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Chemical oxidative synthesis and characterization of poly(o-phenylenediamine) doped with different acids

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ARTICLE INFORMATION

ABSTRACT

Poly o-phenylenediamine (PoPD) doped with different acids such as hydrochloric, sulfuric, formic, phosphoric and glacial acetic acids was synthesized by a chemical oxidative polymerization technique using potassium dichromate as oxidizing agent. The polymer products were characterized by FT-IR and UV-visible spectroscopy. The FT-IR spectra showed shift to lower wave number in case of PoPD-H_2SO_4 and PoPD-H_3PO_4, indicating that the doping degree of PoPD in H_2SO_4 and H_3PO_4 are the greatest. A successful doping of PoPD in H_3PO_4 was observed in UV-vis spectroscopy. The three steps decomposition observed from the thermogravimetric analysis (TGA). The second step loss related to the loss of the dopant is found to be higher in H_3PO_4 doped polymer. The electrical conductivity values of PoPD-H_2SO_4 and PoPD-H_3PO_4 are found to be the highest among the other acids.

1. Introduction

Polyaniline (PANI) as an electrically conductive polymer has attracted considerable attention, because of its excellent environmental stability in the electro conducting form and electrical and optical properties [1,2]. It has different applications in many high performance devices [3-8]. Polymerization of conducting polymer may be performed by chemical [9] or electro-chemical [10] methods. Different chemical oxidizing agents, such as potassium dichromate [11,12], potassium iodate [13], hydrogen peroxide [14], ferric chloride or ammonium persulfate [15] were used. The applications of polyaniline are limited due to its poor processability [16]. Several studies have been done in order to improve the solubility of polyaniline, such as using functionalized protonic acids as dopant [17-19] or the polymerization of aniline derivatives. The substituted group of aniline affects not only the polymerrization reaction but also the properties of the polymer obtained. It is believed that the investigations of polymers synthesized from aromatic diamine are more attractive since they exhibit more novel multi-functionality than polyaniline. Phenylenediamines are a class of aniline derivatives having an extra-NH_2 group in the *o*-, *m*- or *p*-position. Although reports are available on polymerization of *m*- and *p*-isomers [20], *o*-phenylenediamine (*o*PD) is the most frequently studied member. Poly(*o*-phenyldiamine) (PoPD) has apparently shown different characteristics of molecular structure and properties when compared with PANI [21]. It has been reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoxaline repeat unit and exhibits unusually high thermsstability [22,23] although a PANI like structure has also been proposed (Scheme 1) [24].

It has been suggested that the first stage of the polymerization mechanism of *o*PD is the monomer oxidation to the corresponding radical cation, followed by radical coupling (head-to-head, head-to-tail and tail-to-tail) yielding conceivably three different dimmers that can be further oxidized (Scheme 2) [25]. The dimmers arising from tail to tail and head to head coupling play a very minor role [26]. The head to tail dimer of *o*PD may be involved in two competitive processes: (a) further radical coupling leading to chain propagation as in formation of PANI and (b) internal coupling (cyclization) leading to phenazine type structures.

