Macromolecules **2006,** *39,* 243−248

Synthesis and Gas Permeation Properties of Para-Substituted Poly(1-chloro-2-phenylacetylenes)

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Received September 12, 2005; Revised Manuscript Received October 23, 2005

ABSTRACT: Para-substituted 1-chloro-2-phenylacetylenes [$ClC{\equiv}CC_6H_4$-*p*-R; R = F (**1**), Cl (**2**), Me (**3**), Br (**4**), I (**5**), CF_3 (**6**), $SiMe_3$ (**7**), $SiEt_3$ (**8**), Si(*n*-Pr)$_3$ (**9**), and Si(*i*-Pr)$_3$ (**10**)] were polymerized with a catalyst generated by UV irradiation of $Mo(CO)_6$ in CCl_4 to provide the corresponding polymers. The formed polymers except poly(**5**) were soluble in common organic solvents and afforded free-standing membranes by the casting method except for poly(**10**) whose molecular weight was rather low. Compared to poly(1-chloro-2-phenylacetylene) (PCPA), all the polymers in this study exhibited high gas permeability. As the size of para-substituents increased, both the fractional free volume (FFV) and gas permeability increased and then decreased. Consequently, poly(**6**), which has a relatively bulky CF_3 group, showed the largest FFV (0.258) and the highest gas permeability (P_{O_2} = 280 barrers). Poly(**9**) and poly(**10**) were more gas-permeable than PCPA despite their small FFV values and showed large diffusion coefficients, which might be due to large local mobility of the substituents.

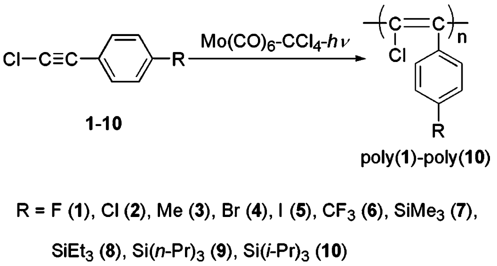
Introduction

Some substituted polyacetylenes exhibit high gas permeability due to the presence of bulky spherical substituents and the rigid main chain composed of alternating double bonds.[1] Among them, poly(1-trimethylsilyl-1-propyne) (PTMSP) is the most gas-permeable, and many studies concerning the gas permeation property of PTMSP have been reported.[1a,2] Most of poly(1-aryl-2-phenylacetylenes) having spherical substituents on the aryl moiety also show high gas permeability.[1c,3] For instance, the oxygen permeability coefficient (P_{O_2}) of poly[1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene] (PTMSDPA) is 1500 barrers,[3c] which is very high among all the synthetic polymers. The membranes of these substituted polyacetylenes can be fabricated by the casting method, while this method cannot be applied to poly(diphenylacetylene) (PDPA) because of its insolubility.[4] Introduction of bulky substituents such as trimethylsilyl group is necessary to obtain soluble PDPAs.

It has been reported that 1-chloro-2-phenylacetylene is polymerized with Mo catalysts to afford solvent-soluble poly(1-chloro-2-phenylacetylene) (PCPA).[5] It is of great interest that a catalyst formed by UV irradiation of $Mo(CO)_6$ in CCl_4 yields PCPA having a weight-average molecular weight (M_w) up to 2 million.[5b] PCPA is soluble in many organic solvents such as toluene, $CHCl_3$, THF, etc., and film-forming. Although the oxygen permeability of PCPA is not very high (P_{O_2} is 5.1 barrers), the oxygen/nitrogen permselectivity (P_{O_2}/P_{N_2}) is as high as 5.0.[6] It is noteworthy that the preparation of membranes of PCPA derivatives having various ring substituents is possible because of their good solubility and film-forming ability. Therefore, PCPA derivatives are interesting polymers to investigate the relationship between gas permeability and ring substituents.

In the present paper we examined at first the polymerization of a series of para-substituted poly(1-chloro-2-phenylacetylenes) catalyzed with $Mo(CO)_6$−CCl_4−*hν* (Scheme 1). The monomers are numbered in the order of increasing size of the para-substituents. Then free-standing membranes were fabricated from the resultant polymers [poly(**1**)−poly(**4**) and poly(**6**)−poly(**9**)] to determine their densities, fractional free volume (FFV), and gas permeability. The diffusivity and solubility of polymer membranes for CO_2 and CH_4 were also studied.

