Optoelectronic properties of thiazole-based polythiophenes

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ABSTRACT: In this work, two thiazole-containing monomers N-(thiazol-2-yl)−2-(thiophen-3-yl)acetamide (ThDBTH) and N,N'-([4,4′-bithiazole]-2,2′-diyl)bis(2-(thiophen-3-yl)acetamide) (Th$_2$DBTH) were synthesized through amidification reaction of 2-(thiophen-3-yl)acetyl chloride with aminothiazole derivatives and characterized by FTIR and ^{1}H and ^{13}C-NMR. The monomers were subjected to electrochemical polymerization and optoelectronic properties of the resultant conducting polymers were investigated. Additionally, copolymerization of ThDBTH in the presence of thiophene was achieved. PThDBTH, PTh$_2$DBTH, and P(ThDBTH-Th) exhibited optical band gaps of 2.15, 2.30, and 1.95 eV, respectively. Switching time and optical contrast of the polymers were evaluated via kinetic studies. The P(ThDBTH-Th) revealed satisfactory switching time and appropriate optical contrast of 1.27 s and 24.97%, respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42206.

INTRODUCTION

Within last 30 years conducting polymers and within the last decade their electrochromic properties have aroused interest both in scientific and commercial society. Among many conjugated polymers, polymers that are based on thiophene derivatives received immense consideration owing to their chemical stability and relative ease in polymerization.[1] Electrochromism refers to the reversible color change of a material upon burst of charge. Various types of materials such as viologens, transition metal oxides, and polymers can be used in the construction of electrochromic devices, which could serve as smart windows, displays, etc. Electrochromic polymers have been the center of attention owing to their promising features such as flexibility, low-power consumption, ease of processing, and low processing cost.[2] Conducting polymers, especially polythiophene[3,4] and polypyrrole[5,6] derivatives, represent a large family of electrochromic materials that are known to possess superior properties. However, products that could be used in daily life applications are yet to be discovered. Incorporation of moieties having different properties in a single repeating unit provides the opportunity to convey properties of these moieties to the polymers as well as to enhance its optical and electrical properties.

Thiazole is a well-known electron-deficient heteroaromatic unit that confines an imine nitrogen in a thiophene unit. Conjugated polymers bearing thiazole units in its structure are well known for demonstrating high mobilities[7] and stacking along the polymer backbone, which gives rise to enhanced π–π interactions and n-dopable polymers. These units find exquisite attention in the field of light-emitting diodes and organic field-effect transistors.[8] Moreover, bithiazole-containing polymers that are chelated with transition metal ions show ferromagnetism.[9,10]

Owing to interesting properties of the thiazole- and thiophene-containing polymers, we proposed the use of thiazole within polythiophene structure through synthesis of two different monomers via simple synthetic approach. These two monomers, abbreviated as ThDBTH [N-(thiazol-2-yl)−2-(thiophen-3-yl)acetamide] and Th$_2$DBTH [N,N'-([4,4′-bithiazole]-2,2′-diyl)-bis(2-(thiophen-3-yl)acetamide)], were characterized by several techniques such as ^{1}H-NMR, ^{13}C-NMR, and FTIR. Electrochemical behavior of ThDBTH and Th$_2$DBTH both in the presence or absence of boronitrifluoride diethyletherate (BFEE) was studied by cyclic voltammetry (CV). Moreover, copolymerization of ThDBTH with thiophene was achieved, where structural and optoelectronic properties of all polymers were investigated by CV, FTIR, elemental analyses, SEM, spectroelectrochemistry, kinetic, and colorimetry studies.

EXPERIMENTAL

Materials

Acetonitrile (ACN) (Merck), dichloromethane (DCM), and BFEE (Sigma) were used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB), tetrabutylammonium hexafluorophosphate (TBAPF$_6$), and LiClO$_4$ were of electroanalytical grade. Thiophene (Th) (Aldrich) was distilled before use,

3-thiophene acetic acid (Aldrich), triethylamine (TEA) (Aldrich), trifluoroacetic acid (TFA) (A.Aesar), 2-aminothiazole (Merck), thionyl chloride (Aldrich), thiourea (Aldrich), and 1,4-dibromobutanedione(Aldrich) were used as received. 2,2′-Diamino-4,4′-bithiazole (DBTH) was synthesized according to literature starting from thiourea and 1,4-dibromobutanedione.[11,12]

Equipment

NMR spectra were recorded with a Bruker Avance Spectrometer at 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR and Varian Agilent VNMRS Spectrometer at 500 MHz for ^{1}H-NMR and 250 MHz for ^{13}C-NMR. Chemical shifts (δ) were given relative to tetramethylsilane (TMS) as the internal standard. The FTIR spectra were recorded on a Brucker Tensor 27 spectrometer. An Ivium stat potentiostat/galvanostat was used for CV studies. A cell equipped with Pt working and counter electrodes, and a Ag/Ag$^+$ reference electrode was used for CV studies, which were carried out at room temperature under nitrogen atmosphere. Spectroelectrochemical and kinetic studies of the polymers were performed on a Thermo Evolution Array UV–Vis spectrophotometer in a quarts cuvette having indium tin oxide electrode (ITO) or tin-doped indium oxide, Pt wire, and Ag wire as working, counter, and pseudo reference electrodes, respectively. Colorimetry measurements were recorded on a Minolta CS-100A Chroma Meter in a proper box having D-50 illumination. Elemental analyses were performed by LECO, CHNS-932. Scanning electron microscopy (SEM) studies were recorded by a ZEİSS-LEO 1430 SEM operating at 15 kV.

