SYNTHESIS AND STRUCTURE INVESTIGATIONS OF FUNCTIONALIZED POLYPYRROLE COPOLYMERS

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Abstract
Copolymer materials were prepared by chemical polymerization from solutions containing binary mixtures of pyrrole and a functionalized pyrrole, such as 3-(1-pyrrolyl)propanoic acid (N-Py) or 4-oxo-4-(1H-pyrrol-3-yl)butanoic acid (3-Py). The molecular structure of the products was determined by FT-IR and MAS solid state 13C NMR spectroscopy. The conformational behaviour of some of these substituted oligopyrroles was studied by ab initio and Density Functional Theory (DFT) methods using the 6-13 G basis set.

1. Introduction

Among conducting polymers, polypyrrole has attracted great interest owing to its high conductivity, redox behavior, relatively high environmental stability and acid-base properties [1]. The potential applications of polypyrrole are numerous and will grow as the improvement in the characteristics of these materials continues [2, 3]. The association of unsubstituted polypyrrole and functionalized polypyrrole within copolymers is a very promising way to meet the specific requirements of physical properties for many types of applications [4].

Our efforts to obtain copolymers were focused on the chemical polymerization method using pyrrole, 4-oxo-4-(pyrrol-3-yl)butanoic acid (3-Py) and 3-(pyrrol-1-yl)propanoic acid (N-Py) as monomers. The acid functions linked to the pyrrole can induce specific properties to the copolymers such as increased solubility or acidity at the one side and can also be useful as functional tools in subsequent chemical transformations, at the other side. Here, we report on the synthesis and investigation of copolymers prepared by chemical polymerization from solutions containing a binary mixture of two different monomeric pyrrole species. This study has involved the determination of copolymer composition using the FT-IR spectroscopy in combination with corresponding data obtained by quantum chemical calculations. In addition, characterization of some products was performed by MAS solid state 13C NMR spectroscopy. The molecular structure and conformational behaviour of some substituted oligopyrroles have been determined by ab initio and Density Functional Theory (DFT) methods using the 6-13 G basis set.

In order to understand the new phenomena and novel structures related to functionalized polypyrroles geometrical and electronic data of functionalized polypyrroles were studied.

2. Experimental

2.1. Materials

Pyrrole, acrylonitrile, trimethylbenzylammonium hydroxide, sodium hydroxide, N-hydroxysuccinimide, benzenesulfonyl chloride, 4-dodecylbenzenesulfonic acid, succinic anhydride, aluminium oxide and hydrochloric acid were purchased from Aldrich Chemical Company and were used as received without further purification. Solvents were dried by distillation under an inert atmosphere. But all reactions were performed under ambient conditions. 4-Oxo-4-(1H-pyrrol-3-yl)butanoic acid (3-Py) was prepared according to known literature procedures [7 - 9]. 3-(1-Pyrrolyl)propanoic acid (N-Py) was synthesized using a procedure based on Blume's [10] method.
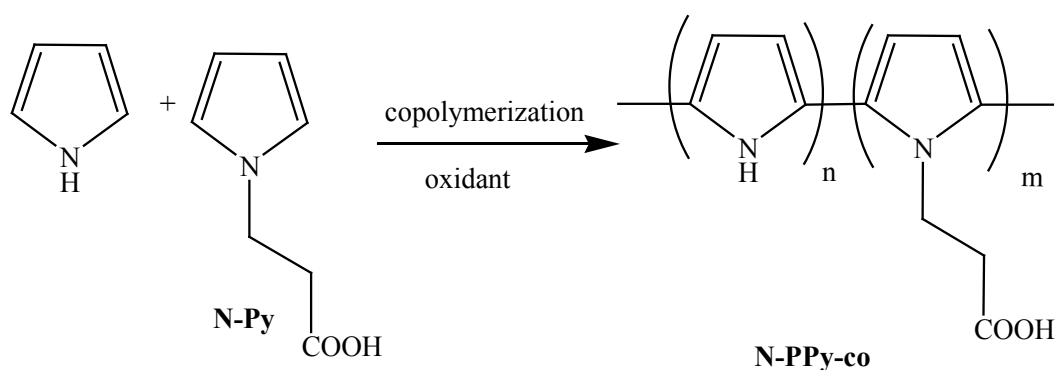
Scheme 1

