Synthesis and Properties of Poly(diphenylacetylenes) Having Hydroxyl Groups

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ABSTRACT: Polymerization of several diphenylacetylene derivatives was carried out by using $TaCl_5$−*n*-Bu_4Sn as catalyst. $C_6H_5C{\equiv}CC_6H_4$-*p*-$OSi(CH_3)_2t$-Bu (**3a**) and $C_6H_5C{\equiv}CC_6H_4$-*m*-$OSi(CH_3)_2t$-Bu (**3b**) provided the corresponding polymers (poly(**3a**), poly(**3b**)) with high molecular weights in good yields, while *p*-*t*-$Bu(CH_3)_2SiOC_6H_4C{\equiv}CC_6H_4$-*p*-$OSi(CH_3)_2t$-Bu (**3c**), *p*-*t*-$Bu(CH_3)_2SiOC_6H_4C{\equiv}CC_6H_4$-*m*-$OSi(CH_3)_2t$-Bu (**3d**), and *m*-*t*-$Bu(CH_3)_2SiOC_6H_4C{\equiv}CC_6H_4$-*m*-$OSi(CH_3)_2t$-Bu (**3e**) did not satisfactorily. Desilylation of poly(**3a**) and poly(**3b**) membranes catalyzed by trifluoroacetic acid yielded poly(diphenylacetylenes) having free hydroxyl groups [poly(**4a**), poly(**4b**)], which are the first examples of highly polar group-carrying poly(diphenylacetylenes). Poly(**3a**) and poly(**3b**) dissolved in nonpolar solvents such as toluene and chloroform, while poly(**4a**) and poly(**4b**) were insoluble in these solvents. According to TGA in air, poly(**3a**) and poly(**3b**) were thermally fairly stable among substituted polyacetylenes, and poly(**4a**) and poly(**4b**) displayed even higher thermal stability. The P_{CO_2}/P_{CH_4} and P_{CO_2}/P_{N_2} permselectivity ratios of poly(**4a**) and poly(**4b**) membranes were as large as 13−46, while keeping relatively high P_{CO_2} values.

Introduction

Polyacetylenes possessing bulky substituents exhibit useful properties including air stability, good solubility, easy membrane fabrication, and high gas permeability, which are not seen in the unsubstituted polyacetylene.[1] Especially, these polymers attract much attention as gas separation membranes applicable to industrial use.[2] Poly(diphenylacetylenes) with bulky spherical substituents are especially interesting since they possess excellent thermal stability and high gas permeability.[3] For example, poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]-acetylene] [poly(**1**)] is readily soluble in common organic solvents and exhibits an onset temperature of weight loss in air up to 450 °C and a large oxygen permeability coefficient (P_{O_2}) of 1550 barrers at 25 °C.[4]

Poly(diphenylacetylene) is an intractable material because it is insoluble and infusible and hence cannot be fabricated into a membrane directly.[5] Consequently, the precursor polymers are necessary to prepare poly(diphenylacetylene) membrane [poly(**2**)], and we have recently succeeded in preparing it by desilylating poly(**1**) membrane (Scheme 1).[6] The desilylation reaction enables the preparation of solvent-insoluble poly(diphenylacetylene) and analogous polymer membranes, which were inaccessible before.[7] Furthermore, being insoluble, this membrane can be used for the separation of organic mixtures as well as gas separation.[8]

Ta and Nb catalysts are effective for the polymerization of disubstituted acetylenes. They, however, become inactive upon addition of protic compounds such as alcohols and carboxylic acids. Accordingly, disubstituted acetylenes with hydroxyl groups cannot be polymerized with these catalysts. A possible approach to obviate this problem would be to polymerize disubstituted acetylene monomers possessing protected hydroxyl groups[9] and then to deprotect the polymers formed therefrom. To our knowledge, there have been no examples of the synthesis of poly(diphenylacetylenes) with highly polar ring substituents including hydroxyl groups. They are expected to show interesting properties and functions since such functional groups would render them more or less polar and hydrophilic. Thus, we invoke the protection/deprotection methodology to prepare hydroxylated poly(diphenylacetylene) membranes.

The present research deals with the synthesis and polymerization of novel diphenylacetylene monomers (**3a**−**e**) (Chart 1) possessing hydroxyl groups protected by bulky silyl groups. We further describe the desilylation of the resultant polymers [poly(**3a**), poly(**3b**)] to yield poly(diphenylacetylenes) having hydroxyl groups [poly(**4a**),[10] poly(**4b**)], properties of the polymers, and gas permeability of the polymer membranes. This paper presents the first synthetic method of poly(diphenylacetylenes) having polar groups.

