Investigation of the Features in Living Anionic Polymerization with Styrene Derivatives Containing Annular Substituents

Hongyuan Bai[1], Zhi Zhang[1], Hongwei Ma*, [1], Li Han[1], Xiaochun Mu[1], Wei Huang[1], Pibo Liu[1], Yibo Wu[2]

1. Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China;

2. Beijing Inst. Petrochem Technol., Beijing Key Lab of Special Elastomer Composite Mat., Beijing 102617, China.

**E-mail: mahw@dlut.edu.cn*

Synthesis of SAs.

SAs were synthesized by Wittig reaction and the whole process of the reaction was performed under argon. Typically, Methyltriphenylphosphonium bromide was added to a three-necked flask under argon. Methyltriphenylphosphonium bromide (59.5 g, 0.17 mol) and dry THF (125 mL) were added into Three-necked flask equipped with a magnetic stir bar. Then the Potassium tert-butoxide (20.3 g dissolved in 100 mL of THF, 0.18 mol) was added into the reaction flask through a constant pressure funnel at 0^{o}C under argon. After the reaction mixture stirred for 2h, CPBE (17.9 g, 0.1 mol), CHBE (19.4 g, 0.1 mol), THNE (15.0 g, 0.1 mol), THBE (15.8 g, 0.1 mol) or META (16.2g, 0.1 mol) was dissolved in 125 mL THF, and drop-wise added into the flask. The mixture reacted under argon for 12 hours at room temperature, and then 10 mL H_2O was added into the flask to quench the reaction. The mixture was poured into a separatory funnel and diluted with saturated sodium chloride solution and extracted with ether for 3 times. Then the organic layer was collected and dried with anhydrous $MgSO_4$ overnight. The turbid fluid was filtrated and concentrated under reduced pressure, and then the flash column chromatography was taken as twice using hexane. Finally, the monomers were purified by vacuum distillation.

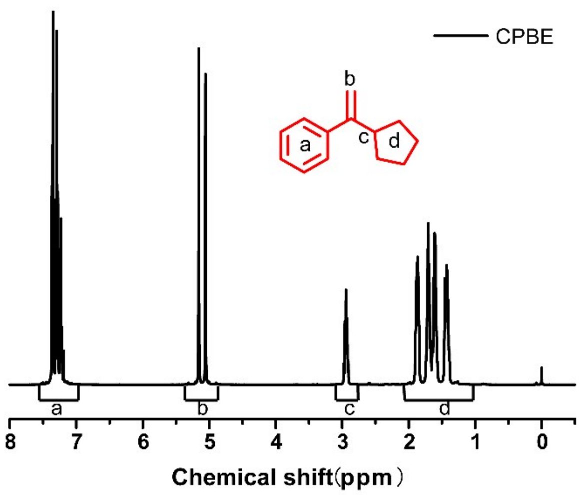
CPBE ^1H NMR (500 MHz, $CDCl_3$): δ 7.65−7.00 (C_6H_5, 5H), 5.20 (C=CH_2, 1H), 5.10 (C=CH_2, 1H), 3.00 (CH, 1H) ,2.10-1.20(C_4H_8, 8H).

CHBE ^1H NMR (500 MHz, $CDCl_3$): δ 7.50−7.24 (C_6H_5, 5H), 5.21 (C=CH_2, 1H), 5.10 (C=CH_2, 1H), 2.50 (CH, 1H) ,2.20-1.150(C_5H_{10}, 10H).

THNE ^1H NMR (500 MHz, $CDCl_3$): δ 7.90−6.80 (C_6H_4, 4H), 5.44 (C=CH_2, 1H), 4.91 (C=CH_2, 1H), 2.89-2.67 (CH_2, 2H) ,2.60-2.40 (CH_2, 2H) ,1.92-1.73(CH_2, 2H).

THBE ^1H NMR (500 MHz, $CDCl_3$): δ 7.50−7.00 (C_6H_4, 4H), 5.09 (C=CH_2, 1H), 4.98 (C=CH_2, 1H), 2.92-2.63 (CH_2, 2H) ,2.52-2.30 (CH_2, 2H) ,1.91-1.67(C_2H_4, 4H).

META ^1H NMR (500 MHz, $CDCl_3$): δ 7.70−6.90 (C_6H_4, 4H), 5.45 (C=CH_2, 1H), 4.95 (C=CH_2, 1H), 3.20-3.00 (CH_2, 2H) ,2.88-2.77 (CH_2, 2H).



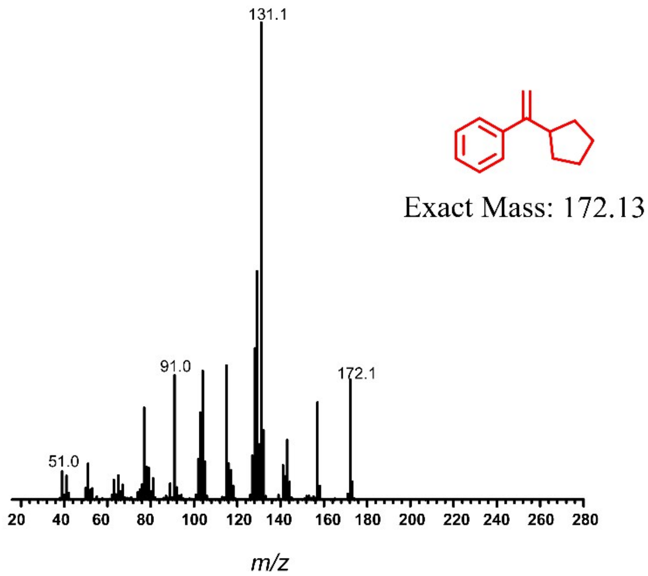
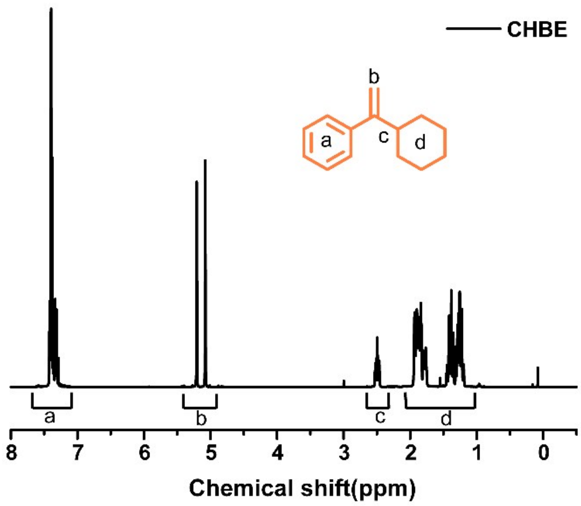


