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Photochemical control of conductivity of polythiophenes with photochromic moieties

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The synthesis, optical and electrical properties of azobenzene-substituted polythiophene derivatives at the 3-position are reported: one without flexible spacer (**PT0**) and the other with a hexamethylene spacer (**PT6**). Photoirradiation of **PT6** at 366 nm caused *trans–cis* isomerization of the azobenzene moiety and this photochromic reaction induced a change in conductivity of the thin film of **PT6**: the conductivity was 1.1×10^{-7} S cm^{-1} before irradiation and 8.3×10^{-7} S cm^{-1} after photoirradiation. After annealing, the conductivity of the film returned to the initial value. The conductivity of a compound without the azobenzene moiety, α-terthienyl (α**T3**), showed no change on photoirradiation at 366 nm.

Introduction

π-Conjugated polymers are a class of materials that exhibit intrinsic conducting properties originating from the polymer chains.[1,2] It is well known that the conductivity of polythiophenes (PTs) can vary in response to minor perturbations in chemical structure, oxidation state, and/or solid state ordering of materials. In particular, chemical doping with I_2 significantly enhances the conductivity of PTs. Recent studies have shown that the conductivity of these materials is sensitive to the regiospecificity of the side chain, which in turn indicates that conformational changes provide large effects on the conductivity.[3–7] Introduction of functional groups to PTs is therefore expected to be favorable from the viewpoint of control of the conductivity.

Photochromic compounds such as azobenzenes and spiropyrans exhibit a reversible structural change due to photochemical reaction on photoirradiation and simultaneously show changes in the spectra in the UV–VIS absorption band.[8–13] Several studies have been performed so far on the conformational change of PTs containing photochromic moieties in the side chain.[14,15] As an alternative to PTs, tetrathiafulvalene derivatives with substituted azobenzenes have been demonstrated to undergo *trans–cis* isomerization upon photoirradiation.[16]

In these studies, however, the conductivity of PTs was not controlled by means of the photochromic reaction. The optical control of conductivity was achieved for the first time by Chen and Liao.[17,18] They used copolymers composed of thiophenes with hexyl side chains and azobenzene moieties in the side chains and showed a change in the conductivity on photoirradiation. They concluded that the enhancement of conductivity on photoirradiation is due to an increase in the number of hopping sites due to the isomerization of azobenzene. The spectra in absorption bands of both azobenzene and conducting units, however, were unchanged before and after photoirradiation. The mechanism of change of the conductivity of polythiophene derivatives on photoirradiation has not been clear. Detailed information on isomerization of the azobenzene affecting the conductivity could not be obtained by absorption spectroscopy.

To obtain a deeper understanding of the mechanism of such photoinduced change in the conductivity, we prepared polythiophene derivatives azobenzene-substituted at the 3-position on thiophene rings with different spacer lengths and evaluated their optical and electrical properties as well as control of their conductivity by photochemical reaction of the azobenzene moieties. The photoinduced change in conductivity was discussed on the basis of the isomerization behavior of the azobenzene introduced to the side chain. We tried to evaluate the change in conductivity of I_2-doped polythiophene derivatives on photoirradiation. However, they absorbed light in the whole visible region and they have very large molar extinction coefficients. Therefore, when we irradiated the I_2-doped polythiophene derivatives, the films absorbed light entirely in the surface region of less than 50 nm thickness and the photochemical reaction could not take place completely across the film. Thus, we used non-doped polythiophene samples in this study.

Experimental

Reagents

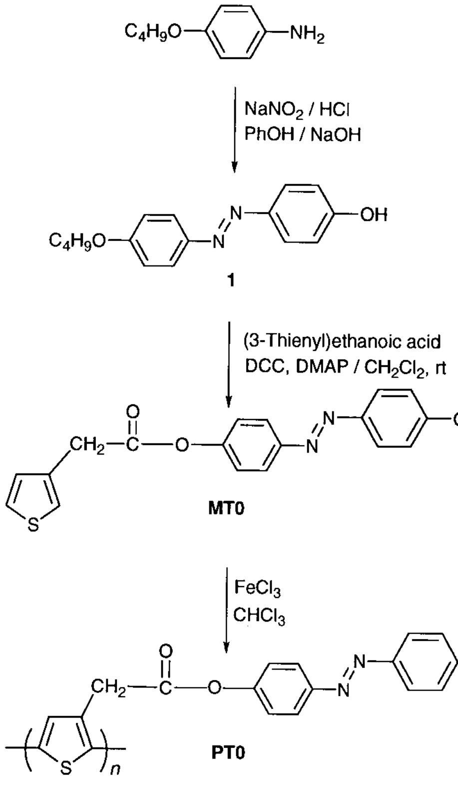
All reagents were purchased from Tokyo Kasei Co. Methylene chloride and chloroform were purified under an argon atmosphere before use. Ferric chloride was dried under vacuum immediately before use. α-Terthienyl was recrystallized from hexane before use.

