

# Structure Dependence of Photochromism of Azobenzene-Functionalized Polythiophene Derivatives

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**ABSTRACT:** Two novel azobenzene-functionalized polythiophene derivatives, poly[4-((4-(phenyl)azo)phenoxy)butyl-3-thienylacetate] (PATH-4) and the copolymer of 3-hexylthiophene and 4-((4-(phenyl)azo)phenoxy)butyl-3-thienylacetate (COP-64) were synthesized. The structure and photoelectronic behavior of both polythiophene derivatives were characterized by NMR, FTIR, UV-vis, XRD, GPC, modulated DSC, and photoluminescence spectroscopy. These new polymers combine photoluminescence property and photochemical

behavior of both polythiophene-conjugated backbones and the photoisomerizable moieties in the side chains. The photoluminescence property of polymers so obtained can be modified reversibly through the photochemical isomerization reaction of the photoactive groups in side chains. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 863–869, 2008

**Key words:** polythiophene derivatives; photochromism; chromophore; azobenzene

## INTRODUCTION

Of the many conjugated polymers, poly(3-alkylthiophenes) have been found to be an unusual class of polymers with good solubility, processibility, environmental stability, electroactivity, and other interesting properties.<sup>1–3</sup> In fact, the use of  $\pi$ -conjugated polymers and oligomers stimulated wide interests for molecular photonic, electronic, and electroluminescent devices.<sup>4–8</sup> The synthesis of 3- and 4-substituted polythiophenes has attracted much interest in the past decade because polythiophenes with suitable substituents not only will have better processibility and stability, but also may possess novel spectroelectrochemical, electrochemical, and optical properties.<sup>9,10</sup> The presence of substituents can even lead to novel physical phenomena that are not found in the unsubstituted parent form. In other words, one can obtain a new material that combines physical properties characteristic of the polythiophene backbone with specific properties of a given substituent. For example, the attachment of photoactive chromophore to the conjugated polythiophene backbone led to the formation of new material with novel dual photochromism.<sup>11,12</sup> Similarly, functionalization of the backbone of polythiophenes with crown ethers or calixarenes led to the fabrication of new types of modified electrode cable of metal complexing.<sup>13–15</sup> Other suc-

cessful attempts of polythiophene functionalization have also been achieved by the addition of functional side groups onto the aromatic backbones, such as redox-active groups,<sup>16,17</sup> mesogenic group,<sup>18</sup> photochromic groups,<sup>19</sup> etc.

In this research, two polythiophene derivatives with photoactive substituents as side chains were synthesized (the synthesis outlines are shown in Scheme 1); the synthesis, characterization, and structure–property relationship of functionalized polythiophenes were also discussed. In particular, we focus our attention on the study of structure-dependence of photochromism, which originates from a combination of conjugated polythiophene backbone and photoactive azobenzene group.

