

Supporting Information

Polymersomes with smectic liquid crystal structure and AIE fluorescence

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1. Characterizations

Nuclear magnetic resonance (NMR)

¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance III HD 400 MHz spectrometer at 298 K. Deuterated chloroform (CDCl₃) was used as the solvent. NMR chemical shifts were recorded in parts per million referenced to the residual solvent proton ($\delta = 7.26$ ppm) for ¹H NMR and carbon ($\delta = 77.1$ ppm) for ¹³C NMR.

Size exclusion chromatography (SEC)

The number-average molecular weights (M_n) and molecular weight distributions of polymers (polydispersity index, *D*) were evaluated by size exclusion chromatography (SEC), using Agilent 1260 Infinity Series GPC (ResiPore 3 μ m, 300 \times 7.5 mm, 1.0 mL/min, UV (250 nm) and refractive index (RI, PLGPC 220) detector. All measurements were performed with THF as the eluent at a flow rate of 1.0 mL/min at 35 °C. Monodisperse polystyrene polymers were used as calibration standards.

Small-angle X-ray scattering (SAXS)

SAXS experiments were carried out on the Xeuss 2.0 apparatus of Laboratoire Léon Brillouin installed in the SWAXS Lab (CEA Saclay, France). The instrument uses a micro-focused Cu K α source (wavelength of 1.54 Å, 8 keV) and a Pilatus3 1M detector (Dectris, Switzerland). One configuration was chosen to cover the broad q range, from 0.09 to 4 nm⁻¹, with the sample to detector distance set to 1.18m. The sample is a fiber drawn by hand with a needle from a molten copolymer at a temperature just below the isotropic-liquid crystal phase.

Polarizing optical microscopy (POM) and differential scanning calorimetry (DSC)

The mesomorphic properties were studied by thermal optical polarizing microscopy using a Leitz Ortholux microscope equipped with a Mettler FP82 hot stage, and differential scanning calorimetry using a Perkin-Elmer DSC7 at the heating and cooling rates of 10 °C min⁻¹.

Fluorescence emission spectroscopy

The fluorescence emission spectroscopy characterization was carried out on a FluoroMax spectrofluorometer. Samples were added to a 1cm quartz cuvette with all flanks transparent.

Ultraviolet–visible spectroscopy (UV-Vis)

UV-vis absorption spectra were measured on a Milton Ray Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS55 and Spex FluoroMax Spectrofluorometer.

Dynamic light scattering (DLS)

Hydrodynamic diameters (D_h) of the self-assemblies and their size distributions in deionized water were measured at 25 °C by dynamic light scattering (DLS, Malvern zetasizer 3000HS, UK) with a 633 nm laser. All measurements were performed with a 90° scattering angle. The sample solution in the scattering cell was equilibrated for 10 min before measurement.

Scanning electron microscopy (SEM)

SEM observations were performed on a Zeiss Leo 1530 FEG-SEM at 10kV. SEM samples were prepared by dropping a drop of the aggregate dispersions onto silicon wafers, followed by freeze-drying or vacuum drying for 3 hours. Before dropping the samples, the silicon wafers were hydrophilized in a bath of 100 mL mixture (70% H₂SO₄: 30% H₂O₂) and then and then cleaned by 20 mL Milli-Q water, Acetone and Ethanol at room temperature respectively. The silicon surface was then dried with liquid nitrogen before use.

Cryo-electron microscopy (Cryo-EM)

Morphologies of the copolymer colloids were characterized by cryo-EM. Images were acquired on a JEOL 2200FS energy-filtered (20 eV) field emission gun electron microscopy operating at 200 kV using a Gatan ssCCD 2048 × 2048 pixels. Samples were prepared by deposition of 5 μL sample solution onto a 200-mesh holey carbon copper grid (Ted Pella Inc., U.S.A.) and the samples were flash-frozen in liquid ethane cooled down at liquid nitrogen.

2. Synthesis of AChol monomer and mPEG-TPE-CTA

The synthesis of AChol monomer was according to the reported procedures.¹ As shown in Figure S1, AChol was synthesized by a one-step reaction between 2-hydroxyethyl acrylate and cholesteryl chloroformate using pyridine as the acid-binding agent. After purification by column chromatography with chloroform and *n*-hexane as the eluents, pure AChol was obtained with a yield of about 72%. AChol has been characterized carefully by NMR. Its ¹H NMR and ¹³C NMR spectra are shown in Figure S2. All the NMR signals could be assigned to the corresponding protons or carbons of AChol, indicating that pure AChol was prepared.