Results and Discussion

Polymerization. The polymerization of diphenylacetylene monomers **3a**−**e** possessing protected hydroxyl groups was carried out using a 1:2 mixture of $TaCl_5$ and *n*-Bu_4Sn as catalyst in toluene solution at 80 °C (Table 1). It has been reported that the $TaCl_5$−*n*-Bu_4Sn catalyst satisfactorily polymerizes disubstituted acetylene monomers to give polymers with high molecular weights in good yields.[1a,b] The polymerization of monomer **3a** produced a polymer in a good yield, whose M_w was as high as 4.0×10^6. The polymerization of monomer **3b** also afforded a polymer in an excellent yield, whose M_w was as high as 1.9×10^6. Thus, monomers **3a** and **3b**, which have a bulky siloxy group in one phenyl group, successfully polymerized to give high molecular weight polymers in high yields. The

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Scheme 1. Synthesis of Poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] [Poly(1)] and Membrane of Poly(diphenylacetylene) [Poly(2)]

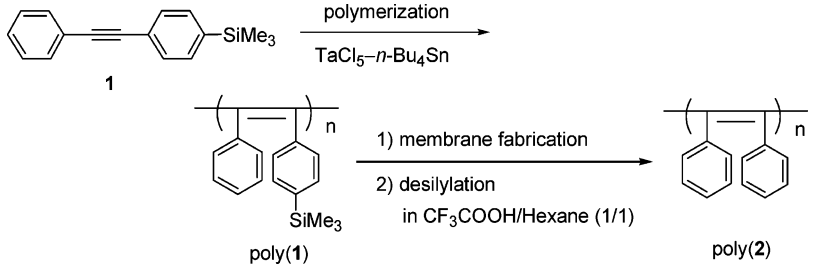
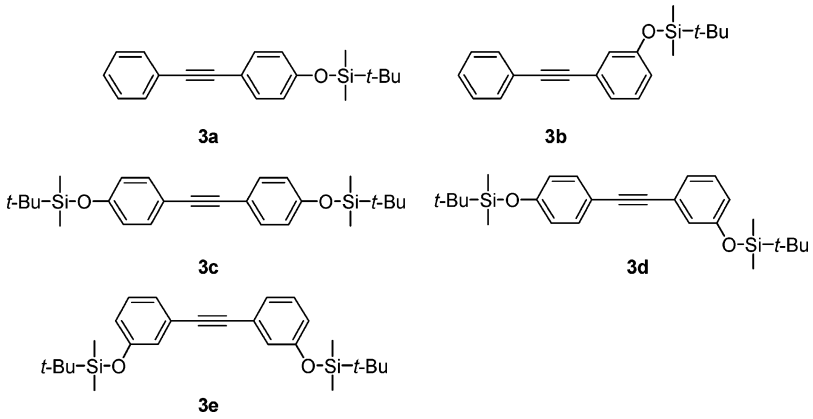


Chart 1. Diphenylacetylene Monomers Having Siloxy Groups



Scheme 2. Synthesis of Poly(diphenylacetylenes) Having Hydroxyl Groups

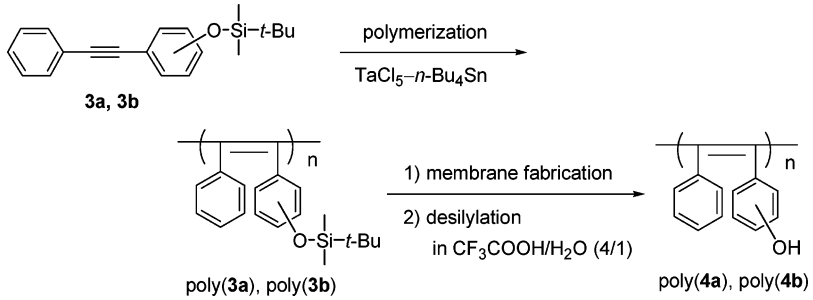


Table 1. Polymerization of 3a–e by $TaCl_5$–*n*-Bu_4Sn[a]

			polymer[b]		
run	monomer	$[M]_0$ (M)	yield (%)	$M_w/10^3$ [c]	M_w/M_n [c]
1	**3a**	0.10	61	4000	12.1
2	**3b**	0.10	72	1900	5.8
3	**3c**	0.10	0		
4	**3c**	0.50	0		
5	**3d**	0.50	48	250	7.6
6	**3e**	0.10	0		
7	**3e**	0.50	0		

