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Synthesis and stable high oxygen permeability of poly(diphenylacetylene)s with two or three trimethylsilyl groups

Giseop Kwak[1], Toshiki Aoki*, Takashi Kaneko

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

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Abstract

We synthesized two new poly(diphenylacetylene)s having two or three trimethylsilyl groups and found these membranes having extremely high oxygen permeabilities of more than 1000 barrers which are of the same order as that for poly[1-(trimethylsilyl)-1-propyne]. Whereas oxygen permeability of poly[1-(trimethylsilyl)-1-propyne] was reported to decrease largely with time, these high oxygen permeabilities were stable for several months. These membranes also showed ethanol permselectivities because of their hydrophobicity. It was found that the introduction of two or three trimethylsilyl groups to poly(diphenylacetylene) was very effective for obtaining stable high oxygen permeable and ethanol permselective membranes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(diphenylacetylene); Trimethylsilyl group; Oxygen permeability

1. Introduction

Polymeric membranes which have high gas permeability are very attractive to use in industry. However, only few polymers which have high oxygen permeability coefficients (P_{O_2}) values more than 1000 barrers are known. Some of silicon (Si)-containing polyacetylenes are highly permeable to gases. In particular, disubstituted polyacetylenes having trimethylsilyl group have attracted much attention because of their extraordinarily high oxygen permeability exceeding 1000 barrers. For instance, P_{O_2} of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] [1] and poly[1-phenyl-2-*p*-(trimethylsilyl)phenylacetylene] [poly(*p*-TMSDP)] [2] reach 6100 and 1100 barrers, respectively. Especially, the P_{O_2} value of poly(TMSP) is the highest of all the polymers. However, the P_{O_2} value reduces with age. For example, after aging for about 3 months, the P_{O_2} value reduced to about 300 barrers [3], which is the same order of P_{O_2} for poly(dimethylsiloxane). To stabilize this high P_{O_2} has been very important and many attempts to stabilize it were made by modifying poly(TMSP) [4,5]. When it was heated at 100 °C for 15 h, the P_{O_2} decreased to less than 1/10 of its initial value. P_{O_2} value of poly(*p*-TMSDP) also decreased to a 1/4 of its original value, when it was aged at 80 °C for 26 h. However, since the extent of decrease of P_{O_2} for poly(*p*-TMSDP) was smaller than for poly(TMSP), diphenylacetylene polymers are promising as membrane materials which have stable high P_{O_2} values.

Almost all polymers including polyacetylenes are water-permselective when aq. ethanol solutions are supplied. However, poly(TMSP) [6,7] shows an ethanol permselectivity similar to that of poly(dimethylsiloxane) [8] which is known to give representative ethanol-permselective membrane. For example, the separation factor (α^{EtOH}) reached 12 when 10 wt% of aq. ethanol solution was fed.

Recently, we found that copolymers of *p*-[tris(trimethylsilyl)silyl]phenylacetylene [*p*-$(Me_3Si)_3SiPA$] containing three trimethylsilyl groups with *p*-(trimethylsilyl)phenylacetylene (*p*-Me_3SiPA) showed high gas permeability. The P_{O_2} values increased monotonously with increasing *p*-$(Me_3Si)_3SiPA$ content and reached 770 barrers for the copolymer containing 80 mol% of *p*-$(Me_3Si)_3SiPA$ [9]. In general, disubstituted polyacetylenes [e.g. substituted poly(diphenylacetylene)s] are more permeable to gases than corresponding monosubstituted ones [e.g. substituted poly(phenylacetylene)s] [10,11]. Hence, it is expected that poly(diphenylacetylene)s with several trimethylsilyl groups show higher gas-permeability. In addition, such polymers are expected to show ethanol-permselectivity because of high permeability and hydrophobicity.

In this communication, we report on the synthesis of two

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* Corresponding author. Tel.: +81-25-262-7280; fax: +81-25-262-7280. *E-mail address:* toshaoki@eng.niigata-u.ac.jp (T. Aoki).

[1] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan.

