Supporting Information

Soluble microporous ladder polymers formed by stepwise nucleophilic substitution of octafluorocyclopentene

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1. Characterization

NMR (^{1}H, ^{13}C, and ^{19}F) spectra were recorded on Bruker UltraShield Avance 400 MHz NMR instrument using deuterated chloroform as solvent at room temperature. Molecular weights and molecular weight distribution of polymers were determined using Waters GPC system equipped with a Waters 515 HPLC pump, 717plus auto sampler, and 2414 refractive-index detector. The following Styragel GPC columns were arranged in a series: guard, HR5E (x2) (30 x 4.6 mm ID), HR1 and HR0.5. THF was used as eluent with flow rate of 1 mL/min and the molecular weight of polymers were calculated against narrow polystyrene standards. MALDI-TOF MS analysis of polymers and model compounds were carried out using Bruker Autoflex speed system with *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix in either positive or negative mode of ionization and the spectra were processed using Polytool software.The nitrogen adsorption/desorption measurements were analyzed using Quantachrome BET analyzer (Autosorb-6) at 25°C in 24 hrs. Prior to analysis the samples were out gassed for 24 hrs at 25°C.

2. Experimental Section

2.1. Materials

Phenol, 4,4′-(hexafluoroisopropylidene)diphenol (6F-BP-A), 4,4′-sulfonyldiphenol (SDP), and bisphenol-A (BP-A) were received with the highest purity from Sigma Aldrich, USA and used without further purification. 4,4'-Dihydroxybenzophenone, (DHBP) 3,5-bis(trifluoro methyl)phenol, and potassium carbonate were received from AlfaAesar, USA. Octafluorocyclopentene (OFCP) was purchased from TCI, Japan. *N,N*-Dimethylformamide (DMF) was purified by Glass contour-6 solvent purification system.

2.2. Linear Polymer Synthesis (Preparation of LIN P4)

A typical polymerization reaction was carried out as given below: Octafluorocyclopentene (0.6 mL, 4.47 mmol) was transferred via syringe into 25 mL of dry DMF under nitrogen atmosphere followed by one equivalent of 4,4′-sulfonyldiphenol (1.119 g, 4.47 mmol) at 25°C. Potassium carbonate (1.85 g, 13.41 mmol) was then added and the reaction was continued for 24 hrs at 25 °C. Then the reaction mixture was poured into deionized water acidified with a few drops of conc. HCl. The white color solid precipitated was separated by filtration. After drying, the white solid was dissolved in THF (3 mL) and precipitated in methanol under vigorous stirring. The precipitate was filtered, washed with methanol and dried in a vacuum oven. Yield: 1.20 g (76%). Molecular weight results by GPC using THF as eluent: M_n = 8900; M_w = 18600; M_w/M_n = 2.1.

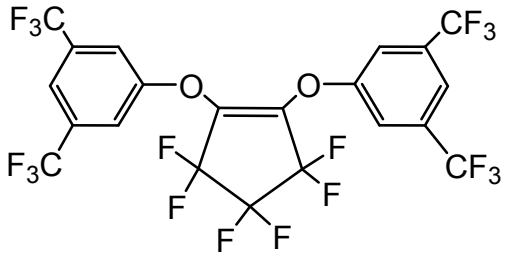
2.3. Synthesis of Ladder Polymer from Linear Polymer (Preparation of LAD P1 by Two Step Process)

LIN P3 (Table 1) (M_n = 7100; M_w = 12300; M_w/M_n = 2.4) (0.15 g, 0.374 mmol) was dissolved in 20 mL of dry DMF under nitrogen atmosphere followed by one equivalent of 4,4′-(hexafluoroisopropylidene)diphenol (126 mg, 0.374 mmol). Potassium carbonate (155 mg, 1.04 mmol) was then added and the reaction was continued for 24 hrs at room temperature. The reaction mixture was then poured into deionized water acidified with few drops of conc. HCl. The solid precipitated was separated by filtration. The dried polymer was purified by precipitating the THF solution of polymer in methanol to yield a white color powder (135 mg, 52%). Molecular weight results by GPC using THF as eluent: M_n = 9800; M_w = 24300; M_w/M_n = 2.5.

