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Supporting information

Macrocyclic poly(α-hydroxyl acid) via DABCO-mediated ROP of O-carboxylanhydride derived from L-phenylalanine even in the presence of alcohol

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Experimental Section.

General Methods.

Anhydrous dichloromethane (DCM), anhydrous dimethylforamide (DMF), anhydrous chloroform (TCM), and L-phenylalanine were purchased from J&K SCIENTIFIC LTD and used without treatment. Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone and stored over 4Å molecular sieves prior to use. Triethylboron (TEB, 1.0 molar tetrahydrofuran solution) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Innochem and used without treatment. 1-Benzyl achohol (BnOH) purchased from Acros was dried with KOH for overnight, following distillation in vacuum three times. $CDCl_3$ was purchased from Cambridge Isotope Laboratories Inc. Use Schlenk tubes in a Vigor glove box under a nitrogen atmosphere to perform all polymerization reactions in a dry, oxygen-free nitrogen atmosphere.

Characterization.

The ^1H NMR was carried out on a 400 MHz or 500 MHz NMR instrument (Bruker Corporation, Germany) at room temperature using $CDCl_3$ (δ = 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR) as solvent. N-H related 2D NMR was carried out on a Bruker Avance III 500WB, Germany using $CDCl_3$ 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 ºC), 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/ionizationtime 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 15m 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 seconds. 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}, conversion% = $I_{1760} / (I_{1760}+ I_{1800})$.[1] Thermal stability is measured by thermogravimetric analysis (TGA) on the TA Q500 analyzer. The test was conducted from room temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on the TA-Q2000 thermal analyzer. At first, the sample was heated to 200 °C at a heating rate of 10 °C/min, then quickly cooled to -80 °C, and maintained at this temperature for 2 minutes. It was then heated to 200 °C at the same heating rate and held at this temperature for 2 minutes, and then cooled to room temperature at a rate of 10 °C/min. The glass transition temperature was obtained from the second heating scanning.

Preparation of $_{\text{L}}$-PheOCA.

As reported[2], 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-3phenylpropanoic acid was afforded in a yield of 81%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.24-7.33 (m, 5H, *Ar*H), 4.53 (dd, *J* = 7.2 Hz, 2H, -C*H*), 3.19- 3.24 (dd, *J* = 14.0 Hz, 1H, C*H$_2$*), 2.98- 3.03 (dd, *J* = 14.0 Hz, 1H, C*H$_2$*).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 40.33 (-CH_2), 71.15 (CH), 127.36 (*Ar*C), 128.79 (*Ar*C), 129.68 (*Ar*C), 135.93 (*Ar*C), 177.87 (C=O).

Preparation of $_{L}$-PheOCA. To a solution of HPPA (36.1 mmol) and activated charcoal (~108 mg) in anhydrous THF (40 mL), triphosgene (24.9 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%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm): 7.34-7.35 (m, 3H, *Ar*H), 7.21-7.23 (m, 2H, *Ar*H), 5.29 (t, *J* = 4.5 Hz, 1H, C*H*), 3.36-3.40 (dd, *J* = 15.0 Hz, 1H, C*H$_2$*), 3.22-3.26 (dd, *J* = 15.0 Hz, 1H, C*H$_2$*).^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm): 36.57 (-CH_2), 80.03 (CH), 128.56 (*Ar*C), 129.31 (*Ar*C), 129.80 (*Ar*C), 131.64 (*Ar*C), 147.92 (OC=OO), 166.44(C=OO).

Polymerization procedure.

A typical procedure for polymerization of $_{\text{L}}$-PheOCA was performed in a 25 mL Schlenk in a Vigor glovebox. The given amount of DABCO, TEB and BnOH was stirred in 1.0 mL anhydrous toluene before taken out from the glovebox. The reaction mixture was then connected to a vacuum line and stirred for 10 min at room temperature, followed by adding 144.2 mg $_{\text{L}}$-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.

References.

1. Quan Y F, and Rong T. J. Am. Chem. Soc., 2017, 139, 6177.
2. 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 TEB or BnOH[a]

Entry	**M:TEB:DABCO:BnOH**[b]	**Time**[c] **h**	**TOF**[d] **h^{-1}**	**$M_{n,exp}$**[e] **Kg/mol**	**$M_{n,mea}$**[f] **Kg/mol**	**Đ** [f]
1	50:0:0.75:0.75	1	95	9.86	6.6	1.23
2	50:0:0.75:1	1	95	9.86	5.9	1.25
3	50:0:0.75:1.5	1	95	9.86	4.5	1.26
4	50:0:0.75:2	1	95	9.86	4.2	1.38
5	50:0.75:1:0	1	95	7.1	71.2	bimodal[g]
6	50:0.75:1.5:0	1	95	4.54	25.6	bimodal[g]
7	50:1:0.75:0	1	95	9.86	72.3	bimodal[g]
8	50:1.5:0.75:0	1	95	9.86	65.7	bimodal[g]
9	50:2:0.75:0	1	95	9.86	49.5	bimodal[g]

[a] Performed at 25 °C. Note: [b] Indicating the feeding molar ratio of L-PheOCA, TEB, DABCO and BnOH. [c] [c] The polymerization time when above 95% monomers were conversed. The monomer conversion was determined by the intensity ratio between 1760 cm^{-1} and 1800 cm^{-1} in FT-IR spectroscopy. Conv.% = I_{1760} / (I_{1760}+ I_{1800}). [d] Indicated turnover frequencies (TOF), TOF = moles of substrate (monomer) consumed per mole of catalyst (initiator) per hour. [e]Calculated by $[M]_0/[DABCO]_0\times$ (M_w of monomer - M_w of CO_2) × monomer conversion. [f] Measured by GPC in THF against polystyrene standards, dispersity indices ($Đ$ = M_w/M_n). [g] With bimodal distribution.

Table S2. ROP of L-PheOCA in different solutions[a]

Run	**Sol**	**M:TEB:DABCO:BnOH**[b]	**Time**[c] **h**	**TOF**[d] **h^{-1}**	**$M_{n,exp}$**[e] **Kg/mol**	**$M_{n,mea}$**[f] **Kg/mol**	**Đ** [f]	**P_m**[g]
1	TOL	50:0.75:0.75:1	0.5	190	9.86	7.9	1.13	0.83
2	DCM	50:0.75:0.75:1	1.5	63.3	9.86	6.4	1.25	0.74
3	TCM	50:0.75:0.75:1	1.5	63.3	9.86	5.5	1.18	0.76
4	THF	50:0.75:0.75:1	2.5	38	9.86	4.9	1.26	0.76
5	DMF	50:0.75:0.75:1	2.5	38	9.86	---	---	---
6	TOL	50:0.75:0.75:1.5	0.5	190	9.86	6.3	1.21	0.77
7	TOL	50:0.75:1:1	0.5	190	7.1	7.8	1.18	0.75

8	TOL	50:0.75:1.5:1	0.5	190	4.9	6.1	1.21	0.79
9	TOL	50:1:1:1	0.5	190	7.1	7.6	1.17	0.78

[a] Performed at 25 °C. Note: [b] Indicating the feeding molar ratio of $_{L}$-PheOCA, TEB, DABCO and BnOH. [c] [c] The polymerization time when above 95% monomers were conversed. The monomer conversion was determined by the intensity ratio between 1760 cm^{-1} and 1800 cm^{-1} in FT-IR spectroscopy. Conv.% = I_{1760} / (I_{1760}+ I_{1800}). [d] Indicated turnover frequencies (TOF), TOF = moles of substrate (monomer) consumed per mole of catalyst (initiator) per hour. [e] Calculated by $[M]_0/[DABCO]_0\times$ (M_w of monomer - M_w of CO_2) × monomer conversion. [f] Measured by GPC in THF against polystyrene standards, dispersity indices ($Đ$ = M_w/M_n). [g] P_m is probability of forming a new isotactic dyad, determined by $^{13}C\{^1H\}$ NMR spectroscopy.

Table S3. Polymerization results at the different monomer conversion[a]

Entry	**Conv.[b]** **%**	**Time[c]** **h**	**TOF[d]** **h^{-1}**	**$M_{n,exp}$[e]** **Kg/mol**	**$M_{n,mea}$[f]** **Kg/mol**	**Đ [f]**
1	25.2	0.16	157.5	4.9	5.86	1.17
2	39.4	0.33	119.4	7.8	8.64	1.18
3	58.5	0.5	117	11.54	12.57	1.12
4	72.7	0.75	96.9	14.34	13.57	1.13
5	80.3	1	80.3	15.84	14.93	1.12
6	86.7	1.25	69.36	17.12	15.44	1.14
7	>95	1.5	63.3	18.73	15.7	1.23

[a] Performed at the feeding ratios of [$_{L}$-PheOCA]/[DABCO]/[TEB]/[BnOH] = 100:0.75:0.75:1 in Tol at 25 °C. [b] The monomer conversion was determined by the intensity ratio between 1760 cm^{-1} and 1800 cm^{-1} in FT-IR spectroscopy, Conv.% = I_{1760} / (I_{1760}+ I_{1800}). [c] The polymerization time at the determined conversion of monomers. [d] Indicated turnover frequencies (TOF), TOF = moles of substrate (monomer) consumed per mole of catalyst (initiator) per hour. [e] Calculated by $[M]_0/[DABCO]_0\times$ (M_w of monomer - M_w of CO_2) × monomer conversion. [f] Measured by GPC in THF against polystyrene standards, dispersity indices ($Đ$ = M_w/M_n).

Table S4. The initiation rate constant (k_i) and the propagation rate constant (k_p) at varying feeding ratios of TEB, DABCO and BnOH

TEB:DABCO:BnOH	**K_i (min^{-1})**	**K_p (min^{-1})**
0:0.5:0	0.0279	0.1684
0:0.75:0	0.0654	0.3055
0:1.0:0	0.1684	0.4629
0.75:0.5:1	0.029	0.072
0.75:0.75:1	0.04569	0.14
0.75:1.5:1	0.0928	0.69
0.75:0.75:1	0.0394	0.1367
1.5:0.75:1	0.0208	0.1081
2:0.75:1	0.0115	0.0902
0.75:0.75:1	0.04368	0.190
0.75:0.75:1.5	0.0314	0.1388
0.75:0.75:2	0.01915	0.0738

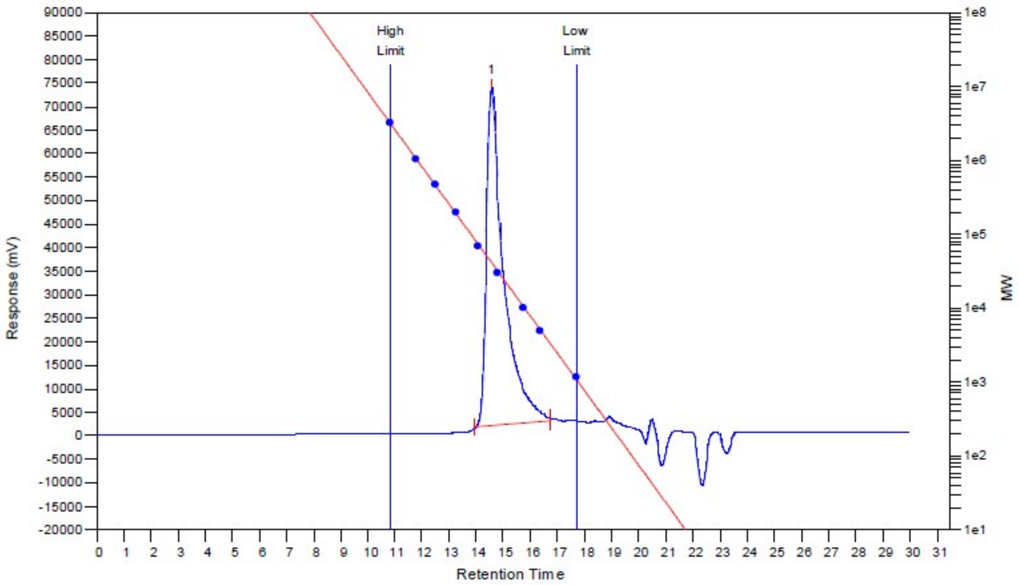


Fig. S1. GPC curves of the resulting polymers via ROP of $_\text{L}$-PheOCA using [DABCO]: [$_\text{L}$-PheOCA] = 0.75:50 (Table 1, run 1).

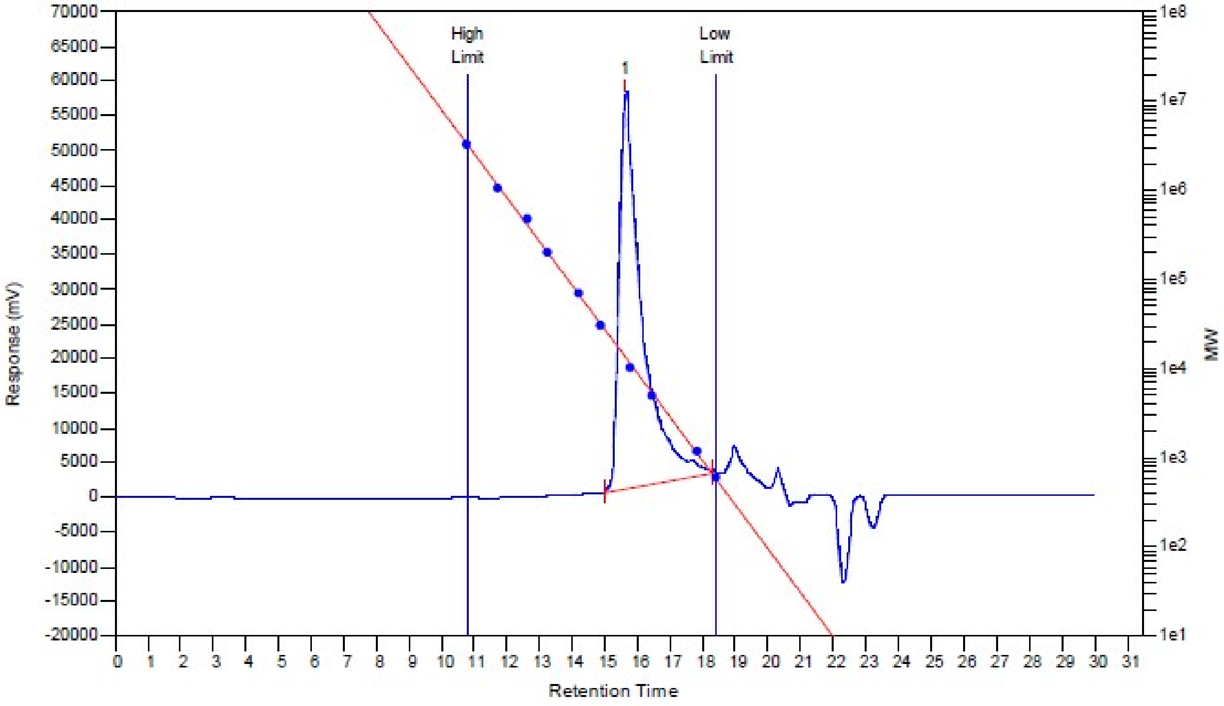
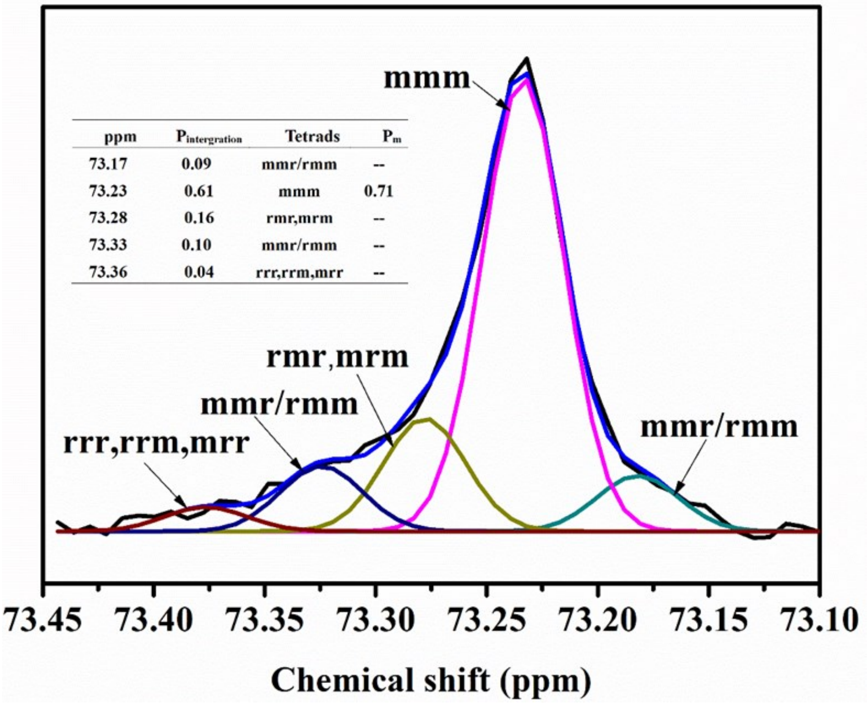


Fig. S2. GPC curves of the resulting polymers via ROP of $_\text{L}$-PheOCA using [DABCO]: [$_\text{L}$-PheOCA] = 0.75:25 (Table 1, run 1).



ppm	$P_{intergration}$	Tetrads	P_m
73.17	0.09	mmr/rmm	--
73.23	0.61	mmm	0.71
73.28	0.16	rmr,mrm	--
73.33	0.10	mmr/rmm	--
73.36	0.04	rrr,rrm,mrr	--

Fig. S3. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[$_L$-PheOCA] = 0.75:50 (Table 1, run 1).

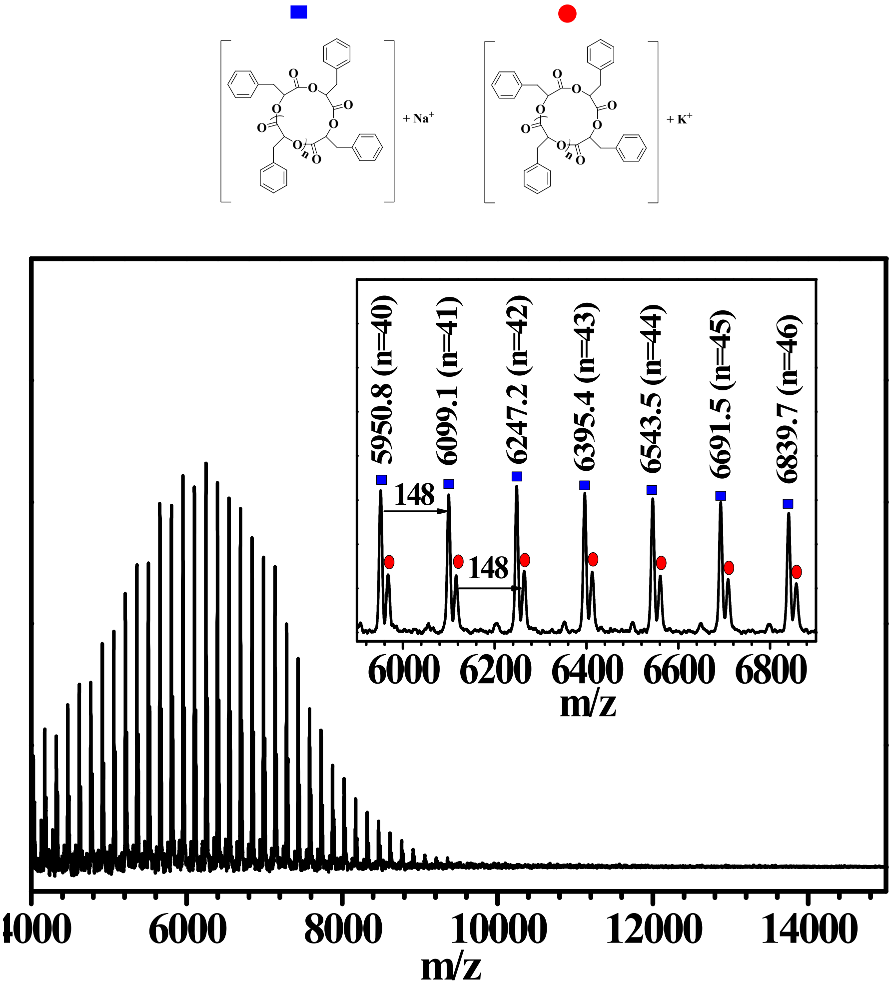


Fig. S4. MALDI-TOF results afforded using [DABCO]:[BnOH]:[$_L$-PheOCA] = 0.75:1:50.

