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RISE IONBIKE

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Table of Content

1 Objective

Protocols for preparation of functionalized PEDOT/biopolymer dispersions and new semiconjugated polymers.

2 Description of tasks

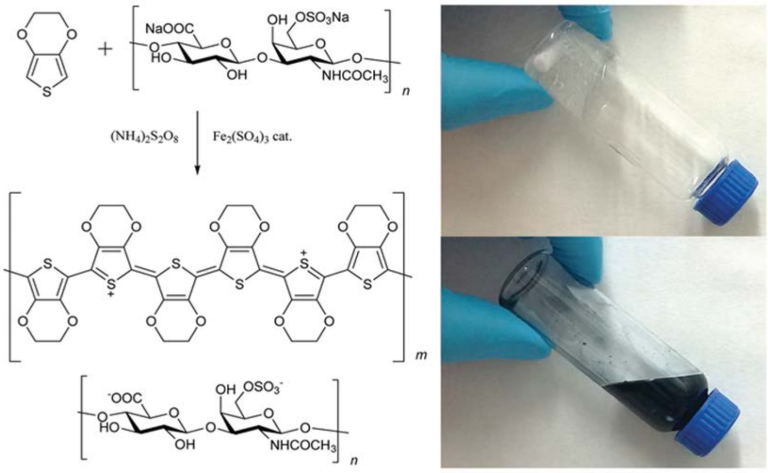
This deliverable corresponds to the activities carried out in the first year of the project of the task 1.4 Preparation of PEDOT/Polysacharide dispersions and new semiconducting polymers. In this period, three main contributions can be highlighted. First, the synthesis of PEDOT/polysaccharide dispersions, the synthesis of a water soluble PEDOT cationic derivative and the synthesis of new functional poly(hexylthiophenes). Nest we will describe the main activities in the three topics:

2.1 Synthesis of PEDOT/polysaccharide dispersions

In most bioelectronics applications, the fine tuning of the interface of conducting polymers and biological molecules or tissues/organisms is a crucial parameter. As one illustrative example, the biotic/abiotic interface for interfacing with live cells can be improved by the incorporation of biological molecules such as nucleotides or proteins for functionality, e.g., for sensing. In this way, the biofunctionalized conductive polymer can enhance their ultimate properties such as biocompatibility and adhesion, and could help to reduce the inflammatory response of a device in living tissue. The two components of PEDOT:PSS are limited, due on the one hand to the lack of functionality of PEDOT and on the other hand to the low biocompatibility of PSS.

A demonstrated strategy to enhance the biocompatibility and reduce the cytotoxicity of conducting polymers like PEDOT is the use of biomolecules as dopants. Thus, the incorporation of biopolymers could be the way to overcome the limitations of PEDOT:PSS dispersions for specific applications. Although PEDOT:PSS has proven to be an appropriate material for cell culture, the aim is to provide an environment that stimulates and persuades cell growth. Within this period we followed our work in the synthesis of different water-based PEDOT:biopolymer dispersions using chemical polymerization.

PEDOT:biopolymer aqueous dispersions synthesized by chemical polymerization have been reported using DNA, sulfated cellulose, dextran sulfonate, hyaluronic acid , heparin, chondroitin sulfate, pectin and guar gum. The synthesis of all of them is very similar and it can be exemplified in Figure 1 for the case of PEDOT:hyalunoric acid dispersions. A typical PEDOT:biopolymer dispersion is synthesized by chemical oxidative polymerization of the EDOT monomer using an oxidant in the presence of a biopolymer as a stabilizer and dopant. However, some parameters vary from one synthesis to another, and these include the PEDOT:biopolymer ratio, reaction temperature, concentration, time and oxidant used. In a typical experimental set-up, these biomolecules and EDOT are firstly dissolved in water; once dissolved, the oxidant is added to the solution. This oxidant can be ammonium persulfate ($(NH_4)_2S_2O_8$), potassium persulfate ($K_2S_2O_8$), iron (III) chloride ($FeCl_3$) or iron (III) p-toluenesulfonate ($(CH_3C_6H_4SO_3)_3Fe$). A catalyst is often employed such as iron (II) sulfate ($Fe_2(SO_4)_3$) to accelerate the reaction kinetics. Once the reaction is complete, the dispersions are purified by ion exchange, filtered and/or dialyzed.