Fig.S1.[1]H NMR and EI-mass spectra of CPBE



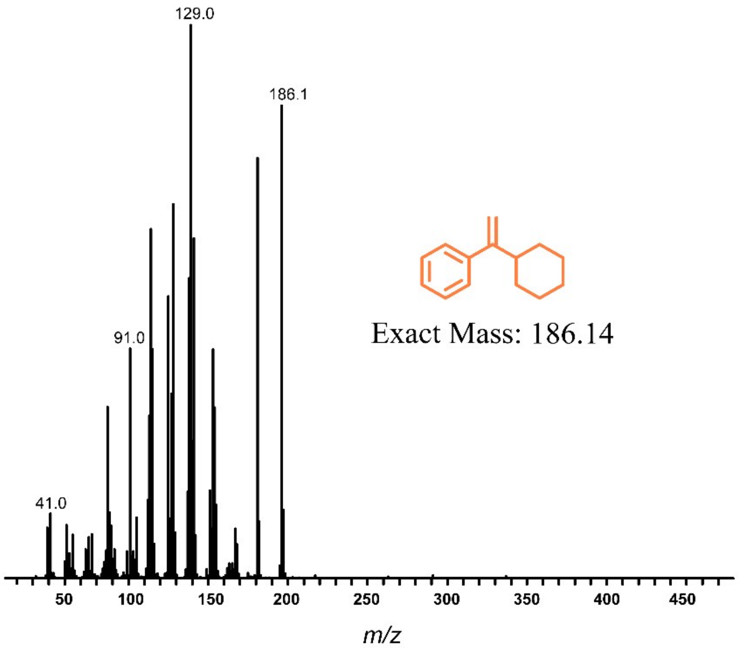


Fig.S2.[1]H NMR and EI-mass spectra of CHBE

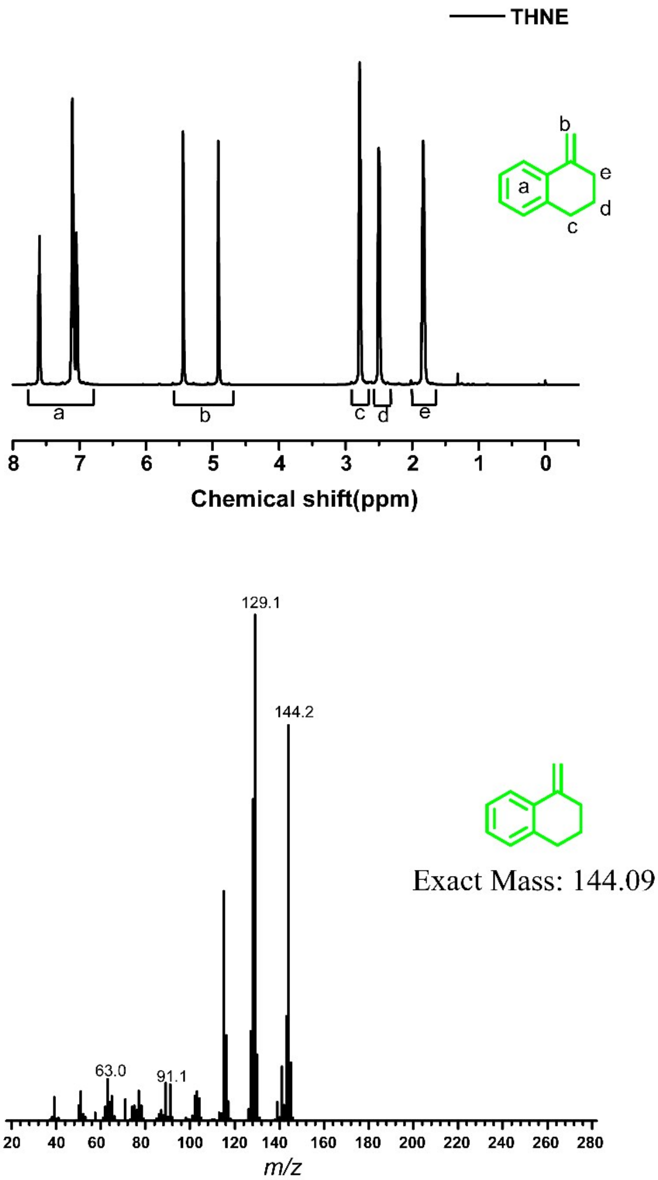
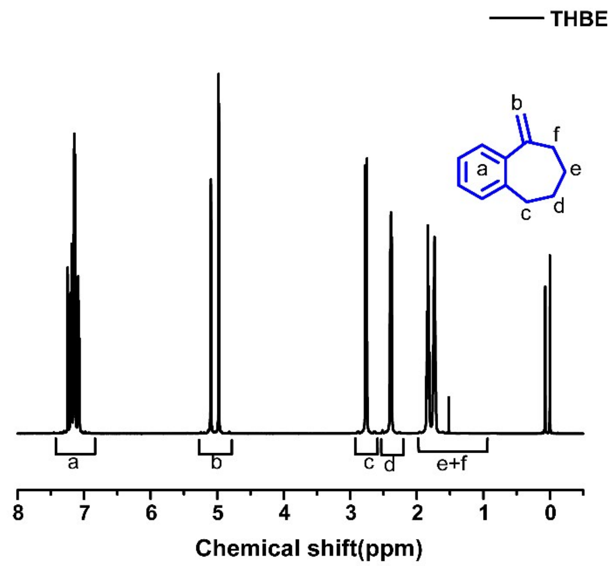


