Macromolecules **2005,** *38,* 2704−2709

Synthesis of Poly(diphenylacetylene) Membranes by Desilylation of Various Precursor Polymers and Their Properties

Toshikazu Sakaguchi,[†] **Kenichi Yumoto,**[†] **Masashi Shiotsuki,**[†] **Fumio Sanda,**[†] **Masakazu Yoshikawa,**[‡] **and Toshio Masuda***[,†]

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Kyoto 615-8510, Japan, and Department of Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, Japan

Received November 17, 2004; Revised Manuscript Received January 12, 2005

ABSTRACT: Diphenylacetylenes having various silyl groups ($PhC{\equiv}CC_6H_4{-}SiR^1R^2R^3$, $SiR^1R^2R^3 = p$-$SiMe_3$, p-$SiMe_2$$i$-Pr, p-$SiEt_3$, p-$SiMe_2$$n$-$C_8H_{17}$, p-$SiMe_2$$n$-$C_{18}H_{37}$, m-$SiMe_3$, m-$SiMe_2$$t$-Bu, **1a**−**g**, respectively) were polymerized with $TaCl_5$−n-Bu_4Sn catalyst to provide high molecular weight polymers. The formed polymers (**2a**−**g**) afforded tough free-standing membranes by casting from toluene solution. Desilylation of these Si-containing polymer membranes was carried out with trifluoroacetic acid. Para-substituted polymers (**2a**−**e**) underwent desilylation completely, while meta-subustituted polymers (**2f** and **2g**) did not. According to thermogravimetric analysis (TGA), both Si-containing and desilylated polymers exhibited high thermal stability, and all the desilylated polymers showed practically the same onset temperature (∼480 °C) of weight loss. The membranes of Si-containing polymers showed lower oxygen permeability as the silyl group became bulkier. The oxygen permeability coefficients ($P(O_2)$ 120−3300 barrers) of desilylated polymer membranes were quite different from each other irrespective of the same polymer structure. When bulkier silyl groups were removed, the oxygen permeability increased to larger extents. In ethanol/water pervaporation, both Si-containing and desilylated polymer membranes showed ethanol permselectivity, indicating that these membranes possess large excess free volumes.

Introduction

Polymerization of substituted acetylenes with transition metal catalysts affords substituted polyacetylenes, which have various substituents and stiff main chain composed of alternating double bonds. Substituted polyacetylenes exhibit interesting features such as chromism, semiconductivity, paramagnetism, gas permeability, etc.[1] Among substituted acetylenes, diphenylacetylene polymerizes in high yield with the $TaCl_5$−n-Bu_4Sn catalyst.[2] The formed polymer is thermally very stable [onset temperature of weight loss (T_0) in air is 500 °C], but insoluble in any solvent. On the other hand, 1-(p-trimethylsilyl)phenyl-2-phenylacetylene (**1a**, Scheme 1) provides a polymer (**2a**) soluble in common organic solvents.[3] **2a** has high molecular weight [weight-average molecular weight (M_w) > 1 × 10^6] and good thermal stability [$T_0 = 420$ °C], and affords a tough free-standing membrane by the casting method. Its oxygen permeability coefficient ($P(O_2)$) reaches 1500 barrers, indicating that this polymer is highly gas-permeable among various polymers.[4]

In a preliminary communication,[5] we reported that the desilylation of the **2a** membrane yields insoluble poly(diphenylacetylene) membrane which otherwise cannot be prepared because of its insolubility. By performing the same procedure, membranes of insoluble poly(diarylacetylene)s having naphthyl or phenanthryl groups can also be prepared.[6] Being insoluble, these membranes can be used for the separation of organic mixtures as well as gas separation. Because of a solid-state reaction, the desilylation reaction seems to generate microvoids in polymer matrix whose size will presumably affect its gas permeability. The size of formed microvoids may be controlled by selecting the size of silyl group of the precursor polymer. In terms of the desilylation of membranes, however, the effects of silyl groups on the gas permeability and the reactivity of desilylation are not well-known yet.

In this research, diphenylacetylenes containing various silyl groups besides trimethylsilyl group (**1a**−**g**, Scheme 1) were polymerized, and free-standing membranes of resultant polymers (**2a**−**e**) were fabricated, which yielded the insoluble membranes of poly(diphenylacetylene)s (**3a**−**e**) upon desilylation. General properties and gas permeability of the polymer membranes (**2** and **3**) were examined, and the variation of gas permeability with desilylation was also investigated.

