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STRUCTURAL PROPERTIES OF POLYTHIOPHENE DOPED WITH FeCl_3

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Abstract. Polythiophene is chemically synthesized and doped with FeCl_3 for 2.5, 5 and 10 h. For structural investigation all samples have been characterized using different techniques. The results of elemental analysis show that with the increase of doping duration the Fe content increases while the S content decreases. FTIR spectrum reveals the complex formation between FeCl_3 and polythiophene. UV-Visible results have been used to calculate band gap energy. Analysis of XRD shows that after polythiophene doping by FeCl_3 some modifications in crystal structure and increase in crystallinity take place. Morphological studies using SEM have been carried out. TGA-DTA results indicate the reduction in T_g values with the increase in dopant concentration as well as increase in thermal stability due to doping.

Keywords: polythiophene, FTIR, UV-Vis spectroscopy, electron microscopy, TGA-DTA.

1. Introduction

Polymer science, both basic and applied, has undergone great development in the last 30 years. The great interest in polymers is due to possibility of combining new chemical functions in a backbone. This opened new fields of applications for macromolecules. After the discovery of iodine doped polyacetylene by McDiarmid and Shirakawa many polymeric structures were synthesized with the aim of improving both the electrical conductivity and the stability of the materials.

Polyheterocyclic in particular polythiophene are thermally and environmentally stable [1]. Many researchers have doped polythiophene and/or its

derivatives using LiBF_4 , NaAsF_6 , NaPF_6 [2], Bu_4NClO_4 , Et_4NBF_4 , Et_4NBF_6 [3], and iodine [4]. Few groups have reported doping of derivatives of polythiophene by FeCl_3 [5, 6] and fabrication of devices using FeCl_3 doped derivatives of polythiophene [7, 8]. However, polythiophene doped with FeCl_3 is not much reported. Hence, in the present work FeCl_3 is used as a dopant.

In the present work polythiophene is chemically synthesized, doped with FeCl_3 for different (2.5, 5 and 10 h) durations. For structural investigation, undoped and all doped samples are characterized using different techniques such as elemental analysis, FTIR analysis, UV-Visible spectroscopy, analysis of wide angle X-ray diffraction, and scanning electron microscopy. Thermal analysis using TGA-DTA technique has also been carried out.

2. Experimental

2.1. Chemical Synthesis

The polythiophene was chemically prepared by catalytic coupling of the Grignard reagent of 2,5-dibromothiophene (Aldrich) by nickel salt [4]. The general procedure consists of stirring 2,5-dibromothiophene with freshly distilled tetrahydrofuran (THF) with magnesium. The catalyst nickel chloride was introduced at the end. The mixture changed color. After 4 h the mixture was cooled and poured into MeOH-HCl. The obtained solid was then washed in hot methanol and dried. The brown powder was further fractionated into two parts by extracting with hot chloroform (CHCl_3). The procedure for chemical synthesis is shown in Fig. 1.

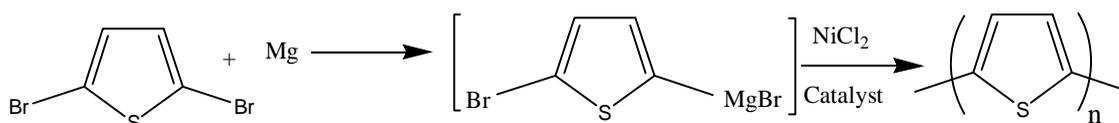


Fig. 1. Polythiophene chemical synthesis steps

The synthesized polymer was undoped using liquid ammonia and then doped using 5 % (weight/volume) aqueous FeCl_3 . Polythiophene powder was immersed in aqueous FeCl_3 for different (2.5, 5 and 10 h) durations with constant stirring to obtain uniform doping. The duration of immersion of polythiophene determines the concentration of dopant. Thus polythiophene was doped with different dopant (FeCl_3) concentration.

