Polymer 54 (2013) 2272–2277

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of silyl-disubstituted poly(*p*-phenylenevinylene) membranes and their gas permeability

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ARTICLE INFO

Article history:
Received 15 December 2012
Received in revised form
27 February 2013
Accepted 4 March 2013
Available online 13 March 2013

Keywords:
Poly(*p*-phenylenevinylene)
Membrane
Gas permeability

ABSTRACT

p-Bis(bromomethyl)benzene with two silyl groups [$SiMe_2$-*n*-C_8H_{17}, $SiMe_3$ (**1a**), $SiMe_2$-*n*-C_8H_{17}, $SiEt_3$ (**1b**), $SiMe_2$-*n*-C_8H_{17}, $SiMe_2$-*n*-C_8H_{17} (**1c**), $SiMe_2$-*n*-C_8H_{17}, $SiMe_2$-*n*-$C_{18}H_{37}$ (**1d**), $SiMe_2$-*n*-$C_{18}H_{37}$, $SiMe_2$-*n*-$C_{18}H_{37}$ (**1e**)] were polymerized by Gilch method to afford silyl-disubstituted poly(*p*-phenylenevinylene)s (**2a**–**e**). The polymers containing $SiMe_3$ groups (**2a**) showed poor solubility and dissolved in only $CHCl_3$. On the other hand, the other polymers (**2b**–**e**) exhibited good solubility in common organic solvents. According to thermogravimetric analysis (TGA), the silyl-disubstituted poly(*p*-phenylenevinylene)s showed high thermal stability (thermal decomposition temperature: $T_d \geq 310$ °C). Polymers **2a**–**e** had relatively high molecular weight over 7.6×10^4, and gave free-standing membranes by solution casting method. Except **2e**, the oxygen permeability coefficients (PO_2) of membranes of the silyl-disubstituted poly(*p*-phenylenevinylene)s increased as increasing alkyl length of silyl groups (**2a**: 5.4, **2b**: 6.0, **2c**: 15.0, **2d**: 20.4 barrers). The membrane of **2e** having two dimethyl-*n*-octadecylsilyl groups in the repeating unit exhibited the lowest gas permeability among the present polymers, and its PO_2 was 1.8 barrers. This is because polymers **2a**–**d** were amorphous while **2e** was crystalline. The PO_2 values for amorphous poly(*p*-phenylenevinylene)s increase in direct proportion to the number of carbon in the side chains.

1. Introduction

Gas permeable polymers have been extensively studied because of their promising application in gas separation membrane [1–5]. A variety 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 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(*p*-phenylenevinylene)s [PPV] bearing various substituents have been intensively researched because of their optical and electronic properties [19–22]. Substituted PPVs are generally synthesized by the polymerization of bis(halomethyl)benzene using potassium *tert*-butoxide as a base, namely Gilch polymerization [23]. It is a simple procedure, and give high molecular weight PPVs. PPVs possess rigid main chain composed of benzene rings and carbon–carbon double bonds, and membranes of PPVs containing bulky substituents such as silyl groups possibly exhibit high gas permeability. Silyl groups are effective as a bulky substituent to improve the gas permeability of polymer membranes because of the steric repulsion and high local mobility of silyl groups [24,25], and a number of silyl-substituted polymers indeed show high gas permeability [26–29]. Among various silyl groups, a trimethylsilyl group is the best substituent for poly(substituted acetylene)s in order to obtain high gas permeable membranes. When a silyl group becomes bulkier than a trimethylsilyl group, the gas permeability of membrane becomes lower [6]. These findings motivated us to examine the gas permeability of membranes of silyl-substituted PPVs, especially trimethylsilyl group-substituted PPV. In our previous study [30], the gas permeability of PPV having long alkyl silyl groups were larger than that of PPV having triethylsilyl and dimethyl-*t*-butylsilyl groups. This tendency is opposite to that for poly(substituted acetylene)s. Unfortunately, the membrane of trimethylsilyl group-substituted PPV had not been obtained because the PPV showed poor solubility.

