

Gas permeation properties of poly(2,5-dialkyl-*p*-phenyleneethynylene) membranes

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Summary

Dipropynylbenzenes with alkyl groups ($\text{CH}_3\text{C}\equiv\text{RC}_6\text{H}_2\text{RC}\equiv\text{CCH}_3$, $\text{R} = n\text{-C}_6\text{H}_{13}$, $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_{10}\text{H}_{21}$, **1a–c**, respectively) were polymerized with $\text{Mo}(\text{CO})_6$ to afford solvent-soluble poly(2,5-dialkyl-*p*-phenyleneethynylene)s (**2a–c**). The polymers (**2a–c**) had high molecular weight over 3×10^4 , and gave free-standing membranes by solution casting method. According to thermogravimetric analysis (TGA), these poly(*p*-phenyleneethynylene)s showed high thermal stability ($T_0 \geq 380^\circ\text{C}$). The densities of membranes of poly(2,5-dialkyl-*p*-phenyleneethynylene)s (**2a–c**) were 0.936–0.965, and their fractional free volume (FFV) were relatively large (ca. 0.14–0.15). The oxygen permeability coefficients (P_{O_2}) of membranes of **2a–c** were 4.88, 7.06, and 16.6 barrers, respectively.

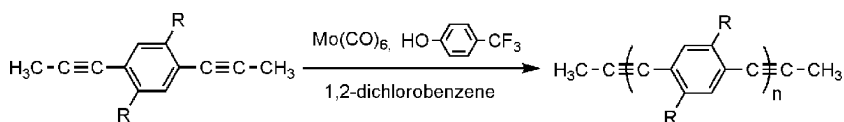
Introduction

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 possibility to simplify the systems and to save energy [1–5]. A huge array of polymers such as substituted polyacetylenes [6–9], polyimides [10–13], polysulfones [14–17], polysiloxanes [18–20], polycarbonates [21–24], cellulose derivatives [25–27] have been studied as gas separation membrane materials. However, there are a few polymers which have sufficient performance to apply to practical use. Therefore, the design and synthesis of novel polymers are essential from the viewpoint of industrial issue.

A variety of poly(phenyleneethynylene)s [PPEs] have been researched intensively because of their optical and electronic properties [28–30]. PPEs possess rigid main chain composed of both benzene ring and triple bond. Substituted polyacetylenes show very high gas permeability because their membranes have large fractional free volume (FFV) due to both their stiff main chain composed of alternating double bonds and the steric repulsion of bulky substituents [8]. This fact indicates that substituted PPEs may exhibit high gas permeability. However, gas permeation properties of membranes of PPEs have never been known so far. Generally, PPEs are synthesized by the palladium-catalyzed polycondensation of diiodobenzene with diethynylbenzene in an amine as solvent [31–35]. However, the obtained PPEs have relatively low

molecular weight, and the degrees of polymerization (P_n) are more in the region of $P_n = 20\text{--}40$. Therefore, PPEs obtained by the palladium-catalyzed polycondensation are difficult to apply for separation membranes. Acyclic diyne metathesis (ADIMET) is reported as another method for synthesis of PPEs [36–39]. ADIMET polymerizations of dipropynylated benzenes by mixing $\text{Mo}(\text{CO})_6$ and a suitable phenol afford high-molecular-weight PPEs in good yields. In most cases, the obtained P_n exceed 50. PPEs obtained by ADIMET polymerization can be used for separation membranes due to their high molecular weights.

In the present study, three types of poly(2,5-dialkyl-*p*-phenyleneethynylene)s, poly(2,5-di-*n*-hexyl-*p*-phenyleneethynylene) (**1a**), poly(2,5-di-*n*-octyl-*p*-phenyleneethynylene) (**1b**), and poly(2,5-di-*n*-decyl-*p*-phenyleneethynylene) (**1c**), were synthesized by ADIMET polymerization to investigate possibility of their application to gas separation membranes. General properties and gas permeability of their free-standing membranes were examined.