In our previous studies [27,28], the effect of different dopants on the structure of polyaniline (PANI) was investigated. In this work, we synthesize poly(*o*-phenylendiamine) by chemical oxidative polymerization method using different acids (HCl, H_2SO_4, HCOOH, CH_3COOH and H_3PO_4) as dopants.
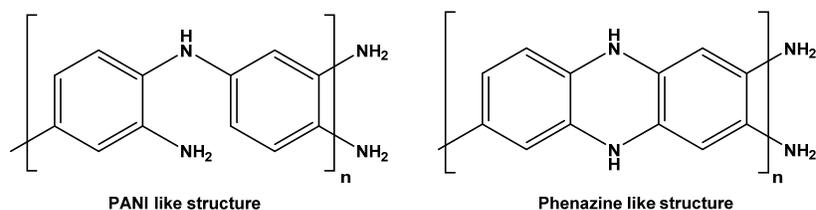
Scheme 1
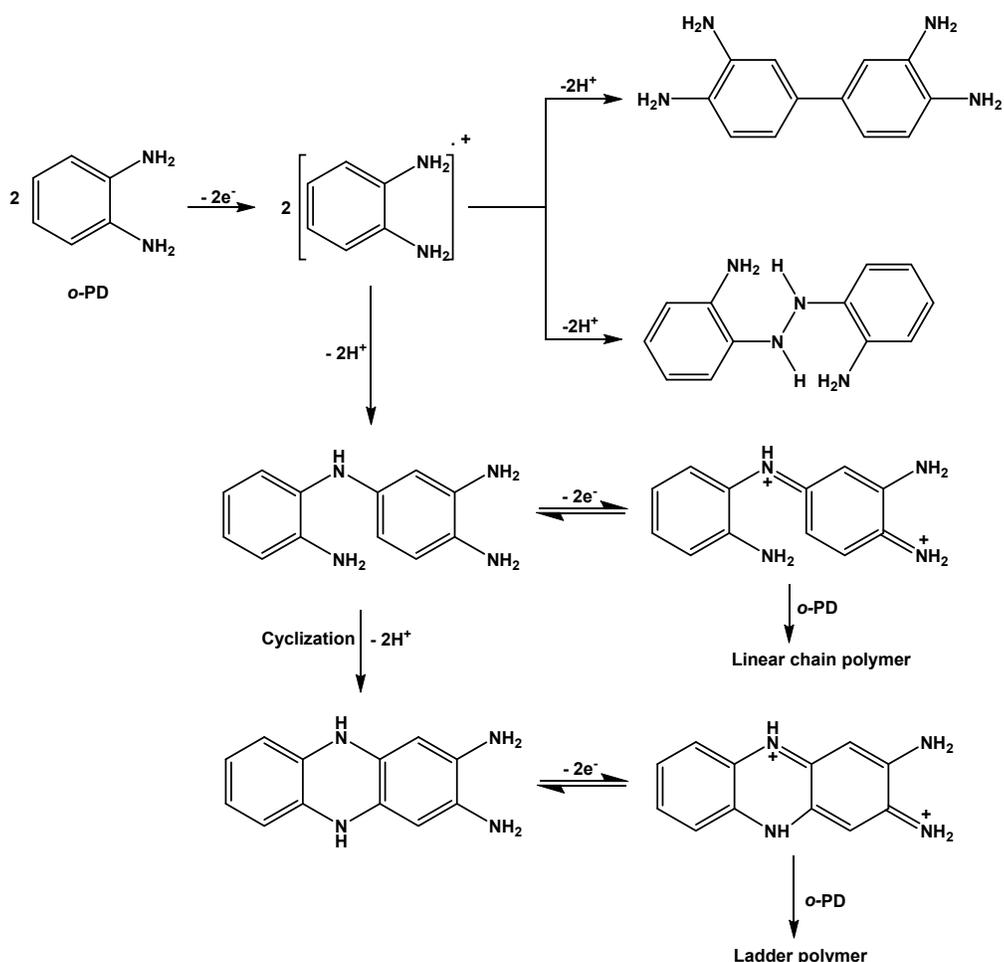
Scheme 2

The effects of the dopant ions on the polymer properties are discussed using FT-IR and UV-visible spectroscopy, TGA analysis and conductivity measurements.

2. Experimental

2.1. Materials

o-Phenylenediamine (*o*PD) (ADWIC, Egypt), potassium dichromate (Merck, Germany), hydrochloric acid (32%), sulfuric acid (98 %), formic acid (98%), glacial acetic acid (99.5%) and phosphoric acid (99%). All these acid used are (Merck, Germany). Acetone and dimethylsulfoxide (DMSO) are used for filtration and UV-visible measurements, respectively.

All chemicals, acids and solvents were used as received without further purification.

