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Synthesis of poly(phenylacetylene)-based polydendrons consisting of a phenyleneethynylene repeating unit, and oxygen/nitrogen permeation behavior of their membranes

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Abstract

Monodendrons consisting of *m*-linked phenyleneethynylene repeating unit with trimethylsilyl-, pentamethyldisiloxanyl- and nonamethyltetrasiloxanyl-peripheral groups were synthesized using the convergent approach. The focal point of monodendrons, terminal acetylene, was polymerized with rhodium catalyst to yield corresponding polydendrons with a high molecular weight. The polydendrons were solubile 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 pemselective membrane. Oxygen permselectivity was increased in polydendrons with a trimethylsilyl group compared to the corresponding zero generation poly(phenylacetylene) derivatives.

Keywords: Dendrimer; Polydendron; Polyacetylene; Silyl group; Oxygen permselectivity

1. Introduction

The chemical structure and/or morphology of polymers play an important role for the permselectivity of nonporous membranes. It is believed that the more homogeneous in horizontal direction membranes are, the better performance they show. 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 nano-scale 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 obtained the corresponding polydendrons by polymerization of the monomers using a rhodium (Rh) catalyst [5]. The polydendrons were mechanically stable and excellent for preparing self-supporting membranes. The first generation polydendron membrane showed an oxygen permselectivity higher than that of the corresponding zero generation poly(phenylacetylene) derivative, poly[[4-(trimethylsilyl)phenyl]acetylene]. Permselective membranes using dendrimers or hyperbranched polymers have also been described elsewhere [6–13].

As dendrimers have no intrinsic ability to form self-supporting membranes, two methods have been described to prepare membranes: use of a porous support to form composite membranes [6–9] or, cross-linking of reactive peripheral groups within the dendrimers [10–13]. Some of them had

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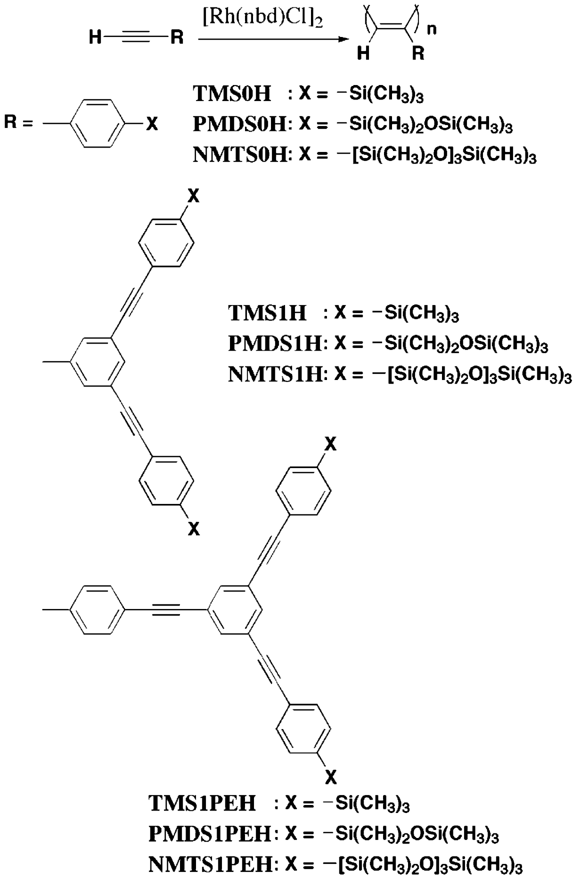

Scheme 1.

the better permselective performance than the corresponding linear polymers. There, our polydendron membranes possess some characteristics as follows: the self-supporting homogeneous membranes are simple to analyze the permeation property, and the shape and space of the dendritic area can be controlled by the shape-persistency of phenyleneethynylene sequences which have geometric restrictions and a lack of conformational freedom. These characteristics are ideal to examine the effect of the branched structure on oxygen/nitrogen permselectivity. In this study, we synthesized polydendrons with various sizes of the rigid and branched area and the flexible peripheral groups as shown in Scheme 1. In addition, we examined the oxygen permselectivity of their membranes in relation to their chemical structures.