Table 1: Synthesis parameters of **N-PPy-co**

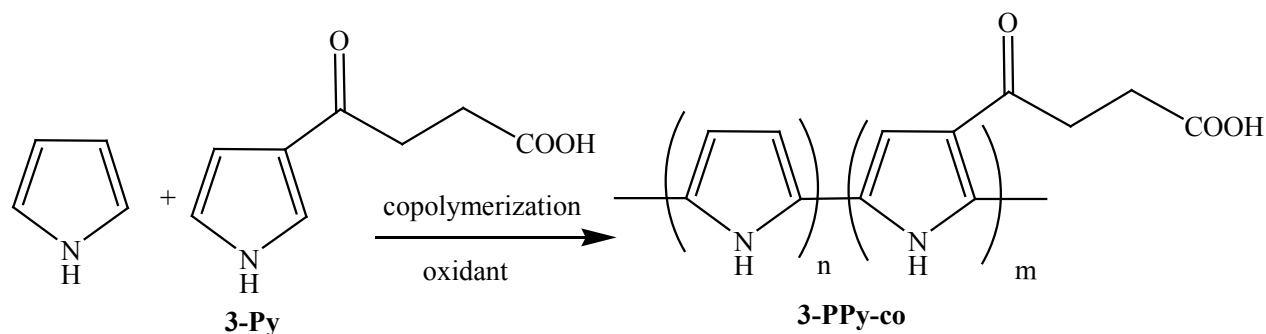| Sample	Mol. ratio Py/N-Py in feed solution	Dopant	monomer/ dopant	Ox.	Ox./ monomer	Time (h)	T(^{0}C)
N-PPy-co 1	1 : 1	DBSA	0.5	APS	0.2	6	rt.
N-PPy-co 2	1 : 3	DBSA	0.5	APS	0.2	6	rt.
N-PPy-co 3	1 : 5	-	-	FeCl$_3$	2.33	10	rt.
N-PPy-co 4	0 : 1	-	-	FeCl$_3$	2.33	10	rt.
N-PPy-co 5	1 : 5	-	-	CuCl$_2$	2.33	14	rt.
N-PPy-co 6	1 : 5	-	-	APS	0.5	6	rt.
N-PPy-co 7	0 : 1	-	-	APS	0.5	8	rt.
N-PPy-co 8	1 : 3	-	-	APS	0.5	6	rt.
N-PPy-co 9	1 : 2	DBSA	0.5	APS	0.5	6	rt.
N-PPy-co 10	1 : 3	DBSA	0.5	APS	0.5	6	< 5
N-PPy-co 11	1 : 2	-	-	APS	0.5	6	rt.
N-PPy-co 12	1 : 1	-	-	APS	0.5	6	rt.
APS: ammonium persulfate, DBSA: dodecylbenzenesulfonic acid							

The reaction parameters were varied to find out the influence of the dopant, the oxidizing reagent, the temperature and the ratio of pyrrole/N-Py on the properties of the resulting copolymers.

b) Synthesis of Poly(pyrrole-co-[4-oxo-4-(1H-pyrrole-3-yl)butanoic acids])

Poly(pyrrole-co-[4-oxo-4(1H-pyrrole-3-yl)butanoic acids]) **(3-PPy-co)** were prepared by chemical oxidation of mixtures of the monomers in aqueous solution (Scheme 2). We performed the co-polymerization in the absence or in the presence of DBSA as dopant. APS and FeCl3 were used as oxidizing agents (Table 2). The pyrrole monomers and DBSA were mixed vigorously with distilled water. An aqueous solution of oxidant was added dropwise to the pyrrole-dopant solution. The mixture was stirred at room temperature for 10 h. The reactions were terminated by adding excess of methanol. The functionalized polypyrroles 3-PPy-co were formed as black powders that were separated by filtration or centrifugation. Because of the low reactivity of 4-oxo-4(1H-pyrrole-3-yl)butanoic acid only two samples of 3-PPy-co were prepared.

Scheme 2

Table 2: Synthesis parameters for **3-PPy-co**

Sample	Mol. ratio Py / 3-Py in feed solution	Ox.	Ox./monomer	Dopant	monomer / dopant	Time (h)
3-PPy-co 1	1 : 3	APS	0.5	DBSA	0.5	10
3-PPy-co 2	1 : 3	FeCl$_3$	2.33	-	0.5	10

2.3. Computational Methods:

Calculations were carried out in Cluj-Napoca on an AMD Opteron cluster running under Linux. The standard B3LYP energies were performed by the Gaussian 03 computer code [5]. The geometry optimization of monomer and one-dimensional polymer chain structures of **N-PPy-co** and **3-PPy-co** conformations was achieved using Pople's 6-311G** basis set. The 3D electron density plots for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were generated using the Gabedit molecular graphics program [6] from Gaussian cube files. To describe the electronic band structures of one-dimensional polymer chains, the periodic boundary conditions were taken into account using a number of twelve k points and a single translation vector (Tv). The band structures of **N-PPy** and **3-PPy** one-dimensional polymer chains were obtained applying the IOP(5/103=10), IOP(5/98=1) and IOP(5/33=1) Gaussian 03 IOP extra keywords.

