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Preparation and characterization of chemically and electrochemically synthesized 3,4-ethylenedioxy pyrrole/pyrrole (EDOP/Py) copolymers

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Abstract. In this study, 3,4-ethylenedioxypyrrole (EDOP) and pyrrole (Py) copolymers were prepared by chemical and electrochemical polymerization methods. The properties of the polymers obtained by both methods were compared. Chemical synthesis of copolymers was carried out with ferric chloride ($FeCl_3$) in the acetonitrile (ACN) environment. The electrochemical synthesis was carried out with lithium perchlorate ($LiClO_4$) electrolyte and suitable oxidation potential range in ACN solution. The properties of polypyrrole (PPy) copolymers were performed with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and conductivity measurements. Depending on the polymerization method and pyrrole amount in copolymer, thermal stability, conductivity and surface morphology were varied.

***Keywords*:** pyrrole; 3,4-ethylenedioxypyrrole; copolymer; chemical polymerization; electrochemical polymerization.

1. Introduction

Conducting polymers were first discovered in 1977 by Shirakawa and co-workers [1]. It is a group of materials attracting attention due to its excellent properties, including electrical, optical and high mechanical properties, easy synthesis and effortless fabrication and high environmental stability [2]. These attractive properties of conducting polymers (CPs) make them useful materials for a wide range of applications, mainly in energy storage [3], electronic and photovoltaic applications [4], electrochromic devices [5], and sensors [6]. Among conducting polymers, polypyrrole (PPy) is an interesting conducting polymer compared to other conjugated polymers such as polyaniline or polythiophene family [7] due to its high charge-carrier mobility, environmental stability, and biocompatibility [8, 9]. The PPy is used in several applications such as biosensors, organic electronics, and electro-chromic devices [10]. Nevertheless, its poor mechanical properties and insolubility in common organic solvents limit the applications of PPy [11]. One of the most important strategies to improve these negative properties is the preparation of copolymers of pyrrole with other compounds [12, 13]. Compared to homopolymerization, copolymerization is an important polymer synthesis approach that allows for a drastic modification of polymer properties. However, functionalization of the pyrrole ring contributes to the development of the application areas of polypyrrole. Further functionalization of polypyrroles can improve their electrocatalytic properties while increasing their selectivity [14]. It is known that the ethylenedioxy substitution served to enhance the optical, electrochemical and electronic properties of polymer [15]. While changing the structure of the pyrrole monomer improves some properties of the polymer, it also brings some disadvantages. Some groups added to the pyrrole structure create steric hindrance and prevent the healthy progress of polymerization. This undesirable situation can be overcome by preparing copolymers of pyrrole derivatives with pyrrole monomer. Thus, by providing copolymerization, both the desired amount of product is obtained and the polypyrrole properties are improved. However, there are limited studies on the synthesis of copolymers of pyrrole and its derivatives with physical properties that are different from those of homopolymers prepared by chemical and electrochemical methods [16, 17].

Considering the above facts, the main objective of the present work is the synthesis and characterization of the copolymers of pyrrole and 3,4-ethylenedioxypyrrole prepared by chemical and electrochemical methods using different monomer ratios (Scheme 1).

However, there was no report on the chemical and electrochemical synthesis and characterization of 3,4-ethylenedioxypyrrole/pyrrole (EDOP/Py) copolymers to the best of our knowledge. In addition, the properties of the copolymers were compared with the properties of their homopolymers. The properties of the obtained polymers are also closely related to the polymerization method. In this study, the effects of chemical and electrochemical polymerization methods on polymer properties were also investigated and compared.