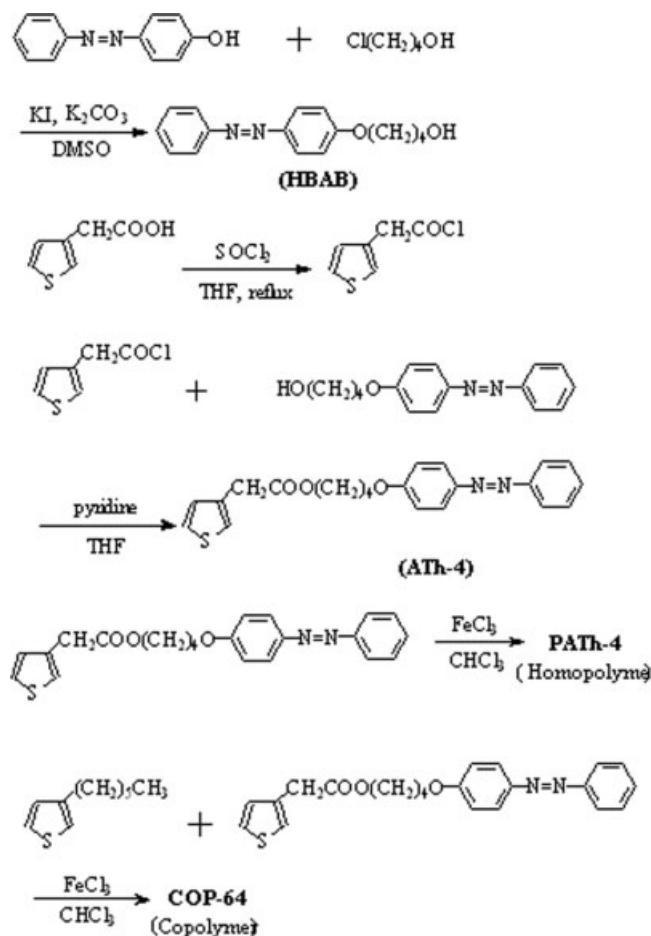
## EXPERIMENTAL

### Synthesis of 4-(4-hydroxybutyloxy)azobenzene

4-(4-Hydroxybutyloxy)azobenzene (HBAB) was synthesized using a procedure similar to the one described by Reck and Ringsdorf.<sup>20</sup> This reaction gave a yellow power (yield, 55%) with a melting point of 100.7°C.

FTIR (KBr,  $\text{cm}^{-1}$ ): 3302 ( $-\text{OH}$ ), 3064 (Ar;  $=\text{CH}$ ), 2864, 2940 (aliphatic;  $\nu_s$  and  $\nu_{as}$  of  $-\text{CH}_2-$ ), 1604, 1583, 1474 (Ar;  $\text{C}=\text{C}$ ), 1501, 1442 ( $\text{N}=\text{N}$ ; cis and trans),<sup>21</sup> 1254, ( $\text{C}-\text{O}-\text{C}$ ;  $\nu_a$ ), 1058 ( $\text{C}-\text{O}-\text{C}$ ;  $\nu_s$ ), 830 (Ar;  $=\text{CH}$ , p-substituted benzene ring), 686, 766 (Ar;  $=\text{CH}$ , monosubstituted benzene ring). <sup>1</sup>H NMR

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**Scheme 1** Synthesis outlines of homopolymer PATH-4 and copolymer COP-64.

(CDCl<sub>3</sub>, 400 MHz, ppm): 1.53 (broad, OH), 1.81 (m, 2H), 1.95 (m, 2H), 3.77 (q, 2H), 4.12 (t, 2H), 7.03 (t, 2H), 7.46 (d, 1H), 7.52 (q, 2H), 7.92 (m, 4H). Anal. calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.11; H, 6.67; N, 10.37; O, 11.85. Found: C, 71.12; H, 6.65; N, 10.35.

#### Synthesis of 3-(4-((4-phenylazo)phenoxy)butyl)thiophenylacetate (ATH-4)

To a two-necked flask equipped with reflux condenser, 0.97 g (6.8 mmol) of 3-thiopheneacetic acid (Aldrich, Beijing, China) was added under N<sub>2</sub> atmosphere; then 5 mL dry THF and 10 mL thionyl chloride (Aldrich) were injected into the flask with a syringe. After the solution was refluxed for 2 h, the excess THF and unreacted SOCl<sub>2</sub> were removed under reduced pressure at the room temperature. The solid residue was dissolved in 10 mL dry THF, and cooled down to 0–5°C by ice bath; then 1.57 g (5.8 mmol) of HBAB and 1 mL pyridine in 15 mL of dry THF were added. After the reaction was stirred for 5 h and the solvent was evaporated out, the product was purified by silica gel column chromatography using chloroform as the

eluant. This reaction gave a yellow crystal (yield, 74%) with a melting point of 87.9°C.

FTIR (KBr, cm<sup>-1</sup>): 3116 (Ar; =CH), 2864, 2940, 2963 (aliphatic; —CH<sub>2</sub>—), 1736 (C=O), 1603, 1581, 1474 (Ar; C=C), 1502, 1441 (N=N; cis and trans)<sup>21</sup> 1248 (C—O—C; ν<sub>a</sub>); 1062 (C—O—C; ν<sub>s</sub>), 830 (Ar; =CH, p-substituted benzene ring), 687, 770 (Ar; =CH, monosubstituted benzene ring). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 1.89 (m, 4H), 3.69 (s, 2H), 4.08 (t, 2H), 4.23 (t, 2H), 7.01 (d, 2H), 7.08 (s, 1H), 7.3 (d, 2H), 7.46 (s, 1H), 7.51 (t, 2H), 7.92 (m, 4H). Anal. calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>SO<sub>3</sub>: C, 67.01; H, 5.58; N, 7.11; S, 8.12; O, 12.18. Found: C, 67.03; H, 5.56; N, 7.10; S, 8.08.

