



Synthesis and oxygen permeation of novel polymers of phenylacetylenes having two hydroxyl groups via different lengths of spacers

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ABSTRACT

Three novel phenylacetylenes having two hydroxyl groups via different kinds of spacers between the two hydroxyl groups and benzyl group were synthesized and polymerized. Two of the resulting polymers having oxyalkylene spacers between the hydroxyl group and benzyl group had good membrane forming ability, relatively high oxygen permselectivity and high oxygen permeability. By introducing the oxyalkylene spacers, the membrane forming abilities and oxygen permselectivity were enhanced. Oxygen permselectivity ($P_{O_2}/P_{N_2} = 2.67$) of the polymer membrane having the longest spacers was higher than that (2.19) of polymer without any spacers. It may be because the columnar content and then defects decreased when the cis-cisoid conformation was changed to cis-transoid conformation. In addition, by decreasing the columnar content of the membrane from the polymer without any spacers, which could be controlled by conditions in membrane preparation, the membrane forming ability and oxygen permselectivity were effectively enhanced (from 2.19 to 2.61) without any drop of oxygen permeability.

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1. Introduction

π -Conjugated polymers like polyacetylenes [1–3] have attracted increasing attention because of their noteworthy physical properties such as electric conductivity, nonlinear susceptibility, high oxygen permeability [4–15] and so on. Among them, poly(phenylacetylene)s are useful because they are usually more stable than other substituted polyacetylenes in the air and can often form self-supporting membranes [16–24]. Some researchers reported the synthesis and oxygen permeability of various poly(phenylacetylene) membranes showing high oxygen permeabilities and relatively high oxygen permselectivities [25–50]. On the other hand, regular structures of poly(phenylacetylene)s such as the conformation of their polymer main chains and the columnar structures in their solid state have been reported [51–59]. Although these regularities are interesting and important because it has possibility to give oxygen permselective membranes with high

selectivity, the control of the structures is not enough for such application.

Recently we have been reporting new one-handed helical poly(phenylacetylene)s by helix-sense-selective polymerization of achiral phenylacetylenes having two hydroxyl groups (for example, **1** in Chart 1) using a chiral catalytic system consisting of [Rh(norbornadiene)Cl]₂ (norbornadiene = NBD) as an initiator and (R)-phenethylamine(PEA) as a cocatalyst [51,52]. The poly(**1**) adopts a tight cis-cisoidal helical conformation [52]. We thought the new types of substituted polyacetylenes having a more regular structure in their main chains, ie, tight cis-cisoidal helical structures can have better performance than other polyacetylenes. The high regularity of poly(**1**) is expected to be applied to oxygen permeation membrane having high selectivity. However, its oxygen permeability has not been reported because its membrane forming ability was not very good. In addition, we thought we needed the new type of substituted polyacetylenes having a more regular structure in its main chain, i.e., a tighter cis-cisoidal helical structure, because it can show better performance than other polyacetylenes. Therefore we designed three new monomers (**2**, **3**, and **4**), which had been expected to give polymers having cis-cisoidal conformation, and measured performances of the resulting polymer membranes.

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To obtain polyphenylacetylenes having regular structures as membrane materials having good membrane forming ability and good permselectivities, and to discuss the relationship between the permselectivity and their regularity containing regular conformations of their polymer main chains and the columnar contents in the solid state, three phenylacetylene monomers having two hydroxyl groups via different kinds of spacers between the two hydroxyl groups and the benzyl group (Chart 1, 2–4) were synthesized and polymerized in this study. In addition, effects of extending the length of the spacers on the membrane forming abilities and their oxygen permselectivity are discussed.

2. Experimental

2.1. Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. The polymerization initiator, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received. Poly(5) and poly(6) were synthesized according to our previous report [53,54].

2.2. Measurements

2.2.1. Measurement of oxygen and nitrogen permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2} : $\text{cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$) and the oxygen separation factor ($\alpha = P_{\text{O}_2}/P_{\text{N}_2}$) were measured by a gas chromatographic method by using YANACO GTR-10 according to our previous report [47]. The diffusion coefficient (D : $\text{cm}^2 \text{ s}^{-1}$) was calculated by the time-lag method represented by $D = L^2/6\theta$, where $L(\text{cm})$ is the thickness of the membrane and $\theta(\text{s})$ is the time-lag.

2.2.2. Other measurements

^1H NMR (400 MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070 and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20 °C (a quartz cell of 1 mm path length; sample concentration: 0.100–2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO). The elongations at break of the membranes were measured at a strain rate of 5 mm/min with a TOM-5 Minebea Co., Ltd. UV-vis spectra were measured with a JASCO V-550 spectropolarimeter. Elemental Analyses were performed by using YANACO MT-3, MT-5, MT-6, and J-SCIENCE LAB CO. Ltd. JM-10 at the Organic Elemental Analysis Research Center (Kyoto University, Japan). X-Ray diffraction diagrams were measured with a Rigaku high resolution X-ray diffractometer RINT2500HR/PC Gigerflex RAD- γ VA.

