Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Synthesis, characterization and association behavior of linear-dendritic amphiphilic diblock copolymers based on poly(ethylene oxide) and a dendron derived from 2,2′-bis(hydroxymethyl)propionic acid

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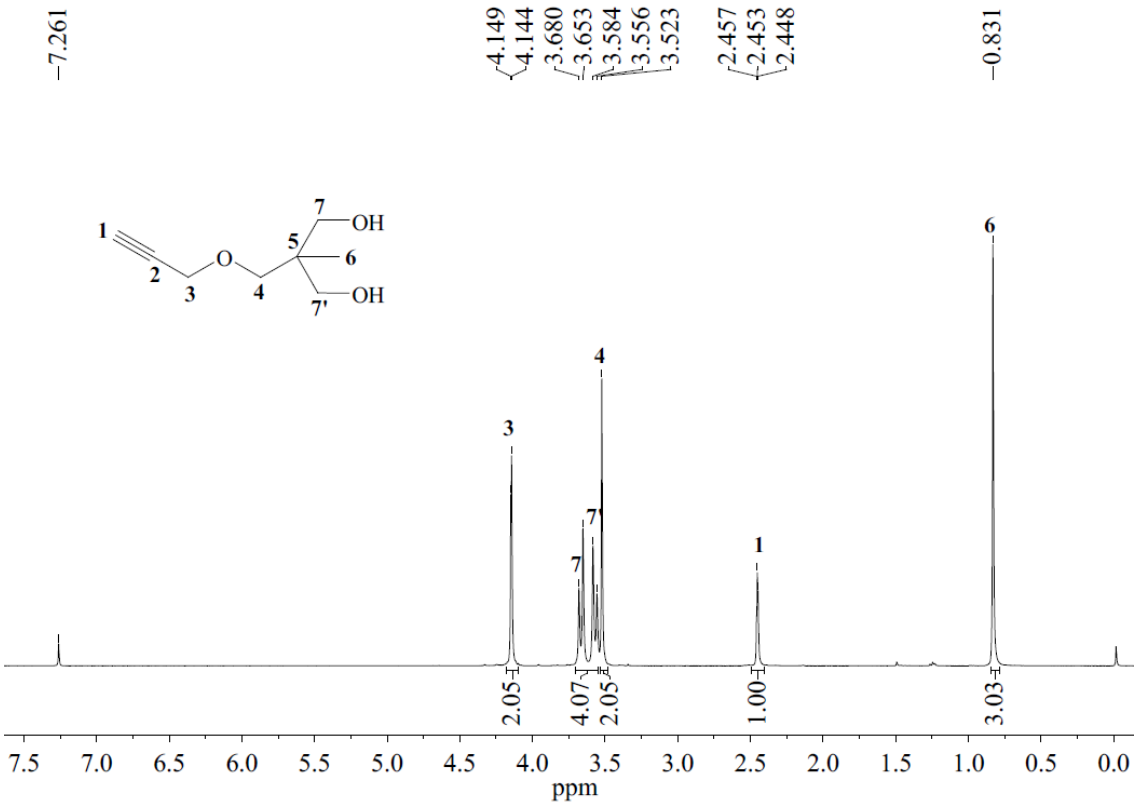
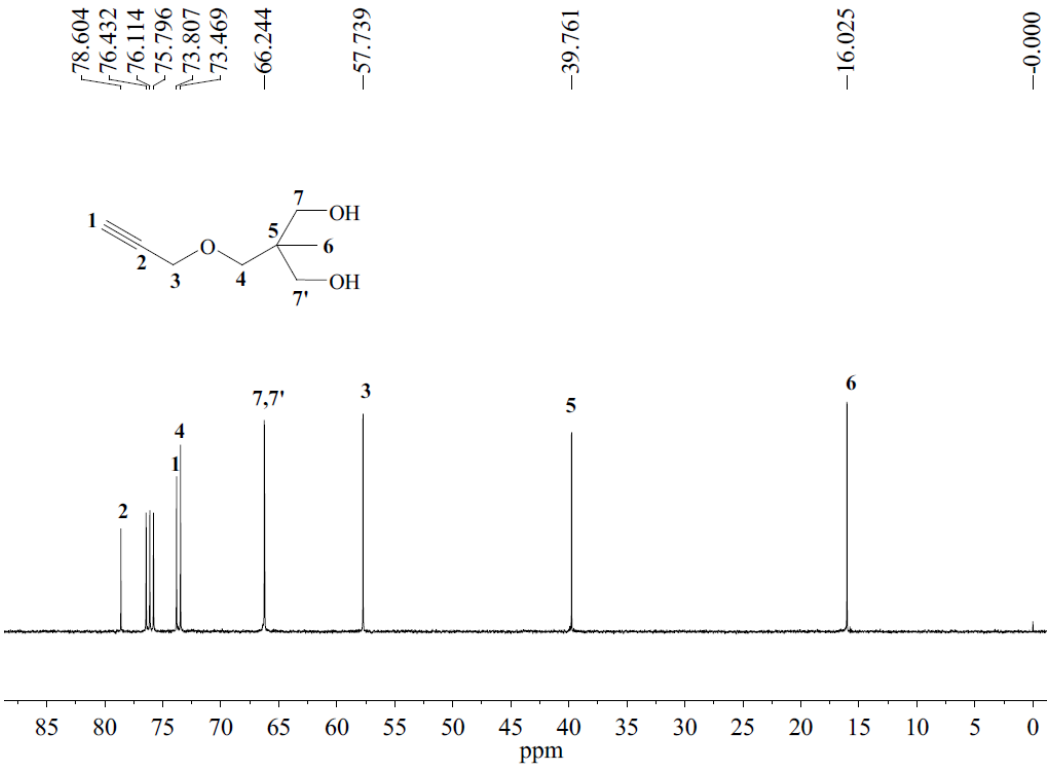
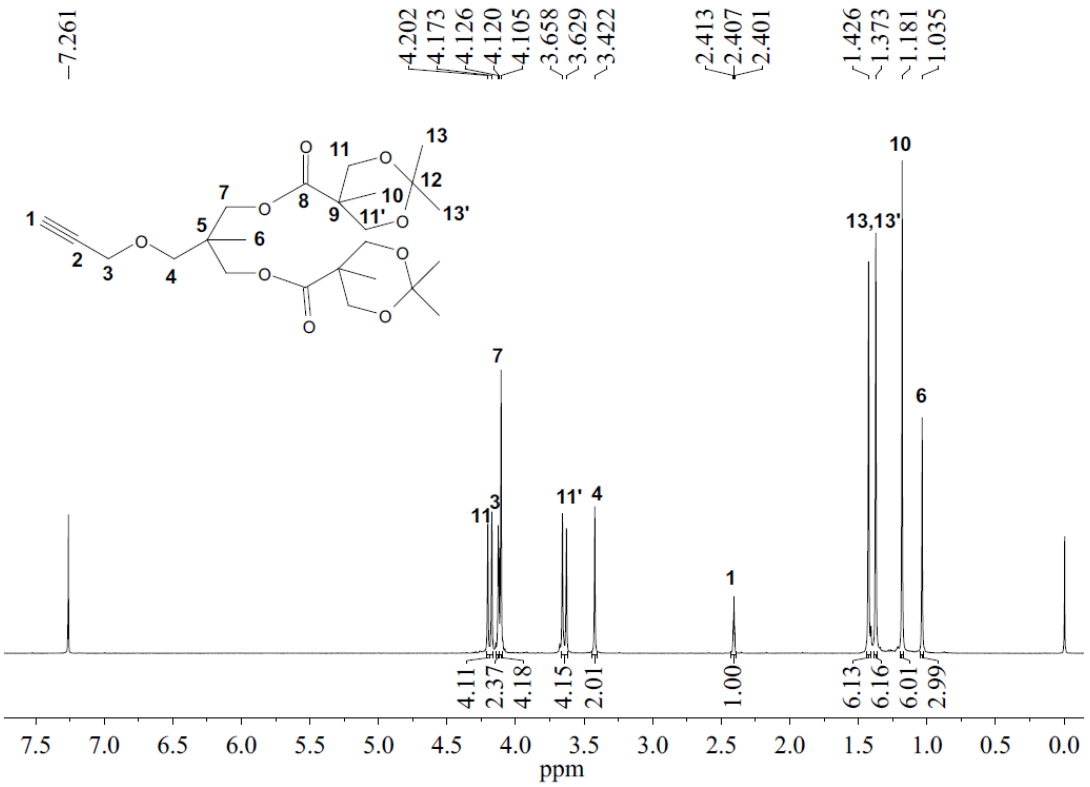
## I. $^{1}$H and $^{13}$C NMR Spectra of the Synthesized Compounds



