Synthesis and Properties of Membranes of Poly(diphenylacetylenes) Having Fluorines and Hydroxyl Groups

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ABSTRACT: Diphenylacetylenes possessing fluorine atom(s) and a siloxy group (**1c**−**i**) were polymerized with $TaCl_5$−*n*-Bu_4Sn. Monomers **1c**−**f** having a siloxy group at the para position of a phenyl ring produced high molecular weight polymers (**2c**−**f**) in good yields. These polymers afforded tough free-standing membranes by casting their toluene solution. Desilylation of the polymer membranes was carried out with trifluoroacetic acid to give membranes of poly(diphenylacetylenes) having fluorine atoms and hydroxyl groups (**3c**−**f**). Polymers **2c**−**f** were soluble in various organic solvents such as toluene, $CHCl_3$, and THF, while polymers **3c**−**f** were insoluble in these solvents. All the polymers **2c**−**f** and **3c**−**f** exhibited high thermal stability. The gas permeability of most membranes in the present study (**2d**−**f** and **3c**−**f**) were higher than those of the corresponding polymers without fluorine atoms (**2a** and **3a**), indicating that incorporation of fluorine atoms into the polymers enhances gas permeability. The P_{CO_2}/P_{N_2} permselectivity ratios of polymers **3c**−**f** were as large as 36−48, and the points of **3c**−**f** in the P_{CO_2} vs P_{CO_2}/P_{N_2} plot were located above Robeson's upper bound.

Introduction

Polyacetylenes with bulky substituents show high thermal stability, good solubility in organic solvents, film-forming ability, and high gas permeability unlike the unsubstituted polyacetylene.[1] High gas permeability of polymers is important from the viewpoint of gas separation technology, and substituted polyacetylenes have attracted much attention as gas separation membranes applicable to practical use.[2] Among substituted polyacetylenes, those from disubstituted monomers with spherical substituents exhibit particularly high gas permeability.[3] For instance, the oxygen permeability coefficient (P_{O_2}) of poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [PTMSDPA] is as large as 1100 barrers.[4] Further, PTMSDPA exhibits good solubility and high thermal stability [the onset temperature of weight loss (T_0) in air is 450 °C].[4]

Membranes of solvent-insoluble polymers like poly(diphenylacetylene) cannot be obtained directly by solution casting.[5] However, we have succeeded in the fabrication of membranes of solvent-insoluble poly(diphenylacetylene) through the desilylation of membranes of PTMSDPA.[6] The desilylation technique enables the preparation of various poly(diarylacetylene) membranes.[7] In addition, being insoluble, their membranes can be applied to the separation of organic liquid mixtures.[8] In a similar way, the desilylation enables the synthesis of poly(diphenylacetylene) having hydroxyl groups at the para or meta position, which was not obtained before because the Ta catalyst is deactivated by protic groups such as the hydroxyl group in the monomer (Scheme 1).[9] Poly(diphenylacetylenes) bearing hydroxyl groups show very high CO_2 permselectivity. However, their gas permeabilities are generally low compared to other poly(diphenylacetylene) derivatives. The improvement of CO_2 permeability without decreasing permselectivity is an important subject to develop novel CO_2 separation membrane materials.

Incorporation of fluorine-containing groups into polymer is one method for increasing gas permeability. In fact, polyacetylene derivatives[10] as well as polysulfone,[11] polycarbonate,[12] polynorbornene,[13] and polyphosphazene[14] have been reported to show higher gas permeability when fluorine atoms are introduced into them. Hence, the synthesis of poly(diphenylacetylenes) having both fluorines and hydroxyl groups is of great interest from the viewpoint of development of novel gas separation membrane materials.

The present study deals with the polymerization and polymer properties of several diphenylacetylene monomers (**1c**−**i**), which have a siloxy group at one phenyl ring and fluorine atoms at the other phenyl ring (Chart 1). We prepared free-standing membranes of resulting polymers (**2c**−**f**) and corresponding desilylated polymers (**3c**−**f**) and elucidated their general properties and gas permeability.

Results and Discussion

Polymerization. The polymerization of monomers **1c**−**i** having both fluorine(s) and a siloxy group was carried out in toluene with $TaCl_5$−*n*-Bu_4Sn (Table 1). The polymerization of monomer **1c** provided a polymer (**2c**) in a good yield, whose weight-average molecular weight (M_w) was over 6×10^6 (run 1). The polymerization of monomers **1d**−**f** also gave high molecular weight polymers (**2d**−**f**) in good yields ($M_w \geq 2.3 \times 10^6$, yield = 64−78%, runs 2−4). The polymerization of a monomer with three fluorine atoms at para and meta positions of one phenyl ring was also attempted, but the formed polymer was insoluble in any solvent such as toluene, $CHCl_3$, and tetrahydrofuran (THF). Monomer **1g**, which has a trifluoromethyl group, did not polymerize under the same conditions as those of **1d**−**f** and also at a 5-fold concentration (runs 5 and 6). This seems to be due to the stronger electron-withdrawing force of the CF_3 group compared to that of the F group. Though monomers **1h** and **1i**, which have a siloxy group at the meta position of a phenyl ring, also yielded polymers **2h** and **2i**; both yields and M_w values of the polymers were relatively low (runs

