Review:

Artificial muscles based on conducting polymers

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Abstract: Natural muscles have mechanical properties that conventional actuators do not possess. These natural machines show large strain, moderate stress, high efficiency and stability, fast response time, high power/weight ratio, long lifetime, etc. In the last years a great interest has arisen to develop materials that mimic natural mechanisms. Conducting polymers have an array of potential applications as artificial muscles since they are capable to produce a moderate displacement when submitted to an electrochemical reaction. This property has been used to fabricate actuator devices that imitate and even improve the performance of natural muscles. For example, conducting polymers show stresses 15 times higher than those generated by mammalian muscles, a high power/weight ratio and a high degree of compliance. However, there are also several responses that need improvement in the actuators based on conducting polymers. Strains are still *c.* 50% lower than in natural muscles. Most of this kind of actuators only work in liquid media. It is necessary to increase the response time and obtain more durable actuators with longer lifetime and higher stability. In spite of these disadvantages, the first actuators based on conducting polymers are being commercialized. This paper presents a brief summary of some of the actuators based on these polymers, focusing on their design, performance and actuation mechanism.

Introduction

The development of materials and devices able to imitate the performance of natural muscles in the direct conversion of electric energy into mechanic energy has always been a challenge to the human being. Taking into account the nature and the operation of its perfect machines, a material is required capable to conduct ions and electrons [1-4]. It should be able to work with electric pulses in the mV region (natural muscles use a potential $\approx$ 175 mV), it should experience a volume variation associated with conformational changes in its structure. It should also have a molecular structure similar to natural muscles; thus, this material should be formed by macromolecular chemistry similar to proteins forming the natural muscles [4]. Also it is desirable to target performances, which equal or exceed those of muscles:

 - Large strains
 - Durability (long lifetime, high stability)
 - High force density (0.1 - 0.5 MPa)
 - Fast response time (0.01 - 0.1 s)
 - High power/weight ratio ($\approx$ 0.1 kW/kg)

In the search for a system with the characteristics named above and capable to imitate the function of natural muscles approximately, the conjugated conducting polymers have arisen as a viable and interesting alternative. In fact, the first actuator that received the name of an artificial muscle was based on a conducting polymer (polypyrrole) and it was reported by Otero et al. in 1992, also named electrochemomechanical device by involving an electrochemical reaction in the mechanic energy generation [5].

Amongst the different materials denominated 'conducting polymers' we will focus on conducting conjugated polymers (CP) that are formed by different families of macromolecules: polyacetylenes, polypyrroles, polythiophenes, polyanilines, etc. [6-24]. The electronic conductivity in conjugated polymers is due to the ease of electronic jumps between chains. These electronic jumps happen thanks to the presence of dopant agents, which modify the electrons amount in the bands. The dopants known as type 'p' remove electrons from the valence band leaving the molecule positively charged. Dopants 'n' add electrons to the conduction band, so, the net charge of the molecule will be negative. This denomination is by direct analogy with classical semiconductor terminology. Through the doping process the charge added to the polymer (or removed) produces a change in the positions of the atoms. These changes produce crystalline islands within the disordered matrix. Several models explain the conductivity by hopping of charge carriers between highly conductive islands and low conductive areas. So, the polymer is converted into an electronic conductor [25-31]. Nevertheless, the conductivity of conducting polymers is very complex and also dependent on preparation and doping [4,32-36]. Doping of the polymers can be done electrochemically or via photodoping. The conjugated polymer can be oxidized (p-doped) or reduced (n-doped) by introducing cations or anions, or photons. Although the word doping is often used in the CPs analogously to solid-state physics, this doping process is different from classical semiconductor doping. In the CPs, the doping is intersticial instead of substitutional and the doping levels are much higher (typically 25%). However, the term 'doping' is also used in the electrochemical terminology to refer to a redox reaction, and 'dopant' to refer to the counterion.

In addition to the variation in conductivity, the state change of conjugated polymers due to doping can produce several effects, e.g., variations in polymer colour, volume and porosity [37-62]. These changes are related to the oxidation state of the polymer and are under electrochemical control: the neutral polymer, the reduced polymer, the oxidized polymer or any intermediate state can be reached by applying the appropriate potential. In this paper we will concentrate on reversible and controllable volume changes in CP and their utilization in the fabrication of actuators.

Volume changes in conducting conjugated polymers

The property of volume change of CPs was reported the first time by Burgmayer and Murray in 1982 [63]. Using PPy membranes they showed that the membrane permeability of certain ions could be changed by two orders of magnitude under polarization at different potentials. From then, the volume changes of several CPs began to be extensively studied [44].

The volume changes in CPs are due to ionic movement produced during an electrochemical reaction. For example, if a p-doped polymer like PPy is oxidized there are two possibilities to maintain electroneutrality: if the polymer is doped with a mobile and small anion (as ClO_4^-) in an electrolytic solution with both mobile cations and

anions, the insertion and de-insertion of the anions during the redox reaction will maintain the electroneutrality (Fig. 1, Fig. 2) [4,63-65]:

$$PPy^+(ClO_4^-) \;+\; e^- \quad \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \quad PPy^0 \;+\; ClO_4^-{}_{aq} \tag{1}$$
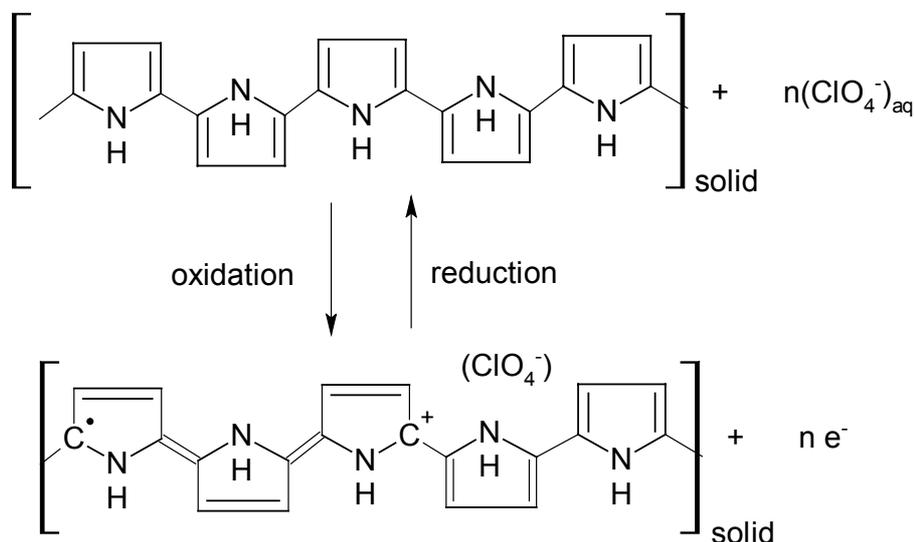
Fig. 1. Sketch representing a redox reaction of PPy in the presence of ClO_4^- anions. To maintain electroneutrality during the oxidation, anions are incorporated inside the polymeric chains according to the number of positive charges formed. Similarly, during reduction, the positive charges are neutralized and the anions get out of the polymer to maintain the electroneutrality
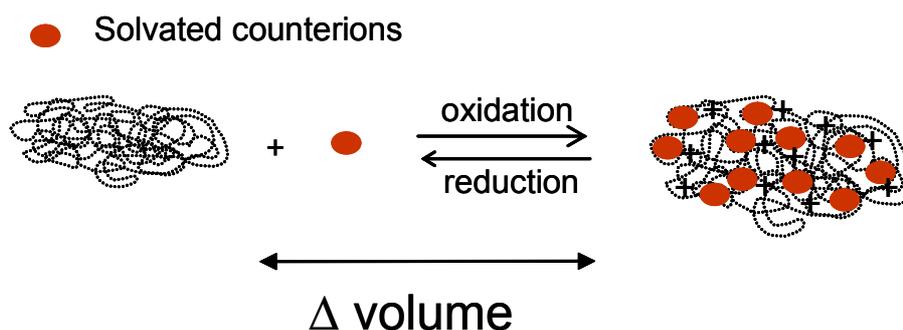
Fig. 2. Picture showing the volume changes in a CP when it is submitted to a redox reaction. In this case, during the oxidation the CP experiences an expansion due to insertion of solvated counterions to neutralize the formed positive charges. In the reduction the positive charges are neutralized by the electrons injected from the potentiostat and the counterions get out to maintain the electroneutrality

If the polymer is doped with a non-mobile and big anion as dodecylbenzenesulfonate (DBS⁻) into an electrolyte containing mobile and small cations X^+, the latter will be inserted and de-inserted during the redox reaction to maintain the electroneutrality:

$$PPy^+(DBS^-) \quad + \quad X^+_{aq} \quad \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \quad PPy^0(DBS^-X^+) \tag{2}$$

Eq. (1) shows that in the first case the CP is expanded during the oxidation due to the insertion of ClO_4^- anions (Fig. 2). In the second case (Eq. (2)) the polymer is expanded during the reduction by insertion of X^+ cations.

Research has shown that the ionic flow in CPs depends on cations' and anions' size, thickness of the CP film, applied voltage and the time scale. The volume change is induced with a voltage change when it modifies the oxidation state of CP. During the volume increase of a CP the inserted ions and its hydrate shell occupy free space. When these get out of the polymer it is shrunk and when they get into the polymer it is expanded. Therefore, the volume change depends on the applied voltage, the electrolyte and the dopant.

According to the properties of volume change observed in CPs, Baughman proposed for the first time (in 1991) to prove the presence of this change of volume by building actuators based on these polymers, which would be able to transform molecular motion into a mechanical movement [65]. The first actuator of this type was obtained by Otero et al., also denominated electro-chemo-mechanical device or artificial muscle due to its similarities with natural muscles [4]. Otero et al. patented this first artificial muscle: a bilayer of $PPy(ClO_4^-)$ with an adherent inactive and flexible polymer, which is named electro-chemo-mechanical device since an electrochemical reaction on the polymer produces conformational changes on its structure, which are finally transformed into a motion. On the other hand, the natural muscles are electro-chemo-mechanical devices since an electric pulse generated in the brain travels through the nervous system until the muscular fibres to produce chemical reactions, which promote conformational changes and mechanic work. Generally the actuators based on CPs are named electro-chemo-mechanic devices.

This bilayer presented motions up to 180° in aqueous solution of $LiClO_4$ [67]. The behaviour of the bilayer was studied in solutions of acetonitrile/$LiClO_4$, propylene carbonate/$LiClO_4$ and water/$LiClO_4$ [68-69]. The greater molecular interaction between solvent and polymer was observed with water as solvent. This supposes a parallel penetration of water and counter ions during the oxidation process giving a more effective swelling of polypyrrole in aqueous solutions. The polymeric swelling occurs easier and in a greater extension when aqueous solutions were used.

Otero et al. developed a model explaining the volume change in PCs taking into in account the electrostatic repulsions between charged polymeric chains [70,71]. According to this model, when a CP as polypyrrole is submitted to an oxidation reaction, positive charges are generated along the polymeric chains. These positive charges produce electrostatic repulsions between them. Due to these repulsions some conformational changes are generated in the polymeric structure. The conformational changes facilitate the insertion of solvated counter ions maintaining the electroneutrality in the polymer. Because of the counter ions the electroneutrality of the polymer is obtained with a consequent increase of its volume. So, when a CP is oxidized its volume is increased proportionally to the formed positive charges. At the same time, when a CP is reduced the positive charges are neutralized with the electrons injected from the potentiostat, the electrostatic repulsions are eliminated diminishing the free volume and the counter ions should get out to maintain the electroneutrality in the polymer. Thus, when the CP is reduced its volume decreases due to the de-insertion of the counter ions from its structure into the electrolyte (Figs.