2.2. Characterization

Elemental analysis of C, H, S elements was carried out by Thermo finnigan, Italy, using FLASH EA 1112 series model and the analysis for Fe was done by Jobin Yvon, France, using JY Ultima-2 model. Fourier transform infrared (FTIR) spectra in the spectral range from 400 to 4000 cm^{-1} was recorded using Shimadzu FTIR-8400S spectrophotometer, operating with normal slit in the 10 min scan mode. A pellet of sample, prepared in KBr, was kept in the sample holder and was directly introduced in the path of infra-red beam. UV-Visible spectra in the range from 230 to 800 nm were recorded in THF solvent using Shimadzu UV-1700 pharma spectrophotometer. The wide angle X-ray diffraction (WAXD) pattern of undoped polythiophene as well as all FeCl_3 doped samples was recorded using Philips Analytical X-Ray B.V. model P W 1710 unit using Cu_αK radiation from a sealed tube operated at 35 KV and 25 mA. The specimen sample in the form of powder was fixed on the rotating stage of the diffractometer. Nickel filtered copper radiation was incident on the sample which was scanned at $1^\circ/\text{min}$ in reflection over the range of $2\theta = 5-40^\circ$. The morphology of all samples has been investigated using JEOL JSM - 6360A analytical scanning electron microscopy.

2.3. Thermal Properties

Thermo gravimetric (TG) and differential thermal analysis (DTA) were carried out using Perkin Elmer, USA Diamond TG/DTA model in the temperature range from 303 to 873 K at a heating rate of $10^\circ/\text{min}$.

3. Results and Discussion

Elemental analysis: The various elements obtained through analysis, within the experimental error limit of 1 %, are represented in Table 1.

From Table 1 it is observed that, as the duration of doping increases, the Fe increases while the S content decreases.

From the FTIR analysis, as shown in Fig. 2, it is observed that a sharp band appears at 788.91cm^{-1} , which is characteristic of the α , α' -coupling of poly-2,5-

thiophene [9], associated with $=\text{C}-\text{H}$ out of plane vibration in undoped polythiophene, indicating that the synthesized sample is polythiophene. Also band at 965cm^{-1} attributed to $\text{C}-\text{Br}$ bands [10] does not appear in FTIR spectrum of synthesized polythiophene confirming that the synthesized sample is polythiophene and the absence of monomer in the synthesized sample. The remaining bands of synthesized sample match very well with the values reported by G. Tourillon [9]. This also confirms that the sample synthesized is polythiophene.

