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Synthesis of poly(1-β-naphthyl-2-phenylacetylene) membranes through desilylation and their properties

Toshikazu Sakaguchi, Giseop Kwak, Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract

The polymerization of 1-β-naphthyl-2-[(*p*-trimethylsilyl)phenyl]acetylene (**8a**) with $TaCl_5$–*n*-Bu_4Sn in cyclohexane provided a high molecular weight polymer (**9a**) ($M_w = 3.4 \times 10^6$). The corresponding monomers having *p*-dimethyl-*t*-butylsilyl and *p*-dimethyl(10-pinanyl)-silyl groups in place of *p*-trimethylsilyl group in **8a** also polymerized in a similar way to give high molecular weight polymers (**9b**, **9c**, respectively; $M_w > 1 \times 10^6$). All these polymers were soluble in many common solvents such as toluene and chloroform, and provided free-standing membranes by casting from toluene solution. The oxygen permeability coefficients (P_{O_2}) of **9a** at 25 °C was as high as 3500 barrers. The membrane of poly(1-β-naphthyl-2-phenylacetylene) (**10a**) was prepared by desilylation of the membrane of **9a** with trifluoroacetic acid. Polymer **10a** was insoluble in any solvents, and showed high thermal stability (the onset temperature of weight loss in air ~470 °C). The P_{O_2} value of **10a** reached 4300 barrers. Not only the membrane of **9c** but also its desilylation product **10c** exhibited large optical rotations ($[\alpha]_D = +2924$ and $+9800°$, respectively) and strong CD signals. This indicates that the membrane of **10c** maintains the helical main chain conformation of **9c** with a large excess one-handed helix sense. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(1-β-naphthyl-2-phenylacetylene); Desilylation; Gas permeability

1. Introduction

It has been known that various disubstituted acetylenes can be polymerized in good yields by $TaCl_5$–cocatalyst [1,2]. Among the monomers, diphenylacetylene (**1**) provides a polymer (**2**) insoluble in any solvents [3] (Scheme 1). The properties of polymer **2** are not well known because of its insolubility. Later it was found that poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (**4**), which is a derivative of *p*-trimethylsilyl group, showed good solubility in various organic solvents [4]; this triggered the synthesis of various poly(diphenylacetylene) derivatives and their characterization [5–9]. Apart from this, it is known that certain Si-containing polyacetylenes show very high gas permeability due to their rigid main chain and spherical substituents. For instance, poly(1-trimethylsilyl-1-propyne) [poly(TMSP)] exhibits the highest gas permeability among all the synthetic polymers, whose oxygen permeability coefficient (P_{O_2}) reaches 4500 barrers [2,10]. Other examples include **4** and poly[*o*,*p*-(bistrimethylsilyl)phenylacetylene] [11], whose P_{O_2} values are 1100 and 450 barrers, respectively. Further it has been revealed that poly[(−)-1-*p*-[dimethyl(10-pinanyl)silyl]phenyl-2-phenylacetylene] having optically active silyl substituents displays strong CD signals due to the helical main chain structure with an excess one-handed helix sense [12].

Recently, we have succeeded in the fabrication of membranes of insoluble poly(diphenylacetylene) (**5**) through the desilylation of membranes of polymer (**4**) catalyzed by proton acids [13]. In general, this methodology is able to provide novel insoluble polymer membranes, which are expected to be advantageous, for instance, in the separation of organic liquid mixtures. Since poly(1-β-naphthyl-2-phenylacetylene) (**7**) [14], poly[1-(*p*-phenylphenyl)-2-phenylacetylene] [14], and poly(1-phenyl-1-hexyne) [15] are also insoluble in any solvents like **2**, their membranes cannot be prepared directly by solution casting. It is, however, expected that such membranes can be prepared by the above-stated ‘desilylation method’ of silyl derivatives.

In the present study, we synthesized 1-β-naphthyl-2-phenylacetylenes with trimethylsilyl, *t*-butyldimethylsilyl, and dimethylpinanylsilyl groups at *para* position of the phenyl group (**8a–c**) as novel monomers, and investigated their polymerization by $TaCl_5$–cocatalyst. All the resulting polymers (**9a–c**) had high molecular weights ($M_w > 3.0 \times 10^6$), dissolved in common solvents, and gave free-standing

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* Corresponding author. Tel.: +81-75-753-5613; fax: +81-75-753-5908.
E-mail address: masuda@adv.polym.kyoto-u.ac.jp (T. Masuda).

