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ARTICLE

New Achiral Phenylacetylene Monomers Having an Oligosiloxanyl Group Most Suitable for Helix-Sense-Selective Polymerization and for Obtaining Good Optical Resolution Membrane Materials

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ABSTRACT: To develop new phenylacetylene monomers more suitable for helix-sense-selective polymerization (HSSP) we reported previously and to improve the efficiency of the HSSP and membrane performance of the resulting polymers, novel phenylacetylenes having a flexible oligosiloxanyl group (S*n*BDHPA) together with the other related three series of monomers were synthesized and polymerized by using a chiral catalytic system and enantioselectivity in permeation of the membranes from the resulting chiral polymers were examined. S*n*BDHPA was the most suitable for the HSSP and the CD absorptions (*G* values) of poly(S*n*BDHPA) were stronger and more stable than those of the corresponding polymers having rigid alkyl groups. The polymers could be fabricated to flexible self-supporting membranes by using solvent-casting method. In addition, enantioselectivity in permeation of one of poly(S*n*BDHPA) membranes was much higher than that of a poly(phenylacetylene) membrane having alkyl groups. This was because the polymers having oligosiloxane groups had high regularity of structures, i.e., chemical structures of the macromolecules such as one handedness and high order structures such as columnar contents in the membranes, and the membranes were flexible and had almost no defects. These good properties as optical resolution membrane materials were caused by flexibility, hydrophobicity, and bulkiness of the oligosiloxane chains. S3BDHPA having a trisiloxanyl group was found to be the best monomer for the HSSP and for obtaining good optical resolution membrane materials.

Introduction

Recently polyacetylenes that have a one-handed helical conformation have received much attention because the chiral structures are expected to enhance these unique properties and create new properties. The authors found an asymmetric-induced polymerization(AIP) that induced a one-handed helical chirality in the main-chain of a poly(phenylacetylene) having a bulky chiral L-menthoxycarbonyl group in 1993.[1a] Although syntheses of many kinds of chiral poly(substituted acetylene)s have been reported,[1−5] there were no reports of obtaining one-handed helical substituted *soluble* polyacetylenes having no other chiral moieties by polymerizing an achiral substituted acetylene with a chiral catalyst.

Recently we have been reporting new helix-sense-selective polymerization (HSSP) of achiral acetylene monomers (Scheme 1).[6] One-handed helical poly(phenylacetylene)s were obtained from achiral phenylacetylenes having two hydroxyl groups, a rigid alkyl group, and no chiral substituents (C*n*DHPA in Chart 1) by use of a chiral catalytic system consist of $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) as a catalyst and (*R*)-phenylethylamine ((*R*)-PEA) as a cocatalyst. There was the first report of obtaining soluble and one-handed helical substituted polyacetylenes having no other chiral moieties.[6a] Among several C*n*DHPAs having a different *n*, C4DHPA having a dodecyl group was the best monomer to obtain chiral polymers having a high M_w, good solubility, large stable Cotton effects in solution and membrane states, a high membrane forming ability, and high crystallinity in the helix-sense-selective polymerization. In addition, a poly(C4DHPA) membrane showed enantioselectivity in permeation. However, regularity of the structures in solution and solid state, and stability of the one-handed helical conformation, strength of the membrane, and enantioselectivity in permeation were low. Therefore, new monomers which are suitable to the HSSP and yield chiral polymers having good properties as membrane materials were desired.

Polydimethylsiloxane (PDMS) has many good properties such as high permeability for many gases and low surface energy. However, since it has no self-supporting-membrane-forming property because of its low glass transition temperature based on the high flexibility of SiO bonds, many kinds of rigid structures as a second component were introduced to PDMS.[7] We found that introduction of short oligosiloxane chains such as disiloxanyl and trisiloxanyl groups was effective to afford advantage of PDMS to the new polymer material containing the rigid second component.[8]

We have been studying optical resolution membranes using poly(chiral substituted acetylene)s prepared by AIP as self-membrane-forming materials.[1a,b,2b,2c,2h] We obtained one-handed helical poly(substituted phenylacetylenes) (poly(C4DHPA) in Chart 1) without the coexistence of any other chiral moieties by a helix-sense-selective polymerization (HSSP) (Scheme 1)[6] and found enantioselectivity in permeation of the one-handed helical polymers.[6h,i] Therefore, we proved directly the effect of the main-chain chirality on enantioselectivity. However, although

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Scheme 1. Helix-Sense-Selective Polymerization (HSSP) of RDHPA

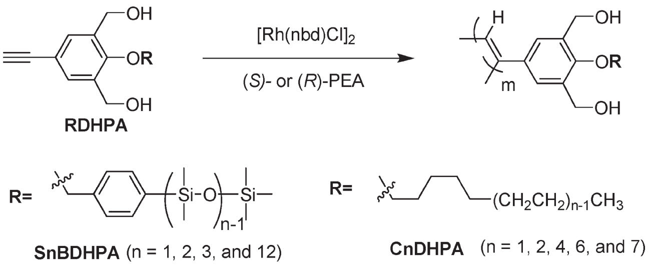


Chart 1. Chemical Structures of S*n*BDHPA and C*n*DHPA

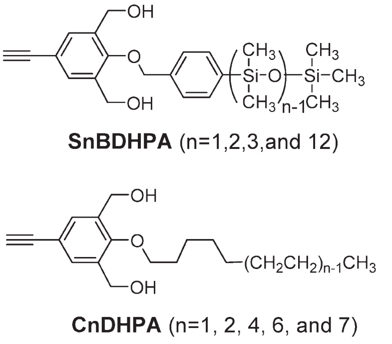
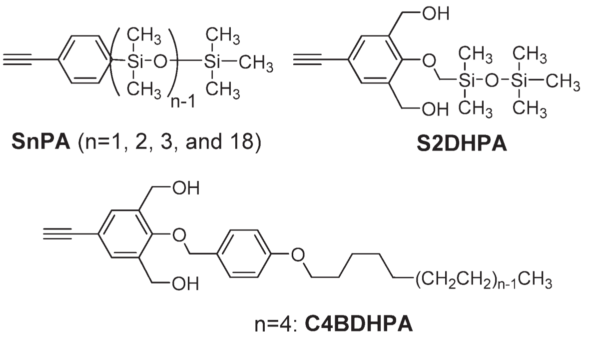


Chart 2. Chemical structures of S*n*PA, S2DHPA, and C4BDHPA



such chiral structures covering all the membrane are expected to show very high enantioselectivity, the selectivity was pretty low because the poly(C4DHPA) membrane was very rigid and therefore tended to make defects. Therefore, other such polymers which can show their potential performance were expected. In order to obtain new chiral polymers, whose chirality is present only in the main chain, having higher stable chiral conformations and better properties as enantioselectively permeable membranes than poly(C*n*DHPA) (Chart 1; C*n*DHPA; the *n* means the number of ethylene units[9]), a series of new achiral monomers having a flexible oligosiloxane chain via a phenylene group (Chart 1, S*n*BDHPA; the *n* means the number of dimethylsiloxane repeating units) instead of a rigid alkyl group in C*n*DHPA was designed, synthesized, and polymerized by using the chiral catalytic system. In addition to S*n*BDHPA, S*n*PAs, S2DHPA, and C4BDHPA (Chart 2) were synthesized and polymerized by using the chiral catalytic system as a reference. The structures in solution and solid state of all of the resulting polymers were examined and discussed compared with those of poly(C*n*DHPA). In addition, performances of the resulting new chiral polymers as materials for enantioselectively permeable membrane were estimated.