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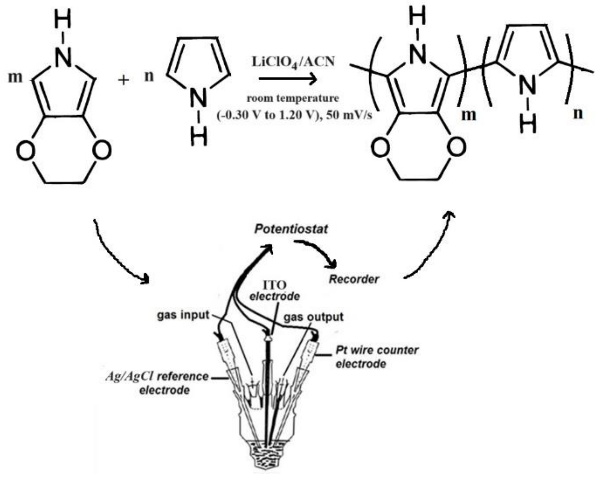

Scheme 1. Structure of the poly (3,4-ethylenedioxypyrrole)/polypyrrole (PEDOP/PPy) copolymer.

2. Experimental

Pyrrole (98%, Aldrich), 3,4-ethylenedioxypyrrole (97%, Aldrich), ferric chloride anhydrous, $FeCl_3$ (99%, Aldrich), lithium perchlorate, $LiClO_4$ (Sigma Aldrich), acetonitrile, CH_3CN, ACN (HPLC grade, Sigma Aldrich) were used as received. The chemical synthesis of polymers was initiated by the dropwise addition of the oxidizing agent ($FeCl_3$) in ACN under constant stirring at 0-5 ºC. The ratio of oxidizing agent to monomer was 1. The reaction was carried out with 0.1 M oxidant so that the monomer concentration was 0.1 M for homopolymers. The chemical synthesis of copolymers was achieved by using monomers (Py/EDOP) with various molar ratios such as 1/4, 2/3, 3/2, 4/1. The total monomer concentration was 0.1 M. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 h. The precipitated polymer was filtered and washed with ACN until the filtrate was colorless. Finally, the polymer was dried at 50 ºC for 24 h under vacuum.

Electrochemical polymerization was done by using three-electrode cell equipped with potentiostat/ galvanostat (CompactStat, Ivium Technologies, Netherlands). Indium tin oxide electrode (ITO), Ag/AgCl and Pt wire were used as working, reference and auxiliary electrode, respectively. The ratio of $LiClO_4$ to monomer was 1. The copolymerization procedure was applied for various feed ratios of the monomers. These ratios were 1/4, 2/3, 3/2, 4/1. The total monomer concentration was 0.1 M. Electrochemical copolymerization procedure was same as electrochemical polymerization procedure of homopolymers. The polymer samples were deposited in ACN solution on the ITO electrode with cyclic voltammetry technique for 50 cycles with a voltage range of -0.30 V to 1.20 V and a scanning rate of 50 mV/s. FTIR spectra were performed between 4000 and 400 cm^{-1} with a 4 cm^{-1} resolution on a Perkin Elmer (Beaconsfield, Buckinghamshire, HP91QA, England). For SEM analysis, Phillips (XL-30S FEG) (Burladingen/Germany) model scanning electron microscope was used. Thermograms of the polymers were recorded using a Perkin Elmer Diamond (Beaconsfield, Buckinghamshire, HP91QA, England) thermogravimetric analyzer in the presence of N_2 atmosphere from 25 to 900 ºC with a heating rate of 10 $ºC·min^{-1}$. The electrical conductivity of polymers was measured using the standard four-probe technique. The direct current electrical conductivity of samples was measured by standard four-probe method using PCI-DAS6014 for a current source, voltameter, and temperature controller. Dry powdered samples were made into pellets using a steel die having 13 mm diameter in a hydraulic press under a pressure of 200 MPa. Conductivity values of samples were calculated according to van der Pauw equation [18].

