

Electronic Supporting Information

Self-Assembly of Amphiphilic Macrocycles Containing Polymeric Liquid Crystal Grafts in Solution

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Materials

Cholesteryl chloroformate (Alfa Aesar, 98%), hydroxyethyl methacrylate (HEMA, TCI), sodium azide (NaN₃, Sigma-Aldrich, ≥ 99.5%), 3-bromo-1-propanol, acryloyl chloride, propargyl alcohol were purchased from Energy Chemical and used as received. Azobis (4-cyano valeric acid) (ACVA), dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from J&K Scientific Ltd. and used as received.

Poly(ethylene glycol) methyl ether methacrylate (OEGMA, Sigma-Aldrich, $M_n = 300$ g/mol) was passed through an alumina column to remove the inhibitor. Copper(I) bromide (CuBr, Adamas) was freshly purified by stirring in acetic acid overnight, washed with acetone, and dried in vacuum. 1,4-dioxane was purchased from Sinopharm Chemical Reagent Co., Ltd. and was dried over CaH_2 and distilled before use. Triethylamine, pyridine, tetrahydrofuran (THF), acetone, benzene, dichloromethane and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. without any further purification. Cholesteryl methacryloyloxy ethyl carbonate (ChEMA), terminal alkyne modified-dithiobenzoate (CPDBP), terminal alkyne modified initiator (ACVAP), 3-azidopropyl acrylate were synthesized as reported previously.¹

Experimental Section

Synthesis of *linear* PChEMA₁₈-Tr

ChEMA (2.0 g, 3.68 mmol), CPDBP (39.0 mg, 0.12 mmol), ACVAP (8.7 mg, 0.024 mmol), and toluene (4.0 mL) were charged into a 10 mL flask and then degassed by three freeze-pump-thaw cycles. The flask was then filled with Ar and placed in an oil bath thermostated at 70 °C. After a predetermined time, the flask was cooled and exposed to air and diluted with THF and the polymer was precipitated in a large amount of methanol. The precipitation procedure was repeated three times, after drying in a vacuum oven overnight at 25 °C, the red product was obtained (1.11 g, yield: 56%).

Synthesis of *linear* PChEMA₁₈-*b*-POEGMA₁₄-Tr

OEGMA (0.60 g, 1.99 mmol), the macro-RAFT agent PChEMA₁₈-Tr (0.95 g, 0.099 mmol), ACVAP (2.6 mg, 0.0075 mmol), and 1,4-dioxane (3.8 mL) were charged into a 10 mL flask and degassed by three freeze-pump-thaw cycles. The flask was then filled with Ar and placed in an oil bath thermostated at 70 °C. After a predetermined time, the flask was cooled and exposed to air and diluted with THF and the polymer was precipitated in a large amount of coldmethanol. The precipitation procedure was repeated, after drying in a vacuum oven overnight at 25 °C, the red product was obtained (1.36 g, yield: 70%).

Synthesis of *linear* PChEMA₁₈-*b*-POEGMA₁₄-N₃

The polymer was synthesized by a one-pot aminolysis/Michael-addition reaction. A 25 mL round-bottom flask was charged with linear PChEMA₁₈-*b*-POEGMA₁₄-Tr (0.85 g, 0.062 mmol) and THF (10 mL). After complete dissolution of the polymer, the solution was degassed by bubbling Ar for at least 40 min, then 3-azidopropyl acrylate (0.48 g, 3.1 mmol) and n-butylamine (0.23 g, 3.1 mmol) were added to the solution. The mixture was allowed to stir at room temperature for 5 h under Ar atmosphere. The polymer was recovered by precipitation into an excess of coldmethanol, after filtered and dried in a vacuum oven overnight at 25 °C, the white product was obtained (0.82 g, yield: 96%).

Synthesis of *cyclic* PChEMA₁₈-*b*-POEGMA₁₄

Toluene (700 mL) was added into a 1 L three-necked round-bottom flask and bubbled with Ar for 4 h to remove oxygen. Then CuBr (203.0 mg, 1.42 mmol) and PMDETA (368.0 mg, 2.12 mmol) were charged into the flask under protection of Ar flow. The

degassed linear precursor (0.10 g, 0.007 mmol) in 20 mL of toluene was added into the CuBr/PMDETA mixture at 70 °C *via* syringe pump very slowly, over 40 h. After the addition of polymer solution was completed, the reaction was allowed to proceed for another period of 24 h. Then, azide resin (100 mg) was added, after 12 h, the mixture was cooled to room temperature and passed through a silica gel column to remove the metal salt. After most of the solvents were removed by a rotary evaporator, the residue was precipitated into coldmethanol. After drying in a vacuum oven overnight at 30 °C, the slightly yellow product was obtained (0.060 g, yield: 60%).

