

THERMAL DECOMPOSITION OF POLYPYRROLES

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The thermal stability of polypyrrole (PPy) samples has been studied by thermogravimetry/mass spectrometry and pyrolysis-gas chromatography/mass spectrometry in inert atmospheres. PPy has been prepared by chemical oxidative polymerization using ferric sulfate as an oxidant and anionic surfactants, such as dodecylbenzenesulfonic acid and sodium dodecylbenzenesulfonate as co-dopants. For comparison we have studied polypyrrole (PPy-SO₄) prepared without any additive. It was found that the presence of anionic surfactants improved the thermal stability of PPy. The decomposition of PPy doped with ferric sulfate and anionic surfactants occurs at relatively high temperature indicating that chemical interactions exist between the polymer and the surfactants.

Keywords: mass spectrometry, polypyrrole, pyrolysis, thermal decomposition, thermal stability, thermogravimetry

Introduction

Polypyrrole (PPy) is attractive as an electrically conducting polymer because of its properties, good electrical conductivity, stability at ambient conditions, and relatively easy way of synthesis. PPy can be prepared by electrochemical polymerization in the form of film. The properties of PPy films, primarily the conductivity, depend on the polymerization conditions and on the type of dopant anion [1, 2]. The limitation for PPy production by this method is the dimension of the electrode. The chemical oxidative polymerization of pyrrole using various oxidants and solvents produces large quantities of PPy in the form of fine powder [3–5]. Defects in the PPy structure and cross-linking of the polymer chains caused a creation of one plus charge per 3–4 pyrrole rings, which is counterbalanced by the building of an oxidant anion into the PPy structure.

The identification of various dopant anions in electrochemically and chemically synthesized PPy can be carried out by mass spectrometry [6]. The pronounced peaks of negative ion spectra confirmed the presence of anion type used in the synthesis of polymer, which is built into its structure. Similarly, time-of-flight secondary ion mass spectrometry was used to perform a systematic characterization of PPy films prepared electrochemically in the presence of chloride, bromide, sulfate and tosylate salts [7]. An ion attributed to the dopant tosylate anions (CH₃C₆H₄SO₃⁻) was observed at *m/z* 171 in the negative ion spectrum of the tosylate-doped PPy. Uyar *et al.* [8] investigated the thermal decomposition

of electrochemically synthesized PPy doped with *p*-toluene sulfonic acid by direct-insertion probe pyrolysis-mass spectrometry. Two PPy structures were proposed: the aromatic form corresponding to the undoped state and the quinoid form corresponding to the doped state. However, the actual cross-linked PPy structure appeared to be more complicated and the relationship between the used dopant and the structure was not totally clarified. It has been shown that PPy films prepared in aqueous media contained high concentration of oxygenated species associated to ketone groups. Pyrolysis experiments also indicated that chemically prepared samples were oxygenated in air more readily and yielded mainly carbonyl and hydroxide groups [9]. For electrochemically synthesized PPy doped with *p*-toluene sulfonic acid, intense toluene, SO₂ and H₂S peaks were recorded at high temperatures, indicating the decomposition of the dopant. The decomposition at high temperatures instead of evaporation at low or moderate temperatures was associated with a strong, probably chemical interaction between the dopant and the host polymer [10].

Chemical oxidative polymerization of pyrrole in the simultaneous presence of oxidant and other substance can improve final electrical, thermooxidative, and hydrolytic stability of the prepared PPy due to the incorporation of bulky hydrophobic component [11, 12]. From the group of anionic, cationic and nonionic surfactants only the anionic surfactants can be incorporated into the conducting polymer structure similarly as the doping anions. This leads to a better stability of PPy towards deprotonation, and to a better stability of the conductivity during thermal ageing [12, 13].

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For the future utilization of conducting polymers, the knowledge of the thermal behavior and stability is important [14, 15]. The aim of this work was the structural study and comparison of the thermal stability of chemically synthesized polypyrroles. As a reference material PPy prepared only in the presence of oxidant – ferric sulfate – was studied, and two other samples prepared in the presence of the same oxidant and the anionic surfactants, dodecylbenzenesulfonic acid and its sodium salt, were synthesized. Morphology of the prepared PPy was studied by scanning electron microscopy. Thermal stability of the samples was investigated using thermogravimetry. Thermogravimetry/mass spectrometry (TG/MS), and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) techniques were applied for the determination of the structures of the decomposition products.

