

Electronic Supplementary Material (ESI) for Polymer Chemistry.

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SUPPORTING INFORMATION

Degradable pH and Redox Dual Responsive Nanoparticles for Efficient Covalent Drug Delivery

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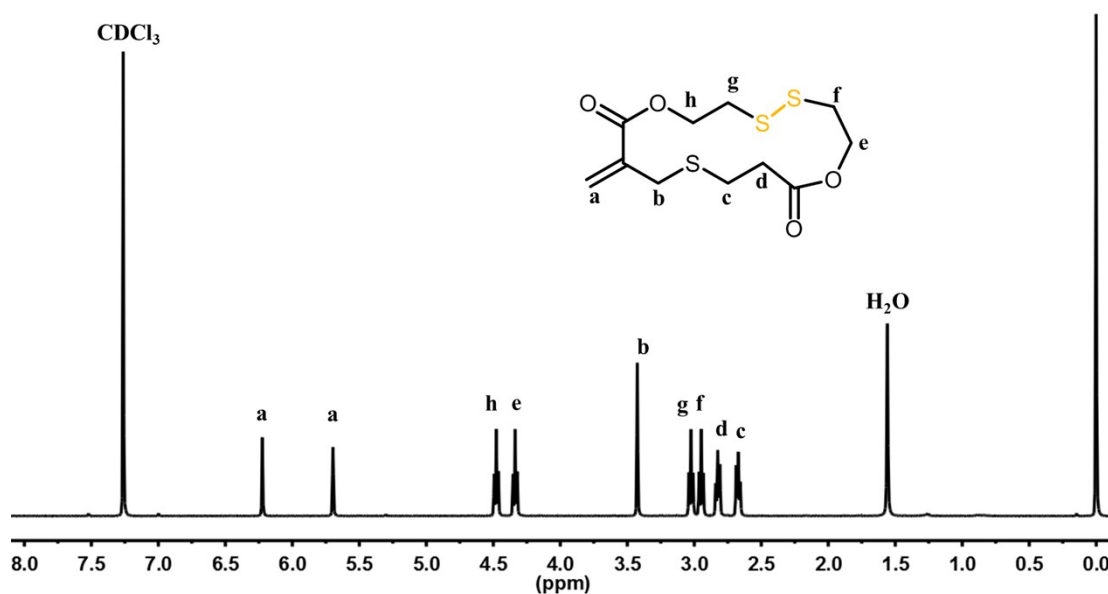


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of MTC monomer.

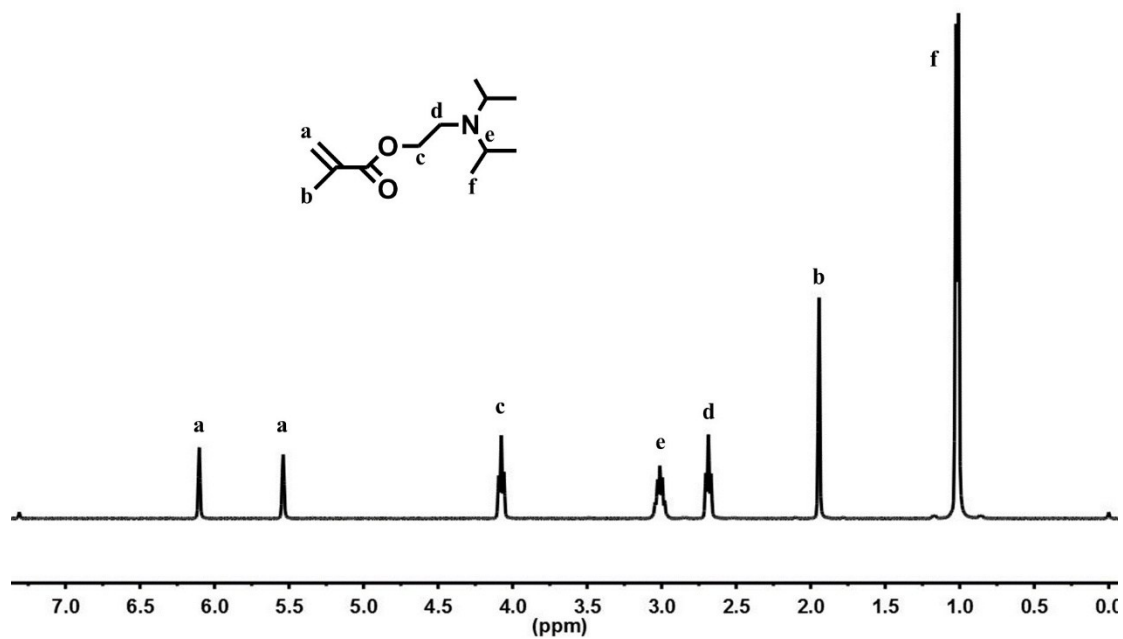


Figure S2. ¹H NMR (400 MHz, CDCl₃) spectrum of DPAEMA monomer.