Scheme 1. Synthesis of Poly(1-chloro-2-phenylacetylene)s with Various Para-Substituents



Results and Discussion

Polymerization. Table 1 shows the results of the polymerization of various monomers **1**−**10** induced by UV irradiation of $Mo(CO)_6$. Monomer **1** polymerized into a polymer [poly(**1**)] in 82% yield, whose weight-average molecular weight (M_w) was as high as 1.7×10^6. The polymerization of **2**−**9** also gave polymers [poly(**2**)−poly(**9**)] in moderate yields (36−87%). Poly(**2**)−poly(**4**) and poly(**6**)−poly(**9**) possessed relatively high molecular weights ($M_w > 3.9 \times 10^5$). The molecular weight of poly(**5**) could not be determined because it was insoluble in common solvents including hexane, CCl_4, toluene, Et_2O, $CHCl_3$, THF, acetone, methanol, DMF, and DMSO. In contrast, the yield and M_w of poly(**10**) were low, which should be due to the steric hindrance of the bulky silyl group of **10**. In the polymerization of substituted acetylenes by group 5 and 6 transition metal catalysts, the bulkiness of monomers remarkably affects the yields and molecular weights of the polymers.[7]

Table 2 summarizes the solubility properties of poly(**1**)−poly(**10**). Poly(**1**) was totally soluble in various organic solvents such as CCl_4, toluene, Et_2O, $CHCl_3$, THF, acetone, and DMF.

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10.1021/ma0519819 CCC: $33.50

Table 1. Polymerization of 1−10[a]

monomer	R	time, h	polymer[b] yield, %	polymer[b] $M_w \times 10^{-3c}$	polymer[b] $M_w/M_n{}^c$
1	F	24	82	1700	1.3
2	Cl	24	55	550	1.5
3	Me	48	48	400	5.4
4	Br	24	87	1500	1.4
5	I	24	65	−[d]	
6	CF_3	24	60	1200	1.6
7	$SiMe_3$	24	52	940	2.2
8	$SiEt_3$	48	36	390	2.2
9	Si(*n*-Pr)$_3$	48	70	1000	2.1
10	Si(*i*-Pr)$_3$	48	9	87	1.7

[a] Polymerized in CCl_4 at 30 °C after catalyst solution was irradiated at 0 °C for 2 h; $[M]_0 = 1.0$ M, $[Mo(CO)_6] = 10$ mM. [b] Methanol-insoluble product. [c] Measured by GPC (polystyrene standard). [d] Insoluble.

Poly(**2**)−poly(**4**) and poly(**6**) showed similar solubility to poly(**1**). Poly(**5**) was insoluble in any solvents described above. Poly(**7**)−poly(**10**) having silyl groups were soluble in nonpolar solvents and completely dissolved even in hexane, while insoluble in polar solvents such as acetone and DMF. It has been reported that PDPA and its derivatives are insoluble in any solvents except for the ones having bulky substituents such as trimethylsilyl and triethylsilyl groups.[3c,4,8] Thus, it can be said that PCPA derivatives are more soluble in organic solvents than are PDPA derivatives.

Density and FFV of Polymer Membranes. Membranes of poly(**1**)−poly(**4**) and poly(**6**)−poly(**9**) were fabricated by casting from polymer solution, while membranes of poly(**5**) and poly(**10**) could not be prepared because poly(**5**) was insoluble and the molecular weight of poly(**9**) was too low. Table 3 lists the densities and FFVs of polymer membranes along with the v_w of substituent R. The FFVs of poly(**2**) and poly(**3**) were 0.214 and 0.228, respectively, being larger than that of PCPA. Further, poly(**6**) and poly(**7**) had larger FFVs than poly(**2**) and poly(**3**) did. This indicates that the polymer chain packing is hampered by steric repulsion with increasing size of the ring substituents. However, the FFVs of poly(**8**) and poly(**9**) having bulkier substituents were smaller than that of PCPA. It seems that the appropriate size of substituent is important to decrease chain packing. The membrane of poly(**1**) exhibited high FFV despite the small substituent, F.[9] This can be accounted for by the idea that chain packing is restricted by intermolecular repulsion caused by the fluorine atoms with high electronegativity, as reported in the case of other fluorine-containing polymers.[10] It can be said that the polymers in this study have large FFVs compared to other conventional gas-permeable polymers such as polysulfones, polyimides, polycarbonates, etc.[11] For example, when polysulfone is modified by silylation and fluorination to reduce the polymer chain packing, its FFV increases to 0.155−0.196.[11b]

Gas Permeation Properties. Table 4 gives the gas permeability of the membranes obtained in the present study. The gas permeability was measured at 25 °C. Figure 1 plots the permeability of PCPA and poly(**1**), poly(**2**), and poly(**4**), all of which have monatomic para-substituents, to various gases at 25 °C as a function of the kinetic diameter of the gases. The gas permeability of poly(**1**), poly(**2**), and poly(**4**) is higher than that of PCPA, and the order is as follows: poly(**1**) > poly(**4**) > poly(**2**) > PCPA. This order agrees well with the order of their FFVs. This also corresponds to the order of the size of para-substituents, except for poly(**1**). Thus, the gas permeability of these polymers depends on their FFVs. The large FFV of poly(**1**) is attributable to the presence of fluorine atoms with high electronegativity and, in turn, weak intermolecular interaction.

