Smectic Polymer Vesicles

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Supplementary Information

SYNTHETICAL PROTOCOLE

The liquid-crystalline (LC) homopolymer PAChol was synthesized by ATRP according to the following protocole. A Schlenk flask with a magnetic stir bar was charged with $Cu^{I}Br$ (14.34 mg, 0.1 mmol), ethyl 2-bromo-2-methylpropionate (19.51 mg, 0.1 mmol), 4,4'-di(*n*-nonyl)-2,2'-bipyridine (81.76 mg, 0.2 mmol) and monomer AChol (528.66 mg, 1 mmol). The flask was degassed by four vacuum-argon cycles. Toluene (1 mL), degassed by

argon bubbling for 30 min, was then introduced into the flask using a syringe purge with argon. The flask was then immersed in an oil bath thermostated at 80 ^{o}C. After 24 h of reaction, the mixture was cooled to room temperature. The resulting polymer solution was poured into a large volume of diethyl ether. The precipitated diblock copolymer was purified 4 times by dissolution in a small amount of dichloromethane and precipitation into a large volume of methanol, and once by dissolution in acetone and precipitation into methanol. The purified polymer was dried under vacuum at room temperature for 3 days. Yield: 0.4336 g (79%).

The side-chain LC diblock copolymers PEG-*b*-PAChol were also synthesized by ATRP. For the synthesis of Copo1, a Schlenk flask with a magnetic stir bar was charged with PEG-Br macroinitiator (0.213g, 0.1 mmol), $Cu^{I}Br$ (28.6 mg, 0.2 mmol), and monomer AChol (0.4 g, 0.76mmol). The flask was degassed for 30 min. Then xylene (0.5 mL) and PMDETA (34.6 mg, 0.2 mmol) were added and the flask was further degassed by three freeze-pump-thaw cycles, and then immersed in an oil bath thermostated at 80ºC. After 24 h of reaction, the mixture was immersed in liquid nitrogen for 10 min and the flask was warmed slowly in ethanol to room temperature. The polymerization mixture was first passed through a short column of aluminum oxide, using CH_2Cl_2 as eluent to remove copper salts. The resulting polymer solution was poured into a large volume of methanol. The removal of unreacted monomer from the polymer was confirmed by the disappearance of the peaks associated with the alkene protons at 5.8 and 6.1 ppm in the ^{1}H NMR spectra of the monomer. The purified polymer was dried under vacuum at room temperature for 2 days. Yield: 0.53g (86%). For the synthesis of Copo2, similar procedure was used except the weight of monomer AChol(0.6 g, 1.14 mmol) and the polymerization time (36 hours).

Table S1 Molecular weights and molecular weight distributions of homopolymers and diblock copolymers PEG_{45}-*b*-PAChol

Samples	$M_{n,NMR}$ (g.mol^{-1})[a]	n_{AChol} [a]	$M_{n,SEC}$ (g.mol^{-1})[b]	M_w/M_n [b]
PEG_{45}-Br	-	-	2300	1.04
Homopolymer PAChol	5230	10	-	1.11
Copo1 (28/72)	7100	10	6000	1.13
Copo2 (20/80)	10200	16	6500	1.14

Notes: [a] Degree of polymerization n_{AChol} and molecular weights calculated by ^{1}H NMR.

[b] Molecular weights and their distributions determined by SEC calibrated with polystyrene standards for homopolymer PAChol and by SEC calibrated with poly(ethylene glycol) standards for PEG_{45}-Br and copolymers.