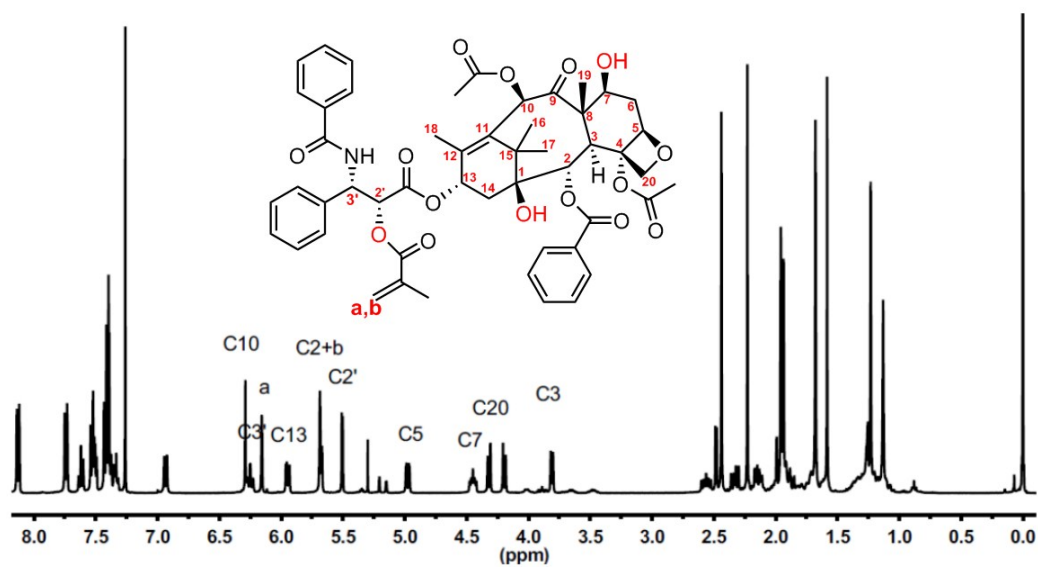


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of PTXMA monomer.

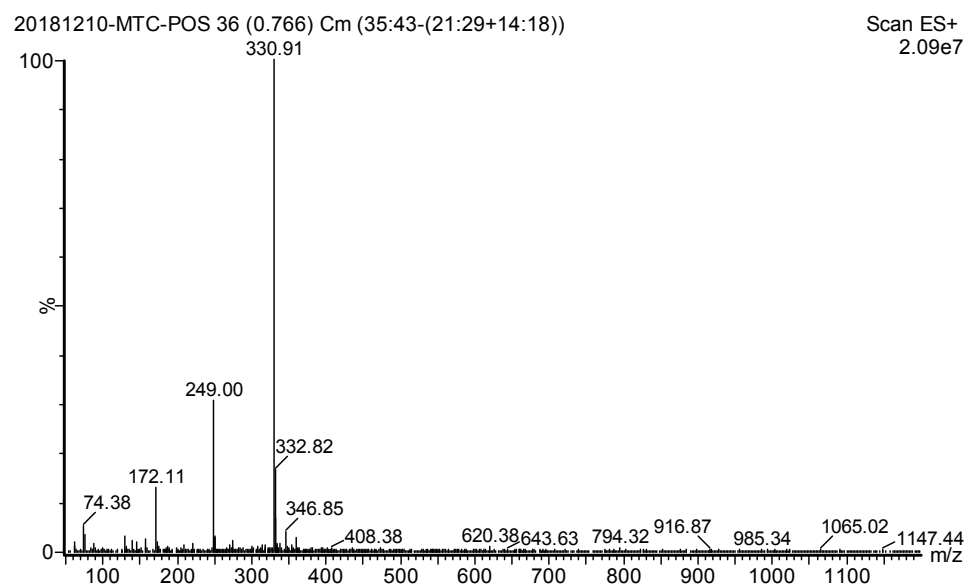


Figure S4. Mass Spectrometry of MTC monomer. ESI-MS m/z: 330.91 [MTC + Na⁺].

