

Supplementary Information for

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

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1. $^1\text{H-NMR}$ Measurements.¹

Stock solutions of PMEO_3MA (2-(2-(2-methoxyethoxy)ethoxy)ethyl methacrylate, 10.0 mg/mL) and aqueous sodium salt solutions (2.0 M) were prepared using D_2O as solvent, respectively. All the testing samples have PMEO_3MA of 3.0 mg/mL, and sodium salt concentrations of 0.01 M to 1.0 M. $^1\text{H-NMR}$ spectra for PMEO_3MA under different sodium salts concentration were obtained on a Bruker AV 400 (400 MHz) spectrometer equipped with Bruker BCU-05 temperature control unit. $^1\text{H-NMR}$ 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_3MA and sodium salt was in the outer capillary tube. As such, the TMS control was never exposed to PMEO_3MA or varying salt concentrations.

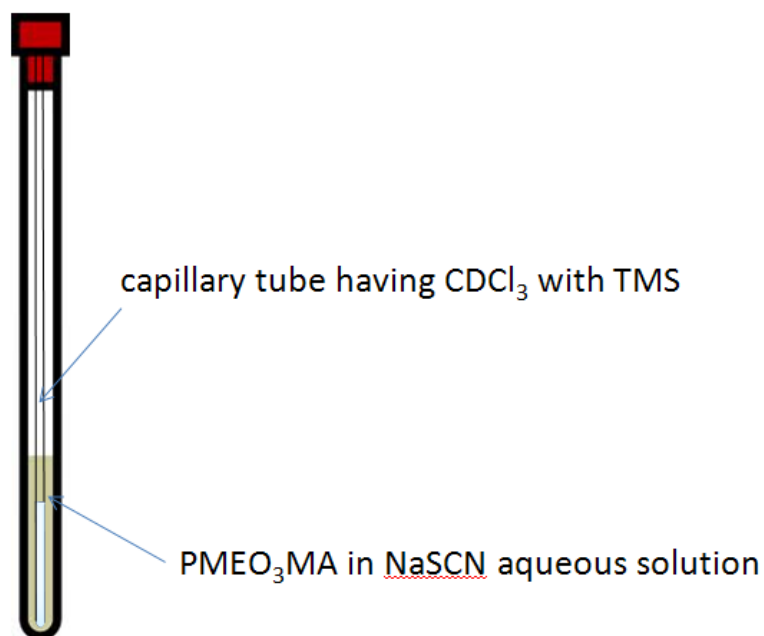


Fig. S1 The illustration depicting $^1\text{H-NMR}$ measurement: the mixed solution of PMEO_3MA and sodium salt was in the NMR tube, and CDCl_3 containing 0.03% TMS was in the inner of the concentric capillary tube.

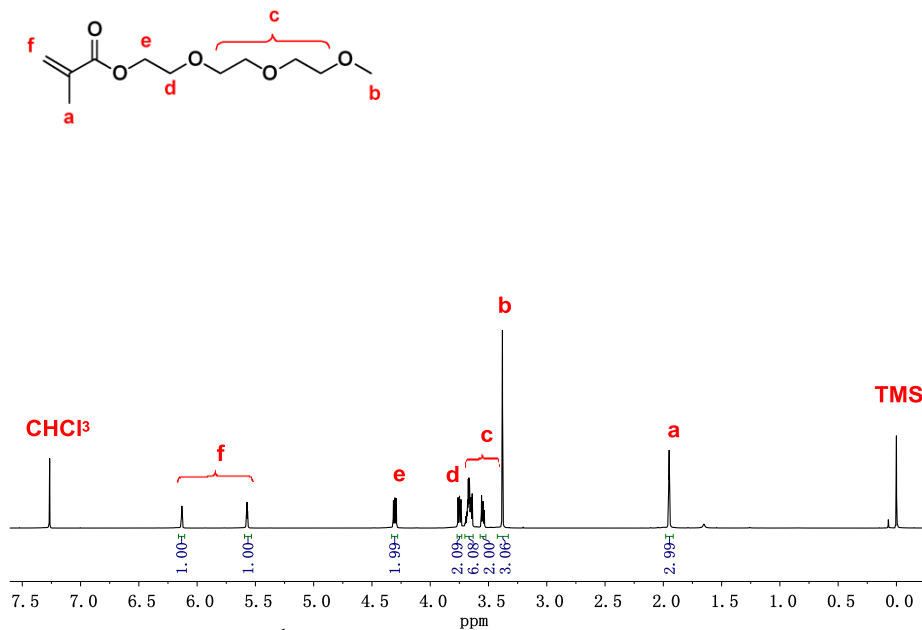


Fig. S2 The ¹H-NMR spectrum of MEO₃MA in CDCl₃.

