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Design and Synthesis of Stimuli-Responsive Conjugated Polymers Having Azobenzene Units in the Main Chain

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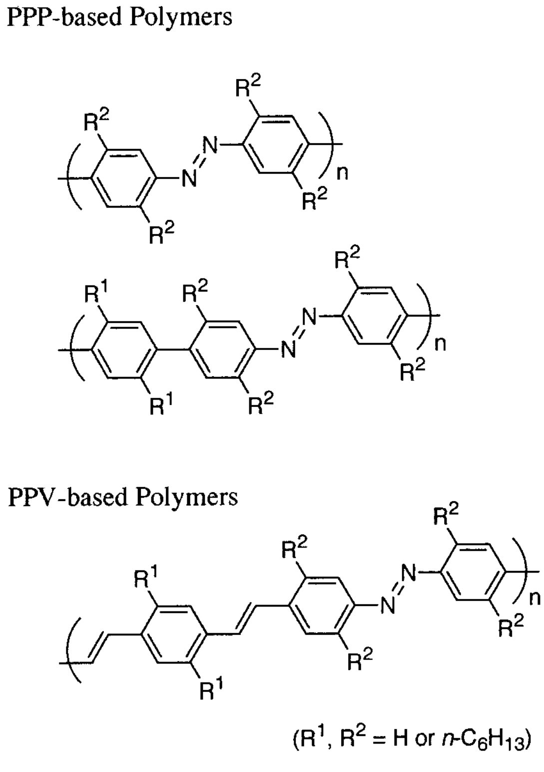
ABSTRACT: Poly(*p*-phenyleneethynylene)- and heteroaromatic-containing poly(phenylene)-based conjugated polymers having photoisomerizable azobenzene units in the main chain were prepared using palladium-catalyzed cross-coupling reaction of 4,4′-diiodoazobenzenes with 1,4-diethynylbenzenes and bis(trimethylstannyl)heteroaromatics, respectively. Polymers possessing *n*-hexyl side chains on the aromatic rings were soluble in common organic solvents such as tetrahydrofuran, chloroform, and toluene. The polymers were thermally stable in air (T_0 > 330 °C). Poly(*p*-phenyleneethynylene)-based polymers (**3**) and thiophene-, furan-, and *N*-methylpyrrole-containing poly(phenylene)-based polymers (**5**) showed remarkably red-shifted absorptions in the visible region (λ_{max} > 400 nm) due to the extended main-chain conjugation, while the pyridine-containing poly(phenylene)-based polymer (**5d**) possesses a low degree of main-chain conjugation (λ_{max} < 380 nm). Polymer **5d** with low degree of main-chain conjugation showed reversible photoisomerization of azobenzene units, which was accompanied by the change in its electrochemical property.

Introduction

Azobenzene is a well-known photoresponsive chromophore, and its photoinduced and thermal geometric isomerizations have been extensively studied over four decades.[1] Azobenzene and its derivatives take both trans (E) and cis (Z) structures with respect to the azo linkage and normally exist in the more stable trans form. The trans isomer of azobenzene has an intense absorption around 320 nm due to the $\pi-\pi^*$ transition, and the cis isomer shows a weak absorption of the $n-\pi^*$ transition around 430 nm.[2] These absorptions enable the reversible isomerization between cis and trans structures upon photoirradiation with ultraviolet or visible light. Azobenzene itself shows no emission in the excited states, so that the photoisomerization proceeds virtually quantitatively.[3] The thermal isomerization from cis to trans isomer also proceeds due to the low activation energy of the cis-to-trans isomerization process. These isomerizations are accompanied by drastic changes in a number of properties such as dipole moment.[4]

Various photoresponsive polymers have been extensively studied to date.[3,5,6] The conformational changes of the polymers induced by the photopromoted or thermally promoted isomerization enable it to tailor the physical and chemical properties, including viscosity, refractive index, conductivity, pH, solubility, wettability, mechanical properties, polymer morphology, and so on. This concept has stimulated many chemists to create a wide variety of photoresponsive polymers, especially those with azobenzene moieties either in the side chains[7−11] or in the main chains,[12−19] with the motivation of producing the light-controllable functional materials. In particular, a recent study has focused on the synthesis of the azobenzene-containing polymers with the liquid crystallinity and the nonlinear optical properties that are typical characteristics of the π-conjugated polymers. Although many types of conjugated polymers, such as poly(*p*-phenylene) (PPP), poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenyleneethynylene) (PPE), and so on, have been synthesized,[20−22] little attention has been paid to the idea that azobenzene itself can be a part of π-conjugative building units.[11−16] Thus, it is of great interest to synthesize conjugated polymers having azobenzenes as conjugative units and to explore novel functions based on the optical, electrical, and magnetic properties.

