Polymer 51 (2010) 2460–2464

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and helix-sense-selective polymerization of a novel phenylacetylene having a trisiloxanyl group and two hydroxyl groups and enantioselective permeability of the resulting chiral polymeric membrane: Effect of the trisiloxanyl group on the polymerization and enantioselective permeability

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ARTICLE INFO

Article history:
Received 16 February 2010
Received in revised form
12 April 2010
Accepted 14 April 2010
Available online 21 April 2010

Keywords:
Helix-sense-selective polymerization
Oligosiloxane chain
Enantioselective permeation

ABSTRACT

To develop a new phenylacetylene monomer suitable for helix-sense-selective polymerization (HSSP) we reported previously and to improve the efficiency of the HSSP and membrane performance of the resulting polymer, a novel phenylacetylene having a trisiloxanyl group (S3BDHPA) was synthesized and polymerized by using a chiral catalytic system and enantioselectivity in permeation of its membrane was examined. S3BDHPA was suitable for the HSSP and the CD absorption of poly(S3BDHPA) was stronger and more stable than that of the corresponding polymer having no siloxanyl groups. In addition, enantioselectivity in permeation of poly(S3BDHPA) was much higher than that of a polymer membrane having no siloxanyl groups. They are thought to be caused by the flexibility and hydrophobicity of the trisiloxane groups.

1. Introduction

Polydimethylsiloxane (PDMS) has many good properties such as high permeability for many gasses and low surface energy. However, since it has no self-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 [1–10]. For example we selected poly (substituted phenylacetylenes) as a second rigid component and synthesized and polymerized siloxane-containing substituted acetylenes and reported selectivity in permeation through the resulting polymeric membranes [11]. 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 [12,13].

We have been studying optical resolution membranes using poly(chiral substituted acetylene)s as self-membrane-forming materials [14–18]. Since they had two kinds of chiral structures, i.e., one-handed helical conformation of the main chain and asymmetric carbons in the pendant groups, it had been difficult to confirm the effect of the main-chain chirality on enantioselectivity [19]. However, we obtained one-handed helical poly(substituted phenylacetylenes)(poly(DoDHPA) in Fig. 1) without the coexistence of any other chiral moieties by a helix-sense-selective polymerization (HSSP) [20–24] and found enantioselectivity in permeation of the one-handed helical polymers [25,26]. Therefore, we proved directly the effect of the main-chain chirality on enantioselectivity. However, the selectivity was pretty low because the poly(DoDHPA) membrane was rigid and therefore tended to make defects.

In the present communication, to develop a new phenylacetylene monomer which is more suitable for our HSSP and to improve membrane performance of the resulting polymer, a novel achiral phenylacetylene (S3BDHPA) having a trisiloxanyl group and two hydroxyl groups was synthesized and chiral poly(S3BDHPA) was synthesized by our HSSP of achiral S3BDHPA (Fig. 1) by using a chiral catalytic system and enantioselective permeation of the resulting polymer membrane was examined. To be compared with S3BDHPA, DoBDHPA which has an alkyl group instead of the oligosiloxanyl group in S3BDHPA was synthesized and polymerized.

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doi:10.1016/j.polymer.2010.04.030

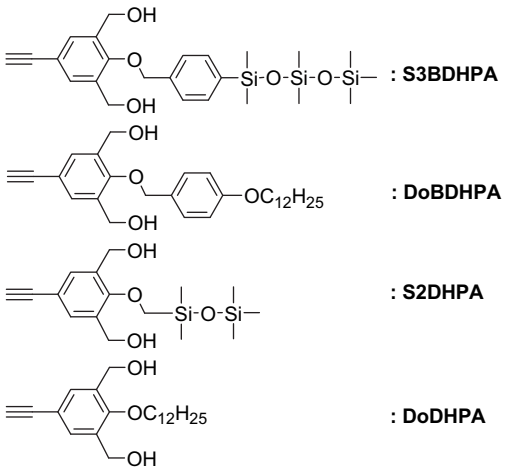


Fig. 1. Chemical structures of S3BDHPA, DoBDHPA, S2DHPA and DoDHPA.

