Supporting Information

Amphiphilic Liquid-Crystal Block Copolymer Nanofibers via RAFT-Mediated Dispersion Polymerization

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1- Characterization of the Chol-TEGA and Chol-TEGMA monomers

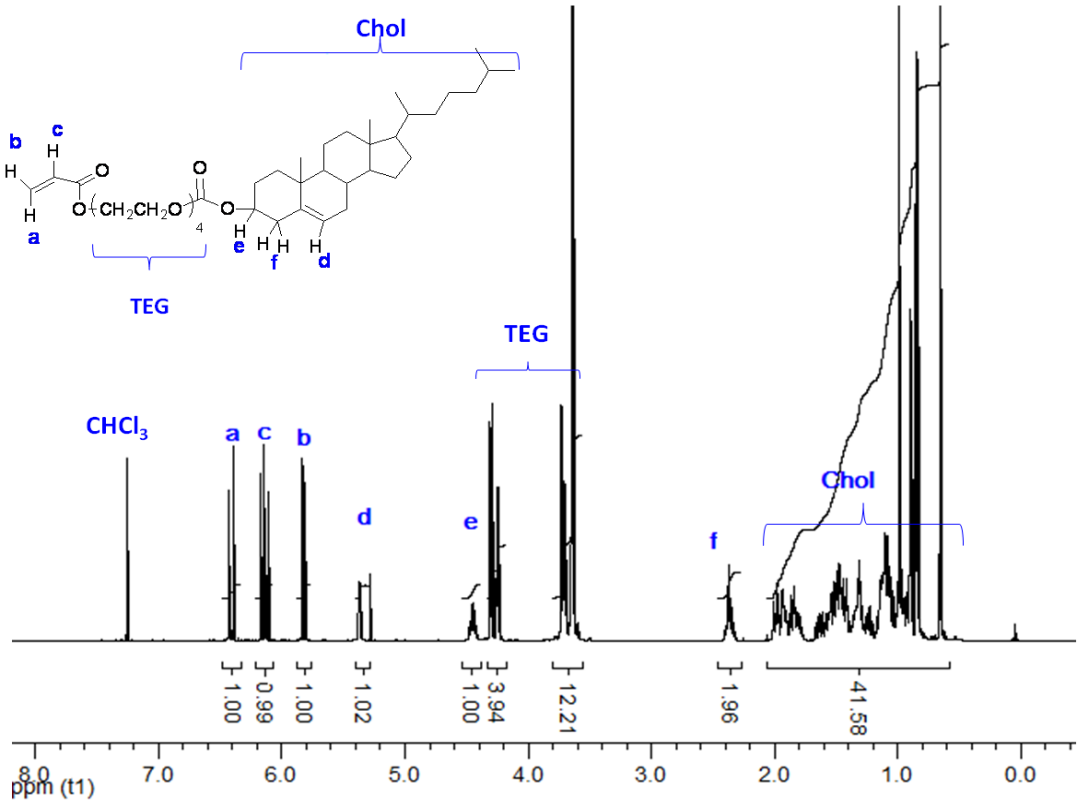

Figure S1. 500 MHz ^{1}H NMR spectrum of Chol-TEGA in $CDCl_3$

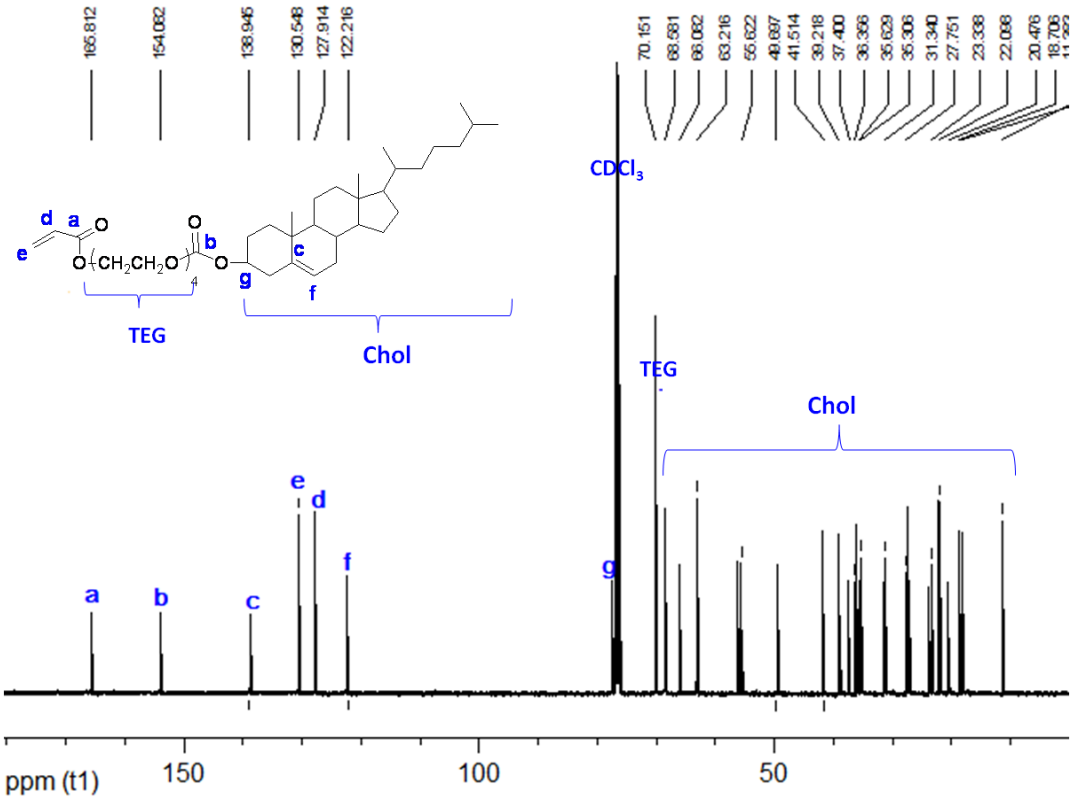

Figure S2. 125 MHz ^{13}C NMR spectrum of Chol-TEGA in $CDCl_3$

