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New conducting pyrrole–thiophene co-polymer from an oligomer precursor: electrochemical characterisation

Fatma A. Al-Yusufy · Stanley Bruckenstein · Walkiria S. Schlindwein

Abstract A new oligomer of N,N'-bis(2-pyrrolyl methy-lene)-3,4-dicyano-2,5-diaminothiophene possessing cyano-substituted thiophene and pyrrole residues linked together by azomethine groups was used for the electrochemical polymerisation of conducting films. The approach used for the oligomer design favours inter-chain interactions through hydrogen bonding and negative charge stability through the cyano substitute thiophene. The oligomer was successfully electropolymerised at 0.67 V vs Ag^+/Ag from 0.1M tetrabutylammonium tetrafluoroborate ($TBABF_4$)/acetoni-trile as a dark blue film on the surface of platinum electrodes. Cyclic voltammetry has been used to investigate the redox behaviour of the films. The electrically conduct-ing polymer showed p-doping/neutralisation behaviour. The effect of different electrolytes such as $TBABF_4$, tetrabutyl-ammonium perchlorate ($TBAClO_4$), lithium perchlorate ($LiClO_4$) and sodium perchlorate ($NaClO_4$) on the redox switching and the stability of the polymer films was investigated. Infrared and UV-vis spectra of oligomer and polymers are presented. The evolution of the film growing process is shown by UV-vis spectroscopy.

F. A. Al-Yusufy · W. S. Schlindwein
Leicester School of Pharmacy, De Montfort University,
The Gateway,
Leicester LE1 9BH, UK

W. S. Schlindwein
e-mail: wss@dmu.ac.uk

F. A. Al-Yusufy
Department of Chemistry, Faculty of Science, Sana'a University,
P.O. Box 11923, Sana'a, Yemen

S. Bruckenstein (✉)
Department of Chemistry, University at Buffalo, SUNY,
Buffalo, NY 14260, USA
e-mail: chemstan@buffalo.edu

Introduction

Historical

The strategy normally used when designing a potential organic molecule involves intensive experimental inves-tigations to find the relationship between its structure and properties. The common approach used to produce mono-mers and oligomers that can lead to conducting polymers is the modification of the precursors by covalent attachment of functional groups with specific activity [1–11].

Recently, several attempts have been made to synthesise polymers containing thiophene or pyrrole linked to phenyl-ene by azomethine units [12–18]. The introduction of electron-withdrawing cyano groups into the conjugated backbone is believed to increase the electron affinity of the molecule, hence inducing the electron transport. In addition, the presence of cyano groups allows close intermolecular contacts in the crystal structure via intermo-lecular hydrogen cyano interactions [19, 20].

The production of electroactive materials by electro-polymerisation basically involves generation of cation radicals as reactive species [7, 10, 21]. Because the elemental step in chain growth involves coupling of two radicals, any structural factors affecting this process will have a crucial effect on the propagation of polymerisa-tion and hence, the structure and properties of the polymer. Lack of coplanarity within the monomer unit could drastically limit the π electron delocalisation along the polymer chain causing a partial loss of its relevant electronic properties [22].

Motivation

Our approach is based on using a one-step reaction to synthesised a new oligomer that possesses cyano-substituted thiophene and pyrrole residues linked together by azomethine moieties (Scheme 1). In this case, the structure of this oligomer would favour (1) inter-chain interactions via hydrogen boding, (2) thermal stability by the addition of nitrogen atoms in the backbone, (3) low polymerisation potential due to the π-conjugation through the three members ring structure and (4) planarity of the structure. With this in mind, we report on the electrochemical polymerisation of the oligomer Py$_2$ThAz as a film and the characterisation of this polymer film using cyclic voltammetry, thermal analysis and UV-vis spectroscopy.

The synthesis and characterisation of the oligomer is reported elsewhere [23].