In our previous studies, we examined the preparation of novel conjugated polymers having azobenzenes in the main chain.[12−14] Application of various palladium-catalyzed coupling methods such as Suzuki coupling and Heck reaction allowed the formation of PPP- and PPV-based polymers:

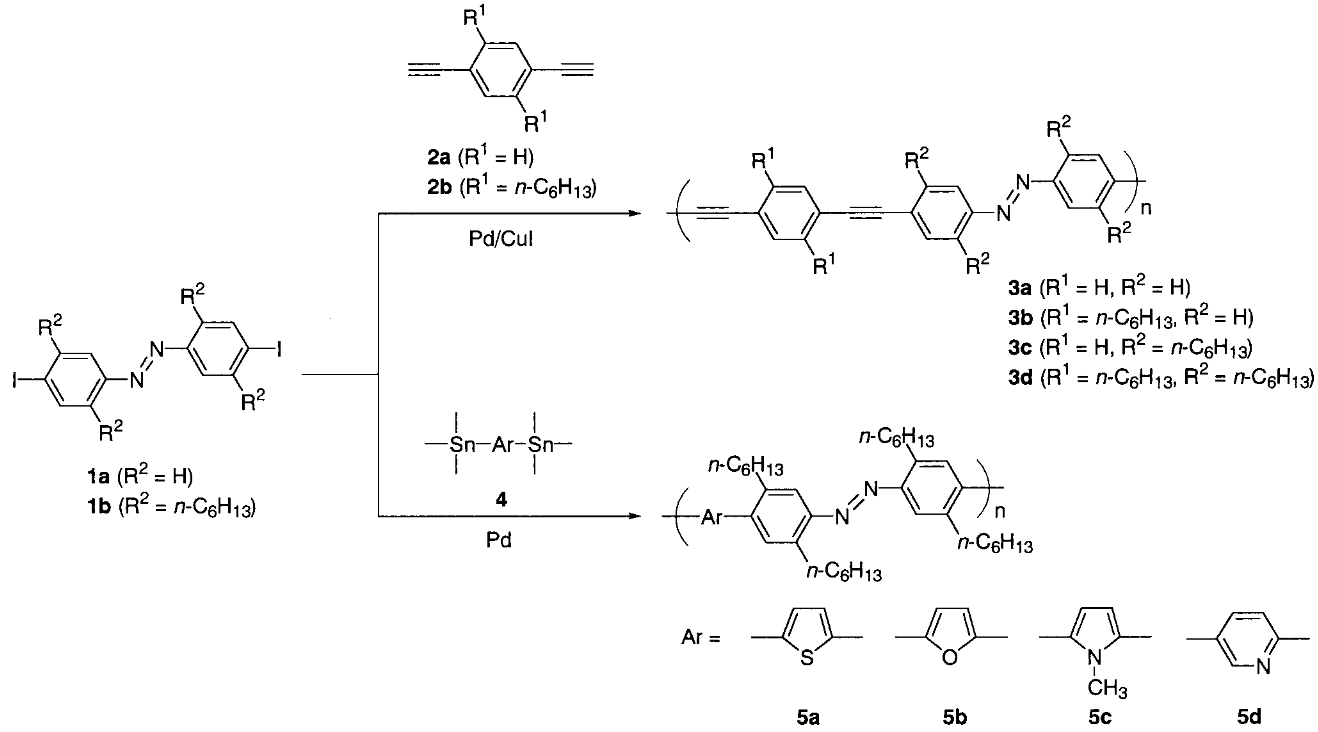

PPP-based Polymers

PPV-based Polymers

(R^1, R^2 = H or n-C_6H_{13})

10.1021/ma002101n CCC: $20.00

Scheme 1



Although the photochemical isomerization of azobenzene in a PPV-based polymer was not effectively achieved,[14] PPP-based polymers showed both the trans-to-cis photoisomerization upon irradiation of ultraviolet light and the cis-to-trans, i.e., reverse isomerization upon irradiation of visible light or by heating.[12,13] Especially, PPP-based polymers with the alternation of phenylene and azobenzene groups rapidly and reversibly isomerize by the photoirradiation and heating. These results stimulated us to design and investigate novel azobenzene-containing conjugated polymers that readily undergo the photoisomerization process.

In the present paper, we report the synthesis of new conjugated polymers (**3**, **5**) having the alternation of azobenzene and various conjugated linkages in the main chain using the well-established palladium-catalyzed coupling methods in order to systematically study the effects of the conjugated linkers on the isomerization behavior. PPE-based polymers (**3**) that are alternating copolymers composed of azobenzene and diethynylbenzene units were prepared by the Heck reaction of 4,4′-diiodoazobenzenes (**1**) with 1,4-diethynylbenzenes (**2**). The Stille reaction of **1** with bis(trimethylstannyl)-heteroaromatics (**4**) was employed for the synthesis of poly(phenylene)-based polymers (**5**) in which azobenzene groups are separated by various heteroaromatics (Scheme 1).