Experimental Section

1. Materials. All the solvents used for monomer synthesis and polymerization were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. The silicon-containing reagents such as trimethylsilylacetylene, trimethylsilanol, hexamethylcyclotrisiloxane (D_3), and dichlorodimethylsilane were purchased from Shinetsu Chemical Co., Ltd., and used as received. DL-Tryptophan and DL-phenylalanine were purchased from Tokyo Chemical Co., Ltd., and were used as received.

2. Synthetic Procedures of all the Monomers (Charts 1 and 2). *2.1. SnBDHPA* (*n* = *1, 2, and 3*) (*Scheme 2*). S1BDHPA, S2BDHPA, and S3BDHPA were synthesized according to the synthetic route shown in Scheme 2. All the of the following reaction procedures were conducted under dry nitrogen.

For the synthesis of compounds **1**−**16**, (Scheme 2) see the Supporting Information.

3,5-Bis(*hydroxymethyl*)*-4-*(*4-trimethylsiliyl-1-phenylmethyloxy*)*-1-phenylacetylene* (*S1BDHPA*). A mixture of sodium hydroxide (252 mg, 6.30 mmol), 2-butanol (10.0 mL), and **14** (510 mg, 1.25 mmol) was refluxed for 2 h at 110 °C. After filtration and concentration, the crude product was purified by silica gel column chromatography to give S1BDHPA as a white solid. Yield: 70.5% (315 mg). R_f = 0.62 (ethyl acetate/hexane = 1/1). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.55 (d, 2H, J = 8 Hz, $PhOCH_2Ph{-}H$), 7.50 (s, 2H, $C{\equiv}CPh{-}H$), 7.40 (d, 2H, J = 8 Hz, $SiPh{-}H$), 4.96 (s, 2H, $PhOCH_2$), 4.67 (d, 4H, J = 6 Hz, $Ph(CH_2OH)_2$), 3.04 (s, 1H, $C{\equiv}CH$), 1.83 (t, 2H, J = 6 Hz, $Ph(CH_2OH)_2$), 0.26 (s, 9H, $Si(CH_3)_3$). IR (KBr): 3600−3100-(OH), 3291 (HC≡C), 2107 (C≡C), 1248 (SiC), 1071 (SiO) cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.10. Found: C, 70.53; H, 7.06.

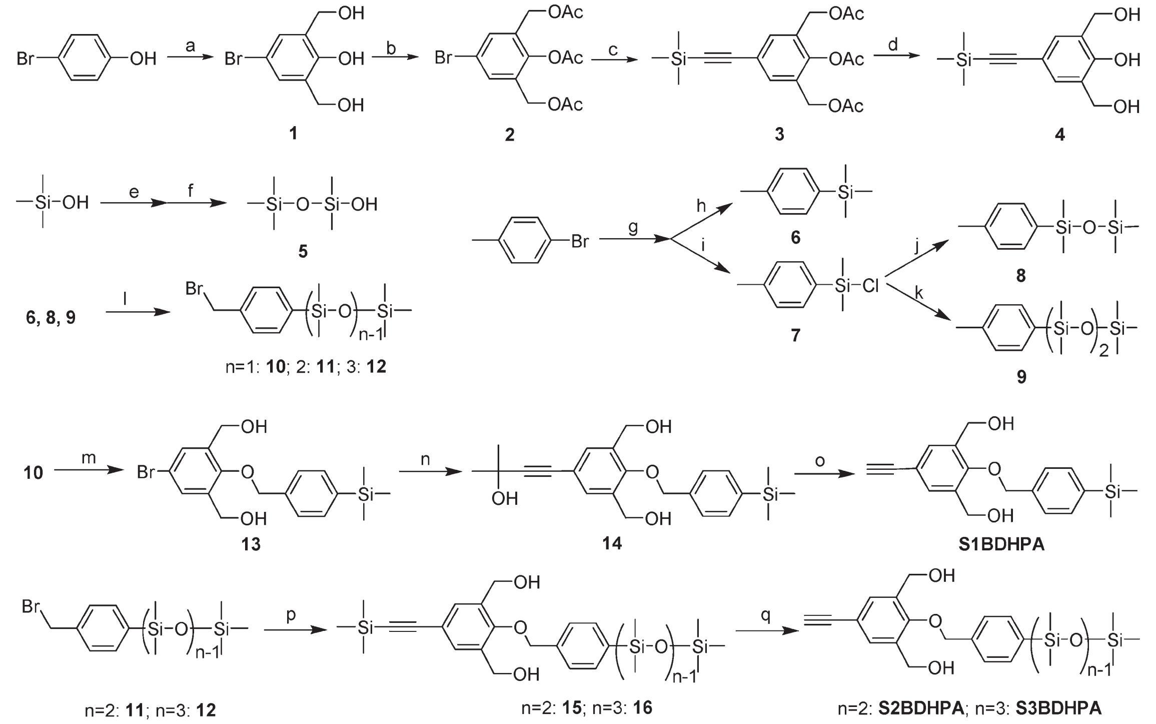
3,5-Bis(*hydroxymethyl*)*-4-*(*4-pentamethyldisiloxanyl-1-phenylmethyloxy*)*-1-phenylacetylene* (*S2BDHPA*). A mixture of potassium carbonate (70.0 mg, 0.504 mmol), **15** (2.10 g, 4.33 mmol), and acetone (140 mL) was refluxed for 24 h at 60 °C. After filtration and concentration, the crude product was purified by silica gel column chromatography to give S2BDHPA as a white solid. Yield: 64.0% (1.14 g). R_f = 0.55 (ethyl acetate/hexane = 1/4). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.57 (d, 2H, J = 8 Hz, $PhOCH_2Ph{-}H$), 7.50 (s, 2H, $C{\equiv}CPh{-}H$), 7.40 (d, 2H, J = 8 Hz, $SiPh{-}H$), 4.96 (s, 2H, $PhOCH_2$), 4.67 (d, 4H, J = 6 Hz, $Ph(CH_2OH)_2$), 3.04 (s, 1H, $C{\equiv}CH$), 1.85 (t, 2H, J = 6 Hz, $Ph(CH_2OH)_2$), 0.31 (s, 6H, $PhSi(CH_3)_2O$), 0.07 (s, 9H, $OSi(CH_3)_3$). IR (KBr): 3600−3100 (OH), 3311 (HC≡C), 2108 (C≡C), 1254 (SiC), 1065 (SiO) cm^{-1}. Anal. Calcd for $C_{22}H_{30}O_4Si_2$: C, 63.73; H, 7.29. Found: C, 63.66; H, 7.24.

3,5-Bis(*hydroxymethyl*)*-4-*(*4-heptamethyltrisiloxanyl-1-phenylmethyloxy*)*-1-phenylacetylene* (*S3BDHPA*). A mixture of **16** (0.512 g, 1.05 mmol), potassium carbonate (50.0 mg, 0.359 mmol), and acetone (30.0 mL) was refluxed for 24 h at 60 °C. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give S3BDHPA as a white viscous solid. Yield: 45.2% (0.232 g). R_f = 0.31 (ethyl acetate/hexane = 1/3). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.59 (d, 2H, J = 8 Hz, $PhOCH_2Ph{-}H$), 7.50 (s, 2H, $C{\equiv}CPh{-}H$), 7.40 (d, 2H, J = 8 Hz, $SiPh{-}H$), 4.96 (s, 2H, $PhOCH_2$), 4.67 (d, 4H, J = 6 Hz, $Ph(CH_2OH)_2$), 3.03 (s, 1H, $C{\equiv}CH$), 1.96 (t, 2H, J = 6 Hz, $Ph(CH_2OH)_2$), 0.33 (s, 6H, $PhSi(CH_3)_2O$), 0.06 (s, 9H, $OSi(CH_3)_3$), 0.03 (s, 6H, $OSi(CH_3)_2O$). IR (KBr): 3600−3100 (OH), 3312 (HC≡C), 2109 (C≡C), 1258 (SiC), 1060 (SiO) cm^{-1}. Anal. Calcd for $C_{24}H_{36}O_5Si_3$: C, 58.97; H, 7.42. Found: C, 58.96; H, 7.49.

