

## Electronic Supplementary Information

### **Hydrogen-Bonding Mediated Self-Assembly of Amphiphilic ABA Triblock Copolymers into Well-Defined Giant Vesicles**

Huiying Wang,<sup>a</sup> Qiang Chen,<sup>a</sup> Zhen Geng,<sup>a</sup> Jingyi Rao,<sup>a</sup> Bijin Xiong,<sup>a</sup> Senbin Chen,<sup>\*a</sup> Frédéric Lortie,<sup>b</sup> Julien Bernard,<sup>b</sup> Wolfgang H. Binder,<sup>c</sup> Jintao Zhu<sup>\*a</sup>

<sup>a</sup>: Key Laboratory of Materials Chemistry for Energy Conversion and Storage, Ministry of Education (HUST), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

E-mail: jtzhu@hust.edu.cn (J. Zhu); senbin@hust.edu.cn (S. Chen)

<sup>b</sup>: Univ Lyon, INSA Lyon, CNRS, IMP UMR 5223, F-69621, Villeurbanne, France

<sup>c</sup>: Chair of Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin Luther University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle (Saale) D-06120, Germany

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## Materials

All the chemicals were purchased from TCI. 2, 2, 2-Trifluoroethyl acrylate (TFEA) and oligo (ethylene glycol) ethyl acrylate (OEGEA) were purified by passing through a column of basic aluminium oxide to removing inhibitors. **1** was synthesized according to a recent report.<sup>[1]</sup> 2, 2'-Azobis(isobutyronitrile) (AIBN) was recrystallized before use from ethanol. Unless otherwise indicated the other chemicals were used without further purification.

## Characterization methods

<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a Bruker AV400 (400 MHz) NMR spectrometer using CDCl<sub>3</sub>, DMSO-d<sub>6</sub> or THF-d<sub>8</sub> as solvent.

Polymers were analyzed by size exclusion chromatography (SEC) running in THF containing 250 ppm BHT (butylated hydroxytoluene) at 30 °C (flow rate: 1 mL·min<sup>-1</sup>), recorded on PL-GPC50 from Agilent (UK), equipped with a set of a PL1110-1520 column, a PL1110-6500 column and a PL1110-6100 column. The average molar mass of polymers was derived from the refractive index signals based on a polystyrene (PS) calibration curve.

Small angle x-ray scattering (SAXS) measurements were conducted with a modified Xeuss system (Xenocs, France) equipped with a Pilatus 300K detector (DECTRIS, Switzerland). The distance of each sample to detector was 1203 mm. The exposure time of each sample was 30 min. After the thermal annealing at 100 °C under vacuum for 12 h, the samples were placed in the hole (d = ~1 mm) which is in the center of the sample holder.

Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC 1 instrument (Switzerland) operating with version 9.1 of STAR software. The amount of the samples for

the DSC measurements was around 5 mg and the measurements were conducted under N<sub>2</sub> flow with a heating and cooling rate of 10 °C/min in the range of -90-100 °C. T<sub>g</sub>'s are estimated by taking the midpoint between the origin and termination temperatures of the overall thermal transition.

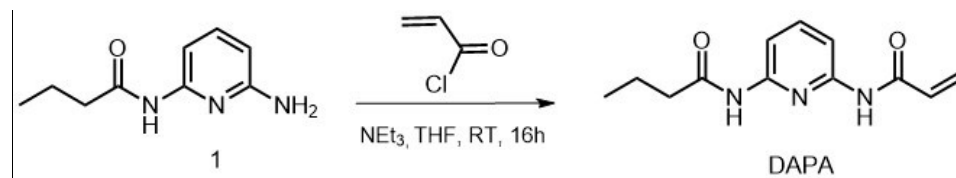
Scanning electron microscopy (SEM) analyses were performed using a SU8010 scanning electron microscope (HITACHI) at an accelerating voltage 3 kV. The sample was dissolved in THF/H<sub>2</sub>O (95/5, v/v) with 2 mg/mL and then spread onto a Si solid. SEM images were taken after spraying gold.