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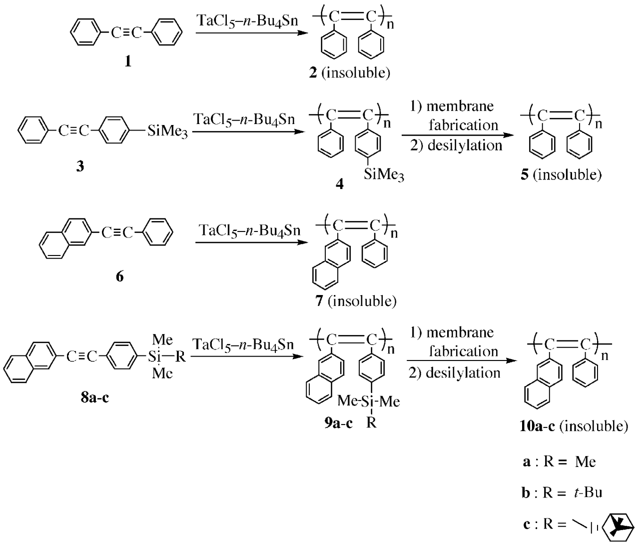


Scheme 1. Preparation of poly(diphenylacetylene) (**5**) and poly(1-β-naphthyl-2-phenylacetylene) (**10a**–**c**) membranes.

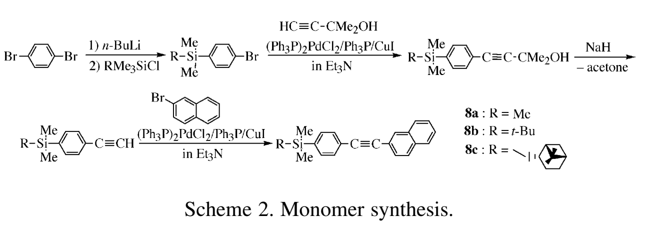
membranes by solution casting. Desilylation of membranes of **9a**–**c** was achieved to give insoluble poly(1-β-naphthyl-2-phenylacetylene) membranes (**10a**–**c**). The gas permeability, CD spectra, and other properties of polymers **9a**–**c** and **10a**–**c** were examined.

2. Experimental

2.1. Materials

$TaCl_5$ and cocatalysts were commercially obtained and used without further purification. Polymerization solvents were purified by the standard methods. 4-Trimethylsilyl-1-ethynylbenzene was prepared according to the literature method [11] (Scheme 2). 4-(*t*-Butyldimethylsilyl)-1-ethynylbenzene was prepared by the same method as for 4-trimethylsilyl-1-ethynylbenzene, by using *t*-butyldimethylchlorosilane as a starting material in place of trimethylchlorosilane. (−)-4-[Dimethyl(10-pinanyl)silyl]-1-ethynylbenzene was prepared according to the literature method [12].

Synthesis of **8a**. A 500 ml three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and flushed with dry nitrogen. 2-Bromonaphthalene (5.00 g, 24.1 mmol), dichlorobis(triphenylphosphine)palladium (56 mg, 0.080 mmol), cuprous iodide (93 mg, 0.48 mmol), triphenylphosphine (85 mg, 0.32 mmol), and triethylamine (160 ml) were placed in the flask. Then, 4-trimethylsilyl-1-ethynylbenzene (4.27 g, 24.5 mmol) in triethylamine (40 ml) solution was added. The reaction mixture was heated at reflux temperature for 5 h. After the triethylamine in the reaction mixture was evaporated, diethyl ether (ca. 300 ml) was added, and the insoluble salt was filtered off. The solution was washed at first with 2N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate, and then concentrated at reduced pressure. Purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product (4.50 g, 62%) as a white solid. mp: 103.0–104.0 °C, purity: >99% (^{1}H NMR). IR (KBr): 2957, 1599, 1250, 1096, 855, 824, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.07 (s, 1H, Ar), 7.85–7.81 (m, 3H, Ar), 7.61–7.49 (m, 7H, Ar), 0.30 (s, 9H). ^{13}C NMR ($CDCl_3$, δ): 141.1, 133.2, 133.0, 132.8, 131.4, 130.7, 128.4, 128.0, 127.8, 126.6, 126.5, 123.5, 120.6, 90.1, 89.9, −1.2. Anal. Calcd for $C_{21}H_{20}Si$: C, 84.0%; H, 6.7%; Si, 9.3%. Found: C, 83.9%; H, 6.7%; Si, 9.4%.