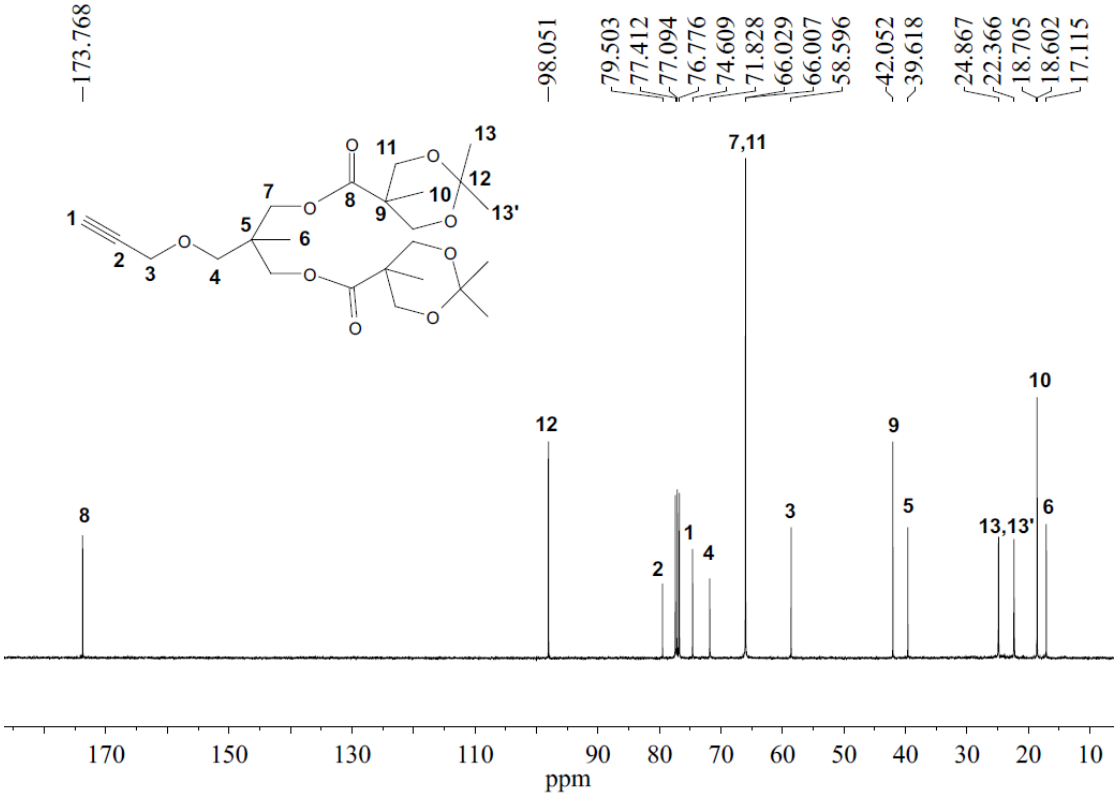

$^{1}$H NMR Spectrum of Compound **3**



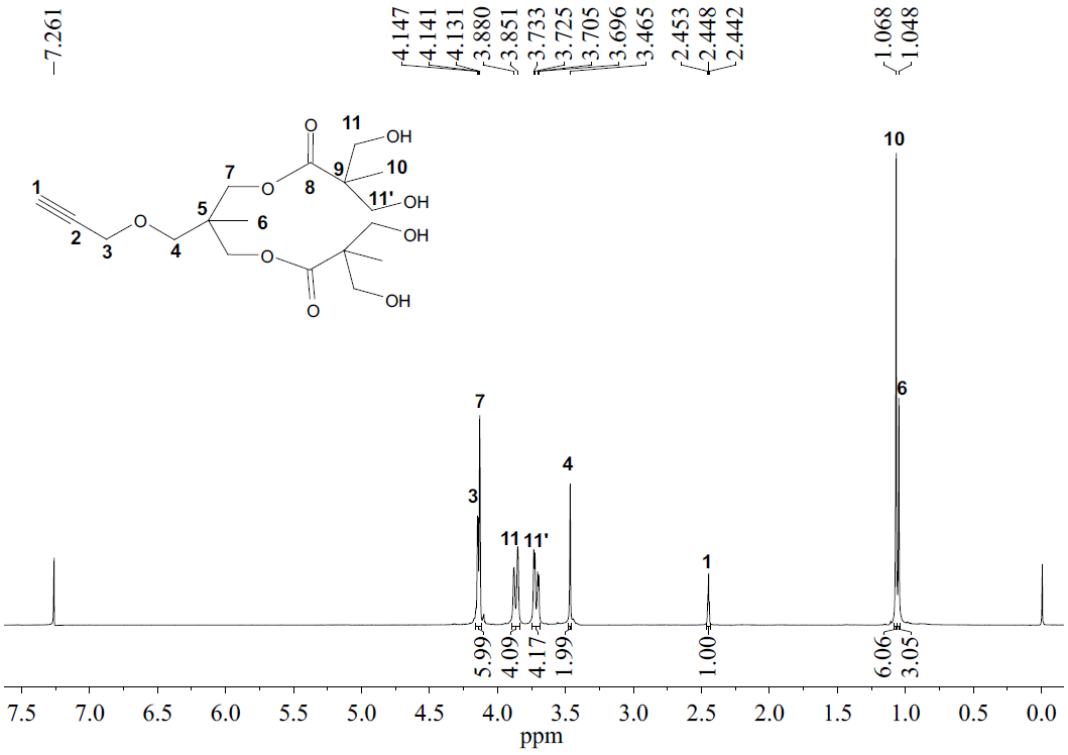

$^{13}$C NMR Spectrum of Compound **3**



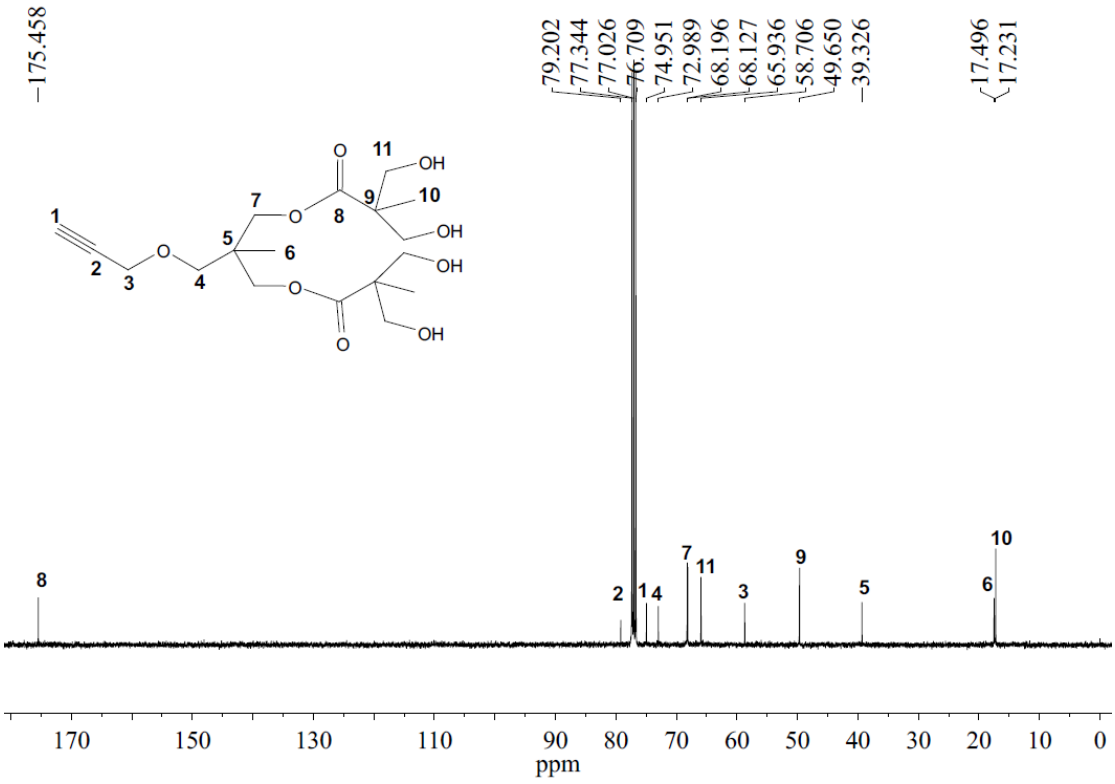

$^{1}$H NMR Spectrum of Compound **5**



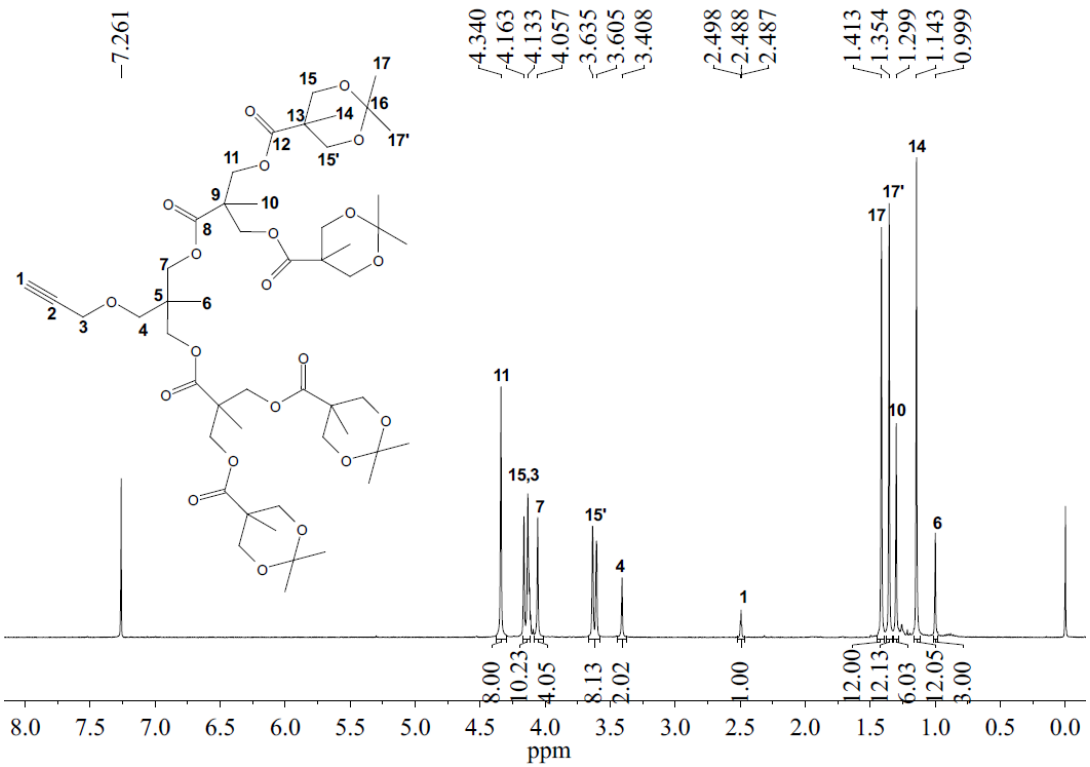

$^{13}$C NMR Spectrum of Compound **5**



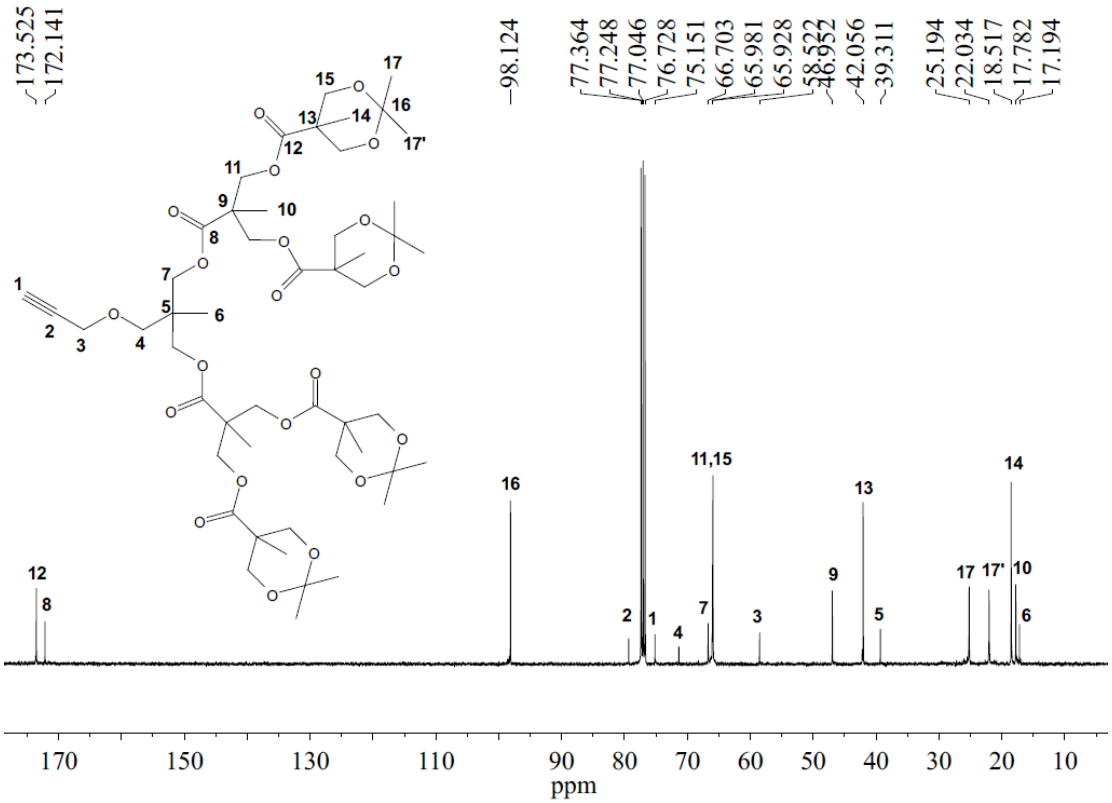

$^{1}$H NMR Spectrum of Compound **6**



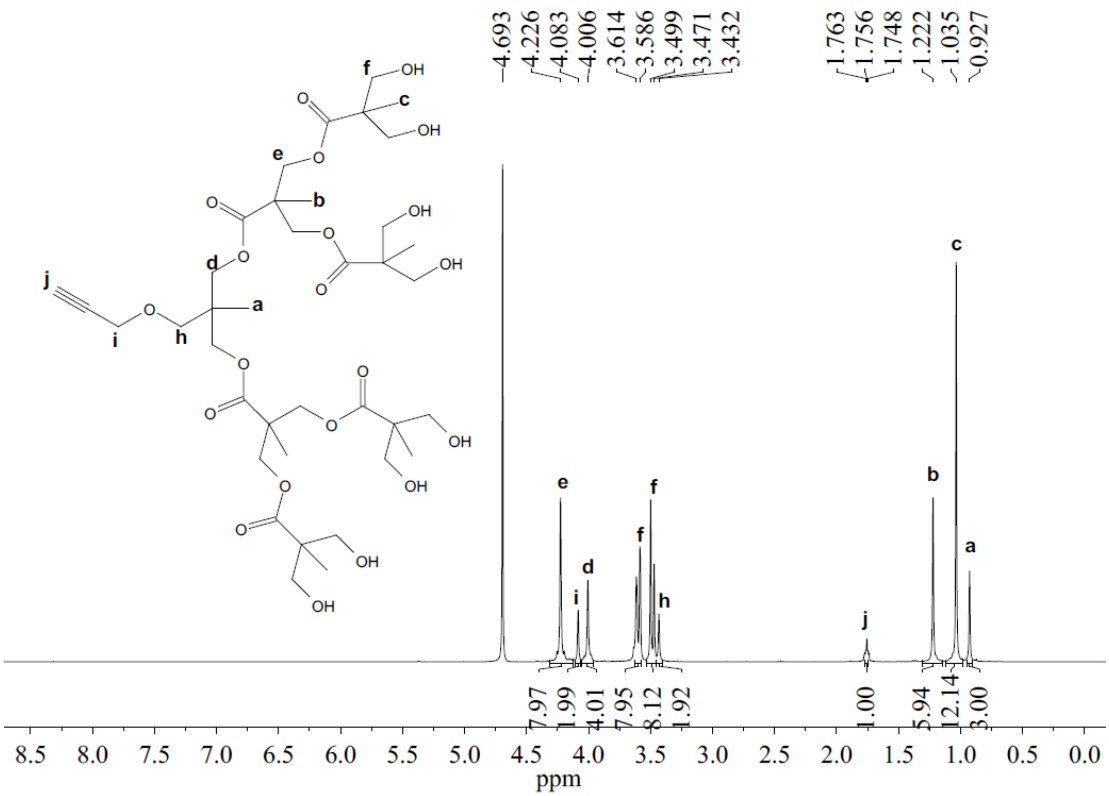

$^{13}$C NMR Spectrum of Compound **6**



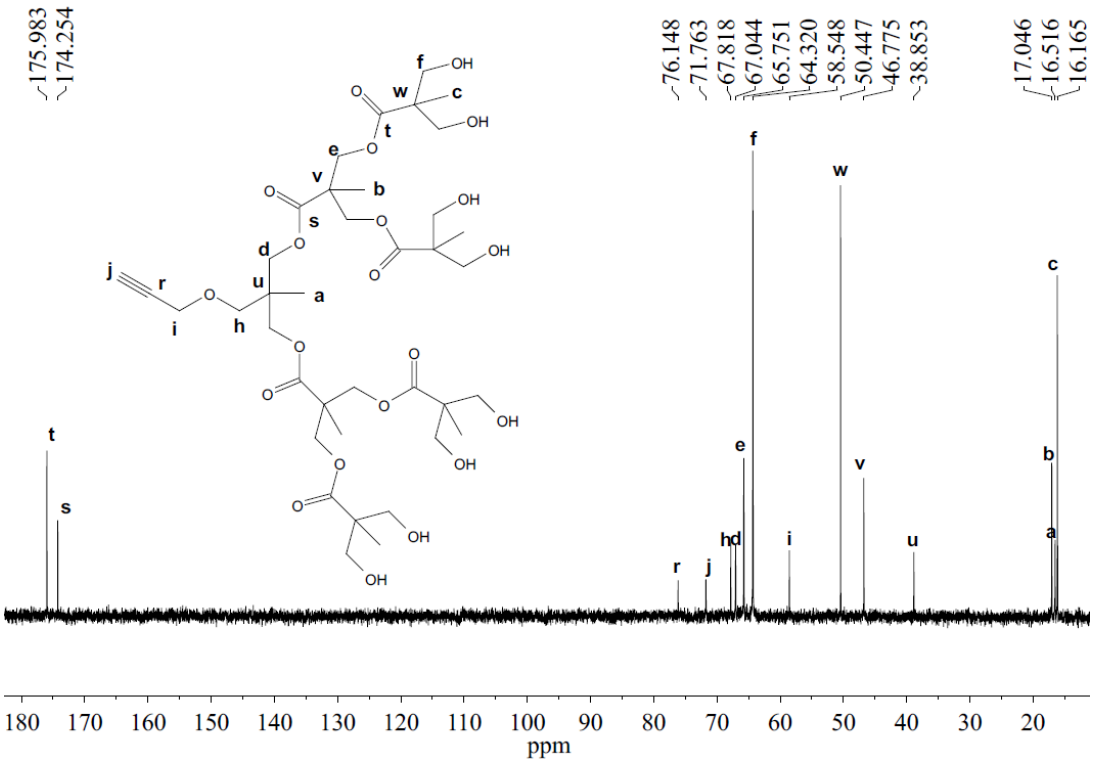

$^{1}$H NMR Spectrum of Compound **7**



