

Electrochemical synthesis of conjugated copolymer poly(3-hexylthiophene-co-dithienopyrrole): Stepwise approach to enhance electro-optical properties

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Abstract:

Electrochemical polymerisation of 3-hexylthiophene (3HT) and electrochemical copolymerisation of 3HT and *N*-benzoyl dithienopyrrole (BDP) were performed to prepare polymer and copolymer films using a linear sweep voltammetry potentiostatic technique with a voltage range from 1.7-1.8 V and a scan rate of 0.1 mV/s. Cyclic voltammetry (CV) curves, Fourier-transform infrared (FTIR) spectra, scanning electron microscope (SEM) images, and UV-Vis absorption spectra of the polymer and copolymer were recorded for analysis and comparison of the electropolymerisation process and properties of the resultant films. The SEM photographs of the copolymer base on 3HT and BDP exhibited a rigid structure with large spherical aggregates with an average size around 200 nm. The copolymer of 3HT and BDP exhibited the band gaps of 2.25 eV which was determined via electrochemical measurement that is higher than of band gaps of homopolymer poly(3-hexylthiophene) (P3HT). The copolymer's energy bandgap HOMO-LUMO was enhanced compared to polymer P3HT. Moreover, the increased conjugation length significantly improved the morphology structure as well as the electrochemical stability of the conjugated copolymer.

Keywords: conjugated polymer, copolymer, electropolymerisation, optoelectronic application, P3HT, thiophene.

Classification numbers: 2.1, 2.3

1. Introduction

Conductive polymers, such as polypyrrole, polythiophene, and polyaniline, have garnered significant attention recently due to their potential applications in various technologies, including electrochemical displays, smart windows, solar cells, sensors, antistatic coatings, catalysis, and redox capacitors [1-4]. Among organic conductive polymers, poly(3-alkylthiophene) and its derivatives, particularly P3HT, are intriguing materials known for their ease of synthesis, good charge carrier mobility, and chemical stability. P3HT has also served as model systems for fundamental research due to its characteristic hair-rod structure, featuring a rigid

conjugated backbone and flexible alkyl side chains, which are favourable for solubilisation [5, 6].

Copolymerisation has emerged as a promising process for creating high-performance conjugated polymers in recent years. Copolymerisation is frequently used to generate a new conjugated polymer with physical and chemical characteristics distinct from and intermediate between those of the constituent homopolymers. However, it is crucial to note that a copolymer significantly differs from a composite and a blend. For example, electropolymerisation (EP) of styrene and pyrrole monomers was performed and found that the product polymer was a copolymer of pyrrole and styrene instead of a composite or blend of polypyrrole and

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polystyrene. The copolymerisation approach has recently been shown to be capable of tuning the wavelength range of light absorption, frontier energy levels, and solubility of conjugated polymers [7, 8]. Notably, P. Acker, et al. (2022) [9] designed the novel N-anisylphenothiazine-bithiophene conjugated copolymer p(APT-T2), which could be a promising material for designing an electrode for energy storage applications due to its intrinsic conductivity combined with the presence of defined redox centers.

Due to the low cost of thiophene monomers and the improved redox potential compared to polypyrrole, polythiophene holds promise for optoelectronic applications [10]. However, the regio-random chemical structure of polythiophene and its derivatives has been shown to provide limited charge transfer in the solid state due to their reduced backbone planarity and disordered molecule packing, which limits their applicability [11]. In contrast, dithiopyrrole has long been recognised for its unique properties, such as excellent thermal and electrical stability, owing to its wide HOMO-LUMO energy gap. Therefore, we attempted to incorporate thiophene with dithienopyrrole units through copolymerisation, aiming to improve polythiophene properties through this specific combination.