2.4. Synthesis of Ladder Polymer - One Step Process (Preparation of LAD P5)

OFCP (0.5 mL, 3.725 mmol) was dissolved in 20 mL of dry DMF under nitrogen atmosphere followed by two equivalents of bisphenol-A (1.7 g, 7.45 mmol). Potassium carbonate (3.08 g, 22.48 mmol) was added and the reaction was stirred for 24 hrs at 55 °C. The reaction mixture was then poured into deionized water acidified by adding few drops of conc. HCl. The white solid thus obtained was separated by filtration. The dried polymer was dissolved in THF and precipitated in methanol to yield a white powder (727 mg: 33%). Molecular weight results by GPC using THF as eluent: M_n = 5900; M_w = 8600; M_w/M_n = 1.5.

Disubstitution of OFCP: Synthesis of 5,5'-((perfluorocyclopent-1-ene-1,2-diyl)bis(oxy)) bis(1,3-bis (trifluoromethyl) benzene)



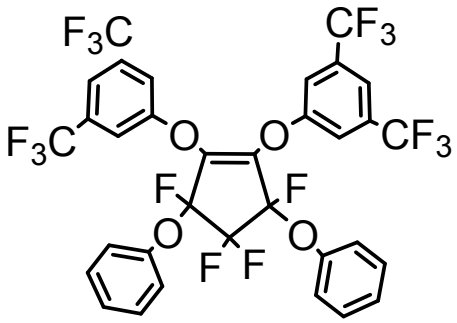
A 50 mL two-neck round bottom flask was charged with 25 mL of dry DMF followed by OFCP (1.0 mL, 7.45 mmol) and 3,5-bis(trifluoromethyl)phenol (2.27 mL, 14.9 mmol) under nitrogen atmosphere. Potassium carbonate (3.09 g, 22.35 mmol) was added and the reaction mixture was stirred for 24 hrs at room temperature. Then the reaction mixture was poured into deionized water acidified with few drops of conc. HCl. The compound separated was extracted with diethyl ether. It was then purified by silica gel column chromatography using ethyl acetate/hexane solvent mixture to yield a colorless viscous liquid of 5,5'-((perfluorocyclopent-1-ene-1,2-diyl)bis(oxy))bis(1,3-bis(trifluoromethyl)benzene) (yield: 93%). The compound was confirmed by NMR spectra (^{1}H, and ^{19}F-NMR) and elemental analyses.

^{1}H NMR ($CDCl_3$, 400.13 MHz, δ): 7.15-7.15 (4H, s), 7.58 (2H, s)

^{19}F NMR ($CDCl_3$, 376.49 MHz, δ): -63.61 (12F, s), -114.58 to -114.59 (4F, t), -130.18 to -130.20 (2F, m)

Elemental analysis Calc'd for C21H6F18O2: C (39.89), H (0.96); Found: C (40.23), H (1.02)

Additional substitution of disubstituted product: 5,5'-((3,4,4,5-tetrafluoro-3,5-diphenoxycyclopent-1-ene-1,2-diyl)bis (oxy))bis(1,3-bis(trifluoromethyl)benzene)



5,5'-((Perfluorocyclopent-1-ene-1,2-diyl)bis(oxy))bis(1,3-bis(trifluoromethyl) benzene) (500 mg, 0.79 mmol) was charged to 50 mL two-neck round bottom flask followed by 15 mL of dry DMF. Two equivalents of phenol (149 mg, 1.63 mmol) followed by potassium carbonate

(328 mg, 2.37 mmol) were added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 hrs. Then the reaction mixture was poured into deionized water acidified with a few drops of conc. HCl. The compound separated was extracted with diethyl ether. The compound was then purified by column chromatography in silica gel using ethyl acetate/hexane solvent mixture to yield a colorless viscous oil of 5,5'-((3,4,4,5-tetrafluoro-3,5-diphenoxycyclopent-1-ene-1,2-diyl)bis(oxy))bis(1,3-bis(trifluoromethyl)benzene) (yield: 85%). The compound was confirmed by NMR (^{1}H, and ^{19}F-NMR) and elemental analyses.

