



## Synthesis, Thermal and Electrochemical Properties of Four New Bis Oxadiazole Copolymers Based on Azo Monomer

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### Abstract

Four new copolymers were synthesized from reaction of bis acid monomer 3-((4-carboxyphenyl)diazenyl)-5-chloro-2-hydroxybenzoic acid with five diacidhydrazide in presence of poly phosphoric acid. The resulted monomers and copolymers have been characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy as well as EIMs technique. The number averages of molecular weights of the copolymers are between 4822 and 9144, and their polydispersity indexes are between 1.02 and 2.15. All the copolymers show good thermal stability with the temperatures higher than 305.86 °C when losing 10% weight under nitrogen. The cyclic voltammetry (CV) measurement and the electrochemical band gaps ( $E_g$ ) of these copolymers are found below 2.00 eV.

**Keywords:** Oxadiazole, Copolymer, Azo, Monomer, Thermal Properties, Electrical Properties.

### Introduction

Besides to utilizing the azo compounds as dyes [1] they exhibited several bioactivity such as anticancer agents [2], antibacterial and antifungal activities [3, 4]. antioxidant properties [5]. Even though, in 2018 Leo, L. *et.al*, [6] found that existence of azo food dyes possess damage effects on cellular inflammatory responses. Furthermore, compounds included azo group in their structure exhibited interesting physical properties like electrochemical [7], fluorescent, chemo sensor for Cu<sup>2+</sup> which can be used in drug analysis [8], light-emitting diodes [9], optical activity [10] and some derivative exhibited significant thermal stability [11].

Azo compounds containing 1, 3, 4-oxadiazole also exhibited fascinating bio and physio properties. Whereas Zhou, W *et.al*, [12] found that the existence of azo group in poly 1,3,4-oxadiazole enhances the ultraviolet resistance. In the other hand, oxadiazole derivatives are one of the most important materials due to their wide applications. In the bioactive field, oxadiazole derivatives exhibit great biological activities such as: antitumor [13], anti-proliferative [14,15] α-

glucosidase inhibitors [16], antioxidant ability [17, 19], anti-inflammatory [20,21] antibacterial [22] and antifungal [23, 24]. Besides, oxadiazole compounds showed interesting results in the physical properties field, such as electrochemical [25, 26] electro-optical [27], Luminescence [28,29] and photo physical properties [30]. In other hand, oxadiazole polymers exhibited interesting properties like optical [31, 32] light-emitting [33] and electrochemical properties [34]. Furthermore, azo compounds showed other properties such as fluorescence optical [35] and thermal properties [36, 38].

We synthesized new dicarboxylic acid containing azo group as a new monomer. Four new bis-1, 3, 4-oxadiazole copolymers were synthesized from the reaction of new monomer with di acid hydrazide in presence of polyphosphoric acid (PPA). All copolymers were identified by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The molecular weight of copolymers, dispersity and degree of polymerization were determined by gel permeation chromatography (GPC). Furthermore, the thermal stability (TS), thermo gravimetric analysis (TGA) and

electrochemical behaviour are determined for these copolymers.

## Experimental

All chemicals were obtained from Sigma Aldrich Company with purity above 95%. Melting point is determined by open capillary tube method by using OMEGA MPS10 electric melting point apparatus. FT-IR spectrums were obtained using a PerkinElmer 400 Fourier Transform Infrared Spectrometer. All  $^1\text{H}$ NMR spectrums were recorded on a Bruker AW MHz spectrometer, DMSO- $d_6$  solvent was used and tetra methyl selaine (TMS) as a reference. A Perkin Elmer Pyris-Diamond TG/DTA was used for measurement of the thermal stability. The molecular weights average and polydispersity (PDI) of the copolymers were analysed using a gel permeation chromatography (GPC) with water 2414 refractive index detector.

