Electronic Supplementary Information for

Fast and switchable ring-opening polymerization of biorenewable omega-substituted lactones towards sustainable copolymers with facile control over monomer sequence

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Experimental section

Materials

Benzyl alcohol (Innochem) was dried and distilled over CaH_2 before use, and solvent toluene (Innochem) was dried by azeotropic distillation and subsequently stored in a glove box. Cyclohexylamine, 3,5-bis(trifluoromethyl)-aniline, isothiocyanatobenzene 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene, 1-isocyanato-3,5-bis (trifluorome-thyl)benzene were purchased from Aladdin and used as received. 1,3-diisopropyl-2-thiourea (Aladdin) and dicyclohexylthiourea(Aladdin) were used as received and 1,3-diphenyl urea (TCI) was recrystallized from ethyl acetate before use. 1,8-Diazabicyclo [5.4.0]-7-undecene (DBU), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IMes, white solid) and *tert*-Butylimino-tris(dimethylamino)phosphorane(t-BuP$_1$) were purchased from Sigma-Aldrich and used as received. ε-decalactone (ε-DL), δ-caprolactone (δ-CL), δ-decalactone (δ-DL) and caprolactone(ε-CL) obtained from Innochem, were dried over CaH_2 for 48 h, then distilled under reduced pressure and stored under a nitrogen atmosphere.

Instruments

Nuclear magnetic resonance (NMR): ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AV spectrometer at 400 MHz and 600 MHz using $CDCl_3$ or benzene-d_6 as solvents.

[1]H diffusion-ordered spectroscopy (DOSY): DOSY spectra was recorded on Bruker AVANCEIIIHD500 spectrometers. DOSY experiments were performed at a steady temperature of 298 K with at least 32 gradient increments using the ledbpgp2s sequence. Complete diffusion was ensured using the T1/T2 module of Topspin and DOSY transformations using either mono, bis- or tri-exponential fitting were performed using the same software after zero filling.

Size exclusion chromatography (SEC): Molecular weights of polymers were

measured using a Shimadzu CBM-20Alite instrument, with HPLC grade THF as the eluent, flowing at 1.0 mL·min $^{-1}$, at 40 °C and using monodisperse polystyrene standards for instrument calibration.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS): MALDI-TOF-MS analyses were performed on a Bruker ultraflextreme MALDI-TOF/TOF equipped with a 337 nm nitrogen laser operating in a positive ion, linear mode. An accelerating voltage of 20 kV was applied. The polymer sample was dissolved in THF at a concentration of 1 mg·mL^{-1}. The cationization agent used was Sodium trifluoroacetate dissolved in THF at a concentration of 1.0 mg·mL^{-1}. The matrix used was dithranol and was dissolved in THF at a concentration of 10 mg·mL^{-1}. Solutions of matrix, salt, and polymer were mixed in a 10:1:1 volume ratio, and then 1.0 μL of mixed solution was spotted on a stainless steel MALDI plate before being air-dried. The spectrum was recorded using reflectron mode.

In situ ATR-IR spectroscopy: In situ ATR-IR measurements were performed under argon atmosphere using a Mettler-Toledo ReactIR 702L spectrometer equipped with a MCT detector and a silver halide DiComp probe. For in situ ATR-IR measurement, the resolution is 8 cm^{-1}, the number of scans is 32 and the test range is from 650 cm^{-1} to 3000 cm^{-1}.

Differential scanning calorimetry (DSC): The thermal properties of polymer samples were measured on a TA Instruments Q-2000 DSC. Samples were analyzed in hermetically sealed aluminum pans. The samples were equilibrated at −80 °C, heated to 100 at 10 °C·min $^{-1}$, and were kept at that temperature for 4 min to erase the thermal history. Subsequently, the samples were cooled to −80 °C at 10 °C·min^{-1}, then kept at that temperature for further 4 min before being heated to 100 °C again. Each sample was entry for three heating/cooling cycles. To erase thermal history, glass transitions and melting endotherms are reported upon the third heating cycle.

Preparation of ureas and thioureas

Ureas and thioureas were prepared according to literature procedures. [1] The ureas (U1,

U2) are prepared by mixing equal amounts of amine and isocyanate in a tetrahydrofuran solution. Tetrahydrofuran is removed under vacuum and then the crude product is purified by washing with DCM under vacuum filtration.[2] Thioureas (TU1, TU2) are similarly prepared by mixing equal amounts of amine and isocyanate in a dichloromethane solution. TU1 is purified by recrystallisation with petroleum ether after removal of the solvent under vacuum.[3] For TU2, the product is purified by removing a portion of the excess dichloromethane by vacuum concentration and precipitating with n-hexane.[4] The final products were kept under vacuum overnight and subsequently stored in a nitrogen-filled glove box.

General polymerization procedure

All polymerizations were performed inside a nitrogen-filled glovebox at ambient temperature. In a typical polymerization process, a stock solution of the initiator benzyl alcohol (BnOH) in the solvent toluene is prepared, followed by direct weighing of a quantity of thiourea/urea and base into a 4.0 mL glass vial equipped with a micro stir bar. An appropriate amount of toluene solution of benzyl alcohol is then added to the vial in order to stir the mixture well, and the monomer is added at last. The vial is then removed from the glove box, with the polymerization carried out by stirring under an external heating bath. A small aliquot of the polymerization mixture was taken out for ^{1}H NMR spectroscopy. The molecular weight M_n and distribution $Đ$ were determined by SEC. Then, the remained crude mixture was precipitated into an excess of cold methanol, filtered and dried in a vacuum at room temperature to a constant weight.

Typical polymerization of ε-DL with (T)U/base (Table 1, entry 1): In a N_2-filled glovebox, U1 (0.050 mmol, 2.5 equiv.) and DBU (0.050 mmol, 2.5 equiv.) were measured into a 4.0 mL glass vial equipped with a stir bar. A stock solution of -OH initiator was prepared by dissolving 20.8 μL of BnOH (0.2 mmol) in 4.0 mL of toluene, and 0.4 mL of the stock solution was added to the vial containing catalysts. The mixture was stirred until homogeneous, then ε-DL (2.0 mmol, 100 equiv.) was added at last. The glass vial was then taken out of the glove box and allowed to stirred at 25 °C for

periods of time. The ε-DL conversion was determined by ^{1}H NMR measurement. The molecular weight M_n and distribution $Đ$ were determined by SEC.

