Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

GSH-responsive polymeric micelles based on the thio-ene reaction for controlled drug release

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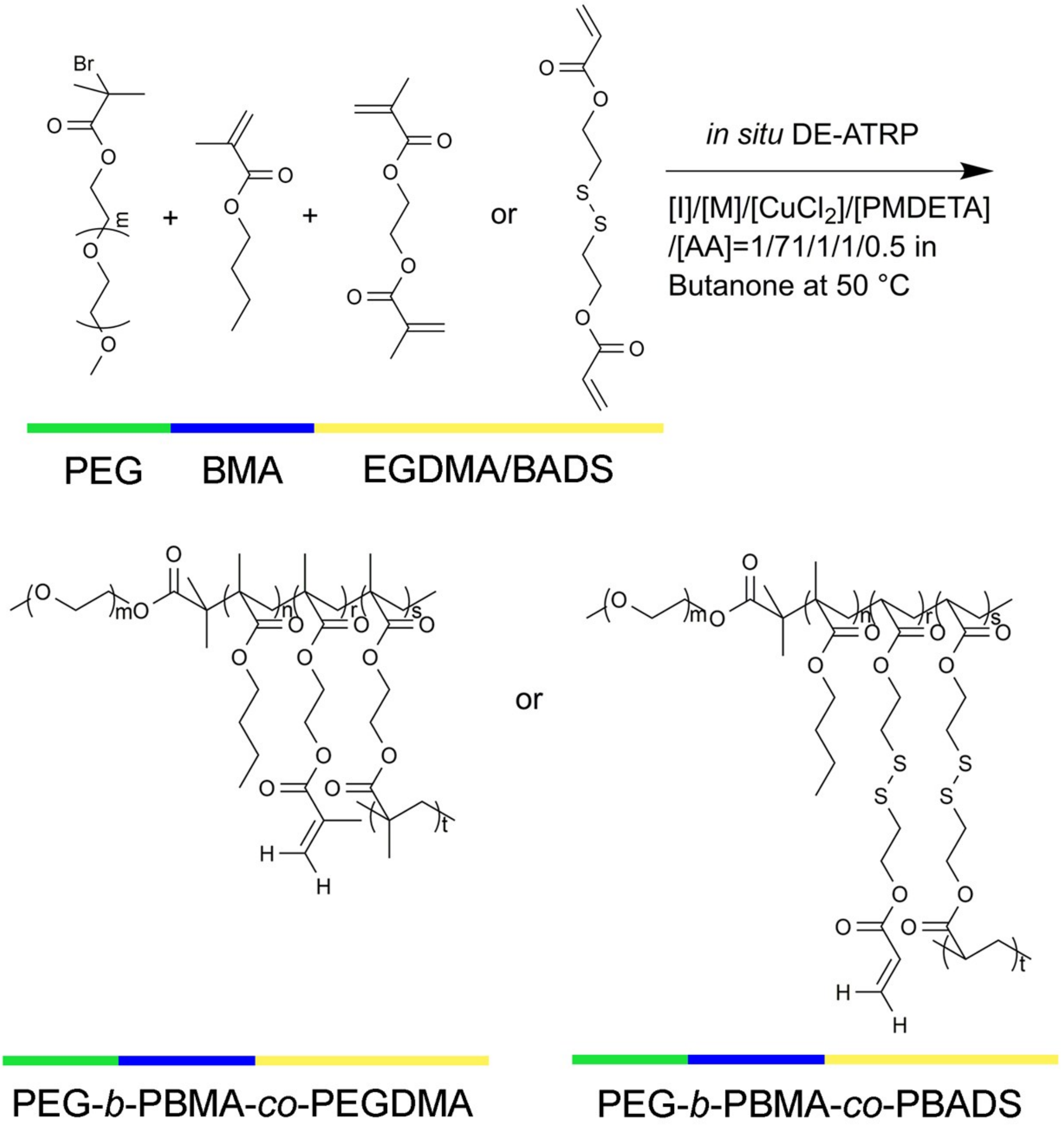
1. Supporting data



Scheme S1. Synthesis of PEG-*b*-PBMA-*co*-PEGDMA (BE) and PEG-*b*-PBMA-*co*-PBADS (BS) by a modified DE-ATRP.