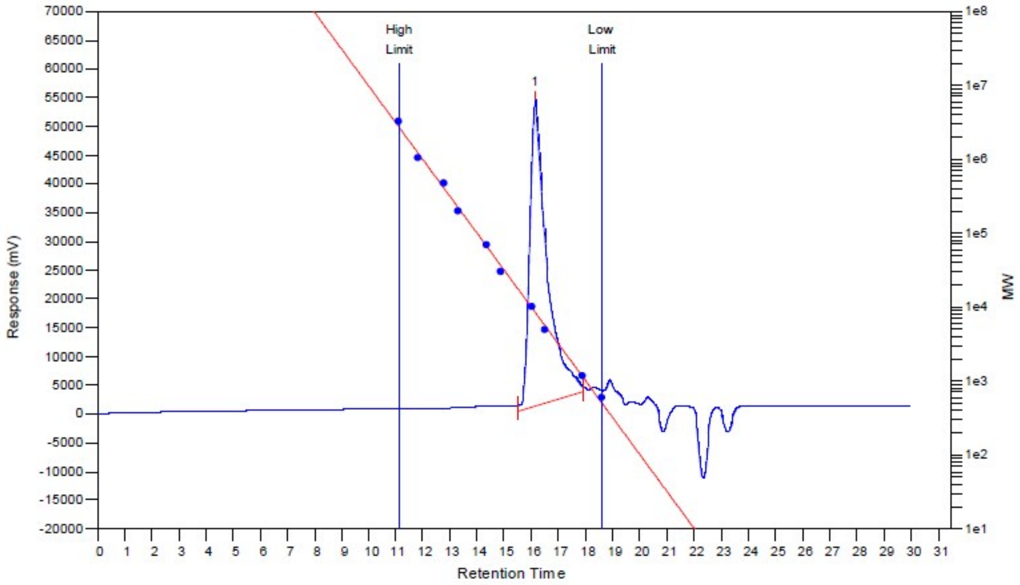
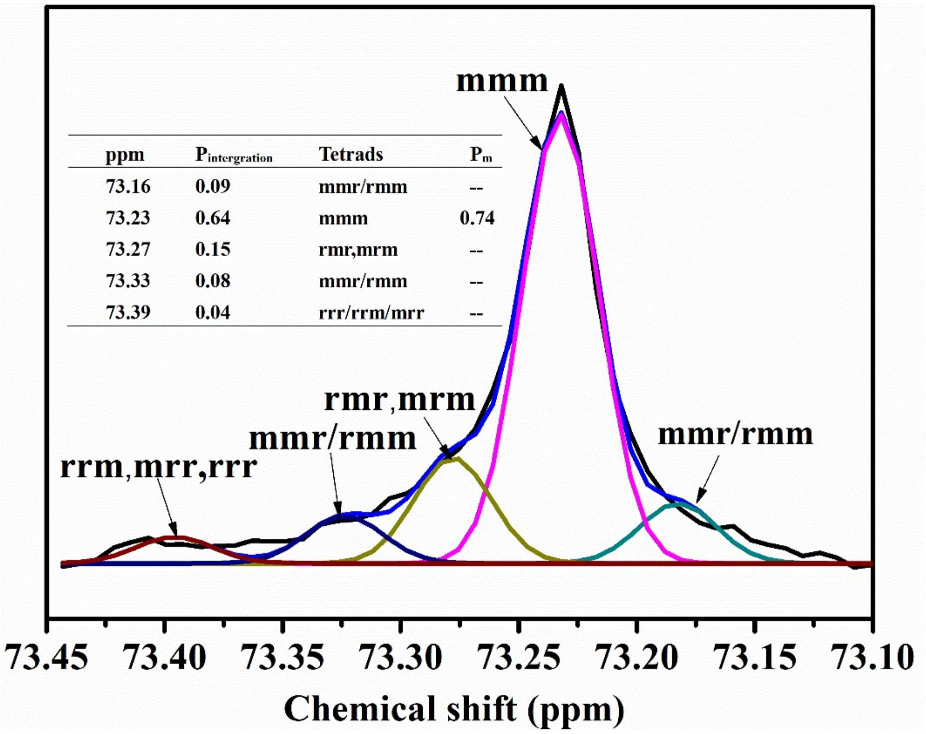


Fig. S5. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[BnOH]: [$_L$-PheOCA] = 0.75:1:50 (Table 1, run 2).



ppm	$P_{intergration}$	Tetrads	P_m
73.16	0.09	mmr/rmm	--
73.23	0.64	mmm	0.74
73.27	0.15	rmr,mrm	--
73.33	0.08	mmr/rmm	--
73.39	0.04	rrr/rrm/mrr	--

Fig. S6. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[BnOH]/[$_L$-PheOCA] = 0.75:1:50 (Table 1, run 2).

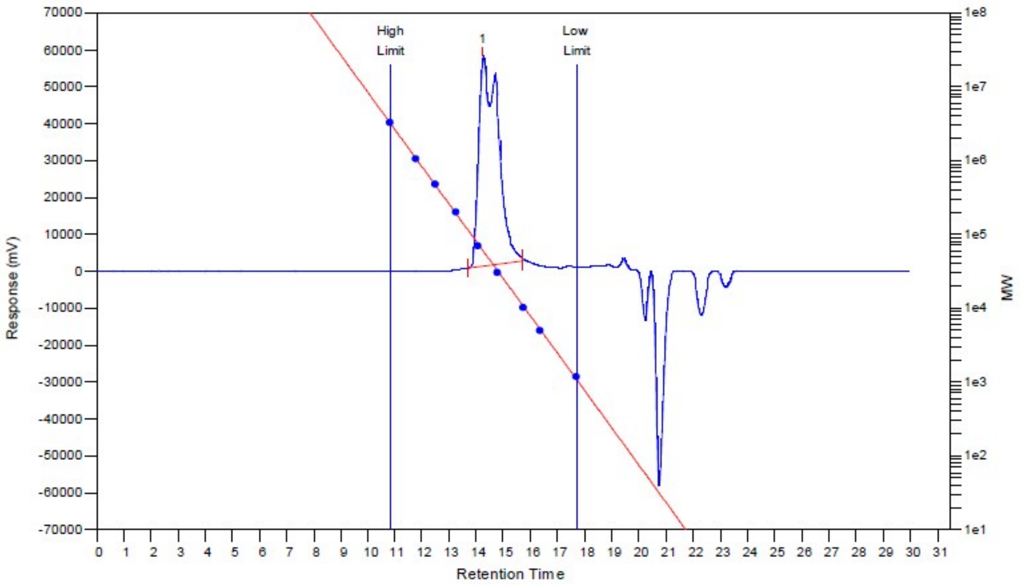
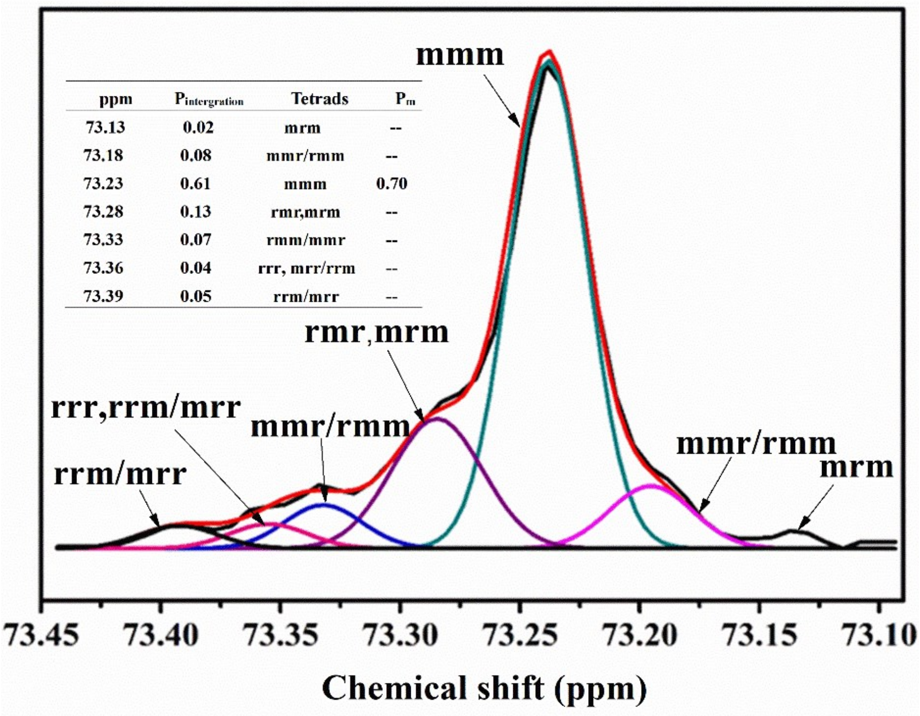


Fig. S7. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]: [$_L$-PheOCA] = 0.75:0.75:50 (Table 1, run 3).



ppm	$P_{intergration}$	Tetrads	P_m
73.13	0.02	mrm	--
73.18	0.08	mmr/rmm	--
73.23	0.61	mmm	0.70
73.28	0.13	rmr,mrm	--
73.33	0.07	rmm/mmr	--
73.36	0.04	rrr, mrr/rrm	--
73.39	0.05	rrm/mrr	--

Fig. S8. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[$_L$-PheOCA] = 0.75:0.75:50 (Table 1, run 3).

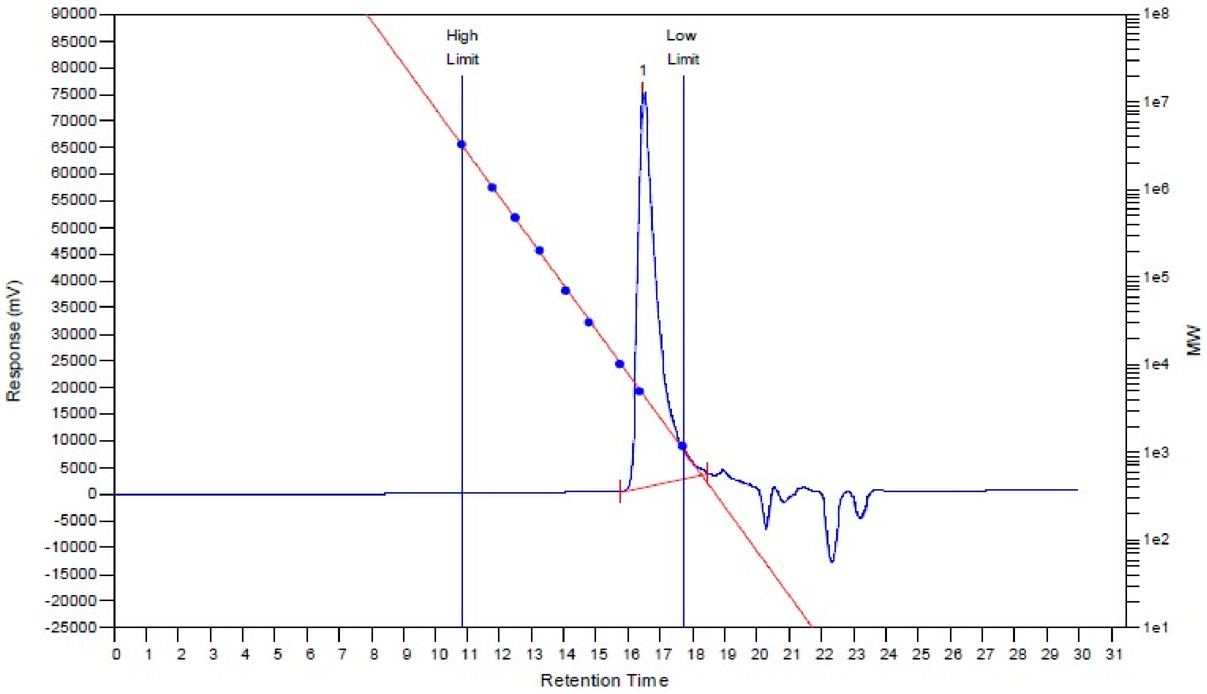


Fig. S9. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] = 0.75:0.75:1:25 (Table 1, run 5).

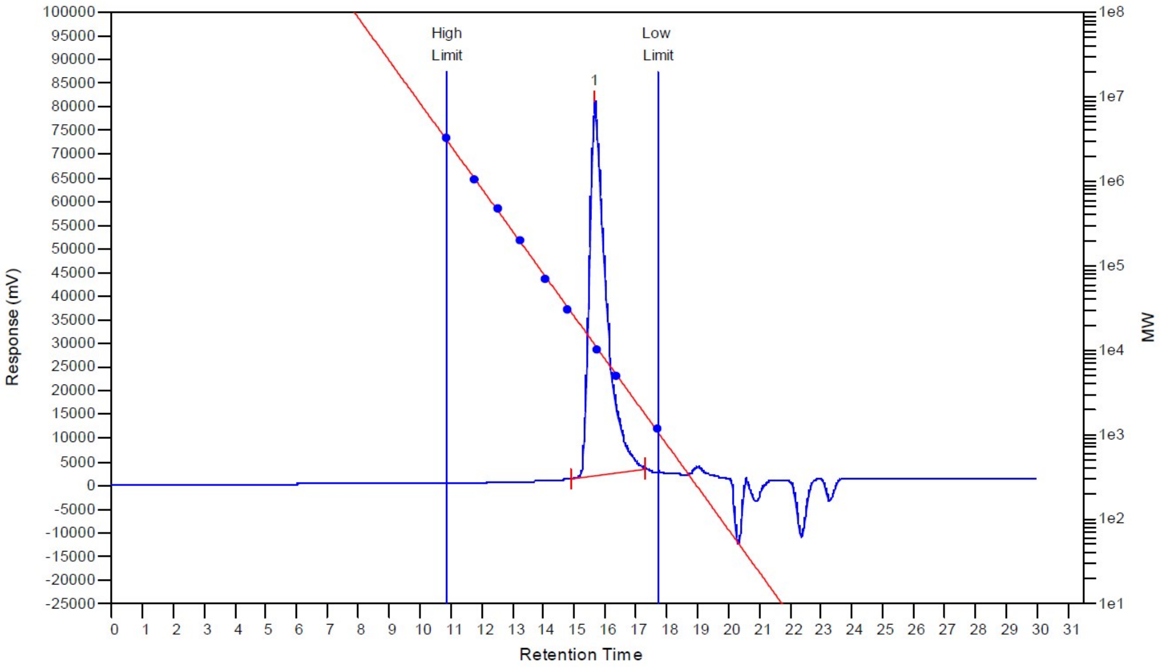


Fig. S10. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] = 0.75:0.75:1:75 (Table 1, run 6).

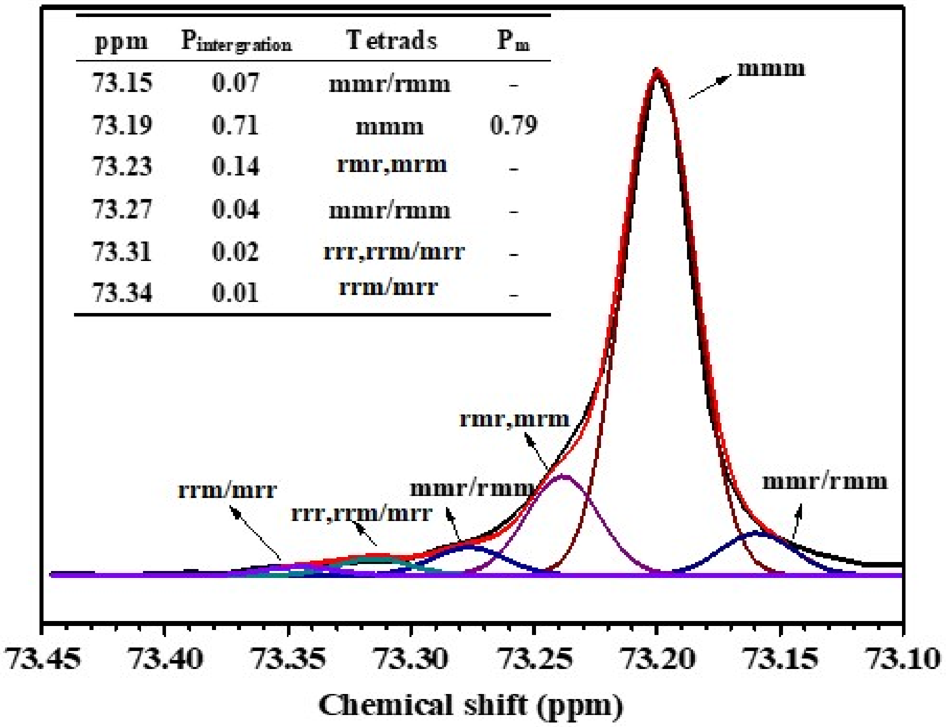


Fig. S11. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{L}$-PheOCA] = 0.75:0.75:1:75 (Table 1, run 6).

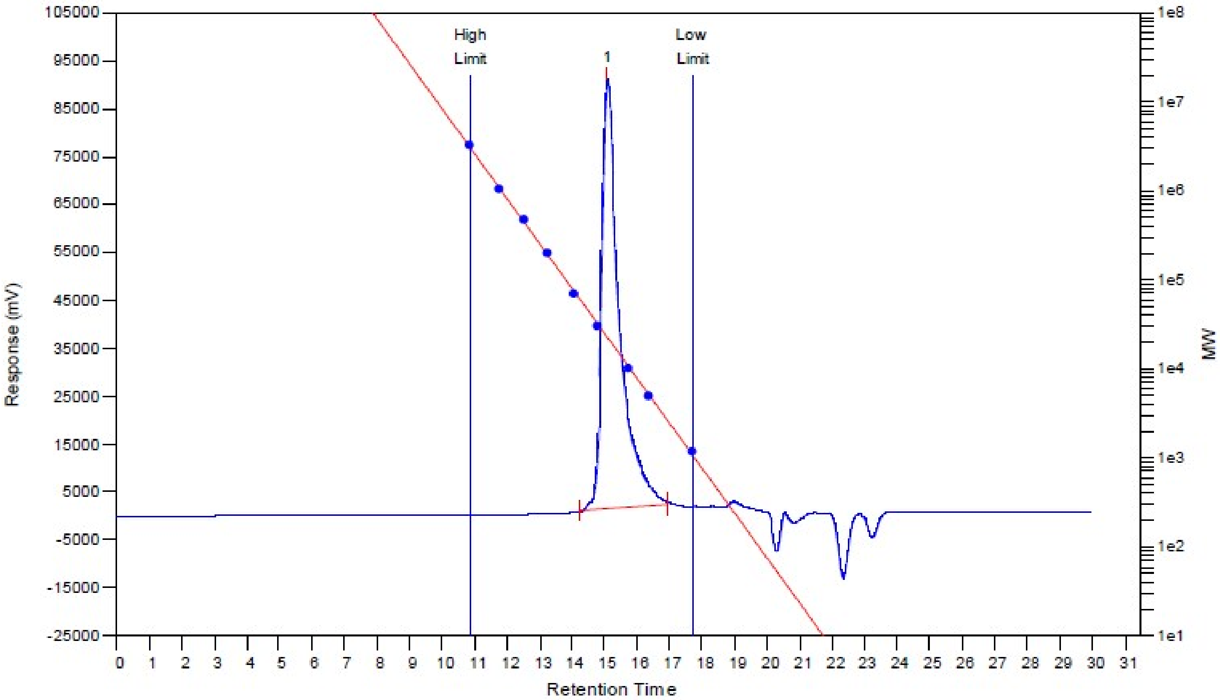
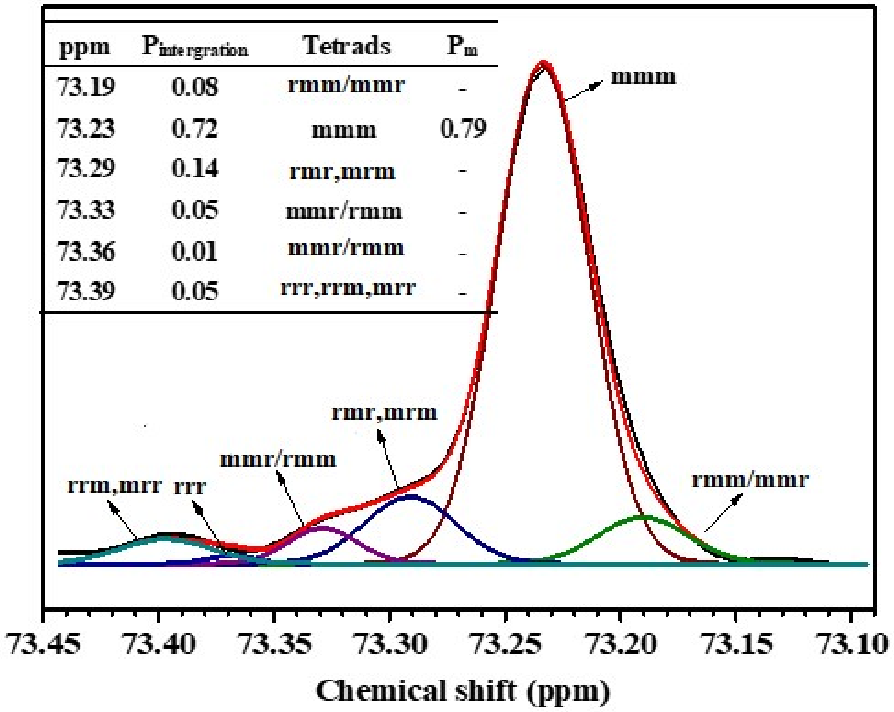


Fig. S12. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] = 0.75:0.75:1:100 (Table 1, run 7).



ppm	$P_{intergration}$	Tetrads	P_m
73.19	0.08	rmm/mmr	-
73.23	0.72	mmm	0.79
73.29	0.14	rmr,mrm	-
73.33	0.05	mmr/rmm	-
73.36	0.01	mmr/rmm	-
73.39	0.05	rrr,rrm,mrr	-

Fig. S13. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:100 (Table 1, run 7).