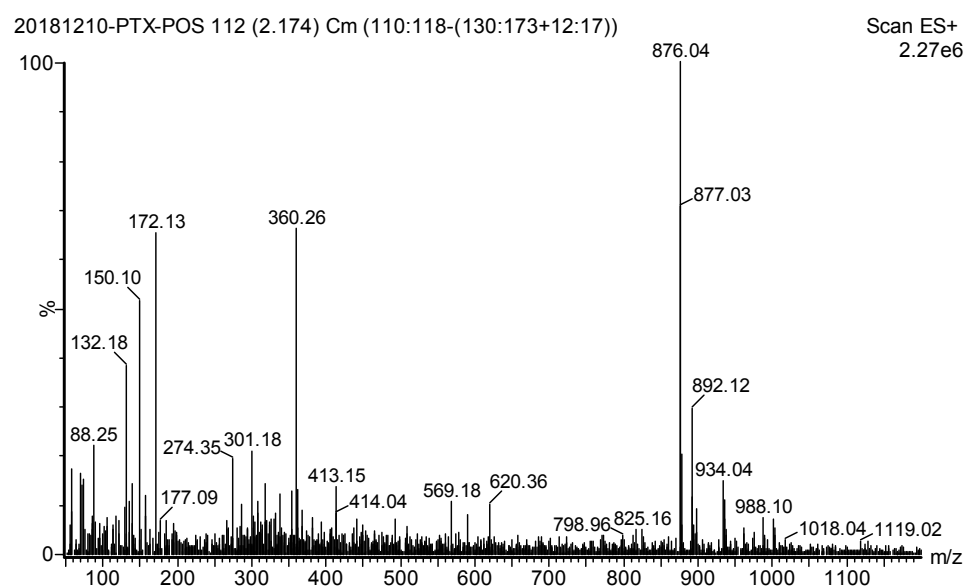


Figure S5. Mass Spectrometry of PTX. ESI-MS m/z: 877.03 [PTX + Na⁺].

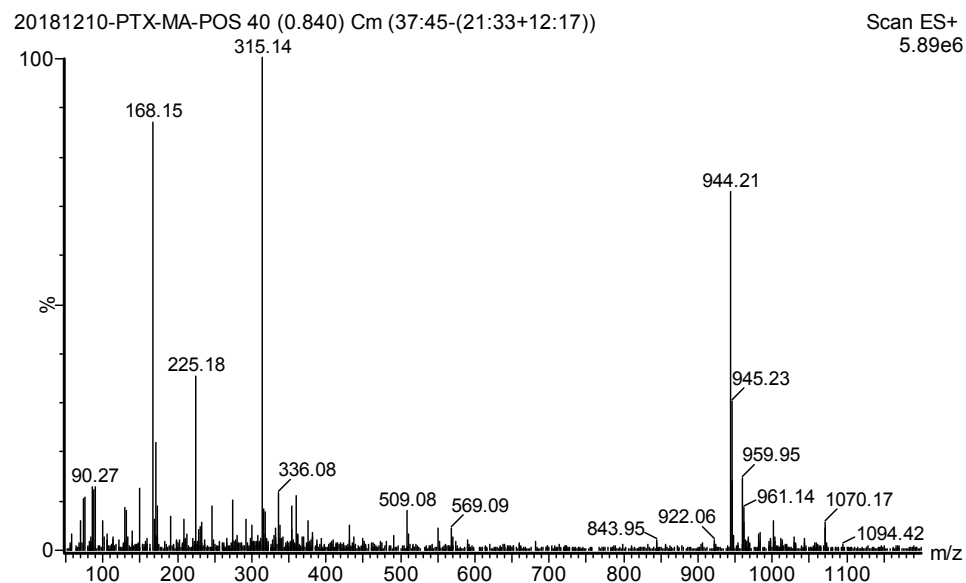


Figure S6. Mass Spectrometry of PTXMA monomer. ESI-MS m/z: 944.21 [PTXMA + Na⁺].