To reveal the tendency of gas permeability and the effect of trimethylsilyl groups for the membranes of PPV, in the present

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http://dx.doi.org/10.1016/j.polymer.2013.03.007

study, bis(bromomethyl)benzenes having two silyl groups were synthesized and then polymerized by Gilch polymerization. The PPVs obtained by this route have at least one long alkyl silyl group in a repeating unit. So, they would exhibit good solubility and afford the free-standing membranes by solution casting. We investigated the gas permeability of membranes of silyl-disubstituted PPVs and discussed the effect of silyl groups on the gas permeability for PPV membranes (Scheme 1).

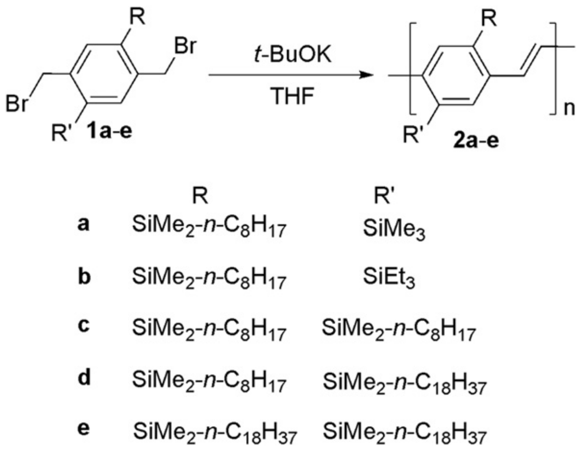
2. Experimental

2.1. 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 three polystyrene gel columns (Shodex K-807L, K-805L, K-804L) 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. 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. Differential scanning calorimetry (DSC) was performed with Rigaku Thermo Plus DSC 8230L. The temperature range was -50 to $+300$ °C and the heating and cooling rates were 5 °C/min. During the measurement, the sample was purged by nitrogen gas. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C under 1 atm upstream pressure.

2.2. Materials

2,5-Dibromo-*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., Ltd. and used without further purification. Various chlorosilanes were purchased from Tokyo Chemical Industry Co., Ltd. THF as polymerization solvent was purified by distillation twice. Monomers **1c** [31] and **1e** [32] were synthesized according to the literatures. The other monomers were synthesized from 2,5-dibromo-*p*-xylene by silylation followed by radical bromination as shown in Scheme 2 according to the literatures [32,33]. The details of the procedures and analytical data of monomers are stated below.



	R	R'
a	$SiMe_2$-*n*-C_8H_{17}	$SiMe_3$
b	$SiMe_2$-*n*-C_8H_{17}	$SiEt_3$
c	$SiMe_2$-*n*-C_8H_{17}	$SiMe_2$-*n*-C_8H_{17}
d	$SiMe_2$-*n*-C_8H_{17}	$SiMe_2$-*n*-$C_{18}H_{37}$
e	$SiMe_2$-*n*-$C_{18}H_{37}$	$SiMe_2$-*n*-$C_{18}H_{37}$

Scheme 1. Synthesis of silyl-disubstituted poly(*p*-phenylenevinylene)s.

2.3. 2-Dimethyl-n-octylsilyl-5-trimethylsilyl-p-bis(bromomethyl) benzene (*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 nitrogen, 2,5-dibromo-*p*-xylene (20 g, 75.9 mmol) and ether (300 mL) were added and cooled at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (47.4 mL, 1.6 M, 75.9 mmol) was added dropwise, and the mixture was stirred for 1 h. Then, a solution of chlorotrimethylsilane (9.9 g, 91.1 mmol) in ether (50 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-bromo-5-trimethylsilyl-*p*-xylene (yield 83%).

Silylation of 2-bromo-5-trimethylsilyl-*p*-xylene was performed by the same method as for 2-bromo-5-trimethylsilyl-*p*-xylene using chlorodimethyl-*n*-octylsilane instead of chlorotrimethylsilane. The obtained crude product was purified by silica gel column chromatography (eluent: hexane) to afford 2-dimethyl-*n*-octylsilyl-5-trimethylsilyl-*p*-xylene (yield 82%).

