Research Article

Polymerization of Phenylacetylene-Based Monodendrons with Alkoxy Peripheral Groups and Oxygen/Nitrogen Permeation Behavior of Their Membranes

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1. Introduction

The chemical structure and/or morphology of polymers play a role in the permselectivity of nonporous membranes. Recently, dendrimers have attracted much attention in organic and polymer chemistry due to their novel properties or functions, which are based on their specific shapes and precisely defined three-dimensional structures [1–3]. Dendrimers are characterized by a regularly— and fractally—branched treelike architecture. This feature provides a nanoscale homogeneous space in the dendrimers particularly suited for rigid molecular architectures. Additionally, the center and periphery of dendrimer molecule can be modified by substituent groups, which may aid molecular recognition [4].

We have previously synthesized monodendron monomers consisting of \( n \)-linked phenyleneethynylene repeating unit with trimethylsilyl peripheral groups and oligo(dimethylsiloxane) chains and obtained the corresponding polydendrons by polymerization of the monomers using a rhodium (Rh) catalyst [5, 6]. The polydendrons were mechanically stable and excellent for preparing self-supporting membranes. The first-generation polydendron (polyTMS1H) membrane showed an oxygen permselectivity higher than that of the corresponding zero-generation poly(phenylacetylene) derivative (polyTMS0H). In this study, we synthesized polydendrons with alkoxy peripheral groups as shown in Scheme 1 because alkyl domain that would have a better gas barrier property than that of oligo(dimethylsiloxane) domain would be suitable to study the effect of dendritic domain on the gas permselectivity. We examined the oxygen permselectivity of their membranes in relation to their chemical structures.

2. Experimental

2.1. Materials. 3,5-Dibromo-1-(3-hydroxyl-3-methylbutynyl)benzene was synthesized as previously described [7].
2.2. Synthesis of Monomers. The general procedure of 3,5-dialkoxybenzyl chloride is as follows. A solution of 3,5-dialkoxybenzyl alcohol (5 mmol), DMF (0.5 mL), and thionyl chloride (10 mmol) in chloroform (25 mL) was stirred at room temperature for 2–12 h. The excess thionyl chloride and solvents were evaporated under reduced pressure, and then the residue was dissolved in diethyl ether. The ether solution was washed with water, then dried over anhydrous sodium sulfate, filtered, and evaporated. Then, 3,5-dialkoxybenzyl chloride was obtained without further purification.

3,5-Diheptyloxybenzyl Chloride. Yield 94%. IR (KBr; cm$^{-1}$): 2872–2936 (C–H). $^1$H NMR (CDCl$_3$, 270 MHz; ppm): $\delta$ 0.91 (t, 6H, $J = 6.8$ Hz, CH$_3$), 1.33 (m, 8H, CH$_2$), 1.44 (m, 4H, CH$_2$), 1.77 (m, 4H, CH$_2$), 3.93 (t, 4H, $J = 6.5$ Hz, CH$_2$O), 4.50 (s, 2H, CH$_2$Cl), 6.39 (t, 1H, $J = 2.4$ Hz, ArH), 6.51 (d, 2H, $J = 2.4$ Hz, ArH). $^{13}$C NMR (CDCl$_3$; ppm): $\delta$ 14.10, 22.66, 25.68, 29.07, 31.55, 46.46, 68.07, 101.17, 106.78, 139.16, 160.26.

3,5-Didodecyloxybenzyl Chloride. Yield 76%. IR (KBr; cm$^{-1}$): 2856–2928 (C–H). $^1$H NMR (CDCl$_3$, 500 MHz; ppm): $\delta$ 0.88 (t, 6H, $J = 6.5$ Hz, CH$_3$), 1.27 (m, 32H, CH$_2$), 1.44 (m, 4H, CH$_2$), 1.76 (m, 4H, CH$_2$), 3.93 (t, 4H, $J = 6.5$ Hz, CH$_2$O), 4.50 (s, 2H, CH$_2$Cl), 6.40 (t, 1H, $J = 2.5$ Hz, ArH), 6.51 (d, 2H, $J = 2.5$ Hz, ArH).

