

Electronic Supplementary Information for

Self-Assembly of Dendron-Helical Polypeptide Copolymers: Organogels and Lyotropic Liquid Crystals

Kyoung Taek Kim, Chiyoung Park, Chulhee Kim, Mitchell A. Winnik,^{*} and Ian Manners^{*}

Experimentals

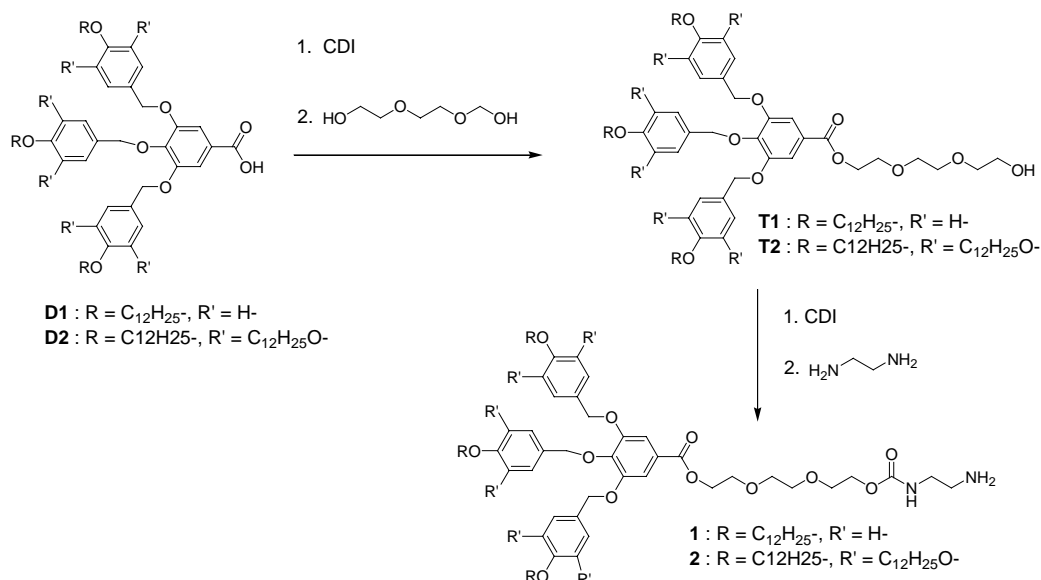
Reagents and Equipment. All reagents were purchased from Aldrich and used as received. DMF, ethyl acetate, and THF were distilled by literature methods.¹ γ -Benzyl-L-glutamate-*N*-carboxyanhydride was synthesized by the literature method.² NMR spectra were recorded on Varian Mercury 400 and Mercury 300 spectrometers with CDCl₃ as a solvent. Molecular weights of the dendron-helical polypeptide (DHP) copolymers (**3-5**) were measured on a Viscotek GPC max system (VE 2001 GPC solvent/sample module and TriSEC Model 302 triple detector array) with THF (0.003 M tetrabutylammonium bromide) as the eluent. FT-IR (Nujol, KBr) was performed on a Perkin Elmer Spectrum One IR Spectrometer. TEM images were obtained on a Phillips CM200 or Hitachi EM600 microscope operated at an acceleration voltage of 80 kV or 75 kV. A carbon-coated copper grid (200 mesh) was used to support the samples. AFM experiments were performed on a SPI 4000 (Seiko Instrument Inc.) and a NanoScope III in a tapping mode using fresh cleaved mica as the substrate. Small angle X-ray scattering (SAXS) experiments were carried out at the 4C1 X-ray beamline of Pohang Accelerator Laboratory (Pohang, Korea). The scattering data were collected using a 2-D CCD detector and the X-ray wavelength was 1.608 Å (Co K α radiation). Powder X-ray diffraction data were collected on a Rigaku RINT-2000 counter diffractometer with a Cu K α radiation source (operated at 40 kV, 40 mA).

For TEM and AFM specimen preparation. The carbon coated copper grid (200 mesh) was gently placed on the organogel. The grid was removed after 30 seconds and air-dried for 1 h. For organogels of copolymer **3**, the TEM specimens were shadowed by coating with Au/Pd (7-8 Å thick) with a tilt angle of 20°. The organogels of copolymers **4** and **5** were observed by TEM without shadowing. For AFM

sample specimen, a fresh-cleaved mica disk (10 mm diameter) was gently tapped on the fraction of the organogel on the filter paper. The mica substrate was then dried for 1 h in ambient condition.

