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ORIGINAL PAPER

# Synthesis and gas permeability of poly (*p*-phenyleneethynylene)s having bulky alkoxy or alkyl groups

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**Abstract** Dipropynylbenzene with branched alkoxy and alkyl groups [$CH_3C\equiv CRC_6H_2RC\equiv CCH_3$, R = 2-methylpropoxy (**1a**), 3-methylbutoxy (**1b**), 4-methylpentoxy (**1c**), cyclohexylmethoxy (**1d**), 2-ethylhexoxy (**1e**), 2-octoxy (**1f**), 2-ethylhexyl (**1g**), and 2-octyl (**1h**)] were polymerized with $Mo(CO)_6$ in the presence of 4-(trifluoromethyl)phenyl to afford poly(2,5-di(alkoxy or alkyl)-*p*-phenyleneethynylene)s (**2a**–**h**). Polymer **2a** was insoluble in any solvents, but the other polymers (**2b**–**h**) were soluble in common organic solvents. The polymers with relatively long side chains (**2e**–**h**) had high molecular weight over $1.6 \times 10^4$ and gave free-standing membranes by solution-casting method. The densities of membranes of **2e**–**h** were 0.914–0.998, and their fractional-free volume values were relatively large (0.094–0.158). The oxygen permeability coefficients of membranes of **2e**–**h** were 18.4, 12.7, 4.85, and 19.3 barrers, respectively. It was found that poly(*p*-phenyleneethynylene) with 2-octyl side groups, which have the branch at the nearest position from main chain, exhibited the highest gas permeability.

**Keywords** Poly(*p*-phenyleneethynylene) · Acyclic diyne metathesis · Membrane · Fractional-free volume · Gas permeability

## Introduction

Development of efficient gas-separation technique has been investigated from the aspect of industrial application. Gas-permeable polymer membranes have attracted much attention because membrane separation of gas mixtures offers energy- and

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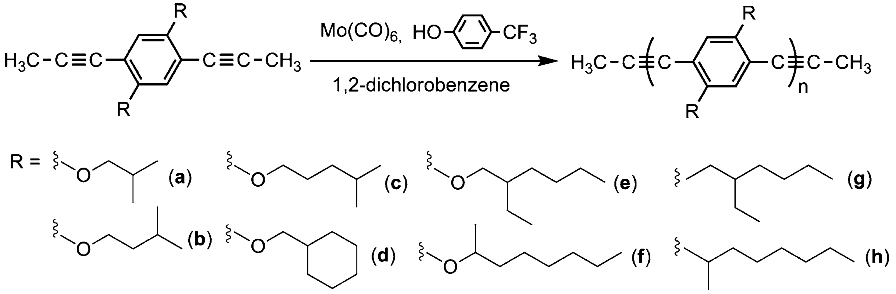
cost-saving relative to the more established processes (e.g., adsorption and cryogenic distillation) [1–5]. Substituted polyacetylenes [6, 7] and polyimides [8, 9] are known to exhibit very high gas permeability because their membranes have large fractional-free volume (FFV) owing to both their stiff main chain and the steric repulsion of bulky substituents. For instance, poly(1-trimethylsilyl-1-propyne) exhibits the highest gas permeability among all the existing polymers [10]. Its oxygen permeability coefficient is around 10,000 barrers, but the permeability is known to be significantly decreased by aging [6, 11]. Many kinds of substituted acetylene polymers and substituted polyimides have been synthesized so far, but 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 development of gas-separation technique employing polymeric membranes.

A variety of poly(phenyleneethynylene)s [PPEs] have been synthesized by acyclic diyne metathesis (ADIMET) polymerization and palladium-catalyzed polycondensation because of their remarkable optical and electronic properties [12–17]. PPEs possess rigid main chain composed of both benzene ring and triple bond. This fact indicates that PPEs may exhibit high gas permeability when they have appropriate substituents. However, gas permeation properties of membranes of PPEs have never been known until our recent report [18]. The paper revealed for the first time that the membranes of poly(2,5-dialkyl-*p*-phenyleneethynylene)s exhibited relatively high gas permeability even the pendant groups were linear alkyl groups. Generally, a spherical bulky substituent lead large FFV compared to a linear alkyl group. Therefore, PPEs having bulky substituents are expected to be of a superior gas permeation property.