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

Table 2. Desilylation of Poly(3a) and Poly(3b) with Trifluoroacetic Acid (TFA)

run	polymer	treatment medium (vol ratio)	time (h)	conv (%)[a]
1	poly(**3a**)	TFA/H_2O (4/1)	24	100
2	poly(**3a**)	TFA/H_2O (2/1)	48	90
3	poly(**3a**)	TFA/methanol (4/1)	48	80
4	poly(**3a**)	TFA/methanol (2/1)	48	30
5	poly(**3a**)	TFA	48	80
6	poly(**3b**)	TFA/H_2O (4/1)	24	100

[a] Determined by TGA (see text for details).

molecular weight distributions of the polymers were appreciably broad (M_w/M_n = 5.8–12.1). On the other hand, the polymerization of monomers **3c** and **3e** did not produce polymers. Monomer **3d** provided a lower molecular weight polymer ($M_w = 2.5 \times 10^5$; $DP_w = 570$) in a moderate yield even at a high monomer concentration ($[M]_0 = 0.50$ M). The inactivity of monomers **3c** and **3e** and the low polymerizability of **3d** may be due to the stetic and/or electronic effect of the two substituents.

Desilylation of Polymer Membranes. High molecular weight is essential for the fabrication of free-standing membranes. As poly(**3a**) and poly(**3b**) possessed high molecular weights ($M_w > 1.0 \times 10^6$), they afforded tough free-standing membranes by casting from toluene solution. The membranes formed from poly(**3a**) and poly(**3b**) were uniform, transparent and yellow. On the other hand, it was difficult to prepare a free-standing membrane from poly(**3d**) because of its rather low molecular weight.

The membrane of poly(**3a**) was immersed in a mixture of trifluoroacetic acid (TFA)/water or TFA/methanol (Table 2). Poly(**3a**) was completely desilylated by using a mixture of TFA/water (4/1) (run 1). After workup by washing with aqueous $NaHCO_3$ solution and water and by the subsequent drying, the desilylation product was dark green and kept the membrane form. The comple-

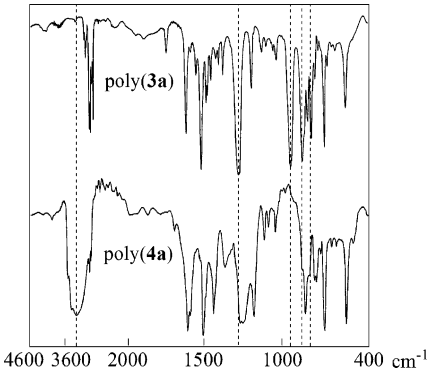


Figure 1. IR spectra of poly(**3a**) and its desilylation product [poly(**4a**)] (KBr pellet).

Table 3. Solubility of the Polymers[a]

	poly(**3a**)	poly(**3b**)	poly(**4a**)	poly(**4b**)
hexane	±	+	−	−
cyclohexane	±	+	−	−
toluene	+	+	−	−
$CHCl_3$	+	+	−	−
THF	+	+	−	−
DMF	−	−	−	+
DMSO	−	−	−	+
methanol	−	−	±	−

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

tion of desilylation was confirmed by IR spectroscopy; i.e., the absorption peaks assignable to the siloxy group at 1260, 912, 855, and 812 cm^{-1} disappeared, and a broad peak due to the hydroxyl group appeared at 3300 cm^{-1} (Figure 1). The degree of desilylation was evaluated by thermogravimetric analysis (TGA) in air; namely, when the silyl group had been partly or completely removed, the amount of ash of SiO_2 remaining above 700 °C in air in TGA decreased proportionally, and hence the degree of desilylation was determined from the amount of ash. The change of the weights of the membranes before and after desilylation was also useful to comfirm the complete desilylation (e.g., poly(**3a**): 53.6 mg; poly(**4a**): observed weight 33.5 mg, calculated weight 33.5 mg). Under the conditions other than those in run 1, poly(**3a**) was not completely desilylated. Poly(**3b**) was completely desilylated by using TFA/water (4/1) in the same way as poly(**3a**). The yellow color of poly(**3b**) membrane turned orange upon desilylation. Thus, the bulky silyl group could be removed using a mixture of TFA/water (4/1) irrespective of the position of the substituents.