Results and Discussion

Polymerization. The polymerization of several novel monomers with silyl groups of various sizes (**1a**−**g**) was carried out in toluene using $TaCl_5$−n-Bu_4Sn as catalyst (Table 1). It is well-known that $TaCl_5$−n-Bu_4Sn achieves a good yield of disubstituted acetylene polymers with high molecular weight,[1a,b] which is essential for fabrication of free-standing membranes. The polymerization of monomer **1a** produced a polymer in good yield, whose M_w was as high as 2.1 × 10^6. Monomers **1b**−**d** also polymerized in a similar way to give polymers in high yields of 80−95%. The polymers from **1c** and **1d** possessed very high molecular weights over M_w > 6 × 10^6. The polymerization of **1e** was conducted with lowering the monomer concentration to 0.10 M owing to the high molecular weight of the monomer, and the formed polymer was isolated by precipitation from acetone because the monomer was hardly soluble in methanol. The M_w of the resultant polymer was as high as 3.0 × 10^6. Thus, it can be said that the para-substituted diphenylacetylenes afford high molecular weight poly-

---

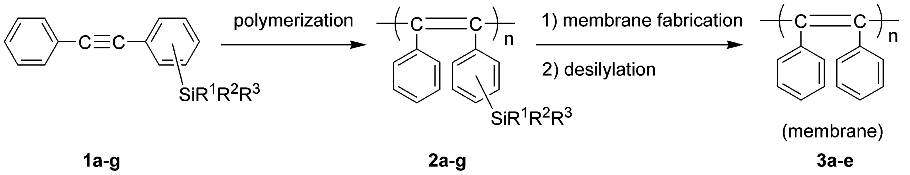
* Corresponding author. E-mail: masuda@adv.polym.kyoto-u.ac.jp.

[†] Kyoto University.

[‡] Kyoto Institute of Technology.

10.1021/ma047632g CCC: $30.25

Scheme 1. Preparation of Various Poly(diphenylacetylene) Membranes via Si-Containing Poly(diphenylacetylene)s



	a	b	c	d	e	f	g
$SiR^1R^2R^3$	p-$SiMe_3$	p-$SiMe_2$i-Pr	p-$SiEt_3$	p-$SiMe_2C_8H_{17}$	p-$SiMe_2C_{18}H_{37}$	m-$SiMe_3$	m-$SiMe_2$t-Bu

Table 1. Polymerization of 1a–g with $TaCl_5$–n-Bu_4Sn[a]

		polymer[b]		
monomer	$[M]_0$	yield (%)	M_w x $10^{-6\,c}$	M_w/M_n[c]
1a	0.50	61	2.1	3.8
1b	0.50	80	5.3	1.8
1c	0.50	95	>6.0	
1d	0.50	89	>6.0	
1e	0.10	69[d]	3.0	3.6
1f	0.50	96	5.7	2.5
1g	0.50	21	0.39	14

[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 calibrated with polystyrenes as standards. [d] Acetone-insoluble product.

Table 2. Solubility of the Polymers[a]

solvent	2a	2b	2c	2d	2e	2f	2 g	3a–e
hexane	−	−	−	+	+	−	+	−
cyclohexane	+	+	+	+	+	+	+	−
toluene	+	+	+	+	+	+	+	−
$CHCl_3$	+	+	+	+	+	+	+	−
THF	+	+	+	+	+	+	+	−
ethanol	−	−	−	−	−	−	−	−
methanol	−	−	−	−	−	−	−	−
DMF	−	−	−	−	−	−	−	−
DMSO	−	−	−	−	−	−	−	−

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

mers in high yields irrespective of bulkiness of para-substituents. The polymerization of monomer **1f** with trimethylsilyl group at meta-position also yielded a high molecular weight polymer. On the other hand, in the case of monomer **1g**, which has a bulkier silyl group at meta position, the polymer yield was as low as 21% and the M_w was no more than 3.9×10^5, which is 1 order of magnitude lower than those of other polymers. It is known that diphenylacetylene with a trimethylsilyl group at the ortho position of a phenyl ring does not undergo polymerization.[7] Thus, it is not unreasonable that diphenylacetylenes with a bulky meta substituent such as **1g** does not smoothly polymerize owing to the steric reason.

Desilylation of Polymer Membranes. The solubility of polymers **2a–g** is summarized in Table 2. The present silyl group-containing poly(diphenylacetylene)s showed good solubility in many low polarity solvents including toluene, chloroform, tetrahydrofuran, and cyclohexane. In addition, polymers **2d** and **2e**, which have long alkyl chains, were completely soluble even in hexane. On the other hand, none of the polymers **2a–g** dissolved in polar solvents such as N,N-dimethylformamide, dimethyl sulfoxide, and lower alcohols such as methanol and ethanol.

Free-standing membranes could be fabricated by casting polymers **2a–g** from toluene solution. The membranes were sufficiently tough and transparent. Their desilylation was carried out in a hexane/trifluoroacetic acid (1:1 volume ratio) mixture at room temperature for 24 h. Desilylation of the membranes of para-substituted polymers **2a–e** proceeded to completion to give membranes of poly(diphenylacetylene)s **3a–e**. On the other hand, desilylation of the membranes of **2f** and **2g**, i.e., meta-substituted polymers, did not reach completion under the same reaction conditions as for the para-substituted counterparts, and hence it was impossible to prepare the membranes of poly(diphenylacetylene) from these polymers. The comparison of IR spectra and weights of membranes before and after desilylation indicated that 68% of the silyl groups of **2f** membrane was removed under the above-stated conditions. The completely desilylated polymers **3a–e** were insoluble in any solvent (Table 2), indicating that the incorporation of silyl groups is essential for the solubility of poly(diphenylacetylene).