In the present study, novel poly[2,5-di(branched alkoxy)-*p*-phenyleneethynylene]s and poly[2,5-di(branched alkyl)-*p*-phenyleneethynylene]s were synthesized to develop membranes of PPEs for gas separation (Scheme 1). The gas permeability of their free-standing membranes was examined, and it was found that PPVs having branched alkoxy and alkyl groups exhibited relatively high gas permeability.



**Scheme 1** Synthesis of poly(2,5-disubstituted-*p*-phenyleneethynylene) derivatives 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 × 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. 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.

### Materials

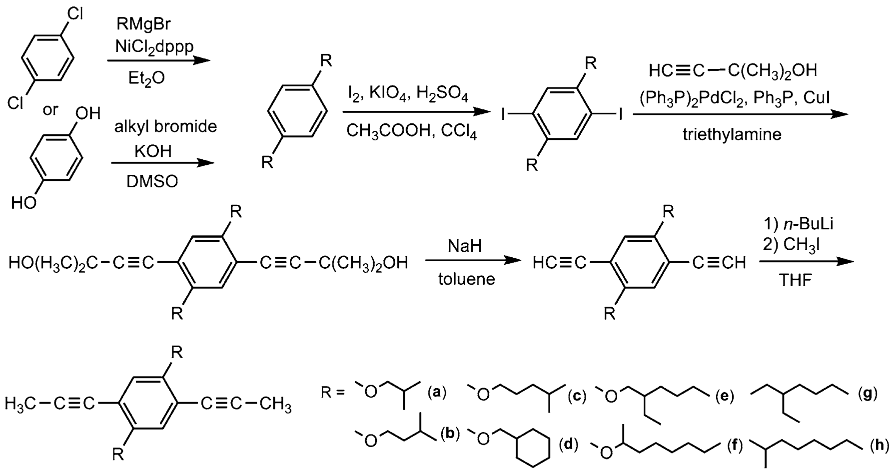
Molybdenum hexacarbonyl, 4-(trifluoromethyl)phenol, 1,4-dichlorobenzene, hydroquinone, 1-bromo-2-methylpropane, 1-bromo-3-methylbutane, 1-bromo-4-methylpentane, (bromomethyl)cyclohexane, 1-bromo-2-ethylhexane, 2-bromodecane, 3-methyl-1-butyne-3-ol, iodomethane, and common organic solvents were commercially obtained from Wako Pure Chemicals, Ind., Ltd., and used without further purification. 1,2-Dichlorobenzene as polymerization solvent was purified by distillation under reduced pressure. 2,5-Bis[(3-methyl)butoxy]-1,4-dipropynylbenzene (**1b**) and 2,5-bis[(2-ethyl)hexyl]-1,4-dipropynylbenzene (**1g**) were prepared according to the literature [19]. The other novel monomers [2,5-dialkoxy-1,4-dipropynylbenzenes (**1a**, **1c**, **1d**, **1e**, and **1f**) and 2,5-di(2-octyl)-1,4-dipropynylbenzene (**1h**)] were newly synthesized as shown in Scheme 2 referring to the literatures [17, 19]. The detailed procedures and analytical data are stated below.

### General procedure for preparation of 1,4-dialkoxybenzene

A suspension of KOH (28 g, 0.50 mol) in DMSO (400 mL) is stirred at room temperature for 3 h under $N_2$. Hydroquinone (22 g, 0.20 mol) and alkyl bromide (0.50 mol) were added and the reaction mixture was stirred for 24 h. The mixture was poured into water, and the aqueous solution was extracted with ether. The organic layer was dried over $MgSO_4$. Ether was evaporated and the crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 9/1) to give desired product.

