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Supporting Information

Non-tortuous Ionic Transport in Robust Micellar Liquid Crystalline Phases with Cubic Symmetry

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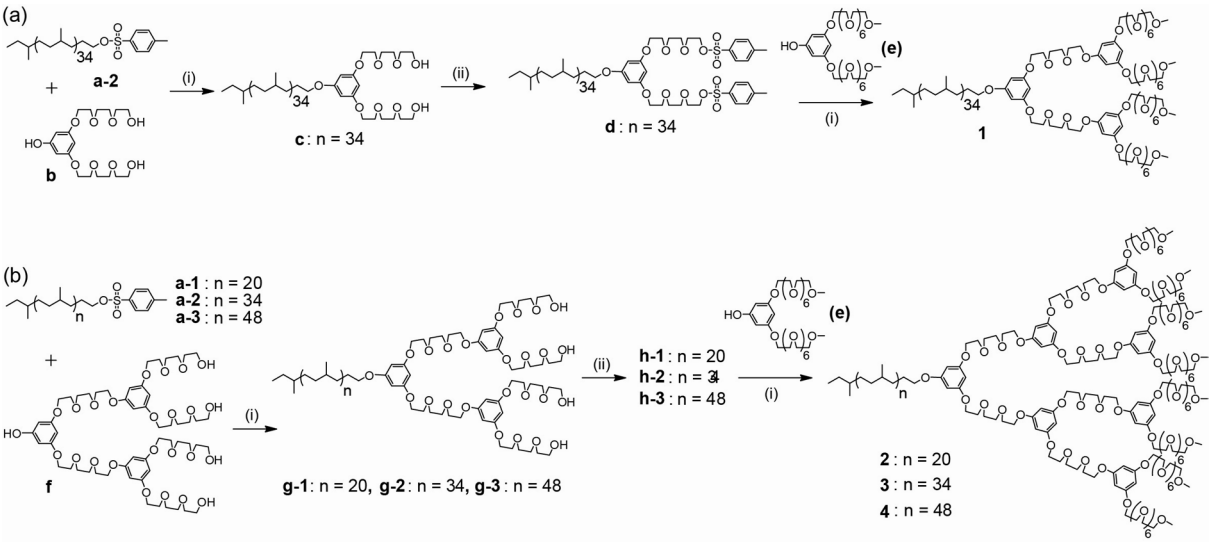
General methods

A Perkin Elmer DSC-7 was used to determine glass transitions, which were reported as the half-way position of the transition heat flow. In all cases, the heating rate was 10 ^{o}C/min. Small angle X-ray scattering (SAXS) measurements were performed in transmission mode with synchrotron radiation at the 10C1 beam line of the Pohang Accelerator Laboratory (PAL), Korea. The sample was held in an aluminum sample holder with films on both sides. The heaing and cooling rates were 2 °C/min. All dynamic mechanical spectroscopy (DMS) data were recorded on a Rheometrics Solid Analyzer RSA 2 equipped with a shear sandwich geometry (0.5-mm thickness). Dynamic mechanical spectrometer was operated at small strain (1%) and low frequency (1 rad/s), and temperature ramps were conducted at 2 °C/min. Dynamic elastic (G´) moduli were recorded as a function of temperature. Ionic conductivities were measured by the complex impedance method using a Schlumberger Solartron 1260 impedance analyzer (frequency range: 10 Hz~10 MHz, applied voltage: 1.0 V) with a temperature controller (heating rate: 2.0 ^{o}C/min) under vacuum. The radius and thickness of the cell in the measurements were 1.9 mm and 1.2 mm, respectively. DC conductivities were practically calculated to be the product of 1/R (Ω^{-1}) times cell constants (cm^{-1}).

Synthesis

The synthesis of the block copolymers was performed mostly with Williamson etherification and tosylation, as outlined in Scheme S1. Linear poly(ethylene-*alt*-propylene) coils (**a-1**, **a-2**, and **a-3**) were prepared by a combination of living anionic polymerization of isoprene, catalytic hydrogenation, and the subsequent tosylation of the hydroxyl end group.[S1] Hydrophilic branching (**b** and **f**) and peripheral (**e**) precursors were prepared using Williamson etherification, tosylation and debenzylation.[S1]



Scheme S1. Synthesis of block copolymer **1**-**4**. Reagents and conditions: (i) K_2CO_3, KI, CH_3CN; (ii) TsCl, pyridine, CH_2Cl_2.

