

Supporting information

Simple Lewis pair of zinc salts and organobases as bifunctional catalysts for controlled ring-opening polymerization of *O*-carboxyanhydrides

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Experimental Section.

General Methods.

All polymerizations were carried out in a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a Vigor glovebox. Anhydrous dichloromethane (DCM), anhydrous dimethylformamide (DMF), anhydrous chloroform (TCM), anhydrous 1,4-dioxane, anhydrous tetrahydrofuran (THF), anhydrous toluene and L-phenylalanine were purchased from J&K SCIENTIFIC LTD and used without treatment. Zn(OTf)₂, Zn(OAc)₂, ZnCl₂, ZnBr₂, ZnI₂ were purchased from Alfa Aesar and used without treatment. Triphosgene purchased from Innochem was used without treatment. 1-Benzyl alcohol, hexanol, trimethylol propane (TMOP) and pentaerythritol (PT) purchased from Acros were dried with KOH for overnight, following distillation in vacuum three times. Single hydroxyl-terminated poly(ethyl glycol) (mPEGOH) and double hydroxyl-terminated poly(ethyl glycol) (HOPEGOH) were treated by azeotropic distillation in toluene. CDCl₃, d₄-THF, C₇D₈ and CD₂Cl₂ were purchased from Cambridge Isotope Laboratories Inc. 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 4-dimethylaminopyridine (DMAP) purchased from Innochem were used without treatment.

Characterization.

The ¹H NMR were carried out on a 400 MHz or 500 MHz NMR instrument (Bruker Corporation, Germany) at room temperature using CDCl₃ (δ = 7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR), C₇D₈ or THF-d₈ as solvent. GPC measurements were carried out by Agilent LC 1260 instrument equipped with a differential refractive-index detector. One guard column and two 7.5 x 300 mm PLgel MIXED-C columns were used. The measurements were performed using THF as eluent (flow rate of 1.0 mL/min at 35 °C), and polystyrene standards were employed for calibration. Polymer solutions with concentrations between 3.0 and 5.0 mg/mL were injected at an injection volume of 40 μL. Desorption/ionization-time of flight mass spectrometer (MALDI-TOF MS) experiments were carried out on a Bruker Autoflex III (laser frequency 100 Hz, 355 nm and detector voltage of 1689 V). *In situ* IR study of monomer polymerization was carried out by using ReactIR 15^m with MCT Detector from METTLER TOLEDO AutoChem. DiComp (Diamond) probe was connected via AgX 6 mm x 2 m Fiber (Silver Halide). Spectra were taken from 2000 cm⁻¹ to 650 cm⁻¹ at 8 wavenumber resolution and the

automatic sampling interval was 15 second. In the process of polymerization, the polymerization solution was taken from the system at the determined time, and spotted on the KBr plate for scanning on FT-IR (Nicolet 6700, the accumulation rate was 16 times with 4 wavenumber resolution). The monomer conversion was determined by the intensity ratio between 1760 cm^{-1} and 1800 cm^{-1} , $\text{conversion\%} = I_{1760} / (I_{1760} + I_{1800})$.¹

Synthesis of OCA monomers

As reported¹, L-PheOCA was synthesized by the modified procedure.

The preparation of 2-hydroxyl-3-phenylpropanoic acid (HPPA). L-Phenylalanine (33.04 g, 200 mmol) in 1 M sulfuric acid was diazotized with 5 M sodium nitrite (3.0 equiv, 600 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and then kept stirring at room temperature overnight. The reaction mixture was extraction with ethyl acetate (3 × 300 mL). The combined extracts were washed with brine (3 × 100 mL), dried over anhydrous MgSO_4 , filtered and evaporated to give a white solid. Upon recrystallization from diethyl ether, pure 2-hydroxyl-3-phenylpropanoic acid was afforded in a yield of 81%. ¹H NMR (CDCl_3 , 400 MHz, δ ppm): 7.24-7.33 (m, 5H, *ArH*), 4.53 (dd, $J = 7.2$ Hz, 2H, -CH), 3.19-3.24 (dd, $J = 14.0$ Hz, 1H, CH_2), 2.98-3.03 (dd, $J = 14.0$ Hz, 1H, CH_2). ¹³C NMR (CDCl_3 , 100 MHz, δ ppm): 40.33 (- CH_2), 71.15 (CH), 127.36 (*ArC*), 128.79 (*ArC*), 129.68 (*ArC*), 135.93 (*ArC*), 177.87 (C=O).

Preparation of L-PheOCA. To a solution of HPPA (30.0 mmol) and activated charcoal (~90 mg) in anhydrous THF (30 mL), triphosgene (20 mmol) was added in one portion. The reaction mixture was stirred for 8 hours at room temperature. The mixture was filtered over celite, the filtrate was concentrated and the resulting residue was recrystallized from THF/hexane (v/v = 6/25) four times to give colourless crystal in a yield of 52%. ¹H NMR (CDCl_3 , 500 MHz, δ ppm): 7.34-7.35 (m, 3H, *ArH*), 7.21-7.23 (m, 2H, *ArH*), 5.29 (t, $J = 4.5$ Hz, 1H, CH), 3.36-3.40 (dd, $J = 15.0$ Hz, 1H, CH_2), 3.22-3.26 (dd, $J = 15.0$ Hz, 1H, CH_2). ¹³C NMR (CDCl_3 , 125 MHz, δ ppm): 36.57 (- CH_2), 80.03 (CH), 128.56 (*ArC*), 129.31 (*ArC*), 129.80 (*ArC*), 131.64 (*ArC*), 147.92 (OC=OO), 166.44(C=OO).

Polymerization procedure.

A typical procedure for polymerization of Phe-OCA was performed in a 25 mL Schlenk in a Vigor glovebox. The given amount of Lewis acid and 1-hexylamine was stirred in 1.0 mL anhydrous THF before taken out from the glovebox. The reaction mixture was then connected

to a vacuum line and stirred for 10 min at 50 °C, followed by adding 144.2 mg PheOCA (0.75 mmol). After a specific time, a small aliquot of polymer solution was taken out for determining monomer conversion. The final reaction solution was precipitated in the mixture of diethyl ether/hexane (v/v = 1/2), and washed twice using the same solution. The obtained polymers were dried under vacuum.

Reference:

[1] Qian Y, Rong T, Yun X X, Lawrence W. D, Timothy M. F, Jian J C. *Biomacromolecules* **2013**, *14*, 920.

Table S1. ROP of L-PheOCA with varying molar ratios of Zn(OAc)₂ and DBU and benzyl alcohol.

run	Zn(OAc)/DBU /[BnOH]/PheOCA ^b	Time (h)	Conv. ^c [%]	M _{n, theo} ^d [kg/mol]	M _{n, SEC} ^e [kg/mol]	Đ ^e
1	2/2/1/50	4	>95	7.1	7.0	1.09
2	2/2/1/50	4+4	>95	7.1	6.9	1.10
3	2/1/1/50	10.0	87	6.5	7.2	1.07
4	2/2/1/50	4.0	>95	7.1	5.8	1.10
5	2/3/1/50	3.7	>95	7.1	6.3	1.11
6	2/4/1/50	3.0	>95	7.1	7.7	1.08
7	3/3/0.5/50	5.5	>95	14.2	13.7	1.12
8	3/3/1/50	1.0	>95	7.1	7.9	1.11
9	3/3/2/50	0.52	>95	3.6	3.9	1.12
10	3/3/3/50	0.40	>95	2.4	2.1	1.14
11	1/3/1/50	4.0	50	3.7	6.2	1.09
12	2/3/1/50	4.0	77	5.7	7.7	1.10
13	2.5/3/1/50	3.5	>95	7.1	6.2	1.16

^a Performed at 25 °C. Note: ^b Indicating the feeding molar ratio of Zn(OAc)₂, DBU and BnOH. ^c The monomer conversion was determined by the intensity ratio between 1760 cm⁻¹ and 1800 cm⁻¹ in FT-IR spectroscopy. Conv.% = I₁₇₆₀ / (I₁₇₆₀ + I₁₈₀₀). ^d Calculated by [M]₀/[I]₀ × (M_w of monomer - M_w of CO₂) × monomer conversion + M_w of initiator. ^e Measured by GPC in THF against polystyrene standards.

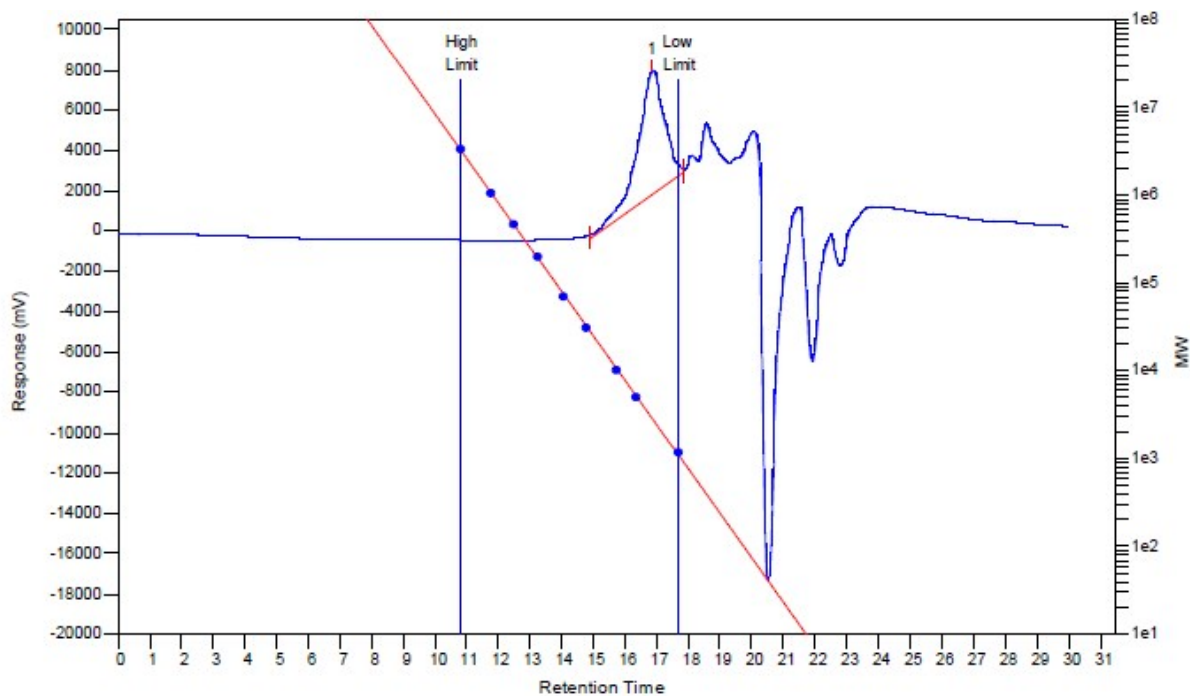


Figure S1. GPC curve of the resulting polymer at the catalysis of DBU only in DCM at 25 °C, $[L\text{-PheOCA}]/[\text{DBU}] = 50:2$.

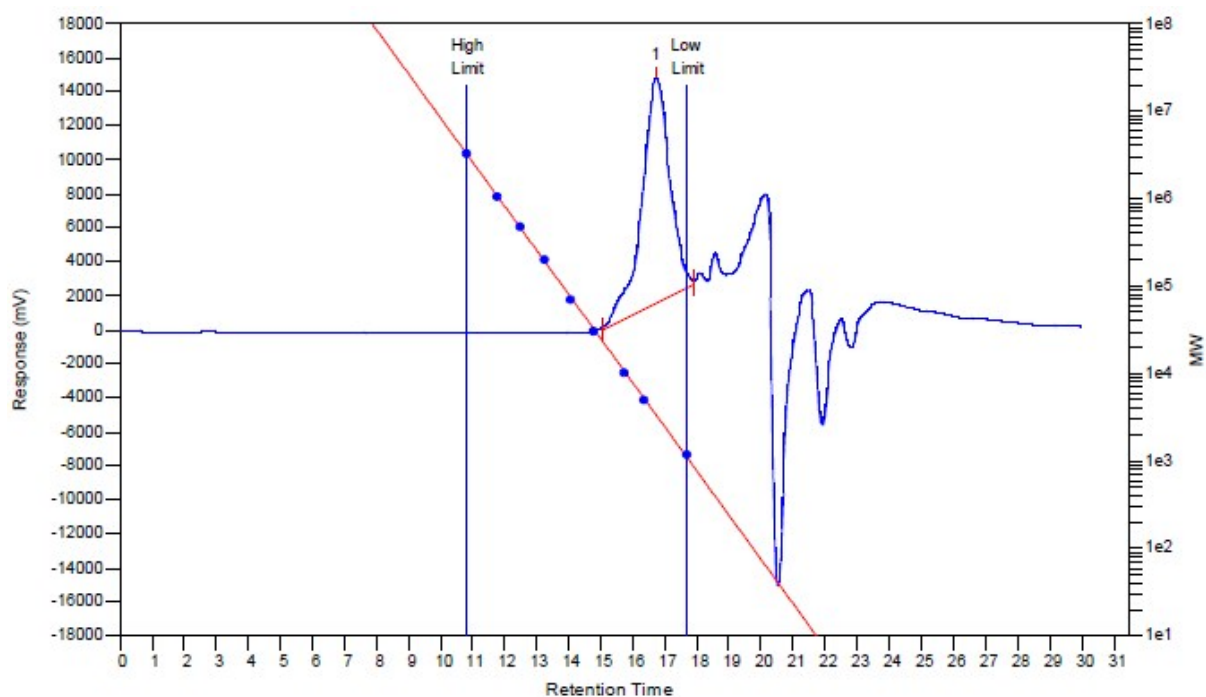


Figure S2. GPC curve of the resulting polymer in the catalysis of DBU and BnOH with molar ratio of 2:1 in DCM at 25 °C, $[L\text{-PheOCA}]/[\text{BnOH}] = 50:1$.

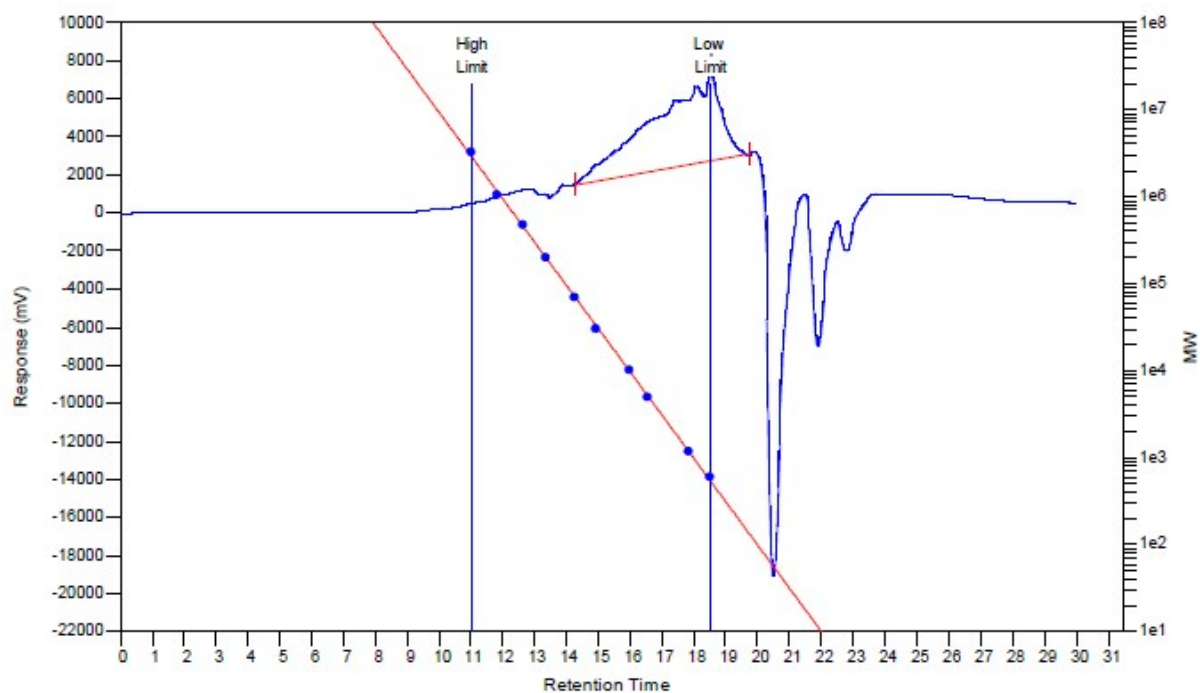


Figure S3. GPC curve of the resulting polymer in the catalysis of DBU and $\text{Zn}(\text{OAc})_2$ in the equimolar in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{DBU}] = 50:1$.

