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Synthesis and characterization of new functionalised pyrrole copolymers

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The preparation of a novel type of pyrrole copolymers is described by chemical oxidative polymerisation of 3-(1-pyrrolyl)-propanoic acid and pyrrole. The copolymers were obtained in water using varied monomer ratios, in the presence of an oxidant agent and with or without a dopant. Investigation of the copolymer molecular structures by NMR spectroscopy, MALDI mass spectrometry and FT-IR spectroscopy showed that the copolymer chains contain substituted and unsubstituted pyrrole with deferring ratios of pyrrole and 3-(1-pyrrolyl)-propanoic acid. SEM investigation revealed that the copolymers morphology is different from that of the homopolymers.

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1. Introduction

It is well known that the electrical conductivity, molecular anisotropy and the environmental and thermal stabilities of polypyrroles can be significantly improved by the judicious choice of dopant anions which are incorporated as counter ions into the oxidized, cationic polypyrrole chains [1-8]. The main drawback of these materials is its poor processability, since it is both infusible and also completely insoluble in all known solvents. In order to overcome this inherent intractability, several strategies have been developed to increase the solubility: (1) Soluble polypyrrole could be prepared via electrochemical polymerisation of alkyl substituted pyrroles [9-11]. (2) Soluble polypyrrole could be also obtained via a counterion-induced processability [12, 13] and (3) Havinga [14] and Heeger et al. [15] prepared water-soluble polypyrroles by electrochemical polymerisation of sulfonyl-substituted pyrrole. There is still a need to find new soluble polypyrroles with the focus to equip them with new properties or to allow further reactions at the functional groups to tether functions to the polymer chain. As a promising option we approached the introduction of other anionic groups as sulfonic groups into polypyrroles.

Copolymerisation, i. e. the incorporation of two or more structurally different monomers into the same polymer chain, is commonly used to control the properties of a polymer. Our efforts were focused on the chemical polymerisation method of copolymers using pyrrole and 3-(1-pyrrolyl)-propanoic acid (NPy) units. The propanoic acid side chains can induce specific properties to the copolymers such as increased solubility or acidity at one side and it can be also useful as functional tools in subsequent chemical transformations, at the other side. Here we report on the synthesis and investigation of copolymer materials prepared by chemical polymerisation from solutions containing a binary mixture of the two different monomeric pyrrole species. This study has involved quantitative determination of copolymer composition using elemental analysis and qualitative comparisons of intensities of IR-adsorption data obtained by FT-IR spectroscopy. In addition, characterization of these materials was performed by scanning electron microscopy (SEM), NMR spectroscopy and MALDI mass spectrometry.

2. Experimental

2.1. Materials

All the reagents 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. 3-(1-Pyrrolyl)-propanoic acid (NPy) was prepared according to known literature procedures [16].

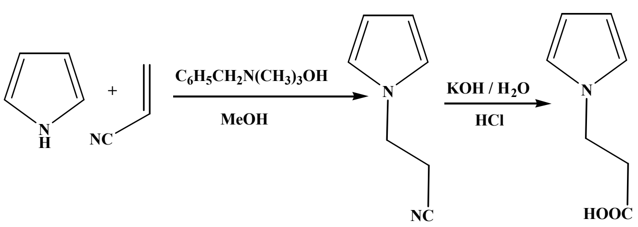
2.2. Instrumentation

Elemental analyses were performed in a LECO CHNS – 932 apparatus. SEM analysis of the pyrrole copolymer was carried out using a JEOL JSM - 5600 LV scanning electron microscop. ^{1}H-NMR and ^{13}C-NMR solution spectra were recorded at 300 MHz and 75 MHz, respectively; with a Bruker AC 300 in $CDCl_3$ as the solvent in 5mm NMR tubes with TMS as internal standard. ^{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 discussion