2.2. Measurements

The FT-IR spectra were recorded using FTIR 8201PC (Shimadzu) instrument by KBr pellet techniques. For measuring the UV-visible absorption spectra, spectro-photometer (UV-1601 Shimadzu) was used. The thermal studies were performed using a Mettler-Toledo 851 thermo-gravimetric analysis (TGA) in a nitrogen atmosphere from room temperature to 600 °C at heating rate of 10 °C/min. A crucible of platinum contain 15 mg of sample was used in the TGA analysis. Conductivity measurements were made at room temperature using conductivity meter (CM-30V).
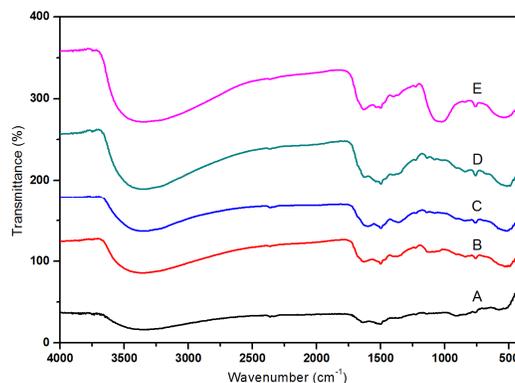
Figure 1. FT-IR spectra of P*o*PD doped with (A) HCl, (B) H_2SO_4, (C) HCOOH, (D) CH_3COOH and (E) H_3PO_4.
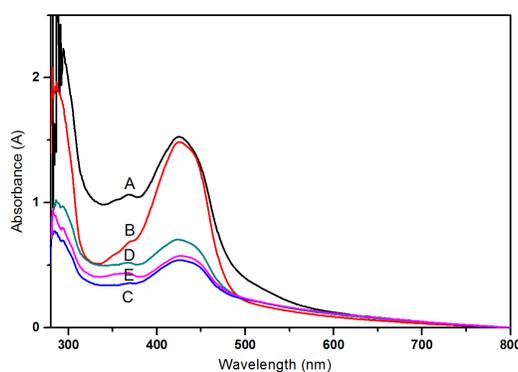
Figure 2. UV-Vis spectra of P*o*PD doped with (A) HCl, (B) H_2SO_4, C) HCOOH, (D) CH_3COOH and (E) H_3PO_4.

2.3. Synthesis of poly(o-phenylenediamine) doped in different acids

The polymer of *o*-phenylenediamine was synthesized by dissolving 1.622 g of *o*-phenylenediamine in 100 mL of 0.1 M HCl in cooled stirred ice bath to produce homogenous solution. Potassium dichromate (4.413 g) was dissolved in 50 mL of 0.1 M HCl and then added to the first solution for 30 minutes with constant stirring. Then remained at room temperature for 24 hours, after this the solution was filtered, washed with acetone and distilled water and the polymer left to dry in oven at 60 °C for 24 hours. The above procedure repeated using 0.1 M H_2SO_4, 0.1 M HCOOH, 0.1 M CH_3COOH and 0.1 M H_3PO_4 acid, respectively.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR is one of the most important methods of spectroscopy; in our work, the importance of FT-IR is concentrated in the comparison of band position for determining groups present in the doped poly *o*-phenylenediamine. Figure 1 shows FT-IR spectrum of P*o*PD doped in different acids.

It shows a broad in the region 3235-3432 cm^{-1} generally assigned to primary and secondary amino groups present in the polymer. The band in the range 1602-1640 cm^{-1} can be assigned to C=C stretching vibrations of the phenazine type structures in the P*o*PD backbone. The bands assigned to C-N stretching vibrations of the quinoid and benzoid rings appear in the ranges 1499-1502 cm^{-1} and 1357-1397 cm^{-1}, respectively. The peaks in the range 834-842 cm^{-1} are due to out of plane bending motion of the C-H bonds of the 1,2,4,5-*tetra*-

substituted benzene nuclei of phenazine units. The presence of the bands between 900-1040 cm^{-1} are due to in-plane bending motion of the C-H bonds of the 1,2,4-trisubstituted benzene rings indicates the presence of open rings in the phenazine units. The signal in the range 512-543 cm^{-1} is assignable to ring deformation. We observed similarity in the FT-IR spectrum for the dopants used indicating the similarity of the oxidation degree in the different dopant used. The intensity of peaks depends on factors such as polymer coil size, the nature polymer-solvent polymer doping. The spectrum of P*o*PD-CH_3COOH (Figure 1.D) has a small intensity band at 1397 cm^{-1}, which is attributed to stretching of C-N band, while a high intensity bands can be observed in the spectrum of P*o*PD-H_2SO_4 (Figure 1.B) and P*o*PD-H_3PO_4 (Figure 1.E) at 1361 and 1359 cm^{-1}, respectively. This shift to lower wavenumber may be attributed that the doping degree of P*o*PD-H_2SO_4 and P*o*PD-H_3PO_4 are the greatest, which prefer the movement of π-electrons and make the displacement to lower wave number.

