Supporting Information

for

Biomacrocyclic Side-Chain Liquid Crystalline Polymers Bearing Cholesterol Mesogens: Facile Synthesis and Topological Effects Study

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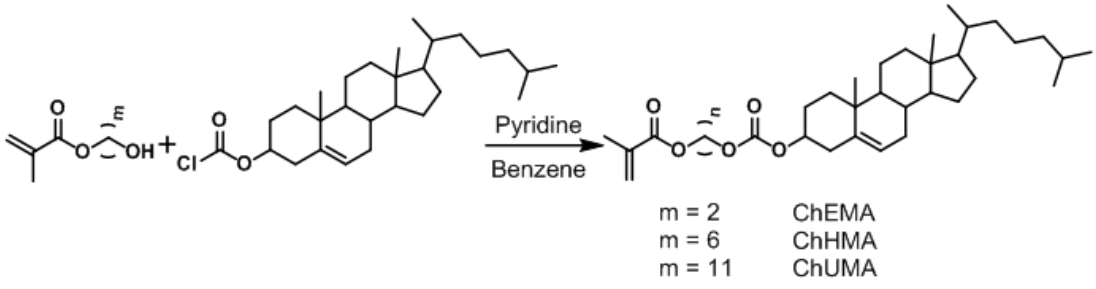
Experimental Section

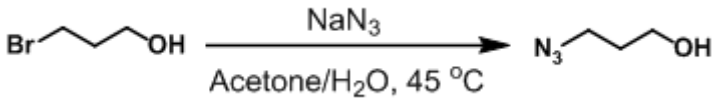
Synthesis of cholesteryl-containing methacrylate monomers



Scheme S1. Synthesis of cholesteryl-containing methacrylate monomers.

The synthetic procedure of ChEMA was as follows: Cholesteryl chloroformate (8.98 g, 20 mmol) and 2-hydroxyethyl methacrylate (5.20 g, 40 mmol) were dissolved in dry benzene (80 mL), the solution was stirred at 45 ^{o}C and then a solution of pyridine (2.05 g, 26 mmol) in dry benzene (10 mL) was added dropwise over 1 h. The mixture was then stirred for additional 5 h. After that, the formed salt was removed by filtration and benzene was removed under reduced pressure, then 150 mL CH_2Cl_2 was added and the solution was washed with distilled water and saturated aqueous NaCl solution for two times, the organic layer was collected and dried over anhydrous $MgSO_4$ overnight. After removal of solvent, the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (v/v = 20/1) as eluent to obtain ChEMA (9.5 g) as a white solid. Yield: 87 %. ChHMA and ChUMA were prepared using similar procedures, only replaced 2-hydroxyethyl methacrylate to 6-hydroxyhexyl methacrylate and 11-hydroxylundecyl methacrylate, respectively. The ^{1}H NMR spectra of ChEMA, ChHMA and ChUMA were shown in Figure S1, Figure S2 and Figure S3, respectively.

Synthesis of 3-azidopropanol

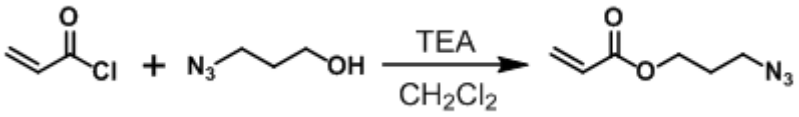


Scheme S2. Synthesis of 3-azidopropanol.

3-Bromobutanol (6.00 g, 0.043 mol) and NaN_3 (5.60 g, 0.086 mmol) were dissolved in acetone/H_2O (v/v = 2/1, 25 mL) under magnetic stirring. The mixture was stirred at 45 ^{o}C for 24 h. Acetone was then removed under reduced pressure, 80 mL of water were added and the mixture was extracted with CH_2Cl_2 (3×50 mL). The

organic layer was collected, dried over anhydrous $MgSO_4$, filtered and evaporated to obtain a colorless oil (3.85 g). Yield: 88 %. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 3.76 (2H, t, C<u>H</u>$_2$-OH), 3.46 (2H, t, C<u>H</u>$_2$-N_3), 1.84 (2H, m, CH_2-C<u>H</u>$_2$-CH_2), 1.66 (1H, s, CH_2-O<u>H</u>).