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Scheme 1. Synthesis of Poly(diphenylacetylenes) Having Hydroxyl Groups

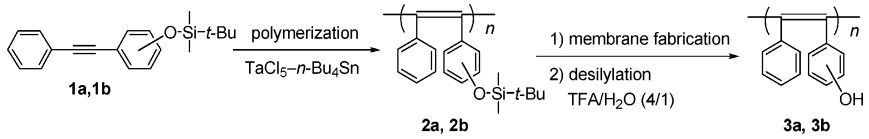


Chart 1. Diphenylacetylene Monomers Bearing Fluorine(s) and/or a Siloxy Group

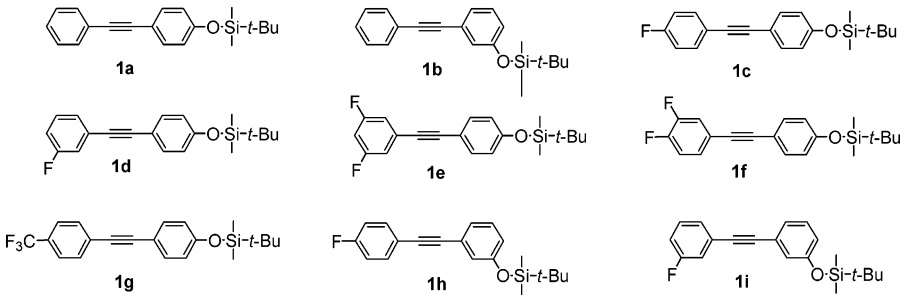


Table 1. Polymerization of 1c−i with $TaCl_5$−*n*-Bu_4Sn[a]

			polymer[b]		
run	monomer	$[M]_0$ (M)	yield (%)	$M_w/10^4$ [c]	M_w/M_n[c]
1	**1c**	0.050	70	>600	
2	**1d**	0.10	71	230	3.0
3	**1e**	0.10	78	>600	
4	**1f**	0.10	64	500	4.8
5	**1g**	0.10	0		
6	**1g**	0.50	0		
7	**1h**	0.10	33	38	4.4
8	**1h**	0.50	20	48	3.8
9	**1i**	0.10	17	45	6.0
10	**1i**	0.50	20	55	4.8

[a] In toluene at 80 °C for 24 h; $[TaCl_5] = 20$ mM, [*n*-Bu_4Sn] = 40 mM. [b] Methanol-insoluble product. [c] Measured by GPC.

7 and 9). The polymer yields and molecular weights did not increase satisfactorily even at a higher monomer concentration of 0.50 M (runs 8 and 10). This may be due to the steric effect of the bulky substituent at the meta position of a phenyl ring. A similar low polymerizability has been reported with several poly(diphenylacetylenes) having bulky silyl groups.[15] This finding suggests that the steric effects in these monomers considerably affect their polymerizability.

Desilylation of Polymer Membranes. The high molecular weight of polymer is an important factor for the fabrication of a free-standing membrane. The M_w values of polymers **2c**−**f** were more than 2 million, and consequently we were able to obtain membranes by casting them from toluene solution. In contrast, the membranes of polymers **2h** and **2i** could not be prepared because the molecular weights of polymers **2h** and **2i** were relatively low.

Desilylation of the membranes of **2c**−**f** was carried out by immersing them in a mixture of TFA/water (4/1 volume ratio). In all the membranes (**2c**−**f**), the silyl group was completely removed with TFA to provide the membranes of hydroxyl-containing polymers **3c**−**f**. The completion of desilylation was confirmed by IR spectroscopy.

Solubility and Thermal Stability of Polymers. The solubility properties of polymers **2c**−**f** and **3c**−**f** are summarized in Table 2. Polymers **2c**−**f** having both fluorine atoms and siloxy groups were soluble in nonpolar solvents such as cyclohexane, toluene, $CHCl_3$, and THF, similarly to polymers **2a** and **2b**.[9a] In contrast, polymers **3c**−**f** having both fluorine atoms and hydroxyl groups were insoluble in nonpolar solvents, while partly soluble in methanol and ethanol. This variation in solubility before and after desilylation should come from the different natures of siloxy and hydroxyl groups. The solubility of polymers **3c**−**f** was similar to that of polymer **3a**, which has no fluorine atoms.

