# CHEMICAL SYNTHESIS OF THIOPHENE-PYRROLE COPOLYMER

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## Abstract

Oligomerization reactions of thiophene and pyrrole monomers and chemical copolymerization of these oligomers were investigated in acetonitrile solutions containing thiophene-$HBF_4$, pyrrole-$HBF_4$ and thiophene-pyrrole-$HBF_4$. According to the results obtained from these studies, chemical oxidative polymerization of pyrrole and thiophene-pyrrole mixture occurs when anhydrous $FeCl_3$ is used as oxidative agent in the presence of various amounts of $HBF_4$. It was observed that homopolymer and copolymer colloids of different compositions are formed, respectively, depending on the concentration of $HBF_4$ used. These polymers were characterized with TGA, DSC, UV-Vis, FTIR techniques and elemental analysis.

## Indroduction

The field of conducting polymers has attracted the interest of many academic and industrial researchers. The properties of these organic polymers have led to use them in various applications, such as anti-static and anti-corrosion coating materials, sensors, batteries and supercapacitors, light emitting diodes, electrochromic devices and transparent electrode materials.[1-6] Conducting polymers can be prepared via chemical or electrochemical polymerization methods. Electropolymerization is generally preferred because it provides a better control of film thickness and morphology. Chemical oxidative polymerization of pyrrole is, on the other hand, an attractive technique to obtain conducting polypyrrole (PPy) in a powdery form for commercial applications. However, the powdery PPy obtained by chemical methods does not reach the desired conductivity values shown by high-quality electrochemically prepared PPy thin films. The synthesis of polypyrrole colloids from aqueous and nonaqueous media is well known.[7-9] For example, the oxidation of the pyrrole monomer can be carried out easily

using ferric chloride, which is used as an oxidizing agent for preparing pyrrole black in solution[10].

The monomers used for the synthesis of conductive copolymers were pyrrole and *N*-substituted pyrrole,[11] aniline and *o*-cynoaniline[12] and thiophene and alkylthiophene.[13] The dimers and trimers of thiophene have also been used for the synthesis of thiophene-pyrrole and thiophene-aniline copolymers as electro-oxidizable starting materials.[14-18] However, there is no chemically synthesized thiophene-pyrrole copolymer from unsubstituted thiophene and pyrrole due to the fact that ferric chloride can easily oxidize pyrrole whereas thiophene cannot be oxidized.

In this work, oligomerization of pyrrole and thiophene and copolymerization of these oligomers were investigated in acidic acetonitrile solution. Thiophene-pyrrole copolymer has been synthesized and characterized using TGA, DSC, UV-Vis, FTIR techniques and elemental analysis.