Figure 2 presents the permeability of PCPA, poly(**3**), and poly(**6**)−poly(**9**), which have polyatomic para-substituents, to various gases at 25 °C as a function of the kinetic diameter of the gases. In correspondence to its larger FFV, poly(**3**) is more permeable to all gases than is PCPA. For example, the P_{O_2} of poly(**3**) was 47 barrers, whereas that of PCPA was 5.1 barrers. The gas permeability of poly(**6**) and poly(**7**), which have even larger FFVs, is very high. Their P_{O_2} values are 280 and 210 barrers, respectively, which are relatively large compared to conventional glassy polymers; e.g., the P_{O_2} values of substituted polysulfones, well-known gas separation materials, are less than 50 barrers.[10a,12]

Poly(**8**) and poly(**9**) exhibited lower gas permeability than poly(**7**), which is attributable to the smaller FFVs of poly(**8**) and poly(**9**). Thus, the gas permeability increased and then decreased with increasing size of para-substituents. It has been reported that the gas permeability decreases as the size of substituents becomes larger; e.g., the P_{O_2} value of PTMSDPA is 1500 barrers,[3c] while those of poly[1-(*p*-triisopropylsilyl)phenyl-2-phenylacetylene] and poly[1-(*p*-triphenylsilyl)phenyl-2-phenylacetylene] are 20 and 3.8 barrers, respectively.[13] Further, the P_{O_2} value of PTMSP is 10 000 barrers, but that of poly(1-triethylsilyl-1-propyne) is no more than 640 barrers.[14] Thus, it seems a general tendency that spherical substituents with appropriate size are useful to achieve high gas permeability in polyacetylenes and that too bulky substituents rather decrease gas permeability. The P_{O_2} values of poly(**8**) and poly(**9**) were 64 and 43 barrers, respectively, which are still higher than that of PCPA despite their lower FFVs than that of PCPA. This may be explained in terms of the effect of local mobility of the substituents,[15] as follows: Gas permeability depends not only on the FFV of polymer membranes but also on the local mobility of the substituents. Triethylsilyl and tripropylsilyl groups are flexible and can rotate, and hence the local mobility of these substituents seems to be large.

Table 2. Solubility of Polymers[a]

polymer R	poly(**1**) F	poly(**2**) Cl	poly(**3**) Me	poly(**4**) Br	poly(**5**) I	poly(**6**) CF_3	poly(**7**) $SiMe_3$	poly(**8**) $SiEt_3$	poly(**9**) Si(*n*-Pr)$_3$	poly(**10**) Si(*i*-Pr)$_3$
hexane	−	−	−	−	−	−	+	+	+	+
CCl_4	+	+	+	+	−	−	+	+	+	+
toluene	+	+	+	+	−	−	+	+	+	+
Et_2O	+	−	+	−	−	+	+	+	+	+
$CHCl_3$	+	+	+	+	−	−	+	+	+	+
THF	+	+	+	+	−	+	+	+	+	+
acetone	+	−	−	−	−	+	−	−	−	−
methanol	−	−	−	−	−	−	−	−	−	−
DMF	+	+	−	+	−	+	−	−	−	−
DMSO	−	−	−	−	−	−	−	−	−	−

[a] Symbols: +, soluble, −, insoluble.

Table 3. Physical Properties of Polymers

polymer	R	υ_w[a] of R, cm^3/mol	density,[b] g/cm^3	FFV[c]
PCPA	H	3.44	1.22	0.210
poly(**1**)	F	5.70	1.31	0.220
poly(**2**)	Cl	12.0	1.34	0.214
poly(**3**)	Me	13.7	1.14	0.228
poly(**4**)	Br	14.4	1.63	0.218
poly(**6**)	CF_3	21.3	1.36	0.258
poly(**7**)	$SiMe_3$	57.6	1.02	0.234
poly(**8**)	$SiEt_3$	88.3	1.03	0.185
poly(**9**)	Si(*n*-Pr)$_3$	118	1.02	0.166

[a] υ_w: van der Waals volume. [b] Determined by hydrostatic weighing. [c] FFV: fractional free volume. Estimated from membrane density.

