

Synthesis and Gas Permeability of Membranes of Silyl-Substituted Poly(*p*-phenylenevinylene)s

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Received 3 December 2009; accepted 22 January 2010

DOI 10.1002/app.32135

Published online 5 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *p*-Bis(bromomethyl)benzene with silyl groups [SiMe₃ (**2a**), SiEt₃ (**2b**), SiMe₂-*t*-Bu (**2c**), SiMe₂-*n*-Bu (**2d**), SiMe₂-*n*-C₈H₁₇ (**2e**), SiMe₂-*n*-C₁₈H₃₇ (**2f**)] were polymerized by a modified Gilch route to afford silyl-substituted poly(*p*-phenylenevinylene)s (**3a–f**). The polymer containing SiMe₃ groups (**3a**) was insoluble in any solvents, while the other polymers (**3b–f**) were soluble in organic solvents. They had relatively high molecular weight over 3.6×10^4 , and gave free-standing membranes by solution casting method. According to thermogravimetric analysis (TGA), the silyl-substituted poly(*p*-phenylenevinylene)s

showed high thermal stability ($T_d \geq 300^\circ\text{C}$). The oxygen permeability coefficients of membranes of the silyl-substituted poly(*p*-phenylenevinylene)s (**3b–f**) were in the range of 3.5–12 barrers, and the poly(*p*-phenylenevinylene)s with long alkyl silyl groups, **3e** and **3f**, exhibited the highest gas permeability among them. This is the first report on gas permeability of poly(*p*-phenylenevinylene)s. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2009–2015, 2010

Key words: membranes; gas permeation; selectivity; poly(*p*-phenylenevinylene); silyl group

INTRODUCTION

Gas permeable polymers have been extensively studied because of their promising application in gas separation membrane.^{1–5} A huge array of polymers such as substituted polyacetylenes,^{6–8} polyimides,^{9–12} polysulfones,^{13–15} polycarbonates^{16–18} have been studied as materials for gas separation membrane. The main chains of these polymers are composed of double bonds, aromatic rings, etc., and they are rigid and restricted in rotation. When such polymers possess spherical bulky substituents, their membranes usually showed large free volume because of the steric repulsion of bulky substituents. Thus, both stiff main chain and bulky substituents are important for high gas permeability. 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.

Poly(phenylenevinylene)s [PPVs] have been intensively researched because of their optical and electronic properties.^{19–22} PPVs possess rigid main chain composed of benzene rings and double bonds, and membranes of PPVs containing bulky substituents

possibly exhibit high gas permeability. Especially, silyl-substituted polymers often show high gas permeability because of the steric repulsion and high local mobility of silyl groups.^{23–26} Synthesis of silyl-substituted PPVs has been reported, and their optical properties have been studied.^{27,28} However, gas permeation properties of membranes of PPVs have never been known so far. Generally, substituted PPVs are synthesized by the polymerization of bis(halomethyl)benzene using potassium *tert*-butoxide as a base, namely Gilch polymerization.²⁹ However, it was reported that the Gilch polymerization gave insoluble PPVs gel even in a monomer having substituents.^{30,31} This may be attributed to extremely high degree of polymerization. Insolubility of polymers is problem from the viewpoint of handling; e.g., characterization, analysis of properties, and preparation of membranes. To solve the solubility problem, a modified Gilch polymerization involving the use of a nonpolymerizable additive such as *p-tert*-butylbenzyl bromide was developed.³¹ The modified Gilch polymerization can control a degree of polymerization, and consequently give soluble high-molecular-weight PPVs.

In the present study, bis(bromomethyl)benzenes having various silyl groups were synthesized, and then polymerized by the modified Gilch polymerization with *p-tert*-butylbenzyl bromide. The free-standing membranes of the silyl-substituted PPVs were prepared by solution casting, and their general properties and gas permeability were investigated.

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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. Thermogravimetric analyses (TGA) were conducted with Rigaku TG-DTA 8078G1 at a 10°C/min heating rate. Thermal decomposition temperature (T_d) 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.

Materials

2-Bromo-*p*-xylene, *n*-butyllithium in hexane, *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), potassium *t*-butoxide, and common organic solvents were commercially obtained from Wako Pure Chemicals Ind., and used without further purification. Various chlorosilanes were purchased from Tokyo Chemical Industry. THF as polymerization solvent was purified by distillation twice. Monomers were synthesized from 2-bromo-*p*-xylene by silylation followed by radical bromination as shown in Scheme 1 according to the literatures.^{32,27} The details of the procedures and analytical data of monomers are stated below.

