

# Synthesis and Conducting and Thermal Properties of Polysilanes Containing Substituted Benzophenanthrene Groups

Meijiang Li,<sup>1</sup> Huayu Qiu,<sup>1</sup> Jianxiong Jiang,<sup>1</sup> Guoqiao Lai,<sup>1</sup> Shengyu Feng<sup>2</sup>

<sup>1</sup>Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Teachers College, Hangzhou, 310012, People's Republic of China

<sup>2</sup>School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People's Republic of China

Received 18 July 2005; accepted 24 April 2006

DOI 10.1002/app.24732

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

**ABSTRACT:** Dichloromethyl(2,9-diphenyl-7,8-benzophenanthryl)silane (**1**) was synthesized by the Diels–Alder reactions of dichloromethylvinylsilane with 2,5-diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone in a sealed tube. Poly[methylphenylsilylene-*co*-(2,9-diphenyl-7,8-benzophenanthryl)methylsilylene] (PMBSI) was obtained by Wurtz-type coupling of dichloromethylphenylsilane and **1** and was characterized with Fourier transform infrared, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>29</sup>Si-NMR, gel permeation chromatography, and ultraviolet and fluorescence spectroscopy. The conducting

properties and thermal properties of the polymer were investigated. Because of the introduction of benzophenanthrene groups into the Si atoms of the polymer, the ultraviolet absorption wavelengths of the PMBSI redshifted significantly in the ultraviolet region, and a strong photoluminescence band could be observed in the visible region. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2445–2450, 2007

**Key words:** conjugated polymers; copolymerization; polysilanes; synthesis

## INTRODUCTION

Polysilanes are one-dimensional, silicon-catenated polymers that possess alkyl and/or aryl groups as side chains, and they have attracted considerable attention because of their interesting properties, such as nonlinear optical properties,<sup>1,2</sup> photoconductivity,<sup>3</sup> electroluminescence,<sup>4,5</sup> semiconducting properties,<sup>6,7</sup> and charge-carrier (hole) transport properties.<sup>8</sup> These characteristics of polysilanes are due to the delocalization of Si–Si  $\sigma$  electrons along the silicon backbone; this is known as  $\sigma$  conjugation.<sup>9</sup> Although solid-state polysilanes have high electric resistance as insulators, they become *p*-type semiconductors in the presence of strong electron acceptors, showing their potential as conducting materials.<sup>10</sup> However, the wide band gap (3–4 eV) has been a barrier to effective interchain doping that is able to cause enough delocalization of electrons in the polymer main chains.

The substitution of the Si skeleton by functional groups is an important candidate for doping techniques. Self-doping to  $\sigma$ -conjugated Si chains could be

realized by some specific side chains, which have strong electron-donating or -accepting properties. In our previous studies, tetraphenylphenyl-substituted polysilanes were studied in detail, and we found that polysilanes with tetraphenylphenyl groups demonstrated intriguing properties such as conductivity by doping with I<sub>2</sub> and nonlinear optical properties due to the  $\pi$ -electron conjugation of the tetraphenylphenyl group.<sup>11,12</sup> Although both the tetraphenylphenyl group and substituted benzophenanthrene group are big  $\pi$ -conjugated groups, the extent of the  $\pi$ -electron conjugation of the latter is more greater than that of the former, and it can be predicted that  $\sigma$ – $\pi$ -conjugated polysilanes with different conjugated groups will demonstrate different properties.

To investigate the effects of conjugated substituted groups on the properties of polysilane, in this study we synthesized and characterized poly[methylphenylsilylene-*co*-(2,9-diphenyl-7,8-benzophenanthryl)-methylsilylene] (PMBSI), and its conducting and thermal properties were also examined.

## EXPERIMENTAL

### Materials

All reactions, unless otherwise noted, were carried out under an atmosphere of dry nitrogen. The solvents, toluene and tetrahydrofuran (THF), were dried over sodium/benzophenone and distilled just before use. All glassware was thoroughly dried in an oven at

Correspondence to: G. Lai (gqlai@hztc.edu.cn) or S. Feng (fsy@sdu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29974016.

Contract grant sponsor: Natural Science Foundation of Zhejiang Province; contract grant number: Y404380.