2.2. 3,5-Bis(*hydroxymethyl*)*-4-*(*4-oligodimethylsiloxanyl-1-phenylmethyloxy*)*-1-phenylacetylene* (*SnBDHPA, Macromonomer* ($\overline{n}_{NMR}$ = *11.7*)) (*Scheme 3*). For the synthesis of compounds **17**−**19** (Scheme 3), see the Supporting Information.

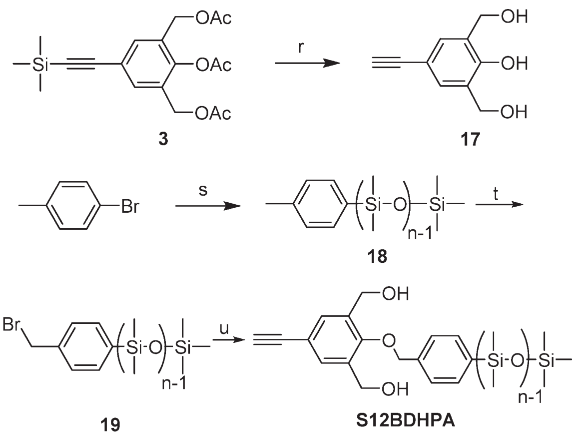
3,5-Bis(*hydroxymethyl*)*-4-*(*4-oligodimethylsiloxanyl-1-phenylmethyloxy*)*-1-phenylacetylene* (*S12BDHPA*). To an acetone solution (5.00 mL) of sodium iodide (200 m, 1.33 mmol), **19** (1.03 g, 1 mmol) was added dropwise at room temperature. The mixture was stirred for 2 h at room temperature. After filtration, the filtrate was added to a mixture of **17** (0.251 g, 1.40

Scheme 2. Synthesis of S*n*BDHPA (*n* = 1, 2, and 3)[a]



[a] Key: (a) CH_2O, 2-propanol, and KOH; (b) Ac_2O and pyridine; (c) PPh_3, CuI, $PdCl_2(PPh_3)_2$, trimethylsilylacetylene, and Et_3N; (d) $LiAlH_4$ and tetrahydrofuran; (e) dichlorodimethylsilane, Et_3N, and Et_2O; (f) $NaHCO_3$ and deionized water; (g) *n*-butyllithium, Et_2O; (h) trimethylchlorosilane; (i) dichlorodimethylsilane; (j) trimethylsilanol, Et_3N, and Et_2O; (k) **5**, Et_3N, and Et_2O; (l) 2, 2′-azobis(isobutyronitrile) (AIBN), *N*-bromosuccinimide (NBS), and CCl_4; (m) **1**, K_2CO_3, and acetone; (n) PPh_3, CuI, $PdCl_2(PPh_3)_2$, 3-hydroxy-3-methyl-1-butyne, and Et_3N; (o) NaOH, 2-butanol; (p) **4**, K_2CO_3, chloroform, and acetone; (q) K_2CO_3 and acetone.

Scheme 3. Synthesis of S12BDHPA, Macromonomer ($\bar{n}_{NMR}$ = 11.7, M_w/M_n = 1.02)[a]



[a] Key: (r) (1) $LiAlH_4$ and tetrahydrofuran and (2) water; (s) (1) *n*-butyllithium, Et_2O, (2) hexamethylcyclotrisiloxane (**D_3**), THF, and (3) trimethylchlorosilane; (t) AIBN, NBS, and CCl_4; (u) (1) NaI and acetone and (2) **17** and K_2CO_3.

mmol), potassium carbonate (0.150 g, 1.08 mmol), and acetone (15.0 mL) with a syringe. The mixture was stirred for 48 h at 45 °C. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give S12BDHPA as white grease-like solid. Yield: 41.1% (0.487 g). R_f = 0.45 (ethyl acetate/hexane = 1/4). ^1H NMR ($CDCl_3$, TMS): δ = 7.58 (d, 2H, *J* = 8 Hz, $PhOCH_2Ph{-}\mathit{H}$), 7.51 (s, 2H, $C{\equiv}CPh{-}\mathit{H}$), 7.42 (d, 2H, *J* = 8 Hz, $SiPh{-}\mathit{H}$), 4.96 (s, 2H, $PhOC\mathit{H}_2$), 4.68 (d, 4H, *J* = 6 Hz, $Ph(C\mathit{H}_2OH)_2$), 3.04 (s, 1H, $C{\equiv}C\mathit{H}$), 1.98 (t, 2H, *J* = 6 Hz, $Ph(CH_2O\mathit{H})_2$), 0.34 (s, 6H, $PhSi(C\mathit{H}_3)_2O$), 0.07−0.03 (br, 67H, $PhSiO(Si(C\mathit{H}_3)_2O)_{n\text{-}2}Si(CH_3)_3$ and $PhSiO(Si(CH_3)_2O)_{n\text{-}2}Si(C\mathit{H}_3)_3$). IR (KBr): 3600−3100 (OH), 3310 ($HC{\equiv}C$), 2110 ($C{\equiv}C$), 1257 (SiC), 1061 (SiO) cm^{-1}. M_w/M_n = 1.02 (by GPC). The degree of polymerization ($\bar{n}$): 12.3 (from calculation for **18**), 11.7 (from ^1H NMR), 13.5 (from GPC)). Anal. Calcd for $C_{41.1}H_{88.1}O_{13.7}Si_{11.7}$: C, 43.68; H 7.86. Found: C, 44.24; H, 7.88.

2.3. 3,5-Bis(hydroxymethyl)-4-(4-dodecyloxy-1-phenylmethyloxy)-1-phenylacetylene (C4BDHPA) (Scheme 4). For the synthesis of compounds **20**−**23**, see the Supporting Information.