### General procedure for preparation of 1,4-dialkylbenzene

To a 500-mL, three-necked, round-bottom flask, equipped with a magnetic stirring bar and dropping funnel, 150 mL of $Et_2O$ and 5.5 g (0.23 mol) of magnesium were



**Scheme 2** Synthesis of 2,4-disubstituted-*p*-dipropynylbenzenes

added. A solution of alkyl bromide (50 g, 0.23 mol) in $Et_2O$ (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 $Et_2O$ (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 HCl aq (1.0 mol/L) and then with water. The solution was dried over $MgSO_4$ and then concentrated at reduced pressure. The crude product was used for next reaction without further purification.

## General procedure for preparation of diiodobenzene

Under $N_2$, 1,4-dialkoxybenzene (0.15 mol), acetic acid (150 mL), sulfuric acid (20 mL), carbon tetrachloride (10 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 were collected by filtration and dissolved in $Et_2O$. The ethereal solution was washed with sodium thiosulfate and then dried over $MgSO_4$. Purification of the crude product by silica gel column chromatography (eluent: hexane/ethyl acetate = 9/1) provided 2,5-dialkoxy-1,4-diiodobenzene.

## General procedure for preparation of diethynylbenzene

After the flask was flushed with nitrogen, 2,5-dialkoxy-1,4-diiodobenzene (0.10 mol), dichlorobis(triphenylphosphine)palladium (0.056 g, 0.08 mmol), cuprous iodide (0.091 g, 0.48 mmol), and triphenylphosphine (0.084 g, 0.32 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 (21 g, 0.25 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 HCl aq (1.0 mol/L) and then with water. The ethereal solution was dried over $MgSO_4$. 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 (4.9 g, 0.20 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 HCl aq (1.0 mol/L) and then with water. The solution was dried over $MgSO_4$. Toluene was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 9/1) to give 2,5-dialkoxy-1,4-diethynylbenzene.

### General procedure for preparation of dipropynylbenzene

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-dialkoxy-1,4-diethynylbenzene (0.020 mol) and 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 (13 mL, 0.20 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 HCl aq (1.0 mol/L) 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/ethyl acetate = 9/1) provided the dipropynylbenzene.

### 2,5-Bis(2-methylpropoxy)-1,4-dipropynylbenzene (**1a**)

$^1$H NMR ($CDCl_3$, ppm): 6.85 (s, 2H, Ar), 3.70 (d, $J = 6.7$ Hz, 4H, Ar–$OCH_2$), 2.09 (s, 6H, $C{\equiv}C{-}CH_3$), 1.26 (m, 2H, Ar–O–$CH_2$–C*H*–$(CH_3)_2$), 1.02 (d, $J = 6.8$ Hz, 12H, Ar–O–$CH_2$–CH–$(C\mathit{H}_3)_2$). $^{13}$C NMR ($CDCl_3$, ppm): 153.6, 117.4, 113.9, 90.8, 76.0, 75.9, 28.3, 19.2, 4.6.

### 2,5-Bis(4-methylpentoxy)-1,4-dipropynylbenzene (**1c**)

$^1$H NMR ($CDCl_3$, ppm): 6.85 (s, 2H, Ar), 3.93 (t, $J = 6.7$ Hz, 4H, Ar–$OCH_2$), 2.10 (s, 6H, $C{\equiv}C{-}CH_3$), 1.80 (m, 4H, Ar–O–$CH_2$–$C\mathit{H}_2$–), 1.62 (m, 2H, Ar–O–$CH_2$–$CH_2$–$CH_2$–C*H*–$(CH_3)_2$), 1.36 (m, 4H, Ar–O–$CH_2$–$CH_2$–$C\mathit{H}_2$–CH–$(CH_3)_2$), 0.91 (d, $J = 6.6$ Hz, 12H, Ar–O–$CH_2$–$CH_2$–$CH_2$–CH–$(C\mathit{H}_3)_2$). $^{13}$C NMR ($CDCl_3$, ppm): 153.4, 117.4, 113.9, 90.9, 75.9, 70.0, 35.1, 27.7, 27.1, 22.6, 4.7.