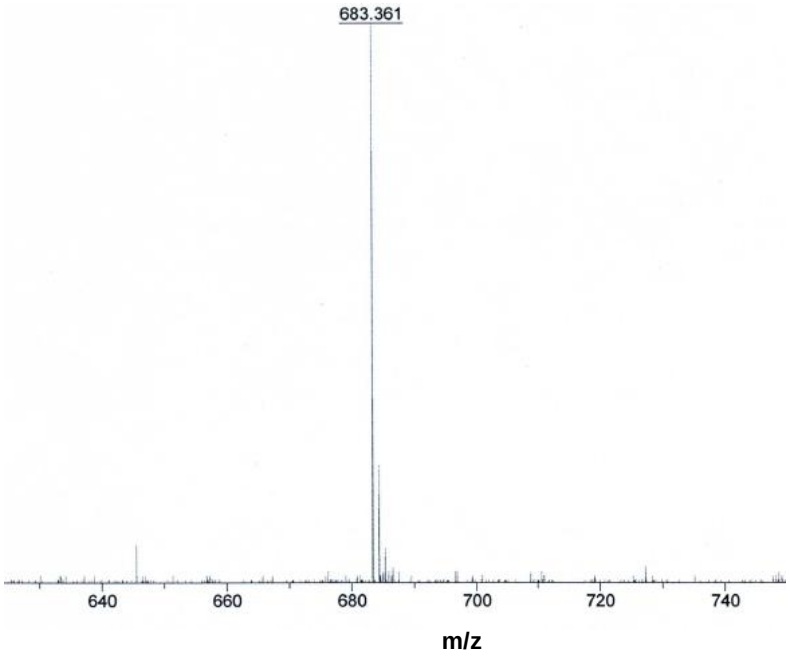

Figure S3. MALDI-TOF MS analysis of Chol-TEGA

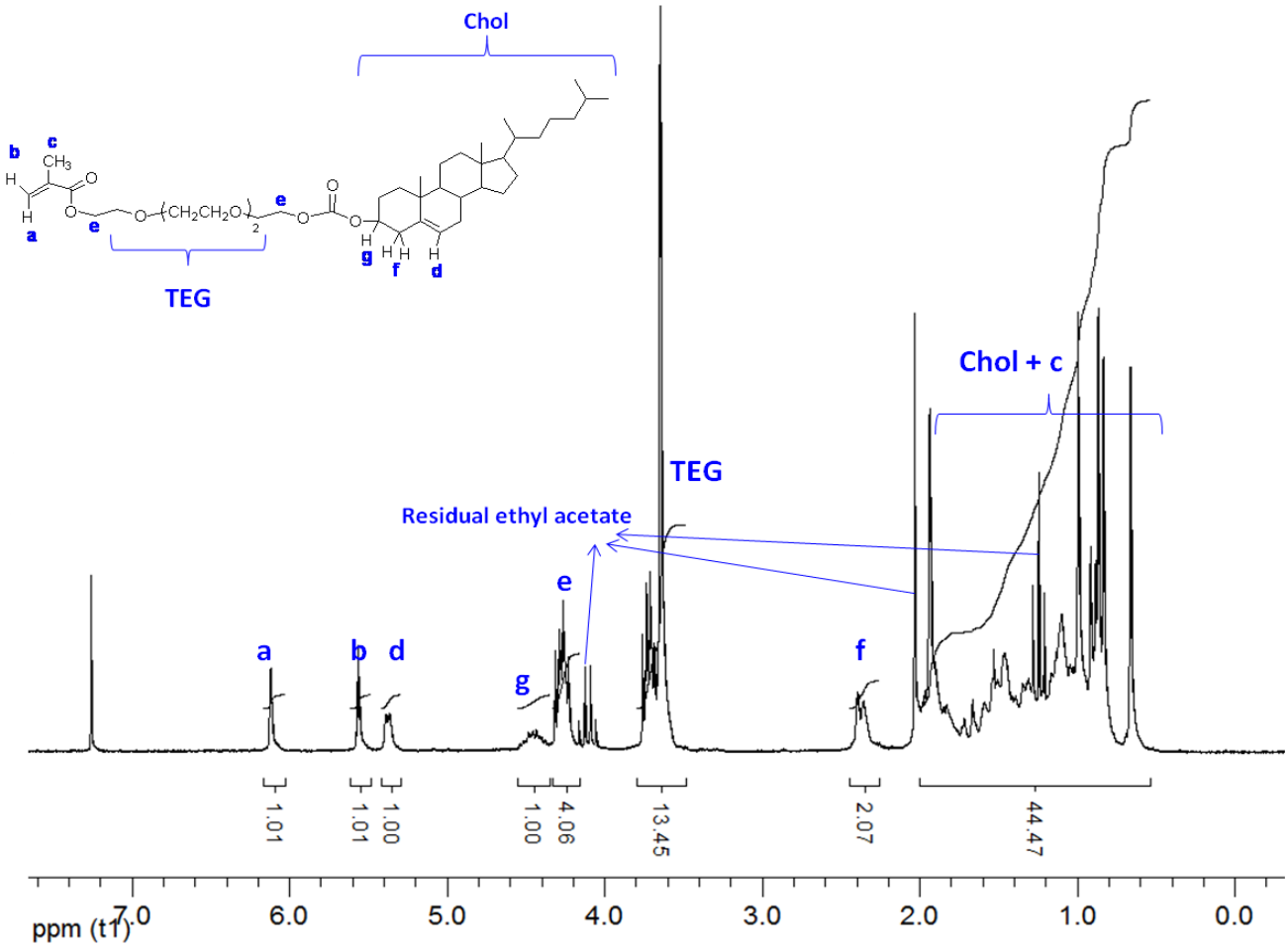

Figure S4. 200 MHz ^{1}H NMR spectrum of Chol-TEGMA in $CDCl_3$.

