

Synthesis and Properties of Novel Metal-Containing Polymers Having Azobenzene Units in the Main Chain

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Poly(phenyleneethynylene)s containing azobenzene and platinum units in the main chain were synthesized by the polycondensation of diethynylazobenzenes with dichlorobis(tributylphosphine)platinum in diethylamine. The corresponding polymers with number-average molecular weights ranging from 7,000 to 108,000 were obtained in 75–97% yields. The polymers were soluble in organic solvents such as chloroform and toluene. The polymers substituted with hexyl groups on the aromatic rings were soluble more than the unsubstituted ones. Some of them underwent *trans*-to-*cis* photoisomerization. In a similar way, polymers containing ferrocene units were also synthesized in 61–92% yields.

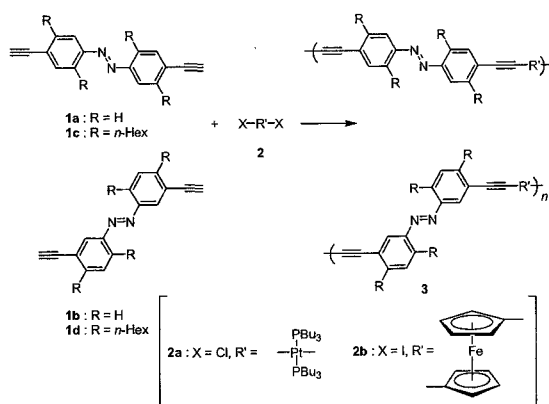
Key words: azobenzene, photoisomerization, metal-containing conjugated polymer

1. INTRODUCTION

Azobenzene undergoes isomerization reversibly by photo-irradiation. *Trans*-azobenzene isomer has an intense absorption around 320 nm due to π - π^* transition, and *cis* isomer has a weak absorption around 430 nm due to n - π^* transition.¹ Ultraviolet (UV)-irradiation isomerizes *trans*-isomer to *cis*-one, and visible light-irradiation does *cis*-one to *trans*-one. The *cis*-to-*trans* isomerization also takes place thermally due to the low activation energy. The isomerization takes place efficiently without accompanying emission.² Many researches concerning azobenzene have been done to utilize it as digital storages, photo-switches, and holographic materials. Azobenzene-containing polymers are widely studied as photo-responsive materials, which include a dendrimer possessing an azobenzene core.³ It isomerizes even by infrared ray at 1597 cm^{-1} , which corresponds to the stretching vibration of the aromatic rings of the shell. Our previous study has revealed that hydrodynamic volume of azobenzene in a solution changes as the isomerization occurs.⁴ We have also focused attention on metal-containing polymers, because they exhibit interesting electrical and optical properties. For example, strong spin-orbit coupling associated with heavy metals enables significant mixing of singlet and triplet states, which makes the spin-forbidden emission (phosphorescence) from triplet excited states partially allowed.⁵ Not being a polymer, azoferrocene isomerizes not only by irradiation at π - π^* transition described above but also by irradiation at 546 nm, corresponding to metal ligand charge transfer from the *d*-orbital of Fe(II) to the π -orbital of Cp-N=N-Cp.⁶ Further, the quantum yield of photoisomerization is ten times higher than that of the irradiation to π - π^* transition. If we incorporate azobenzene and metal in polymers, we may obtain novel materials which show interesting properties based on the synergistic effect of them. This article deals with

synthesis of metal-containing conjugated polymers having azobenzene units in the main chain by the polycondensation of diethynylazobenzenes (1a–d) with dichlorobis(tributylphosphine)platinum (2a) and diiodoferrocene (2b) (Scheme 1).