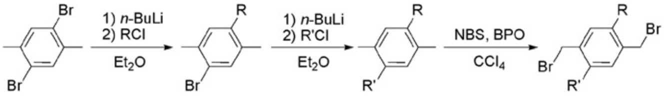
2-Dimethyl-*n*-octylsilyl-5-trimethylsilyl-*p*-xylene (8.8 g, 25.2 mmol), NBS (9.0 g, 50.5 mmol), BPO (68 mg, 0.28 mmol), and CCl_4 (200 mL) were charged into a 500 mL flask equipped with a reflux condenser. The mixture was stirred at 80 °C under N_2 for 1 h. The solution was washed with water three 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-dimethyl-*n*-octylsilyl-5-trimethylsilyl -*p*-bis(bromomethyl)benzene (yield 25%). ^{1}H NMR ($CDCl_3$, ppm): 7.52 (s, 1H, Ar), 7.50 (s, 1H, Ar), 4.60 (s, 2H, CH_2Br), 4.59 (s, 2H, CH_2Br), 1.35–1.20 (m, 12H, $SiCH_2\text{-}(CH_2)_6\text{-}CH_3$), 0.87 (t, $J = 7.1$ Hz, 5H, $SiCH_2\text{-}(CH_2)_6\text{-}CH_3$), 0.40 (s, 9H, $Si(CH_3)_3$), 0.38 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 142.2, 142.0, 140.8, 140.3, 137.7, 137.4, 34.2, 34.1, 33.5, 31.9, 29.2, 23.9, 22.7, 16.4, 14.1, 0.3, -1.5. Anal. Calcd for $C_{21}H_{38}Br_2Si_2$: C, 49.80; H, 7.56; Br, 31.55; Si, 11.09. Found: C, 49.48; H, 7.16.

2.4. 2-Dimethyl-n-octylsilyl-5-triethylsilyl-p-bis(bromomethyl) benzene (*1b*)

This monomer was prepared by the same method as for **1a** (Overall yield 12%). ^{1}H NMR ($CDCl_3$, ppm): 7.50 (s, 1H, Ar), 7.48 (s, 1H, Ar), 4.58 (s, 2H, CH_2Br), 4.57 (s, 2H, CH_2Br), 1.34–1.18 (m, 12H, $SiCH_2\text{-}(CH_2)_6\text{-}CH_3$), 1.00–0.85 (m, 20H, $SiCH_2\text{-}(CH_2)_6\text{-}CH_3$, $Si(CH_2CH_3)_3$), 0.38 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 142.4, 141.9, 139.9, 138.4, 137.8, 137.7, 34.4, 34.3, 33.5, 31.9, 29.2, 23.9, 22.7, 16.4, 14.1, 7.6, 4.2, -1.6. Anal. Calcd for $C_{24}H_{44}Br_2Si_2$: C, 52.55; H, 8.08; Br, 29.13; Si, 10.24. Found: C, 52.30; H, 8.20.

2.5. 2-Dimethyl-n-octylsilyl-5-dimethyl-n-octadecylsilyl-p-bis(bromomethyl)benzene (*1d*)

This monomer was prepared by the same method as for **1a** (Overall yield 9%). ^{1}H NMR ($CDCl_3$, ppm): 7.50 (s, 2H, Ar), 4.58 (s, 4H,



Scheme 2. Monomer synthesis scheme.

