

## Supporting Information

### Synthesis and Self-assembly of Amphiphilic Semi-brush and Dual Brush Block Copolymers.

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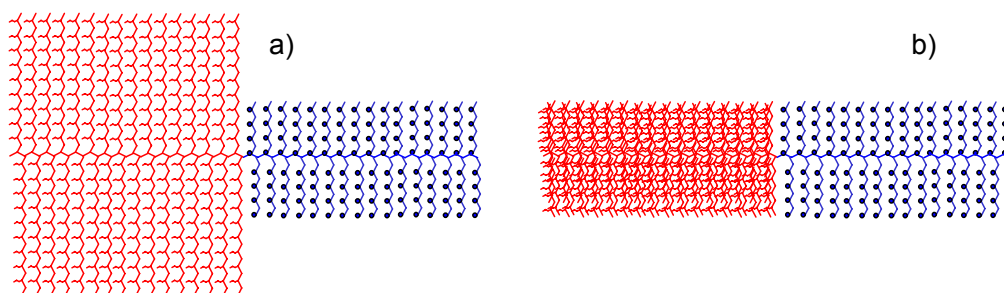
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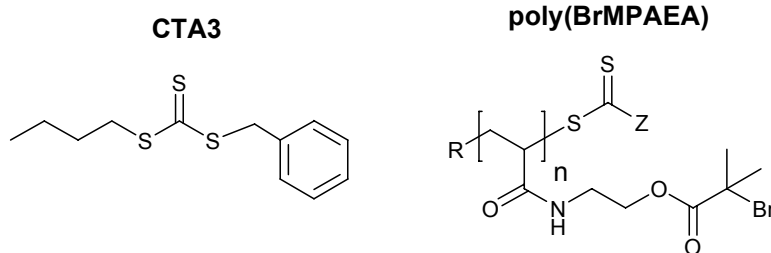
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**Scheme S1:** shape of an amphiphilic dual brush with unequal graft lengths (a) in a non-selective solvent, and (b) in a selective solvent for the shorter grafts.



**Table S1.** Monofunctional RAFT chain transfer agents (CTA) used, and reactive macroRAFTagents (brush precursors) prepared.



**Synthesis of BrMPAEA.** Acryloylchloride (4.75 mL, 58 mmol) in dry ethyl acetate (15 mL) was added dropwise to a stirred solution of ethanolamine (3.0 g, 49 mmol) and NaOH (2.32 g in 10 mL H<sub>2</sub>O) in ethylacetat (25 mL dry) at 0 °C, and subsequently stirred over night at ambient temperature. The organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate / methanol 10:1) to afford 2.42 g of the intermediate N-(2-hydroxyethyl)acrylamide. To this colorless oil, dry THF (40 mL) and triethylamine (4.4 mL, 31.5 mmol) were added. After stirring for 10 min at 0°C, as solution of 2-bromoisobutyryl bromide (3.1 mL, 25.2 mmol) in dry THF (15 mL) was added dropwise and the reaction was allowed to proceed over night. The mixture was successively extracted with acidic ice-water (0.5M HCl), aq NaHCO<sub>3</sub>, and ethyl acetate. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane / ethyl acetate 1:1, *R<sub>f</sub>* = 0.15) to afford the desired product as colorless oil. Yield: 1.67 g (13 % over two steps).

Elemental analysis (C<sub>9</sub>H<sub>14</sub>BrNO<sub>3</sub>, *M<sub>r</sub>* = 264.11 g/mol): Calc: C 40.93, H 5.34, N 5.30; Found: C 41.13, H 4.83, N 5.21.

EI-MS (positive ions): 265 (M+1)<sup>+</sup>.