Thermal Stability of the Polymers. The thermal stability of polymers **2a–g** and **3a–e** was examined by TGA in air (Figures 1 and 2). The onset temperature of weight loss (T_0) for polymer **2a** was 420 °C, showing its high thermal stability. The T_0 values of polymers **2b** and **2c** were 350 and 300 °C, respectively, while those

Figure 1. TGA curves of silyl group-containing poly(diphenylacetylene)s **2a–g** (in air, heating rate 10 °C min^{-1}).

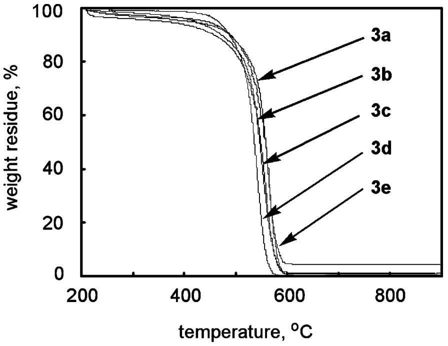


Figure 2. TGA curves of poly(diphenylacetylene)s **3a–e** obtained by desilylation (in air, heating rate 10 °C min^{-1}).

Table 3. Oxygen Permeability ($P(O_2)$) and Oxygen/Nitrogen Separation Factor ($P(O_2)/P(N_2)$) of the Polymer Membranes

	2		3	
polymer	$P(O_2)^a$	$P(O_2)/P(N_2)$	$P(O_2)^a$	$P(O_2)/P(N_2)$
a	1500	2.2	910	2.2
b	500	2.3	2100	1.6
c	550	2.1	2500	1.5
d	28	3.2	3300	1.5
e	20	3.8	120	2.8
f	1700	1.7		
g	1000	2.3		

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

Table 4. $P(O_2)$ and $P(O_2)/P(N_2)$ of 3a after Conditioning with Various Solvents

solvent	$P(O_2)$ (barrer)^a	$P(O_2)/P(N_2)^a$
methanol	910	2.2
ethanol	1100	1.6
1-propanol	610	2.2
2-butanol	760	1.6
acetone	420	2.6
THF	420	1.8
toluene	530	2.1
hexane	510	2.0

[a] Measured at 25 °C after membrane **3a** was immersed in each solvent and then dried to constant weight at room temperature.

of **2d** and **2e**, which have long alkyl chains, were as low as around 260 °C. The values of **2f** and **2g** were 420 and 380 °C, respectively. These results imply that the thermal degradation of these polymers occurs at the silyl moiety at first and that the thermal stability decreases as the alkyl chain on the silyl groups becomes longer. It is interesting to compare the values of these polymers with the much lower T_0 (~200 °C) of para-substituted poly(phenylacetylenes).[8] When **2a**−**g** were heated in air above 800 °C, the ash composed of silica remained, whose amount agreed with the expected value in every case.

The desilylated polymers **3a**−**e** exhibit practically identical TGA curves to each other, and their T_0 values are all approximately 480 °C. This temperature is higher than those of the starting Si-containing polymers, which means that the thermal stability improves upon desilylation. This finding is consistent with the idea that the thermal decomposition of silyl group-containing polymers takes place at the silyl group at first. The practically identical TGA curves of the desilylated polymers show that the thermal stability depends on the polymer structure obtained after desilylation and is independent of that before desilylation.

Oxygen Permeability of the Polymers. Polymer membranes **2a**−**g** and **3a**−**e** were immersed in methanol for 24 h and dried to constant weight at room temperature, and then their permeability was measured at 25 °C (Table 3). The $P(O_2)$ value of membrane **2a** at 25 °C was 1500 barrers, while that of **3a** (the product of desilylation of membrane **2a**) was 910 barrers, which is somewhat smaller than that of **2a**. Though we reported before[5] that the $P(O_2)$ of **3a** reaches 6000 barrers, we were unable to reproduce this high permeability thereafter. Freeman also determined the $P(O_2)$ of **3a** to be 850 barrers.[9] It is, anyhow, noteworthy that poly(diphenylacetylene) **3a** exhibits high oxygen permeability up to ca. 1000 barrers although it has no spherical groups. By comparison, poly(phenylacetylene) is much less permeable to oxygen ($P(O_2) = 6.0$ barrers[10]). This means that microvoids are generated in **3a** at the position where silyl groups were present in **2a** and that the microvoids are retained due to the highly stiff polymer structure.

The $P(O_2)$ values of the membranes **2b** and **2c**, which have bulky silyl groups, were smaller than that of **2a**, and 500 and 550 barrers, respectively. A tendency has been known that, as the spherical substituent of polyacetylenes becomes bulkier, the gas permeability decreases.[11] This has been explained in terms of the local mobility of substituents.[12] The present finding agrees with this tendency. The $P(O_2)$ values of the desilylated polymer membranes **3b** and **3c** were 2100 and 2500 barrers, respectively, which are, interestingly, much larger than those of **2b** and **2c**. This obvious increase of permeability is considered to be due to the formation of large microvoids by removal of bulky silyl groups. The $P(O_2)$ values of membranes **2d** and **2e**, which have long alkyl chains, were no more than 28 and 20 barrers, respectively, which is compatible with previous results that polyacetylenes with long alkyl groups show relatively low gas permeability.[13] In sharp contrast to **2d**, the $P(O_2)$ of membrane **3d** reached up to 3300 barrers. This seems due to the generation of large microvoids by removal of bulky silyl group. On the other hand, the $P(O_2)$ value of membrane **3e** was 120 barrers, where the increase of gas permeability upon desilylation is not very large. Membrane **2e** considerably swelled due to high affinity to the desilylation solvent mixture, and consequently it shrank pretty much during desilylation. This should have more or less depressed the formation of microvoids.

