

Supplementary Information

Ring-opening metathesis polymerization with 2-5 orders of rate increment

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Table S1. Summary of polymerization rate at different conditions

Fig. S1 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [HCl] = 1 : 2. Measured rate of polymerization $k_{obs} = 5.52 \times 10^{-3} \text{ s}^{-1}$.

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Fig. S3 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.28 \times 10^{-2} \text{ s}^{-1}$.

Fig. S4 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [HCl] = 1 : 8. Measured rate of polymerization $k_{obs} = 1.72 \times 10^{-2} \text{ s}^{-1}$.

Fig. S5 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [HCl] = 1 : 16. Measured rate of polymerization $k_{obs} = 1.72 \times 10^{-2} \text{ s}^{-1}$.

Fig. S6 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 1600 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 5.98 \times 10^{-3} \text{ s}^{-1}$.

Fig. S7 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 3200 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.03 \times 10^{-3} \text{ s}^{-1}$.

Fig. S8 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [H₂SO₄] = 1 : 4. Measured rate of polymerization $k_{obs} = 3.11 \times 10^{-2} \text{ s}^{-1}$.

Fig. S9 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [BF₃] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.66 \times 10^{-2} \text{ s}^{-1}$.

Fig. S10 Kinetic plot of COE (1 M) polymerization at 233 K with G3-BrPy in THF at [G3] : [COE] = 1 : 800 and [G3-BrPy]:[HCl]=1 : 4. Measured rate of polymerization $k_{obs} = 1.10 \times 10^{-2} \text{ min}^{-1}$.

Fig. S11 Kinetic plot of cycloheptene (1 M) polymerization at 233 K with G3 in THF at [G3] : [cycloheptene] = 1 : 800 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.84 \times 10^{-3} \text{ s}^{-1}$.

Fig. S12 Kinetic plot of cyclopentene (1 M) polymerization at 233 K with G3 in THF at [G3] :

[cyclopentene] = 1 : 800 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.10 \times 10^{-2} \text{ s}^{-1}$.

Fig. S13 Kinetic plot of NBE-PLLA macromonomer polymerization with G3 at [G3] : [NBE-PLLA] = 1 : 400. Measured rate of polymerization $k_{obs} = 3.22 \times 10^{-3} \text{ min}^{-1}$.

Fig. S14 Demonstrative ^1H NMR spectrum of the kinetic track for COE polymerization at 233 K with [G3] : [HCl] = 1 : 8 after 7 min of the reaction.

Fig. S15 ^1H NMR spectrum of the synthesized NBE-PLLA macromonomer.

Fig. S16 ^1H NMR spectrum of the synthesized 3-isopropyl-COE monomer.

Fig. S17 ^1H NMR spectrum of the synthesized poly(3-isopropyl-COE).

I. Materials

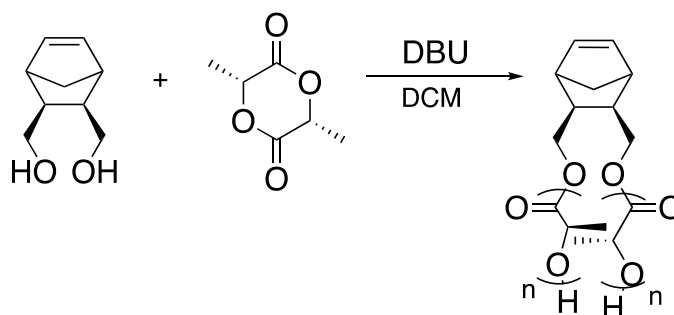
Grubbs' 2nd generation catalyst was purchased from Coach Chem. *Cis*-cyclooctene was purchased from Acros Organics. *Cis*-cyclopentene, *cis*-cycloheptene, ethyl vinyl ether, 1-lactide, and 5-norbornene-2-*exo* (dimethanol-NBE), 3-*exo*-dimethanol, and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purchased from TCI Chemicals. All solvents were dried by molecular sieves before usage. Hydrochloric acid (36.0%), sulfuric acid, and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Trifluoroacetic acid ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) was purchased from Adamas and used as received.

Grubbs' 3rd generation catalysts were synthesized from Grubbs' 2nd generation catalyst using pyridine or 3-bromo-pyridine as ligand for substitution following the established method from reference.^[1] The cyclooctene derivative, 3-isopropyl-COE, was synthesized via a similar route reported previously.^[2]

II. Methods

All NMR experiments were recorded on Bruker 600 MHz or Bruker 700 MHz. Gel permeation chromatography was performed using a Malvern Vescotek GPC (TDA 305 equipped with two T6000M columns) using THF (stabilized) as eluent at a 1 mL min^{-1} flow rate at $35 \text{ }^\circ\text{C}$. The molecular weight and molecular weight distribution were determined using polystyrene standard according to RI signal. All the reaction at 233 K was performed using an EYELA Low TEMP. PAIRSTIRRER PSL-1400.

III. Synthesis of macromonomer NBE-PLA



To a solution of *L*-lactide (10 g) in CH_2Cl_2 (70 mL), a CH_2Cl_2 solution (20 mL) containing dimethanol-NBE (385 mg) and DBU (760 mg) was added. The reaction was stirred at room temperature for 120 s and then quenched with excess amount of acetic acid. The solution was then

concentrated and precipitated using methanol for 6 times for purification to obtain pure white powder (7.9 g) as the macromonomer NBE-PLA. The number-average molecular weight was determined by GPC to be 3.6 kDa with $D = 1.13$ using polystyrene (PS) standard. The number-average molecular weight determined from NMR to be 5.0 kDa. The difference between NMR and GPC reflects the difference between the size of PLLA and PS in THF. The molecular weight determined by NMR was used for the calculation of monomer concentration and catalyst loading.

IV. General polymerization procedure at 233 K

The reaction kinetics studied at 233 K involves different monomers, acids, etc. However, all the experiments followed similar procedure: ($[G3] : [HCl] = 1 : 4$, kinetic measurement at 1 min, COE as monomer with $[M] = 1 \text{ M}$, $[G3] : [COE] = 1 : 800$).

Catalyst preparation:

HCl (36.0%) was first diluted in THF to prepare a 0.25 mol L^{-1} HCl/THF solution. To a THF solution with G3 (2.25 mg in $50 \mu\text{L}$) was added $50 \mu\text{L}$ of the HCl/THF solution. The solution was kept at 233 K for further usage.