Transmission electron microscopy (TEM) analyses were conducted with a HT7700 transmission electron microscope (HITACHI) at an accelerating voltage 100 kV. The sample was dissolved in THF/H<sub>2</sub>O (95/5, v/v) with 2 mg/mL and spread onto a Cu grid coated with a Carbon-film. After 1 min, excess solution was blotted off with filter paper and air-dried before the measurement. TEM images were taken directly without staining.

For imaging their topography by atomic force microscopy (AFM), the polymer aggregates were immobilized on a Si solid support by drop coating films from a THF/H<sub>2</sub>O (95/5, v/v) solution. AFM imaging was carried out with a SPM-9700 (HITACHI) operating in tapping mode in air at room temperature.

Dynamic light scattering (DLS) measurements were conducted in THF/H<sub>2</sub>O (95/5, v/v) solution with 2 mg/mL at room temperature using a Nano-ZS90 using Zetasizer software.

Confocal laser scanning microscope (CLSM) measurement was conducted with an Olympus FV1200 (Tokyo, Japan) using 100× objective. The sample was dissolved in THF/H<sub>2</sub>O (95/5, v/v, c = 2 mg/mL) and mixed with trace amount of Rhodamine B. One drop of the obtained solution was placed on microscopic glass slide for the measurement.



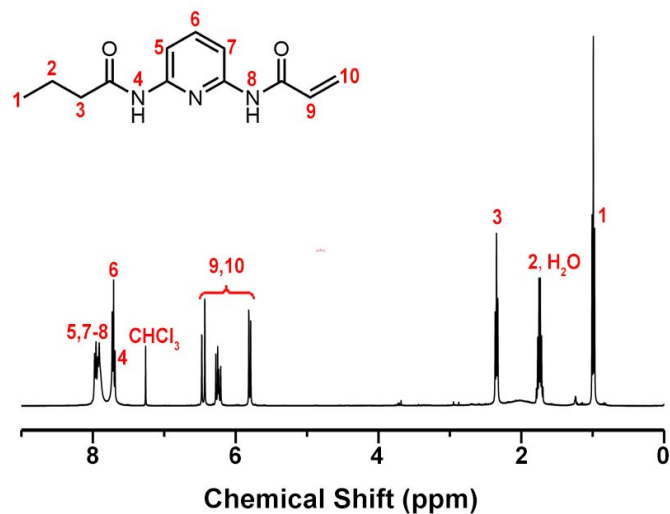
**Figure S1:** Synthetic route to DAPA monomer.

**Synthesis of DAPA (Figure S1).**

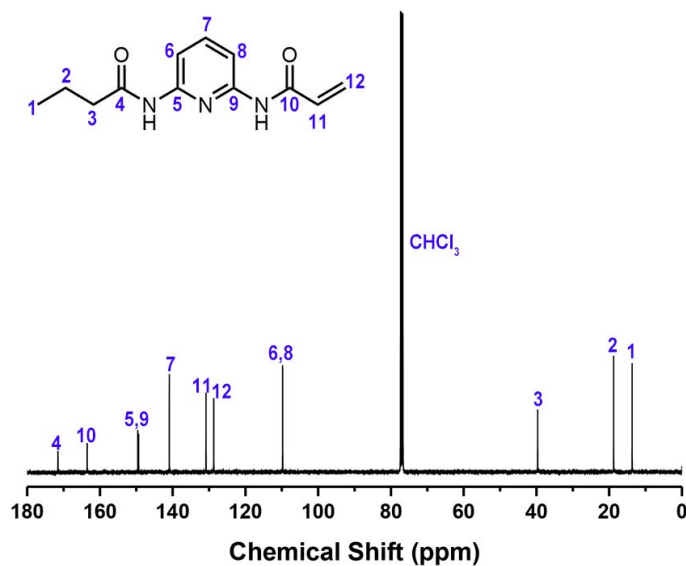
The amidation reaction of **1** with acryloyl chloride was implemented under Ar atmosphere. Typically, to a stirred solution of **1** (3.73 g, 0.0208 mol) and triethylamine (8.7 ml, 0.0627 mol) in anhydrous THF, an excess of acryloyl chloride (5.1 ml, 0.0627 mol) was added dropwise at 0 °C. Then the mixture was allowed to stir at room temperature for 16 h. Then dichloromethane was added to disperse the mixture which was successively extracted with sodium bicarbonate, brine, and water. The organic phase was dried with anhydrous magnesium sulfate and purified by column chromatography on silica (dichloromethane/methanol, 100/3, v/v) to give DAPA monomer as a white solid (1.7 g, 35%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, **Figure S2**) δ (ppm): 1.0 (t, 3H), 1.75 (m, 2H), 2.35 (t, 2H), 5.80 (dd, 1H), 6.24 (quart, 1H), 6.44 (dd, 1H), 7.66 (br, 1H), 7.71 (t, 1H), 7.80 (br, 1H), 7.92 (d, 1H), 7.96 (d, 1H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, **Figure S3**) δ (ppm): 171.5, 163.5, 149.4, 149.2, 141, 130.8, 128.8, 109.7, 39.6, 18.7, 13.7.