## Results and Discussion

Acetonitrile solutions containing thiophene-$HBF_4$ (1:1) and pyrrole-$HBF_4$ (1:1) were prepared and examined using UV-vis spectrometer. As seen in curve (a) in Figure 1, there are no absorption bands for thiophene-$HBF_4$ mixture between 250-500 nm. The absorption bands of pyrrole and thiophene monomers were reported to be below 250 nm.[19,20] In the curve (b) in Figure 1, there are two broad absorption bands at 310 nm and 456 nm, which belong to pyrrole oligomers.[20] The band at 456 nm was assigned to the interband transition (from valence to conduction band).[21] These UV-vis. results indicate that pyrrole oligomers are formed by catalytic reactions of these monomers with $HBF_4$ in dilute acidic media, whereas thiophene oligomers are not formed under the same conditions. The UV-vis spectrum obtained from thiophene-pyrrole-$HBF_4$ mixture also shows two broad absorption bands at 329 nm and 472 nm (Figure 1c). It is clearly seen that thiophene-pyrrole oligomers are also formed with different absorption characteristics than those of pyrrole oligomers. A red shift in the absorption maxima of pyrrole-thiophene oligomers with respect to pyrrole oligomers indicates that thiophene rings are added to pyrrole oligomers causing an additional increase in the conjugation length.
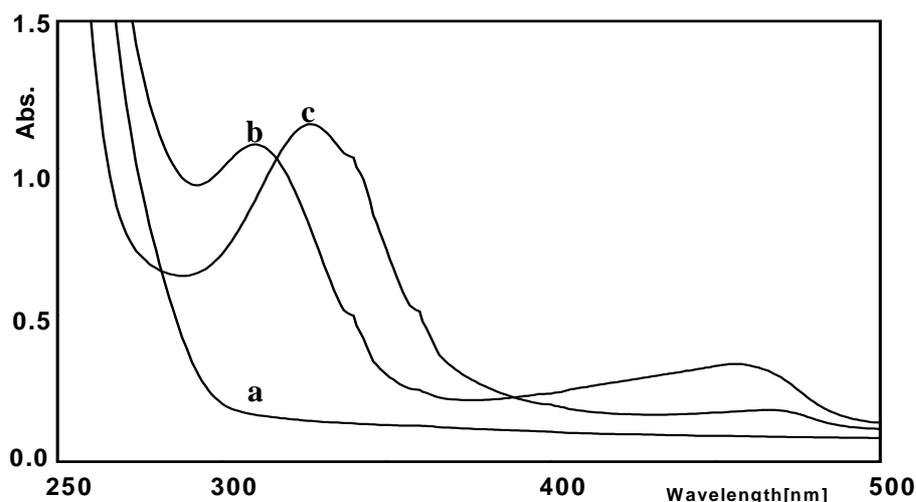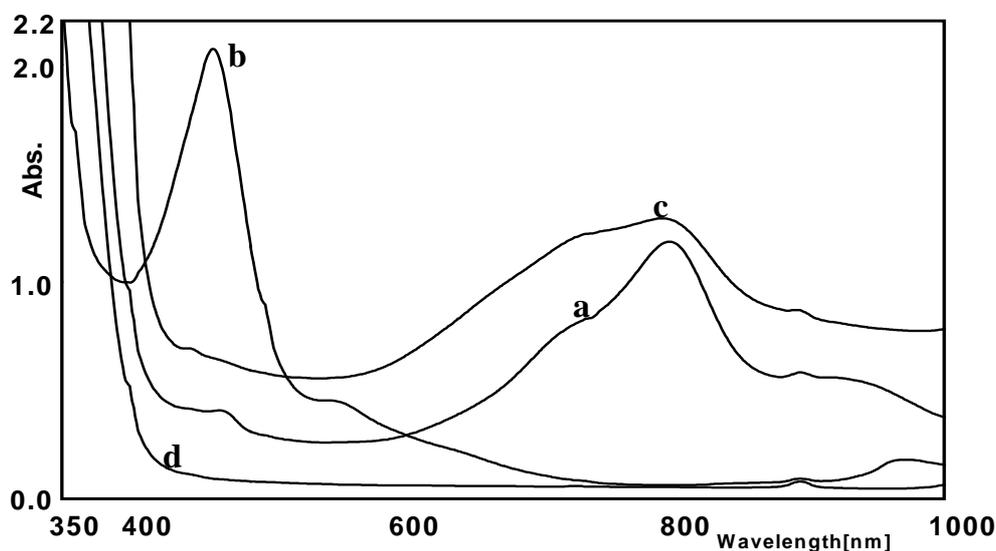
**Figure 1.** UV-vis spectra of (a) thiophene-HBF$_4$ mixture (1:1), (b) pyrrole-HBF$_4$ mixture (1:1), (c) thiophene-pyrrole-HBF$_4$ mixture (1:1:2), (The concentrations of species, C = 0.001M).

Figure 2 compares the UV-vis spectra of the pyrrole and thiophene solutions upon addition of FeCl$_3$ alone without HBF$_4$. As seen in Figure 2a there is a broad absorption band for pyrrole-FeCl$_3$ solution. The band maximum observed at 800 nm belongs to soluble forms of polypyrrole formed in acetonitrile. This band was assigned to the transition from the valence band into the bipolaron band.[21] The UV-vis spectrum of thiophene-FeCl$_3$ solution has no absorption bands indicating that neither oligomers nor soluble forms of the polymer are formed (Figure 2d). The UV-vis spectrum of the pyrrole-thiophene mixture upon the addition of FeCl$_3$ (Figure 2c) is similar to that in Figure 2a, giving evidence that thiophene does not oligomerize or polymerize with the addition of FeCl$_3$. The additions of HBF$_4$ and then FeCl$_3$ to pyrrole-thiophene solutions cause the formation of insoluble and soluble polymers. Figure 2b shows the UV-vis spectrum of the soluble portion of this copolymer. The conjugation length is apparently shorter here because of the intervening thiophene rings between the polypyrrole chains (as was the case in thiophene-aniline copolymer),[22] causing a blue shift in the absorption maximum.