3,5-Bis(3,5-dihexyloxybenzyloxy)benzyl chloride. Yield 99%. IR (KBr; cm$^{-1}$): 2868–2944 (C–H). $^1$H NMR (CDCl$_3$, 270 MHz; ppm): $\delta$ 0.90 (t, 12H, $J = 7.0$ Hz, CH$_3$), 1.34 (m, 16H, CH$_2$), 1.45 (m, 8H, CH$_2$), 1.76 (m, 8H, CH$_2$), 3.93 (t, 8H, $J = 6.5$ Hz, CH$_2$O), 4.50 (s, 2H, CH$_2$Cl), 4.94 (s, 4H, CH$_2$), 6.40 (t, 2H, $J = 2.2$ Hz, ArH), 6.51 (d, 4H, $J = 2.2$ Hz, ArH), 6.55 (t, 1H, $J = 2.2$ Hz, ArH), 6.62 (d, 2H, $J = 2.2$ Hz, ArH). $^{13}$C NMR (CDCl$_3$; ppm): $\delta$ 14.14, 22.68, 25.79, 29.27, 31.64, 46.35, 68.04, 70.15, 100.75, 101.99, 105.62, 107.53, 138.62, 139.34, 159.88, 160.33.

4-Bromo-1-(3,5-dimethoxybenzyloxy)benzene. A mixture of 4-bromophenol (13 g, 74 mmol), 3,5-dimethoxybenzyl chloride (15 g, 81 mmol), K$_2$CO$_3$ (22 g, 0.16 mol), and 18-crown-6 (3.0 g, 11 mmol) in acetone (200 mL) was refluxed for 18 h. After removal of the solvent, the residue was extracted with dichloromethane. The organic layer was washed with brine, then dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by silica-gel column separation with dichloromethane/hexane (1/1 v/v) as an eluent to give 4-bromo-1-(3,5-dimethoxybenzyloxy)benzene (19 g, 58 mmol). Yield 78%; mp 75$^\circ$C. TLC (dichloromethane/hexane (1/1 v/v); $R_f = 0.14$). IR (KBr; cm$^{-1}$): 2844–2944 (C–H). $^1$H NMR (CDCl$_3$, 270 MHz; ppm): $\delta$ 3.77 (s, 6H, CH$_3$), 4.96 (s, 2H, CH$_2$), 6.41 (t, 1H, $J = 2.4$ Hz, ArH), 6.55 (d, 2H, $J = 2.4$ Hz, ArH), 6.83 (d, 2H, $J = 8.9$ Hz, ArH), 7.36 (d, 2H, $J = 8.9$ Hz, ArH), $^{13}$C NMR (CDCl$_3$; ppm): $\delta$ 55.36, 70.10, 99.80, 105.05, 113.04, 116.58, 132.13, 138.78, 157.57, 160.85.
1-(3,5-Dimethoxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene. 2-Methyl-3-butyn-2-ol (10 mL, 0.10 mol) was added to a triethylamine solution (110 mL) of 4-bromo-1-(3,5-dimethoxybenzyl)benzene (18 g, 55 mmol), bis(triphenylphosphine)palladium (II) chloride (0.14 g, 0.2 mmol), triphenylphosphine (0.72 g, 2.7 mmol), and copper (I) iodide (0.34 g, 1.8 mmol) under a nitrogen atmosphere. The solution was stirred for 18 h at 90°C. After cooling, the mixture was treated with aqueous 4 N HCl, extracted with dichloromethane, and washed with brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure.

The crude product was purified by silica gel column separation with dichloromethane as an eluent to give 1-(3,5-dimethoxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene (5.5 g, 17 mmol). Yield 31%. TLC (dichloromethane): Rf = 0.88 (t, 6H, CH2), 1.26 (m, 32H, CH2), 1.43 (m, 4H, CH2), 1.76 (m, 4H, CH2), 3.92 (t, 4H, J = 6.8 Hz, CH2O), 4.95 (s, 2H, CH2O), 6.40 (t, 1H, J = 2.0 Hz, ArH), 6.53 (d, 2H, J = 2.0 Hz, ArH), 6.88 (d, 2H, J = 8.5 Hz, ArH), 7.34 (d, 2H, J = 8.9 Hz, ArH).

