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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 permselity. 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.

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

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application. Recently we have been reporting new one-handed helical polv(phenylacetylene)s, by helix-sense-selective, polymerization, of

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

y(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, $[Rh(nbd)Cl]_2$ (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} : cm³(STP) cm cm⁻² s⁻¹ cm Hg⁻¹) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) were measured by a gas chromatographic method by using YANACO GTR-10 according to our previous report [47]. The diffusion coefficient (D: cm² s⁻¹) was calculated by the time-lag method represented by $D = L^2/6\theta$, where L(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 $(M_{\rm p} \text{ and } M_{\rm w})$ 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-YVA.

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, (CH₂OH)₂), 4.51 (d, 4H, Ph(CH₂OH)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(400MH_Z, CDCl₃, TMS, δ): 7.49 (s, 2H, PhH), 4.70 (d, 4H, Ph(CH₂OH)₂), 3.85 (t, 2H, OCH₂CH₂(CH₂)₉CH₃), 1.97 (t, 2H, (CH₂OH)₂), 1.80 (m, 2H, OCH₂CH₂(CH₂)₉CH₃), 1.50-1.20 (m, 18H, OCH₂CH₂(CH₂)₉CH₃), 0.88 (t, 3H, OCH₂CH₂(CH₂)₉CH₃).

2.3.1.3. 1-Dodecyloxy-2,6-bis(hydroxymethyl)-4-(3-hydroxy-3methyl-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 (Et₃N, 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 silicagel column chromatography. The crude solid was recrystallized from dichloromethane/hexane (1/10). Yield: 81.5% (white solid), $R_{\rm f} = 0.27$ (ethyl acetate/hexane = 1/1). ¹H NMR(400MH₇, CDCl₃, TMS, δ): 7.45 (s, 2H, PhH), 4.67 (d, 4H, Ph(CH₂OH)₂), 3.86 (t, 2H, OCH₂CH₂(CH₂)₉CH₃), 2.14 (s, 1H, C(CH₃)₂OH), 1.94 (t, 2H, (CH₂OH)₂), 1.79 (m, 2H, OCH₂CH₂(CH₂)₉CH₃), 1.60 (s, 6H, C(CH₃)₂), 1.50-1.20 (m, 18H, OCH₂CH₂(CH₂)₉CH₃), 0.88 (t, 3H, OCH₂CH₂(CH₂)₉CH₃).

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), $R_{\rm f} = 0.24$ (ethyl acetate/hexane = 1/4). ¹H NMR(400MH_Z, CDCl₃, TMS, δ): 7.49 (s, 2H, PhH), 4.70 (d, 4H, Ph(CH₂OH)₂), 3.90 (t, 2H, OCH₂CH₂(CH₂)₉CH₃), 3.04 (s, 1H, C≡CH), 1.96 (t, 2H, (CH₂OH)₂), 1.81 2H. $OCH_2CH_2(CH_2)_9CH_3),$ 1.50-1.20 (m. (m, 18H. OCH₂CH₂(CH₂)₉CH₃), 0.88 (t, 3H, OCH₂CH₂(CH₂)₉CH₃). Anal.calcd for C₂₂H₃₄O₃: 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), CBr₄ (3.23 g, 9.73 mmol), PPh₃ (2.27 g, 8.67 mmol), and CH₂Cl₂ (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(400MH_Z, CDCl₃, TMS, δ): 7.50 (s, 2H, PhH), 4.48 (s, 4H, PhCH₂Br), 4.09 (t, 2H, PhOCH₂CH₂), 3.06 (s, 1H, \equiv CH), 1.89(tt, 2H, OCH₂CH₂CH₂), 1.54-1.27 (m,18H, OCH₂CH₂(CH₂)₉CH₃), 0.88 (t,3H, OCH₂CH₂(CH₂)₉CH₃).