Typical polymerization of δ-CL with (T)U/base (Table S1, entry 2): In a N$_2$-filled glovebox, U2 (0.050 mmol, 2.5 equiv.) and IMes (0.050 mmol, 2.5 equiv.) were measured into a 4.0 mL glass vial equipped with a stir bar. A stock solution of -OH initiator was prepared by dissolving 20.8 μL of BnOH (0.2 mmol) in 4.0 mL of toluene, and 0.4 mL of the stock solution was added to the vial containing catalysts. The mixture was stirred until homogeneous, then δ-CL (2.0 mmol, 100 equiv.) was added at last. The glass vial was then taken out of the glove box and allowed to stirred at 25 °C for periods of time. The δ-CL conversion was determined by ^{1}H NMR measurement. The molecular weight M_n and distribution $Đ$ were determined by SEC.

Typical polymerization of δ-DL with (T)U/base (Table S2, entry 2): In a N$_2$-filled glovebox, U2 (0.050 mmol, 2.5 equiv.) and IMes (0.050 mmol, 2.5 equiv.) were measured into a 4.0 mL glass vial equipped with a stir bar. A stock solution of -OH initiator was prepared by dissolving 20.8 μL of BnOH (0.2 mmol) in 4.0 mL of toluene, and 0.4 mL of the stock solution was added to the vial containing catalysts. The mixture was stirred until homogeneous, then δ-DL (2.0 mmol, 100 equiv.) was added at last. The glass vial was then taken out of the glove box and allowed to stirred at 25 °C for periods of time. The δ-DL conversion was determined by ^{1}H NMR measurement. The molecular weight M_n and distribution $Đ$ were determined by SEC.

Typical copolymerization of ε-CL and ε-DL with (T)U/base (Table 2, entry 1): In a N$_2$-filled glovebox, U2 (0.050 mmol, 2.5 equiv.) and IMes (0.050 mmol, 2.5 equiv.) were measured into a 4.0 mL glass vial equipped with a stir bar. Then ε-CL (2.0 mmol, 100 equiv.) and ε-DL (2.0 mmol, 100 equiv.) was added. A stock solution of -OH initiator was prepared by dissolving 20.8 μL of BnOH (0.2 mmol) in 4.0 mL of toluene, and 0.4 mL of the stock solution was added to the vial. The glass vial was then taken out of the glove box and allowed to stirred at 25 °C for periods of time. The monomer conversion was determined by ^{1}H NMR measurement. The molecular weight M_n and

distribution Đ were determined by SEC.

Copolymerization of ε-CL and ε-DL with (T)U/IMes for *in situ* ATR-IR spectroscopy: In a N_2-filled glovebox, (T)U (0.025 mmol, 2.5 equiv.) and IMes (0.025 mmol, 2.5 equiv.) were measured into a 4.0 mL glass vial equipped with a stir bar. Then ε-CL (1.0 mmol, 100 equiv.) and ε-DL (1.0 mmol, 100 equiv.) was added. For U2/IMes, the amount of ε-DL added was reduced to 0.5 mmol to shorten the reaction time. A stock solution of -OH initiator was prepared by dissolving 20.8 μL of BnOH (0.2 mmol) in 4.0 mL of toluene, and 0.4 mL of the stock solution was added to the vial.

Figures and tables

Table S1. ROPs of δ-CL mediated by (T)U/IMes catalyst systems [a]

entry	catalysts	t (h)	conv.[b] (%)	TOF[c] (h^{-1})	$M_{n,theo}$[d] (kDa)	$M_{n,SEC}$[e] (kDa)	Đ[e]
1	U1/IMes	1	82	33	9.5	7.7	1.29
2	U2/IMes	20 min	79	95	9.1	7.6	1.09
3	U3/IMes	10 min	84	202	9.8	6.4	1.36
4	TU1/IMes	48	78	0.5	9.0	6.1	1.26
5	TU2/IMes	4	82	8	9.6	8.9	1.21
6	TU3/IMes	2 min	83	996	9.6	9.4	1.31

[a] Polymerizations were performed in dry toluene at 25 °C with $[\delta\text{-CL}]_0$ = 5 M; $[\delta\text{-CL}]/[(T)U]/[Base]/[I]$ = 100/2.5/2.5/1; I = BnOH. [b] Monomer conversion determined by ^{1}H NMR in CDCl$_3$ using integrals of the characteristic signals. [c] Turnover frequency (TOF) = mole of consumed monomer/mole of (thio)urea catalyst per hour. [d] $M_{n,theo}$ = $M_{(\delta\text{-CL})} \times ([\delta\text{-CL}]_0/[I]_0) \times$ conv. + $M_{(BnOH)}$. [e] Determined by SEC in THF at a flow rate of 1.0·min^{-1} at 40 °C, calibrated with polystyrene standards.

Table S2. ROPs of δ-DL mediated by (T)U/IMes catalyst systems [a]

entry	catalysts	t (h)	conv.[b] (%)	TOF[c] (h^{-1})	$M_{n,theo}$[d] (kDa)	$M_{n,SEC}$[e] (kDa)	Đ[e]
1	U1/IMes	48	72	0.6	12.4	11.7	1.19
2	U2/IMes	1	65	26	11.2	8.2	1.09
3	U3/IMes	20 min	70	84	12.0	10.3	1.26
4	TU1/IMes	120	69	0.2	11.8	8.4	1.08
5	TU2/IMes	24	63	1	10.8	8.8	1.09
6	TU3/IMes	5 min	69	331	11.9	10.2	1.19