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

polymer	R	*P*, barrers					
		He	H_2	O_2	N_2	CO_2	CH_4
PCPA	H	23	29	5.1	1.0	23	1.3
poly(**1**)	F	100	160	37	9.9	220	14
poly(**2**)	Cl	48	80	17	3.5	100	6.3
poly(**3**)	Me	130	180	47	13	250	24
poly(**4**)	Br	60	110	23	5.8	130	14
poly(**6**)	CF_3	420	600	280	120	1500	180
poly(**7**)	$SiMe_3$	200	400	210	72	990	220
poly(**8**)	$SiEt_3$	76	140	64	22	320	64
poly(**9**)	Si(*n*-Pr)$_3$	48	100	43	14	220	47

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

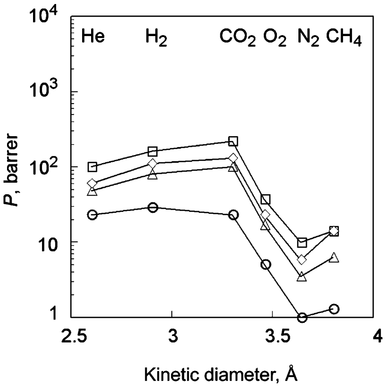


Figure 1. Gas permeability coefficients (*P*) of poly(1-chloro-2-phenylacetylenes) with halogens [para-substituent = H [○, PCPA], F [□, poly(**1**)], Cl [△, poly(**2**)], Br [◇, poly(**4**)].

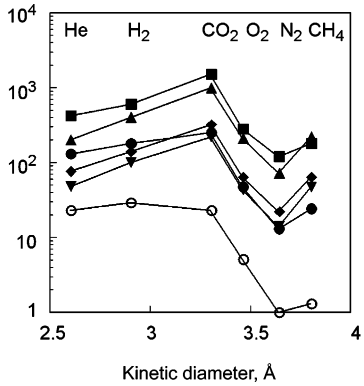


Figure 2. Gas permeability coefficients (*P*) of poly(1-chloro-2-phenylacetylenes) with polyatomic groups [para-substituent = H [○, PCPA], Me [●, poly(**3**)], CF_3 [■, poly(**6**)], $SiMe_3$ [▲, poly(**7**)], $SiEt_3$ [♦, poly(**8**)], Si(*n*-Pr)$_3$ [▼, poly(**9**)].

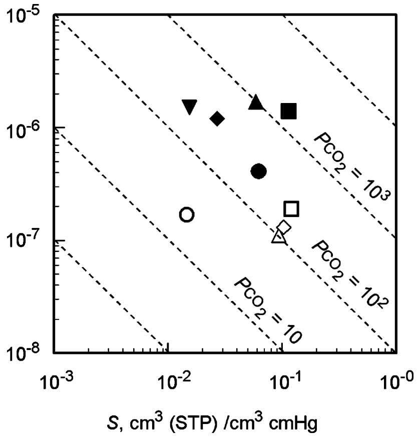


Figure 3. CO_2 diffusion coefficients (*D*) and solubility coefficients (*S*) of poly(1-chloro-2-phenylacetylenes) with para-substituents (R). R: H [○, PCPA], F [□, poly(**1**)], Cl [△, poly(**2**)], Me [●, poly(**3**)], Br [◇, poly(**4**)], CF_3 [■, poly(**6**)], $SiMe_3$ [▲, poly(**7**)], $SiEt_3$ [♦, poly(**8**)], Si(*n*-Pr)$_3$ [▼, poly(**9**)]. The unit of P_{CO_2} is barrer.