Fig.S3.[1]H NMR and EI-mass spectra of THNE



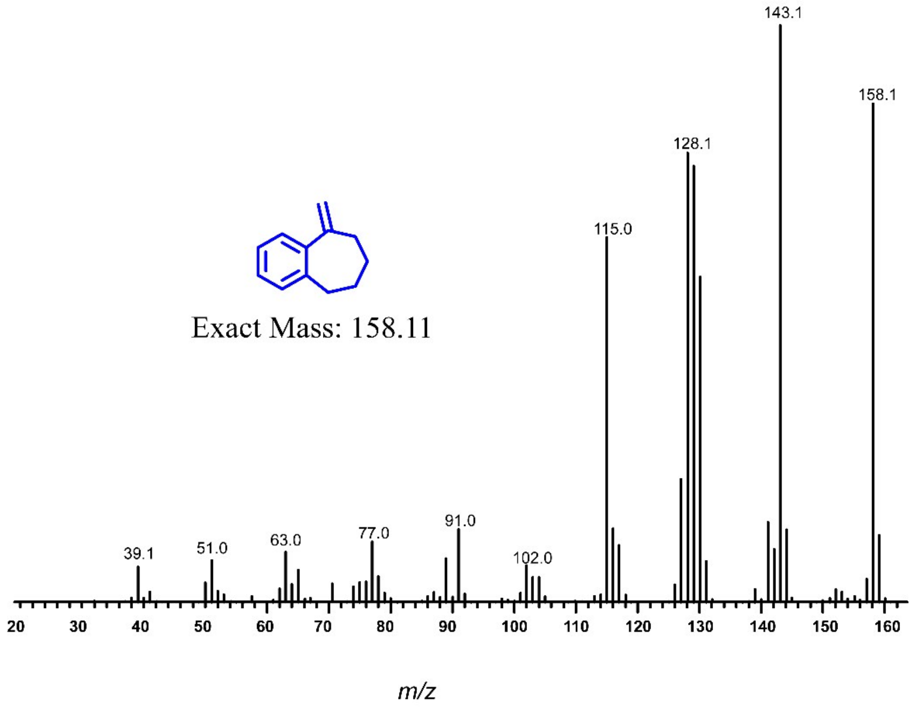
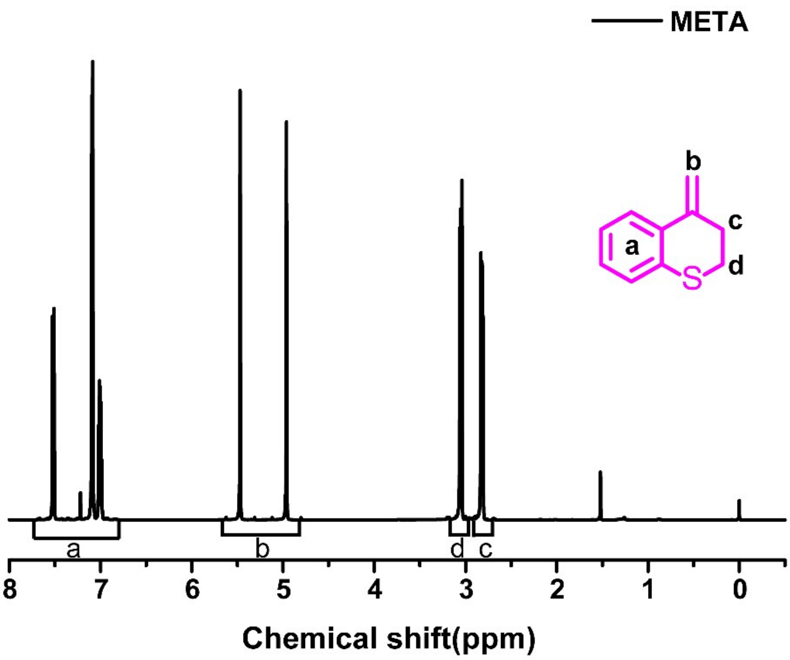