4-Dodecyloxy-3,5-bis(2-hydroxyethyloxymethyl)phenyl-

acetylene (2)

Sodium hydride (144 mg, 3.00 mmol) was added to a solution of compound **10** (300 mg, 0.600 mmol) and ethylene glycol (0.330 mL, 6.00 mmol) in THF (60.0 mL). The mixture was refluxed for 3 days, and water (60 mL) was added. The resulting aqueous layer was extracted with ethyl acetate. The organic layer was dried over MgSO₄, and evaporated to dryness. The product was purified with silica gel chromatography to give monomer **2**. Yield: 68.6% (white solid), $R_f = 0.23$ (ethyl acetate/hexane = 1/2). ¹H NMR(400MH_Z, CDCl₃, TMS, δ): 7.43 (s, 2H, PhH), 4.50 (d, 4H, PhCH₂O), 3.76 (t, 2H, PhOCH₂), 3.70(td, 4H, OCH₂CH₂OH), 3.55 (t, 4H, OCH₂CH₂OH), 2.96 (s, 1H, C=CH), 1.93 (t, 2H, OCH₂CH₂OH), 1.72(tt, 2H, OCH₂CH₂CH₂), 1.45-1.19 (m, 18H, (CH₂)₉CH₃), 0.81 (t, 3H, (CH₂)₉CH₃). IR(KBr): 3310(OH), 3280(H–C=), 2840(CH), 2095(C=C). Anal.calcd for C₂₆H₄₂O₅: C 71.85, H 9.74, O 18.41; found: C 71.89, H 9.75, O 18.21.

2.3.1.6. 4-Dodecyloxy-3,5-bis(4-hydroxybutyloxymethyl)phenylacetylene (3). Sodium hydride (150 mg, 3.20 mmol) was added to a solution of compound 10 (300 mg, 0.640 mmol) and 1,4-butanediol (0.560 mL, 6.35 mmol) in THF (60.0 mL). The mixture was refluxed for 3 days, and water (60 mL) was added. The resulting aqueous layer was extracted with ethyl acetate. The organic layer was dried over MgSO₄, and evaporated to dryness. The product was purified with silica gel chromatography. Yield: 76.0% (colorless liquid), $R_{\rm f} = 0.12$ (ethyl acetate/hexane = 1/2). ¹H NMR(400MH₇, CDCl₃, TMS, δ), 7.48 (s, 2H, PhH), 4.50 (s, 4H, PhCH₂O), 3.81 (t, 2H, PhOCH₂), 3.64(td, 4H, CH₂(CH₂)₂CH₂OH), 3.53 (t, 4H, OCH₂(CH₂)₂CH₂OH), 3.01 (s, 1H, C=CH), 1.93 (t, 2H, CH₂CH₂OH), 1.78(tt, 2H, OCH₂CH₂CH₂), 1.65 (m, 8H, CH₂(CH₂)₂CH₂OH), 1.45-1.26 (m, 18H, OCH₂CH₂(CH₂)₉CH₃), 0.81 (t, 3H, OCH₂CH₂(CH₂)₉CH₃).IR(KBr): 3397(OH), 3296(H-C≡), 2840(CH), 2095(C≡C). Anal.calcd for C₃₀H₅₀O₅: C 73.43, H 10.27, O 16.30; found: C 72.77, H 10.28, O 16.43.

2.3.1.7. 4-Dodecyloxy-3,5-bis(2-hydroxybenzyl-1-oxy)methylphenylacetylene (4). Catechol (349 mg, 3.18 mmol), compound 10 (300 mg, 0.635 mmol), potassium carbonate (439 mg, 3.18 mmol), and acetone (60.0 mL) were put in a 100 mL flask. The solution was refluxed for 48 h and cooled to room temperature. Unreacted potassium carbonate was removed by filtration and the solution was concentrated by evaporation. The crude product was purified by silica-gel column chromatography. Yield: 80% (white solid), $R_{\rm f} = 0.38$ (ethyl acetate/hexane = 1/4). ¹H NMR(400MH₇, THF- d_8 , TMS, δ), 7.57 (s, 2H, PhH), 6.95-6.81 (m, 8H, (OPhHOH)₂), 5.71 (s, 2H, $(OPhOH)_{2}$). 5.08 (s, 4H, (PhCH₂O)₂), 3.87 (t. 2H. OCH₂CH₂(CH₂)₉CH₃), 3.05 (s, 1H, C=CH), 1.78 (m, 2H, OCH₂CH₂(CH₂)₉CH₃), 1.34-1.17 (m, 18H, OCH₂CH₂(CH₂)₉CH₃), 0.86 (t, 3H, $OCH_2CH_2(CH_2)_9CH_3$). IR(KBr): 3340(OH), 3285(H-C=), 2840(CH), 2095(C=C). Anal.calcd for C₃₄H₄₂O₅: C 76.95, H 7.98, O 15.07; found: C 76.95, H 8.62, O 15.07.

