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Synthesis, characterization and structure dependence of thermochromism of polythiophene derivatives

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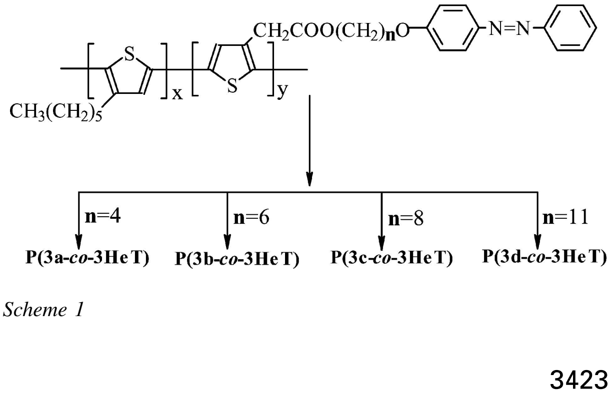
In order to investigate the effect of the bulky pendant group and the spacer length between the pendant group and polythiophene main chain on the optical property of polythiophene backbone, a series of polythiophene derivatives were synthesized via copolymerization of 3-hexylthiophene with four different types of 4-((4-(phenyl)azo)phenoxy)alkyl-3-thienylacetate. The alkyl spacers with different lengths, i.e., butyl, hexyl, octyl and undecyl groups were used between the bulky azobenzene group and the thiophene ring. The compositions and structures of these polythiophene derivatives were characterized. The structural dependence of thermochromic behaviour of these copolymers were systematically studied and results compared with poly(3-hexylthiophene) (P3HeT). A thermochromic temperature coefficient (C_{TC}) was defined for the first time in an attempt to quantitatively compare the sensitivity of the thermochromism in the copolymers. The results have shown that these copolymers with a bulky azobenzene group in side chain have a higher (C_{TC}) value than P3HT and the C_{TC} value of the copolymers increase with increasing the spacer length.

1. 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 [1–4]. Moreover, in comparison with other conjugated polymers, polythiophenes are relatively easy to be functionlized, and the attachment of substituents through β-carbons has relatively little impact on electronic properties of the conjugated backbone. Polythiophenes with suitable substituents in 3-position not only will have better processibility and stability, but may also possess novel electrical, electrochemical and optical properties [5, 6]. Moreover, the presence of substituents in 3-position can even lead to novel physical phenomena that are not found in the unsubstituted parent form. For example, the attachment of photoactive substituents to the conjugated polythiophere backbone let to the formation of new material with novel dual photochromism [7, 8]. Similarly functionalization of the backbone of polythiophenes with crown ethers or calixarenes let to the fabrication of new types of modified electrode cable of metal complexing [9–11]. The introduction of photochromic chromophore as a side group to the conjugated polythiophene backbone significantly alters electrochemical and spectroelectrochemical behavior [12] as well as conductivity [13] of these new polymers as compared to the corresponding parent forms. Furthermore, other successful attempts of polythiophene functionalization have also been achieved by the addition of functional side groups onto the aromatic backbones, such as redox-active groups [14, 15], mesogenic group [16], and photochromic groups [17], etc. Therefore, synthesis of 3-substituted polythiophenes has attracted much interest both from synthetic considerations as well as from material science.

In this work, a series of polythiophene derivatives (see Scheme 1) with a bulky azobenzene pendent in the side chain were studied. The structure-dependence of thermochromism of polythiophene derivatives is discussed. One of the objectives of this work is to investigate whether and how the bulky azobenzene group and the spacer length between the azobenzene group and polythiophene main chain affects the optical properties



Scheme 1

of the polythiophene main chain. It is believed that a better understanding of the structure-property relationships can not only be useful for the improvement of the physical properties of polythiophenes but can also be helpful for the rational design of various conjugated polymers.

