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### Synthesis and Characterization of Thiophen-3-yl Acetic Acid 4-Pyrrol-1-yl Phenyl Ester and its Conducting Polymers

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## Synthesis and Characterization of Thiophen-3-yl Acetic Acid 4-Pyrrol-1-yl Phenyl Ester and its Conducting Polymers

**Bahar Bingöl**  
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*Thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) monomer was synthesized via reaction of thiophen-3-yl acetyl chloride with 4-pyrrol-1-yl phenol. Homopolymers were achieved by using electrochemical and chemical polymerization techniques. Copolymers of TAPE with bithiophene or pyrrole were synthesized by potentiostatic electrochemical polymerization in acetonitrile-tetrabutylammonium tetrafluoroborate (TBABF) solvent-electrolyte couple. The chemical structures were confirmed by both Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA) were used to examine the thermal behavior of the polymers. The morphologies of the films were investigated by Scanning Electron Microscope (SEM). Two-probe technique was used to measure the conductivities of the samples. Moreover, investigations of electrochromic and spectroelectrochemical properties of poly(TAPE-co-BiTh) carried out and the characteristics of dual type electrochromic device based on poly(TAPE-co-BiTh) and poly(3,4-ethylenedioxythiophene) (PEDOT) were reported.*

**Keywords:** N-substituted pyrroles, conducting polymers, electrochromism, spectroelectrochemistry

### INTRODUCTION

Conducting polymers have several applications including rechargeable batteries [1], sensors [2], membranes [3], light emitting diodes

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[4], optical displays [5], electrochromic devices [6], and enzyme immobilization matrices [7]. Limiting the spectrum of applications, conducting polymers suffer from the disadvantages of being insoluble, infusible, and exhibiting poor mechanical and physical properties. In every field of their application the introduction of substituents on the polymer backbone has proved to be an ingenious way of optimizing their physical and chemical properties [8]. Grafting of flexible hydrocarbon chains has been used to improve solubility and processability [9]; linear or cyclized polyethers [10] and fluorinated [11] groups were used to control the molecular structure of the chains.

Chemical and electrochemical polymerization of pyrrole derivatives substituted at the 1 or 3 position may lead to conducting polymers with useful modified properties. Although it is well known that such substituted pyrroles give polymers whose conductivities decrease with the steric hindrance of the substituent [12–18], alkyl- or arylpyrroles can be used for the synthesis of a wide variety of chemically modified polymer films. Using this approach, several dipyrrolyl monomers were synthesized and polymerized, in which two pyrroles are separated by a spacer [19].

The present work describes the synthesis of a new N-substituted pyrrole, thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE), which also bears a thiophene moiety in the structure. The homopolymers of TAPE were achieved both by using electrochemical and chemical polymerization techniques. In addition, copolymers of TAPE in the presence of bithiophene and pyrrole were studied. The second part of this work reports the electrochromic properties of poly(TAPE-co-BiTh), which belong to the most interesting properties of conducting polymers. Electrochromism is defined as the persistent change of optical properties of a material induced by reversible redox processes. For various applications, electrochromic devices based on conducting polymers have become a recent focus of research because all electroactive and conducting polymers are potentially electrochromic materials [20].

## EXPERIMENTAL

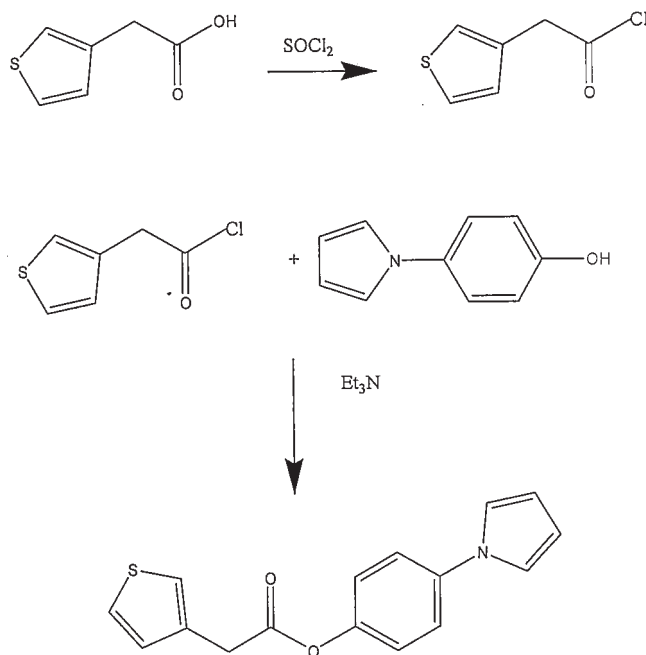
### Materials

4-pyrrol-1-yl phenol, 3-thiophene acetic acid, thionyl chloride, pyrrole, 2,2'-bithiophene, nitromethane, tetrabutylammonium tetrafluoroborate (TBAFB), ferric chloride, propylene carbonate (PC), polymethylmethacrylate (PMMA), and ethylene dioxy thiophene (EDOT) were purchased from Aldrich and used as received. Triethylamine (TEA) (Merck), dichloromethane (DCM) (Merck), methanol (Merck),

acetonitrile (ACN) (Merck), and tetrachloromethane (Riedel-de-Haen) were used without further purification.