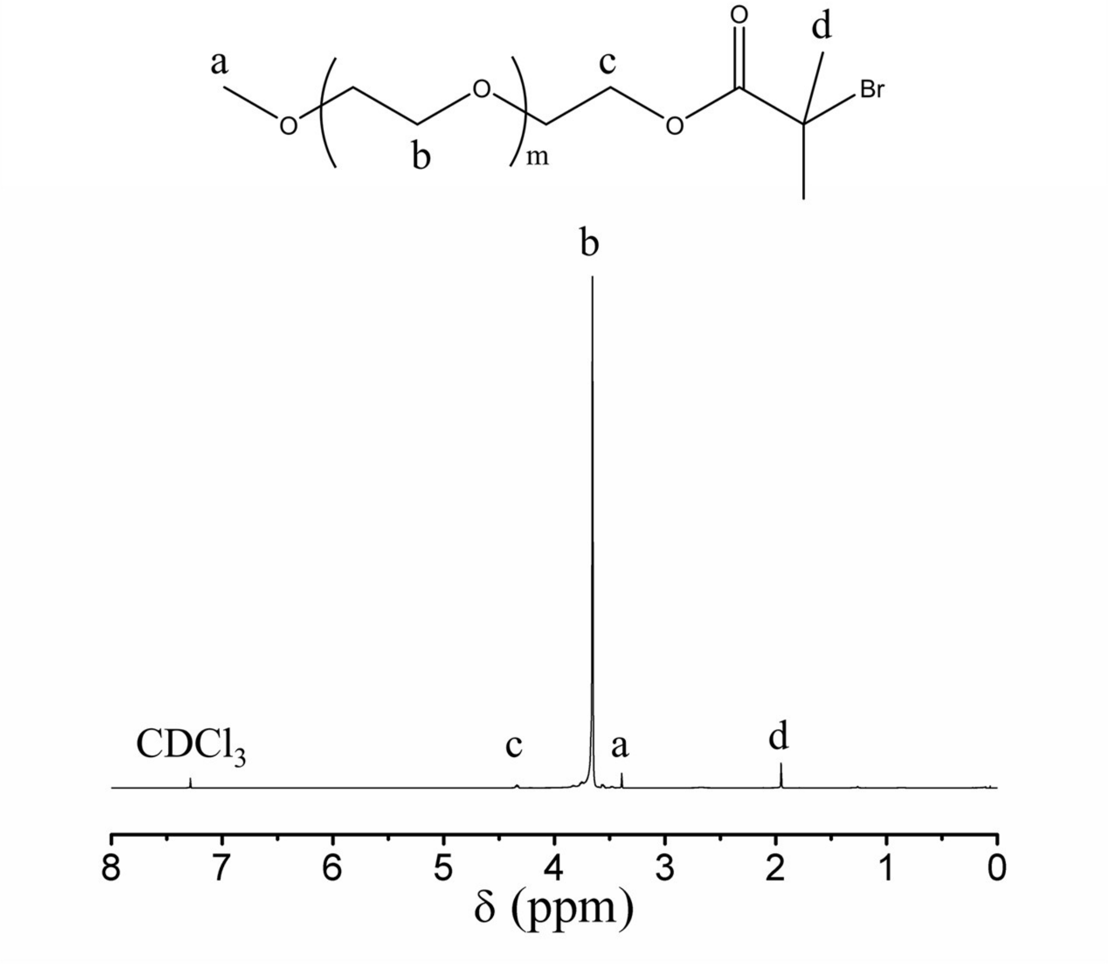


Fig. S1 ^{1}H NMR spectra of PEG2K macroinitiaor.