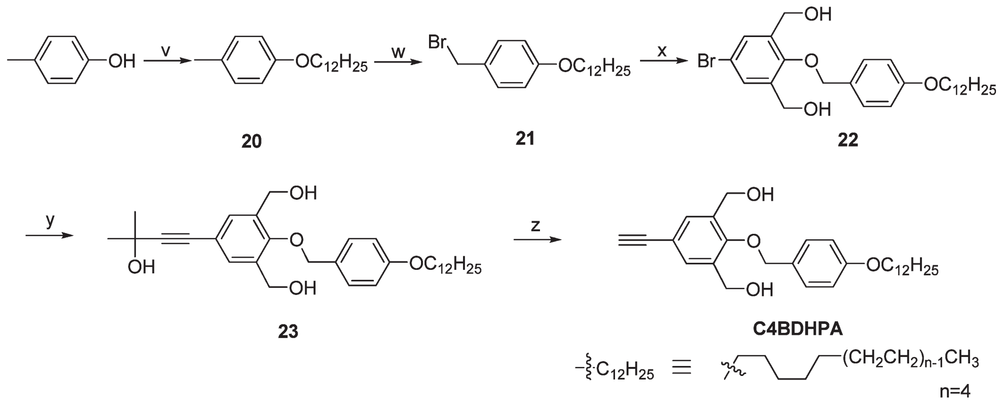
A reaction and purification similar to those for S1BDHPA were run with **23** instead of **14** to give C4BDHPA as a white solid. Yield: 49.4% (1.71 g). R_f = 0.27 (ethyl acetate/hexane = 1/2). ^1H NMR ($CDCl_3$, TMS): δ = 7.49 (s, 2H, $PhCH_2OPh\text{-}\mathit{H}$), 7.30 (d, 2H, *J* = 8 Hz, $C_{12}H_{25}OPh{-}\mathit{H}$), 6.90 (d, 2H, *J* = 8 Hz, $PhOCH_2Ph{-}\mathit{H}$), 4.88 (s, 2H, $PhOC\mathit{H}_2Ph$), 4.63 (d, 4H, *J* = 6 Hz, $Ph(C\mathit{H}_2OH)_2$), 3.95 (t, 2H, *J* = 7 Hz, $OC\mathit{H}_2CH_2$), 3.05 (s, 1H, $C{\equiv}C\mathit{H}$), 2.04 (t, 2H, *J* = 6 Hz, $Ph(CH_2O\mathit{H})_2$), 1.78 (tt, 2H, J_1 = J_2 = 7 Hz, $OCH_2C\mathit{H}_2CH_2$), 1.26−1.51 (m, 18H, $CH_2\text{-}(C\mathit{H}_2)_9CH_3$), 0.88(t, 3H, $CH_2C\mathit{H}_3$). IR (KBr): 3600−3050 (OH), 3308 ($HC{\equiv}C$), 3000−2800(CH), 2116 ($C{\equiv}C$), 1200−1000 (CO) cm^{-1}. Anal. Calcd for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found: C, 76.87; H, 8.84.

2.4. SnPA (n = 1, 2, 3, and 18) (Chart 2). According to a similar method we reported previously, S*n*PAs (*n* = 1, 2, 3, and 18) were prepared and polymerized.[2g] Synthetic routes similar to S*n*BDHPAs (*n* = 1, 2, 3, and 12) were run with 1,4-dibromobenzene instead of **1** as a starting compound. The detail of synthesis and polymerization of S*n*PA will be reported in another paper in near future.

2.5. S2DHPA (Chart 2). According to a method we report previously S2DHPA was prepared.[8a,2g] The synthesis similar to S2BDHPA was run with chloromethylpentamethyldisiloxane instead of **11**.

3. Helix-Sense-Selective Polymerization (HSSP) of S*n*BDHPA and C4BDHPA. A typical procedure was as follows. A solution

Scheme 4. Synthesis of C4BDHPA[a]



[a] (v) 1-Bromododecane, KOH, deionized water, and ethanol; (w) AIBN, NBS, and CCl_4; (x) **1**, K_2CO_3, and acetone; (y) PPh_3, CuI, $PdCl_2(PPh_3)_2$, 3-hydroxy-3-methyl-1-butyne, and Et_3N; (z) NaOH, 2-butanol.

Table 1. Helix-Sense-Selective Polymerization of an Oligosiloxane or an Alkyl Group Containing Phenylacetylene Monomers [a]

			polymer			
no.	monomer	yield (%)	M_w[b] ($\times 10^6$)	M_w/M_n[b]	$\|G\|_{307}$[c] (deg)	DMSO content[d] (vol %)
1	S1BDHPA	47.4	3.7	8.7	36	26
2	S2BDHPA	69.2	6.8	6.1	50	33
3	S3BDHPA	93.0	22.9	7.6	74	> 50
4	S12BDHPA	72.1	7.5	10.4	48	> 50
5	S2DHPA	(15.0)[e]	(0.1)[f]	(1.4)[f]	0	...[g]
6[h]	C1DHPA	(95.8)[i]	...[i]	...[i]	...[i]	...[i]
7[h]	C2DHPA	24.8	1.0	5.0	59	...
8[h]	C4DHPA	59.6	7.7	3.8	54	< 10
9[h]	C6DHPA	28.0	6.7	4.7	21	...
10[h]	C7DHPA	26.7	1.1	4.7	33	< 10
11	C4BDHPA	92.5	7.9	4.0	7	< 10
12	S1PA	91.6	0.8	2.8	0	...[g]
13	S2PA	80.1	0.7	2.1	0	...[g]
14	S3PA	95.0	0.8	2.4	0	...[g]
15	S18PA	78.9	0.9	2.1	0	...[g]

[a] See the experimental section for reaction conditions. [b] By GPC correlating polystyrene standard with THF eluent. [c] $G_{307} = [\theta]_{307}\,\varepsilon^{-1} \times 10^2$ at 307 nm in THF. [d] DMSO content (vol %) in DMSO/THF when the CD signals of the polymers disappeared (see Figure 3). [e] Partly soluble. [f] Soluble part in THF. [g] No CD absorptions. [h] From ref 6i. [i] Totally insoluble.

of $[Rh(nbd)Cl]_2$ (1.32 mg, 2.80 μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (73.4 μL, 0.56 mmol) in toluene (0.70 mL) was added to a toluene (0.30 mL) solution of S3BDHPA (70 mg, 0.14 mmol). The reaction solution was stirred at room temperature for 12 h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and dried *in vacuo* to give a red solid. ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 7.54−7.31 (br, 6H, Ph−H), 5.89 (br, cis proton in the main chain), 4.75 (br, 2H, PhOCH_2Ph), 4.38(br, 4H, Ph(CH_2OH)$_2$), 1.84 (br, 2H, Ph(CH$_2$OH)$_2$), 0.34−0.04 (br, 21H, SiCH_3). *cis*-proton content in the main chain (*cis* %) = 89.4.

Other polymerizations were carried out similarly (Scheme 1).

Poly(*S1BDHPA*). ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 7.55−7.33 (br, 6H, Ph−H), 5.83 (br, cis proton in the main chain), 4.71 (br, 2H, PhOCH_2Ph), 4.32 (br, 4H, Ph(CH_2OH)$_2$), 1.92 (br, 2H, Ph(CH$_2$OH)$_2$), 0.34−0.18 (br, 9H, SiCH_3). *Cis* % = 81.6

Poly(*S2BDHPA*). ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 7.52−7.37 (br, 6H, Ph−H), 5.87(br, cis proton in the main chain), 4.74 (br, 2H, PhOCH_2Ph), 4.37 (br, 4H, Ph(CH_2OH)$_2$), 1.88 (br, 2H, Ph(CH$_2$OH)$_2$), 0.34−0.08 (br, 15H, SiCH_3). *Cis* % = 84.3

Poly(*S12BDHPA*). ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 7.51−7.33 (br, 6H, Ph−H), 5.81 (br, cis proton in the main chain), 4.76 (br, 2H, PhOCH_2Ph), 4.35 (br, 4H, Ph(CH_2OH)$_2$), 1.93 (br, 2H, Ph(CH$_2$OH)$_2$), 0.34−0.04 (br, 73H, SiCH_3). *Cis* % = 81.4

Poly(*C4BDHPA*). ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 6.50−7.50 (m, 6H, Ph−H), 5.83(br, cis proton in the main chain), 4.63 (br, 2H, PhOCH_2Ph), 4.32 (br, 4H, Ph(CH_2OH)$_2$), 3.79 (br, 2H, OCH_2CH$_2$), 1.83 (br, 2H, Ph(CH$_2$OH)$_2$), 1.71 (br, 2H, OCH$_2$CH_2), 1.15−1.52 (br, 18H, CH$_2$(CH_2)$_9$CH$_3$), 0.88(br, 3H, CH$_2$CH_3). *Cis* % = 72.3

The other characterizations are summarized in Tables 1 and S1.