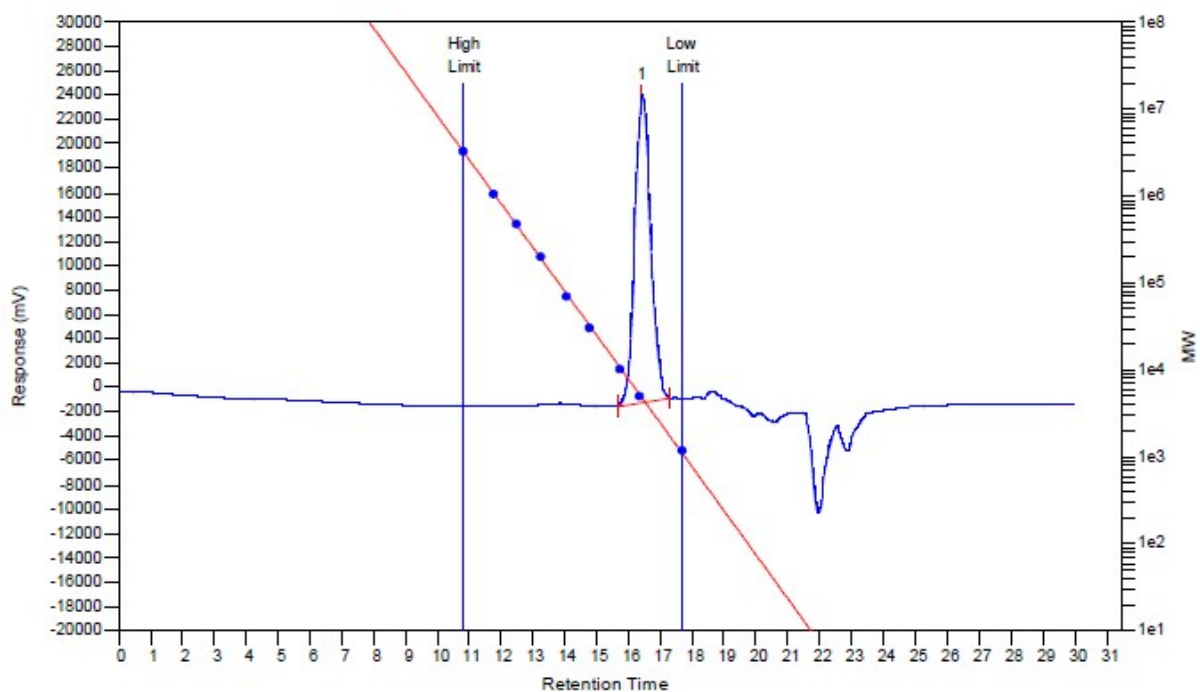


Figure S4. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH in the equimolar in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

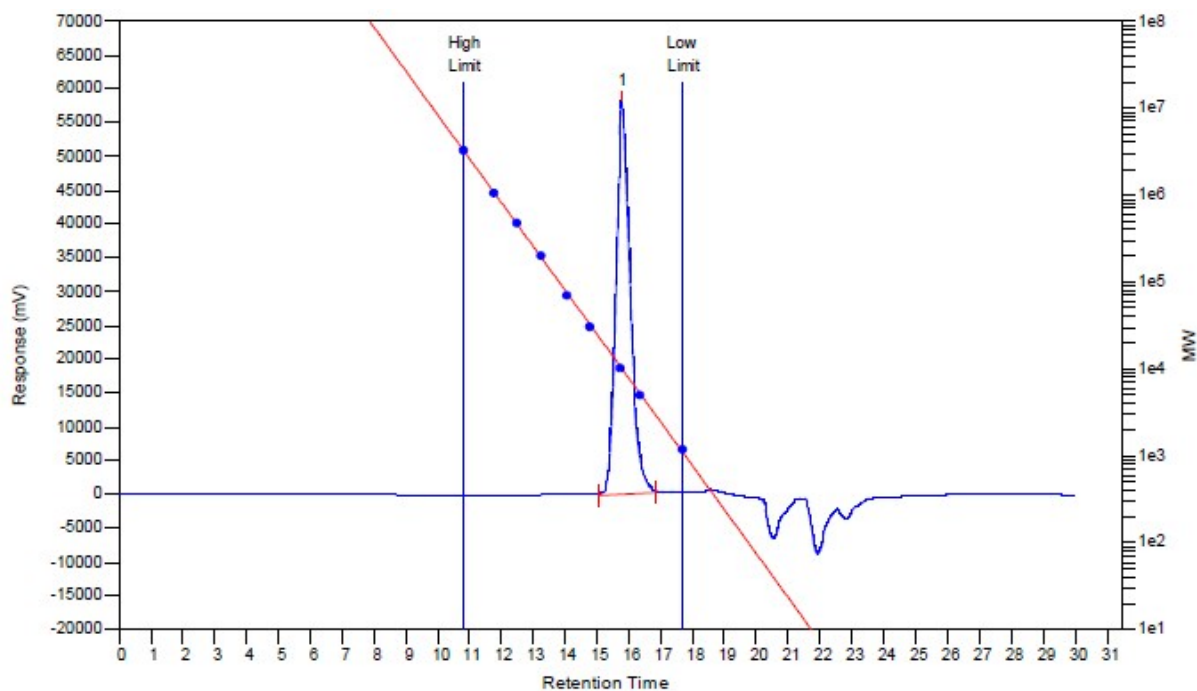


Figure S5. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

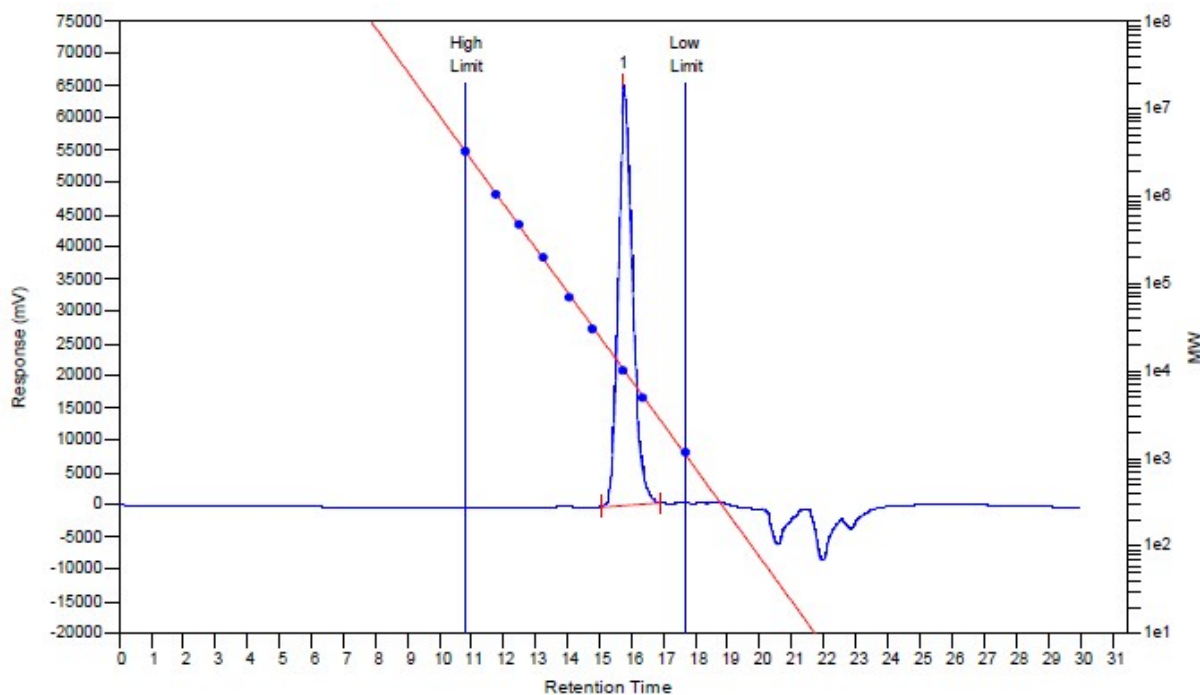


Figure S6. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 3:3:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

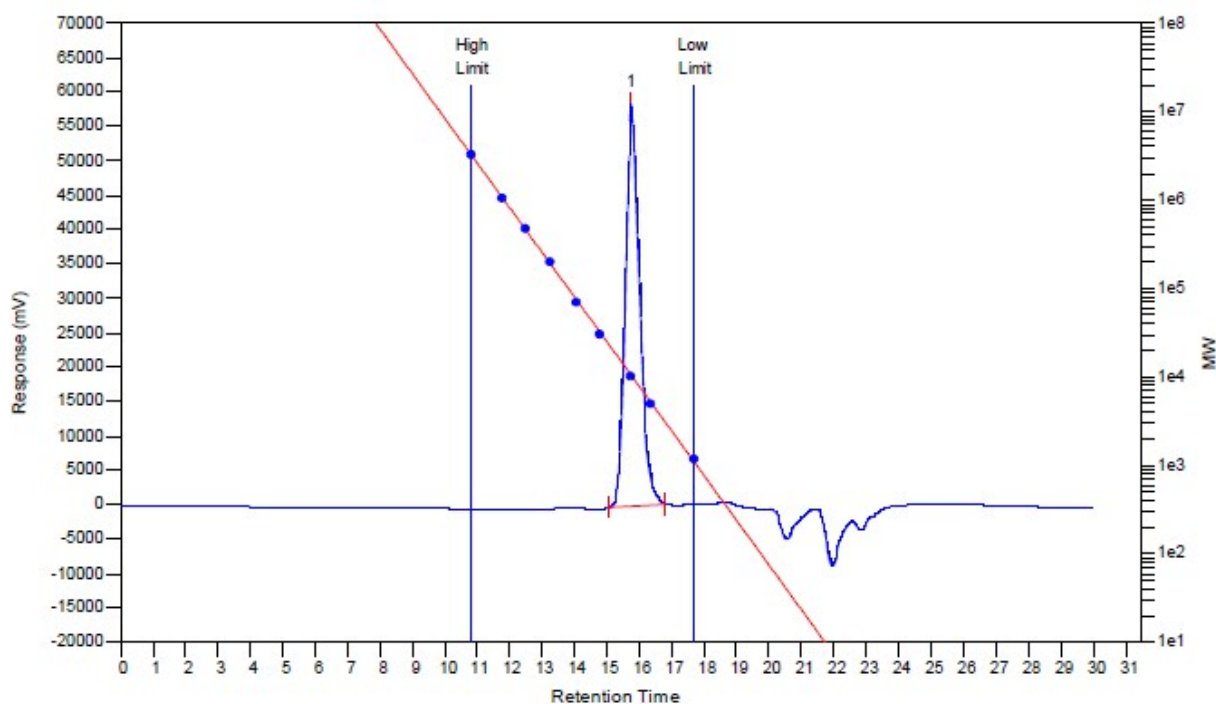


Figure S7. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 4:4:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

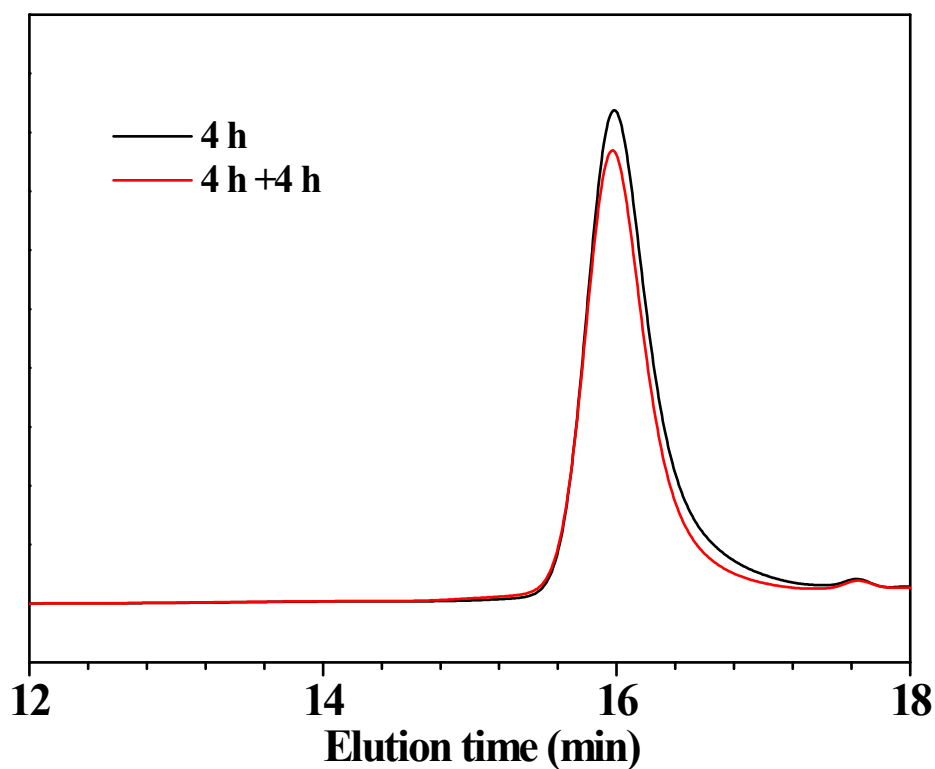


Figure S8. GPC curves of PheOCA polymerization for 4 h and 8 h.

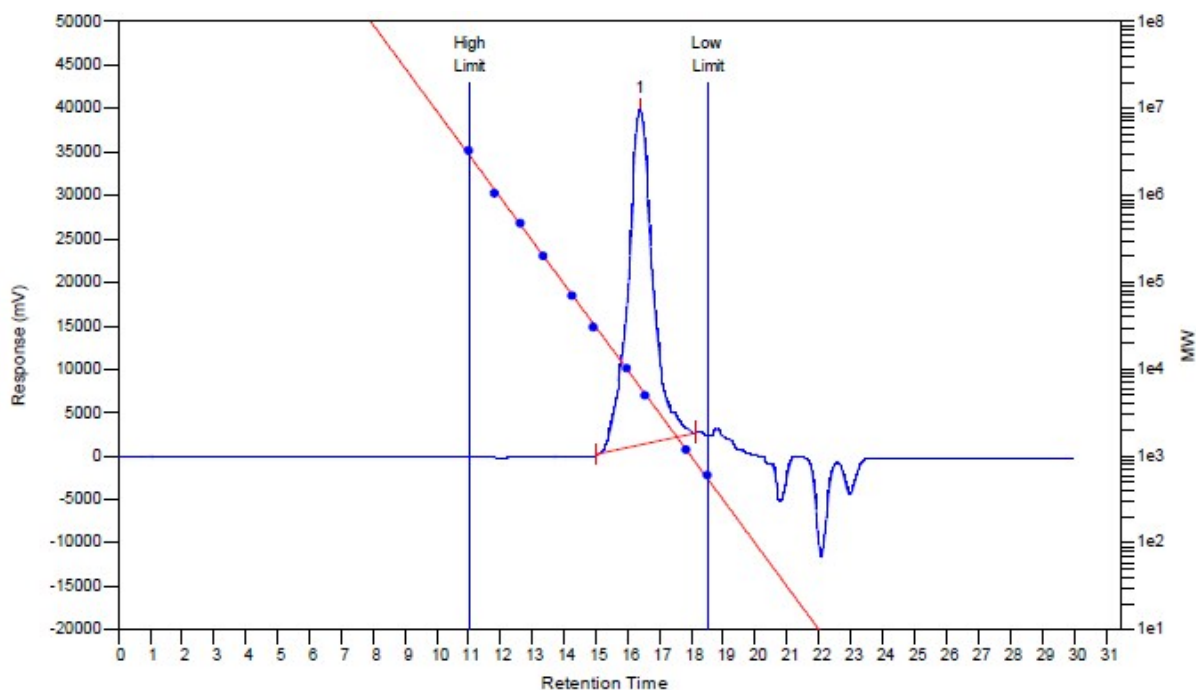


Figure S9. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 4:4:1 in DCM at 25 °C. $[\text{L-PheOCA}]/[\text{BnOH}] = 25:1$.

