

## SUPPLEMENTARY INFORMATION

### **Aqueous Self-Assembly of Poly(ethylene oxide)-block-Poly( $\epsilon$ -caprolactone) (PEO-*b*-PCL) Copolymers: Disparate Diblock Copolymer Compositions Give Rise to Nano- and Meso-Scale Bilayered Vesicles**

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### **Materials and Methods**

$\epsilon$ -caprolactone ( $\epsilon$ -CL, Aldrich) was dried over calcium hydride ( $\text{CaH}_2$ ) at room temperature for 48 h and distilled under reduced pressure. Monomethoxyl poly(ethylene oxide) (MePEO) homopolymers featuring a terminal hydroxyl group and molecular weights of 5000, 2000, 1100 and 750, were purchased from Fluka. Higher molecular weight MePEO homopolymers ( $M_n = 1100, 2000$  and 5000) were purified by dissolution in tetrahydrofuran (THF), followed by precipitation into ether, and subsequent drying at 40 °C under reduced pressure (10 mm Hg) for 24 h. Stannous octoate ( $\text{SnOct}_2$ ) (Sigma, USA) and 1,6-hexanediol (Aldrich, Germany) were used as received. Ethylene oxide (EO, Aldrich) was purified by passage through potassium hydroxide, condensed onto  $\text{CaH}_2$ , stirred for 2 h, and distilled. Naphthalene was recrystallized from ether. THF was

distilled over Na mirror under nitrogen. Other chemicals were commercially available and used as received.

**Ring-Opening Polymerization Reaction Conditions.** Monomethoxyl poly(ethylene oxide) (MePEO) was delivered to a flamed-dried flask under argon gas (Ar). A known mass of  $\epsilon$ -CL monomer was then injected into the flask via syringe, after which two drops of SnOct<sub>2</sub> were added to the reaction mixture. The flask was connected to a vacuum line, evacuated, and immersed in an oil bath at 130 °C. A progressive increase in viscosity of the homogeneous mixture was evident as the polymerization reaction progressed. After 24 h, the volatiles were removed; the recovered solid residue was dissolved in methylene chloride, precipitated with cold methanol/hexane (4 °C), and dried under vacuum.

**Anionic Living Polymerization Reaction Conditions.** A flame-dried flask was purged with Ar, and charged with 30 mL of anhydrous tetrahydrofuran (THF), acetonitrile (0.55 mL, 10 mmol), and potassium naphthalenide (5 ml of a 1 M THF solution). After vigorous stirring at 20 °C for 70 min, the mixture was cooled in an ice-water bath, upon which distilled EO was added via syringe. The polymerization reaction was carried out at ambient temperature; a 5 mL sample of the cyano-terminated PEO reaction product was removed, treated with an acetone solution containing acetic acid, precipitated with excess diethyl ether, dried under vacuum at room temperature, and the molecular weight of PEO block was analyzed via GPC and NMR spectroscopy.  $\epsilon$ -CL, dissolved in THF to provide a specific  $\epsilon$ -CL:EO mole ratio, was added to the remaining reaction mixture of CN-PEO. After 10 min at 0 °C, the polymerization was quenched by adding a small

amount of acetic acid and poured into acetone. The reaction product was further purified by precipitation in diethyl ether and dried under vacuum at 40 °C for two days.

**Copolymer Characterization.** PEO polymers and copolymers were characterized by  $^1\text{H}$  NMR spectroscopy (Bruker 500 MHz NMR system); **Fig. S1** displays a representative  $^1\text{H}$  NMR spectrum. Note in this figure the appearance of a resonance at  $\sim 4.20$  ppm (d), consistent with the terminal methylene end group of the PEO block in the  $^1\text{H}$  NMR spectrum, which indicates that the final reaction products were limited to only diblock copolymers of PEO and PCL. The sharp weak resonance at 3.38 ppm and the intense peak at 3.65 ppm correspond to methyl (a,  $\text{CH}_3\text{O}$ - terminated PEO) and methylene groups (b, repeat unit of MePEO), respectively. Resonances at 2.23 ppm, 1.63 ppm, 1.38 ppm and 4.06 ppm were assigned to protons in PCL repeat units (e, f, g, and h methylenes). The peak at 3.65 ppm (the methylene proton signal for the PEO block) and the triplet at 2.23 ppm (the methylene proton signal of the caprolactone repeating units, e,  $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), were used to establish the degree of PCL block polymerization and  $M_n$ .  $^1\text{H}$  NMR spectroscopy was further utilized to characterize the number-average molecular weight of PEO from the calculated ethylene oxide repeat unit number, by comparison of the integrated intensities of the resonances that corresponded to the end groups (i.e.  $\text{CH}_3\text{O}$ - or  $\text{CNCH}_2\text{CH}_2$ -). The key difference between the  $^1\text{H}$  NMR spectra of CN-PEO-*b*-PCL and MePEO-*b*-PCL diblock copolymers is highlighted by two weak signals around 2.51 ppm and 1.90 ppm which correspond respectively to  $\alpha$ - and  $\beta$ - $\text{CH}_2$  groups at the diblock copolymer CN terminus (**Fig. S2**).

Weight-average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) values for each copolymer formulation were determined using a GPC system that featured two

columns (PLgel 5 $\mu$ m mixed C, 300  $\times$  7.5 mm, linear MW operating range: 200-2,000,000 g/mol) connected in series, and laser light scattering and refractive index detectors (PD2040 High Temperature Laser Light Scattering Detector, Enterprise System, Precision Technologies). THF was utilized as the eluting solvent. PEO standards were used to calibrate copolymers molecular weights determined from refractive index data. Two types of weight-average molecular masses were calculated from refractive index data using PEO standard samples and laser light scattering data (**Table S3**).