Linear and *cyclic* PChEMA₁₃-*b*-POEGMA₁₅ were prepared using similar procedures.

The numbers of repeated units ($m_{[\text{ChEMA}]}$, $n_{[\text{OEGMA}]}$) and the number average molecular weight ($M_{n,\text{NMR}}$) of the resultant RAFT polymers was calculated from their ¹H NMR spectra (Figure S4 and Figure S6) by Formulate S1 and S4:

$$m_{[\text{ChEMA}]} / n_{[\text{OEGMA}]} = [(I_{5.31-5.46}) / (I_{4.64-4.71} / 2)] / [(I_{3.33-3.41} / 3) / (I_{4.64-4.71} / 2)] \quad \text{Formulate S1}$$

$$M_{n,\text{NMR}} = m \times M_{\text{ChEMA}} + n \times M_{\text{OEGMA}} + M_{\text{CPDBP}} \quad \text{Formulate S2}$$

M_{CPDBP} : the molecular mass of the RAFT agent CPDBP.

Table S1. Characterization data of *linear* and *cyclic* LC amphiphilic diblock copolymers

sample	M_n^a (g/mol)	M_n^b (g/mol)	M_w/M_n^b	f_{PChEMA}^c (wt %)
<i>linear</i> PChEMA ₁₃ - <i>b</i> -POEGMA ₁₅	11900	12300	1.12	61
<i>cyclic</i> PChEMA ₁₃ - <i>b</i> -POEGMA ₁₅		11300	1.12	
<i>linear</i> PChEMA ₁₈ - <i>b</i> -POEGMA ₁₄	14200	14400	1.11	70
<i>cyclic</i> PChEMA ₁₈ - <i>b</i> -POEGMA ₁₄		13200	1.12	

^aMeasured by ¹H NMR spectra. ^bDetermined by GPC measurements. ^cPChEMA weight fraction in

the PChEMA-*b*-POEGMA diblock copolymers.

Self-assembly of linear and cyclic copolymers in 1,4-dioxane/H₂O solution

The solution self-assembly of linear and cyclic amphiphilic LC copolymers was performed at the exact identical conditions for systematic study. Typically, the sample was first completely dissolved in 1,4-dioxane, with an initial concentration of 1.0 mg/mL. The polymer solutions were filtered through a PTFE filter with 0.22 µm pore size to remove any dusts to obtain the stock solution. Milli-Q water was then slowly added (0.1 mL/h) to 1.0 mL of the stock solution under gentle shaking at room temperature until the final water content reached 60 wt%. The stable micelles could be obtained by dialyzing the micelle solution against deionized water for 2 days to remove all the organic solvent.

Characterization

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by a TOSOH HLC-8320 size exclusion chromatography equipped with refractive-index and UV detectors using two TSKgel Super Mutipore HZ-N (4.6×150 mm, 3 µm beads size) columns arranged in series, and it can separate polymers in the molecular weight range from 500~1.9×10⁵ g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software, and molecular weights were calculated with polymethyl methacrylate (PMMA) standards. FT-IR spectra were obtained on a Bruker TENSOR-27 FT-IR spectrometer by mixing polymer with KBr as tablets. ¹H NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) using

tetramethylsilane (TMS) as the internal standard at room temperature, NMR samples were prepared with concentration of ~20 mg/mL in CDCl₃. SAXS experiments were used to identify the phase structures of the LCs, which were performed using a high-flux X-ray instrument (SAXSess mc², Anton Paar) equipped with line collimation system and a 2200 W sealed-tube X-ray generator (CuK α , λ = 0.154 nm). Samples were wrapped into aluminum foils and sandwiched in a steel sample holder. The X-ray scattering patterns were recorded in vacuum on an imaging-plate (IP). The scattering peak positions were calibrated with silver behenate. A temperature control unit (Anton paar TC300) in conjunction with the SAXSess mc² was utilized to study the structure evolution as a function of temperature. Samples for TEM observation were prepared by placing a drop of self-assembled polymer solution onto a carbon-coated copper grid. After 30 s, the excess fluid was removed with a piece of filter paper. Then a drop of staining agent phosphotungstic acid (1 wt%) was placed on the grid, and after 30 s, the excess solution was removed with a piece of filter paper and the grid was left to dry under the ambient conditions. Transmission electron microscopy (TEM) was recorded on HITACHI HT7700 at a 120 kV accelerating voltage. Hydrodynamic diameter (D_h) was measured by dynamic light scattering (DLS) using Brookhaven's NanoBrook 90Plus PALS instrument at 25 °C at a scattering angle of 90°. The surface morphology was measured by atomic force microscope (AFM) with a tapping mode (Veeco Instruments Inc., Nanoscope IV). The self-assembled polymer solution was dropped onto precleaned silicon wafer and was then left to dry under the ambient conditions.

