Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for

Supramolecular polymer fabricated by click polymerization from supramonomer

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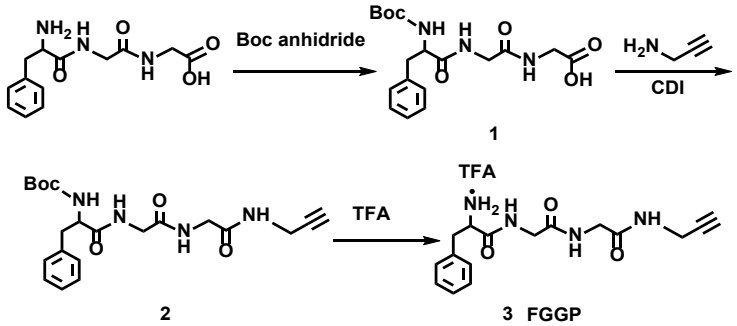
1. Experimental Section



Scheme S1. Synthesis route of FGGP.

Compound 1 FGG (83.8mg,0.3 mmol) was dissolved into 1 mL 0.5 mol/L Na_2CO_3 aqueous solution, and 1 mL THF containing Boc_2O (98.2 mg, 4.5 mmol) was added dropwise into the solution in the ice-water bath with stirring. After 30 min, the mixture was warmed up to room temperature, and kept reaction for 12 h. The solution was then acidified by dilute HCl (0.5 mol/L) until pH = 1, with white precipitate generated. The solution was extracted with ethyl acetate (3×5 mL). The organic phase were then mixed, dried over $MgSO_4$ and filtered. After concentration in vacuo, the product was purified by column chromatography (silica, CH_2Cl_2/CH_3OH= 10:1) to give the product (102.4 mg, 90%) as a white powder. ^1H NMR (400 MHz, CD_3OD, ppm): δ = 7.30 -7.19 (m, 5H), 5.20 (1H), 4.27 (dd, 1H), 3.96 - 3.74 (m, 4H), 3.17 - 3.12 (dd, 1H), 2.90 - 2.84 (dd, 1H), 1.37 (s, 9H).

Compound 2 Compound **1**(75.8mg, 0.2 mmol) was dissolved into 1 mL anhydrous CH_2Cl_2, then *N*, *N*′-carbonyldiimidazole (71.3 mg, 0.44 mmol) was added into the solution. The solution was stirred under N_2 atmosphere for 6 h at room temperature. Then propargyl amine (11.0 mg, 0.2 mmol) was added. The solution was stirred for another 6 h at room temperature. Then 10mL dilute HCl (0.5 mol/L) was added into the solution. The solution was extracted with CH_2Cl_2 (3×5 mL). The organic phase were mixed, dried over $MgSO_4$ and filtered. After concentration in vacuo, the product was purified by column chromatography (silica, CH_2Cl_2/CH_3OH = 10: 1) to give the product (74.9 mg,

95%) as a white solid.^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.30 - 7.21 (m, 5H), 4.24 (dd, 1H), 3.97 (d, J = 2.5Hz, 2H), 3.92 (d, J = 16.7, 1H), 3.85 (s, 2H), 3.73 (d, 1H), 3.13 (dd, 1H), 2.88 (dd, 1H), 2.57 (t, J = 2.5 Hz, 1H), 1.37 (s, 9H).

Compound 3 Compound **2** (74.9 mg, 0.18 mmol) was stirred in CF_3COOH/CH_2Cl_2 (1:1, 1mL) for 1 h at room temperature. The solvent was removed in vacuo, and the obtained sticky solid was precipitated by diethyl ether. The precipitate was collected by filtration and washed with diethyl ether. After dried in vacuo to obtain light yellow powder (67.6 mg, 99%).^{1}H NMR (400 MHz, D_2O, ppm): δ = 7.44 - 7.32 (m, 5H), 4.33 (dd, 1H), 4.04 - 3.90 (m, 6H), 3.25 (d, J = 7.2Hz, 2H), 2.63 (s, 1H). ESI-MS: m/z=317.1 $[M+H]^+$.

Click Polymerization FGGP (1.72 mg, 4 μmol) and CB[8] (2 μmol) were first dissolved in 1 mL water to obtain supramonomer FGGP-CB solution (2 mM), then N_3-PEG-N_3 (4.12 mg, 2 μmol) was dissolved in solution. The solution was bubbled by argon for 30 min, then ascorbic acid (0.18 mg, 1 μmol) and $CuSO_4 \cdot 5H_2O$ (0.13 mg, 0.5 μmol) were added into the solution. The solution was sealed up, and click polymerization was performed assisted by ultrasound oscillation for 2 h.

2. Characterization of supramonomer

The formation of the supramonomer was evidenced by ESI-MS (Figure S1). The molecular weight of CB[8] is 1329.12 Da, while FGGP is 316.36 Da, therefore, the mass-to-charge ratio of molecular ion peak at 981.85 strongly indicated doubly charged supramonomers.

