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COPOLYMERIZATION OF POLY (O-PHENYLENEDIAMINE-CO-O/P-TOLUIDINE) VIA THE CHEMICAL OXIDATIVE TECHNIQUE: SYNTHESIS AND CHARACTERIZATION

KOPOLIMERIZACIJA POLI (O-FENILENDIAMINA-CO-O/P-TOLUIDINA) S TEHNIKO KEMIJSKE OKSIDACIJE: SINTEZA IN KARAKTERIZACIJA

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Chemical oxidative copolymerization of *o*-phenylenediamine -co-*o*/*p*-toluidine at different molar ratios of monomer was performed using potassium dichromate as an oxidant. The resulting copolymers were investigated using Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy. In the copolymer, the intensity of the band at 1005 cm^{-1} is substantially decreased due to the -CH_3 bending vibrations. A hyposochromic shift is observed in UV-visible spectroscopy. The electrical-conductivity values obtained for the *o*-toluidine copolymers are higher than those for the *p*-toluidine copolymers.

Keywords: *o*-phenylenediamine, *o*-toluidine, *p*-toluidine, conductivity, chemical oxidativeness, FTIR

Izvedena je bila kemijska oksidativna kopolimerizacija *o*-fenilendiamina-co-*o*/*p*-toluidina pri različnih molarnih razmerjih monomera, z uporabo kalijevega dikromata kot oksidanta. Nastali kopolimeri so bili preiskovani z uporabo infrardeče spektroskopije s Fourierjevo transformacijo (FTIR) in UV-vidno spektroskopijo. V kopolimeru je intenziteta pasu pri 1005 cm^{-1} občutno zmanjšana zaradi upogibnih vibracij -CH_3. V UV vidnem spektru je opažen zamik v spektralnem pasu. Vrednosti električne prevodnosti dobljene pri *o*-toluidin kopolimerih so višje kot pri *p*-toluidin kopolimerih.

Ključne besede: *o*-fenilendiamin, *o*-toluidin, *p*-toluidin, prevodnost, kemijska oksidativnost, FTIR

1 INTRODUCTION

Intrinsically conductive polymers have become an efficient alternative to inorganic conductors in many practical applications in the recent decade.[1] Polyaniline, poly toluidine, polypyrrole, poly aminopyridine, polythiophene and poly phenylenediamine are examples of conductive polymers, showing high conductivity. Polyaniline is an important member of the intrinsically conductive polymers because of the ease of its preparation, an excellent environmental stability, interchangeable oxidation states, electrical and optical properties, economic costs,[2–4] and because they can be used for chemical sensors,[5,6] electromagnetic shielding,[7] electrochemical and corrosion devices.[8–9] Polymerization of a conducting polymer may be performed with chemical[10] or electrochemical[11] methods. Different chemical oxidizing agents such as potassium dichromate,[12–14] potassium iodate,[15] hydrogen peroxide,[16] ferric chloride or ammonium persulphate[17] can be used. The application of polyaniline is limited because of its poor processability,[18] which is true for most conducting polymers.

A good method to obtain soluble conductive polymers is the polymerization of aniline derivatives. Poly phenylenediamine homopolymer has attracted attention because it has been reported to be a high aromatic polymer containing a 2,3-diamino phenazine or quinoxaline repeat unit and exhibiting an unusually high thermostability.[19–21] In recent years, copolymerization has been developed as one of the most essential and alternative strategies for modifying physical and chemical properties of conducting polymers. These copolymers show characteristics reasonably different from those of the homo polymer.[22,23] Thus, copolymerization can be a convenient synthetic method and a process for preparing new conducting materials with improved properties. However, the conductivity and solubility of the phenylenediamine homopolymer are low.[19–21] Copolymerization of o-phenylenediamine with o/p toluidine might be one of the best methods. A close analysis of the literature shows a large number of reports on the chemical and electrochemical synthesis of polytoluidine and its copolymer with aniline and other substituted anilines.[24–33] Electrochemical copolymerization of o-phenylenediamine with *o*-toluidine has been reported.[34] So far, there has been no report on copolymerization of o-phenylenediamine with *o*/*p* toluidine using the chemical oxidative method. Toluidines are derivatives of aniline where a – CH_3 group is substituted in the aromatic ring at the *o*-, *m*- or *p*- positions. In this work, a chemical oxidative copolymerization of o-phenylenediamine with *o*/*p* toluidine at different molar ratios of monomer was synthesized and characterized using FTIR, UV-visible spectroscopy and conductivity measurements.