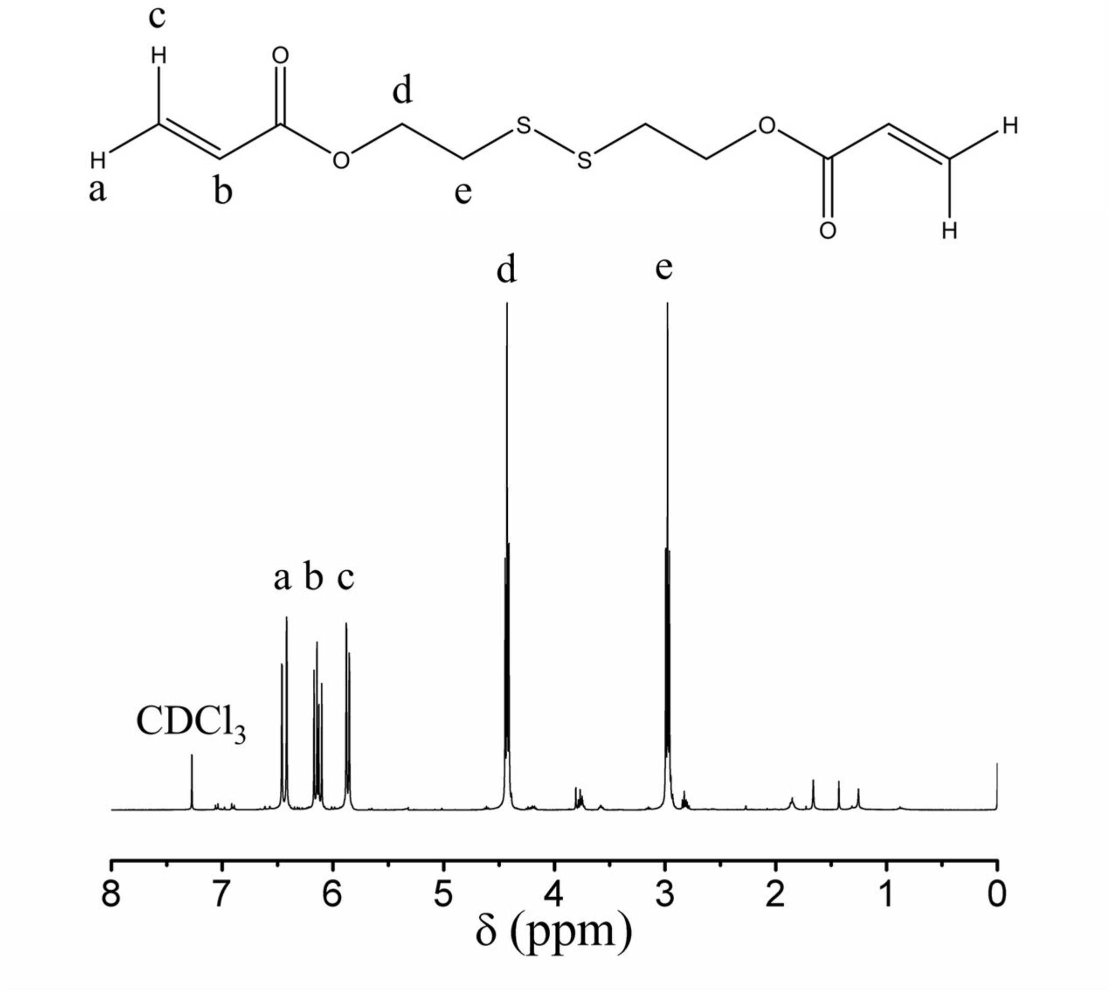


Fig. S2 ^{1}H NMR spectra of bis(2-acryloyl)oxyethyl disulphide (BADS).

