

Supporting Information

Supramolecular polymers synthesized by thiol-ene click polymerization from supramonomers

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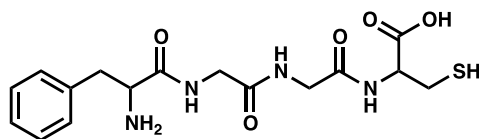
1. Methods:

^1H NMR, ^{13}C NMR and DOSY NMR were recorded on a JOEL JNM-ECA400 apparatus (400 MHz). Asymmetric Flow Field Flow Fractionation experiments (AsF-FFF) were performed by Wyatt Technology Eclipse 3+ with multi-angle light scattering detector (DAWN HELEOS-II), ultraviolet and differential refraction detector (OptilabrEX). ESI mass spectra were recorded by Thermo Fisher DSQ. ITC study was carried out with a Microcal VP-ITC apparatus at 298.15 K.

2. Material Characterization

Tetrapeptide FGGC was purchased from GL Biochem (Shanghai) Ltd, while Mal-PEG-Mal was purchased from Seebio Biotech (Shanghai) Ltd. Both these two chemicals were characterized thoroughly after received.

a. Characterization of FGGC



^1H NMR (JOEL JNM-ECA400, 400 MHz, D_2O , 25 °C): δ (ppm) = 2.84 (2H), 3.09 (2H), 3.80 (2H), 3.86 (2H), 4.17 (1H), 4.48 (1H), 7.17 (2H), 7.27 (3H). (Fig. S1)

ESI: m/z 383.14 $[\text{M}+\text{H}]^+$, 405.12 $[\text{M}+\text{Na}]^+$

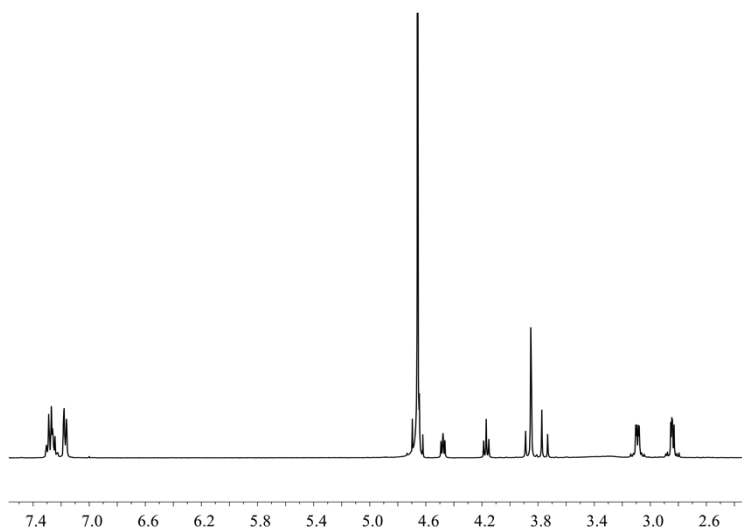
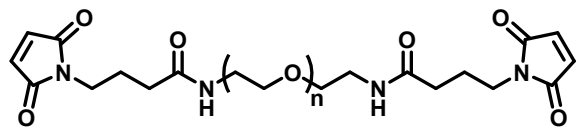


Fig. S1 ^1H NMR of FGGC (400 MHz, D_2O)

b. Characterization of Mal-PEG-Mal



$^1\text{H NMR}$ (JOEL JNM-ECA400, 400 MHz, D_2O , 25 °C): δ (ppm) = 1.60 (4H), 2.38 (4H), 3.06 (4H), 3.40 (4H), 3.40-3.70 (PEG backbone), 6.75 (4H) (Fig. S2)