Synthesis of 2-trimethylsilyl-*p*-xylene (1a)

A 500 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. After flushing the flask with nitro-

gen, 2-bromo-*p*-xylene (10 g, 54 mmol) and ether (200 mL) were added and cooled at 0°C. At the same temperature, a hexane solution of *n*-butyllithium (35 mL, 1.6 M, 56 mmol) was added dropwise, and the mixture was stirred for 1 h. Then, a solution of chlorotrimethylsilane (6.1 g, 56 mmol) in ether (25 mL) was added dropwise at 0°C, and stirring was continued further for 12 h at room temperature. The reaction mixture was washed with water, and dried over anhydrous sodium sulfate. Ether was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane) to afford 2-trimethylsilyl-*p*-xylene (9.4 g, 53 mmol, yield 98%).

^1H -NMR (CDCl_3 , ppm): 7.20 (s, 1H, Ar), 7.07 (d, $J = 7.8$ Hz, 1H, Ar), 7.05 (d, $J = 7.8$ Hz, 1H, Ar), 2.40 (s, 3H, Ar- CH_3), 2.32 (s, 3H, Ar- CH_3), 0.40 (s, 9H, $\text{Si}(\text{CH}_3)_3$). ^{13}C -NMR (CDCl_3 , ppm): 140.1, 138.5, 135.9, 133.7, 129.8, 129.4, 22.4, 21.2, 0.28.

Synthesis of 2-trimethylsilyl-*p*-bis(bromomethyl)benzene (2a)

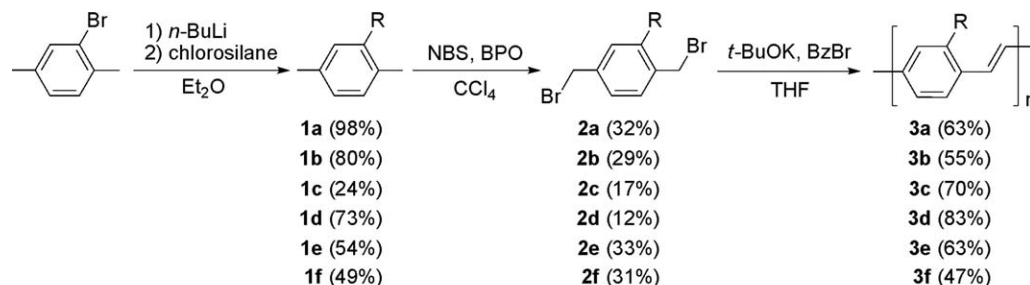
2-Trimethylsilyl-*p*-xylene (5.0 g, 28 mmol), NBS (10 g, 56 mmol), BPO (68 mg, 0.28 mmol), and CCl_4 (200 mL) were charged into a 500 mL flask. The mixture was stirred at 80°C under N_2 for 4 h. The solution was washed with water three times, and then dried over anhydrous sodium sulfate. After filtration and evaporation, the residue was purified by silica gel column chromatography (eluent: hexane) to afford 2-trimethylsilyl-*p*-bis(bromomethyl)benzene (2.8 g, 9.0 mmol, yield 32%).

^1H -NMR (CDCl_3 , ppm): 7.46–7.39 (m, 3H, Ar), 4.60 (s, 2H, Ar- $\text{CH}_2\text{-Br}$), 4.48 (s, 2H, Ar- $\text{CH}_2\text{-Br}$), 0.40 (s, 9H, $\text{Si}(\text{CH}_3)_3$). ^{13}C -NMR (CDCl_3 , ppm): 143.3, 139.9, 136.9, 135.3, 131.4, 130.4, 33.7, 33.2, 0.29.

Synthesis of 2-triethylsilyl-*p*-xylene (1b)

This monomer was prepared by the same method as for 1a (Yield 80%).

^1H -NMR (CDCl_3 , ppm): 7.21 (s, 1H, Ar), 7.06 (d, $J = 7.7$ Hz, 1H, Ar), 7.04 (d, $J = 7.7$ Hz, 1H, Ar), 2.38



R = SiMe_3 (a), SiEt_3 (b), $\text{SiMe}_2\text{-}t\text{-Bu}$ (c), $\text{SiMe}_2\text{-}n\text{-Bu}$ (d), $\text{SiMe}_2\text{-}n\text{-C}_8\text{H}_{17}$ (e), $\text{SiMe}_2\text{-}n\text{-C}_{18}\text{H}_{37}$ (f)

Scheme 1 Synthetic route of silyl-substituted PPVs.

