

Synthesis and characterization of poly(N-(2-(thiophen-3-yl)methylcarbonyloxyethyl) maleimide) and its spectroelectrochemical properties

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Abstract A new monomer; N-(2-(thiophen-3-yl)methylcarbonyloxyethyl) maleimide (NMT) was synthesized. The chemical structure of the monomer was characterized by Nuclear Magnetic Resonance ($^1\text{H-NMR}$) and Fourier Transform Infrared (FTIR) Spectroscopy. Electrochemical polymerization of NMT was performed in acetonitrile (AN)/borontrifluoride ethylether (BFEE) solvent mixture (1:1, v/v) where tetrabutylammonium tetrafluoroborate (TBAFB) was utilized as the supporting electrolyte. The resulting conducting polymer was characterized by Fourier Transform Infrared (FTIR) Spectroscopy, thermal analyses and Scanning Electron Microscopy (SEM). Electrical conductivity was measured by the four-probe technique. The spectroelectrochemical behavior and switching ability of P(NMT) film were investigated by UV–Vis spectrophotometry. P(NMT) revealed color changes between yellow and blue in the reduced and oxidized states respectively.

Keywords Conducting polymers · Electrochemical polymerization · Polythiophenes · Spectroelectrochemistry

1 Introduction

In the late 1970s, conjugated polymers were identified as future new materials that would lead to the next generation of electronic and optical devices. Polythi-

ophenes are an important representative class of conducting polymers that can be used as electrical conductors [1], nonlinear optical devices [1], polymer light-emitting diodes [2], sensors [3], batteries [4], artificial noses and muscles [5], transistors [6] and electrochromic devices [7].

Synthesis of new polythiophene derivatives with improved conductivity and processing properties is an important part of conducting polymer research [8]. This area has attracted great attention since substitution of a flexible side group can improve the stability, fusibility, and processibility of thiophene without much affecting the environmental stability and electrical conductivity [9–11].

Because of their diverse variations of color and high contrast ratios, functionalized polythiophenes have become potential electrochromic materials. An electrochromic material is one that changes color in a reversible manner by an electrochemical reaction, and the phenomenon is called electrochromism [12]. A number of conjugated polymers have colors both in the oxidized and reduced states. The color exhibited by the polymer is determined by the band gap energy (E_g), defined as the onset of the π to π^* transition [13]. An important point in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modifications. Polyheterocycles have proved to be of special interest due to their stability under ambient conditions.

In this study, we synthesized a new thiophene monomer containing a maleimide group namely N-(2-(thiophen-3-yl)methylcarbonyloxyethyl) maleimide (NMT). Electrochemical polymerization of NMT was achieved in ACN:BFEE (1:1, v/v) using tetrabutylammonium tetrafluoroborate (TBAFB) as the supporting

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electrolyte. The resultant polymer was characterized by cyclic voltammetry, FTIR, DSC, SEM, and conductivity measurements. The second part of the study was devoted to investigate an interesting property of conducting polymers, the ability to switch reversibly between the two states of different optical properties, “electrochromism”. Consecutively, we investigated the optoelectrochemistry and measured the L , a and b values of P(NMT) coated on ITO glass via constant potential electrolysis.

Polymers of *N*-substituted maleimides and their derivatives can be classified as polyimides, an important class of high performance engineering plastics. This provides the polymers with superior mechanical and thermal stability [14]. In order to enhance the mechanical and thermal stability of conducting polymer, future study will concern the electropolymerization of the macromonomer obtained through the polymerization of the maleimide functional group.

2 Experimental

2.1 Materials

Maleic anhydride (Sigma), ethanolamine (Aldrich), furan (Sigma), 3-thiophene acetic acid (Aldrich), dichloromethane (DCM) (Merck), ethyl acetate (Aldrich), ethanol (Aldrich), thionyl chloride (Aldrich), tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), borontrifluoride ethylether (BFEE) (Sigma), acetonitrile (AN) (Merck) were used without further purification.