**Figure S2:**  $^1\text{H}$  NMR spectrum of DAPA monomer, recorded in  $\text{CDCl}_3$  at  $27^\circ\text{C}$ .



**Figure S3:**  $^{13}\text{C}$  NMR spectrum of DAPA monomer, recorded in  $\text{CDCl}_3$  at  $27^\circ\text{C}$ .

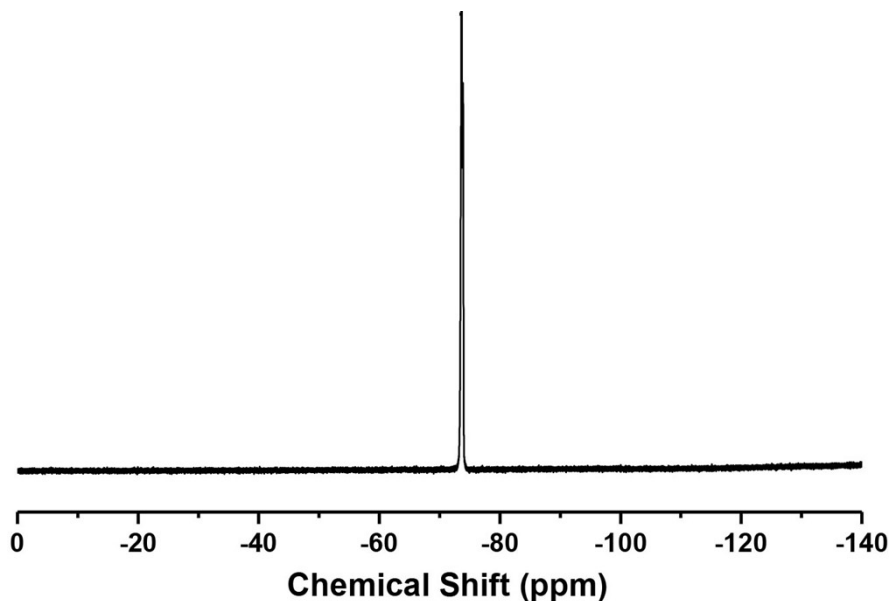
### *Homopolymerization of OEGEA.*

Solution homopolymerization of OEGEA was carried out using DBTTC as RAFT agent, and AIBN as initiator. Typically, solution polymerization of OEGEA (5.53 mL,  $3 \times 10^{-2}$  mol) was carried out using DBTTC (0.29 g,  $1 \times 10^{-3}$  mol), AIBN ( $1.64 \times 10^{-2}$  g,  $1 \times 10^{-4}$  mol) and DMF (5.5 mL). The mixture was transferred into microwave reaction tube sealed with rubber stopper, which was deoxygenated by Ar

bubbling for ~30 min at 0 °C. Then the tube was put in an oil bath thermostated at 70 °C. The reaction was stopped by immersing the tube into ice water bath 3 h later. The mixture was then precipitated into MeOH/H<sub>2</sub>O (1/2, v/v) to remove excess monomer. The polymer was dried under vacuum and characterized by <sup>1</sup>H NMR and SEC (**Figure S7**). The molar mass of the pure POEGEA was characterized using <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) from the relative integration of the ester protons of POEGEA backbone (-O-CH<sub>2</sub>-CH<sub>2</sub>-, 2(m+n)H, δ = 4.10 ppm, with (m+n) being the degree of polymerization) and of the characteristic aromatic protons of DBTTC (phH, 10H, δ = 7.10-7.35 ppm).