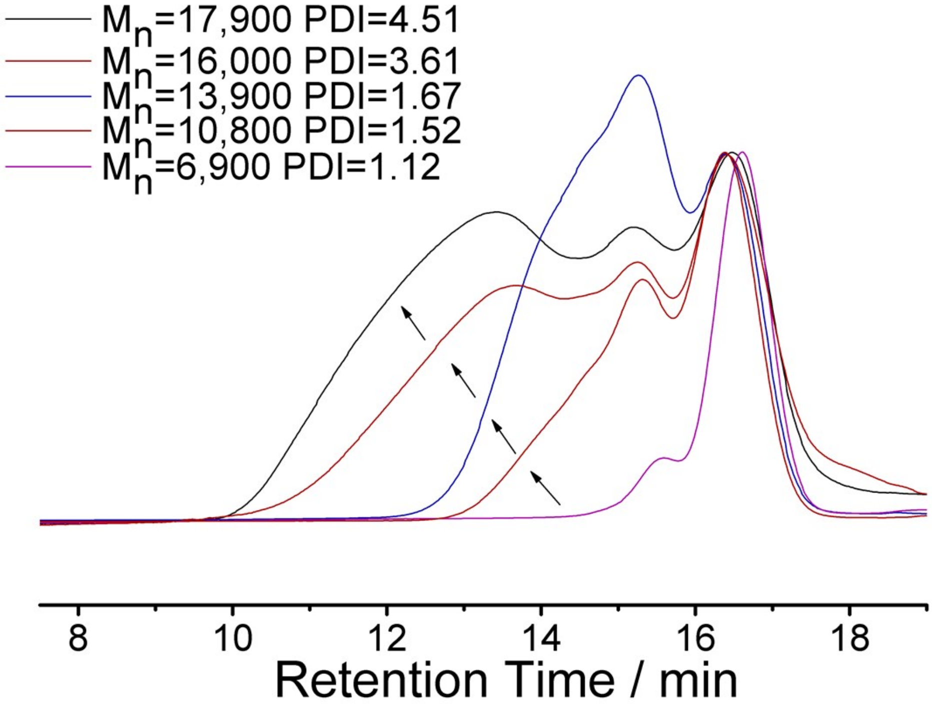


Fig. S3. Gel permeation chromatograms of BS with different molecular weights. All polymers are purified.

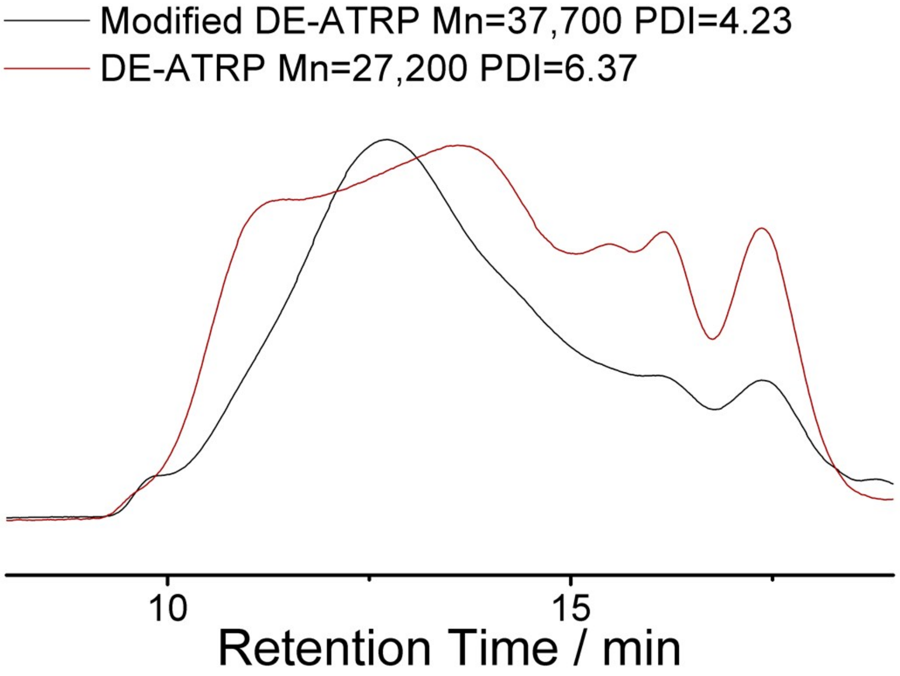


Fig. S4. Gel permeation chromatograms of BE synthesized by DE-ATRP and modified DE-ATRP, 50˚C, 24h.

