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ORIGINAL PAPER

Synthesis of poly(*p*-phenyleneethynylene)s bearing oligo-ethylene glycols and their gas permeation properties

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Abstract 1,4-Diiodobenzenes bearing oligo-ethylene glycols [IRC_6H_2IR, R = $OCH_2CH_2OCH_3$ (**1a**), $O(CH_2CH_2O)_2CH_3$ (**1b**), $O(CH_2CH_2O)_3CH_3$ (**1c**)] were polymerized with 1,4-diethynylbenzene in the presence of Pd/Cu catalyst to afford poly(*p*-phenyleneethynylene)s bearing oligo-ethylene glycols (**2a–c**), respectively. Polymer **2a** was insoluble in any solvents, but the other polymers (**2b**, **2c**) were soluble in $CHCl_3$. The weight-average molecular weights of **2b** and **2c** were 5.4×10^4 and 9.6×10^4, respectively, and they gave free-standing membranes by solution-casting method. The densities of membranes of **2b** and **2c** were 1.26 and 1.22 g/cm^3, respectively, and their carbon dioxide permeability coefficients were 12.9 and 13.5 barrers, respectively. The CO_2/N_2 separation factor of membrane of **2b** was as large as 33.7. Membrane of **3b**, which contains triethylene glycols, exhibited higher CO_2 permselectivity, and the CO_2/N_2 separation factor was 50.0.

Keywords Poly(*p*-phenyleneethynylene) · Ethylene glycol · Membrane · Fractional free volume · Gas permeability · Carbon dioxide

Introduction

The separation and storage of the carbon dioxide is important for the preservation of the environment at the current state. The membrane-separation technology can offer a competitive way of separation of carbon dioxide in a relatively low cost and energy conservation [1–3]. Poly(ethylene glycol) is considered as attractive materials for CO_2 separation owing to the fact that the polar ether oxygen has a strong affinity to CO_2 molecule [4, 5]. Therefore, there have been numerous studies

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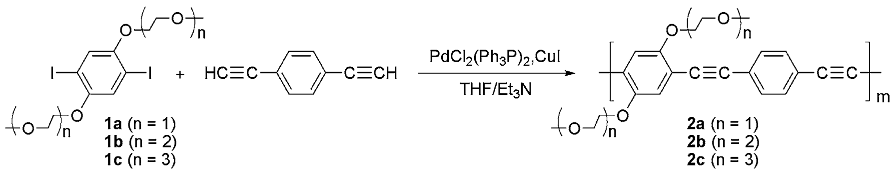


Scheme 1 Synthesis of poly(*p*-phenyleneethynylene)s bearing oligo-ethylene glycols by Pd/Cu-catalyzed polycondensation

on polymers containing poly(ethylene glycol)s for CO_2/N_2 separation [6–12]. However, poly(ethylene glycol) with high molecular weight shows a strong tendency to crystallize, which reduces CO_2 permeability. In order to obtain a novel material with high CO_2/N_2 separation factor and high CO_2 permeability, we designed conjugated polymers bearing oligo-ethylene glycols in the side chains. The rigid main chain of conjugated polymer offers high gas permeability and membrane-forming ability. For instance, poly(diphenylacetylene) bearing oligo-ethylene glycols exhibited high CO_2 permeability ($PCO_2 = 660$ barrers) and relatively high CO_2/N_2 separation factor ($PCO_2/PN_2 = 28.8$) [12]. The CO_2 permeability of poly(diphenylacetylene) is enough high, however, the CO_2/N_2 separation factor is not satisfactory for a practical use. Therefore, a novel conjugated polymer possessing high concentration of ethylene glycol should be synthesized.

We reported that poly(2,5-dialkoxy-*p*-phenyleneethynylene)s (PPEs) exhibited relatively high gas permeability [13] which indicates a possibility of PPEs for a material of gas-separation membrane. Generally, PPEs have been synthesized by acyclic diene metathesis (ADIMET) polymerization and palladium-catalyzed polycondensation [14–20]. The palladium catalyst is tolerant of polar groups such as ethylene glycol. Therefore, PPEs bearing ethylene glycols are expected to be easily synthesized by palladium-catalyzed polycondensation.

