Self-assembly of Amphiphilic Liquid Crystal Polymers Obtained From A Cyclopropane -1,1-Dicarboxylate Bearing A Cholesteryl Mesogen

Lin Jia,[†] Ming Liu,[‡] Blandine Brissault,[‡] Aurélie Di-Cicco,[†] Pierre-Antoine Albouy,[§] Jacques Penelle,[‡] Sylvie Boileau,[‡] Valessa Barbier,[‡,*] Min-Hui Li[†*]

[†] Institut Curie, CNRS, Université Pierre et Marie Curie, Laboratoire Physico-Chimie Curie, UMR168, 26 rue d'Ulm, 75248 Paris CEDEX 05, France.

[‡] Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS, Université Paris-Est, 2-8 rue Henri Dunant, 94320 Thiais, France.

[§] Université Paris-Sud, CNRS, Laboratoire de Physique des Solides, UMR8502, 91405 Orsay CEDEX, France.

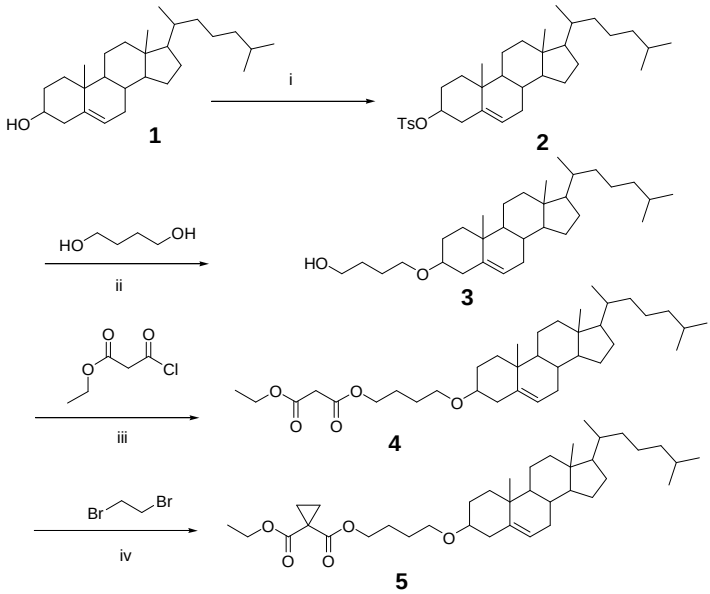
[*] Corresponding author:

e-mail: min-hui.li@curie.fr, Tel.: 33 1 56246763, Fax: 33 1 40510636 (MHL)

e-mail: barbier@icmpe.cnrs.fr, Tel: 33 1 49781194 , Fax: 33 1 49781208 (VB)

Supporting Information

1. Synthesis of 4-(cholesteryl)butyl ethyl cyclopropane-1,1-dicarboxylate, liquid crystal monomer.



(i) TsCl, Pyridine. (ii) Dioxane, reflux. (iii) Et_3N,CH_2Cl_2, 0^oC~ 25^oC. (iv) K_2CO_3, DMSO/CH_2Cl_2=1:1, 25^oC, 3 days

Scheme SI-1. Synthetic route for liquid crystal monomer.

Cholesteryl tosylate (**2**)**. 2** was synthesized from cholesterol (25 g, 64.5 mmol) and tosyl chloride (25 g, 131.5 mmol) by refluxing for 24 h in 200 mL pyridine. The solution was added to 1.8 L of a 5% K_2CO_3 aqueous solution, and stirred for one hour at 4 ^oC. A solid was recovered by filtration, then dissolved in 400 mL dichloromethane. After washing with distilled water, the organic phase was dried over anhydrous Na_2SO_4, then concentrated by rotary evaporation. The solid product was purified by recrystallization from acetone. Yield 27.4 g (80.6%). ^1H NMR (300 MHz $CDCl_3$): δ 7.80 (d, 2H, aromatic para-), 7.33 (d, 2H aromatic para-), 5.30 (d, 1H, -C(CH-)=C<u>H</u>-), 4.32 (m, 1H, -C<u>H</u>(CH_2-)-OTs), 2.45 (s, 3H, C<u>H</u>$_3$- aromatic), 0.66-2.40(m, 43H, -C<u>H</u>$_3$, -C<u>H</u>(CH_3)-, -C<u>H</u>-, -C<u>H</u>$_2$-, alkyl protons).

