# Synthesis of Poly(*p*-phenylene)-Based Photoresponsive Conjugated Polymers Having Azobenzene Units in the Main Chain

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*Received March 13, 2000; Revised Manuscript Received May 19, 2000*

ABSTRACT: Poly(*p*-phenylene)-based novel conjugated polymers having photoisomerizable azobenzene units in the main chain were prepared by the palladium-catalyzed Suzuki coupling of 1,3-propanediol diesters of 1,4-phenylenediboronic acids with 4,4′-diiodoazobenzenes, and the reversible cis−trans isomerizations of azobenzene units were achieved. Despite their stiff structures, the polymers are soluble in common organic solvents such as chloroform, toluene, and tetrahydrofuran if either or both of the monomers possess *n*-hexyl side chains on the aromatic rings. The resulting polymers possess high molecular weights ($M_n > 7 \times 10^3$) and are thermally stable ($T_0 >$ 350 °C) and fluorescent. The azobenzene units in the conjugated polymer backbone underwent the photochemical cis−trans reversible isomerizations in both tetrahydrofuran and toluene upon irradiation with UV light of appropriate wavelengths at 20 °C. The thermal cis-to-trans isomerization was also readily accomplished in toluene at 80 °C. Moreover, the solid-state photochemical trans-to-cis isomerization took place at 20 °C. These isomerization processes were accompanied by the change in the three-dimensional hydrodynamic volume of the polymer, which was evidenced by size exclusion chromatography.

## 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 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.[4a] 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 a number of drastic changes in properties such as dipole moment.[3]

Various photoresponsive polymers have been extensively studied to date.[4] The conformational changes of the polymers induced by the photopromoted or thermally promoted isomerization enable 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[5,6] or in the main chains,[7,8] with the motivation of producing the light-controlled 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 $\pi$-conjugated polymers.

Although many types of conjugated polymers have been synthesized,[9] little attention has been paid to the idea that azobenzene itself can be a part of $\pi$-conjugative building units.[8] Thus, it is of great interest to synthesize conjugated polymers having azobenzenes as conjugative units and to explore novel excellent functions based on the optical, electrical, and magnetic properties. The previous reports were limited to the preparation of poly(*p*-phenylene) (PPP),[8a,d] poly(phenyleneethynylene),[8b] poly(phenylenevinylene) (PPV)[8c] having azobenzenes in the main chains, and polyacetylenes[6] with azobenzenes in the side chains. Furthermore, the profile of the isomerization has not been discussed for the conjugated polymers having azobenzene groups in the main chains.

In a previous study, we have succeeded in the synthesis of novel PPV-based conjugated polymers bearing azobenzene functional groups in the main chain[8c] by using the Heck reaction.[11] One of those polymers showed a remarkable red-shifted absorption in the visible region ($\lambda_{max} >$ 450 nm) due to its expanded main-chain conjugation. Unfortunately, the photochemical isomerization of azobenzene in these PPV-based polymers was not effectively achieved. The following points seem responsible for this unsatisfactory result: (i) the enhanced stability of the ground state of trans azobenzene, based on the prolonged $\pi$-conjugation length of the backbone, and (ii) the photoinduced side reactions, e.g., cyclization to phenanthlyl rings of the carbon−carbon double bond in PPV. Thus, it is still a challenging and interesting subject to design and construct azobenzene-containing conjugated polymers that readily undergo photoisomerization process.

PPP[12−14] is also a typical conjugated polymer, and much effort has been made to synthesize soluble PPP derivatives because of the rigid rodlike main-chain structure. The $\lambda_{max}$ of PPPs generally remains in the region below 400 nm in solutions,[12] which means the reduced $\pi$-conjugation compared with that of PPV. Additionally, the absence of double bonds in the main