CH_2Br), 1.34–1.21 (m, 44H, $SiCH_2–(CH_2)_6–CH_3$, $SiCH_2–(CH_2)_{16}–CH_3$), 0.90–0.83 (m, 10H, $SiCH_2–(CH_2)_6–CH_3$, $SiCH_2–(CH_2)_{16}–CH_3$), 0.38 (s, 12H, $Si(CH_3)_2$, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 142.1, 140.1, 137.7, 34.3, 33.52, 33.51, 31.92, 31.91, 29.70, 29.68, 29.66, 29.59, 29.4, 29.3, 29.24, 29.22, 23.9, 22.69, 22.66, 16.4, 14.1, −1.5. Anal. Calcd for $C_{38}H_{72}Br_2Si_2$: C, 61.27; H, 9.74; Br, 21.45; Si, 7.54. Found: C, 60.96; H, 9.65.

2.6. Polymerization

Polymerization was carried out in a round-bottom flask equipped with a dropping funnel and a three-way stopcock under dry nitrogen. A detailed procedure of polymerization is as follows: Monomer **1a** (1.01 g) and dry THF (30 mL) were charged in the flask. To this solution was slowly added a solution of potassium *tert*-butoxide (1.35 g) in dry THF (20 mL) at 0 °C. After 2 h, the reaction mixture was then poured into the mixture of methanol and acetone (1:1). The precipitate was dissolved in chloroform and reprecipitated in the mixture of methanol and acetone. Its yield was determined by gravimetry.

2.7. Membrane preparation

Membranes of **2b**–**e** were prepared by casting toluene solution of polymers (concn. 1.0–2.0 wt%) onto a glass plate. The plate was covered with a glass vessel to slow down solvent evaporation (ca. 3 days). After drying, the membrane was peeled off, and it was further dried at 25 °C under reduced pressure for 24 h. However, membrane of **2a** was prepared by casting $CHCl_3$ solution of the polymer because **2a** did not dissolved in toluene completely. The thickness of membranes used for measurement is in the range of 50–80 μm.

2.8. Fractional free volume (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:

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

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. An aqueous sodium nitrate was used as the auxiliary liquid. FFV is calculated by the following equation:

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

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 [34].

3. Results and discussion

3.1. Synthesis of silyl-disubstituted PPV

The monomers can be easily polymerized by the Gilch polymerization using potassium *tert*-butoxide as a base in dry THF. In the present study, relatively high molecular weight polymers are desired in order to prepare free-standing membranes by solution casting. Then, the polymerizations of monomer **1a** were examined under various conditions (Table 1). Increase of polymerization temperature hardly affected the yield and molecular weight of the resultant polymers (runs 1 and 2), but increase of concentration of base improved the M_n of the resultant polymers (run 3). When the polymerization was operated at higher concentrations of monomer and base, the yield and M_n of the polymer became 63% and 76,600, respectively (run 4). However, the polymerization at much higher concentrations of monomer and base afforded an insoluble polymer (run 5). Therefore, the polymerizations of the other monomers were examined under the same conditions as those of run 4 in Table 1. The silyl-disubstituted PPVs (**3b**–**e**) were obtained in relatively high yields, whose M_n's were in the range of 98,700–260,000 (Table 2).

Table 1
Polymerization of monomer **1a** in THF.

Run	$[M]_0$ [mM]	$[t\text{-BuOK}]_0$ [mM]	Temp. [°C]	Time [h]	Yield[a] [%]	M_n[b]	M_w/M_n[b]
1	20	60	0	2	49	12,600	8.48
2	20	60	25	15	41	17,300	6.53
3	20	120	0	2	49	32,300	7.22
4	40	240	0	2	63	76,600	4.11
5	80	480	0	2	82	insoluble	

[a] Acetone-insoluble product.
[b] Measured by GPC.

The ^1H NMR spectra of polymers were measured in $CDCl_3$ (Fig. 1). In all the spectra, two broad peaks at around 7.90 and 7.45 ppm were observed, which are assigned to the protons on the vinylene segments and benzene rings, respectively. The peaks assigned to the protons on alkyl silyl groups were observed at around 1.40, 0.85, and 0.45 ppm. In the spectra of **2a** and **2b**, 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 [35]. The amount of bisbenzyl defects is calculated to be approximately 8.5% based on the peak intensity ratio of bisbenzyl moiety to vinylene moiety. Polymers **2c**–**e** should have the structural defect in the backbone, but the peak could not be observed probably because the peak intensity is too low toword the peak intensity of alkyl groups.

