Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Self-Assembly of Luminescent Triblock Bottlebrush Copolymers in Solution

Feng Shao, Yonghui Wang, Christopher M. Tonge, Ethan R. Sauvé and Zachary M. Hudson

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Z1.

Tel: +1-604-822-3266; Fax: +1-604-822-2847; e-mail: zhudson@chem.ubc.ca

Table of Contents

Calculations

The total molecular weight of the BBCPs is determined from the sum of the molecular weight of each brush multiplied by the degree of polymerization (DP) of that brush (eq. **S1**). Herein, DP_{nBuA} denotes the DP of monomer to give macromonomer, while $DP_{nBuA\text{-}MM}$ denotes the DP of macromonomer to give bottlebrush.

$$M_{n,total} = DP_{nBuA\text{-}MM} \times M_{n,nBuA\text{-}MM} + DP_{PSBr\text{-}MM} \times M_{n,PSBr\text{-}MM} + DP_{(CzBA\text{-}co\text{-}PAPOMA)\text{-}MM} \times M_{n,(CzBA\text{-}co\text{-}PAPOMA)\text{-}MM} \quad \textbf{(S1)}$$

M_n for each macromonomer was determined using the ratio of a diagnostic peak for each monomer in the ^{1}H NMR spectrum relative to the norbornene olefin peak at δ = 6.31 ppm. These peaks were chosen as the three MMs did not have any overlapping signals in those regions of their ^{1}H NMR spectra.

nBuA-MM: δ = 3.86–4.34 ppm (2H, peak A);

PS^{Br}-MM: δ = 6.18–7.26 ppm (2H, peak B):

(CzBA-*co*-PAPOMA)-MM: δ = 4.60–5.51 ppm for **CzBA** (2H, peak C)

For a BBCP, M_n (nBuA block) was determined by SEC from an aliquot using triple detection. In this case, $M_{n,total} = M_n$ (nBuA block), so $DP_{nBuA\text{-}MM}$ may be determined by:

$$DP_{nBuA\text{-}MM} = M_{n,total} / M_{n,nBuA\text{-}MM}$$

In the ^{1}H NMR spectrum of a triblock BBCP, the integration of peak A (I_A) may then be assigned the value $I_A = DP_{nBuA} \times DP_{nBuA\text{-}MM} \times 2$.

In other words, I_A (the number of protons per bottlebrush) is equal to the number of macromonomers/bottlebrush × the number of monomers/macromonomer × 2 protons/monomer.

Subsequently, precise integration values for peaks B and C (I_B and I_C) may be determined by relative integration (both peaks also represent 2 protons/monomer).

DP_{PSBr} and $DP_{(CzBA\text{-}co\text{-}PAPOMA)}$ may then be determined by:

$DP_{PSBr\text{-}MM} = I_B / (2 \times DP_{PSBr})$ and $DP_{(CzBA\text{-}co\text{-}PAPOMA)\text{-}MM} = I_C / (2 \times DP_{CzBA})$.

Additional Figures

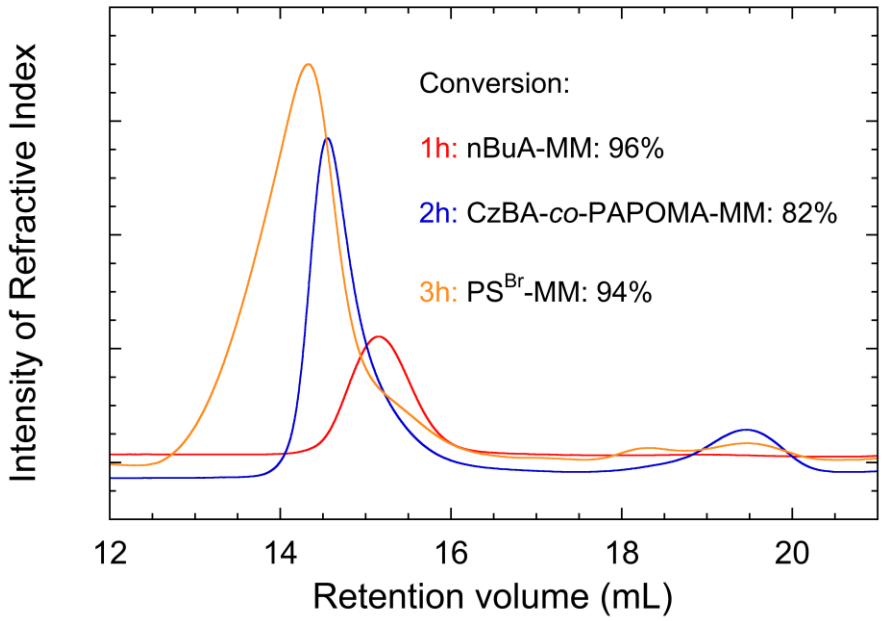

Figure S1. GPC characterization for the preparation of BBCP **2**.