### ***Chain extension of POEGEA via the copolymerization of DAPA/TFEA.***

Solution copolymerization of DAPA/TFEA was carried out using POEGEA as macroRAFT agent, and AIBN as initiator. Typically, chain extension of POEGEA with DAPA (0.7 g, 3×10<sup>-3</sup> mol) and TFEA (0.76 mL, 6×10<sup>-3</sup> mol) was carried out using POEGEA (0.38 g, 1×10<sup>-4</sup> mol), AIBN (1.64× 10<sup>-3</sup> g, 1×10<sup>-5</sup> mol) and DMF (1.9 mL). The mixture was transferred into microwave reaction tube sealed with rubber stopper, which was deoxygenated by argon bubbling for ~30 min at 0 °C. Then the tube was put in an oil bath thermostated at 70 °C. The reaction was stopped by immersing the tube into ice water bath 3 h later. The mixture was then precipitated into MeOH/H<sub>2</sub>O (1/1, v/v) to purify the polymer. The polymer was dried under vacuum and characterized by <sup>1</sup>H NMR, <sup>19</sup>F NMR (**Figure S4**) and SEC (**Figure S6**). The molar mass of the pure POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA was characterized using <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) from the relative integration of the ester protons of POEGEA backbone (-O-CH<sub>2</sub>-CH<sub>2</sub>-, 2(m+n)H, δ = 4.10 ppm, with (m+n) being the degree of polymerization), PTFEA backbone (-O-CH<sub>2</sub>-CF<sub>3</sub>, 2(o+p)H, δ = 4.66 ppm, with (o+p) being the degree of polymerization), the alkyl protons of DAPA backbone (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, 3(x+y)H, δ = 0.87 ppm, with (x+y) being the degree of polymerization) and of the characteristic aromatic protons of DBTTC (phH, 10H, δ = 7.10-7.35 ppm).



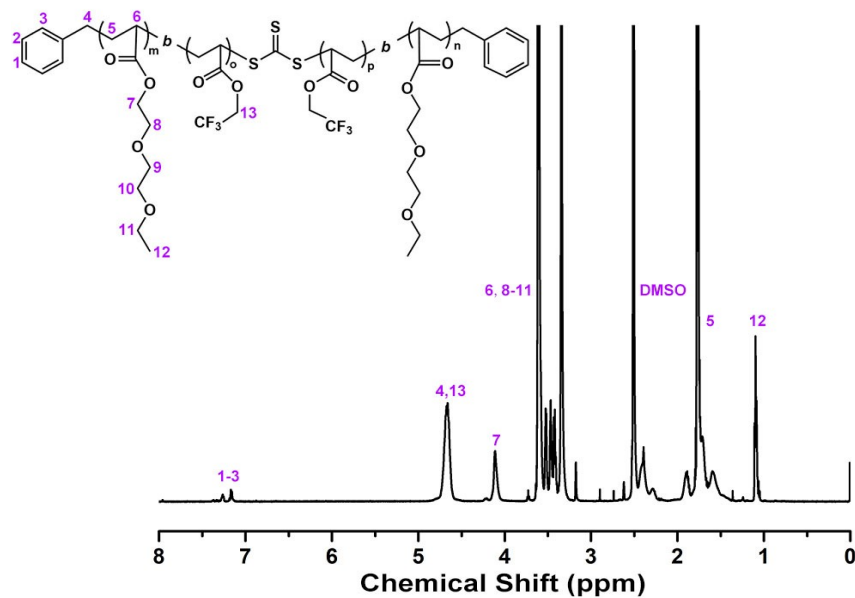
**Figure S4:**  $^{19}\text{F}$  NMR spectrum of the H-bonding amphiphilic ABA triblock copolymer: POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA, recorded in DMSO- $\text{d}_6$  at 27 °C.