3.2. Solubility and thermal stability of silyl-disubstituted PPV

The solubility of silyl-dusbstituted substituted PPVs is summarized in Table 3. Trimethylsilyl-substituted PPV (**2a**) showed poor solubility. Polymer **2a** was soluble only in $CHCl_3$, and partly soluble in hexane, toluene, CH_2Cl_2, and THF. Specifically, most part of **2a** was completely soluble in toluene and THF, but a small amount of insoluble part was observed in those solvents. On the other hands, PPVs having two long alkyl silyl groups in a repeating unit (**2b**–**e**) exhibited relatively good solubility, and they totally dissolved in toluene, $CHCl_3$, CH_2Cl_2, and THF.

The thermal stability of silyl-disubstituted PPVs in N_2 was evaluated by TGA (Fig. 2). Except for polymer **2c**, thermal

Table 2
Polymerization of monomers **1b**–**e**.[a]

Run	Monomer	yield[b] [%]	M_n[c]	M_w/M_n[c]
1[d]	**1b**	49	125,000	4.59
2	**1c**	40	98,700	3.97
3	**1d**	77	260,000	2.91
4	**1e**	81	226,000	2.23

[a] In THF at 0 °C for 2 h; $[M]_0$ = 40 mM, [t-BuOK] = 240 mM.
[b] Acetone-insoluble product.
[c] Measured by GPC.
[d] $[M]_0$ = 80 mM, [t-BuOK] = 480 mM.

