

Preparation and Properties of Disilane and Disiloxane Unit-Fused Poly(diphenylamine)

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ABSTRACT: Disilane unit-fused poly(diphenylamine) (poly(10,11-dihydro-10,11-disila-5,10,10,11,11-pentamethyl-5H-dibenz[b,f]azepine-2,8-diyl), PDSiAzep) were prepared and properties of these compounds were studied. Oxidation of PDSiAzep led to related disiloxane-fused poly(diphenylamine) (poly(5,7-disila-6-oxa-5,5,7,7,12-pentamethyl-5,6,7,12-tetrahydrodibenz[b,g]azocine-3,9-diyl) PSiO). These polymers have new heterocyclic unit. Not only UV and Cyclic voltammetry (CV) measurements but also X-ray crystallography of the related dibromide suggested that the structure of the bridging unit affected π -conjugation through the N atom. The highest conductivities of electrochemically doped PDSiAzep and PSiO were 2.0×10^{-4} and 1.3×10^{-2} , respectively. Turn-on bias voltage of a double layer electroluminescent device comprising PDSiAzep was higher than that of PSiO. These electrical properties were depended on effective π -conjugation through the N atom.

KEY WORDS Diphenylamine / Dibenzazepine / Cyclic Voltammetry / X-ray Crystal Structure /

Phenazasiline, monosilane unit-fused diphenylamine derivative, and related polymers are potentially useful materials such as hole transporting layer for EL devices,^{1a} antioxidants,^{1b} additives for jet-engine lubricants,^{1c} thermally stable polymers,^{2a} and electrochromic polymers.^{2b} We have already reported preparation and properties of phenazasiline-containing π -conjugated polymers.³ The resulting polymers displayed high efficiency as hole transporting polymeric materials^{3a} and interesting electrochromism.^{3b} We also reported that the substituent on N atom of poly(phenazasiline) was more effective for electrical properties than that of Si atom although dihedral angles between two benzene atoms were changed by the substituent on the Si atom.³

On the other hand, we also reported the study of the effect of Si-bridging unit of monosilane and disilane unit-fused diphenylamines by spectroelectrochemical measurement.^{3b,4} From the reports, the Si unit exerts influence on the electronic structure of diphenylamine unit. This influence seems to affect the property of electronic device. So, we here report preparation and properties of disilane and disiloxane unit-fused poly(diphenylamine), and comparison of poly(phenazasiline).

EXPERIMENTAL

Reagent

N-Methyl-2,2',4,4'-tetrabromodiphenylamine was prepared by the reported method.⁵ Other chemicals were used as purchased.

Measurement

Infrared (IR) spectra were recorded on a JASCO FT-IR 610 spectrometer. Nuclear magnetic resonance (NMR) spectra in solutions were taken using a Bruker ARX-300 spectrometer. UV-vis spectra were recorded on a Shimadzu UV-3100 and Hitachi U-3500 spectrometers. Molecular weights of polymers were measured with a GPC system equipped with a Shimadzu LC-6A high-pressure pump, Shodex KF-80 M (pore size: 6 mm), KF-802 (pore size: 6 mm), and KF-801 (pore size: 6 mm) columns, and Shimadzu RID-2A, Shodex SE-61 (RI) detectors using tetrahydrofuran (THF) eluent and polystyrene standards.

Cyclic voltammetry (CV) was measured as follows. Electrochemical control of the experiments was achieved using BAS electrochemical analyzer model 660. A three electrodes system was used, consisting of a Glassy Carbon (GC) electrode (BAS, 3 mm in diameter) as the working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ (10 mM AgNO₃) reference

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electrode. Tetrabutylammonium perchlorate (TBAP) was used for electrolyte. Spectroelectrochemical properties of polymer⁴ and conductivity of electrochemically doped polymer film⁶ were measured by the reported method, respectively.

Preparation of 2,8-Dibromo-10,11-dihydro-10,11-disila-5,10,10,11,11-pentamethyl-5H-dibenz[b,f]azepine 1