Synthesis of 3-azidopropyl acrylate



Scheme S3. Synthesis of 3-azidopropyl acrylate.

3-Azidopropanol (3.85 g, 0.038 mol), TEA (5.00g, 0.049 mol) were dissolved in 60 mL anhydrous CH_2Cl_2 under magnetic stirring. The solution was cooled to 0 ^{o}C in an ice bath and acryloyl chloride (4.48 g, 0.049 mol) diluting in 15 mL CH_2Cl_2 was slowly added dropwise over 1 h. The mixtures were allowed to warm up to room temperature and stir for another 24 h. The formed salt was removed by filtration and the solution was washed two times with distilled water and saturated aqueous NaCl solution, the organic layer was collected and dried over anhydrous $MgSO_4$ overnight. After removal of solvent, the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (v/v = 20/1) as eluent to obtain 3-azidopropyl acrylate (3.20 g) as a light yellow oil. Yield: 54 %. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 6.39 (1H, d, C<u>H</u>$_a$H$_b$=CH-), 6.14 (1H, q, CH$_a$H$_b$=C<u>H</u>-), 5.83 (1H, d, CH$_a$<u>H</u>$_b$=CH-), 4.26 (2H, t, CH_2-C<u>H</u>$_2$-O-), 3.42 (2H, t, C<u>H</u>$_2$-N_3), 1.96 (2H, m, CH_2-C<u>H</u>$_2$-CH_2). Tips: The organic azide compound is very sensitive to heat, which should be immediately used for the next step reaction, long period storage even in the fridge might induce the self-

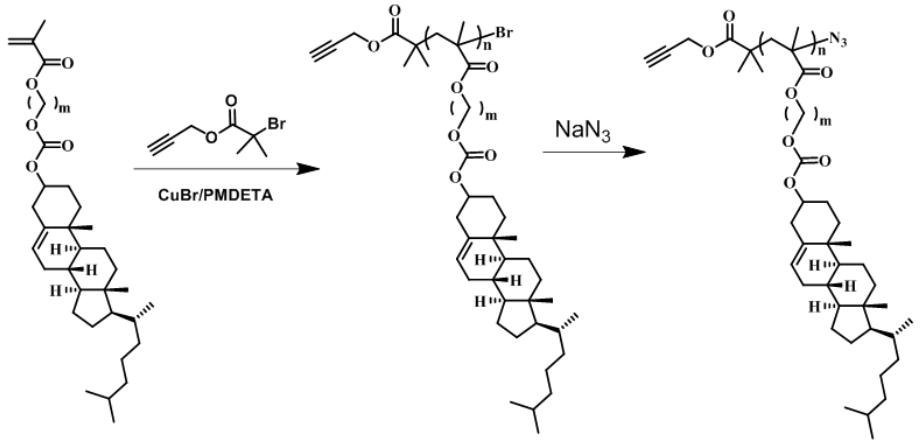
polymerization.

The number of repeated units (n) and the number average molecular weight ($M_{n,NMR}$) of the resultant RAFT polymers was calculated from their ^{1}H NMR spectra by Formulate S1 and S4:

$$n = (I_{5.31\text{-}5.46})/(I_{4.64\text{-}4.71}/2) \quad \text{Formulate S1}$$

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

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



Scheme S4. Synthetic routes of polymeric linear precursors *via* ATRP.

Azidation process of polymer prepared by ATRP:

1.0 g linear PChHMA-Br and NaN_3 in a 20-fold molar excess were dissolved in a 10 mL of DMF/anisole (2/3, v/v) mixed solvents in a round-bottom flask. The reaction mixture was stirred at 50 ^oC for 24 h (afterwards, we even rise the temperature up to 70 ^oC), collected by filtration to remove residual sodium salts before purification by precipitation into methanol, followed by filtrating and drying in vacuo at 25 ^oC to give a white solid.