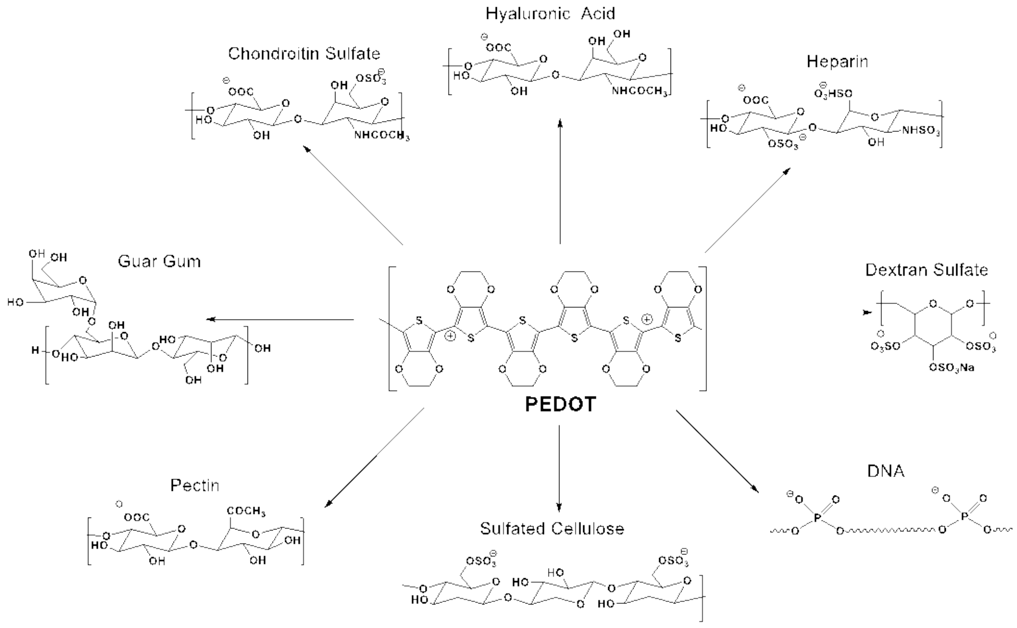
Scheme 1. Synthetic route to PEDOT:hyaluronic acid aqueous dispersions.

The PEDOT:biopolymer dispersions have a macroscopic aspect similar to PEDOT:PSS dispersions. As it can be seen in the picture of Scheme 1 , dark blue dispersions are obtained. The dispersions are formed by PEDOT particles of sizes between 100–500 nm stabilized by the biopolymer. Particle size and morphology can be studied by UV-spectroscopy, light-scattering, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Similarly to PEDOT:PSS, the PEDOT:biopolymer dispersions can be processed in the form of thin films or the solution formulated to be inkjet printed, extrusion printed and spray coated. The electrochemical properties of the PEDOT:biopolymer films, for instance PEDOT:dextran sulfate or PEDOT:DNA present similar features to PEDOT:PSS.

Furthermore, the electrical conductivity of drop-casted or spin-coated films presents similar values to pristine PEDOT:PSS without further treatments of between 10^{-1}–10 S cm^{-1}. Using this chemical polymerization method, different PEDOT:biopolymer dispersions have been prepared as shown in Scheme 2 and summarized in Table 1. The advantages of each PEDOT:biopolymer material in comparison to PEDOT:PSS are discussed here. In the case of the PEDOT:DNA complex, the main advantages are its higher conductivity with respect to PEDOT:PSS and its non-acidic nature In the case of PEDOT:sulfate cellulose, it shows a higher conductivity than PEDOT:PSS which has been attributed to a higher proportion of PEDOT chains of quinoid structure than in PEDOT:PSS. In the case of PEDOT:glycosaminoglycans, they provide functional support in neuroregenerative processes and in the case of chondroitin sulfate, additional protection in oxidative milieu. Although some of these dispersions were already reported in the scientific literature (some by us) the work here was to reproduce and to establish solid synthetic protocols for the scale-up synthesis of the dispersions. Within IONBIKE protocols for the synthesis of 1 L PEDOT/biopolymer dispersions were established.