2.4. Spectroscopy

^{13}C-NMR spectra of solid copolymers were performed with a 400 MHz Tesla using MAS. FT-IR spectra were carried out on a JASCO FTIR 610 spectrophotometer.

**3. Results and Discussions**

A series of pyrrole copolymers **N-PPy-co** (see Table 1) and **3-PPy-co** (see Table 2) were obtained by chemical polymerization. The effect of monomer ratios, oxidizing reagents (APS, FeCl3, CuCl2), oxidation reagent / monomer ratios, temperatures and reaction times and of DBSA as dopant was investigated. In order to assign IR-data and to get information about the orbital structure as well as the band gap theoretical studies of **N-PPy-co** and **3-PPy-co** were performed. In the first part the geometry structures of the **N-Py** and **3-Py** monomers as well as the **N-PPy-co** and **3-PPy-co** oligomers, are described. In the second part, the band structures, electron affinities and ionization potential values of the oligomer conformations are presented. Discussions of the structural changes of **N-PPy-co** and **3-PPy-co** caused by the functional molecular fragments in the polypyrrole structure and of the electron conduction properties follow. The calculated IR frequency

values are compared with experimental spectra and MAS ^{13}C NMR spectra of two **N-PPy-co** samples are discussed.

3.1. Geometry.

Conformations of **N-Py** and **3-Py** monomers are shown in Fig. 1, where O atoms are denoted with red color, blue color represents N atoms, gray color C atoms and white color H atoms. Analogous conformations of oligomers are shown in Fig. 2. The **N-Py** monomer structure is composed of the pyrrole ring and the 2-carboxy-ethyl molecular fragment bound to the ring N atom, while in the other monomer structure **3-Py** a 3-carboxy-propionyl fragment is attached to position 3 of the pyrrole ring. The oligomer structures **N-tri-Py-co** and **3-tri-Py-co** contain the same molecular fragments as the monomers, but instead of a single pyrrole ring three pyrrole units are included. Each geometry of monomers and oligomers was optimized at B3LYP density functional theory level using the 6-311G** Pople's basis set with polarization functions (d orbitals on heavy atoms and p orbitals on H atoms). The infinite chain of a polypyrrole backbone presents a nearly linear and planar structure where the location of the N atoms at adjacent pyrrol rings is found at alternating sides [11]. It can be expected that the introduction of additional molecular fragments into different positions of the pyrrole ring will distort the highly ordered polypyrrole backbone structure. This fact depends very much on the geometry of the fragment structures. Precisely, if one considers the geometry at C atoms along the oligopyrrole chain in **N-tri-Py-co** and **3-tri-Py-co** (Fig. 2) one can see that in the former case all three pyrrole rings are distorted, i. e. out of plane. In the latter case only one pair of pyrrole rings are distorted while the other pair is kept in one plane due to intramolecular hydrogen bonding between the carbonyl O atom of the side chain in the central ring with the NH hydrogen atom of the adjacent ring. The distance of the H…O intramolecular hydrogen bond is 1.7657 Å. It can be assumed that this difference in the conformational structures affects the electronic and other properties of the respective polypyrrole. This is especially likely in the first oligomer case **(N-tri-Py-co)** where the different pyrrole rings are distorted by more than 20° against each other. In the second case **(3-tri-Py-co)** the situation is different, since two rings are kept in the same plane.
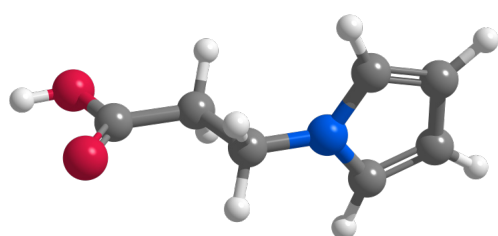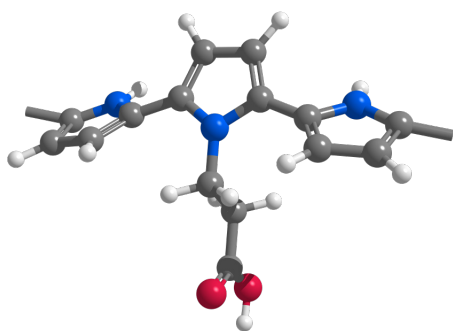