#### Synthesis of poly[3-(4-((4-phenylazo)phenoxy)butyl)thiophenylacetate] (PATH-4)

The polymerization was carried out by chemical oxidation using anhydrous FeCl<sub>3</sub> according to a procedure similar to that of Daoust and Leclerc.<sup>22</sup> A dark brown powder was obtained with a yield of 39%.

#### Synthesis of copolymer of 3-(4-((4-phenylazo)phenoxy)butyl)thiophenylacetate and 3-hexylthiophene (COP-64)

The copolymerization was carried out by seed-polymerization method using anhydrous FeCl<sub>3</sub> as oxidant. In a 50-mL Schlenk reaction flask, 0.9 g (5.5 mmol) of anhydrous FeCl<sub>3</sub> was quickly added, which was subsequently evacuated and flushed with argon three times. Then 15 mL of anhydrous CHCl<sub>3</sub> was syringed into the reactor at 0–5°C, followed by the addition of 0.2 g (0.51 mmol) monomer in 3 mL CHCl<sub>3</sub> in one portion. After 10 min, a solution of 3-hexylthiophene (3HT) in 5 mL of CHCl<sub>3</sub> was added in a dropwise manner for 20 min. Then the reaction mixture was stirred at the room temperature for some time. The polymerization reaction was terminated by the addition of 200 mL of methanol. The precipitated polymer was then washed repeatedly with water and methanol, and dedoped in aqueous ammonia. Finally the copolymer was further purified in a Soxhlet apparatus with methanol for 24 h. The obtained product was a brownish-black powder and the yield was 56%.

#### Measurements

FTIR spectra were recorded on a PerkinElmer System 2000 FTIR spectrometer. NMR spectra were recorded on a BRUKER 400 NMR spectrometer at 400 MHz. The elemental analyses were carried out with a mitamura riken kogyo micro elementary analyzer. Differential scanning calorimetry (DSC) analyses were performed at 5°C/min on a TA instruments using 2920 modulated DSC (model 2920). Molecular weights of samples were measured by gel permeation chromatography (GPC),

**TABLE I**  
Compositions and Average Molecular Weights  
of PATH-4 and COP-64

Sample	Initial feed	Composition <sup>a</sup>		$M_n$ ( $10^{-3}$ )	$M_w$ ( $10^{-4}$ )	$M_w/M_n$
	(3TH : ATH-4) (mol/mol)	(3TH : ATH-4) (mol/mol)				
PATH-4	–	–		5.39	1.43	2.65
COP-64	5.80 : 1	8.62 : 1		32.5	5.46	1.68

<sup>a</sup> Calculated from <sup>1</sup>H NMR.

waters 410; eluent, THF) calibrated with monodispersed polystyrene standards. X-ray diffractions of polymer films on glass slides were measured using a Rigaku Rint 2000 X-ray diffractometer and operated at 40 kV and 30 mA. The data were collected from 1.5° to 40° (2 $\theta$ ) at a scan rate of 2°/min. UV–vis spectra were obtained using an UV–vis recording spectrophotometer (Shimadzu, model UV-2501PC). Fluorescence measurements were conducted on a Shimadzu RF5000 spectrofluorophotometer. The photochromic experiments were carried out using an ARC lamp (Oriel, model 68910; 200–500 W) as the light source. The monochromatic light peaked at 360 and 410 nm was isolated using filter (models 58650 and 59285).

## RESULTS AND DISCUSSION

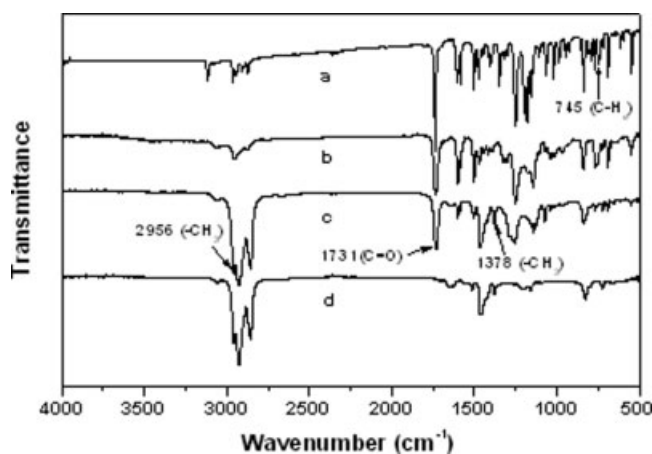
All polymerization processes, including homopolymerization and copolymerization, in our research were carried out under lower temperature and controlled addition of monomer because  $\alpha$ – $\alpha'$  coupling can be considered predominant during the polymerization process carried out under these experimental conditions. The oxidative polymerization of monomer Ath-4 in the presence of FeCl<sub>3</sub> was easy to carry out without any difficulties. For the copolymerization of Ath-4 and 3-HT, however, to obtain the copolymer, the seed-oxidation polymerization technique was used. That is, the monomer ATH-4 was first initiated by FeCl<sub>3</sub> and polymerized to form the polymer active species with moderate molecular weights; then the polymer active species was used to initiate the polymerization of 3-HT to form copolymer. It should be also stressed that the amount of oxidant FeCl<sub>3</sub> used in copolymerization was strictly controlled in case the formation of P3HT homopolymer in the second step.

