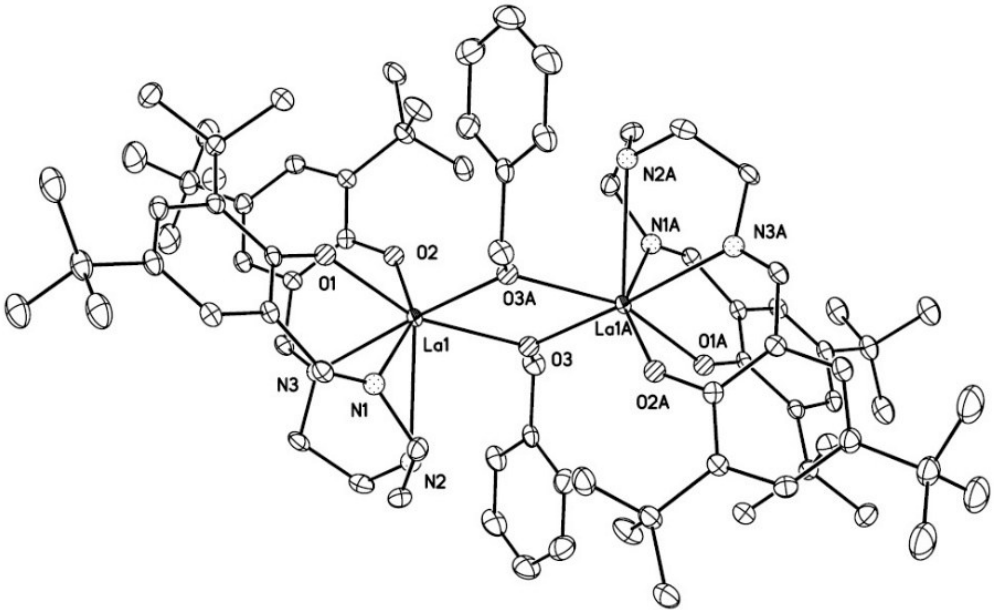

Fig. S**10.** The structure of complex **4**

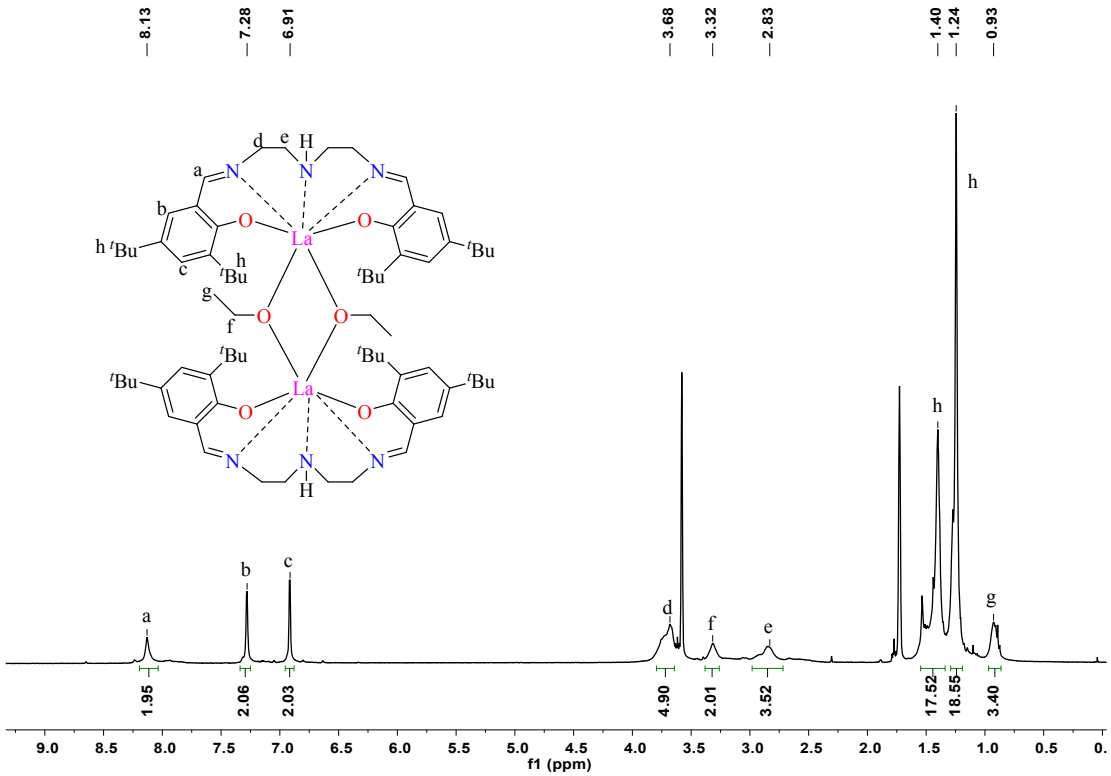

Fig. S**11**. ^{1}H NMR spectrum of complex **5** in THF-d_8

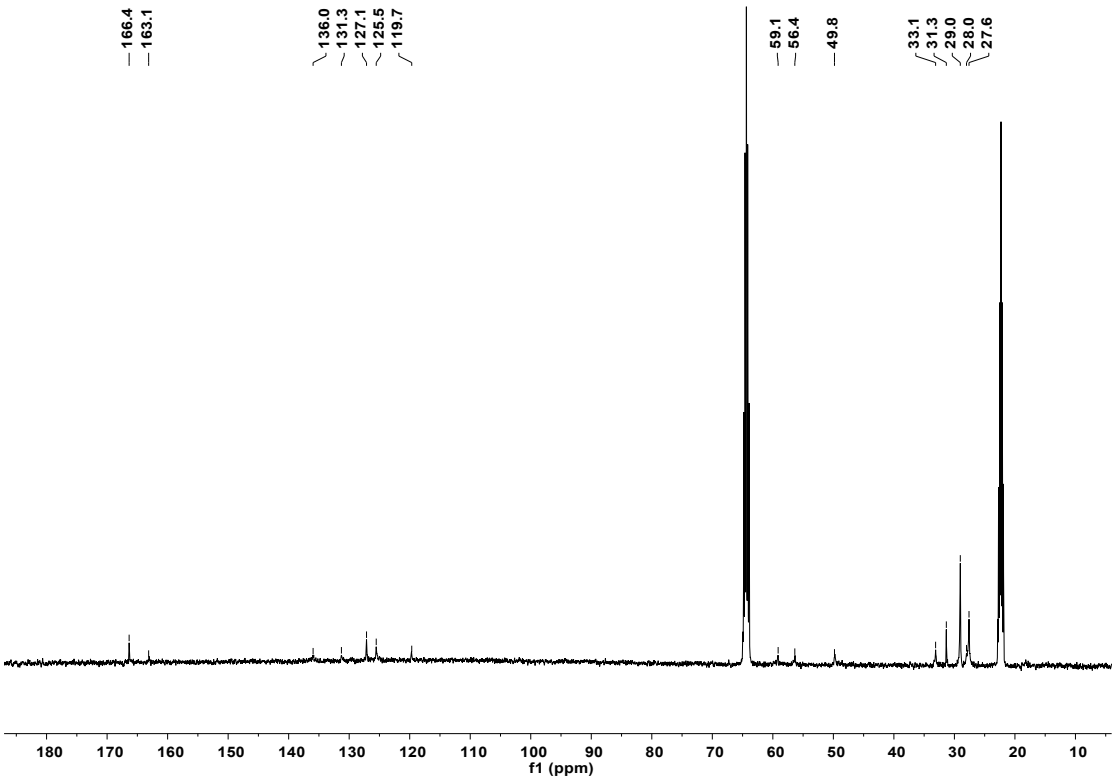

Fig. S**12**. ^{13}C NMR spectrum of complex **5** in THF-d_8

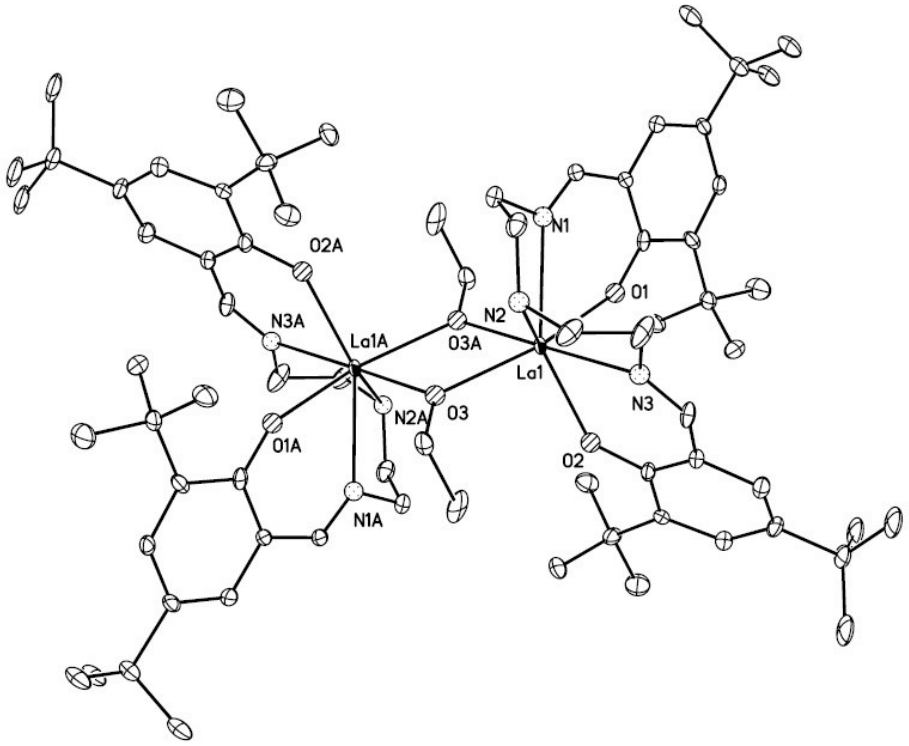

Fig. S**13.** The structure of complex **5**

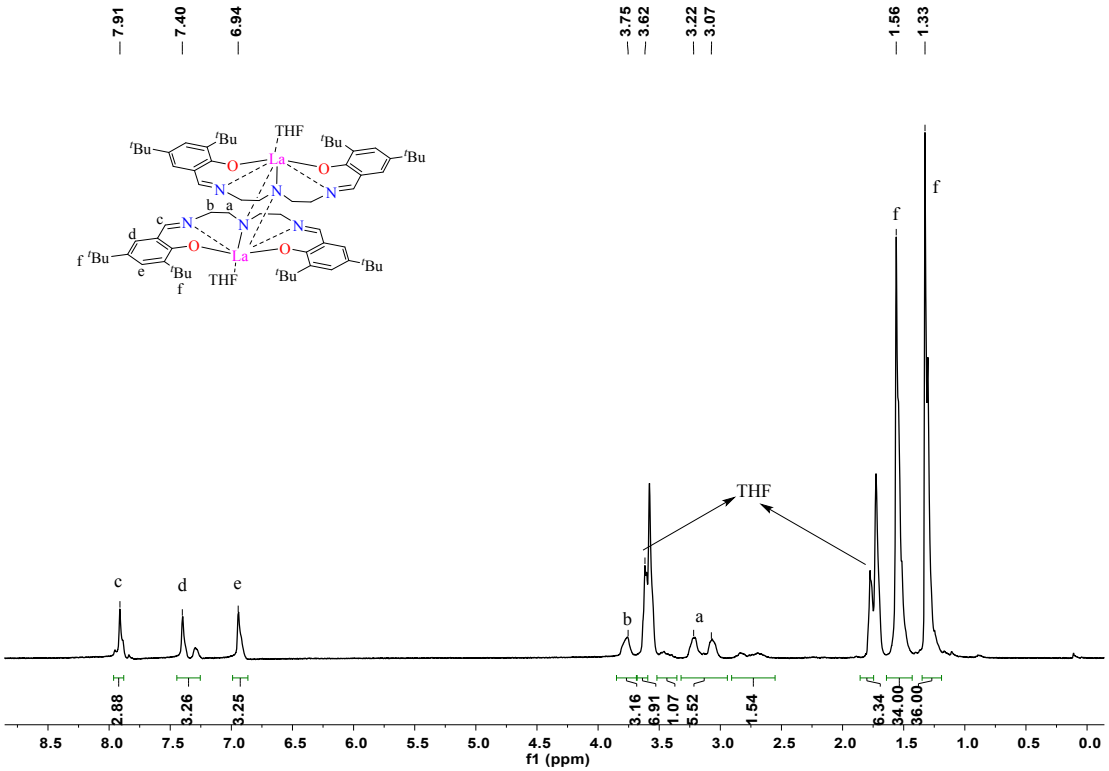

Fig. S**14**. ^{1}H NMR spectrum of complex **6** in THF-d_8

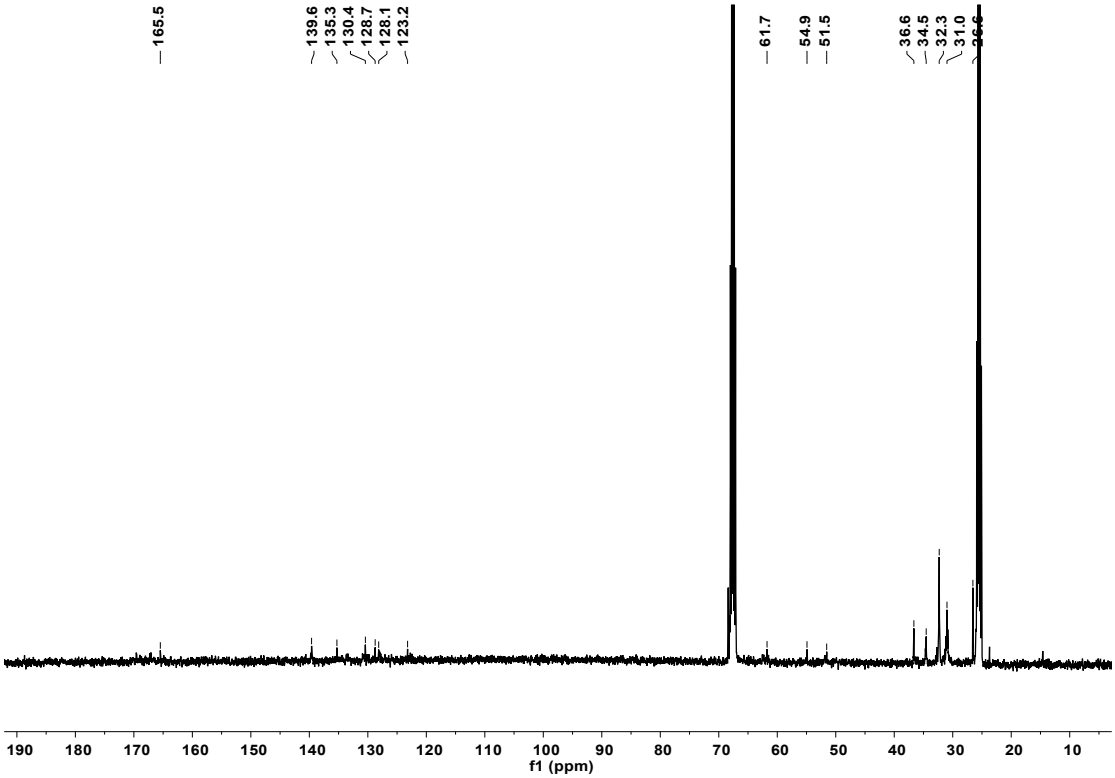

Fig. S**15**. ^{13}C NMR spectrum of complex **6** in THF-d_8