### Synthesis of 3-((4- carboxyphenyl) diazenyl)- 5- chloro- 2- hydroxybenzoic acid (monomer)

4-aminobenzoic acid (6.85 g, 50 mmol) was dissolved in 20 mL of 4-N-hydrochloric acid. The mixture was left to cool until  $0^\circ\text{C}$ . Sodium nitrite (6.9 g, 100 mmol) was dissolved in 6 mL of distilled water and cooled to  $0^\circ\text{C}$ , then added drop wise to previous mixture through 30 minutes. The least mixture was added drop wise to a cooled solution at  $0^\circ\text{C}$  of 5-chlorosalicylic acid (8.62 g, 50 mmol) which dissolved in 25 mL of 4 N sodium hydroxide .After that the mixture was stirred at  $20\text{-}25^\circ\text{C}$  after adjusting pH of the solution at 4-5 using 2% hydrochloric acid. The orange precipitation was filtered from the solution and washed with distilled water.

Then it was dried under vacuum oven at  $50^\circ\text{C}$  for two hours.

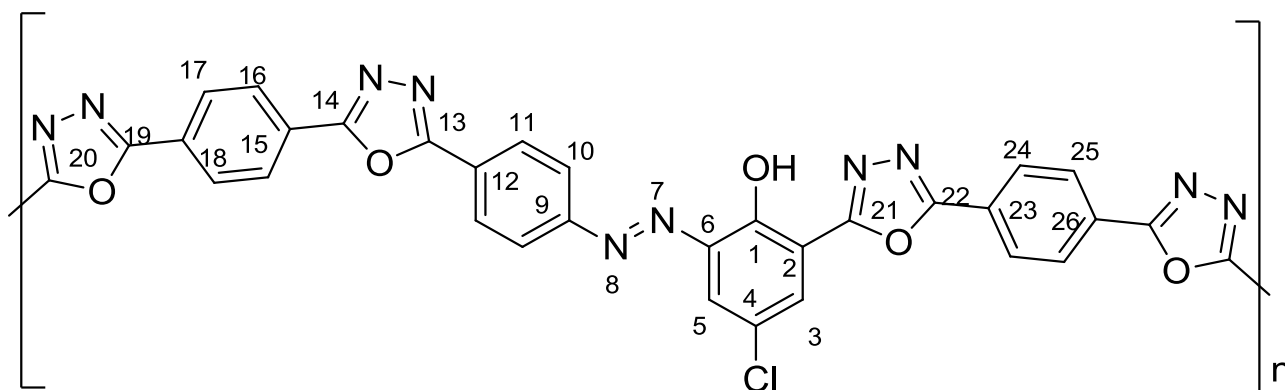
11.84 g of 3-((4-carboxyphenyl) diazenyl)-5-chloro-2-hydroxybenzoic acid monomer was obtained and characterized as following details: 74% yield, mp  $283^\circ\text{C}$ . FT-IR,  $\nu$ , 3213 (OH), 3042 ( $\text{C}_{\text{ar}}\text{-H}$ ), 2309 (N=N), 1782 and 1667 (C=O), 1564-1493 (C=C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 400 MHz):7.03(2H, d, J 8.2 Hz, H10), 7.69 (1H,d, J=2.18 Hz,H5), 7.87 (2H,d,J 8.24,H11),7.92 (1H,d,J 2.2,H3),9.66 (bs,1H,OH). $^{13}\text{C}$ NMR,  $\delta$  (ppm, DMSO- $d_6$ , 100 MHz):118.79 (1C,C2), 123.14 (2C,C10) ,127.3 (1C,C6),128.54 (1C,C4), 130.05 (1C,C5), 131.81 (2C,C11), 132.64 (1C,C12). 134.37 (1C,C3), 154.21 (1C,C9), 155.86 (1C,C1), 169.67 (1C,C=O), 170.43 (1C,C=O). $M^+ = 320$ , 15%, for  $[\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}_5]^+ m/z=172$ , 100% for  $[\text{C}_7\text{H}_4\text{ClO}_3]^+, m/z=122$ , 11% for  $[\text{C}_7\text{H}_5\text{O}_2]^+$ .

### General Synthesis of the Four New Copolymers (cop1- cop4)

A mixture of 3-((4-carboxyphenyl) diazenyl)-5-chloro-2-hydroxybenzoic acid monomer (0.32g, 1mmol) and bis acid hydrazide (1mmol) was grinded together to obtain a fine powder and added to 10 mL of polyphosphoric acid at  $140^\circ\text{C}$ . The mixture was left under heating at  $140\text{-}150^\circ\text{C}$  for 16 hours.

