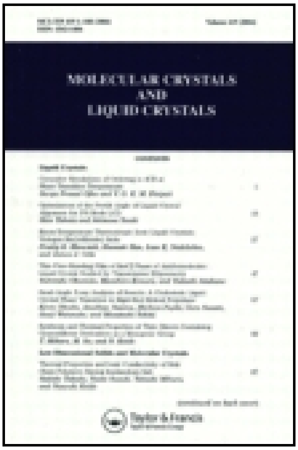

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Solution Processible Sulfosuccinate Doped Polypyrrole: Preparation, Spectroscopic and Spectroelectrochemical Characterization

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SOLUTION PROCESSIBLE SULFOSUCCINATE DOPED POLYPYRROLE: PREPARATION, SPECTROSCOPIC AND SPECTROELECTROCHEMICAL CHARACTERIZATION

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Oxidative polymerization of pyrrole in the presence of salts of two diesters of sulfosuccinic acid, namely sodium di(ethylhexyl) sulfosuccinate (abbreviated as NaDEHSS) or sodium dihexylsulfosuccinate (abbreviated as NaDHSS) have been investigated. It has been demonstrated that the processibility of the resulting polymer depends on the selection of an appropriate oxidant/dopant couple. If ammonium peroxydisulfate is used as the oxidizing agent the resulting polypyrrole combines solution processibility with spectroscopic and spectroelectrochemical properties of classical intractable doped polypyrrole. For these reasons polypyrrole doped with sulfosuccinate anions can be considered as a very promising material for the fabrication of polymer modified electrodes in various sensing devices or as a material for the fabrication of hole transporting layers in polymer photovolatic cells.

Keywords: diesters of sulfosuccinic acid; polypyrrole; solution processibility

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INTRODUCTION

Polypyrrole, although intensively studied in the past two decades because of its interesting electronic and electrochemical behavior, has so far very limited technological applications due to its intractability [1]. Therefore, any improvement in the processing of this polymer is of crucial importance. In 1992 Cao *et al.* [2], when working on new forms of polyaniline, developed the concept of so called "dopant induced processibility". In this approach the intractable polymer is being doped with specially designed dopant anions, containing solubilizing or plasticizing groups [3,4]. As a result, insoluble neutral polymer becomes solution processible after doping. Recently, the same concept was applied to polypyrrole by Oh *et al.* [5]. These authors showed that polypyrrole doped with anions originating from di(2-ethylhexyl) ester of sulfosuccinic acid (abbreviated as $DEHSS^-$) becomes solution processible. Moreover solution cast films of polypyrrole-di(ethylhexyl) sulfosuccinate show reasonably good conductivity of *ca.* 3 S/cm and excellent stretchability. Dialkyl or dialkoxy sulfosuccinates show similar influence on the properties of polyaniline improving its mechanical properties combined with conductivity exceeding 100 S/cm for unoriented samples [6,7].

In this communication we report on the preparation and spectroscopic properties of processible polypyrrole doped with $DEHSS^-$ and with another anion originating from the same family of diesters, namely dihexyl sulfosuccinate anion ($DHSS^-$). In particular we present the studies of the influence of the polymerization conditions on the processibility and electrical conductivity of the resulting polypyrrole-sulfosuccinate. We also describe voltammetric properties of these new polypyrrole based systems and discuss UV-vis spectral response on the increasing electrode polarization potential.

EXPERIMENTAL

Chemicals

Pyrrole (Loba – Chemie) was vacuum distilled prior to the use. Sodium dihexyl sulfosuccinate (NaDHSS) was prepared in the reaction of maleic anhydride (Laboratory BDH Reagent) with 1-hexanol (Merck) to give dihexyl maleate. The resulting ester was then sulfonated with sodium hydrogen sulfite (CHEMAN, Poland) following the procedure described in [8]. Other reagents i.e. sodium di(2-ethylhexyl) suflosuccinate (NaDEHSS) (Aldrich), ammonium peroxydisulfate, $(NH_4)_2S_2O_8$ (Aldrich), iron chloride, $FeCl_3$ (Fluka), iron sulfate, $Fe_2(SO_4)_3$ (POCh, Poland), hydrogen peroxide

H_2O_2 (Chempur, Poland), tetrabutylammonium tetrafluroborate Bu_4NBF_4 (Aldrich), chloroform (POCh, Poland), N-methyl-2-pyrrolidinone (NMP) (BASF), toluene (Chempur), acetonitrile (anhydrous Aldrich), were used as received.