[a] Polymerizations were performed in dry toluene at 25 °C with $[\delta\text{-DL}]_0$ = 5 M; $[\delta\text{-DL}]/[(T)U]/[Base]/[I]$ = 100/2.5/2.5/1; I = BnOH. [b] Monomer conversion determined by ^{1}H NMR in CDCl$_3$ using integrals of the characteristic signals. [c] Turnover frequency (TOF) = mole of consumed monomer/mole of (thio)urea catalyst per hour. [d] $M_{n,theo}$ = $M_{(\delta\text{-DL})} \times ([\varepsilon\text{-DL}]_0/[I]_0) \times$ conv. + $M_{(BnOH)}$. [e] Determined by SEC in THF at a flow rate of 1.0·min^{-1} at 40 °C, calibrated with polystyrene standards.
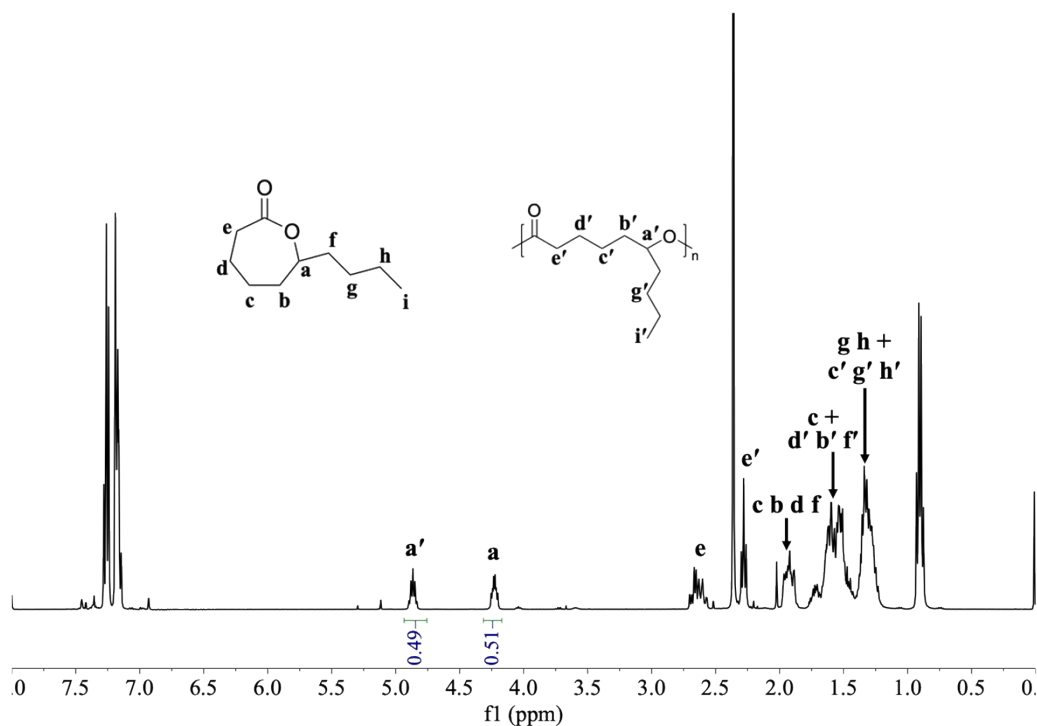
Figure S1. ^{1}H NMR spectrum (CDCl$_3$, 298 K) of an aliquot from the polymerization mixture in ROP of ε-DL (Table 1, entry 3).

Calculation of monomer conversion in ROPs of omega-substituted lactones

As shown in Figures S1, the monomer conversion can be calculated from the integrals of the characteristic signals assigned to the monomer and polymer (peaks a and a′).

The monomer conversion was determined using the equation shown below:

$$conv. (\%) = \frac{I_{a'}}{I_a + I_{a'}} \times 100\%$$

I_a and $I_{a'}$ are the integrals of peak a and a′ in ^{1}H NMR spectrum.
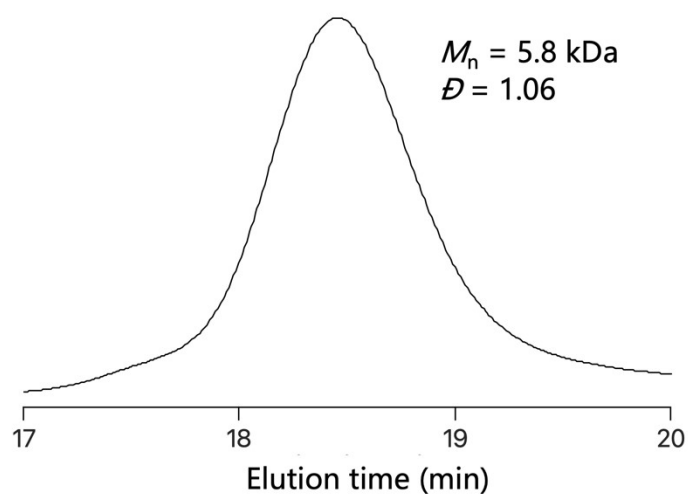
Figure S2. SEC trace of P (ε-DL) obtained by U2/BEMP (Table 1, entry 5).
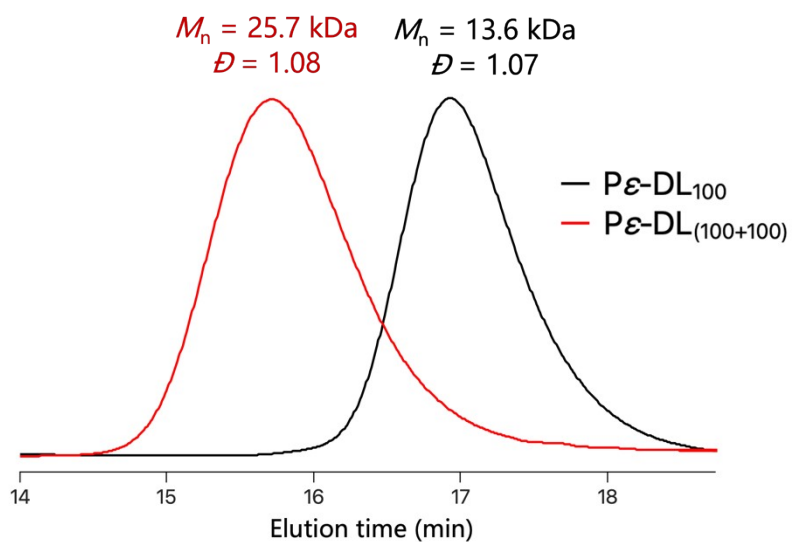
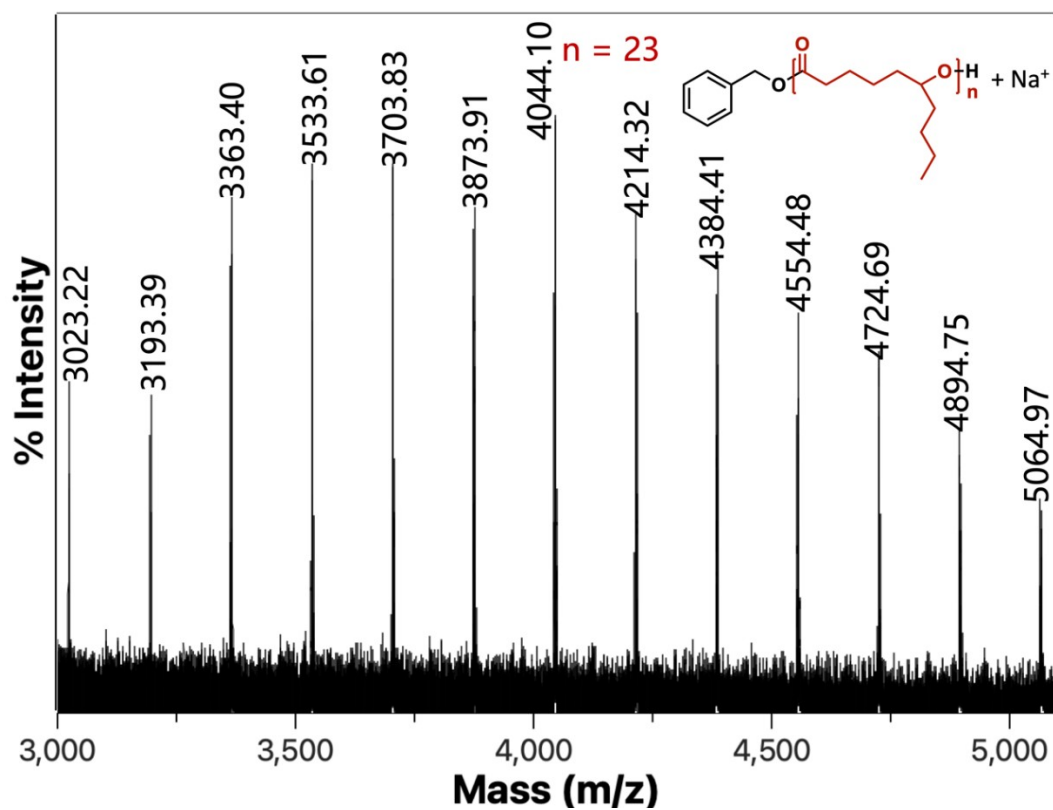**Figure S3.** SEC traces of P(ε-DL) obtained by sequential addition of two batches of ε-DL.