***Chain extension of POEGEA via the homopolymerization of TFEA.***

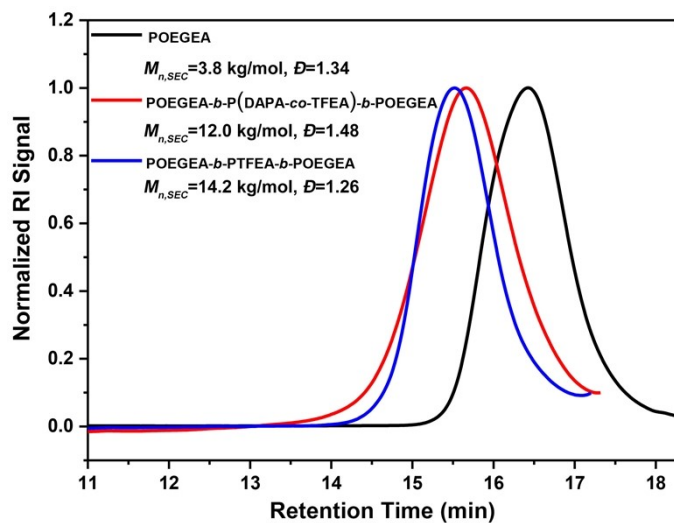
Solution homopolymerization of TFEA was carried out using POEGEA as macroRAFT agent, and AIBN as initiator. Typically, chain extension of POEGEA with TFEA (1.14 mL,  $9 \times 10^{-3}$  mol) was carried out using POEGEA (0.38 g,  $1 \times 10^{-4}$  mol), AIBN ( $1.64 \times 10^{-3}$  g,  $1 \times 10^{-5}$  mol) and DMF (1.9 mL). The mixture was transferred into microwave reaction tube sealed with rubber stopper, which was deoxygenated by argon bubbling for ~30 min at 0 °C. Then the tube was put in an oil bath thermostated at 70 °C. The reaction was stopped by immersing the tube into ice water bath 3 h later. The mixture was put into a dialysis bag and dialyzed against THF to purify the polymer. The polymer was dried under vacuum and characterized by  $^1\text{H}$  NMR (**Figure S5**), and SEC (**Figure S6**). The molar mass of the pure POEGEA-*b*-PTFEA-*b*-POEGEA was characterized using  $^1\text{H}$  NMR (DMSO- $\text{d}_6$ ) from the relative integration of the ester protons of POEGEA backbone ( $-\text{O}-\text{CH}_2-\text{CH}_2-$ ,  $2(m+n)\text{H}$ ,  $\delta = 4.10$  ppm, with  $(m+n)$  being the degree



of polymerization), PTFEA backbone ( $-\text{O}-\text{CH}_2-\text{CF}_3$ ,  $2(o+p)\text{H}$ ,  $\delta = 4.66$  ppm, with  $(o+p)$  being the degree of polymerization), and of the characteristic aromatic protons of DBTTC ( $\text{phH}$ ,  $10\text{H}$ ,  $\delta = 7.10-7.35$  ppm).

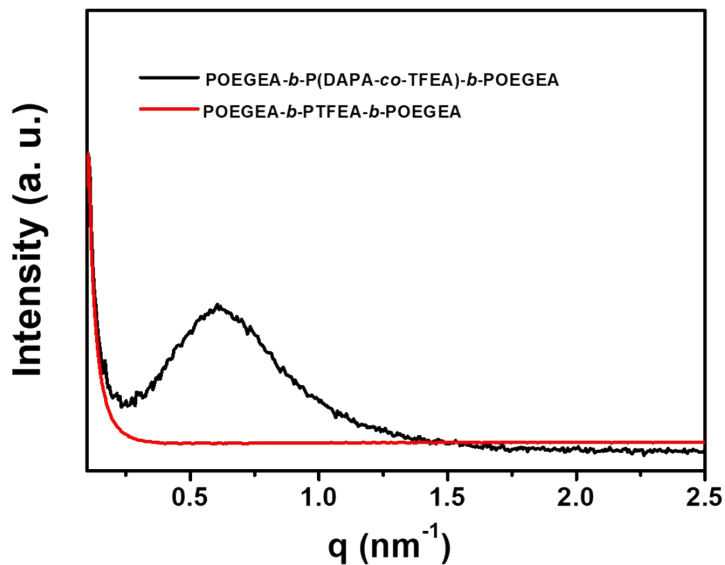


**Figure S5:**  $^1\text{H}$  NMR spectrum of the amphiphilic triblock copolymer: POEGEA-*b*-PTFEA-*b*-POEGEA, recorded in DMSO- $\text{d}_6$  at 27 °C.