2. Experimental details

2.1. Synthesis

4-(4-Hydroxybutyloxy)azobenzene (2a): To a 250 ml three-neck round flask containing 100 ml of anhydrous dimethyl sulfoxide, 5.25 g (26.5 mmol) of 4-phenylazophenol (1a) and 5.53 ml (53.5 mmol) of 4-chloro-1-butanol were added, then 0.25 g of potassium iodide (catalyst) and 7.5 g (54.5 mmol) potassium carbonate were added. The reaction mixture was magnetically stirred and maintained at 110°C by an oil bath for about 8 h. The reaction solution was cooled to room temperature and the salts were filtered out with a Buchner funnel. The filtrate was poured into a fourfold volume of ice-cold water with stirring, then left to stay for overnight. The precipitate was filtered and washed with water for several times, and then it was recrystallized in methanol twice. The product was a yellow powder and the yield is 55%. FT-IR (KBr, cm^{-1}): 3302 (—OH); 3064 (Ar; =CH); 2864, 2940 (aliphatic; ν_s and ν_{as} of $-CH_2-$); 1604, 1583, 1474 (Ar; C=C); 1501, 1442 (N=N; cis and trans); 1254; (C—O—C; ν_{as}); 1058 (C—O—C; ν_a); 830 (Ar;—CH; *p*-substituted benzene ring); 686, 766 (Ar;—CH; mono-substituted benzene ring). ^{1}H NMR ($CDCl_3$, 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 $C_{16}H_{18}N_2O_2$: C, 71.11; H, 6.67; N, 10.37; O, 11.85. Found: C, 71.12; H, 6.65; N, 10.35.

4-(6-Hydroxyhexyloxy)azobenzene (2b), 4-(8-Hydroxyoctyloxy)azobenzene (2c) and *4-(11-Hydroxyundecyloxy)azobenzene (2d)* was synthesized using the same synthetic procedure as for 2a.

Synthesis of 3-(4-((4-phenylazo)phenoxyl)butyl) thienylacetate (3a): To a two-necked flask equipped with a reflux condenser, 0.97 g (6.8 mmol) of 3-thiopheneacetic acid (Aldrich) was added under N_2 atmosphere. Then 5 ml dry THF and 10 ml thionyl chloride (Aldrich) were injected into the flask with a syringe through a rubber septum. After the solution was refluxed for 2 h, the excess THF and unreacted $SOCl_2$ were removed under reduced pressure at 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 4-(4-Hydroxybutyloxy)azobenzene (2a) and 1 ml pyridine in 15 ml of dry THF was added. The reaction mixture was stirred for 5 h, after while the solvent was evacuated by rotary evaporation. The product was purified by the silica gel column chromatography using chloroform as the eluant. This reaction gave a yellow crystal with a 64% yield. FT-IR (KBr, cm^{-1}): 3116 (Ar; = CH); 2864, 2940, 2963 (aliphatic; $-CH_2-$); 1736 (C=O); 1603, 1581, 1474 (Ar; C=C); 1502, 1441 (N=N; cis and trans); 1248; (C—O—C; ν_{as}); 1062 (C—O—C; ν_a); 830 (Ar; =CH; *p*-substituted benzene ring); 687, 770 (Ar; =CH; mono-substituted benzene ring). ^{1}H NMR ($CDCl_3$, 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 $C_{22}H_{22}N_2SO_3$: 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.

3-(6-((4-phenylazo)phenoxyl)hexyl)thienylacetate-(3b), 3-(8-((4-phenylazo)phenoxyl)octyl)thienylacetate (3c) and *3-(11-((4-phenylazo)phenoxyl) undecyl)thienylacetate (3d)* was synthesized using the same synthetic procedure as for 3a.

Synthesis of copolymer of 3-(4-((4-phenylazo) phenoxyl)butyl)thienylacetate and 3-hexylthiophene (P(3a-co-3HeT)). The copolymerization was carried out by seed-polymerization method using anhydrous $FeCl_3$ as catalyst. In a 50 ml Schlenk reaction flask, 0.9 g (5.5 mmol) of anhydrous $FeCl_3$ was quickly put into the flask, which was subsequently evacuated and flushed with argon three times. Then 15 ml of anhydrous $CHCl_3$ was injected into the reactor at 0–5°C by syringe. This was followed by the addition of 0.2 g (0.51 mmol) monomer 3a in 3 ml $CHCl_3$. After a period of time, 0.2 g (1.19 mmol) of 3-hexylthiophene (3HeT) in 5 ml of $CHCl_3$ was added in dropwise manner for 20 min. Then the reaction mixture was stirred at the room temperature for about 4 h. The polymerization reaction was eventually 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 extracted in a Soxhlet apparatus with methanol for 24 hours. $Mw = 6.09\times10^4$, $Mw/Mn = 1.70$.

