

Supporting Information

Synthesis and Extremely High Gas Permeability of Polyacetylenes Containing

Indan/Tetrahydronaphthalene Groups

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General Considerations. Tantalum(V) chloride (TaCl_5 , Aldrich) was used without further purification. Tetrabutyltin ($n\text{-Bu}_4\text{Sn}$, Wako) was used after distillation. Cyclohexane, benzene, and dichloromethane were distilled from calcium hydride under dry nitrogen prior to use. α -Methylstyrene (Aldrich), *tert*-butyl alcohol (Aldrich), 2-phenyl-2-propanol (Wako), thionyl chloride (Wako), titanium(IV) chloride (1.0 M in methylene chloride, Aldrich), 2,3-dimethyl-2-butene (Aldrich), and 2,5-dichloro-2,5-dimethylhexane (Wako) were used as received without further purification. 1,1,3,3-tetramethylindan,¹ 1,1,2,2,3,3-hexamethylindan,² and 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene³ were prepared according to the literature methods. Monomers **1–3** were synthesized referring to the literature concerning iodination and ethynylation.^{4,5}

Molecular weights of polymers were estimated by gel permeation chromatography (CHCl_3 as eluent, polystyrene calibration). IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. NMR spectra were recorded on a JEOL EX-400

spectrometer. The melting points were measured with a Yanaco micro melting point apparatus. Elemental analysis of monomers was carried out at the Microanalytical Center of Kyoto University. UV-vis spectra were recorded on a Shimadzu UV-2200 spectrophotometer. Thermogravimetric analysis (TGA) was conducted in air with a Perkin-Elmer TGA7 thermal analyzer.

1-(1,1,3,3-tetramethylindan-5-yl)-2-phenylacetylene (1).

A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, 1,1,3,3-tetramethylindan (16.4 g, 94 mmol), iodine (9.5 g, 37 mmol), and periodic acid (4.3 g, 19 mmol) was dissolved in acetic acid aqueous solution (100 mL, 80%) containing sulfuric acid (3.0 mL). The reaction mixture was stirred at 80 °C for 20 h. After H₂O (200 mL) was added, the solution was extracted with diethyl ether. The organic layer was washed first with 1 M Na₂S₂O₃·5H₂O aq (5 × 200 mL) and then with H₂O (3 × 200 mL). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 5-iodo-1,1,3,3-tetramethylindan as a colorless liquid; yield 20%. ¹H NMR (CDCl₃) δ (ppm): 7.50 (dd, ³J = 8.0 Hz, ⁴J = 1.6 Hz, 1H, Ar), 7.42 (d, J = 1.6 Hz, 1H, Ar), 6.87 (d, J = 8.0 Hz, 1H, Ar), 1.81 (s, 2H, CH₂), 1.28 (s, 6H, CH₃), 1.28 (s, 6H, CH₃). ¹³C NMR (CDCl₃) δ (ppm): 153.9, 151.0, 135.6, 131.9, 124.7, 91.8, 56.3, 42.6, 42.4, 31.4, 31.3. A 300 mL

three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar.

After the flask was flushed with nitrogen, 5-iodo-1,1,3,3-tetramethylindan (5.6 g, 19 mmol), dichlorobis(triphenylphosphine)palladium (0.070 g, 0.10 mmol), cuprous iodide (0.11 g, 0.58 mmol) and triphenylphosphine (0.10 g, 0.38 mmol) were placed in the flask and dissolved in triethylamine (100 mL) at room temperature. Then, a solution of phenylacetylene (2.6 g, 25 mmol) in triethylamine (20 mL) was added dropwise, and stirring was continued at room temperature for 5 h. After that, triethylamine in the reaction mixture was evaporated off, and then ether (200 mL) was added to the residual mass. Solvent-insoluble solid was filtered off, and the filtrate was washed with 1 M HCl aq. and then with water (3 × 200 mL). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a colorless liquid; yield 80%. IR (KBr, cm^{-1}): 2958, 2360, 1597, 1493, 1315, 1065, 891, 829, 756, 690, 521. ^1H NMR (CDCl_3) δ (ppm): 7.54–7.51 (m, 2H, Ar), 7.30–7.38 (m, 5H, Ar), 7.09 (d, $J = 8.0$ Hz, 1H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{13}C NMR (CDCl_3) δ (ppm): 151.9, 151.4, 131.5, 130.4, 128.3, 128.0, 125.9, 123.6, 122.6, 121.4, 90.1, 88.3, 56.5, 42.6, 42.5, 31.4, 31.3. Anal. Calcd for $\text{C}_{21}\text{H}_{22}$: C, 91.92; H, 8.08. Found: C, 91.93; H, 8.26.

1-(1,1,2,2,3,3-hexamethylindan-5-yl)-2-phenylacetylene (2).

5-Iodo-1,1,2,2,3,3-hexamethylindan was prepared by the same method as for

5-iodo-1,1,3,3-tetramethylindan using 1,1,2,2,3,3-hexamethylindan instead of 1,1,3,3-tetramethylindan to give a white solid; yield 90%, mp 72–74 °C. ^1H NMR (CDCl_3) δ (ppm): 7.50 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H, Ar), 7.42 (d, $J = 1.6$ Hz, 1H, Ar), 6.88 (d, $J = 8.0$ Hz, 1H, Ar), 1.18 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR (CDCl_3) δ (ppm): 153.3, 150.3, 135.6, 131.9, 124.8, 91.6, 48.5, 47.8, 47.5, 27.3, 27.2, 21.4.

