Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Polymer Chain Editing: Functionality "Knock-in", "Knock-out" and Replacement via Cross Metathesis Reaction and Thiol-Michael Addition

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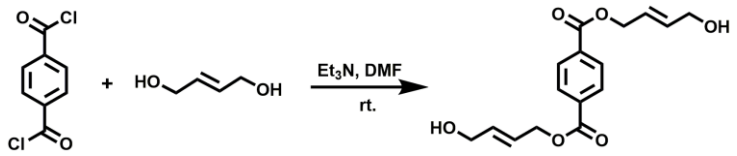
Experiments

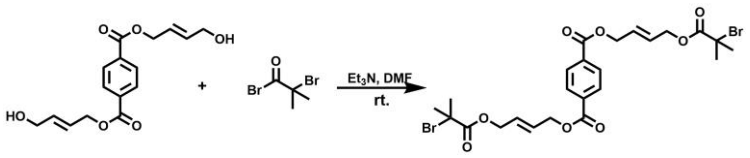
Synthesis of ATRP initiator 1~3

The ATRP initiator *but-2-ene-1, 4-diyl Bis(2-bromoisobutyrate)* (**1**) was prepared according to the previously reported literatures.[1, 2]

Preparation of bis(4-(2-bromoisobutyrate)-but-2-en-1-yl)terephthlalate ***(2):***

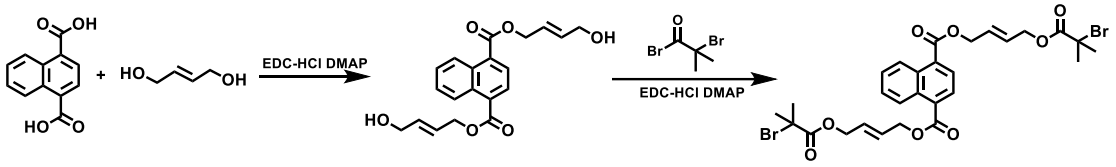


15 g *cis*-2-butene-1,4-diol(14 mL, 170 mmol, 5 equiv.), trimethylamine(34 mL, 244 mmol, 7.5 equiv.) and DMF (60 mL) were mixed in an oven-dried 250 mL Schlenk flask under argon atmosphere, then the flask was cooled to 0 ºC with ice. 6.8 g Terephthaloyl Chloride (33.5 mmol, 1 equiv.) in 15 mL DMF was added dropwise to the mixture, and a white precipitate developed. After stirring at room temperature overnight, the salt formed in the reaction is filtered and the reaction mixture was evaporated, the residue was redissolved in DCM and washed with $NaHCO_3$ aqueous, brine and dried over anhydrous $MgSO_4$. The product was purified by silica gel chromatography with an eluant of DCM and MeOH (v/ v =6: 1), to give the product *bis(4-hydroxybut-2-en-1-yl)terephthlalate* as a light yellow solid in 78 % yield. ^{1}H NMR: δ(TMS, ppm), 4.34 (d, 4H, -C**H**$_2$-OH), 4.97 (d, 4H, -C**H**$_2$-O-C=O), 5.77 (m, 2H, HO-CH$_2$-C**H**=CH-), 5.93 (m, 2H, -CH=C**H**-CH2-O-C=O), 8.09 (s, 4H, -Ar**H**).



The obtained bis(4-hydroxybut-2-en-1-yl) terephthlalate (1.8 g, 5.8 mmol, 1 equiv.), 4.3 g DMAP(35.2 mmol, 6 equiv.), and DMF (20 mL)were mixed in an oven-dried Schlenk flask under argon atmosphere, then the flask was cooled to 0 ºC. 2-bromoisobutyryl bromide (8 g, 35.2 mmol, 6 equiv.) with 30 mL DMF was added dropwise to the mixture, and a light yellow precipitate developed. After stirring at room temperature overnight, the reaction mixture was diluted with 200 mL water and extracted with EtOAc for three times, the organic layer was washed with $NaHCO_3$

aqueous, brine and dried over anhydrous $MgSO_4$. The product was purified by silica gel chromatography with an eluant of pure DCM to give the difunctional initiator **2** as a light yellow oil in 83 % yield. ^{1}H NMR ($CDCl_3$): δ (TMS, ppm), 1.98 (s, 12H, -C**H$_3$**), 4.88&5.08 (d, 8H, -O-C**H$_2$**-), 5.88 (m, 4H, -C**H**=C**H-**), 8.14 (s, 4H, -**ArH**). ^{13}C NMR ($CDCl_3$): 171.44 (O=**C**-O), 165.48 (Ph-**C**=O) 129.67&133.85 (-**Ar**), 128.49&129.67 (-**C**H=**C**H-), 60.96&61.47 (-O-**C**H_2-), 55.51 (-**C**H-Br), 30.72 (-**C**H_3).



The synthetic procedure of Naph-core initiator (**3)** is similar to the Benz-core initiator (**2**), the overall yield for two steps is 51 %. ^{1}H NMR ($CDCl_3$): δ (TMS, ppm), 1.89 (s, 12H, -C**H$_3$**), 4.85&5.09 (d, 8H, -O-C**H$_2$**-), 5.88&6.05 (m, 4H, -C**H**=C**H-**), 7.67&8.12&8.86 (m, 6H, -**ArH**). ^{13}C NMR ($CDCl_3$): 171.41 (O=**C**-O), 166.73 (Ph-**C**=O) 125.93, 127.84, 131.45, 131.51 (-**Ar**H), 127.92&128.53 (-**C**H=**C**H-), 60.99&61.47 (-O-**C**H_2-), 55.54 (-**C**H-Br), 30.73 (-**C**H_3).

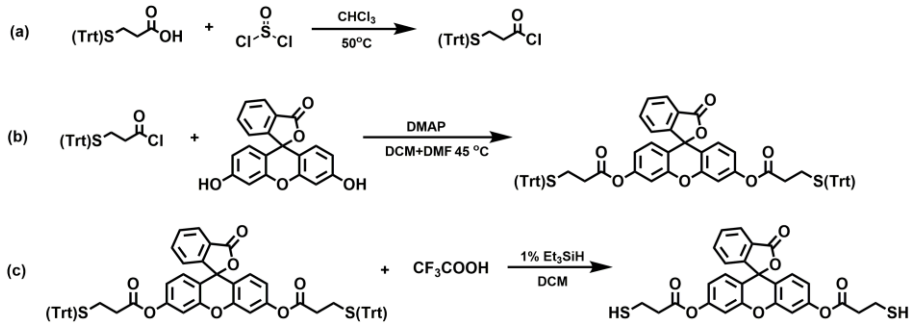
Synthesis of P2 by using initiator 2.

MMA (15 mL, 14.16 g, 0.141 mol), CH_3CN (8 mL), CuBr (0.292 g, 2.03 mmol) and bPy (0.947 g, 6.10 mmol) were mixed with magnetic striation in a 100 mL Schlenk flask and subsequently degassed via three freeze-pump-thaw cycles. The Schlenk flask was backfilled with argon, and initiator **2** (0.62 g, 1.01 mmol) was added. Two more freeze-pump-thaw cycles were performed. The flask was then sealed under argon and placed in a pre-heated oil bath at 80 °C. The polymerization was stopped by cooling with liquid nitrogen after 60 mins. The mixture was diluted with THF and passed through a neutral alumina column twice to remove the copper catalyst and precipitated into a 10 folds volume of hexane. After filtration, the product P2 was obtained as a white powder. Yield: 41%, $M_{n,GPC}$ =6300 Da, $Đ$ = 1.15.

Synthesis of P3 by using initiator 3.

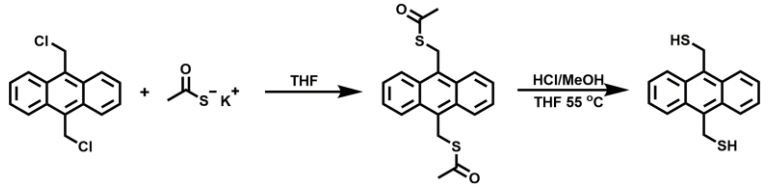
MMA (16 mL, 15.10 g, 0.151 mol), CH_3CN (8 mL), CuBr (0.292 g, 2.03 mmol) and bPy (0.950 g, 6.10 mmol) were mixed with magnetic striation in a 100 mL Schlenk flask and subsequently degassed via three freeze-pump-thaw cycles. The Schlenk flask was backfilled with argon, and initiator **3** (0.66 g, 0.99 mmol) was added. Two more freeze-pump-thaw cycles were performed. The flask was then sealed under argon and placed in a pre-heated oil bath at 80 °C. The polymerization was stopped by cooling with liquid nitrogen after 75 mins. The mixture was diluted with THF and passed through a neutral alumina column twice to remove the copper catalyst and precipitated into a 10 folds volume of hexane. After filtration, the product P3 was obtained as a white powder. Yield: 56%, $M_{n,GPC}$ =10700 Da, $Đ$ = 1.15.

Synthesis of dithiol compound containing fluorescein (CP3) and anthryl (CP4) functionality



20 g 3-(Tritylthio)propionic acid (57.4 mmol, 1 equiv.) and $CHCl_3$ (150 mL) were mixed in an oven-dried 500 mL three-neck flask under argon atmosphere, then the flask was cooled to 0 ºC in ice bath. 6.3 mL $SOCl_2$ (10.3 g, 86.6 mmol, 1.5 equiv) was added dropwise to the mixture. After refluxing for 8 hours, excess chloroform and $SOCl_2$ were distilled (1 M NaOH was prepared bath to treat the acid gas distilled from the reaction flask), 4.78 g fluorescein (14.4 mmol, 0.25 equiv)and 3.51 g DMAP(28.7 mmol, 0.5 equiv) with 50 mL DMF was added to the mixture，after stirring in the ice bath for 2 hours, raise the temperature to 50 ºC and stirring overnight. The salt formed in the reaction is filtered and the reaction mixture was evaporated, the product was purified by silica gel chromatography with an eluant of DCM and EtOAc (v/ v =6: 1), to give a yellow powder.

Deprotection: 0.1 g (0.1 mmol) was dissolved in 1 mL DCM, TFA (40 % in DCM with 1 % Et_3SiH) was added and the reaction allowed to stir for 30 minutes at room temperature. The organic solvents were evaporated to dryness. The crude mixture was purified by silica gel chromatography using pure DCM as eluent to afford **CP3** and used in the further coupling reaction. ^{1}H NMR ($CDCl_3$): δ (TMS, ppm), 1.75 (t, 2H, -S**H**), 2.88-2.98 (m, 8H, O=C-C**H$_2$**C**H$_2$**-SH), 6.88-6.95 (m, 4H), 7.09-7.22 (m, 3H), 7.60-7.75 (m, 2H), 8.02-8.07 (d, 1H).



1 g Bis(chloromethyl)anthracene (3.6 mmol, 1equiv.) was dissolved in 10 mL of THF with 8 mmol of KSAc (0.916 g, 2.2 equiv.) under the protection of argon. The mixture was stirred at room temperature about 2 h. The organic solvents were evaporated to dryness and redissolved in DCM, the organic layer was washed by $NaHCO_3$ aqueous and brine. The crude thioacetate obtained was pure enough to use directly in the next step. The deacetylation reaction was carried out by adding 1 mL of HCl in 2 mL methanol to a solution of the thioacetate in $CHCl_3$ and stirring at 55 °C for 12 h. The dithiol product was washed by $NaHCO_3$ aqueous， brine and dried over by $MgSO_4$. The obtained product **CP4** was used directly in the coupling reaction. ^{1}H NMR ($CDCl_3$): δ (TMS, ppm), 4.75 (d, 2H, -C**H$_2$**-SH), 7.61-7.64 (m, 4H, **-ArH**), 8.33-8.36 (m, 4H, **-ArH**).

Recombination of the cleaved intermediate via thiol-Michael addition reaction using dithiols.