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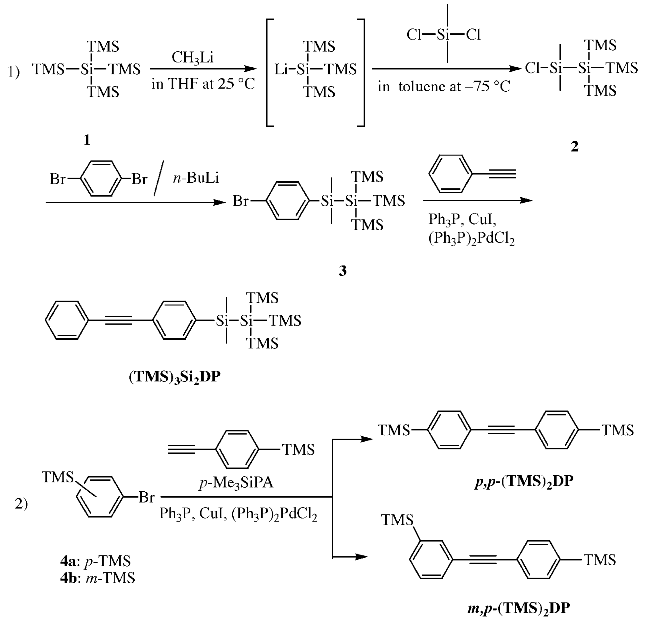

Scheme 1. Synthesis of diphenylacetylenes with two or three trimethylsilyl (TMS) groups.

or three trimethylsilyl-containing poly(diphenylacetylene)s, i.e. poly[1-{p-{2′,2′-bis(trimethylsilyl)pentamethyltrisilanyl} phenyl}]-2-phenylacetylene, poly[(TMS)$_3$Si$_2$DP], having three trimethylsilyl groups, and poly[1-(m-trimethylsilyl)phenyl-2-(p-trimethylsilyl)phenylacetylene], poly[m,p-(TMS)$_2$DP], having two trimethylsilyl groups, their extremely high oxygen permeabilities (P_{O_2}), and stability of the high P_{O_2}s. In addition, ethanol pervaporation behavior of the resulting polymers will be described.

2. Experimental

2.1. Monomer synthesis (Scheme 1)

Tetrakis(trimethylsilyl)silane (**1**): This compound was prepared according to the literature [12].

Crude 2′,2′-bis(trimethylsilyl)pentamethyltrisilanyl chloride (**2**): A 300-ml round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, compound **1** (10 g, 31.2 mmol) and dry THF (100 ml) were placed in the flask at 25 °C. At the same temperature, a THF/cumene(10/90) solution of methyllithium (31.2 ml, 1.0 M, 31.2 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. After evaporating THF and cumene, toluene (40 ml) was added. At −78 °C, dimethyldichlorosilane 3.8 ml (31.2 mmol) was added dropwise, and the reaction mixture was stirred at room temperature overnight. Toluene was evaporated, and the crude product, **2** was obtained as a yellow solid.

p-[2′,2′-bis(trimethylsilyl)pentamethyltrisilanyl]bromobenzene (**3**): A 300-ml round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, p-dibromobenzene (7.4 g, 31.2 mmol) and diethyl ether (50 ml) were placed in the flask at 0 °C. At the same temperature, a hexane solution of n-butyllithium (18.8 ml, 1.6 M, 31.2 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. A solution of the crude compound **2** (10.2 g) in diethyl ether (30 ml) was added dropwise, and stirring was continued overnight. After removal of insoluble salts by filtration, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (hexane) to give the desired product (yield 2.6 g, 17%) as a colorless solid. ^{1}H NMR (CDCl$_3$): δ 7.46–7.40 (4H, aromatic), 0.49 (6H, –Si(CH_3)$_2$–), and 0.16 (27H, –[Si(CH_3)$_3$]$_3$) ppm.

1-[p-{2′,2′-bis(trimethylsilyl)pentamethyltrisilanyl}phenyl] -2-phenylacetylene [(TMS)$_3$Si$_2$DP]: A 200-ml round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and flushed with dry nitrogen. Triethylamine (50 ml), (Ph$_3$P)$_2$PdCl$_2$ (10 mg, 120 μmol), CuI (10 mg, 47 μmol), PPh$_3$ (20 mg, 760 μmol), phenylacetylene (0.87 ml, 7.5 mmol) and compound **3** (2.5 g, 5.3 mmol) were placed in the flask, and the mixture was stirred for 3 h at 80 °C. After the completion of the reaction has been confirmed by thin layer chromatography (TLC), triethylamine was evaporated. The crude product was purified by flash column chromatography (hexane) to give the desired product (yield 1.1 g, 44%) as a colorless solid. IR (KBr): 3032, 2956, 2220, 1604, 1508, 1242, 1096, 823 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.55–7.48 (9H, aromatic), 0.53 (6H, –Si(CH_3)$_2$–), 0.17 (27H, –[Si(CH_3)$_3$]$_3$) ppm. ^{29}Si NMR (CDCl$_3$): δ −9.5 (3Si, –[Si(CH$_3$)$_3$]$_3$), −12.7 (1H, –Si(CH$_3$)$_2$–), −85.6 (1H, –SiC$_6$H$_4$–) ppm. Anal. calcd for (C$_{25}$H$_{42}$Si$_5$)$_n$: C, 62.19; H, 8.71. Found: C, 63.88; H, 8.54.