Synthesis of ThDBTH and Th$_2$DBTH

A mixture of 3-thiophene acetic acid (0.5 g, 3.5 mmol) and thionyl chloride (0.48 g, 4.1 mmol) was placed in a 50-mL round bottom flask and then refluxed. After 3 h excess thionyl chloride was removed by vacuum. Later, the crude liquid product was added to a aminothiazole-containing [1.25 mmol for 2-aminothiazole (BTH) or 0.44 mmol for DBTH] THF (10 mL) solution at 0°C and stirred for about 4 h. The crude products were purified on a silica gel column while eluting with 100 : 7 CHCl$_3$: MeOH. ThDBTH and Th$_2$DBTH were achieved with a yield of 42 and 39%, respectively. For ThDBTH: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 11.23 (s, 1H), 7.48 (d, $J = 3.6$ Hz, 1H), 7.41 (dd, $J = 4.9, 3.0$ Hz, 1H), 7.31 (s, 1H), 7.12 (dd, $J = 4.9, 1.3$ Hz, 1H), 7.06 (d, $J = 3.6$ Hz, 1H), 3.96 (s, 2H). ^{13}C-NMR (250 MHz, CDCl$_3$) δ 168.18, 158.78, 136.84, 132.78, 128.24, 127.11, 124.00, 113.90, 37.69. FTIR (KBr, cm^{-1}): 3264, 3174, 3106, 3037, 2946, 2883, 2734, 1684, 1567, 1429, 1333, 1270, 1241, 1192, 1165, 1126, 1062, 973, 814, 757, 718, 669, 624, 551, and 514. For Th$_2$DBTH: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 9.08 (s, 1H), 7.41–7.38 (m, 1H), 7.20 (s, 1H), 7.56–7.03 (m, 1H), 6.81 (s, 1H), 3.85 (s, 2H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ 157.66, 145.08, 132.58, 128.36, 127.58, 124.58, 109.36, 104.83, 37.83. FTIR (KBr, cm^{-1}): 3319, 3266, 3206, 3146, 3079, 2926, 2832, 2718, 1637, 1557, 1431, 1224, 871, 798, 767, 706, 561, 526, and 504.

Electrochemical Polymerization

Polymerization of ThDBTH was achieved potentiodynamically, in the presence of 50 mg monomer, 0.1 M TBAFB in BFEE between 0.0 and 2.0 V, in an electrolysis cell equipped with Pt working and counter electrodes and a Ag/Ag$^+$ reference electrode. Thiophene was used as the comonomer for the synthesis of P(ThDBTH-Th). ThDBTH (50 mg) was dissolved in 5 mL BFEE and 1 μL of Th was introduced into the electrolysis cell containing TBAFB. The films were prepared potentiodynamically by scanning the potential between 0.0 and 1.5 V on ITO glass electrodes. Conducting homopolymer of Th$_2$DBTH was achieved under constant potential electrolysis. Fifty milligrams of Th$_2$DBTH was dissolved in 5 mL BFEE and the solution was introduced into a single-compartment electrolysis cell equipped with Pt working and counter electrodes and a Ag/Ag$^+$ reference electrode. During these studies, TBAFB was used as the supporting electrolyte.

RESULTS AND DISCUSSION

The monomers ThDBTH and Th$_2$DBTH were prepared via a amidification reaction between 2-(thiophen-3-yl)acetyl chloride and corresponding aminothiazole derivative as illustrated in Scheme 1. The structures of the monomers were confirmed by FTIR and ^{1}H and ^{13}C-NMR (Figure 1) analyses.

Electrochemical Polymerization

To investigate the electrochemical behavior of ThDBTH, a CV experiment was performed in TBAFB/ACN supporting electrolyte/solvent system. As reflected in the voltammogram [Figure 2(a)], the monomer exhibited an irreversible electroactivity having an onset at 1.4 V. However, the current intensity sharply decreased upon repetitive cycles. Despite utilization of various solvents (acetonitrile and dichloromethane) and supporting electrolytes (TBAPF$_6$ and LiCIO$_4$) polymer formation was not observed.

In 1995 Xue and coworkers reported the low-potential electrochemical synthesis of polythiophene in BFEE.[13] It was found out that the resultant polymer had higher effective mean conjugation length with remarkable mechanical strength. Linear sweep voltammetry studies showed that the oxidation potential of thiophene was reduced to 1.3 V vs. standart calomel electrode (SCE),[14] which is lower than the overoxidation potential (1.4–1.5 V vs. SCE) of the polymer. Other studies on electrochemical polymerization of bithiophene,[15] terthiophene,[16] and pyrrole in isopropyl alcohol[17] were performed by taking the advantage of the decrease in the oxidation potential of the monomers. Additionally, owing to the decrease in the oxidation potential, reactive metals such as aluminum, nickel,[18] and copper oxide[19] were shown to be useful as the working electrodes for electropolymerization of thiophene. Thus, to benefit from its positive impact, we pursued continuous linear sweep experiments in BFEE, which contains 0.1 M TBAFB. In accordance with the literature, ThDBTH revealed lower oxidation peak (1.2 V) in BFEE and continuous deposition of the polymer onto the WE was monitored by the increase in the polymer's anodic (1.5 V) and cathodic peak (1.1 V) currents [Figure 2(b)]. Free-standing conducting polymer films of ThDBTH were successfully synthesized. However, contrary to its main-chain analogs,[20,21] n-type doping was not available, presumably due to lower degree of stacking. Figure 3 represents the FTIR spectra of ThDBTH and its homopolymer, where ThDBTH revealed the
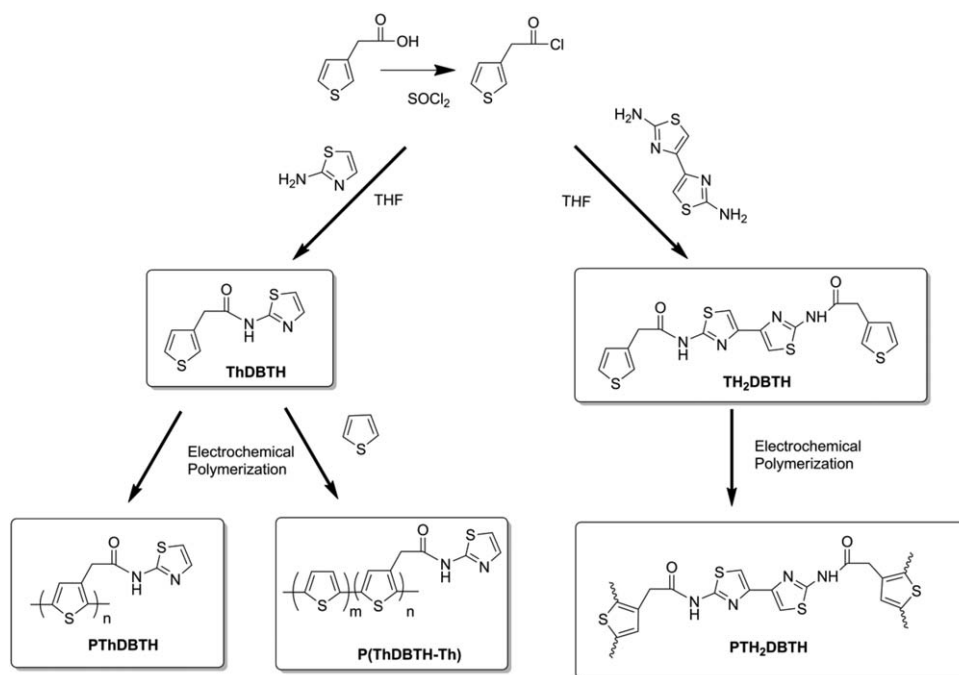
Scheme 1. Schematic representation of monomers and polymers.