In this study, novel poly(*p*-phenyleneethynylene)s bearing oligo-ethylene glycols were synthesized by polycondensation with Pd/Cu catalyst to develop materials for CO_2 separation (Scheme 1). The gas permeability of their free-standing membranes was examined, and it was found that PPEs bearing diethylene glycols or triethylene glycols exhibited pretty high CO_2 permselectivity.

Experimental

Measurements

The molecular weight distributions (MWDs) 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. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Jeol LA-500 instrument in $CDCl_3$

at room temperature. Thermogravimetric analyses (TGA) were conducted with Rigaku TG-DTA 8078G1 under N_2 at a 10 °C/min heating rate. Thermal decomposition temperature was defined as the temperature of 5% weight loss of the sample. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C under 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. The D value was determined by the time lag method using the following equation:

$$D = l^2/6\theta, \qquad (1)$$

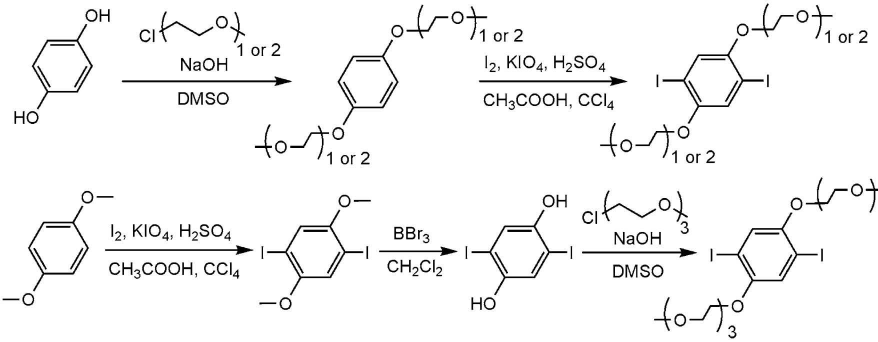
here, l is the membrane thickness and θ is the time lag, which is given by the intercept of the asymptotic line of time–pressure curve to the time axis. The S value was calculated by using equation $S = P/D$.

Materials

2-Chloroethanol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, hydroquinone, 1,4-dimethoxybenzene, boron tribromide, iodine, potassium periodic acid, sulfuric acid, sodium hydroxide, triphenylphosphine, cuprous iodide, palladium (II) chloride, 1,4-diethynylbenzene, and common organic solvents were commercially obtained from Wako Pure Chemicals, Ind., Ltd., and used without further purification. 1-Chloro-2-(2-methoxyethoxy)ethane [$ClCH_2CH_2OCH_2CH_2OCH_3$] and 1-chloro-2-[2-(2-methoxyethoxy)ethoxy]ethane [$ClCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$] were synthesized according to the literature [21]. Monomers **1a**–**c** were synthesized as shown in Scheme 2 referring to the literatures [22, 23]. The analytical data of monomers **1a**–**c** are described below.

2,5-Bis(2-methoxyethoxy)-1,4-diiodobenzene (**1a**)

^1H NMR ($CDCl_3$, ppm): 7.24 (s, 2H, Ar), 4.09 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–), 3.78 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2), 3.48 (s, 6H, –O–CH_3). ^{13}C NMR ($CDCl_3$, ppm): 153.2, 123.6, 86.5, 70.9, 70.2, and 59.5.



Scheme 2 Synthesis of 2,5-disubstituted-1,4-diiodobenzenes

2,5-Bis[2-(2-methoxyethoxy)ethoxy]-1,4-diiodobenzene (**1b**)

^{1}H NMR ($CDCl_3$, ppm): 7.23 (s, 2H, Ar), 4.11 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–), 3.89 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–), 3.79 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–), 3.59 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–), 3.41 (s, 6H, –O–CH_3). ^{13}C NMR ($CDCl_3$, ppm): 153.1, 123.4, 86.4, 72.0, 71.0, 70.3, 69.6, and 59.2.