General Properties of the Polymers. The solubility of the present polymers was examined (Table 3). Poly(**3a**) and poly(**3b**) possessing bulky siloxy groups

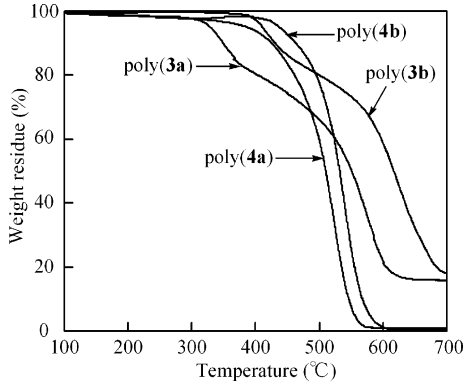


Figure 2. TGA curves of the polymers (in air, heating rate 10 °C min^{-1}).

dissolved in many relatively nonpolar solvents such as toluene, chloroform, and THF, similarly to other poly(diphenylacetylene) derivatives.[3] In contrast, poly(**4a**) was insoluble in such solvents but partly soluble in methanol and ethanol. Poly(**4b**) was insoluble in the nonpolar solvents, methanol and ethanol, while soluble in highly polar solvents such as DMSO and DMF. This variation in solubility with desilylation is remarkable and noteworthy, which should be reflective of incorporation of hydroxyl groups.

The onset temperatures (T_0) of weight loss of poly(**3a**) and poly(**3b**) were 320 and 390 °C in air, respectively, which indicates fair thermal stability among substituted polyacetylenes (Table 4). These polymers showed two-stage weight loss in TGA measured in air, suggesting that the silyl group is at first eliminated (Figure 2). The T_0 values of poly(**4a**) and poly(**4b**) were 360 and 420 °C and even higher than those of poly(**3a**) and poly(**3b**).

Poly(**3a**) exhibited two absorption maxima at λ_{max} = 373 and 429 nm in the UV−vis spectrum (Table 4) similarly to other poly(diphenylacetylene) derivatives; e.g., for poly(**1**) λ_{max} = 375 and 430 nm.[4] Poly(**3b**) also showed a UV−vis spectrum close to that of poly(**3a**).

As seen in Table 4, the Young's moduli (E), tensile strengths (σ_B), and elongations at break (γ_B) of poly(**3a**) and poly(**3b**) resembled those of poly(**1**); that is, all these polymers were very hard and brittle and could hardly be elongated. This seems to be common in poly(diphenylacetylene) derivatives.[11] Poly(**4a**) and poly(**4b**) were mechanically even harder due to the presence of hydroxyl groups.

Density and Fractional Free Volume (FFV) of the Polymers. The densities of polymer membranes were measured to calculate the fractional free volume (FFV). FFV (cm^3 of free volume/cm^3 of polymer) is often used to estimate the efficiency of chain packing and the

Table 4. Comparison of Properties of the Polymers[a]

	poly(**1**)[b]	poly(**3a**)	poly(**3b**)	poly(**4a**)	poly(**4b**)
T_0[c] (°C)	420	320	390	360	420
λ_{max} (nm)	375, 430	373, 429[d]	370, 421[e]		
ϵ_{max} (M^{-1} cm^{-1})	4300, 4800	4800, 5400[d]	5200, 5800[e]		
E[f] (MPa)	1460	920	1800	2160	3500
σ_B[f] (MPa)	19	19	17	26	46
γ_B[f] (%)	1.5	2.2	1.0	1.2	1.3
density[g] (g/cm^3)	0.91	0.993	0.976	1.217	1.189
FFV[h]	0.26	0.177	0.190	0.0805	0.102

[a] Obtained with $TaCl_5$ as catalyst at 80 °C for 24 h. [b] Data from refs 4, 11, and 14. [c] Onset temperature of weight loss in TGA measured in air. [d] Measured in $CHCl_3$, concentration 1.27 × 10^{-4} mol/L. [e] Measured in $CHCl_3$, concentration 1.34 × 10^{-4} mol/L. [f] E = Young's modulus, σ_B = tensile strength, and γ_B = elongation at break. [g] Determined by hydrostatic weighing. [h] FFV values were calculated from membrane densities (see text).