Experimental

Materials

Pyrrole (Merck-Schuchardt) was purified by distillation under reduced pressure and stored in a refrigerator at about 4°C before use. The oxidant, ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, Merck) and the surfactants: sodium dodecylbenzenesulfonate (DBSNa, Fluka) and dodecylbenzenesulfonic acid (DBSA, Fluka) were used as received.

Chemical preparation of polypyrrole

$\text{Fe}_2(\text{SO}_4)_3$ oxidant (0.01 mol) was dissolved in 100 mL of distilled water and mixed with 0.004 mol of the surfactant dissolved in 100 mL distilled water and stirred for 15 min. Pyrrole of 0.015 mol (1 mL) was dispersed in 50 mL of water and inserted dropwise into the stirred mixture. The molar ratio pyrrole/anionic surfactant was 3.75. The polymerization was carried out for 4 h at room temperature at moderate stirring. The precipitated PPy was filtrated off, washed with distilled water and dried in a vacuum dryer at 60°C for 8 h.

The reversed procedure, when anionic surfactant and monomer were first mixed and then the same amount of oxidant was added, was used for the preparation of the control sample and it is marked as PPy-SO₄ – DBSA (r). PPy-SO₄ was synthesized by the same procedure without the addition of any surfactant. The abbreviation and characterization of the samples are listed in Table 1.

Methods

Thermogravimetry/mass spectrometry

The TG/MS system is built of a Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC quadrupole mass spectrometer. Typically 1–2 mg samples were placed into the platinum sample pan and heated at a 20°C min⁻¹ rate in argon atmosphere. Portions of the volatile products were introduced into the mass spectrometer through a glass lined metal capillary transfer line heated to 300°C. The quadrupole mass spectrometer operated at 70 eV. The intensity of the products was normalized to the sample mass and the intensity of the ³⁸Ar isotope in order to avoid errors caused by the shift in the sensitivity of the mass spectrometer.

Pyrolysis-gas chromatography/mass spectrometry

Pyrolysis experiments were carried out on a Pyroprobe 2000 pyrolyzer (Chemical Data Systems). About 1–2 mg samples were pyrolyzed at 400 and 500°C for 20 s in a quartz tube using helium as a carrier gas. Analysis of the volatile products was accomplished on line with a GC/MS (Agilent Techn. Inc. 6890 GC, 5973 MSD) using HP-5MS capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness). The pyrolysis interface and the GC injector were kept at 280°C. The GC oven was programmed to hold at 50°C for 1 min and then increase to 300°C at a rate of 10°C min⁻¹. The mass spectrometer operated at 70 eV in the EI mode. The mass range of 14–600 Da was scanned.

Table 1 Elemental composition (mass%) of polypyrrole chemically synthesized in the presence of surfactants, polymerization yield and conductivity

Sample	Anionic surfactant	C	H	N	S	S/N/ mol mol ⁻¹	Yield/ g g ⁻¹ Py	σ/S cm ⁻¹
PPy-SO ₄	–	50.59 59.28 ^a	3.7 3.73 ^a	14.5 17.28 ^a	4.37 6.60 ^a	0.13 0.17 ^a	0.97 1.23 ^a	0.12
PPy-SO ₄ –DBSA	Dodecylbenzenesulfonic acid	65.06	7.30	6.50	6.68	0.45	1.62	1.9
PPy-SO ₄ –DBSA (r) ^b	Dodecylbenzenesulfonic acid	65.31	7.43	7.89	6.25	0.35	1.50	7.8
PPy-SO ₄ –DBSNa	Sodium dodecylbenzenesulfonate	67.26	7.05	5.96	6.35	0.47	1.27	4.7

^aCalculated value, ^bReversed preparation method (Experimental)