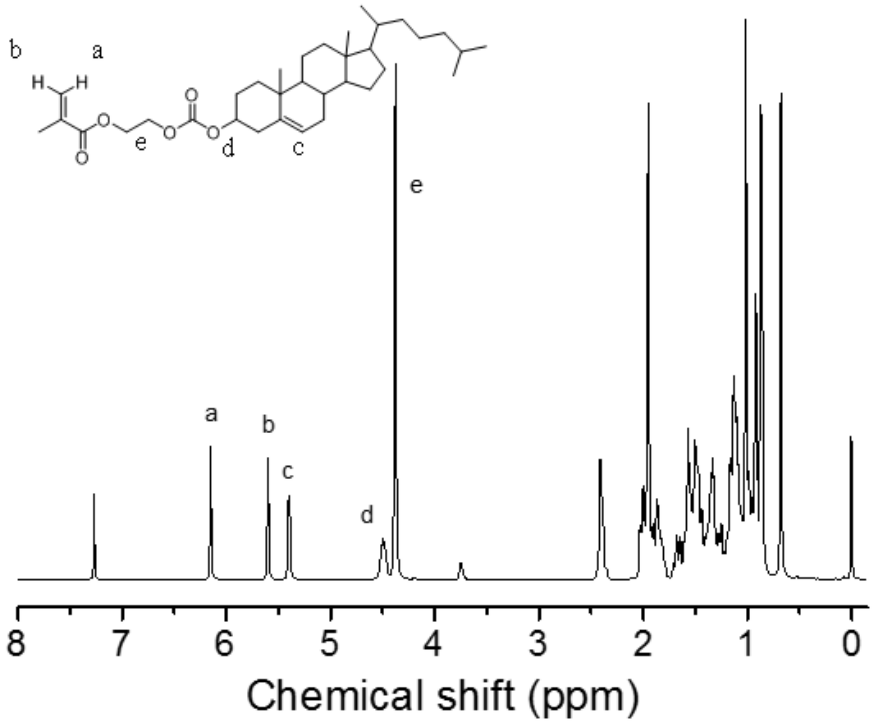


Figure S1. ^{1}H NMR spectrum of ChEMA.

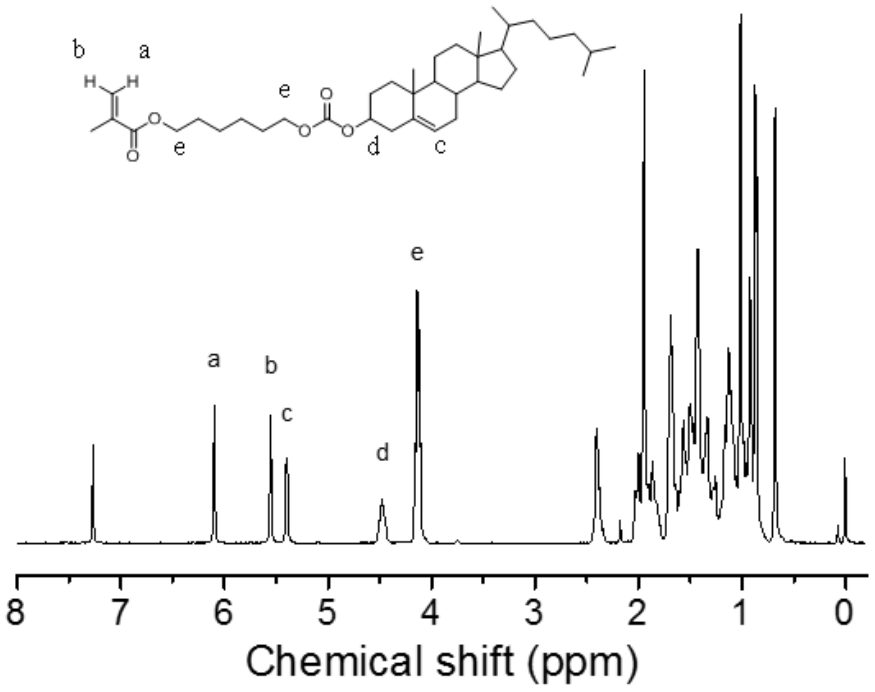


Figure S2. ^{1}H NMR spectrum of ChHMA.

