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Supporting Information

Temperature-Triggered Reversible Micellar Self-Assembly of Linear-Dendritic Block Copolymers

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Experimental

Materials. 2-(2-Methoxyethoxy)ethyl methacrylate (MEO2MA, 95%, Aldrich) was purified by passing the neat liquid through a column filled with alumina to remove the inhibitor. Palladium (10 wt % on activated carbon), N-N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), poly-(ethylene glycol) bis(carboxymethyl) ether (HOOC-PEG-COOH), 4,4'-dinonyl-2,2'-bipyridine (dNbpy, 97%), and Copper(I) bromide were purchased from Aldrich and used as received. Dowex 50WX2-100 H+ resin was purchased from Lancaster Synthesis Inc. All other chemicals used in this work were purchased from Aldrich and Alfa Aesar and used without further purification.

Characterization. ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometers with $CDCl_3$ as a solvent. Gel permeation chromatography (GPC) measurements were carried out to obtain molecular weight and polydispersity as

measured against polystyrene standards in tetrahydrofuran (THF) solution using a Water Breeze 1525 HPLC system equipped with four Styragel HT columns operated at 35 °C, series 2414 refractive index detector, series 1525 binary HPLC pump, and 717plus autosampler. A flow rate of 1.0 mL/min was used. The apparent molecular weights and polydispersities (M_w/M_n) were determined using WinGPC 6.0 software from Polymer Standards Services (PSS). Tapping-mode atomic force microscopy (AFM) measurements were conducted in air with a Dimension 3100 system (Digital Instruments, Santa Barbara, CA) operated under ambient conditions. Multi-angle dynamic light scattering (DLS) study was performed by photon correlation spectroscopy using a Brookhaven Instruments, Co. (Holtsville, NY) system consisting of a model BI-200SM goniometer, a model EMI-9865 photomultiplier, a model BI-9000AT digital correlator, and a Coherent Innova 90C Series ion laser (Santa Clara, CA) operated at 514 nm. All measurements were made at 25 (0.1 °C; 1.0 mg/mL of polymer was dissolved intowater and filtered using a 0.45-*í*m Acrodisc syringe filter (PallCo., Ann Arbor, MI) before measurements. All determinations were made in triplicate and averaged.

Synthesis

B16COOH, 1 was prepared as previously reported[1].

Dendritic initiator, B16Br, 2. B16Br, 2, was prepared by the coupling reaction between B16COOH, 1 and 2-Hydroxyethyl bromoisobutyrate in dichloromethane, in the presence of N-N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). 2-Hydroxyethyl bromoisobutyrate (0.21 g, 1.0 mmol), DCC (0.25 g, 1.2 mmol) and DMAP (0.03 g, 0.012 mmol) were dissolved in 40 mL of dichloromethane. B16COOH, 1 (2.2 g,, 1.05 mmol) in 5 mL CH_2Cl_2 was added dropwise to the solution while the solution was

kept in an ice bath. The reaction mixture was stirred for 12 h. The resulting precipitate was filtered off, and the solvent was evaporated to give a viscous liquid, which was purified by silica gel column chromatography using ethyl acetate/hexane (3:7) as the solvent. A yield of 73% was obtained after purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.4-3.6 (overlapped, 60H, CH_2 in dendrimer, 4H, -OCH_2CH_2O-), 1.55-1.0 (overlapped, 48H, CH3, 21H, CH3, 24H, CH3). GPC: M_n = 1,800 g/mol; PDI = 1.05.

B16-*b*-PMEO2MA, 3. MEO2MA (1.88 g, 0.1 mol), B16Br, 2 (0.21 g, 0.1 mmol), dNbpy (0.082 g, 0.2 mmol) and anisole (1.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. Oxygen was removed by three freeze-pump-thaw cycles, and CuBr (0.0143 g, 0.1 mmol) was added under nitrogen. The polymerization was conducted at 50 °C for 2 h. The reaction was stopped by opening the flask to air, and the catalyst was removed by passing the solution through a neutral alumina column. The polymer was precipitated by addition to hexane, and dried under high vacuum at room temperature for 12 h. (DP of PMEO2MA = 40, as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.1 (24H, CH_2 in dendrimer), 3.8-3.6 (overlapped, 36H in dendrimer, 2H, -OC-O-CH_2-CH_2-O-CH_2CH_2-O-CH_3 in PMEO2MA), 3.4 (9H, -OC-O-CH_2-CH_2-O-CH_2CH_2-O-CH_3 in PMEO2MA), 1.7-0.8 (overlapped, 48H, CH_3, 21H, CH_3, 24H, CH_3). GPC: M_n = 8,500 g/mol; PDI = 1.18.