Table 5. Gas Permeability Coefficients (*P*) of the Polymers[a]

	P (barrer[b])								
polymer	H_2	He	CO_2	O_2	N_2	CH_4	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	P_{CO_2}/P_{N_2}
poly(**3a**)[c]	330	170	810	160	50	160	3.2	5.1	16.2
poly(**3b**)[c]	380	210	880	190	67	170	2.8	5.2	13.1
poly(**4a**)[d]	56	38	110	8.0	2.4	2.3	3.3	47.8	45.8
poly(**4b**)[d]	86	46	130	15	5.1	9.6	2.9	13.5	25.5

[a] *P* values measured at 25 °C. [b] 1 barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$. [c] Methanol-conditioned. [d] Hexane-conditioned.

amount of space (free volume) available for gas permeation in a polymer matrix. It is defined as[12]

$$\mathrm{FFV} = \frac{v_{\mathrm{SP}} - v_0}{v_{\mathrm{SP}}} \approx \frac{v_{\mathrm{SP}} - 1.3v_{\mathrm{W}}}{v_{\mathrm{SP}}}$$

where v_{sp} and v_0 are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. It is usually assumed that v_0 is 1.3 times as large as the van der Waals volume (v_W), which is calculated by the group contribution methods.[13]

The FFV values of poly(**3a**) and poly(**3b**) were 0.18−0.19, which are more or less smaller than that of poly(**1**)[14] (FFV = 0.26). Desilylation of poly(**3a**) and poly(**3b**) resulted in shrinkage of the polymer membranes, and the densities became higher than those before desilylation (Table 4). Simultaneously, the FFV of poly(**3a**) decreased from 0.177 to 0.0805, and that of poly(**3b**) did from 0.190 to 0.102. This is explicable by the idea that the shrinkage of the membranes due to intermolecular hydrogen bonding predominates over the formation of microvoids due to elimination of the bulky silyl groups in the solid state.

Gas Permeability of the Polymer Membranes. The polymer membranes were conditioned beforehand by immersing in methanol [for poly(**3a**) and poly(**3b**)] or in hexane [for poly(**4a**) and poly(**4b**)] for 24 h and subsequently drying to constant weight at room temperature. Then their gas permeability was measured at 25 °C (Table 5).

The oxygen permeability coefficient (P_{O_2}) of poly(**3a**) was 160 barrers, which is relatively small among those of poly(diphenylacetylene) derivatives; e.g., poly(**1**): P_{O_2} = 1550 barrers, P_{O_2}/P_{N_2} = 3.0;[6] poly[1-phenyl-2-[*p*-(isopropyldimethylsilyl)phenyl]acetylene: P_{O_2} = 500 barrers, P_{O_2}/P_{N_2} = 2.3.[15] The permeability of poly(**3a**) to other gases was also relatively low. The permeability of poly(**3b**) with *meta*-hydroxyl group was somewhat higher to every gas than of the *para*-counterpart, poly(**3a**). The P_{O_2} values of desilylated polymers poly(**4a**) and poly(**4b**) were 8.0 and 15 barrers, respectively, which demonstrate significant decreases of gas permeability after desilylation, presumably owing to the decrease of FFV. In general, polymers bearing hydroxyl groups such as poly(vinyl alcohol) (P_{O_2} = 0.00665 barrers) commonly show very low gas permeability and can be utilized as gas barrier membranes.[16] When this is taken into account, the relatively high gas permeability of poly(**4a**) and poly(**4b**) suggests fairly sparse structures as are common for sterically crowded substituted polyacetylenes.

The gas separation factors for oxygen and nitrogen (P_{O_2}/P_{N_2}) of poly(**3a**) and poly(**4a**) were 3.2 and 3.3, which are very close to each other. A similar tendency was observed in the case of poly(**3b**) and poly(**4b**). In contrast, the gas separation factors of CO_2 and methane (P_{CO_2}/P_{CH_4}) and of CO_2 and nitrogen (P_{CO_2}/P_{N_2}) of poly(**4a**) and poly(**4b**) were 14−48 and appreciably large,[17]

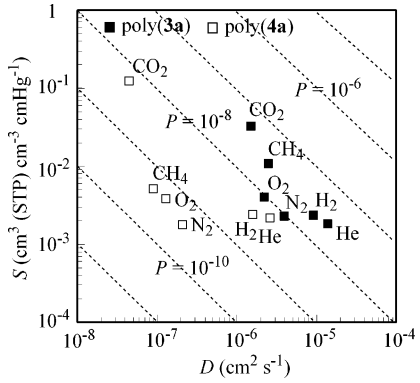


Figure 3. Plot of diffusion coefficient (*D*) vs solubility coefficient (*S*) of poly(**3a**) and poly(**4a**).