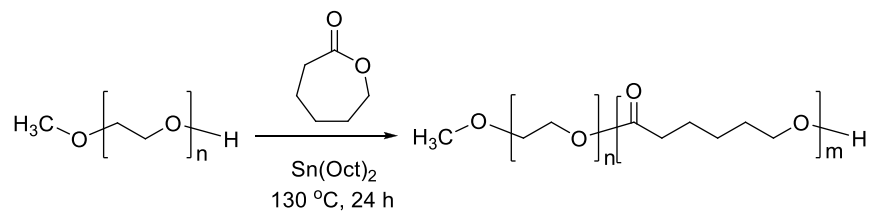
**Characterization of Sample Morphology.** Confocal laser scanning microscopy (BioRad Radiance 2000) and epifluorescent optical microscopy (Zeiss Axiovert 200) were employed to characterize the meso-scale self-assembled aqueous morphologies of the biodegradable polymer compositions that featured dispersed Nile Red (1:99 dye:polymer). The instruments were equipped with 488 nm excitation and 505 nm long-pass emission filters for these experiments.

Nanometric polymersomes were prepared as described above and characterized by cryogenic transmission electron microscopy (cryo-TEM). Vitreous samples were prepared within a controlled environment vitrification system (Vitrobot). A droplet of solution ( $\sim$ 10  $\mu$ l) was deposited on a copper TEM grid coated with a porous polymer film. A thin film ( $<$  300 nm) was obtained by blotting with filter paper. After allowing the sample sufficient time to relax from any residual stresses imparted during blotting ( $\sim$ 30 s), the grid was plunge-cooled in liquid ethane at its freezing point ( $-180$   $^{\circ}$ C), resulting in vitrification of the aqueous film. Sample grids were examined in a FEI

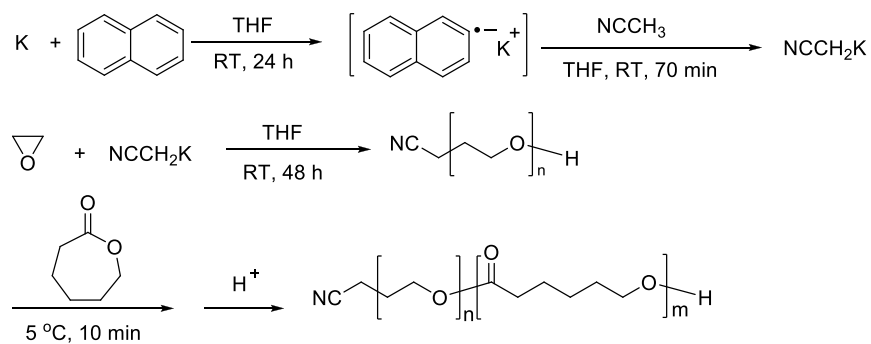
Tecnai G<sup>2</sup> Twin transmission electron microscope operating at 200 kV, and images were recorded with a Gatan 724 Multiscan digital camera.

A comparative analysis of the morphologies of self-assembled structures generated as a function of preparative method (thin-film hydration vs. organic co-solvent/water injection/extraction) shows that while the morphologies of nanoscale assemblies are similar for both methods for a given polymer composition, the  $\mu\text{m}$ -sized morphologies generated via thin film hydration differed from those derived from co-solvent injection.

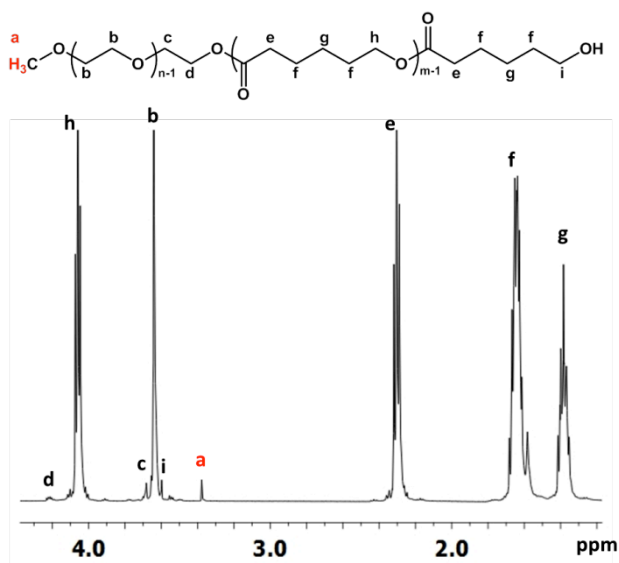
**Dynamic Light Scattering (DLS).** Dynamic light scattering was performed using a DynaPro Titan dynamic light-scattering instrument (Wyatt Technology Inc.) that applied vertically polarized laser light of wavelength 829 nm. The DLS instrument was calibrated with BSA standard (2 mg ml<sup>-1</sup> in PBS buffer, 25 °C). Light-scattering studies were carried out in the concentration range of 0.1 - 0.5 mg mL<sup>-1</sup> polymersomes in DI H<sub>2</sub>O. Prior to DLS, The quartz cell was rinsed several times with filtered water and then filled with the filtered sample solution. The data obtained in each case were the average of 50 runs, each of 10s duration. The temperature was maintained at 25 °C. Data were collected and analyzed using the DYNAMICS software for the DynaPro Titan instrument (Wyatt Technology Inc.)



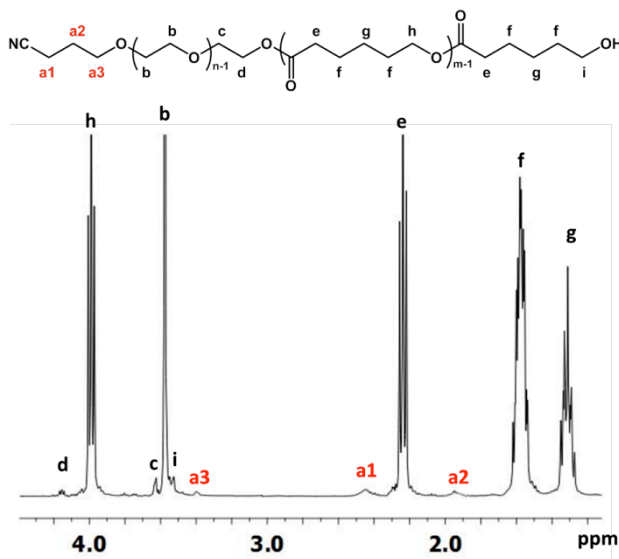
**Scheme S1.** Synthesis of PEO-*b*-PCL diblock copolymers by ring-opening polymerization.