Synthesis of copolymer of 3-(6-((4-phenylazo) phenoxyl)hexyl)thienylacetate and 3-hexylthiophene (P(3b-co-3HeT)). P(3b-co-3HeT) was similarly synthesized. $Mw = 6.21\times10^4$, $Mw/Mn = 1.65$.

Synthesis of copolymer of 3-(8-((4-phenylazo)-phenoxyl)octyl)thienylacetate and 3-hexylthiophene (P(3c-co-3HeT)). P(3c-co-3HeT) was similarly synthesized. $Mw = 5.89\times10^4$, $Mw/Mn = 1.73$.

Synthesis of copolymer of 3-(11-((4-phenylazo)phenoxyl) undecyl)thienylacetate and 3-hexylthiophene (P(3d-co-3HeT)). P(3d-*co*-3HeT) was similarly synthesized. $Mw = 5.97\times10^4$, $Mw/Mn = 1.69$.

Synthesis of poly(3-hexylthiophene) (P3HeT). P3HT was similarly synthesized. $Mw = 5.34\times10^4$, $Mw/Mn = 1.42$.

2.2. Characterization

FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. NMR spectra were recorded on a BRUKER 400 NMR spectrometer at 400 MHz in deuterated chloroform with TMS as an internal standard. The elemental analyses were carried out with a Mitamura Riken Kogyo Micro Elementary Analyzer. Molecular weights analysis were performed by a waters 410 Gel Permeation Chromatography (GPC), using

TABLE I Compositions and physical properties of polythiophene derivatives

		Head-to-tail content (mol %)		
Samples	Composition[a] (3n:3HeT) (mol/mol)	3n units (n = a, b, c and d)	3HeT segments	T_{TC} ($\times 10^{2}$) ($^{\circ}C^{-1}$)
P(3a-*co*-3HeT)	1:2.76	50	79	1.37
P(3b-*co*-3HeT)	1:3.03	55	82	1.46
P(3c-*co*-3HeT)	1:2.87	48	83	1.79
P(3d-*co*-3HeT)	1:2.92	53	80	3.03
P3HeT	–	–	79	1.36

[a]Calculated from ^{1}H-NMR.

THF as eluent, calibrated with polystyrene standards samples. X-ray diffractions of polymer films on glass slides were measured using a Rigaku Rint 2000 X-ray Diffractometer and operated at 40 kV, 30 mA, the data were collected from 1.5 to 40°C (2θ) at a scan rate of 2°C/min. The thermochromic properties were measured using a UV-Vis recording spectrophotometer (Shimadzu, Model UV-2501PC), with a temperature control unit of the maximum error of ±1°C and a temperature range of 25–250°C. To prepare thin films, the copolymer was dissolved in chloroform, filtered, and then the solution was deposited by casting method onto clean quartz slides and finally dried under vacuum for 24 h.

3. Results and discussion

The four copolymers obtained could be cast into good quality films from chloroform solutions similar to P3HeT homopolymer. The copolymers were relatively stable and no spectral changes were detected for samples stored in dark over a period of three months. The chemical structure and compositions of four copolymers as well as P3HeT homopolymer were analyzed by ^{1}H NMR. The obtained results are summarized in Table I. Typical ^{1}H NMR spectrum for copolymer P(3b-*co*-3HeT) is shown in Fig. 1 as an example and the spectra of the other copolymers are similar. By comparison to the spectra of two monomers, the following assignments corresponding to the protons of 3-hexylthiophene (3HeT) units can be made: 0.93 ($-CH_3$), 1.36, 1.45 ($-CH_2CH_2CH_2-Me$), 1.61, 1.71 (β-CH_2-) [18], 2.56, 2.82 (α-CH_2-) [18]. The peaks assigned to the azobenzene-functionalized thiophene units are as follows: 1.36, 1.45 ($-(CH_2)_4-$), 3.58, 3.79 ($-CH_2-COO-$), 4.18 ($-COO-CH_2-$), 3.96 ($-CH_2-O-Ar$), 7.00, 7.48, 7.87 (protons of phenylene rings). The peak at 7.00 ascribable to the β'-proton of thiophene ring of both azobenzene-based thiophene units and 3HeT units overlaps with that associated with the phenylene ring. The ^{1}H NMR signals at $\delta = 2.56$ and 2.82 ppm correspond to the α-CH_2-group of the 3HeT unit for the head-to-head and head-to-tail coupling, respectively. The intensities of these two peaks suggest the presence of about 82% of head-to-tail coupling in the 3HeT units of copolymer P(3b-*co*-3HeT). Similarly, the peaks at $\delta = 3.58$ and 3.79 ppm correspond to the α-CH_2-group of azobenzene-based thiophene units for the head-to-head and head-to-tail coupling, respectively. The intensities of these two peaks indicate the presence of 55% head-to-tail linkages among the azobenzene-based thiophene units. Furthermore, the small but distinct peak at 3.48 ppm is suggested to be due to the α-CH_2-units of the mixed coupling between the azobenzene-based thiophene unit and a 3-hexylthiophene-unit [19].

