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STRUCTURAL, THERMAL AND ELECTRICAL PROPERTIES OF DOPED POLY(3,4-ETHYLENEDIOXYTHIOPHENE)

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Abstract. Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically synthesized, undoped and then re-doped using FeCl₃ as well as camphorsulfonic acid (CSA). FT-IR results confirm the nature of the synthesized and doped samples. XRD analysis indicates crystal structure modification after doping and was also used to calculate crystallinity of samples. Crystallinity increases after FeCl₃ doping, whereas it reduces due to CSA doping. TGA-DTA results show reduction in T_g value for FeCl₃ doped sample while it increases for CSA doped samples compared to that of undoped PEDOT. Reduction in T_g indicates plasticizing effect of FeCl₃ whereas increase in T_g show anti-plasticizing effect of CSA in PEDOT. Conductivity (σ) value increases by two orders of magnitude after doping. Log σ vs. $1/T$ graph show metallic nature of undoped PEDOT above 308 K, however both doped samples show semiconducting nature from 301 to 383 K.

Keywords: poly(3,4-ethylenedioxythiophene), FT-IR, TGA-DTA, electrical conductivity.

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most prominent conjugated polymers, which was developed at the Bayer AG research laboratories in Germany during the late 1980s to give a soluble conducting polymer. However it was initially found to be insoluble when prepared using standard oxidative chemical or electrochemical method, but exhibited interesting properties with a very high (300 S/cm) conductivity [1-3]. To make water-soluble poly(styrene sulfonic acid) (PSA) was used as a dopant during polymerization. This combination resulted in a water-soluble system with good film forming properties with excellent stability and high visible light transmissivity [4, 5] but at the cost of conductivity (~10 S/cm). This made it an excellent

candidate for several industrial applications including material for photographic film, electroluminescent lamps [6], electronic devices [7], sensors and textile [8].

In this paper chemical synthesis, structural and thermal analysis as well as d.c. electrical conductivity measurements of undoped and FeCl₃ as well as camphorsulfonic acid (CSA) doped PEDOT are reported.

2. Experimental

2.1. Sample Preparation: Chemical Synthesis and Doping

PEDOT was chemically synthesized as reported by Corradi *et al.* [9] with slight modifications. For synthesis 1.42 g (0.01 mol) of monomer-EDOT was mixed in 140 ml of distilled water. The reaction mixture was stirred for 15 min. To this mixture 4.05 g (0.025 mol) of anhydrous FeCl₃ was added. The above mixture was then stirred for 24 h at 348 K in oil bath. Precipitate obtained was filtered using glass crucible. It was then washed with methanol and distilled water alternately till the filtrate became colorless. It was initially dried in oven at 473 K for 15 min to remove water contents and then dried in natural atmosphere till it got completely dried.

The above synthesized and dried powder was undoped using aqueous hydrazine for 6.5 h. The undoped PEDOT was re-doped using 5 % (w/v) aqueous FeCl₃ as well as CSA for 5 h with constant magnetic stirring to obtain uniform doping.

2.2. Characterization

Elemental analysis (C, H, N, S and O) of all samples was carried out using FLASH EA 1112 model (ThermoFinnigan, Italy). ICP-atomic emission spectroscopy (JY Ultima-2 model, Jobin Yvon, France) was used

to detect Fe contents in all samples. FT-IR was carried out in the spectral range of 400–4000 cm^{-1} using Shimadzu FTIR-8400S spectrophotometer. The wide angle X-ray diffraction (WAXD) patterns were recorded using Bruker Advanced X-ray diffractometer within a range of $2\theta = 5\text{--}45^\circ$. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using Diamond TG/DTA model (Perkin Elmer, USA) in the temperature range from 300 to 873 K at the heating rate of 283 K/min. D.C. electrical conductivity (σ) measurements of undoped and all doped PEDOT samples in the temperature range from 301 to 383 K with a step of 5 K were carried out using four probe method.

3. Results and Discussion

3.1. Elemental Analysis

The various elements obtained through analysis are tabulated in Table 1.

From Table 1 it is observed that in case of FeCl_3 doped PEDOT, sulfur content decreases while Fe content increases compared to undoped PEDOT indicating that it quite likely that S of PEDOT is getting replaced by Fe after doping with FeCl_3 . S content is also found to decrease even after doping by CSA.

