

Supporting Information for

Reductively and Hydrolytically Dual Degradable Nanoparticles by “Click” Crosslinking of Multifunctional Diblock Copolymer

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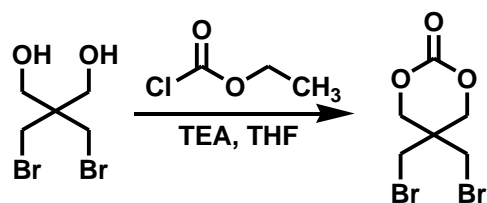
Synthesis of 5,5-dibromomethyl trimethylene carbonate (Scheme S1; DBTC).

Dibromoneopentyl glycol (8.9 g, 34 mmol) and ethyl chloroformate (6.5 mL, 68 mmol) were dissolved in 250 mL anhydrous THF, then the mixture was stirred at 0 °C for 30 min, TEA (9.5 mL, 68 mmol) was added dropwise within 25 min. The solution was stirred overnight at room temperature. After filtering the precipitate, the filtrate was concentrated on a rotary evaporator, the concentrated oil-like liquid was precipitated into ethyl ether. 4.95 g of the resulting white solid in 50.6 % yield was

obtained after drying the product under vacuum overnight. Fig. S1 shows ^1H NMR spectrum of the product. ^1H NMR (400 MHz, CDCl_3), d: 4.41(s, 4H, $-\text{OCH}_2-$), 3.59 (s, 4H, $-\text{CH}_2\text{Br}$).

Synthesis and Characterization of propargyl 3,3'-dithiopropionate (Scheme S2).

2.1 g of 3,3'-dithiodipropionic acid (10 mmol) and 1.2 g of KOH (21.5 mmol) were dissolved in 25 mL DMF, stirred at 100 °C for 1.5 h. Then 2.38 g of propargyl bromide (20 mmol) was added dropwise to the solution during 0.5 h. After that, the mixture was stirred and reacted at 70 °C for 72 h, then terminated the reaction by cooling to room temperature. After filtration and concentration on a rotary evaporator, the residue was dissolved in CH_2Cl_2 and then washed three times with distilled water. Dried the organic layer with anhydrous MgSO_4 , and then removed CH_2Cl_2 in vacuum to obtain the product. 1.35 g of a brown viscous liquid in 47% yield was obtained after drying the product under vacuum overnight. Fig. S2 shows ^1H NMR spectrum of the product. ^1H NMR (400 MHz, CDCl_3), d: 2.5 (s, 2H, $-\text{CH}_2\text{C}\equiv\text{CH}$), 2.7 (t, 4H, $-\text{CH}_2\text{CO}-$), 2.9 (t, 4H, $-\text{SCH}_2-$), 4.7 (m, 4H, $-\text{CH}_2\text{C}\equiv\text{CH}$). Unfortunately, the DMF solvent was not removed completely for its high boiling point. However, the amount of DMF in the product could be calculated by the integral ratio of corresponding proton in ^1H NMR spectrum and the following “click” reaction was carried out in DMF media, which makes it possible to proceed the “click” reaction precisely.



Scheme S1 Synthesis of 5,5-dibromomethyl trimethylene carbonate(DBTC).



Scheme S2 Synthesis of propargyl 3,3'-dithiopropionate.

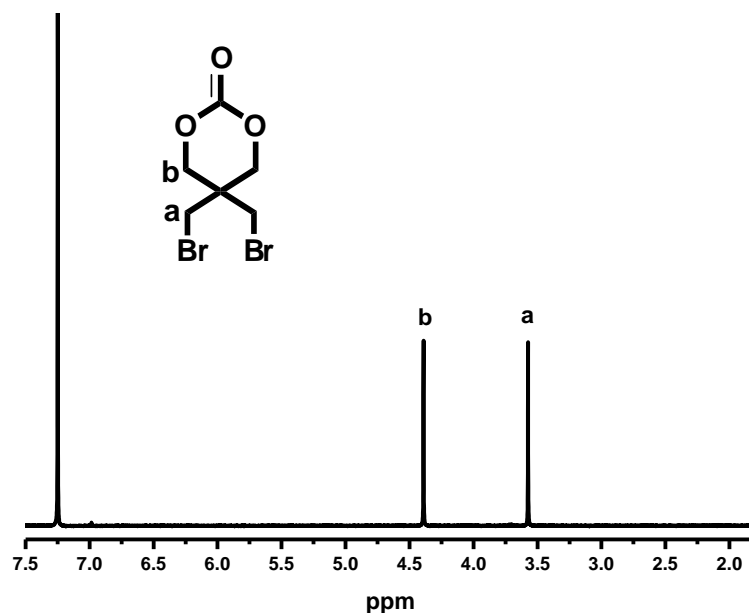


Fig. S1 ¹H NMR spectrum of 5,5-dibromomethyl trimethylene carbonate (DBTC).

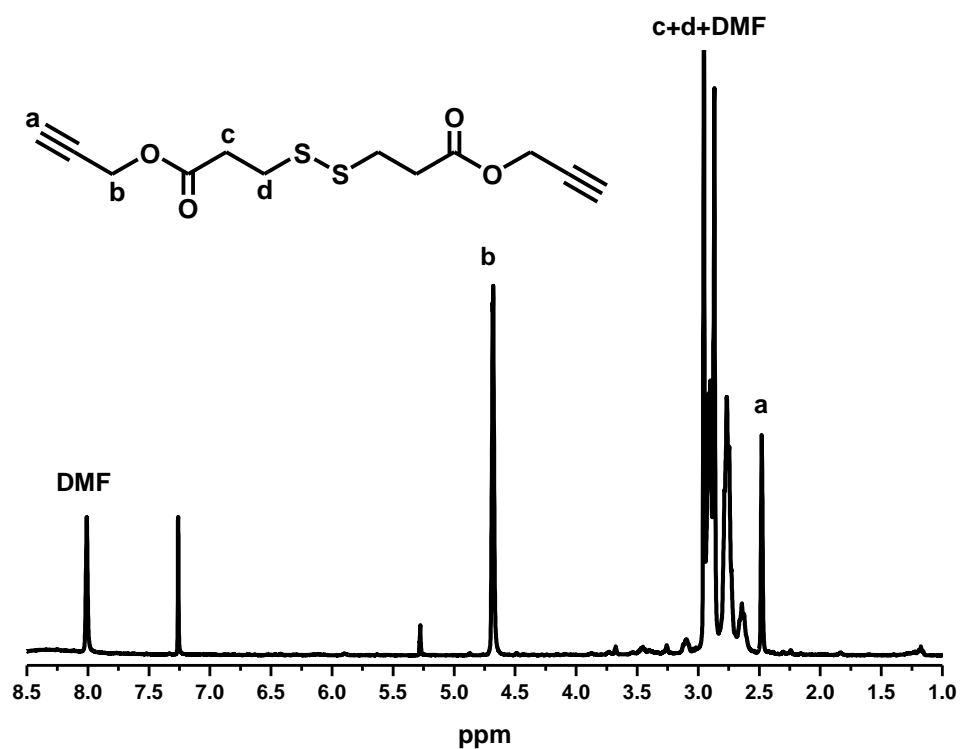


Fig. S2 ¹H NMR spectrum of propargyl 3,3'-dithiopropionate.