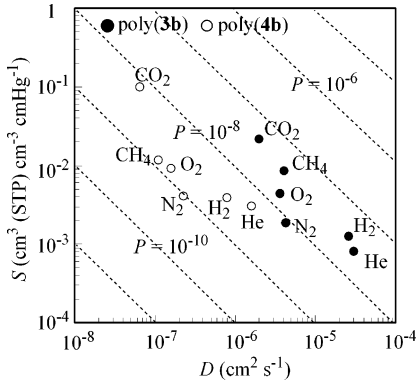


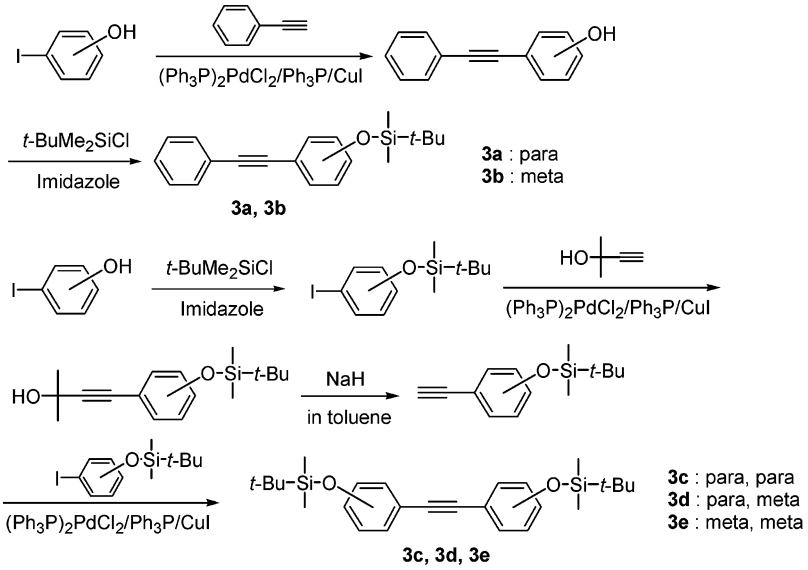
Figure 4. Plot of diffusion coefficient (*D*) vs solubility coefficient (*S*) of poly(**3b**) and poly(**4b**).

indicating that the separation performance for CO_2 remarkably improves upon desilylation. The increases of separation factors of poly(**4a**) against poly(**3a**) were fairly larger than those with poly(**4b**) vs poly(**3b**). It is especially noteworthy that the P_{CO_2}/P_{CH_4} value of poly(**4a**) is located out of the Robeson's upper bound.[18] The methane permeability, P_{CH_4}, remarkably decreases compared to those of not only CO_2 but also small-size gases (H_2, He) upon desilylation. This is reasonable because methane is nonpolar and fairly bulky.

The gas permeability coefficient (*P*) was inspected in more detail by dividing into the gas solubility coefficient (*S*) and gas diffusion coefficient (*D*). The calculation method is explained in the experimental part. The *D* and *S* of poly(**3a**) and poly(**4a**) are plotted in Figure 3 and those of poly(**3b**) and poly(**4b**) in Figure 4.

The *S* of every gas except CO_2 hardly changed upon desilylation, while the *D* significantly decreased. The decrease of *D* can be accounted for both by the elimination of the silyl groups possessing high mobility and by the decrease of FFV. The obvious increase of *S* of CO_2 in both poly(**3a**) and poly(**3b**) can be explained by the idea that the CO_2 molecule strongly interacts with the hydroxyl groups of the polymers.

Scheme 3. Synthesis of Diphenylacetylene Monomers Having Siloxy Groups



Conclusions

In this article, we have demonstrated the synthesis of novel poly(diphenylacetylene) derivatives possessing hydroxyl groups protected with bulky silyl groups and their transformation into poly(diphenylacetylenes) having hydroxyl groups by desilylation using a mixture of TFA/water (4/1). Thus, the synthesis of a new class of polar poly(diphenylacetylene) membranes was achieved. The poly(diphenylacetylenes) with hydroxyl groups showed unique solubility properties. The gas permeability of the poly(diphenylacetylenes) having hydroxyl groups was lower than that of the polymers before desilylation, probably owing to the decrease of microvoids resulting from intermolecular hydrogen bonding. Nevertheless, the relatively high gas permeability of the hydroxylated poly(diphenylacetylenes) among hydroxyl group-bearing polymers suggests a fairly sparse structure as seen in many substituted polyacetylenes. In addition, the membranes of the hydroxylated poly(diphenylacetylenes) exhibited outstanding CO_2 permeability as well as separation performance for CO_2 against methane and nitrogen, which could be explained by the increase of solubility of CO_2 in the polymer membranes, resulting from strong interaction between CO_2 molecules and the hydroxyl groups. Thus, poly(diphenylacetylenes) with polar groups proved to show unique properties, and syntheses of other polar group-containing polymers are in progress.