2.3. Synthesis of the poly(2)-poly(4) (Scheme 1)

2.3.1. Synthesis of new monomers 2–4 (Scheme 1)

2.3.1.1. 4-Bromo-2,6-bis(hydroxymethyl)-1-phenol (7). A formaldehyde aqueous solution (37.0 wt%, 300 mL, 4.00 mol) was added dropwise to a solution of 4-bromophenol (51.1 g, 0.295 mol) and potassium hydroxide (18.5 g, 0.393 mol) in 2-propanol (100 mL), and the solution was heated and stirred at 40 °C for 89 h. The resulting solution was cooled to room temperature and poured into 0.1 mol/L hydrochloric acid (1000 mL) with stirring. The solution was allowed to stand for about 6 h to give a red viscous solid as a

precipitate. After removing the red solid by decantation, the supernatant solution was allowed to stand for 2 days to yield a white solid as a precipitate. The solid was filtered, washed with chloroform, and dried to give a white solid. Yield: 63.4% (43.6 g). ^1H NMR (400 MHz, DMSO- d_6 , δ): 8.78 (s, 1H, PhOH), 7.29 (s, 2H, PhH), 5.33 (t, 2H, $(\text{CH}_2\text{OH})_2$), 4.51 (d, 4H, Ph $(\text{CH}_2\text{OH})_2$).

2.3.1.2. 4-Bromo-2,6-bis(hydroxymethyl)-1-dodecyloxybenzene (8). 1-Bromododecane (5.90 mL, 23.6 mmol) was added to the solution of **7** (5.00 g, 21.5 mmol) and potassium carbonate (8.25 g, 59.7 mmol) in acetone (100 mL). The solution was refluxed under stirring for 48 h. After cooling to room temperature, unreacted potassium carbonate was filtered off and the solvent was evaporated to give a crude product. The crude product was purified by silica-gel column chromatography. Yield: 64.3% (white solid), $R_f = 0.27$ (ethyl acetate/hexane = 1/4). ^1H NMR(400MHz, CDCl_3 , TMS, δ): 7.49 (s, 2H, PhH), 4.70 (d, 4H, Ph $(\text{CH}_2\text{OH})_2$), 3.85 (t, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.97 (t, 2H, $(\text{CH}_2\text{OH})_2$), 1.80 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.50–1.20 (m, 18H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (t, 3H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$).

2.3.1.3. 1-Dodecyloxy-2,6-bis(hydroxymethyl)-4-(3-hydroxy-3-methyl-1-butynyl)benzene (9). 2-Methyl-3-butyn-2-ol (2.30 mL, 27.6 mmol) was added to a mixture of **8** (13.8 mmol), tribenzylphosphine (0.430 g, 1.66 mmol), copper(I) iodide (0.290 g, 1.52 mmol) and bis(tribenzylphosphine)palladium(II) chloride (0.430 g, 0.620 mmol) in dry triethylamine (Et_3N , 100 mL). The solution was stirred at room temperature for 12 h and refluxed for 24 h. The resulting solid was removed by filtration and the solution was concentrated. The formed brown liquid was purified by silica-gel column chromatography. The crude solid was recrystallized from dichloromethane/hexane (1/10). Yield: 81.5% (white solid), $R_f = 0.27$ (ethyl acetate/hexane = 1/1). ^1H NMR(400MHz, CDCl_3 , TMS, δ): 7.45 (s, 2H, PhH), 4.67 (d, 4H, Ph $(\text{CH}_2\text{OH})_2$), 3.86 (t, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 2.14 (s, 1H, $\text{C}(\text{CH}_3)_2\text{OH}$), 1.94 (t, 2H, $(\text{CH}_2\text{OH})_2$), 1.79 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.60 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.50–1.20 (m, 18H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (t, 3H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$).

2.3.1.4. 4-Dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (1). A mixture of **9** (11.4 mmol) and sodium hydride (60% in oil, 0.450 g, 11.3 mmol) in dry toluene (400 mL) was refluxed for 20 min. After cooling the mixture to room temperature, the resulting solid was removed by filtration and the solvent was concentrated. The crude product was dissolved in diethyl ether, and then the solution was washed with 0.1 M HCl aqueous solution. The organic layer was dried with anhydrous sodium sulfate. After removing the formed salt by filtration, the organic layer was concentrated. The obtained solid was purified by silica-gel column chromatography and by recrystallization from hexane. Yield: 67.2% (white solid), $R_f = 0.24$ (ethyl acetate/hexane = 1/4). ^1H NMR(400MHz, CDCl_3 , TMS, δ): 7.49 (s, 2H, PhH), 4.70 (d, 4H, Ph $(\text{CH}_2\text{OH})_2$), 3.90 (t, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 3.04 (s, 1H, $\text{C}\equiv\text{CH}$), 1.96 (t, 2H, $(\text{CH}_2\text{OH})_2$), 1.81 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.50–1.20 (m, 18H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (t, 3H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$). Anal. calcd for $\text{C}_{22}\text{H}_{34}\text{O}_3$: C 76.26, H 9.89; Found: C 76.56, H 9.76.

2.3.1.5. 4-Dodecyloxy-3,5-bis(bromomethyl)phenylacetylene (10). **1** (1.00 g, 2.89 mmol), CBr_4 (3.23 g, 9.73 mmol), PPh_3 (2.27 g, 8.67 mmol), and CH_2Cl_2 (40.0 mL) were put in a 100 mL flask. The solution was stirred for 4 h in an ice bath and then the solvent was removed by evaporation. The crude solid was purified by silica-gel column chromatography to give compound **10**. Yield: 88.5% (white solid), $R_f = 0.14$ (Hexane). ^1H NMR(400MHz, CDCl_3 , TMS, δ): 7.50 (s, 2H, PhH), 4.48 (s, 4H, Ph CH_2Br), 4.09 (t, 2H, $\text{PhOCH}_2\text{CH}_2$), 3.06 (s, 1H,

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