

Supporting Information for:

**Unexpected Toroidal Micelles formed from St/MMA Gradient
Copolymers**

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1. ^1H NMR and GPC Characterization of Styrene (St)/methyl methacrylate (MMA) gradient copolymer $\text{PS}_{266}\text{-grad-PMMA}_{200}$

Detailed information of synthesis and characterization of $\text{PS}_{266}\text{-grad-PMMA}_{200}$ was reported in reference.[1] Aliquots (≈ 0.3 mL) of the reaction mixture were precipitated in hexane and purified at different reaction times during polymerization. Gel permeation chromatography (GPC) characterization was recorded by a Waters 410 instrument with polystyrene as standards and THF as eluent. ^1H NMR spectra of the gradient copolymers were recorded on a Bruker AV-300 with CDCl_3 as solvent. ^1H NMR and GPC results of these gradient copolymers were shown in figure S1 and figure S2. The profile along gradient polymer chain in figure 1a in original manuscript is drawn based on figure S1 and figure S2.

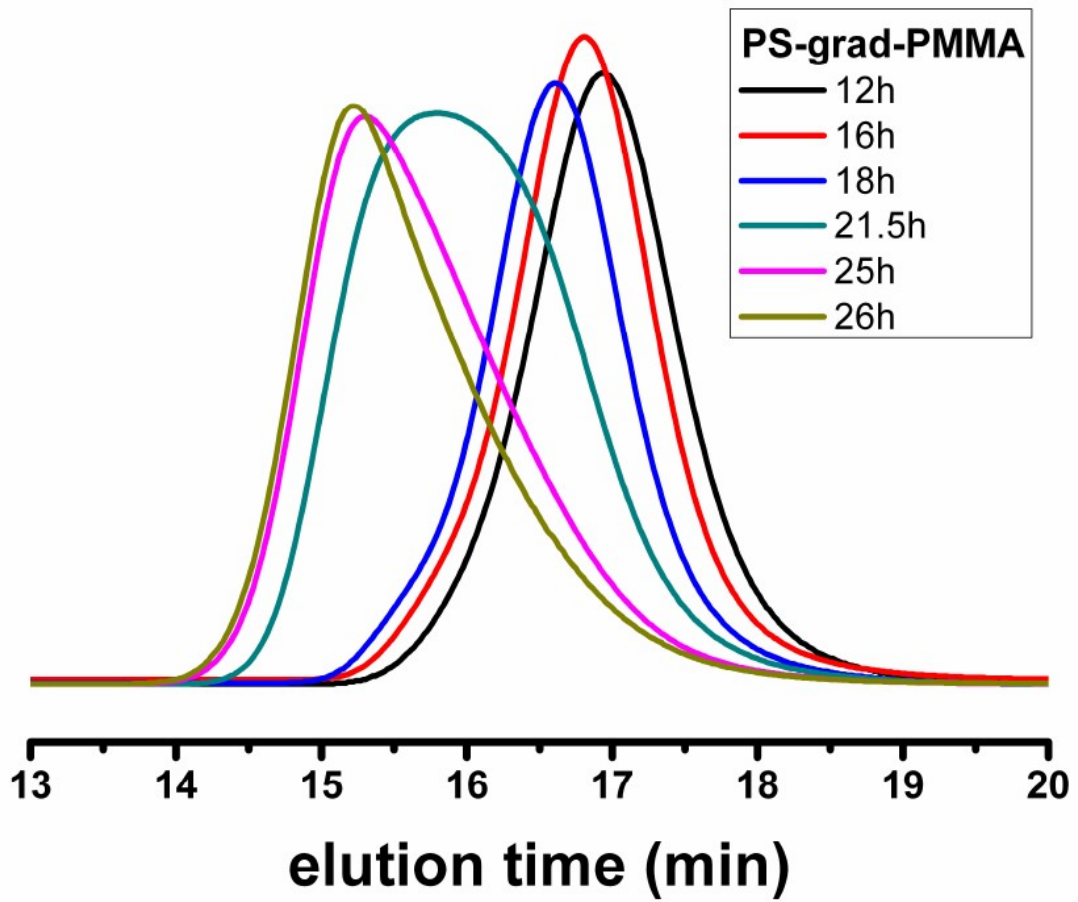


Figure S1. Elution time of St/MMA gradient copolymers from GPC.