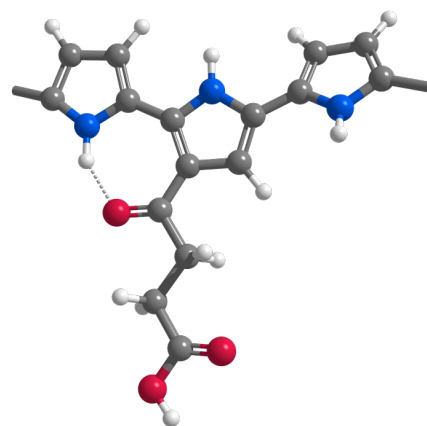3-(1-pyrrolyl)-propanoic acid (**N-Py**)
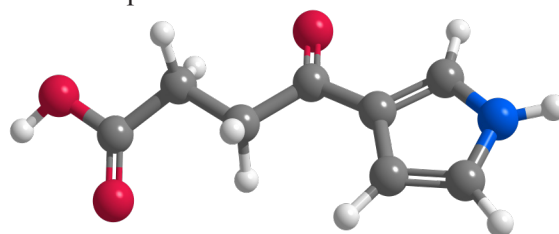
4-oxo-4(1*H*-pyrrol-3-yl)butanoic acid (**3-Py**)

Fig. 1: Calculated Geometries of **N-Py** and **3-Py** monomers

3-(1-pyrrolyl)-propanoic acid trimer with pyrrole (**N-*tri*-Py-co**)

4-oxo-4(1*H*-pyrrol-3-yl)butanoic acid trimer with pyrrole (**3-*tri*-Py-co**)

Fig. 2: Calculated Geometries of **N-tri-Py-co** and **3-tri-Py-co.**

a. HOMO orbital of **N-*tri*-PPy-co**

b. LUMO orbital of **N-*tri*-PPy-co**

c. HOMO orbital of oligopyrrole fragment structure of **N-*tri*-PPy-co**

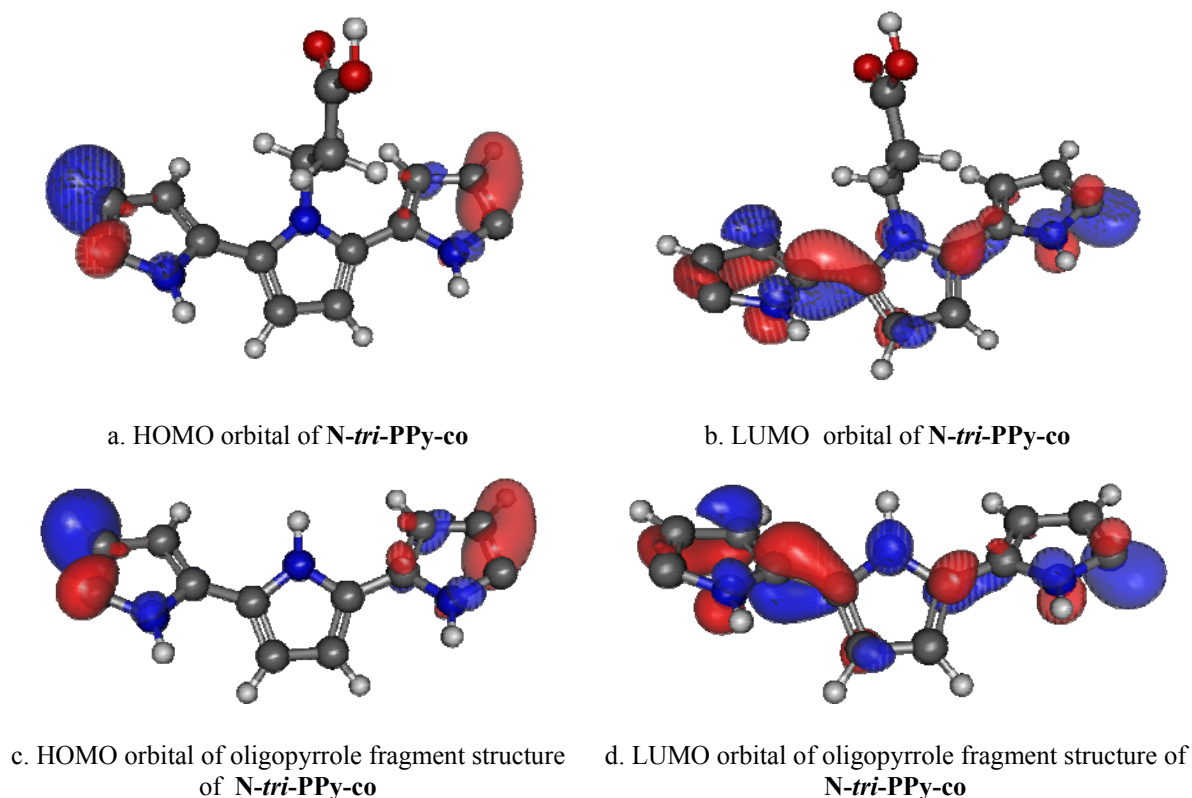d. LUMO orbital of oligopyrrole fragment structure of **N-*tri*-PPy-co**