3. Results and discussion

3.1. FTIR results

The FTIR spectra of the PPys and Py/EDOP copolymers synthesized by chemical and electrochemical methods were examined (Figure 1a-d). Figures 1a and b are spectra of PPys synthesized by chemical and electrochemical methods which are similar to that reported in the literature [19]. The FTIR spectra of Py/EDOP (1/4) copolymers are shown in Fig. 1c and d as examples for identification of copolymer structures. The broad bands at around 3435-3486 cm^{-1} are due to the N-H and O-H stretching for all polymers. The weak bands between the range of 2930 and 2860 cm^{-1} are caused by the CH_2 stretching. These bands shifted to the range of 2924 and 2853 cm^{-1} in the copolymer spectra (Fig. 1c, d). The band attributed to the C=C stretching of pyrrole ring is seen at around 1645 cm^{-1}. The band observed in the range of 1434-1467 cm^{-1} are the =C-H stretching peaks in the pyrrole rings. The band at about 1400 cm^{-1} are assigned to the CH_2 deformations also which is more visible in the chemically synthesized copolymer spectrum (Fig. 1c). However, bands in the range of 1000 and 1280 cm^{-1} shows the combination of N-H out-of-plane bending, C-H in-plane bending and C-N stretching for all polymers. The sharp bands observed in the range of 1059-1087 cm^{-1} are the characteristic bands belonging to the stretching vibrations of C-O-C group in EDOP structure in copolymer spectrum (Fig. 1c, d) [20]. These results show that the specific bands caused by Py and EDOP units were observed in the spectra confirming the formation of the copolymers. The chemically and electrochemically synthesized polymers were quite different from each other. Polypyrrole synthesized by electrochemical route has lower intensity bands than that of chemically synthesized. This may be due to the limited amount of product synthesized by electrochemical method. Electrochemically synthesized copolymer has more intense bands than chemically synthesized copolymer. This can be explained by the high conductivity of electrochemically synthesized copolymers [21].

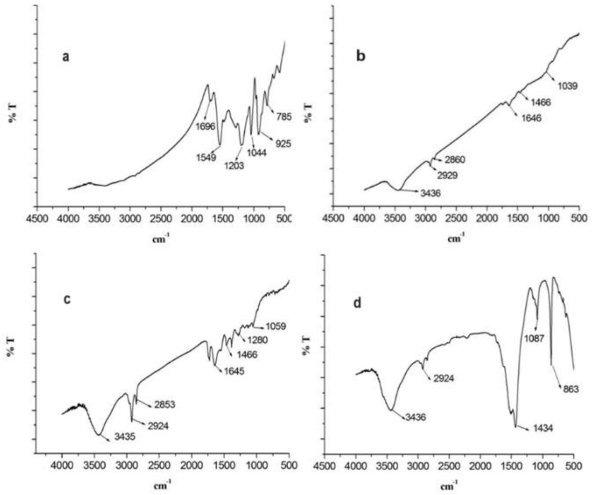

Figure 1. FTIR spectra of PPy (chemical) (a), PPy (electrochemical) (b), Py/EDOP (1/4) copolymer (chemical) (c), Py/EDOP (1/4) copolymer (electrochemical) (d).

3.2. TGA results

Figures 2 and 3 show the TGA curves of the different samples. Tables 1 and 2 indicate the thermal degradation temperatures and the residue values (%) at 900 ºC obtained from these curves of chemically and electrochemically synthesized polymers, respectively. The low weight loss (~10%) shown in the range of 80-110 ºC is due to humidity and small molar mass components in the polymer matrix being removed from polymer structures [22]. All the samples indicate two-step weight loss except that step. First thermal degradation step of the polymer samples indicates the removing of dopant anions from polymer structure. The second degradation steps are related to decomposition of the polymer chains.

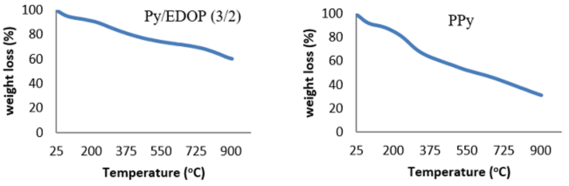

Figure 2. TGA thermographs of chemically synthesized polymers.