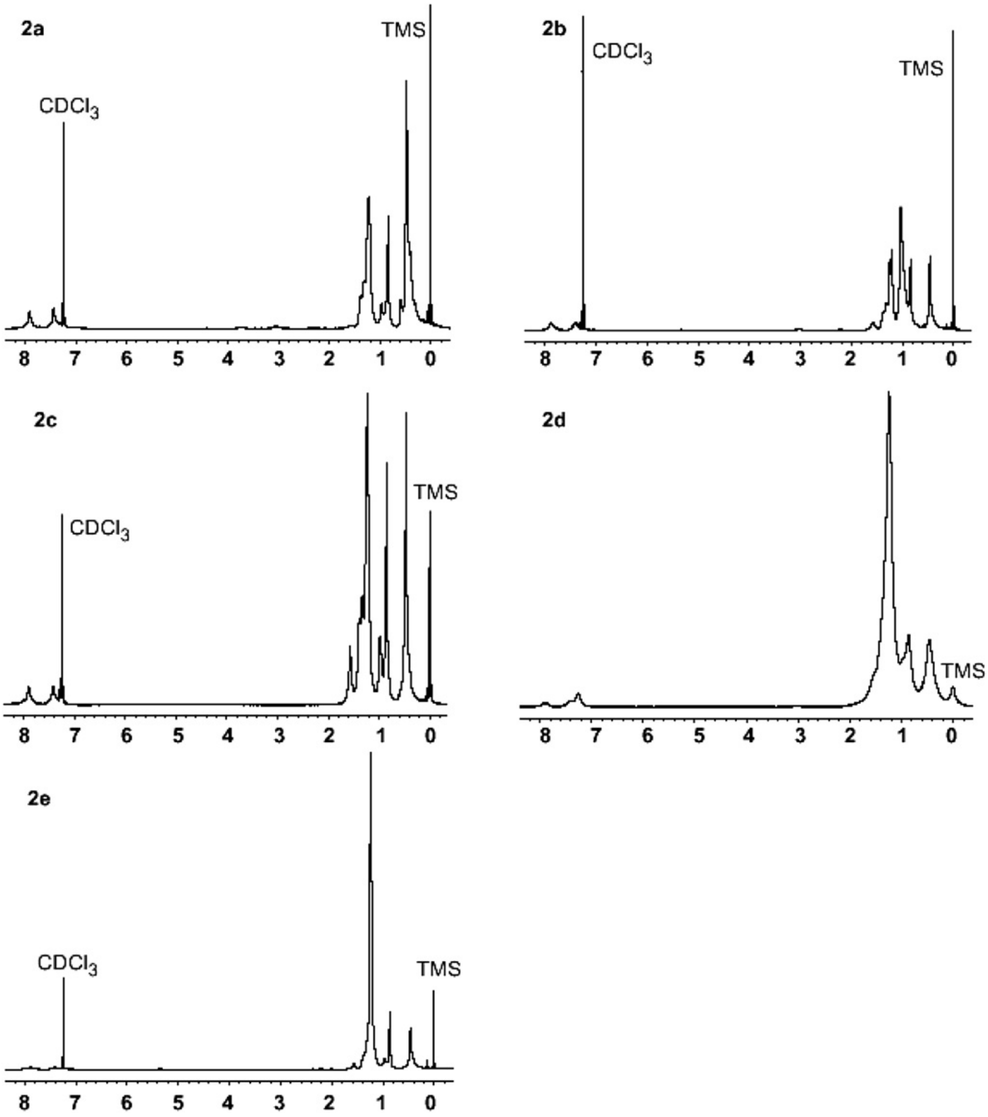


Fig. 1. ^{1}H NMR spectra of **2a**–**e** in $CHCl_3$.

decomposition temperatures (5% weight loss) of the PPVs were over 310 °C, indicating good thermal stability. The weight loss patterns are similar for all the silyl-disubstituted PPVs. The weight losses became from around 230 °C, and the weights greatly decreased to around 500 °C, and then they were slightly decreased. On the basis of the percentage of weight loss consideration, it was found that the PPVs lose silyl side groups in the first, and then decomposition of the main chains occurred. The decomposition temperature of **2c** was 410 °C, which is higher than those of the other silyl-disubstituted PPVs. The weight residue was approximately 40% at 500 °C, and the value does not correspond to the

Table 3
Solubility of polymers.[a]

Polymer	Hexane	Toluene	$CHCl_3$	CH_2Cl_2	THF	Acetone	DMF	DMSO
2a	±	±	+	±	±	−	−	−
2b	±	+	+	+	+	−	−	−
2c	±	+	+	+	+	−	−	−
2d	+	+	+	+	+	−	−	−
2e	+	+	+	+	+	−	−	−

[a] Symbols; +: soluble, ±: partly soluble, −: insoluble.

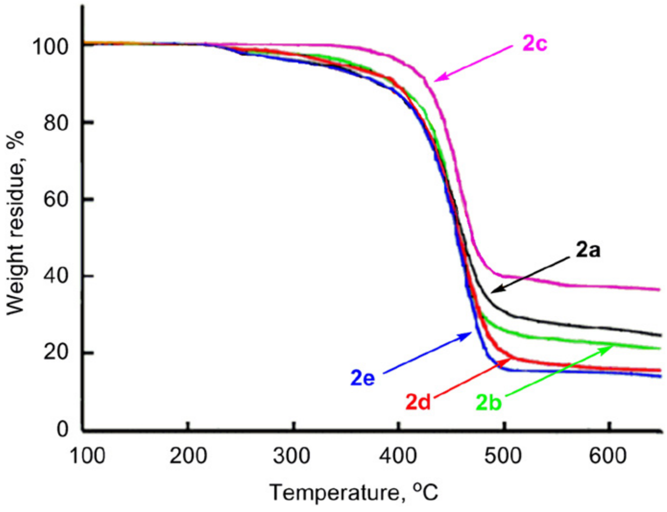


Fig. 2. TGA thermograms of polymers **2a**–**e** (in N_2, heating rate 10 °C/min).

Table 4
Gas permeability coefficients (P)[a] and densities of membranes at 25 °C.