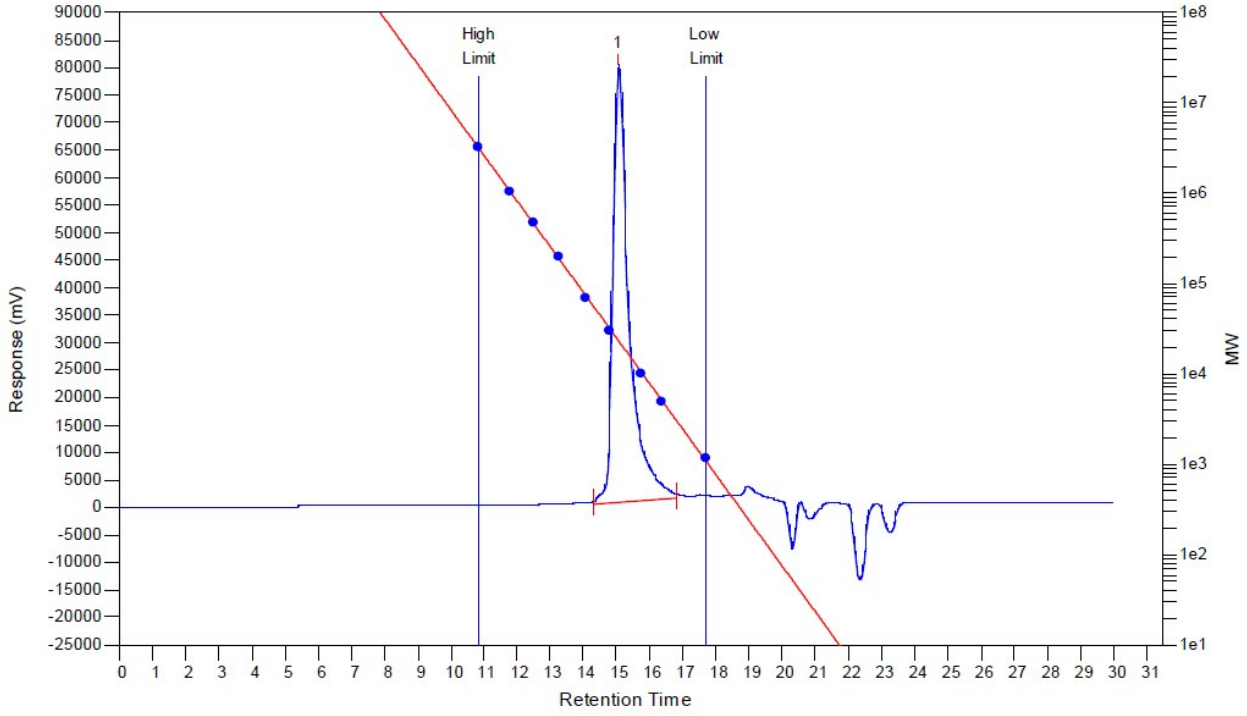
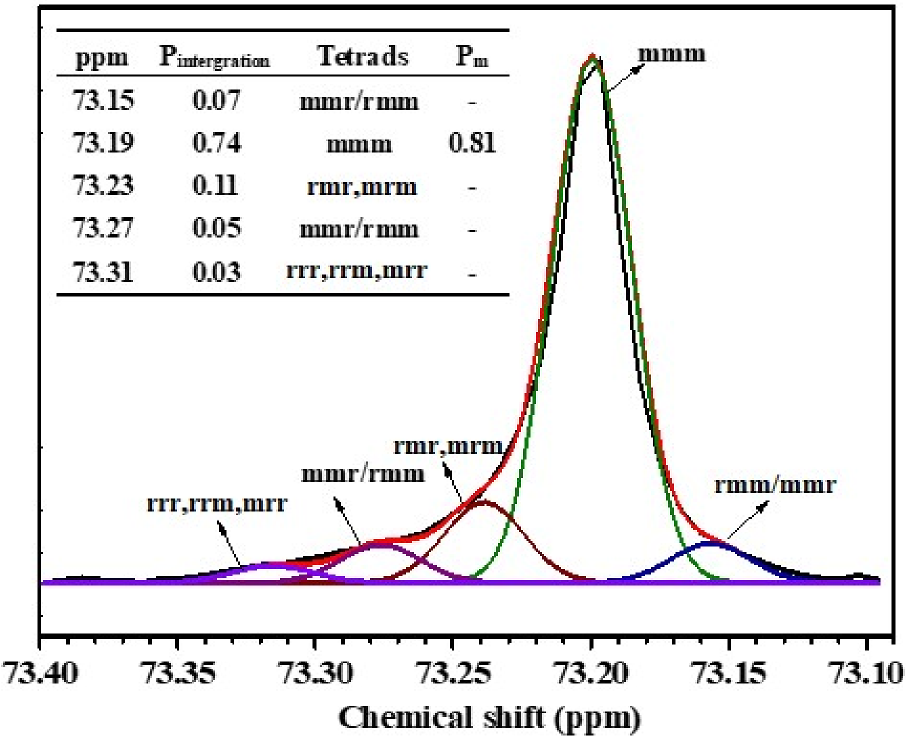


Fig. S14. GPC curves of the resulting polymers via ROP of $_{\text{L}}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:150 (Table 1, run 8).



ppm	$P_{intergration}$	Tetrads	P_m
73.15	0.07	mmr/rmm	-
73.19	0.74	mmm	0.81
73.23	0.11	rmr,mrm	-
73.27	0.05	mmr/rmm	-
73.31	0.03	rrr,rrm,mrr	-

Fig. S15. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 0.75:0.75:1:150 (Table 1, run 8).

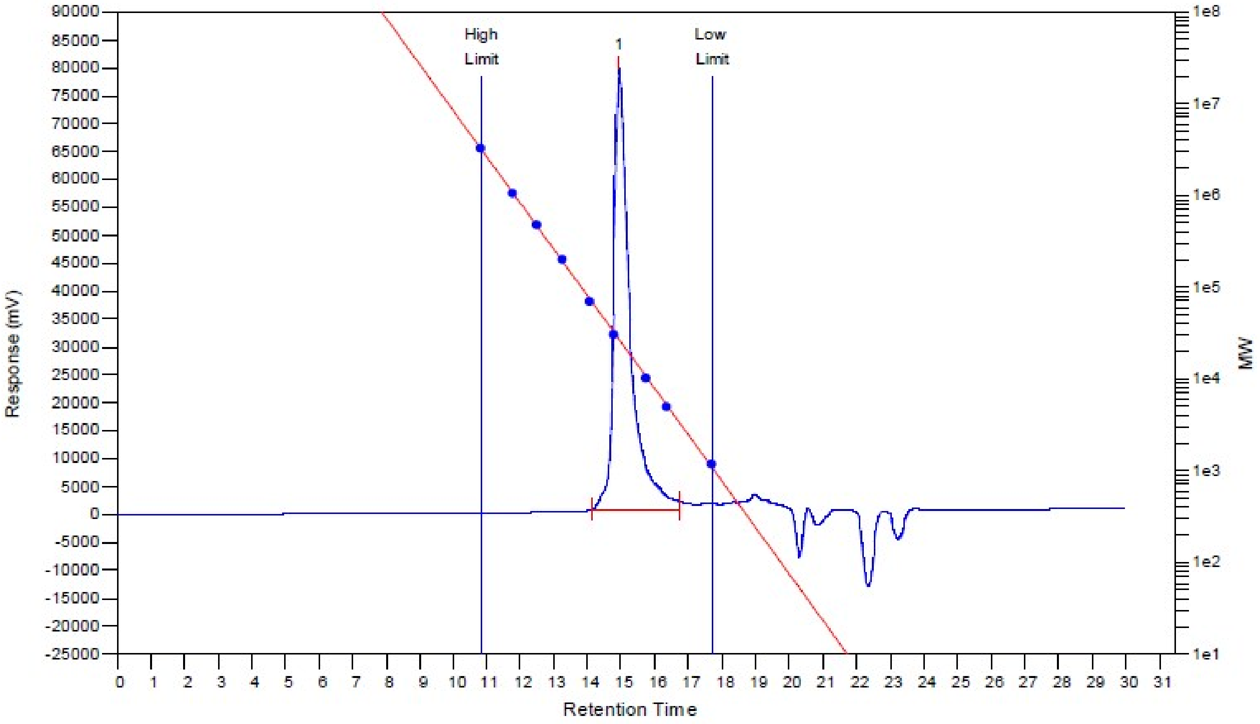
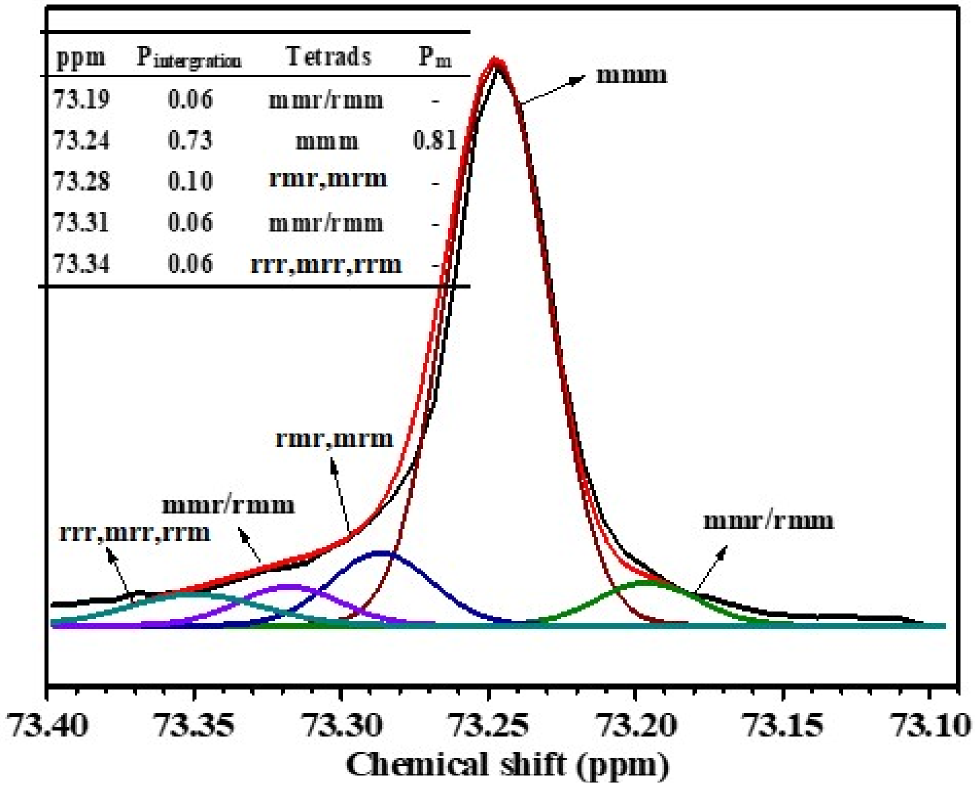


Fig. S16. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] = 0.75:0.75:1:200 (Table 1, run 9).



ppm	$P_{intergration}$	Tetrads	P_m
73.19	0.06	mmr/rmm	-
73.24	0.73	mmm	0.81
73.28	0.10	rmr,mrm	-
73.31	0.06	mmr/rmm	-
73.34	0.06	rrr,mrr,rrm	-

Fig. S17. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:200 (Table 1, run 9).

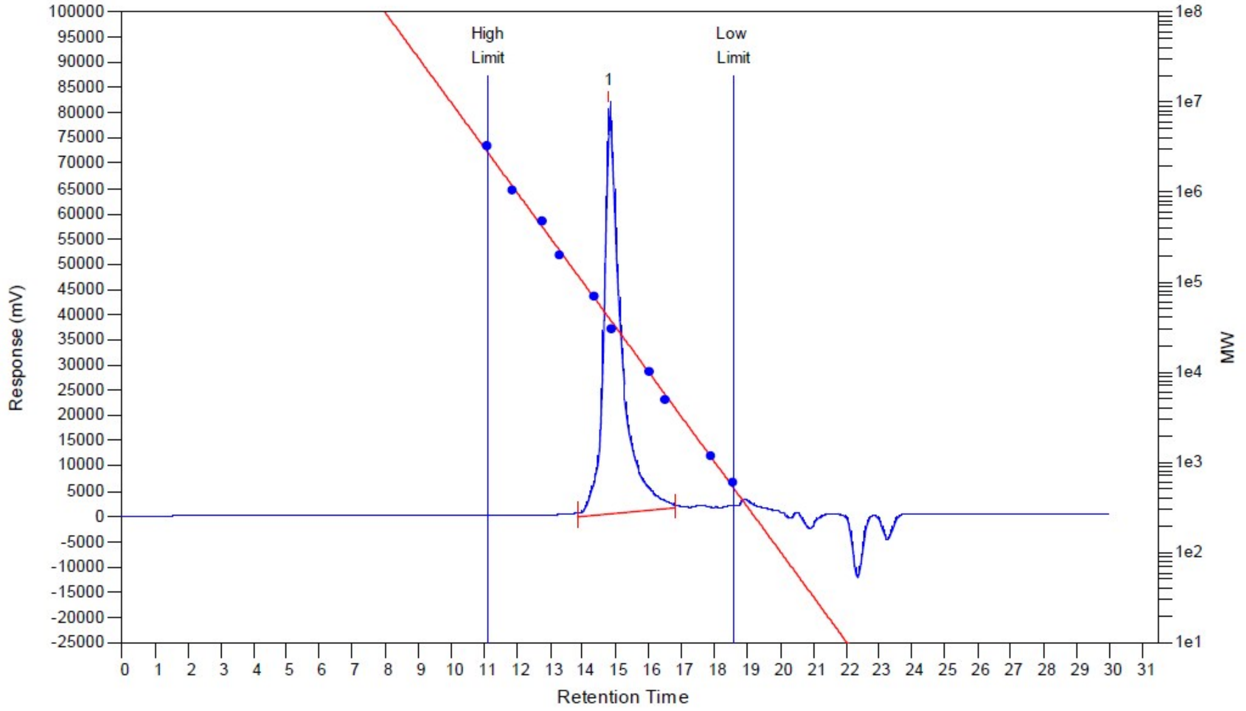
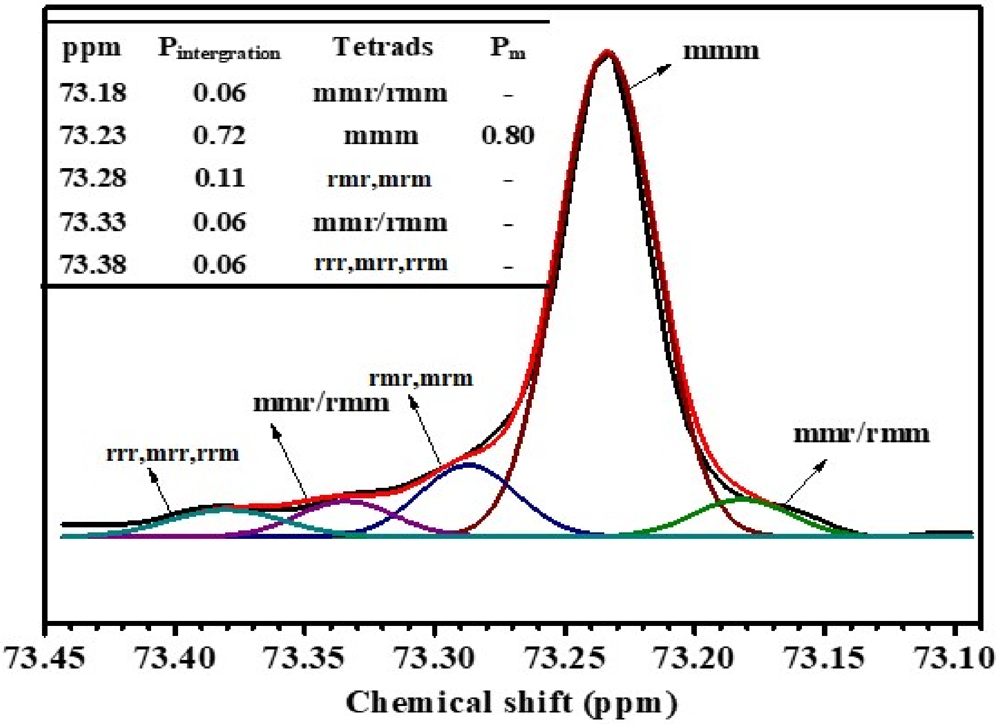


Fig. S18. GPC curves of the resulting polymers via ROP of $_{\text{L}}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:250 (Table 1, run 10).



ppm	$P_{intergration}$	Tetrads	P_m
73.18	0.06	mmr/rmm	-
73.23	0.72	mmm	0.80
73.28	0.11	rmr,mrm	-
73.33	0.06	mmr/rmm	-
73.38	0.06	rrr,mrr,rrm	-

Fig. S19. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[L-PheOCA] = 0.75:0.75:1:250 (Table 1, run 10).

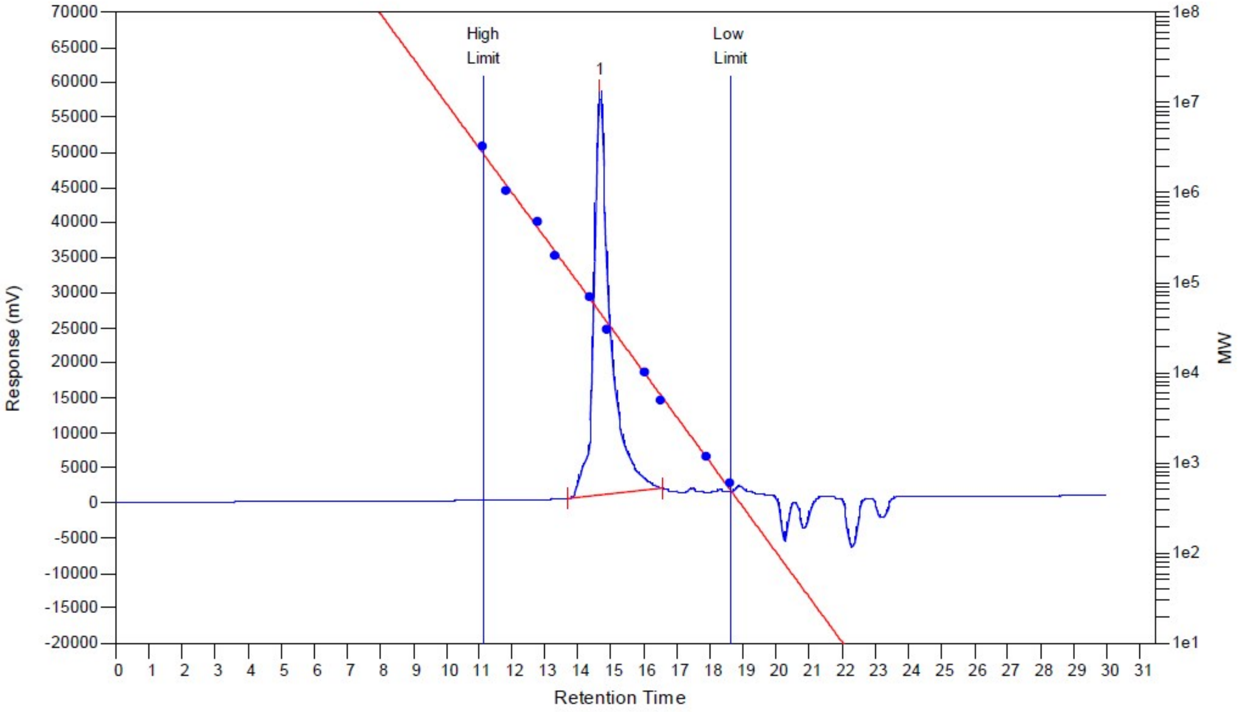
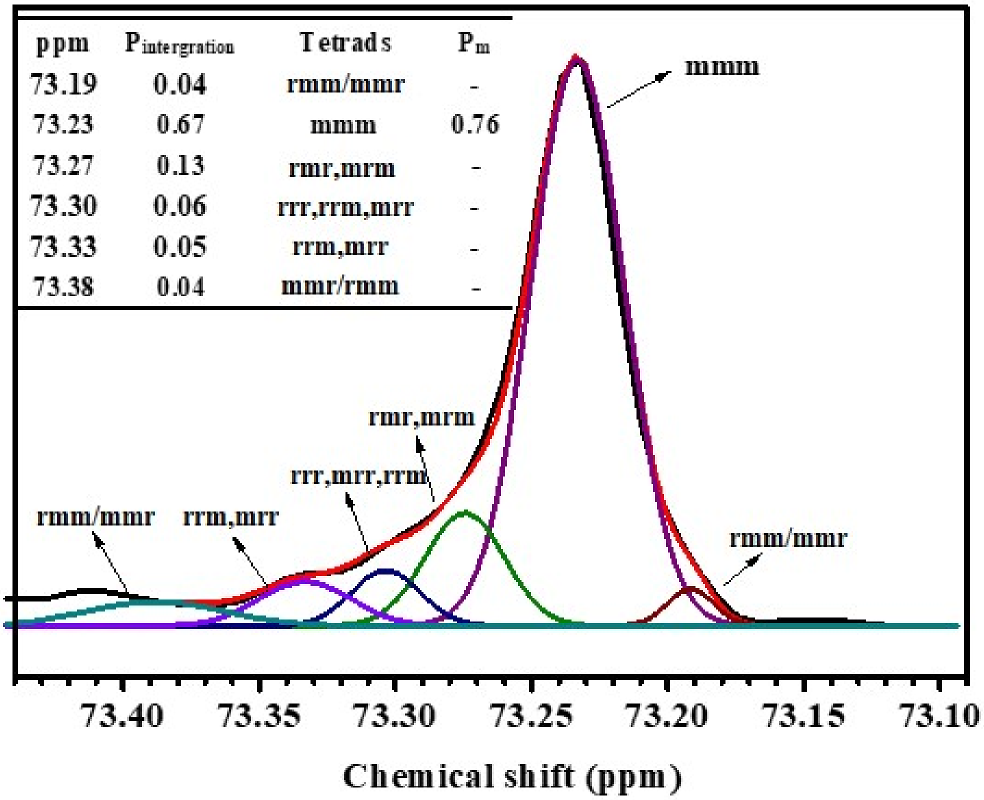


Fig. S20. GPC curves of the resulting polymers via ROP of L-PheOCA using [DABCO]:[TEB]:[BnOH]:[L-PheOCA] = 0.75:0.75:1:300 (Table 1, run 11).



ppm	$P_{intergration}$	Tetrads	P_m
73.19	0.04	rmm/mmr	-
73.23	0.67	mmm	0.76
73.27	0.13	rmr,mrm	-
73.30	0.06	rrr,rrm,mrr	-
73.33	0.05	rrm,mrr	-
73.38	0.04	mmr/rmm	-

Fig. S21. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\mathrm{L}}$-PheOCA] = 0.75:0.75:1:300 (Table 1, run 11).

