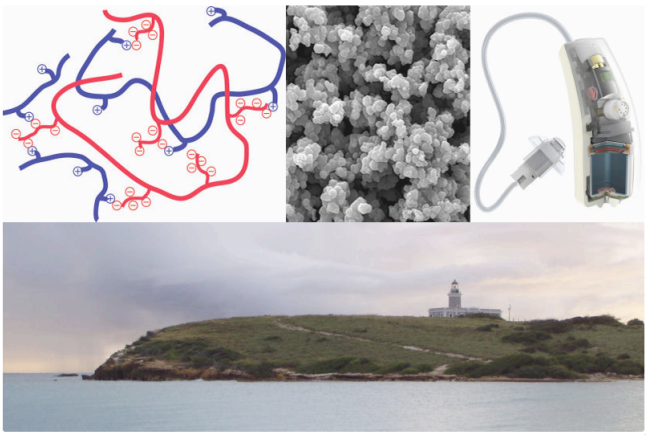

Organization

- Polymer Division of the Slovak Chemical Society
- Polymer Institute, Slovak Academy of Sciences, Bratislava
- Technical University of Denmark, Lyngby
- Danish Society for Polymer Technology
- Associazione Italiana di Scienza e Tecnologia delle Macromolecole
- Universtiy of Pisa, Dept. of Chemistry & Industrial Chemistry, Pisa
- University of East Piemonte, Alessandria
- University of Milan

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INVITED LECTURES

IL 1

SURFACES, INTERFACES AND ORGANIC BIONICS

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Abstract

Effective interfacing of biological systems with man-made materials and structures should revolutionise medical science.

Interfacing biology and electronics (bionics) has already resulted in prosthetics such as the bionic ear and the bionic eye, treatments for Parkinson's disease and epilepsy. At present the performance of such devices and the realization of others remains limited by the fidelity of information that can be transmitted across the electrode-cellular interface[1,2].

A number of significant advances have occurred and these have fuelled progress in bionics.

- Discovery of new organic conductors (including graphene, carbon nanotubes and inherently conducting polymers)[3,4].
- Development of new fabrication strategies (including 3D printing) that enable the realization of complex structures with control over spatial distribution of composition[5,6,7].
- Development of new biofabrication tools giving unprecedented insights into biomolecular events occurring at the interface with new electrodes[8].

Here, we will present our recent contribution to each of these areas.

We will do so in the context of our pursuit of devices for real clinical applications to enable the realization of

- Implanted conduits for nerve and muscle regeneration.
- Implanted bionic devices for epilepsy detection and control.

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IL 2

ELECTROACTIVE FABRICS FOR TISSUE ENGINEERING AND SOFT ROBOTICS

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Abstract

Electroactive polymers (EAP) such as conducting polymers are interesting materials not only for printed, low cost electronics, photovoltaics and light emitting devices but also for use in soft actuators. These "smart" materials deform in response to electrical simulation and are often addressed as artificial muscles due to their functional similarity with natural muscles. The materials operate at low voltages, can use aqueous electrolytes and have been shown to be biocompatible. In addition since the materials are both ion and electronic conductive they can be an interface between traditional hard electronics that communicate by electrons and soft, wet biological materials such as tissue and cells that predominantly communicate by ionic signals. This makes the materials interesting candidates for bioelectronic applications including tissue engineering. Likewise the fact that they are lightweight and operate silently makes them suitable as compliant actuators for soft robotics.

Tissue engineering and stem cell therapy are the promising treatments of cardiac infarctions. The stem cell niche is vital for the proliferation and differentiation of stem cells and tissue regeneration. An artificial carrier, e.g. a scaffold, is needed to introduce stem cells into the host tissue as direct injection of stem cells showed fast stem cell death. We are currently developing EAP scaffolding fabrics for cardiac tissue engineering. The electrospun EAP scaffold mimics the extracellular matrix and provides a 3D microenvironment that can be easily tuned during fabrication, such as controllable fibre dimensions, alignment, and coating. In addition, the scaffold provides electrical and electromechanical stimulation[1] to the stem cells which are important external stimuli to stem cell differentiation. This stimulation is expected to increase the differentiation ratio of stem cells into cardiomyocytes[2,3]. Excellent biocompatibility was achieved using primary cardiovascular progenitor cells[4]. We present the fabrication, electrochemical and electromechanical characterisation as well as the response of the stem cells to the scaffolds and to the stimulation.

Likewise we can use advanced textile technology to create a new type of soft actuators: electroactive textiles. Textile technology allows for a rational assembly of fibres. We developed new EAP based fibres, or yarn, employing a metal-free combined chemical-electrochemical synthesis route[5] and assembled them in to EAP fabrics that show enhanced performance over individual fibres. We will present the fabrication and characterisation of these fibres and fabrics as well as their performance as linear actuators.

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IL 3

CONDUCTIVE POLYMER HYBRIDS: THE ROLE OF COUPLING AGENTS AND SURFACTANTS

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Abstract

Conductive polymer hybrids are the subject of numerous studies. These materials provide the possibility to design devices with a new functionality, where the best of both organic and inorganic, or insulating organic and conductive organic can be utilized. Conductive polymer hybrids concern so many applications such as coatings, fillers, sensors, adsorbents, nanocomposites, and so on. However, one key issue is to control the interface using surfactants or coupling agents.

Herein we summarize our findings on the use of surfactants [1] or coupling agents such as silanes [2] and aryl diazonium salts [3] for making:

- adherent coatings on inorganic and flexible organic substrates (PET, PEN)
- intercalated and exfoliated clay-polypyrrole nanocomposites
- core-shell carbon nanotube-polyaniline nanocomposites
- fillers for thermoplastics and thermosets

to name but a few applications.

The emphasis will be on the paramount role of the surface modifiers or coupling agents in improving adhesion of the conductive polymer to the substrate and the effect on the performances of the hybrid conductive systems.

Acknowledgements

Part of this work has been supported by IFCEPAR/CEFIPRA through the Flexi-Sensors project No 4705-2.

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IL 4

CONDUCTIVE PDMS ELASTOMERS: HOW TO OBTAIN AN EFFICIENT DISTRIBUTION OF FILLERS

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Abstract

Polydimethylsiloxane (PDMS) elastomers employing conductive fillers are used in many applications for e.g. flexible electrode materials or with lower amounts of fillers for high capacitance elastomers. Traditionally, the most commonly applied filler in such applications has been carbon black, which through high loading results in sufficiently high conductivities. During recent years, the range of conductive fillers has been extended to include i.e. expanded graphite, single walled carbon nanotubes and multi walled carbon nanotubes (MWCNTs), whereof in particular MWCNTs are interesting due to their outstanding electrical and mechanical properties. However, the use of MWCNTs for many new applications requires efficient processing strategies in order to result in elastomers with an efficient and reproducible dispersion of the nanomaterial. If efficient dispersion of the nanomaterial in the PDMS precursors is achieved, the mixture should furthermore be able to crosslink without interference from the nanofiller[1]. There are several possible pathways to obtain such dispersions, where these could be divided into two main strategies, direct mixing using processing equipment or modification of the MWCNTs followed by traditional preparation of the crosslinked elastomer. Both pathways have been investigated and the presentation will outline results from both approaches.

Direct processing of the MWCNTs together with PDMS prepolymers by mechanical mixing, sonication, speedmixing or roll milling have been investigated. It is very clear that in order to obtain sufficiently effective dispersion, it is necessary to use the more efficient methods such as roll milling or speed mixing to distribute the fillers. As an alternative to direct mixing, modification of MWCNTs is a well-known approach to ease dispersion of nanomaterials. This can be done by surface initiated polymerizations by e.g. atom transfer radical polymerization (ATRP) using compatibilizing monomers. Through the surface initiated polymerization a thin coating of polymer is introduced on the MWCNTs to prevent agglomeration and permit much easier dispersion into the targeted polymer such as a PDMS prepolymer.

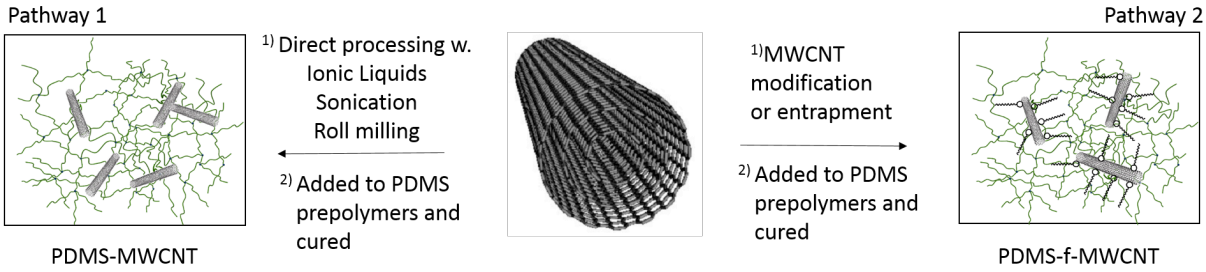

Figure 1: Dispersing MWCNT effectively in PDMS by Pathway 1: Direct processing or Pathway 2: Modification or entrapment and subsequent crosslinking.

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IL 5

SYNTHETIC STRATEGIES TOWARDS ANION AND PROTON EXCHANGE MEMBRANES WITH ENHANCED MORPHOLOGICAL CONTROL AND CONDUCTIVITY

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Abstract

Durable polymers functionalized with acidic and basic groups are currently developed for proton- and anion-exchange membranes (PEMs and AEMs, respectively) for various electrochemical applications such as fuel cells and batteries.[1] For the fuel cell applications, the present main challenges in the development of both proton conducting PEMs and hydroxide ion conducting AEMs are to improve stability and the transport properties.

We are pursuing several approaches to aromatic PEMs and AEMs where sulfonic acid and quaternary ammonium (QA) groups, respectively, are concentrated to side chains or selected segments in the polymeric structure to induce a higher level of organization and conductivity in the membranes. For example, nanostructured PEMs with excellent performance and high proton conductivity at low relative humidity (RH) were achieved by preparing multiblock copolymers with rigid blocks having very high sulfonic acid concentrations.[2] Using a new sulfonation strategy, we have recently in collaboration with other research groups synthesized and studied "hypersulfonated" aromatic polymers with extremely high acid concentrations (Fig. 1a) leading to proton conductivities of up to 90 mS cm^{-1} at 120 °C and 50% RH.[3] When it comes to AEMs, we have recently attached QA groups to poly(phenylene oxide)s via flexible and stable spacers (Fig. 1b) by using a straightforward synthetic route involving bromoalkylation and quaternization.[4] These materials showed efficient phase separation, significantly enhanced OH^- conductivity (Fig. 1d) and far superior alkaline stability in relation to corresponding polymers with QA groups traditionally placed in benzylic positions directly on the backbone (Fig. 1c). In the present paper we will discuss recent findings regarding molecular design principles, synthetic procedures and important structure-property relationships of these and other new PEM and AEM materials.

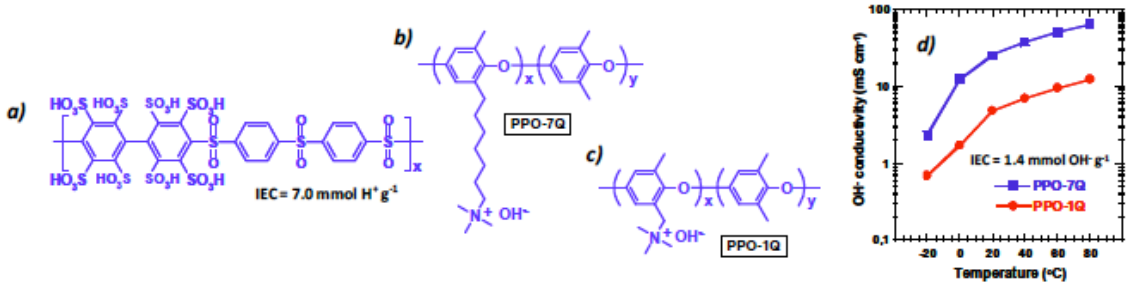

Figure 1 *a)* A "Hypersulfonated" poly(arylene sulfone); *b)* poly(phenylene oxide) with QA groups on fexible alkyl spacers; *c)* poly(phenylene oxide) with QA groups placed in benzylic positions; *d)* OH^- conductivity of AEMs based on the latter two polymers (IEC = Ion Exchange Capacity).

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IL 6

Towards Commercialization of Micro Fuel Cells

JAN H. HALES [1], CHRISTIAN KALLESØE, TORSTEN LUND-OLESEN, LEIF H. CHRISTENSEN

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Abstract

More than 95 percent of today's hearing aids use disposable zinc air batteries, which have several drawbacks for both end-user and manufacturers of hearing instruments. A general issue in the industry relates to the ever increasing demand for electrical energy as the functionality of the hearing instruments expands to encompass wireless connectivity, allowing e.g. direct mobile phone connection or access to other devices involving audio streaming. Elevated energy demands results in increased exchange frequency of the employed disposable batteries, which directly affects the end-user through the associated dexterity challenge of replacing the tiny button cell batteries. The increased amounts of disposable batteries will in turn also pose an environmental challenge.

The presented work enables the replacement of zinc air batteries in hearing aids by utilizing methanol based passive micro fuel cells. The goal is to achieve a fuel cell powered hearing aid that can be "recharged" within 30 seconds by replenishing the methanol. The fuel exchange is handled by a user-friendly docking station, shown in figure 1(c) that interfaces with the fuel cell embedded in the hearing aid as indicated in figure 1(b). In order to achieve the required energy and power densities, the main components comprising passive fuel cells in the Direct Methanol Fuel Cell (DMFC) category, have been investigated for further development and optimization. The presentation will focus on the specific areas involving synthesis of catalyst nanoparticles and the efforts in finding the optimum proton conducting polymer membrane. Furthermore, durability issues and the related impact on miniaturization and industrialization will be discussed. First prototypes of the technology have been manufactured and the processes are now being developed towards commercialization in 2017/18.

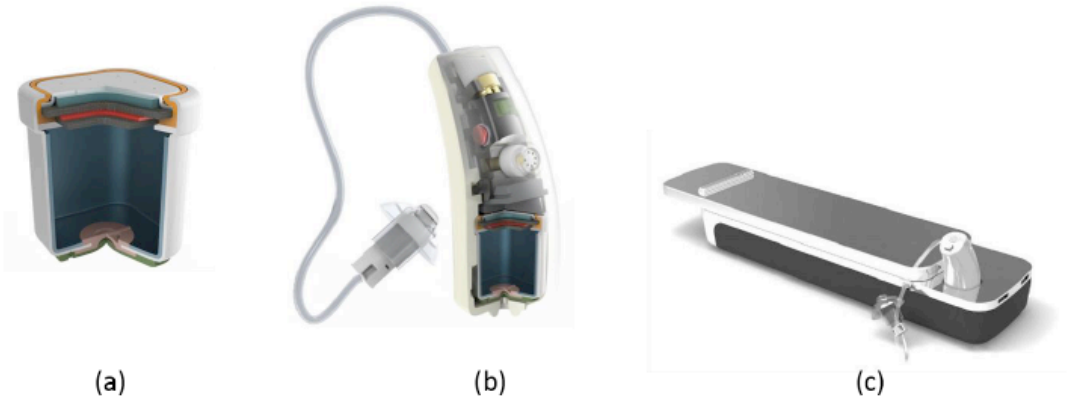

Figure 1. System overview showing: (a) the passive micro fuel cell, (b) the hearing aid with embedded fuel cell and (c) the docking station for recharging the hearing aid.

Acknowledgements

The presented work is funded by Innovation Fund Denmark and realised in collaboration with Aarhus University, Technical University of Denmark, AH Metal Solution A/S, Sonion A/S and Widex A/S.

IL 7

HIERARCHICAL STRUCTURE AND ELECTRICAL PROPERTIES OF PEDOT/PSS AND APPLICATIONS TO ORGANIC DEVICES

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Abstract

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) is a conducting polymer having a hierarchical structure (Fig.1). The sequence of monomer units of PEDOT and PSS (primary structure) forms a poly-ion complex between PEDOT cations and PSS anions through electrostatic interactions (secondary structure). The poly-ion complex disperses in water as a colloidal gel particle (tertiary structure) with a diameter of several tens nm where hydrophobic PEDOT molecules aggregate to form physical crosslinks of the PSS chains. Therefore, the PEDOT/PSS colloidal gel particles can be shaped into various shapes such as thin coatings on various substrates[1], fibers[2], and free-standing thick films[3] (quaternary structure). It is one of the most successful conductive polymers, having superior electrical and thermal stability especially in the conductive state, and this provides potential applications to organic electronics such as antistatic coating, capacitors, hole-injection layers of organic light-emitting diodes, and transparent electrodes of touch panels and solar cells as an alternative of indium tin oxide (ITO)[4]. However, little is known about correlation between hierarchical structures and electrical conductivity, which is crucially important for the practical applications to highly conductive transparent electrodes for flexible, stretchable, and wearable electronics.

In this talk, the hierarchical structure of the PEDOT/PSS will be investigated to clarify the mechanism for the improvement of electrical conductivity. It was found that electrical conductivity significantly increased by few orders of magnitude in the presence of a secondary dopant such as ethylene glycol and dimethyl sulfoxide, which can be associated with the improvement of both intra- and inter-particle transfer of charge carriers[5] caused by (i) crystallization of PEDOT molecules[6], (ii) removal of the insulating PSS from the surface of the PEDOT/PSS particles, and (iii) aggregation of the particles. Furthermore, synthesis of highly conductive PEDOT/PSS and applications to organic devices such as capacitors[7], touch panels[8], flexible speakers, and compliant electrodes for soft actuators[9], will be demonstrated.

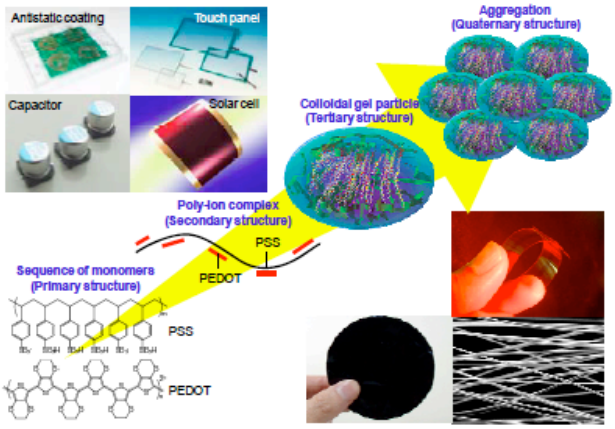

Fig.1 Hierarchical structure and applications of PEDOT/PSS.

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IL 8

TOWARDS SOLAR FUELS FROM CONJUGATED POLYMER PHOTOELECTRODES

GRAEME SUPPES PATRICK FORTIN, PANKAJ CHOWDHURY AND STEVEN HOLDCROFT *

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Abstract

The photovoltaic (PV) industry is undergoing rapid growth. Inorganic-based semiconductor materials currently dominate the PV industry. However, organic semiconductors are being intensely investigated because they offer roll-to-roll manufacturing alternatives. However, to overcome temporal variations in sunlight, solar energy needs to be efficiently converted into chemical fuel that can be stored, transported, and used upon demand. An approach is the photoelectrolysis of water, which typically employ inorganic semiconducting materials.

In this talk, conjugated polymers are examined for photocathode activity in aqueous solutions. Photoelectrochemistry at p-type organic semiconductor in acidic and neutral conditions will be presented and discussed. The origin of photoelectrochemical cathodic current will be described with the view to water splitting and "charging" of various redox couples.