Characterization of monomers and polymers

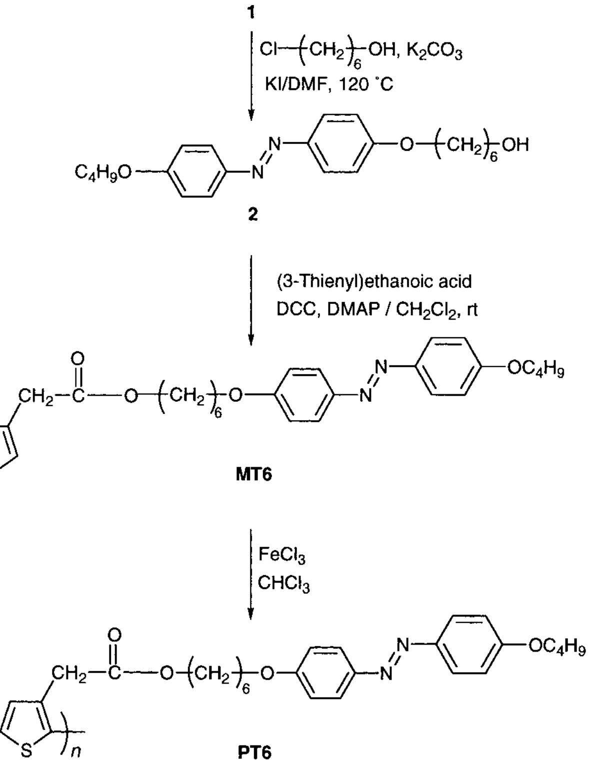
^{1}H-NMR spectra were recorded with a JEOL-400 (400 MHz) spectrometer. Molecular weight was determined by GPC (Tosoh HLC-802; column, GMH6 $\times$ 2 + G4000H8; eluent, chloroform) calibrated with standard polystyrenes. Glass transition temperature (T_g) was determined with a differential scanning calorimeter (DSC; Seiko I&E SSC-5000) operated at a heating rate of 10 °C min^{-1}. Melting points were determined with an Olympus Model BHSP polarizing microscope equipped with Mettler hot stage Models FP-80 and FP-82. IR spectra were recorded with a JEOL FT/IR-3 spectrometer.

Preparation of thiophene derivatives

Azobenzene-substituted polythiophene derivatives at the 3-position were synthesized following the synthetic route shown in Scheme 1 and Scheme 2.



Scheme 1 Synthetic route to **PT0**.



Scheme 2 Synthetic route to **PT6**.

4-Butoxy-4′-hydroxyazobenzene (1)[19]. Butoxyaniline (6.91 g, 41.9 mmol) was dissolved in acidified water (15 ml HCl–75 ml water) and diazotized with sodium nitrite (2.89 g, 41.9 mmol) in an ice bath. Aqueous phenol (3.94 g, 41.9 mmol) was added to the resulting diazonium salt solution while stirring for 2 h at 0 °C. The crude product was collected by filtration and purified by column chromatography on silica gel (eluent, $CHCl_3$). Recrystallization from hexane gave 7.04 g of compound **1** as a dark yellow solid (plates, yield 62%): mp 110 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, t, $J=7.0$ Hz, $-CH_3$), 1.39–1.54 (2H, m, $-CH_2CH_3$), 1.63–1.82 (2H, m, $-CH_2CH_2CH_3$), 4.03 (2H, t, $J=7.7$ Hz, $-OCH_2CH_2CH_2CH_3$), 5.29 (1H, br, -OH), 6.94 (2H, d, $J=8.8$ Hz, 3-H, 5-H), 7.01 (2H, d, $J=8.4$ Hz, 3′-H, 5′-H), 7.82 (2H, d, $J=8.4$ Hz, 2′-H, 6′-H), 7.84 (2H, d, $J=8.8$ Hz, 2-H, 6-H). IR (KBr, cm^{-1}) 3480, 1600, 1580, 1500, 1250, 850, 820. Anal. Calcd. for $C_{16}H_{18}N_2O_2$: C, 71.11; H, 6.67; N, 10.37. Found: C, 71.10; H, 6.83; N, 10.16%.