110–120°C and cooled *in vacuo* to room temperature. Dichloromethylvinylsilane and dichloromethylphenylsilane were obtained from Acros Organics Co. (Geel, Belgium). 2,5-Diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone was prepared according to the literature.<sup>13</sup>

### Synthesis of dichloromethyl (2,9-diphenyl-7,8-benzophenanthryl)silane (1)

Dichloromethylvinylsilane (8.4 g, 0.06 mol), 150 mL of toluene, and 15.3 g (0.04 mol) of 2,5-diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone were sealed in an evacuated glass tube and heated in a hydrogenation bomb at 230°C for 10 h. After the tube was cooled and opened, the toluene and volatile silicone compounds were evaporated. The residue was purified by a silica gel column under N<sub>2</sub> protection, with drying toluene as the eluent, to give the pure product.

Yield: 90%. ANAL. Calcd: C, 75.46%; H, 4.46%. Found: C, 75.42%; H, 4.41%. Mass spectrometry: *m/e* 494 (M<sup>+</sup>).

### Preparation of PMBSI

In a 100-mL, three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 1.04 g (45 mmol) of sodium and 30 mL of dry toluene. The contents of the flask were heated to refluxing under a nitrogen atmosphere and then stirred vigorously to prepared the sodium dispersion. To this were added a toluene solution of 4.93 g (10 mmol) of 1 and 1.91 g (10 mmol) of dichloromethylphenylsilane and 4.0 mL of diglyme over a period of 30 min at 90–100°C, and then the mixture was heated to refluxing for 10 h. The remaining sodium was decomposed with a 1 : 1 mixture of ethanol and acetic acid. The resulting mixture was then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with toluene. The organic layer and extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. The solvent was evaporated to give a solid product, which was first dissolved in THF and then purified three times by reprecipitation from methanol/isopropyl alcohol to give 3.56 g (65% yield) of the polymer as a yellow solid.

### Structural characterization

The molecular weight was determined by gel permeation chromatography with 4- $\mu$  Styragel columns calibrated with polystyrene standards (10<sup>5</sup>-, 10<sup>4</sup>-, 10<sup>3</sup>-, and 500-Å porosity) and with toluene as the eluant at a flow rate of 2 mL/min. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were determined with a JEOL model JNM-EX 270 spectrometer (Tokyo, Japan). <sup>29</sup>Si-NMR spectra were determined with a NIC NB-300 spectrometer (Madison, WI) in deuteriochloroform. The determination of the ratio of MePhSi units to MeArSi (Ar = 2,9-diphenyl-7,8-benzophenanthryl) units (*m*) in the polymer was car-

ried out by the integration of the <sup>1</sup>H-NMR signals for the different groups. Mass spectra were taken on an NS 902 mass spectrometer (A.E.I Ltd., Manchester, England). Elemental analyses were performed on an EA-1110 instrument (CE Instruments, Milan, Italy). Fourier transform infrared (FTIR) spectra were examined in the region of 4000–400 cm<sup>-1</sup> on KBr pellets with a Nicolet FTIR 5DX spectrometer (Madison, WI). Ultraviolet (UV) spectra were measured with a Shimadzu UV-2501PC spectrophotometer (Kyoto, Japan). Photoluminescence spectra were recorded with a Perkin-Elmer LS-5013 (Edinburg, UK). Thermogravimetric analysis (TGA) was carried out with a Rheometric Scientific thermogravimetric analyzer (Piscataway, NJ).

### Measurement of the conductivity in air

A THF solution of PMBSI (5 wt %) was spin-coated onto a quartz plate with a spinner and dried under reduced pressure to give solid films with a thickness of 0.05–0.1 mm. The films were then treated with I<sub>2</sub> vapor for 5 h, and the excess of I<sub>2</sub> was removed under reduced pressure (1 mmHg) for 30 min. After the resulting films were allowed to stand in air for 2 h, the conductivity of the films was measured by the four-probe method.