Scheme 2. Monomer synthesis.

Synthesis of **8b**. This monomer was prepared in the same way using 4-(*t*-butyldimethylsilyl)-1-ethynylbenzene. Yield 48%, mp: 91.0–92.5 °C, purity: >99% (^{1}H NMR). IR (KBr): 2955, 1599, 1250, 1094, 860, 822, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.07 (s, 1H, Ar), 7.84–7.80 (m, 3H, Ar), 7.62–7.48 (m, 7H, Ar), 0.88 (s, 9H), 0.30 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 143.7, 138.6, 134.4, 132.8, 131.4, 130.4, 128.4, 128.0, 127.8, 126.7, 126.5, 123.5, 120.6, 90.3, 89.9, 26.4, 16.9, −6.3. Anal. Calcd for $C_{24}H_{26}Si$: C, 84.2%, H, 7.7%, Si, 8.1%. Found: C, 84.2%, H, 7.7%, Si, 8.1%.

Synthesis of **8c**. This monomer was prepared similarly from (−)-4-[dimethyl(10-pinanyl)silyl]-1-ethynylbenzene. Yield 60%, mp: 63.0–64.0 °C, purity: >99% (^{1}H NMR). IR (KBr): 2982, 1599, 1248, 1098, 864, 822, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.05 (s, 1H, Ar), 7.83–7.78 (m, 3H, Ar), 7.60–7.47 (m, 7H, Ar), 2.18–0.68 (m, 11H), 1.14 (s, 3H), 0.77 (s, 3H), 0.28 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 141.0, 133.5, 133.0, 132.8, 131.4, 130.6, 128.4, 128.0, 127.8, 126.6, 126.5, 123.3, 120.6, 90.1, 90.0, 49.2, 40.6, 39.5, 31.1, 26.9, 25.5, 24.7, 23.8, 22.9, 20.0, −1.9, −2.1. Anal. Calcd for $C_{30}H_{34}Si$: C, 85.3%; H, 8.1%; Si, 6.6%. Found: C, 85.0%; H, 8.2%; Si, 6.8%.

2.2. Polymerization

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. The polymerization conditions were as follows: 80 °C, 24 h, $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, $[Cocat] = 40$ mM. A detailed procedure of polymerization has been described elsewhere [7]. Polymers were isolated by precipitation into a large amount of methanol, and polymer yields were determined by gravimetry.

2.3. Desilylation

Membranes (thickness ca. 20–40 μm) of **9a**–**c** were fabricated by casting toluene solution of the polymers (conc. ca. 1.0–1.5 wt%) onto a glass plate. Applying basically the same method as for the desilylation of **4** [13], the desilylation reaction of the present membranes was carried out as follows: a polymer membrane was immersed in a mixture of hexane/trifluoroacetic acid (volume ratio 1:1) at room temperature for 24 h; the orange membrane gradually turned dark green. To neutralize the remaining acid in the polymer matrix, the membrane was then immersed in a mixture of hexane/triethylamine (volume rate 1:1) at room temperature for 24 h. The color of the membrane changed from dark green to red. Finally, the membrane was immersed in methanol for 24 h to remove residual impurities, washed with methanol, and dried to constant weight at room temperature for 24 h. The completion of desilylation was confirmed by the IR spectra of the membranes before and after reaction; the IR spectra of the membranes of **10a–c** exhibited no absorptions at 1250, 1120, and 860 cm^{-1}, which were seen in **9a–c**. The weights of the membranes decreased upon desilylation to the values anticipated for desilylation, which also supports the completion of the reaction (e.g. **9a**: 67.6 mg, **10a**: found, 51.4 mg, calcd, 51.4 mg).

2.4. Characterization

The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ as eluent, polystyrene calibration). IR and UV–Vis spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer and a Shimadzu UV-2200 spectrophotometer, respectively. NMR spectra were observed on a JEOL EX-400 spectrometer. Thermogravimetric analysis (TGA) were conducted in air with a Perkin–Elmer TGA7 thermal analyzer. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus. CD spectra were recorded with a Jasco J-600 spectropolarimeter. Since the solid-state CD spectra hardly changed with measuring conditions, the influence of birefringence is denied. Specific rotations were measured with a Jasco V-530 spectropolarimeter. The $[\alpha]_D$ values of membranes were calculated based on observed α values and evaluation of concentrations from the UV–Vis spectra of polymer membranes and polymer solutions.