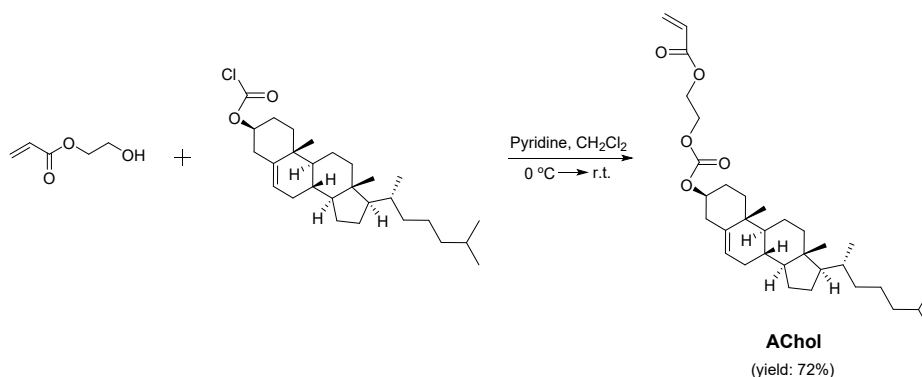


Figure S1. Synthetic route to AChol monomer.

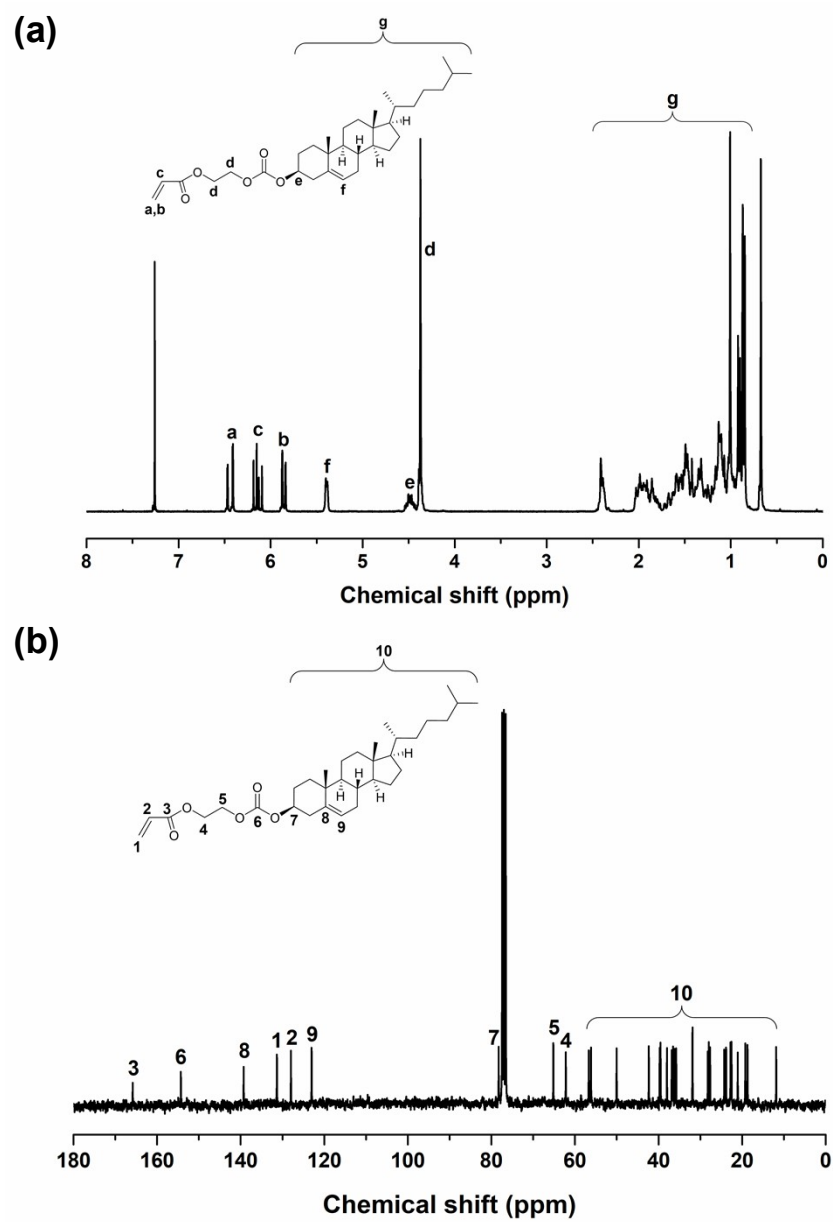


Figure S2. ^1H NMR and ^{13}C NMR spectra of AChol. CDCl_3 , 400 MHz, 297 K.