2,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-1,4-diiodobenzene (**1c**)

^{1}H NMR ($CDCl_3$, ppm): 7.23 (s, 2H, Ar), 4.10 (t, $J = 5.0$ Hz, 4H, Ar–O–CH_2–), 3.88 (t, $J = 5.0$ Hz, 4H, Ar–O–CH_2–CH_2–), 3.79 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–), 3.69 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–), 3.67 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2–), 3.56 (t, $J = 4.8$ Hz, 4H, Ar–O–CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2–), 3.38 (s, 6H, –O–CH_3). ^{13}C NMR ($CDCl_3$, ppm): 153.1, 123.4, 86.4, 71.9, 71.1, 70.7, 70.6, 70.2, 69.6, and 59.0.

Polymerization

Polymerization was carried out in a glass flask equipped with a three-way stopcock under dry nitrogen at 60 °C. A detailed procedure of polymerization is as follows: Monomer **1a** (0.57 g, 1.2 mmol), 1,4-diethynylbenzene (0.15 g, 1.2 mmol), $PdCl_2(Ph_3P)_2$ (0.011 g, 0.016 mmol), CuI (0.042 g, 0.22 mmol), triethylamine (1.5 mL), and chloroform (20 mL) were placed in a 100-mL glass flask. The reaction mixture was heated at 60 °C, and stirred for 24 h. Polymerization was quenched with a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol. Its yield was determined by gravimetry.

Membrane preparation

Polymer membranes (thickness ca. 60–80 μm) were prepared by casting $CHCl_3$ solutions of the polymers (concentration 1.0 wt%) onto a glass plate. The plate was covered with a glass vessel to slow down solvent evaporation (ca. 2 days). After drying, the membrane was peeled off, and it was further dried at room temperature under reduced pressure for 24 h.

Fractional free volume of polymer membranes

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

$$\rho = \rho_0 \times M_A / (M_A - M_L), \tag{2}$$

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. Ion-exchanged water was used as the auxiliary liquid.

Fractional free volume (FFV) is calculated by the following equation:

$$\mathrm{FFV} = \left(v_{sp} - v_o\right)/v_{sp} \approx \left(v_{sp} - 1.3v_w\right)/v_{sp}, \tag{3}$$

where v_{sp} is the polymer specific volume, and v_o is the occupied volume of the polymer. The occupied volume is typically estimated as 1.3 times the van der Waals volume (v_w), which is calculated using the group contribution method [24].

Results and discussion

Polymerization

The polycondensations of monomers **1a–c** with 1,4-diethynylbenzene were carried out using $PdCl_2(Ph_3P)_2/CuI$ catalyst in $CHCl_3$ at 60 °C, whose results are summarized in Table 1. The polymerization of **1a** and 1,4-diethynylbenzene provided a polymer (**2a**) in 92% yield. However, a precipitation was formed during the polymerization, and polymer **2a** was insoluble in any solvents. Monomer **1b** polymerized with 1,4-diethynylbenzene to give a solvent-soluble polymer **2b**, whose number-average molecular weight was 11,400. Monomer **1c** also polymerized to afford a solvent-soluble polymer **2c** with relatively high molecular weights ($M_n = 23{,}900$). However, the complete insoluble polymers **2b** and **2c** were formed when the polymerizations were operated for 24 h.

Figure 1 shows ^1H NMR spectra of polymers **2b** and **2c** in $CDCl_3$. The ^1H NMR spectrum of **2b** shows five signals derived from oxyethylene unit and two signals in the aromatic region assigned to the protons of the oxyethylenes-substituted benzene ring at 7.02 ppm and the 1,4-diethynylbenzene unit at 7.45 ppm. The integrated intensity of the peak at 7.45 ppm is twice as large as the intensity of the peak at 7.02, indicating that the polymerization of **1b** with 1,4-diethynylbenzene afforded

