Supporting Information

Core-bound Polymeric Micellar System Based on Photocrosslinking of Thymine

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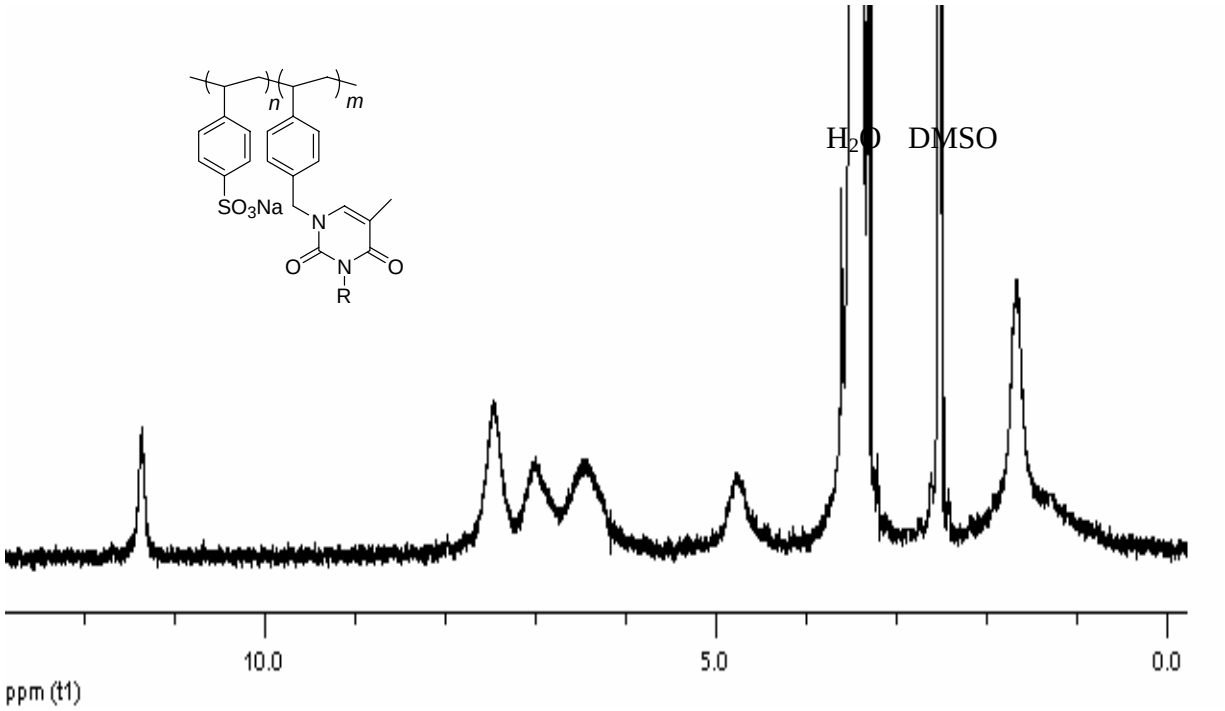
Materials and Measurements. All reagents and materials were purchased from Sigma-Aldrich in the purest form available and used as received. The thymine functionalized monomer VBT was synthesized from *p*-vinylbenzylchloride and thymine in aqueous ethanol. NMR spectra were taken on a Bruker 500 MHz NMR spectrometer. IRs were recorded using a Thermo Electron Corp. class 1 laser product. Molecular weights were measured using an Agilent 1100 series gel permeation chromatography (GPC) with Agilent GPC data analysis software equipped with RID using G4000PW_{XL} columns. Calibration curves were obtained using poly(styrene sulfonic acid sodium salt) standards.

Copolymer Synthesis. VPS (1.0 g, 4.85 mmol) was dissolved in 10 mL of 50% ethylene glycol/water and TEMPO (74 mg 0.47 mmol) was then added. $Na_2S_2O_5$ (34 mg, 0.18 mmol) and $K_2S_2O_8$ (64 mg, 0.24 mmol) were then added and the solution was heated at 60 °C for 1 h under nitrogen. The mixture became clear and was stirred at 125 °C for 5 h under nitrogen to prepare homo VPS polymer. VBT (1.18 g, 4.85mmol) was then added to the homo VPS polymer solution and stirring continued at 125 °C under nitrogen for 5h. The polymerized product was purified by adding the solution to 200 mL of acetone. The resulting solids were collected by filtration and dried under vacuum. IR: $\nu_{N\text{-}H}$ = 3195, $\nu_{C=O}$ = 1672. M_n = 7.9× 10^4, M_w/M_n = 1.73.

^{1}H-NMR of Poly(VBT(1)-*b*-VPS(1))-H in DMSO-*d6*



Micellar Aggregates Formation. A typical block copolymer (0.1 g) in DMSO 10 mL was transferred through a 0.45 μm filter into a pre-swollen semi-permeable membrane (Spectra/Por, SPEC-TRUM, molecular weight cutoff, 3500), and dialyzed against 1 L of water for 24 h to form a micellar aggregates. The dialysate water was exchange after 2, 5, and 8 h.