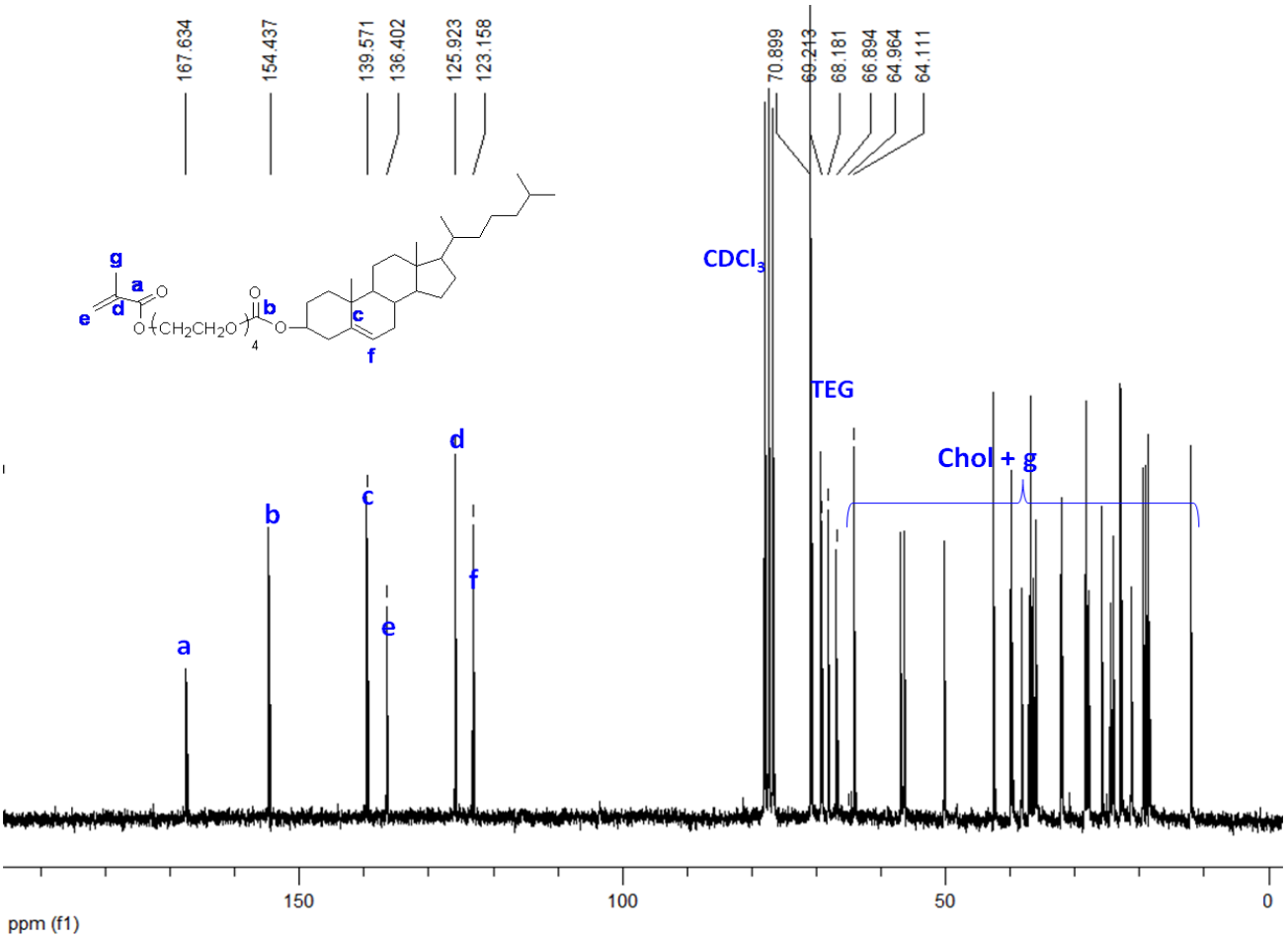

Figure S5. 63 MHz ^{13}C NMR spectrum of Chol-TEGMA in $CDCl_3$.

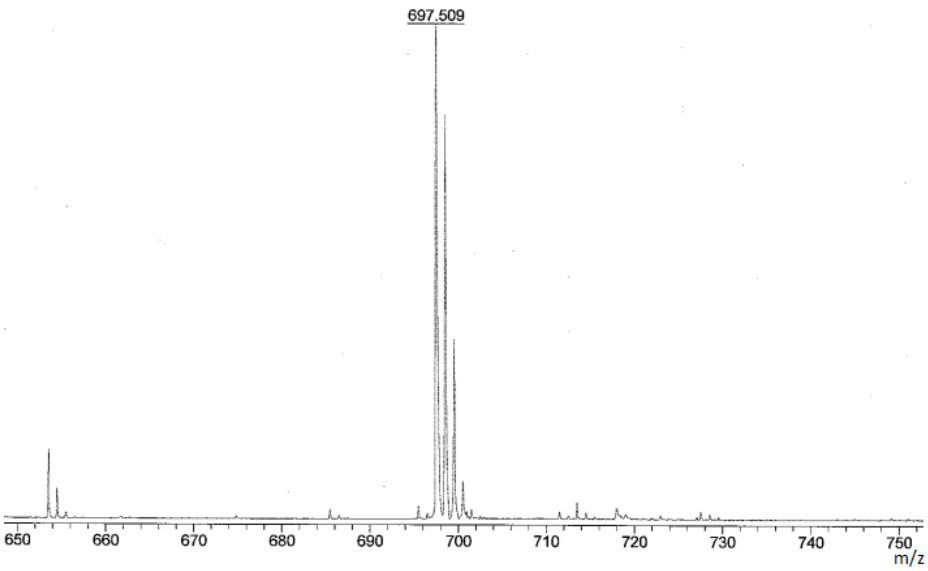

Figure S6. MALDI-TOF MS analysis of Chol-TEGMA

2- Synthesis and characterization of the P(Chol-TEGA) and P(Chol-TEGMA) homopolymers

In a typical experiment, the polymerization of Chol-TEGA (0.51 g, 7.7×10^{-4} mol) was carried out in a 5 mL septum-sealed flask with DTTC (12.5 mg, 3.4×10^{-5} mol) as a reversible chain transfer agent and ACPA (0.2 mg, 7.1×10^{-6} mol) as an initiator in 1,4-dioxane (0.75 mL). The mixture was deoxygenated with nitrogen for 30 min at 0°C, and placed in a thermostated oil bath at 80 °C under stirring. After 21 hours, the polymerization was quenched by immersion of the flask in ice water. The polymer was purified by 3 successive precipitations in acetone at room temperature and dried under vacuum. The polymerization results were: 92% conversion, M_n^{TD} = 1.9×10^4 g.mol^{-1}, M_w/M_n = 1.22, dn/dc = 0.094 mL.g^{-1}.