Polymerization:

To a 2 mL vial equipped with a stir bar was added *cis*-cyclooctene (55 mg) in THF (total $500 \mu\text{L}$). The vial was placed under 233 K for 20 min for temperature equilibration. A total $20 \mu\text{L}$ of the catalyst solution prepared as mentioned above was added via syringe into the solution. The reaction was kept for 60 s before quenching with $800 \mu\text{L}$ ethyl vinyl ether solution in THF ($v : v = 1 : 1$) via syringe. A part of the solution ($100 \mu\text{L}$) was added into $600 \mu\text{L}$ of *d*-chloroform for NMR experiments to study the conversion of the monomer.

All other kinetic experiments were performed following this procedure with specified monomer, acid, catalyst, catalyst loading, acid loading, etc.

V. Polymerization of 3-isopropyl-COE at 40 °C

($[C] : [M] = 1 : 800$) To a 2 mL vial equipped with a stir bar was added 3-isopropyl-COE (200 mg). The vial was placed at 40 °C for 20 min. A total $52.8 \mu\text{L}$ of the catalyst prepared as described above in *section IV* was added into the monomer to initiate the polymerization. The polymerization kinetics was tracked by extracting reaction aliquots ($20 \mu\text{L}$) into ethyl vinyl ether every minute upon initiation. NMR was used to analyze the monomer conversion. The final polymer obtained after 1 h of the reaction could be hardly dissolved in THF or chloroform.

($[C] : [M] = 1 : 100$) To a 2 mL vial equipped with a stir bar was added 3-isopropyl-COE (200 mg). The vial was placed at 40 °C for 20 min. HCl (36.0%) was first diluted in THF to prepare a 0.25 mol L^{-1} HCl/THF solution. To a vial with G3 (18 mg) was added $400 \mu\text{L}$ of the HCl/THF solution. A total $211.2 \mu\text{L}$ of the catalyst solution was added. The reaction was kept at 40 °C for 30 min before quenching with ethyl vinyl ether. The resultant polymer was precipitated using methanol for three times and then subjected to NMR study.

VI. Polymerization of macromonomer NBE-PLLA at 40 °C

Macromonomer NBE-PLLA was first dissolved into THF to acquire a 200 mg mL⁻¹ macromonomer solution (0.04 M). The macromonomer solution was then added into 4 individual 2 mL vials (1 mL in each vial). HCl (0.5 M in THF) was then added into the 4 vials (A, B, C, and D) with a volume of 0 μL (A), 0 μL (B), 10 μL (C), and 20 μL (D). G3 catalyst solution without acid in THF was prepared with a concentration of 7.27 mg mL⁻¹ and G3 catalyst solution with HCl was prepared as stated in **section IV**. For vial A, C, and D, 10 μL of the G3 catalyst solution without acid was added and then their polymerization kinetics were tracked. For vial B, 1.6 μL of the G3 solution (with HCl, [G3] : [HCl] = 1 : 4) was added and then the polymerization kinetics was tracked.

Reference

- (1) Sanford, M. S.; Love, J. A.; Grubbs, R. H. A versatile precursor for the synthesis of new ruthenium olefin metathesis catalysts. *Organometallics* **2001**, *20*, 5314-5318.
- (2) Radlauer, M. R.; Matta, M. E.; Hillmyer, M. A. Regioselective cross metathesis for block and heterotelechelic polymer synthesis. *Polym. Chem.* **2016**, *7*, 6269-6278.

Table S1. Summary of polymerization rate at different conditions¹

1. All polymerizations (expected for the norbornene experiment with HCl) were performed at 233 K with G3 catalyst at [G3] : [monomer] = 1 : 800 and [G3] : [acid] = 1 : 4.
2. The polymerization of norbornene was performed at 233 K with G3 catalyst at [G3] : [monomer] = 1 : 16000 and [G3] : [acid] = 1 : 4.

monomer	acid	solvent	time	conversion (%)	estimated k_{obs} (s^{-1})
norbornene	--	THF	6 h	76.13	3.52×10^{-5}
norbornene ²	HCl	THF	20 s	12.97	6.95×10^{-3}
cyclooctadiene	--	THF	6 h	8.36	3.87×10^{-6}
cyclooctadiene	HCl	THF	15 s	20.02	1.49×10^{-2}
cyclooctadiene	HCl	THF	40 s	39.76	1.27×10^{-2}
cyclooctene	--	THF	6 h	3.47	1.61×10^{-6}
cyclooctene	--	toluene	6 h	0.97	4.49×10^{-7}
cyclooctene	HCl	toluene	10 s	86.16	1.81×10^{-1}
cyclooctene	HCl	toluene	15 s	93.41	1.98×10^{-1}
cyclooctene	--	chloroform	6 h	0.81	3.77×10^{-7}
cyclooctene	HCl	chloroform	5 s	27.28	6.37×10^{-2}
cyclooctene	HCl	chloroform	15 s	71.01	8.26×10^{-2}
cyclooctene	--	DCM	6 h	0.50	2.30×10^{-7}
cyclooctene	HCl	DCM	5 s	7.90	1.51×10^{-2}
cyclooctene	HCl	DCM	10 s	16.35	1.52×10^{-2}
cyclooctene	HCl	acetone	6 h	1.39	6.44×10^{-7}
cyclooctene	HCl	acetone	5 s	2.41	4.90×10^{-3}
cyclooctene	HCl	acetone	10 s	3.79	3.79×10^{-3}
cyclooctene	H ₃ PO ₄	THF	60 s	0.70	1.16×10^{-4}
cyclooctene	H ₃ PO ₄	THF	75 s	0.77	1.02×10^{-4}
cyclopentene	--	THF	6 h	12.28	5.69×10^{-6}
cycloheptene	--	THF	6 h	1.07	4.95×10^{-7}