### 2,5-Bis(cyclohexylmethoxy)-1,4-dipropynylbenzene (**1d**)

$^1$H NMR ($CDCl_3$, ppm): 6.84 (s, 2H, Ar), 3.73 (d, $J = 6.4$ Hz, 4H, Ar–$OCH_2$), 2.09 (s, 6H, $C{\equiv}C{-}CH_3$), 1.89–1.64 (m, 12H, cyclohexyl), 1.32–1.04 (m, 10H, cyclohexyl). $^{13}$C NMR ($CDCl_3$, ppm): 153.7, 117.6, 114.0, 90.8, 76.0, 75.2, 37.6, 29.8, 26.6, 25.8, 4.7.

2,5-Bis(2-ethylhexoxy)-1,4-dipropynylbenzene (**1e**)

$^1$H NMR ($CDCl_3$, ppm): 6.85 (s, 2H, Ar), 3.81 (d, $J = 6.0$ Hz, 4H, Ar–$OCH_2$), 2.08 (s, 6H, $C{\equiv}C{-}CH_3$), 1.75 (quint, $J = 6.0$ Hz, 2H, Ar–O–$CH_2$–C$H$–), 1.54–1.18 (m, 16H, Ar–O–$CH_2$–CH–($CH_2CH_3$)$CH_2CH_2CH_2$$CH_3$), 0.96–0.85 (m, 12H, Ar–O–$CH_2$–CH–($CH_2CH_3$)$CH_2CH_2CH_2CH_3$). $^{13}$C NMR ($CDCl_3$, ppm): 153.8, 117.3, 114.0, 90.8, 76.0, 72.4, 39.4, 30.6, 29.0, 24.0, 23.1, 14.1, 11.2, 4.6.

2,5-Bis(2-octoxy)-1,4-dipropynylbenzene (**1f**)

$^1$H NMR ($CDCl_3$, ppm): 6.85 (s, 2H, Ar), 4.23 (sext, $J = 6.1$ Hz, 2H, Ar–OCH), 2.08 (s, 6H, $C{\equiv}C{-}CH_3$), 1.72–1.24 (m, 26H, Ar–O–CH($CH_3$)$CH_2CH_2CH_2CH_2CH_2$ $CH_3$), 0.88 (t, $J = 7.0$ Hz, 6H, Ar–O–CH($CH_3$)$CH_2CH_2CH_2CH_2CH_2CH_3$). $^{13}$C NMR ($CDCl_3$, ppm): 153.1, 120.9, 115.7, 90.5, 76.7, 76.3, 36.6, 31.8, 29.3, 25.4, 22.6, 19.9, 14.1, 4.7.

2,5-Bis(2-octyl)-1,4-dipropynylbenzene (**1h**)

$^1$H NMR ($CDCl_3$, ppm): 6.85 (s, 2H, Ar), 3.18 (sext, $J = 7.1$ Hz, 2H, Ar–CH), 2.09(s, 6H, $C{\equiv}C{-}CH_3$), 1.62–1.15 (m, 26H, Ar–CH($CH_3$)$CH_2CH_2CH_2CH_2$ $CH_2CH_3$), 0.86 (t, $J = 7.0$ Hz, 6H, Ar–CH($CH_3$)$CH_2CH_2CH_2CH_2CH_2CH_3$). $^{13}$C NMR ($CDCl_3$, ppm): 146.4, 129.2, 122.6, 89.7, 78.8, 37.8, 36.0, 31.8, 29.4, 27.4, 22.7, 21.2, 14.1, 4.5.

## 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** (0.49 g), $Mo(CO)_6$ (0.020 g), 4-(trifluoromethyl)phenol (0.24 g), and 1,2-dichlorobenzene (15 mL) were placed in a 30-mL glass tube. The reaction mixture was heated at 150 °C, removing 2-butyne by a slow stream of nitrogen. After 90 min, polymerization was quenched with a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol. In order to remove the phenol, the polymer was dissolved in chloroform and washed with 10% sodium hydroxide. Its yield was determined by gravimetry.