Experimental Section

Materials. $TaCl_5$ as main catalyst was commercially obtained (Strem) and used without further purification. *n*-Bu_4Sn (Wako, Japan) as cocatalyst was used after distillation. *p*-Iodophenol, *m*-iodophenol, and common solvents such as toluene, ether, and methanol (Wako, Japan) were employed without further purification. Phenylacetylene and *tert*-butyldimethylchlorosilane were purchased from Aldrich. Monomers were synthesized according to Scheme 3, referring to the literature for ethynylation[19] and silylation.[20] Their synthesis and analytical data are detailed below.

1-Phenyl-2-*p*-(*tert*-butyldimethylsiloxy)phenylacetylene (3a). As the first step,[19] a 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and flushed with dry nitrogen. *p*-Iodophenol (25 g, 110 mmol), phenylacetylene (12 g, 110 mmol), bis(triphenylphosphine)palladium dichloride (0.80 g, 1.1 mmol), triphenylphosphine (1.2 g, 4.6 mmol), cuprous iodide (1.3 g, 6.8 mmol), and triethylamine (300 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 (300 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/ethyl acetate = 9/1) provided the desired product [1-phenyl-2-(*p*-hydroxyphenyl)-acetylene] (yield 14 g, 61%) as a white solid. As the second step,[20] a 500 mL three-necked flask was equipped with a dropping funnel and a magnetic stirring bar and flushed with nitrogen. 1-Phenyl-2-(*p*-hydroxyphenyl)acetylene (13 g, 65 mmol), imidazole (13 g, 200 mmol), and *N*,*N*-dimethylformamide (100 mL) were placed in the flask. Then, a solution of *tert*-butyldimethylchlorosilane (13.6 g, 90 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 aqueous sodium hydroxide. The ethereal solution was dried over anhydrous sodium sulfate and then concentrated at reduced pressure. The crude product was purified by flash column chromatography (eluent: hexane) to provide the desired product (new compound; yield 13.3 g, 67%) as a colorless liquid. Purity >99% (^{1}H NMR). IR (KBr): 2957, 1595, 1490, 1260, 880, 852, 843, 615, 497 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.67 (d, 2H, Ar), 7.57 (d, 2H, Ar), 7.37−7.47 (m, 3H, Ar), 6.93 (d, 2H, Ar), 1.13 (s, 9H), 0.33 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 155.9, 133.0, 131.4, 128.3, 127.9, 123.5, 120.2, 116.0, 89.4, 88.2, 25.6, 18.2, −4.5. Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

1-Phenyl-2-*m*-(*tert*-butyldimethylsiloxy)phenylacetylene (3b). This monomer was prepared by the same method as for **3a** using *m*-iodophenol as the starting compound instead of *p*-iodophenol. Yield 70%, colorless liquid, purity >99% (^{1}H NMR). IR (KBr): 2956, 1590, 1494, 1264, 973, 878, 839, 537, 457 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.53 (d, 2H, Ar), 7.32−7.34 (m, 3H, Ar), 7.18 (t, H, Ar), 7.14 (d, H, Ar), 7.00 (s, H, Ar), 6.81 (d, H, Ar), 0.99 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 155.9, 133.0, 131.4, 128.3, 127.9, 123.5, 120.2, 116.0, 89.4, 88.2, 25.6, 18.2, −4.5. Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

***p*,*p*′-Bis(*tert*-butyldimethylsiloxy)diphenylacetylene (3c).** *p*-(*tert*-Butyldimethylsiloxy)iodobenzene and *p*-(*tert*-butyldimethylsiloxy)phenylacetylene were prepared according to a literature procedure.[21] A 500 mL three-necked flask was

equipped with a three-way stopcock and a magnetic stirring bar and flushed with dry nitrogen. *p*-(*tert*-Butyldimethylsiloxy)iodobenzene (5.2 g, 15.6 mmol), *p*-(*tert*-butyldimethylsiloxy)phenylacetylene (3.0 g, 13.0 mmol), bis(triphenylphosphine)palladium dichloride (0.090 g, 0.13 mmol), triphenylphosphine (0.14 g, 0.52 mmol), cuprous iodide (0.15 g, 0.78 mmol), and triethylamine (80 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 4.0 g, 72%) as a white solid. Purity >99% (^{1}H NMR). IR (KBr): 2957, 1603, 1260, 916, 855, 812, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37 (d, 4H, Ar), 6.79 (d, 4H, Ar), 0.98 (s, 18H), 0.20 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 155.6, 132.8, 120.1, 116.3, 88.1, 25.6, 18.3, −4.4. Anal. Calcd for $C_{20}H_{24}$OSi: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