Scheme 1



2. RESULTS AND DISCUSSION

2.1 Polycondensation

The results of the polycondensation are summarized in Table I. The polycondensation of diethynylazobenzenes with the Pt complex was carried out using CuI as a catalyst in Et_2NH at the solvent-refluxing temperature for 24 h. The polycondensation with diiodoferrocene was conducted using CuI and $\text{Pd}(\text{PPh}_3)_4$ as catalysts in *i*-Pr₂NH at 70 °C for 96 h. In run 1, the polycondensation proceeded heterogeneously due to poor solubility of the ethynylbenzene monomer 1a having azo group at *para*-position. As the result, the number-average molecular weight (M_n) of the obtained polymer was as

low as 7,000. On the other hand, the monomer **1b** having azo group at *meta*-position to the ethynyl group, and the monomers **1c** and **1d** having hexyl group afforded solvent-soluble polymers with relatively high M_n (20,200–108,000) (runs 3, 5, 6). In the polycondensation of Fe-containing monomer **2b** with non-hexylated monomers **1a** and **1b**, the M_n of the formed polymers was very low ($< 1,000$, runs 2 and 4). Meanwhile, the M_n of the polymer obtained by the polycondensation of **2b** with hexylated monomer **1d** reached 3,200 (run 7). This difference was presumably resulted by the same reason in the case of Pt-containing polymers.

The structures of these polymers were confirmed by IR and ^1H NMR spectroscopies. The polymers exhibited no peak assignable to $\text{C}\equiv\text{CH}$ stretching vibration around $3,200\text{ cm}^{-1}$ and no signal assignable to $\text{C}\equiv\text{CH}$ around 3.2 ppm in the IR and ^1H NMR spectra, respectively.

Table 1 Polycondensation of **1** with **2**^a

run	1	2	polymer	yield ^b (%)	M_n^c	M_w/M_n^c
1	1a	2a	3aa	96	7,000	1.5
2	1a	2b	3ab	92	800 ^d	1.2
3	1b	2a	3ba	75	20,200	2.2
4	1b	2b	3bb	61	900 ^d	1.8
5	1c	2a	3ca	97	108,000	4.7
6	1d	2a	3da	80	20,400	2.4
7	1d	2b	3db	92 ^e	3,200	1.7

^a With **2a**: $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 50\text{ mM}$, $[\text{CuI}] = 1\text{ mM}$ in Et_2NH with refluxing for 24 h. With **2b**: $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 50\text{ mM}$, $[\text{CuI}] = [\text{Pd}(\text{PPh}_3)_4] = 2\text{ mM}$ in $i\text{-Pr}_2\text{NH}$ at $70\text{ }^\circ\text{C}$ for 96 h. ^b Acetone-insoluble part. ^c Estimated by GPC eluted by CHCl_3 , polystyrene calibration. ^d The polymer was mostly insoluble in CHCl_3 . ^e Isolated by preparative HPLC.

2.2 Polymer properties

All the Pt-containing polymers were soluble in toluene, CHCl_3 , CH_2Cl_2 , THF, while insoluble in acetone and methanol. The Fe-containing polymers **3ab** and **3bb** were hardly soluble in CHCl_3 , and insoluble in acetone, methanol, DMSO. The polymer **3db** having hexyl groups was soluble in toluene and CHCl_3 , but insoluble in methanol and acetone.

Thermogravimetric analysis (TGA) of the polymers indicated that they were thermally stable in air. The weight loss-beginning temperatures of **3aa**, **3ba**, **3ca** and **3da** were 300, 270, 290, and $285\text{ }^\circ\text{C}$, respectively.

Fig. 1 depicts the UV-vis spectra of the polymers **3aa** and **3ca**. The monomer **1a** exhibited a sharp absorption peak at 350 nm assignable to $\pi\text{-}\pi^*$ transition of *trans* azobenzene, while the polymers **3aa** and **3ca** exhibited broad absorption peaks at 446 and 460 nm, respectively. Compared to the monomer, the absorption peaks of these polymers were red-shifted about in 100 nm. This fact indicates that the conjugation length of the polymers extended along the main chain. The absorption peaks of **3ba** and **3da** were also red-shifted from those of the monomers **1b** and **1d**, but the degrees were small. It can be considered that the conjugation does not so

extend, presumably due to the *meta* linkage of the polymer main chain.

2.3 *Cis-trans* photo-isomerization

The polymers **3aa** and **3ca** with *para*-linkage did not show any spectroscopic change upon UV and visible light irradiation. Namely, no isomerization of azobenzene moiety of the polymers took place. This may be responsible to overlap of the $\pi\text{-}\pi^*$ and the $n\text{-}\pi^*$ transitions due to long conjugation. Consequently, it may be difficult to irradiate the $\pi\text{-}\pi^*$ transition of the *trans* azobenzene selectively.