After cooling the mixture to  $20^\circ\text{C}$ , it was poured into 100 mL crashed ice under stirring and the pH was adjusted carefully to 5-6 by cooling saturated solution of sodium bicarbonate. Then, mixture was left under stirring for one hour. The resulting copolymer was extracted by DCM ( $3 \times 40\text{mL}$ ). The organic layer of the copolymer was washed with water and brine, then dried using magnesium sulphate and evaporated under a reduced pressure.

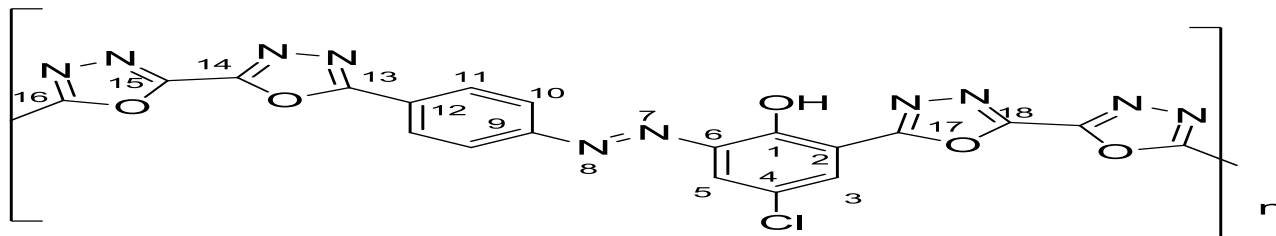
### Synthesis of Copolymer 1 (Cop1)



This copolymer was resulted from reaction of the monomer (3-((4-carboxyphenyl) diazenyl)-5-chloro-2-hydroxybenzoic acid) with terephthalic dihydrazide. The obtained compound was a glassy brown compound with the following specification: Yield 52.7%. IR,  $\nu$ , 3377 (OH), 3039 ( $C_{ar}$ -H), 2298 (N=N), 1619 (C=N), 1581-1498 (C=C)  $cm^{-1}$ .  $^1H$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 400 MHz): 7.09(2H, d, J 7.96 Hz, H10), 7.74(1H,d, J=2.22 Hz,H5),7.88 (8H, s, H16,H17,H24& H25), 7.94(2H,d,J

8.24,H11),8.05 (1H,d,J 2.2,H3), 9.72 (bs,1H,OH).  $^{13}C$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 100 MHz):113.34 (1C,C2), 126.81(4C, C15, C18,C23, C26), C 127.14 (2C,C10), 127.39 (1C,C6), 128.35(8C,C16, C17,C24,C25), 129.54(1C,C4), 129.55 (1C,C12), 130.05 (1C,C5), 131.81(2C,C11),. 132.51 (1C, C3), 150.91 (1C, C1), 154.21 (1C, C9), 163.72 &164.09 and 164.88 for (C=N of oxadiazole rings).

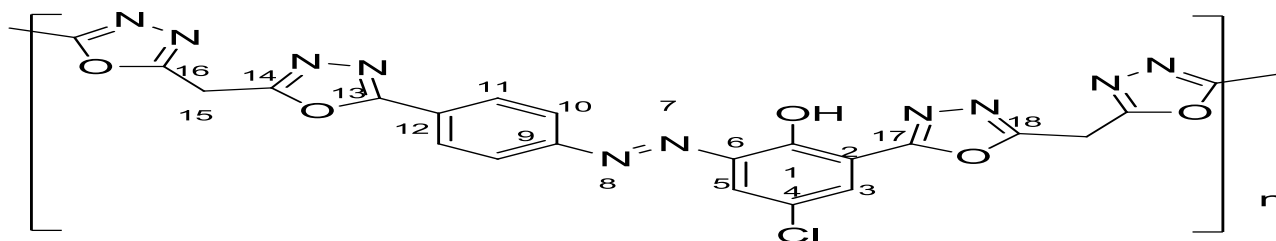
### Synthesis of Copolymer 2 (Cop2)



This copolymer was obtained from reaction of the new monomer with oxalic dihydrazide. The product was dark orange: yield 58.66%, IR,  $\nu$ , 3364 (OH), 3044( $C_{ar}$ -H), 2301(N=N) 1616 (C=N), 1564-1493 (C=C) $cm^{-1}$ .  $^1H$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 400 MHz): 7.11(2H, d, J 7.96 Hz, H10), 7.70(1H,d, J=1.98 Hz,H5), 7.98(2H,d, J 8.0, H11), 8.05 (1H,d, J 2.21,

H3),9.89 (bs,1H,OH).  $^{13}C$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 100 MHz):117.91 (1C, C2), 127.45 (1C, C6), 129.82 (1C, C4), 129.62 (1C, C12), 130.11(1C, C5), 131.78 (2C, C11), 132.79 (1C, C3), 151.07 (1C, C1), 154.13 (1C, C9), 163.55, 164.33 and 165.02 for (C=N of oxadiazole rings).