Strategies for modifying the main conjugation length of optoelectronic materials, such as organic solar cells, dye-sensitised solar cells, organic field-effect transistors, and electrochromism, have recently received considerable attention to enhance their physical and chemical properties. Additionally, electrochemical polymerisation is well-known as a simple, fast, efficient, and cost-effective method to prepare polymer films by employing an electric field. This method also offers several advantages: (1) It is highly effective for synthesising polymer films because the reaction may be completed in several seconds or minutes, whereas the conventional method requires several hours or days, and the prepared films only form on the electrodes without any visible signs of a reaction in the solution; (2) The electrochemical reaction may be carried out at ambient conditions, in contrast to the severe conditions, high temperatures, and inert environments required for conventional chemical synthesis; (3) Instead of requiring specialised catalysts and expensive complexants for solution-phase synthesis, the electropolymerisation approach employs inexpensive supporting electrolytes [12-14]. Therefore, extending the main chain's conjugation length via electrochemical polymerisation is effective for optoelectronic applications.

In this work, the electrochemical polymerisation of 3HT and the electrochemical copolymerisation of 3HT and BDP were prepared using linear sweep voltammetry potentiostatic technique. FTIR spectroscopy was used to characterise and study the chemical structure of the obtained polymer and copolymer. Most importantly, the resultant polymer and copolymer were further examined for their morphological, optical, and electrical properties to assess the efficiency of the copolymerisation approach.

2. Materials and methods

2.1. Materials

3HT (99%), N-benzoyl dithieno[3,2-b:2'3'-d]pyrrole (98%), and Lithi perchlorate (LiClO_4 , 98%) were purchased from Acros Organic and used as received.

Chloroform (CHCl_3 , 99.5%) was purchased from Fisher/Acros and dried using molecular sieves under N_2 . Acetonitrile (CH_3CN , 99%) and methanone (99%) were purchased from Fisher/Acros and used as received.

2.2. Characterisation

FTIR spectra, collected as the average of 64 scans with a resolution of 4 cm^{-1} , were recorded from the KBr disk on the FTIR Bruker Tensor 27. UV-vis absorption spectra of polymers in solution were recorded on an Ocean Optics USB2000 spectrometer over a wavelength range of 200-1100 nm. Surface morphology analysis of polymers coated specimen surfaces was performed by SEM (model Jeol JSM-6480 LV). The AUTOLAB equipment (Utrecht, Netherlands) was used to measure the electrochemical properties of molecules. The AUTOLAB software is NOVA 1.11. The electrochemical experiments used an ITO glass as a working electrode, Pt as a counter electrode, and an Ag/Ag^+ reference electrode. The solutions were prepared with 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) in acetonitrile. Ag/Ag^+ reference electrode (0.1 M AgNO_3 /0.1 M TBAPF₆ in CH_3CN ; 0.320 V and SCE) was used as a reference potential.

2.3. Investigation the onset oxidation potentials (E_{onset}) of monomers 3HT and N-benzoyl dithieno[3,2-b:2'3'-d]pyrrole (BDP)

First, the electrochemical experiment of the 3HT was conducted by adding 3HT (0.27 ml, 1.5 mmol) and LiClO_4 (319.2 mg, 3.0 mmol) to acetonitrile (30 ml) in

an electrochemical cell, using an indium tin oxide (ITO) glass as a working electrode and platinum disk as a counter electrode. Then the mixture was subjected to CV at a voltage range of 0-2 V, with a scan rate of 0.1 mV/s.

The same experiment was applied to the monomer BDP, in the electrochemical cell BDP (16.98 mg, 0.06 mmol), LiClO₄ (319.2 mg, 3 mmol), and acetonitrile (30 ml). The electrochemical experiment was conducted using ITO glass and Pt as working and counter electrodes, respectively, with an applied voltage of 0-2 V and a scan rate of 0.1 mV/s.

2.4. Electrochemical polymerisation of 3HT

For electrochemical polymerisation of 3HT, the electrolyte consisted of 3HT monomer (0.27 ml, 1.5 mmol) and LiClO₄ (319.2 mg, 3 mmol) dispersed in acetonitrile (30 ml). The ITO glass and Pt were used as working and counter electrodes, respectively. The P3HT was electrochemically polymerised at the voltage of 1.7-1.8 V and a scan rate of 0.1 mV/s for about 15 min. After that, the thin-film on ITO glass was soaked in acetonitrile for 15 min to remove small molecules and dried in a vacuum oven at 50°C for 24 h.