2 EXPERIMENTAL PART

2.1 Materials

o-phenylenediamine (*o*-PD), o-touidine (*o*T), p-toluidine (*p*T) (ADWIC, Egypt), potassium dichromate ($K_2Cr_2O_7$), ammonium persulfate ($(NH_4)_2S_2O_3$) (Merk, Germany), hydrochloric acid (HCl 32 %), formic acid (HCOOH 98 %) and glacial acetic acid (CH_3COOH 99.5 %) (Merk-Germany), dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) were used for the UV-visible and conductivity measurements, respectively. All the chemicals, acids and solvents were used as received without any further purification.

2.2 Measurements

The FTIR spectra were recorded with a FTIR 8201PC (SHIMADZU) instrument using KBr pellets techniques. For measuring the UV-visible absorption spectra, a spectrophotometer (UV-1601 SHIMADZU) was used. Conductivity measurements were made at room temperature using a conductivity meter (CM-30V).

2.3 Synthesis of poly (o-phenylenediamine – Co –o/p-toluidine)copolymer

2.3.1 Synthesis of poly o-phenylenediamine

The polymer of *o*-phenylenediamine was synthesized by dissolving 1.622 g of *o*-phenylenediamine in 100 mL of 0.1M HCL in a stirred ice bath to produce a homogenous solution. 4.413 g of potassium dichromate was dissolved in 50 mL of 0.1M HCL and added to the first solution for 30 min while being constantly stirred, then it was left at room temperature for 24 h. After this the solution was filtered, washed with acetone and distilled water and the polymer was left to dry in an oven at 60 °C for 24 h.

2.3.2 Synthesis of poly o- and p- toluidine

Poly (*o*- and *p*- toluidine) were synthesized with chemical oxidative polymerization of *o*- and *p*- toluidine in an acidic media. 5 mL of *o*T was dissolved in 300 mL of 1M formic acid and kept at 0 °C; 11.4 g of $K_2Cr_2O_7$ was dissolved in 200 mL of 1M formic acid also at 0 °C and added dropwise under constant stirring to the (*o*T/HCOOH) solution over a period of 20 min. The resulting dark green solution was maintained under constant stirring for 24 h. The solution was filtered and then washed with distilled water; the black powder of poly *o*-toluidine was left to dry in air for one week, while 2.5 mL of *p*T was dissolved in 150 mL of 1M HCL and kept at 0 °C; 5.7 g of $K_2Cr_2O_7$ was also dissolved in 100 mL of 1M HCL at 0 °C and added dropwise under constant stirring to the (*p*T/HCL) solution over a period of 20 min. The resulting dark red solution was maintained under constant stirring for 24 h. The solution was filtered and then washed with distilled water, and the black red powder of poly *p*-toluidine was left to dry in air for one week.