2. Experimental section

2.1. Synthesis of 1-(1-heptamethyltrisiloxanyl)-4-{4-ethynyl-2,6-bis(hydroxymethyl)-1-phenoxymethyl} benzene (S3BDHPA)

According to the synthetic route shown in Scheme 1, S3BDHPA was synthesized via compounds **1**–**9** in 18.2% total yield. All the following reaction procedures were conducted under dry nitrogen. For the detail of synthesis of **1**–**7**, see supporting information.

2.1.1. 1-Heptamethyltrisiloxanyl-4-bromomethylbenzene (**8**) [27]

To a mixture of *N*-bromosuccinimide (7.1 g, 40 mmol), 2, 2′-azobisisobutyronitrile (AIBN) (98.4 mg, 0.6 mmol), and CCl_4 (80 mL), a CCl_4 solution of **7** (6.57 g, 40 mmol, 20 mL) was added dropwise at room temperature. The mixture was stirred for 8 h at 80 °C. After filtration, the solution was concentrated. The crude product was purified by silica-gel column chromatography to give **8** as a clear liquid. Yield: 76.7% (2.9 g). Rf = 0.73 (ethyl acetate/hexane = 1/16). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.52 (d, 2H, J = 8 Hz, $BrCH_2Ph-\underline{H}$), 7.36(d, 2H, J = 8 Hz, $SiPh-\underline{H}$), 4.47 (s, 2H, $BrC\underline{H}_2$), 0.31 (s, 6H, $PhSi(C\underline{H}_3)_2$), 0.05 (s, 9H, $Si(C\underline{H}_3)_3$), 0.02 (s, 6H, $OSi(C\underline{H}_3)_2O$).

2.1.2. 1-(1-Heptamethyltrisiloxanyl)-4-{4-(trimethylsiliylethynyl)-2,6-bis(hydroxymethyl)-1-phenoxymethyl}benzene (**9**) [20,26]

According to a similar method we reported previously, **9** was synthesized. The crude product was purified by silica-gel column chromatography to give **9** as a white solid. Yield: 65.7% (1.12 g). Rf = 0.35 (ethyl acetate/hexane = 1/3). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.56 (d, 2H, J = 8 Hz, $PhOCH_2Ph-\underline{H}$), 7.47 (s, 2H, $C\equiv CPh-\underline{H}$), 7.38 (d, 2H, J = 8 Hz, $SiPh-\underline{H}$), 4.95 (s, 2H, $PhOC\underline{H}_2$), 4.64 (d, 4H, J = 6 Hz, $PhC\underline{H}_2OH$), 1.88 (t, 2H, J = 6 Hz, $O\underline{H}$), 0.33 (s, 6H, $PhSi(C\underline{H}_3)_2$), 0.22 (s, 9H, $C\equiv CSi(C\underline{H}_3)_3$), 0.06 (s, 9H, $OSi(C\underline{H}_3)_3$), 0.03 (s, 6H, $OSi(C\underline{H}_3)_2O$).

2.1.3. 1-(1-Heptamethyltrisiloxanyl)-4-{4-ethynyl-2,6-bis(hydroxymethyl)-1-phenoxymethyl}benzene (S3BDHPA)