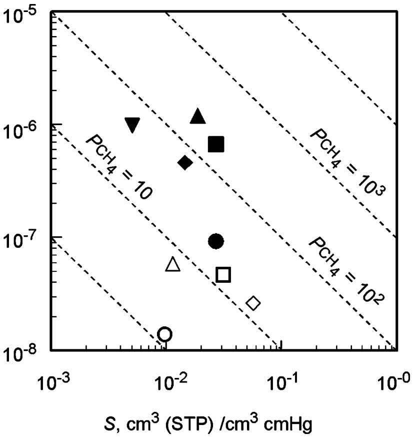
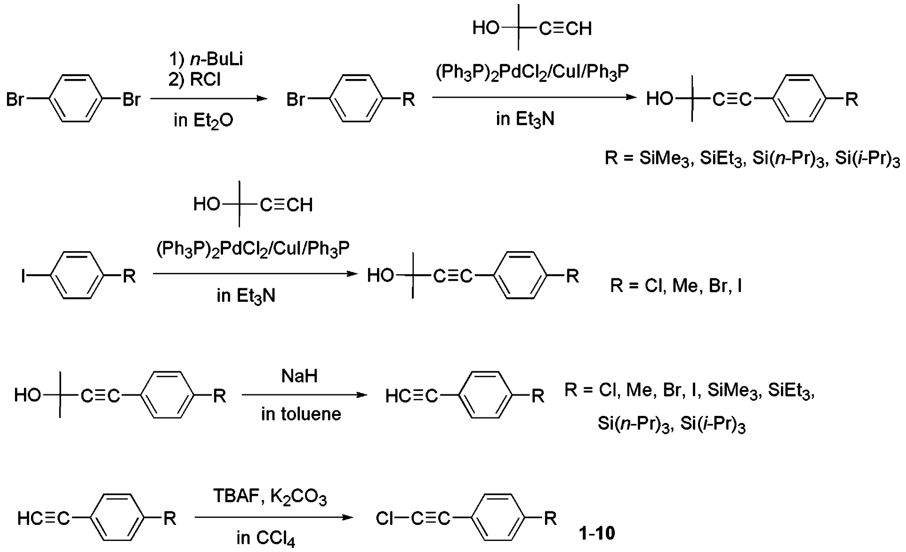


Figure 4. CH_4 diffusion coefficients (*D*) and solubility coefficients (*S*) of poly(1-chloro-2-phenylacetylenes) with para-substituents (R). R: H [○, PCPA], F [□, poly(**1**)], Cl [△, poly(**2**)], Me [●, poly(**3**)], Br [◇, poly(**4**)], CF_3 [■, poly(**6**)], $SiMe_3$ [▲, poly(**7**)], $SiEt_3$ [♦, poly(**8**)], Si(*n*-Pr)$_3$ [▼, poly(**9**)]. The unit of P_{CH_4} is barrer.

Gas Diffusivity and Solubility. Figure 3 depicts the CO_2 diffusivity coefficients (D_{CO_2}) and CO_2 solubility coefficients (S_{CO_2}) of polymer membranes. From Figure 3, we can divide the present polymers into three kinds according to the magnitude of *D* and *S* values compared to those of PCPA, namely, (i) those with large *S* [poly(**1**), poly(**2**), poly(**4**)], (ii) those with large *S* and *D* [poly(**6**), poly(**7**)], and (iii) those with large *D* [poly(**8**), poly(**9**)]. In other words, polymers with monatomic groups have large *S* values, those with polyatomic groups with appropriate sizes such as poly(**6**) and poly(**7**) have both large *S* and *D* values, and those with very bulky groups [poly(**8**), poly(**9**)] have large *D* values. This suggests the following things: (i) the monatomic ring substituents increase FFV and are polar, resulting in the increase of the *S* value, and (ii) the polyatomic bulky substituents do not increase FFV but increase local mobility, leading to the increase of the *D* value. It is thought that polyatomic substituents with suitable sizes such as CF_3 and $SiMe_3$ enhance both *S* and *D* values.

Figure 4 depicts the relationship between the CH_4 diffusion coefficients (D_{CH_4}) and CH_4 solubility coefficients (S_{CH_4}) of polymer membranes. A tendency more or less similar to the case of CO_2 is observed in Figure 4. Thus, as compared to PCPA, halogen-containing polymers possess somewhat large *S* and *D* values, whereas polymers having polyatomic substituents have clearly large *D* values. It is obvious that the higher CH_4 permeability of poly(**8**) and poly(**9**) than that of PCPA originates from their large *D* values.

Scheme 2. Synthesis of 1-Chloro-2-phenylacetylene Monomers



Conclusions

Poly(1-chloro-2-phenylacetylene) derivatives having various substituents at the para-position of the phenyl ring, poly(**1**)−poly(**10**), were synthesized by polymerization using the Mo(CO)$_6$−CCl$_4$−$h\nu$ catalyst. Among these polymers, poly(**1**)−poly(**4**) and poly(**6**)−poly(**9**) had high molecular weight and were solvent-soluble and film-forming. The FFVs of poly(**6**) and poly(**7**), which have CF$_3$ and SiMe$_3$ groups, respectively, were larger than those of the other polymers. It is considered that polymer chain packing is hampered by steric repulsion when the polymer has substituents of appropriate sizes. Consequently, poly(**6**) and poly(**7**) exhibited higher gas permeability than the other polymers in this study. As the size of para-substituents increased, the gas permeability at first increased and then decreased. This can be mainly explained in terms of the change of FFV with the size of the substituents. Further, gas permeability was divided into diffusivity and solubility, and it was found that the polymers with monatomic substituents show more or less large *S* values, whereas those with polyatomic substituents display fairly large *D* values.