2.2 Equipment

A Voltalab PST50 potentiostat was used for the cyclic voltammetric studies. NMR spectra of the monomers were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) using CDCl_3 as the solvent and tetramethylsilane as the internal standard relative to which the chemical shifts (δ) are given. The FTIR spectrum was recorded on a Nicolet 510 FTIR spectrometer. The surface morphology of the polymer film was analyzed using a JEOL JSM-6400 scanning electron microscope. A Solartron 1285 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis. An Agilent 8453 UV–Vis spectrophotometer was used to perform the spectroelectrochemical studies of copolymers and the characterization of the devices. Colorimetry measurements were done via a Minolta CS-100 spectrophotometer.

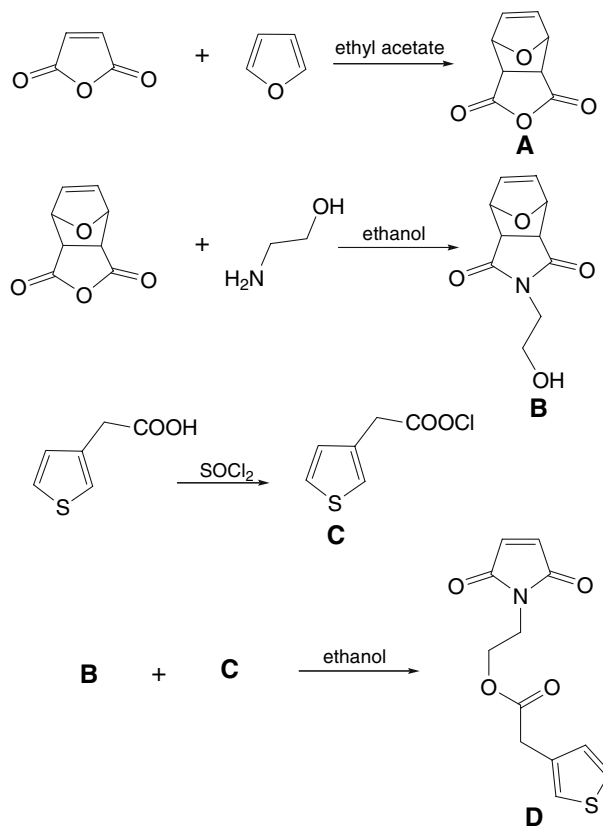
2.3 Synthesis of the monomer

2.3.1 Synthesis of 3, 6-endoxo-1, 2, 3, 6-tetrahydrophthalic anhydride (**A**)

The 3, 6-endoxo-1, 2, 3, 6-tetrahydrophthalic anhydride (**A**) (Scheme 1) was synthesized according to the method described by Narita et al. [15]. Maleic anhydride (20 g, 20.4 mmol) and ethyl acetate (25.5 ml) were mixed in a 100 ml round-bottomed flask. Furan (17.35 g, 25.5 mmol) was added and the reaction mixture was stirred overnight at room temperature. The precipitate 18.15 g (89%) was filtered and washed with ethyl acetate, m.p. 107 °C.

2.3.2 Synthesis of 2-hydroxy-*N*-ethyl-3, 6-endoxo-1, 2, 3, 6-tetrahydrophthalimide (**B**)

The synthesis of 2-hydroxy-*N*-ethyl-3, 6-endoxo-1, 2, 3, 6-tetrahydrophthalimide (**B**) (Scheme 1) was carried



Scheme 1 Synthesis route of NMT

out in accordance with the method described by Narita et al. [15]. Ethanolamine (0.38 g, 6.17 mmol) in ethanol (5 ml) was added drop-wise to slurry of **A** (10 g, 6 mmol) in ethanol (15 ml) in a 50 ml round-bottomed flask. This mixture was then refluxed for 4 h. After

cooling to room temperature, a white solid had formed. The crude product was filtered and washed with ethanol followed by petroleum ether yielding 7.27 g (58%) of a white crystalline solid as the final product, m.p. 132 °C.