Table 1. Available PEDOT:biomolecule dispersions prepared by chemical oxidative polymerization. Achieved conductivities, particle size and morphology

PEDOT:biopolymer.	Conductivity (S·cm−1)	Particle size and morph.
PEDOT:dextran sulfate 92	7	394–691 nm
PEDOT:DNA 96	1	50 nm fibers
PEDOT:heparin 93	0.05–0.001	>1 µm spheres
PEDOT:chondroitin Sulfate 93	0.075–0.002	500 nm spheres
PEDOT:hyaluronic acid 93	0.071–0.003	200 nm spheres
PEDOT:sulfated cellulose 91	0.576	250–350 nm
PEDOT:pectin 94	<0.01	-
PEDOT:guar gum 95	0.028–0.129	100–300 nm spheres

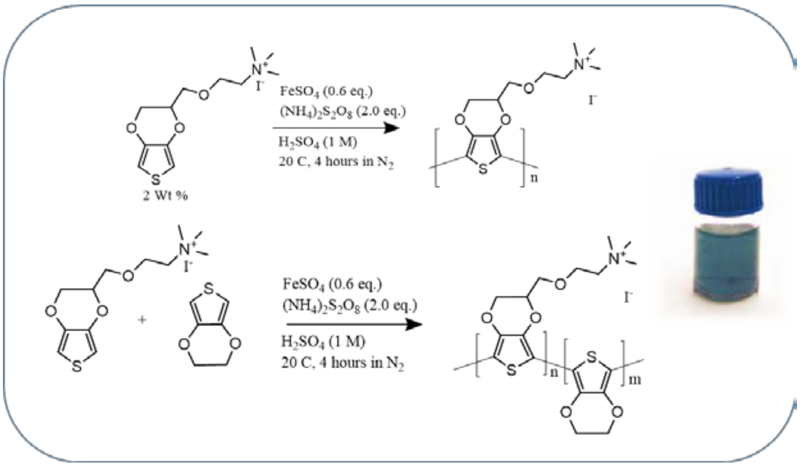


Scheme 2. PEDOT:biopolymer dispersions employing hyaluronic acid, heparin, chondroitin sulfate, dextran sulfate, DNA, sulfated cellulose, pectin, and guar gum.

To sum up, in this period we prepared a number of PEDOT/biopolymer aqueous dispersions. These dispersions could be processed in the forms of thin conductive films. Within IONBIKE Rise in the next periods those dispersions will be investigated to produced biocompatible iongels which show mixed ionic and electronic conductivities.

2.2 Synthesis of cationic water soluble PEDOT derivative

Among the different electrically conducting polymers used in bioelectronics, the conducting polymer PEDOT (poly(3.4ethylenedioxythiophene) is the most popular one. PEDOT is usually processed from an aqueous dispersion as in the case of commercially available PEDOT/PSS in the forms of transparent conducting films that can be used as conducting layers, hole transporting layers in difference devices such as OECTs as well as for cell-growth and stimulation. Recently, anionic water soluble PEDOT-S materials were also developed which offers some advantages such as the self-doping nature and the real water solubility of it thanks to the presence of sulfonate groups. In any case, both PEDOT/PSS or PEDOT-S are anionic polyelectrolytes which may not interact and complex with naturally abundant anionic groups available in biomolecules such as carboxylates. For this reason, the goal in this period was to develop a water soluble and processable PEDOT-N polymer with cationic nature.



Scheme 3: Synthetic route towards new water soluble cationic PEDOT-N

The synthetic route towards water soluble PEDOT-N materials is described in Scheme 3. For this purpose, we designed an EDOT cationic monomer having an quaternary ammonium group. This monomer was homopolymerized as shown in the upper reaction or copolymerized with EDOT monomer. The polymerization was carried out by using a chemical oxidating agent such as ammonium peroxidisulfate in the present of a catalytic amount of Iron sulphate in an acidic aqueous media for 4 hours at 20 ºC. After reaction a dark blue precipitate was obtained which was further filtered and cleaned with water several times. In the second case a series of copolymers having different amount of EDOT_N monomer and EDOT were synthesized. In all the cases the yields of the reaction were higher than 85 %. As an initial proof of concept the obtained PEDOT-N powder was dissolved in water leading to a blueish solution typical color of conductive PEDOT materials. Next, the obtained (co)polymers were characterized by UV-VIS and FTIR as shown in Figure 1.