P1-cm-LA-C1: The cleaved intermediate P1-*cm*-LA (150 mg, 0.0577 mmol) was dissolved in DMSO (2 mL) under argon in a 10 mL Schlenk tube. 1,4-butanediol bis(thioglycolate) (C1) (6.87 mg, 0.0289 mmol) in DMSO with *n*-Bu_3P (5.85 mg, 0.0289 mmol) were added by syringe under inert atmosphere of argon. The reaction mixture was stirred at room temperature. GPC and NMR were used to monitor the reaction. After 24 hours, the mixture was diluted with 50 mL $CHCl_3$ and washed by 0.1 M HCl. After precipitation in CH_3OH/H_2O (v: v= 7: 3) twice and dried under vacuum

for 24 h, a light gray crude product was obtained and further purified with preparative SEC to afford the final product. Yield: 57.5 %, $M_{n\ GPC\ P1\text{-}cm\text{-}LA\text{-}C1}$ = 5900 Da, $Đ$ = 1.16. The overall yield of the P1-*cm*-EA-C1 was 46.6 % after the cleavage and recombination reaction.

P1-cm-LA-C2: P1-*cm*-LA-C2 was prepared and purified by the previously described procedure, except that 150 mg of P1-*cm*-LA (0.0577 mmol), 5.27 mg of *meso*-2,3-dimercaptosuccinic acid (C2, 0.0289 mmol), and 5.85 mg of *n*-Bu_3P (0.0289 mmol) were used. Yield = 48%. $M_{n\ GPC\ P1\text{-}cm\text{-}LA\text{-}C2}$ =5700 Da, $Đ$ = 1.19. The overall yield of the P1-*cm*-EA-C2 was 38.9 % after the cleavage and recombination reaction.

P2-cm-EA-CP2: P2-*cm*-EA-CP2 was prepared and purified by the previously described procedure, except that 200 mg of P2-*cm*-EA (0.0683 mmol), 6.21 mg of *meso*-2,3-dimercaptosuccinic acid (0.0341 mmol), and 6.90 mg of *n*-Bu_3P (0.0341 mmol) were used. Yield = 57.8%. $M_{n\ GPC\ P2\text{-}cm\text{-}EA\text{-}CP2}$ =5900 Da, $Đ$ = 1.18. The overall yield of the P2-*cm*-EA-CP2 was 53.3 % after the cleavage and recombination reaction.

P3-cm-EA-CP1: P3-*cm*-EA-CP1 was prepared and purified by the previously described procedure, except that 200 mg of P3-*cm*-EA (0.0476 mmol), 2.58 mg of 1,3-propanedithiol (CP1, 0.0238 mmol), and 4.82 mg of *n*-Bu_3P (0.0238 mmol) were used. Yield = 63.6%. $M_{n\ GPC\ P3\text{-}cm\text{-}EA\text{-}CP1}$ =10700 Da, $Đ$ = 1.16. The overall yield of the P3-*cm*-EA-CP1 was 58.9 % after the cleavage and recombination reaction.

P3-cm-EA-CP2: P3-*cm*-EA-CP2 was prepared and purified by the previously described procedure, except that 200 mg of P3-*cm*-EA (0.0476 mmol), 4.34 mg of *meso*-2,3-dimercaptosuccinic acid (0.0238 mmol), and 4.82 mg of *n*-Bu_3P (0.0238 mmol) were used. Yield = 50.8%. $M_{n\ GPC\ P3\text{-}cm\text{-}EA\text{-}CP2}$ =9800 Da, $Đ$ = 1.18. The overall yield of the P3-*cm*-EA-CP2 was 47.0 % after the cleavage and recombination reaction.

P3-cm-EA-CP3: P3-*cm*-EA-CP3 was prepared and purified by the previously described procedure, except that 250 mg of P3-*cm*-EA (0.0595 mmol), 15.11 mg of **CP3** (0.0298 mmol), and 6.02 mg of *n*-Bu_3P (0.0298 mmol) were used. Yield = 42.8%. $M_{n\ GPC\ P3\text{-}cm\text{-}EA\text{-}CP3}$ =11100 Da, $Đ$ = 1.18. The overall yield of the P3-*cm*-EA-CP3 was 39.6 % after

the cleavage and recombination reaction.

P3-cm-EA-CP4: P3-*cm*-EA-CP4 was prepared and purified by the previously described procedure, except that 200 mg of P3-*cm*-EA (0.0476 mmol), 6.43 mg of **CP4** (0.0238 mmol), and 4.81 mg of *n*-Bu_3P (0.0238 mmol) were used. Yield: 55.2%, $M_{n\ GPC\ P3\text{-}cm\text{-}EA\text{-}CP4}$ =10800 Da, $Đ$ = 1.18. The overall yield of the P3-*cm*-EA-CP4 was 51.1 % after the cleavage and recombination reaction.

Characterization data

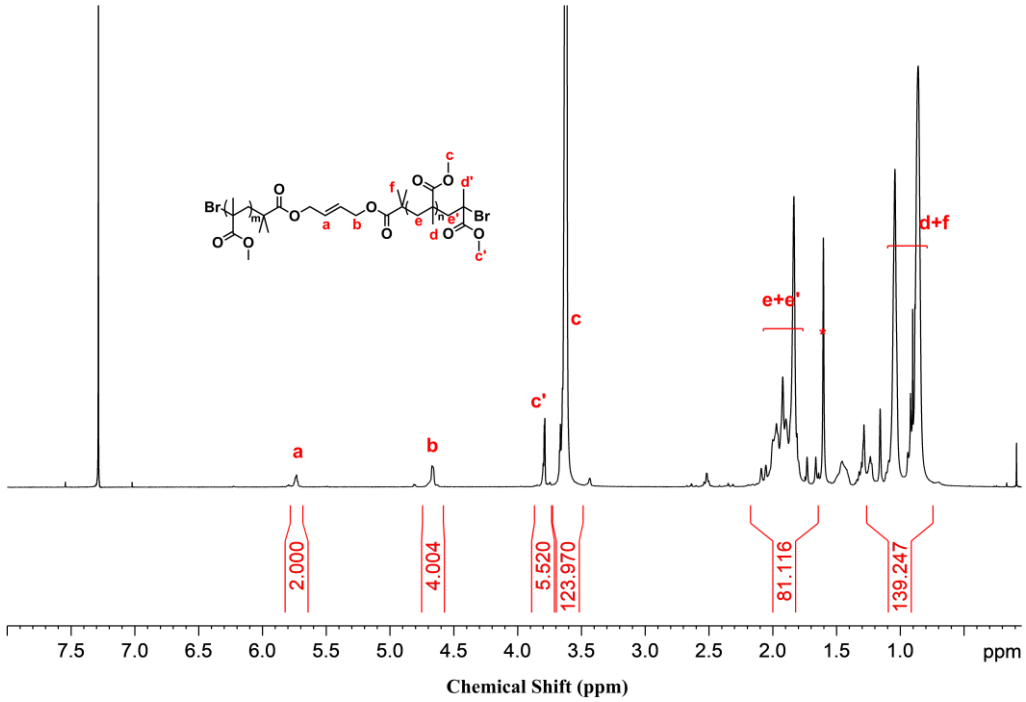


Figure S1 ^{1}H NMR spectrum of P1 in $CDCl_3$.

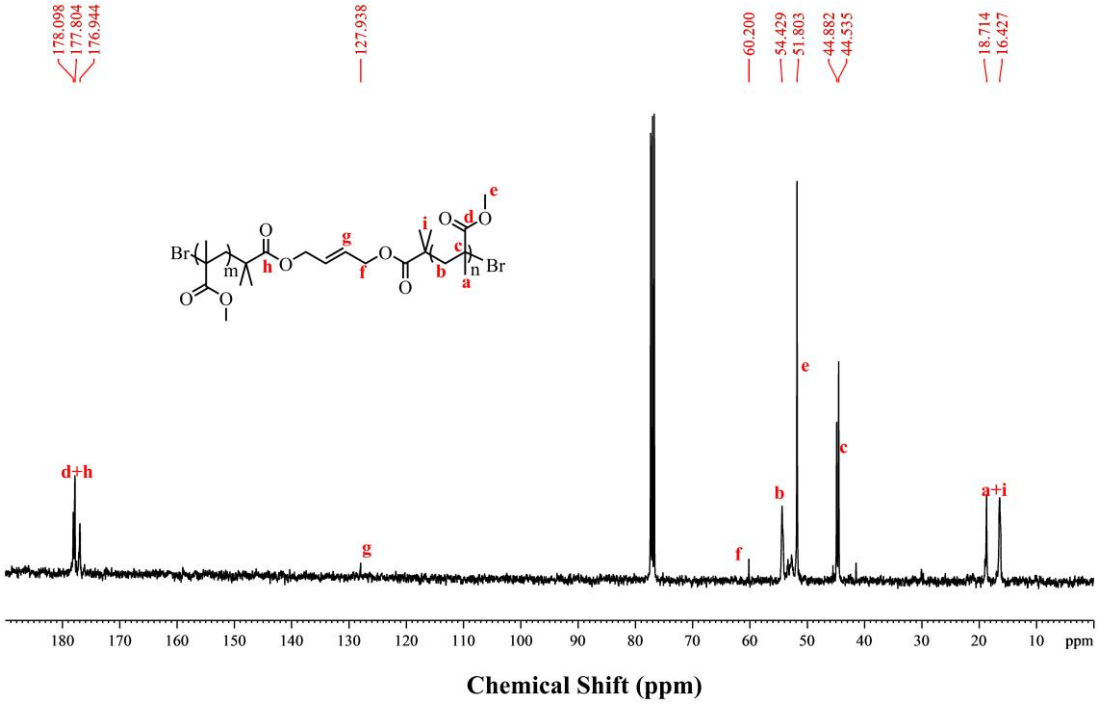


Figure S2 ^{13}C NMR spectrum of P1 in $CDCl_3$.

NMR spectra of ATRP initiators 2 and 3

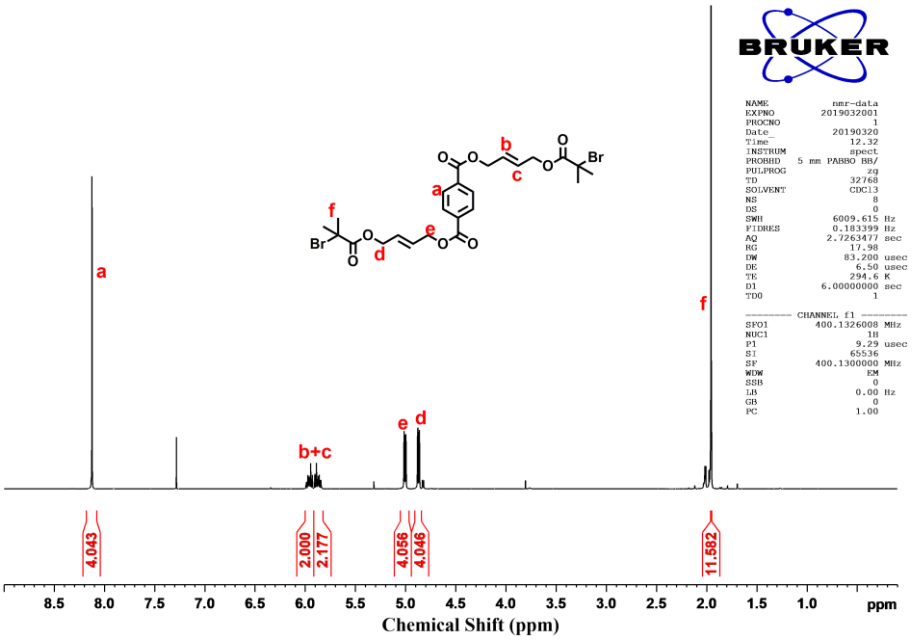


Figure S3 ^{1}H NMR spectrum of bis (4-(2-bromoisobutyrate)-but-2-en-1-yl) terephthlalate (**2**) in $CDCl_3$.