Both PATH-4 and COP-64 were found to be partially soluble in chloroform, THF, and methylene chloride. Only the soluble part was used to characterize and carry out the measurements of optical properties. The composition and molecular weight as well as the polydispersity index of both polymers are listed in Table I. It can be seen that the real composition (3HT : ATH-4) of COP-64 is higher than that of the initial feed because the insoluble part of the copolymer is significantly enriched in ATH-4 units when compared with

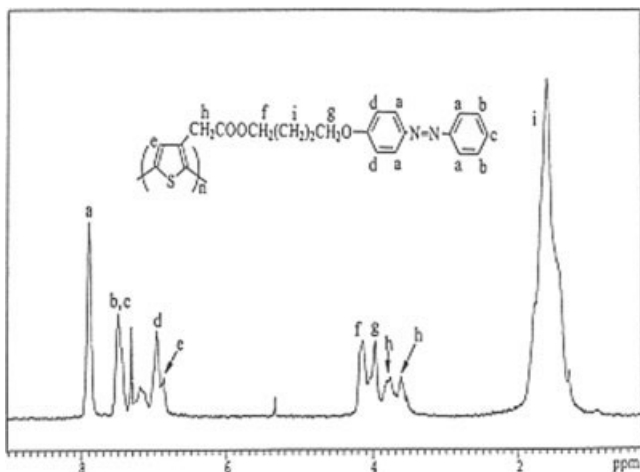
the soluble fraction. Furthermore, COP-64 has higher molecular weight and lower molecular weight distribution when compared with PATH-4.

Figure 1 illustrates the FTIR spectra of polymer PATH-4 and copolymer COP-64, along with spectrum of the monomer ATH-4. For comparison, the spectrum of poly(3-HT) (P3HT) is also presented in Figure 1. The polymerization and copolymerization processes are confirmed by the disappearance of the band at 745 cm<sup>-1</sup>, which is attributable to C–H <sub>$\alpha$</sub>  out-of-plane deformation vibration of thiophene rings. Spectral features of the ester derivatives of ATH-4 are clearly seen in the copolymer spectrum, especially the band at 1731 and 1252 cm<sup>-1</sup>, which can be ascribable to carbonyl (C=O) stretching vibration and C–O–C stretching vibration ( $\nu_{as}$ ) respectively. Furthermore, the absorption bands occurring at 1378 cm<sup>-1</sup> (–CH<sub>3</sub>,  $\delta_s$  deformation vibration) and 2956 cm<sup>-1</sup> (–CH<sub>3</sub>,  $\nu_{as}$  stretching vibration) in COP-64 are characteristic of 3-HT blocks; thus the present FTIR data support the existence of Ath-4 and 3-HT segments in copolymer. It is necessary to mention that some of the FTIR bands associated with the polythiophene backbone strongly superimpose with those originating from the chromophore. For example, the peak at 830 cm<sup>-1</sup> (Ar; =CH, p-substituted benzene ring) in azobenzene is very close to the peak at 827 cm<sup>-1</sup> associated with the out-of-plane C–H <sub>$\beta$</sub>  deformation vibration of thiophene rings, which is characteristic of 2,3,5-trisubstituted thiophene ring.<sup>23–25</sup>

Figure 2 shows the <sup>1</sup>H NMR of homopolymer PATH-4. On the basis of the comparison with the spectrum of monomer, we can assign the following peaks for PATH-4: 1.54 (–(CH<sub>2</sub>)<sub>4</sub>–), 3.57, 3.75 (–CH<sub>2</sub>–COO–), 3.93 (–CH<sub>2</sub>–O–Ar), 4.10 (–COO–CH<sub>2</sub>–), 6.93, 7.46, 7.86 (protons of phenylene rings), 6.90 ( $\beta'$ -proton of thiophene ring). The small peak located around 7.15 is not well resolved and has multiplet splitting, which is due to the  $\beta'$ -proton of the