2.3.2. Polymerization of new monomers 2-4 (Scheme 1)

A typical procedure for **2** was as follows: A solution of [Rh(nbd) $Cl]_2$ (2.12 mg, 4.60 µmol) and (*S*)- or (*R*)-phenethylamine (PEA) (118 µl, 0.920 mmol) in dry toluene (1.44 mL) was added to a dry toluene (1.44 mL) solution of **2** (100 mg, 230 µmol). The reaction solution was stirred at room temperature for 4 h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other polymerization of new monomers 3 and 4 were carried out similarly.

Poly(**2**): ¹H NMR(400MH_Z, CDCl₃, TMS, δ): 6.74 (br, Ph*H* and trans proton in the main chain), 5.57 (br, cis proton in the main chain), 4.25 (br, PhCH₂O), 3.74-3.30 (br, PhOCH₂CH₂ and OCH₂-CH₂OH), 1.85-1.26 (br, CH₂CH₂OH and OCH₂(CH₂)₁₀CH₃), 0.88 (s, 3H, OCH₂(CH₂)₁₀CH₃). IR(KBr): 3310(OH), 2840(CH).

Poly(**3**): ¹H NMR(400MH_Z, CDCl₃, TMS, δ), 6.51 (br, Ph*H* and trans proton in the main chain), 5.44 (br, cis proton in the main chain), 4.08(br, PhCH₂O), 3.36-2.97 (br, PhOCH₂ CH₂, OCH₂(CH₂)₂-CH₂OH and CH₂CH₂OH), 1.37-1.20 (br, CH₂(CH₂)₂CH₂OH and OCH₂(CH₂)₁₀CH₃), 0.81 (s, 3H, OCH₂(CH₂)₁₀CH₃). IR(KBr): 3397(OH), 2840(CH).

Poly(**4**): ¹H NMR(400MH_Z, THF- d_8 , TMS, δ), 6.47 (br, PhH and trans proton in the main chain), 5.60 (br, OPhOH and cis proton in the main chain), 4.50 (br, PhCH₂O), 3.43(br, OCH₂CH₂(CH₂)₉CH₃), 1.17-1.00 (br, OCH₂CH₂(CH₂)₉CH₃ and OCH₂CH₂(CH₂)₉CH₃), 0.81 (s, 3H, OCH₂CH₂(CH₂)₉CH₃). IR(KBr): 3340(OH), 2840(CH).

2.4. Membrane preparation

A typical membrane fabrication method for poly(**2**) was as follows: A solution of the poly(**2**) (0.0600-10.0 wt%) in dry toluene (40.0 mg/mL) was cast on a poly(tetrafluoroethylene) sheet (4 cm²). After evaporating of the solvent for 12 h at 25 °C, the membranes were detached from the sheet and dried in *vacuo* for 24 h. Thickness (L) of the membranes was 50.0–80.0 μ m. Other polymer membranes were carried out similarly.

3. Results and discussion

3.1. Synthesis and polymerization of novel phenylacetylene monomers having two hydroxyl groups (Table 1, Scheme 1)

As described in the introduction part, we reported a phenylacetylene(1) (Chart 1) having two hydroxyl groups without any spacers between the two hydroxyl groups and benzyl group was polymerized to give the corresponding tight cis-cisoidal one handed helical polymer [51,52]. In addition, the solid from this regular polymer was reported to include a columnar structure [55–59]. However its oxygen permeability has not been reported because its membrane forming ability was not very good. To obtain polymers as membrane materials having good membrane forming ability from such novel phenylacetylenes having two hydroxyl groups, three novel phenylacetylenes having two hydroxyl groups via different kinds of the spacers between the two hydroxyl groups and benzyl group (Chart 1, 2–4) were synthesized and polymerized by using the $[Rh(nbd)Cl]_2/(R)$ -PEA as catalytic system (Scheme 1). The new monomers 2-4, were obtained via the monomer 1 in 23-38% yields according to Scheme 1. The polymerization gave high *Mw* of poly(**2**) and poly(**3**) in high yields(Table 1, Nos. 2 and 3). Especially M_w of poly(**3**) was 20 times higher than that of poly(**1**) (Table 1, Nos. 1 and 3), although the M_w of poly(4) was lower than that of poly(1).