1-(3,5-Didodecyloxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene. 2-Methyl-3-butyn-2-ol (1.2 mL, 12 mmol) was added to a triethylamine solution (110 mL) of 4-bromo-1-(3,5-didodecyloxybenzyl)benzene (4.0 g, 6.3 mmol), bis(triphenylphosphine)palladium (II) chloride (1.6 mg, 0.0022 mmol), triphenylphosphine (2.8 mg, 0.010 mmol), and copper (I) iodide (1.5 mg, 0.0077 mmol) under a nitrogen atmosphere. The solution was stirred for 24 h at 90°C. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation with dichloromethane/hexane (1/2 v/v) as an eluent to give 1-(3,5-didodecyloxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene (1.6 g, 2.5 mmol). Yield 40%. IR (KBr; cm−1): 3324 (–OH), 2856–2928 (C–H).

Catalytic amounts of sodium hydride were added to a toluene solution (12 mL) of 1-(3,5-didodecyloxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene (0.90 g, 1.4 mmol). The solution was refluxed for 3 h under a nitrogen atmosphere. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation with dichloromethane/hexane (1/1 v/v) and hexane as an eluent to give DGOPA (0.45 g, 0.78 mmol). Yield 55%. TLC (dichloromethane/hexane (1/1 v/v)): Rf = 0.71. IR (KBr; cm−1): 3328 (C=C), 2856–2924 (C=C), 2121 (C=C). 1H NMR (CDCl3, 500 MHz; ppm): δ 0.88 (t, 6H, J = 7.0 Hz, CH2O), 1.26 (m, 32H, CH2), 1.43 (m, 4H, CH2), 1.76 (m, 4H, CH2), 2.99 (s, 1H, C=C–H), 3.92 (t, 4H, J = 6.5 Hz, CH2O), 4.98 (s, 2H, CH2O), 6.40 (t, 1H, J = 2.0 Hz, ArH), 6.53 (d, 2H, J = 2.0 Hz, ArH), 6.88 (d, 2H, J = 8.5 Hz, ArH), 7.34 (d, 2H, J = 8.9 Hz, ArH).

1-(3,5-Diiodoxybenzyl)-4-(3-hydroxy-3-methylbutynyl)benzene. A mixture of 4-iodophenol (18 g, 80 mmol), 3,5-diiodoxybenzyl chloride (29 g, 88 mmol), K2CO3 (24 g, 18 mmol), and 18-crown-6 (23 g, 88 mmol) in acetonitrile (530 mL) was refluxed for 8 h. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation with...
dichloromethane/hexane (1/3 v/v) as an eluent to give 4-iodo-1-(3,5-dihexyloxybenzoyl)benzene (37 g, 53 mmol).

Yield 91%. TLC (dichloromethane/hexane (1/3 v/v); Rf = 0.40. IR (KBr; cm⁻¹): 2872–2936 (C–H). 1H NMR (CDCl₃, 270 MHz; ppm): δ 0.90 (t, 6H, J = 6.8 Hz, CH₃), 1.33 (m, 8H, CH₂), 1.44 (m, 4H, CH₂), 1.76 (m, 4H, CH₂), 2.92 (s, 1H, C=C=H), 3.93 (t, 4H, J = 6.6 Hz, CH₂O), 4.96 (s, 2H, CH₂O), 6.40 (t, 1H, J = 2.4 Hz, ArH), 6.53 (d, 2H, J = 9.3 Hz, ArH), 7.53 (d, 2H, J = 9.3 Hz, ArH). 13C NMR (CDCl₃; ppm): δ 14.13, 22.68, 25.79, 29.27, 31.64, 68.08, 70.08, 82.99, 100.72, 105.48, 117.22, 138.07, 138.57, 158.43, 160.39.