2.3.3 Synthesis of thiophen-3-yl-acetyl chloride

3-Thiophene acetic acid (7 mmol) was dissolved in 10 ml dichloromethane and reacted with excess thionyl chloride (14 mmol, where thionyl chloride was added dropwise while cooling in an ice bath 0 °C). The chlorination reaction was carried out overnight at room temperature, which yields thiophen-3-yl-acetyl chloride (yield 92%).

2.3.4 Synthesis of *N*-(2-(thiophen-3-yl)methylcarbonyloxyethyl) maleimide (NMT)

A solution of **B** (0.8 g (0.004 mol)) in 10 ml dichloromethane containing 0.4 g (0.004 mol) triethylamine (TEA), was added dropwise in 0.5 h. onto 0.72 g (0.0045 mol) 3-thiophene acetyl chloride in an ice bath and under nitrogen atmosphere. The esterification was carried out overnight at room temperature. After cooling the solution, the solid product was filtered off and washed with ethanol.

2.4 Cyclic voltammetry (CV)

The oxidation/reduction behavior of the monomer (NMT) was investigated by CV. The system consisted of a potentiostat and a CV cell containing platinum foil working and counter electrodes and a Ag/Ag⁺ reference electrode. Measurements were carried out in AN:BFEE (1:1, v/v) solvent mixture and TBAFB supporting electrolyte.

2.5 Synthesis of conducting polymer of NMT

Preparative electrochemical homopolymerization was performed under potentiostatic conditions in a one-compartment cell. 40 mg MT were dissolved in AN:BFEE (1:1, v/v) solvent mixture where 0.2 M TBAFB was used as the supporting electrolyte. Electrolyses were carried out at 1.6 V in a cell equipped with Pt working and counter electrodes and Ag/Ag⁺ reference electrode at room temperature for 1 h. The free standing films were washed with AN several times to remove unreacted monomer and TBAFB.

2.6 Spectroelectrochemistry

Spectroelectrochemical analyses of the polymer were carried out to understand the band structure of the product. For spectroelectrochemical studies, the polymer film was deposited potentiostatically at 1.6 V vs Ag/Ag⁺ from a solution of 40 mg MT in AN:BFEE (1:1, v/v)/TBAFB solvent–electrolyte couple on indium tin oxide-coated glass slide (ITO) UV–Vis spectra of the film were recorded at various potentials in AN:BFEE/TBAFB.

2.7 Switching

A square wave potential step method coupled with optical spectroscopy was used to investigate the switching times and contrast for these polymers. In this double potential step experiment, the potential was set at an initial potential (where the conducting polymer was in one of its extreme states) for 5 s and stepped to a second potential for another 5 s, before being switched back to the initial potential. During the experiment the percent transmittance (%T) and switching times at λ_{\max} of the polymer were measured using a UV–Vis spectrophotometer.

2.8 Colorimetry study of polymer

Colorimetry analysis was run in order to study the color of the sample. In order to assign a quantitative scale to color measurements, the Commission Internationale de l'Eclairage (International Commission of Illumination) color spaces 1976 Lab system was chosen due to its common use in industry [13]. The film prepared for spectroelectrochemical studies was switched in AN:BFEE/TBAFB (0.2M) and its colors at fully reduced and oxidized states were measured using a Minolta CS-100 spectrophotometer.

