

SUPPORTING INFORMATION

Inhomogeneous-Collapse Driven Micelle-Vesicle Transition of Amphiphilic Block

Copolymers

Biaolan Liu, Jian Wang, Yu Zhang, Shuaishuai Wu, Geying Ru* and Jiwen Feng*

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, National Center for Magnetic Resonance in Wuhan, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China;

*Corresponding author.

E-mail: jwfeng@wipm.ac.cn (J.W. Feng). Tel: 86-27-87197343. Fax: 86-27-87199291.

gyru@wipm.ac.cn (G.Y. Ru). Tel: 86-27-87197883.

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1. Block copolymer synthesis

1.1 Materials.

N-isopropylacrylamide (99%, NIPA; J&K Chemical Co., Ltd.), *N*, *N*¹-diethylaminoethylmethacrylate (DEAEMA; Sigma-Aldrich), *N*, *N*¹-dimethylaminoethylmethacrylate (DMAEMA; Sigma-Aldrich), 4, 4'-azobis(4-cyanopentanoic acid) (V-501; Sigma-Aldrich), di(thiobenzoyl) disulfide (Sigma-Aldrich). The solvent 99.9% deuterium water was purchased from Cambridge Isotope Laboratory. Other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2 RAFT polymerization.

The chain transfer agent 4-cyanopentanoic acid dithiobenzoate (CPADB) was prepared according to the methods reported in the literature.¹ The block copolymers were synthesized according to procedures described in the literatures.²⁻³ A mixture solution of CPADB (173.3 mg, 0.621 mmol), DMAEMA (10.6g, 0.0675 mol) or DEAEMA (12.0 g, 0.0649 mol) and V-501 (43.5mg, 0.155 mmol) in 16 mL of redistilled dioxane were added to a 50 mL reaction flask. The solution was degassed by three freeze-vacuum-thaw cycles and then placed in a preheated oil bath at 343 K. The reaction was terminated after 24 h by cooling the solution in ice bath. The products (PDMAEMA and PDEAEMA) were then purified by precipitation into a large excess of heptanes or n-hexane for two times and dried under vacuum to a constant weight.

The block copolymer PDEAEMA₁₃₃-b-PNIPA₃₂₂ was synthesized as follows: PDMAEMA (1.04 g), NIPA (2.41 g, 0.0213 mmol) and V-501 (6.3 mg, 0.0225 mmol) were dissolved in 14 mL dioxane in a flask. The solution was degassed by three freeze-vacuum-thaw cycles and then polymerized at 343 K for 24 h. The reaction was stopped by cooling the solution in ice bath. The

product was purified by precipitation in hexanes and dialyzed against distilled water for several days (MWCO 20 kD), and then dried to constant weight. In the case of PDMAEMA₉₅-b-PNIPA₂₂₈ synthesis, PDEAEMA (1.04 g), NIPA (1.81 g, 0.0160 mmol) and V-501 (3.8 mg, 0.0136 mmol) were dissolved in 14 mL dioxane in a flask. And polymerization time was 48 h.

2. Micellization of PDEAEMA₁₃₃-b-PNIPA₃₂₂ at room temperature

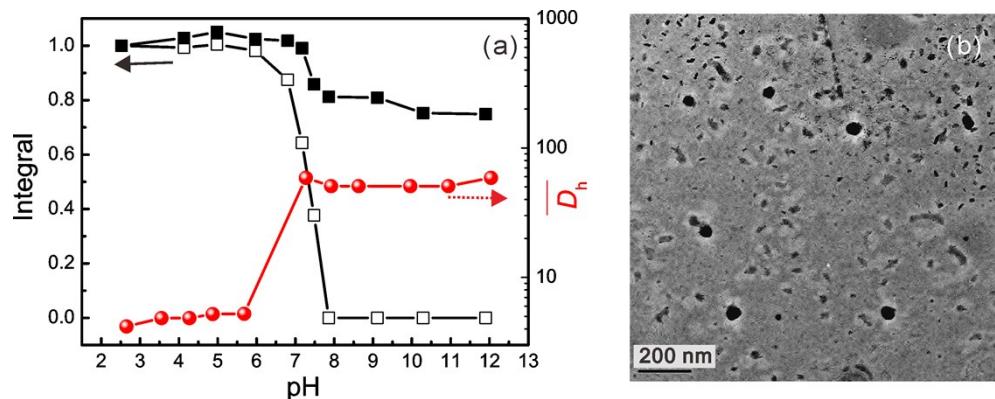


Figure S1 (a) NMR integral of side chain proton peak (PNIPA-*NCH* (filled symbols) and PDEAEMA- $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ (open symbols)) and average hydrodynamic diameters (\overline{D}_h) at variable solution pH at 298 K; (b) TEM micrographs of micelles in alkaline solution at 298 K.

