Supporting Information for

Catalytic *Living ROMP: Block Copolymers from Macro-Chain Transfer Agents*

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Contents

Materials

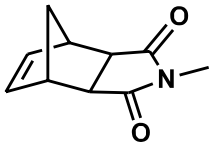
Grubbs' 2nd generation catalyst, 2,3-Dihydrofuran, *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride, α-Bromoisobutyryl bromide (BIBB), ethylene glycol vinyl ether, 4-(vinyloxy)butan-1-ol , ethyl vinyl ether , methylamine solution , aniline and stannous octoate were purchased from Sigma Aldrich. All other reagents and solvents were purchased from Acros organics or Sigma Aldrich and used without further purification. Monomers **M1**, **M2** and 2-(vinyloxy)ethyl 2-bromo-2-methylpropanoate were synthesized according to the previously reported procedure.[1,2] Deuterated solvents ($CDCl_3$) was purchased from Cambridge Isotope Laboratories Inc.

Characterization

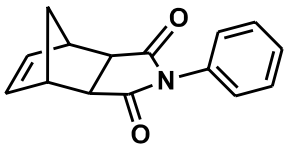
All NMR spectra (^1H, ^{13}C, DOSY) were recorded on a Bruker Avance III 400 MHz NMR spectrometer (^1H NMR 400 MHz, ^{13}C-NMR 101 MHz). Relative molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) with DMF and $CHCl_3$ as eluents. The DMF GPC is an automated Agilent 1260 Infinity II HPLC system equipped with one Agilent PolarGel M guard column (particle size = 8 µm) and two Agilent PolarGel M columns (ID = 7.5 mm, L = 300 mm, particle size = 8 µm). Signals were recorded an interferometric refractometer (Agilent 1260 series). Samples were run using DMF + 0.05M LiBr as the eluent at 60 °C and a flow rate of 1.0 mL/min. Molecular weights were determined based on narrow molecular weight poly(ethylene oxide) calibration standards. The $CHCl_3$ GPC is an automated Agilent Technologies 1260 Infinity II GPC system (pump, autosample, RI detector) with two MZ-Gel SDplus Linear columns (5 µm, 300×8.0mm), a MZ-Gel SDplus Linear precolumn (5 µm, 50×8.0mm) at a flow rate of 1mL/min for samples measured in $CHCl_3$. The samples were run at 40 °C and the chloroform GPC was calibrated with PSS-polymer polystyrene standards.

Monomers and Macro-Chain Transfer Agents (m-CTAs) Used

Monomers



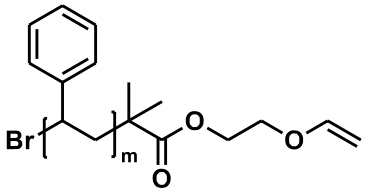
M1



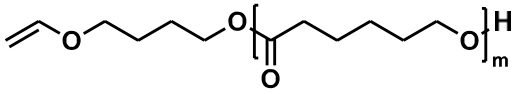
M2

2,3-DHF

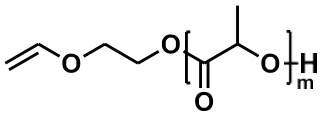
Macro-Chain transfer agent



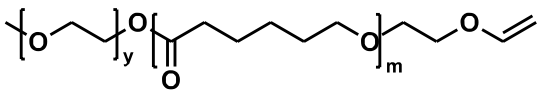
m-CTA1



m-CTA2



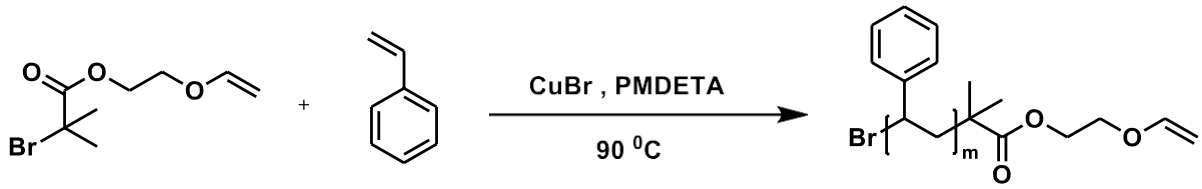
m-CTA3



m-CTA4

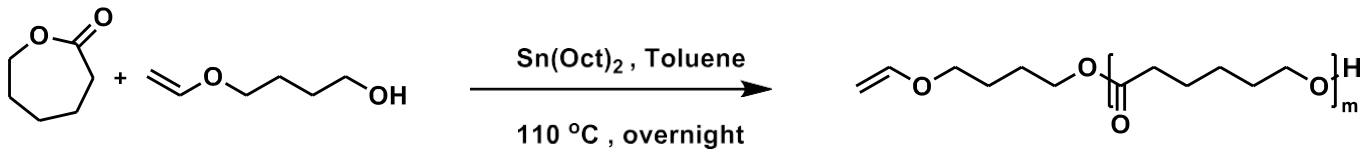
Synthesis of Macro-Chain Transfer Agents (m-CTAs)

Synthesis of Polystyrene (PS) Vinyl Ether Macro-Chain Transfer Agent (m-CTA1)



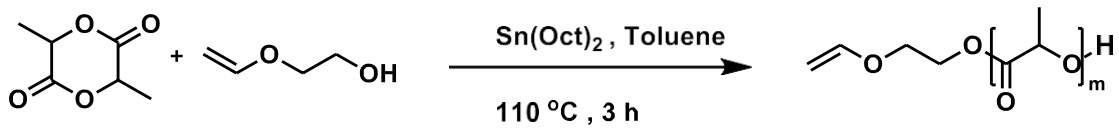
A mixture of 2-(vinyloxy)ethyl 2-bromo-2-methylpropanoate (initiator) (1 equiv. , 91.05 mg) and styrene (50 equiv., 2.0 g) were taken in Schlenk flask and degassed carefully for three times . CuBr (1 equiv., 55.09 mg) was weighed inside the glove box in another Schlenk flask and taken out from the glove box. A stock solution of *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA) (199.68 mg) in toluene (0.3 mL) was also prepared and degassed as before. Then the mixture of the initiator P14 and styrene were transferred into the Schlenk flask containing CuBr followed by the addition of 0.1 mL of PMDTA (1 equiv., 66.56 mg) stock solution in toluene. The resulting solution was stirred at 90 ^{0}C for 24 h. The reaction mixture was then cooled at room temperature, diluted with DCM, and passed through basic alumina to remove the copper salt. Then the solvent was removed under reduced pressure and the concentrated solution obtained was precipitated from cold methanol to give the m-CTA1 as white solid. ($M_{n\ (SEC,\ CHCl_3)}$ =3.12kDa, Đ = 1.16)

Synthesis of Polycaprolactone (PCL) Vinyl Ether Macro-Chain Transfer Agent (m-CTA2)



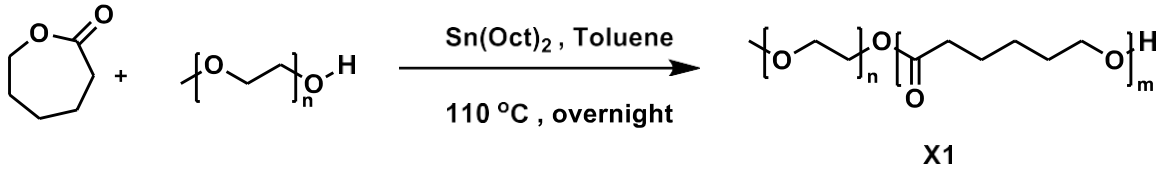
Synthesized according to the reported procedure.[3] 4-(vinyloxy)butan-1-ol (1 equiv. , 593.66 mg) , $Sn(oct)_2$ (0.1 equiv. , 207.04 mg) , and caprolactone monomer (12 equiv., 7 g) were taken in a Schlenk flask and dissolved in 30 mL of anhydrous toluene. Then the whole reaction mixture was stirred at 110 ^{0}C for 24 h under argon atmosphere. Upon completion of the reaction, the solvent was removed under vacuum and the concentrated solution obtained was precipitated from cold hexane to give the m-CTA2 as white solid. ($M_{n\ (SEC,\ CHCl_3)}$ =2.21 kDa, Đ = 1.22)

Synthesis of Polylactide (PLA) Vinyl Ether Macro-Chain Transfer Agent (m-CTA3)

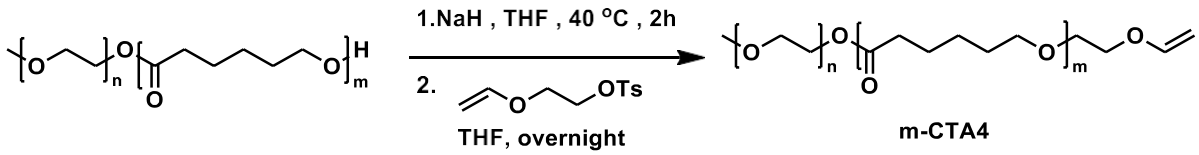


2-(vinyloxy)ethan-1-ol (1 equiv. , 183.40 mg) , $Sn(oct)_2$ (0.1 equiv. , 84.32 mg) , and L-lactide monomer (10 equiv., 3 g) were taken in a Schlenk flask containing 15 mL of anhydrous toluene. Then the whole solution was stirred at 110 ^{0}C for 3 h under argon atmosphere. After that reaction the mixture was cooled down and the solvent was removed under vacuum. The concentrated solution obtained was then precipitated from cold methanol to give the m-CTA3 as white powder. ($M_{n\ (SEC,\ DMF)}$ =1.93 kDa, Đ = 1.18)

Synthesis of Polyethylene glycol-Polycaprolactone (PEG-PCL) Vinyl Ether Macro-Chain Transfer Agent (m-CTA4)

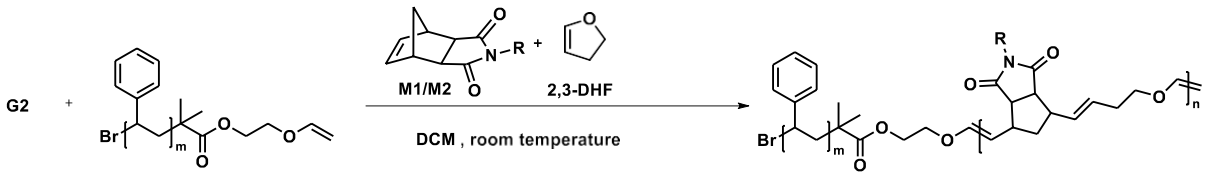


PEG_{2k}-monomethyl ether (1 equiv., 2.0 g), $Sn(oct)_2$ (0.1 equiv. , 40.51 mg) , and caprolactone monomer (14 equiv., 1.6 g) were taken in a Schlenk flask containing 10 mL of anhydrous toluene. Then the whole solution was stirred at 110 ^{0}C for 24 h under argon atmosphere. After that reaction the mixture was cooled down and the solvent was removed under vacuum. The concentrated solution obtained was then precipitated from cold diethyl ether to give the **X1** as white powder. ($M_{n\ (SEC,\ DMF)}$ =4.11 kDa, Đ = 1.23)



NaH (60% dispersion in mineral oil, 36 mg, and 3 equiv.) was dissolved in dry THF (4 mL) taken in a 25 mL round bottom flask and was cooled to 0^{0}C. Then, polymer **X1** (600 mg, 1 equiv.) in dry THF (5mL) was added slowly to it, and the reaction mixture was stirred at room temperature for 2h. Then 2-(vinyloxy)ethyl 4-methylbenzenesulfonate ((364 mg, 10 equiv.) was dissolved in 3 mL of dry THF and added to the flask and stirred for overnight at room temperature. Upon completion of the reaction, the solution was concentrated in vacuum and precipitated in cold diethyl ether (10-fold excess) for three times. Then the precipitate was filtered and dried in vacuum to give the macro-chain transfer agent **m-CTA4** as white solid. ($M_{n\ (SEC,\ DMF)}$ =4.16 kDa, Đ = 1.23)

Procedure for one-pot synthesis of Polystyrene (PS)-ROMP di-block copolymers using Polystyrene (PS) Vinyl Ether Macro-Chain Transfer Agent (m-CTA1)



A Schlenk flask containing **m-CTA1** (10-80 equiv.) was closed, evacuated, and backfilled with argon three times, then dry degassed DCM (0.5 mL) was added to it. **G2** catalyst (1.0 mg ,1 equiv.) was also dissolved in dry degassed DCM (0.5 mL) and was quickly added to the polystyrene vinyl ether macro-chain transfer agent solution ensuring efficient mixing. To this solution, a mixture of monomer (**M1 or M2**) and **2,3 DHF** (1:2 ratio) which were also dissolved in dry degassed DCM (0.2 M with respect to DHF) was added quickly and the combined solution was stirred at room temperature until the desired monomer conversion was reached. The polymerization was then quenched by adding ethyl vinyl ether and solvent was removed under reduced pressure. The concentrated solution obtained was precipitated from cold methanol to give the ROMP-Polystyrene di-block copolymers **P1 – P6**.

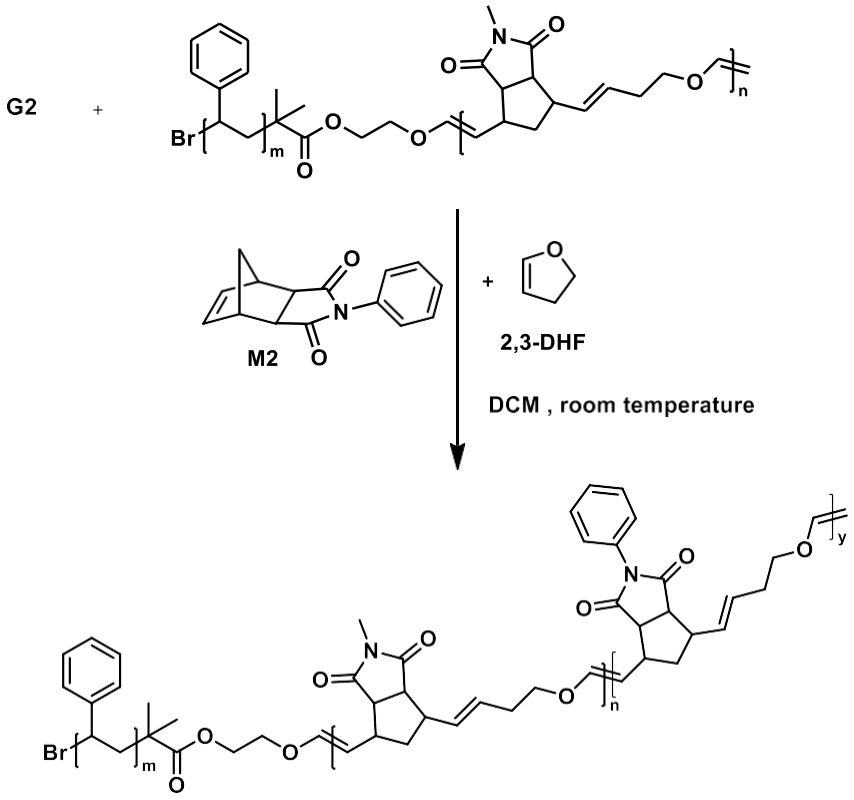
Table S1: One-pot Catalytic Living Copolymerization Data of Monomers M1 and M2 with 2,3-DHF using macro-chain transfer agents m-CTA1

Entry	**Polymer**	**Monomer (M)**	**G2:CTA:M:DHF**	**Monomer (M) conversion (%)[a]**	**M_n (Non catalytic) (kDa)**	**M_n (catalytic, monomer/m-CTA) (theo; kDa)**	**M_n (obs.) ($CHCl_3$; kDa)**	**Đ**
1	P1	M1	1:10:600:1200	> 90	151.32	16.43	16.89	1.33
2	P2	M1	1:15:600:1200	> 91	151.32	12.09	12.78	1.34
3	P3	M1	1:30:600:1200	> 92	151.32	7.64	8.46	1.33
4[b]	P4	M1	1:40:600:1200	> 90	151.32	6.43	6.87	1.27
5	P5	M1	1:80:6000:12000	> 94	1482.1	20.51	21.48	1.35
6	P6	M2	1:40:800:16000	> 92	200.81	8.82	9.31	1.31

[a] conversion of monomer (**M1-M2**) determined by ^{1}H NMR spectroscopy

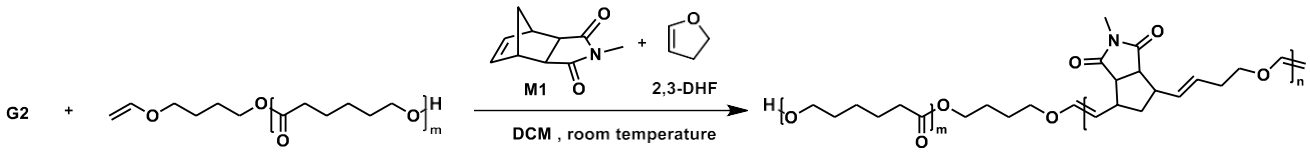
[b] Polymer **P4** was not quenched with vinyl ether.

Procedure for one-pot synthesis of Polystyrene (PS)-ROMP-ROMP tri-block terpolymer



G2 (1 equiv., 0.5 mg) and polymer **P4** (20 equiv., 76.0 mg) were dissolved in dry degassed DCM (1 mL) in a Schlenk flask under argon. To this solution, a mixture of monomer **M2** (800 equiv., 112.71 mg) and **2,3 DHF** (1600 equiv., 66.01 mg) which were also dissolved in dry degassed DCM (4.71 mL, 0.20 M with respect to the 2,3-DHF) was transferred quickly and the combined solution was stirred at room temperature for overnight. The polymerization was then quenched by adding ethyl vinyl ether (after > 93 % conversion of **M2)** and solvent was removed under reduced pressure. The concentrated solution obtained was precipitated from cold methanol to give the tri-block copolymer **P7**. ($M_{n\ (SEC,\ CHCl3)}$ =33.47 kDa, Đ = 1.39)

Procedure for one-pot synthesis of Polycaprolactone (PCL)-ROMP di-block copolymers using Polycaprolactone (PCL) Vinyl Ether Macro-Chain Transfer Agent (m-CTA2)

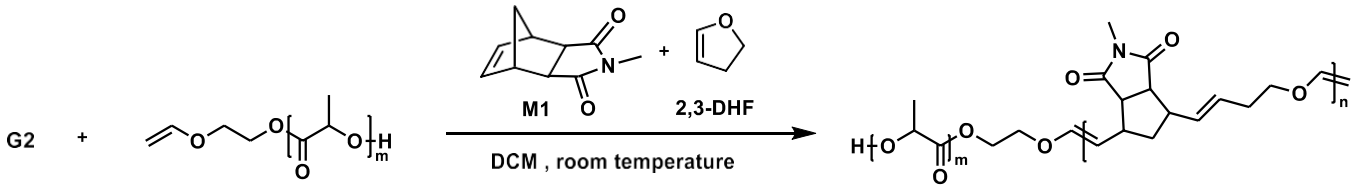


A Schlenk flask containing **m-CTA2** (10 or 80 equiv.) was closed, evacuated and backfilled with argon three times, then dry degassed DCM (0.5 mL) was added to it. **G2** catalyst (1.0 mg ,1 equiv.) was also dissolved in dry degassed DCM (0.5 mL) and was quickly added to the polycaprolactone vinyl ether macro- chain transfer agent solution ensuring efficient mixing. To this solution, a mixture of monomer (**M1 or M2**) and **2,3 DHF** (1:2 ratio) which were also dissolved in dry degassed DCM (0.2 M with respect to DHF) was added quickly and the combined solution was stirred at room temperature until the desired monomer conversion was reached. The polymerization was then quenched by adding ethyl vinyl ether and solvent was removed under reduced pressure. The concentrated solution obtained was precipitated from cold methanol to give the ROMP-Polycaprolactone di-block copolymers **P8** and **P9**.