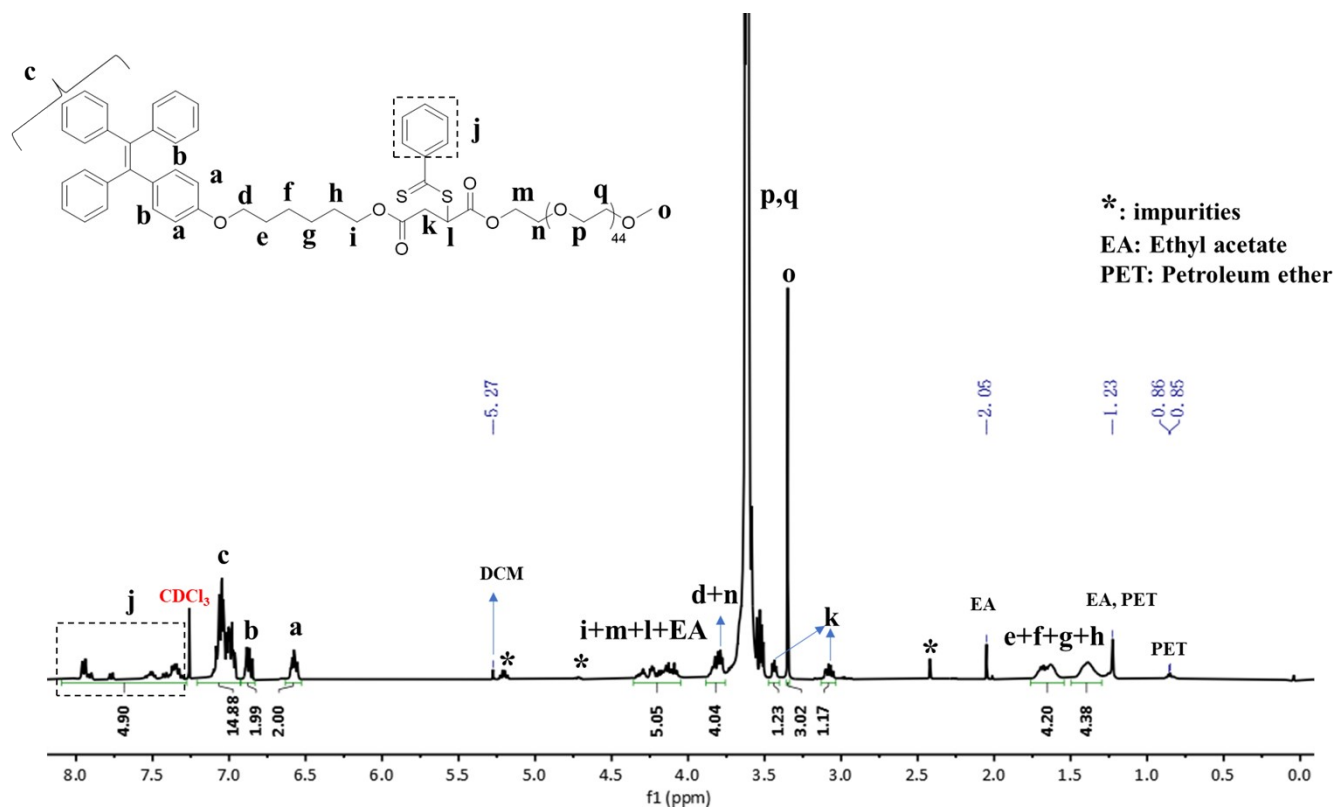


Figure S3. ¹H NMR spectrum of mPEG-TPE-CTA. CDCl₃, 400 MHz, 297 K.

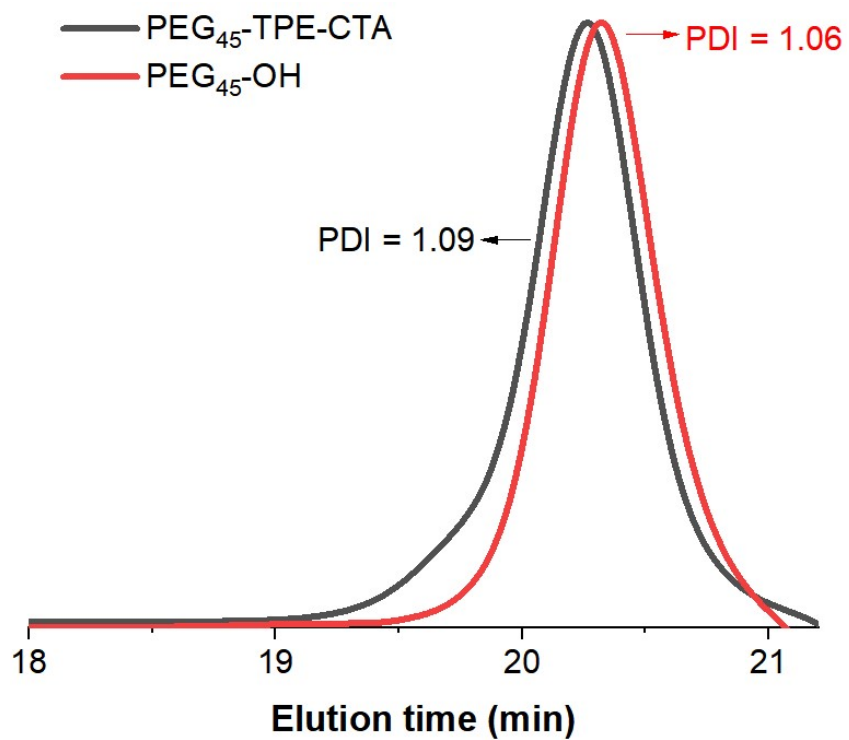


Figure S4. GPC traces of mPEG-OH and mPEG-TPE-CTA with THF as the eluent.