2.3.3 Synthesis of poly (o-phenylenediamine – Co – o-/p- toluidine)copolymer

1.54 g *o*PD and 0.5133 mL *o*T/*p*T were added to 150 mL of 1M glacial acetic acid in a 500 mL single-neck glass flask at 40 °C . 13.68 g ($(NH_4)_2S_2O_8$) was dissolved separately in 14 mL distilled water to prepare an oxidant solution. The monomer solution was then stirred and treated with the oxidant solution added dropwise at an adding rate of one drop every three seconds for 30 min at 40 °C. Immediately after the first few drops, the reaction solution turned violet in the case of *o*T and blackish green in the case of *p*T. After 1 h, the copolymer acetate was isolated from the reaction mixture with filtration and washed with the excess of distilled water to remove the oxidant and oligomers. A whitish

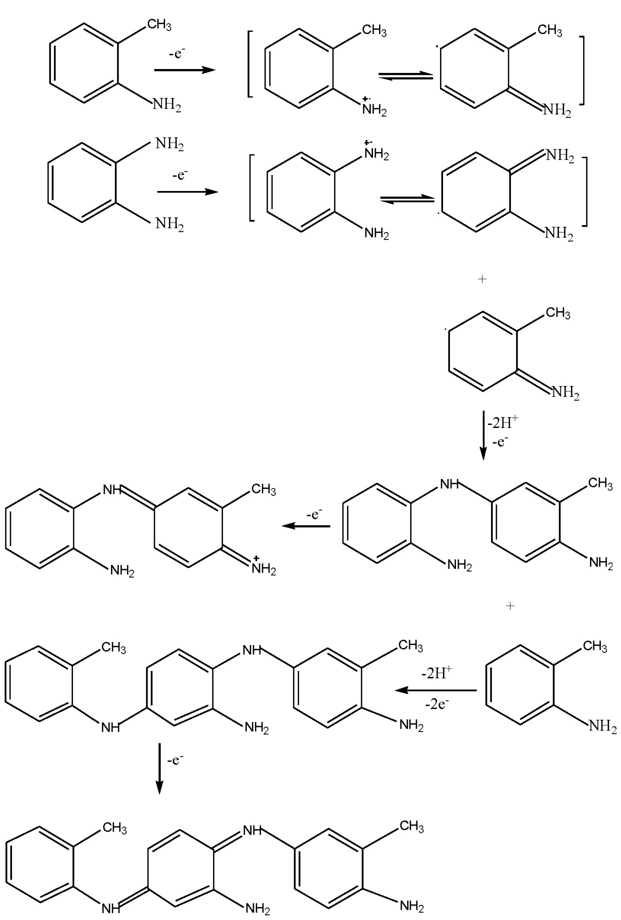

Figure 1: Scheme of copolymerization mechanism of poly (*o*-phenylenediamine-Co-*o*-toluidine) copolymer

Slika 1: Shema mehanizma kopolimerizacije poli (*o*-fenilendiamin in *o*-toluidin) kopolimera violet solid powder and a greenish brown solid powder for *o*T and *p*-T copolymers, respectively, were left to dry in the oven at 118 °C for 48 h and then dry in air for one week. The above procedure was repeated at various molar ratios of the monomers *o*T and *p*T at the feeds of 0.50 and 0.25 molar of *o*PD, respectively.

3 RESULTS AND DISCUSSION

3.1 Synthesis of poly (o-phenylenediamine – Co – o-/p-toluidine)copolymer

Toluidines are derivatives of aniline where a $–CH_3$ group is substituted in the aromatic ring at the *o*-, *m*- or *p*- positions. Schemes in **Figures 1** and **2** represent the copolymerization mechanism of poly (*o*-phenylenediamine-Co-*o*-/*p*-toluidine)copolymer, respectively.

3.2 FTIR spectra of poly (o-phenylenediamine – Co - o / p- toluidine) copolymer

Figure 3 shows the FTIR spectra of poly *o*-phenylenediamine, poly *o*-toluidine and poly *p*-toluidine, respectively.