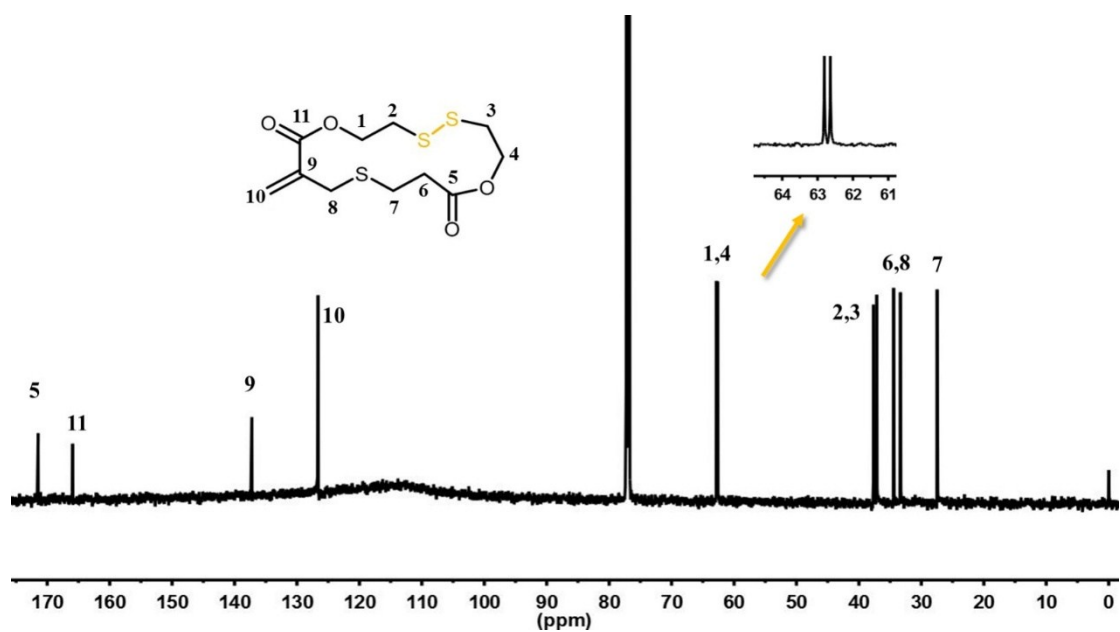


Figure S7. ¹³C NMR (400 MHz, CDCl₃) spectrum of MTC monomer.

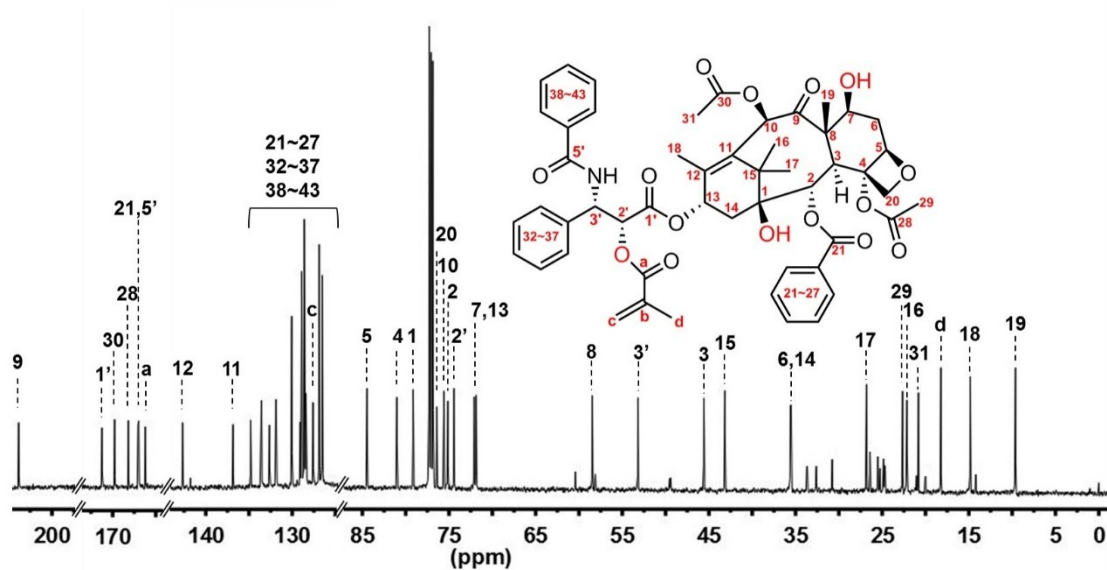


Figure S8. ^{13}C NMR (400 MHz, CDCl_3) spectrum of PTXMA monomer. There are some solvent peaks as we used dichloromethane, dimethylformamide, tetrahydrofuran, ethyl acetate and *n*-hexane during the synthesis and purification of the PTXMA.

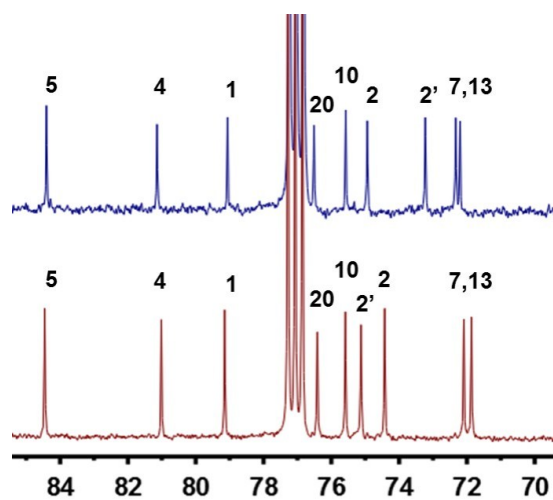


Figure S9. ^{13}C NMR (400 MHz, CDCl_3) spectrum of PTX (upper) compared with PTXMA (blow).