**Scheme S2.** Synthesis of PEO-*b*-PCL diblock copolymers by anionic living polymerization.



**Figure S1.** Representative  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of a monomethoxy terminated PEO-*b*-PCL diblock copolymer.



**Figure S2.** Representative  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of a CN terminated PEO-*b*-PCL diblock copolymer.

**Table S1.** Extent to which Vesicles Comprise the Visually Observed Meso-Scale and Nanoscale Morphologies Prepared from PEO-b-PCL Diblock Copolymers via Thin-Film Hydration in Aqueous Media.

PEO-b-PCL Copolymers <sup>a</sup>	f <sub>PEO</sub> <sup>b</sup>	μm-Mor. <sup>c</sup>	Extent to which vesicles comprise the visually observed morphologie <sup>d</sup>	nm-Mor. <sup>e</sup>	Extent to which vesicles comprise the visually observed morphologie <sup>d</sup>
PEO(0.75K)-b-PCL(2.9K)	0.21	MS,IP	0	V,S	D
PEO(1.1K)-b-PCL(2.9K)	0.27	MS, IP	0	V,S	D
PEO(1.1K)-b-PCL(3.7K)	0.23	MS, IP	0	V,S	D
PEO(1.1K)-b-PCL(6.3K)	0.15	MS, IP	0	V,S	C
PEO(1.1K)-b-PCL(7.0K)	0.14	IP,MS	0	V,S	C
PEO(1.1K)-b-PCL(7.7K)	0.12	IP	0	S,V	A
PEO(1.5K)-b-PCL(6.3K)	0.19	MS, IP	0	V,S	D
PEO(1.5K)-b-PCL(10.4K)	0.13	IP	0	S,V	C
PEO(2K)-b-PCL(7.4K)	0.21	IP,MS	A	V,S	D
PEO(2K)-b-PCL(9.5K)	0.17	V,IP	D	V,S	D
PEO(2K)-b-PCL(12K)	0.14	V,IP	D	V,S	D
PEO(2K)-b-PCL(15K)	0.12	IP,V	A	S,V	C
PEO(2k)-b-PCL(18k)	0.1	IP	0	S,V	A
PEO(2.6K)-b-PCL(11.2K)	0.19	V, IP	D	V,S	D
PEO(2.6K)-b-PCL(12.3K)	0.17	IP,V	C	V,S	D
PEO(2.6K)-b-PCL(13.9K)	0.16	IP,V	A	V,S	C
PEO(2.6K)-b-PCL(15.5K)	0.14	IP,V	A	S,V	C
PEO(3K)-b-PCL(16.5K)	0.15	IP,V	A	V,S	C
PEO(3K)-b-PCL(19K)	0.14	IP,V	A	S,V	A
PEO(3K)-b-PCL(20.5K)	0.13	IP,V	A	S,V	A
PEO(3.8K)-b-PCL(17K)	0.18	IP,V	A	V,S	D
PEO(3.8K)-b-PCL(17.7K)	0.17	IP,V	C	V,S	D
PEO(3.8K)-b-PCL(20K)	0.16	IP,V	A	S,V	C
PEO(3.8K)-b-PCL(22.2K)	0.15	IP,V	A	S,V	A

<sup>a</sup>Number-average molecular weight of PEO-b-PCL diblock copolymers as determined by

<sup>b</sup>1H NMR spectroscopy. <sup>c</sup>Weight fraction of the PEO block as determined by 1H NMR



data. <sup>c</sup>Determined qualitatively from fluorescence confocal and laser optical microscopic studies of the self-assembled structures formed from thin film rehydration of 50:1 copolymer: Nile Red films. Observed polymersome and irregularly shaped particle (IP) diameters ranged from less than 1  $\mu\text{m}$  to greater than 30  $\mu\text{m}$ ; microsphere (MS) diameters ranged from  $\sim 5 - 30 \mu\text{m}$ ; vesicle (V) diameters spanned  $\sim 5 - 50 \mu\text{m}$ . In the cases of mixed morphologies, the major component is written first. <sup>d</sup>The approximate, qualitative extent to which vesicles comprise the visually observed morphologies was visually estimated from fluorescence confocal and laser optical microscopic studies: D (dominant morphology) – Vesicles define the most prevalently observed morphological structure; C (common morphology) – Vesicles define one of the commonly observed morphological structures; A (atypical morphology) – Vesicles are observed, but such structures are less common than other observed morphologies. <sup>e</sup>Determined qualitatively from cryogenic transmission electron microscopic studies of the self-assembled structures formed from thin film rehydration of 50:1 copolymer:Nile Red films followed by extrusion through a 400 nm porosity membrane (S = spherical micelles, V = vesicle, P = precipitate; for systems exhibiting mixed morphologies, the majority component is noted first).

**Table S2.** Molecular details of all polymers synthesized.

Block Copolymers	PEO length (Da)	PCL length (Da)	$f_{\text{PEO}}$
OCL (PEO- <i>b</i> -PCL)	0.75K	2.9K, 5.8K, 9K	0.07-0.21
	1.1K	2.9K, 3.7K, 6.3K, 7K, 7.7K, 9.5K, 13K	0.08-0.27
	1.5K	6.3K, 10.4K, 12.4K, 13.7K,	0.10-0.19
	2K	7.4K, 9.5K, 12K, 15K, 18K, 22K	0.08-0.27
	2.6K	11.2K, 12.3K, 13.9K, 15.5K	0.14-0.19
	3K	16.5K, 19K, 20.5K, 24.7K, 25.8K	0.10-0.15
	3.8K	17K, 17.7K, 20K, 22.2K	0.15-0.18
	5K	10K, 16K, 22K, 26K, 32K, 52K	0.09-0.33
	5.8K	22K, 23.8K, 24K, 30.2K, 33.6K, 37.7K, 41.2K	0.12-0.21