4-(4-Butoxyphenyldiazenyl)phenyl (3-thienyl)ethanoate (MT0).[20] Under an argon atmosphere, 6.12 g (30.0 mmol) of *N,N′*(DCC) in 100 ml of CH_2Cl_2 were added to a solution of **1** (3.27 g, 11.0 mmol), (3-thienyl)ethanoic acid (1.56 g, 11.0 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.14 g, 1.1 mmol). The mixture was stirred for 20 h at room temperature, and the reaction was monitored by thin layer chromatography. The precipitated salt was filtered off and the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent, $CHCl_3$). Recrystallization of crude product from ethanol–acetone (7 : 1) gave 3.64 g of **MT0** as an orange solid (powder, yield 84%): mp 129 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, t, $J=6.9$ Hz, $-CH_3$), 1.48–1.56 (2H, m, $-CH_2CH_3$), 1.78–1.86 (2H, m, $-CH_2CH_2CH_3$), 3.94 (2H, s, Th-CH_2COO-), 4.08 (2H, t, $J=7.7$ Hz, $-OCH_2CH_2CH_2CH_3$), 7.00 (2H, d, $J=8.5$ Hz, 3-H, 5-H), 7.16 (1H, d, $J=5.7$ Hz, Th-4-H), 7.22 (2H, d, $J=8.9$ Hz, 3′-H, 5′-H), 7.29 (1H, s, Th-2-H), 7.35 (1H, d, $J=5.7$ Hz, Th-5-H), 7.87 (2H, d, $J=8.5$ Hz, 2-H, 6-H), 7.89 (2H, d, $J=8.9$ Hz, 2′-H, 6′-H). IR (KBr, cm^{-1}) 2960, 2940, 2880, 1750, 1600, 1580, 1490, 1230, 840, 730. Anal. Calcd for $C_{22}H_{22}SN_2O_3$: C, 67.00; H, 5.58; S, 8.11; N, 7.11. Found: C, 66.77; H, 5.63; S, 8.22; N, 7.21%.

Poly[4-(4-butoxyphenyldiazenyl)phenyl (3-thienyl)ethanoate] (PT0).[21] To the mixture of **MT0** (1.18 g, 3.01 mmol) and $FeCl_3$ (1.95 g, 12.0 mmol) was added slowly anhydrous $CHCl_3$(20 ml) and the resulting solution was stirred at room temperature for 10 h under vacuum. The reaction mixture was poured into 900 ml of acetone, and the precipitate formed was filtered off, washed with acetone and with methanol several times, and dried under vacuum. Ionic impurities were removed completely from the polymer by successive washing with concentrated ammonia (5%, 10 ml) and 1 M HCl (10 ml). This procedure was repeated five times. Pure polymer was dried under vacuum to give 0.127 g of **PT0** as a brown solid (yield 10.7%), which was insoluble in common solvents: T_g 30 °C. Anal. Calcd for $(C_{22}H_{20}SN_2O_3)_n$: C, 67.34; H, 5.10; S, 8.16; N, 7.14. Found: C, 67.54; H, 5.38; S, 8.14; N, 6.83%.

Because of insolubility, no stereoregularity of the thiophene units could be determined.

4-Butoxy-4′-(6-hydroxyhexyloxy)azobenzene (2). A small amount of KI, **1** (3.27 g, 11.0 mmol), 6-chlorohexan-1-ol (1.64 g, 12.0 mmol) and K_2CO_3 (1.40 g, 11.0 mmol) were dissolved in dimethylformamide (150 ml) and allowed to stir for 10 h at 120 °C. The reaction was monitored by thin layer chromatography, and upon adding water (500 ml), a pale yellow solid was precipitated. The residue was dissolved in $CHCl_3$ and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by recrystallization from hexane to give 3.51 g of **2** as a pale yellow solid (powder, yield 86%): mp 119 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, t, $J=7.3$ Hz, $-CH_3$), 1.25 (1H, br, -OH), 1.44–1.61 (6H, m, $-CH_2CH_3$, $-OCH'_2CH'_2(CH'_2)_2$), 1.64–1.70 (2H, m, $-CH'_2CH'_2OH$), 1.77–1.88 (4H, m, $-OCH_2CH_2$, $-OCH'_2CH'_2$), 3.67 (2H, br, $J=7.5$ Hz, $-CH'_2CH'_2OH$), 4.04 (4H, t, $J=7.7$ Hz, $-OCH_2CH_2$, $-OCH''_2CH'_2$), 6.98 (4H, d, $J=8.5$ Hz, 3-H, 5-H, 3′-H, 5′-H), 7.86 (4H, d, $J=8.5$ Hz, 2-H, 6-H, 2′-H, 6′-H). IR (KBr, cm^{-1}) 3510, 2910, 1600, 1580, 1500, 1220, 840. Anal. Calcd. for $C_{22}H_{30}N_2O_3$: C, 71.35; H, 8.11; N, 7.57. Found: C, 71.23; H, 8.12; N, 7.77%.