A mixture of **9** (0.5 g, 0.9 mmol), potassium carbonate (50 mg, 0.36 mmol), and acetone (30 mL) was refluxed for 24 h at 60 °C. After filtration, the solution was concentrated. The crude product was purified by silica-gel column chromatography to give S3BDHPA as a white wax solid. Yield: 41.0% (0.208g). Rf = 0.31 (ethyl acetate/hexane = 1/3). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.59 (d, 2H, J = 8 Hz, $PhOCH_2Ph-\underline{H}$), 7.50 (s, 2H, $C\equiv CPh-\underline{H}$), 7.40 (d, 2H, J = 8 Hz, $SiPh-\underline{H}$), 4.96 (s, 2H, $PhOC\underline{H}_2$), 4.67 (d, 4H, J = 6 Hz, $PhC\underline{H}_2OH$), 3.03 (s, 1H, $C\equiv C\underline{H}$), 1.96 (t, 2H, J = 6 Hz, $O\underline{H}$), 0.33 (s, 6H, $PhSi(C\underline{H}_3)_2$), 0.06 (s, 9H, $Si(C\underline{H}_3)_3$), 0.03 (s, 6H, $OSi(C\underline{H}_3)_2O$). IR (KBr): 3600–3100 (OH), 3312($HC\equiv C$), 2109($C\equiv C$), 1258(SiC), 1060 cm^{-1}(SiO). $C_{24}H_{36}O_5Si_3$ (488.2): Cacld. C 58.97, H 7.42; found: C 58.96, H 7.49.

2.2. Synthesis of 1-dodecyloxy-4-{4-ethynyl-2,6-bis(hydroxymethyl)-1-phenoxymethyl}- benzene (DoBDHPA)

DoBDHPA (Fig. 1) was synthesized similarly to S3BDHPA.[1] ^{1}H NMR ($CDCl_3$, TMS): δ = 7.49(s, 2H, $Ph-\underline{H}$), 7.30(d, 2H, J = 8 Hz, $\underline{H}-Ph-OC_{12}H_{25}$), 6.90(d, 2H, J = 8 Hz, $PhOCH_2Ph-\underline{H}$), 4.88(s, 2H, OCH_2Ph), 4.63(d, 4H, J = 6 Hz, $C\underline{H}_2OH$), 3.95(t, 2H, J = 7 Hz, $OC\underline{H}_2(CH_2)_{10}$), 3.05(s, 1H, $C\equiv C\underline{H}$), 2.04(t, 2H, J = 6 Hz, $CH_2O\underline{H}$), 1.78 (p, 2H, J = 7 Hz, OCH_2 $C\underline{H}_2$ $(CH_2)_9$), 1.26–1.51(m,18H, $CH_2(C\underline{H}_2)_9CH_3$), 0.88(t, 3H, J = 7 Hz, $C\underline{H}_3$).

2.3. Helix-sense-selective polymerization (HSSP) [20,26]

A solution of $[Rh(nbd)Cl]_2$ (1.32 mg, 2.8 μmol) and (*S*)- or (*R*)-phenylethylamine (73.4 μl, 0.56 mmol) in toluene (0.7 mL) was added to a solution of S3BDHPA (70 mg, 0.14 mmol) in toluene (0.3 mL). 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 polymer. ^{1}H NMR (DMSO-d_6/CCl_4 = 1/5): δ = 7.54–7.31 (br, 6H, $Ph-\underline{H}$), 5.89(br, cis proton in the main chain), 4.75(br, 2H, $PhOC\underline{H}_2Ph$), 4.38(br, 4H, $C\underline{H}_2OH$), 0.34–0.04(br, 21H, $SiC\underline{H}_3$); IR (KBr): 3600–3100(OH), 1256(SiC), 1051 cm^{-1}(SiO). Polymerization of DoBDHPA was carried out similarly. The other characterizations are summarized in Table 1.

2.4. Membrane preparation [14–19]

A toluene solution of the polymer (6–9 wt.-% (w/v)) was cast onto a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24 h at rt, the polymer membrane was detached from the sheet and dried *in vacuo* for 24 h at rt. The thicknesses were 68.0 and 70.1 μm.