Table S2: One-pot Catalytic Living Copolymerization Data of Monomers M1 and M2 with 2,3-DHF using macro-chain transfer agents m-CTA1

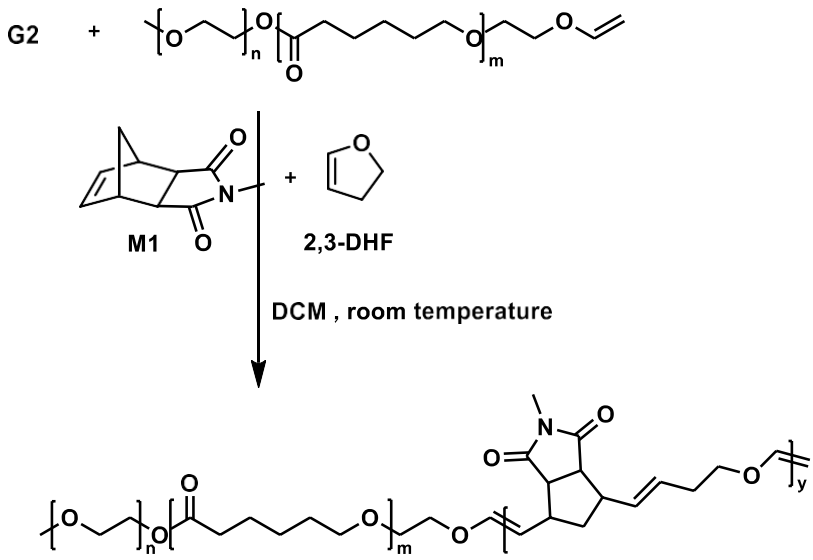
Entry	**Polymer**	**Monomer (M)**	**G2:CTA:M:DHF**	**Monomer (M) conversion (%)[a]**	**M_n (Non catalytic) (kDa)**	**M_n (catalytic, monomer /m-CTA) (theo; kDa)**	**M_n (obs.) ($CHCl_3$; kDa)**	**Đ**
1	P8	M1	1:10:500:1000	> 95		13.93	14.81	1.34
2	P9	M1	1:80:3000:6000	> 93		10.81	11.36	1.30

Procedure for one-pot synthesis of Polylactide (PLA)-ROMP di-block copolymer using Polylactide (PLA) Vinyl Ether Macro-Chain Transfer Agent (m-CTA3)



A Schlenk flask containing **m-CTA3** (50 equiv.) was closed, evacuated, and backfilled with argon three times, then dry degassed DCM (0.5 mL) was added to it. **G2** catalyst (1.0 mg ,1 equiv.) was also dissolved in dry degassed DCM (0.5 mL) and was quickly added to the polylactide vinyl ether macro-chain transfer agent solution ensuring efficient mixing. To this solution, a mixture of monomer **M1** (2000 equiv.) and **2,3 DHF** (4000 equiv.) which were also dissolved in dry degassed DCM (0.2 M with respect to DHF) was added quickly and the combined solution was stirred at room temperature for overnight. The polymerization (> 95 % monomer conversion) was then quenched by adding ethyl vinyl ether and solvent was removed under reduced pressure. The concentrated solution obtained was precipitated from cold methanol to give the ROMP-Polylactide di-block copolymers **P10.** ($M_{n\,(SEC,\,DMF)}$ =21.86 kDa, Đ = 1.32)

Procedure for one-pot synthesis of Polyethylene glycol (PEG)-Polycaprolactone (PCL)-ROMP tri-block terpolymer using Polyethylene glycol (PEG)-Polycaprolactone (PCL) Vinyl Ether Macro-Chain Transfer Agent (m-CTA4)



A Schlenk flask containing **m-CTA4** (50 equiv.) was closed, evacuated and backfilled with argon three times, then dry degassed DCM (0.5 mL) was added to it. **G2** catalyst (1.0 mg ,1 equiv.) was also dissolved in dry degassed DCM (0.5 mL) and was quickly added to the polyethylene glycol-polycaprolactone vinyl ether macro-chain transfer agent solution ensuring efficient mixing. To this solution, a mixture of monomer **M1** (5000 equiv.) and **2,3 DHF** (10000 equiv.) which were also dissolved in dry degassed DCM (0.2 M with respect to DHF) was added quickly and the combined solution was stirred at room temperature for overnight. The polymerization (> 94 % monomer conversion) was then quenched by adding ethyl vinyl ether and solvent was removed under reduced pressure. The concentrated solution obtained was precipitated from cold methanol to give the Polyethylene glycol-Polycaprolactone-ROMP tri-block terpolymer **P11.** ($M_{n\ (SEC,\ DMF)}$ =27.68 kDa, Đ = 1.35)

SEC DATA

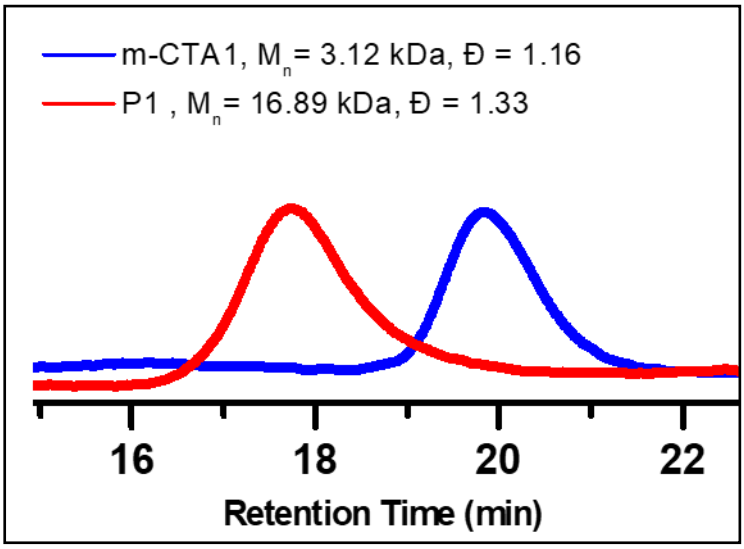


Fig S1: Refractive index ($CHCl_3$) traces of **m-CTA1** and di-block copolymer **P1**

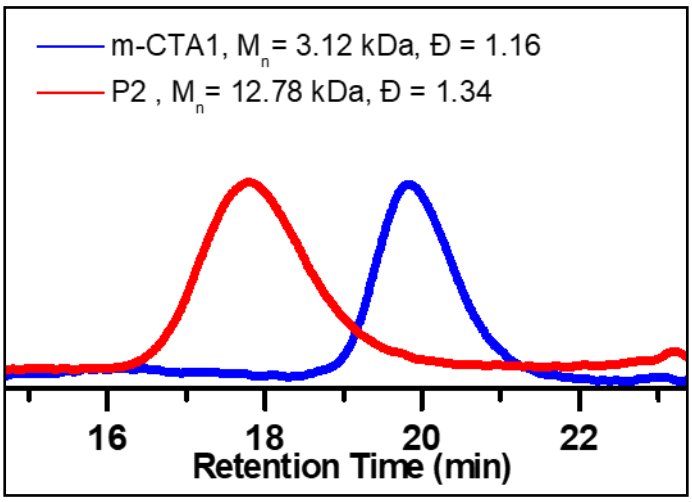


Fig S2: Refractive index ($CHCl_3$) traces of **m-CTA1** and PS-ROMP di-block copolymer **P2**

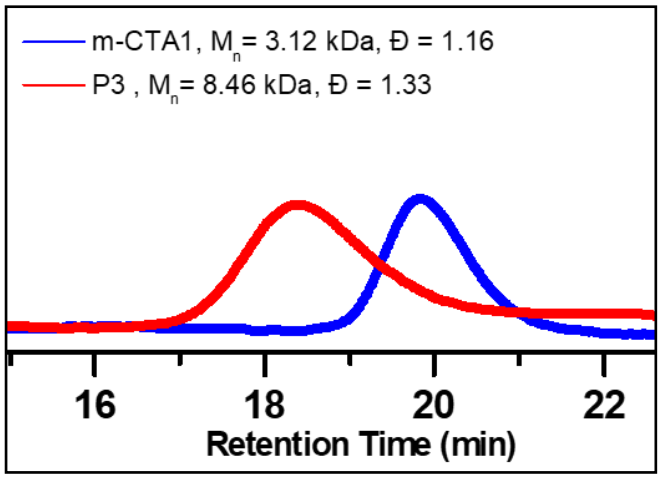


Fig S3: Refractive index ($CHCl_3$) traces of **m-CTA1** and PS-ROMP di-block copolymer **P3**

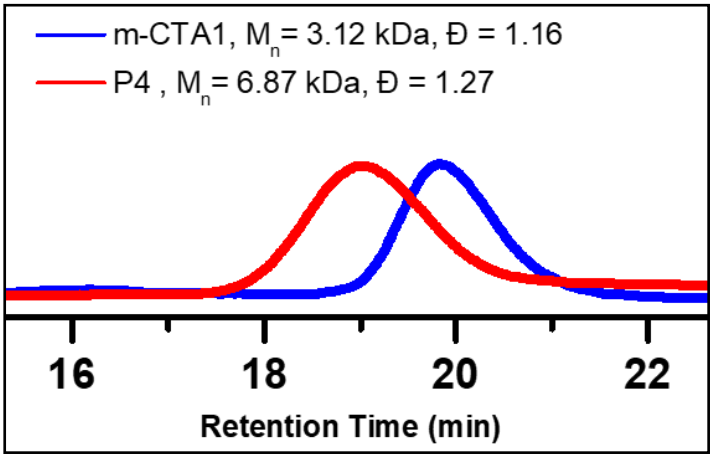


Fig S4: Refractive index ($CHCl_3$) traces of **m-CTA1** and PS-ROMP di-block copolymer **P4**

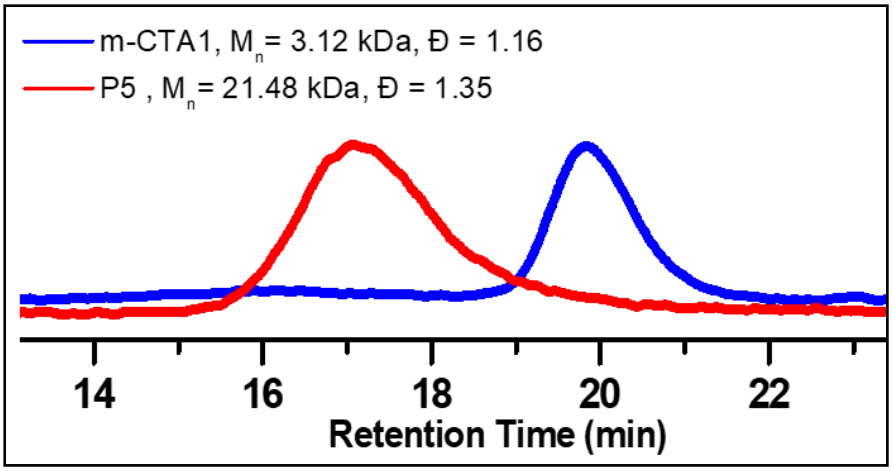


Fig S5: Refractive index ($CHCl_3$) traces of **m-CTA1** and PS-ROMP di-block copolymer **P5**

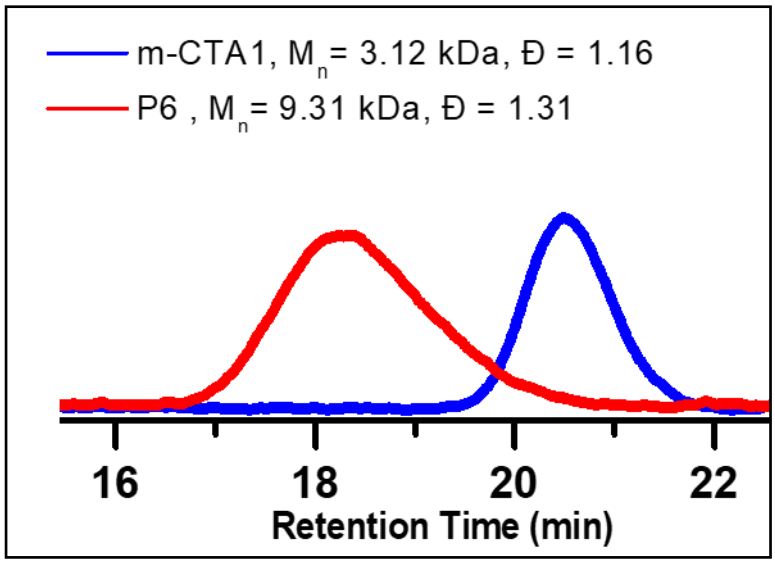


Fig S6: Refractive index ($CHCl_3$) traces of **m-CTA1** and PS-ROMP di-block copolymer **P6**

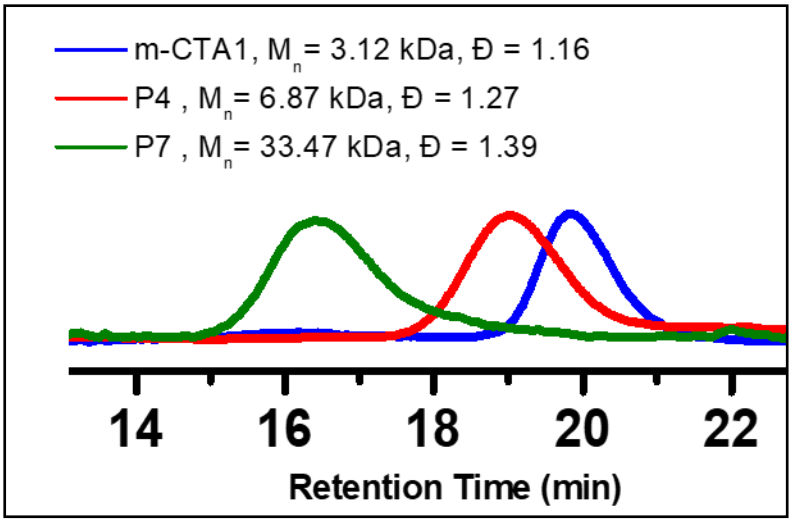


Fig S7: Refractive index ($CHCl_3$) traces of **m-CTA1**, PS-ROMP di-block copolymer **P4** and PS-ROMP-ROMP tri-block terpolymer **P7**

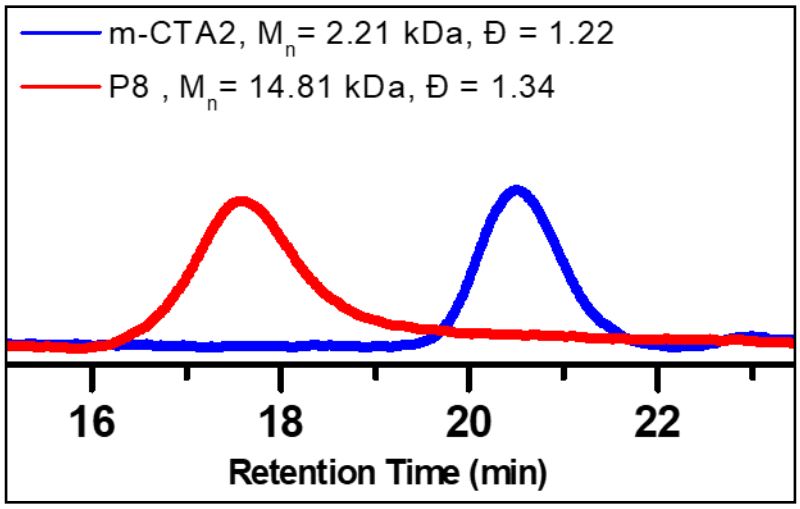


Fig S8: Refractive index ($CHCl_3$) traces of **m-CTA2** and PCL-ROMP di-block copolymer **P8**

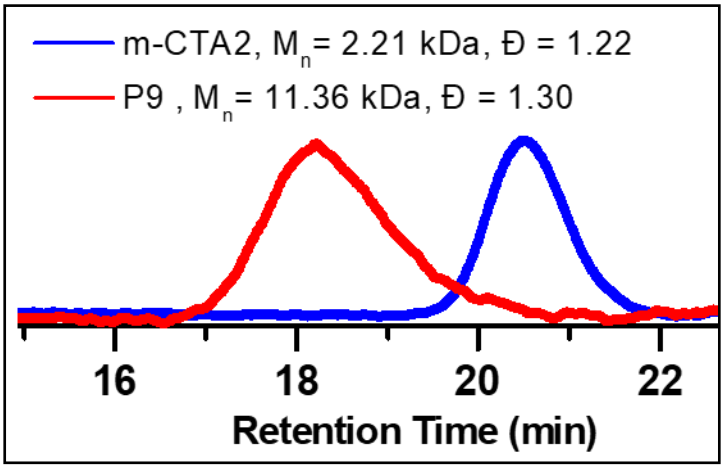


Fig S9: Refractive index ($CHCl_3$) traces of **m-CTA2** and PCL-ROMP di-block copolymer **P9**

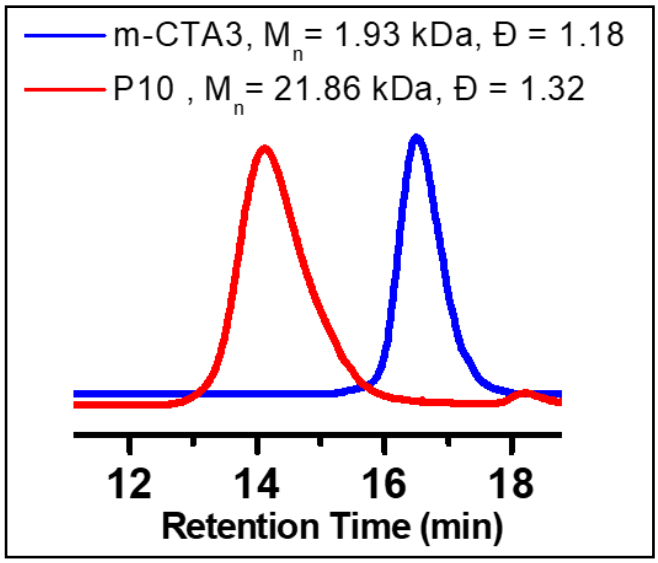


Fig S10: Refractive index (DMF) traces of **m-CTA3** and PLA-ROMP di-block copolymer **P10**

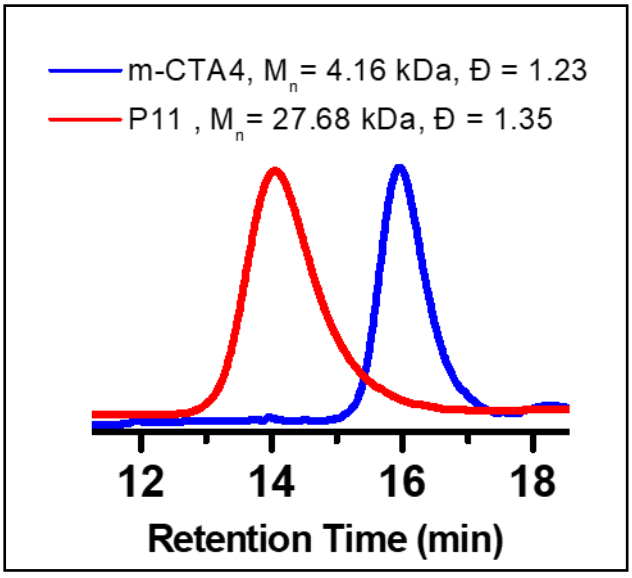


Fig S11: Refractive index (DMF) traces of **m-CTA4** and PEG-PLA-ROMP tri-block terpolymer **P11**

Degradation Studies

Procedure

One drop of 1M HCl was added to a 6 mg/mL solution of diblock copolymer **P5** in dichloromethane , and the resulting mixture was stirred at room temperature. SEC ($CHCl_3$) analysis of the crude mixture shows the complete degradation of the ROMP block within 30 min whereas the polystyrene block did not degrade under these conditions.