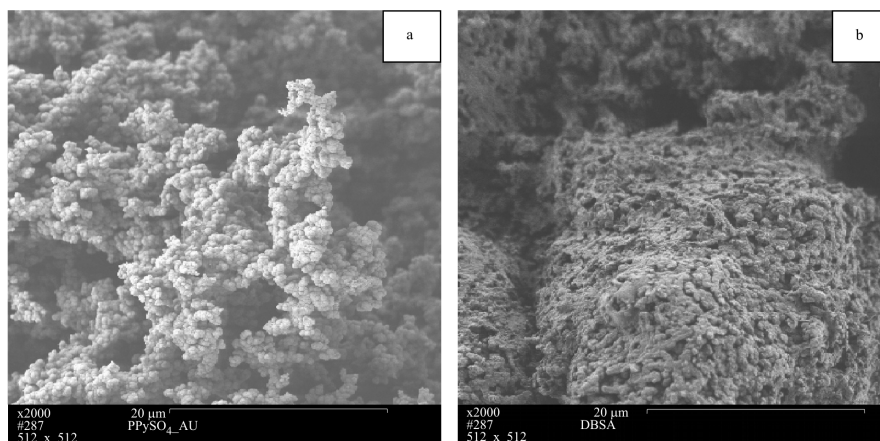


Fig. 1 SEM micrographs of a – PPY-SO₄ and b – PPY prepared in the presence of anionic surfactant, PPY-SO₄-DBSA

Results and discussion

Table 1 presents the results of the elemental analysis of chemically prepared PPy, the polymerization yield and the conductivity of samples. The expected content of the elements in primary PPY-SO₄ was calculated assuming that one positive charge is created for three pyrrole rings, which has to be balanced by the anion of the oxidant molecule. The SO₄²⁻ anion can thus compensate the positive charge of six pyrrole rings. The polymerization yield given in the table represents the amount of polymer prepared from one gram of monomer. The polymerization yield of PPY-SO₄ reached 79% of the theoretical value. PPy is hygroscopic and contains water. The presence of C–O, C–OH and C=O bonds in the PPy samples evident from IR study, indicates an oxygen uptake due to oxidation [16]. The amount of water adsorbed in PPy and oxygen bounding into polymer chains reduce the content of all other elements compared to the theoretically calculated values. The polymerization yield significantly increased when surfactants were used in the polymerization. The amount of carbon, hydrogen, and sulfur are higher in the surfactant-containing samples than the experimental values for PPY-SO₄. The increase in sulfur content indicates that the sulfur containing anionic part of the surfactant is incorporated into the PPy structure, similarly as the anion of oxidant. The S/N ratio represents the doping level for one pyrrole ring in the PPy chain. This parameter is significantly higher in the surfactant-containing samples than theoretically calculated for PPY-SO₄.

The conductivity of PPY-SO₄ synthesized from water solution containing monomer and Fe₂(SO₄)₃ as oxidant is 0.12 S cm⁻¹. Additives like anionic surfactants increase the conductivity of chemically synthesized PPy [11–13]. The presence of anionic surfactants NaDBS and DBSA during polymerization increases the conductivity of the final product to 1.9–7.8 S cm⁻¹

that is at least one order of magnitude higher value than the conductivity of surfactant-free PPY-SO₄.

Figure 1 compares the morphology of PPY-SO₄ and PPy sample prepared with the same oxidant and anionic surfactant, PPY-SO₄-DBSA. The SEM study of PPY-SO₄ sample shows the presence of globular particles of about 1 μm in diameter (Fig. 1a). At the same magnification, the SEM micrograph of PPY-SO₄-DBSA (Fig. 1b) reveals connecting particles of deformed globules which are smaller compared to particles of surfactant free PPY-SO₄. PPY-SO₄-DBSA powder looks more compact compared to the PPY-SO₄ structure.

Figure 2 shows the thermogravimetric curves of the polypyrrole samples at 20°C min⁻¹ heating rate in argon atmosphere. Most of the samples have some adsorbed moisture, which is released up to 120°C. Polypyrrole doped only with SO₄²⁻ anion (PPY-SO₄) starts to decompose at a relatively low temperature (150°C) and the maximum rate of decomposition takes place at about 250°C. Polypyrrole samples doped with SO₄²⁻ anion in the presence of anionic surfactants have significantly higher thermal stability: the decomposition commences above 200°C. It is in agreement with the thermal behavior in oxidative atmosphere studied previously [12]. The decomposition of PPy prepared in the presence of the surfactants occurs roughly in two stages. The first step takes place between 200 and 400°C, while a sharp peak can be observed on the DTG curves between 400 and 550°C.