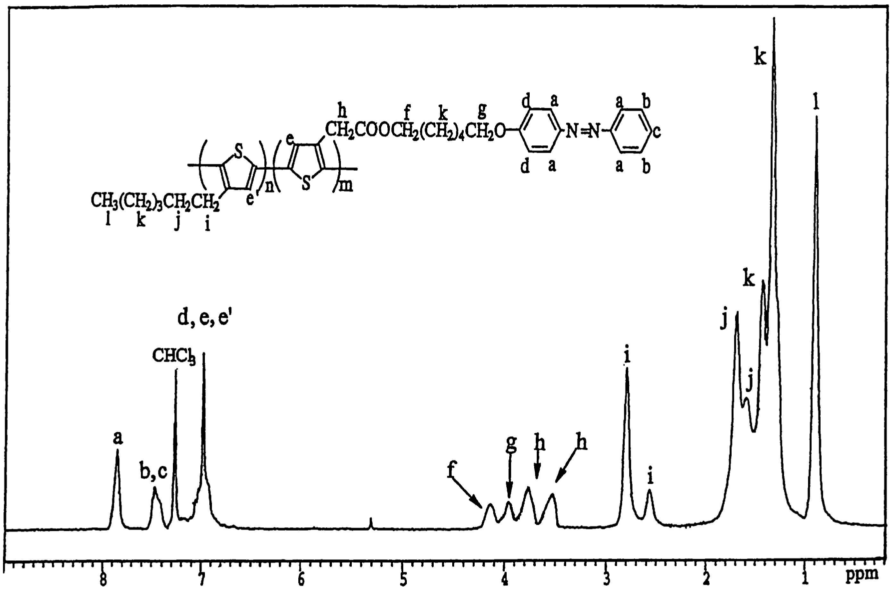


Figure 1 ^{1}H NMR spectrum of the copolymer P(3b-*co*-3HeT).

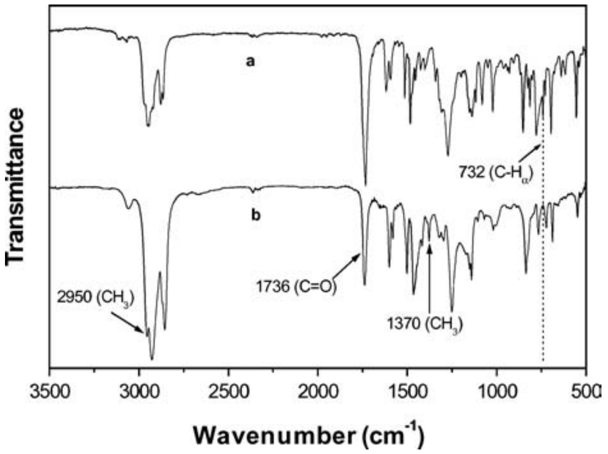


Figure 2 FT-IR spectra of (a) monomer (3b) and (b) copolymer P(3b-*co*-3HeT).

The FT-IR spectrum for copolymer P(3b-*co*-3HeT) is shown in Fig. 2 as curve b. The FT-IR spectrum for monomer 3-(4-((4-phenylazo) phenoxyl)butyl)thienylacetate (3b) is shown in curves a for a comparison. The copolymerization reaction can be monitored by the disappearance of the band located around 732 cm^{-1}, the C—H$_\alpha$ out-of-plane deformation vibration of thiophene rings. The peaks at around 1736 and 1260 cm^{-1} are due to the carbonyl (C=O) stretching vibration and C—O—C stretching vibration (ν_{as}) respectively. The absorption bands at about 1370 cm^{-1} (—CH$_3$, δ_s deformation vibration) and 2950 cm^{-1} (—CH$_3$, ν_{as} stretching vibration) indicate the existence of 3-alkylthiophene blocks. It should be mentioned that some FTIR peaks of polythiophene backbone are overlap with those from azobenzene moiety. For example, the peak at 835 cm^{-1} (Ar; =CH, *p*-substituted benzene ring) in azobenzene is very close to the peak at 830 cm^{-1} associated with the out-of-plane C—H$_\beta$ deformation vibration of thiophene rings, which is characteristic of 2,3,5-trisubstituted thiophene ring [20–22]. Similar result was also observed for the other three copolymers.

