# Designing new interpenetrated polymer actuators based on polypyrrole for medical micro-systems

## Introduction

Electroactive polymers (EAP) are polymer materials whose shape can be modified when voltage is applied. Depending on the specific material, they may either bend or have a linear motion (they can shrink or expand). As actuators, they can undergo a significant amount of deformation. These materials can provide solutions for engineering technology in areas where conventional actuators have their limitations, especially in areas where sub-millimeter and micrometer actuators are required. There are several EAP actuator materials and designs proposed, but each of them still has significant drawbacks. The current project aims to solve some problems by proposing a novel approach by combining a novel preparation technology using a well-known and understood material and a high competence in control and modeling of such kind of materials.

**The main goal of the project is the design, preparation, characterization, developing manufacturing technology (both in micro and ordinary scale), control and modeling of layered bending-type conducting polymer actuators based on interpenetrated networks of polypyrrole (PPy) as the working material and a polyethylene oxide (PEO) (or some copolymer of PEO ) interlayer.**

## Background information

EAP actuators have several advantages compared to conventional actuators. They are mechanically simpler, lightweight and easy to miniaturize, they are flexible and soft and have a high number of degrees of freedom; their motion is noiseless, and due to the low metal concentration they are quite insensitive to electromagnetic fields. Because of these properties, EAP materials might have considerable potential in areas where conventional actuators and sensors would not make it, e.g. in liquid environments and/or for applications where size or weight are important constraints. They are especially well adapted in biotech areas, like microfluidics or for microsurgery tools which operate in blood and tissue environment.

## Polypyrrole

Polypyrrole is and has been a popular material for basically composing conductive polymer based actuators[[1]](#endnote-2). The actuation is subsequent to the volume change of the polymer film caused by doping and dedoping processes. Both anion-driven and cation–driven actuators have been proposed.

In order to create usable devices, a wide variety of engineered bending and linear actuators have been proposed. The layered bending actuator is perhaps the simplest design; in the bilayer configuration, it consists of one inert nonconductive layer (*e.g.* adhesive tape) and a working layer of polypyrrole[[2]](#endnote-3). Actuation is due to the shrinking and swelling of the conducting polymer layer relative to the supporting layer. Trilayer designs consist of an insulating supporting interlayer (again possibly adhesive tape) and two working conducting polymer layers on each side. Actuation is created by applying potential between the two sides of the actuator which causes one side to shrink and the other to swell, resulting in the bending motion of the actuator[[3]](#endnote-4). Five layers actuators have construction like conductive polymer/metal/interlayer/metal/conductive polymer[[4]](#endnote-5). The metal sheet enhances the conductivity of the surface. The linear designs are more complex, some examples include coil-spring-based[[5]](#endnote-6), tube-encapsulated[[6]](#endnote-7) and stacked/combined bending actuators[[7]](#endnote-8),[[8]](#endnote-9).

But two serious problems will occur:

* The common problem of all (metal) electrode based conducting polymer devices is the delamination during long time actuation; this is due to the swelling and shrinking in three dimensions[[9]](#endnote-10),[[10]](#endnote-11).
* Dependence on the surrounding solution to be the source for the mobile ionic species. The metal layer indeed prevents from using the interlayer as ions and solvent source.

One option to overcome the last problem is a trilayer design which uses a polymer electrolyte as the interlayer to store the mobile ions[[11]](#endnote-12). This is not possible with metallic layers. Such actuators are capable of working both in air and solutions, but still have a tendency to delaminate after some work-cycles.

The isolation of the actuator from the outside environment is especially important in case of biomedical applications. Polypyrrole is a biocompatible material, but it tends to uptake various substances from biomaterials, resulting in an unreliable behavior of the actuation. To overcome this issue, actuators with self-contained sources of ions are preferred.

## Interpenetrated Networks of Conductive Polymers

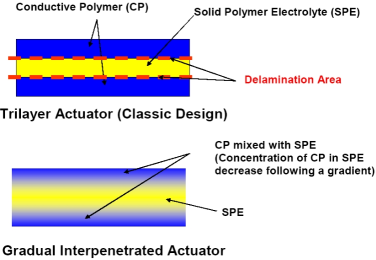
**We have introduced several innovations based on Inter-Penetrated Networks (IPN) Conductive Polymers (CP) technique (also called conjugated polymers).** The IPNs are a blend of polymers that are synthesized at the same time. Contrary to copolymers, their chains remain independent, but they are, however, entangled and physically cross-linked. They are defined as a combination of minimum 2 (commonly cross-linked) polymers that are synthesized in juxtaposition[[12]](#endnote-13),[[13]](#endnote-14). As the networks are entangled, this technique can be used even with polymers that cannot be mixed with each other. Good interpenetration is reached when the right concentration of monomers, cross-linking agents and catalysts are used[[14]](#endnote-15); the components are introduced at the same time, but their networks must be formed separately, by using two different kinetics[[15]](#endnote-16) or two different mechanisms.