2.5. Electrochemical copolymerisation of 3HT and BDP

For electrochemical polymerisation of the copolymer from 3HT and BDP, the electrolyte consisted of monomer 3HT (0.27 ml, 1.5 mmol), BDP (16.98 mg, 0.06 mmol) and LiClO₄ (319.2 mg, 3 mmol) dispersed in acetonitrile (30 ml). The ITO glass and Pt were used as working and counter electrodes, respectively. The copolymer was electrochemically polymerised at the voltage of 1.7-1.8 V, with a scan rate of 0.1 mV/s for about 15 min. After that, the thin-film on ITO glass was soaked in acetonitrile for 15 min to remove small molecules and dried in a vacuum oven at 50°C for 24 h.

3. Results and discussion

3.1. Electrochemical polymerisation of 3HT and electrochemical copolymerisation of 3HT and BDP

Before conducting the electropolymerisation to synthesise P3HT and copolymer, the onset oxidation potentials (E_{onset}) of monomers 3HT and BDP were investigated from their CV (Fig. 1). The figure shows that the E_{onset} of 3HT and BDP was initiated at 1.4 and 1 V, respectively, and BDP

also exhibits oxidation peaks at 1.16 and 1.7 V. Based on the results, the voltage for the electropolymerisation should be above the E_{onset} of both monomers. Therefore, the polymer P3HT and copolymer were prepared by linear sweep voltammetry potentiostatic technique with a voltage range from 1.7-1.8 V and a scan rate of 0.1 mV/s.

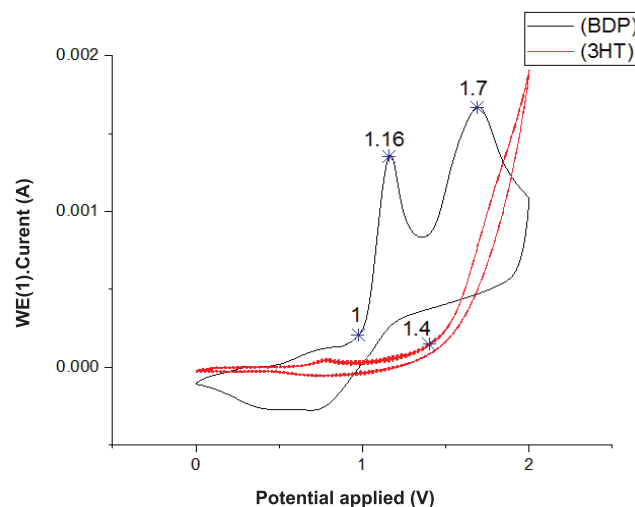


Fig. 1. CV of monomers 3HT and BDP with the range of voltage from 0-2 V and a scan rate of 0.1 mV/s.

The acquired current-voltage (I-V) characteristic curves for the electropolymerisation to synthesise polymer P3HT and copolymer are shown in Fig. 2. The current intensity increases gradually with the increase in applied voltage for both electropolymerisations. The prepared conductive polymers exhibited good electrochemical redox activity, as evidenced by the significant growth of the corresponding conductive polymers on the ITO glass.

After the successful electropolymerisations of both polymers, P3HT and copolymer, the chemical structure was characterised using FTIR spectroscopy. FTIR spectroscopy was scanned in the frequency region of 400-4000 cm⁻¹ using an infrared spectrometer by employing the KBr pellet technique. In the case of P3HT, Fig. 3 and Table 1 exhibit bands from 2927-2854 cm⁻¹ attributed to the C-H stretching vibrations of the ethyl-hexyl group and C-H linkage in the aromatic structure. Aromatic C=C stretching, and C-H deformation vibrations correspond to the characteristic band between 1700 and 1610 cm⁻¹. The band from 1245 to 970 cm⁻¹ is ascribed to the C-S stretching vibrations of thiophene structures. The FTIR result clearly indicated that the electropolymerisation has been performed successfully to obtain the conjugated polymer P3HT.