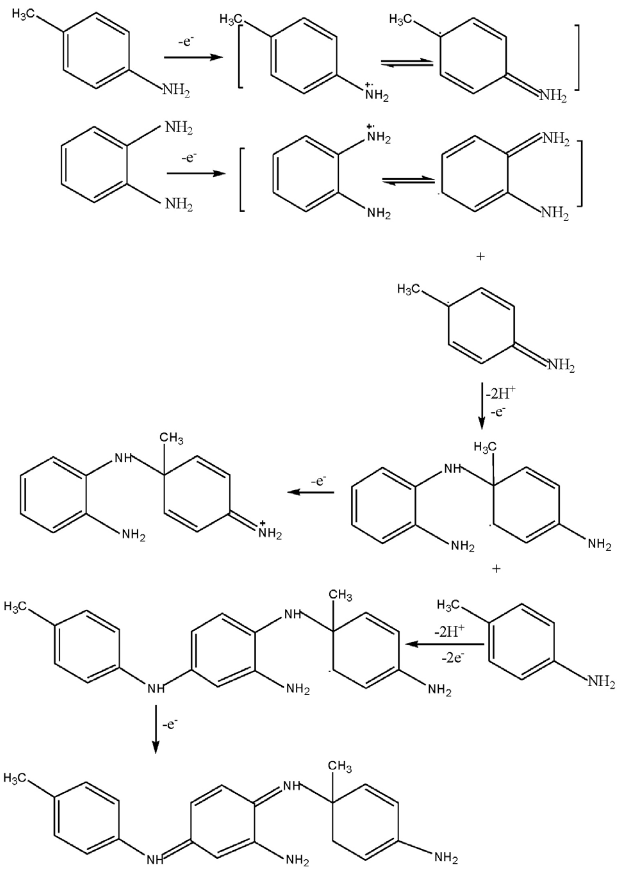

Figure 2: Scheme of copolymerization mechanism of poly (*o*-phenylenediamine-Co-*p*-toluidine) copolymer

Slika 2: Shema mehanizma kopolimerizacije poli (*o*-fenilendiamin in *p*-toluidin) kopolimera

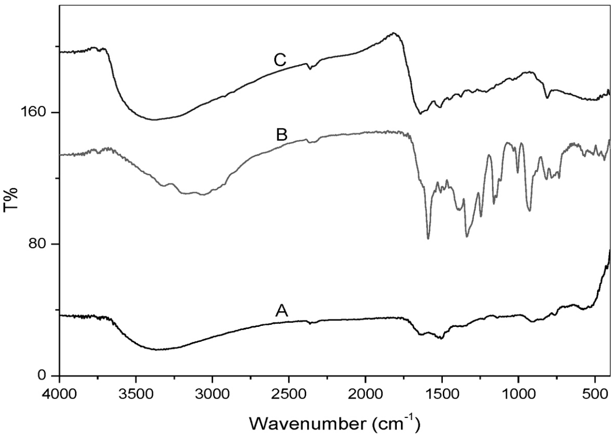

Figure 3: FTIR spectra of: A) poly *o*-phenylenediamine, B) poly *o*-toluidine and C) poly *p*-toluidine

Slika 3: FTIR-spekter: A) poli *o*-fenilendiamina, B) poli *o*-toluidina in C) poli *p*-toluidina

A weak band is observed at 3326–3391 cm^{-1} characteristic of the $–NH_2$ and N-H stretching, another one is observed at 1640–1525 cm^{-1} assigned to the quinoid and benzenoid phenyl ring for poly o-phenylenediamine (**Figure 3** (A), the signal due to the C-H in-plane bending vibratio is observed at 1161 cm^{-1}. **Figure 3** (B and C) shows the frequency peaks at (2917, 1638, 1450, 1301, 1207, 1157, 920) cm^{-1} that are attributed to the C-H stretching of the substituent methyl group, C=C stretching vibrations of quinoid rings, C=C stretching vibrations of benzoid rings, C-N stretching vibrations of quinoid rings, C-N stretching vibrations of benzoid rings, C-H in-plane bending vibrations and 1, 2, 4- tri substituted aromatic rings, respectively. The signal at 567 cm^{-1} is due to the C-H out-of-plane bending vibration. The peak at 3063 cm^{-1} in **Figure 3** (B and C) is caused by the C-H stretch modes of the substituent methyl group. **Figure 4** shows the FTIR spectra of poly