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Compounds c, g-1, g-2, and g-3. Compounds **c**, **g-1**, **g-2**, and **g-3** were synthesized using the similar procedure except for the stoichiometry of reactants and purification. A representative synthesis is described for compound **g-1**. To a solution of compound **a-1** (1.97 g, 1.24 mmol, 2.0 equiv), **f** (0.7 g, 0.62 mmol, 1.0 equiv) in anhydrous acetonitrile (7 mL) and THF (21 mL) were added K_2CO_3 (256 mg, 1.85 mmol, 3.0 equiv) and KI (205 mg, 1.23 mmol, 2.0 equiv). The reaction mixture was stirred for 48 h at 95 °C under nitrogen. The resulting solution was cooled to room temperature, and concentrated under reduced pressure. The resulting mixture was dissolved with CH_2Cl_2, carefully treated with diluted aqueous HCl solution, washed with brine. After removal of the solvent under reduced pressure, the residue was purified by silica-column chromatography (CH_2Cl_2:CH_3OH = 19:1) to yield a colourless viscous oil (1.42 g, 89%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, C*H*$_3$), 0.97-1.45 (br, C*H* and C*H*$_2$), 2.58 (t, 4H), 3.61 (m, 8H), 3.71 (m, 32H), 3.84 (m, 16H), 3.89 (t, 2H), 4.07 (m, 16H), 6.08 (s, 4H), 6.11 (s, 5H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.9, 24.7, 32.9, 33.3, 37.6, 61.9, 67.5, 69.8, 70.5, 70.9, 72.7, 94.6, 160.6. M_w/M_n (GPC) = 1.03.

Compound c. Reaction condition: compound **2b** (5.4 g, 2.16 mmol, 1.0 equiv), compound **5** (2.53 g, 6.48 mmol, 3.0 equiv), K_2CO_3 (1.35 g, 9.72 mmol, 4.5 equiv), KI (360 mg, 2.16 mmol, 1.0 equiv) in anhydrous acetonitrile (30 mL) and THF (60 mL) at 95 °C for 48 h. Purification: a repetitive dissolution/precipitation method with CH_2Cl_2/methanol. Yield: 96%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 2.58 (t, 2H), 3.61 (m, 4H), 3.71 (m, 12H), 3.84 (m, 4H), 3.89 (t, 2H), 4.07 (m, 4H), 6.09 (s, 2H), 6.13 (s, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.9, 24.7, 33.0, 37.6, 61.9, 67.5, 69.8, 70.6, 71.0, 72.6, 113.1, 113.2, 160.5. M_w/M_n (GPC) = 1.03.

Compound g-2. Reaction condition: compound **2b** (1.91 g, 0.75 mmol, 1.0 equiv), compound **7** (1.27 g, 1.12 mmol, 1.5 equiv), K_2CO_3 (467 mg, 3.38 mmol, 4.5 equiv), KI (104 mg, 0.75 mmol, 1.0 equiv) in anhydrous acetonitrile (7 mL) and THF (28 mL) at 95 °C for 48 h. Purification: a repetitive dissolution/precipitation method with CH_2Cl_2/methanol. Yield: 92%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 2.58 (t, 4H), 3.61 (m, 8H), 3.71 (m, 32H), 3.84 (m, 16H), 3.89 (t, 2H), 4.07 (m, 16H), 6.08 (s, 4H), 6.11 (s, 5H). ^{13}C NMR ($CDCl_3$, δ, ppm): 20.0, 24.7, 33.0, 33.3, 37.6, 61.9, 67.5, 69.8, 70.6, 71.0, 72.7, 94.6, 160.5. M_w/M_n (GPC) = 1.02.

Compound g-3. Reaction condition: compound **2c** (1.89 g, 0.54 mmol, 1.0 equiv), compound **7** (0.76 g, 0.67 mmol, 1.24 equiv), K_2CO_3 (277 mg, 2.0 mmol, 3.9 equiv), KI (91 mg, 0.54 mmol, 1.0 equiv) in anhydrous acetonitrile (7 mL) and THF (35 mL) at 95 °C for 48 h. Purification: a repetitive dissolution/precipitation method with CH_2Cl_2/methanol. Yield: 74%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 144H, C*H*$_3$), 0.97-1.45 (br, 336H, C*H* and C*H*$_2$), 2.58 (t, 4H) 3.61 (m, 8H), 3.71 (m, 32H), 3.84 (m, 16H), 3.89 (t, 2H), 4.07 (m, 16H), 6.08 (s, 4H), 6.11 (s, 5H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.9, 24.6, 33.0, 33.3, 37.7, 61.9, 67.5, 69.8, 70.6, 71.0, 72.7, 94.6, 160.5. M_w/M_n (GPC) = 1.02.