The $P(O_2)$ values of membranes **2f** and **2g** with silyl groups at meta position were 1700 and 1000 barrers, respectively, which are slightly higher than those of para-substituted analogues (**2a**, 1500 barrers; **2b**, 500 barrers; **2** with p-SiMe$_2$-t-Bu is insoluble[14]). Unfortunately, the oxygen permeability of their desilylated membranes (**3f** and **3g**) could not be measured because their desilylation did not proceed completely. The oxygen/nitrogen separation factors ($P(O_2)/P(N_2)$) of all the polymer membranes **2** and **3** were in the range 1.5−3.8, and the values tended to decrease as the $P(O_2)$ increased. These results agree with the general tendency of gas permeation through polymer membranes.[15]

Effect of Swelling Solvents on the Oxygen Permeability. As mentioned above, the prepared polymer membranes were subsequently immersed in methanol, and dried to constant weight at room temperature prior to permeability measurements. If measured without this operation, the permeability generally assumes lower values, because, when immersed in methanol, polymer membranes swell to eventually have larger excess free volumes upon drying. Thus, the effect of various conditioning agents on the oxygen permeability of membrane **3a** was investigated (Table 4). When **3a** was conditioned with ethanol, the $P(O_2)$ value was 1100 barrers and slightly larger than that with methanol. When 1-propanol and 2-butanol were used, the $P(O_2)$ values were somewhat smaller, and 610 and 760 barrers, respectively. The polymer chains seem to become mobile due to high affinity to these alcohols, and the swollen membranes should shrink during the drying process. The $P(O_2)$ values after treatment with acetone, THF, toluene, and hexane which have relatively high affinity to **3a** were all 420−530 barrers and fairly small. Thus, we can say that rather low affinity solvents such

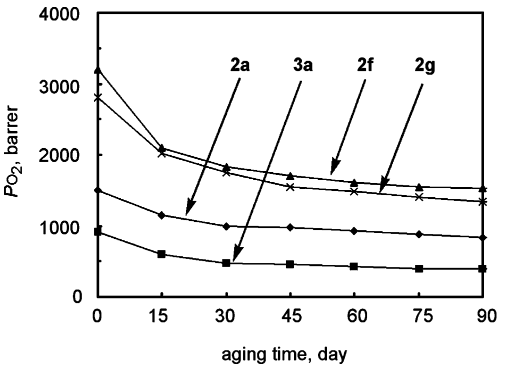


Figure 3. Effect of aging time on the oxygen permeability of polymers **2a**, **3a**, **2f**, and **3g** (stored in air at 25 °C).

Table 5. Gas Diffusion and Solubility Coefficients (*D* and *S*)[a]

		H_2	O_2	N_2	CO_2	CH_4
2a	P^b	3100	1700	900	6900	2800
	10^3S^c	9.9	9.0	3.8	58	25
	10^7D^d	320	240	190	120	110
3a	P^b	2700	1300	800	5300	2200
	10^3S^c	8.1	12	10	87	38
	10^7D^d	340	110	75	62	57

[a] Measured at 25 °C by the "time lag" method. [b] In the unit of barrer (1 barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$). [c] In the units of cm^3 (STP) cm^{-3} $cmHg^{-1}$. [d] In the units of cm^2 s^{-1}.

as methanol and ethanol are useful as agents for conditioning substituted polyacetylene membranes to achieve high gas permeability. In the case of high affinity solvents, substituted polyacetylene membranes shrink during drying, resulting in the decrease of excess free volume and, in turn, low gas permeability.

Variation of Oxygen Permeability with Aging Time. The variation of oxygen permeability with aging time was examined by storing the membranes at room temperature in air (Figure 3). The $P(O_2)$ value of membrane **2a** decreased from 1500 to 1150 barrers in 15 days and further to 1000 barrers after 30 days and then practically leveled off. Similarly, the $P(O_2)$ values of membranes **3a**, **2f**, and **2g** decreased with time to about a half of their initial values. This variation with aging time is accounted for by the reduction of excess free volume, in other words, the relaxation of polymer conformation. After 90 days, these membranes were immersed in methanol for 24 h and dried to constant weight; consequently, their $P(O_2)$ values were restored to the initial ones owing to the recovery of the initial unrelaxed polymer molecular structure. For instance, though the $P(O_2)$ of membrane **2a** was 950 barrers after 90 days, it increased to ca. 1450 barrers when the membrane was immersed in methanol for 24 h and dried to constant weight. This variation of the permeability of polymer membranes with aging time is a general tendency observed for highly gas-permeable disubstituted acetylene polymers.[6,16] Although poly(1-trimethylsilyl-1-propyne) [poly(TMSP)] exhibits the highest gas permeability among all the polymers, its $P(O_2)$ value remarkably decreases from 6000 to around 100 barrers.[16a] On the other hand, the present polymers and other poly(diarylacetylene)s[6] feature rather small time dependence of $P(O_2)$, since their permeability only decreases to a half of their initial values.

