

## Synthesis and Characterization of Some Novel Monomers and Copolyesters Containing Bispyrazole or Bisdihydroisoxazole with Studying the Effect of TiO<sub>2</sub> Nanoparticles on their Electrical Conductivity

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**Abstract:** In this study, attempting to obtain new electrically-conducting polymers, six conjugated copolyesters have been synthesized. First, bispyrazole and bisdihydroisoxazole heterocyclics monomers were obtained from close-closing of bischalcone derivatives by hydrazine and hydroxylammonium chloride, respectively. The Bispyrazole Heterocyclic monomer (BHZH) was used in the preparation of PHZT, PHZP, PHZO and dihydroisoxazole heterocyclic monomer (BHAH) was used in the preparation of PHAT, PHAP, PHAO. The structure of the monomers and the repeating units present in the copolyesters chain was confirmed by FT-IR, <sup>1</sup>H-NMR spectroscopic techniques, Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) also the thermal properties of these copolyesters were evaluated by Thermo Gravimetric Analysis (TGA), the electrical conductivity results indicated the prepared copolyesters lie semiconductors region, in addition. The effect of increasing the TiO<sub>2</sub> nanoparticles concentration as a filler and the frequency on the electrical conductivity of the prepared copolyester was analyzed, the results showed the increase of electrical conductivity with increasing concentration of TiO<sub>2</sub> nanoparticles and the frequency.

**Key words:** Bispyrazole, bisdihydroisoxazole, copolyesters, TiO, nanoparticles, electrical conductivity, XRD

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### INTRODUCTION

Conducting polymers (Cps) have attracted significant attention due to their use in commercial applications such as electronic elements (Lu *et al.*, 2011), rechargeable batteries (Wang, 2015; Kenin *et al.*, 2018), optical switching elements (Davidenko and Kokozay, 2017), sensors (Dodabalapur, 2006; Kumar *et al.*, 2015), electrostatic charge dissipation, electromagnetic interference EMI shielding (Sudirman *et al.*, 2012; Chandrasekhar and Naishadham, 1999), excellent NLO properties (Pietrangelo *et al.*, 2008), molecular devices and membranes which originates from their high electrical conductivity (Hackett *et al.*, 2017; Bryan *et al.*, 2016). Cps are a superb choice because of their long p-conjugation length with their good electrical conductivity (10<sup>-3</sup>-10<sup>-5</sup>) s/cm (Phang *et al.*, 2008) and it have surprising properties of having high electrical conductivity and can display a range of properties from semiconducting to close metallic behavior or it can have a greater range of electrical conductivity than inorganic semiconductors (Dubey and Leclerc, 2011; Kose and Ramteke, 2012).

Most electrically-conducting polymers are containing conjugated backbone, i.e., alternating double and single bonds (Mahmood, 2017) which is accepted to be not only a basic condition for electrical conductivity as well as it is also a major cause of the characteristic ability and good mechanical properties of these polymers (Khattab, 2008). The synthesis of electrically conductivities polymers with conjugated -C = C- bonds requires the controlled coupling of a large number of monomers (Khattab, 2007). So, through simple modifications of their molecular structure, their physical and chemical properties can be adjusted in a fairly large range such as definite structures were incorporated in the backbone of the for studying the effect of molecular structure on the electronic, physical and electrical properties of the polymers (Khattab, 2008) also polymer adjustments give methods for studying the effects of chain flexibility (Amborski, 1962), symmetry and molecular hardness on conductivity and knowledge of the structural reliance of conductivity with the mechanism of conduction in polymers will allow the synthesis and manufacture of conductive polymers films (Imam, 2013;

Vilcakova *et al.*, 2002), the attention in conjugated polymers has increased because these polymers combine some properties of both metals and polymers (Caseri, 2000).