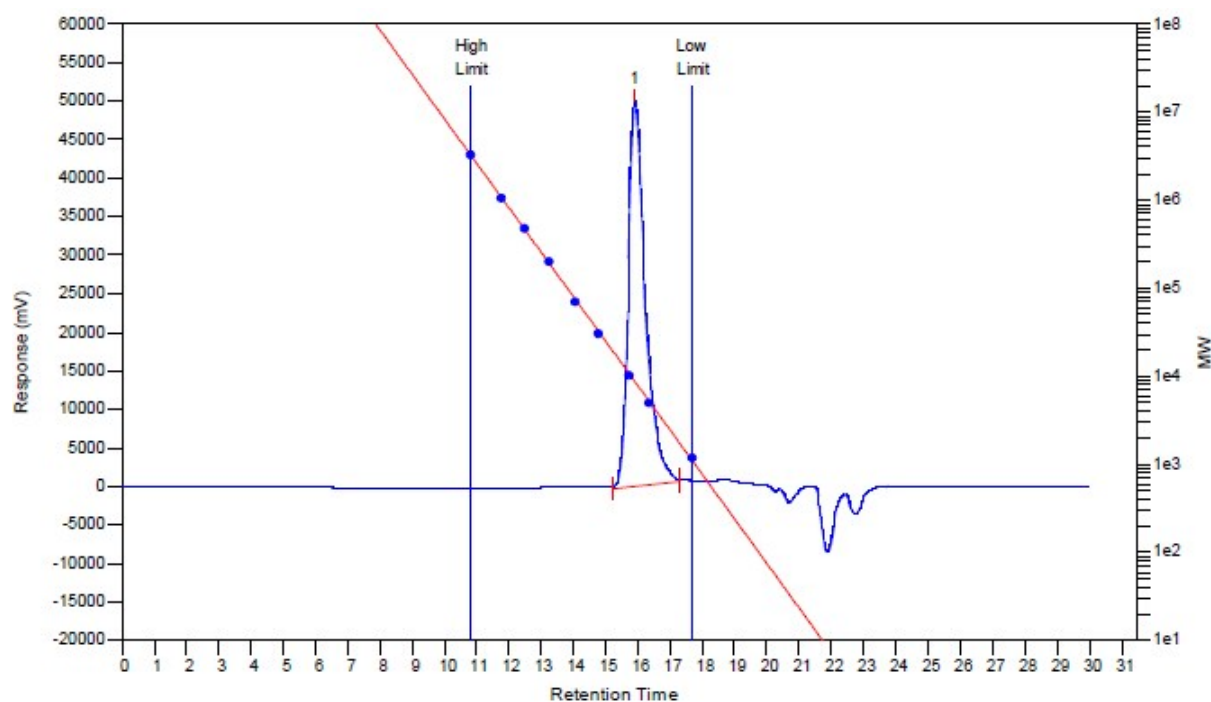


Figure S10. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 4:4:1 in DCM at 25 °C. $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

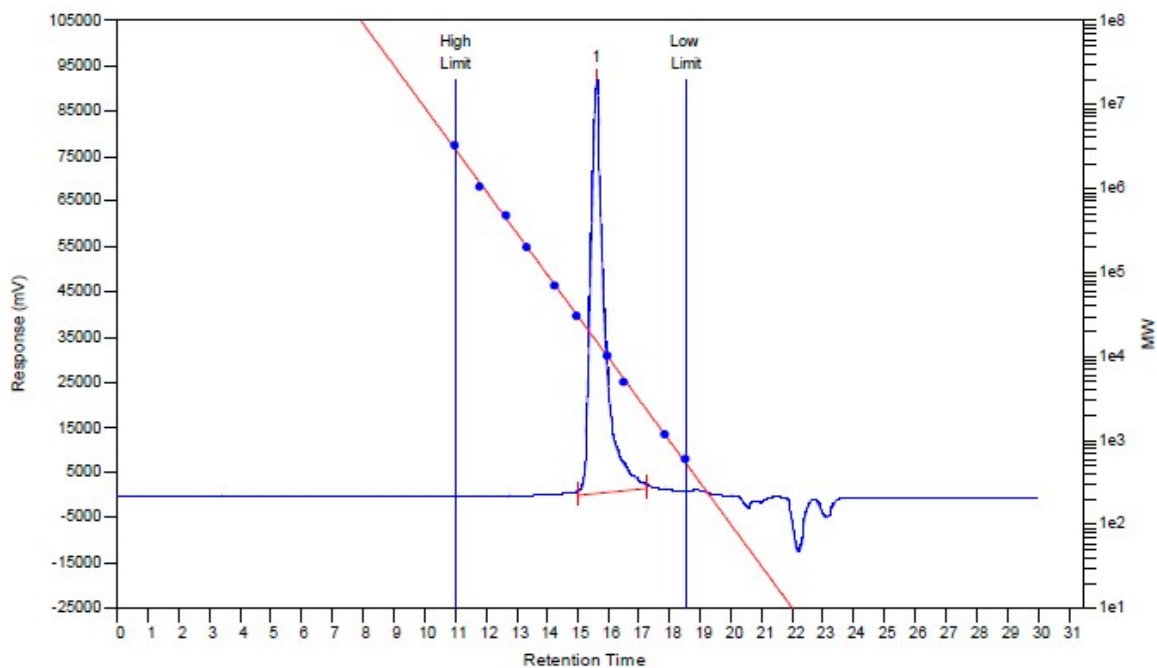


Figure S11. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 4:4:1 in DCM at 25 °C. $[\text{L-PheOCA}]/[\text{BnOH}] = 75:1$.

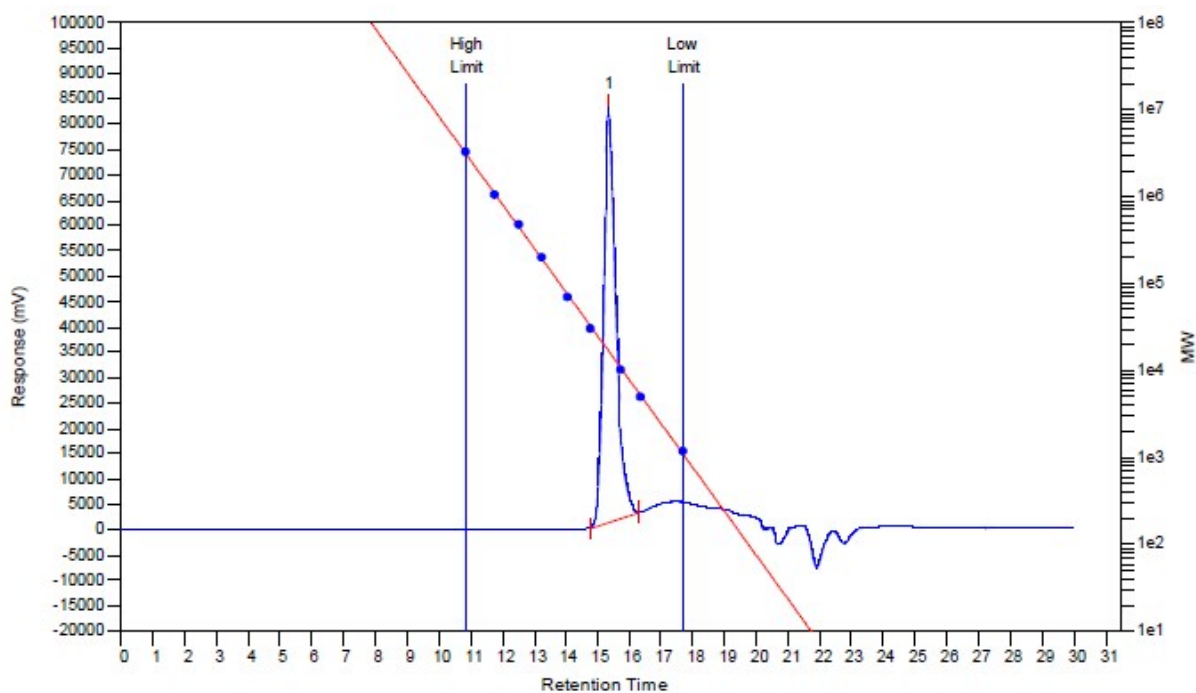


Figure S12. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 4:4:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 100:1$.

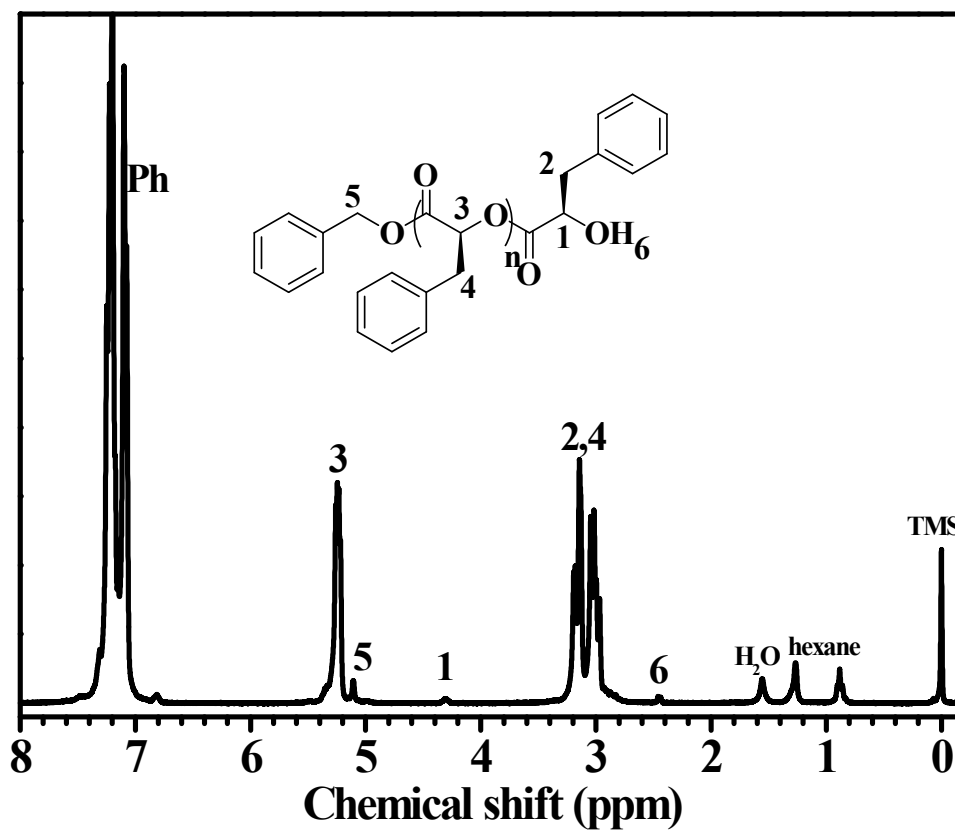


Figure S13. ^1H NMR spectrum of the polymer obtained with the molar ratio of $\text{Zn}(\text{OAc})_2$, DBU, BnOH and L-PheOCA to 2:2:1:50.

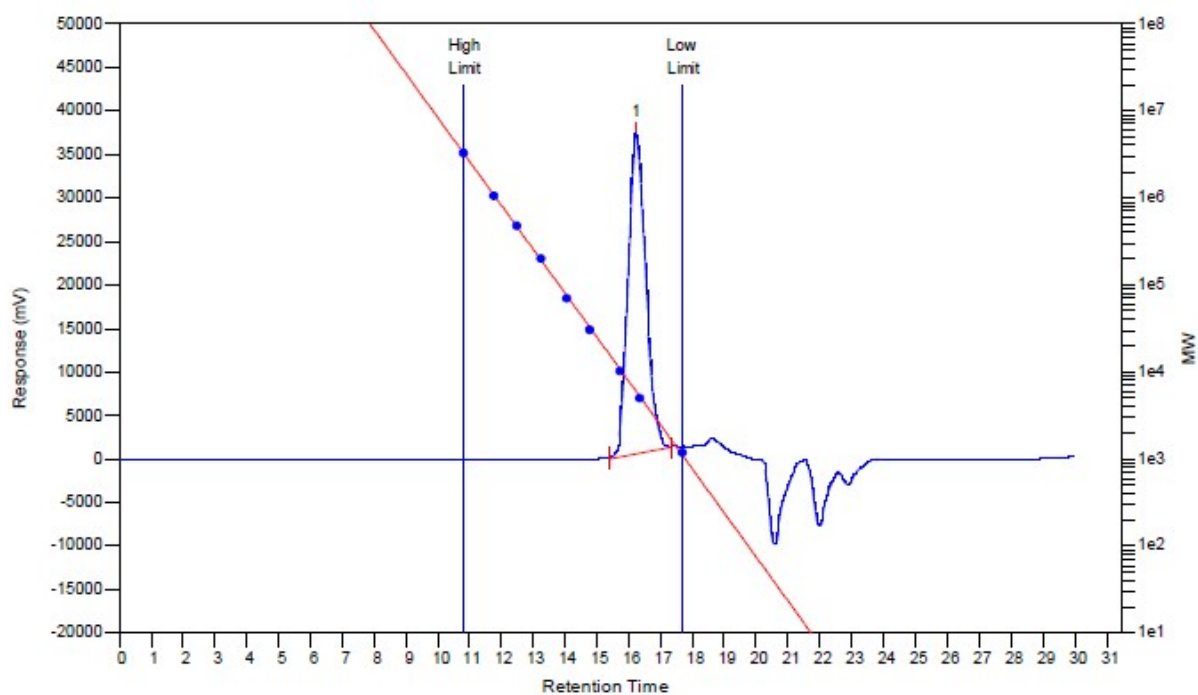


Figure S14. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH

with molar ratio of 2:2:1 in THF at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

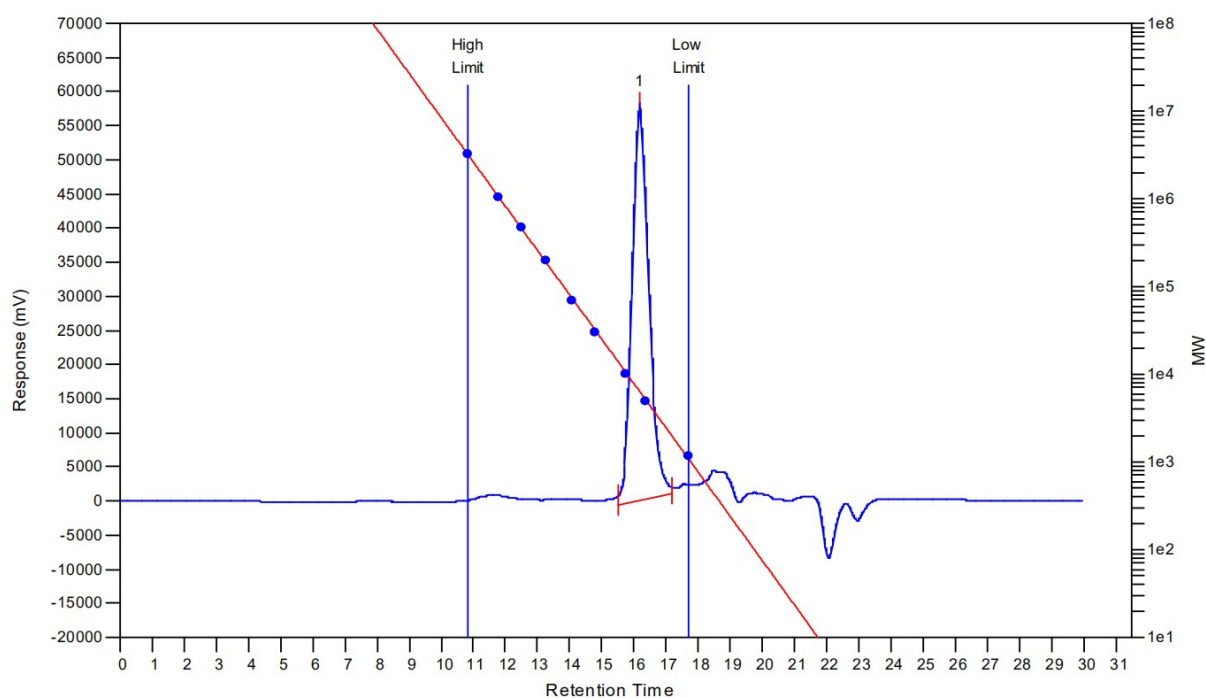


Figure S15. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 2:2:1 in dioxane at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

