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Synthesis and Gas Permeability of Novel Poly(diphenylacetylenes) Having Polyethylene Glycol Moieties

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Summary

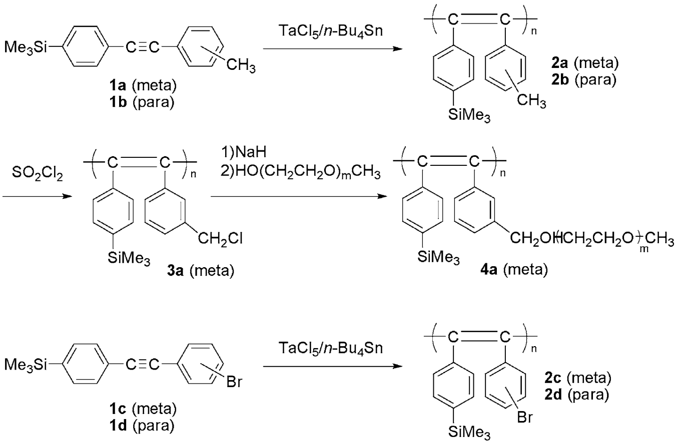
4-Trimethylsilyldiphenylacetylenes with methyl group or bromine atom ($Me_3SiC_6H_4C{\equiv}CC_6H_4R$, R = *m*-$CH_3$, *p*-$CH_3$, *m*-Br, *p*-Br, **1a–d**, respectively) were polymerized with $TaCl_5$/*n*-Bu_4Sn to afford poly(diphenylacetylene) derivatives (**2a–d**). The polymers (**2a–d**) had high molecular weight over $5{\times}10^5$, and gave free-standing membranes by solution casting method. Chlorination of the obtained poly[1-(3-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene] was carried out by using sulfuryl chloride, and then substitution of polyethylene glycol was performed to give poly(diphenylacetylene) possessing polyethylene glycol moieties. Its carbon dioxide permeability (P_{CO_2}) and permselectivity (P_{CO_2}/P_{N_2}) were 2,970 barrers and 9.0, respectively.

Introduction

Substituted acetylene polymers have been synthesized by the polymerization with transition metal catalysts [1–4]. Substituted acetylene polymers exhibit interesting features such as chromism, semiconductivity, paramagnetism, gas permeability, etc. Among substituted acetylenes, diphenylacetylene derivatives polymerize with the $TaCl_5$/*n*-Bu_4Sn catalyst system. The formed poly(diphenylacetylene) derivatives exhibit relatively high gas permeability [5–8], and are expected to be applicable for gas separation membranes. For instance, 1-phenyl-2-(4-trimethylsilyl)phenylacetylene polymerizes to give high-molecular-weight poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] in high yield. Its carbon dioxide permeability coefficient (P_{CO_2}) reaches 4,700 barrers [9], indicating that poly(TMSDPA) is highly CO_2-permeable among various polymers. Carbon dioxide permselectivity (P_{CO_2}/P_{N_2}) is, however, not large enough to be applied for practical use.

It is known that carbon dioxide tend to interact with polar groups in the polymer membranes [10]. Therefore, polymer membranes possessing polar groups show high CO_2 solubility and solubility selectivity. The polymer membranes with ether oxygen moieties such as polyethylene glycol [PEG] are considered to be favorable for CO_2 separation membrane because they have appropriate polarity [11], and it has been reported that PEG membranes exhibit high CO_2 permselectivity [12,13]. This fact suggests that incorporation of PEG moieties to poly(diphenylacetylene) may increase CO_2 permselectivity as maintaining high CO_2 permeability.

In the present work, four kinds of poly(diphenylacetylene) derivatives, poly[1-(3-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene] (**2a**), poly[1-(4-methylphenyl)-2-(4-tri-methylsilyl)phenylacetylene] (**2b**), poly[1-(3-bromophenyl)-2-(4-trimethylsilyl) phenylacetylene] (**2c**), and poly[1-(4-bromophenyl)-2-(4-trimethylsilyl)phenylacetylene] (**2d**) were synthesized, and PEG-substitution was carried out to investigate possibility of their application for gas separation membranes. General properties and gas permeability of their free-standing membranes were examined.