3.2. FT-IR Analysis

Fig. 1 shows FT-IR spectra of undoped and FeCl_3 doped, as well as CSA doped PEDOT. The synthesized polymer after treatment with hydrazine gives rise to the IR spectrum as depicted in Fig. 1A.

The band appearing at 840.99 cm^{-1} could be ascribed to vibration mode of C–S bond in thiophene ring. The band at 890 cm^{-1} associated to the bending mode of C–H bond in EDOT monomer disappears after polymerization indicating that formation of PEDOT molecular chains with $\alpha\text{--}\alpha'$ coupling [10]. The presence of band at 918.15 cm^{-1} is due to ethylenedioxy ring deformation mode. A very strong band at 1060.88 and 1193.98 cm^{-1} is characteristic band of C–O [11]. The band at 1141.90 cm^{-1} is assigned to stretching mode of ethylenedioxy group. Also a very strong band observed at 1340.57 cm^{-1}

is C=C characteristic band [11]. A band observed at 1500.67 cm^{-1} is due to ring vibration mode of thiophene ring [12]. Furthermore a weak characteristic CH_2 stretching of the dioxethylene bridge (2850–3000 cm^{-1}) confirms that the synthesized polymer is PEDOT and is coupled at $\alpha\text{--}\alpha'$ position.

After doping PEDOT by FeCl_3 for 5 h, a new band appears at 570.95 cm^{-1} . This band is not observed in undoped PEDOT. It has been reported by D. Pavia *et al.* [13] that the bands within 550–780 cm^{-1} are associated to C–Cl. Thus it appears that due to doping by FeCl_3 , C–Cl bonding must take place. A band appearing at 918.15 cm^{-1} in undoped PEDOT shifts to 925.86 cm^{-1} in FeCl_3 doped PEDOT, indicating that ethylenedioxy ring deforms after doping. This might be due to the fact that Cl from FeCl_3 forms a bond with C of ethylenedioxy ring resulting in C–Cl band, which appears in IR-spectra at 570.95 cm^{-1} . It is also observed that after doping PEDOT by FeCl_3 , a band at 840.99 cm^{-1} associated to vibration mode of C–S bond in thiophene ring shifts to 837.13 cm^{-1} .

It can be therefore concluded that Fe of FeCl_3 might be getting attached to (and/or replacing) S of thiophene ring causing thiophene ring to deform and results in shift of band. Moreover, a shift in characteristic band of C–O appearing at 1060.88 cm^{-1} and 1193.98 cm^{-1} in undoped PEDOT to 1055.10 and 1205.55 cm^{-1} , respectively, after doping it by FeCl_3 indicates that Fe must bond with O of ethylenedioxy ring. Furthermore a shift in band from 1500.67 cm^{-1} appearing in undoped PEDOT to 1518.03 cm^{-1} in FeCl_3 doped PEDOT associated to ring vibration modes of thiophene ring (1350–1500 cm^{-1}) indicates a change in structure of substituted thiophene. It appears from this shift/change that the double bond of thiophene ring changes its position and a double bond appears between *b-b'* position of thiophene rings. The possible change in structure of PEDOT after doping it by FeCl_3 is shown in Figs. 2a and 2b.

Thus appearance of new band and shifting of some of the bands indicates FeCl_3 is getting doped in PEDOT and forms a complex with PEDOT chain where Cl gets attached with C of thiophene ring at *b* position and Fe gets attached with S of thiophene and/or O of ethylenedioxy ring.

Table 1

Percentage of C, H, N, S, O and Fe elements

Sample	C, %	H, %	N, %	S, %	O, %	Fe, ppm
Undoped PEDOT	43.83	3.31	1.25	21.11	26.45	1891
5 h FeCl_3 doped PEDOT	40.87	3.40	1.05	19.50	26.88	4719
5 h CSA doped PEDOT	43.94	3.48	1.10	20.00	25.67	1924