1-[4-(3,5-DiheXyloxyBenzoyl)phenyl]-2-trimethylsilylacetylene. Trimethylsilylacetylene (19 mL, 0.14 mol) was added to a triethylamine solution (140 mL) of 4-iodo-1-(3,5-dihexyloxybenzoyl)benzene (36 g, 70 mmol), bis(triphenylphosphine)palladium (II) chloride (84 mg, 0.12 mmol), triphenylphosphine (87 mg, 0.33 mmol), and copper (I) iodide (46 mg, 0.24 mmol) under a nitrogen atmosphere. The solution was stirred for 10 h at 60°C. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation with dichloromethane/hexane (1/2 v/v) as an eluent to give 1-[4-(3,5-dihexyloxybenzoyl)phenyl]-2-trimethylsilylacetylene (25 g, 53 mmol).

Yield 76%. IR (KBr; cm⁻¹): 2872–2964 (C–H), 2160 (C=C). 1H NMR (CDCl₃, 270 MHz; ppm): δ 0.24 (s, 9H, Si(CH₃)₃), 0.91 (t, 6H, J = 6.8 Hz, CH₃), 1.33 (m, 8H, CH₂), 1.45 (m, 4H, CH₂), 1.76 (m, 4H, CH₂), 3.93 (t, 4H, J = 6.5 Hz, CH₂O), 4.98 (s, 2H, CH₂O), 6.40 (t, 1H, J = 2.4 Hz, ArH), 6.53 (d, 2H, J = 2.4 Hz, ArH), 6.88 (d, 2H, J = 8.9 Hz, ArH), 7.39 (d, 2H, J = 8.9 Hz, ArH). 13C NMR (CDCl₃; ppm): δ 0.17, 14.14, 22.68, 25.79, 29.26, 31.64, 68.05, 69.97, 92.46, 100.71, 105.07, 105.49, 114.64, 115.39, 133.33, 138.58, 158.69, 160.35.

[4-(3,5-DiheXyloxyBenzoyl)phenyl]acetylene (HG0PA). A mixture of 1-[4-(3,5-dihexyloxybenzoyl)phenyl]-2-trimethylsilylacetylene (4.8 g, 10 mmol) and K₂CO₃ (0.14 g, 1.0 mmol) in methanol (200 mL) was stirred at room temperature for 20 h. After removal of the solvent, the residue was extracted with dichloromethane. The organic layer was washed with brine, then dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by silica gel column separation with dichloromethane/hexane/hexane (1/4 v/v) as an eluent to give HG0PA (3.5 g, 8.4 mmol). Yield 84%. TLC (dichloromethane/hexane (1/4 v/v); Rf = 0.76. IR (KBr; cm⁻¹): 3332 (C=C=H), 2860–2932 (C–H), 2160 (C=C). 1H NMR (CDCl₃, 270 MHz; ppm): δ 0.90 (t, 6H, J = 6.8 Hz, CH₃), 1.33 (m, 8H, CH₂), 1.44 (m, 4H, CH₂), 1.76 (m, 4H, CH₂), 2.99 (s, 1H, C=C=H), 3.93 (t, 4H, J = 6.6 Hz, CH₂O), 4.96 (s, 2H, CH₂O), 6.40 (t, 1H, J = 2.2 Hz, ArH), 6.53 (d, 2H, J = 2.2 Hz, ArH), 6.89 (d, 2H, J = 8.9 Hz, ArH), 7.41 (d, 2H, J = 8.9 Hz, ArH). 13C NMR (CDCl₃; ppm): δ 14.13, 22.68, 25.79, 29.27, 31.64, 68.08, 70.04, 75.82, 83.60, 100.75, 105.53, 114.31, 114.77, 133.47, 138.57, 158.92, 160.39.