### Synthesis of Thiophen-3-yl Acetic Acid 4-Pyrrol-1-yl Phenyl Ester (TAPE)

3-thiophene acetic acid (0.007 mole) was dissolved in 10 mL dichloromethane and reacted with excess thionyl chloride (0.014 mole, where thionyl chloride was added dropwise while cooling in ice bath 0°C). The chlorination reaction was carried out overnight at room temperature, which yields thiophen-3-yl-acetyl chloride as 1.04 g solid (yield 92%). 4-pyrrol-1-yl-phenol (0.0065 mole) and triethylamine (TEA) (0.008 mole) were mixed at 0°C. The esterification reaction was started with the addition of this mixture to the product obtained in the first step. The product was dissolved in 50 mL DCM and extracted twice with NaOH. The organic layer was dried over CaCl<sub>2</sub> and the solvent was removed by rotaevaporatory. The final product was 1.0 g solid (yield: 54%) (Scheme 1).



**SCHEME 1** Synthesis route of TAPE monomer.

## Cyclic Voltammetry (CV)

The oxidation/reduction behavior of the monomer (TAPE), TAPE in the presence of bithiophene (BiTh) and pyrrole (Py) were investigated by CV. The system consists of a potentiostat (Wenking POS 2), an X-Y recorder and a CV cell containing platinum foil working and counter electrodes and a Ag/Ag<sup>+</sup> reference electrode. Measurements were carried out in ACN-TBAFB solvent-electrolyte couple under nitrogen atmosphere at room temperature.

## Synthesis of Homopolymers of TAPE

A Wenking POS 73 Potentiostat was used to supply a constant potential in the electrochemical polymerization. Homopolymerization of TAPE was carried out in the presence of 100 mg monomer dissolved in 20 mL ACN and 0.1 M TBAFB supporting electrolyte. The polymerization reaction was allowed to proceed at 1.5 V for 2 h. After electrolysis, the product was washed with ACN to remove unreacted monomer and excess TBAFB.

## Synthesis of Copolymers of TAPE with Bithiophene

35 mg of TAPE and 35 mg bithiophene were dissolved in 20 mL ACN. Tetrabutylammonium tetrafluoroborate (TBAFB; 0.1 M) was used as the supporting electrolyte. Electrolysis was performed at 1.4 V and it was allowed to proceed until black polymer films are formed (1 h). ACN was used to wash the films to remove unreacted monomer and excess TBAFB.

## Synthesis of Copolymers of TAPE with Pyrrole

100 mg monomer was dissolved in 20 mL ACN and 0.1 M TBAFB was used as the supporting electrolyte. Electrochemical polymerization was started by application of 1.2 V vs. Ag/Ag<sup>+</sup> reference electrode. After 5 min, 30  $\mu$ L pyrrole were introduced to the electrolysis medium. After electrolysis, films were washed several times with ACN to eliminate the presence of unreacted monomer and excess TBAFB.

## Chemical Polymerization of TAPE with Ferric Chloride

To carry out the oxidative polymerization of TAPE, monomer ( $3.53 \times 10^{-4}$  mole) was dissolved in 5 mL CCl<sub>4</sub> at 0°C. FeCl<sub>3</sub> 6H<sub>2</sub>O ( $14.12 \times 10^{-4}$  mole) in 15 mL CH<sub>3</sub>NO<sub>2</sub> was later added dropwise to

the solution. The reaction was carried out for 24 h with constant stirring. Methanol was used as the nonsolvent and a black solid product was obtained after filtration.

## Electrochromic Studies and Spectroelectrochemistry of Poly(TAPE-co-BiTh)

Spectroelectrochemical studies were carried on a HP8453A UV-VIS spectrophotometer. Colorimetry measurements were done with a Coloreye XTH Spectrophotometer (GretagMacbeth).

To carry out spectroelectrochemical and electrochromic studies, copolymer films were synthesized on indium tin oxide (ITO) coated glass. Copolymer films deposited on ITO-coated glass were used both for spectroelectrochemistry and electrochromic measurements in TBAFB (0.1M)/ACN with Ag/Ag<sup>+</sup> as the reference electrode and a Pt wire as the auxiliary electrode. Films were deposited on ITO-coated glass slides and dried under atmospheric conditions.

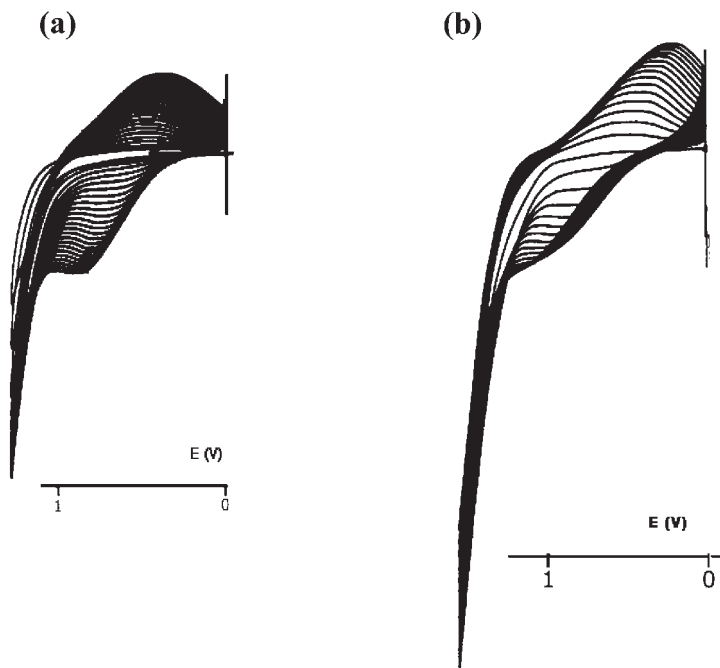
### Preparation of Electrochromic Device