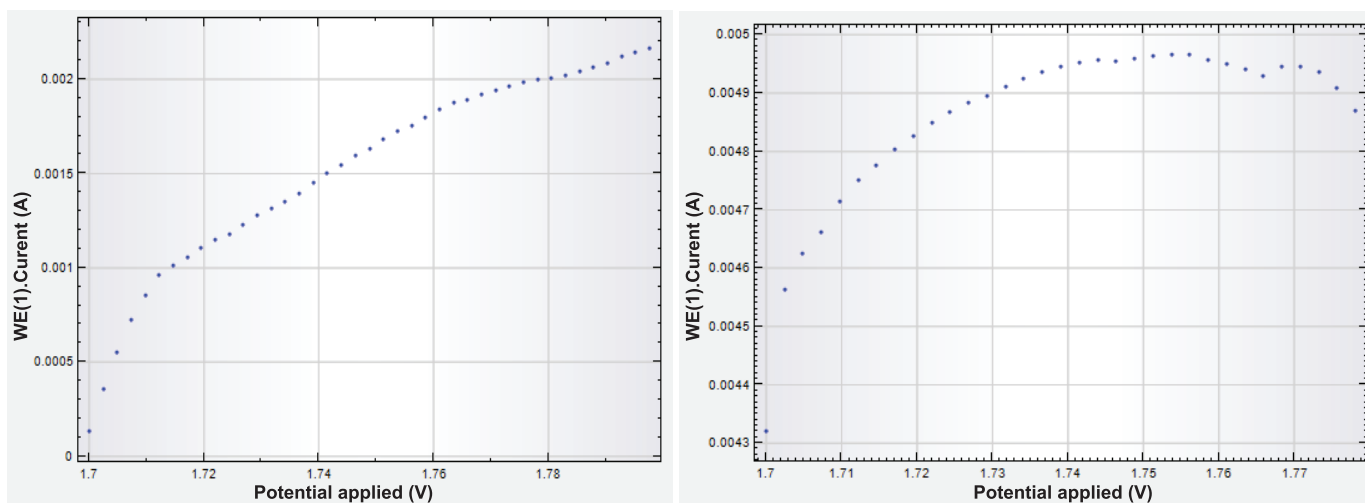


Fig. 2. Current-voltage (I-V) graphs of the electropolymerisations to synthesise P3HT (left) and copolymer (right).

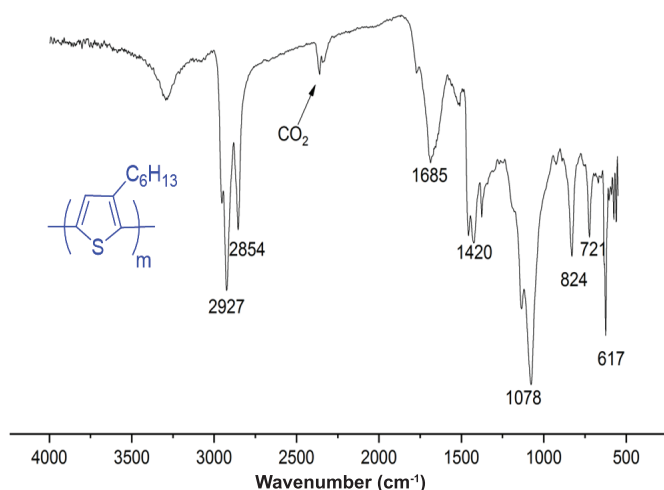


Fig. 3. FTIR spectrum of polymer P3HT.

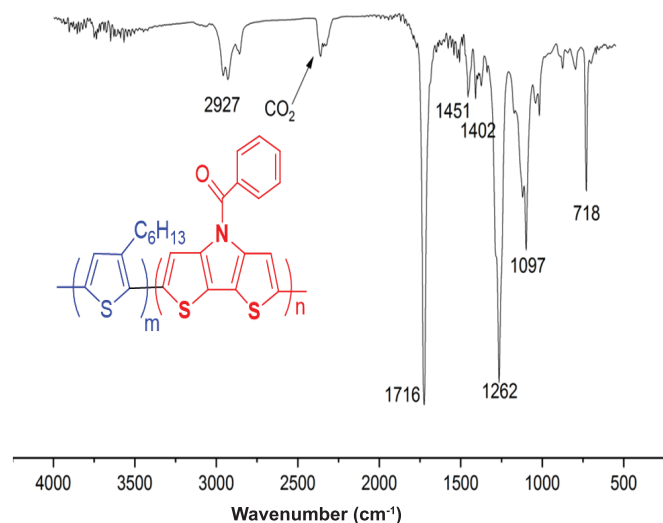


Fig. 4. FTIR spectrum of copolymer from 3HT and BDP.