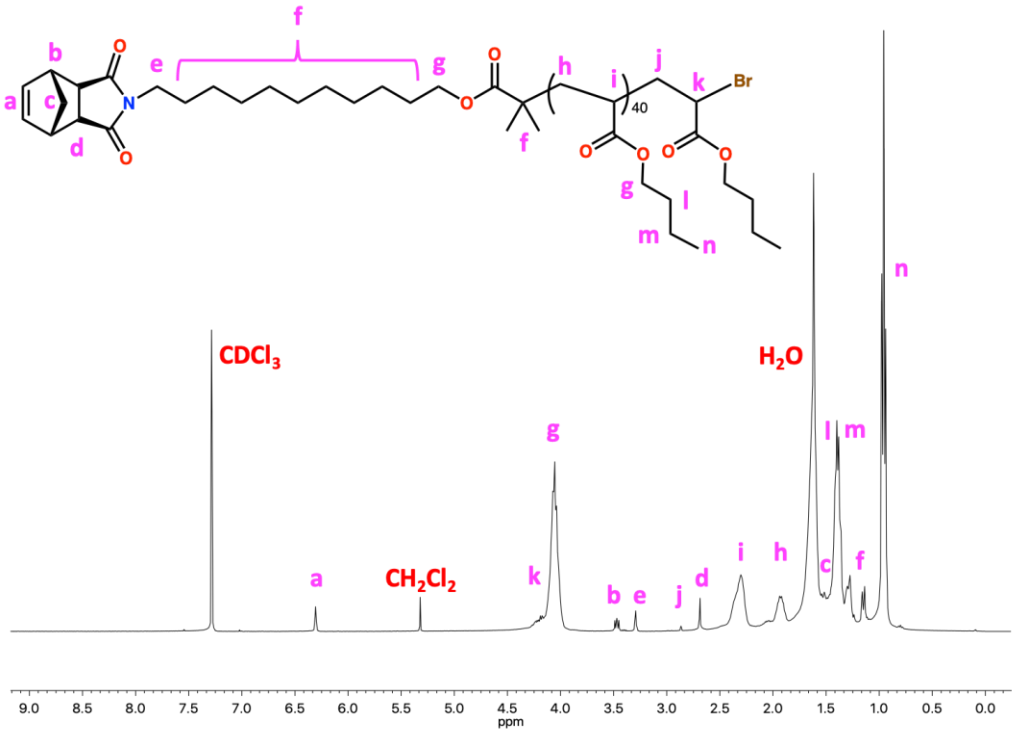

Figure S2. ^{1}H NMR spectrum of **nBuA-MM** in $CDCl_3$.

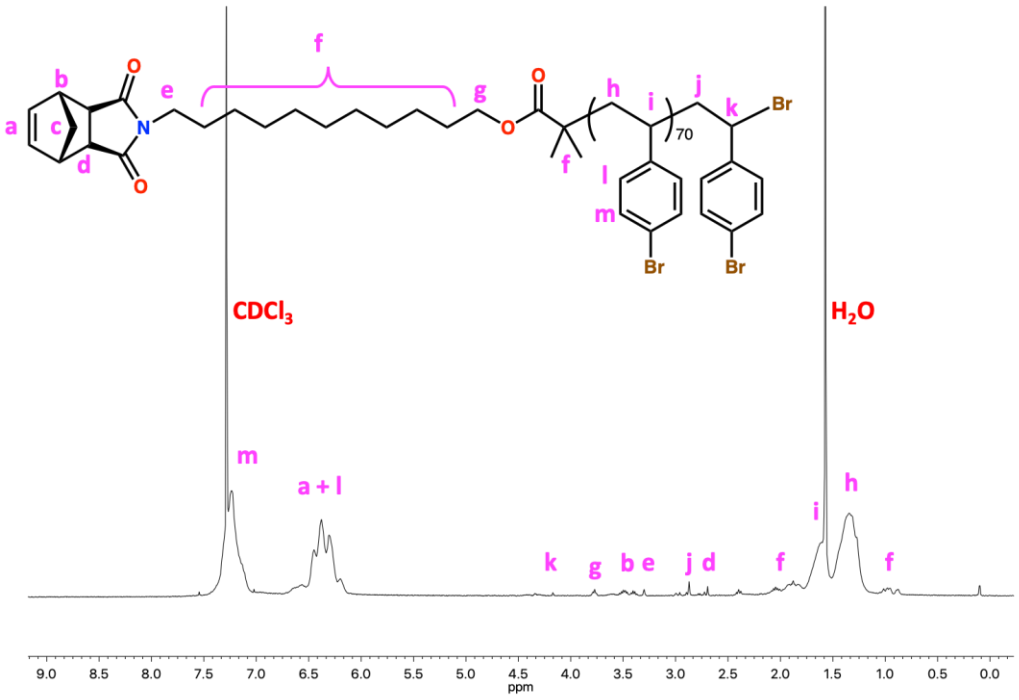

Figure S3. ^{1}H NMR spectrum of **PS^{Br}-MM** in $CDCl_3$.

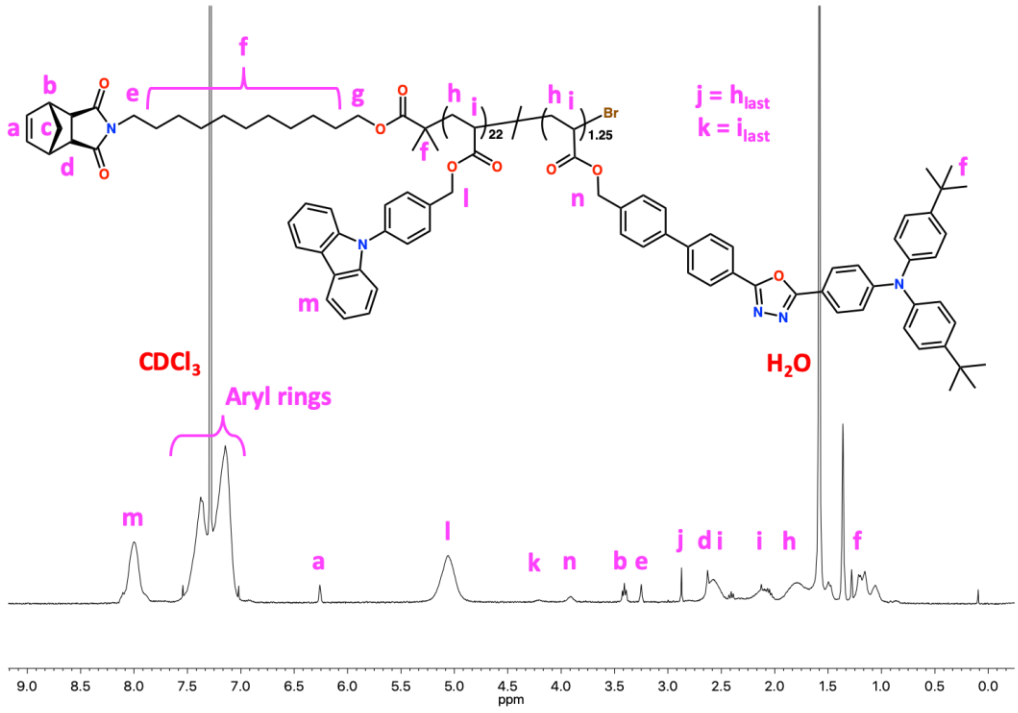

Figure S4. ^{1}H NMR spectrum of **CzBA-*co*-PAPOMA-MM** in $CDCl_3$.