following absorptions at 3103 cm^{-1} (aromatic C—H), 2953, 2888 cm^{-1} (aliphatic C—H), 1685 cm^{-1} (C=O stretching, amid I band), 1569 cm^{-1} (C=N), 761 cm^{-1} (thienylene out-of-plane

C—Hα stretching), 1165, 1061 cm^{-1} (in-plane C—H deformations), 1426, 1338 cm^{-1} (aromatic C=C, C—C ring stretchings), 665, 625 cm^{-1} (C—S—C stretching).[22,23] Upon
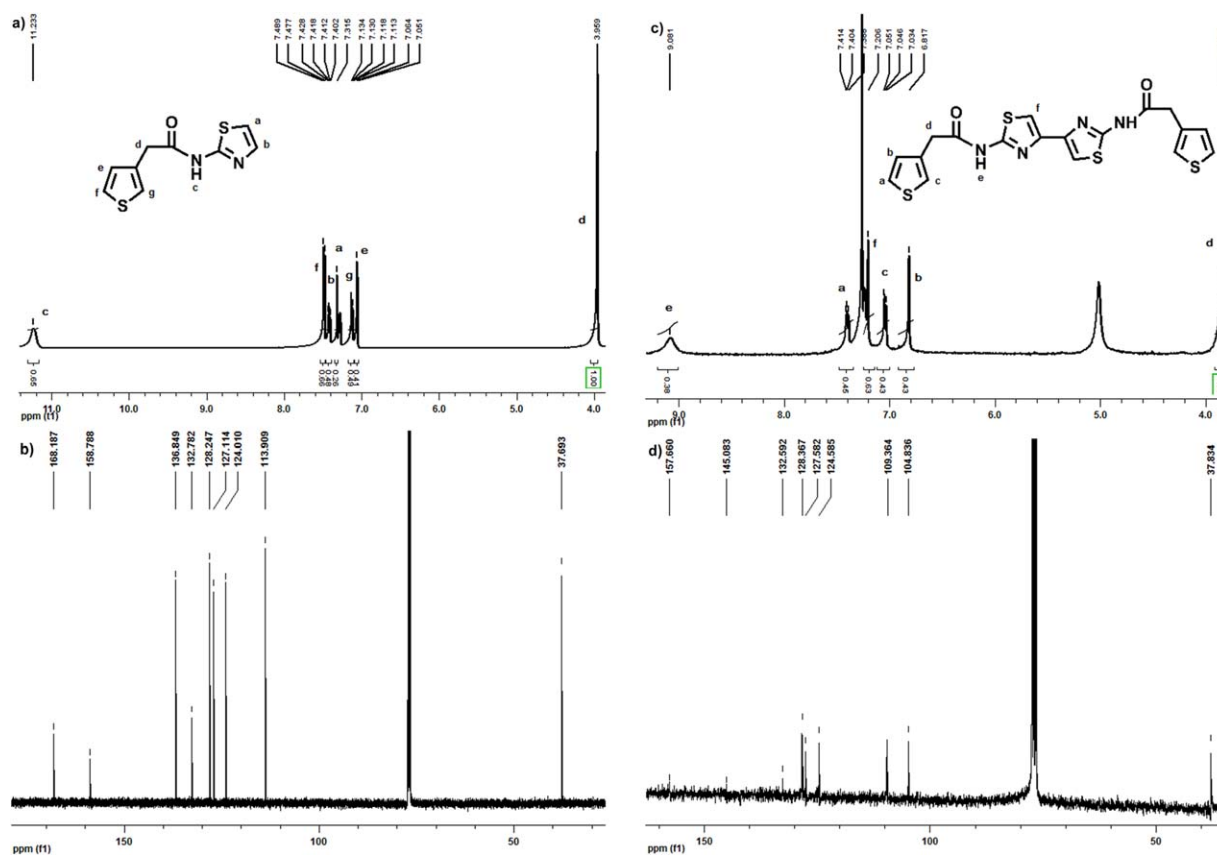
Figure 1. (a) ^{1}H-NMR spectra of ThDBTH in CDCl$_3$; (b) ^{13}C-NMR spectra of ThDBTH in CDCl$_3$; (c) ^{1}H-NMR spectra of Th$_2$DBTH in CDCl$_3$; and (d) ^{13}C-NMR spectra of Th$_2$DBTH in CDCl$_3$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
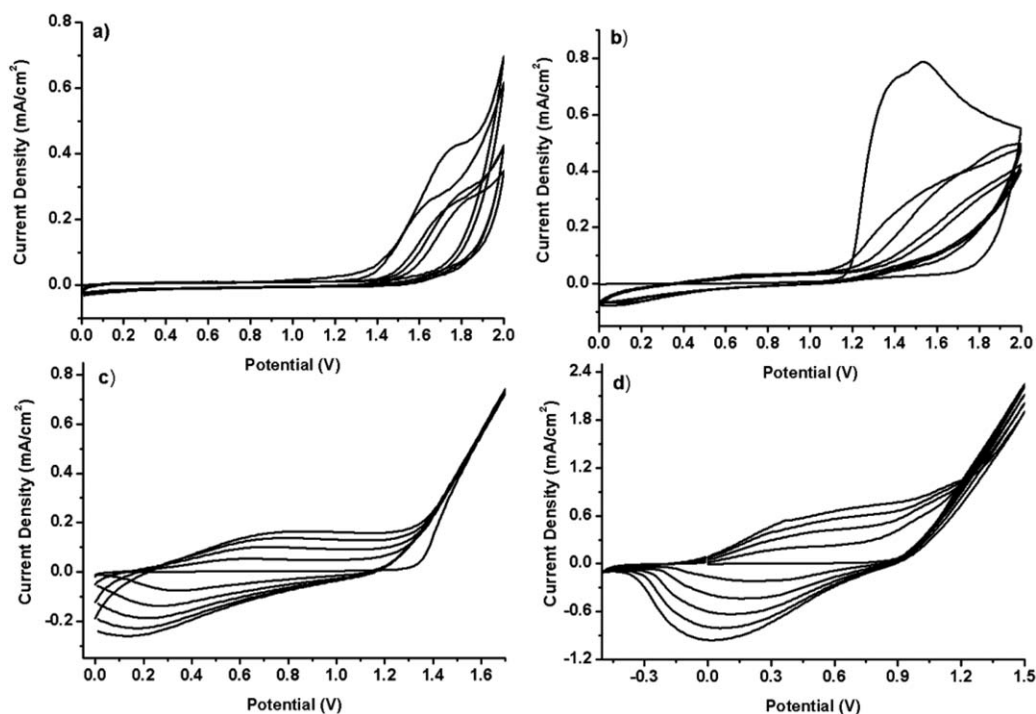
Figure 2. Cyclic voltammogram of (a) ThDBTH in 0.1 M TBAFB/ACN; (b) ThDBTH in 0.1 M TBAFB/BFEE; (c) ThDBTH in the presence of thiophene and 0.1 M TBAFB/BFEE; and (d) thiophene in 0.1 M TBAFB/BFEE, with a scan rate of 100 mV/s.