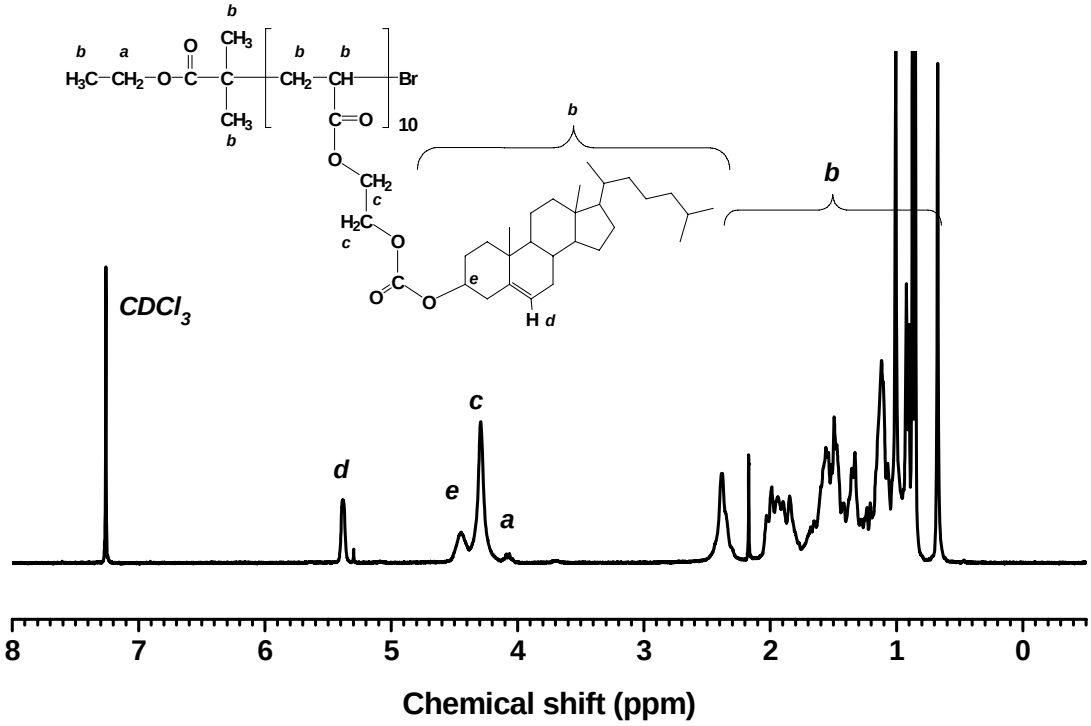

Figure S1. 300 MHz ^{1}H NMR spectrum of the LC homopolymer PAChol

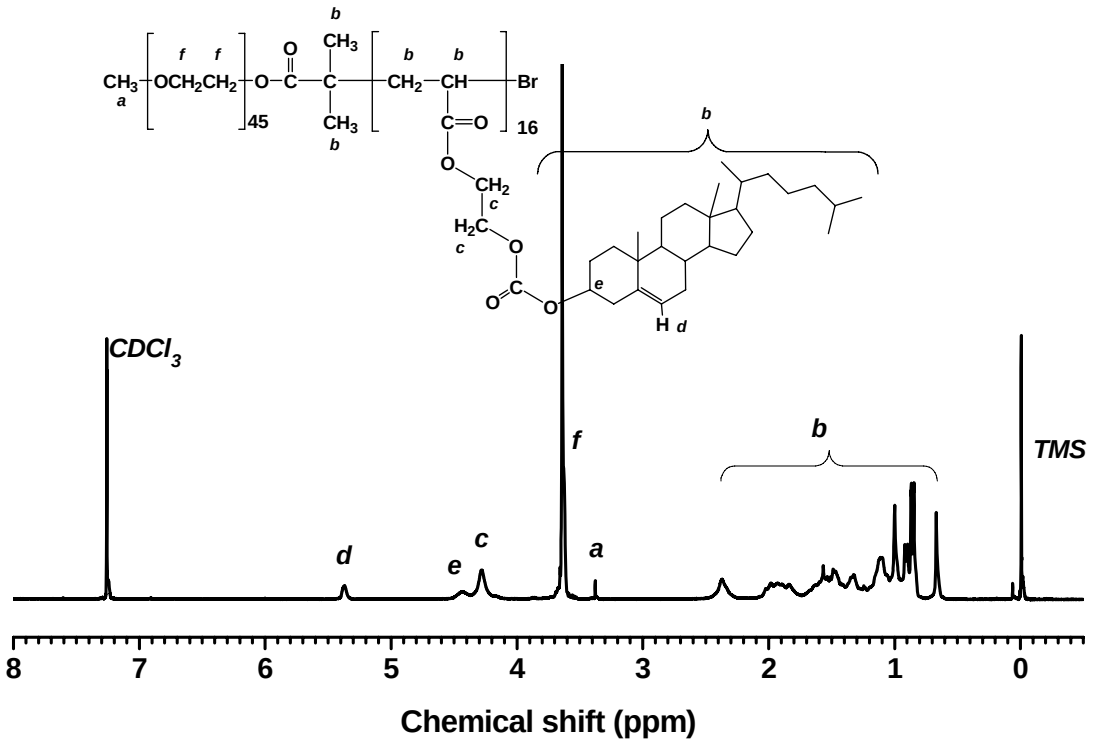

Figure S2. 300 MHz ^{1}H NMR spectrum of the LC diblock copolymer PEG-*b*-PAChol (20/80)