3 Results and discussion

3.1 FT-IR and NMR spectra

The identification of NMT was carried out by FT-IR spectroscopy. Figure 1 (a) shows the FT-IR spectrum of NMT in the range 4,000–500 cm⁻¹. The absorption bands at 1,543, 1,410, 855, 788 and 665 cm⁻¹ are due to the vibrations of C-H and C=C bonds of thiophene rings. 3,100 cm⁻¹ band is attributed to CH stretching of maleimide and two peaks at 1,735 and 1,697 cm⁻¹ are related to CO stretching vibrations of ester and

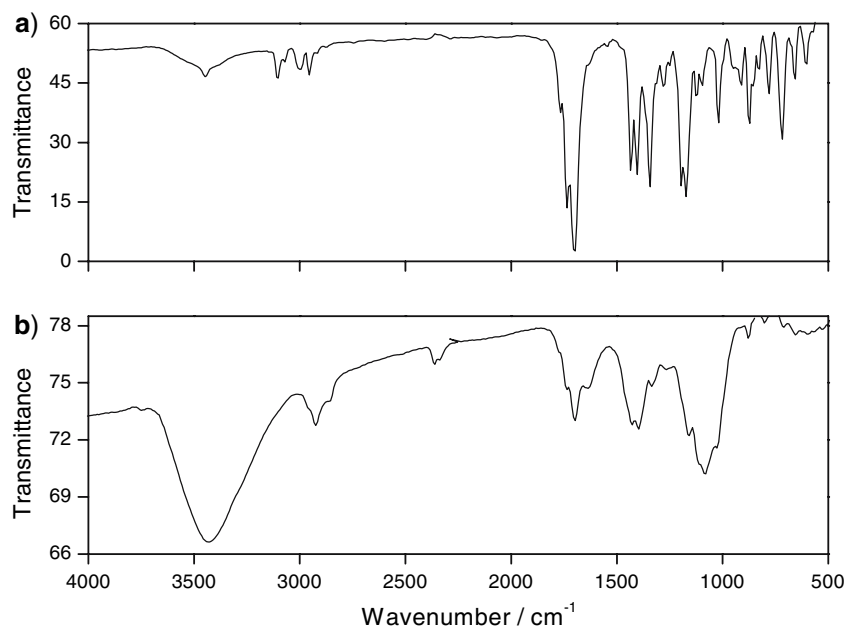


Fig. 1 FTIR spectrum of the (a) monomer (NMT) (b) electrochemically prepared polymer P(NMT)

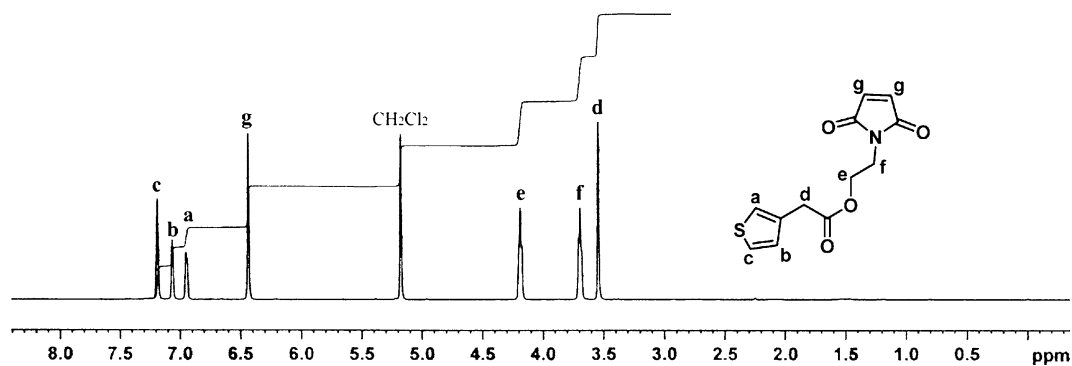


Fig. 2 NMR spectrum of the monomer (NMT)

maleimide ring respectively. Peaks at 2,948 and 2,867 cm⁻¹ correspond to aliphatic methylene stretchings and the bands in the region of 1,100–1,250 cm⁻¹ is due to C-O-C symmetric and asymmetric stretching vibrations of spacer methyl chain [16].

As seen in Fig. 1(b), as well as the characteristic monomer peaks, FTIR spectra of P(NMT) also contain a new shoulder at 1,637 cm⁻¹ indicating the polyconjugation upon polymerization and the peak at 1,083 cm⁻¹ showing the presence of the dopant ion (BF₄⁻).