Poly(TAPE-co-BiTh) film was coated onto an ITO electrode by cycling between 0 and 1.6 V versus Ag/Ag<sup>+</sup>. A solution of 3,4-ethylenedioxythiophene (EDOT) (10 mM) and TBAFB/ACN (0.1M) was used to deposit PEDOT film at the ITO electrode by cycling between -1.0 and +1.0 V versus Ag/Ag<sup>+</sup>. The polymerizations were performed with a Solartron 1285 Potentiostat. Gel electrolyte was spread on the coated sides of ITO electrodes, which were later placed in sandwich configuration under atmospheric conditions. The gel electrolyte for electrochromic device based on polymethylmetacrylate (PMMA) was plasticized by 1,2-propylenecarbonate to form a highly transparent and conductive gel. The composition of casting solution by weight ratio of ACN:PC:PMMA:TBAFB was 70:20:7:3. The spectroelectrochemistry study of the devices was performed with Agilent 8453 UV-Vis Spectrometer.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry

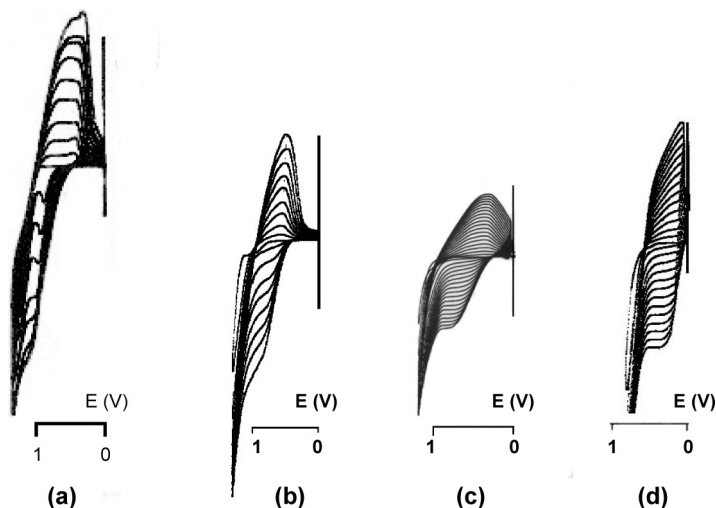
Cyclic voltammogram of homopolymer of TAPE in acetonitrile showed an oxidation peak at 0.8 V and a reduction peak at 0.4 V implying that TAPE is electroactive. When the regions from 0 V to 1.3 V (Figure 1a) and to 1.5 V (Figure 1b) were scanned, it was found that the electroactivity increases with increasing scan number.



**FIGURE 1** Cyclic voltammograms of TAPE in scan range (a) 0–1.3 V (b) 0–1.5 V.

Cyclic voltammograms in the region between  $-0.5\text{ V}$  and  $+1.7\text{ V}$  revealed both an oxidation and a reduction peak, where both increase in height during the first six runs. However, after the sixth run the disappearance of the oxidation peak and a shift for the reduction peak were observed.

To determine the route of polymerization, oxidation/reduction behavior of the starting materials, namely, 4-pyrrol-1-yl phenol and thiophen-3-yl acetic acid, were investigated. It was observed that thiophen-3-yl acetic acid has an oxidation peak at  $1.9\text{ V}$ . On the other hand, 4-pyrrol-1-yl phenol revealed oxidation and reduction peaks at  $0.5\text{ V}$  and  $0.4\text{ V}$ , respectively. This implies that homopolymerization goes from the pyrrole moiety of TAPE because the applied voltage is only enough for generation of pyrrole radical cation. Because the applied voltage was increased, overoxidation of pyrrole unit takes place yielding a decrease in electroactivity after the sixth run for TAPE when a potential of  $1.7\text{ V}$  is applied.



**FIGURE 2** Cyclic voltammograms for (a) TAPE/BiTh, (b) BiTh, (c) TAPE/Py, (d) Py.

After the addition of bithiophene to the solution, an oxidation peak at 0.7 V and a reduction peak at 0.6 V were observed revealing an increase in height with increasing scan number (Figure 2a). This redox behavior is completely different than that of pure polybithiophene, which has oxidation and reduction peaks at 1.30 V and 0.5 V, respectively (Figure 2b). This huge difference in CVs may indicate an interaction between TAPE and bithiophene, possibly a copolymer formation. BiTh was preferred instead of thiophene because lower potential is required for its oxidation, enabling the polymerization to be performed under milder conditions, decreasing the probability of overoxidizing the monomer during the polymerization.

CV of TAPE in the presence of pyrrole revealed an oxidation peak at 0.6 V and a reduction peak at 0.1 V (Figure 2c). Addition of pyrrole to the reaction medium also made a significant difference compared to that of poly(TAPE) (Figure 1a) and pure polypyrrole cyclic voltammogram (Figure 2d). The earlier argument about a possible interaction between TAPE and pyrrole may also be valid in this case.