Elemental analysis results of polymers (A, B, C and D) are given in Table 1. As can be seen in this table, the increasing amount of sulfur was found in the polymers (A, B, and C) as the concentration of HBF$_4$ was increased. Since thiophene oligomers are not formed in dilute acidic medium the amount of the sulfur in these polymer samples stems

from the chemical polymerization of thiophene-pyrrole oligomers which form upon nucleophilic addition of thiophene to protonated pyrrole cation or to protonated cations of pyrrole oligomers, as shown below.



**Figure 2.** UV-vis spectra of (a) pyrrole-FeCl$_3$ mixture (1:1), (b) pyrrole-thiophene-HBF$_4$-FeCl$_3$ (1:1:2:2) mixture, (c) pyrrole-thiophene-FeCl$_3$ (1:1:2), (d) thiophene-FeCl$_3$ mixture (1:1) (The concentrations of species, C=0.001M).

The amount of sulfur in the sample D is very low because of the fact that thiophene oligomers are not formed in dilute acidic medium. If the thiophene oligomers were to form in dilute acidic solution, FeCl$_3$ could oxidize them to produce polymer.[18] It is possible that the thiophene oligomers may form in concentrated acidic media and can react with FeCl$_3$ to produce copolymer as reported in literature.[18] Thus, the oxidation of both thiophene oligomers and thiophene-pyrrole oligomers by FeCl$_3$ cause an increase in the amount of sulfur in the polymer.

As seen in the TGA and DSC curves in Figure 3 and 4, the weight loss temperatures (Figure 3) and DSC behaviors (Figure 4) of the homopolymer and copolymer are different from each other. While the weight loss temperature is 220 °C for pyrrole homopolymer, the weight losses of copolymer (sample B) are about 100 °C and 300 °C. Figure 3b shows that in addition to the copolymer the sample B is a mixture, which contains also some polypyrrole. It is known that the weight loss temperatures for polythiophene prepared electrochemically is 67.8 °C and 210 °C, which are different

than the above values.[23] The comparison of the TGA curves of polypyrrole and thiophene-pyrrole copolymer shows that the latter has a higher maximum weight loss temperature of 300 °C whereas the polypyrrole decomposes at 220 °C. In addition the homopolymer looses 41.7% of its weight up to 800 °C whereas copolymer looses 55.1%

**Table 1.** Elemental analysis results for Samples A, B and C were prepared from A, B and C solutions given experimental section and for sample D prepared as follows. Pyrrole-HBF$_4$ and thiophene-HBF$_4$ solutions of the same concentrations were prepared separately. After 24 h, these solutions were mixed and 0.02 mol of ferric chloride was then added to this mixture.

| Samples (Pyrrole-Thiophene-HBF$_4$) | %N | %S |
|---|---|---|
| A (1:1:1) | 8.50 | 1.68 |
| B (1:1:2) | 8.29 | 6.21 |
| C (1:1:3) | 4.51 | 16.4 |
| D | 10.7 | 0.933 |
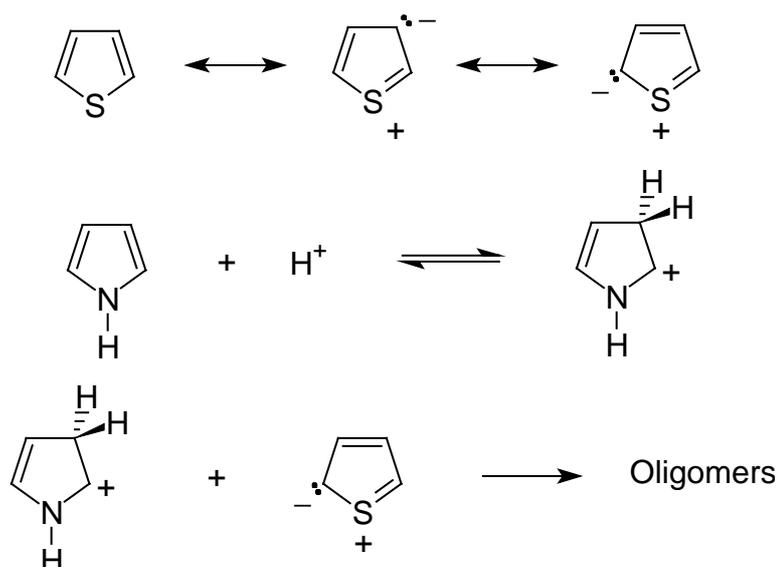


