

Supporting Information for

Star amphiphilic block copolymers: synthesis via polymerization-induced self-assembly and crosslinking within nanoparticles, solution and interfacial properties

Sijia Qian^a, Rui Liu^a, Guang Han^{*:b}, Keyu Shi^{*:a}, and Wangqing Zhang^{a,c}

^a Key Laboratory of Functional Polymer Materials of the Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

^b State Key Laboratory of Special Functional Waterproof Materials, Beijing Oriental Yuhong Waterproof Technology Co., Ltd, Beijing 100123, China.

^c Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.

1 Equations

The aggregation number N_{agg} of linear block copolymer micelles or the arm number N_{arm} of star block copolymer micelles was calculated as follows:

$$N_{\text{agg}} = \frac{\pi D^3 d_p N_A}{6M_{n,\text{NMR}}} \quad \text{or} \quad N_{\text{arm}} = \frac{\pi D^3 d_p N_A}{6M_{n,\text{NMR}}}$$

where d_p is the polymer density, D is the diameter of the micelle core, N_A is Avogadro's number, and M is the polymer molecular weight or molar mass of an arm in star block copolymers. Based on N_{agg} or N_{arm} , the molar mass of a single nanosphere of the block copolymer can be obtained by Equation S1.

$$M_{n,\text{th}} = \frac{[\text{monomer}]_0 \times M_{\text{monomer}}}{[\text{RAFT}]_0} \times \text{conversion} + M_{\text{RAFT}} \quad (\text{S1})$$

$$M_{\text{TEM}} = N_{\text{agg}} \times M_n \quad \text{or} \quad N_{\text{arm}} \times M_n \quad (\text{S2})$$

2 Preparation of linear and star PNIPAM₉₉-*b*-PS₁₉₀ micelles

Herein, take 1.0 mg/mL linear PNIPAM₉₉-*b*-PS₁₉₀ micelles as an example, the linear PNIPAM₉₉-*b*-PS₁₉₀ was dissolved in THF to obtain a 2.5 mg/mL solution at room temperature. Into the PNIPAM₉₉-*b*-PS₁₉₀ solution, deionized water was added at a rate of 1

drop every 10 s with stirring. As the deionized water was added, micelles were formed when the solution became turbid. The drops of water continued until the block copolymer concentration reached to 1.5 mg/mL. The micellar solution was dialyzed against water for 3 days to remove THF and the resultant colloidal dispersion with 1.0 mg/mL concentration was kept at room temperature for further use. The preparation of 0.2, 1.2, 3.0, 6.0 or 12.0 mg/mL linear PNIPAM₉₉-*b*-PS₁₉₀ micelles is similar, but just 0.5, 3.0, 7.5, 15.0 or 60.0 mg/mL PNIPAM₉₉-*b*-PS₁₉₀ solution in THF was used. Star s-PNIPAM₉₉-*b*-PS₁₉₀ nanospheres with different polymer concentration were prepared similarly.