While the formed poly(1) was partly precipitated during polymerization i.e., the polymerization solution could not maintain its homogeneity, no precipitation was observed by the end of polymerization of **2** and **3**.

It is thought to be caused by the fact that the introduction of longer flexible spacers between the two hydroxyl groups and the benzyl group in 2 and 3 enhanced the solubilities of the monomers and their polymers compared with those of 1 and poly(1) which has no spacers, and therefore homogeneity of the polymerization system could be kept during polymerization. The polymerization system of 4 could not keep its homogeneity during polymerization since the benzene ring as a spacer decreased the solubility of the monomer and its polymer. Therefore, the polymerization gave a



Scheme 1. Synthetic routes to new polymers (poly(2)-poly(4)).

low *Mw* poly(**4**) in a low yield. In the case of **5** having a shorter alkyl group than **1**, the yield and *Mw* were also low (Table 1, No. 5) because solubilities of **5** and poly(**5**) were low. The yield of polymerization of **6** having a benzyloxy group as a spacer, and *Mw* and solubility of poly(**6**) were similar to those of **1** and poly(**1**).

We previously reported that polymers from monomers having no spacers between the hydroxyl groups and benzyl group, i.e., poly(1) [51], poly(5) [53] and poly(6) [54], were optically active (Table 1, Nos. 1, 5 and 6; [G] = 54, 59 and 7deg, Fig. S1) and their main chain took cis-cisoid one-handed helical conformations which are maintained by intramolecular hydrogen bonds of the hydroxyl groups [52]. On the other hand, three novel polymers of the corresponding monomers having two hydroxyl groups in this study, i.e., poly(2), poly(3), and poly(4) were optically inactive ([G] = 0, Table 1, Nos. 2–4). Because we found most of polymers prepared from achiral phenylacetylenes having two hydroxyl groups by using chiral catalytic system such as poly(1) showed CD signals based on their stable one handed tight cis-cisoidal conformation, this finding can indicate that these polymers' main chain consisted of more extended and unstable cis-transoid helical conformations. We also reported that in ¹H NMR spectra, the peaks of polymers having tight cis-cisoidal conformations were very broad because of their very low molecular motion. In fact, the peaks for poly(**5**) and poly(**6**) in ¹H NMR spectra were very broad similar to poly(**1**). However, the peaks of poly(**2**), poly(**3**), and poly(**4**) were sharp in ¹H NMR spectra. To discuss the broadness, the peak width($W_{1/2}$) at the half-height of the methyl peak in ¹H NMR spectra of poly(**2**), poly(**3**), and poly(**4**) were much smaller than that of poly(**1**). The finding indicates the molecular motion of poly(**2**).

Polymerization of novel phenylacetylenes	(1-6)	having	two l	hydroxyl	groups.
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No.	Monomer	Yield (%)	$M_{\rm w}{}^{\rm a}(10^6)$	$M_{\rm w}/M_{\rm n}^{\rm a}$	W _{1/2} ^b (ppm)	G ₃₀₇ ^c (deg)	v_{OH}^{d} (cm ⁻¹)	Solubility ^e	Membrane forming ability ^f
1	1	92.0	2.5	3.8	0.22	54	3300	++	+
2	2	85.5	2.3	4.0	0.034	0	3438	+++	+++
3	3	89.5	39	6.5	0.036	0	3400	++	++
4	4	42.0	0.57	3.1	0.056 ^g	0	3352	++	_
5	5 ^h	24.8	1.0	5.0	_	59	_	+	_
6	6 ⁱ	92.5	7.9	4.0	-	7	-	++	+

^a By GPC correlating polystyrene standard (eluent: THF).

^b Peak width at half-height of -CH₃ in ¹H NMR spectra in CDCl₃.

^c $|G|_{307} = [\theta]_{307} \varepsilon^{-1} \times 10^2$ at 307 nm in THF.

^d The O-H vibration absorption bands from IR spectra at r.t. (3.0 g/L) in CHCl₃.

^e In CHCl₃; +++: high soluble; ++: soluble; +:partly soluble.

^f +++: Very flexible; ++: flexible; +: brittle; -: no membrane forming ability.

^g In THF-d₈.

^h From Ref. [53].

ⁱ From Ref. [54].

Table 2

Oxygen permeation through membranes of novel polymers of polyphenylacetylenes (1–3) having two hydroxyl groups.