Table 1. IR absorption wavenumbers (cm⁻¹) and their functional group of P3HT and copolymer.

P3HT	Copolymer	Functional group
Wavenumbers (cm ⁻¹)		
2927	2927	Methylene C-H stretch
2854	2854	Methyl C-H stretch
1685	1716	C=C aromatic ring stretch
1420	1451, 1402	Methyl and methylene C-H bend
-	1262	C-N aromatic stretch
1078	1097	C-S stretch
824	718	Aromatic C-H bend

Similarly, the presence of chemical functional groups in the copolymer has been identified by the FTIR spectrum, as shown in Fig. 4. The spectrum indicates bands in the range of 2927-2854 cm⁻¹ relating to the -CH₂ and -CH₃ stretching and peak at 1451-1402 cm⁻¹ relating to the -CH₃ and -CH₂ bending, while the C=C stretching mode of the aromatic ring is exhibited in the peak at 1716 cm⁻¹. Moreover, the peaks at 1262 cm⁻¹ indicate the existence of C-N of pyrrole structures. This investigation has demonstrated that the electropolymerisation of monomers 3HT and BDP has been performed successfully to generate the copolymer.

3.2. Structure analysed of the P3HT and copolymer using SEM

The morphology of P3HT and copolymer films formed on the electrodes was investigated using SEM. SEM

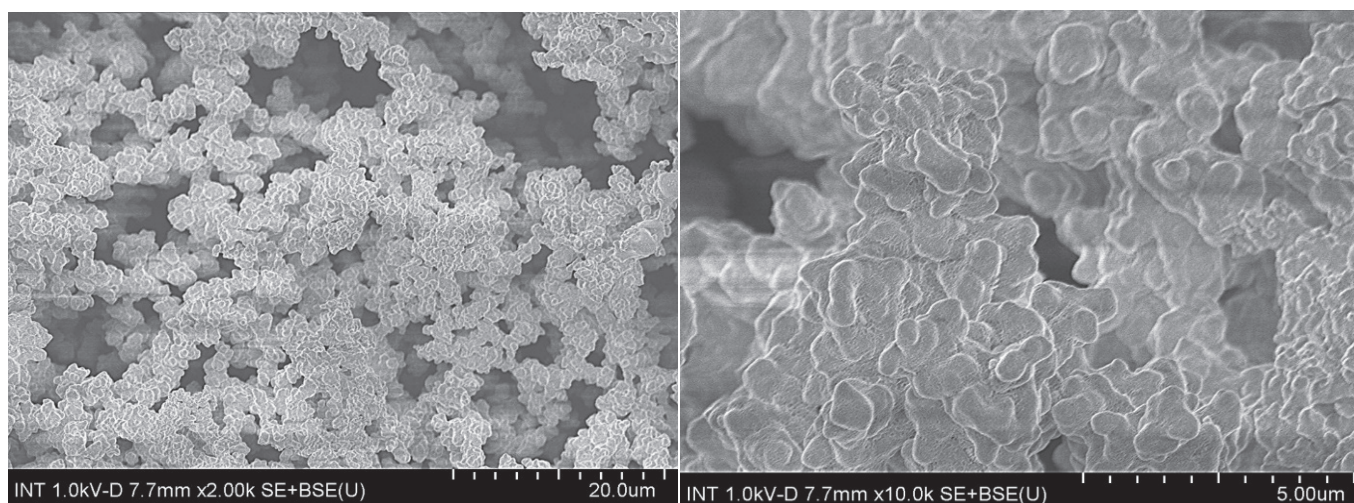


Fig. 5. SEM images of polymer P3HT.

micrographs of the P3HT film were shown in Fig. 5. A low magnification (2,000x, Fig. 5, left) image of the P3HT sample revealed a “coral-like” morphology, whereas a high magnification (10,000x, Fig. 5, right) image revealed large amounts of small spherical particles separated by empty pores. In fact, the decrease in the polymer’s regularity, which is evident in the globular forms, might be caused by structural defects such as reticulation, cross-linking, and α,β - coupling instead of α,α' -coupling between thiophene units [15].