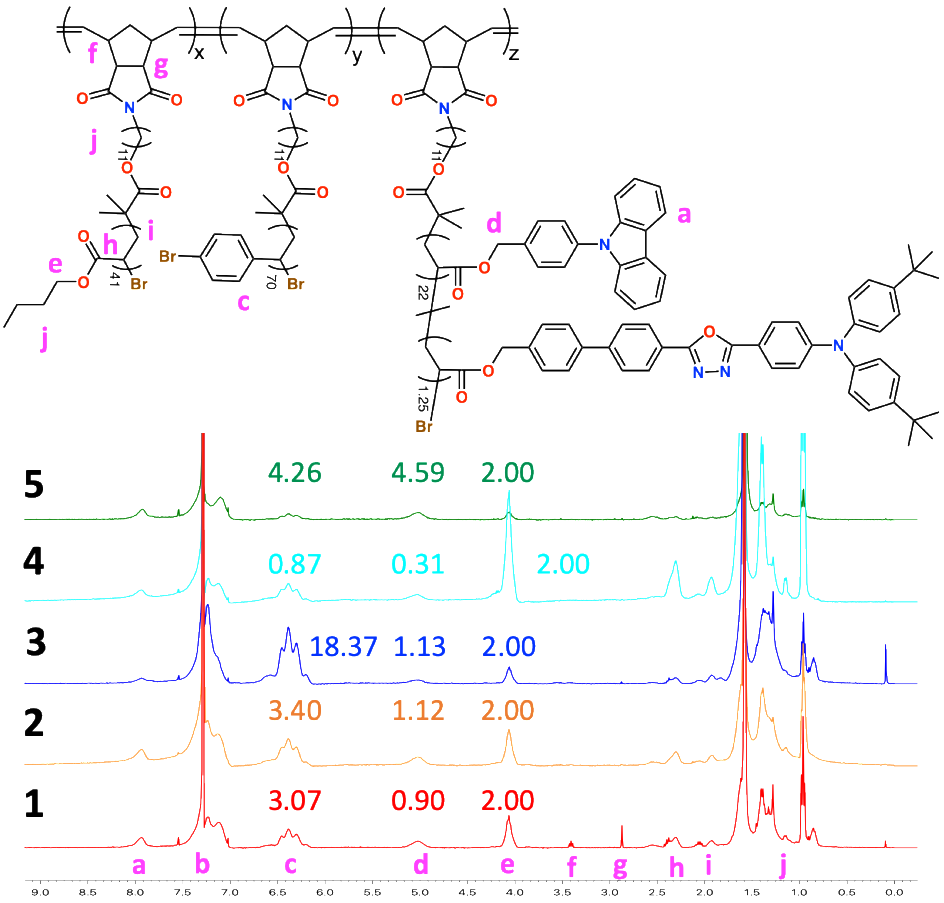

Figure S5. ^{1}H NMR spectrum of BBCPs **1**–**5** in $CDCl_3$. The integrated area of peaks c, d and e (with corresponding values) were used to determine the degree of polymerization of poly(norbornene) backbone for the **PS^{Br}-MM** and **CzBA-*co*-PAPOMA-MM** blocks. For the first block **nBuA-MM**, the degree of polymerization of the poly(norbornene) backbone was determined by SEC; **b**: aryl protons.

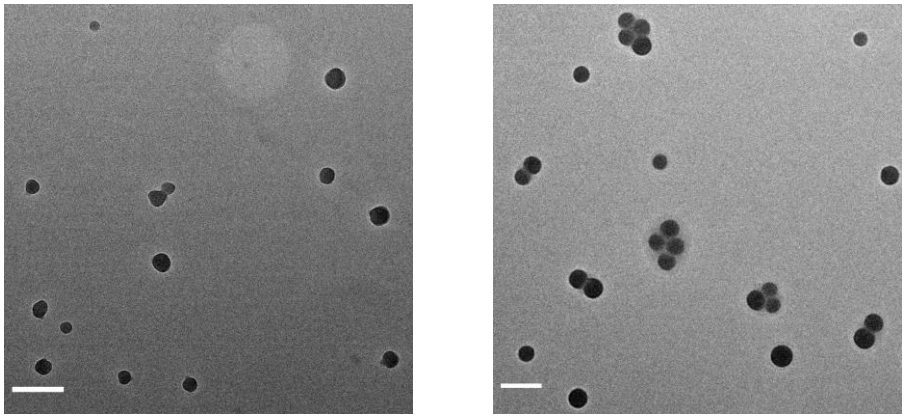

Figure S6. TEM images of triblock BBCP **5** in TFE after self-assembly. Left: **5** in THF solution directly self-assembled in TFE; right: **5** in THF solution dialyzed into TFE; Scale bars = 200 nm.

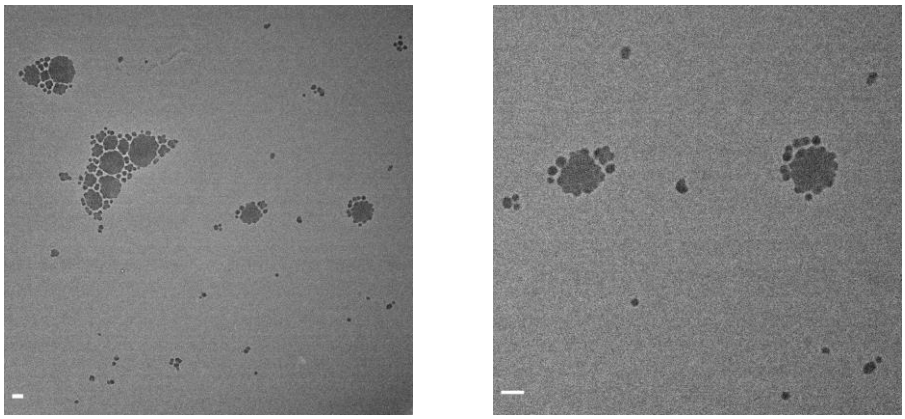

Figure S7. TEM images of triblock BBCP **2** after self-assembly in EtOAc with a concentration of 0.01 mg/mL. Scale bars = 200 nm (left) and 500 nm (right).

