Preparation and Properties of π-Conjugated Polymer with Phenazasiline Units

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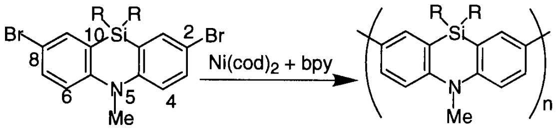
Poly(phenazasiline)s (PPhenaz) and related phenazasiline copolymers having arylenediethyndiyl units in the backbone (PPhE) were prepared by organometallic processes. PPhenaz films show reversible electrochromic behavior upon electrochemical treatment. A double layer electroluminescent device comprising PPhenaz with n-C_8H_{17} groups bound to the silicon displays high performance similar to those comprising a typical hole-transport material, poly(*N*-vinylcarbazole).

Phenazasiline derivatives are potentially useful materials such as hole transporting layer for EL devices[1] and antioxidant.[2] Phenazasiline-containing polyesters and polyamides possess high thermal stability.[3] Casalbore-Miceri and coworkers synthesized phenazasiline homopolymers by electrochemical oxidation of trimethylphenazasiline and examined electrochromic behaviors,[4] but the structure of the polymers, the juncture of repeat units in particular, is not clear. Transition metal complex-assisted reductive coupling and related reactions starting with dihalogenated aromatic compounds have been known to provide reliable synthetic methods to obtain structurally well-defined π-conjugated polymers.[5-7] In this paper, we report preparation of phenazasiline-containing polymers by reductive coupling of dibromophenazasiline and phenazasiline-acetylene-phenylene copolymers by the reaction of dibromophenazasiline with diethynylbenzenes. The resulting polymers displayed interesting electochromism and high efficiency as hole transporting polymeric material.

Poly(phenazasiline-2,8-diyl)s (PPhenaz) were synthesized by the reductive coupling of 2,8-dibromo-5,10-dihydro-5-methylphenazasilines **1a-c**[8] (eq 1, Table 1).[6,9] For instance, to a mixture of $Ni(cod)_2$ (0.168 g, 0.6 mmol, cod = 1,5-cyclooctadiene), cod (0.375 cm^3) and 2,2'-bipyridyl (0.100 g, 0.6 mmol) in toluene (10 cm^3) was added phenazasiline **1b** (0.297 g, 0.5 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 175 mg (4.0 mmol monomer unit, 80%) of analytically pure PPhenaz-b. PPhenaz-a and -c were also obtained similarly. All these polymers are soluble in CF_3COOH. However, their solubilities in usual organic solvents like chloroform, 1,2-dichloroethane, and THF were in the order PPhenaz-c < PPhenaz-a < PPhenaz-b, and the solubilities of PPhenaz-a and PPhenaz-c in THF were somewhat limited.



(1)

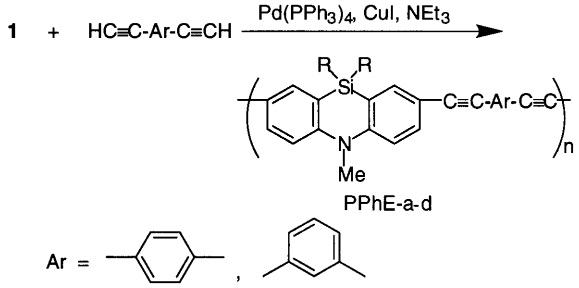
1a, b, c PPhenaz-a, -b, -c

a: R = Me, b: R = n-C_8H_{17}, c: R = Ph

$Ni(cod)_2$ = bis(1,5-cyclooctadiene)nickel(0), bpy = 2,2'-bipyridyl

Copolymers, poly[(phenazasiline-2,8-diyl)(phenylenediethynyl)] (PPhE), were synthesized by palladium-catalyzed polycondensation between **1** and diethynylbenzenes (eq 2, Table 1).[7]

For example, a mixture of phenazasiline **1b** (0.5 mmol), 1,3-diethynylbenzene (0.51 mmol), and triethylamine (1 cm^3) in toluene (10 cm^3) was heated in the presence of CuI (5 mg) and