(s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 0.95 (t, *J* = 8.1 Hz, 9H, Si-(CH₂CH₃)₃), 0.85 (q, *J* = 8.1 Hz, 6H, Si-(CH₂-CH₃)₃). ¹³C-NMR (CDCl₃, ppm): 140.6, 136.1, 135.1, 133.7, 129.7, 129.6, 22.4, 21.1, 7.6, 4.0.

Synthesis of 2-triethylsilyl-*p*-bisbromomethylbenzene (2b)

This monomer was prepared by the same method as for **2a** (yield 29%).

¹H-NMR (CDCl₃, ppm): 7.45 (s, 1H, Ar), 7.43 (d, *J* = 7.9 Hz, 1H, Ar), 7.39 (d, *J* = 7.9 Hz, 1H, Ar), 4.58 (s, 2H, Ar-CH₂-Br), 4.48 (s, 2H, Ar-CH₂-Br), 0.97 (t, *J* = 8.1 Hz, 9H, Si-CH₂CH₃), 0.92 (q, *J* = 8.1 Hz, 6H, Si-CH₂-CH₃). ¹³C-NMR (CDCl₃, ppm): 143.7, 137.0, 136.7, 136.2, 131.6, 130.2, 33.9, 33.3, 7.5, 4.2.

Synthesis of 2-dimethyl-*t*-butylsilyl-*p*-xylene (1c)

This monomer was prepared by the same method as for **1a** (yield 24%).

¹H-NMR (CDCl₃, ppm): 7.62 (s, 1H, Ar), 7.43 (d, *J* = 7.7 Hz, 1H, Ar), 7.41 (d, *J* = 7.7 Hz, 1H, Ar), 2.77 (s, 3H, Ar-CH₃), 2.68 (s, 3H, Ar-CH₃), 0.71 (s, 9H, SiC(CH₃)₃), 0.32 (s, 6H, Si(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 140.9, 136.8, 135.7, 133.4, 130.0, 129.7, 26.9, 23.7, 21.1, 18.1, -3.1.

Synthesis of 2-dimethyl-*n*-butylsilyl-*p*-bisbromomethylbenzene (2c)

This monomer was prepared by the same method as for **2a** (yield 17%).

¹H-NMR (CDCl₃, ppm): 7.45–7.35 (m, 3H, Ar), 4.58 (s, 2H, Ar-CH₂-Br), 4.47 (s, 2H, Ar-CH₂-Br), 0.78 (s, 9H, SiC(CH₃)₃), 0.35 (s, 6H, Si(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 142.8, 138.1, 136.9, 135.6, 132.0, 131.1, 33.6, 33.3, 22.0, 18.5, -2.5.

Synthesis of 2-dimethyl-*n*-butylsilyl-*p*-xylene (1d)

This monomer was prepared by the same method as for **1a** (yield 73%).

¹H-NMR (CDCl₃, ppm): 7.29 (s, 1H, Ar), 7.12 (d, *J* = 7.7 Hz, 1H, Ar), 7.09 (d, *J* = 7.7 Hz, 1H, Ar), 2.45 (s, 3H, Ar-CH₃), 2.36 (s, 3H, Ar-CH₃), 1.46–1.30 (m, 4H, Si-CH₂CH₂CH₂CH₃), 0.93 (t, *J* = 7.2 Hz, 3H, Si-CH₂CH₂CH₂CH₃), 0.86 (t, *J* = 7.2 Hz, 2H, Si-CH₂CH₂CH₂CH₃), 0.35 (s, 6H, Si-(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 140.4, 137.4, 135.3, 133.9, 129.8, 129.7, 26.6, 26.3, 22.5, 21.1, 15.8, 13.8, -1.9.

Synthesis of 2-dimethyl-*n*-butylsilyl-*p*-bisbromomethylbenzene (2d)

This monomer was prepared by the same method as for **2a** (yield 12%).

¹H-NMR (CDCl₃, ppm): 7.45–7.35 (m, 3H, Ar), 4.59 (s, 2H, Ar-CH₂-Br), 4.47 (s, 2H, Ar-CH₂-Br), 1.38–1.25 (m, 4H, Si-CH₂CH₂CH₂CH₃), 0.88 (t, *J* = 7.0 Hz, 3H, Si-CH₂CH₂CH₂CH₃), 0.84 (t, *J* = 7.2 Hz, 2H, Si-CH₂CH₂CH₂CH₃), 0.38 (s, 6H, Si(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 143.4, 139.3, 136.8, 135.5, 131.5, 130.3, 33.7, 33.2, 26.4, 26.1, 16.2, 13.7, -1.5.