To a dispersion of *N*-methyl-2,2',4,4'-tetrabromodiphenylamine (4.04 g, 8.1 mmol) in dry ether (35 cm³) was added 1.6 M hexane solution of *n*-butyllithium (11 cm³, 17.6 mmol) at 0 °C under N₂. After the reaction mixture became homogeneous, 1,2-dichloro-1,1,2,2-tetramethyldisilane (1.51 g, 8.1 mmol) was added to the solution at 0 °C and stirred overnight at room temperature. The reaction mixture was purified by silica gel column chromatography (eluent = hexane) to give 1.40 g (3.1 mmol) of **1**. Yield was 38%. mp: 151–152 °C. ¹H NMR: δ 0.37 (s, 12 H), 3.15 (s, 3 H), 7.36 (d, 2 H), 7.47 (dd, 2 H), 7.52 (d, 2 H). ¹³C NMR: δ 156.72, 142.26, 137.05, 133.27, 124.62, 120.09, 43.20, –1.69, –4.41 ppm. ²⁹Si NMR: δ –26.28. Anal. Found: C, 44.4; H, 4.6; N, 3.1%. Calcd. for C₁₇H₂₁Br₂NSi₂: C, 44.8; H, 4.7; N, 3.1%.

Preparation of Poly(10,11-dihydro-10,11-disila-5,10,10,11,11-pentamethyl-5H-dibenz[b,f]azepine-2,8-diyl) (PDSiAzep)

To a mixture of Ni(cod)₂ (3.52 g, 12.8 mmol, cod = 1,5-cyclooctadiene), cod (1 cm³) and bpy (2.00 g, 12.8 mmol, bpy = 2,2'-bipyridyl) in toluene (100 cm³) was added disilane monomer **1** (4.84 g, 10.6 mmol) and the mixture was heated at 60 °C for 48 h. A white powder precipitated upon pouring the mixture to methanol was successively washed with 2 M aqueous hydrochloric acid, methanol and hexane, and was dissolved in THF. Reprecipitation into methanol afforded 2.52 g (8.52 mmol monomer unit) of PDSiAzep. Yield was 80%. ¹H NMR: δ 0.33 (s, 12 H), 3.22 (s, 3 H), 7.2–7.8 (m, 6 H). ¹³C NMR: δ 157.40, 139.35, 139.65, 133.25, 129.21, 122.84, 43.37, –1.56, –4.33. Anal. Found: C, 67.9; H, 7.0; N, 4.5%. Calcd for (C₁₇H₂₁NSi·0.3 H₂O)_n: C, 67.9; H, 7.2; N, 4.7%.

Preparation of 3,9-Dibromo-5,7-disila-6-oxa-5,5,7,7,12-pentamethyl-5,6,7,12-tetrahydrodibenz[b,g]azocine 2

Trimethylamine oxide dihydrate (0.38 g, 3.4 mmol) was added to the solution of **1** (1.38 g, 3.0 mmol) in benzene (20 cm³). The reaction mixture was heated at 85 °C and stirred for 24 h. Then, this mixture was passed through silica gel column chromatography (eluent = hexane). Recrystallization of the crude

product from dichloromethane/methanol gave 1.14 g (2.4 mmol) of **2**. Yield was 80%. mp: 119–119.5 °C. ¹H NMR: δ 0.17 (s, 6 H), 0.49 (s, 6 H), 3.10 (s, 3 H), 7.2–7.6 (m, 6 H). ¹³C NMR: δ 156.53, 140.61, 137.35, 133.66, 125.35, 118.73, 45.77, 1.81, 0.41. ²⁹Si NMR: δ –0.45. Anal. Found: C, 43.4; H, 4.5; N, 3.0; Br 34.3%. Calcd. for C₁₇H₂₁Br₂NOSi₂: C, 43.3; H, 4.5; N, 3.0; Br 33.9%.

Preparation of Poly(5,7-disila-6-oxa-5,5,7,7,12-pentamethyl-5,6,7,12-tetrahydrodibenz[b,g]azocine-3,9-diyl) (PSiO)

Preparation from reaction of PDSiAzep (PSiO-NO). Reaction of 115 mg (0.38 mmol of monomer unit) of PDSiAzep with 59.4 mg (0.53 mmol) of trimethylamine oxide dihydrate afforded 103 mg (0.33 mmol monomer unit) of PSiO-NO. Yield was 85%. ¹H NMR: δ 0.11 (s, 6 H), 0.46 (s, 6 H), 3.20 (s, 3 H), 7.2–7.6 (m, 6 H). ¹³C NMR: δ 157.42, 148.04, 137.16, 133.62, 129.61, 123.82, 45.91, 2.07, 0.54. Anal. Found: C, 65.2; H, 6.7; N, 4.2%. Calcd for (C₁₇H₂₁NOSi₂)_n: C, 65.5; H, 6.8; N, 4.5%.

