Synthesis and Gas Permeation Properties of Poly(diarylacetylene)s Having Substituted and Twisted Biphenyl Moieties

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ABSTRACT: Diarylacetylene monomers containing substituted biphenyl (**1a–f**) and anthryl (**1g**) groups were synthesized and then polymerized with $TaCl_5$-n-Bu_4Sn catalyst to produce the corresponding poly(diarylacetylene)s (**2a–g**). Polymers **2a–f** were soluble in common organic solvents such as cyclohexane, toluene, and chloroform. According to thermogravimetric analysis, the onset temperatures of weight loss of the polymers were over 400 °C in air, indicating considerably high thermal stability. Free-standing membranes **2a** and **2c–e** were prepared by the solution casting method. Desilylation of Si-containing membrane **2c** was carried out with trifluoroacetic acid to afford **3c**. All the polymer membranes, especially those having twisted biphenyl groups, exhibited high gas permeability; for example, their oxygen permeability (P_{O_2}) values ranged from 130 to 1400 barrers. Membrane **2d** having two chlorine atoms in the biphenyl group showed the highest gas permeability (P_{O_2} = 1400 barrers) among the present polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 861–868, 2010

KEYWORDS: gas permeation; membranes; polyacetylenes

INTRODUCTION Substituted polyacetylenes have attracted much attention among scientists because of a variety of functions, such as optical nonlinearity, photoconductivity, liquid crystallinity, helicity, and high gas permeability.[1–5] As an important class of separation membrane materials, substituted polyacetylenes are characterized by high gas permeability and high vapor/gas permselectivity, which are strikingly different from those of conventional glassy polymers.[6–10] The unique permeation properties of these polymers originate from their stiff main chain composed of alternating double bonds, bulky pendant groups, and low cohesive energy structure. One of them, poly(1-trimethylsilyl-1-propyne) [poly-(TMSP)] is the most permeable polymeric materials among all the existing polymers, and many studies have been reported concerning its permeation properties to date.[11–15] Since the discovery of poly(TMSP), considerable effort has been devoted to the synthesis and study on gas permeation properties of new substituted polyacetylenes aiming at the development of novel separation membrane materials.

Poly(diarylacetylene) derivatives are another important type of highly permeable polymers. For instance, poly[1-phenyl-2-(p-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] exhibits excellent thermal stability and high gas permeability; its oxygen permeability coefficient (P_{O_2}) is as large as 1500 barrers, and the onset temperature of weight loss is 420 °C,[16,17] which is clearly higher than that of poly(TMSP) (300 °C).[12]

Poly(diarylacetylene)s have the possibility that a variety of chemical structures can be accessed by the modification of the precursor monomers to tailor polymer properties desired for specific applications. Biphenyl-containing polymers have been extensively studied for applications as liquid crystalline materials, light-emitting diodes, proton exchange membranes, and gas separation membranes. Recent examples of such polymers include polyacetylenes,[18] poly(isothianaphthene methine),[19] poly(ether sulfone)s,[20] poly(2,7-carbazole)s,[21] poly(phenylenevinylene)s,[22] and polyimides.[23] It is known that incorporation of biphenyl groups contributes for improving the thermal stability of the polymers. The bulky biphenyl group is expected to affect the polymer chain packing and in turn the gas permeation properties of polymer membranes. However, only a few biphenyl-based poly(diarylacetylene)s have been reported so far. Although polymers **2h** and **2i** in Chart 1 have been synthesized, they are insoluble in any solvents.[24] Introduction of a very bulky *tert*-butyldimethylsiloxy group onto the biphenyl group of **2h** solubilizes the polymer (**2j**), but the gas permeability of the polymer is fairly low (e.g., P_{O_2} 73 barrers).[25] On the other hand, incorporation of moderately bulky and spherical groups, such as *tert*-butyl and trimethylsilyl, into poly(diarylacetylene)s has been recognized to not only improve solubility but also favor high gas permeability. Thus, we synthesized poly(diarylacetylene)s having biphenyl moieties substituted with *tert*-butyl,
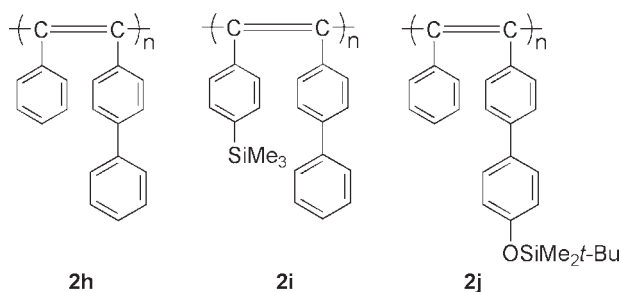
CHART 1 Previous examples of poly(diarylacetylene)s having biphenyl moieties.

methyl, and chlorine groups, because such polymers are expected to show good solubility due to the substituents, excellent thermal stability due to the poly(diarylacetylene) structure, and high gas permeability due to the more or less twisted structure of the biphenyl moiety.