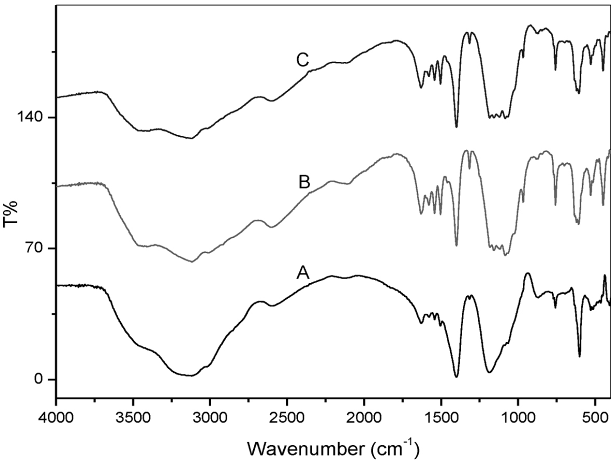

Figure 4: FTIR spectra of poly (*o*PD-Co-*o*T) copolymer with different molar ratios of *o*PD: A) 0.25, B) 0.50, C) 0.75

Slika 4: FTIR-spektri poli (*o*PD in *o*T) kopolimera z različnimi molskimi razmerji *o*PD: A) 0,25, B) 0,50, C) 0, 75 (*o*PD-Co-*o*T) copolymer with different molar ratios of *o*PD.

Most of the bands show variations in the intensity and position. The spectra of the copolymer show the main bands corresponding to the N-H stretching vibrations and ring stretching vibrations of quinoid and benzeoid structures. The intensity of the N-H stretching vibrations in the region between 3470–3010 cm^{-1} increases with the increasing *o*PD feed concentration, indicating an increase in the number of primary and secondary amino groups in the copolymer structure. The band at 1590 cm^{-1} (**Figure 3** (B)) and the band at 1627 cm^{-1} (**Figure 3** (C)) correspond to the C=C stretching vibrations of the aromatic rings. This signal is shifted to 1630 cm^{-1} in the copolymer, **Figure 4**. The intensity of the two bands centered at 1497 cm^{-1} and 600 cm^{-1} greatly increases with the increasing *o*PD feed concentration (**Figure 4**), while the 1497 cm^{-1} band in the copolymer indicates the presence of phenazine-type structures in the copolymer backbone. These cyclic structures in the copolymer are either due to the presence of *o*PD blocks or may result from the cyclization of the adjacent *o*PD and *o*T units in the copolymer chain. On the other hand, the intensity of the band at 1005 cm^{-1}, due to the –CH$_3$ bending vibrations, substantially decreases in the copolymer. This is indicative of a gradual decrease in the *o*T units in the copolymer structure with the increasing *o*PD feed concentration.

Figure 5 shows the FTIR spectra of poly(*o*PD-Co-*p*T) copolymer with different molar ratios of *o*PD.

In general, with some exceptions, the spectral characteristics of the copolymers are very similar to those of P*o*PD. The intensity of the broad band, in the region of 3000–3353 cm^{-1} increases with the increasing *o*PD feed concentration. The band corresponding to the quinoid stretching vibrations occurs at 1616 cm^{-1} for the copolymer. The intensity of this band was also found to increase with the increasing *o*PD feed concentration. The incorporation of the p-toluidine moiety in the copolymer was indicated by the appearance of the characteristic C-H stretching of the substituent methyl group, which was observed as a very weak band at 2917 cm^{-1}. As in o-toluidine, the intensity of the band at 1029 cm^{-1}, due to the -CH$_3$ bending vibrations, substantially decreases in the copolymer.