Fig.S4. ^{1}H NMR and EI-mass spectra of THBE



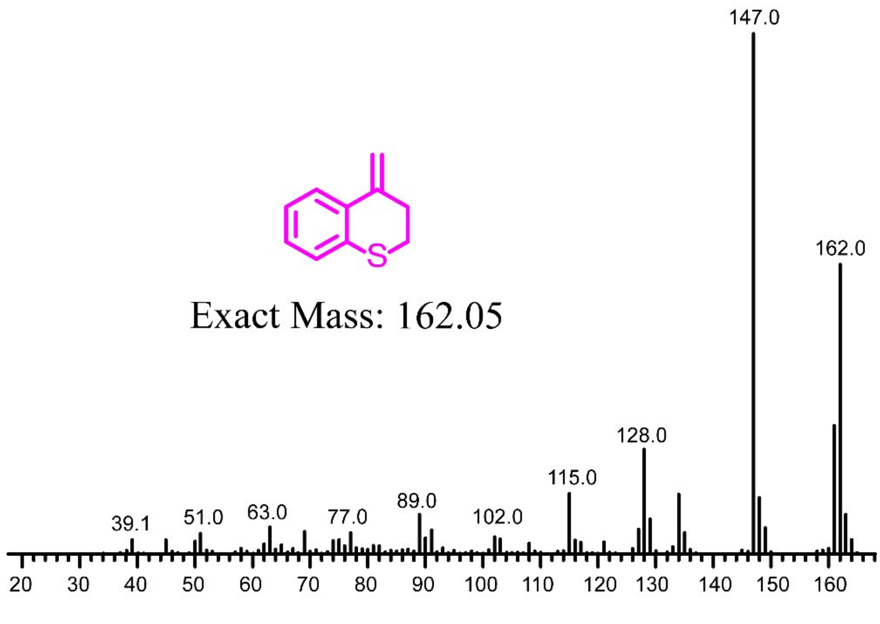


Fig.S5.[1]H NMR and EI-mass spectra of META

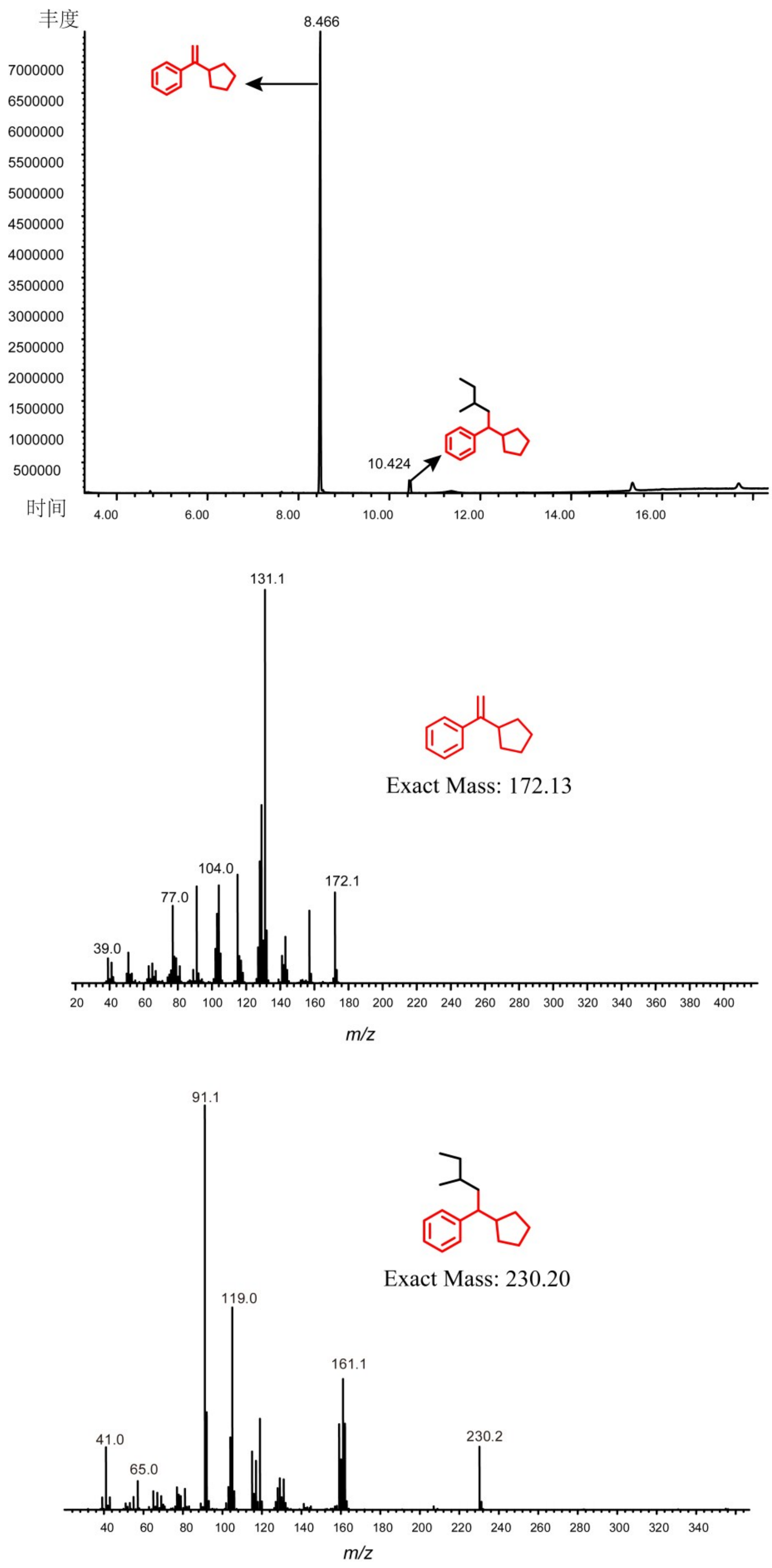


Fig.S6. GC curves and mass spectra of CPBE and Mono-adducts CPBE during living anionic homopolymerization

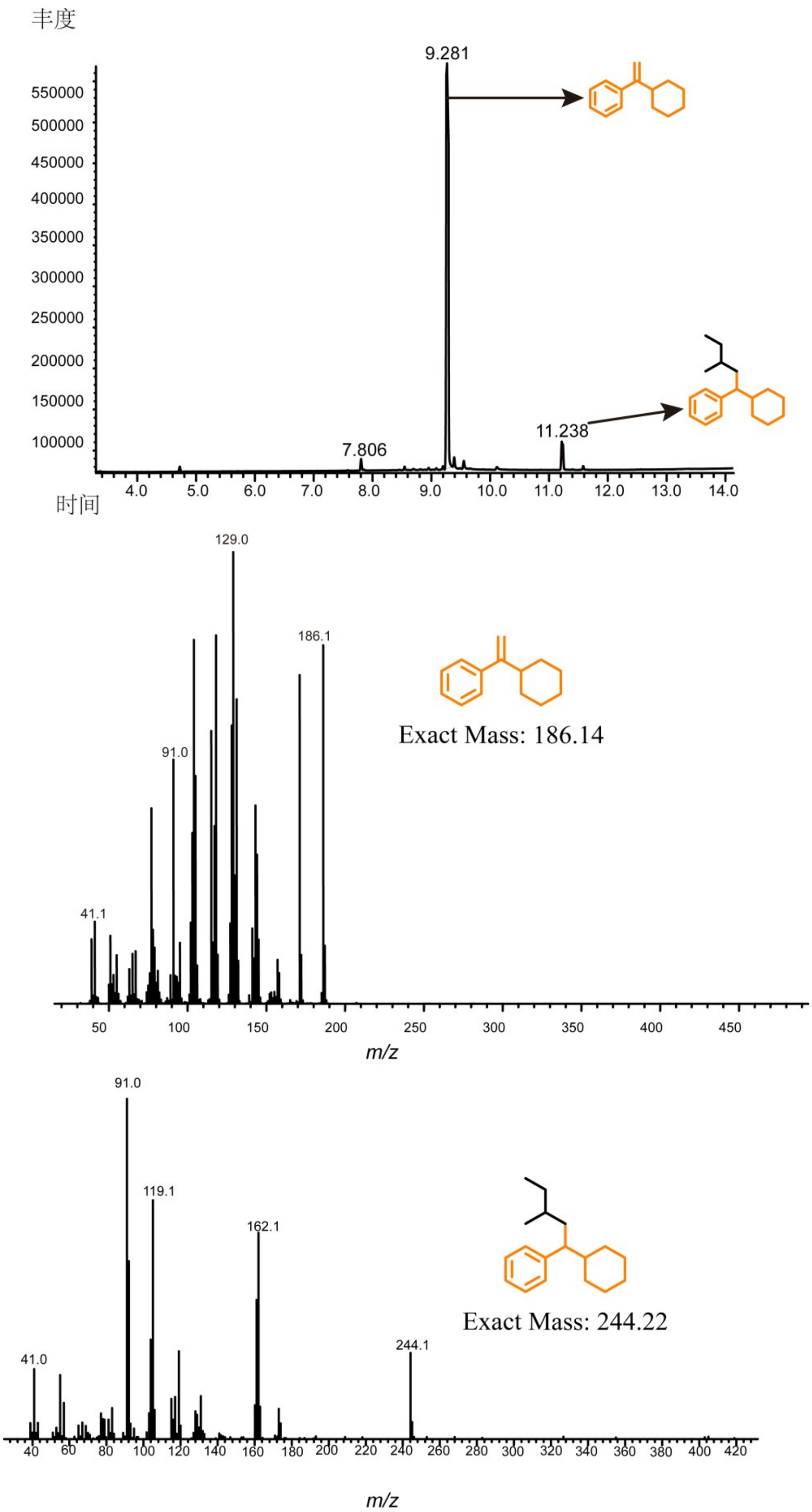


Fig.S7. GC curves and mass spectra of CHBE and Mono-adducts CHBE during living anionic homopolymerization