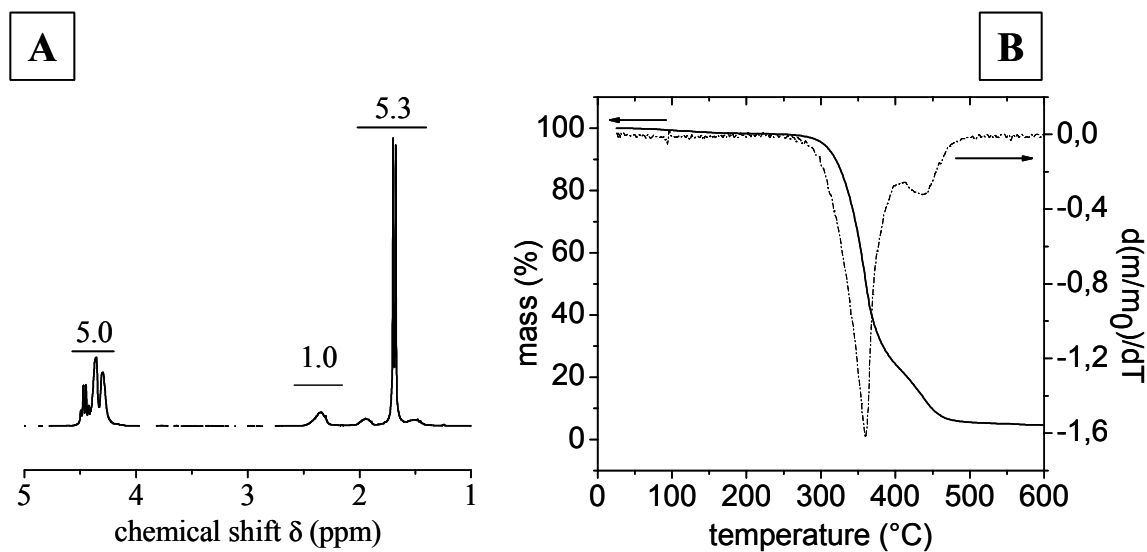
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 1.90 (s, 6 H, -CH<sub>3</sub>), 3.64 (q, *J* = 5.45 Hz, 2 H, -CON-CH<sub>2</sub>-), 4.29 (t, *J* = 5.45 Hz, 2 H, -CH<sub>2</sub>-OOC-), 5.65 (dd, *J* = 10.11, 1.54 Hz, 1 H, CH=C-CON- (E)), 6.1 (dd, *J* = 17.02, 10.11 Hz, 1 H, CH=C-CON- (Z)), 6.26 (dd, *J* = 17.02, 1.54 Hz, 1 H, =CH-CON-), 6.3 (s br, 1 H, NH).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 31.0 (-CH<sub>3</sub>), 38.9 (NH-CH<sub>2</sub>-), 64.8 (CH<sub>2</sub>-O), 127.4 (=CH), 130.9 (=CH<sub>2</sub>), 166.5 (CONH), 172.0 (-COO-). IR (KBr, selected bands, in cm<sup>-1</sup>): 3283, 2976, 1734, 1657, 1540, 1463, 1272, 1159, 1106, 1026, 983, 958.

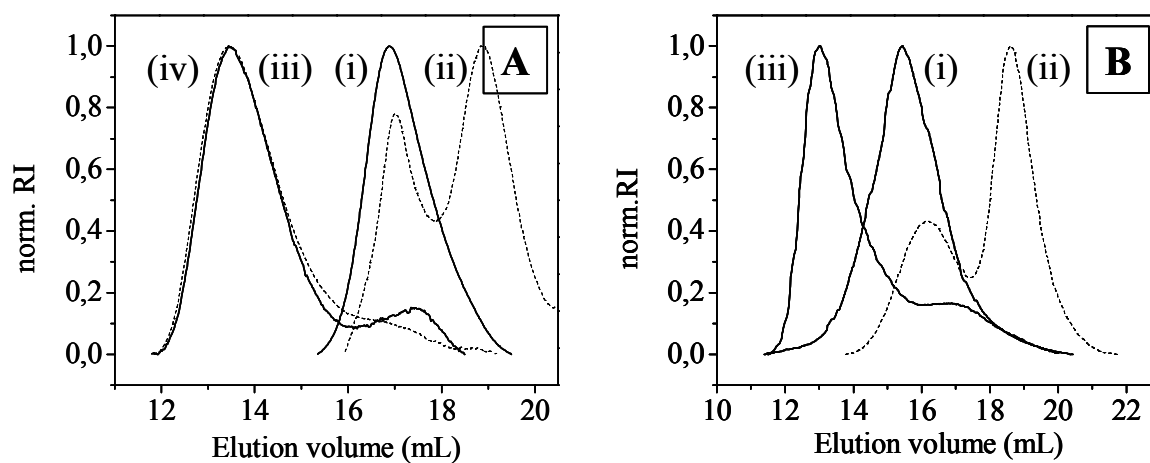
**Table S2:** Synthesis and characterization of RAFT-polymerized inimer (conditions: 65°C, initiated by AIBN).