Table 1

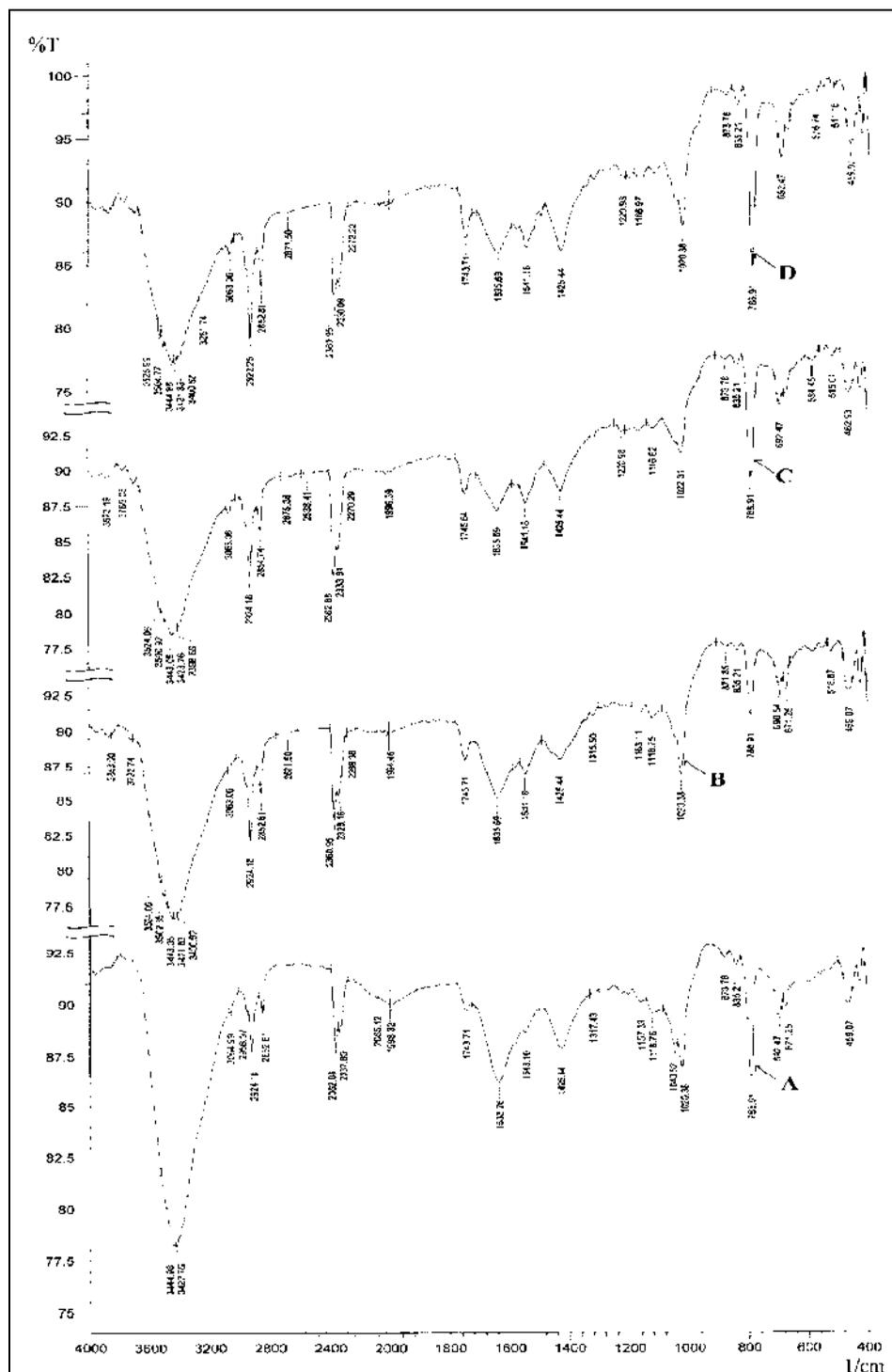
Percentage of C, H, S and Fe elements in undoped and FeCl_3 doped polythiophene

Sample	C, %	H, %	S, %	Fe, $\mu\text{g}/\text{gm}$
Undoped PT	51.16	2.41	43.03	3.70
2.5 h FeCl_3 doped PT	50.81	2.39	28.08	537.4
5 h FeCl_3 doped PT	51.28	2.44	26.28	2348.3
10 h FeCl_3 doped PT	50.28	2.66	25.02	3583.6

In 2.5, 5 and 10 h FeCl_3 doped samples new bands appear at 580cm^{-1} , 584.45cm^{-1} and 576.74cm^{-1} respectively, whereas these bands are not observed in undoped polythiophene. It has been reported by D. Pavia *et al.* [11] that the bands with $550-780\text{cm}^{-1}$ are associated to $\text{C}-\text{Cl}$. Thus it appears that due to doping by FeCl_3 , $\text{C}-\text{Cl}$ bonding must be taking place. Also it is observed that the bands associated with $\text{C}=\text{C}$ stretching are slightly shifting after doping. The characteristic bands of polythiophene associated with $=\text{C}-\text{H}$ out of plane bend and appearing at 788.91cm^{-1} in undoped polythiophene does not show any shift after doping. It should also be noticed that bands of undoped polythiophene due to ν cycles appearing at 1425.44 and 1220.98cm^{-1} do not show any change after doping. However slight changes are observed in $\text{C}-\text{H}$ band appearing at 692.47 and 671.25cm^{-1} band after doping. Only in 2.5 h sample 692.47cm^{-1} shift to 690.54cm^{-1} and in 5 h and 10 h doped samples shoulders appear at 671.25cm^{-1} band. All this indicates that FeCl_3 forms a complex with polythiophene chain where Cl^- of FeCl_3 gets attached probably at $\text{C}=\text{C}$ of polythiophene. Also from the results of elemental analysis it is observed that with doping duration increase the Fe^+ content increases, indicating that Fe^+ also gets doped in polythiophene and forms a complex. Moreover, results of elemental analysis also show that the S content decreases as doping duration increases, indicating that it is quite likely that S of polythiophene is getting replaced by Fe^+ after doping. J. Breadas *et al.* [12] in their theoretical studies reported that polythiophene when doped with sodium goes closer to carbon than sulfur. It is therefore quite likely that when polythiophene is doped with FeCl_3 ,