Experimental

Materials and methods

The solvents, N,N-dimethylformamide (DMF), anhydrous (Aldrich, 99.8%), and acetonitrile (Aldrich, 99.5+%), were used as received. The supporting electrolytes, tetrabutylammonium tetrafluoroborate (TBABF$_4$; Aldrich, 99%), tetrabutylammonium perchlorate (TBAClO$_4$; Aldrich, 99%), lithium perchlorate (LiClO$_4$; Aldrich, 99.99%) and sodium perchlorate (NaClO$_4$; Aldrich 99%) were also used as received.

The UV-vis spectra were carried out using Unicam UV/Vis spectrometer. The thermogravimetric analysis was performed using thermogravimetric analysis (TGA) 7 from Perkin Elmer at 10 °C/min from 30 to 500 °C.

Electrochemical measurements

Electrochemical studies were carried out using a PGSTAT30 Windsor potentiostat. A glass cell with three compartments separated by porous disks equipped with platinum electrodes was used. All the potentials were measured vs a Ag$^+$/Ag reference electrode. The reference
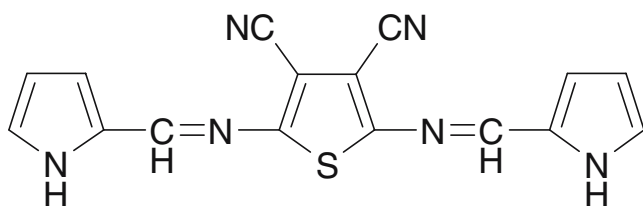
electrode was calibrated before each experiment with respect to the ferrocenium/ferrocene (Fc$^+$/Fc) redox couple. The potential of the Ag$^+$/Ag reference electrode was generally 0.12 V.

A 0.25 cm^2 platinum disc (Aldrich, 99.99%) was used as the working electrode and two platinum meshes were used as counter electrodes. The cell configuration is reported elsewhere [24]. The solutions were deaerated by passing nitrogen before the measurements and during the measurements the nitrogen flow was maintained over the solution. The oligomer was electropolymerised in the working electrode compartment from an acetonitrile solution of 0.025 M Py$_2$ThAz with 0.1 M TBABF$_4$ as supporting electrolyte. The other electrode compartments were filled with the same electrolyte but without the oligomer. Before each experiment, the Pt meshes used as counter electrodes were cleaned by burning in a propane flame, and the working electrode was cleaned with acid, followed by neutralisation using base solution, then washed with acetone, and finally dried. It was then placed in the working electrode compartment close to the Luggin capillary of the reference electrode compartment. Polymerisation was performed potentiostatically at 0.67 V vs Ag$^+$/Ag (see below). For all the experiments, the polymer films were deposited by passing 85 mC cm^{-2} of charge at the polymerisation potential. The redox potentials and the stability of the polymer films were determined from cyclic voltammetry (see Tables 1 and 2 and Fig. 5).

A one compartment electrochemical cell, with a Luggin capillary for the reference electrode (Ag$^+$/Ag), was used in the studies using different electrolytes. Platinum was used as counter and working electrodes. The polymer films were cycled in 0.1 M of electrolyte/acetonitrile solutions for 90 cycles after a pre-conditioning step of 10 cycles to obtain a steady-state response. All the cyclic voltammograms were acquired at a scan rate of 50 mV s^{-1} in the potential range of −0.5 to 1.0 V.

Table 1 Cathodic and anodic peak potentials obtained from the cyclic voltammograms of polymer films in different electrolyte/acetonitrile solutions

Electrolyte solution	Ep^a (V)			
	1st cycle		90th cycle	
	+	−	+	−
LiClO$_4$	0.970	0.445	0.876	0.331
TBAClO$_4$	0.982	0.419	0.786	0.484
TBABF$_4$	0.839	0.588	0.741	0.556
NaClO$_4$	0.838	0.602	0.760^b	0.537

+, anodic; −, cathodic
[a] Peak potential
[b] 20th cycle

Scheme 1 N,N'-bis(2-pyrrolylmethylene)-3,4-dicyano-2,5-diaminothiophene (Py$_2$ThAz)

Table 2 Charge density and charge loss obtained from the cyclic voltammograms of polymer films in different electrolyte/acetonitrile solutions