Scheme 1. Synthesis of poly(diphenylacetylene) derivatives

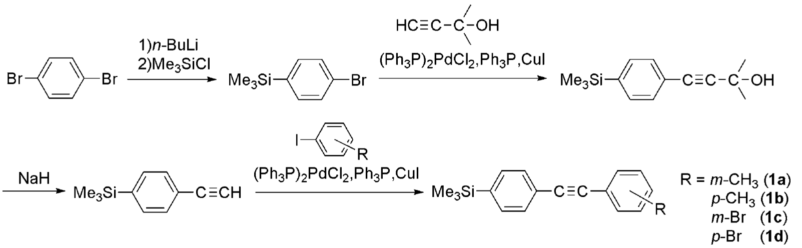
Experimental

Measurements

The molecular weight distributions (MWDs) of polymers were measured by gel permeation chromatography (GPC) in THF (at a 1.0 mL/min flow rate) at 40°C on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex A-80M × 2 and KF-802.5 × 1) and a Shimadzu RID-6A refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from chromatograms based on a polystyrene calibration. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Jeol LA-500 instrument in $CDCl_3$ at room temperature. IR spectra were recorded on a Shimadzu FTIR-8600PC spectrophotometer. Elemental analyses 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

Tantalum chloride (Aldrich) as main catalyst was used without further purification, while *n*-Bu_4Sn (Wako, Japan) as cocatalyst was purified by distillation. *p*-Dibromobenzene, 3-methyl-1-butyne-3-ol, *m*-iodotoluene, *p*-iodotoluene, *m*-bromoiodobenzene, *p*-bromoiodobenzene, and common organic solvents were commercially obtained from Wako, Japan and used without further purification. Polyethylene glycol mono methyl ether [M_n = 350] was purchased from Alfa Aesar and used without purification. Toluene as polymerization solvent was purified by distillation under reduced pressure. 1-(3-Methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1a**), 1-(4-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1b**), 1-(3-bromophenyl)-2-(4-trimethysilyl)phenylacetylene (**1c**), and 1-(4-bromophenyl)-2-[4-(trimethylsilyl)-phenyl]acetylene (**1d**) were synthesized as shown in Scheme 2 according to the literatures [14,15]. The details of the procedures and analytical data of **1a–d** are stated below.



Scheme 2. Synthesis of diphenylacetylene monomers

1-(3-Methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (1a)

A 500-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, dichlorobis(triphenylphosphine)palladium (0.075 g, 0.10 mmol), triphenylphosphine (0.11 g, 0.40 mmol), cuprous iodide (0.12 g, 0.60 mmol), and *m*-iodotoluene (5.9 g, 27 mmol) were placed in the flask and dissolved in triethylamine (100 mL) at room temperature. Then, a solution of *p*-trimethylsilylphenylacetylene (4.7 g, 27 mmol) in triethylamine (50 mL) was added, and stirring was continued for 3 h at 40°C. After the triethylamine in the reaction mixture was evaporated, ether (ca. 300 mL) was added, and the insoluble salt was filtered off. The solution was washed with hydrochloric acid (1.0 mol/L) and then with water. The ethereal solution was dried over anhydrous sodium sulfate. After filtration, ether was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane) to provide the desired product (3.6 g, 0.014 mol, 50%) as colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.52 (s, 4H, Ar), 7.40 (s, 1H, Ar), 7.37 (d, J = 7.6 Hz, 1H, Ar), 7.26 (t, J = 7.6 Hz, 1H, Ar), 7.17 (d, J = 7.6 Hz, 1H, Ar), 2.36 (s, 3H, Ar-CH_3), 0.28 (s, 9H, Si-$(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 140.9, 138.0, 133.2, 132.2, 130.6, 129.1, 128.7, 128.2, 123.6, 123.1, 89.9, 89.2, 21.2, 1.2. Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.47; H, 7.81.