of its original weight. In the DSC curves, the peaks at 111 °C (endothermic) and 212 °C (exothermic) in Figure 4a belong to homopolymer of polypyrrole. In Figure 4b, there are three peaks at 111 °C (endothermic), 183 °C (exothermic) and 338 °C (endothermic). The peaks at 111 °C and 183 °C belong to polypyrrole homopolymer in the presence of sample B as in Figure 4a. The peak at 338 °C (not observed in Figure 4b) in Figure 4a is due to degradation of copolymer as shown in TGA curve around 300 °C (Figure 3b). These two findings also confirm that the polymers were different in nature.
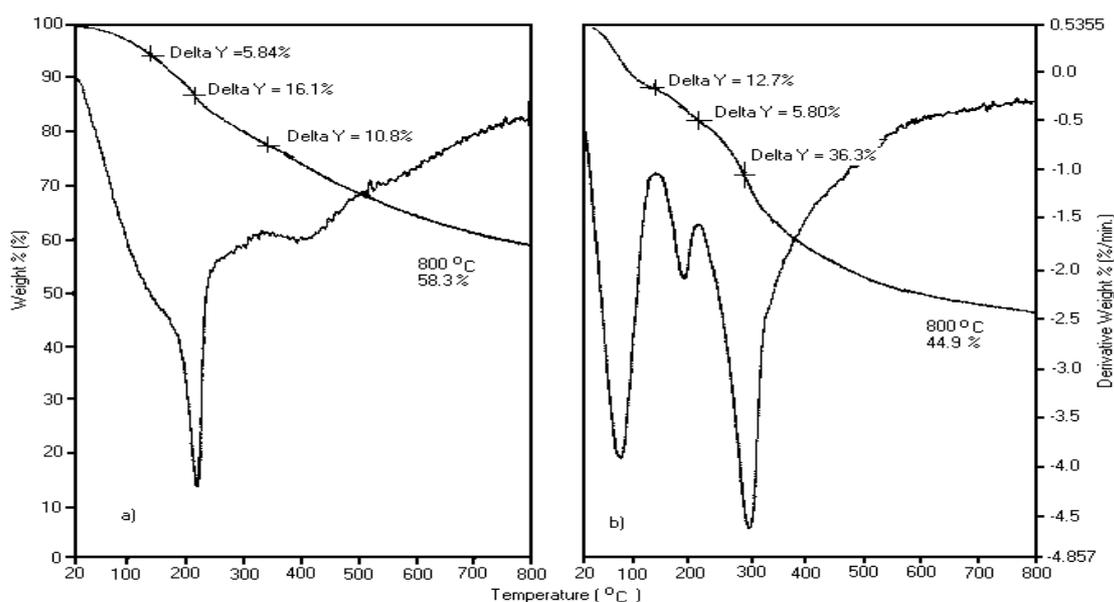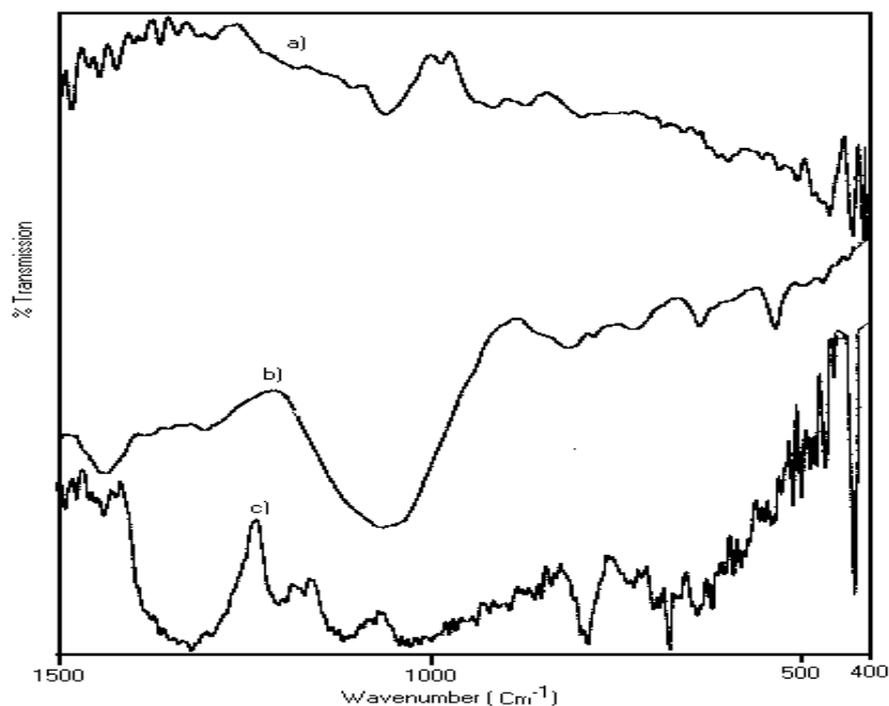
**Figure 3.** TGA curves for (a) polypyrrole homopolymer, (b) sample B prepared from B solution that contains 0.01 mol pyrrole, 0.01 mol thiophene and 0.02 mol HBF$_4$.
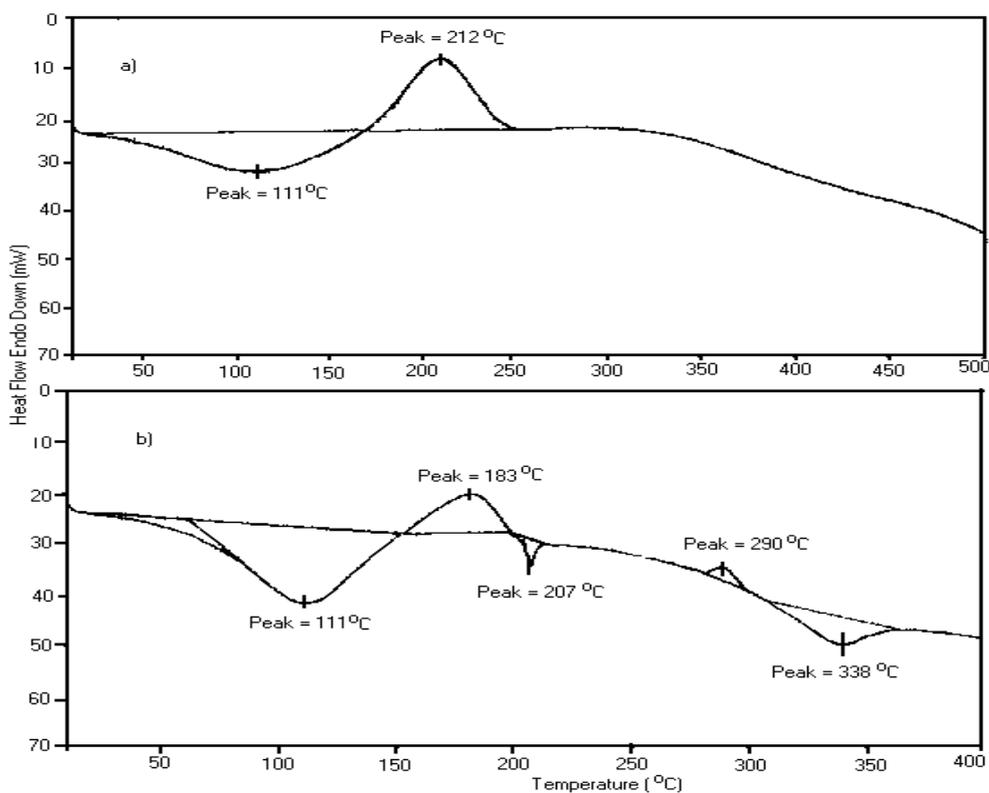