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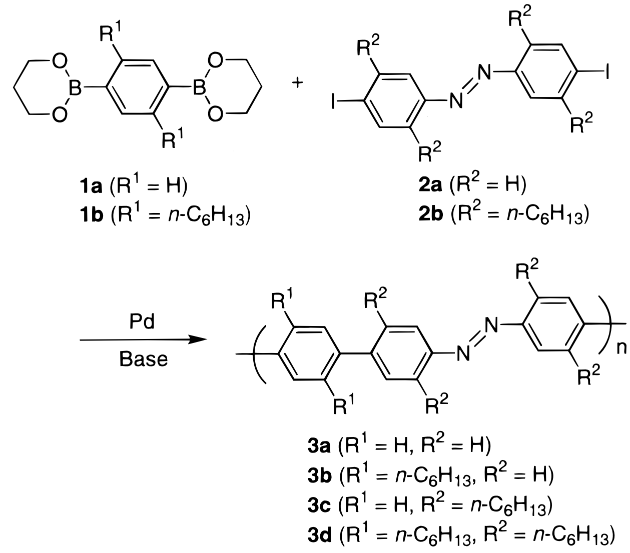
10.1021/ma0004559 CCC: $19.00

**Scheme 1**



chain excludes possible photoinduced side reactions observed in PPV. These facts give a prospect that the azobenzene-containing PPP functions as a photoresponsive $\pi$-conjugated polymer. Only one example was reported for the synthesis of azobenzene-containing PPP that was synthesized by the Ni(0)-catalyzed polymerization of 4,4′-dibromoazobenzene.[8a] However, detailed characterization was not performed. Our preliminary experiment also suggested that this synthetic method is not suitable for the production of a high molecular weight PPP from dihaloazobenzene with alkyl side chains. This is because of an avoidable side reaction, probably the reduction of the N═N bond, which is corroborated by the observation of the N−H stretching around 3400 $cm^{-1}$.

In the present paper, we report on the synthesis of novel PPP-based conjugated polymers having azobenzene units in the main chain by utilizing the Pd-catalyzed Suzuki coupling.[13,14] This route has proven to nicely provide high molecular weight polymers in excellent yields. The photoinduced cis−trans isomerizations of the formed polymers are also described. To our knowledge, this is the first example of the reversible isomerization about azobenzene units in the conjugated polymer backbone.

## Results and Discussion

**Polymerization.** Several kinds of PPPs have been synthesized by using the Suzuki coupling, and various polymerization conditions were examined for each PPP.[14a] To obtain polymers with high molecular weight in good yield, there are several important factors to be optimized, e.g., catalyst, solvent, base, and so on, which vary with individual monomers. Thus, one should establish the optimal coupling conditions in polymerizing novel monomers. In this study, the 1,3-propanediol diesters of 1,4-phenylenediboronic acids **1** and 4,4′-diiodoazobenzenes **2** were employed for the coupling reaction (Scheme 1), and polymerization conditions were examined because **2** had not been used as monomers in the Suzuki coupling.

Palladium complexes that catalyze the Suzuki coupling include $Pd(PPh_3)_4$,[14b] $PdCl_2(PPh_3)_2$ $PdCl_2(dppf)$[14c] (dppf = 1,1′-bis(diphenylphosphino)ferrocene), $Pd(dba)_2$, $Pd(OAc)_2$, etc. Palladium catalysts with phosphine ligands are generally used since they are thermally stable. $PdCl_2(dppf)$ is known to be more active as catalyst than $Pd(PPh_3)_4$ in many cases.[14a] Thus, we chose here $Pd(PPh_3)_4$ as a Pd(0) catalyst and $PdCl_2(dppf)$ as a Pd(II) catalyst.

We examined polymerization solvents as the first factor to be optimized. PPPs have been prepared by the Suzuki coupling in various solvents such as toluene, benzene, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMAc). In the present study, toluene and DMAc were employed in the coupling of **1b** with **2a**, the results of which are summarized in Table 1. Polymerizations were carried out at 110 °C for 48 h. The toluene/water system gave polymers, but their molecular weights were no more than a few thousand (runs 1, 2). In contrast, polymers with high molecular weights were obtained in high yield in a DMAc/water mixture (runs 3, 4). This suggests that, since the resulting polymer is soluble in toluene and insoluble in DMAc, it is not an important factor whether the polymerization solvent is a good solvent of the polymer or not. The polymerization in DMAc in the absence of water resulted in decreases in the yield and molecular weight of polymer (runs 5, 6). Thus, the results of runs 1−6 prove that the DMAc/water mixture is the most favorable for this coupling.