The synthesis of the P(Chol-TEGMA) homopolymer was performed accordingly with PTTC as a RAFT agent: 80 % conversion, M_n^{TD} = 1.38×10^4 g.mol^{-1}, M_w/M_n = 1.17, dn/dc = 0.099 mL.g^{-1}.

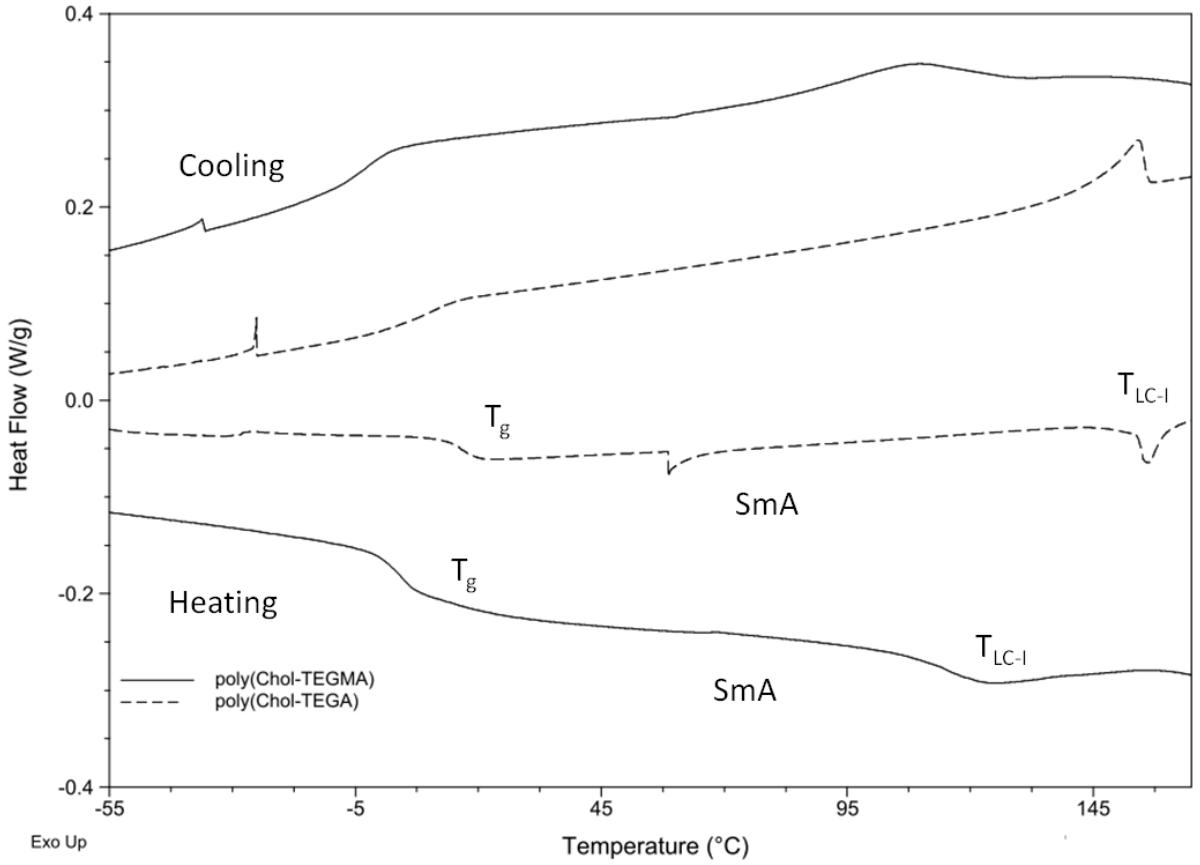

Figure S7. DSC thermograms of the poly(Chol-TEGMA) and poly(Chol-TEGA) homopolymers at heating and cooling rate 10 °C.min^{-1}.

Table S1. Thermal properties and smectic layer spacing *d* for the P(Chol-TEGA) and P(Chol-TEGMA) homopolymers in bulk.

Sample	M_n^{TD} (kg.mol^{-1})	T_g (°C)	(Heating)		(Cooling)		Smectic layer spacing *d* (nm)
			T_{LC-I} (°C)	Enthalpy (J/g)	T_{LC-I} (°C)	Enthalpy (J/g)	
P(Chol-TEGA)	19.0	16.3	154	3.2	156	4.9	5.5
P(Chol-TEGMA)	19.8	-0.2	102	3.1	124	3.4	5.6

Glass transition temperature (T_g) was measured by DSC with a heating rate of 10 °C.min^{-1}, liquid crystal-isotropic transition temperature (T_{LC-I}) and transition enthalpy were measured by DSC second cycle with heating or cooling rate 5 °C.min^{-1}. Smectic layer spacing *d* was calculated from SAXS.