^{1}H NMR ($CDCl_3$, 400.13 MHz, δ): 6.59 (2H, s), 6.90 (2H, s), 7.12 – 7.17 (2H, m), 7.29-7.30 (8H, d), 7.34 (1H, s), 7.41 (1H, s)

^{19}F NMR ($CDCl_3$, 376.49 MHz, δ): -63.54 (6F,s), -63.61 (6F, s), -114.63 (2F, s), -124.88 to -124.90 (2F, t)

Elemental analysis Calc'd for C33H16F16O4 C (50.79), H (2.07); Found: C (51.00), H (1.73)

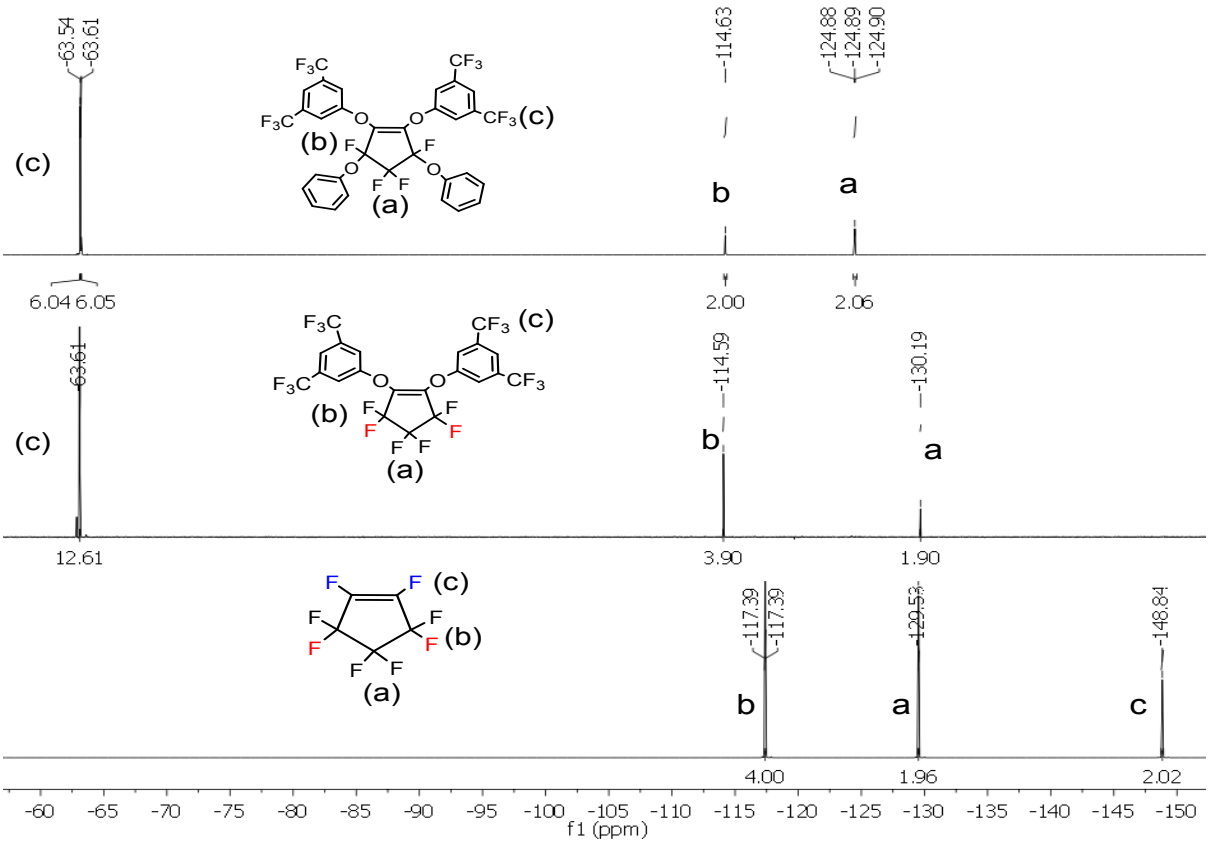


Fig. S1 ^{19}F-NMR spectra of OFCP, di- and tetrasubstituted compounds.