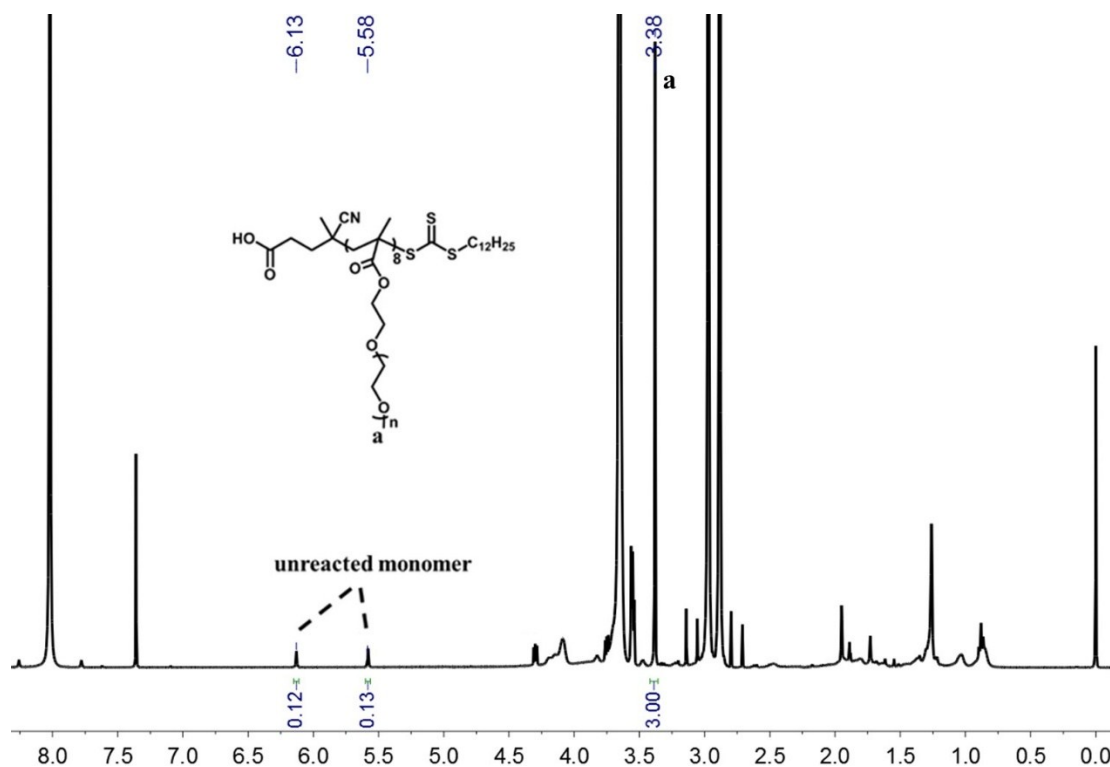


Figure S10. ^1H NMR (400 MHz, CDCl_3) spectrum of crude product POEGMA₈ Macro-CTA.

From the ^1H NMR data we used peak a and unreacted monomer to calculate the repeat units. We set peak a as 3 which represent the methyl group of the OEGMA (no matter reacted or not) and integrated it against the unreacted double bond (the integral is 0.13). Thus, the conversion of Macro-CTA is about 87 %, and the repeat units $9 \times 0.87 \approx 8$. The M_n of POEGMA₈ Macro-CTA 403(the molecular weight of DTTCP)+ $8 \times 475=4203$. We use the same method to calculate the M_n of group 2 and 3. Compared with the peak a, in group we use peak f, g shown in Figure 1 to calculate the repeated units. And in group 3 we used peak f, g, 2' and d shown in Figure 1 to calculate the repeated units and M_n .