Preparation by Dehalogenative Polycondensation (PSiO-Ni). Reaction of 0.52 g of **2** with 0.37 g of Ni(cod)₂ and 0.20 g of bpy afforded 318 mg (1.0 mmol monomer unit) of PSiO-Ni. Yield was 93%. *M*_w = 2.6 × 10⁴ and *M*_n = 1.2 × 10⁴. Anal. Found: C, 65.2; H, 7.4; N, 4.5%. Calcd for (C₁₇H₂₁NOSi₂)_n: C, 65.5; H, 6.8; N, 4.5%.

Preparation of Poly(5,10-dihydro-5H-phenazasiline-2,8-diyl) (PPhenaz)^{3a}

*Preparation of 2,8-Dibromo-5,10-dihydro-5,10,10-trimethyl-5H-phenazasiline 3a.*⁵ Monomer **3a** was prepared by the same method as **1**. Reaction of 1.19 g (2.4 mmol) of *N*-methyl-2,2',4,4'-tetrabromodiphenylamine, 3 cm³ of 1.6 M hexane solution of *n*-butyllithium, and 0.31 g of dichlorodimethylsilane afforded 0.57 g of **3a** as a colorless crystal. Yield was 60%. mp: 151–152 °C (lit.⁵ 148–149 °C). ¹H NMR: δ 0.44 (s, 6 H), 3.47 (s, 3 H), 6.91 (d, 2 H), 7.44 (dd, 2 H), 7.55 (d, 2 H). ¹³C NMR: δ 148.39, 135.40, 132.71, 125.76, 117.10, 113.89, 38.37, –2.36. ²⁹Si NMR: δ –20.93.

Preparation by Poly(5,10-dihydro-5,10,10-trimethyl-5H-phenazasiline-2,8-diyl) (PPhenaz-a). Reaction of 398 mg (1 mmol) of **3a** with 0.33 g (1.2 mmol) of Ni(cod)₂ and 0.19 g (1.2 mmol) of bpy afforded 188 mg (0.79 mmol monomer unit) of PPhenaz-a. Yield was 79%. ¹H NMR: δ 0.54 (s, 6 H), 3.64 (s, 3 H), 7.1–7.8 (m, 6 H). ¹³C NMR: δ 149.73, 132.99, 131.40, 128.46, 123.41, 115.35, 38.31, –1.85. Anal. Found: C, 74.6; H, 6.7; N, 5.5%. Calcd for (C₁₅H₁₅NSi·0.3 H₂O)_n: C,

74.2; H, 6.5; N, 5.8%.

Preparation of 2,8-Dibromo-5,10-dihydro-10,10-di-(*n*-octyl)-5-methyl-5H-phenazasiline 3b. Monomer **3b** was prepared by the same method as **3a**. Reaction of 5.08 g (10.2 mmol) of *N*-methyl-2,2',4,4'-tetrabromodiphenylamine, 14 cm³ of 1.6 M hexane solution of *n*-butyllithium, and 2.93 g of dichloro-di-(*n*-octyl)silane afforded 4.51 g (7.6 mmol) of **3b**. Yield was 75%. mp: 44–48 °C. ¹H NMR: δ: 0.5–1.6 (m, 34 H), 3.45 (s, 3 H), 6.92 (d, 2 H), 7.47 (dd, 2 H), 7.62 (d, 2 H). ¹³C NMR: δ 149.81, 135.67, 132.64, 123.92, 117.23, 113.58, 38.50, 33.36, 31.87, 29.20, 29.07, 23.51, 22.68, 14.13, 13.05. ²⁹Si NMR: δ –20.93. Anal. Found: C, 58.6; H, 7.4; N, 2.3; Br, 27.3%. Calcd for C₂₉H₄₃Br₂NSi: C, 58.9; H, 7.3; N, 2.4; Br, 26.9%.

Preparation by Poly(5,10-dihydro-5,10-dihydro-10,10-di-(*n*-octyl)-5-methyl-5H-phenazasiline-2,8-diyl) (PPhenaz-b). Reaction of 888 mg (1.50 mmol) of **3b** with 0.50 g of Ni(cod)₂ and 0.28 g of bpy afforded 584 mg (1.35 mmol monomer unit) of PPhenaz-b. Yield was 90%. ¹H NMR: δ 0.5–1.6 (m, 34 H), 3.62 (s, 3 H), 7.1–7.8 (m, 6 H). ¹³C NMR: δ 150.13, 132.55, 131.77, 128.21, 121.37, 115.42, 38.39, 33.69, 31.92, 29.32, 29.27, 23.87, 22.67, 14.11, 13.50. Anal. Found: C, 77.5; H, 10.0; N, 3.3%. Calcd for (C₂₉H₄₃NSi·H₂O)_n: C, 77.4; H, 9.7; N, 3.1%.