Scheme 1. Synthesis of poly(2,5-dialkyl-*p*-phenyleneethynylene)s by ADIMET polymerization

Experimental

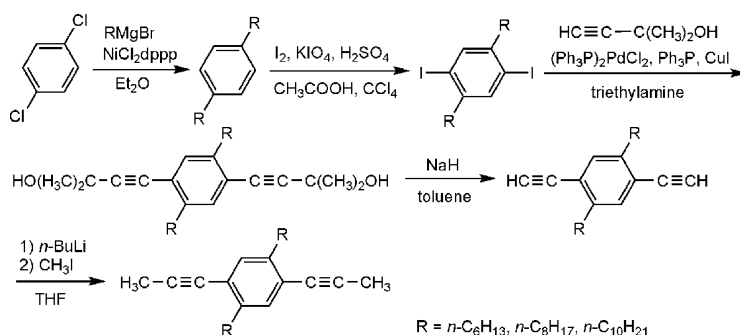
Measurements

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 \times 1 and K-804L \times 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. IR spectra were recorded on a Shimadzu FTIR-8600PC spectrophotometer. Elemental analyses of monomers were performed at the Microanalytical Center of Kyoto University. Thermogravimetric analyses (TGA) were conducted with Rigaku TG-DTA 8078G1 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.

Materials

Molybdenum hexacarbonyl, 4-trifluoromethylphenol, 1,4-dichlorobenzene, 1-bromohexane, 1-bromooctane, 1-bromodecane, 3-methyl-1-butyne-3-ol, iodomethane, and common organic solvents were commercially obtained from Wako, Japan and used without further purification. 1,2-Dichlorobenzene as polymerization solvent was purified by distillation under reduced pressure. 2,5-Dihexyl-*p*-dipropynylbenzene (**1a**)

and 2,5-dioctyl-*p*-dipropynylbenzene (**1b**) were synthesized as shown in Scheme 2 according to the literatures [37, 38]. 2,5-Didodecyl-*p*-dipropynylbenzene (**1c**) was synthesized in the same method as for **1a** and **1b**. The details of the procedures and analytical data of **1c** are stated below.



Scheme 2. Synthesis of a series of 2,5-dialkyl-*p*-dipropynylbenzenes

2,5-Didodecyl-*p*-dipropynylbenzene (**1c**)

To a 500 mL, three-necked, round-bottom flask, equipped with a magnetic stirring bar and dropping funnel, were added 150 mL of Et₂O and 5.5 g (0.23 mol) of magnesium. A solution of bromodecane (50 g, 0.23 mol) in Et₂O (50 mL) was slowly added to the flask through dropping funnel at 0°C, and the mixture was stirred for 24 h at room temperature. 1,4-Dichlorobenzene (13 g, 0.090 mol) in Et₂O (50 mL) and [1,3-bis(diphenylphosphino)propane]dichloronickel (II) were slowly added to the mixture at 0°C, and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture was washed with hydrochloric acid (1.0 mol/L) and then with water. The solution was dried over anhydrous sodium sulfate, and then concentrated at reduced pressure. The crude product was used for next reaction without purification.

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, the crude product (32 g), acetic acid (150 mL), sulfuric acid (20 mL), potassium periodic acid (5.2 g, 0.023 mol), and iodine (28 g, 0.11 mol) were added into the flask, and the mixture was stirred at 90°C for 15 h. The reaction mixture was cooled down to room temperature and poured into 800 mL of cold water. The precipitates was collected by filtration and dissolved in Et₂O. The ethereal solution was washed with sodium thiosulfate three times, and then dried over anhydrous sodium sulfate. Purification of the crude product by silica gel column chromatography (eluent: hexane) provided 2,5-didodecyl-*p*-diiodobenzene (20 g, 61%) as white solid.

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, 2,5-didodecyl-*p*-diiodobenzene (20 g, 0.032 mol), dichlorobis(triphenylphosphine)palladium (0.077 g, 0.11 mmol), cuprous iodide (0.12 g, 0.64 mmol), and triphenylphosphine (0.11 g, 0.43 mmol) were placed in the flask and dissolved in triethylamine (250 mL) at room temperature. Then, a solution of 3-methyl-1-butyne-3-ol (5.5 g, 0.064 mol) in triethylamine (50 mL) was added, and stirring was continued for 5 h at 80°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 placed in another flask equipped with a reflux condenser and magnetic stirring bar. Toluene (200 mL) and sodium hydride (1.4 g, 0.057 mol) were added into the flask and stirred at reflux temperature for 3 h. After cooling to room temperature, the reaction mixture was washed with hydrochloric acid (1.0 mol/L) and then with water. The solution was dried over anhydrous sodium sulfate. Toluene was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane) to give 2,5-didecyl-*p*-diethynylbenzene (7.9 g, 0.021 mol, 69%) as white solid.