### TGA of PMBSI and poly[methyl (2,9-diphenyl-7,8-benzophenanthryl)silane] (PBSI)

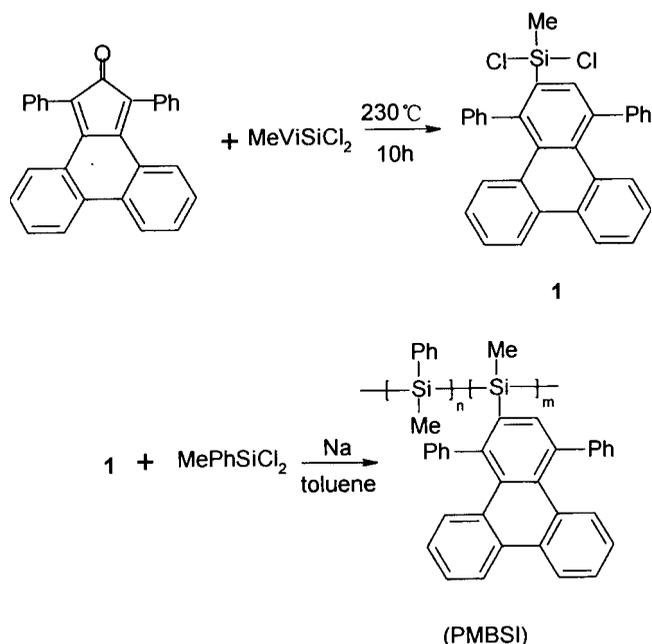
On a platinum plate was placed 4–5 mg of PMBSI or PBSI, and the plate was heated from room temperature to 700°C at a rate of 10°C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Synthesis of 1

The synthetic strategy used to obtain the monomer and desired polymer from simple starting materials is outlined in Scheme 1.

There are two methods for introducing functional groups such as condensed ring groups into organosilicon compounds with Diels–Alder reactions. First, vinylsilane reacts with cyclopentadienones containing functional groups in a sealed tube at a high temperature.<sup>14</sup> Second, vinylsilane reacts with cyclopentadienones at the refluxing temperature in a high-boiling-point solvent in an open system.<sup>15</sup> It has been reported that two competing reactions take place in the first method (see Scheme 2).<sup>14</sup> The ratios of the two products are determined by the reaction conditions and the properties of the groups bonded to the Si atom. In the second method, H<sub>2</sub> can easily get out, and cracking of the Si–Ar bond by the H<sub>2</sub> molecule can be prevented at high temperatures. However, because of the low boiling point of dichlorome-

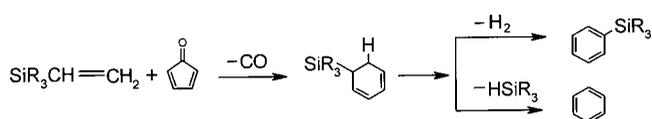


Scheme 1 Synthetic route to **1** and PMBSI.

thylvinylsilane and the resultant low reaction temperature, the expected product (**1**) was not obtained after a long period of refluxing under nitrogen gas in an open system.

Dichloromethylvinylsilane and 2,5-diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone were reacted in toluene in a sealed tube at 230°C for 10 h, the solution turned from black green to yellow, and **1** was obtained. Its structure was confirmed by IR and  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR, and the data are listed in Table I. From the  $^1\text{H}$ -NMR spectroscopy data, we have concluded that the chemical shift at 0.15 ppm is attributable to the absorption of protons of Si—CH<sub>3</sub>, whereas the chemical shifts at 6.8–7.2 ppm belong to the absorptions of protons of Ar—H. From the  $^{13}\text{C}$ -NMR spectroscopy data, we have learned that the chemical shift at 2.3 ppm belongs to the carbon of the Si—CH<sub>3</sub> group, and the chemical shifts at 126.9–131.5 ppm are attributable to the carbons of the aromatic ring. From the  $^{29}\text{Si}$ -NMR spectroscopy data, we have also learned that the chemical shift at 15.6 ppm can be attributed to the Si atom of SiMeArCl<sub>2</sub>. The analytical results show that the structure of compound **1** agreed with the expected structure.

The IR spectrum of compound **1** is shown as Figure 1. The C—H stretching vibrations of Si—CH<sub>3</sub> can be seen at 2916 cm<sup>-1</sup>. The peaks between 1600 and 1400 cm<sup>-1</sup>



Scheme 2 Reaction of vinylsilane with cyclopentadiene in a sealed tube at a high temperature.