## Characterization

Homopolymers of TAPE were synthesized both by electrochemical and chemical polymerization methods. Moreover, electrochemical



polymerizations of TAPE in the presence of bithiophene or pyrrole were tried, and both of them were successful in ACN/TBAFB solvent-electrolyte couple (Scheme 2).

## NMR

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of monomer were generated on a Bruker-Instrument-NMR Spectrometer (DP-400) monomer with  $\text{CDCl}_3$  as the solvent, and the chemical shifts ( $\delta$ ) are given relative to tetramethylsilane as the internal standard.

$^1\text{H}$ -NMR spectrum of monomer (Figure 3):  $^1\text{H}$ -NMR ( $\delta$ , ppm): 7.0 (m, 2H) and 6.2 (m, 2H) from pyrrole ring, 7.2 (m, 2H) and 7.3 (m, 2H) from benzene ring, 6.8 (m, 1H), 6.85 (m, 1H) and 7.1 (m, 1H) from thiophene ring and 3.9 (s, 2H) from  $\text{CO-CH}_2$ .

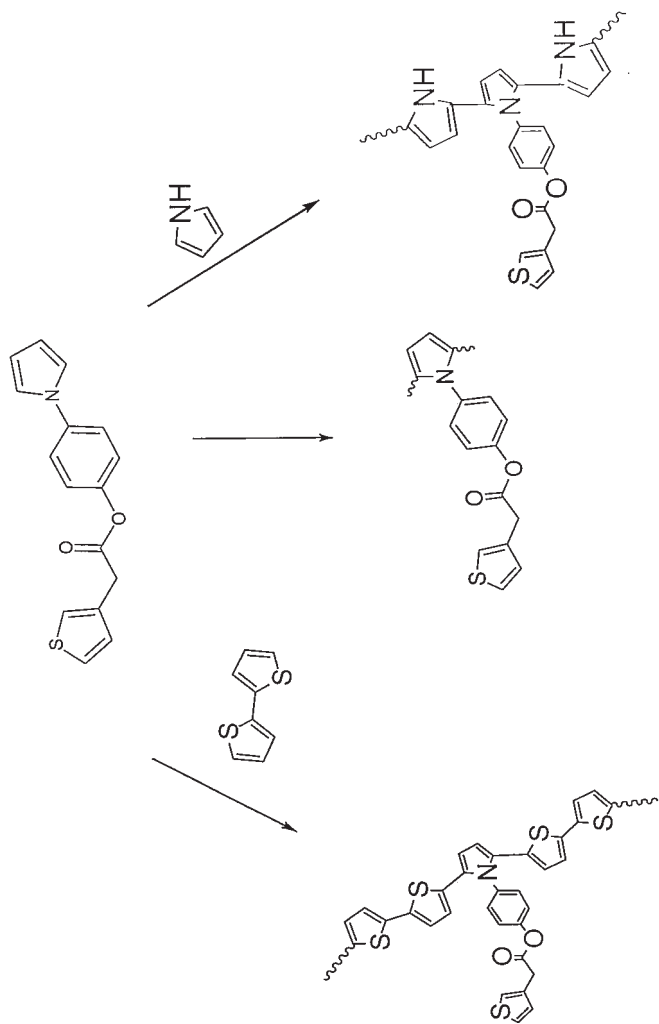
$^{13}\text{C}$ -NMR spectrum of the monomer:  $^{13}\text{C}$ -NMR ( $\delta$ , ppm): 168 from CO, 122, 121 from benzene ring, 118, 109 from pyrrole ring, 127, 131 from thiophene ring, 34 from the aliphatic group.

## FTIR

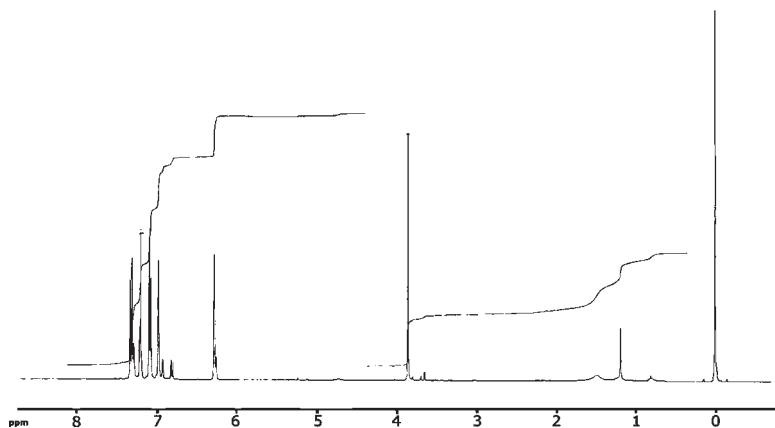
The FTIR spectrum of monomer (Figure 4) exhibits some characteristic features of N-substituted pyrroles. The absorption bands at 720, 3157, and 3131 are due to the in-phase cis out-of-plane movement of  $\text{HC=CH}$ ; bands at 1012 and 1071  $\text{cm}^{-1}$  correspond to C-H stretchings of N-substituted pyrroles [21]. The intense peak at 1753  $\text{cm}^{-1}$  may be attributed to the C=O stretching vibrations, and C-O-C stretching vibrations are observed in the region of 1100–1204  $\text{cm}^{-1}$ . The absorption band at 1548  $\text{cm}^{-1}$  indicates the presence of benzene ring. Absorption bands in the region of 808–857  $\text{cm}^{-1}$  may be due to the thiophene moiety.