1 and 2). Otero et al. supported their model with density measurements in PPy films: in the oxidized state the film mass is 50% higher than in the reduced state due to incorporation of counter ions [71]. Besides, Tourillon and Garnier demonstrated the reorganization processes of the polymeric chains, accompanied by the expulsion of anions towards the electrolytic medium by XPS measurements [72]. However, a complete picture of the nature of the volume changes in CPs has not yet been determined.

Pei and Inganäs studied the behaviour of PPy(DBS⁻) films. They observed an increase of mass when cations and hydration shells were inserted in the CP and a decrease when they were excluded [73]. So, the CP was swollen during reduction and was shrunk during oxidation (Eq. (2)). Smela and Gadegaard studied the volume change *in situ* in these films by atomic force microscopy. They found that film thickness increased between 30 - 40% in the reduced state compared to the oxidized state [74].

Polyaniline (PANI) is another one of the most used CPs to make actuators. Okabayashi et al. were the first to determine a volume variation in PANI according to its oxidation state [75]. They observed the weight change of PANI in propylene carbonate/LiClO$_4$ during a redox reaction by an electrogravimetric method. During the oxidation, the weight of the polymer increased up to 8 times due to the insertion of solvated ClO$_4^-$ anions. The species concerned with the doping/undoping process is ClO$_4^-$ solvated with propylene carbonate molecules. They also observed that the solubility of the doping molecule affects the electroactivity of the polymer. The use of a dopant soluble in the electrolyte is preferable to improve the undoping/doping process. A similar value of volume change was found for PPy in LiClO$_4$/propylene carbonate according to *in situ* bulk measurements of Slama and Tanguy [76].

The emeraldine form of PANI also can be electrochemically oxidized or reduced in aqueous acid resulting in pernigraniline (PS) and leuco-emeraldine (LS) salts, respectively, as is shown in Fig. 3. The redox reaction occurs with motion of protons and electrons in strong acid (pH < 3). The addition of protons and electrons to nitrogens is observed during the reduction; this leads to ring changes from phenyl to quinoid structure upon oxidation and *vice versa* during the reduction (Fig. 3). In this case, the structural changes (phenyl ↔ quinoid) are the cause of strain of the PANI. In the reduced state the polymer is more compact than in the oxidized state, as was demonstrated by Kaneto et al. [77]

Polythiophene (PT) and its derivatives are not as well studied as PPy and PANI but they are also a subject of research as actuators at the moment. Most actuators based on PTs have been fabricated from monomers synthesized for particular actuation purposes. Tourillon and Garnier studied the electrochemical properties of substituted PTs and the effect of the counter ion, the solvent and the polymer structure on these properties [78].

The swelling of the polymer was observed when this was oxidized. For example, it was demonstrated that in polymethylthiophene the thickness varies from 160 nm in the undoped state to 200 nm in the oxidized doped state. The doping level was determined by elemental microanalysis to about 25% (one positive charge developed in every 4 monomeric units). Although it was not sufficiently clarified, the authors reported that the effect of the dopant does not appear to be substantially determining the electrochemical properties of the thiophene derivatives. This remark was based on the i = f(V) curves. These do not show differences if the counter ion BF$_4^-$ is replaced by CF$_3$SO$_3^-$. This behaviour was found by the authors when studying the

role of different anions (BF$_4^-$, ClO$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$) in polymers derived from thiophene. This result absolutely differs from studies carried out for polypyrroles [79,80, 34]. In electrogenerated polypyrroles the anion change in the electrolyte has a profound effect on the electrochemical response. The authors attributed this unexpected behaviour to different types of morphology: the polythiophene derivatives show a fibrillar structure, whereas polypyrrole is much more compact. This causes that for PPy a higher potential is necessary for obtaining an amount of free volume when more voluminous anions are used [80]. Concerning the effect of the solvent, its polarity and its swelling properties affect the electrochemical characteristics of the polymers according to the i = *f*(V) curves recorded by the authors. Additional research is necessary to generalize the effect of the type of dopant on the electrochemical properties of these thiophenes. For example, it would be desirable to study the effect of the counterion on the electrical conductivity of these polymers and to make a structural analysis of the polymer under the different conditions.
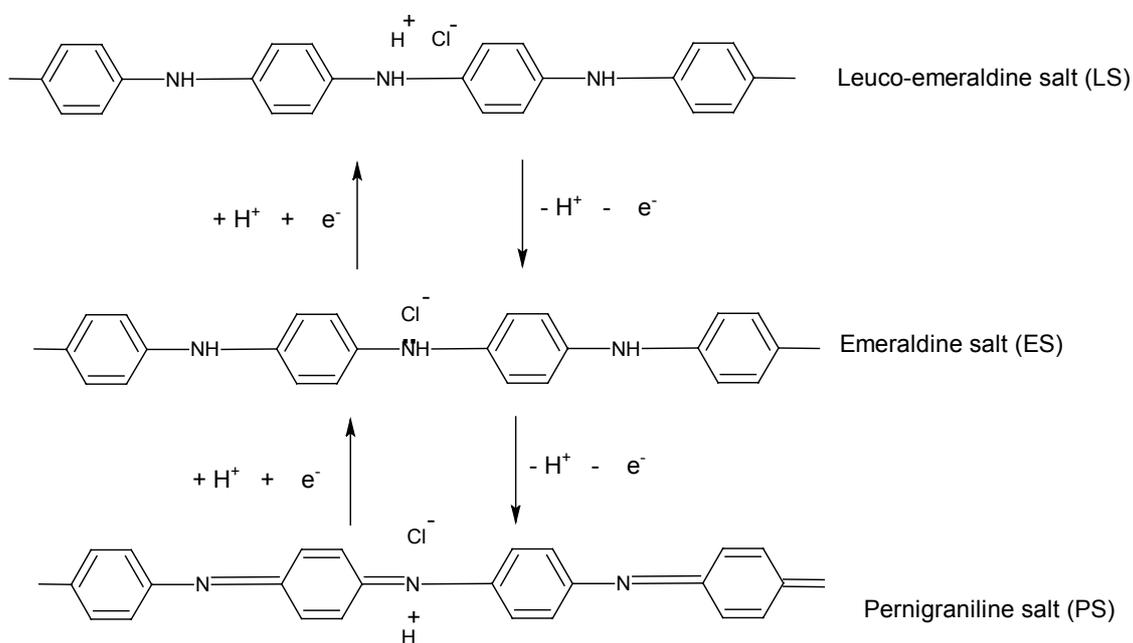
Fig. 3. Redox cycle of PANI in HCl aqueous solution. The emeraldine salt is oxidized into pernigraniline (PS) salt or reduced into leuco-emeraldine (LS) salt [77]

Unlike PPy and PANI actuators, in the PT actuators the actuation mechanism is not simply due to ion intercalation in the polymer chains. In this class of materials the actuation results from π-π stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement, which promotes large strains. One possible molecular rearrangement is the formation of π-dimers by the tendency of orbitals to align due to Pauli´s exclusion principle during oxidation of the material. In Fig. 4 is shown the actuation mechanism of a material composed by hinge molecules (like a calixarene) interconnected with rigid chains of thiophene. The thiophene chains attract each other in the oxidized state, thus contracting the material. This strain is reversible during the reduction of the polymer [54]. So, these novel polymers hold the promise of improving the speed limits of the PPy and PANI actuators caused by the ionic diffusion rate.
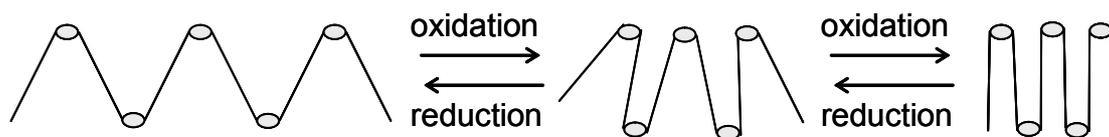
○ Hinge molecules (for example, calix [4] arene)

╲ Rigid rods: Thiophene chains

Fig. 4. Picture showing the actuation mechanism of a molecular actuator based on PT chains interconnected with a highly versatile molecule like a calixarene [54]

Similarities with natural muscles

Natural muscles are devices able to convert chemical energy into mechanical energy and heat at a constant temperature. In general, the muscular motion starts with an electric pulse generated from the brain into the nervous system, which promotes an increase of Ca^{2+} concentration around the muscular fibres. This increase of ionic concentration originates conformational changes in the troponin-tropomyosin complex and consequently the muscular contraction. All these processes occur in aqueous medium and at constant temperature [1-3,81]. A sketch of the mechanism is shown in ref. [82]

So, a natural muscle is an electro-chemo-mechanical device (involving an electric signal which initiates chemical reactions that lead to production of mechanical energy) whose active part is a complex material (proteins + water + ions + small organic molecules).

The actuators based on conducting polymers or artificial muscles show several similarities of operation and structure with the natural muscles and also some differences. The resemblances can be summarized as follows [4]:

 - These polymers show reversible processes of oxidation and reduction, which promote the insertion and the de-insertion of ions of their structure and, therefore, conformational changes, which cause volume changes that generate a motion. In the natural muscles, chemical reactions promote ionic concentration variations (Ca^{2+}), conformational changes in the muscular structure (troponin-tropomiosyn) and finally the muscular contraction.

 - Electric pulses linked to chemical reactions are involved in movement generation.

 - In these polymers like in natural muscles a controlled mechanical motion is observed.

 - There is a direct conversion from chemical energy into mechanical energy.

 - The polymers work in aqueous solutions of ionized salts and at constant temperature.

 - The conducting polymers have a macromolecular structure comparable with the proteinic structure of natural muscles.

The differences between muscles based on conducting polymers and natural muscles are [4]:

- The driving power in natural muscles is the chemical energy produced by combustion of glucose at constant temperature. In conducting polymers the driving power is the electric charge consumed during the redox reaction.

- The reversibility of the muscular motion is achieved by the operation of a second muscle. In conducting polymers both contraction and expansion of the material are observed due to insertion and de-insertion of ions from its structure.

Actuation principles

An electro-chemo-mechanical actuator or artificial muscle based on CP has three fundamental parts: an anode, a cathode and an electrolyte. Both anode and cathode can be made of CP. The electrolyte can be either liquid or solid. In the first case the actuators only work in liquid medium. With a solid electrolyte the actuator operates in the air. These actuators work by electrochemical transfer of ions between the electrodes through the electrolyte. The mass and volume of electrolyte can be minimized. Thus, the electrolyte amount could be the strictly necessary for the observation of ionic conductivity. The ionic movement and the subsequent volume change in CP are the fundaments of the motion in these actuators.

The volume changes in the CP can be transformed into movement using several kinds of devices. For example, bilayer, multilayer and fibre devices have been used. These devices elongate, shrink, and bend, in aqueous medium or air.

Other types of ionic polymer - artificial muscles

Ionic polymer-metal composites (IPMCs)

Around 1950, the reversible dilation and contraction of IPMCs were observed [83]. From then, these materials have been widely studied and evaluated as sensors, batteries and artificial muscles [83-90].