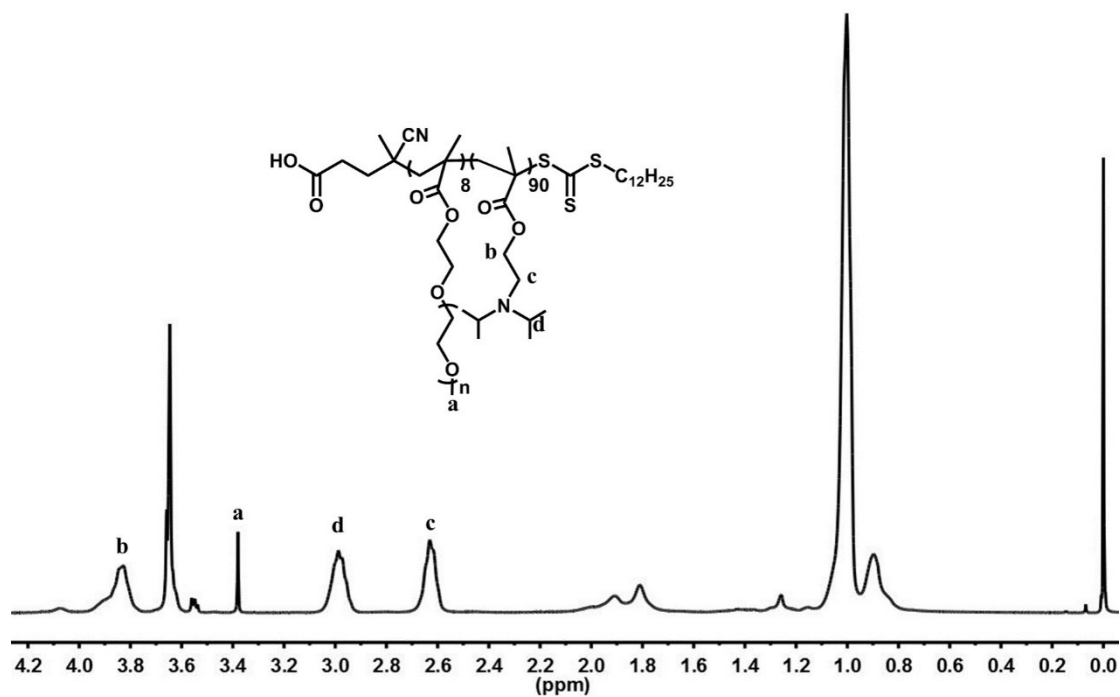


Figure S11. ^1H NMR (400 MHz, CDCl_3) spectrum of $\text{OEGMA}_8\text{-}b\text{-PDPAEMA}_{90}$.

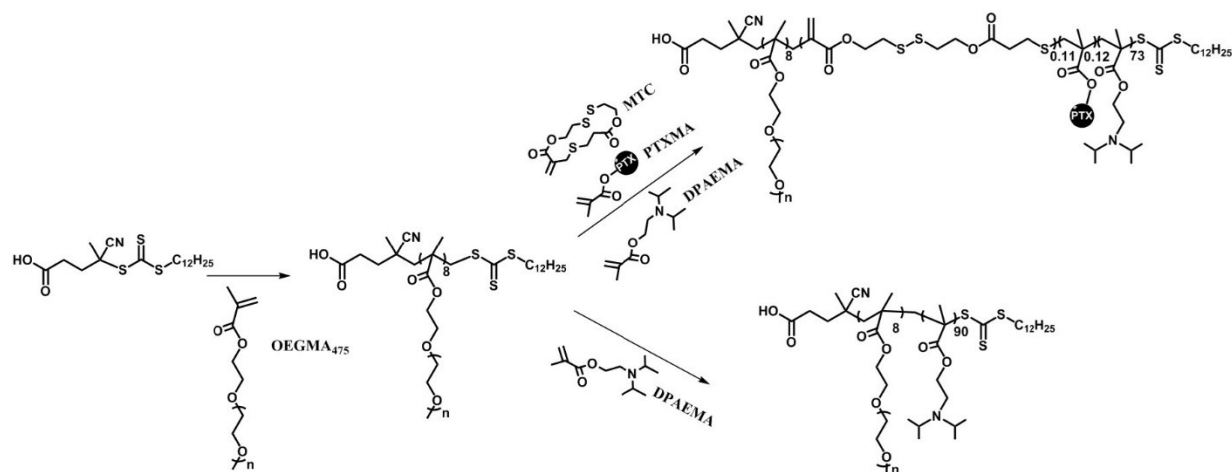


Figure S12. Synthesis of diblock copolymers $\text{POEGMA}_8\text{-}b\text{-P}(\text{DPAEMA}_{73}\text{-co-PTXMA}_{0.12}\text{-co-MTC}_{0.11})$ and $\text{POEGMA}_8\text{-}b\text{-PDPAEMA}_{90}$ via RAFT polymerization.