Synthesis of 2-dimethyl-*n*-octylsilyl-*p*-xylene (1e)

This monomer was prepared by the same method as for **1a** (yield 54%).

¹H-NMR (CDCl₃, ppm): 7.23 (s, 1H, Ar), 7.06 (d, *J* = 7.2 Hz, 1H, Ar), 7.04 (d, *J* = 7.2 Hz, 1H, Ar), 2.39 (s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 1.32–1.18 (m, 12H, Si-CH₂-(CH₂)₆-CH₃), 0.87 (t, *J* = 6.9 Hz, 3H, Si-CH₂-(CH₂)₆-CH₃), 0.80 (t, *J* = 7.9 Hz, 2H, Si-CH₂-(CH₂)₆-CH₃), 0.29 (s, 6H, Si-(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 140.4, 137.5, 135.3, 133.9, 129.8, 129.7, 33.6, 31.9, 29.3, 24.0, 22.7, 22.5, 21.1, 16.1, 14.1, -1.8.

Synthesis of 2-dimethyl-*n*-octylsilyl-*p*-bisbromomethylbenzene (2e)

This monomer was prepared by the same method as for **2a** (yield 33%).

¹H-NMR (CDCl₃, ppm): 7.48–7.37 (m, 3H, Ar), 4.59 (s, 2H, Ar-CH₂-Br), 4.47 (s, 2H, Ar-CH₂-Br), 1.35–1.22 (m, 12H, Si-CH₂-(CH₂)₆-CH₃), 0.88–0.84 (m, 5H, Si-CH₂-(CH₂)₆-CH₃), 0.38 (s, 6H, Si-(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 143.4, 139.3, 136.9, 135.5, 131.5, 130.3, 33.7, 33.5, 33.2, 31.9, 30.9, 29.2, 23.9, 22.6, 16.5, 14.1, -1.5.

Synthesis of 2-dimethyl-*n*-octadecylsilyl-*p*-xylene (1f)

This monomer was prepared by the same method as for **1a** (yield 49%).

¹H-NMR (CDCl₃, ppm): 7.29 (s, 1H, Ar), 7.12 (d, *J* = 6.8 Hz, 1H, Ar), 7.09 (d, *J* = 6.8 Hz, 1H, Ar), 2.45 (s, 3H, Ar-CH₃), 2.36 (s, 3H, Ar-CH₃), 1.40–1.25 (m, 32H, Si-CH₂-(CH₂)₁₆-CH₃), 0.94 (t, *J* = 6.7 Hz, 3H, Si-CH₂-(CH₂)₁₆-CH₃), 0.86 (t, *J* = 7.4 Hz, 2H, Si-CH₂-(CH₂)₁₆-CH₃), 0.359 (s, 6H, Si-(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 140.4, 137.5, 135.3, 133.9, 129.8, 129.7, 33.6, 32.0, 29.72, 29.69, 29.66, 29.42, 29.38, 29.32, 23.9, 22.7, 22.5, 21.1, 16.1, 14.1, -1.8.

Synthesis of 2-dimethyl-*n*-octadecylsilyl-*p*-bisbromomethylbenzene (2f)

This monomer was prepared by the same method as for **2a** (yield 31%).

¹H-NMR (CDCl₃, ppm): 7.46–7.38 (m, 3H, Ar), 4.59 (s, 2H, Ar-CH₂-Br), 4.47 (s, 2H, Ar-CH₂-Br), 1.34–1.20 (m, 32H, Si-CH₂-(CH₂)₁₆-CH₃), 0.90–0.84

(m, 5H, Si—CH₂—(CH₂)₁₆—CH₃), 0.38 (s, 6H, Si—(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): 143.4, 139.3, 136.9, 135.5, 131.5, 130.3, 33.7, 33.5, 33.2, 31.9, 29.71, 29.69, 29.67, 29.64, 29.56, 29.4, 29.3, 23.9, 22.7, 16.5, 14.1, -1.5.

Polymerization

Polymerization was carried out in a round-bottom flask equipped with a dropping funnel and a three-way stopcock under dry nitrogen at 0°C. A detailed procedure of polymerization is as follows: Monomer **2b** (0.57 g), benzyl bromide (0.056 g), and dry THF (30 mL) were placed in the flask. To this solution was slowly added a solution of potassium *tert*-butoxide (0.56 g) in dry THF (20 mL) at 0°C. After 24 h, the reaction mixture was then poured into the mixture of methanol and acetone (1 : 1). The precipitate was redissolved in chloroform and reprecipitated in the mixture of methanol and acetone. Its yield was determined by gravimetry.