This type of material is obtained from an ionic polymer with ion exchanging capability, which is then chemically treated with an ionic salt solution of a metal and then chemically reduced to yield ionic polymer metal composites. Typical ion exchange polymers are the following: perfluorinated alkenes terminated by ionic groups, styrene/divinylbenzene-based polymers in which the ionic groups have been substituted on the phenyl rings, where the nitrogen atom is fixed to an ionic group [91]. These polymers exhibit large dynamic deformation if placed in an electric field varying with time. Reversing the process, dynamic deformation of such polymers produces dynamic electric fields. A relatively low voltage (1 - 10 V) is required to stimulate bending in IPMCs, where the base polymer provides channels for the mobility of positive ions in a fixed network of negative ions on interconnected clusters (in the case of perfluorinated membranes, which are the most studied) and promoting deflections around 2 cm and responses from 0.1 to 1 s under DC activation [92]. The ionic content of the IPMCs is an important factor in the electromechanical response of these materials. Diffusion and Coulomb forces (ion transport and electrophoretic solvent transport) are considered as the driving mechanism responsible for the bending and the associated effects. Due to their ability to absorb large amounts of polar solvents, when equilibrated with aqueous solutions, IPMCs swell to absorb a certain amount of water. Swelling results from the affinity of water to the fixed ion-exchanging sites and the moving counter ions. Oppositely to the actuation mechanism of CPs, the bending in the IPMCs is partially related to migration of mobile ions

within the polymer caused by an applied electric field. Bending results for sodium cations and platinum metallization have been shown. This capability was enhanced using Li$^+$, tetra-n-butylammonium and other types of cations with gold metallization [93-95]. A silicon-based coating has been developed that maintains the moisture in the IPMC actuators for several months and allows working in the air [96].

The first prototypes of actuator tools based on IPMCs have been built. For example, a dust wiper fabricated with perfluorocarboxylated gold composite with two types of cations, tetra-n-butylammonium and lithium, and a 4-finger gripper that was used to grab small objects.

The main points to improve in this type of actuators are as follows:

 - Because of their sensibility to dehydration, it is necessary improve the protecting coating for long-term operation and residual deformation.

 - Electrolysis at > 1.03 V causes degradation.

 - Under DC voltage, IPMCs don't maintain the induced bending and retract after several seconds. Upon removal of the electric field an overshoot bending occurs in the opposite direction moving towards the steady state position.

Electroactive polymer gels

A gel is described as an intermediate between a liquid and a solid and consists of a polymer network and interstitial fluid. The properties of the gel are defined by the interaction between the polymer and the liquid. Polymer gels have the ability to swell, shrink, bend and curl with the application of a stimulus. These stimuli can be anything from pH, solvent and temperature changes to electric stimulation. One of the key features of polymer gels is their ability to drastically change volume. The expansion and contraction of gels depends on the diffusion of water or solvent in and out of the matrix. The gels' rubber elasticity, polymer-polymer affinity and the hydrogen ion pressure are all factors that affect the rate and quantity of the volume change.

The study of gels chemically actuated as muscles was initiated on poly(acrylic acid) gels by Osada in 1987 [97]. These polymers showed a large expansion on being moved from an acidic solution to a base. However, they were quite weak and the response is slow. From then, a number of new gel systems were developed with stronger responses, such as poly(vinyl alcohol) blended with poly(acrylic acid) and poly(allylamine hydrochloride), poly(vinyl alcohol), and saponified polyacrylonitrile (PAN) fibres [98]. For example, moving from acid to base, PAN fibres will change in length by about 70% in about 5 s and will generate a force of 1.2 MPa.

The first studies of volume changes on polymer gels induced by an electric field dated from 1965 [84]. The type of deformation depends on the pH of the surrounding solution, the salt concentration, the position of the gel relative to the electrodes, and the shape of the gel. The volume change of a polymer gel under an electric field is based upon the transport of mobile ions in the gel and in the surrounding solution. The conformational changes and the electrorepulsive interactions promoted by the ionic mobility cause the shrinking and the swelling of the gel [99]. Axial displacements are more common and large voltages to actuate are required.

The force generated by a gel muscle can range from 0.001 to 0.2 MPa with response times from 1 to 1000 s [99]. Some materials studied as gel muscle are: poly(vinyl acetate) gel film, poly(vinyl acetate) – poly(sodium acrylate), poly(acrylic acid) – poly(vinyl alcohol). One type of polymer gels is known as hydrogels. A hydrogel is a

water-swollen three-dimensional network of hydrophilic homopolymers or copolymers with cross-links formed by covalent or ionic bonds. Hydrogels are capable of swelling up to 250% and the time required to perform these results can take as long as 10 to 10^4 s. Although it is much more desirable to use an electrically driven actuator than a chemically actuated one, electric field associated systems are not as good as those using a change in solvent composition [100].

Due to the important deformation of a gel with a relatively high speed, polymer gels had been applied to the fabrication of systems that exhibit motion. For example, a hand with four gel fingers which can hold a 9 g object [101], a fish with a tail of gel film, which can swim at a velocity of 2 cm/s under an AC electric field of 0.5 Hz. A polymer gel with two hooks that performs a looping action at 25 cm/min has been fabricated [86].

The most gel actuators using electric field function only immersed in a solution. However, Shiga et al. designed a mechanical hand with two smart gel fingers that works in air and which can catch an object weighing 0.2 g [99,102]. In spite of the important advances in the performance of polymer gels, these exhibit relaxation of their position when the electric field is switched off. So, a deformation towards the opposite direction is shown in the absence of the field. This and the high voltages required constitute an important disadvantage compared to the CPs. Some authors suggest that composites can be manufactured with a better performance by combining both gels and CPs or gels with traditional polymers [103].

Actuators based on conducting polymers

Actuators working in liquid medium

Linear actuators

The simplest actuators are the linear actuators, which are formed just by a CP film. The actuation principle is based on longitudinal expansion and contraction of the polymer due to the insertion and de-insertion of ions. With this kind of device the influence of ionic flow has been studied in both doped CPs with anions of different sizes (mobile and non-mobile) and in a great variety of electrolytes.

Della Santa characterized the mechanical behaviour of a simple freestanding PPy film doped with benzenesulfonate anions (BS⁻) working in an electrochemical cell [81]. The PPy(BS⁻) film was obtained under the trade name Lutamer. The actuator was 90 mm long and 1 mm wide and it was immersed in an electrolyte of 10^{-2} M sodium benzenesulfonate in a mixture of acetonitrile and water. The material had an electrical conductivity of 150 S/cm in its fully doped state. An extremity of the strip was mechanically fixed by a gold clamp that provides electric contact. The other extremity of the strip was fixed to a computer driven servo-controlled actuator, which was used for measuring both force and displacement. The PPy film was also connected to a potentiostat as working electrode through the gold clamp; a Pt sheet was used as counter electrode and a standard calomel electrode (SCE) as reference (Fig. 5).

The characterization of this actuator strip was made in its wet and stabilized state. A stabilization period was needed since the PPy(BS⁻) film considerably changes its properties when immersed in an electrolyte solution and during the first electrochemical cycles; it was found that when the polymer is immersed in the electrolytic

solution, it undergoes a free swelling that produces a linear dimension variation by 2%. During the cycling (CV: cyclic voltametry) of the polymer (±1V) the most BS-anions leave the film and Na^+ becomes the dominating moving ion species. The elastic modulus of the polymer decreases with cycling until a final constant value equal to 660 ± 40 MPa which is 50% lower than the initial value. After a pre-conditioning of 20 cycles of CV, the actuator was characterized by means of a square wave (SW) current, taking measurements of length changes and developed force.
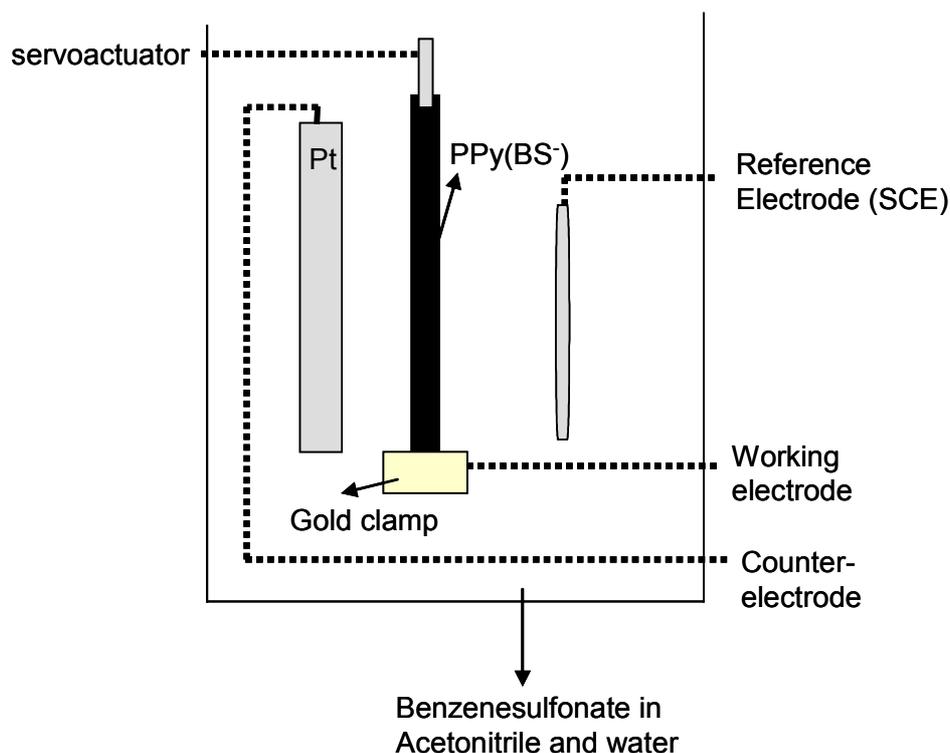
Fig. 5. Picture of an electrochemical cell containing a linear actuator of PPy(BS⁻), which acts as working electrode. The counter electrode is a Platinum sheet and as reference a SCE was used

The elongation and contraction of the actuator was related to the amount of charge exchanged every cycle: an average value of length change to charge ratio of 1 mm/C was computed for values of charge between 0.25 - 0.3 C. For charges higher than 0.3 C, the lifetime of the actuator decreased considerably. Experiments have also demonstrated that the electrical conductivity of the material decreased due to the loss of BS⁻ dopants. The force developed by this actuator was around 3 MPa.

Hutchison et al. developed PPy-based electromechanical actuators in different designs. One of these designs was a freestanding film working as a linear actuator [104]. PPy was prepared galvanostatically from a solution of 0.1 M pyrrole, 0.1 M 4-toluenesulfonic acid sodium salt (pTS) and 1 M sodium perchlorate for 30 - 60 min to give films of 4 - 40 μm thickness. PPy was grown as film on polished stainless steel and peeled off after growth. The films were tested directly or were sputter-coated with Pt on one side before mechanical testing. As electrolyte 1 M $NaNO_3$ or $NaClO_4$ solution was used. Electric contacts were applied through carbon cement and the actuation potential was typically in the range from -0.8 to +0.4 V vs. an Ag/AgCl electrode. The actuator was evaluated in a tensile testing machine. In the electro-

chemical cell the PPy film acts as a working electrode; there is further a stainless steel counter electrode and a Ag/AgCl reference electrode (Fig. 6).