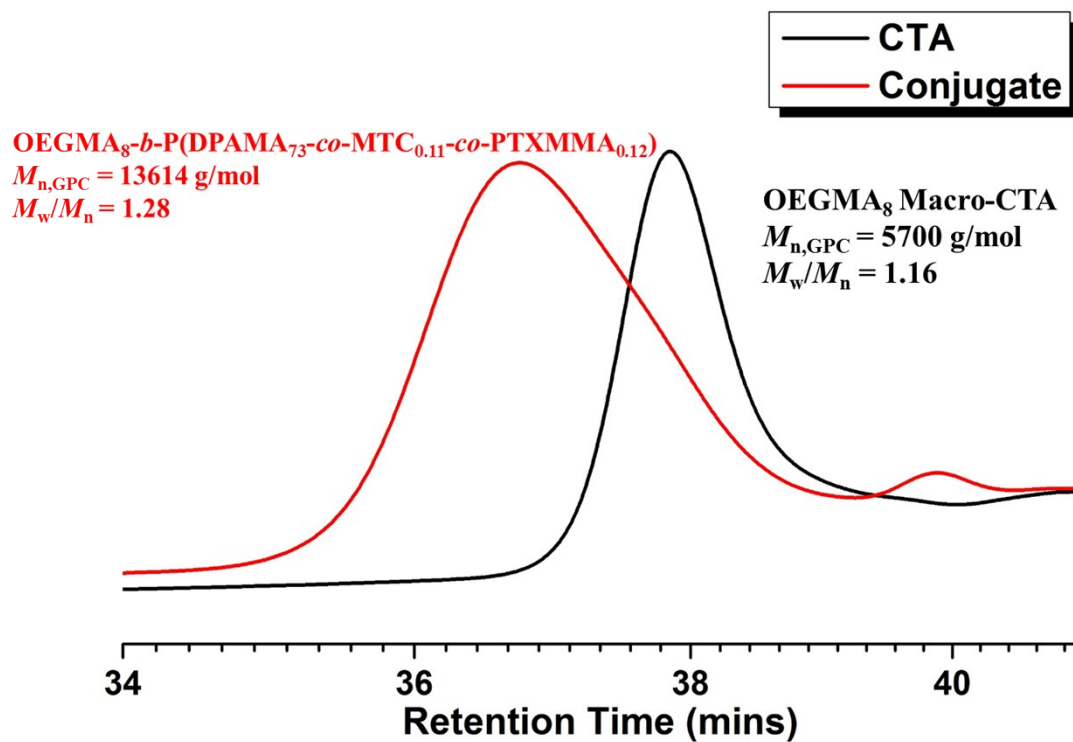
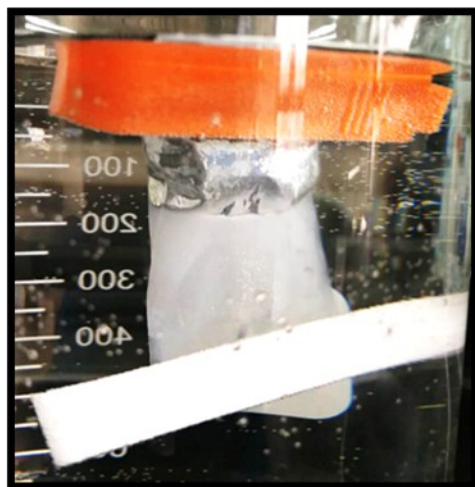


Figure S13. GPC traces of POEGMA₈-*b*-P(DPAEMA₇₃-*co*-PTXMMA_{0.12}-*co*-MTC_{0.11}) and POEGMA₈ Macro-CTA using DMAc as mobile phase.

pH= 7.4



pH= 5.0

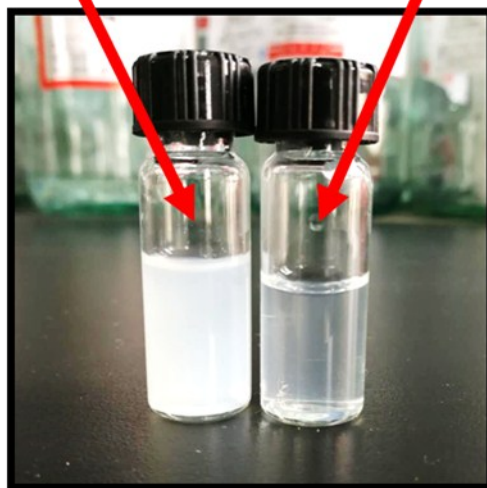
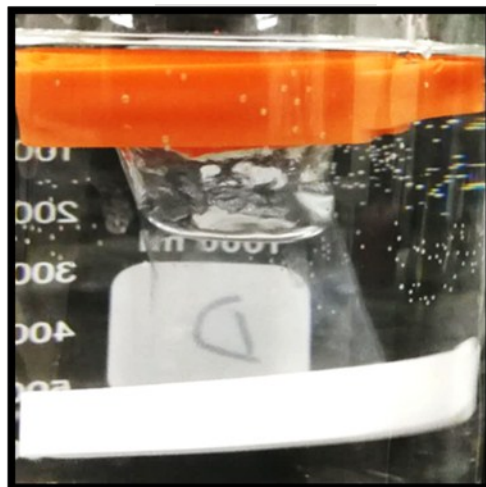


Figure S14. The pH responsiveness of the aqueous solution of self-assemblies observed by naked eyes. The solubility of DPAEMA has changed from hydrophobic to hydrophilic which can be clearly observed. The sample changed from turbid to clear under the acidic condition.

