Synthesis of PEG-Functionalized Poly(diphenylacetylene)s and Their Gas Permeation Properties

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ABSTRACT: The polymerizations of 1-(3-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1a**) and 1-(4-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1b**) were carried out with $TaCl_5$-n-Bu_4Sn to give relatively high-molecular-weight polymers (**2a** and **2b**) ($M_n > 5 \times 10^5$). The obtained polymers were brominated by using benzoyl peroxide and N-bromosuccinimide first, followed by substitution reaction of three types of polyethylene glycol. When diethylene glycol was used as a reagent on substitution reaction of meta-substituted polymer, PEG-functionalized poly(diphenylacetylene) with the highest content of oxyethylene unit [**4a(2)**] was obtained, and the degree of substitution was 0.60. The degrees of substitution decreased to 0.15 and 0.08 when the polyethylene glycols with higher molecular weights were used. PEG-substitution reaction to the para-substituted polymers was difficult to proceed, and hence the degree of substitution was 0.18 even when diethylene glycol was used. The CO_2/N_2 separation factor of PEG-functionalized polymer [**4a(2)**] was as large as 28.8, although that of **2a** was 7.41. The other PEG-functionalized polymers also exhibited high CO_2 permselectivity, and their CO_2/N_2 separation factors were over 20. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3504–3509, 2009

Key words: poly(diphenylacetylene); polyethylene glycol; membrane; gas permeation; carbon dioxide

INTRODUCTION

Development of efficient gas-separation systems has been investigated from the aspect of industrial application. Gas-permeable polymer membranes have attracted much attention because they have a possibility to simplify the systems and to save energy.[1–5] Some substituted acetylene polymers are superior in gas permeability due to both their stiff main chain composed of alternating double bonds and the steric repulsion of spherical side groups.[6–8] Generally, disubstituted acetylene polymers are highly gas-permeable and stable in air compared with those from monosubstituted ones. Therefore, the former polymers are promising as gas- separation membranes. For instance, poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] is highly gas-permeable and thermally very stable.[9,10] Its carbon dioxide permeability coefficient (P_{CO_2}) reaches 4700 barrers,[9] indicating that poly(TMSDPA) is one of the most CO_2-permeable polymers among all the synthetic polymers. However, carbon dioxide permselectivity (P_{CO_2}/P_{N_2}) is not large enough to apply to practical use.

It is known that carbon dioxide tend to interact with polar groups in the polymer membranes.[11] 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,[12] and it has been reported that PEG membranes exhibit high CO_2 permselectivity.[13,14] This fact suggests that incorporation of PEG moieties to poly(diphenylacetylene) may increase CO_2 permselectivity as maintaining high CO_2 permeability. In our previous work,[15] poly(TMSDPA)s having PEG moieties were synthesized from poly[1-(3-chloromethylphenyl)-2-(4-trimethylsilyl)phenylacetylene] by substitution of polyethylene glycol monomethyl ether, with the degree of PEG-substitution being as low as 0.20. Its P_{CO_2} and P_{CO_2}/P_{N_2} values were 2970 barrers and 9.00, respectively, which revealed that the incorporation of PEG improves CO_2 permselectivity of poly(TMSDPA). However, its CO_2 permeability and permselectivity were still insufficient for CO_2 separation membranes.

In this work, to synthesize CO_2 permselective PEG-functionalized poly(diphenylacetylene) membranes with high degree of substitution, substitution reaction of polyethylene glycol monomethyl ether was examined for poly[1-(3-bromomethylphenyl)-2-

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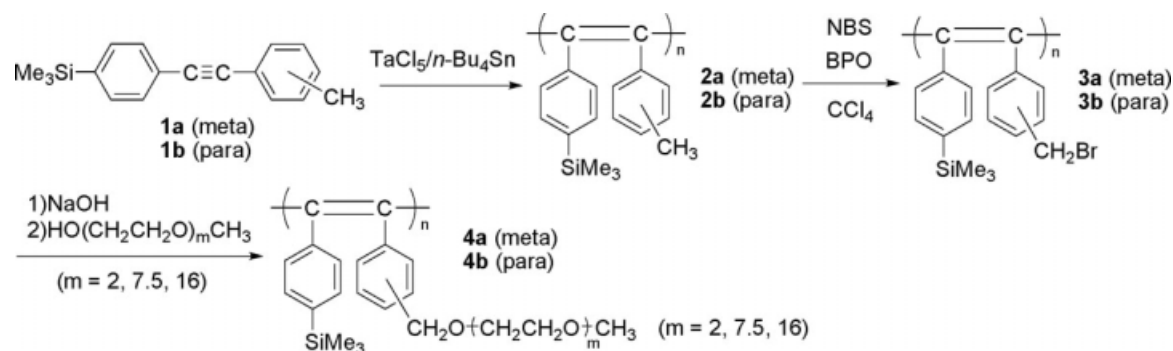
Scheme 1 Synthesis of PEG-functionalized poly(diphenylacetylene)s.