These researchers found that the force density observed in platinised PPy films along the entire length is almost six times higher than for an unplatinised film. This fact is due to a better electrical conductivity along the PPy allowing maximum actuation. On the contrary, in the unplatinised films only a small region around the electric contact would experience a sufficient potential to carry out the redox reactions (Fig. 6 A, B). However, the platinised films were both very brittle and difficult to handle.
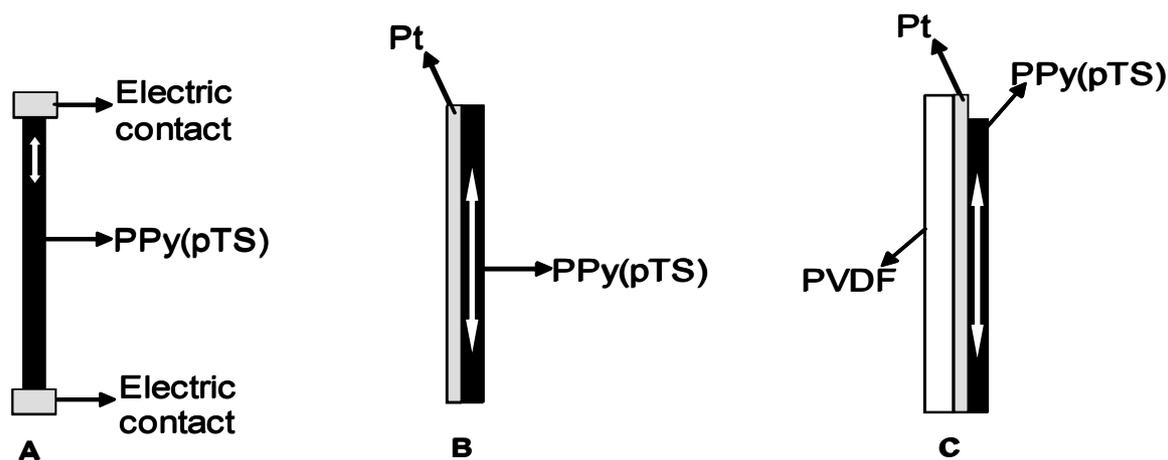
Fig. 6. A schematic diagram for, A: a linear actuator of freestanding PPy(pTS), B: an actuator with platinised PPy(pTS) film, and C: a bilayer formed by a platinised PPy film over a PVDF layer

The evaluation of the influence of the scan rate on the movement of the PPy(pTS) films demonstrated that the scan rate shows a correlation with the charge consumed during the redox reaction. The authors also reported a linear relationship between the consumed charge during the cycle and the force generated by the film, which demonstrates the faradic nature of the actuation process.

Lu et al. showed results on the synthesis, fabrication and operation of CP devices working in ionic liquids composed of 1-butyl-3-methylimidazolium cations (BMIM$^+$) together with anions such as tetrafluoroborate (BF$_4^-$) or hexafluorophosphate (PF$_6^-$) [83]. The authors used these materials as electrolytes since they satisfy the requirements: high ionic conductivity, large electrochemical windows, low volatility, fast ion mobility during the redox reaction, and environmental stability.

Ionic liquids are organic or inorganic salts that are liquid at room temperature (or reaction temperature) which are being employed as substitutes for most organic and inorganic compounds. These salts show very good dissolution, high thermal stability, non-flammability, with higher viscosities than either aqueous or organic electrolytes at room temperature, and they can also be obtained in a very dry state. One of their major advantages is the optimization of compound characteristics through a broad choice of anion and cation combination (tailor-made electrolytes).

The actuation properties of PANI emeraldine base fibres with ionic liquids were studied. The linear actuation performance for the leucoemeraldine/emeraldine salt redox couple in (BMIM$^+$)(BF$_4^-$) was measured under isometric and isotonic

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conditions. The fibre had a length of 10 mm, 59 µm diameter, and was doped with trifluoromethanesulfonic acid. The electrochemical-actuation measurements were carried out using an electrochemical cell whit the polymer fibre as the working electrode, a Pt wire as the counter electrode and a silver wire as the reference electrode at a potential between -0.4 V and +0.7 V. One end of the fibre was clamped on the bottom of the electrochemical cell contacting a platinum plate. The other end of the fibre was fixed on the tip of a dual-mode lever arm system. The fibre was partially immersed into electrolyte (only the lower portion ~ 1cm). The actuation mechanism showed that the fibre shrunk when the CP was oxidized to the emeraldine salt and expanded upon reduction. The cation incorporation at cathodic potentials and expulsed at anodic potentials is the predominant mechanism during actuation. The actuation mechanism of PANI fibres with ionic liquids does not involve the loss or gain of solvated protons; thus, the authors did not observe a pH dependence toward actuation. Charge/discharge measurements showed that the reduction rate is faster than the oxidation in this electrolyte [105,106].

The results found for performance were similar to those reported by Mazzoldi et al. for PANI linear actuator in aqueous and gel electrolytes [107]. The isotonic strain measured during voltametric cycles reached a maximum of 0.28% and the force generated was 0.005 N. The ratio of the mass lifted to the mass of fibre was $2 \cdot 10^4$. The energy density for one cycle was 10 kJ/m^3 and the specific work performed was 5.6 J/kg.

As for some other actuators, both the strain and the stress in the fibre were proportional to the consumed charge during a redox cycle. They calculated a strain to charge ratio of 0.031% and a stress to charge ratio of 0.18 MPa·mC^{-1}. The reduction process was faster than the oxidation process in $(BMIM^+)(BF_4^-)$ due to the incorporation of imidazolium cations. This worked for 10 000 redox cycles without losing any strain or stress. This represents an advantage of ionic liquids with respect to both aqueous and organic electrolytes [105].

These researchers also fabricated actuators as a yarn based on these PANI fibres and operated them in ionic liquids. This yarn was prepared from twisted 20 Panion-triflate fibres, which are commercially available through Santa Fe Science and Technology. This actuator with yarn shape was operated in $(BMIM^+)(BF_4^-)$ and had a better performance compared with a single PANI fibre-actuator working in the same media at lower cycling potentials: the linear strain was almost 4 times higher than of a single PANI fibre, and the force generated for the yarn was 5.6 times of that of a single fibre. According to the authors, this can be due to the increase of charge injection obtained by cycling to higher potentials [105].

$PPy(PF_6)$ tubes grown on top of a helical Pt wire were also evaluated as actuators both in tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in propylene carbonate (PC) and pure $(BMIM^+)(PF_6^-)$. In order to synthesize this tube a 125 µm Pt wire was used with another Pt wire of 25 µm wrapped around it as a spiral. Over this assembly was deposited a PPy coating in an electrochemical cell. The central Pt wire was removed and two short Pt wires were inserted into the tube at both ends to make good electrical contact and sealed with epoxy (Fig. 7). Pt was used for improving the charge distribution throughout the device [105,106].

The evaluation of this device was made in an electrochemical cell with the $PPy(PF_6)$ tube as working electrode, and an auxiliary electrode of another CP. A square wave $\pm 5V$ was applied to the PPy tube during around 6000 cycles. The results showed that for a few hundred cycles the linear strain and the displacement rate were very

similar for an ionic liquid as electrolyte and for an organic electrolyte (tetrabutyl-ammonium hexafluorophosphate in propylene carbonate (PC-TBAPF$_6$)). However, the charge as a fraction of the charge exchanged during the 100th cycle, called normalized charge by the authors, with respect to displacement decreased greatly in PC-TBAPF$_6$ after 2000 cycles. The authors attributed this decrease in performance to a mechanical and electronic breakdown of the backbone because of a nucleophilic attack from the electrolyte on PPy(PF$_6$) at high potentials and/or electrochemical decomposition of propylene carbonate. During the reduction process, the actuator evaluated in an ionic liquid was expanded, presumably owing to the incorporation of the large imidazolium cation. With the actuator operated in an ionic liquid very little irreversible degradation of the polymer occurred after 6000 redox cycles and very good results were obtained for the performance of the actuator: 1.6% of strain at a 3.2%/s rate of displacement [105].

Pt wire of 125 μm

Pt wire of 25 μm

Connection of Pt wire solded with epoxy
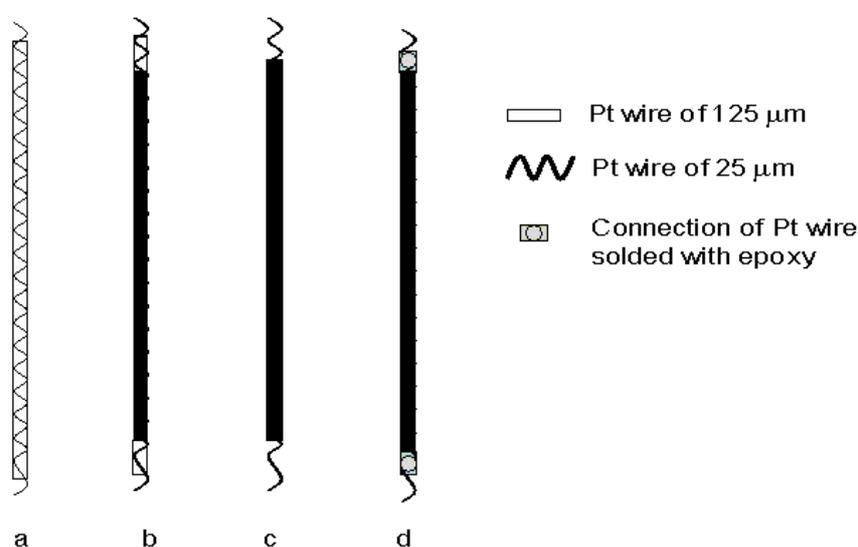
Fig. 7. Sketch of the assembly of an actuator based on PPy(PF$_6$) tubes. a: An electrode formed by a Pt wire of 125 μm wrapped with a Pt wire of 25 μm was used as working electrode. b: PPy(PF$_6$) was deposited around of the spiral. c: The wider Pt wire was removed from the assembly. d: Two Pt wires were sealed on each end part of the spiral with epoxy to be used as electric connections [106]

Bending actuators

As it was mentioned previously, the first actuator based on CP was made combining a PPy film with a non-volume changing layer into a bilayer structure. This was a bilayer: PPy doped with ClO$_4^-$ / adherent tape and it was reported in 1992 by Otero et al. [5] The original idea to design this actuator was based on a bimetallic thermo-meter where two metallic plates with different thermal expansion coefficient are welded side to side. An increase of temperature gives a separation of atoms higher in a plate than in the other one. Consequently there is an increase in the length of the first plate greater than the second one. The macroscopic result is a bending of the bilayer maintaining the plate with higher thermal expansion coefficient on the convex side. Taking as fixed point an end part of the bilayer this will describe an angular movement proportional to the temperature change. A decrease of the temperature will produce an opposite movement.

The first bilayer actuator (PPy(ClO_4^-)/adherent tape) was used to evaluate the volume change mechanism in PPy under electrochemical stimulation [5]. These PPy films were electrogenerated over a stainless steel electrode in acetonitrile with 2% water, 0.2 M of pyrrole and 0.1 M of $LiClO_4$. The electropolymerization was potentio-dynamical (-0.32 V during 2 s and +0.87 V during 8 s vs. Ag/AgCl in 6300 s) to obtain homogeneous, flexible and smooth films. The coated steel was removed from the polymerization solution in an oxidized state to prevent oxygen attack (this attack would decrease the oxidation/reduction capacity). PPy films of 13 µm thickness, 3 mg weight, 2 cm length and 1.5 cm width were obtained passing 28 C during the synthesis. The thickness of the PPy films is controlled through the electric charge of polymerization. The relationship between charge of polymerization and mass of polymer is shown in Fig. 8; Eq. (3) relates the mass of the polymeric film to its thickness.