p- or m-(Trimethylsilyl)bromobenzenes (**4a**, **4b**): These compounds were synthesized according to the literature [13].

1-(p-Trimethylsilyl)phenyl-2-(p-trimethylsilyl)phenylacetylene [p,p-(Me$_3$Si)$_2$DPA]: A 200-ml round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and flushed with dry nitrogen. Triethylamine (50 ml), (Ph$_3$P)$_2$PdCl$_2$ (5 mg, 60 μmol), CuI (5 mg, 30 μmol), PPh$_3$ (10 mg, 380 μmol), p-Me$_3$SiPA [13] (1.2 g, 6.9 mmol) and compound **4a** (1.6 g, 6.9 mmol) were placed in the flask, and the mixture was stirred for 3 h at 80 °C. After the completion of the reaction has been confirmed by TLC, triethylamine was evaporated. The crude product was purified by flash column chromatography (hexane) to give the desired product (yield 1.6 g, 70%) as a colorless solid. IR (KBr): 2964, 2260, 1600, 1508, 1252, 1104, 842 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.50 (8H, aromatic), 0.27 (18H, 2-Si(CH_3)$_3$) ppm.

1-(m-Trimethylsilyl)phenyl-2-(p-trimethylsilyl)phenylacetylene [m,p-(Me$_3$Si)$_2$DPA]: This compound was prepared similarly to synthesis of p,p-(Me$_3$Si)$_2$DPA by

Table 1
Synthesis and properties of polydiphenylacetylenes and polypropyne having trimethylsilyl groups (polymerized with $TaCl_5$–nBu_4Sn in toluene for 24 h: $[M]_0 = 1.0\,M$; [cat]/[cocat] = 0.5)

Run	Monomer (M)	$[M]/[TaCl_5]$	Polymer						
			Yield (%)	$10^{-5} \times M_w$ [a]	M_w/M_n [a]	P_{O_2} (10^{-3} barrer)	α [b]	d [c]	V_F [d]
1	$(TMS)_3Si_2DP$	5.2	40	3.4	7.0	1.3	2.1	0.88	0.21
2	m,p-$(TMS)_2DP$	6.4	29	4.8	6.9	1.1	2.4	0.85	0.27
3	p,p-$(TMS)_2DP$	12.5	55			Insoluble			
4 [e]	p-TMSDP	25	85	22	2.9	1.1	2.1	0.91 [f]	0.26 [f]
5 [g]	TMSP	50	100	8.5	1.4	6.1	1.7	0.75 [h]	0.29 [f]

[a] Determined by GPC.
[b] $\alpha = P_{O_2}/P_{N_2}$.
[c] Density determined by floatig method.
[d] Free volume fraction.
[e] Ref. [2].
[f] Ref. [17].
[g] Ref. [1].
[h] Ref. [21].

using compound **4b**. Yield 1.4 g, 63%. ^1H NMR ($CDCl_3$): δ 7.70–7.34 (8H, aromatic), 0.29 (9H, m-$Si(CH_3)_3$), 0.28 (9H, p-$Si(CH_3)_3$) ppm.

2.2. Polymerization

Polymerizations were carried out under dry nitrogen according to the procedure described elsewhere [2]. The polymerization mixtures were diluted with toluene, and were poured into a large amount of methanol under stirring to precipitate the formed polymers. The polymers were filtered off and dried to constant weights.