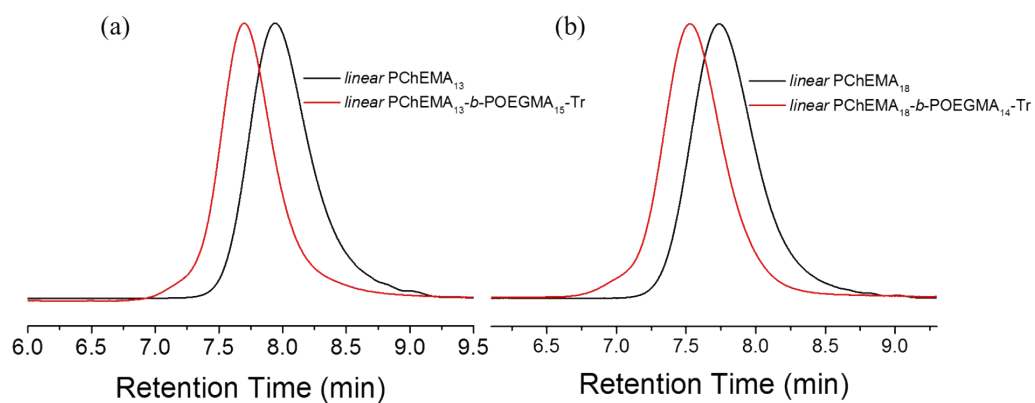


Figure S1. GPC traces of (a) *linear* PChEMA₁₃ and *linear* PChEMA₁₃-*b*-POEGMA₁₅ (after chain extension), (b) *linear* PChEMA₁₈ and *linear* PChEMA₁₈-*b*-POEGMA₁₄ (after chain extension).

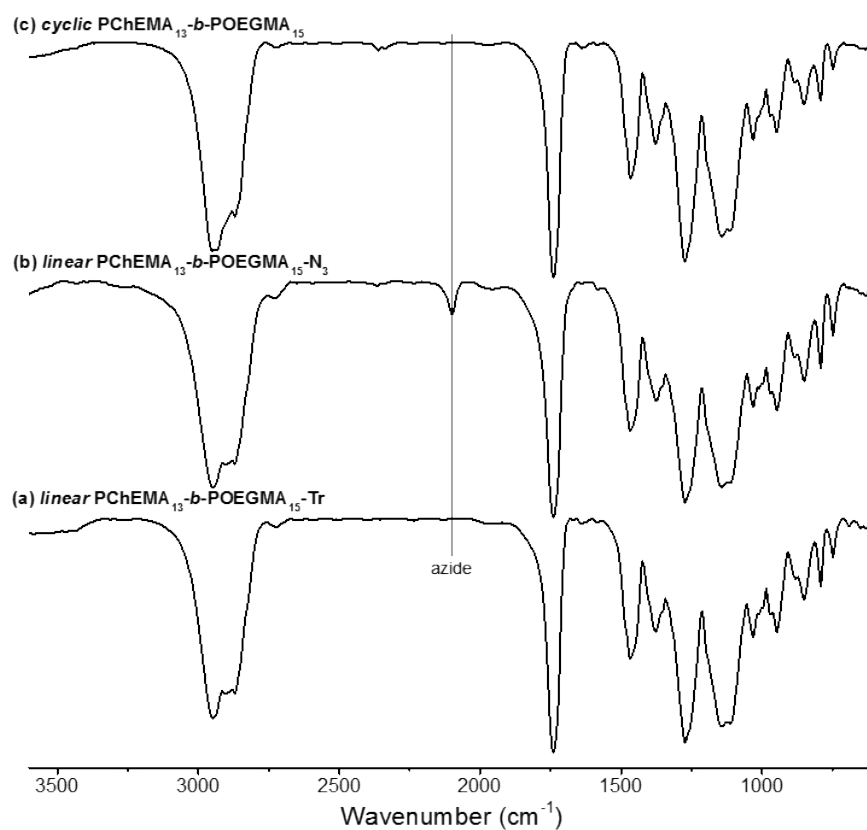


Figure S2. FT-IR spectra of (a) *linear* PChEMA₁₃-*b*-POEGMA₁₅-Tr, (b) *linear* PChEMA₁₃-*b*-POEGMA₁₅-N₃, and (c) *cyclic* PChEMA₁₃-*b*-POEGMA₁₅.