In this study, we report the polymerization of diarylacetylene monomers containing a substituted biphenyl or an anthryl group (Scheme 1, **1a–g**). Free-standing membranes were fabricated from several resultant polymers, and desilylation of the membrane was accomplished with trifluoroacetic acid. Then, general properties and gas permeability of the obtained polymers were examined.

EXPERIMENTAL

General

Molecular weights of polymers were estimated by gel permeation chromatography on a Shimadzu PU/SPD-6A/UV-975 chromatograph equipped with polystyrene columns (Showa Denko Shodex K-805, K-806, and K-807) using $CHCl_3$ as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standard. NMR spectra were recorded on a JEOL EX-400 spectrometer. Melting points were measured with a Yanaco micromelting point apparatus. Elemental analysis of monomers was carried out at the Microanalytical Center of Kyoto University. Thermogravimetric analysis (TGA) was conducted in air with a Shimadzu TGA-50 thermal analyzer.

Materials

Tantalum(V) chloride ($TaCl_5$, Aldrich) was used without further purification. Tetra-n-butyltin (n-Bu_4Sn, Wako) was used after distillation. 4-(Trimethylsilyl)phenylacetylene was donated by NOF. Phenylacetylene (Aldrich), 4-bromo-4′-tert-butylbiphenyl (TCI), 1-bromo-4-iodobenzene, tert-butyl-3,5-dimethylbenzene, 1,4-di-tert-butylbenzene, 9-bromoanthracene, trifluoroacetic acid (TFA), and common solvents (Wako Pure Chemical) were used without further purification, except toluene, as a polymerization solvent, that was purified by the standard method. Diphenylacetylene-4-boronic acid and 4-(trimethylsilyl)diphenylacetylene-4′-boronic acid were prepared according to the literature procedures.[26] 5-tert-Butyl-2-iodo-1,3-dimethylbenzene and 2,5-di-tert-butyliodobenzene were prepared according to the literature methods.[27] Monomers were synthesized referring to the literature of Suzuki coupling[28,29] and ethynylation reactions[30,31] (Scheme 2).

1-Phenyl-2-(4′-tert-butyl-biphenyl-4-yl)acetylene (1a)