3.2. UV-Visible spectroscopy

The UV-Visible spectra of P*o*PD synthesized in different dopants (HCl, H_2SO_4, HCOOH, CH_3COOH and H_3PO_4), respectively, are shown in Figure 2. Two characteristic absorption peaks were found in the range 282-429 nm. The peak at 294 nm is attributed to the benzene π-π* electronic transition, while the peak at 429 nm ascribed to the n-π* electronic transition. A blue shift will be observed from the band at 294 to 282 nm as shown in Figure 2.E, may be attributed that P*o*PD doped in H_3PO_4 cause lower the degree of conjugation as well as hindering charge transfer between chains, this indicate a successful doping of H_3PO_4 in P*o*PD.

3.3. Electrical conductivity

The electrical conductivity of the P*o*PD-HCl, P*o*PD-H$_2$SO$_4$, P*o*PD-HCOOH, P*o*PD-CH$_3$COOH and P*o*PD-H$_3$PO$_4$ at room temperature is presented in Table 1.

Table 1. Electrical conductivity of P*o*PD in different acids dopants at room temperature.

Polymer	Conductivity (S.cm^{-1})
P*o*PD-HCl	1.44
P*o*PD-H$_2$SO$_4$	2.07
P*o*PD-HCOOH	1.15
P*o*PD-CH$_3$COOH	0.85
P*o*PD-H$_3$PO$_4$	2.06

From Table 1, the conductivity were found to be in the order P*o*PD-H$_2$SO$_4$ = P*o*PD-H$_3$PO$_4$ > P*o*PD-HCl > P*o*PD-HCOOH > P*o*PD-CH$_3$COOH. The lower value of the conductivity in the case of P*o*PD-CH$_3$COOH is attributed to the decrease of the efficiency of charge transfer between the polymer chains when CH$_3$COOH used as a dopant for P*o*PD. However, the electrical conductivity values of P*o*PD-H$_2$SO$_4$ and P*o*PD-H$_3$PO$_4$ are the highest indicating that the doping degree of P*o*PD doped with these acids are the best. Figure 3 shows the effect of the temperature upon the conductivity of P*o*PD synthesized in different dopants.
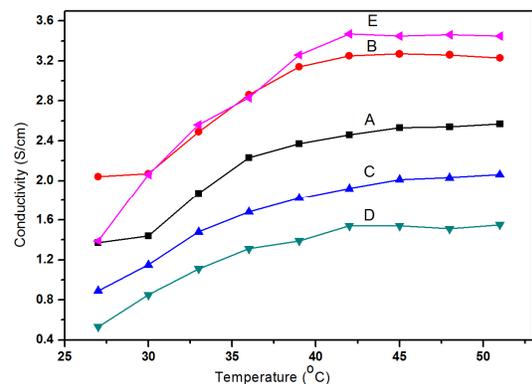
Figure 3. The temperature dependent conductivity plot of P*o*PD doped in different acids, (A) HCl, (B) H$_2$SO$_4$, (C) HCOOH, (D) CH$_3$COOH and (E) H$_3$PO$_4$.

It can be observed that the conductivity increased with the increase in temperature in the different acid dopants, which is characteristic of thermal activated behavior and is in good agreement with literature [29]. The increase in conductivity is attributed to the increase in the temperature [30]. In addition, it should be expected that the molecular motion becomes non negligible in the high temperature ranges, which leads to the recombined ion and/or relocation of the dopant ion [31].

3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is used to determine physical and chemical changes that result in changes in mass when a material is heated. Figure 4 shows TGA and derivative thermo-gravimetry (DTGA) for samples of doped P*o*PD-HCl, P*o*PD-H$_2$SO$_4$, P*o*PD-HCOOH, P*o*PD-CH$_3$COOH and P*o*PD-H$_3$PO$_4$, respectively.