Solubility and Diffusivity of Gases in the Polymer Membranes. Table 5 lists the permeability, solubility, and diffusion coefficients (*P*, *S*, and *D*) of **2a** and **3a** for various gases. Among the *P* values for the five gases examined, the $P(CO_2)$ was the largest, while the $P(N_2)$ was the smallest in both **2a** and **3a**. The gas permeation through membrane can be inspected by dividing into the solution and diffusion terms theoretically with rubbery polymers and approximately with glassy polymers. In general, the *S* value increases with increasing critical temperature of gases, while the *D* value decreases with increasing molecular diameter of gases in any polymers. Both **2a** and **3a** also display this tendency.

When the gas solubilities for **2a** with **3a** are compared, most of the *S* values of **3a** are larger than those of **2a** (Table 5). The gas solubility in polymer membrane is considered to increase with increasing free volume in polymer membrane,[17] and hence the increase of gas solubility after desilylation suggests the increase of free volume in polymer membrane. On the other hand, the *D* values of **3a** were smaller than those of **2a** for most gases. This can be accounted for by the large local mobility of trimethylsilyl group. The local mobility of substituents plays an important role for gas diffusivity; i.e., the gas diffusivity becomes large when the polymer has substituents with large local mobility such as trimethylsilyl group.[12] To summarize, the desilylation of **2a** membrane results in larger gas solubility but smaller diffusivity, and consequently, the gas permeability either remains about the same or becomes somewhat smaller.

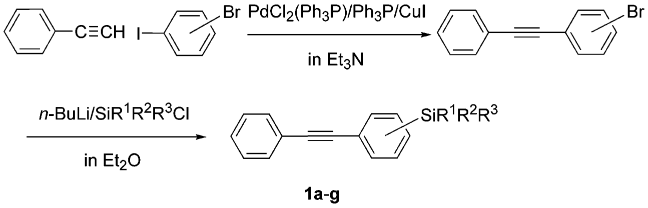
Table 6. Pervaporation of EtOH/H₂O Mixtures through the Polymer Membranes[a]

polymer	X_{EtOH}[b]	Y_{EtOH}[c]	α_{EtOH/H_2O}[d]	10^3R/(g m m^{-2} h^{-1})
2a	0.0985	0.419	6.60	3.28
2b	0.0994	0.354	4.97	1.27
2c	0.119	0.371	4.38	1.39
2d	0.0994	0.193	2.14	2.32
2e	0.0978	0.290	2.86	1.93
2f	0.0941	0.347	5.10	5.11
2g	0.0970	0.481	8.64	2.08
3a	0.101	0.392	5.74	3.18
3b	0.0972	0.467	8.12	6.45
3c	0.0971	0.485	8.76	8.45
3d	0.0982	0.464	7.95	4.27
3e	0.0989	0.339	4.54	2.71

[a] At 30 °C; downstream pressure 267 Pa (2 mmHg). [b] Weight fraction of ethanol in the feed. [c] Weight fraction of ethanol in the permeate. [d] $\alpha_{EtOH/H_2O} = (Y_{EtOH}/Y_{H_2O})/(X_{EtOH}/X_{H_2O})$.

Pervaporation of the Ethanol/Water Mixture. The pervaporation experiments of ethanol/water mixture were performed using polymer membranes **2a**–**g** and **3a**–**e**, whose results are shown in Table 6. The separation factor α_{EtOH/H_2O} of membrane **2a** was 6.60, which is similar to that of poly[1-*β*-naphthyl-2-(*p*-trimethylsilyl)phenylacetylene][18] ($\alpha_{EtOH/H_2O} = 5.30$). Although this value is smaller than those of poly(TMSP)[19] and poly(dimethylsiloxane)[20] (17.0 and 8.65, respectively), it indicates ethanol permselectivity. Other Si-containing polymer membranes **2b**–**g** also permeated ethanol preferentially. These results are interesting and important because most polymers show water permselectivity in ethanol/water pervaporation. For instance, the values of separation factor $\alpha_{H_2O/EtOH}$ values for cellulose acetate, nylon, and polyacrylonitrile having polar groups are fairly large (8.5–70),[21] and even polyethylene and polystyrene, which are hydrophobic polymers, display water permselectivity, whose $\alpha_{H_2O/EtOH}$ values are roughly 1.7 and 12, respectively.[22,23] This is because the ethanol molecule is bulkier than the water

Scheme 2. Synthesis of Monomers 1a−g



molecule and hence usually difficult to permeate through polymer membranes. The high ethanol permselectivity of the present polymers is attributable to the presence of microvoids therein as well as their hydrophobicity. In particular, the former seems to be operative in ethanol permselectivity. The permeation rate (R) is also considerably increased by the presence of microvoids, and hence highly ethanol-permselective membranes show large fluxes. It is further noted that the ethanol permselectivity and permeation rate of polymer membranes **3b−e** are larger than those of the corresponding Si-containing polymer membranes. This indicates that a large number of microvoids are generated upon desilylation.