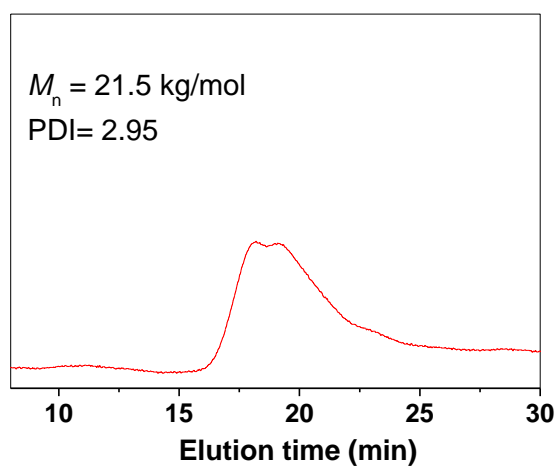


Fig. S3 GPC curve of the PME₀₃MA prepared via AIBN initiated traditional free radical polymerization.

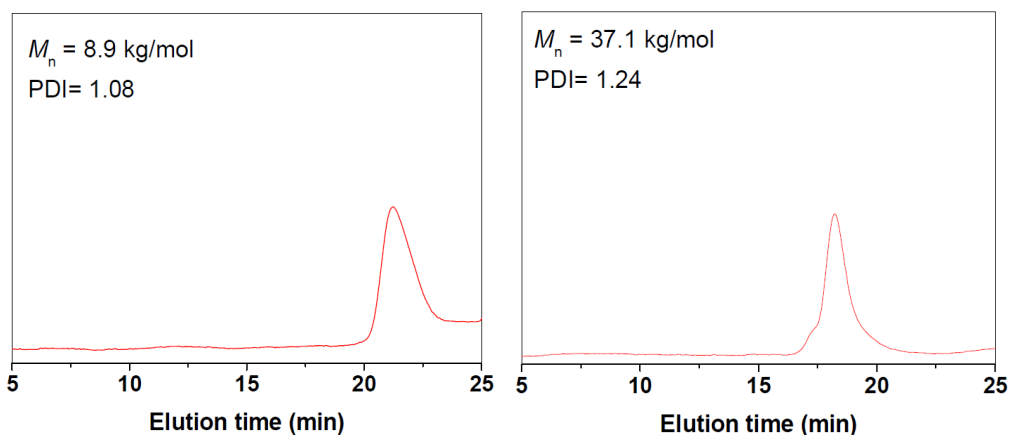


Fig. S4 GPC curves of the homopolymer of PMEO₃MAs with different molecular weights prepared from RAFT polymerization.

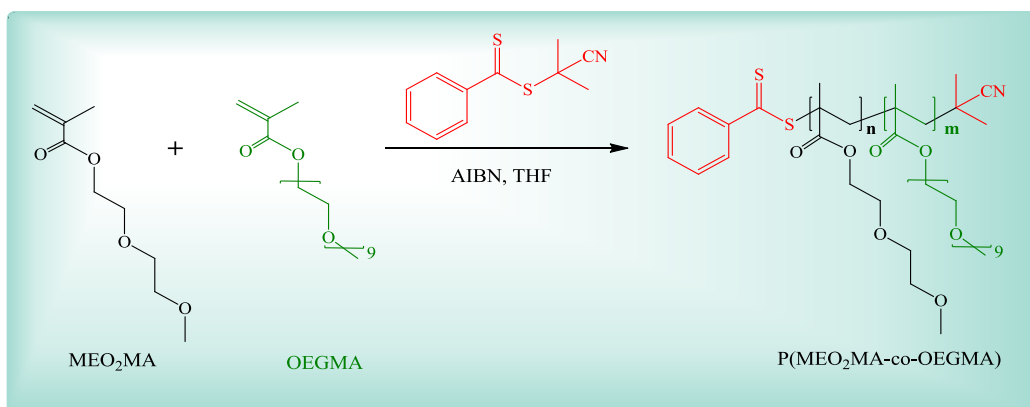


Fig. S5 Synthesis of PEG-based copolymer P(MEO₂MA-*co*-OEGMA) via RAFT polymerization.