Fe⁺ might be going closer to carbon than sulfur or it may replace the sulfur. This might be due to the fact that both Fe and sulfur atoms have a net positive charge. The complex formed by Fe⁺ ions with polythiophene chain cannot be detected using FTIR as the wavelength range of all Fe⁺ complex bands lie below 300 cm⁻¹ [13]. However,

as the S content is found to be decreased, it is likely that Fe⁺ ions occupy the position of S ions after doping. Thus shifting of some of the bands in undoped polythiophene and appearance of some extra bands in IR spectrum of doped samples indicate that a complex formation between the dopant molecule and polythiophene has taken place.



For easy comparison the various absorption bands observed have been tabulated in Table 2.

Table 2

Values of IR absorption peaks of chemically synthesized and FeCl₃ doped polythiophene

For undoped PT in the present work, cm ⁻¹	For 2.5 h doped PT, cm ⁻¹	For 5 h doped PT, cm ⁻¹	For 10 h doped PT, cm ⁻¹	Association
1543.1 and 1633.76	1541.18 and 1635.69	1541.18 and 1635.69	1541.18 and 1635.69	C=C stretch
1425.44	1425.44	1425.44	1425.44	ν cycle
1220.98	1220.98	1220.98	1220.98	ν cycle
1020.38	1020.38	1022.31	1020.38	C-H in plane bend
788.91	788.91	788.91	788.91	C-H out of plane bend
692.47 and 671.25	690.54 and 671.25	692.47 and 671.25	692.47 and 671.25	C _γ -H
-----	580	584.45	576.74	C-Cl

Table 3

Values of peak positions (2θ), crystallite size, crystallinity, glass transition temperature (T_g) and temperature for 5% weight loss of undoped and FeCl₃ doped polythiophene

Sample	XRD analysis			Thermal analysis	
	Peak position at 2θ ⁰	Crystallite size (D _{hkl}), Å	Crystallinity, %	T _g , K	5% weight loss temperature, K
Undoped PT	a) 19.7 b) 23 c) 26.3 d) 28	a) 60.53 b) 44.26 c) 30.62 d) 40.98	66	521	528
2.5 h doped PT	a) 19.7 b) 23 c) 28	a) 60.53 b) 21.17 c) 49.14	72	504	458
5 h doped PT	a) 19.7 b) 23.2 c) 27.7	a) 60.53 b) 48.70 c) 61.42	74	468	553
10 h. doped PT	a) 19.8 b) 22.8 c) 28	a) 46.12 b) 32.44 c) 29.80	78	471	529

The UV-Visible spectra of undoped as well as 10 h doped sample showed an absorption peak at 416 nm whereas for 2.5 h and 5 h doped samples it is at 420 nm, corresponding to bang gap energy of 2.98 and 2.95 eV, respectively. It has been reported by G. Tourillon [9] that maximum absorption value is 480 nm for long chain polythiophene synthesized electrochemically. However it has also been reported by the same author that “this maximum shifts to the blue absorption range 418 nm, if

this polymer is chemically synthesized and is related to impurities (Mg, Ni) and structural defects”.