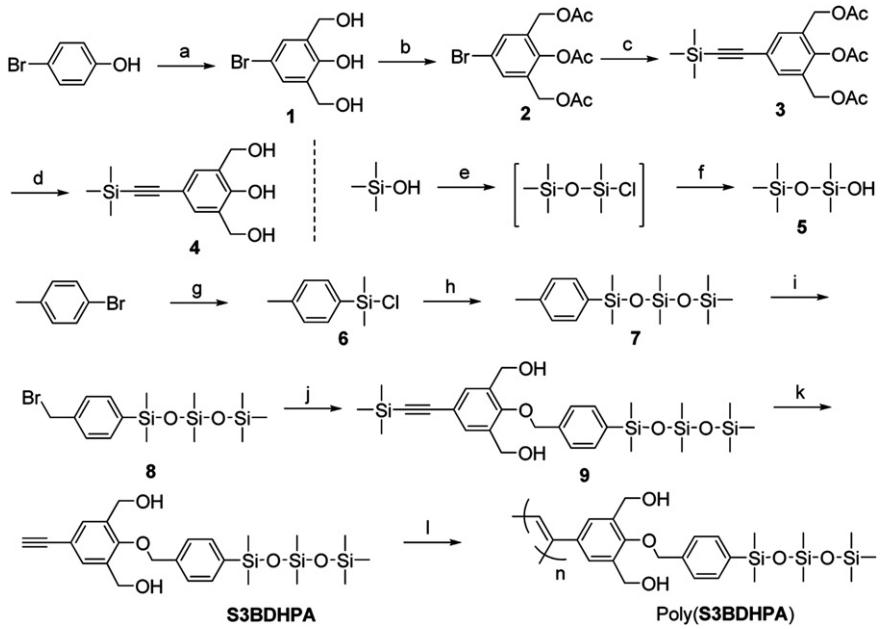
2.5. Measurement of contact angles and elongations at break of the membrane

Contact angles of distilled water droplets on the membranes were measured with a DM301, Kyowa Interface Science Co., LTD. The elongations at break of the membranes were measured at a strain rate of 5 mm/min with a TOM-5 Minebea Co., Ltd.

2.6. Enantioselective permeation [14–19,25,26]

The polymer membrane was placed between a disproportionate two-chamber cell, whose chamber volumes on the feed side and permeate sides were 150 and 20 mL, respectively. An aqueous solution of a DL-tryptophan (Trp) or DL-phenylalanine (Phe) (0.05wt.-% (w/v)) and deionized water were supplied in the feed and permeate side chambers, respectively. After a permeation period with stirring at room temperature, the solute in permeate side was concentrated and analyzed by an HPLC with a chiral column (CROWNPAK CR (+)). Permeability coefficients (P (m^2/s)) were calculated according to the same manner we reported previously [15], and diffusion coefficients (D (m^2/s)) and solubility coefficients (S (m^3/m^3)) were calculated by using the following equations: $D = L^2/6\theta$ and $S = P/D$, where L (m) is the thickness of the membrane and θ (s) is the time lag. For tryptophan,

[1] The detail will be reported somewhere in the near future.



Scheme 1. Synthesis and helix-sense-selective polymerization (HSSP) of S3BDHPA. (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 dry tetrahydrofuran; (e) dichlorodimethylsilane, Et_3N, and dry Et_2O; (f) $NaHCO_3$ and deionized water; (g) *n*-butyllithium, dichlorodimethylsilane, and dry Et_2O; (h) 5, Et_3N, and dry Et_2O; (i) 2, 2-Azobisisobutyronitrile (AIBN), *N*-Bromosuccinimide (NBS), and CCl_4; (j) the same as c; (k) K_2CO_3 and acetone; (l) $[Rh(nbd)Cl]_2$, chiral phenylethylamine, and toluene.