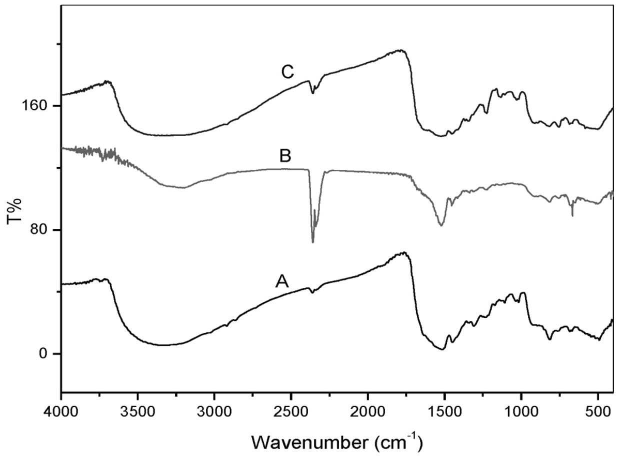

Figure 5: FTIR spectra of poly (*o*PD-Co-*P*T) copolymer with different molar ratios of *o*PD: A) 0.25, B) 0.50, C) 0.75

Slika 5: FTIR-spektri poli (*o*PD in PT) kopolimera z različnimi molskimi razmerji *o*PD: A) 0,25, B) 0,50 in C) 0,75

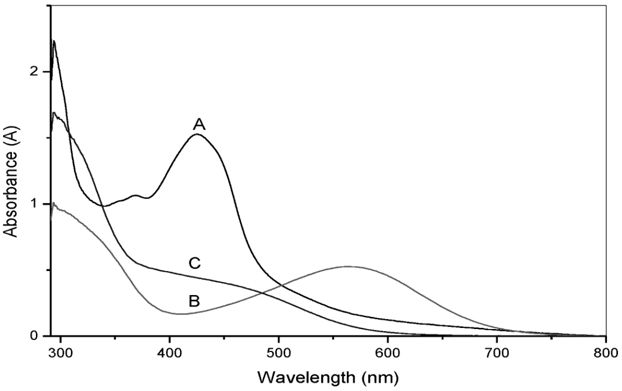

Figure 6: UV-VIS spectra of: A) poly *o*-phenylenediamine, B) poly *o*-toluidine and C) *p*-toluidine

Slika 6: UV-VIS spektri: A) poli *o*-fenilendiamin, B) poli *o*-toluidin in C) *p*-toluidin

3.3 UV-visible spectra of poly (o-phenylenediamine – Co - o / p- toluidine) copolymer

Figure 6 shows the UV-visible spectra of poly *o*-phenylenediamine, poly *o*-toluidine and poly *p*-toluidine, respectively.

Figures 7 and **8** show the UV-visible spectra of poly (*o*PD-Co-*o*T) and poly (*o*PD-Co-*p*T)copolymers, respectively, with different molar ratios of *o*PD. In **Figures 6**, **7** and **8**, for UV-visible spectra of homopolymers and copolymers, two characteristic absorption peaks were found at around 290 nm and in a range of 417–563 nm corresponding to the benzene π-π^* electronic transition and n-π^* electronic transition. A hyposochromic shift from 550 nm in the o-toluidine copolymer to 450 nm in

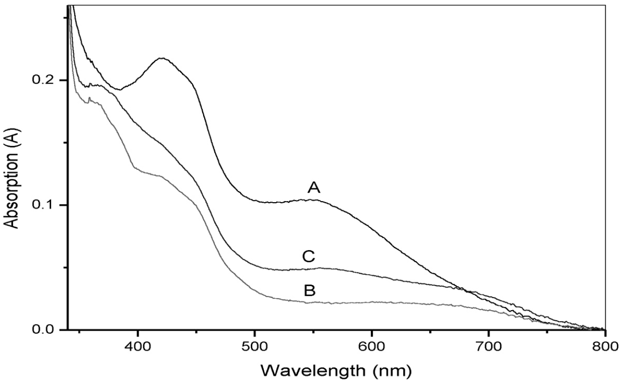

Figure 7: UV-VIS spectra of poly (*o*PD-Co-*o*T) copolymer with different molar ratios of *o*PD: A) 0.25, B) 0.50 and C) 0.75