4-Cholesteryloxy-butan-1-ol (**3**). 1,4-Butandiol (5.8 g, 64.5 mmol) was first dissolved in 300 mL of dry dioxane, and cholesteryl tosylate (**2**) (7 g, 12.9 mmol) was added to the solution. The mixture

was refluxed for 48 h. Dioxane was then removed by distillation, and the solid product was dissolved in 200 mL dichloromethane. The solution was washed three times with a saturated $NaHCO_3$ aqueous solution, then with distilled water. The washed solution was dried over anhydrous Na_2SO_4. Finally, after dichloromethane removal, the product was purified by column chromatography with silica gel (eluent: ethyl acetate/hexane 1/20, *v*/*v*) to yield compound **3**. Yield 7.5 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.33-5.35 (d, 1H, -C(CH_2-)=C<u>H</u>-), 3.62-3.66 (t, 2H, -C<u>H</u>$_2$-OH), 3.42-3.46 (t, 2H, -C<u>H</u>$_2$-O-CH-), 3.12 (m, 1H, -C<u>H</u>O-), 0.67-2.40 (m, 47H, -C<u>H</u>$_3$, -C<u>H</u>(CH_3)-, -C<u>H</u>-, -C<u>H</u>$_2$-, alkyl protons) (see Fig. SI-1 for ^{1}H NMR spectra).

4-Cholesteryloxy-butyl ethyl malonate (**4**). Ethyl malonyl chloride (2.5 g, 16.6 mmol) in dichloromethane (20 mL) was added dropwise to a solution of 4-cholesteryloxy butanol (**3**) (5 g, 11.0 mmol) and triethylamine (1.65 g, 16.6 mmol) in dichloromethane (50 mL) at 0°C. The mixture was stirred for 2 days at room temperature. CH_2Cl_2 (100 mL) was then added to the filtrated solution, and the resulting organic phase was washed three times with a saturated $NaHCO_3$ aqueous solution (80 mL), then with distilled water (50 mL). The organic phase was dried over Na_2SO_4, then concentrated by rotary evaporation to yield a crude product. The pure compound **4** was obtained after purification by column chromatography (silica gel, eluent: ethyl acetate/hexane 1/5, *v*/*v*). Yield 4.2 g (67.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.33-5.35 (d, 1H, -C(CH_2-)=C<u>H</u>-), 4.15-4.23(m, 4H, -C<u>H</u>$_2$-O-CO-), 3.45-3.49 (t, 2H, -C<u>H</u>$_2$-O-CH-), 3.36 (s, 2H, -O-CO-C<u>H</u>$_2$-CO-O-), 3.12 (m, 1H, -C<u>H</u>O-), 0.67-2.40 (m, 50H, -C<u>H</u>$_3$, -C<u>H</u>(CH_3)-, -C<u>H</u>-, -C<u>H</u>$_2$-, alkyl proton) (see Fig. SI-2 for ^{1}H NMR spectra).

4-(Cholesteryl)butyl ethyl cyclopropane-1,1-dicarboxylate (**5**). A mixture of **4** (2.8 g, 4.8 mmol), 1,2-dibromoethane (1.83 g, 9.6 mmol), anhydrous carbonate K_2CO_3 (4.0 g, 28.8 mmol) in 5 mL

DMSO/CH_2Cl_2 (*v/v=1/1*) was stirred vigorously for 3 days at room temperature. 30 mL of water were then added to the resulting mixture and extracted five times with 30 mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were washed three times with distilled water, then dried over Na_2SO_4. CH_2Cl_2 was evaporated, and the residue was purified by column chromatography (silica gel, EtOAc/hexane 1/6, *v/v*) to yield monomer **5**. In order to reach the high purity necessary for anionic polymerization, monomer **5** was purified several times by column chromatography. Yield 2.4 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.33-5.35 (d, 1H, -C(CH_2-)=C<u>H</u>-), 4.15-4.23(m, 4H, -C<u>H</u>$_2$-O-CO-), 3.45-3.49(t, 2H, -C<u>H</u>$_2$-O-CH-), 3.12 (m, 1H, -C<u>H</u>O-), 0.67-2.40 (m, 54H, -C<u>H</u>$_3$, -C<u>H</u>(CH_3)-, -C<u>H</u>-, -C<u>H</u>$_2$-, alkyl protons) (see Fig. SI-3 for ^{1}H NMR spectra).