3. Results and discussion

3.1. Polymerization

The polymerization of poly[1-β-naphthyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (**8a**) with $TaCl_5$–*n*-Bu_4Sn in cyclohexane at 80 °C produced a high molecular weight polymer (**9a**; yield ca. 60%, M_w 3.4×10^6), which was soluble in toluene, $CHCl_3$, and so forth (Table 1, run 1). When toluene was used as polymerization solvent, a similar polymer yield was achieved, but the M_w of the polymer was lower and 6.0×10^5 (run 2). In cyclohexane, the polymerization system became solid because of the formation of high molecular weight polymer. The reason for the high molecular weight in cyclohexane may be the formation of a less amount of active species due to the lower solubility of catalyst components in cyclohexane than in toluene.

Table 1
Polymerization of **8a–c** by $TaCl_5$–cocatalyst (polymerized at 80 °C for 24 h; $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, [Cocat] = 40 mM)

Run	Cocatalyst	Solvent	Polymer[a]		
			Yield (%)	M_w (10^3)[b]	M_n (10^3)[b]
Monomer: **8a**					
1	*n*-Bu_4Sn	Cyclohexane	59	3400	700
2	*n*-Bu_4Sn	Toluene	54	600	100
3	Et_3SiH	Cyclohexane	64	900	60
4	Et_3SiH	Toluene	60	340	30
5	Et_3SiH	Benzene	26	400	35
6	Et_3SiH	Chlorobenzene	22	300	20
7	Et_3SiH	*o*-dichlorobenxene	47	140	10
8	Et_3SiH	1,2-Dichloroethane	4	50	2
9	Et_3SiH	CCl_4	0	–	–
Monomer: **8b**					
10	*n*-Bu_4Sn	Cyclohexane	56	1200	220
11	*n*-Bu_4Sn	Toluene	21	620	80
Monomer: **8c**					
12	*n*-Bu_4Sn	Cyclohexane	69[c]	1300	110
13	*n*-Bu_4Sn	Toluene	44[c]	300	20

[a] Methanol-insoluble product.
[b] Measured by GPC.
[c] Acetone-insoluble product.

When Et_3SiH was used as cocatalyst in place of *n*-Bu_4Sn, the molecular weight of polymers decreased in both cyclohexane and toluene, though the polymer yields were similar. The effect of various solvents was examined by using Et_3SiH as cocatalyst (runs 3–9). Benzene, chlorobenzene, and *o*-dichlorobenzene as solvents gave similar or lower yields and molecular weights of polymer compared to toluene. Further, polymerization did not or hardly proceeded in 1,2-dichloroethane and carbon tetrachloride, the reason for which is not clear at present. From these results, it is concluded that the polymerization catalyzed by $TaCl_5$–*n*-Bu_4Sn in cyclohexane solution is the most favorable among the polymerizations examined to obtain a high molecular weight polymer in high yield.

Polymerization of monomers **8b** and **8c** in cyclohexane and toluene was examined (runs 10–13). In cyclohexane, the polymer yields reached about 55–70%, and the M_w values of polymers exceeded one million. Thus the polymerization behavior of these monomers resemble that of monomer **8a**, although the polymer molecular weights of **8b** and **8c** were not so high.

3.2. Polymer properties

Properties of **9a–c** were examined by using the polymer

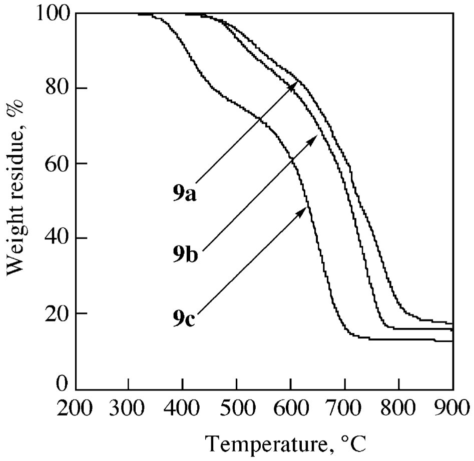


Fig. 1. TGA curves of **9a**–**c** (in air, heating rate 10 °C min^{-1}).

samples obtained by the polymerization with $TaCl_5$–*n*-Bu_4Sn in cyclohexane (Table 1, runs 1, 10, and 12).