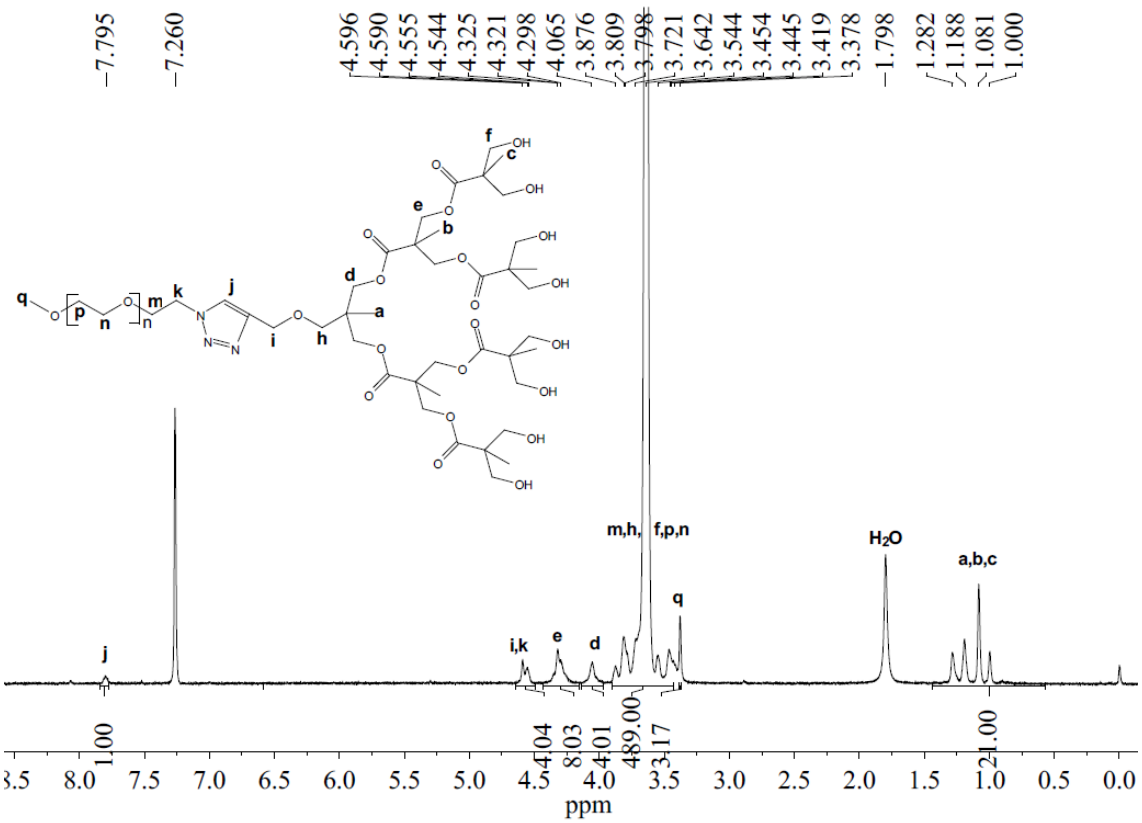

$^{13}$C NMR Spectrum of Compound **7**



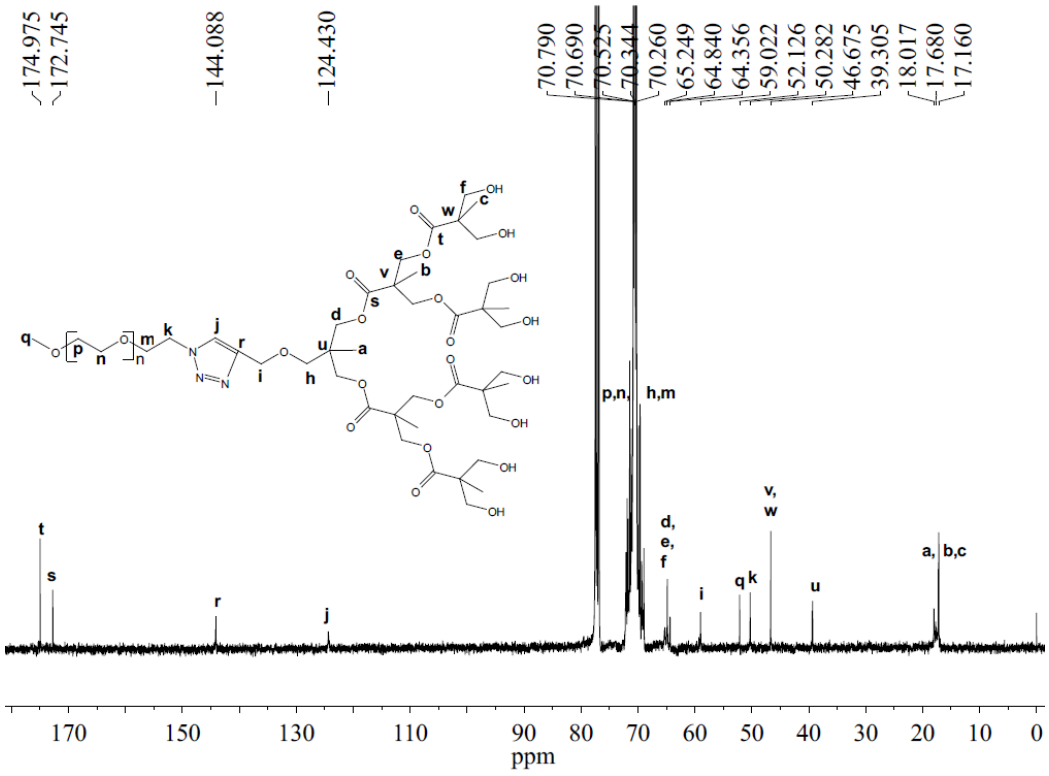

$^{1}$H NMR Spectrum of Compound **8**



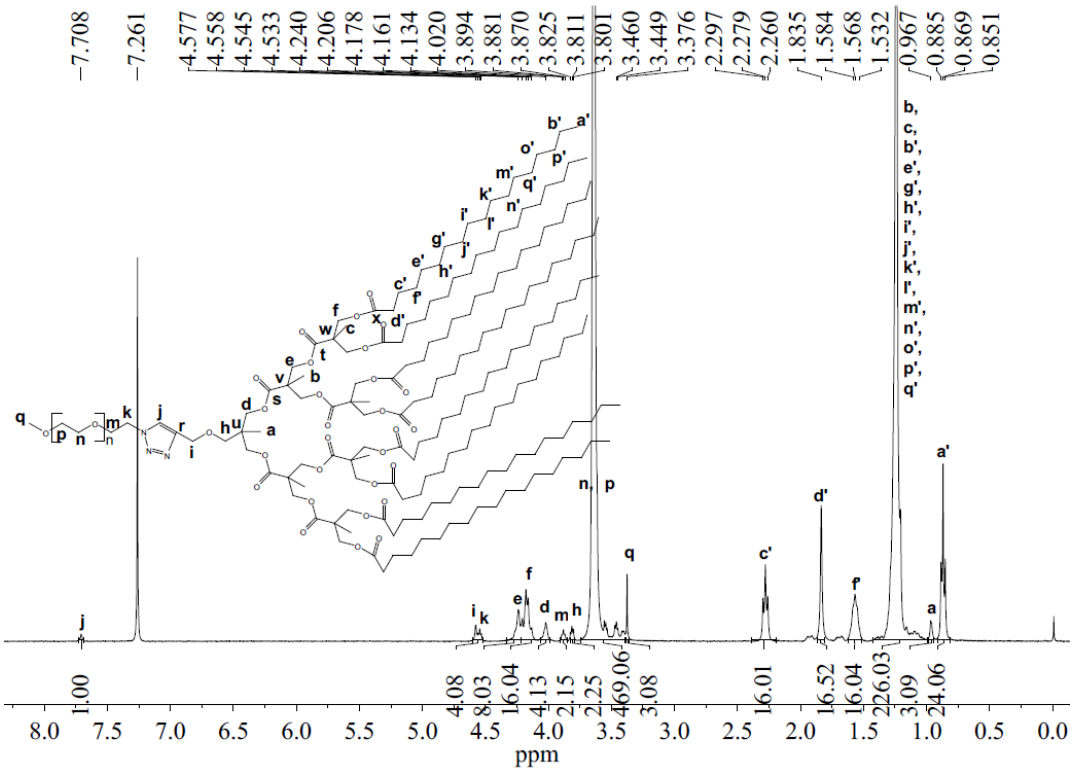

$^{13}$C NMR Spectrum of Compound **8**



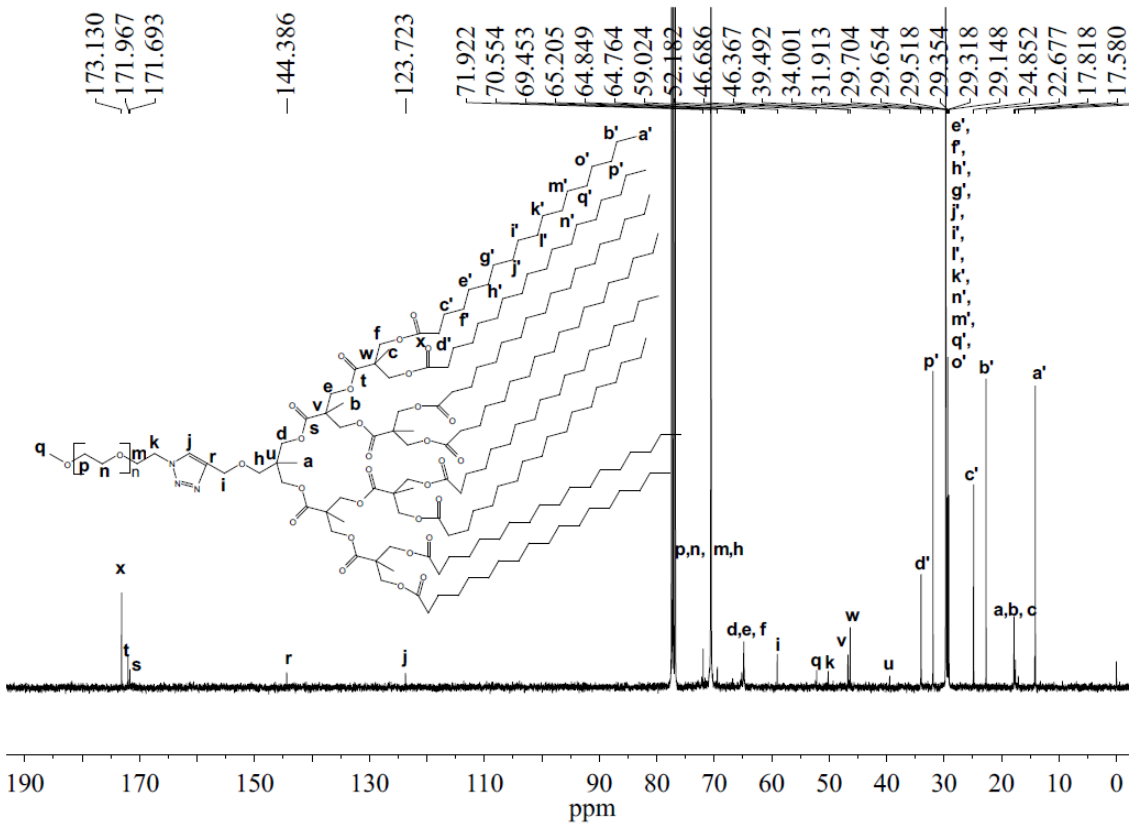

$^{1}$H NMR Spectrum of Compound **10**



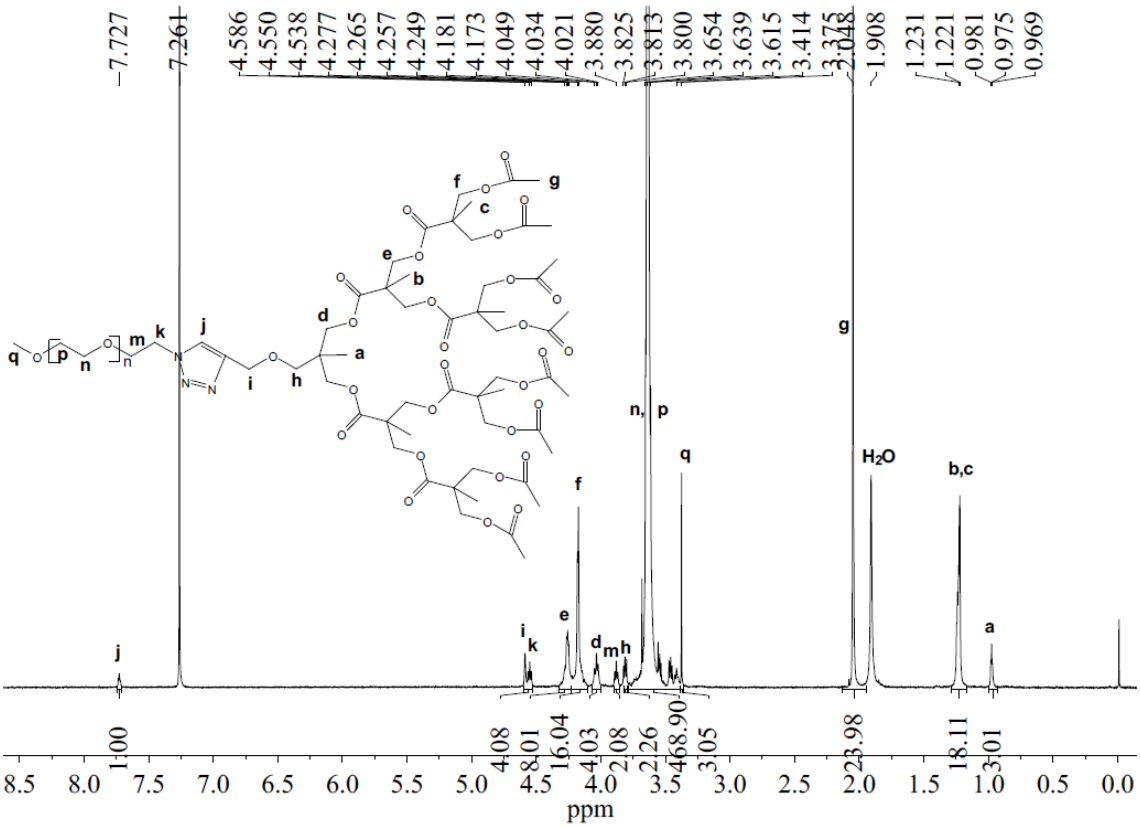

$^{13}$C NMR Spectrum of Compound **10**



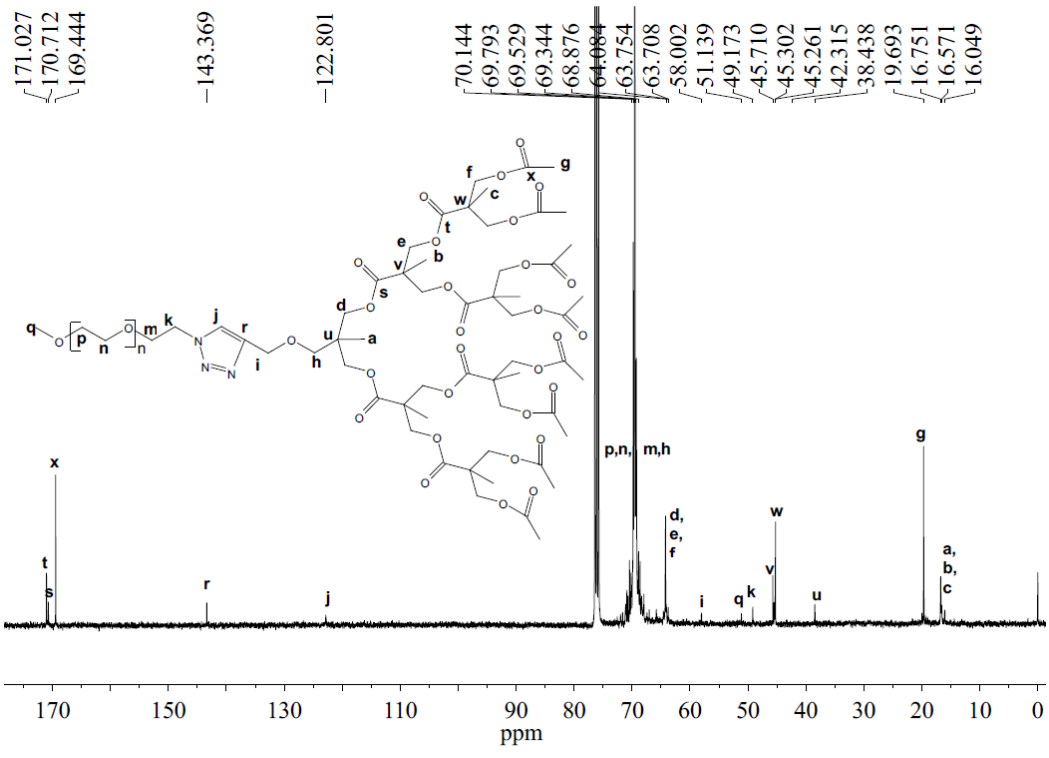

$^{1}$H NMR Spectrum of Compound **11**




$^{13}$C NMR Spectrum of Compound **11**

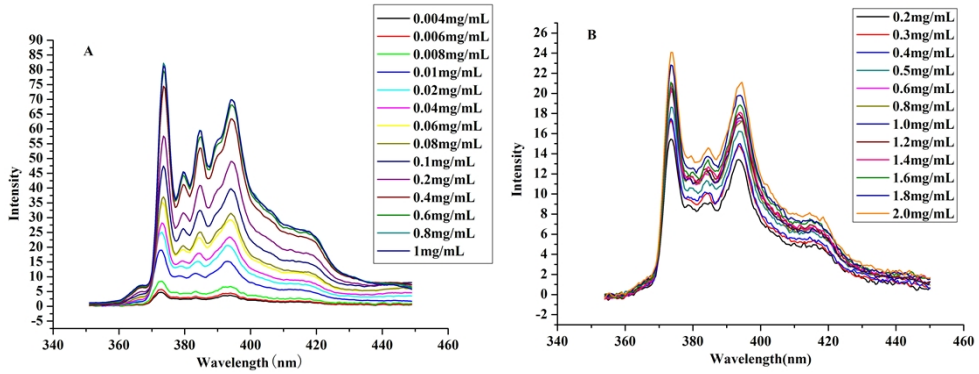



$^{1}$H NMR Spectrum of Compound **12**




