Research Article

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

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Monodendron monomers with alkoxy peripheral groups were synthesized, and the focal point of monodendrons, terminal acetylene, was polymerized with rhodium catalyst to yield corresponding polydendrons with a high molecular weight. The polydendrons were soluble in common organic solvents and readily formed membranes. Oxygen permselectivity was improved in the polydendrons with a space-persistent dendritic crowd. It was found that the well-defined dendritic and rod-like structure of the polydendrons was useful for permselective membrane.

1. Introduction

The chemical structure and/or morphology of polymers play an important role for 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 *m*-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 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-hydroxy-3-methylbutynyl)benzene was synthesized as previously described [7].

SCHEME 1

3,5-Dimethoxybenzyl chloride [8], 3,5-dihexyloxybenzyl alcohol [9], 3,5-didodecyloxybenzyl alcohol [10], 3,5-bis(3,5-dihexyloxybenzyloxy)benzyl alcohol [11], and (4-hexyloxyphenyl)acetylene (**Hex0H**) [12] were synthesized according to the literature procedures. (Bicyclo [2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ($[\text{Rh}(\text{nbd})\text{Cl}]_2$) (Aldrich Co.), bis(triphenylphosphine)palladium(II) chloride (Aldrich Co.), and *n*-butyllithium (Kanto Chemical Co., Inc., 1.6 M in hexane) were used without further purification. Other conventional reagents were used as received or purified by conventional method.

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-Dihexyloxybenzyl Chloride. Yield 94%. IR (KBr; cm^{-1}): 2872–2936 (C–H). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 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_2O), 4.50 (s, 2H, CH_2Cl), 6.39 (t, 1H, $J = 2.4$ Hz, ArH), 6.51 (d, 2H, $J = 2.4$ Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 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). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 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_2O), 4.50 (s, 2H, CH_2Cl), 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). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 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_2O), 4.50 (s, 2H, CH_2Cl), 4.94 (s, 4H, CH_2O), 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): δ 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_2CO_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°C. TLC (dichloromethane/hexane (1/1 v/v)): $R_f = 0.14$. IR (KBr; cm^{-1}): 2844–2944 (C–H). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 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): δ 55.36, 70.10, 99.80, 105.05, 113.04, 116.58, 132.13, 138.78, 157.57, 160.85.

1-(3,5-Dimethoxybenzyloxy)-4-(3-hydroxyl-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-dimethoxybenzyloxy)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-dimethoxybenzyloxy)-4-(3-hydroxyl-3-methylbutynyl)benzene (5.5 g, 17 mmol). Yield 31%. TLC (dichloromethane): R_f = 0.15. IR (KBr; cm^{-1}): 3324 (–OH), 2848–2988 (C–H), 2228 (C≡C). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 1.61 (s, 6H, CH_3), 2.11 (s, 1H, –OH), 3.79 (s, 6H, CH_3), 4.99 (s, 2H, CH_2), 6.41 (t, 1H, J = 2.2 Hz, ArH), 6.56 (d, 2H, J = 2.2 Hz, ArH), 6.88 (d, 2H, J = 8.9 Hz, ArH), 7.34 (d, 2H, J = 8.9 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 31.61, 55.36, 65.61, 69.89, 81.89, 92.45, 99.82, 105.08, 114.69, 115.03, 132.94, 138.81, 158.44, 160.82.

[4-(3,5-Dimethoxybenzyloxy)phenyl]acetylene (MG0PA). Sodium hydride (2.0 g, 50 mmol) was added to a toluene solution (65 mL) of 1-(3,5-dimethoxybenzyloxy)-4-(3-hydroxyl-3-methylbutynyl)benzene (5.5 g, 17 mmol). The solution was refluxed for 2 h under a nitrogen atmosphere. After cooling, the mixture was treated with water, 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 MG0PA (1.1 g, 4.3 mmol). Yield 25%; mp 60°C. TLC (hexane): R_f = 0.75. IR (KBr; cm^{-1}): 3296 (≡C–H), 2848–2988 (C–H), 2112 (C≡C). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 3.00 (s, 1H, C≡C–H), 3.78 (s, 6H, CH_3), 4.98 (s, 2H, CH_2), 6.40 (t, 1H, J = 1.9 Hz, ArH), 6.55 (d, 2H, J = 1.9 Hz, ArH), 6.89 (d, 2H, J = 8.9 Hz, ArH), 7.41 (d, 2H, J = 8.9 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 55.32, 69.87, 75.96, 83.53, 99.80, 105.04, 114.31, 114.70, 133.43, 138.71, 158.79, 160.81.