In general, the Suzuki coupling requires the assistance of bases during the catalytic cycle, and the kind of the base strongly affects the reaction rate. Especially, the addition of strong bases such as $Ba(OH)_2$, NaOH, and $K_3PO_4$ produces a remarkable accelerating effect on the coupling if the monomers tolerate the strong basic conditions.[13] Thus, we employed NaOH (runs 7, 8) instead of $K_2CO_3$ (runs 3, 4). Use of NaOH enhanced the polymer molecular weight with $Pd(PPh_3)_4$ as catalyst (run 7 vs 3) and resulted in quantitative polymer formation with $PdCl_2(dppf)$ (run 8 vs 4). These results indicate that $K_2CO_3$ is useful as a base in the coupling of **1** with **2** but that NaOH is more favorable for this reaction.

Another factor to be optimized is the palladium catalyst. The polymerization with $PdCl_2(dppf)$ was much faster than that with $Pd(PPh_3)_4$, as evidenced by the faster color change of the polymerization solution with $PdCl_2(dppf)$. However, no significant difference in the molecular weight and the yield was observed between these catalysts. The colors of the resulting polymers are basically orange, but that of $PdCl_2(dppf)$-based polymers was darker than that of the $Pd(PPh_3)_4$-based polymers. This darker color is probably due to either the unremovable catalyst residues or the structural defects generated by side reactions during polymerization.

In summary, the coupling of **1b** with **2a** proceeded well in the presence of both $Pd(PPh_3)_4$ and aqueous NaOH in DMAc at 110 °C to give polymer **3b** with high molecular weight in high yield (run 7). These conditions were applied to other monomer combinations, affording polymers **3a**, **3c**, and **3d** in good yields as orange powders (runs 9−11). The $^1H$ NMR spectra in $CDCl_3$ agreed with their expected structures.

**Polymer Properties.** Optical and thermal properties of **3** are summarized in Table 2. Whereas **3a** was completely insoluble in any organic solvent due to its stiff structure, **3b**−**d** with alkyl side chains were soluble in common organic solvents such as chloroform, toluene, and THF. The wavelengths of absorption maximum ($\lambda_{max}$) in the UV/vis spectra of **3b**−**d** in chloroform were

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

| | monomer | | | | | polymer | | |
|---|---|---|---|---|---|---|---|---|
| run | **1** | **2** | catalyst | solvent[b] | base | **3** | yield (%)[c] | $M_n$ ($M_w/M_n$)[d] |
| 1 | **1b** | **2a** | $Pd(PPh_3)_4$ | toluene/$H_2O$ | $K_2CO_3$ | | 62 | 1660 (1.4) |
| 2 | **1b** | **2a** | $PdCl_2(dppf)$ | toluene/$H_2O$ | $K_2CO_3$ | | 49 | 1550 (1.4) |
| 3 | **1b** | **2a** | $Pd(PPh_3)_4$ | DMAc/$H_2O$ | $K_2CO_3$ | | 100 | 6780 (1.7) |
| 4 | **1b** | **2a** | $PdCl_2(dppf)$ | DMAc/$H_2O$ | $K_2CO_3$ | | 88 | 9700 (2.0) |
| 5 | **1b** | **2a** | $Pd(PPh_3)_4$ | DMAc | $K_2CO_3$ | | 72 | 2890 (1.7) |
| 6 | **1b** | **2a** | $PdCl_2(dppf)$ | DMAc | $K_2CO_3$ | | 88 | 3410 (1.9) |
| 7 | **1b** | **2a** | $Pd(PPh_3)_4$ | DMAc/$H_2O$ | NaOH | **3b** | 100 | 7700 (1.8) |
| 8 | **1b** | **2a** | $PdCl_2(dppf)$ | DMAc/$H_2O$ | NaOH | | 100 | 8470 (1.8) |
| 9 | **1b** | **2b** | $Pd(PPh_3)_4$ | DMAc/$H_2O$ | NaOH | **3d** | 97 | 8540 (2.0) |
| 10 | **1a** | **2b** | $Pd(PPh_3)_4$ | DMAc/$H_2O$ | NaOH | **3c** | 99 | 7390 (1.6) |
| 11 | **1a** | **2a** | $Pd(PPh_3)_4$ | DMAc/$H_2O$ | NaOH | **3a** | 89 | insoluble |

[a] $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 80$ mM, [Pd] = 2.4 mM, $[\text{base}]_0/[\mathbf{1}]_0 = 4$, 110 °C, 48 h. [b] The volume ratio of toluene or DMAc to water in the mixed solvents was 25:4. [c] Methanol-insoluble part. [d] THF-soluble part. Estimated by GPC (THF, PSt).

**Table 2. Optical and Thermal Properties of 3**

| | | | $T_0$ (°C)[c] | |
|---|---|---|---|---|
| polymer | $\lambda_{max}$ (nm)[a] | $\lambda_{emi}$ (nm)[b] | in air | in $N_2$ |
| **3a** | | | 384 | 432 |
| **3b** | 368 | 413, 490 | 383 | 362 |
| **3c** | 369 | 413, 436, 494 | 364 | 357 |
| **3d** | 378 | 424, 499 | 362 | 349 |

[a] In $CHCl_3$. [b] The peak emission wavelength in $CHCl_3$ excited at $\lambda_{max}$. [c] The onset temparature of decomposition.

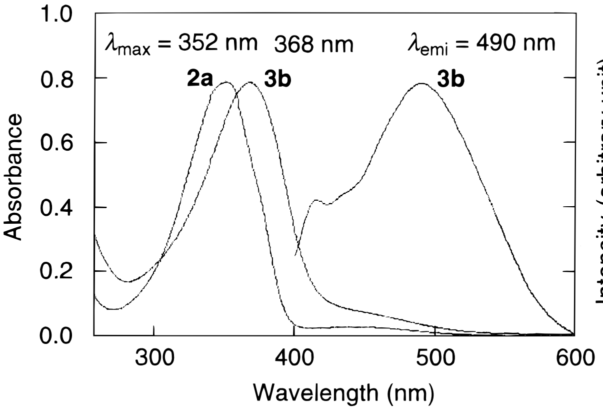


**Figure 1.** UV/vis spectra of **2a** and **3b** in $CHCl_3$ and emission spectrum of **3b** in $CHCl_3$ (excited at 368 nm).

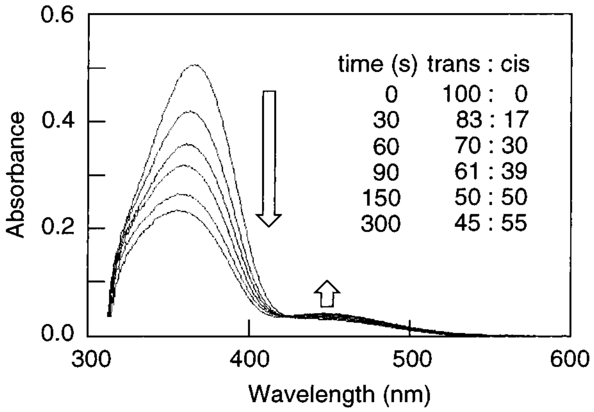


**Figure 2.** Variation of the UV/vis spectrum of **3b** in toluene at 20 °C upon irradiation at 300 nm < $\lambda_1$ < 400 nm.

around 368–378 nm. These absorptions are characteristic of the $\pi-\pi^*$ transition of the *trans*-azobenzenes and obviously red-shifted compared to those of the corresponding monomers **2**. For example, the $\lambda_{max}$ of **3b** was red-shifted by 16 nm against **2a** (Figure 1). This suggests that these polymers that contain azobenzene units in the main chain generate moderately long $\pi$-conjugation systems. In other words, the azobenzene units behave as conjugative building units in the main chain. When polymers **3b**–**d** were excited at their $\lambda_{max}$ in chloroform solution, a few weak emission peaks were detected above 410 nm, among which the major peaks were around 490–499 nm. Because azobenzene itself is known to show no emission,[4a] this emission peaks are probably derived from the terphenyl units in the main chain.

All of the polymers **3** were thermally highly stable in both air and nitrogen, and their onset temperatures of decomposition ($T_0$) were higher than ca. 350 °C. The $T_0$ value in air decreased by 20 °C when the polymer possessed the alkyl side chains on the azoaromatic rings. Polymers are normally more stable in nitrogen than in air, and the $T_0$ value of **3a** in nitrogen was 48 °C higher than in air. In the cases of **3b**–**d**, however, the $T_0$ values in air and nitrogen were similar to each other.

**Cis–Trans Isomerization.** Polymer **3b** was used for the investigation of the isomerization of azobenzene in the main chain. The photoirradiations in solution were carried out both in toluene and in THF, and the temperature was kept at 20 °C to inhibit the thermal cis-to-trans isomerization. In both solutions, **3b** possessed a strong absorption in the region from 300 to 400 nm ($\lambda_{max}$ = 365 nm) attributable to the $\pi-\pi^*$ transition bands of the *trans*-azobenzene units. Thus, the irradiation at 300 nm < $\lambda_1$ < 400 nm should be effective in trans-to-cis photoisomerization.

The variation of the UV/vis absorption spectrum in toluene upon irradiation at $\lambda_1$ is shown in Figure 2. Under irradiation at $\lambda_1$, the strong absorption band due to a $\pi-\pi^*$ transition at 365 nm rapidly decreased, while the weak absorption band due to n–$\pi^*$ transition around 450 nm increased. The absorption at 365 nm decreased to 45% of the initial value as soon as 300 s and leveled off. Assuming that the azobenzene units were all in the stable trans form at the initial stage, the isomerized **3b** has 45% trans and 55% cis contents. Simultaneously, the absorption maximum slightly shifted to the shorter wavelength, which can be explained in terms of a decrease of conjugation with increasing cis content. This suggests that the electrical properties based on the $\pi$-conjugation are controllable by the isomerization of azobenzene in the conjugated polymer backbone.

As stated above, the absorption around 450 nm increased in the trans-to-cis isomerization. This implies that the irradiation at $\lambda_2$ > 450 nm will effectively cause the reverse isomerization. Thus, photoinduced cis-to-

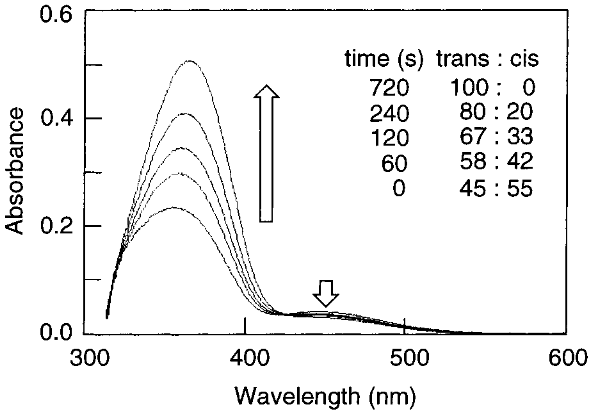


**Figure 3.** Variation of the UV/vis spectrum of **3b** in toluene at 20 °C upon irradiation at $\lambda_2 > 450$ nm after irradiation at 300 nm $< \lambda_1 <$ 400 nm for 300 s.

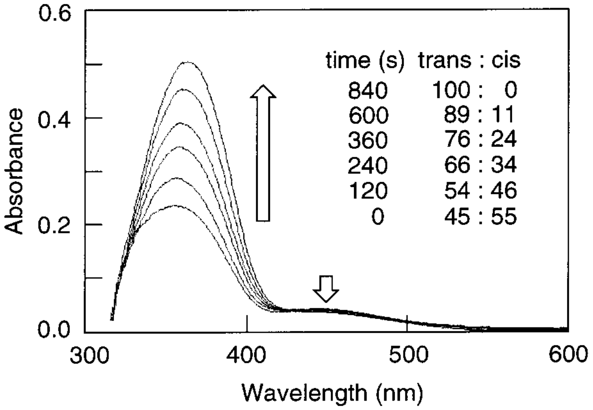


**Figure 4.** Variation of the UV/vis spectrum of **3b** in toluene at 80 °C in the dark after irradiation at 300 nm $< \lambda_1 <$ 400 nm for 300 s.