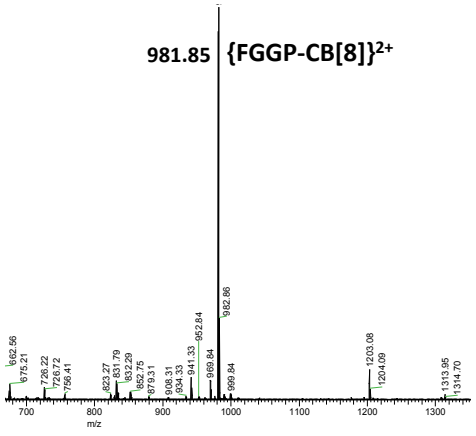


Figure S1.ESI-MS spectrum of supramonomer (FGGP-CB[8]) .

In the FTIR spectra (Figure S2), the azide group band at 2100 cm^{-1} disappeared, indicating completion of the click polymerization.

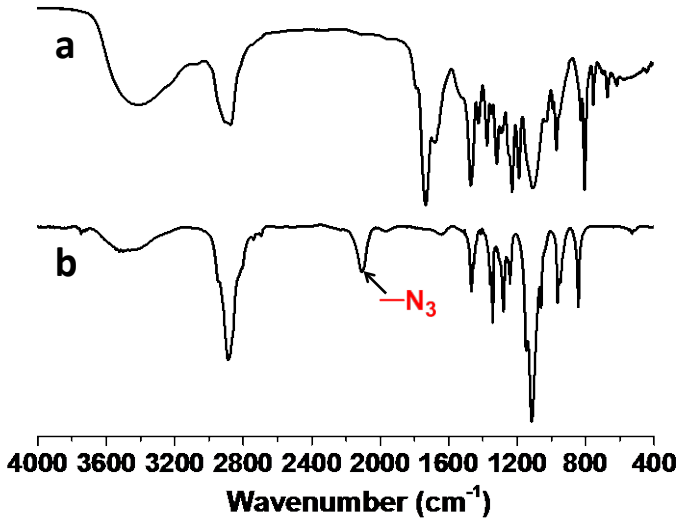


Figure S2. FTIR spectra of (a) supramolecular polymer and (b) N_3-PEG-N_3.

3. Degradation of supramolecular polymer

As shown in Figure S3, on adding triethylamine, the ^{1}H NMR signals of the aromatic group of FGGP shifted downfield and returned to the state before complexing with CB[8]. This suggests decomposition of the FGGP–CB[8] complex, leading to depolymerization of the supramolecular polymer.

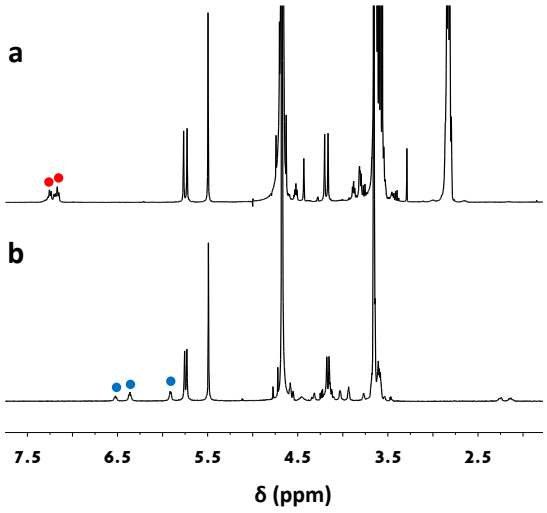


Figure S3. ^{1}H NMR spectra of supramolecular polymers after (a) and before (b) degenerated by TEA.

4. Characterization of one-pot supramolecular polymerization

As indicated by the ^{1}H NMR spectrum (Figure S4), the supramonomers were formed in minutes by rapid complexation between FGGP and CB[8]. However, at the same time, the click reaction was still at the initial stage. Click reactions finally completed after 2 h. These results

indicated that the supramolecular complexation and click reaction did not interfere with each other. Supramolecular polymers can therefore be constructed simply by simultaneously mixing FGGP, CB[8], and N_3-PEG-N_3.

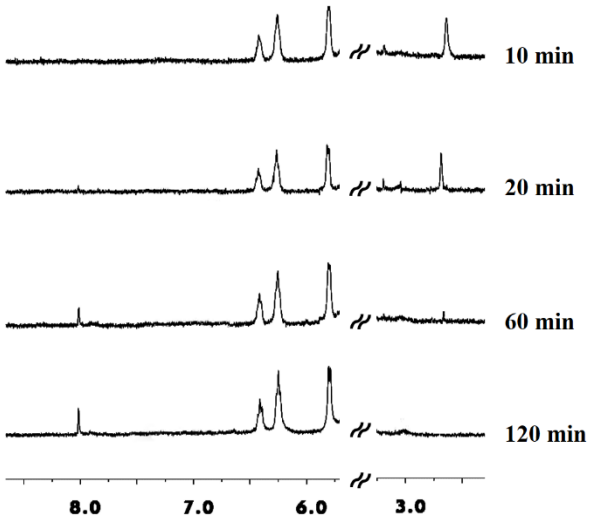


Figure S4. A series of ^{1}H NMR spectra of polymerization with different reaction times. Supramolecular complexation was completed within 10 min, while click reaction was completed in 2 h.