Table 2. Solubility of the Polymers[a]

	2c	**2d**	**2e**	**2f**	**3c**	**3d**	**3e**	**3f**
hexane	±	+	+	+	−	−	−	−
cyclohexane	+	+	+	+	−	−	−	−
toluene	+	+	+	+	−	−	−	−
$CHCl_3$	+	+	+	+	−	−	−	−
THF	+	+	+	+	−	−	−	−
methanol	−	−	−	−	±	±	±	±
DMF	−	−	−	−	−	−	−	−
DMSO	−	−	−	−	−	−	−	−

[a] +: soluble; ±: partly soluble; −: insoluble.

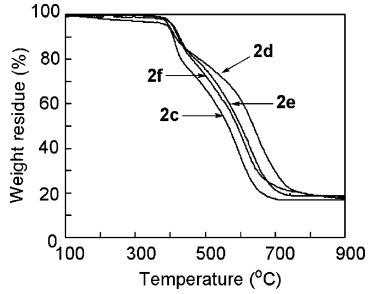


Figure 1. TGA curves of **2c**−**f** (in air, heating rate 10 °C min^{-1}).

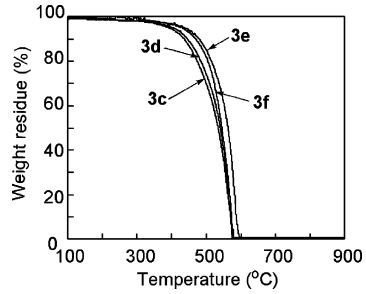


Figure 2. TGA curves of **3c**−**f** (in air, heating rate 10 °C min^{-1}).

The thermal stability of polymers **2c**−**f** and **3c**−**f** was examined with TGA in air (Figures 1 and 2). The onset temperatures of weight loss (T_0) of polymers **2c**−**f** were ∼360 °C, showing their high thermal stability. The T_0 value of polymer **2a**, which has no fluorine atoms, is also 360 °C.[9a] Thus, introduction of fluorine atoms hardly affects the thermal stability of these polymers. When polymers **2c**−**f** were heated to 800 °C in air, SiO_2 remained as the residue, whose amounts agreed with the expected values. All the T_0 values of desilylated

Table 3. Density and FFV of the Polymer Membranes

	2		3	
polymer	density[a] (g/cm^3)	FFV[b]	density[a] (g/cm^3)	FFV[b]
a	0.99	0.177	1.22	0.081
c	1.03	0.176	1.27	0.099
d	1.02	0.187	1.26	0.105
e	1.05	0.195	1.34	0.095
f	1.06	0.187	1.33	0.104

[a] Determined by hydrostatic weighing. [b] FFV: fractional free volume. Calculated from membrane density.

polymers **3c**−**f** were ∼320 °C, which are also the same as that of polymer **3a** (T_0 = 320 °C). The practically identical TGA curves of polymers in Figure 2 also indicate that the thermal stability of these polymers is independent of the presence of fluorine atoms.

Density and FFV of Polymer Membranes. Table 3 lists the densities and FFVs of the polymer membranes. The FFV value of membrane of **2c** was 0.176, which is almost the same as that of **2a** (FFV = 0.177).[9a] The FFVs of membranes of **2d**−**f** were 0.187−0.195, being larger than that of **2a**. Desilylation led to the shrinkage of the membranes, which resulted in the increase of densities. Accordingly, the FFVs of membranes of **3c**−**f** were smaller than those of membranes before desilylation. This can be accounted for by intermolecular hydrogen bonding. It is noteworthy that membranes of **3c**−**f** possessing both fluorine atoms and hydroxyl groups exhibited higher FFVs than the membrane of **3a** did. This can be explained by the idea that the chain packing is inhibited by repulsive force between fluorine atoms that have high electronegativity.

Gas Permeability. Table 4 summarizes the gas permeability coefficients of the polymer membranes. The oxygen permeability coefficient (P_{O_2}) of **2c** having a fluorine atom at the para position of the phenyl ring was 100 barrers, which was somewhat smaller than that of **2a** (P_{O_2} = 160 barrers). However, the P_{O_2} of **2d** with a fluorine atom at the meta position of the phenyl ring was as high as 340 barrers. Polymer **2e** possessing two fluorine atoms at meta positions of one phenyl ring displayed the highest oxygen permeability among the present polymers, whose P_{O_2} value was 590 barrers. This value was ∼4 times as large as that of **2a**. Similar tendencies were observed with other gases; i.e., polymer **2e** was more permeable to gases than were other polymers. Polymer **2f**, which has two fluorines at meta and para positions, also showed high oxygen permeability, whose P_{O_2} was 370 barrers.

The gas permeability of the membranes of desilylated polymers **3c**−**f** significantly decreased compared to those of siloxy-containing polymers **2c**−**f**. For instance, the P_{O_2} value of **3e** was no more than 23 barrers, while that of **2e** was 590 barrers. This behavior should stem from the large decrease of FFV upon desilylation. Interestingly, polymers **3c**−**f** having fluorine atoms showed higher gas permeability than polymer **3a** did.