4. Preparation and Characterization of the Membranes.[1,2,10] According to our previous reports, the membranes were prepared and measured. For details, see the Supporting Information.

5. Measurements.[1,2,10] According to our previous reports, the polymers and membranes were measured. For details, see the Supporting Information.

Results and Discussion

Achievement of the Helix-Sense-Selective Polymerization of New Achiral Monomers and Macromonomer Having an Oligosiloxane Chain. To obtain new monomers which are suitable for the HSSP,[6a] a series of new phenylacetylene monomers having a flexible oligosiloxane chain and two hydroxymethyl groups (Chart 1, S*n*BDHPA (*n* = 1, 2, 3, and 12)) were synthesized and polymerized by using the chiral catalytic system(Scheme 1). As a result, all of the S*n*BDHPAs monomers whose *n* values are 1 to 12 were found to be suitable to the HSSP since all the resulting polymers showed Cotton effects at wavelengths around 430 and 307 nm assigned to absorption of the conjugated main chain and the pendant groups, respectively, in spite of no chiral groups

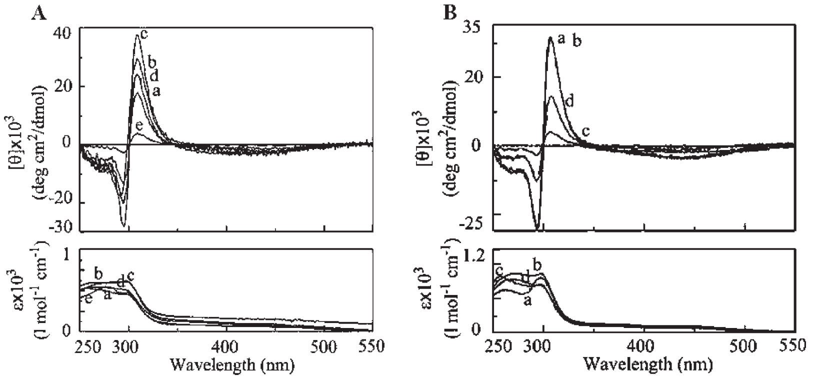


Figure 1. CD and UV spectra in THF at 20 °C of (A) poly(S*n*BDHPA) (a, $n = 1$; b, $n = 2$; c, $n = 3$; and d, $n = 12$) and (e) poly(C4BDHPA) prepared by using (*S*)-PEA/[Rh(nbd)Cl]$_2$ in this study, and (B) poly(C*n*DHPA) (a, $n = 2$; b, $n = 4$; c, $n = 6$; and d, $n = 7$) prepared by using (*R*)-PEA/[Rh(nbd)Cl]$_2$ from ref 6i.

Table 2. Structures of Membranes of poly(S*n*BDHPA)s and poly(C*n*DHPA)s estimated by XRD

no.[a]	polymer	2θ[b] (deg)	lattice spacing, d[c] (Å)	columnar diameter, l[d] (Å) calcd[e]	columnar diameter, l[d] (Å) obsd.	columnar diameter, l[d] (Å) obsd./calcd (%)	columnar content[f] (%)
2	poly(S2BDHPA)	3.80	23.2	33.6	26.8	79.8	59.0
3	poly(S3BDHPA)	3.04	29.1	38.8	33.6	86.6	65.9
4	poly(S12BDHPA)	2.02	43.7	75.2	50.5	67.2	47.5
7[g]	poly(C2DHPA)	4.92	17.9	33.4	20.7	62.0	65.5
8[g]	poly(C4DHPA)	4.32	20.4	42.2	23.7	56.2	62.0
9[g]	poly(C6DHPA)	3.94	22.4	52.2	25.9	49.6	37.2
10[g]	poly(C7DHPA)	h	h	56.8	h	h	h
11	poly(C4BDHPA)	3.44	25.7	55.0	29.7	54.0	60.3

[a] The numbers correspond to those in Table 1. [b] (100) reflection. [c] Calculated from $2d(\sin\theta) = n\lambda$, where $n = 1$ and $\lambda = 1.54$ Å. [d] $l = d/\sin 60°$. [e] By using MM2 calculation using a model having no interpenetration of the side chains. [f] The ratio of the area of the column to the total area. [g] From ref 6i. [h] No peaks for crystalline.

in the starting monomers (Figure 1A and Table 1, nos. 1−4). Since the shapes of the absorption peaks of poly(S*n*BDHPA)s were similar to those of poly(C*n*DHPA)s (Figure 1B) prepared by using the same chiral catalytic system,[6i] they were thought to have a one-handed helical main chain which was the same as poly(C*n*DHPA)s.

Effects of the Chemical Structures of the Monomers on the Helix-Sense-Selective Polymerization and One-Handed Helicity of the Resulting Polymers. The results of the HSSP (Scheme 1) of S*n*BDHPAs (Chart 1) together with the other related monomers, C*n*DHPAs, C4BDHPA, S2DHPA, and S*n*PAs which were synthesized according to Schemes 2−4 are summarized in Table 1. C*n*DHPAs (Chart 1) have a rigid alkyl group and no phenylene spacers, C4BDHPA (Chart 2 and Scheme 4) has a rigid alkyl group instead of a flexible oligosiloxanyl group in S*n*BDHPAs (Chart 1), S2DHPA (Chart 2) has a flexible disiloxanyl group and no phenylene spacers, and S*n*PAs (Chart 2) have a flexible oligosiloxanyl group, no hydroxyl groups, and no phenylene spacers.

When we compared the average values of *G* between the two kinds of polymers, poly(S*n*BDHPA)s (Table 1, nos. 1−4) showed a higher *G* value than that of poly(C*n*DHPA)s (Table 1, nos. 6−10). When we compared *G* values between the two polymers which had a similar number of atoms (*n*) in the side chains and the same spacer(phenylene spacer) in the monomer units, poly(S3BDHPA) (Chart 1 and Table 1, no. 3) showed a much higher *G* value than poly(C4BDHPA) (Chart 2 and Table 1, no. 11) as shown in Figure 1 (parts c and e). Therefore, introduction of a flexible oligosiloxane chain gave much better effect on *G* values than that of a rigid alkyl chain. The phenylene spacers in C*n*BDHPA and S*n*BDHPA had a bad effect because poly(C4BDHPA)(Table 1, no. 11) had a much lower *G* value than poly(C4DHPA) (Table 1, no. 8). Since S*n*DHPAs had been thought to be the best structure judging from the two above findings, S2DHPA(Chart 2) without any phenylene spacers was synthesized and polymerized by using the same chiral catalytic system. However, unexpectedly it gave only an insoluble polymer (Tables 1 and 2, no. 5). In addition, the total yield of the monomer was low. Therefore, we selected and used S*n*BDHPA with a phenylene spacer instead of S*n*DHPA in this study.

In the case of S*n*PAs without hydroxymethyl groups(Table 1, nos. 12−15), they were not suitable to the HSSP. In addition, their MWs of the resulting polymers were much lower than those of poly(S*n*BDHPA)s and poly(C*n*DHPA)s having two hydroxymethyl groups. Therefore, the two hydroxyl groups in the monomers were found to largely enhance MW of the resulting polymers.