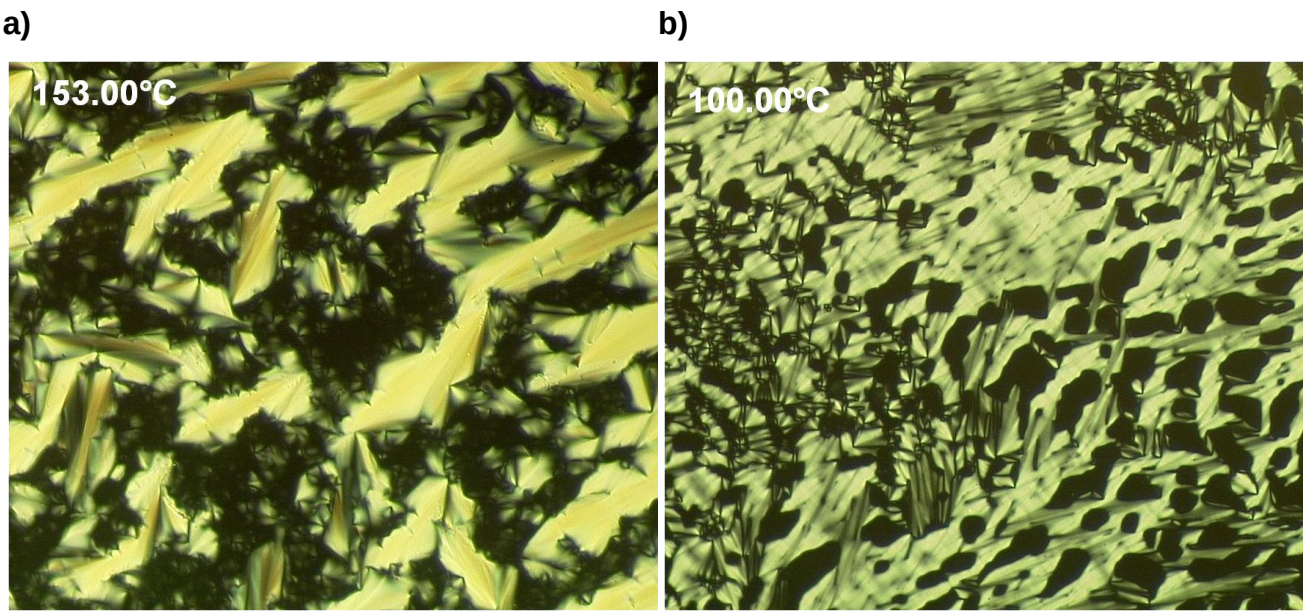

Figure S8. Polarizing optical micrographs (POM) of homopolymers a) Poly(Chol-TEGA), b) Poly(Chol-TEGMA).

3- P(AA-*co*-PEGA)-*b*-P(Chol-TEGA) block copolymers prepared via RAFT dispersion polymerization at a 1 M monomer concentration

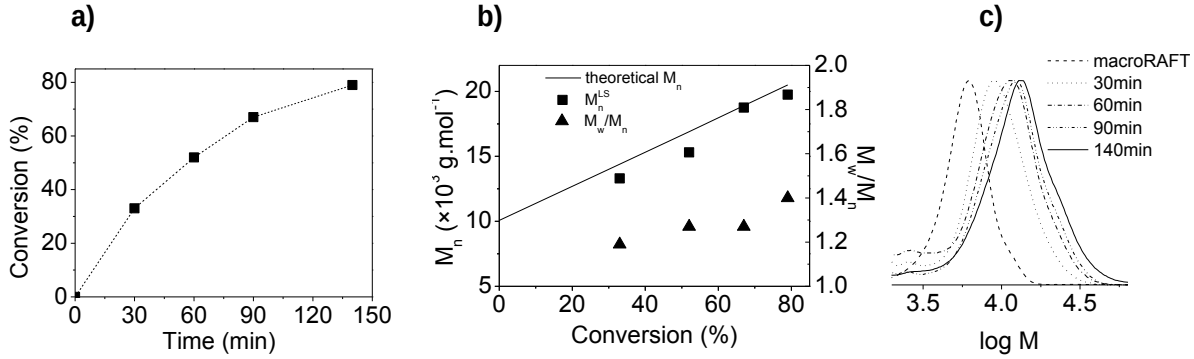

Figure S9. Polymerization of Chol-ATEG in the presence of the P(AA-*co*-PEGA) macroRAFT agent in ethanol/water (95:5, v:v) at 80°C, $[M]_0$ = 1.0 mol.L^{-1}, $[M]_0/[\text{macroRAFT}]_0$ = 20 (Table 1, entry **A6**). a) Evolution of the monomer conversion with time; b) evolution of the number-average molar mass (M_n^{TD}) and polydispersity index (M_w/M_n) with monomer conversion; c) evolution of SEC traces with conversion.