On the other hand, when the polymer **3ba** with *meta*-linkage was irradiated by UV light at $300\text{ nm} < \lambda < 400\text{ nm}$ in CHCl_3 , the intense of absorption at 330 nm decreased by 9% (Fig. 2). When this sample was further irradiated by visible light at $400\text{ nm} < \lambda < 500\text{ nm}$, the intense of absorption at 330 nm increased (Fig. 3). An isosbestic point was observed at 420 nm during these processes. It can be concluded that the *trans* azobenzene moiety of the polymer main chain partly isomerized to *cis* form by UV-irradiation, and re-isomerized to *trans* form by visible light-irradiation. It is proved that the efficiency of photo-isomerization is low but reversible isomerization of azobenzene moieties occurs. The difference of isomerization behavior between the polymers with *para*- and *meta*-linkages may be caused by the difference in the conjugated lengths. The latter polymer has shorter conjugated length than that of the former, and the degree of overlap of $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions is small. Another *meta*-substituted polymer **3da** slightly isomerized from *trans* to *cis* form by UV-irradiation, but the absorption did not recover by additional visible light-irradiation.

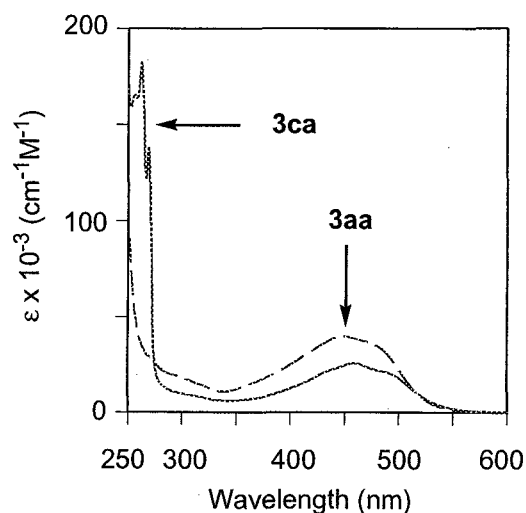


Fig. 1 UV-vis spectra of **3aa** and **3ca** measured in CHCl_3 (0.004 mM).

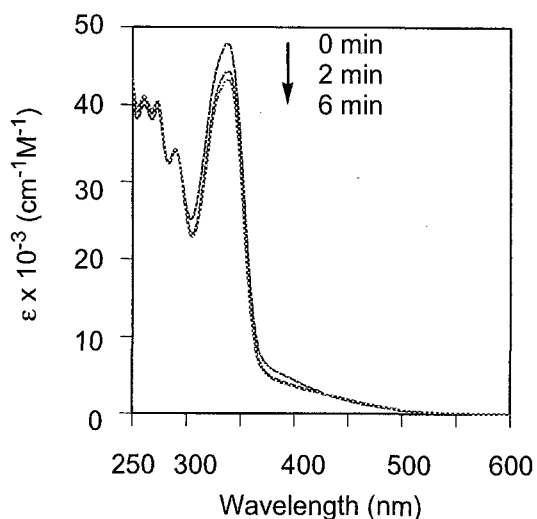


Fig. 2 Variation of the UV-vis spectra of **3ba** measured in CHCl_3 (0.025 mM) upon irradiation at $300 < \lambda < 400$ nm.

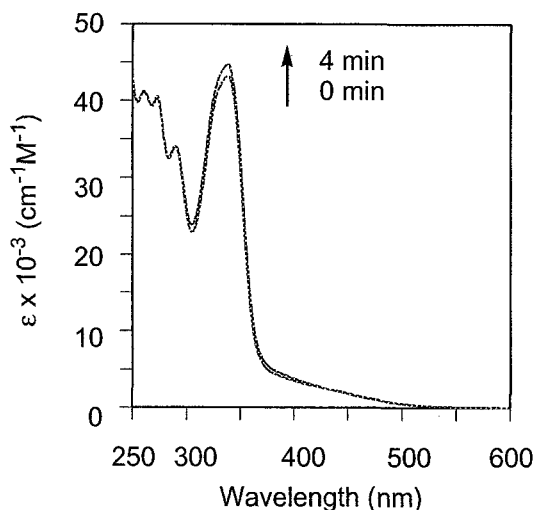


Fig. 3 Variation of the UV-vis spectra of **3ba** measured in CHCl_3 (0.025 mM) upon irradiation at $400 < \lambda < 500$ nm (after irradiation at $300 < \lambda < 400$ nm for 10 min).