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, 2,5-didecyl-*p*-diethynylbenzene (7.9 g, 0.021 mol) and tetrahydrofuran (THF) (200 mL) were added into the flask. *n*-Butyllithium hexane solution (1.6 mol/L, 28 mL, 0.044 mol) was slowly added at -78°C through dropping funnel, and the mixture was stirred for 1 h at -78°C . Keeping the low temperature of the reaction mixture, iodomethane (14 mL, 0.22 mol) was added through dropping funnel. After the addition, the reaction mixture was stirred at room temperature for 3 h. After the THF in the reaction mixture was evaporated, ether (ca. 200 mL) was added. The solution was washed with 1N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate. Purification of the crude product by silica gel column chromatography (eluent: hexane) provided the desired product (7.0 g, 0.016 mol, 76%) as white solid. IR (KBr, cm^{-1}): 2949, 2868, 2228, 1491, 1426, 1426, 1371, 1250, 994, 895, 724. ^1H NMR (CDCl_3 , ppm): 7.16 (s, 2H, Ar), 2.65 (t, $J = 7.7$ Hz, 4H, Ar- CH_2), 2.08 (s, 6H, $\text{C}\equiv\text{C}-\text{CH}_3$), 1.58 (m, 4H, Ar- CH_2-CH_2), 1.31–1.26 (m, 28H, Ar- $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_7$), 0.88 (t, $J = 7.1$ Hz, 6H, Ar- $\text{CH}_2-\text{CH}_2-(\text{CH}_2)_7-\text{CH}_3$). ^{13}C NMR (CDCl_3 , ppm): 141.7, 132.1, 122.5, 89.7, 78.5, 33.8, 31.9, 30.4, 29.66, 29.58, 29.47, 29.41, 29.3, 22.7, 14.1, 4.5. Anal. Calcd. for $\text{C}_{32}\text{H}_{50}$: C, 88.41; H, 11.59. Found: C, 88.32; H, 11.69.

Polymerization

Polymerization was carried out in a glass tube equipped with a three-way stopcock under dry nitrogen at 150°C . A detailed procedure of polymerization is as follows: Monomer **1a** (0.50 g), $\text{Mo}(\text{CO})_6$ (0.019 g), 4-(trifluoromethyl)phenol (0.25 g), and 1,2-dichlorobenzene (16 mL) were placed in a 30-mL glass tube. The reaction mixture was heated at 150°C , removing butyne by a slow stream of nitrogen. After 24 h, polymerization was quenched with a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol. To remove the phenol, the polymer was dissolved in chloroform, and washed with 10% sodium hydroxide. Its yield was determined by gravimetry.

Membrane preparation

Membranes (thickness ca. 50–80 μm) of **2a–c** were prepared by casting carbon tetrachloride solution of the polymers (concn. 1.0–1.5 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.

FFV of polymer membranes

The densities of membranes were 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:

$$\rho = \rho_0 \times M_A / (M_A - M_L) \quad (1)$$

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

FFV is calculated by the following equation:

$$\text{FFV} = (v_{\text{sp}} - v_0) / v_{\text{sp}} \approx (v_{\text{sp}} - 1.3 v_w) / v_{\text{sp}} \quad (2)$$

where v_{sp} is the polymer specific volume, and v_0 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 [40].

Results and discussion

Polymerization

The polymerizations of 2,5-dialkyl-*p*-dipropynylbenzenes **1a–c** were carried out by using $\text{Mo}(\text{CO})_6/p$ -(trifluoromethyl)phenol catalyst in 1,2-dichlorobenzene at 150°C by referring to the literature [37], whose results are summarized in Table 1.

At first, the effect of initial monomer concentration was examined (entries 1–3). The polymerization of **1a** afforded polymer (**2a**) with relatively high molecular weight in good yield ($M_n = 7.7 \times 10^3$, yield = 80%). When the initial monomer concentration increased, the M_n of obtained polymers decreased. The polymerization was carried out for 16 and 48 h (entries 4 and 5). When polymerization time was 16 h, the M_n of obtained polymer was similar to that of the polymer obtained for 24 h, but the polymer yield was lower and 24%. On the other hand, the polymerization of **1a** for 48 h gave high-molecular-weight polymer in good yield ($M_n = 16 \times 10^3$, yield = 78%). When the polymerization catalyst concentration ($[\text{Mo}(\text{CO})_6]$) was increased and 3.0 mM, the M_n of obtained polymer reached up to 31×10^3 irrespective of shorter polymerization time (entry 6). From these results, it is concluded that the polymerization in high catalyst concentration is the most favorable among the polymerizations examined to obtain a high-molecular-weight polymer in high yield.