4-Bromo-1-(3,5-didodecyloxybenzyloxy)benzene. A mixture of 4-bromophenol (1.9 g, 11 mmol), 3,5-didodecyloxybenzyl chloride (6.0 g, 12 mmol), K_2CO_3 (3.3 g, 24 mmol), and 18-crown-6 (3.2 g, 12 mmol) in acetone (60 mL) was refluxed for 87 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 (1/2 v/v) as an eluent to give 4-bromo-1-(3,5-didodecyloxybenzyloxy)benzene (5.3 g, 8.3 mmol). Yield 76%. TLC (dichloromethane/hexane (1/2 v/v)): R_f = 0.90. IR (KBr; cm^{-1}): 2856–2928 (C–H). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.88 (t, 6H, J = 6.8 Hz, CH_3), 1.26 (m, 32H, CH_2), 1.43 (m, 4H, CH_2), 1.76 (m, 4H,

CH_2), 3.92 (t, 4H, J = 6.8 Hz, CH_2O), 4.95 (s, 2H, CH_2O), 6.40 (t, 1H, J = 2.3 Hz, ArH), 6.52 (d, 2H, J = 2.3 Hz, ArH), 6.84 (d, 2H, J = 8.8 Hz, ArH), 7.36 (d, 2H, J = 8.8 Hz, ArH).

1-(3,5-Didodecyloxybenzyloxy)-4-(3-hydroxyl-3-methylbutynyl)benzene. 2-Methyl-3-butyn-2-ol (1.2 mL, 12 mmol) was added to a triethylamine solution (12 mL) of 4-bromo-1-(3,5-didodecyloxybenzyloxy)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-didodecyloxybenzyloxy)-4-(3-hydroxyl-3-methylbutynyl)benzene (1.6 g, 2.5 mmol). Yield 40%. IR (KBr; cm^{-1}): 3324 (–OH), 2856–2928 (C–H), 2240 (C≡C). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.88 (t, 6H, J = 6.5 Hz, CH_3), 1.26 (m, 32H, CH_2), 1.42 (m, 4H, CH_2), 1.60 (s, 6H, CH_3), 1.76 (m, 4H, CH_2), 2.04 (s, 1H, –OH), 3.92 (t, 4H, J = 6.5 Hz, CH_2O), 4.98 (s, 2H, CH_2O), 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 = 8.5 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 14.18, 22.67, 26.03, 29.23, 29.34, 29.38, 29.56, 29.58, 29.62, 29.65, 31.56, 31.91, 65.63, 68.07, 70.01, 81.96, 92.44, 100.79, 105.60, 114.80, 115.05, 133.04, 138.75, 158.70, 160.53.

[4-(3,5-Didodecyloxybenzyloxy)phenyl]acetylene (DG0PA). Catalytic amounts of sodium hydride were added to a toluene solution (12 mL) of 1-(3,5-didodecyloxybenzyloxy)-4-(3-hydroxyl-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 DG0PA (0.45 g, 0.78 mmol). Yield 55%. TLC (dichloromethane/hexane (1/1 v/v)): R_f = 0.71. IR (KBr; cm^{-1}): 3328 (≡C–H), 2856–2924 (C–H), 2112 (C≡C). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.88 (t, 6H, J = 7.0 Hz, CH_3), 1.26 (m, 32H, CH_2), 1.43 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 2.99 (s, 1H, C≡C–H), 3.92 (t, 4H, J = 6.5 Hz, CH_2O), 4.98 (s, 2H, CH_2O), 6.40 (t, 1H, J = 2.0 Hz, ArH), 6.53 (d, 2H, J = 2.0 Hz, ArH), 6.90 (d, 2H, J = 8.5 Hz, ArH), 7.41 (d, 2H, J = 8.5 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 14.11, 22.68, 26.03, 29.23, 29.34, 29.38, 29.56, 29.59, 29.63, 29.65, 31.91, 68.06, 70.02, 75.81, 83.60, 100.78, 105.56, 114.38, 114.83, 133.56, 138.66, 159.06, 160.53.