The NMR spectrum of the monomer (Fig. 2) shows resonance signals of thiophene, CH₂ and maleimide protons of relative intensities corresponding to the number and type of protons.

¹H-NMR (CDCl₃) δ ppm: 7.17–7.21 (m, 1H, H_a), 7.06 (s, 1H, H_b), 6.95 (d, 1H, H_c), 6.44 (s, 2H, H_g), 4.19

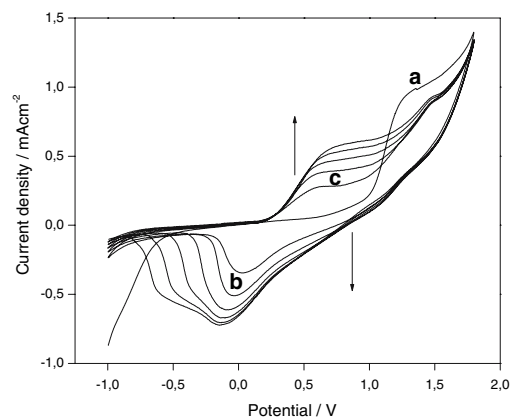


Fig. 3 Cyclic voltammograms of the monomer (NMT) in BFEE/AN at 250 mV sec⁻¹

Fig. 4 (a) Cyclic voltammogram of P(NMT) in monomer free AN:BFEE (1:1, v/v) at different scan rates (b) Anodic and cathodic peak currents as a function of the scan rate

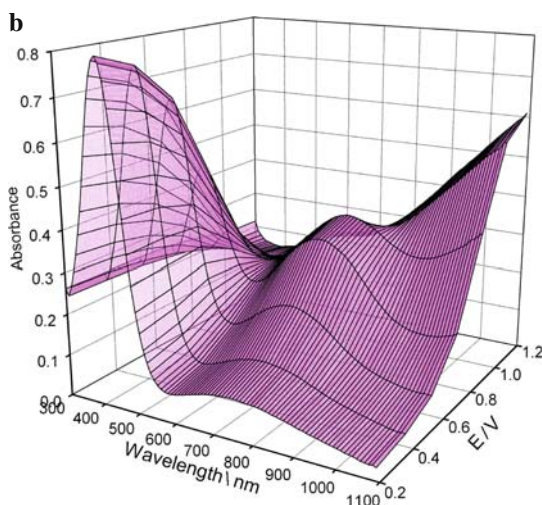
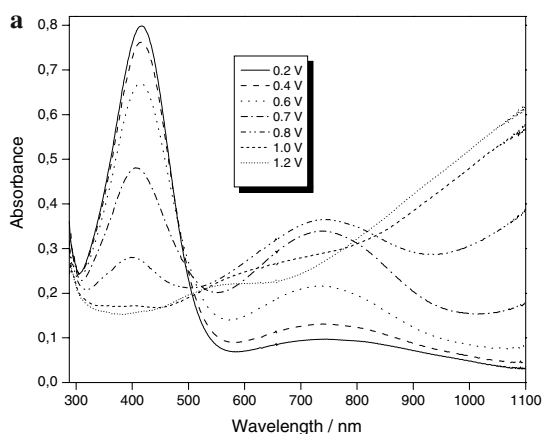
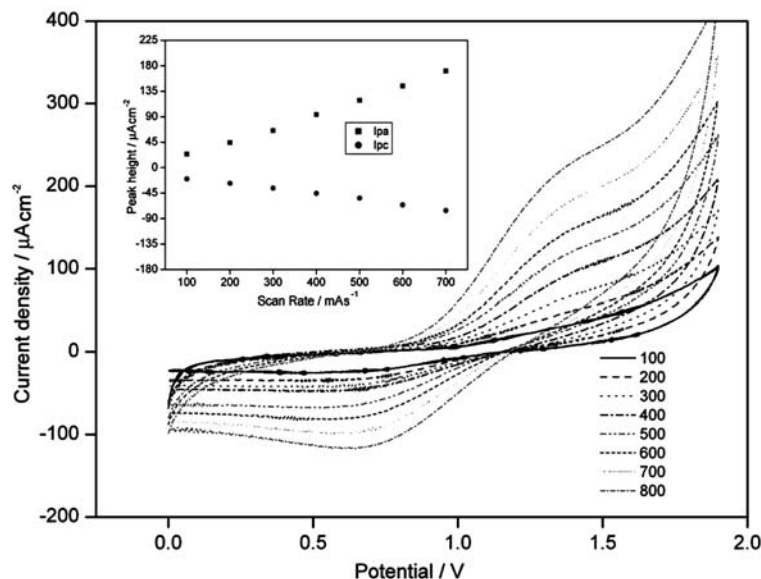


