

SHORT COMMUNICATIONS

Preparation of Phenazasiline-containing Poly(arylene)s and Their Use as Functional Additives in Resins

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Phenazasiline-containing polymers could be functional materials because phenazasiline contains both diphenylamine and diphenylsilane structure. The preparation and properties of poly(phenazasiline)s (Scheme 1) have been described.^{1,2} Poly(phenazasiline) has shown a high efficiency as a hole transporting layer of electroluminescent (EL) devices^{1a} and has an interesting electrochromism.^{1b} It is also useful for extension fixation of DNA.^{1c} However, phenazasiline-containing polymers have color and fluorescence. The color and fluorescence property is important for industrial applications such as an additive for coloring in plastics (resins), EL devices, or light-emitting diode panels. Polymers have good thermal stability.³ Thus polymers seem to be useful as a functional additive in resins by using a thermal melting process usually used in processing resins.

We have previously reported the preparation of poly(phenazasiline) with various substituents on the N and Si atoms,^{1,2} but the related copolymer with phenazasiline was not systematically explored. We synthe-

sized the phenazasiline-containing poly(aryleneethynylene), indicating that the absorption λ_{\max} shifted by 10 nm.^{1a} Color variation is also important for industrial applications. Thus we were optimistic of preparation of a copolymer with an aromatic unit to change the color of phenazasiline. In this study, we prepared a phenazasiline-containing poly(arylene) (PAR), and used the polymer as functional additive. We also studied the fluorescence energy resonance transfer (FRET) between the phenazasiline-containing polymers as the probe in the transparent resin when two polymers were used simultaneously.

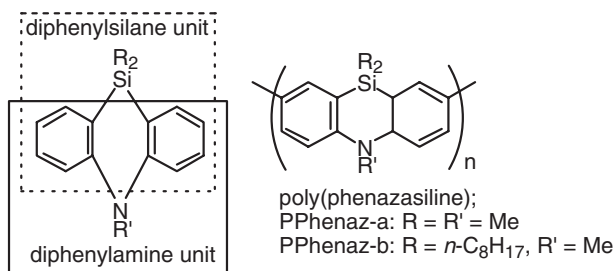
EXPERIMENTAL

Reagent

Reagents 2,5-bis(trimethylstannyl)thiophene,^{4a} 2,5-dihexyloxy-1,4-diboronic acid,^{4b} 2,8-dibromo-5,10,10-trimethylphenazasiline (**1a**),⁵ 2,8-dibromo-10,10-dioctyl-5-methylphenazasiline (**1b**),⁵ and poly(5,10,10-trimethylphenazasiline-2,8-diyl) (PPhenaz-a)⁵ were prepared as previously described. Other chemicals were used as purchased.

Measurement

NMR spectra in solution were taken by using a Bruker ARX-300 and JEOL-EX 400 spectrometers. Absorption spectra were spectro measured by using a Hitachi U-3250 and JASCO V-570 spectrometers. A cyclic voltammogram (CV)^{1b,5} was taken and the conductivity⁶ of the polymers was measured as previously described. The film used for the measurement



Scheme 1.

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was cast from 1,2-dichloroethane.

Fluorescence and excitation spectra were measured by using a Hitachi 4010 spectrometer. Fluorescence spectra were excited at the absorption λ_{\max} light. Excitation spectra were monitored at the fluorescence λ_{\max} light.

Polymer Preparation

Preparation of Poly(5,10,10-trimethylphenazasiline-2,8-diyl-alt-thiophene-2,5-diyl) PAR-a. Pd(PPh₃)₄ (32.8 mg, 0.028 mmol) was added under N₂ to the toluene (15 mL) solution containing **1a** (210 mg, 0.53 mmol) and 2,5-bis(trimethylstannyl)thiophene (218 mg, 0.53 mmol) while stirring. After stirring for 48 h at 90 °C, the reaction mixture was poured into methanol. The obtained powder was successively washed with KF solution, water, methanol and hexane. A yellow powder (166 mg) was resulted. ¹H NMR (CDCl₃): δ 7.1–7.8 (m, 8H), 3.61 (s, 3H), 0.54 (s, 6H). Anal. Found: C, 71.7; H, 5.2; N, 3.8; S, 10.4%. Calculated for (C₁₉H₁₇NSSi)_n: C, 71.4; H, 5.4; N, 4.4; S, 10.0%.