Nanocomposites are a modern category of materials that have high physical, thermal and mechanical properties compared with traditional composites (micro composites) (Balazs *et al.*, 2006; Hamming *et al.*, 2009) and polymers nanocomposite is a polymer that has been reinforced with a little quantity (<5% wt.) of nanosized particles (Levitsky *et al.*, 2009), the heterogeneous-conducting polymer nanocomposites principally for organic-inorganic nanocomposites have an interest of scientists in the last decade (Su and Kuramoto, 2000) owing to their enhanced properties arising from the reinforcement of nanofiller, so, nanoscale reinforcement materials using to improve the electrical and optical properties of the polymers (Bora *et al.*, 2013; Potts *et al.*, 2011) such as thin films of nanocrystalline TiO<sub>2</sub> have significant applications in the field of optoelectronic materials (Potts *et al.*, 2011) also considered photocatalytic material (Fleming *et al.*, 2005; Arango *et al.*, 1999) can be used to form thin films in dye-sensitized solar cells and anti-reflection coatings (Okada *et al.*, 2006). Although, there are many reports on the heterogeneous-conducting polymer nanocomposites but one special interest is the incorporation of inorganic nanoclusters with conducting polymers because the resulting nanocomposites may possess unique electrical and optical properties (Su and Kuramoto, 2000; Yavuz and Gok, 2007). However, there are no reports on study of the synthesis and characterization of copolyesters containing bispyrazolines and bisdihydroisoxazole moiety as a different heterocyclic ring which aromatic heterocyclic has less than aromatic nature such as a furan, pyrrole and thiophene. So, this study deals with the synthesis of copolyesters by the poly condensation of (BHAH or BHZH) and diacid chlorides and also studying the effect of TiO<sub>2</sub> nanoparticle on their electrical conductivity.

## MATERIALS AND METHODS

**Experimental:** Terephthalaldehyde, oxalyl chloride (Sigma Aldrich), terephthalic acid, phthalic acid, acetone, 4-hydroxyacetophenone (Spectrochem Puriss grade), hydroxylamine hydrochloride, 4-hydroxybenzaldehyde (LobaChemie AR), hydrazine hydrate (80%) (Merck), TiO<sub>2</sub> nanoparticles were purchased from (Sigma Aldrich). Thionyl chloride sulphuric acid and sodium hydroxide (Rankem) were used as received. All other materials were used after purification.

**Synthesis of Bischalconediol (BH):** (1, 4-phenylene) bis (1-(4-hydroxyphenyl) prop-2-en-1-one): method preparing bis-chalcone compounds are same stated in the study (Podkoscielny and Kultys, 1976) syntheses 1-4 should be described in the study two similar molar quantity of

4-hydroxyacetophenone (2.76 g, 0.02 mol) was added into conical flask 100 mL and was dissolved in 25 mL of ethanol absolute. The 20% aqueous NaOH solution (2 g, 0.02 mol) was poured gently into the conical flask containing 4-hydroxyacetophenone and the mixture was stirred for about 10 min. Terephthalaldehyde (1.34 g, 0.01 mol) was added into conical flask. The mix was mixed vigorously at 0-4°C for 4 h and kept in the refrigerator for 24 h, 3M glacial acetic acid was added until the solution was neutralized (Konagaya and Tokai, 2000) as yellowish green powder; yield: 60%. The obtained precipitate was filtered off washed and dried and recrystallized from ethanol. The completion of this reaction was monitored by TLC (methanol: Benzene) (1:4).

**Monomer synthesis of (BHAH):** 4, 4-(1, 4-phenylene bis (isoxazole-5, 3-diyl)) diphenol: according to general procedure, compound Bischalcone (BH) (1.85 g, 0.005 mol) was dissolved in 25 mL of ethanol and sodium hydroxide solution (0.5 g NaOH in 10 mL of water) was poured gently into the conical flask containing bischalcone and was stirred for about 10 min, hydroxylamine hydrochloride (1.39 g, 0.02 mol) was dissolved in 25 mL of ethanol and was added into conical flask containing bischalcone MA. The mixture was refluxed with stirring on a water bath at 70°C for 7 h then the mixture was cooled with stirring at room temperature overnight, the precipitate was concentrated under vacuum, poured into ice water and after that 3M HCl was added until the solution was neutralized as yellowish green powder; yield: 73%. The obtained precipitate was filtered off washed and dried and recrystallized from ethanol. The completion of the reaction was monitored by TLC (methanol: Benzene) (1:4) (Majeed, 2013).

**Synthesis of monomer (BHZH):** 4, 4-(1, 4-phenylene bis (1H-pyrazole-5, 3-diyl)) diphenol: according to general procedure, compound a mixture of Bischalcone (BH) (1.85 g, 0.005 mol) and hydrazine hydrate (80%) (1 g, 0.02 mol) in ethanol (30 mL) was heated under reflux with stirring on a water bath at 70°C for 10 h then the mixture was cooled with stirring at room temperature overnight, the precipitate was concentrated under vacuum, poured into ice water and after that 3M HCl was added until the solution was neutralized as yellowish green powder; yield: 60%. The obtained precipitate was filtered off, washed, dried and recrystallized from ethanol. The completion of the reaction was monitored by TLC (methanol: Benzene) (1:4) (Majeed, 2013).