Fig. 5 Optoelectrochemical Spectrum of P(NMT) at applied potentials between 0.2 and 1.2 V (a) 2D (b) 3D

(t, 2H, $j = 20$ Hz, H_c), 3.70 (t, 2H, $j = 20$ Hz, H_f), 3.54 (s, 2H, H_d).

3.2 Cyclic voltammetry

In the cyclic voltammogram of NMT (Fig. 3), at 1.34 V (a) the monomer is oxidized to its radical cation. Monomer oxidation is immediately followed by chemical coupling that yields oligomers in the vicinity of the electrode. Once these oligomers reach a certain length they precipitate onto the electrode surface where the chains can continue to grow in length the electroactivity of the polymer deposited onto the WE can be monitored by the appearance of a peak (−0.35 V) corresponding to the reduction of the oxidized polymer while scanning in the cathodic direction (b). A second positive scan reveals another oxidation peak (0.64 V) at a lower potential than the monomer oxidation peak (c). This is due to the oxidized polymer. Another noticeable fact is the increase in monomer oxidation peak current in the subsequent scans. As the peak current is directly proportional to the electrode area, this increase in the peak current may be attributed to an increase in the WE area due to the electrodeposited polymer.

3.3 Scan rate dependence of the peak currents

Polymer films prepared by constant potential electrolysis (1.8 V) were washed with AN, and their redox switching in monomer-free electrolyte showed a single,

well-defined redox process. The current response was directly proportional to the scan rate, indicating that the polymer film was electroactive and adhered well to the electrode. The anodic and cathodic peak currents show a linear dependence on scan rate as illustrated, in Fig. 4. This demonstrates that the electrochemical processes are reversible and not diffusion limited, even at very high scan rates.

3.4 Conductivity

The conductivity of P(NMT) was measured as $2.8 \times 10^{-5} \text{ S cm}^{-1}$ by the four-probe technique. Conductivity values of electrode and solution sides were found to be of the same order of magnitude. This observation revealed the homogeneity of the film.

3.5 Spectroelectrochemistry of conducting copolymers

The film was deposited on ITO via potentiostatic electrochemical polymerization of NMT (0.1 mol l^{-1}) in the presence of 0.1 mol l^{-1} TBAFB in BFEE/AN (1:1, v/v) at +1.6V. P(NMT) coated ITO was investigated by UV–visible spectroscopy in the monomer free electrolytic system by switching between +0.2 V and +1.2 V (Fig. 5). The onset energy for the π – π^* transition (electronic band gap) was 2.34 eV and λ_{max} was found to be 417 nm. There was a gradual decrease in the peak intensity at 417 nm upon increase in the applied potential, which was accompanied by an increase in the intensity of peaks at 733 nm due to the formation of charge carrier bands (Fig. 5). The appearance of the peak at 733 nm may be attributed to the evolution of a polaron band.