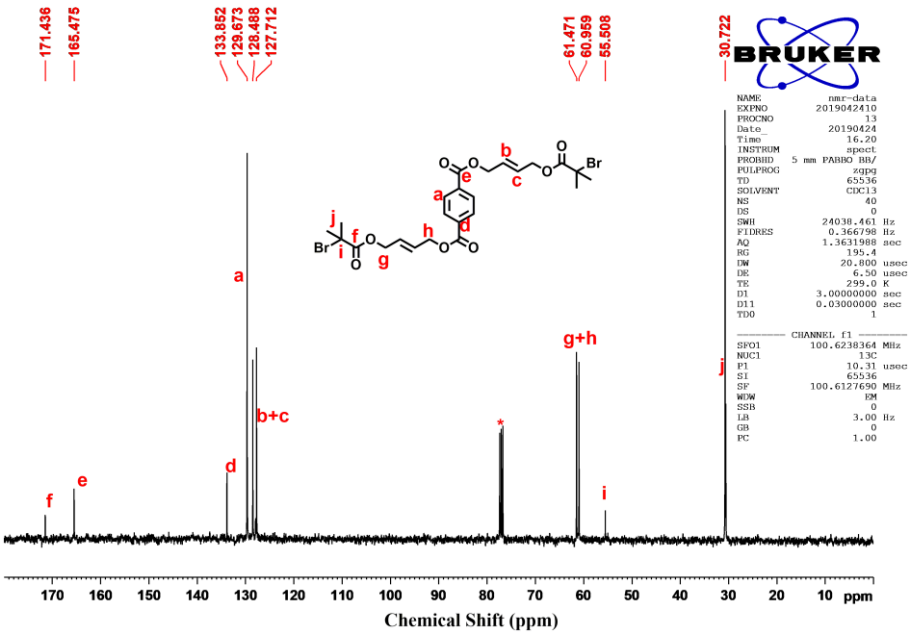


Figure S4 ^{13}C NMR spectrum of bis(4-(2-bromoisobutyrate)-but-2-en-1-yl)terephthlalate (**2**) in $CDCl_3$.

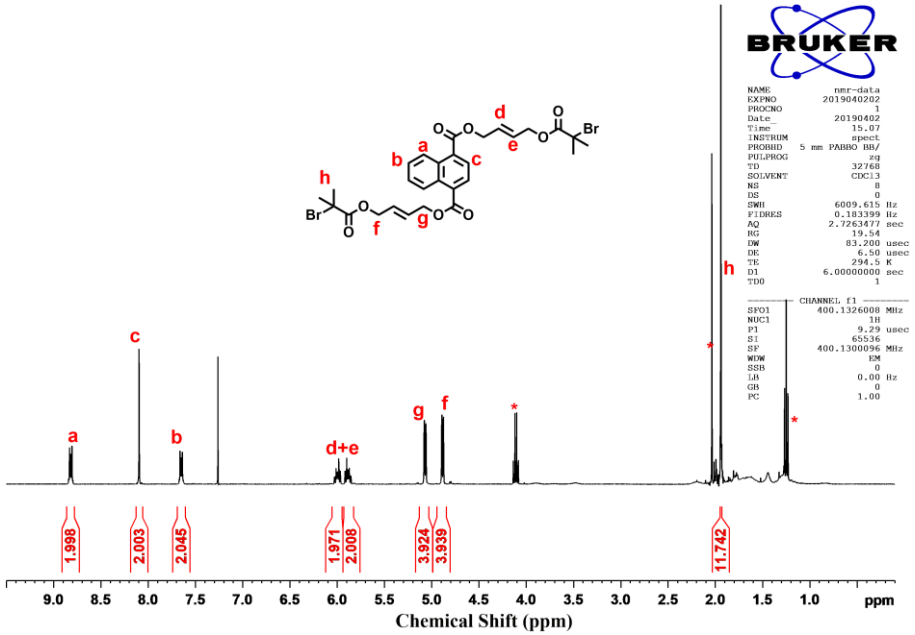


Figure S5 ^{1}H NMR spectrum of bis(4-hydroxybut-2-en-1-yl) naphthalene-1,4-dicarboxylate (**3**) in $CDCl_3$.

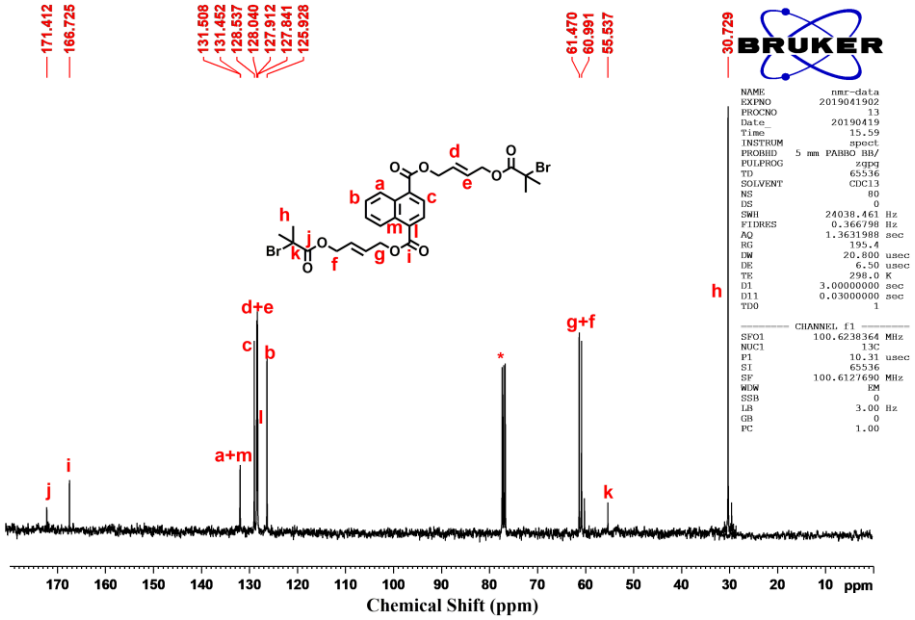


Figure S6 ^{13}C NMR spectrum of bis(4-hydroxybut-2-en-1-yl) naphthalene-1,4-dicarboxylate (**3**) in $CDCl_3$.

NMR spectra of ATRP products P2 and P3

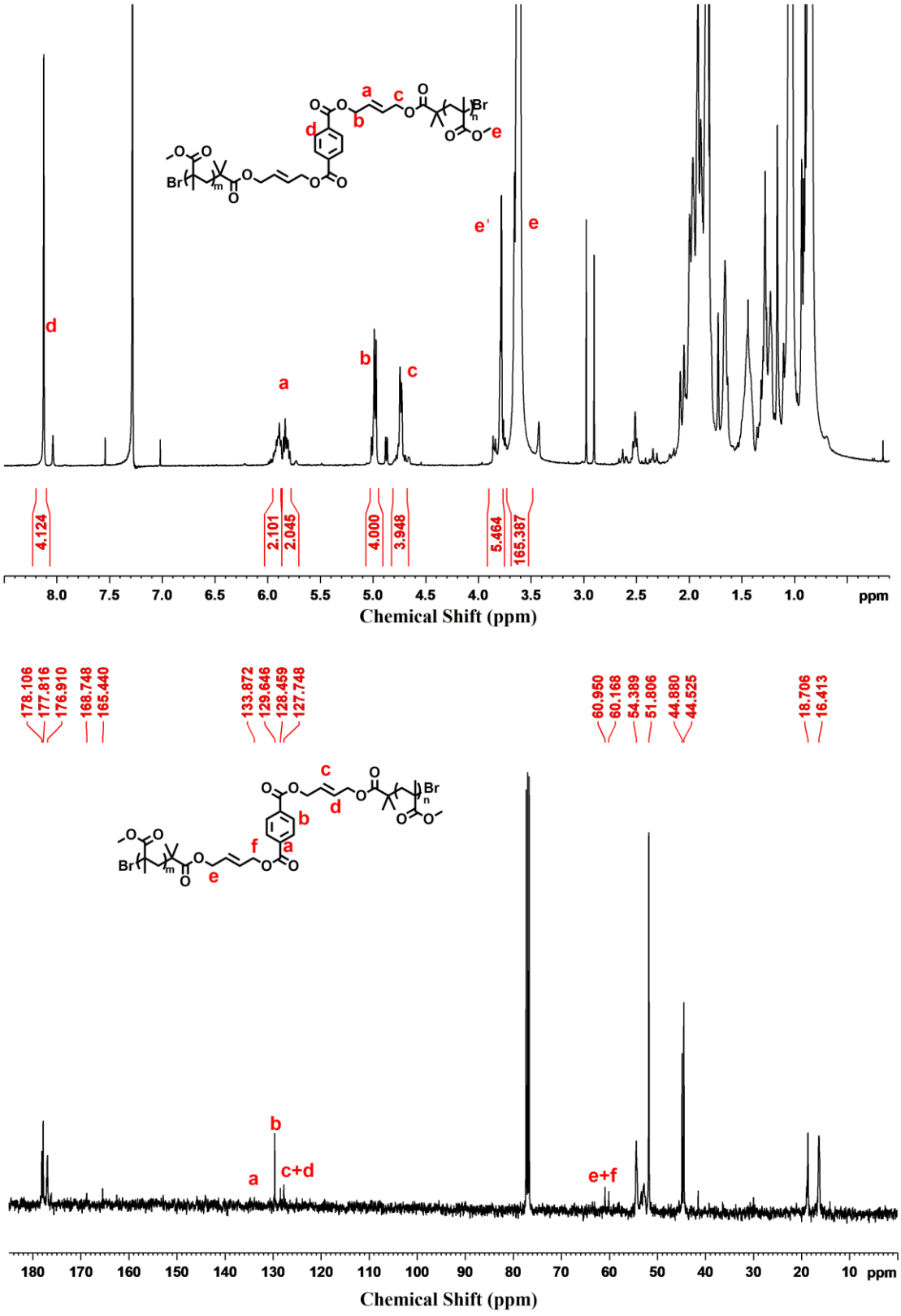


Figure S7 ^{1}H NMR and ^{13}C NMR spectra of P2 in $CDCl_3$.

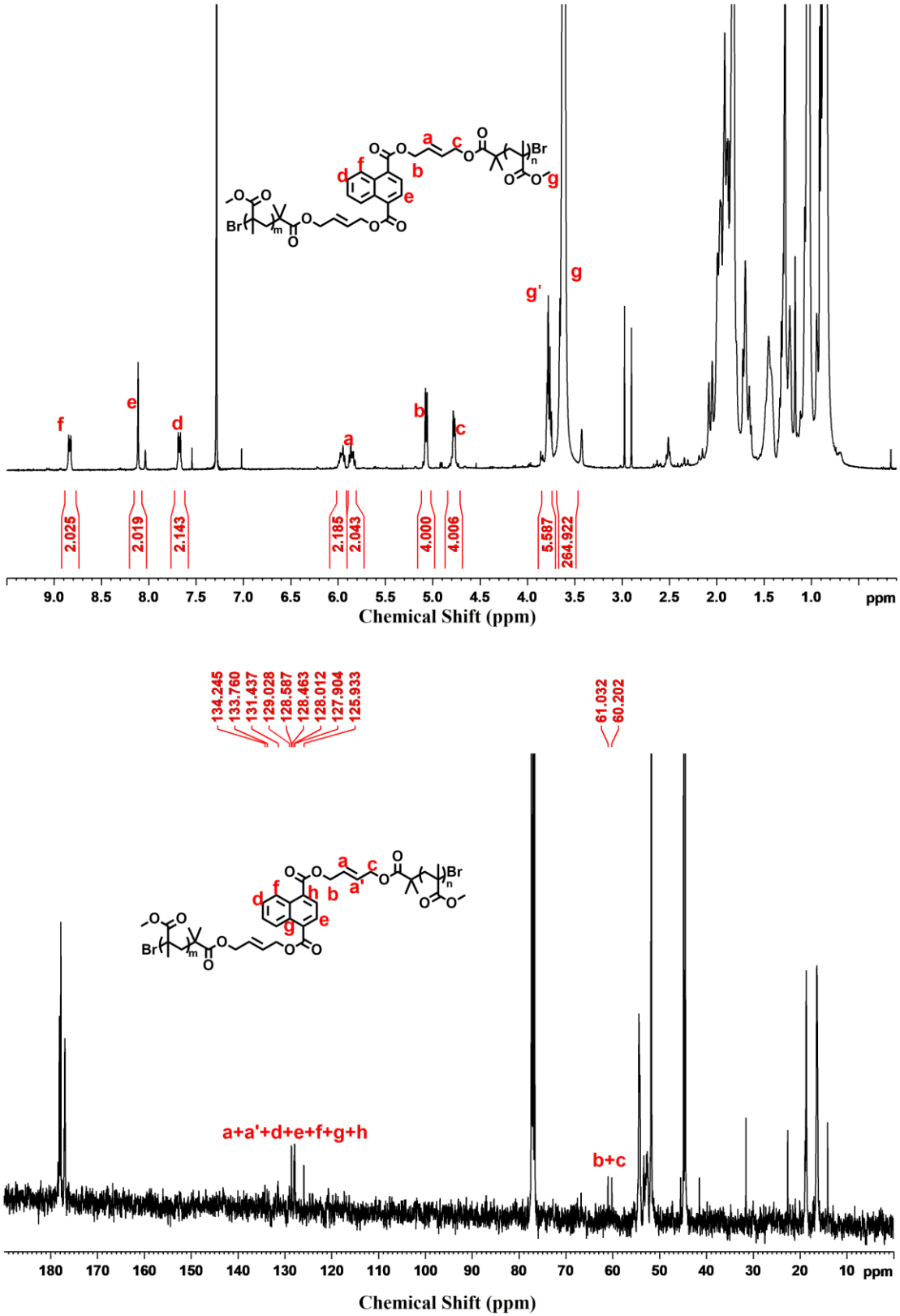


Figure S8 ^{1}H NMR and ^{13}C NMR spectra of P3 in $CDCl_3$.