**Table S3.** GPC and  $^1\text{H}$  NMR Characterization Data for PEO-*b*-PCL Diblock Copolymers.

PEO- <i>b</i> -PCL Copolymers <sup>a</sup>	$f_{\text{PEO}}^b$	$M_n^b$	$M_w^c$	PDI <sup>c</sup>	$M_w^d$
PEO(5.8K)- <i>b</i> -PCL(24K)	0.20	29800	27800	1.24	28100
PEO(5.8K)- <i>b</i> -PCL(33.6K)	0.15	39400	28500	1.20	31100
PEO(5K)- <i>b</i> -PCL(22K)	0.18	27000	25300	1.37	24000
PEO(5K)- <i>b</i> -PCL(26K)	0.16	31000	31400	1.32	36200
PEO(3.8K)- <i>b</i> -PCL(17K)	0.18	20800	15100	1.20	18900
PEO(3.8K)- <i>b</i> -PCL(20K)	0.16	23800	17600	1.25	19100
PEO(3.8K)- <i>b</i> -PCL(22.2K)	0.15	26000	19200	1.26	22100
PEO(3K)- <i>b</i> -PCL(16.5K)	0.15	19000	16700	1.23	17300
PEO(3K)- <i>b</i> -PCL(19K)	0.14	22000	19400	1.24	19400
PEO(2.6K)- <i>b</i> -PCL(11.2K)	0.19	13800	16200	1.27	19000
PEO(2.6K)- <i>b</i> -PCL(12.3K)	0.17	14900	17300	1.25	20600
PEO(2.6K)- <i>b</i> -PCL(15.5K)	0.14	18100	19600	1.25	24100
PEO(2K)- <i>b</i> -PCL(9.5K)	0.17	11500	12500	1.14	16300
PEO(2K)- <i>b</i> -PCL(12K)	0.14	14000	13700	1.21	15400
PEO(2K)- <i>b</i> -PCL(15K)	0.12	17000	16100	1.21	18300

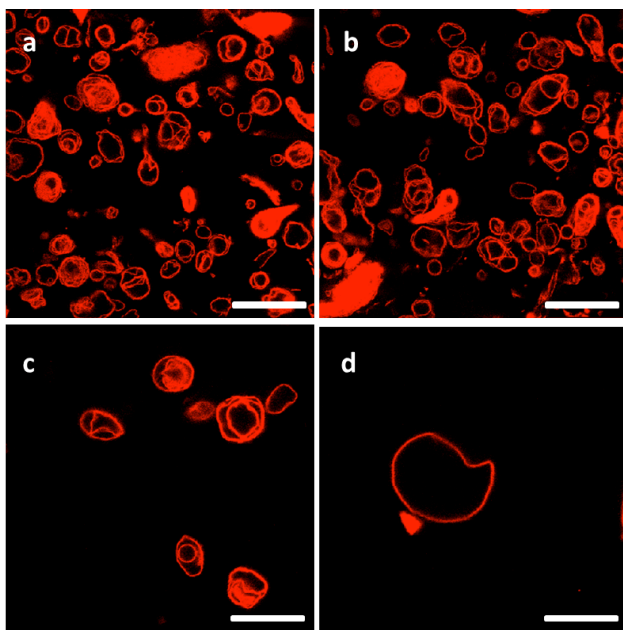
<sup>a</sup>Number-average molecular weight of PEO-*b*-PCL diblock copolymers as determined by  $^1\text{H}$  NMR spectroscopy. <sup>b</sup>Weight fraction of the PEO block as determined by  $^1\text{H}$  NMR data. <sup>c</sup>Polydispersity index and weight-average molecular weight of PEO-*b*-PCL diblock copolymers as determined from dynamic light scattering (DLS) data of samples analyzed by gel permeation chromatography (GPC). <sup>d</sup>Weight-average molecular weight of PEO-*b*-PCL diblock copolymers calculated from refractive index (RI) data of samples analyzed by GPC using PEO standard samples as calibrants.

**Table S4.** Polymers that Self-Assemble into Polymersomes.

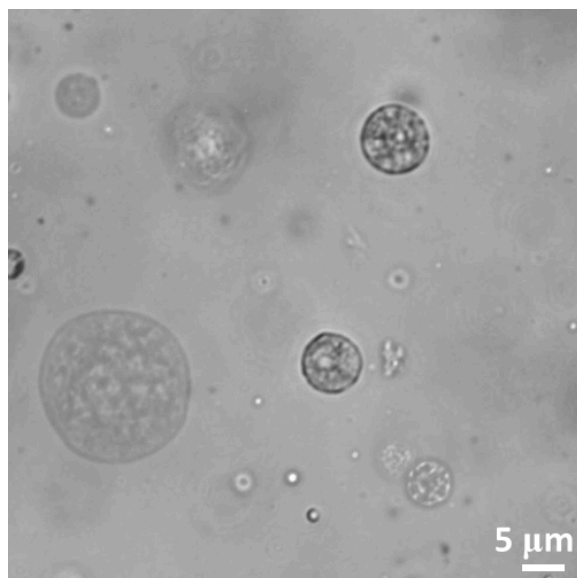
PEO- <i>b</i> -PCL Copolymers	$M_w^a$	$f_{PEO}^b$	Morphology <sup>c</sup>	D (DLS) <sup>d</sup>
PEO(0.75K)- <i>b</i> -PCL(2.9K)	3.65K	0.21	V	71 nm
PEO(1.1K)- <i>b</i> -PCL(2.9K)	4K	0.27	V	101.8 nm
PEO(1.1K)- <i>b</i> -PCL(3.7K)	4.8K	0.23	V	124 nm
PEO(1.1K)- <i>b</i> -PCL(6.3K)	7.4K	0.15	V,S	135.9 nm
PEO(1.1K)- <i>b</i> -PCL(7.0K)	8.1K	0.14	V,S	142.2 nm
PEO(1.1K)- <i>b</i> -PCL(7.7K)	8.8K	0.12	S,V	151.4 nm
PEO(1.5K)- <i>b</i> -PCL(6.3K)	7.8K	0.19	V	146.3 nm
PEO(1.5K)- <i>b</i> -PCL(10.4K)	11.9K	0.13	S,V	172.5 nm
PEO(2K)- <i>b</i> -PCL(7.4K)	9.4K	0.21	V	187 nm
PEO(2K)- <i>b</i> -PCL(9.5K)	11.5K	0.17	V	203 nm
PEO(2K)- <i>b</i> -PCL(12K)	14K	0.14	V,S	212.6 nm
PEO(2K)- <i>b</i> -PCL(15K)	17K	0.12	S,V	221 nm
PEO(2k)- <i>b</i> -PCL(18k)	20K	0.1	S,V	268 nm
PEO(2.6K)- <i>b</i> -PCL(11.2K)	13.8K	0.19	V	208.5 nm
PEO(2.6K)- <i>b</i> -PCL(12.3K)	14.9K	0.17	V	212.1 nm
PEO(2.6K)- <i>b</i> -PCL(13.9K)	16.5K	0.16	V,S	215.4 nm
PEO(2.6K)- <i>b</i> -PCL(15.5K)	18.1K	0.14	S,V	228.2 nm
PEO(3K)- <i>b</i> -PCL(16.5K)	19.5K	0.15	V,S	192.4 nm
PEO(3K)- <i>b</i> -PCL(19K)	22K	0.14	S,V	229 nm
PEO(3K)- <i>b</i> -PCL(20.5K)	23.5K	0.13	S,V	245 nm
PEO(3.8K)- <i>b</i> -PCL(17K)	20.5K	0.18	V,S	214 nm
PEO(3.8K)- <i>b</i> -PCL(17.7K)	21.5K	0.17	V,S	220.4 nm
PEO(3.8K)- <i>b</i> -PCL(20K)	23.8K	0.16	S,V	256 nm
PEO(3.8K)- <i>b</i> -PCL(22.2K)	26K	0.15	S,V	260.6 nm