2. Synthesis and characterization of the macro-initiator α-methoxy-ω-(3-mercapto propionyl) polyethylene glycol (PEG_{45}-SH) (M_n=2000) (according to ref.[1])

MPEG-OH (α-methoxy-ω-hydroxy polyethylene glycol) (M_n = 2000, 20 g, 0.01 mol) and MPA (3-mercaptopropionic acid) (5.3 g, 0.05 mol) was stirred at 50°C under nitrogen until the full dissolution of MPA. Toluene (20 mL) and $HfCl_4 \cdot 2THF$ (250 mg, 0.52 mmol) were then added. The reaction flask was equipped with an azeotropic distillation apparatus and the mixture was refluxed at 130°C under nitrogen for 16 h. Toluene was removed under reduced pressure. The recovered polymer was precipitated twice in diethyl ether. Yield: 19 g (95%). (see Fig. SI-4 for ^{1}H NMR spectra).

3. ^{1}H NMR spectra

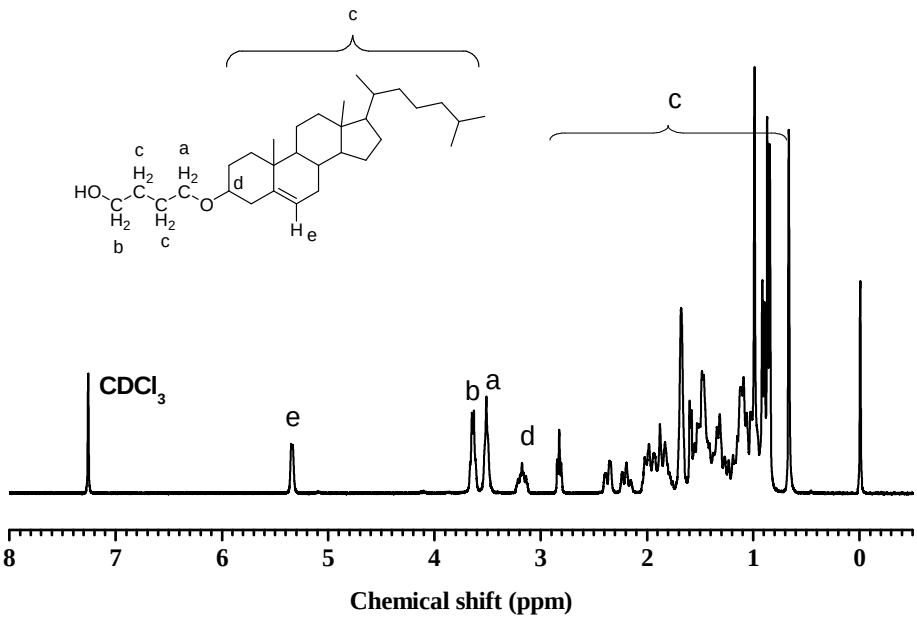


Figure SI-1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-Cholesteryloxy-butan-1-ol** (**3**)