Experimental Section

General Data. 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. Thermogravimetric analysis (TGA) was conducted in air with a Perkin-Elmer TGA7 thermal analyzer.

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C. 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 S values were calculated by using equation $S = P/D$.

The permeation experiments of ethanol/water mixture were performed by an ordinary pervaporation technique and permeates were analyzed by a Shimadzu GC-8APT gas chromatograph equipped with a 3.0-m long column packed with poly(ethylene glycol) 20 M [Chromosorb W (AW-DMCS)].

Materials. $TaCl_5$ (Strem) as main catalyst was used without further purification, while n-Bu_4Sn (Wako, Japan) as cocatalyst was purified by distillation. Bromoiodobenzenes (Wako, Japan) were used without further purification. Solvents for polymerization were purified by the usual methods. Phenylacetylene (Aldrich) and various alkylchlorosilanes (Tokyo Kasei, Japan) were commercially obtained. Monomers were synthesized according to Scheme 2 with reference to the literature of ethynylation[24] and silylation.[25] 1-Phenyl-2-(*p*-bromo)phenylacetylene and 1-phenyl-2-(*m*-bromo)phenylacetylene were synthesized by the reaction of phenylacetylene with *p*- and *m*-bromoiodobenzenes, respectively.[3b] Monomers **1a** and **1f** were prepared according to the literature procedure.[3b] The synthesis and analytical data of other monomers are as follows.

1-Phenyl-2-(*p*-dimethylisopropylsilyl)phenylacetylene (1b). A 500 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 1-phenyl-2-(*p*-bromo)phenylacetylene (20 g, 0.078 mol) and ether (250 mL) were added and cooled at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (58 mL, 1.6 M, 93 mmol) was added dropwise, and the mixture was stirred for 1 h. Then, a solution of dimethylisopropylchlorosilane (13 g, 95 mmol) in ether (50 mL) was added dropwise at 0 °C, and stirring was continued further for 5 h at room temperature. After the completion of the reaction was confirmed by TLC, ice−water (50 mL) was added. The reaction mixture was washed with water, and dried over anhydrous sodium sulfate. Ether was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane) to give the desired product (12 g, 56%) as colorless liquid. Purity >99% (^{1}H NMR). IR (KBr, cm^{-1}): 2859, 1598, 1560, 1508, 1248, 1100, 995, 916, 824, 807, 760. ^{1}H NMR ($CDCl_3$, ppm): 7.54−7.46 (m, 6H, Ar), 7.34−7.32 (m, 3H, Ar), 0.95 (d, 6H, $SiCHC\mathit{H}_3$), 0.94 (m, 1H, $SiC\mathit{H}$), 0.25 (s, 6H, $SiC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, ppm): 139.2, 133.8, 131.6, 130.5, 128.3, 128.2, 123.4, 123.3, 89.8, 89.5, 17.5, 13.8, −5.4. Anal. Calcd for $C_{19}H_{22}Si$: C, 81.9; H, 8.0; Si, 10.1. Found: C, 82.0; H, 7.8; Si, 10.2.

1-Phenyl-2-(*p*-triethylsilyl)phenylacetylene (1c). This monomer was prepared by the same method as for **1b** using triethylchlorosilane instead of dimethylisopropylchlorosilane to give a colorless liquid, yield 65%, purity >99% (^{1}H NMR). IR (KBr, cm^{-1}): 2874, 1599, 1560, 1507, 1099, 1011, 913, 821, 755. ^{1}H NMR ($CDCl_3$, ppm): 7.57−7.48 (m, 6H, Ar), 7.38−7.30 (m, 3H, Ar), 0.96 (t, 9H, $SiCH_2C\mathit{H}_3$), 0.80 (q, 6H, $SiC\mathit{H}_2$). ^{13}C NMR ($CDCl_3$, ppm): 138.1, 134.1, 133.0, 131.6, 130.6, 128.3, 128.2, 123.4, 89.7, 89.6, 7.3, 3.2. Anal. Calcd for $C_{20}H_{24}Si$: C, 82.1; H, 8.3; Si, 9.6. Found: C, 81.7; H, 7.5; Si, 10.8.

1-Phenyl-2-(*p*-dimethyloctylsilyl)phenylacetylene (1d). The identical procedure to that of **1b** was applied except using dimethyloctylchlorosilane in place of dimethylisopropylchlorosilane as a colorless liquid, yield 28%, purity >99% (^{1}H NMR). IR (KBr, cm^{-1}): 2854, 1654, 1560, 1508, 1248, 1101, 821, 754. ^{1}H NMR ($CDCl_3$, ppm): 7.54−7.46 (m, 6H, Ar), 7.36−7.32 (m, 3H, Ar), 1.29−1.23 (m, 12H, $SiCH_2(C\mathit{H}_2)_6$), 0.87 (t, 3H, $SiCH_2(CH_2)_6C\mathit{H}_3$), 0.74 (t, 2H, $SiC\mathit{H}_2$), 0.26 (s, 6H, $SiC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, ppm): 140.3, 133.4, 131.6, 130.6, 128.3, 128.2, 123.5, 123.3, 89.7, 89.6, 33.9, 31.9, 29.3, 23.8, 22.7, 15.6, 14.1, −3.1, −3.4. Anal. Calcd for $C_{24}H_{32}Si$: C, 82.7; H, 9.3; Si, 8.0. Found: C, 82.7; H, 9.4; Si, 7.9.