Results and Discussion

Polymerization. Several kinds of PPE derivatives have been synthesized by utilizing the palladium-catalyzed coupling of dihalobenzenes with diethynylbenzenes under the Heck conditions.[23,24] In this study, we employed one of the typical polymerization conditions in the coupling of **1** with **2** (Scheme 1), and the results are summarized in Table 1. Polymerization with PdCl$_2$(PPh$_3$)$_2$ and CuI in *N*,*N*-dimethylformamide (DMF) and triethylamine at 80 °C for 24 h gave polymers **3a**−**d** in quantitative yields. The polymers were orange to dark red solids, and **3b**−**d** having alkyl pendants were soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene.

Table 1. Pd-Catalyzed Polymerization of 1 with 2[a]

polymer	yield[b] (%)	M_n[c] (g mol^{-1})	M_w[c] (g mol^{-1})	T_0[d] (°C)	λ_{max}[e] (nm)
3a	100	[f]	[f]	384	
3b	100	4790	13 000	349	410
3c	100	20 900	114 000	336	422
3d	100	12 300	47 100	347	422

[a] [**1**] = [**2**] = 50 mM, [PdCl$_2$(PPh$_3$)$_2$] = 0.50 mM, [CuI] = 2.0 mM, 80 °C, 24 h. [b] Methanol-insoluble part. [c] Estimated by GPC (THF, PSt). [d] The onset temperature of weight loss in air determined by TGA (heating rate, 10 °C/min). [e] In CHCl$_3$. [f] Insoluble.

Heteroaromatic-containing functional polymers are usually studied from the viewpoint of their interesting electrochemical properties.[25] They can be prepared by the palladium-catalyzed Stille reaction because heteroaromatics such as thiophene and furan are easily introduced in the polymer backbone by the cross-coupling reaction of dihaloarenes with bis(trialkylstannyl)heteroaromatics under mild conditions.[26,27] One of the typical polymerization conditions was employed in the coupling of **1b** with bis(trimethylstannyl)heteroaromatics based on thiophene (**4a**), furan (**4b**), *N*-methylpyrrole (**4c**), and pyridine (**4d**) (Scheme 1), and the results are summarized in Table 2. Polymerization with PdCl$_2$(PPh$_3$)$_2$ in DMF at 110 °C for 48 h gave polymers **5a**−**d** in moderate to good yields. The polymers are soluble in common organic solvents such as THF, chloroform, and toluene.

NMR and IR spectra of all soluble polymers, **3b**−**d** and **5**, supported the formation of polymers with expected structures. For example, IR spectra of **3** showed absorptions around 2200 cm^{-1}, which indicates the presence of the disubstituted C≡C groups in the main chain. In the ^{1}H NMR spectrum of **5a**, which is illustrated as a typical example in Figure 1a, all signals

Table 2. Pd-Catalyzed Polymerization of 1b with 4[a]

polymer	yield[b] (%)	M_n[c] (g mol^{-1})	M_w[c] (g mol^{-1})	T_0[d] (°C)	λ_{max}[e] (nm)	E_{pa}[f] (V)	E_{pc}[f] (V)
5a	92	66 700	137 000	334	415	+1.29	+1.23
5b	95	14 500	29 000	334	469	+1.29	+1.26
5c	87	5730	12 900	337	402	+1.22	−1.17
5d	58	2580	3780	335	373	+1.24	−1.18

[a] [**1b**] = 75.0 mM, [**4**] = 76.5 mM, [PdCl$_2$(PPh$_3$)$_2$] = 1.5 mM, 110 °C, 48 h. [b] Methanol-insoluble part. [c] Estimated by GPC (THF, PSt). [d] The onset temperature of weight loss in air determined by TGA (heating rate, 10 °C/min). [e] In CHCl$_3$. [f] The anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}) vs Ag/Ag$^+$ electrode.