After homopolymerization of TAPE, a band at 720  $\text{cm}^{-1}$  due to out-of-plane bending or ring bending disappears. This is a characteristic feature of poly(N-substituted pyrrole)s [22]. The presence of C=O group and benzene ring was confirmed by the presence of absorption bands at 1750  $\text{cm}^{-1}$  and 1598  $\text{cm}^{-1}$ , respectively. Moreover, the shoulder at 1040  $\text{cm}^{-1}$  reveals that dopant ion is present in the structure, which confirms that polymerization reaction took place.

After chemical polymerization of TAPE, a new band appears at 1616  $\text{cm}^{-1}$  indicating the conjugation in addition to characteristic bands of TAPE monomer. Besides, chemically synthesized poly(TAPE) was insoluble in common solvents such as ACN and DCM, in which the monomer is soluble. This may also indicate that chemical polymerization of TAPE was achieved.

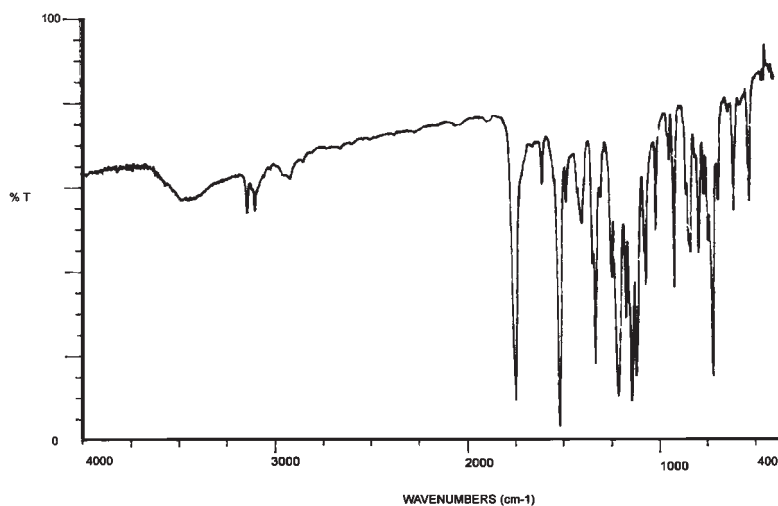


**SCHEME 2** Synthesis of conducting poly(TAPE) and copolymers of TAPE with bithiophene and pyrrole.



**FIGURE 3**  $^1\text{H-NMR}$  spectrum of the monomer.

The FTIR spectrum of electrochemically synthesized copolymer of TAPE/BiTh shows the presence of carbonyl group at  $1753\text{ cm}^{-1}$ , and benzene ring was observed at  $1548\text{ cm}^{-1}$ . Incorporation of tetrafluoroborate ions in the structure may be inferred by the presence of a strong absorption peak at  $1080\text{ cm}^{-1}$ . Other than these, ester groups were also observed. These results indicate that copolymers of TAPE with bithiophene were achieved because carbonyl functionality and benzene ring exist only in the monomer.



**FIGURE 4** FTIR spectrum of the monomer.

The characteristic functional groups of monomer were also present in the FTIR spectrum of copolymer of TAPE with pyrrole. No absorption bands are observed at 730, 3140, 1012, and 1071  $\text{cm}^{-1}$ , which can be used as an evidence for the polymerization from 2, 5 positions of pyrrole ring [23].

## Thermal Analysis

Thermal analyses of monomer and homopolymers were conducted by DSC in the range 30°C to 425°C at a heating rate of 10°C/min under  $\text{N}_2$  atmosphere.

DSC thermogram of the monomer shows a sharp melting point at 88.5°C. It is stable up to 210°C and it begins to decompose at 210°C (Figure 5).

In the DSC thermogram of the homopolymer, there are two endothermic transitions at 86°C due to removal of the solvent, ACN, and at 383°C corresponding to the decomposition of homopolymer.

For copolymer of TAPE with bithiophene, the DSC thermogram revealed several endothermic transitions at 109°C, 182°C, 303°C, and 378°C. The first transition may be attributed to the removal of solvent from the matrix, the second is due to removal of tetrafluoroborate ions from the system, and the last two transitions show the decomposition of the copolymer.

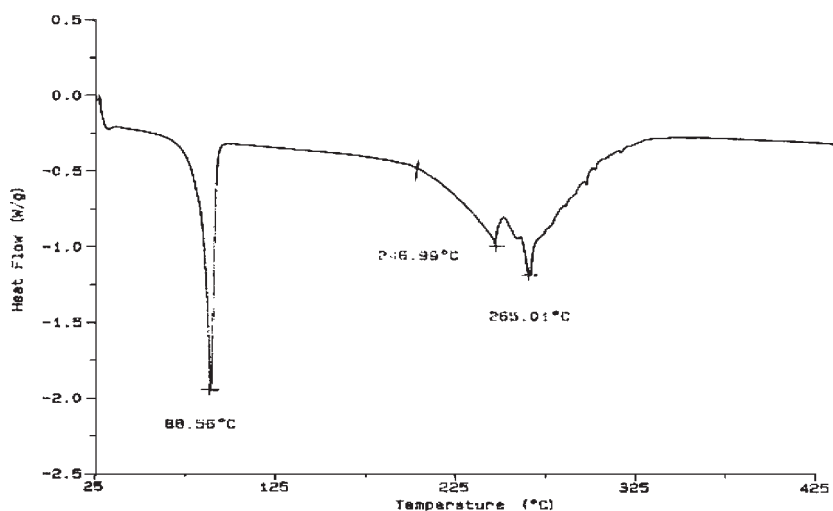


FIGURE 5 DSC thermogram of the monomer.