6-[4-(4-Butoxyphenyldiazenyl)phenoxy]hexyl (3-thienyl) ethanoate (MT6).[20] **MT6** was synthesized following the procedure described for **MT0**, using 3.36 g (9.01 mmol) of **2** and 1.27 g (9.01 mmol) of (3-thienyl)ethanoic acid. The crude product was purified by recrystallization from ethanol–acetone (5:1) to give 3.41 g of **MT6** as an orange solid (powder, yield 77%): mp 104 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.00 (3H, t, $J=6.9$ Hz, -CH_3), 1.40–1.47 (2H, m, $\text{-C}H_2\text{CH}_3$), 1.49–1.56 (4H, m, $\text{-C}H_2\text{CH}_2\text{CH}_3$), 1.63–1.72 (2H, m, $\text{-COO-CH}'_2\text{C}H'_2$), 1.75–1.85 (4H, m, $\text{-OCH}_2\text{C}H_2$), 3.7 (2H, s, $\text{Th-C}H_2\text{COO}$), 4.04 (4H, t, $J=7.6$ Hz, $\text{-OC}H_2\text{CH}_2$, $\text{-OC}H'_2\text{CH}'_2$), 4.13 (2H, t, $J=7.2$ Hz, $\text{-COOC}H'_2\text{CH}'_2\text{CH}_2$), 6.98 (4H, d, $J=8.7$ Hz, 3-H, 5-H, 3′-H, 5′-H), 7.05 (1H, d, $J=5.7$ Hz, Th-4-H), 7.16 (1H, s, Th-2-H), 7.28 (1H, d, $J=5.7$ Hz, Th-5-H), 7.89 (4H, d, $J=8.7$ Hz, Be-2-H, 6-H, 2′-H, 6′-H). IR (KBr, cm^{-1}) 2980, 2940, 2880, 1730, 1600, 1580, 1490, 1250, 1070, 1030. Anal. Calcd. for $C_{28}H_{34}SN_2O_4$: C, 68.01; H, 6.88; S, 6.48; N, 5.67. Found: C, 68.25; H, 6.77; S, 6.46; N, 5.77%.

Poly[6-{4-(4-butoxyphenyldiazenyl)phenoxy}hexyl (3-thienyl)ethanoate] (PT6). **PT6** was synthesized following the procedure described for **PT0** using 1.00 g (2.01 mmol) of **2** and 1.29 g (8.01 mmol) of $FeCl_3$. Pure **PT6** was obtained as a brown solid (0.057 g, 5.7% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (3H, t, $J=6.9$ Hz, -CH_3), 1.20–1.80 (12H, m, $\text{-(C}H_2)_6\text{CH}_3$), 3.60 (1H, br, $\text{Th-C}H_2\text{COO}$, for Head-to-Head), 3.70 (1H, br, $\text{Th-C}H_2\text{COO}$, for Head-to-Tail), 3.86 (2H, br, $\text{-OC}H'_2\text{CH}'_2$), 3.97 (2H, br, $\text{-OC}H_2\text{CH}_2$), 4.13 (2H, br, 7.2 Hz, $\text{-COO-C}H'_2\text{CH}_2$), 6.84 (2H, d, $J=8.5$ Hz, Be-3′-H, 5′-H), 6.98 (2H, d, $J=8.7$ Hz, Be-3-H, 5-H), 7.16 (1H, br, Th-4-H), 7.82 (4H, d, $J=8.5$ Hz, Be-2-H, 6-H, 2′-H, 6′-H). IR (film) 3090, 3050, 2920, 1750, 1625, 1600, 1540, 1250, 1150, 820. Anal. Calcd for $(C_{28}H_{32}SN_2O_4)_n$: C, 68.29; H, 6.50; S, 6.50; N, 5.69. Found: C, 68.05; H, 6.80; S, 6.76; N, 5.97%. $T_g < -100$ °C; $M_n = 2.3 \times 10^4$ ($CHCl_3$; polystyrene standards); $M_w/M_n = 5.1$.