Compounds d, h-1, h-2, and h-3. Compounds **d**, **h-1**, **h-2**, and **h-3** were synthesized using the same procedure. A representative synthesis is described for compound **h-1**. To a solution of **g-1** (1.34 g, 0.52 mmol, 1.0 equiv) and 4-toluenesulfonyl chloride (1.97 g, 10.4 mmol, 20 equiv) in anhydrous CH_2Cl_2 (60 mL) was added pyridine (0.84 mL, 10.4 mmol, 20 equiv). The reaction mixture was stirred for 24 h at room temperature. The resulting mixture was treated with diluted aqueous HCl solution, and washed with brine. After removal of the solvent under reduced pressure, the residue was purified by flash silica-column chromatographies (CH_2Cl_2:EtOAc = 9:1 to 7:3) to yield a yellowish viscous solid (1.34 g, 81%). M_w/M_n (GPC) = 1.03. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, C*H*$_3$), 0.97-1.45 (br, C*H* and C*H*$_2$), 2.42 (s, 12H), 3.56-3.98 (m, 48H), 4.03 (m, 16H), 4.15 (t, 8H), 6.08 (s, 4H), 6.11 (s, 5H), 7.32 (d, 8H), 7.78 (d, 8H).

Compound d. Yield: 92%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 2.42 (s, 6H), 3.56-3.98 (m, 12H), 4.03 (m, 4H), 4.15 (t, 4H), 6.08 (s, 3H), 7.32 (d, 4H), 7.78 (d, 4H). M_w/M_n (GPC) = 1.03.

Compound h-2. Yield: 55%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 2.42 (s, 12H), 3.56-3.98 (m, 48H), 4.03 (m, 16H), 4.15 (t, 8H), 6.08 (s, 4H), 6.09 (s, 5H), 7.32 (d, 8H), 7.78 (d, 8H). M_w/M_n (GPC) = 1.02.

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Compound h-3. Yield: 66%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 2.42 (s, 12H), 3.56-3.98 (m, 48H), 4.03 (m, 16H), 4.15 (t, 8H), 6.08 (s, 4H), 6.09 (s, 5H), 7.32 (d, 8H), 7.78 (d, 8H). M_w/M_n (GPC) = 1.02.

Block copolymers. Block copolymers **1-4** were synthesized using the same procedure. A representative synthesis is described for **2**. To a solution of **h-1** (1.27 g, 0.39 mmol, 1.0 equiv) and **e** (1.88 g, 2.38 mmol, 6.0 equiv) in anhydrous acetonitrile (13 mL) and THF (32 mL) were added K_2CO_3 (495 mg, 3.57 mmol, 9.0 equiv) and KI (132 mg, 0.79 mmol, 2.0 equiv). The reaction mixture was stirred for 48 h at 95 °C under nitrogen environment. The resulting solution was cooled to room temperature, and concentrated under reduced pressure. The resulting mixture was redissolved with CH_2Cl_2, and carefully treated with diluted aqueous HCl solution. The organic layer was washed with brine. After removal of the solvent under reduced pressure, the residue was purified by flash silica-column chromatography (CH_2Cl_2:CH_3OH = 49:1 to 19:1) and a preparative GPC to yield a yellowish viscous solid (1.47 g, 66%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 60H, C*H*$_3$), 0.97-1.45 (br, 140H, C*H* and C*H*$_2$), 3.37 (s, 24H), 3.53 (t, 16H), 3.60-3.79 (br, 232H), 3.82 (m, 40H), 4.05 (t, 40H), 6.08 (s, 21H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.6, 24.4, 32.7, 37.5, 59.0, 67.3, 69.6, 70.5, 94.2, 160.4. M_w/M_n (GPC) = 1.02.
1. Yield: 71%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 3.37 (s, 12H), 3.53 (t, 8H), 3.60-3.79 (br, 112H), 3.82 (m, 16H), 4.05 (t, 16H), 6.08 (s, 9H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.8, 24.5, 32.8, 37.5, 59.0, 67.4, 69.7, 70.7, 71.9, 94.3, 160.5.M_w/M_n (GPC) = 1.02.
3. Yield: 62%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 102H, C*H*$_3$), 0.97-1.45 (br, 238H, C*H* and C*H*$_2$), 3.37 (s, 24H), 3.53 (t, 16H), 3.60-3.79 (br, 232H), 3.82 (m, 40H), 4.05 (t, 40H), 6.08 (s, 21H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.6, 24.4, 32.7, 37.5, 59.0, 67.3, 69.6, 70.5, 94.2, 160.4. M_w/M_n (GPC) = 1.02.
4. Yield: 74%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 144H, C*H*$_3$), 0.97-1.45 (br, 336H, C*H* and C*H*$_2$), 3.37 (s, 24H), 3.53 (t, 16H), 3.60-3.79 (br, 232H), 3.82 (m, 40H), 4.05 (t, 40H), 6.08 (s, 21H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.7, 24.4, 32.7, 37.5, 59.0, 67.3, 69.6, 70.6, 94.2, 160.4. M_w/M_n (GPC) = 1.02.

