Supporting Information

Supramolecular polymers synthesized by thiol-ene click polymerization from supramonomers

Qiao Song, Fei Li, Liulin Yang, Zhiqiang Wang and Xi Zhang*

The Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

1. Methods:

$^1$H 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

![Structure of FGGC](image)

$^1$H NMR (JOEL JNM-ECA400, 400 MHz, D$_2$O, 25 °C): $\delta$ (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 [M+H]$^+$, 405.12 [M+Na]$^+$

![NMR spectrum of FGGC](image)
b. Characterization of Mal-PEG-Mal

\[
\text{\includegraphics[width=0.5\textwidth]{structure.png}}
\]

\textbf{\textsuperscript{1}H NMR} (JOEL JNM-ECA400, 400 MHz, D\textsubscript{2}O, 25 °C): \( \delta \) (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 \textsuperscript{1}H NMR of Mal-PEG-Mal (400 MHz, D\textsubscript{2}O)](image)

\textbf{\textsuperscript{13}C NMR} (JOEL JNM-ECA400, 100 MHz, D\textsubscript{2}O, 25 °C) \( \delta \) (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 \textsuperscript{13}C NMR of Mal-PEG-Mal (100 MHz, D\textsubscript{2}O)](image)
3. Characterization of supramonomers

Fig. S4 ESI-MS spectrum of supramonomers.


Fig. S5 $^1$H NMR spectra of supramolecular polymers in comparison with Mal-PEG-Mal and supramonomers (400 MHz, D$_2$O).

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

The pH of the solution was adjusted by deuterium chloride (in D$_2$O) and sodium deuteroxide (in D$_2$O). 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 DCl (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:

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\frac{d[\text{product}]}{dt} = k[\text{thiol}][\text{ene}]
\]
Thus, we are able to get the relationship between conversion and time, \( conversion = \frac{kt}{kt+1} \)

Upon monitoring the reaction via \textit{in situ} \(^1\text{H} \) 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.