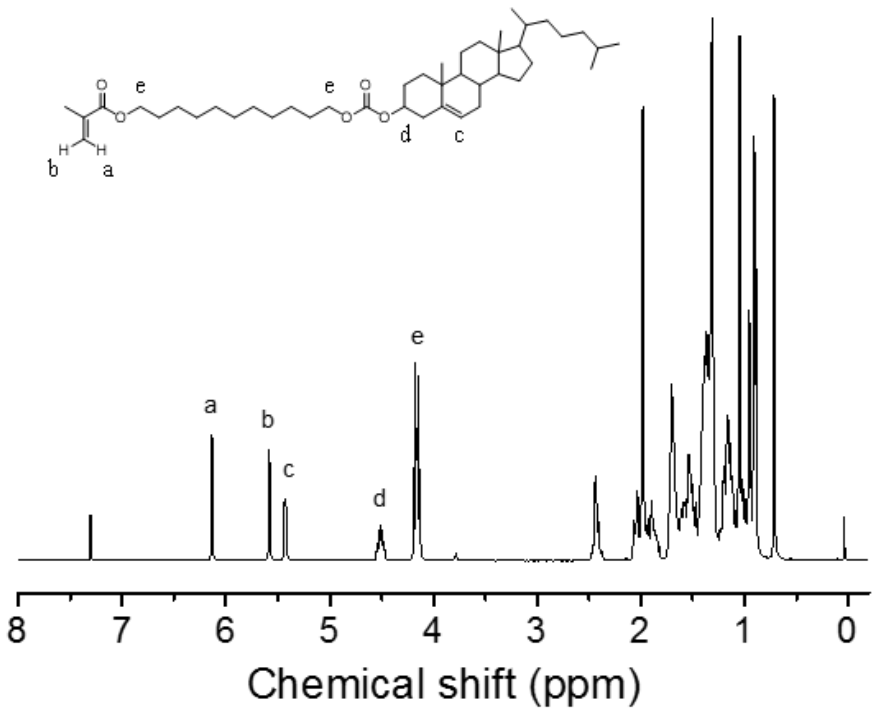


Figure S3. ^{1}H NMR spectrum of ChUMA.

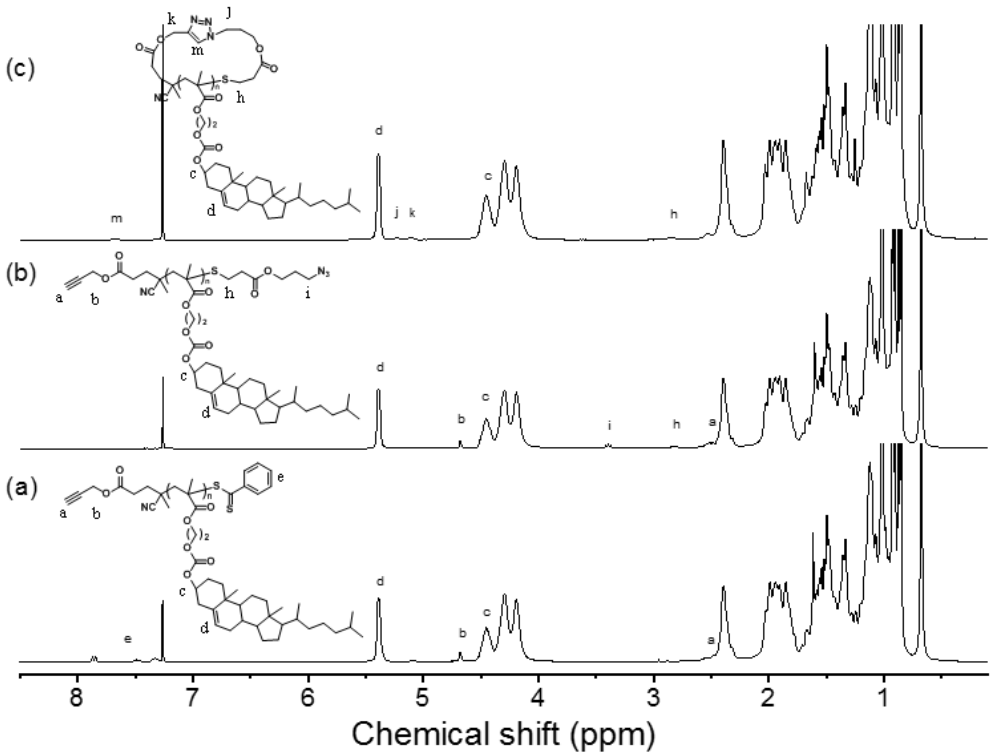


Figure S4. ^{1}H NMR spectra of (a) *linear* PChEMA-Tr, (b) *linear* PChEMA-N_3, and (c) *cyclic* PChEMA.