Table 1 Results of polycondensations of **1a–c** with 1,4-diethynylbenzene

Monomers	Time (h)	Polymer[a]		
		Yield (%)	M_n^b	M_w/M_n^b
1a	24	92	Insoluble	
1b	1.5	71	11,400	4.7
1b	24	93	Insoluble	
1c	1.5	65	23,900	4.0
1c	24	88	Insoluble	

In $CHCl_3$ at 60 °C; $(M)_0 = (\text{1,4-diethynylbenzene})_0 = 0.060$ M, $[PdCl_2(Ph_3P)_2] = 0.8$ mM, $[CuI] = 11$ mM, $[Et_3N] = 0.72$ M

[a] Methanol insoluble product

[b] Measured by GPC (polystyrene calibration)

an alternating copolymer. The ^{1}H NMR spectrum of **2c** also indicates the generation of an alternating copolymer. The spectrum shows seven signals derived from the oxyethylene unit and two signals derived from the aromatic protons.

Solubility and thermal property

The solubility properties of polymers **2a**–**c** were studied, whose results are summarized in Table 2. Polymer **2a** with the shortest oxyethylene chains in this study was insoluble in any solvents. Polymer **2b** was completely soluble in $CHCl_3$, and partially soluble in CCl_4, toluene, and THF. Polymer **2c** bearing the longest

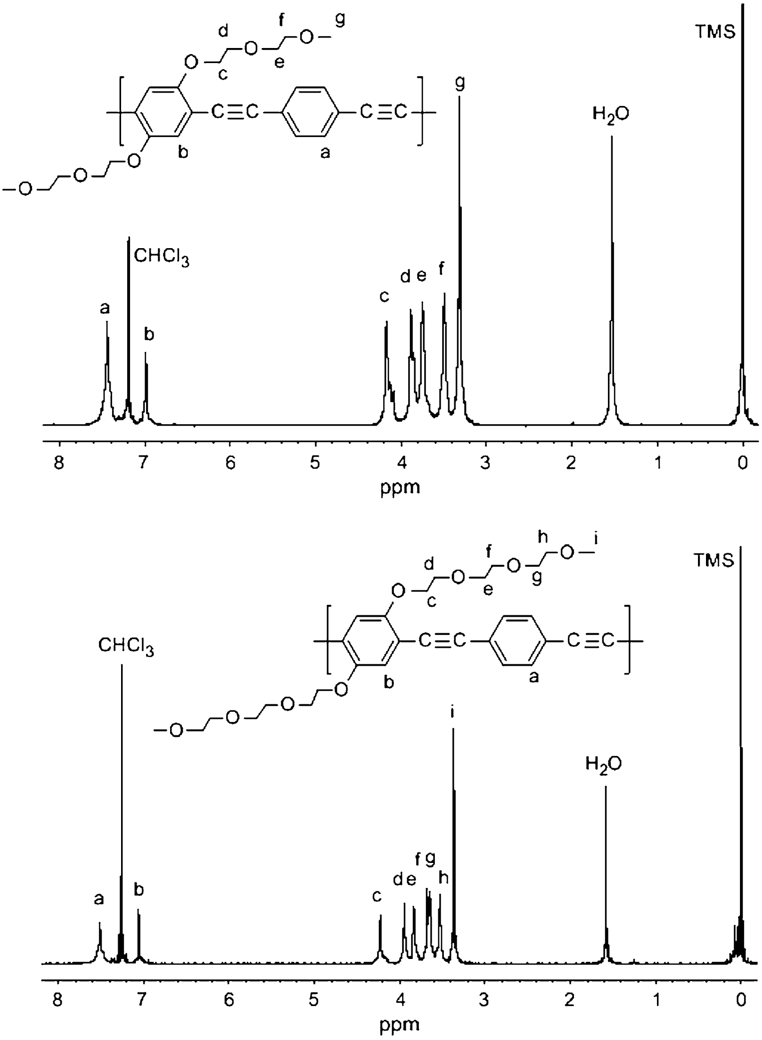


Fig. 1 ^{1}H NMR spectra of polymers **2b** (*top*) and **2c** (*bottom*) in $CDCl_3$

oxyethylene chains dissolved in $CHCl_3$ and THF, while it was insoluble in hexane, CCl_4, and toluene. Neither **2b** nor **2c** dissolved in polar solvents such as acetone, methanol, *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO).