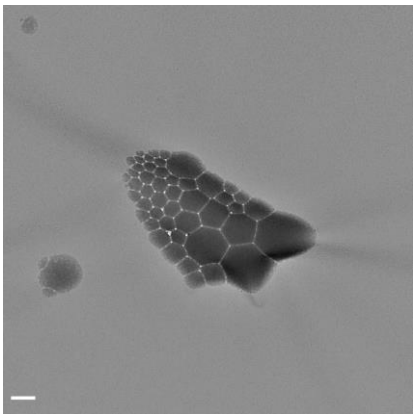

Figure S8. TEM image of triblock BBCP **3** after self-assembly in EtOAc with a concentration of 0.01 mg/mL. Scale bar = 500 nm.

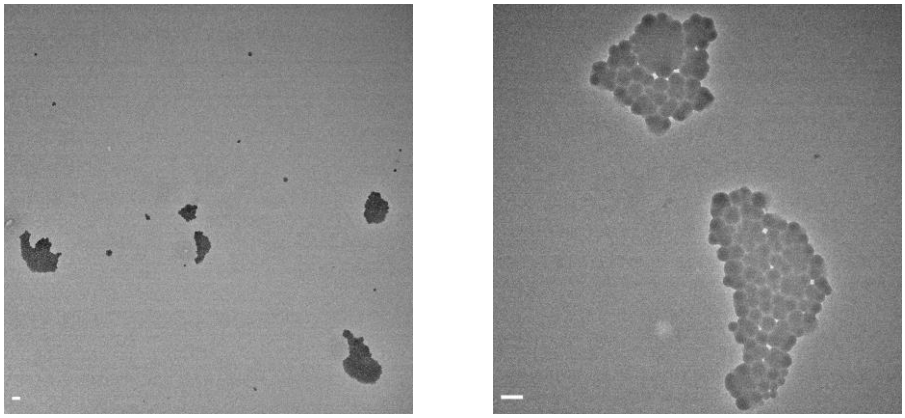

Figure S9. TEM images of triblock BBCP **5** after self-assembly in EtOAc with a concentration of 0.01 mg/mL. Scale bar = 200 nm (left) and 500 nm (right).

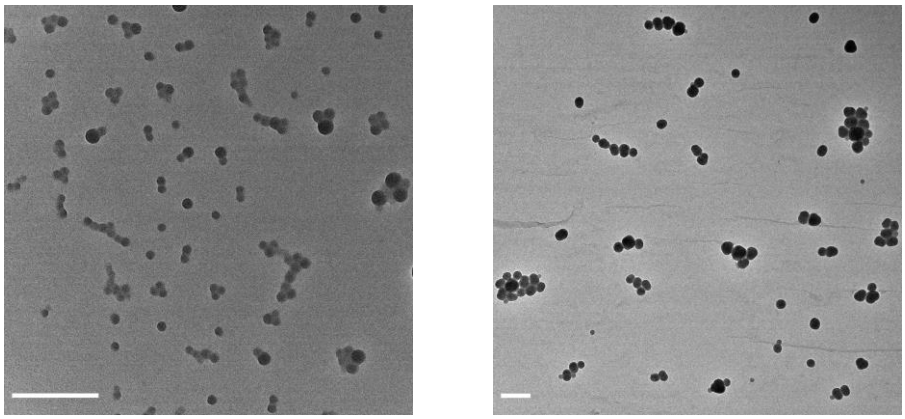

Figure S10. Wider TEM images of triblock BBCPs **4** (left) and **5** (right) after self-assembly in EtOAc followed by dialysis into TFE. Scale bar = 500 nm.

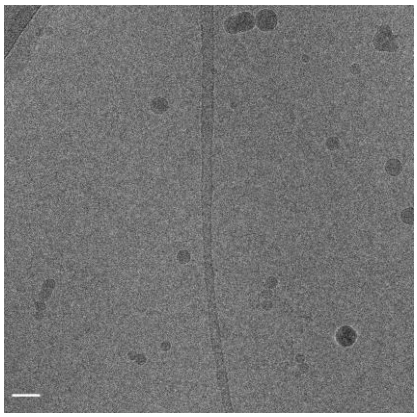

Figure S11. Cryo-TEM image of triblock BBCP **4** self-assembled in EtOAc and then dialyzed into TFE. Scale bar = 50 nm.

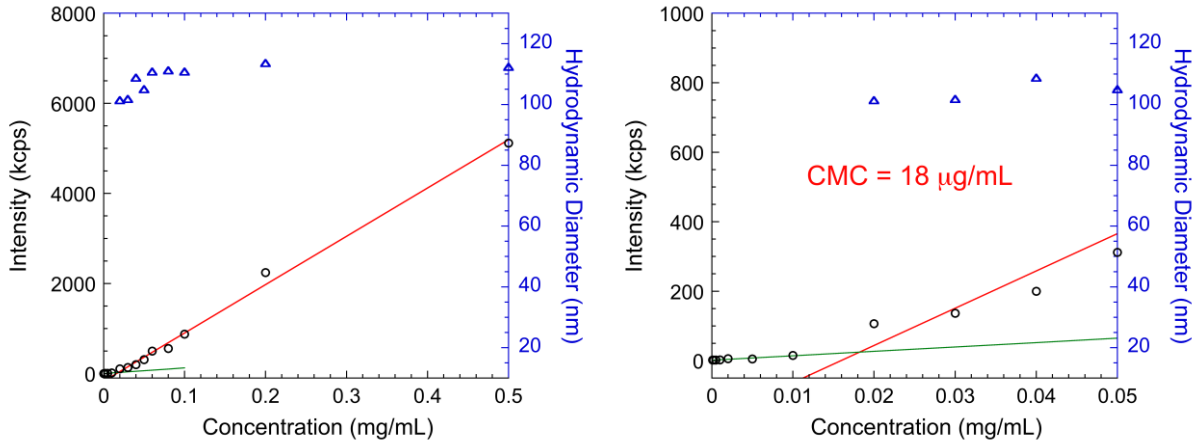

Figure S12. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **1** in TFE at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