**TABLE 1** Conductivity Values of the Polymers

Sample	Conductivity (S/cm)
Poly(TAPE)	$2 \times 10^{-10}$
Poly(TAPE-co-BiTh)	$1 \times 10^{-6}$
Poly(TAPE-co-Py)	$5 \times 10^{-6}$

## Conductivity Measurements

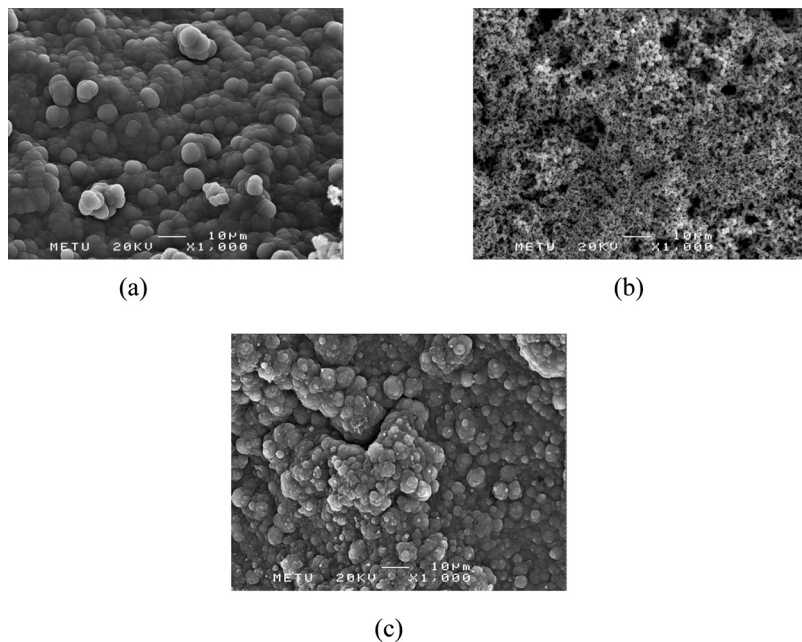
Electrical conductivity measurements of the copolymers were carried out by using the two-probe technique. The conductivity of the homopolymer was measured via two-probe technique because of the poor quality of the films, which is in accordance with the literature. It has already been shown that N-substituted pyrrole monomers yield electrically conducting polymer films of poor quality when the substituent is ethyl or larger [12–13]. Conductivity values of the samples are given in Table 1.

The order of magnitude of the conductivity of the homopolymer was found as  $2 \times 10^{-10}$  S/cm. The best films were obtained from the polymerization of TAPE with Py, the conductivity of which was measured as  $5 \times 10^{-6}$  S/cm. The conductivity of both electrode sides of poly(TAPE-co-Py) were of the same order of magnitude, which reveals the homogeneity of the films. The conductivity of poly(TAPE-co-BiTh) was measured as  $1 \times 10^{-6}$  S/cm. The low conductivities are in agreement with the previous results reported in the literature for poly(N-substituted pyrrole)s and its copolymers [22, 24–25]. The conductivity of the homopolymer is improved by introduction of pyrrole and bithiophene to the matrix.

## Morphologies of Polymer Films

The surface morphologies of homopolymers and copolymers were investigated by Scanning Electron Microscope. SEM micrographs of the solution side and electrode side differ from each other significantly. Some globule-like droplets were observed on the solution side of poly(TAPE) film (Figure 6a). On the other hand, the electrode side of poly(TAPE) film has flat-plane structure with some cracks.

As far as SEM micrographs of copolymers of TAPE with BiTh are concerned, the solution sides of the copolymer films differ from those of pure polybithiophene considerably. This may be used as an evidence of the presence of copolymerization of monomer (TAPE) with bithiophene. The surface of the solution side of pure polybithiophene has



**FIGURE 6** SEM Micrographs of (a) solution side of poly(TAPE), (b) solution side of poly(TAPE-co-BiTh), (c) solution side of poly(TAPE-co-Py).

a sponge-like structure. The solution side of TAPE/BiTh films shows granular-like structure, whereas its electrode side is smooth (Figure 6b).

In SEM micrographs the solution side of SEM micrographs of  $\text{BF}_4^-$  doped copolymers of TAPE with Py, a significant difference of morphology were observed compared to the cauliflower structure of pure Py, which might be arising from the copolymerization of TAPE with Py. The solution side of the polymer shows globule-like droplets that are significantly smaller than those of the solution side of poly(TAPE), which excludes the probability of synthesis pure poly(TAPE) (Figure 6c).