A 500-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 4-bromo-4′-tert-
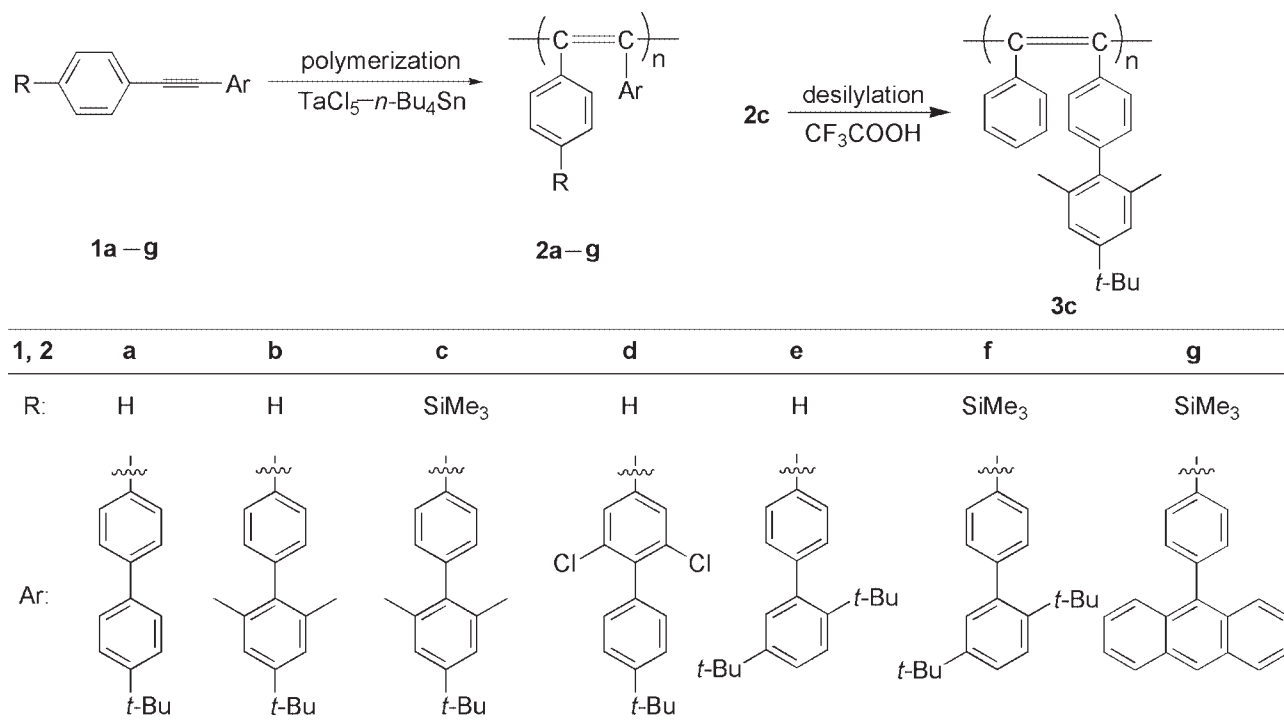
SCHEME 1 Synthesis of poly(diarylacetylene)s having biphenyl or anthryl moieties.
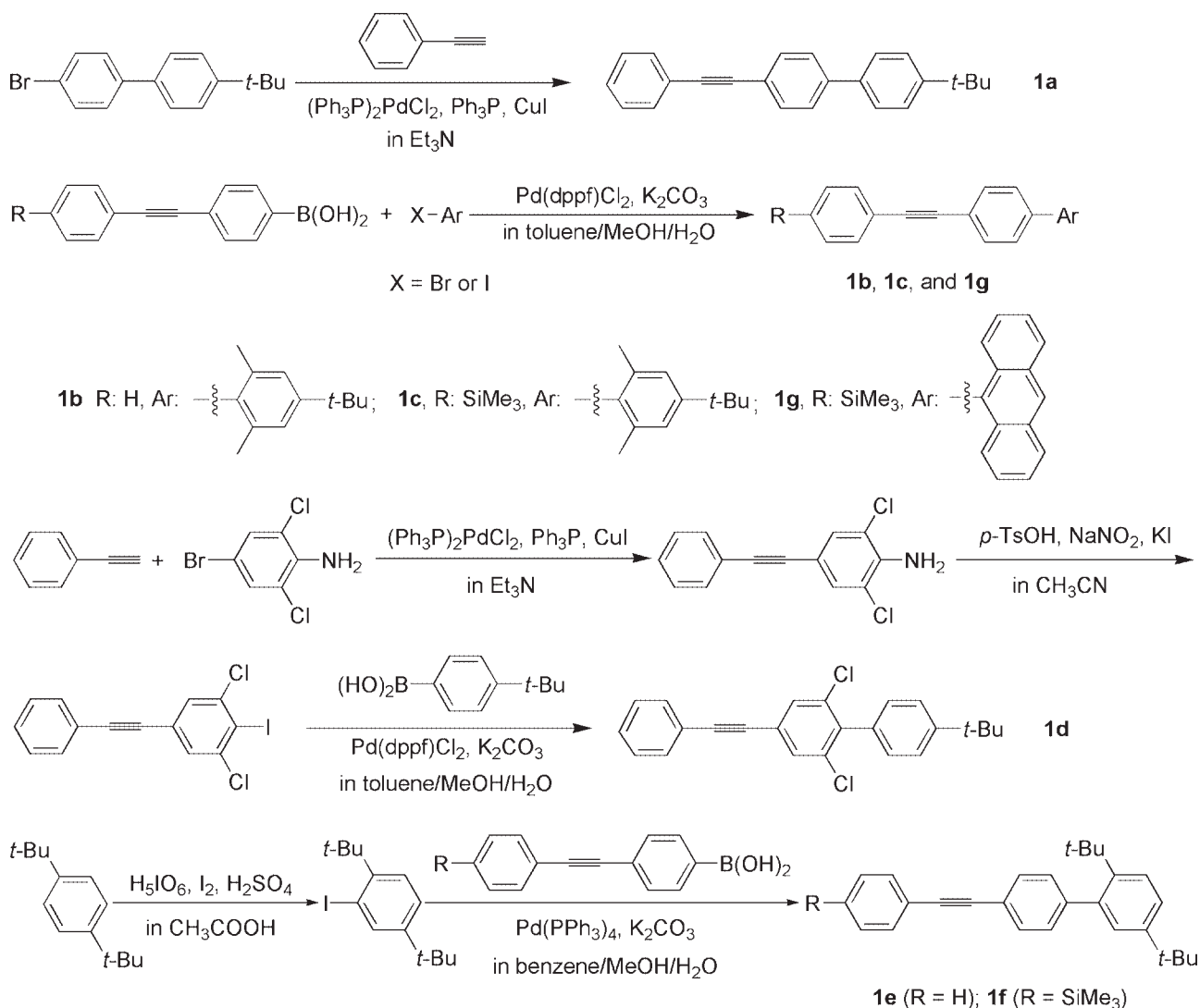
SCHEME 2 Synthesis of diarylacetylene monomers having biphenyl or anthryl moieties.