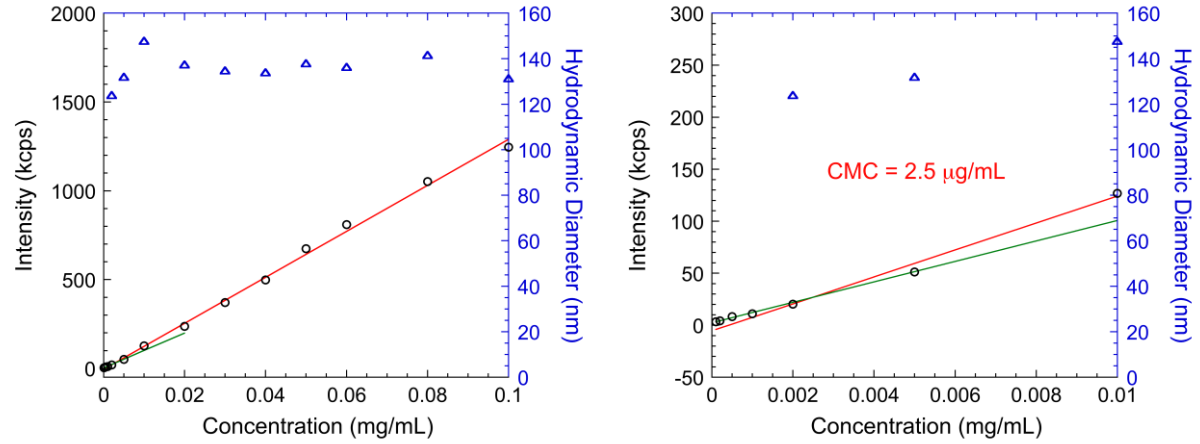

Figure S13. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **1** in EtOAc at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

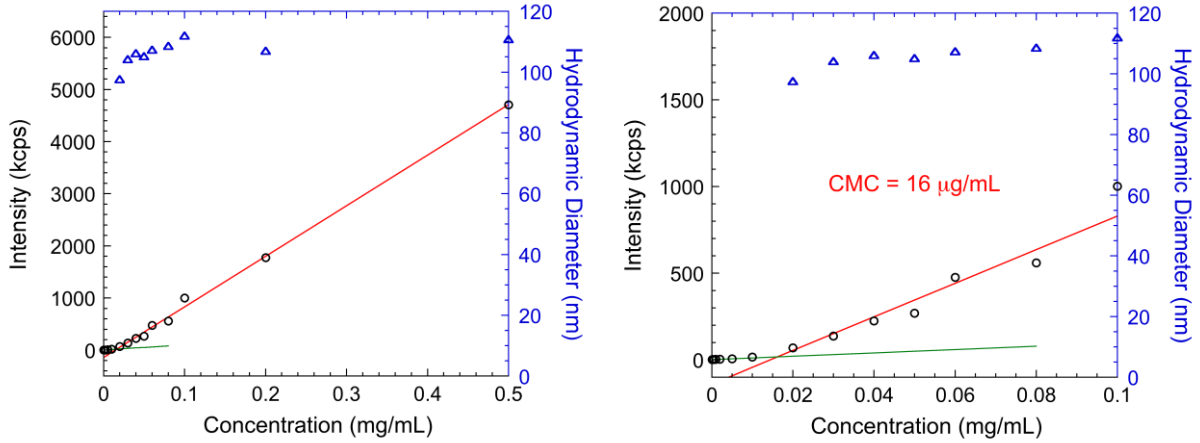

Figure S14. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **2** in TFE at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

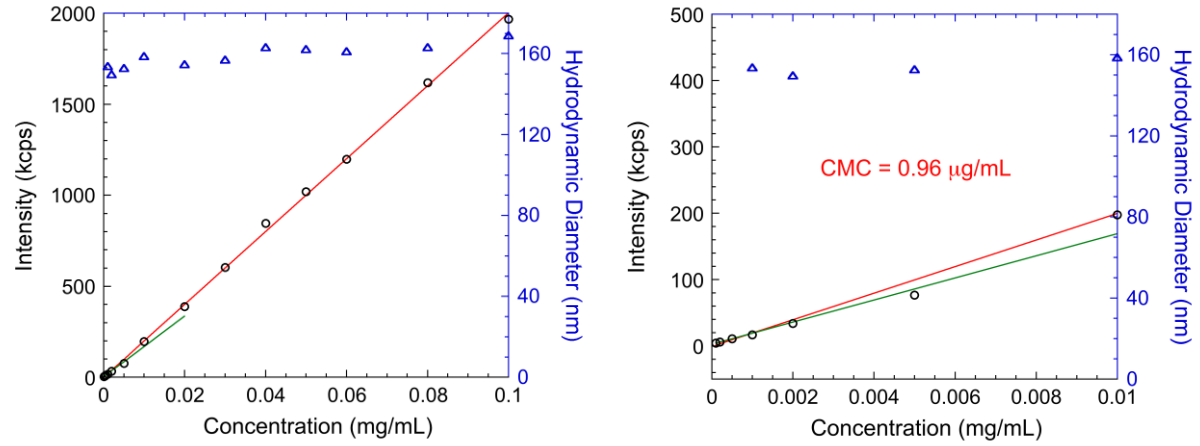

Figure S15. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **2** in EtOAc at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