(4-trimethylsilyl)phenylacetylene] (**2a**) and poly[1-(4-bromomethylphenyl)-2-(4-trimethylsilyl)phenylacetylene] (**2b**). To study the effect of PEG-length on gas permeability, three kinds of polyethylene glycol monomethyl ethers were used for PEG-substitution (Scheme 1). Gas permeability and permselectivity of free-standing membranes of PEG-functionalized poly (diphenylacetylene)s were investigated.

EXPERIMENTAL

Measurements

The molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) in chloroform (at a 1.0 mL/min flow rate) at 40°C on a Shimadzu LC-10AD chromatograph equipped with four polystyrene gel columns (Shodex K-805L × 1 and K-804L × 3) 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. Gas permeability coefficients were measured with a Rika-seiki K-315-N gas permeability apparatus at 25°C and 1 atm upstream pressure. The permeability coefficient P expressed in barrer unit (1 barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}) was calculated from the slope of the steady-state line.

Materials

Tantalum chloride (Aldrich) as main catalyst was used without further purification, whereas n-Bu$_4$Sn (Wako, Japan) as cocatalyst was purified by distillation. p-dibromobenzene, 3-methyl-1-butyne-3-ol, m-iodotoluene, p-iodotoluene, N-bromosuccinimide, benzoyl peroxide, and common organic solvents were commercially obtained from Wako, Japan and used without further purification. Di(ethylene glycol) methyl ether [PEG(2)] was purchased from Aldrich and used without purification. Polyethylene glycol mono methyl ethers (M_n = 350 [PEG(7.5)] and M_n = 750 [PEG(16)]) were purchased from Alfa Aesar and used without purification. Toluene as polymerization solvent was purified by distillation. 1-(3-Methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1a**) and 1-(4-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene (**1b**) were synthesized as shown in Scheme 2 according to the literatures.[16,17] The details of the procedures and analytical data of **1a** and **1b** are stated in the previous article.[15]
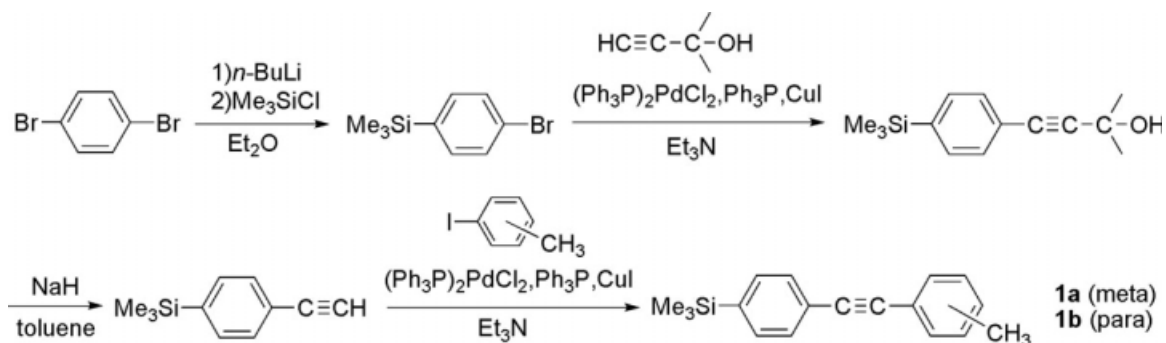
Scheme 2 Synthesis of diphenylacetylene monomers.

Polymerization procedure

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen at 80°C for 24 h under the following conditions: $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, $[n\text{-Bu}_4Sn] = 40$ 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), $n\text{-Bu}_4Sn$ (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 continued 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 by gravimetry.

Bromination and PEG-substitution procedures

Bromination[18] and substitution reactions of PEG[19] were performed according to the literatures. A detailed procedure of reaction is as follows:

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, N-bromosuccinimide (0.067 g) and benzoyl peroxide (1.8 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 acetone to precipitate the polymer and to remove the residual regents. The polymer (**3a**) was collected by using a glass filter and dried under vacuum for 24 h.