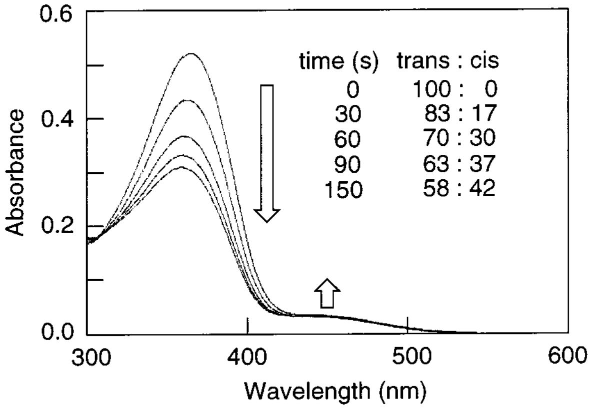


**Figure 5.** Variation of the UV/vis spectrum of **3b** in THF at 20 °C upon irradiation at 300 nm $< \lambda_1 <$ 400 nm.

trans isomerization was examined by irradiation at $\lambda_2$ of the sample with a 55% cis content (Figure 3). As a result, the absorption at 365 nm increased with irradiation at $\lambda_2$, and the spectrum was restored to that of the initial nonirradiated sample after irradiation for 720 s. This sample (cis content 55%) was also subjected to the thermal cis-to-trans isomerization at 80 °C in the dark. As illustrated in Figure 4, the spectrum was again restored to that of the nonirradiated sample after 840 s. These results manifest that the azobenzene units in the conjugated polymer backbone do isomerize reversibly by the photo- or thermochemical procedures.

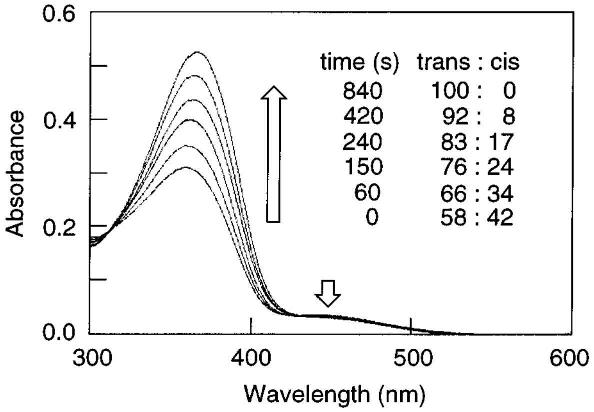


**Figure 6.** Variation of the UV/vis spectrum of **3b** in THF at 20 °C upon irradiation at $\lambda_2 > 450$ nm after irradiation at 300 nm $< \lambda_1 <$ 400 nm for 150 s.

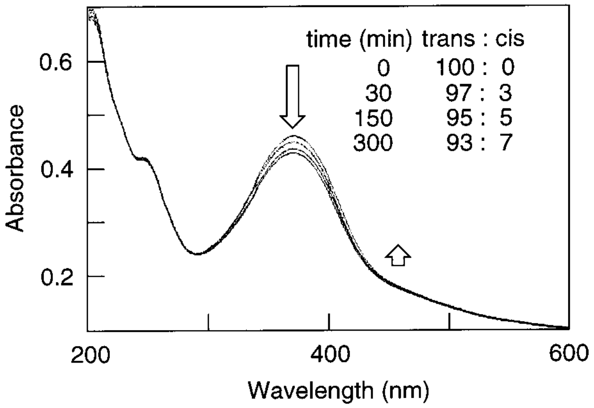


**Figure 7.** Variation of the UV/vis spectrum of **3b** in film at 20 °C upon irradiation at 300 nm $< \lambda_1 <$ 400 nm.

The photoinduced reversible cis–trans isomerizations were next conducted in THF (Figures 5 and 6). Upon irradiation at $\lambda_1$ for 150 s, **3b** isomerized, whose cis content reached 42%, and then completely recovered the all-trans form by irradiation at $\lambda_2$ for 840 s. Both trans-to-cis and cis-to-trans isomerizations were somewhat slower in THF than in toluene (see Figures 2, 3, 5, and 6). This can be explained in terms of the mobility of the stiff polymer chain in solutions and the better solubility of **3b** in toluene than in THF. The trans-to-cis isomerization was also achieved in the solid state (Figure 7), although slugguish as expected; e.g., 7% of the azobenzene units isomerized after 300 min.

