Supporting Information

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

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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.

CTA3

poly(BrMPAEA)
**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 H₂O) in ethyl acetate (25 mL dry) at 0 °C, and subsequently stirred overnight at ambient temperature. The organic phase was separated, dried over Na₂SO₄, 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 overnight. The mixture was successively extracted with acidic ice-water (0.5M HCl), aq NaHCO₃, and ethyl acetate. The combined organic phases were dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane / ethyl acetate 1:1, \( R_f = 0.15 \)) to afford the desired product as colorless oil. Yield: 1.67 g (13 % over two steps).

Elemental analysis (C₉H₁₄BrNO₃, \( M_r = 264.11 \text{ g/mol} \)): 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⁺+) .

\(^1\)H NMR (300 MHz, CDCl₃): \( \delta \) (ppm): 1.90 (s, 6 H, -CH₃), 3.64 (q, \( J = 5.45 \text{ Hz} \), 2 H, -CON-CH₂-), 4.29 (t, \( J = 5.45 \text{ Hz} \), 2 H, -CH₂-OOC-), 5.65 (dd, \( J = 10.11, 1.54 \text{ Hz} \), 1 H, CH=CON- (E)), 6.1 (dd, \( J = 17.02, 10.11 \text{ Hz} \), 1 H, CH=C-CON- (Z)), 6.26 (dd, \( J = 17.02, 1.54 \text{ Hz} \), 1 H, =CH-CON-), 6.3 (s br, 1 H, NH).

\(^1\)C-NMR (75 MHz, CDCl₃) \( \delta \) (ppm): 31.0 (-CH₃), 38.9 (NH-CH₂-), 64.8 (CH₂-O), 127.4 (=CH), 130.9 (=CH₂), 166.5 (CONH), 172.0 (-COO-). IR (KBr, selected bands, in cm⁻¹): 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).

<table>
<thead>
<tr>
<th>polymer (^a)</th>
<th>RAFT agent</th>
<th>conv. ([%]/[\text{h}] ) (^b)</th>
<th>theory (^c)</th>
<th>SEC analysis</th>
<th>spectroscopic analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (BrMPAEA) (_\text{62})</td>
<td>CTA3</td>
<td>31/14.5</td>
<td>17</td>
<td>( M_n \times 10^3 ) ([\text{g mol}^{-1}])</td>
<td>( M_n \times 10^3 ) ([\text{g mol}^{-1}])</td>
</tr>
</tbody>
</table>

\(^a\) Conditions for poly(BrMPAEA): \([\text{Monomer}]/[\text{CTA}]/[\text{Initiator}] = 200/1/0.1 \text{ in THF}; \)

\(^b\) Determined by \(^1\)H-NMR analysis of the crude product.

\(^c\) Calculated according to equation: \( M_{n,\text{theor.}} = (\text{conversion} \times M_{n,\text{monomer}} \times [\text{M}] / [\text{CTA}] ) + M_{n,\text{CTA}} \).

\(^d\) Eluent NMP, RI detection, calibrated by polystyrene standards.

\(^e\) Calculated by end group analysis via UV band (\( \lambda = 309 \text{ nm} \), \( \varepsilon_{\text{CTA3}} = 14,700 \text{ L·mol}^{-1·cm}^{-1} \text{ in CH}_2\text{Cl}_2 \)).
**Fig. S1.**  
A) $^1$H NMR spectra of poly(ClPEA) in CDCl$_3$.  
B) TGA plot (continuous line) of poly(ClPEA), and derivative DTG plot (dashed line) of poly(ClPEA).

**Fig. S2.**  
A) SEC traces of: (i, continuous line) (PEG)$_{858}$, (ii, dashed line) (PEG)$_{429}$-b-(ClPEA)$_{470}$-b-(PEG)$_{429}$, (iii, continuous line) TriB-2, and (iv, dashed line) TriB-3.  
B) SEC traces of (i, continuous line) (ClPEA)$_{680}$, (ii, dashed line) (PEG)$_{375}$-b-(ClPEA)$_{680}$-b-(PEG)$_{375}$, and (iii, continuous line) TriB-4 in THF as eluent.
Fig. S3. DSC traces of studied polymers:
A) (i) (ClPEA), (ii) (PEGA)$_{192}$-b-(ClPEA)$_{72}$-b-(PEGA)$_{192}$, (iii) TriB-1;
B) (i) (PEGA)$_{450}$-b-(ClPEA)$_{450}$-b-(PEGA)$_{450}$ (ii) TriB-2 (iii) TriB-3.

Fig. S4. A) $^1$H NMR spectra of TriB-1 in D$_2$O.
B) Dynamic light scattering analysis of 0.1 wt% aqueous dispersions at 25 °C of
(i) (PEGA)$_{192}$-b-(ClPEA)$_{72}$-b-(PEGA)$_{192}$;
(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 (equation S1)
where $I(0)$ is directly related to the molecular weight $M_w$ of the aggregates by:

$$I(0) = \Phi \cdot (SLD_p - SLD_0)^2 \cdot \frac{M_w}{\rho_p \cdot N_{Av}} \quad \text{(equation S2)}$$

Here $\Phi$ is the volume fraction of the dispersed particles, $SLD_p$ and $SLD_0$ the scattering length densities of particle and solvent, $\rho_p$ the particle density, and $N_{Av}$ 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)$_{192}$-b-(CIPEA)$_{72}$-b-(PEGA)$_{192}$ in D$_2$O and the derived dual brush TriB-1 b) in D$_2$O and c), d) in D$_2$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$_2$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 Mw and radius of gyration Rg obtained via SLS-analyses of precursor \((\text{PEGA})_{192}\text{-b-(ClPEA)}_{72}\text{-b-(PEGA)}_{192}\) and the derived dual brush TriB-1

<table>
<thead>
<tr>
<th>Plot</th>
<th>polymer</th>
<th>Mw((q^2) / \text{ g/mol})</th>
<th>Rg / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guinier</td>
<td>((\text{PEGA})<em>{192}\text{-b-(ClPEA)}</em>{72}\text{-b-(PEGA)}_{192})</td>
<td>3.40E+06</td>
<td>76.1</td>
</tr>
<tr>
<td>Guinier</td>
<td>TriB-1 in D(_2)O</td>
<td>2.45E+07</td>
<td>60.9</td>
</tr>
<tr>
<td>Guinier</td>
<td>TriB-1 in D(_2)O/DMF (10/1)</td>
<td>4.84E+09</td>
<td>226.3</td>
</tr>
<tr>
<td>Guinier (larger q-range)</td>
<td>TriB-1 in D(_2)O/DMF (10/1)</td>
<td>3.13E+08</td>
<td>102.1</td>
</tr>
<tr>
<td>Berry</td>
<td>TriB-1 in D(_2)O/DMF (10/1)</td>
<td>3.10E+09</td>
<td>265.2</td>
</tr>
</tbody>
</table>

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