Preparation of EL Device

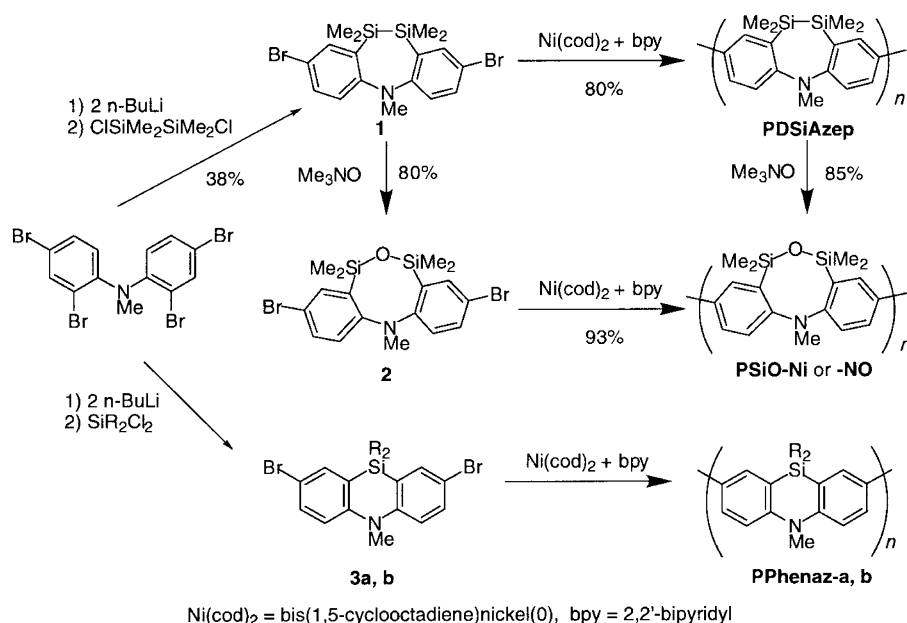
A thin films (30–40 nm) of the polymers were prepared by spin coating, from a solution of polymer in 1,2-dichloroethane on an anode, indium-tin oxide (ITO) coated on a glass substrate with a sheet resistance of 15 Ω cm⁻¹ (Asahi Glass Co.). An electron

transporting-emitting layer was then prepared by vacuum deposition of tris(8-quinolinolato) aluminum(III) (Alq₃) at 1 × 10⁻⁵ Torr with a thickness of 60–70 nm on the polymer film. Finally a layer of magnesium-silver alloy with an atomic ratio of 10 : 1 was deposited on the Alq₃ layer surface as the top electrode at 1 × 10⁻⁵ Torr. The actual thickness of each layer on the EL devices was measured with a Sloan Dektak 3030 surface profiler. The emitting area was 0.5 × 0.5 cm². Luminance was measured with a Topcon BM-7 luminance meter at room temperature.

RESULTS AND DISCUSSION

Preparation of Disilane-Unit Fused Poly(diphenylamine)

Scheme 1 illustrates the preparation of poly(10,11-dihydro-10,11-disila-5,10,10,11,11-pentamethyl-5H-dibenz[b,f]azepine-2,8-diyl) (PDSiAzep), a disilane unit-fused poly(diphenylamine). Selective dilithiation of *N*-methyl-2,2',4,4'-tetrabromodiphenylamine using *n*-butyllithium in ether followed by addition of 1,2-dichloro-1,1,2,2-tetramethyldisilane produced **1** as colorless crystal. Polymer PDSiAzep was prepared through dehalogenative polycondensation of related dibromide **1** with zerovalent nickel complex.^{3a,3c,7} PDSiAzep is soluble in usual organic solvents like THF, CHCl₃, and toluene, whereas PPhenaz-a shows high solubility only in CF₃COOH. As shown in Figure 1a and Table I, ²⁹Si NMR spectrum of PDSiAzep exhibits a signal in the region characteristic of the monomer **1**.



Scheme 1.