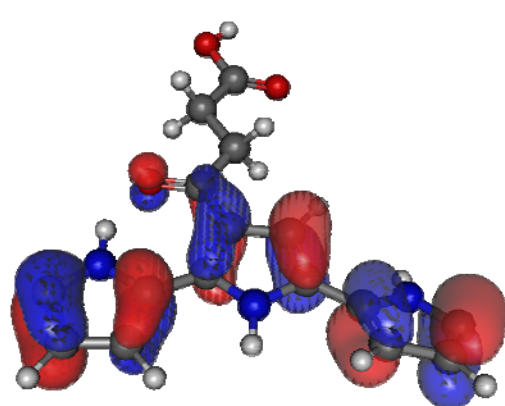**Fig. 3:** HOMO and LUMO orbitals of **3-tri-PPy-co** and the corresponding oligopyrrole fragment

3.2. Electron Densities and Band Structures.

In order to have a global idea about the electron conduction mechanisms in polypyrroles we studied the band structure of the infinite chain polymers as well as the HOMO – LUMO energy gaps of the oligomer conformations. In Fig. 3 and Fig. 4, respectively, the 3D electron density maps of HOMO and LUMO orbitals for **N-tri-PPy-co** and **3-tri-PPy-co** oligomers are presented with and without functional molecular fragments.

There is practically no difference in the two orbital maps of the HOMOs of **N-tri-PPy-co** (Fig. 3a) and the corresponding oligopyrrole fragment (Fig. 3c). These points to the fact that the incorporation of the fragment containing the side chain at the N-atom into an unsubstituted polypyrrole, maintains the HOMO orbital considerably localized. Thus, no improvement of electron conductibility can be expected in this way. Moreover, the polypyrrole chain suffers a distortion of neighbored pyrrole rings due to the 2-carboxy-ethyl molecular fragment attached to the N-atom and hereby the polypyrrole's delocalized π-electron system becomes more local-

ized, which can lead to lower electron conductivity. Similar to HOMOs, the LUMOs (Fig. 3b and 3d) remain unchanged, but in contrast to the HOMOs, the LUMOs present a very large delocalization in both cases. The opposite situation is found in the **3-tri-PPy-co** system where the 3-carboxy-propionyl fragment enhances the electron conductivity by extending the delocalized π electron system due to the presence of the conjugated C=O bond.

In addition, we also calculated the energetic band structure of these three one dimensional polypyrroles **PPy, N-PPy-co** and **3-PPy-co** (see Fig. 5). Regarding to **N-PPy-co** there is practically no difference to **PPy** in the band structure topology. Thus, the introduction of the 2-carboxy-ethyl side chain to the N-atom of the pyrrole could not give a qualitative change in the conduction mechanism. The band width of the **N-PPy-co** HOCO (highest occupied crystal orbital) is 0.044 eV and that of the LUCO (lowest unoccupied crystal orbital) is 0.073 eV. The gap is 2.68 eV. In case of the simple **PPy** chain 0.023 eV was obtained for the HOCO width, 0.073 eV for the LUCO width and 3.02 eV for the
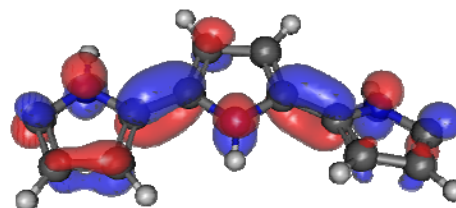
a. HOMO orbital of **3-*tri*-PPy-co** structure
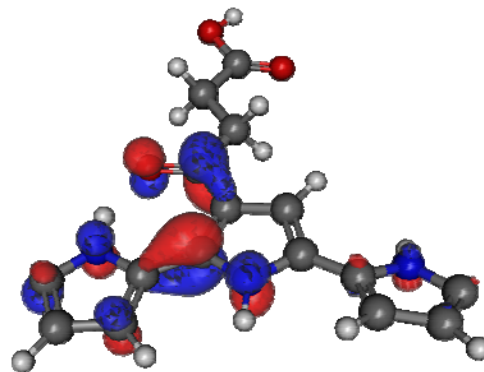
b. LUMO orbital of **3-*tri*-PPy-co** structure
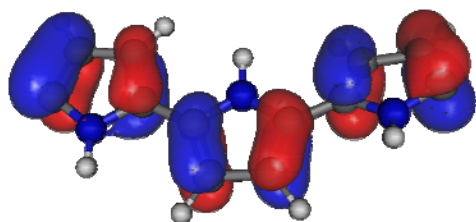
c. HOMO orbital of the oligopyrrole fragment structure of **3-*tri*-PPy-co**

d. The LUMO orbital of the oligopyrrole structure of **3-*tri*-PPy-co**

Fig. 4: HOMO and LUMO orbitals of **3-tri-PPy-co** and corresponding oligopyrrole structure

gap. However, the analysis of the band structure of the **3-PPy-co**, where the side chain is connected to position 3, reveals significant and interesting differences to the simple **PPy** system (Fig. 5c). First, the **3-PPy-co** band is shifted down compared with the simple PPy band position, but the HOCO-LUCO gap decreases by 0.2 eV. On the other hand, the **3-PPy-co** LUCO band width became smaller (the **3-PPy-co** band width is 0.045 eV, while the simple **PPy** band width is 0.626 eV). Furthermore, another bound (energetically negative value) wide band line was found in this **3-PPy-co** system, which could increase the electron affinity and the electron conductibility of the system. We have also calculated the electron affinities and ionization potentials for both the **N-PPy-co** and the **3-PPy-co** system. The electron affinities were calculated 3.10 eV and 3.28 eV, while the ionization potentials were 5.67 eV and 5.56 eV, respectively.
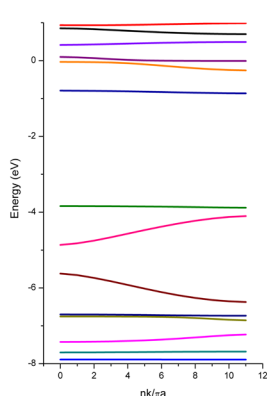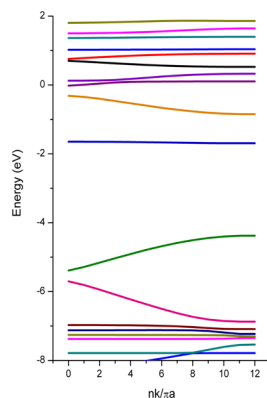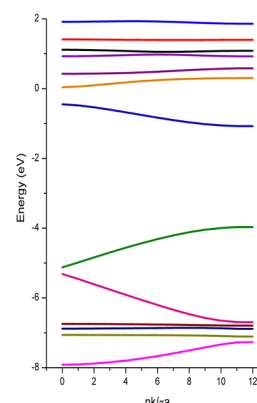

Fig. 5a

Fig. 5b

Fig. 5c

Fig. 5: 5a: Band structure of **PPy,** 5b: Band structure of **N-PPy-co** and 5c: Band structure of **3-PPy-co** as one-dimensional polymer molecular structure.

3.4 FTIR Spectra.

In order to study the influence of different groups attached to the polypyrrole chain we performed normal mode analysis, where the different normal mode vibrations are assigned to the corresponding absorption peaks of the experimental IR spectra obtained from the functionalized polypyrrole structures **N-PPy** and **3-PPy.** Based on the previous consideration, the calculated IR frequency lines are shown in Fig. 6 for the monomer **N-Py** and the polymer **N-PPy-co** systems, while Fig. 7 presents the analogous results for the **3-Py** and **3-PPy-co** system. The assignment of normal mode vibrations to different vibration frequencies was made using the Molden [12] molecular visualization graphics program. Comparing the experimental spectra of both oligomer systems one can see only a few differences in the spectral profiles. These points to the