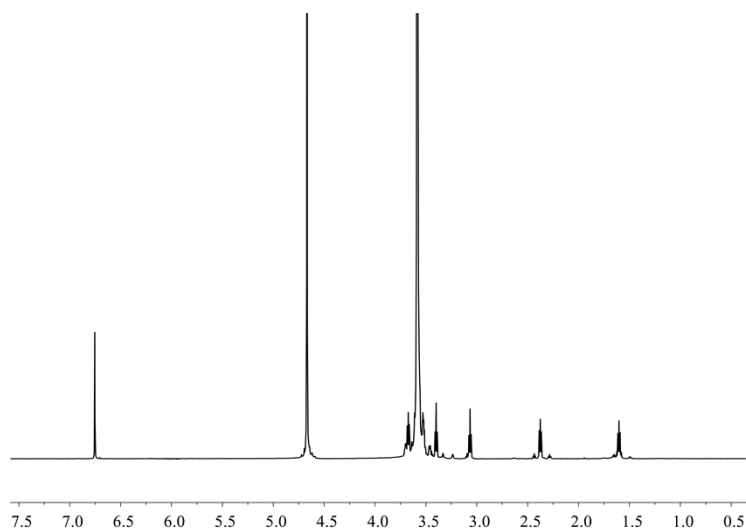


Fig. S2 $^1\text{H NMR}$ of Mal-PEG-Mal (400 MHz, D_2O)

$^{13}\text{C NMR}$ (JOEL JNM-ECA400, 100 MHz, D_2O , 25 °C) δ (ppm) = 173.33, 172.54, 134.49, 69.61 (PEG backbone), 68.37, 36.39, 34.77, 34.55, 28.15, as shown in Fig. S3.

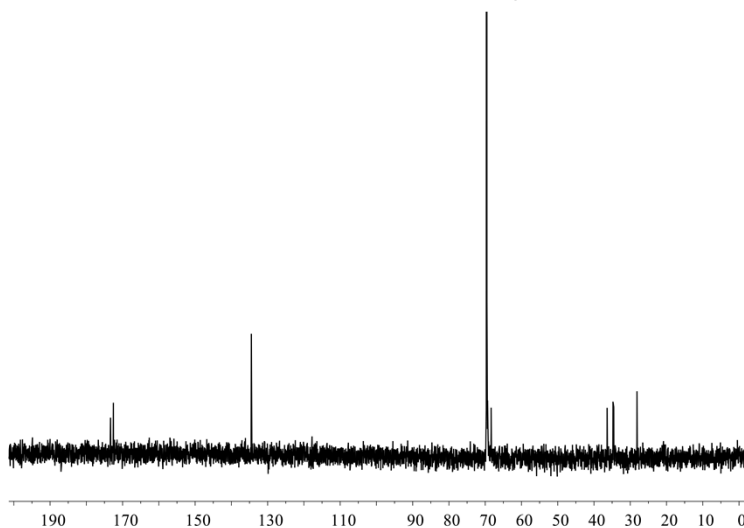


Fig. S3 $^{13}\text{C NMR}$ of Mal-PEG-Mal (100 MHz, D_2O)