polymer <sup>a)</sup>	RAFT agent	conv. [%]/[h] <sup>b)</sup>	theory <sup>c)</sup>		SEC		spectroscopic analysis	
			<i>M<sub>n</sub></i> × 10 <sup>-3</sup> [g mol <sup>-1</sup> ]	<i>M<sub>n</sub></i> × 10 <sup>-3</sup> [g mol <sup>-1</sup> ]	PDI	<i>M<sub>n</sub></i> × 10 <sup>3</sup> [g mol <sup>-1</sup> ]	Z/R <sup>h)</sup>	
<b>1</b> (BrMPAEA) <sub>62</sub>	CTA3	31/14.5	17	3.9 <sup>d)</sup>	2.18	67 <sup>e)</sup>	-	

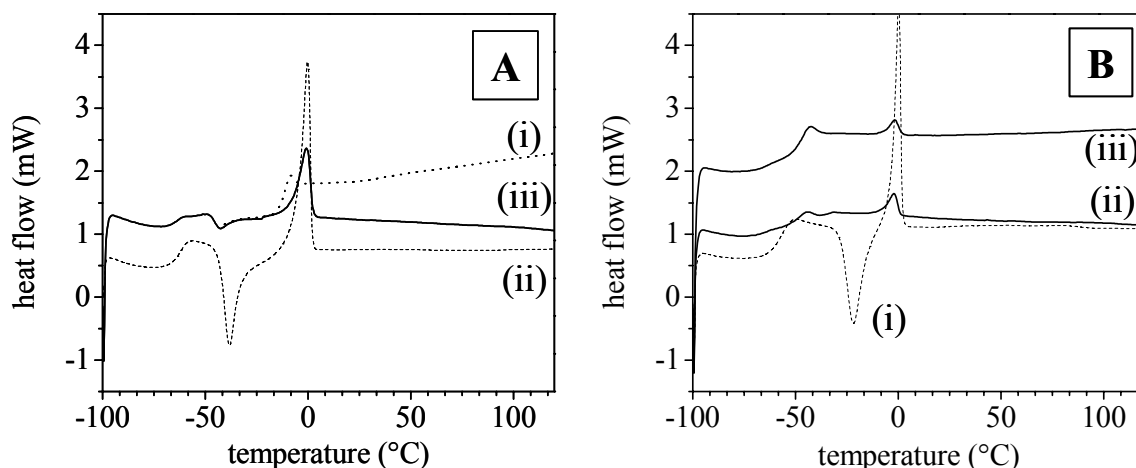
a) Conditions for poly(BrMPAEA): [Monomer]/[CTA]/[Initiator] = 200/1/0.1 in THF;  
b) Determined by <sup>1</sup>H-NMR analysis of the crude product.  
c) Calculated according to equation: *M<sub>n,theor.</sub>* = (conversion × *M<sub>r,monomer</sub>* × [M] / [CTA]) + *M<sub>r,CTA</sub>*.  
d) Eluent NMP, RI detection, calibrated by polystyrene standards.  
e) Calculated by end group analysis via UV band (λ = 309 nm, ε<sub>CTA3</sub> = 14,700 L·mol<sup>-1</sup>·cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).