IL 9

USE OF POLYMERS FOR HIGH-ENERGY-DENSITY BATTERIES

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The storage of energy is a challenge for the effective use of regenerative energy sources like wind and solar energy. Efficient and high-energy-density batteries could help in this respect and at the same time make e-mobilty more acceptable due to more affordable batteries with higher range. Besides other concepts LiS-batteries would provide a solution since they promise a much higher energy-density and capacity compared to conventional Li-ion batteries. There are however still many problems to be solved. Polymers can be used for the design of cathodes which contain sulfur in a porous conductive structure[1]. Nanoporous carbon cathodes for lithium sulfur batteries can be produced by pyrolysis of gyroid replicas based on polystyrene-poly-4-vinyl pyridine (PS-P4VP) block copolymer sacrificial templates. A free standing gyroid carbon network with highly ordered and interconnected porous structure is fabricated by impregnating the carbon precursor solution into the gyroid block copolymer nanotemplates and subsequently carbonizing them at elevated temperature in an inert media. A wide range of analytical tools are employed to characterize fabricated porous carbon materials[2]. Prepared nanostructures exhibit a fascinating morphology with high surface area and uniform porosity with interconnected three dimensional networks. Those nanoporous templates with gyroid structure provide high cycling stability of lithium sulfur batteries over more than 100 cycles. Other routes based on polymer hybrid structures will be discussed. Further aspects include optimization of separator and electrolyte to minimize so-called polysulfur shuttle and dendride formation which limit battery lifetime.

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IL 10

RADIATION-GRAFTED ANION-EXCHANGE POLYMER ELECTROLYTES FOR ELECTROCHEMICAL APPLICATIONS

JULIA PONCE CONZALEZ, TERRENCE R. WILLSON, GABRIELA STEHLIKOVA, SIMON D. POYNTON, SAM MURPHY, ROBERT C. T. SLADE, DANIEL K. WHELLIGAN, IAN HAMERTON, JOHN R. VARCOE

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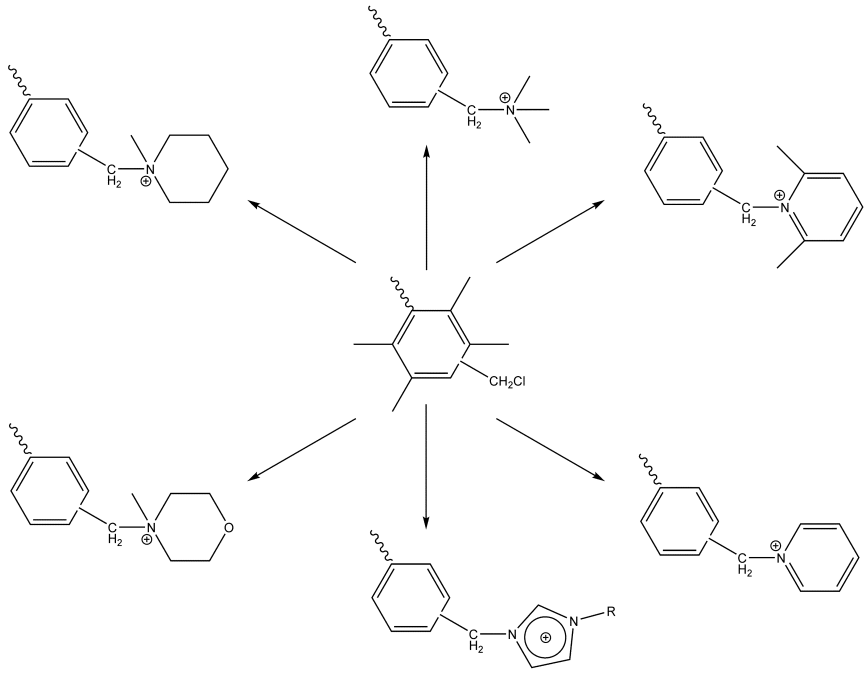
Abstract

This talk will discuss anion-exchange membranes (AEM) for application in a diversity of clean energy technologies [Varcoe *et al.*, *Energy Environ. Sci.*, 2014, **7**, 3135]. These include alkaline polymer electrolyte fuel cells (APEFC) and reverse electrodialysis (RED) cells. These technologies include the application of the AEMs in both neutral and alkaline pH conditions.

This presentation will present recent research into radiation-grafted anion-exchange membranes (AEM), which are anion-conducting polymer electrolytes that contain a variety of morphologies and chemistries. Small-scale experiments have been conducted and synthesis protocols have been developed. The ultimate aim is to use this methodology for the repeatable production of large (lab-scale) batches of materials (*e.g.* square-metre-sized batches of AEM). Such a development will enable a large number of tests and experiments to be conducted on the same batch of material. This facilitates materials research by allowing the comparison of AEMs where a single variable has varied between different samples. For-example different AEMs can be synthesised that have the same ion-exchange capacities and polymer backbones but where the chemistries of the cationic head-groups is varied.

The radiation-grafted AEMs (with similar ion-exchange capacities) discussed possess a diverse range of cationic chemistries, such as benzyltrialkylammonium, benzylimidazoliums, benzylpyridiniums, and benzylpiperaziniums. Some of these AEMs are being utilised in APEFCs (in high pH conditions), whilst others can only be applied to systems with neutral pHs (*e.g.* AEMs for use in RED cells). As well as characterisation, the ionic conductivities of these materials have been evaluated.



IL 11

CONDUCTING POLYMERIC COMPOSITES

JÜRGEN PIONTECK

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Abstract

The success of polymeric materials is based on their ease of production and processing, as well as their broad variety of properties, which opens up multifaceted applications and makes them indispensable in daily life. One of the typical properties of conventional polymers is their insulating character and thus polymers are widely used to insulate electrical wiring and cables and electrical equipment. Otherwise, the insulating character can cause electrostatic charging resulting in electric sparks, limiting applications in explosive environment or sensible electronics and surfaces. Even electrical conductivity may be desired for applications in apparatus engineering, as conductive glues, solder paste, coatings, EMI shielding, etc.
To provide antistatic or electrical conductive properties to conventional polymers, different approaches are possible [1] and a very successful way is the addition of conductive fillers due to the permanence of electrical properties, variability of possible fillers, and possible simultaneous improvement of mechanical strength, heat transport properties and stability of the polymer matrix.
This contribution gives an overview about different fillers for antistatic and conductive modification of conventional polymers, the effect of the filler geometry on the electrical percolation concentration, and factors influencing the dispersion and distribution of conductive fillers in the polymer matrix [2,3]. The resulting morphologies will be correlated with the observed electrical and other properties and examples for application of such conductive filler e.g. as sensor for liquids [4], vapours [5], or strain [6] or EMI shielding [7] will be given.

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ORAL CONTRIBUTIONS

OC1

COORDINATION-BASED MOLECULAR ASSEMBLIES AS ELECTROCHROM MATERIALS: ULTRA-HIGH SWITCHING STABILITY AND COLORATION EFFICIENCIES[1]

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Abstract

Electrochromic polymer-based devices are increasingly being used in display technology, solar
smart windows, and sensors.[2] In contrast to the well-developed field of polymer chemistry, relat
few examples of molecular architectures with efficient electrochromic properties are known. In
study we used a dip-coating process to generate molecular assemblies (**MA**) from metal polypy
complexes cross-linked with $PdCl_2$.[3,4] These polypyridyl complexes are considered
chromophores for fabricating electrochromic materials, due to their excellent stability and
absorption that greatly depends on their oxidation state. The number of pyridine moieties o
chromophores is varied to control (i) the materials' stability, (ii) color, (iii) redox-chemistry, and
the film growth (i.e., linear *vs.* exponential). We also observed that minor structural differences
the pyridine-bipyridine bond order) at the molecular level become apparent when the stability
electrochromic properties (Figure 1) are examined. The **MA**s exhibit high coloration efficiencies
are extremely stable: they are thermally robust and have exceptionally high (spectro)electroche
activity. Furthermore, we demonstrated the formation of a first-generation solid-state set-up.[1,5]

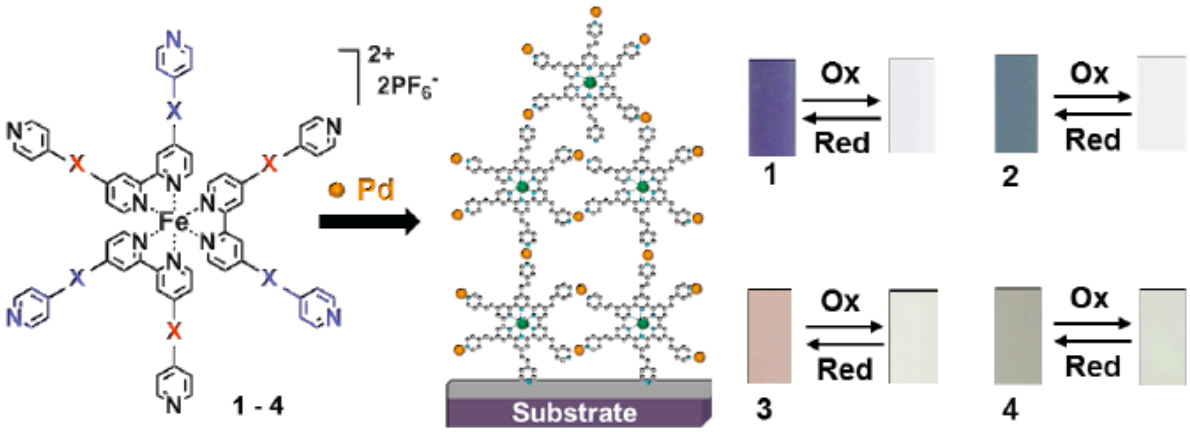

Figure 1: Left: The formation of the surface-confined metal-organic molecular assemblies (**MA**).
Right: Photographs of **MA1-4** showing the colored (Fe^{2+}) and the bleached (Fe^{3+}) states.
(**X** = H_2C-CH_2 , HC=CH or C≡C).

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OC2

SU8-GRAPHENE: A NEW PHOTO-PATTERNABLE CONDUCTIVE POLYMER COMPOSITE

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Abstract

SU8 epoxy is a photo-resist with great intrinsic properties such as high thermal stability, chemical and mechanical robustness along with high sensitivity to UV. Having eight reactive epoxy sites in each monomer molecule, a high degree of cross-linking is attainable for SU8 after photo-activation and thermal treatment. These characteristics make SU8 one of the most favorable polymers for MEMS applications, pattern transfer and fabrication of high aspect ratio structures[1]. However, besides the attractive features, SU8 has few drawbacks: it is an electrically insulating material with very low thermal conductivity; it is brittle and has high internal stresses which can lead to bending of the structures[2,3]. Addition of fillers has been shown to partially overcome these drawbacks[4,5].

Graphene, due to its advantageous electronic and mechanical properties as well as good chemical stability, is considered as a promising material for nanoelectronic and optoelectronic devices. Having a very high specific surface area ($2600 m^2 g^{-1}$ [6]) enables high electrical conductivities for composites with a low loading of graphene fillers.

In this work, we present SU8-graphene-based nanocomposite containing reduced graphene oxide (RGO) flakes, as a new patternable conductive polymer with electrical properties superior to other graphene-based polymer composites[7]. Our composites preserve the photo-patternability after optimization of UV lithography parameters and well-defined structures can be drawn at wafer scale. Scanning and transmission electron microscopy were used to analyze the microstructures of the composites. Chemical contribution of the RGO fillers within the matrix, before and after crosslinking of the polymer matrix, was investigated by FTIR and FTraman spectroscopy.

Electrical and mechanical properties of these composites can be controlled by tuning the content of graphene flakes within the SU8 matrix. Electrical conduction of the composite samples containing various volume fractions of RGO was measured using two and four probe methods. We showed that the conductivity (σ) behavior of the composites as a function of volume fraction (ϕ) is not consistent with the classical percolation model of transport. Instead, we suggest that the composite conductivity results from tunneling processes between the graphene flakes: $\sigma = \sigma_0 e^{-\frac{2\delta(\phi)}{\xi}}$, where, ξ is the tunneling decay length, and $\delta(\phi)$ is typical distance between two particle surfaces. High electrical conductivities compare to pure SU8, even at very low filler loadings, is a result of homogeneous dispersion of the flexible graphene flakes in the SU8 matrix.

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OC3

INFLUENCE OF GRAPHITE NANOPLATELETS 8gnp9 DISPERSION ON THE THERMAL CONDUCTIVITY OF HDPE COMPOSITES PREPARED USING MELT MIXING

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Abstract

A series of composites based on high density polyethylene (HDPE) with graphite nano platelets (GNP) was prepared by melt mixing using a Branbeder mixing Plasticorder k07-176/A. The GNP material was pre-dispersed using ultrasonification of dry powders using differents conditions. GNP contents of 3, 5, 6 and 7 wt% were used. The dispersion of the GNP within the composites was studied using light Microscopy on thin sections of pressed plates in two directions. The state of dispersion was quantified using the agglomerate area ratio. Thermal and Electrical conductivity were measure and related to the state of dispersion and pre-treatment conditions. It was found for composites with 5 wt% of GNP, the ration area decreases improved GNP dispersion, while with the addition of 7 wt% does not improved GNP dispersion due to size agglomeration in composites. The experimental results revealed that GNP could be dispersed in the form of nano sheets in the HDPE matrix.

OC 4

CONDUCTIVITY AND FLAMMABILITY OF SMART TEXTILES BASED ON EXPANDED GRAPHITE-POLYMERIC NANOCOMPOSITES

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New textiles also called smart textiles usually contain metal fibres or other elements as sensors. In the current study, we tried to prepare conductive textiles by surface coating of PES, cotton, and PES/cotton mixture with polymeric composites containing expanded graphite [1]. The conductivity, flammability, thermostability and contact angles were measured before and after washing of coated textiles with detergents.

Electrical conductivity of all untreated textiles was about 10^{-14} S/cm. The surface treatment with conducting suspension of graphite led to substantially higher values of the conductivity. SEM study demonstrated the quality of surface treatment by polymeric matrix Axilat containing graphite. The coating remains preserved also after series of 5 cycle washing.

Flammability of textiles was investigated by the cone calorimeter. Parameters characterising the burning processes as heat release rate, time to ignition, total oxygen consumed, total smoke released, effective heat of combustion as well as calculated value of maximum rate of heat emission (MARHE) will be presented.

TGA results showed that washing lowered the onset temperature, the first step of degradation of washed samples probably due to using detergent SDS. The second step of TGA curves depended on the textile type. Textile treatment with polymeric matrices has an impact on thermal stability of washed samples – it lowers the onset of degradation, depending on the textile type. From studied textile treated PES samples showed the best thermostability.

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OC5

POLYSILANE/FULLERENE NANOCOMPOSITE AS A MATERIAL FOR POLYMER SOLAR CELLS

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Abstract

In the past decades, silicon-based inorganic solar cells have achieved significant development; their power conversion efficiency has reached over 20%. Yet, bulk heterojunction (BHJ) polymer solar cells (PSCs) have drawn great attention because of the advantages of easy fabrication, low cost, light weigh and flexibility.

PSCs are commonly composed of a photoactive blend film of a conjugated polymer (donor) and fullerene/fullerene derivative (acceptor) sandwiched between a PEDOT:PSS coated ITO (positive electrode) and a low-work function metal (negative electrode). When light irradiates on the PSCs through the transparent ITO electrode, the semiconducting donor and acceptor materials in the photoactive layer absorb photons to form excitons (bounded electron-hole pairs), then the excitons diffuse to the donor/acceptor interfaces where the excitons dissociate into electrons and holes. The dissociated electrons and holes then move to and are collected by negative and positive electrode, respectively, to realize the photon-to-electron conversion.

The most representative polymer donor and fullerene derivative acceptor used in the PSCs are regioregular poly-(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{60}BM$), respectively, and the power conversion efficiency (PCE) of the PSCs based on P3HT/$PC_{60}BM$ reached reproducibly over 4%. Further PCE improvement in PSCs demands novel donor and acceptor photovoltaic materials elaboration. In this aspect, polysilanes seem to be a promising donor material. They belong to a class of σ-conjugated polymers and exhibit intrinsic electric conductivity, broad photoluminescence and transparency in the visible region.

In this presentation, we report on formation and investigation of PSCs, which photoactive layer is based on diphenylsilane/methylsilane copolymer (PSHDF) and $PC_{70}BM$, the last being a C_{70} derivative. The cyclic voltammograms of PSHDF and $PC_{70}BM$ allowed estimation of their electron HOMO and LUMO energy levels and conclusion on potential increasing efficiency of the PSHDF/$PC_{70}BM$ system as compared with PCE of the P3HT/$PC_{60}BM$ system.

We synthesized a highly soluble PSHDF copolymer in a microwave reactor using a Wurtz reaction. In the UV-vis spectra of the PSHDF/fullerene nanocomposite, we found a strong bathochromic shift of the absorption band as compared with a neat copolymer, whereas in the luminescence spectra of this nanocomposite, we detected an intensive luminescence quenching. Both findings indicate formation of intermolecular charge transfer complex between PSHDF and fullerene. This phenomenon evidences formation of BHJ structure in the nanocomposite for the photoactive layer of PSCs.

PSCs of the conventional structure ITO/PEDOT:PSS/BHJ/LiF/Al (BHJ = PSHDF/$PC_{70}BM$) were constructed and their functional characteristics were determined. Optimization of PSHDF/$PC_{70}BM$ ratio and active layer thickness are in progress.

Financial supports from the Russian Foundation of Basic Research (grant 13-03-00033) is gratefully acknowledged.

OC6

ELECTRICAL RESISTIVITY OF MELT MIXED PCL – MWCNT COMPOSITES: INFLUENCE OF AGGLOMERATE DISPERSION AND NANOTUBE LENGTH UPON VARIATION OF MIXING SPEED

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Abstract

Even if polymers are normally excellent electrical isolators, for some applications electric discharge behaviour or conductivity is desired. A suitable way to produce such composites is melt mixing with conductive nanoparticles, like carbon based materials. Carbon nanotubes owing a very high aspect ratio are candidates which promise to reach electrical percolation at quite low loadings.
One crucial point in producing such nanocomposites is the filler dispersion, as such materials form agglomerates in micrometer size upon synthesis. Such primary agglomerates are difficult to disperse due to strong van-der-Waals forces and entanglements between the tubes. However, especially for mechanical properties, but also for their processability and e.g. surface properties, samples free of primary agglomerates are advantageous. Concerning electrical properties, the content of individualized tubes able to form the conductive network together with remaining primary agglomerates as well as their effective length are decisive for the electrical percolation threshold. Next to the polymer and nanotubes characteristics and their interactions, the mixing conditions can significantly influence the achievable state of dispersion. Increasing input of mixing energy leads to better dispersion but also reduces the length of the nanotubes. As both are influencing the electrical properties, this study aims to find optimum conditions for achieving minimum electrical resistivity at a given MWCNT content.
Poly(caprolactone) (PCL) was chosen as the matrix and composites containing 0.5 wt% multiwalled carbon nanotubes (MWCNTs) which is near the electrical percolation threshold were investigated[1]. They were produced by melt-mixing in a small-scale compounder by varying the rotation speed between 25 and 400 rpm at a constant mixing time of 2 min at 90°C. By that, different levels of dispersion, as assessed by quantitative analysis of area ratio of remaining primary agglomerates from light microscopy, were achieved. With increasing screw speed the state of dispersion increases and levels off starting at about 100 rpm. The differences in dispersion up to a rotation speed 75 rpm could be clearly shown also in melt rheological measurements where samples with better dispersion resulted in higher complex viscosity and storage modulus values especially at low measuring frequencies. In addition, shortening of the MWCNTs was investigated using TEM investigations on tubes recovered after dissolution of the PCL matrix of the composites. The shortening increased with mixing speed. The mean lengths after processing were between 40 % (25 rpm) and 31 % (400 rpm) related to the initial length of the nanotubes. Both effects, improved dispersion and nanotube shortening, are clearly reflected in the electrical resistivity values of compression molded samples. Here, up to 75 rpm a decrease in resistivity from about 1 E11 Ohm-cm towards 2500 Ohm-cm due to the better dispersion was observed. However, when using mixing speeds above 75 rpm, where the state of dispersion had leveled off, again an increase in resistivity up to 1 E10 Ohm-cm was found reflecting the reduction in the nanotubes' aspect ratio.
In summary, for the selected nanotube concentration of 0.5 wt%, temperature and mixing time conditions, 75 rpm seems to be an optimum where already good dispersion is achieved, CNT shortening is not too much pronounced, and the lowest electrical resistivity could be observed.
Acknowledgements: We gratefully acknowledge the financial support from INTELTEX (Intelligent multi-reactive textiles integrating nano-filler based CPC-fibres), a European Integrated Project supported by the Sixth Framework Programme for Research and Technological Development of the European Commission (NMP2-CT-2006-026626). We thank Nanocyl S.A. (Sambreville, Belgium) for providing the MWCNT material.