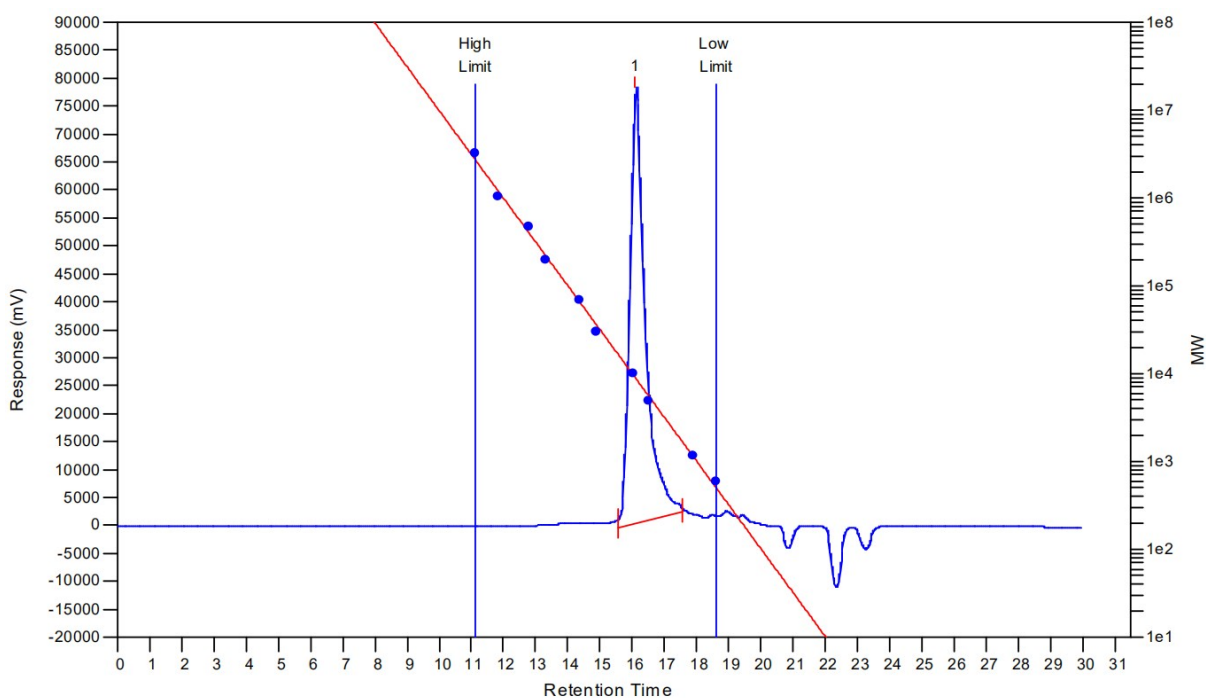


Figure S16. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 2:2:1 in CHCl_3 at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

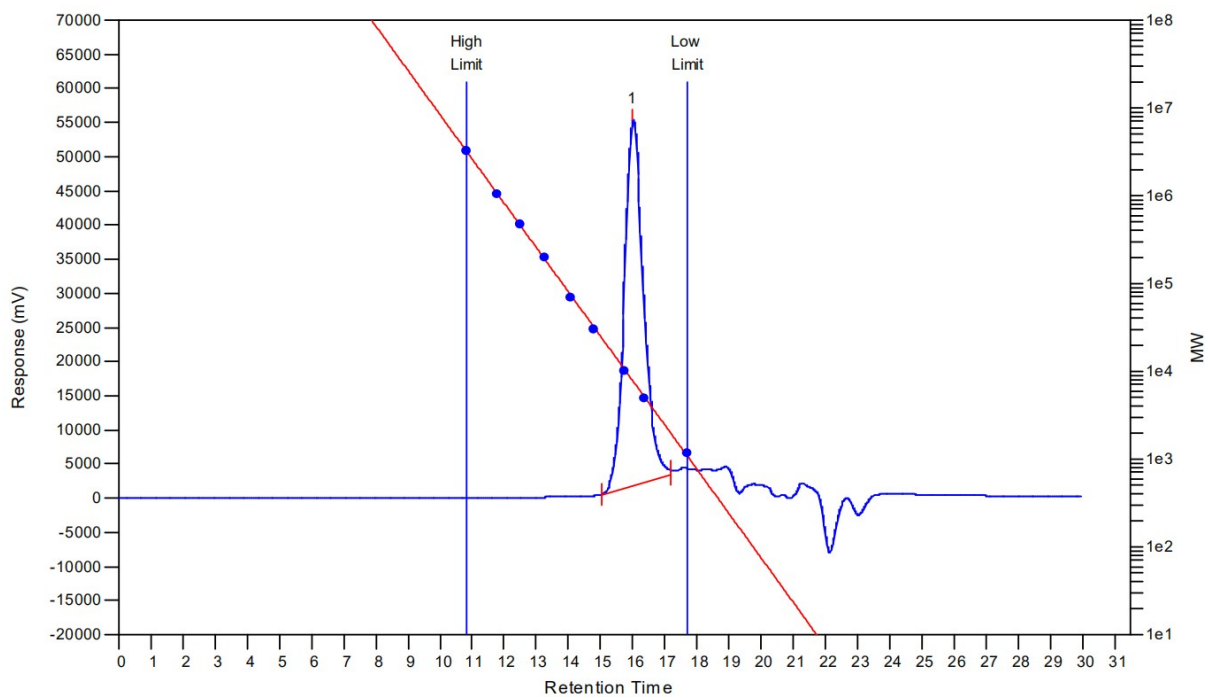


Figure S17. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and BnOH with molar ratio of 2:2:1 in toluene at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

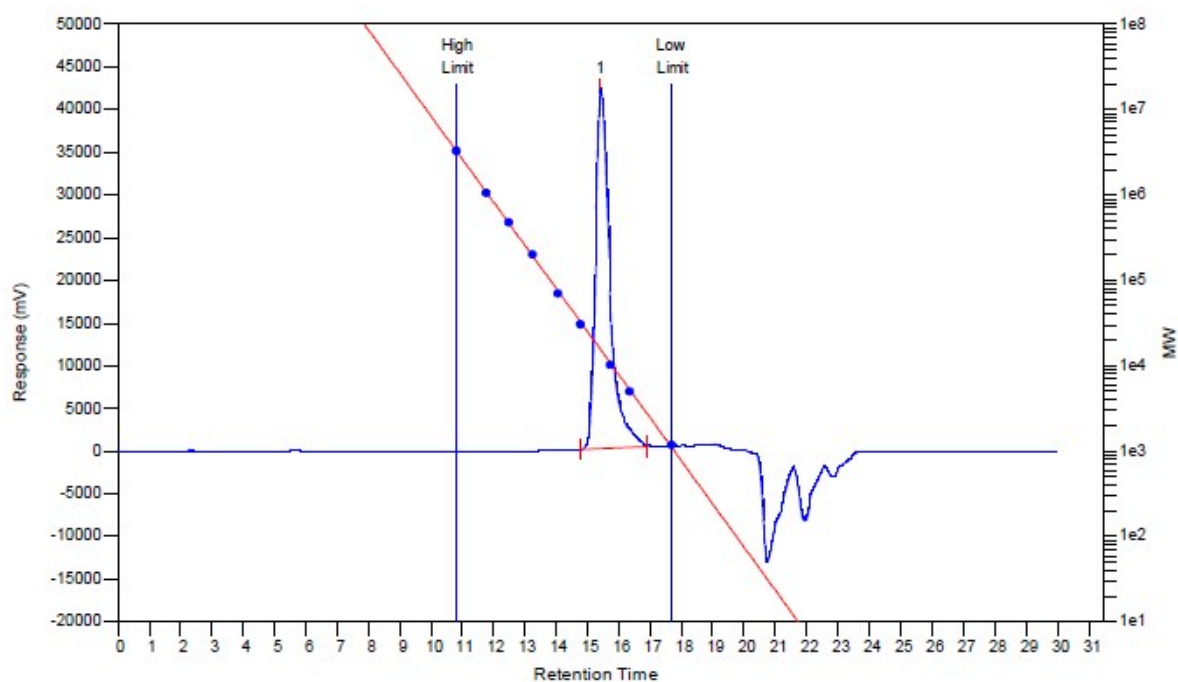


Figure S18. GPC curve of the resulting polymer in the catalysis of ZnCl_2 , DBU and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

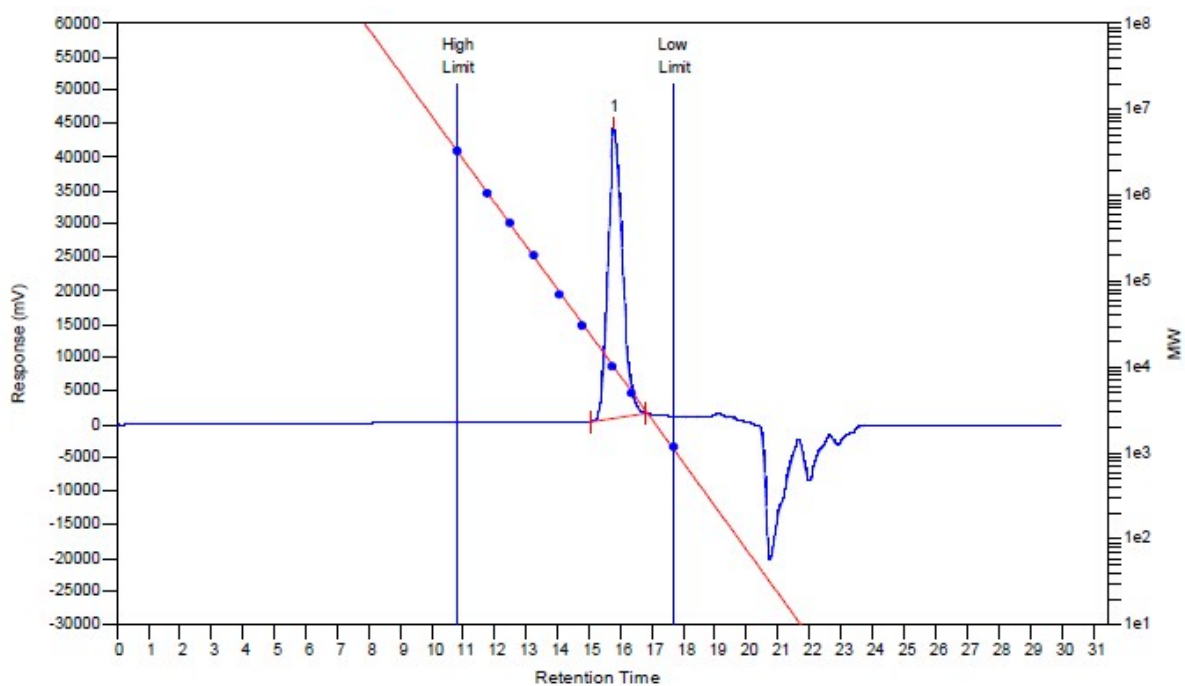


Figure S19. GPC curve of the resulting polymer in the catalysis of ZnBr_2 , DBU and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

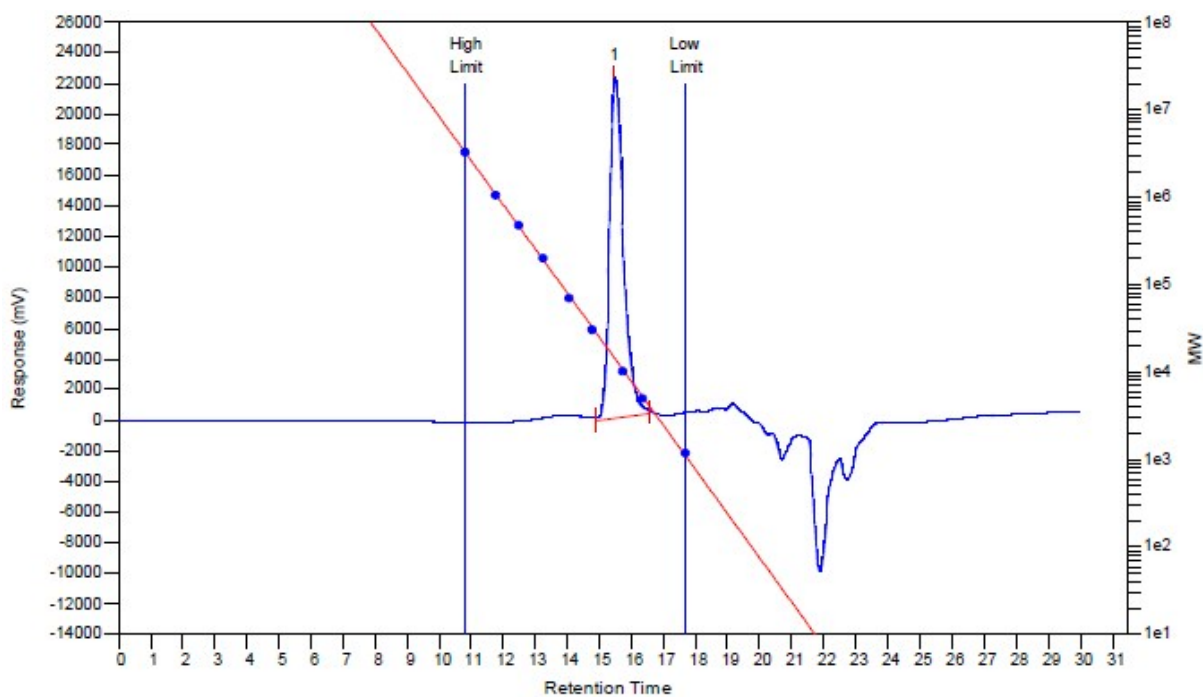


Figure S20. GPC curve of the resulting polymer in the catalysis of ZnI_2 , DBU and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

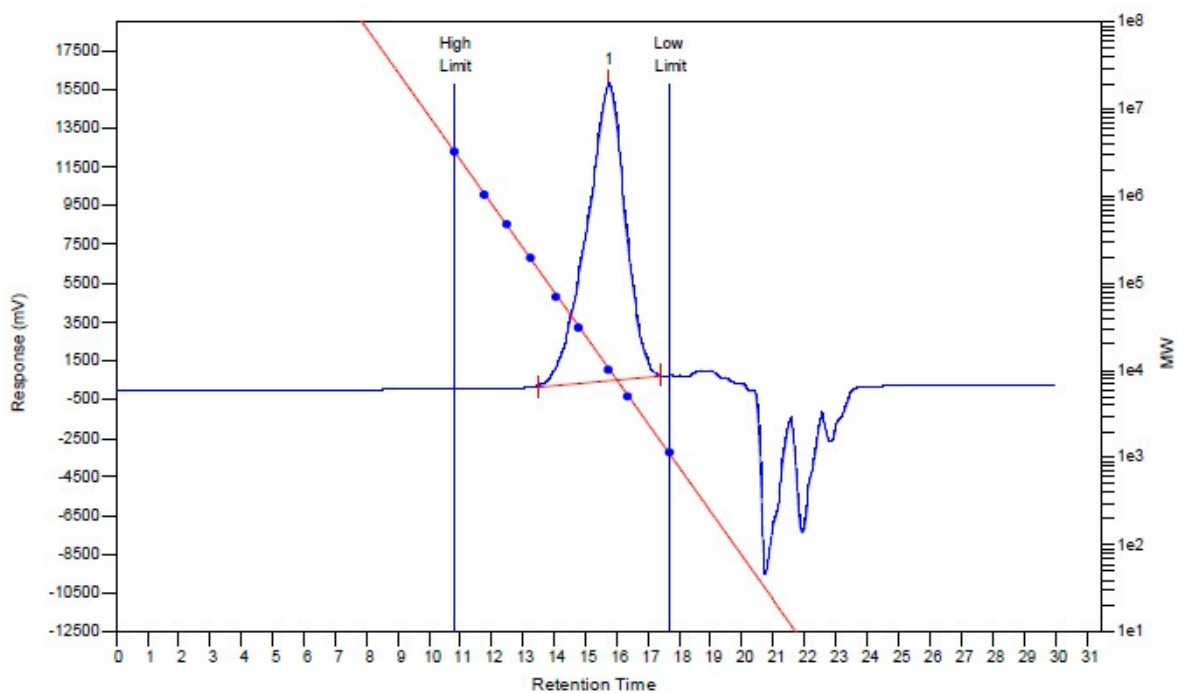


Figure S21. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OTf})_2$, DBU and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