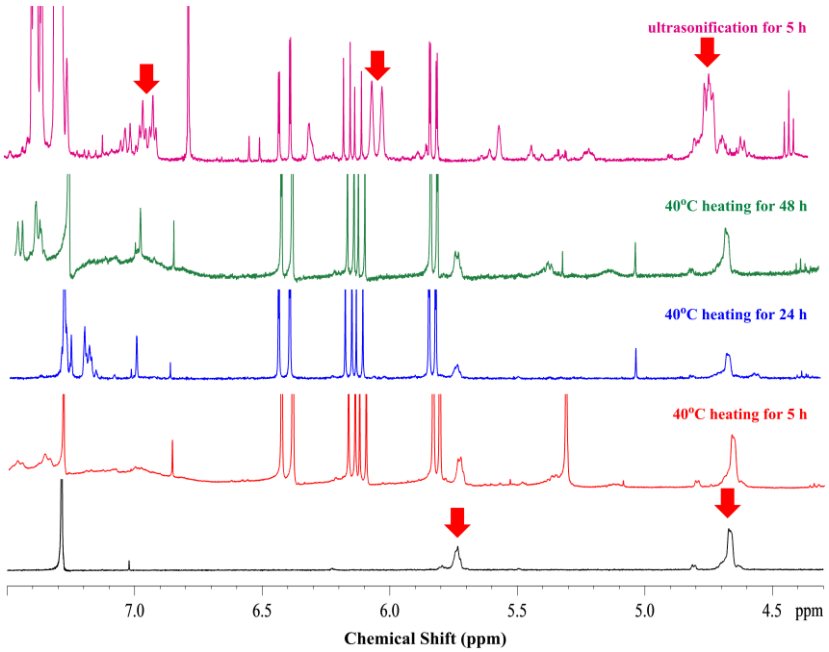


Figure S9 ^{1}H NMR spectra of the CM reaction between P1 and LA under different conditions (black: P1, red: 40 °C for 5 h; blue: 40 °C for 24 h; green: 40 °C for 48 h, purple: ultrasonication for 5 h).

Table S1. Cross-metathesis cleavage products of P1 with different acrylates.

Polymer	CM partner	eq.[a]	$M_{n,GPC}$ (Da)[b]	$M_{n,NMR}$ (Da)[c]	$M_{n.MALDI}$ (Da)[d]	$Đ$ [b]	Conv. (%)[c]	Yield (%)[e]
P1	-	-	6100	4800	-	1.15	-	-
P1-*cm*-LA	LA	5	3800	2600	2500	1.15	99	81
P1-*cm*-AA	AA	5	3500	2400	2100	1.15	99	86
P1-*cm*-HFBA	HFBA	5	3700	2600	2250	1.15	99	88
P1-*cm*-HEA	HEA	5	3700	2500	1840	1.17	99	78
P1-*cm*-NIPAM	NIPAM	5	3600	2500	1900	1.17	99	83
P1-*cm*-FMA	FMA	3	3700	2700	2470	1.15	99	83

[a]Related to the internal double bonds. [b]Determined by GPC in THF using PMMA as standards. [c]Calculated from ^{1}H NMR spectroscopy. [d]Calculated from MALDI-TOF MS spectroscopy. [e]Isolated yield after precipitation

NMR spectra of CM reaction products

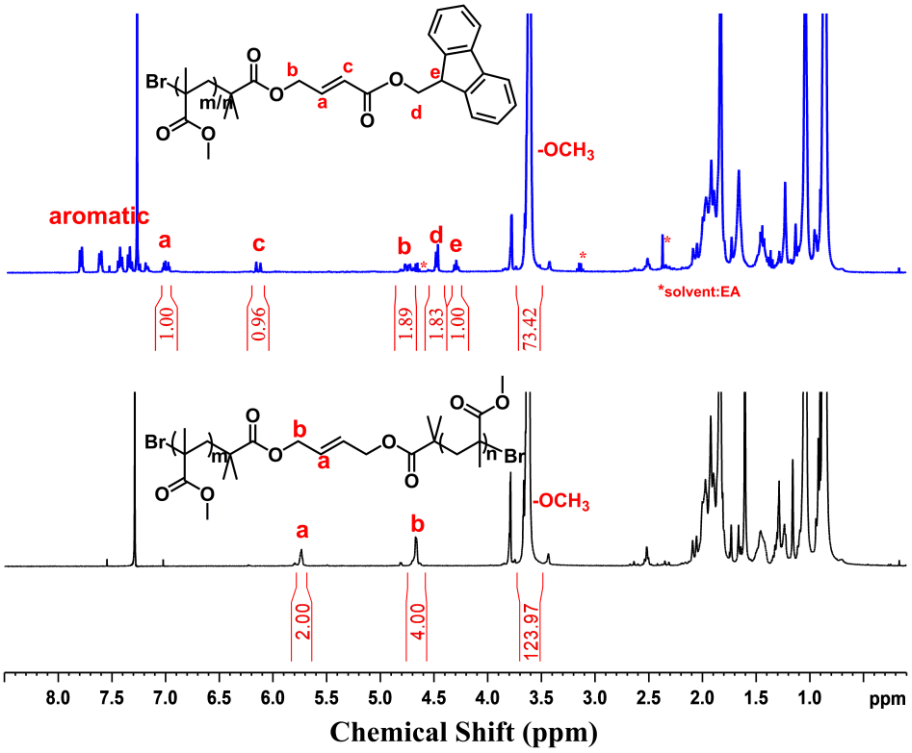


Figure S10 ^{1}H NMR spectra of P1 (black) and its cross metathesis product P1-*cm*-FMA (blue).

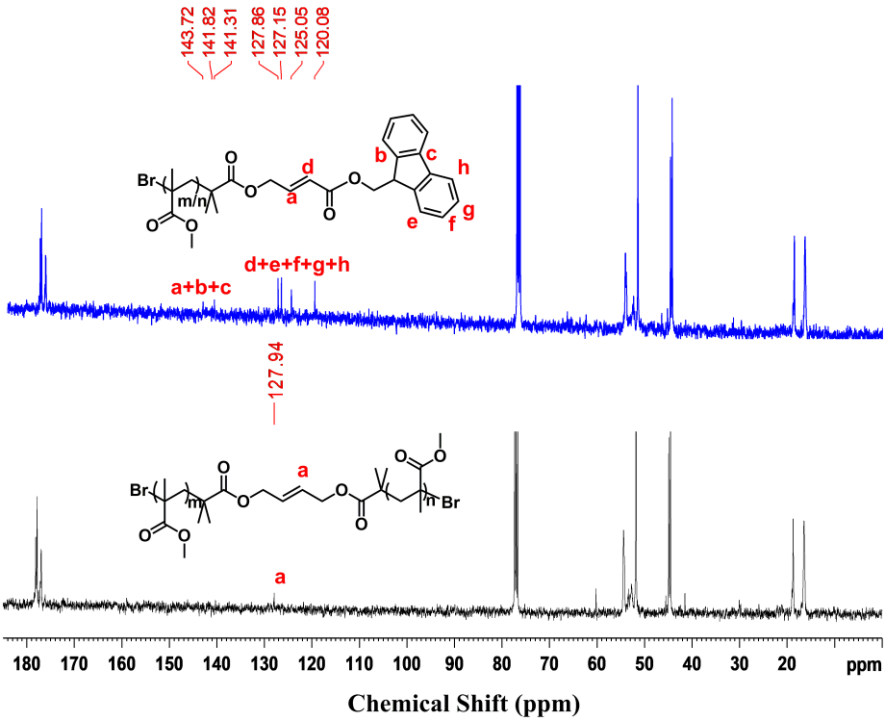


Figure S11 ^{13}C NMR spectra of P1 (black) and its cross metathesis product P1-*cm*-FMA (blue).

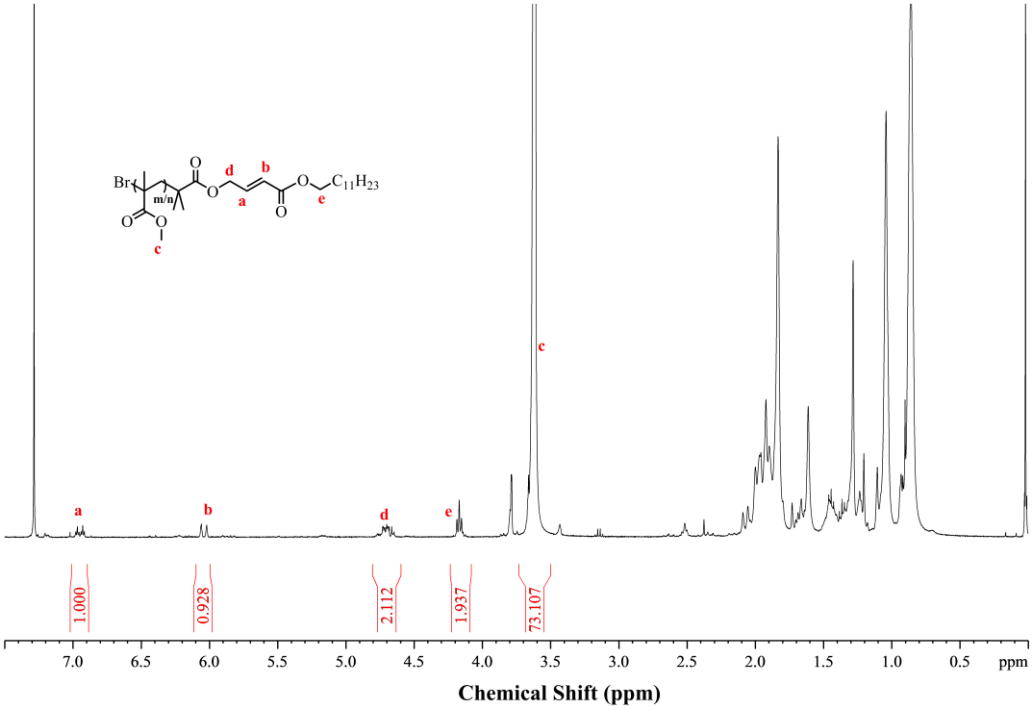


Figure S12 ^{1}H NMR spectrum of P1-*cm*-LA in $CDCl_3$.

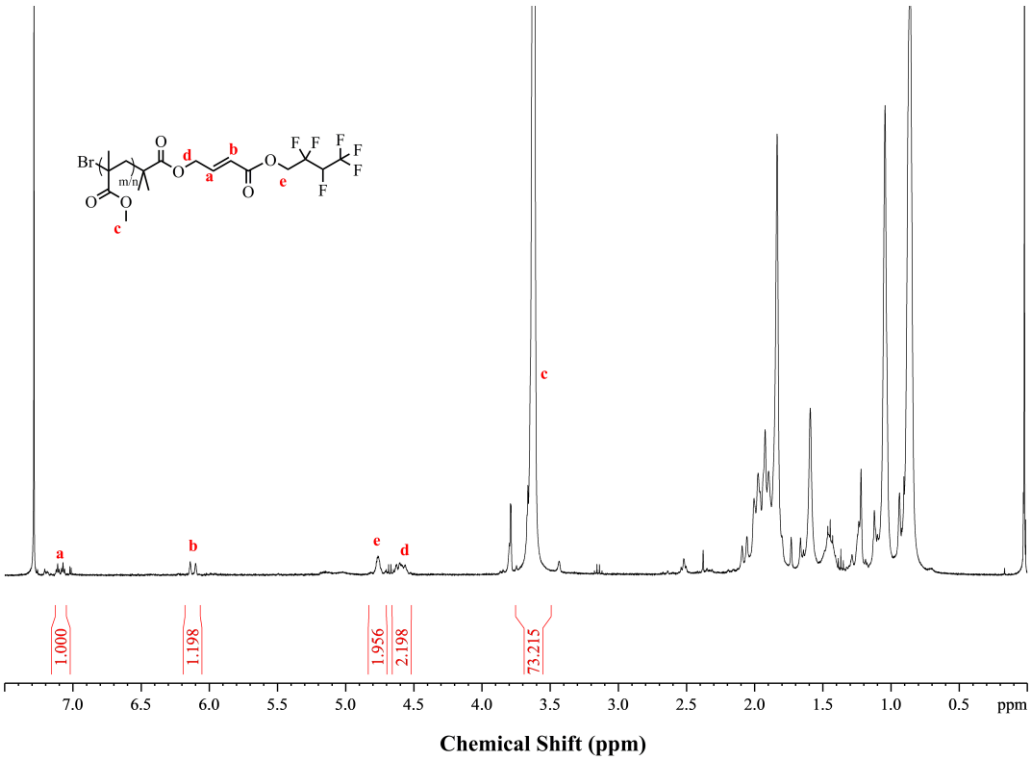


Figure S13 ^{1}H NMR spectrum of P1-*cm*-HFBA in $CDCl_3$.