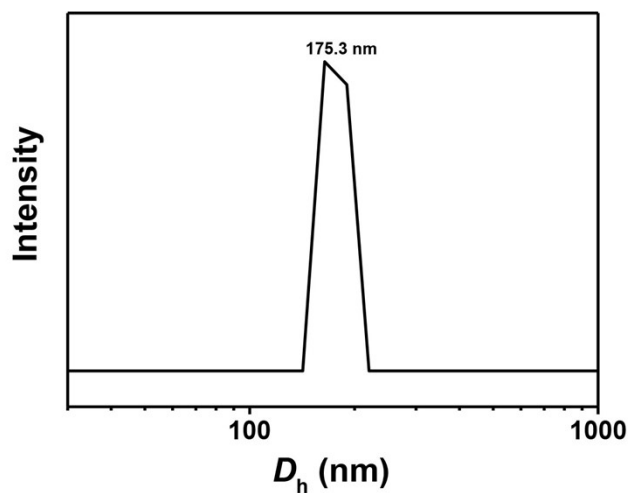
**Figure S6:** Evolution of the normalized RI signals for POEGEA, POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA, and POEGEA-*b*-PTFEA-*b*-POEGEA.

**SAXS results of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA, and POEGEA-*b*-PTFEA-*b*-POEGEA**



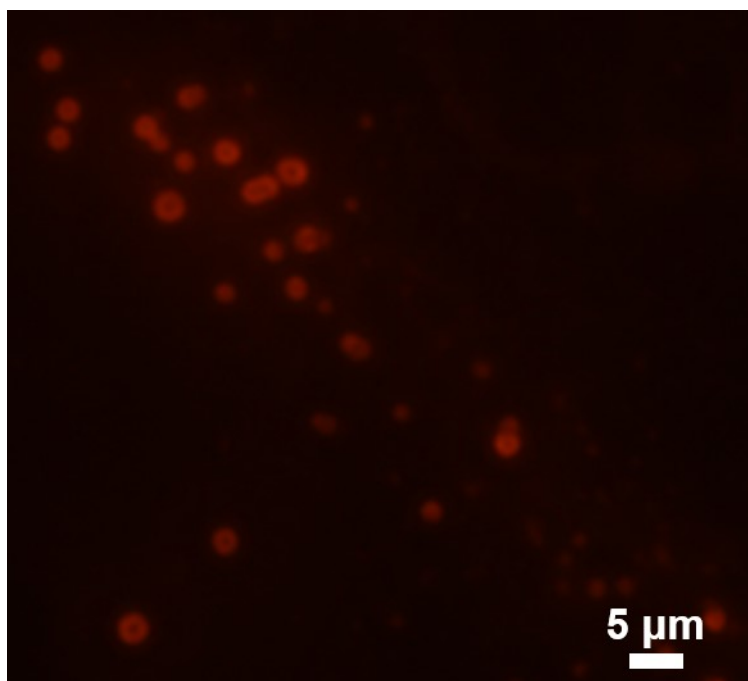
**Figure S7:** One dimensional SAXS curves of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA, and POEGEA-*b*-PTFEA-*b*-POEGEA.

**DLS result of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA**



**Figure S8:** DLS result of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA in THF/H<sub>2</sub>O (95/5, v/v), c = 2 mg/mL.

## CLSM result of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA



**Figure S9:** CLSM result of POEGEA-*b*-P(DAPA-*co*-TFEA)-*b*-POEGEA.

## References

- [1] Chen, S.; Rocher, M.; Ladaviere, C.; Gerard, J.-F.; Lortie, F.; Bernard, J., *Polym. Chem.* 2012, **3**, 3157-3165.