1-(4-Methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (1b)

This monomer was prepared by the same method as for **1a** using *p*-iodotoluene instead of *m*-iodotoluene. Yield 36%, white solid. ^{1}H NMR ($CDCl_3$, ppm): 7.51 (s, 4H, Ar), 7.45 (d, J = 8.0 Hz, 2H, Ar), 7.17 (d, J = 8.0 Hz, 2H, Ar), 2.38 (s, 3H, Ar-CH_3) 0.29 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 140.7, 138.3, 133.2, 131.5, 130.6, 129.1, 123.7, 120.2, 89.9, 88.9, 21.5, -1.2. Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.72; H, 7.67.

*1-(3-Bromophenyl)-2-(4-trimethylsilyl)phenylacetylene (**1c**)*

This monomer was prepared by the same method as for **1a** using *m*-bromoiodobenzene instead of *m*-iodotoluene. Yield 44%, white solid. ^{1}H NMR ($CDCl_3$, ppm): 7.70 (s, 1H, Ar), 7.51 (s, 4H, Ar), 7.47 (d, J = 7.8 Hz, 1H, Ar), 7.46 (d, J = 7.8 Hz, 1H, Ar), 7.22 (t, J = 7.8 Hz, 1H, Ar), 0.29 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 141.5, 134.3, 133.3, 131.3, 130.7, 130.1, 129.7, 125.3, 122.9, 122.1, 90.8, 88.1, -1.3. Anal. Calcd. for $C_{17}H_{17}Si$: C, 62.00; H, 5.20. Found: C, 62.03; H, 5.18.

*1-(4-Bromophenyl)-2-(4-trimethylsilyl)phenylacetylene (**1d**)*

This monomer was prepared by the same method as for **1a** using *p*-bromoiodobenzene instead of *m*-iodotoluene. Yield 48%, white solid. ^{1}H NMR ($CDCl_3$, ppm): 7.51 (s, 4H, Ar), 7.48 (d, J = 8.6 Hz, 2H, Ar), 7.40 (d, J = 8.6 Hz, 2H, Ar), 0.29 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 141.4, 133.2, 133.0, 131.6, 130.6, 123.1, 122.4, 122.3, 90.7, 88.6, -1.3. Anal. Calcd. for $C_{17}H_{17}Si$: C, 62.00; H, 5.20. Found: C, 61.93; H, 5.24.

Polymerization

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen at 80 °C for 3 h under the following conditions: $[M]_0$ = 0.20 M, $[TaCl_5]$ = 20 mM, [*n*-Bu_4Sn] = 40 mM. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube by mixing monomer **1a** (0.53 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. Then the monomer solution was added to the catalyst solution. Polymerization was carried out at 80°C for 3 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 by gravimetry.

Chlorination and PEG-substitution reaction

Chlorination [16] and substitution reaction of PEG [17] were performed according to the literatures.

A 100-mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, polymer **2a** (0.10 g) was placed in the flask and dissolved in carbon tetrachloride (50 mL) at room temperature. Then, sulfuryl chloride (0.015 g) and BPO (0.10 mg) were added, and stirring was continued for 2 h at 75°C. After the reaction, the reaction mixture was poured into a large excess of methanol and the obtained polymer (**3a**) was collected by using glass filter as insoluble product.

A 200-mL flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, polyethylene glycol monomethyl ether (0.44 g), sodium hydride (0.050 g), and THF (50 mL) were placed in the flask. Then, a solution of **3a** (0.075 g) in THF (50 mL) was added, and stirring was continued for 2 h at room temperature. The reaction mixture was poured into methanol, and then polymer **4a** was collected by glass filter. Further, the obtained polymer was dissolved in chloroform and washed with water three times.

Membrane preparation

Membranes (thickness ca. 50–80 μm) of **2a–d**, **3a**, and **4a** were prepared by casting toluene solution of the polymers (concn. 0.5–1.0 wt%) onto a glass plate. The plate was covered with a glass vessel to slow down solvent evaporation (ca. 3–5 days). After drying, the membrane was immersed into methanol for 24 h, and dried again at an ambient condition for 24 h.