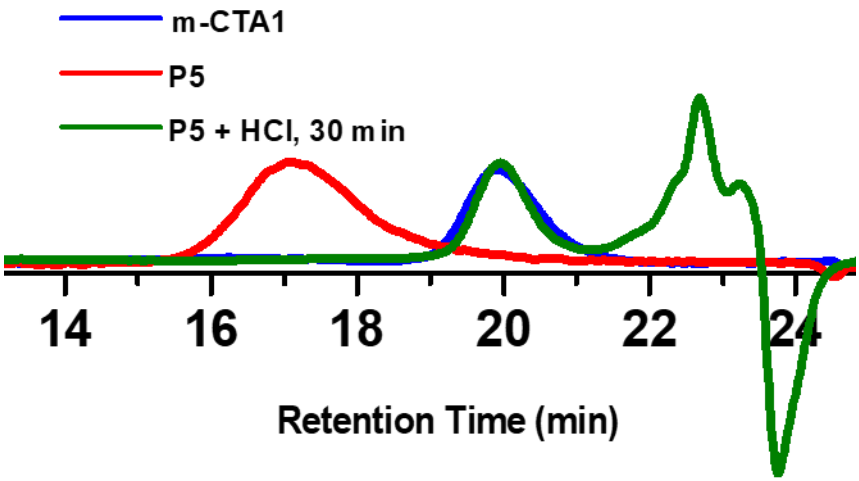


Fig S12: Refractive index ($CHCl_3$) trace of degradation of PS-ROMP di-block copolymer **P5**

DOSY DATA

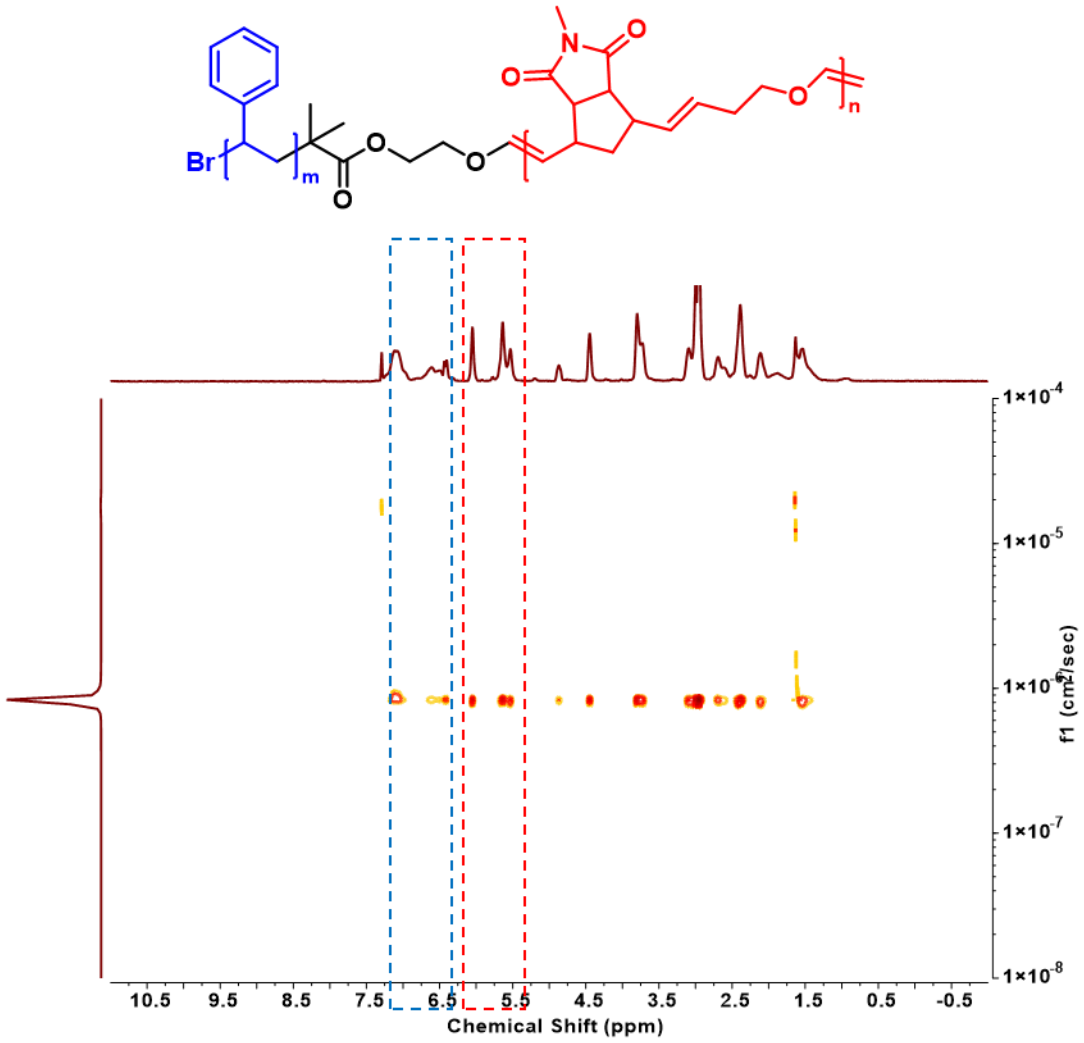


Fig S13: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P1**

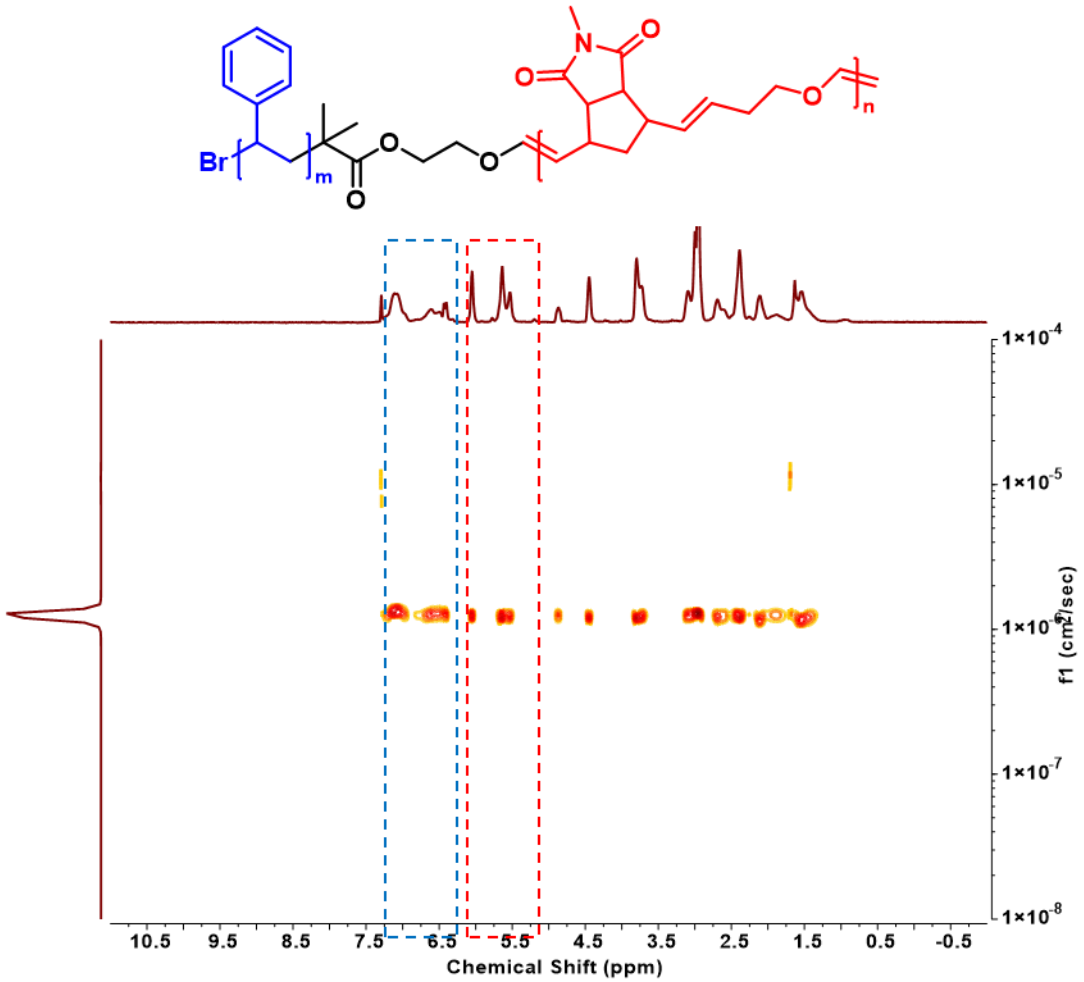


Fig S14: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P2**

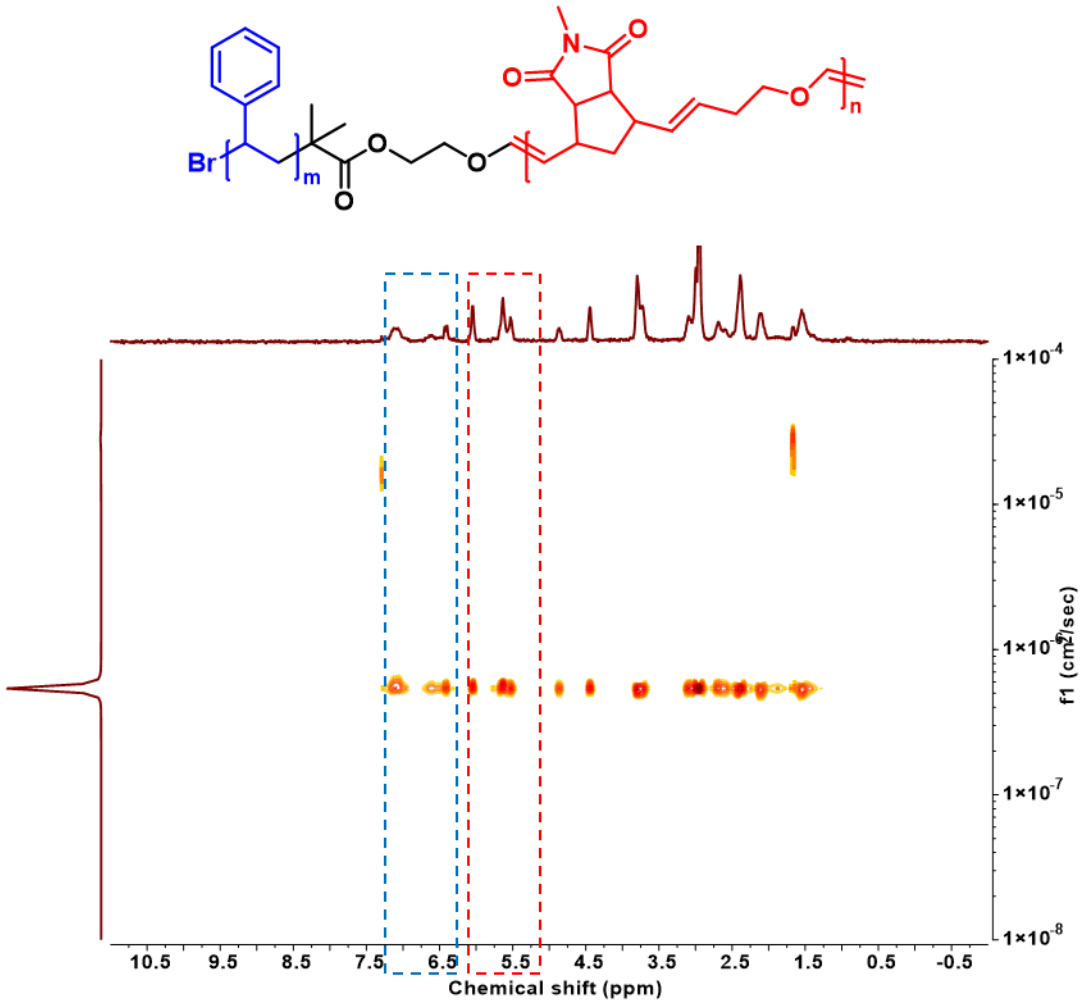


Fig S15: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P3**

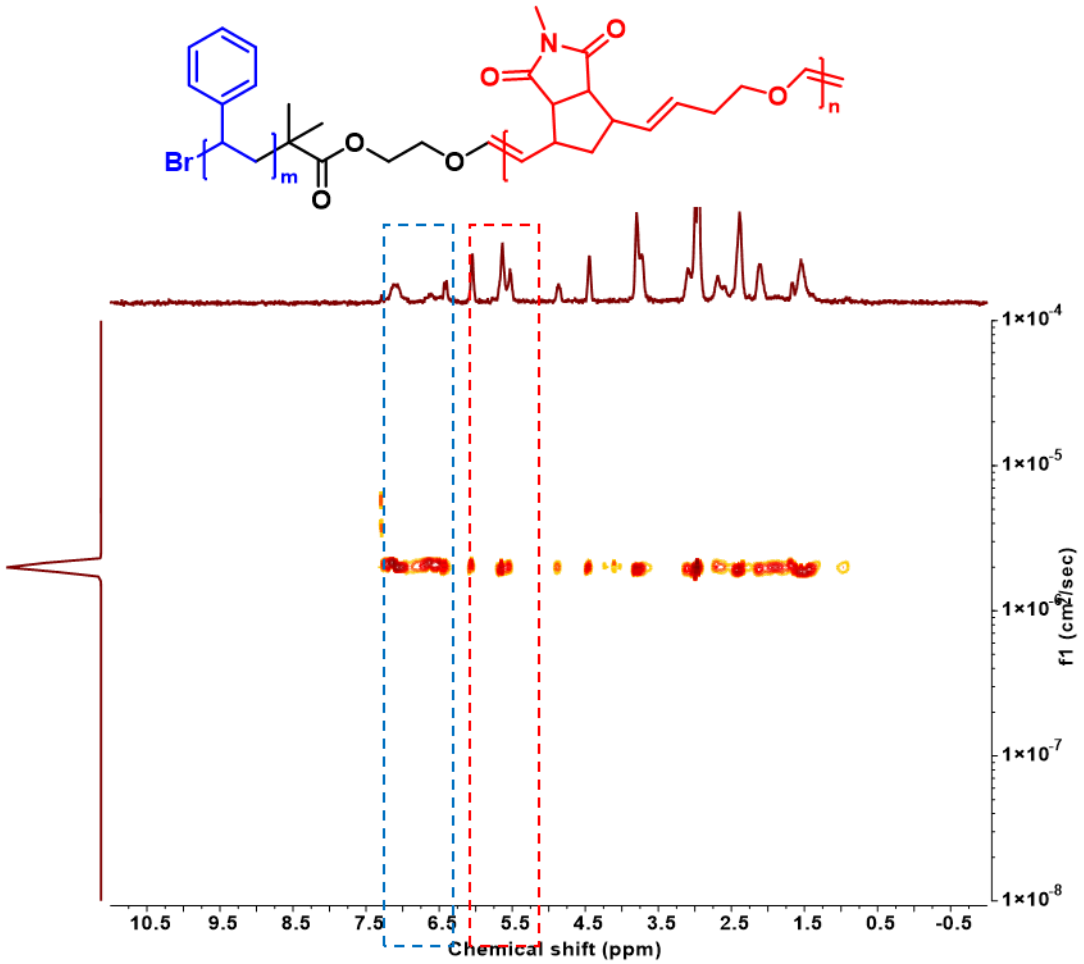


Fig S16: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P4**

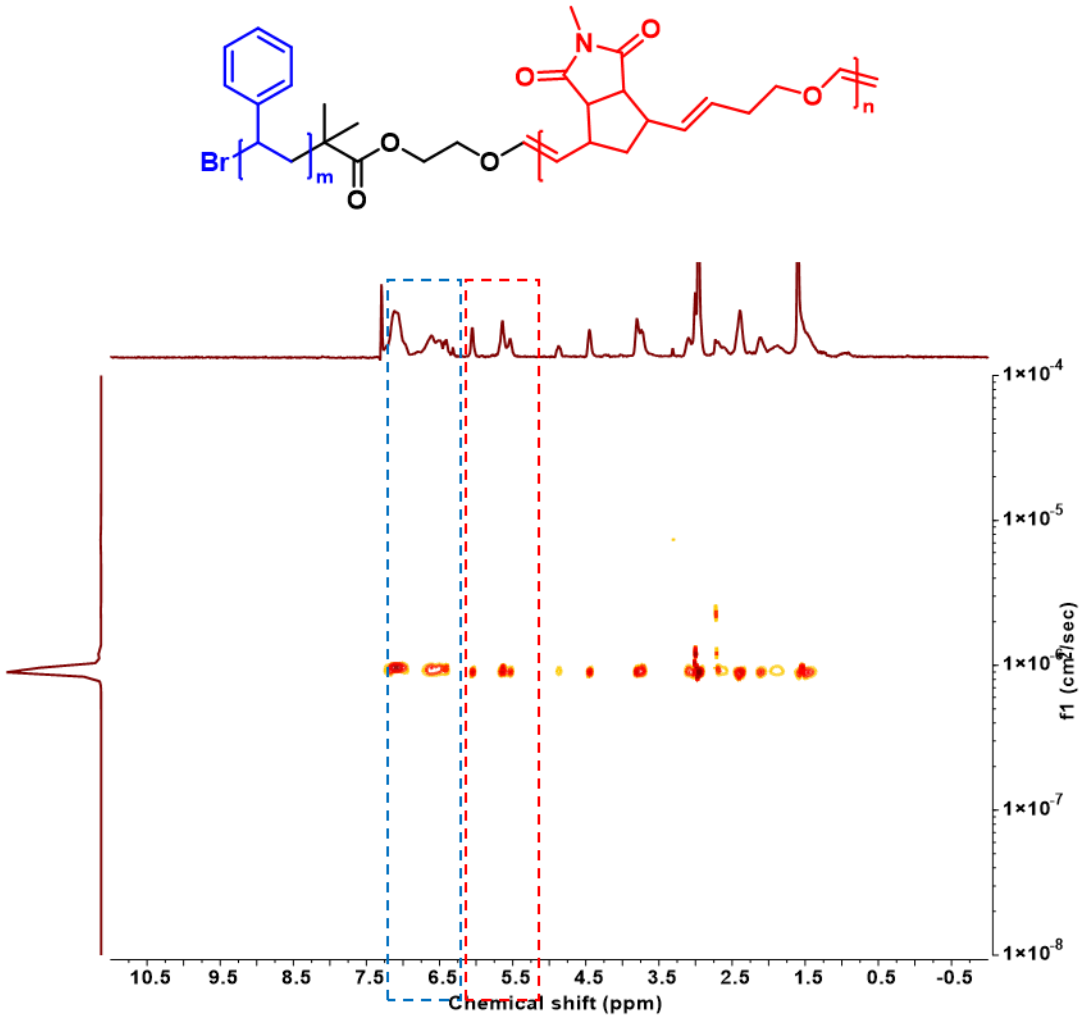


Fig S17: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P5**

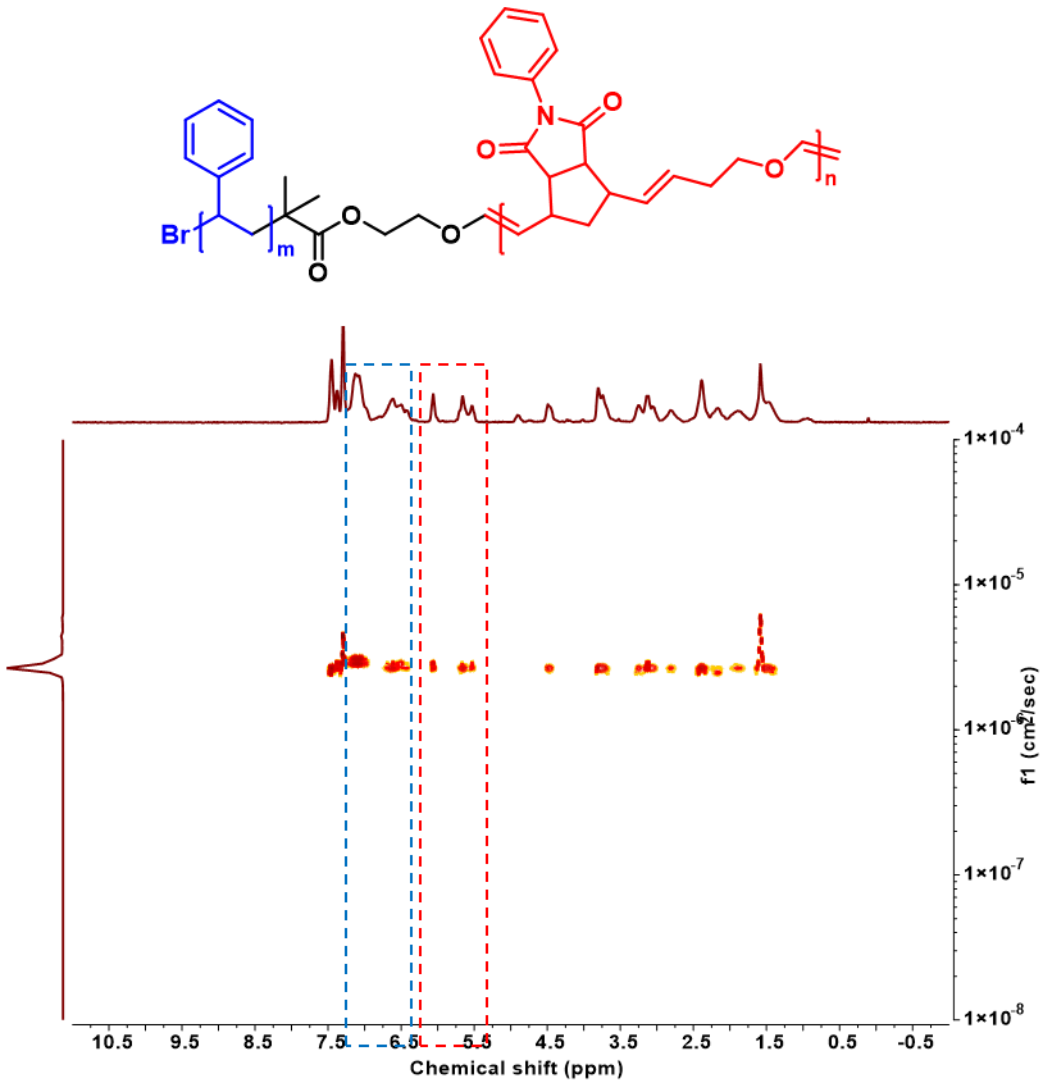


Fig S18: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP di-block copolymer **P6**