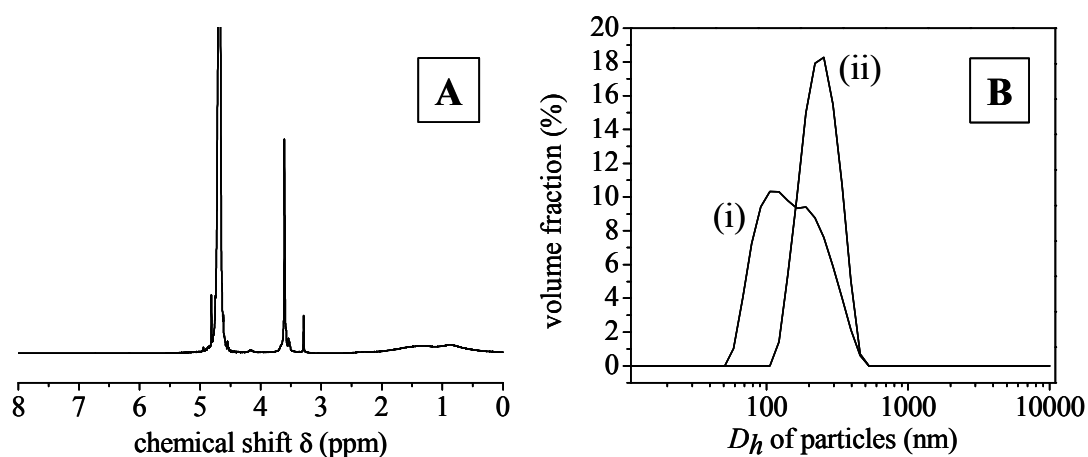
**Fig. S1.** A)  $^1\text{H}$  NMR spectra of **poly(CIPEA)** in  $\text{CDCl}_3$ .  
 B) TGA plot (continuous line) of **poly(CIPEA)**, and derivative DTG plot (dashed line) of **poly(CIPEA)**.



**Fig. S2.** A) SEC traces of: (i, continuous line) **(PEGA)<sub>858</sub>**,  
 (ii, dashed line) **(PEGA)<sub>429</sub>-b-(CIPEA)<sub>470</sub>-b-(PEGA)<sub>429</sub>**,  
 (iii, continuous line) **TriB-2**,  
 and (iv, dashed line) **TriB-3**.  
 B) SEC traces of (i, continuous line) **(CIPEA)<sub>680</sub>**,  
 (ii, dashed line) **(PEGA)<sub>375</sub>-b-(CIPEA)<sub>680</sub>-b-(PEGA)<sub>375</sub>**,  
 and (iii, continuous line) **TriB-4** in THF as eluent.



**Fig. S3.** DSC traces of studied polymers:  
 A) (i) (CIPEA), (ii) (PEGA)<sub>192</sub>-b-(CIPEA)<sub>72</sub>-b-(PEGA)<sub>192</sub>, (iii) TriB-1;  
 B) (i) (PEGA)<sub>450</sub>-b-(CIPEA)<sub>450</sub>-b-(PEGA)<sub>450</sub> (ii) TriB-2 (iii) TriB-3.



**Fig. S4.** A) <sup>1</sup>H NMR spectra of TriB-1 in D<sub>2</sub>O.  
 B) Dynamic light scattering analysis of 0.1 wt% aqueous dispersions at 25 °C of  
 (i) (PEGA)<sub>192</sub>-b-(CIPEA)<sub>72</sub>-b-(PEGA)<sub>192</sub>;  
 (ii) TriB-1, prepared by protocol A: Volume fraction distribution of aggregates' hydrodynamic diameter.

### SANS Data Analysis

In a first approach the data were analyzed in a model-independent way. Here we applied the Guinier approximation (eq. S1) from which we can derive the radius of gyration,  $R_g$ , and the scattering intensity extrapolated to zero scattering angle,  $I(0)$ .

$$I(q) = I(0) \cdot \exp\left(-q^2 \cdot R_g^2 / 3\right) \quad (\text{equation S1})$$