4-Iodo-1-[3,5-bis(3,5-dihexyloxybenzoyl)benzoyl]benzene (HG1PA). A mixture of 1-[4-(3,5-bis(3,5-dihexyloxybenzoyl)benzoyl]phenyl]-2-trimethylsilylacetylene (3.5 g, 4.0 mmol) and K₂CO₃ (78 mg, 0.57 mmol) in methanol/diethyl ether (160 mL/50 mL) was stirred at room temperature for 24 h. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation
with dichloromethane/hexane (1/1 v/v) as an eluent to give HG1PA (2.3 g, 2.8 mmol). Yield 69%. TLC (dichloromethane/hexane (1/1 v/v)); Rf = 0.43. IR (KBr; cm\(^{-1}\)): 3296 (=C–H), 2864–2940 (C–H), 2112 (C=–C). \(^1\)H NMR (CDCl\(_3\), 270 MHz; ppm): δ 0.90 (t, 12H, J = 6.5 Hz, CH\(_3\)), 1.33 (m, 16H, CH\(_3\)), 1.45 (m, 8H, CH\(_2\)), 1.76 (m, 8H, CH\(_2\)), 2.99 (s, 1H, C=–C–H), 3.93 (s, 8H, CH\(_2\)), 4.94 (s, 4H, CH\(_2\)O), 4.99 (s, 2H, CH\(_2\)O), 6.40 (t, 2H, J = 2.2 Hz, ArH), 6.54 (d, 4H, J = 2.2 Hz, ArH), 6.56 (t, 1H, J = 2.2 Hz, ArH), 6.64 (d, 2H, J = 7.2 Hz, ArH), 6.88 (d, 2H, J = 8.8 Hz, ArH), 7.41 (d, 2H, J = 8.8 Hz, ArH). \(^{13}\)C NMR (CDCl\(_3\); ppm): δ 14.03, 22.59, 25.68, 29.14, 31.41, 31.56, 65.58, 68.10, 80.87, 86.52, 90.39, 94.62, 114.58, 123.28, 124.25, 131.11, 133.35, 135.38, 137.72, 159.82, 159.99, 160.35, 160.59.

1-(3-Hydroxy-3-methylbutynyl)-3,5-bis[(4-hexyloxyphenyl)ethynyl]benzene. A triethylamine (40 mL) solution of 4-[2-(3,5-dibromophenyl)ethylphenyl]-1-(3-hydroxyl-3-methylbutynyl) benzene (11 g, 35 mmol), **Hex0H** (14 g, 70 mmol), bis(triphenylphosphine)palladium (II) chloride (0.23 g, 0.33 mmol), triphenylphosphine (0.47 g, 1.8 mmol), and copper (I) iodide (0.24 g, 1.3 mmol) was stirred for 16 h at 95°C under a nitrogen atmosphere. The mixture was worked up in the same manner as described above, and the crude product was purified by silica gel column separation with dichloromethane as an eluent to give 1-(3-hydroxy-3-methylbutynyl)-3,5-bis[(4-hexyloxyphenyl)ethynyl]benzene. (12 g, 21 mmol). Yield 60%. TLC (dichloromethane): Rf = 0.34. IR (KBr; cm\(^{-1}\)): 3464 (–OH), 2960 (C–H), 2221 (C=–C). \(^1\)H NMR (CDCl\(_3\), 500 MHz; ppm): δ 0.91 (t, 6H, J = 7.0 Hz, CH\(_3\)), 1.35 (m, 8H, CH\(_3\)), 1.46 (m, 4H, CH\(_2\)), 1.62 (s, 6H, CH\(_3\)), 1.79 (m, 4H, CH\(_2\)), 2.01 (s, 1H, OH), 3.97 (t, 4H, J = 6.7 Hz, CH\(_2\)O), 6.87 (d, 4H, J = 8.8 Hz, ArH), 7.44 (d, 4H, J = 8.8 Hz, ArH), 7.48 (d, 2H, J = 2.0 Hz, ArH), 7.57 (t, 1H, J = 2.0 Hz, ArH). \(^{13}\)C NMR (CDCl\(_3\); ppm): δ 14.03, 22.59, 25.68, 29.14, 31.41, 31.56, 65.58, 68.10, 80.87, 86.52, 90.39, 94.62, 114.58, 123.28, 124.25, 131.11, 133.35, 135.38, 137.72, 159.82, 159.99, 160.46.