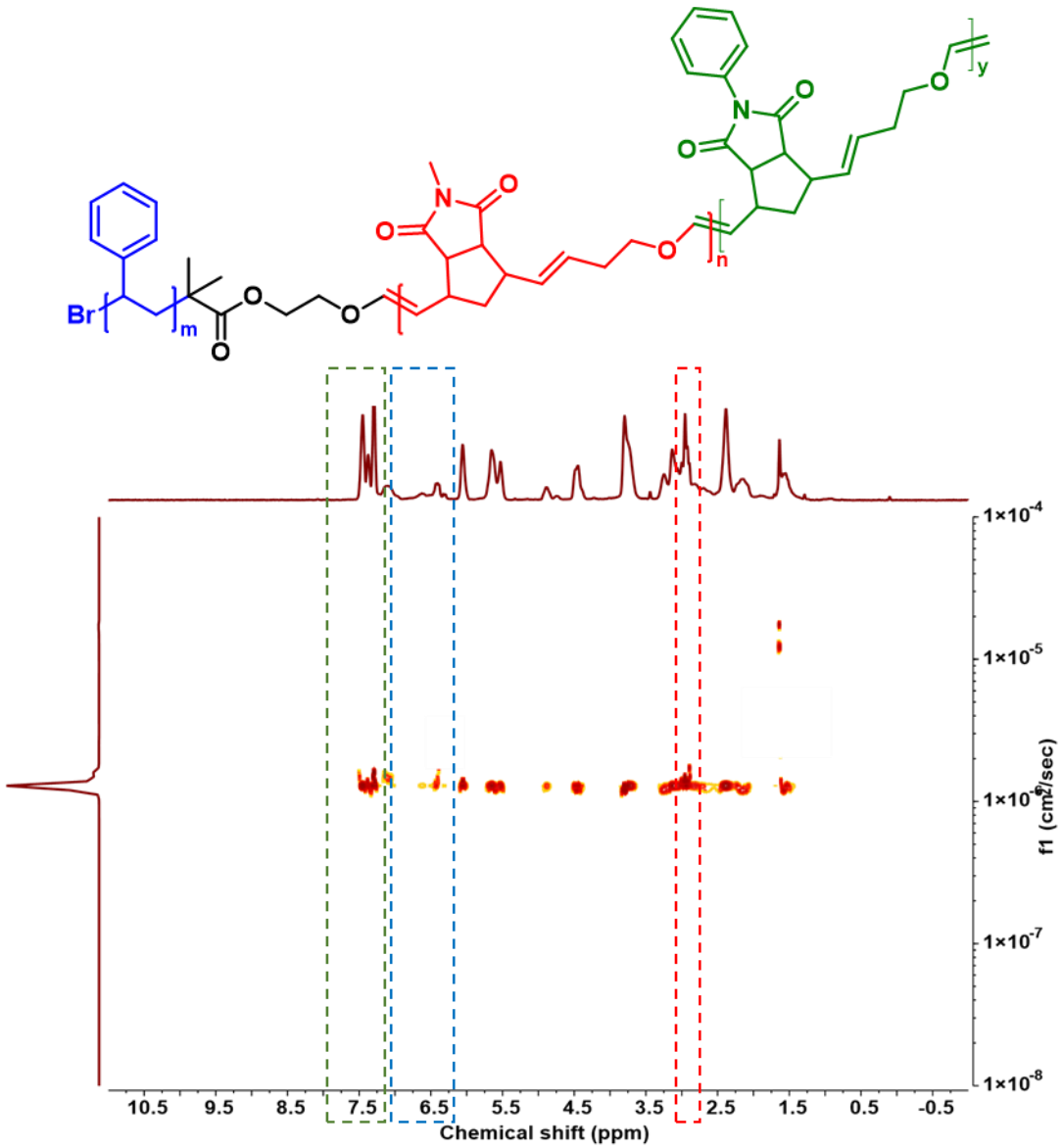


Fig S19: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PS-ROMP-ROMP tri-block copolymer **P7.**

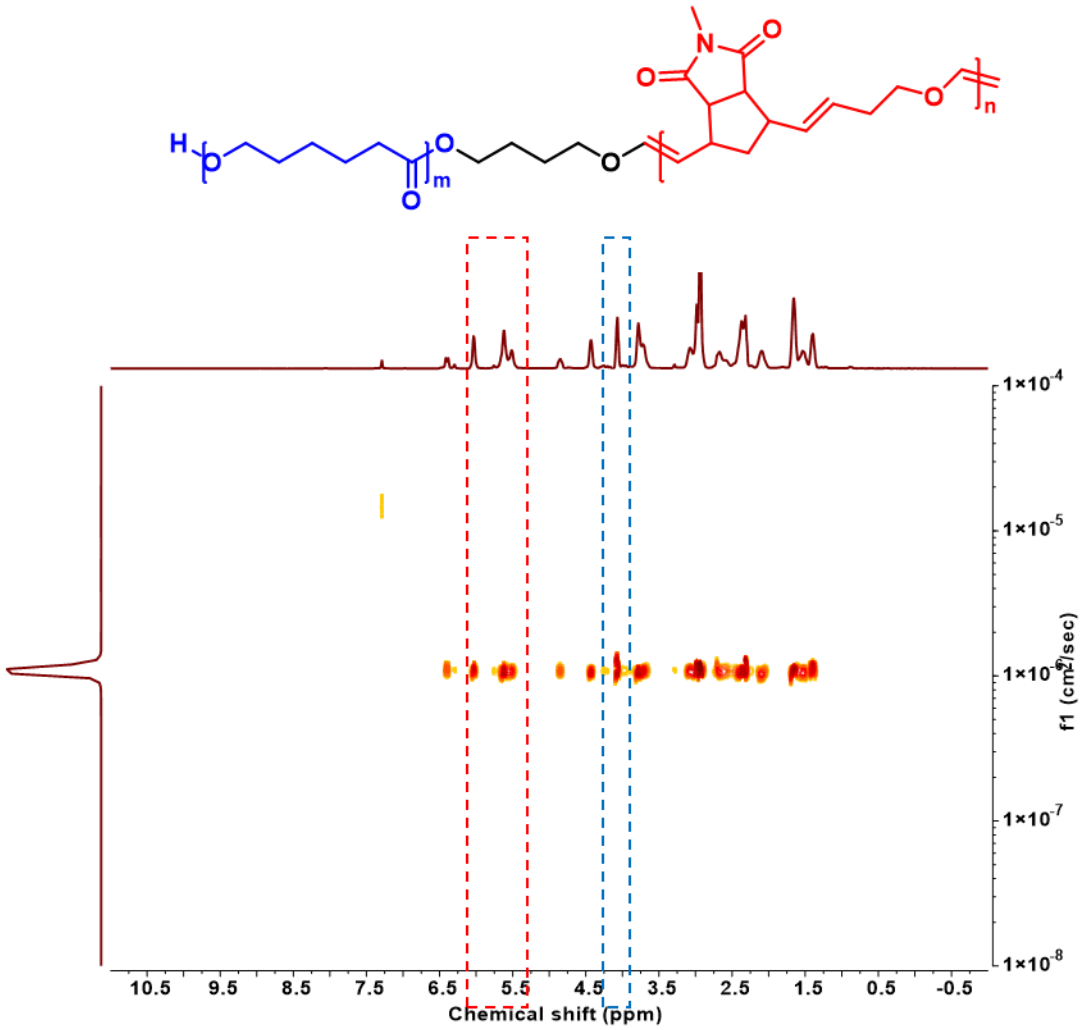


Fig S20: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PCL-ROMP di-block copolymer **P8.**

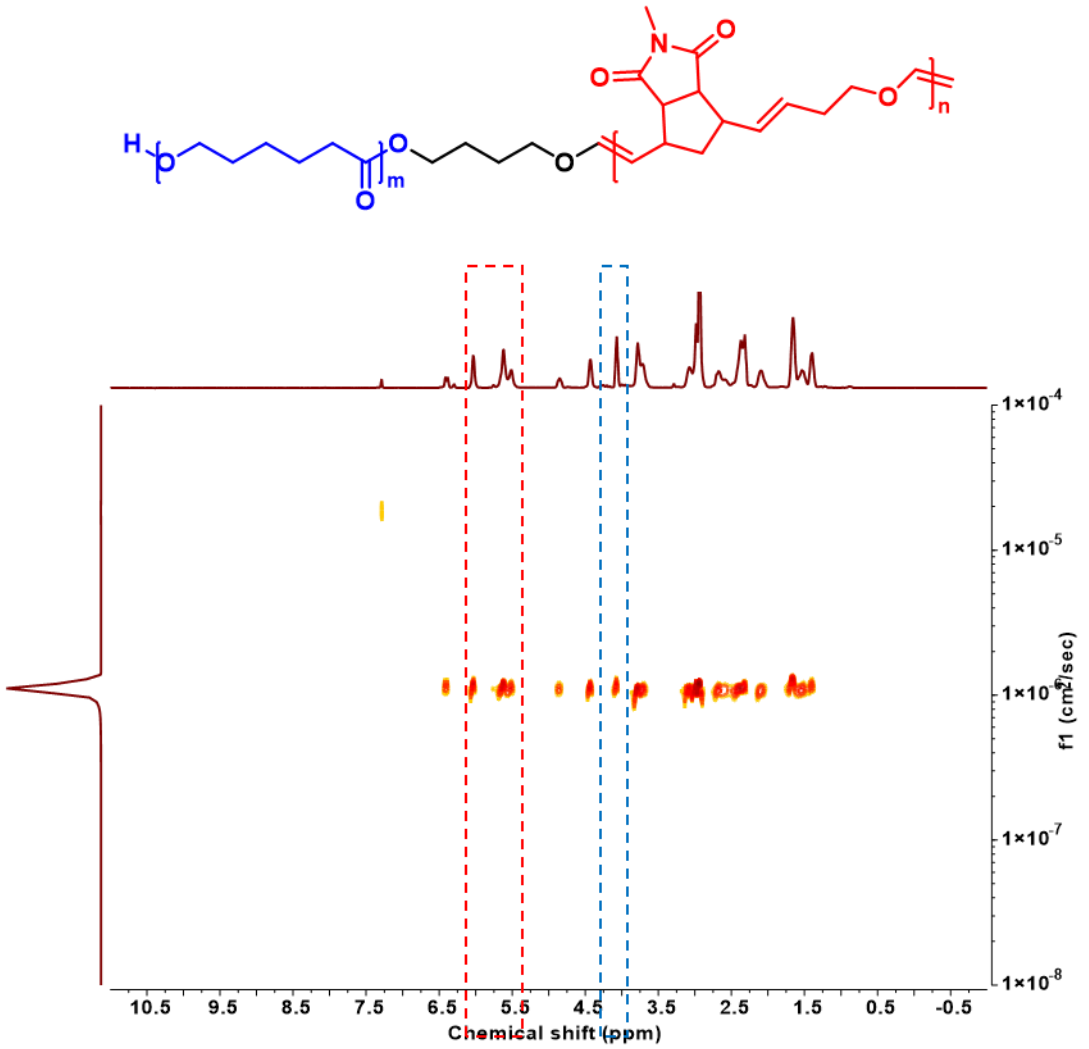


Fig S21: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PCL-ROMP di-block copolymer **P9.**

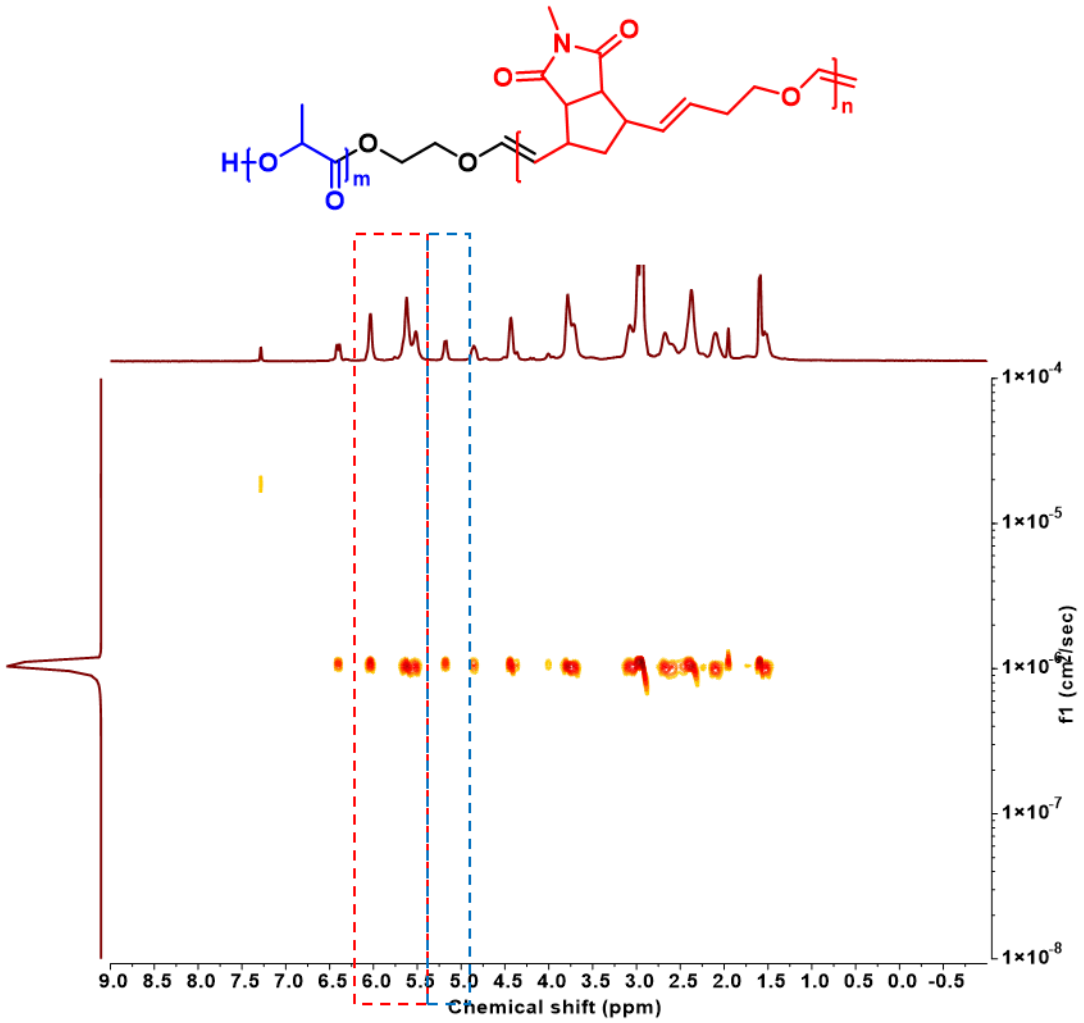


Fig S22: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PCL-ROMP di-block copolymer **P10.**

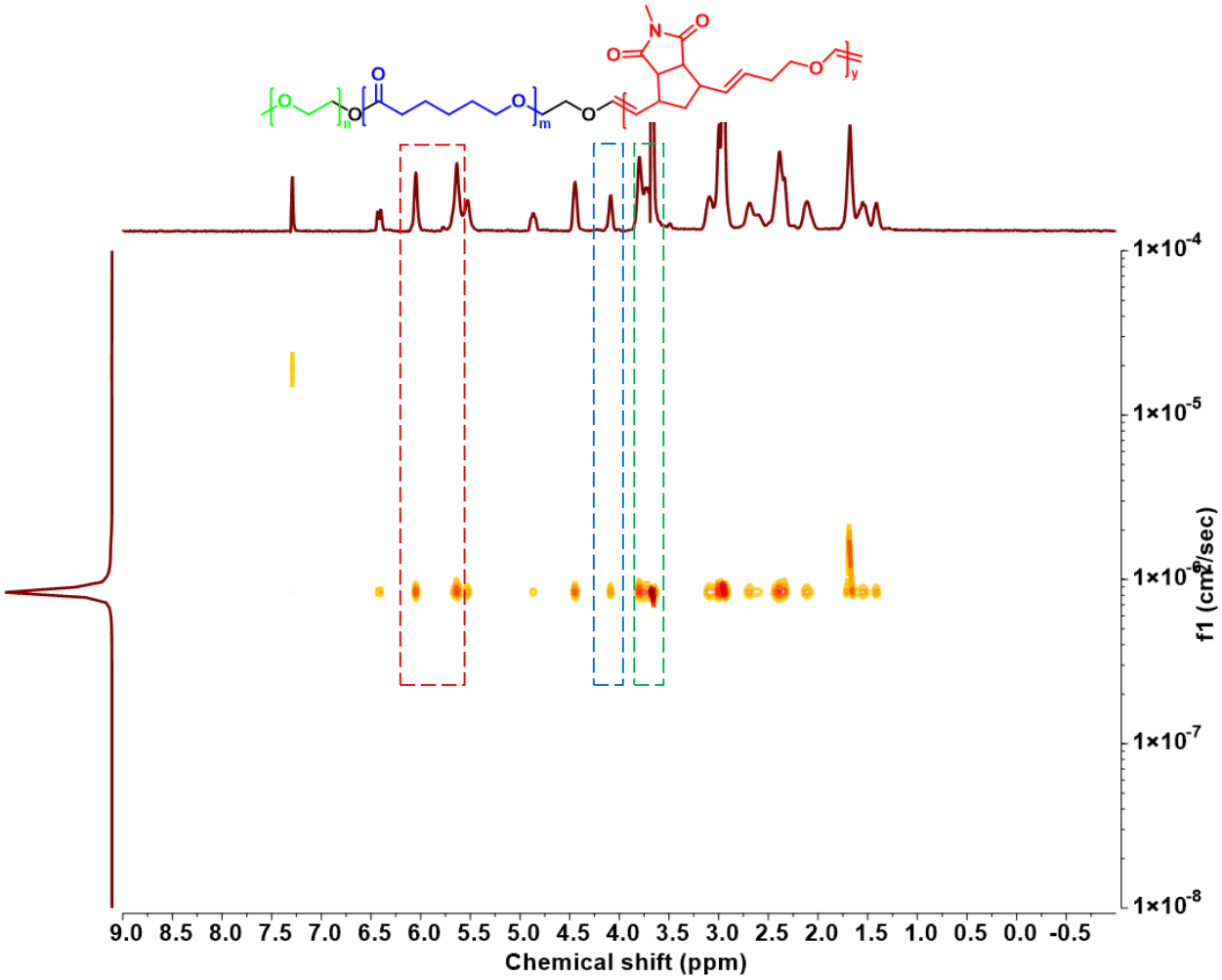


Fig S23: DOSY NMR spectrum (400 MHz, $CDCl_3$) of PEG-PCL-ROMP tri-block terpolymer **P11.**