homopolymerization of ThDBTH, most of the characteristic peaks of the monomer remained unperturbed, such as carbonyl stretching at 1680 cm^{-1} and C=N stretching at 1551 cm^{-1}. However, the band at 761 cm^{-1} indicating C—Hα stretching of the thiophene moiety of the monomer disappeared completely on the spectra of the homopolymer. The shoulder at 1652 cm^{-1} and the intense band at 1084 cm^{-1} were assigned to be due to the formation of polyconjugation upon polymerization, and the presence of dopant anion, respectively.

Similar to ThDBTH, electrochemical behavior of Th$_2$DBTH was examined in the same electrolyte system while scanning the potential between 0.0 and 2.0 V. The monomer revealed an irreversible oxidation peak onset at 1.1 V and maximum at 1.7 V whose intensity decreased upon consecutive cycles. Nevertheless, a thin film of PTh$_2$DBTH was coated on ITO electrode and it was subjected to spectroscopic analysis. In literature, composite electrolyte system made up of TFA, BFEE, and acetonitrile was used for electrochemical polymerization of benzene[24] and 3-chlorothiophene.[25] To overcome the loss of electroactivity problem, we also used TFA-containing composite electrolyte systems. However, a well-defined redox behavior was still not observed.

Electrochemical Copolymerization

Other than chemical tailoring, copolymerization is one of the most efficient approaches for tuning the properties of conducting polymers. Throughout sometime, many studies have focused on electrochemical copolymerization where copolymerization of thiophene with fluorene,[26,27] selenophene,[28] naphthalene dimide,[29] binaphthyl,[30] thiazole,[31] pyridine, and quinoxaline[32] was achieved. With these efforts, numerous novel conducting polymers have been prepared with distinct superior properties,

such as enhanced electrical conductivity and electrochemical activity, fine tuning of band gap, and color of the polymer. Thus, the next step of our study was to proceed toward copolymerization.

For this purpose, continuous linear sweep voltammetry studies were pursued in the presence of thiophene under the same experimental conditions. As seen in Figure 2(c), there was a drastic change in the voltammogram; both the increase in the increments between consecutive cycles and the oxidation potential of the material were different than those of both monomer and pure thiophene, which in fact could be interpreted as the formation of copolymer. The resultant copolymer [P(ThDBTH-Th)] revealed lower oxidation (0.6 V) and reduction (0.3 V) potentials compared to its parent polymer, PThDBTH.