butylbiphenyl (5.0 g, 17 mmol), bis(triphenylphosphine)palladium dichloride (53 mg, 0.08 mmol), cuprous iodide (88 mg, 0.48 mmol), and triphenylphosphine (80 mg, 0.32 mmol) were placed in the flask and dissolved in triethylamine (150 mL) at room temperature. Then, a solution of phenylacetylene (2.0 g, 20 mmol) in triethylamine (20 mL) was added, and the reaction mixture was heated at reflux temperature for 5 h. Triethylamine in the reaction mixture was evaporated off, and then diethyl ether (200 mL) was added to the residual mass. Solvent-insoluble solid was filtered off, and the filtrate was washed with 1 M HCl aq. and then with water. The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a white solid (3.5 g, 65%).

^{1}H NMR (400 MHz, δ, CDCl$_3$): 7.59–7.23 (br, 13H, Ar), 1.35 (s, 9H, CCH_3). ^{13}C NMR (100 MHz, δ, CDCl$_3$): 150.2, 140.3, 136.9, 131.5, 131.1, 127.8, 127.7, 126.3, 126.1, 125.3, 122.8, 121.3, 89.5, 88.9, 34.1, 30.9. Anal. Calcd. for C$_{24}$H$_{22}$: C, 92.90; H, 7.10. Found: C, 92.53; H, 7.13.

1-Phenyl-2-(4′-tert-butyl-2′,6′-dimethylbiphenyl-4-yl)acetylene (1b)

A 100-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, diphenylacetylene-4-boronic acid (1.5 g, 6.8 mmol), 4-*tert*-butyl-2,6-dimethyliodobenzene (2.3 g, 8.1 mmol), 1,1′-bis(diphenylphosphino)ferrocene palladium(II) dichloride [Pd(dppf)Cl$_2$, 49 mg, 0.068 mmol], potassium carbonate (K$_2$CO$_3$, 1.9 g, 14 mmol), toluene (5 mL), methanol (5 mL), and H$_2$O (5 mL) were placed in the flask. Then, the reaction mixture was heated at 80 °C for 6 h. After that the solution was extracted with diethyl ether. The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to provide the desired product (1.5 g, 65%) as a white solid; mp 158.0–159.0 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.59–7.13 (m, 11H, Ar), 2.05 (s, 6H, CH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 150.0, 141.5, 138.3, 135.4, 131.6, 131.5, 129.5,

128.3, 128.2, 124.4, 123.4, 121.4, 89.4, 89.3, 34.3, 31.4, 21.1. Anal. Calcd. for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.44; H, 7.65.

1-(4-Timethylsilylphenyl)-2-(4′-tert-butyl-2′,6′-dimethylbi-phenyl-4-yl)acetylene (1c)

This monomer was prepared by the same method as for monomer **1b** using 4-(trimethylsilyl)diphenylacetylene-4′-boronic acid instead of diphenylacetylene-4-boronic acid to give a white solid; yield 70%, mp 155.5–157.0 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.59–7.13 (m, 10H, Ar), 2.05 (s, 6H, CH_3), 1.35 (s, 9H, C(CH_3)$_3$), 0.28 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 150.0, 141.5, 140.0, 138.3, 135.4, 133.2, 131.7, 130.7, 129.5, 124.4, 123.6, 121.4, 89.8, 89.5, 34.3, 31.4, 21.1, −1.2. Anal. Calcd. for $C_{29}H_{34}Si$: C, 84.82; H, 8.34. Found: C, 84.53; H, 8.37.

1-Phenyl-2-(2,6-dichloro-4′-tert-butylbiphenyl-4-yl)acety-lene (1d)

A 500-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 4-bromo-2,6-dichloroaniline (12 g, 50 mmol), bis(triphenylphosphine)palladium dichloride (351 mg, 0.50 mmol), cuprous iodide (571 mg, 3.0 mmol), and triphenylphosphine (525 mg, 2.0 mmol) were placed in the flask. Then, triethylamine (300 mL) and phenylacetylene (6.1 g, 60 mmol) were added, and the reaction mixture was heated at reflux temperature for 7 h. After that triethylamine in the reaction mixture was evaporated off, and then diethyl ether (200 mL) was added to the residual mass. Solvent-insoluble solid was filtered off, and the filtrate was washed with 1 M HCl aq. and then with water. The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 30/1) to give 1-phenyl-2-(4-amino-3,5-dichlorophenyl)acetylene as a red solid (6.2 g, 47%).