No.	Membrane	Solvent	Membrane forming ability ^a	<i>P</i> ₀₂ ^b	$P_{\rm O_2}/P_{\rm N_2}$	<i>D</i> ₀₂ ^c	D_{O_2}/D_{N_2}
1	Poly(1)	CHCl ₃	+	1.39	2.19	1.16	1.04
2	Poly(2)	THF	+++	0.13	2.60	0.41	1.45
3	Poly(3)	THF	++	0.16	2.67	0.50	1.34

^a +++: Very flexible; ++: flexible; +: brittle.

^b In 10^{-8} cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹.

^c In 10^{-6} cm² s⁻¹.



Fig. 1. Oxygen permeation through membranes of novel polymers of phenylacetylenes (1–3) having two hydroxyl groups.

poly(**4**) is higher than that of poly(**1**). We also reported the stable cis-cisoidal conformation in poly(**1**) was maintained only by their intramolecular hydrogen bonds. In the IR spectra of poly(**1**)-poly(**4**) in chloroform (Fig. S2), the wavenumber of O–H vibration absorption bands of poly(**2**), poly(**3**), and poly(**4**) were higher than that of poly(**1**). The observation shows their hydrogen bonds in poly(**2**), poly(**3**), and poly(**4**) were weaker than those in poly(**1**). In conclusion, all the results on CD, UV, NMR, and IR above mentioned indicate that with increase of the spacer length, the hydrogen bonds had become weaker and their tight cis-cisoidal one-handed helical main chain structures could not be maintained and was



Fig. 2. XRD of novel polymers of phenylacetylenes (1-4) having two hydroxyl groups.

converted to cis-transoid racemic helical structure. Therefore, the main chains became more flexible by extending the spacers of the side groups.

3.2. Fabrication and characterization of their membranes (Table 1)

Poly(2) and poly(3) could be easily fabricated into selfsupporting membranes which were tough enough to be applied as oxygen permselective membranes. Their good membrane forming abilities are attributed to the good solubility and high Mw, respectively (Table 1). On the other hand, poly(4) and poly(5) showed no self-supporting membrane forming ability due to their low M_w and poor solubility, respectively. Although poly(1) and poly(6) had self-membrane forming ability, they were much brittler than poly(2) and poly(3). Poly(2) and poly(3) membranes have higher flexibility and higher elongation at break than those of poly(1) whose reason is discussed later.

3.3. Enhancement of oxygen permselectivities of the membranes by changing the chemical structures of the polymers (Table 2, Fig. 1)

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}) through the membranes of polyphenylacetylenes, poly(**1**), poly(**2**) and poly(**3**) were newly determined as shown in Table 2 and Fig. 1. By extending the length of the spacers between the two hydroxyl groups and benzyl group, membrane forming abilities and oxygen permselectivities were highly enhanced. In particular, the polymer membrane from the monomer (**3**) having the longest spacer, i.e., butyloxy, showed the highest oxygen permselectivity ($P_{O_2}/P_{N_2} = 2.67$) which was 1.2 times higher than poly(**1**) without spacers ($P_{O_2}/P_{N_2} = 2.19$), although the P_{O_2} values of poly(**2**) and

Fable 3	
Characterization of membranes of novel polymers of phenylacetylenes (1–6) having two hydroxyl groups.	

No.	Polymer	Lattice spacing $(d)^a$ (Å)	Columnar diameter ^b (Å)	Columnar content ^c (%)	Tensile strength (Kg/cm ²)	Elongation at break (%)	Membrane forming ability ^d
1	Poly(1)	20.42	23.58	85.9	113.7	10.8	+
2	Poly(2)	26.74	30.88	43.6	103.3	175	+++
3	Poly(3)	26.58	30.69	36.8	223.1	50.0	++
4	Poly(4)	28.65	33.08	13.8	_	_	-
5	Poly(5) ^e	17.90	20.70	65.5	_	_	-
6	Poly(6) ^f	25.70	29.70	60.3	128.5	7.60	+

^a Calculated from the following equations: 2d sin θ = n λ , where n = 1 and λ = 1.54 Å.

^b d/sin 60.

^c The ratio of the area of columnar region to the area of the entire region.

^d +++: Very flexible; ++: flexible; +: brittle; -: no membrane forming ability.

e From Ref. [53].

^f From Ref. [54].

 Table 4

 Oxygen permeation through membranes of novel polymers of polyphenylacetylenes

 (1) having two hydroxyl groups prepared by using different solvents.