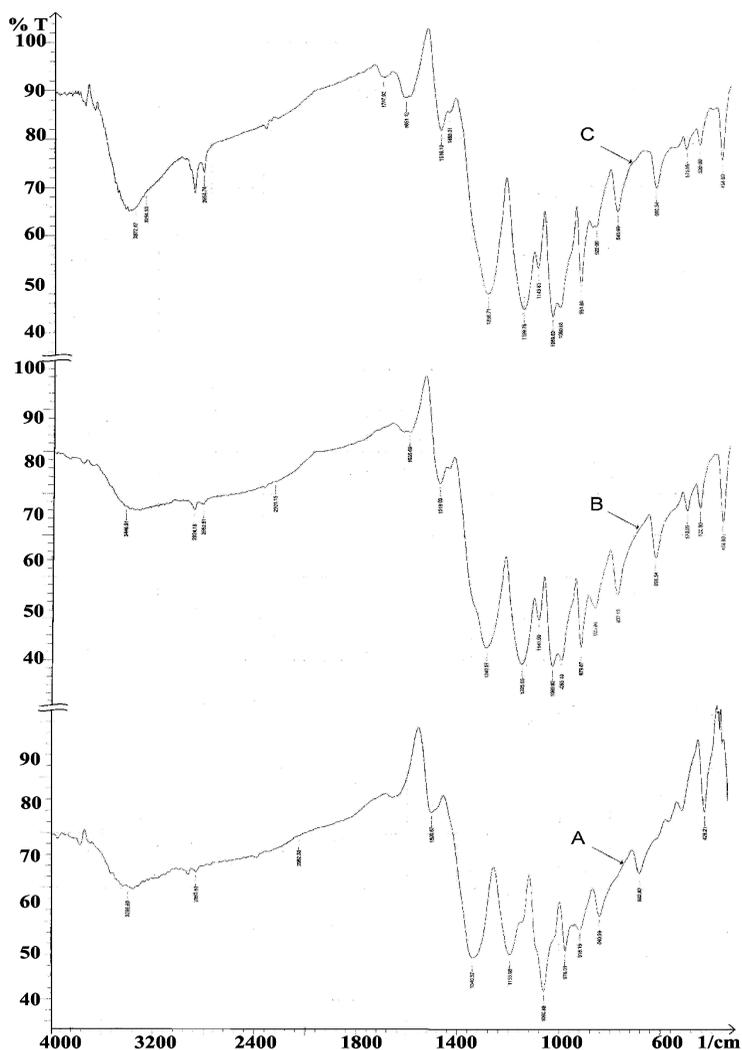


Fig. 1. FT-IR spectra of undoped (A), 5 h FeCl_3 doped (B) and 5 h CSA doped (C) PEDOT

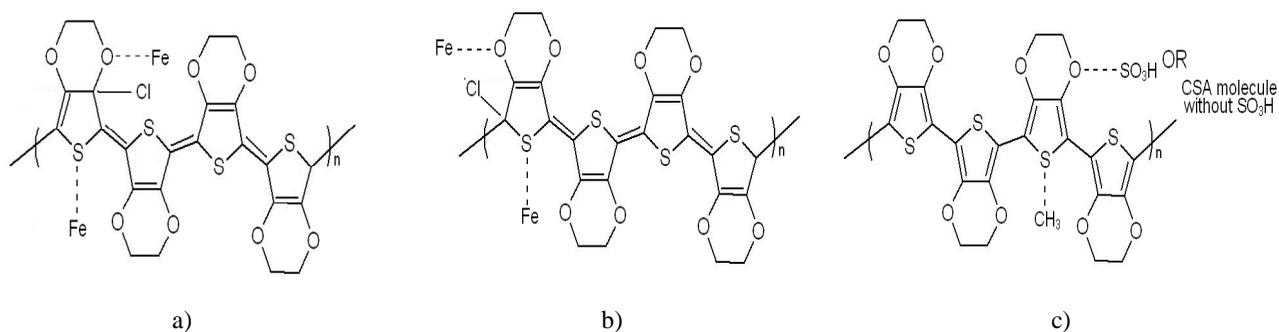


Fig. 2. Change in PEDOT structure due to doping by CSA

After doping undoped PEDOT by CSA for 5 h new bands appear at 1089.82 , 1483.31 and 1737.92 cm^{-1} associated to S-Aryl, asymmetric deformation of $\text{CH}_3\text{-S}$ band and to C=O, respectively. These bands are not observed in undoped PEDOT. A band appearing at 918.15 cm^{-1} in

undoped PEDOT shifts to 922.00 cm^{-1} in CSA doped PEDOT, indicating that ethylenedioxy ring deforms after doping. Moreover a shift in characteristic band of C-O appearing at 1193.98 cm^{-1} after doping by CSA indicates that SO_3H group, probably after getting detached from

CSA, forms a band or interaction with O of ethylenedioxy ring or CSA molecule after detaching SO_3H group gets attached to O of ethylenedioxy ring and deforms it. A shift in band from 1500.67 cm^{-1} appearing in undoped PEDOT to 1516.10 cm^{-1} in CSA doped sample associated to ring vibration modes of thiophene ring ($1350\text{--}1500\text{ cm}^{-1}$) indicates that one of the CH_3 group of CSA moiety either forms bond or interacts with S of thiophene ring, giving a new band at 1483.31 cm^{-1} . Furthermore appearance of strong and medium bands at 2924.18 and 2854.74 cm^{-1} , respectively, indicates presence of alkane group in CSA doped PEDOT. Similarly a band at 1737.92 cm^{-1} associated to $\text{C}=\text{O}$ is observed in CSA doped PEDOT.