In conclusion, the chemical structure of S*n*BDHPAs was the best to the HSSP among the five kinds of achiral monomers, that is, S*n*BDHPAs, S*n*DHPA, C*n*DHPAs, C*n*BDHPA, and S*n*PA. In particular, the *G* value of poly(S3BDHPA) was the highest (Table 1, no. 3) in all the polymers listed in Table 1 in this study. Therefore, S3BDHPA is the best monomer to the HSSP which we developed at present. In addition, poly(S3BDHPA) had the highest solubility and the highest MW in this study.

In the case of the HSSP of C*n*DHPAs in our previous study, with increasing *n*, the *G* values decreased as shown in Figures 1B and 2 (the open symbols) and the monomers whose *n* values were less than 2 (for example, C1DHPA) gave insoluble polymers (Table 1, no. 6).[6i] We thought the long alkyl chains ($n > 5$; nos. 9 and 10 in Table 1) disturbed regular structures of the main chain and the short alkyl chains ($n < 2$; no. 1 in Table 1) could not prevent *inter*-molecular hydrogen bonds followed by insolubilization of the resulting polymers. On the other hand, in the case of the HSSP of S*n*BDHPAs in this study, with increasing $n = 1$ to 3,

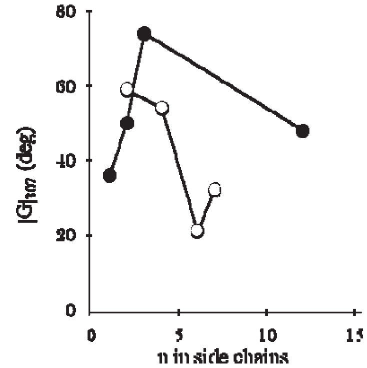


Figure 2. Plots of G values versus the n values in the side chains of the polymers. Key: (●) poly(SnBDHPA) (n = 1, 2, 3, and 12) in this study; (○) poly(CnDHPA) (n = 2, 4, 6, and 7) from ref 6i.

the G values increased as shown in Figures 1A and 2 (the solid symbols) and highly soluble polymers having high MW were obtained even when n = 1 (Table 1, no. 1). Therefore, the introduction of an oligosiloxane chain had better effect on the formation of regular conformation in the chiral polymers produced by the HSSP. Since generally oligosiloxane chains have high mobility and hydrophobicity, they could promote formation of a regular conformation, that is, one-handed helicity of the resulting polymers during polymerization in nonpolar solvent without insolubilization by *inter*molecular hydrogen bonds. When the n exceeded 3 (Table 1, no. 4), G values decreased similarly to those of poly(CnDHPA) ($n > 5$). As a result, the plot of G values versus n values had a maximum at n = 3 (the solid symbols in Figure 2). Even for poly(S12BDHPA) having long siloxane chains in the series of poly(SnBDHPA), the G value of the polymer remained more than 60% of the maximum value for poly(S3BDHPA) and much stronger than that of poly(C7DHPA) having a smaller n than poly(S12BDHPA) in the side groups. On the other hand in the series of poly(CnDHPA), the G value of poly(C7DHPA) was less than 60% of the maximum G value for poly(C2DHPA). This may be because the flexible and hydrophobic siloxane chains were more effective in maintaining higher regularity of the one-handed main chain even when the side chains were long.

When we consider the pentamethylene group between the oligoethylene group and the oxygen atom as a spacer in CnDHPA(Chart 1) instead of the phenylene spacer in SnBDHPA, the corresponding monomers of S1BDHPA, S2BDHPA, and S3BDHPA having a similar number (n) of skeleton atoms in the substituents are C1DHPA, C2DHPA, and C4DHPA, respectively, in this study. When we compare all the values such as yields, M_w, and G values between SnBDHPA and CnDHPA having a similar number (n) of atoms in the substituents, all the values of SnBDHPA were higher than those of CnDHPA except for G values for poly(S2BDHPA) and poly(C2DHPA) (Table 1, nos. 2 and 7). For example, S1BDHPA (Table 1, no. 1) gave a soluble chiral polymer but C1DHPA (Table 1, no. 6) gave only an insoluble product, and S3BDHPA (Table 1, no. 3) gave a soluble chiral polymer with a higher yield, a higher M_w, and higher G than C4DHPA (Table 1, no. 8). Therefore, introduction of a flexible short siloxane chain had a much better effect on obtaining soluble chiral polymers having better characteristics in higher yields by the HSSP than that of a rigid alkyl group. Among them, S3BDHPA was the best.

The much better effect of the short siloxane chains on the HSSP is thought to be caused by their higher solubilization effect (for the detail of solubilities of the monomers and polymers, see Table S1 and its explanation in the Supporting Information). As mentioned above, poly(S3BDHPA) showed the best for all the properties (Table 1, no. 3). It may be because the polymerization of S3BDHPA proceeded in homogeneous system due to high solubility of the monomer and the corresponding polymer (Table S1, no. 3). Relatively low MW values of poly(S1BDHPA) and poly(S2BDHPA) having shorter oligosiloxane side chains were thought to be because that solubilities of S1BDHPA, S2BDHPA, and their polymers were not high enough to keep homogeneous system during polymerization. Although poly(C6DHPA) had also as high a solubility as poly(S3BDHPA) (Table S1), the G value was much lower than that of poly(S3BDHPA) (Table 1, nos. 9 and 3). The fact indicated that long alkyl chains in poly(C6DHPA) enhanced solubility but disturbed the regular main chain structure. On the other hand, short siloxane chains in poly(S3BDHPA) enhanced solubility without disturbing the regular main chain structure. Therefore, short oligosiloxane chains were found to be a much better substituent to obtain better monomers which are suitable to the HSSP and give more regulated structures of the resulting polymers. Among SnBDHPAs, S3BDHPA was the best.

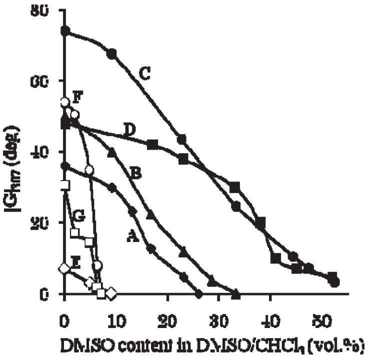


Figure 3. Plots of $|G|_{307}$ values of the polymers at 307 nm versus DMSO contents in DMSO/THF at 20 °C. Key: (A) poly(S1BDHPA) (◆); (**B**) poly(S2BDHPA) (▲); (C) poly(S3BDHPA) (●); (D) poly(S12BDHPA) (■); (E) poly(C4BDHPA) (◇); (F) poly(C4DHPA) (○); (G) poly(C7DHPA) (□). Letters A−G correspond to those in Figure S1. $G_{307} = [\theta]_{307}\,\varepsilon^{-1} \times 10^2$.

Effects of the Oligosiloxane Chains on Stability in Solution of the One-Handed Helical Conformation in the Chiral Polymers Prepared by the Helix-Sense-Selective Polymerization. As described above, the one-handed helical conformation of poly(CnDHPA) was maintained by *intra*molecular hydrogen bonds between hydroxyl groups.[6] Therefore, when a polar solvent was added to the solution of poly(CnDHPA) showing Cotton effects, the intensities of CD absorptions decreased and then disappeared because the intramolecular hydrogen bonds were broken by the polar solvent. Oligosiloxanes are hydrophobic and therefore they were expected to protect the *intra*molecular hydrogen bonds in poly(SnBDHPA). In order to investigate such effects, a polar solvent, DMSO, was added to THF solutions of poly(SnBDHPA)s showing Cotton effects similarly to poly(CnDHPA). The results are shown in Figures 3 and S1, parts A−D. In the all poly(SnBDHPA)s, with increasing DMSO, the intensity of CD peaks decreased and finally disappeared or almost disappeared similarly to poly(CnDHPA) (Figures 3 and S1, parts F and G). Therefore, the one-handed helical main chain was also supported by the *intra*molecular hydrogen bonds.