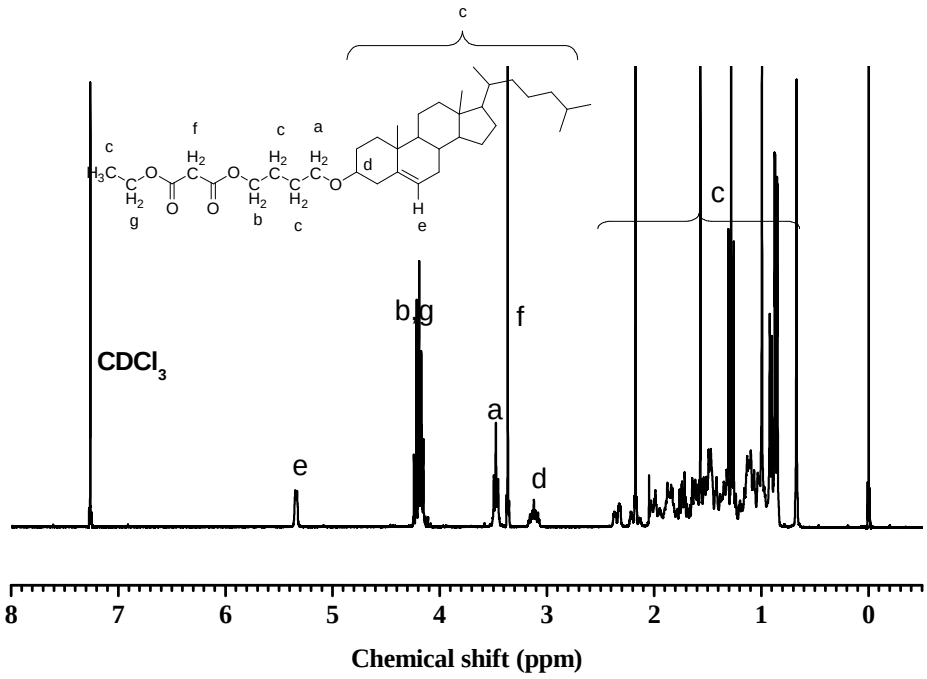


Figure SI-2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-Cholesteryloxy-butyl ethyl malonate** (**4**).

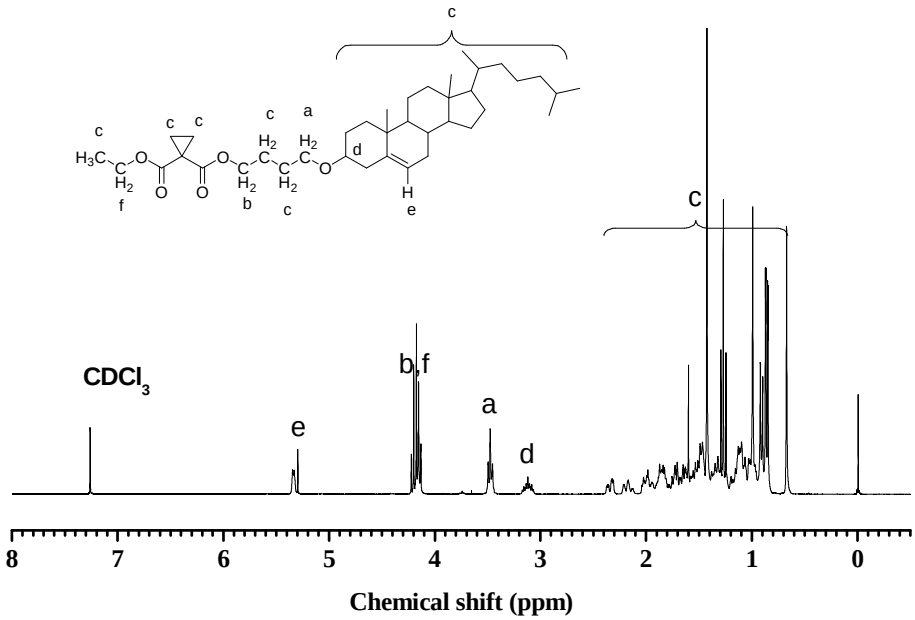


Figure SI-3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-(Cholesteryl)butyl ethyl cyclopropane-1,1-dicarboxylate** (**5**)