Figure : Principle of using interpenetrated networks for conductive polymer actuators.

The goal here is to bind the conductive polymer network with the isolating polymer network directly with the IPN technique, instead of sticking metal on isolating polymer, and growing CP on metal (see ).

Such systems have several advantages:

* The delamination problem from the interlayer/electrode material is solved.
* No metal electrodes are used.
* No physical barrier to isolate polymer (the SPE) and the conductive polymer part. The SPE may be used as solvent and ions tank for the electroactive CP part.
* It enables the working of the actuator almost in every environment, as it does not need any more external ions. It can work in the air. It also avoids difficult contamination issues in biological applications.
* A better ionic mobility inside conductive polymer, due to the mixing with insulative layer. (Insulative layers are porous materials selected for their strong ionic conduction)

The system which contains PEDOT (3,4-ethylenedioxythiophene) as for the conductive polymer and a PEO dangling chains ladder network and PB (Polybutadiene) as for SPE layer have been reported[[16]](#endnote-17).

The choice of the polymer electrolyte system is critical when operating in the air. Aqueous solutions or organic solvents containing electrolytes were first used, but the drying process could not be prevented. The most promising results are obtained with a room temperature ionic liquid, 1-ethyl-3-metylazolium bis-(trifluoromethylsulfonyl)imide. These actuators can achieve in air more than 7\*106 bendings from 1 to 18Hz under an applied potential in the range of 2 to 5V.

The material described can be modeled based on finite element modeling[[17]](#endnote-18)and physical models[[18]](#endnote-19).

A new, faster fabrication technique based on microwaves was developed[[19]](#endnote-20) (from ~16 hours fabrication time (before); to a few minutes time (after)). Beyond reducing strongly the reaction time, more precise and proper control of the fabrication conditions have been achieved. It enhances reproducibility and performances. It also enables the using of precise masking techniques in order to obtain various shapes of the actuator. Actuators with linear movements were made altogether with the chemical fabrication step. A chemical wirings is also integrated into the fabrication. Electric connection wires can be made from the same conductive polymer material, during the same fabrication step.

However, these innovations were done with systems based on the PEDOT conductive polymer. PEDOT is known to be at least 3 times less efficient than polypyrrole for actuation. **By using a better conductive polymer,** with the improvements made for this PEDOT system, namely: Interpenetrated Network, linear actuation shapes, chemically integrated wiring, **would probably allow obtaining a new, very efficient actuator**.

## Biomedical applications

Biomedical applications are among the most promising ones for the kind of actuators we aim to achieve in the project. Private societies like Micromuscle AB, Infinite Biomedical Technologies or Molecular Mechanisms, or research groups like the Smela group in Mechanical Engineering Department in Maryland or the IPRI lab in Wollongong have chosen this application field for their own conductive polymer actuators. Possible applications are:

* Steerable guidewires, active coatings for medical devices.
* Coatings for voltage controlled drug delivery.
* Microvalves, seals, microvials or micropups for Microfluidics or Lab-on-chips
* Medical micro-implements and micro-robots.

For these ongoing projects, electrochemically deposited polypyrrole actuators have mainly been used; these have weaker performances and less longevity than the interpenetrated networks of polypyrrole actuators that we propose; better biomedical devices should therefore be obtained by this way.

## Research goals

**The main goal of the project is the design, preparation, characterization, developing manufacturing technology (both in micro and ordinary scale), control and modeling of layered bending-type conducting polymer actuators.**

The first goal of the project is the design, **preparation, and study of layered bending-type conducting polymer actuators based on interpenetrated networks of polypyrrole (PPy) as the working material and a polyethylene oxide (PEO) (or some copolymer of PEO ) interlayer**. The benefits of this design over conventional three-layer conducting polymer actuators are:

* No (metal) electrodes used and no delamination from the interlayer/electrode material.
* Enables the use of ionic liquids as dopants (ionic liquids never evaporate, thus permitting the use of such actuators in open air for months).
* Self contained source of ions. We do not need external solvent or other kind of ion source. It can be easily isolated from environment.

To achieve that we will work on the following issues:

* The optimization of the chemical synthesis conditions of the polypyrrole layer (including the oxidizing agent – Fe3+ or alternatives).
* The optimization of the type and chemical composition of the interlayer polymers.
* The optimization of the relative thicknesses of the layers.
* The choice of optimal solvent and the mobile ionic species.
* The comparison of chemically and electrochemically synthesized polypyrrole films.

