Supplementary Information for

Anion-dipole interactions regulating the self-assembled nanostructures of polymers

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1. \(^1\text{H}-\text{NMR Measurements.}\)

Stock solutions of PMEO\textsubscript{3}MA (2-(2-(2-methoxyethoxy)ethoxy)ethyl methacrylate, 10.0 mg/mL) and aqueous sodium salt solutions (2.0 M) were prepared using D\textsubscript{2}O as solvent, respectively. All the testing samples have PMEO\textsubscript{3}MA of 3.0 mg/mL, and sodium salt concentrations of 0.01 M to 1.0 M. \(^1\text{H}-\text{NMR spectra for PMEO}_3\text{MA under different sodium salts concentration were obtained on a Bruck AV 400 (400 MHz) spectrometer equipped with Bruck BCU-05 temperature control unit.} \(^1\text{H}-\text{NMR spectra were recorded with NMR tubes adapted with coaxial inserts. CDCl}_3 containing 0.03\% TMS was in the inner of the concentric capillary tube, while the mixed solution of PMEO\textsubscript{3}MA and sodium salt was in the outer capillary tube. As such, the TMS control was never exposed to PMEO\textsubscript{3}MA or varying salt concentrations.}

![Fig. S1 The illustration depicting \(^1\text{H}-\text{NMR measurement: the mixed solution of PMEO}_3\text{MA and sodium salt was in the NMR tube, and CDCl}_3 containing 0.03\% TMS was in the inner of the concentric capillary tube.}](attachment:image.png)
**Fig. S2** The $^1$H-NMR spectrum of MEO$_3$MA in CDCl$_3$.

**Fig. S3** GPC curve of the PMEO$_3$MA prepared via AIBN initiated traditional free radical polymerization.

$M_n = 21.5$ kg/mol
PDI = 2.95
Fig. S4 GPC curves of the homopolymer of PMEO$_3$MAs with different molecular weights prepared from RAFT polymerization.

Fig. S5 Synthesis of PEG-based copolymer P(MEO$_2$MA-co-OEGMA) via RAFT polymerization.

Fig. S6 GPC curve of the copolymer P(MEO$_2$MA-co-OEGMA) prepared from RAFT polymerization.
Fig. S7 TEM images for the self-assembled nanostructures from copolymer P(MEO$_2$MA-co-OEGMA) in NaSCN solution with different concentrations.

2. Calculation of $K_A$

Apparent equilibrium association constants ($K_A$) of CHn unit with SCN$^-$ were abstracted from isotherm fitting of the $^1$H-NMR data of P(MEO$_3$MA) in the presence of NaSCN at 300 K and 323 K. To calculate association constants at other temperatures, Arrhenius equation was used: ln($k_2/k_1$) = -$E_a$(1/$T_2$-1/$T_1$)/R. First, the apparent activation energy ($E_a$) for each binding site was obtained from Arrhenius equation using the known $K_A$ at 300 K and 323 K, then association constants at other temperatures were obtained from Arrhenius equation using the $E_a$.

3. Calculation of amount of CH$_n$ units bound with SCN$^-$ based on the following equation.

$$\text{CH}_n + \text{SCN}^- \xrightarrow{K_A} \text{CH}_n^-\text{SCN}^-$$

$$K_A(\text{average}) = \frac{[\text{CH}_n^-\text{SCN}^-]}{[\text{CH}_n] \times [\text{SCN}^-]}$$

$$= \frac{([\text{CH}_n^-\text{SCN}^-])}{([\text{CH}_n]_0 - [\text{CH}_n^-\text{SCN}^-]) \times ([\text{SCN}^-]_0 - [\text{CH}_n^-\text{SCN}^-])}$$

$^1$H-NMR spectra of P(MEO$_3$MA) with different NaSCN concentration were carried out in D$_2$O. The CDCl$_3$ containing 0.03% TMS was in the inner of the concentric capillary tube, and the spectra were externally referenced to TMS.
**Table S1.** The $K_A$ values for various CH$_n$ units in PMEO$_3$MA at different temperatures.

<table>
<thead>
<tr>
<th>CH$_n$ position</th>
<th>300 K</th>
<th>323 K</th>
<th>328 K</th>
<th>330 K</th>
<th>333 K</th>
<th>340 K</th>
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<tr>
<td>1</td>
<td>15.3</td>
<td>8.93</td>
<td>8.02</td>
<td>7.69</td>
<td>7.23</td>
<td>6.29</td>
</tr>
<tr>
<td>2</td>
<td>8.1</td>
<td>4.55</td>
<td>4.05</td>
<td>3.87</td>
<td>3.62</td>
<td>3.12</td>
</tr>
<tr>
<td>3</td>
<td>11.2</td>
<td>5.99</td>
<td>5.29</td>
<td>5.04</td>
<td>4.69</td>
<td>3.98</td>
</tr>
<tr>
<td>4</td>
<td>10.5</td>
<td>4.97</td>
<td>4.28</td>
<td>4.04</td>
<td>3.71</td>
<td>3.05</td>
</tr>
<tr>
<td>5</td>
<td>17.3</td>
<td>9.43</td>
<td>8.36</td>
<td>7.97</td>
<td>7.44</td>
<td>6.35</td>
</tr>
<tr>
<td>average$^a$</td>
<td>12.1</td>
<td>6.55</td>
<td>5.80</td>
<td>5.53</td>
<td>5.15</td>
<td>4.39</td>
</tr>
</tbody>
</table>

The average association constant $K_A$(average)=$(K_{A1}+K_{A2}+3*K_{A3}+K_{A4}+K_{A5})/7$.

4. **Morphology control of the self-assembled nanostructures by using SCN$^{-}$ ion.**

For regulating the morphology of the self-assembled nanostructures, different amount of NaSCN were added into PMEO$_3$MA solutions (PMEO$_3$MA concentration is 3.0 mg/mL), and these solutions were heated to the temperature above their LCSTs.

![Transmittance Change](image)

**Fig. S8** Transmittance change of the PMEO$_3$MA (3.0 mg/mL) in water at different concentration of NaSCN with temperature. The PMEO$_3$MA was prepared via AIBN initiated traditional free radical polymerization.
Fig. S9 ITC titration curves showing that there is no interaction of the prepared PMEO₃MA with Na₂SO₄. The PMEO₃MA was prepared via AIBN initiated traditional free radical polymerization.

![Fig. S9 ITC titration curves](image)

Fig. S10 TEM images for the self-assembled nanostructures from the prepared PMEO₃MA in Na₂SO₄ aqueous solution with various concentrations. The PMEO₃MA was prepared via AIBN initiated traditional free radical polymerization.

![Fig. S10 TEM images](image)
Fig. S11 TEM images for the self-assembled nanostructures from the prepared neutral polar PMEO$_3$MA in NH$_4$SCN solution with different concentrations. The PMEO$_3$MA was prepared via AIBN initiated traditional free radical polymerization.

Fig. S12 The effect of molecular weight of homopolymer on the self-assembly in NaSCN solution. a) Homopolymer PMEO$_3$MA with different molecular weight prepared via RAFT polymerization. b) TEM images for the self-assembled nanostructures from the prepared homopolymer of PMEO$_3$MA with molecular weight of 8.9 kg/mol and 37.1 kg/mol in NaSCN solution.

References: