

# Thermal and Physical Properties of Poly(tetraphenyl-*p*-silphenylenesiloxane-*co*-tetramethyl-*p*-silphenylenesiloxane)s

Hitoshi Ito, Eiichi Akiyama\*, Yu Nagase\*\* and Saburo Fukui\*\*

Ebara Research Co., Ltd, 4-2-1 Honfujisawa, Fujisawa, Kanagawa 251-8502, Japan

Fax: +81-466-81-7220, e-mail: itoh.hitoshi@er.ebara.com

\*Sagami Chemical Research Center, 2743-1, Hayakawa, Ayase, Kanagawa 251-1193, Japan

Fax: +81-467-77-4113, e-mail: akiyama@sagami.or.jp

\*\*Department of Applied Chemistry, School of Engineering, Tokai University,

1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Fax: +81-463-50-2012, e-mail: yunagase@keyaki.cc.u-tokai.ac.jp

The thermal degradation behavior in nitrogen and the thermal mechanical properties of poly(tetraphenyl-*p*-silphenylenesiloxane-*co*-tetramethyl-*p*-silphenylenesiloxane)s, Poly(PS-*co*-MS)s, were investigated by using the thermogravimetry analysis and the thermal mechanical analysis. Poly(PS-*co*-MS)s showed high  $T_{d5}$ , which presented a temperature of 5 % weight loss, in nitrogen ( $T_{d5} = \sim 500$  °C), and their molecular weights affected on the thermal degradation behavior. Each copolymer had a softening point,  $T_s$ , related to a glass transition temperature and/or a melting point. The copolymer of the unit ratio PS/MS = 86/14 showed relatively high thermal mechanical stability ( $T_s = 147$  °C). The gas permeability with self-standing copolymer membranes were investigated. The gas permeability of the membranes considerably lower than that of a polydimethylsiloxane membrane and decreased with an increase of PS unit ratio. The dielectric constants,  $\epsilon$ , of the copolymers were evaluated by using the optically method to range from 2.3 to 3.0.

Key words: Polysilarylenesiloxane, Copolymerization, Thermal degradation behavior, Thermal mechanical analysis, Gas permeability, Dielectric constant.

## 1. INTRODUCTION

Silicon containing materials are practically important because these have been used in wide variety of engineering applications. For example, poly(dimethylsiloxane), PDMS, and their derivatives have been used as oxygen-enriching membranes although the selectivity of oxygen is not enough [1, 2]. Silicon dioxide and the related materials are used as low dielectric constant materials in semiconductor devices [3, 4]. A new material having lower dielectric constant,  $\epsilon$ , than that of SiO<sub>2</sub>, however, is required in order to improve the device performance. Not only a value of  $\epsilon$  but a high thermal degradation temperature,  $T_d$ , a high glass transition temperature,  $T_g$ , and an affinity between an insulator and a silicon wafer are required. On the other hand, we reported that some kinds of silicon-containing polymers of fully aromatic polysilarylenesiloxanes showed no weight loss in air below 500 °C, and had high melting point,  $T_m$ , above 300 °C in our previous papers [5, 6]. Unfortunately, these were insoluble polymers, and could not be processed into thin films or self-standing membranes. Therefore, we prepared poly(tetraphenyl-*p*-silphenylene siloxane-*co*-tetramethyl-*p*-silphenylenesiloxane), Poly(PS-*co*-MS), in order to obtain soluble polymers, and reported their thermal properties in air in the last our report [7]. These polymers showed high  $T_d$  (around 500 °C) in air and showed  $T_g$  in proportional to the PS unit ratio. However, their thermal degradation behaviors in inert gas and their thermal mechanical properties are not

be revealed. Therefore, in this paper, thermal degradation behavior in nitrogen gas and thermal mechanical properties of the Poly(PS-*co*-MS)s are investigated by using the thermogravimetric analysis, TGA, and the thermal mechanical analysis, TMA, respectively. Furthermore, because the solubility of Poly(PS-*co*-MS) to common solvents was improved by copolymerization, a gas permeability and a dielectric constant as physical properties are studied. The self-standing membranes for the gas permeation measurements were made by the casting method. The thin films for the optical measurements in order to evaluate the dielectric constants were obtained by the spin-coating method. Then these physical properties will be discussed.

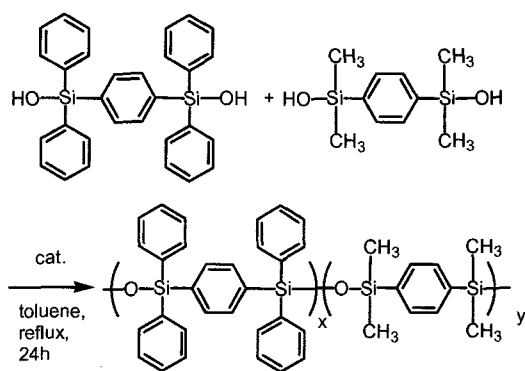
## 2. EXPERIMENTAL

### 2.1. Preparation of copolymers

Poly(PS-*co*-MS)s were synthesized in refluxed toluene in the presence of basic catalyst, according to our previous report [7] (CP series in Scheme). The molar compositions in the obtained copolymers, which were determined from the ratios of the integrated peak intensities of methyl protons and those of the phenyl protons of <sup>1</sup>H-NMR spectra, and their molecular weights were listed in Table I.

### 2.2. Thermal analysis

TGA was performed by using a Shimadzu DTG 60A at a heating rate of 10 °C·min<sup>-1</sup> with a nitrogen flow rate of 50 ml·min<sup>-1</sup> to study the thermal degradation behavior.



Scheme

Table I. Characterizations of polymers

Polymer	Composition <sup>b</sup> (mol %) x/y	$\bar{M}_n^c$ /10 <sup>4</sup>	$\bar{M}_w^c$ /10 <sup>4</sup>	$\bar{M}_w/\bar{M}_n$
PolyPS	100/0	—	—	—
CP-a	86/14	6.1	9.2	1.5
CP-b	70/30	3.7	5.6	1.5
CP-c	48/52	14	26	1.8
CP-d	24/76	29	47	1.6
CP-e	9/91	11	16	1.5
PolyMS <sup>a</sup>	0/100	21	34	1.7

<sup>a</sup> Polymerized in benzene at 80 °C. <sup>b</sup> Determined by <sup>1</sup>H-NMR.

<sup>c</sup>  $\bar{M}_n$  and  $\bar{M}_w$  are the number-average molecular weight and weight-average molecular weight, respectively.

TMA was performed on a Shimadzu TMA 60 using a penetration probe of 0.5 mm diameter under a constantly applied load of 50 g at a heating rate of 10 °C·min<sup>-1</sup> with a nitrogen flow rate of 50 ml·min<sup>-1</sup>.

### 2.3. The preparation of membranes

Toluene solutions containing 3 wt.% of the copolymer were cast on polytetrafluoroethylene sheets put at level, and the solvent was evaporated for a few days. Before measuring gas permeation, the membranes were dried in *vacuo* and cut into circle pieces 25 mm in diameter. The thicknesses of the membranes were used in the range of 100-300 μm.

### 2.4. Measurements of membrane densities

The density of each copolymer membrane was calculated from a precise weight and a precise volume of the product of a film area and a thickness, which was measured with a precision digital micrometer.

### 2.5. Measurements of gas permeability coefficients

Gas permeation measurements were conducted according to the vacuum method using a K-315N-01 (Tsukuba Rika Seiki) at 30 °C. A pressure on the permeation side was monitored with a BARATRON® Pressure Transducer. The permeability coefficients, *P*, were calculated from the slope of time-pressure curves, *dp/dt*, at steady state. The diffusion coefficients were calculated from the membrane thickness, *l*, and time lag, *θ*, according to the following equation,  $D = l^2/\theta$ . The solubility coefficients were also calculated by the equation,  $S = P/D$ .

### 2.6. Measurements of the thicknesses and the refractive indices

The copolymers were spin-coated from 1 wt.% solution in toluene on silicon wafers (Mitsubishi

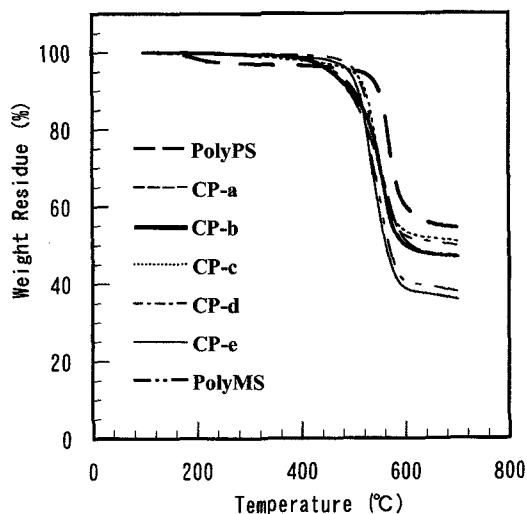


Fig. 1 TGA curves of copolymers in nitrogen.

Table II. Thermal degradation behavior of polymers

Polymer	in nitrogen		in air	
	$T_{d5}^a$ (°C)	Weight Residue <sup>b</sup> (%)	$T_{d5}^a$ (°C)	Weight Residue <sup>b</sup> (%)
PolyPS	511	54.4	539	27.3
CP-a	458	46.6	464	25.1
CP-b	457	46.9	470	28.6
CP-c	497	50.7	524	34.3
CP-d	505	49.6	513	43.2
CP-e	492	36.0	519	41.8
PolyMS	464	37.8	516	35.0

<sup>a</sup> The temperature of the 5 % weight loss determined from TG curve. <sup>b</sup> The ratio of weight residue at 700 °C.

Material) with a spin coater ACT-300A (Active) at 500 rpm. Refractive indices and thicknesses of copolymer films were measured by using the standard ellipsometric method on a DHA-XAS (Mizojiri Optical Co., Ltd.) at wavelength of 632.8 nm, and at an incident irradiation angle of 70°. Extinction coefficients of zero were used approximately.

## 3. RESULTS AND DISCUSSION

### 3.1. Thermal degradation behavior in nitrogen

The TGA curves of copolymers (CP series), PolyPS and PolyMS under nitrogen flow are shown in Fig. 1. CP series and PolyMS indicated weight loss processes of single step. In the case of PolyPS, the small weight loss (~2.8 %) was observed at 180-250 °C. This weight loss would be caused by the condensation between chain-end silanols as mentioned in the previous report [6]. The main thermal degradation started from around 520 °C. It was revealed that the fully aromatic polysilylenesiloxane such as PolyPS showed high thermal stability in nitrogen. As summarized in Table II, the temperature of 5 % weight loss,  $T_{d5}$ , of the CP series when the PS unit ratio was lower than 50 % increased with the increase of the PS unit ratio. To the contrary, the  $T_{d5}$  of the CP-a and b of high PS unit ratio (>70 %) decreased with the increase of PS unit ratio. The molecular weights of CP-a and b were considerably lower than those of the other CP series as listed in Table I. Considering the PolyPS was thermally stable below

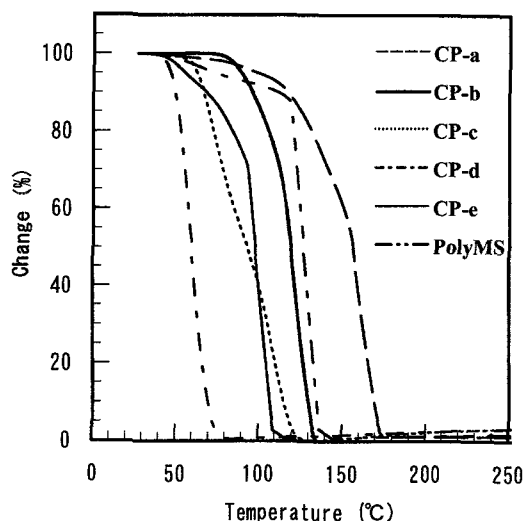


Fig. 2 TMA curves of copolymers.

520 °C, the reduced thermal stability of CP-a and b would be caused by the decomposition of the chain-end silanols arising from the MS units. These results showed that the molecular weights of copolymers greatly affected on the thermal stability of copolymers in similar to the thermal stability in air reported in our previous paper [7]. Additionally, the weight residues at 700 °C in nitrogen increased with an increase of PS unit ratio. On the other hand, the weight residues in air decreased with an increase of PS unit ratio. This indicated that the PS units were more stable under nitrogen than under air in the high temperature region.

### 3.2. Thermal mechanical properties

The TMA curves of CP series and PolyMS are shown in Fig. 2. TMA of PolyPS could not be conducted because this polymer was fine powder. The softening points,  $T_s$ , were determined as the intersection of the tangents of two linear segments in TMA curves. CP-e softened at room temperature, therefore,  $T_s$  could not be evaluated. However, CP-e looked like a solid state, and was not waxy or gammy material at a room temperature. The  $T_s$ 's estimated from the TMA curves are listed in Table III. The  $T_g$  and  $T_m$  estimated by using the differential scanning calorimetry have already been reported in our previous paper [7], and are also listed in Table III. The  $T_s$  increased with an increase of PS unit ratio. This would result from an increase of a rigid segment consisted of PS unit.  $T_s$  of CP-b and c were close to  $T_g$ . This indicated that the softening of copolymers was caused by the glass transition phenomena. CP-a exhibited relatively high  $T_s$  of 147 °C, which was 20 °C higher than  $T_g$ . Considering the  $T_m$  of

Table III. Thermal properties of polymers

Polymer	$T_g^a$ (°C)	$T_m^a$ (°C)	$T_s^c$ (°C)
PolyPS	—	323	—
CP-a	127	317	147
CP-b	96	—	101
CP-c	62	—	64
CP-d	22	—	49
CP-e	-3.8	(123) <sup>b</sup>	—
PolyMS	—	132	120

<sup>a</sup> Determined by DSC on the second heating scan. <sup>b</sup> Determined by DSC on the first heating scan. <sup>c</sup> The softening point determined by the TMA.

317 °C for CP-a, the crystal region should not yet melt around  $T_s$ . Consequently, the large amorphous region due to the low crystallization degree would suppress the thermal mechanical stability of CP-a. On the other hand, the  $T_s$  of CP-d was also higher than the  $T_g$ . This stabilization would be attributed to the high molecular weight, so that the  $T_s$  of CP-d also resulted from the glass transition phenomenon. For CP-e, the  $T_m$  was observed on the first heating scan only. Under the measurement condition of heating and cooling rates of  $\pm 10$  °C·min<sup>-1</sup>, CP-e during the second heating scan would stand in a super-cooling state to exhibit only a glass transition.

### 3.3. The preparation of membranes

The membranes were prepared from the toluene solution of each copolymer by the casting method on the polytetrafluoroethylene sheets. However, the membranes of CP-a and b were brittle and fragile, and could not be obtained as self-standing membranes. On the other hand, CP-c, d, e and PolyMS could be obtained as tough membranes of their thickness in the range of 100-300  $\mu$ m. Thus difference of processability into membranes would be mainly caused by the different molecular weights as listed in Table I. Unfortunately, the copolymers, which have the same composition as CP-a and b, and have high molecular weights suitable for the membrane preparation, could not be obtained. As a result, the gas permeabilities of CP-c, d, e and PolyMS membranes were measured.

### 3.4. Gas permeabilities

Permeation measurements of hydrogen, oxygen, nitrogen and carbon dioxide gasses for the CP-c, d, e and PolyMS membranes were conducted at 30 °C. Unfortunately, the measurements for CP-e and PolyMS membranes were not successfully finished because the no negligible pressure changes of a permeate side arising