2.3. Measurements

The weight- and number-average molecular weights (M_w and M_n, respectively) of polymers were determined by gel permeation chromatography (GPC); Hitachi 655A-11 Liquid Chromatograph, eluent THF, polystyrene calibration. ^1H NMR spectra were measured in $CDCl_3$ solution at 25 °C on a Varian Gemini 200H (200 MHz) NMR spectrometer. Oxygen and nitrogen permeability coefficients and ethanol and water permeation rates were measured by gas chromatographic method using YANACO GTR-10 and YANACO GTR-12L, respectively. The fractional free volumes (FFV) were calculated from film density determined by floating method and specific van der Waals volume estimated by van Krevelen's group contribution method [14,15].

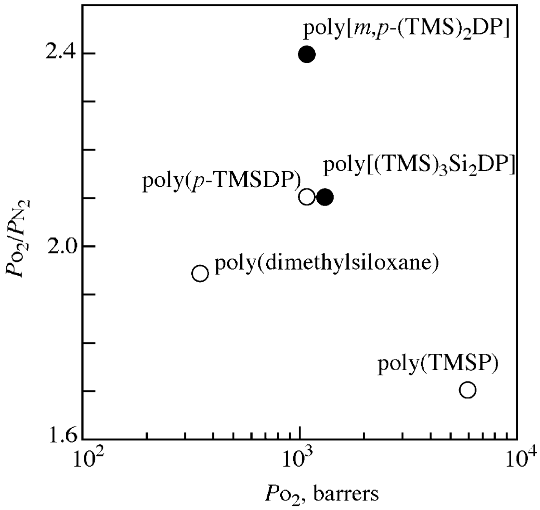

Fig. 1. Plot of oxygen permselectivity (P_{O_2}/P_{N_2}) vs. oxygen permeability coefficient (P_{O_2}) of membranes from poly[$(TMS)_3Si_2DP$] and poly[m,p-$(TMS)_2DP$] together with other highly permeable polymers (see Table 1).

3. Results and discussion

Table 1 shows the results of the polymerization of the monomers. First, although we tried to polymerize the monomers at the same conditions ($[M]_0 = 0.5$ M, $[M]/[TaCl_5] = 25$) as polymerization of p-TMSDP (No. 4 in Table 1) [2], little or no polymers were obtained at this condition. When we changed the polymerization conditions to $[M]_0 = 1.0$ M and $[M]/[TaCl_5] \sim 5$, $(TMS)_3Si_2DP$ and m,p-$(TMS)_2DP$ afforded polymers in proper yields. The polymerization of $(TMS)_3Si_2DP$ by $TaCl_5$–n-Bu_4Sn in toluene at 80 °C gave a polymer with high molecular weight (M_w) of 3.4×10^5 in yield of 40%. Although p,p-$(TMS)_2DP$ afforded polymer insoluble in general organic solvents such as chloroform, THF, and toluene, m,p-$(TMS)_2DP$ provided a polymer which has M_w of 4.8×10^5 and was soluble in various organic solvents. The polymerization yield of m,p-$(TMS)_2DP$ was slightly lower than that of p,p-$(TMS)_2DP$. It might be attributed to the larger steric hindrance of m,p-$(TMS)_2DP$ as compared to p,p-$(TMS)_2DP$. The IR spectra of the resulting polymers (Table 1, runs 1–3) exhibited no absorption at about 2220 cm^{-1} ($\upsilon_{C\equiv C}$) that was seen in monomers. Poly[$(TMS)_3Si_2DP$] and poly[m,p-$(TMS)_2DP$]

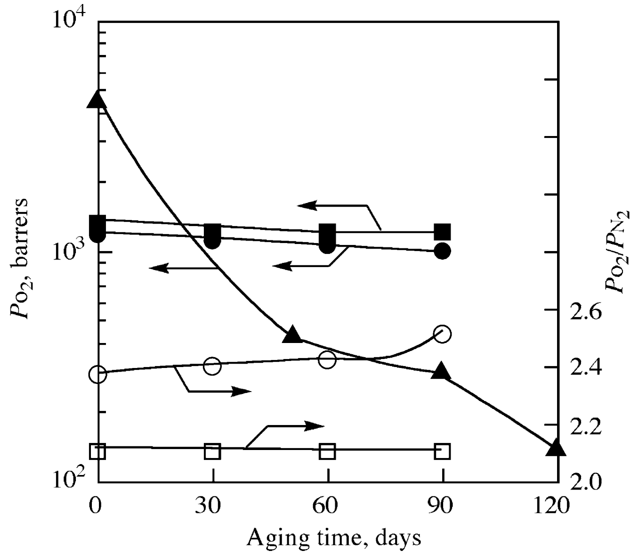

Fig. 2. Effect of aging time on P_{O_2} and P_{O_2}/P_{N_2} of poly[$(TMS)_3Si_2$DP], poly[*m*,*p*-$(TMS)_2$DP], and poly(TMSP) membrane. ■ □: poly[$(TMS)_3Si_2$DP] (25 °C, in air), ● ○: poly[*m*,*p*-$(TMS)_2$DP] (25 °C, in air), ▲: poly(TMSP) (30 °C, in vacuo).