Micellar Aggregates Characterization. DLS measurements were performed using a Malvern Zetasizer Nano series Nano-ZS with 4 mW He-Ne laser at a laser wavelength of 633 nm at 25 °C. Dispersion Technology Software 4.2 was used to calculate the average diameter of the micellar aggregates. 0.5 mg/mL block copolymer micelle solution was used for the measurement. For the TEM measurement, a drop of the 0.5 mg/mL block copolymer micellar aggregate solution was placed on a 200 mesh formvar carbon coated copper grid. After removing the excess, the sample was negatively stained by using 0.1 % uranyl acetate. The sample was dried in vacuum and measured using a Philips EM 400T equipped with an AMT digital camera (Accelerating voltage: 100 kV, Bright filed image). The AFM sample was prepared by depositing the block copolymer micellar aggregate solution onto freshly cleaved mica and dried in air. The AFM measurement was carried out in the tapping mode

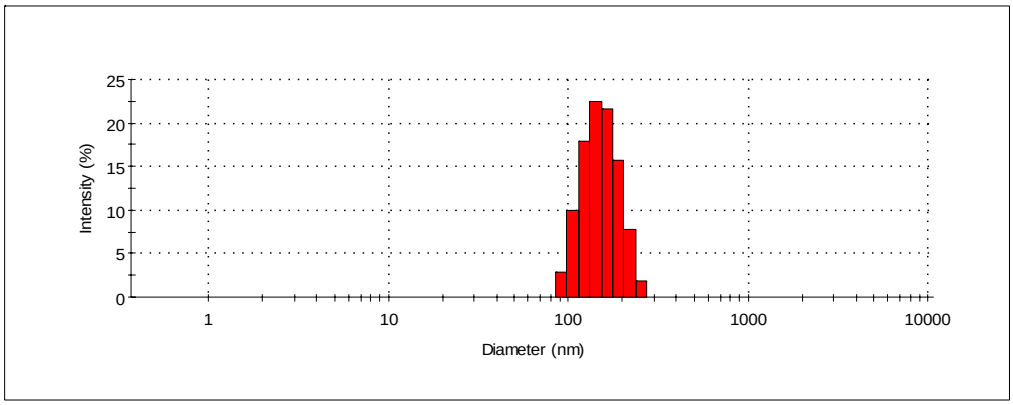
with a PSIA Corp. XE-150 equipped with Si-N tip with the backside coated with Al (spring constant: 40 N/m).

Table S1. Size of formed block copolymer micellar aggregates by DLS.[a]

entry	polymer code	irradiation (J/cm^2)	average diameter (nm)
1	poly(VBT(1)-*b*-VPS(1))-L	0	87
2	poly(VBT(1)-*b*-VPS(1))-H	0	164
3	poly(VBT(1)-*b*-VPS(1))-H	0.3	166
4	poly(VBT(1)-*b*-VPS(1))-H	5.0	160
5	poly(VBT(1)-*b*-VPS(1))-H	10.0	157
6	poly(VMT(1)-*b*-VPS(1))	0	48

[a] All of the measurement was carried out using 0.5 mg/mL micelle solution.

DLS size distribution date of Poly(VBT(1)-*b*-VPS(1))-H micellar aggregates



Size distribution of the prepared poly(VBT(1)-*b*-VPS(1))-H by dialysis method

Photocrosslinking. A solution of the block copolymer micellar aggregates (5.0 mg/mL) was crosslinked in a quartz glass tube by irradiation at short wave UV (XL 1000 UV Crosslinker, Spectronics Co.) with 0.3, 5, 10 J/cm^2. After photocrosslinking, the UV spectra of each solution was obtained with an Agilent 8453 UV-Visible Spectrophotometer.

Critical Micelle Concentration (CMC) Measurement. The CMC of the micellar aggregates were estimated by fluorescence spectroscopy using pyrene as a probe. An acetone solution of pyrene (6.0×10^{-2} M) was prepared and added to water to give a pyrene concentration of 12.0×10^{-7} M. The acetone in the solution was than evaporated to form an acetone-free pyrene solution. This pyrene solution (2 mL) was mixed together with solutions of the block copolymer micellar aggregate solutions (2 mL) with concentrations ranging from 5.0×10^{-5} to 5.0 mg/ml. The final concentration of pyrene in each sample solution was 6.0×10^{-7} M and the final concentration of the block copolymer micelles solutions were 2.5×10^{-5} to 2.5 mg/ml. To measure the CMC of the crosslinked micellar aggregates, the crosslinked micellar aggregate solutions (0.3, 5 J) were diluted to a concentration range of 5.0×10^{-5} to 5.0 mg/ml and measured by the same procedure as the uncrosslinked micelles. The measurements were carried out at the emission wavelength of 395 nm and excitation wavelength of 333 nm using Perkin Elmer LS55 Spectrofluorometer.