Supporting Information for

A New Level of Hierarchical Structure Control by Use of Supramolecular Self-assembled Dendronized Block Copolymers

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1. Synthesis of homopolymers and block copolymers

Materials

The first and second generation dendronized macromonomers (**MG1** and **MG2**) and polymers (**PG1** and **PG2**) were synthesized according to a previous report[1]. Dendronized block copolymer with poly(N-isopropyl acrylamide) block was prepared by reversible addition fragmentation chain transfer polymerization[2]. Methoxy diethylene glycol methacrylate (**MeDEG-MA**) was purchased and purified by silica gel chromatography before use. Other reagents and solvents were purchased at reagent grade and used without further purification. All reactions and polymerizations were run under a nitrogen atmosphere. Macherey-Nagel pre-coated TLC plates (silica gel 60 G/UV$_{254}$, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm, 230-400 mesh) was used as the stationary phase for column chromatography. All samples were dried thoroughly under vacuum prior to analytical measurements to remove strongly adhering solvent molecules.

Characterization

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 500 (^{1}H: 500 MHz) spectrometers at room temperature using $CDCl_3$ or CD_3OD as solvent, and chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. *Gel Permeation Chromatography* (*GPC) measurements* were carried out by using a PL-GPC 220 instrument with a 2×PL-Gel Mix-B LS column set (2×30 cm) equipped with refractive index (RI), viscosity, and light scattering (LS; 15 ^{o} and 90 ^{o} angles) detectors, and LiBr (1 g/L) in DMF as eluent at 45 ^{o}C. Universal calibration was performed with

poly(methyl methacrylate) standards in the range of M_p = 2680 to 3900000 (Polymer Laboratories Ltd, UK). *Differential Scanning Calorimetry (DSC)* measurements were performed on a DSC Q1000 differential scanning calorimeter from TA Instruments in a temperature range of -80 ~ +150 °C with a heating rate of 10 $°C \cdot min^{-1}$. Samples of a total weight ranging between 3 - 10 mg were closed into aluminum pans of 40 μL, covered by a holed cap, and analyzed under a nitrogen atmosphere. The glass transition temperature (T_g) was determined in the second heating run. *UV/vis turbidity measurements* were carried out for the lower critical solution temperature (LCST) determination on a Varian Cary 100 Bio UV/vis spectrophotometer equipped with a thermostatically regulated bath. Solutions of the polymers in de-ionized water (with concentration from 0.05 wt% to 4 wt%) were filtered with a 0.45 μm filter before adding into a cuvette (path length 1 cm), which was placed in the spectrophotometer and heated or cooled at a rate of 0.2 $°C \cdot min^{-1}$. The absorptions of the solution at λ = 500 nm were recorded every minute.

Synthesis

Typical ATRP procedure for synthesis of oligoethylene oxide polymethacrylates (PMeDEG$_{500}$): Into a Schlenk tube were added the monomer **MeDEG-MA** (21.25 mmol), DMF (4 mL), CuCl (0.04 mmol), and pentamethyldiethyltriamine (PMDETA; 0.13 mmol) and the resulting mixture was immediately degassed several times by freeze-pump-thaw cycles. Upon addition of the initiator ethyl 2-bromoisobutyrate (0.04 mmol), the system turned homogeneously blue to green, indicating the start of the polymerization. The mixture was kept at 80 °C for a predetermined time. After cooled down to room temperature, the catalyst was removed by filtration through a short silica column, and the resulting polymer was purified on a silica column with dichloromethane (DCM) as eluent. GPC results: M_n = 99,600, PDI = 1.28. ^{1}H NMR ($CDCl_3$): δ = 0.88-1.22 (br, 3H, CH_3), 1.79-1.89 (br, 2H, CH_2), 3.38 (br, 3H, CH_3), 3.54-3.66 (br, 6H, CH_2), 4.09 (br, 2H, CH_2).