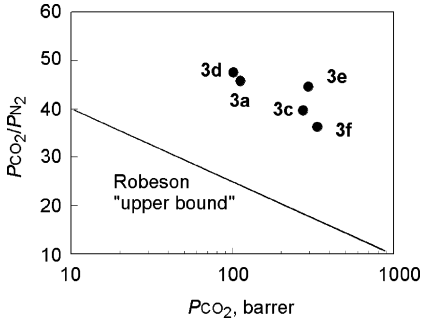


Figure 3. Plot of permselectivity vs permeability for the CO_2/N_2 gas pair.

The separation factors of oxygen against nitrogen (P_{O_2}/P_{N_2}) in polymers **2c**−**f** and **3c**−**f** were 2.1−2.6 and 2.7−5.7, respectively, which are similar to each other group. In contrast, the separation factors of CO_2 against N_2 (P_{CO_2}/P_{N_2}) in polymers **3c**−**f** were 36−48 and appreciably larger than 11−13 of polymers **2c**−**f**, indicating that the separation performance for CO_2 remarkably improves upon desilylation. Such improvement of separation performance is also observed in the case of polymers **2a** and **3a**. For instance, the P_{CO_2}/P_{N_2} value of polymer **3a** is as large as 46, which is close to those of the present polymers. However, the CO_2 permeability of polymers **3e** and **3f** is larger than that of polymer **3a**, and hence they are more promising as CO_2 separation membranes. The separation factors of CO_2 against CH_4 (P_{CO_2}/P_{CH_4}) in polymers **3c**−**f** were also fairly large and 18−32. It was found that introduction of fluorine atoms improved CO_2 permeability without decreasing very much the separation performance for CO_2. It is noteworthy that the points of **3c**−**f** as well as of **3a** in the CO_2 vs CO_2/N_2 plot are located above Robeson's upper bound[16] (Figure 3).

Diffusivity and Solubility of Gases. The gas permeability of polymers can be divided into two factors, namely, the diffusion and solution terms theoretically in the case of rubbery polymers and approximately with glassy polymers.[17] To inspect the gas permeability of the present polymers in more detail, gas diffusion coefficients (D) and gas solubility coefficients (S) were calculated. Tables 5 and 6 list the D and S values, respectively, of **2c**−**f** and **3c**−**f** for N_2, CO_2, and CH_4. In general, the D value decreases with increasing critical volume of gases in any polymer, while the S value increases with increasing critical temperature of gases. The polymers in the present study also showed this tendency; e.g., the diffusivity of CO_2 was somewhat lower than that of N_2, while the solubility of CO_2 was much higher than that of N_2.

Table 4. Gas Permeability Coefficients (P) of the Polymer Membranes[a]

	P (barrer[b])								
polymer[c]	He	H_2	CO_2	O_2	N_2	CH_4	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
2a	170	330	810	160	50	160	3.2	16.2	5.1
2c	140	230	590	100	46	110	2.2	12.8	5.4
2d	350	650	1680	340	130	340	2.6	12.9	4.9
2e	610	1100	2950	590	280	650	2.1	10.5	4.5
2f	390	700	2100	370	170	410	2.2	12.4	5.1
3a	38	56	110	8.0	2.4	2.3	3.3	45.8	47.8
3c	52	110	270	25	6.8	15	3.7	39.7	18.0
3d	44	63	100	12	2.1	3.3	5.7	47.6	30.3
3e	71	110	290	23	6.5	9.2	3.5	44.6	31.5
3f	71	100	330	25	9.1	12	2.7	36.3	27.5

[a] P values measured at 25 °C. [b] 1 barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}. [c] Polymers **2a** and **2c**−**f** were conditioned with methanol before measurements, while polymers **3a** and **3c**−**f** were conditioned with hexane.

Table 5. Gas Diffusion Coefficients[a] (*D*) of the Polymer Membranes

	10^7 *D* (cm^2 s^{-1})					
	polymers **2**			polymers **3**		
	N_2	CO_2	CH_4	N_2	CO_2	CH_4
critical vol (cm^3/mol)	89.8	93.9	99.2	89.8	93.9	99.2
a	32	25	15	1.3	0.89	0.45
c	11	7.0	5.8	3.5	1.7	0.75
d	30	27	15	2.4	1.5	0.60
e	40	39	17	2.0	1.5	0.62
f	32	28	18	2.5	2.3	1.1

[a] Determined by the "time lag" method at 25 °C.