The TGA thermograms for polymers **2a**–**c** are shown in Fig. 2, which indicates two decomposition processes for each of the three polymers. The first process, starting at about 260 °C, is attributed to the degradation of the ethylene glycol side chains. The weight loss at the first process has been running until around 400 °C, and the percentage of weight loss corresponds to the content of oxyethylene unit in each polymer. The second process, starting at about 400 °C, was attributed to the degradation of the main chains.

Density and FFV

Free-standing membranes of polymers **2b** and **2c** could be prepared by solution-casting. However, the membranes of polymer **2a** could not be obtained because it was insoluble in any solvents. Densities and fractional free volume of membranes of **2b** and **2c** are listed in Table 3. The densities of membranes of **2b** and **2c** were 1.26 and 1.22 g/cm^3, respectively, which are much larger than those of poly(*p*-phenyleneethynylene)s with alkyl side groups; e.g., the densities of poly(2,5-dihexyl-*p*-phenyleneethynylene), poly(2,5-didecyl-*p*-phenyleneethynylene), and poly[2,5-di(2-octyl)-*p*-phenyleneethynylene] are 0.965, 0.936, and 0.914 g/cm^3, respectively [13, 25]. The FFV values of

Table 2 Solubility of the polymers

	Hexane	CCl_4	Toluene	$CHCl_3$	THF	Acetone	DMF	DMSO
2a	–	–	–	–	–	–	–	–
2b	–	±	±	+	±	–	–	–
2c	–	–	–	+	+	–	–	–

+ Soluble, ± partially soluble, – insoluble

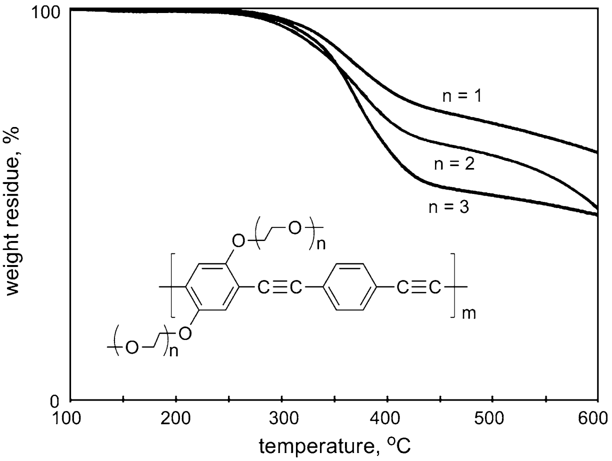


Fig. 2 TGA thermograms of polymers **2a**–**2c** (in N_2, heating rate 10 °C min^{-1})

Table 3 Density, FFV, and gas permeability coefficients (*P*) of polymer membranes

	Density (g/cm^3)	FFV	PN_2 (barrer)[a]	PO_2 (barrer)[a]	PCO_2 (barrer)[a]	PCO_2/PN_2	$DCO_2^b \times 10^{-7}$	$SCO_2^c \times 10^{-3}$
2b	1.26	0.062	0.38	1.12	12.9	33.7	2.13	5.97
2c	1.22	0.073	0.27	0.96	13.5	50.0	1.42	9.45

[a] 1 Barrer = 1×10^{-10} cm^3(STP) cm/(cm^2 s cmHg)

[b] In the units of cm^2/s

[c] In the units of cm^3(STP)/(cm^3 cmHg)

membranes of **2b** and **2c** were 0.062 and 0.073, respectively. They are much smaller than those of the alkyl-substituted poly(*p*-phenyleneethynylene)s (FFV = 0.140–0.158) [13, 25]. Polymers **2b** and **2c** possess polar ethylene glycol side groups, and thus form dense membranes due to the strong intermolecular interaction of the side chains.