The trans-to-cis isomerization of azobenzene in the PPP backbone should be accompanied by a change of hydrodynamic volume in solution. Such a change was observed by size exclusion chromatography (SEC) with other polymers.[7e] Figure 8 shows the chromatograms of nonirradiated and irradiated **3b** in THF. The SEC curve clearly shifted toward a low molecular weight region after irradiation at $\lambda_1$, and then the original SEC curve was recovered after irradiation at $\lambda_2$, which manifests that the isomerization is reversible and that photodegradation of **3b** is negligible.[15] The relative number-average molecular weight was reduced from 7700 to 4290 by isomerization to a 40% cis content. This result supports the idea that the cis–trans isomerizations lead to a change in the three-dimensional hydrodynamic volume.

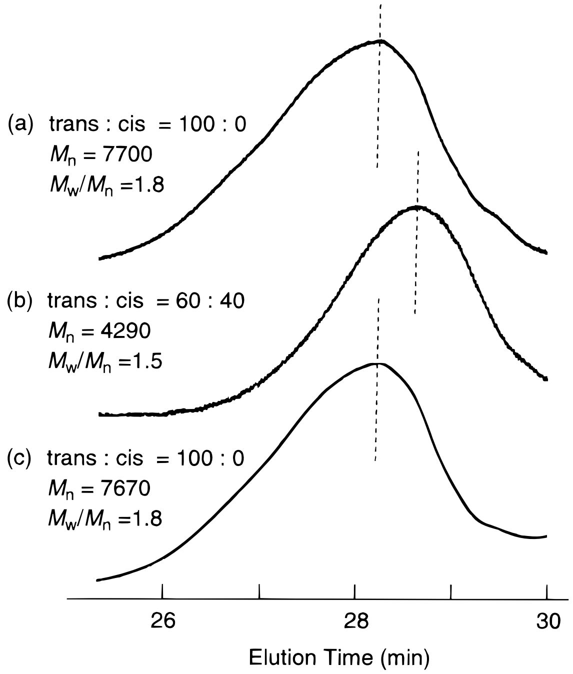


**Figure 8.** Size exclusion chromatograms of **3b** (a) before and (b) after irradiation at 300 nm < $\lambda_1$ < 400 nm and (c) after additional irradiation at $\lambda_2$ > 450 nm. (Samples b and c were prepared by irradiation in THF at 20 °C for 120 and 900 s, respectively; measured in THF at 40 °C.)

## Conclusions

Novel PPP-based conjugated polymers having photoisomerizable azobenzene units in the main chain were successfully synthesized by using the palladium-catalyzed Suzuki coupling reaction. The produced polymer **3b** underwent the photoinduced or thermally induced reversible cis−trans isomerizations of azobenzenes in the conjugated polymer backbone, which was monitored by the UV/vis absorption spectroscopy. The isomerizations occurred both in solution and in film. The trans-to-cis isomerization proceeded faster than the reverse isomerization, and the polymer isomerized faster in toluene than in THF. Similar photopromoted and thermally promoted cis−trans isomerizations took place in the soluble polymers, **3c** and **3d**, as well. This is the first example of the reversible isomerization of the azobenzene unit in the conjugated polymer backbone. The stimuli responsibility of the present conjugated polymers would allow them to be applied to molecular sensors, switches, and so forth.

## Experimental Section

**General.** SEC analyses were carried out using two Shodex KF 805L columns (eluent, THF) after calibration with standard polystyrenes. Melting points were measured with a Yanaco micro melting point apparatus. IR, UV/vis, NMR, and emission spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, a JEOL EX-400 spectrometer, and a JASCO FP-750 spectrophotometer, respectively. Thermogravimetric analyses (TGA) were conducted in air or nitrogen on a Perkin-Elmer TGA7 thermal analyzer at a heating rate of 10 °C/min. Ether, THF, and toluene were dried over sodium/benzophenone and distilled under nitrogen. DMAc was dried over CaO and KOH and distilled at reduced pressure. **1a** was prepared by esterification of 1,4-phenylenediboronic acid according to the literature.[14a] **1b**,[14a,16a] **2a**,[16b] **2b**,[8c] and $PdCl_2(dppf)$[16c] were prepared according to the literature. $Pd(PPh_3)_4$ and 1,4-phenylenediboronic acid were purchased from Wako Pure Chemicals Co., Jpn., and Tokyo Kasei Co., Jpn., respectively.