Table I. The data of the polymers

Polymer	^{29}Si NMR/ δ^a	$M_w/10^4^b$	UV $\lambda_{\text{max}}/\text{nm}^c$	Conductivity/ Scm^{-1d}
PDSiAzep	-27.04	4.4 (2.0)	274 (1.3)	2.0×10^{-4}
PSiO-NO	-0.85	5.1 (2.2)	315 (2.2)	1.3×10^{-2}
PPhenaz-a	-21.66	1.9 (2.9) ^e	361 ^e	4.0
PPhenaz-b	-19.52	2.6 (2.2)	366 (2.6)	1.7×10

^aIn CDCl_3 at room temperature. ^bDetermined by GPC (THF, polystyrene standards). The figures in the parentheses are M_w/M_n . ^c CHCl_3 solution. The figures in the parentheses are $\epsilon/10^4$. ^dElectrochemically doped cast film. ^e CHCl_3 soluble part.

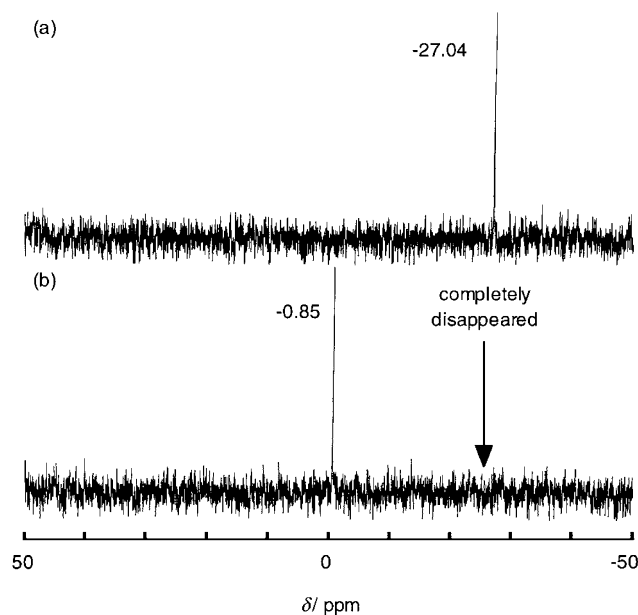


Figure 1. ^{29}Si NMR spectra of (a) PDSiAzep and (b) PSiO-NO.

Preparation of Disiloxane-Unit Fused Poly(diphenylamine)

As shown in Scheme 1, the reaction between **1** and PDSiAzep which were disilane type compounds and excess amount of trimethylamine oxide⁸ gave disiloxane type compounds **2** and PSiO-NO in good yields, respectively. Dehalogenative polycondensation of **2** also afforded PSiO-Ni. Both PSiO-NO and PSiO-Ni were soluble in usual organic solvents like THF, CHCl_3 , CH_2Cl_2 , and toluene. ^{29}Si NMR spectrum of PSiO-NO exhibits a signal in the region characteristic of the monomer **2** (Figure 1b and Table I). ^{29}Si NMR spectrum of PSiO-NO (Figure 1) also indicates that Si-Si unit of PDSiAzep was completely converted to the Si-O-Si unit without occurring another reaction.

UV-vis Spectra

As shown in Table I, UV-vis λ_{max} of CHCl_3 solution of the polymers were in the order PPhenaz > PSiO-NO > PDSiAzep. To investigate the effect of the structure, the X-ray analysis of the monomers were carried out. The results of X-ray crystallography are summarized in Table II and ORETP drawings are depicted in

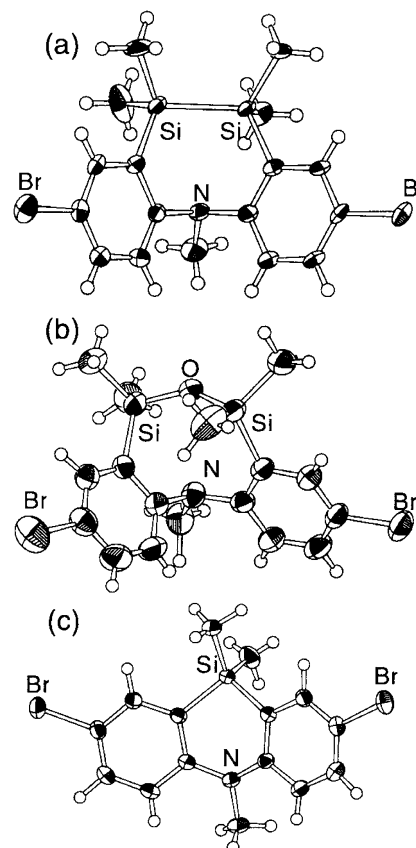


Figure 2. ORTEP drawings of (a) **1**, (b) **2**, and (c) **3a**.