Figure S4. MALDI-TOF mass spectrum of P(ε-DL) produced with U2/BEMP as catalyst (M_n = 5.8 kDa, Đ = 1.06)
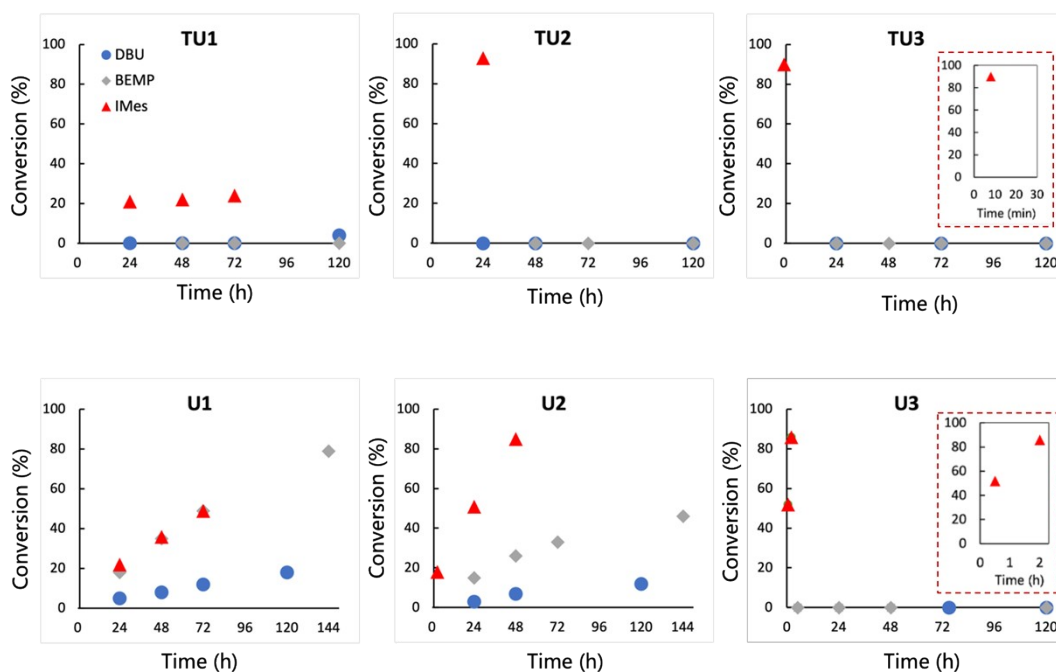
Figure S5. Plots of conversion vs. time for ROPs of ε-DL mediated by (thio)urea/base catalyst systems.

The activity trends and reaction mechanisms of (thio)urea/base catalyst systems:

The activity of the (thio)urea/base catalyst systems showed unique trends. For a given U or TU catalyst, a stronger base usually leads to a faster reaction rate. The order of reaction rates is IMes (18~24) > BEMP (16.5) > DBU (13.9) with the same (thio)urea.

Besides, these differences and trends in activity can be explained by two mechanisms. When the organic base is not strong enough to deprotonate the (thio)urea, i.e. when its pK_a value is significantly less than that of the (thio)urea, the polymerization is dominated by a cooperative

mechanism. Under this mechanism, the activity of the (thio)urea/base catalyst system is positively correlated with the acidity of the (thio)urea. As when using DBU (pK_a = 13.9), the observed trend in activity is U2 > U3 (16 < pK_a < 20).