A 200-mL flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, di(ethylene glycol) methyl ether (0.13 g), sodium hydroxide (0.044 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 a glass filter. The obtained polymer was washed with methanol and dried under vacuum.

Membrane preparation

Membranes (thickness ca. 40–80 μm) of **2a–d**, **3a**, and **4a** were prepared at 25°C by casting toluene solution of the polymers (concn 0.50–1.0 wt %) onto a Teflon flat plate. The plate was covered with a glass vessel to slow down solvent evaporation (ca. 3–

5 days). After drying, the membrane was peeled off, and further dried under vacuum at 25°C for 24 h.

RESULTS AND DISCUSSION

Polymerization, bromination, and PEG-substitution

In our previous study, high-molecular-weight poly[1-(3-methylphenyl)-2-(4-trimethylsilyl)phenylacetylene] and poly[1-(4-methylphenyl)-2-(4-trimethylsilyl)-phenylacetylene] were obtained by the polymerization with $TaCl_5/n\text{-Bu}_4Sn$ catalyst[15]; however, it was difficult to treat them in polymer reaction because of high viscosity of polymer solution. In this study, the polymerization was performed under the conditions of lower monomer concentration to decrease molecular weights of the polymers. The results of polymerizations were summarized in Table I. The polymerization of **1a** afforded a polymer (**2a**) with a relatively high-molecular weight in good yield ($M_n = 5.3 \times 10^5$, yield = 80%) (entry 1). Monomer **1b** also polymerized with $TaCl_5/n\text{-Bu}_4Sn$ to give a polymer (**2b**) in good yield, where the M_n value was as high as 9.8×10^5 (entry 2). Their molecular weights were slightly lower than those in previous ones.[15] They were still high enough to fabricate tough free-standing membranes.

Figure 1 depicts the IR spectra of polymer **2a**, brominated polymer **3a**, and PEG-functionalized polymer **4a**. The polymers **4a(2)**, **4a(7.5)**, and **4a(16)** represent the polymers substituted by PEG(2), PEG(7.5), and PEG(16), respectively. The spectrum of **3a** exhibited the absorptions at about 1200 and 590 cm^{-1} derived from C—Br stretching, which was not seen in the spectrum of **2a**. To calculate the degree of bromination, the spectrum of the equimolar mixture of monomer **1a** and a benzyl bromide were used as a reference. The ratio of absorptions at 1250 ($\delta_{\prime SiC—H}$) and 590 cm^{-1} ($\delta_{\prime C—Br}$) in spectrum of **3a** was compared with that in spectrum of the reference. Degree of bromination was estimated to be about 0.65. In the spectrum of **4a(2)**, the strong and slightly broad absorption at about 1100 cm^{-1} derived from C—O—C stretching was appeared

TABLE I
Polymerization of Diphenylacetylene Derivatives with $TaCl_5$-$n\text{-Bu}_4Sn$[a]

Entry	Monomer	Polymer[b]		
		Yield (%)	$M_n/10^4$[c]	M_w/M_n[c]
1	**1a**	80	53	2.9
2	**1b**	83	98	3.4

[a] In toluene at 80°C for 3 h; $[M]_0 = 0.20$ M, $[TaCl_5]_0 = 20$ mM, $[n\text{Bu}_4Sn]_0 = 40$ mM.
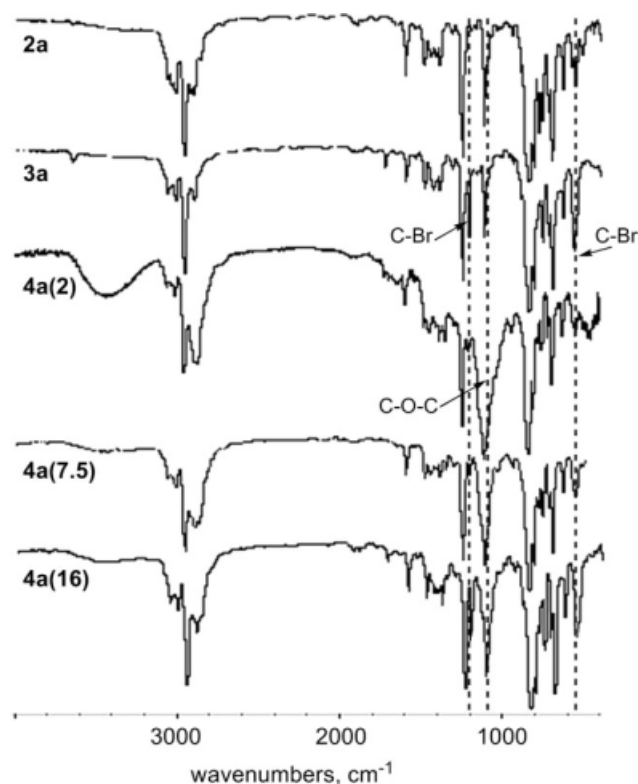[b] Methanol-insoluble product.
[c] Measured by GPC.