With reference to the reported method,[32] a 1-L three-necked flask containing 1-phenyl-2-(4-amino-3,5-dichlorophenyl)acetylene (6.2 g, 24 mmol), p-toluenesulfonic acid (14 g, 71 mmol), and acetonitrile (140 mL) was cooled to 10–15 °C. Then, a solution of NaNO$_2$ (3.3 g, 47 mmol) and KI (9.8 g, 59 mmol) in H$_2$O (15 mL) was added dropwise. To the reaction mixture were added NaHCO$_3$ (1 M; until pH = 9–10) and Na$_2$S$_2$O$_3$ (2 M, 350 mL). After extracting the organic compounds with diethyl ether and evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 1-phenyl-2-(3,5-dichloro-4-iodophenyl)acetylene as a white solid (4.6 g, 52%).

Monomer **1d** was prepared by the same method as for monomer **1b** using 4-tert-butylphenylboronic acid and 1-phenyl-2-(3,5-dichloro-4-iodophenyl)acetylene instead of diphenylacetylene-4-boronic acid and 4-tert-butyl-2,6-dimethyliodobenzene to give a white solid (2.1 g, 52%); mp 168.0–169.0 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.55–7.18 (m, 11H, Ar), 1.37 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 151.1, 139.5,

135.0, 133.3, 131.8, 130.7, 129.1, 128.9, 128.5, 125.1, 124.3, 122.4, 91.5, 86.7, 34.7, 31.3. Anal. Calcd. for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.31. Found: C, 76.11; H, 5.18.

1-Phenyl-2-(2′,5′-di-tert-butylbiphenyl-4-yl)acetylene (1e)

A 200-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, diphenylacetylene-4-boronic acid (3.1 g, 14 mmol), 2,5-di-tert-butyliodobenzene (4.0 g, 14 mmol), tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$,3.2 g, 3.6 mmol], K$_2$CO$_3$ (4.8 g, 35 mmol), benzene (48 mL), methanol (32 mL), and H$_2$O (10 mL) were placed in the flask. Then, the reaction mixture was heated at 80 °C for 5 h. After that the solution was extracted with diethyl ether. The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to provide the desired product (1.5 g, 30%) as a white solid; mp 174.6–175.6 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.56–6.97 (m, 12H, Ar), 1.30 (s, 9H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 147.5, 146.0, 144.6, 140.9, 131.6, 130.4, 130.2, 129.1, 128.3, 126.4, 126.3, 124.2, 123.4, 121.3, 89.4, 89.3, 36.1, 34.1, 32.7, 31.3. Anal. Calcd. for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.49; H, 8.54.

1-(4-Trimethylsilylphenyl)-2-(2′,5′-di-tert-butylbiphenyl-4-yl)acetylene (1f)

This monomer was prepared by the same method as for monomer **1e** using 4-(trimethylsilyl)diphenylacetylene-4′-boronic acid instead of diphenylacetylene-4-boronic acid to give a white solid; yield 30%, mp 205.0–206.0 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.53–6.97 (m, 10H, Ar), 1.30 (s, 9H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$), 0.28 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 147.5, 146.0, 144.6, 141.0, 140.9, 133.2, 130.7, 130.5, 130.2, 129.2, 126.4, 124.2, 123.6, 121.4, 89.8, 89.5, 36.1, 34.1, 32.7, 31.3, −1.2. Anal. Calcd. for $C_{31}H_{38}Si$: C, 84.87; H, 8.73. Found: C, 84.42; H, 8.72.

1-(4-Trimethylsilylphenyl)-2-(4-(9-anthryl)phenyl)acety-lene (1g)

This monomer was prepared by the same method as for monomer **1b** using 4-(trimethylsilyl)diphenylacetylene-4′-boronic acid and 9-bromoanthracene instead of diphenylacetylene-4-boronic acid and 4-tert-butyl-2,6-dimethyliodobenzene to give a white solid; yield 30%, mp 206.1–207.1 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.49–7.34 (m, 17H, Ar), 0.30 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 141.2, 139.0, 136.2, 133.3, 131.6, 131.4, 131.3, 130.7, 130.0, 128.4, 126.8, 126.6, 125.5, 125.1, 123.5, 122.5, 90.1, 89.7, −1.2. Anal. Calcd. for $C_{31}H_{26}Si$: C, 87.27; H, 6.14. Found: C, 87.43; H, 6.13.