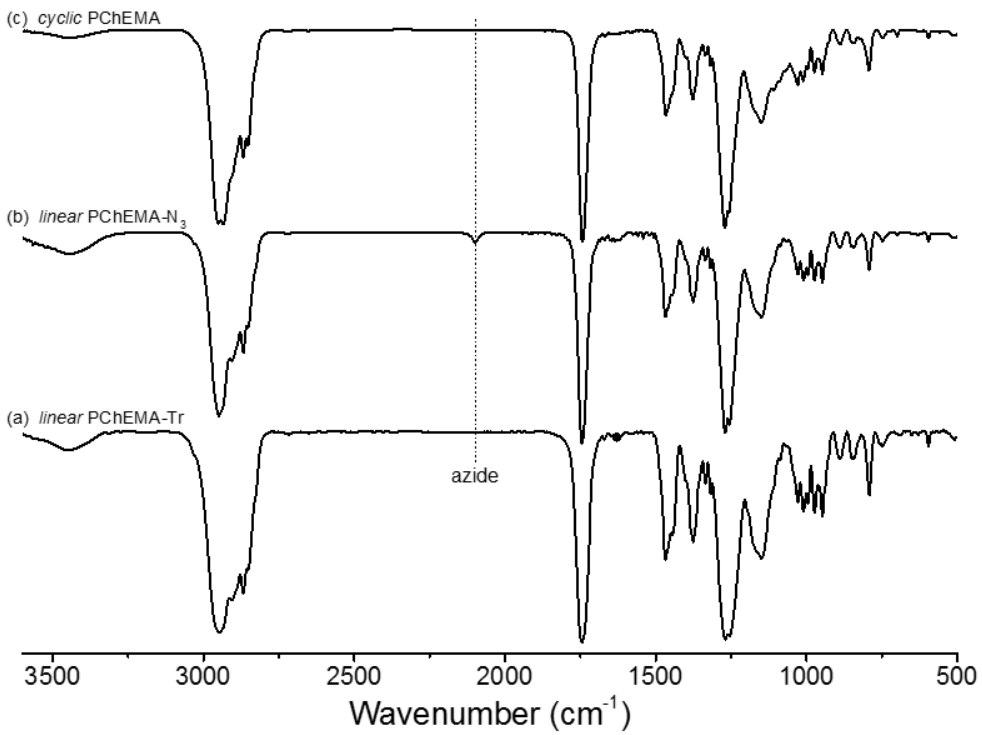


Figure S5. FT-IR spectra of (a) *linear* PChEMA-Tr, (b) *linear* PChEMA-N_3, and (c) *cyclic* PChEMA.