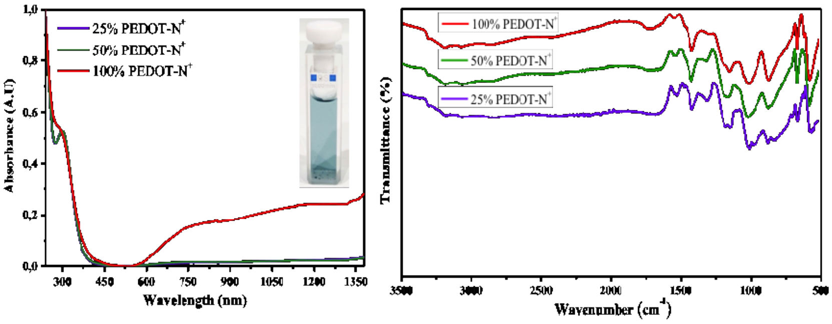


Figure 1: Left side, UV-VIS spectra of aqueous solution of PEDOT-N copolymers and right side,FTIR spectra of PEDOT-N copolymers

As it can be seen in the UV spectra, the PEDOT-N copolymers show the typical blue color and absorption bands of conductive PEDOT. This is a broad bipolaron band after 600 nm that goes well into the near-visible range. In the case of the PEDOT-N homopolymer this band is more intense than in the case of the copolymers probably due to its higher solubility in water. The FTIR bands of all the copolymers show the typical bands associated with PEDOT thiophene backbone. Some differences are observed in the relative intensity of the bands which is associated to the different EDOT-N/EDOT units ratio.

Then the different aqueous solutions were analysed deposited onto a TEM grid in order to analyse the type of particles formed by PEDOT-N copolymers. As it can be seen in the Figure 2 in the PEDOT-N homopolymer image is not possible to see the presence of any spherical particle in solution. Which proves that PEDOT-N+ is a real solution of PEDOT. However in the case of the copolymers between EDOT-N and EDOT spherical particles are observed. Those particles are smaller at high ammounts of EDOT-N+ 50% (20-40 nm) than in the case of smaller ammounts of EDOT-N+ 25% where big particle aggregrates are observed. In the case of the copolymers it seens to indicate that more than a real solution, a dispersion of PEDOT particle is obtained as in the case of commercially available PEDOT/PSS. In anycase all the copolymers are stable in water for more than 2 days.

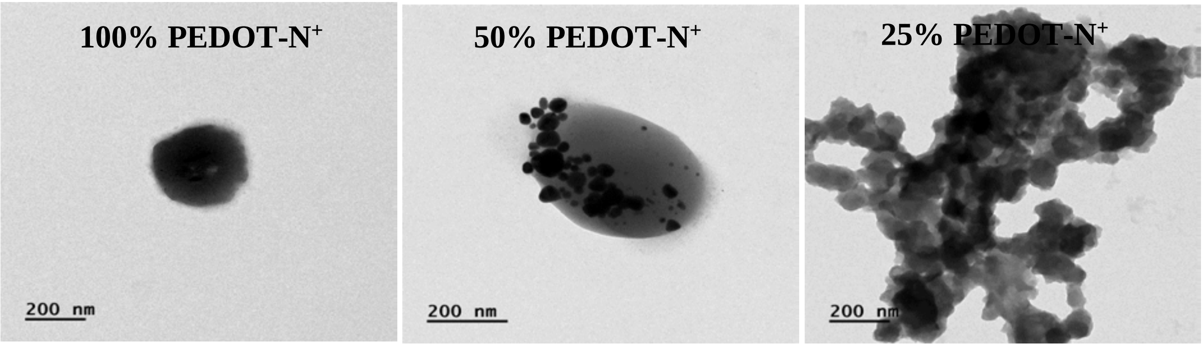


Figure 2: TEM images of PEDOT-N and PEDOT-N-PEDOT copolymers having 50% EDOT-N units and 25 % EDOT-N units respectively

After confirming the water solubility and the chemical structure of the PEDOT-N copolymers we verified its properties and the conductivity of its films after casting. As it can be seen in the Table the zeta potential results show that the PEDOT-N copolymers are cationically charged and the potential increases with the amount of EDOT-N cationic units in the copolymes. Furthermore, the conductivity of the films is in the order of 10^{-2}-10^{-1} S/cm. There is a trend in the electrical conductivity and the values are higher in the case of copolymers with higher PEDOT content. It is worth to note that the values are similar to the non-treated commercially available PEDOT/PSS dispersions.