Membrane preparation

Membranes (thickness about 30–50 μm) of **3b–f** were prepared by casting CHCl₃ 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 (about 3 days). After drying, the membrane was peeled off, and it was further dried at 25°C under reduced pressure for 24 h.

RESULTS AND DISCUSSION

Synthesis of Silylated PPV

The synthetic route for silylated PPV as outlined in Scheme 1. The monomers were synthesized by radical bromination of 2-alkylsilyl-*p*-xylenes (**1a–f**), which were obtained through silylation of 2-bromo-*p*-xylenes using *n*-BuLi and then the corresponding silylation agents. When chlorodimethyl-*t*-butylsilane, chlorodimethyl-*n*-octylsilane, and chlorodimethyl-*n*-

C₁₈H₃₇ were used as silylation agents, the yields became relatively low, which may be attributed to the bulkiness of the silylation agents. Monomer yields after radical bromination were low in all the monomers, which is because radical bromination affords multibrominated xylenes and unbrominated xylenes as well as desired monomers. The monomers can be easily polymerized by the Gilch polymerization using potassium *tert*-butoxide as base in dry THF at 0°C. Unsubstituted PPV is known to be insoluble, and side chain-containing monomers are usually used to obtain soluble PPVs. In this study, various silyl-substituted PPVs were synthesized, but they were insoluble in any solvents when the polymerizations were operated in the absence of benzyl bromide. Therefore, their polymerizations were operated in controlling the concentrations of monomer and benzyl bromide (Table I). The polymerization of trimethylsilyl group-containing monomer gave an insoluble PPV. The other silyl-substituted PPVs (**3b–f**) were obtained in relatively high yields, whose *M_n*'s were in the range 36,000–204,000. However, the polymers of **3b–d** were not completely soluble in CHCl₃, and their *M_n*'s were measured using CHCl₃-soluble parts of the polymers.

The ¹H-NMR spectra of **3e** and **3f** were measured in CDCl₃ although the spectra of **3a–d** could not be measured because of their poor solubility in organic solvents. The ¹H-NMR spectra of **2e** and **3e** are shown in Figure 1. In the spectrum of **2e**, two peaks at around 4.6 ppm assigned to the benzyl protons were observed, while the peaks disappeared in the spectrum of **3e**. In the spectrum of **3e**, the broad peak at around 7.75 ppm was observed, which is assigned to the protons on the vinylene segments. There are two broad peaks at around 7.50 and 7.05 ppm assigned to the protons on the phenylene rings. The peaks assigned to the protons on dimethyl-*n*-octylsilyl groups were observed at around 1.30, 0.85, and 0.45 ppm. Figure 2 depicts the ¹H-NMR spectra of **2f** and **3f**. In the spectrum of **3f**, the peaks assigned to the protons on the vinylene, phenylene,

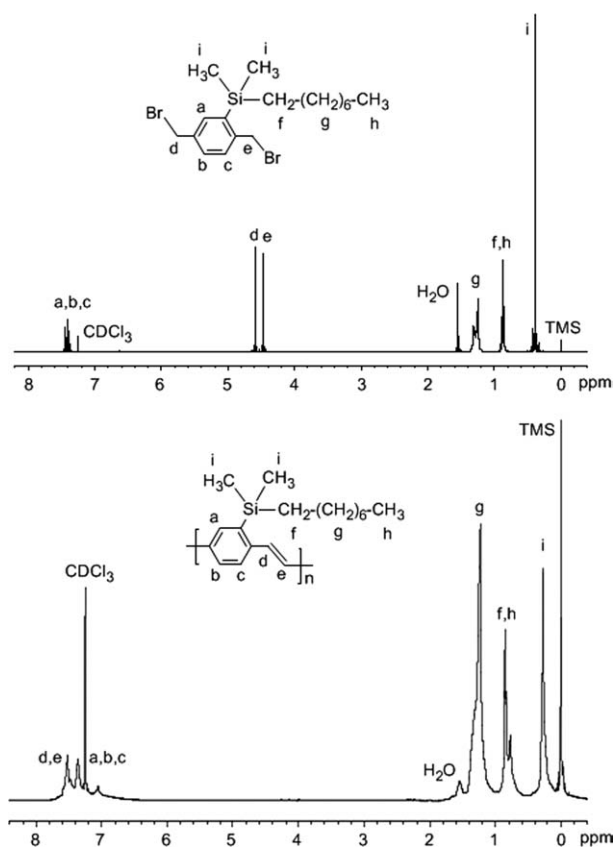
TABLE I
Polymerization of Silyl-Substituted Monomers^a