Slika 7: UV-VIS spektri poli (*o*PD in *o*T) kopolimera z različnimi molskimi razmerji *o*PD: A) 0,25, B) 0,50 in C) 0,75

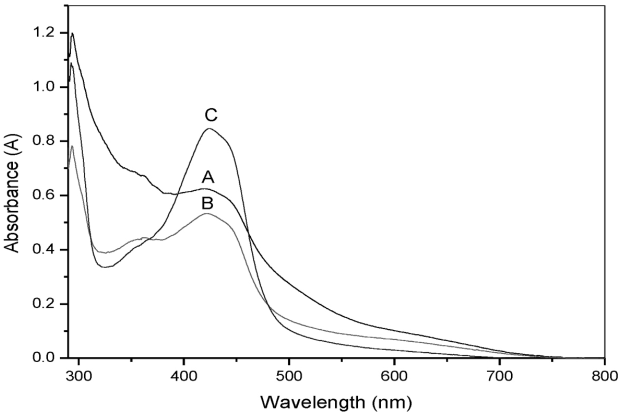

Figure 8: UV-VIS spectra of poly (*o*PD - Co- *p*T) copolymer with different molar ratio of *o*PD: A) 0.25, B) 0.50 and C) 0.75.

Slika 8: UV-VIS spektri poli (*o*PD in *p*T) kopolimera z različnimi molskimi razmerji *o*PD: A) 0,25, B) 0,50 in C) 0,75

the p-toluidine copolymer implies a decrease in the extent of conjugation and an increase in the band gap. These bands correspond to the excitation transition of the quinoid rings. It can be observed that these bands increase when the o-phenylenediamine in the copolymer is increased. This blue shift with the increasing o-phenylenediamine in the copolymer is due to the steric effect of the substituents, indicating a successful copolymerization.

3.4 Electrical conductivity

Table 1: shows electrical conductivity of poly (*o*-phenylenediamine –Co-*o*/*p*-toluidine) copolymer at room temperature in DMF

Tabela 1: Električna prevodnost poli (*o*-fenilendiamina in *o*/*p*-toluidin) kopolimera pri sobni temperaturi v DMF

Polymer	Conductivity (S/cm)
P*o*PD	2.23
P*o*T	1.43
P*p*T	2.04
P(*o*PD-Co-*o*T)25	3.39
P(*o*PD-Co-*o*T)50	3.42
P(*o*PD-Co-*o*T)75	4.65
P(*o*PD-Co-*p*T)25	1.615
P(*o*PD-Co-*p*T)50	1.878
P(*o*PD-Co-*p*T)75	1.898

It can be seen that the conductivity increases as the amount of *o*-phenylenediamine increases in the copolymers. In general, o-isomer gives higher conductivity values than the other isomers; the small values of the conductivity in the case of poly (*o*-phenylenediamine–Co-*p*-toluidine) copolymer compared with the conductivity value of *o*-phenylenediamine may indicate that *p*-toluidine is not a good enough polymer to make a copolymer with *o*-phenylenediamine.

5 CONCLUSION

The synthesis of the copolymerization of *o*-phenylenediamine with *o* / *p*-toluidine was characterized using FTIR and UV-Vis spectroscopy. The intensity of the band at 1005 cm^{-1} that is due to the -CH_3 bending vibrations, substantially decreases in the copolymer. A hypsochromic shift from 550 nm in the *o*-toluidine copolymer to 450 nm in the *p*-toluidine copolymer implies a decrease in the extent of conjugation and an increase in the band gap. In general, ortho-isomers give higher conductivity values than the other isomers; so the obtained conductivity values that are higher for the *o*-toluidine copolymer than for the *p*-toluidine copolymer, indicate that *p*-toluidine is not a good enough polymer able to make a copolymer with *o*-phenylenediamine.

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