No.	Membrane	Solvent	$P_{O_2}^{a}$	P_{O_2}/P_{N_2}	$D_{0_2}{}^{b}$	$D_{\mathrm{O}_2}/D_{\mathrm{N}_2}$
1	Poly(1-a)	CHCl ₃	1.39	2.19	1.16	1.04
2	Poly(1-b)	toluene/CHCl ₃ (1/1 (v/v))	1.41	2.61	1.80	1.19
3	Poly(1-c)	pyridine	1.46	2.07	1.37	1.19

^a In 10^{-8} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹

^b In 10^{-6} cm² s⁻¹.



Fig. 3. Oxygen permeation through membranes of phenylacetylene (1) having two hydroxyl groups prepared by using different solvents.

poly(**3**) were lower than that of poly(**1**). To discuss the reason of this change in P_{O_2} and P_{O_2}/P_{N_2} , diffusion coefficients (*D*) were determined from the time lags (Table 2). The higher P_{O_2}/P_{N_2} values and lower P_{O_2} values of poly(**2**) and poly(**3**) membranes were caused by the higher D_{O_2}/D_{N_2} values and lower D_{O_2} values of them. Judging from this fact and the better membrane forming ability of poly(**2**) and poly(**3**), these higher P_{O_2}/P_{N_2} and lower P_{O_2} may be caused by dense and defect-free structures of poly(**2**) and poly(**3**) membranes.

3.4. Reasons for the improvements of oxygen permselectivities by changing the chemical structures of the polymers (Table 3, Fig. 2)

As described above (Table 1), although 1 was reported to produce a tight cis-cisoidal one handed helical polymer by the same polymerization condition as that in this study [51,52], it was estimated that the polymers from **2–4** did not have tight cis-cisoidal one handed helical main chains but had loose cis-transoidal racemic helical main chains, judging from their sharper peaks in $NMR(W_{1/2})$ and the absorption bands for OH at higher wave lengths and the UV absorption peaks(Fig. S1). In addition, poly(2) and poly(3) showed better membrane forming abilities and oxygen permselectivitie than poly(1). Therefore, it is thought that one of the reason for these improvements were change of a tight cis-cisoid helicity to a loose cis-transoid helicity in the main-chain conformation. Table 3 lists the results of measurements of XRD (Fig. 2) and mechanical strength for the six polymer membranes. The columnar content of poly(2), poly(3), and poly(4) (Table 3, Nos. 2–4) were much lower than that of poly(1), poly(5) and poly(6) (Table 3, Nos. 1, 5 and 6) whose main chain took regular cis-cisoidal helical conformation. Poly(2) and poly(3) membranes had higher flexibility and higher elongation at break (175 and 50%) than poly(1)(10.8%). It may be caused by their loose helical conformation and lower columnar contents. Although usually polymer membranes having a higher crystallinity show higher permeability and lower permselectivity, these results for poly(1), poly(2), and poly(3) were opposite. It may be caused by the presence of some molecular size defects in poly(1).

In conclusion, by changing the length of the spacers of the monomers between the two hydroxyl groups and benzyl group, the conformations of the polymer main chains were controlled from cis-cisoid to cis-transoid, resulting in decrease of their columnar contents. As a result, the membrane forming ability and oxygen permselectivity were highly enhanced, although the oxygen permeability decreased.

3.5. Enhancements of oxygen permselectivities of the membranes from the same polymers by changing preparation conditions (Table 4, Fig. 3)

As we discussed above, to enhance the membrane forming ability and oxygen permselectivity, the columnar content should be lower. It has been achieved by changing the monomer structures,



Chart 1. Chemical structures of monomers having two hydroxyl groups in this study (1–6).

Table 5	
Characterization of membranes of novel polymers of polyphenylacetylene (1) having two hydroxyl groups prepared by	/ using different solvents.

No.	Membrane	Solvent	Condition	Lattice spacing $(d)^a$ (Å)	Columnar diameter ^b (Å)	Columnar content ^c (%)	Membrane strength ^d
1	Poly(1-a)	CHCl ₃	25°C/101 KPa	20.42	23.58	85.9	+
2	Poly(1-b)	toluene/CHCl ₃ (1/1 (v/v))	25°C/101 KPa	20.53	23.71	67.8	+++
3	Poly(1-c)	pyridine	45°C/61 KPa	20.62	23.81	29.0	++

^a Determined by XRD, calculated from the following equations: 2d $\sin\theta = n\lambda$, where n = 1 and $\lambda = 1.54$ Å.