Polymers **9a**–**c** showed good solubility unlike **7**, which has no silyl groups; i.e. they completely dissolved in common solvents such as toluene, chloroform, tetrahydrofuran (THF), cyclohexane, carbon tetrachloride, chlorobenzene, anisole, etc. They were partly soluble in hexane and diethyl ether. Polymer **9c** was more soluble than the other polymers; e.g. it completely dissolved in *o*-dichlorobenzene, whereas **9a** and **9b** only partly dissolved in it. None of them dissolved in polar solvents such as DMF, DMSO, and lower alcohols. Free-standing membranes of **9a**–**c** could be fabricated by casting them from toluene solution.

TGA of **9a**–**c** were conducted in air (Fig. 1). The onset temperatures of weight loss (T_0) of **9a**–**c** were 450, 440, and 340 °C, respectively, indicating very high thermal stability of **9a** and **9b**. The thermal stability of **9c** is somewhat lower, suggesting that the pinanyl group tends to remove at high temperatures. The TGA profiles of **10a**–**c** (the desilylation products from **9a**–**c**) and **7** (the direct polymerization product) are shown in Fig. 2. These polymers, which are all structurally just poly(1-β-naphthyl-2-phenylacetylene)s, show high T_0 values of around 470 °C and similar TGA curves to one another, indicating high thermal stability. This is important upon application when it is taken into account that the T_0 value of highly gas-permeable poly(TMSP) is 330 °C and relatively low [16].

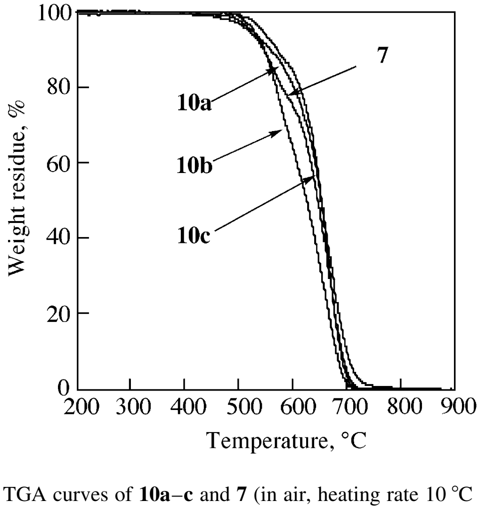


Fig. 2. TGA curves of **10a**–**c** and **7** (in air, heating rate 10 °C min^{-1}).

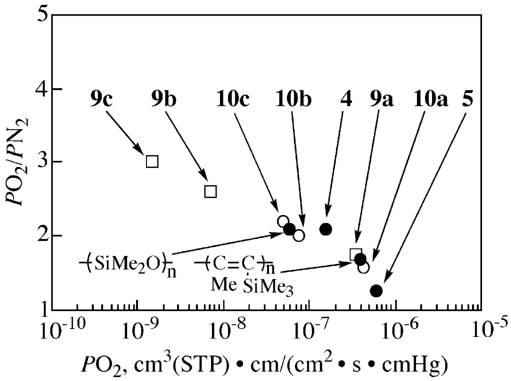


Fig. 3. Oxygen permeability coefficient (P_{O_2}) and P_{O_2}/P_{N_2} of present polymers (25 °C) (data from this study and Refs. [10,13,19]).

3.3. Gas permeability

The oxygen permeability coefficients (P_{O_2}) of **9a** at 25 °C was 3500 barrers, which is about three times as high as that of **4** (1100 barrers) which is the corresponding poly(diphenylacetylene) derivative (Fig. 3); thus this P_{O_2} value is one of the highest values among all the polymers. The P_{O_2} value of **10a**, the corresponding desilylated polymer of **9a**, was 4300 barrers at 25 °C, which is somewhat larger than that of **9a**. The permeability coefficients of **9a** and **10a** to various gasses are shown in Table 2. It is noticed that the values of **10a** are larger than those of **9a** in most cases. In addition to high gas permeability, **10a** is insoluble in any solvents and thermally very stable; all these properties are advantageous when the development of gas-separation membranes is considered.

The P_{O_2} values of **9b** and **9c** at 25 °C were 70 and 15 barrers, which are much smaller than that of **9a** (3500 barrers). These results mean that the introduction of bulkier silyl groups onto poly(1-β-naphthyl-2-phenylacetylene) leads to remarkable decreases in gas permeability. Such a tendency has also been observed in poly(diphenylacetylene) derivatives [17,18].