$$e = \frac{m}{A \cdot \rho} \qquad (3)$$

Where e = thickness in cm, m = mass in g, A = area in cm^2, ρ = density in $g \cdot cm^{-3}$.
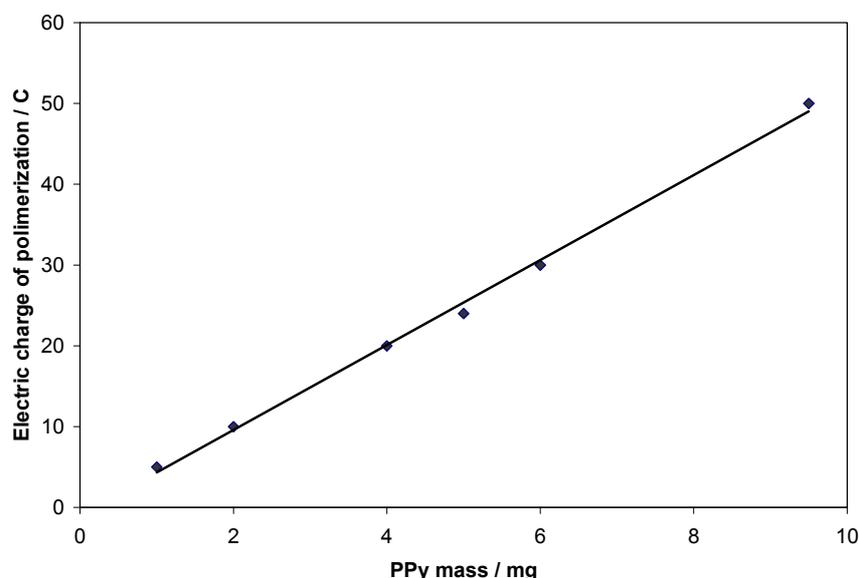
Fig. 8. Electric charge consumed during the polymerization of a PPy film by the method patented by Otero et al. [68,108]

The PPy film over the working electrode was peeled off with a commercial adherent and flexible tape. This bilayer was evaluated in an aqueous solution of $LiClO_4$. As counter electrode a platinum plate was used, the PPy film was connected to the potentiostat as working electrode. A SCE was used as reference. According to the model explained in the Introduction, the PPy film experiences volume changes during redox reactions. These volume changes are transformed to a self-bending of the bilayer system comparable to the bimetallic thermometer (Fig. 9). This device moves, covering angles up to 360° in $LiClO_4$ aqueous solution. The movement rate is greater during the reduction than during the oxidation of PPy. During the oxidation the bilayer bends with a rate of 0.3 rad/s and during the reduction with 0.5 rad/s in 1 M $LiClO_4$ aqueous solution when a potential of ± 1 V was applied [109]. The difference is due to ionic diffusion during the redox reaction. The rate of reduction is faster than the

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rate of oxidation. In the reduced state the polymeric structure is closed and in the oxidized state it is open. The opening of the structure is easier to perform than the closing, making the reduction process faster. This conclusion was achieved from the work of Otero and Santamaría related with the redox behaviour of thin PPy films [110]. They evaluated and optimized the necessary time to complete the oxidation/ reduction processes in PPy(ClO$_4^-$) films. They found than the times required for the oxidation reactions are longer than the reduction times. For example, in a PPy film of 2.22 µm thickness the oxidation/reduction time ratio is 4.59 s/3.4 s. According to this a flexible and open polymeric structure will be desired to carry out an easy and fast oxidation. So, the polymerization conditions of the CP film play an important role for the performance of this actuator [110,4].
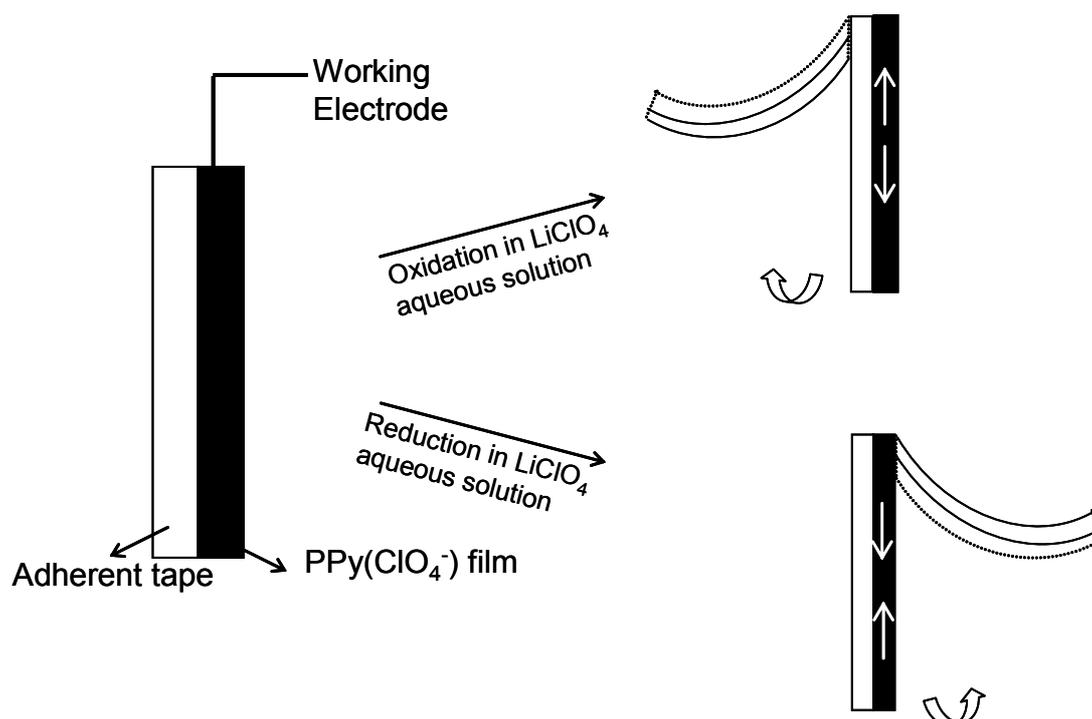
Fig. 9. Bilayer device formed by a PPy(ClO$_4^-$) film and an adherent tape. The motion is produced by volume changes in PPy during a redox reaction. For example, during the oxidation of the PPy film it is expanded by the insertion of ClO$_4^-$ anions from the electrolyte. The PPy film is expanded and the adherent tape is shrunk, so, the device bends into the adherent tape. The opposite movement is obtained when the polarity is changed

Reproducibility of the macroscopic movement was very high using these bilayers. In order to test the reproducibility, four different devices were checked in 1 M LiClO$_4$ aqueous solution under a constant voltage of 1 V during a 90° angular movement relative to the vertical position. Through a cathodic potential (-1 V) the electro-chemical reaction and the consequent direction of movement were reversed. The average times required to describe 90° and 180° during oxidation were 4.5 ± 0.31 s and 11.21 ± 0.54 s, respectively, with a decrease in the movement rate during the final part. Under reduction the movement rates were higher: 2.56 ± 0.05 s and 6.09 ± 0.46 s to describe 90° and 180°, respectively. In general, the reproducibility was very high showing deviations of less than 5% [109].

Otero and Sansiñena also found than the bilayer (PPy doped with ClO_4^- / adherent tape) is capable of generating mechanical work [110]. In order to test the behaviour of the bilayer under these conditions a piece of steel of known mass ($\approx$ 1 g) was attached to the bottom of the bilayer. When the bilayer was submitted to oxidation/ reduction processes the time required to describe 90° under oxidation was 5.32 $\pm$ 0.95 s and for 180° 13.95 $\pm$ 2.76 s as average of four bilayers. During the reduction process the measured times were 2.27 $\pm$ 0.41 and 12.2 $\pm$ 1.75 s for 90° and 180°, respectively. Under conditions of mechanical work the reproducibility decreases and deviations are around 20% [109]. The influence of the electrolyte concentration on bilayer movement was also studied. The electrolyte concentrations evaluated were from 0.1 to 0.75 M $LiClO_4$ aqueous solution under a constant anodic current of 15 mA or constant voltage of 1 V vs. SCE. From the experimental results the researchers concluded that there is a direct dependence between described angle and consumed charge during the movement. This relation does not depend either on electrolyte concentration or on electrical conditions. Also an increase of the electrolyte concentration promotes an easier entrance of anions into the polymer structure [113-115].

Both the direction and movement rate of the bilayer (PPy doped with ClO_4^- / adherent tape) are controlled by the electric charge consumed during the movement. So, it is possible to locate the actuator at any angle and with the desired rate. Sansiñena demonstrated that it is possible to obtain a straight calibration, which correlates the consumed charge with the angle [108]. Thus, this actuator has electrochemo-positioning properties so that an electrochemical reaction controls both its position and movement rate.

The reaction times are shorter for thinner films [116]. This is due to the fact that the switching rate between two states is limited by the ionic diffusion.

Onoda et al. reported the fabrication of actuators from cylindrical PPy pipe [117]. To prepare the cylindrical PPy an electrochemical cell containing an aqueous solution of *p*-toluenesulfonic acid sodium salt (p-TSNa, 1 M), a Ni plate as counter electrode and a Ag reference electrode were used. The working electrode was a Ni wire (0.2 mm diameter) in 2 M pyrrole and a slender pipe made of polytetrafluoroethylene (PTFE) was attached on top of the Ni wire; PPy was deposited on top of the Ni wire by constant current flow. The cylindrical PPy fibre obtained showed an extremely smooth and uniform outer surface and a very insular inner surface. The inner surface was in contact with electrolyte during PPy synthesis and the outer surface was in contact with a PTFE slender during the synthesis. The conductivity of the fibre on the outer surface showed an anisotropy, being much higher in the growth direction ($\approx$ 100 S/cm) than in the perpendicular direction. However, the conductivity of the fibre on the inner surface did not show a significant anisotropy and it was smaller than on the outer surface.

To measure the electro-chemo-mechanical properties of the material, the cylindrical PPy pipe was cut into a strip (2 cm x 0.31 cm). When the PPy was submitted to a redox process it experiences a bending. The electrical connections were made so that both the outer surface and the inner surface alternately acted as working electrode (Fig. 10). The auxiliary electrode was a metallic plate. The PPy strip bent in the direction of the surface in contact with PTFE during undoping and the movement was contrary during the doping. This is a result of film contraction during reduction and its expansion during oxidation. The PPy film is straight in the oxidized state and bends to the outer surface by reduction. The actuator showed a total displacement of about 6 mm during cyclic voltametry in TSNa 1 M aqueous solution under a sweep

rate of 15 mV/s and potentials between 0.5 and -1.5 V vs. Ag/Ag$^+$. The response time required to bend over 90° during the reduction was approximately 1 s. However, the same movement during the oxidation of PPy took several seconds. The authors suggested that this anomalous behaviour could be due to the difficulty of dopant transfer between the inner surface and the outer one [117].
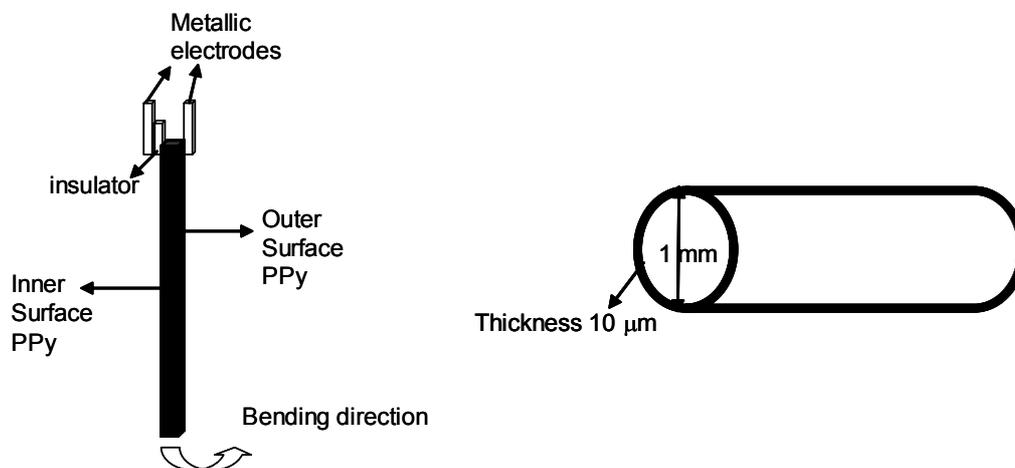
Fig. 10. Sketch showing the structure and work of an actuator of cylindrical PPy fibre

Baughman et al. also showed a bilayer formed by a copolymer of 3-methylthiophene and 3-n-octylthiophene covered over one side with a gold film. This device was evaluated in propylene carbonate solution with LiClO$_4$ together with a Li counter electrode [44,50]. The electrochemical doping of the polymer with ClO$_4^-$ produced an expansion of the CP with respect to the gold coating; this generated a bending of the device. With electrochemical undoping the opposite movement was produced. Some authors have denominated electromechanical actuators those based on CP [50]. An electromechanic actuator directly converts electrical energy into mechanical energy such as piezoelectric and electrostrictive materials. CP actuators make the same conversion of energy. However, they are really electrochemical mechanical actuators, so the term electro-chemo-mechanical is more precise and suitable.