$P_D = 4.17 \times 10^{-16}$ m^2/s, $P_L = 0.67 \times 10^{-16}$ m^2/s, $\alpha = P_D/P_L = 6.25$; $D_D = 1.60 \times 10^{-14}$ m^2/s, $D_D/D_L = 5.09$; $S_D = P_D/D_D = 2.61 \times 10^{-2}$ m^3/m^3, $S_D/S_L = 1.22$. For phenylalanine, $P_D = 7.31 \times 10^{-16}$ m^2/s, $P_L = 1.68 \times 10^{-16}$ m^2/s, $\alpha = P_D/P_L = 4.35$; $D_D = 3.10 \times 10^{-14}$ m^2/s, $D_D/D_L = 3.88$; $S_D = P_D/D_D = 2.36 \times 10^{-2}$ m^3/m^3, $S_D/S_L = 1.13$.

3. Results and discussion

3.1. Achievement of helix-sense-selective polymerization (HSSP) of S3BDHPA

Poly(S3BDHPA), obtained by using a chiral catalytic system, i.e., $[Rh(nbd)Cl]_2$ and (*S*)-phenylethylamine [20], showed Cotton effects at wavelengths around 430 nm and 307 nm which are assigned to the main chain and the pendant groups, respectively, as shown in Fig. 2A. The shape of the absorption peaks was similar to that of poly(DoDHPA) prepared by using the same chiral catalytic system by us [20–26]. Therefore, a novel monomer, S3BDHPA was found to be suitable for the HSSP. The results of HSSP of S3BDHPA and the other related monomers, DoBDHPA and S2DHPA [28] are summarized in Table 1. DoBDHPA has a rigid alkyl group instead of a flexible siloxanyl group in S3BDHPA and S2DHPA has a flexible disiloxanyl group and no phenylene groups (Fig. 1). Poly(S3BDHPA) showed a much higher M_w than that of poly(DoBDHPA) (Table 1). It is thought to be because that introduction of the oligosiloxane chain enhanced the solubility of S3BDHP A and its polymer compared with those of DoBDHPA and kept homogeneous polymerization system during polymerization. In case of S2DHPA, since solubilities in nonpolar solvents of the monomer and its polymer were poor, it was not suitable for polymerization including the HSSP.

3.2. Effects of the siloxane chains on regularity and stability of the one-handed helicity of poly(S3BDHPA)

As shown in Fig. 2A, poly(S3BDHPA) showed much higher CD intensity in chloroform than poly(DoBDHPA). This may be because the flexible short siloxane chains did not obstruct the formation of the one-handed main chain compared with the rigid alkyl chains in poly(DoBDHPA).

As we reported previously, main chain chiralities of polymers prepared by the HSSP of phenylacetylene monomers having two

Table 1
Helix-sense-selective polymerization of S3BDHPA, DoBDHPA, and S2DHPA and properties of the resulting polymers.

Monomer	Yield (%)	Polymer					Membrane	
		M_w[a] $\times 10^6$	Cis% [b]	$[\theta]$[c] $\times 10^3$ deg· cm^2/dmol	Stability of $[\theta]$[d] vol.-%	Solubility[e]	Elongation at break[f] (%)	Contact angle[g] °
S3BDHPA	93.3	40.1	89	39.6	52.4	++	14.9	104.4
DoBDHPA	92.5	7.9	72	3.2	10.0	+	7.6	88.3
S2DHPA	15.0	0.1				−		

[a] By GPC correlating polystyrene standard with tetrahedron eluent.
[b] By ^{1}H NMR.
[c] Molar ellipticity at 307 nm in CD spectrum in chloroform.
[d] DMSO content (vol.-%) in DMSO/$CHCl_3$ when CD signals of the polymers disappeared.
[e] In chloroform and toluene; ++, easily soluble; +, soluble; −, insoluble.
[f] Membrane elongation at break at strain rate 5 mm/min.
[g] Contact angles of distilled water droplets.