$^{13}$C NMR Spectrum of Compound **12**

## II. Fluorescence spectra for PEO-b-G3-$(C_{18}H_{35}O_2)_8$ and PEO-b-G3-$(C_2H_3O_2)_8$




**SI-Fig.1**. Steady-state fluorescence excitation spectra monitored at for the pyrene probe in an aqueous solution of PEO-b-G3-$(C_{18}H_{35}O_2)_8$ (A) and PEO-b-G3-$(C_2H_3O_2)_8$ (B) at various concentration at 25 ºC.

## III. Determination of Micellar Aggregation Numbers of PEO-b-G3-$(C_{18}H_{35}O_2)_8$ and PEO-b-G3-$(C_2H_3O_2)_8$

The Experimental Procedures

The pyrene solution in acetone ($6 \times 10^{-4}$ M, prepared prior to use) was added to the 100 mL volumetric flask and the acetone was removed at reduced pressure at 35 ºC for 2 h. Then the solution of PEO(5k)-b-G3-$(C_{18}H_{35}O_2)_8$ (1mg/mL) was added to the volumetric flask to make solutions with a pyrene concentration of $6 \times 10^{-7}$ M. In addition, the different volumes of cetylpyridinium chloride (CPC) solution in methanol ($2 \times 10^{-4}$ M, prepared prior to use) were added to the other series of 10 mL volumetric flasks and the methanol was removed at reduced pressure at 35 ºC for 2 h. Finally the solution of PEO(5k)-b-G3-$(C_{18}H_{35}O_2)_8$ including