Measurements of photoisomerization and conductivity

The sample solution was irradiated with light at 366 nm, which was isolated from a 500 W high-pressure mercury lamp by the use of glass filters (Toshiba UV-35 + UV-D36A). The photoisomerization was followed spectroscopically with a Hitachi UV-320 spectrometer and a Shimadzu UV-200 spectrometer.

Fig. 1 shows the experimental setup used for the observation of change in conductivity induced by photoirradiation. The sample film was prepared by casting the polymer solution in chloroform onto a glass substrate and by drying completely under reduced pressure. The samples were prepared at a size of 1 × 1 cm^2. The size of the sample films was measured with a micrometer three times and a mean value was taken. The thickness of the films was estimated by UV absorption spectroscopy. The conductivity of the films was measured with an Advantest R-8340A resistance meter using the two-probe method.

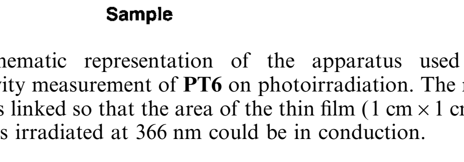


Fig. 1 Schematic representation of the apparatus used for the conductivity measurement of **PT6** on photoirradiation. The resistance meter was linked so that the area of the thin film (1 cm × 1 cm square) which was irradiated at 366 nm could be in conduction.

Results and discussion

Characterization of polymers

It was found that **PT0** is insoluble in common organic solvents. The low solubility of **PT0** may be explained in terms of a compact morphology, which results from the absence of any degrees of freedom between the polymer chain and the azobenzene moiety. In contrast, **PT6** is soluble. The number-average molecular weight was 23000. ^{1}H-NMR spectra provide useful information on the substitution pattern in the polymer backbone. Previous reports have shown that α-methylene protons directly attached to the thiophene ring can be resolved into two different diads: head-to-tail (H–T) and head-to-head (H–H).[22–27] The two peaks around 3.7 ppm come from the methylene group between the ester group and the thiophene ring. The expanded ^{1}H-NMR spectrum of **PT6** (Fig. 2) shows that **PT6** has a stereorandom chain structure with equal distribution of H–T and H–H linkages.

It is well known that when thiophenes are polymerized by the chemical oxidation coupling method with $FeCl_3$, polymers obtained contain both regular (H–H linkage) and irregular (H–T linkage) polymers.[28–30] The irregular parts are more soluble than the regular ones, and the irregular parts are removed during work-up. Yamamoto and co-workers have demonstrated that 2,5-disubstituted-3-alkylpolythiophenes have characteristic IR absorption peaks due to aromatic C–H out-of-plane vibrations around 820 cm^{-1}.[31] In this study, IR spectra of the polymers have also demonstrated that **PT6** is linked at the 2,5-positions of the thiophene rings.

DSC measurements revealed that the glass transition temperature (T_g) of **PT6** is below −100 °C, and is lower than that for **PT0** (30 °C). It has been reported that T_g decreased when the 3-position of the thiophene ring was substituted with a long alkoxyphenyl group.[32,33] In general, the T_g of polymers with longer conjugation is expected to be higher than those with shorter conjugation because of the increased stiffness of the polymer backbone. From this argument, the very low value of T_g of **PT6** may be due to six methylene spacers incorporated in the side chain which decrease rigidity of thiophene units. In other words, **PT6** may be a highly amorphous material.

Photoisomerization of PT6 in solution

Fig. 3 shows the change in absorption spectra of **PT6** in $CHCl_3$ (3.3×10^{-5} M) after photoirradiation at 366 nm at room tem-

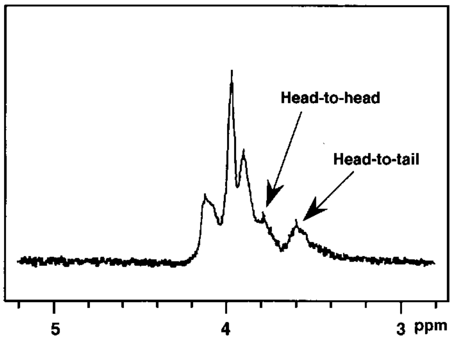


Fig. 2 ^{1}H-NMR spectrum of **PT6** in the region of the methylene protons directly attached to the thiophene ring.