### Electrochromic Properties of Copolymer

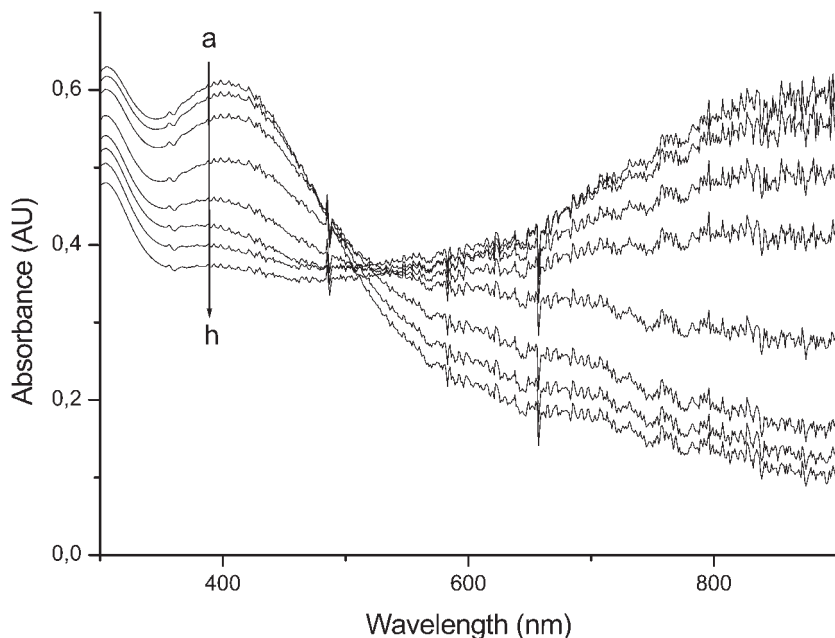
The electrochemical switching of the copolymer of TAPE with bithiophene was studied. The copolymer film was coated on an ITO electrode by application of +1.4 V vs.  $\text{Ag}/\text{Ag}^+$  reference electrode. The electrochromism and optoelectrochemical analysis switching studies were performed in ACN/TBAFB (0.1M) solvent-electrolyte couple. Upon switching of copolymer film between -1.4 and +1.4 V, transparent

**TABLE 2** Electrochromic Properties of Polymers

Polymer	$\lambda_{\max}$ (nm)	$E_g$ (eV)	Color (red)	Color (ox)	L	a	b
Poly (2,2'bithiophene)	480	1.1–1.2	Orange red	blue	(ox) 77	-11	-30
					(red) 60	10	22
Poly (TAPE-co-2,2' bithiophene)	410	1.99	brownish	Pale blue	(ox) 84	5	-7
					(red) 72	14	23

pale blue and brownish colors were observed for the oxidized and neutral states, respectively. The electrochromic properties of the polymers are summarized in Table 2.

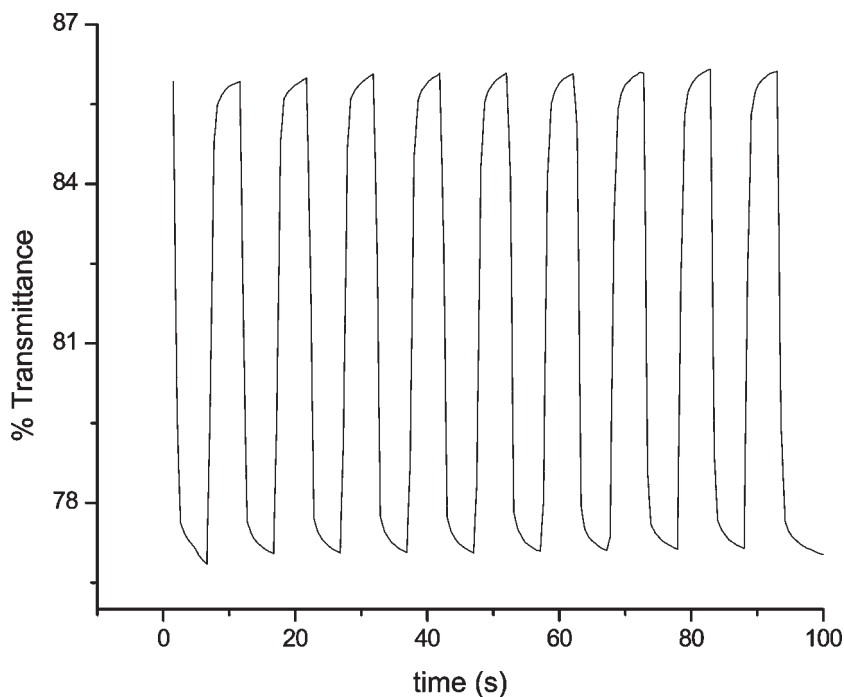
Optoelectrochemical analysis was performed to clarify the electronic structure of the copolymer and to determine its optical behavior upon doping. To carry out the optoelectrochemical analysis, the film



**FIGURE 7** Optoelectrochemical Spectrum of poly(TAPE-co-BiTh) at applied potentials between 0.0 and +1.3 V (a) 0.0 V, (b) +0.4 V, (c) +0.6 V, (d) +0.8 V, (e) +1.0 V, (f) +1.1, (g) +1.2 V, (h) +1.3 V.

deposited onto ITO coated glass was placed in a UV cuvette for spectroelectrochemistry experiment after being washed with an electrolyte solution, which does not contain any monomer. By application of a potential ranging from 0.0 V to 1.3 V, a series of UV-VIS spectra were collected (Figure 7). To determine the reversibility of the film, another series of potential ranging from 1.3 V to 0.0 V were applied. The  $\lambda_{\max}$  value for the  $\pi \rightarrow \pi^*$  transition in the completely reduced state of poly(TAPE-co-BiTh) was found to be 410 nm. The electronic band gap is defined as the onset energy for the  $\pi \rightarrow \pi^*$  transition and it was determined as 1.99 eV for the copolymer. On the other hand, pure poly(BiTh) has a peak absorbance at 480 nm and has a band gap of 1.1–1.2 eV [26].