1-(3-Hydroxy-3-methylbutynyl)-3,5-bis[(4-hexyloxyphenyl)ethylphenyl] (Hex1H). 1-(3-Hydroxy-3-methylbutynyl)-3,5-bis[(4-hexyloxyphenyl)ethylphenyl] benzene (12 g, 22 mmol) was allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica gel column separation with dichloromethane and hexane as an eluent to give Hex1H (9.0 g, 18 mmol). Yield 82%. TLC (dichloromethane): Rf = 0.93. IR (NaCl; cm\(^{-1}\)): 3308 (=C–H), 2932 (C–H), 2208 (C=–C). \(^1\)H NMR (CDCl\(_3\), 500 MHz; ppm): δ 0.91 (t, 6H, J = 7.0 Hz, CH\(_3\)), 1.35 (m, 8H, CH\(_3\)), 1.43 (m, 4H, CH\(_2\)), 1.78 (m, 4H, CH\(_2\)), 3.09 (s, 1H, CH=C–C=H), 3.97 (t, 4H, J = 6.8 Hz, CH\(_2\)O), 6.87 (d, 4H, J = 9.0 Hz, ArH), 7.44 (d, 4H, J = 9.0 Hz, ArH), 7.55 (d, 2H, J = 1.5 Hz, ArH), 7.62 (t, 1H, J = 1.5 Hz, ArH). \(^{13}\)C NMR (CDCl\(_3\); ppm): δ 14.03, 22.59, 25.69, 29.14, 31.57, 68.11, 78.03, 82.21, 86.39, 90.75, 114.52, 114.59, 122.68, 124.37, 133.14, 133.99, 134.31, 159.51.

2.3. Polymerization. An appropriate amount of monomers (typically, 0.5–1.0 g) was placed in a Schlenk tube equipped with a three-way stopcock, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. Freshly distilled solvent was transferred to the tube, and the monomers were dissolved with stirring. The determined amount of [Rh(nbd)Cl]\(_2\) and triethylamine dissolved in the solvent was added to the stirred monomers solution. The detailed polymerization conditions are tabulated in Table 1. The reaction solution was poured into methanol or methanol/benzene (3/2 v/v) to yield polymer precipitate. The precipitate was washed with the precipitant and then dried in vacuo to give a yellow polymer.

2.4. Membrane Preparation. A 5 wt% (w/v) solution of a polymer in chloroform or toluene was cast on a Teflon sheet, and the solvent was evaporated at room temperature. The resulting solid membrane was detached from the sheet and dried in vacuo for 24 hr. Thickness (L) of the membranes was 70–160 μm.

2.5. Measurement of Oxygen and Nitrogen Permeability. Oxygen and nitrogen permeability coefficients (P\(_{O2}\) and P\(_{N2}\): cm\(^3\)(STP) cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\)) and the oxygen separation factor (α = P\(_{O2}\)/P\(_{N2}\)) were measured by a gas chromatographic method using YANACO GTR-10 according to [13].

2.6. Other Measurements. IR spectra were measured with a Hitachi IR 270-30 spectrometer. NMR (\(^1\)H, \(^{13}\)C) spectra were measured with a Varian Unity 500SW (500 MHz) or a JEOL GXS-270 (270 MHz) spectrometer. Average molecular weights (M\(_{n}\) and M\(_{w}\)) were evaluated by coupling of gel permeation chromatography and low angle laser light scattering (GPC-LALLS) at 40°C on THF eluent using Tosoh Liquid Chromatograph instruments with SD-8000, CCPD, C0-8010, LS-8000, RI-8011, and PP8010. The optical spectra were measured with a JASCO Ubest V-550DS UV-vis spectrometer. The wide-angle X-ray scattering measurements were performed using a Rigaku Geigerflex with a graphite-monochromatized Cu Kα radiation, which was supplied at 40 kV and 20 mA.