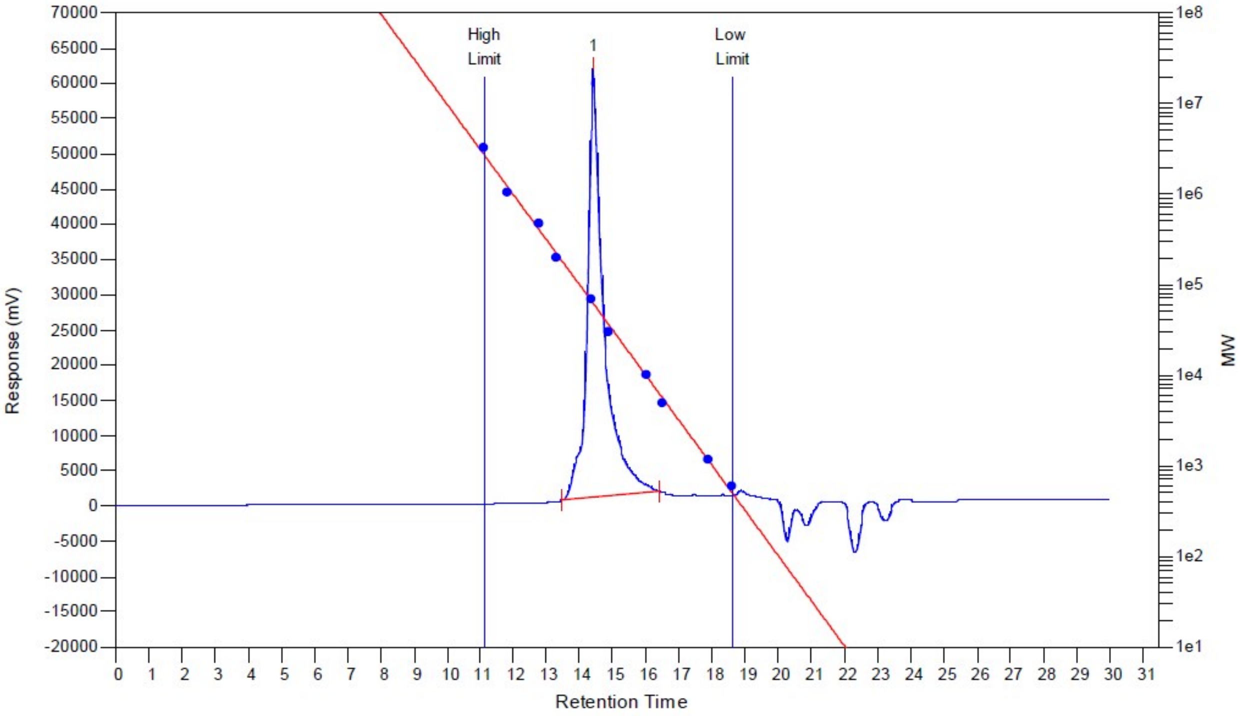
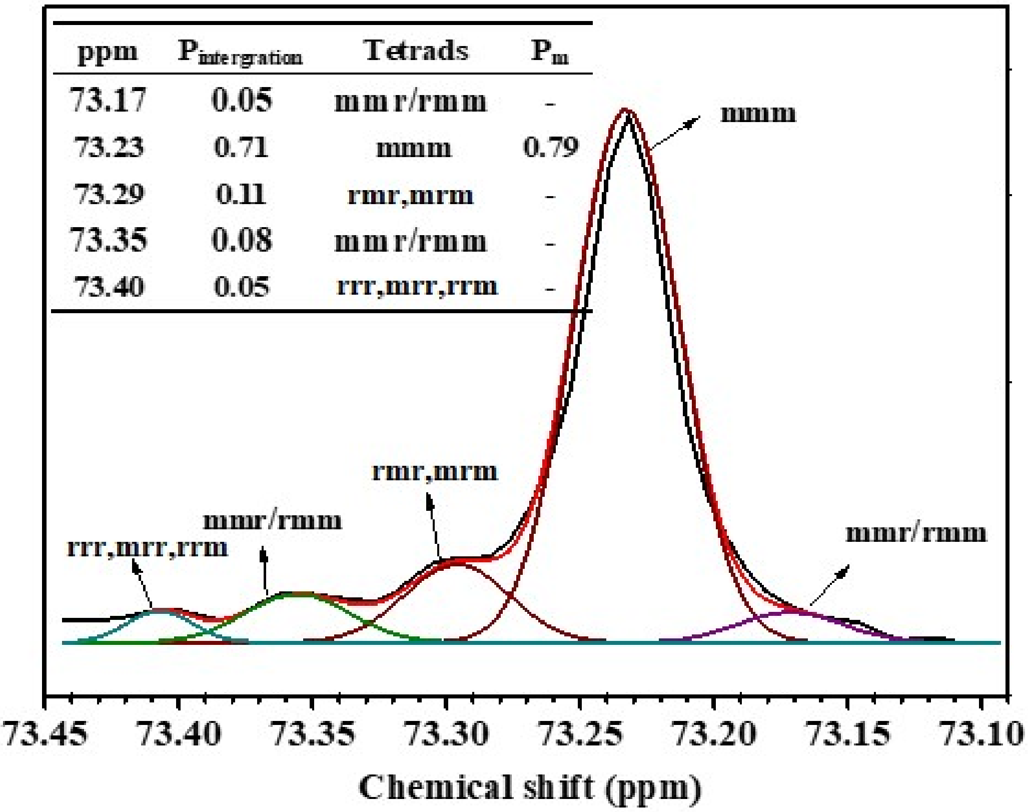


Fig. S22. GPC curves of the resulting polymers via ROP of $_{\mathrm{L}}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{\mathrm{L}}$-PheOCA] = 0.75:0.75:1:400 (Table 1, run 12).



ppm	$P_{intergration}$	Tetrads	P_m
73.17	0.05	mmr/rmm	-
73.23	0.71	mmm	0.79
73.29	0.11	rmr,mrm	-
73.35	0.08	mmr/rmm	-
73.40	0.05	rrr,mrr,rrm	-

Fig. S23. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 0.75:0.75:1:400 (Table 1, run 12).

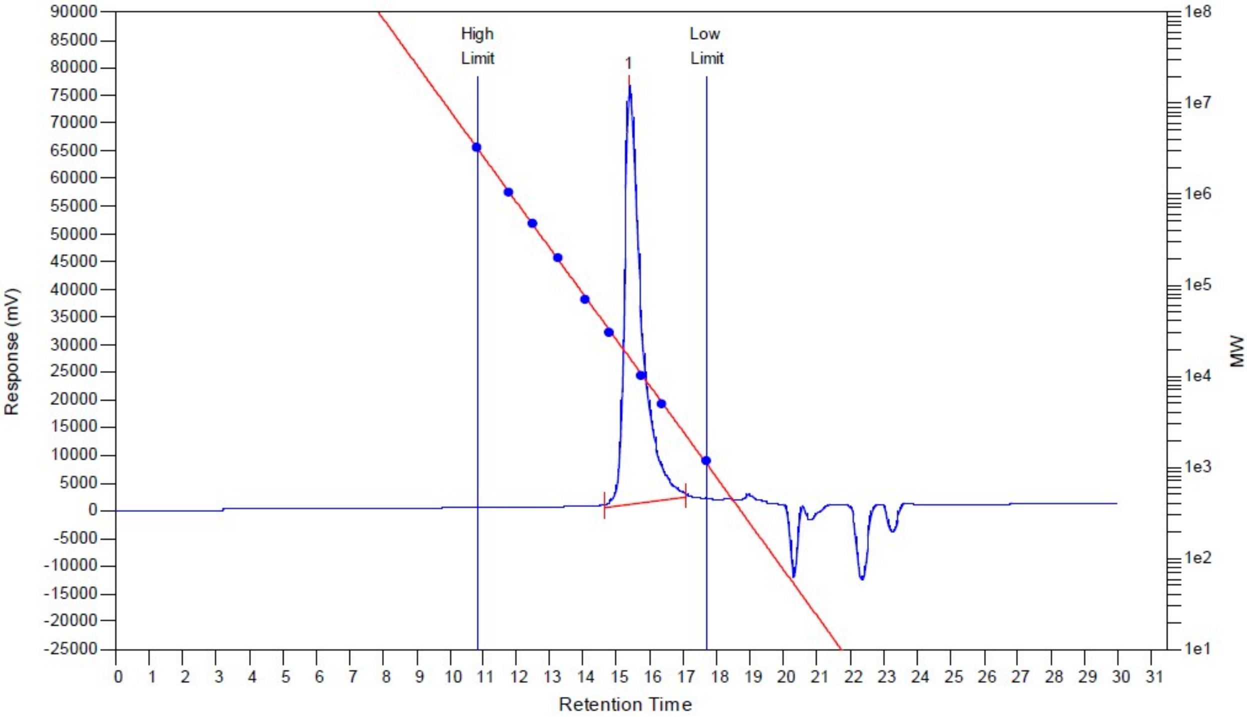
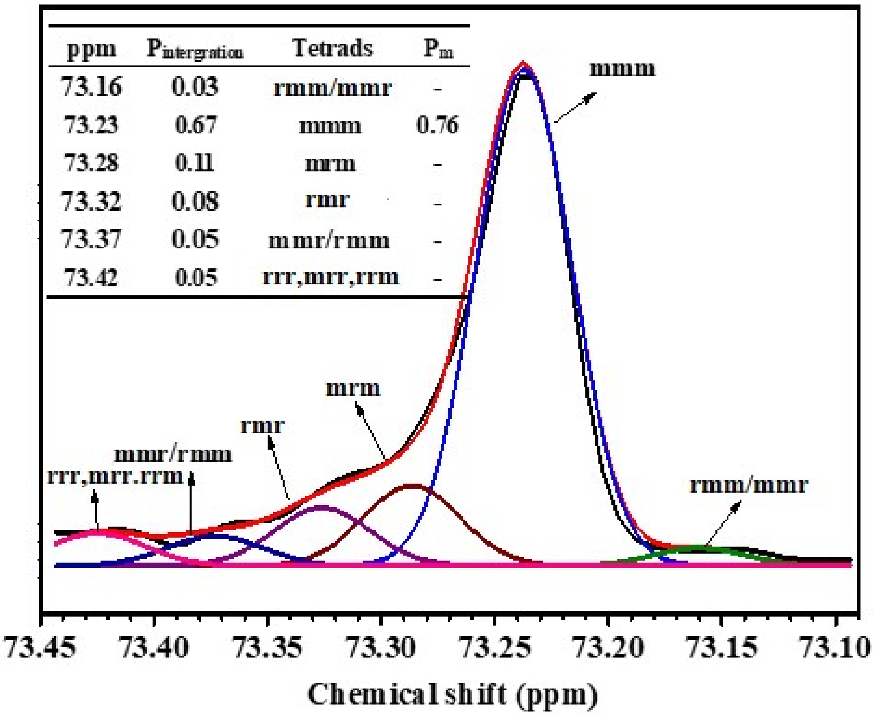


Fig. S24. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] = 0.75:0.75:1:(50/50) (Table 1, run 13).



ppm	$P_{intergration}$	Tetrads	P_m
73.16	0.03	rmm/mmr	-
73.23	0.67	mmm	0.76
73.28	0.11	mrm	-
73.32	0.08	rmr	-
73.37	0.05	mmr/rmm	-
73.42	0.05	rrr,mrr,rrm	-

Fig. S25. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:(50/50) (Table 1, run 13).

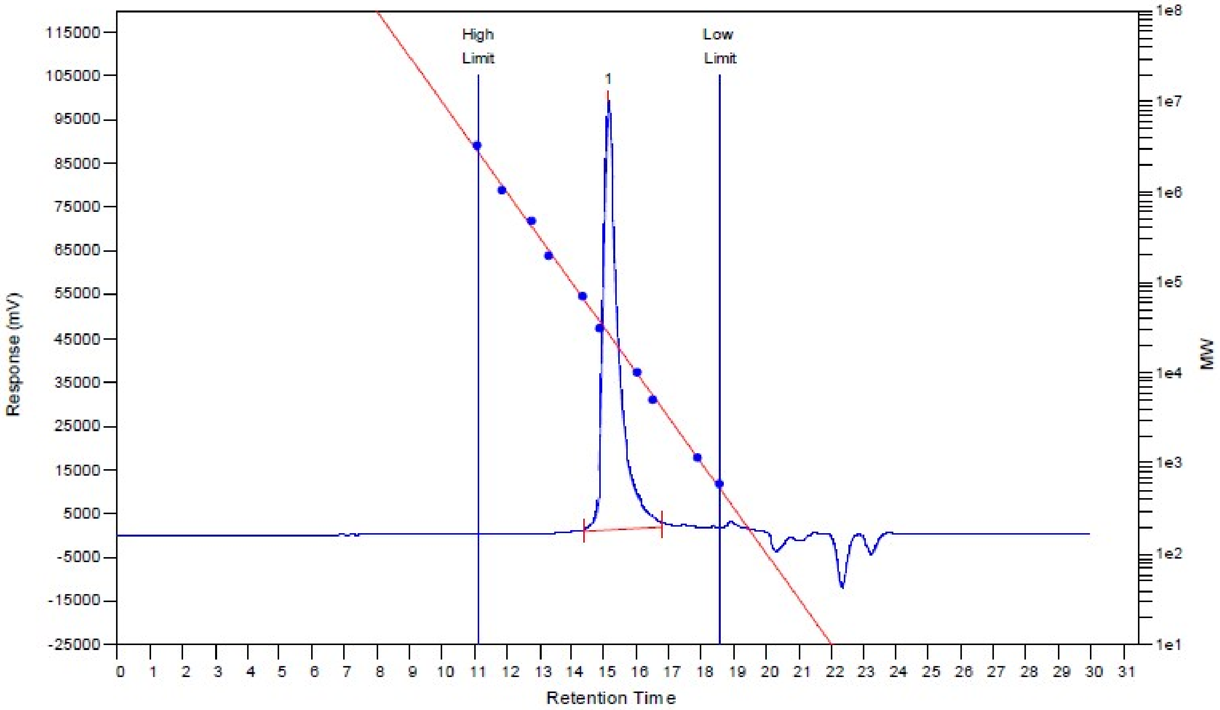
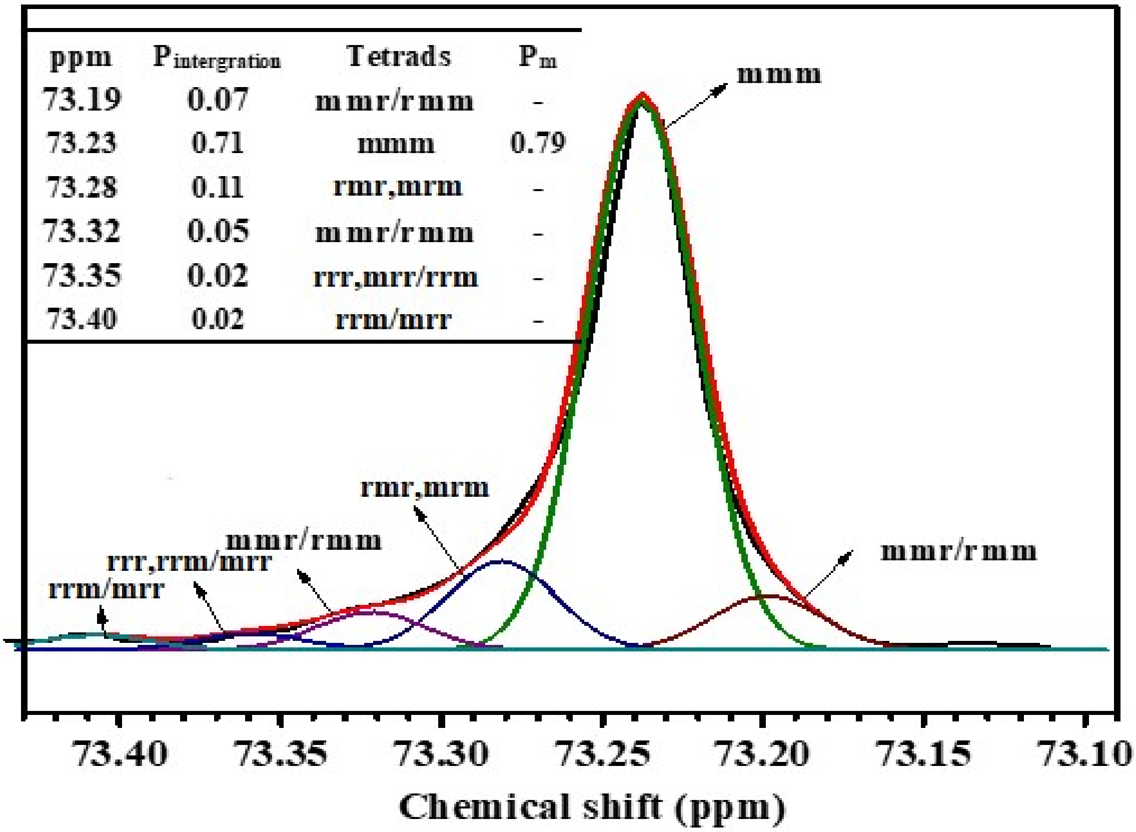


Fig. S26. GPC curves of the resulting polymers via ROP of $_{\text{L}}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:(50/50/50) (Table 1, run 14).



ppm	$P_{intergration}$	Tetrads	P_m
73.19	0.07	mmr/rmm	-
73.23	0.71	mmm	0.79
73.28	0.11	rmr,mrm	-
73.32	0.05	mmr/rmm	-
73.35	0.02	rrr,mrr/rrm	-
73.40	0.02	rrm/mrr	-

Fig. S27. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[L-PheOCA] = 0.75:0.75:1:(50/50/50) (Table 1, run 14).

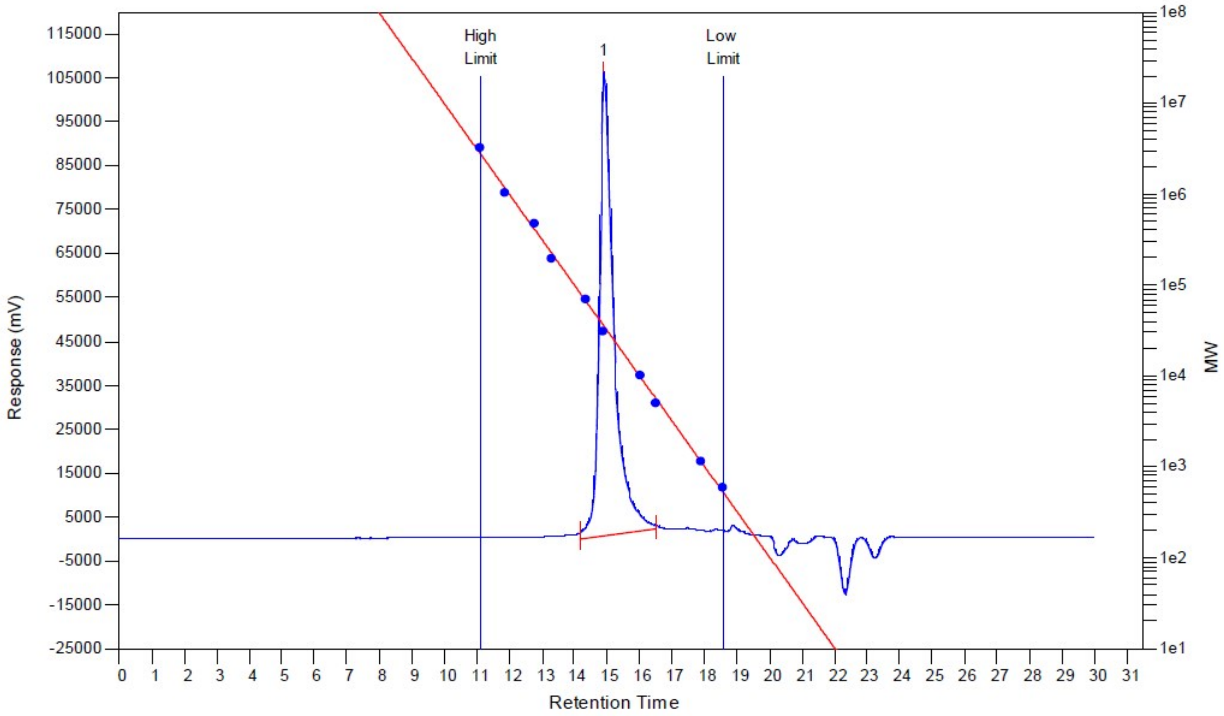
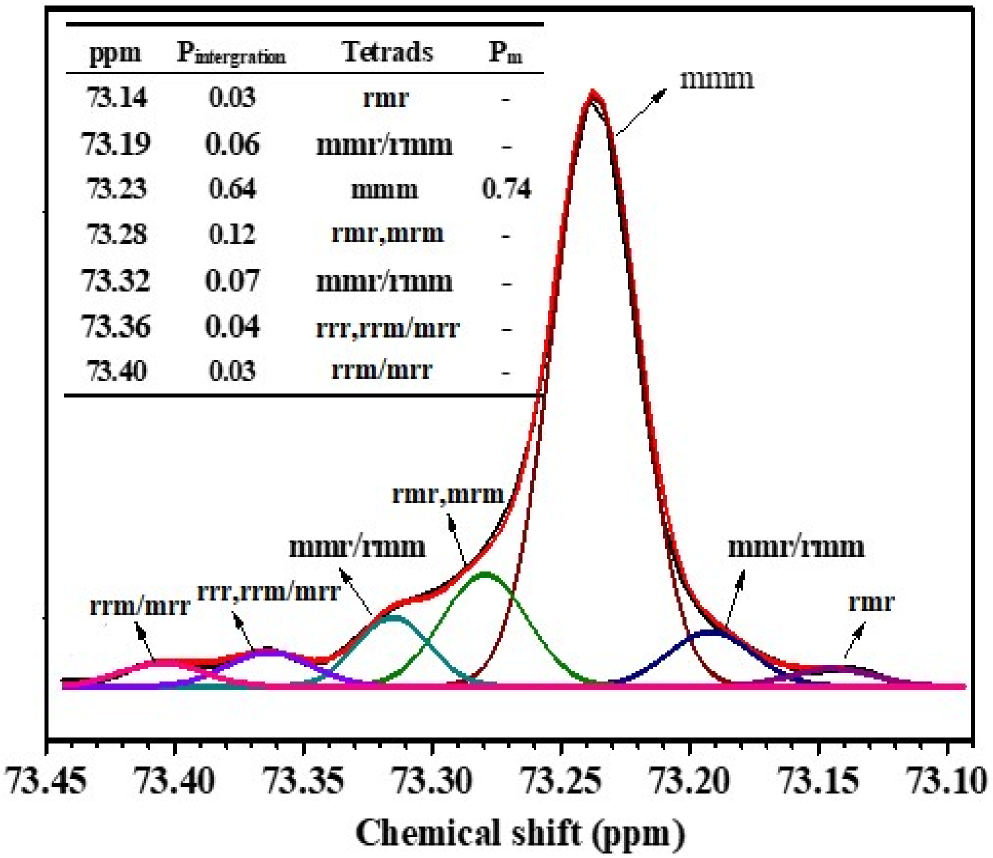


Fig. S28. GPC curves of the resulting polymers via ROP of L-PheOCA using [DABCO]:[TEB]:[BnOH]:[L-PheOCA] = 0.75:0.75:1:(50/50/50/50) (Table 1, run 15).



ppm	$P_{intergration}$	Tetrads	P_m
73.14	0.03	rmr	-
73.19	0.06	mmr/rmm	-
73.23	0.64	mmm	0.74
73.28	0.12	rmr,mrm	-
73.32	0.07	mmr/rmm	-
73.36	0.04	rrr,rrm/mrr	-
73.40	0.03	rrm/mrr	-

Fig. S29. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 0.75:0.75:1:(50/50/50/50) (Table 1, run 15).