They named this bilayer 'unimorph device' because this system has only one active electro-chemo-mechanic electrode. Consequently, a bimorph device will use both an electromechanic anode and cathode in a unique device. The 'unimorph' and 'bimorph' terms are typical of the piezoelectric materials. However, Baughman et al. have extensively utilized them for the CP actuators.

For example, a simple electrochemical bimorph cell consists of a polymer electrode strip and a polymer counter electrode strip cemented together by a polymeric electrolyte, which electronically separates these electrodes. And an electrochemical unimorph cell will consist, for example, of a polymer electrode strip glued to an inactive and flexible polymer.

Pei and Inganäs have studied different bilayers of conjugated polymers, such as PANI, PPy, and poly(3-octylthiophene) (P$_3$OT) as active materials and different dopant ions [118-120]. The first of these bilayers was a strip of PPy and polyethylene (PE) layer bound together (PPy/PE). This strip bends due to volume changes in the PPy layer. This self-induced bending of a bilayer is also called bending beam method. With this method *in situ* volume changes can be measured in CP during an electrochemical redox reaction.

To form a PPy/PE bilayer, a PE film of 150 µm thickness was coated with a gold layer of 0.2 µm thickness by vacuum evaporation. The Au film acts as the carrier and current collector. This Au/PE layer was used as the working electrode to electro-chemically polymerize pyrrole in an aqueous solution containing pyrrole and sodium tosylate, $LiClO_4$ or sodium dodecylbenzenesulfonate (DBS^-Na^+). A potential of 0.75 V was applied and pyrrole was oxidatively polymerized onto Au/PE to form a PPy/PE laminate (with Au in between). The thickness of the PPy film was typically between 10 - 15 µm (Fig. 11). PPy/PE had an area of 2.3 cm x 0.25 cm [120].

PE layer (150 µm)

PPy film (10-15 µm)

Au coating (0.2 µm)
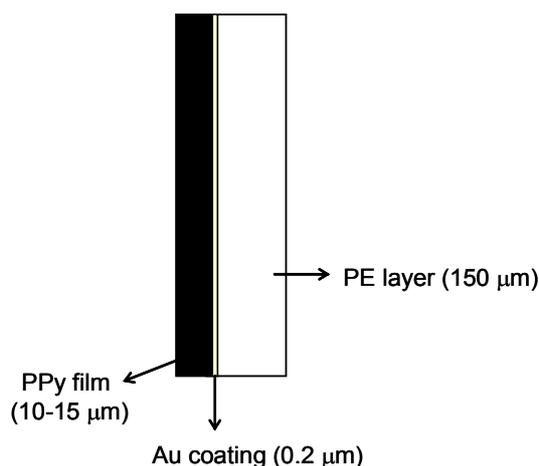
Fig. 11. Bilayer formed by a polyethylene (PE) layer and a PPy film. A gold film placed between PE and PPy acts as current collector. This bilayer works as working electrode in an electrochemical cell containing a liquid electrolyte. A gold wire is used as counter electrode; the reference electrode is Ag/AgCl

These actuators work in a liquid electrolyte with an inactive counter electrode (Au-coated Si wafer or Au wire) separately of the bilayer. The bilayer PPy/PE is the working electrode. As reference electrode a commercial Ag/AgCl was used. The movement of these bilayers was microscopic (around 0.1 cm) with a movement rate around 0.5 mm/s. By holding the potential fixed at any value within the potential limits (-0.85 V and +0.3 V) it is possible to locate the microactuator in intermediate positions [119,21]. These PPy/PE bilayers could be bending for many cycles without significant loss of the maximum bending degree. $PPy^0(TsO)$/PE showed the highest loss of bending which was about 0.02 cm^{-1} after 13 h of cycling. The bilayer $PPy(ClO_4^-)$/PE showed a better curvature amplitude than $PPy^0(TsO)$/PE and also a higher movement speed. The highest curvature was with $PPy(DBS^-)$/PE and was about 0.14 cm^{-1} with a speed of 0.5 mm/s. The average life of $PPy(DBS^-)$/PE was 100 cycles with a loss of the maximum bending of 0.02 cm^{-1}, and 40 cycles of life for $PPy(ClO_4^-)$ with a bending loss of 0.002 cm^{-1}. During the test of these bilayers Pei and Inganäs observed that the oxidation is faster in $PPy(DBS^-)$ films where DBS^- is the large anion dodecylbenzenesulfonate. This is due to cationic flow; the faster process is the expulsion of cations [118]. From these results Pei and Inganäs suggested that the bilayer PPy(DBS)/PE could be interesting as artificial muscles.

After the test of Au/PPy bilayers these researchers observed that standard methods of photolithography and micromachining could be used to fabricate microactuators. The used methods to fabricate these microactuators involved sequential deposition and removal steps. In this case, the deposition of the polymer occurs via electro-polymerization on patterned electrodes (Au-coated Si wafers). The gold layer is

covered with a patterned photoresist layer that allows PPy to be deposited only on the exposed Au surfaces. After PPy deposition, the photoresist layer can be removed with ethanol leaving a patterned PPy layer. For the release of PPy microactuators they used two methods, differential adhesion or sacrificial layer. Differential adhesion is based on the poor adhesion between Au and Si. A Cr layer is patterned on a Si surface to obtain adhesive and non-adhesive areas. Over this layer an Au layer is deposited and PPy is electrodeposited. PPy is patterned so that the Cr layer works as an anchor holding to the surface. The major part of the bilayer (PPy/Au) is in contact with Si (poor adhesion). So, activating the bilayer causes it to pull itself free [121-123]. For a more detailed description of the microfabrication of CP micro-actuators, I refer to Smela [122].

Smela et al. studied bilayers made of a layer of PPy and a layer of gold and they demonstrated that these could be used as hinges to lift and position rigid components [121,123]. The bending of the hinges was electrically controlled and reversible allowing precise positioning. The bilayers were fabricated with a technique based on differential adhesion. They made thin gold strips on the surface of a silicon wafer; one end of each strip was attached to the wafer, the other was free to move. On the strips they grew a PPy(DBS-) film. To evaluate the motion the wafer was immersed in an aqueous solution of NaDBS, a gold wire was used as counter electrode and Ag/AgCl as a reference electrode. By applying a voltage between -1 and 0 V against Ag/AgCl, shrinkage or swelling of the PC was obtained. Stiff strips (they were made of benzocyclobutene) folded over while bilayers bent into spirals (up to 360°) during the oxidation of PPy. By combining a number of hinges and plates, self-opening and closing boxes were also constructed [123].

Smela et al. also demonstrated PPy/Au hinges to be able to lift plates of silicon and polysilicon [124]. These hinges showed high strength; they were capable to lift 40 000 times their own weight with a good reproducibility. The hinges rotate the plates between 0° and 180°. The evaluations showed that thickness of PPy influences the performance of the actuator, but the Au layer thickness did not affect the performance appreciably. In general, thinner films move faster. These results show that these bilayers could be useful to fabricate tools on the micrometer scale.

However, if it is desired to fabricate more complex microdevices, addressable and controllable microactuators (e.g., devices able to open and close boxes or to manipulate cells) the differential adhesion is not suited for this. These more complex microactuators were built by micromachining technology. For this intended use, a topography of two dissimilar materials is patterned (Ti on a thermally oxidized Si wafer). This layer is the sacrificial layer. Next, a thin Cr adhesion layer and the Au structural layer are evaporated, what is followed by deposition of other microparts like rigid plates of benzocyclobutene, which mechanically connect the bilayers. Then, PPy was electrodeposited and patterned. Finally, etching of the microactuator and underetching the sacrificial layer was conducted. After fabrication post processing is possible.

Jager et al. also had manufactured on-chip microelectrodes (100 µm x 150 µm Au counter electrode and 50 µm x 100 µm Ag/AgCl reference electrode) [125]. In order to study these microactuators video sequences were recorded or images were taken with a microscope combined with a camera. The operation potential was typically between -0.7 V and -0.3 V vs. Ag/AgCl. The microactuators are themselves free from the surface after a few activation cycles. The typical response time of the micro-actuators to bend using potential steps is 1 - 2 s. The speed and the position of the actuator can be controlled by the applied current.

Using these microactuators, several micro tools that operate in liquid medium were fabricated: microfingers, lifting plates, microarms, closable microvials and micro-valves. The microfingers (gold strip with a thin layer of PPy) curled into spirals and they can be used to touch or even grab small objects with suitable geometries. The researchers had fabricated arrays of microfingers. For example, an array of 250 µm length grabs a 30 µm glass fibre. These microfingers not only can be used to touch and grab objects, they may also be used to establish electric contact to the object [52,121].

By combining bilayers and rigid plates, they manufactured self-opening and closing boxes (six sides of 300 µm x 300 µm). Using this device Jager et al. developed a cell clinic [121,126]. This is a micomachined cavity that can be closed with a lid (100 µm x 100 µm wide and 20 µm deep). The lid is activated by two PPy hinges. These microvials were not only operated in NaDBS solution, but also in cell culture medium. The performance was as when they were operated in NaDBS. They placed on the bottom of the microvials two sensors for impedance measurements on pigment cells. The possibility of using impedance to characterise intracellular processes was demonstrated.

They also have fabricated and operated microrobots. These microrobots were manu-factured linking together microactuators (PPy/Au bilayers) with stiff components [53,121,127]. A microrobot is composed by an elbow, a wrist and a hand with 4 to 2 fingers (670 µm total length). This microarm picks up, lifts and moves small objects over the surface (see Fig. 12). Although these microactuators are limited to liquid environments they have been operated in a number of interesting salt solutions, including blood plasma, urine and cell medium.

Lu and Mattes fabricated bending actuators from emeraldine base dissolved in *N*-methyl-2-pyrrolidone (NMP) to study the electroactivity of the films [129]. The PANI films obtained had conductivities between 1 - 10 S/cm (acid doping). They coated the polymer film with one layer of gold to improve the conductivity along its length. These metallized films were doped in 1 M acidic aqueous solution for 24 h and then dried in vacuum for 24 h. The electroactivity of these films was studied in lithium perchlorate/ propylene carbonate from -0.4 to +0.8 V vs. Ag/Ag$^+$. The electroactivity of the films doped with soluble anions in the electrolyte was much better than for films doped with insoluble anions in the electrolyte, which is in accord with the results shown by Okabayashi [75]. This was due to the difficult expansion of the anions into the electrolyte. The actuation properties of PANI films coated with a layer of gold were evaluated connecting the film to the potentiostat through a gold clamp. The bending motion of the actuator was recorded using a video camera. The bending of the films was only observed for films doped with soluble anions. The best results were for PANI films doped with CF_3SO_3H. The highest angle was 99° in propylene carbonate during stimulation from -0.4 V to 0.8 V vs. Ag/Ag$^+$ at a scan rate of 5 mV/s.