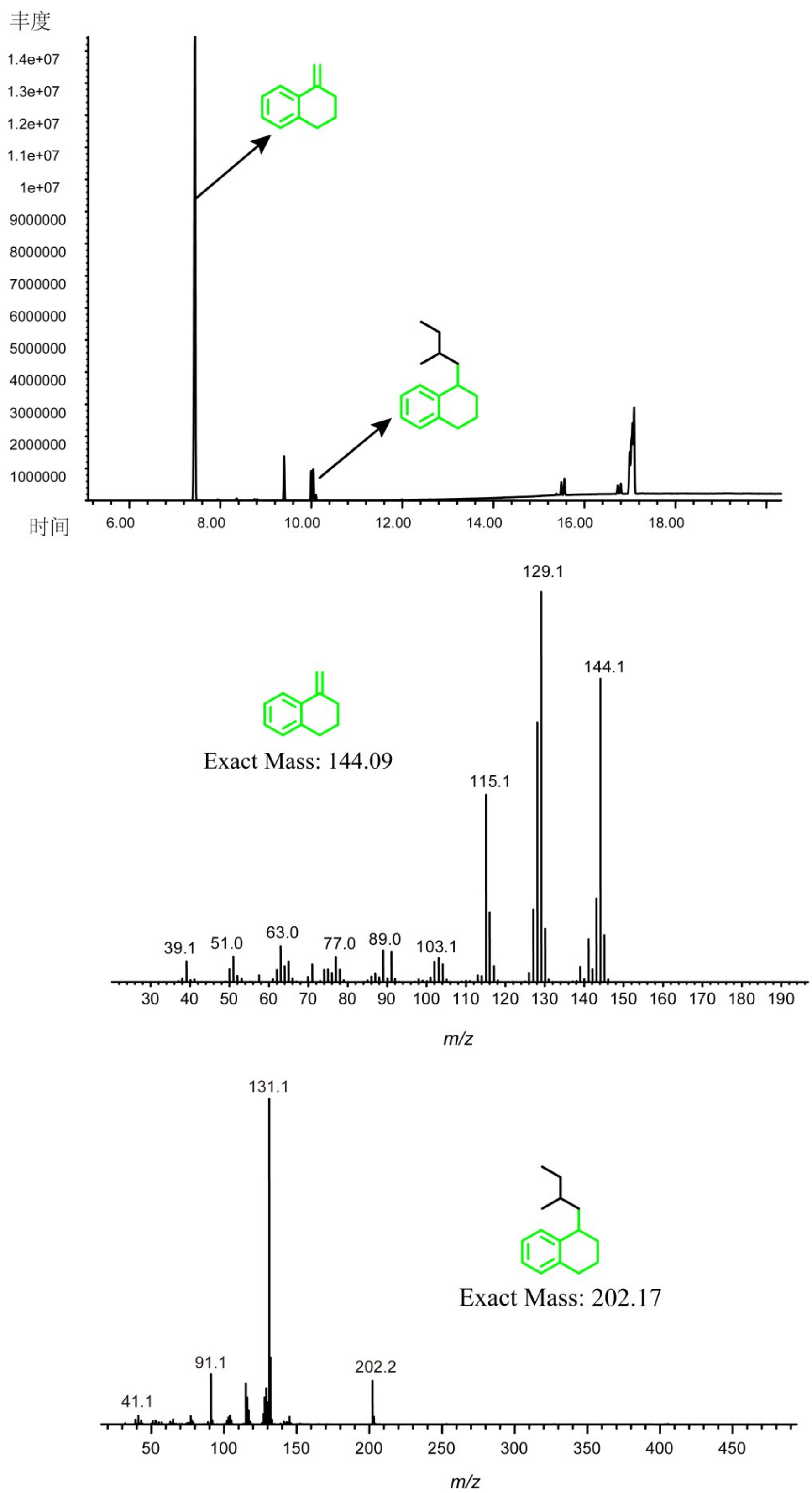
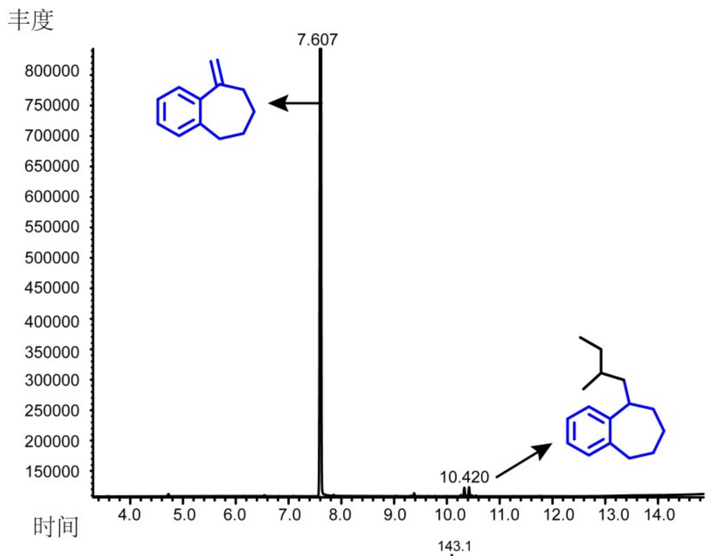
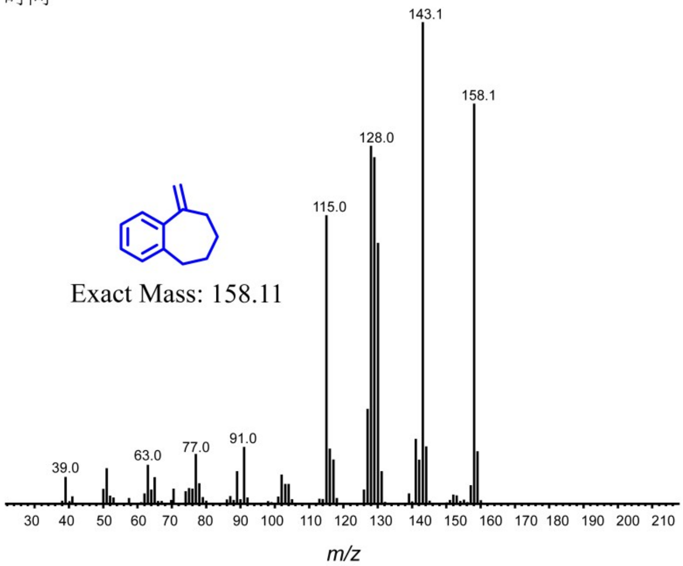


Fig. S8. GC curves and mass spectra of THNE and Mono-adducts THNE during living anionic homopolymerization





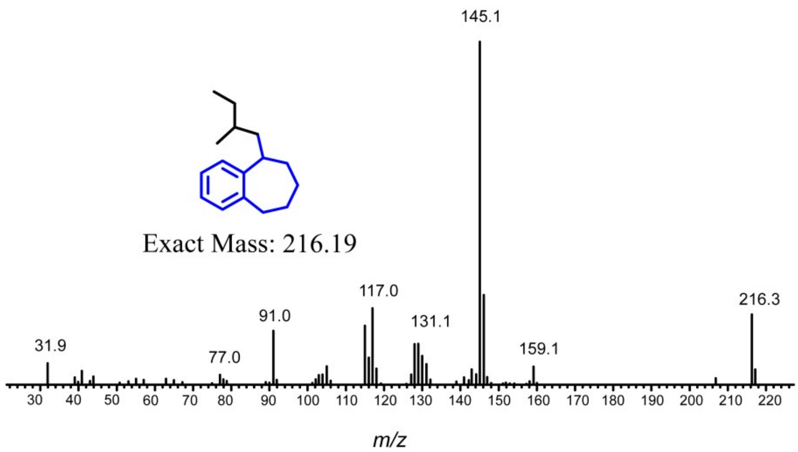


Fig. S9. GC curves and mass spectra of THBE and Mono-adducts THBE during living anionic homopolymerization