Table 2
Gas permeability coefficients (*P*) of **9a** and **10a**

Polymer	P^a						P_{O_2}/P_{N_2}
	He	H_2	O_2	N_2	CO_2	CH_4	
9a	2400	4400	3500	2000	10 000	3600	1.8
10a	3300	4700	4300	2700	13 000	2500	1.6

[a] At 25 °C in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (=1 barrer).

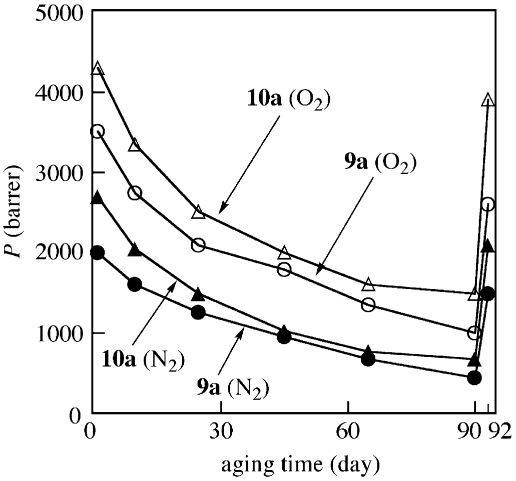


Fig. 4. Effect of aging time on the oxygen and nitrogen permeability of **9a** and **10a** (stored at 25 °C in air). The data after 92 days are based on the membranes which were conditioned in methanol.

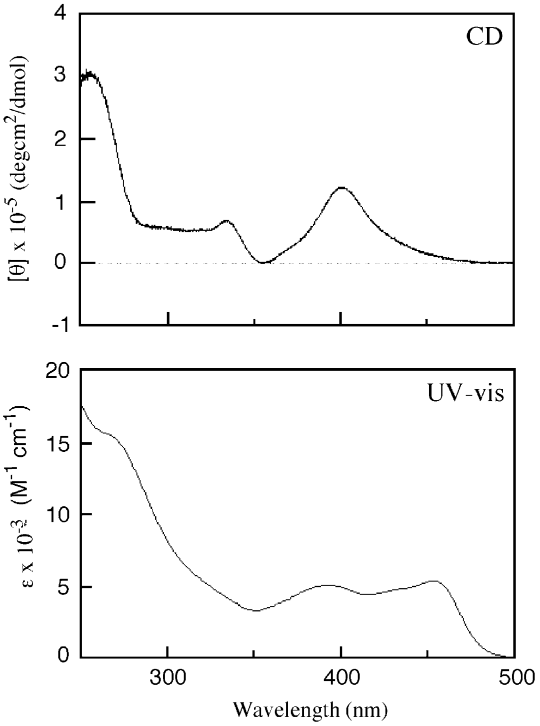


Fig. 5. CD and UV–Vis spectra of **9c** in solution ($CHCl_3$, 9.47×10^{-5} mol l^{-1}, 25 °C).

The P_{O_2} value of **10b** was 750 barrers, indicating a large increase upon desilylation (cf. the P_{O_2} of **9b**: 70 barrers). Polymer **10c** showed a similar tendency; i.e. the P_{O_2} value increased from 15 to 500 barrers upon desilylation. It is noteworthy that such a large increase in P_{O_2} upon desilylation is not seen in the highly permeable polymer **9a**. An interesting point is that, although all of **10a–c** have the same molecular structure, they have different numbers and sizes of molecular-scale voids, leading to different gas permeability. However, the membranes of **9b** and **9c** were so weak that more detailed study of their gas permeability was unfortunately impossible.

The effect of aging time on P_{O_2} and P_{N_2} was examined by keeping the membranes of **9a** and **10a** at 25 °C in air. As seen in Fig. 4, the P_{O_2} values of **9a** and **10a** decreased from 3500 and 4300 to 1000 and 1500 barrers after 90 days, respectively. It seems that the P_{O_2} of both **9a** and **10a** becomes nearly constant after 90 days. The P_{N_2} of these polymers also shows a similar tendency. Highly gas-permeable polyacetylenes tend to exhibit such a tendency; i.e. their permeability more or less decreases with time, although the degree of the permeability decrease depends on each polymer. For instance, the P_{O_2} value of poly(TMSP) decreases from ca. 5000 to ca. 100 barrers after about 100 days [20], while that of poly[1-(trimethylgermyl)-1-propyne] only slightly decreases from ca. 8000 to ca. 6000 barrers after 90 days [21]. Quite interestingly, the decreased P_{O_2} and P_{N_2} values of these polymer membranes, **9a** and **10a**, were virtually completely restored to the initial ones when the membranes were immersed in methanol for 24 h. A similar behavior has been observed with poly(TMSP) [20,22].