On the other hand, SEM photographs of the copolymer prepared from 3HT and BDP exhibited a more rigid structure (2,000x, Fig. 6, left; 10,000x, Fig. 6, right) with large spherical aggregates (5-7 mm) of small-sized particles

with an average size of around 200 nm. In general, the macroscopic structure of P3HT is relatively loose compared to the copolymer. This comparison also confirms that the electrochemical copolymerisation was performed successfully to generate the 3HT-BDP copolymer.

3.3. Optical properties of the P3HT and copolymer

The optical properties of P3HT and the copolymer were characterised and compared using UV-Vis absorption. According to Fig. 7, the maximum absorption peak of the copolymer is at 430 nm, which is red-shifted compared to that of P3HT, which is at 390 nm. This effect results from the fact that larger molecules absorb light at longer wavelengths than smaller ones because they are more polarisable as they grow in size.

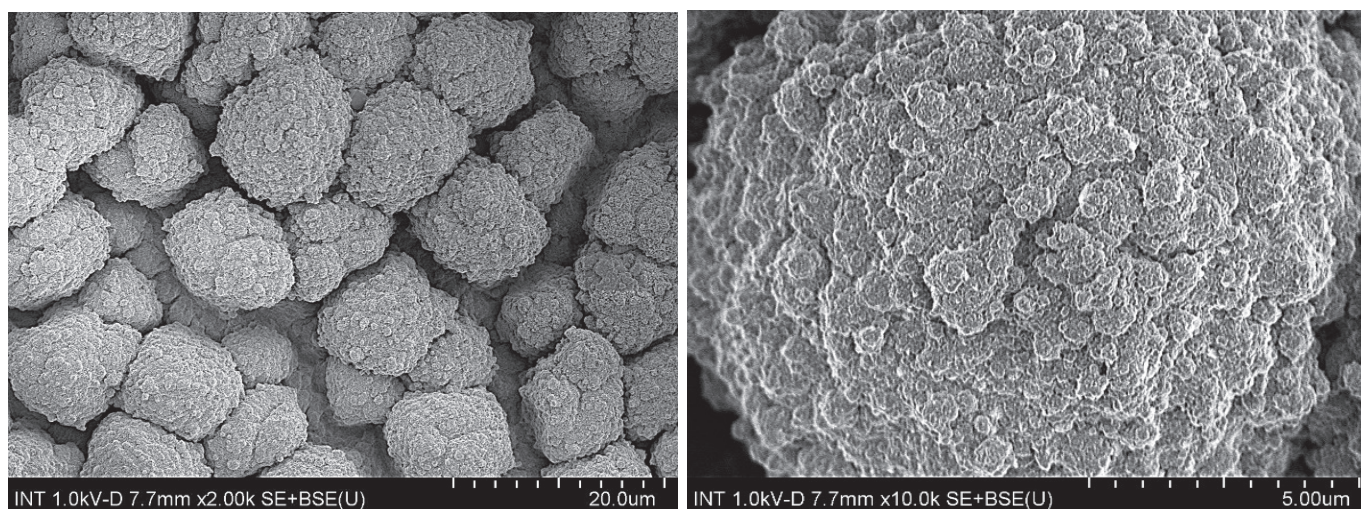


Fig. 6. SEM images of the copolymer.