Preparation of Poly(10,10-dioctyl-5-methylphenazasiline-2,8-diyl-alt-thiophene-2,5-diyl) PAR-b. The reaction of **1b** (584 mg, 1.0 mmol), 2,5-bis(trimethylstannyl)thiophene (404 mg, 1.0 mmol), and Pd(PPh₃)₄ (56 mg, 0.05 mmol) produced 459 mg of PAR-b as a yellow powder. ¹H NMR (CDCl₃): δ 6.8–8.0 (m, 8H), 3.58 (s, 3H), 0.8–2.0 (m, 34H). ¹³C NMR (CDCl₃): δ 150.35, 130.76, 128.90, 127.44, 125.53, 122.72, 121.45, 115.58, 38.54, 33.45, 31.92, 29.27, 29.16, 23.73, 22.68, 14.12, 13.43.

Preparation of Poly(10,10-dioctyl-5-methylphenazasiline-2,8-diyl-alt-1,4-dihexyloxybenzene-2,5-diyl) PAR-c. Two molar of Na₂CO₃ (aq) (11 mL) was added under N₂ to toluene solution (10 mL) containing **1b** (328 mg, 0.055 mmol) and 2,5-dihexyloxy-1,4-diboronic acid (202 mg, 0.55 mmol). Then, Pd(PPh₃)₄ (28 mg, 0.028 mmol) was added to the suspension, and stirred at 90 °C for 48 h. The reaction mixture was poured into methanol to stop the reaction, and the obtained precipitate was filtrated. The precipitate was washed by 1 M HCl and then in methanol, and then was dried in a vacuum and 368 mg of PAR-c as a white powder was produced. ¹H NMR (CDCl₃): δ 6.8–8.0 (m, 8H), 3.95 (t, 4H), 3.63 (s, 3H), 0.8–2.0 (m, 54H).

Addition of Polymer to the Resin

Preparation of Poly(lactic acid) (PLA)-containing Masterbatch. PPhenaz-a (1 mg) and PLA (10 g) were mixed and were put into a mixed extruder. Kneading the mixture at 180 °C gave a PPhenaz-containing masterbatch (PLA-m1). A PAR-containing masterbatch (PLA-m2) was obtained similarly.

Preparation of Poly(styrene) (PS)-containing Masterbatch. PPhenaz-a (1 mg) and PS (10 g) were mixed and were put into the mixed extruder. Kneading the mixture at 220 °C gave a PPhenaz-containing masterbatch (PS-m1). A PAR-containing masterbatch (PS-m2) was obtained similarly.

Resin Molding

Resin Containing One Additive. A mixture of PLA-m1 (0.15 g) and PLA (1.35 g) was put into a mixed extruder. Kneading the mixture at 180 °C and injection-molding gave a dumbbell-shaped resin (PLA-1, Table II). Resins PLA-2, PS-1, and PS-2 were prepared similarly (PS-1 and PS-2 were kneaded at 220 °C).

Resin Containing Two Additives. A mixture of PLA-m1 (0.15 g), PLA-m2 (0.45 g) and PLA (0.90 g) was put into a mixed extruder. Kneading the mixture at 180 °C and injection-molding gave dumbbell-shaped resin (PLA-3, Table II). Resins PLA-4, PS-3, and PS-4 were prepared similarly (PS-3 and PS-4 were kneaded at 220 °C).