SAXS studies of copolymers. Toluene gels of **3** and **4** were slowly dried under ambient atmosphere for 24 h. Under synchrotron X-ray source (Pohang Acceleration Laboratories, Pohang, Korea), wet toluene gels of **3** and **4** also gave the peaks at the identical locations in SAXS experiments with smaller intensities of the signal compared to the dried gels. For liquid crystal of **4**, both concentrated THF solution of **4** and the solid **4** after drying the THF solution were used for SAXS experiments. Similar to the experimental results from the organogels, the location of the peak remained unchanged but the intensity of the peaks decreased in solution samples.

Effect of hydrogen bonding for the gelation. 5 vol % of methanol was added to the toluene solution of the block copolymers. The solution exhibited thermoreversible gelation in the presence of methanol. Addition of large amount of methanol to the organogels induced shrinkage of the gel into dense solid.



Synthesis of dendron 1. The second generation dendron (**D1**) was prepared by the method reported by Percec *et al.*³ **D1** (4.96 g, 5 mmol) and 1,1'-carbonyldiimidazole (CDI) (0.97 g, 6 mmol) were reacted in dry THF (60 ml) at room temperature for 4h under a purified N₂ atmosphere. The solution was cooled to

0 °C and 50 mL of a THF solution of triethylene glycol (7.5 g, 50 mmol) was added, while the temperature was kept at 0 °C. The solution was stirred for 1 h at 0 °C and then stirred at 50 °C for 8 h. Solvents were removed under reduced pressure. The crude mixture was dissolved in CH₂Cl₂ and extracted with brine three times. The organic layer was dried with anhydrous MgSO₄. A concentrated solution was precipitated in acetone. A white glassy solid **T1** was obtained after filtering and drying under vacuum for 24 h. Yield: 5.1g (91%) ¹H NMR (δ=ppm, CDCl₃, 400MHz) 7.34 (s, 2H), 7.27 (d, *J*=8 Hz, 4H), 7.18 (d, *J*=9.2 Hz, 2H), 6.83 (d, *J*=8.8 Hz, 4H), 6.69 (d, *J*=8.4 Hz, 2H), 4.99 (s, 4H), 4.95 (s, 2H), 4.41 (t, *J*=4.8 Hz, 2H), 3.85-3.93 (m, 6H), 3.77 (t, *J*=4.8 Hz, 2H), 3.64-3.66 (m, 6H), 3.54-3.56 (m, 2H), 1.68-1.75 (m, 6H), 1.22-1.41 (br, 54H), 0.83 (t, *J*=6.8 Hz, 9H). ¹³C NMR (δ=ppm, CDCl₃, 400MHz) 166.22, 159.05, 152.65, 142.67, 130.26, 129.47, 129.30, 128.64, 124.89, 114.49, 114.12, 109.46, 74.72, 72.54, 71.17, 70.74, 70.43, 69.35, 68.09, 68.00, 64.03, 61.80, 31.95, 29.70, 29.67, 29.64, 29.63, 29.48, 29.46, 26.11, 22.72, 14.14.

T1 (4.5 g, 4 mmol) was reacted with ethylene diamine (6 g, 100 mmol) via the preparation method described above. The crude product was purified by the column chromatography (neutral alumina, CH₂Cl₂/methanol (90/10 % v/v)). Yield: 2.37 g (49 %). ¹H NMR (δ=ppm, CDCl₃, 400MHz) 7.36 (s, 2H), 7.31 (d, *J*=8.4 Hz, 4H), 7.21 (d, *J*=8.8 Hz, 2H), 6.86 (d, *J*=8.4 Hz, 4H), 6.72 (d, *J*=8.8 Hz, 2H), 6.12 (br, NH), 5.02 (s, 4H), 4.97 (s, 2H), 4.45 (t, *J*=5.2 Hz, 2H), 4.18-4.20 (br, 2H), 3.88-3.96 (m, 6H), 3.81 (t, *J*=4.4 Hz, 2H), 3.62-3.68 (br, 4H), 3.35-3.39 (m, 2H), 2.99-3.01 (m, 2H), 1.72-1.81 (m, 6H), 1.26-1.46 (br, 54H), 0.87 (t, *J*=7.2 Hz, 9H). ¹³C NMR (δ=ppm, CDCl₃, 400MHz) 166.22, 159.02, 152.62, 142.67, 130.20, 129.38, 129.30, 128.51, 124.84, 114.43, 114.08, 109.35, 74.72, 71.15, 70.42, 70.38, 69.61, 69.27, 68.05, 67.96, 64.10, 63.85, 31.90, 29.66, 29.62, 29.44, 29.34, 29.30, 26.06, 22.67, 14.10. Low Res. Mass (ESI) calcd. for C₇₃H₁₁₅N₂O₁₂ 1212.7 (M+H), found 1211.9. High Res. Mass (ESI) calcd. for C₇₃H₁₁₅N₂O₁₂ (M+H) 1211.8492, found 1211.8444.