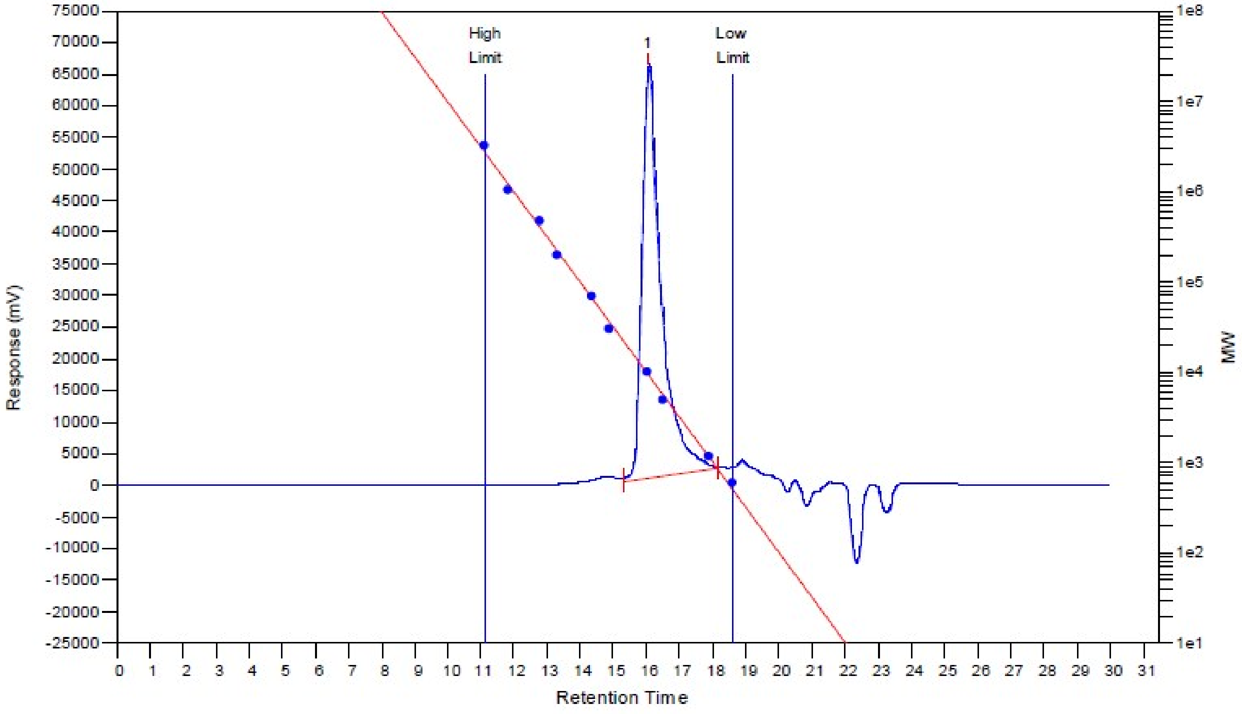


Fig. S30. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[BnOH]:[$_L$-PheOCA] = 0.75:0.75:50 in Tol (Table S1, run 1).

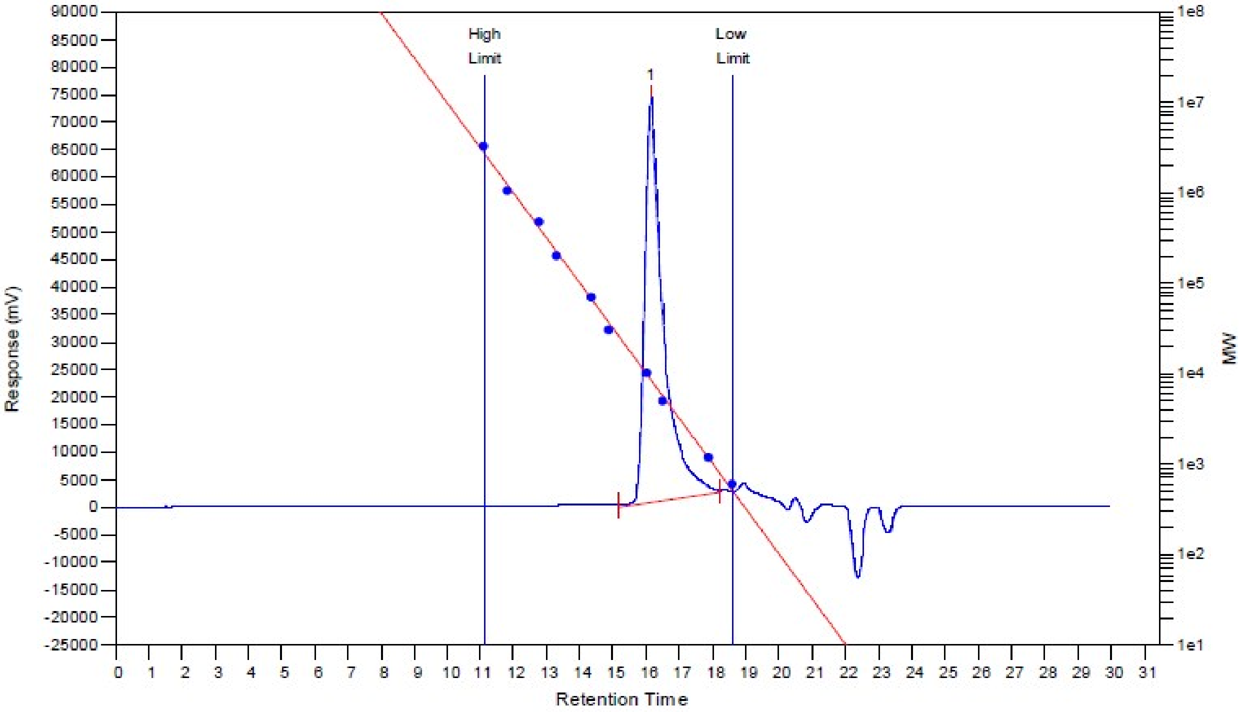


Fig. S31. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[BnOH]:[$_{L}$-PheOCA] = 0.75:1:50 in Tol (Table S1, run 2).

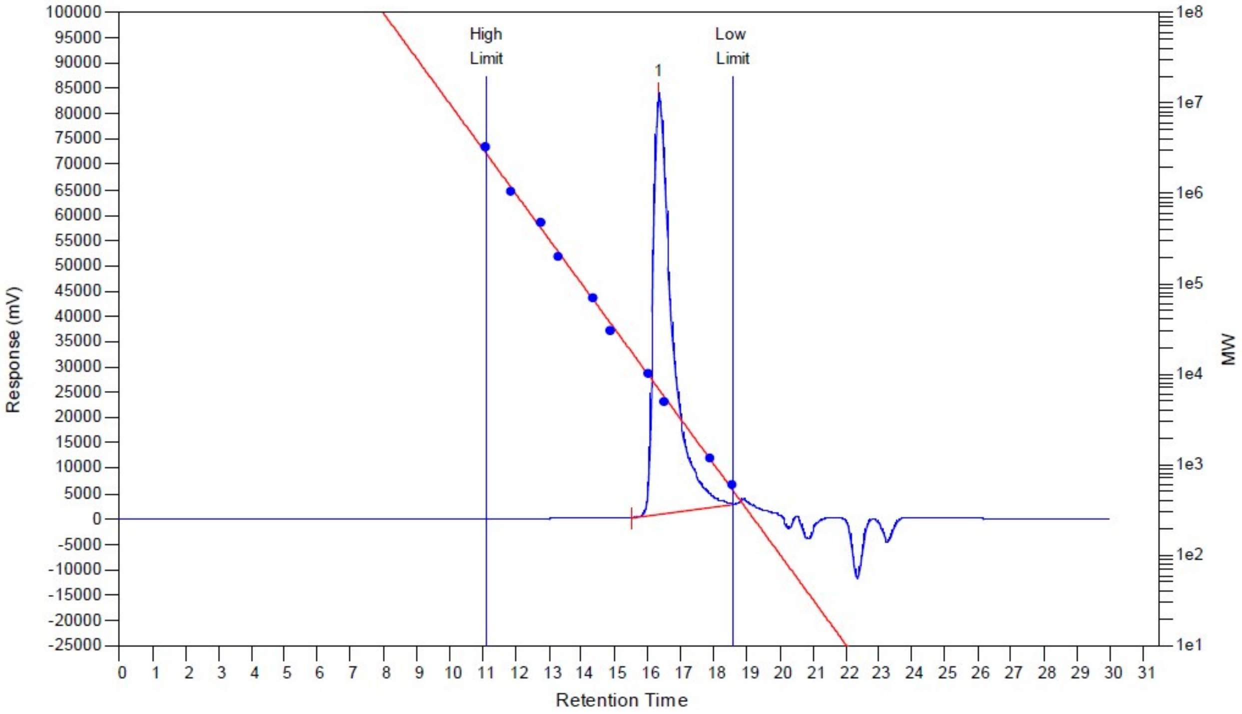


Fig. S32. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[BnOH]:[$_{L}$-PheOCA] = 0.75:1.5:50 in Tol (Table S1, run 3).

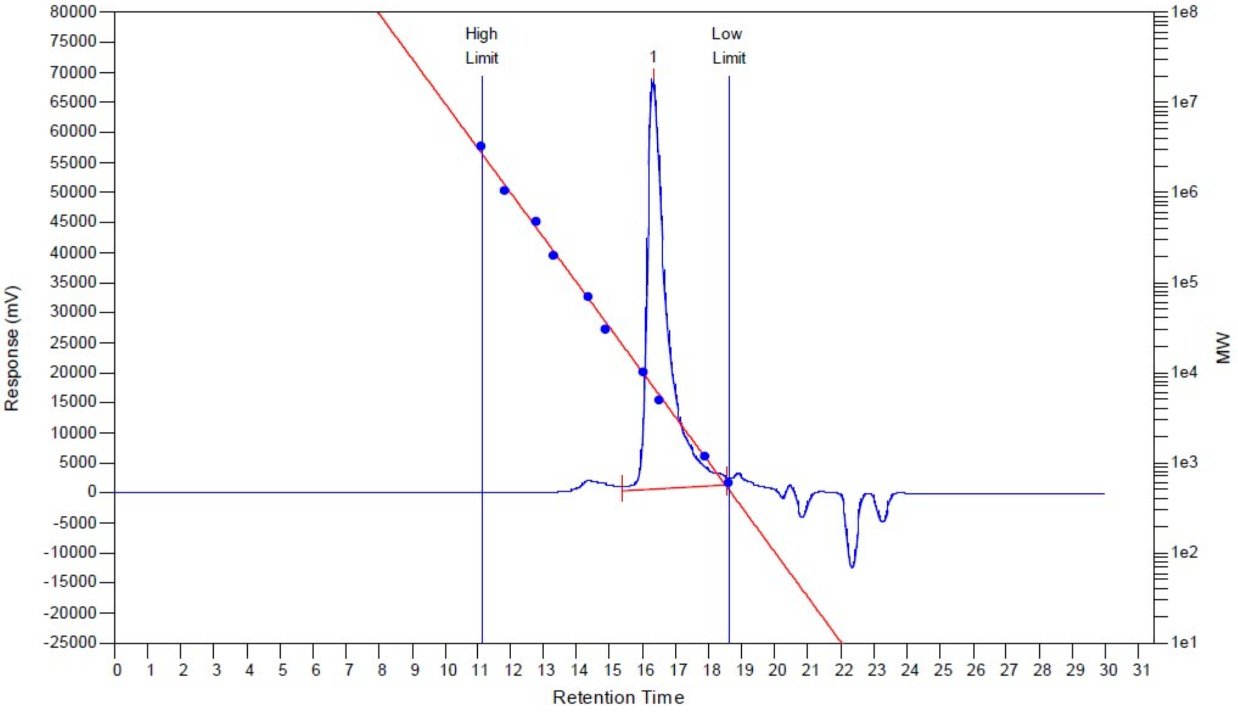


Fig. S33. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[BnOH]:[$_{L}$-PheOCA] = 0.75:2:50 in Tol (Table S1, run 4).

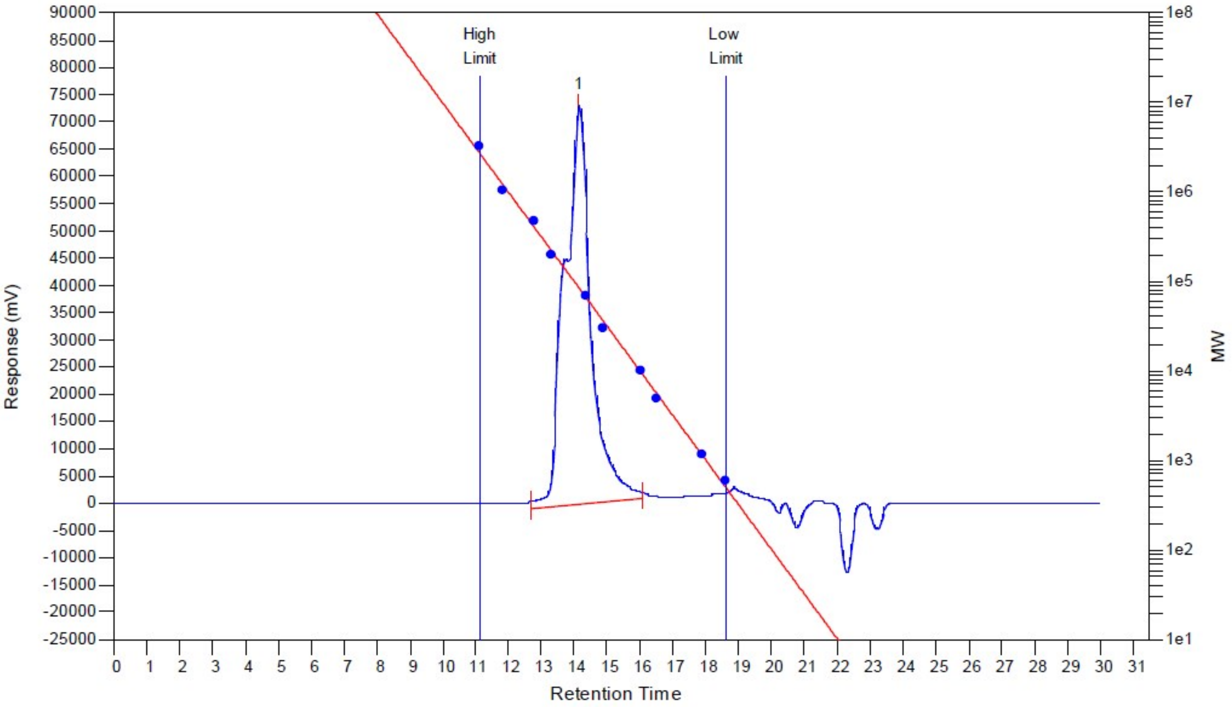


Fig. S34. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[$_{L}$-PheOCA] =1:0.75:50 in Tol (Table S1, run 5).

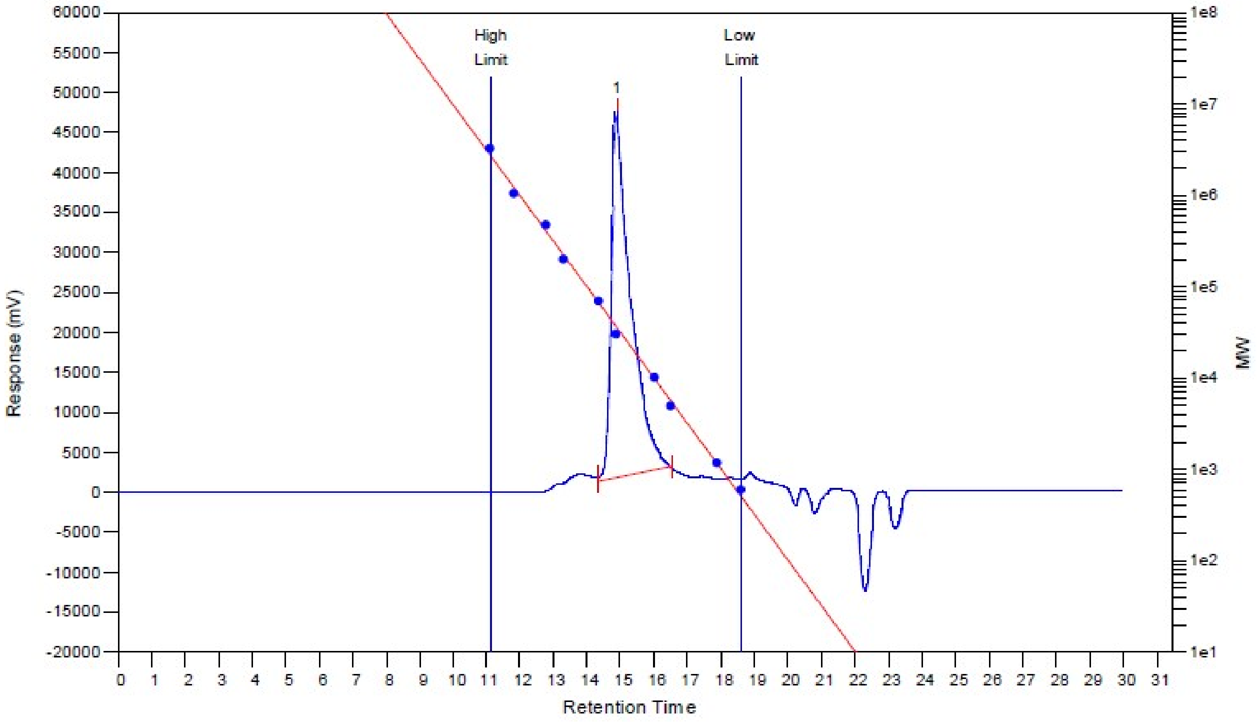


Fig. S35. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[$_L$-PheOCA] =1.5:0.75:50 in Tol (Table S1, run 6).

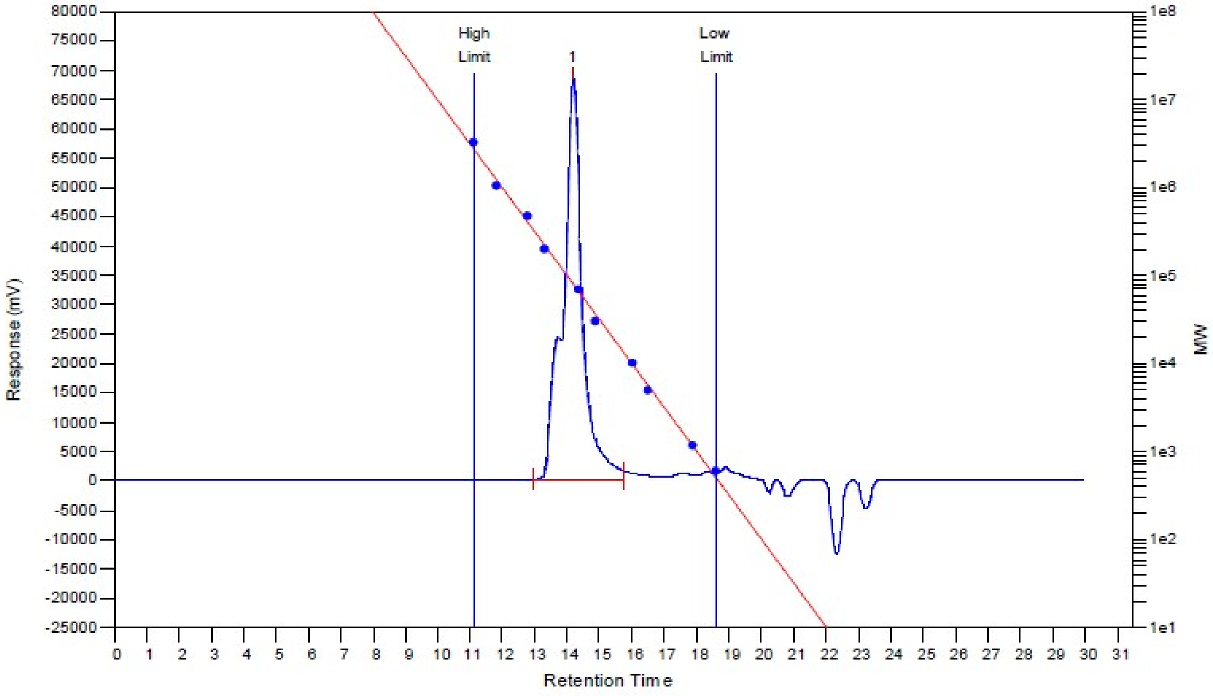


Fig. S36. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[$_L$-PheOCA] =0.75:1:50 in Tol (Table S1, run 7).

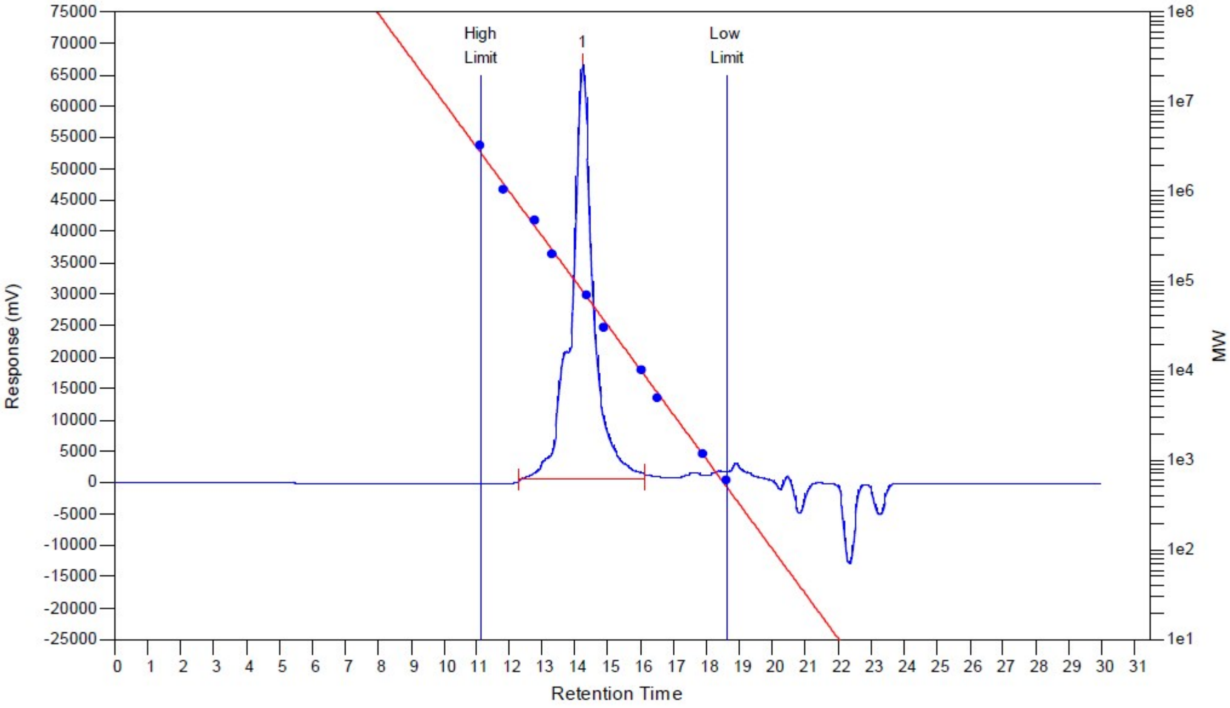


Fig. S37. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[$_L$-PheOCA] =0.75:1.5:50 in Tol (Table S1, run 8).