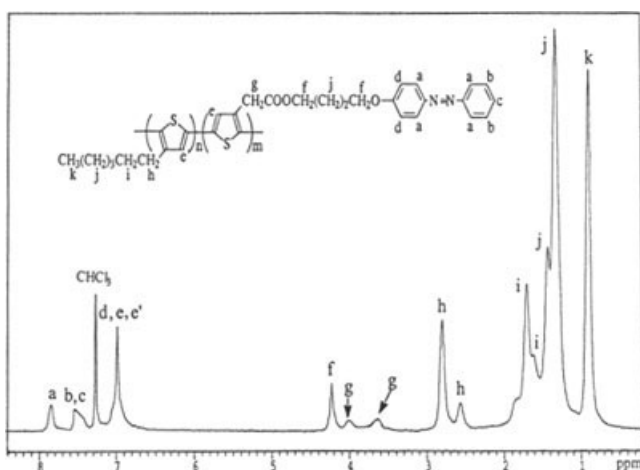


**Figure 1** FTIR spectra of (a) monomer ATH-4, (b) PATH-4, (c) COP-64, and (d) P3HT.



**Figure 2**  $^1\text{H}$  NMR spectrum of homopolymer PATH-4.

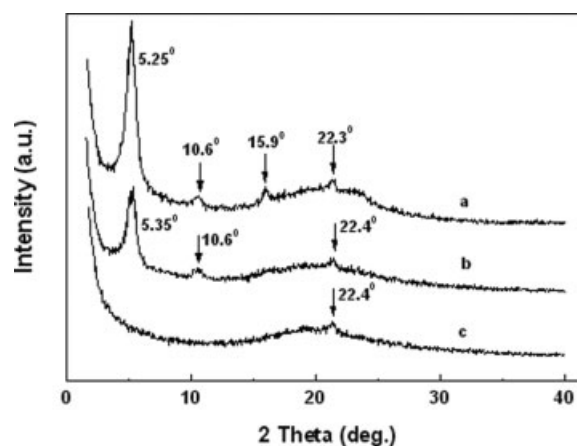
thiophene ring for various regioisomeric units in the polymer chain. Previous reports have shown that the oxidative polymerization of  $\beta$ -substituted thiophene monomer with ferric chloride always led to two different types of couplings: head-to-tail and head-to-head. The two peaks located at 3.57 and 3.75 ppm arise from the methylene protons between the ester group and the thiophene ring, which show that PATH-4 has a stereorandom chain structure with almost equal distribution of head-to-tail and head-to-head linkages along the polymer chain. From the  $^1\text{H}$  NMR spectrum of the copolymer of ATH-4 with 3-HT (Fig. 3), the following assignments corresponding to the protons of 3-HT unit can be given: 0.90 ( $-\text{CH}_3$ ), 1.34, 1.43 ( $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Me}$ ), 1.59, 1.70 ( $\beta\text{-CH}_2-$ ), 2.54, 2.80 ( $\alpha\text{-CH}_2-$ ). The peaks assigned to the ATH-4 unit are as follows: 1.34, 1.42 ( $-(\text{CH}_2)_2-$ ), 3.59, 3.96 ( $-\text{CH}_2-\text{COO}-$ ), 4.22 ( $-\text{COO}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{O}-\text{Ar}$ ), 6.98, 7.46, 7.84 (protons of phenylene rings). The peak at 6.98 ascribable to the  $\beta'$ -proton of thio-



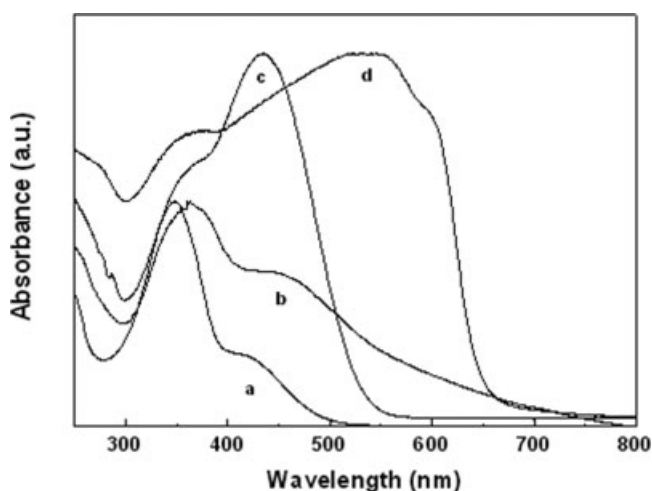
**Figure 3**  $^1\text{H}$  NMR spectrum of copolymer COP-64.

phene ring of both ATH-4 and 3-HT units overlaps with that associated with the phenylene ring. Variations in configuration and location of some peaks of ATH-4 unit in copolymer COP-64 when compared with those of homopolymer PATH-4 indicate that the adjacent structure and chemical environment of some protons have been changed, which supports the formation of copolymer.