4-Iodo-1-(3,5-dihexyloxybenzyloxy)benzene. A mixture of 4-iodophenol (18 g, 80 mmol), 3,5-dihexyloxybenzyl chloride (29 g, 88 mmol), K_2CO_3 (24 g, 18 mmol), and 18-crown-6 (23 g, 88 mmol) in acetone (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-dihexyloxybenzyloxy)benzene (37 g, 73 mmol). Yield 91%. TLC (dichloromethane/hexane (1/3 v/v)): R_f = 0.40. IR (KBr; cm^{-1}): 2872–2936 (C–H). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 0.90 (t, 6H, J = 6.8 Hz, CH_3), 1.32 (m, 8H, CH_2), 1.44 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 3.92 (t, 4H, J = 6.8 Hz, CH_2O), 4.94 (s, 2H, CH_2O), 6.39 (t, 1H, J = 2.2 Hz, ArH), 6.52 (d, 2H, J = 2.2 Hz, ArH), 6.73 (d, 2H, J = 9.3 Hz, ArH), 7.53 (d, 2H, J = 9.3 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 14.13, 22.68, 25.79, 29.27, 31.64, 68.07, 70.08, 82.99, 100.72, 105.48, 117.22, 138.07, 138.57, 158.43, 160.39.

1-[4-(3,5-Dihexyloxybenzyloxy)phenyl]-2-trimethylsilylacetylene. Trimethylsilylacetylene (19 mL, 0.14 mol) was added to a triethylamine solution (140 mL) of 4-iodo-1-(3,5-dihexyloxybenzyloxy)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-dihexyloxybenzyloxy)phenyl]-2-trimethylsilylacetylene (25 g, 53 mmol). Yield 76%. IR (KBr; cm^{-1}): 2872–2964 (C–H), 2160 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 0.24 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.91 (t, 6H, J = 6.8 Hz, CH_3), 1.33 (m, 8H, CH_2), 1.45 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 3.93 (t, 4H, J = 6.5 Hz, CH_2O), 4.98 (s, 2H, CH_2O), 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). ^{13}C NMR (CDCl_3 ; 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-Dihexyloxybenzyloxy)phenyl]acetylene (HG0PA). A mixture of 1-[4-(3,5-dihexyloxybenzyloxy)phenyl]-2-trimethylsilylacetylene (4.8 g, 10 mmol) and K_2CO_3 (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 (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)): R_f = 0.76. IR (KBr; cm^{-1}): 3332 ($\equiv\text{C-H}$), 2860–2932 (C–H), 2160 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 0.90 (t, 6H, J = 6.8 Hz, CH_3), 1.33 (m, 8H, CH_2), 1.44 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 2.99 (s, 1H, $\text{C}\equiv\text{C-H}$), 3.93 (t, 4H, J = 6.6 Hz, CH_2O), 4.96 (s, 2H, CH_2O), 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). ^{13}C NMR (CDCl_3 ; 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-dihexyloxybenzyloxy)benzyloxy]benzene. A mixture of 4-iodophenol (3.7 g, 17 mmol), 3,5-bis(3,5-dihexyloxybenzyloxy)benzyl chloride (13 g, 17 mmol), K_2CO_3 (4.7 g, 34 mmol), and 18-crown-6 (0.56 g, 2.1 mmol) in acetone (130 mL) was refluxed for 115 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 ethyl acetate/hexane (1/8 v/v) as an eluent to give 4-iodo-1-[3,5-bis(3,5-dihexyloxybenzyloxy)benzyloxy]benzene (11 g, 12 mmol). Yield 72%. TLC (ethyl acetate/hexane (1/8 v/v)): R_f = 0.64. IR (KBr; cm^{-1}): 2864–2936 (C–H). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 0.90 (t, 12H, J = 6.9 Hz, CH_3), 1.33 (m, 16H, CH_2), 1.45 (m, 8H, CH_2), 1.76 (m, 8H, CH_2), 3.93 (t, 8H, J = 6.6 Hz, CH_2O), 4.94 (s, 4H, CH_2O), 4.95 (s, 2H, CH_2O), 6.40 (t, 2H, J = 2.2 Hz, ArH), 6.54 (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), 6.71 (d, 2H, J = 9.0 Hz, ArH), 7.53 (d, 2H, J = 9.0 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 14.15, 22.69, 25.80, 29.28, 31.64, 68.05, 69.93, 70.13, 83.07, 100.69, 101.50, 105.62, 106.11, 117.20, 138.07, 138.70, 138.75, 158.31, 159.97, 160.32.