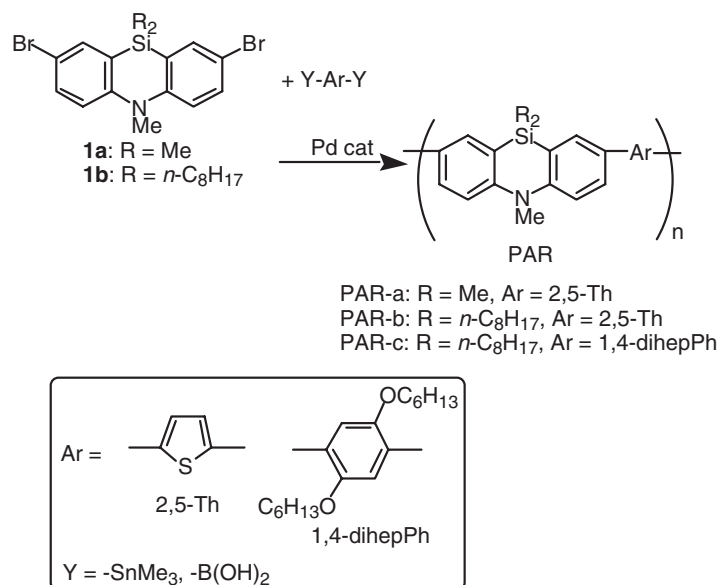
RESULTS AND DISCUSSIONS

Preparation and Properties of Phenazasiline-containing Poly(arylene)s

We believed various phenazasiline-containing polymers could be prepared because the poly(phenazasiline) was prepared from a reaction of the related dibromophenazasiline.^{1a,2,4,5,7} So, a reaction between dibromophenazasiline and distannyl- or diboryl-aromatic compound by a palladium-catalyzed system was done to prepare phenazasiline-containing poly(arylene)s (PAR, Scheme 2).^{4,5} Table I shows the results of polymerizations. PARs were obtained at a high yield. The color of the PAR was changed by introducing an aromatic unit (Ar in Scheme 1 and Table I). The thienylene-containing polymer was yellow and phenylene-containing polymer was white. Polymers with a long alkyl or alkoxy chain (PAR-b and PAR-c) had good solubility in usual organic solvents, such as CHCl₃, THF, and toluene, but the solubility of PAR-a was low. The ²⁹Si NMR spectrum of PAR showed signals in the region characteristic of related phenazasiline derivatives.^{1a,2,5,8}

Even though prepared by the same method, the observed molecular weight of PAR-a was lower for PAR-b, which may be because of the low solubility of PAR-a whose molecular weight was measured only for the THF-soluble part.

The absorption λ_{\max} of the phenylene-type copolymer (PAR-c) in CHCl₃ was almost the same as for the related homopolymer PPhenaz-b.^{1,2,5} This relationship was the same as for diphenylamine-containing poly-



Scheme 2.

Table I. Results of preparation of PAR and data of phenazasiline-containing polymers

Polymer	PAR-a	PAR-b	PAR-c	PPhenaz-a ^a
R	Me	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	Me
Ar	2,5-Th	2,5-Th	1,4-dihepPh	—
Y	SnMe ₃	SnMe ₃	B(OH) ₂	—
Color	yellow	yellow	white	white
Yield/%	98	91	94	
M _w /10 ^{-3b}	2.0 (1.3) ^c	11.6 (1.6)	21.0 (2.3)	18.5 (2.9) ^{a,c}
²⁹ Si NMR/ δ^d	-21.45	-19.50	-20.21	-21.6 ^a
Absorption $\lambda_{\max}/\text{nm}^e$	400 ^c	405	359	361 ^{a,c}
Fluorescence $\lambda_{\max}/\text{nm}^e$	453 ^c	460	415	403 ^c
Conductivity/S cm ^{-1f}	g	1.8	0.43	4.0 ^a
p-doping/ V vs. Ag/Ag ⁺	E_{pa} g	0.52 0.48	0.63 0.59	0.47 ^a 0.37 ^a
n-doping/ V vs. Ag/Ag ⁺	E_{pc} g	-2.70 -2.65	h	h

^aFrom ref 1b. ^bGPC (THF, polystyrene standards). The figure in the parenthesis is M_w/M_n . ^cSolvent soluble part. ^dIn CDCl₃. ^eCHCl₃ solution. ^fElectrochemically doped cast film. ^gNot Measured. ^hNot determined from CV.

(arylene)s,^{4c} implying that the absorption λ_{\max} of phenazasiline derivatives depend on their diphenylamine unit.^{1b} However, the absorption λ_{\max} of CHCl₃ solution of thienylene-type copolymers (PAR-a and -b) were longer than related phenazasiline homopolymers, indicating that introducing a thienylene unit to phenazasiline polymer causes a long-wave shift to the absorption λ_{\max} .^{4d,e} The fluorescence color changed markedly from purple for PPhenaz-a to blue for PAR-a and PAR-b. The successful longer wavelength was probably due to the electron of the N atom of phenazasiline delocalizing to the thienyl moiety.

The CV of the PAR film showed reversible electrochemical p-doping, which is observed in phenazasi-

line derivatives,^{1b,2,8} and the CV of the PAR-b film showed reversible n-doping; PAR-c had no reduction process. The conductivity of electrochemically p-doped cast film was almost the same as for poly(phenazasiline).⁵

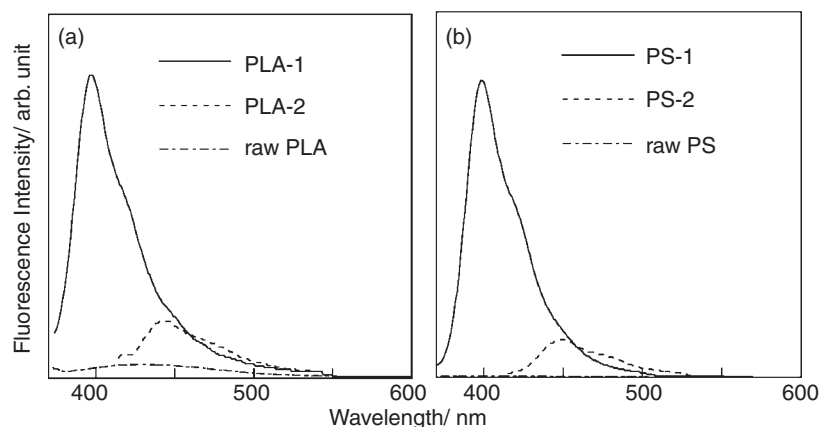
Use of Phenazasiline-containing Polymer as a Functional Additive in Resin