X-ray diffraction patterns of P3HeT and copolymer films on glass slide cast from chloroform solution are shown in Fig. 3. For P3HeT, three diffraction peaks were observed at low angle region corresponding to the first-, second- and third-order reflection, respectively. For copolymers, however, only two diffraction peaks were observed at low angle region corresponding to the first- and second-order reflection. This indicates that a lower degree of space filling of the side chain exists in copolymers than in P3HeT due to the presence of bulky chromophore groups and more polar carbonyl groups that hinder the intercalation of the side chains. Furthermore, at wide angle region, in addition to a broad amorphous peak, a small but distinct diffraction peak at 21.5°C was also observed for some copolymers, which can be ascribed to the spacing between two successive stacking planes of coplanar subchains [23].

Thermochromic phenomena of polythiophene derivatives may be extremely useful due to the strong blue shift in the visible region with the thermally induced disordering of the side chains [5]. It has been reported [24] that chromic phenomena can be induced via a large range of external stimuli, which can lead to the development of novel affinitychromic and thermochromic materials such as affinitychromic sensor, optical temperature indicator as well as thermal recording materials. The thermochromic behavior of four copolymers with different spacer lengths was evaluated. Since the shape of spectra are generally similar for these copolymers, the spectral changes of P(3b-*co*-3HeT) as a function of heating temperature is shown in Fig. 4 as a typical example. Upon heating, an absorption band at 500 nm related to a planar (or nearly planar) conjugated backbone showed a strong blue shift with increasing the heating temperature. At last, this absorption band shifted to around 425 nm and no appreciable change was found any more when the heating temperature reached to 210°C and further increased. The latter should be characteristic of a twisted (less conjugated) form of the polythiophene backbone [25]. Moreover, the thermochromic effect was found to be reversible for all the four copolymers in solid film, and, upon cooling, the copolymer film recovers its initial absorption spectrum. A clear isosbestic point is also observed, revealing the co-operative twisting of the azobenzene-functionalized polythiophene backbone. In addition, as shown in Fig. 4, the thermochromic process does not affect the

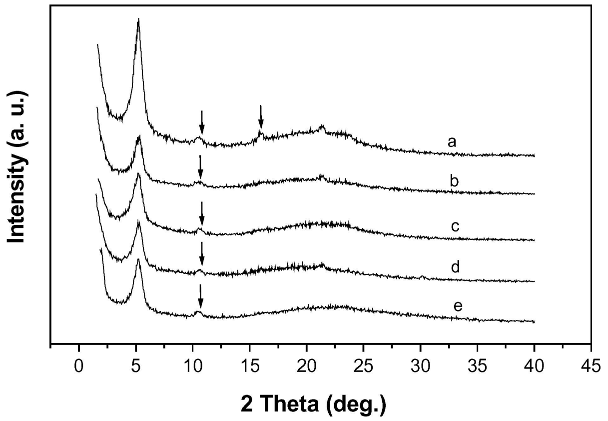


Figure 3 X-ray diffraction patterns of polymer films cast from chloroform solutions: (a) P3HT; (b) P(3a-*co*-3HeT); (c) P(3b-*co*-3HeT); (d) P(3c-*co*-3HeT); and (e) P(3d-*co*-3HeT).

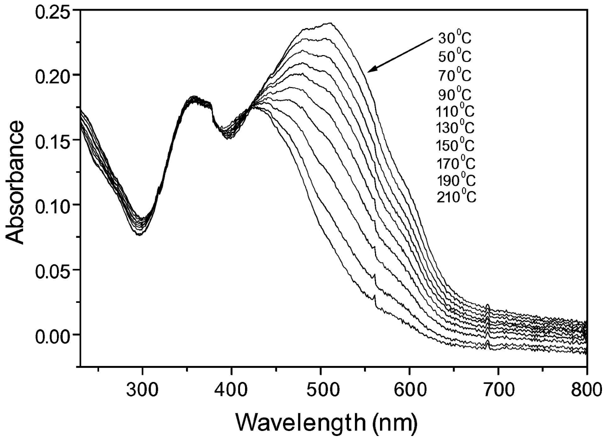


Figure 4 Temperature-dependent UV-visible absorption spectra of copolymer P(3b-*co*-3HeT) film.