3. EXPERIMENTAL

3.1 Measurements.

^1H NMR (400 MHz), IR, and UV-vis spectra were recorded on a JOEL EX-400 spectrometer, a Shimadzu FTIR-8100 spectrophotometer, and a Shimadzu UV-2200 spectrophotometer, respectively. Melting points were measured by a Yanaco micro melting point apparatus. The molecular weight of polymers were determined by GPC on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806) using CHCl_3 as an eluent, calibrated by polystyrene standards. TGA was conducted on a Perkin-Elmer TGA7 thermal analyzer at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in air.

Elemental analysis was carried out at the Kyoto University Elemental Analysis Center.

3.2 Reagents.

Unless otherwise stated, reagents were commercially obtained and used without purification. Bis(3-iodophenyl)diazene,⁷ bis(3-iodo-4,6-dihexylphenyl)diazene,⁸ bis(4-iodophenyl)diazene,⁷ bis(4-iodo-2,5-dihexylphenyl)diazene,⁸ dichloro bis(tributylphosphine)platinum(II) (**2a**),⁹ and 1,1'-diiodoferrocene (**2b**)¹⁰ were synthesized according to the literature method.

3.3 Monomer synthesis

Bis(3-ethynylphenyl)diazene (**1b**)

A solution of bis(3-iodophenyl)diazene (5 g, 11.5 mmol) in *i*-Pr₂NH (250 ml) was added trimethylsilylacetylene (7.3 ml, 52.7 mmol), CuI (30 mg 0.16 mmol) and PdCl₂(PPh₃)₂ (65.0 mg, 0.093 mmol), then stirred with refluxing for 3 h under dry nitrogen. After evaporation of *i*-Pr₂NH, the residual mixture was extracted by Et₂O. The organic layer was washed with water, and dried over MgSO₄. It was filtrated and concentrated by rotary evaporation. To a solution of the crude product (4.46 g) in THF (50 ml) and MeOH (17 ml) was added 1 M solution of tetrabutylammonium fluoride in THF (40 ml). The resulting mixture was stirred at $0 \text{ }^\circ\text{C}$ for 40 min. Water (100 ml) was added to the mixture, and it was extracted by Et₂O. The organic layer was dried over MgSO₄, filtrated and evaporated. Recrystallization from hot acetone and MeOH gave brown solid (1.65 g, 7.17 mmol, 60%). Mp $134 \text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl₃, δ): 3.16 (s, 2H), 7.49 (d, $J = 4.1 \text{ Hz}$, 2H), 7.63 (d, $J = 4.1 \text{ Hz}$, 2H), 7.92 (d, $J = 4.1 \text{ Hz}$, 2H), 8.05 (s, 2H) IR (KBr): $3284 (\nu_{\text{C}\equiv\text{CH}}) \text{ cm}^{-1}$. Anal. Calcd for C₆H₁₀N₂: C, 83.45%; H, 4.38%; N, 12.17%. Found: C, 83.17%; H, 4.67%; N, 12.00%.

Bis(4-ethynylphenyl)diazene (**1a**)

This compound was synthesized from bis(4-iodophenyl)diazene in a manner similar to **1b**. ^1H NMR (acetone-*d*₆, δ): 3.82 (s, 2H), 7.75 (d, $J = 7.9 \text{ Hz}$, 4H), 7.96 (d, $J = 7.9 \text{ Hz}$, 4H) IR (KBr): $3270 (\nu_{\text{C}\equiv\text{CH}}) \text{ cm}^{-1}$. Anal. Calcd for C₆H₁₀N₂: C, 83.45%; H, 4.38%; N, 12.17%. Found: C, 83.65%; H, 4.43%; N, 12.19%.

Bis(4-ethynyl-2,5-dihexylphenyl)diazene (**1c**)

This compound was synthesized from bis(4-iodo-2,5-dihexylphenyl)diazene in a manner similar to **1b**. ^1H NMR (CDCl₃, δ): 0.95 (m, 12H), 1.24–1.66 (m, 32H), 2.79 (t, $J = 6.3 \text{ Hz}$, 4H), 3.07 (t, $J = 6.2 \text{ Hz}$, 4H), 3.38 (s, 2H), 7.45 (s, 2H), 7.48 (s, 2H).