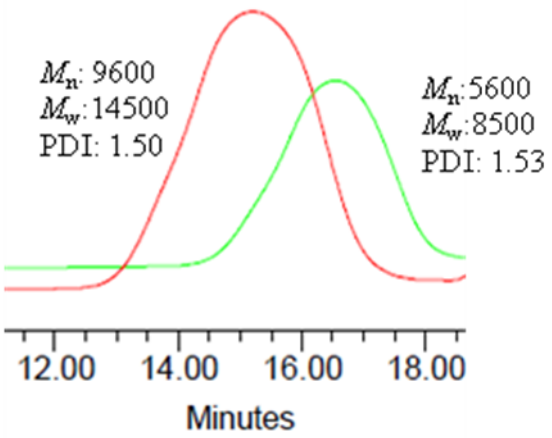


Fig. S2 Gel permeation chromatogram of (a) linear polymer, BP-A-OFCP (green) and (b) ladder polymer BP-A-OFCP-6F-BP-A (red).

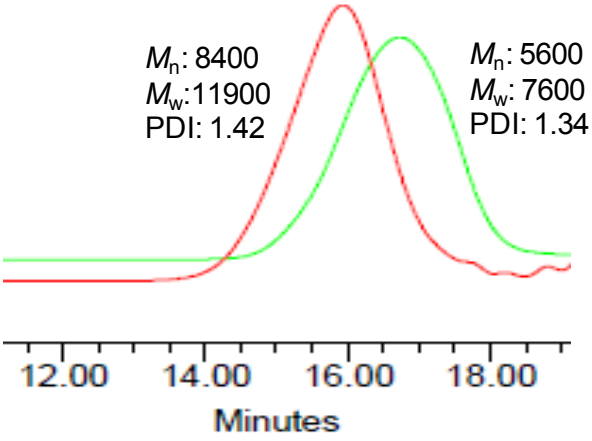


Fig. S3 Gel permeation chromatogram of (a) linear polymer, DHBP-OFCP (green) and (b) ladder polymer, DHBP-OFCP-6F-BP-A (red).

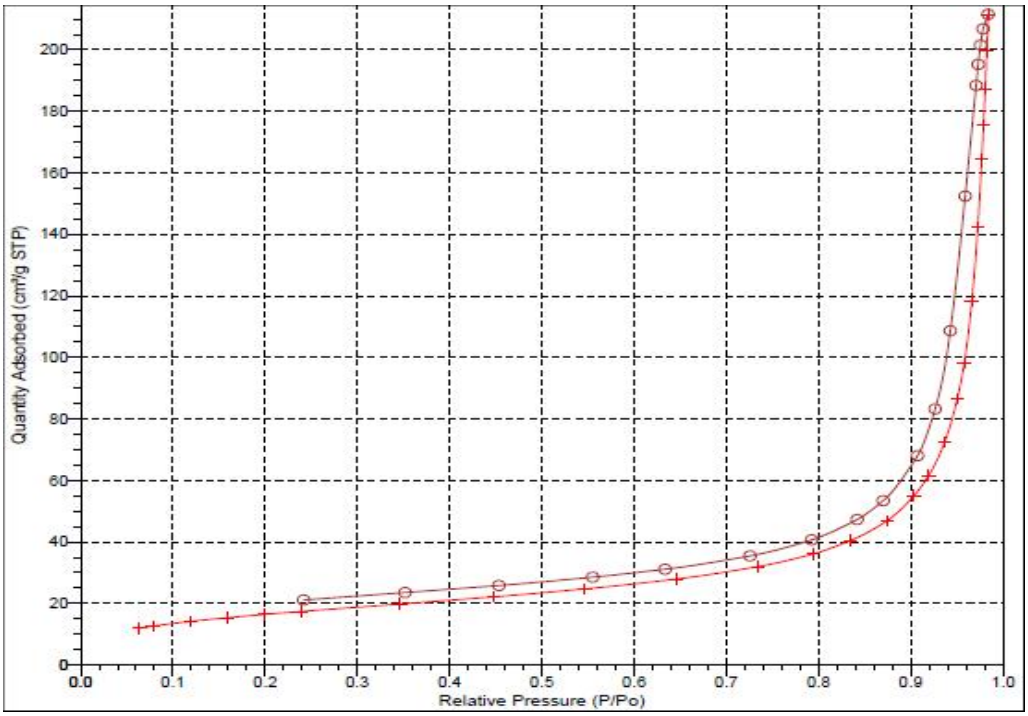


Fig. S4 The nitrogen adsorption/desorption isotherm of LAD P6.