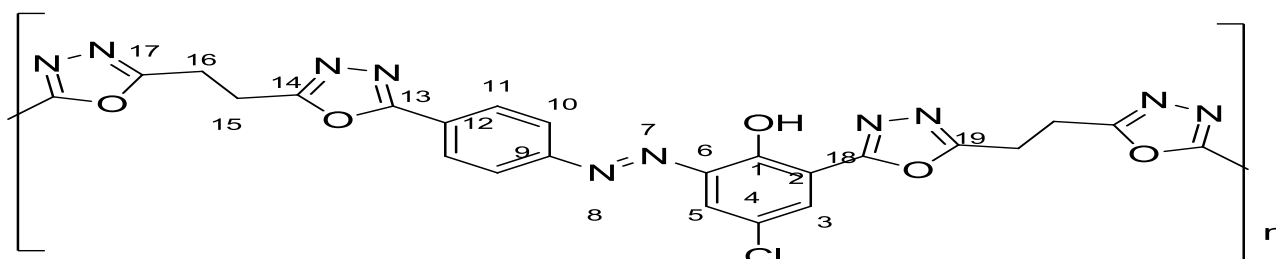
### Synthesis of Copolymer 3 (Cop3)



This copolymer was obtained from reaction of the new monomer with malonic dihydrazide, the product was glassy red: yield 59.2%, IR,  $\nu$ , 3361 (OH), 3063( $C_{ar}$ -H), 2963-2858 (C- $H_{aliph}$ ), 2294(N=N), 1622 (C=N), 1598-1504 (C=C)  $cm^{-1}$ .  $^1H$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 400 MHz): 3.87( 4H,s,H15), 7.15(2H, d, 8.0 Hz, H10), 7.72 (1H,d, J=2.2 Hz,H5), 7.97(2H,d, J

8.2, H11), 8.04 (1H,d, J 2.2, H3),9.89(bs,1H,OH).  $^{13}C$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 100 MHz):25.4(2C, CH $_2$ ), 118.09 (1C, C2), 127.48 (1C, C6), 129.62 (1C, C4), 129.78 (1C, C12), 130.15(1C, C5), 131.80 (2C, C11), 132.84 (1C, C3), 151.12 (1C, C1), 154.17 (1C,C9), 163.89 ,164.81, and 164.92 for (C=N of oxadiazole rings).

### Synthesis of Copolymer 4 (Cop4)



This copolymer was obtained from reaction of the monomer with succinic dihydrazide, the product was pale orange compound, yield 48.6%, IR,  $\nu$ , 3378 (OH), 3035 ( $C_{ar}$ -H), 2916-2866 ( $C-H_{aliph}$ ), 1620 ( $C=N$ ), 1584-1498 ( $C=C$ ) $cm^{-1}$ .  $^1H$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 400 MHz): 3.56 (8H,s,H15& H16), 7.12(2H, d, 8.4 Hz, H10), 7.71 (1H,d,  $J=2.0$  Hz,H5), 7.94 (2H,d,  $J$  8.1, H11), 8.08 (1H,d,  $J$  2.24, H3), 9.91 (bs,1H,OH).