*3.4. Helical conformation of **9c** and **10c***

A solution of polymer **9c**, which has chiral dimethylpinanylsilyl groups, showed a large optical rotation ($[\alpha]_D = +2924°$; $CHCl_3$, $c = 9.47 \times 10^{-5}$ mol l^{-1}), and displayed strong CD signals in the UV–Vis region (Fig. 5). The specific rotation of monomer **8c** was much smaller, and opposite in sign to that of **9c**. These findings indicate that the main chain of **9c** exists in helical conformation with a large excess one-handed helix sense. Further, a membrane of **9c** was fabricated by casting a toluene solution of the polymer onto a quartz plate, and its $[\alpha]_D$ value and CD spectrum were examined. The $[\alpha]_D$ value was as large as +3390°, and CD signals were observed in the same region as for absorption (Fig. 6), although some differences are seen from those in solution. Thus, the helical structure was confirmed also in the solid state. It is reasonable to think that this helical structure of the main chain is induced by the presence of the chiral side groups.

Quite interestingly, the desilylated polymer membrane, **10c**, also exhibited a very large optical rotation ($[\alpha]_D = +9800°$), and intense CD signals in the UV–Vis region (Fig. 6). This manifests that **10c** also retains helical main chain conformation with a large excess one-handed helix sense. This finding agrees with the result of poly(diphenylacetylene) [13]. It is noteworthy that **10c** shows virtually the same chiroptical properties as for **9c** despite the absence of any chiral side groups; this means that the chirooptical properties of both **9c** and **10c** are substantially based on the main-chain helical structure. This is a new type of chiral memory apart from previous examples of different types [23]. Since the

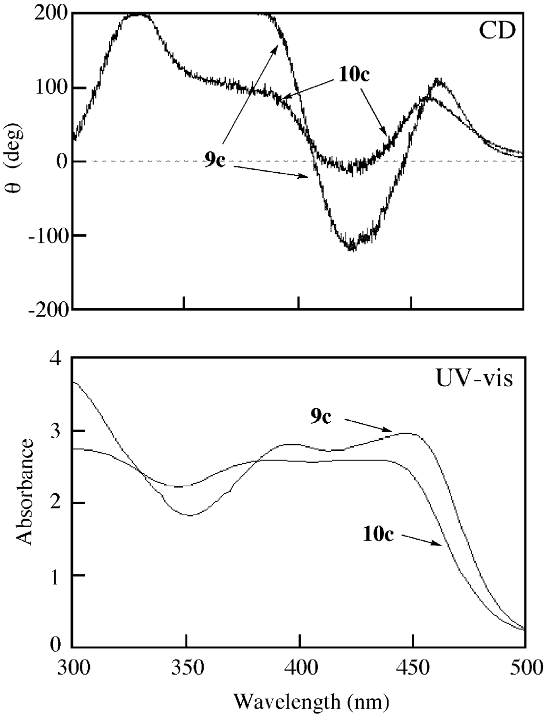


Fig. 6. CD and UV–Vis spectra of **9c** and **10c** in the solid state (25 °C).

membrane of **10c** is insoluble in any solvents, its application as chiral separation membrane is an interesting subject, and such research is now underway.

4. Conclusions

Polymer **9a** exhibited extremely high gas permeability, which is close to that of poly(TMSP) and higher than that of **4**. Polymer **10a** obtained through desilylation showed high gas permeability of the same level as **9a** despite the absence of any spherical substituents. Further, polymer **10c**, which was prepared by the desilylation of **9c**, turned out to possess a helical conformation with a large excess one-handed helix sense in the main chain irrespective of the absence of any chiral pendant groups. This finding corresponds with the result of poly(diphenylacetylene) obtained in the same way. Thus, the desilylation method is a novel and interesting method to prepare the membranes of poly(diarylacetylenes), and the resulting polymer membranes are expected to show unique properties and various functions.

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