Hutchison et al. reported devices based on PPy films (thickness: 4 - 40 µm) deposited over a poly(vinylidene fluoride) (PVDF) membrane covered with Pt and operated in $NaNO_3$ solution (Fig. 6C) [104]. These actuators worked with voltages between -0.8 and +0.4 V vs. Ag/AgCl. As counter electrode a stainless steel plate was used. The evaluation of the mechanical properties of this device showed that it generates a force of 0.025 N/mm (per width) and a relative stress with respect to total thickness of 0.18 MPa. However, it is too inflexible to be optimized as actuator due to the substrate. These researchers also studied the influence of a current collector in the actuators. They demonstrated that a Pt film deposited over the PPy film increases

the tensile stresses even 6 times. Although the Pt film decreases the flexibility of the device this is compensated by an increasing force due to a better redox performance.
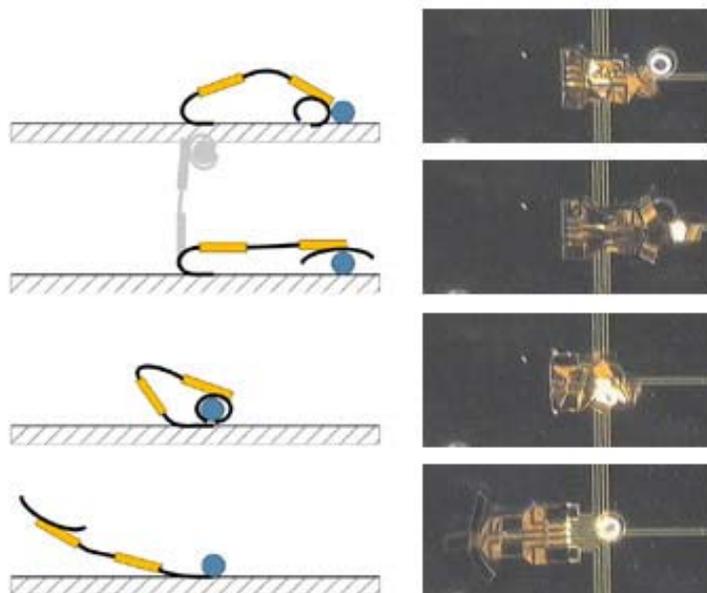
Fig. 12. Sequence of a microrobot based on PPy(DBS⁻) grabbing and lifting a 100 µm glass bead [128] (by courtesy of E. Jager, www.micromuscle.com)

The following step of the research of Hutchison et al. was the development of multi-composed actuator devices [104]. With this intention, PPy-coated fibre polyester electrodes were fabricated and combined in order to increase the polymer surface area (Fig. 13). The goal was to obtain an equivalent geometry and a configuration similar to laminated PPy films, which have a typical substrate thickness of 100 µm, a PPy coating thickness of 20 µm and a flat configuration. The conducting polymer area fraction of these laminated films is 0.3. The bundled fibre actuators were obtained by combining different numbers of PPy-coated fibre electrodes. A typical array was 50 fibers per bundle with 20 µm fibre thickness, a coating thickness of 20 µm and a bundle diameter of 0.25 mm. For this bundled actuator a conducting polymer area fraction of 0.64 was obtained. The bundled fibre actuator was used as working electrode, the counter electrode was a stainless steel electrode and as reference an Ag/AgCl electrode was used. The device was operated in 1 M NaNO$_3$ solution. The bundled fibre actuator showed generated stress and force much higher than the laminated actuator (6.8 MPa with respect to the PPy cross-sectional area and 0.1 N/mm per unit width). Besides, this design can be easily scaled. However, the bundled actuator showed the disadvantage that the fibres tended to congeal together after coating.

Otero and Sansiñena reported a triple layer actuator based on PPy(ClO$_4$⁻). This actuator is formed by an adherent polymer layer sandwiched between two PPy(ClO$_4$⁻) films. The synthesis of these PPy(ClO$_4$⁻) films was the same as for the bilayers PPy(ClO$_4$⁻)/adherent tape (see p. 15). During electrodeposition the two faces of the working electrode were covered by PPy(ClO$_4$⁻). Once the synthesis was finished the working electrode was washed and dried. A double-sided tape was used to peel off a film of PPy(ClO$_4$⁻) covering an electrode face. With the other side of the tape the other PPy(ClO$_4$⁻) film was peeled off. So, a triple layer PPy(ClO$_4$⁻)/adherent tape/

PPy(ClO$_4^-$) was formed. This actuator was 2 cm long and 1.5 cm wide; each PPy(ClO$_4^-$) film was 13 µm thick. The triple layer actuator only acts in a liquid electrolyte. To test the triple layer, one of the PPy(ClO$_4^-$) films was connected as a working electrode to the potentiostat and the other film of PPy(ClO$_4^-$) as a counter electrode. The connection of the reference electrode was short-circuited with the counter electrode. A drop of silver cement with a copper yarn were used to make the connections between the PPy(ClO$_4^-$) films and the potentiostat (Fig. 14).
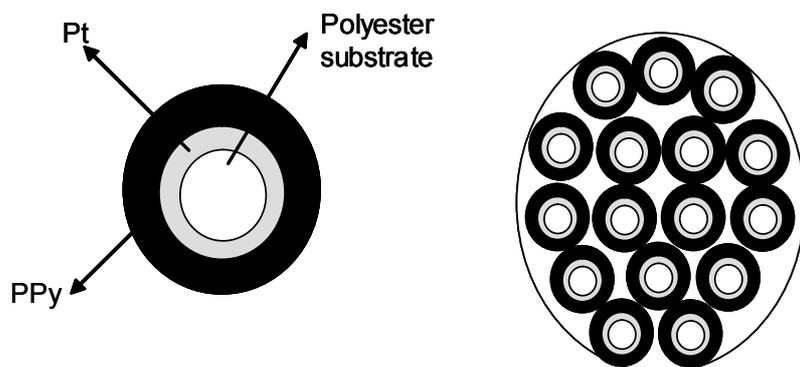
Fig. 13. Schematic drawing showing a bundled fibre actuator. The left drawing shows the composition of each fibre: the substrate coated with a Pt film and a PPy film grown over the Pt. Approximately 50 fibres are bundled to form the actuator which acts as a working electrode in an electrochemical cell with a liquid electrolyte of 1 M NaNO$_3$ [104]
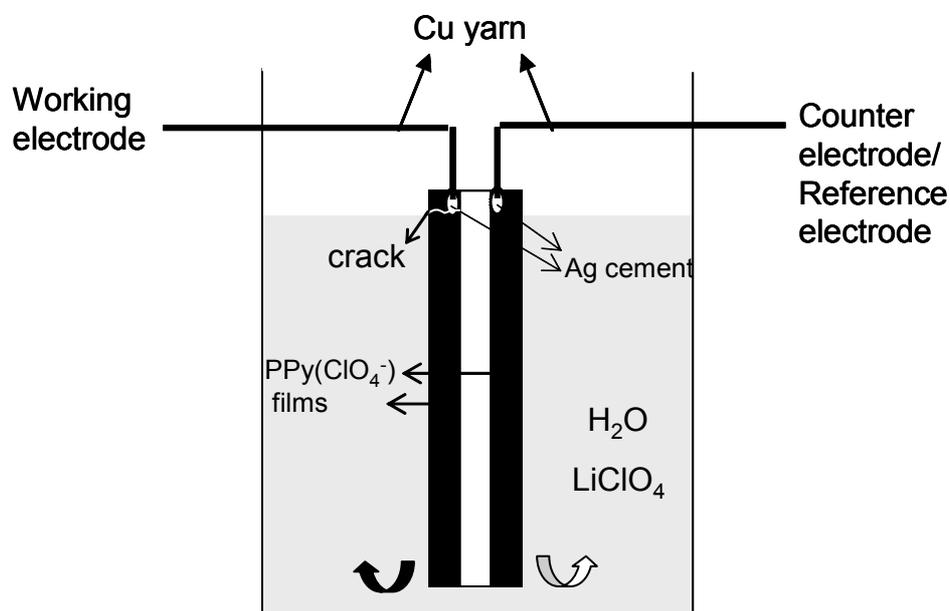
Fig. 14. Picture of a triple layer actuator PPy(ClO$_4^-$)/adherent tape/PPy(ClO$_4^-$).The electric connections were made with silver cement and Cu yarn so that one PPy film acts as working electrode and the other film as counter electrode. The reference electrode was short-circuited with the counter electrode. This actuator worked in an aqueous solution of LiClO$_4$. The triple layer bent when submitted to a redox cycle. The movement was towards the film that was reduced (cathode). In order to invert the movement direction the polarity was changed. Also the place is shown where the crack is formed that limits the lifetime of the triple layer

The performance of the triple layer was studied in aqueous solution of $LiClO_4$ under chronoamperometry and chronopotentiometry. This actuator showed a bending movement when submitted to a redox cycle; the achieved movements can be up to 360°. The bending is based on the expansion of the anode and the contraction of the cathode due to the insertion and de-insertion of ClO_4^- anions. The intermediate polymer should be flexible, adherent and an insulator to allow bending of the actuator without short-circuits.

Otero and Cortés showed that the direction and movement rate of this actuator are controlled by the applied current during the redox cycle. When the actuator was studied during different movements under constant currents and constant potentials the results demonstrated that the charge consumed is independent of the electric conditions and is proportional to the bending angle (Fig. 15) [130,131]. Thus, we have a perfect control of the final position of the material: once defined both, initial and final angle, through Fig. 15 the required electric charge can be defined; it corresponds to the variation of the volume under control of the electrochemical reaction. As a consequence it indicates that the time required to attain the new position is the lower the higher the experimental current: there exists a perfect control of the movement by the magnitude of the current and the sense of the current flow. The charge consumed is not only independent of electric conditions; it is also independent of the electrolyte concentration and the temperature, as can be seen in Tab. 1 [48,131]. These results show the charge consumed by the triple layer during a 90° movement at different temperatures and electrolyte concentrations under galvanostatic conditions (10 mA).

This actuator generates a force able to lift up to 180 times its own weight; this value is low compared to other actuators based on PPy. Some preliminary tests show that a better adhesion between PPy films and adherent tape improves the mechanical work generated by the actuator [130]. As well, this same loss of adhesion limits the lifetime of the actuator since it produces a crack in the PPy films formed at the zone between the air and the solution and close to the electric contact (Fig. 14). This crack breaks the electric contact between potentiostat and actuator, the full rupture of the electric contact is produced after around 112 cycles of 180°. The improvement of the adhesion between layers increases the lifetime of this actuator [130].