Bis(3-ethynyl-4,6-dihexylphenyl)diazene (**1d**)

This compound was synthesized from bis(3-iodo-4,6-dihexylphenyl)diazene in a manner similar to **1b**. The product was purified by SiO₂-column chromatography eluted with hexane

to obtain dark red oil in 62% yield. ^1H NMR (CDCl_3 , δ): 0.75–1.75 (m, 44H), 2.80 (t, $J = 6.2$ Hz, 4H), 3.10 (t, $J = 6.2$ Hz, 4H), 3.21 (s, 2H), 7.16 (s, 2H), 7.71 (s, 2H), IR (KBr): 3314 ($\nu_{\text{C=CH}}$) cm^{-1} . Anal. Calcd for $\text{C}_{40}\text{H}_{58}\text{N}_2$: C, 84.75%; H, 10.31%; N, 4.94%. Found: C, 82.02%; H, 10.09%; N, 4.87%.

3.4 Polymer synthesis^{11, 12}

All the polycondensations were carried out under nitrogen. The solvents were purified by standard method before use. The conditions were summarized in Table I. After heating the reaction mixture for a set time, the reaction mixture was concentrated by rotary evaporation. In the case of **3aa**, the resulting solid was washed with acetone. In the same way, **3ab** and **3bb** were washed with methanol. **3db** was separated from the residual monomers and catalysts by preparative HPLC. In the other cases, the resulting solid was dissolved in a small amount of CHCl_3 , and the solution was poured into a large amount of acetone, then a precipitate polymer was isolated by filtration.

3.5 Spectroscopic data of polymers

3aa IR (KBr): 2957, 2093, 1587, 1147 cm^{-1} , ^1H NMR (CDCl_3 , δ): 0.94 (t, $J = 6.2$ Hz, 18H), 1.41–1.63 (m, 24H), 1.96–2.27 (m, 12H), 7.37–7.40 (m, 4H), 7.77–7.80 (m, 4H). **3ab** IR (KBr): 2201 ($\nu_{\text{C=C}}$) cm^{-1} . **3ba** IR (KBr): 2957, 2099, 1560, 1541, 1508 cm^{-1} , ^1H NMR (CDCl_3 , δ): 0.94 (t, $J = 6.2$ Hz, 18H), 1.42–1.64 (m, 24H), 2.15–2.17 (m, 12H), 7.34–7.35 (m, 4H), 7.65–7.66 (m, 2H), 7.80 (s, 2H). **3bb** IR (KBr): 2260 ($\nu_{\text{C=C}}$) cm^{-1} . **3ca** IR (neat): 2959, 2085, 1216, 1147 cm^{-1} , ^1H NMR (CDCl_3 , δ): 0.88–2.18 (m, 98H), 2.85–3.10 (m, 8H), 7.22–7.44 (m, 4H). **3da** IR (neat): 2957, 2096, 1464 cm^{-1} , ^1H NMR (CDCl_3 , δ): 0.83–2.11 (m, 98H), 2.85–3.07 (m, 8H), 7.04 (s, 2H), 7.48 (s, 2H). **3db** IR (KBr): 2213 ($\nu_{\text{C=C}}$) cm^{-1} , ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 8.0$ Hz, 12H), 1.21–1.69 (m, 32H), 2.83–2.87 (m, 4H), 3.12 (s, 4H), 4.24–4.34 (m, 4H), 4.44–4.54 (m, 4H), 7.12–7.17 (m, 2H), 7.66–7.76 (m, 2H).

3.6 Photo-irradiation

A sample solution was irradiated in a quartz glass tube with a 400 W high-pressure mercury lamp (Fuji Glass Work HB-400). To irradiate at $300 \text{ nm} < \lambda < 400 \text{ nm}$, Pyrex glass and Toshiba D33S filters were used. To irradiate at $400 \text{ nm} < \lambda < 500 \text{ nm}$, a Toshiba L42 filter was used. The distance between the sample and lamp was 30 cm.

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