Usually, raw resins are functionalized by addition of additives. Our group has improved mechanical properties of resin by adding compatibilizers^{9a} and layered silicate.^{9b} Adding phenazasiline-containing polymers to raw resins seems to give a new function to resin. Therefore, phenazasiline-containing polymer

Table II. Data of prepared polymer-added resins. Scheme 3 shows the chemical structure of added polymers PPhenaz-a and PAR-a

Resin	PPhenaz-a contents/wt %	PAR-a contents/wt %	Resin ^a	Absorption λ_{\max}/nm	Fluorescence $\lambda_{\max}/\text{nm}^b$	Excitation λ_{\max}/nm
PLA-m1	0.01	0	PLA			
PLA-m2	0	0.01	PLA			
PLA-1	0.001	0	PLA	369	401	363
PLA-2	0	0.001	PLA	390	445 ^c	403
PLA-3	0.001	0.003	PLA	d	402, 447	389
PLA-4	0.001	0.006	PLA	d	402, 451	409
PS-m1	0.01	0	PS			
PS-m2	0	0.01	PS			
PS-1	0.001	0	PS	369	401	363
PS-2	0	0.001	PS	390	451 ^c	405
PS-3	0.001	0.003	PS	d	401, 448	409
PS-4	0.001	0.006	PS	d	401, 451	412

^aPLA: poly(lactic acid). PS: poly(styrene). ^bExcited at PPhenaz-a λ_{\max} . ^cExcited at PAR-a λ_{\max} . ^dNot measured.

**Figure 1.** Fluorescence spectra of PPhenaz-a- or PAR-a-added resins. Irradiated at absorption λ_{\max} of the polymers. The resin was PLA (a) and PS (b).

and raw resin were molded by melting using heat. Table II shows the absorption and fluorescence data of polymer-added resins PLA-1, PLA-2, PS-1, and PS-2. The absorption and fluorescence λ_{\max} of the resins were almost the same as polymers in the organic solvent. Excitation λ_{\max} was almost the same as absorption λ_{\max} . These results suggest that polymers have good dispersibility to the resins by even the molding by melting. Absorption, fluorescence, and excitation λ_{\max} of the polymer-added resin did not depend on raw resin (Table II). Even though only 0.001 wt % of the polymer was added, the fluorescence of polymer-added resins was much stronger than for related raw resins (Figure 1), suggesting that polymers are useful as fluorescence additives in the transparent resin.

FRET by Mixing of Additives

Energy transfer is important for the antenna function of organic solar cells¹⁰ and environmental probes

in resins.¹¹ The π -conjugated polymer has long-distance exciton transfer in itself, and thus efficient energy transfer in resins is predictable. In this study, successful change in electron band on the π -conjugate was induced by introducing thienylene. Thus, energy transfer between PPhenaz-a and the thienylene unit-containing PAR-a was investigated. Various contents of PPhenaz-a and PAR-a were added to the resin (Table II). Figure 2a shows the fluorescence spectra of PLA containing 0.001 wt % of PPhenaz-a at various concentration of PAR-a. With increasing concentration of PAR-a, the peak at 400 nm based on PPhenaz-a decreased and the peak at 450 nm based on PAR-a increased. The increasing fluorescence at 450 nm indicates that polymers in resins do not phase separately to self-quench fluorescence but homogeneously distribute in resins. Similar results were obtained when PS was used as a resin (Figure 2b). These results show that the excitation energy transfer occurs from PPhenaz-a to PAR-a.