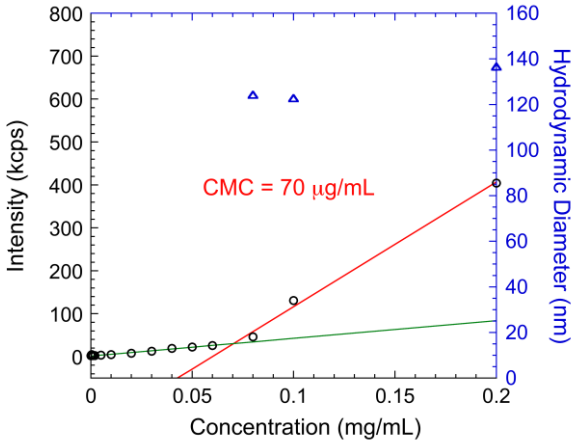

Figure S16. Dynamic light scattering plots of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **3** in TFE at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

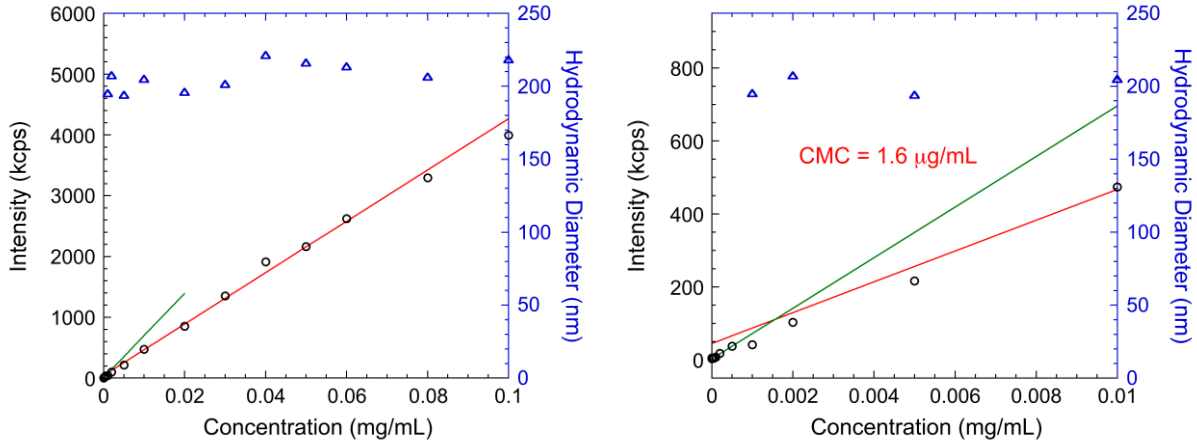

Figure S17. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **3** in EtOAc at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

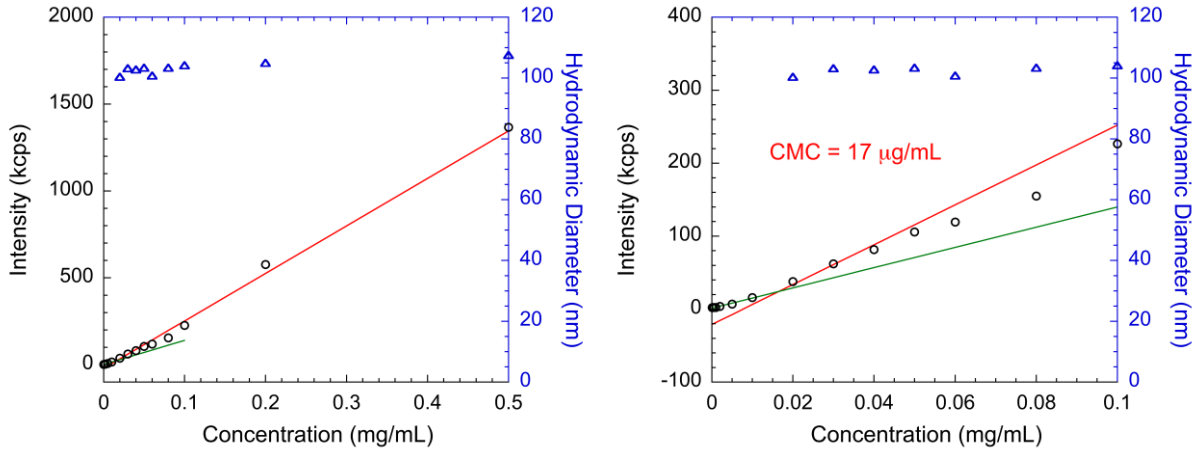

Figure S18. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **4** in TFE at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

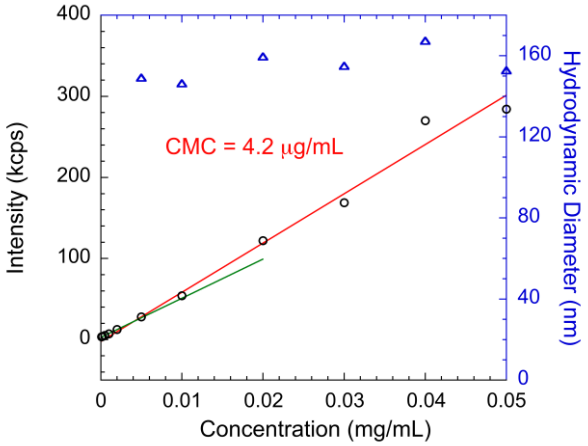

Figure S19. Dynamic light scattering plots of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **4** in EtOAc at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

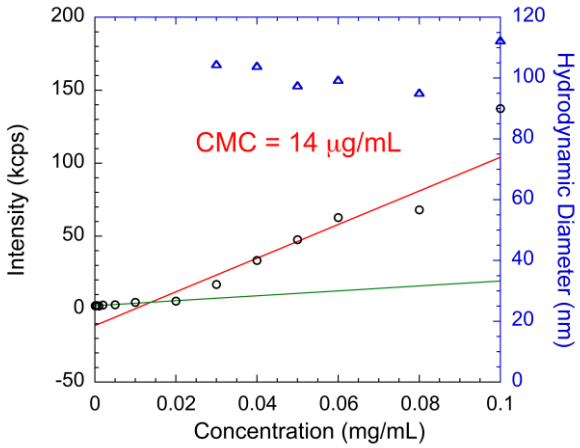

Figure S20. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **5** in TFE at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