Typical ATRP procedure for synthesis of block copolymers (PMeDEG$_{500}$Boc-PG1$_{344}$): Into a Schlenk tube were added the dendronized G1 macromonomer (2.04 mmol), DMF (1 mL), CuBr (0.02 mmol), and PMDETA (0.06 mmol), and the resulting mixture was immediately degassed several times by freeze-pump-thaw cycles, then polymer initiator PMeDEG (0.02 mmol based on Br) was added. The mixture was kept at 90 °C for a predetermined time. After cooling to room temperature, the catalyst was removed by filtration through a short silica column and the resulting polymer purified by precipitation from DCM solution into diethyl ether twice. GPC results: M_n = 155,500, PDI = 1.36. ^{1}H NMR ($CDCl_3$): δ = 0.93-1.02 (br, CH_3), 1.44 (br, CH_3), 1.75 (br, CH_2), 2.55 (br, CH_2), 3.08 (br, CH_2), 3.44 (br, CH_3), 3.61-3.72 (br, CH_2), 4.14 (br, CH_2), 6.93 (br, CH).

Typical ATRP procedure for synthesis of block copolymers (PMeDEG$_{380}$Boc-PG2$_{32}$): Into a Schlenk tube were added the dendronized G1 or G2 macromonomer (0.44 mmol), DMF (1 mL), CuBr (0.015 mmol), and PMDETA (0.044 mmol), and the resulting mixture was immediately degassed several times by freeze-pump-thaw cycles, then polymer initiator PMeDEG (0.02 mmol based on Br) was added. The mixture was kept at 90 °C for a predetermined time. After cooling to room temperature, the catalyst was removed by filtration through a short silica column and the resulting polymer was purified by precipitation from DCM solution into diethyl ether twice. GPC results: M_n = 149,900, PDI = 1.31. ^{1}H NMR ($CDCl_3$): δ = 0.92-1.08 (br, CH_3), 1.40 (br, CH_3), 1.77-1.94 (br, CH_2), 2.50 (br, CH_2), 2.98 (br, CH_2), 3.44 (br, CH_3), 3.61-3.66 (br, CH_2), 4.15 (br, CH_2), 6.95 (br, CH), 7.05 (br, CH).

De-protection of the block copolymers (PMeDEG-PG1 or PMeDEG-PG2): Copolymer was dissolved in trifluoroacetic acid at 0 ^{o}C under N_2 protection, and mixture stirred for 12 h at room temperature. After quenched with excess amount of MeOH, evaporation in vacuum afforded slight yellowish product with quantitative yield.

2. Physical Characterization of the complexes

Thermal treatment

Steric crowding of dendrons may greatly reduce conformations of the backbone chains, causing the backbone to elongate. Consequently, the dendronized polymers may appear as rigid rods, giving low molecular mobility and additional resistance for dendronzed block copolymers to achieve the equilibrium state. In this study, without particular statement, all the block copolymers are treated by casting at 60 ^{o}C from their 1-butanol solutions, annealing within saturated 1-butanol vapor at 60 ^{o}C for 48h and then thermally annealing at 140 ^{o}C for over 24h.

WAXS profile of PG_{190}-SO_4C_8

WAXS profile of the polymer complexed with the surfactant C8 (PG_{190}-SO_4C_8) is shown in Figure S1. It presents only a single broad peak, indicating an amorphous state. In this specific case the alkyl tails length is not long enough to induce microphase segregation between the lipid tail and the dendronized polymer.

Structures at the block copolymer length scale

Figure S2 shows the typical TEM images of dendronized block copolymers complexed with sulfate alkyl tails at the block copolymer length scale. a, $PMeDEG_{500}PG1_{344}$-SO_4C_{12}. b, $PMeDEG_{380}PG2_{32}$-SO_4C_{14}. c, $PNiPAM_{45}PG1_{425}$-SO_4C_{18}. Clearly, a cylindrical structure is observed for $PMeDEG_{500}PG1_{344}$-SO_4C_{12}, while lamellar structures are observed for $PMeDEG_{380}PG2_{32}$-SO_4C_{14} (periodicity ~67nm) and $PNiPAM_{45}PG1_{425}$-SO_4C_{18} (periodicity is ~27nm).