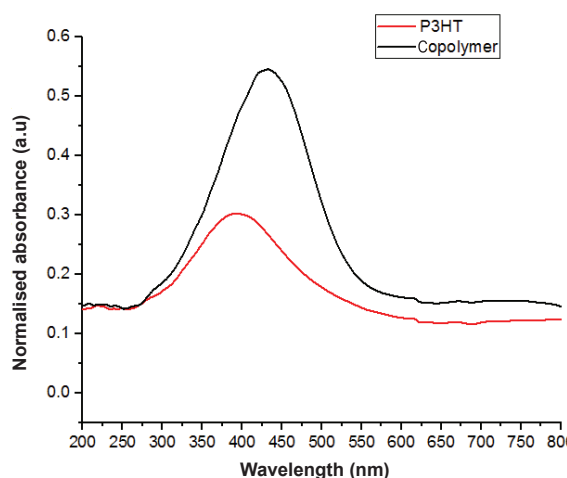


Fig. 7. UV-Vis absorption spectrum of P3HT (red line) and copolymer (black line) at 0.5 mg.ml⁻¹ in chloroform.

Another important parameter of the optical properties is the energy bandgap of the polymer, which can be determined using the UV-Vis absorption spectrum. Using the Planck equation ($E_g = 1240/\lambda_{\text{onset}}$), the calculated energy bandgap of P3HT and the copolymer are 2.16 and 2.25 eV, respectively. The results indicate that both polymers have a high value

of optical bandgap (above 2 eV), making them useful for high-temperature optical devices such as LEDs, lasers, or solar cells. However, the copolymer has a higher value due to the increased number of conjugated bonds in its structure.

3.4. Electrochemical properties of P3HT and copolymer

The electrochemical behaviours of P3HT and the copolymer were examined using the CV method to gain a better understanding of their electrochemical activity. Both the polymer and copolymer exhibited distinct redox peaks with hysteresis (potential drift) between the anodic and cathodic peak potentials. Slow heterogeneous electron transfer, the mutual transformation of various electronic species, local polymer chain rearrangement, and electronic charging of the interfacial exchange at the metal/polymer and polymer/solution interfaces were attributed to the potential shifts of the redox peaks among the CVs [4].

The stability of both polymers was also investigated, with a total of four cycles performed, as shown in Figs. 8A, 8B. P3HT's redox activity was sustained at around 70% after four cycles of scanning, exhibiting generally good redox activity. However, the increased conjugation length significantly improved the electrochemical stability of the copolymer, achieving stability above 90% after four

