

Synthesis and Metal-like Luster of Novel Polyaniline Analogs Containing Azobenzene Unit

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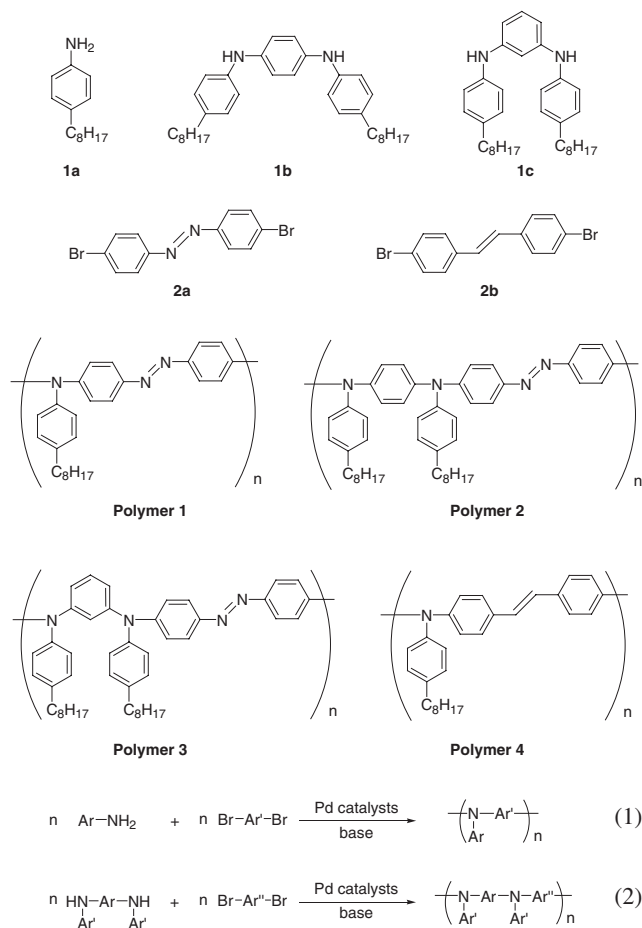
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Pd-catalyzed polycondensations of aniline derivatives and 4,4'-dibromoazobenzene afford polyaniline analogs containing an azobenzene unit in good yields. The obtained polymers are red in solution and in thin-film states, whereas they exhibit green metal-like luster in thick-film states.

Azobenzene is a well-known photoresponsive molecule that undergoes photoinduced and thermal trans-cis isomerization. A large number of polymers containing azobenzene moieties have been used in liquid crystalline materials,¹ actuators,² and surface relief grafting³ because the trans-cis isomerization induces a large geometric change around the azobenzene moiety, resulting in morphological and mechanical changes. Owing to the strong absorption in the visible region, azobenzene structures are commonly found in dyes such as methyl orange. Although many dye-containing π -conjugated polymers have been developed for light-harvesting and light-emitting materials,⁴ there are only a few examples of π -conjugated polymers with an azobenzene unit in a main chain.⁵ Such azobenzene-containing π -conjugated polymers are high potential materials for third-order nonlinearities.⁶ Therefore, a new polymer with an azobenzene unit is expected to have interesting optical properties. Since the introduction of an electron-donating amino group confers redox ability and enables the enhancement of the absorption coefficient of a dye molecule, we focused on the incorporation of aminoazobenzene derivatives into the main chain of polymers for the development of new optical materials. Herein, we report the syntheses of new polyaniline analogs with an azobenzene unit by polycondensation using a Pd-catalyzed C-N coupling reaction.⁷ The optical properties, such as metal-like luster, of these polymers are also presented.

Polymer with an azobenzene unit (**Polymer 1**) was obtained in 94% yield ($M_n = 10300$) by the polycondensation of 4-octylaniline (**1a**) and 4,4'-dibromoazobenzene (**2a**) for 24 h at 100 °C using Pd₂(dba)₃ (dba: dibenzylideneacetone) and P(*t*-Bu)₃·HBF₄ in the presence of *t*-BuONa (eq 1 in Scheme 1 and see Supporting Information).⁸ The monomers **1b** and **1c** were prepared for the syntheses of the polymers with an additional phenylene unit. *para*-Linked and *meta*-linked polymers, i.e., **Polymers 2** and **3**, were synthesized in 98% ($M_n = 22100$) and 91% ($M_n = 6500$) yields from **1b** and **1c**, respectively, similarly to **Polymer 1** (eq 2). In the preparation of **Polymer 2**, P(*t*-Bu)₃·HBF₄ with Pd₂(dba)₃ gave a higher molecular weight polymer than those synthesized with DPPF⁹ ($M_n = 6500$) and X-phos¹⁰ ($M_n = 7200$) as the ligand. The high efficiency of the P(*t*-Bu)₃ ligand for the preparation of poly(triarylamine) analogs has also been reported in the literature.⁷ The polymerization