Thus shifting of some of the bands and appearance of new bands indicates that CSA is getting doped in PEDOT chains and attached to S of thiophene and/or SO_3H group or CSA molecule after detaching SO_3H group gets attached to O of ethylenedioxy ring. The change in structure of PEDOT after doping it by CSA is shown in Fig 2c.

3.3. XRD Analysis

Fig. 3 shows XRD scans of undoped and FeCl_3 , as well as CSA doped PEDOT samples. Peaks around 6 and 11° , which are common in all cases, are due to the distance between the dopant and the S atom of thiophene ring. A peak around 6 and 11° in undoped PEDOT is due to remaining traces of salt in the dedoped PEDOT [14]. The broad peak between $2\theta = 20^\circ$ and 30° indicates that particle size is in nanoscale. The particle size increases after doping; however the overall particle size is in nanoscale region [15]. The intense peak in undoped PEDOT at $2\theta = 32.96^\circ$ and 35.88° represents the population of crystallites in that plane [16]. Table 2 summarizes the result of wide angle X-ray diffractions. The peaks are found to be shifted after doping, indicating that the crystal structure has been modified after doping PEDOT by FeCl_3 as well as by CSA.

In the present work Manjunath *et al* [17] analysis is used to calculate the crystallinity of undoped and doped PEDOT samples with 5 to 8 % error. It is observed that after doping PEDOT by FeCl_3 crystallinity increases whereas it decreases due to doping by CSA compared to crystallinity of undoped PEDOT. Due to complex formed by PEDOT with Fe^+ ions in FeCl_3 doped samples; Fe^+ ions pull PEDOT chains in such a manner that chains are systematically arranged leading to increase in crystallinity and the sample shows amorphous nature. However after doping PEDOT by CSA attachment of CSA with PEDOT disturbs the regular arrangement of PEDOT chains as CSA is heavy and big size molecule and hence reduces the crystallinity. It has been reported in literature that crystallinity of polymers ranges from fully amorphous to

well developed crystal depending on their method of preparation. Hence polymeric samples of PEDOT can be considered as polycrystalline aggregates.

3.4. Thermal Analysis

The results of thermal analysis are tabulated in Table 3. From Table 3 it is observed that after doping PEDOT by FeCl_3 , glass transition temperature (T_g) value decreases. Reduction in T_g value due to doping indicates plasticizing effect of dopant (FeCl_3) molecule. The externally added dopant reduces the interchain interaction in the polymer. It causes chains to skate on one another, making it more flexible. Thus it works as a plasticizer. From Table 3 it is also observed that due to doping of PEDOT by CSA, T_g value increases compared to that of undoped PEDOT. The increase in T_g value indicates antiplasticizing effect of dopant (CSA) molecule. It results in decrease in free volume of the mixture, which in turn causes the stiffening of polymer chains and hence rises in T_g . Results of TGA analysis of all samples are shown in Fig. 4. It indicates that the undoped PEDOT is stable up to about 523 K . The weight loss from 423 K possibly results from the low weight oligomer. Major decomposition occurs in the region between 553 and 673 K .