(2)

PPhE-a-d

1,4-phenylene 1,3-phenylene

Table 1. Preparation of phenazasiline-containing π-conjugated polymers

Polymer	R	-Ar-	Method[a]	Solvent	Yield/%	*M*w/10^3 [b]	NMR/δ		λmax/nm[c]	
							^{29}Si	^{13}C of -*C*≡*C*-[d]	UV	EM[e]
PPhenaz-a	Me		A	Toluene	79	9.0 (2.3)[f]	-21.66[g]		361[f]	403[f]
PPhenaz-b	n-C_8H_{17}		A	DMF	50	5.0 (1.5)	-19.52[g]		364	
PPhenaz-b	n-C_8H_{17}		A	Toluene	80	20.8 (2.2)			366	405
PPhenaz-c	Ph		A	DMF	77	Nd[h]	-28.50[d]		366[f]	405[f]
PPhE-a	n-C_8H_{17}	1,4-phenylene	B	Toluene	37	4.7 (2.0)	-19.47[g]	91.0	377	426
PPhE-b	n-C_8H_{17}	1,3-phenylene	B	Toluene	32	8.5 (1.2)	-19.47[g]	89.9	354	418
PPhE-c	Ph	1,4-phenylene	B	Toluene	51	5.1 (1.5)[f]	-28.74[d]	91.4	379[f]	425[f]
PPhE-d	Ph	1,3-phenylene	B	Toluene	38	6.4 (1.5)[f]	-29.24[d]	90.1	359[f]	396, 417[f]

[a]Reaction conditions. Method A: $Ni(cod)_2$ and bpy 0.6 mmol, **1** 0.5 mmol, solvent 10 cm^3, 60 °C, 48 h. Method B: **1** and diethynylbenzene 0.5 mmol, CuI and $Pd(PPh_3)_4$ 0.025 mmol, triethylamine 1 cm^3, and toluene 10 cm^3, 60 °C, 48 h. DMF = N,N-dimethylformamide. [b]Determined by GPC ($CHCl_3$, polystyrene standards). The figure in the parenthesis is *M*w/*M*n. [c]$CHCl_3$ solution. [d]Determined by CP MAS method. [e]Excited by light in the near UV λmax region. [f]Data for $CHCl_3$-soluble fractions. [g]In $CDCl_3$. [h]Not determined because of the low solubility.

$Pd(PPh_3)_4$ at 60 °C for 48 h and was poured into methanol to precipitate a yellow orange powder, which was washed with hexane and methanol to give a 37% yield of analytically pure PPhE-b. Despite the presence of the phenazasiline ring, PPhE-a, -b, -c, and -d are less soluble in CF_3COOH than the PPhenaz family. PPhE-a and -b having long alkyl chains on the Si atom are more soluble in chloroform than the phenyl substituted PPhE-c and -d.

Synthetic and spectroscopic data for these polymers are summarized in Table 1. ^1H NMR spectra of these polymers confirm the proposed structures as exemplified by the spectrum of PPhenaz-b (Figure 1). ^{13}C CP-MAS NMR spectra of PPhE display signals at about δ 90, which are assignable to the C≡C unit. ^{29}Si NMR spectra of the polymers also exhibit a signal in the region characteristic of the phenazasiline ring.[10]

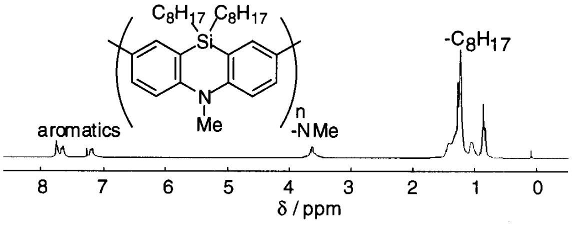


Figure 1. ^1H -NMR spectrum of PPhenaz-b (in $CDCl_3$).

UV and fluorescence data of the polymers are also summarized in Table 1. PPhE-a and -c with 1,4-phenylene unit show higher λmax values than PPhE-b and -d with 1,3-phenylene unit, suggesting the extended π-conjugation system.