Electrolyte solution	Charge density (mC cm^{-2})				Charge loss per 90 cycles (%)	
	1st cycle		90th cycle			
	+	−	+	−	+	−
LiClO$_4$	2.18	2.66	1.87	2.13	14.2	19.9
TBAClO$_4$	2.89	2.72	1.15	1.33	60.2	51.1
TBABF$_4$	1.12	1.07	0.31	0.30	72.5	71.9
NaClO$_4$	0.59	0.58	0.20[a]	0.23	65.2[a]	60.0

[a] 20th cycle

Results and discussion

Oligomer

The oligomer, Py$_2$ThAz, synthesis and characterisation are reported elsewhere [23]. Analysis of Py$_2$ThAz by single crystal diffraction [23] reveals extensive hydrogen bonding between the cyano groups and the N–H bonds of the pyrrole rings. The X-ray results show that the molecule was not totally planar. As a result of this distortion, the solid state of the oligomer adopted a zig-zag structure.

The thermal stability of the oligomer was investigated by TGA. The main loss in weight (11%) occurred at 297.6 °C. The incorporation of nitrogen atoms into the conjugated molecular chains aided in the thermal stability of this material.

Potentiodynamic polymerisation

The redox behaviour of the Py$_2$ThAz was investigated using cyclic voltammetry in the potential range −0.1 to 1.2 V. The initial cycles showed two distinct oxidation peaks that increased with the number of cycles and merged to almost one peak at higher potential (Fig. 1). The polymer or the oxidised species formed at this higher potential showed no redox response when the potential cycled in a fresh electrolyte solution. These results, as shown below, indicate that the polymerisation of the Py$_2$ThAz is very sensitive to the positive polymerisation potentials to which it is exposed. Too positive potentials can generate electrochemical inactive species due to the formation of defects within the polymer chain. As a result of this, the electrochemical polymerisation potential was investigated potentiostatically.

Potentiostatic polymerisation

A series of charge-time curves at fixed potentials were performed. For applied potentials lower than the polymerisation potential, the current was less than 0.1 μA.cm^{-2},
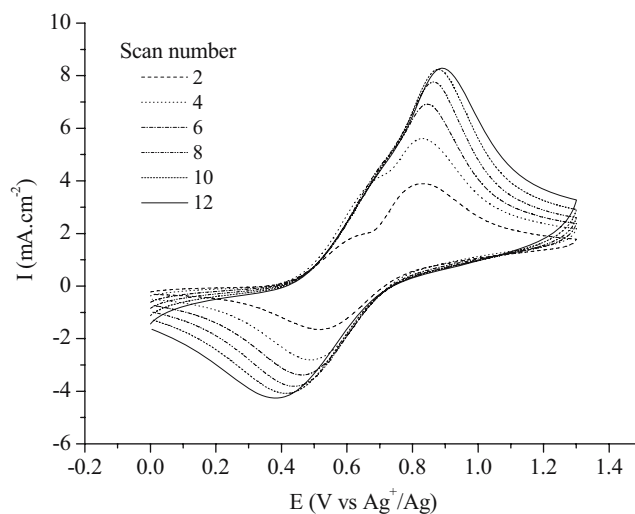
Fig. 1 Cyclic voltammograms of poly(Py$_2$ThAz) potentiodynamically grown from a solution of 0.025 M of oligomer in 0.1 M of TBABF$_4$ as supporting electrolyte in acetonitrile

similar to the value obtained in the absence of the oligomer. Once the applied potential reached the polymerisation potential, after induction period of 5–75 s, the deposition current increased continuously. The increase in current with time is due to the concurrent increase in the surface area of the growing film. Generally, after several hundred seconds of polymerisation, the current attained a steady state value corresponding to a balance between the growth of the polymer film's surface area and concentration polarisation.

The electropolymerisation potential for the oligomer was determined by increasing the potential to the working electrode in 10 mV steps and was defined as the least positive potential at which an increase in the electrode current with time was observed [25]. The electropolymerisation potential of the oligomer was found to be 0.67 V against Ag$^+$/Ag.