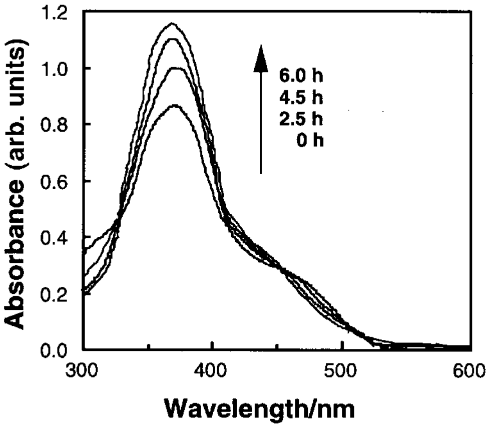


Fig. 3 Change in absorption spectrum of **PT6** in chloroform. The sample solution was left in the dark at room temperature after photoirradiation at 366 nm. [**PT6**]$=3.3\times10^{-5}$ M (based on monomer unit).

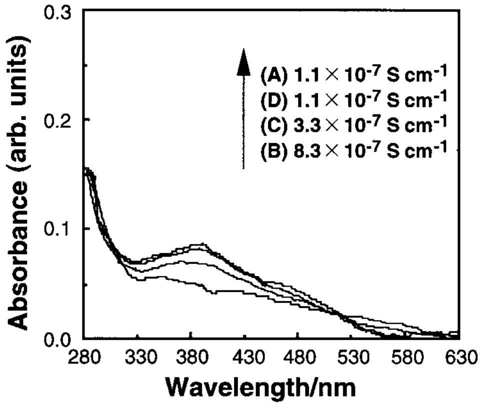


Fig. 4 Absorption spectra of thin film of **PT6** (A), before irradiation; (B), after irradiation at 366 nm; (C), after annealing at 70 °C for 5 h; (D), after annealing at 70 °C for 9 h. The conductivity of **PT6** was measured in the dark at room temperature.

perature (24 °C). The absorption at 370 nm is due to the π–π* transition of the azobenzene moieties in **PT6**. Taking into account the literature data,[34,35] the broad band around 450 nm can be assigned to the sum of the absorption due to the n–π* transition of the azobenzene moiety and the π–π* transition of the π-conjugation of the polythiophene backbone, which suggests a short π-conjugation length in **PT6**. When **PT6** was irradiated at 366 nm in $CHCl_3$, the absorbance at 370 nm decreased and that at 470 nm increased. This means that *trans–cis* isomerization of the azobenzene moieties was induced on photoirradiation. After photoirradiation, the sample solution was kept in the dark at room temperature. It was found that the absorbance at 370 nm increased and that at 470 nm decreased as shown in Fig. 3, indicating that *cis–trans* isomerization took place thermally, and after 6 h the absorption spectrum returned to the initial one.

Effect of photoirradiation on conductivity of PT6

Since the extinction coefficient of the π–π* transition of the azobenzene chromophore at 366 nm is very large ($>3\times10^4$, Fig. 3), photons are absorbed entirely in the surface region of less than 1 μm. This means that thin films with thickness less than 1 μm are needed to bring about the photochemical reaction completely across the films. Using the setup shown in Fig. 1, a thin film of **PT6** (thickness, 300 nm) which was connected to the resistance meter, was irradiated at 366 nm, and the resistance was measured. The conductivity (σ/S cm^{-1}) was calculated by the following equation [eqn. (1)],

$$\sigma=(1/R)\times(l/U) \qquad (1)$$

where R is resistance/Ω, l is length of the film, and U is the conducting area (3.0×10^{-5} cm^2). Fig. 4 shows the absorption spectra of a thin film of **PT6** annealed at 70 °C after photoirradiation, as well as the values of conductivity. Photoirradiation at 366 nm brought about a decrease of the absorbance at 380 nm and an increase at 550 nm, while the conductivity of the thin film was 1.1×10^{-7} S cm^{-1} (300 GΩ) before irradiation and 8.3×10^{-7} S cm^{-1} (40 GΩ) after photoirradiation at 366 nm (Fig. 4B). After annealing at 70 °C for 5 h, the conductivity of the thin film changed to 3.3×10^{-7} S cm^{-1} (120 GΩ) along with the increase of the absorbance in the UV region and the decrease in the longer wavelength region (Fig. 4C). After annealing at the same temperature for 9 h, the conductivity returned to its initial value (Fig. 4D). These results indicate that the conductivity of the polythiophene can be controlled reversibly by the isomerization of the azobenzene chromophores covalently attached to the thiophene rings.