NMR DATA

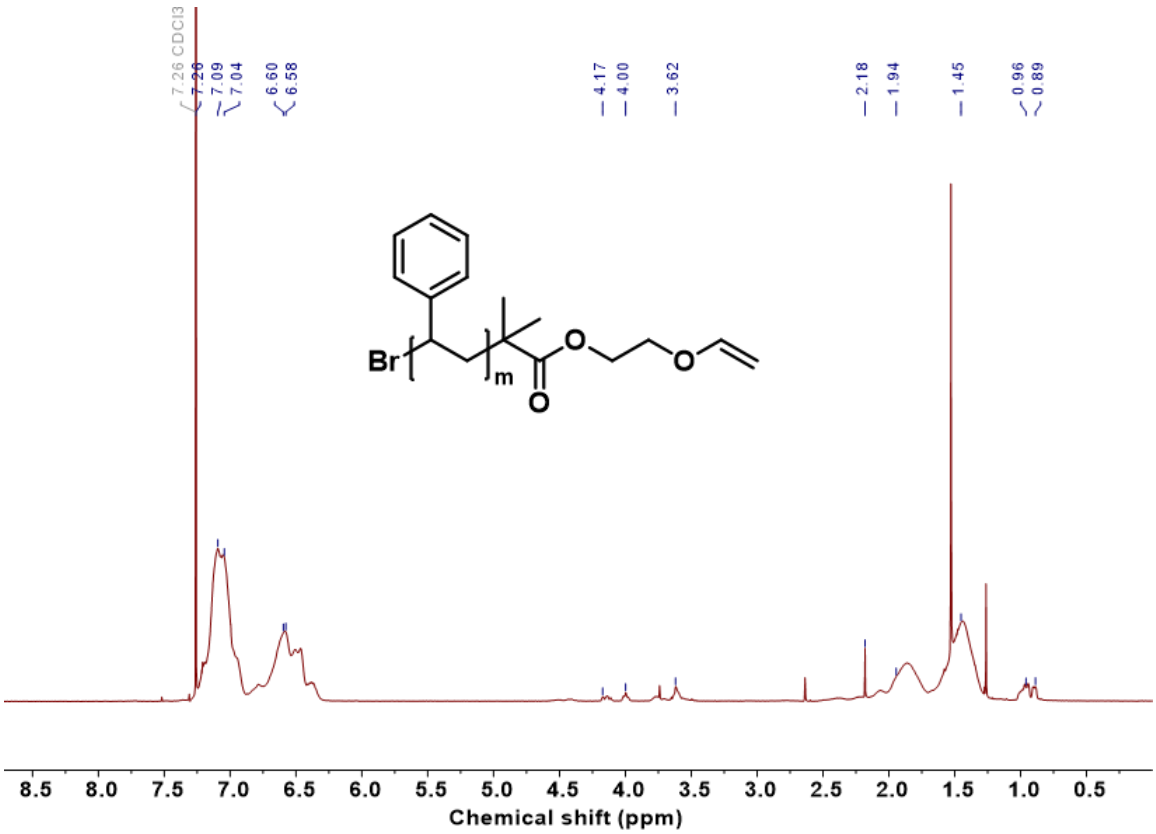


Fig S24: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **m-CTA1.**

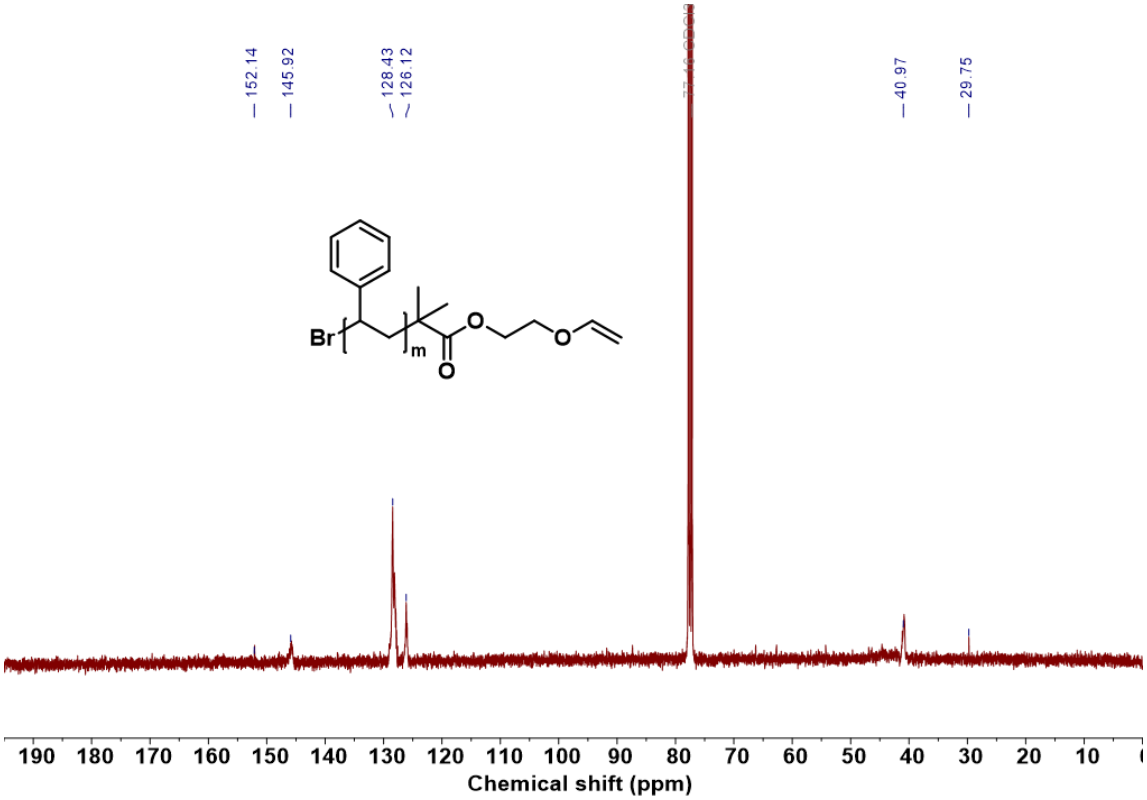


Fig S25: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **m-CTA1**

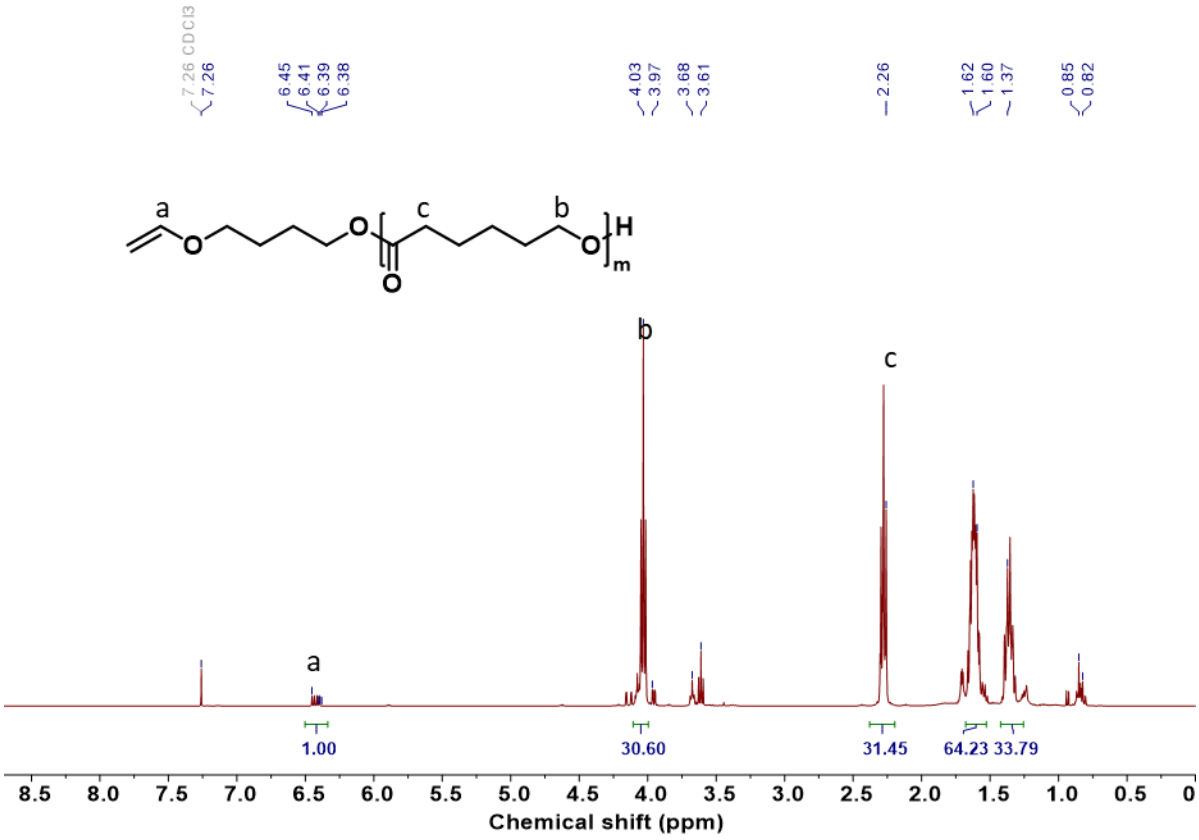


Fig S26: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **m-CTA2**

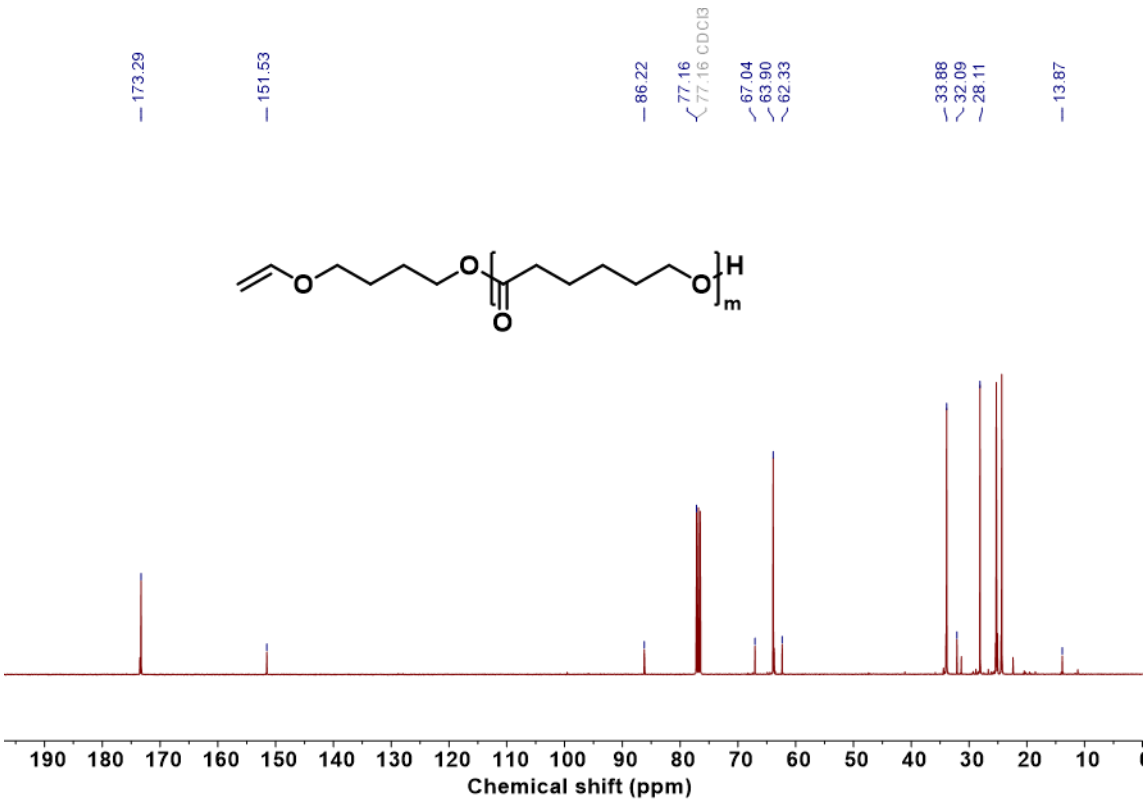


Fig S27: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **m-CTA2**

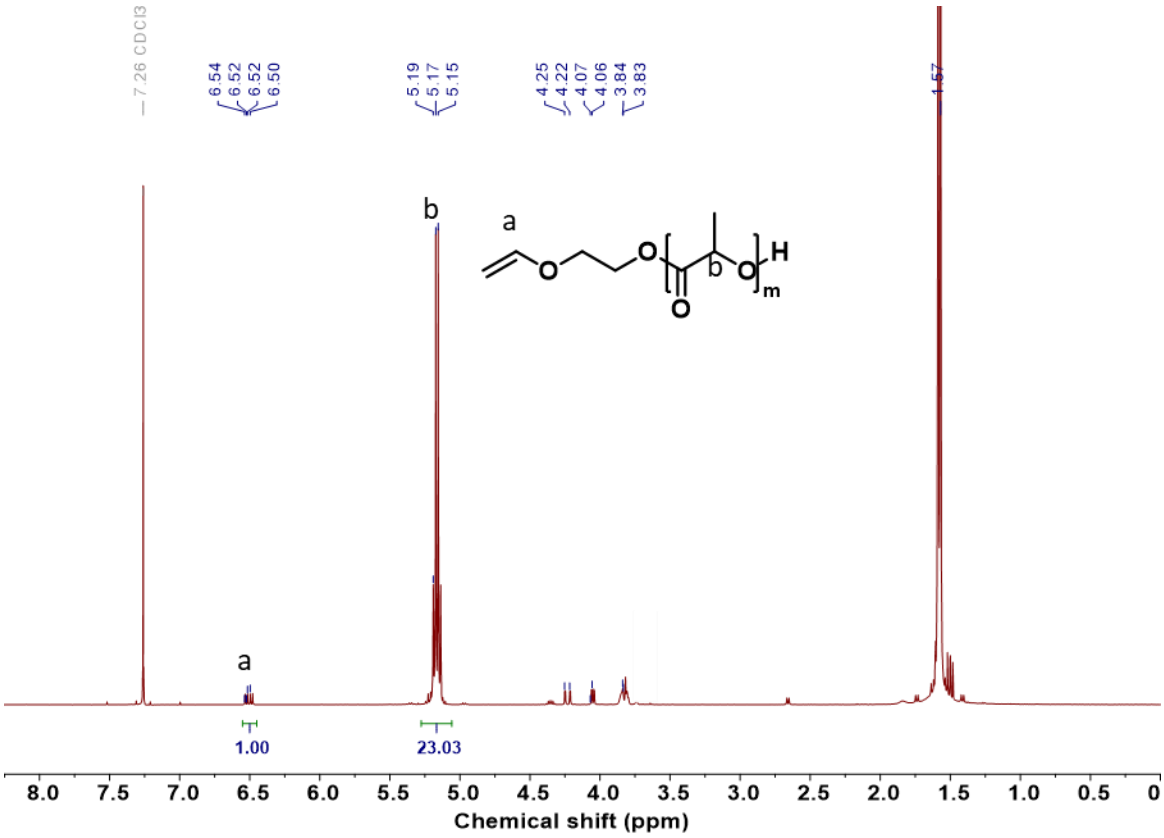


Fig S28: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **m-CTA3**

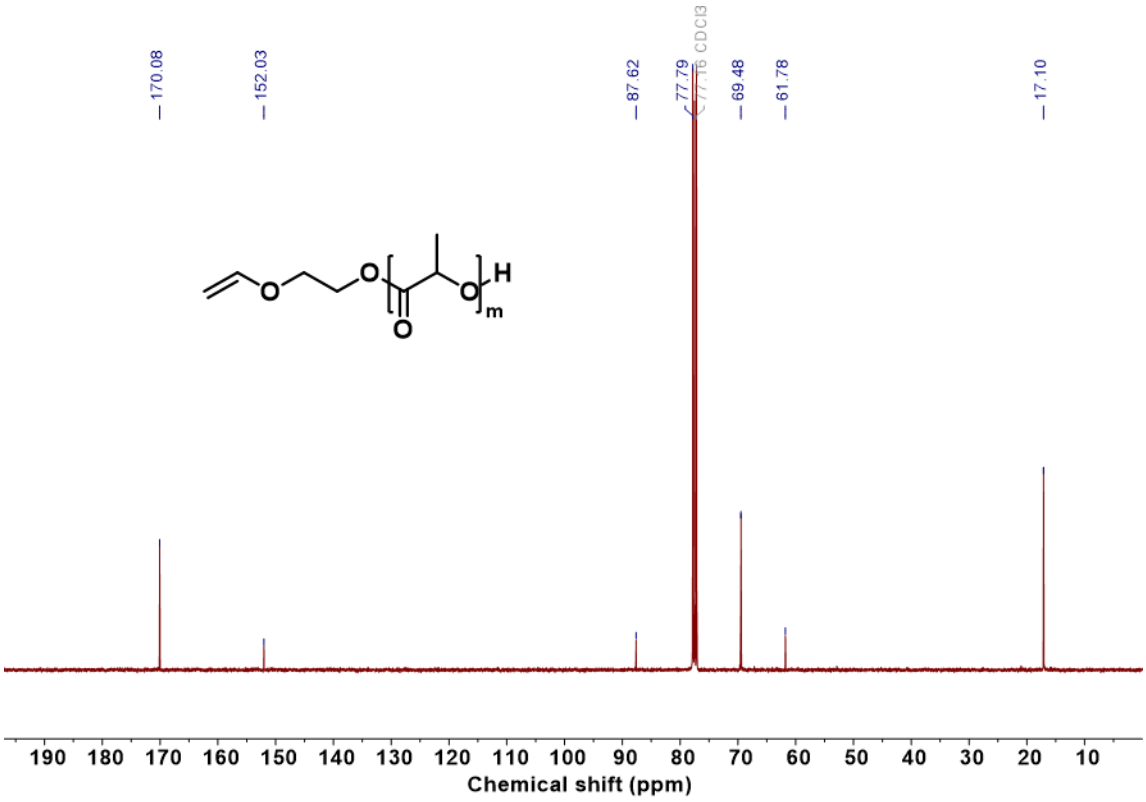


Fig S29: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **m-CTA3**

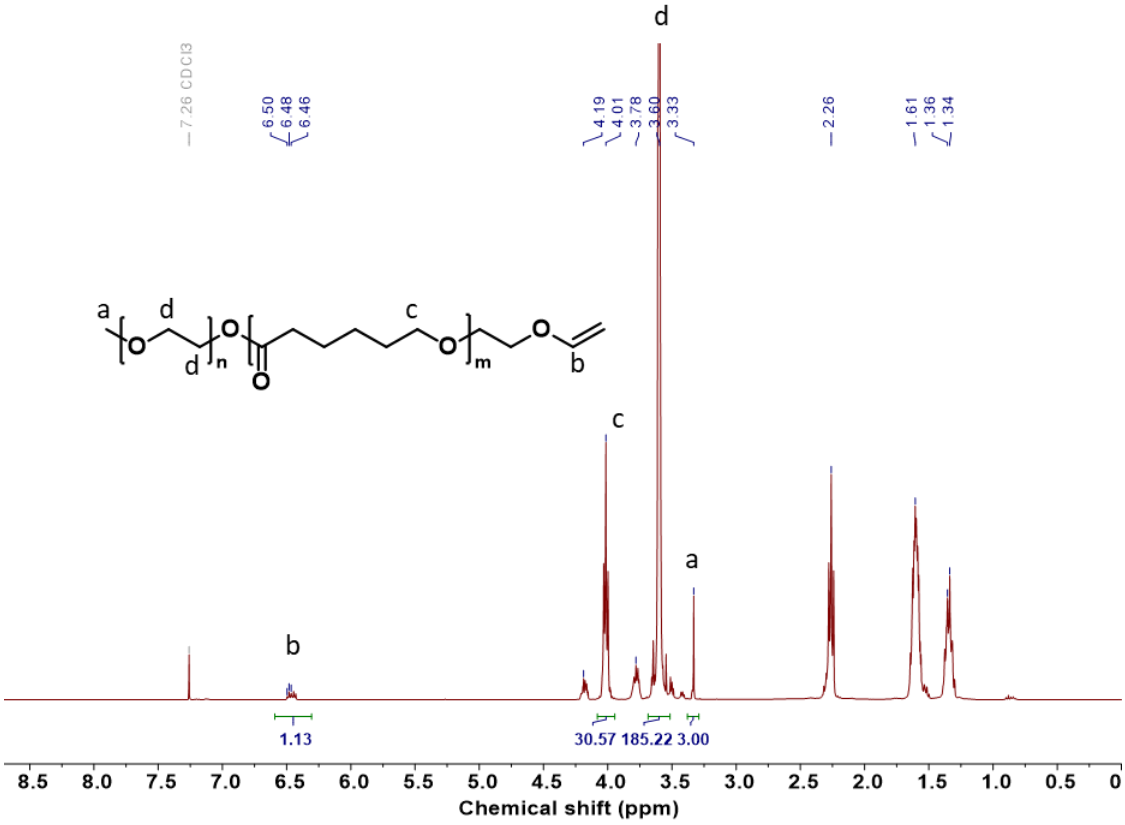


Fig S30: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **m-CTA4**

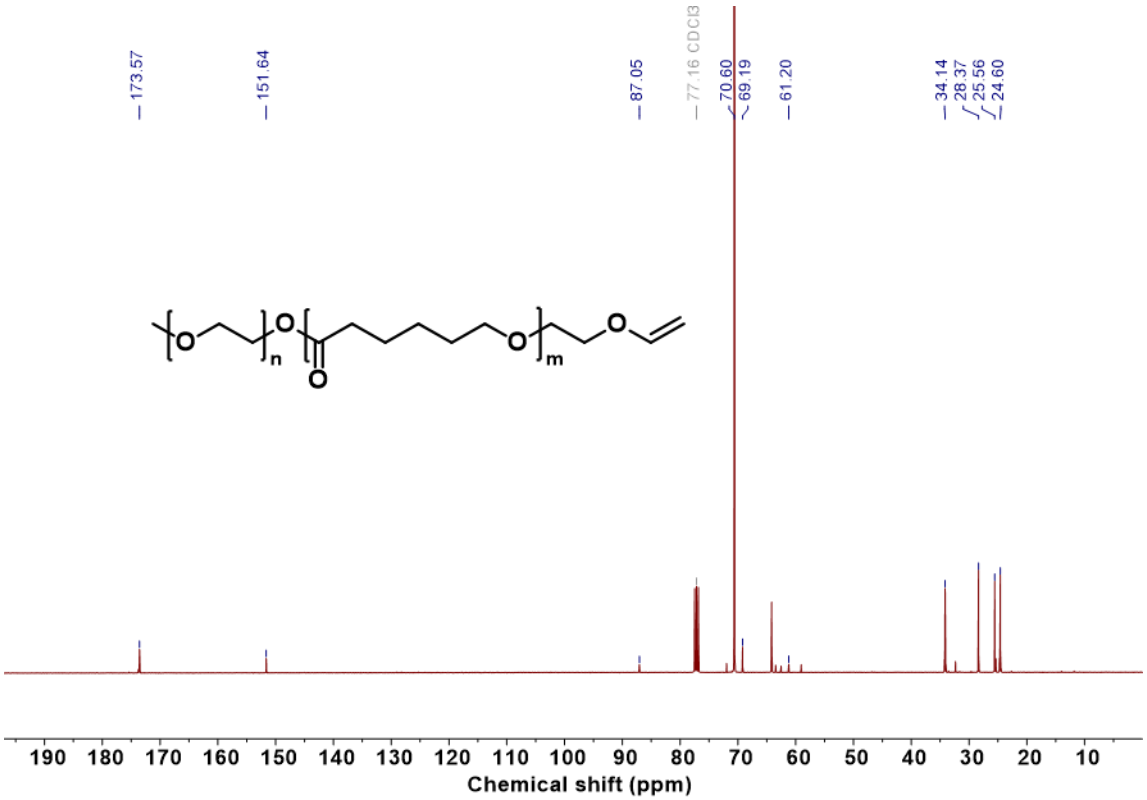


Fig S31: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **m-CTA4**