Figure 1 IR spectra of meta-substituted poly(diphenylacetylene)s.

although it was not observed in the spectra of **2a** and **3a**. In addition, the absorptions at about 1200 and 590 cm^{-1} almost disappeared after substitution of PEG(2). These findings indicate that PEG moieties were substituted to polymer **3a**. The absorption beyond 3000 cm^{-1} was observed, which is due to H$_2$O adsorbed on polymer surface. Degree of substitution was calculated from the comparison of the ratio of absorptions at 1250 ($\delta_{,SiC-H}$) and 590 cm^{-1} ($\delta_{,C-Br}$) in the spectrum of **3a** and **4a(2)**; i.e., it was estimated from decrease of C—Br bond. Thus, the degree of PEG-substitution was found to be about 0.60.

The absorptions at 1100 cm^{-1} derived from C—O—C stretching in the spectra of **4a(7.5)** and **4a(16)** were weak compared with that in spectrum of **4a(2)**. This suggests that the degrees of substitution were much lower than that in the case of **4a(2)**. From the strength of absorption at 1100 cm^{-1}, the degrees of substitution of PEG(7.5) and PEG(16) were estimated to be about 0.15 and 0.08, respectively. It was found that substitution of PEG becomes more difficult as a molecular weight of PEG becomes higher. This may be mainly due to the poor solubility of **4a(7.5)** and **4a(16)**. In the case of substitution of PEG(2), the polymer solution was homogenous during substitution reaction. On the other hand, polymers **4a(7.5)** and **4a(16)** were readily pre-

cipitated after addition of PEG(7.5) and PEG(16) to the solution of **3a**. Consequently, the highest content of oxyethylene unit was achieved when a PEG with the lowest molecular weight was used as a reactant.

The IR spectra of the para-substituted polymers, **2b**, **3b**, and **4b(2)**, were shown in Figure 2. As the same as the meta-substituted polymers, the absorptions at about 1200 and 590 cm^{-1} derived from C—Br were observed in spectrum of **3b**. However, they were much smaller than those of **3a**, indicating low degree of bromination. The para-substituted polymer showed low solubility, and partially precipitated during the bromination. In the spectrum of **4b(2)**, the weak absorption at 1100 cm^{-1} derived from C—O was observed, which suggests that the content of oxyethylene is very low. The degree of PEG-substitution was estimated to be 0.18 from the comparison of IR spectra in the same way as the case of the meta-substituted polymers. When PEG(7.5) and PEG(16) were used instead of PEG(2), the substitution reaction hardly occurred. Therefore, **4b(7.5)** and **4b(16)** could not be obtained.

Solubility

The solubility of polymers **2**, **3**, and **4** are summarized in Table II. Polymer **2a** was soluble in toluene, CHCl$_3$, Et$_2$O, and THF, but insoluble in polar solvents such as acetone, methanol, and dimethyl sulfoxide. Polymer **3a**, which is a brominated polymer, also showed good solubility in relatively low-polar solvents and totally dissolved in toluene, CHCl$_3$, and so far. Polymer **4a(2)**, which is a PEG(2)-functionalized polymer, exhibited the similar solubility to that of **3a** except that polymer **4a(2)** did not dissolved in Et$_2$O. Polymers having longer polyethylene glycols showed poor solubility. Polymer **4a(7.5)** did
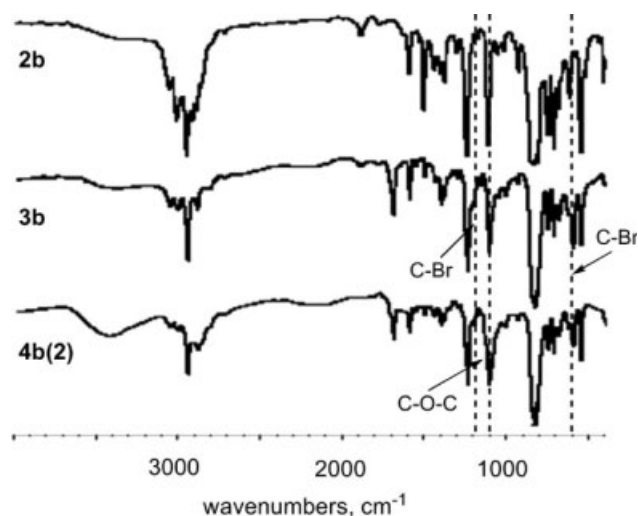