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OC7

THE LATEX METHOD: A FACILE ROUTE TO IMPROVED CONDUCTIVITY AND OPTICAL TRANSPARENCY BY 2D ALIGNMENT OF MULTI-WALLED CARBON NANOTUBES

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Abstract

The latex method[1] is a means of preparing carbon nanotube composites where the exfoliation of carbon nanotubes is carried out in an aqueous surfactant which can be mixed with a polymer latex resulting in fewer processing steps. Composites prepared by this means have been found to have reasonably good conductive percolation thresholds[2] compared to some solvent mixing techniques and have opened up routes to some novel functional materials.[3]

In this work, polystyrene latexes were prepared ranging from 100 nm to >1 μm in diamter and MWCNT with average length of 1 - 1.5 μm with sodium dodecyl sulphate as surfactant. A concept we call "Double Confinement"[4] which is somewhat similar to double percolation,[5] is a simple protocol (Figure 1) developed to produce nanocomposite films with low percolation thresholds and high conductivities. Here a combined effect of particle size control, mixing, freeze-drying and an enhanced compression molding technique was found to produce a 2D aligned carbon nanotube network which resulted in a maximum conductivity of 66 S/m at 1 wt% MWCNT and with a percolation threshold between 0.1 and 0.15 wt% MWCNT loading. The 2D alignment was confirmed by percolation theory and scanning electron microscopy. The effects are attributed to the physical properties of the latex in combination with the enhanced compression molding technique.

Moreover, the 2D aligned MWCNT networks improve the transparent/translucent qualities of the films and allow for little loss in bulk conductivity when the thickess is reduced resulting in better transparency at higher CNT loading (Figure 2).

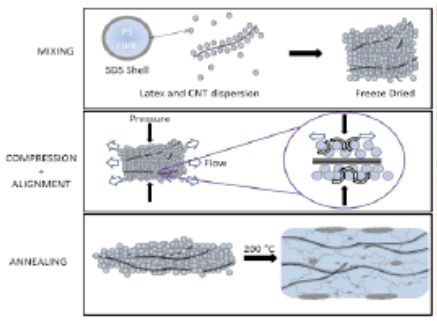

Figure 1 Protocol for preparing 2D aligned MWCNT composites

Figure 2. Semi-Transparent 30 μm film 0.4 wt% Loading MWCNT; 6 S/m

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OC8

TAILOR MADE COPOLYMER FOR IMPROVED DISPERSION AND COMPATIBILITY OF MWCNT IN WATERBORNE UV-CURABLE COATINGS

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Abstract

Ever since the discovery of carbon nanotubes (CNT) they have been a hot topic in the field of nanotechnology, showing great potential towards many applications. However, despite the extensive research that has been done, the optimal use of pristine CNT for the production of electrically conductive systems are still being investigated, especially for water based UV-curable polyurethane dispersion (UV-PUD) coatings. The shortcoming of CNT can be attributed to the π-π interactions among them, limiting their exfoliation into solvents and/or matrices. Even though the use of classical surfactants such as sodium dodecyl sulfate (SDS) leads to well dispersed CNT in water, processing of such dispersions into coatings can be less than ideal.

A polydimethylsiloxane (PDMS) based block copolymer can act as a compatibilizer[1] by forming an ancherpoint between CNT and matrix, thereby improving the dispersion quality and the interfacial interactions between CNT and matrix. In this work a PDMS block interacted with multiwalled CNT (MWCNT) through CH-π interactions while the other block consisted of an ionic polyurethane block compatible with a UV-PUD matrix. The exfoliation of CNT into water using ultrasonication was monitored using UV-Vis spectroscopy.[2] The localization of CNT in the PDMS phase of the dispersed block copolymer resulted in a nucleating effect of CNT on the crystallization kinetics of PDMS, which was visible using differential scanning calorimetry (DSC).

The produced aqueous CNT dispersions are suitable for the formulation of UV-PUD coating systems. Before coalescence of the colloidally dispersed PU-nanoparticles upon drying (film formation), they form a segregated structure similar to the latex technology leading to low electrical percolation thresholds (~ 0.1 weight percent of CNT). Cross-linking of the UV-PUD coatings increased the glass transition of the PU phase showing no significant reduction in conversion despite the presence of CNT. This was due to the good dispersion quality in the CNT-filled coatings leading to a low percolation threshold which in turn improved the translucency. Even at low CNT loadings were the produced coatings suitable as electrostatic discharge (ESD) coatings showing conductivity in the range of 0.1 S/m.

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OC9

CROSS-LINKED POLY(ARYLENE ETHER KETONE) ELECTROLYTE MEMBRANES CONTAINING HYGROSCOPIC PROTON CONDUCTORS FOR FUEL CELL APPLICATION

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Abstract

Sulfonated poly(arylene ether ketone) (SPAEK) fuel cell membranes were prepared in a cross-linked structure to enhance their dimensional and mechanical stability. Sulfonated mesoporous benzene-silica (SMBS) hygroscopic conductors were embedded in the membranes to lessen their dehydration in the low humid environment. Synthesis of the cross-linked SPAEK (CSPAEK) and its precursor was confirmed using ^{1}H-NMR spectroscopy and FT-IR spectroscopy. The effects of sulfonation degree (SD) and hygroscopic conductors on the membranes properties such as proton conductivity, methanol crossover, and thermal and mechanical stability were analyzed. The prepared CSPAEK membranes were thermally stable up to 250^{o}C without any chemical degradation. While the CSPAEK membranes containing hygroscopic proton conductors exhibited superior conductivity to that of Nafion®117, those with a cross-linking percent of less than 20% showed lower methanol permeability. Although the water uptake of the composite membranes was higher than that of the pristine membranes, no mechanical failure was observed.

Acknowledgment
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OC10

A new chemical stabilizing strategy for better performances and durability of PEMFC

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Among ionomer membrane uses, our work focuses on proton exchange membrane (PEM) for fuel cell (FC). In such devices the proton conducting polymer membrane traditionally used is Nafion which belongs to the perfluorosulfonic acide (PFSA) family. Despite its good properties up to 80°C, the loss of its mechanical properties as well as drying issues at higher temperatures prevent future developments. Therefore, there is currently an increasing interest in using alternative membranes that are capable of operating at higher temperatures. Popular candidates are polyaromatic polymers (for example sPEEK) which present good mechanical properties at high temperatures. However the conductivity and durability in FC of sPEEK are lower than that of Nafion.

The key to understanding the difference in proton conductivity between Nafion and sPEEK can be found in their specific microstructures. Nafion structure shows on the same polymer chain both extreme hydrophobicity of the backbone and high hydrophilicity of the sulfonic groups attached to the pendant chains. In presence of water, this leads to a well-defined nano-separation between hydrophilic and hydrophobic areas, which gives rise to the formation of proton conduction paths. At the opposite, for sPEEK membranes the nano-phase separation is less defined due to its higher polymer backbone rigidity, the lower hydrophobicity of its hydrocarbon backbone and finally the lower acidity of its sulfonic groups compared to that of Nafion. Hydrophilic channels are thus narrower and less connected than in Nafion. This leads to a lower swelling, a decrease of water and proton transport coefficients and as a consequence to lower FC performances (Fig.1). Moreover, sPEEK backbone is much more sensitive to H_2O_2, a byproduct generated during fuel cell operation and responsible for the oxidative degradation of the membrane. Through chain scissions, the membrane loses its mechanical properties and becomes more porous to gases resulting in FC failure. Thus the lifetime of a sPEEK based PEMFC is only a few hundred hours against several thousand hours with Nafion (Fig.1). However the better mechanical properties observed at high temperature, as well as a potential lower cost and lower environmental impact make it worth trying to improve sPEEK membrane conductivity and durability. Indeed, the performances of this membrane can be significantly improved by a suitable hydrothermal treatment or a pre-oxidation, up to becoming equivalent to that of Nafion (Fig.1).

SAXS analyses (Fig.2) performed on hydrothermally treated membrane show that the increase in molecular mobility induced by the pretreatment (water, temperature, H_2O_2 concentration) allows a gradual nano-structuration of the membrane. Obviously once the membrane performances are upgraded, the challenge is to be able to avoid the membrane degradation in FC to reach more than thousands of hours of operation. In order to do so, we developed an original strategy based on the insertion of a stabilizing network in the hydrophilic channels where the oxidizing agents produced in FC are located. This talk will be focused on the ambivalent effects of ageing and how it can be used to develop more efficient membranes. To fully characterize the physical and chemical properties of this composite membrane and their evolution during operation in FC, we developed an innovative AFM-Raman coupling set-up. It allows collecting topographic, mechanical and thermomechanical AFM data colocalized with chemical information obtained by Raman spectroscopy. (see "Co-localized AFM-Raman setup : a powerful tool to study PEMFC membrane stabilization by active nano-networks" poster).

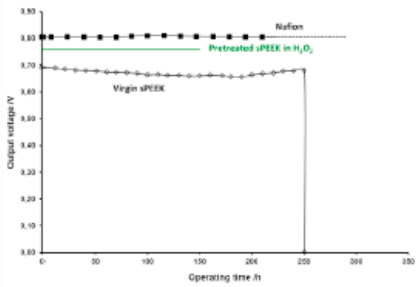

Fig.1: Evolution of output voltage of FC based on Nafion, virgin or pretreated in H_2O_2 sPEEK membranes.

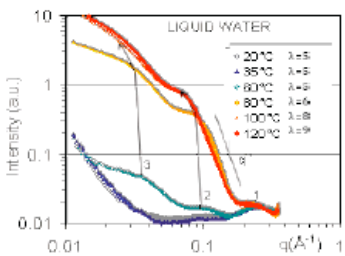

Fig.2: SAXS profiles of sPEEK membranes (liquid water conditioning) after 96h of hydrothermal treatment at 20, 35, 60, 80, 100 and 120°C.

OC 11

HIGHLY PROTON CONDUCTIVE MEMBRANES BASED ON POLYMERIZED IONIC LIQUIDS FOR NON-HUMIDIFIED FUEL CELL APPLICATION

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Abstract

Proton Exchange Membrane Fuel Cells (PEMFCs) are a promising technology for power generation due to their high energetic efficiency and low environmental impact. However, it is necessary to overcome some technical obstacles before their commercialization. One of the issues that must be addressed is the development of high proton conducting membranes under non-humidified conditions which allow working at temperatures above 80 ºC and eliminate the management of water. Ionic liquids have attracted increasing interest as electrolytes in fuel cells because of their unique properties such as high conductivity in anhydrous conditions, high thermal and chemical stability, negligible vapour pressure and large electrochemical window[1]. Nevertheless, it is important to take into account that PEMFCs require solid electrolytes. One innovative technique toward achieving this quality is the polymerization of ionic liquid monomers[2].

In this work, electrolytes consisting in polymerized ionic liquids were developed for proton exchange membranes fuel cell without external humidification. Different protic ionic liquids were chosen for this application due to its enhanced ionic conductivity. The thermal stability, water content and ionic conductivity of the polymeric electrolytes were measured. Fuel cell tests and ionic conductivity experiments at different temperatures show the great potential of these ionic liquid-based polymers as proton exchange membranes[3].

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OC12

ON THE CONDUCTIVITY MECHANISM IN POLYMERIZED PROTIC IONIC LIQUID [HSO_3-BVIM][OTF]: DIELECTRIC RELAXATION STUDIES

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Abstract

Polymerized ionic liquids (poly-ILs) are a special class of ionic conductors formed by the mobile cations or anions and the repeating counterionic species covalently bonded to the polymer backbone. Due to the combination of the unique properties of ionic liquids with macromolecular architecture of polymers, poly-ILs have become the attractive candidates for potential applications in energy storage and electrochemical devices. However, to design any process involving polymerized ionic conductors on an industrial scale, it is necessary to know some physical properties, such as molecular mobility and electric conductivity. In this talk, we show that the broadband dielectric spectroscopy (BDS) is a very powerful experimental tool for understanding the molecular-level dynamics in ion-containing liquids and polymers as well as recognizing the type of charge transport mechanism in these systems. [1] Herein, we investigate the molecular dynamics and ions transport properties of newly designed material, polymerized imidazolium-based protic ionic liquid [HSO_3-BVIm][OTf]. The monomer is also examined as a reference. The results of dielectric measurements, analyzed in modulus $M^*(f)$ and conductivity $\sigma^*(f)$ formalisms, combined with differential scanning calorimetry experiments, have revealed a fundamental difference between the conducting properties of examined polymer membrane and its low-molecular weight counterpart. Our findings have indicated a strong decoupling between electric conductivity and segmental dynamics when the ionic transport is controlled by fast proton hopping through the dense hydrogen-bond network. Finally, we also provided a deep understanding on the effect of water on the value of the glass transition temperature, decoupling phenomenon and conductivity mechanism of examined polymer membrane. Based on our experimental results one can assume that using poly-[HSO_3-BVIm][OTf] as a polyelectrolyte one can avoid the serious problem of water management observed for commercial membranes for low temperature fuel cell applications.

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Acknowledgements
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OC13

EFFECT OF COMPRESSION ON THE ION CONDUCTION IN POLYMERIZED IONIC LIQUID Poly(BuVIm)NTf

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Abstract

Polymerized ionic liquids (PolyILs) have received considerable attention in recent years due to their potential as electrolytes in batteries and fuel cells. From the application's point of view in electrochemical devices, an unique feature of PolyILs is a specific combination of mechanical stiffness of a polymer and high ionic conductivity of ionic liquid. However, there is still a lack of satisfactory understanding of ion conduction mechanism in these materials [1]. In this talk we present a systematic analysis of the broadband dielectric measurements of poly 1-vinyl-3-butyl imidazolium 2bis(trifluoromethylsulfonyl)imide over a wide pressure range with the aim of understanding the ion conduction process. The pressure dependence of ion conductivity is analysed in terms of the activation volume reflecting volume requirements for local ion diffusion.

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Acknowledgement
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OC14

A NEW PEDOT POLYMER BEARING TEMPO MOIETIES FOR ELECTROCHEMICAL ENERGY STORAGE

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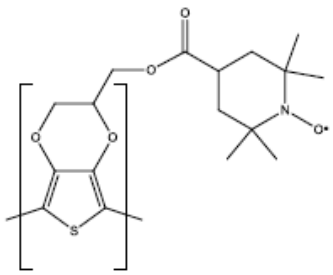
Poly(3,4-ethylene-dioxy)-thiophene (PEDOT) is one of the most interesting conducting polymers because of its high conductivity and excellent environmental stability[1]. Moreover, polymers with radical moieties such as the stable (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) nitroxide radical possess very fast electron-transfer reactivity, being able to increase the capability and cycling stability of batteries. In order to combine both properties, we chose TEMPO nitroxide radical[2] as pendant group of PEDOT.

In this study, we present the electrochemical synthesis of a new PEDOT polymer bearing TEMPO moieties. The electropolymerization was carried out in acetonitrile and dichloromethane by different techniques: cyclic voltammetry, chronoamperometry and chronopotentiometry. Two different oxidation-reduction processes were observed in the polymer electrochemical characterization, as shown in Fig. 1.

a



b

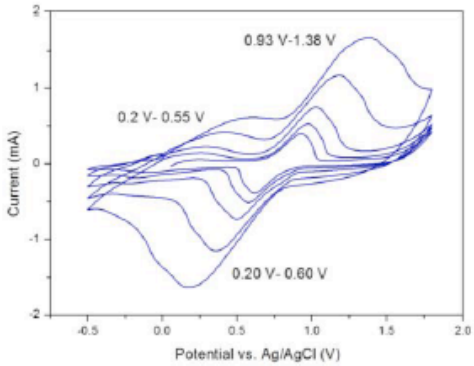


Figure 1. (a) Chemical structure of PEDOT polymer bearing TEMPO moieties. (b) Electrochemical characterization of electrodeposited polymer in 0.1 M $TBAPF_6$ dichloromethane solution at 5, 7.5, 10, 15, 20 mV/s.

The use of polymers in batteries offers several advantages over the inorganic materials used nowadays in batteries, such as high rate capacity, low weight, low toxicity, processability and recyclability[3]. Therefore, our polymer has been tested as cathode additive in rechargeable lithium batteries. A summary of the results obtained using the polymer as mediator in $LiFePO_4$ cathodes will be presented.

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OC15

Conductive and thermoelectric materials based on PEDOT

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Abstract

Conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) meet a wide range of applications as transparent electrodes, hole injecting layers or thermoelectric materials for low temperature applications[1]. Here we present the synthesis of highly conductive PEDOT using iron(III)trifluoromethanesulfonate as oxidant. Low temperature electrical conductivity measurements showed that the polymer exhibits a true metallic behaviour which is even strengthened by an acid doping step leading to conductivities up to 2273 S cm^{-1} at an unprecedented 45.5 % oxidation state. X-ray photoemission spectroscopy (XPS) and time of flight - secondary ion mass spectrometry (ToF-SIMS) analyses demonstrate a full exchange of the trifluoromethanesulfonate anions by hydrogen sulfate counterions after doping with sulfuric acid. The 80 % increase of the electrical conductivity obtained with this treatment is explained by the enhancement of both the charge carrier concentration and the mean size of the crystalline domains.[2] The use of these new high performance metallic polymers in printed electronics would significantly extend the range of possible applications.

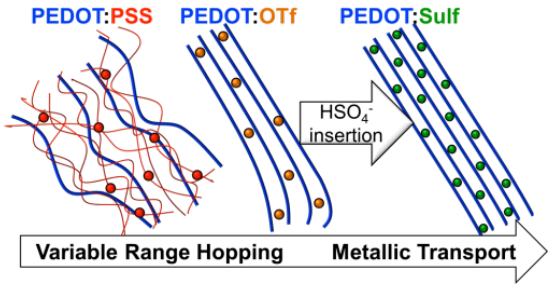

Figure 1: Electronic transport in new PEDOT-based materials

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OC16

All-atom molecular dynamics simulation of the structural, thermodynamic, and packing properties of the pure amorphous and pure crystalline phases of P3HT and PQT semiconducting polymers

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Abstract

Semiconducting polymers are promising materials for a variety of applications in organic electronics due to their unique combination of opto-electronic properties (such as ease of preparation and low cost manufacturing). Polythiophenes represent one broad family of polymeric semiconductors. Among them, poly-3-hexylthiophene (or P3HT, Figure 1)[1] and poly[5,5'-bis(3-alkyl-2-thienyl)-2,2'-bithiophene] (or PQT, Figure 2) are two of the most widely investigated conjugated polymers due to their relatively high carrier mobility (0.1 cm^2/Vs and 0.18 cm^2/Vs respectively)[2] coupled with a high degree of solubility and stability.