Monomer	[M] ₀ , M	[BzBr], mM	[<i>t</i> -BuOK], M	Yield ^b (%)	<i>M_n</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
2a	0.060	8.0	0.20	63	Insoluble	
2b	0.030	6.5	0.10	55	68,000	4.3
2c	0.020	4.0	0.10	70	45,000	9.2
2d	0.040	7.5	0.10	83	204,000	2.1
2e	0.030	3.0	0.10	63	101,000	5.0
2f	0.030	3.0	0.10	47	36,000	5.3

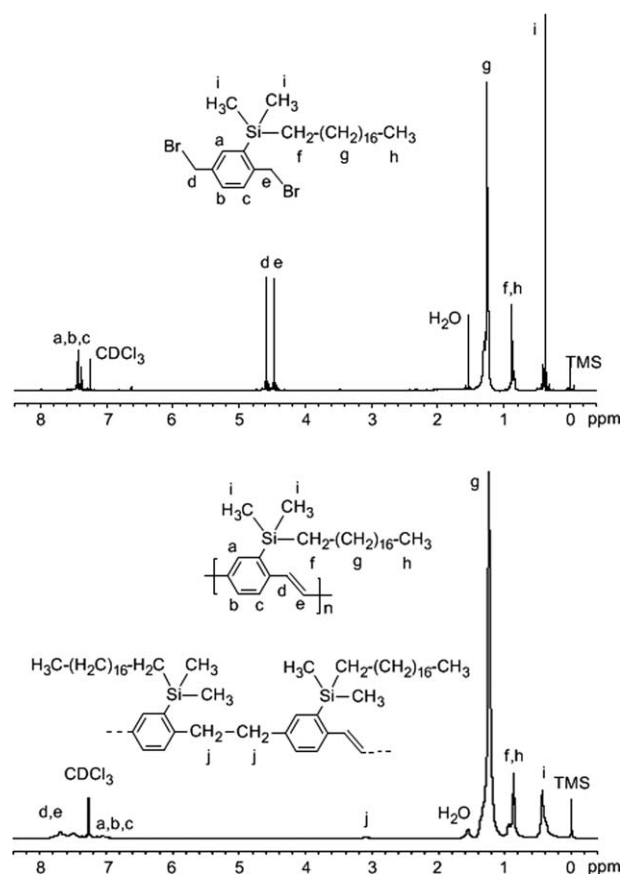
^a Polymerized at 0°C for 24 h.

^b Methanol/acetone (1/1)-insoluble product.

^c Measured by GPC (polystyrene standard).

Figure 1 $^1\text{H-NMR}$ spectra of **2e** and **3e**.

and silyl segments were observed. In addition, a very weak peak around 3.1 ppm is observed, which originates from the resonance of bisbenzyl moieties. This is a type of structural defect in the PPV backbone. It is reported that such defect is formed by the head-to-head linkage of *p*-xylylene intermediates during polymerization.³³ The amount of bisbenzyl defects is calculated to be 3.8% based on the peak intensity ratio of bisbenzyl moiety to dimethylsilyl group. It is considered that the structural defect does not intensely affect the property of PPV because the content of bisbenzyl moieties was very small.

Figure 2 $^1\text{H-NMR}$ spectra of **2f** and **3f**.

Solubility and thermal stability of silylated-PPV

The solubility of silyl-substituted PPV is summarized in Table II. Trimethylsilyl-substituted PPV (**3a**) was insoluble in any solvents. Triethylsilyl- and dimethyl-*n*-butylsilyl-substituted PPVs (**3b** and **3d**) showed better solubility, and they partially dissolved in CHCl_3 , THF, and CH_2Cl_2 . The solubility of dimethyl-*t*-butylsilyl-substituted PPV (**3c**) was low, and it was slightly soluble in CHCl_3 and THF. On the other hands, long alkyl silyl-substituted PPVs (**3e** and **3f**) exhibited relatively good solubility, and they totally dissolved in CHCl_3 .

The thermal stability of silyl-substituted PPVs in N_2 was evaluated by TGA (Fig. 3). Except for

TABLE II
Solubility of Silylated PPVs^a

Polymer	Hexane	Toluene	CHCl_3	THF	Et_2O	CH_2Cl_2	Acetone	Methanol
3a	—	—	—	—	—	—	—	—
3b	—	—	±	±	—	±	—	—
3c	—	—	±	±	—	—	—	—
3d	—	±	±	±	—	±	—	—
3e	—	±	+	±	—	±	—	—
3f	—	±	+	±	—	±	—	—

^a Symbols: + soluble, ± partially soluble, — insoluble.