Py$_2$ThAz was then successfully electropolymerised at 0.67 V vs Ag$^+$/Ag from 0.1 M TBABF$_4$ in acetonitrile as dark blue film on the surface of the platinum electrode. It was difficult, however, to obtain a completely insoluble polymer. The formation of soluble low molar mass polymers was observed by the colour change of the oligomer/electrolyte solution from orange to dark brown. Several studies have reported that slight solubility of the oligomer limits the degree of electropolymerisation [7, 10, 14]. According to the X-ray crystallography studies [23] of the Py$_2$ThAz structure, the slight solubility of the oligomer could be attributed to the intermolecular hydrogen cyano interactions. In addition, the distorted structure, with one pyrrole ring twisted out of plane, is another factor that might influence on the polymerisation process [10, 13, 22].

The thickness of the film was controlled by performing electropolymerisation at different charge depositions 26, 85, 110 and 138 mC cm^{-2} correspondent to 10, 20, 30 and

40 min, respectively, for the same oligomer solution. It was observed that after 20 min of deposition, the solid polymer falls off the working electrode surface into the oligomer solution. Therefore, a 20-min deposition time (85 mC cm^{-2}) was chosen for all the measurements. The as-deposited polymer was neutralised by scanning the potential from an open circuit potential to 0.0 V. The neutral polymer films were then transferred to fresh acetonitrile-based electrolyte solutions for the subsequent cyclic voltammetry studies.

Cyclic voltammetry

The cyclic voltammogram for the polymer, in the potential range −1.5 to 1.0 V and at a scan rate of 20 mV s^{-1}, showed only oxidation/neutralisation (*p*-doping/neutralisation; Fig. 2).

Different scan rates (10, 20, 30, 40 and 50 mV s^{-1}) were applied to the polymer, and a linear behaviour of square root of the scan rate against peak current oxidation was obtained; however, the redox behaviour was not completely reversible [26], although the deposition was diffusion controlled (Fig. 3).

For slow scan rates (10 mV s^{-1}), the current–voltage curves show a 'tail' just before 1.0 V. This is probably due to further oxidation of electroactive species trapped in the polymer matrix that need higher potentials for oxidation compared to the oligomer. This behaviour was further investigated by cycling the polymer film between the same potentials (−0.5–1.0 V) at 10 mV s^{-1} for several cycles.

Figure 4 shows these cyclic voltammograms of the polymer film in 0.1 M TBABF$_4$/acetonitrile. Potential cycling at lower scan rates (10 mV s^{-1}) caused peak potentials to shift to more negative values. After reaching its most negative potential value (~12th cycle), the cyclic
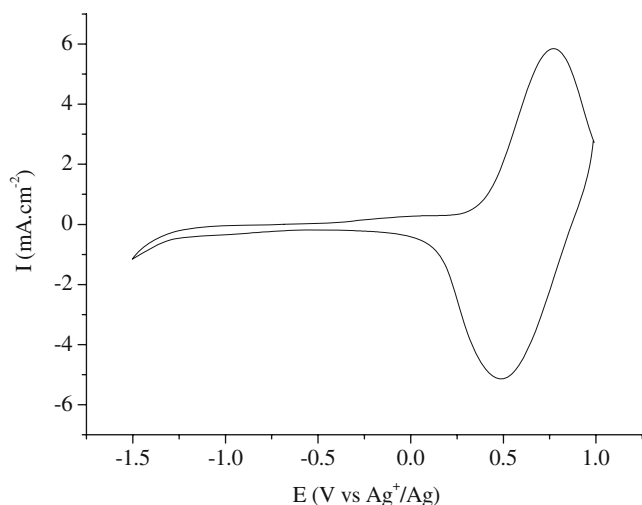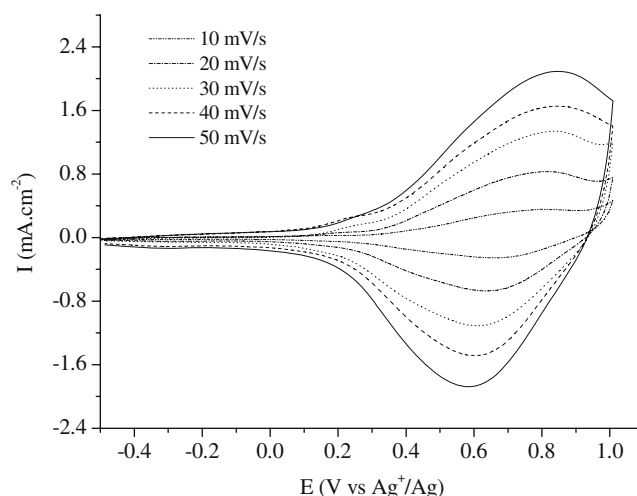

