Conducting polymer actuators based on interpenetrated networks

# 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 solution 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 they still have significant drawbacks. We try to solve at least some problems by proposing novel approach by combining a novel preparation technology, well-known material and 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. Due to these properties, it is suggested that EAP materials have high potential in areas where the conventional actuators and sensors still have some disadvantages, e.g. in liquid environments and/or for applications where size or weight are important features. They are especially well adapted in biotech areas, like microfluidics or for microsurgery tools which should work in blood and tissue environment.

## Polypyrrole

Polypyrrole is and has been the most common material for constructing conductive polymer based actuators at present time [[1]](#endnote-2). The actuation is due to the volume change of the polymer film caused by these doping and dedoping processes. Both anion-driven and cation–driven actuators have been proposed. An anion–driven actuator swells upon doping as the anions (together with some solvent) move into the polymer matrix to compensate for the charge buildup on the polypyrrole chains. A cation-driven actuator swells upon dedoping as the cations (and solvent) is incorporated into the film to compensate the negative charge, as the anionic species are immobile (or have low mobility) and cannot leave the polymer matrix.

In order to create usable devices, a wide variety of bending and linear actuator constructions 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. Another alternative design is the trilayer version, consisting 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). An extension of this design is the five layer version, where the interlayer is covered by a metal electrode on each side on which the conducting polymer layers are either deposited or attached[[4]](#endnote-5). Five layers actuators have construction like conductive polymer/metal/interlayer/metal/conductive polymer, due to fabrication ease (in this case, conductive polymer can be fabricated accurately by electroplating; moreover, 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 intrinsic tendency of the material will delaminate during the long time actuation due to swell and shrink in all three dimensions causing the eventual failure of adhesion from the electrode surface[[9]](#endnote-10),[[10]](#endnote-11)..**
* **Another shortcoming of such designs is the systems 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 nd solvent source.**

One option two overcome the last problem is a trilayer design is to use 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 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 fully biocompatible material. However it tends to uptake various substances from biomaterials, rendering the behavior of the actuation unreliable. Also, for reliable performance, an actuator cannot depend on external electrolytes as a source of dopant ions, therefore, actuators with self-contained sources of ions are preferred.

## Interpenetrated Network of Conductive Polymers

**We have introduced several innovations were introduced based on InterPenetrated Networks (IPN) Conductive Polymers (CP) technique.** 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 crosslinked . They are defined as a combination of minimum 2 (commonly crosslinked) 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, crosslinking 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 was 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 Figure 1).

Such systems have several advantages:

* The delamination problem from the interlayer/electrode material is completely 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 drying process could not be prevented. The most promizing 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 18 Hz under an applied potential in the range of 2 to 5V

Figure . Finite-element simulations of more efficient, linear moving actuator shapes.

The material described by model based on finite element modeling[[17]](#endnote-18)and physical models[[18]](#endnote-19)

New, much quicker fabrication techniques based on microwaves were developed[[19]](#endnote-20) (from ~16 hours fabrication time (before); to a few minutes time (after)). Beyond reducing strongly the reaction time, they have several advantages like more precise and more proper control of the fabrication conditions. It enhances reproducibility and performances. It also enables the using of masks, in order to obtain the new shapes of previously modeled best designs. Actuators with linear movements were then made in just one chemical step. A chemical wiringos 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 PEDOT conductive polymer. PEDOT is known to be minimum 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 permit to obtain a new, very efficient actuator**.

# 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
* 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. W e do not need external solvent or other kind of ion source.
* Can be easily isolated from environment.

To achieve that we will work on issues like:

* 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 designs on the same surface will permit new kinds of deformation of actuators.
* Using of conductive polymer wires to connect actuators with external electrodes will permit to avoid using bulky clips.

**The third goal is to develop models to explain the electromechanical behavior, predict properties and realtime control 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 modelling tools which are scalable and with high accuracy.
* Analytical and numerical electromechanical models for real-time closed loop control. These models should be exploited by engineers to make electromechanical simulations for evaluation and prototyping actuators in actual systems.

# Methodology

The cause of the project requires skills of engineering as well as preparative and electrochemistry from the 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 of the electroactive material. Polypyrrole is 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 very limited 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, rendering 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 mobilities 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 morfology 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 well trained specialist is available. Electromechanical measurements will be performed on experimental measurement system at Estonian host institute. The setup is National Instruments equipment based system which contains fast camera (up ti 400 fps), IR laser distance measurement sensor, several DAQ I/O capabilities and wide range of static and dynamic force measurement sensors. Simplified schematic overview of the system is given in Figure X.

Physics based models

FEM modeling, realtime electrochemical control

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# Expected results

The main expected result of the project is the recipy (Alvo: no-no-no---the main result is to make a prototype which uses the materials we provide technology for...!) to prepare interpenetrated conducting polymer actuators of polypyrrole, that are durable for extended periods of actuation.

The scientific results will be published in the leading international journals of the field ("Advanced Materials", "Synthetic Metals", "Smart Materials and Structures", 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

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# 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)