X-ray diffraction patterns of the polymer and copolymer films on glass slide cast from chloroform solution are shown in Figure 4. Upon scanning from  $1.5^\circ$  to  $40^\circ$ , at a scan rate of  $2^\circ\text{C}/\text{min}$ , three separate diffraction peaks appeared in COP-64 diffraction patterns: a very intense peak with a maximum intensity at  $5.35^\circ$ , and two small but distinct diffraction peaks centered around at  $10.6^\circ$  and  $22.4^\circ$ , respectively. In addition, a broad amorphous peak near  $20^\circ$  is also observed for copolymer COP-64. The crystallinity of COP-64 is lower than that of P3HT as indicated by the less sharp diffraction peak in the XRD spectrum (compare curves a and b of Fig. 4). Unlike the case of P3HT, in which three orders of reflection were present with maxima at  $5.25^\circ$ ,  $10.6^\circ$ , and  $15.9^\circ$ , respectively [Fig. 4(a)], only the first- and second-order reflection of COP-64 sample were observed. This reveals that a lower degree of space filling of the side chains exists in COP-64 than in P3HT<sup>26</sup> probably due to the presence of the bigger chromophore groups and more polar carbonyl groups, which hinder the intercalation of the side chains. This explanation can also be supported by the XRD results of homopolymer PATH-4, in which only a small diffraction peak at  $\sim 22^\circ$  appeared in addition to a broad amorphous peak at wide-angle region. The small diffraction peaks centered at  $\sim 22^\circ$  corresponding to a  $d$ -spacing of 3.9 Å for COP-64 and PATH-4 can be ascribed to the spacing between two successive stacking planes of coplanar subchains as has already been assigned for P3HT.<sup>26,27</sup>



**Figure 4** X-ray diffraction patterns of polymer films cast from chloroform solutions: (a) P3HT, (b) COP-64, and (c) PATH-4.



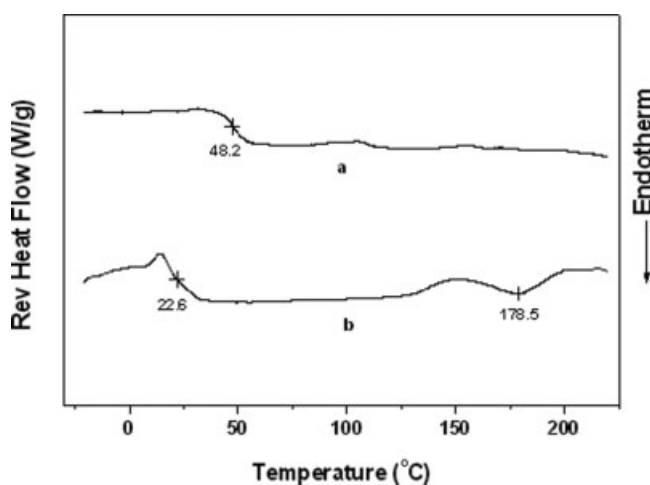
**Figure 5** UV-vis absorbance spectra of PATH-4 (a) in chloroform solution, (b) in the solid state and COP-64, (c) in chloroform solution, and (d) in the solid state.