The second goal is **the integration of these synthesized actuators into effective applications and prototypes**, with the aim of reaching small size systems.

* The optimization of the overall design (shape, size, contacts, etc) of the actuators for various applications .
* Using of masks for enabling electroactive parts and inert parts on the same surface, will permitting new kinds of deformation of actuators.
* Using conductive polymer wires to connect actuators with external electrodes will permit to avoid using bulky clips.
* Integration of actuators in prototypes, especially biomedical oriented prototypes like microvalves, pumps and drug release devices.

**The third goal is to develop models to explain the electromechanical behavior, to predict properties and perform real-time control of the actuator:**

* Physics based models to describe the system.
* Precise models based on multi-scale finite element analysis technique to bridge chemical engineers and mechanical engineers by providing them testing and modeling tools which are scalable and with high accuracy.
* Analytical and numerical electromechanical models for real-time closed loop control. Engineers use them to make electromechanical simulations for evaluation and prototyping actuators in actual systems.

## Methodology

This project requires skills from engineering as well as preparative and electrochemistry from the in-site personnel. Details of the work include raw materials synthesis and characterization. The optimization of the actuator and its materials requires experiments in material characterization, electrochemical behavior (ion mobility), mechanical performance (measurement of strain and stress), etc.

An important difference from the majority of works published on polypyrrole-based actuators will be the actual synthesis process of the electroactive material. Polypyrrole is commonly obtained by the oxidative electrodeposition of pyrrole from the solution of some supporting electrolyte. Due to the nonconductive properties of the interlayer, this approach is not (fully) applicable, and instead, polypyrrole will be mostly synthesized chemically, using mild oxidizers (*e.g.* Fe3+). There is not much information available on the comparison of the behavior of chemically and electrochemically synthesized polypyrrole films as actuator material. The chemical oxidative polymerization is in principle just as straightforward as the electrochemical synthesis. However, just as in case of the electrochemical procedure, the various conditions of the process define many of the properties of the resulting polymer, making the control of those properties a matter of paramount importance. It has been shown that the solvent, redox potential, monomer concentration and temperature all play an important role[[20]](#endnote-21),[[21]](#endnote-22) Using reduced redox potentials (by adding Fe2+ to the solution) and methanol as the solvent have shown the best results in terms of conductivity. The best conditions for the present actuator application need to be established during the project. Laboratory space and necessary equipment for organic polymer synthesis are available.

Voltamperometry is the standard method for the synthesis and electrochemical study of conducting polymers, allowing the estimation of film thickness, ion mobility inside the film, and also the monitoring of ongoing processes. It will be used extensively for the characterization of the materials and the optimization of the design. High-quality equipment for performing electrochemistry experiments will be available.

Spectroscopic measurements for the study of the conjugation length, structure, charge distribution, etc of the polymers will be carried out applying several techniques, including UV/Vis (in co-operation with the Institute of Physics), IR (Institute of Chemistry), Raman (Uppsala and/or Inst. of Physics). There is ongoing collaboration with all of these institutions.

SEM is an important and powerful tool for studying the morphology of the cross sections of the actuators. The equipment is available in the Institute of Physics.

The surface of the synthesized actuators can also be studied using AFM. The formation of the conducting polymer, the thickness and the roughness for the surface will be studied. The equipment and a well trained specialist are available.Electromechanical measurements will be performed on the experimental measurement system at the host institute. The setup is National Instruments equipment based system which contains a fast camera (up to 400 fps), IR laser distance measurement sensor, several DAQ I/O capabilities and wide range of static and dynamic force measurement sensors.

Integration into prototypes will require the development of the technologies needed to work at small sizes like masking based on the experience obtained from PEDOT and wiring using conductive polymers for wires (See, J. Citérin works in CV).

Modelling the systems, developing and verification the control algorithms of the systems will be performed by using COMSOL Multphysics, LabView and MatLab software developing environments.

**Active international collaboration with CNRS will be expected.**

## Expected results

**The main expected result is a fully operational tiny actuator which uses the IPN-CP-PPy material. This actuator should be usable and implemented in early biomedical prototypes.**

To achieve this main result we will:

* Develop a recipe to prepare interpenetrated conducting polymer actuators of polypyrrole that are durable for extended periods of actuation.
* Develop technology and knowhow to prepare prototypes with tiny actuators.
* Develop models and control algorithms for the developed materials and systems.
* Develop prototypes focused on biomedical fields concerns, *e.g.* using blood as a solution. In a second step, prototyping will be oriented toward well-fitted applications like valves and pumps and compared to existing devices.
* Publish scientific results in the leading international journals of the field ("Advanced Materials", "Synthetic Metals", "Smart Materials and Structures", “IEEE Transactions”, etc.).
* The usable designs and applications of the novel actuators will be investigated and collaboration partners for the actual use of the actuators will be searched for.