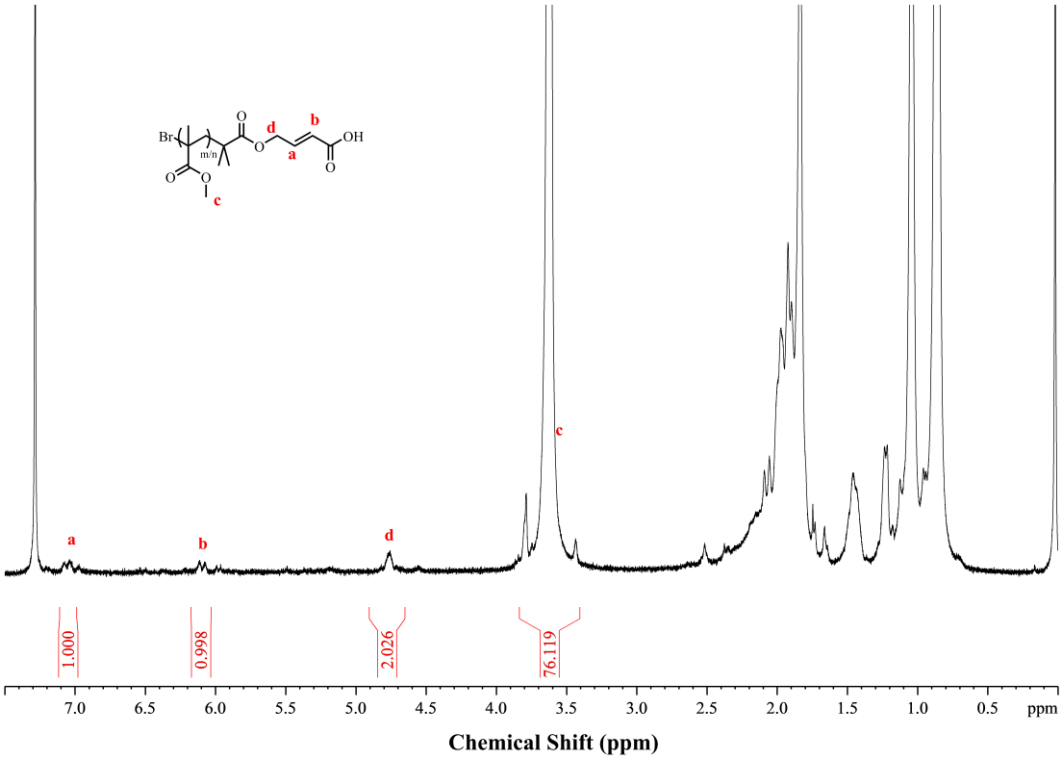


Figure S14 ^{1}H NMR spectrum of P1-*cm*-AA in $CDCl_3$.

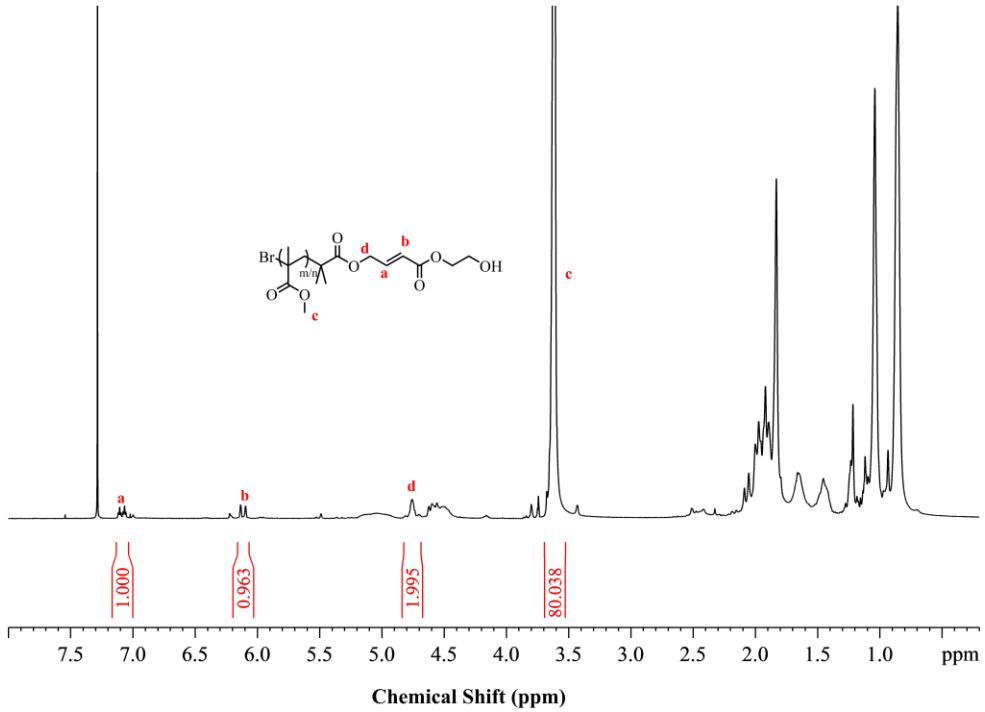


Figure S15 ^{1}H NMR spectrum of P1-*cm*-HEA in $CDCl_3$.

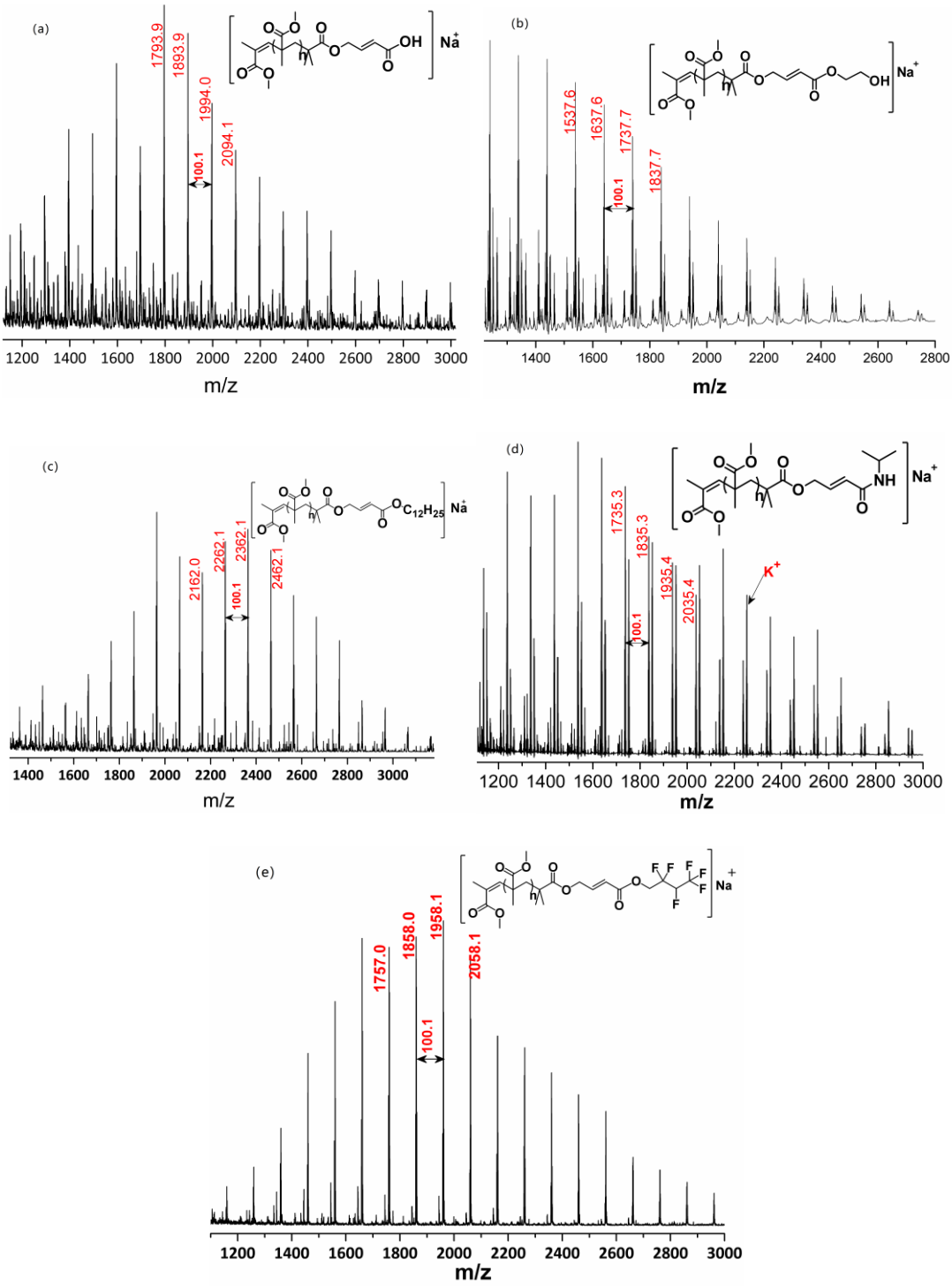


Figure S16 MALDI-TOF MS spectra of different P1-*cm* products

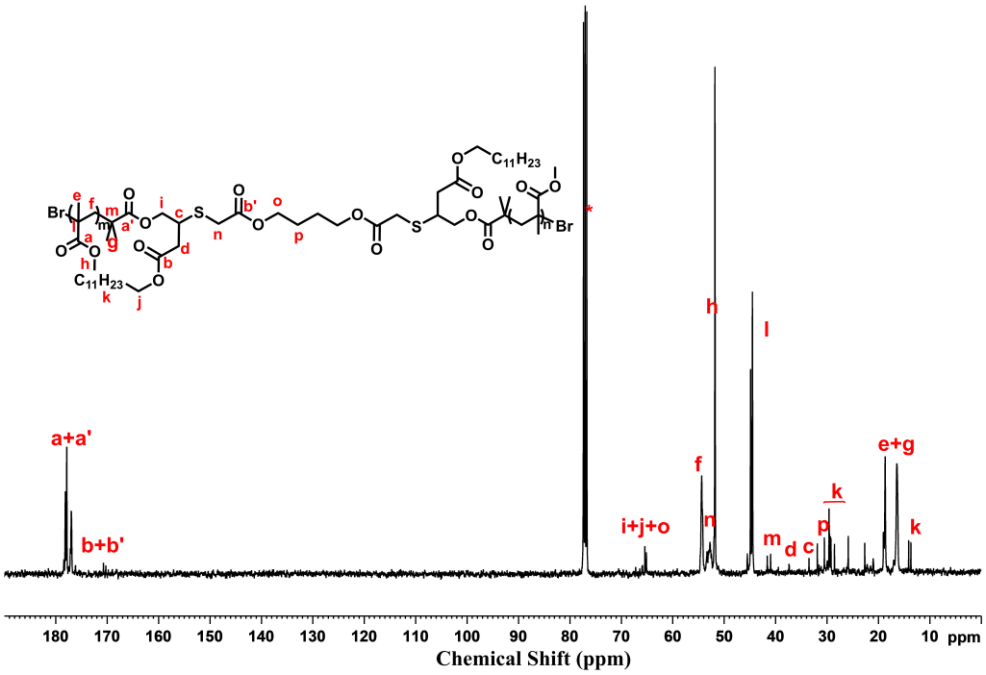


Figure S17 ^{13}C NMR spectrum of P1-*cm*-LA-C1 in $CDCl_3$.