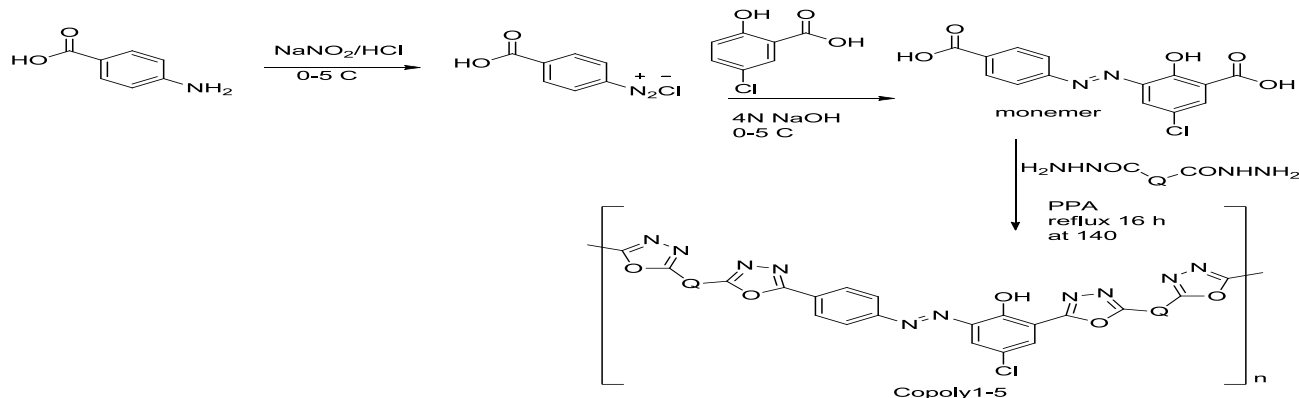
$^{13}C$  NMR,  $\delta$  (ppm, DMSO- $d_6$ , 100 MHz): 32.93 (4C,  $CH_2$ ), 118.16 (1C, C2), 127.51 (1C, C6), 129.58 (1C, C4), 129.79 (1C, C12), 130.11(1C,

C5), 131.85 (2C, C11), 132.89 (1C, C3), 151.18 (1C, C1), 154.07 (1C,C9), 164.82,164.81 and 164.94 for ( $C=N$  of oxadiazole rings).

## Result and Discussion

### Chemistry

Four copolymers were successfully synthesized from the reaction of 3-((4-carboxyphenyl) diazenyl)-5-chloro-2-hydroxybenzoic acid as a monomer with acid dihydrazide in the presence of PPA as shown in Scheme 1.



Scheme 1: synthetic role of synthesized cop 1-cop 4

The new monomer and fourth new copolymers (cop1-cop4) were identified by FT-IR,  $^1H$ -NMR and  $^{13}C$  NMR and EIMs for the monomer. The FT-IR of monomer showed the expected signals such as the hydroxyl group of carboxylic acid and phenol at 3213  $cm^{-1}$  as well the azo group ( $N=N$ ) was detected as weak signal at 2309  $cm^{-1}$ , while the carbonyl of carboxylic acid was detected at 1667  $cm^{-1}$ . The  $^1H$ -NMR showed that the two doublet peak at 7.03 and 7.87 ppm. These doublet peaks were related to the two protons with  $J = 8.2$  and 8.24 Hz respectively.

This was attributed to 1, 2 splitting between H10 and H11. Furthermore, NMR showed that the doublet peak at 7.69 ppm for one proton (H5) with  $J = 2.18$  Hz is attributed to 1,3 splitting [39], while the peak of H3 located at 7.92 ppm with  $J = 2.2$ . The hydroxyl group of phenol was detected as broad singlet due to hydrogen bonding capability [40]. The two hydroxyl groups of two carboxylic acid were undistinguished by  $^1H$  NMR and that could be attributed to inter hydrogen bonding between the carboxylic

acid and phenol group and intra hydrogen bonding for the second carboxyl group [41, 42].

Although, the  $^1H$  NMR spectrum do not exhibited the hydrogen of carboxylic acid,  $^{13}C$  NMR exhibited the two carbons of two carboxylic acid groups at 169.67 and 170.43 ppm respectively. The  $^{13}C$  NMR spectrum also detected all expected carbons. The electron ionization mass spectroscopy (EIMs) displayed the molecular ion as carbocation radical  $M^+ = 320$ , 15%, for  $[C_{14}H_9ClN_2O_5]^+$  while the base peak was located as carbo-cation  $[C_7H_4ClO_3]^+$ , 100% as well the rest fragmentations confirmed the monomer structure.