<sup>a</sup>Number-average molecular weight of PEO-*b*-PCL diblock copolymers as determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup>Weight fraction of the PEO block as determined by <sup>1</sup>H NMR data. <sup>c</sup>Determined qualitatively from cryogenic transmission electron microscopic studies of the self-assembled structures formed from thin film rehydration of 50:1 copolymer: Nile Red films followed by extrusion through 400 nm membrane (S = spherical micelles,

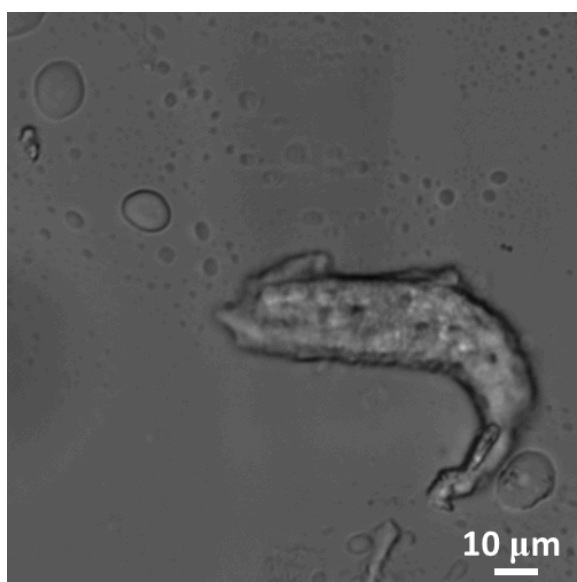
V = vesicle, P = precipitate; in the cases of mixed morphologies the majority component is written first). <sup>d</sup>Average diameter of the vesicles/micelles determined by dynamic light scattering (DLS).



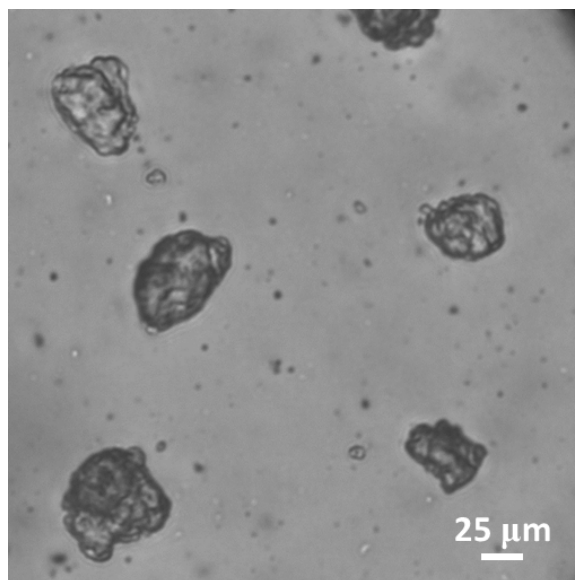
**Fig. S3** Scanning fluorescence confocal micrographs ( $\lambda_{\text{ex}} = 488 \text{ nm}$ ) of PEO(2K)-b-PCL(12K)-based vesicles, containing membrane-encapsulated Nile Red (peak emission = 603 nm) in DI water at 25 °C, that display continuous spherical morphology but jagged edges suggestive of solid vesicle membranes. Scale bar = 5  $\mu\text{m}$ .



**Figure S4.** Optical microscopic images of microspheres derived from thin-film hydration of 99:1 PEO(5K)-*b*-PCL(10K):Nile Red in DI water at 25 °C.