3.1. Synthesis of monomer

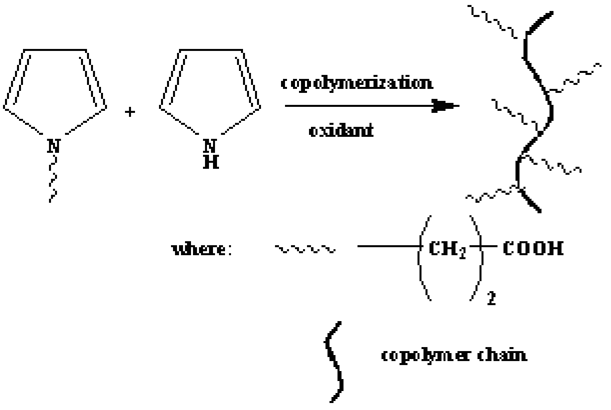
Synthesis of 3-(1-pyrrolyl)-propanoic acid (N-Py) was accomplished using a procedure analogous to Blume`s method [16] which was modified (Scheme 1). A flask equipped with an internal thermometer was charged with pyrrole (7.4 ml, 110 mmol) and trimethylbenzylammonium hydroxide (2.22 ml, 1.6 mmol 40 wt % solution in methanol). To this solution acrylonitrile (5.7 ml, 110 mmol) was added without allowing the reaction temperature to rise above 40^0C. After the addition was complete, the reaction was stirred for 24 h. The resulting crude pyrrole-1-yl-propionitril was then hydrolysed by adding potassium hydroxide (7.8 g, 142.8 mmol) in 20 ml water to the reaction mixture and heating under reflux for 2 h. After allowing the reaction to cool to room temperature, the product was isolated by acidification with 6 N HCl followed by threefold extraction with diethyl. The combined organic extracts were dried over anhydrous sodium sulphate and the solvent was removed in vacuum to give the product which was purified by distillation (b.p. 119-124^0 C/3 mm, m.p. 59-61^0 C).



Scheme 1: Synthesis of 3-(1-pyrrolyl)-propanoic acid.

3.2. Synthesis of copolymers

Pyrrole copolymers were prepared by chemical oxidation of the monomers in aqueous solution (Scheme 2). We performed the copolymerisation in the absence or in the presence of a dopant (dodecybenzensulfonic acid). Several oxidising agents (see Table 1) were used. The synthesis parameters of all functionalised polypyrrole samples are given in Table 1. The monomeric pyrrole and the dopant (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 r.t. for various time intervals between 6 and 10 h (Table 1). The reactions were terminated by adding excess of methanol. The functionalized polypyrroles were formed as black powders that were separated by filtration or centrifugation. The filtrates have a black colour, indicating a certain solubility of the products. In addition, the solubility of the powders PPy-co 1, PPy-co 2 and PPy-co 10 were investigated in a bit more detail. It turned out that these products were soluble in organic solvents (chloroform, methanol, and ethanol) and in water.



Scheme 2: Synthesis of copolymers.

Table 1. The synthesis parameters for pyrrole copolymers

Sample	Mol. ratio Py : N-Py in feed solution	Dopant	monomer/ dopant	Ox.	oxidant/ monomer	Time (h)	T(^{0}C)
PPy-co 1	1 : 1	DBSA	0.5	APS	0.2	6	rt.
PPy-co 2	1 : 3	DBSA	0.5	APS	0.2	6	rt.
PPy-co 3	1 : 5	-	-	$FeCl_3$	2.33	10	rt.
PPy-co 4	0 : 1	-	-	$FeCl_3$	2.33	10	rt.
PPy-co 5	1 : 5	-	-	$CuCl_2$	2.33	52	rt.
PPy-co 6	1 : 5	-	-	APS	0.5	6	rt.
PPy-co 7	0 : 1	-	-	APS	0.5	8	rt.
PPy-co 8	1 : 3	-	-	APS	0.5	6	rt.
PPy-co 9	1 : 2	DBSA	0.5	APS	0.5	6	rt.
PPy-co 10	1 : 3	DBSA	0.5	APS	0.5	6	< 5
PPy-co 11	1 : 2	-	-	APS	0.5	6	rt.
PPy-co 12	1 : 1	-	-	APS	0.5	6	rt.

APS: ammonium persulfate, DBSA: dodecylbenzolsulfonic acid

The reaction parameters were varied to find out the influence of the dopant, the temperature and the ratio of pyrrole/3-(1-pyrrolyl)-propanoic acid to the properties of the resulting copolymers.

It has to be mentioned that a fine black powder was obtained for the sample PPy-co 10 polymerised at low temperature (T<5^0C) and the separation from the solution was possible only by centrifugation. Another special case, which has to be mentioned, is the sample PPy-co 5, where $CuCl_2$ was used as oxidising agent. After 52 h at room temperature a dark green solution was obtained instead of precipitation of a black powder. It is known that pyrrol oligomers are entirely soluble in water and have a dark green colour. Thus we assume that oligomers rather than polymers were formed in the case of sample PPy-co 5.