DE-ATRP:[I]/[$CuCl_2$]/[PMDETA]/[AA]=1/0.25/0.25/0.05

Modified DE-ATRP:[I]/[$CuCl_2$]/[PMDETA]/[AA]=1/1/1/0.5

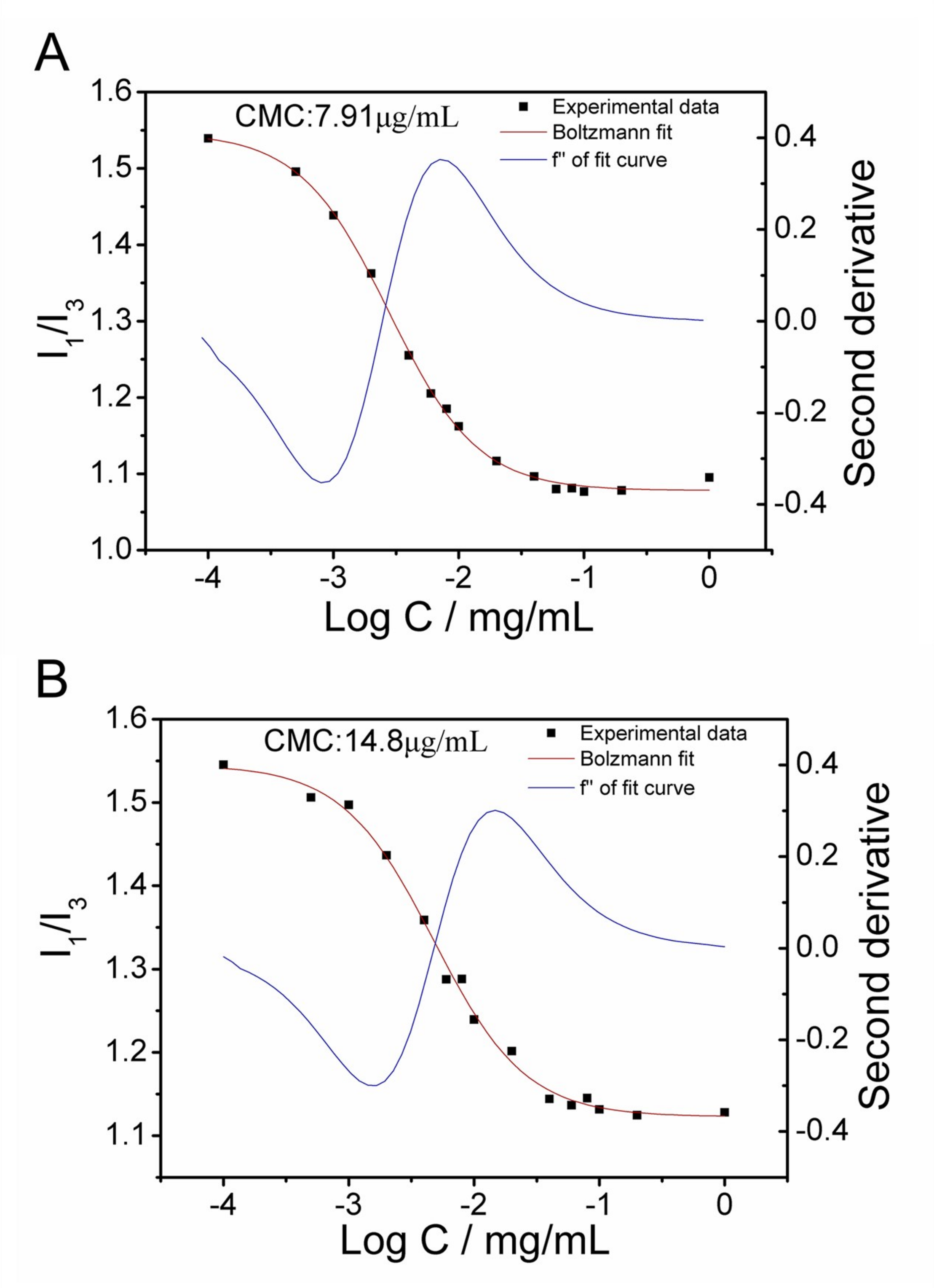


Fig. S5. Plots of fluorescence emission intensity ratio I1/I3 (I373/I383) versus concentration of BE (A) and BS (B) copolymers.