Table IV. Gas permeation behavior of polymers

Code	density g/cm <sup>3</sup>	$P_{H_2}$	$P_{O_2}$	$P_{N_2}$	$P_{CO_2}$	$D_{H_2}$	$D_{O_2}$	$D_{N_2}$	$D_{CO_2}$	$S_{H_2}$	$S_{O_2}$	$S_{N_2}$	$S_{CO_2}$
		(Barrer) <sup>c</sup>				(10 <sup>-7</sup> cm <sup>2</sup> ·sec <sup>-1</sup> )				(10 <sup>-4</sup> cm <sup>3</sup> (s.t.p.)·cm <sup>3</sup> ·cmHg <sup>-1</sup> )			
CP-c	1.0	28	4.5	1.1	1.1	176	4.4	2.5	2.7	1.6	10	4.4	75
CP-d	0.92	37	6.1	1.7	1.7	585	7.6	7.6	8.9	0.63	8.0	2.2	46
PolyMS	0.71	—	8.8 <sup>d</sup>	2.8 <sup>d</sup>	—	—	—	—	—	—	—	—	—
PDMS <sup>a</sup>	—	890	800	400	3800	1400	340	340	220	6.6	24	12	170
PSt <sup>b</sup>	1.0-1.1	23	2.6	0.79	11	436	1.1	—	0.58	0.53	24	—	181

<sup>a</sup> Ref. 9. <sup>b</sup> Ref 10. <sup>c</sup>  $1.0 \times 10^{-10}$  [cm<sup>3</sup> (s.t.p.)·cm·cm<sup>2</sup>·sec<sup>-1</sup>·cmHg<sup>-1</sup>]. <sup>d</sup> Ref 8.

**Table V.** The refractive indices and dielectric constants of polymer films

Polymer	$n^a$	$d^a$ (nm)	$\epsilon^b$
<b>PolyPS</b>	—	—	2.9-3.0 <sup>c</sup>
<b>CP-a</b>	1.72	389	3.0
<b>CP-b</b>	1.61	866	2.6
<b>CP-c</b>	1.59	636	2.5
<b>CP-d</b>	1.57	704	2.5
<b>CP-e</b>	1.54	138	2.4
<b>PolyMS</b>	1.52	209	2.3

<sup>a</sup> Determined by ellipsometric method at wavelength of 632.8 nm.

<sup>b</sup> Optically estimated dielectric constant:  $\epsilon=n^2$ . <sup>c</sup> Evaluated by extrapolation of the linear  $\epsilon$  vs. PS molar ratio.

from a gas leak. Then, the evaluation for the PolyMS membrane was referred to our previous paper [8]. The gas permeabilities of all gasses decreased with an increase of PS unit ratio. Permeability coefficient,  $P$ , diffusion coefficient,  $D$ , and solubility coefficient,  $S$ , calculated from the obtained pressure curve are summarized in Table IV, together with values for a poly(dimethylsiloxane), PDMS, and a polystyrene, PSt, referred to the literature [9, 10]. PDMS, which has been well known as a material for an oxygen-enriching membrane, indicates relatively high  $S_{O_2}$ ,  $S_{CO_2}$  and  $D_{H_2}$  compared with the case of  $N_2$  gas. CP-c, e and PolyMS indicated distinctly low values of permeation parameters against all gasses compared with PDMS, in spite of these contained the same structure of dimethylsiloxane unit to a PDMS. On the other hand, it was found that the gas permeation behavior of PSt was very similar to that of CP-c and d. The PS unit introduced into the structure of PolyMS would behave as the same as the side-chain phenyl group of PSt. The densities of the membranes of CP-c, e and PolyMS are also presented in Table IV. The densities increased with an increase of PS unit ratio. The density of CP-c was 1.0, and approximately coincided with that of PSt as shown in Table IV.

### 3.5. Refractive indices and dielectric constants of copolymer films

The refractive indices and the thicknesses of the thin films were measured by using the standard ellipsometric method as listed in Table V. The optically estimated  $\epsilon$  according to the Maxwell's equation,  $\epsilon = n^2$  [11], are also summarized in Table V. PolyPS could not be dissolved in common solvents to be prepared as a thin film by the spin-coating method. Therefore, the refractive index was not evaluated by ellipsometry. Then, the  $\epsilon$  of PolyPS estimated by the extrapolating of the linear  $\epsilon$  vs. PS molar ratio to be approximately 2.9-3.0. The  $\epsilon$  increased with an increase of PS unit ratio. This resulted from the introduction of phenyl groups, which have relatively higher polarizability. The  $\epsilon$ 's of CP series ranged from 2.3 to 3.0. These values were lower than those of conventional  $SiO_2$  of  $\epsilon = 3.9$ , polyimide of  $\epsilon = 2.9-3.9$  [11], fluorinated polyimides of  $\epsilon = 2.33-2.50$  [12, 13], and semi-aromatic polyimides of  $\epsilon = 2.72-2.83$  [14,15]. PSt of  $\epsilon = 2.49-2.61$  [10] shows the very similar value to CP series. Therefore, CP series will be candidates for new low  $\epsilon$  materials if the thermal mechanical stability is improved. Unfortunately there is