Figure 2 IR spectra of para-substituted poly(diphenylacetylene)s.

TABLE II
Solubility of Poly(diphenylacetylene) Derivatives

Polymer	Hexane	Toluene	$CHCl_3$	Et_2O	THF	Methanol	DMSO
2a	±	+	+	+	+	−	−
3a	−	+	+	+	+	−	−
4a(2)	−	+	+	−	+	−	−
4a(7.5)	−	+	−	−	−	−	−
4a(16)	−	−	−	−	−	−	−
2b	±	+	+	+	+	−	−
3b	−	+	+	−	±	−	−
4b(2)	−	+	±	−	±	−	−

+, soluble; ±, partially soluble; −, insoluble.

not dissolved in any solvents except toluene. Polymer **4a(16)** was insoluble in any solvents. The solubility of **2b** was almost same as that of **2a**. Polymer **3b** was soluble in toluene and $CHCl_3$ and partially soluble in THF. Polymer **4b(2)** exhibited less solubility than **4a(2)**, it was soluble in only toluene.

Gas permeability of polymer membranes

The free-standing membranes of polymers **2a**, **3a**, **4a(2)**, **4a(7.5)**, **2b**, **3b**, and **4b(2)** were prepared by casting toluene solution onto Teflon flat plate, whereas the free-standing membranes of **4a(16)** could not be prepared by solution-casting because of its insolubility. The permeability of membranes of meta-substituted polymers [**2a**, **3a**, **4a(2)**, and **4a(7.5)**] to carbon dioxide, oxygen, and nitrogen was examined at 25°C (Table III). The carbon dioxide permeability coefficient (P_{CO_2}) of membrane of **2a** was 5750 barrers. The P_{CO_2} value of **3a** was 4630 barrers, which is close to that of **2a**. The P_{CO_2} and P_{N_2} values of **3a** were 1240 and 656 barrers, respectively. These values are also close to those of **2a**. Bromination did not significantly affect the gas permeability of this membrane. The carbon dioxide and nitrogen separation factors (P_{CO_2}/P_{N_2}) of **2a** and **3a** were 7.41 and 7.06, respectively, and these permselectivity is not high. For instance, the P_{CO_2}/P_{N_2} values of high gas-permeable disubstituted acetylene polymers are normally in the range of 5.0–12.0.[20–24] On the other

hand, PEG-functionalized poly(diphenylacetylene) derivatives showed high-CO_2 permselectivity. The P_{CO_2}/P_{N_2} value of membrane of **4a(2)** was as large as 28.8, and its P_{CO_2} value was 660 barrers. High CO_2 permselectivity of **4a(2)** is thought to be due to the high affinity of PEG units and CO_2 molecules, and decrease of CO_2 permeability is thought to be due to the increase of polymer chain packing. Introduction of polar groups such as PEG to a polymer generally strengthens intermolecular force, which facilitates molecular packing. The CO_2 permselectivity of **4a(7.5)** was slightly lower than that of **4a(2)**. This is reasonable because the content of oxyethylene unit in **4a(7.5)** is lower than that in **4a(2)**.