Polymerization Procedure

Polymerizations were performed using toluene as a solvent in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations: [TaCl$_5$] = 20 mM, [n-Bu$_4$Sn] = 40 mM. The

TABLE 1 Polymerization of Monomers **1a–g** by TaCl$_5$-n-Bu$_4$Sn Catalyst[a]

Monomer	[M]$_0$ (M)	Polymer[b]		
		Yield (%)	$M_w \times 10^{-6}$[c]	M_w/M_n[c]
1a	0.20	58	2.5	1.6
1b	0.20	83	>6.0	–
1c	0.20	83	>6.0	–
1d	0.10	80	4.9	3.3
1e	0.20	74	1.6	3.0
1f	0.20	53	0.91	3.1
1g	0.10	82	–[d]	–[d]

[a] Polymerization in toluene at 80 °C for 24 h; [TaCl$_5$] = 20 mM, [n-Bu$_4$Sn] = 40 mM.
[b] Methanol-insoluble product.
[c] Determined by GPC, eluted with CHCl$_3$ (polystyrenes as standards).
[d] Insoluble in any solvents.

formed polymers were isolated by precipitation into a large amount of methanol and dried to constant weight. The polymer yields were determined by gravimetry.

Membrane Fabrication and Desilylation

The membranes (thickness ca. 80–120 μm) of polymers **2a–f** were fabricated by casting from toluene solution of the polymer (concentration ca. 0.50–1.0 wt %) onto a flat-bottomed Petri dish. Then, the dish was covered with a glass vessel to slow solvent evaporation (ca. 4–7 days). Actually, the membrane of **2b** was too brittle to be free standing. After a membrane was formed, the membrane was peeled off, and it was immersed in methanol for 24 h and dried to constant weight at room temperature for 24 h. With reference to the method described in the literature,[33] the desilylation reaction of polymer membrane **2c** was carried out using trifluoroacetic acid.

Measurement of Gas Permeability

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with a MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated to 0.3 Pa, whereas the upstream side was filled with a gas at about 1 atm (10^5 Pa), and the increase of pressure in a downstream receiving vessel was measured. The P-values were calculated from the slopes of time–pressure curves in the steady state where Fick's law held.

RESULTS AND DISCUSSION

Polymerization

As described in the Experimental section, diarylacetylene monomers containing substituted biphenyl (anthryl) groups were synthesized by applying the Suzuki and Sonogashira coupling reactions, namely palladium-catalyzed aromatization and ethynylation and other reactions (see Scheme 2). The synthetic reactions all proceeded in moderate to good yields,

and all the monomers were identified by ^{1}H and ^{13}C NMR spectroscopies besides elemental analysis.

The polymerization of diarylacetylene monomers **1a–g** was carried out in toluene by using TaCl$_5$-n-Bu$_4$Sn catalyst, whose results are summarized in Table 1. It is known that TaCl$_5$-n-Bu$_4$Sn is an effective catalyst for the polymerization of sterically crowded diphenylacetylene derivatives to provide polymers having high molecular weights,[1,34] which is essential for fabrication of free-standing membranes. In this study, the polymerization of monomer **1a**, which possesses the p-$tert$-butylbiphenyl group, gave a soluble polymer (**2a**) in a good yield (58%), whose weight-average molecular weight (M_w) was 2.5 × 10^6. Monomers **1b–d** having ortho methyl or chlorine substituents in addition to p-$tert$-butyl group on the biphenyl moiety also provided polymers in high yields (~80%), and their M_w values were as high as 4.9 × 10^6 and above. Monomers **1e** and **1f** with two $tert$-butyl groups on the terminal phenyl group of biphenyl afforded polymers with lower M_w (1.6 × 10^6 and 0.9 × 10^6, respectively) than those of **1a–d**, which is due to the steric hindrance of the bulky $tert$-butyl groups. On the other hand, polymer **2g** obtained from monomer **1g**, which has an anthryl substituent on a phenyl ring, was insoluble in any organic solvents. Thus, except **1g**, all the present monomers having substituted biphenyl groups successfully polymerized into high-molecular-weight soluble polymers in good yields.

Solubility and Thermal Stability of the Polymers

The solubility of polymer is an essential factor for membrane fabrication by solution casting. Hence, the solubility of the formed polymers in various solvents was examined (Table 2). According to our previous study, polymer **2h**, which has just planar groups but no flexible groups, is insoluble in any organic solvents. In contrast, all the present polymers having substituted biphenyl groups, **2a–f**, dissolved in common non-polar or low-polarity solvents such as toluene, chloroform, and THF. In particular, the good solubility of **2a**, which has just the p-$tert$-butylbiphenyl moiety, means that the p-$tert$-butyl group is effective enough to solubilize this type of polymers. The good solubility due to the incorporation of the p-$tert$-butyl group is attributable to two reasons; that is, one is that the p-$tert$-butyl group has sufficient surface to interact with a solvent and is locally quite mobile, namely its

TABLE 2 Solubility of Polymers **2a–g**[a]

	2a	2b	2c	2d	2e	2f	2g
Hexane	–	–	–	–	–	–	–
Cyclohexane	±	+	+	+	+	+	–
Toluene	+	+	+	+	+	+	–
CHCl$_3$	+	+	+	+	+	+	–
THF	+	+	+	+	+	+	–
Methanol	–	–	–	–	–	–	–
DMF	–	–	–	–	–	–	–
DMSO	–	–	–	–	–	–	–