3.3. Elemental micro-analyses

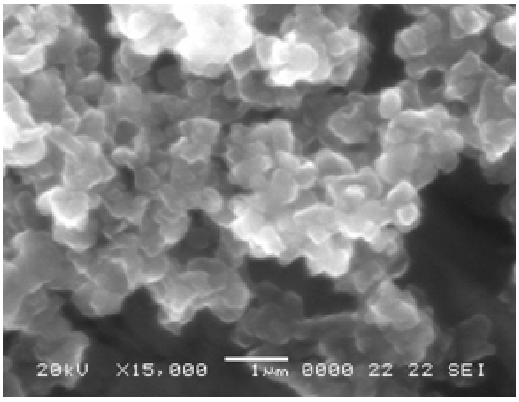
The results of elemental analysis of some representative copolymers samples are given in Table 2. It turned out that higher sulphur concentrations were found in the samples prepared by the addition of the dopant DBS to the polymerisation solution. However, sulphur is also present at low concentrations in the samples prepared without the dopant DBS, due to the insertion of the sulphate from the oxidant APS.

Table 2. Results of elemental analysis of Polypyrrole copolymers.

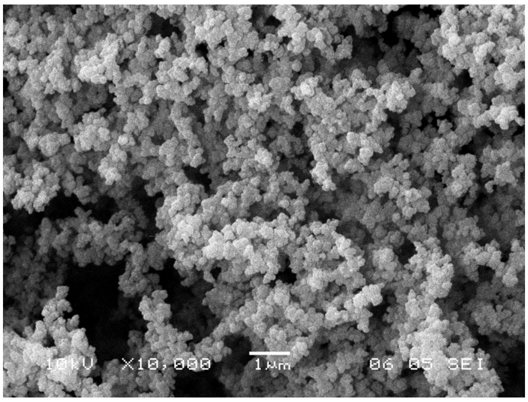
Sample	C (%)	H (%)	N (%)	S (%)
PPy-co1	51.64	4.45	13.15	5.26
PPy-co 2	51.62	4.31	12.53	4.72
PPy-co 8	54.15	4.58	12.42	1.86
PPy-co 9	53.78	5.44	10.95	3.32
PPy-co 10	60.85	6.59	7.57	4.24
PPy-co 11	53.45	4.56	12.43	2.36
PPy-co 12	52.44	4.73	13.72	3.23

3.4. Scanning electron microscopy analysis

The difference between the structure of pyrrole copolymer and that of polypyrrole can be observed in the SEM images (Fig. 1). The morphology of the copolymer PPy-co 11 (1b) shows that the particles are uniform and have a smaller size (around 100 nm) as compared with polypyrrole (1a).



a



b

Fig. 1. SEM imagines of (a) polypyrrole, (b) PPy-co 11.

3.5. NMR spectroscopy

3.5.1. ^{1}H-NMR analysis:

N-substituted polypyrroles are known to have significantly lower conductivities than their unsubstituted or 3-substituted counterparts. Thanks to its solubility in $CDCl_3$, the copolymer PPy-co 2 could be characterized by NMR spectroscopy in $CDCl_3$ solution (Figure 2b).

As can be seen from Figure 2, the spectrum of the copolymer PPy-co 2 (2b) resembles that of monomeric 3-(1-pyrrolyl)-propanoic acid (2a) in the aliphatic region ($\delta < 4$ ppm). As expected, the signals in the polymer spectrum (2b) are broader and less resolved than in the monomer (2a). In the aromatic region, the signals corresponding to the protons of the pyrrole ring and the benzene ring of the dopant appear overlapped. The proton belonging to the carboxyl group appear as singlet at the chemical shift $\delta = 9.2$ ppm.

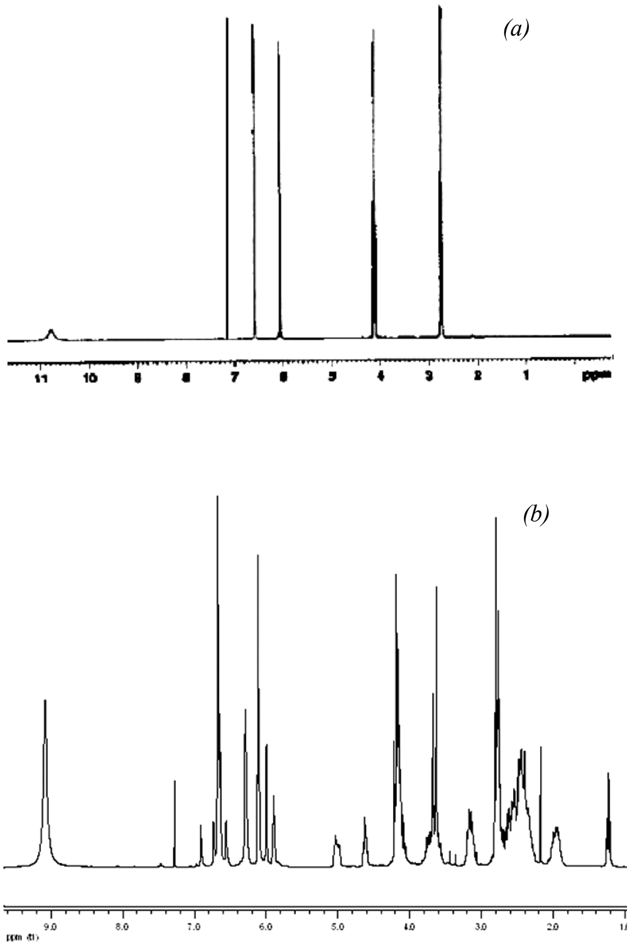


Fig. 2. ^{1}H-NMR spectra (a) 3-(1-pyrrolyl)-propanoic acid; (b) PPy-co 2 in $CDCl_3$ at 300 MHz.

3.5.2. ^{13}C- NMR experiment

^{13}C-NMR experiments with PPy-co 1 and PPy-co 3 were implemented in solid state using the MAS method (see Fig. 3a and 3b, respectively). Three peaks can be distinguished. The broader peak in the region 20 - 60 ppm belongs to methylene carbon atoms of the dopant (DBSA) and the N-substituent of the functionalized pyrrol rings. The major peak appears at 120 – 150 ppm and corresponds 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. As expected the relative peak intensity of COOH and the CH_2 –groups versus the ring carbon atoms increases with increasing amount of N-functionalized pyrrol.

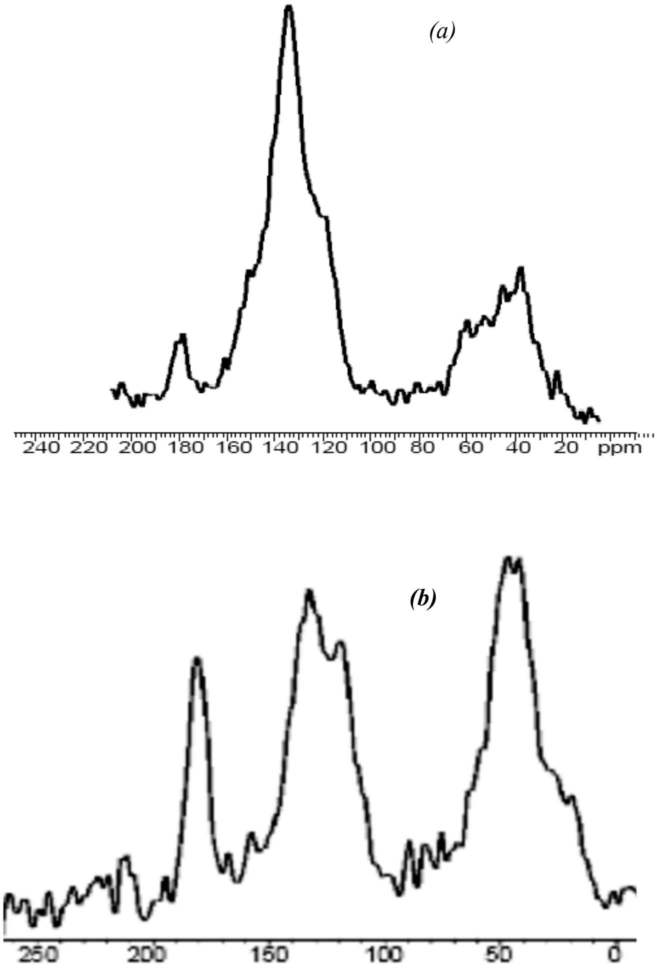


Fig. 3. MAS ^{13}C-NMR solid state spectrum of a) PPy-co 1 and b) PPy-co 3

3.6. MALDI analysis

MALDI spectrum of the sample PPy-co 10, an undoped functionalized polypyrrole, (Figure 4), sample preparation from $CHCl_3$-solution shows peaks in the range of m/z = 700 – 900 corresponding to degrees of polymerization DP = 9- 12 but also lower masses belonging to shorter oligomers.