The optical properties of both neutral polymers were also analyzed, and their UV-vis absorbance spectra in the solid and in solution are given in Figure 5. It should be noticed that the second absorbance band of COP-64 associated with the conjugated polythiophene backbones showed a much more obvious bathochromic shift in the solid than in chloroform solution. The maximum bathochromic shift is more than 100 nm (548 vs. 436 nm). This reveals that the packing of polymer chains in the condensed phase is anticipated to favor a coplanar arrangement of the adjacent thiophene rings, which results in a bathochromic shift in the absorbance in comparison with the solution-phase polymer. Similar UV-vis absorbance changes were also observed for PATH-4 in the solid and in the solution. But in this case, the second absorbance band associated with the conjugated polythiophene backbones in the solid exhibited a red shift of only 23 nm in comparison with that in chloroform solution (448 vs. 425 nm in the case of solution). The difference in band gap between COP-64 and PATH-4 probably arises from their different steric interactions among the side chains. It is known that these steric interactions can induce a nonplanar conformation and, eventually, reduce the effective conjugation length.<sup>22</sup> Too strong side-chain steric interactions among PATH-4 molecules make most PATH-4 chains to adopt a nonplanar conformation even in the solid. Therefore, no obvious nonplanar-to-planar conformational transition can take place between in solution and in the solid state. Furthermore, it is very interesting to note that the first absorbance band related to  $\pi$ - $\pi^*$  transition of trans isomers of the azobenzene for PATH-4 also showed a bathochromic shift of about 17 nm (365 vs. 348 nm) in the solid when compared with that in chloroform solution. This might be related to the

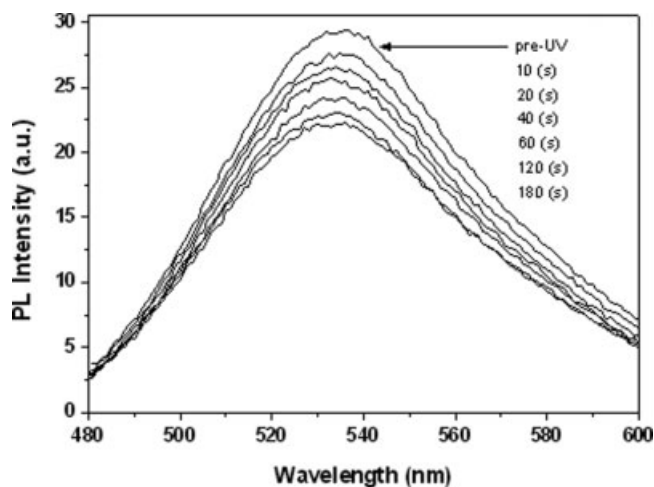
solvatochromic effect; however, this point is highly speculative and a deeper understanding of this phenomenon will require additional studies to characterize it more completely.

Figure 6 shows MDSC thermograms of PATH-4 and copolymer COP-64. When the samples were subjected to the heating scan from  $-30$  to  $230^\circ\text{C}$ , COP-64 displayed two apparent transitions as indicated by the reversing heat flow curves. The first one at  $22.6^\circ\text{C}$  can be assigned to the glass transition temperature  $T_g$ , and the second one around  $178.5^\circ\text{C}$  is the melting temperature of copolymer. For PATH-4, however, only one transition at  $48.2^\circ\text{C}$  appeared during the heating scan, which corresponds to the glass transition. This further confirms the amorphous structure of PATH-4. These results also reveal that COP-64 has a much higher ordered phase when compared with PATH-4; they also indicate that the flexible side chain can provide a higher free volume, allowing the molecular chains to realign more easily than the rigid side chain, which agree well with the XRD results.

The effects of trans-cis isomerization of photoactive azobenzene groups on photoluminescence properties of both polymer main chains were also investigated. Upon irradiation by the UV light of 362 nm, the intensity of fluorescence of PATH-4 was found to decrease with UV irradiation (Fig. 7). On the other hand, the above-mentioned process is also reversible; when the irradiated samples were irradiated by the visible light of 410 nm, the intensity of fluorescence steadily increased up to the starting value before irradiation (see Fig. 8). These results indicate that the optical properties of the azobenzene-functionalized polythiophene can be controlled reversibly by the photoinduced isomerization of the photoactive groups covalently attached to the thiophene rings. For copolymer COP-64, however, the emission intensity change is less prominent (Fig. 9). It is well known that the properties