**General preparation of phthaloyl chloride of terephthaloyl chloride oxalyl chloride (Podkoscielny and Kultys, 1976; Konagaya and Tokai, 2000):** Phthaloyl chloride was prepared by refluxing phthalic acid with an excess amount of thionyl chloride in the presence of a slight amount of DMF as catalyst for 4 h.

The unreacted thionyl chloride was distilled off under vacuum. The obtained product was solidified on cooling in an ice bath.

**General synthesis of polymer 1-6:** The monomer BHZH or BHAH (0.003 mol) was dissolved in DCM 20 and 2 mL of pyridine used in a three-necked 125 mL round flask, solution of (terephthaloyl chloride, phthaloyl chloride or oxalyl chloride) (0.003 mol) in 5 ML of DCM did moderately add inside 5 min through the funnel at 0-5°C temperature below strong stirring. The mix was stirred continuously at RT to 30 min in a nitrogen atmosphere. The reaction was stirred maintained overnight at RT and then acidified by 1:1 diHCl. The precipitated polyester did washed by methanol, filtered and dried in a vacuum oven.

**Characterization and analytical techniques:** FTIR spectra: FTIR spectra of M1(KBr)  $\nu(\text{cm}^{-1})$ : 3448 s(C-OH), 1685 s( $\delta\text{C} = \text{O}$ ), 1596-1501s (C = C<sub>Ar</sub>), 1342 m(C-O). <sup>1</sup>H-NMR spectra (DMSO-d<sub>6</sub>)  $\delta$ ppm: 6.65-6.94dd (4H, CH-Ar), 7.42 -7.73 (4H, CH = CH), 7.93-8.06dd (4H, CH-Ar), 8.12 (4H, CH-Ar), 10.03 (2H-OH).

FTIR spectra of BHAH(KBr)  $\nu(\text{cm}^{-1})$ : 3523 s(C-OH) 1658 s( $\delta\text{C} = \text{N}$ ), 1587-1508s (C = C<sub>Ar</sub>), 1359 m(C-O). <sup>1</sup>H-NMR spectra (DMSO-d<sub>6</sub>)  $\delta$ ppm: 6.86 (2H, CH = C), 7.21-7.33 dd (4H, CH-Ar), 7.49-7.67dd (4H, CH-Ar), 7.86-8.10 dd (4H, CH-Ar), 9.90 (2H-OH), 10.51(2HNH). FTIR spectra of BHZH (KBr)  $\nu(\text{cm}^{-1})$ : 3226 s(C-OH) 1620 s( $\delta\text{C} = \text{N}$ ), 1569-1508s (C = C<sub>Ar</sub>), 1359 m(C-O). <sup>1</sup>H-NMR spectra (DMSO-d<sub>6</sub>)  $\delta$ ppm: 6.74 (2H, CH = C), 7.15-7.33 dd (4H, CH-Ar), 7.50-7.77 dd (4H, CH-Ar), 7.88-7.96 dd (4H, CH-Ar), 10.17 2H-OH. FTIR spectra of PHAT (KBr)  $\nu(\text{cm}^{-1})$ : 3340 m (N-H), 1733 m( $\delta\text{C} = \text{O}$  ester), 1683 m (C = N), 1600-1506 m (C = C<sub>Ar</sub>), 1263 m (C-O). FTIR spectra of PHAP(KBr)  $\nu(\text{cm}^{-1})$ : 1737 m ( $\delta\text{C} = \text{O}$  ester), 1689 m (C = N), 1604-1504 m (C = C<sub>Ar</sub>), 1283 m (C-O). Poly3 IR spectrum (KBr)  $\nu(\text{cm}^{-1})$ : 3224 m (N-H), 1722 m ( $\delta\text{C} = \text{O}$  ester), 1658 m (C = N), 1602-1512 m (C = C<sub>Ar</sub>), 1274 m (C-O). FTIR spectra of PHZP (KBr)  $\nu(\text{cm}^{-1})$ : 1743 m ( $\delta\text{C} = \text{O}$  ester), 1666 m (C = N), 1604-1503 m (C = C<sub>Ar</sub>), 1265 m (C-O). FTIR spectra of PHAO (KBr)  $\nu(\text{cm}^{-1})$ : 3438 m (N-H), 1768 m ( $\delta\text{C} = \text{O}$  ester), 1666 m (C = N), 1600-1510 m (C = C<sub>Ar</sub>), 1278 m(C-O). FTIR spectra of PHZO (KBr)  $\nu(\text{cm}^{-1})$ : 1749 m( $\delta\text{C} = \text{O}$  ester), 1652 m (C = N), 1604-1510 m (C = C<sub>Ar</sub>), 1282 m (C-O) (Fig. 1).