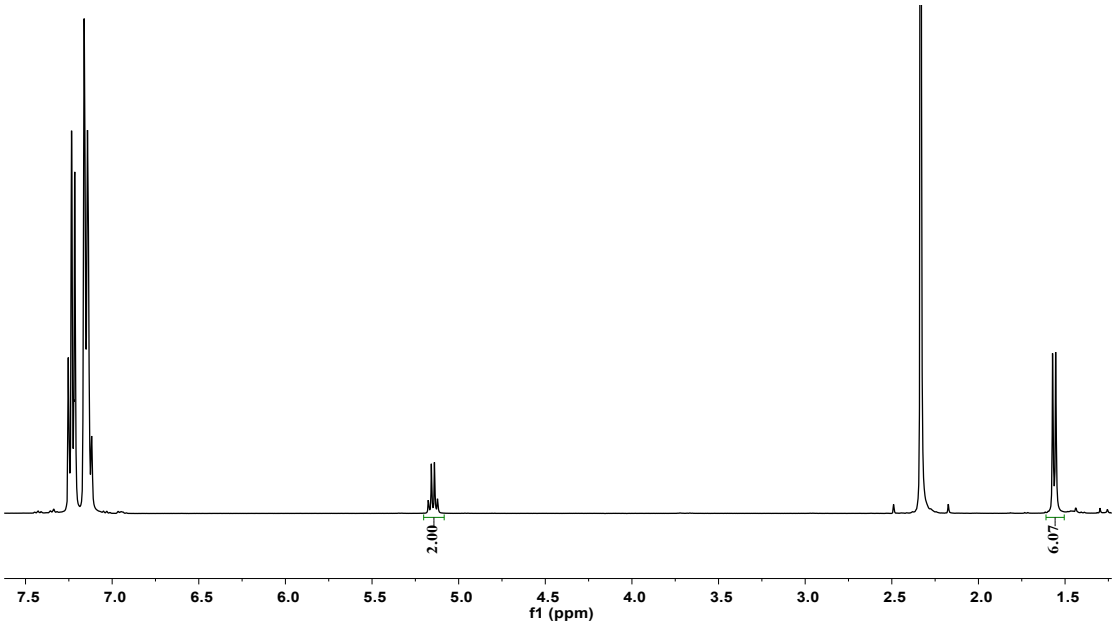

Fig. S**16**. ^{1}H NMR spectrum of homopolymer of L-LA: Entry **4** in Table **1**.

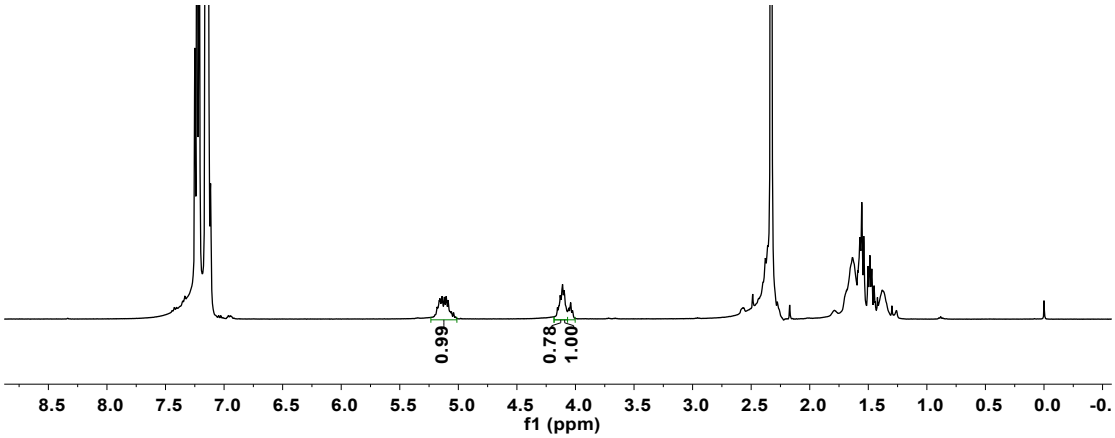

Fig. S**17**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL: Entry **2** in Table **2**

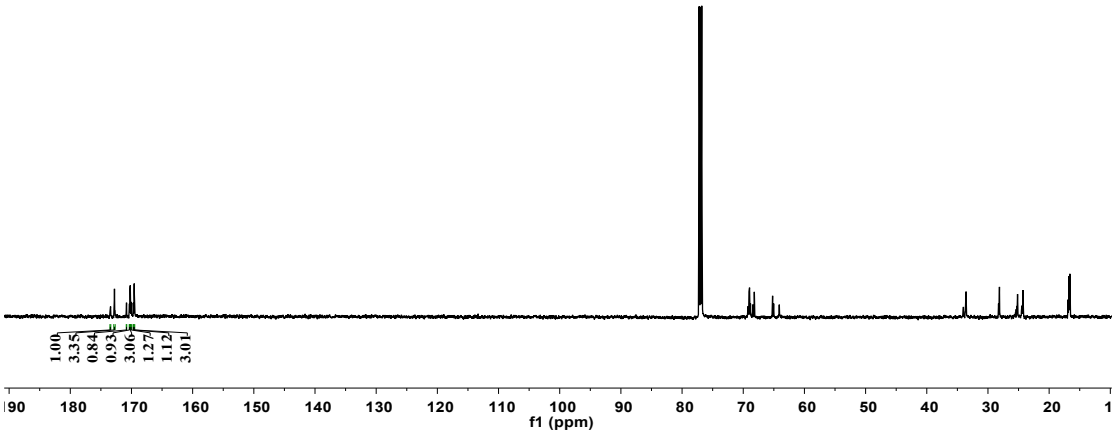

Fig. S**18**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **2** in Table **2**

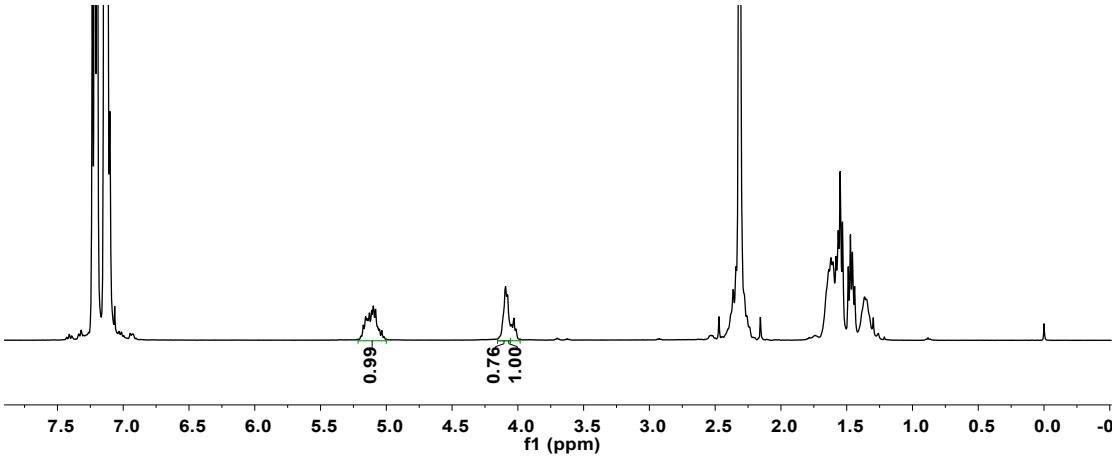

Fig. S**19**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL: Entry **4** in Table **2**