Here we will present results about the nano-scale structure of these two systems as obtained through detailed all-atom Molecular Dynamics (MD) simulations in the *NPT* statistical ensemble by employing the very accurate DREIDING[3] force-field. We have separately simulated the pure crystalline and pure amorphous phases of the two systems, and studied the dependence of their conformational and configurational properties on temperature. For both crystalline and amorphous domains, we have investigated the temperature effects on the distribution of dihedral angles along the hexyl chain branches and along the backbone of the chains, on all radial distribution functions, on chain packing and chain conformation, and on chain interdigitation. We will highlight and analyze differences in these properties between the two polymers in order to get insight on the effect that side group arrangement along the main chain backbone can have on the overall system structure and morphology.

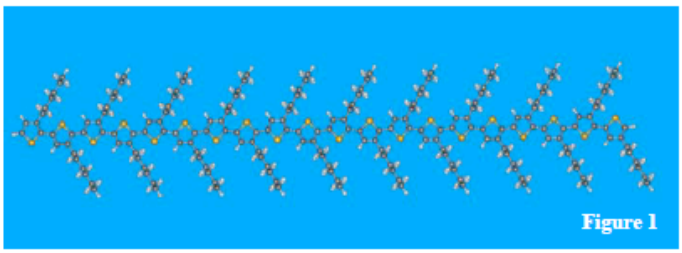
Figure 1

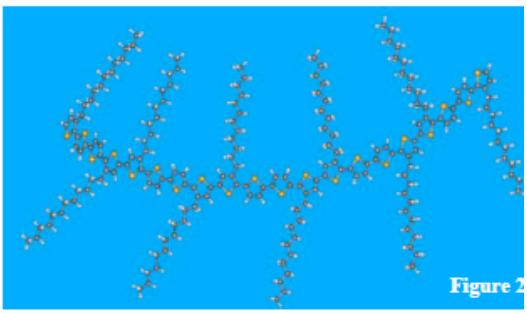
Figure 2

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OC17

IN SITU INFRARED SPECTROSCOPY OF OLIGOANILINE INTERMEDIATES CREATED UNDER ALKALINE CONDITIONS

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Abstract

The progress of the oxidation of aniline with ammonium peroxydisulfate (APS) in an alkaline aqueous medium has been monitored in situ by attenuated total reflection (ATR) Fourier transform infrared spectroscopy.

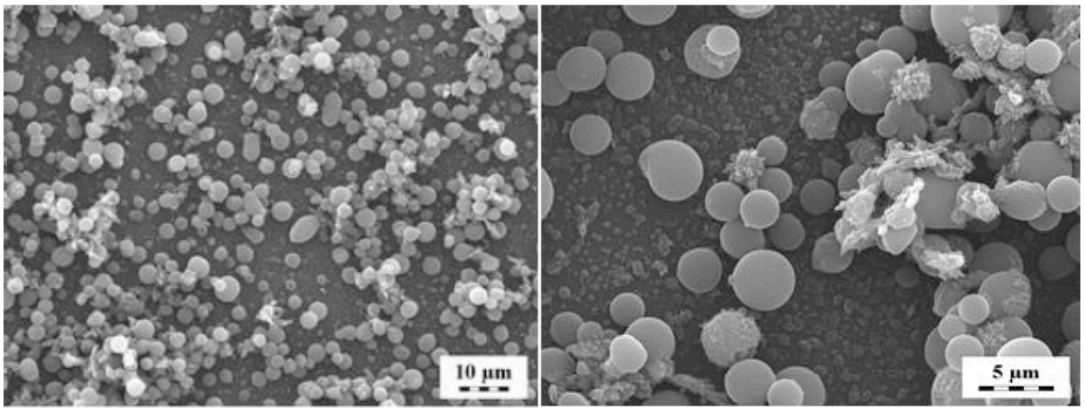

Fig. 1. Scanning electron micrograph of the films obtained by the oxidation of aniline with APS in 0.5 M ammonium hydroxide solution on silicon support.

When aniline is oxidized in alkaline media, oligoaniline microspheres were formed (Fig. 1). Under alkaline conditions, aniline oligomers are the exclusive product of aniline oxidation, but they are essential for the understanding of oxidation chemistry.
The growth of the microspheres and of the film at the ATR crystal surface as well as the changes proceeding in the surrounding aqueous medium are reflected in the spectra. The evolution of the spectra and the changes in the molecular structure occurring during aniline oxidation in alkaline medium are discussed with the help of differential spectra.
The detection of the spectral bands created at the various times of the early stages of aniline oxidation in the ATR FTIR spectra substantially extends the information about the formation of the produced structures. Several processes connected with the various stages of aniline oxidation were distinguished. The progress of hydrolysis of the aniline in water and further an oxidation of phenol to the benzoquinone imines in the presence of APS in alkaline medium predicted by Surwade[1] were detected in the spectra in real time.
The molecular structure of the final film deposited on ATR crystal and of the powdered sample precipitated under the same conditions is also discussed. The solid oxidation product is composed of oligomers, mainly trimers to octamers, of various molecular structures incorporating in addition to aniline constitutional units of *p*-benzoquinone or *p*-benzoquinoneimine moieties.

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OC18

Conducting filler ageing: XPS, FTIR and electrical conductivity study

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Abstract

Polypyrrole (PPy) as electroconductive polymer has potential in applications as sensors, flexible parts in electronic devices, electromagnetic shielding, artificial muscles, etc. Polypyrrole is also potential conducting filler for thermoplastics. As shown previously, surfactants affect the size, conductivity and surface chemistry of polypyrrole powder particles [1] and lead to better dispersion throughout the polymeric matrix [2]. From the application point of view it is useful to know degradation of its electroactivity and thus its lifetime of usability.

Five PPy samples were chemically synthesized with different oxidants and dopants or surfactant, namely $FeCl_3$, $FeCl_3.6H2O$, $Fe_2(SO_4)_3$, $(NH_4)_2S_2O_8$ and $FeCl_3$ + dodecyl benzene sulfonic acid (DBSA). Prepared PPy's were aged in our laboratory at ambient air and at temperature 24 ± 2 °C, not directly exposed to the sun. We tried to follow the chemical changes in matured samples by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and confronted these changes with the decrease of electrical conductivity of studied samples. Elemental analysis (EA) was performed as well.

From XPS results it can be concluded that oxygen seems to attack preferably the alpha position of pyrrole unit creating thus N-C=O carbonyl group. In the case of PPy-SO_4 and PPy-S_2O_8 the chains are clearly shorter as determined by FTIR with the highest amount of carbonyl groups just after polymerization. Additionally, sulphate group most probably reacts with polymer chains to create sulfonic functional group, what can be also a reason for shorter polymeric chains of PPy. The best result of electrical conductivity stability was achieved when higher amount of surfactant DBS^- was incorporated into the PPy. High amount of DBS^- provides enough anions to maintain high doping level after Cl^- depletion. Additionally, high amount of DBS alkyl chains effectively prevents PPy to oxidize on air.

Acknowledgement.
This work was financially supported by Slovak projects APVV 0593-11, VEGA No. 02/0149/14, and VEGA No. 1/0601/15.

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OC19

PRODUCTION OF HYDROGEN USING HETERO-SYSTEM: POLYPYRROLE/TIO2 UNDER VISIBLE LIGHT

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Abstract

The research on alternative eco-friendly energy resources constitutes one of the challenges in the 21 century. Due to their possible applications in the conversion of the solar energy into electrical and/or chemical forms, the semiconductor materials have found very interest from both academic and industrial points of view. It was admitted that is estimated that very little part of the solar energy is efficiently used. Because of its abundance, there are several technologies developed to use this natural energy in order to diminish the dependence of the fossil fuels, mainly considered as responsible of the greenhouse gases. It is reported that the organic semiconductor materials can be used in photocatalytic processes in order to generate the hydrogen using a renewable energy source such as solar energy [1].

Among them, the polymer materials are successfully applied in water splitting process. Our aim in this contribution is focused on the photo electrochemical properties and photocatalytic hydrogen production. The photoactivity is improved on hetero-systems PANI/TiO_2 which inhibit considerably the lost of electron/hole (e^-/h^+) pairs and shifts the spectral photoresponse of TiO_2 toward longer wavelengths. We have focused our efforts particularly on the pH effect allowing the best hydrogen production efficiency. As an example, Figure 1 shows the evolution of hydrogen as a function pH.

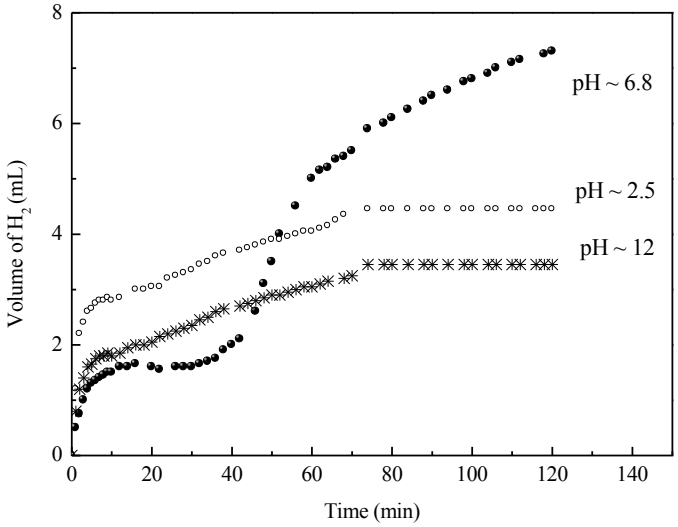

Figure 1: Hydrogen evolution using hetero system PPy/TiO_2 versus pH.

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OC20

USING SMALL ANGLE SCATTERING TO INVESTIGATE THE MORPHOLOGY AND TRACK WATER IN BLOCK COPOLYMER IONOMER MEMBRANES

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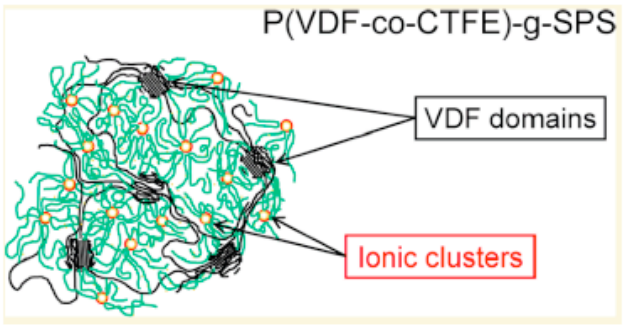
Abstract

Small angle scattering is a powerful technique to investigate the morphology of block copolymer ionomer and can also give insights on the localization of water in the membrane. Ultimately, the objective is to point out the correlation between the structure, the water swelling and the proton conductivity. In this paper we present scattering data collected on two series of fluorous copolymers bearing polystyrene grafts sulfonated from 0 to 100%.[1] Those data reveal a disordered, partially phase-separated system consisting of fluorous domains in a partially sulfonated polystyrene matrix with aggregation of ion-rich domains within the matrix. The size of the fluorous domains depends on graft density, and their packing depends on the graft chain length. The spacing of the ion-rich domains is remarkably independent of either graft chain length or charge content. The impact of the morphology on the swelling and then on conductivity will be discussed.[2]



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OC21

CHAIN GROWTH SYNTHESIS OF N-TYPE SEMICONDUCTING POLYMERS P(NDI2OD-T2) AND ITS ULTRA-THIN TRANSISTORS

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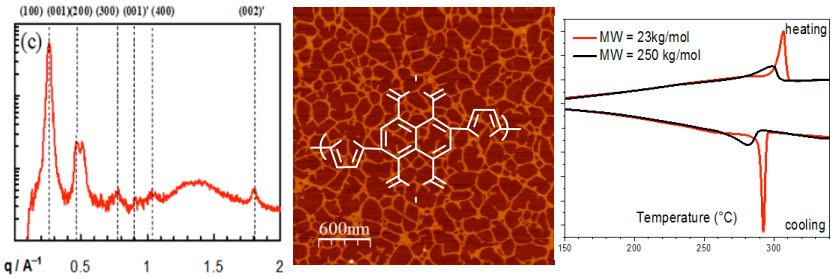
Abstract

Control over the molecular weight (MW) of π-conjugated polymers is crucial for the fabrication of highly performing photovoltaic devices and field-effect transistors (FETs). Recently, we discovered an unusual chain-growth catalyst transfer polycondensation method for preparation of highly performing n-type polymer P(NDI2OD-T2) and other donor-acceptor polymers, MW of which can be controlled.[1] In this contribution we will report new chemistry aspects of this polymerization. Afterwards, we will report fabrication of highly performing ultra-thin P(NDI2OD-T2) FETs.[2] We will particularly show that relatively thin FETs with the thickness of ~ 15 nm exhibit electron mobility of ~ 0.45 cm²/Vs. Further reduction of the active film thickness lads to somewhat decreased mobility values, however, even 5-2 nm thick P(NDI2OD-T2) FETs still exhibit substantial mobilities of 0.02-0.01 cm2/Vs. Interestingly, the lowest MW sample (23 kg/mol) exhibited higher mobility than the highest MW one (250 kg/mol) measured for thicker devices (50-15 nm). This is a rather unusual behavior since typically charge carrier mobility increases with the MW. We attribute this result to the high crystallinity of the lowest MW sample, as confirmed by DSC and XRD studies (Scheme 1).



Scheme 1.

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OC22

AMBIPOLAR POLYMERS AND MOLECULAR GLASSES FOR OPTOELECTRONIC APPLICATIONS

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Abstract

Growing interest has been recently focused on finding materials with ambipolar charge-transporting characters for the application in organic light emiting diodes (OLEDs) and in some other optoelectronic or electronic devices[1]. Ambipolar polymers and molecular materials recently synthesized and studied in the author's laboratories are reviewed.

Carbazolyl-containing polyethers, exhibiting high triplet energies were found to be effective host materials for the emitting layer of phosphorescent OLEDs[2,3]. There is an indirect evidence that these materials when protected from air are capable of transporting both positive and negative charges[Errore. Il segnalibro non è definito.]. Carbazolyl-containing glass-forming stable free radicals have appeared to be effective ambipolar organic semiconductors, with electron mobilities approaching 10^{-2} cm^2/Vs and hole mobilities reaching 10^{-3} cm^2/Vs at high electric fields in air[4]. Carbazole trimers with different linking topology represent another group of glass-forming ambipolar molecular materials[5]. 2,7-Di(9-carbazolyl)-9-(2-ethylhexyl)carbazole was found to show very high electron mobility ($\mu_e = 2\times10^{-3}$ $cm^2V^{-1}s^{-1}$ at an electric field of 1.8×10^5 V/cm) and reasonably high hole mobility ($\mu_h = 8\times10^{-4}$ $cm^2V^{-1}s^{-1}$). Since 3,6-di(9-carbazolyl)carbazoles exhibit high triplet energy and ambipolar charge transport, they were successfully used for the development of single layer electrophosphorescent devices with external quantum efficiencies of 8-9% for blue and 13-14% for green and 10% for white devices. They also showed good performance in the single-layer fluorescent OLEDs[6] and as electron-injecting materials in OLEDs based on the triple-singlet energy transfer[7] [5]. Ambipolar charge transport was also observed in carbazolyl substituted perylene bisimides under ambient conditions[8]. Depending on the linking topolygy of carbazolyl groups either hole transport or electron transport is more efficient. Time-of-flight mobilities in these materials reach 10^{-3} $cm^2V^{-1}s^{-1}$ at high electric fields for both holes and electrons. Molecular glasses of the recently synthesized conjugated derivatives of triphenylamine and 1,8-naphthalimide were also found to be capable of transporting both holes and electrons in air[9,10].

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OC23

Thin and uniform clay-containing polyelectrolyte multilayers as ceramic coating on separator for lithium-sulfur batteries

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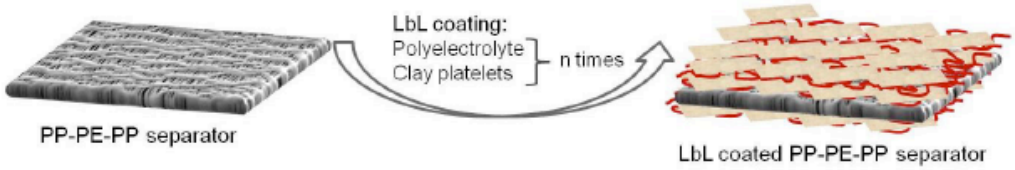
Abstract

Polymer nanocomposites uniquely combine the properties of inorganic and organic components providing the opportunities to develop novel advanced materials. The layer-by-layer (LbL) assembling allows forming the films with the thickness from several nanometers to several microns. It provides a versatile means to create polymeric thin films, allowing nanometer-scale control over the spatial distribution of ionized species within the membrane. In this work the LbL technique was used to form clay-containing ceramic coating on surface of polyolefin based commercial separator as shown on figure.

The safety problems of the batteries, which are at the heart of our technological development, providing mobility and energy independence in various small and large-scale applications, have recently received considerable attention. It is due to the increased potential for fire and/or explosion under unwanted conditions, such as hard internal shorts, overcharging and other uncontrolled conditions. In this respect battery separators play a key role, since it is placed between the positive and the negative electrodes to prevent physical contact of the electrodes while enabling free ionic transport and isolating electronic flow. The currently used separators, based on microporous polyolefin membranes offer excellent mechanical strength and chemical stability; they shrink, soften and even melt at high temperatures. However, melting causes short circuiting between the electrodes in the case of unusual heat generation.



The thermal stability of polyolefin based commercial separator was improved by deposition of a thin (~100 nm) (clay/polyethyleneimine)$_n$ (clay/PEI)$_n$ and (clay/ polyacrylic acid)$_n$ (clay/PAA)$_n$ coatings on its surface by the LbL technique. The investigation of surface properties of coated of PP-PE-PE Celgard 2320 separator showed the forming of uniform, highly wettable and ion-conductive ceramic coatings. Furthermore testing the full cell within them indicated, that the system (clay/PEI)$_n$ significantly improved the electrochemical performance of battery by preventing a shuttle effect of soluble species. The optimum number of layers for systems (clay/PEI)$_n$ and (clay/PAA)$_n$ was found as 7 and 5 correspondingly.

Acknowledgements
This research was supported by the Research Grant from Nazarbayev University and Ministry of Education and Science of Kazakhstan.

OC24

HIGHLY CONDUCTIVE SINGLE-ION Li^+ ELECTROLYTES BASED ON BLOCK COPOLYMERS CONTAINING POLY(TETRAFLUOROSTYRENESULFONATE) AND POLY(ETHYLENE OXIDE)

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Abstract

Lithium-ion battery technologies, which are based on liquid electrolytes, have been greatly successful for consumer electronics. However, the intrinsic instability of the electrolyte typically requires special safety measures which result in increased cost and reduced energy (power) density, which is especially problematic in automotive applications. The use of solid polymer electrolytes, i.e., a salt dissolved in a polar polymer, would eliminate the use of liquids. Still, the fraction of charge carried by lithium ions is characteristically below 1/5th, leading to concentration gradients which limit the power performance.[1] In single-ion conductors (SICs), the anions are tethered to the polymer and only the Li^+ is transported in the electrolyte. Hence, the use of polymeric SICs potentially solves many of the issues originating from the use of liquids and free salts.[2] However, most SICs show low conductivities because of a low degree of ion-dissociation and slow dynamics of the polymer chains.