Table 6. Gas Solubility Coefficients[a] (*S*) of the Polymer Membranes

	10^3*S* (cm^3 (STP) cm^{-3} $cmHg^{-1}$)					
	polymers **2**			polymers **3**		
	N_2	CH_4	CO_2	N_2	CH_4	CO_2
critical temp (K)	126.2	190.4	304.1	126.2	190.4	304.1
a	1.6	11	32	1.8	5.1	124
c	4.2	19	84	1.9	20	159
d	4.3	23	62	0.88	5.5	67
e	7.0	38	76	3.3	15	193
f	5.3	23	75	3.6	11	143

[a] Calculated by using quotients, *P*/*D*.

As shown in Table 5, the *D* value of every gas significantly decreased after desilylation. For instance, the *D* value of CO_2 in the units of 10^{-7} cm^2 s^{-1} changed from 39 to 1.5 upon desilylation of **2e**. The decrease of diffusivity can be accounted for by both the decrease of FFV and the loss of local mobility[18] of silyl groups upon desilylation. The *D* values of polymers **3c**−**f** were somewhat larger than that of **3a**, indicating that incorporation of fluorine atoms leads to the increase in diffusivity.

Quite interestingly, the *S* values of N_2 and CH_4 tend to decrease upon desilylation of any of **2a** and **2c**−**f**, while the *S* of CO_2 increases. These results can be explained by the idea that the CO_2 molecule strongly interacts with the hydroxyl group of the polymers. The *S* values of polymers **3c**, **3e**, and **3f** having fluorine atoms were somewhat larger than that of **3a**.

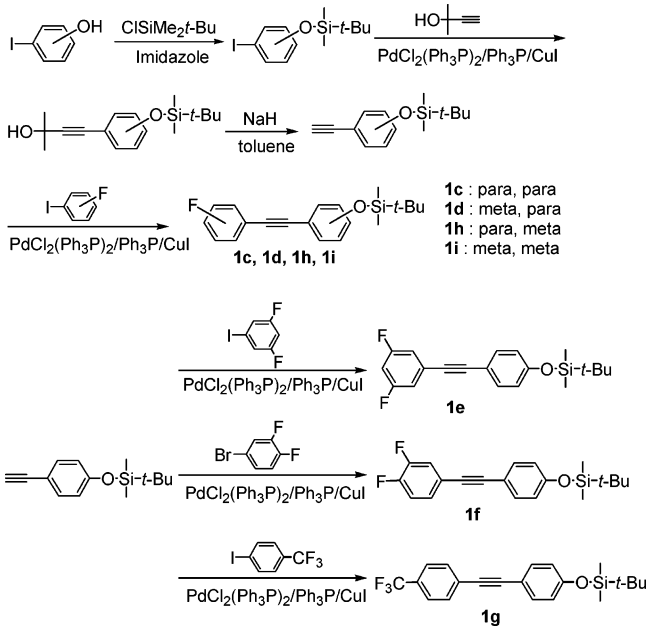
Conclusions

We synthesized novel poly(diphenylacetylenes) having both fluorine atoms and siloxy groups (**2c**−**f**, **2h**, and **2i**) by the polymerization of the corresponding monomers (**1c**−**f**, **1h**, and **1i**) with $TaCl_5$−*n*-Bu_4Sn and then prepared poly(diphenylacetylenes) having both fluorine atoms and hydroxyl groups (**3c**−**f**) by desilylation of the precursor polymers (**2c**−**f**) using a mixture of TFA/H_2O. The solubility and thermal stability of polymers **2c**−**f** and **3c**−**f** were similar to those of **2a** and **3a**, respectively. The membranes of polymers **3c**−**f** exhibited excellent separation performance for CO_2 against nitrogen and methane like polymer **3a**, which is mainly explained by the increase of solubility of CO_2 in the polymer membranes. The P_{CO_2} of polymer **3e** was 290 barrers and 2.6 times as large as that of **3a**. Thus, poly(diphenylacetylenes) bearing both fluorine atoms and hydroxyl groups proved to show moderate CO_2 permeability and high CO_2 permselectivity, and hence they are promising candidates of CO_2 separation membranes.

Experimental Section

General. The molecular weights of polymers were estimated by gel permeation chromatography ($CHCl_3$ as eluent, polystyrene calibration). IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. NMR spectra were observed on a JEOL EX-400 spectrometer. Elemental analyses of monomers were performed at the Microanalytical Center of Kyoto University. Thermogravimetric analyses (TGA) were conducted in air with a Parkin-Elmer TGA7 thermal analyzer. Gas permeability coefficients of polymers were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

Scheme 2. Synthesis of Fluorine- and Siloxy-Containing Diphenylacetylene Monomers



$TaCl_5$ was commercially obtained (Strem) and used without further purification. *n*-Bu_4Sn (Wako, Japan) was used after distillation. *p*-Iodophenol, *m*-iodophenol, 4-(4-fluorophenylethynyl)-phenol, and common solvents (Wako, Japan) were employed without further purification. Phenylacetylene and *tert*-butyldimethylchlorosilane were purchased from Aldrich. *p*-(*tert*-Butyldimethylsiloxy)phenylacetylene was prepared according to a literature procedure.[19] Monomers were synthesized according to Scheme 2, referring to the literature for ethynylation[20] and silylation.[21] Their synthesis and analytical data are detailed below.