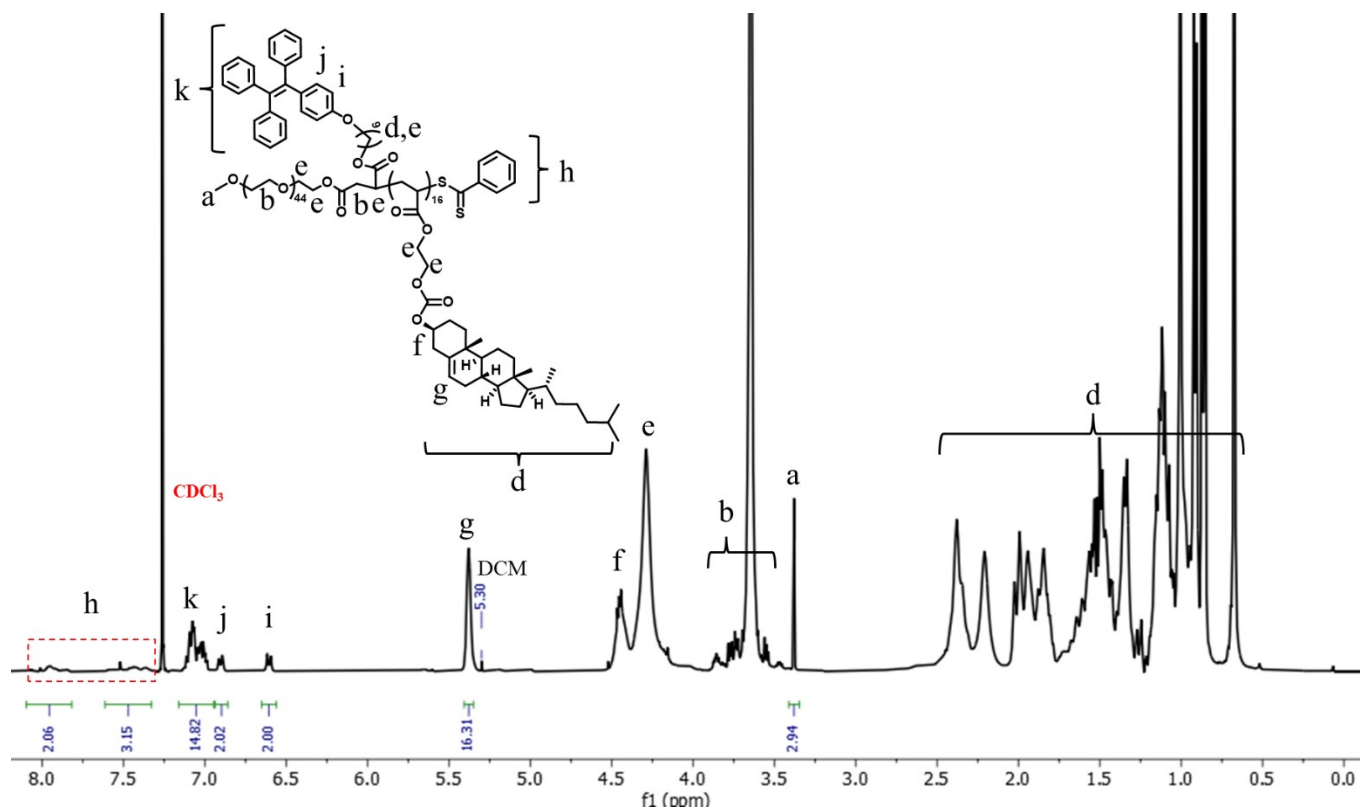


Figure S5. ¹H NMR spectrum of PEG₄₅-TPE-*b*-PACHol₁₆ copolymer. CDCl₃, 400 MHz, 297 K.