Figure 3(c) reflects the FTIR spectrum of the copolymer having similar vibrational signals as of the homopolymer; such as aromatic C—H, aliphatic C—H, aromatic C=C, C—C ring stretching, and dopant-related peaks around 1084 cm^{-1}. As polythiophene (PTh) does not contain strongly stretching C=O and C=N groups, presence of these bands at 1694 cm^{-1} (C=O) and 1537 cm^{-1} (C=N) could be considered as the proof of successive copolymerization. Moreover, evolution of the new peak at 793 cm^{-1} is in accordance with the FTIR spectra of pristine polythiophene [Figure 3(d)]. To further prove the successive electrochemical copolymerization and determine the composition of the copolymer we have performed elemental analyses (Table I) on PThDBTH, P(ThDBTH-Th). When we compare weight percentages of S and N of the two polymers, it is clear that the copolymer is higher in sulfur content. As the comonomer (thiophene) contains only S as the heteroatom,
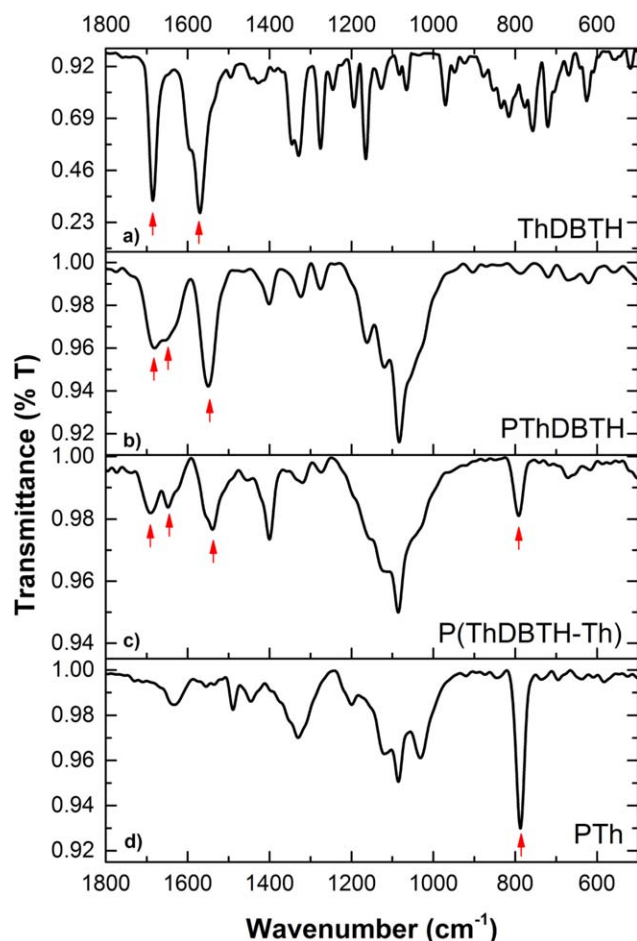
Figure 3. FTIR spectrum of (a) ThDBTH, (b) PThDBTH, (c) P(ThDBTH-Th), and (d) PTh. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

such result ensures inclusion of thiophene units within the copolymer backbone and formation of a true copolymer. Moreover, by considering the molar S/N ratio we could roughly estimate that for every ThDBTH unit within the copolymer structure there are five thiophene units, which is in accordance with the relative increase in the molar C/N ratio also.

Figure 4(a,b,d) represents the SEM images of PThDBTH, PTh, and P(ThDBTH-Th) under same magnification, respectively. As we could see PTh exhibits its well-known compact cauliflower-like appearance upon enlargement [Figure 4(c)], whereas PThDBTH revealed a much more coarser globular structure. The copolymer, on the other hand, presented a different more open morphology from PThDBTH and pure PTh, which further supported the formation of a true copolymer.

Electrochromic Properties of ThDBTH-Based Polymers

To investigate the optoelectronic properties of PThDBTH, the polymer film was deposited on ITO via potentiodynamic electrochemical polymerization of ThDBTH (0.01 M) in the presence of BFEE and TBAFB between 0.0 and 2.0 V. Optoelectronic characterization (Figure 5) of the polymer was performed in a UV–Vis spectrophotometer while incrementally increasing the applied potential between 0.0 and 2.1 V in the same monomer-free elec-

trolyte system. The electronic band gap of the polymer was calculated as 2.15 eV, which is slightly higher than that of PTh (1.99 eV), which was synthesized under the same conditions. It is well known that the nature of the substituted group (both electronic and steric) generally affects optoelectronic properties of conjugated polymers. It has been demonstrated that the alkyl side chains with steric hindrance could cause significant inter-ring twisting, thereby giving rise to a substantial reduction in π-stacking, blue shift in λ_{max}, and increase in the band gap.

At 0.0 V PThDBTH revealed a broad absorption (π–$\pi^\star$ transitions) with λ_{max} of 420 nm. At this state the polymer appeared in yellow color. Amplification of the applied potential resulted in reduction in the intensity of π–$\pi^\star$ transitions along with evolution of new bands located at 710 nm. Upon further oxidation, new charge carriers were formed leading to new absorption at longer wavelengths (beyond 940 nm). In accordance with former studies,[33] these transitions are attributed to polaron and bipolaron charge carrier band formations, respectively. However, despite variation of polarization medium and potential the polymer did not reveal reversible coloration upon repetitive switching.

Later on, we have investigated the spectral behavior of PTh$_2$DBTH in a similar manner. At 0.0 V PTh$_2$DBTH was in neutral state having π–$\pi^\star$ transition at 415 nm. Upon amplification of applied potential this transition diminishes and a new transition at 850 nm evolved. However, it was not possible to reversibly switch this material between its oxidized and reduced forms more than once.