Poly(SnBDHPA)s showed much higher CD stabilities to solvent polarity. Even though the DMSO content exceeded 50 vol %, the CD signals of poly(S3BDHPA) and poly(S12BDHPA) were maintained (Figures 3 and S1, parts C and D), while the CD signals of poly(C*n*DHPA)s and poly(C4BDHPA) disappeared (Figures 3 and S1, parts E, F, and G) even when the DMSO content was less than 10 vol % as shown in Figure 3. The contents of DMSO for poly(S*n*BDHPA)s when the CD signals disappeared were much higher than those of poly(C*n*DHPA) as shown in the first column from the right in Table 1. The fact indicated that stabilities of the one-handed helicity of poly(S*n*BDHPA)s to polar solvents were much higher than those of poly(C*n*DHPA)s. We thought that the introduction of hydrophobic oligosiloxane chains formed a hydrophobic field to protect the intramolecular hydrogen bonds inside the field from being broken by the external polar molecules.

The content of DMSO (vol %) when the CD signals completely disappeared increased with increasing *n* as shown in Figure 3.

The stabilities of the one-handed helical main chain of poly(S*n*BDHPA) in solution to aging and heating were high similarly to that of poly(C*n*DHPA). The times which were needed to decrease to the half value of the original ones in solution were 147 and 132 days for poly(S3BDHPA) and poly(C4DHPA), respectively. The stability of the one-handed main chain of poly(S3BDHPA) to heating was as high as that of poly(C4DHPA) as shown in Figure S2 in the Supporting Information.

Effects of the Oligosiloxane Chains on Structures and Properties of the Chiral Polymers Prepared by the Helix-Sense-Selective Polymerization in Solid State. The XRD diagrams of the membranes made from the poly(S*n*BDHPA)s together with poly(C*n*DHPA) are shown in Figure S3 in the Supporting Information and values for the solid structures for the membranes determined by the results of XRD are summarized in Table 2. Since peaks attributed to (100) reflections in a crystalline were observed, we estimated they have a pseudohexagonal structure similarly to poly(C*n*DHPA) (Figure S3B) we reported before.[6i]

Calculated values for the columnar diameters (*l*) determined by using a model, where no interpenetrating of the side chains between polymer molecules was supposed to occur, were larger than observed values as shown in Table 2. Therefore, the real side chains of all the polymer molecules intermolecularly interpenetrated each other to some extent. The calculated and observed columnar diameters (*l*) increased with increasing *n* in poly(S*n*BDHPA) similarly to those in poly(C*n*DHPA) as expected (Table 2).

The observed diameters (*l*) of poly(S*n*BDHPA)s determined by XRD were longer than those of poly(C*n*DHPA) although the calculated values were almost the same when we compared the two kinds of polymers having similar *n* of the side chains. For example, the observed *l* value of poly(S2BDHPA) (Table 2, no. 2) was higher than that of poly(C2DHPA) (Table 2, no.7) in spite of almost the same calculated values. This may be because bulkiness of side chains of poly(S*n*BDHPA) was higher than those of poly(C*n*DHPA). In the case of the bulkier oligosiloxane substituents in poly(S*n*BDHPA), since it was more difficult for the side chains to interpenetrate into the side chains of other polymer molecules, the observed *l* values in poly(S*n*BDHPA) were higher than those in poly(C*n*DHPA). Therefore, to obtain membranes having columnar structures having *l* values closer to the calculated ones, bulkier oligosiloxane chains were more suitable.

The columnar contents of poly(S*n*BDHPA) and poly(C*n*DHPA) calculated are listed in Table 2. In the case of poly(C*n*DHPA), with increasing n, the content decreased. On the other hand, the plot of the columnar contents versus *n* values in poly(S*n*BDHPA) (Figure 4) showed a behavior similarly to the plot of the intensity of *G* values versus *n* values as mentioned in Figure 2, that is, it had a maximum at $n = 3$. Poly(S3BDHPA) showed the highest columnar content in poly(S*n*BDHPA)s, and poly(S2BDHPA) and poly(S12BDHPA) showed lower columnar content than poly(S3BDHPA). The findings indicated the following two things. One is that the polymers having higher regularity in the polymer molecules had higher regularity in the solid state as shown in Figure 5. The other is that poly(S3BDHPA) having the highest regularity in the one-handed helical conformation in solution had the highest regular structure also in solid state.

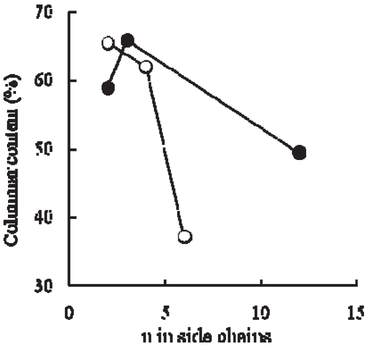


Figure 4. Plots of the columnar contents versus the *n* values in the side chains of the polymers. Key: (●) poly(S*n*BDHPA) ($n = 2, 3$, and 12) in this study; (○) poly(C*n*DHPA) ($n = 2, 4$, and 6) from ref 6i.

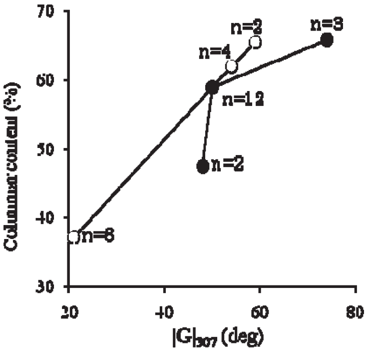


Figure 5. Plots of the columnar contents versus the $|G|_{307}$ values at 307 nm of the polymers. Key: (●) poly(S*n*BDHPA) ($n = 2, 3$, and 12) in this study; (○) poly(C*n*DHPA) ($n = 2, 4$, and 6) from ref 6i.

Since the polymers having longer side chains such as poly(S12BDHPA), poly(C6DHPA), and poly(C7DHPA) had lower columnar contents, longer side chains were found to disturb regular structures both in the polymer conformation and in solid state. Although poly(S12BDHPA) had longer siloxane side chains, it showed much higher columnar content than poly(C7DHPA) having shorter alkyl side chains showing no peaks in XRD. In summary, to obtain chiral polymers having the highest regularity both in solution and solid state by the HSSP, S3BDHPA was found to have the best structure as a monomer for the HSSP.

Several characterizations of membranes from the chiral polymers are summarized in Table 3. Homopolymers from the phenylacetylens having two hydroxyl groups and side chains whose *n* values are 3 and 4, i.e., poly(S3BDHPA), poly(C4DHPA), and poly(C4BDHPA) had self-supporting-membrane-froming ability (Table 3, nos. 3, 8, and 11). The decreasing order of flexibility of the three membranes were poly(S3BDHPA) > poly(C4DHPA) > poly(C4BDHPA) judging from the values of elongation at break (Table 3).