From Figure 4, it can be seen that the total weight loss of P*o*PD doped with different acids is around 40% by raising its temperature at a rate of 10 °C/min from 25 to 600 °C in air. The polymers exhibit two weight loss processes at 84-150 and 240-450 °C, the first loss may be due to loss of water molecules and dopant acids in the polymer P*o*PD at different acids, and the other loss may be due to loss of oligomers (low molecular weight) and breakage of the weak bond in the polymers.
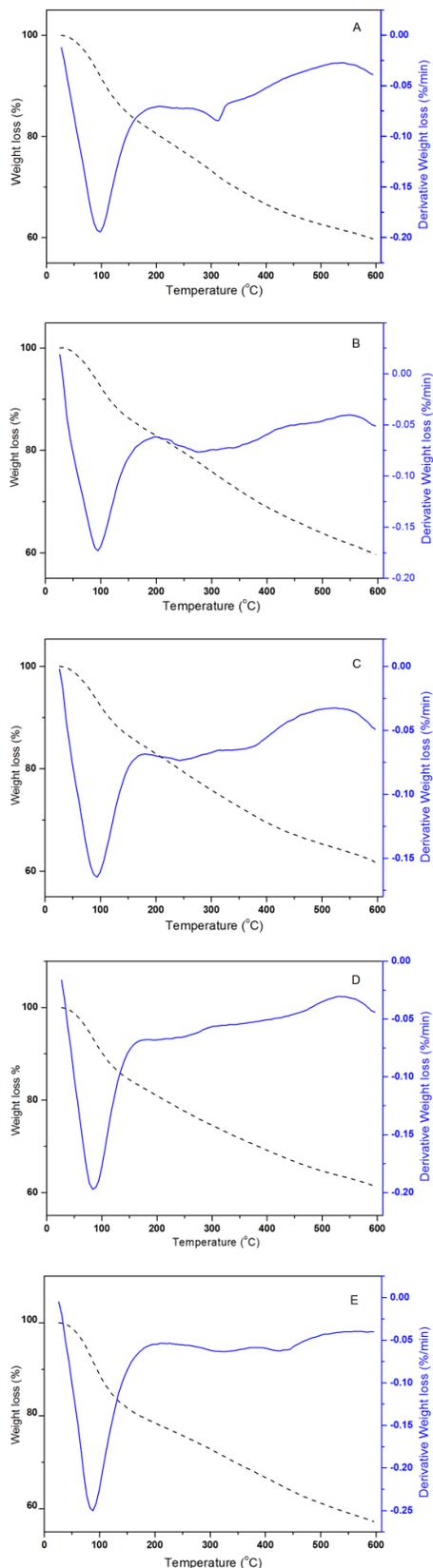
Figure 4. TGA and DTGA of P*o*PD doped with different acids, (A) HCl, (B) H$_2$SO$_4$, (C) HCOOH, (D) CH$_3$COOH and (E) H$_3$PO$_4$.

The total weight residual of P*o*PD with different acids is around 60% at 600 °C, these indicated that the polymers prepared may be stable at 600 °C and when the polymers heated over 600 °C may be observed the complete decomposition of the backbone of the P*o*PD (benzenoid and quinoid) units. It can be observed that the total weight loss of P*o*PD-H_3PO_4 (43%) is greater than weight loss of P*o*PD in the other dopant, the total weight loss were found to be in the order, P*o*PD-H_3PO_4 (43%) > P*o*PD-HCl = P*o*PD-H_2SO_4 (40%) > P*o*PD-HCOOH = P*o*PD-CH_3COOH (38%). The loss of dopant increases in P*o*PD-H_3PO_4 and decreases in the other acids dopants. This may be attributed thatP*o*PD-H_3PO_4 loses a greater weight than P*o*PD in the other dopants under study in this temperature range (84-150 °C) i.e. the doping level of P*o*PD with H_3PO_4 is the highest between the other dopants used in this study.

4. Conclusions

The electrical conductivity values of *o*-phenylenediamine doped with H_2SO_4 and H_3PO_4 are the highest, indicating that the doping degree of P*o*PD with these acids are the most optimal. This fact is noted also in FT-IR and UV-Visible spectra. TGA data indicates that the loss of dopant increases in P*o*PD-H_3PO_4 and decrease in the other dopants, this may be attributed that P*o*PD-H_3PO_4 loses a greater weight than P*o*PD in other acids, that means that the doping level of P*o*PD with H_3PO_4 is the highest.