TABLE I  
 $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR Chemical Shifts for **1**

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	$^{29}\text{Si}$ (ppm)	Assignment
0.15	2.3		Me—Si
6.8, 6.9, 7.1, 7.2	126.9–131.5		Ar—Si
		15.6	Si—MeArCl <sub>2</sub>

are attributed to the absorption of the substituted benzophenanthryl and phenyl groups. The strong band at 1260 cm<sup>-1</sup> is attributed to the CH<sub>3</sub> symmetric deformation vibration of the Si—CH<sub>3</sub> group. The plane swing vibration of CH<sub>3</sub> and stretching vibration of Si—C bond of the Si—CH<sub>3</sub> group appear at 758 cm<sup>-1</sup>. There is a weak band at 3050 cm<sup>-1</sup> that can be attributed to the C—H stretching vibration of the aromatic ring. A strong absorption corresponding to the stretching vibration of the Si—C bond and the vibration of the aromatic ring of Si—Ar groups can be observed at 1050 and 1075 cm<sup>-1</sup>. Because of the hydrolysis reaction of the Si—Cl bond of compound **1** during the examination of the IR spectra of compound **1**, an absorption peak at 3400 cm<sup>-1</sup> can be observed, and it can be attributed to the absorption of the Si—OH group.

No 2,9-diphenyl-7,8-benzophenanthrene was formed in the reaction, perhaps because the great conjugated interaction of the 2,5-diphenyl-9,10-benzophenanthryl group with the Si atom prevented the cracking of the Si—Ar bond at high temperatures. This was similar to the preparation of dichloromethyltetraphenylphenylsilane. From experimental data, we know that it takes 10 h at 230°C to complete the Diels–Alder reaction for 2,5-diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone and dichloromethylvinylsilane, which is 10 h less than the time for the reaction of tetraphenylcyclopentadienone and dichloromethylvinylsilane.<sup>15</sup> Perhaps this is true because the planar structure of 2,5-diphenyl-3,4-(*o,o'*-biphenylene)cyclopentadienone makes  $\pi$  electrons of the conjugated system delocalize more extensively than the nonplanar structure of tetraphenylcyclopentadienone.

### Preparation of PMBSI

The cocondensation of MePhSiCl<sub>2</sub> and **1** with a sodium dispersion in refluxing toluene resulted in a soluble copolymer (PMBSI) in a 65% yield. It was soluble in such solvents as toluene, THF, dichloromethane, and chloroform. Table II summarizes the polymerization results for PMBSI and homopolymer PBSI.

The molecular weight of PMBSI was lower than that of alkyl- or aryl-substituted polysilane copolymers; the number-average molecular weight was greater than 10<sup>4</sup> at least. We also obtained the homopolymer (PBSI; number-average molecular weight < 3000) of **1** with the usual condensation method, and an attempt to prepare a high-molecular-weight homopolymer

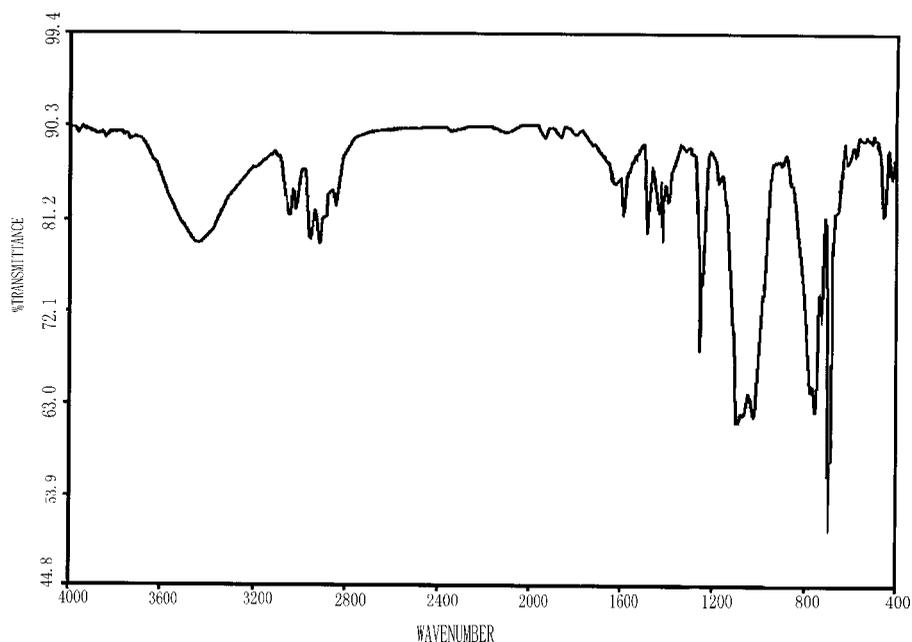


Figure 1 IR spectrum of 1.

was unsuccessful. From Table II, we can conclude that with the ratio of MePhSi units to MeArSi (Ar = 2,9-diphenyl-7,8-benzophenanthryl) units increasing, the molecular weights of the polymer increased. Perhaps this was caused by the impurity of monomer 1 and the large steric congestion of the substituted condensed ring group.