When the pK_a value of the base is greater than the pK_a value of the (thio)urea, this leads to the deprotonation of the (thio)urea and polymerization therefore proceeds via the anionic mechanism. Under this mechanism, the activity of the (thio)urea anion decreases as the acidity of the (thio)urea increases, as thiourea anion with higher basicity is more favourable to activate the alcohol nucleophiles.[2] When using U3/TU3 with the largest pK_a with IMes, the activity reaches its maximum, which could be due to the highest activity of 'matching' mechanism. The increase in activity with increasing basicity of the base bound to a given (thio)urea can also be attributed to the change from a cooperative mechanism to a more active anionic mechanism.
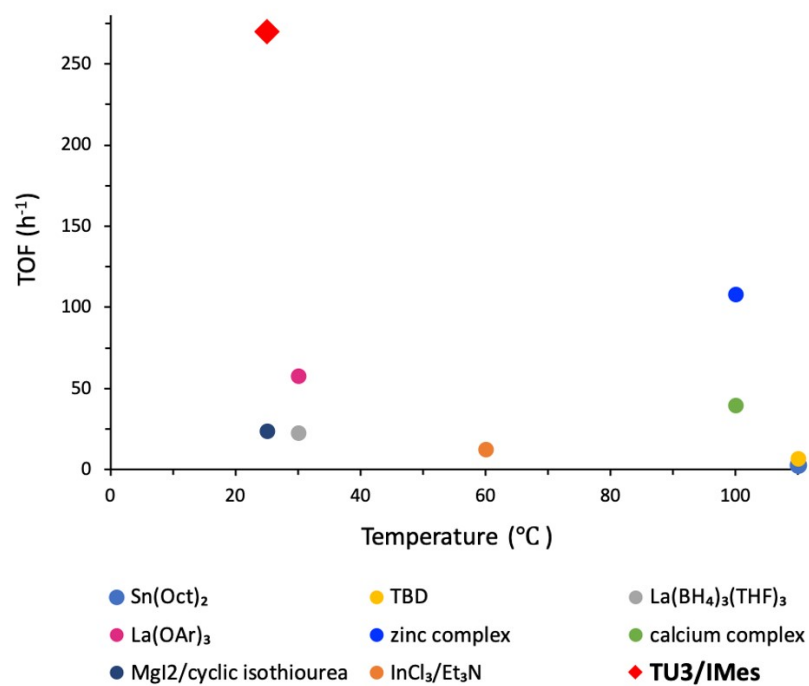
Figure S6. Comparison of TOF values against temperature in ROP of ε-DL with catalysts in previous studies[5-9] and TU3/IMes in this work.
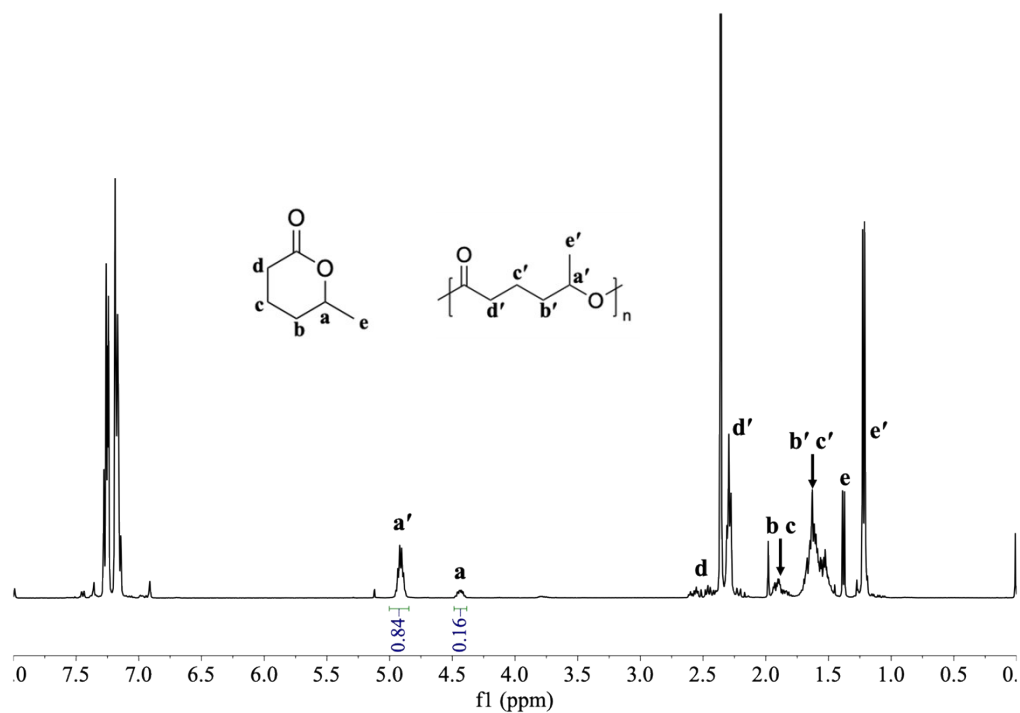
Figure S7. [^1]H NMR spectrum (CDCl₃, 298 K) of an aliquot from the polymerization mixture in ROP of δ-CL (Table S1, entry 3).
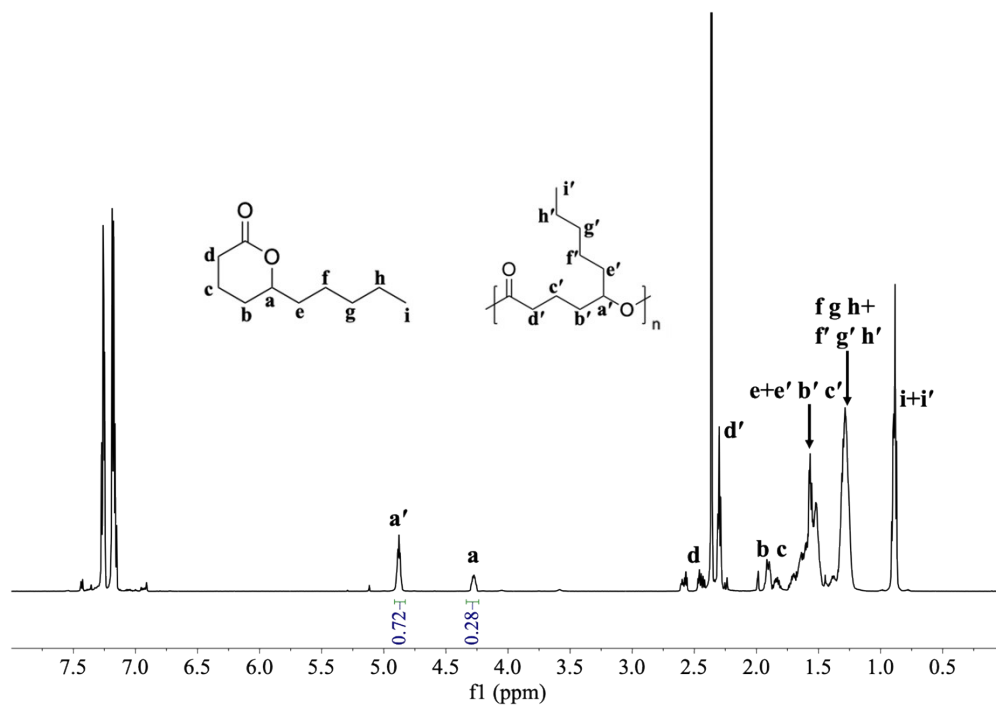

Figure S8. [^1]H NMR spectrum (CDCl₃, 298 K) of an aliquot from the polymerization mixture in ROP of δ-DL (Table S2, entry 1).
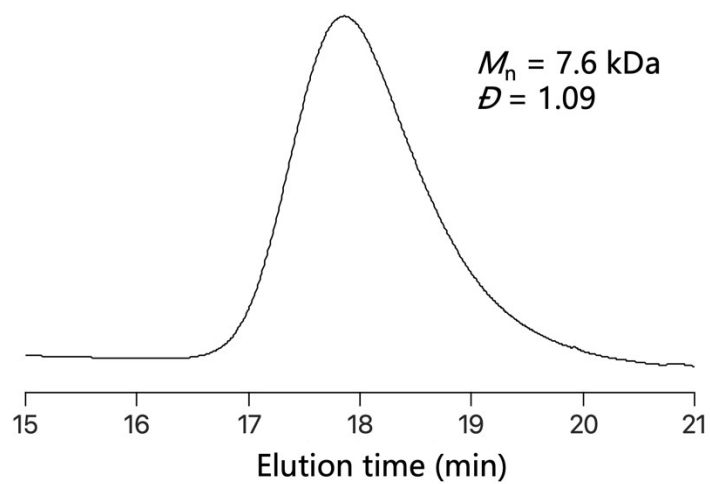
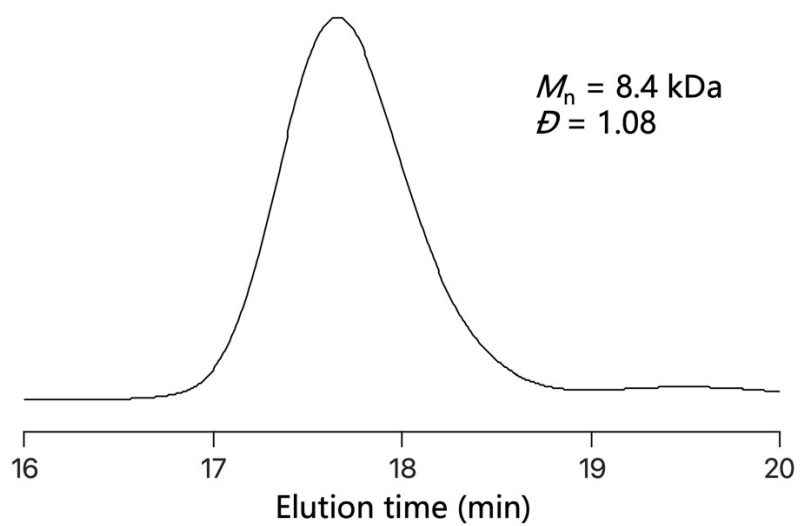**Figure S9.** SEC trace of P(δ-CL) obtained by U2/IMes (Table S1, entry 2).