1-[4-[3,5-Bis(3,5-dihexyloxybenzyloxy)benzyloxy]phenyl]-2-trimethylsilylacetylene. Trimethylsilylacetylene (1.4 mL, 10 mmol) was added to a triethylamine solution (10 mL) of 4-iodo-1-[3,5-bis(3,5-dihexyloxybenzyloxy)benzyloxy]benzene (4.6 g, 5.0 mmol), bis(triphenylphosphine)palladium (II) chloride (10 mg, 0.015 mmol), triphenylphosphine (4.2 mg, 0.016 mmol), and copper (I) iodide (17 mg, 0.090 mmol) under a nitrogen atmosphere. The solution was stirred for 14 h at 75°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-bis(3,5-dihexyloxybenzyloxy)benzyloxy]phenyl]-2-trimethylsilylacetylene (3.5 g, 4.0 mmol). Yield 79%. IR (KBr; cm^{-1}): 2864–2936 (C–H), 2160 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.24 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.90 (t, 12H, J = 7.0 Hz, CH_3), 1.33 (m, 16H, CH_2), 1.45 (m, 8H, CH_2), 1.76 (m, 8H, CH_2), 3.93 (t, 8H, J = 6.8 Hz, CH_2O), 4.94 (s, 4H, CH_2O), 4.99 (s, 2H, CH_2O), 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), 6.63 (d, 2H, J = 2.2 Hz, ArH), 6.86 (d, 2H, J = 9.0 Hz, ArH), 7.38 (d, 2H, J = 9.0 Hz, ArH). ^{13}C NMR (CDCl_3 ; ppm): δ 0.04, 14.03, 22.59, 25.72, 29.21, 31.57, 68.05, 69.85, 70.15, 92.53, 100.79, 101.60, 105.11, 105.69, 106.22, 114.72, 115.55, 133.44, 138.86, 138.92, 158.76, 160.13, 160.49.

{4-[3,5-Bis(3,5-dihexyloxybenzyloxy)benzyloxy]phenyl}acetylene (HG1PA). A mixture of 1-[4-[3,5-bis(3,5-dihexyloxybenzyloxy)benzyloxy]phenyl]-2-trimethylsilylacetylene (3.5 g, 4.0 mmol) and K_2CO_3 (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)): $R_f = 0.43$. IR (KBr; cm^{-1}): 3296 ($\equiv\text{C-H}$), 2864–2940 (C–H), 2112 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 270 MHz; ppm): δ 0.90 (t, 12H, $J = 6.5$ Hz, CH_3), 1.33 (m, 16H, CH_2), 1.45 (m, 8H, CH_2), 1.76 (m, 8H, CH_2), 2.99 (s, 1H, $\text{C}\equiv\text{C-H}$), 3.93 (t, 8H, $J = 6.5$ Hz, CH_2O), 4.94 (s, 4H, CH_2O), 4.99 (s, 2H, CH_2O), 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, $J = 2.2$ 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 14.16, 22.70, 25.81, 29.29, 31.66, 68.06, 69.90, 70.15, 75.86, 83.58, 100.72, 101.54, 105.63, 106.16, 114.36, 114.77, 133.47, 138.72, 138.77, 158.82, 159.99, 160.35.

1-(3-Hydroxyl-3-methylbutynyl)-3,5-bis [(4-hexyloxyphenyl) ethynyl]benzene. A triethylamine (40 mL) solution of 4-[2-(3,5-dibromophenyl)ethynyl]-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-hydroxyl-3-methylbutynyl)-3,5-bis [(4-hexyloxyphenyl) ethynyl]benzene. (12 g, 21 mmol). Yield 60%. TLC (dichloromethane): $R_f = 0.34$. IR (KBr; cm^{-1}): 3464 ($-\text{OH}$), 2960 (C–H), 2212 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.91 (t, 6H, $J = 7.0$ Hz, CH_3), 1.35 (m, 8H, CH_2), 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_2O), 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, 90.59, 94.62, 114.58, 123.28, 124.25, 133.11, 133.35, 133.58, 133.74, 159.46.