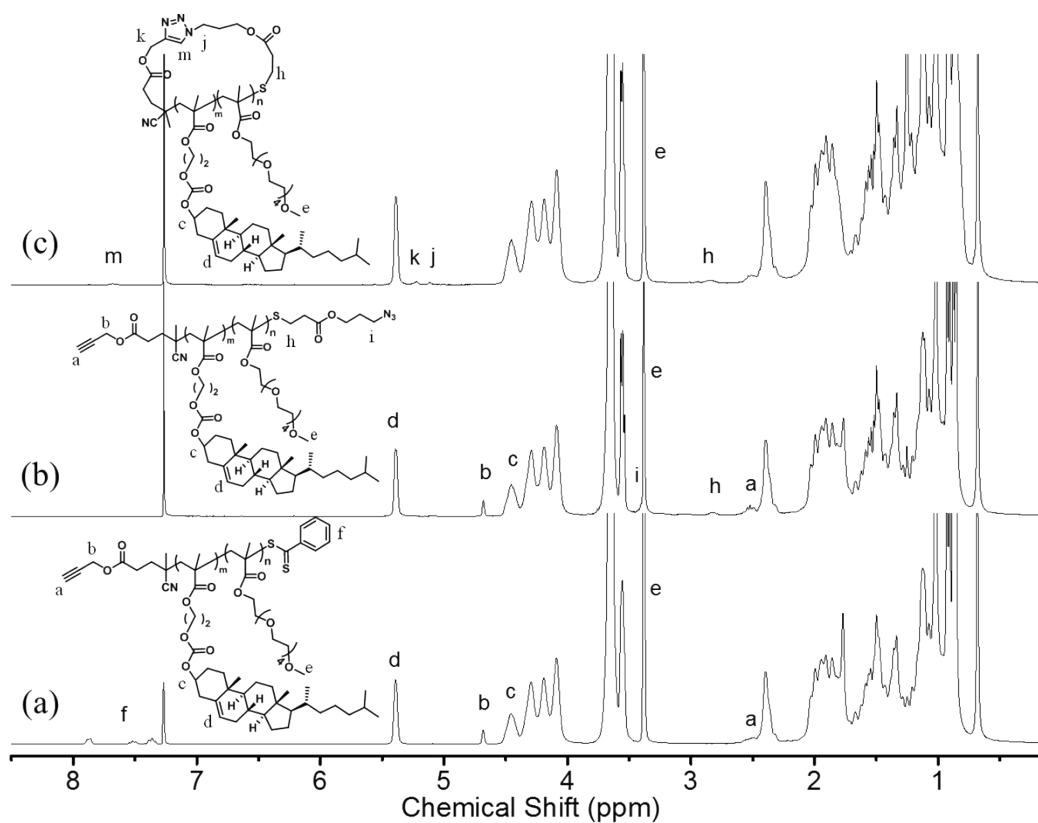


Figure S3. ^1H NMR spectra of (a) *linear* PChEMA₁₃-*b*-POEGMA₁₅-Tr, (b) *linear* PChEMA₁₃-*b*-POEGMA₁₅-N₃, and (c) *cyclic* PChEMA₁₃-*b*-POEGMA₁₅.