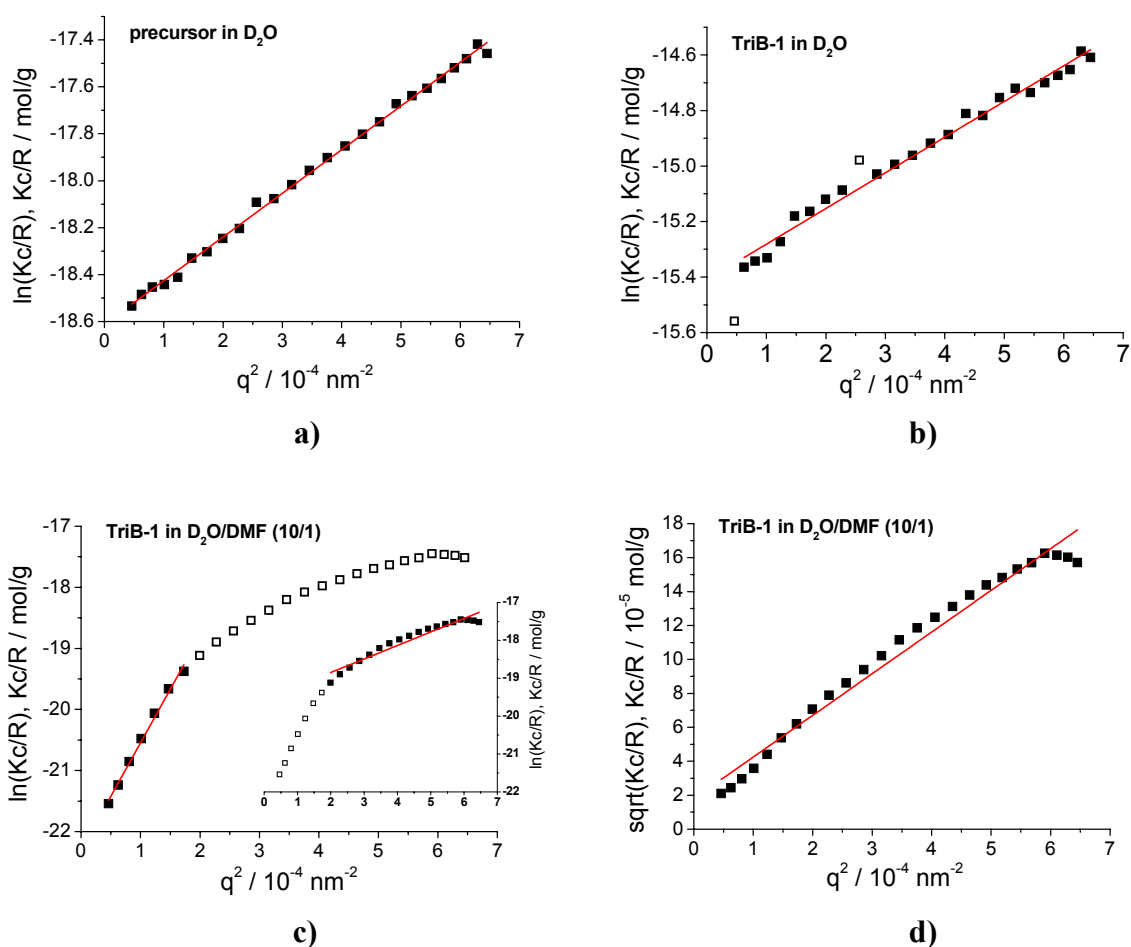
where  $I(0)$  is directly related to the molecular weight  $M_w$  of the aggregates by:

$$I(0) = \Phi \cdot (\text{SLD}_p - \text{SLD}_0)^2 \cdot \frac{M_w}{\rho_p \cdot N_{\text{Av}}} \quad (\text{equation S2})$$

Here  $\Phi$  is the volume fraction of the dispersed particles,  $\text{SLD}_p$  and  $\text{SLD}_0$  the scattering length densities of particle and solvent,  $\rho_p$  the particle density, and  $N_{\text{Av}}$  the Avogadro's number.

From the molecular weight one can then directly calculate the radius of a compact aggregate (neglecting any solvation) by taking into account the polymer density assumed to be 1.13 and 1.05 g/ml for the semi-brush and the dual brush copolymer, respectively.