In order to confirm that the change in the conductivity of **PT6** is due to the isomerization of the azobenzene moieties, the same measurement was performed using α-terthienyl (α**T3**) without the azobenzene moiety. As shown in Fig. 5, photoirradiation at 366 nm caused no change in the spectrum nor in the conductivity (8.3×10^{-7} S cm^{-1}, 120 GΩ) of a thin film of α**T3** (thickness, 400 nm). Therefore, the change of the conductivity in **PT6** resulted from the isomerization of the azobenzene moieties.

It might be possible that the change in the conductivity is due to release of strain in the sample film associated with the change in molecular shape of the azobenzene moieties on photoisomerization. To see if this is the case, the thin film of **PT6** was annealed at 70 °C for 10 h in order to release the strain before photoirradiation (Fig. 6). Annealing before irradiation caused no change in the absorption spectra and the conductivity within the experimental error. When this annealed film was irradiated at 366 nm, the conductivity increased in a similar manner to Fig. 4, although the absolute value of conductivity after irradiation was smaller than that in Fig. 4, and when the film was left in the dark at the same temperature for 6 h, the conductivity was restored to the initial value. From these results, it is clear that the change in conductivity of **PT6** was induced by isomerization of the azobenzene moieties, not by the release of strain of the polymer film.

Mechanism of photoinduced change in conduction of PT6

Conductivity (σ) is expressed by eqn. (2)

$$\sigma=ne\mu \qquad (2)$$

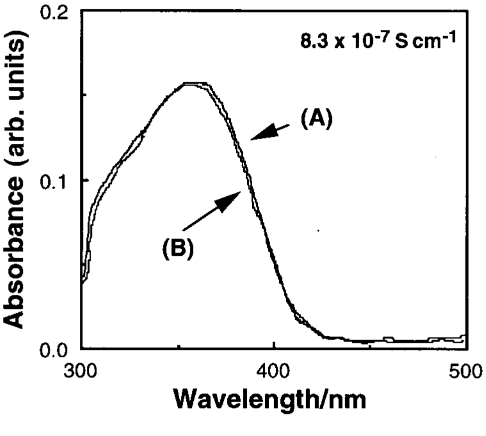


Fig. 5 Absorption spectra of a thin film of α**T3** (A), before irradiation; (B), after irradiation at 366 nm.

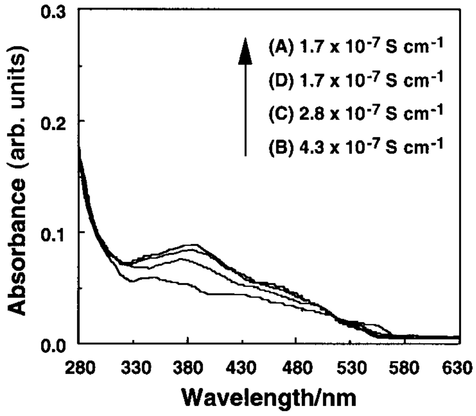


Fig. 6 Absorption spectra of a thin film of **PT6** (A), before irradiation; (B), after irradiation at 366 nm; (C), after annealing at 70 °C for 3 h; (D), after annealing at 70 °C for 6 h. The conductivity of **PT6** was measured in the dark at room temperature. The thin film of **PT6** was annealed at 70 °C for 10 h before photoirradiation.

where n is the number of carriers, e is the charge of carriers, and μ is the mobility of carriers. **PT6** is a very amorphous material as discussed above, and in such amorphous materials, hopping of carriers plays an important role in the conduction mechanism. In **PT6**, since the conducting units of polymer chains are distributed randomly, it is assumed that the hopping of carriers occurs partially along the polymer backbone. It has been reported that the solid-state UV–VIS absorption spectra of regiochemically random polymers (H–T, >50%) show the maximum absorption around 500 nm for the π–π^* transition of π-conjugated units, while those of regioregular polymers (H–T, >98%) show a much longer maximum absorption wavelength around 550 nm.[34,35] In this study, the change in absorbance around 530 nm, which might be assigned to the π–π^* transition of the conducting units with enhanced regularity of polymer backbone and/or to the charge transfer complex, was observed before and after photoirradiation. On irradiation the conductivity increased with a concomitant increase in absorbance around 530 nm. This result means the isomerization of the azobenzene moieties affects both the number and the mobility of carriers.