Among chemically synthesized polymers, the initial thermal degradation temperatures of the polymer main chains were examined. It is seen that the Py/EDOP (3/2) copolymer has the highest thermal stability at 250 ºC according to the percentage residual values at 900 ºC amount of pyrrole for the copolymer structure. Among the chemically synthesized polymers the highest residual value (60%) belongs to Py/EDOP (3/2) copolymer.

The electrochemically synthesized polymers were investigated thermally also. The initial thermal degradation temperatures of the polymer main chains were examined. Py/EDOP (3/2) and PPy are the polymers with the highest thermal decomposition temperature. Among the electrochemically synthesized polymers, the highest percentage residual value at 900 ºC belongs to PPy. When the copolymers were evaluated among themselves, it is seen that the percentage residual values of copolymers at 900 ºC increases as the increment of pyrrole amount in the copolymer structures.

Table 1. Thermal degradation temperatures of chemically synthesized polymers

	T_i (ºC)	T_m (ºC)	T_f (ºC)	Residue at 900 ˚C (%)
Py/EDOP copolymer (1/4)	25 240 550	112.5 340 655	100 440 760	37
Py/EDOP copolymer (2/3)	25 230 440	60 300 475	95 370 510	9
Py/EDOP copolymer (3/2)	25 250 480	57.5 365 685	90 480 890	60
Py/EDOP copolymer (4/1)	25 220 580	60 300 715	95 380 850	53
PPy	25 220 540	112.5 280 610	100 340 680	32

T_i: initial decomposition temperature; T_m: maximum decomposition temperature; T_f: final decomposition temperature.

Table 2. Thermal degradation temperatures of electrochemically synthesized polymers

	T_i (ºC)	T_m (ºC)	T_f (ºC)	Residue at 900 °C (%)
PEDOP	25 230 600	112.5 285 695	100 340 790	18

Py/EDOP copolymer (2/3)	25	57.5	90	22
	220	285	350	
	780	825	870	
Py/EDOP copolymer (3/2)	25	67.5	110	51
	250	310	370	
	610	710	810	
Py/EDOP copolymer (4/1)	25	112.5	100	52
	200	290	380	
	380	580	780	
PPy	25	57.5	90	83
	250	315	380	
	380	560	740	

T_i: initial decomposition temperature; T_m: maximum decomposition temperature; T_f: final decomposition temperature.

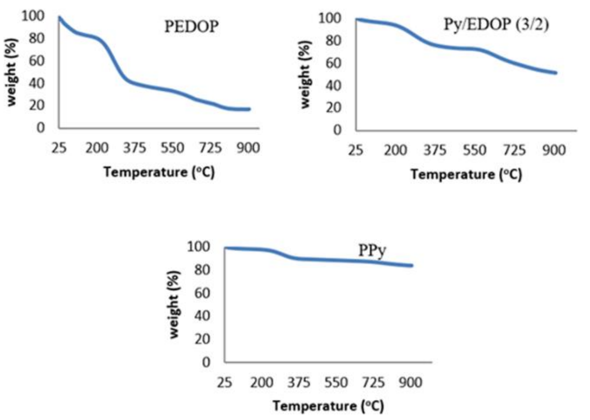

Figure 3. TGA thermographs of electrochemically synthesized polymers.

When the chemically and electrochemically synthesized polymer samples with the same ratio were compared, the initial decomposition temperatures and residual values at 900 °C were different from each other. Although the residual values of chemically synthesized copolymers do not give any systematic results depending on the amount of polypyrrole in the copolymer structure, it was observed that the residual values of the copolymers increased proportionally with the increase in the amount of polypyrrole in the electrochemically synthesized copolymers. It can be concluded that the electrochemically synthesized copolymers were more properly arranged than the chemically synthesized copolymers. Because electrochemical polymerization is more controlled method than chemical polymerization especially in terms of oxidation potential.