### Characterization of PMBSI

A typical IR spectrum of PMBSI is shown in Figure 2. The C—H stretching vibrations of Si—CH<sub>3</sub> can be seen at 2900 and 2950 cm<sup>-1</sup>. The vibrations of the aromatic ring and deformation vibrations of the side chains appear in the fingerprint region between 1600 and 1300 cm<sup>-1</sup>. The strong band at 1255 cm<sup>-1</sup> can be

attributed to the CH<sub>3</sub> symmetric deformation vibration of the Si—CH<sub>3</sub> group. The plane swing vibration of CH<sub>3</sub> and stretching vibration of the Si—C bond of the Si—CH<sub>3</sub> group appear at 760 cm<sup>-1</sup>. The peaks at 3077 and 3021 cm<sup>-1</sup> can be attributed to the C—H stretching vibration of the aromatic ring. A strong absorption corresponding to the stretching vibration of the Si—C bond and the vibration of the aromatic ring of the Si—Ar groups can be observed at 1028, 700, and 1073 cm<sup>-1</sup>. The band at 475 cm<sup>-1</sup> can be attributed to the Si—Si stretching vibration. This is fully in agreement with the expected polymeric structures.

Further support for the structure of PMBSI was obtained from <sup>1</sup>H-, <sup>13</sup>C-, and <sup>29</sup>Si-NMR spectra. The spectral data are reported in Table III. From the <sup>1</sup>H-NMR spectroscopy data in Table III, we can conclude that the chemical shift at 0.3 ppm should be attributed

TABLE II  
Properties of PMBSI and PBSI

Polymer	$M_w^a$	$M_w/M_n^a$	UV $\lambda_{max}$ (nm)		$m^b$
			in THF	Fluorescence $\lambda_{max}$ (nm) in THF	
PMBSI <sup>c</sup>	8960	2.04	234, 260, 330 <sup>d</sup>	475	5.8
PMBSI <sup>e</sup>	6740	1.95	235, 261, 320 <sup>d</sup>	450	3.7
PBSI	2830	1.60	231, 258	405	0

<sup>a</sup> $M_w$  and  $M_n$ , weight and number average molecular weights relatively determined to polystyrene calibration standards.

<sup>b</sup>The molar ratio of MePhSi to MeArSi unit in the PMBSI.

<sup>c</sup>The copolymer was prepared by MePhSiCl<sub>2</sub> and 1 with equal molar ratio.

<sup>d</sup>The maximum absorption wavelength of the shoulder.

<sup>e</sup>The copolymer was prepared by MePhSiCl<sub>2</sub> and 1 with 0.5 molar ratio.

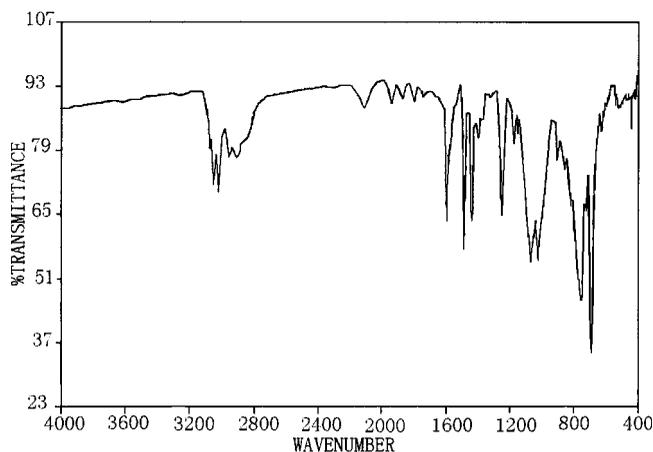


Figure 2 IR spectrum of PMBSI.