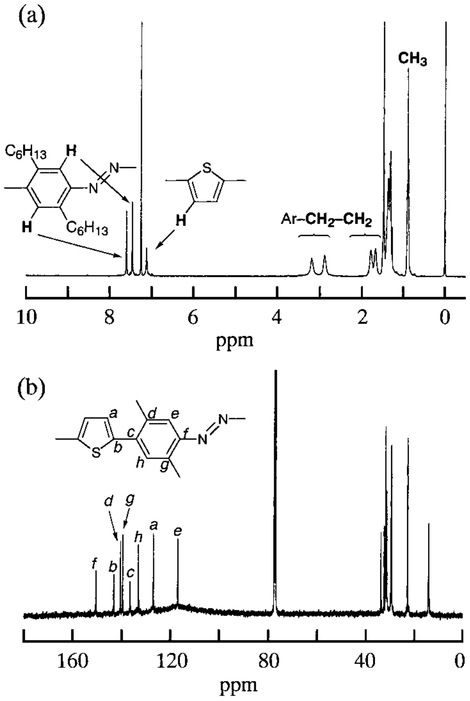


Figure 1. (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum of **5a** in CDCl$_3$.

were clearly detected, and the ratio of the integrated intensities of the aromatic and methylene protons supported the formation of the expected polymer. The number of carbon signals (Figure 1b) also coincided with that of structure **5a**. Although the elemental analysis data for the soluble polymers **3b**−**d** and **5a**−**d** were relatively close to the calculated values, those of polymer **5d** disagreed with the theoretical value calculated on the basis of its repeating unit. This is probably due to its low molecular weight since the found values for polymer **5d** agreed with values estimated by assuming that one C−I bond remained at one of the polymer ends.

Polymer Properties. Thermogravimetric analyses (TGA) in air indicated very high thermal stability of polymers **3** and **5** (Tables 1 and 2). No weight loss was observed up to 320 °C for any polymers. The glass transition temperature was not detected below 300 °C. Figure 2 shows the UV/vis absorption spectra of monomers **1** and polymers **3** and **5** in chloroform. Monomers **1a** and **1b** showed the absorption maxima (λ_{max}) at 352 and 364 nm, respectively, due to the π−π* transition of *trans*-azobenzene units. Polymers **3b**−**d** possess λ_{max} at 410, 422, and 422 nm, respectively, which are more than 50 nm red-shifted compared with the λ_{max} of the corresponding azobenzene monomers **1**. This clearly reveals that PPE-based polymers have very extended conjugation along the main chain. The λ_{max} of polymers **5a**−**c** with five-membered heterocycles also located in the visible region (> 400 nm) in chloroform. Polymer **5b** has λ_{max} at the longest wavelength (469 nm) among the azobenzene-containing polymers we have synthesized.[12−14] In contrast, polymer **5d** with six-membered heterocycles exhibited the λ_{max} at the UV region (373 nm), indicating its low degree of main-chain conjugation. Both a strong absorption of the π−π* transition and a weak one due to the n−π* transition of **5d** can be seen in the UV (300−430 nm) and visible regions (430−550 nm), respectively, while only one broad absorption was observed for polymers **3b**−**d** and **5a**−**c**. This is probably due to the overlapping of the wide absorption of the main-chain chromophore with that of the n−π* transition of azobenzene units.

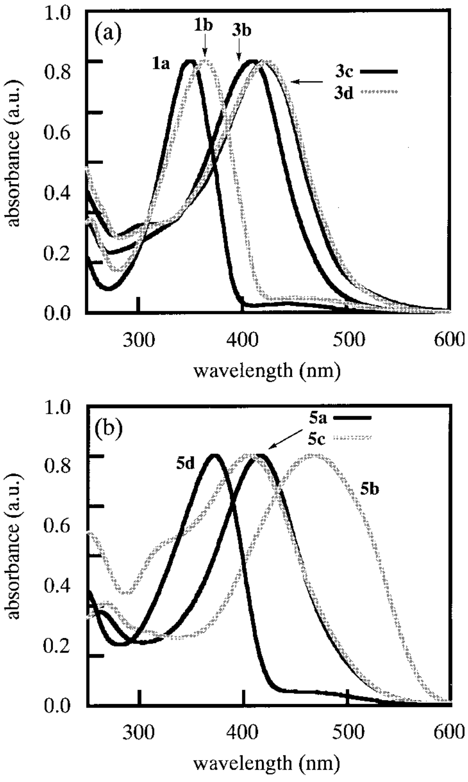


Figure 2. UV/vis absorption spectra of (a) **1a**, **1b**, **3b**−**d** and (b) **5a**−**d** in CHCl$_3$.

We found by the cyclic voltammetric analysis that the electrochemical reduction and oxidation of heteroaromatic-containing polymers **5a**−**d** take place reversibly in dichloromethane (CH$_2$Cl$_2$). These electrochemical properties were based on the reduction and oxidation of the conjugated π-electron system along the polymer backbone since monomer **1b** showed no redox peak in CH$_2$Cl$_2$. The electrochemical oxidations were achieved with thiophene (**5a**)- and furan-containing polymers (**5b**), and p-doping was observed at an anodic peak potential (E_{pa}) of 1.3 V (vs Ag/Ag$^+$). *N*-Methylpyrrole (**5c**)- and pyridine-containing polymers (**5d**) underwent the electrochemical reduction at a cathodic peak potential (E_{pc}) of −1.2 V (Table 2).