Figure 2. These monomers had bent structures between two benzene units. However, as shown in Tables I and II, there was no correlation between the dihedral angle of two benzene atoms and UV-vis λ_{max} of the polymers. On the other hand, as shown in Table II, the sums of the angles around the N of **1**, **2**, and **3a** are 337.8° , 341.2° , and 358.5° , respectively. The order of flatness around the N atom of the monomers was the same order as UV-vis λ_{max} of the related polymers.

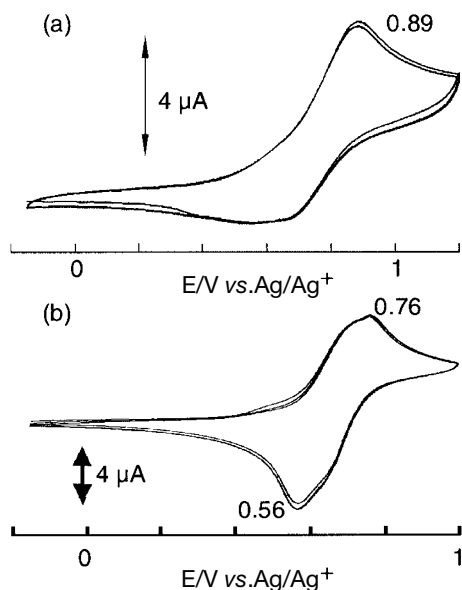
By the way, UV-vis λ_{max} of CHCl_3 solution of PSiO-Ni was 313 nm, which was almost the same region of PSiO-NO. This result seems to indicate that the properties of PSiO are not so much changed by the synthetic method.

Electrochemical Behavior

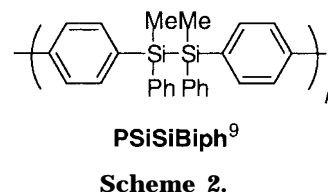
CV of the PDSiAzep was shown in Figure 3a. CV

Table II. Structure parameter of **1**, **2**, and **3a** from crystal structure

	1	2	3a	
formula	C ₁₇ H ₂₁ Br ₂ NSi ₂	C ₁₇ H ₂₁ Br ₂ NOSi ₂	C ₁₅ H ₁₅ Br ₂ NSi	
molecular weight	455.34	471.34	397.18	
space group	orthorhombic, P2 ₁ 2 ₁ 2 ₁ (No 19)	monoclinic, P2 ₁ /c (No 14)	triclinic, P1 (No 2)	
Cell dimensions	<i>a</i> / Å	11.441(3)	9.273(3)	9.125(4)
	<i>b</i> / Å	15.307(3)	26.020(3)	10.011(6)
	<i>c</i> / Å	11.282(3)	8.536(2)	9.066(3)
	α / deg			93.00(4)
	β / deg		90.99(2)	92.71(4)
	γ / deg			110.23(4)
	<i>V</i> / Å ³	1975.9(7)	2059.4(8)	774.1(7)
Z	4	4	2	
<i>D</i> _{calc} / g cm ⁻³	1.531	1.52	1.704	
<i>R</i>	0.053	0.041	0.029	
<i>R</i> _w	0.072	0.063	0.045	
Selected bond angle/deg	C _{Ar1} -N-C _{Ar2}	109.2(6)	114.2(3)	123.9(2)
	C _{Ar1} -N-C _{Me}	114.0(6)	110.7(4)	117.5(2)
	C _{Ar2} -N-C _{Me}	114.6(6)	116.3(4)	117.1(2)
	Sum of bond angle around the N atom	337.8	341.2	358.5
Dihedral angle between two benzene atoms	107.38	102.92	151.23	

**Figure 3.** CV curve of CH₂Cl₂ solution of (a) PDSiAzep and (b) PSiO containing TBAP (0.1 M) at 50 mV s⁻¹.

curves of poly(diphenylamine) derivatives are always reversible.^{3,7b} However, although PDSiAzep was poly(diphenylamine) derivatives, the CV was irreversible. Oxidation potential of PDSiAzep film (at about 0.84 V, irreversible) was lower than related that of poly(biphenylenedisilanyl) PSiSiBiph (in Scheme 2, at 1.21 and 1.56 V, irreversible)^{9a} which was PDSiAzep without bridging N atom. To understand the detailed oxidation mechanism, spectroelec-