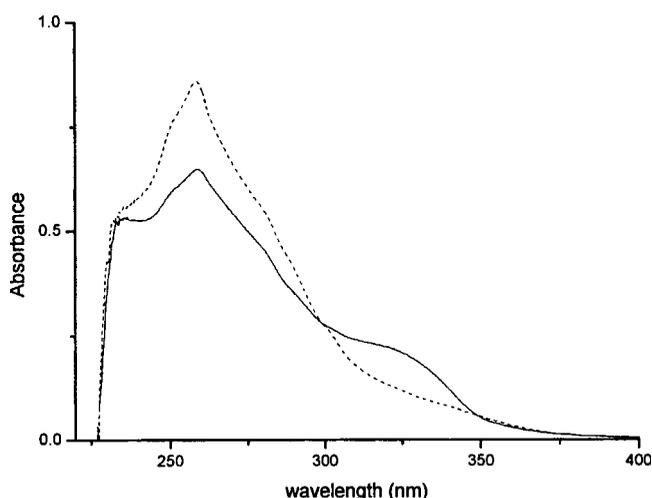
TABLE III  
 $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR Chemical Shifts for PMBSI

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	$^{29}\text{Si}$ (ppm)	Assignment
0.3 (m)	3.0 (s)	–39.0–41.2 (br)	Me–Si
		–48.5–52.3 (br)	PhMeSi
6.4–7.2 (br)	123.6–132.8 (br)		MeArSi
			Ar–Si

to the absorption of protons of Si–CH<sub>3</sub>, whereas the chemical shifts at 6.4–7.2 ppm belong to the absorptions of protons of Ar–H. From the  $^{13}\text{C}$ -NMR spectroscopy data in Table III, we can learn that the chemical shift at 3.0 ppm belongs to the carbon of the Si–CH<sub>3</sub> group, and the chemical shifts at 123.6–132.8 ppm can be attributed to the carbons of the aromatic ring. From the  $^{29}\text{Si}$ -NMR spectroscopy data in Table III, we also can know that the chemical shift at –39.0–41.2 ppm can be attributed to the Si atom of Si–MePh, and the chemical shift at –48.5–52.3 ppm belongs to the Si of Si–MeAr. These well agree with the structures of PMBSI. The mass spectrum of the polymer showed fragments derived from (methylphenyl)Si, (methylphenyl)Si–(MeAr)Si, and MeArSi moieties, with higher abundances for the former two. This is in accordance with the observed high *m* value and suggests that PMBSI is a random copolymer rather than an alternating or block copolymer.

#### UV absorption and fluorescence emission properties of PMBSI and PBSI

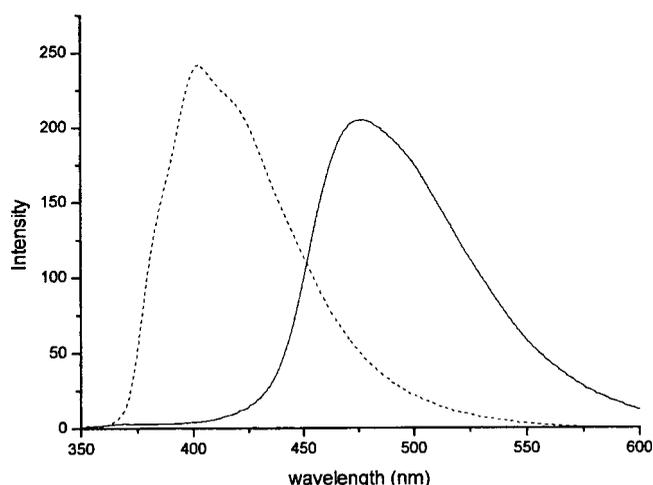
The UV spectra for PMBSI and PBSI in THF solutions are shown in Figure 3. Figure 3 shows that PMBSI exhibits two strong absorption peaks at 234 and 260 nm in a THF solution. They can be attributed to the  $\pi$ – $\pi^*$  absorption of phenyl and condensed ring groups.