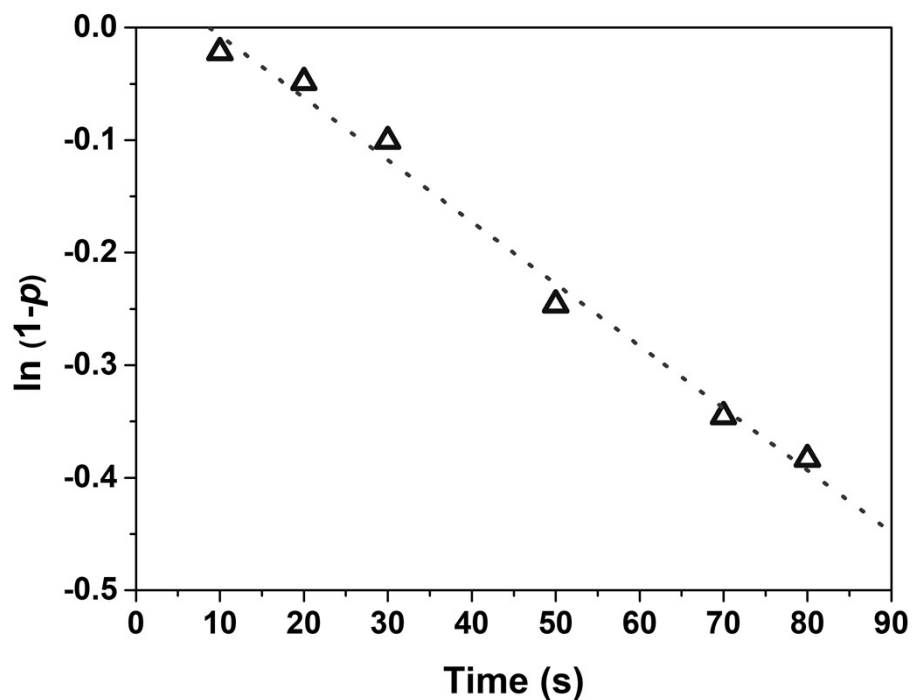


Fig. S1 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 800$ and $[G3] : [HCl] = 1 : 2$. Measured rate of polymerization $k_{obs} = 5.52 \times 10^{-3} \text{ s}^{-1}$.

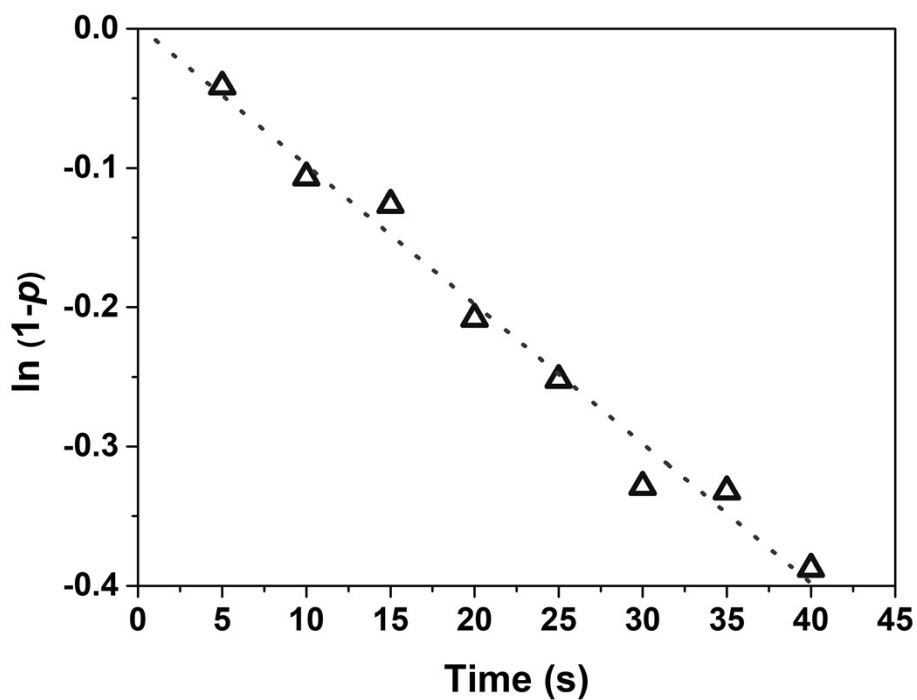


Fig. S2 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 800$ and $[G3] : [HCl] = 1 : 3$. Measured rate of polymerization $k_{obs} = 1.00 \times 10^{-2} \text{ s}^{-1}$.

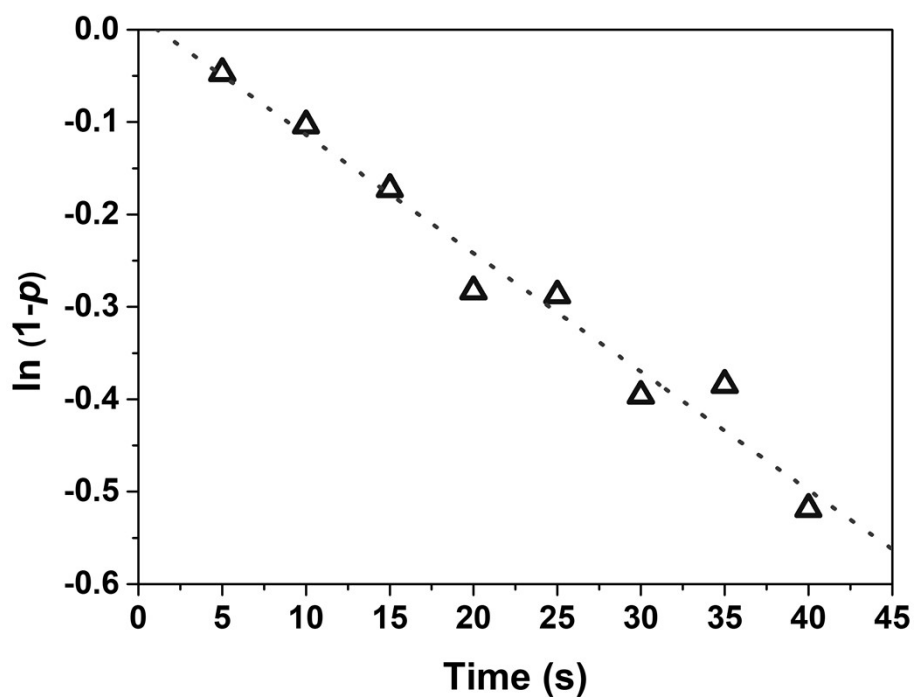


Fig. S3 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 800$ and $[G3] : [HCl] = 1 : 4$. Measured rate of polymerization $k_{obs} = 1.28 \times 10^{-2} \text{ s}^{-1}$.