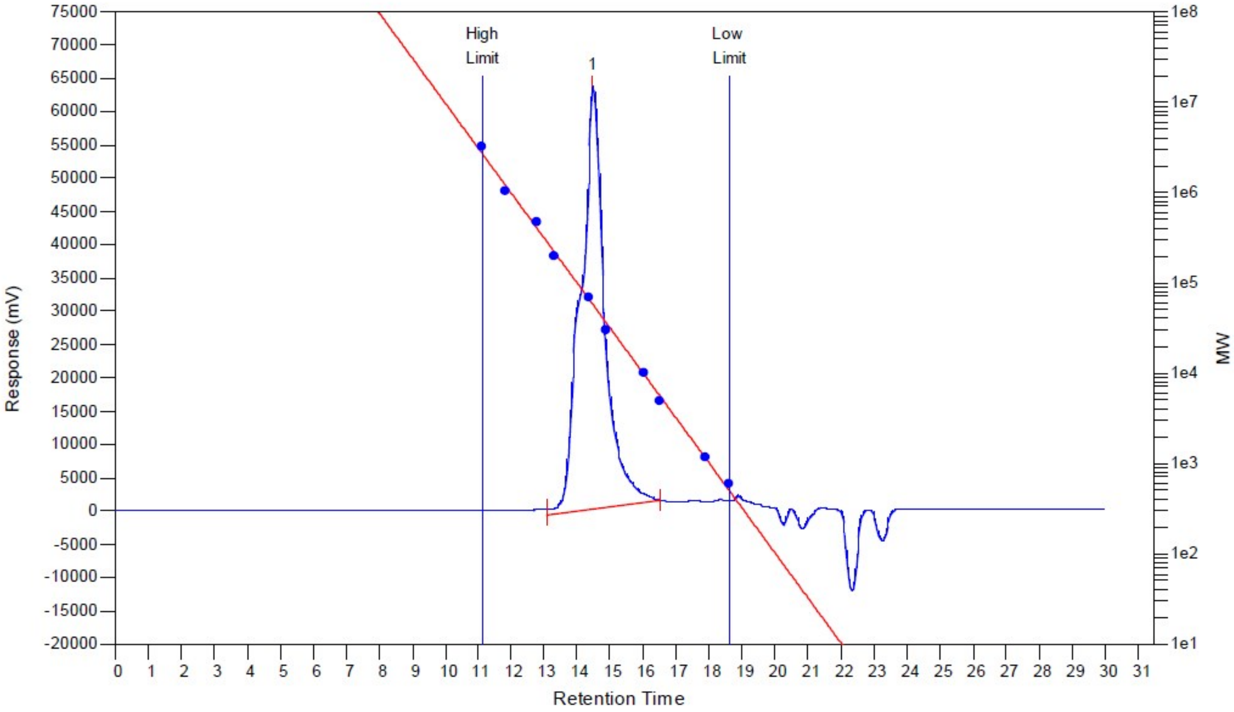


Fig. S38. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[$_L$-PheOCA] =0.75:2:50 in Tol (Table S1, run 9).

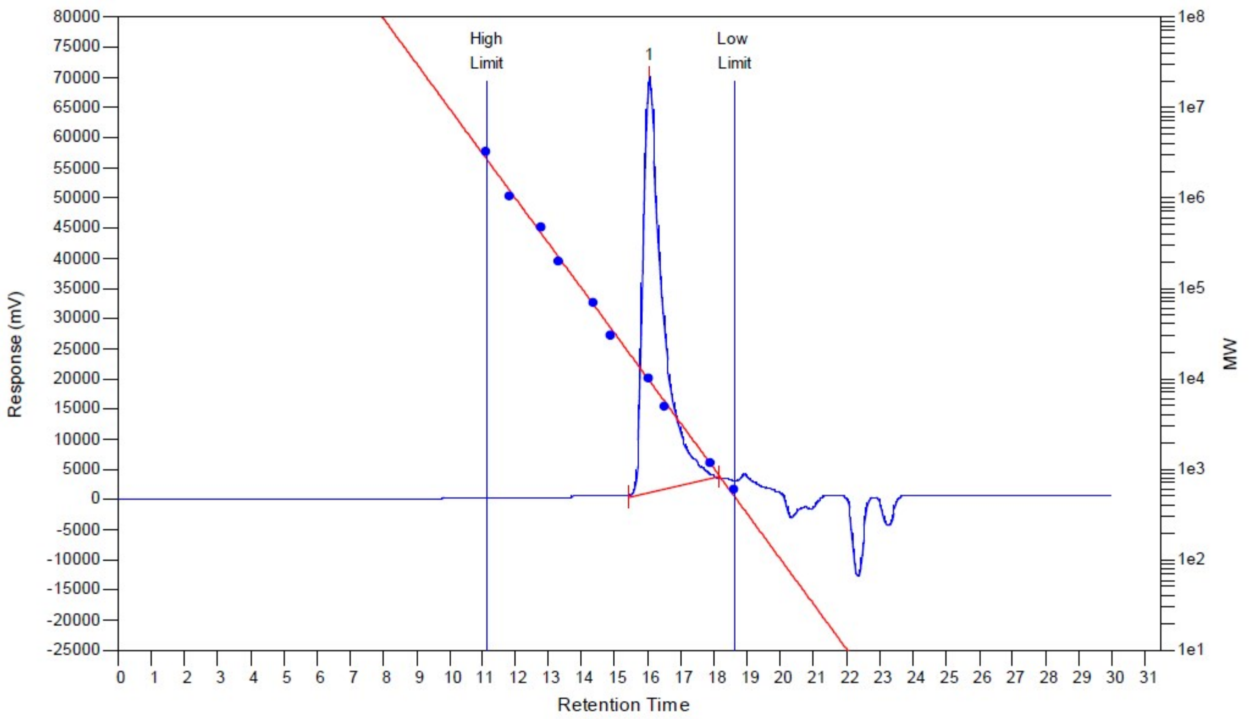


Fig. S39. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] =0.75:0.75:1:50 in CH_2Cl_2 (Table S2, run 2)

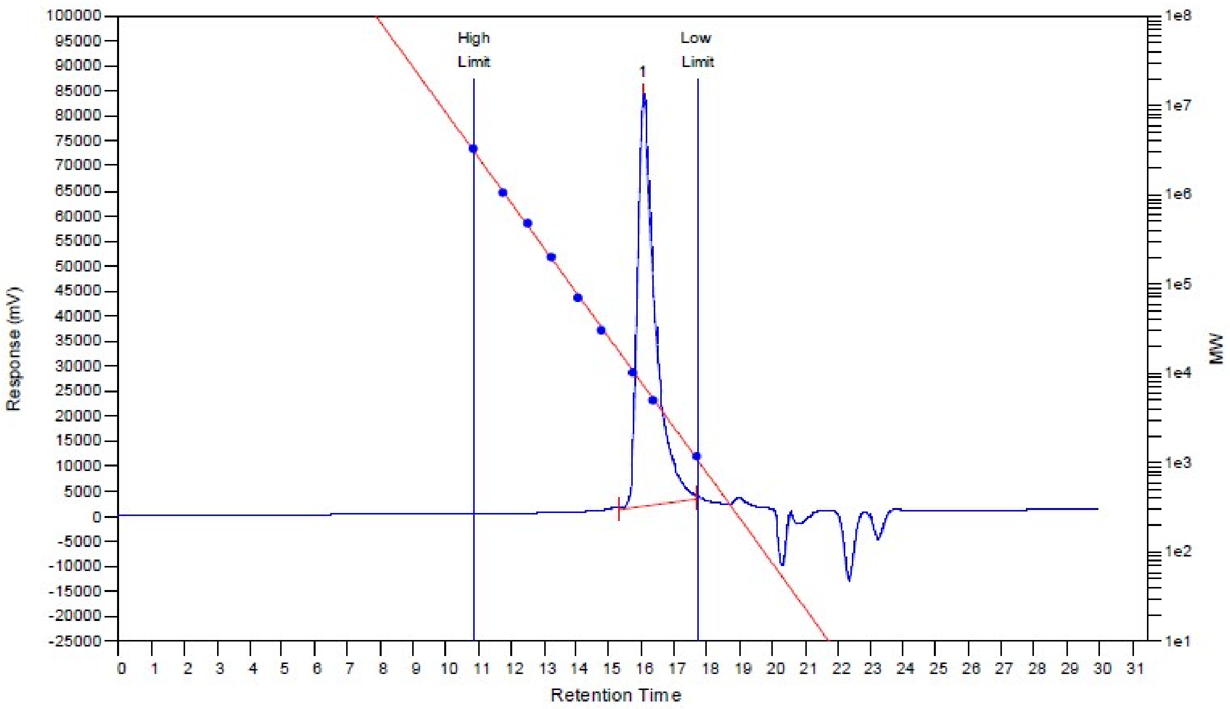


Fig. S40. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] =0.75:0.75:1:50 in $CHCl_3$ (Table S2, run 3).

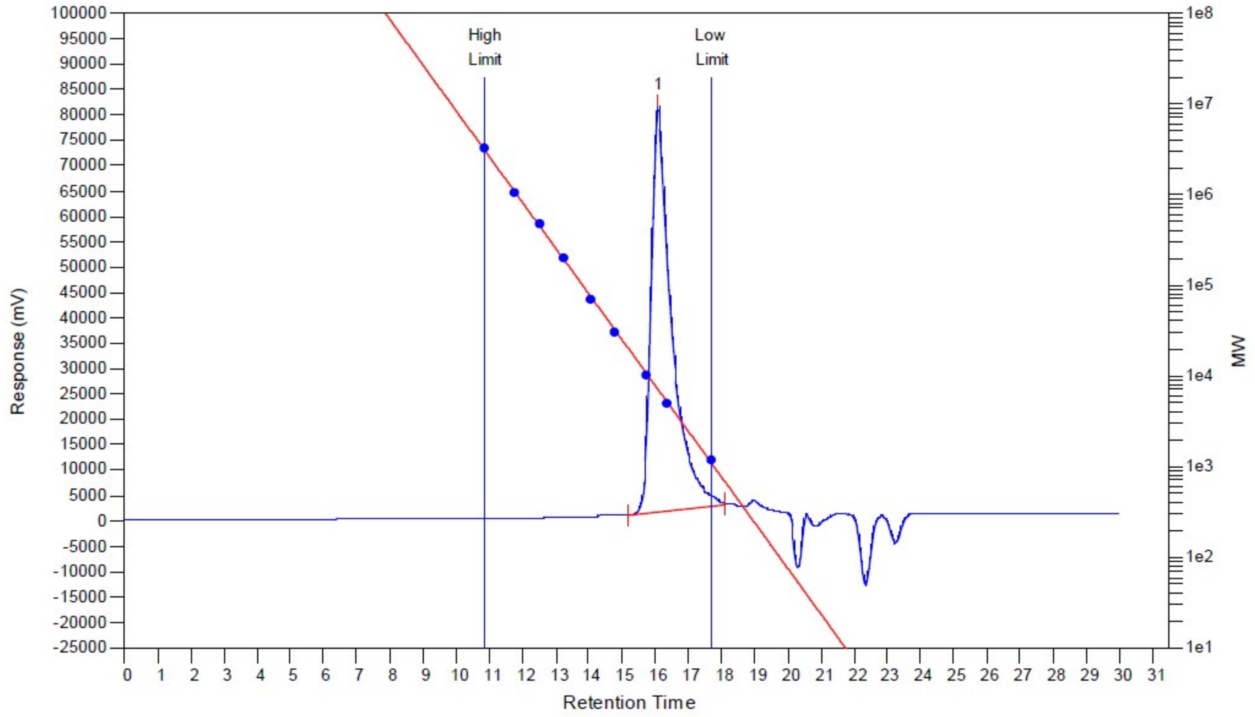


Fig. S41. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] =0.75:0.75:1:50 in THF (Table S2, run 4).

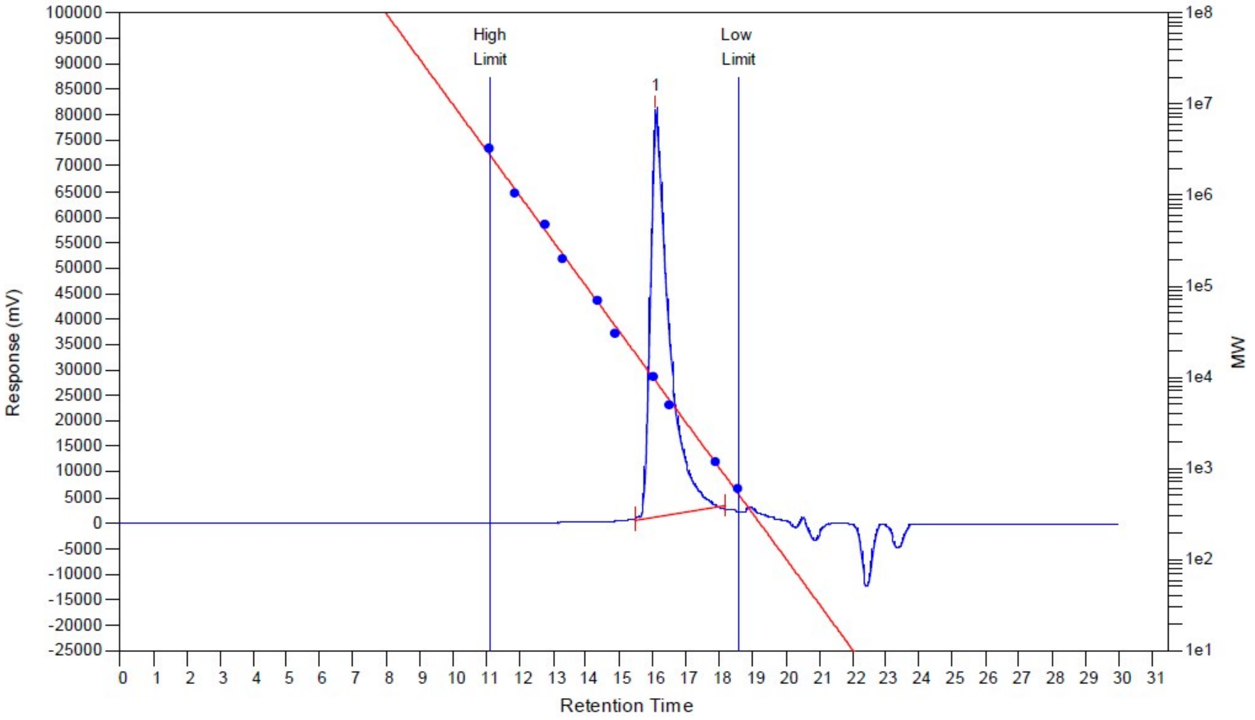


Fig. S42. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] =0.75:0.75:1:50 in Tol (Table S2, run 6).

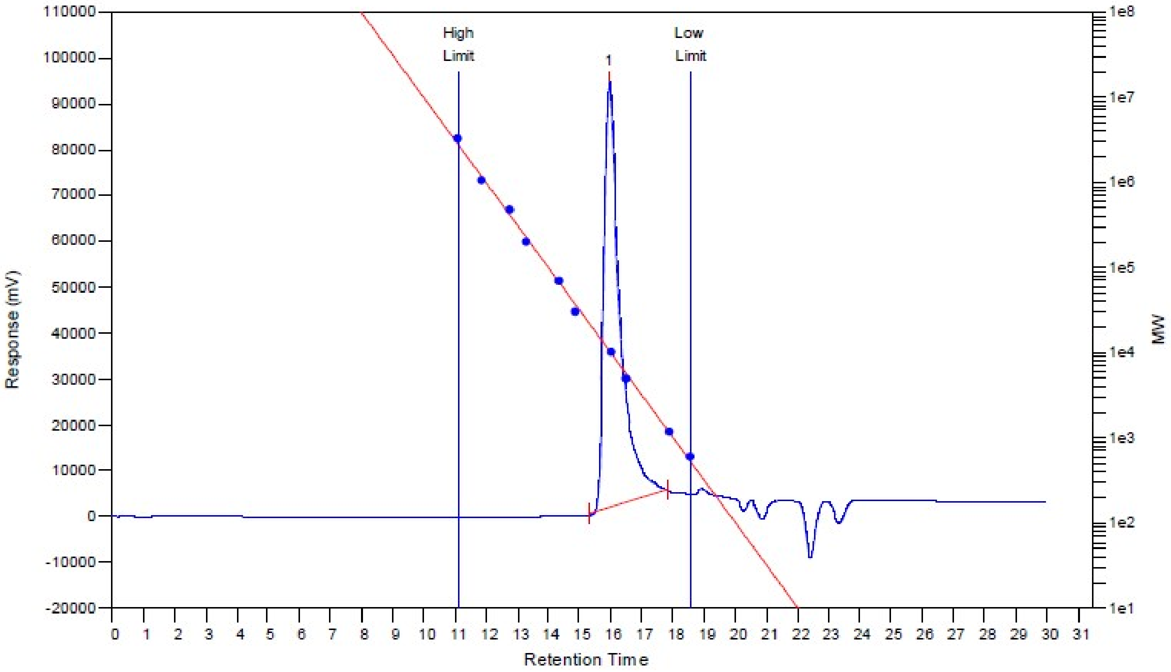


Fig. S43. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] =1:0.75:1:50 in Tol (Table S2, run 7).

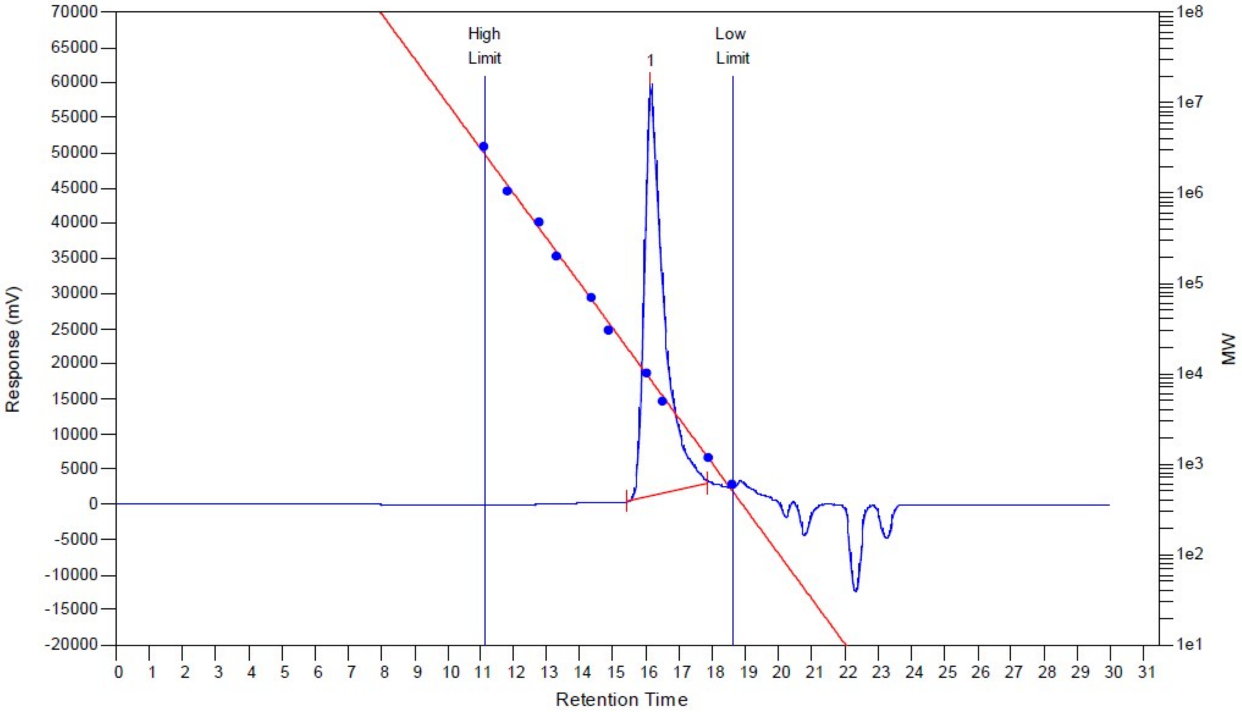


Fig. S44. GPC curves of the resulting polymers via ROP of $_L$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_L$-PheOCA] =1.5:0.75:1:50 in Tol (Table S2, run 8).