Finally, optoelectronic properties of the copolymer films were investigated. For this purpose, P(ThDBTH-Th) films were deposited onto ITO via potentiodynamic cycling between 0.0 and 1.7 V in TBAFB/BFEE. In neutral state the copolymer displayed orange appearance having a λ_{max} of 480 nm ($E_g = 1.95$ eV), which is considerably different than pure polythiophene ($\lambda_{max} = 497$ nm, red) and PThDBTH ($\lambda_{max} = 420$ nm, yellow). Upon rise in the applied voltage, evolution of the new bands centered at 710 nm and beyond 970 nm was recorded (Figure 6), which were accompanied by gradual decrease in the intensity of the bands at λ_{max} 420 nm. At the ultimate oxidation the copolymer appeared in blue with an intensified absorption in NIR region. As seen in Figure 7 PThDBTH displayed color transition from yellow to blue. The copolymer, on the other hand, revealed orange to blue coloration, which is different from both polythiophene (red-blue) and PThDBTH. However, owing to subjective nature of color, which depends on lighting, viewing angle, etc., we performed colorimetry studies to provide an objective and quantitative practice. Table II reflects the results of the colorimetry studies where L defines relative luminance, a,b defines the hue and saturation of the material on a typical $L^\star a^\star b^\star$- CIE system.
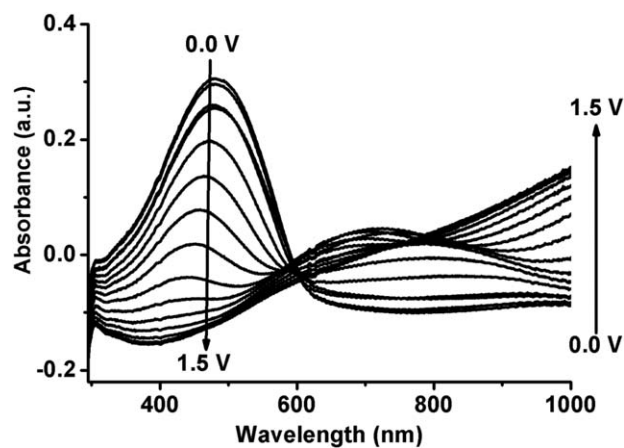
Table I. Elemental Analysis of PThDBTH and P(ThDBTH-Th)

| Material	C %	H %	N %	S %
PThDBTH	22.27	3.53	5.90	12.49
P(ThDBTH–Th)	37.25	3.00	2.93	22.65
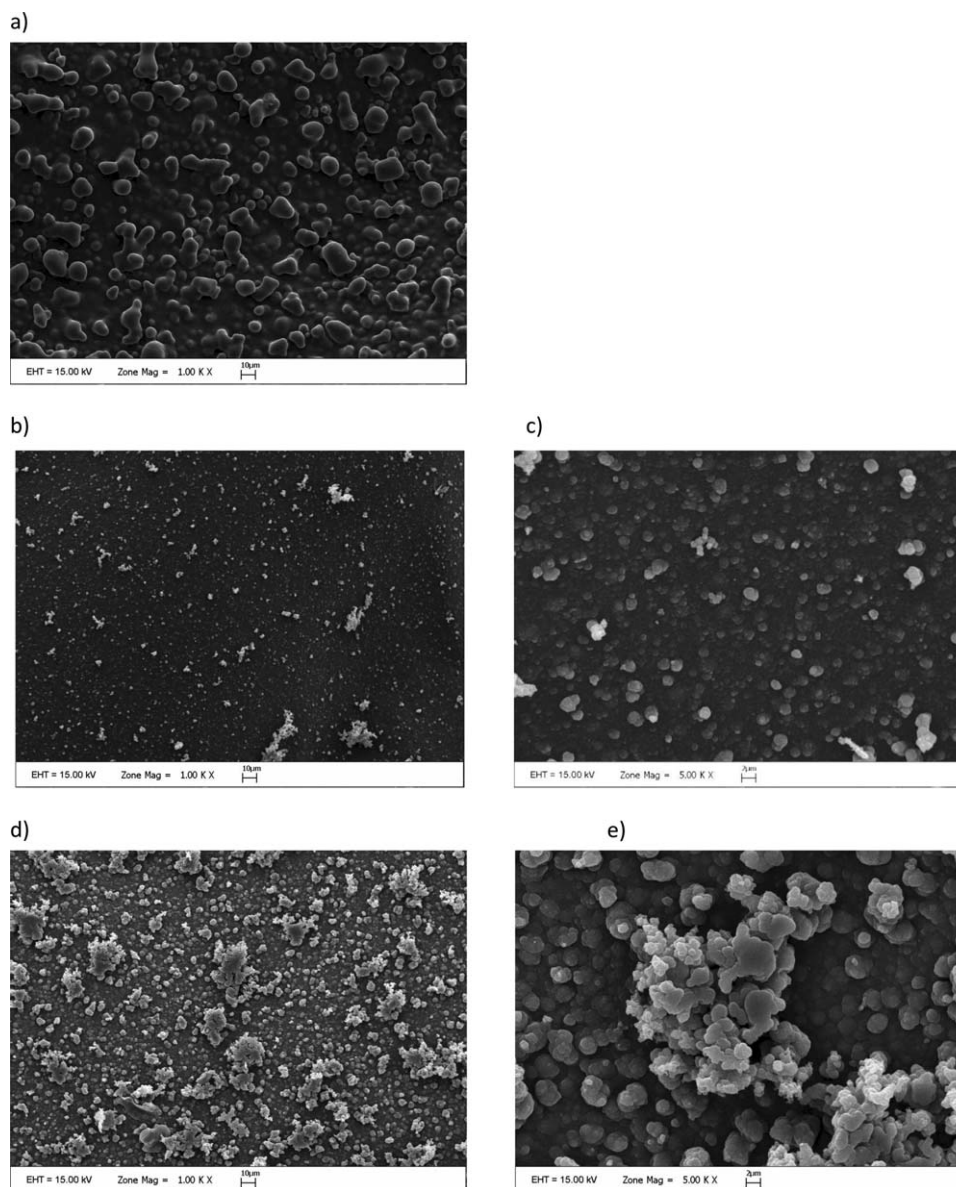
Figure 4. SEM micrographs of (a) PThDBTH (1000 X), (b) PTh (1000 X), (c) PTh (5000 X), (d) P(ThDBTH-Th) (1000 X) and (e) P(ThDBTH-Th) (5000 X).
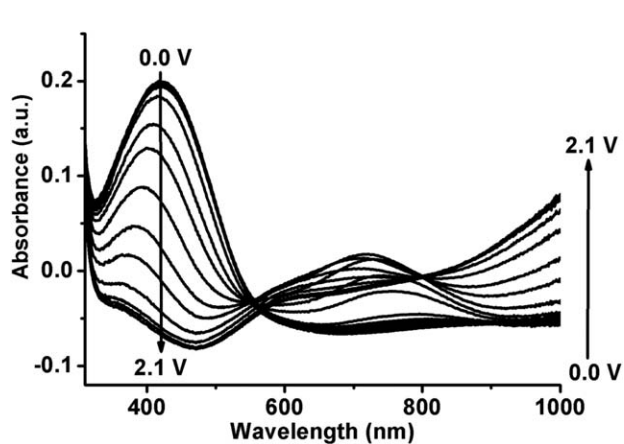
Figure 5. Spectroelectrochemistry study of PThDBTH at applied potentials between 0.0 and 2.1 V in 0.1 M TBAFB/DCM.