1-(4-Fluoro)phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene (1c). A 500 mL three-necked flask was equipped with a dropping funnel and a magnetic stirring bar and was flushed with nitrogen. 4-(4-Fluorophenylethynyl)phenol (10 g, 47 mmol), imidazole (9.4 g, 140 mmol), and *N*,*N*-dimethylformamide (100 mL) were placed in the flask. Then, a solution of *tert*-butyldimethylchlorosilane (10 g, 66 mmol) in *N*,*N*-dimethylformamide (80 mL) was added dropwise at 0 °C for 30 min, and then the reaction mixture was stirred for an additional 10 h at room temperature. After ether (100 mL) was added, the solution was washed with water and then with 1 N NaOH(aq). The ethereal solution was dried over anhydrous sodium sulfate and then concentrated at reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane) to provide the desired product (new compound; yield 5.7 g, 74%) as a white solid; mp 73.0−73.8 °C. IR (KBr): 2959, 1604, 1264, 1157, 915, 829, 781, 547 cm^{-1}. ^1H NMR ($CDCl_3$): 7.47 (dd, J = 8.8 Hz, J = 5.2 Hz, 2H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.02 (vt, J = 8.8 Hz, 2H, Ar), 6.81 (d, J = 8.8 Hz, 2H, Ar), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): 162.1 (d, J = 249 Hz, 1C, Ar), 155.8 (1C, Ar), 133.1 (d, J = 8.2 Hz, 2C, Ar), 132.8 (2C, Ar), 120.1 (2C, Ar), 119.5 (d, J = 3.3 Hz, 1C Ar), 115.6 (1C, Ar), 115.4 (d, J = 22 Hz, 2C, Ar), 88.9 (1C, C≡C), 87.0 (1C, C≡C), 25.7 (3C, CCH_3), 18.2 (1C, CCH_3), −4.4 (2C, $SiCH_3$). Anal. Calcd for $C_{20}H_{23}FOSi$: C, 73.6; H, 7.1. Found: C, 73.3; H, 7.1.

1-(3-Fluoro)phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene (1d). A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed

with dry nitrogen. *p*-(*tert*-Butyldimethylsiloxy)phenylacetylene (10 g, 43 mmol), *m*-fluoroiodobenzene (11.5 g, 52 mmol), bis-(triphenylphosphine)palladium dichloride (0.30 g, 0.43 mmol), triphenylphosphine (0.45 g, 1.7 mmol), cuprous iodide (0.49 g, 2.6 mmol), and triethylamine (200 mL) were placed in the flask. The reaction mixture was stirred at room temperature for 2 h. After the triethylamine in the reaction mixture was evaporated, ether (150 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate followed by rotary evaporation of ether. Purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product (new compound; yield 8.5 g, 61%) as a colorless liquid. IR (KBr): 2957, 1510, 1263, 912, 841, 783, 713, 681 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40 (d, $J = 8.8$ Hz, 2H, Ar), 7.31−7.24 (m, 2H, Ar), 7.18 (d, $J = 9.6$ Hz, 1H, Ar), 7.08−6.97 (m, 1H, Ar), 6.81 (d, $J = 8.8$ Hz, 2H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 162.3 (d, $J = 245$ Hz, 1C, Ar), 156.2 (1C, Ar), 133.1 (2C, Ar), 129.8 (d, $J = 9.5$ Hz, 1C, Ar), 127.3 (1C, Ar), 125.4 (d, $J = 9.5$ Hz, 1C, Ar), 120.2 (2C, Ar), 118.1 (d, $J = 22$ Hz, 1C, Ar), 115.4 (1C, Ar), 115.1 (d, $J = 22$ Hz, 1C, Ar), 90.3 (1C, C≡C), 87.0 (1C, C≡C), 25.7 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{20}H_{23}FOSi$: C, 73.6; H, 7.1. Found: C, 73.4; H, 7.0.