Table S1. Synthesis of LC amphiphilic PEG-TPE-*b*-PACHol diblock copolymer.^a

Sample	[AChol]/ [mPEG-TPE-CTA]/[AIBN] ^b	Yield ^c
PEG ₄₅ -TPE- <i>b</i> -PACHol ₁₁	5:1:0.2	57%
PEG ₄₅ -TPE- <i>b</i> -PACHol ₁₄	7:1:0.2	64%
PEG ₄₅ -TPE- <i>b</i> -PACHol ₁₆	10:1:0.2	67%
PEG ₄₅ -TPE- <i>b</i> -PACHol ₂₂	15:1:0.2	76%
PEG ₄₅ -TPE- <i>b</i> -PACHol ₄₃	30:1:0.2	51%

- All the polymerization trials were performed using mPEG-TPE-CTA ($M_{n,NMR} = 2680$ Da, $D = 1.16$) as the chain transfer agent in 1,4-dioxane at 80 °C; polymerization time: 24 h; concentration of mPEG-TPE-CTA: 0.028 M.
- Molar ratio.
- Degree of polymerization (DP), M_n and yield were calculated by ¹H NMR.

3. Supplementary data of liquid crystal properties of PEG₄₅-TPE-*b*-PACHol_n (n =11, 14, 16)

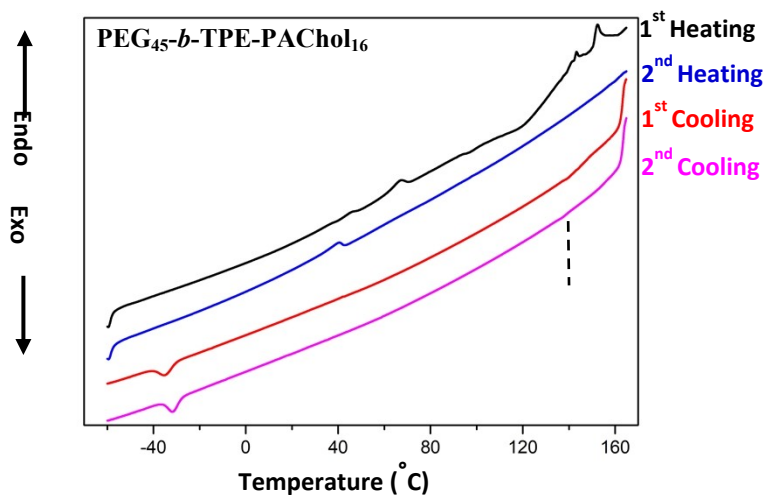


Figure S6. The DCS curves of PEG₄₅-TPE-*b*-PACHol₁₆. The scan rate was ± 10 °C/min. The vertical dotted line indicates the smectic-isotropic (SmA-I) transition position of the hydrophobic block PACHol₁₆.

Table S2. Phase transition temperatures of PEG₄₅-TPE-*b*-PACHol₁₆ obtained by DSC (± 10 °C/min)

Process	PEG Melting (T_m) or Recrystallization (T_{cr})	PACHol ₁₆ SmA-I	PACHol ₁₆ T_g	PACHol ₁₆ melting
1 st Heating	45.7 °C (0.58 J/g)		66.9 °C (2.25 J/g)	143.2 °C, 152.4 °C (24.58 J/g)
1 st Cooling	-34.7 °C (-3.66 J/g)	139.8 °C (-0.11 J/g)		--
2 nd Heating	40.2 °C (0.79 J/g)	<i>Signal too flat</i>		--
2 nd Cooling	-31.5 °C (-4.00 J/g)	137.0 °C (-0.11 J/g)		--

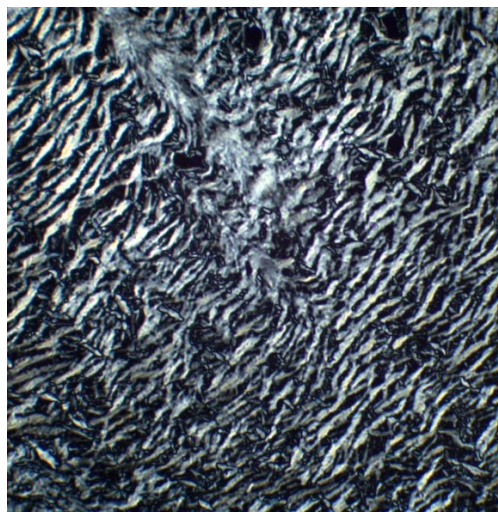


Figure S7. POM textures of PEG₄₅-TPE-*b*-PACHol₁₆ at 25°C.