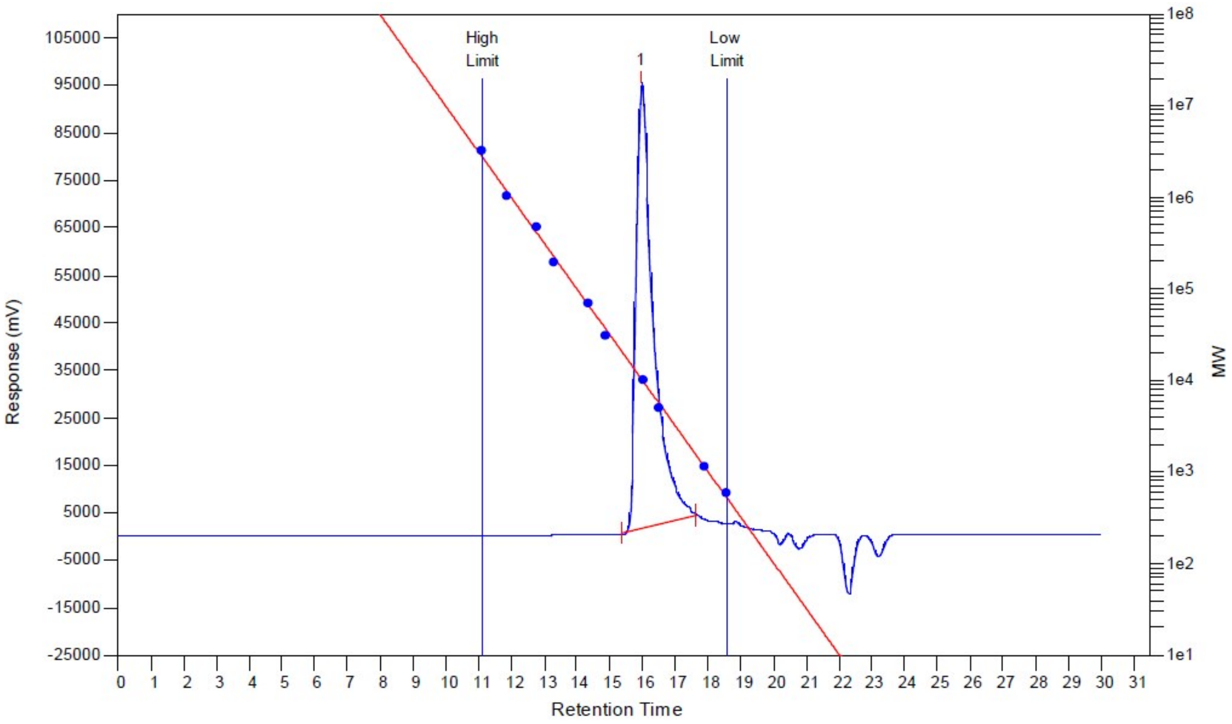
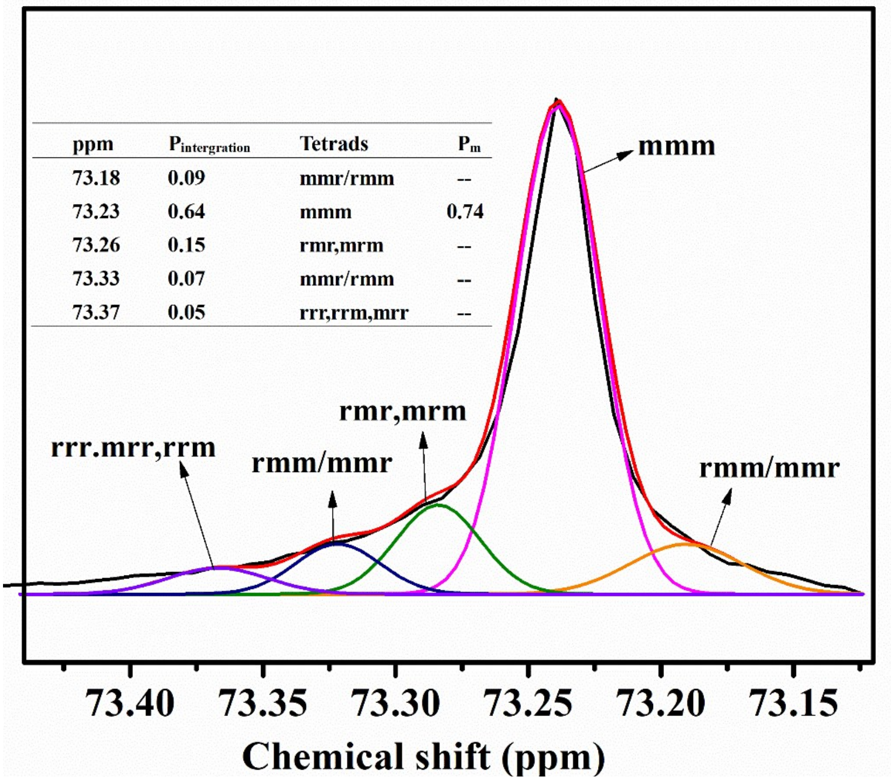
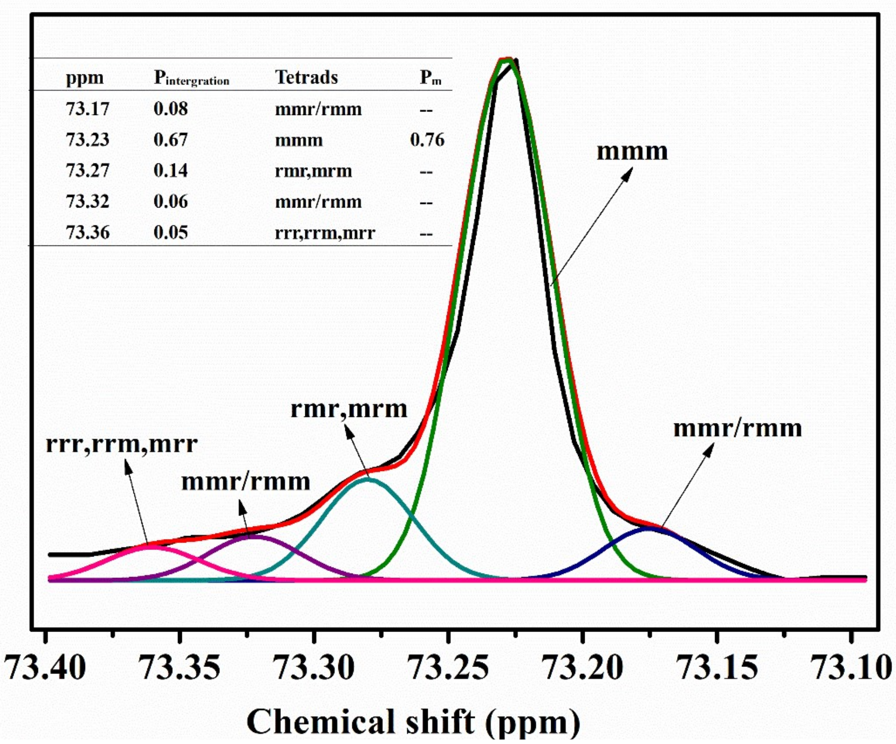


Fig. S45. GPC curves of the resulting polymers via ROP of $_{L}$-PheOCA using [DABCO]:[TEB]:[BnOH]:[$_{L}$-PheOCA] =1:1:1:50 in Tol (Table S2, run 9).



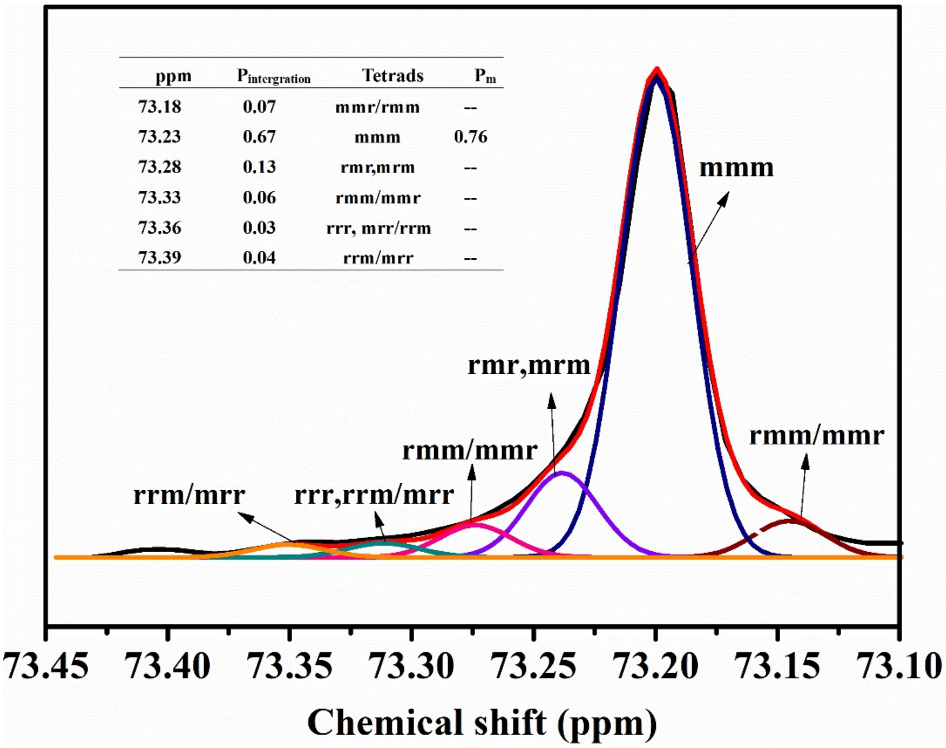
ppm	$P_{intergration}$	Tetrads	P_m
73.18	0.09	mmr/rmm	--
73.23	0.64	mmm	0.74
73.26	0.15	rmr,mrm	--
73.33	0.07	mmr/rmm	--
73.37	0.05	rrr,rrm,mrr	--

Fig. S46. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{L}$-PheOCA] = 0.75:0.75:1:50 in CH_2Cl_2 (Table S2, run 2).



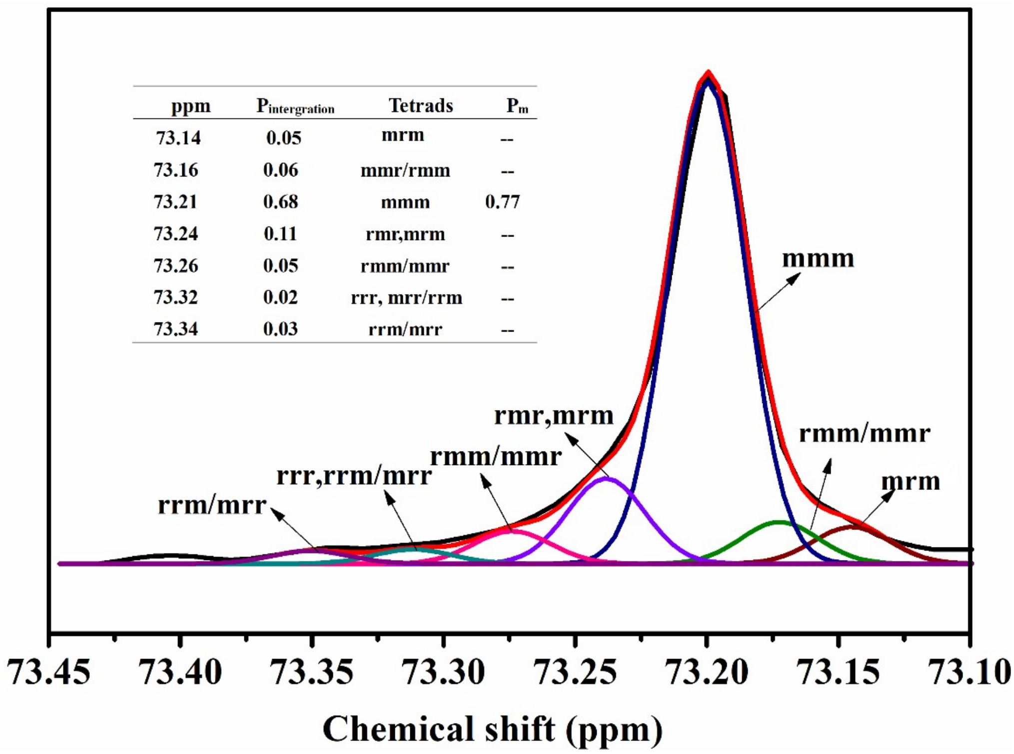
ppm	$P_{\text{intergration}}$	Tetrads	P_m
73.17	0.08	mmr/rmm	--
73.23	0.67	mmm	0.76
73.27	0.14	rmr,mrm	--
73.32	0.06	mmr/rmm	--
73.36	0.05	rrr,rrm,mrr	--

Fig. S47. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:50 in $CHCl_3$ (Table S2, run 3).



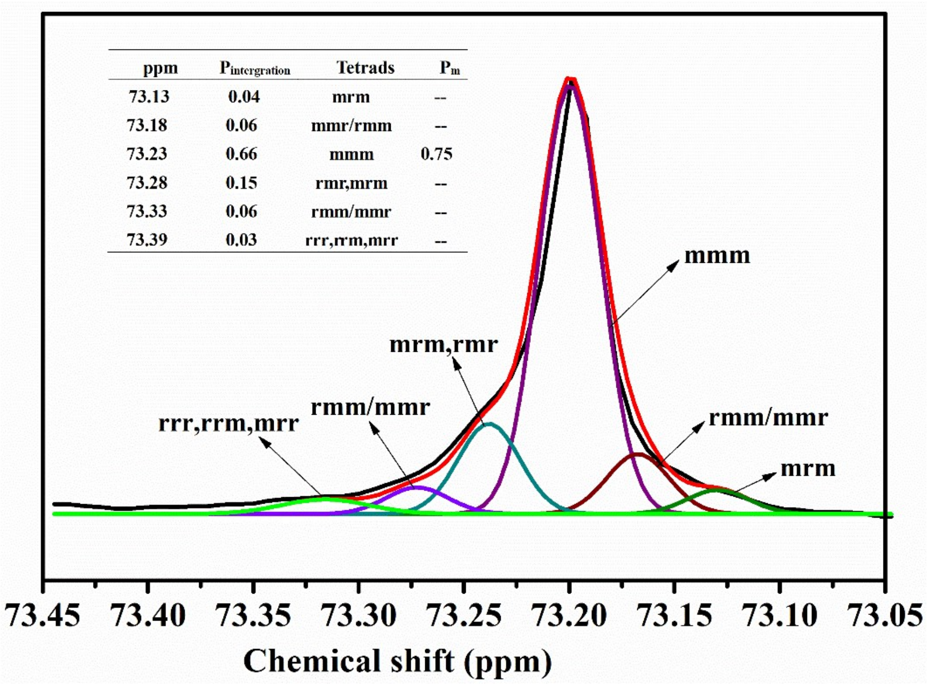
ppm	$P_{\text{intergration}}$	Tetrads	P_m
73.18	0.07	mmr/rmm	--
73.23	0.67	mmm	0.76
73.28	0.13	rmr,mrm	--
73.33	0.06	rmm/mmr	--
73.36	0.03	rrr, mrr/rrm	--
73.39	0.04	rrm/mrr	--

Fig. S48. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1:50 in THF (Table S2, run 4).



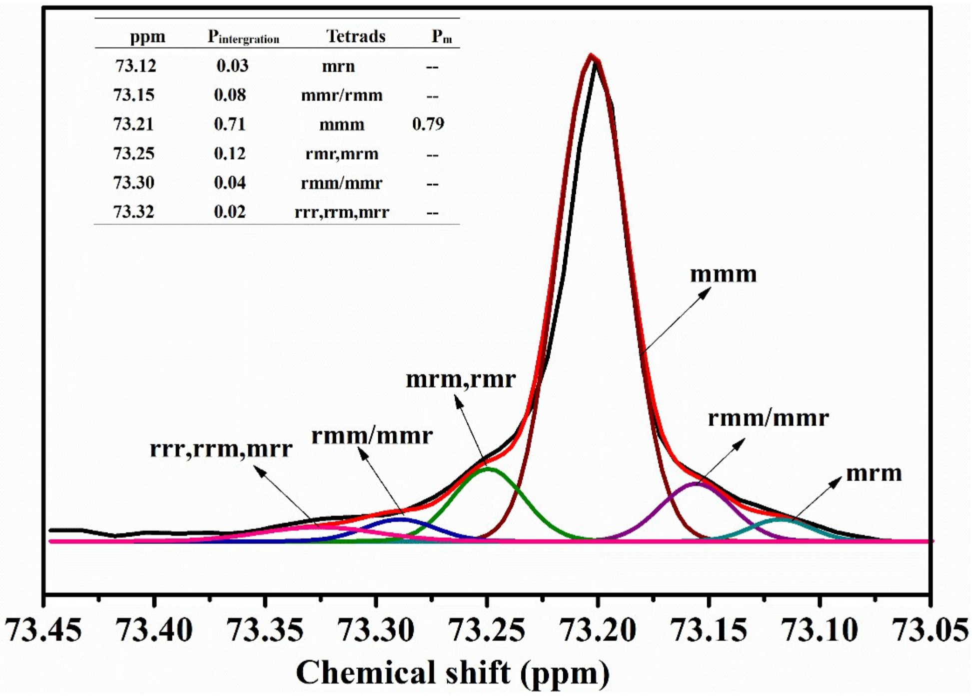
ppm	P_{intergration}	Tetrads	P_m
73.14	0.05	mrm	--
73.16	0.06	mmr/rmm	--
73.21	0.68	mmm	0.77
73.24	0.11	rmr,mrm	--
73.26	0.05	rmm/mmr	--
73.32	0.02	rrr, mrr/rrm	--
73.34	0.03	rrm/mrr	--

Fig. S49. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 0.75:0.75:1.5:50 in Tol (Table S2, run 6).



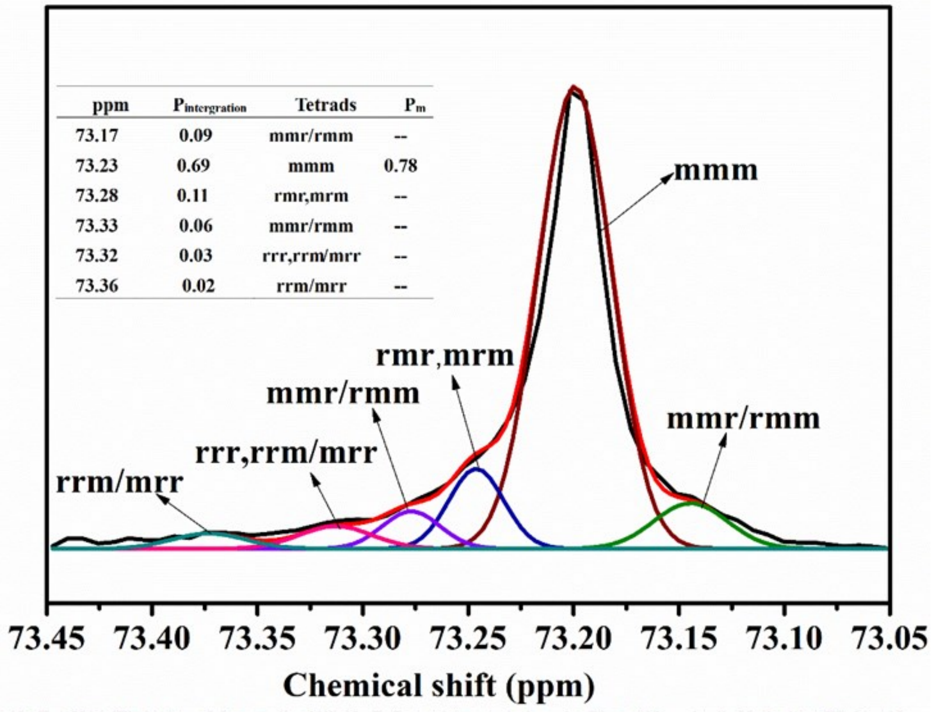
ppm	P_{intergration}	Tetrads	P_m
73.13	0.04	mrm	--
73.18	0.06	mmr/rmm	--
73.23	0.66	mmm	0.75
73.28	0.15	rmr,mrm	--
73.33	0.06	rmm/mmr	--
73.39	0.03	rrr,rrm,mrr	--

Fig. S50. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_{\text{L}}$-PheOCA] = 1:0.75:1:50 in Tol (Table S2, run 7).



ppm	$P_{intergration}$	Tetrads	P_m
73.12	0.03	mrn	--
73.15	0.08	mmr/rmm	--
73.21	0.71	mmm	0.79
73.25	0.12	rmr,mrm	--
73.30	0.04	rmm/mmr	--
73.32	0.02	rrr,rrm,mrr	--

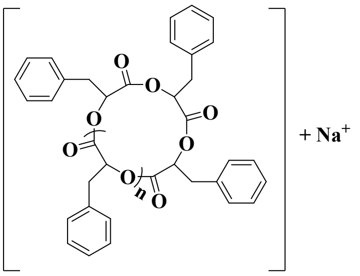
Fig. S51. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 1.5:0.75:1:50 in Tol (Table S2, run 8).



ppm	$P_{intergration}$	Tetrads	P_m
73.17	0.09	mmr/rmm	--
73.23	0.69	mmm	0.78
73.28	0.11	rmr,mrm	--
73.33	0.06	mmr/rmm	--
73.32	0.03	rrr,rrm/mrr	--
73.36	0.02	rrm/mrr	--

Fig. S52. Proposed tetrad stereosequence assignments for the methine carbon of ^{13}C NMR spectrum of cyclic polymer carried out at the feeding ratio of [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 1:1:1:50 in Tol (Table S2, run 9).

●



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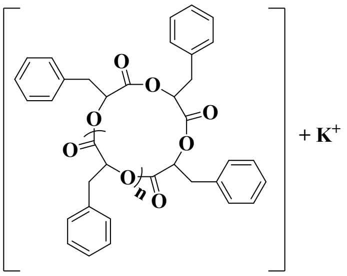


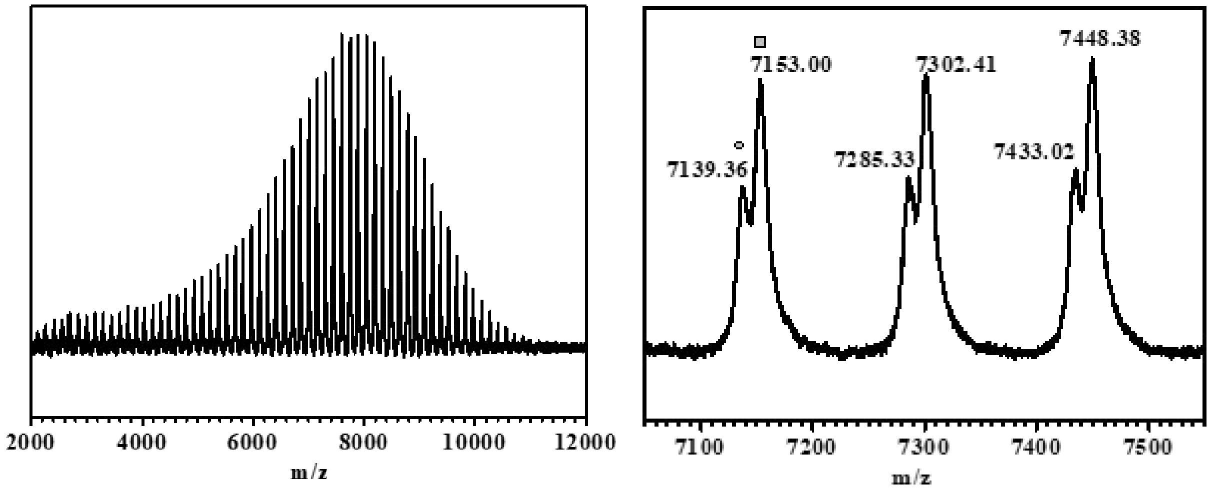


Fig. S53. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 0.75:0.75:1:50 in CH_2Cl_2 (Table S2, run 2).