The dynamic electrochromic experiment of poly(TAPE-co-BiTh) was carried out at 498 nm, where maximum transmittance difference between oxidized and neutral states was achieved. The time required for poly(TAPE-co-BiTh) film to change its redox state was found as 1.6 s (Figure 8), which is determined upon application of a square wave potential.



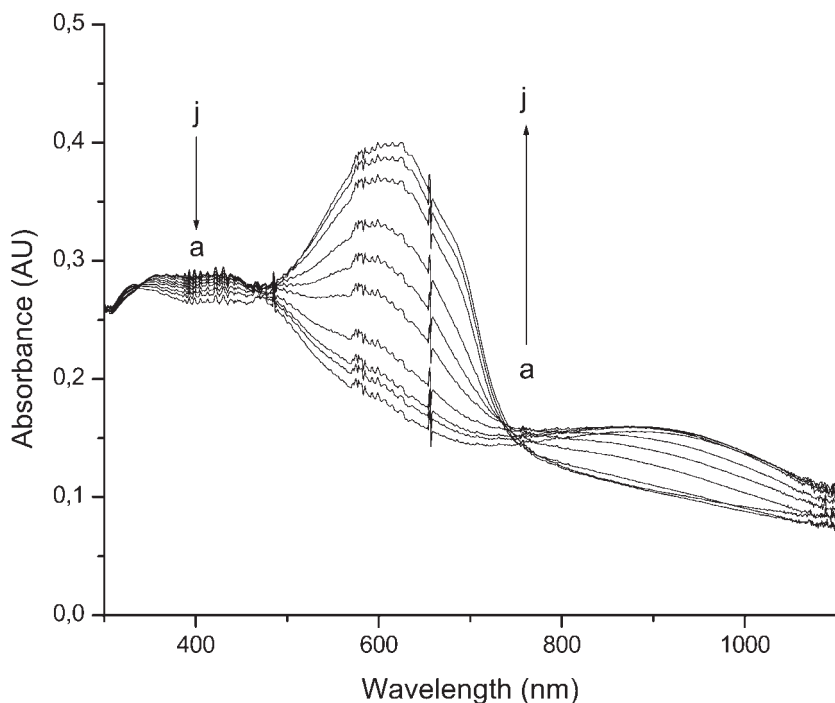
**FIGURE 8** Dynamic electrochromic study of poly(TAPE-co-BiTh) at 498 nm.



## Characteristics of Electrochromic Device

While constructing the electrochromic device, one polymer film must be placed in its oxidized state and the other in its neutral state. Upon application of a voltage, one of the polymer films is oxidized, whereas the other is neutralized, resulting in a color change. The observed colors are blue and brownish with the colorimetry parameters  $L$ ,  $a$ ,  $b$  values of (41, -7, -11) and (38, 4, 25) respectively.

Spectroelectrochemistry is used to investigate the optical properties of the device upon doping and dedoping processes. Optoelectrochemical spectra of dual type electrochromic device are shown in Figure 9. The color turned blue at 0.8 V, the wavelength of maximum absorption was at 612 nm, the blue color of the device was attributed to the absorption of neutral PEDOT, because poly(TAPE-co-BiTh) on the opposite electrode changed to a bleached oxidized form. The color turned brownish at 0.6 V; the wavelength of maximum absorption



**FIGURE 9** Optoelectrochemical Spectrum of poly(TAPE-co-BiTh) at applied potentials (a) -0.2 V, (b) +0.2, (c) +0.4 V, (d) +0.6 V, (e) +0.8 V, (f) +0.9, (g) +1.0 V, (h) +1.2 V, (i) +1.4 V, (j) +1.6 V.

was 402 nm. The brownish color is attributed to the absorption of reduced poly(TAPE-co-BiTh) because PEDOT on the opposite electrode turned to the bleached oxidized form. The results revealed that the time required to reach 90% of ultimate % T was 1.6 s.

The stability test of this electrochromic device was carried out by using cyclic voltammetry to observe the current change for studying the long-term stability of the electrochromic device. Cyclic voltammogram of the device was recorded by sweeping the voltage between 0.0 and 1.7 V with a scan rate of 250, which reveals a little difference in intensity of current between the 1st and the 300th cycle.

## CONCLUSION

Thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) monomer was synthesized successfully. The syntheses of the homopolymer and copolymers of TAPE were achieved by using acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couple, by constant potential electrolysis. The controlled addition of FeCl<sub>3</sub> at low temperature resulted in the synthesis of poly(TAPE) chemically.

Furthermore, the electrochromic and spectroelectrochemical properties of poly(TAPE-co-BiTh) films were investigated. Moreover, a dual type electrochromic device based on poly(TAPE-co-BiTh) and poly(3,4-ethylenedioxythiophene) was constructed and its characteristics were studied.

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