Polymerization

Pyrrole oxidative polymerization procedure, in its main part similar to that reported in [8], can be described as follows. 0.022 mole of the sulfosuccinate (NaDEHSS or NaDHSS) were dissolved in 90 ml of water. To this solution, subsequently cooled to 5°C, 3 g of pyrrole (0.045 mole) were added. The mixture was vigorously stirred and additionally cooled to 0°C. At this stage the oxidant solution was slowly added drop-wise. Four types of oxidizing agents were tested: ammonium peroxydisulfate, iron chloride, iron sulfate and hydrogen peroxide. The exact compositions were as follows: 0.019 mole of $FeCl_3$ in 80 ml of H_2O, 0.011 mole of $Fe_2(SO_4)_3$ 200 ml of H_2O. In the cases of $(NH_4)_2S_2O_8$ and H_2O_2 the content of the oxidant was twice lower because the molecules of iron chloride and iron sulfate are one electron oxidizers whereas the molecules of ammonium peroxydisulfate and hydrogen peroxide are two electron ones. Thus, in the former case the composition of the oxidizing solution was as follows: 2.14 g of $(NH_4)_2S_2O_8$ in 20 ml of H_2O. In the latter case 3.65 g of sulfosuccinic acid were added to the solution of 1.06 g of 30% H_2O_2 in 20 ml of H_2O, in order to assure low pH of the oxidizing medium. The oxidizing/polymerizing reaction was carried out during 20 h at the temperature of 0°C. It was terminated by addition of 150 ml of methanol. The precipitated polymer was then filtered using a Büchner funnel and washed repeatedly with water/methanol mixture. Finally the obtained polymer powder was vacuum dried till constant mass.

Characterization Techniques

FTIR spectra of the investigated polymers were obtained using the KBr pellets technique. Conductivity measurements were carried out either on pressed pellets or on solution cast films using the standard 4-point technique with pressure contacts.

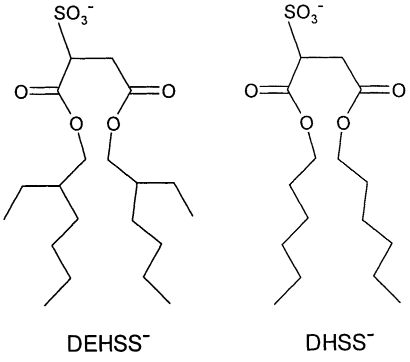
Solid state UV-vis-NIR spectra of sulfosuccinate doped polypyrrole were recorded on a Perkin-Elmer λ900 spectrometer equipped with a cryostat operating in the temperature range of 77–523 K. The spectra of thin polymer layers were recorded in the range from 190 to 296 K.

The Raman spectra were obtained using a FT Raman Bruker RFS 100 spectrometer with the near-IR excitation line (1064 nm).

All electrochemical and spectroelectrochemical experiments were carried out in acetonitrile solution of 0.1 M tetrabutylammonium tetrafluoroborate in single compartment cell with platinum gauze counter electrode and Ag/AgCl reference electrode using AUTOLAB potentiostat (Ecochemie, the Netherlands). For cyclic voltammetry investigations thin layers of the polymers were deposited on a platinum electrode by casting from chloroform solution. For spectroelectrochemical studies the polypyrrole films were cast on indium tin oxide (ITO) coated glass substrate and absorption spectra were taken using Lambda 2 (Perkin Elmer) spectrometer.

RESULTS

The doping anions tested in this research are shown in Scheme 1. Both doping agents render polypyrrole solution processible provided that they are used in combination with an appropriate oxidizing/polymerizing agent. Out of four oxidizing agents tested only ammonium peroxydisulfate yields solution processible polymer. The use of iron sulfate and iron chloride results in intractable conductive powders whereas oxidative polymerization with hydrogen peroxide leads to a pasty material of poor conductivity. The results of the conductivity measurements are collected in Table 1. Powders of intractable polypyrrole show significantly higher conductivity as compared to films of processible polypyrrole cast from solution. These differences in processibility and conductivity may have their origin in various factors such as different doping anion, different doping level or different supramolecular organization for the same doping anion. The case of polypyrrole obtained with iron chloride is easy to explain, since the elemental analysis shows only a small content of sulphur – one sulphur atom per 11 pyrrole unit. This means that sulfosuccinate is not the dominant dopant