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. Melting points of monomers were determined by a Yanako micromelting point apparatus. Elemental analyses of monomers were performed at the Microanalytical Center of Kyoto University. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

Materials. Mo(CO)$_6$ was purchased from Aldrich (Japan) and used without further purification. Tetra-*n*-butylammonium fluoride (1 mol/L in THF) and a series of alkylsilyl chlorides were purchased from TCI (Japan). Other chemicals and organic solvents were purchased from Wako (Japan) and used without further purification. CCl$_4$ was purified by distillation. *p*-(Trimethylsilyl)phenylacetylene, *p*-(triethylsilyl)phenylacetylene, *p*-(tri-*n*-propylsilyl)phenylacetylene, *p*-(triisopropylsilyl)phenylacetylene were prepared by successive silylation[16] and ethynylation[17] of *p*-dibromobenzene according to the literature (Scheme 2). *p*-Methylphenylacetylene, *p*-chlorophenylacetylene, *p*-bromophenylacetylene, and *p*-iodophenylacetylene were prepared via the same routes as in the literature of ethynylation.[17] *p*-Fluorophenylacetylene and *p*-trifluoromethylphenylacetylene were purchased from Wako (Japan). PCPA was prepared by the same method as in the literature to compare with the results of this study.[5b] Monomers **1**−**10** were synthesized as shown in Scheme 2 referring to the literature,[18] the details of which are stated below.

Monomer Synthesis. 1-Chloro-2-(*p*-fluorophenyl)acetylene (**1**) was prepared as follows: A 100 mL flask was equipped a three-way stopcock and a magnetic stirring bar and flushed with dry nitrogen. *p*-Fluorophenylacetylene (1.8 g, 15 mmol), potassium carbonate (2.1 g, 15 mmol), and CCl$_4$ (15 mL) were fed in the flask. Then, a solution of tetra-*n*-butylammonium fluoride in THF (0.50 mol/L, 1.6 mL, 0.8 mmol) was added, and the resulting mixture was stirred for 2 h at room temperature. After the completion of the reaction was confirmed by TLC, a small amount of methanol was added. The solution was washed at first with 1 N hydrochloric acid and then with water. The solution was dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. Purification of the crude product by distillation under reduced pressure provided the desired product (1.7 g, 72%) as a colorless liquid. IR (KBr): 3052, 2226, 1892, 1647, 1603, 1507, 1464, 1385, 1296, 1237, 1157, 1094, 1015, 889, 835, 803, 588, 525 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.42 (dd, J = 8.8 Hz, J = 5.2 Hz, 2H, Ar), 7.00 (dd, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$, δ): 162.6 (d, J = 249 Hz, 1C), 133.8 (d, J = 8.2 Hz, 2C), 118.1 (d, J = 3.3 Hz, 1C), 115.6 (d, J = 22.3 Hz, 2C), 68.4, 67.8. Anal. Calcd for C$_8$H$_4$ClF: C, 62.2%; H, 2.6%. Found: C, 62.0%; H, 2.5%.

1-Chloro-2-(*p*-chlorophenyl)acetylene (**2**) was prepared by the same method as for **1** by using *p*-chlorophenylacetylene instead of *p*-fluorophenylacetylene as a starting compound. Yield 83%, white solid, mp 57.5−59.0 °C. IR (KBr): 2926, 2855, 2220, 1898, 1642, 1592, 1487, 1400, 1266, 1219, 1111, 1090, 1015, 955, 885, 824, 573, 515, 492 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.35 (d, J = 8.0 Hz, 2H, Ar), 7.28 (d, J = 8.0 Hz, Ar). ^{13}C NMR (CDCl$_3$, δ): 134.7, 133.1, 128.7, 120.6, 69.1, 68.3. Anal. Calcd for C$_8$H$_4$Cl$_2$: C, 56.2%; H, 2.4%. Found: C, 55.8%; H, 2.2%.

1-Chloro-2-(*p*-methylphenyl)acetylene (**3**) was prepared from *p*-methylphenylacetylene in the same way as for **1**. Yield 41%, colorless liquid. IR (KBr): 3030, 2922, 2222, 1906, 1609, 1509, 1449, 1181, 1105, 1040, 887, 814, 781, 521 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.32 (d, J = 8.0 Hz, 2H, Ar), 7.11 (d, J = 8.0 Hz, 2H, Ar), 2.34 (s, 3H, CH_3). ^{13}C NMR (CDCl$_3$, δ): 138.7, 131.8, 129.1, 119.0, 69.5, 67.1, 21.5. Anal. Calcd for C$_9$H$_7$Cl: C, 71.8%; H, 4.7%. Found: C, 72.0%; H, 4.5%.