fact that the pyrrole vibration intensity contribution to the resultant spectral shape is significant and the specific fragment intensities are mostly shielded. At the same time, in case of the **N-PPy-co** system the theoretical spectrum presents two intense lines at 1116.7 cm-1 and 1761.1 cm-1 (Fig. 6). Both lines are characteristic for the 2-carboxyethyl group. The first line can be assigned to the CH2 group's rocking vibration and is in good agreement with the measured band, while the second represents a typical C=O bond stretching vibration and is found at lower wave numbers in the measured spectrum. Between these two intense lines of the calculated spectrum several frequency lines are seen, which are characteristic to the **N-PPy-co** common vibration motions from which the 1372 cm-1 and 1409 cm-1 represent the C-N bond stretching.
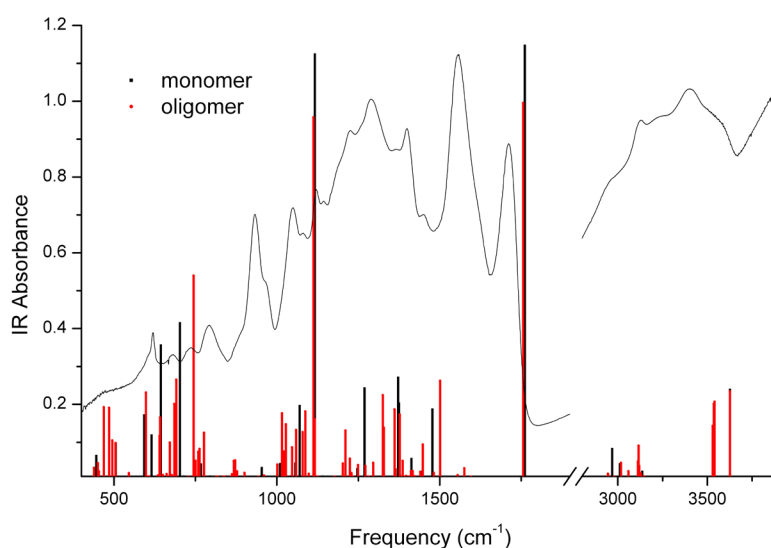

Fig. 6: Theoretical IR absporption peaks of monomer **N-Py** and oligomer **N-tri-PPy-co** and measured IR-spectrum of **N-PPy-co**

In case of **3-PPy-co** the measured spectrum is in better agreement with calculated values. More lines of intensive absorption are found by calculation (Fig. 7). The most interesting 3-carboxy-propionyl group normal modes are the two C=O bond stretching vibrations which appear very clearly separated from each other. While the ester carbonyl group shows an IR-band at 1720-1750, the keto group absorbs at

1715 cm-1. The strong frequency shift of the keto group to 1715 cm-1 is attributed to the intramolecular hydrogen-bond effect on the C=O vibration (see also Fig. 2). This effect of intramolecular hydrogen-bond can be observed in the experimental spectra. Furthermore, we found two important normal modes whose vibrations present a very large delocalization of pyrrole ring absorption. This means that not only

a few atoms of the oligomer structure take part in the collective motion but the whole PPy chain and the 3-carboxy-propionyl group as well. These vibrations are found at 901 cm⁻¹ and 1502 cm⁻¹, where the second frequency value has a much larger intensity than the first one. In general, the other frequency lines in the spectral domain of 900 – 1550 cm-1 with significant line intensities present a mixed normal motion of localized pyrrole vibrations and also localized attached group vibrations. The difference

between certain normal modes is given by the vibrational amplitude of the localized molecular groups. Anyway, from the complexity of the shape of experimental spectra it may be concluded that the "infinite" functionalized polypyrrole chain has a very complicated secondary structure and the linearity of the chain could be only an approximation. This very complicated secondary conformation also influences the other physical properties of these materials.
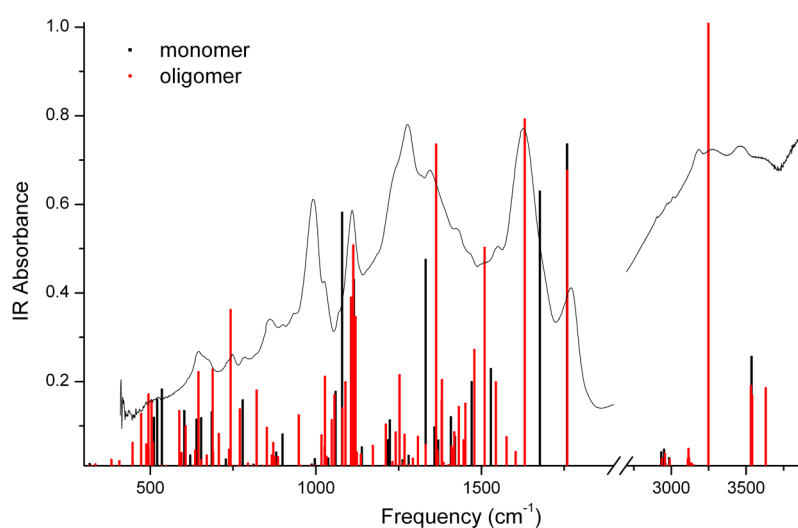