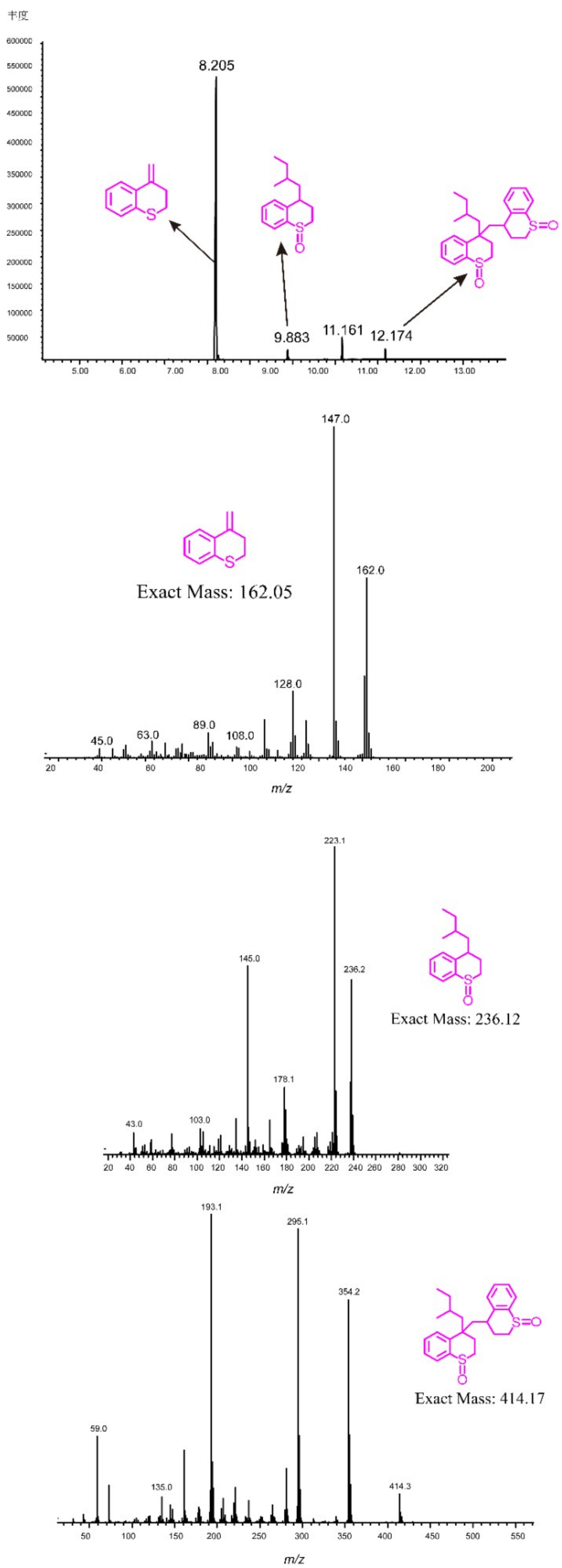


Fig. S10. GC curves and mass spectra of META, Mono-adducts META and Di-adducts META during living anionic homopolymerization

CPBE $\frac{3N_S + 11N_{SA}}{5N_S + 5N_{SA}} = \frac{Area(\delta 2.9 - 0.8) - Area(\delta 1.53 - 1.515) - 3}{Area(\delta 6.0 - 7.5) - Area(\delta 7.27 - 7.24)}$; (1)

CHBE $\frac{3N_S + 13N_{SA}}{5N_S + 5N_{SA}} = \frac{Area(\delta 2.9 - 0.8) - Area(\delta 1.53 - 1.515) - 3}{Area(\delta 6.0 - 7.5) - Area(\delta 7.27 - 7.24)}$ (2)

THNE $\frac{3N_S + 8N_{SA}}{5N_S + 4N_{SA}} = \frac{Area(\delta 2.9 - 0.8) - Area(\delta 1.53 - 1.515) - 3}{Area(\delta 6.0 - 7.5) - Area(\delta 7.27 - 7.24)}$; (3)

THBE $\frac{3N_S + 10N_{SA}}{5N_S + 4N_{SA}} = \frac{Area(\delta 2.9 - 0.8) - Area(\delta 1.53 - 1.515) - 3}{Area(\delta 6.0 - 7.5) - Area(\delta 7.27 - 7.24)}$ (4)

META $\frac{3N_S + 6N_{SA}}{5N_S + 4N_{SA}} = \frac{Area(\delta 2.9 - 0.8) - Area(\delta 1.53 - 1.515) - 3}{Area(\delta 6.0 - 7.5) - Area(\delta 7.27 - 7.24)}$ (5)

Equation S1-S5. The method to calculate the number of N_{St} and N_{SA} in chains