The FT-IR of cop 4 showed that the OH signal was at 3378-3361  $cm^{-1}$ . The weak signal of azo group appeared at 2304-2294  $cm^{-1}$ . The significant peak of  $C=N$  of the oxadiazole rings were located at 1622-1616  $cm^{-1}$ . Furthermore, the aliphatic C-H for cop3 and cop4 were located in range 2963-2858  $cm^{-1}$ . The  $^1H$  NMR spectra exhibited

interesting signal peak at 7.88 ppm for eight protons clearly referring to the presence of two 1, 4-phenolyl groups.

Furthermore, the spectrum of cop3 showed an interesting peak as singlet at 3.87, integrated for four which attributed to two group  $CH_2$  (H15) while the singlet at 3.56

ppm for cop4 integrated to eight proton refer to existence of two groups of CH<sub>2</sub>CH<sub>2</sub> attached to the bisoxadiazole (H15 and H16). These interesting peaks are considered the best indicator to confirm formation of the copolymer. The other peaks appeared as were expected area. The <sup>13</sup>C NMR spectra displayed new significant peak which confirm the proposed structure of the copolymers such as the peaks at rang 163.55-165.02 ppm which attributed to existence of four oxadiazole ring and two are in different electronic environments. The existence of two new carbons at, 126.81 and 128.35 attributed to 1, 4-phetholyl group in cop1.

Furthermore, carbon at 25.4 for two CH<sub>2</sub> in cop3 and carbon at 32.93 ppm for two symmetrical CH<sub>2</sub>CH<sub>2</sub> attached two oxadiazole rings considering best evidence for formation the copolymers (cop1-4). Existence of small peak at 169.20-170.15 is most possibly attributed to terminal group (COOH). The average number of molecular weights (M<sub>n</sub>) of the copolymers varies from 4822 to 9144 and the degrees of polymerization (DP) range from 10-17. All the copolymers show narrow molecular weight distribution (PDI) as depicted in Table 1.

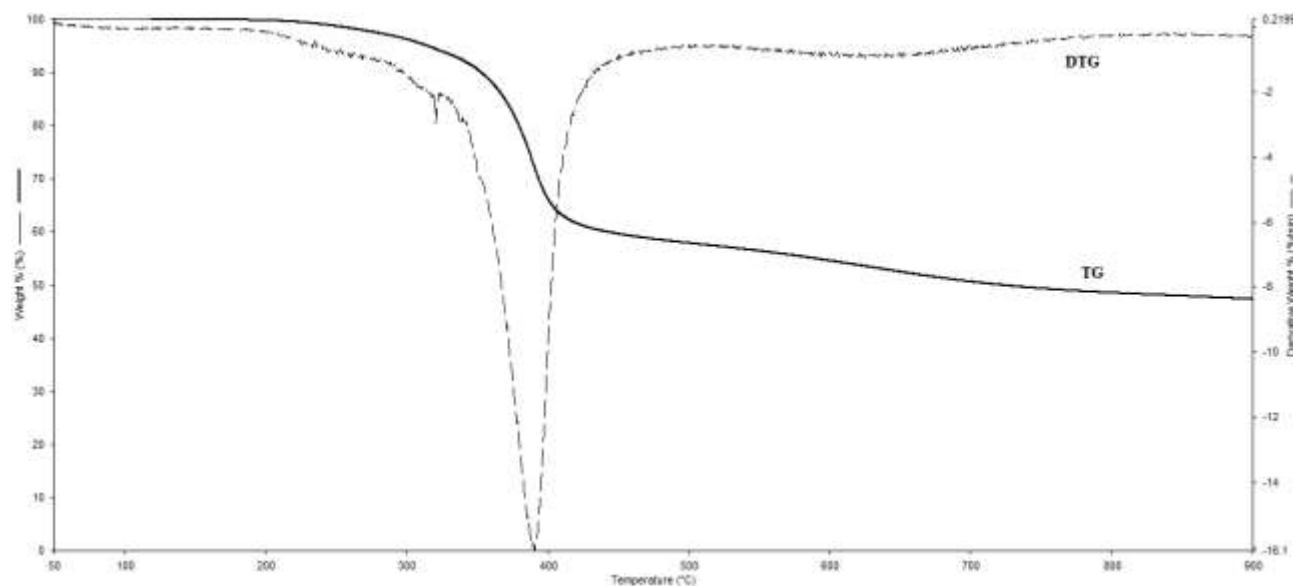
**Table 1: Percentage yield and characteristics of the copolymers (cop1-cop4)**