## Membrane preparation

Polymer membranes (thickness ca. 60–80 μm) were prepared by casting toluene solutions 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 peeled off, and it was further dried at 25 °C under reduced pressure 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 ($\rho_0$) is needed, and the membrane density ($\rho$) is given by the following equation:

$$\rho = \rho \times M_A/(M_A - M_L), \tag{1}$$

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:

$$\mathrm{FFV} = \left(v_{sp} - v_0\right)/v_{sp} \approx \left(v_{sp} - 1.3\, v_w\right)/v_{sp}, \tag{2}$$

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 [20].

## Results and discussion

### Polymerization

The polymerizations of monomers **1a–h** were carried out using $Mo(CO)_6$/4-(trifluoromethyl)phenol catalyst in 1,2-dichlorobenzene at 150 °C by referring to the literature [17], whose results are summarized in Table 1. The polymerization of **1a**

**Table 1** Results of ADIMET polymerization

| Run | Monomer | Time (h) | Polymer[a] | | | | |
|---|---|---|---|---|---|---|---|
| | | | Yield (%) | $M_n$[b] | $M_w/M_n$[b] | DP[c] | DP[d] |
| 1 | **1a** | 1.5 | 54 | Insoluble | | | |
| 2 | **1b** | 1.5 | 68 | 1,800 | 6.6 | 6.56 | 23.1 |
| 3 | **1b** | 5.0 | 62 | Insoluble | | | |
| 4 | **1c** | 1.5 | 56 | 8,660 | 13.0 | 28.6 | 18.2 |
| 5 | **1d** | 1.5 | 60 | 2,860 | 2.8 | 8.76 | 12.5 |
| 6 | **1e** | 5.0 | 78 | 17,200 | 6.5 | 47.8 | –[e] |
| 7 | **1f** | 2.5 | 65 | 16,900 | 10.4 | 47.0 | –[e] |
| 8 | **1g** | 5.0 | 63 | 41,300 | 5.7 | 126 | –[e] |
| 9 | **1h** | 3.0 | 61 | 44,700 | 3.5 | 137 | –[e] |

In 1,2-dichlorobenzene at 150 °C; $[M]_0 = 0.10$ M, $[Mo(CO)_6] = 5.0$ mM, $[p\text{-}CF_3C_6H_4OH] = 0.10$ M

[a] Methanol-insoluble product

[b] Measured by GPC (polystyrene calibration)