trochemical properties of PDSiAzep were studied. As shown in Figure 4a, absorption bands assigned as polaron of PDSiAzep were observed at about 480 and 1400 nm at lower potential. When the potential was higher, polaron states in PDSiAzep were transformed to bipolaron states indicating the absorption band at about 540 nm (Figure 4b). On further oxidation, the absorption bands were disappeared (Figure 4c), maybe because of instability of bipolaron state of PDSiAzep. We reported the mechanism of electrochemical oxidation of 2,8-diphenyl-10,11-dihydro-10,11-disila-5,10,10,11,11-pentamethyl-5H-dibenz[b,f]azepine **1b**,⁴ which could be said the model compound for PDSiAzep. The report suggests that Si-Si bond cleavage occurs before oxidation of N atom, which does not have aromatic amine property by electrochemical oxidation of **1b**, and the report agrees with the result of spectroelectrochemistry of the polymer. UV, CV, and spectroelectrochemistry of PDSiAzep suggest that the N atom in PDSiAzep works as electron-donating substituent rather than substituent which expand π -conjugation system like poly(phenazasiline).

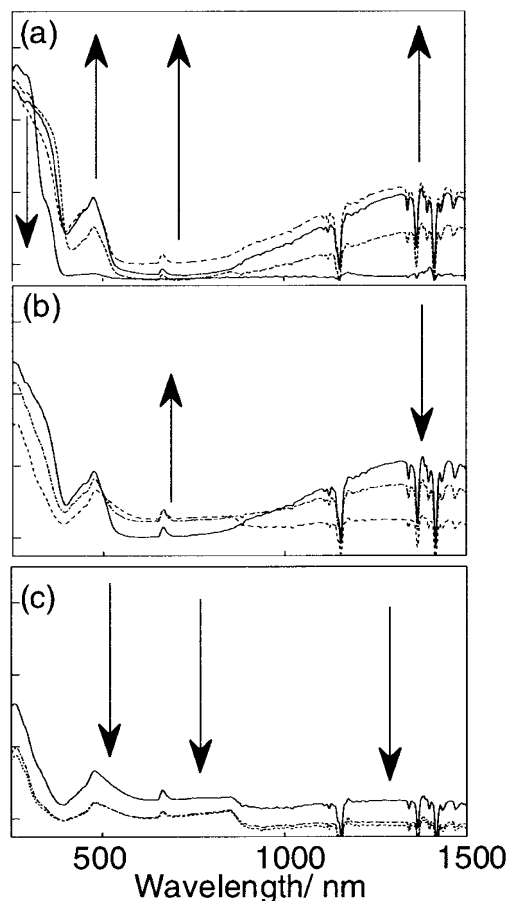


Figure 4. Absorption spectral changes during oxidation at constant potentials. (a) The solution of PDSiAzep in CH_2Cl_2 containing 0.1 M TBAP at -0.15 V, $+0.2$ V, $+0.3$ V, $+0.4$ V, $+0.45$ V, and $+0.55$ V in the arrow direction, and (b) at $+0.7$ V, $+0.75$ V, and $+0.8$ V, and (c) $+0.8$ V, $+0.9$ V, and $+1.0$ V in the arrow direction.

On the other hand, as shown in Figure 3b, CV of PSiO shows reversible redox behavior. In spite of CV of poly(diphenylamine) always show two reversible peaks,^{3,7b} CV of PSiO seems to show only one peak. To understand of the detailed oxidation mechanism, spectroelectrochemical measurements of PSiO were carried out (Figure 5). As shown in Figure 5a, absorption bands assigned as polaron of PSiO were observed at about 465 and 1035 nm at lower potential. At higher potential (> 0.6 V), polaron states in PSiO were transformed to bipolaron states indicating the absorption band at about 510 nm (Figure 5b). From Figure 3b and 5, the CV shows two-step reversible oxidation behavior. On the other hand, CV of 1,3-diphenyl-1,1,3,3-tetramethylsiloxane did not show electrochemical activity in the sweep range between -0.15 to 1 V vs. Ag/Ag^+ . These results suggest that CV of PSiO shows typical redox of poly(diphenylamine) without electrochemical influence on Si–O–Si unit. The results also suggest that N atom of PSiO extend π -conjugation system and this agrees with the result of the X-ray crystallography of the related monomer **2**.