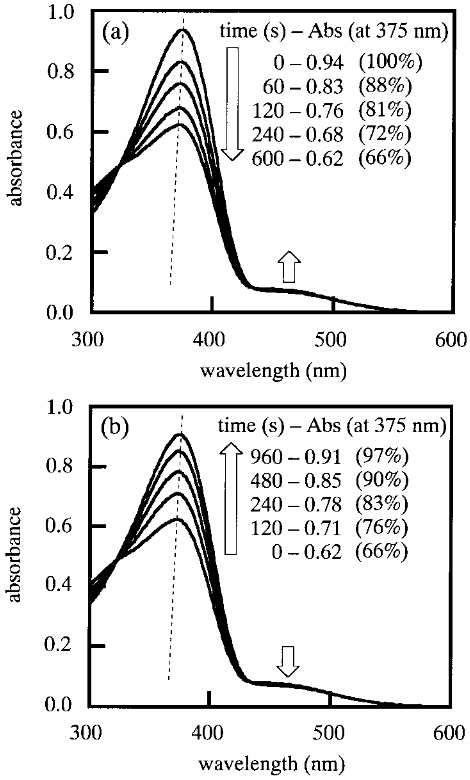


Figure 3. Variation of the UV/vis spectrum of **5d** in toluene at 20 °C upon (a) irradiation at 300 nm < λ_1 < 400 nm and (b) additional irradiation at λ_2 > 470 nm. The dotted lines explain the shift of the absorption maximum.

Cis–Trans Isomerizations. We have previously achieved the trans-to-cis photoisomerization of azobenzene unit in the main chain of the PPP-type polymers under the irradiation at 300 nm < λ_1 < 400 nm that roughly corresponds to the absorption range of *trans*-azobenzene units. Thus, UV irradiations at λ_1 were carried out for polymers **3b–d** and **5a–d** in toluene, and the isomerization of azobenzene units was monitored by the UV/vis absorption spectra. The variation of the UV/vis absorption spectrum of **5d** in toluene at 20 °C upon the irradiation at λ_1 is shown in Figure 3a.

As seen in Figure 3a, the strong absorption in the range 323–435 nm, attributed to the π–π* transition bands of the *trans*-azobenzene units (λ_{max} at 375 nm in toluene), rapidly decreased upon UV irradiation, while the weak absorption in the range 435–502 nm, attributed to the n–π* transition bands of the *cis*-azobenzene units, increased. The absorption at 375 nm decreased to 66% of the initial value after 600 s and leveled off. The isosbestic points were observed at 323, 435, and 502 nm. These spectral changes clearly indicate that the azobenzene units in the conjugated polymer backbone underwent the trans-to-cis isomerization. Assuming that all azobenzene units are in the stable trans form at the initial stage and that the absorption at 375 nm is derived only from the *trans*-azobenzene units, it can be estimated that **5d** has 66% trans and 34% cis contents at the photostationary state under the irradiation at λ_1 in toluene. UV irradiation was also carried out in THF and chloroform solutions, and similar spectral changes were observed under the irradiation at λ_1 in both solvents. The absorption at λ_{max} decreased and leveled off at 76% and 66% of the initial value in THF and chloroform, respectively.

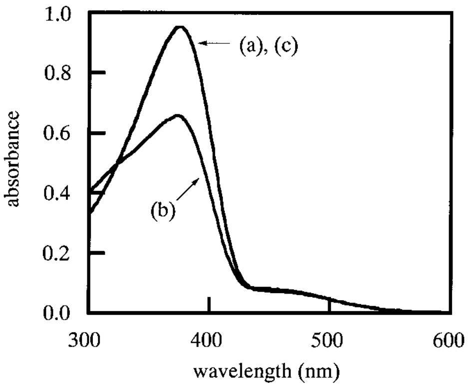


Figure 4. Variation of the UV/vis spectrum of **5d** in toluene (a) before and (b) after irradiation at 300 nm < λ_1 < 400 nm for 600 s and (c) after heating the UV-irradiated sample at 80 °C for 300 s in the dark.

To achieve the cis-to-trans photoisomerization, the visible-light irradiation at λ_2 > 470 nm was carried out after the irradiation at λ_1 for 600 s in toluene (Figure 3b). As a result, the absorption of 323–435 nm increased, and the absorption of 435–502 nm decreased due to the cis-to-trans photoisomerization. The isosbestic points were observed at 323, 435, and 502 nm. When the UV-irradiated sample was heated at 80 °C in the dark, similar thermally induced cis-to-trans isomerization occurred, and the spectrum was restored to that of the nonirradiated sample after 300 s (Figure 4). These results clearly show that pyridine-containing polymer **5d** do isomerize reversibly by the photo- or thermochemical procedures, and photodegradation is negligible.