SCHEME 1

TABLE 1 Room Conductivuty (σ) of Sulfosuccinate Doped Polypyrrole

Sample	Oxidant	Morphology	σ [S/cm]
PPy(DEHSS)	$(NH_4)_2S_2O_8$	Pressed pellet	1.5×10^{-2}
PPy(DEHSS)	$(NH_4)_2S_2O_8$	Film cast from:	
		$CHCl_3$	1×10^{-3}
		toluene	4×10^{-3}
		NMP	1×10^{-3}
PPy(DEHSS)	$FeCl_3$	Pressed pellet	2
PPy(DEHSS)	$Fe_2(SO_4)_3$	Pressed pellet	10
PPy(DHSS)	$(NH_4)_2S_2O_8$	Film cast from:	
		NMP	2×10^{-3}
		DMF	1.4×10^{-3}
		DMSO	3×10^{-4}

anion and the polymer is preferentially doped with chloride ion present in the reaction medium. Preferential doping of polypyrrole with Cl^-, in the reaction media containing various anionic species, has been reported [9]. It is especially pronounced in cases where the anions competing for doping are bulky as for example sulfosuccinates studied in this research. Elemental analysis shows however that polypyrrole is doped with the same sulfosuccinate dopant if ammonium peroxydisulfate or iron sulfate are used as the oxidizing agent. In both case the elemental analysis can be very well fitted assuming the following general formula of the doped polymer: $(PPy)^+{}_x(DEHSS)^-$ (see Table 2).

The main difference between intractable polypyrrole obtained with iron sulfate and that prepared with ammonium peroxydisulfate, which is solution processible, is the doping level. It is significantly higher in the former case. Doping of the polymer with sulfosuccinate anions should produce two effects which are opposite in nature. Increasing doping level results in an increase of the number of ester groups introduced to the polymer matrix which should facilitate its dissolution. On the other hand the charge imposed on the polymer chain also increases with the increasing doping level which renders the system more stiff and ionic in nature and by consequence more difficult to dissolve. Evidently at the doping level achieved with ammonium peroxydisulfate oxidant a delicate compromise between these two opposite phenomena is achieved whereas in the case of iron sulfate oxidant this optimum, for polymer dissolution, doping level is exceeded.

The presence of sulfosuccinate anions in solution processible polypyrrole is clearly manifested in its IR spectrum (Fig. 1). To a first approximation the spectrum of $(PPy)^+{}_{3.67}(DEHSS)^-$ can be treated as a superposition of the spectrum of oxidized polypyrrole and that of the

TABLE 2 Elemental Analysis of Polypyrrole-sulfosuccinates Obtained with Different Oxidizing Agents

	%C	%H	%N	%S
$Fe_2(SO_4)_3$oxidant				
Calc for $(PPy)_{2.75}$ DEHSS	62.03	7.54	6.42	5.36
Found	60.48	7.32	6.42	5.32
$(NH_4)_2S_2O_8$ oxidant				
Calc for $(PPy)_{3.67}$ DEHSS	63.10	7.28	7.79	4.85
Found	61.90	7.42	7.80	4.85

dopant. The principal bands attributed to the vibration of the polypyrrole chain [5,10,11] at 1554 cm^{-1}, 1481 cm^{-1}, 1380 cm^{-1}, 1288 cm^{-1}, 1039 cm^{-1}, 962 cm^{-1}, 914 cm^{-1} and 788 cm^{-1} are accompanied by peaks characteristic of the vibrations of the dopant anions. In particular the bands originating from the C-H stretchings in the alkyl substituents of the ester group can be distinguish in the spectral range 2850–2950 cm^{-1} together with a clear peak at 1732 cm^{-1} which is due to $C = O$ stretching deformations. The broad peak at 1207 cm^{-1} can be interpreted as a result of the overlap of the band originating from the dopant (at 1220 cm^{-1} in NaDEHSS) and the band ascribed to pyrrole ring breathing (at 1185 cm^{-1} in $(PPy)_xCl$).