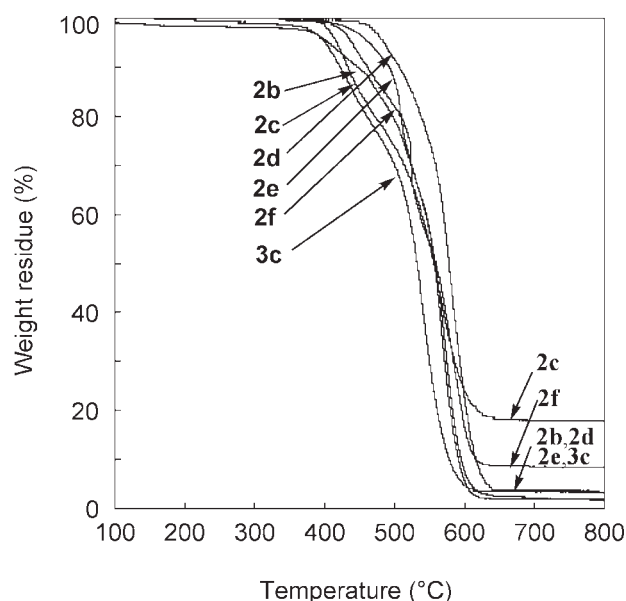[a] Symbols: +, soluble; ±, partly soluble; –, insoluble.

FIGURE 1 TGA curves of the polymers (in air, heating rate 10 °C/min).

methyl groups can easily rotate, and the other reason is that the introduction of the *p-tert*-butyl group gives rise to a large imbalance of the two side groups of the polymers. With respect to the latter reason, it is noted that poly(diphenylacetylene) and **2i**, whose two side groups are the same or similar in size, are insoluble.[10] All the present polymers were insoluble in highly polar solvents such as methanol, DMF, and DMSO.

The thermal stability of polymers was examined by TGA measured in air (Fig. 1). The onset temperatures of weight loss of all the polymers were above 400 °C, which are similar to that of thermally stable poly(PTMSDPA) (420 °C)[17] and much higher than those of aliphatic disubstituted acetylene polymers such as poly(TMSP) (330 °C).[12] The results of the TGA analysis indicate that the present polymers have excellent thermal stability, which seems to be due to the "jacket effect" of the bulky aryl groups that protect the double bonds in the main chain from air oxidation.[35]

Fabrication and Desilylation of Polymer Membranes

Free-standing membranes could be fabricated by casting polymers **2a** and **2c–f** from toluene solution, whereas the membranes of **2b** and **2g** could not be prepared because of their brittleness and insolubility, respectively. The formed membranes were uniform, yellow, and transparent. A membrane of polymer **3c**, which has the same structure as that of **2b**, was prepared by desilylation of **2c**. The desilylation reaction was carried out in a trifluoroacetic acid/H_2O (9:1 volume ratio) mixture at room temperature for 24 h. The completion of desilylation could be confirmed by TGA analysis; namely, when Si-containing polymer **2c** was heated above 700 °C, the weight residue composed of SiO_2 remained, whereas no residue was detected with the desilylated **3c** (Fig. 1).

Gas Permeation Properties of the Polymers

The gas permeability coefficients of membranes **2a** and **2c–e**, and desilylated membrane **3c** to various gases measured at 25 °C are listed in Table 3. The membrane of **2f** was mechanically too weak to measure the permeability. As seen from Table 3, **2a**, which has just the *p-tert*-butylbiphenyl group, showed the lowest gas permeability among the present polymers. Thus, the P_{O_2} value of **2a** remained 130 barrers. However, this value is still about twice as that of polymer **2j** containing flexible siloxy groups (P_{O_2} = 73 barrers). We have previously reported that the incorporation of flexible groups in the polymer accompanies a decrease in gas permeability; for example, the P_{O_2} value of poly(TMSDPA) is 1500 barrers, whereas that of poly[1-phenyl-2-*p*-(dimethyl-*tert*-butylsiloxy)phenylacetylene] is 160 barrers.[36]

The other present polymer membranes **2c–e** and **3c** exhibited higher gas permeability than **2a** did. The common feature of the former polymers is the more twisted structure of the biphenyl moiety due to the presence of ortho substituents. For instance, the P_{O_2} of **2c** was 760 barrers, which is very close to that of poly(dimethylsiloxane) (P_{O_2} = 780 barrers,[37] Fig. 2), a typical polymer well known to have the highest gas permeability among all the rubbery polymers. The P_{O_2} value of **3c** obtained by the desilylation of **2c** was 1100 barrers, which is even higher than that of its precursor **2c** and relatively close to that of poly(TMSDPA) (1500 barrers). This increase of gas permeability after desilylation can be explained by the idea that microvoids rather increase in number and/or size upon desilylation in the solid state for such stiff polymers.[24] Polymer **2e** also displayed fairly high oxygen permeability (P_{O_2} = 810 barrers). Among all the biphenyl-containing poly(diarylacetylene)s, polymer **2d** exhibited the highest permeability to various gases. Its P_{O_2} was as high as 1400 barrers, which is about the same as that of poly(TMSDPA) and very large among all the synthetic polymers, although smaller than that of poly(TMSP) (P_{O_2} ~ 10,000 barrers).