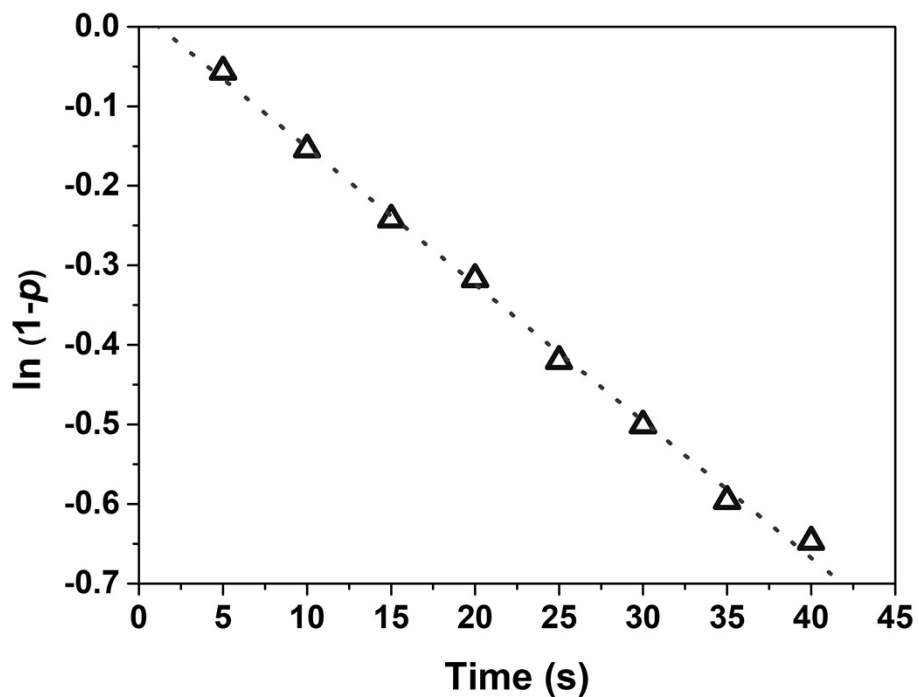


Fig. S4 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 800$ and $[G3] : [HCl] = 1 : 8$. Measured rate of polymerization $k_{obs} = 1.72 \times 10^{-2} \text{ s}^{-1}$.

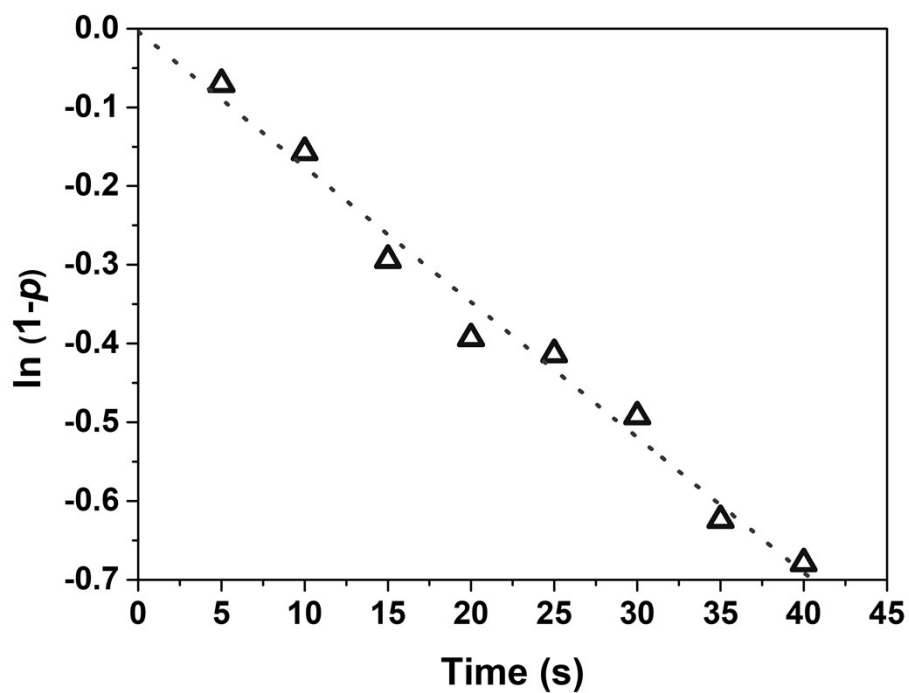


Fig. S5 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [HCl] = 1 : 16. Measured rate of polymerization $k_{obs} = 1.72 \times 10^{-2} \text{ s}^{-1}$.

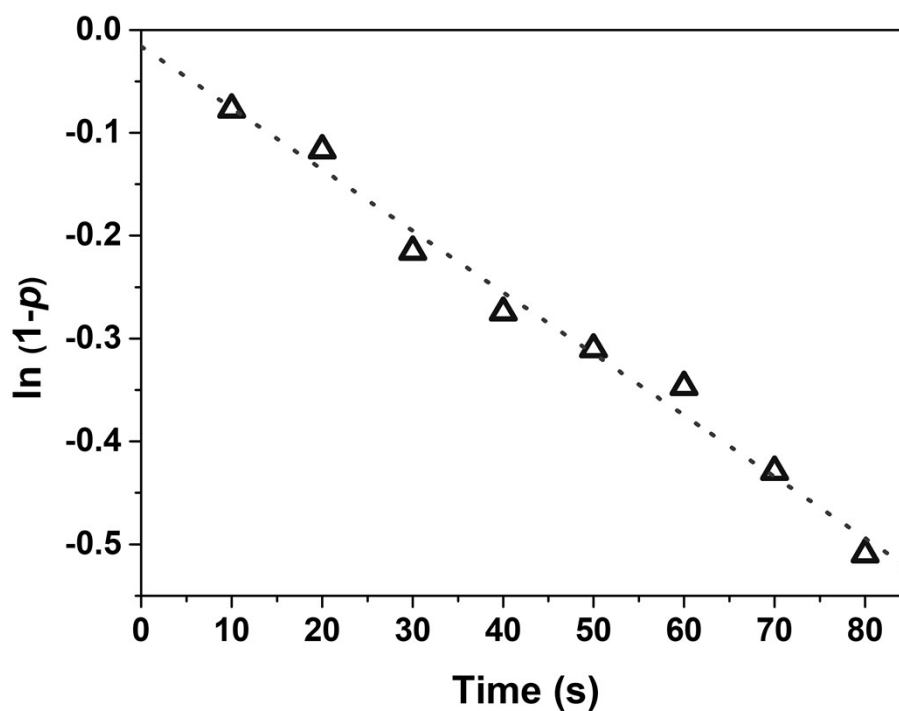


Fig. S6 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 1600 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 5.98 \times 10^{-3} \text{ s}^{-1}$.