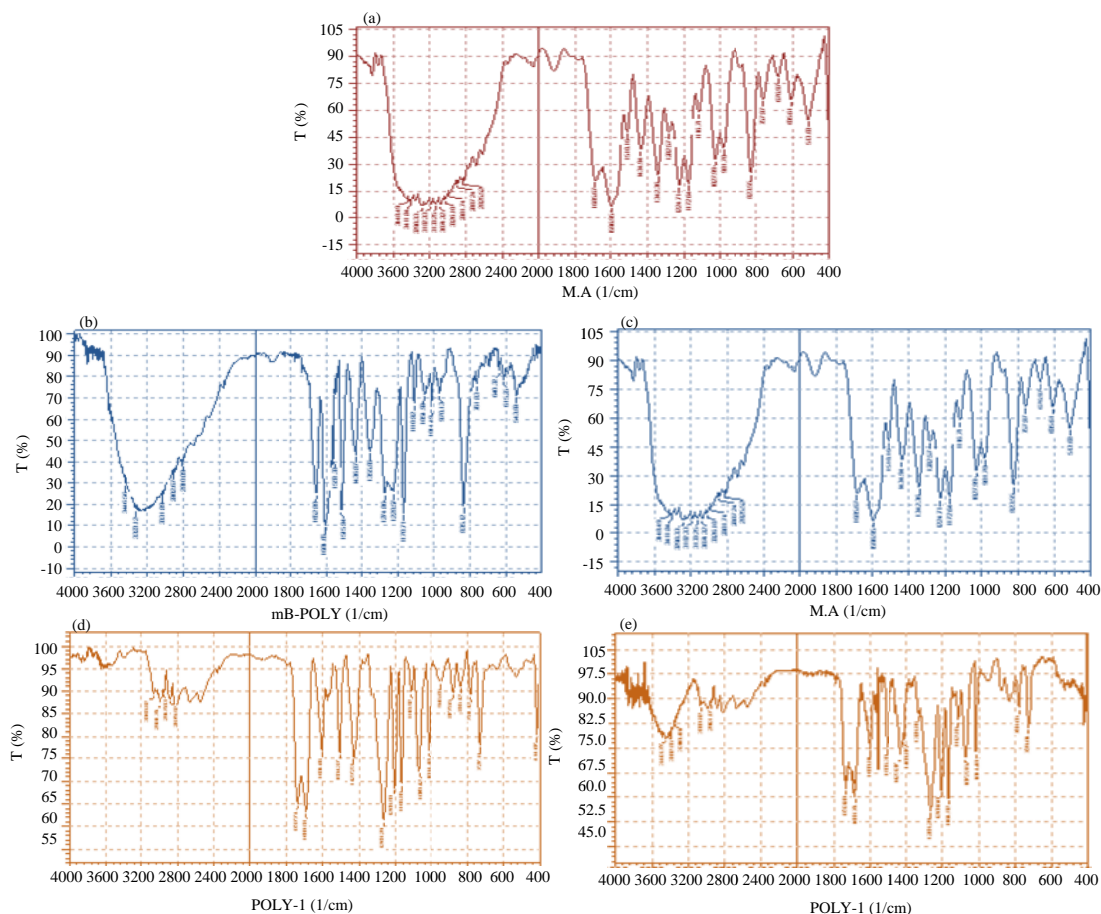


Fig. 1: Continue

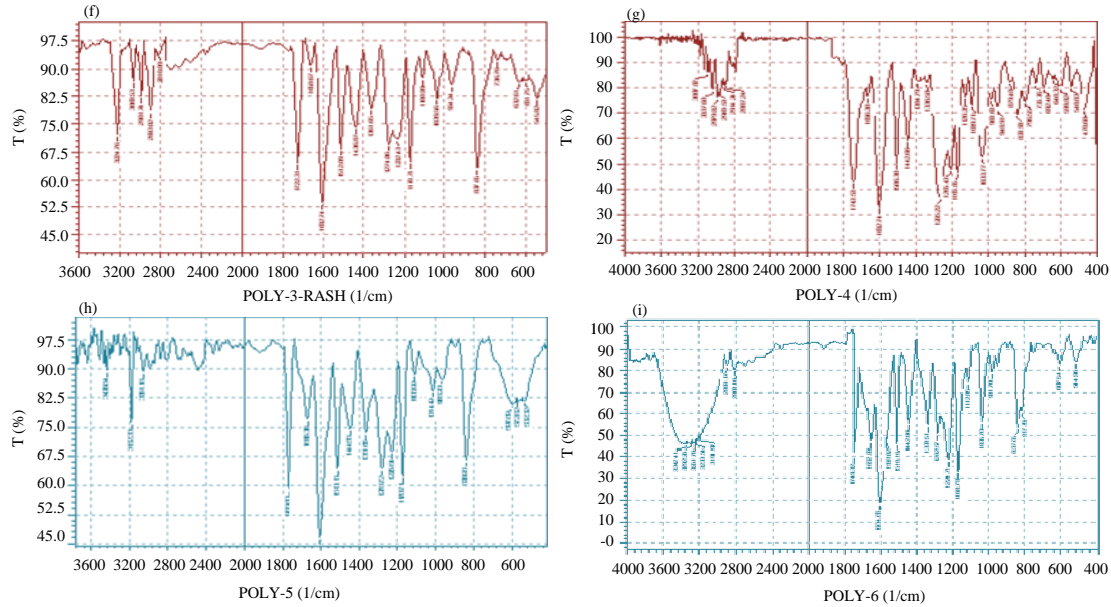


Fig. 1(a-i): FTIR spectrum for copolyesters illustrates the XRD patterns of all copolyester. The diffraction pattern of PHAT and PHZT shows three characteristic peaks at  $2\theta = 17.4^\circ, 26.8^\circ$  and  $29.3^\circ$ , indicating a high degree of crystallinity, PHAP, PHZP, PHAO and PHZO shows a very weak reflection at  $2\theta = 21^\circ$ . This feature may be attributed to the formation of strong hydrogen bonds between the oxygen or nitrogen for heterocyclic and the bulky aromatic

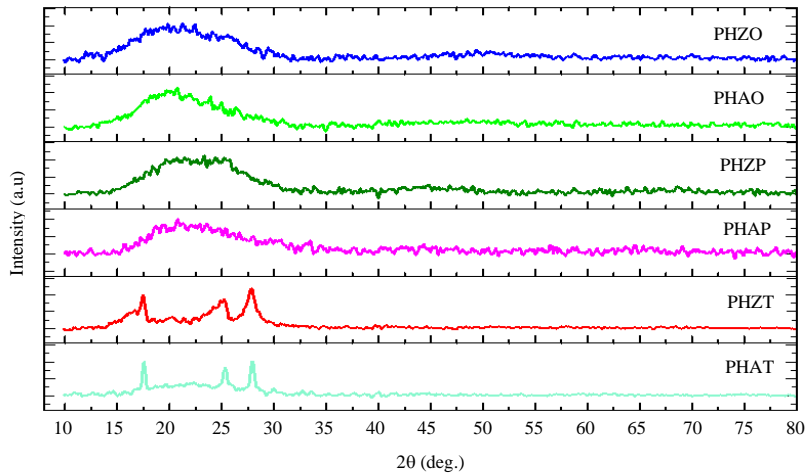


Fig. 2: XRD patterns of copolyesterdgd

**X-Ray Diffraction (XRD) analysis**

**Thermogravimetric analysis:** Thermal properties of the prepared copolyesters were evaluated with Thermo Gravimetric Analysis (TGA) in N<sub>2</sub> atmosphere, TGA curves are shown for the PHAH, PHZH and PHAO to indicated four steps of weight loss (Fig. 2).

Primary step beginning at of 272.4-303.7°C which is attributed to the removal all of the O<sub>2</sub>-containing functional groups. The second stage at around 303- 450°C

which happens enough to the removal of most of the oxygen-containing functional groups through the chemical reduction process.

The next stages (3th at about 500°C and 4th at about 600°C) indicate the polymer chain break which can start to the production of gases 29 and the and the glass transition temperature (T<sub>g</sub>) at 303 VC of PHAH, 321.3 of PHZH and 321.9 VC of PHAP did determine by Differential Scanning Calorimetry (DSC), so, the polymers showed fairly good thermal stability.