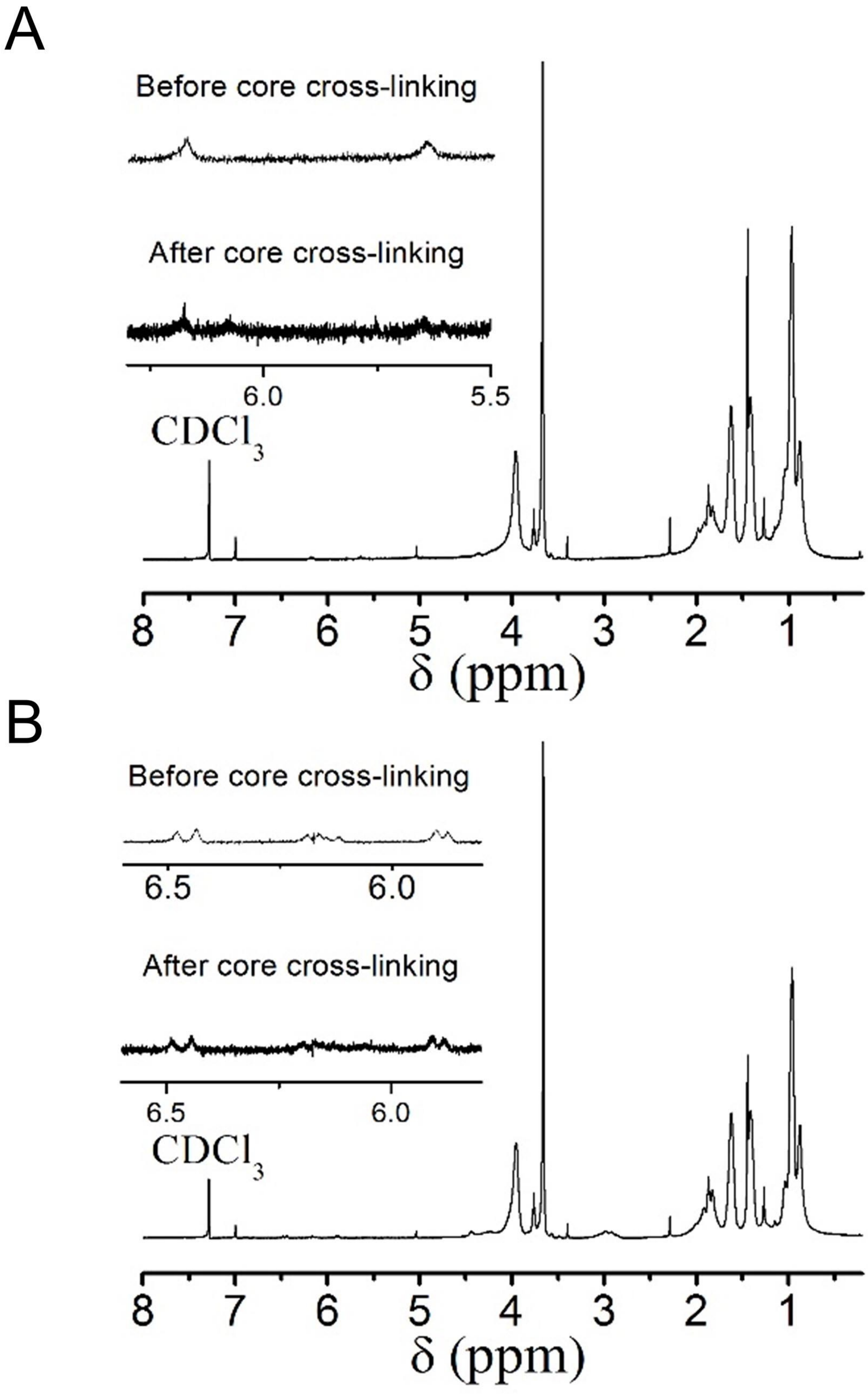