1-Chloro-2-(*p*-bromophenyl)acetylene (**4**) was prepared similarly to **1** from *p*-bromophenylacetylene. Yield 64%, white solid, mp 81.0−83.0 °C. IR (KBr): 2222, 1898, 1584, 1483, 1393, 1267, 1067, 1011, 957, 885, 816, 513 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.43 (d, J = 8.4 Hz, 2H, Ar), 7.30 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR

($CDCl_3$, δ): 133.3, 131.6, 122.9, 121.0, 69.3, 68.4. Anal. Calcd for C_8H_4BrCl: C, 44.6%; H, 1.9%. Found: C, 44.6%; H, 1.9%.

1-Chloro-2-(*p*-iodophenyl)acetylene (**5**) was prepared similarly to **1** from *p*-iodophenylacetylene. Yield 77%, white solid, mp 79.5−80.5 °C. IR (KBr): 2222, 1898, 1578, 1482, 1388, 1262, 1109, 1055, 1007, 884, 814, 536, 513 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.64 (d, $J = 8.0$ Hz, 2H, Ar), 7.16 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, δ): 137.5, 133.4, 121.6, 94.6, 69.6, 68.5. Anal. Calcd for C_8H_4ClI: C, 36.6%; H, 1.5%. Found: C, 36.2%; H, 1.6%.

1-Chloro-2-(*p*-trifluoromethylphenyl)acetylene (**6**) was prepared similarly to **1** from *p*-(trifluoromethyl)phenylacetylene. Yield 64%, white solid, mp <30.0 °C. IR (KBr): 2226, 1923, 1794, 1676, 1616, 1576, 1404, 1323, 1171, 1132, 1105, 1067, 1019, 891, 841, 770, 737, 669, 596, 517 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.56 (d, $J = 8.4$ Hz, 2H, Ar), 7.53 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, δ): 132.2, 130.3 (q, $J = 33.1$ Hz, 1C), 125.9, 125.3 (q, $J = 4.1$ Hz, 2C), 123.8 (q, $J = 272$ Hz, 1C), 70.9, 68.1. Anal. Calcd for $C_9H_4ClF_3$: C, 52.8%; H, 2.0%. Found: C, 52.7%; H, 2.2%.

1-Chloro-2-(*p*-trimethylsilylphenyl)acetylene (**7**) was similar to **1** from *p*-(trimethylsilyl)phenylacetylene. Yield 64%, white solid, mp 39.0−41.0 °C. IR (KBr): 2957, 2926, 2359, 2220, 1923, 1595, 1458, 1391, 1370, 1306, 1250, 1105, 841, 820, 758, 529 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.44 (d, $J = 8.4$ Hz, 2H, Ar), 7.39 (d, $J = 8.4$ Hz, 2H, Ar), 0.25 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, δ): 141.5, 133.2, 131.0, 122.3, 69.5, 68.3, −1.2. Anal. Calcd for $C_{11}H_{13}ClSi$: C, 63.3%; H, 6.3%. Found: C, 63.7%; H, 6.6%.

1-Chloro-2-(p-triethylsilylphenyl)acetylene (**8**) was prepared from *p*-(triethylsilyl)phenylacetylene in the same way as for **1**. Yield 75%, colorless liquid. IR (KBr): 2955, 2876, 2220, 1595, 1458, 1416, 1393, 1306, 1238, 1103, 1007, 887, 727, 531 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.42 (d, $J = 6.8$ Hz, 2H, Ar), 7.40 (d, $J = 6.8$ Hz, 2H, Ar), 0.95 (t, $J = 8.0$ Hz, 9H, $SiCH_2CH_3$), 0.77 (q, $J = 8.0$ Hz, 6H, $SiCH_2$). ^{13}C NMR ($CDCl_3$, δ): 138.6, 134.0, 130.9, 122.3, 69.5, 68.3, 7.4, 3.3. Anal. Calcd for $C_{14}H_{19}ClSi$: C, 67.0%, H, 7.6%. Found: C, 67.2%, H, 7.8%.