Membrane	PO_2	PN_2	PCO_2	PO_2/PN_2	PCO_2/PN_2	density [g/cm^3]	FFV
2a	5.4	1.5	22	3.7	15	1.02	0.095
2b	6.0	1.6	23	3.8	15	1.00	0.095
2c	15	4.9	67	3.0	14	0.950	0.14
2d	20	7.1	100	2.9	14	0.929	0.15
2e	1.8	0.60	9.2	3.0	15	0.976	0.10

[a] In the unit of barrer (1 barrer = 1×10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}).

percentage of weight loss for silyl side groups. However, a convincing explanation could not be provided for the distinct result of **2c**.

3.3. Gas permeability of membranes of silylated PPVs

The free-standing membranes of **2a**–**e** could be prepared by solution casting. The gas permeability coefficients, separation factors, and fractional free volume (FFV) are shown in Table 4. The oxygen permeability coefficients (PO_2) of membranes of **2a** and **2b** were 5.4 and 6.0 barrers, respectively. The other gas permeability and separation factors of **2a** were almost the same as those of **2b**. The FFVs of these two membranes were also the same, which suggests that long alkyl silyl groups mainly control the formation of membranes and the difference between trimethylsilyl and triethylsilyl dose not affect the gas permeability. Dimethyl-*n*-octylsilyl group-disubstituted PPV (**2c**) exhibited higher gas permeability than **2a** and **2b**, and dimethyl-*n*-octylsilyl and dimethyl-*n*-octadecylsilyl groups-substituted PPV (**2d**) showed even higher gas permeability than **2c**. For example, the PO_2 of **2c** and **2d** were 15 and 20 barrers, respectively, which are more than twice as large as those of **2a** and **2b**. The separation factors of **2c** and **2d** were smaller than those of **2a** and **2b**, which agrees with the general tendency that highly gas permeable polymers show low gas separation ability. The FFV values of **2c** and **2d** were also much larger than those of **2a** and **2b**. These results indicated that a long alkyl chain is important for the gas permeability in substituted PPV. The high gas permeability of PPV having long alkyl chains would be due to that flexible alkyl chains assist gas diffusion and long chains prevent π–π stacking of conjugated main chains. On the contrary, dimethyl-*n*-octadecylsilyl group-disubstituted PPV (**2e**) showed the lowest gas permeability among the disubstituted PPVs in the present study. The low gas permeability of membrane of **2e** is due to that **2e** is a crystalline polymer. The membrane of **2e** was translucent, and the membranes of **2a**–**d** were transparent. The DSC thermograms on first heating scan of membranes of **2a**–**e** are shown in Fig. 3. In the thermograms of **2a**–**d**, there is no peak in the present temperature range, while polymer **2e** showed melting of crystallites around 28 °C, indicating that membrane of **2e** contains crystalline parts.

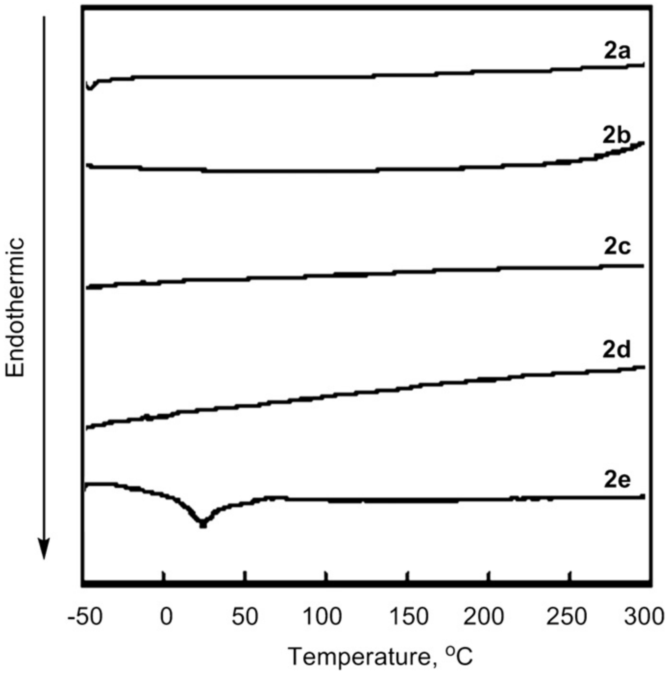


Fig. 3. DSC thermograms of membranes **2a**–**e** (in N_2, heating rate 5 °C/min, first heating scan).