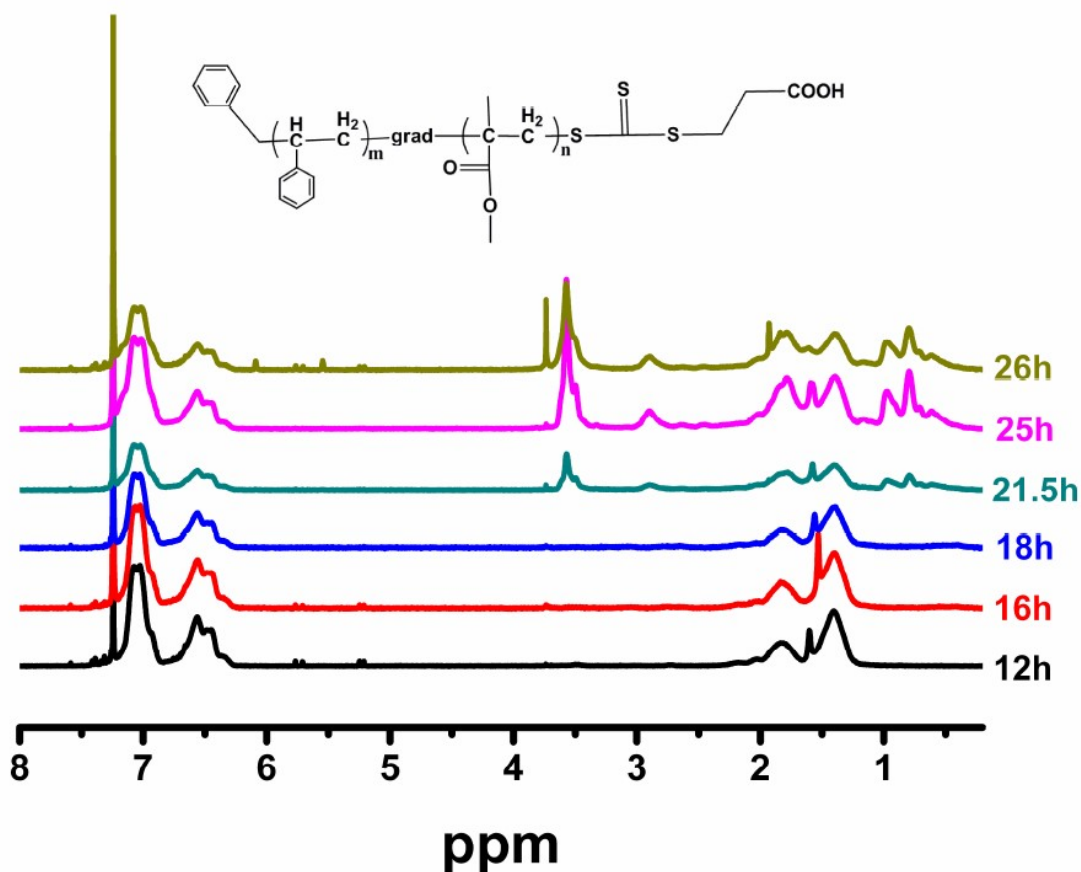


Figure S2. ¹H NMR of St/MMA gradient copolymers during the copolymerization.

2. Determination of viscosity of acetone/water mixture at different temperature.

The viscosity of the mixture of acetone and water was determined by a nondestructive way reported in previous study.[1] Monodispersed silica microspheres ($R \sim 140\text{nm}$) were used to determine the viscosity, since the silica spheres are hard spheres whose size can not be affected by the solvent conditions. The value of viscosity can be calculated according to Stocks-Einstein equation $\eta = k_b T / 6\pi R_h D$, the diffusion coefficient could be

obtained by laser light scattering experiments. Table S1 summaries the viscosity of the mixed solvents at different temperatures.

Table S1. viscosity of acetone/water mixture (water content: 0.099w/w) at different temperatures.

T/K	η /cp
288	0.4884
298	0.4207
320	0.3215

Reference:

[1] C. Zheng, H. Y. Huang, T. B. He, *Macromol. Rapid Commun.* **2013**, 34, 1654.