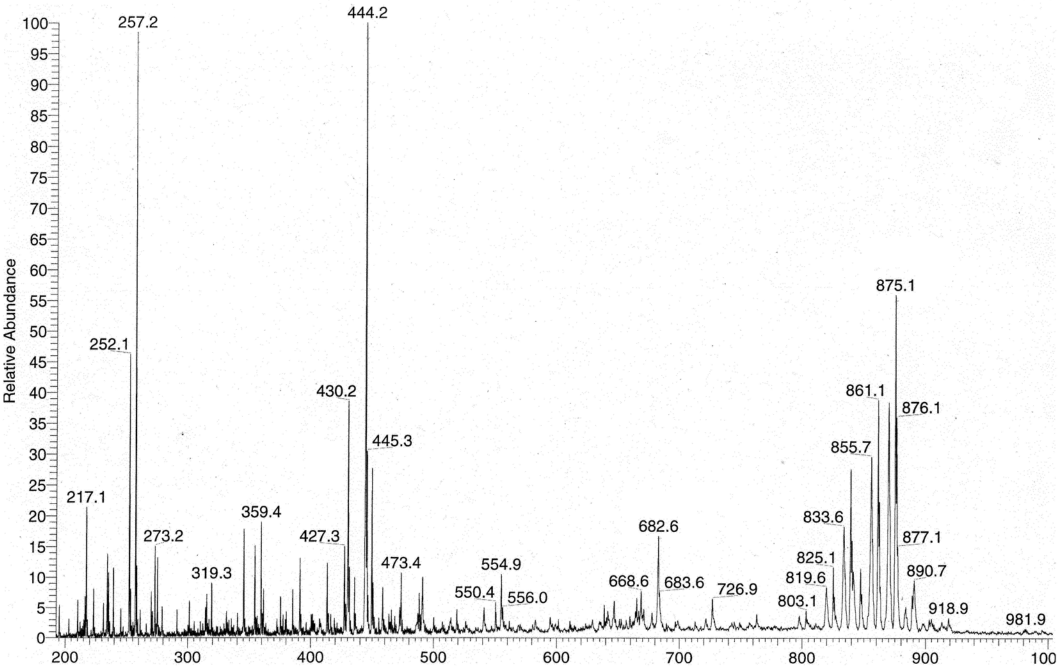


Fig. 4 MALDI spectrum of PPy-co 10

Table 3. Peak positions (cm^{-1}) of IR-adsorption bands of pure PPy and copolymers: PPy-co 6, PPy-co 7, PPy-co 8, PPy-co 10

PPy(DBS) ν (cm^{-1})	PPy-co6 ν (cm^{-1})	PPy-co 7 ν (cm^{-1})	PPy-co 8 ν (cm^{-1})	PPy-co 10 ν (cm^{-1})	Band assignments
3440	3374	3422	3400		N-H and -OH-
-	1714	1717	1712	1705	–C=O-
1552	1559		1559	1535	C=C/C-C
1465	1400	1400	1400	1454	Ring breathing with contribution from C=C/C-C and C-N
1294	1297		1289	1285	C-H in-plane bend
1198	1210	1202		1149	Ring breathing
1037	1047		1050	1029	C-H in-plane bend
914	932		932	914	Ring deformation
790	790	789	793	794	Ring deformation on β-carbon

3.7. FTIR spectroscopy

The molecular structure for pyrrole copolymers prepared from binary solution mixtures were also investigated using FT-IR spectroscopy. Although these data do not provide a quantitative determination of the copolymer composition, they nevertheless could clearly show again that under these polymerization conditions the 3-(1-pyrrolyl)-propanoic acid is incorporated into the copolymer. For comparison the FT-IR spectra of polypyrrole and of some representative copolymer samples are shown in Figure 5. One can see that the peak positions and relative bands intensities in the copolymers spectra are affected by the unsubstituted pyrrole/substituted pyrrole ratio. Table 3 presents the peak positions of the main characteristic absorption bands. The spectra of all copolymers as well as of the N-functionalized homopolymer (PPy-co 7) contain an intense adsorption band with the maximum situated in the range of 1705 – 1717 cm^{-1}, which ascribed to the –C=O group. The adsorption bands of the pyrrole ring vibrations are found at lower frequencies in the spectra for copolymers as compared to that of pure polypyrrole (see Table 3).