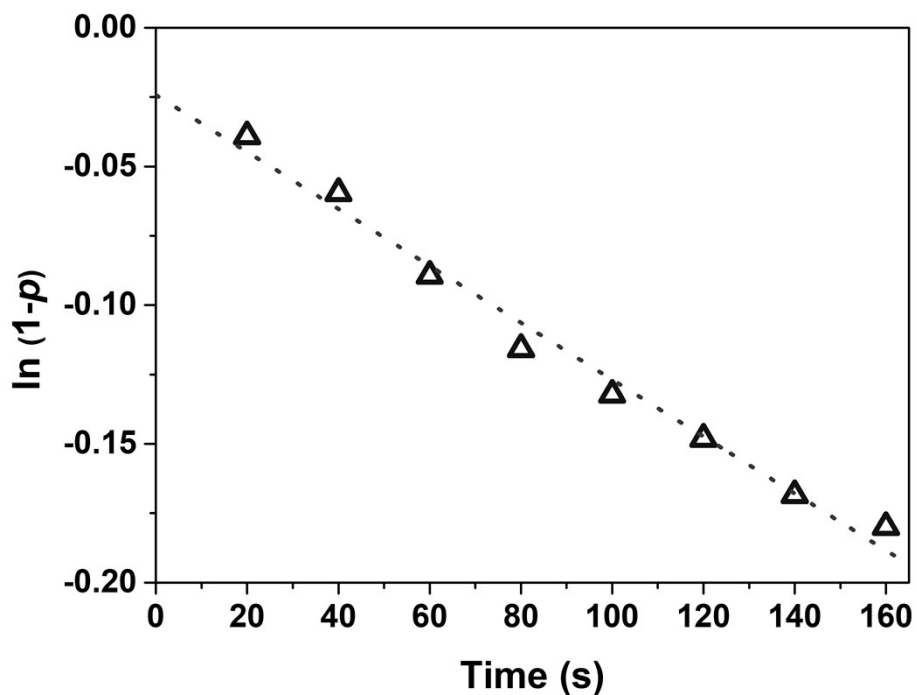


Fig. S7 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 3200$ and $[G3] : [HCl] = 1 : 4$. Measured rate of polymerization $k_{obs} = 1.03 \times 10^{-3} \text{ s}^{-1}$.

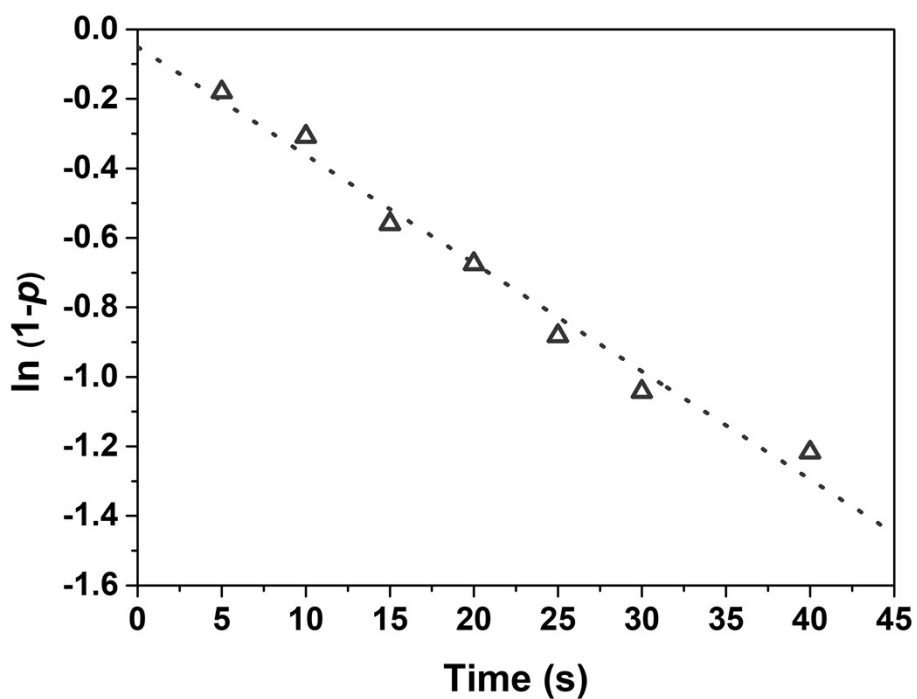


Fig. S8 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at $[G3] : [COE] = 1 : 800$ and $[G3] : [H_2SO_4] = 1 : 4$. Measured rate of polymerization $k_{obs} = 3.11 \times 10^{-2} \text{ s}^{-1}$.

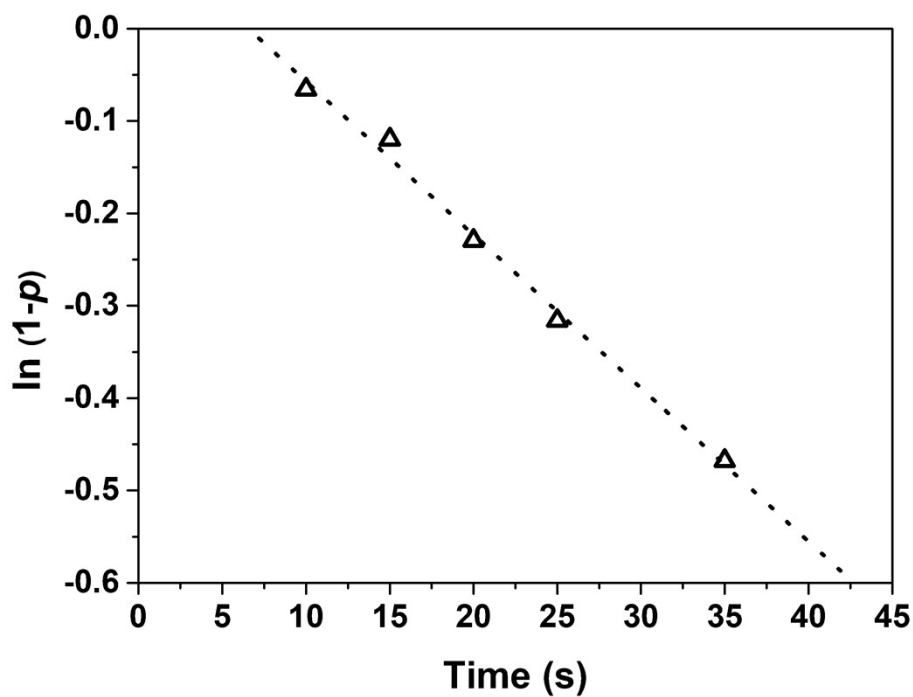


Fig. S9 Kinetic plot of COE (1 M) polymerization at 233 K with G3 in THF at [G3] : [COE] = 1 : 800 and [G3] : [BF₃] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.66 \times 10^{-2} \text{ s}^{-1}$.