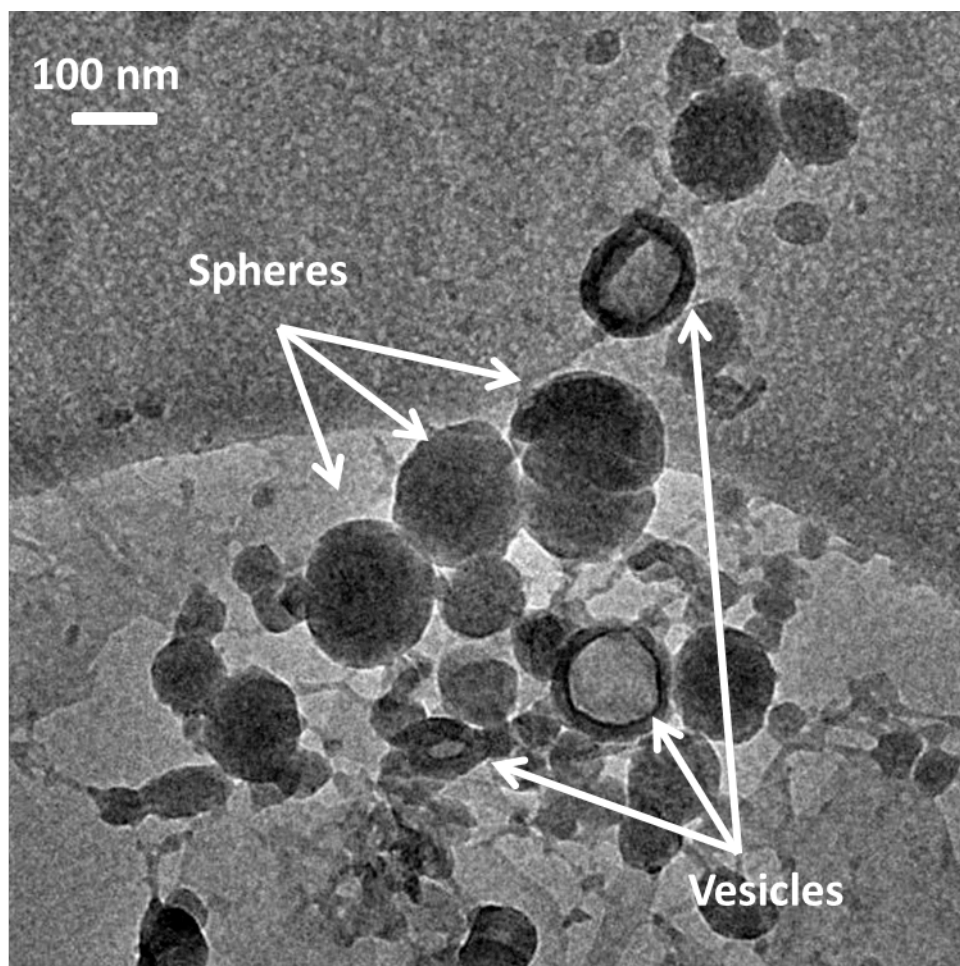


**Figure S5.** Optical microscopic images of irregular particles and a few polymersomes derived from thin-film hydration of 99:1 PEO(2K)-*b*-PCL(15K):Nile Red in DI water at 25 °C.

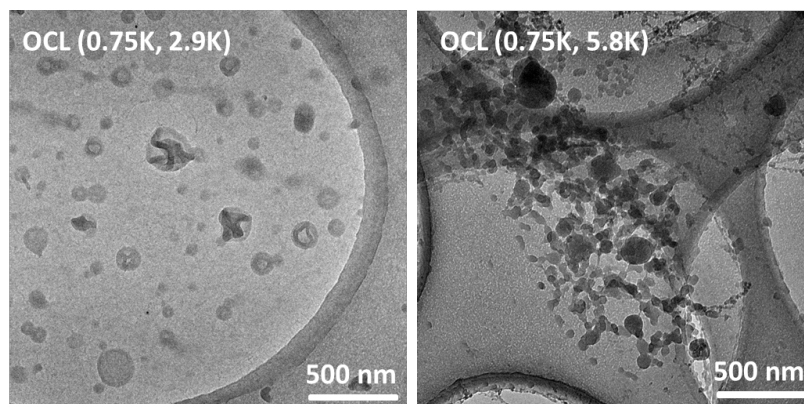


**Figure S6.** Optical microscopic images of irregular particles derived from thin-film hydration of 99:1 PEO(2K)-*b*-PCL(22K):Nile Red in DI water at 25 °C.