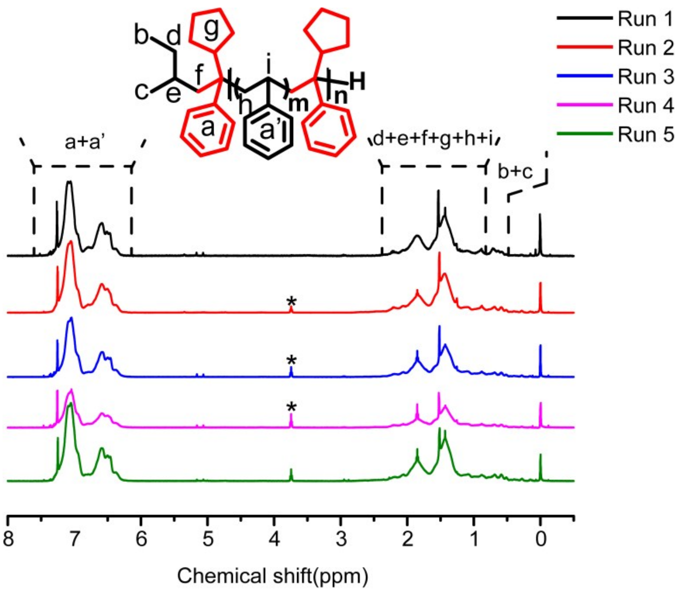


Fig.S11. ^{1}H NMR spectra result of the copolymer of CPBE with St

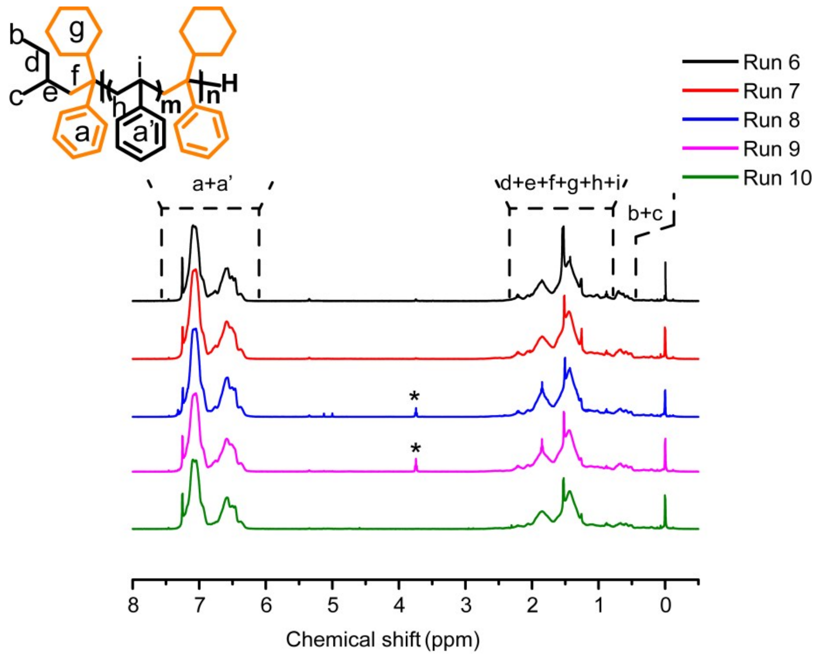


Fig.S12. [1]H NMR spectra result of the copolymer of CHBE with St

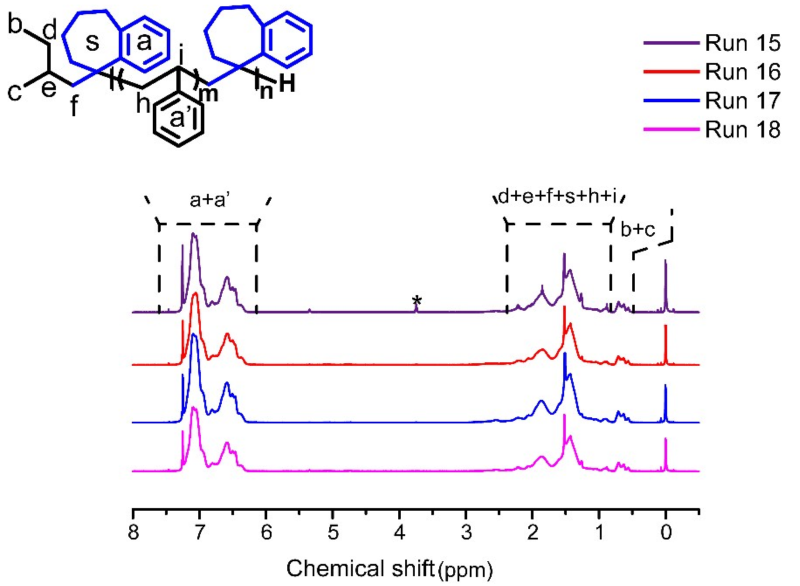


Fig. S13. [1]H NMR spectra result of the copolymer of THBE with St

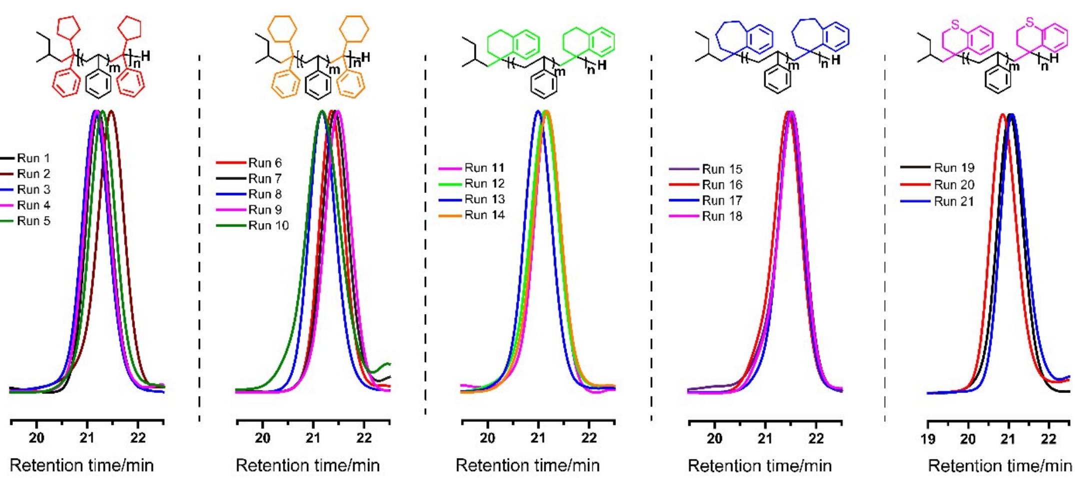


Fig. S14. SEC curves of copolymers of St and SAs