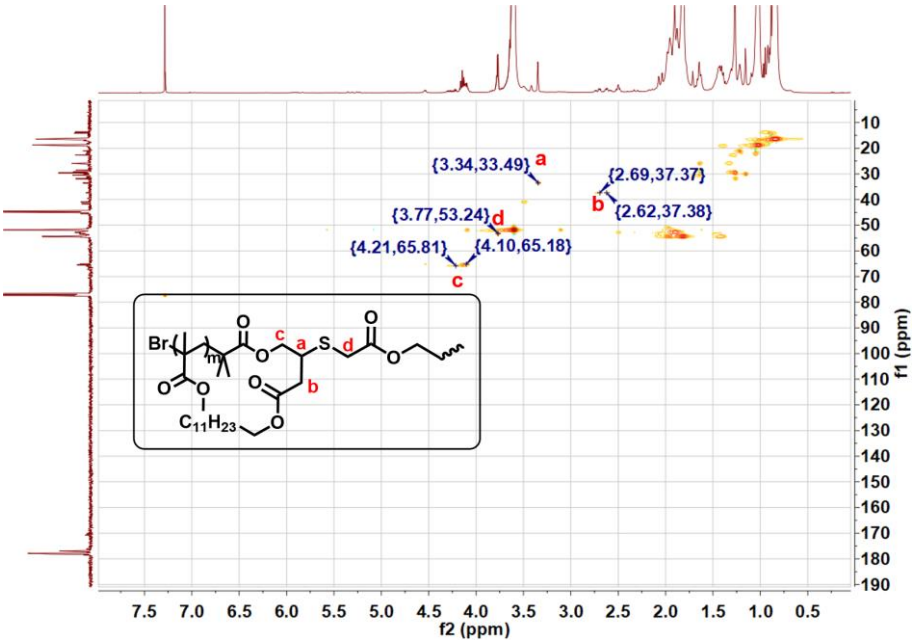


Figure S18 ^{1}H-^{13}C HSQC spectrum of P1-*cm*-LA-C1.

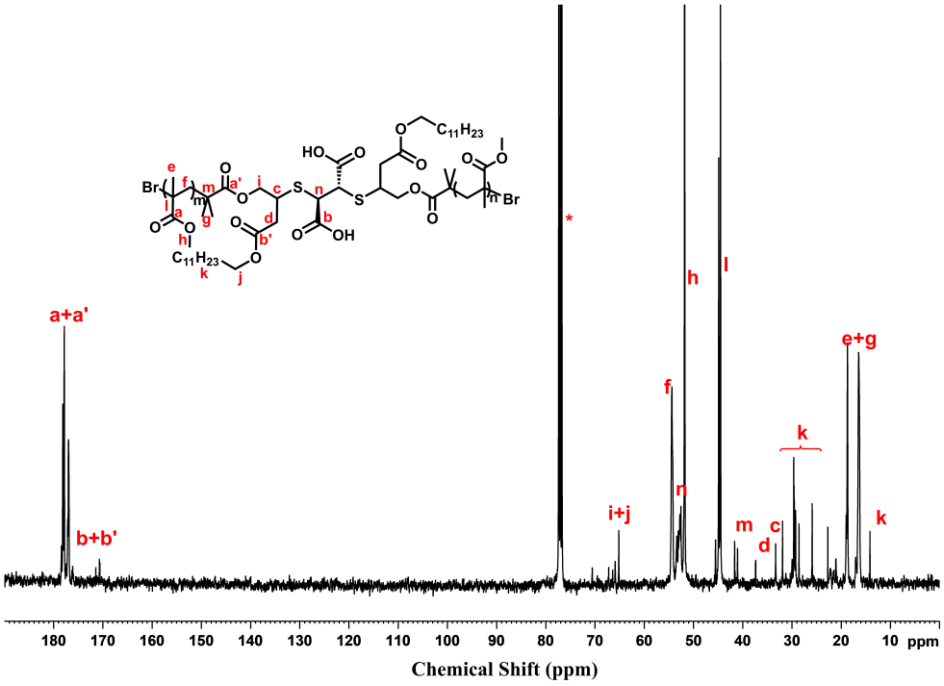


Figure S19 ^{13}C NMR spectrum of P1-*cm*-LA-C2 in $CDCl_3$.

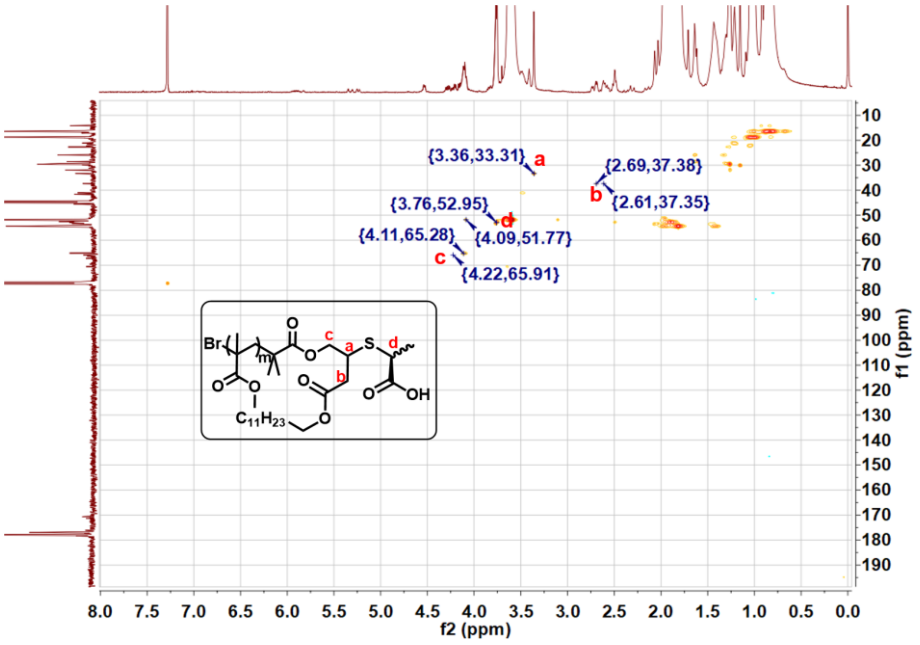


Figure S20 ^{1}H-^{13}C HSQC spectrum of P1-*cm*-LA-C2.

Table S2 Characterization of cross metathesis products between P2 or P3 and ethyl acrylates.

Polymer	$M_{n,GPC}$ (Da)[a]	$M_{n,NMR}$ (Da)[b]	DP[b]	$Đ$[a]	Yield (%)[c]
P2-*cm*-EA	3400	2930	26	1.16	92.3%
P3-*cm*-EA	5800	4200	41	1.16	92.6%

[a]$M_{n\ GPC}$ was determined by GPC in THF, using PMMA standards. [b] Calculated from ^{1}H NMR spectroscopy. [c]Isolated yield after precipitation.

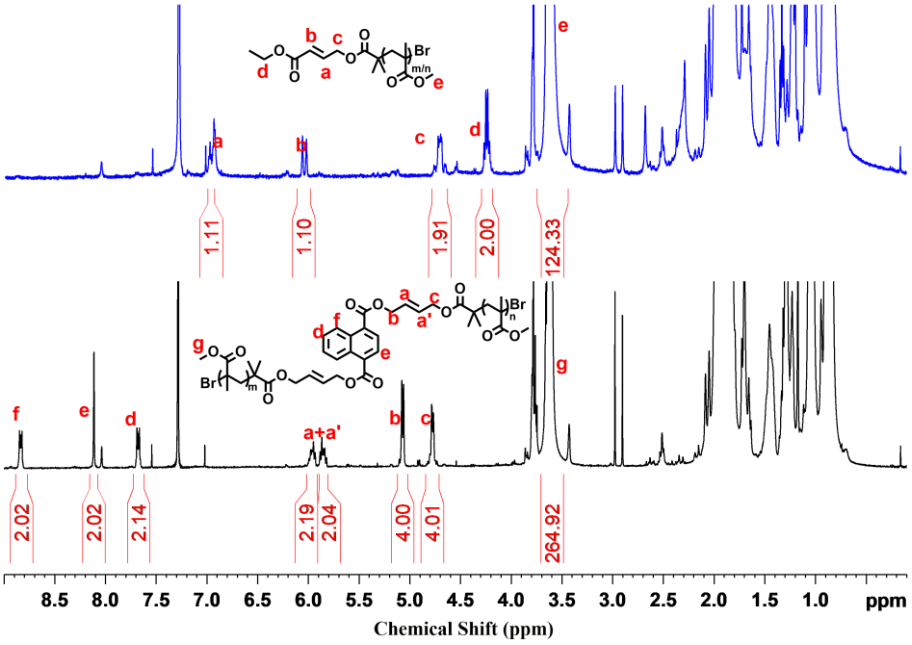


Figure S21 Comparison of ^{1}H NMR spectra of P3 and its CM product P3-*cm*-EA in $CDCl_3$.

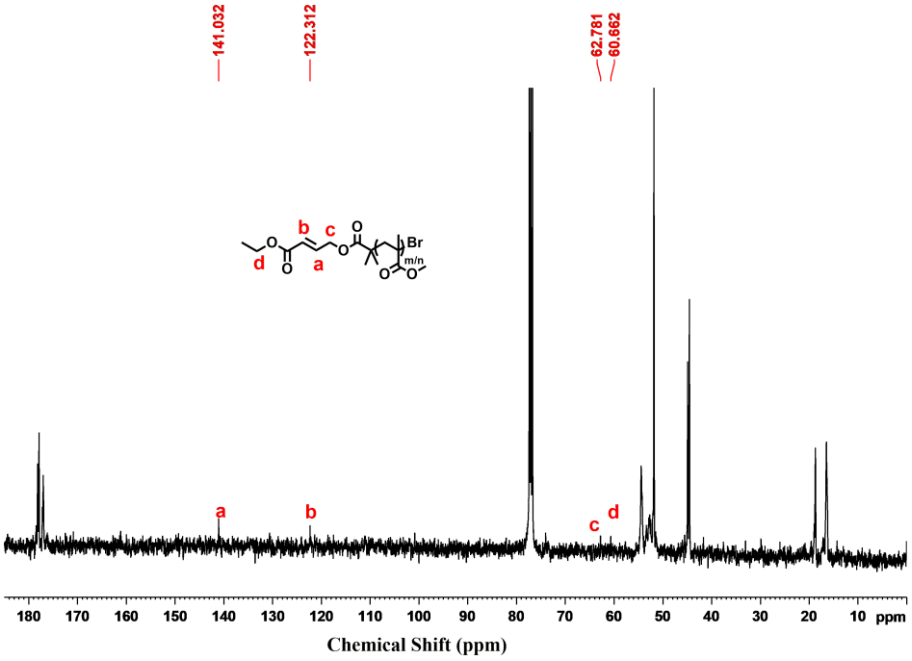


Figure S22 ^{13}C NMR spectrum of P3-*cm*-EA in $CDCl_3$.

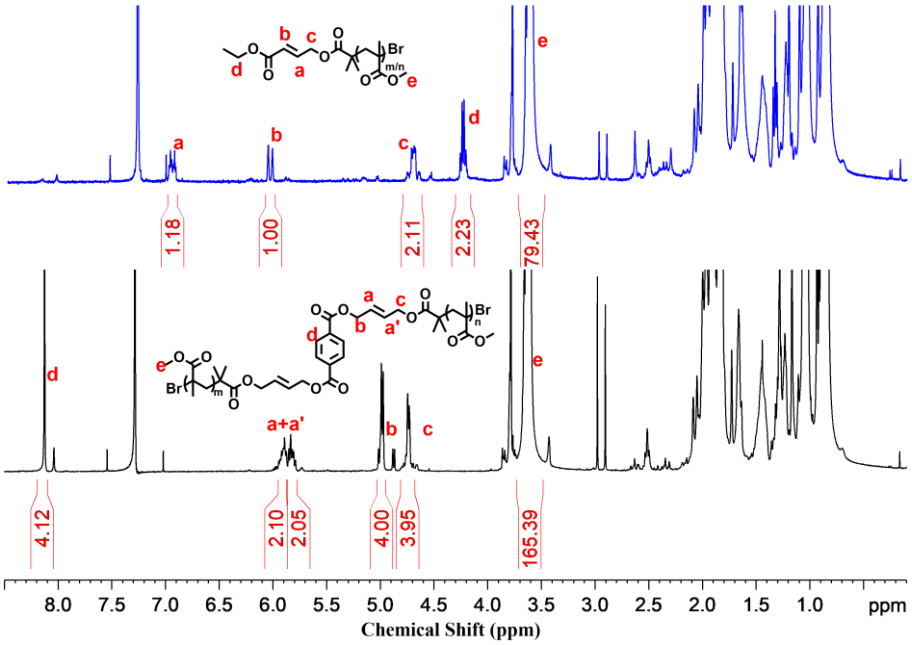


Figure S23 Comparison of ^{1}H NMR spectra of P2 and its CM product P2-*cm*-EA in $CDCl_3$.