On the other hand, no change in the spectra of polymers **3b–d** and **5a–c** was recognized under irradiation, which suggests that polymers having expanded main-chain conjugation do not undergo trans-to-cis photoisomerization of azobenzene units. This is probably because, as seen in Figure 2, the absorption of the n–π* transition (weak absorption around 450 nm) of azobenzene is completely overlapped with the π–π* transition which is largely red-shifted due to the extended main-chain conjugation. Therefore, photoirradiation around the absorption maximum causes no change of the equilibrium between the trans and cis forms. Our previous studies have shown that the photoisomerization was unsuccessful with PPV-based polymers having high degree of main-chain conjugation (λ_{max} > 420 nm).[14] On the other hand, the PPP-based polymers, which possess limited conjugation (λ_{max} < 380 nm), readily isomerized reversibly.[12,13] Thus, one can conclude that the degree of the main-chain conjugation is an important factor to achieve the photoisomerization of azobenzene units in the conjugated polymer backbone and that, for designing photoresponsive polymers, their λ_{max} should be located in the UV region.

As illustrated by dotted lines in Figure 3, the cis–trans isomerization was accompanied by the slight shift of λ_{max}, which can be explained in terms of the change of the main-chain conjugation length due to the isomerization of azobenzene. This suggests that the electrical properties based on the π-conjugation are controllable by the isomerization of azobenzene units in the main chain. To clarify this property change, cyclic voltammetric analyses were carried out, and the cyclic voltammograms of **5d** before and after the UV irradiation in CH_2Cl_2 solution are shown in Figure 5. An obvious

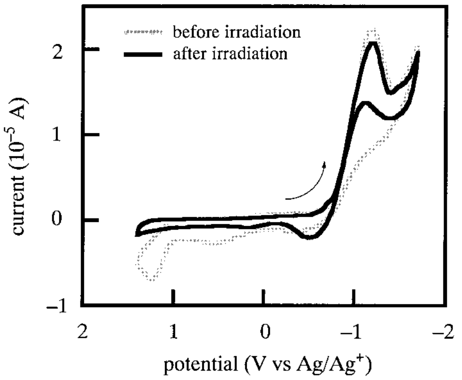


Figure 5. Cyclic voltammograms of **5d** in CH_2Cl_2 containing 0.1 M *n*-Bu_4NBF_4 before and after irradiation at 300 nm $< \lambda_1 <$ 400 nm for 600 s.

change, especially in the cathodic wave, was recognized after the trans-to-cis isomerization. That is, before isomerization, electrochemical n-doping and undoping take place at −1.1 and 1.2 V (vs Ag/Ag$^+$). On the other hand, the irradiated sample showed no distinct undoping peak around 1.2 V but was undoped around −0.6 V. This suggests that the n-doped state is unstabilized by the photoirraiation. This CV curve of UV-irradiated **5d** was again restored to that of the original one after the cis-to-trans reverse isomerization. These results mean that the manipulation of electrochemical properties of conjugated polymers by external stimuli is possible by incorporating stimuli-responsible conjugated molecules in the main chain.

Summary. We have prepared various PPE- and poly(phenylene)-based conjugated polymers having photoisomerizable azobenzene units in the main chain by the palladium-catalyzed couplings. According to the UV/vis absorption spectra, the main chains of PPE-based polymer **3b**−**d** and thiophene-, furan-, and *N*-methylpyrrole-containing polymers **5a**−**c** have widely extended π-conjugation length, while the pyridine-containing polymer **5d** has a low degree of main-chain conjugation. This conjugation length plays an important role for the cis−trans isomerization of azobenzene units in the conjugated polymer backbone. The pyridine-containing polymer **5d** underwent the photoinduced or thermally induced reversible cis−trans isomerizations, which was evidenced by the variation of the UV/vis absorption spectrum. The reversible electrochemical reduction and oxidation were achieved with heteroaromatic-containing polymers **5a**−**d**; p-doping was achieved with **5a** and **5b**, and n-doping takes place for **5c** and **5d**. The isomerization was accompanied by the change of the electrochemical properties. The stimuli responsibility of the present conjugated polymer would allow them to be applied to optical switching devices, molecular sensors, and so forth.