pyrene ($6 \times 10^{-7}$ M) was added to the series of 10 mL volumetric flasks to make the CPC concentrations from $0.4 \times 10^{-7}$ M to $2 \times 10^{-7}$ M.

The solution preparation for PEO(5k)-b-G3-$(C_2H_3O_2)_8$ (2 mg/mL) was obtained according to the same procedure as that of PEO(5k)-b-G3-$(C_{18}H_{35}O_2)_8$.

The aggregation numbers for both copolymers in aqueous solution can be calculated by use of eqs 1 and 2:[1-3]

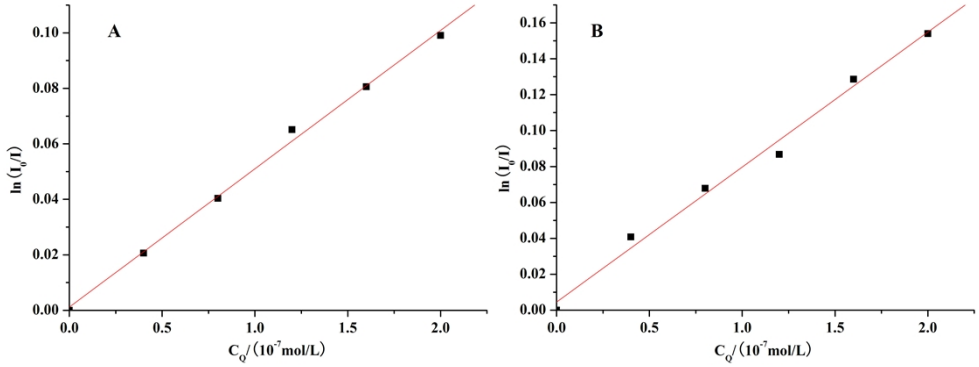
$$\ln\left(\frac{I_0}{I}\right) = \frac{[Q]}{[mic]} \qquad (1)$$

$$N_{agg} = \frac{c - cmc}{[mic]} \qquad (2)$$