Figure 6. Spectroelectrochemistry study of P(ThDBTH-Th) at applied potentials between 0.0 and 1.5 V in 0.1 M TBAFB/DCM.
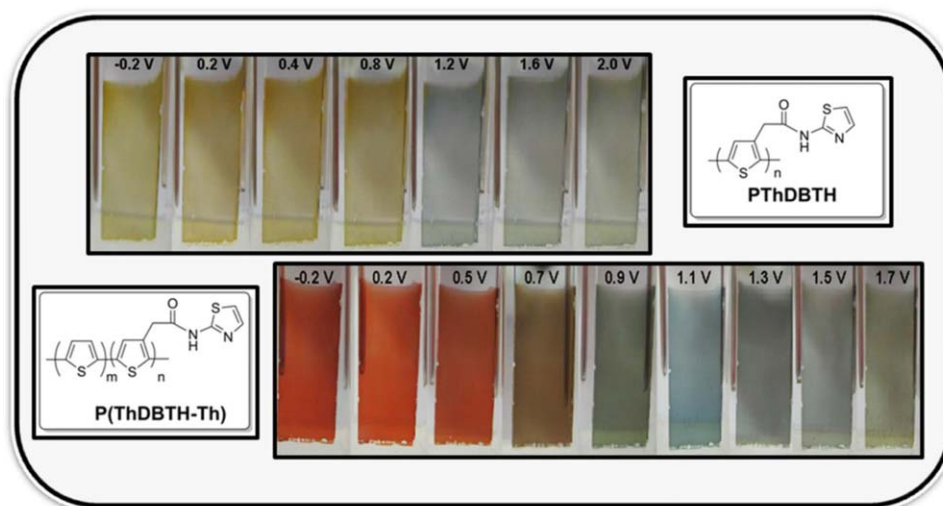
Figure 7. Images of PThDBTH and P(ThDBTH-Th). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The capability of a polymer to change rapidly between its extreme states is important for daily life applications such as displays. Kinetic studies can monitor these types of properties by measuring switching time and percent transmittance change of the polymer upon applied potential. It is conventional to use a square wave potential step method coupled with optical spectroscopy. In this experiment, the potential was set at an initial potential for a set period of time, and was stepped to a second potential for a set period of time (10 s), before being switched back to the initial potential again. Kinetic studies were performed within the light of spectroelectrochemistry studies, as it involves the information about the potentials to be applied for a full switch and wavelength of maximum contrast. The switching time of P(ThDBTH-Th) was determined by monitoring the %T change at 480 nm through switching of the applied potential in a square wave form between 0.0 and 1.0 V with a residence time of 10 s. The optical contrast was measured as the difference between %T in the neutral and oxidized forms and noted as 24.76%. Contrary to its homopolymer, the copolymer has good stability with 1.27 s of switching time (Figure 8). Interestingly, the switching time of the copolymer was slightly lower than that of pristine PTh (1.36 s), which was synthesized under same experimental conditions. Former studies[34–37] underlined the critical role of film morphology on switching proper-

ties of the conducting polymers, where a correlation between the switching time and diffusion distance of the dopant ions was drawn. It was found that polymer films having a more open morphology possess faster switching speeds. Such reasoning is in accordance with the SEM studies of the polymers (Figure 4), where P(ThDBTH-Th) displayed a more open morphology compared to its parent homopolymers.

As the last part of our study, coloration efficiency of the copolymer was calculated. Coloration efficiency, which could be described as the alteration of optical density per introduced charge, provides a quantitative measure for effective use of charge. In accordance with literature,[38] we have calculated the coloration efficiency of the copolymer to be 698 cm^2/C, which is suitable for small area devices.

CONCLUSION

In this study, we proposed the use of thiazole ring in polythiophene structure and investigated the optoelectronic properties of these polymers. For this purpose, two different thiazole-containing monomers (ThDBTH and Th_2DBTH) were synthesized via basic synthetic approach. CV was utilized as the major characterization technique to acquire information about electrochemical behavior of monomers. Preliminary studies were

Table II. Electrochromic Properties of the Polymers

Material	λ_{max} (nm)	E_g (eV)	Color (Ox)	Color (Red)	L	a	b
PThDBTH	420	2.15	Blue	Yellow	(ox) 88	−1	6
					(red) 89	4	13
P(ThDBTH-Th)	480	1.95	Blue	Orange	(ox) 69	−2	5
					(red) 56	37	37
PTh	495	1.99	Blue	Red	(ox) 47	−7	−2
					(red) 51	52	46

ox, oxidized state; red, reduced state.
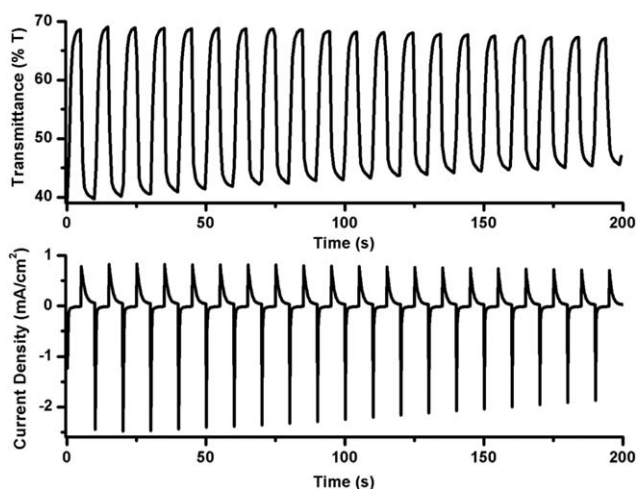
Figure 8. Electrochromic switching, (a) transmittance change, and (b) current change monitored at 480 nm for P(ThDBTH-Th).