Experimental Section

General. GPC analyses were carried out using two Shodex KF 805L columns (eluent, THF) after calibration with standard polystyrenes. IR, UV/vis, and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a JASCO V-550 spectrometer, and a JEOL EX-400 spectrometer, respectively. Thermogravimetric analyses (TGA) were conducted in air on a Perkin-Elmer TGA7 thermal analyzer at a heating rate of 10 °C/min. DSC measurements were carried out using a Perkin-Elmer Pyris 1 differential scanning calorimeter. Cyclic voltammetric analyses were carried out in dichloromethane solution of tetrabutylammonium tetrafluoroborate (0.1 M) and polymer (50 mg/L) with a three-electrode system composed of Ag/Ag$^+$ electrode, Pt reference electrode, and Pt wire counter electrode, by using an ALS/chi ALS600A-n analyzer at a scanning rate of 0.1 V/s.

Photoirradiation. Photoirradiations were carried out at 20 °C with a 400 W high-pressure mercury lamp equipped with a power source (HB-400, Fuji Glass Work). The appropriate wavelengths were selected either with a Pyrex glass and a UV-D33S filter (Toshiba) for irradiation at 300 nm $< \lambda_1 <$ 400 nm or with a Y-47 filter (Toshiba) for irradiation at $\lambda_2 >$ 470 nm. The distance between a lamp and samples was 30 cm. Samples in solution were placed in a quartz cell. The photo- or thermochemical cis−trans isomerizations were monitored by the change of absorbance.

Materials. *N*,*N*-Dimethylformamide (DMF) was distilled over calcium hydride. 4,4′-Diiodoazobenzene (**1a**),[14] 2,2′,5,5′-tetrahexyl-4,4′-diiodoazobenzene (**1b**),[14] 1,4-diethynyl-2,5-dihexylbenznene (**2b**),[28] 2,5-bis(trimethylstannyl)thiophene (**4a**),[29] 2,5-bis(trimethylstannyl)furan (**4b**),[29] 2,5-bis(trimethylstannyl)pyrrole (**4c**),[30] and 2,5-bis(trimethylstannyl)pyridine (**4d**),[31] were synthesized according to the literature. 1,4-Diethynylbenzene (**2a**) was purchased from Tokyo Kasei, Co. and recrystallized from hexane.

Polymer 3a. A solution of $PdCl_2(PPh_3)_2$ (3.5 mg, 0.0050 mmol) and CuI (3.8 mg, 0.020 mmol) in DMF (8.0 mL) and triethylamine (2.0 mL) was added to a **1a** (217 mg, 0.50 mmol) and **2a** (63 mg, 0.50 mmol) placed in a 30 mL round-bottom flask charged with nitrogen. The mixture was stirred at 80 °C for 24 and then poured into 300 mL of methanol. The precipitate was filtered and washed with methanol to give **3a** (330 mg) as an orange powder in 100% yield. IR (KBr): 3019, 2955, 2924, 2855, 1599, 1559, 1483, 1464, 1458, 1377, 1266, 1179, 947, 905, 806, 723 cm^{-1}. Anal. Calcd for $(C_{22}H_{12}N_2)_n$: C, 86.82; H, 3.97; N, 9.20. Found: C, 69.28; H, 3.46; N, 6.63; I, 12.35.

Polymer 3b. Polymerization of **1a** with **2b** was performed similarly to the case of **3a** to give **3b** as an orange powder in 100% yield ^{1}H NMR ($CDCl_3$): δ 0.80−0.97 (CH_3), 1.10−1.89 ($ArCH_2CH_2CH_2CH_2CH_2$), 2.86−3.38 ($ArCH_2$), 7.06−7.20 ($C{\equiv}CArH$), 7.40−7.68 ($N{=}N{-}ArH$). IR (KBr): 3019, 2955, 2924, 2855, 1599, 1559, 1483, 1464, 1458, 1377, 1266, 1179, 947, 905, 806, 723 cm^{-1}. Anal. Calcd for $(C_{34}H_{36}N_2)_n$: C, 86.40; H, 7.68; N, 5.93. Found: C, 85.01; H, 7.95; N, 4.37; I, 2.07.

Polymer 3c. Polymerization of **1b** with **2a** was performed similarly to the case of **3a** to give **3c** as a dark-red powder in 100% yield. ^{1}H NMR ($CDCl_3$): δ 0.80−0.97 (CH_3), 1.10−1.89 ($ArCH_2CH_2CH_2CH_2CH_2$), 2.86−3.38 ($ArCH_2$), 7.06−7.20 ($C{\equiv}CArH$), 7.40−7.68 ($N{=}N{-}ArH$). IR (KBr): 3019, 2955, 2924, 2855, 1599, 1559, 1483, 1464, 1458, 1377, 1266, 1179, 947, 905, 806, 723 cm^{-1}. Anal. Calcd for $(C_{46}H_{60}N_2)_n$: C, 86.19; H, 9.43; N, 4.37. Found: C, 85.09; H, 9.47; N, 4.27; I, 0.78.