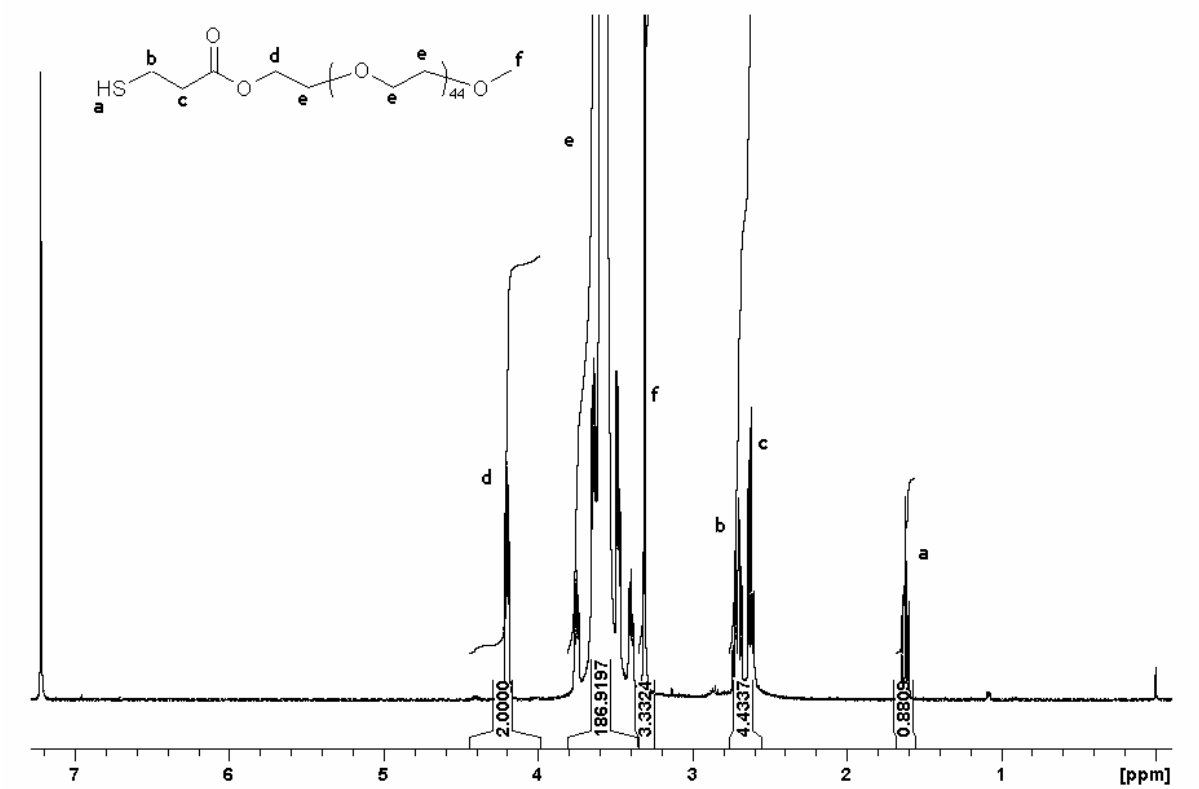


Figure SI-4. ^{1}H NMR spectrum of PEG_{45}-SH (400 MHz, $CDCl_3$, room temperature).