It has also been reported by T. Yamamoto *et al.* [14] that polythiophene film deposited showed an absorption peak at about 430 nm and the film was insoluble in hot CHCl₃, indicating that polythiophene had a molecular weight higher than about 1400. R. McClough [15] reported that polythiophene polymers of molecular weight greater than 3000 are not soluble in hot chloroform.

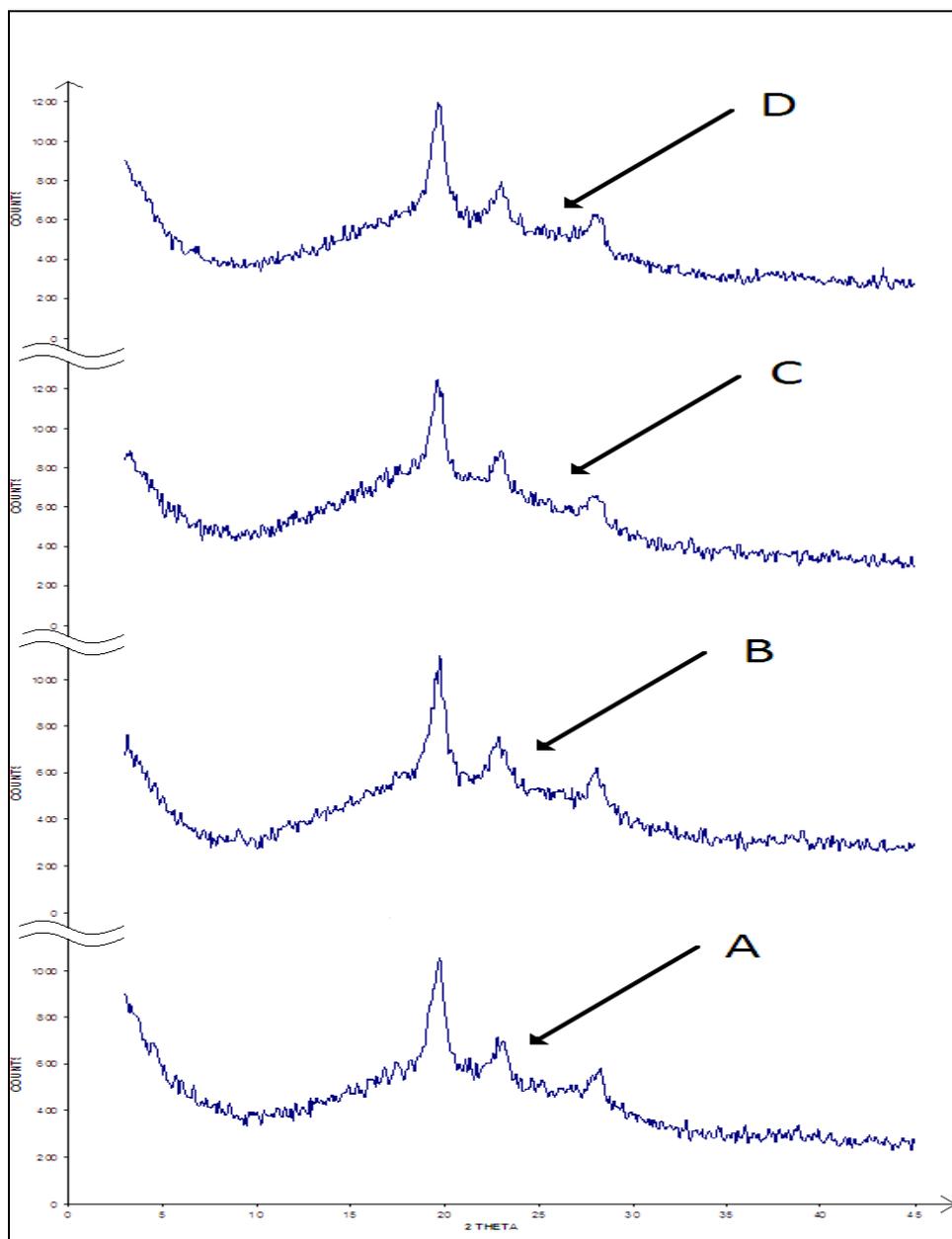


Fig. 3. XRD scan of undoped (A); 2.5 h (B); 5 h (C) and 10 h (D) FeCl₃ doped polythiophene

In the present work the brown powder was fractionated into two parts by hot CHCl₃ for about 50 h and insoluble powder was used as a final product. Also UV-Visible results indicate an absorption peak of undoped polythiophene at 416 nm. This in turn indicates that inherent impurities of Mg and/or Ni are present and the synthesized polymer has a molecular weight greater than 3000.