[c] Degree of polymerization calculated from GPC

[d] Degree of polymerization calculated from $^1$H NMR

[e] Not determined

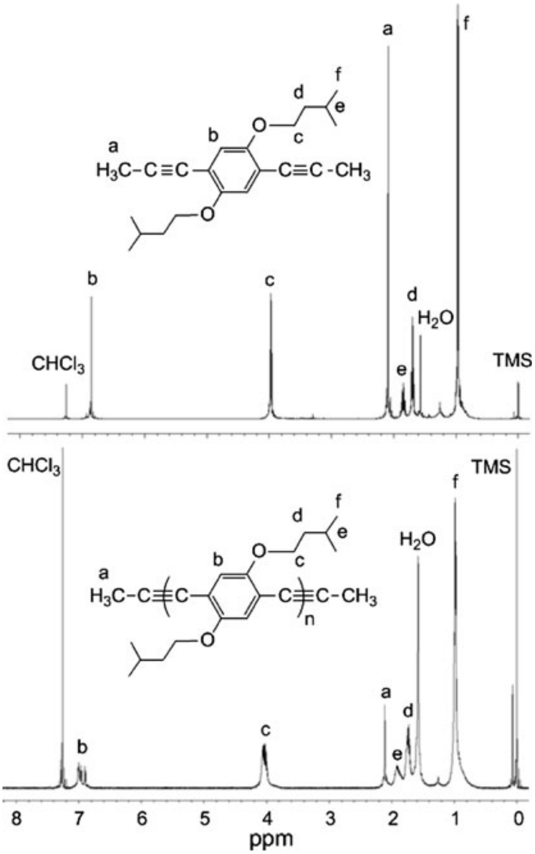


**Fig. 1** $^1$H NMR spectra of monomer **1b** and polymer **2b**

afforded polymer (**2a**) in 54% yield, but **2a** was insoluble in any solvents (run 1). Monomer **1b** polymerized for 1.5 h to give a solvent-soluble polymer **2b**, whose number-average molecular weight was as low as 1,800 (run 2). When the polymerization time became longer than 5 h, the resultant polymer became insoluble in any solvents (run 3). Monomers **1c** and **1d** also polymerized to afford solvent-soluble polymers **2c** and **2d**, respectively, when the polymerization time was 1.5 h (runs 4 and 5). Since polymers **2a**–**d** do not possess enough long side groups, solvent-soluble polymers with high molecular weight could not be obtained. On the other hand, monomers **1e**–**h** have relatively long substituents as pendant groups, and the polymerizations of **1e**–**h** afforded solvent-soluble polymers with relatively high molecular weights ($M_n$ > 16,900) (runs 6–9).

Figure 1 shows $^1$H NMR spectra of monomer **1b** and polymer **2b** obtained by the polymerization for 1.5 h (Table 1, run 2). Polymer **2b** exhibits peaks derived from alkyl group (c)–(f) and benzene ring (b) similar to monomer **1b**. The singlet peak of the propyne end groups at 2.05 ppm was observed in spectrum of **2b**. The degree of polymerization was determined to be 23.1 by comparing the integrated intensities

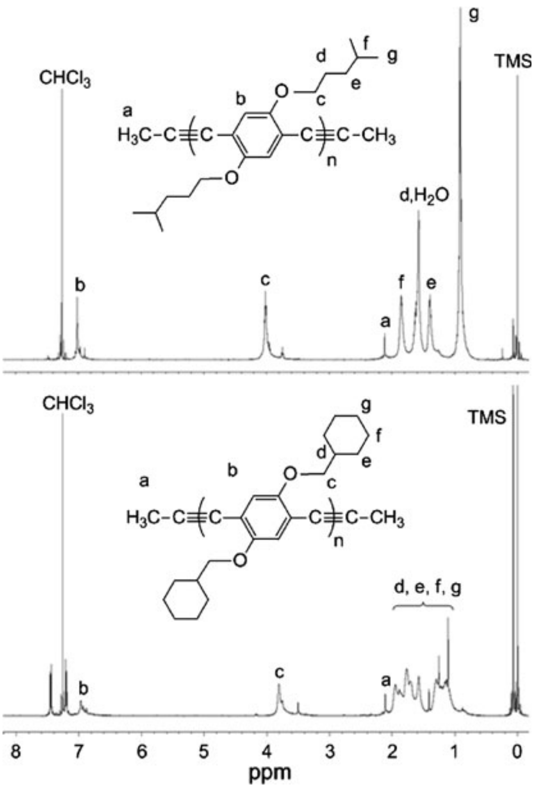


**Fig. 2** $^1$H NMR spectra of polymers **2c** and **2d**

of the peaks due to propyne (a) to methylene (c). From GPC measurement, the degree of polymerization of **2b** was 6.56, which is smaller than that from $^1$H NMR. This is unsuspected because the GPC method using polystyrene calibration is known to lead to errors in the determination of the absolute molecular weight in the case of rigid polymers [17]. The $^1$H NMR spectra of polymers **2c** and **2d** are shown in Fig. 2. In both spectra, the small peaks of the propyne end groups were observed at 2.05 ppm. The degrees of polymerization of **2c** and **2d** were 18.2 and 12.5, respectively, based on the peak intensity ratio of the end groups (a) and methylene groups (c). Figure 3 depicts $^1$H NMR spectra of **2e**–**h**, which are in accord with the expected chemical structures and exhibited no peaks due to propyne end groups because of high molecular weights of **2e**–**h**. Therefore, the degrees of polymerization could not be determined by $^1$H NMR.