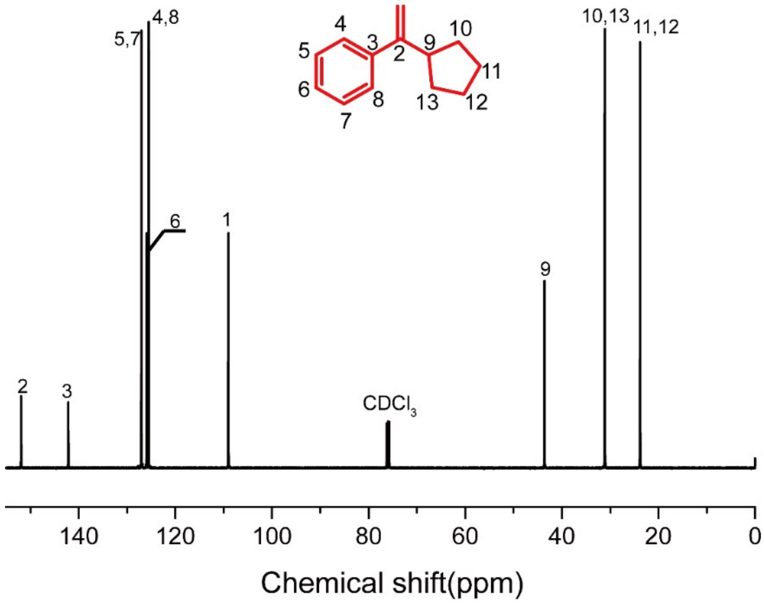


Fig. S15. ^{13}C NMR spectra of CPBE

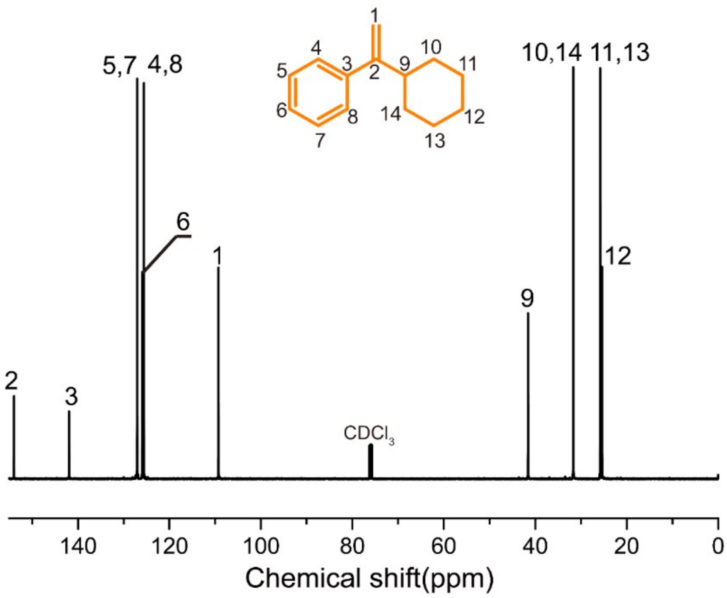


Fig. S16. ^{13}C NMR spectra of CHBE

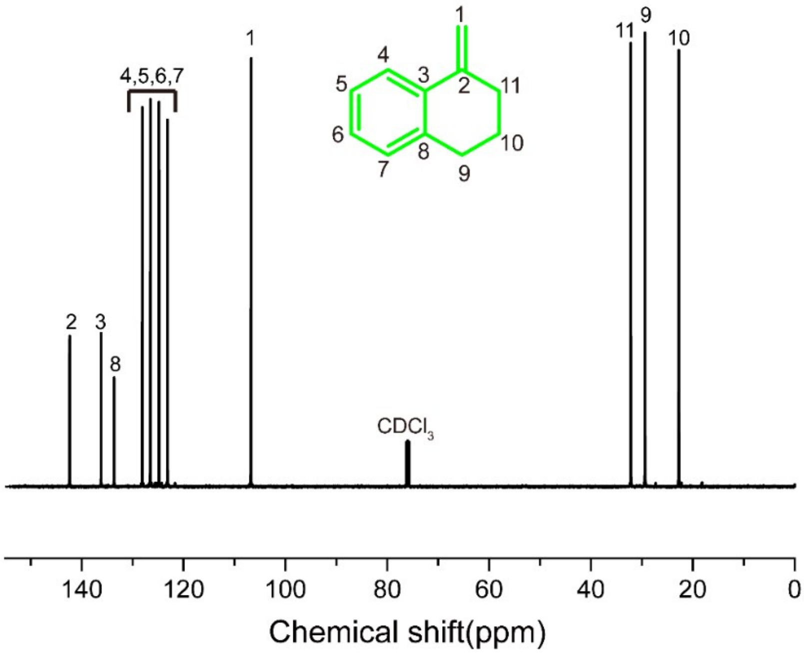


Fig. S17. ^{13}C NMR spectra of THNE

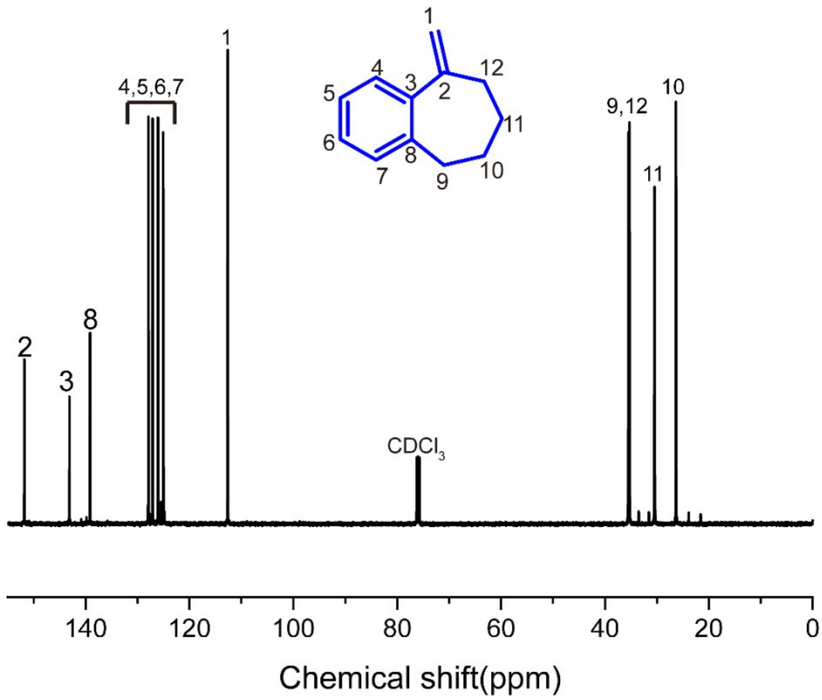


Fig. S18.^{13}C NMR spectra of THBE

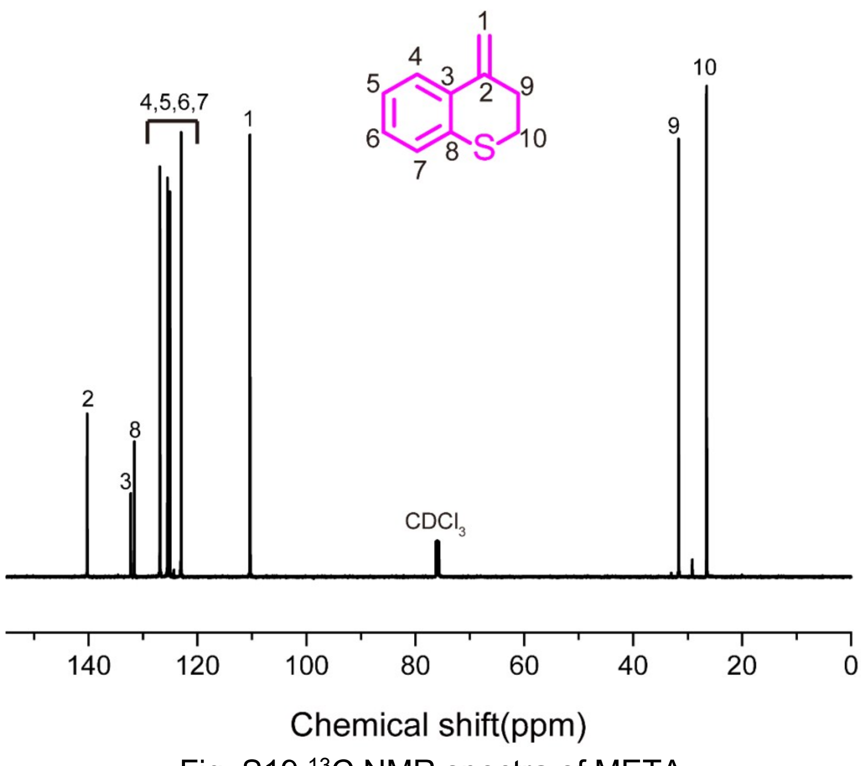


Fig. S19.^{13}C NMR spectra of META