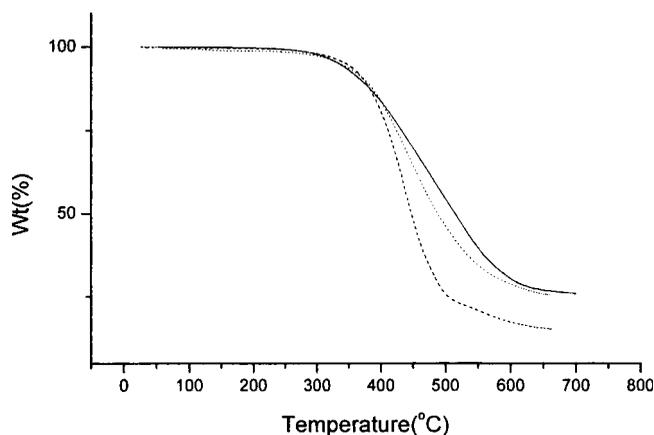
**Figure 3** UV absorption spectra of PMBSI and PBSI in THF at 0.05 mM (base molar unit). Solid and dotted line show the absorption spectra of PMBSI and PBSI in THF, respectively.

In addition to the  $\pi$ – $\pi^*$  absorption bands, a shoulder feature can be observed in the region of 300–350 nm and ascribed to the absorption of  $\sigma$ – $\sigma^*$  of the Si–Si bonds; the absorption edge of PMBSI shows a considerable redshift in comparison with that of polymethylphenylsilane, which shows a strong and sharp absorption peak at 337 nm,<sup>16</sup> indicating that just like the tetraphenylphenyl group, the substituted benzophenanthryl group is a big  $\pi$ -conjugated system, and the  $\pi$  electrons of the substituted benzophenanthryl group make the  $\sigma$  electrons in Si–Si bonds delocalize extensively. In other words, the conjugated interaction between the  $2p\pi$  orbitals of the aromatic ring and the  $3d\pi$  orbitals of the silicon backbone increases after the introduction of the 2,9-diphenyl-7,8-benzophenanthryl groups into the side chains of PMBSI. Notably, in comparison with PMBSI, PBSI shows only two absorption peaks at 231 and 258 nm, and no obvious shoulder feature can be observed in the region of 300–500 nm. Maybe this is caused by the low polymerization degree of homopolymer PBSI, and the absorption of  $\sigma$ – $\sigma^*$  of the Si–Si bonds blueshifts from that of PMBSI.

The fluorescence spectra of PMBSI and PBSI in dilute THF are shown in Figure 4. One broad emission appears in the visible region with a bandwidth at the half-height of 80 nm, and no emission in the near-UV region can be observed, unlike typical polymethylphenylsilanes, which show a strong and sharp emission peak at 353 nm,<sup>16</sup> indicating that the increased conjugative interaction leads to a redshift of the fluorescence emission. In comparison with that of tetraphenylphenyl-substituted polysilanes, the maximum emission band of PMBSI redshifts 10 nm,<sup>15</sup> also indicating that polysilanes with more effective  $\pi$ -conjugation groups demonstrate more intriguing optical properties, and it is predicted that this copolymer



**Figure 4** Fluorescence spectra of PMBSI and PBSI in THF at 10 mM (base molar unit). Solid and dotted line indicate the emission spectra of PMBSI and PBSI in THF, respectively.



**Figure 5** TGA profile of PMBSI, PBSI, and polymethylphenylsilane. Solid, dotted, and dashed line denote the thermogravimetric curve of PBSI, PMBSI and polymethylphenylsilane, respectively.

could be a candidate for light-emitting materials in the manufacture of light-emitting diodes. In comparison with that of homopolymer PBSI, the maximum emission peak of PMBSI redshifts 70 nm, indicating that with an increasing polymerization degree, the conjugated extent of  $\sigma$ -electron delocalization along the Si—Si backbone becomes stronger; this is identical to the result shown in the UV absorption spectrum.

### Conducting properties of PMBSI and PBSI

Like other polysilanes, PMBSI is an insulator. However, when a thin film of PMBSI, which was prepared on a quartz plate by the spin coating of a 5 wt % THF solution, was doped with  $I_2$  at 40–50°C *in vacuo*, a conducting film was obtained. The conductivity of the film was determined by the four-probe method. The conductivity of the PMBSI thin film doped with  $I_2$  was measured to be 35.0 S/m in air, and it was higher than that of polysilanes with tetraphenylphenyl groups. With the same method, the conductivity of a PBSI thin film doped with  $I_2$  was measured to be 0.54 S/m, which was about 100 times lower than that of PMBSI. According to previous studies of doping effects on the electronic properties of polysilanes,<sup>12,17</sup> by the  $I_2$  doping of PMBSI, a strong interaction could occur between the big  $\pi$ -conjugated 2,9-diphenyl-7,8-benzophenanthryl substitute and  $I$ , and the  $\sigma$ - $\pi$  conjugated main chains play an important role in the doping of this system.