**Figure 4.** DSC curves for (a) polypyrrole homopolymer, (b) sample B prepared from B solution that contains 0.01 mol pyrrole, 0.01 mol thiophene and 0.02 mol HBF$_4$.

Furthermore, the comparison of the IR spectra of polypyrrole, sample B obtained from solution B and polythiophene prepared electrochemically also support the above conclusion (Figure 5). The absorption bands of polymers are at 1321, 782, 673 and 420 cm$^{-1}$ for polythiophene, 1492-1268 (10 bands), 1037, 447 and 416 cm$^{-1}$ for polypyrrole and 1421, 1051, 622 and 520 cm$^{-1}$ for copolymer (sample B).



**Figure 5.** Infrared spectra for (a) polypyrrole, (b) sample B prepared from B solution that contains 0.01 mol pyrrole, 0.01 mol thiophene and 0.02 mol HBF$_4$, (c) polythiophene prepared electrochemically.

It can thus be concluded that polymer synthesized from solution containing of thiophene, pyrrole and HBF$_4$ via chemical oxidative polymerization is a copolymer of thiophene-pyrrole.

It must be added that the dry conductivity value of the copolymer is too low to be measured.

## Conclusions

The UV-vis studies showed that pyrrole oligomers are formed whereas thiophene oligomers are not and thiophene reacts with pyrrole to produce thiophene-pyrrole

oligomers in acidic media. Thiophene-pyrrole copolymer can be synthesized by the oxidation of these oligomers with $FeCl_3$. If the acid concentration is low, the amount of sulfur in the copolymer is also low. The amount of sulfur in the polymer increases with increasing acid concentration in the polymerization medium. For example the elemental analysis results of sample B in Table 1 leads to the conclusion that approximately one thiophene ring is incorporated in the structure of sample B for every three pyrrole rings, This case indicates that the amount of sulfur in the polymer can be controlled with control of acid concentration during polymerization.

## Experimental

Pyrrole (97%, Aldrich) was filtered through basic alumina and thiophene (99%, Merck) was distilled before use. Anhydrous acetonitrile (99.8%, Aldrich), diethylether complex of tetrafluoroboric ($HBF_4$) (85%, Aldrich) and anhydrous iron trichloride ($FeCl_3$) (99%, Fluka) were used as received.

All of the studies were performed at room temperatures. The UV-vis and IR spectra were obtained using Jasco V-530 and Jasco FT/IR 430 spectrometers respectively. The compositions of the polymers were examined using LECO CHNS-932 apparatus. DSC and TGA curves were obtained with Perkin Elmer Pyris 1 instrument.

### Synthesis of Polymers

In the synthesis of homopolymer of pyrrole, 2.0 mL pyrrole taken from 5 M pyrrole-acetonitrile solution (0.01 mol) and equivalent amount of $HBF_4$ (0.01 mol) were mixed and the equivalent amount of ferric chloride was then added to this mixture and stirred at room temperature for 3h. A black colloidal solution was obtained upon addition of ferric chloride. The resulting black PPy precipitate was filtered.

In the synthesis of copolymers (A, B and C samples), 0.01 mol of pyrrole and 0.01 mol of thiophene were mixed and varying amounts of $HBF_4$ (0.01, 0.02, 0.03 mol) was then added to these mixtures to obtain the A, B and C solutions (the polymers prepared from A, B and C solutions were named as A, B and C given in Table 1 respectively). The ratio of the pyrrole-thiophene-$HBF_4$ in the A, B and C solutions are 1:1:1, 1:1:2 and 1:1:3 respectively. These solutions were kept for 24h to ensure complete oligomerization reaction to take place. After 24h, 0.02 mol of ferric chloride was added to each solution

and the solutions were stirred at room temperature for 3h. The resulting black polymers were then filtered

The sample D given in Table 1 was prepared as follows. Pyrrole-HBF$_4$ (1:1) and thiophene-HBF$_4$ (1:1) solutions were prepared separately. After 24 h, these solutions were mixed and 0.02 mol of ferric chloride was then added to this mixture. The black polymer precipitated was filtered.

The colloidal polymer samples (homopolymer and copolymer) were subjected to multiple rinsing procedures with acetonitrile to remove any residual ferric and ferrous chloride and then dried under vacuum.

## Acknowledgements

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## Povzetek

Študirali smo reakcijo oligomerizacije tiofenskega in pirolnega monomera in kemijsko kopolimerizacijo nastalih oligomerov v raztopini acetonitrila ob prisotnosti tiofena-HBF$_4$, pirola-HBF$_4$ in tiofen-pirola-HBF$_4$. Glede na dobljene rezultate v tej študiji lahko povzamemo, da poteče kemijska oksidativna polimerizacija pirola in tiofen-pirolne mešanice, kadar uporabimo anhidridni FeCl$_3$ kot oksidativno sredstvo v prisotnosti različnih količin HBF$_4$. Opazili smo, da se tvorijo homopolimerni in kopolimerni koloidi različnih sestav, glede na koncentracijo HBF$_4$. Polimere smo okarakterizirali z TGA, DSC, UV-VIS in FTIR tehnikami ter z elementno analizo.