Monomer **1b** also polymerized with $\text{Mo}(\text{CO})_6/p$ -(trifluoromethyl)phenol to give the polymers in good yields both for 4 and 6 h, where the M_n values were as high as 36 and 41×10^3 , respectively (entries 7 and 8). The difference of polymerizability between **1a** and **1b** is presumably derived from the purity of the monomers because **1a** and **1b** have a similar chemical structure. Polymerization of **1c** in 3.0 mM of catalyst concentration also provided high-molecular-weight polymer compared to in 1.0 mM of catalyst concentration (entries 9 and 10).

Figure 1 shows ^1H NMR spectra of monomer **1c** and polymer **2c** obtained by the polymerization in 3.0 mM of catalyst concentration (Table 1, entry 10). Polymer **2c** exhibits peaks derived from alkyl group c–f and benzene ring b similar to monomer **1c**. Although the propyne end group should appear as a singlet at 2.05 ppm, the end group could not be detected because of high molecular weight of polymer **2c**.

Therefore, the degree of polymerization could not be estimated by end group integration. Polymers **2a** and **2b** also exhibit the similar peaks to corresponding monomers except propyne end groups, and the degrees of polymerization could not be calculated from proton NMR. It is noteworthy that the high-molecular-weight poly(*p*-phenyleneethynylene)s having hexyl, octyl, and decyl groups could be synthesized by ADIMET polymerization of the corresponding dipropynylated benzene.

Table 1. ADIMET polymerization of monomers **1a–c**^a

Monomer	[M] ₀ (M)	[Mo(CO) ₆] (mM)	Time (h)	polymer ^b		
				Yield (%)	<i>M_n</i> /10 ^{3c}	<i>M_w</i> / <i>M_n</i> ^c
1a	0.10	1.0	24	80	7.7	3.7
	0.20	1.0	24	89	3.4	2.1
	0.50	1.0	24	68	6.5	3.1
	0.10	1.0	16	24	9.9	3.2
	0.10	1.0	48	78	16	3.9
	0.10	3.0	9	62	31	7.3
1b	0.10	1.0	4	70	36	6.2
	0.10	1.0	6	73	41	7.2
1c	0.10	1.0	24	78	4.8	1.9
	0.10	3.0	9	57	30	2.9

^ain 1,2-dichlorobenzene at 150°C; [*p*-(trifluoromethyl)phenol] = 0.10 M; ^bmethanol-insoluble product; ^cmeasured by GPC

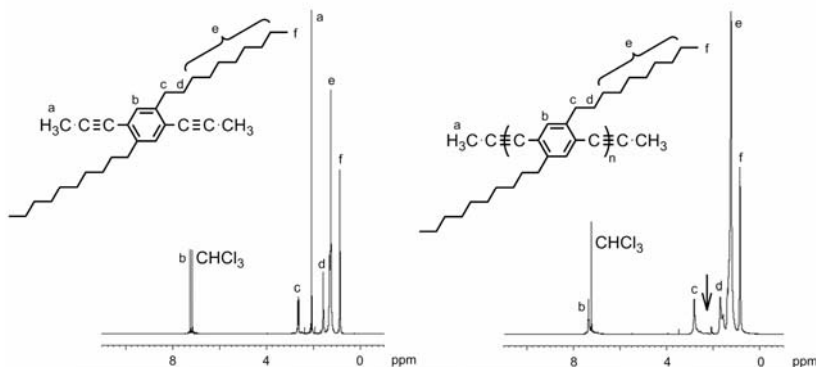


Figure 1. ¹H NMR spectra of monomer **1c** and polymer **2c**

Solubility and thermal properties of the polymers **2a–c**

Properties of polymers **2a–c** were examined by using the polymer samples with the highest molecular weights among this study (Table 1, entries 6, 8, and 10, respectively).

The solubility properties of polymers **2a–c** were studied, whose results are summarized in Table 2. Although poly(*p*-phenyleneethynylene) without alkyl groups was insoluble in any solvents, polymer **2a** with hexyl groups totally dissolved in CCl₄ and CHCl₃. It was insoluble in hexane, toluene, ethyl ether, tetrahydrofuran (THF), CH₂Cl₂, and polar solvents such as acetone, methanol, *N,N*-dimethylformamide, and

dimethyl sulfoxide. Polymer **2b** showed similar solubility properties to that of **2a**, while **2b** was partly soluble in THF. Polymer **2c** showed good solubility and dissolved even in toluene, THF, CH_2Cl_2 as well as CCl_4 and CHCl_3 .