Cyclic voltammetry (CV) of PPhenaz films cast from trifluoroacetic acid shows that the films are more readily oxidized than those cast from 1,2-dichloroethane, presumably associated with the former being protonated. PPhenaz displayed an interesting electrochromism upon electrochemical oxidation. Thus, a PPhenaz-c film cast on an ITO glass plate from trifluoroacetic acid[11] was colorless when neutral, but the color changed to yellow, red, and finally purple with increase in the electrode potential to +1.0 V (*vs.* Ag/Ag$^+$). As the CV curves in Figure 2 show, the behavior was reversible. The multiple oxidation process found for the PPhenaz-c film cast from trifluoroacetic acid, different from the one cast from dichloroethane,[12] is presumably associated with protonation/deprotonation process. On the other hand, the CV curves of PPhE films showed irreversible peaks.

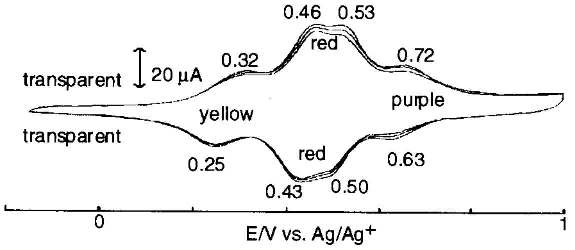


Figure 2. CV curves of PPhenaz-c film laid on a ITO electrode cast from CF_3COOH. In a CH_3CN solution of $[Bu_4N][ClO_4]$ (0.1 M). At 50 mVs^{-1}

By using PPhenaz-b as a hole-transport layer and Alq_3 [tris(8-quinolinolato)aluminum(III)] as an electron-transport-emitting layer respectively, a double layer EL device comprising ITO/PPhenaz-b (thickness: 40 nm)/ Alq_3 (60 nm)/Mg:Ag was fabricated with the PPhenez-b being spin-coated. As shown in Figure 3, the current density of the EL device increases with applied voltage from about 5 V and the current density reaches 800 mA cm^{-2} at 14 V. The electrical properties of the device are almost the same as that of a device with a typical hole-transport material, poly(*N*-vinylcarbazole).[13] The luminance, which is green emission only from Alq_3, starts at a low voltage such as 5 V and a maximum luminance of 5500 cdm^{-2} is achieved at 13 V. The PPhenez-b has the ionization potential of 5.4 – 5.5 eV as measured with a Riken AC-1, indicating that the hole injection to this polymer is smooth. The electron affinity of the PPhenez-b may be about 2.0 eV[14] and results in the high electron-blocking property. The use of the polymer PPhenez-b as a hole transporting layer in the device therefore enables efficient electroluminescence from the emitting layer, Alq_3.

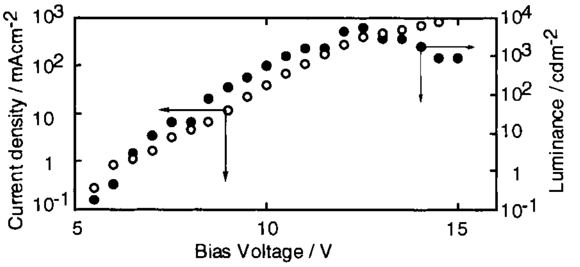


Figure 3. Current density-voltage (○) and luminance-voltage (●) characteristics of a typical ITO/PPhenaz-b/Alq_3/Mg:Ag cell.

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References and Notes

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9 PPhenaz-b: Anal. Found: C, 77.5; H, 10.0; N, 3.3; Br, 0.2%. Calcd for $(C_{29}H_{43}NSi{\cdot}H_2O)_n$: C, 77.4; H, 9.7; N, 3.1%.
10 ^{29}Si-NMR data in $CDCl_3$. **1a**: δ -20.93. **1b**: δ -19.03. **1c**: δ -29.32.
11 The film was dried *in vacuo* after cast to exclude the acid.
12 Oxidation peaks of PPhenaz-c cast from 1,2-dichloroethane were Epa1 = 0.63 and Epa2 = 0.74 V vs Ag/Ag$^+$.
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