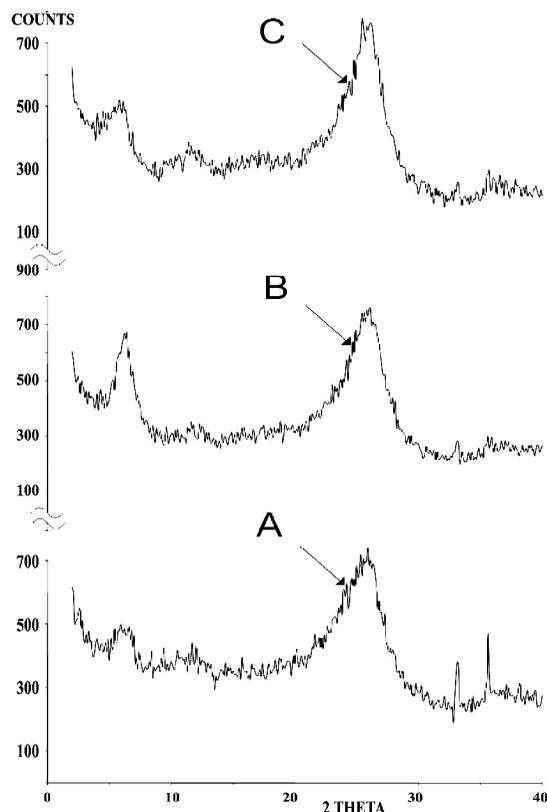


Fig. 3. XRD scan of undoped (A), 5 h FeCl_3 doped (B) and 5 h CSA doped (C) PEDOT

Table 2

Values of peak positions (2θ) and crystallinity from XRD pattern of undoped and doped PEDOT

Sample	Peak position at $2\theta^{\circ}$	Crystallinity, %
Undoped PEDOT	a) 6.11 b) 11.67 c) 25.56 d) 32.96 e) 35.84	30
5 h FeCl_3 doped PEDOT	a) 6.29 b) 11.67 c) 25.76 d) 33.10 e) 37.37	46
5 h CSA doped PEDOT	a) 5.74 b) 11.11 c) 25.76 d) 32.46 e) 36.58	22

Table 3

Glass transition temperature and weight loss temperature values for undoped, 5 h FeCl_3 doped and 5 h CSA doped PEDOT

Sample	Glass transition temperature (T_g), K	Weight loss temperature, K			
		5 %	10 %	15 %	20 %
Undoped PEDOT	600	456	538	558	569
5 h FeCl_3 doped PEDOT	552	367	487	529	544
5 h CSA doped PEDOT	625	380	536	562	576

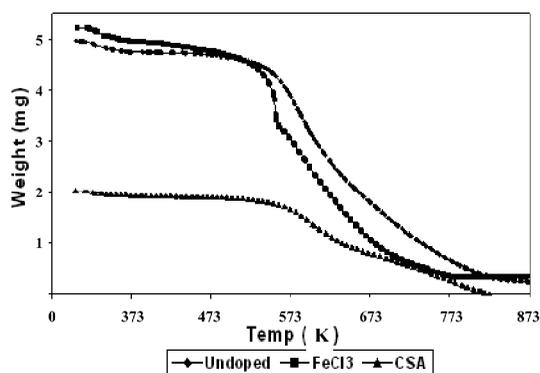
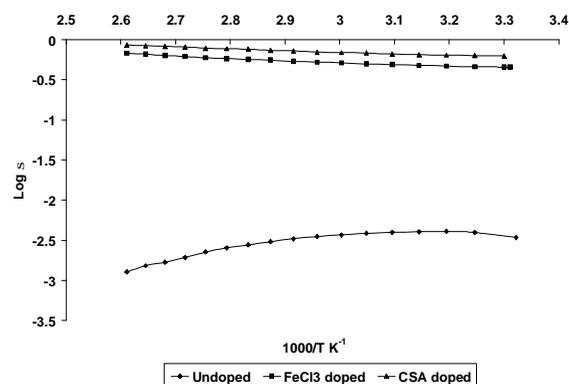
Fig. 4. TGA curve of undoped, 5 hr. FeCl_3 and 5 hr. CSA doped PEDOT

Fig. 4 also shows TGA curves of FeCl_3 doped and CSA doped PEDOT. From these curves it is observed that FeCl_3 doped sample is stable up to about 383 K and major decomposition of this sample occurs between 473 and 623 K. However CSA doped sample is stable up to about 523 K and major decomposition occurs in the region of 593–748 K. It is observed that in case of CSA doped sample decomposition above 20 % occurs at a higher temperature. In case of CSA doped PEDOT sample 5 % weight loss occurs at much lower temperature compared to that of undoped sample, while 10 % weight

Fig. 5. $\text{Log}\sigma$ vs. $1/T$ for undoped, 5 hr. FeCl_3 doped and 5 hr. CSA doped PEDOT

loss in both undoped and CSA doped samples occurs at nearly the same temperature. However above 10 % further weight loss in CSA doped sample occurs at higher temperatures compared to that of undoped PEDOT sample. This may be because dopant (CSA) molecule may be getting lost at slower rate above 536 K.