### Thermal properties of PMBSI and PBSI

The thermal behaviors of PMBSI, PBSI, and polymethylphenylsilane were examined with TGA in a nitrogen atmosphere. The thermogravimetric curves for the thermal degradation of the three polymers are shown in Figure 5. The apparent weight loss of all three polymers began at approximately 300°C; most

weight loss of PMBSI and PBSI happened in the temperature range of 350–600°C, but the most weight loss of polymethylphenylsilane happened from 350 to 500°C. Figure 5 shows that at the same weight-loss percentage, the corresponding temperature of PBSI was highest, and that of polymethylphenylsilane was lowest. Therefore, PBSI has better thermal stability than polymethylphenylsilane, and the heat resistance of copolymer PMBSI is between those of PBSI and polymethylphenylsilane.

## CONCLUSIONS

PMBSI can be prepared with dichloromethylphenylsilane and **1** via a Wurtz-type reductive condensation reaction. The structural characterization, UV absorption, and fluorescence emission, and conducting and thermal properties of the polymer have been investigated. Like polysilanes with tetraphenylphenyl groups, PMBSI exhibits excellent conducting properties in air after doping with  $I_2$ , and the maximum UV absorption and fluorescence emission bands redshift significantly. Because the 2,9-diphenyl-7,8-benzophenanthryl group has more effective conjugation interaction with Si—Si bonds than the tetraphenylphenyl group, the optical and conducting properties of PMBSI are improved over those of polysilanes with tetraphenylphenyl groups. PMBSI and PBSI have similar thermal stability; the total weight losses from room temperature to 700°C have been calculated to be about 75% of the initial weights in an atmosphere of  $N_2$ .

## References

- Hasegawa, T.; Iwasa, Y.; Kishida, H.; Koda, T.; Tokura, Y.; Tachibana, H.; Kawabata, Y. *Phys Rev B* 1992, 45, 6317.
- Yoshida, M. *Mol Cryst Liq Cryst* 1999, 327, 71.
- Kepler, R. G.; Zeigler, J. M.; Havrah, L. A.; Kurtz, S. R. *Phys Rev B* 1987, 5, 2818.
- Suzuki, H.; Hoshino, S.; Matsumoto, N. *Thin Solid Films* 1998, 331, 64.
- Suzuki, H.; Hoshino, S.; Furukawa, K.; Ebata, K.; Yuan, C. H.; Bleyl, I. *Polym Adv Technol* 2000, 11, 460.
- Kobayashi, T.; Hatayama, K.; Shirakawa, H. *Organometallics* 1998, 17, 1646.
- Matsumoto, N. *Jpn J Appl Phys* 1998, 37, 5425.
- Baessler, H.; Borsenberger, P. M.; Perry, R. J. *J Polym Sci Part B: Polym Phys* 1994, 32, 1677.
- Matsumoto, N.; Takeda, K.; Teramae, H.; Fujino, M. In *Silicon-Based Polymer Science*; Zeigler, J. M.; Gordon Fearon, F. W.; Eds.; ACS Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990.
- Trefonas, P.; West, R.; Miller, R. D.; Hofer, D. *J Polym Sci Polym Lett Ed* 1983, 21, 823.
- Shi, B. C.; Li, G. W.; Zhang, M. G.; Li, G. *Silicone Mater* 1997, 6, 1.
- Du, Z. D.; Chen, J. H.; Feng, S. Y. *Acta Polym Sinica* 1988, 2, 81.
- Dilthey, W. *J Prakt Chem* 1935, 143, 189.
- Freeburger, M. E.; Spialter, L. J. *J Org Chem* 1970, 35, 652.
- Chen, J. H.; Feng, S. Y.; Du, Z. D. *Chem J Chin Univ* 1986, 7, 1150.
- Miller, R. D.; Michl, J. *Chem Rev* 1989, 89, 1359.
- Ueno, H.; Kojima, H.; Kakimoto, M. *Denki Zairyo Gijutsu Zasshi* 1994, 3, 19.