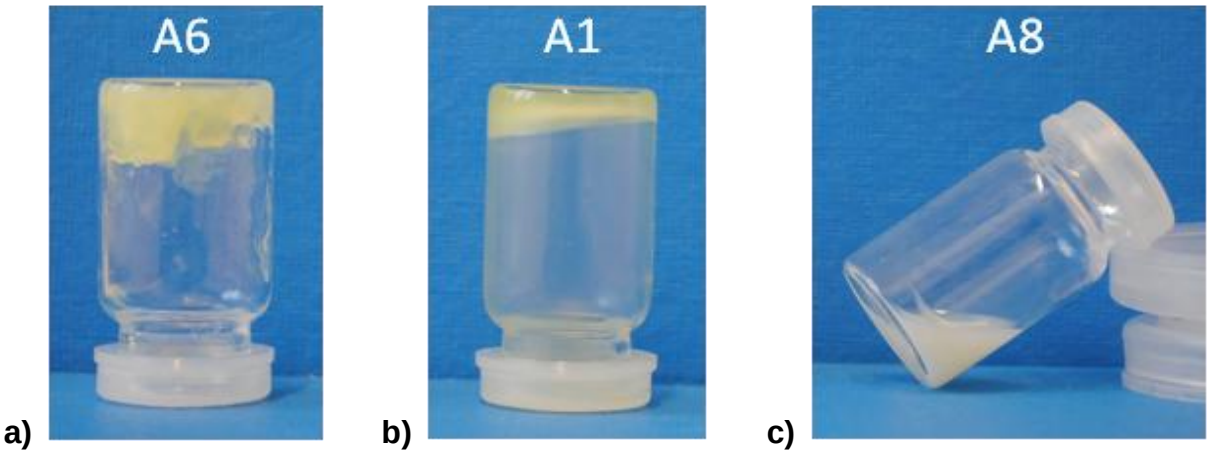

Figure S10. Aspect of the polymer dispersions obtained at different monomer concentrations: a) **A6** ($[M]_0$ = 1 M); b) **A1** ($[M]_0$ = 0.5 M); c) **A8** ($[M]_0$ = 0.29 M).

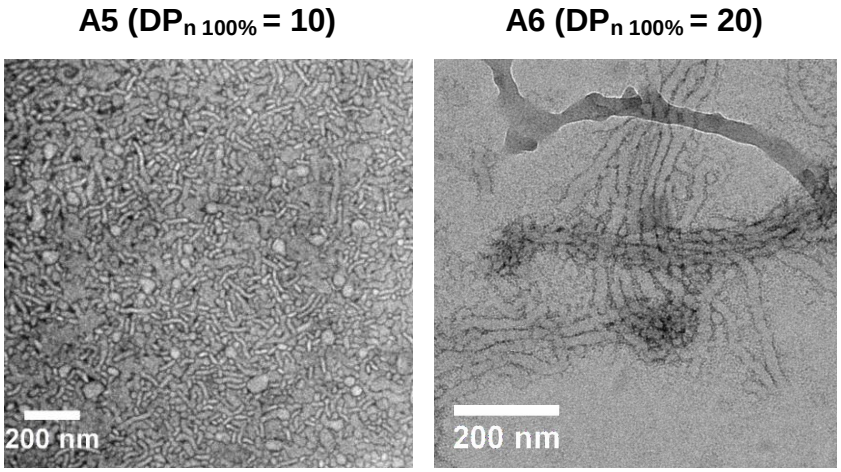

Figure S11. TEM micrographs of the P(AA-*co*-PEGA)-*b*-P(Chol-TEGA) copolymer assemblies. Experiments **A5** and **A6** performed in ethanol/water mixture (95/5) ($[\text{Chol-TEGA}]_0$ = 1.0 M).

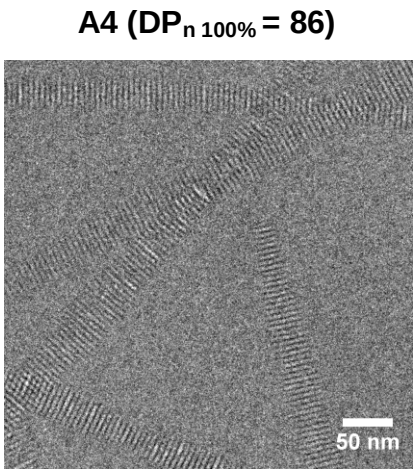

Figure S12. Cryo-TEM image of the P(AA-*co*-PEGA)-*b*-P(Chol-TEGA) copolymer nanofibers. Experiment **A4** performed in ethanol/water mixture (95/5) ($[\text{Chol-TEGA}]_0$ = 0.5 M).