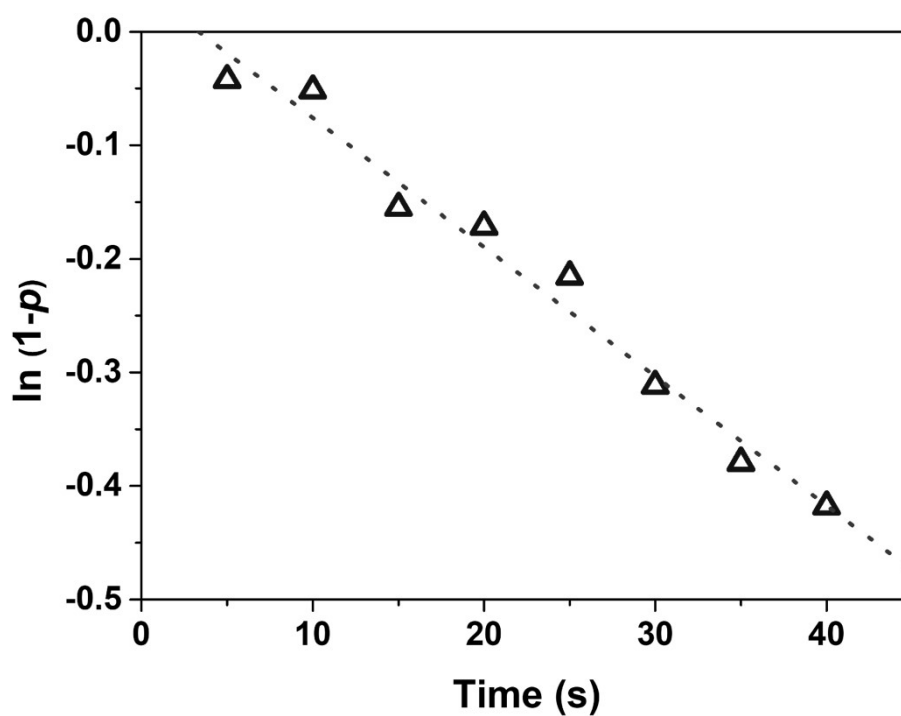


Fig. S10 Kinetic plot of COE (1 M) polymerization at 233 K with G3-BrPy in THF at [G3] : [COE] = 1 : 800 and [G3-BrPy] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.10 \times 10^{-2} \text{ min}^{-1}$.

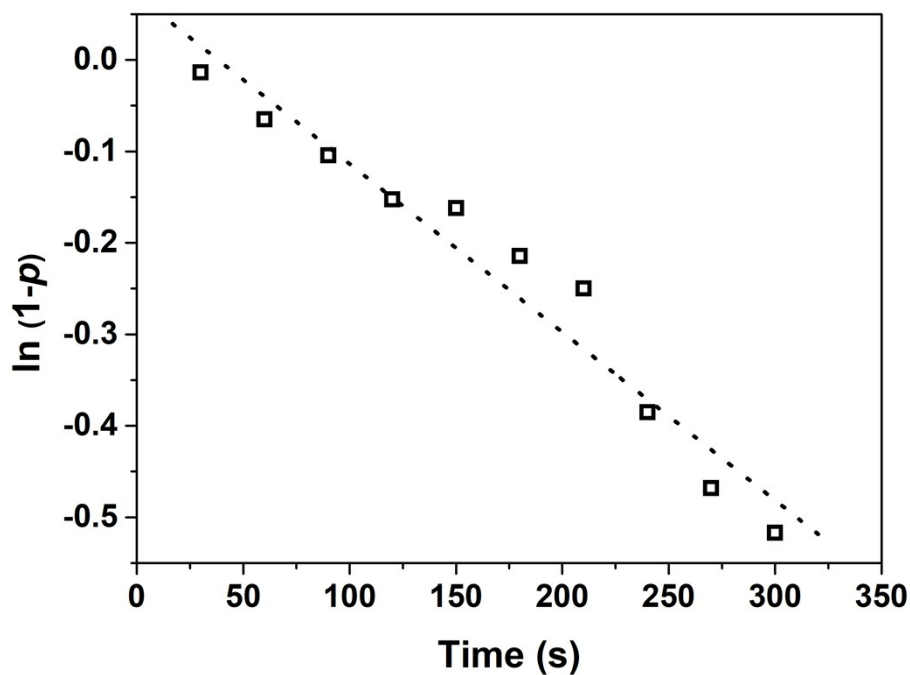


Fig. S11 Kinetic plot of cycloheptene (1 M) polymerization at 233 K with G3 in THF at [G3] : [cycloheptene] = 1 : 800 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.84 \times 10^{-3} \text{ s}^{-1}$.

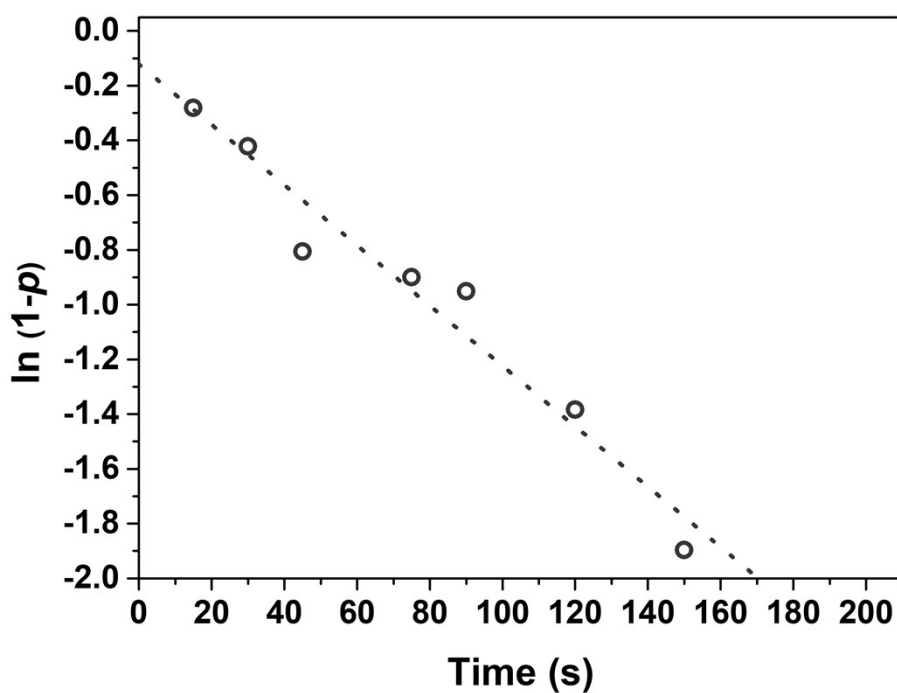


Fig. S12 Kinetic plot of cyclopentene (1 M) polymerization at 233 K with G3 in THF at [G3] : [cyclopentene] = 1 : 800 and [G3] : [HCl] = 1 : 4. Measured rate of polymerization $k_{obs} = 1.10 \times 10^{-2} \text{ s}^{-1}$.

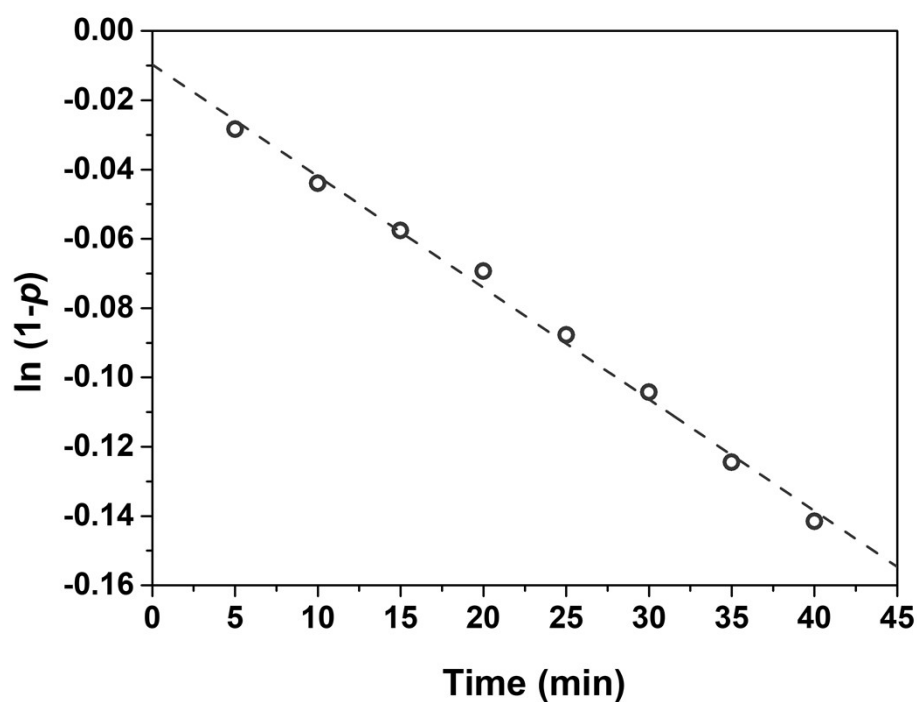


Fig. S13 Kinetic plot of NBE-PLLA macromonomer polymerization (0.05 M) with G3 at [G3] : [NBE-PLLA] = 1 : 400. Measured rate of polymerization $k_{obs} = 3.22 \times 10^{-3} \text{ min}^{-1}$.

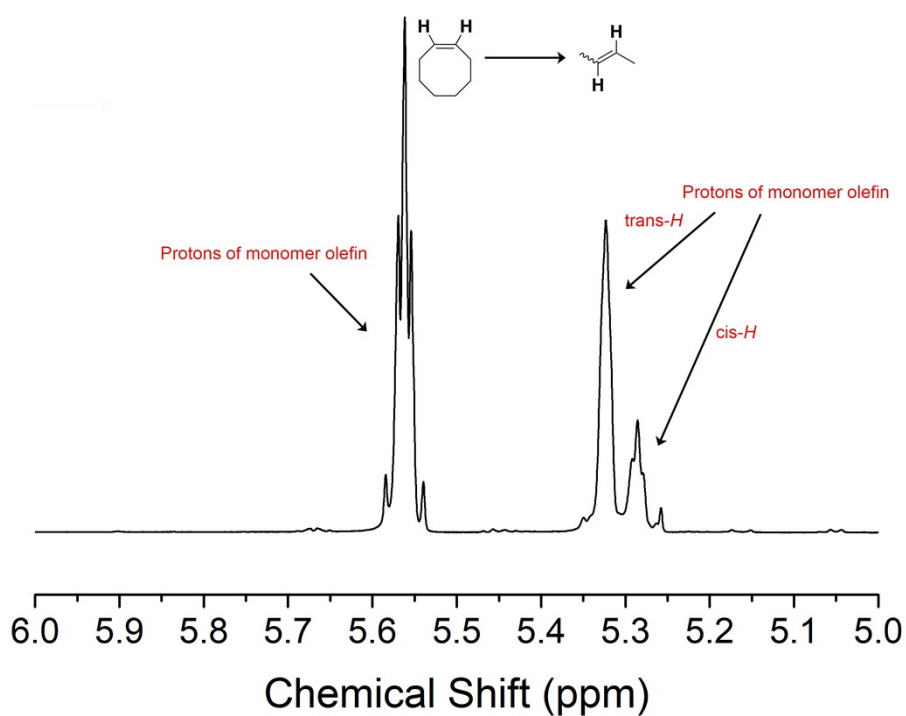


Fig. S14 Demonstrative ^1H NMR spectrum of the kinetic track for COE polymerization at 233 K with [G3] : [HCl] = 1 : 8 after 7 min of the reaction.