References

[1]. Wang, P. C.; Liu, L. H.; Mengistie, D. A. *Displays* **2013**, *34*, 301-314.
[2]. Jaymand, M. *Progress Polym. Sci.* **2013**, *38*, 1287-1306.
[3]. Steffens, C.; Manzoli, A.; Oliveira, J. E. *Sensors Actuat. B: Chem.* **2014**, *191*, 643-649.
[4]. Wang, L.; Hua, E.; Liang M. *Biosens. Bioelect.* **2014**, *51*, 201-207.
[5]. Talwar, V.; Singh, O.; Singh, R. *Sensors Actuat. B: Chem.* **2014**, *191*, 276-282.
[6]. Moon, Y.; Yun, J.; Kim, H. *J. Ind. Eng. Chem.* **2013**, *19*, 493-497.
[7]. Gupta, G.; Birbilis, N.; Cook, A. B.; Khanna, A. S. *Corrosion Sci.* **2013**, *67*, 256-267.
[8]. Karthikaiselvi, R.; Subhashini, S. *J. Assoc. Arab Uni. Basic Appl. Sci.* **2014**, *16*, 74-82.
[9]. Gopodinova, K.; Terlemezyan, L. *Progress Polym. Sci.* **1998**, *38*, 1832-1908.
[10]. Gurunathan, K.; Murugan, A. V.; Marimuthu, R.; Mulik, U. P.; Amalnerkar, D. P. *Mater. Chem. Phys.* **1999**, *61*, 173-191.
[11]. Chowdhury, P.; Saha, B. *Indian J. Chem. Tech.* **2005**, *12*, 671-675.
[12]. Sayyah, S. M.; Khaliel, A. B.; Aboud, A.; Mohamad, S. M. *Int. J. Polym. Sci.* **2014**, ID: 520910, 1-16.
[13]. Hirase, R.; Shikata, T.; Shirai, M. *Synth. Met.* **2004**, *146*, 73-77.
[14]. Gopalakrishnan, K.; Elango, M.; Thamilsevan, M. *Arch. Phys. Res.* **2012**, *3*, 315-319.
[15]. Molapo, K.; Ndangili, P. M.; Ajayi, R. F. *Int. J. Electrochem. Sci.* **2012**, *7*, 11859-11875.
[16]. Cao, Y.; Smith, P.; Heeger, A. *Synth. Met.* **1992**, *48*, 91-97.
[17]. Kang, Y.; Lee, M.; Rhee, S. *Synth. Met.* **1993**, *57*, 3471-3482.
[18]. Kang, Y.; Lee, M.; Rhee, S. *Synth. Met.* **1992**, *52*, 319-328.
[19]. Pron, A.; Laska, J.; Osterholm, J. E.; Smith, P. *Polymer*, **1993**, *34*, 4235-4240.
[20]. Cataldo, F. *Eur. Polym. J.* **1996**, *32*, 43-50.
[21]. Li, X. G.; Huang, M. R.; Duan, W.; Yang, Y. L. *Chem. Rev.* **2002**, *102*, 2925-3030.
[22]. Premasiri, A. H.; Euler, W. B. *Macromol. Chem. Phys.* **1995**, *196*, 3655-3666.
[23]. Chan, H. S. O.; Ng, S. C.; Hor, T. S. A.; Sun, J.; Tan, K. L.; Tan, B. T. G. *Eur. Polym. J.* **1991**, *27*, 1303-1308.
[24]. Yano, J. *J. Polym. Sci. A: Polym. Chem.* **1995**, *33*, 2435-2441.
[25]. Barbero, C.; Silber, J. J.; Sereno, L. *J. Electroanal. Chem. Interf. Electrochem.* **1989**, *263*, 333-352.
[26]. Losito, I.; Palmisano, F.; Zambonin, P. G. *Anal. Chem.* **2003**, *75*, 4988-4995.
[27]. Melad, O. *J. Res. Updates Polym. Sci.* **2015**, *4*, 134-138.
[28]. Melad, O.; Jarur, M. *Chem. Chem. Tech.* **2016**, *1*, 41-44.
[29]. Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1987**, *36*, 3475-3478.
[30]. Kobayashi, A.; Ishikawa, H.; Amano, K.; Satoh, M.; Hasegawa, E. *J. Appl. Phys.* **1993**, *74*, 296-299.
[31]. Kulkarni, M. V.; Viswanath, A. K.; Marimuthu, R.; Seth, T. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 2043-2049.