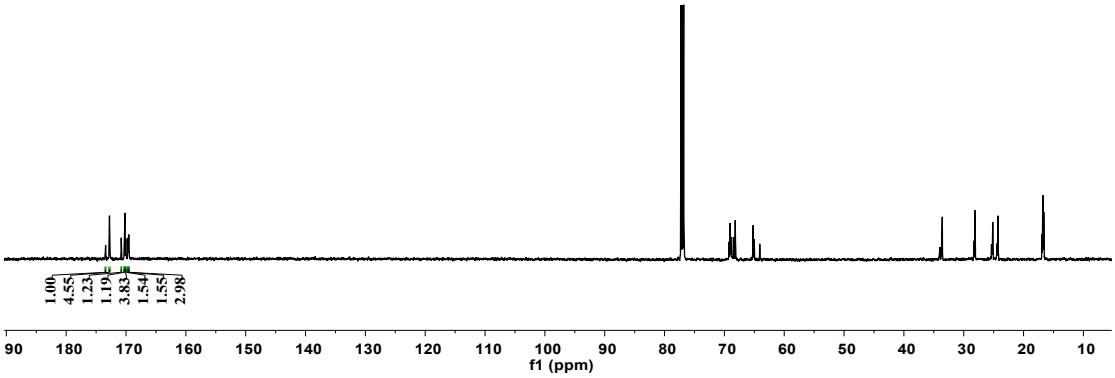

Fig. S**20**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **4** in Table **2**

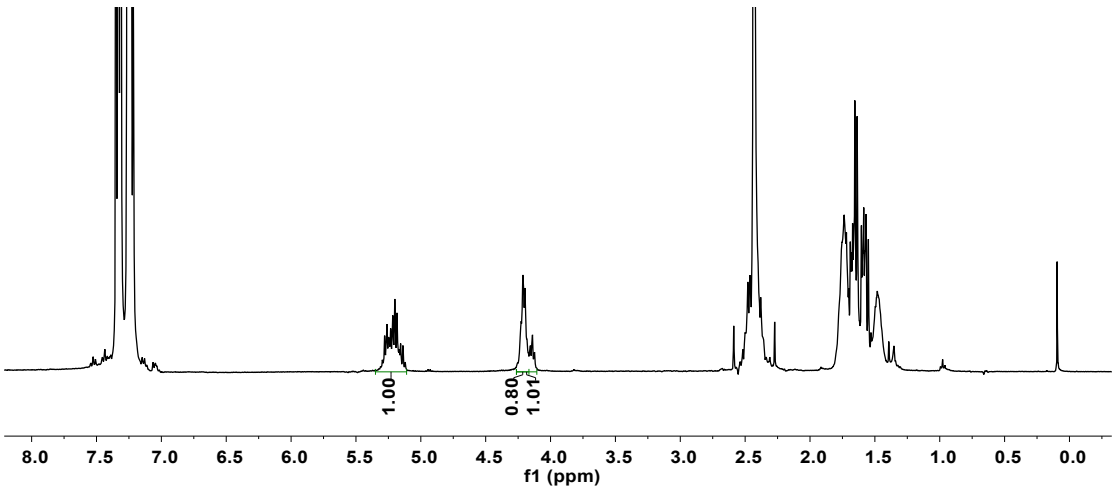

Fig. S**21**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL: Entry **5** in Table **2**

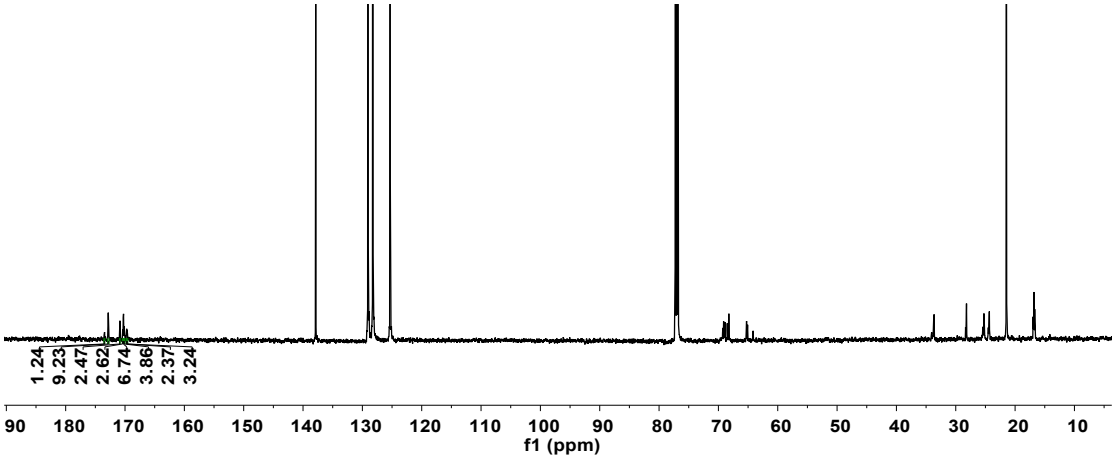

Fig. S**22**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **5** in Table **2**

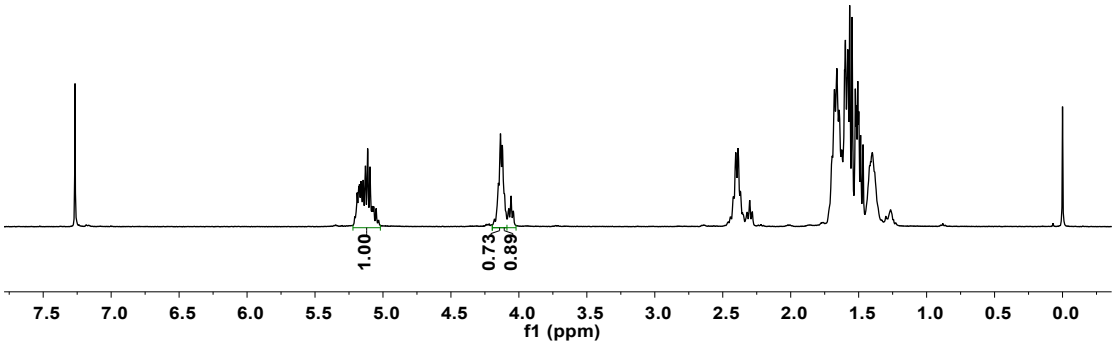

Fig. S**23**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL: Entry **6** in Table **2**

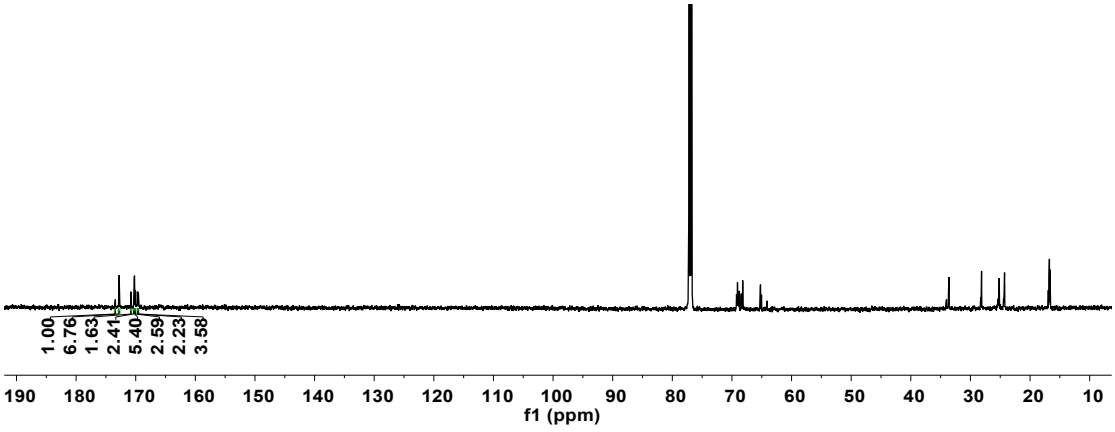

Fig. S**24**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **6** in Table **2**

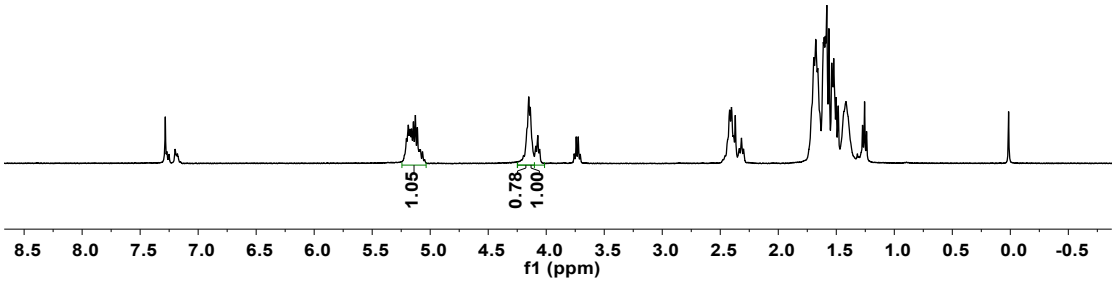

Fig. S**25**. [1]H NMR spectrum of copolymer of L-LA and ε-CL: Entry **7** in Table **2**

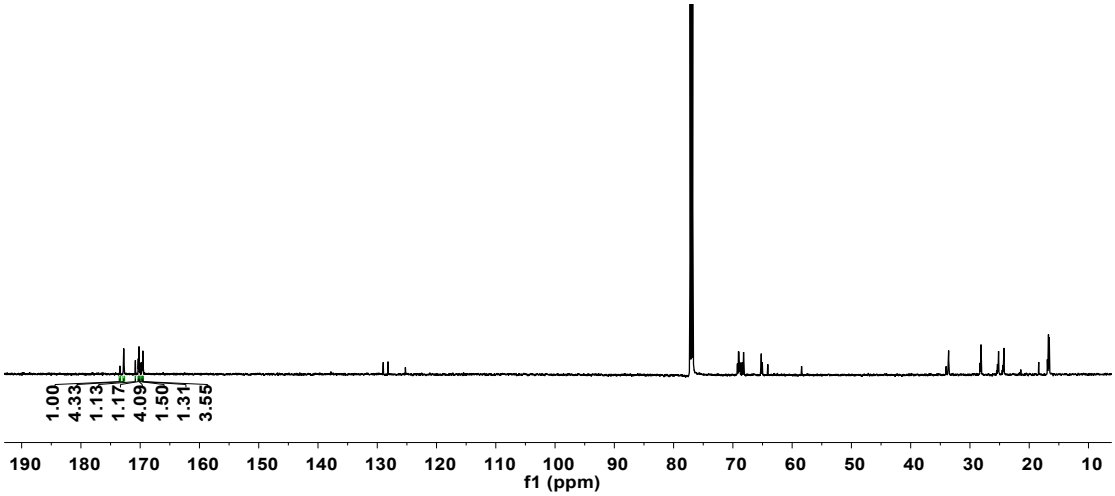

Fig. S**26**. [13]C NMR spectrum of copolymer of L-LA and ε-CL: Entry **7** in Table **2**