3. Characterization of supramonomers

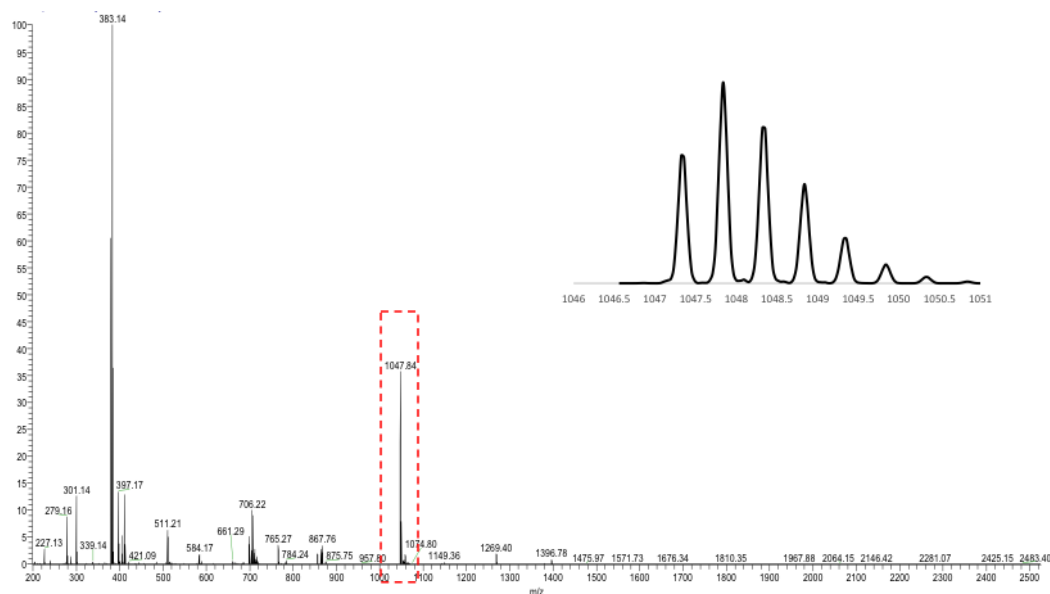


Fig. S4 ESI-MS spectrum of supramonomers.

4. Formation of supramolecular polymers.

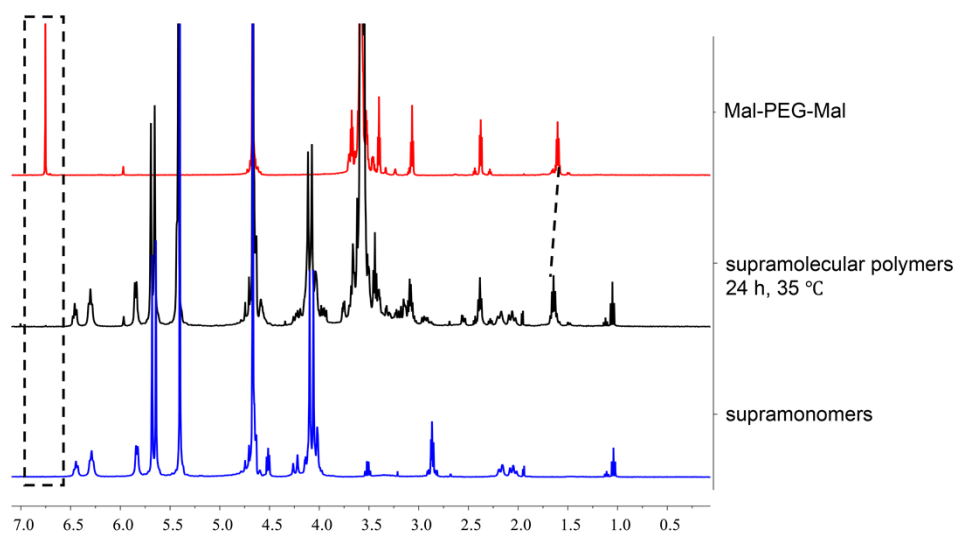


Fig. S5 ¹H NMR spectra of supramolecular polymers in comparison with Mal-PEG-Mal and supramonomers (400 MHz, D₂O).

5. Reaction dynamics of thiol-ene reaction between supramonomers and Mal-PEG-Mal.

The pH of the solution was adjusted by deuterium chloride (in D₂O) and sodium deuteroxide (in D₂O). Generally, the pH of the solution without adjustment is 2.54. Adding 25 μL NaOD (100 mM) into 1 mL solution can tune the pH to 4.34. The addition of 25 μL and 50 μL DCI (1 M) will lead to pH=1.19 and 0.73 respectively.

Based on the reaction: [thiol]+[ene]→[product], the equation can be expressed as following, while k is reaction rate constant:

$$d[\text{product}]/dt=k[\text{thiol}][\text{ene}]$$

Thus, we are able to get the relationship between conversion and time, $conversion=kt/(kt+1)$
Upon monitoring the reaction via *in situ* ^1H NMR, a series of *conversion* and *t* can be acquired at certain pH and temperature. In this way, using least-squares analysis, the rate constant *k* can be calculated.