3. Results and Discussion

3.1. Polymerization of Monodendron Monomers. The monodendron monomers were polymerized by Rh catalyst, [Rh(nbd)Cl]\(_2\), in the presence of triethylamine cocatalyst. The polymerization mixtures were purified by precipitating into methanol or methanol/benzene (9/1-3/2 v/v) to yield the corresponding polydendrons as yellow powders. It is well known that the Rh catalyst can selectively promote the polymerization of monosubstituted acetylenes [14–19]. Moreover, we have previously demonstrated that TMSI1H, PMDS1H, and NMTS1H polymerize at the terminal acetylene group of the focal point [7]. The same catalyst system promotes the polymerization of HG1PA and Hex1H to yield the corresponding polymers as shown in Table 1. HG0PA...
and DG0PA gave highly soluble polymers with a high degree of polymerization ($DP > 10^3$) in spite of the larger peripheral groups in comparison with MG0PA. The yield and the degree of polymerization of polydendrons (i.e., poly(HG1PA) and poly(Hex1H1)) are similar to those of the corresponding zero-generation polymers (i.e., poly(HG0PA) and poly(Hex1H)), since the first-generation dendrons are not too crowded to affect the polymerization ability.

### 3.2. Structure of Polydendrons

The polymerization of the monodendrons at the terminal acetylene group of focal point was confirmed by means of IR and $^1$H NMR; for example, in IR and $^1$H NMR spectra of poly(Hex1H), the peaks assignable to the terminal acetylene group of the monodendron Hex1H, that is, 3308 cm$^{-1}$ (the stretching vibration of the $\equiv$C–H bond) in IR spectrum and $\delta$ 3.09 (s, $1^H$, $\equiv$C–H) in $^1$H NMR, completely disappeared. The visible absorption maxima ($\lambda_{max}$) of polydendrons significantly increased due to the construction of the dendritic structure, that is, poly(Hex0H) (400 nm) to poly(Hex1H) (455 nm), and poly(HG0PA) (400 nm) to poly(HG1PA) (441 nm). A bathochromic shift has been reported for some ortho- and meta-substituted poly(phenylacetylene)s in comparison with the simple or para-substituted poly(phenylacetylene) [20–24]. This bathochromic shift indicates a developed $\pi$-conjugation in the main chain of polydendrons and suggests that steric hindrance and repulsion among bulky substituents at the $m$-position formed the extended main chain structure. This resulted in a highly twisted dihedral angle between the main chain and the attached phenyl rings and was counteracted by slightly or moderately twisted single bonds of the main chain. The visible absorption maxima ($\lambda_{max}$) of the first-generation polydendrons were significantly increased due to the effect of the bulky substituent at the $m$-position in comparison with the corresponding zero-generation polymers poly(HG0PA) and poly(Hex1H).

The wide-angle X-ray scattering (WAXS) of poly(HG0PA) and poly(HG1PA) was measured in film states (Table 2). The sharp peaks were observed at $2\theta = 3$–4°, and these sharp crystalline peaks are attributed to the (100) reflection of the pseudohexagonal lattice of rod-like molecules [7, 25]. The interplanar $d$ spacing of the polymers increased with increasing generation, while the density seldom decreased. These data suggest that the increase of $d$ spacing is related to the increase of the column diameter with the generation. The column diameter of the polymers estimated from $d$ spacing is only slightly smaller than that of molecular modeling. The molecular modeling was performed on the assumption of a fully extended conformation for side-chain monodendrons and distorted cis-transoid main chain conformation (dihedral angle = 130 deg), as described in [7]. The column diameter difference between the values estimated from $d$ spacing and from molecular modeling suggests that the flexible alkyl chain as the peripheral group was bent and/or the columns slightly overlapped each other in the part of the peripheral group.