For **2**: The same procedure was used. The crude product was purified by the column chromatography (silica, THF/CH₂Cl₂ (50/50 % v/v)). A light yellow gummy solid was obtained. Yield: 0.83 g (62 %). ¹H

NMR (δ =ppm, CDCl₃, 400MHz) 7.40 (s, 2H), 6.63 (s, 4H), 6.59 (s, 2H), 5.02 (s, 6H), 4.45 (t, J =4.8 Hz, 2H), 4.18-4.21 (br, 2H), 3.86-3.94 (m, 14H), 3.82 (t, J =5.2 Hz, 2H), 3.74 (t, J =6.4 Hz, 4H), 3.63-3.70 (m, 6H), 3.17-3.21 (m, 2H), 2.78 (t, J =5.6 Hz, 2H), 1.25-1.77 (m), 0.87 (t, J =6.8 Hz, 27H). ¹³C NMR (δ =ppm, CDCl₃, 400MHz) 166.07, 156.62, 153.26, 153.01, 152.56, 142.71, 137.85, 137.77, 132.36, 131.64, 125.19, 109.78, 106.15, 75.14, 73.37, 73.29, 71.71, 70.60, 70.78, 69.64, 69.29, 69.06, 68.85, 64.19, 63.78, 43.68, 41.64, 43.68, 41.64, 31.92, 30.39, 29.79, 29.73, 29.68, 29.57, 29.49, 29.45, 29.39, 29.37, 26.21, 26.19, 26.16, 22.67, 14.08. Mass (MALDI-TOF) calcd. for C₁₄₅H₂₅₈N₂O₁₈ (M) 2317.60, found 2318.1.

Polymerization of 3-5. Polymerizations were conducted with γ -benzyl-L-glutamate-N-carboxyanhydride and the dendron **1** and **2** in a DMF/THF mixture in a drybox under a purified N₂ atmosphere. As a representative procedure: Polymer **3**: To a 5 ml THF solution of **1** (120 mg, 0.1 mmol), 5 ml DMF solution of γ -benzyl-L-glutamate NCA (0.92 g, 3.5 mmol) was added at once. The flask was sealed with a rubber septum and the reaction was allowed to proceed for 72 h at room temperature. The solution was precipitated in cold diethyl ether and the resulting white powder was collected and washed with diethyl ether and methanol. Vacuum drying of the product gave a white powder (710 mg, 91 %). ¹H NMR (δ =ppm, CDCl₃, 400MHz) 8.15-8.45 (br, NH), 7.24-7.37 (br, m, Ar), 6.86 (d, J = 8.4 Hz, 4H), 6.73 (d, J = 8.8 Hz, 2H), 4.97-5.03 (br, m, Ph-CH₂-), 4.39-4.40 (br), 3.89-3.96 (m), 3.57 (br), 2.10-2.60 (br, β , γ CH₂), 1.74-1.79 (m), 1.43-1.45 (br), 1.26 (s), 0.87 (t, J = 6.8 Hz). Dp_n (PBLG) = 30 (¹H NMR). GPC (THF/[nBu₄N]Br 0.003M) M_n = 29,450 g/mol, PDI (M_w/M_n) = 1.18. FT-IR (cm⁻¹, Nujol, KBr): 1651 (amide I), 1544 (amide II). For **4** (900 mg, 84 %): Dp_n (PBLG) = 43 (¹H NMR). GPC (THF/[nBu₄N]Br 0.003M) M_n = 34,100 g/mol, PDI (M_w/M_n) = 1.18. FT-IR (cm⁻¹, Nujol, KBr): 1650 (amide I), 1544 (amide II).