The gas permeability coefficients of membranes of para-substituted polymers [**2b**, **3b**, and **4b(2)**] were shown in Table IV. These results were similar to those of the meta-substituted polymers. The P_{CO_2} value of membrane of **2b** was as large as 9500 barrers, which is somewhat larger than that of **2a**. The P_{CO_2} value of membrane of brominated polymer **3b** was 3100 barrers. The P_{CO_2}/P_{N_2} values of membranes of **2b** and **3b** were 10.3 and 9.01 barrers, respectively. These polymer membranes also exhibited usual CO_2 permselectivity. After substitution of PEG(2) into **3b**, the CO_2 permeability decreased to 629 barrers and the permselectivity increased up to 22.5. This permselectivity is relatively high and near those of **4a(2)** and **4a(7.5)** irrespective of low content of oxyethylene unit, indicating that the introduction of PEG at para-position of phenyl rings greater

TABLE III
Gas Permeability Coefficients (P)[a] and Selectivity of 2a, 3a, 4a(2), and 4a(7.5)

polymer	DS[b]	P_{CO_2}	P_{O_2}	P_{N_2}	P_{CO_2}/P_{N_2}	P_{O_2}/P_{N_2}
2a	−	5750	1160	776	7.41	1.50
3a	−	4630	1240	656	7.06	1.89
4a(2)	0.60	660	68.8	22.9	28.8	3.00
4a(7.5)	0.15	251	35.1	10.0	25.1	3.51

[a] Permeability coefficients measured at 25°C and at 1 atm upstream pressure. In the units of 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$ (= 1 barrer).
[b] Degree of PEG substitution.

TABLE IV
Gas Permeability Coefficients (P)[a] and Selectivity of 2b, 3b, and 4b(2)

Polymer	DS[b]	P_{CO_2}	P_{O_2}	P_{N_2}	P_{CO_2}/P_{N_2}	P_{O_2}/P_{N_2}
2b	−	9500	2400	920	10.3	2.61
3b	−	3110	690	345	9.01	2.00
4b(2)	0.18	629	89.1	28.0	22.5	3.14

[a] Permeability coefficients measured at 25°C and at 1 atm upstream pressure. In the units of 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$ (= 1 barrer).
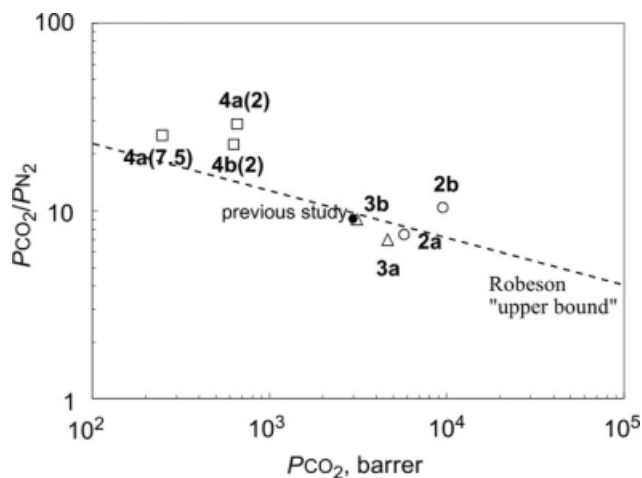[b] Degree of PEG substitution.

Figure 3 Permselectivity versus permeability for the CO_2/N_2 gas pair. The data of previous study (●) from Ref. 15.

effects on CO_2 permselectivity than that at meta-position does.

Figure 3 depicts the CO_2 permeability coefficients (P_{CO_2}) and CO_2 permselectivity (P_{CO_2}/P_{N_2}) of the present polymers. The data of poly(diphenylacetylene) having PEG moieties presented in our previous article[15] is also plotted in Figure 3. It is obviously observed from Figure 3 that the PEG-functionalized polymers [**4a(2)**, **4a(7.5)**, and **4b(2)**] exhibited much higher CO_2 permselectivity than the polymers without PEG moieties and even the previous polymer having PEG moieties. These PEG-functionalized polymers still showed high CO_2 permeability, and their data were located above Robeson's upper bound.[25,26] Thus, PEG-functionalized poly(diphenylacetylene)s proved to show high CO_2 permeability and high CO_2 permselectivity, and hence they are promising candidates of CO_2 separation membranes.

CONCLUSIONS

Substitution reaction of polyethylene glycols with different molecular weights to high gas-permeable poly(diphenylacetylene)s has been successfully carried out using poly[1-(3-bromomethylphenyl)-2-(4-trimethylsilyl)phenylacetylene] as a reactant. The degrees of substitution were calculated from the IR spectra of the resultant polymers. It was found that the degree of substitution became lower as molecular weight of polyethylene glycol became higher. High CO_2 permselectivity was achieved by the introduction of PEG(2) to a poly(diphenylacetylene) derivative, and its P_{CO_2}/P_{N_2} reached up to 28.8. Its P_{CO_2} value was 660 barrers, which is still very high.

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