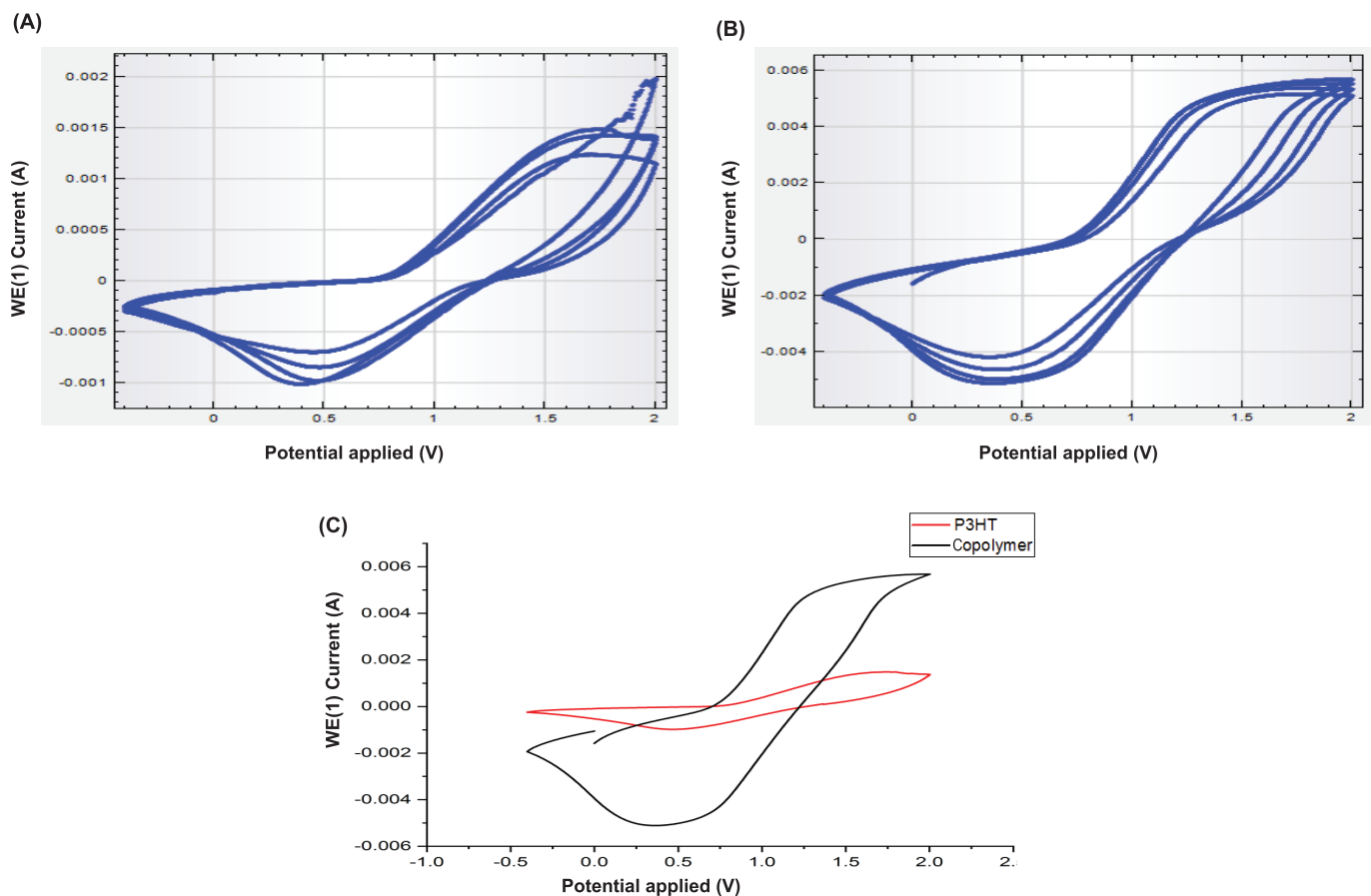


Fig. 8. CVs of (A) P3HT, (B) copolymer, and (C) first cycle of P3HT and copolymer.

scanning cycles. Furthermore, CV was employed to evaluate the HOMO and LUMO energy levels of the polymer using an empirical equation. The results are shown in Table 2. The experimental HOMO of the copolymer exhibited an elevated value, attributed to the increase in the conjugation length in the structure.

Table 2. Electrochemical properties and calculation parameters of P3HT and copolymer.

Compound	E_{pa} (V)	i_{pa} (mA)	E_{pc} (V)	i_{pc} (mA)	E_g (eV)	(V)	HOMO* (eV)	LUMO* (eV)
P3HT	1.53	1.23	0.50	1.3	2.16	0.82	-5.22	-3.06
Copolymer	1.28	3.8	0.65	5	2.25	0.74	-5.14	-2.89
HOMO* = $-(4.4+) \text{ eV (Ag/Ag}^+)$					LUMO* = $E_g + \text{HOMO}$			

HOMO: highest occupied molecular orbital; LOMO: least unoccupied molecular orbital; *: excited energy state.

4. Conclusions

3HT and BDP were used as precursor monomers to construct a conjugated copolymer through electrochemical copolymerisation using a linear sweep voltammetry potentiostatic technique. The structure, optical, and electrical properties of the copolymer were analysed and compared with the polymer P3HT, which was also synthesised using the same method. The comparison highlighted the improvement in the morphology and HOMO-LUMO energy gap of the copolymer, which significantly enhances the electrochemical stability of the material. This study has demonstrated that electropolymerisation is a highly applicable, straightforward, and efficient approach for preparing conductive polymers and copolymers for diverse optoelectronic applications.

CRedit author statement

Thao Phuong Le Nguyen: Conceptualisation, Methodology, Formal analysis; Cam Hong Thi Nguyen, Tam Hoang Luu: Software, Data curation, Validation; Thuy Thu Truong, Bao Kim Doan, Thiet Quoc Nguyen: Visualisation, Investigation; Ha Tran Nguyen: Conceptualisation, Methodology, Formal analysis, Supervision, Writing original draft preparation, Writing - Reviewing and Editing, Project administration.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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