Figure S1 shows the pH-variable NMR integral of side chain proton peak and average hydrodynamic diameters of PDEAEMA-b-PNIPA in aqueous solution at 298 K and the TEM image of micelles formed in alkaline solution. As shown in Figure S1(a), the integral of PDEAEMA- $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ drops sharply around pH 7, accompanied by a small but substantial decrease of PNIPA-*NCH* intensity. This indicates that the PDEAEMA segments undergo a hydrophobic collapse around pH 7. The small integral loss (about 20%) of PNIPA protons can be attributed to the motion-limited PNIPA segments located at the interface between the PDEAEMA core and PNIPA shell. It is obviously showed by the DLS results that the PDEAEMA-b-PNIPA

self-assembles into aggregates with an average hydrodynamic diameter ($\overline{D_h}$) of about 40 ~ 50 nm when the pH increases to above 7. (for simplicity, $\overline{D_h}$ was defined to be the peak value at maximum volume percent) Similar aggregation behavior of PDEAEMA₉₈-b-PNIPA₃₉₂ with higher PNIPA mass fraction was previously reported by Smith et al. and spherical particles were observed at pH 9.⁴ The nominally hydrophilic PNIPA mass fraction of the present PDEAEMA₁₃₃-b-PNIPA₃₂₂ below the LCST is ~ 59% at which spherical micelles are expected. However, the aggregates of PDEAEMA₁₃₃-b-PNIPA₃₂₂ at pH 12 exhibit coexistence of spherical and axiolitic nanoparticles as seen from the TEM image in Figure S1(b). It is worth pointing out that the real hydrophilic PNIPA mass fraction calculated from the data in Figure S1(a) (the collapsed PNIPA segments at core-shell interface was excluded) is about 45% at which worm-like micelles are expected. The coexisting morphologies were reported previously.^{2, 5}

3. Inhomogeneous-collapse of PNIPA block

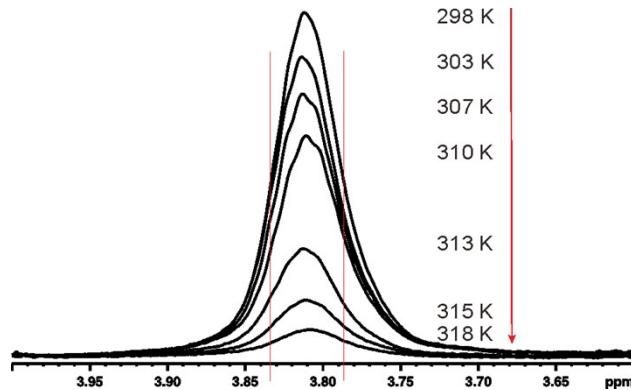


Figure S2 NMR peak of PNIPA_NCH in PDEAEMA-b-PNIPA alkaline solution (pH 12) at variable temperature

As showed in Figure S2, the line width of PNIPA_NCH does not change obviously with temperature, supporting the inhomogeneous-collapse speculation of PNIPA block on the micelle shell.

4. LCST transition of PNIPA chain in homopolymers and block copolymers

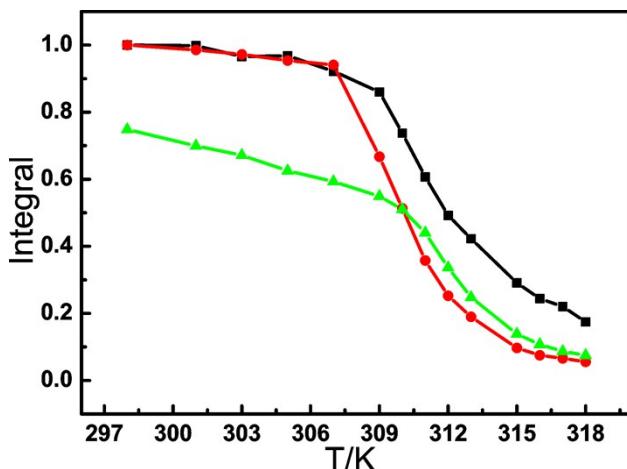


Figure S3 NMR integral variation of PNIPA_CHAIN in PNIPA homopolymer (square) and PDMAEMA-b-PNIPA (circle), PDEAEMA-b-PNIPA (triangle) in alkaline solution (pH=12).

*The homopolymer PNIPA was synthesized in the same procedure as PDMAEMA and PDEAEMA.

5. References for supporting information

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