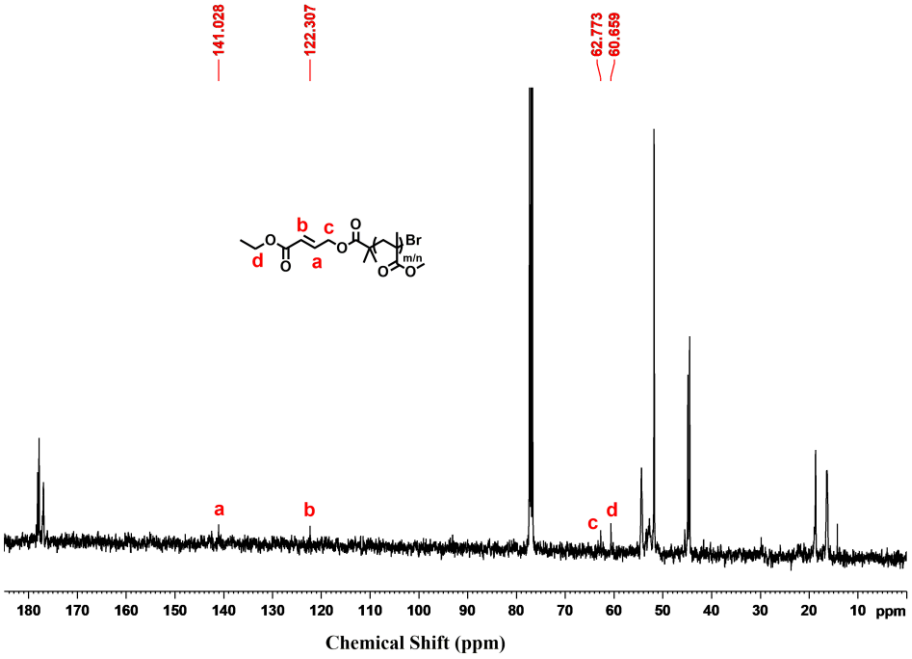


Figure S24 ^{13}C NMR spectrum of P2-*cm*-EA in $CDCl_3$.

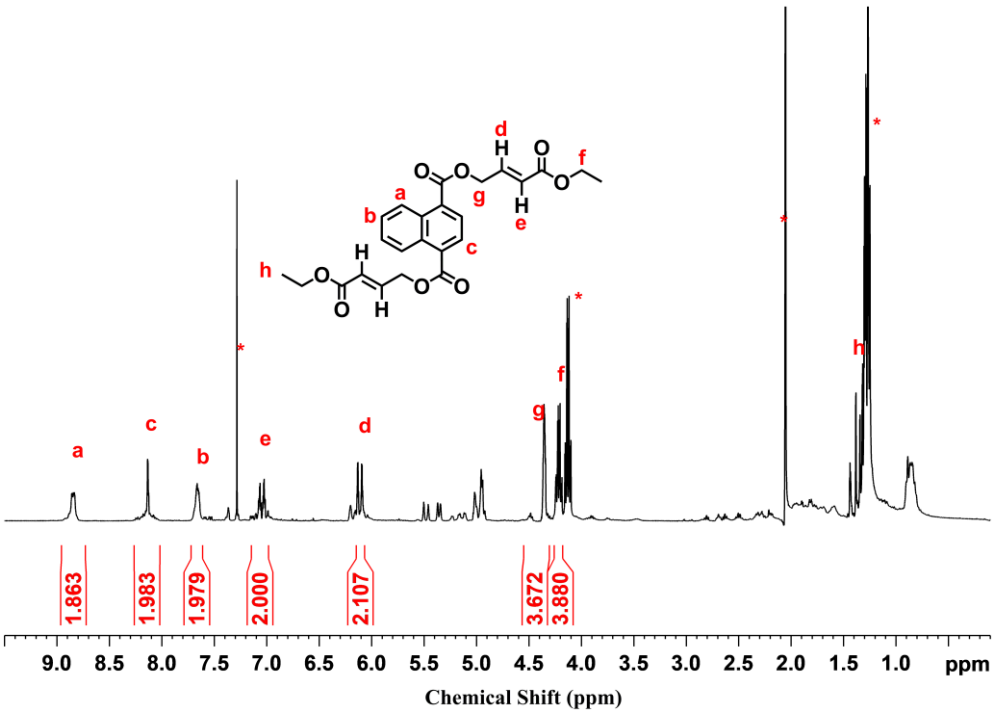


Figure S25 ^{1}H NMR spectrum of the released naphthyl- compound in $CDCl_3$

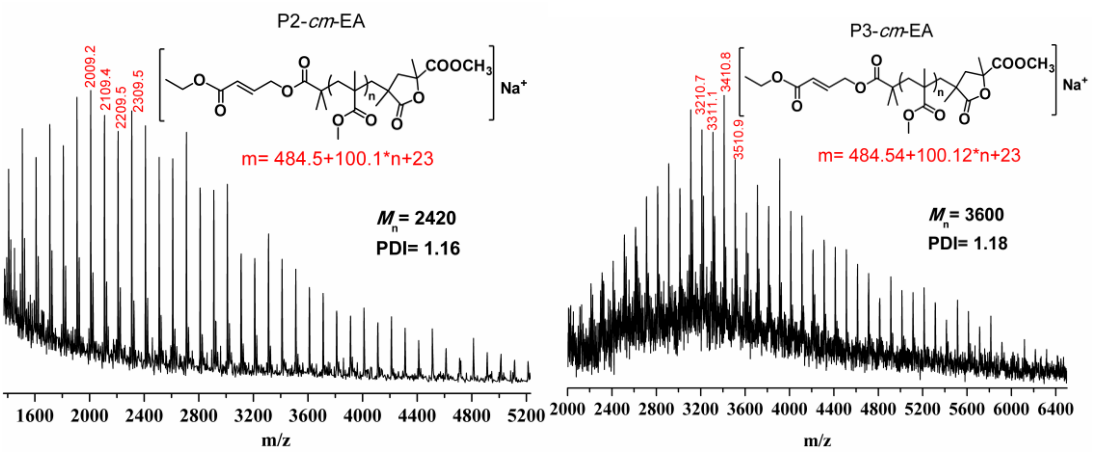


Figure S26 MALDI-TOF MS spectra of P2-*cm*-EA and P3-*cm*-EA.

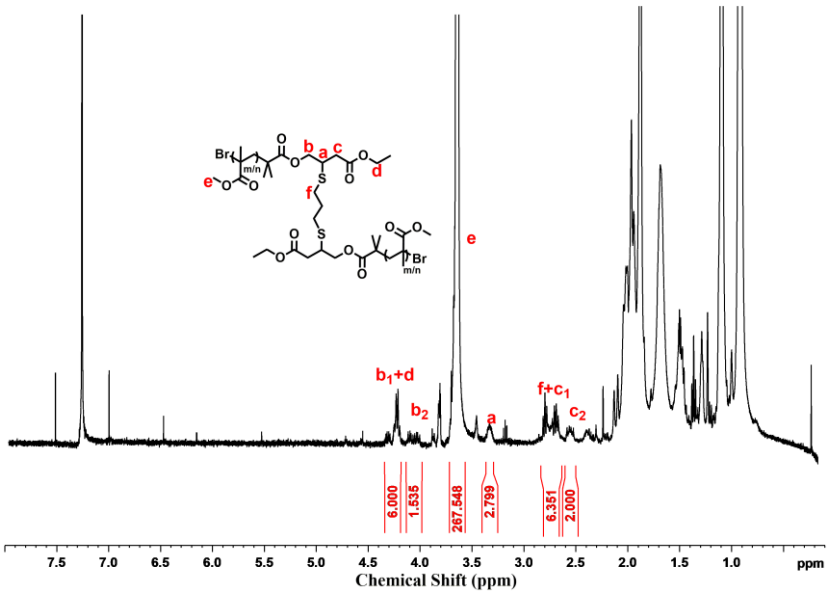


Figure S27 ^{1}H NMR spectrum of P3-*cm*-EA-CP1 in $CDCl_3$.

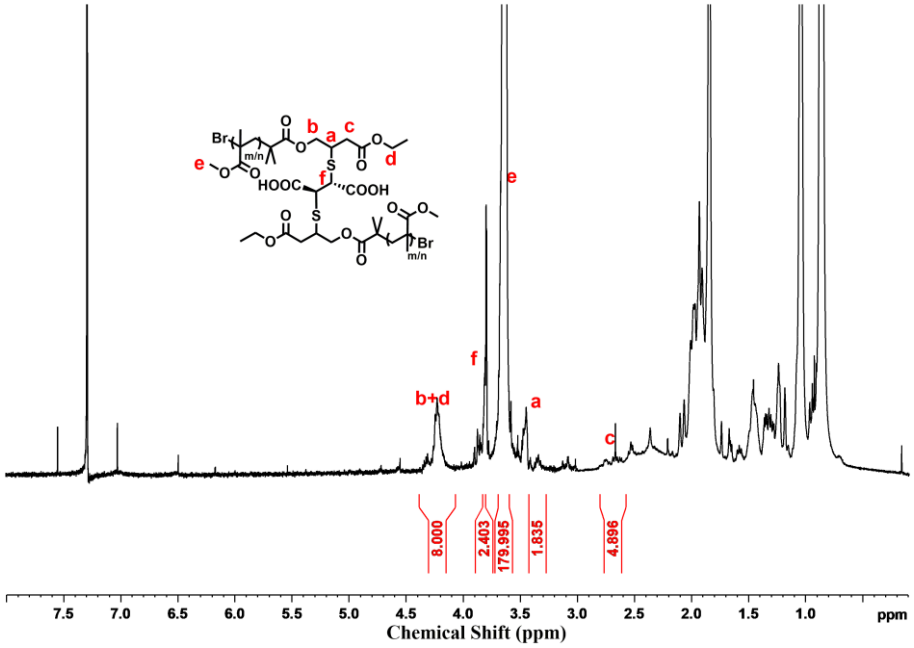


Figure S28 ^{1}H NMR spectrum of P2-*cm*-EA-CP2 in $CDCl_3$

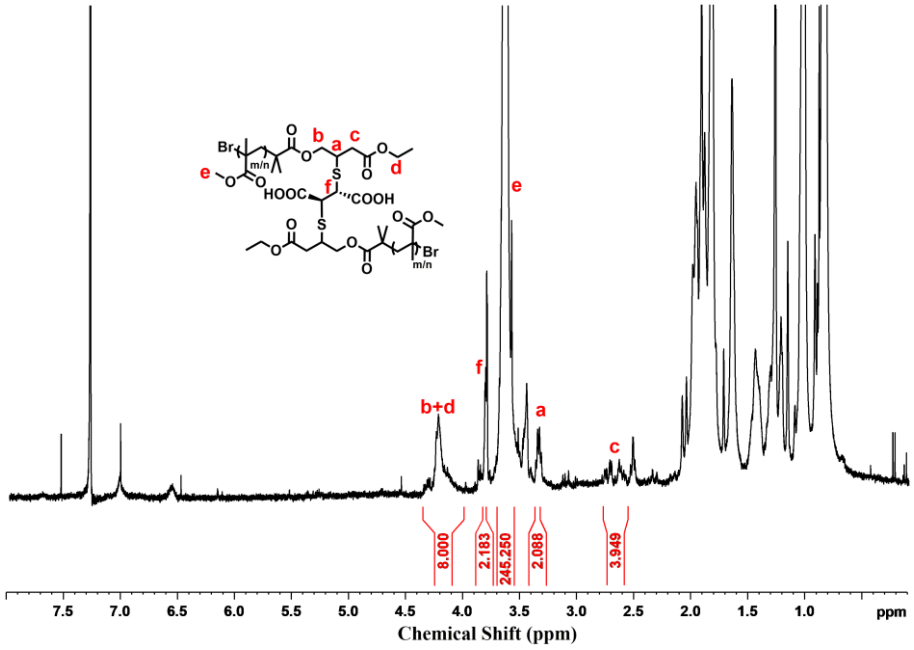


Figure S29 ^{1}H NMR spectrum of P3-*cm*-EA-CP2 in $CDCl_3$.