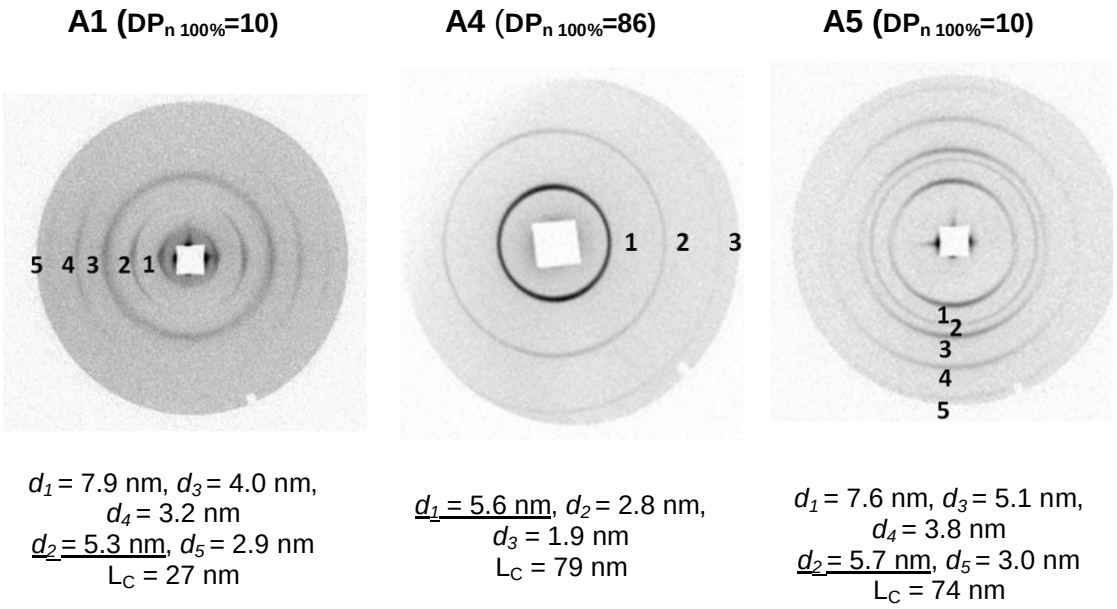

Figure S13. X-ray scattering patterns and calculations for P(AA-*co*-PEGA)-*b*-P(Chol-TEGA) copolymers dispersions **A1, A4** and **A5** in ethanol/water mixture (95/5). The underlined *d* values correspond to the smectic layer spacing and L_c is the correlation length of the smectic structure.

4- Characterization of the *in situ* formed P(MAA-*co*-PEGMA)-*b*-P(Chol-TEGMA) nano-assemblies

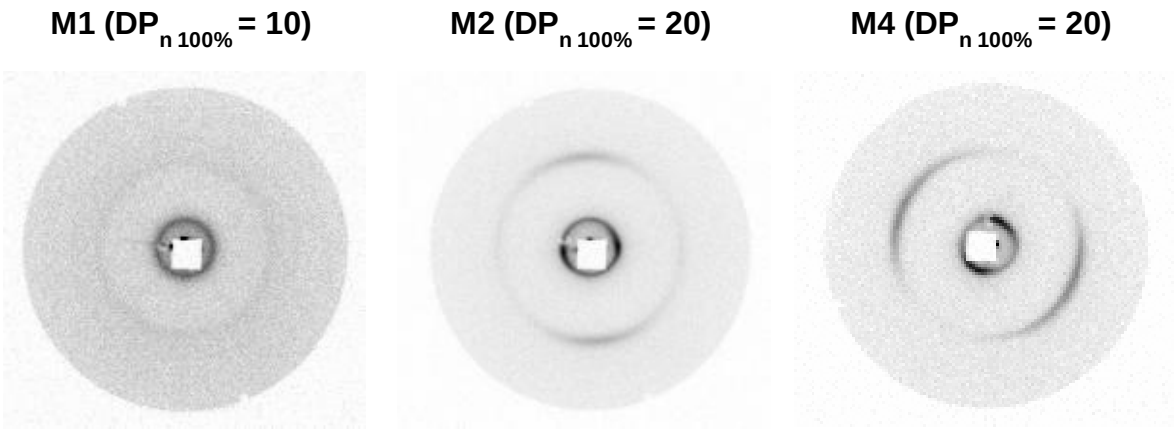

Figure S14. X-ray scattering patterns and calculated smectic layer spacings *d* for P(MAA-*co*-PEGMA)-*b*-P(Chol-TEGMA) copolymers dispersions **M1, M2** and **M4** in ethanol/water mixture (95/5). *d* is the smectic layer spacing.