Fig. 7: Theoretical IR absporption peaks of monomer **3-Py** and oligomer **3-tri-PPy-co** and measured IR-spectrum of **3-PPy-co 1**

3.4. MAS ¹³C- NMR Experiment

In order to analyze the functionalized polypyrrole chain also ¹³C-NMR solid state investigations were carried out. ¹³C-NMR experiments with **N-PPy-co 1** and **N-PPy-co 3** were implemented in solid state using the MAS method (see Fig. 8a and 8b,
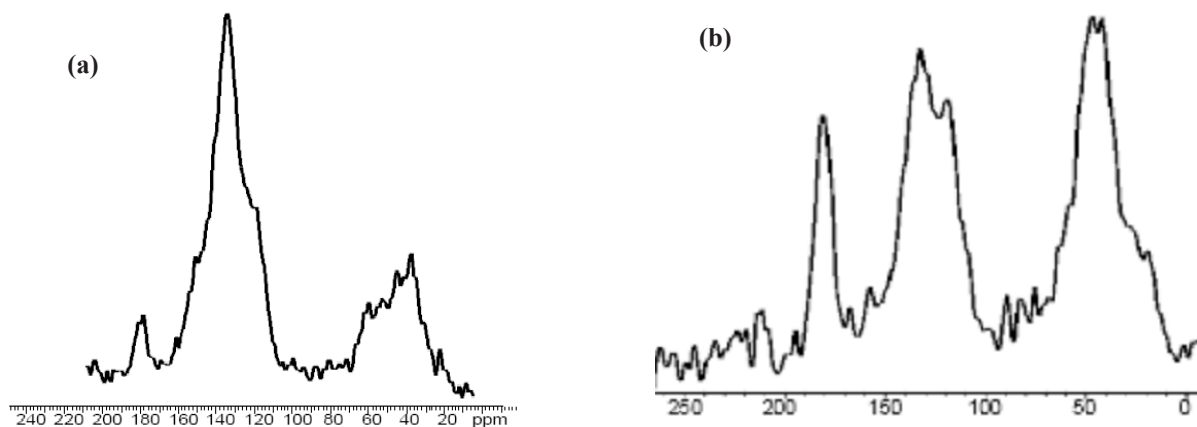

Fig. 8. MAS ¹³C-NMR solid state spectrum of (a) **N-PPy-co 1** and (b) **N-PPy-co 3**

respectively). Three peaks can be distinguished. The broader peaks in the region 20 - 60 ppm belong to methylene carbon atoms of the dopant (DBSA) and of the carboxyethyl group attached to the N-atoms of the functionalized pyrrole rings. The major peaks appear at 120 – 150 ppm and correspond well with α and β carbon atoms of pyrrole rings. The downfield peak at 180 ppm belongs to the carboxyl carbon atom COOH, proving that the 3-(1-pyrrolyl)-propanoic acid is included into the polypyrrole chain in both cases. The relative peak intensities of COOH and the CH2–groups versus the α and β ring carbon atoms in the spectra of **N-PPy-co 1** as compared with **N-PPy-co 3** increase showing the higher incorporation of the N-functionalized pyrrole N-Py in the latter copolymer. While unsubstitued polypyrrole shows only one peak in the 140 ppm region [13] an additional peak is found at about 120 ppm in the copolymers **N-PPy-co 1** and **N-PPy-co 3** (Fig. 8). This phenomenon is caused by changes in conformation and conjugation within the polypyrrole backbone.

4. Conclusions

Novel functionalized polypyrroles were prepared by chemical copolymerization of 3-(1-pyrrolyl)propanoic acid and 4-oxo-4(1*H-pyrrole*-3-yl)butanoic acid with unsubstituted pyrrole in different ratios. MAS solid state ^{13}C-NMR spectra of pyrrole copolymers were recorded showing the characteristic peaks of and reflect the effect of the ratios of monomers.

Quantum chemical *ab initio* calculations at B3LYP density functional theory level, using 6-311G** basis set were performed to achieve geometry configuration, band structure, electron affinity, ionization potential and IR absorption spectra in cases of **N-PPy** and **3-PPy.** The results show that attaching different side chains to different positions of the polypyrrole chain causes changes in the physical properties of the polypyrrole system. Thus, substituents could increase or decrease the electron conductibility and enlarge or reduce the band line width or the HOCO-LUCO gap. Key absorption peaks of the IR-spectra were tried to predict by these calculations too. In the other hand, the "infinite" linear ap-

proximation of the functionalized polypyrrole chain is not able to perfectly describe the different properties of the systems perfectly and therefore more complicated 3D structure have to be considered.

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