In the Raman spectrum of $(PPy)^+_{3.67}(DEHSS)^-$ (Fig. 2) only bands characteristic of the oxidised polymer chain are present whereas no peaks

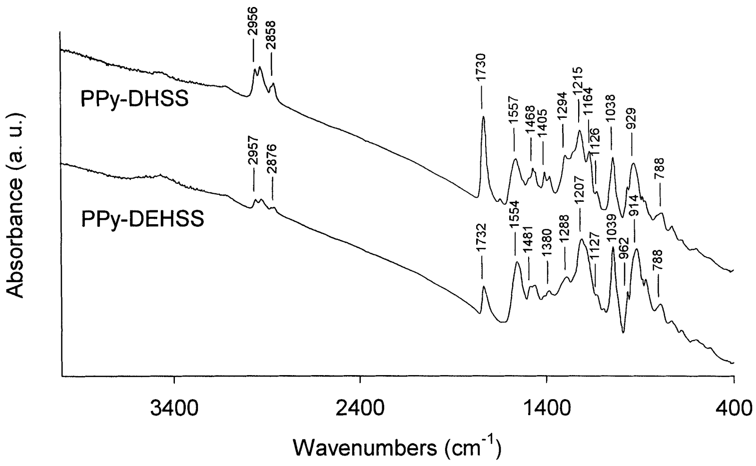


FIGURE 1 FTIR spectra of PPy-DHSS and PPy-DEHSS.

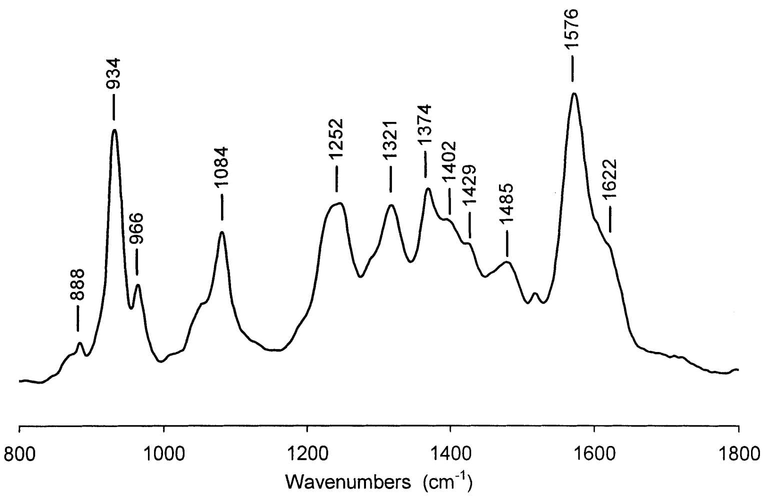


FIGURE 2 Raman spectrum of PPy-DEHSS.

which could be ascribed to the dopant anions are detected. This is not unexpected since the bands originating from the oxidised polymer chain undergo strong resonant enhancement for the applied excitation line ($\lambda_{exc} = 1064\,nm$) rendering other raman bands "invisible". The oxidized chain can adopt the charge, imposed upon the doping reaction, in two storage configurations: in a form of radical cations (polarons) or diactions (bipolarons). For $(PPy)^+_{3.67}(DEHSS)^-$ the dications are predominant charge storage configurations as judged from the intensity of the bands at 934 cm^{-1}, 1084 cm^{-1} and 1374 cm^{-1} characteristic of this species [12–14].

It has recently been demonstrated [6,7] that polyaniline doped with plasticizing dopants such as sulfosuccinates or sulfophthalates exhibits the phenomenon of thermochromism at unusually low temperatures. In polyconjugated systems thermochromism is always registered at temperatures exceeding glass transition temperature, Tg, since it requires chain conformation changes. Its occurrence at sub-zero temperatures, in polyaniline doped with sulfosuccinate ions, unequivocally shows that the polymer is plasticized with the introduced dopant which leads to a significant lowering of the Tg value. Very similar low temperature thermochromism is also observed in the case of solution processible $(PPy)^+_{3.67}(DEHSS)^-$. Figure 3 shows UV-vis-NIR spectra of thin films of this polymer deposited on a quartz substrate by casting from NMP solution. The spectrum registered at room temperature is very similar to that reported in [5] and consists of a relatively sharp peak at 430 nm and a broad absorption