Fig. 3 Current–voltage curves of the poly(Py$_2$ThAz) as a function of scan rate

voltammogram lost its reversible-like character. The peak potential then shifted to more positive values, and eventually, the redox response died off and the polymer film became non-conducting. These results suggest that at potentials of 1.0 V or above and cycling at low scan rates (e.g. 10 mV s^{-1}) can lead, via further oxidation, to species that have no redox response. Using higher scan rates (e.g. 50 mV s^{-1}), further oxidation is less favoured and the subsequent shifts of the peak potential do not occur.

Stability in different electrolytes

The effects of different electrolytes such as TBABF$_4$, TBAClO$_4$, LiClO$_4$ and NaClO$_4$ on the redox behaviour and the stability of the polymer films were investigated.

The stability of the polymer films during doping was determined from the charge in the reduction peak over
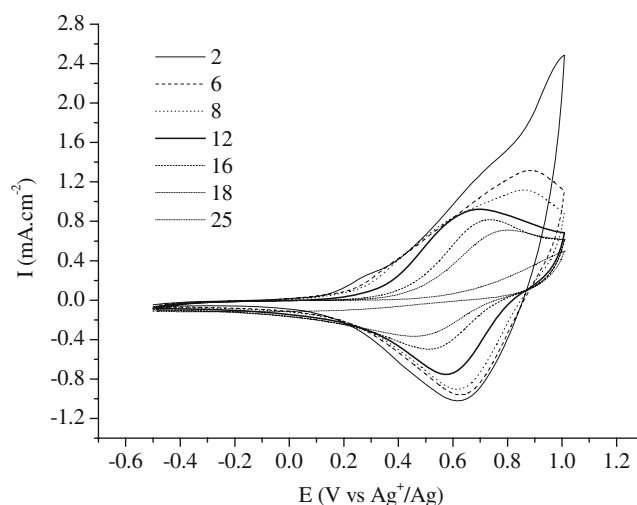

Fig. 2 Cyclic voltammogram of poly(Py$_2$ThAz) over the range of −1.5–1.0 V in 0.1 M of TBABF$_4$ as supporting electrolyte in acetonitrile