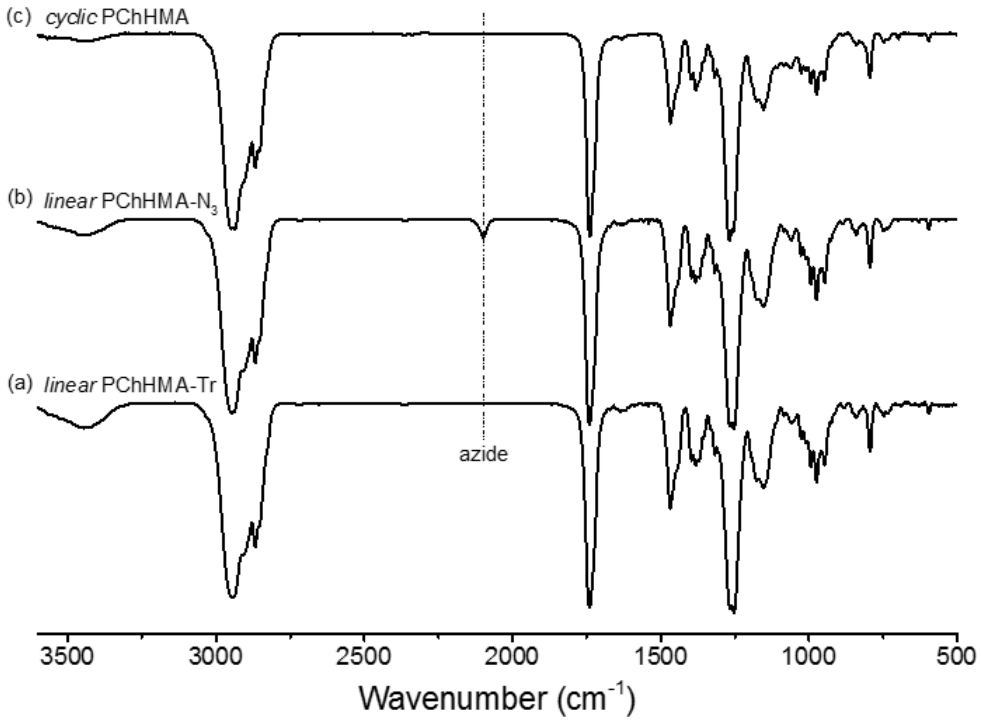


Figure S6. FT-IR spectra of (a) *linear* PChHMA-Tr, (b) *linear* PChHMA-N_3, and (c) *cyclic* PChHMA.

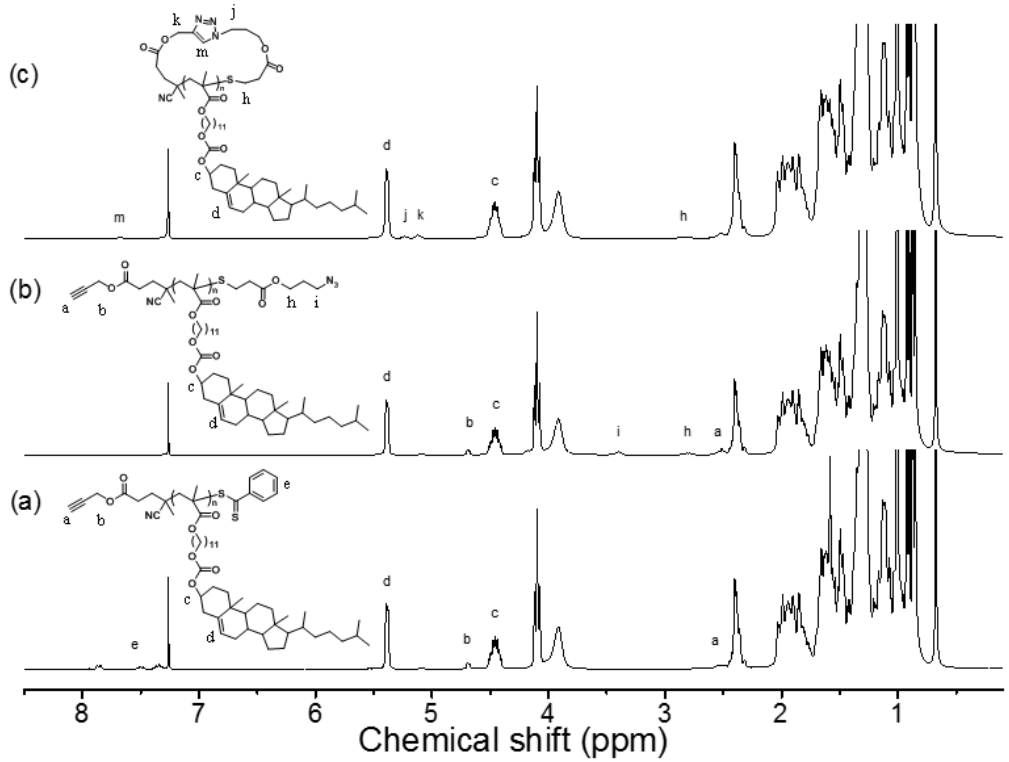


Figure S7. ^{1}H NMR spectra of (a) *linear* PChUMA-Tr, (b) *linear* PChUMA-N_3, and (c) *cyclic* PChUMA.