### 3.3. Oxygen Permselectivity of Polydendron Membranes

The polymers were soluble in common organic solvents, such as chloroform, toluene, and tetrahydrofuran. The polymers poly(HG0PA), poly(Hex0H), and poly(Hex1H) exhibited good film-forming abilities depending on their degree of polymerization and formed a self-supporting film colored orange due to $\pi$-conjugated main chain chromophore by the solvent-casting method.

Oxygen and nitrogen permeation were measured using air as feed gas at 298 K and 76 cmHg using poly(HG0PA), poly(Hex0H), and poly(Hex1H) membranes. Figure 1 shows the relationship between the oxygen permeability coefficient ($P_O_2$) and the oxygen separation factor ($\alpha = P_O_2/P_N_2$) for the polydendron membranes with the zero-generation polymer (poly(TMS0H), poly(PMDS0H), and poly(NMTS0H)) membranes. The oxygen permeability coefficient ($P_O_2$) of the membranes formed by first-generation polydendrons were smaller than that of the corresponding zero-generation poly(phenylacetylene) derivative. It seems that this behavior was caused by the low mobility of the stiff and crowded dendritic structure. The zero-generation poly(phenylacetylene) derivatives show a balance between

**Table 1: Polymerization of phenylacetylene monodendrons with alkyl peripheral groups using [Rh(nbd)CL]$_2$**

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Yield (%)</th>
<th>$M_w$ (×10$^3$)</th>
<th>$M_w/M_n$</th>
<th>$DP$ (×10$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG0PA</td>
<td>60</td>
<td>0.92</td>
<td>1.4</td>
<td>3.4</td>
</tr>
<tr>
<td>HG0PA$^d$</td>
<td>87</td>
<td>2.4</td>
<td>1.8</td>
<td>5.9</td>
</tr>
<tr>
<td>DG0PA$^c$</td>
<td>65</td>
<td>2.8</td>
<td>2.7</td>
<td>4.9</td>
</tr>
<tr>
<td>HG1PA</td>
<td>92</td>
<td>6.1</td>
<td>1.7</td>
<td>7.4</td>
</tr>
<tr>
<td>Hex0H$^f$</td>
<td>49</td>
<td>5.3$^g$</td>
<td>5.2$^g$</td>
<td>2.6</td>
</tr>
<tr>
<td>Hex1H$^f$</td>
<td>35</td>
<td>8.2$^g$</td>
<td>3.0$^g$</td>
<td>1.6</td>
</tr>
</tbody>
</table>

$^a$ Triethylamine, $[M]_0 = 0.5$ mol/l, $[M]_0/[Cat]_0 = 2500$, 25° C, 3 hr, precipitated with MeOH/benzene (9/1 v/v).

$^b$ Determined from GPC-LALLS.

$^c$ Calculated from $M_n$.

$^d$ Ether, $[triethylamine]_0/[Cat]_0 = 20$.

$^e$ $[M]_0/[Cat]_0 = 5000$.

$^f$ Chloroform, $[M]_0/[Cat]_0 = 1000$, $[triethylamine]_0/[Cat]_0 = 20$.

$^g$ Determined from GPC calibrated by polystyrene standard.
and poly(TMS0H) cis extended conformation for side-chain monodendrons and distorted from molecular modeling, which was performed as described in text. (The molecular modeling was performed on the assumption of a fully extended conformation for side-chain monodendrons and distorted cis-transoid main chain conformation (dihedral angle $\theta = 130$ deg), as described in [7].)

The phenylacetylene monomers consisting of monodendron with alkoxy peripheral groups were successfully polymerized with a Rh catalyst, $[\text{Rh(nbd)}\text{Cl}]_2$, to yield corresponding polydendrons with high molecular weight, in spite of the bulkiness of the dendritic residue and the peripheral groups. The polydendrons were fabricated to self-supporting membranes, and the membrane formed by the polydendron of first generation, poly(Hex1H), showed an oxygen permselectivity higher than that of the corresponding zero-generation poly(phenylacetylene) derivatives.

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### References

7. T. Kaneko, M. Asano, K. Yamamoto, and T. Aoki, “Polymerization of phenylacetylene-based monodendrons and structure of