No.	Yield (%)	Colour	Mol. Wt. (g/mol)	Poly dispersity	Degree of polymerization
cop1	52.7	Glassy brown	7836	1.33	12
cop2	58.66	Dark orange	4822	1.21	10
cop3	59.2	Red	9144	2.04	17
cop4	48.6	Pale orange	8528	1.37	16

### Thermal Stability

The thermal stability of the synthesized copolymers was screened by thermo gravimetric analysis (TGA). Utilizing a PerkinElmer Pyris-Diamond TG/DTA thermo balance under nitrogen gas as inert atmosphere at a heating rate of 10 °C/min starting from 50 °C to 900 °C. The weight of sample under test was 10-15 mg for cop1-cop4. Figure 1 shows that the TGA thermo grams of copolymer (cop3), which was typically similar to rest of the copolymers. The detailed thermal data of cop1-cop4 is shown in Table 2. Figure 1 and Table 2 clearly show the onset decomposition

temperatures of all the copolymers which were more than 367 °C. These results indicated that the polybisoxadiazole containing azo group exhibited significant thermal stability. Furthermore, Figure 1 shows that the derivative temperature of (cop3), where the decomposition was occurred through a single decomposition step. Temperatures at 10% weight loss were recorded in the range of 323.80-356.28 °C. So, Table 2 shows major weight loss of about 50% in the range of 445-670 °C. The copolymers containing 1, 4-phethyl group moiety (cop1) lose the major weight (50%) at very high temperature compared to the copolymers containing alkyl group moiety (cop2-cop4).



**Figure 1: TGA curves of copolymer cop1**

In addition, the glass transition temperatures ( $T_g$ ) of the copolymers (cop1-cop4) were achieved by DSC under nitrogen

atmosphere, as well as no detectable phase transition showed in all copolymers.

**Table 2: Thermal properties of copolymers cop1-cop4**

Copolymers	Temperature (°C) corresponding to				Char yield (%) at 700 °C
	Onset	10% Wt loss	50% Wt loss	DTp	
cop1	373.36	325.24	491.83	390.22	33.74
cop2	367.47	348.48	447.35	389.38	35.93
cop3	376.80	355.56	453.74	392.34	45.32
cop4	370.73	342.70	462.19	380.69	43.13

**Electrochemical Properties**

Cyclic voltammetry (CV) analysis for the synthesized copolymer was carried out to evaluate the electrochemical properties and to determine the HOMO and LUMO energy levels, which are important for locating the band gaps. The experiments were accomplished in a 0.1 M tetrabutyl ammonium perchlorate (TBAP) as a supporting electrolyte in an anhydrous acetonitrile ( $CH_3CN$ ) utilizing a thin film coated on an indium-tin-oxide (ITO) glass substrate as working electrode at room temperature. The CV curves were obtained by using AgCl/Ag as a reference electrode, so the scan rate was 50 mV s<sup>-1</sup> in a potential

range (-2.0 V - +2.0 V). Figure 2 shows a typical CV curve of the copolymer (cop2). All the copolymers exhibited irreversible redox processes with onset oxidation (p-doping) and reduction (n-doping). The oxidation (p-doping) started at 0.85, 0.91, 0.89, and 1.03, V for cop1-cop4 respectively. The reduction processes (n-dopping) started at -53, -0.61, -0.65, -0.64, and -0.89 V for the compounds (cop1-cop4) respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels and the electrochemical energy gaps ( $E_g$ ) of the corresponding copolymers have been determined using the oxidation onset ( $E_{onset}$ ) following the equations:

$$LUMO = -E_{red} - 4.71 \text{ eV}$$

$$HOMO = -E_{ox} - 4.71 \text{ eV}$$

$$E_g = -(E_{HOMO} - E_{LUMO})$$

Where  $E_{red}$  and  $E_{ox}$  are the onset potentials for reduction and oxidation relative to the Ag/Ag+ reference electrode respectively [43]. The HOMO energy levels of the copolymers were calculated to equal -5.62, -5.69, -5.8 and -5.74 eV; the LUMO energy levels were estimated to equal -4.09, -4.05, -3.93 and -3.91 for (cop1-cop4) respectively. The results were tabulated and shown in Table 3. This table shows that the synthesized copolymers containing  $(CH_2)_2$  as Q group have the lowest HOMO energy value among all the copolymers (cop1-cop4). The present of  $(CH_2)_2$  may play pivotal role to lower the HOMO energy level. This electrochemical behaviour of copolymers (cop1-cop4) can be well