		25%	**50%**	**100%**	**PEDOT-N^+ Cl^-**
Zeta Potential	Zeta potential (mV)	12,8	14,8	20,6	
Conductivity	Conductivity (S/Cm)	0,1242	0,0623	0,0318	0,0438
DLS	Z Average (nm) | Std d.	30790 ± 2445	6046 ± 1563	2658 ± 1088	

Next, the conductive PEDOT-N films were characterized by SEM microscopy. As it can be seen in images the PEDOT-N homopolymer after casting shows a continuous structure typically obtained from a soluble polymer precursor. The film surface is quite regular and the films is continuous. However in the case of PEDOT-N copolymers the SEM image shows the structure of a irregular film typically obtained from an nanoparticle dispersion. Although continuous films are obtained the surface is quite rough. This effect is clearly observed in the copolymers with higher amount of EDOT vs EDOT-N+ and it is clearly related to the TEM pictures of the solution/dispersions.

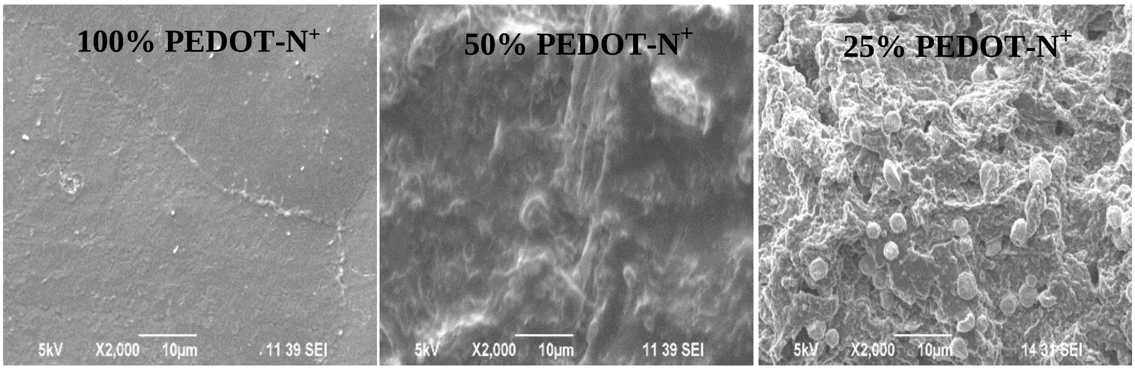


Figure 3: SEM images of films obtained from PEDOT-N and PEDOT-N-PEDOT copolymers having 50% EDOT-N units and 25 % EDOT-N units respectively

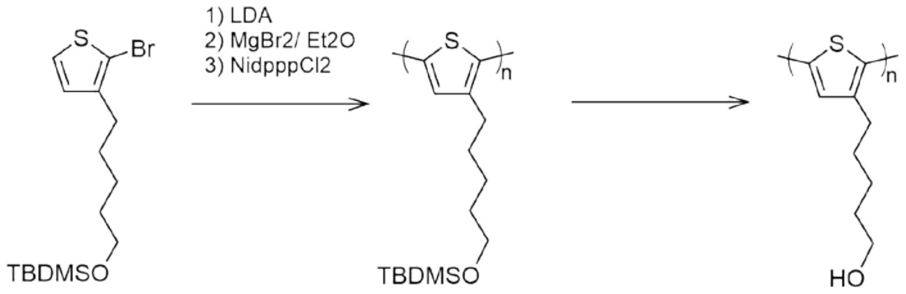
To finish we investigated the processabiity of the PEDOT-N+ materials. As illustrated before, thin conductive polymer films could be obtained by simple casting from the aqueous solution. The films showed electrical conductivity levels similar to other commercially available PEDOT/PSS materials. Furthermore, we wanted to show that the PEDOT-N+ copolymers could be further processed and integrated into a hydrogel material. For this purpose, different ammounts of PEDOT-N homopolymer were dissolved in the presence of PEGDA-diacrylate and a photoinitiator. By simple photopolymerization different conducting hydrogels could be easily prepared as shown in the figure 4.