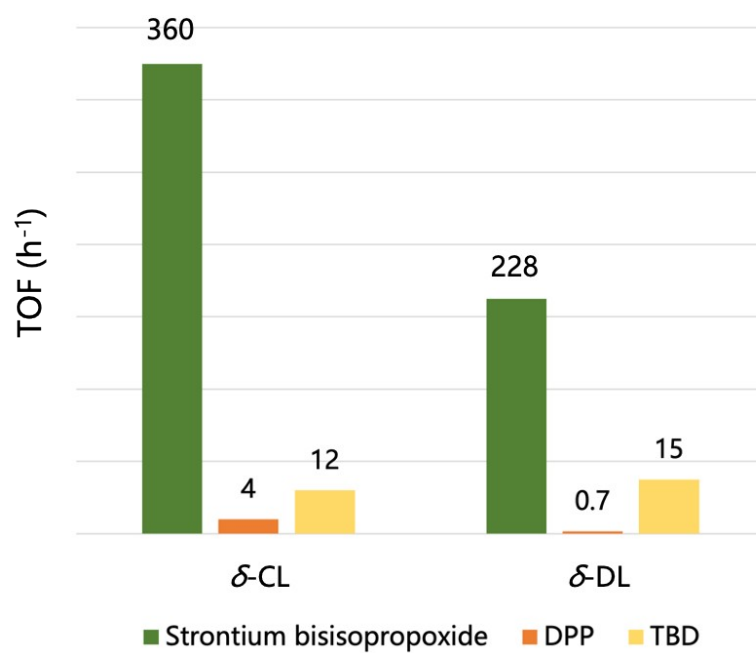**Figure S10.** SEC trace of P(δ-DL) obtained by TU1/IMes (Table S2, entry 4).

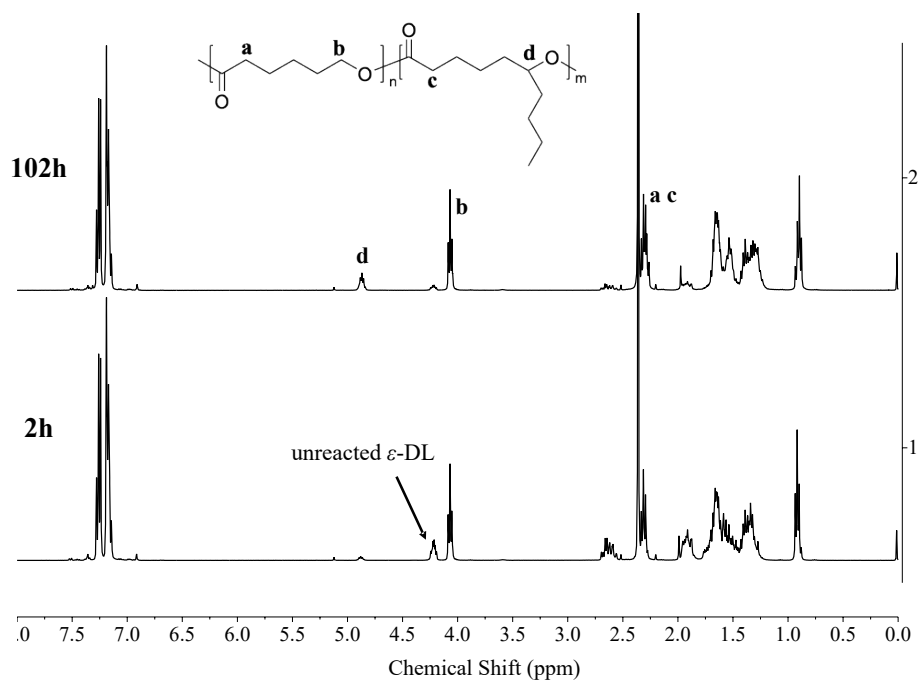**Figure S11.** TOF values at room temperature for catalysts commonly used in ROP of δ-CL and δ-DL.[10-13]

Figure S12. ^{1}H NMR spectrum (CDCl$_3$, 298 K) of aliquots from the polymerization mixture in ring-opening copolymerization of ε-CL and ε-DL by U2/IMes (Table 2, entry 1).