Fig. 4 Cyclic voltammogram of the poly(Py$_2$ThAz) as a function of number of cycles in 0.1 M of TBABF$_4$ as supporting electrolyte in acetonitrile at 10 mV s^{-1}
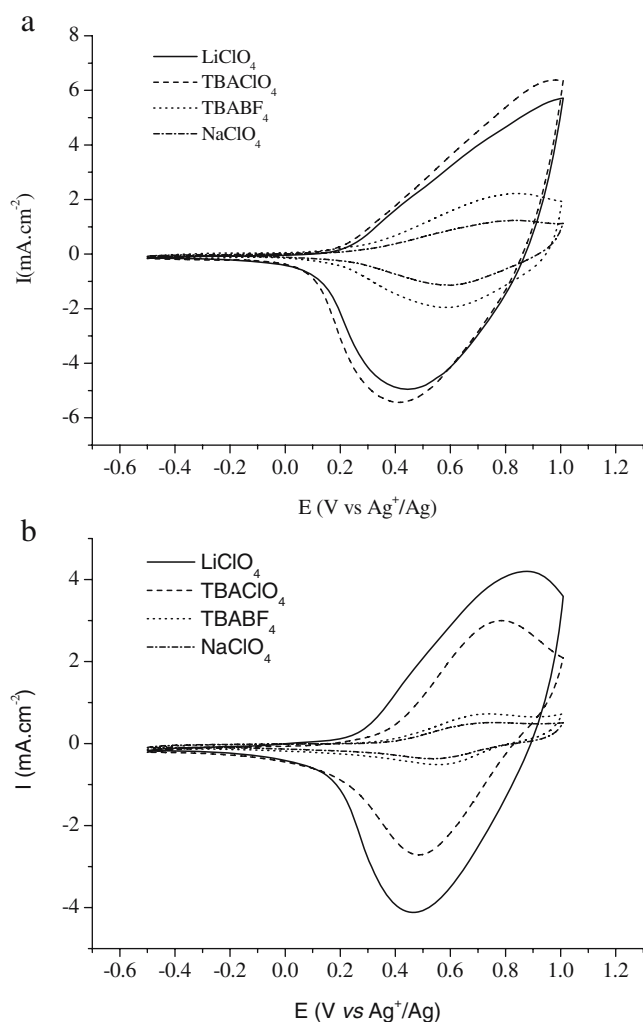
Fig. 5 Cyclic voltammograms for poly(Py$_2$ThAz) in 0.1 M of LiClO$_4$, TBAClO$_4$, TBABF$_4$, and NaClO$_4$ electrolytes. **a** 1st cycle, **b** 90th cycle (except for the NaClO$_4$, which is the 20th cycle)

multiple cycles. The average percentage charge loss (CL) per cycle was calculated from the charge under the neutralisation wave of the voltammogram for the *p*-doping. This is obtained from the following equation:

$$CL = \left[\frac{Q_1 - Q_r}{Q_1} \right] \frac{1}{n} 100\%$$

where Q_1 is the reduction charge in the first cycle, Q_r is the reduction charge in the *n*th cycle and *n* is the number of cycles. For all measurements reported in this paper, the tenth cycle was taken as the first cycle, and the cycles before that are considered a pre-conditioning step [27].

Tables 1 and 2 show how the different electrolytes affect the response of the polymer films to redox switching in acetonitrile-based electrolyte solutions. Of all the salts, LiClO$_4$ showed the highest stability effect on the polymer film with only about 14–20% charge loss after 90 cycles.

Figure 5 shows the cyclic voltammograms for the polymers in 0.1 M of LiClO$_4$, TBAClO$_4$, TBABF$_4$ and

NaClO$_4$ electrolyte solutions for the 1st and 90th *p*-doping/ undoping cycles (except for the NaClO$_4$, which is the 20th cycle). NaClO$_4$ had considerably lower charge density and stability, with about 60% charge loss only after 20 cycles compared to LiClO$_4$ and TBAClO$_4$. Previous studies on the effect of similar electrolytes on the redox behaviour of poly (vinylferrocene) in propylene carbonate gave similar results in the case of NaClO$_4$. This has been attributed to the solvation structure of the electrolyte and the role it plays in the ion mobility [27].

For all the electrolyte solutions the peak potential Ep, for the polymer films was shifted to lower potentials as the number of cycles increased. This could be attributed to further polymerisation of low molecular polymer molecules to form higher molar masses, which can be more easily oxidized at lower potentials [7]. The influence of the anion, ClO$_4^-$, proved to be significant. For the same cation (TBA$^+$), the polymer is more stable in ClO$_4^-$ compared to BF$_4^-$. Referring to the hard acid–hard base theory of Pearson [28], ClO$_4^-$ is a hard base, and the polymer could be considered a hard acid due to the presence of the two strong electron-withdrawing cyano groups in the repeat unit of polymer chains. Therefore, one would expect ClO$_4^-$ to stabilise the polymer cation radicals more than BF$_4^-$. Overall, LiClO$_4$ proved to be the most promising electrolyte, among the ones studied, for poly(Py$_2$ThAz).