Figure 4: Pictures of hydrogels containing different amount of PEDOT-N polymers.

To sum up, in this deliverable we show the synthesis of a new water soluble and processable cationic PEDOT-N copolymer. The PEDOT-N materials show the typical features of PEDOT such as UV absorbance, bipolarond band, electrical conductivity values and film formation ability. By modifying the EDOT-N and EDOT ratio different copolymers were obtained. The PEDOT—N homopolymer show the higher solubility in water and best quality films. By increasing the amount of EDOT, PEDOT nanoparticle aqueous dispersions were obtained which leaded to more irregular films but with slightly higher conductivity values. The water solubility of PEDOT-N materials allows its processability also in the form of hydrogels. In the next months we will investigate the incorporation of PEDOT-N polmers into ionogels which show mixed ionic/electronic conductivity.

2.3 Synthesis of new semiconducting polymers

Initial focus for the synthesis of ion precursors was centred around designing building blocks that can conduct ions as well as electronic charge carriers. As a promising alternative to currently employed motives, we explored the use of hydroxyhexyl-functionalized side-chains combined with backbones that have been developed for the organic thin-film transistor- and solar cell- field was selected. We selected poly[3-(6-hydroxy)hexyl thiophene] (P3HHT) as model system: i) because hydroxyl groups render conjugated polymer semiconductors hydrophilic and, thus, more compatible with biological enviromentments. Ii) their synthesis is facile, requiring only a protection and deprotection step with respect to typical synthetic procedures. iii) the hydroxyl group is well distanced from the aromatic moiety of the monomer and, thus, does not affect its reactivity during polymerization, yielding highly regioregular polymers as the final product, in contrast to e.g. materials with oligoethylenegycol-based side chains.



Scheme 4. Synthesis route selected towards poly[3-(6-hydroxy)hexyl thiophene] (P3HHT)

P3HHT polymers were successfully synthesized. Gel Permeation Chromatography of P3HHT precursor revealed a number-average molecular weight, M_n of 41000 g/mol and a weight-average molecular weight of M_w = 66000 g/mol (Đ = 1.6). After deprotection of the side-groups, a M_n of 25000 g/mol and M_w = 41000 g/mol was obtained.

Beneficially, P3HHT films show water contact angles comparable with PEDOT:PSS films prepared from typical formulations used in state-of-the-art bioelectronics devices (see Figure 1), suggesting good surface hydrophilicity, important for the envisioned use of such materials in bioelectronics applications. Moreover, simple passive swelling experiments performed with Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) show only a minor change in thickness during swelling (+2.4%) for a 92-nm P3HHT film upon exposure to flowing 0.1 M electrolyte solution, the common concentration used in benchmarking organic electrochemical transistor (OECT) materials. This is swelling is minute compared to cross-linked PEDOT:PSS which shows a volume change of up to 90% leading to sever device stability issues; and even glycolated mixed conductors (p(g2T-TT) usually show volume changes of around 10-15% that can result in device failure after multiple cycling. In the next period we will investigate the use of those polymers in OECT devices within WP3.

3 Description of work & main achievements

Within this first year of the project, we established the protocols for preparation of functionalized PEDOT/biopolymer dispersions and new semiconjugated polymers. The main achievements were:

- Scale-up synthesis up to 1 L of PEDOT/biopolymer dispersons which is applicable to many different types of biopolymers
- Development of a new cationic PEDOT derivative, PEDOT-N which is water soluble and can be used to develop new ionogels.
- Synthesis of new hydroxyl functional P3HT semiconducting type polymer derivatives.

4 Deviations from the workplan

The work was carried out without deviations from the workplan.

5 Performance of the partners

The development of PEDOTs whithin this deliverable was carried out at partner UPV/EHU, during the secondments visit from/to Deakin University, Universidad de Rio Cuarto and Universidad Nacional de Litoral. The development of new semiconducting polymers was carried out at LCPO in collaboration with KAUST.

6 Conclusions

The activitities and results carried out during the first year of the project showed that this deliverable was fulfilled in a very satisfactory manner.