3.3. SEM results

Figures 4 and 5 represent the morphologies of chemically and electrochemically synthesized polymers, respectively. When SEM micrographs of chemically synthesized homopolymers and copolymers are examined, it is seen that the particle size gradually decreases with the increase of the pyrrole amount in the structure. Reducing the particle size allows for more regular stacking. However, the chemically synthesized PPy appears to have the most regular stacking.

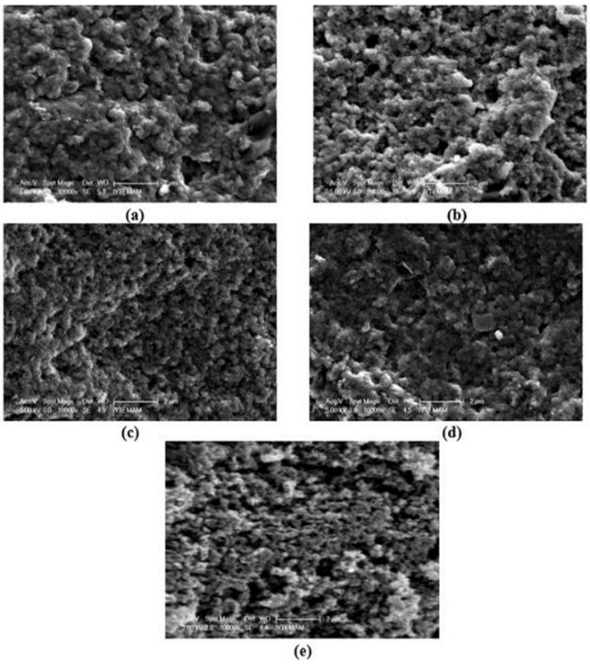
(a) (b) (c) (d) (e)

Figure 4. SEM micrographs of chemically synthesized Py/EDOP (1/4) (a), Py/EDOP (2/3) (b), Py/EDOP (3/2) (c), Py/EDOP (4/1) (d), PPy (e).

When the SEM micrographs of the electrochemically synthesized polymers are examined, the surface morphology changes with the increase in the amount of pyrrole (Figure 4). As the amount of pyrrole increases, the cauliflower-like morphology of the polypyrrole attracts more attention. However, no systematic change has been observed towards polypyrrole, on the contrary, quite different morphological structures were observed.

SEM micrographs of chemically and electrochemically synthesized polymers were compared. It is seen that electrochemically synthesized polymers have a more regular and in conjunction with each other structure. This regular structure affects the conductivity values and thermal stability of the polymer. Electrochemically synthesized PPy has a higher conductivity than the chemically synthesized polymer sample due to its more uniform stacking. Electrochemically synthesized Py/EDOP (2/3) exhibits a more regular morphology than chemically synthesized. Accordingly, as seen from the TGA results, the residual value at 900 ºC increases. SEM results support conductivity and TGA results.

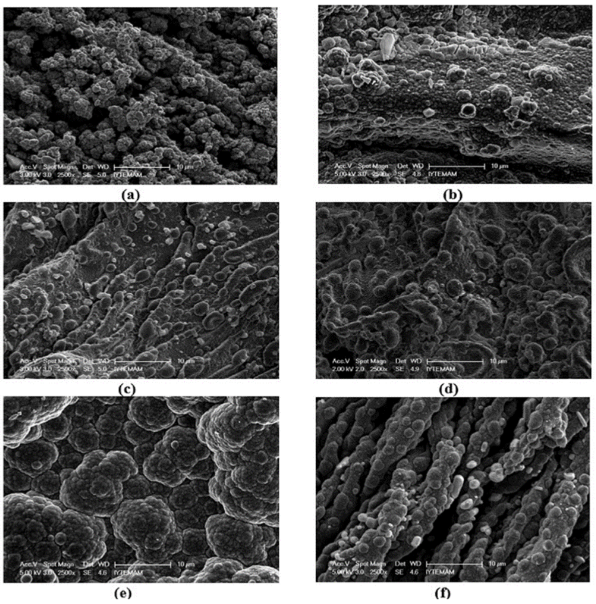

Figure 5. SEM micrographs of electrochemically synthesized PEDOP (a), Py/EDOP (1/4) (b), Py/EDOP (2/3) (c), Py/EDOP (3/2) (d), Py/EDOP (4/1) (e), PPy (f).