were soluble in toluene, THF, and $CHCl_3$, but insoluble in hexane, acetone, DMF, and DMSO. A free-standing films (thickness 100–120 μm) were prepared by casting toluene solutions of these two polymers.

Poly[$(TMS)_3Si_2$DP] and poly[*m*,*p*-$(TMS)_2$DP] in this study exhibited the same orders of magnitude of P_{O_2} value as poly(TMSP) which has the highest P_{O_2} value in all the polymers (Fig. 1). By introducing more trimethylsilyl group to a phenyl group of poly(*p*-TMSDP), the α value increased with maintaining the high P_{O_2} [poly[*m*,*p*-$(TMS)_2$DP]], while poly[$(TMS)_3Si_2$DP] which has three trimethylsilyl groups showed higher P_{O_2} than poly(*p*-TMSDP) which has one trimethylsilyl group per monomer unit and kept the same α value as poly(*p*-TMSDP) (Fig. 1). On the other hand, it was reported that polydiphenylacetylenes containing branched alkylsilyl groups such as triisopropyl groups or bulky aryl groups such as triphenylsilyl groups showed 1/100–1/1000 times lower P_{O_2} than poly(TMSP) [16]. Therefore, branched oligosilyl groups which contains three trimethylsilyl groups in poly[$(TMS)_3Si_2$DP] was found to be very effective to enhance P_{O_2} in contrast to triisopropyl or triphenyl groups. In conclusion, two or three trimethylsilyl groups played an important role in these new polydiphenylacetylenes. To discuss this high P_{O_2}, FFV were estimated from density (*d*) as shown in Table 1. Since these new polymers showed high FFV values and low densities similarly to those for poly(*p*-TMSDP) [17] and poly(TMSP) [18], the introduction of two or three trimethylsilyl groups to polydiphenylacetylenes was found to be suitable for preventing polymer chains from packing. Although poly(TMSP) and poly(*p*-TMSDP) have extremely high P_{O_2} value more than 1000 barrers, the P_{O_2} values tend to decrease with aging. We examined the effect of aging time on P_{O_2} in these new polymers (Fig. 2). As a result, the P_{O_2} values hardly changed for 90 days at 25 °C. Moreover, even at 50 °C, almost no decrease was observed. It can be concluded that the oxygen permeability of these polymers is fairly stable to aging and this behavior is much different from poly(TMSP) [3]. This is very convenient for practical use. In case of poly[*m*,*p*-$(TMS)_2$DP], since the structure is more symmetric than poly(*p*-TMSDP), the distribution of free volume and microvoids may be uniform in size. Therefore, it may have almost no large free volumes and microvoids. As a result, lower decrease in P_{O_2} during aging and high α may be attained. The reason why the aging effect was small in poly[$(TMS)_3Si_2$DP] is not clear at present. In summary, introduction of several trimethylsilyl groups was found to be effective for keeping high P_{O_2}.

Poly(TMSP) and poly(*p*-TMSDP) show ethanol permselectivity in ethanol/water pervaporation (PV) owing to its high diffusivity and hydrophobicity [19,20]. Poly[*m*,*p*-$(TMS)_2$DP] and poly[$(TMS)_3Si_2$DP] were also hydrophobic because their contact angles toward water were 84 and 83°, respectively, which were between that of poly(*p*-TMSDP) (83°) [19] and that of poly(TMSP) (90°) [20]. Therefore, these new polymers were also expected to have ethanol-permselectivity. In fact, α^{EtOH} of these polymers were 6.2 and 6.0, respectively, between poly(*p*-TMSDP) (3.1) [19] and poly(TMSP) (11.0) [20] when 0.7 wt% of aq. ethanol solution was supplied. In conclusion, the present polymers were more ethanol-permselective because of higher hydrophobicity than poly(*p*-TMSDP).

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