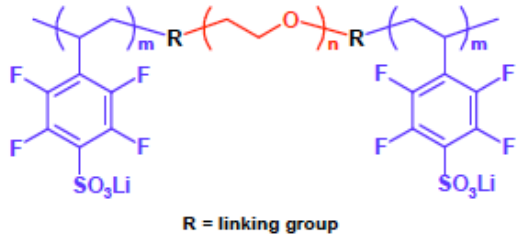

Figure 1 Structure of triblock copolymer containing poly(tetrafluorostyrenesulfonate) and PEO blocks.[3]

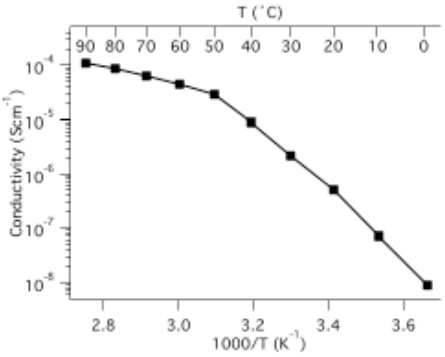

Figure 2 Lithium ion conductivity of a triblock copolymer SIC with [EO]/[Li] =10.

The present work focuses on high-temperature polymeric SICs. A series of BAB-type triblock copolymer conductors having a central poly(ethylene oxide) (PEO) block and flanking poly(tetrafluorostyrenesulfonate) blocks in various block ratios were designed and synthesized (Fig. 1). Because of the electron-withdrawing character of the fluorinated aromatic rings, Li^+ can be expected to be highly dissociated and conducted through the dynamics of the PEO chains. Partial PEO crystallinity reduced the conductivity below approx. 45 °C. According to both thermal and morphological characterizations, the miscibility of the blocks increased above this temperature that greatly enhanced the ion transport. The highest lithium ion conductivity of the series reached 4.5×10^{-5} S cm^{-1} at 60 °C (Fig. 2). This value thus exceeds the high-temperature Li^+ conductivity of current state-of-the-art block copolymer SICs.[4]

We thank the Swedish Energy Agency for funding of the project "High Temperature Lithium Batteries" (proj. 37722-1).

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OC25

ELECTRICAL AND CONDUCTIVITY PROPERTIES OF PVA/ODA-MMT AND PVP/ODA-MMT PREINTERCALATED NANOCOMPOSITES AS HIGH-OHMIC POLYMER SOLID POLYELECTROLYTES.

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Abstract

WITHDRAWN

OC26

NANOSTRUCTURED HYBRID ELECTROLYTES FOR ENERGY CONVERSION

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Abstract

WITHDRAWN

OC27

MOLECULAR WIRE FORMATION FROM POLY[2,7-(9,9-DIOCTYLFLUORENE-*ALT*-(5,5' BITHIOPHENE/CUCURBIT[7]URIL)] POLYROTAXANE COPOLYMER

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Abstract

Conjugated polymers (CP) have attracted intensive attention in the last years, as promising active hole-transporting materials, which possess a wide range of applications in electro-optical devices. Unfortunately, the use of these materials is often affected by several limitations including undesirable aggregation, which leads to low photoluminescence quantum yield values (PLQE). Based on the combined structural and optical studies, the most successful approach is devoted to copolymerization of fluorene with the other arenes. Among them, the encapsulation of CP with suitable macrocycle molecules represents an attractive approach to achieve control over molecular rigidity, prevention of aggregation, improved PLQE, and surface-morphological characteristics of the resulting conjugated polyrotaxanes. This approach has been applied by incorporating chemically-modified CDs [1]. Recently, CP having cucurbit[7]uril (CB7) as host molecules have been reported and they showed significantly enhancements of the morphological and surface characteristics [2].

Our study relies on the investigation of the optical, electrochemical behaviors, morphology, surface free-energies as well as transport properties of poly[(9,9-dioctylfluorene-*alt*-bithiophene/cucurbit[7]uril)] (**PF-BT•CB7**) main-chain polyrotaxane, as depicted in the structure chart in Figure 1.

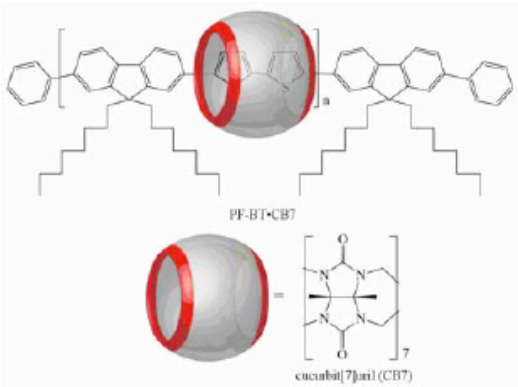

Figure 1. Chemical structure of **PF-BT•CB7** copolymer

The CB7 encapsulation leads to distinct improvements in the photophysical and morphological characteristics compared with those of the corresponding **PF-BT** non-rotaxane counterpart. **PF-BT•CB7** has a less flexible conformation of macromolecular chains and a higher tendency to organize itself into linear ribbons in the solid state. In addition, the negatively charged carbonyl portals of CB7 have a significant contribution to the surface free-energy.

Acknowledgements
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OC28

CONDUCTIVE POLYMER COMPOSITES REINFORCED BY METALLIC NANOWIRES

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Abstract

The conductive polymer composites reinforced with a low content of high aspect ratio conductive fillers can significantly improve the electrical properties of the pure polymer matrix and maintain its mechanical properties. Percolation phenomenon is dependent on the apparent aspect ratio of the filler. Very low percolation threshold were obtained with introduction of carbon nanotubes (CNTs). Above the percolation threshold (p_c < 5 vol %), the literature shows that the conductivity value of CNTs composites levels off at an upper limit[1] of about 10^{-1} $S.m^{-1}$. Metallic nanowires (NW) have attracted much attention because of their higher intrinsic electrical conductivity[2].

In this work, metallic nanowires were synthesized by electrochemical and polyol ways giving an uniform high aspect ratio ($\xi \sim 200$). The polyol process suggests an easy way to produce several grams of silver nanowires. Nanowires polymer composites were elaborated by addition of NW in semi-crystalline matrices [2, 3].The conductivity of melt-pressed composite films has been studied as a function of NWs volume fraction. It shows a very low percolation threshold near 1 vol%. At the percolation threshold p_c, the volume electrical conductivity of nanocomposites increases from 10^{-12} $S.m^{-1}$ to 10^{2} $S.m^{-1}$. The surface resistivity above the percolation threshold reaches a low value near 1 Ω/□ . The influence of metallic nanowires on composites mechanical properties was studied and compared with spherical nanoparticles. Composites reach an electrical conductivity 10^3 times higher than the one of CNTs nanocomposites. Below 5 vol%, nanocomposites remain ductile and flexible[4].

Despite moderate aspect ratio regarding CNTs, metallic nanowires represent a very promising route to improve the electrical conductivity in polymer matrix composites.

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OC29

CHIRAL CONDUCTIVE POLYMERS AS SPIN FILTERS

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Abstract

The introduction of conducting polymers to organic electronics has revolutionized the technology and conducting polymers are now part of the OLED based appliances. Recently spin-LED/OLED have been suggested for improving the efficiency of LEDs and OLEDs and a spin-OLED was indeed demonstrated[1,2]. In this device, electrons injected into and from the light-emitting species have their spin predetermined: therefore, the formation of the non-emitting triplet state is avoided. The control of the spin in these devices tipically requires a magnetic element that defines the spin orientation, but the integration of this component with OLED technology is challenging because of material constraints and effects at the interfaces that can affect charge and spin injection. Here we show that by using chiral conductive polymers[3] (CCPs) it is possible to inject spins with very high spin selectivity. The spin selectivity observed results from the chiral-induced spin selectivity (CISS) effect reported recently[4]. This finding introduces the possibility of producing spin-OLEDs without any magnetic component and without introducing additional production restrictions.

We investigated spin-selective electron transport through poly{[methyl *N* -(tert-butoxycarbonyl)-S-3-thienyl- L -cysteinate]-cothiophene} (PCT-L)[5]. Measurements were performed in two configurations: in an electrochemical cell at room temperature (Fig.A) or in a solid state device at various temperatures (Fig.B)[6].

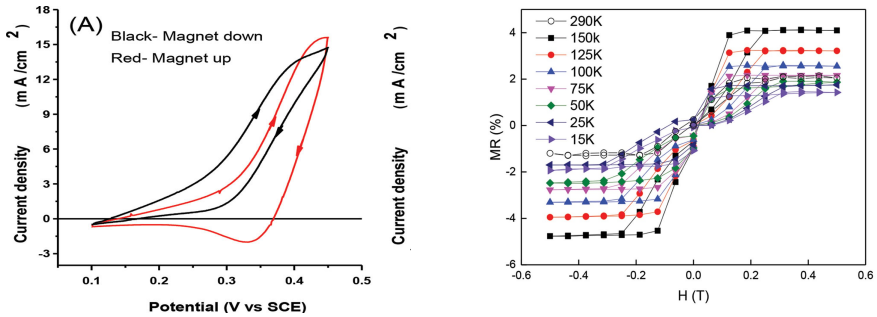

Fig.A: CV plots for a PCT-L coated Ni working electrode with ferrocene as the redox couple. Black and red curves correspond to a plot taken when the Ni is magnetized down or up, respectively. **Fig.B**: Magnetoresistance curves obtained with a solid-state device composed of PCT-L using an external magnetic field up to 0.5T at different temperatures.

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OC30

THERMAL BEHAVIOR AND ELECTRICAL PROPERTIES OF POLYMER BLENDS AND INTERPOLYMER COMPLEXES BASED ON POLY(STYRENE-CO-METHACRYLIC ACID) AND POLY(N-N-DIMETHYLACRYLAMIDE-CO-4-VINYLPYRIDINE).

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Abstract

Novel materials of optimized properties as nano-structured blends or interpolymer complexes with specific morphologies may be prepared by simply mixing pairs of a proton-acceptor and proton-donor polymers in a common solvent and by monitoring the nature and density of interactions that occurred between the constituents of the mixtures.

Varying the densities of interacting species within poly (N,N-dimethylacrylamide-*co*-4-vinylpyridine) (PDMA4VP) containing two proton accepting sites of different strength and poly(styrene-*co*-methacrylic acid) (PSMA), new materials as miscible blends or inter-polymer complexes were elaborated and characterized with the aim to use them as proton conducting membranes**.**

FTIR spectroscopy analysis confirmed that competing specific interactions of different nature and strength carboxyl-pyridine, carboxyl-amide and carboxyl-carboxyl occurred within these systems.

The thermal properties of the synthesized copolymers and their various blends or interpolymer complexes were investigated by differential scanning calorimetry (DSC) and thermogravimetry (TGA).

Although a single glass transition temperature (Tg), higher than those calculated from the weight average values of the pure polymers was depicted with all compositions of these systems, different Tg-composition behaviours were observed with interpolymer complexes compared to miscible blends.

Denser and stronger specific interactions occurred within the interpolymer complexes that led to stiffer materials, of Tg higher than those of the individual constituents, varying slightly with the initial composition compared to those obtained miscible blends.

In agreement with FTIR spectroscopy results, the Tg-composition curves of these systems were analyzed using equations in the literature and confirmed that the presence of 4-vinylpyridine (4VP) units in PDMA4VP copolymers increased the average strength of intermolecular interactions in the PDMA4VP/PSMA systems.

A thermogravimetric analysis showed that the thermal behaviour observed with the interpolymer complexes was different from those of the blends and the individual constituents.

Results of a preliminary investigation on electrical properties of the synthesized copolymers and some of their blends and inter-polymer complexes were determined and will be presented.

POSTER CONTRIBUTIONS

P1

SYNTHESIS AND CHARACTERIZATION OF PEDOT/PSS WITH CONDUCTIVITIES HIGHER THAN 1000 S/CM

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Abstract

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) (Fig.1) in the form of an water dispersion as colloidal gel particles is one of the most successful conductive polymers during the last two decatedes. Because of its processability, transparency, high electrical conductivity and thermal stability, the PEDOT/PSS has potential applications to electrical and optical devices such as transparent electrodes for touch panels and flexible displays[1]. So far, the highest electrical conductivity of ca. 1000 S/cm has been reported for the PH1000 grade of the PEDOT/PSS by Heraeus[2]. However, it is still lower compared to indium tin oxide (ITO > 1000 S/cm) for the applications to the transparent electrodes.

In this study, highly conductive PEDOT/PSS was newly synthesized at various polymerization temperatures and characterized by means of Raman spectra, X-ray photoelectron spectra (XPS), wide-angle X-ray diffraction analysis (XRD), and conductive atomic force microscopy (C-AFM). It was found that the electrical conductivity increased with decreasing the polymerization temperature and the value reached as high as 1145 S/cm at 0 °C (Fig.2) which is higher than that of the PH1000. The Raman spectra suggested that the the lower the polymerization temperature, the higher the polymerization degree of PEDOT, while the XPS spectra clearly demonstrated that the composition ratio between the PEDOT and PSS was nearly constant. On the other hand, the XRD pattern indicated that the crystallite size normal to the (020) planes of the PEDOT crystals slightly increased as the polymerization temperature became lower. The C-AFM clearly demonstrated that the decrease of polymerization temperature resulted in an increase of the number of conductive particles, while the morphology was almost the same. The results allowed us to conclude that the high electrical conductivites over 1000 S/cm would be associated with the slow rate of radical formation at low temperatures. Therefore, polymerization degree of the PEDOT molecules increased prefarable to form large crystallites, which significantly improved transport of charge carriers between the highly conductive particles.

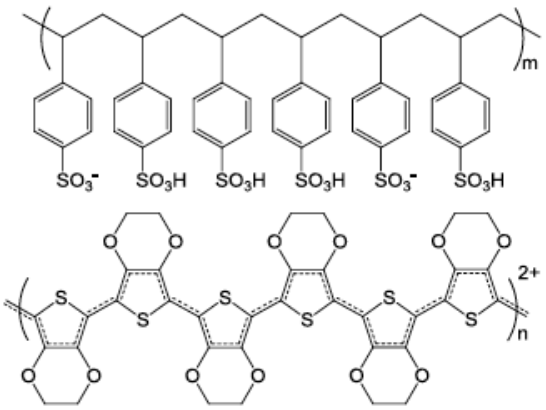

Fig.1 Chemical structure of PEDOT/PSS.

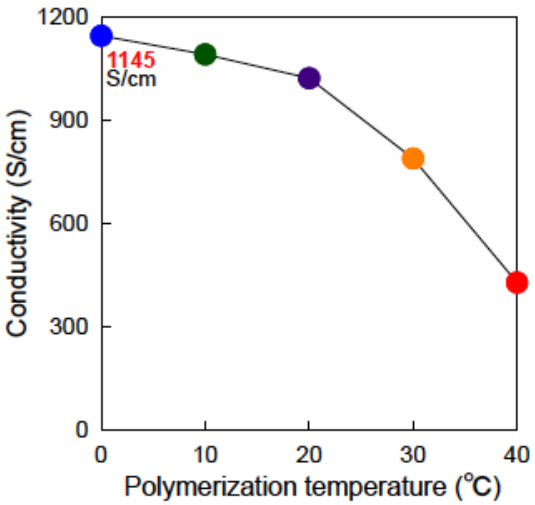

Fig.2 Dependence of electrical conductivity on polymerization temperature of PEDOT/PSS.

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P2

EFFECTIVE ELECTRICAL CONDUCTIVITY OF CNT-EPOXY NANOCOMPOSITES

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Abstract

The electrical conductivity of carbon nanotube (CNT)-epoxy composites was investigated analytically and experimentally. The theoretical predictions of the effective electrical conductivity of CNT-epoxy composites calculated by an analytical model developed on the basis of the micromechanics of composites. The parametric analysis carried out revealed an influence of geometrical and electrical parameters of the micromechanical model on the effective conductivity of CNT-epoxy nanocomposite. The nanocomposites made from the DGEBA-based and RTM6 epoxy resins filled with different weight content of Baytubes C150P and N7000 multi-walled carbon nanotubes were prepared. The experimental values of the electrical conductivity of the nanocomposites were compared with those calculated by means of the analytical model.

P3

DISPERSION VERSUS DISTRIBUTION: CRITICAL BALANCE TO ACHIEVE CONDUCTING COMPOSITES

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Abstract

The aim of this work is to investigate the influence of polyamide ratio and nanotubes source on dielectric and morphological behaviour of PA66/PA6/MWCNT composites.

Two polyamides, PA66, PA6 and CNT (NC7000, Nanocyl) pre-dispersed at 15 wt.% in PA66 and PA6 were used. The content of CNT was fixed at 3 wt.% in all nanocomposites.

From the Light Microscopy images, the agglomerate area ratio along with the average value of agglomerate size were calculated and matched with the conductivity values (see Table 1).

The highest conductivity values correspond to nanocomposites with high ratio A/A_0 and relatively big agglomerates (the worst state of dispersion). It seems as if the conductivity was more related to the agglomerate distribution than the CNT dispersion within the matrix.

PA66/PA6/CNT	A/A_0	Agglomerate $\overline{A}$ (µm²)	σ *(S/cm)
25/75(MB)/3	14.9% ± 2.0%	1593 ± 595	$1.4.10^{-6}$
50/50(MB)/3	38.5% ± 3.2%	2117 ± 690	$8.5.10^{-5}$
75/25(MB)/3	14.4% ± 1.2%	1266 ± 246	$6.0.10^{-7}$
25(MB)/75/3	2.5% ± 0.9%	438 ± 158	$1.1.10^{-10}$
50(MB)/50/3	34.4% ± 0.9%	2488 ± 869	$7.7.10^{-6}$
75(MB)/25/3	3.5% ± 0.7%	591 ± 318	$1.4.10^{-8}$

Table 1: Agglomerate area ratio A/A_0, agglomerate $\overline{A}$ and conductivity values (*at 1.000 Hz). MB indicates the matrix where nanotubes are pre-dispersed.

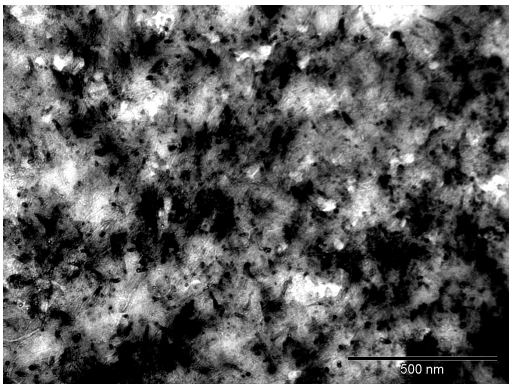

Figure 1: TEM image of 50(MB)/50/3 composite

The worst dispersion of CNTs was measured in 50/50 PA66/PA6 composites (Figure 1), although their agglomerates are better distributed in the matrix than in the other two ratios of polyamides. This fact favours a greater number of CNT-CNT interactions, encourages electrical network formation and, as a result, higher conductivity values are achieved[1].

For the other polyamide ratios, the better distribution and electrical properties, have been achieved when MWCNT are predispersed in PA6, with lower viscosity[2].

Acknowledgements. Authors acknowledge the financial support to Xunta de Galicia-FEDER (Program of Consolidation and structuring competitive research units (GRC2014/036).