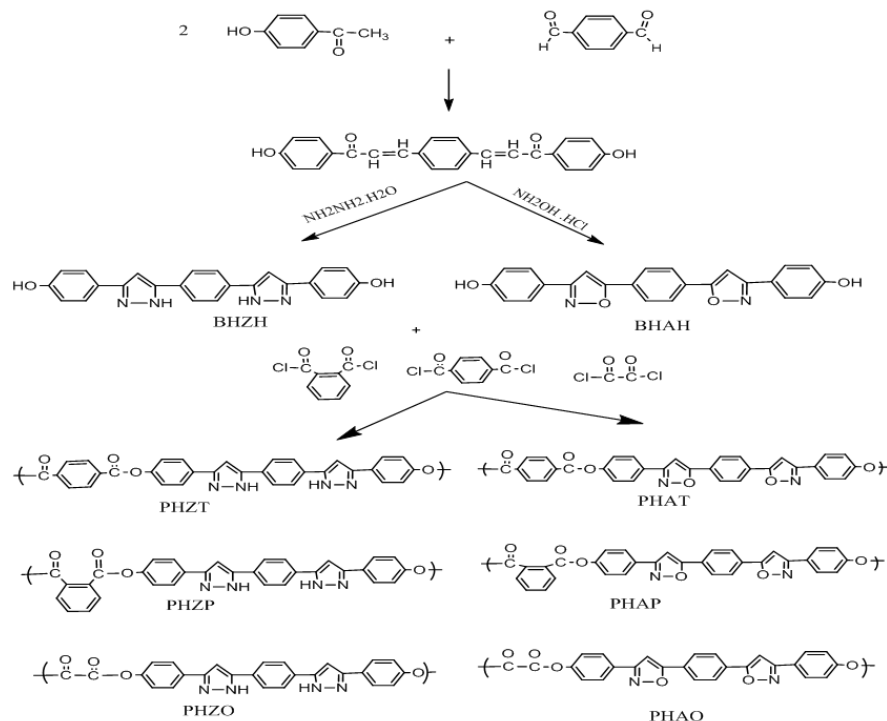


Fig. 3: Measurement of electrical conductivity of the prepared copolyesters at room temperature was carried out using LCR electronic test technique to measure the Inductance (L), Capacitance (C) and Resistance (R) of frequency range 50 Hz-1 MHz

## RESULTS AND DISCUSSION

Figure 3 shows the chemical structures of the prepared polymers. It is clearly noticed that the chemical structures of the investigated polymers are very important in affecting the measured conductivity. It is also shown that the nature of the chain containing the pyrazoline and dihydroisoxazole is important of the polymers for improving their molecular organization in thin films. The samples with a thickness about 0.2 and 1 cm diameter were prepared for this study as shown in Table 1.

From the electrical conductivity measured, it may be observed that all the samples are semiconducting in nature and the data showed an enhancing in conductivity via polyester ( $\sigma \sim 10^{-11}$  ohm $^{-1}$  cm) (Amborski, 1962; Shahab *et al.*, 2009) or poly azomethine ( $\sigma \sim 1.0069 \times 10^{-9}$  ohm $^{-1}$ .cm $^{-1}$ ) (Khatab and Al-Chalabi, 2013) by many order of magnitude. In our opinion, this phenomenon may be explained by two manners: firstly: the ester group with unshared pair of electrons can lead to a molecular association with the pyrazoline or dihydroisoxazole heterocyclic among the chain, this will enhance the movement of charge carriers through the polymer chain then increasing conductivity (Su and Kuramoto, 2000).

Table 1: Gives the real, imaginary-permittivity ( $\epsilon'$  and  $\epsilon''$ ) and electrical conductivity of the prepared pure copolymers

Polymer	$\sigma/\Omega^{-1} \cdot \text{cm}^{-1}$	$\epsilon''$	$\epsilon'$
I	3.25575E-09	1.171595207	10.1533513
II	1.14353E-07	41.15058817	28.93852895
III	2.75405E-08	9.910581429	28.47786394
VI	1.94048E-08	6.982913869	21.3675455
V	2.31687E-09	0.833737286	7.373638328
VII	2.71275E-08	9.761969897	11.75447013

Second: the flexibility can be improved by coupling the pyrazoline or dihydroisoxazole heterocyclic with an ester group enhancing the conductivity leading to an increase the flexibility of the polymer chain but there should be significant coupling to the electronic degrees of freedom.