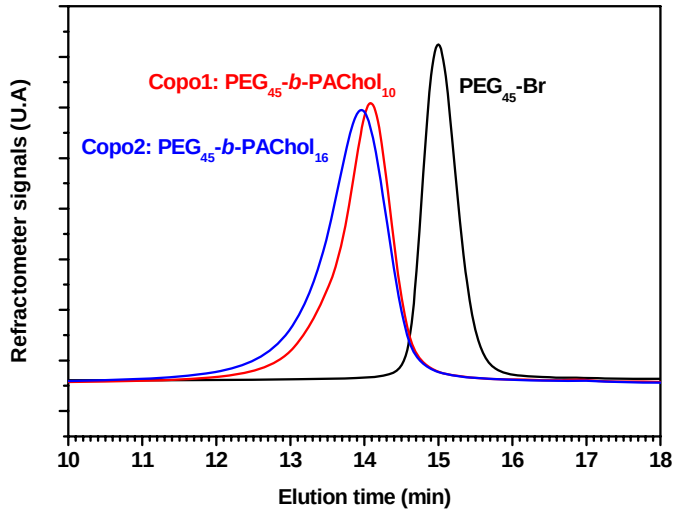

Figure S3. SEC curves of the LC block copolymers and macro-initiator PEG_{45}-Br.

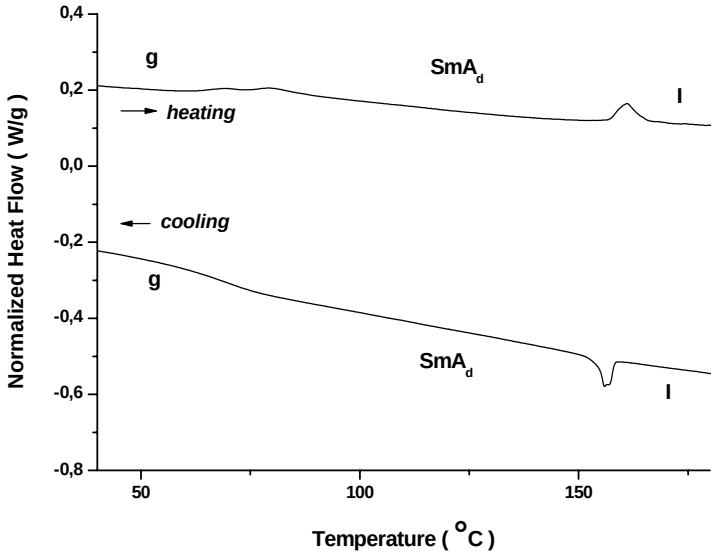

Figure S4. DSC curves of the LC homopolymer PAChol on heating and cooling at 10ºC.min^{-1}