Preparation of ionic samples 1-Li$^+$-4-Li$^+$. The preparation was done by mixing each block copolymer solution in dry THF with an appropriate volume of 0.1 M lithium triflate solution in dry THF, followed by slow evaporation of the solvent under reduced pressure at room temperature. The samples were then dried in a vacuum oven at 100 ^{o}C for 24 hours to maintain constant mass.

Reference
S1. J. Song and B.-K. Cho, *Soft Matter*, 2012, **8**, 3419.

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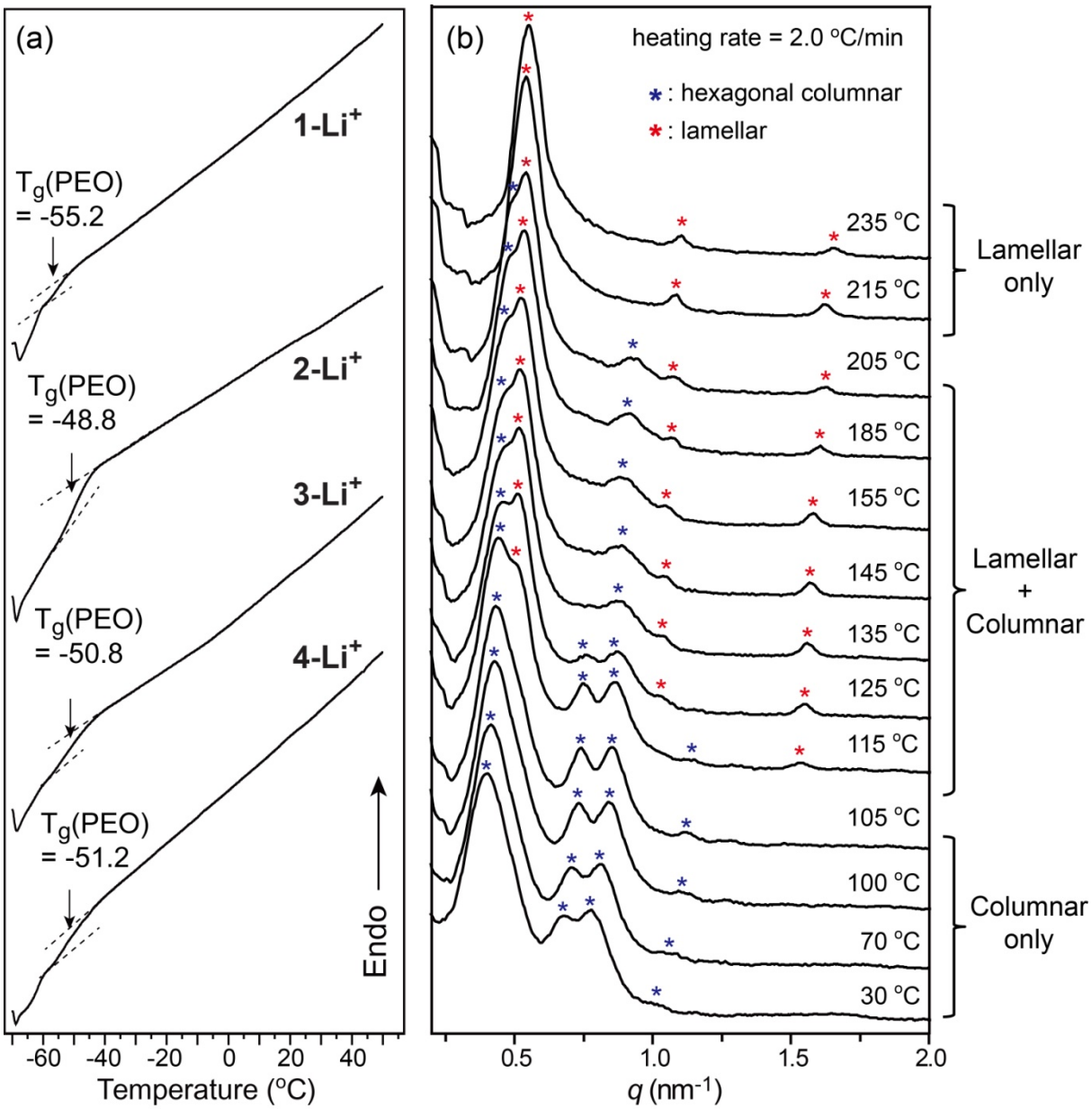

Fig. S1 (a) DSC thermograms of ionic samples, and (b) the SAXS data of **4-Li**$^+$ as a function of temperature.