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P4

RHEOLOGICAL MONITORING OF POLYAMIDE66/POLYAMIDE 6/MULTI-WALLED CARBON NANOTUBES COMPOSITES

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Abstract

Polyamide 66 (PA66) and polyamide 6 (PA6) are widely used in electronic appliances, vehicles and sophisticated machinery, owing to its good mechanical strength and chemical resistance. Fitting the PA66/PA6 ratio, the desired mechanical properties can be obtained. Besides, if conducting nanofiller, as multiwalled carbon nanotubes (MWCNTs), is added, the nanocomposites obtained could show interesting physical properties.

In this work, polymer nanocomposites were obtained melt-mixing 3 wt.% MWCNT in polyamide 66/polyamide 6 (PA66/PA6) blends with different polyamide ratios. The nanotubes were initially pre-dispersed in two different masterbatches (with PA66 or PA6 matrix, respectively). The main objective of this study is to analyze the influence of polyamide ratio and nanotube source on the rheological behavior of these composites. Previously, different electrical behaviors were observed because electrical percolation takes place before when the nanotubes are included in a PA6 matrix. In this study, the rheological behavior of composites will be related with their electrical properties[1].

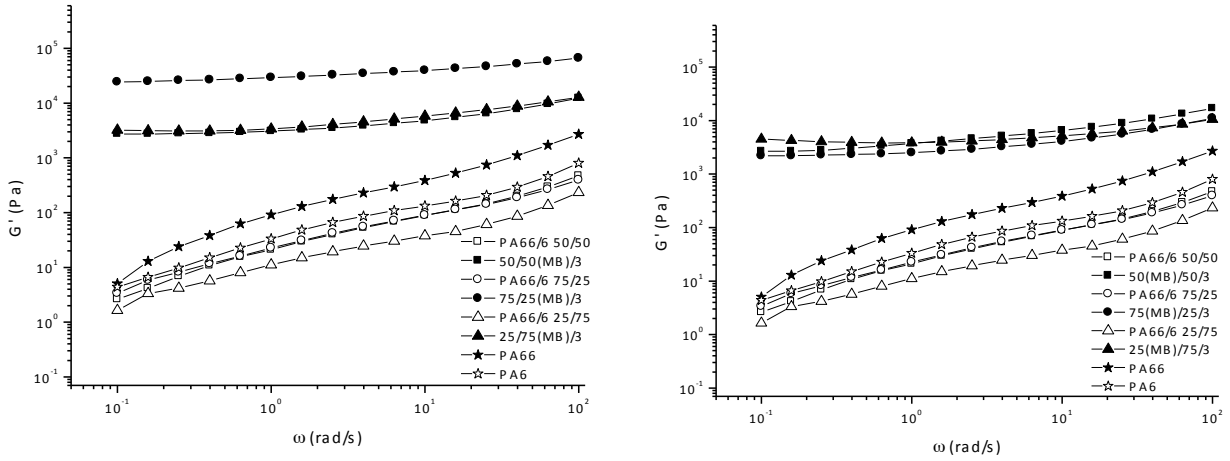

Figure. The effect of the ratio PA66/6 on the G' for composites

All composites, independent of polyamide ratio, are rheologically percolated but differences in electrical and rheological percolation states could be highlighted.

The differences are related with unlike requirements for rheological and electrical percolation threshold[2] (CNT-polymer network in one case, CNT-CNT networks, in the other one). The data display that matrix viscosity, miscibility between polyamides, and the use of a different masterbatch, are key aspects which determine the formation of CNT-polymer and CNT-CNT networks. The prevalence of one or another one originates the differences observed in rheological and electrical properties[3].

Acknowledgements. Authors acknowledge the financial support to Xunta de Galicia-FEDER (Program of Consolidation and structuring competitive research units (GRC2014/036)

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P5

FACTORIAL EXPERIMENTAL DESIGN ON SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES BY CVD USING Co/Mn BIMETALLIC CATALYST

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Abstract

Carbon nanotubes (CNT) are of great interest in nanotechnology, especially when used as additives in polymer nanocomposites due to properties improvements, such as: mechanical reinforcement, electrical and thermal conductivities, controlled drug release. Since their discovery, studies on multi-walled (MWCNT) or single-wall (SWCNT) follow three typical synthesis methods: catalytic chemical vapor deposition (CVD), arc discharge and laser vaporization. Several works apprise that CVD tends to produce nanotubes with less impurities and large scale processing at low cost. The properties of CNT obtained by CVD rely on various synthesis parameters: temperature, time, flow rate of precursors, type of catalyst and so on. The aim of this research is to explore routes on MWCNT synthesis via CVD using statistically designed experiments to evaluate any significant processing parameter. A factorial design has been applied for temperature, flow rate of CH_4/N_2 and time (Table I). The responses variables are: mass yield, thermal stability (Ea), quality (ratio on D/G Raman bands) and morphology. The MWCNT are characterized by TGA, Raman, TEM and SEM analyses. TEM and SEM micrographs (Fig.1) show a bamboo-like MWCNT morphology, with almost ten concentric walls and diameters around 30 nm. The statistical analyses show temperature as a significant factor for all the studied responses (95% of confidence). The higher yield and thermal stability (Ea) and better quality (lower D/G ratio) are found at the higher 950 °C level. The CH_4:N_2 rate is significant only for the thermal stability. The interaction between temperature and CH_4:N_2 is significant for the D/G ratio.

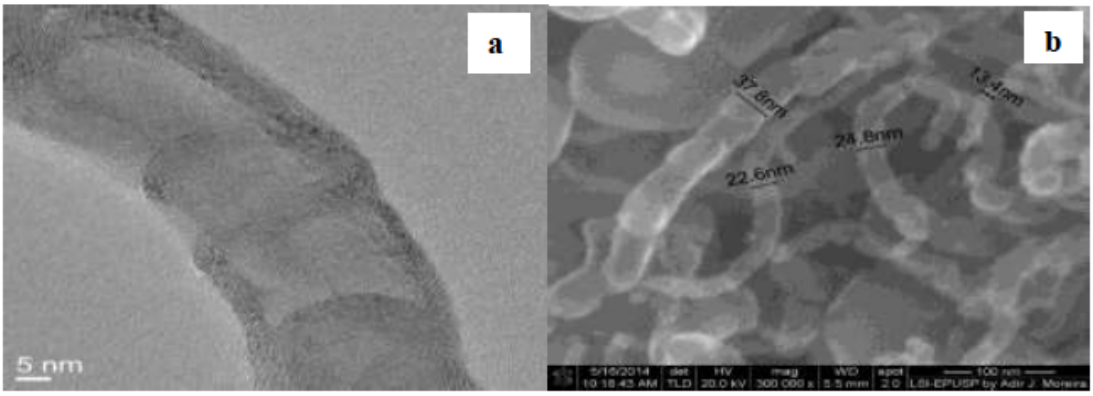

Fig.1: Micrograph of MWCNT: MET (a) and SEM (b), at the conditions: 850°C; 3:1 CH4:N2; 5 min.

Table I: Factorial experimental design (2^3 + center point)

Factors		Levels		
		-1	0	1
X1	T (°C)	850	900	950
X2	CH_4:N_2	1:1	2:1	3:1
X3	Time (min)	5	15	25

Acknowledgements: LNNano-LNLS and CNPq / CAPES for the financial support.

P6

SYNTHESIS OF PMMA/MWCNT NANOCOMPOSITES BY IN SITU POLYMERIZATION USING ULTRASONIC PROBE STIRRING

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Abstract

Research on polymeric nanocomposites is of great interest in both academia and industry. It is still a challenging to obtain the complete dispersion of nanoparticles into polymer matrix although many methods, including in situ polymerization, melt blending, and solution blending, have been studied in the literature. Poly(methyl methacrylate) (PMMA) is a typical transparent amorphous polymer. Nanocomposites of multiwalled carbon nanotubes (MWCNT) in very small amounts (1 to 3 wt%) dispersed into poly(methyl methacrylate) (PMMA) matrix could have a high potential for applications whereupon conductivity, transparency, flexibility and low specific weight are required. In this work, nanocomposites of PMMA/MWCNT are synthetized by *in situ* solution polymerization and ultrasonically agitated (probe sonicator) to improve nanoparticles dispersion into the polymer matrix. A 2^3 factorial experimental design (Table I) was used to study the effect of synthesis variables on the electrical resistance of PMMA/MWNCT thin films. Sheet resistance measured by the four-points method range from 5.7 to 29.2 kΩ/sq; lower resistances were found at the high levels of energy and MMA/AIBN ratio, for chloroform, and at the low levels for the solvents mixture. High resolution TEMs (Fig. 1) showed that nanoparticles are interconnected and disperse without special orientation.

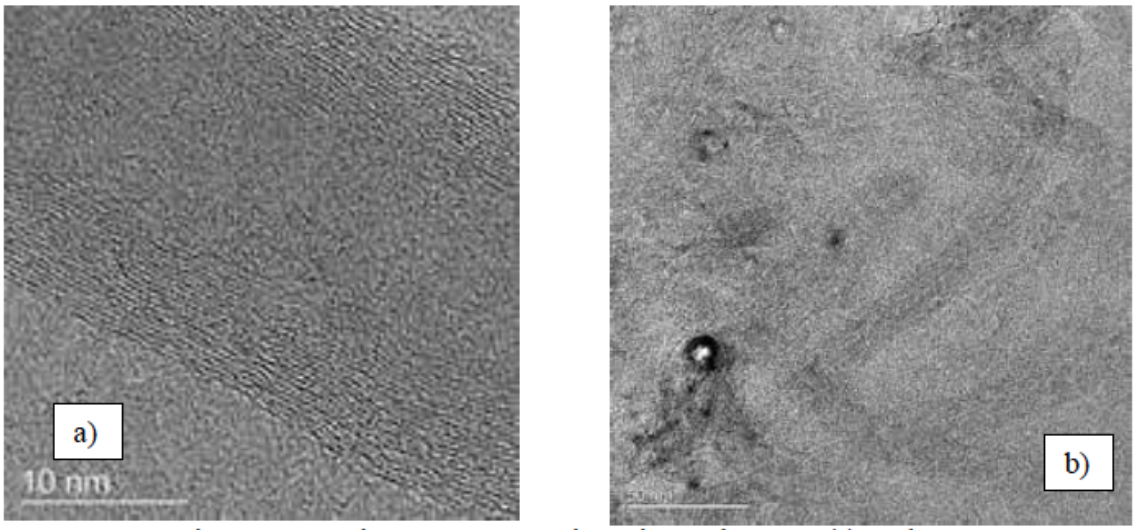

Fig 1. HRTEM images: MWCNT integrity, scale 10 nm (a), and randomly interconnected, scale 50 nm (b), into PMMA matrix.

Table I: Factors and levels of 2^3 experimental design (MMA: monomer/AIBN: initiator)

Factors	Levels	
	-1	1
Solvent	Chloroform	Chloroform/Toluene
MMA/AIBN	200:1	400:1
Sonication energy (kJ)	120	240

Acknowledgements: LNNano-LNLS- Brazilian Synchrotron Light Laboratory; Prof. P.C.M.L. Miranda (IQ/Unicamp); Prof. I. Pereyra, Prof. M.N.P. Carreño, Igor Abe (PSI/EPUSP); J. M. Bressanin, F. Buzzolin (FEQ/Unicamp); CNPq for the financial support.

P7

ONE- AND TWO-STEP SYNTHESIS OF POLYPHENYLENE COPOLYMERS IN THE PRESENCE OF NICKEL COMPLEX

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WITHDRAWN

P8

CONDUCTING ELECTROSPUN POLYCAPROLACTONE/POLYPYRROLE FIBERS

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Intrinsically conducting polymers (ICP) are ideal for wide range of applications with the benefit of easier processing and higher flexibility than inorganic metals. They are also less expensive and lighter than metals. ICP are studied for many application including biological and chemical sensors, transparent electronic devices, resistors, actuators, etc. Most studied conducting polymers are polypyrrole (PPy), polyaniline, polythiophene and their derivates. Various methods are used for PPy synthesis, as electrochemical polymerization, chemical oxidative polymerisation, etc. [1]. The rising demand for these polymers calls for the new kind of conductive polymers, nanocomposites or hybrids. New combined materials, prepared by coating of various substrates with PPy, can find applications as antistatic materials, anti-corrosion coating, radiation shielding, but also a new category of application is opening in organic electronic or medical using [2].

Polycaprolactone (PCL) was synthesised in 1930s. It is a hydrophobic, semi crystalline polymer, crystallinity tends to decrease with increasing molecular weight. PCL is used for its good solubility, low melting point and mixture compatibility. These are also the reasons for which PCL is studied in the biomedical field.

First step of our research was preparation of electrospun poly(ε-caprolactone) fibres at a nano and submicron scale. The study of controlled electrospinning parameters such as applied voltage, tip-collector-distance and polymer concentration was made. Dimethylformamide (DMF), chloroform, dimethyl dichlormethane (DCM), and DMF/DCM (ratio 1:1) were used as solvents. Solutions of PCL with the concentration between 5 wt.% and 15 wt.% were spinned. The results showed that the electrospun fibres from 15 wt.% solution using DMF/DCM as solvent in the ratio 1:1 with the flow rate 0.5mL/h, applied voltage 9 kV, are without any defects in the structure.

These electrospun mats were further coated by conducting polymer, polypyrrole. We studied the influence of polymerization conditions, including using combination of oxidant and surfactant during chemical oxidative polymerization of pyrrole monomer on quality of depth penetration of conductive polymer into fibrous mats. Various analytical methods e.g. XPS, SEM were used to characterization of the morphology and structure of prepared fibrous composite. The interesting properties of these composites recommended them as material for biological and medical use.

Acknowledgement: This work was financially supported by project VEGA 2/0149/14 and project COST MP 1206.

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P9

A NEW POLYTHIOPHENE WITH LC SIDE CHAINS FOR BHJ SOLAR CELLS

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Abstract

In the last years, the semiconducting polymers have reached an increasing importance for the production of organic-based photovoltaic solar cells (OPV)s. In fact, these materials are easy to process and quite inexpensive. However, the control of the nanoscale morphology or microstructure of the active layer in hybrid solar cells is critical to ensure high device performance. We report on the synthesis of a new thiophenic monomer, functionalized in the side chains with a molecule showing a liquid crystal (LC) behavior, i.e. the 3-[6-(4-oxy-4'-cyanobiphenyl)hexyl]thiophene (T6CB). It has been obtained using a SN2 reaction on the thiophenic intermediate 3-(6-bromohexyl)thiophene (Figure 1), with good yield (90%).

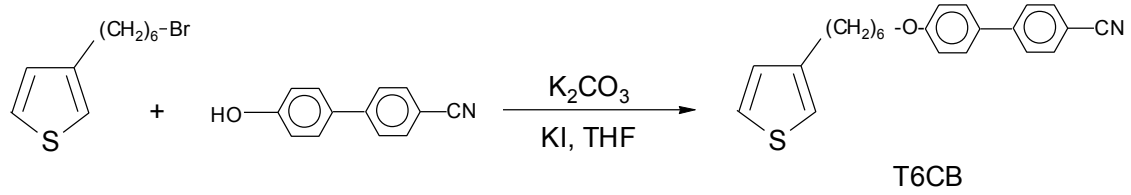

Figure 1. Synthesis of monomer T6CB

Since the homopolymer of T6CB was insoluble in common organic solvents, the monomer has been copolymerized with 3-hexylthiophene to give a soluble and filmable copolyer which has been exploited for the assembling of a bulk heterojunction polymeric solar cell.

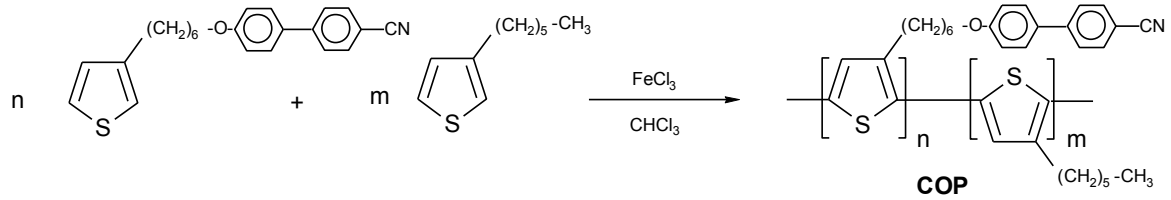

Figure 2. Synthesis of the LC copolymer.

The spontaneous orientation of cyano-biphenyl moieties should lead to a well-ordered morphology when subjected to a process of thermal annealing, thus favoring the alignment of the macromolecular chains[1]. In fact, COP has shown a LC behavior, as confirmed by the images obtained with the optical microscope in polarized light.

Lastly, after a suitable annealing procedure, the power conversion efficiency of COP reached the 3.56%, evidencing a significant increase with respect to the un-annealed counterpart (2.95%).

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P10

SYNTHESIS OF CONJUGATED ONOR-ACCEPTOR OLIGOMERS AND POLYMERS FOR APPLICATIONS IN BULK HETEROJUNCTION (BHJ) AND SINGLE COMPONENT (SMOC) SOLAR CELLS

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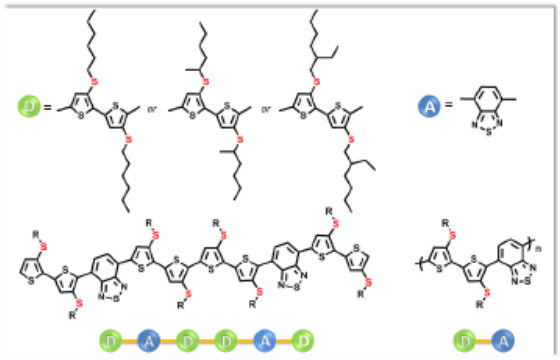
Abstract

In the last decade the study of conjugated semiconducting thiophene derivatives has received much attention for their potential application in low-cost production of solar cells on flexible substrates.[1] Recently, organic solar cells made of one single photoactive material, containing donor and acceptor moieties in the same molecule, have been also investigated.[2]

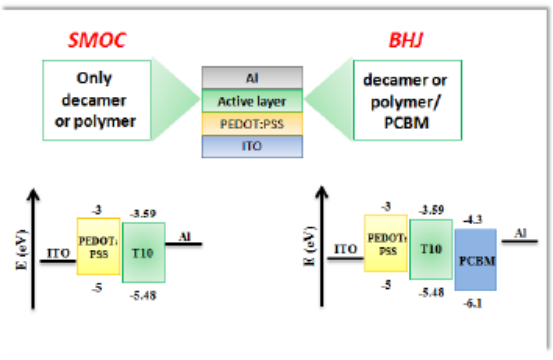
The aim of this work was to synthesize *small-bandgap* decamers and polymers made of alternating donor and acceptor units, namely bis(3,4'-thioalkyl)-2,2'-bithiophene and 2,1,3-benzothiadiazole, respectively. The compounds were synthesized with a high degree of purity in aqueous solvents with the assistance of microwave (MW) and ultrasound (US) irradiation. The molecular structure of the synthesized compounds is shown in Scheme 1.

The newly synthesized decamers and polymers were characterized in solution and in thin film by means UV-vis and PL spectroscopies, Cyclic Voltammetry, X-ray diffraction, Atomic Force Microscopy (AFM). Surface photovoltage maps of cast films of decamers and polymers in blend with PCBM or as pure compounds were obtained through Kelvin Probe Force Microscopy indicating that under illumination charge generation and separation were obtained in both cases.