The intensities of the absorption band characteristic for the collective vibration mode of intra-ring and inter-ring C=C/C-C, located around 1550 cm^{-1}, decrease with the increase of substituted pyrrole monomer concentration (see Figure 5). For the N-functionalized homopolymer sample PPy-co 7 this band is very weak. This fact indicates a reduction of the effective conjugation length of the polymeric chains due to the conformational modifications induced by the substituted pyrrole[1].

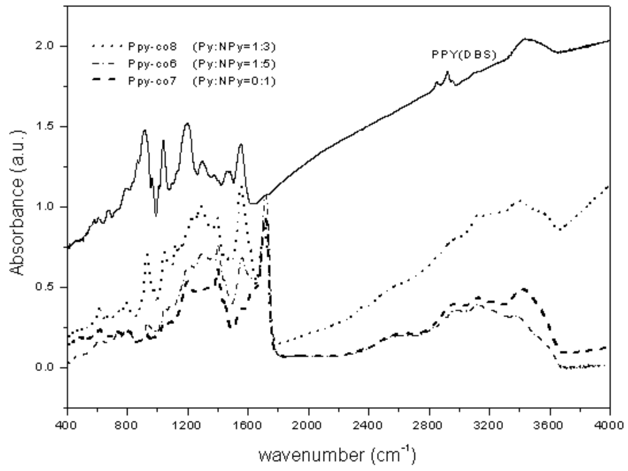


Fig. 5 FT-IR spectra of PPy, PPy-co6 , PPy-co7 , PPy-co8

The absorption bands characteristic for pyrrole ring vibrations are sensitive to the oxidation degree of the polymer. In Fig. 6 one can compare the FT-IR spectra of PPy doped with DBS and of two copolymers PPy-co 8 prepared without dopant and PPy-co 10 prepared with dopant DBS. The absorption bands which are typical for pyrrole ring vibrations shift to lower frequencies in the spectrum of the sample PPy-co 10 as compared with PPy-co 8, showing an increase of the oxidation level due to dopant addition.

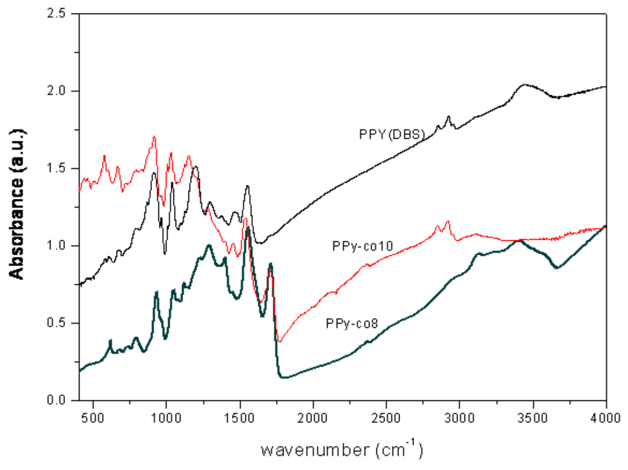


Fig. 6. FT-IR spectra of PPy, PPy-co 8 and PPy-co 10

4. Conclusions

Novel N-substituted polypyrroles were prepared by chemical polymerization of 3-(1-pyrrolyl)-propanoic acid. The morphology of the resultant copolymers shows smaller and uniform particles as compared with polypyrrole. The incorporation of the N-functionalized pyrrol in the copolymer chain can be seen in MAS ^{13}C-NMR spectra as well as in FTIR spectra. FT-IR spectroscopy of pyrrole copolymers further shows that conjugation length of the chains is influenced by the unsubstituted pyrrole/substituted pyrrole ratio. Some of the copolymers showed an increased solubility in organic solvents and in water.

The control of the substituted pyrrole copolymers properties by the synthesis parameters makes these materials suitable for further functionalisation by biomolecules and also for the easy functionalization of inorganic nanoparticles.

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