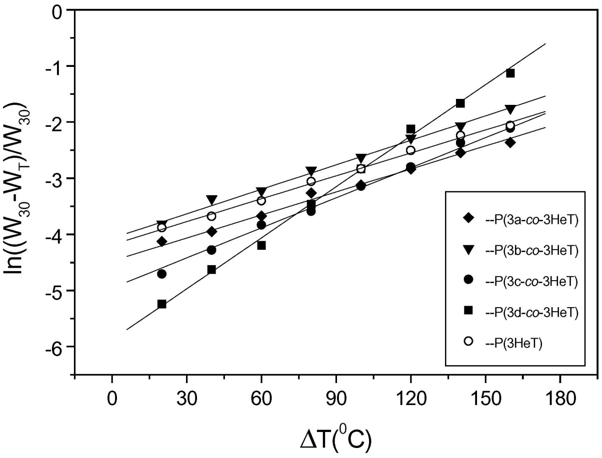


Figure 5 Plots of $\ln((W_{30} - W_T)/W_{30})$ vs. temperature change (ΔT).

absorption band associated with the π–π^* transition of *trans* isomer of the azobenzene chromophore. It is believed that, at elevated temperature during the thermochromism measurement, the azobenzene groups should have *trans* configuration.

In order to quantify the dependence of the thermochromic process upon the spacer length between the azobenzene group and main chain, the logarithm of the change of wavelength at maximum absorption $\ln[(W_{30} - W_T)/W_{30}]$ is plotted against temperature change ($\Delta T = T - T_{30}$), where W_{30} and W_T are the wavelengths of absorption peaks at the temperature of 30°C and T°C, respectively. The slope of plots of $\ln[(W_{30}\text{-}W_T)/W_{30}]$ against ΔT is defined as thermochromic temperature coefficient (C_{TC}). The plots are shown in Fig. 5, and the values of C_{TC} are obtained using linear curve fitting and summarized in Table I. It can been seen that the C_{TC} value increases with the spacer length between azobezene groups and the main chains. In fact the C_{TC} value for P(3a-*co*-3HeT) is comparable to that of poly(3-hexylthiophene) but for P(3d-*co*-3HeT) this value is more than doubled comparing with poly(3-hexylthiophene). It is a relatively well-known phenomenon that [5, 26, 27] the thermochromism of substituted polythiophenes arises from a delicate balance between repulsive side chains steric interactions and attractive interchain interactions, with the latter interactions being necessary to stabilize the low-temperature planar conformation. It is believed that the temperature effect for the steric interaction is more pronounced for bulkier side groups, hence, polythiophene with a longer pendant side chain should give a larger value of C_{TC}. Furthermore, it has been reported that [24, 28] in regioregular polyalkylthiophenes there are cooperative thermochromic transitions of the backbone, whereas in non-regioregular polyalkylthiophenes only localized conformational defects can be created along the backbone. In this study, the regioregularity of the azobenzene substituted thiophene units are similar (48–55%) for the copolymers although it is substantially lower than the hexylthiophene units (79–83%). However, the bulkier azobenzene thiophene segments are expected to influence the twisting of the conjugated polythiophene backbone and hence higher C_{TC} values were observed in the copolymers as compared with P3HeT. This strong dependence of the thermochromic properties upon the type of substituents can be explained by a cooperative formation of intramolecular and intermolecular assemblies, which would be reversibly broken through thermally induced side chain disordering [24].

4. Conclusion

Investigations on thermochromism of a series of polythiophene derivatives with different spacer length between the bulky azobenzene group and polythiophene main chain have indicated that the side chain structure such as nature of the substituents has a strong influence on the conformation and optical properties of the resulting polythiophene derivatives. A higher thermochromic temperature coefficient (C_{TC}) was observed in the copolymers than in P3HeT. And the C_{TC} value of the copolymers was found to increase with increasing the spacer length. This suggests that the bulkier pendant groups in the side chain are more easily to cause the conformational changes in the polythiophene backbone at elevated temperature. This may be attributed to the difference in steric effect of the pendent during the heating process.

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