Calculation of sequence lengths of ε-CL and ε-DL in ε-CL/ε-DL copolymer
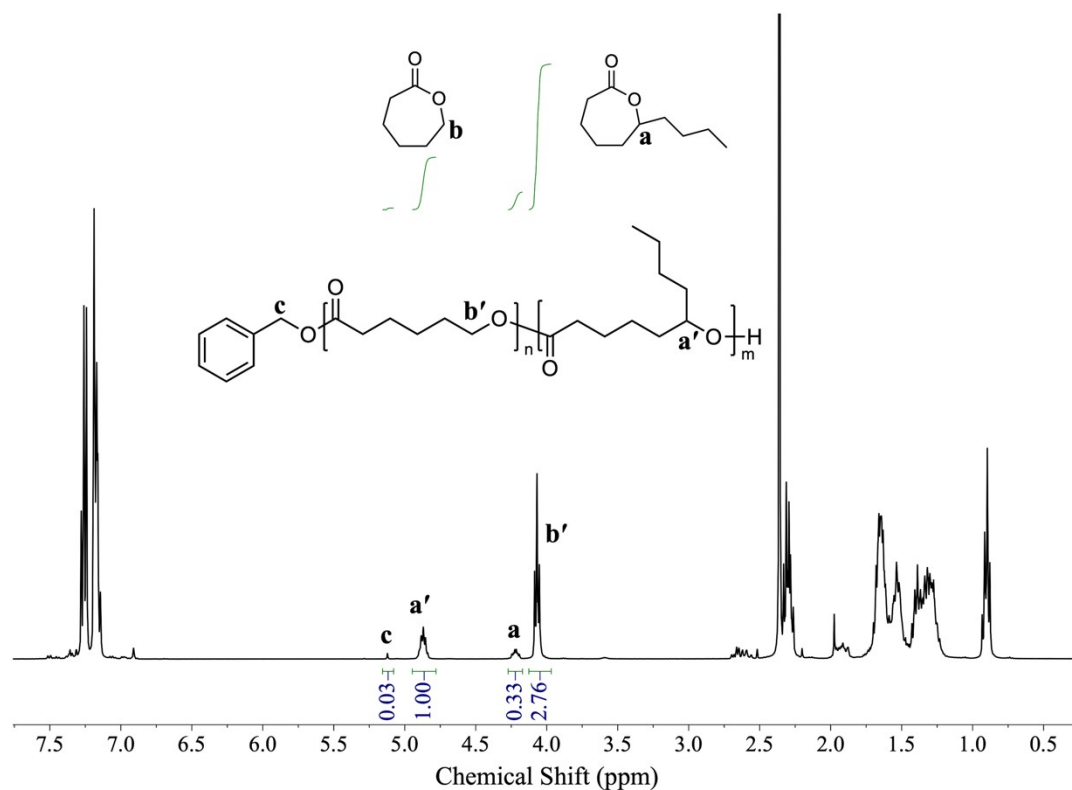

Figure S13. ^{1}H NMR spectrum (CDCl$_3$, 298 K) of the ring-opening copolymerization of ε-CL and ε-DL by U2/IMes (Table 2, entry 1).

The sequence lengths of ε-CL and ε-DL can be calculated from the integrals of the characteristic signals assigned to the monomer unit (peaks a′ and b′) and the initiator (peaks c) in the polymer chain. As shown in Figures S14, in the copolymer prepared by U2/IMes, the sequence lengths of ε-CL and ε-DL were calculated as follows:

$$len(\varepsilon - DL) = \frac{I_{a'}}{I_c/2} = 67$$

$$len(\varepsilon - CL) = \frac{I_{b'}}{I_c} = 92$$

Table S3. Copolymerization of ε-DL and ε-CL catalyzed by (T)U/base catalyst systems. [a]

Entry	catalyst(s)	[ε-CL]/ [ε-DL]	conv. ε-CL (%) [b]	conv. ε-DL (%) [b]	$M_{n,theo}$[c] (kDa)	$M_{n,NMR}$[d] (kDa)	ε-CL/ε-DL[e]
1	U2/IMes	100/100	99	75	23.3	22.0	92/67
2	U3/IMes	100/100	99	86	26.0	24.5	95/80
3	U3/IMes	50/100	99	93	21.6	18.4	45/93
4	TU3/IMes	100/100	99	92	27.1	28.0	100/97

[a] Polymerizations were performed in dry toluene at 25 °C with [ε-CL]$_0$ = 2.5 M; [(T)U]/[Base]/[I] = 2.5/2.5/1; I = BnOH. [b] Monomer conversion determined by ^{1}H NMR in CDCl$_3$ using integrals of the characteristic signals. [c] $M_{n,theo} = M_{(\varepsilon\text{-CL})} \times ([\varepsilon\text{-CL}]_0/[I]_0) \times$ conv. $+ M_{(\varepsilon\text{-DL})} \times ([\varepsilon\text{-DL}]_0/[I]_0) \times$ conv. $+ M_{(BnOH)}$. [d] Determined by the integration of suitable signals from the ^{1}H NMR spectra. [e] Sequence lengths of ε-CL and ε-DL in polymer chain from the ^{1}H NMR spectra.
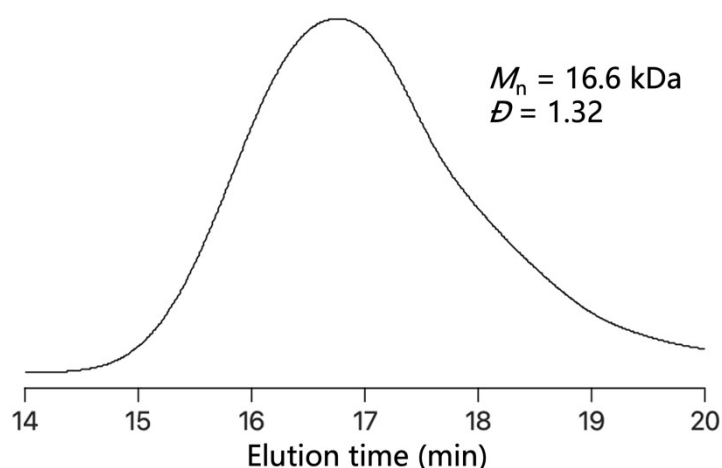

Figure S14. SEC trace of ε-CL/ε-DL copolymer obtained by U2/IMes (Table 2, entry 1).
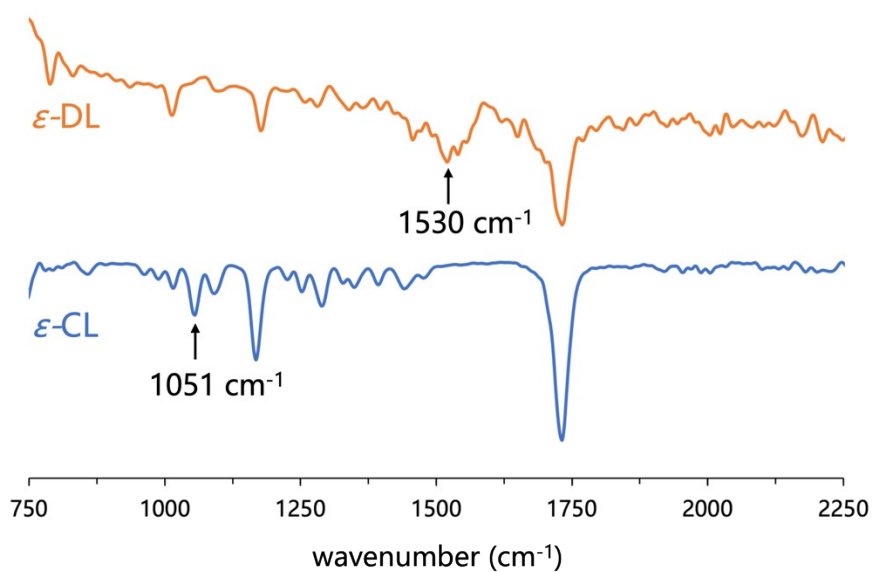
Figure S15. FTIR spectra of the ε-CL and ε-DL monomers.