Scheme 1. Structures of monomers and polymers **1–4**.

procedure is facile for the polycondensation of **1a** and **2b** providing the comparative polymer, **Polymer 4**, having a stilbene unit instead of an azobenzene unit (87% yield, $M_n = 13300$).

Polymers 1–4 are soluble in CHCl₃, CHCl₂CHCl₂, and THF. The fabrication of thin films and self-supporting films is possible by spin-coating and solvent-cast methods on a glass plate, respectively. The electrochemical properties of **Polymers 1–4** were investigated by cyclic voltammetry in film states. The cast films of **Polymers 1–4** on an ITO electrode give rise to an electrochemical redox active cycle in an acetonitrile solution of *n*-Bu₄NPF₆ (Figure S1).⁸ In the case of **Polymer 2**, two well-resolved waves were observed in the positive potential region. The separation of the oxidation wave indicates an electrical

Table 1. Electrochemical and optical properties of **Polymers 1–4**

	Electrochemical properties ^a			Absorption			
				Solution ^d		Thin film ^c	Reflection
	E_{pa}/V^b	E_{pc}/V^b	$E^{o'}/V^c$	λ_{max}/nm	$\epsilon/L mol^{-1} cm^{-1}$	λ_{max}/nm	λ_{max}/nm
Polymer 1	0.786	0.578	0.682	515	23700	510, 541 ^f	559, 518 ^f
Polymer 2	0.576, 0.798	0.374, 0.628	0.475, 0.713	501	29300	490	542
Polymer 3	0.915	0.606	0.761	461	28100	470, 510 ^f	524
Polymer 4	0.608	0.207	0.408	409	23600	422	461

^aCyclic voltammetry of polymers was measured in an acetonitrile solution of 0.1 M *n*-Bu₄NPF₆ with 0.1 M AgNO₃/Ag reference. Sweep rate: 100 mV s⁻¹. ^b E_{pa} and E_{pc} correspond to the anodic and cathodic peak potentials, respectively. ^c $E^{o'} = (E_{pa} + E_{pc})/2$. ^dIn CHCl₃. ^eThe thin films and the thick films were fabricated by a cast method on a quartz plate and a glass plate, respectively. ^fShoulder peak.

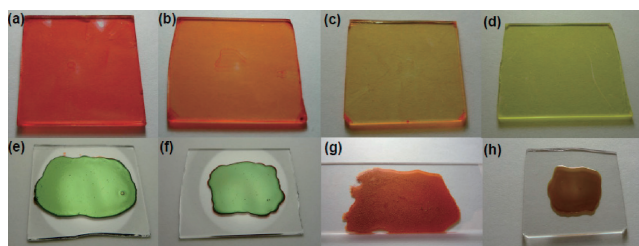


Figure 1. Photographs of the thin films of (a) **Polymer 1**, (b) **Polymer 2**, (c) **Polymer 3**, (d) **Polymer 4**, and the thick films of (e) **Polymer 1**, (f) **Polymer 2**, (g) **Polymer 3**, (h) **Polymer 4**.

communication between nitrogen atoms through a *para*-phenylene unit. Since electrical communications through azobenzene and *meta*-phenylene units are unfavorable, **Polymers 1** and **3** do not exhibit resolved waves. The peak potentials of the polymers are summarized in Table 1. Owing to the electron-withdrawing property of the azobenzene unit, the peak potentials of **Polymers 1–3** were observed at a higher oxidation potential than those of the *N*-substituted polyaniline derivatives and **Polymer 4**.^{7i,11}