It is clear that these results completely exhibited that inserting metal nanoparticles for conduction polymers will increase the electrical conductivity, so when copolyester was mixed with TiO<sub>2</sub> nanoparticle, the electrical conductivity was increased because these materials have the advantage of excellent electrical conductivity. These advances could lead to commercial applications in the near future (Dubey and Leclerc, 2011). In addition the ratio of electrical conductivity enhances with increased weight ratio of TiO<sub>2</sub> fillers nanosized which revealed the trade-off relationship between the electrical conductivity (Chen *et al.*, 2019) (Table 2).

The conduction mechanism in our investigated nanocomposites results from the hopping process of charge carriers as a charge transport passes into the polymer in conducting polymer systems, a mechanism of transport is also similar to this in amorphous semiconductors (hopping carrier) (Caseri, 2000; Shumaila *et al.*, 2013). The agent defining the conductivity is the transport movement, along with the carrier concentration. The doping method produces a generous supply of possible carriers but to contribute to conductivity they must be mobile. There are at least three factors contributing to the carrier mobility: single chain or intramolecular transport, interchain transport and interparticle contact (Imam, 2013). These three factors comprise a complicated resistive network which determines the effective mobility of the transmitters. So, the flux and since, the conductivity is prepared on both a microscopic (intro and interchain) and a macroscopic

(interparticle) level, so, the enhanced conductivity observed in samples holding nanosized TiO<sub>2</sub> implies either increased charge injection from the electrodes or increased mobility of the injected charge in transit through the sample (Fleming *et al.*, 2005). This behaviour is in an agreement (Al-Maiyaly, 2013; Nesic *et al.*, 1996) as the increasing tendency of conductivity for polyester was also reported by Xu *et al.* (2005), Su and Kuramoto (2000). This excitation involves the transfer of electrons from the HOMO to the LUMO of the organic semiconductor for colored compounds which is the case for conjugated polymers (Khattab *et al.*, 2008).

Figure 4 tells the difference of electrical conductivity at room temperature with frequency in the extent of 50 Hz<sup>-1</sup> MHz. The data show that the conductivity increases with increasing of frequency and shows a small dip at higher frequencies (Fleming *et al.*, 2005). The same variation was obtained for samples with different TiO<sub>2</sub> nanoparticles content (0.1, 0.2). The behavior dependent on frequency can be illustrated on the bases of interface charge polarisation (Max-well Wagner-Sillars effect) (Li *et al.*, 2009; Smith, 2009). This phenomenon takes place in heterocyclic systems like metal-polymer composites owing to the accumulation of charges carriers at the interfaces. Vishnuardhan *et al.* have reported that the conductivity of pure polypyrrole is (1.26×10<sup>-4</sup> s/cm) at 10-5 Hz. Where Fig. 5 showed the electrical conductivity of copolyestersnanocomposite (1.06×10<sup>-6</sup> s/m) at the same frequency than pure copolyesters. The improvement of electrical conductivity for nanocomposite comes from the effective dispersion of nanophotoadductin the polypyrrole films which might help the formation of a more efficient network for charge transport in the polypyrrole films, resulting in higher conductivities.

Figure 6 observation tells us that all copolyesters show similar behavior up to 1.13386E-06 at the frequency of 1809.5 Hz and after that the conductivity increases significantly. With the increase in TiO<sub>2</sub> nanoparticles content in copolyesters and increased at higher frequencies. The increase in conductivity is mainly due to an extended chain length of copolyester which helps in a polarisation of charge carriers between localized sites and offers a lot of conductive path.

Table 2: Gives of the real, imaginary-permittivity (ε' and ε'') and electrical conductivity of the prepared copolymers both in the pure state and doped with different concentrations of nanosized TiO<sub>2</sub>