2. Experimental

2.1. Materials

[4-(Trimethylsilyl)phenyl]acetylene (TMS0H) [14], [4-(pentamethyldisiloxanyl)phenyl]acetylene (PMDS0H) [15], [4-(nonamethyltetrasiloxanyl)phenyl]acetylene (NMTS0H) [15], 3,5-dibromo-1-(3-hydroxyl-3-methylbutynyl)benzene [16], 4-bromo-1-(3-hydroxyl-3-methylbutynyl)benzene [17], TMS1H [16], PMDS1H [16] and NMTS1H [16] were synthesized as previously described. (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ([Rh(nbd)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

2.2.1. 3,5-Dibromophenylacetylene

Sodium hydride (3.3 g, 83 mmol) was added to a toluene solution (126 ml) of 3,5-dibromo-1-(3-hydroxyl-3-methylbutynyl)benzene (18 g, 57 mmol). The solution was heated to 100 °C and stirred for 2 h under a nitrogen flow. The reaction solution was washed with water, then dried over anhydrous sodium sulfate. The crude product was purified by silica-gel column separation with hexane as an eluent to give 3,5-dibromophenylacetylene (13 g, 50 mmol). Yield 87%; mp 85–87 °C. TLC (hexane): $R_f = 0.64$. IR (KBr; cm^{-1}): 3300 (≡C–H), 2316 (C≡C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 3.15 (s, 1H, C≡C–H), 7.68 (d, 2H, $J = 1.5$ Hz, ArH), 7.95 (t, 1H, $J = 1.5$ Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 79.82, 80.57, 122.58, 132.98, 133.54, 134.63. Anal. calcd. for ($C_{30}H_{30}Si_2$): C, 80.7; H, 6.8. Found: C, 80.5; H, 7.1.

2.2.2. 1-(3-Hydroxyl-3-methylbutynyl)-4-iodobenzene

2-Methyl-3-butyn-2-ol (2.8 ml, 30 mmol) was added to a triethylamine/pyridine solution (200 ml/133 ml) of 1,4-diiodobenzene (10 g, 30 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.14 g, 0.2 mmol), triphenylphosphine (0.24 g, 0.92 mmol) and copper(I) iodide (0.12 g, 0.63 mmol) under a nitrogen atmosphere. The solution was stirred for 18 h at 50 °C. The mixture was filtered off, and the filtrate was evaporated, then extracted with chloroform, and washed with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether, and washed with 10% HCl. The ether layer was dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was dissolved in benzene (150 ml), and ethylene diamine (30 ml) was added to the solution. The solution was heated at 80 °C for 20 min. After cooling, the mixture was filtered off, and the filtrate was washed with 10% HCl and water, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by silica-gel column separation with chloroform as an eluent to give 1-(3-hydroxyl-3-methylbutynyl)-4-iodobenzene (4.8 g, 17 mmol). Yield 55%; mp 81–83 °C. TLC (chloroform): $R_f = 0.28$. IR (KBr; cm^{-1}): 3484 (–OH), 2988 (C–H), 2356 (C≡C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 1.61 (s, 6H, CH$_3$), 2.14 (s, 1H, –OH), 7.13 (d, 2H, $J = 8.5$ Hz, ArH), 7.63 (t, 1H, $J = 8.5$ Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 31.37, 65.59, 81.22, 94.09, 95.15, 122.22, 133.12, 137.38.

2.2.3. 4-[2-(3,5-Dibromophenyl)ethynyl]-1-(3-hydroxyl-3-methylbutynyl)benzene

A triethylamine (40 ml) solution of 1-(3-hydroxyl-3-methylbutynyl)-4-iodobenzene (4.3 g, 15 mmol), 3,5-dibromo-