Where $I_0$ and $I$ are the emission intensities at a certain wavelength in the absence and presence of the added fluorescence quencher, respectively, and $[Q]$ is the concentration of the fluorescence quencher. $[mic]$ is the micellar concentration in solution, and $c$ is the total concentration of the copolymer.

The emission spectra of these solutions were recorded and the logarithm of the intensity ratio $I_0 / I$ at a specific wavelength (383 nm) was plotted against the quencher concentration $[Q]$, according

to eq 1. Thus a straight line through the origin with a slope equal to 1 / [*mic*] can be determined, and the aggregation number can be calculated according to eq 2.




**SI-Fig.2**. $\ln(I_0/I)$ of pyrene fluorescence intensity as a function of CPC concentration in PEO-b-G3-$(C_{18}H_{35}O_2)_8$ and PEO-b-G3-$(C_2H_3O_2)_8$ micelles solutions. [Py] = $6.0 \times 10^{-7}$ M.
(A) PEO-b-G3-$(C_{18}H_{35}O_2)_8$ (1 mg/mL), (B) PEO-b-G3-$(C_2H_3O_2)_8$ (2 mg/mL).

## References:

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2. N. J. Turro and A.Yekta, *J. Am.Chem. Soc.*, 1978, **100**, 5951-5952.

3. J. V. Stam, S. Depaemelaere and F. C. D. Schryver, *J. Chem. Educ.*, 1998, **75**, 93-98.