***p*,*m*′-Bis(*tert*-butyldimethylsiloxy)diphenylacetylene (3d).** This monomer was prepared by the same method as for **3c** using *m*-(*tert*-butyldimethylsiloxy)iodobenzene instead of *p*-(*tert*-butyldimethylsiloxy)iodobenzene. Yield 82%, colorless liquid, purity >99% (^{1}H NMR). IR (KBr): 2956, 1600, 1494, 1257, 973, 878, 839, 617, 543, 462 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.40 (d, 2H, Ar), 7.17 (t, H, Ar), 7.10 (d, H, Ar), 6.98 (d, H, Ar), 6.81 (d, H, Ar), 6.79 (d, 2H, Ar), 0.99 (s, 9H), 0.98 (s, 9H), 0.21 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 155.9, 155.4, 133.0, 129.5, 129.3, 125.7, 124.7, 123.8, 122.9, 121.7, 120.2, 116.0, 89.1, 88.1, 25.7, 18.2, −4.4. Anal. Calcd for $C_{20}H_{24}$OSi: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

***m*,*m*′-Bis(*tert*-butyldimethylsiloxy)diphenylacetylene (3e).** This monomer was prepared by the same method as for **3c** using *m*-(*tert*-butyldimethylsiloxy)iodobenzene and *m*-(*tert*-butyldimethylsiloxy)phenylacetylene instead of *p*-(*tert*-butyldimethylsiloxy)iodobenzene and *p*-(*tert*-butyldimethylsiloxy)phenylacetylene. Yield 71%, colorless liquid, purity >99% (^{1}H NMR). IR (KBr): 2956, 1596, 1494, 1262, 970, 878, 839, 542, 460 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.18 (t, 2H, Ar), 7.12 (d, 2H, Ar), 7.00 (s, 2H, Ar), 6.81 (d, 2H, Ar), 0.99 (s, 18H), 0.21 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 155.4, 129.3, 124.9, 124.2, 123.0, 120.5, 88.9, 25.7, 18.2, −4.4. Anal. Calcd for $C_{20}H_{24}$OSi: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

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: $[M]_0$ = 0.10 M, $[TaCl_5]$ = 20 mM, $[n\text{-}Bu_4Sn]$ = 40 mM. The formed polymers were isolated by precipitation into a large amount of methanol, and the polymer yields were determined by gravimetry. Sharp ^{1}H and ^{13}C NMR spectra of these polymers was not observed because of too high viscosity of the solutions. Poly(**3a**); IR (film): 2960, 1605, 1490, 1263, 912, 855, 812, 781, 690, 548 cm^{-1}. Poly(**3b**); IR (film): 2959, 1597, 1481, 1270, 968, 880, 839, 780, 688, 527 cm^{-1}.

Membrane Fabrication and Desilylation. Membranes (thickness ca. 30−80 μm) of poly(**3a**) and poly(**3b**) were fabricated by casting toluene solution of the polymers (concentration ca. 0.50−1.0 wt %) onto a Petri dish. The dish was covered with a glass vessel to slow down solvent evaporation (ca. 3−5 days). With reference to the method described in the literature,[6] the desilylation reaction of the membranes of poly(**3a**) and poly(**3b**) was carried out using trifluoroacetic acid as acid catalyst. A detailed method of desilylation of membranes is as follows: A membrane of polymer was immersed in a mixture of trifluoroacetic acid 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, washed with water, 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. Sharp ^{1}H and ^{13}C NMR spectra of poly(**4a**) and poly(**4b**) were not observed because of either insolubility or high viscosity of solution. Poly(**4a**); IR (film): 3300, 1595, 1490, 1232, 777, 690, 524 cm^{-1}. Poly(**4b**); IR (film): 3300, 1579, 1482, 1230, 780, 689, 523 cm^{-1}.

Measurements. 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 analyses (TGA) were conducted in air with a Parkin-Elmer TGA7 thermal analyzer. Tensile tests were carried out at 25 °C at a strain rate of 0.5 mm/min on a Tensilon model RTM-500 (Orientec Co.). A typical specimen was 50 mm in length, 5.0 mm in width, and 30 μm in thickness.

The densities of membranes were 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 equation:

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

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. Aqueous Na_2NO_3 solution was used as the auxiliary liquid.

The gas permeability coefficients (P) of polymers were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C. The P values were calculated from the slopes of time−pressure curves in the steady state where Fick's law holds.[23] 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 the equation $S \equiv P/D$.

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