explained by the relationship between the structures and electrochemical. This results in a shift of the HOMO energy level to lower energy [44], and the conjugation of the copolymers hence lower the energy levels between HOMO and LUMO. The results as summarized in Table 3 show that the synthesized copolymers have electrochemical band gap of less than 2.00 eV. As a result of this property, they can potentially be applied in heterojunction solar cells [45, 46]. The HOMO energy level of copolymers (cop1-cop4) is comparable with the most widely used hole-transporting material 4,4'-bis(1-naphthylphenylamino)biphenyl (NBP) [47].

**Table 3: The Electrochemical data of copolymers (cop1-cop4)**

Copolymers	$E_{red}^b(V)$	$E_{ox}^b(V)$	$E_{LUMO}^c(eV)$	$E_{HOMO}^c(eV)$	$E_g^d(eV)$
cop1	-0.62	0.91	-4.09	-5.62	1.53
cop2	-0.66	0.98	-4.05	-5.69	1.64
cop3	-0.78	1.09	-3.93	-5.8	1.87
cop4	-0.74	1.03	-3.97	-5.74	1.77

- Cyclic voltammogram curves of the drop coated film measured in 0.1M TBAP acetonitrile solution at a scan rate of 50mVs-1 at room temperature (versus Ag/Ag+).
- Onset oxidation (P-doping) and reduction (n-dopping) potentials versus Ag/Ag+.
- Predestined from the onset oxidation and reduction potential by utilize  $E_{HOMO} = -E_{ox} - 4.71eV$  and  $E_{LUMO} = -E_{red} - 4.71eV$
- Electrochemical band gaps determined using  $E_g = -(E_{HOMO} - E_{LUMO})$ .

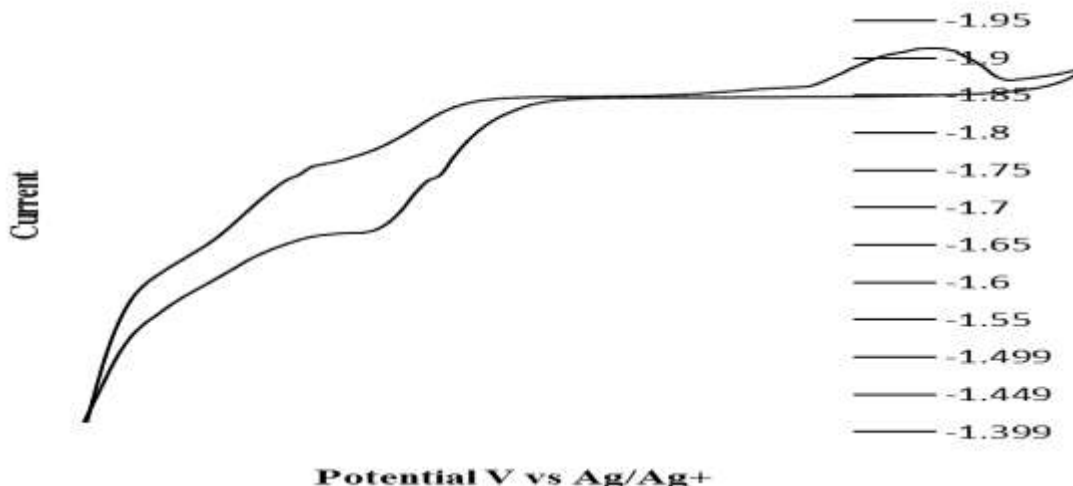


Figure 2: Cyclic voltammograms of cop2 in CH<sub>3</sub>CN at scan rate 50 mVs<sup>-1</sup>

## Conclusion

Four bis 1,3,4-oxadiazole containing azo copolymer successfully synthesized from reaction of the di carboxylic acid 3-((4-carboxyphenyl)diazonyl)-5-chloro-2-hydroxy benzoic acid as a monomer and di acid hydrazide in the presence of PPA. These copolymers exhibited interesting thermal stability and electrochemical properties

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