## SLS Data Analysis

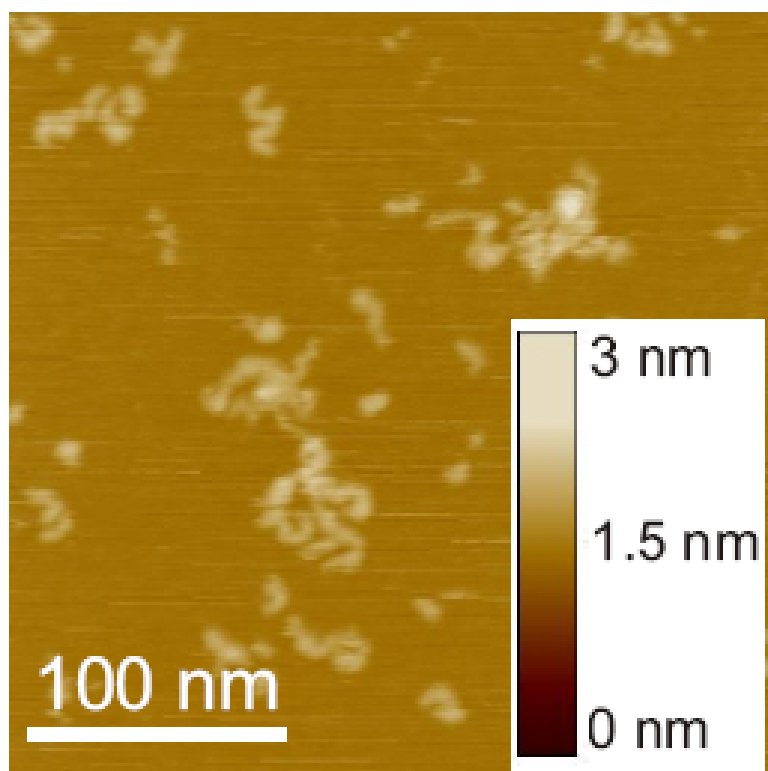


**Fig. S5.** Guinier- a), b), c) and Berry-Plot d) of SLS-data for a) precursor **(PEGA)<sub>192</sub>-b-(CIPEA)<sub>72</sub>-b-(PEGA)<sub>192</sub>** in D<sub>2</sub>O and the derived dual brush **TriB-1** b) in D<sub>2</sub>O and c), d) in D<sub>2</sub>O/DMF (10/1) at 25 °C; used ! and neglected ∇ data-points for the fit

Static light scattering data were analysed by means of the Guinier approximation according to eq. S1. Concerning the validity of Guinier approximation fit of TriB-1 in D<sub>2</sub>O/DMF (10/1) was done only for low scattering angles due to its non-linear curve behavior. Repeating measurements of this sample appeared always in the same manner.

**Table S3:** Molecular weight  $M_w$  and radius of gyration  $R_g$  obtained via SLS-analyses of precursor  $(\text{PEGA})_{192}\text{-b-(CIPEA)}_{72}\text{-b-(PEGA)}_{192}$  and the derived dual brush TriB-1

Plot	polymer	$M_w(q^2) / \text{g/mol}$	$R_g / \text{nm}$
Guinier	$(\text{PEGA})_{192}\text{-b-(CIPEA)}_{72}\text{-b-(PEGA)}_{192}$	3.40E+06	76.1
Guinier	TriB-1 in $\text{D}_2\text{O}$	2.45E+07	60.9
Guinier	TriB-1 in $\text{D}_2\text{O/DMF}$ (10/1)	4.84E+09	226.3
Guinier (larger q-range)	TriB-1 in $\text{D}_2\text{O/DMF}$ (10/1)	3.13E+08	102.1
Berry	TriB-1 in $\text{D}_2\text{O/DMF}$ (10/1)	3.10E+09	265.2



**Fig. S6.** SFM height image of the semi-brush block copolymer precursor  $(\text{PEGA})_{375}\text{-b-(CIPEA)}_{680}\text{-b-(PEGA)}_{375}$ .