Results and discussion

Polymerization

The polymerizations of diphenylacetylene derivatives **1a–d** were carried out with $TaCl_5/n\text{-}Bu_4Sn$ in toluene at 80°C, whose results are summarized in Table 1. It is known that the polymerization with $TaCl_5/n\text{-}Bu_4Sn$ achieves good yield of disubstituted acetylene polymers with high molecular weight [1,2], which is essential for fabrication of free-standing membranes.

The polymerization of **1a** afforded a polymer (**2a**) with high molecular weight in good yield ($M_n = 8.0 \times 10^4$, yield = 84%) (entry 1). Monomer **1b** also polymerized with $TaCl_5/n\text{-}Bu_4Sn$ to give the polymer in good yield, where the M_n value was as high as 275×10^4 (entry 2). Polymerizations of Br-containing monomers **1c** and **1d** provided high-molecular-weight polymers (entries 3 and 4). Noteworthy is that novel high-molecular-weight poly(diphenylacetylene)s having methyl groups or bromine atoms could be synthesized by the polymerization of the corresponding disubstituted acetylene monomers.

Table 1. Polymerization of diphenylacetylene monomers **1a–d**[a]

		polymer[b]		
entry	monomer	Yield (%)	$M_n/10^4$[c]	M_w/M_n[c]
1	**1a**	84	80	2.4
2	**1b**	85	275	2.5
3	**1c**	92	93	3.0
4	**1d**	72	54	3.5

[a]in toluene at 80 °C for 3h; $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM; [b]methanol-insoluble product; [c]measured by GPC

Chlorination and PEG-substitution reaction

Figure 1 depicts the IR spectra of polymers **2a**, **3a**, and **4a**. The spectrum of **3a**, which is chlorinated polymer, exhibited the absorption at ca. 1050 cm^{-1} derived from C-Cl stretching, which was not seen in the spectrum of **2a**. In the spectrum of **4a**, the absorption at ca. 1100 cm^{-1} derived from C-O-C stretching was stronger than that in **3a**. Further, the absorption at ca. 1050 cm^{-1} in the spectrum **4a** decreased compared with that in **3a**. These findings indicate that PEG moieties were substituted to polymer **2a**. Degrees of substitution were calculated from the elemental analyses of **2a**, **3a**, and **4a**. The weight ratio of chlorine in **3a** was found to be 6.38%. The theoretical weight ratio of chlorine should be 11.86% when one chlorine atom is substituted to the repeating unit. From these results, degree of chlorination was found to be ca. 0.54. The weight ratios of carbon and hydrogen in **4a** were found to be 72.78 and 6.84%, respectively, although they are theoretically 81.76 and 7.62% in 2a, 53.08 and 9.21% in a polyethylene glycol moiety. Therefore, degree of PEG-substitution was estimated to be ca. 0.25.

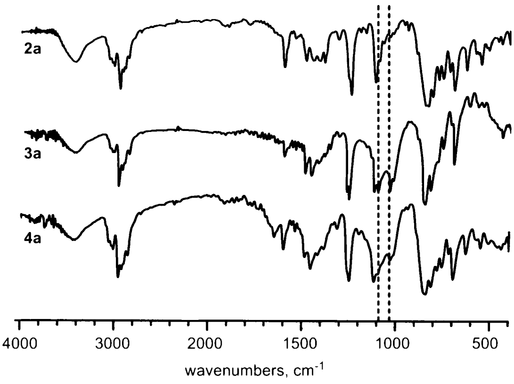


Figure 1. IR spectra of **2a**, **3a**, and **4a**

*Solubility properties of the polymers **2a–d**, **3a**, and **4a***

The solubility properties of polymers **2a–d**, **3a**, and **4a** were studied, whose results are summarized in Table 2. Polymers **2a–d** showed similar solubility properties to each other, and totally dissolved in toluene, $CHCl_3$, Et_2O, THF, and CH_2Cl_2. They were insoluble in polar solvents such as acetone, methanol, and dimethyl sulfoxide. Polymer **3a**, which is chlorinated polymer, also showed good solubility in relatively low polar solvents and dissolved in toluene, $CHCl_3$, and so on, while insoluble in hexane. Polymer **4a**, which is polyethylene glycol-substituted polymer, exhibited the same solubility as that of **2a**. It was found that these poly(diphenylacetylene) derivatives exhibited similar solubility properties even in polyethylene glycol-substituted one. This is reasonable because the PEG content of polymer **4a** is relatively small.