In order to clarify the effect of surfactants on the thermal behavior of the polypyrrole samples, the release of volatile products was monitored during the decomposition with thermogravimetry/mass spectrometry (TG/MS). Figure 3 presents the mass spectrometric curves of the major products beside the thermogravimetric curves of the samples. PPY-SO₄ starts to decompose with the scission of the doping anions releasing SO₂ (Fig. 3a). We could not detect any pyrrole formation during the pyrolysis; however,

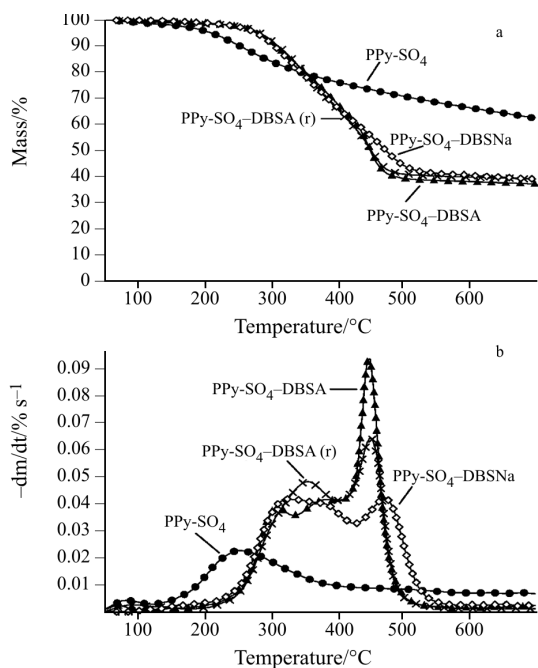


Fig. 2 a – TG and b – DTG curves of polypyrrole samples at 20°C min⁻¹ heating rate in argon atmosphere

smaller nitrogen-containing molecules have been monitored indicating the scission of the pyrrole rings. Nitrogen oxide (m/z 30 NO⁺) was evolved from 300 till 700°C. It should be noted that m/z 30 is also the main MS fragment ion of NO₂, so it might be released, too. The source of oxygen might be the SO₄²⁻ group or the oxygen bonded to PPy structure. The

amount of oxygen can be calculated from the results of elemental analysis as a difference of the sum of detected elements to 100%. At high temperatures HCN is evolved by the cleavage of the pyrrole rings.

The surfactant-containing samples decompose roughly in two stages (Figs 3b–d). SO₂ and a small amount of pyrrole are monitored at lower temperatures (250–400°C). HCN evolution was not monitored from these samples. The sharp second DTG peak corresponds to the evolution of the decomposition products of the surfactants. Mainly aliphatic hydrocarbon fragments and toluene are detected at this stage. The evolution of SO₂ occurs in a wide temperature interval. The lower temperature peak can be attributed to the scission of the SO₄²⁻ groups, whereas the high temperature peak may originate from the sulfonate groups of the surfactants. The two peaks of SO₂ can be clearly distinguished during the decomposition of PPy-SO₄-DBSNa. However, the sulfonate SO₂ peak is shifted to slightly lower temperature in the case of the samples prepared in the presence of DBSA. The decomposition of the alkylbenzene groups also occurs at a slightly higher temperature (about 20°C) in the DBSNa treated samples in comparison with the acid form of the surfactant. The different preparation methods of the PPy-SO₄-DBSA result in similar composition, although the sharp decomposition peak of the PPy-SO₄-DBSA is more intense than in the case of the sample prepared by the reverse method. It can be concluded from the evolution curves of the products that the first decomposition stage corresponds to the