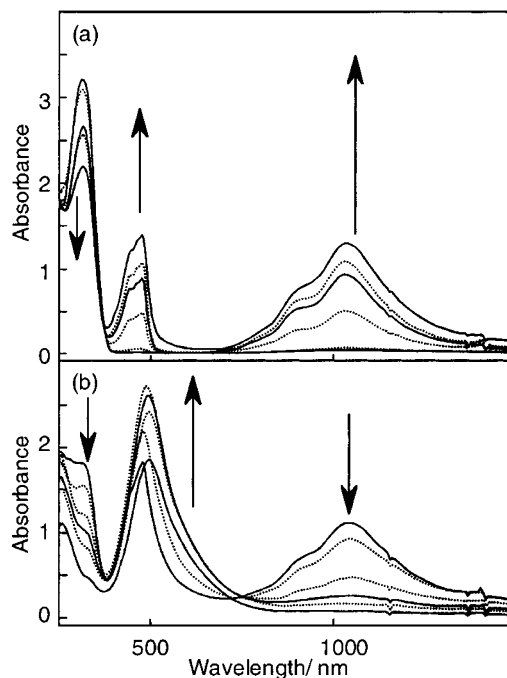


Figure 5. Absorption spectral changes during oxidation at constant potentials. (a) The solution of PSiO in CH_2Cl_2 containing 0.1 M TBAP at -0.15 V, $+0.2$ V, $+0.3$ V, $+0.4$ V, $+0.45$ V, and $+0.55$ V in the arrow direction. (b) The solution of PSiO in CH_2Cl_2 containing 0.1 M TBAP at $+0.6$ V, $+0.65$ V, $+0.7$ V, $+0.75$ V, $+0.8$ V, and $+0.9$ V in the arrow direction.

As shown in Table I, the conductivity of electrochemically doped PDSiAzep and PSiO-NO were about 2.0×10^{-4} and $1.3 \times 10^{-2} \text{ Scm}^{-1}$, respectively. Conductivities of the polymers were lower than PPhenaz. The difference of conductivity seems to come from effective π -conjugation through the N atom.

Electroluminescent Device

EL properties of the device which was fabricated by using the polymers as a hole-transport layer are shown in Figure 6. EL data of PPhenaz-b^{3a} and PSiSiBiph^{9b} (Scheme 2) are also given in Figure 6 for comparison.

From Figure 6, turn-on bias voltage of PSiO-NO and PPhenaz-b was lower than that of PDSiAzep, indicating the higher hole injection properties of PSiO-NO and PPhenaz-b. From the data of CV, UV, and X-ray crystallography of model compound, turn-on bias voltage of this type EL device, which has poly(arylamine) type polymer as a hole-transport layer, seems to depend on the effective π -conjugation through the N atom. Expansion of the π -conjugation of polymers may play a key role for the high hole injection properties.

On the other hand, as shown in Figure 6a, current-voltage characteristic of PDSiAzep was better than that of PSiSiBiph. The result shows introduction of N atom is effective for the properties of the hole transporting material of EL device though the N atom of the

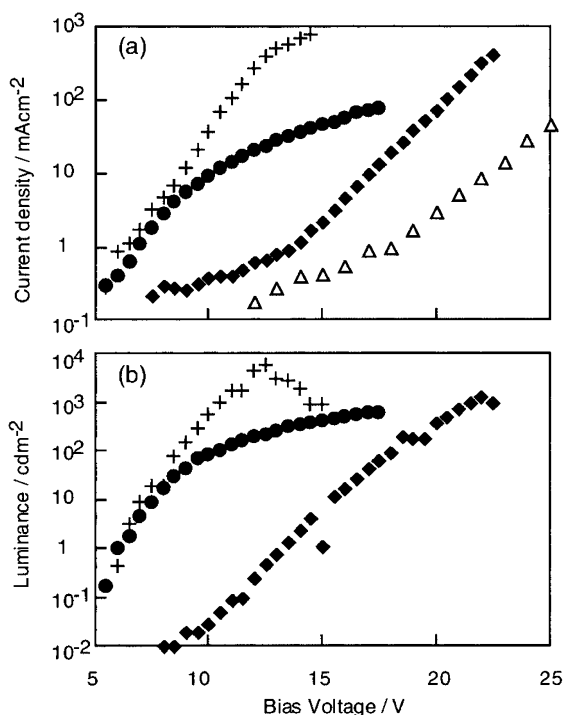


Figure 6. (a) Current density-voltage and (b) luminance-voltage characteristics of the EL device having polymers (◆) PDSiAzep; (●) PSiO-NO; (+) PPhenaz-b;^{3a} and (△) PSiSiBiph^{9b} as the hole-transporting material.

diphenylamine unit did not expand π -conjugation.

CONCLUSION

Disilane and disiloxane unit-fused poly(diphenylamine) (PDSiAzep and PSiO) were prepared and properties of these compounds were studied. Fusing unit of the polymers influences on effective π -conjugation length. The effective π -conjugation length influences electronic property such as electric conductivity of the polymer and characteristics of EL device with the polymer as the hole-transport layer.

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