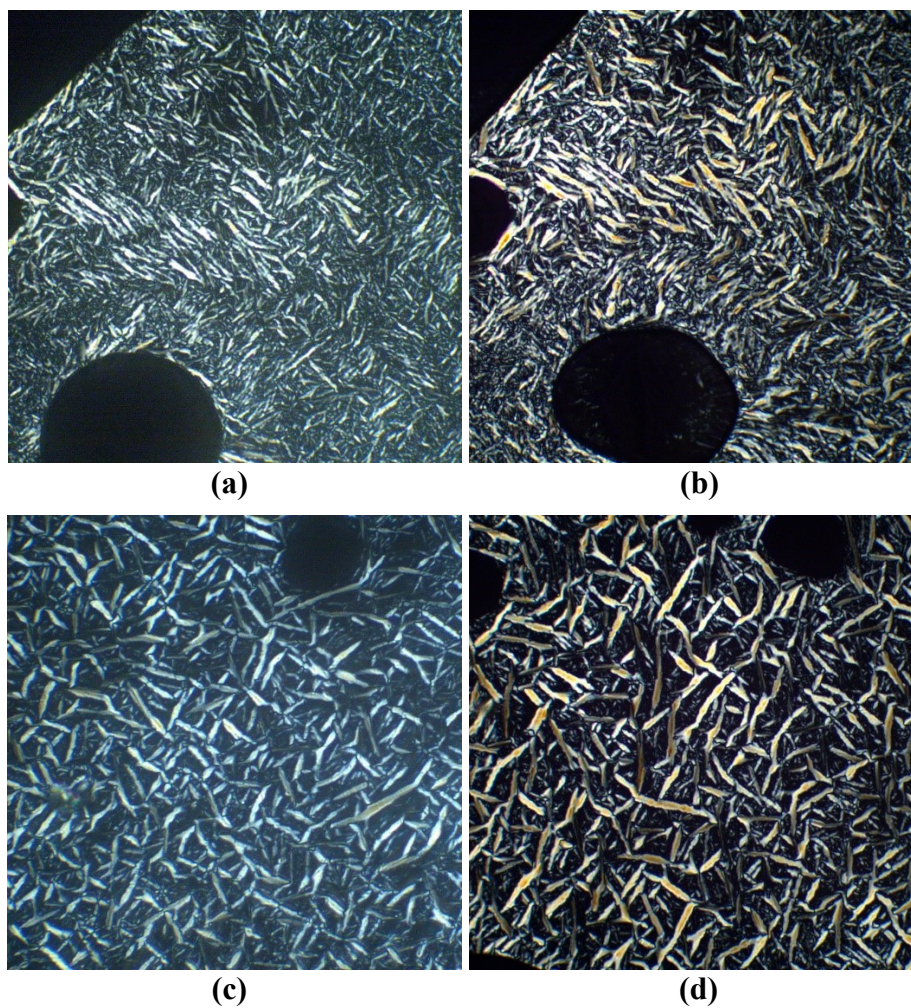


Figure S8. POM textures of PEG₄₅-TPE-*b*-PACHol_n. (a-b) n = 14 at 120°C (a) and 25°C (b). (c-d) n = 11 at 117°C (c) and 25°C (d).

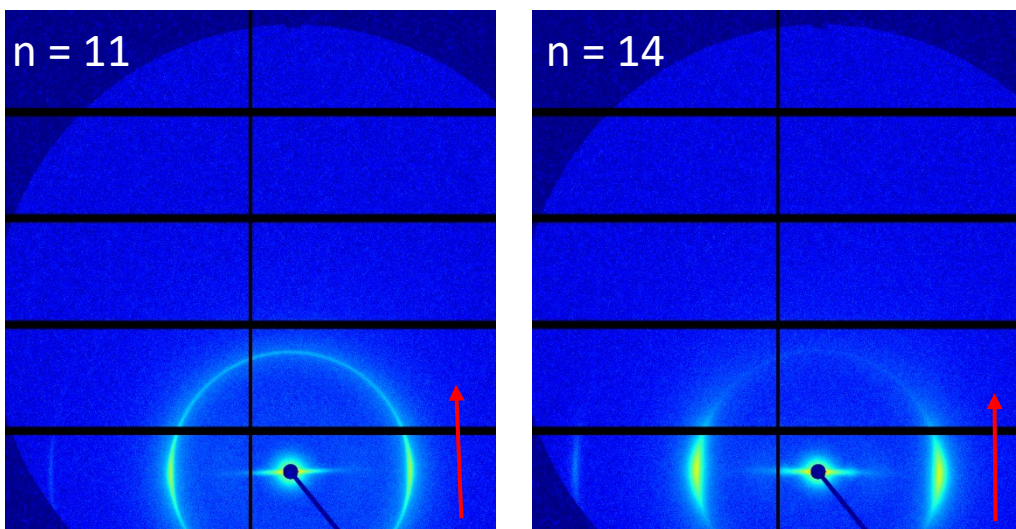
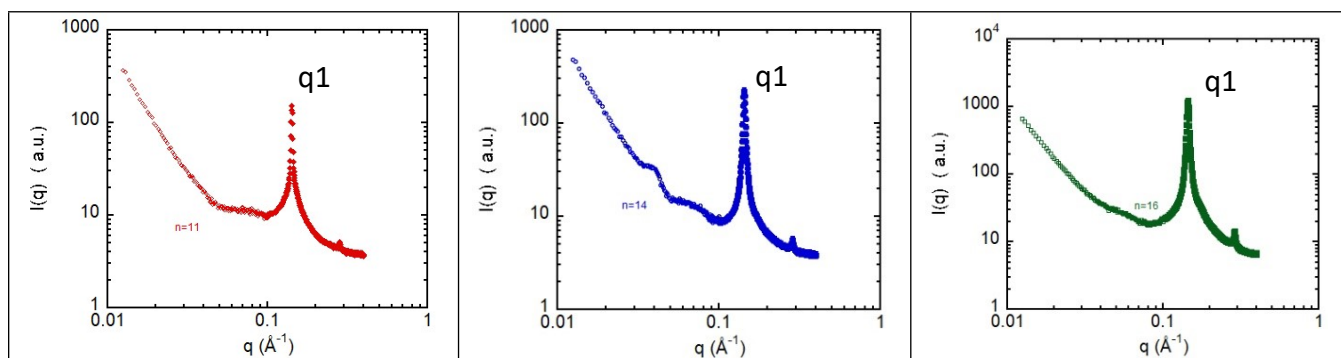