**Photoirradiation.** UV irradiations 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-45 filter (Toshiba) for irradiation at $\lambda_2$ > 450 nm. The distance between a lamp and samples was 30 cm. Samples in toluene or THF solution were placed in a quartz cell equipped with a glass cap. A chloroform solution of polymer was cast onto a quartz plate to give a film sample for photoisomerization. The photo- or thermochemical cis−trans isomerizations were monitored by the change of absorbance.

**Polymer 3a. 3a** was prepared by the same procedure as **3b** described below. IR (KBr): 3040, 1597, 1483, 1401, 1229, 1159, 1109, 1003, 864, 824, 768, 731, 689, 571, 532 $cm^{-1}$. Anal. Calcd for $(C_{18}H_{12}N_2)_n$: C, 84.35; H, 4.72; N, 10.93. Found: C, 75.77; H, 4.54; N, 9.36; I, 7.32.

**Polymer 3b.** A sealable 10 mL ampule was charged with **1b** (166 mg, 0.40 mmol), **2a** (174 mg, 0.40 mmol), $Pd(PPh_3)_4$ (13.9 mg, 0.012 mmol), NaOH (64 mg, 1.6 mmol), DMAc (5.0 mL), water (0.80 mL), and a stirring bar. The mixture was degassed twice by the freeze−pump−thaw procedure, and then the ampule was sealed off with a gas burner under vacuum, followed by stirring at 110 °C for 48 h. Then the ampule was opened, and the reaction mixture was poured into 100 mL of methanol. The precipitated solids (crude polymer product) were filtrated and washed with water/methanol (1:1) and then with methanol. After drying in a vacuum, the polymer was redissolved in toluene and reprecipitated into methanol to give **3b** as orange powder in 100% yield. IR (KBr): 2955, 2926, 2857, 1599, 1483, 1223, 1156, 1011, 855, 573 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.80−0.96 (6H, $CH_3$), 1.13−1.37 (12H, $CH_3CH_2CH_2CH_2$), 1.47−1.65 (4H, $ArCH_2CH_2$), 2.53−2.78 (4H, $ArCH_2$), 7.20−7.32 (2H, Ar*H*), 7.49−7.64 and 7.98−8.13 (4H and 4H, N−Ar′*H*). Anal. Calcd for $(C_{36}H_{36}N_2)_n$: C, 84.86; H, 8.55; N, 6.60. Found: C,82.02; H, 8.44; N, 5.91; I, 0.55.

**Polymer 3c. 3c** was prepared by the same procedure as for **3b**. IR (KBr): 2957, 2926, 2857, 1603, 1480, 1458, 1377, 1183, 986, 905, 849, 536 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.77−0.96 (12H, $CH_3$), 1.11−1.90 (32H, $CH_3CH_2CH_2CH_2CH_2$), 2.57−2.80 and 3.05−3.33 (4H and 4H, N−Ar′$CH_2$), 7.21−7.75 (8H, Ar*H* and N−Ar′*H*). Anal. Calcd for $(C_{42}H_{60}N_2)_n$: C, 85.08; H, 10.20; N, 4.72. Found: C,82.31; H, 9.76; N, 4.52; I, 1.98.

**Polymer 3d. 3d** was prepared by the same procedure as for **3b**. IR (KBr): 2957, 2926, 2855, 1603, 1480, 1466, 1458, 1379, 1179, 905, 723 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.77−0.98 (18H, CH3), 1.16−1.90 (48H, $CH_3CH_2CH_2CH_2CH_2$), 2.24−2.58 (8H, Ar$CH_2$ and N−Ar′$CH_2$), 3.00−3.42 (4H, N−Ar′ $CH_2$), 7.04−7.68 (6H, Ar*H* and N−Ar′*H*). Anal. Calcd for $(C_{54}H_{84}N_2)_n$: C, 85.20; H, 11.12; N, 3.68. Found: C, 84.18; H, 10.78; N, 3.37; I, 0.81.

**Acknowledgment.** This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture and Sports, Japan.

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MA0004559