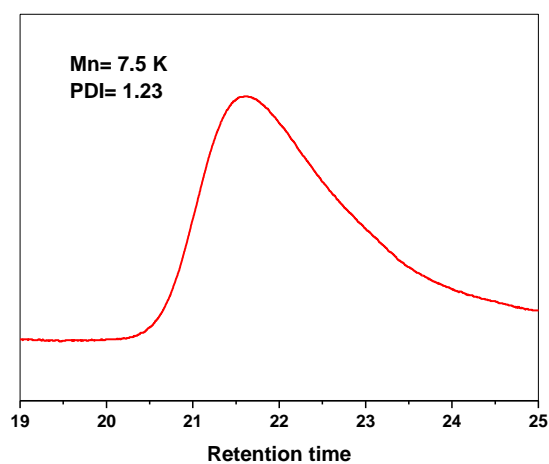


Fig. S6 GPC curve of the copolymer P(MEO₂MA-*co*-OEGMA) prepared from RAFT polymerization.

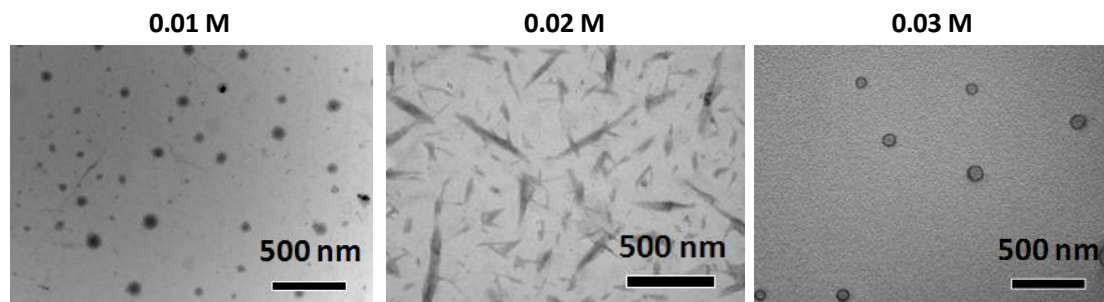


Fig. S7 TEM images for the self-assembled nanostructures from copolymer P(MEO₂MA-co-OEGMA) in NaSCN solution with different concentrations.

2. Calculation of K_A

Apparent equilibrium association constants (K_A) of CH_n unit with SCN⁻ were abstracted from isotherm fitting of the ¹H-NMR data of PMEO₃MA 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.

$$\begin{aligned}
 \text{CH}_n + \text{SCN}^- &\xrightleftharpoons{K_A} \text{CH}_n \cdots \text{SCN}^- \\
 K_A(\text{average}) &= \frac{[\text{CH}_n \cdots \text{SCN}^-]}{[\text{CH}_n] \times [\text{SCN}^-]} \\
 &= \frac{[\text{CH}_n \cdots \text{SCN}^-]}{([\text{CH}_n]_0 - [\text{CH}_n \cdots \text{SCN}^-]) \times ([\text{SCN}^-]_0 - [\text{CH}_n \cdots \text{SCN}^-])}
 \end{aligned}$$

¹H-NMR spectra of PMEO₃MA with different NaSCN concentration were carried out in D₂O. The CDCl₃ 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 $PMEO_3MA$ at different temperatures.

	300 K	323 K	328 K	330 K	333 K	340 K
CH_n position	$K_A(M^{-1})$	$K_A(M^{-1})$	$K_A(M^{-1})$	$K_A(M^{-1})$	$K_A(M^{-1})$	$K_A(M^{-1})$
1	15.3	8.93	8.02	7.69	7.23	6.29
2	8.1	4.55	4.05	3.87	3.62	3.12
3	11.2	5.99	5.29	5.04	4.69	3.98
4	10.5	4.97	4.28	4.04	3.71	3.05
5	17.3	9.43	8.36	7.97	7.44	6.35
average ^a	12.1	6.55	5.80	5.53	5.15	4.39

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

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 $PMEO_3MA$ solutions ($PMEO_3MA$ concentration is 3.0 mg/mL), and these solutions were heated to the temperature above their LCSTs.