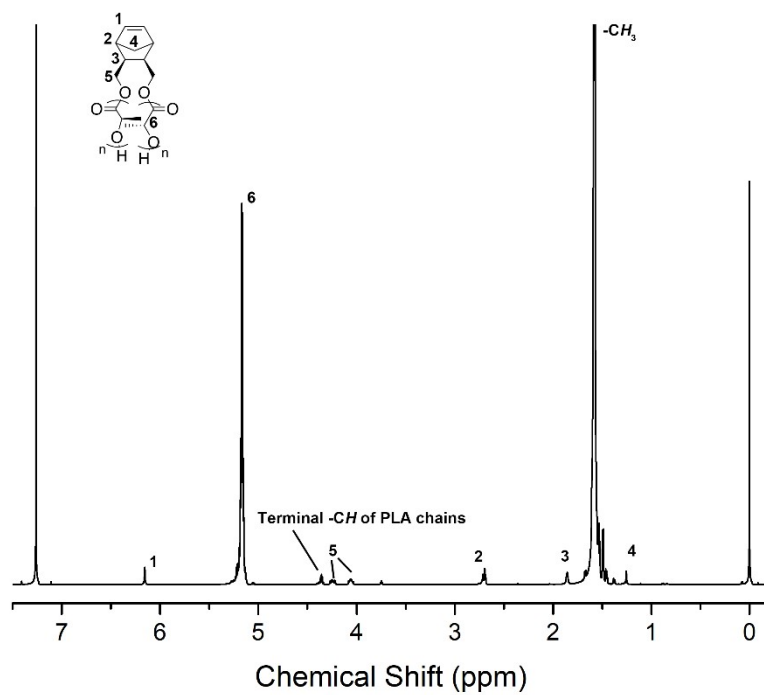


Fig. S15 ^1H NMR spectrum of the synthesized NBE-PLLA macromonomer.

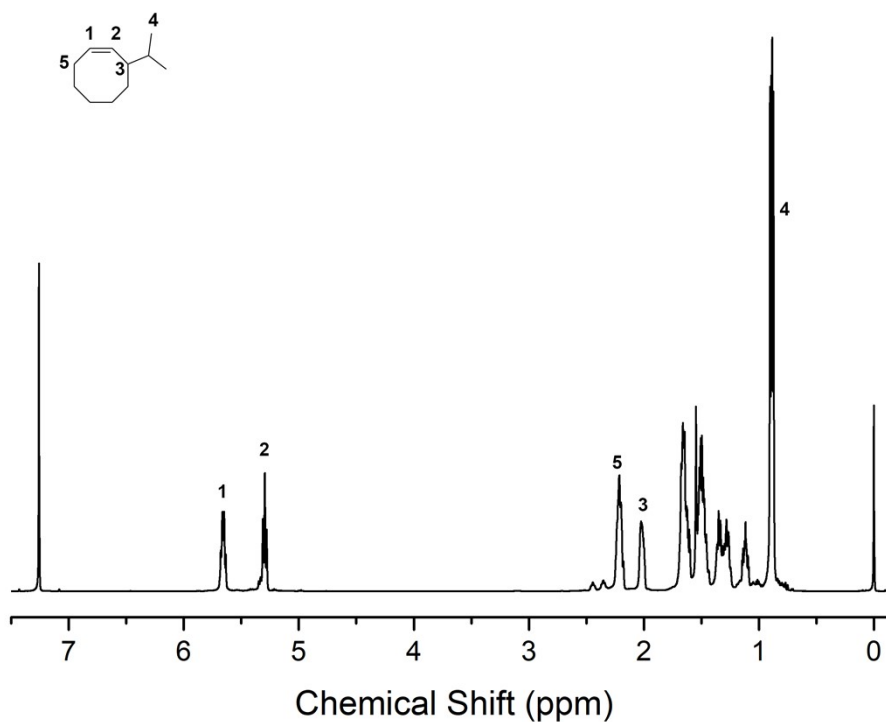


Fig. S16 ^1H NMR spectrum of the synthesized 3-isopropyl-COE monomer.

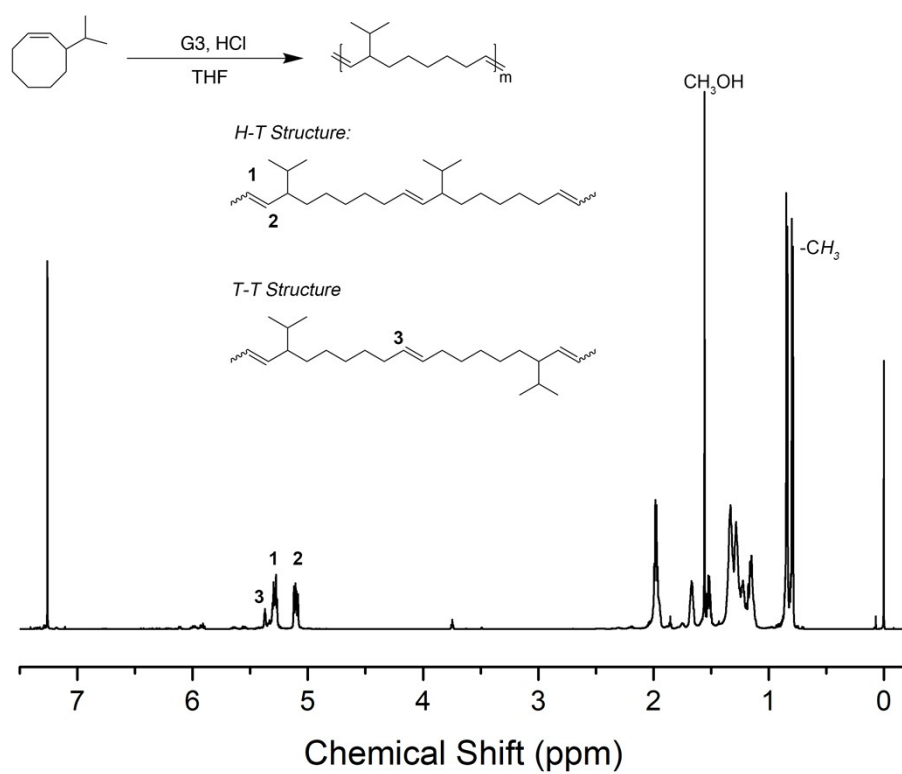


Fig. S17 ¹H NMR spectrum of the synthesized poly(3-isopropyl-COE).