Polymer/Polymer: TiO <sub>2</sub> nanoparticles	σ/ Ω-1. cm-1	ε''	ε'
<b>I</b>			
1:0.0	3.25575E-09	1.171595207	10.1533513
1:0.1	1.7330E-06	0.031288683	2.238103238
1:0.2	1.00294E-06	0.023167975	1.83872815
<b>II</b>			
1:0.0	1.14353E-07	41.15058817	28.93852895
1:0.1	1.0372E-06	0.029948574	2.495714515
1:0.2	2.41322E-06	0.09494689	1.680475928
<b>III</b>			
1:0.0	1.40176E-06	0.053965383	1.690115347
1:0.1	1.38363E-06	0.042718215	3.583742833
1:0.2	1.3113E-06	0.049946034	1.64651479
<b>VI</b>			
1:0.0	1.94048E-08	32.72307089	5.074052331
1:0.1	1.38145E-07	0.012936478	3.563767963
1:0.2	1.22836E-06	0.05566921	0.56180452
<b>V</b>			
1:0.0	2.31687E-09	0.833737286	7.373638328
1:0.1	1.47697E-06	0.026574799	1.238918383
1:0.2	1.0527E-06	0.02673162	1.684412099
<b>VII</b>			
1:0.0	2.71275E-08	9.761969897	11.75447013
1:0.1	1.01102E-06	0.019890174	1.255692804
1:0.2	1.55052E-06	0.059692593	1.281506943

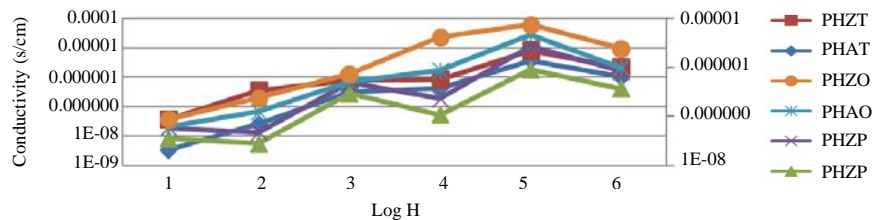


Fig. 4: Electrical conductivity of pure copolyesters with different frequencies

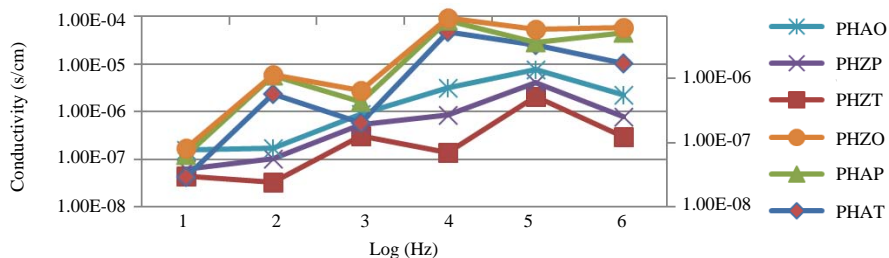


Fig. 5: Electrical conductivity of doped copolyesters by 0.1% wt. concentration of TiO<sub>2</sub> nanoparticles and different frequencies

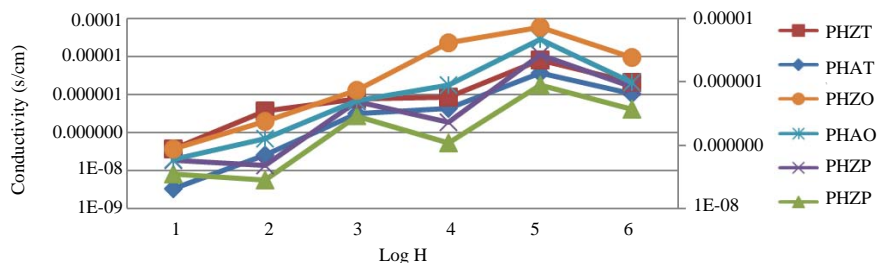


Fig. 6: Electrical conductivity of doped copolyesters by 0.2% wt. concentration of TiO<sub>2</sub> nanoparticles and different frequencies

## CONCLUSION

New monomers containing bispyrazole and bishydroisoxazoleheterocyclics were synthesized and characterized. The structures of the synthesized polymers were confirmed by means of FTIR and NMR spectroscopy. By polycondensation of each monomer with terephthaloylchloride, phthaloyl chloride, oxalyl chloride, six conjugated polyesters have been obtained. TGA showed that the temperatures of maximum weight-loss rate are above 550°C and the DSC measurements revealed the existence of glass transition and melting temperatures. Our results indicate that the electrical conductivity of pure and doped polymers by different TiO<sub>2</sub> nanoparticle ratios (0.1, 0.2%) lies in the semiconductors region and in addition, the electrical conductivity increased with the increase of the TiO<sub>2</sub> nanoparticle concentration and increase frequency. Also the highest electrical conductivity was obtained for the PHZO/TiO<sub>2</sub> nanoparticle (0.2% wt.).

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