1-Chloro-2-(*p*-tri-*n*-propylsilylphenyl)acetylene (**9**) was prepared similarly to **1** from *p*-(tri-*n*-propylsilyl)phenylacetylene. Yield 70%, colorless liquid. IR (KBr): 2955, 2868, 2220, 1915, 1595, 1460, 1410, 1373, 1333, 1101, 1065, 1003, 887, 820, 720, 530 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.42 (d, $J = 8.0$ Hz, 2H, Ar), 7.39 (d, $J = 8.0$ Hz, 2H, Ar), 1.37−1.28 (m, 6H, $SiCH_2CH_2$), 0.95 (t, $J = 7.2$ Hz, 9H, $SiCH_2CH_2CH_3$), 0.77 (t, $J = 8.8$ Hz, 6H, $SiCH_2$). ^{13}C NMR ($CDCl_3$, δ): 139.4, 133.9, 130.9, 122.2, 69.6, 68.2, 18.5, 17.4, 15.1. Anal. Calcd for $C_{17}H_{25}ClSi$: C, 69.7%; H, 8.6%. Found: C, 69.8%; H, 8.8%.

1-Chloro-2-(*p*-triisopropylsilylphenyl)acetylene (**10**) was prepared similarly to **1** from *p*-(triisopropylsilyl)phenylacetylene. Yield 74%, white solid, mp 38.5−40.0 °C. IR (KBr): 2944, 2867, 2220, 1595, 1464, 1391, 1368, 1308, 1250, 1098, 1073, 1015, 995, 920, 884, 820, 710, 681, 646, 569, 536, 517 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.43 (d, $J = 8.4$ Hz, 2H, Ar), 7.40 (d, $J = 8.4$ Hz, 2H, Ar), 1.44−1.35 (m, 3H, SiC*H*), 1.06 (d, $J = 7.6$ Hz, 18H, $SiCHCH_3$). ^{13}C NMR ($CDCl_3$, δ): 136.2, 135.1, 130.7, 122.1, 69.5, 68.3, 18.2, 10.7. Anal. Calcd for $C_{17}H_{25}ClSi$: C, 69.7%; H, 8.6%. Found: C, 69.7%; H, 8.7%.

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 in CCl_4 at 30 °C for 24 h under the following conditions: $[M]_0 = 1.0$ M, $[Mo(CO)_6] = 10$ mM. The catalyst solution was UV irradiated at 0 °C for 2 h. A detailed procedure of the polymerization is as follows: A monomer solution was prepared in a Schlenk tube by mixing monomer **1** (0.46 g) and CCl_4 (2.0 mL). Another Schlenk tube was charged with $Mo(CO)_6$ (7.9 mg) and CCl_4 (1.0 mL); this catalyst solution was irradiated by a 400 W Hg lamp at 0 °C for 2 h. Then the monomer solution was added to the catalyst solution. Polymerization was continued at 30 °C for 24 h, which was quenched with a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol, and its yield was determined gravimetrically.

Membrane Fabrication. Membranes (thickness ca. 30−100 μm) of poly(**1**)−poly(**4**) and poly(**7**)−(**9**) were fabricated by casting toluene solution of the polymers (concentration ca. 1.0−2.0 wt %) onto a Petri dish. Membrane of poly(**6**) was prepared by casting perfluorobenzene solution of the polymer. The Petri dish was covered with a glass vessel to slow solvent evaporation (ca. 3−5 days).

Density and FFV of Polymer Membranes. The densities of membranes were determined by hydrostatic weighing using a Mettler Toledo balance and a density determination kit. In this method, a liquid with a known density (ρ_0) is needed, and the membrane density (ρ) is given by the following equation:

$$\rho = \rho_0 M_A/(M_A - M_L) \tag{1}$$

where M_A and M_L are the weights of the membrane in air and in auxiliary liquid (aqueous $NaNO_3$; $\rho_0 = 1.258$ g/mL), respectively.

FFV is calculated by the following equation:

$$\mathrm{FFV} = (\upsilon_{sp} - \upsilon_0)/\upsilon_{sp} \approx (\upsilon_{sp} - 1.3\upsilon_w)/\upsilon_{sp} \tag{2}$$

where υ_{sp} and υ_0 are the specific and occupied volumes of the polymer, respectively. The occupied volume is typically 1.3 times larger than the van der Waals volume (υ_w), which is calculated by the group contribution methods.[19]

Gas Diffusivity and Solubility of Polymer Membranes. The *P* values were calculated from the slopes of time−pressure curves in the steady state where Fick's law holds.[6] The *D* values were determined by the time lag method using the following equation:

$$D = l^2/6\theta \tag{3}$$

where *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 *S* values were calculated by using the equation $S = P/D$.

Acknowledgment. This research was partly supported by a grant-in-aid for scientific research from the Ministry of Education, Science, Culture and Sports, Japan.

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MA0519819