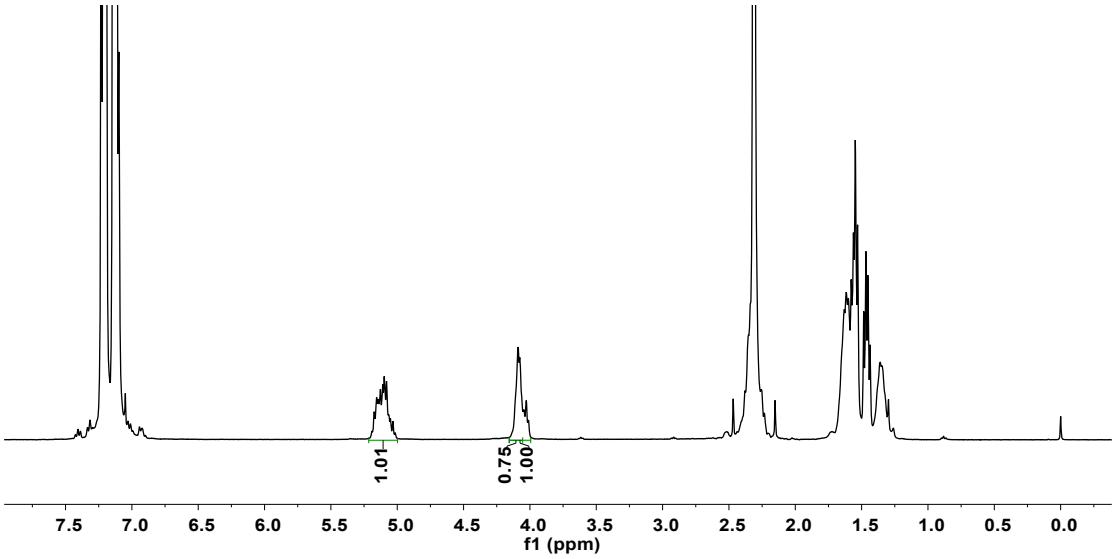

Fig. S**27**. [1]H NMR spectrum of copolymer of L-LA and ε-CL: Entry **9** in Table **2**

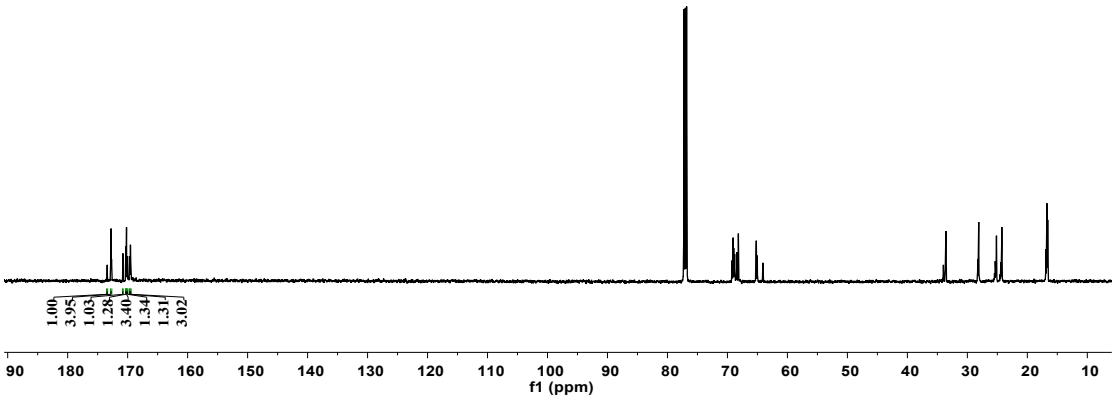

Fig. S**28**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **9** in Table **2**

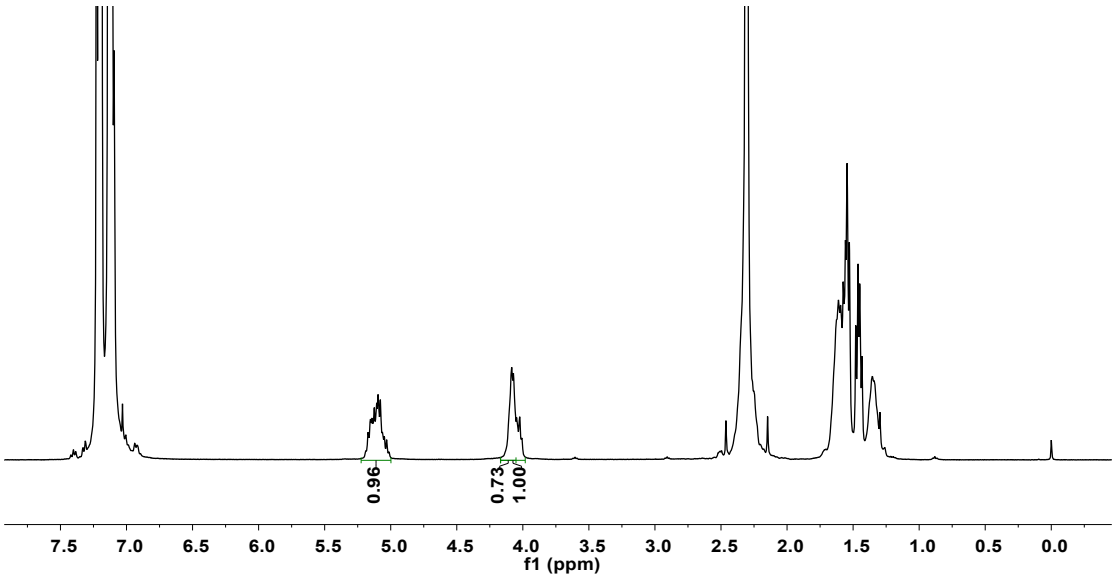

Fig. S**29**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL: Entry **11** in Table **2**

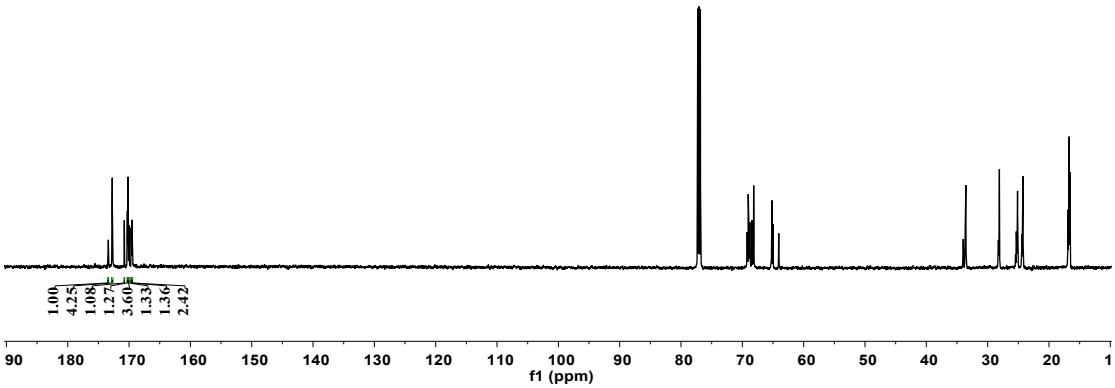

Fig. S**30**. ^{13}C NMR spectrum of copolymer of L-LA and ε-CL: Entry **11** in Table **2**

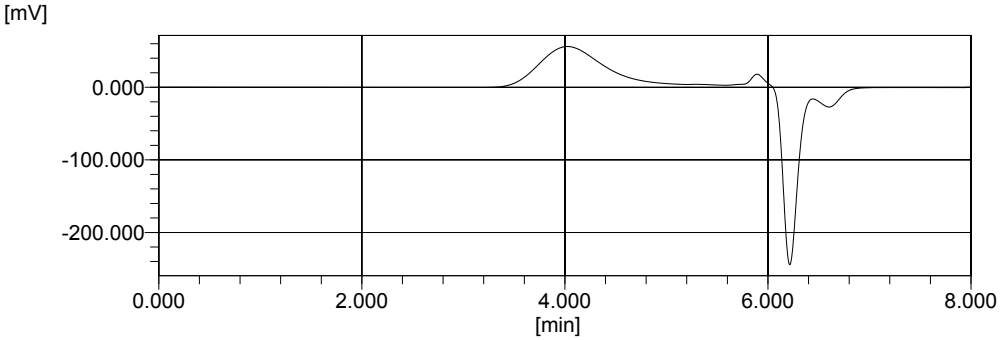

Fig. S**31**. GPC trace of resulting copolymer obtained by complex **3**: Entry **1** in Table **2**

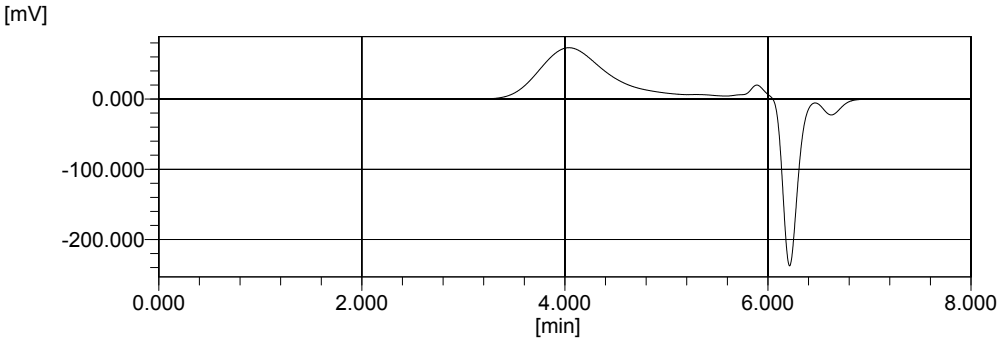

Fig. S**32**. GPC trace of resulting copolymer obtained by complex **3**: Entry **2** in Table **2**