Finally, application in bulk heterojunction and single component photovoltaic devices demonstrated that the compounds may act not only as donors in BHJ solar cells but also as both donors and acceptors in single photoactive material solar cells (Scheme 2).



Scheme 1. Molecular structure of the synthesized compounds



Scheme 2. Schematic representation of the device structure

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P11

SYNTHESIS AND CHARACTERIZATION OF INDICO-CONTAINING CONJUGATED POLYMERS

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Indigo as a very stable chromophore is of outstanding interest as building block for conjugated polymers for organic electronics applications. Because of its stability it is used to dye the famous 'blue jeans'.[1] It's strong blue absorption is based on the crossed assembly of electron-accepting and electron-donating building blocks. Due to its stability in solid state, polymers containing indigo units have been proposed for application in organic solar cells.[2] Low bandgap copolymers containing isoindigo have shown high power conversion efficiencies in bulk heterojunction-type OPV devices of up to 6.3%.[3]
Via Suzuki coupling of dibromoindigo and a fluorenediboronic ester alternating indigo-fluorene copolymers have been synthesized with a maximum degree of polymerization of eleven.[4] For investigation of the photophysical properties also a model compound, a fluorene-indigo-fluorene - trimer - has been synthesized. (Figure 1, left)

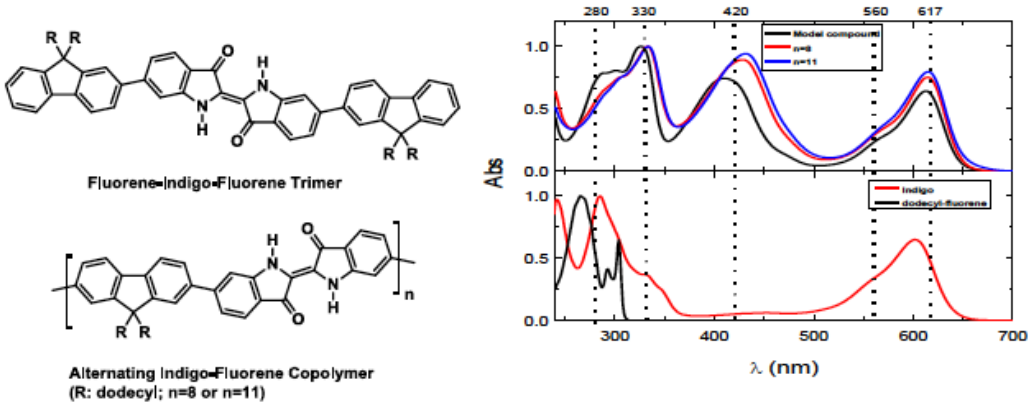

Figure 1: left: chemical structures of a fluorene-indigo-fluorene trimer and the alternating indigo-fluorene copolymer; right: absorption spectra of copolymers, the model compound, indigo, and 9,9-dialkylfluorene (dashed line are guidelines to the eyes).

The alternating copolymer shows absorption maxima at 333, 431, and 615 nm. (Figure 1, right) Hereby, the absorption band at 431 nm is assigned to a delocalized charge-transfer transition that is dependent on the molecular weight (length) of the copolymers. The absorption band at 615 nm corresponds to a transition of the electronically localized indigo chromophore.

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P12

SYNTHESIS OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/TiO_2 PHOTOCATALYTIC POLYMER NANOCOMPOSITES

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Abstract

Environmental problems associated with water pollution have persistently been an important issue over recent decades, correlated negatively with the health and ecosystem. Photocatalysis is established as an effective and sustainable water treatment technology offering a perspective for the degradation of many organic water pollutants, converting them to biodegradable compounds or completely mineralizing them into carbon dioxide and water. Titanium dioxide, TiO_2, is one of the most important photocatalyst, which is widely used due to its chemical stability and high photocatalytic activity. It is also inexpensive and harmless to the human population and the environment. However, relatively high recombination rate of electron-hole pair in excited TiO_2 restricts its photocatalytic activity thus hindering its practical application in the water treatment processes. Conducting polymers with extended π-conjugated electron system and satisfactory environmental stability can act as stable photo-sensitizer to sensitize TiO_2. As typical n-type semiconductors, conducting polymers can absorb a broad spectrum of ultraviolet and visible light (190–800 nm) irradiation[1]. Because of that the main goal of this work was to exploit the sensitizing capacities of conducting polymers to produce TiO_2-based photocatalyst with enhanced photocatalytic properties. For this purpose nanocomposite of poly(3,4-ethylenedioxythiophene) (PEDOT) and TiO_2 was synthesized by oxidative chemical polymerization with two different oxidants, $FeCl_3$ and ammonium persulfate (APS). Polymerization was carried out in batch reactor at room temperature for 24 h in nitrogen atmosphere with HCl as the dopant. To determine effect of oxidant on structure of synthesized PEDOT/TiO_2 nanocomposite infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used. To determine polymerization degree TG analysis was used. FT-IR results showed typical vibrations for PEDOT and Ti-O, and thus confirmed successful synthesis of polymer photocatalyst nanocomposites. A significant influence of oxidant agent on the morphology had been confirmed by XRD and SEM. Samples synthesized with $FeCl_3$ showed highly crystalline morphology while samples prepared with APS had more sphere-like amorphous morphology. The results demonstrate that the redox potential of used oxidizing agents has a key role in tailoring the properties of PEDOT nanocomposites.

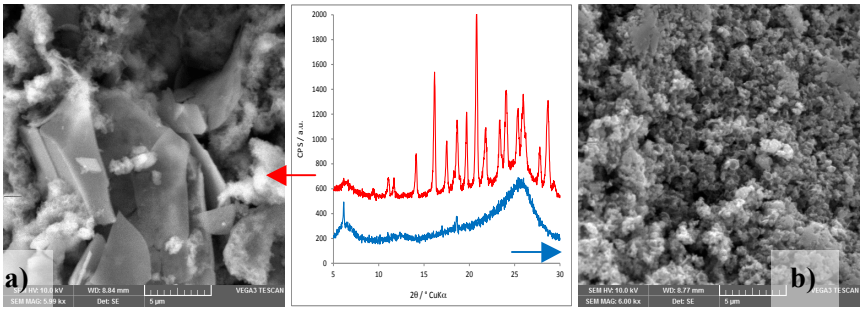

Figure 1. SEM pictures and XRD results of PEDOT synthesized with a) $FeCl_3$ and b) APS oxidant

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P13

CO-LOCALIZED AFM-RAMAN SETUP: A POWERFUL TOOL TO STUDY POLYMER HYBRID MEMBRANE WITH AN ACTIVE NANO-NETWORKS FOR PEMFC

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We present here a co-localized AFM-Raman setup, developed to be a key element in our strategy to design hybrid membranes for proton exchange membrane fuel cell (PEMFC) . Indeed, co-localization of these two instruments makes it possible to get topographic, mechanical, thermo-mechanical and chemical mappings for the same spot of the membrane with a nano to micro-resolution.

During the co-localized characterization the sample is successively analyzed by the AFM and the confocal Raman microspectrometer. The AFM is able to give quantitative mechanical properties of the sample at the nanoscale, based on the acquisition of thousands of force-distance curves per image. Each pixel contains a force curve that can be analyzed in order to provide mechanical properties such as Modulus, Adhesion, Deformation and Dissipation, simultaneously acquired with the topographic information of the sample at high resolution. Special care must be taken with calibration issues in order to access real and comparable quantitative mechanical properties, as well as analysis conditions like indentation depth, applied force, and tip shape and size. Confocal Raman microspectroscopy is a straightforward complementary technique to access chemical and structural information at a micro-scale, which can be correlated to differences in mechanical properties measured by AFM.

We will give illustrations of the interest of these co-localized data for a better understanding of the structure-properties relationship and stabilization mechanism of hybrid membranes designed with an active nanonetwork in our lab (see "A new chemical stabilizing strategy for better performances and durability of PEMFC" talk).

Finally we will also stress out the importance of the sample preparation for such analysis. We used cryo-ultramicrotomy to open cross-sections of the membranes for both AFM and Raman analysis. Using a diamond knife we operated at -100ºC to produce very flat surfaces with minimum damage to the structure to be studied. In addition, cryo-cutting provides thin slices of the membrane suitable for complementary structure analysis with TEM or STEM, or even 3DTEM.

P14

ELECTRO CONDUCTIVE COMPOSITES WITH SEGREGATED STRUCTURE: POLYMER/REDUCED GRAPHENE OXIDE

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One of the most promising approaches to the development of electro conductive composites is the formation of segregated structure with conductive filler placed on the surface of polymer powder. Such filler creates a conductive network at ultra-low content of electro conductive material. Traditionally conductive polymer composites are obtained by uniform distribution of filler in polymer matrix. The conductivity of these materials is achieved when the quantity of the filler is higher than the percolation threshold.

In this study conductive polymer composites with segregated structure were made from different polymer matrixes and reduced graphene oxide (rGO). Graphene oxide (GO) was synthesized from graphite powder using Hummer's method[1] with varied quantity of $KMnO_4$ (2 or 3 g $KMnO_4$ per 1 g of graphite) followed by immersion in H_2O for several days. Then GO was fractionated by centrifugation to three fractions: heavy, middle (M) and floaty (F). Study of gaseous products of thermal reduction of GO showed that heavy fraction of graphene oxide was weakly oxidized. For this reason composites were prepared only using floaty and middle fractions. Fluoropolymer F-42, polytetrafluoroethylene and ultra-high-molecular-weight polyethylene were used as composite matrix. Composites were synthesized by thermal treatment at 200°C and chemical treatment at small amount of hydrazine vapor at room temperature. Hydrazine reduction (HR) for the preparing of rGO/polymer composites with segregated structure allows getting higher electro conductivity than thermal reduction. The conductivity of samples prepared by HR is more than 10-folds higher than that of samples prepared by thermal reduction. The conductivity of composites with segregated structure reaches 1.43 $S*cm^{-1}$ at filler concentration 0.25-0.5 % (Fig. 1). The conductivity of composites obtained by hydrazine reduction at 95 °C was 1.7-1.8 times higher as compared with HR at room temperature. Mechanical properties were also investigated.

Reduction of graphene oxide by small amount of hydrazine vapor at room or 95 °C temperatures allows using polymers which have a processing temperature less than 160 °C for this application.

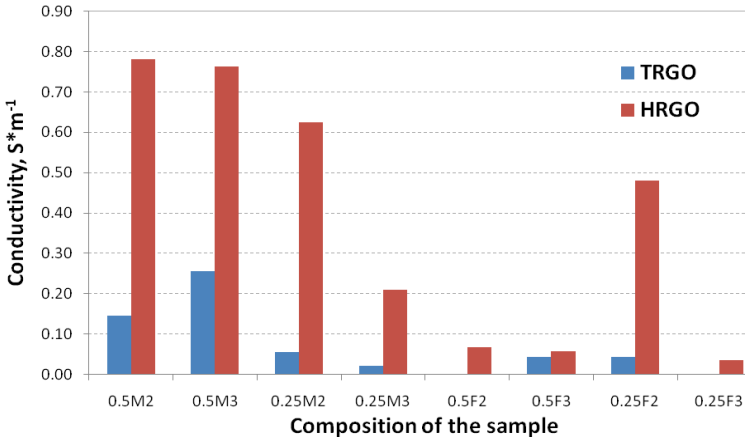

Figure 1. Electrical conductivity of F-42/rGO composite samples. TRGO - thermally reduced graphite oxide, HRGO - graphene oxide reduced by hydrazine. **0.5M2** composition consists of 0.5% (**0.5**) of rGO obtained from middle (**M**) fraction of GO synthesised with 2 g (**2**) of $KMnO_4$ per 1 g of the graphite.

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P15

SYNTHESIS OF NOVEL CONDUCTIVE COMPOSITE WITH CONJUGATED WATER-SOLUBLE POLYFLUORENE AND GRAPHENE OXIDE USING RADIATION FOR HOLE TRANSPORTING LAYER IN ORGANIC SOLAR CELLS

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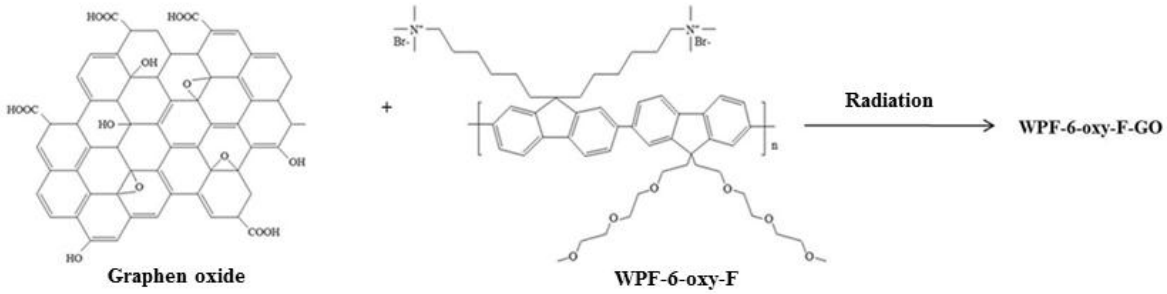
Abstract

Conjugated polymer-based organic solar cells (OSCs) have the merits of low-cost, lightweight and flexibility, which enable their mass production, large-area production and roll-to-roll process. As an effort to obtain a better power conversion efficiency (PCE), a charge transport layer is introduced between the electrode and active layer to improve the efficiency of carrier transport in OSCs. There are some charge transport materials, such as conductive polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS). In particular, PEDOT:PSS is widely used as a hole transporting layer (HTL) or transparent electrode in OSCs because of high conductivity and solution-processibility. However, as PEDOT:PSS has several drawbacks including a high acidic nature, hygroscopic property and inhomogeneous electrical property, so these problems are related to the ITO anode corrosion, and device stability[1]. Therefore, PEDOT:PSS should be needed to replacement of new hole transporting layer.

To replace PEDOT:PSS, graphene oxide (GO) and 9-bis((6'-(N,N,N-trimethylammonium) hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-(2-methoxyethoxy) ethoxy)ethyl)-9-fluorene)) dibromide (WPF-6-oxy-F) were simply blended and then this blended solution (WPF-6-oxy-F-GO) was treated with electron beam to induce the reaction between WPF-6-oxy-F and GO. After electron beam treatment, conductivity of WFP-6-oxy-F-GO was improved due to efficient π-π packing formed C-N bonds between two materials by electron beam energy. This WPF-6-oxy-F-GO composite was used as a HTL between the active layer and anode in OSCs. As a result, the PCE of OSCs was dramatically enhanced ~6.72% by introducing WPF-6-oxy-F-GO with electron beam treatment as a HTL. Compared with each WPF-6-oxy-F-GO composite with electron beam or without, PCE was enhanced from 5.24% to 6.72%, and fill-factor (FF) and short circuit current density (J_{sc}) also improved from 55.30% to 63.30%, 9.40 mA/cm^2 to 14.56 mA/cm^2, respectively.



Scheme 1. *The structure of the materials and the fabrication process of WPF-6-oxy-F-GO*

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P16

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE/TiO_2 COMPOSITES AS A PHOTOCATALYST

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Abstract

The great advantage of conductive polymers is that their chemical, physical and optical properties can be adjusted according to the demand of application. In this study the structure of conductive polymer polypyrrole (PPy) was studied during the chemical synthesis. It is of great importance to explore the appropriate structure of polypyrrole that can induce activation of TiO_2 photocatalysts since the synthesis of organic/inorganic hybrid materials can result in a synergistic and complementary feature, increasing TiO_2 photocatalytic efficiency. As conductive polymers are also photosensitive they can be activated by light absorption, which starts the transition of electrons from a conductive polymer by injection in the conductive band of TiO_2. However, despite intensive research, the relationship between structure and conductivity is still not completely understood. It is assumed that the conductivity increases with a higher degree of crystallinity but this is not confirmed for all conducting polymers, only for some of them.

In this paper different conditions of synthesis of pure polypyrrole and polypyrrole titanium dioxide (PPy-TiO_2) composite were studied. Samples of polypyrrole, TiO_2 and polypyrrole/TiO_2 composites were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetry (CV). The results show that due to the changes in the fraction of oxidant during the synthesis of PPy its structure was changed, and thus the conductivity.

P17

BLOOD COAGULATION AND PLATELET ADHESION ON POLYANILINE FILMS

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Abstract

Conducting polyaniline (PANI) has immense potential with regard to practical applications in the biomedicine[1]. As all materials being used *in vivo* will come into a contact with blood at some point, hemocompatibility is one of the major biocompatibility parameters. The contact of any material with blood induces multiple defensive mechanisms, such as the activation of coagulation cascade, platelet adhesion or the triggering of complementary systems. The hemocompatibility of a material can be affected by modification with synthetic polymers and/or copolymers with heparin-like activity[2]. For example, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) was shown as a material acting against blood clotting[3,4]. The present study is focused on the investigation of changes in blood coagulation and platelet adhesion induced by the surfaces of PANI hydrochloride (PANI-Cl) and PANI modified by PAMPSA. The PANI-PAMPSA films were prepared using two procedures. In the first one, PANI base was reprotonated with PAMPSA solution (PANI-PAMPSA). In the second procedure, PAMPSA was added prior to the polymerization into the reaction mixture (PANI-REACT). The anticoagulation activity was determined *via* monitoring the following coagulation parameters: thrombin clotting time (TCT); activated partial thromboplastin time (aPTT); and prothrombin time (PT). The interaction with coagulation factors X, V and II was also studied.

Table 1. Blood coagulation and platelet adhesion induced by different PANI surfaces.

	PANI-Cl	**PANI-PAMPSA**	**PANI-REACT**
Anticoagulation activity	physiological	coagulation inhibited	physiological
Platelet adhesion	physiological	significantly decreased	decreased

As can be seen in Table 1, pristine PANI-Cl influenced neither coagulation nor platelet adhesion. Also PANI-REACT did not have any significant effect on the coagulation. Nevertheless, the platelet adhesion notably decreased on both PANI surfaces modified with PAMPSA. Moreover, PANI-PAMPSA completely hindered coagulation. These results highlight the significant potential of this surface modification with respect to application in biomedicine. The combined conductivity, anticoagulation activity, and ability to decrease platelet adhesion observed on PANI surface coated with PAMPSA open up new possibilities for this polymer to be used, not only as a biomaterial but also in blood-contacting devices, such as catheters or blood vessel grafts.

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P18

CALCULATION AND EXPERIMENTAL DETERMINATION OF PIEZORESISTIVITY TENSOR COMPONENTS OF UNIDIRECTIONAL FIBRE REINFORCED PLASTICS

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Abstract

Fiber reinforced plastics (FRPs) made of electric conductive carbon fibers and electric insulator epoxy resin or nonconductive glass fibres and conductive epoxy resin filled with carbon fiber nanotubes possess a self-sensing monitoring function of the damage accumulations (fiber breakages, delaminations, etc.) by means of their electric resistance change during mechanical loading. Evaluation of the piezoresistive behavior of unidirectional FRP laminates are carried out by using the uniaxial tensile tests of the specimens 0 and 90°, where reinforcing fibers were directed along and transverse to the loading direction. The components of piezoresistive tensor of UD FRPs are calculated by means of the gage factors of the tensioned specimens 0 and 90° experimentally determined in accordance to the relative surface electrical resistance changes, when electrical current flowed along or across the reinforcing carbon fibers.