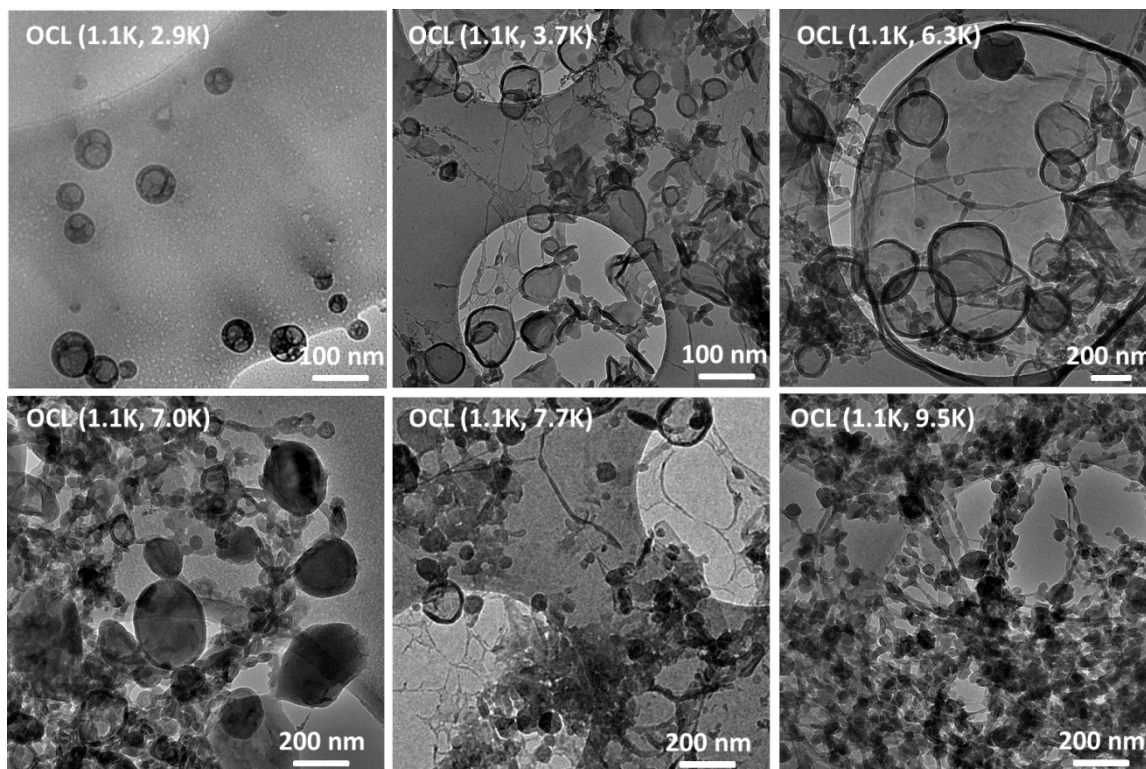




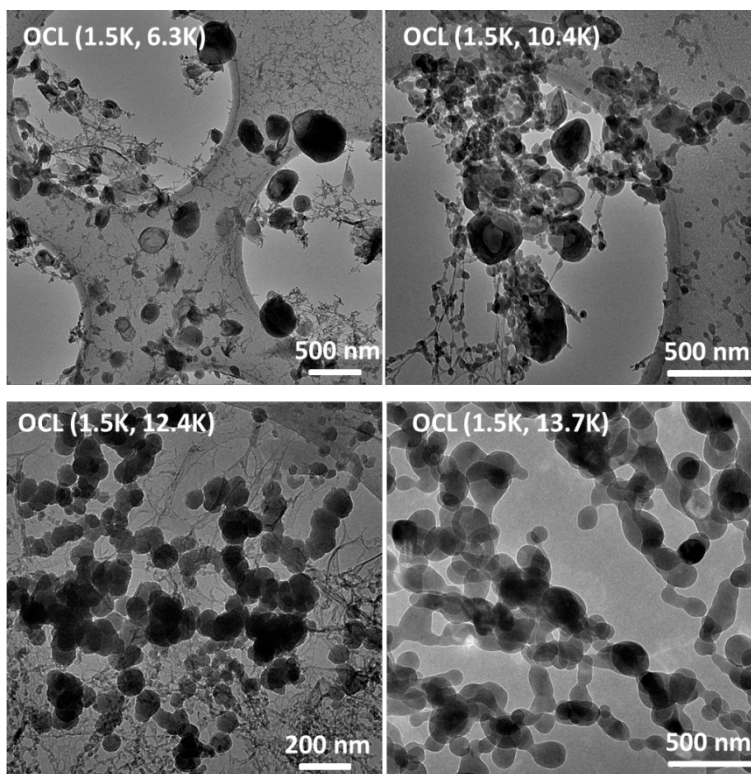
**Figure S7.** Representative Cryo-TEM image shows a mixture of vesicle and spheres in nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(2.6K)-*b*-PCL(15.5K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



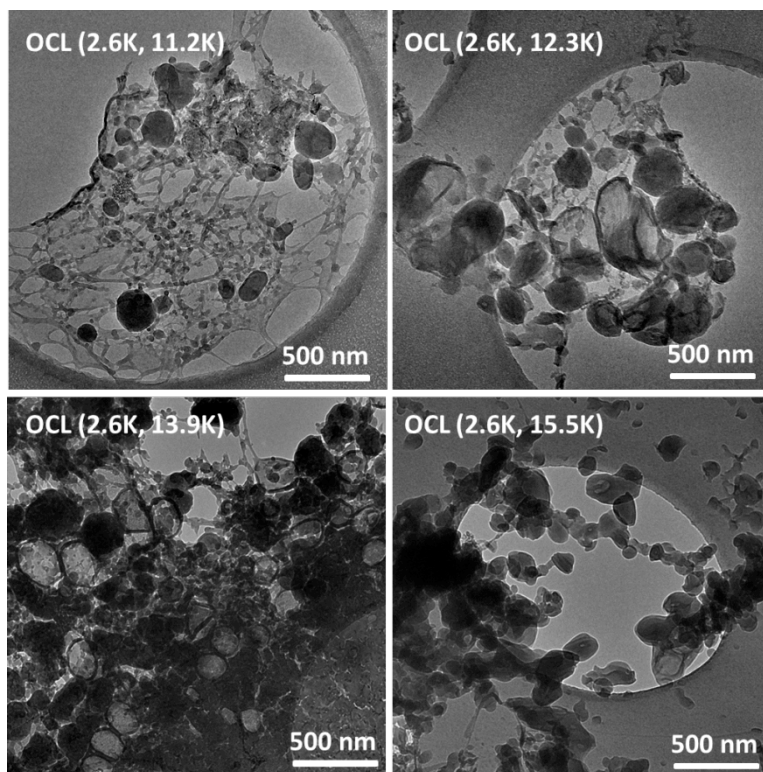
**Figure S8.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(0.75K)-*b*-PCL(2.9, 5.8K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



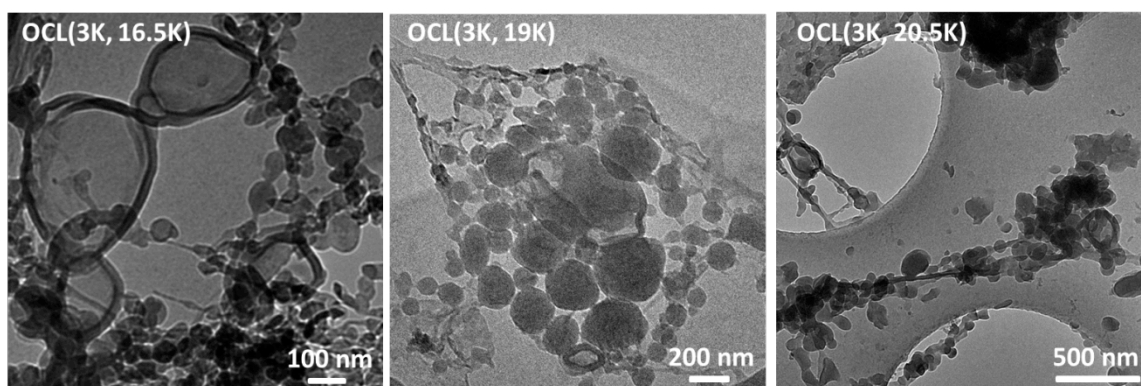
**Figure S9.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(1.1K)-*b*-PCL(2.9 – 9.5K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