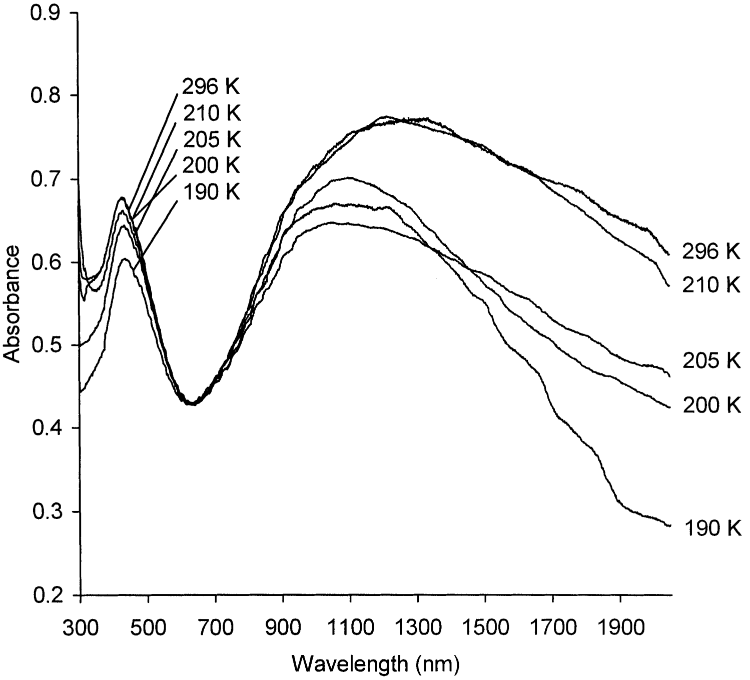


FIGURE 3 UV-Vis-NIR spectra of thin film of PPy-DEHSS registered for the temperature range of 296–190 K.

covering essentially whole NIR region of the spectrum. The latter one is ascribed to delocalized charge carriers (dications) and can be considered as a spectroscopic manifestation of the metallic character of the doped polymer. As seen from Figure 3 upon lowering of the temperature, the NIR band ascribed to charge carriers narrows implying their increasing localization and by consequence less metallic character. It is interesting to note that this line narrowing starts below 210 K i.e. in the same temperature range as in the case of polyaniline doped with the same dopant [7].

$(PPy)^{+}{}_{3.67}(DEHSS)^{-}$ prepared by chemical oxidation with $(NH_4)_2S_2O_8$ is electroactive and can be electrochemically de-doped and re-doped. Its cyclic voltammogram, recorded in Bu_4NBF_4/acetonitrile electrolyte, is presented in Figure 4. It should be noted here that in polyconjugated macromolecular systems the first voltammogram is distinctly different from the consecutive ones because of so called “memory effect” closely associated with the relaxation phenomena in the polymer matrix [15]. After few cycles the shape of the cv curve stabilizes. In the stable cycle the de-doping process gives rise to a cathodic peak with maximum at −0.36 V. This

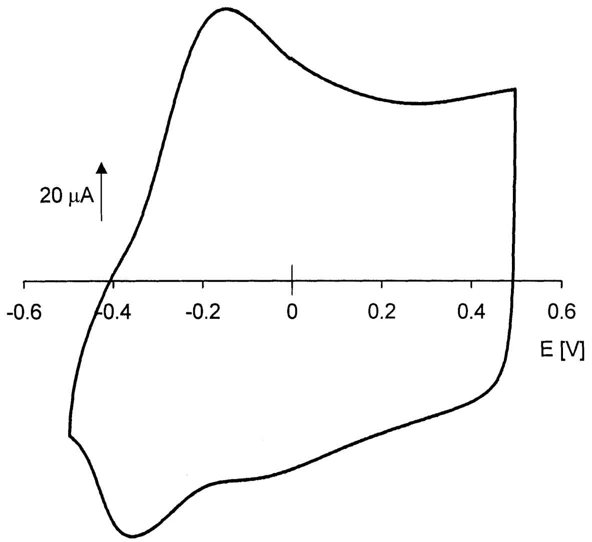


FIGURE 4 Cyclic voltammogram of PPy-DEHS film on platinum electrode registered in 0.1 M Bu_4NBF_4/acetonitrile solution at 50 mV/s. Potentials measured versus Ag/AgCl reference electrode.