Polymer 3d. Polymerization of **1b** with **2b** was performed similarly to the case of **3a** to give **3d** as a red-orange powder in 100% yield. ^{1}H NMR ($CDCl_3$): δ 0.80−0.97 (CH_3), 1.10−1.89 ($ArCH_2CH_2CH_2CH_2CH_2$), 2.86−3.38 ($ArCH_2$), 7.06−7.20 ($C{\equiv}CArH$), 7.40−7.68 ($N{=}N{-}ArH$). IR (KBr): 3019, 2955, 2924, 2855, 1599, 1559, 1483, 1464, 1458, 1377, 1266, 1179, 947, 905, 806, 723 cm^{-1}. Anal. Calcd for $(C_{58}H_{84}N_2)_n$: C, 86.08; H, 10.46; N, 3.46. Found: C, 83.92; H, 10.46; N, 3.30; I, 1.24.

Polymer 5a. A solution of DMF (8.0 mL) containing **1b** (462 mg, 0.600 mmol), **4a** (251 mg, 0.612 mmol), and $PdCl_2(PPh_3)_2$ (8.4 mg, 0.012 mmol) in a 30 mL round-bottom flask charged with nitrogen was stirred at 110 °C for 48 h. The reaction mixture was poured into 300 mL of methanol. The precipitate was filtered and washed with methanol. After drying in a vacuum, the polymer was extracted with chloroform in a Soxhlet apparatus, and then the resulting extract was concentrated and reprecipitated into methanol to give **5a** (330 mg) as an orange powder in 92% yield. ^{1}H NMR ($CDCl_3$): δ 0.80−0.97 (CH_3), 1.10−1.89 ($ArCH_2CH_2CH_2CH_2CH_2$), 2.86−3.38 ($ArCH_2$), 7.06−7.20 (thienyl-*H*), 7.40−7.68 ($N{=}N{-}ArH$). IR (KBr): 3019, 2955, 2924, 2855, 1599, 1559, 1483, 1464, 1458, 1377, 1266, 1179, 947, 905, 806, 723 cm^{-1}. Anal. Calcd for $(C_{40}H_{58}N_2S)_n$: C, 80.21; H, 9.76; N, 4.68; S, 5.35. Found: C, 79.49; H, 9.81; N, 4.42; I, 0.53.

Polymer 5b. Polymerization of **1b** with **4b** was performed similarly to the case of **5a** to give **5b** as a red powder in 95% yield. ^{1}H NMR (CDCl$_3$): δ 0.80−1.01 (CH_3), 1.18−1.88 (ArCH$_2$$CH_2CH_2CH_2CH_2$), 2.88−3.35 (Ar$CH_2$), 6.71−6.84 (furil-$H$), 7.50−7.81 (N═N−Ar$H$). IR (KBr): 3019, 2955, 2924, 2872, 2855, 1601, 1559, 1489, 1466, 1377, 1283, 1208, 1184, 907, 779, 723 cm^{-1}. Anal. Calcd for $(C_{40}H_{58}N_2O)_n$: C, 82.42; H, 10.03; N, 4.81; O, 2.74. Found: C, 80.91; H, 10.29; N, 4.48; I, 1.01.

Polymer 5c. Polymerization of **1b** with **4c** was performed similarly to the case of **5a** to give **3c** as an orange powder in 87% yield. ^{1}H NMR (CDCl$_3$): δ 0.88−0.97 (CH_3), 1.15−1.83 (ArCH$_2$$CH_2CH_2CH_2CH_2$), 2.58−3.30 (Ar$CH_2$ and NCH_3), 6.19−6.30 (pyrrolyl-H), 7.20−7.66 (N═N−ArH). IR (KBr): 2955, 2926, 2855, 1603, 1466, 1458, 1439, 1377, 1254, 1165, 907, 723 cm^{-1}. Anal. Calcd for $(C_{41}H_{61}N_3)_n$: C, 82.63; H, 10.32; N, 7.05. Found: C, 81.21; H, 10.05; N, 6.72; I, 1.92.

Polymer 5d. Polymerization of **1b** with **4d** was performed similarly to the case of **5a** to give **5d** as a brown-orange powder in 58% yield. ^{1}H NMR (CDCl$_3$): δ 0.76−1.00 (CH_3), 1.10−1.86 (ArCH$_2$$CH_2CH_2CH_2CH_2$), 2.57−3.28 (Ar$CH_2$), 7.13−7.90 and 8.61−8.85 (ArH). IR (KBr): 3017, 2957, 2924, 2857, 1592, 1468, 1458, 1377, 1180, 905, 851, 723 cm^{-1}. Anal. Calcd for $(C_{41}H_{59}N_3)_n$: C, 82.91; H, 10.01; N, 7.07. Found: C, 78.14; H, 9.30; N, 6.69; I, 3.27.

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