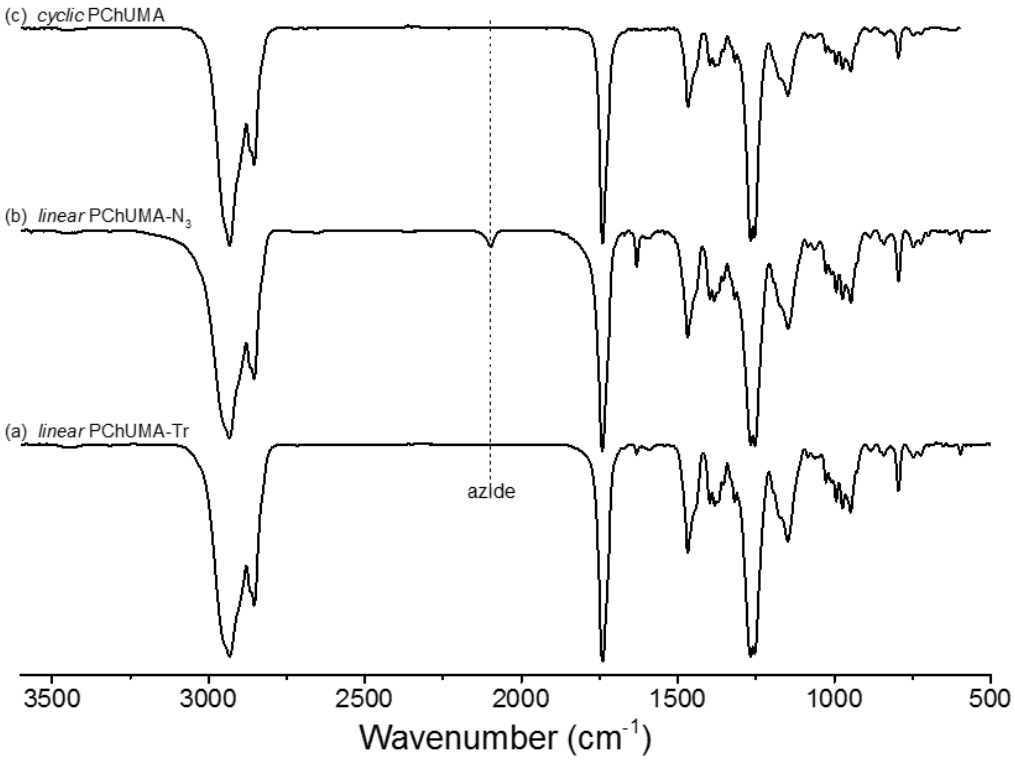
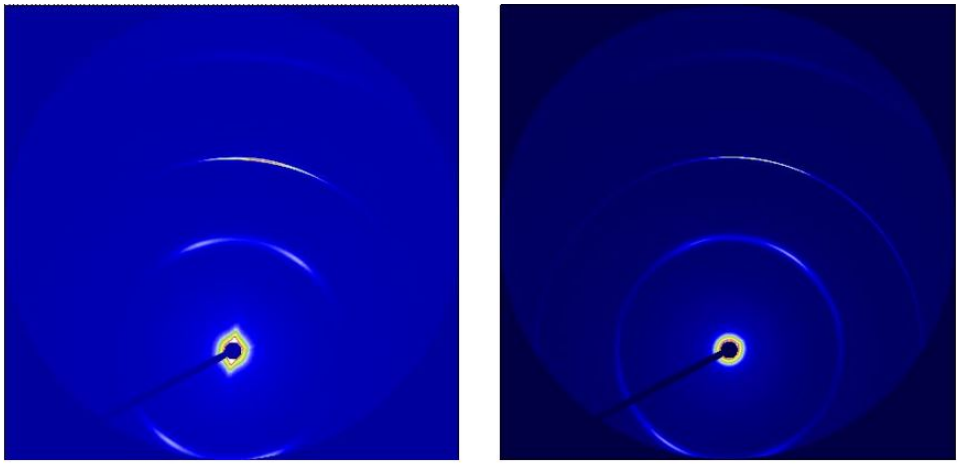


Figure S8. FT-IR spectra of (a) *linear* PChUMA-Tr, (b) *linear* PChUMA-N_3, and (c) *cyclic* PChUMA.



linear-PChUMA *cyclic*-PChUMA

Figure S9. 2D SAXS profiles of *linear*, *cyclic* PChUMA recorded, respectively.