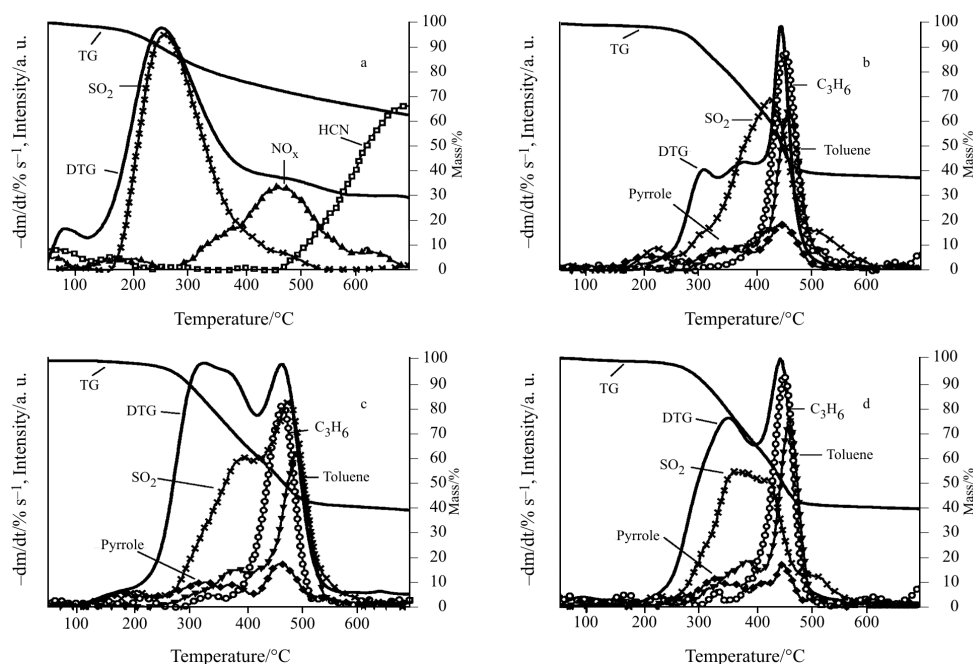


Fig. 3 Thermogravimetric and mass spectrometric curves of a – PPy-SO₄, b – PPy-SO₄-DBSA, c – PPy-SO₄-DBSNa and d – PPy-SO₄-DBSA (r). The monitored ions: m/z 27 (HCN), m/z 30 (NO_x), m/z 42 (C₃H₆), m/z 64 (SO₂), m/z 67 (pyrrole), m/z 91 (toluene)

scission of PPy-SO₄ segments of the polymer, while the devolatilization of the surfactant moieties takes place at higher temperatures.

For comparison we studied the thermal behavior of the two surfactants (Fig. 4). Dodecylbenzenesulfonic acid (DBSA) has low thermal stability; it decomposes between 150 and 300°C with the formation of a few percents of char residue. However, sodium dodecylbenzenesulfonate (DBSNa) decomposes at much higher temperature, between 380 and 480°C. Its decomposition occurs at similar temperature as the decomposition of the surfactant moieties in the polymers. It appears that dodecylbenzenesulfonate groups are present in the polypyrrole samples in ionic form independently of the preparation method and the original form of the surfactant (acid or sodium salt). During the decomposition of DBSNa, apparently sodium sulfate or other sulfur-containing salt is left behind. However, the residue is much higher than expected indicating that char formation also plays a role during the decomposition of DBSNa.

More detailed product analysis was performed by the use of pyrolysis-GC/MS. The scission of sulfonate groups results in the release of SO₂ from each sample. The acid form of the pure surfactant decomposes at low temperature with the cleavage of the sulfonate groups and the evaporation of the residual alkylbenzene moieties as displayed in the pyrogram in Fig. 5a. The surfactant contains various isomers of decyl, undecyl, dodecyl and tridecyl

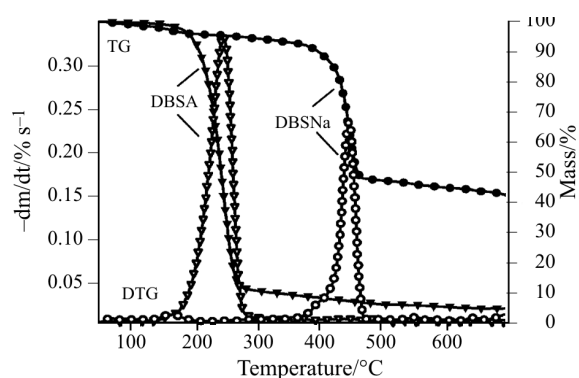


Fig. 4 TG and DTG curves of dodecylbenzenesulfonic acid (DBSA) and sodium dodecylbenzenesulfonate (DBSNa) surfactants