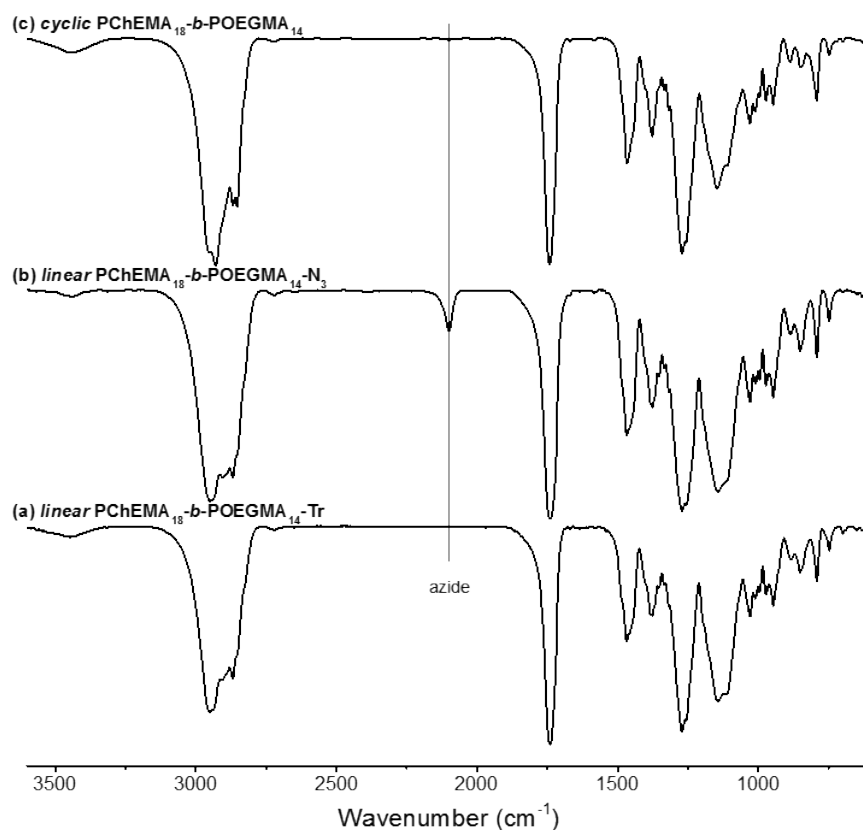


Figure S4. FT-IR spectra of (a) *linear* PChEMA₁₈-*b*-POEGMA₁₄-Tr, (b)

*linear*PChEMA₁₈-*b*-POEGMA₁₄-N₃, and (c) *cyclic* PChEMA₁₈-*b*-POEGMA₁₄.

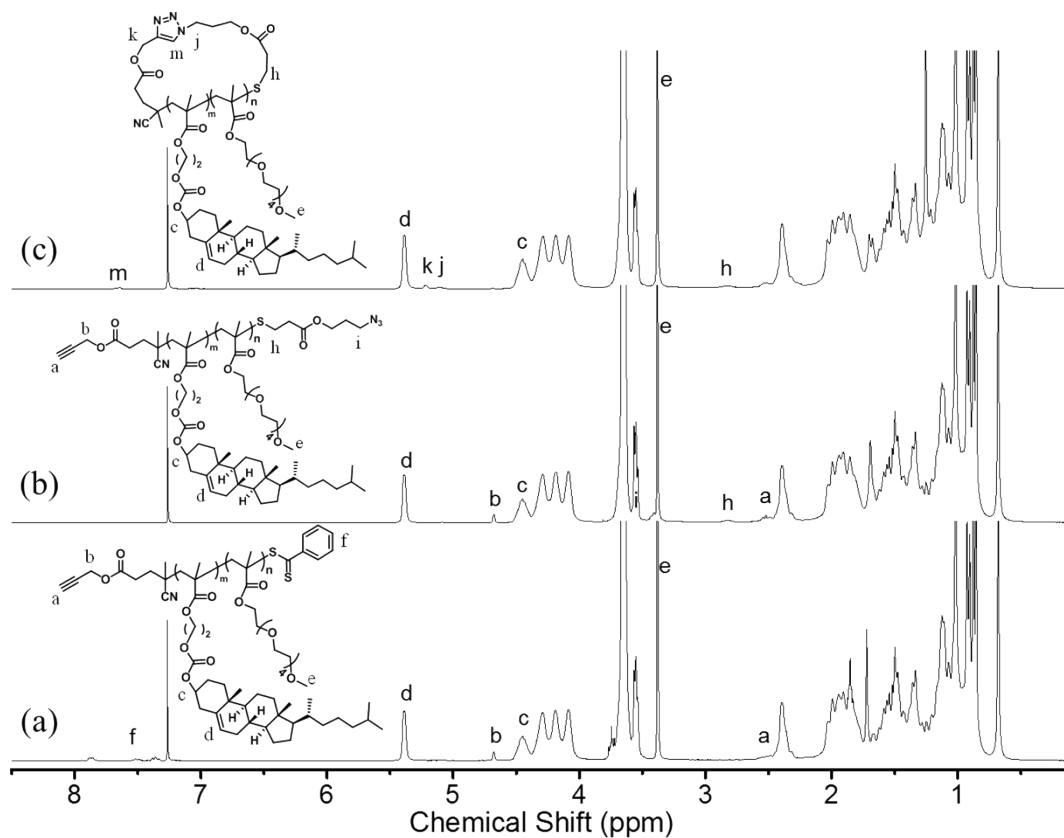


Figure S5. ¹H NMR spectra of (a) *linear* PChEMA₁₈-*b*-POEGMA₁₄-Tr, (b) *linear*PChEMA₁₈-*b*-POEGMA₁₄-N₃, and (c) *cyclic* PChEMA₁₈-*b*-POEGMA₁₄.