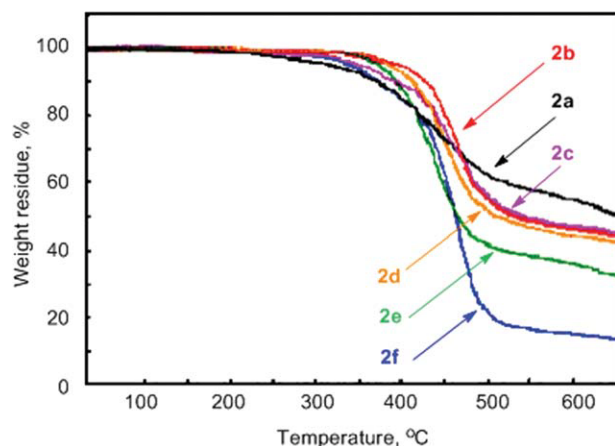


Figure 3 Thermogravimetric analysis of silyl-substituted PPVs in N_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer **3a**, thermal decomposition temperatures (5% weight loss) of the PPVs (**3b–f**) were over 350°C , indicating good thermal stability. PPVs having trimethylsilyl groups (**3a**) exhibited lower decomposition temperature, which may be related to its lower molecular weight. The polymer **3a** was immediately precipitated during the polymerization, and therefore the molecular weight of **3a** is expected not to increase sufficiently. The weight-loss patterns are similar for all the silyl-substituted PPVs. The weight losses became from around 300°C , and the weights greatly decreased to around 500°C , and then they were gradually decreased. Based on the percentage of weight loss consideration, it was found that the PPVs lose silyl side groups in the first, then decomposition of the main chains occurred.

Gas permeability of membranes of silylated PPVs

The free-standing membranes of silyl-substituted PPV could be prepared by solution-casting except for trimethylsilyl-substituted PPV (**3a**). Polymers **3b–d** could not completely dissolve in organic solvents, and their membranes were fabricated using CHCl_3 -soluble parts. Their gas permeability coefficients and

separation factors are shown in Table III. The oxygen permeability coefficients (PO_2) of membranes of **3b** and **3c** were 6.6 and 6.5 barrers, respectively. The PO_2 of membrane of **3d** was 3.5 barrers, which is half of those of **3b** and **3c**. These results suggest that spherical bulky substituents such as triethylsilyl- and dimethyl-*t*-butylsilyl groups are effective in increase of gas permeability on PPVs. However, dimethyl-*n*-octylsilyl group-containing PPV (**3e**) showed relatively high gas permeability, and its PO_2 value was 12 barrers, which is roughly twice as large as those of polymers **3b** and **3c**. The PO_2 of membrane of dimethyl-*n*-octadecylsilyl group-containing PPV (**3f**) was 12 barrers, which is the same as that of membranes of **3e**. This may be accounted for by the flexibility of enough long alkyl groups to improve gas diffusion in the polymer matrix. Our previous article showed that gas permeability increased as increasing alkyl length of side groups in poly(*p*-phenylene ethynylene) [$-\text{C}\equiv\text{C}-\text{C}_6\text{H}_2\text{R}_2-\text{R}=\text{n}-\text{C}_6\text{H}_{13}$, $\text{n}-\text{C}_8\text{H}_{17}$, $\text{n}-\text{C}_{10}\text{H}_{21}$].³⁴ It is revealed that PPV exhibits high gas permeability when the polymer had long alkyl groups, as is the case for poly(*p*-phenylene ethynylene)s. The permeability 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 of **3e** and **3f** were almost the same, and they are higher than those of **3b–d**.

CONCLUSIONS

This article first revealed the gas permeability of membranes of substituted poly(*p*-phenylenevinylene)s. Poly(*p*-phenylenevinylene)s with relatively bulky silyl groups showed solvent-solubility, and gave their tough free-standing membranes by solution-casting. PPVs having relatively long alkyl silyl groups showed higher gas permeability than PPVs having short alkyl silyl groups and spherical silyl groups. The silyl-substituted PPVs had good thermal stability, excellent film-forming ability, and easy polymerization procedure, and hence they are promising for novel polymer materials as gas separation membranes.