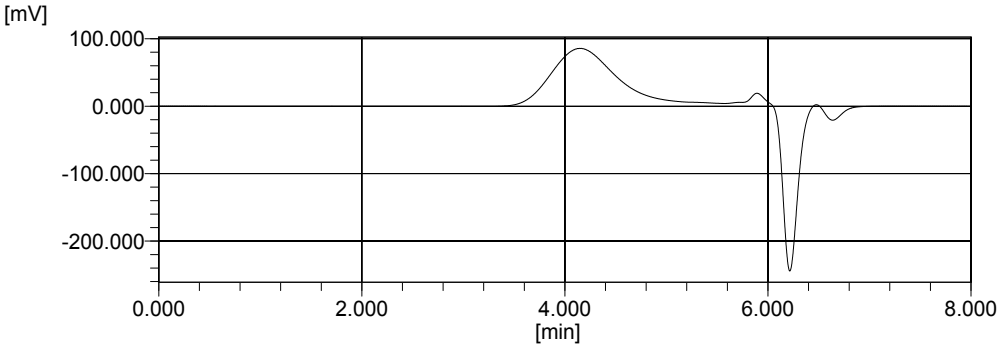

Fig. S**33**. GPC trace of resulting copolymer obtained by complex **3**: Entry **3** in Table **2**

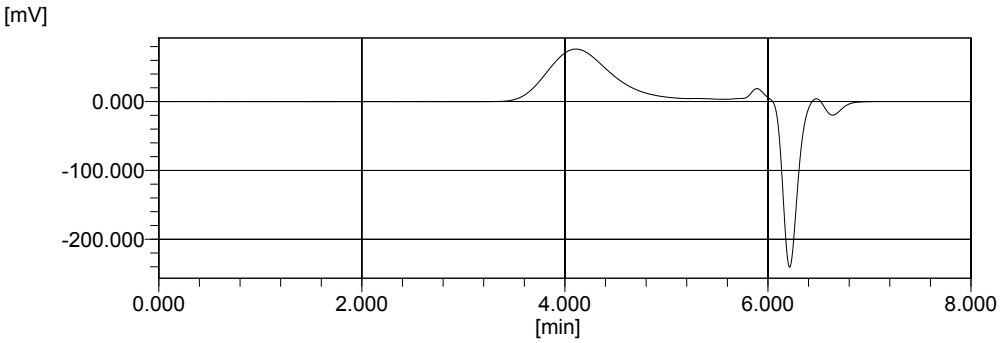

Fig. S**34**. GPC trace of resulting copolymer obtained by complex **3**: Entry **4** in Table **2**

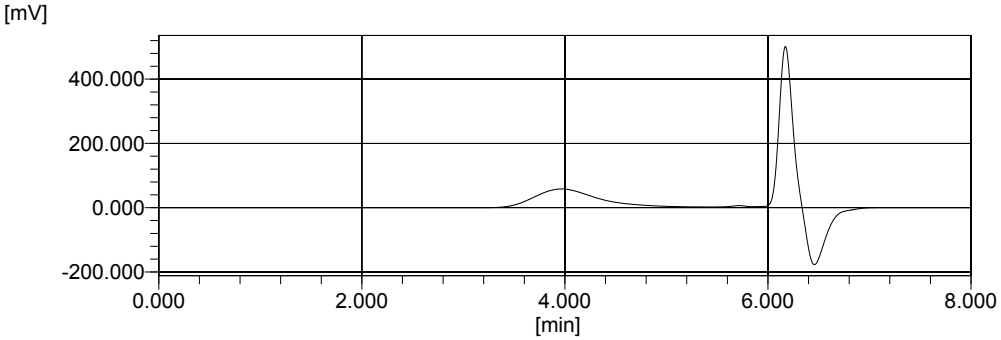

Fig. S**35**. GPC trace of resulting copolymer obtained by complex **3**: Entry **5** in Table **2**

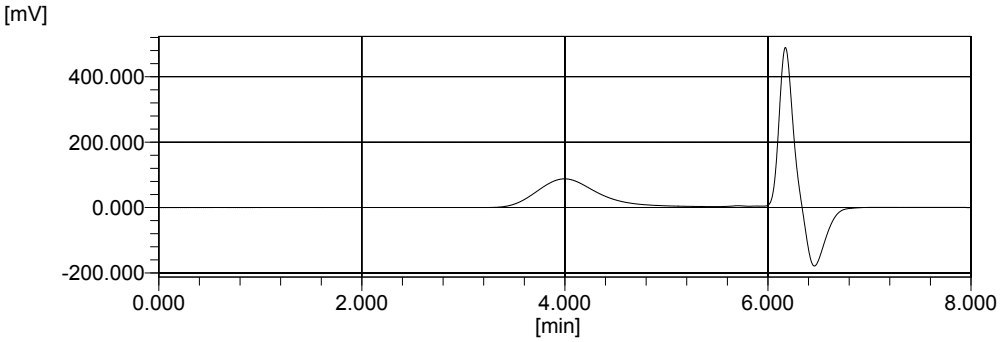

Fig. S**36**. GPC trace of resulting copolymer obtained by complex **3**: Entry **6** in Table **2**

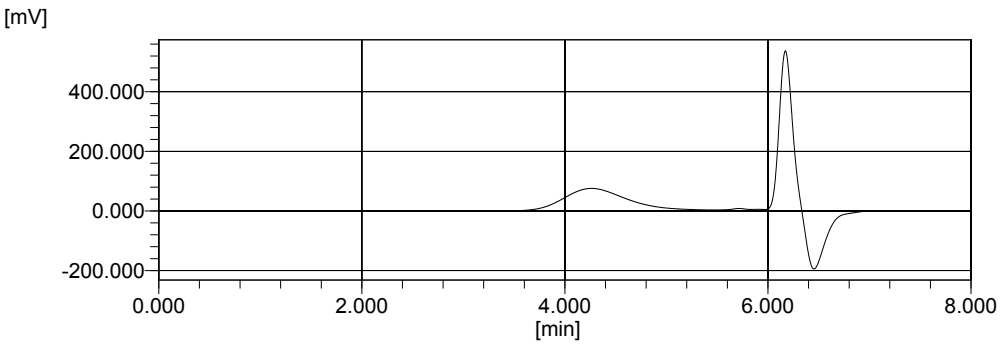

Fig. S**37**. GPC trace of resulting copolymer obtained by complex **3**: Entry **7** in Table **2**

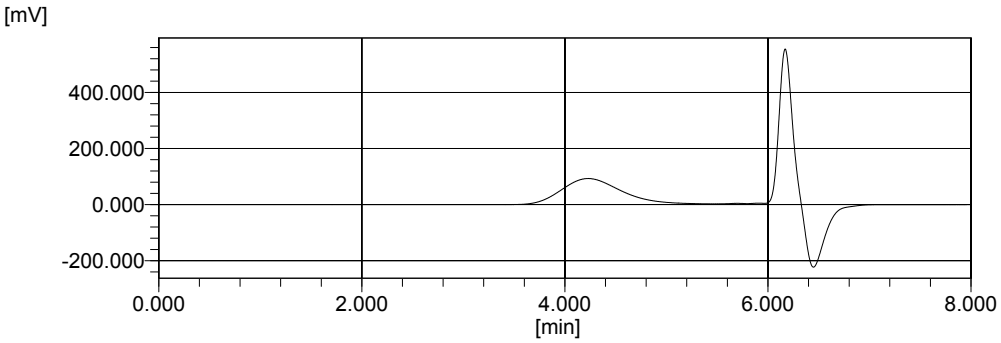

Fig. S**38**. GPC trace of resulting copolymer obtained by complex **3**: Entry **8** in Table **2**

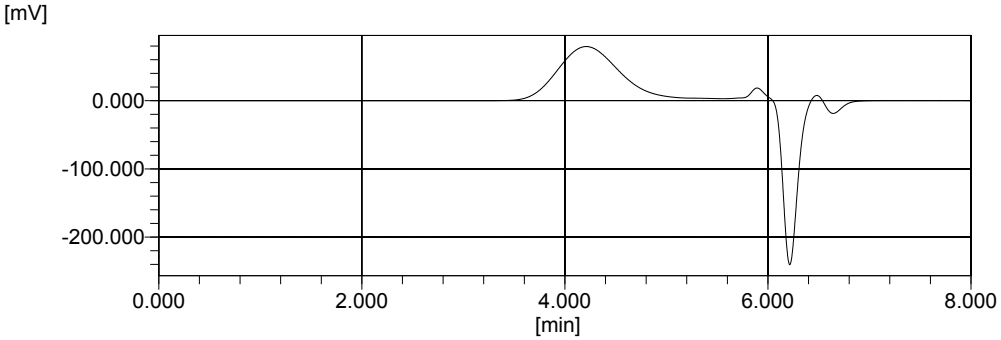

Fig. S**39**. GPC trace of resulting copolymer obtained by complex **3**: Entry **9** in Table **2**

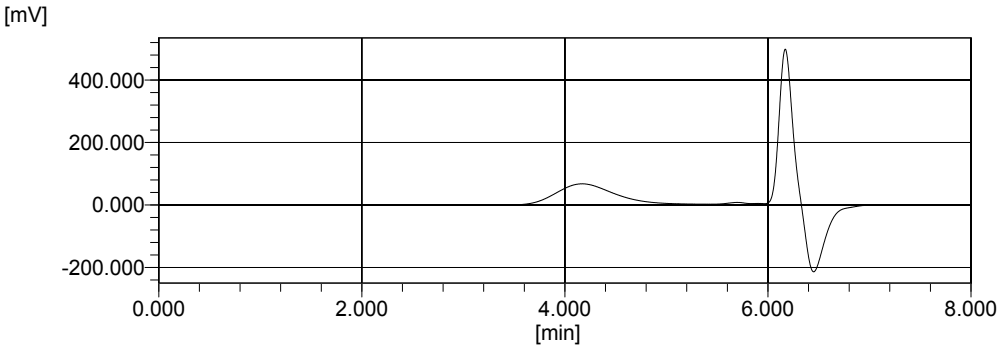

Fig. S**40**. GPC trace of resulting copolymer obtained by complex **3**: Entry **10** in Table **2**

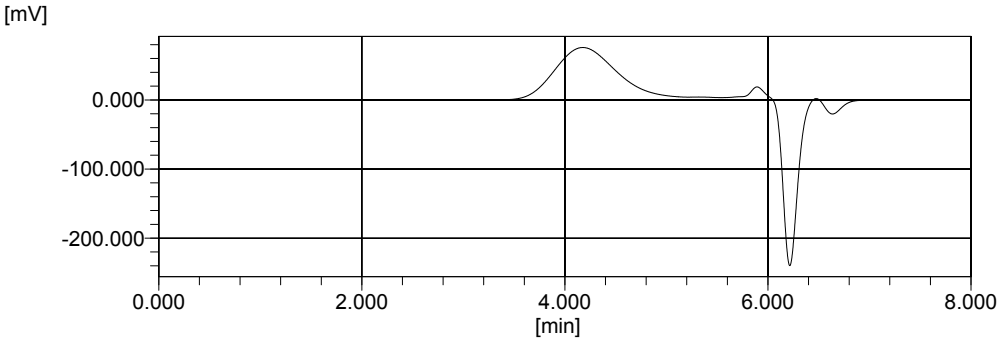

Fig. S**41**. GPC trace of resulting copolymer obtained by complex **3**: Entry **11** in Table **2**