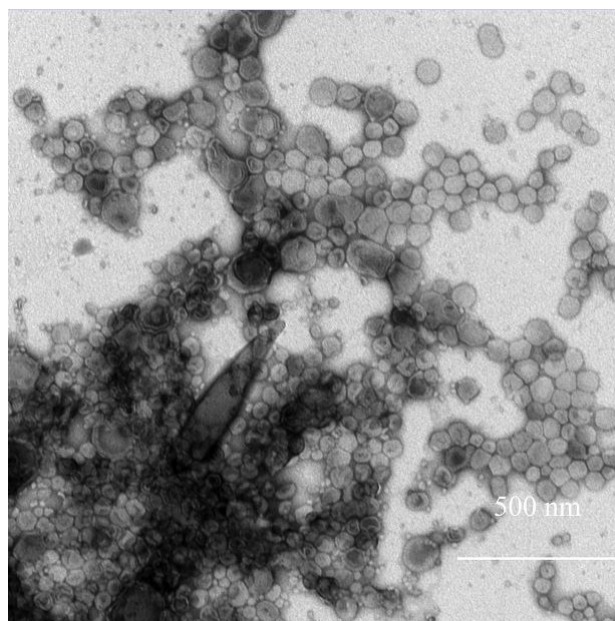


Figure S6. TEM image (stained with phosphotungstic acid) of self-assembled

morphologies of *cyclic* PChEMA₁₃-*b*-POEGMA₁₅ in 1,4-dioxane/H₂O (1/1.5). The initial concentration was 1.0 mg/mL.

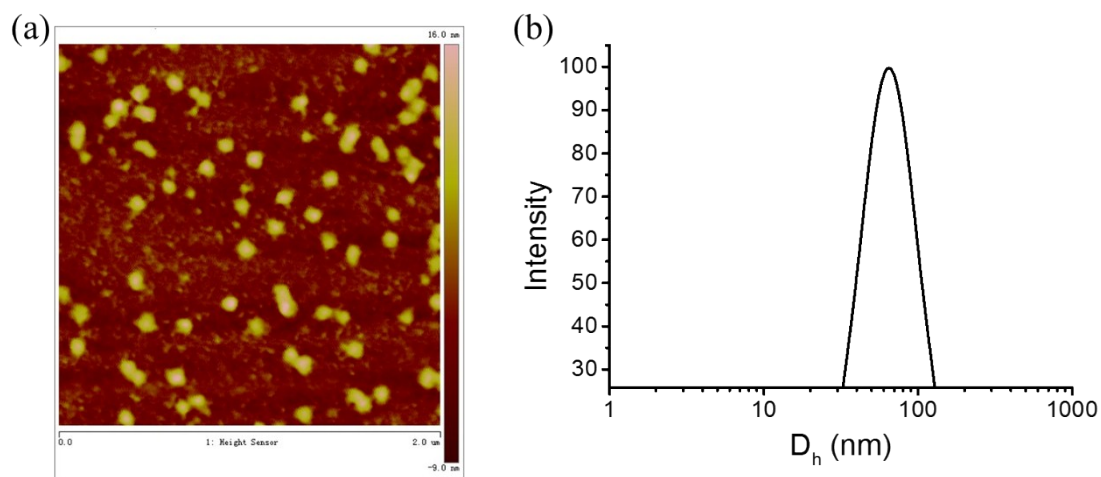


Figure S7. Characterization of vesicles formed by *cyclic* PChEMA₁₃-*b*-POEGMA₁₅ in 1,4-dioxane/H₂O (1/1.5): (a) AFM image; (b) hydrodynamic diameters (D_h) distributions determined by DLS.

References

- (1) Zhou, F.; Li, Y. W.; Jiang, G. Q.; Zhang, Z. B.; Tu, Y. F.; Chen, X. F.; Zhou, N. C.; Zhu, X. L. *Polym. Chem.* **2015**, *6*, 6885-6893.