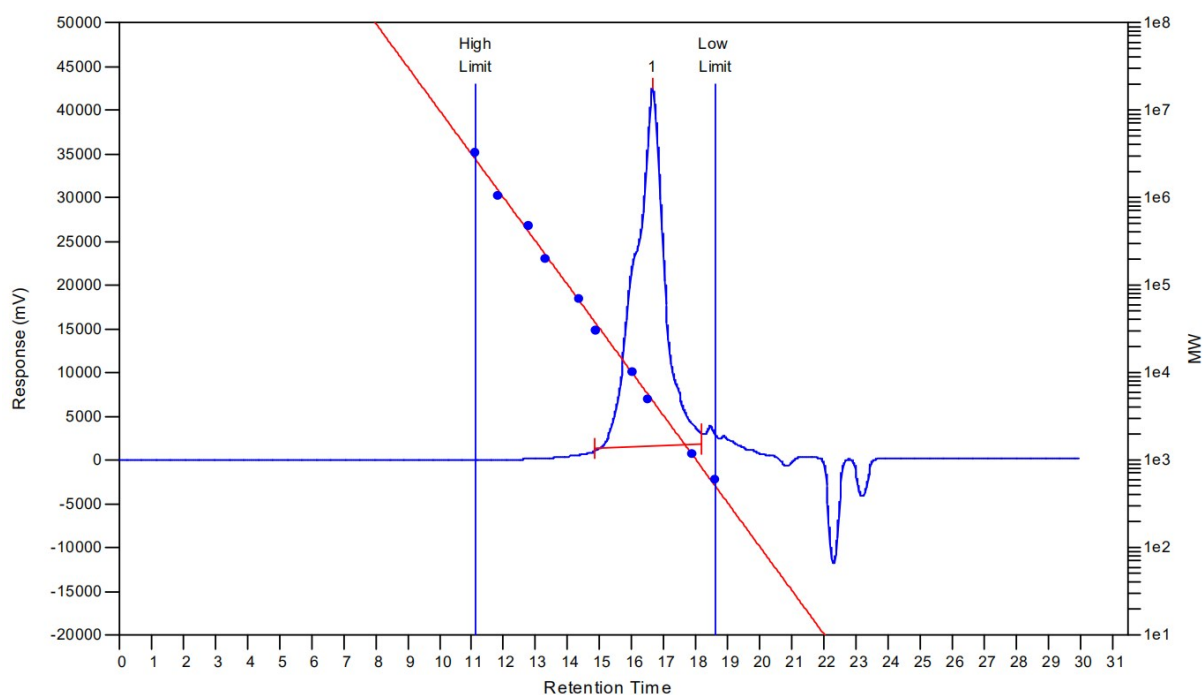


Figure S22. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBN and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

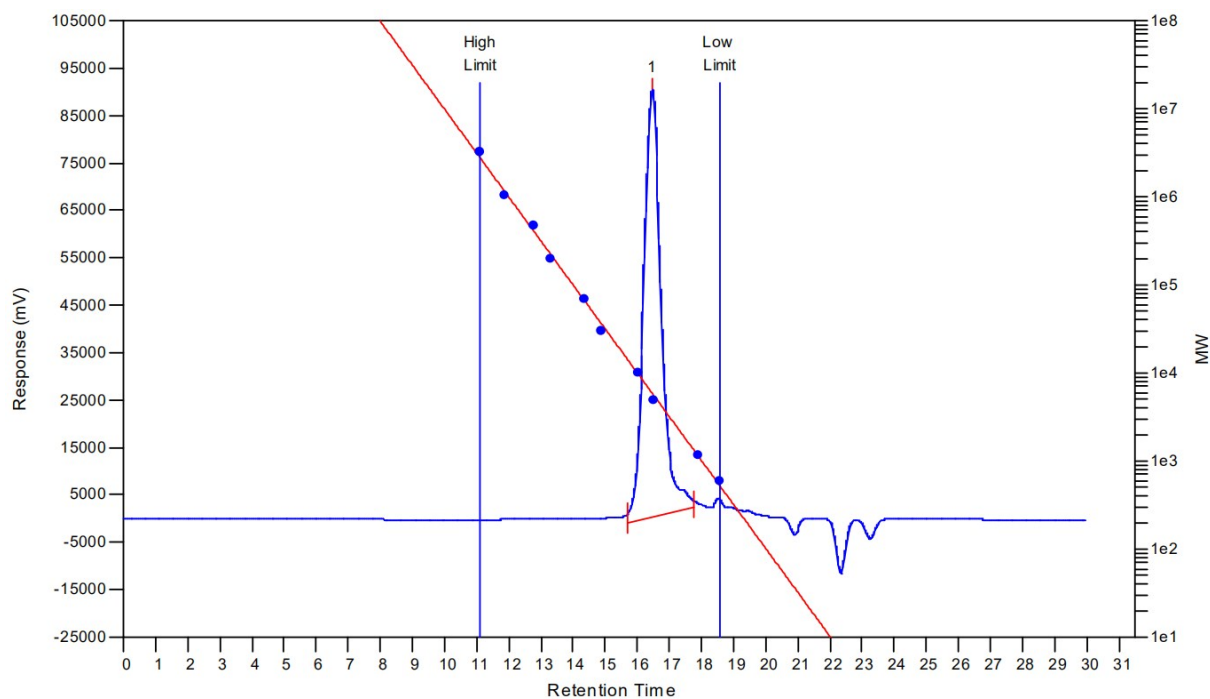


Figure S23. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, MTBD and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

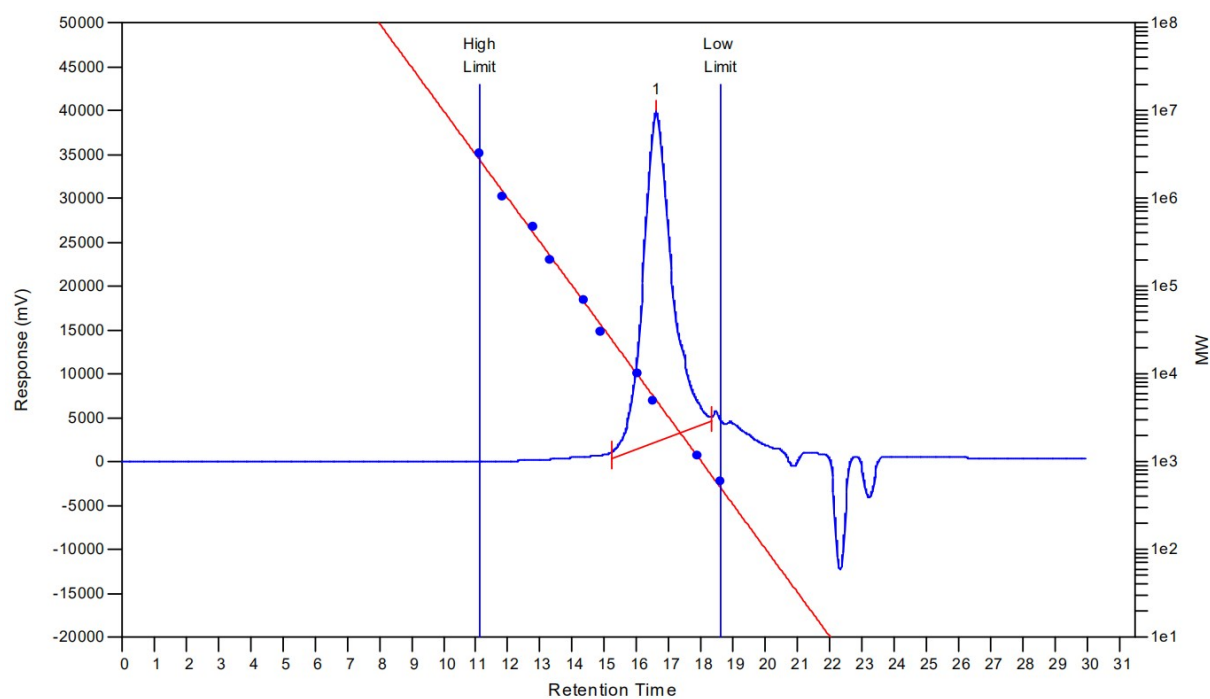


Figure S24. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, TBD and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

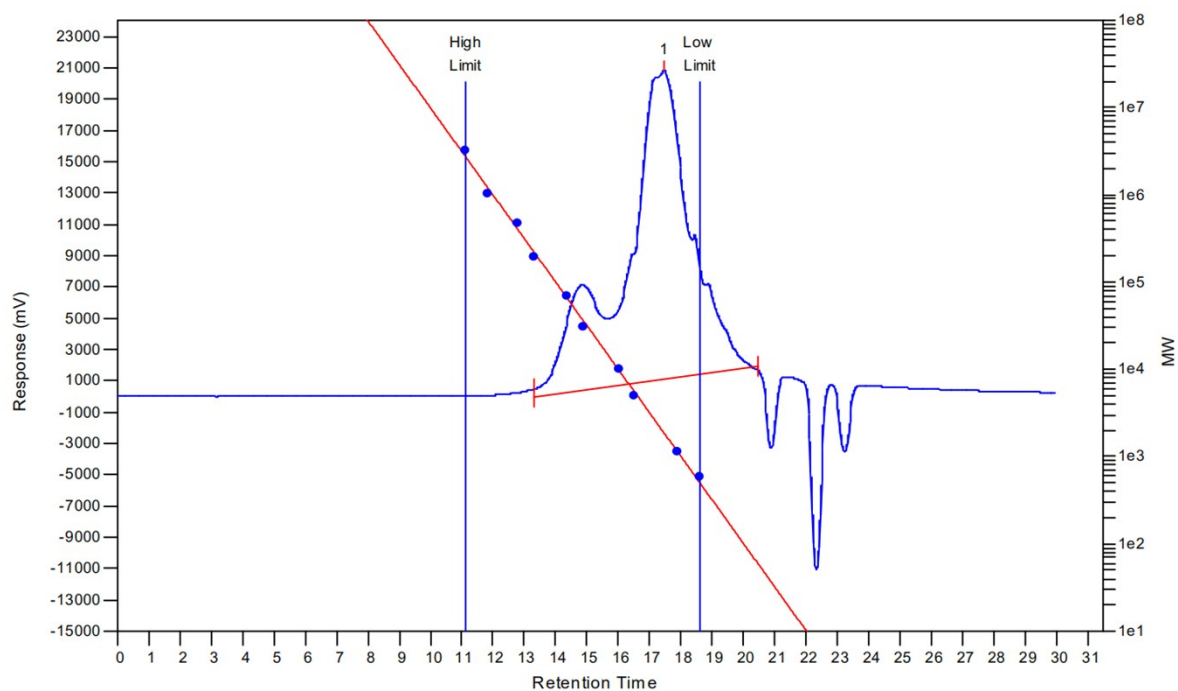


Figure S25. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DMAP and BnOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{BnOH}] = 50:1$.

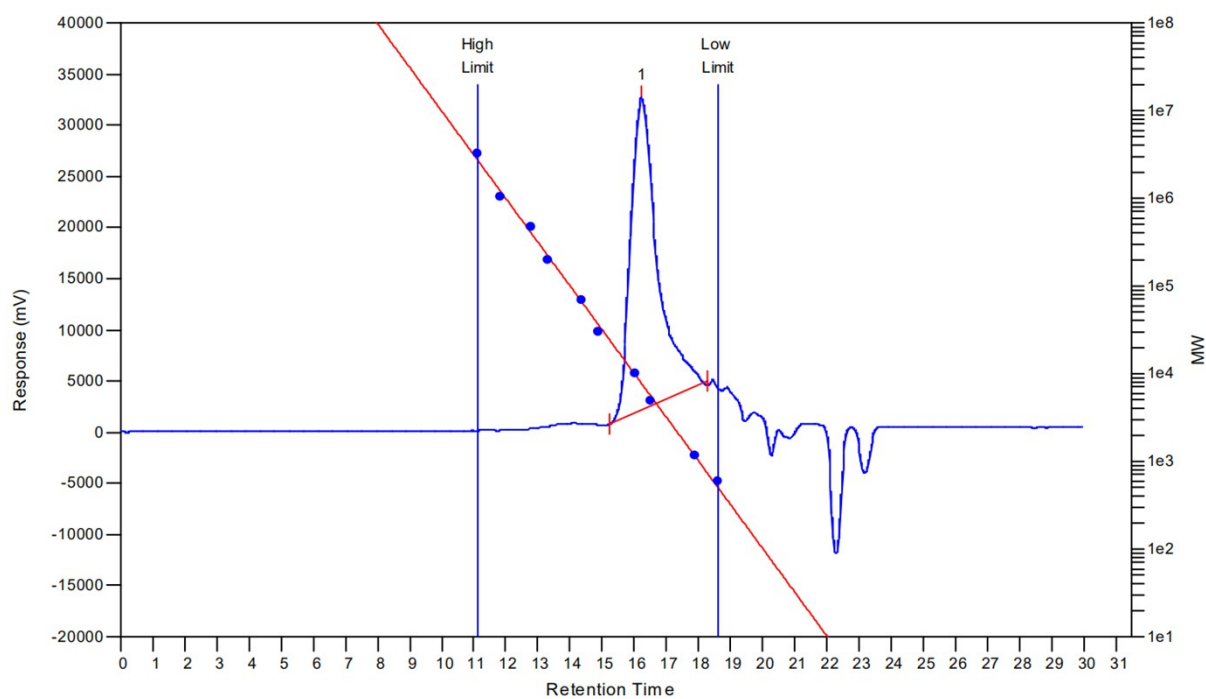


Figure S26. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and HexOH with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{HexOH}] = 50:1$.

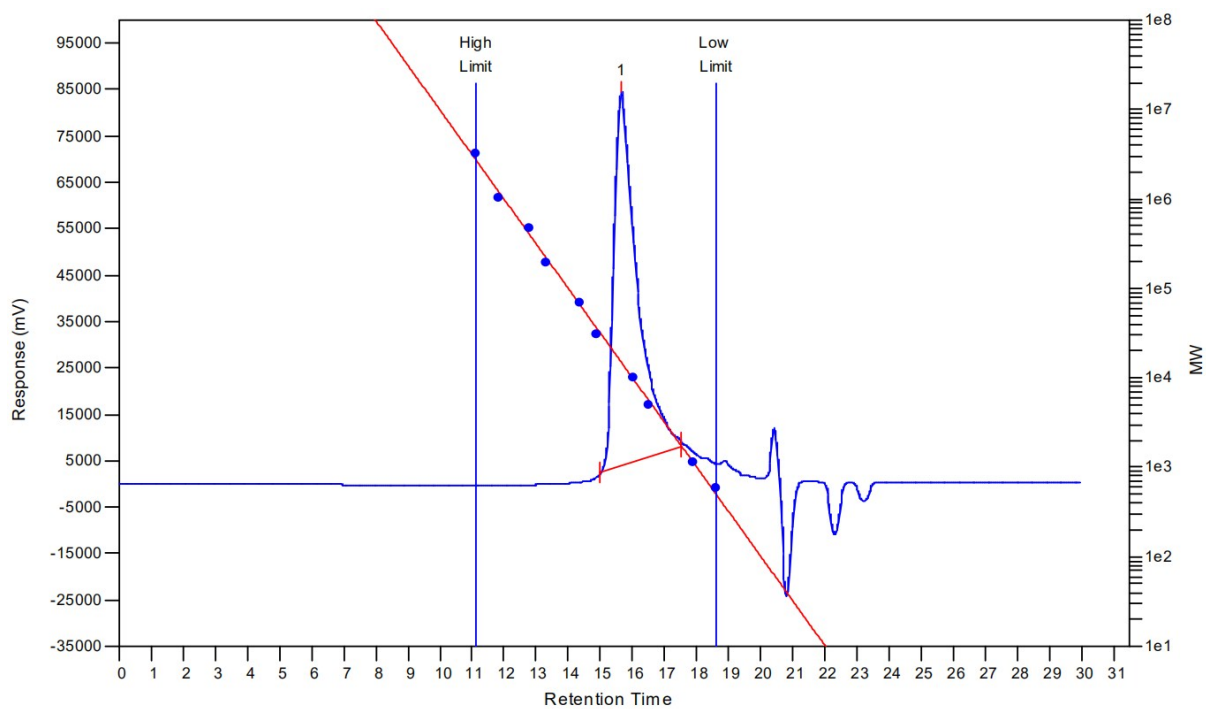


Figure S27. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and TMOP with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{OH}] = 25:1$.