## Solubility

The solubility properties of polymers **2a**–**h** were studied, whose results are summarized in Table 2. Polymer **2a** with the smallest side groups in this study was insoluble in any solvents, while polymers **2b** and **2c** were totally dissolved in $CCl_4$,

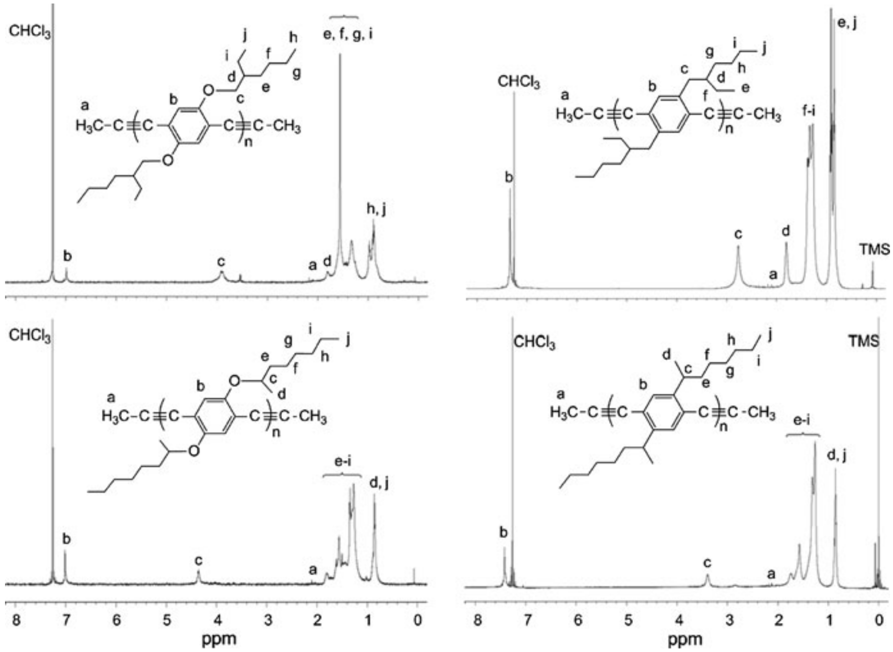


**Fig. 3** $^1$H NMR spectra of polymers **2e**, **2f**, **2g**, and **2h**

**Table 2** Solubility of the polymers

| | Hexane | $CCl_4$ | Toluene | $CHCl_3$ | THF | $CH_2Cl_2$ | Acetone | DMSO |
|---|---|---|---|---|---|---|---|---|
| **2a** (–)[a] | – | – | – | – | – | – | – | – |
| **2b** (1,800) | ± | + | + | + | + | + | – | – |
| **2c** (8,660) | ± | + | + | + | + | + | – | – |
| **2d** (2,860) | – | ± | ± | + | ± | ± | – | – |
| **2e** (17,200) | + | + | + | + | + | + | – | – |
| **2f** (16,900) | ± | + | + | + | + | + | – | – |
| **2g** (41,300) | ± | + | + | + | + | + | – | – |
| **2h** (44,700) | – | + | + | + | + | + | – | – |

*Symbols*: + soluble, ± partially soluble, − insoluble

[a] Figure in *parenthesis* represents the number-average molecular weight

toluene, $CHCl_3$, THF, and $CH_2Cl_2$. They were partially soluble in hexane and insoluble in polar solvents such as acetone, methanol, *N*,*N*-dimethylformamide, and dimethylsulfoxide (DMSO). Polymer **2d** containing cyclohexylmethoxy groups showed poor solubility properties, and it was soluble in $CHCl_3$ and partially soluble in $CCl_4$, toluene, THF, and $CH_2Cl_2$. However, polymers **2b**–**d** became insoluble when the degrees of polymerization increased. On the other hand, polymers **2e**–**h** showed good solubility and completely dissolved in toluene, THF, $CH_2Cl_2$ as well as $CCl_4$ and $CHCl_3$ irrespective of their relatively high molecular weights.