de-doping can consist of the transformation of macromolecules of polycationic nature into neutral ones. This process must be accompanied either by the removal of the dopant anions from the polymer matrix or by incorporation of cations originating from the electrolyte to the polymer matrix. Since the sulfosuccinate dopants are rather bulky and their diffusion coefficient is in the polymer matrix is rather low, the latter process seems more probable. Moreover de-doping via cations incorporation was reported for PPy doped with dodecylsulfate on the basis of spectroscopic studies of the polymer in the reduced state [11]. Anyhow, electrochemical quartz microbalance and spectroscopic studies of the polymer in the reduced and doped states must be carried out in order to verify the de-doping mechanism proposed above. Such investigations are in progress. The doping of neutral polymer is manifested by an anodic peak at −0.14 V. This doping, which converts neutral polymer chains into polycations, must proceed via cation removal if the neutral polymer contains dopant anions and cations neutralizing them or alternatively via incorporation of anions originating from the electrolyte. If the de-doping mechanism involves cation incorporation the re-doping mechanism must automatically proceed via cation removal. Unusually high capacitive current observed in the potential range from 0 V to 0.5 V is characteristic of the majority of electroactive conjugated polymers [16].

In Figure 5 the results of UV-vis-NIR (till 1100 nm) spectroelectrochemical investigations are presented. The open circuit voltage of a $(PPy)^{+}_{3.67}$ $(DEHSS)^{-}$ thin film, deposited on a platinum electrode, is +0.14 V. The polarisation of the electrode to −0.3 V results in a total transformation of the polymer spectrum. At E = −0.3 V the spectrum is characteristic of neutral PPy with only one peak at 390 nm. Re-doping of the polymer at E = +0.4 V results in a bathochromic shift of the band characteristic of the neutral polymer and the appearance of a broad band extending towards near infrared which is characteristic of the doped state. One must however note that the spectrum of as prepared $(PPy)^{+}_{3.67}(DEHSS)^{-}$ and that of the polymer electrochemically de-doped and then re-doped are different although both show features of the doped state. This means that the de-doping and re-doping processes must be more complex than describe above and in addition to simple cation injection and ejection may involve other phenomena which influence polymer chain conformation.

Preliminary experiments show that solution processible polypyrroles studied in this research can be used as hole transporting layers in organic photovoltaic cells [17].

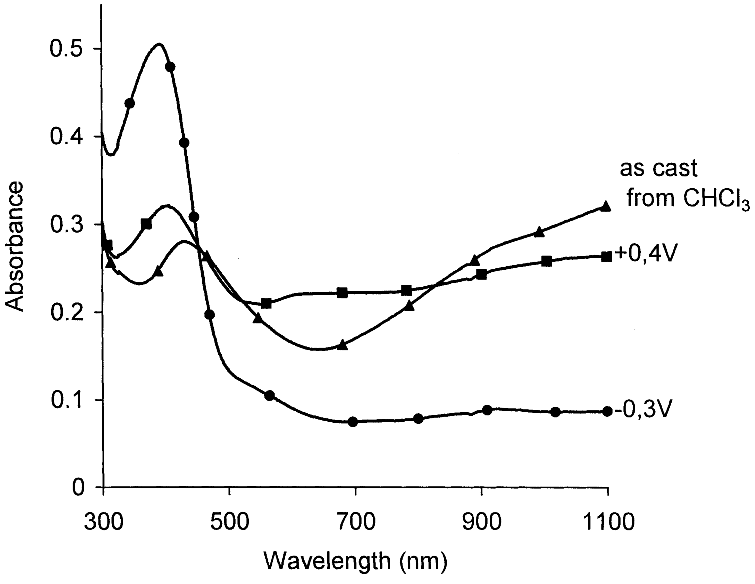


FIGURE 5 UV-Vis-NIR spectra of thin film of PPy-DEHSS registered at different potentials in 0.1 M Bu_4NBF_4/acetonitrile solution.

CONCLUSIONS

To summarize, we have demonstrated that solution processible PPy obtained by chemical oxidation of pyrrole with ammonium peroxydisulfate in the presence of sulfosuccinate anions shows very interesting spectroscopic properties including low temperature thermochromism, reported for the first time for doped polypyrrole. Moreover thin layers of this solution processible polymer are electroactive and show cyclic voltammograms very similar to those recorded for electrochemically synthesized polypyrroles. This last property is of significant practical importance because it facilitates the fabrication of polypyrrole based hole transporting layers in polymer photovoltaic cells as well as the fabrication of modified electrodes for various sensing applications.

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