PEOB16-b-PEO2MA, 4. The acetonide protective groups of B16-*b*-PMEO2MA, 3, were deprotected by stirring in methanol in the presence of an acidic Dowex 50W-X2 resin for 18 h. The deprotected product (0.049 g, 0.005 mmol, based on theoretical molecular weight), DCC (0.12 g, 0.55 mmol) and DMAP (0.0006 g, 0.005 mmol) were dissolved in dichloromethane (20 mL). After 10 min flushing with argon, HOOC-PEG-

COOH (MW = 600 g/mol) (0.3 g, 0.5 mmol) in 5 mL dichloromethane was added dropwise to the solution for 24 h. The precipitate was filtered off, and the solvent was evaporated to give a viscous liquid. The resulting product was dialyzed against distilled water for 48 h by a Spectra/Porcellulose ester membrane with a MW cutoff of 10 000 g/mol from Spectrum Laboratories. The dialyzed product was dried under vacuum.). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.3-4.0 (60H in dendrimer, CH_2), 3.6 (640H, in dendritic PEO, CH_2, 2H, -OC-O-CH_2-CH_2-O-CH_2CH_2-O-CH_3 in PMEO2MA), 3.4 (9H, -OC-O-CH_2-CH_2-O-CH_2CH_2-O-CH_3 in PMEO2MA), 1.8-0.6 (overlapped, 48H, CH_3, 21H, CH_3, 24H, CH_3). GPC: M_n = 11,100 g/mol; PDI = 1.15.