1-Phenyl-2-(*p*-dimethyloctadecylsilyl)phenylacetylene (1e). This monomer was also prepared by the same method as for **1b** using dimethyloctadecylchlorosilane instead of dimethylisopropylchlorosilane as a white solid, yield 78%, mp 35.0−36.0 °C, purity >99% (^{1}H NMR). IR (KBr, cm^{-1}): 2850, 1599, 1560, 1508, 1255, 1101, 850, 819, 757. ^{1}H NMR ($CDCl_3$, ppm): 7.56−7.50 (m, 6H, Ar), 7.36−7.34 (m, 3H, Ar), 1.31 (m, 32H, $SiCH_2(C\mathit{H}_2)_{16}$), 0.90 (t, 3H, $SiCH_2(CH_2)_{16}C\mathit{H}_3$), 0.75 (t, 2H, $SiC\mathit{H}_2$), 0.27 (s, 6H, $SiC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, ppm): 140.4, 133.5, 131.6, 130.6, 128.3, 128.2, 123.5, 123.3, 89.7, 89.6, 33.6, 31.9, 29.92, 29.86, 29.83, 29.82, 29.78, 29.71, 29.68, 29.67, 29.6, 29.4, 29.3, 23.8, 22.7, 15.6, 14.1, −3.0, −3.1. Anal. Calcd for $C_{34}H_{52}Si$: C, 83.5; H, 10.7; Si, 5.8. Found: C, 83.3; H, 10.8; Si, 5.9.

1-Phenyl-2-(*m*-*t*-butyldimethylsilyl)phenylacetylene (1 g). This monomer was prepared by the same method as for **1b** using *tert*-butyldimethylchlorosilane and 1-phenyl-2-(*m*-bromo)phenylacetylene instead of dimethylisopropylchlorosilane and 1-phenyl-2-(*p*-bromo)phenylacetylene as a colorless liquid, yield 64%, purity >99% (^{1}H NMR). IR (KBr, cm^{-1}): 2853, 1598, 1560, 1508, 1491, 1250, 1112, 882, 832, 757. ^{1}H NMR ($CDCl_3$, ppm): 7.68 (s, 1H, Ar), 7.60−7.54 (m, 3H, Ar), 7.49 (s, 1H, Ar), 7.37−7.32 (m, 4H, Ar), 0.94 (s, 9H, $SiCC\mathit{H}_3$), 0.31 (s, 6H, $SiC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, ppm): 138.0, 137.4, 134.1, 131.9, 131.5, 128.2, 128.1, 127.3, 123.3, 122.5, 89.8, 89.3, 26.4, 16.8, 6.3. Anal. Calcd for $C_{20}H_{24}Si$: C, 82.1; H, 8.3; Si, 9.6. Found: C, 82.6; H, 8.1; Si, 9.3.

Polymerization. Polymerizations were carried out in a Schlenk tube, equipped with a three-way stopcock, under dry nitrogen. Unless otherwise specified, the reaction was carried out at 80 °C for 24 h under the following conditions: $[M]_0 = 0.50$ M, $[TaCl_5] = 20$ mM, and $[n\text{-}Bu_4Sn] = 40$ mM. A detailed procedure of polymerization is as follows: The monomer solution was prepared in a Schlenk tube by mixing monomer **1a** (1.3 g) and toluene (5.0 mL). Another Schlenk tube was charged with $TaCl_5$ (71 mg), n-Bu_4Sn (0.13 mL), and toluene (4.9 mL); this catalyst solution was aged at 80 °C for 10 min, and then monomer solution was added to it. Polymerization was run at 80 °C for 24 h, which was quenched with a small amount of methanol. The resulting polymer was isolated by precipitation into a large excess of methanol, and its yield was determined gravimetrically.

Membrane Fabrication and Desilylation. Membranes (thickness ca. 20−50 μm) of polymers (**2a**−**g**) were fabricated by casting their toluene solution (concentrated ca. 0.50−1.0 wt %) into a Petri dish. The plate was covered with a glass vessel to slow solvent evaporation (ca. 3−5 days). After a membrane formed, it was immersed in methanol for 24 h and dried to constant weight at room temperature for 24 h. As shown in the literature,[5] the desilylation of the membranes of **2a**−**g** was carried out using trifluoroacetic acid. A detailed procedure is as follows: The polymer membrane of **2a** was immersed in a mixture of hexane/trifluoroacetic acid (1:1 volume ratio) at room temperature for 24 h. To remove the remaining acid in the polymer matrix, the membrane was immersed in a mixture of hexane/triethylamine at room temperature for 24 h. Finally, it was immersed in methanol for 24 h to remove residual impurities, washed with methanol, and dried to constant weight at room temperature for 24 h. The completion of desilylation was confirmed by IR spectra of the polymer membranes before and after the reaction; the IR spectra of the membrane of **3a** exhibited no absorptions at ca. 1250, 1120, and 860 cm^{-1}, which were seen in **2a**. After desilylation, the weight of the **3a** membrane decreased to the values anticipated for desilylation, which also confirmed the completion of the reaction.