groups on the benzene rings as the pyrogram reveals. DBSNa surfactant decomposes at higher temperature (Fig. 4). The pyrogram (Fig. 5b) shows that scission of the alkylbenzene segments results in the formation of various hydrocarbon compounds. The strong fragmentation is accompanied by high char yield as detected by thermogravimetry. This scission mechanism is apparently catalyzed by the presence of the sodium ions. No fragmentation was observed from the PPy samples prepared in the presence of the surfactants and the pyrograms of the 3 samples are very similar. The pyrogram of the PPy-SO₄-DBSA is displayed in Fig. 6a as an example. The product distribution of the polymer is similar to DBSA except that minor amount

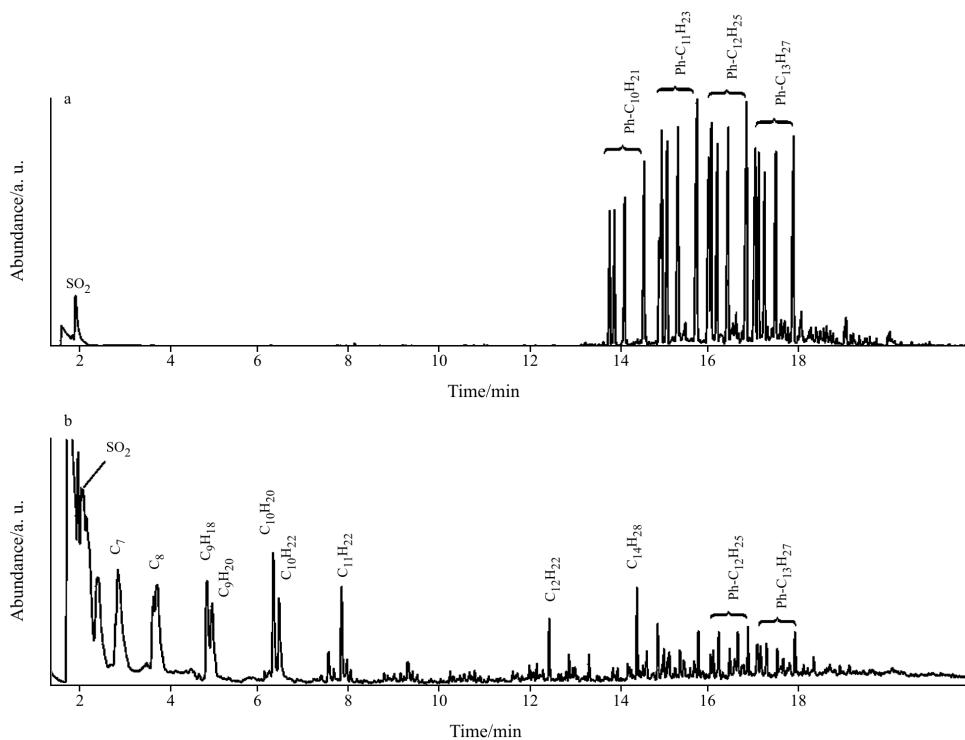


Fig. 5 Pyrolysis products of a – DBSA at 400°C and b – DBSNa at 500°C pyrolysis temperature

of pyrrole was detected from PPy-SO₄-DBSA. PPy-SO₄ prepared without surfactant (Fig. 6b) produces mostly SO₂ which can be derived from the doping anions. We could not detect any pyrrole formation that can be explained partly by the low amount of hydrogen in this sample. The release of pyrrole requires 2 hydrogen atoms which is available in the surfactant molecules, thus more pyrrole is formed from the samples containing surfactants. Furthermore, the differences in the decomposition of surfactant-free PPy-SO₄ and surfactant-containing PPy can be also explained by differences in the network structure of these samples. During polymerization pyrrole rings are coupled through α - α positions creating the main polymer chain. However, β -coupling also occurs resulting in cross-linked PPy structure. When anionic surfactant is added into the polymerization solution it is built into the PPy structure as a co-dopant. The bulky surfactant anion sterically hinders the cross-linking through the β -position. Thus, the created network is less extended comparing to the network of the surfactant-free PPy-SO₄. As a consequence of the extended network structure in PPy-SO₄, no pyrrole evolution was monitored during pyrolysis, however, the release of HCN and NO_x was observed indicating the scission of pyrrole rings. The conductivity measurements confirm the differences in network structure of these two PPy types. The conductivity of surfactant-free PPy-SO₄ is lower in comparison with the surfactant-containing PPy (Table 1) because the network structure formed in PPy-SO₄ causes conformation defects of the chains.