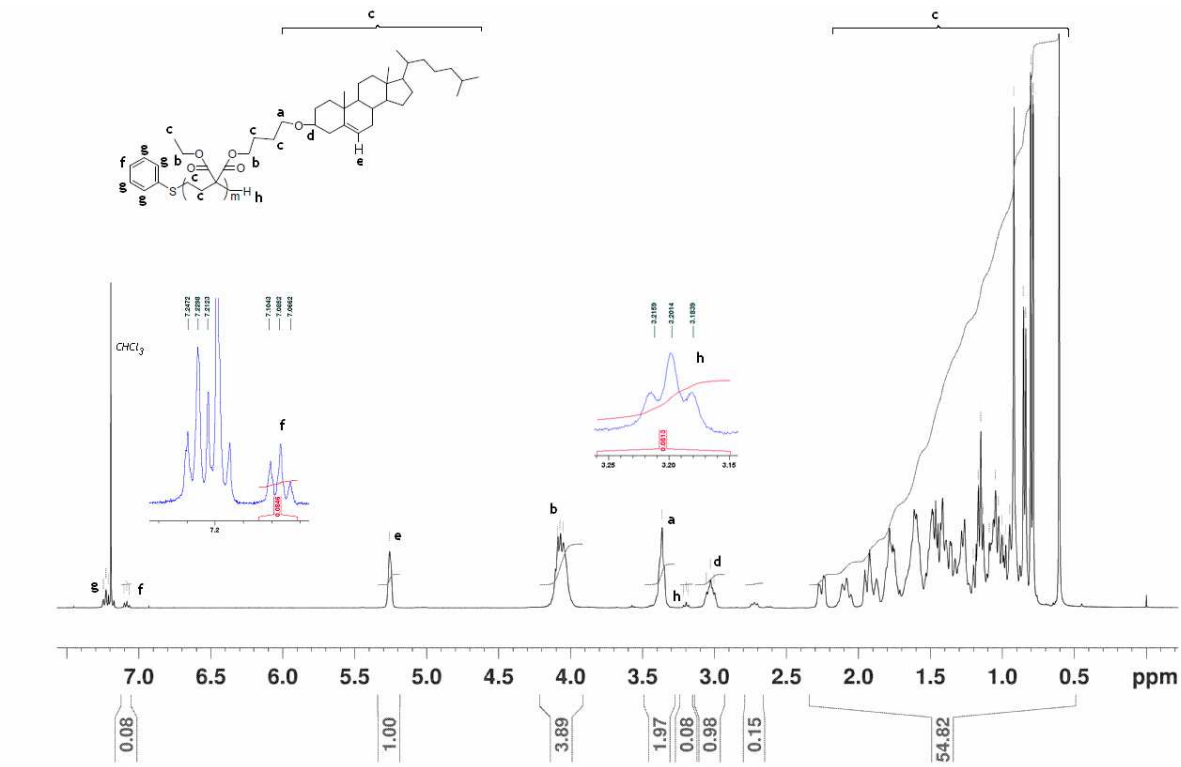


Figure SI-5. ^{1}H NMR spectrum of **PCpEChol** homopolymer (400 MHz, $CDCl_3$, room temperature).

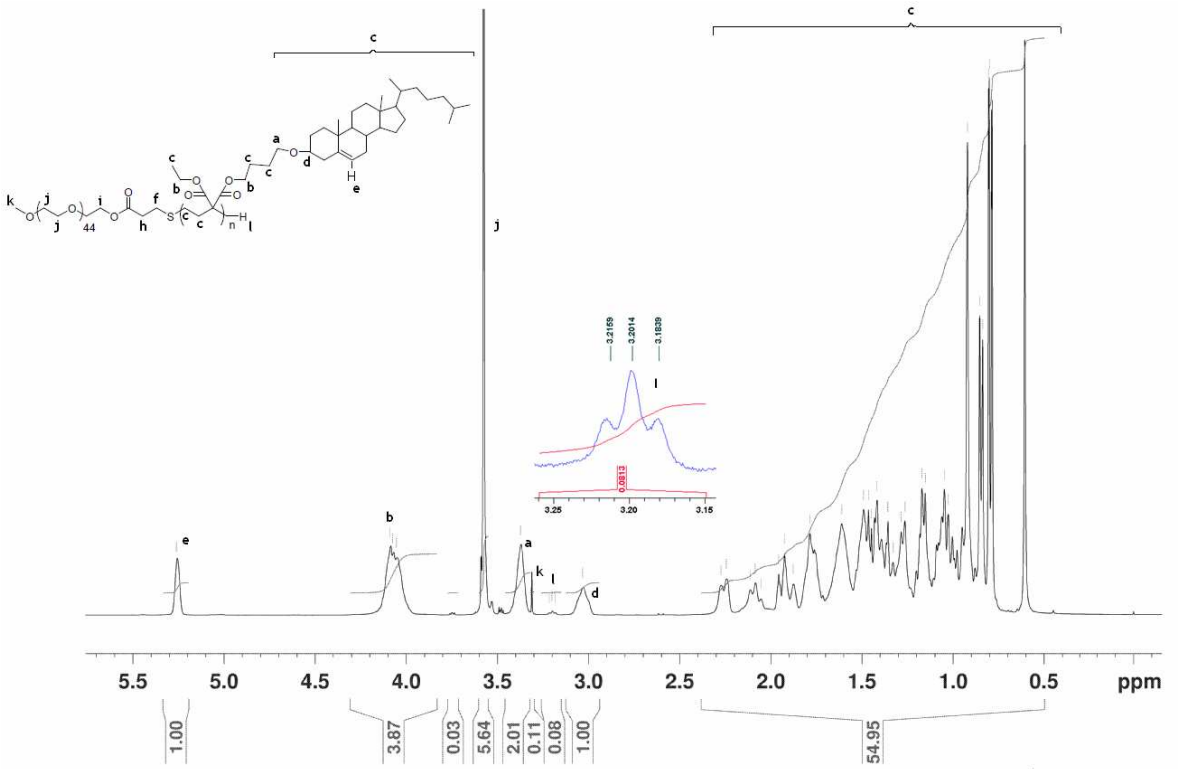
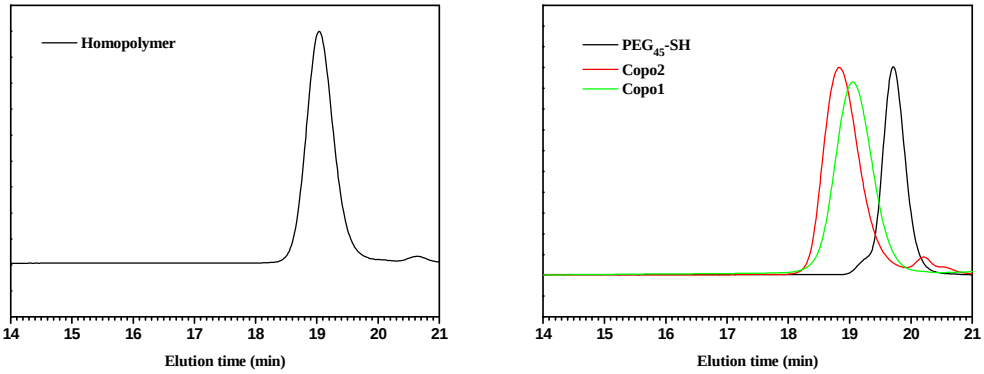