UV-Vis spectra

The electronic absorption spectra for the oligomer and the polymer were recorded using DMF as a solvent. Polymer films, deposited potentiostatically at different times (5, 10 and 20 min), were washed thoroughly in acetonitrile to remove the salt from the films and then characterized by UV-vis spectroscopy. Figure 6 shows the visible region of
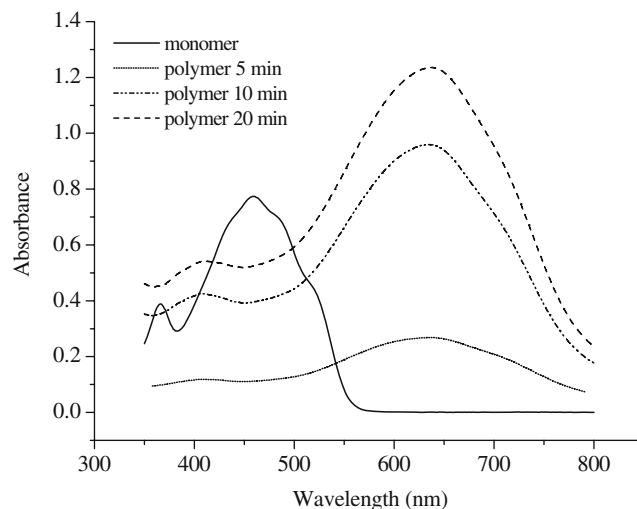

Fig. 6 UV-Vis absorption spectra of the oligomer and the polymer samples deposited at different time intervals

the absorption spectra for the oligomer and the polymer samples deposited at different time intervals. There are no major differences in the UV region (not shown) of the spectra for the oligomer and the polymers. They all show several absorption bands in the UV region due to the thiophene and the pyrrole rings in the chemical structures. Differences are clear in the visible region of the spectra. The oligomer shows two absorption bands, one narrow at 366 nm and the other broad band at 459 nm with shoulders at 480 and 518 nm. On comparison, the polymers showed a large absorption band shift to longer wavelengths. The absorption bands are much broader in the polymers than in the oligomer spectrum. The two absorption bands in the polymer spectra are observed at 407 and 636 nm with a shoulder at about 700 nm. This is attributed to the extension of the π-conjugation as a consequence of polymerization. Furthermore, the colour change of the oligomer from orange to dark blue on polymerization is characteristic of the π-conjugation length [12]. The absorption spectra of the polymers at different deposition times showed no change in position of the bands. This indicates that they have the same conjugation block dimension in the chain lengths that had reached a critical length in the first few minutes [13].

Conclusions

A novel oligomeric species Py$_2$ThAz can be electropolymerised to form p-doped film on the electrode. The polymer can be formed either by constant potential or by using cyclic voltammetry. For voltage scan rates between 10 and 50 mV s^{-1}, the oxidation peak currents for a film cycled between −1.5 to 1.0 V vs Ag$^+$/Ag reference electroscan rate that demonstrated diffusion control in acetonitrile 0.1 M TBABF$_4$ containing 0.25 M oligomer. Repetitive voltage cycling between −0.5 and 1.0 V had two effects at 10 mV s^{-1}. First, the peak oxidation current shifted to less positive potentials, presumably because oligomers and short chain polymer were oxidised to longer chain polymers. Second, on repetitive cycles scan rates, the oxidation current peak shifted more positively and eventually died off, presumably because of over oxidation of the desirable longer chain polymer. Studies of the stability of the polymer to long term potential cycling (up to 90 cycles) with TBABF$_4$, TBAClO$_4$, LiClO$_4$ and NaClO$_4$ demonstrated that the most stable performance occurred in LiClO$_4$. For LiClO$_4$, on the 90th cycle, the charge loss was 14% on the oxidation cycle and 20% on the reduction cycle. The synthesis of the oligomer, and presumably derivatives of it, is extremely simple to achieve in one step at very low cost.

We believe that by suitable choice of oligomers/monomers analogous to Py$_2$ThAz, polymers that have the improved geometry and stability can be produced. Furthermore, the one step synthetic approach should be generally applicable in these cases.

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