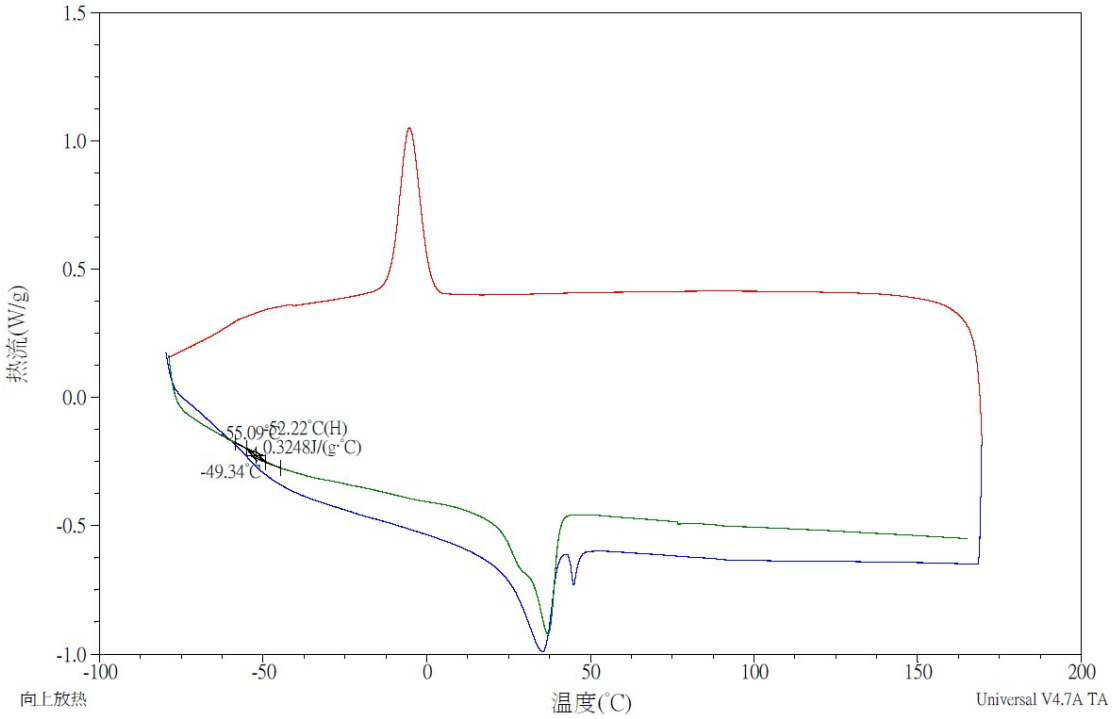

Fig. S**42**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **1** in Table **3**

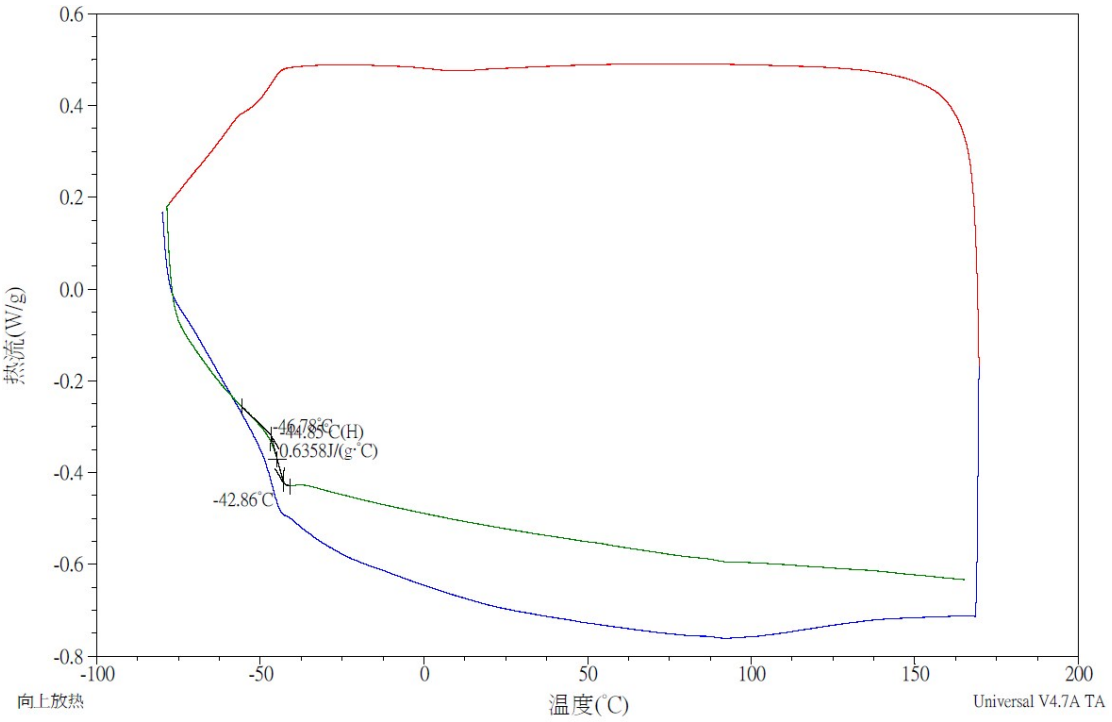

Fig. S**43**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **2** in Table **3**

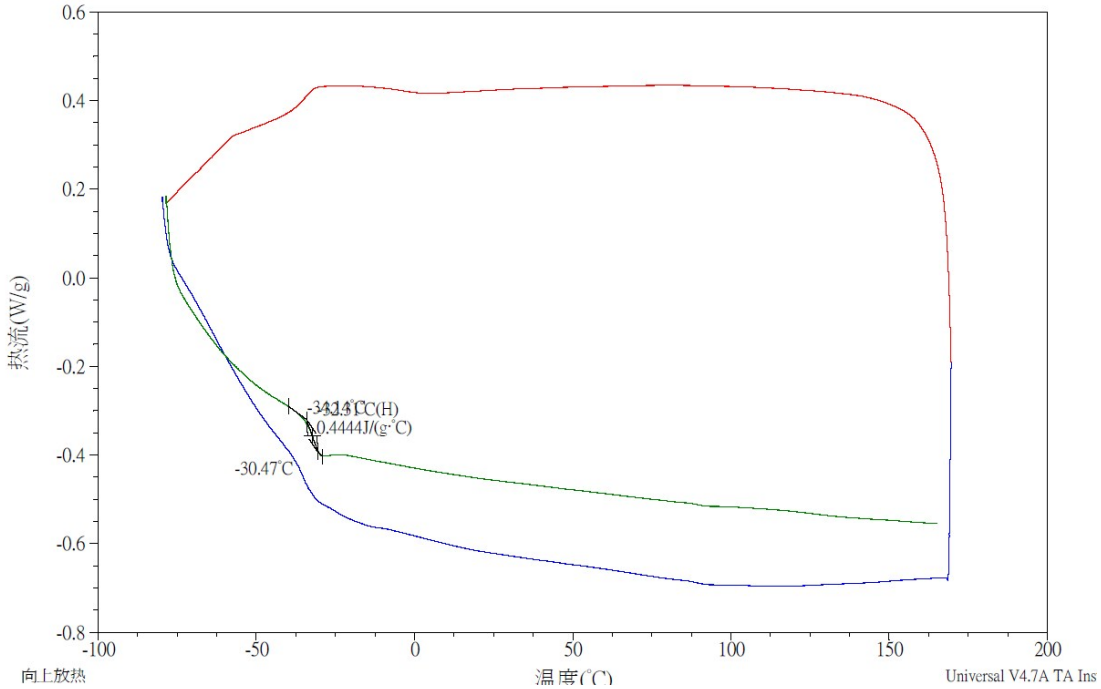

Fig. S**44**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **3** in Table **3**

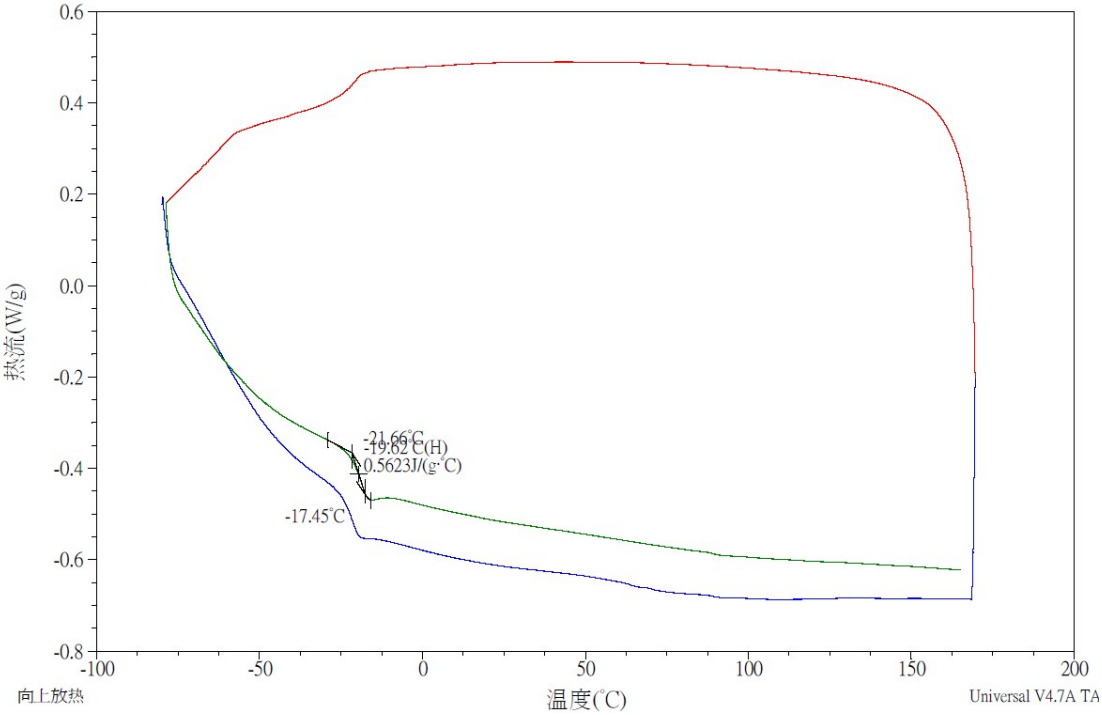

Fig. S**45**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **4** in Table **3**