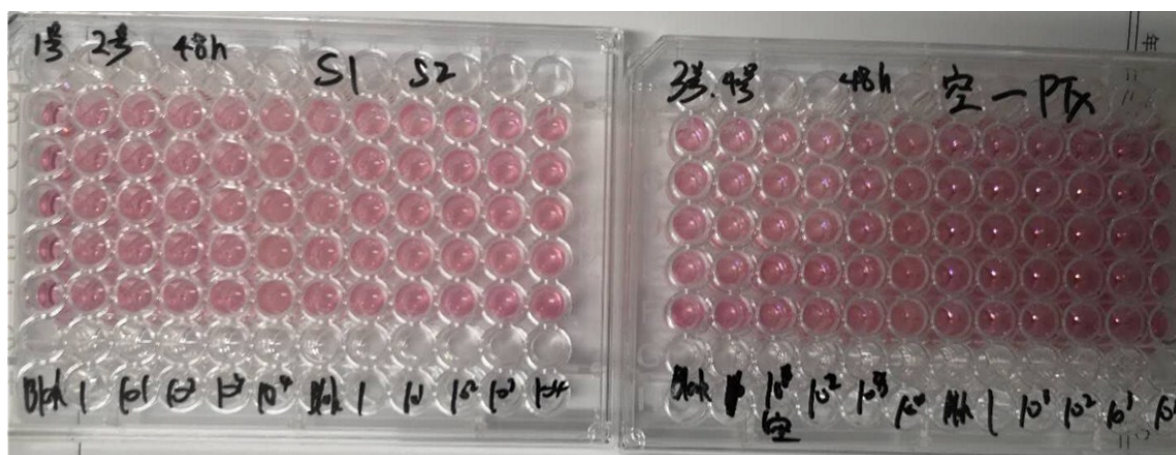


Figure S15. In vitro study before adding MTT.

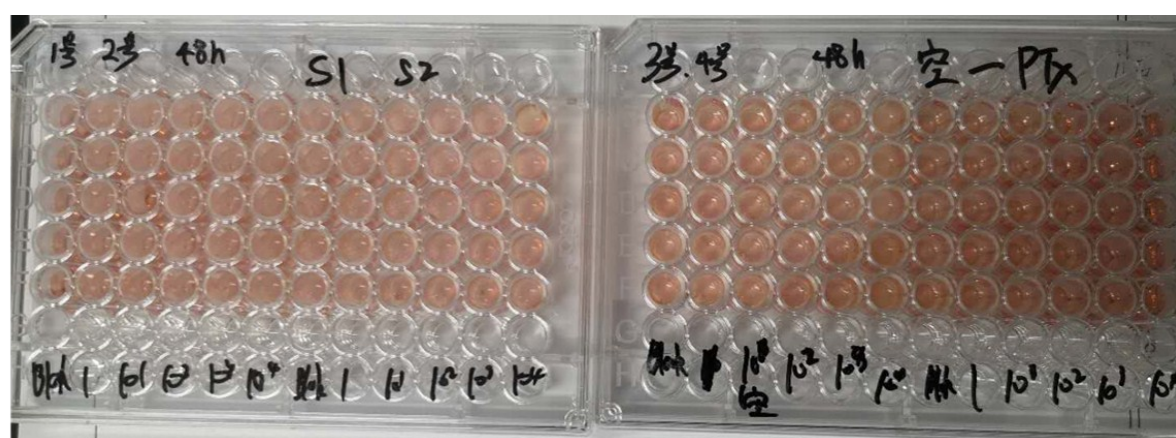


Figure S16. The color change of the system in vitro study after adding MTT (200 μ L, 0.5 mg/mL).

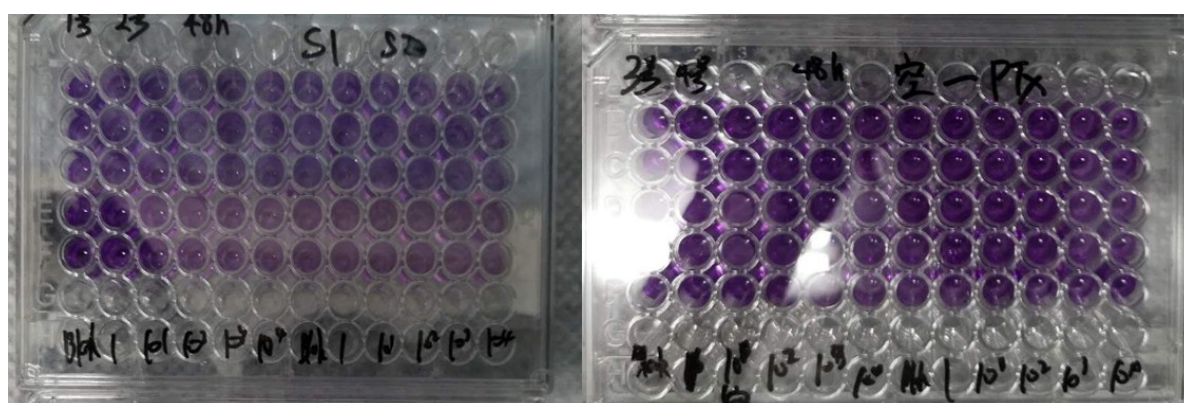


Figure S17. The color change of the system in vitro study after adding DMSO (150 μ L).