P19

LAYER-BY-LAYER DEPOSITION OF NANOCOLLOIDS ON THE GOLD ELECTRODE

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Abstract

Ionic liquids (IL) are generally defined as salts that melt at or below 100 °C to afford liquids composed solely of cations and anions.[1] While IL are widely used in organic chemistry (e. g., as a solvent), their applications in materials research are quite rare. The most attractive properties of IL include: a low vapour pressure which allows using them in vacuum technologies; a wide electrochemical window (up to 6 V); high specific conductivity (in the range of tens of $mS \cdot cm^{-1}$) thermal stability up to 400 °C.[2] Another good feature of ionic liquids is the formation of nanoparticles and their stability. This makes them perspective for applications in catalysis as well as for fabrication of chemical sensors.
Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF_4) with copper nanoparticles were prepared by sputtering of nanoparticles on the surface of the liquid. The ultra-thin nanocomposite layer containing Cu nanoparticles and conducting polymer polyaniline (PANI) and poly(sodium-4 styrenesulfonate) (PSS) was prepared by Layer-by-Layer (LbL) deposition. This technique is based on electrostatic interaction of oppositely charged species which are repeatedly adsorbed on the surface[3] and presents a simple and low-cost method for the formation of thin composite layers from conducting and non-conducting substrates. Here we performed an LbL-deposition of nanoparticles from ionic liquid. First, PANI was deposited to the surface of gold electrode. Then PSS layer was deposited. At the next step nanoparticles were deposited from ionic liquid and finally PSS was deposited again to stabilize the multilayer structure. Then the whole procedure of deposition of four layers was repeated several times. The nanocomposite formed by this way on the gold surface was studied by cyclic voltammetry (CV). The potential scanning from -0.2 V till +0.7 V at scan rate 100 mV/s was used. CV shows a strong signal in the oxidative part of graph which can be assigned to Cu oxidation. The peak decreased with increasing number of scans. This can indicate that the copper content on the electrode surface decreased. Morphology of the LbL surface was studied with scanning electron microscopy. X-ray photoelectron spectroscopy showed that Cu is in the metallic state.
The results demonstrate a high potential of LbL deposition of nanoparticles from ionic liquids. The formed copper containing nanocomposite can be used for electrocatalytical oxidation of glucose in non-enzymatic glucose sensors.

Acknowledgement. This work was financially supported by BMFB project POLYCON (Germany), and by APVV-0593-11 and VEGA 2/0149/14 projects (Slovakia).

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P20

PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURED MATERIALS BASED ON POLYPYRROLE AND TiO_2 (PPy/TiO_2). APPLICATIONS TO ELECTROCHEMICAL GENERATORS

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Abstract

This work focuses on the development and characterization of nanostructured materials based on Polypyrrole and titanium dioxide (PPy/TiO_2) for applications to electrochemical generators. The composite materials between Polypyrrole and titanium dioxide of anatase type at different percentages (3 to 15% of TiO_2) used as reinforcements were prepared via insitu polymerization with manganese dioxyde MnO_2 in aqueous medium. Initially, MnO_2 was chemically synthesized by oxidation of Mn^{2+} in the presence of an oxidizing agent in aqueous medium. The elaborated materials were then characterized by FTIR, DSC, TGA, SEM, EDX, UV-Vis, DRX, measurement of electrical conductivity and their capacitive performances studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS).
The effective specific capacity is a factor that determines the electrochemical behavior of the supercapacitor, it is determined to virgin polypyrrole and its composites by cyclic voltammetry. The incorporation of TiO_2 in the polypyrrole matrix has a remarkable effect on the electrical conductivity and the electrochemical performance capacitance supercapacitors.

Keywords: Polypyrrole, MnO_2, TiO_2 anatase, FTIR, DSC, TGA, DRX, EIS, conductivity, supercapacitors,

P21

A COMPREHENSIVE STUDY AND CHARACTERIZATION OF COLLOIDAL EMERALDINE-BASE

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WITHDRAWN

P22

PHOTO-THERMAL ACTUATION OF ETHYLENE VINYL ACETATE NANOCOMPOSITES CONTAINING CARBON NANOTUBES

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Abstract

The contribution presents a part of comprehensive research focused on reversible photo-thermal actuation of nanocomposites based on ethylene vinyl acetate (EVA) filled with modified single- and multi-wall carbon nanotubes (SWCNT, MWCNT)[1]. In general, actuators have ability to change their dimension upon external stimulus. Polymer/carbon nanotubes (CNT) nanocomposites represent promising materials for designing and fabricating new stimuli responsive materials[2]. However, the extent of final property depends on several parameters including the size of the particles, aspect ratio, degree of dispersion and alignment in the polymeric matrix[3]. CNT possess multifunctional characteristics, and also respond to light irradiation in wide range of optical wavelength. New photo-actuating materials based on the commercial elastomer EVA and well-dispersed CNT have been developed as potential materials for the fabrication of smart actuators. The photo-thermal actuation effect of the prepared nanocomposites containing different quantity of nanofiller will be discussed.
The photo-thermal actuation measurements were performed for stretched strips by dynamic mechanical analyser (DMA) equipped by light-emitted diode (LED). The best actuation responses were measured for the nanocomposite containing a lower amount of modified MWCNT, and 0.1 wt.% was the optimal concentration of the nanofiller. During illumination of the sample by red LED the stress increases measured by DMA, which indicated contraction of the nanocomposite, reaching values in the range of 100 kPa. The highest stress changes were found only for the nanocomposites filled with MWCNT compared to SWCNT due to higher aspect ratio and improved ability of absorption light and convert it more efficiently to heat. The presence of higher amount of MWCNT lead to lower photo-thermal actuation response of nanocomposite because of increased stiffness of the samples and decreasing the polymer chain flexibility. The mechanism of the elastomer-CNT actuators will be reported, alignment study of CNT within the polymeric matrix, effect of photo-thermal actuation results as measured actuation stresses in response to light, long–term stability. This contribution also will reports new modified MWCNT in the presence of dyes such as Rhodamine and the low cost Congo Red which both have "aniline" moiety which can further be reacted with $NaNO_2$ in order to obtain in situ the corresponding diazotized dyes that are expected to readily react with the carbon nanotubes through radical coupling [4]. The preliminary results of the photo-thermal actuation of samples filled with dye-labelled CNT will be discussed.

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P23

SYNTHESIS, PHOTOPHYSICAL AND MORPHOLOGICAL PROPERTIES OF AZOMETHINE PERSYLILATED α-CYCLODEXTRIN MAIN-CHAIN POLYROTAXANE

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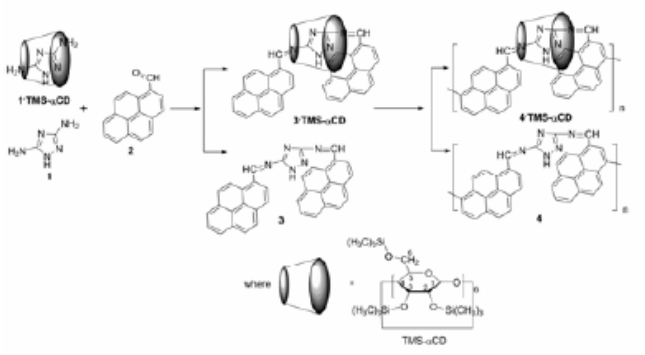
Abstract

Aromatic poly(azomethine)s (PAMs) have received particular interest due to their interesting electro-optical properties that make them as potential alternative to traditional inorganic semiconductors. Unfortunately, the use of PAMs is often affected by several limitations including their rather low solubility in common organic solvents associated with undesirable aggregation and high-melting temperature. To overcome this drawback, the encapsulation of PAMs into macrocycle cavities is a topic of continuous interest [1-3]. Therefore, we decided to explore the effect of hexakis(2,3,6-trimethylsilyl) α-cyclodextrin (TMS-αCD) encapsulation, as an alternative approach to bring some benefits on the photophysical characteristics of PAMs. Therefore, we synthesized a 2-rotaxane azomethine monomer (**3•TMS-αCD**) through a condensation reaction between 3,5–diamino-1,2,4-triazole (1) encapsulated into hexakis(2,3,6-trimethylsilyl) α-cyclodextrin cavity (**1•TMS-αCD**) and 1-pyrenecarboxaldehyde (2). The oxidative coupling of **3•TMS-αCD** afforded then **4•TMS-αCD** azomethine polyrotaxane, Scheme 1.



Scheme 1. The synthetic procedure for the polyrotaxane **4•TMS-αCD** and its non-rotaxane **4** counterpart

The optical, electrochemical, morphological, surface free-energies, as well as transport properties of **4•TMS-αCD** polyrotaxane have been investigated and compared with those of the reference **4**. The polyrotaxane was soluble in toluene/DMF1/1 v/v mixture and displayed useful levels of thermal stability and higher fluorescence quantum yield (Φ_{PL}) in DMF solutions. Φ_{PL} improvement was further reflected in the fluorescence lifetime (τ_F), significantly longer than that of the starting monomer **3•TMS-αCD** (7.8 *vs* 0.89 ns). In addition, a smoother surface with the smaller grains uniformly distributed on the surface, as well as lower surface free-energy, combined with energy gap (3.32 *vs* 3.76 eV) represent noticeable advantages of azomethine backbones encapsulation by TMS-αCD.

Acknowledgements
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REDOX-ACTIVE POLYIMIDE–POLYETHER BLOCK COPOLYMERS AS ELECTRODE MATERIALS FOR LITHIUM BATTERIES

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Abstract

Redox-active polyimide–polyether multi-block copolymers were synthesized by polycondensation reaction of aromatic dianhydrides with α-ω-diamino poly(ethylene oxide). Polyimide-*b*-polyether block copolymers showed microphase separation between a hard-polyimide domain and a soft-polyether domain as observed by Atomic Force Microscopy. The block copolymers were investigated as cathodes for polymer/lithium metal batteries. Polymer cathodes were formulated where the block copolymer had a dual role as active material and binder, with a small amount of carbon black, *i.e.* 15 wt% (*cf.* AFM images below). Naphthalene polyimides showed higher discharge voltages, higher specific capacities as well as better cycling performance, compared to pyromellitic polyimides. The longest PEO blocks resulted in a better performance as electrodes. The best performing naphthalene polyimide-b-PEO2000 presented an excellent value of discharge capacity of 170 mA h.g^{-1}, stable after 100 cycles at a current density of 1Li$^+$/5 h and considering the polyimide as the active material. The average discharge plateaus were 2.51 V and 2.37 V *vs.* Li$^+$/Li.[1]

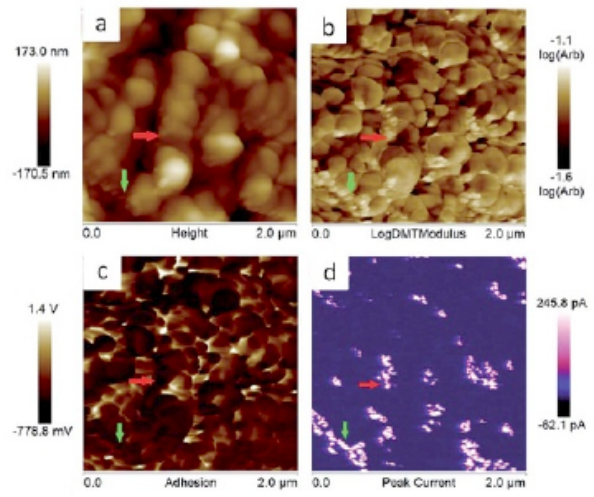

Figure. AFM images collected in the PeakForce TUNA mode, using a DC sample bias of 1 V on sample naphthalene polyimide-b-PEO600 loaded with 15wt% of carbon black. (a) Topography, (b) elastic modulus in log scale, (c) adhesion force and (d) peak current images. The red and green arrows are pointing on the same domains in all four pictures.

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PEDOT/PSS/POLYGLYCERIN COMPOSITE FOR STRETCHABLE ELECTRODES

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Abstract

Stretchable and highly conductive electrodes are of great importance for organic electronics. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) as a water dispersion of colloidal particles is one of the most successful conducting polymers because of its high electrical conductivity, transparency, and thermal stability. The PEDOT/PSS films are, however, hard and brittle due to the hydrogen bonding between sulfonic acid groups of the PSS on the surface of the colloidal particles. Previously, we have developed stretchable and highly conductive PEDOT/PSS films by adding sugar alcohols (SAs) such as xylitol[1] and applied to compliant electrodes for small, lightweight, flexible, and noiseless soft actuators and artificial muscles[2]. However, the PEDOT/PSS/SA electrodes required subsequent heating above the melting point of the SA with poor thermal stability.

In this study, thermally stable, stretchable, and highly conductive PEDOT/PSS films and coatings were fabricated by adding polyglycerin (PG) instead of the SAs. The electrical conductivity, thermal stability, and mechanical properties of the resulting PEDOT/PSS/PG films were investigated by means of four-point method, thermogravimetric analysis, and tensile measurements. It was found that no notable weight loss was observed between 100 and 200 °C, indicative of superior thermal stability of the PEDOT/PSS/PG films. As shown in Fig.1, the electrical conductivity increased at PG concentrations higher than 40 wt% and reached as high as 411 S/cm at 60 wt%, which is mainly associated with the crystallization of PEDOT molecules preferable to the transport of charge carriers. A further increase of the PG concentration brought about the decrease of conductivity due to the decrease of a relative PEDOT content in the film. On the other hand, a clear indication of the importance of PG was seen in the mechanical properties. Young's modulus and tensile strength gradually decreased with increasing the PG concentration, which can be explained in terms of the plasticizing effect of the PG. It should be noted that elongation at break was significantly improved by adding PG and attained 27% at PG concentration of 50 wt%. The results allowed us to conclude that the PEDOT/PSS/PG films had great advantages as the stretchable and highly conductive electrodes for the applications to flexible, printed, stretchable, and wearable electronics.

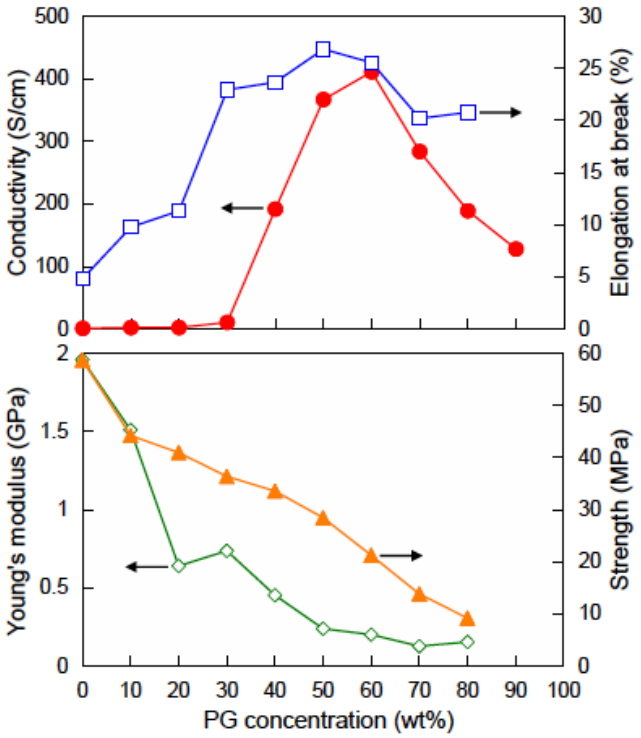

Fig.1 Dependence of electrical conductivity and tensile properties of PEDOT/PSS/PG films on PG concentration.

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EFFECT OF THE PROCESSING CONDITIONS ON ELECTRICAL TRANSPORT PHENOMENA IN PP/MWCNTS COMPOSITES

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Abstract

Carbon nanotubes (CNTs) are widely known to be able to considerably modify the electrical properties of the polymer matrix in which they are embedded, even at very low filler content[1] [2]. It is reported that polymer/CNT composites show high strength and stiffness combined with electrical conductivity at relatively low concentrations of CNTs[3].
The final properties of the polymer composites based on CNTs are strongly affected by the processing techniques, which can modify the eventual orientation and aggregation[4].
In this work, polypropylene (PP) composites filled with multi-walled carbon nanotubes (MWCNTs) were developed. The MWCNT dispersion was performed in a co-rotating twin-screw extruder, and the obtained composite was injection molded to obtain the desired specimens for characterization. Electrical characterization was performed in the three main direction, i.e. the one longitudinal to the flux of the molten material, while filling the mold - and the two transversals, in order to thoroughly correlate the electrical behavior to the morphology, studied by scanning electron microscopy. The aim of this work is to investigate the influence of the processing technologies (injection molding and extrusion) on the electrical resistivity of PP/MWCNT composites.
As a result, the two external surfaces of the sample directly in contact with the mold contain a less amount of MWCNTs, and this results in a higher resistivity along the through-thickness direction. As far as extrusion conditions are concerned, it is remarkable to notice the resistivity of the composites is higher when MWCNTs are embedded at the end of the extruder than at the middle of it. In fact, the morphological analysis demonstrates that a longer extrusion process for the MWCNTs could reduce the aspect ratio of the fillers and, consequently, the efficiency in their electrical properties.

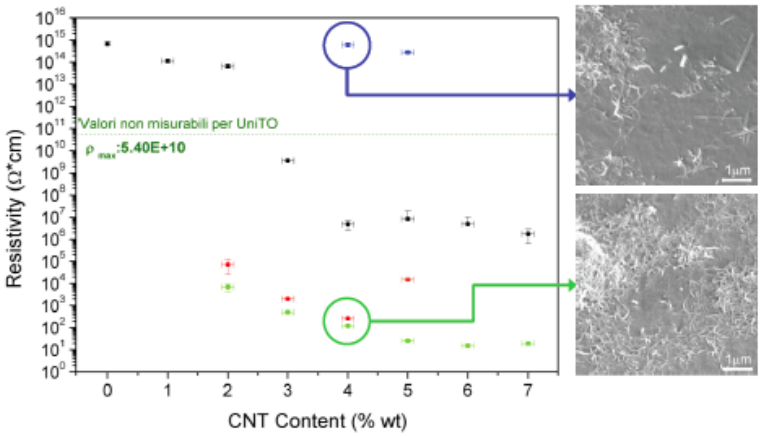

Figure 1. Resistivity and SEM of CNT-based composites: different dimensions measurements for compounds where CNTs were assayed in the middle (red, green and black lines) and at the end of the extruder (orange and blue lines

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TITLE POLYYNE COMPOUNDS AS PRECURSORS FOR POLYMERIC CONDUCTING MATERIALS

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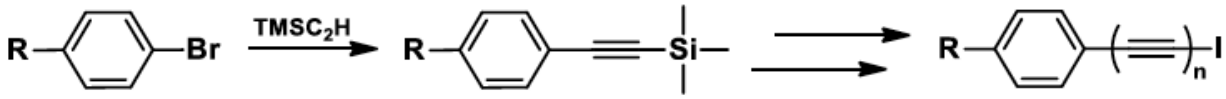
Abstract

Organic and organometallic polyynes have been attracting a constant interest of the scientific community for more than fifty years. Such species are regarded as a model compounds of the hypothetical linear allotropic form of carbon - carbyne and as precursor of numerous materials including conducting ones. 1-Halopolyynes are a rare group of polyynes which possess interesting physicochemical properties and essential application potential *via* for instance crystal-to-crystal topochemical polymerization.

In this contribution we present our recent advances in the synthesis of long chain 1-halopolyynes. The synthesis of a series of novel 1-iodopolyynes with carbon chain up to the decapentayne is presented. 1-Iodopolyynes were obtained using an iterative procedure that included Sonogashira coupling followed by halogenation and chain elongation *via* Cadiot-Chodkiewicz. All polyynes were fully characterized using spectroscopic methods. Moreover, unprecedented single crystal X-ray structures were obtained for some of the 1-iodopolyynes.



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