Table 2. Solubility of polymers **2a–c**^a

	hexane	CCl_4	toluene	CHCl_3	Et_2O	THF	CH_2Cl_2	acetone	DMSO
2a	–	+	–	+	–	–	–	–	–
2b	–	+	–	+	–	±	–	–	–
2c	–	+	+	+	–	+	+	–	–

^aSymbols: + soluble, ± partly soluble, – insoluble

The thermal stability of polymers **2a–c** was examined by thermogravimetric analysis in N_2 (Figure 2). Thermal decomposition temperatures (5% weight loss) of **2a**, **2b**, and **2c** were all approximately 350°C , indicating good thermal stability. This initial decomposition is attributed to the decomposition of the alkyl side chains, and the decomposition starting at around 500°C is attributed to the decomposition of the main chain [41].

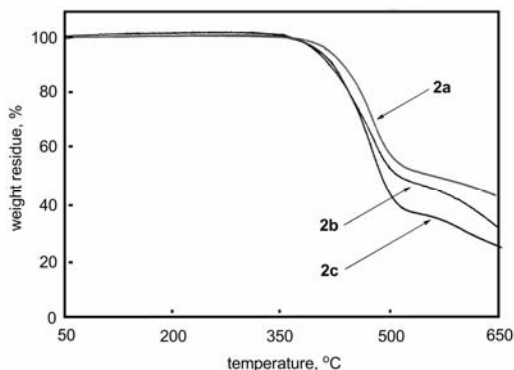


Figure 2. TGA curves of polymers (in N_2 , heating rate $10^\circ\text{C}/\text{min}$)

Density, FFV, and gas permeability of polymer membranes

The densities and fractional free volume (FFV) of membranes of **2a–c** are listed in Table 3. The densities of membranes of **2a–c** were 0.965 , 0.953 , and $0.936 \text{ g}/\text{cm}^3$, respectively, which are relatively low among hydrocarbon polymers; e.g., the densities of crystalline polystyrene, amorphous polystyrene, and poly(*p*-phenylenevinylene) are 1.12 , 1.04 , $1.24 \text{ g}/\text{cm}^3$, respectively [42]. The fractional free volumes (FFVs) of membranes of **2a–c** were 0.140 , 0.141 , and 0.150 , respectively. Polymer **2c** has the largest FFV value among these three poly(2,5-dialkyl-*p*-phenyleneethynylene)s. These results indicate that long alkyl chain prevents polymer chain to pack together.

The permeability of membranes of **2a–c** to oxygen, nitrogen, and carbon dioxide was examined at 25°C (Table 3). The oxygen permeability coefficients (P_{O_2}) of membranes of polymers (**2a–c**) were 4.88 , 7.06 , 16.6 barrers, respectively. The P_{O_2} values increase as alkyl chain becomes longer. This trend is in agreement with the result of fractional free volume of membranes. Interestingly, the P_{O_2} value of decyl

group-containing **2c** is nearly to that of natural rubber, which is rubbery polymer and known to be relatively high gas permeable [43]. The permeability of **2a–c** to other gases such as N₂ and CO₂ exhibited similar tendencies to the case of oxygen. The N₂ and CO₂ permeability coefficients (P_{N_2} and P_{CO_2}) of **2c** were 5.86 and 74.3 barrers, respectively, and the largest among those of the present polymers. The oxygen/nitrogen separation factors (P_{O_2}/P_{N_2}) of all the polymers **2a–c** were in the range of 2.70–3.24.

Table 3. Density, FFV, and gas permeability coefficients (P)^a of polymer membranes

	density(g/cm ³)	FFV	P_{O_2}	P_{N_2}	P_{CO_2}
2a	0.965	0.140	4.88	1.81	22.7
2b	0.953	0.141	7.06	2.18	34.4
2c	0.936	0.150	16.6	5.86	74.3

^ain the units of 1×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ (= 1 barrer)

Conclusions

Poly(*p*-phenyleneethynylene)s possessing different kinds of alkyl groups such as hexyl, octyl, and decyl groups were synthesized by ADIMET polymerization. The free-standing membranes of polymers (**2a–c**) could be prepared by solvent-casting method. Polymers **2a–c** exhibited high thermal stability ($T_0 \sim 380^\circ\text{C}$). The FFVs of membranes of poly(2,5-dialkyl-*p*-phenyleneethynylene)s (**2a–c**) were appreciably large, and they showed high gas permeability. This study is the first example of permeability of poly(phenyleneethynylene)s although electronic properties of various poly(*p*-phenyleneethynylene)s have been reported.

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