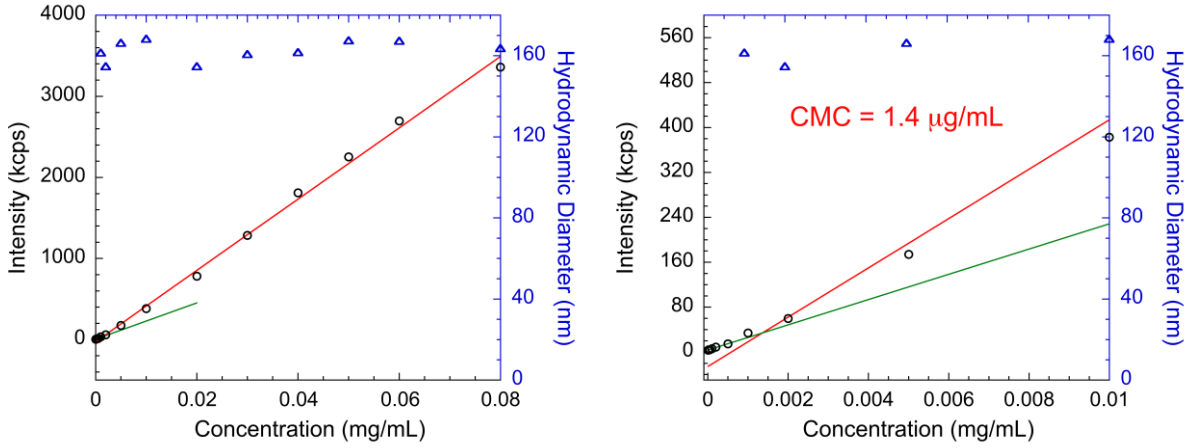

Figure S21. Dynamic light scattering plots (left) and zoom (right) of intensity of scattered light (black circle) and hydrodynamic radius (blue triangle) obtained for BBCP **5** in EtOAc at various concentrations. The intersection of the two lines in the intensity data corresponds to the critical micelle concentration (CMC) of the sample.

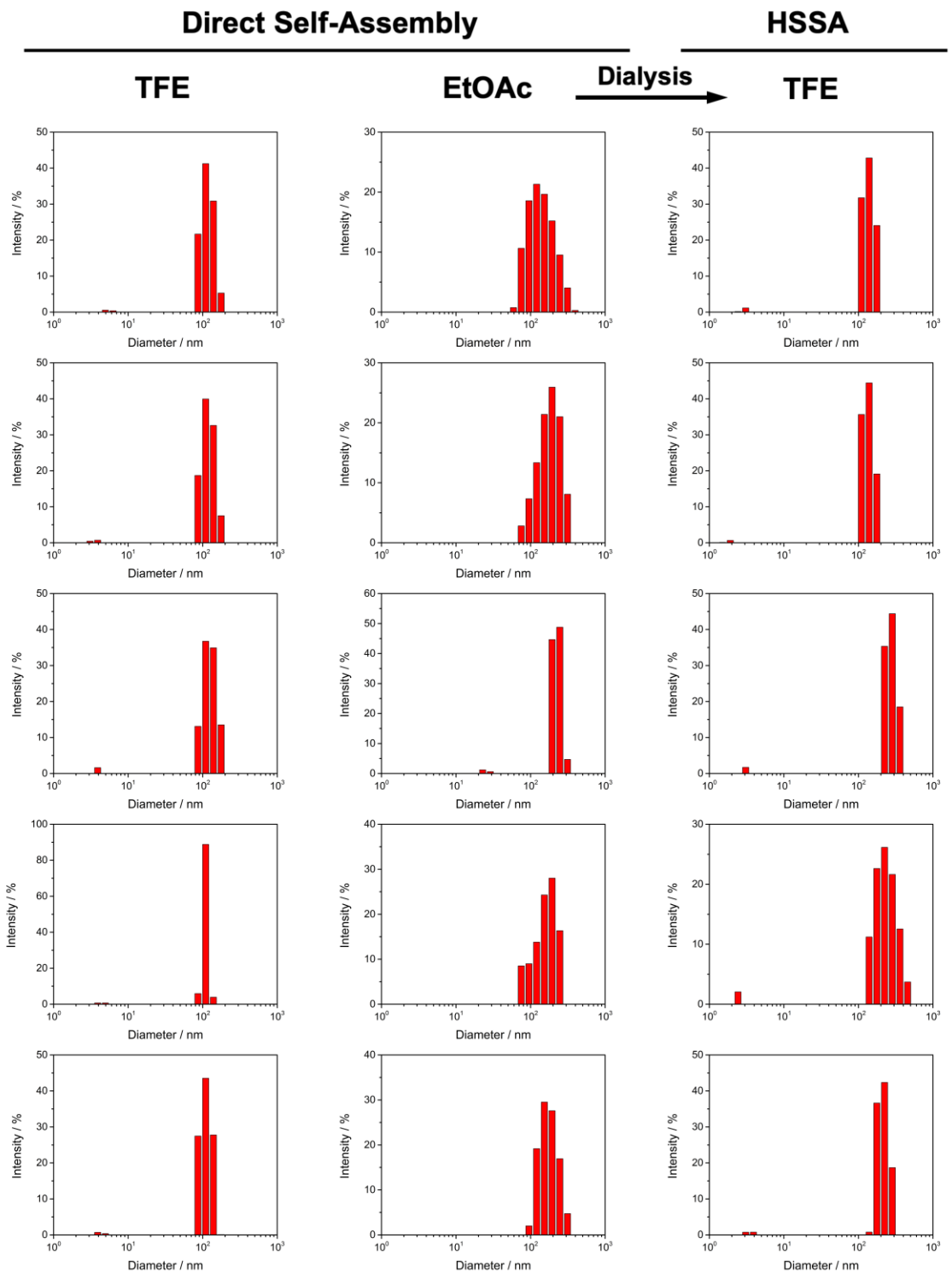

Figure S22. Intensity weighted particle size distribution by DLS using a quadratic cumulant fit of triblock BBCPs **1**–**5** (from top to bottom in order) after self-assembly.