3.4. Conductivity results

The conductivity values of the chemically and electrochemically synthesized polymer samples are given in Table 3. Conductivity measurements of chemically synthesized copolymers could not be taken due to the inability to prepare pellets properly. Since they are obtained in film form, this problem has not been experienced in polymers synthesized electrochemically. When the conductivity values of the electrochemically synthesized polymers are examined, it is seen that the conductivity values increase with the increase in the amount of pyrrole. Electrochemically synthesized Py/EDOP (2/3) and Py/EDOP (3/2) have the highest conductivity values. Their conductivity values are $29.9x10^{-2}$ S·cm^{-1} and $30.4x10^{-2}$ S·cm^{-1}, respectively. The conductivity value of electrochemically synthesized PPy ($18.4x10^{-2}$ S·cm^{-1}) is about two higher than that of chemically synthesized PPy ($10.1x10^{-2}$ S·cm^{-1}). The obtained conductivity values may be due to the electrochemically synthesized polymer being more regular morphologically. This copolymer was found to have a helical cone-like morphology, possibly useful in future sensing applications, and showed both higher conductivity and better thermal stability than PPy. These improved properties result from the enhanced conjugation in the copolymer main chain. As a result, formation of copolymer structure contributed to the conductivity. Additionally, preparing the copolymer of Py and EDOP electrochemically had a positive effect on the conductivity properties.

Table 3. Conductivity values of polymers

Sample	**Conductivity (S·cm^{-1})**
Py/EDOP (1/4)	$19.9x10^{-2}$
Py/EDOP (2/3)	$29.9x10^{-2}$
Py/EDOP (3/2)	$30.4x10^{-2}$
Py/EDOP (4/1)	$25.5x10^{-2}$
Electrochemically synthesized PPy	$18.4x10^{-2}$
Chemically synthesized PPy	$10.1x10^{-2}$

4. Conclusions

Copolymers of pyrrole (Py) and 3,4-ethylenedioxypyrrole (EDOP) were prepared by chemical and electrochemical polymerization methods. The properties of polymers obtained by both methods were compared particularly. All samples were successfully characterized with FTIR, TGA, SEM and the conductivity measurements. Spectroscopic, thermal, morphological and conductivity properties of polymers were affected by the monomer ratio. FTIR studies show that the specific bands caused by Py and EDOP units are observed in the spectra of copolymers, confirming the formation of the copolymers. The percentage residual values at 900 ºC depending on the amount of pyrrole for the copolymer structure were evaluated. Among the chemically synthesized polymers, the highest thermal stability (250 ºC) and residual value (60%) belongs to Py/EDOP (3/2) copolymer. When the copolymers synthesized electrochemically were evaluated among themselves, it is seen that the percentage residual values of copolymers at 900 ºC increase as the increment of pyrrole amount in the copolymer structures. SEM results of polymers indicates that the electrochemically synthesized polymers have more regular structure than that of chemically synthesized polymers. The conductivity values exhibit that the electrochemical method improves the conductivity properties of copolymers. Furthermore, formation of Py/EDOP copolymer structure supports the conductivity. Besides, electrochemically synthesized Py/EDOP (2/3) and Py/EDOP (3/2) copolymers have the highest conductivity values. In this study, electrochemical synthesize has been found to be an effective way to create material, Py/EDOP copolymer, with better properties than that of PPy and PEDOT.

Conflict of interest

The authors declare that there is no conflict of interest.

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