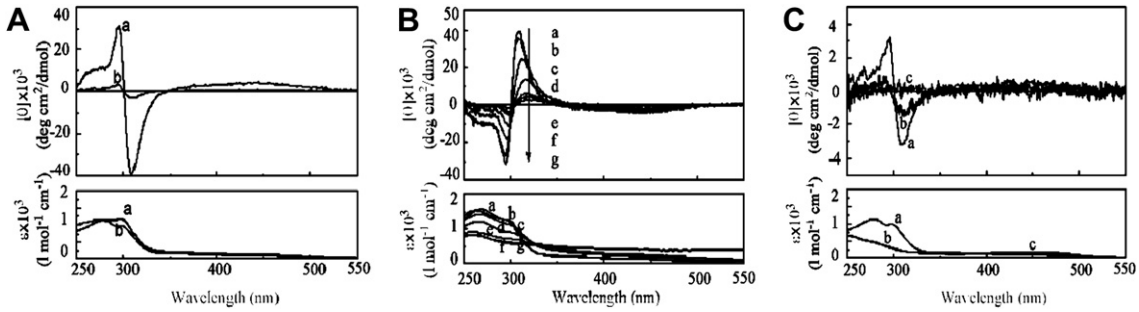


Fig. 2. CD and UV spectra of (A): a: poly(S3BDHPA), b: poly(DoBDHPA) prepared by using (*R*)-PEA in chloroform at 20 °C; (B): poly(S3BDHPA) prepared by using (*S*)-PEA in DMSO/$CHCl_3$ having different contents (vol.-%) of DMSO (a, 0; b, 9; c, 23; d, 33; e, 44; f, 50; g, 52) at 20 °C; (C): poly(DoBDHPA) prepared by using (*R*)-PEA in DMSO/$CHCl_3$ having a different content(vol.-%) of DMSO (a, 0; b, 5; c, 10) at 20 °C.

hydroxyl groups were not stable to polarity of solvents [20]. In this study, effects of polarity of solvents (the content (vol.-%) of DMSO in various two-component solvents, DMSO/$CHCl_3$) on CD stability of poly(S3BDHPA) and poly(DoBDHPA) were examined. Even though the DMSO content exceeded 50 vol.-%, the CD signal of poly (S3BDHPA) was maintained (Fig. 2B), while the CD signal of poly (DoBDHPA) disappeared when the DMSO content was only 10 vol.-%.(Fig. 2C) . The facts indicated that poly(S3BDHPA) has a much higher CD stability for polarity of solvents. As we reported before [20,26], since intramolecular hydrogen bonds stabilized the one-handed helical backbones of polymers prepared by the HSSP of phenylacetylene monomers having two hydroxyl groups, molecules of polar solvents collapsed the one-handed helical conformation by breaking the intramolecular hydrogen bonds. The introduction of hydrophobic oligosiloxane chains can form a hydrophobic field to protect the intramolecular hydrogen bonds inside the field from being broken by the external polar molecules. Therefore, poly(S3BDHPA) having hydrophobic siloxane chains showed much higher CD stability for polarity of solvents. In summary, the introduction of the short siloxane chains was found to be very effective in enhancing the regularity and stability of the one-handed helicity.