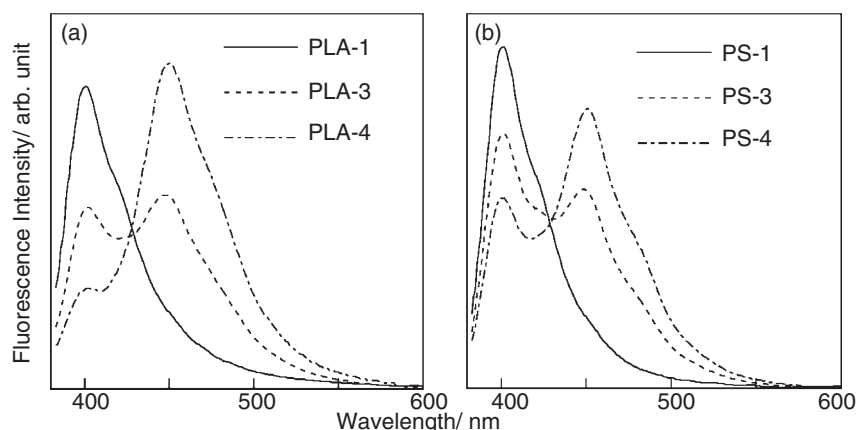
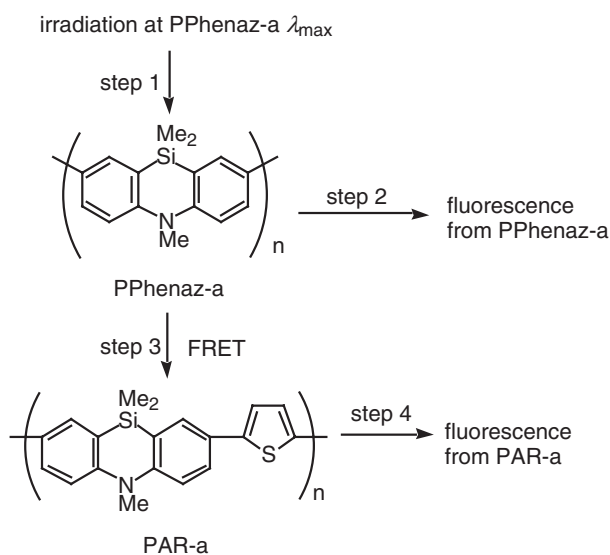


Figure 2. Fluorescence spectra of polymer-added resins with various contents of PPhenaz-a and PAR-a. Irradiated at absorption λ_{\max} of PLA-1 or PS-1 (see Table II). The resin was PLA (a) and PS (b).



The most probable mechanism for the observed FRET is the Förster dipole–dipole interaction. Scheme 3 seems to show the FRET mechanism. First, irradiation at PPhenaz-a λ_{\max} (step 1 in Scheme 3) causes emission at about 400 nm from PPhenaz-a (step 2, ex PLA-1). When PAR-a does not exist near PPhenaz-a, the emission is only from PPhenaz-a (step 3, ex PLA-3 and PLA-4). However, the emission based on PPhenaz-a overlapped with absorption of PAR-a (Table II). Therefore, fluorescence energy from PPhenaz-a transfers to PAR-a (step 4), and then, the fluorescence from PAR-a increases.

Figure 3 shows the change in I_0/I by adding the PAR-a to the PLA and PS. The increase of I_0/I in PLA is larger than for PS, indicating a larger FRET (about 1.5 times) between PPhenaz-a and PAR-a in PLA than for PS. Thus, PPhenaz-a and PAR-a act as sensitive probes of the difference in internal micro environment in resins, suggesting that phenazasiline-

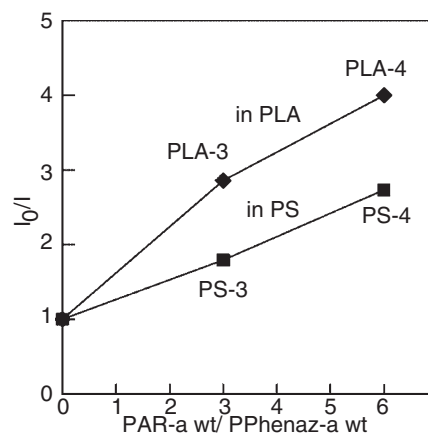


Figure 3. Plots for I_0/I for polymer-containing resin vs. weight ratio of PAR-a/PPhenaz-a. The resin was PLA (◆) and PS (■). I_0 : the fluorescence intensity of PPhenaz-a-containing resin without PAR-a. I : the fluorescence intensity of PPhenaz-a-containing resin in the presence of PAR-a. Both I_0 and I were measured at Fluorescence λ_{\max} of PS-1 and PLA-1, respectively.

containing polymers are useful as an environment probe in resins.

In conclusion, we prepared phenazasiline-containing poly(arylene)s (PAR), and introduced a thienylene unit into the polymer to successfully induce color change. Phenazasiline-containing polymers are useful as a fluorescence additive in resins because polymers have good compatibility with resin. The energy transfer shows that phenazasiline-containing polymers are useful as environment probes.

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