Polymers 1–3 are red in solution and in a thin-film state (Figure 1). In contrast, **Polymer 4** is pale yellow owing to the absence of an azo structure in its polymer chain. UV–vis spectroscopy clearly indicates the difference in color (Figure S2).⁸ The electrical oxidation of the polymer changes the color of the films from red or yellow to blue. The absorbance maxima (λ_{max}) of the polymers in a solution state are close to those in a thin-film state (Table 1). In general, the λ_{max} of a π -conjugated polymer in a thin-film appears at longer wavelength than that in solution. This unusual phenomenon is probably due to inefficient π – π stacking in the thin-film state because of the bulky and bent structure of the triphenylamine unit. The most interesting optical property of **Polymer 1** is its green metal-like luster in a thick-film state, which has no light transmittance in the visible region due to strong absorption (Figure 1e). Figure 2a shows the absorption spectrum of **Polymer 1** in a thin-film state and reflection spectra in a thick-film state. The thickness of the thin-film and thick-film are 0.063 and 17 μ m, respectively. In the case of film more than 6.8 μ m thick, the film of **Polymer 1** clearly exhibits metal-like luster (Figure S3).⁸ One can assume that the metal-like luster originates from the structural color caused by microstructures on the scale of the visible region wavelength.¹²

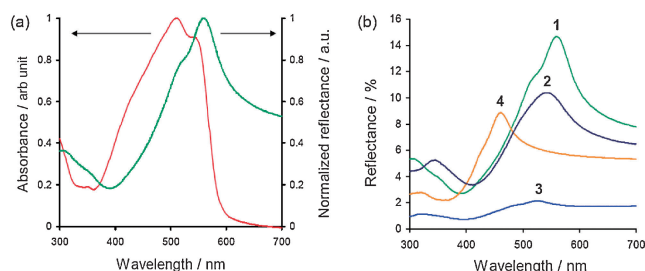


Figure 2. (a) Absorption spectrum of **Polymer 1** in the thin film state (red) and reflection spectrum in the thick film state (green). (b) Reflection spectra of **Polymers 1–4** in the thick film state.

To determine whether or not the metal-like luster is due to the structural color, XRD analysis was carried out. The result shows a broad diffraction at approximately 4.3 \AA indicating only a loose interchain π – π -stacking interaction (Figure S4).⁸ In addition, the reflection peak does not depend on the angle of incident light (Figure S5),⁸ which is different from the angle dependence of incident light in materials with structural color.^{13,14} On the basis of these results, the structural color is unlikely to be the reason for the metal-like luster. **Polymer 1** in Figure 2 exhibits reflectance at 559 nm, since its reflectance is fairly high owing to its strong light absorption in the visible region. It is considered that the strong light absorption might be attributed to the π – π^* -electronic transition of azobenzene in the polymer main chain. A similar metal-like luster and a reflective property were observed for **Polymer 2** (Figures 1f and 2b). In contrast, **Polymer 3** exhibits no metal-like luster or clear reflection probably because of the low film-forming ability and rough surface of the film resulting in the scattering of incident light (Figures 1g and 2b). These observations suggest that the essential conditions for the appearance of metal-like luster are not only the existence of an azobenzene dye but also other factors such as the smoothness of the film surface. The thick film of **Polymer 4** exhibits no metal-like luster, as shown in Figure 1h, although Figure 2b shows the reflection of **Polymer 4** at 461 nm. The lack of metal-like luster is probably due to the reflection region being close to the ultraviolet region.

Recently, there have been some reports on π -conjugated polymers showing metal-like luster.^{14,15} In the structure of these polymers, donor and acceptor units are connected by π -conjugated linkages. Since **Polymers 1** and **2** also have donor

(amine) and acceptor (azobenzene) units in their polymer chain, the charge-transfer structure may also have a crucial role in the metal-like luster.

In summary, we synthesized novel polyaniline analogs containing an azobenzene unit. Thick films of the polymers exhibit green metal-like luster. Detailed investigation of the origin of the metal-like luster and the control of the color of the metal-like luster by a redox or protonation reaction of the amino group is in progress.