Figure SI-6. ^{1}H NMR spectrum of **PEG$_{45}$-*b*-PCpEChol** (Copo2) (400 MHz, $CDCl_3$, room temperature).



(a) (b)

Figure SI-7. SEC curves of homopolymer **PCpEChol** (a) and amphiphilic diblock copolymers **PEG$_{45}$-*b*-PCpEChol** Copo1 & 2 with their macro-initiator PEG$_{45}$-SH (b).

4. Supplemental information on monomer and polymer characterization

Table SI-1. Transition temperatures and enthalpies (in brackets) of LC monomer and homopolymer obtained by DSC analysis (T taken as the peak temperatures in DSC thermograms).

Samples	**Scan** (5ºC min^{-1})	**T_{SmA-N*} (℃) (ΔH /J g^{-1})**	**T_{N*-I} (℃) (ΔH /J g^{-1})**	**T_g (℃)**
Monomer (**5**)	Heating	19.6 (0.617)	23.8 (0.523)	-
	Cooling	16.7 (-0.644)	21.3 (-0.527)	-
Homopolymer (PCpEChol)	Heating	121.2	123.2 (3.89)[a]	-
	Cooling	118.9	122.2 (-3.87)[b]	32.6

[a,b] The enthalpies are for transitions SmA-N*-I, because the peaks of SmA-N* transition and N*-I transition are fused.