1-(3,5-Difluoro)phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene (1e). This monomer was prepared by the same method as for **1d** using 1-bromo-3,5-difluorobenzene instead of *m*-fluoroiodobenzene. Yield 70%; colorless liquid. IR (KBr): 2957, 1510, 1271, 1122, 989, 912, 839, 808, 783, 689, 671 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39 (d, $J = 8.8$ Hz, 2H, Ar), 7.00 (d, $J = 8.8$ Hz, 2H, Ar), 6.81 (d, $J = 8.8$ Hz, 2H, Ar), 6.76 (t, $J = 8.8$ Hz, 1H, Ar), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 162.6 (dd, $J = 248$ Hz, $J = 13$ Hz, 2C, Ar), 156.5 (1C, Ar), 133.2 (2C, Ar), 126.3 (t, $J = 12$ Hz, 1C, Ar), 120.3 (2C, Ar), 114.9 (1C, Ar), 114.3 (dd, $J = 19$ Hz, $J = 7.4$ Hz, 2C, Ar), 103.9 (t, $J = 25$ Hz, 1C, Ar), 91.5 (1C, C≡C), 86.1 (1C, C≡C), 25.6 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{20}H_{22}F_2OSi$: C, 69.7; H, 6.4. Found: C, 69.8; H, 6.5.

1-(3,4-Difluoro)phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene (1f). This monomer was prepared by the same method as for **1d** using 3,5-difluoroiodobenzene instead of *m*-fluoroiodobenzene. Yield 71%, white solid; mp 33.9−34.8 °C. IR (KBr): 2954, 1518, 1263, 1120, 953, 906, 837, 812, 781, 711, 602 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38 (d, $J = 8.8$ Hz, 2H, Ar), 7.29 (vt, $J = 10$ Hz, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H, Ar), 7.24−7.18 (m, 1H, Ar), 7.11 (dd, $J = 18.4$ Hz, $J = 8.4$ Hz, 1H, Ar), 6.81 (d, $J = 8.8$ Hz, 2H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3 (1C, Ar), 150.2 (dd, $J = 250$ Hz, $J = 12$ Hz, 1C, Ar), 149.9 (dd, $J = 250$ Hz, $J = 12$ Hz, 1C, Ar), 133.0 (2C, Ar), 127.9 (dd, $J = 5.8$ Hz, $J = 3.3$ Hz, 1C, Ar), 120.4 (dd, $J = 8.2$ Hz, $J = 4.1$ Hz, 1C, Ar), 120.3 (2C, Ar), 120.2 (d, $J = 18$ Hz, 1C, Ar), 117.3 (d, $J = 18$ Hz, 1C, Ar), 115.3 (1C, Ar), 89.9 (1C, C≡C), 86.1 (1C, C≡C), 25.7 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{20}H_{22}F_2OSi$: C, 69.7; H, 6.4. Found: C, 69.5; H, 6.6.

1-(4-Trifluoromethyl)phenyl-2-(4-*tert*-butyldimethylsiloxy)-phenylacetylene (1g). This monomer was prepared by the same method as for **1d** using 4-iodobenzotrifluoride instead of *m*-fluoroiodobenzene. Yield 85%, colorless liquid. IR (KBr): 2959, 1520, 1263, 1134, 916, 841, 806, 781, 679, 598 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.59 (brs, 4H, Ar), 7.42 (d, $J = 8.4$ Hz, 2H, Ar), 6.82 (d, $J = 8.4$ Hz, 2H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 156.5 (1C, Ar), 133.2 (2C, Ar), 131.6 (2C, Ar), 129.5 (q, $J = 33$ Hz, 1C, Ar), 127.5 (1C, Ar), 125.1 (q, $J = 3.3$ Hz, 2C, Ar), 124.0 (q, $J = 272$ Hz, 1C, Ar), 120.3 (2C, Ar), 115.3 (1C, Ar), 92.0 (1C, C≡C), 86.9 (1C, C≡C), 25.6 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{21}H_{23}F_3OSi$: C, 67.0; H, 6.2. Found: C, 67.1; H, 6.2.

1-(4-Fluoro)phenyl-2-(3-*tert*-butyldimethylsiloxy)phenylacetylene (1h). This monomer was prepared by the same method as for **1d** using *m*-(*tert*-butyldimethylsiloxy)phenylacetylene and *p*-fluoroiodobenzene instead of *p*-(*tert*-butyldimethylsiloxy)phenylacetylene and *m*-fluoroiodobenzene, respectively. Yield 76%, white solid, mp 53.8−55.3 °C. IR (KBr): 2928, 1512, 1262, 978, 833, 802, 779, 713, 690, 528 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (dd, $J = 8.8$ Hz, $J = 5.6$ Hz, 2H, Ar), 7.20 (t, $J = 8.0$ Hz, 1H, Ar), 7.12 (d, $J = 8.0$ Hz, 1H, Ar), 7.04 (vt, $J = 8.8$ Hz, 2H, Ar), 7.00 (s, 1H, Ar), 6.82 (d, $J = 8.0$ Hz, 1H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 162.4 (d, $J = 250$ Hz, 1C, Ar), 155.4 (1C, Ar), 133.4 (d, $J = 8.3$ Hz, 2C, Ar), 129.4 (1C, Ar), 124.7 (1C, Ar), 124.0 (1C, Ar), 123.0 (1C, Ar), 120.6 (1C, Ar), 119.3 (1C, Ar), 115.5 (d, $J = 22$ Hz, 2C, Ar), 88.9 (1C, C≡C), 88.0 (1C, C≡C), 25.7 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{20}H_{23}FOSi$: C, 73.6; H, 7.1. Found: C, 73.4; H, 7.3.