For the block copolymers consisting of one PNiPAM coil block and one 2nd generation dendronized block, no microphase separation was observed at the block copolymer length scale. This is presumably due to increased miscibility of both blocks occurring owing to the presence of the amides in both blocks, and thus, internal hydrogen bonds.

Additional TEM analysis for Figure 3

In Figure 3a and b, poorly organized alkyl tail columns appear to be correlated with large dendronized polymer domains (e.g. 65~67nm vs ~5nm liquid crystalline periodicity), while well organized lipid lamellae are found in systems with lower large scale periodicities in Figure 3c (~27 nm vs ~5nm liquid crystalline periodicity).

Reference

1. Zhang, A., *et al.* Efficient synthesis of high molar mass, first- to fourth-Generation distributed dendronized polymers by the macromonomer approach. *Chem. Eur. J.* **9**, 6083–6092 (2003).

2. Cheng, C., *et al.* Synthesis of thermally switchable poly(N-isopropylacrylamide-block-dendronized methacrylate)s. *Macromolecules* **40**, 220-227 (2007).

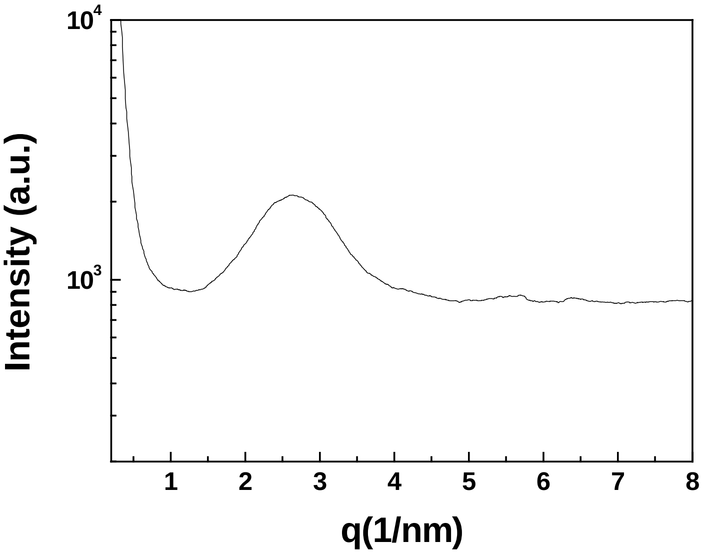

Figure S1. WAXS profile of PG_{190}-SO_4C_8.

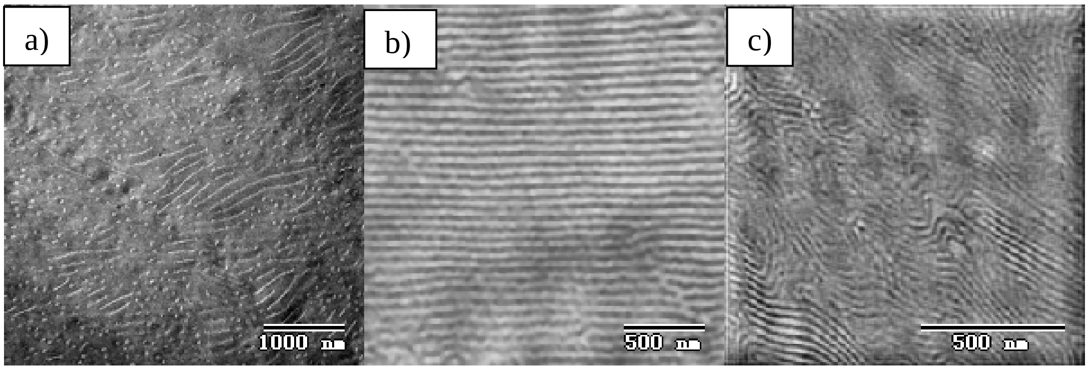

Figure S2. Typical TEM images of dendronized block copolymers complexed with sulfate alkyl tails at the block copolymer length scale. a) $PMeDEG_{500}PG1_{344}$-SO_4C_{12}. b) $PMeDEG_{380}PG2_{32}$-SO_4C_{14}. c) $PNiPAM_{425}PG1_{45}$-SO_4C_{18}.