Conclusions

PPy chemically synthesized in the presence of anionic surfactants has different structure and thermal stability than the surfactant free PPy. SEM study showed that the presence of the anionic surfactant in the polymerization mixture strongly influenced the morphology and consequently the conductivity of the prepared PPy. PPy-SO₄ decomposes at a relatively low temperature with the evolution of SO₂. At higher temperature NO_x and HCN formation was observed demonstrating the scission of the pyrrole rings. The thermal stability of PPy-SO₄ increases when the synthesis was carried out in the presence of anionic surfactants. The decomposition of PPy doped with ferric sulfate and anionic surfactants can be divided into two main stages: the first one can be attributed to the decomposition of PPy-SO₄ segments, while the cleavage of dodecylbenzenesulfonate groups occurs at higher temperatures (400–550°C). The surfactant-containing PPy-SO₄ samples release pyrrole during decomposition. However, the cleavage of the pyrrole rings was not observed: no HCN and NO_x formation was detected. It indicates that these samples have less cross-linked structure than the surfactant-free PPy-SO₄. Dedoping and dopant decomposition take place during heating: evolution of SO₂ from sulfate and sulfonate groups as well as release of hydrocarbons from the dodecylbenzenesulfonate groups were observed. The relatively high decomposition temperature of the surfactant moieties indicates that chemical interactions occur between polypyrrole and the surfactants. The

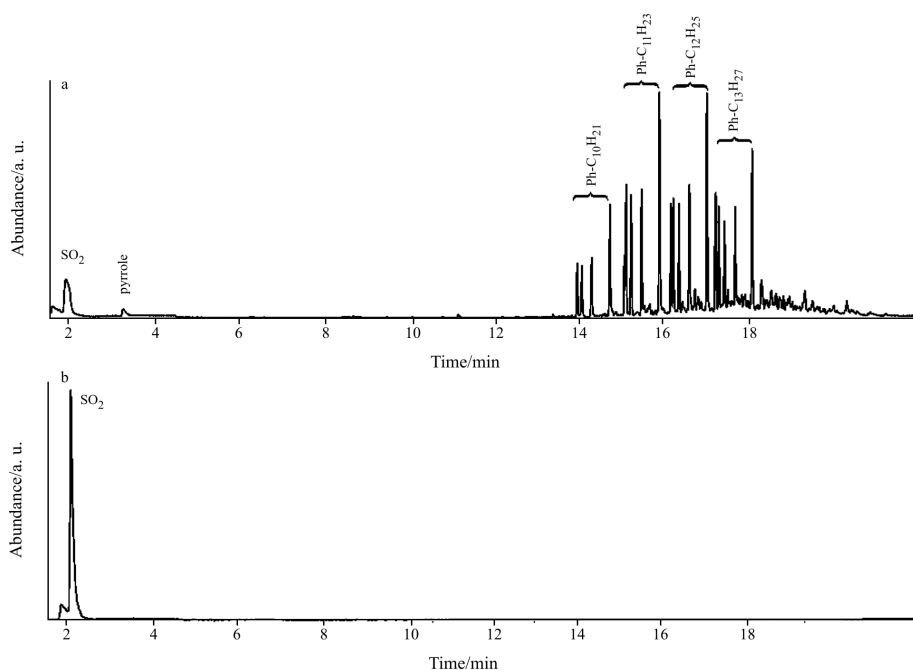


Fig. 6 Pyrolysis products of a – PPy-SO₄-DBSA and b – PPy-SO₄ at 400°C pyrolysis temperature

various preparation methods resulted in similar chemical composition of polypyrrole, although the amount of surfactant ions in the polymer samples is slightly different.

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