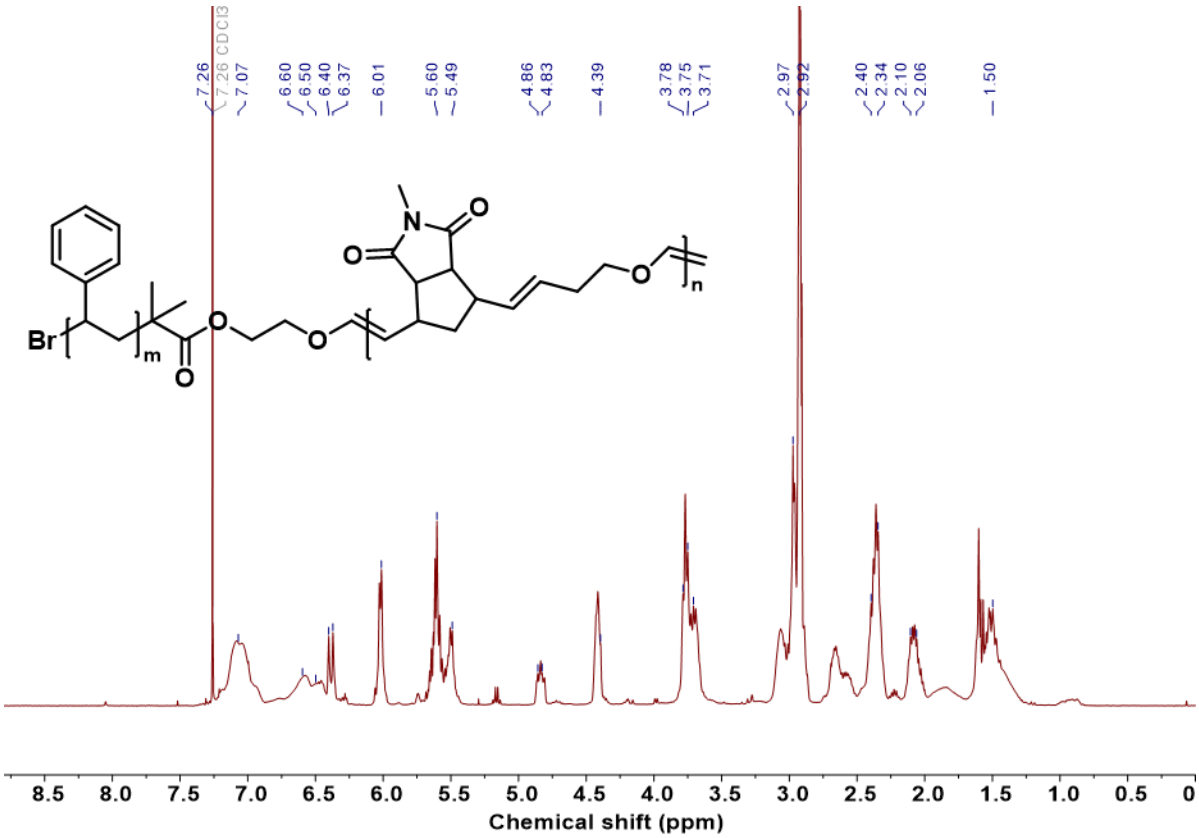


Fig S32: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P1**

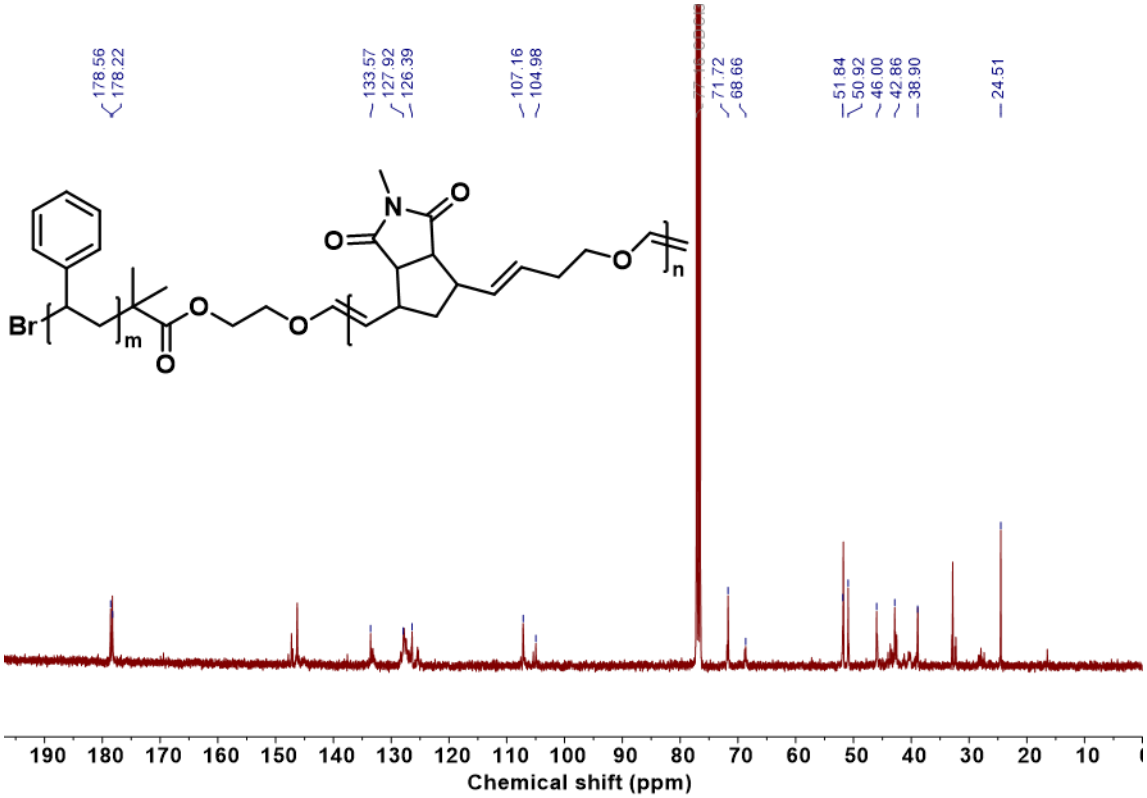


Fig S33: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P1**

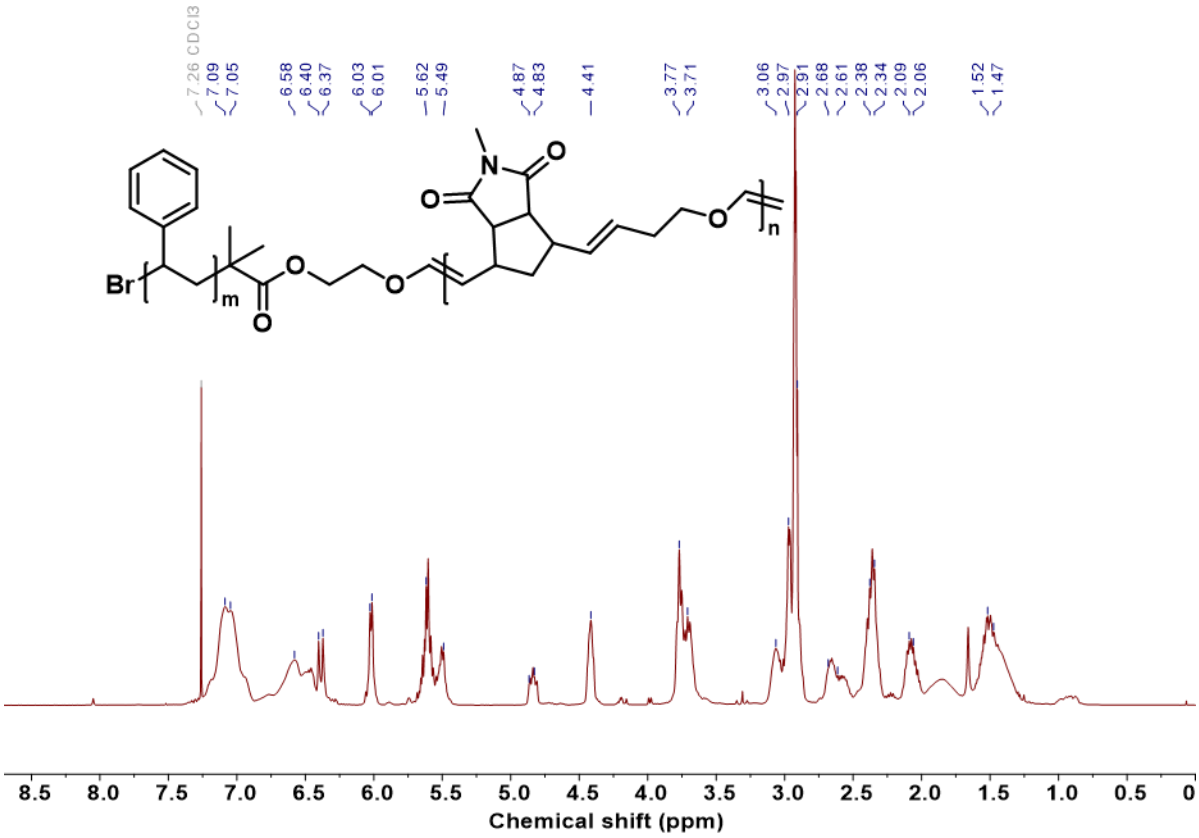


Fig S34: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P2**

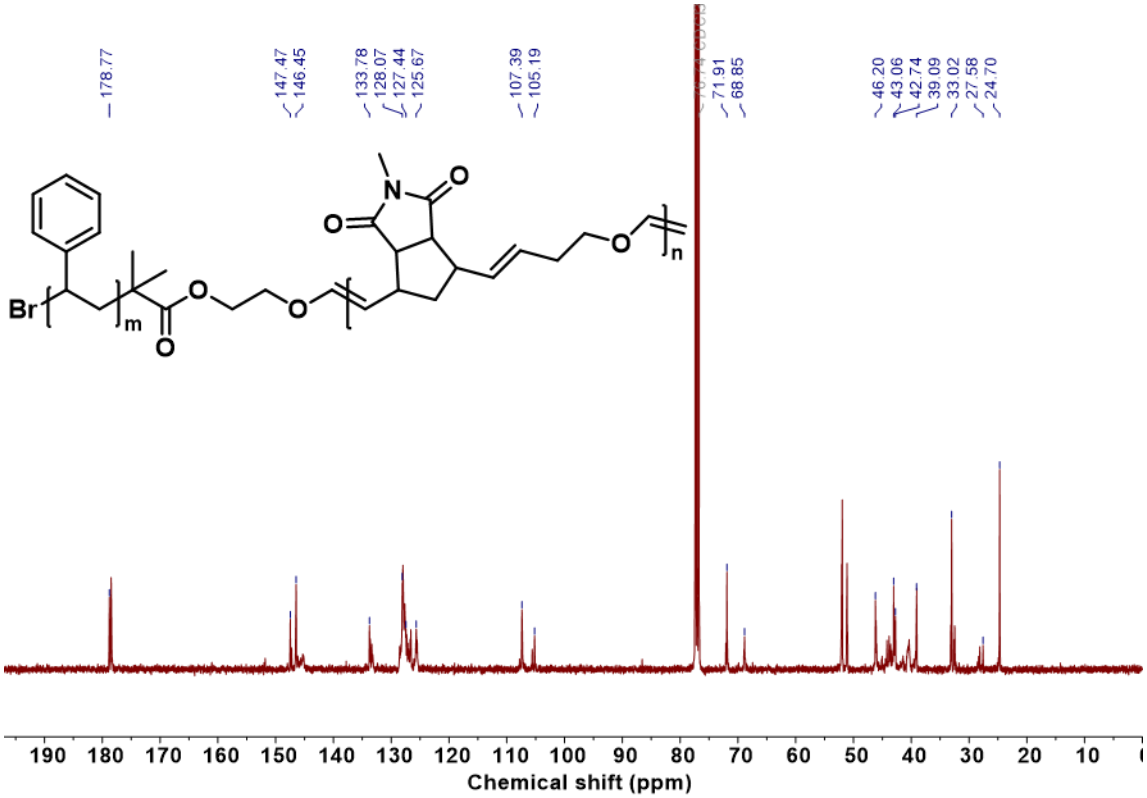


Fig S35: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P2**

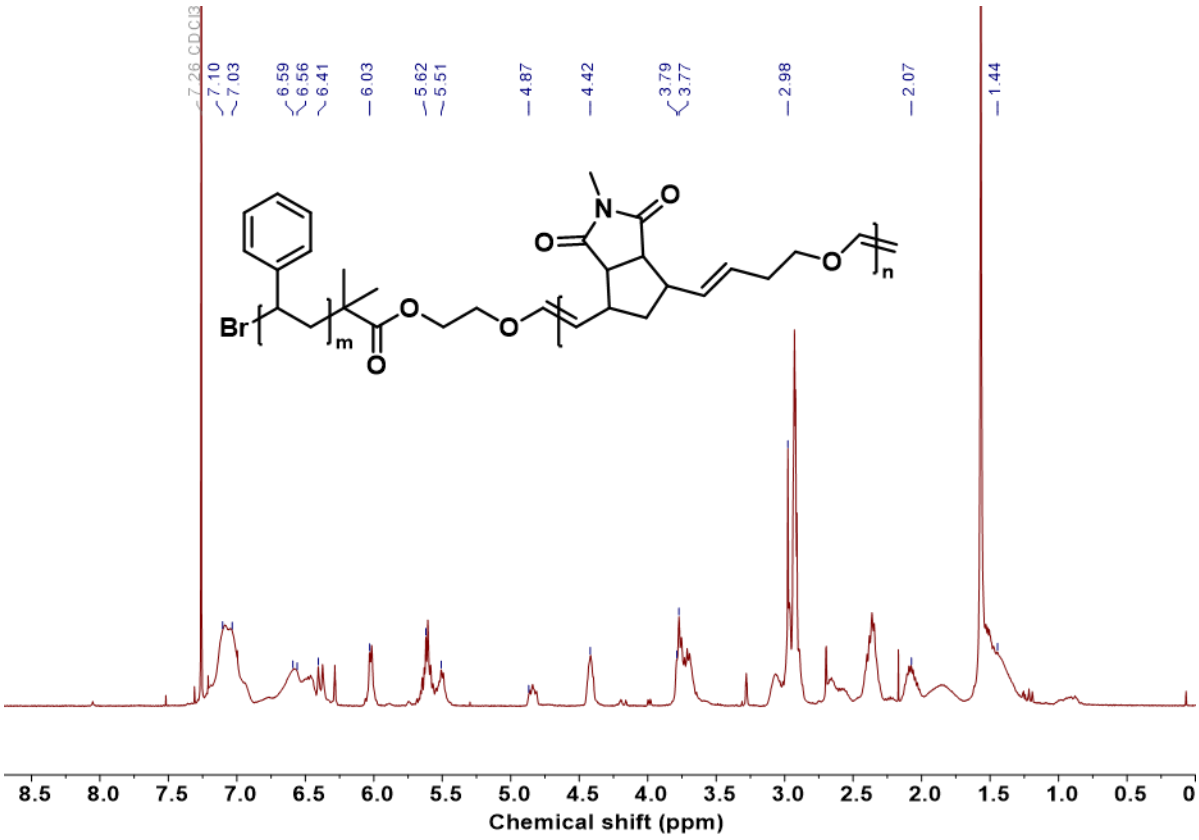


Fig S36: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P3**

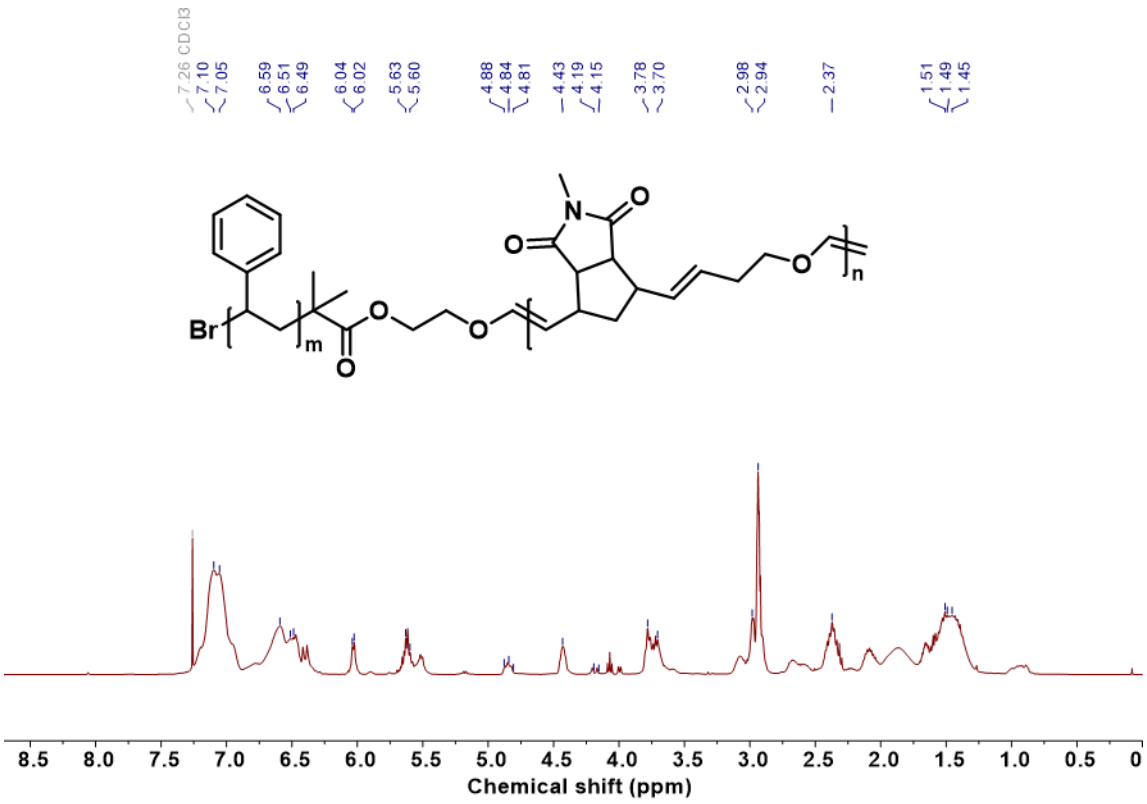


Fig S37: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P4**

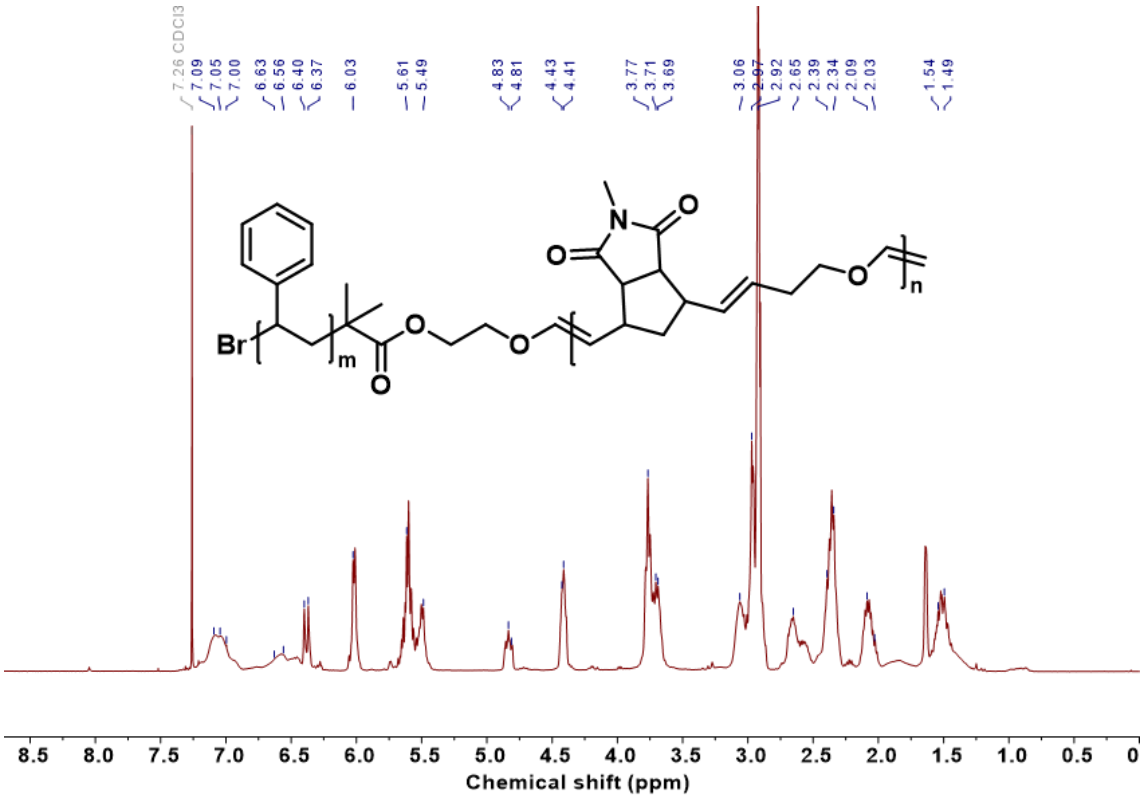


Fig S38: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P5**

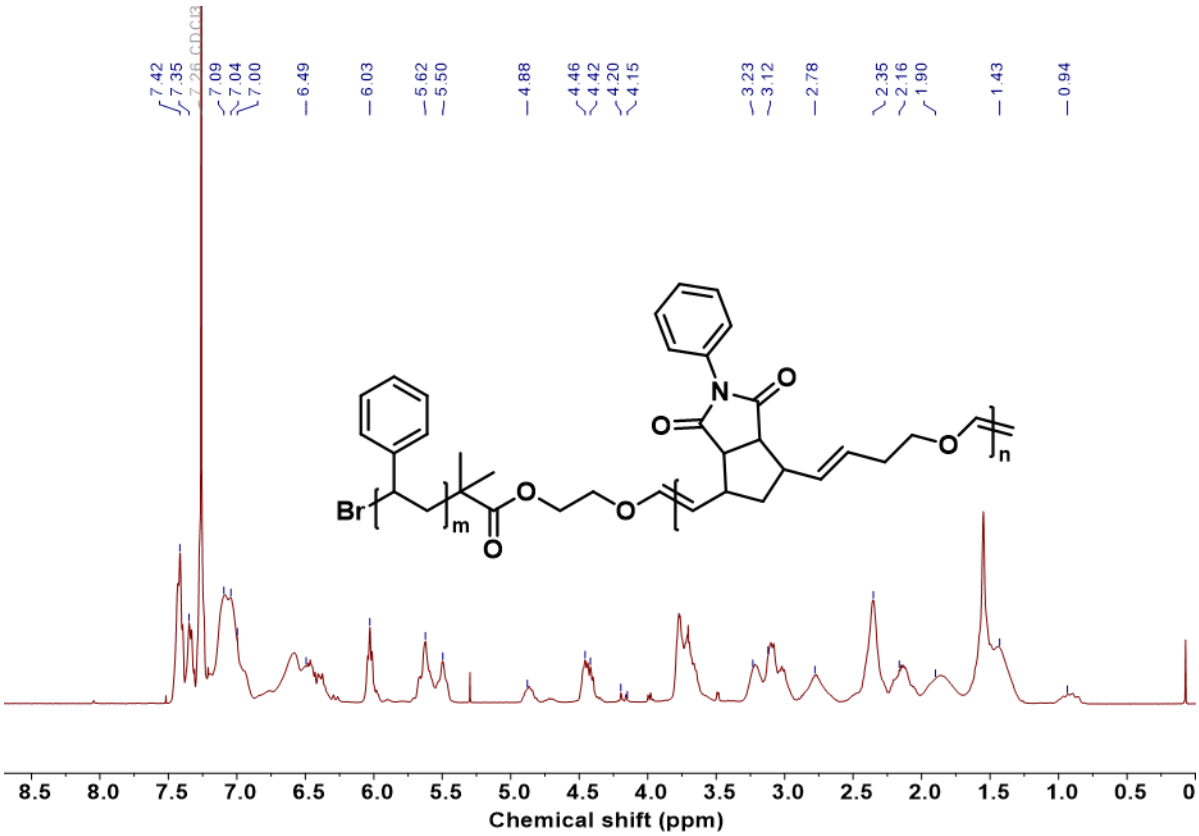


Fig S39: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P6**

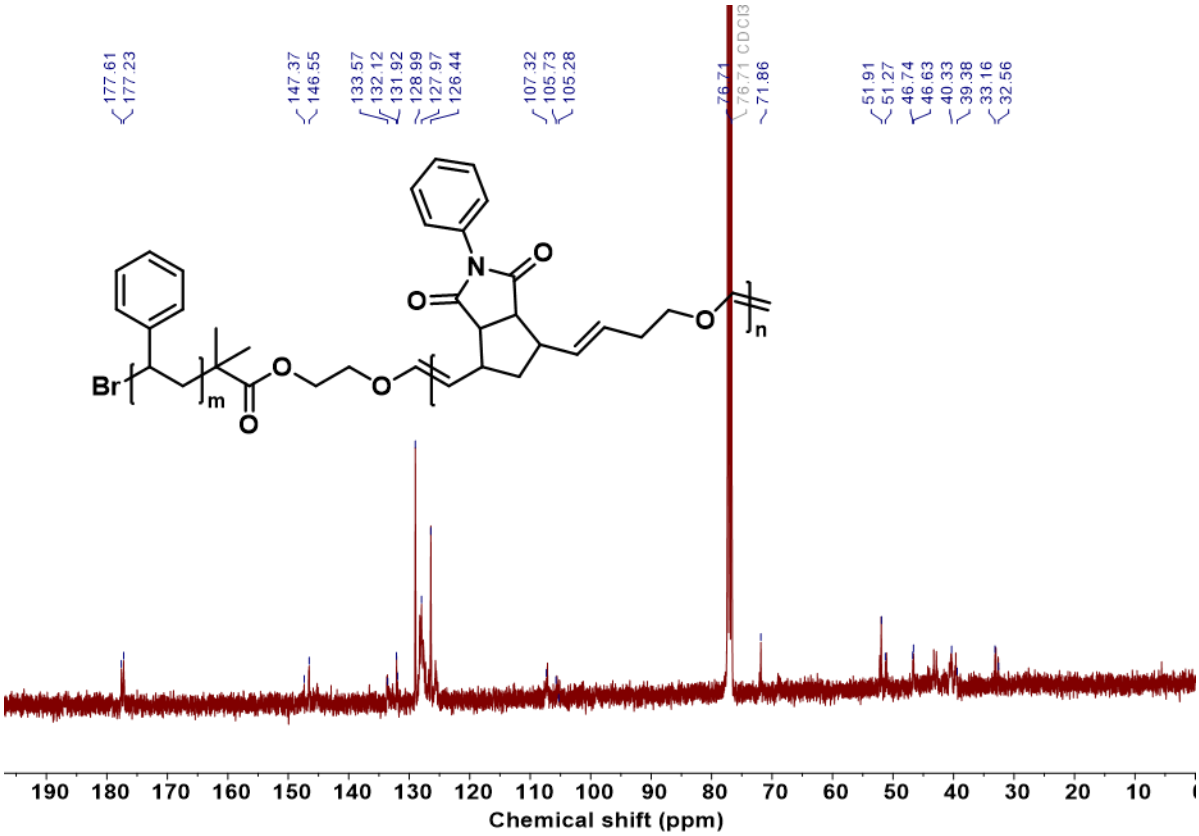