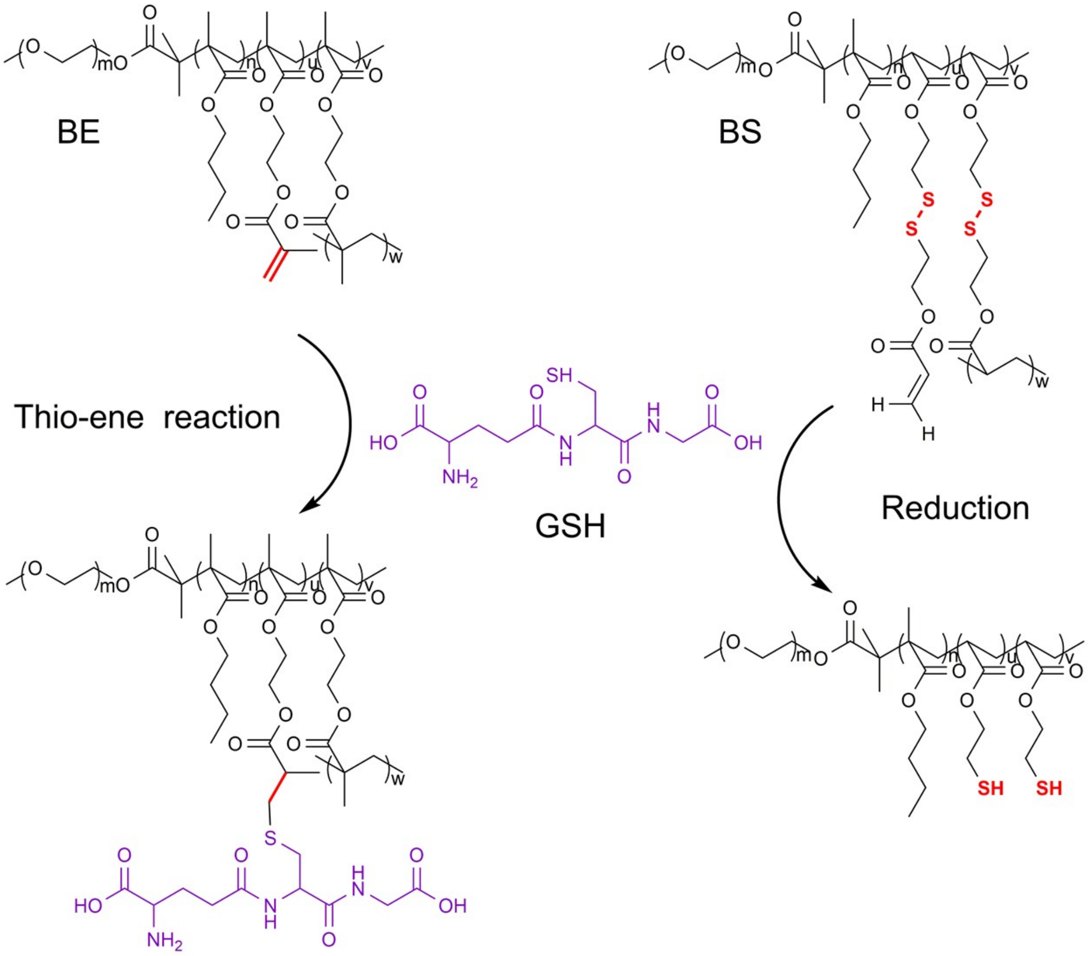