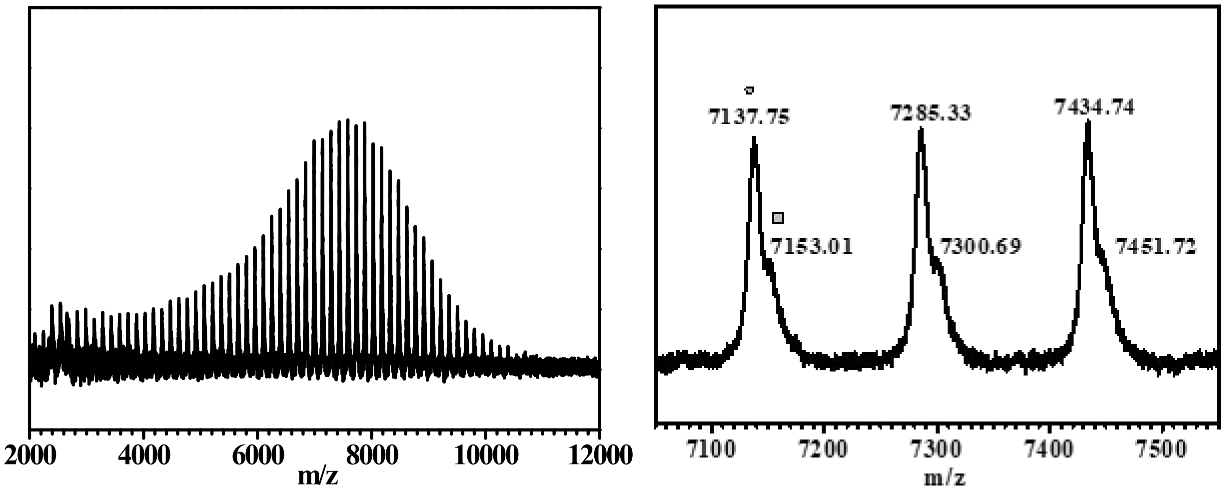


Fig. S54. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[$_L$-PheOCA] = 0.75:0.75:1:50 in $CHCl_3$ (Table S2, run 3).

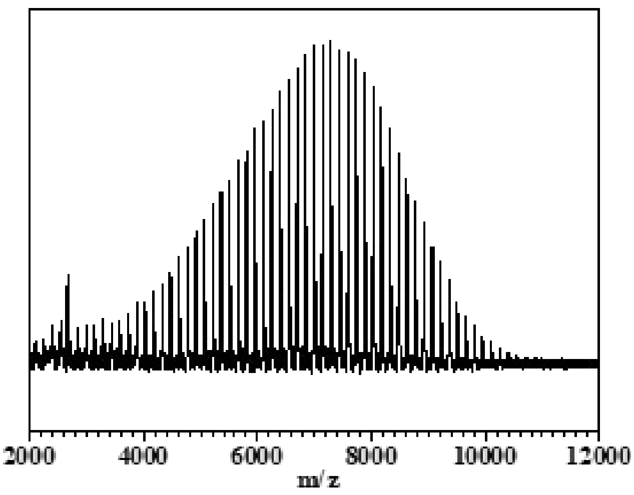


Fig. S55. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[L-PheOCA] = 0.75:0.75:1:50 in THF (Table S2, run 4).

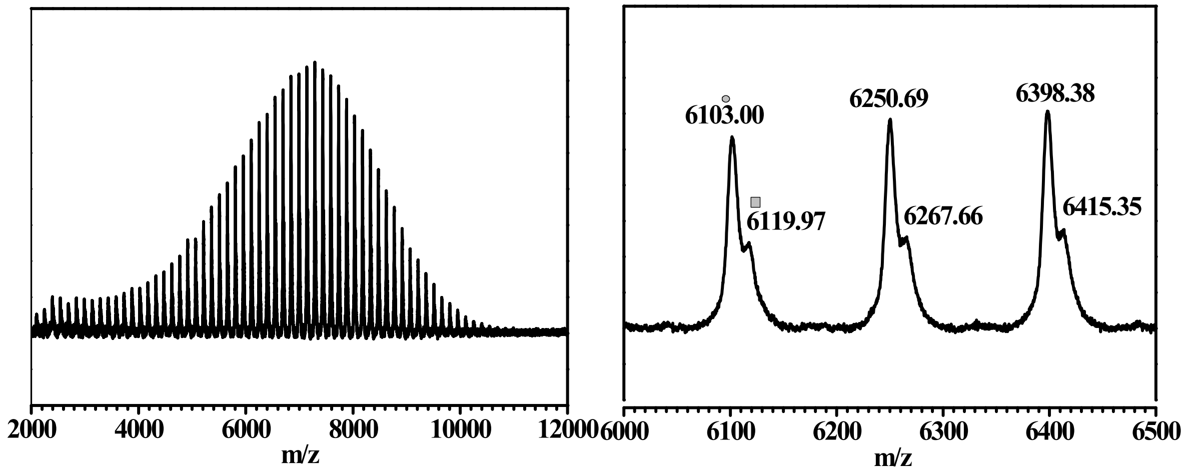


Fig. S56. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[L-PheOCA] = 0.75:0.75:1.5:50 in Tol (Table S2, run 6).

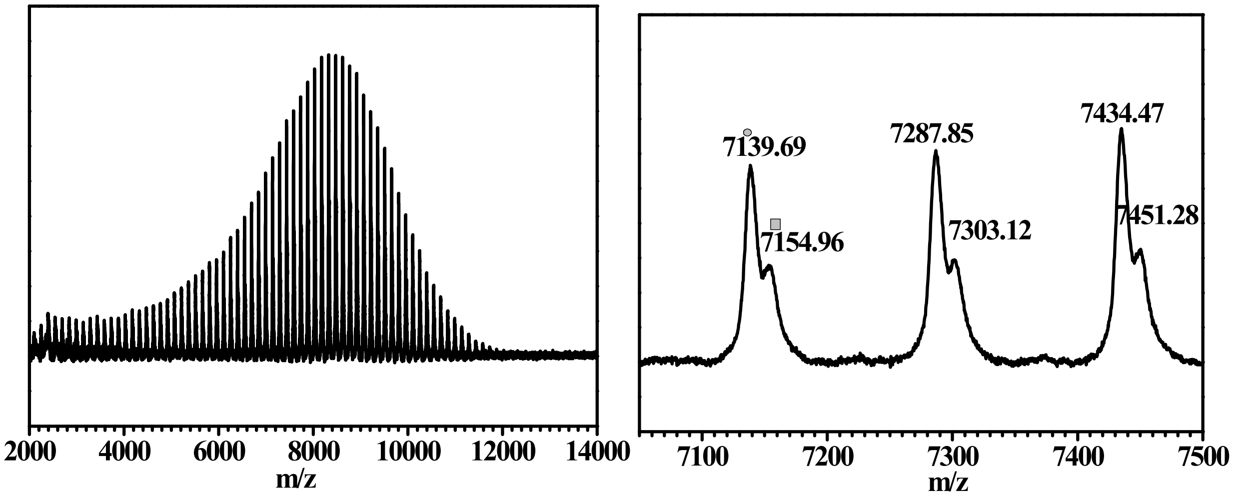


Fig. S57. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[L-PheOCA] = 1:0.75:1:50 in Tol (Table S2, run 7).

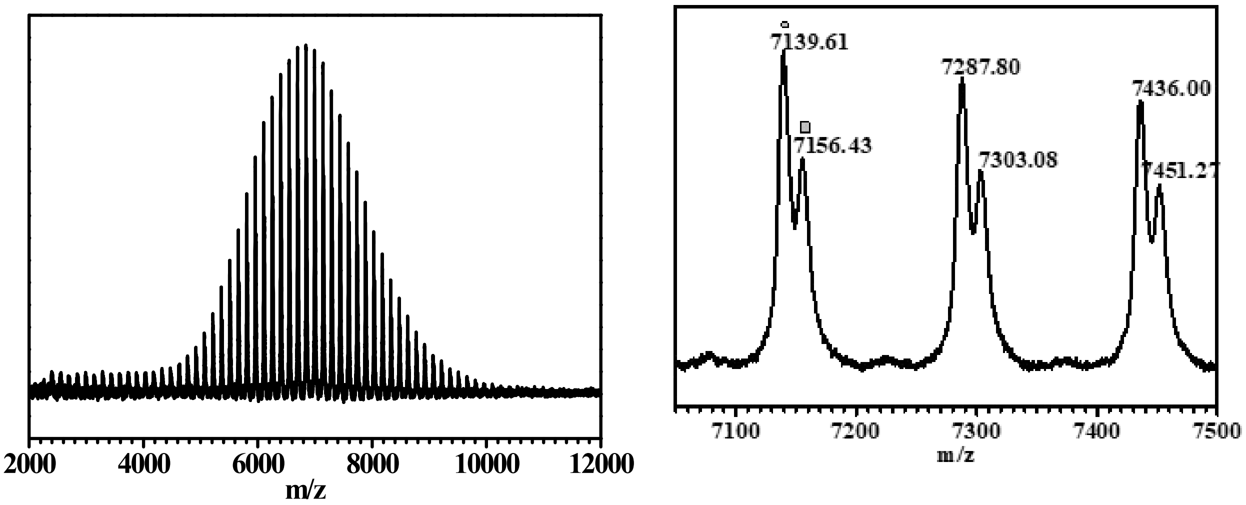


Fig. S58. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[$_{L}$-PheOCA] = 1.5:0.75:1:50 in Tol (Table S2, run 8).

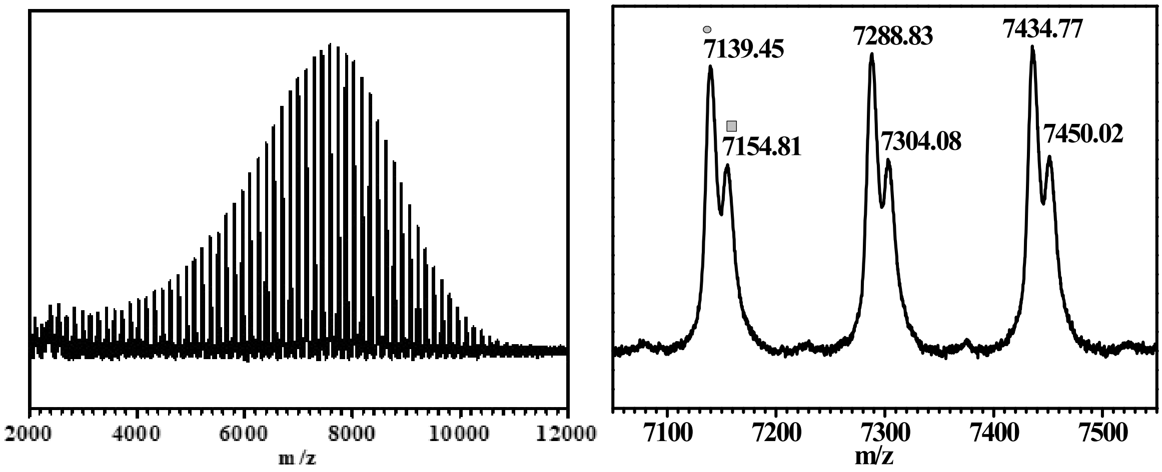


Fig. S59. MALDI-TOF result of the resulting polymers conducted using [DABCO]/[TEB]/[BnOH]/[$_{L}$-PheOCA] = 1::1:50 in Tol (Table S2, run 9).

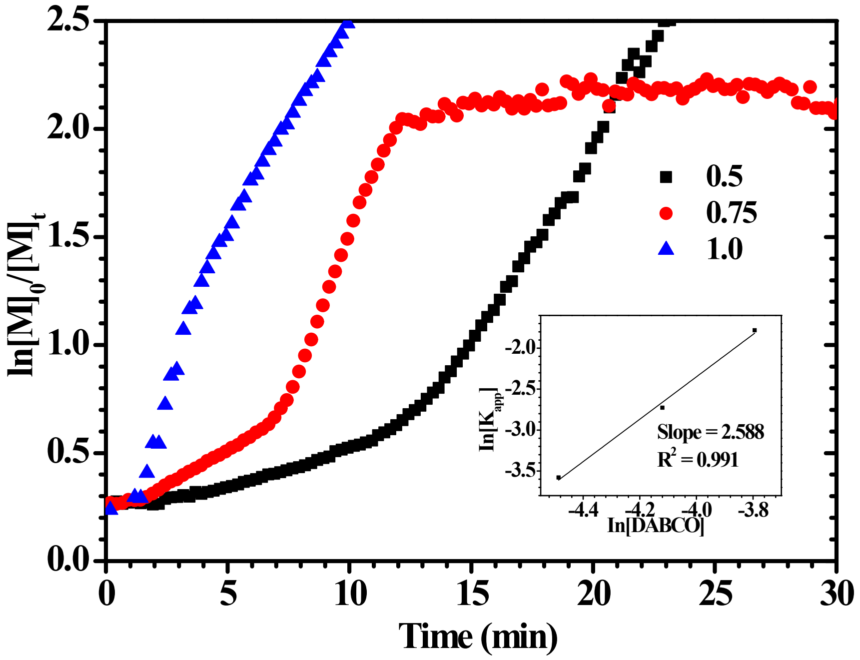
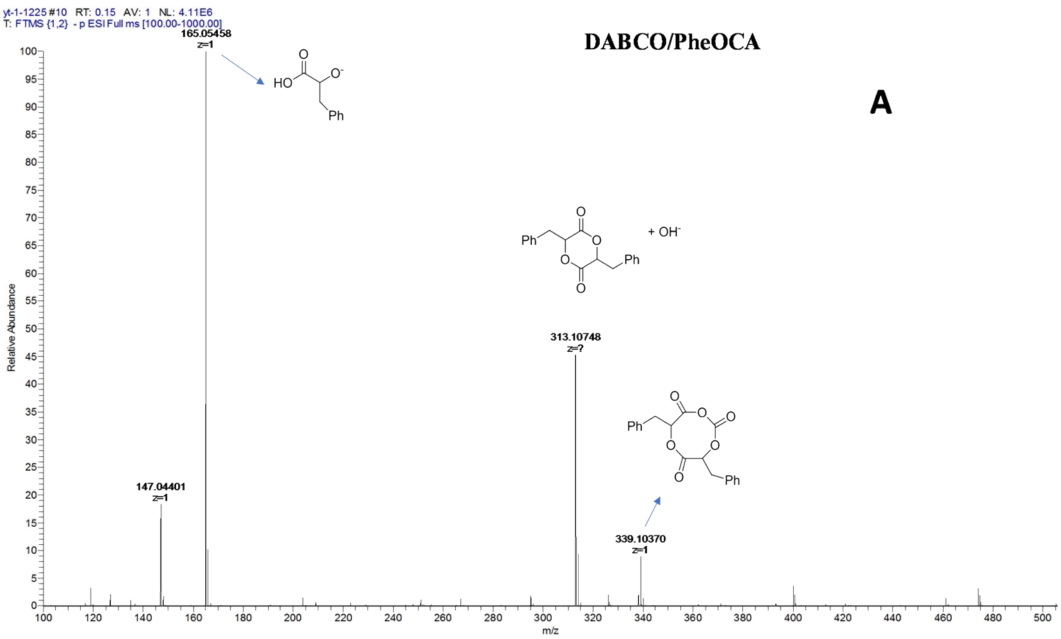


Fig. S60. Kinetic plots for ROP of $_{\text{L}}$-PheOCA (0.75 M) dependence of varying DABCO concentrations:



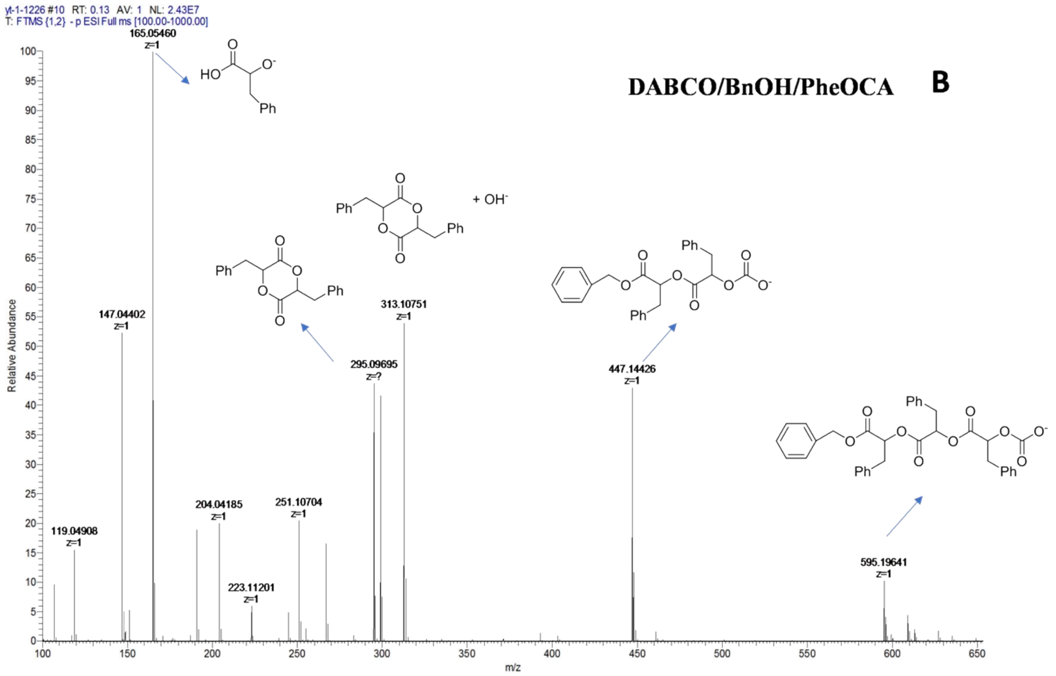


Fig. S61. ESI-MS results of polymerization carried out with [DABCO]/[$_L$-PheOCA]/ = 1:1 (A); [DABCO]/[BnOH]/[$_L$-PheOCA] = 0.75:1:1 (B).

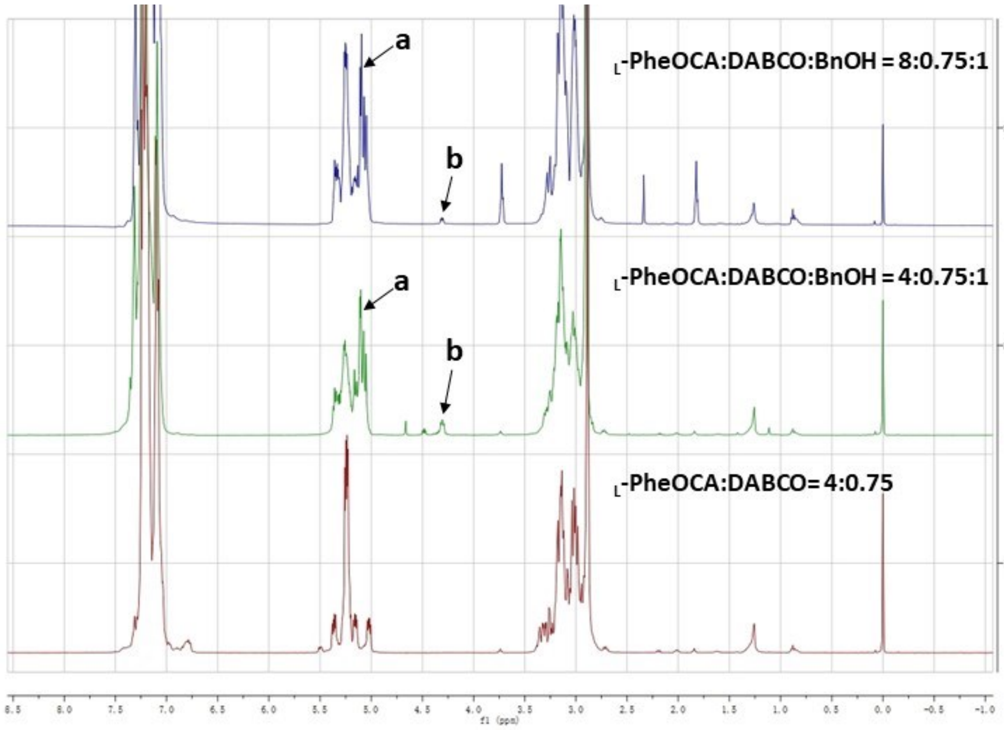


Fig. S62. ^{1}H NMR spectra of polymerization systems performed with [$_L$-PheOCA]/[DABCO]/[BnOH] =4:0.75:1 and $_L$-PheOCA/DABCO =4:0.75.

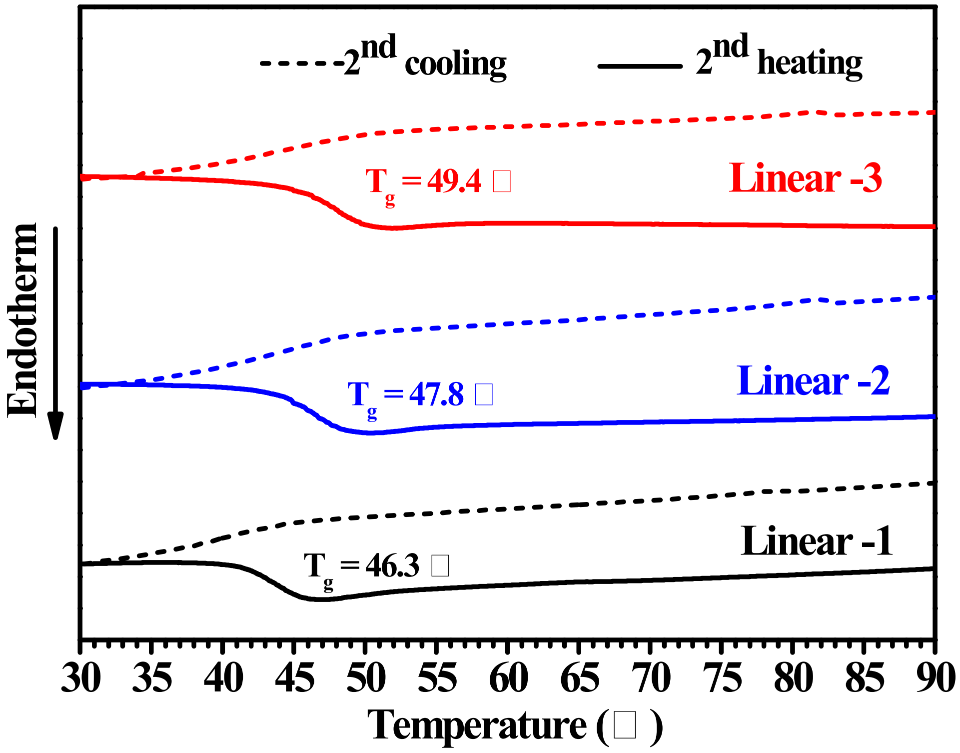


Fig. S63. DSC curves of the second time heating and cooling at 10 °C /min for four linear polymers. Linear-1: M_n = 6.9 KDa, Đ = 1.10; Linear-2: M_n =11.92 KDa, Đ = 1.11; Linear-3: M_n = 15.96 KDa, Đ = 1.14.