Monomer **2** was prepared by the same method as for monomer **1** using 5-iodo-1,1,2,2,3,3-hexamethylindan instead of 5-iodo-1,1,3,3-tetramethylindan to give a white solid; yield 85%, mp 136–138 °C. IR (KBr, cm^{-1}): 2981, 2950, 1597, 1493, 1373, 1111, 887, 833, 756, 690, 532. ^1H NMR (CDCl_3) δ (ppm): 7.54–7.51 (m, 2H, Ar), 7.39–7.30 (m, 5H, Ar), 7.10 (d, $J = 8.0$ Hz, 1H, Ar), 1.18 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR (CDCl_3) δ (ppm): 153.3, 150.3, 135.6, 131.9, 124.8, 91.6, 48.5, 47.8, 47.5, 27.3, 27.2, 21.4. Anal. Calcd for $\text{C}_{23}\text{H}_{26}$: C, 91.34; H, 8.66. Found: C, 91.57; H, 8.72.

1-(1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene-6-yl)-2-phenylacetylene (3).

6-Iodo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene was prepared by the same method as for 5-iodo-1,1,3,3-tetramethylindan using 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene instead of 1,1,3,3-tetramethylindan to give a white solid; yield 88%, mp 58–60 °C. ^1H NMR (CDCl_3) δ (ppm): 7.59 (s, 1H, Ar), 7.42 (d, $J = 8.4$ Hz, 1H, Ar), 7.03 (d, $J = 8.4$ Hz, 1H, Ar), 1.66 (virtual s, 4H, CH_2), 1.26 (s, 6H, CH_3), 1.25 (s, 6H, CH_3). ^{13}C NMR (CDCl_3) δ (ppm): 147.7, 144.6, 135.6, 134.6, 128.7, 91.1, 34.8,

34.3, 34.1, 31.7, 31.7, 31.7. Monomer **3** was prepared by the same method as for monomer **1** using 6-iodo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene instead of 5-iodo-1,1,3,3-tetramethylindan, and was purified by silica gel column chromatography (eluent: hexane), then by preparative high performance liquid chromatography (HPLC) to give a white solid; yield 80%, mp 69–70 °C. IR (KBr, cm^{-1}): 3059, 2958, 1597, 1493, 1362, 1065, 891, 829, 752, 690, 540. ^1H NMR (CDCl_3) δ (ppm): 7.54–7.53 (m, 2H, Ar), 7.52 (s, 1H, Ar), 7.34–7.30 (m, 3H, Ar), 7.28 (s, 2H, Ar), 1.69 (virtual s, 4H, CH_2), 1.30 (s, 6H, CH_3), 1.28 (s, 6H, CH_3). ^{13}C NMR (CDCl_3) δ (ppm): 145.5, 145.0, 131.6, 129.9, 128.7, 128.3, 128.0, 126.6, 123.6, 120.1, 89.9, 88.2, 35.0, 34.9, 34.3, 34.2, 31.8, 31.7. Anal. Calad for $\text{C}_{22}\text{H}_{24}$: C, 91.61; H, 8.39. Found: C, 91.59; H, 8.30.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations: $[\text{M}]_0 = 0.20 \text{ M}$, $[\text{TaCl}_5] = 20 \text{ mM}$, $[\textit{n}\text{-Bu}_4\text{Sn}] = 40 \text{ mM}$. The formed polymers were isolated by precipitation into a large amount of methanol, and dried to constant weight; the polymer yields were determined by gravimetry. Sharp ^1H and ^{13}C NMR spectra of these polymers could not be observed because of high viscosity of solution. Poly(**1**); IR (KBr pellet): 2594, 1489, 1362, 1315, 1192, 1072, 890, 818, 760, 690, 517. Poly(**2**); IR (KBr pellet): 2594, 1489, 1373, 1261, 1157, 1111, 887, 818, 760, 690, 532. Poly(**3**); IR (KBr pellet): 2962, 1600, 1493, 1462, 1389, 1362, 1261, 1014, 806, 690, 532.

Membrane fabrication and desilylation. The membranes (thickness ca. 80–120 μm) were fabricated by casting from toluene [poly(1) and poly(2)] or chloroform solution [poly(3)] of the polymers (concentration ca. 0.50–1.0 wt%) onto a flat-bottomed Petri dish. Then, the dish was covered with a glass vessel to slow solvent evaporation (ca. 3–5 days). After membranes were prepared, they were immersed in methanol for 24 h and dried to constant weight at room temperature for 24 h.

Measurement of gas permeabilities. Gas permeability coefficients (P) of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with a MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated to 0.3 Pa, while the upstream side was filled with a gas at about 1 atm (10^5 Pa), and the increase of pressure in a downstream receiving vessel was measured. The P values were calculated from the slopes of time-pressure curves in the steady state where Fick's law held.

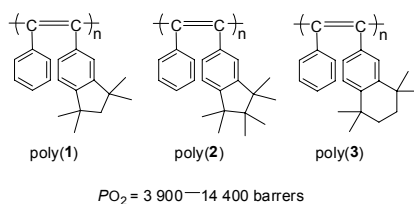
Notes and references

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Polyacetylenes as gas-separation membranes: Acetylenic monomers containing a polymethylated indan or tetrahydronaphthalene moiety were polymerized with $TaCl_5$ - n - Bu_4Sn catalyst to give high molecular weight polymers. Free-standing membranes were fabricated by the casting method. All of the polymer membranes showed unexpected high gas permeability. Poly(1) and poly(2) are the most permeable to gases among all the aromatic polyacetylenes.

Keywords: gas separation · membranes · polymerization · polymers · substituted polyacetylenes