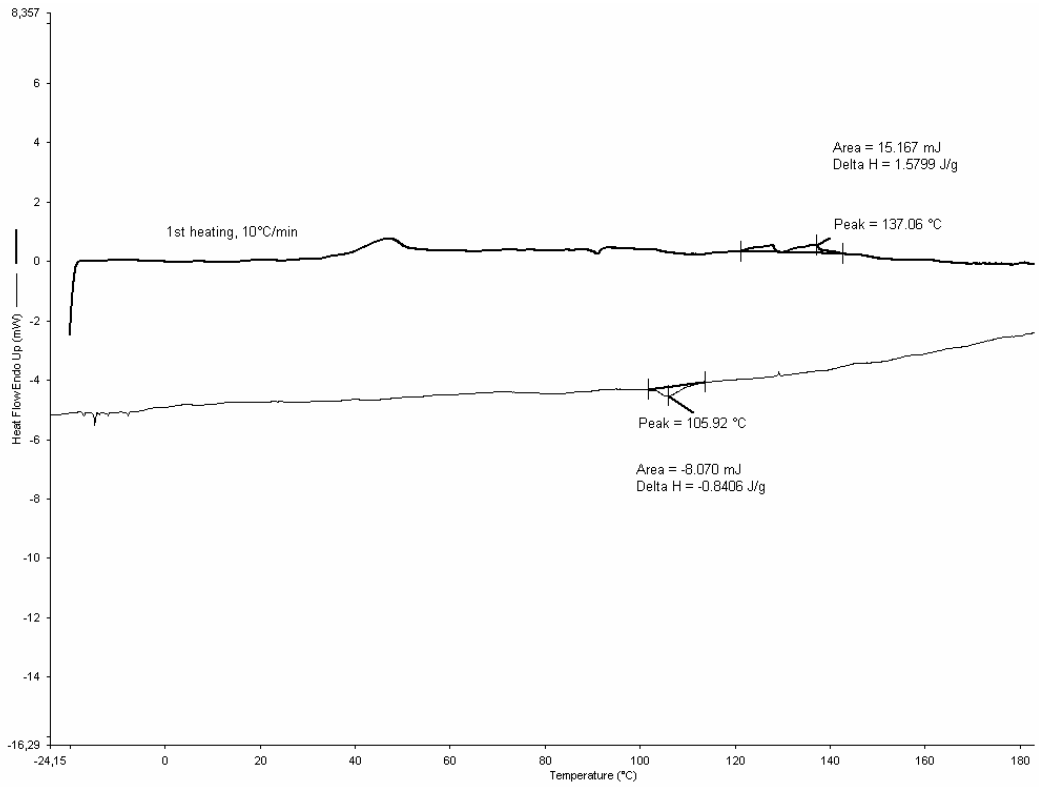


Figure SI-8. DSC thermograms for Copo1. Heating and cooling rates are 10°C/min.

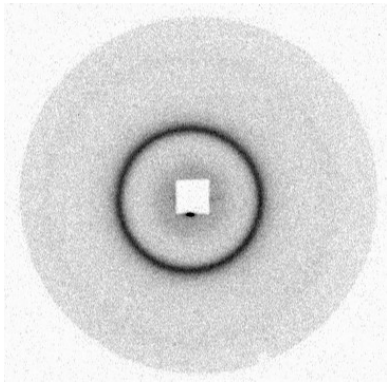


Figure SI-9. SAXS pattern of Copo2 at 25°C. The smectic period deduced is P = 4.58 nm.

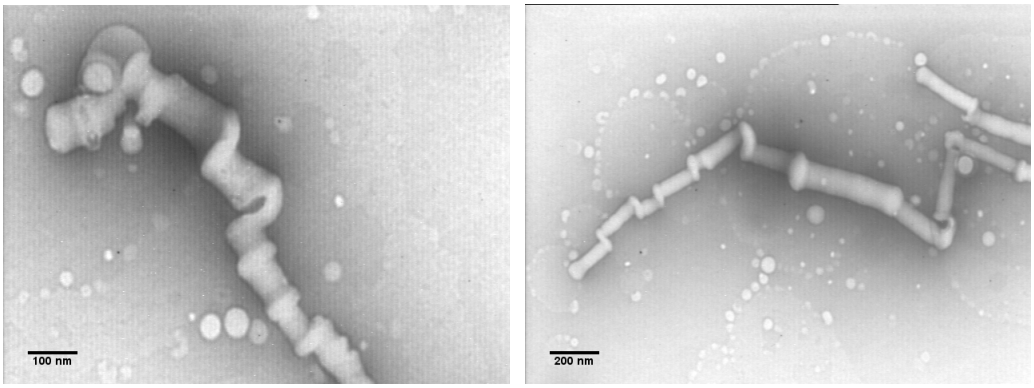


Figure SI-10. Classical TEM images with negative staining of fold ribbons formed by Copo1 with a starting polymer concentration of 0.1 wt % in dioxane. Scale bar = 200 nm.

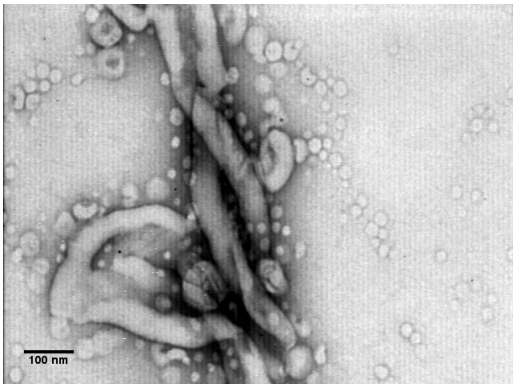


Figure SI-11. Classical TEM image with negative staining of twisted membranes formed by Copo2 with a starting polymer concentration of 0.5 wt % in dioxane. Scale bar = 100 nm.

References

1. Wan, D.; Pu, H.; Yang, G. *Reactive and Functional Polymers* **2008,** 68, (2), 431-435.