## Density and FFV

Free-standing membranes of polymers **2e**–**h** could be prepared by solution-casting. However, the membranes of polymers **2a**–**d** could not be obtained because polymer **2a** was insoluble in any solvents and polymers **2b**–**d** with solubility in toluene did not have enough high molecular weights. Densities and FFV of membranes of **2e**–**h** are listed in Table 3. The densities of membranes of **2e**–**h** were 0.985, 0.998, 0.984, and 0.914 g/cm$^3$, respectively, which are relatively low among hydrocarbon polymers; for example, the densities of crystalline polystyrene, amorphous polystyrene, and poly(*p*-phenylenevinylene) are 1.12, 1.04, and 1.24 g/cm$^3$, respectively [21]. The FFVs of membranes of **2e**–**h** were 0.136, 0.124, 0.094, and 0.150, respectively. Polymer **2h** has the largest FFV value among these four poly(2,5-disubstituted-*p*-phenyleneethynylene)s. This seems to imply that the bulkiness close the benzene ring is important for the formation of a sparse membrane, and the substituent with the branch at the carbon adjacent to benzene ring efficiently prevents polymer chain to pack together.

## Gas permeability

The gas permeability of membranes of **2e**–**h** to oxygen, nitrogen, and carbon dioxide was examined at 25 °C (Table 3). Their gas permeability exhibited an anticipated result from their FFV data. The oxygen permeability coefficients ($PO_2$) of membranes of polymers (**2e** and **2f**), which have alkoxy side groups, were 18.4 and 12.7 barrers, respectively. Both the alkoxy-containing PPEs are comparable and showed relatively high gas permeability. The $PO_2$ value of membrane of **2g** was 4.85 and much smaller than those of **2e** and **2f**. The higher $PO_2$ of **2e** and **2f** than that of **2g** may come from the existence of flexible alkoxy linkages in the former polymers. In contrast, the $PO_2$ of **2h** was 19.3 barrers, much higher than that of **2g**. This fact shows that the existence of branch points in the vicinity of the main chain phenylenes is effective for gas permeability. We reported that the $PO_2$ values of PPVs having *n*-hexyl and *n*-octyl substituents were 4.88 and 7.06 barrers [18]. Compared to linear alkyl groups, branched alkoxy and alkyl with the branch at the carbon adjacent to backbone are good for increase of gas permeability as pendant groups of PPE. The permeability of **2e**–**h** to other gases such as $N_2$ and $CO_2$ exhibited similar tendencies to the case of oxygen. The $N_2$ and $CO_2$ permeability coefficients ($PN_2$ and $PCO_2$) of **2h** were 6.37 and 84.2 barrers, respectively, and the

**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] | $PO_2/PN_2$ |
|---|---|---|---|---|---|---|
| **2e** | 0.985 | 0.136 | 6.18 | 18.4 | 83.6 | 2.98 |
| **2f** | 0.998 | 0.124 | 4.12 | 12.7 | 56.0 | 3.08 |
| **2g** | 0.984 | 0.094 | 1.26 | 4.85 | 17.5 | 3.85 |
| **2h** | 0.914 | 0.158 | 6.37 | 19.3 | 84.2 | 3.03 |

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

largest among those of the present polymers. The oxygen/nitrogen separation factors ($PO_2/PN_2$) of all the polymers **2e**–**h** were in the range of 2.98–3.85. The $PO_2/PN_2$ of **2g**, which showed the lowest permeability, was the largest, and the $PO_2/PN_2$ of **2h**, which showed the highest permeability, was the smallest. It was recognized that the permeability and separation factor are trade-off relationship as the separation factor generally decreases with increasing permeability [22]. The gas permeation properties of the present polymers are well agreed with trade-off relationship.

## Conclusions

Poly(*p*-phenyleneethynylene)s having branched alkoxy groups or branched alkyl groups (**2a**–**h**) were synthesized by ADIMET polymerization. Poly(*p*-phenyleneethynylene)s possessing relatively long side groups (**2e**–**h**) had high molecular weights and good solvent-solubility, and gave their free-standing membranes by solvent-casting method. The FFVs of membranes of poly(2,5-dialkyl-*p*-phenyleneethynylene)s (**2e**–**h**) were appreciably large and they showed high gas permeability. Especially, membrane of **2h** which has 2-octyl groups exhibited the largest FFV value and the highest gas permeability. This implies that the bulkiness of side groups around phenylene-backbone is important to prevent poly(*p*-phenyleneethynylene)s to pack together in the membrane-formation process.

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