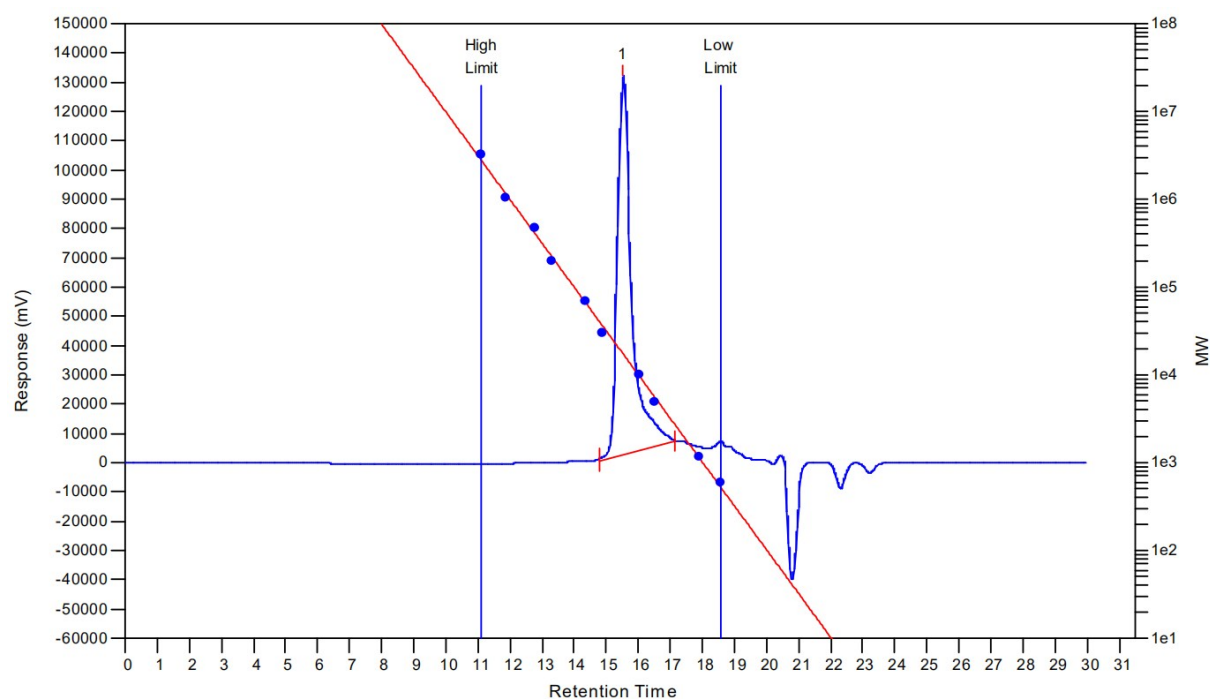


Figure S28. GPC curve of the resulting polymer in the catalysis of $\text{Zn}(\text{OAc})_2$, DBU and PT with molar ratio of 2:2:1 in DCM at 25 °C, $[\text{L-PheOCA}]/[\text{OH}] = 25:1$.

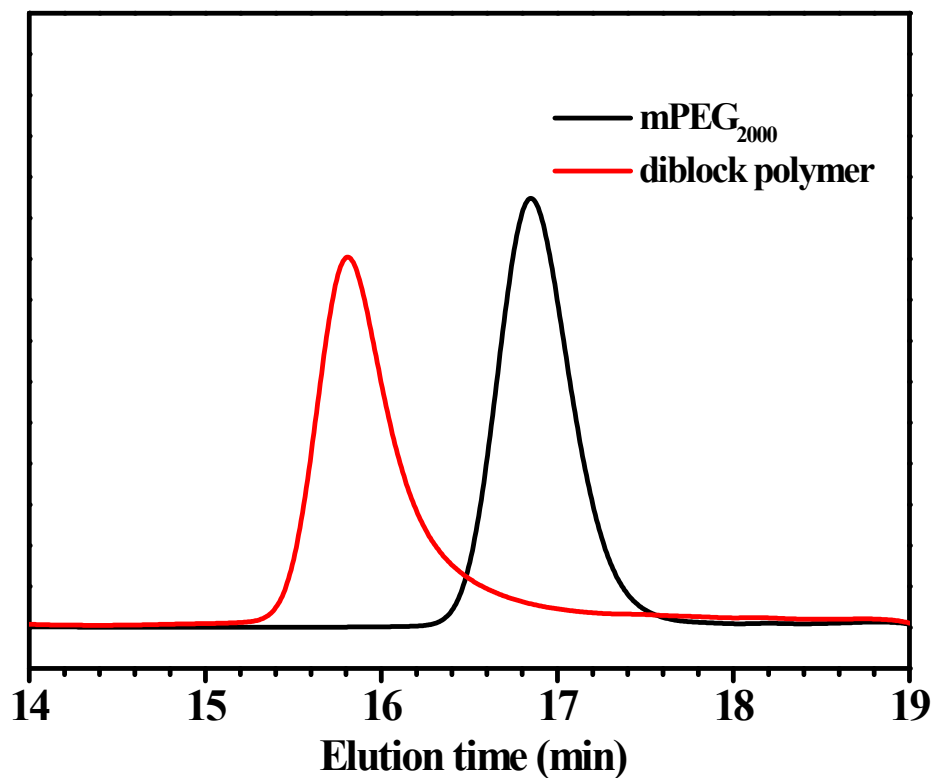


Figure S29. GPC curves of the resulting diblock amphiphilic polymer in the catalysis of Zn(OAc)₂, DBU and mPEGOH with molar ratio of 2:2:1 in DCM at 25 °C, [L-PheOCA]/[OH] = 50:1.

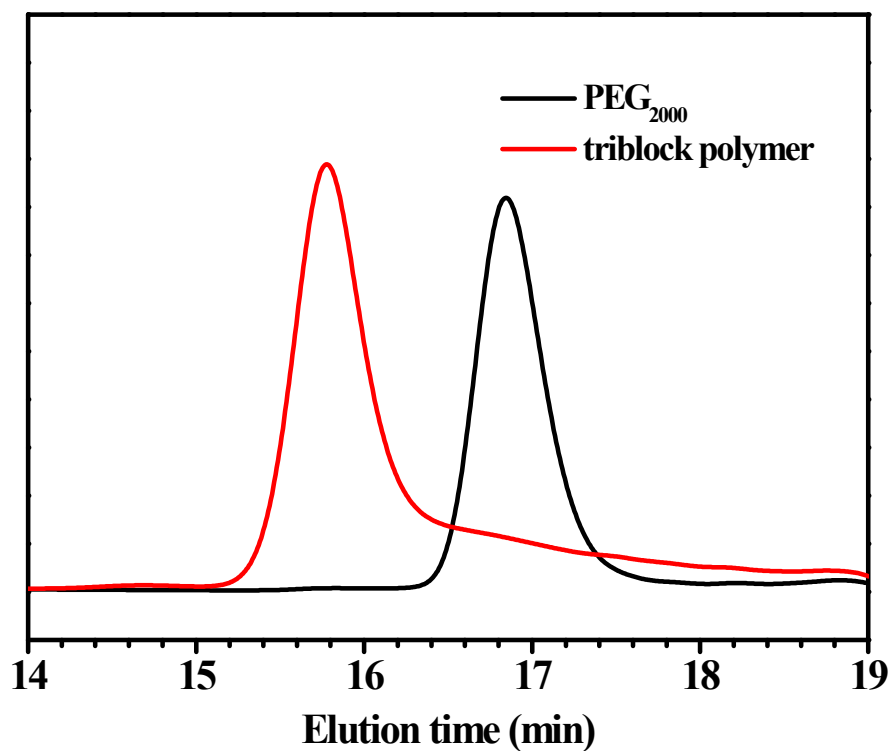


Figure S30. GPC curves of the resulting triblock amphiphilic polymer in the catalysis of Zn(OAc)₂, DBU and HOPEGOH with molar ratio of 4:4:1 in DCM at 25 °C, [L-PheOCA]/[OH] = 25:1.

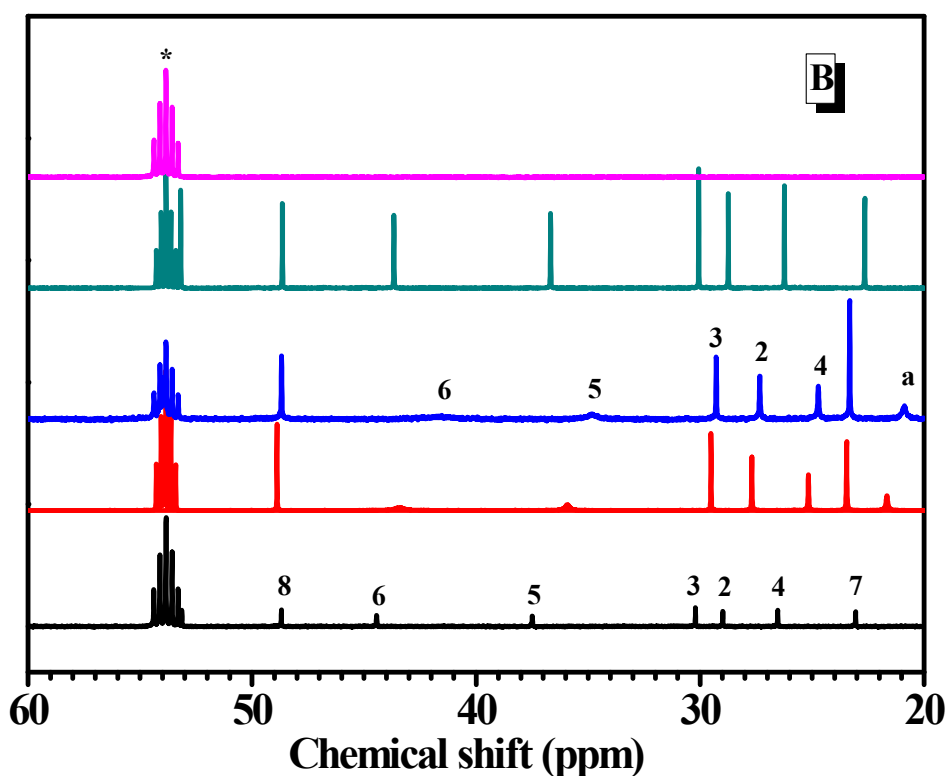
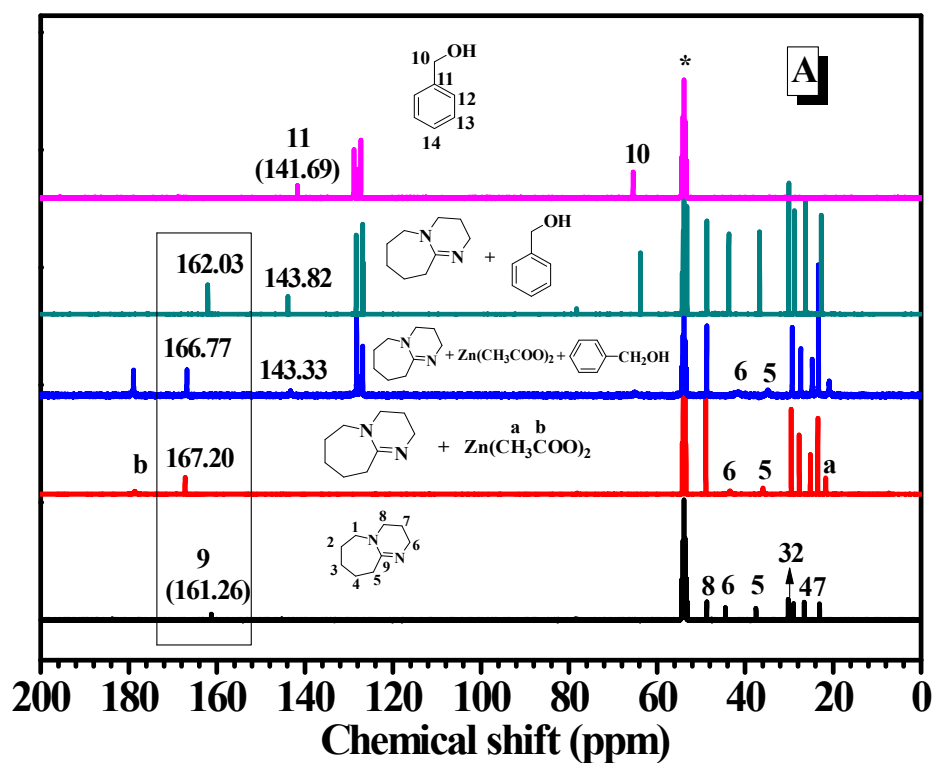


Figure S31. ^{13}C NMR spectra of DBU, BnOH, the combinations of DBU and BnOH, DBU and $\text{Zn}(\text{OAc})_2$, DBU and $\text{Zn}(\text{OAc})_2$ and BnOH (a); The correspondingly expanded spectra in the chemical shift range of 20 and 60 ppm (b). The peaks marked as asterisk were CD_2Cl_2 .

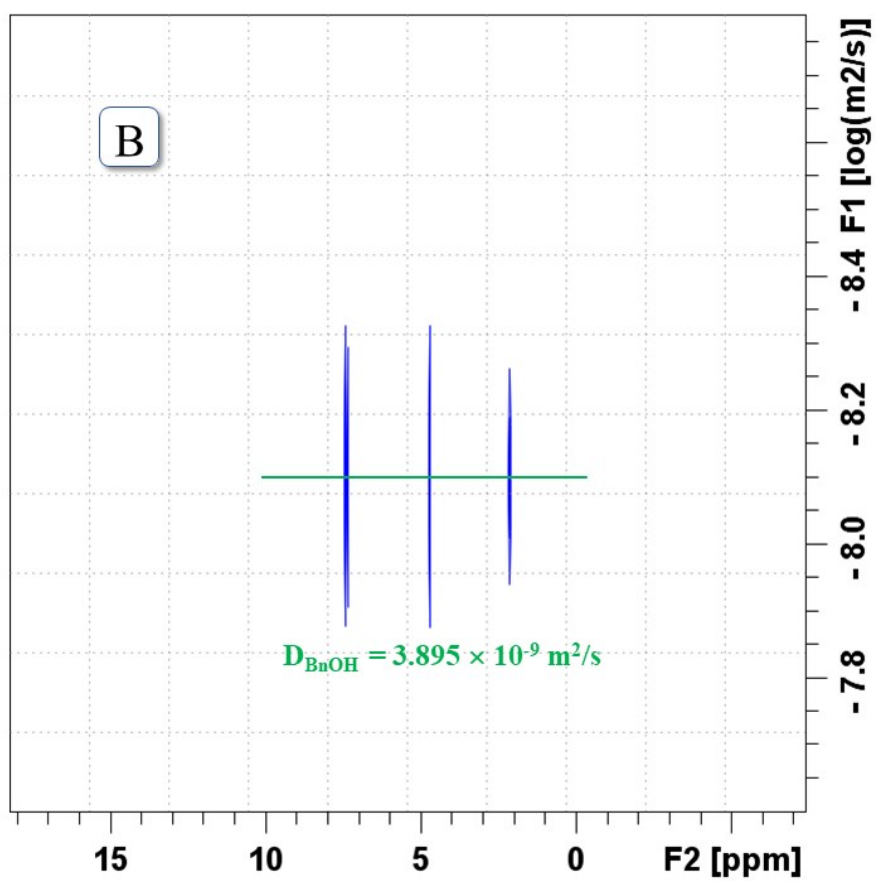
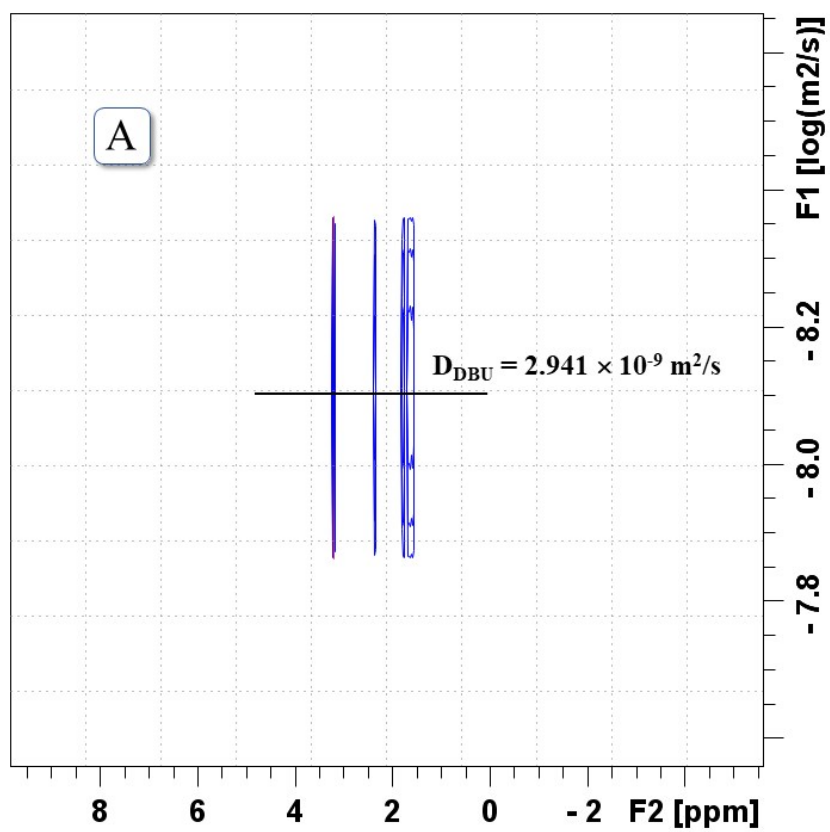


Figure S32. DOSY spectra of DBU (A) and BnOH (B).