a trade-off between high  $T_g$  and low  $\epsilon$  as shown in Table II and Table V on a present stage of our study. PolyPS had relatively low  $\epsilon$  of 2.9-3.0, and showed high  $T_d$  (over 500 °C) and high  $T_m$  of 323 °C. For an instance, an improvement of processing by the directly melt-polycondensation reaction [6] will be necessary to be applied to insulator materials.

### 4. Conclusions

The thermal degradation behavior in nitrogen and thermal mechanical properties of poly(tetraphenyl-*p*-silphenylenesiloxane-co-tetramethyl-*p*-silphenylene siloxane)s were investigated by using TGA and TMA. As a result, these showed high  $T_{d5}$  in nitrogen (around 500 °C) and the molecular weights of copolymers played an important role for  $T_{d5}$ . All copolymer had  $T_s$  related to  $T_g$  and/or  $T_m$ . CP-a had the highest  $T_s$  of 147 °C, that is, showed relatively high thermal mechanical stability. The gas permeabilities of the self-standing membranes were investigated. The gas permeabilities decreased with an increase of PS unit ratio. The gas permeation behavior of CP-c and d was very similar to a polystyrene. The  $\epsilon$  of copolymers evaluated by the optically method. The  $\epsilon$  values of CP series ranged from 2.3 to 3.0, and were relatively lower than those of conventional  $SiO_2$  and polyimide films. The membrane density and  $\epsilon$  values of CP-c also showed similar to those of polystyrene. Consequently, a possibility of CP series for a new low  $\epsilon$  material was suggested in this paper.

### 5. References

- [1] B. S. R. Reddy and U. Senthilkumar, *J. Sci. Ind. Res.*, **62**, 666-677 (2003).
- [2] R. W. Baker, *Ind. Eng. Chem. Res.*, **41**, 1393-1411 (2002).
- [3] T. Homma, *Mat. Sci. Eng.*, **R23**, 243-285 (1998).
- [4] K. Maex, M. R. Baklanov, D. Shamiryan, F. Lacopi, S. H. Brongersma and Z. S. Yanovistkaya, *J. Appl. Phys.*, **93**, 8793-8841 (2003).
- [5] H. Ito, E. Akiyama, T. Kawakami, Y. Nagase, A. Yamamoto and S. Fukui, *Trans. Mat. Res. Soc. Jpn.*, in press.
- [6] H. Ito, E. Akiyama, Y. Nagase, A. Yamamoto and S. Fukui, *Polym. J.*, in press.
- [7] H. Ito, E. Akiyama, Y. Nagase and S. Fukui, *Polym. J.*, submitted.
- [8] Y. Nagase, J. Ochiai, K. Matsui and M. Uchikura, *Polymer*, **29**, 740-745 (1988).
- [9] T. C. Merkel, V. I. Bondar, K. Nagai, B. D. Freeman and I Pinnau. *J. Polym. Sci. Part B: Polym. Phys.*, **38** 415-434 (2000).
- [10] "POLYMER HANDBOOK", Ed. by J. Brandrup and E. H. Immergut, JOHN WILY & SONS, New York (1975) pp.III 236.
- [11] J. O. Simpson and A. K. St. Clair, *Thin Solid Films* **308-309**, 480-485 (1997).
- [12] G. Hougham, G. Tesoro, A. Viehbeck, and J. D. Chapple-sokol, *Macromolecules*, **27**, 5964-5971 (1994).
- [13] Y. Watanabe, Y. Shibusaki, S. Ando and M. Ueda, *Polym. J.*, **37**, 270-276 (2005).
- [14] D. Boese, H. Lee, Y. Yoon, J. D. Swlen and J. F. Rabolt, *J. Polym. Sci. Part B: Polym. Phys.*, **30**, 1321-1327 (1992).