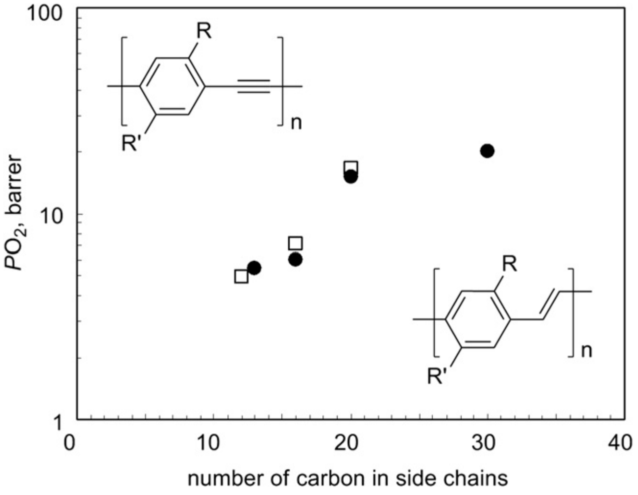


Fig. 4. Relationship between the PO_2 and the number of carbon in polymer side chains for poly(*p*-phenylenevinylene)s (●) and poly(*p*-phenyleneethynylene)s (□).

The relation between the gas permeability and the length of side chains in the membranes of PPVs is the same as that in poly(*p*-phenyleneethynylene)s (PPE) having long alkyl groups we reported [36]; i.e., the gas permeability increases as the alkyl side chains become longer in PPV and PPE. In poly(diphenylacetylene)s, however, the effect of substituents is opposite to PPV and PPE [37]. When poly(diphenylacetylene), one of the highest gas permeable polymers [6], has spherical bulky substituents such as trimethylsilyl groups as a side group, the polymer forms a sparse membrane (FFV = 0.26 [38]) because the stacking between polymer chains is prevented by steric repulsion of bulky substituents [39]. On the other hands, the FFV value drastically decreases when poly(diphenylacetylene) possesses long alkyl groups. This would be due to that the flexible long alkyl chains occupy the molecular-scale voids indigenous to poly(diphenylacetylene) membrane. In contrast to poly(diphenylacetylene), PPV and PPE afford rather dense membranes and they have little molecular-scale voids. Therefore, the role of long alkyl chains on PPV and PPE is different from that on poly(diphenylacetylene).

In PPV and PPE, the PO_2 versus the number of carbon in the side chains is plotted in Fig. 4. Interestingly, the PO_2 values increase in direct proportion to the number of carbon regardless of polymer backbone, suggesting that the percentage of flexible alkyl side chain mainly affects the gas permeability. It is concluded that the long alkyl chains would play a role of gas diffusion area as well as generate free volume on PPV and PPE.

4. Conclusions

This paper revealed the gas permeability of membranes of silyl-disubstituted poly(*p*-phenylenevinylene)s. Poly(*p*-phenylenevinylene)s with long alkyl silyl groups such as dimethyl-*n*-octylsilyl and dimethyl-*n*-octadecyl groups had relatively high molecular weights and good solubility, and afford their tough free-standing membranes by solution casting. The PPVs having two long alkyl silyl groups in a repeating unit showed higher gas permeability than PPVs having a long alkyl silyl group in a repeating unit. However, the PPV having two dimethyl-*n*-octadecylsilyl groups in a repeating unit exhibited the lowest gas permeability because of its crystallinity. It is found that the long alkyl chains would play roles of gas diffusion matrix as well as generate free volume in PPV and PPE.

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