Fig S40: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P6**

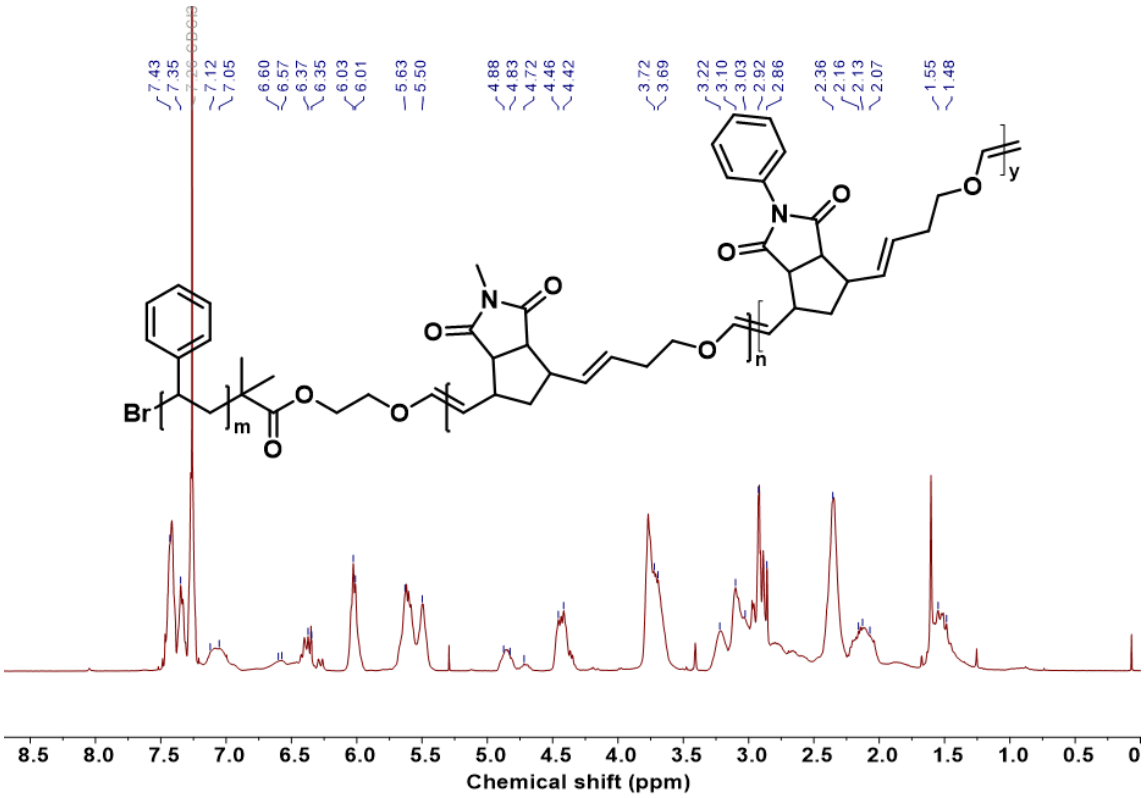


Fig S41: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P7**

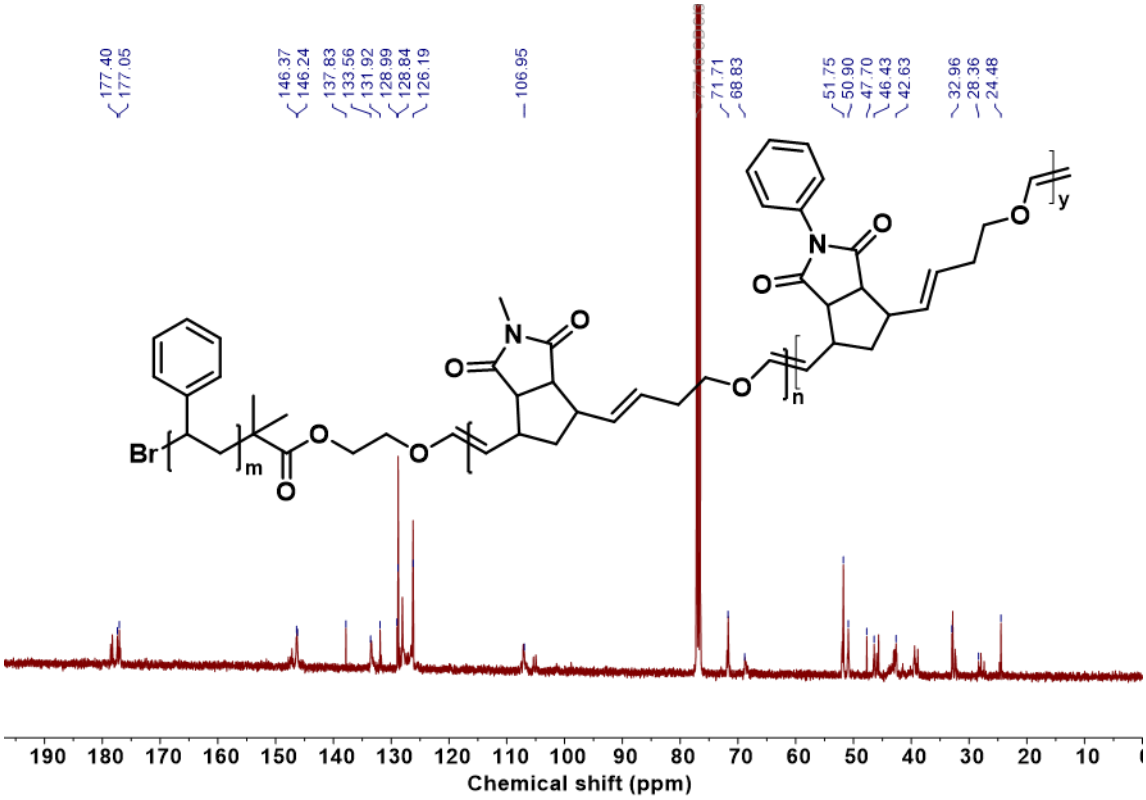


Fig S42: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P7**

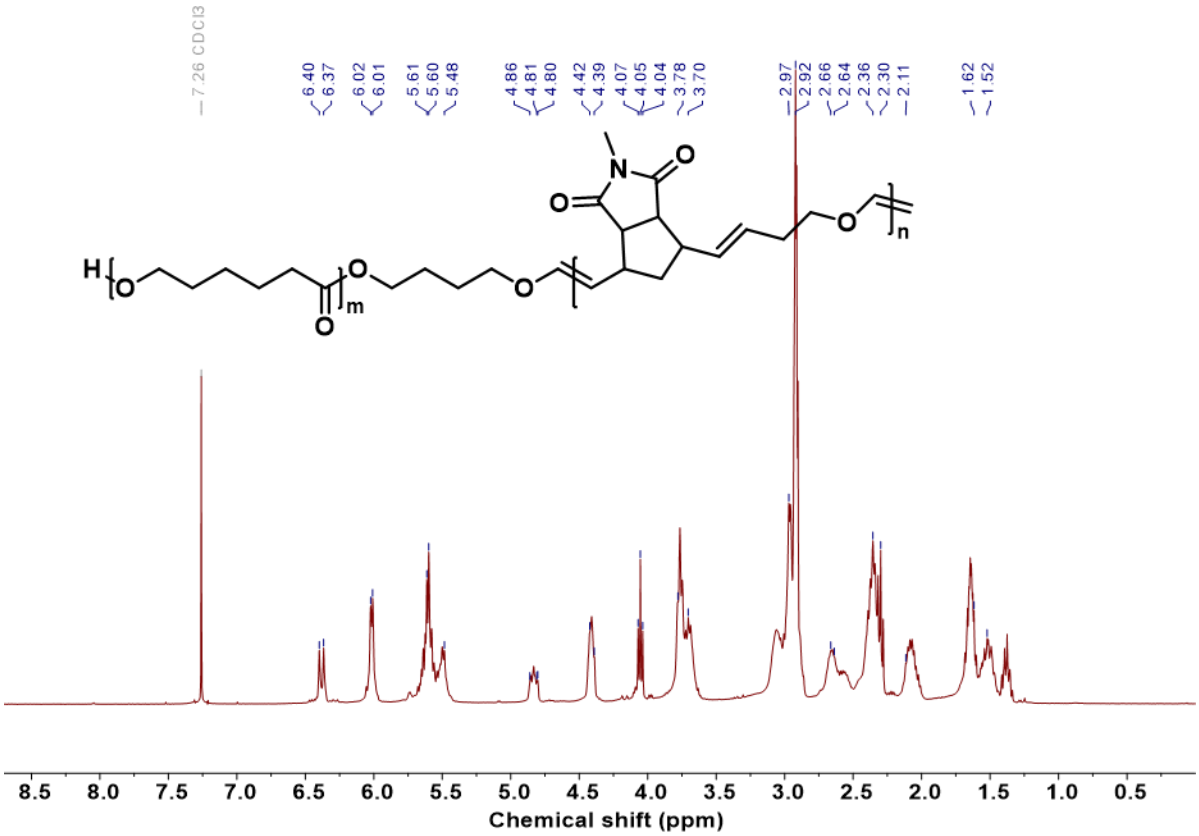


Fig S43: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P8**

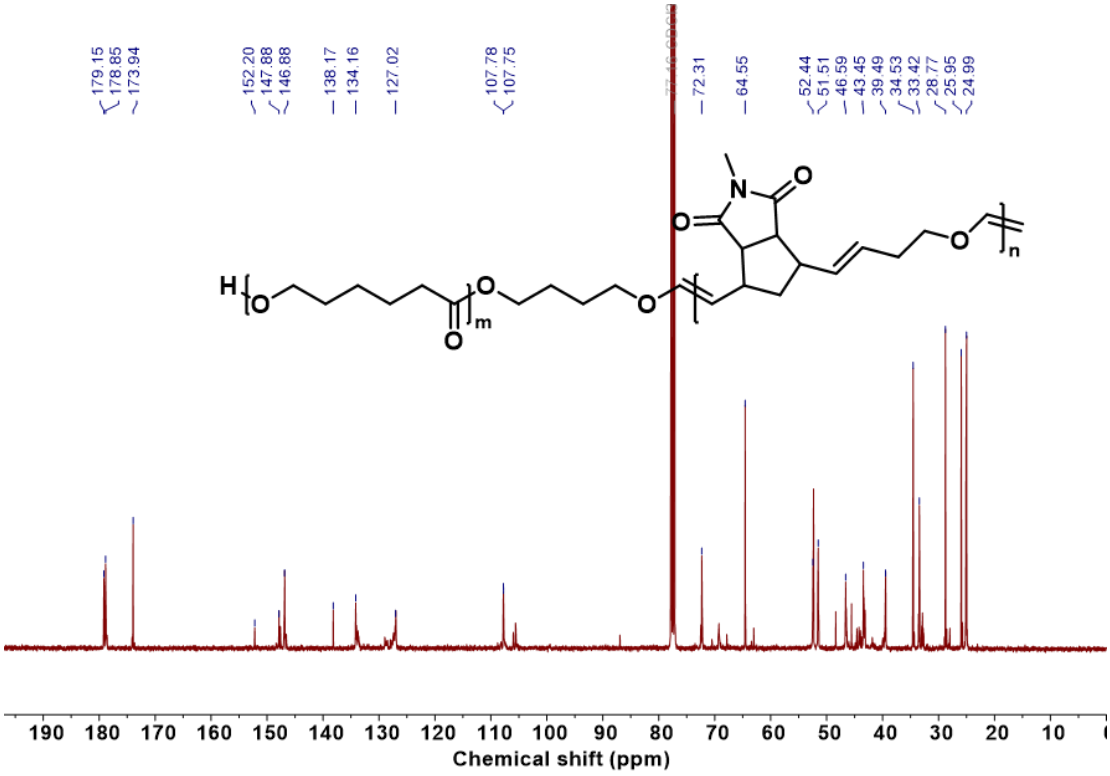


Fig S44: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P8**

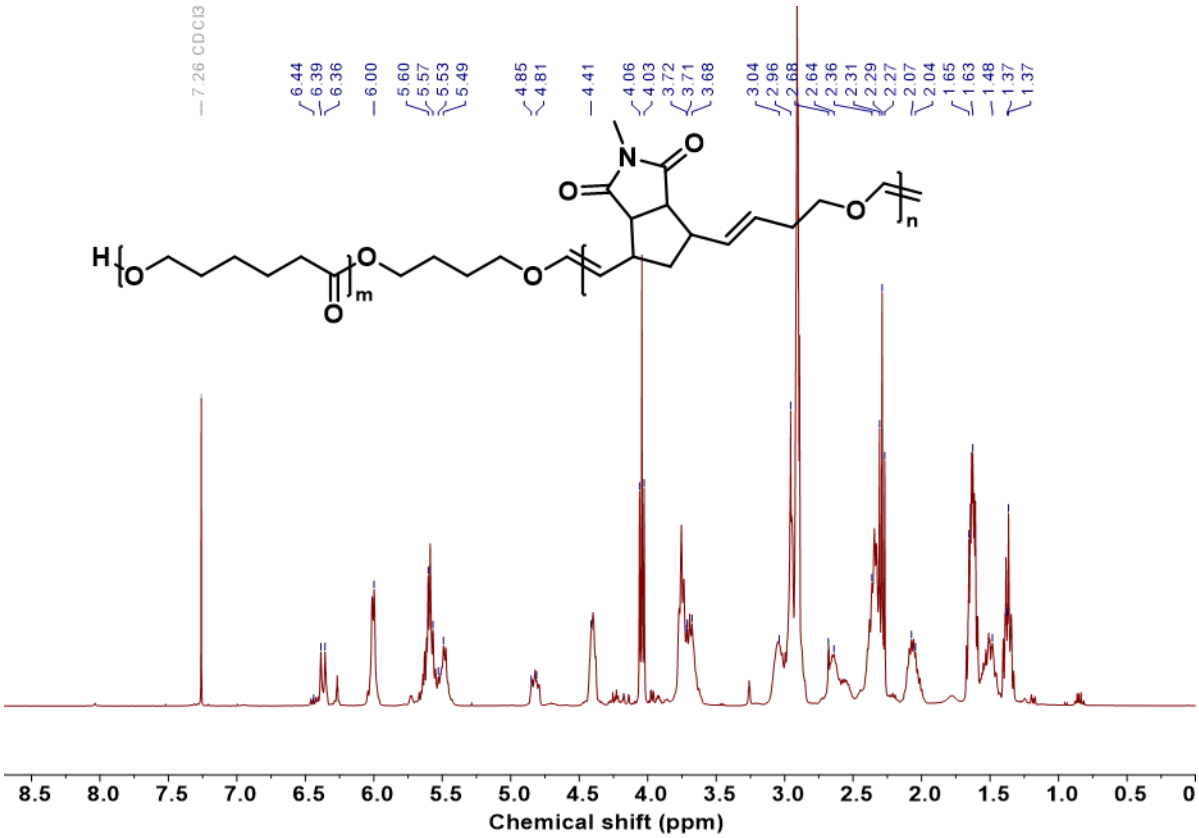


Fig S45: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P9**

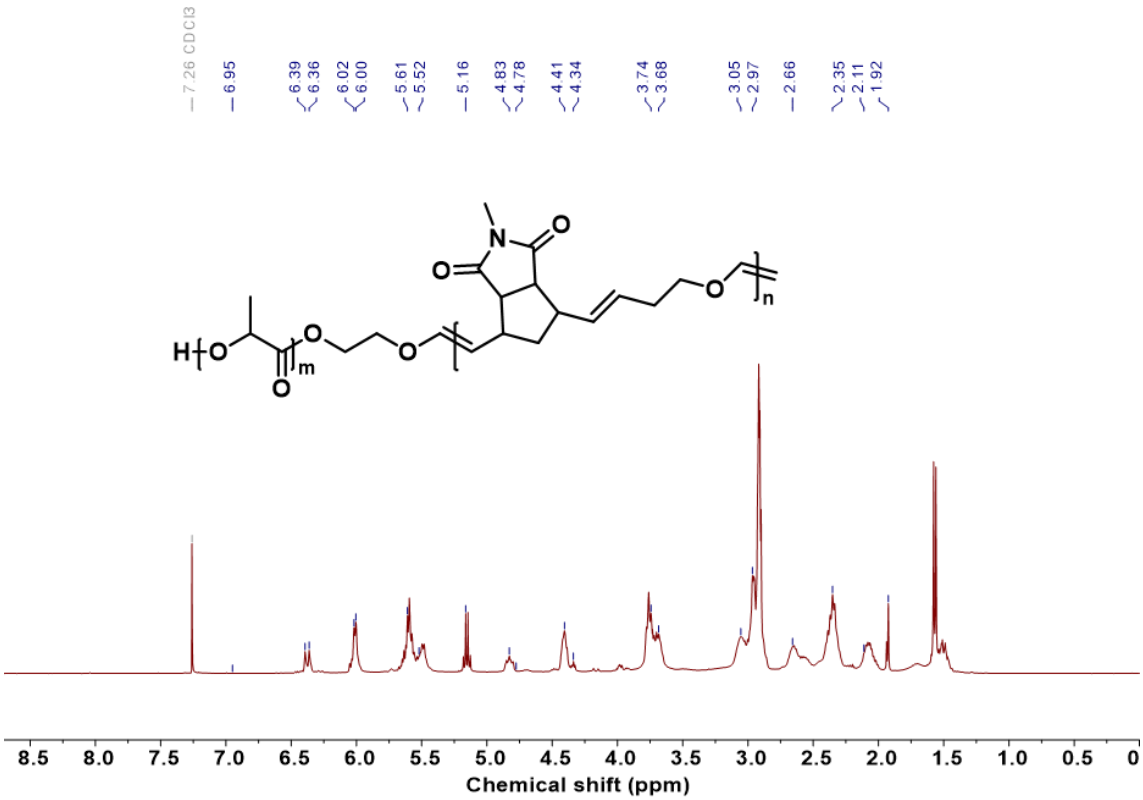


Fig S46: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P10**

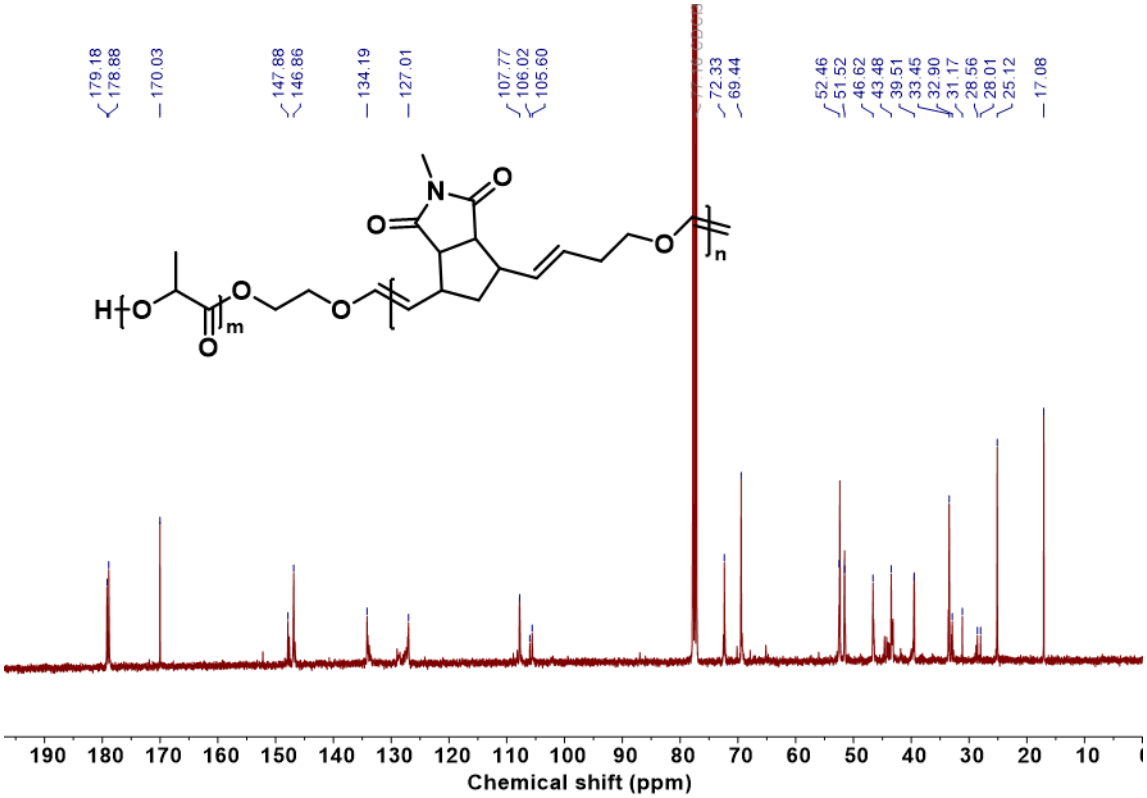


Fig S47: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P10**

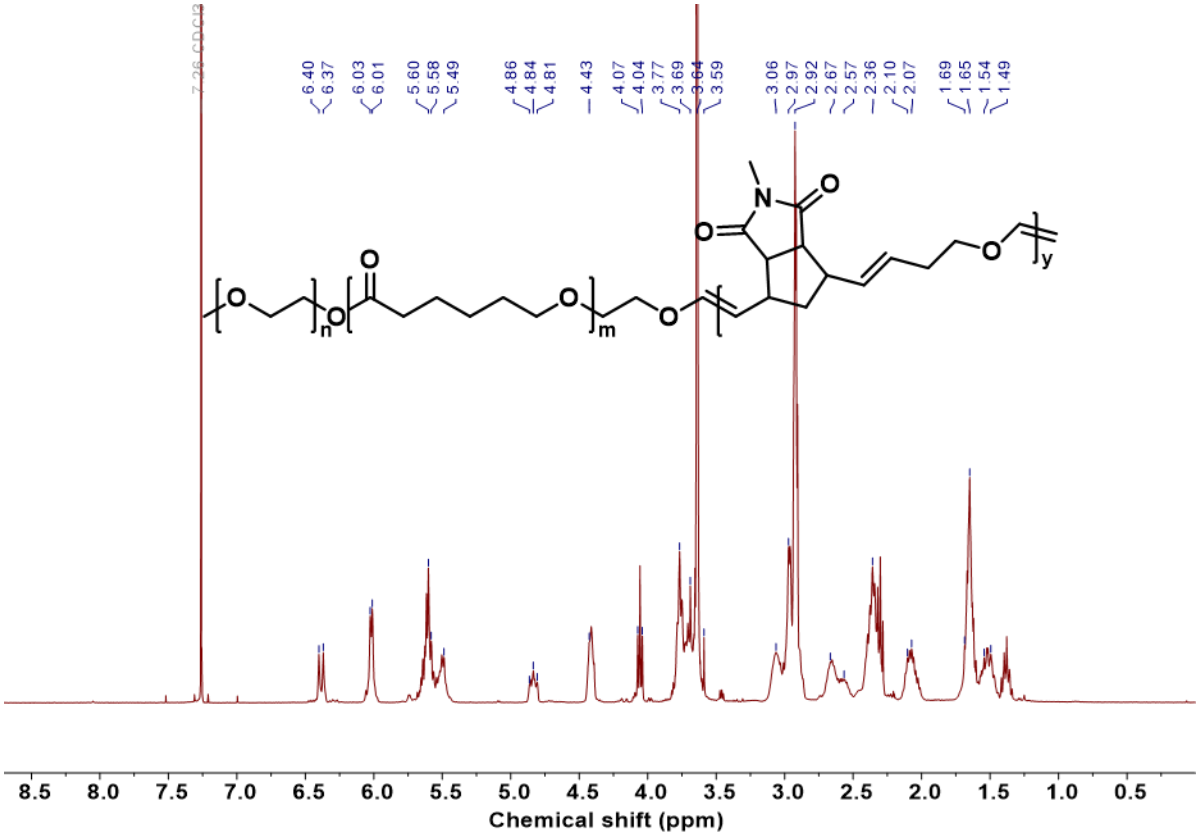


Fig S48: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polymer **P11**