For **5** (780 mg, 87 %): ¹H NMR (δ =ppm, CDCl₃, 400MHz) 8.31 (br, NH), 7.25 (br, m, Ph), 6.63 (s, 4H), 6.59 (s, 2H), 5.03 (br, Ph-CH₂-), 3.70-4.00 (br, -OCH₂-, α -CH), 2.10-2.60 (br, β , γ CH₂), 1.74-1.79 (m), 1.43-1.45 (br), 1.25 (s), 0.87 (t, J = 6.8 Hz). DP_n (PBLG) = 78 (¹H NMR), GPC (THF/[nBu₄N]Br

0.003M) $M_n = 48,900$ g/mol, PDI (M_w/M_n) = 1.21. FT-IR (cm^{-1} , Nujol, KBr): 1651 (amide I), 1543 (amide II).

References

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2. Poché, D. S.; Moore, M. J.; Bowles, J. L. *Synth. Commun.* **1999**, *29*, 843-854.
3. Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539-1555.

Figure S1. A and B. AFM height (A) and phase (B) images of the dried toluene gel of **4**. C. The height profile of the AFM image of the toluene gel of **4**.

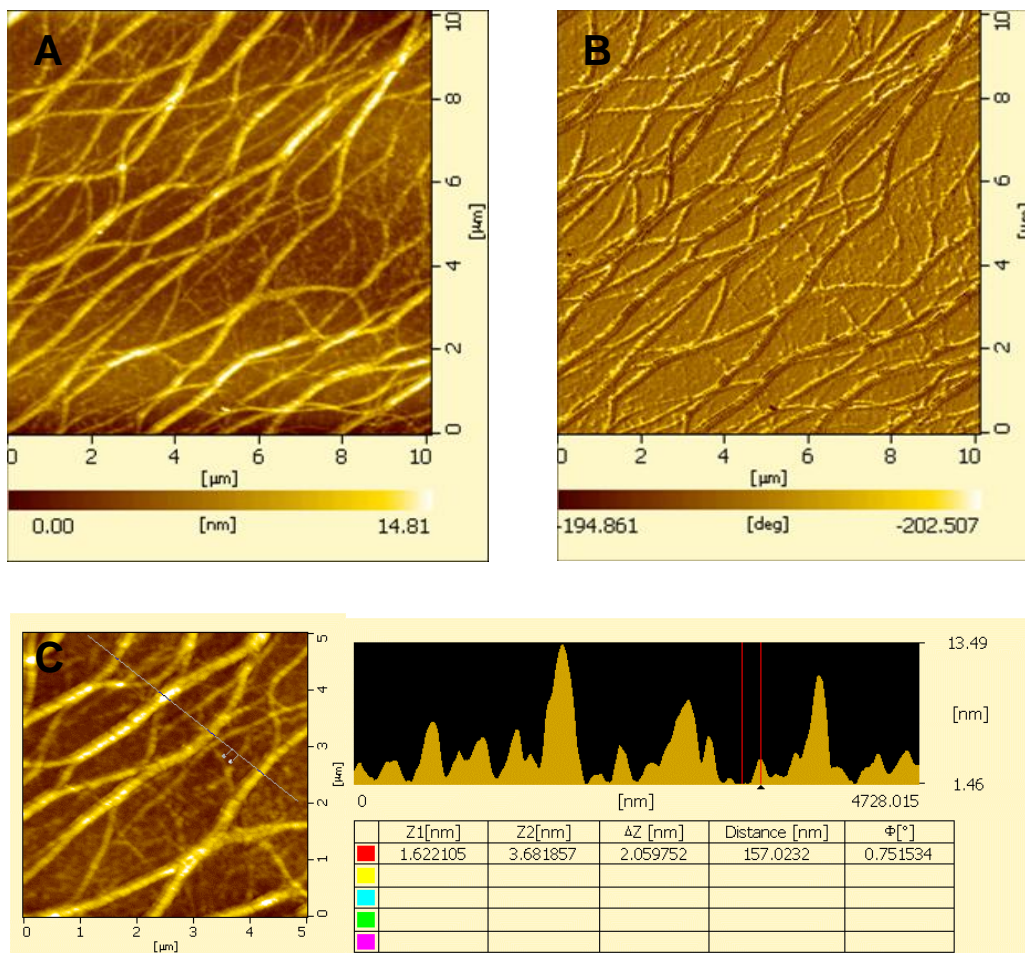


Figure S2. A and B. AFM height (A) and phase (B) images of the dried toluene gel of **5**. C. The height profile of the AFM image of the toluene gel of **5**.