Figure S16. DOSY NMR spectrum of the polymer obtained from the ring-opening copolymerization of ε-CL and ε-DL by U2/IMes.
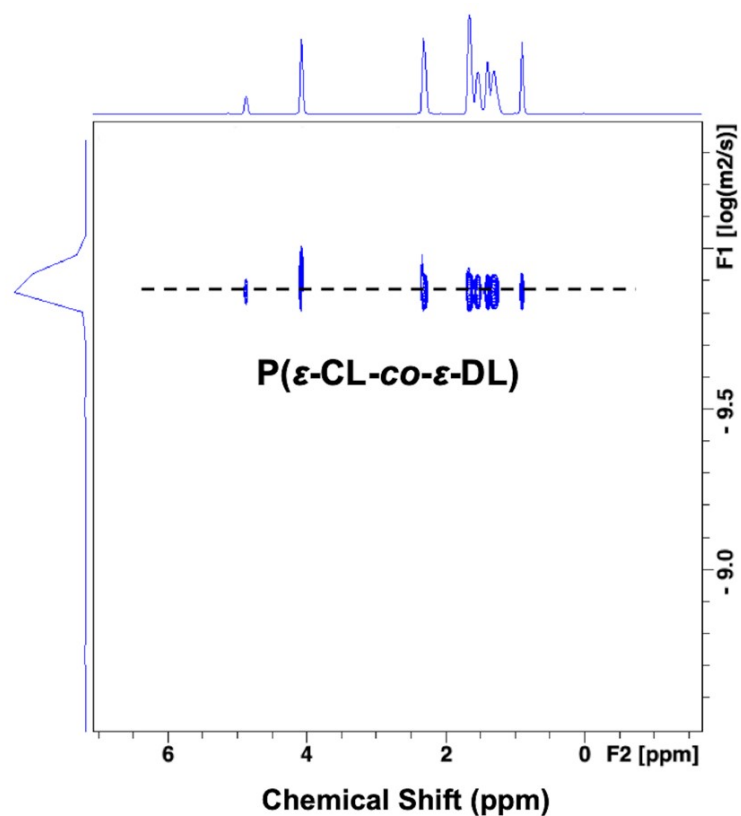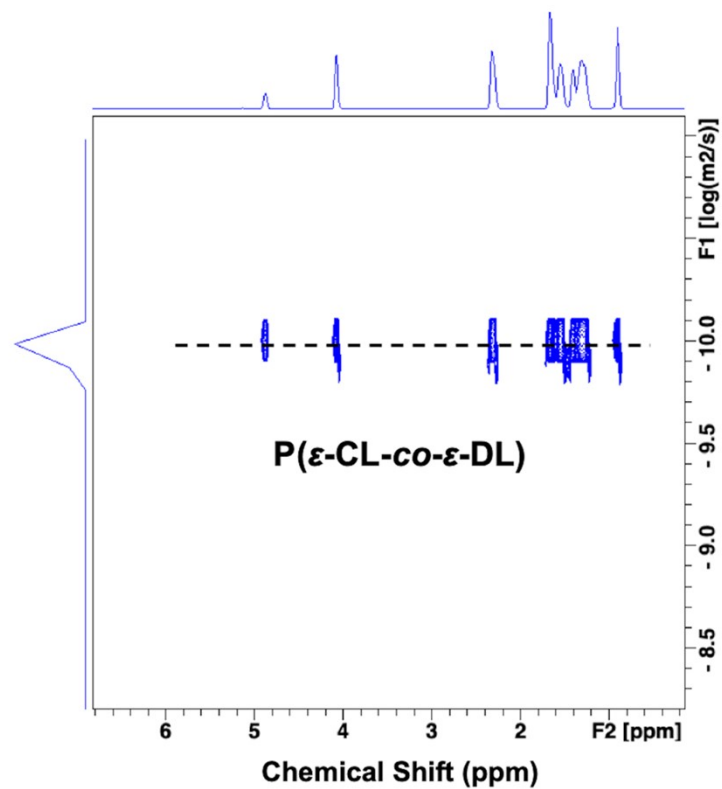
Figure S17. DOSY NMR spectrum of the polymer obtained from the ring-opening copolymerization of ε-CL and ε-DL by U3/IMes.
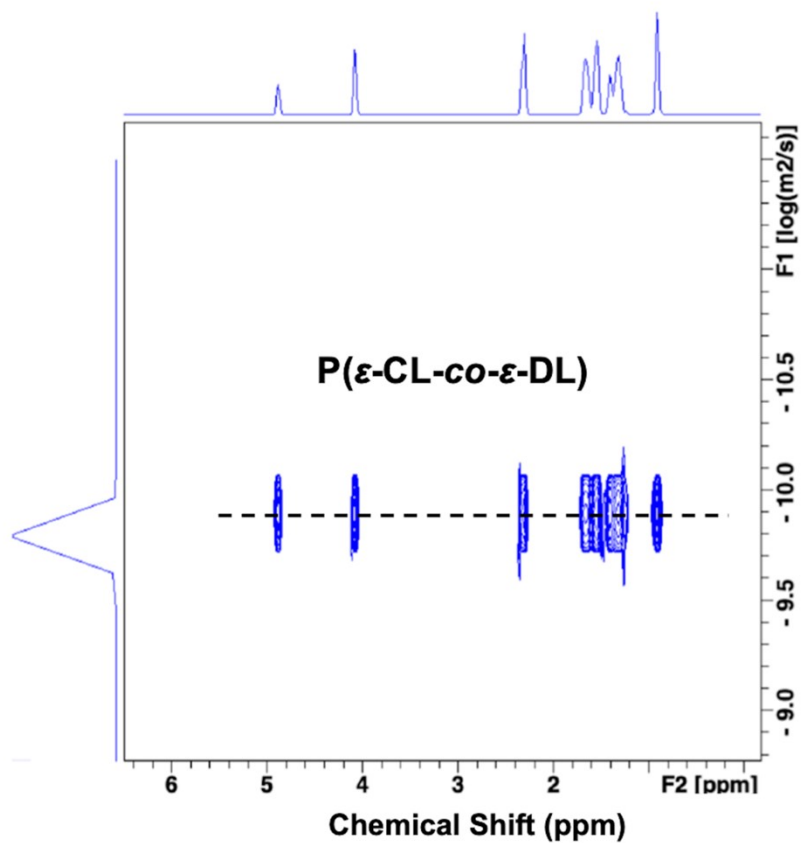
Figure S18. DOSY NMR spectrum of the polymer obtained from the ring-opening copolymerization of *ε*-CL and *ε*-DL by TU3/IMes.

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