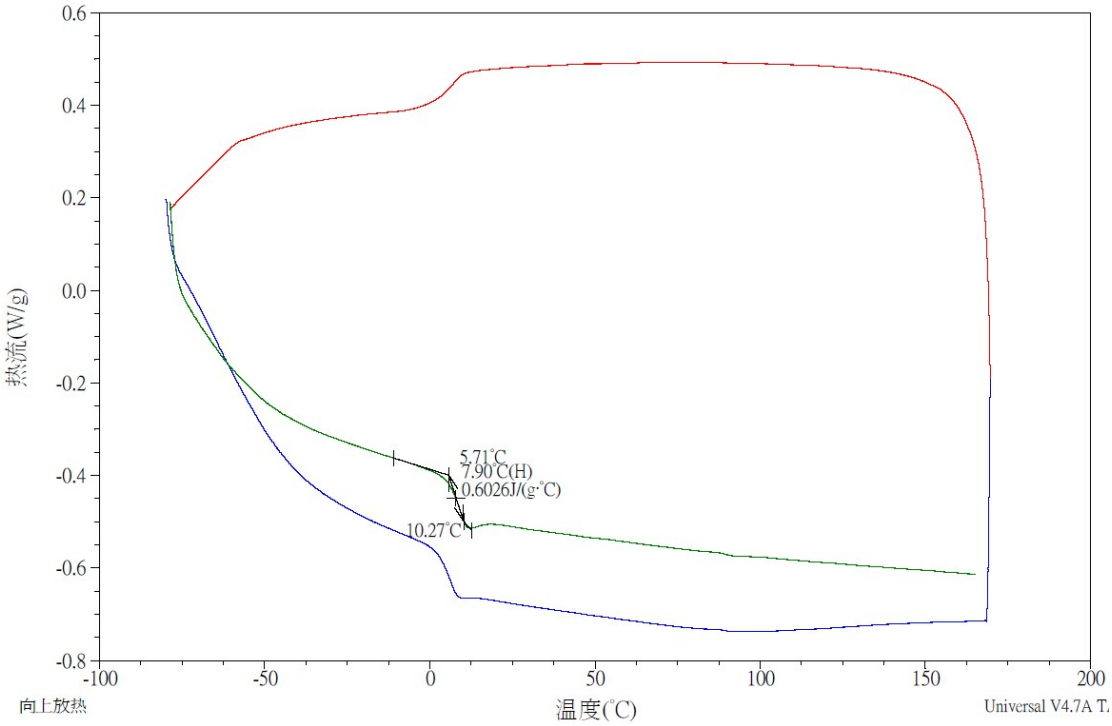

Fig. S**46**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **5** in Table **3**

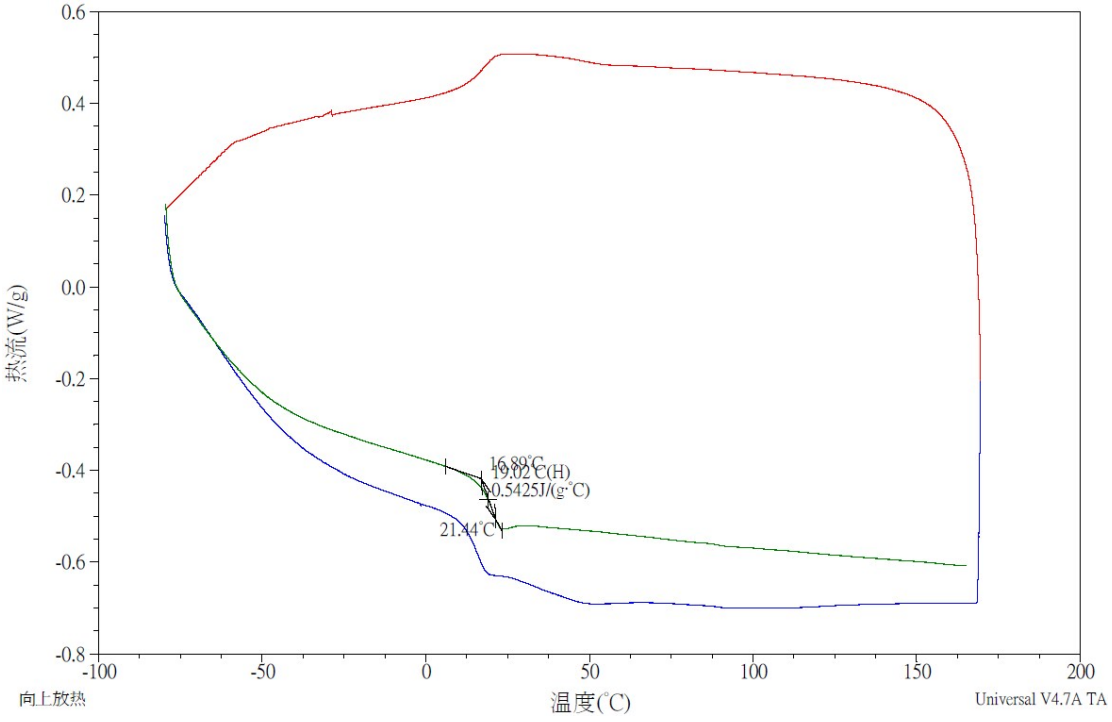

Fig. S**47**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **6** in Table **3**

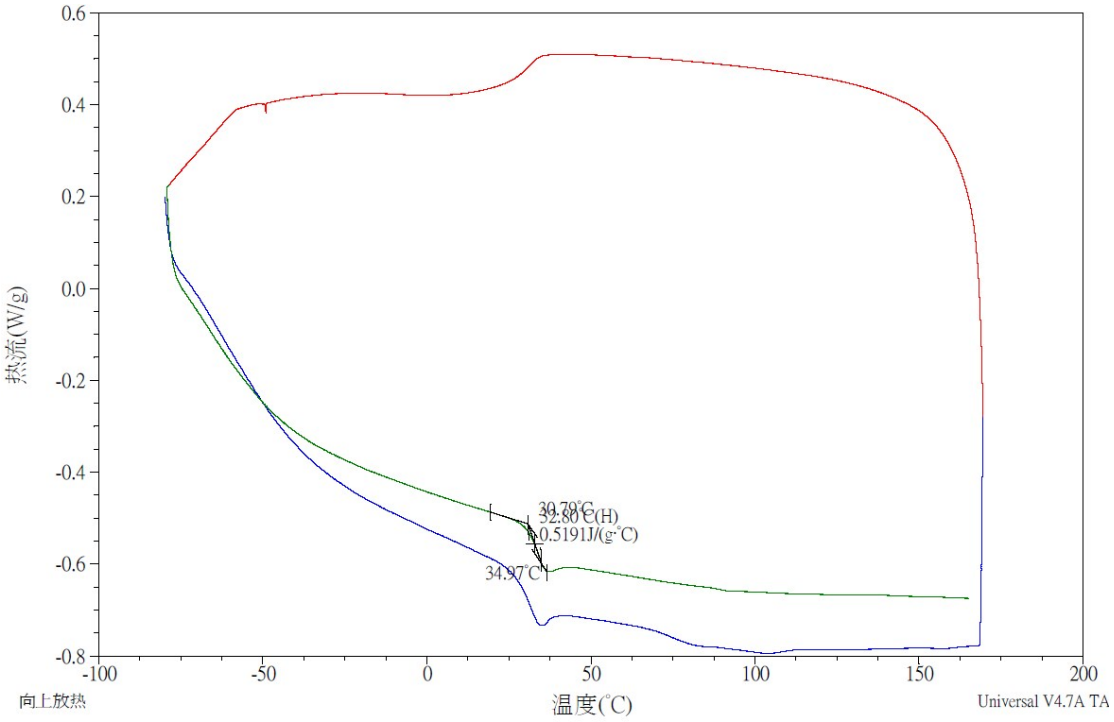

Fig. S**48**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **7** in Table **3**

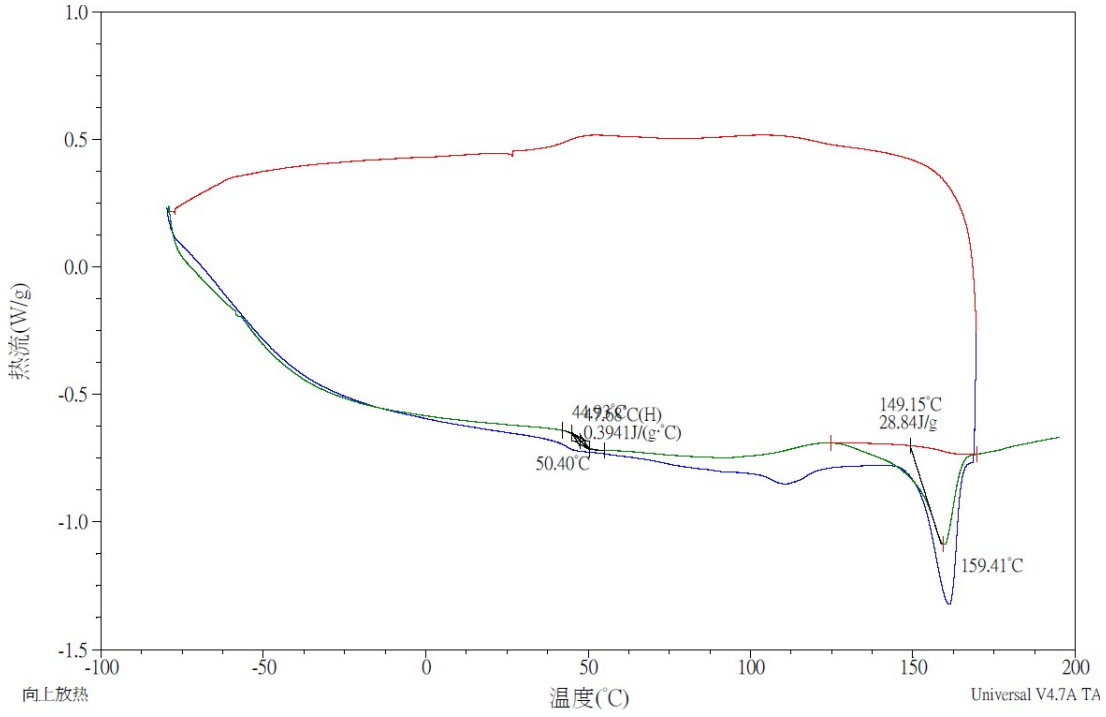

Fig. S**49**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **8** in Table **3**

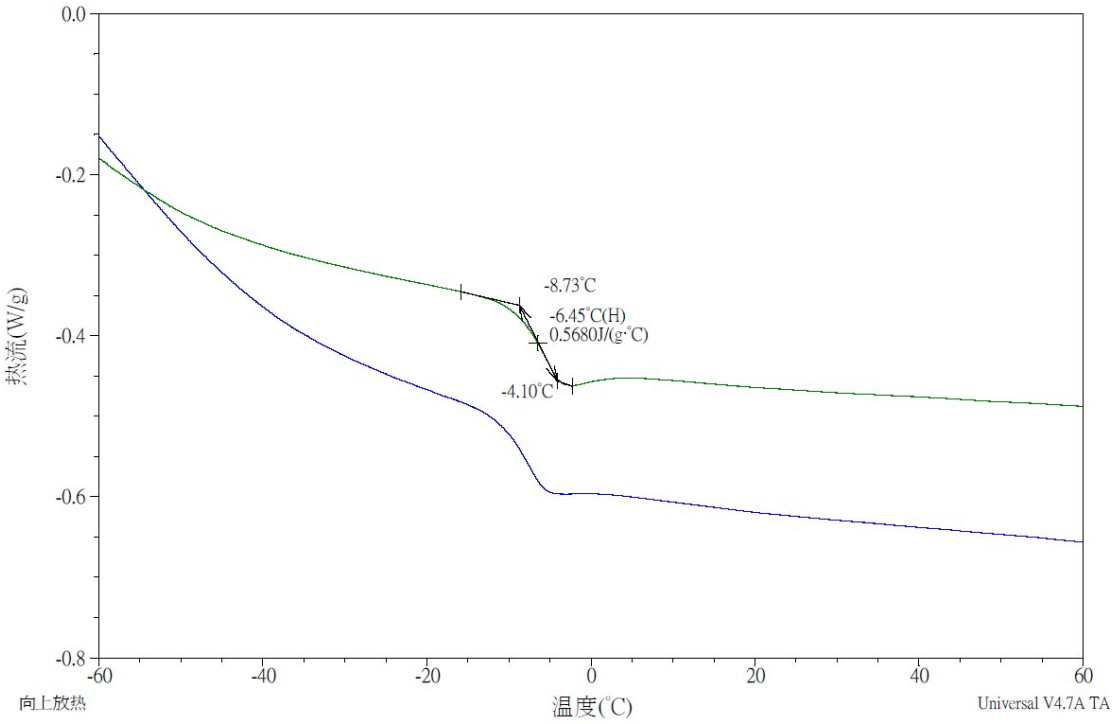

Fig. S**50**. DSC curve of the resulting copolymer obtained by complex **3**: Entry **9** in Table **3**