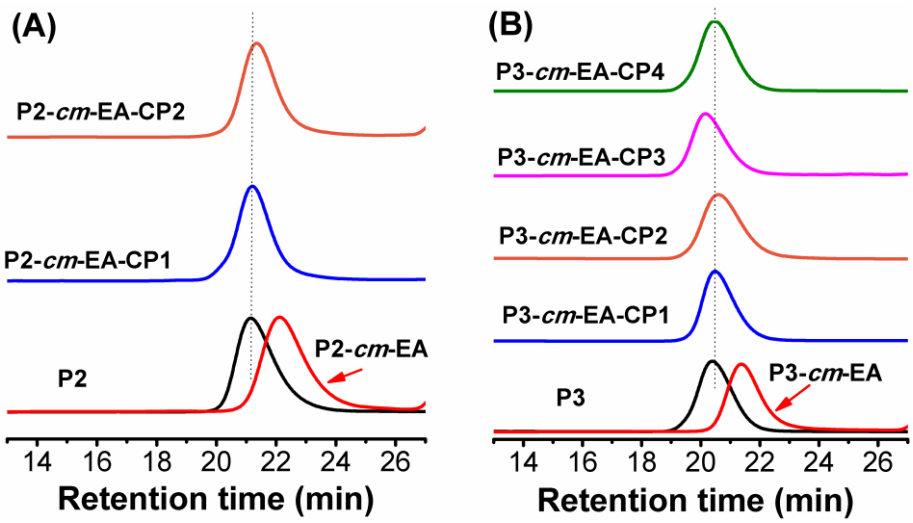


Figure S30 GPC curves of the coupling reaction between (A) P2-*cm*-EA (B) P3-*cm*-EA with different dithiol compound.

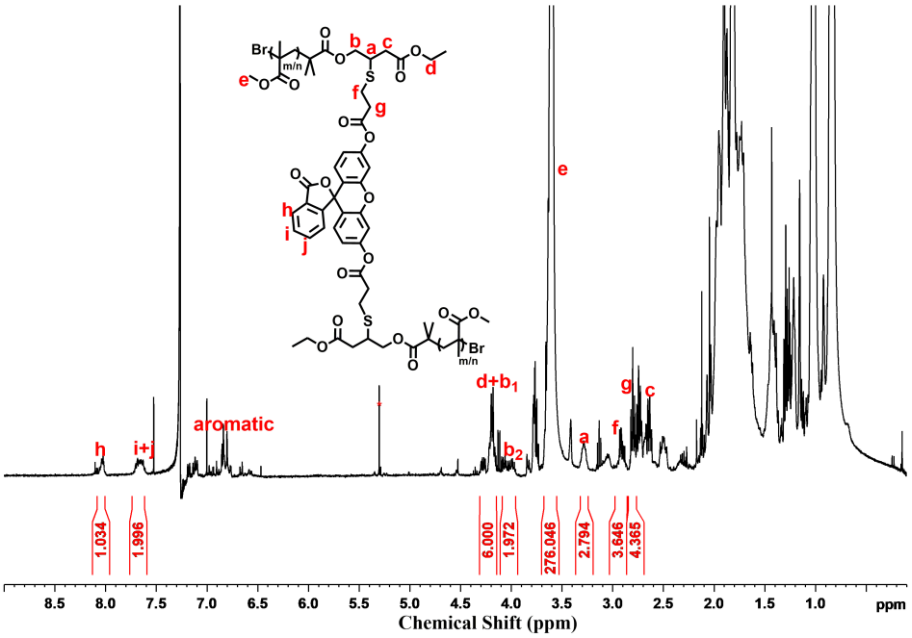


Figure S31 ^{1}H NMR spectrum of P3-*cm*-EA-CP3 in $CDCl_3$.

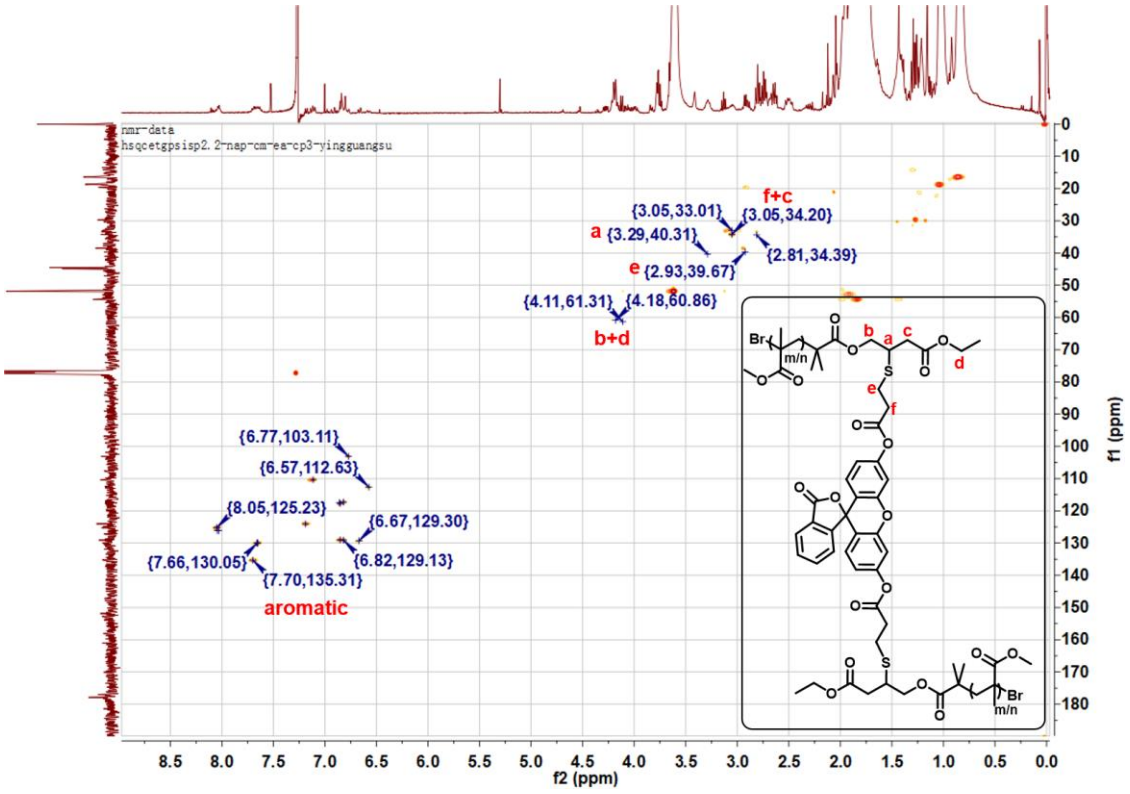


Figure S32 ^{1}H-^{13}C HSQC spectrum of P3-*cm*-EA-CP3 in $CDCl_3$.

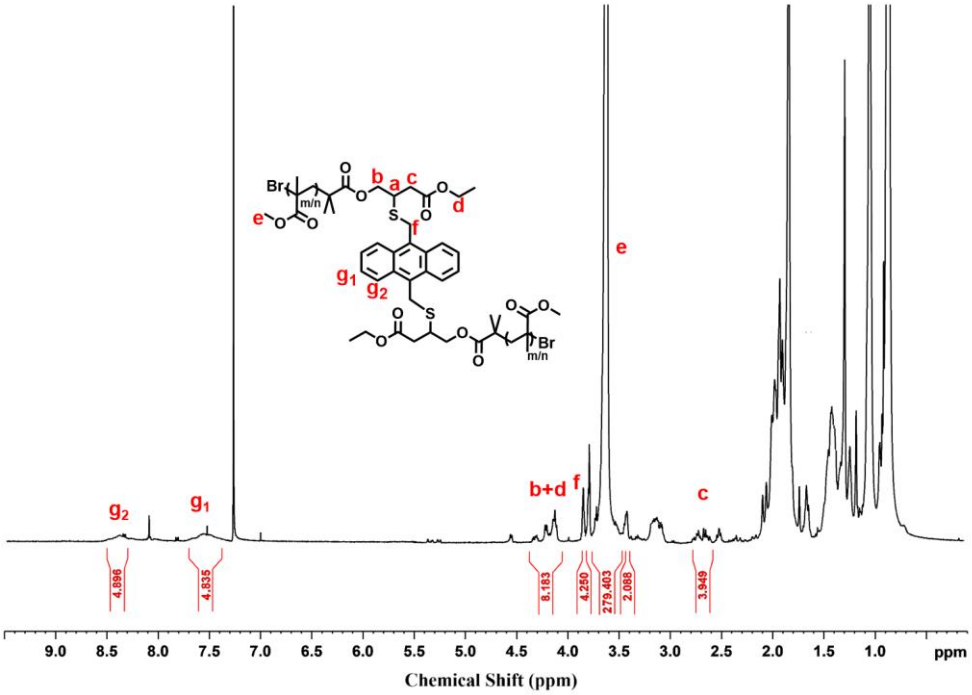


Figure S33 ^{1}H NMR spectrum of P3-*cm*-EA-CP4 in $CDCl_3$.

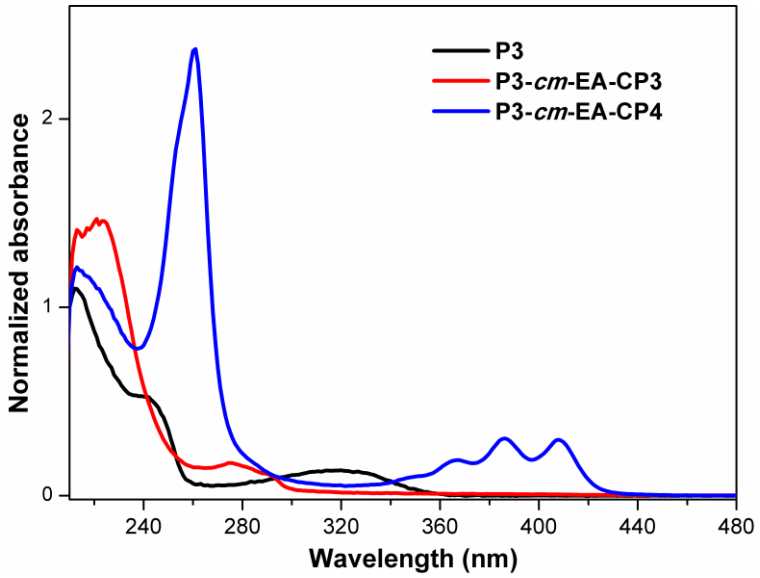


Figure S34 Comparison of the UV spectra of P3 before and after functionality replacement process.

Table S3 Characterization of products after different processes from P3.

Process	Polymer	$M_{n,GPC}$ (Da) [a]	$M_{n,NMR}$ (Da) [b]	$Đ$ [a]	DP [b]	Functionality
ATRP	P3	10700	9500	1.15	88	naphthyl
Cleavage	P3-*cm*-EA	5800	4200	1.16	41	-
Knock-out	P3-*cm*-EA-CP1	10700	9570	1.16	89	n/a
Replacement	P3-*cm*-EA-CP2	9800	8940	1.18	82	dicarboxyl
	P3-*cm*-EA-CP3	11100	10260	1.18	92	fluorescein
	P3-*cm*-EA-CP4	10800	10100	1.18	93	anthryl

[a] $M_{n\ GPC}$ was determined by GPC in THF, using PMMA standards. [b] Calculated from ^{1}H NMR spectroscopy.

References

1. Matson, J. B.; Grubbs, R. H., ROMP-ATRP block copolymers prepared from monotelechelic poly (oxa) norbornenes using a difunctional terminating agent. *Macromolecules* **2008,** *41* (15), 5626-5631.
2. Matson, J. B.; Grubbs, R. H., Monotelechelic Poly(oxa)norbornenes by Ring-Opening Metathesis Polymerization Using Direct End-Capping and Cross-Metathesis. *Macromolecules* **2010,** *43* (1), 213-221.