References

1. Pinnau, I.; Freeman, B. D. *Advanced Materials for Membrane Separation*, ACS Symposium Series; American Chemical Society: Washington, 2004; 876.
2. Tsujita, Y. *Prog Polym Sci* 2003, 28, 1377.
3. Nunes, S. P.; Peinemann, K. V. *Membrane Technology in the Chemical Industry*; Wiley: New York, 2001.
4. Pandey, P.; Chauhan, R. S. *Prog Polym Sci* 2001, 26, 853.
5. Baker, R. W. *Ind Eng Chem Res* 2002, 41, 1393.
6. Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog Polym Sci* 2001, 26, 721.
7. Aoki, T. *Prog Polym Sci* 1999, 24, 951.
8. Sakaguchi, T.; Yumoto, K.; Shida, Y.; Shiotsuki, M.; Sanda, F.; Masuda, T. *J Polym Sci Part A: Polym Chem* 2006, 44, 5028.

TABLE III
Gas Permeability Coefficients (P)^a and Selectivity of Membranes of Silyl-Substituted PPVs

membrane	PN_2	PO_2	PCO_2	PO_2/PN_2	PCO_2/PN_2
3b	1.8	6.6	24	3.7	13
3c	1.5	6.5	26	4.3	17
3d	1.1	3.5	14	3.2	13
3e	3.9	12	60	3.1	15
3f	4.5	12	61	2.7	14

^a In the units of barrer ($1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm/cm}^2 \text{ sec}$).

9. Wind, J. D.; Paul, D. R.; Koros, W. J. *J Membr Sci* 2004, 228, 227.
10. Heuchel, M.; Hofmann, D.; Pullumbi, P. *Macromolecules* 2004, 37, 201.
11. Ayala, D.; Lozano, A. E.; Abajo, J. D.; Garcia-Perez, C.; De La Campa, J. G.; Peineman, K. V.; Freeman, B. D.; Prabhakar, R. *J Membr Sci* 2003, 215, 61.
12. Burns, R. L.; Koros, W. J. *Macromolecules* 2003, 36, 2374.
13. Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S.; Lee, K. J.; Jho, J. Y. *Macromolecules* 2004, 37, 1403.
14. Kim, I. W.; Lee, K. J.; Jho, J. Y.; Park, H. C.; Won, J.; Kang, Y. S.; Guiver, M. D.; Robertson, G. P.; Dai, Y. *Macromolecules* 2001, 34, 2908.
15. Ghosal, K.; Chen, R. T.; Freeman, B. D.; Daly, W. H.; Negulescu, I. I. *Macromolecules* 1996, 29, 4360.
16. Laot, C. M.; Marand, E.; Schmittmann, B.; Zia, R. K. P. *Macromolecules* 2003, 36, 8673.
17. Lopez-Gonzalez, M. M. C.; Saiz, E.; Guzman, J.; Riande, E. *Macromolecules* 2001, 34, 4999.
18. Chen, S. H.; Ruaan, R. C.; Lai, J. Y. *J Membr Sci* 1997, 134, 143.
19. Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem Rev* 2009, 109, 897.
20. Kim, J.; Swager, T. M. *Nature (London)* 2001, 411, 1030.
21. Sato, T.; Jiang, D. L.; Aida, T. *J Am Chem Soc* 1999, 121, 10658.
22. Ding, L.; Egbe, D. A. M.; Karasz, F. E. *Macromolecules* 2004, 37, 6124.
23. Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J Am Chem Soc* 1983, 105, 7473.
24. Tsuchihara, K.; Masuda, T.; Higashimura, T. *J Am Chem Soc* 1991, 113, 8548.
25. Kim, H. S.; Kim, Y. H.; Ahn, S. K.; Kwon, S. K. *Macromolecules* 2003, 36, 2327.
26. Kim, Y. H.; Ahn, S. K.; Kim, Y. S.; Kwon, S. K. *J Polym Sci Part A: Polym Chem* 2002, 40, 4288.
27. Chen, Z. K.; Huang, W.; Wang, L. H.; Kang, E. T.; Chen, B. J.; Lee, C. S.; Lee, S. T. *Macromolecules* 2000, 33, 9015.
28. Wang, L. H.; Chen, Z. K.; Kang, E. T.; Meng, H.; Huang, W. *Synth Met* 1999, 105, 85.
29. Gilch, H. G.; Wheelwright, W. L. *J Polym Sci: A-1* 1966, 4, 1337.
30. Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J Am Chem Soc* 1998, 120, 231.
31. Hsieh, B. R.; Yu, Y.; Vanlaeken, A. C.; Lee, H. *Macromolecules* 1997, 30, 8094.
32. Sakaguchi, T.; Yumoto, K.; Shiotsuki, M.; Sanda, F.; Yoshikawa, M.; Masuda, T. *Macromolecules* 2005, 38, 2704.
33. Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* 1999, 32, 4925.
34. Sakaguchi, T.; Nojiri, D.; Hashimoto, T. *Polym Bull* 2008, 60, 271.