Table 3 summarizes the result of wide angle X-ray diffractions as well as results of thermal analysis. From the XRD analysis, as shown in Fig. 3, it is observed that four peaks appear in undoped polythiophene at 2θ values

of 19.66, 23, 26.33 and 28°. After doping these peaks are found to have shifted, particularly the peak appearing at 26.33° in undoped polythiophene does not appear in doped polythiophene. This shows that the crystal structure has been modified after doping. It has been reported in literature that crystallinity of polythiophene ranges from fully amorphous to well developed crystal depending on their method of preparation. The degree of crystallinity is a measure of the volume by fraction of crystalline part of the material. In the present work Manjunath *et al.* [16] analysis is used to calculate the crystallinity of undoped and doped polythiophene samples with 8 to 10 % error. It

is observed that after doping there is an increase in crystallinity. It is also found that crystallinity increases with the increase in concentration of dopant as is evident from Table 3. Due to the complex formed by polythiophene with Fe^+ ions in FeCl_3 doped samples Fe^+ ions pull polythiophene chains in such a manner that chains are systematically arranged leading to increase in crystallinity and all the samples show semi-crystalline nature.

Table 3 also summaries crystallite size determined using Scherrer equation. From Table 3 it is found that in case of 5 h doped sample crystallite size is the largest among the samples reported. However its crystallinity is less than that of 10 h doped sample. This in turn indicates that 5 h doped sample contains a smaller number of larger size crystals. In case of 2.5 h and 10 h doped samples though the crystallinity is higher than in undoped samples, crystallite size is small, indicating that these samples contain more small-sized crystals.

Scanning electron microscope pictures (Fig. 4) shows that undoped polythiophene (Fig. 4A) contains collection of small globules. After doping it by FeCl_3 for 2.5 h duration (Fig. 4B) the globules are dispersed and form slightly separated aggregates. With further increase in dopant (FeCl_3) molecules these aggregates increase in size and are slightly separated in 5 h doped sample (Fig. 4C). However, if the concentration of dopant continues to increase (10 h sample, Fig. 4D), the aggregate decreases in size.

The results of thermal analysis show that after doping polythiophene by FeCl_3 values of glass transition temperature (T_g) decrease. Reduction in T_g values due to doping indicates plasticizing effect of dopant molecules. Addition of special substances (plasticizers) into a polymer results in a decrease in the effectiveness of intermolecular (interchain) interaction in polymer. The macroscopic effect of plasticizing usually brings about a reduction in the T_g . Both low-molecular and high-molecular substances are used as plasticizers. One of the most important requirements which plasticizer must meet is its compatibility with the polymer being plasticized [17]. V. Kargin *et al.* [18] reported that there are two types of plasticizers, namely interstructural plasticizer and intrastructural plasticizer. In intrastructural plasticizer T_g continuously drops with the increasing amount of plasticizer and this type of plasticizer gets implanted between polymer molecules, whereas an interstructural plasticizer mixes with polymer to a limited extent destroying some structure while other structures remain un-destroyed. In this type of plasticizer T_g drops up to a definite value and further introduction of plasticizer does not have such an effect.

It is observed from Table 3 that when FeCl_3 is introduced in polythiophene, T_g decreases fast up to 5 h doping and thereafter T_g is not much affected by further (10 h doping) increase in plasticizer. This observation allows us to conclude that FeCl_3 acts as an interstructural plasticizer.