{3,5-Bis [(4-hexyloxyphenyl)ethynyl]phenyl} acetylene (Hex1H). 1-(3-Hydroxyl-3-methylbutynyl)-3,5-bis [(4-hexyloxyphenyl)ethynyl]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): $R_f = 0.93$. IR (NaCl; cm^{-1}): 3308 ($\equiv\text{C-H}$), 2932 (C–H), 2208 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 500 MHz; ppm): δ 0.91 (t, 6H, $J = 7.0$ Hz, CH_3), 1.35 (m, 8H, CH_2), 1.43 (m, 4H, CH_2), 1.78 (m, 4H, CH_2), 3.09 (s, 1H, $\text{C}\equiv\text{C-H}$), 3.97 (t, 4H, $J = 6.8$ Hz, CH_2O), 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 $[\text{Rh}(\text{nbd})\text{Cl}]_2$ 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_{O_2} and P_{N_2} ; $\text{cm}^3(\text{STP})\text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$) and the oxygen separation factor ($\alpha = P_{\text{O}_2}/P_{\text{N}_2}$) 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 (^1H , ^{13}C) spectra were measured with a Varian Unity 500SW (500 MHz) or a JEOL GSX-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, CO-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 K α 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, $[\text{Rh}(\text{nbd})\text{Cl}]_2$, in the presence of triethylamine cocatalyst. The polymerization mixtures were purified by precipitating into methanol or methanol/benzene (9/1-4/3 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 **TMS1H**, **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**

TABLE 1: Polymerization of phenylacetylene monodendrons with alkyl peripheral groups using $[\text{Rh}(\text{nbd})\text{CL}]_2^{\text{a}}$.

Monomers	Yield (%)	M_w^{b} ($\times 10^6$)	M_w / M_n^{b}	DP^{c} ($\times 10^3$)
MG0PA	60	0.92	1.4	3.4
HG0PA^d	87	2.4	1.8	5.9
DG0PA^c	65	2.8	2.7	4.9
HG1PA	92	6.1	1.7	7.4
Hex0H^f	49	5.3 ^g	5.2 ^g	2.6
Hex1H^f	35	8.2 ^g	3.0 ^g	1.6

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

^b Determined from GPC-LALLS.

^c Calculated from M_w .

^d Ether, $[\text{triethylamine}]_0/[Cat]_0 = 20$.

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

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

^g Determined from GPC calibrated by polystyrene standard.

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(**Hex1H**)) 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 ^1H NMR; for example, in IR and ^1H 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 $\equiv\text{C}-\text{H}$ bond) in IR spectrum and δ 3.09 (s, 1H, $\equiv\text{C}-\text{H}$) in ^1H NMR, completely disappeared. The visible absorption maxima (λ_{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 π -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 (λ_{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 $2\theta = 3 - 4^\circ$, 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°), 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 π -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 ($\alpha = P_{\text{O}_2}/P_{\text{N}_2}$) 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 2: Column structure of polydendrons.

Polymers	Generation number	Density ^a (g/cm ³)	2θ ^b (deg)	d spacing ^c (Å)	Column diameter	
					WAXS ^d (Å)	Calcd ^e (Å)
poly(HG1PA) ^f	1	1.068	3.1	30.5	35.2	43.0
poly(HG0PA) ^f	0	1.062	3.3	28.7	33.1	36.7

^a Determined by floating method containing error of ± 0.005 .^b Crystalline peak of the wide-angle X-ray scattering (WAXS) of the polymers.^c Estimated from 2θ .^d Estimated from d (column diameter = $2d/\sqrt{3}$).^e Estimated 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 = 130 deg), as described in [7].)

FIGURE 1: Permselectivity of poly(phenylacetylene) analogue membranes for O₂/N₂ separation. Poly(phenylacetylene) (PPA) and poly(TMS0H) from [13], poly(PMDS0H), poly(NMTS0H), poly(TMS1H), and poly(PMDS1H) from [6].

the oxygen permeability coefficient and oxygen separation factor. However, the oxygen permselectivity of the polydendrons with a trimethylsilyl group, poly(TMS1H), shows good performance in comparison with corresponding zero-generation poly(phenylacetylene) derivatives. In comparison, polydendrons with oligo(dimethylsiloxane) peripheral groups (i.e., poly(PMDS1H)) exhibited similar trend to that of the corresponding zero-generation poly(phenylacetylene) derivatives. On the other hand, polymers and polydendrons with alkoxy peripheral groups exhibited the lower oxygen permeability coefficient due to the alkyl domain that would have better gas barrier property than oligo(dimethylsiloxane) domain. But the oxygen permselectivity of poly(Hex1H) shows good performance in comparison with the trend between polyethylene and poly(Hex0H). These results suggest that the space-persistence due to the stiff and crowded dendritic structure play an important role in the high performance of the oxygen permselectivity, while the effect of the peripheral group was similar to that of the corresponding zero-generation poly(phenylacetylene) derivatives.

4. Conclusions

The phenylacetylene monomers consisting of monodendron with alkoxy peripheral groups were successfully polymerized with a Rh catalyst, [Rh(nbd)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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