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References and Notes

- 1 a) A. S. Matharu, S. Jeeva, P. S. Ramanujam, *Chem. Soc. Rev.* **2007**, *36*, 1868. b) C. Ruslim, K. Ichimura, *Adv. Mater.* **2001**, *13*, 641. c) G. Iftime, F. L. Labarthe, A. Natansohn, P. Rochon, *J. Am. Chem. Soc.* **2000**, *122*, 12646.
- 2 a) T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem., Int. Ed.* **2007**, *46*, 506. b) T. J. White, S. V. Serak, N. V. Tabiryan, R. A. Vaia, T. J. Bunning, *J. Mater. Chem.* **2009**, *19*, 1080. c) Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
- 3 a) A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139. b) N. Zettsu, T. Ogasawara, N. Mizoshita, S. Nagano, T. Seki, *Adv. Mater.* **2008**, *20*, 516. c) T. Fukuda, H. Matsuda, T. Shiraga, T. Kimura, M. Kato, N. K. Viswanathan, J. Kumar, S. K. Tripathy, *Macromolecules* **2000**, *33*, 4220.
- 4 a) A. Ajayaghosh, *Chem. Soc. Rev.* **2003**, *32*, 181. b) E. Zhou, Q. Wei, S. Yamakawa, Y. Zhang, K. Tajima, C. Yang, K. Hashimoto, *Macromolecules* **2010**, *43*, 821. c) K. Becker, J. M. Lupton, *J. Am. Chem. Soc.* **2006**, *128*, 6468. d) A. Nagai, Y. Chujo, *Macromolecules* **2010**, *43*, 193.
- 5 a) A. Izumi, M. Teraguchi, R. Nomura, T. Masuda, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1057. b) A. Izumi, M. Teraguchi, R. Nomura, T. Masuda, *Macromolecules* **2000**, *33*, 5347. c) A. Izumi, R. Nomura, T. Masuda, *Macromolecules* **2001**, *34*, 4342.
- 6 D. Kuciauskas, M. J. Porsch, S. Pakalnis, K. M. Lott, M. E. Wright, *J. Phys. Chem. B* **2003**, *107*, 1559.
- 7 a) T. Kanbara, A. Honma, K. Hasegawa, *Chem. Lett.* **1996**, 1135. b) T. Kanbara, M. Oshima, T. Imayasu, K. Hasegawa, *Macromolecules* **1998**, *31*, 8725. c) F. E. Goodson, S. I. Hauck, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 7527. d) M. Jikei, R. Mori, S. Kawauchi, M. Kakimoto, Y. Taniguchi, *Polym. J.* **2002**, *34*, 550. e) R. E. Ward, T. Y. Meyer, *Macromolecules* **2003**, *36*, 4368. f) I. Shen, M. C. McCairn, J. J. Morrison, M. I. Turner, *Macromol. Rapid Commun.* **2007**, *28*, 449. g) J. Kuwabara, H. Mori, T. Teratani, M. Akita, T. Kanbara, *Macromol. Rapid Commun.* **2009**, *30*, 997. h) T. Yasuda, T. Suzuki, M. Takahashi, T. Tsutsui, *Chem. Lett.* **2009**, *38*, 1040. i) T. Michinobu, H. Kumazawa, E. Otsuki, H. Usui, K. Shigehara, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3880.
- 8 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 9 1,1'-Bis(diphenylphosphino)ferrocene.
- 10 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl.
- 11 M. Horie, I. Yamaguchi, T. Yamamoto, *Macromolecules* **2006**, *39*, 7493.
- 12 S. Kinoshita, S. Yoshioka, Y. Fujii, N. Okamoto, *Forma* **2002**, *17*, 103.
- 13 a) H. Goto, *Adv. Funct. Mater.* **2009**, *19*, 1335. b) G. I. Márk, Z. Vértessy, K. Kertész, Z. Bálint, L. P. Birò, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2009**, *80*, 051903. c) Y. Ding, S. Xu, Z. L. Wang, *J. Appl. Phys.* **2009**, *106*, 074702.
- 14 I. Yamaguchi, A. Kado, T. Fukuda, H. Fukumoto, T. Yamamoto, M. Sato, *Eur. Polym. J.* **2010**, *46*, 1119.
- 15 a) T. Morikita, I. Yamaguchi, T. Yamamoto, *Adv. Mater.* **2001**, *13*, 1862. b) C. G. Bangcuyo, U. Evans, M. L. Myrick, U. H. F. Bunz, *Macromolecules* **2001**, *34*, 7592. c) T. Yamamoto, Q. Fang, T. Morikita, *Macromolecules* **2003**, *36*, 4262. d) I. Yamaguchi, S. Shingai, M. Sato, *Macromolecules* **2008**, *41*, 6292.