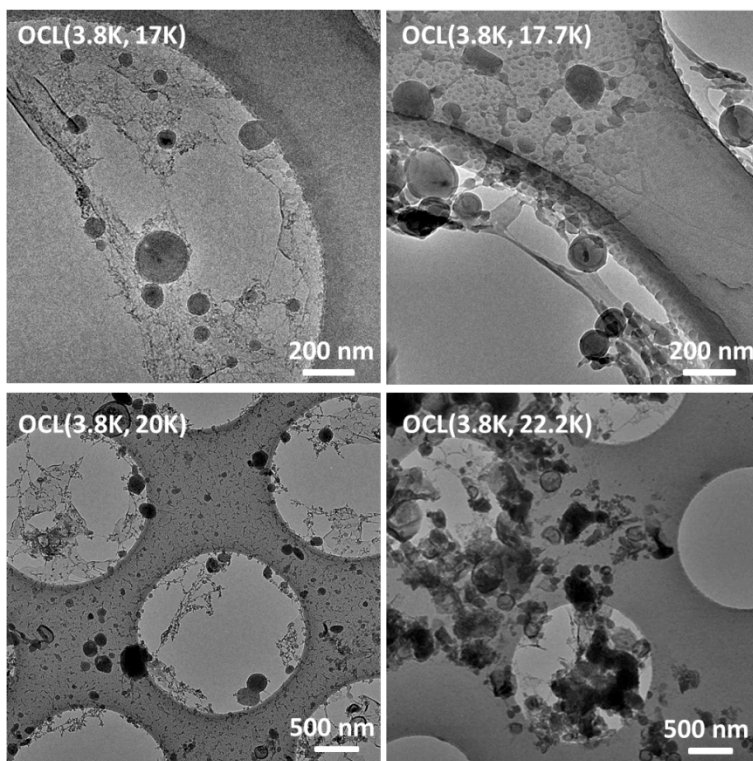
**Figure S10.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(1.5K)-*b*-PCL(6.3 – 13.7K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



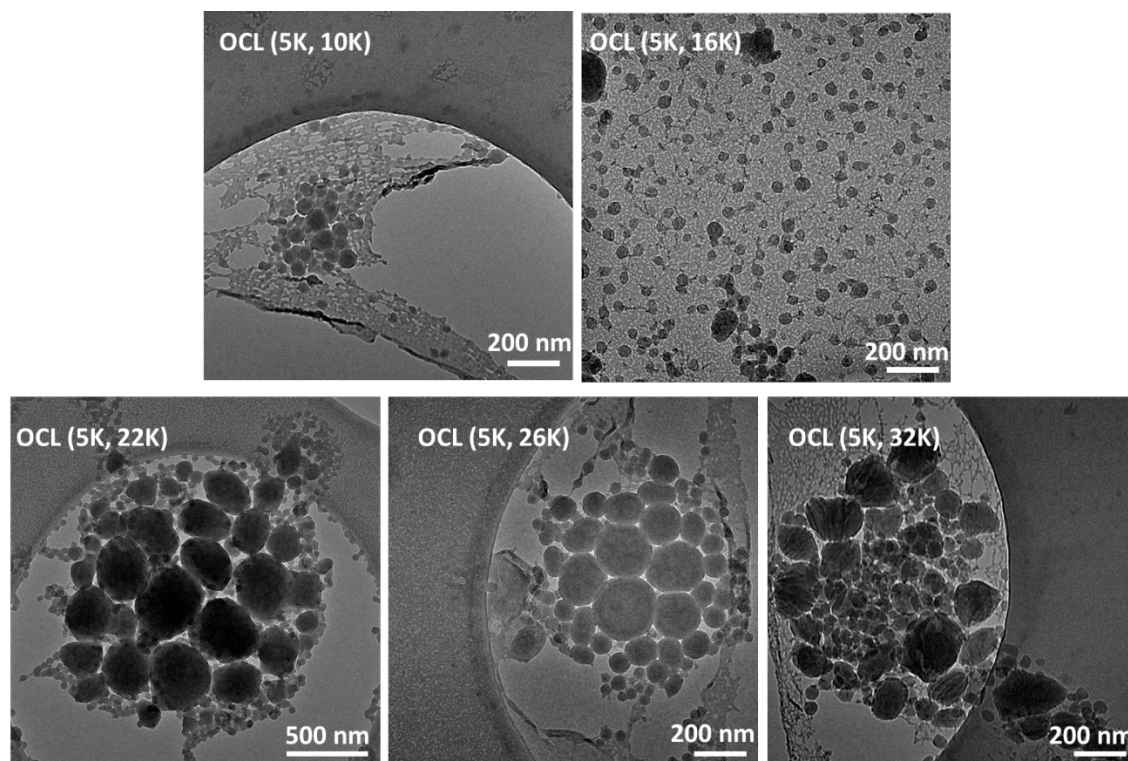
**Figure S11.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(2.6K)-*b*-PCL(11.2 – 15.5K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



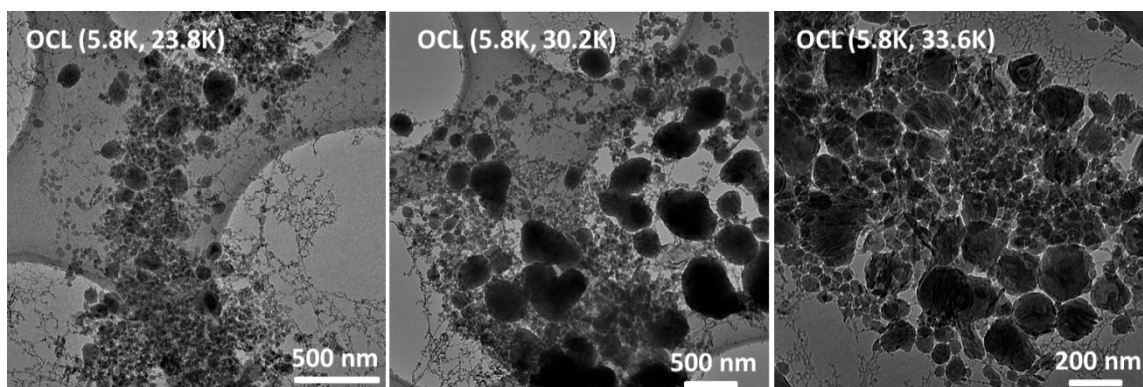
**Figure S12.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(3K)-*b*-PCL(16.5, 19K, 20.5K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



**Figure S13.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(3.8K)-*b*-PCL(17 – 22.2K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



**Figure S14.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(5K)-*b*-PCL(10 - 32K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.



**Figure S15.** Cryo-TEM images of nano-scale PEO-*b*-PCL diblock copolymers OCL PEO(5.8K)-*b*-PCL(23.8K, 30.2K, 33.6K) particles in aqueous suspensions obtained via thin-film hydration and subsequent self-assembly.