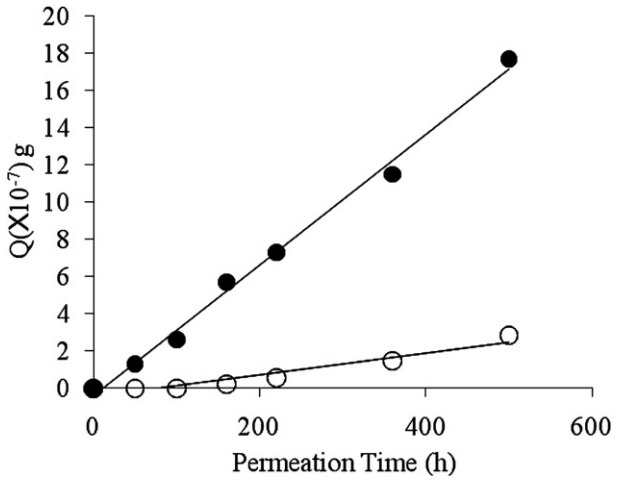


Fig. 3. Plots of quantity (*Q*) of permeated D-tryptophan (●) and L-tryptophan (○) vs permeation time through a poly(S3BDHPA) membrane (thickness = 70.1 μm) at 20 °C; feed = 0.05 wt.-% aqueous solution, pH = 2. $P_D = 4.17 \times 10^{-16}$ m^2/s, $P_L = 0.67 \times 10^{-16}$ m^2/s, $\alpha = P_D/P_L = 6.25$; $D_D = 1.60 \times 10^{-14}$ m^2/s, $D_D/D_L = 5.09$; $S_D = P_D/D_D = 2.61 \times 10^{-2}$ m^3/m^3, $S_D/S_L = 1.22$.

3.3. Effects of the oligosiloxane chains on the performance for its permselective membrane

Poly(S3BDHPA) can be easily fabricated into a self-supporting membrane. The membrane has a higher flexibility and a higher elongation at break (Table 1) than that of poly(DoBDHPA) due to flexibility of the siloxane chains.

Enantioselectivity of a poly(S3BDHPA) membrane was observed in concentration-driven permeation of a racemic aqueous solution of tryptophan (Fig. 3). The enantioselectivity of a poly(S3BDHPA) membrane($\alpha = P_D/P_L = 6.25$) was extremely higher than that of a poly(DoDHPA) membrane we reported before($\alpha = 1.22$) [25], while the permeability ($P = P_D + P_L = 4.84 \times 10^{-16}$ m^2/s) of the poly (S3BDHPA) membrane was much lower than that of the poly (DoDHPA) membrane ($P = 8.33 \times 10^{-13}$ m^2/s) [25]. For the permeation of a racemic aqueous solution of phenylalanine, a poly (S3BDHPA) membrane also showed a high enantioselectivity ($\alpha = P_D/P_L = 4.35$) and a relatively low permeability ($P = 8.90 \times 10^{-16}$ m^2/s).

There are mainly the following three reasons why the selectivity was so high. (1) Judging from the CD intensities (Fig. 2A and Table 1), poly(S3BDHPA) has a higher degree of the one handedness, i.e., a higher enantiomeric excess than poly(DoDHPA). 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(DoDHPA) containing rigid alkyl chains tended to have some defects because of the rigid alkyl side chains, poly(DoDHPA) 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 1). (3)As the contact angle values of water droplets shown in Table 1, poly (S3BDHPA) membrane was more hydrophobic. Therefore, permeability of the aqueous solution was very low. However, the selectivity was not lowered because the solvent, water could not produce any defects in the membrane.

4. Conclusions

A novel monomer suitable for the helix-sense-selective polymerization (HSSP) was successfully synthesized. By introducing a flexible and hydrophobic trisiloxanyl group to a phenylacetylene monomer, the resulting polymer prepared by the HSSP showed stronger and more stable CD signals. The findings indicated the one-handed helicity had higher regularity and more stability. In

addition, a membrane from the one-handed helical poly (S3BDHPA) showed good membrane performance such as higher strength and higher permselectivity. They are thought to be caused by the flexibility and hydrophobicity of the trisiloxane groups. At present S3BDHPA is the best monomer in the several monomers that we found suitable for our HSSP judging from the high regularity of the main chain and the best performance as a permeation membrane.

Acknowledgments

Partial financial support through a Grant-in-Aid for Scientific Research (B) (Nos. 16350061 and 19350054) from *the Japan Society for the Promotion of Science*, and a Grant-in-Aid for Scientific Research in a Priority Area "Super-Hierarchical Structures" (Nos. 18039011 and 19022009) from *the Ministry of Education*, *Culture*, *Sports*, *Science and Technology*, *Japan*, through *an Asahi Glass Foundation*, through *the Iketani Science and Technology Foundation*, and through a Grant for Promotion of *Niigata University* Research Projects is gratefully acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.04.030.

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