Table 2. Solubility of polymers **2a–d**, **3a**, and **4a**[a]

	hexane	toluene	$CHCl_3$	Et_2O	THF	CH_2Cl_2	acetone	DMSO
2a–d	±	+	+	+	+	+	–	–
3a	–	+	+	+	+	+	–	–
4a	±	+	+	+	+	+	–	–

[a] symbols: + soluble, ± partly soluble, – insoluble

Gas permeability of polymer membranes

The permeability of membranes of **2a–d** to oxygen, nitrogen, and carbon dioxide was examined at 25°C (Table 3). The carbon dioxide permeability coefficients (P_{CO_2}) of membranes of polymers (**2a–d**) were 3060, 9500, 6270, 5400 barrers, respectively. The P_{CO_2} value of poly(TMSDPA) is 4700 barrers, which is nearly to those of the present polymers. It has been reported that the P_{CO_2} values of trimethylsilyl group-containing poly(diarylacetylene) derivatives are in the range of 2100–14000 barrers [18–21]. Therefore, the present polymers **2a–d** were found to show high CO_2 permeability similarly to other poly(diarylacetylene) derivatives. The permeability coefficients of **2a–d** to other gases such as oxygen and nitrogen were also large. These values are larger than that of poly(dimethylsiloxane) [22], which exhibits the highest gas permeability among all the rubbery polymers.

Table 3. Gas permeability coefficients (*P*)[a] and permselectivity of membranes of **2a–d**

	P_{O_2}	P_{N_2}	P_{CO_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
2a	880	450	3060	1.96	6.80
2b	2400	920	9500	2.61	10.3
2c	1920	1200	6270	1.60	5.23
2d	1160	520	5400	2.23	10.4

[a]in the units of 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$ (= 1 barrer)

The results of gas permeability of **2a**, **3a**, and **4a** were shown in Table 4. The P_{CO_2} value of **3a**, which is chlorinated polymer, was 5150 barrers and slightly increased compared with that of **2a**. Carbon dioxide permselectivity (P_{CO_2}/P_{N_2}) of **3a** also improved up to 7.15 from 6.80. PEG-substituted poly(diphenylacetylene) **4a** showed the highest permselectivity among these three polymers, and its P_{CO_2}/P_{N_2} was 9.00. The P_{CO_2} value of **4a** was almost same as that of **2a** irrespective of higher permselectivity. Generally, a trade-off relationship and an upper boundary line are present [23]; i.e. CO_2 permeability decreases when CO_2 permselectivity increases. This finding indicates that PEG moieties in polymer **4a** interact with CO_2 to increase CO_2 solubility in polymer matrix. It was found that the introduction of PEG moieties improves CO_2 permselectivity of poly(diphenylacetylene) derivative without decreasing CO_2 permeability.

Table 4. Gas permeability coefficients (*P*)[a] and permselectivityof membranes of **2a**, **3a**, and **4a**

	P_{O_2}	P_{N_2}	P_{CO_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
2a	800	450	3060	1.96	6.80
3a	1310	720	5150	1.82	7.15
4a	880	330	2970	2.67	9.00

[a]in the units of 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$ (= 1 barrer)

Conclusions

Novel poly(diphenylacetylene)s possessing methyl groups or bromine atoms were synthesized by metathesis polymerization with $TaCl_5$/*n*-Bu_4Sn. Polyethylene glycol-substituted poly(diphenylacetylene) was obtained by the polymer reaction of methyl group-containing poly(diphenylacetylene). Membrane of PEG-substituted poly(diphenylacetylene) exhibited high CO_2 permselectivity compared with membrane of poly(diphenylacetylene) without PEG moieties. It was found that the incorporation of polyethylene glycol moieties to poly(diphenylacetylene) improves CO_2 permselectivity of the polymer membrane.

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