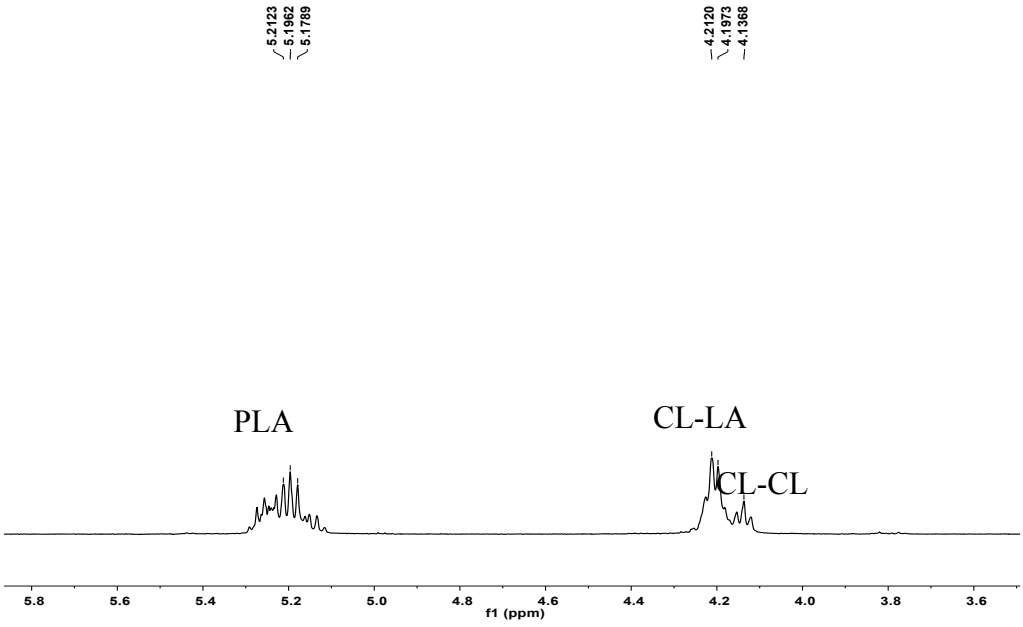

Fig. S**51**. ^{1}H NMR spectrum of copolymer of L-LA and ε-CL (Sequential copolymerization of LA and CL)

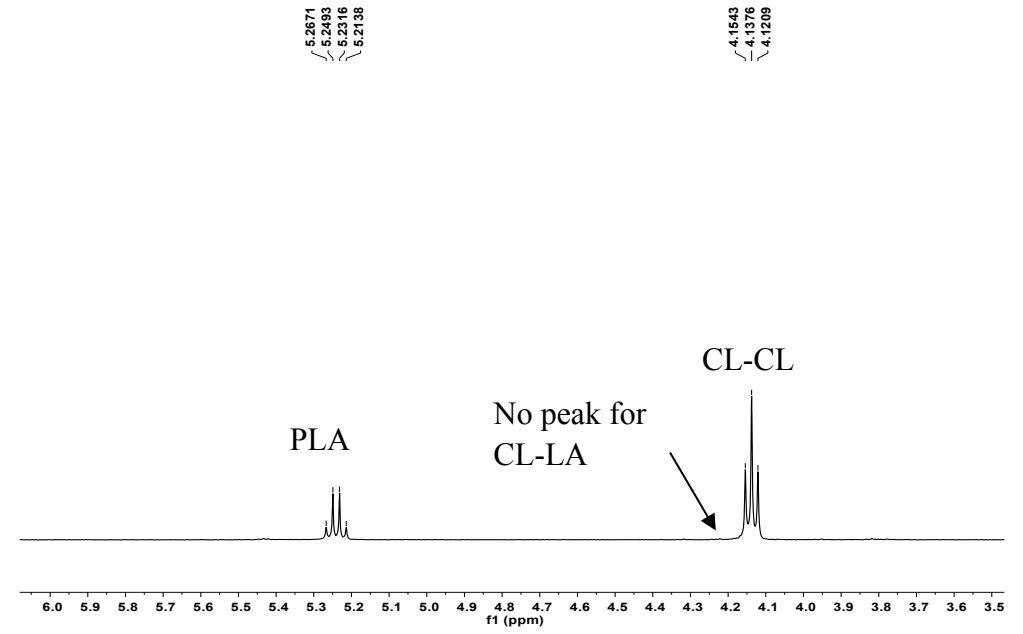

Fig. S**52**. ^{1}H NMR spectrum of copolymer of ε-CL and L-LA (Sequential copolymerization of CL and LA)

Table S1 Sequential copolymerization of LA and CL initiated by complex **3**[a]

Entry	Cat.	1st feed		2nd feed		C_{CL}, C_{LA}[b] (%)	CL:LA[c] (%)	CL-LA/CL-CL[d]
		$[LA]_0:[I]_0$	t_1	$[CL]_0$	t_2			
1	**3**	200:1	2 min	200	3 h	99, 99	50:50	78:22

[a] Polymerization conditions: $([\varepsilon\text{-CL}]_0 + [\text{L-LA}]_0):[I]_0 = 400:1$, in toluene, 60 ℃, 3h. [b] Monomer conversion was determined by ^{1}H NMR spectroscopy. [c] CL/LA molar ratio in the copolymer. [d] (CL-LA)/(CL-CL) in the copolymer.

Table S2 Sequential copolymerization of CL and LA initiated by the complex **3**[a]

Entry	Cat.	1st feed		2nd feed		C_{CL}, C_{LA}[b] (%)	CL:LA[c] (%)	CL-LA/CL-CL[d]
		$[CL]_0:[I]_0$	t_1	$[LA]_0$	t_2			
1	**3**	200:1	2 min	200	3 h	99, 40	70:30	0:100

[a] Polymerization conditions: $([\varepsilon\text{-CL}]_0 + [\text{L-LA}]_0):[I]_0 = 400:1$, in toluene, 60 ℃, 3h. [b] Monomer conversion was determined by ^{1}H NMR spectroscopy. [c] CL/LA mole ratio in the copolymer. [d] (CL-LA)/(CL-CL) in the copolymer.

Table S3 Crystallographic data for complexes **1-5**

Complex	**1**·2.5THF	**2**·THF	**3**·4THF	**4**·3THF	**5**·4THF
Formula	$C_{63}H_{102}N_3O_6$.	$C_{46}H_{76}N_3O_5L$	$C_{90}H_{148}N_6O_{10}L$	$C_{94}H_{140}N_6O_9L$	$C_{88}H_{144}N_6O_{10}L$
M_r	1144.39	890.01	1751.97	1775.94	1723.91
T/K	223(2)	223(2)	223(2)	223(2)	223(2)
Crystal	Tetragonal	Triclinic	Triclinic	Triclinic	Triclinic
Space	I 41/a	P -1	P -1	P -1	P -1
Crystal	0.50×0.40×0.	0.75×0.40×0.3	0.50×0.40×0.4	0.50×0.40×0.4	0.40×0.20×0.2
a/Å	28.6963(3)	10.3685(4)	12.1234(6)	12.9998(5)	12.0092(6)
b/Å	28.6963(3)	13.2339(5)	13.8634(5)	14.5735(5)	13.9383(6)
c/Å	33.2864(6)	18.9841(8)	15.2486(6)	15.2374(7)	14.9998(5)
α/°	90.00	101.370(3)	94.997(3)	114.717(4)	95.089(3)
β/°	90.00	105.032(4)	107.017(4)	101.976(4)	107.153(4)
γ/°	90.00	92.632(3)	104.611(4)	104.959(3)	104.278(4)
V/Å^3	27410.6(7)	2453.43(17)	2355.25(18)	2364.13(16)	2287.12(17)
Z	8	2	1	1	1
D_c/g·cm^{-3}	1.109	1.205	1.246	1.247	1.251
μ/mm^{-1}	0.669	0.913	7.402	0.947	0.970
F(000)	9760	940	924	932	908
θ_{max}/°	26.4	26.4	73.9	26.4	26.4

Collect	62531	22733	16901	23213	21967
Unique	14028	9994	9463	9648	9331
No. of	659	489	488	484	425
GOF	1.109	1.065	1.050	1.058	1.090
R	0.0474	0.0452	0.0520	0.0392	0.0948
wR_2	0.1426	0.1181	0.1365	0.1018	0.2627
R_{int}	0.0389	0.0343	0.0546	0.0336	0.1480

Table S4 Select bond lengths (Å) and bond angles (deg) for complexes **1-5**

Bond	**1**	**2**	**Bond**	**3**	**4**	**5**
La-O1	2.318(3)	2.357(3)	La1-O1	2.339(3)	2.365(2)	2.346(5)
La-O2	2.358(3)	2.346(3)	La1-O2	2.370(3)	2.320(2)	2.327(4)
La-O3	2.286(3)	2.203(3)	La1-O3	2.463(3)	2.468(2)	2.446(5)
La-O4	2.703(3)	2.671(3)	La1-O3A	2.423(3)	2.439(2)	2.425(5)
La-N1	2.722(3)	2.761(3)	La1-N1	2.652(4)	2.619(3)	2.652(6)
La-N2	2.767(3)	2.764(3)	La1-N2	2.827(4)	2.805(3)	2.795(6)
La-N3	2.693(3)	2.679(4)	La1-N3	2.657(4)	2.638(3)	2.648(6)
Bond	**1**	**2**	**Bond angles**	**3**	**4**	**5**
O2-La-N3	67.80(10)	68.40(11)	O1-La1-N1	69.41(12)	68.07(8)	67.43(17)
N1-La-N3	115.64(10)	122.53(13)	O2-La1-N1	87.34(14)	152.52(9)	151.70(2)
N1-La-O1	67.43(10)	66.66(9)	O3-La1-N1	110.08(13)	115.41(9)	112.27(18)
O2-La-O1	96.10(9)	98.97(9)	O1-La1-O3A	112.37(12)	92.75(8)	90.90(17)
N1-La-O3	108.72(11)	113.15(10)	O3-La1-O3A	68.76(12)	68.04(9)	68.58(18)
O4-La-O3	175.34(10))					