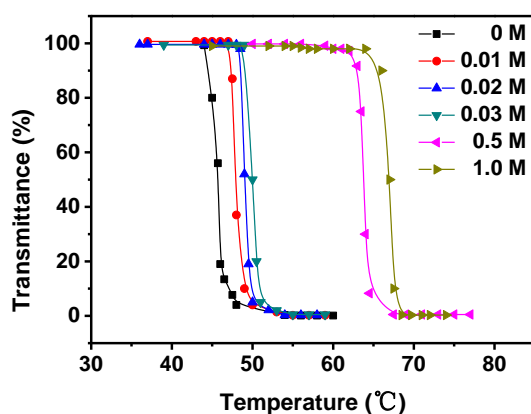


Fig. S8 Transmittance change of the $PMEO_3MA$ (3.0 mg/mL) in water at different concentration of $NaSCN$ with temperature. The $PMEO_3MA$ was prepared via AIBN initiated traditional free radical polymerization.

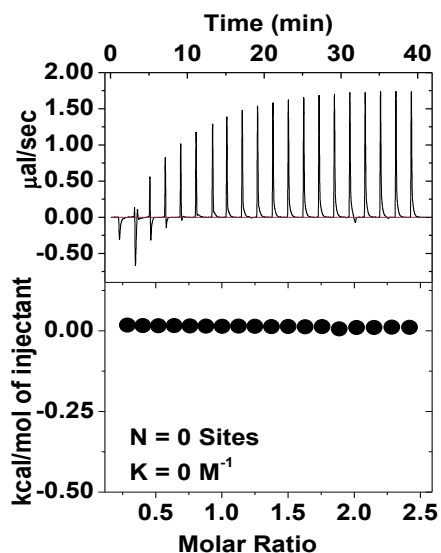


Fig. S9 ITC titration curves showing that there is no interaction of the prepared PME₃MA with Na₂SO₄. The PME₃MA was prepared via AIBN initiated traditional free radical polymerization.

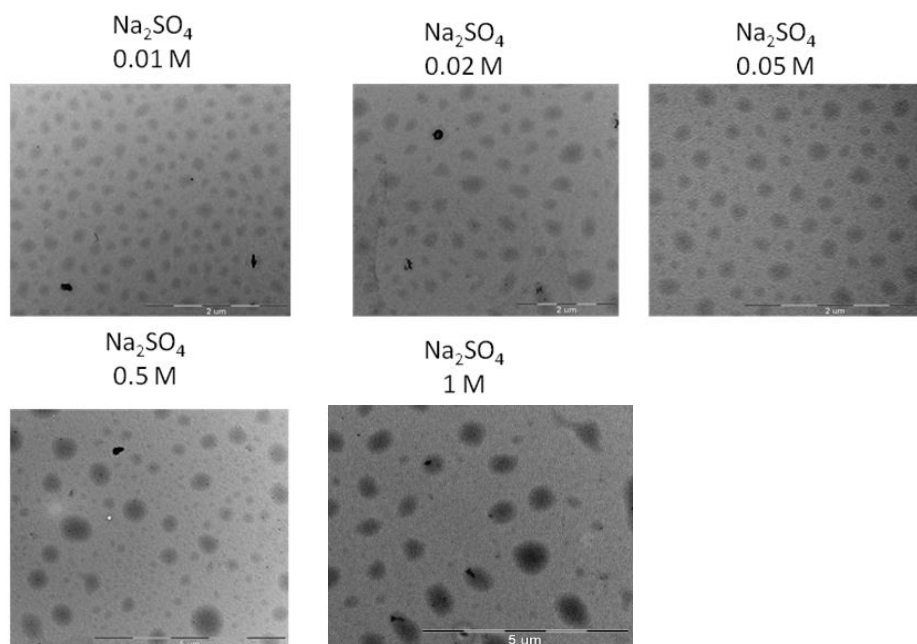


Fig. S10 TEM images for the self-assembled nanostructures from the prepared PME₃MA in Na₂SO₄ aqueous solution with various concentrations. The PME₃MA was prepared via AIBN initiated traditional free radical polymerization.