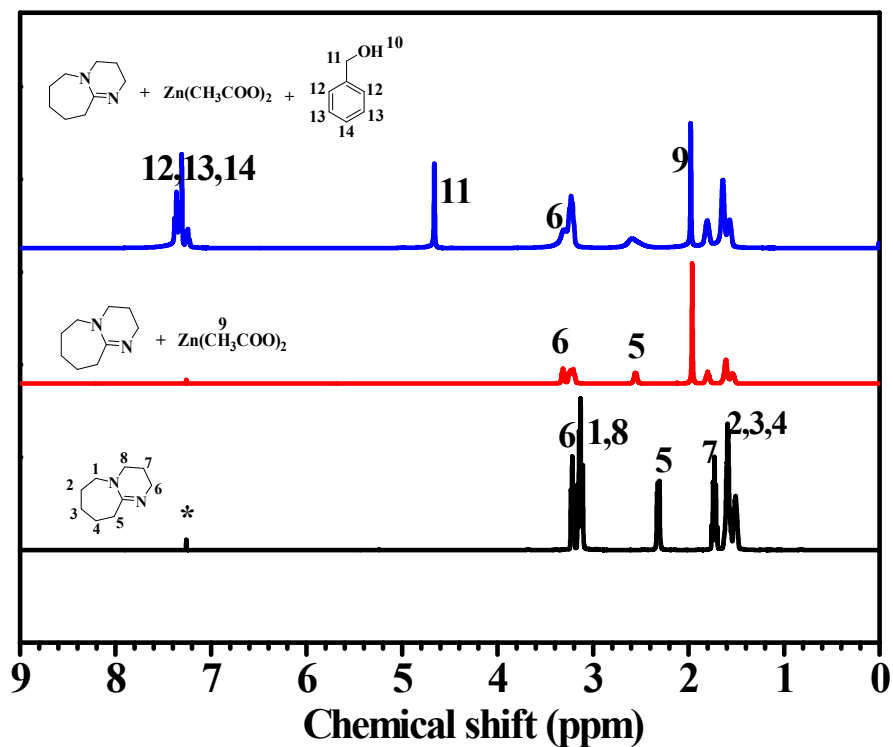


Figure S33. ^1H NMR spectra of $\text{Zn}(\text{OAc})_2$, DBU and BnOH in CDCl_3 . The peaks marked as asterisk were deuterated CDCl_3 .

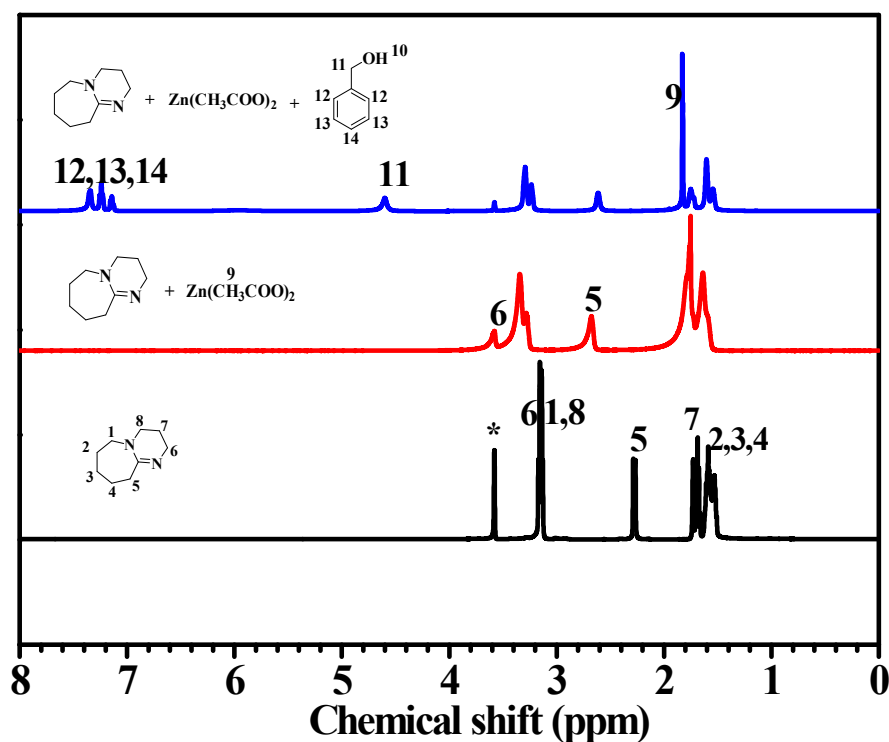


Figure S34. ^1H NMR spectra of $\text{Zn}(\text{OAc})_2$, DBU and BnOH in d_4 -THF. The peaks marked as asterisk were deuterated THF.

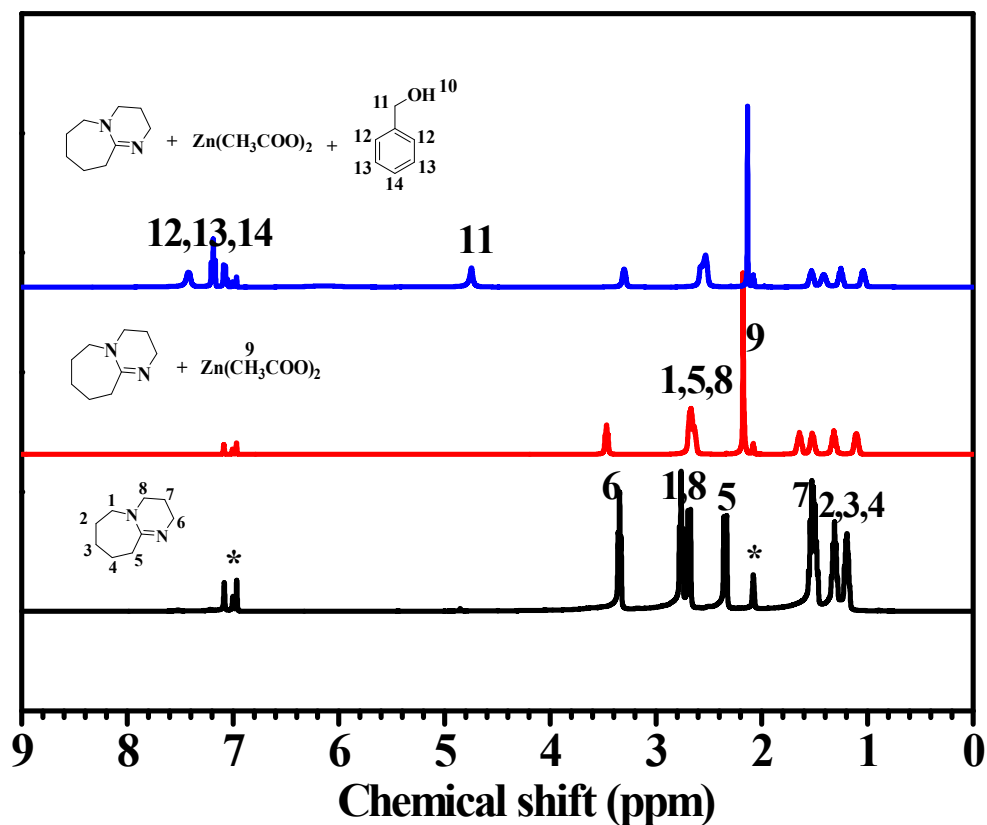


Figure S35. ^1H NMR spectra of $\text{Zn}(\text{OAc})_2$, DBU and BnOH in d_8 -toluene. The peaks marked as asterisk were deuterated toluene.

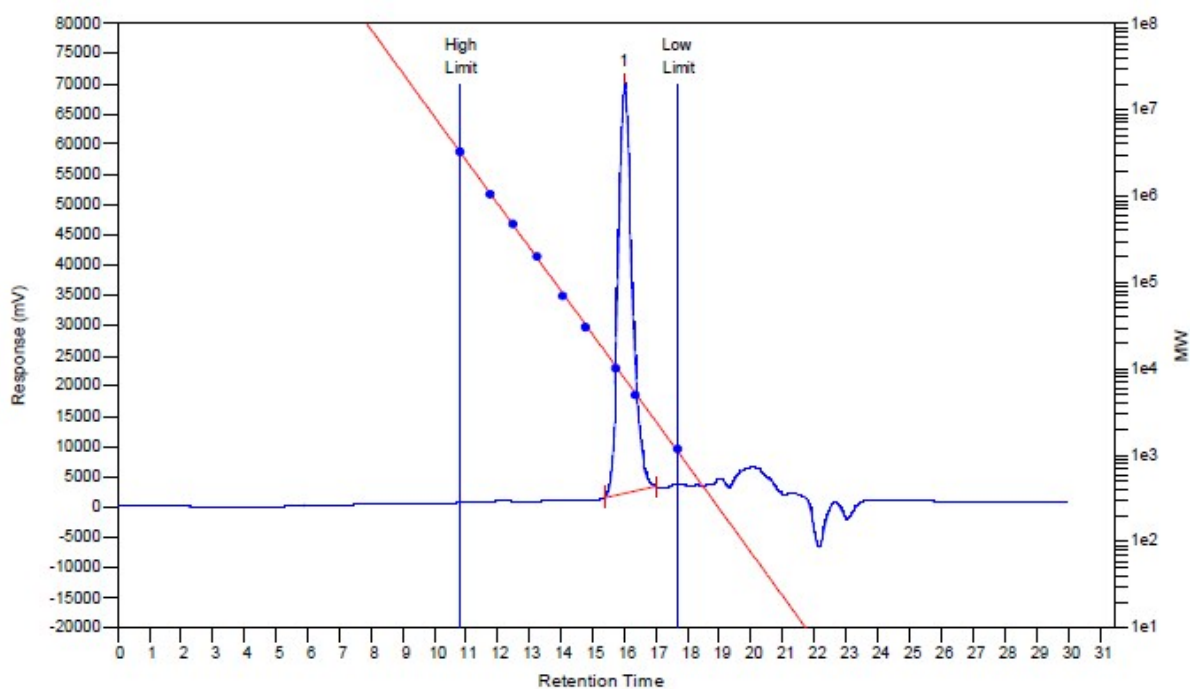


Figure S36. GPC curve of the polymer obtained at $[\text{L-PheOCA}] = 0.75 \text{ M}$; $[\text{Zn}(\text{OAc})_2] = 0.030 \text{ M}$; $[\text{BnOH}] = 0.015 \text{ M}$; $[\text{DBU}]/[\text{Zn}(\text{OAc})_2] = 1:2$.

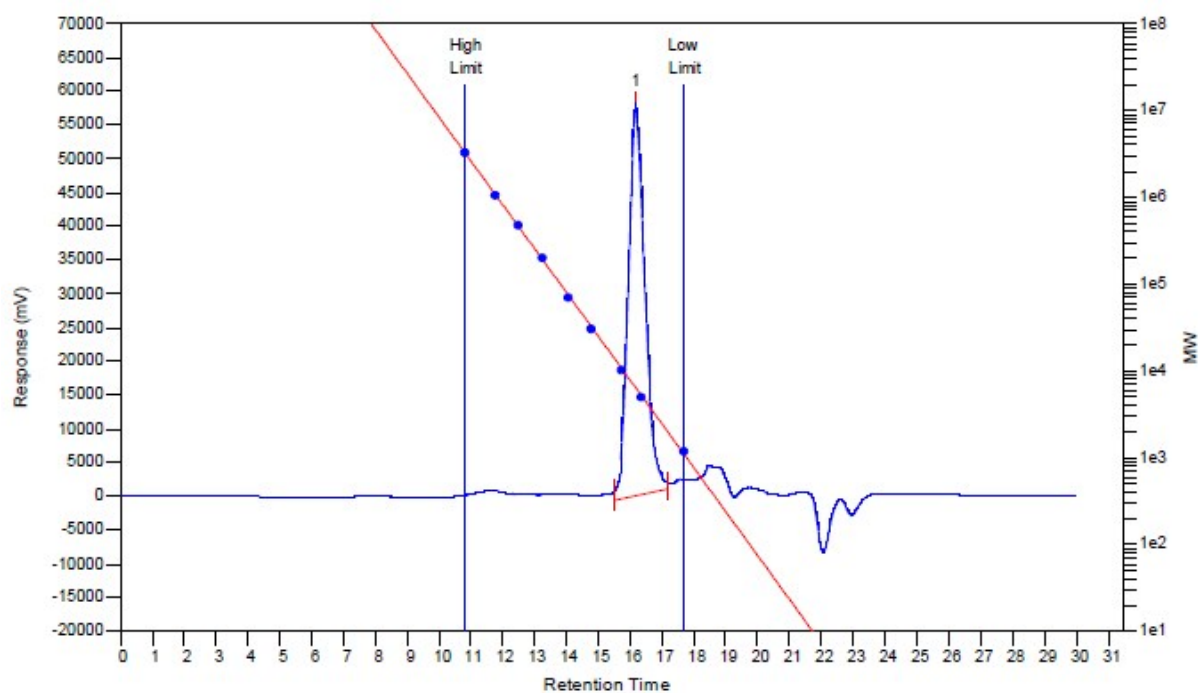


Figure S37. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75\text{ M}$; $[\text{Zn}(\text{OAc})_2] = 0.030\text{ M}$; $[\text{BnOH}] = 0.015\text{ M}$; $[\text{DBU}]/[\text{Zn}(\text{OAc})_2] = 2:2$.