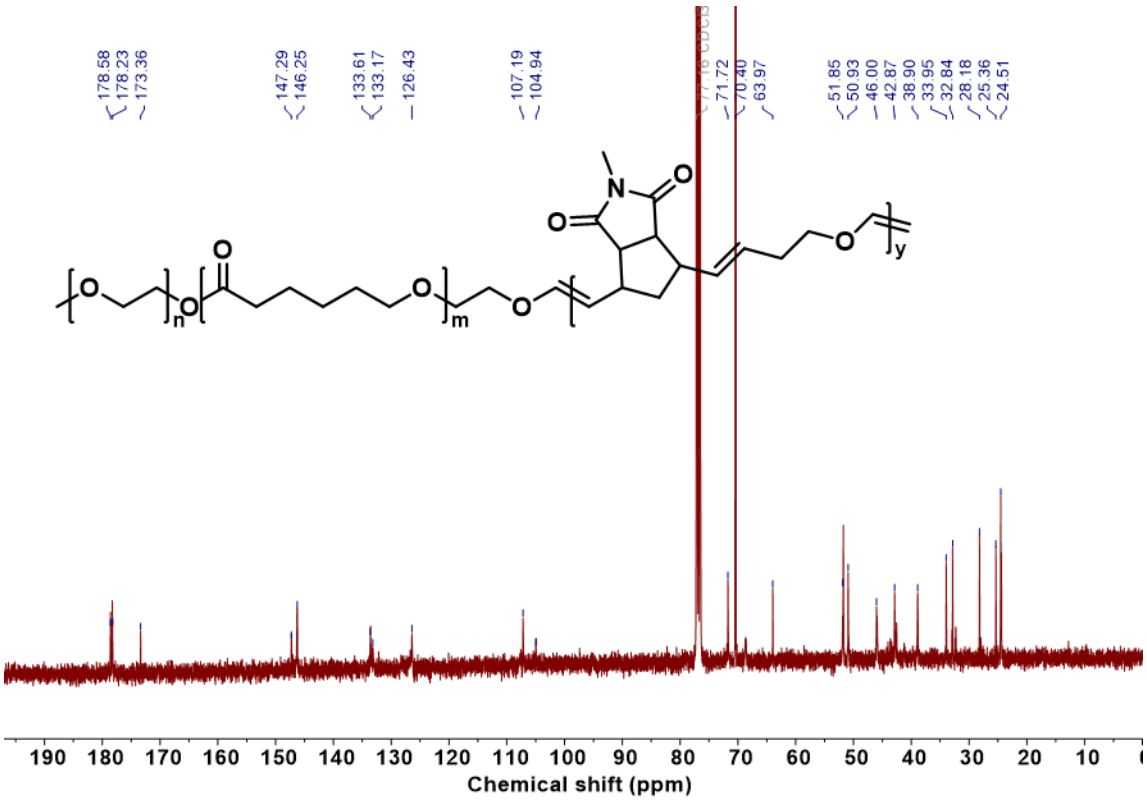


Fig S49: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of polymer **P11**

REFERENCES

(1) Liu, P.; Yasir, M.; Kilbinger, A. F. M. Catalytic Living Ring Opening Metathesis Polymerisation: The Importance of Ring Strain in Chain Transfer Agents. *Angew. Chemie - Int. Ed.* **2019**, *58* (43), 15278–15282. https://doi.org/10.1002/anie.201907921.

(2) Yang, Y. Y.; Hu, H.; Wang, X.; Yang, F.; Shen, H.; Xu, F. J.; Wu, D. C. Acid-Labile Poly(Glycidyl Methacrylate)-Based Star Gene Vectors. *ACS Appl. Mater. Interfaces* **2015**, *7* (22), 12238–12248. https://doi.org/10.1021/acsami.5b02733.

(3) Liow, S. S.; Lipik, V. T.; Widjaja, L. K.; Abadie, M. J. M. Synthesis, Characterization and Photopolymerization of Vinyl Ether and Acrylate Functionalized Hybrid Oligo-Caprolactone. *J. Polym. Res.* **2012**, *19* (1). https://doi.org/10.1007/s10965-011-9748-6.