1-(3-Fluoro)phenyl-2-(3-*tert*-butyldimethylsiloxy)phenylacetylene (1i). This monomer was prepared by the same method as for **1d** using *m*-(*tert*-butyldimethylsiloxy)phenylacetylene instead of *p*-(*tert*-butyldimethylsiloxy)phenylacetylene. Yield 60%, colorless liquid. IR (KBr): 2957, 1491, 1265, 982, 930, 874, 837, 783, 721, 681 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.32−7.27 (m, 2H, Ar), 7.24−7.20 (m, 1H, Ar), 7.19 (d, $J = 8.0$ Hz, 1H, Ar), 7.13 (d, $J = 8.0$ Hz, 1H, Ar), 7.06−6.98 (m, 2H, Ar), 6.83 (d, $J = 8.0$ Hz, 1H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 162.3 (d, $J = 246$ Hz, 1C, Ar), 155.5 (1C, Ar), 129.8 (d, $J = 9.1$ Hz, 1C, Ar), 129.4 (1C, Ar), 127.4 (1C, Ar), 125.0 (d, $J = 9.1$ Hz, 1C, Ar), 124.9 (1C, Ar), 123.7 (1C, Ar), 123.1 (1C, Ar), 120.9 (1C, Ar), 118.3 (d, $J = 22$ Hz, 1C, Ar), 115.5 (d, $J = 22$ Hz, 1C, Ar), 90.1 (1C, C≡C), 87.8 (1C, C≡C), 25.7 (3C, C*C*H_3), 18.2 (1C, *C*CH_3), −4.4 (2C, SiCH_3). Anal. Calcd for $C_{20}H_{23}FOSi$: C, 73.6; H, 7.1. Found: C, 73.7; H, 7.2.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. Unless otherwise specified, the polymerizations were carried out at 80 °C for 24 h at the following concentrations: [$TaCl_5$] = 20 mM, [*n*-Bu_4Sn] = 40 mM. The formed polymers were isolated by precipitation into a large amount of methanol, and the polymer yields were determined by gravimetry.

Membrane Fabrication and Desilylation. Membranes (thickness ca. 50−120 μm) of polymers **2c**−**f** were fabricated by casting toluene solution of the polymers (concentration ca. 0.50−1.0 wt %) onto a flat-bottomed Petri dish. The dish was covered with a glass vessel to slow solvent evaporation (ca. 3−5 days). With reference to the method described in the literature,[9] the desilylation reaction of the membranes of **2c**−**f** was carried out using TFA as acid catalyst. A detailed method of desilylation of membranes is as follows: A membrane was immersed in a mixture of TFA and water (volume ratio 4:1) at room temperature for 24 h. To neutralize the remaining acid in the polymer matrix, the membrane was then immersed in aqueous $NaHCO_3$ solution at room temperature for 24 h and then dried in air at room temperature. Finally, the membrane was immersed in hexane for 24 h to remove residual impurities and dried to constant weight at room temperature for 24 h.

Membrane Density. Membrane density was determined by hydrostatic weighing using a Mettler Toledo balance (model AG204, Switzerland) and a density determination kit.[22] In this method, a liquid with known density (ρ_0) is needed, and the membrane density (ρ) is given by the following equations:

$$\rho = \frac{M_A}{M_A - M_L}\rho_0$$

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. Aqueous $NaNO_3$ solution was used as the auxiliary liquid.

Density and Fractional Free Volume (FFV) of Polymer Membranes. FFV (cm^3 of free volume/cm^3 of polymer) is commonly used to estimate the efficiency of chain packing and the amount of space (free volume) available for gas permeation in a polymer matrix. It is defined as[23]

$$\mathrm{FFV} = \frac{v_{sp} - v_0}{v_{sp}} \approx \frac{v_{sp} - 1.3v_w}{v_{sp}}$$

where v_{sp} and v_0 are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. Typically, v_0 is 1.3 times larger than the van der Waals volume (v_w), which is calculated by the group contribution methods.[24]

Measurement of Gas Permeabilities. The P values were calculated from the slopes of time−pressure curves in the steady state where Fick's law holds.[25] The D values were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

Here, l is the membrane thickness and θ is the time lag, which is given by the intercept of the asymptotic line of the time−pressure curve to the time axis. The membrane thickness was controlled so that the time lag would be in the range 10−300 s, preferably 30−150 s. When the time lag was <10 s, the error of measurement became relatively large. If the time lag was, on the contrary, >300 s, the error based on baseline drift became serious. The S values were calculated by using equation $S \equiv P/D$.

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