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-\textit{b}-PBMA-\textit{co}-PEGDMA (BE) and PEG-\textit{b}-PBMA-\textit{co}-PBADS (BS) by a modified DE-ATRP.

\[ \text{PEG} \quad \text{BMA} \quad \text{EGDMA/BADS} \]

\[ \text{PEG-}b\text{-PBMA-}co\text{-PEGDMA} \quad \text{PEG-}b\text{-PBMA-}co\text{-PBADS} \]
Fig. S1 $^1$H NMR spectra of PEG2K macroinitiator.
Fig. S2 $^1$H NMR spectra of bis(2-acryloyloxyethyl 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]/[CuCl₂]/[PMDETA]/[AA] = 1/0.25/0.25/0.05
Modified DE-ATRP: [I]/[CuCl₂]/[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.

Before GSH response $M_n=16,000$ PDI=3.61
After GSH response $M_n=9,800$ PDI=1.91
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): 

$$\frac{M_n}{7000}$$

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

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

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

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

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

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

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