Conclusions

We propose here two hypotheses to interpret the observed phenomenon. One is the conformational change of the polymer backbone. The properties of *cis*-azobenzene are very different from those of *trans*-azobenzene, *e.g.*, the polarity of *cis*-azobenzene is much higher than that of *trans*-azobenzene. When properties of a polymer matrix such as density are changed due to *trans–cis* photoisomerization, the coplanarity of the thiophene rings may be increased. The other hypothesis is the formation of a charge transfer complex. It may be possible that a charge transfer complex is formed between *cis*-azobenzene as an electron-withdrawing group and the thiophene ring as an electron-donating group, which results in a similar effect to doping and enhances the conductivity with an increase in the concentration of the *cis* form. Although it is not clear at the present stage of research which hypothesis is correct, our focus is not only on the conformational change but also on the formation of the charge transfer complex. From the results obtained in the present study, photoresponsive polythiophene derivatives are promising materials in view of the reversible control of electrical properties by light.

References

1 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
2 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Dekker: New York, 1986, Vol. 1 and 2.
3 R. D. McCullough and S. P. Williams. *J. Am. Chem. Soc.*, 1993, **115**, 11608.
4 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.
5 T.-A. Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1992, **114**, 10087.
6 C. A. Sandstedt, R. D. Rieke and C. J. Eckhardt, *Chem. Mater.*, 1995, **7**, 1057.
7 K. Faid, M. Frechette, M. Ranger, L. Mazerolle, I. Levesque, M. Leclerc, T.-A. Chen and R. D. Rieke, *Chem. Mater.*, 1995, **7**, 1390.
8 G. H. Brown, *Photochromism*, *Techniques of Chemistry*, Vol. III, Wiley Interscience, 1971.
9 M. Irie, M. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894.
10 T. Saika, M. Irie and T. Shimidzu, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2123.
11 K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1993, **115**, 6442.
12 K. Sayo and M. Irie, *J. Phys. Chem.*, 1992, **96**, 7671.
13 G. M. Tsivgoulis and J.-M. Lehn, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1119.
14 A. Yassar, C. Moustrou, H. Korri-Youssoufi, A. Samat, R. Gugliemetti and F. Garnier, *Macromolecules*, 1995, **28**, 4548.
15 I. Levesque and M. Leclerc, *Macromolecules*, 1997, **30**, 4347.
16 L. M. Goldenberg, M. R. Bryce, S. Wegener, M. C. Petty, J. P. Cresswell, I. K. Lednev, R. E. Hester and J. N. Moore, *J. Mater. Chem.*, 1997, **7**, 2033.
17 S. A. Chen and C. S. Liao, *Synth. Met.*, 1993, **55–57**, 4950.
18 S. A. Chen and C. S. Liao, *Makromol. Chem. Rapid Commun.*, 1993, **14**, 69.
19 T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, 1991, **182B**, 357.
20 A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 1989, **19**, 307.
21 K. Yoshino, S. Hayashi and R. Sugimoto, *Jpn. J. Appl. Phys.*, 1984, **23**, L899.
22 T. Yamamoto, K. Sanechika and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1497, 1503.
23 T. Yamamoto, *J. Synth. Org. Chem. Jpn.*, 1995, **53**, 77.
24 M. R. Anderson, D. Selse, H. Jarvinen, T. Hjertberg, O. Inganas, O. Wennerstorm and J. E. Osterholm, *Macromolecules*, 1994, **27**, 6503.
25 R. M. S. Maior, K. Hinkelmann, H. Eckent and F. Wudl, *Macromolecules*, 1990, **23**, 1268.
26 M. Sato and H. Morii, *Macromolecules*, 1991, **24**, 1196.
27 M. Leclerc, M. F. Diaz and G. Wegner, *Makromol. Chem.*, 1989, **190**, 3105.
28 T. Yamamoto, D. Komarudin, M. Arai, B. L. Lee, H. Suganuma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda and H. Matsuda, *J. Am. Chem. Soc.*, 1998, **120**, 2047.
29 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.
30 G. Barbarella, A. Bongini and M. Zambianchi, *Macromolecules*, 1994, **27**, 3039.
31 Y. Miyazaki and T. Yamamoto, *Synth. Met.*, 1994, **64**, 69.
32 P. L. Burtlett and K. Birkin, *Synth. Met.*, 1993, **61**, 15.
33 T. M. Sweger and M. J. Marsella, *Adv. Mater.*, 1994, **6**, 595.
34 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.
35 R. D. McCullough and S. P. Williams, *J. Am. Chem. Soc.*, 1993, **115**, 4910.

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