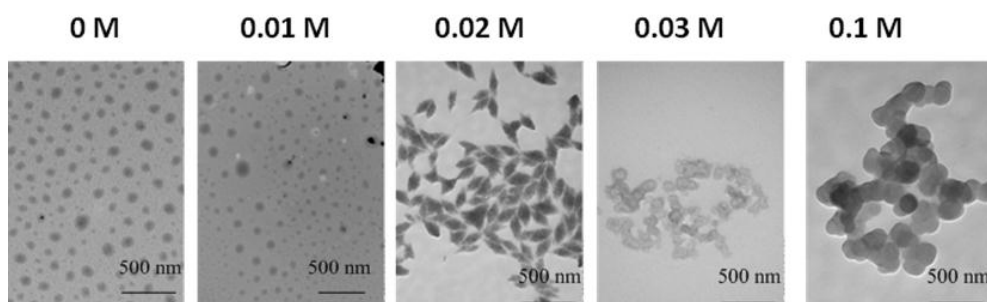


Fig. S11 TEM images for the self-assembled nanostructures from the prepared neutral polar PME₃MA in NH₄SCN solution with different concentrations. The PME₃MA was prepared via AIBN initiated traditional free radical polymerization.

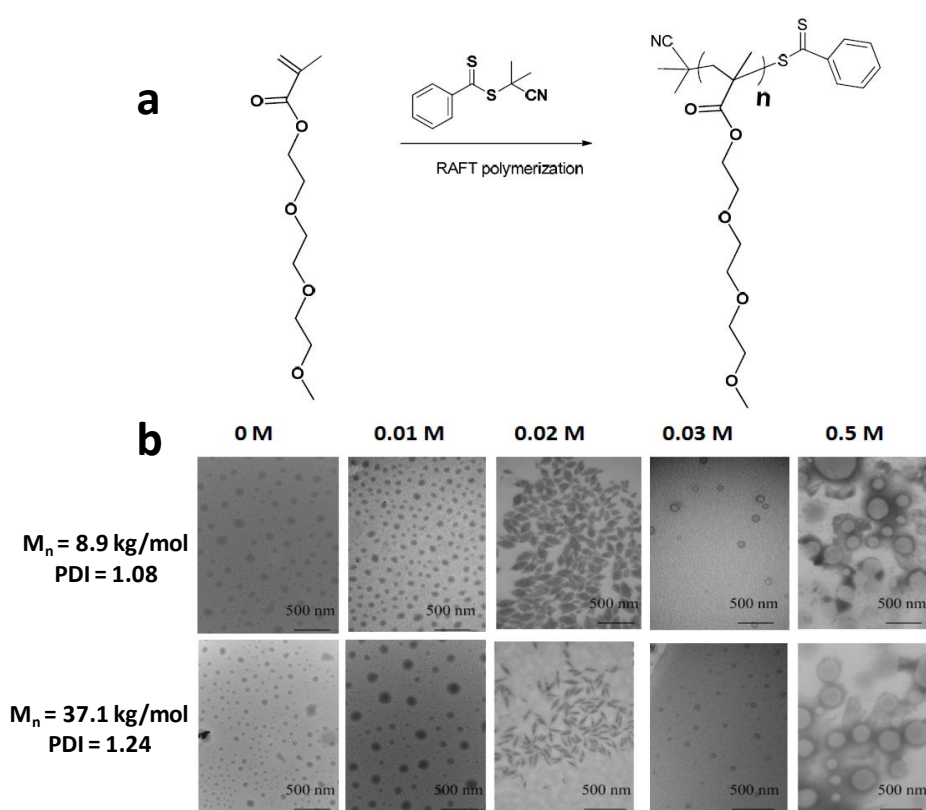


Fig. S12 The effect of molecular weight of homopolymer on the self-assembly in NaSCN solution. a) Homopolymer PME₃MA with different molecular weight prepared via RAFT polymerization. b) TEM images for the self-assembled nanostructures from the prepared homopolymer of PME₃MA with molecular weight of 8.9 kg/mol and 37.1 kg/mol in NaSCN solution.

References:

1. K. B. Rembert, J. Paterová, J. Heyda, C. Hilty, P. Jungwirth, and P. S. Cremer, Molecular Mechanisms of Ion-Specific Effects on Proteins. *J. Am. Chem. Soc.* **134**, 10039.