Figure S9. SAXS of PEG₄₅-TPE-*b*-PACHol_n (n = 11 left, n = 14 right) at 25°C. The red arrow indicates the fiber drawing direction.



	Low q peak	Low q Bump	q1		q2	
	Å ⁻¹	Å ⁻¹	Å ⁻¹	d (nm)	Å ⁻¹	q2/q1
n = 11		0.69	0.1419	4.42789288	0.283	1.99436223
n = 14	0.040	0.63	0.1429	4.39690693	0.2861	2.00209937
n = 16		0.57	0.1447	4.34221147	0.2878	1.98894264

Figure S10. Data analyses of SAXS of PEG₄₅-TPE-*b*-PACHol_n (n = 11, 14, 16) at 25°C. q1 and q2 correspond to the signals of aligned smectic A phase. Low q bump and peak correspond the microphase separation of PEG and PACHol blocks (bump signals give lengths of about 9nm, 10nm and 11nm for n = 11, 14 and 16, respectively).

4. Supplementary data of self-assembly of PEG₄₅-TPE-*b*-PACHol₁₆

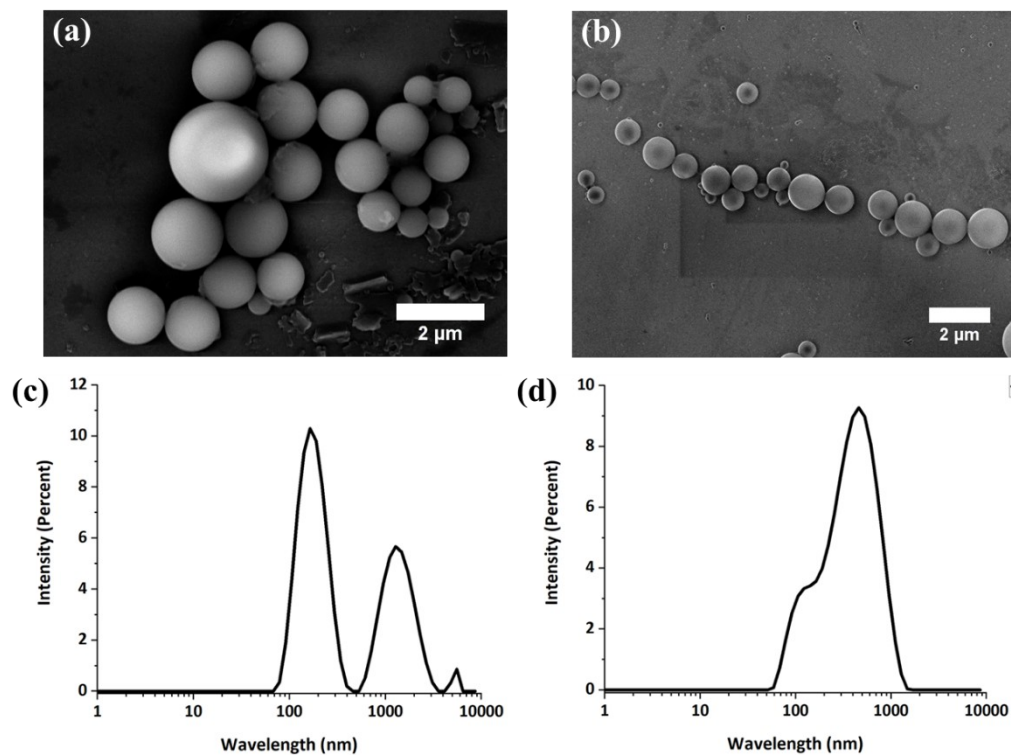


Figure S11. Supplemental SEM images of the self-assemblies formed from the diblock copolymer PEG₄₅-TPE-*b*-PACHol₁₆ in THF/water system at a concentration of 2 mg/mL (a) and of 1mg/mL (b), and their intensity profile of size distribution by DLS at 2 mg/mL (c) and of 1mg/mL (d).

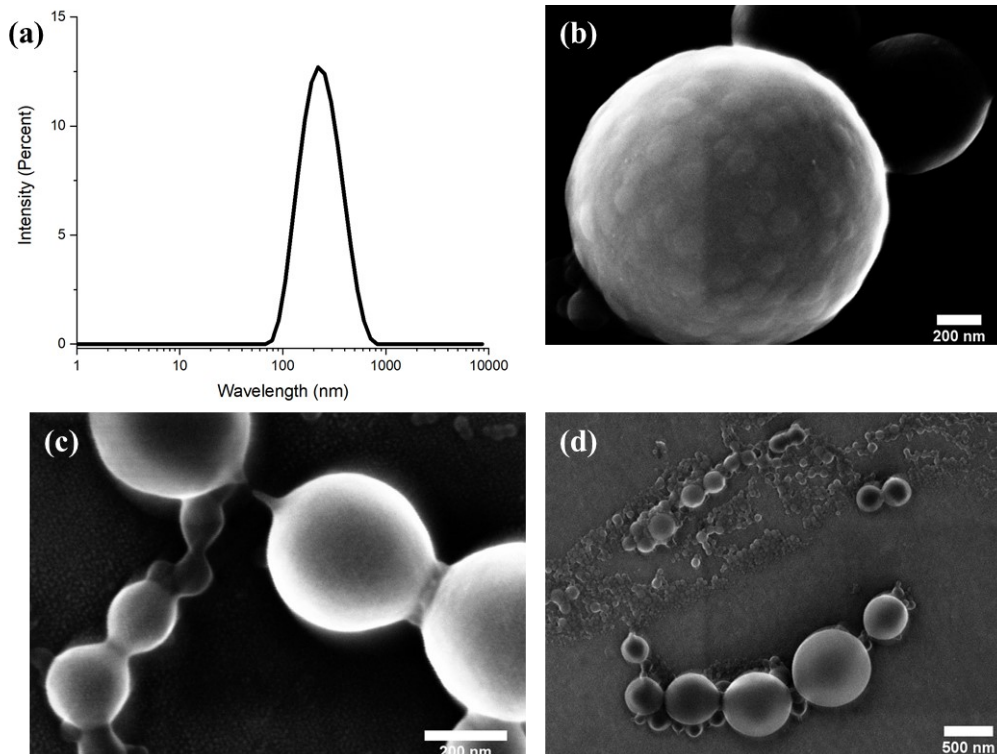


Figure S12. The DLS profile (a) and SEM pictures (b-d) of the self-assemblies formed from the diblock copolymer PEG₄₅-TPE-*b*-PACHol₁₆ in THF/water system at a concentration of 10 mg/mL.

5. Fluorescence quantum yield measurement

Quantum yield of the AIE polymersomers in aqueous solution were obtained by comparing the integrated fluorescence spectra of the self-assembly solution with the fluorescence spectrum of a standard fluorogen, 9,10-diphenylanthracene, in ethanol (excitation wavelength: 355 nm) with corrections of refractive index differences using equation:²

$$\phi_2 = \phi_1 \times \frac{n_2^2}{n_1^2} \times \frac{F_2}{F_1} \times \frac{A_1}{A_2}$$

ϕ_2 is the quantum yield of the sample to be measured; ϕ_1 is the quantum yield of a standard sample; n_1 and n_2 are the refractive indexes of the standard solution and of sample solution, respectively; F_1 and F_2 are the integral areas of emission intensities in the fluorescence spectra of the standard and sample solution, respectively; A_1 and A_2 are the absorption intensity of standard and sample solution respectively, which are kept lower than 0.05. Here, the refractive index of ethanol is $n_1 = 1.366$ and that of water is $n_2 = 1.333$ at room temperature. The quantum yield of 9,10-diphenylanthracene is 0.96 in ethanol at room

temperature (1 $\mu\text{g/mL}$; $\lambda_{\text{ex}} = 355 \text{ nm}$).

References

1. Piñol, R.; Jia, L.; Gubellini, F.; Lévy, D.; Albouy, P.-A.; Keller, P.; Cao, A.; Li, M.-H. *Macromolecules* **2007**, *40*, 5625-5627.
2. Lu, H.; Su, F.; Mei, Q.; Tian, Y.; Tian, W.; Johnson, R. H.; Meldrum, D. R. *J. Mater. Chem.* **2012**, *22*, 9890-9900.