3.6 In situ polymerization

In situ UV–Vis spectra were taken during the course of polymerization. We investigated the in situ electrochemical polymerization at 1.8 V in TBAFB/BFEE:AN every 10 s time interval (Fig. 6).

3.7 Switching

During the switching experiment, the % transmittance (%T) at λ_{max} (417 nm) was measured. The polymer film was synthesized on ITO-coated glass slides under constant potential conditions. The %T was then mon-

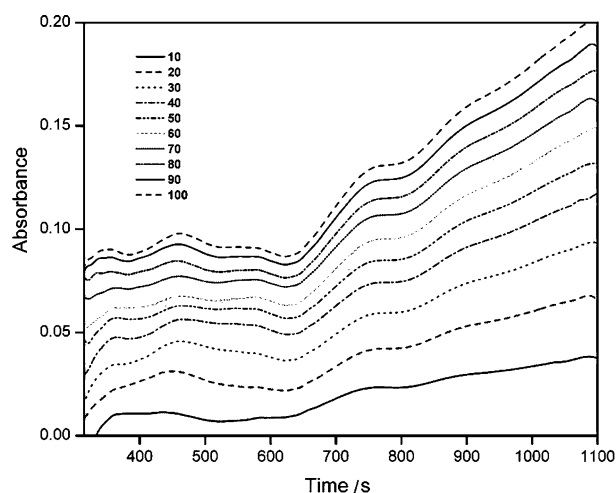


Fig. 6 UV–Vis absorption spectra for the course of polymerization of NMT in BFEE/AN (spectra were recorded for every 5 min)

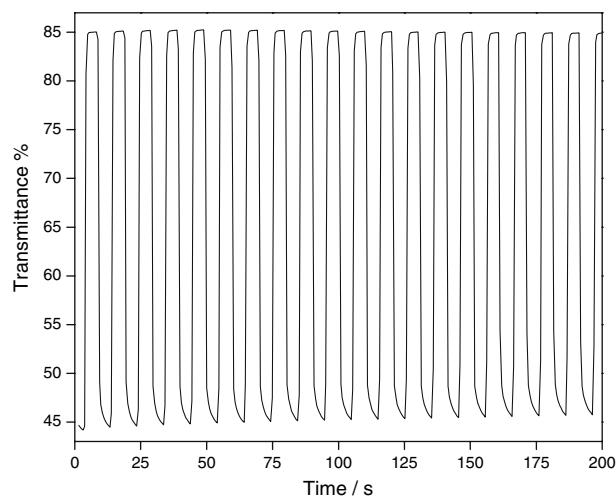


Fig. 7 Electrochromic switching, optical absorbance monitored for P(NMT) at 417 nm in the presence of 0.1 M TBAFB in BFEE/AN

itored at λ_{max} while the polymer was switched between +0.2 V and +1.2 V. The contrast was measured as the difference between %T in the reduced and oxidized forms and noted as 41%. As seen in Fig. 7, P(NMT) has reasonable stability and a switching time (1.75 s).

3.8 Colorimetry

L, a and b values of the films, where L corresponds to luminance, and a, b values to color coordinates, were measured at the fully oxidized and fully reduced states and the data are given in Table 1. P(NMT) was blue in its oxidized state and yellow in its reduced state.

4 Conclusions

A new monomer; N-(2-(thiophen-3-yl)methylcarbonyloxyethyl) maleimide (NMT) was successfully synthesized and characterized via NMR and FTIR. The conducting polymer of NMT was synthesized potentiostatically in AN:BFEE (1:1, v/v) using TBAFB (0.1 M) as electrolyte. P(NMT) was characterized via FTIR, SEM, DSC and conductivity measurement. Spectroelectrochemical analyses revealed that the homopolymer of NMT has an electronic band gap of 2.34 eV. The contrast was measured as the difference between %T in the reduced and oxidized forms. P(NMT) has good optical contrast (41%) and switching time (1.7 s).

The results highlight superior properties of the homopolymer, which may be a potential material for electrochromic devices.

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