Gas permeability

The gas permeability of membranes of **2b** and **2c** to nitrogen, oxygen, and carbon dioxide was examined at 25 °C (Table 3). The nitrogen permeability coefficients (PN_2) of membranes of **2b** and **2c** were 0.38 and 0.27 barrers, respectively, whose values are one magnitude smaller than PPEs with alkyl or alkoxy groups [13, 25]. The oxygen permeability coefficients (PO_2) of membranes of **2b** and **2c** are also much smaller than those of other PPEs. The lower gas permeability of membranes of **2b** and **2c** can be accounted for by the fact that their membranes exhibit small FFV values compared to PPEs with alkyl or alkoxy groups. The PN_2 and PO_2 values of **2c** are slightly smaller than those of **2b**, respectively. However, the PCO_2 value of **2c** is larger than that of **2b**, which may come from the higher content of ethylene glycol of **2c**. The gas permeability of polymers can be divided into two factors, namely, the diffusion and solution terms theoretically in the case of rubbery polymers and approximately with glassy polymers [26]. The *D* value of CO_2 in membrane of **2c** was 1.42×10^{-7} cm^2/s, and that in membrane of **2b** were 2.13×10^{-7} cm^2/s. Interestingly, the *S* value of CO_2 in membrane of **2c** was much larger than that of **2b**. This result can be explained by the idea that the CO_2 molecule strongly interacts with oxyethylene unit of the polymer. Unfortunately, the *D* and *S* values of N_2 and O_2 could be estimated because the time lags on N_2 and O_2 permeability measurements could not be clearly observed.

Figure 3 depicts the CO_2 permeability coefficients (PCO_2) and CO_2/N_2 separation factor (PCO_2/PN_2) of the present polymers. The data of poly(*p*-phenyleneethynylene)s having alkyl or alkoxy groups [13, 25] are also plotted in Fig. 3. It is clearly observed from Fig. 3 that the PPEs in this study (**2b**, **2c**) exhibited much higher CO_2 permselectivity than the PPEs possessing alkyl and alkoxy groups. The data in this study get close to Robeson's upper bound [27], indicating that they are the promising candidates of CO_2 separation membranes.

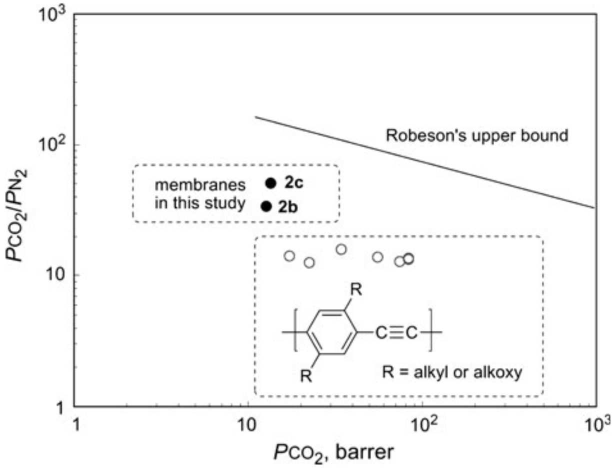


Fig. 3 Permselectivity versus permeability for the CO_2/N_2 gas pair. The data of previous study (*open circle*) from [13, 25]

Conclusions

Poly(*p*-phenyleneethynylene)s bearing ethylene glycols (**2a**–**c**) were synthesized by Pd/Cu-catalyzed polycondensation with 1,4-diethynylbenzene. Poly(*p*-phenyleneethynylene) bearing monoethylene glycols (**2a**) was insoluble, but poly(*p*-phenyleneethynylene)s with diethylene glycols and triethylene glycols (**2b**, **2c**) exhibited solvent-solubility, and gave their free-standing membranes by solution-casting. The PCO_2/PN_2 of membranes of **2b** and **2c** were 33.7 and 50.0, respectively. These permselectivity is pretty high compared to the previously-reported poly(*p*-phenyleneethynylene)s. This implies that introduction of oligo-ethylene glycol is effective in improvement of CO_2 permselectivity on membranes of poly(*p*-phenyleneethynylene)s.

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