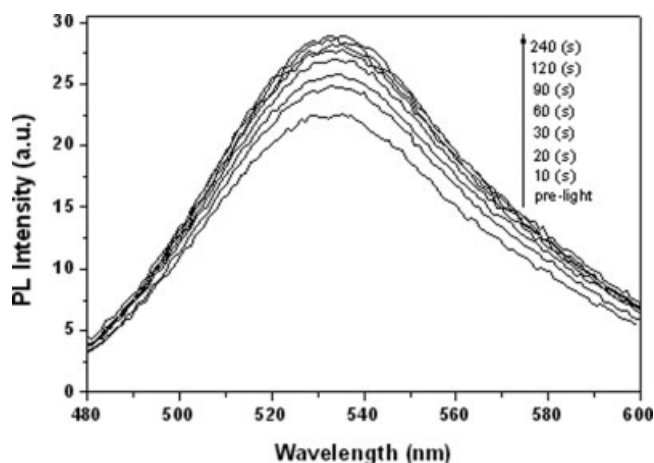


**Figure 6** MDSC thermograms of (a) PATH-4 and (b) COP-64.

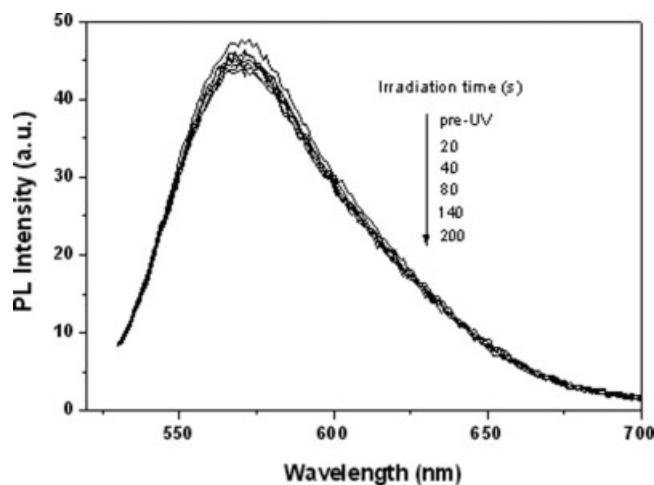


**Figure 7** Photoluminescence spectra of PATH-4 in chloroform for a 460-nm-excitation wavelength with different irradiation time by the UV light at 362 nm (1.68 mW).

of *cis*-azobenzene are very different from those of *trans*-azobenzene. For an unsubstituted azobenzene, when the linear *trans*-isomers changes to the bent *cis*-isomers, the distance between the *para*-carbon atoms decreases from 9 to 5.5 Å and the dipole moment increases from 0 to 3.0 D. Thus, the *trans*-*cis* photoisomerization will bring about a structural rearrangement in the azobenzene side chains, producing steric pressure and electronic interactions that could force changes in the conformation of polymer main chain. The torsion angle between the thiophene rings of main chain decreases with the reorganization of azobenzene chromophore side chains, which will result in an increase in the overlapping of the neighboring  $p_z$  atomic orbital; hence, the degree of conjugation (coplanarity) of polythiophene backbone will increase accordingly. It has been reported that the twisted form of the conju-



**Figure 8** Photoluminescence spectral changes of the irradiated PATH-4 in chloroform for a 460-nm-excitation wavelength with different irradiation time by the visible light of 410 nm (1.68 mW).



**Figure 9** Photoluminescence spectra of COP-64 in chloroform for a 518-nm-excitation wavelength with different irradiation time at 362 nm (1.68 mW).

gated polymer backbone shows fluorescence whereas the planar form does not emit at all.<sup>28,29</sup> It has been suggested that the conformational defects (a twisted conformation) can act as traps for energy migration and therefore inhibit nonradiative decay.<sup>30,31</sup> The increase in coplanarity of the thiophene rings caused by photoinduced isomerization of pendent azobenzene chromophore will thus bring about the enhancement of nonradiative decay of excited species.<sup>29,31</sup> Hence, the photoluminescence intensity of PATH4 decreases with the increase in UV irradiation time. For copolymer COP-64, the smaller change in fluorescence intensity with the photoisomerization of azobenzene chromophore can be attributed to the lower content of chromophore in the side chain of copolymer which is not high enough to induce distinct change in coplanarity of polythiophene backbone.

## CONCLUSIONS

Investigations on photochromism of azobenzene-functionalized polythiophenes have indicated that the polymer structure has a strong influence on the conformation and optical properties of the resulting polythiophene derivatives. The *trans*-*cis* photoisomerization of azobenzene chromophore in the side chain has profound effect on the photoluminescence associated with the conjugated polythiophene. The fluorescence intensity was found to decrease with UV irradiation for homopolymer PATH-4. However, for copolymer COP-64, the change of fluorescence intensity was much reduced. The results indicate that the *trans*-*cis* isomerization of the azobenzene group to induce the structural change in the polythiophene backbone has diminished in copolymers because of the lower content of photoactive chromophore in the side chain. The synthesis of photoresponsive polythiophene de-

rivatives opens up a new approach to the development of novel photochromic polymers.

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