^b d/sin 60.

^c The ratio of the area of columnar region to the area of the entire region.

^d +++:Very flexible; ++: flexible; +:brittle.

i.e., the length of the spacer. Although poly(1) had highly regular chemical structures, their membrane performance was poor because of very high columnar content (85.9%) when it was prepared from chloroform solution. Therefore, we tried to decrease of the columnar content of poly(1) by changing solvents in membrane preparation. Solvents with different polarities and boiling points, such as toluene and pyridine, were used for membrane fabrication. Table 4 and Fig. 3 show the results of measurement of oxygen permeation behavior for the three poly(1) membranes prepared by three different conditions, i.e., poly(1-a), poly(1-b), and poly(1-c). The P_{O_2}/P_{N_2} was successfully improved from 2.19(poly(1-a)) to 2.61(poly(1-b)) with no decrease of P_{O_2} when toluene/CHCl₃(1/1(v/ v)) was used as a two component solvent (Table 4, Nos. 1 and 2). The increase in P_{O_2}/P_{N_2} was caused by increase in D_{O_2}/D_{N_2} . When we used pyridine as a solvent (Table 4, No. 3), P_{O_2} increased but P_{O_2}/P_{N_2} decreased (poly(1-c)).

3.6. Reason for the improvements of oxygen permselectivities by changing preparation conditions(*Table 5, Fig. S3*)

To discuss the reason for the improvement of P_{O_2}/P_{N_2} for poly(1) and the best performance of poly(1-b), XRD for the three membranes were measured(Fig. S3). Table 5 shows the results of XRD measurement for the three poly(1) membranes prepared by three different conditions, i.e., poly(1-a), poly(1-b), and poly(1-c). By changing the polarity and boiling point of the casting solvent for the membrane fabrication, the columnar contents were highly changed. When solvents having a high boiling point, i.e., toluene and pyridine were used, the original columnar content of poly(1a) (85.9%) largely decreased to 67.8 and 29.0%. Contrary to the decrease, the membrane forming ability highly increased. Poly(1-b) membrane having an intermediate columnar content, showed the best performance as an oxygen permselective membrane. By decreasing the columnar contents, the membrane became denser and flexible and as a result the defects, which had been included in the original membrane poly(**1-a**), may be decreased. Therefore the potential ability of the regular structure in poly(1), which can efficiently separate oxygen and nitrogen, could be used and emerged in poly(1-b) membrane.

In conclusion, by decreasing the columnar content of the membrane prepared from the same polymer by changing conditions in membrane preparation, membrane forming abilities and oxygen permselectivities were successfully enhanced without any drop of oxygen permeability.

4. Conclusions

Three phenylacetylene monomers having two hydroxyl groups via different kinds of spacers between the two hydroxyl groups and benzyl group were synthesized and polymerized by using a $[Rh(nbd)Cl]_2/(R)$ -phenethylamine(PEA) catalytic system. The polymerization gave poly(**2**) and poly(**3**) having high molecular weights and good solubility in high yields. Especially *Mw* of poly(**2**) was 20

times higher than that of poly(1) having no spacers. These polymers could be easily fabricated into self-supporting membranes which were tough enough to be applied as oxygen permselective membranes. By extending the length of the spacers, the membrane forming abilities and oxygen permselectivities were highly enhanced. In particular, the poly(2) having the longest spacers, i.e., butyloxy groups showed the highest oxygen permselectivity $(P_{O_2}/P_{N_2} = 2.67)$ which was 1.2 times higher than that of poly(1) $(P_{O_2}/P_{N_2} = 2.19)$. Because the conformation of poly(**2**) and poly(**3**) is an extended cis-transoidal and that of poly(1) is a tight cis-cisoidal, the columnar contents of poly(2) and poly(3) were lower than that of poly(1). In addition, by using solvents having lower solubilities, i.e., toluene, the columnar contents of poly(1) (85.9%) were decreased to 67.8, respectively. As a result, oxygen permselectivities were also substantially enhanced without any drop of oxygen permeability. This may be because the intermediate columnar content decrease the defects in the membrane and as a result the regular structure was effectively used for the separation. This is an ideal improvement.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.11.042.

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