## Relevance to research project in host institution in Estonia

Intelligent Materials and Systems Laboratory (<http://www.ims.ut.ee>) is an interdisciplinary research group established in 2003 in University of Tartu, Institute of Technology. Labs main research activity is focusing on development and exploitation of ion-conducting electroactive polymers, so the planned work fits into their profile completely.

Planned work has straightforward connection to applied targeted financing project “Ionic Electroactive Polymer Materials, Control and Applications” 2008-2013.

## References

1. Y. Osada, D.E. DeRossi, Eds. Polymer Sensors and Actuators, Springer, 2000, p 217. [↑](#endnote-ref-2)
2. T.F. Otero, J.M. Sansiñena, Adv. Mater. 10 (1998) 491-494. [↑](#endnote-ref-3)
3. E. Smela, Adv. Mater. 15 (2003) 481-494. [↑](#endnote-ref-4)
4. G. Alici, P. Metz, G. M. Spinks, Smart Mater. Struct. 15 (2006) 243–252. [↑](#endnote-ref-5)
5. S. Hara, T. Zama, W. Takashima, K. Kaneto, Synth. Metals 146 (2004) 47–55. [↑](#endnote-ref-6)
6. J. D. Madden ), R. A. Cush, T. S. Kanigan, C. J. Brenan, I. W. Hunter, Synthetic Metals 105(1999) 61–64. [↑](#endnote-ref-7)
7. T.F. Otero, M.T. Cortés, G. Vázquez Arenas, Electrochimica Acta 53 (2007) 1252–1258. [↑](#endnote-ref-8)
8. T.F. Otero, M. Broschart, J. Appl. Electrochem. 36 (2006) 205-214 [↑](#endnote-ref-9)
9. E.W.H. Jager, E. Smela, O. Inganas, Science 290 (2000) 1540–1545. [↑](#endnote-ref-10)
10. . Maw, E. Smela, K. Yoshida, P. Sommer-Larsen, R.B. Stein, Sen. Actuators A, 89, (2001), 175–184. [↑](#endnote-ref-11)
11. E. Smela, Adv. Mater. 15 (2003) 481-494. [↑](#endnote-ref-12)
12. ] L. H. Sperling, D. Klempner, L. A. Utracki Eds, “Interpenetrating polymer Networks”, Washington (1991), American Chemical Society. [↑](#endnote-ref-13)
13. L. H. Sperling, Polym. Eng. Sci., 87, 16, (1976). [↑](#endnote-ref-14)
14. L. H. Sperling, V. Mishra, “RIPs around the world :sciences and engineering” Wiley (1997). [↑](#endnote-ref-15)
15. C. Rouf, S. Derrough, J.-J. André, J.-M. Widmaier, G.C. Meyer, L. H. Sperling, D. Klempner, L. A. Utracki Eds “Interpenetrating polymer networks”, Washington (1991), American Chemical Society, 143 [↑](#endnote-ref-16)
16. J. Citérin, A. Kheddar, M. Hafez, F. Vidal, C. Plesse, D. Teyssié, C. Chevrot, “Characterization of a new interpenetrated network conductive polymer (IPN-CP) as a potential actuator that works in air conditions”, IEEE/RSJ IROS 2004, 28 Sept.-2 Oct. 2004, Sendai, Japan. pp. 913 - 918 vol.1 [↑](#endnote-ref-17)
17. J. Citérin, G. Turbelin, A. Kheddar, F. Vidal, C. Chevrot, “New design methods and simulation of linear actuators using ionic polymers”, IEEE International, Conference on Robotics and Biomimetics ROBIO, 29 June – 03 Jul. 2005, Honk Kong, China. pp. 438-443 [↑](#endnote-ref-18)
18. Catherine Gauthier, Cédric Plesse, Frédéric Vidal, Jean-Marc Pelletier, Claude Chevrot and Dominique Teyssié “Polybutadiene/poly(ethylene oxide) based IPNs, Part II: Mechanical modelling and LiClO4 loading as tools for IPN morphology investigation”, Polymer (2007), 48,26,7476-7483. [↑](#endnote-ref-19)
19. J. Citérin, A. Kheddar, “IPN-CP actuators with improved fabrication process”, IEEE International Conference on Robotics and Biomimetics (ROBIO), December 2007, Sanya, China. [↑](#endnote-ref-20)
20. S. Machida, S. Miyata, Synth. Metals, 31 (1989) 311-318. [↑](#endnote-ref-21)
21. . E. Whang, J. H. Han, H. S. Nalwa, T. Watanabe, S. Miyata, Synth. Metals, 43 (1991) 3043-3048. [↑](#endnote-ref-22)