Table 3. Characterization of Membranes from the Chiral Polymers Prepared by the HSSP

no.[a]	polymer	Si %[b]	self-supporting-membrane-forming property	appearance	elongation at break[c] (%)	contact angle[d] (deg)
1	poly(S1BDHPA)	21.5	−	very brittle	...[e]	...[e]
2	poly(S2BDHPA)	35.5	+	brittle	...[e]	97.6
3	poly(S3BDHPA)	45.3	+++	flexible	14.9	104
4	poly(S12BDHPA)	76.8	−	viscous	...[e]	...[e]
6	poly(C1DHPA)	0	−	(insoluble)	...[e]	...[e]
7	poly(C2DHPA)	0	+	brittle	...[e]	...[e]
8	poly(C4DHPA)	0	++	rigid	10.8	90.0
11	poly(C4BDHPA)	0	++	rigid	7.6	88.3
12[f]	poly(S1PA)	42.0	++	rigid	...[e]	...[e]
15[f]	poly(S18PA)	92.8	−	viscous	...[e]	...[e]
16[f]	PDMS	100	− −	(liquid)	...[e]	(108)[g]

[a] The numbers correspond to those in Table 1. [b] Weight percentage of trimethyl or dimethylsiloxanyl units in the polymers. [c] At a strain rate of 5 mm/min. [d] Distilled water droplets. [e] Poor membrane forming ability. [f] Achiral polymers. [g] For a cross-linked membrane from ref 11.

Table 4. Enantioselective Permeation of Aqueous Solutions of DL-Trp and DL-Phe through the Polymeric Membranes

run	membrane	racemate	$P \times 10^{15}$ (m^2/s)[a]	α (= P_D/P_L)	$D \times 10^{14}$ (m^2/s)[b]	D_D/D_L	$S \times 10^2$ (m^3/m^3)[c]	S_D/S_L
1	poly(S3BDHPA)	Trp	0.47	6.3	1.9	5.1	2.5	1.2
2		Phe	0.89	4.4	3.9	3.9	2.3	1.1
3[d]	poly(C4DHPA)	Trp	2250	3.0	97.8	1.4	230	2.2
4[d]		Phe	790	1.2	53.6	1.5	147	0.8

[a] Permeability coefficient. [b] Diffusion coefficient. [c] Solubility coefficient. [d] From refs 6c and6i.

In summary, introduction of a short oligosiloxane chain in S*n*BDHPA was effective in obtaining stable one-handed helical polymers having good properties as membrane materials, while introduction of a phenylene spacer in C*n*BDHPA decreased regularity and flexibility of the resulting polymer membranes. In particualr, poly(S3BDHPA) was the best membrane material because it had the best self-supporting-membrane-forming ability and the highest regularities both in molecular structures and molecular assembly structures among the polymers prepared by the HSSP of the achiral phenylacetylenes.

Performances as Optical Resolution Membranes of the Chiral Polymers Prepared by the Helix-Sense-Selective Polymerization. As mentioned in the Introduction, we had already reported that poly(C4DHPA) membranes showed enantioselectivity in permeation of the racemate of two amino acids such as tryptophan (Trp) and phenylalanine (Phe).[6h,i] It was the first example that supported directly the chiral recognition ability of the one-handed helical structure because it was the first experimental result for the polyacetylenes which had chiral structures only in the main chain without the coexistence of any other chiral moieties. Since membranes from such chiral polymers can have molecular-sized chirality which covered all over the membrane, they were expected to have high enantioselectivity in permeation. However, the selectivities were very low. It may be caused by defects in the membranes judging from the facts that they were rigid and their permeabilities were very high (Table 4, runs 3 and 4 and Figure S4B).

Since the poly(S3BDHPA) has the highest regular structures and the best performance as membrane materials as mentioned above, we expected that poly(S3BDHPA) membranes could be applied to optical resolution membranes having much higher performance. In fact, poly(S3BDHPA) could be easily fabricated into a self-supporting membrane by solvent casting method. In addition, the membrane had a higher flexibility and a higher elongation at break (Table 3) than that of other polymers due to flexibility of the siloxane chains.

Concentration-driven permeation of racemic aqueous solutions of tryptophan (Trp) and phenylalanine (Phe) were carried out. The results are shown in Table 4, runs 1 and 2 and Figure S4A. Enantioselectivities in permeation through poly(S3BDHPA) membranes were observed(Figure S4). In addition, they showed higher enantioselectivities (α) in permeation than poly(C4DHPA) membranes. As we discussed the mechanism of the enantioselective permeations through other polymeric chiral membranes, to realize high selectivity in permeations, *S* and *D* values must be low because the dense structures of the membranes should be maintained during permeations.[2b] Since poly(S3BDHPA) membranes were highly hydrophobic judging from the values of contact angles of water(Table 3), they had low interaction with the solvent, i.e., water. Therefore, the membranes could keep dense structures during permeations of aqueous solutions. In addition, since the membranes were flexible due to flexible oligosiloxane chains, they had no or small amounts of defects. As a result, much higher selectivities, i.e., higher ratios of permeability coefficients for D-isomers to those for L-isomers were observed because the ratios of diffusion coefficients for D-isomers to those for L-isomers were enhanced as shown in Table 3.

In summary, there are mainly the following three reasons why the selectivity of poly(S3BDHPA) was so high. (1) Judging from the *G* values (Table 1), poly(S3BDHPA) has a higher degree of the one handedness, i.e., a higher enantiomeric excess than poly(C4DHPA). Therefore, poly(S3BDHPA) can have a higher enantioselectivity. (2) Since the flexible siloxane chains worked as an internal plasticizer in the membrane, the resulting poly(S3BDHPA) membrane may have less defects where no selective permeation occurred. Therefore, the membrane showed higher selectivity and lower permeability. On the other hand, since poly(C4DHPA) containing rigid alkyl chains tended to have some defects because of the rigid alkyl side chains, poly(C4DHPA) membranes showed higher permeability and lower permselectivity than the poly(S3BDHPA) membrane. The difference of the flexibility of the two membranes was observed in the values of elongation at break (Table 3). (3) As the contact angle values of water droplets shown in Table 3, poly(S3BDHPA) membrane was more hydrophobic. Therefore, permeability of the aqueous solution was very low and the selectivity was not lowered because the solvent, water could not produce any defects in the membrane.

Conclusions

Novel phenylacetylenes having an oligosiloxanyl group (S*n*BDHPA) and the other related three series of phenylacetylene monomers were synthesized and polymerized by using a chiral catalytic system and enantioselectivity in permeation of their membranes were examined. S*n*BDHPA was suitable for the helix-sense-selective polymerization (HSSP) and the CD absorptions (*G* values) of poly(S*n*BDHPA)s were the strongest and the one-handed helicities were the most stable among the five kinds of monomers. Enantioselectivity in permeation of poly(S3BDHPA) was much higher than that of a polymer membrane having alkyl groups. This was because the polymers having oligosiloxane groups had high regularity of structures, i.e., chemical structures of the macromolecules such as one handedness and high order structures such as columnar contents in the membranes and the membranes were flexible and had almost no defects. These good properties as optical resolution membrane materials were caused by flexibility, hydrophobicity, and bulkiness of the oligosiloxane chains. Therefore, S*n*BDHPAs were the best monomers suitable for the HSSP and for obtaining chiral polymers having the best properties as membrane materials and in particular S3BDHPA was the best monomer among S*n*BDHPAs.

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Supporting Information Available: Text giving procedures of synthesis of **1**−**23** and membrane preparation, and measurements, figures showing original charts of CDs (Figures S1 and S2) and XRD (Figure S3) and plots of permeation (Figure S4), and a table of solubilities of the monomers and polymers (Table S1) with its explanation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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