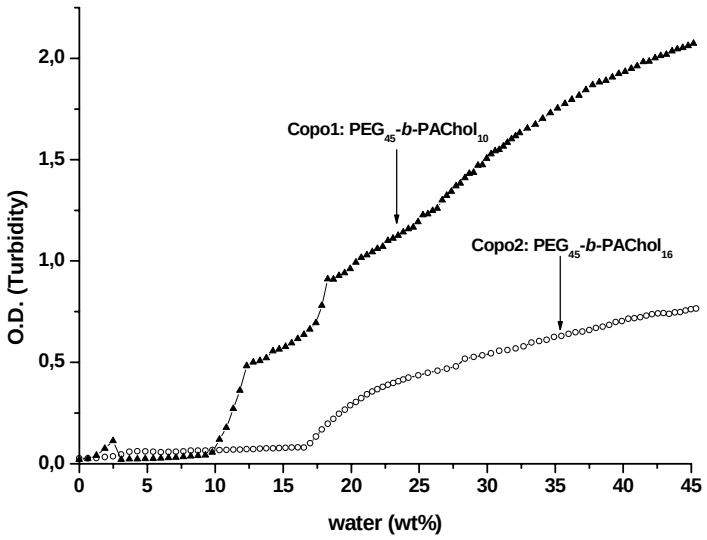

Figure S5. Turbidity (optical density) curves of Copo1 (o) and Copo2 (▲) solutions in dioxane as a function of the amount of water added (starting concentration was 1.0wt% in dioxane).

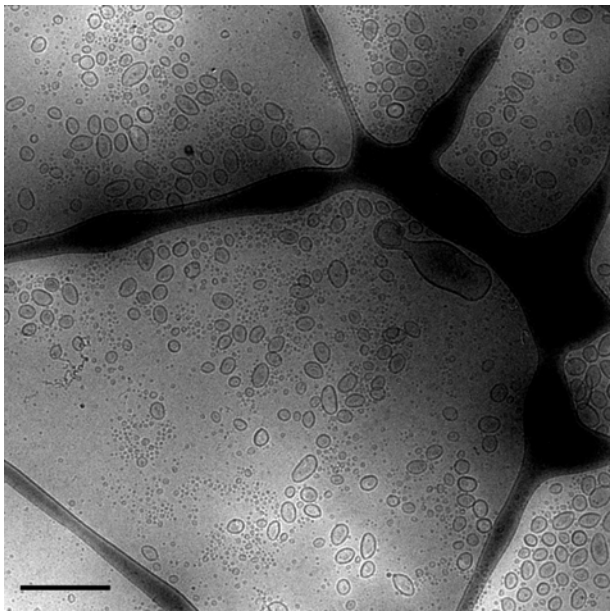

Figure S6. Cryo-TEM image of Copol at 3000 magnification. Scale bar = 1 μm.

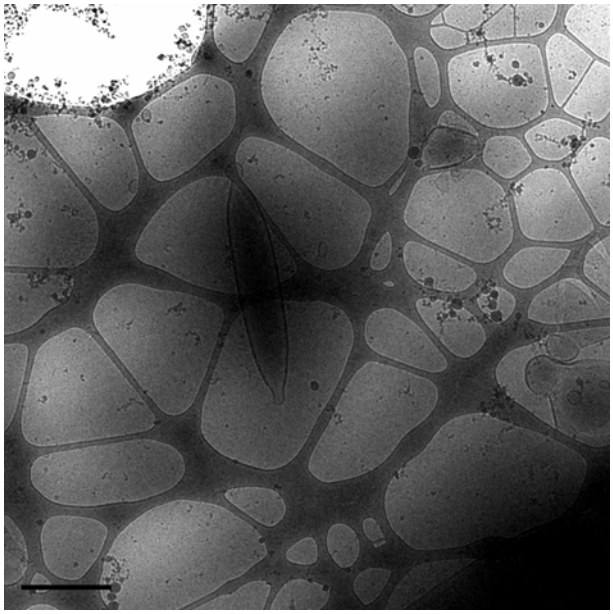

Figure S7. Cryo-TEM image of Copo2 at 3000 magnification. Scale bar = 1 μm.