Based on the above experimental findings, the following discussions are possible about the gas permeability of the present polymers: (i) the twisted biphenyl structure[26,38] induced by methyl, chlorine, or *tert*-butyl groups at the ortho position(s) is favorable for the generation of excess free volume;

TABLE 3 Gas Permeability Coefficients (*P*) of Polymer Membranes

Polymer	P (Barrer[a])						
	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
2a	170	330	130	46	840	120	2.8
2c	660	1,500	760	360	3,300	990	2.1
3c	780	1,900	1,100	520	4,500	1,500	2.1
2d	920	2,400	1,400	740	6,100	2,100	1.9
2e	820	1,800	810	370	3,100	990	2.2

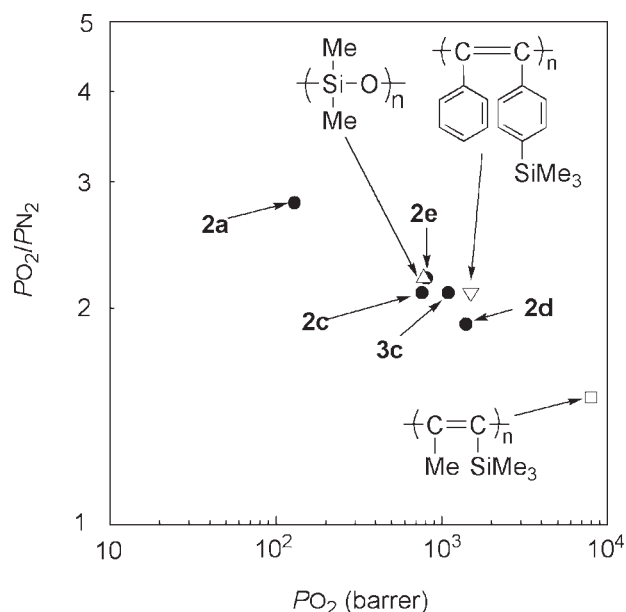[a] At 25 °C in the units of 1 × 10^{-10} cm³ (STP) cm/(cm² s cmHg) (= 1 barrer).

FIGURE 2 Oxygen permeability coefficient (PO_2) and PO_2/PN_2 of the present polymer membranes.

(ii) the large local mobility of *tert*-butyl groups promotes the diffusion of gases through the membrane;[39] and (iii) intersegmental packing of the polymer chain of **2d** is inhibited by the repulsion of highly electronegative chlorine atoms to produce a sparse structure in the polymer matrix. Similar and even obvious effects have been observed in previous studies of poly(diarylacetylene)s carrying indanyl/fluorenyl groups.[40–42]

The permeability of the membranes to other gases, such as He, H_2, N_2, CO_2, and CH_4, showed similar tendencies. The separation factors of oxygen against nitrogen (PO_2/PN_2) of the present polymers were in a range of 1.9–2.8. A tradeoff relationship is observed between permeability and permselectivity, namely, more permeable polymers are generally less permselective and vice versa.[43]

CONCLUSIONS

In this study, new poly(diarylacetylene)s having substituted biphenyl (**2a–f**) and anthracene (**2g**) moieties were synthesized by the polymerization of the corresponding monomers with $TaCl_5$-*n*-Bu_4Sn catalyst. The present polymers had high molecular weight and showed good solubility in common organic solvents except **2g**, and they had high thermal stability. Polymers **2a** and **2c–e** afforded free-standing membranes when casted from their toluene solution. Desilylation of a membrane of trimethylsilyl-containing polymer **2c** was achieved with trifluoroacetic acid to give membrane **3c**. All the present polymer membranes exhibited fairly high gas permeability. The PO_2 value of polymer **2c** was 760 barrers, which is almost the same as that of poly(dimethylsiloxane). The gas permeability of the desilylated polymer **3c** became larger than that of **2c**. Polymer **2d** bearing chlorine atoms in the biphenyl moieties showed the highest PO_2 value of 1400

barrers among the present polymers, which is about the same as that of poly(TMSDPA). The results of this study indicate that the incorporation of methyl/chlorine groups in the biphenyl moieties clearly enhances the gas permeability of the present polymers.

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