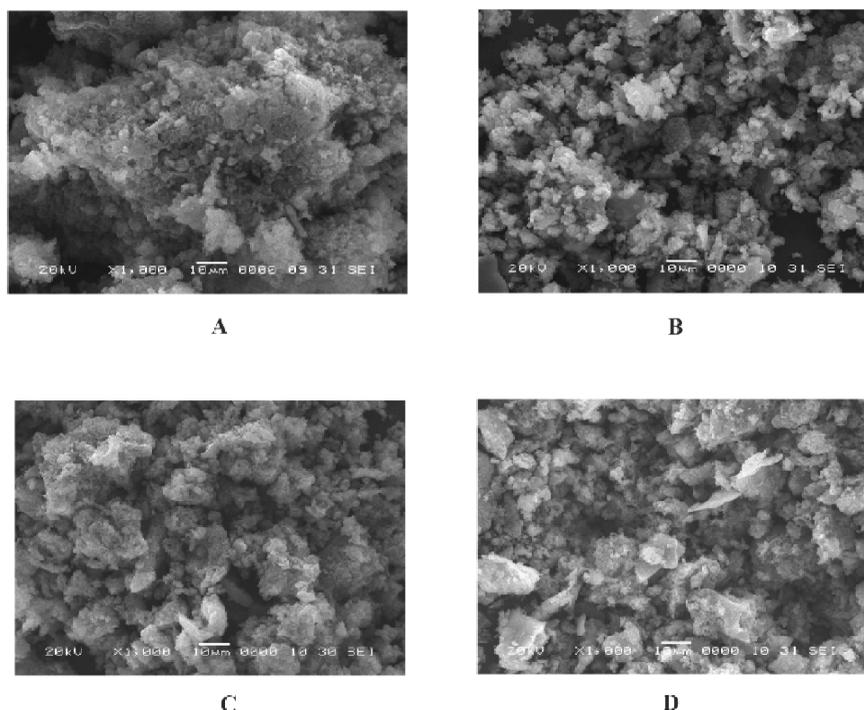


Fig. 4. SEM micrographs of undoped (A); 2.5 h (B); 5 h (C) and 10 h (D) FeCl_3 doped polythiophene

It is also observed that except 2.5 h doped sample 5 % weight loss takes place at higher temperature compared to that for undoped polythiophene. This indicates that except for 2.5 h doped sample thermal stability of polythiophene slightly increases after doping.

4. Conclusions

Polythiophene can be doped with FeCl₃ with the formation of a complex. As the duration of doping increases, the Fe content increases while the S content decreases. From the UV-Visible spectrum it is observed that molecular weight of chemically synthesized polythiophene is about 3000. Also due to doping of polythiophene by FeCl₃ crystal structure gets modified and crystallinity increases. Crystallinity increases with the increase in concentration of the dopant. The SEM micrographs indicate morphological modifications due to doping. Glass transition temperature (*T_g*) decreases after doping, indicating that dopant acts as a plasticizer. Thermal stability, in general, increases due to doping.

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СТРУКТУРНІ ВЛАСТИВОСТІ ПОЛІТІОФЕНУ, ПРОМОТОВАНОГО FeCl₃

Анотація. Проведено синтез політіофену, промотованого FeCl₃ протягом 2,5, 5 і 10 год. Для структурних досліджень використовувались різні методики. За результатами елементного аналізу встановлено, що зі збільшенням часу промотування вміст заліза збільшується, а вміст сірки зменшується. Фур'є-спектроскопія підтверджує утворення комплексу між FeCl₃ і політіофеном. Спектрофотометричний аналіз використано для розрахунку енергії забороненої зони. Встановлено, що після промотування політіофену FeCl₃ відбуваються деякі зміни в кристалічній структурі полімеру та зростає його кристалічність. Морфологічні дослідження проведені з використанням СЕМ. Результати термогравиметричного аналізу свідчать про зменшення значення температури склування зі збільшенням концентрації промотора, а також про збільшення термічної стабільності.

Ключові слова: політіофен, Фур'є-спектроскопія, електронна мікроскопія, термогравиметричний аналіз.