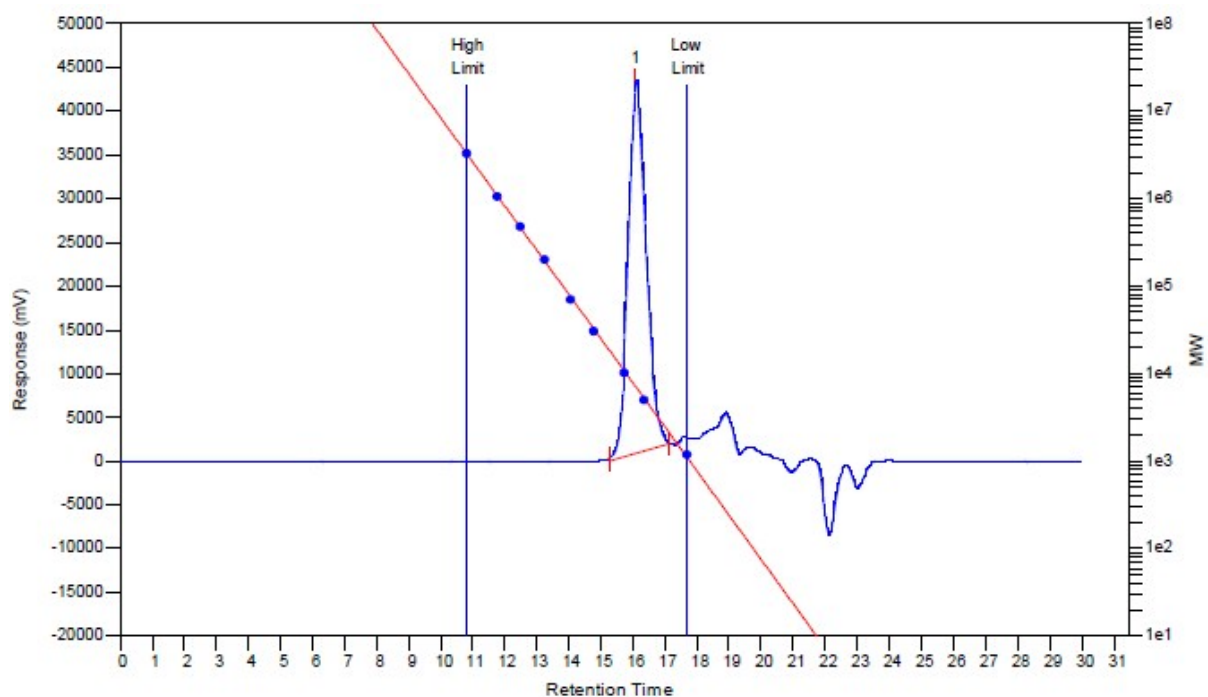


Figure S38. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75\text{ M}$; $[\text{Zn}(\text{OAc})_2] = 0.030\text{ M}$; $[\text{BnOH}] = 0.015\text{ M}$; $[\text{DBU}]/[\text{Zn}(\text{OAc})_2] = 3:2$.

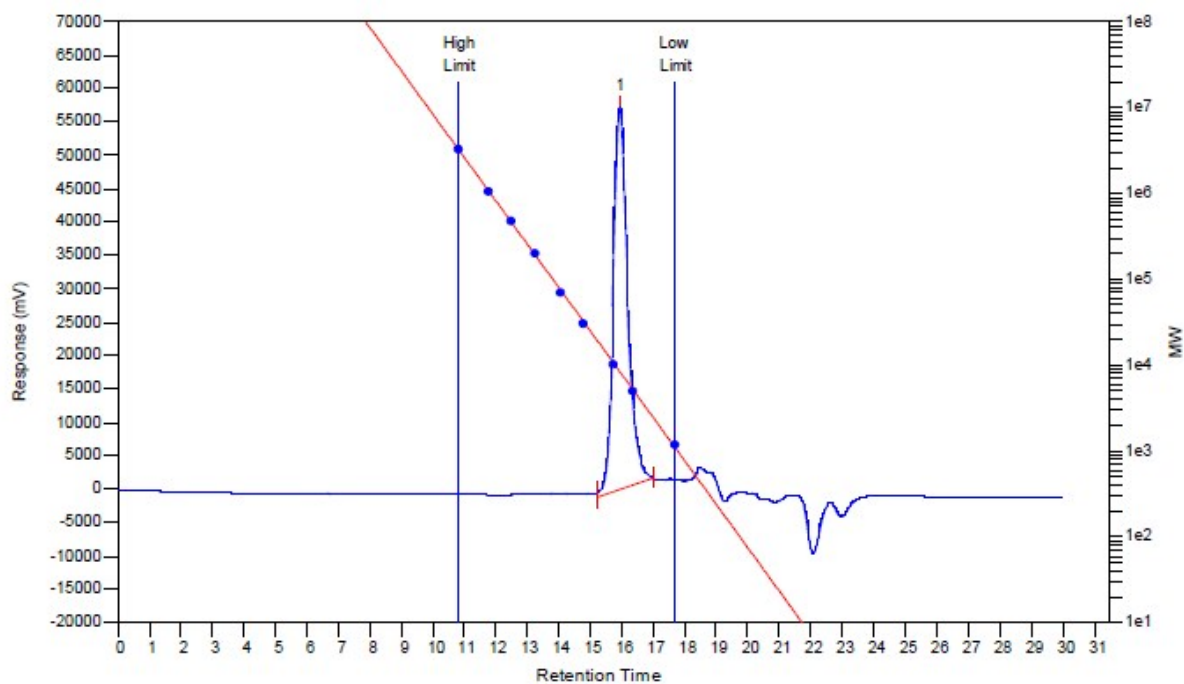


Figure S39. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75 \text{ M}$; $[\text{Zn}(\text{OAc})_2] = 0.030 \text{ M}$; $[\text{BnOH}] = 0.015 \text{ M}$; $[\text{DBU}]/[\text{Zn}(\text{OAc})_2] = 4:2$.

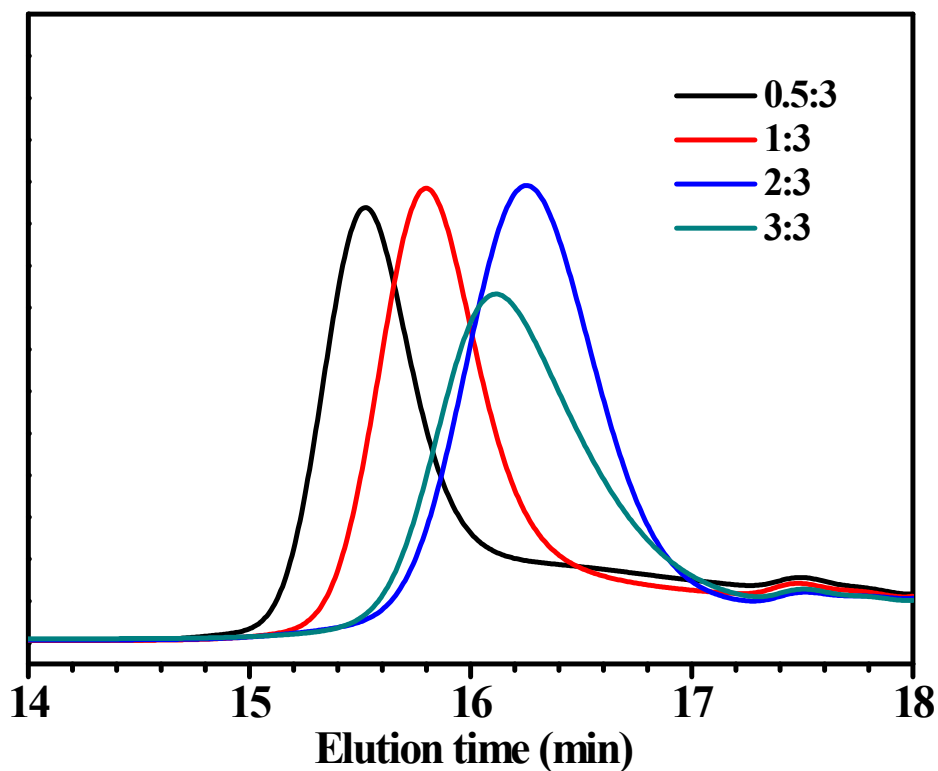


Figure S40. GPC curves of polymers obtained by varying feeding ratios of BnOH to DBU. $[\text{Zn}(\text{OAc})_2] = [\text{DBU}] = 0.045 \text{ M}$, $[L\text{-PheOCA}] = 0.75 \text{ M}$.

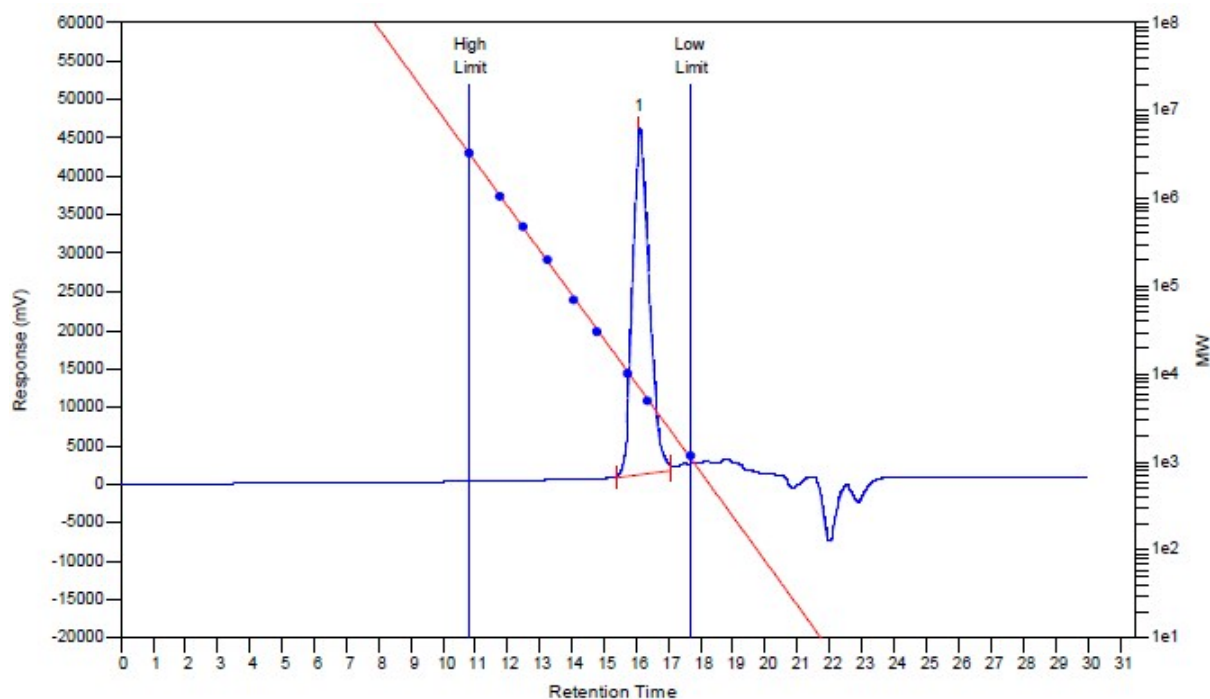


Figure S41. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75 \text{ M}$; $[\text{DBU}] = 0.045 \text{ M}$; $[\text{BnOH}] = 0.015 \text{ M}$; $[\text{Zn}(\text{OAc})_2]/[\text{DBU}] = 1:3$.

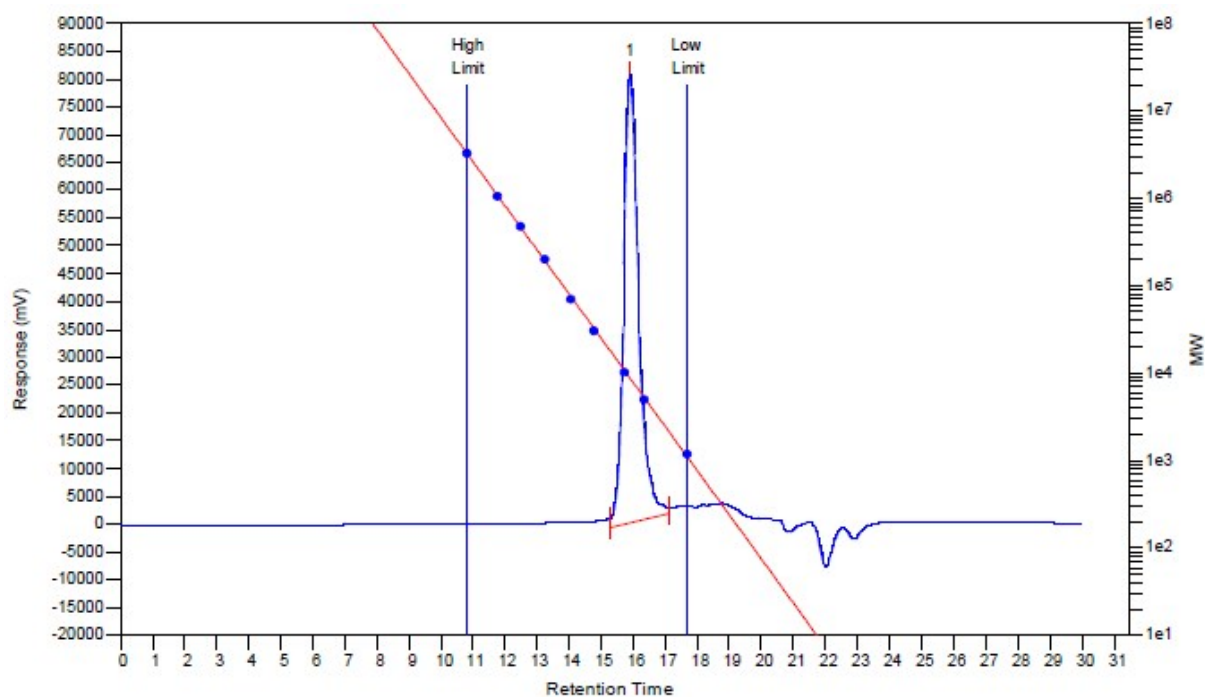


Figure S42. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75 \text{ M}$; $[\text{DBU}] = 0.045 \text{ M}$; $[\text{BnOH}] = 0.015 \text{ M}$; $[\text{Zn}(\text{OAc})_2]/[\text{DBU}] = 2:3$.

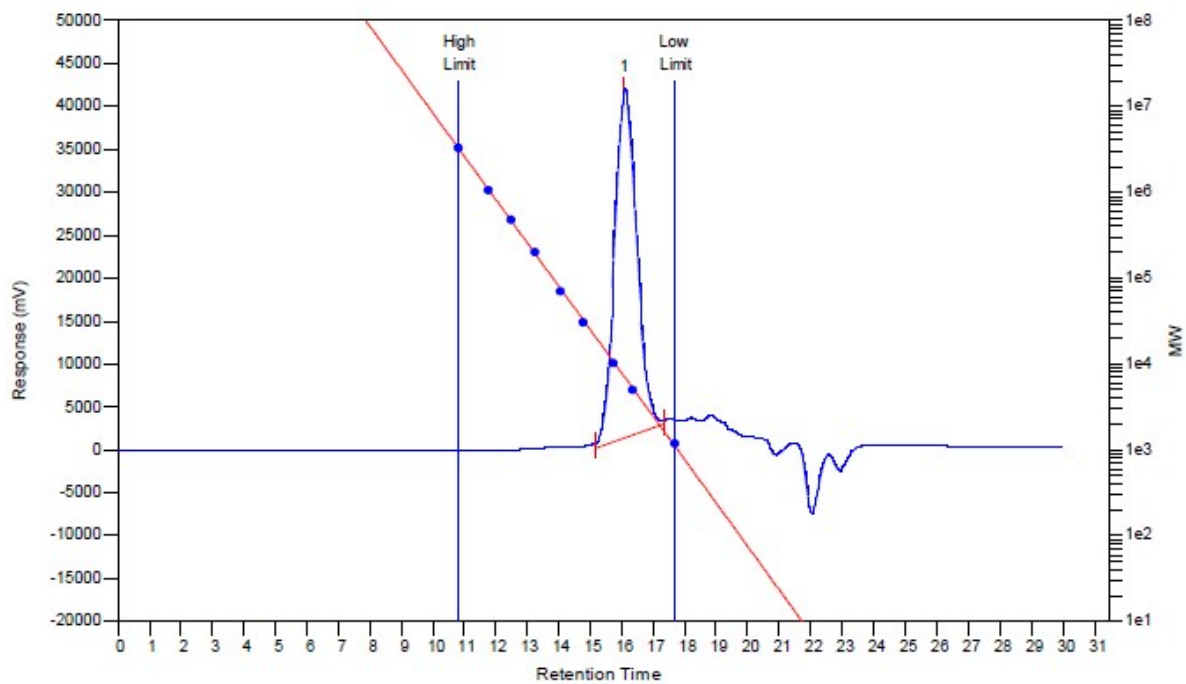


Figure S43. GPC curve of the polymer obtained at $[L\text{-PheOCA}] = 0.75 \text{ M}$; $[\text{DBU}] = 0.045 \text{ M}$; $[\text{BnOH}] = 0.015 \text{ M}$; $[\text{Zn}(\text{OAc})_2]/[\text{DBU}] = 2.5:3$.