Fig. S6. ^{1}H NMR spectra of BE (A) and BS (B) before and after 48 hrs core cross-linking.



Scheme S2. The reaction mechanism of GSH response for BE and BS.

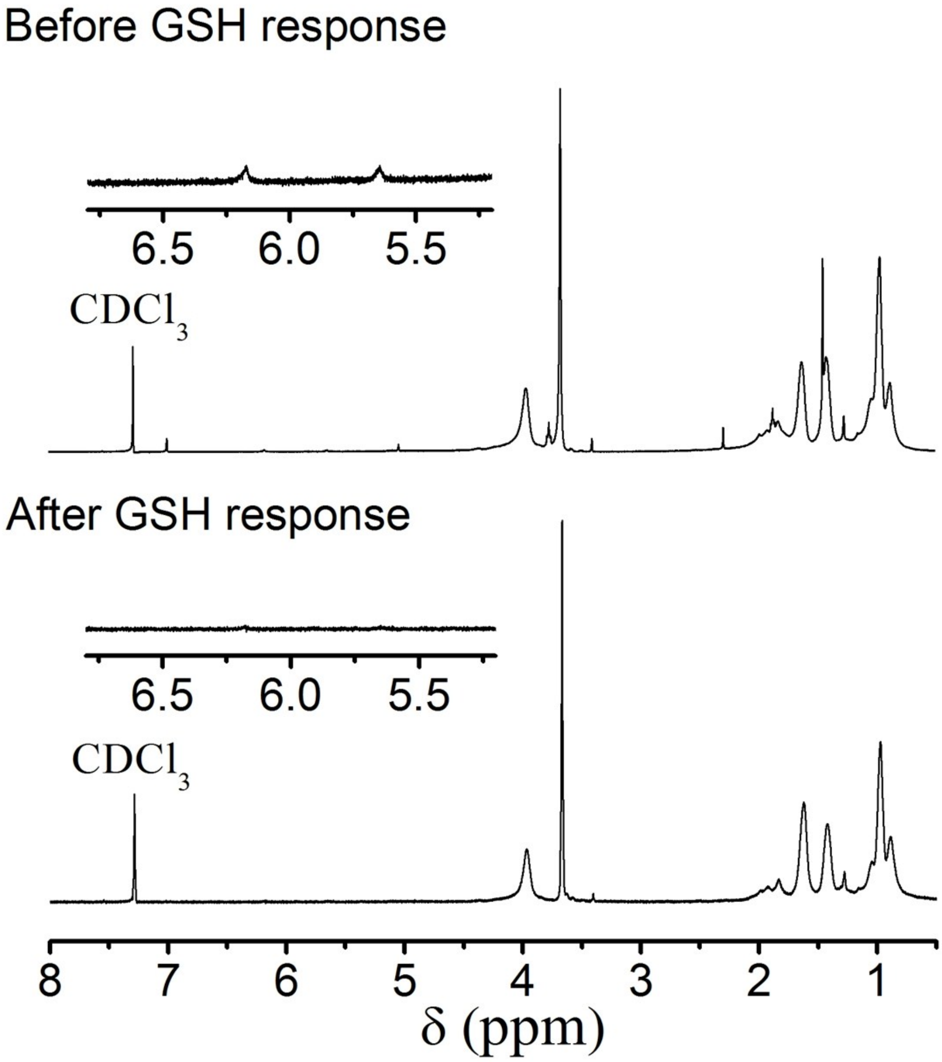


Fig. S7. ^{1}H NMR spectra of BE before and after GSH response for 24 hrs.

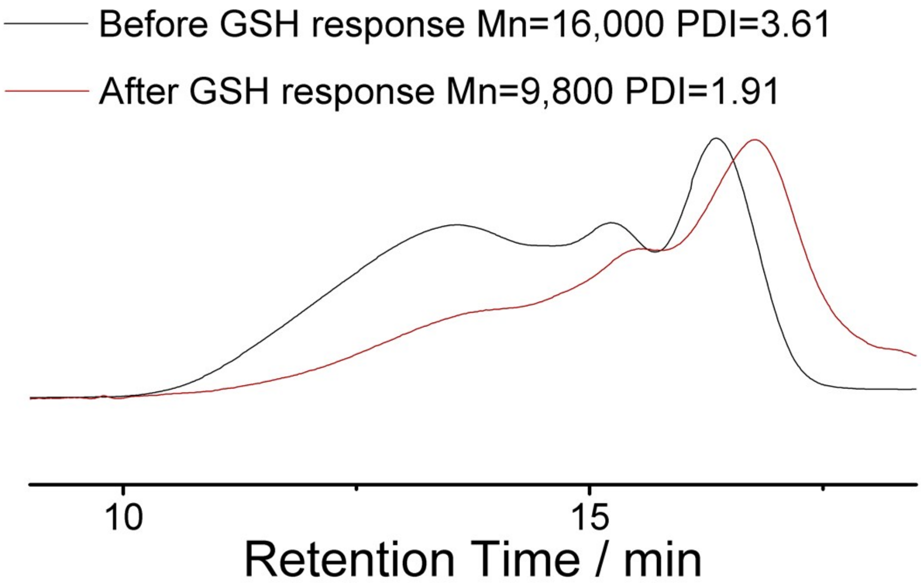


Fig. S8. Gel permeation chromatograms of BS before and after GSH response for 24 hrs.

2. Branched percent calculation

The M_n of cyclized molecules is ~7000, we can calculate the average number of cyclized molecules that branched together from the M_n of polymers (we set the number of initiator as 1):

$$\frac{Mn}{7000}$$

The number of double-vinyl monomers consumed in branching reaction:

$$\frac{Mn}{7000} - 1$$

We know the ratio of double-vinyl monomers/initiator=R from ^1H NMR (R=6.3 for BE and 5.1 for BS). So the total number of double-vinyl monomers:

$$\frac{Mn}{7000} \times R$$

Finally, we can calculate the branched percent (%):

$$BP(\%) = \frac{\frac{Mn}{7000} - 1}{Mn/7000} \times \frac{1}{R} \times 100\%$$

The equation is based on an assumption that no cross link net existing in polymers.