performed in TBAFB/ACN-supporting electrolyte/solvent system. Both monomers revealed irreversible electroactivity at around 1.2 V, which sharply decreased upon consecutive scans. To overcome such problem similar type of experiments were performed in the presence of BFEE. In both cases it was possible to synthesize polymer films upon scanning between 0.0 and 2.0 V. Additionally, copolymer of ThDBTH with thiophene was synthesized in the presence of BFEE at constant potential electrolysis. Spectroelectrochemistry experiments were performed to investigate key properties of all polymers. Switching time and optical contrast of all polymers were evaluated via kinetic studies. Band gap of PThDBTH, P(ThDBTH-Th), and PTh$_2$DBTH was found to be 2.15, 1.95, and 2.30 eV, respectively. P(ThDBTH-Th) exhibited a switching time of 1.27 s and optical contrast of 24.76%. Results implied the possible use of these materials in electrochromic devices owing to their satisfactory electrochromic properties.

ACKNOWLEDGMENTS

REFERENCES

1. Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
2. Abidin, T.; Zhang, Q.; Wang, K.-L.; Liaw, D.-J. *Polymer* **2014**, *55*, 5293.
3. Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.
4. Sonmez, G. *Chem. Commun.* **2005**, *42*, 5251.
5. Camurlu, P. *RSC Adv.* **2014**, *4*, 55832.
6. Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121.
7. Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996.
8. Lin, Y.; Fan, H.; Li, Y.; Zhan, X. *Adv. Mater.* **2012**, *24*, 3087.
9. Yang, J.; Sun, W.; Zhou, Z.; Shen, Z. *J. Appl. Polym. Sci.* **2006**, *101*, 443.
10. Yang, J.; Sun, W.; Jiang, H.; Shen, Z. *Polymer* **2005**, *46*, 10478.
11. Lin, W.; Sun, W.; Yang, J.; Shen, Z. *Mater. Chem. Phys.* **2008**, *112*, 617.
12. Camurlu, P.; Gültekin, C. *Smart Mater. Struct.* **2012**, *21*, 025019.
13. Shi, G.; Jin, S.; Xue, G.; Li, C. *Science* **1995**, *267*, 994.
14. Jin, S.; Xue, G. *Macromolecules* **1997**, *30*, 5753.
15. Zhang, D.; Qin, J.; Xue, G. *Synth. Met.* **1999**, *106*, 161.
16. Zhang, D.; Qin, J.; Xue, G. *Synth. Met.* **1999**, *100*, 285.
17. Xu, J. K.; Shi, G. Q.; Qu, L. T.; Zhang, J. X. *Synth. Met.* **2003**, 135, 221.
18. Li, C.; Shi, G.; Liang, Y.; Sha, Z. *Polymer* **1997**, *38*, 6421.
19. Wang, X.; Shi, G.; Liang, Y. *Electrochem. Commun.* **1999**, *1*, 536.
20. Politis, J. K.; Curtis, M. D. *Chem. Mater.* **1998**, *10*, 1713.
21. Yamamoto, T.; Suganuma, H.; Maruyama, T.; Kubota, K. *J. Chem. Soc. Chem. Commun.* **1995**, *16*, 1613.
22. Rasch, B.; Novák, P.; Vielstich, W. *Synth. Met.* **1991**, *1*, 2963.
23. Kvarnström, C.; Ivaska, A.; Neugebauer, H. Advanced Functional Molecules and Polymers; Nalwa, H. S., Ed.; Gordon and Breach Sci. Publ.: Tokyo, **2001**; Vol. 2., Chapter 6, pp 139–170.
24. Li, C.; Shi, G.; Liang, Y. *J. Electroanal. Chem.* **1998**, *455*, 1.
25. Xu, J.; Shi, G.; Xu, Z.; Chen, F.; Hong, X. *J. Electroanal. Chem.* **2001**, *514*, 16.
26. Liu, B.; Yu, W.; Lai, Y.; Huang, W. *Macromolecules* **2000**, *33*, 8945.
27. Lim, E.; Jung, B.; Shim, H. *Macromolecules* **2003**, *36*, 4288.
28. Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. *J. Am. Chem. Soc.* **2010**, *132*, 8546.
29. Durban, M. M.; Kazarinoff, P. D.; Luscombe, C. K. *Macromolecules* **2010**, *43*, 6348.
30. Pina, J.; Melo, J. S.; Burrows, H. D.; Maçanita, A. L.; Galbrecht, F.; Bünnagel, T.; Scherf, U. *Macromolecules* **2009**, *42*, 1710.
31. Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986.
32. Lin, B.; Yamamoto, T. *Macromolecules* **1999**, *32*, 1375.
33. Fesser, K.; Bishop, A. R.; Campbell, D. K. *Phys. Rev. B* **1983**, *27*, 4804.
34. Yashima, H.; Kobayashi, M.; Lee, K.-B.; Chung, D.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1987**, *134*, 46.
35. Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 4401.
36. Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, *13*, 634.
37. Poverenov, E.; Li, M.; Bitler, A.; Bendikov, M. *Chem. Mater.* **2010**, *22*, 4019.
38. Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559.