3.5. Electrical Conductivity Measurements

Conductivity measurements of undoped and all doped PEDOT samples were carried out using four probe technique in the temperature range of 302–383 K with a

step of 5 K. The conductivity values of undoped, FeCl₃ and CSA doped PEDOT samples at room temperature (302 K) are $3.41 \cdot 10^{-3}$, $4.55 \cdot 10^{-1}$ and $6.24 \cdot 10^{-1}$ S/cm, respectively. It is evident that conductivity increases by two orders of magnitude after doping.

Due to doping greater number of +ve and -ve ions gets attached to the polymer chain. When electric field is applied the attached charge carriers give away extra electrons. These electrons then get carried over polymeric chains and conductivity increases. It is also observed from the Table that CSA doped sample has highest conductivity among the samples studied.

3.6. Variation of Conductivity with Temperature

Fig. 5 shows $\log \sigma$ vs. $1/T$ graph for undoped and doped PEDOT samples. From the graph it is observed that, in case of undoped PEDOT initially (from 302 to 313 K) conductivity increases. This increase in conductivity with rise in temperature indicates semiconducting behavior of the undoped sample. From 318 to 483 K conductivity decreases with the increase in temperature, indicating metallic behavior in this temperature range. However for all doped PEDOT samples conductivity increases with the increase in temperature from room temperature to 483 K, indicating semiconducting nature of the material. The activation energy calculations show that for undoped sample it is $7.39 \cdot 10^{-2}$ eV in semiconducting region near room temperature whereas it is $5.45 \cdot 10^{-3}$ and $1.02 \cdot 10^{-2}$ eV for FeCl₃ doped and CSA doped sample, respectively. The activation energy for doped samples are found to increase with the increase in temperature and is $2.62 \cdot 10^{-2}$ and $1.85 \cdot 10^{-2}$ eV for FeCl₃ doped and CSA doped sample, respectively, in the temperature range of 333–378 K.

The activation energy for FeCl₃ doped sample is lower than that of undoped and CSA doped sample. However with rise in temperature, the activation energy increases rapidly in case of FeCl₃ doped sample compared to that of CSA doped sample.

4. Conclusions

Poly(3,4-ethylenediontheophene) (PEDOT) can be doped with FeCl₃ as well as with CSA and both dopant forms complex with PEDOT. The crystal structure gets modified after doping PEDOT by FeCl₃ and CSA. Broadening of diffraction line in XRD pattern of all the samples at about $2\theta \approx 25-26^\circ$ indicates that the particle size for undoped and for the doped samples are in nano scale. Glass transition temperature (T_g) decreases after doping PEDOT by FeCl₃ indicating that FeCl₃ dopant acts as a plasticizer, while T_g increases after doping by CSA indicating that CSA acts as an anti-plasticizer in PEDOT. Conductivity increases by two orders of magnitude after doping. Undoped PEDOT show metallic nature above

308 K, however both doped samples show semiconducting nature from 302 to 383 K.

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СТРУКТУРНІ, ТЕРМІЧНІ І ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ДОПОВАНОГО ПОЛІ(3,4-ЕТИЛЕНДІОКСІТІОФЕНУ)

Анотація. Хімічно синтезовано недопований і допований за допомогою FeCl₃ і камфор сульфокислоти (КСК) полі(3,4-етилендіоксітіофен) (ПЕДОТ). За допомогою Фур'є-спектроскопії підтверджено природу синтезованого і допованого зразків. За допомогою дифракції рентгенівських променів встановлено кристалічну структуру після допування і розрахована кристалічність зразків. Показано, що кристалічність збільшується після допування FeCl₃, але знижується при допуванні КСК. За результатами ТГА-ДТА встановлено, що значення температури сипування (T_g) для зразка, допованого FeCl₃, знижується, а для зразка, допованого КСК – збільшується, у порівнянні з недопованим ПЕДОТ. Зниження T_g вказує на пластифікуючий ефект FeCl₃, тоді як збільшення T_g – на антипластифікуючий ефект КСК в ПЕДОТ. Визначено, що після допування значення електропровідності (σ) збільшується на два порядки. Залежність $\log \sigma - 1/T$ вказує на металічну природу недопованого ПЕДОТ за температури вище 308 К, і напівпровідникову природу обох допованих зразків в інтервалі 301–383 К.

Ключові слова: полі(3,4-етилендіоксітіофен), Фур'є-спектроскопія, ТГА-ДТА, електропровідність.