Additional AFM images

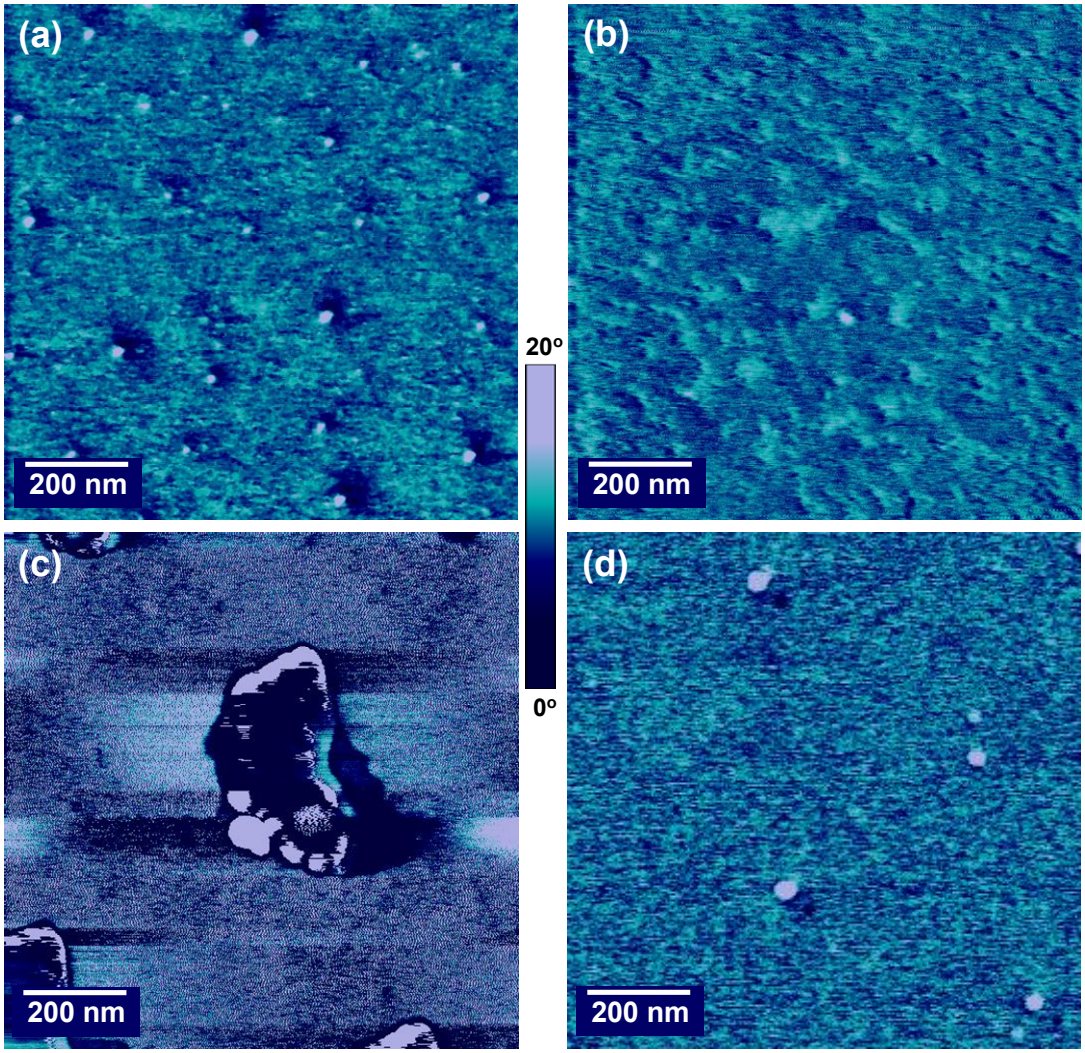

Figure S1. AFM height images of aqueous solutions of PMEO2MA-*b*-B16PEO **4** solutions spin-coated on a silicon wafer under various conditions a) the original micelles of PMEO2MA-*b*-B16PEO **4** at 50 ^{o}C; b) the disrupted micelles after cooling to 25 ^{o}C; c) the regenerated micelles after heating to 50 ^{o}C for 1 min; d) the regenerated micelles after continuous heating at 50 ^{o}C for 120 min.

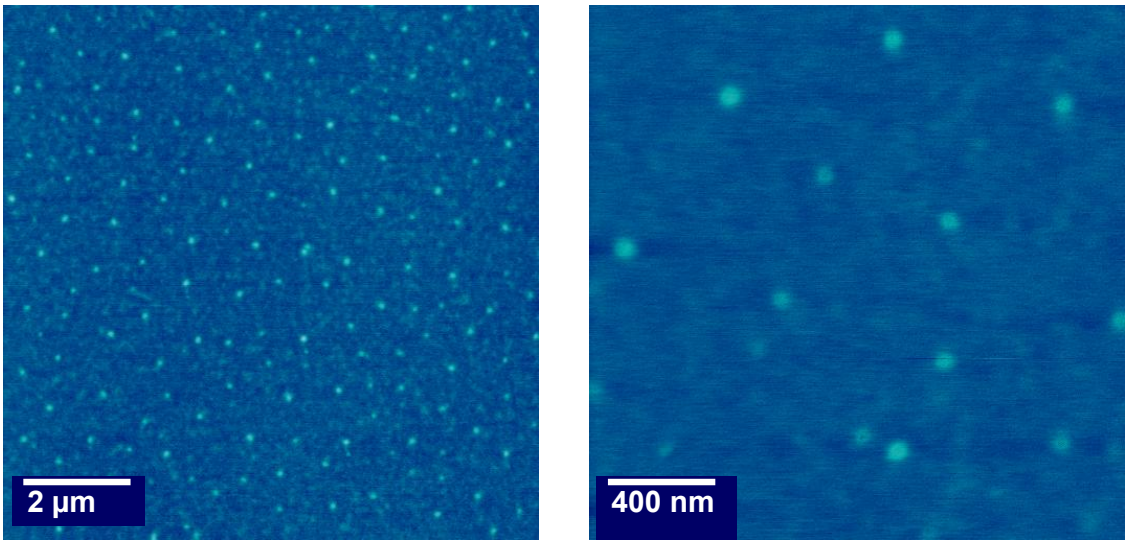

Figure S2. AFM height images of the regenerated micelles after continuous heating at 50 ^{o}C for 60 min of PMEO2MA-*b*-B16PEO **4** spin-coated on silicon wafer.

1 **L. Tian, and P. T. Hammond, *Chem. Mater.* 2006, 18, 3976**