Acknowledgment. The authors thank Dr. Giseop Kwak at Nara Institute of Science and Technology for his valuable suggestions. This research was supported by a grant-in-aid for scientific research from the Ministry of Education, Science, Culture, and Sports (Japan).

References and Notes

(1) For reviews of substituted polyacetylenes, see: (a) Masuda, T.; Sanda, F. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Vol. 3 Chapter 3. 11, 2003. (b) Nomura, R.; Masuda, T. In *Encyclopedia of Polymer Science and Technology*; Kroshwitz, J. I., Ed.; Wiley: New York, 2003; Vol. IA, p 1. (c) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721. (d) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645. (e) Tabata, M.; Sone, T.; Sadahiro, Y. *Macromol. Chem. Phys.* **1999**, *200*, 265.
(2) Niki, A.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1553.
(3) (a) Tsuchihara, K.; Masuda, T.; Higashimura, T. *J. Am. Chem. Soc.* **1991**, *113*, 8548. (b) Tsuchihara, K.; Masuda, T.; Higashimura, T. *Macromolecules* **1992**, *25*, 5816.
(4) (a) Freeman, B. D.; Pinnau, I. *Advanced Materials for Membrane Separation*; ACS Symposium Series 876; American Chemical Society: Washington, DC, 2004. (b) Nunes, S. P.; Peinemann, K. V. *Membrane Technology in the Chemical Industry*; Wiley: New York, 2001. (c) Koros, W. J.; Mahajan, R. *J. Membr. Sci.* **2000**, *175*, 181. (d) Tsujita, Y. *Prog. Polym. Sci.* **2003**, *28*, 1377. (e) Pandey, P.; Chauhan, R. S. *Prog. Polym. Sci.* **2001**, *26*, 853.
(5) Teraguchi, M.; Masuda, T. *Macromolecules* **2002**, *35*, 1149.
(6) (a) Sakaguchi, T.; Shiotsuki, M.; Masuda, T. *Macromolecules*, **2004**, *37*, 4104. (b) Sakaguchi, T.; Kwak, G.; Masuda, T. *Polymer* **2002**, *43*, 3937.
(7) Kouzai, H.; Masuda, T. Unpublished data.
(8) Fujita, Y.; Misumi, Y.; Tabata, M.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 3157.
(9) Freeman, B. D. Personal communication.
(10) Aoki, T.; Nakahara, H.; Hayakawa, Y.; Kokai, M.; Oikawa, E. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 849.
(11) (a) Nagai, K.; Toy, L. G.; Freeman, B. D.; Teraguchi, M.; Masuda, T. *Polym. Mater. Sci. Eng.* **1999**, *81*, 531. (b) Aoki, T.; Kobayashi, Y.; Kaneko, T.; Oikawa, E.; Yamamura, Y.; Fujita, Y.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules*, **1999**, *32*, 79. (c) Teraguchi, M.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4546.
(12) (a) Kanaya, T.; Teraguchi, M.; Masuda, T.; Kaji, K. *Polymer* **1999**, *40*, 7157. (b) Kanaya, T.; Tsukushi, I.; Kaji, K.; Sakaguchi, T.; Kwak, G.; Masuda, T. *Macromolecules* **2002**, *35*, 5559.
(13) Masuda, T.; Iguchi, Y.; Tang, B. Z.; Higashimura, T. *Polymer* **1988**, *29*, 2041.
(14) Tsuchihara, K.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 547.
(15) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.
(16) (a) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M.; Masuda, T.; Higashimura, T. *Koubunshi Ronbunshu* **1986**, *43*, 747. (b) Nagai, K.; Higuchi, A.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 289. (c) Kwak, G.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2964.
(17) Hu, C. C.; Chang, C. S.; Ruaan, R. C.; Lai, J. Y. *J. Membr. Sci.* **2003**, *226*, 51.
(18) Sakaguchi, T.; Yumoto, K.; Kwak, G.; Yoshikawa, M.; Masuda, T. *Polym. Bull. (Berlin)* **2002**, *48*, 271.
(19) (a) Masuda, T.; Tang, B. Z.; Higashimura, T. *Polym. J.* **1986**, *18*, 565. (b) Ishihara, K.; Nagase, Y.; Matsui, K. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 43. (c) Masuda, T.; Takatsuka, M.; Tang, B. Z.; Higashimura, T. *J. Membr. Sci.* **1990**, *49*, 69.
(20) Miyata, T.; Obata, S.; Uragami, T. *Macromolecules* **1999**, *32*, 3712.
(21) (a) Nagy, E.; Borlai, O.; Ujhidy, A. *J. Membr. Sci.* **1980**, *7*, 109. (b) Mulder, M. H. V.; Oude, H. J.; Hegeman, H.; Smolders, C. A. *J. Membr. Sci.* **1983**, *16*, 269.
(22) Eustache, H.; Histi, G. *J. Membr. Sci.* **1981**, *8*, 105.
(23) Uragami, T.; Morikawa, T. *Makromol. Chem.* **1989**, *190*, 399.
(24) (a) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
(25) Habich, D.; Effenverger, F. *Synthesis* **1979**, 841.

MA047632G