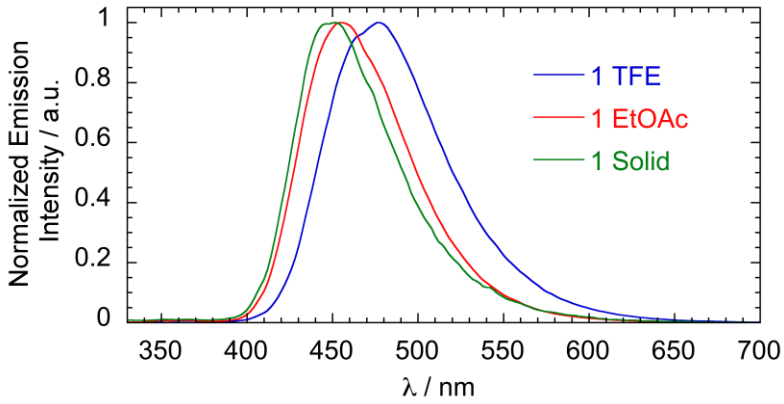

Figure S23. Photoluminescence spectra for micelles of BBCP **1** (as representative for other BBCPs) in TEF and EtOAc at 0.1 mg/mL and in solid state. λ_{ex} = 300 nm.

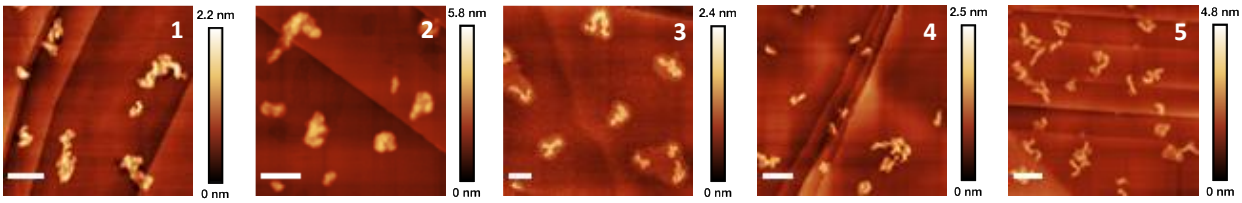

Figure S24. Zoomed AFM height images of BBCPs 1–5 on HOPG, spin-coated from 4:1 chloroform:chlorobenzene (scale bar = 100 nm).

Additional Tables

Table S1. Characterization details for **nBuA-MM**, **PS^{Br}-MM** and **(CzBA-*co*-PAPOMA)-MM**.

Macromonomer	M_n[a] (kDa)	M_n[b] (kDa)	DP[b]	$Đ$[a]
nBuA-MM	4.60	5.40	41	1.16
PS^{Br}-MM	12.3	1.34	70	1.06
(CzBA-*co*-PAPOMA)-MM	8.30	8.30	22 + 1.25[c]	1.16

[a] determined by SEC in THF; [b] determined using ^{1}H NMR. [c] CzBA + PAPOMA

Table S2. Solubility test for obtained macromolecules of **nBuA-MM**, **PS^{Br}-MM** and **(CzBA-*co*-PAPOMA)-MM**.

Solvent	nBuA-MM	PS^{Br}-MM	CzBA-*co*-PAPOMA-MM	Evaluation
H_2O	×	×	×	**0**
THF	√	√	√	**3**
DCM	√	√	√	**3**
$CHCl_3$	√	√	√	**3**
EtOAc	√	√	×	**2**
MeCN	√	×	×	**1**
DMF	**Partial**	√	√	**2.5**
DMSO	×	**Partial**	×	**0.5**
MeOH	×	×	×	**0**
EtOH	√	×	×	**1**
Et_2O	√	×	×	**1**
TFE (CF_3CH_2OH)	√	×	×	**1**
Acetone	**Partial**	√	×	**1.5**
Hexane	√	×	×	**1**
Cyclohexane	√	√	×	**2**
Toluene	√	√	√	**3**
Benzene	√	√	√	**3**
1,4-Dioxane	√	√	√	**3**
Anisole	**Partial**	√	√	**2.5**
1,2-Dichloroethane	**Partial**	√	√	**2.5**
Isopropanol	√	×	×	**1**

Note: Solubility was assessed by adding 2 mg of each macromonomer to a 4 mL vial with 1 mL solvent. The vials were sonicated for 120 seconds, then allowed to stand and examined with the naked eye. Soluble = (√) – 1, sparingly soluble = 0.5, insoluble = (×) – 0.

Table S3. DLS data for BBCPs **1**–**5**.

BBCPs	**1**		**2**		**3**		**4**		**5**	
M_n(NMR) [a]	1.00		1.31		2.22		1.00		1.34	
Solvent	TFE	EtOAc	TFE	EtOAc	TFE	EtOAc	TFE	EtOAc	TFE	EtOAc
CMC [b]	18.0	2.50	16.0	0.960	70.0	1.60	17.0	4.20	14.0	1.40
CMC [c]	17.9	2.49	12.2	0.730	31.4	0.719	16.9	4.18	10.5	1.05
d maximum [d]	113.6	147.8	112.0	174.8	136.6	267.6	107.6	167.4	115.8	175.0
d minimum [d]	101.4	124.0	97.6	149.8	108.4	194.2	100.4	146.4	95.2	154.8
d average [d]	108.2	135.6	106.0	160.4	120.1	214.5	103.8	149.2	105.9	164.3

[a] in MDa; [b] in μg/mL; [c] in nM (10^{-9} mol/mL); [d] hydrodynamic diameter in nm.