This triple layer actuator also shows sensory characteristics. The variation of the electric energy consumed by the triple layer under galvanostatic condition has a direct relation to the electrolyte concentration, the temperature and the pushed weight [51,131,132]. So, if the electric energy consumed is known it is possible to determine any of these parameters. Particularly, the tactile sensibility found in this material is very interesting [51]. Through several experiments we have demonstrated that when the actuator encounters an obstacle it pushes it away with the same speed regardless of its weight, but with an energy related to the object weight found. The triple layer 'feels' the resistance that its motion encounters. We proposed a model in which the contact of the triple layer with an obstacle promotes conformational changes in the PPy generating more compact conformations. An obstacle and the subsequent compaction of the PPy films generate a rise of electric energy consumed by the triple layer to cause stronger mechanical forces and to maintain the same speed of movement. These structural changes are stored in the polymer as a memory effect. This effect could only be erased by the flow of a contrary current which promotes the opposite electrochemical reaction returning the actuator to its initial position.
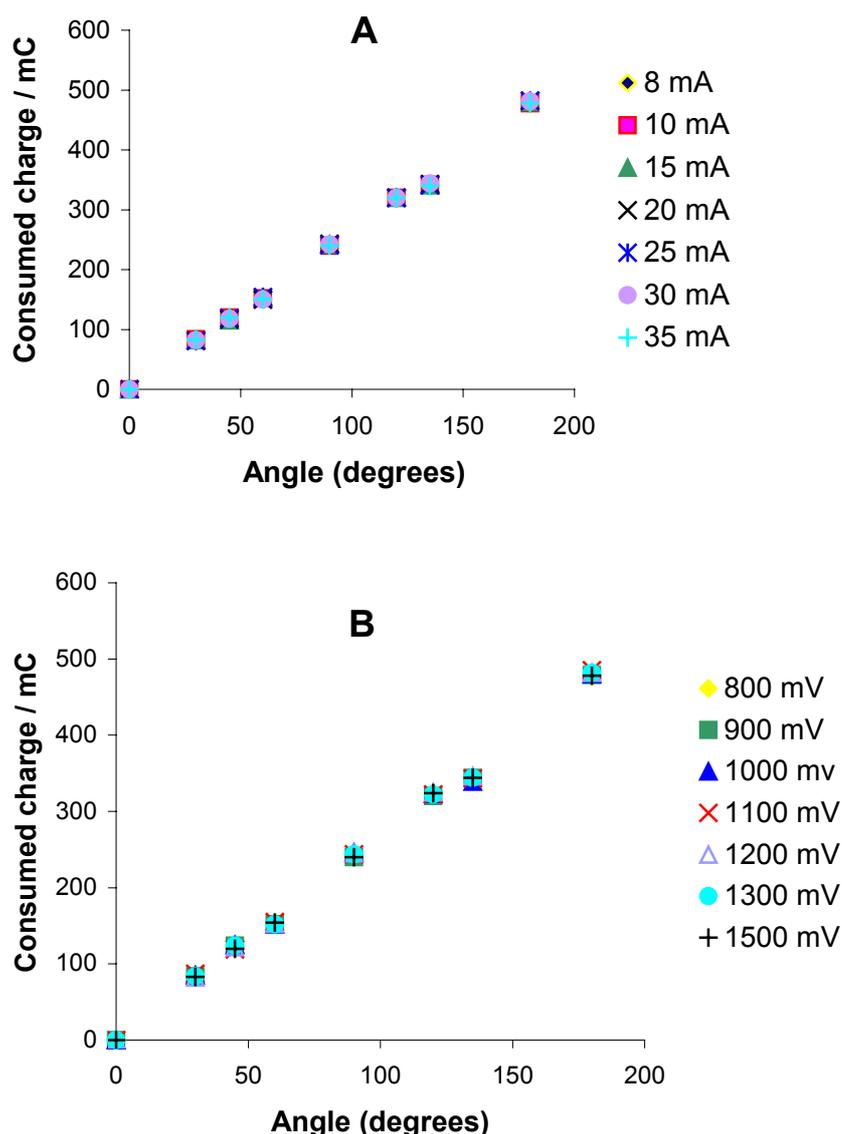
Fig. 15. Charge consumed by the triple layer actuator PPy(ClO$_4^-$)/adherent tape/ PPy(ClO$_4^-$) during movements of 30°, 45°, 60°, 90°, 120°, 135° and 180° and under different electrical conditions; A: with constant currents of 8, 10, 15, 20, 25, 30 and 35 mA; B: with constant potentials of 800, 900, 1000, 1100, 1200, 1300, 1400, 1500 and 1600 mV

Tab 1. Consumed charge by the triple layer actuator PPy(ClO$_4^-$)/adherent tape/ PPy(ClO$_4^-$) during a 90° movement at different electrolyte concentrations (at 25°C) and temperatures ([LiClO$_4$] = 1 mol/L). The test was carried out under a constant current of 10 mA

	[LiClO$_4$] / (mol·L^{-1})					Temperature in °C				
	0.05	0.1	0.25	0.5	1	5	15	25	35	50
Q / mC	252	252	250	254	252	241	242	243	245	243

Different devices, which carry out specific tasks, were fabricated with this triple layer, e.g., a device capable to develop macroscopic longitudinal movement [130]. This device shows longitudinal strains up to 60% of its own length. In order to fabricate this device, two triple layers were placed face to face so that the upper part and the end part of each triple layer were joined together. The electric contacts were made so that the PPy internal films worked as counter electrode and the outer films were the working electrode. The device was operated from a potentiostat so that the current through each triple layer was the same and the movement rate too. According to the disposition of each triple layer and the same speed, the device experiences a movement of opening and closing, as a valve, when submitted to an electric current.

Other devices which execute motions like a hinge also were fabricated from triple layers $PPy(ClO_4^-)$/adherent tape/$PPy(ClO_4^-)$. For example, an articulate device formed by two triple layers and three both rigid and inactive plastic plates placed according to the following disposition: plate-triple layer-plate-triple layer-plate. Each triple layer was connected to a different potentiostat, so that they could move independently. During the operation of this device in an aqueous solution of $LiClO_4$ a current was applied to each triple layer so that each one acted as a hinge moving towards the direction and desired rate. The movement of this device could be similar to the finger movement. With an optimized device of this kind it should be possible to carry out positioning jobs of an active head placed on one of the plates. Besides, assemblies of up to three of these devices have been fabricated increasing the versatility of the motion [130].

A device like a gripper formed by four triple layers $PPy(ClO_4^-)$/adherent tape/$PPy(ClO_4^-)$ was fabricated. A handle was placed in the end part of each triple layer. The four triple layers were assembled so that they worked jointly as a gripper; all triple layers were connected to the same potentiostat. To operate this device a current flow was applied to the triple layers so that each one bended in the same direction, which is related to the polarity. Due to the disposition of the triple layers their bending produced an opening and closing motion. With this mechanism it is possible to pick up, to lift, and to move a small object (for example, a dice). It was demonstrated that this actuator is suitable to fabricate devices intended for the manipulation of samples [130].

Kaneto et al. fabricated a triple layer solid actuator based on PANI whose actuation is based on structural changes resulting from a redox reaction by proton transfer between films (Fig. 3) [77]. The emeraldine salt (ES) film was obtained from 12% (w/v) emeraldine base powder dissolved in *N*-methyl-2-pyrrolidone and then casted on a glass substrate. This film was peeled off and stretched and then treated with 1 M HCl to obtain ES films.

The operation of these actuators is based on the expansion of the emeraldine salt film during its oxidation and its contraction upon reduction. So, a PANI film can be connected as the working electrode and another as the counter electrode. The actuator was fabricated from two ES films (8 mm x 25 mm x 50 μm, 8 mg) and a double-sided cellophane tape of 90 μm thickness: ES/cellophane tape/ES. The electric contacts were made placing two Pt foils between the ES films and the tape at the upper part of the triple layer (Fig. 16). They called this actuator a 'backbone-type' one. The actuator was operated in 1 M HCl solution.

In its straight state the potential difference between the PANI films is 0 V. When a potential is applied, the actuator bends in either direction depending on the polarity. The maximum bending of this actuator was 1% taken as $\Delta\ell/\Delta\ell_0$ ($\Delta\ell$: increment

elongation, $\Delta\ell_0$: original length), which was substantially lower than of other bending triple layer actuators. The lifetime observed was 200 cycles at 1.5 V of operation.
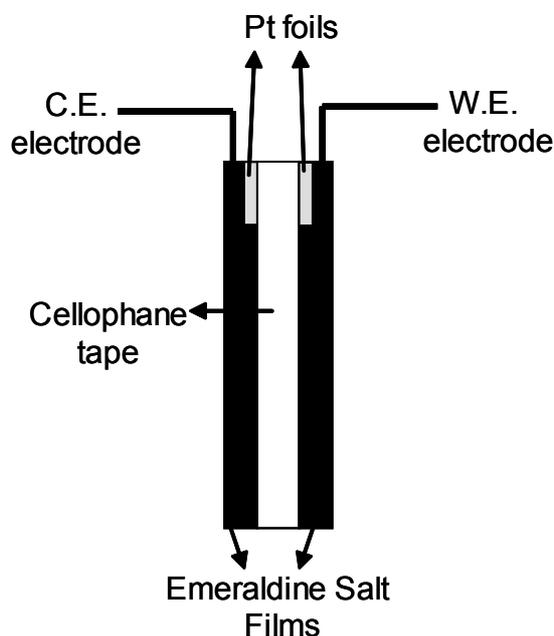
Fig. 16. A sketch showing the design of a backbone-type actuator of PANI

Anquetil et al. reported the synthesis of novel macromolecular actuators based on PT oligomers and calix[4]arene molecules [54]. Calix[4]arene is a highly versatile molecule, which shows a number of different conformations thus allowing shape-changing abilities. The authors had used bithiophene and quaterthiophene groups as rod chains integrated with the arenes that act as hinges. The CP films were grown from solution of calix[4]arene-bithiophene or quaterthiophene (QT) monomer, tetra-ethylammonium hexafluorophosphate (TEAP) and polyanions as the sulfated poly(β-hydroxyether) (S-PHE) in acetonitrile (AN). The incorporation of polyanions improves the mechanical properties of the conducting film. The authors varied the deposition concentrations to find optimal parameters towards mechanically strong films. In these materials the S-PHE electrolyte is acting as a matrix, thus, a soft polyanion is desirable to allow conformational rearrangement of the polymer.

The obtained films were between 120 and 150 µm thick. Once polymerized the films were peeled off the working electrode, rinsed and allowed to dry for 24 h. The characteristics of a poly(QT)/S-PHE film were: conductivity of 10^{-1} S·m^{-1}, tensile strength of 20 MPa (dry) and 1.3 MPa (soaked in AN). The evaluation of actuation properties was carried out over a strip of poly(QT) (2.25 mm long, 0.375 mm wide and 80 µm thick) using the bending method. Operation voltage was $\pm$5V vs. Ag/AgCl applied through a pair of stainless steel tweezers in an electrochemical cell containing 0.1 M TEAP and a counter electrode of stainless steel. The actuation was monitored with a digital video camera; the reversible strains observed were about 20% with a curvature radius of 55°. The authors theoretically estimated that a molecule of calix[4]arene-quaterthiophene would produce at the most 92 pN of average active force.

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Linear actuators

Mazzoldi et al. developed a linear actuator prototype based on PANI fibre. This actuator is formed by a PANI fibre doped with $HClO_4$ and embedded into a solid polymer electrolyte (SPE) matrix. As counter electrode serves a copper wire winding along the SPE external surface (Fig. 17) [107].
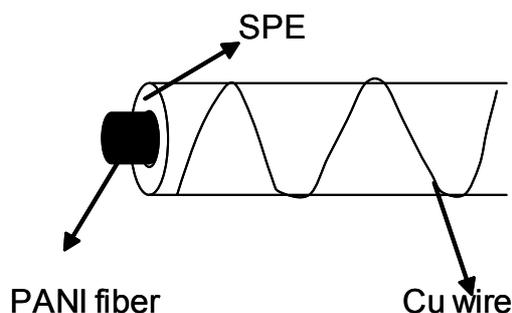
Fig. 17. Schematic diagram of a polyaniline (PANI)/solid polymeric electrolyte (SPE)/ Cu dry actuator

In order to produce the PANI fibres the authors used the method reported by Tzou and Gregory [133] based on extrusion through a spinnerette. Undoped powdered PANI was dissolved in *N,N'*-dimethylpropylene urea. Then the CP was extruded, immersed in a coagulation bath and drawn. The doping process was conducted by immersion of the fibre in 1 M $HClO_4$ for 24 h; then it was dried in an oven at 50°C for 1 h. The SPE was prepared using propylene carbonate, ethylene carbonate, poly-acrylonitrile and cupric perchlorate according to the procedure of Croce et al. [134] The result was a transparent and solid membrane with elastomeric properties over the PANI fibre.

In order to test the actuator, its lowest extremity was mechanically fixed with a clamp. The upper extremity of the actuator was fixed to the displacement transducer or the servo-controlled actuator. Measurements of sample length changes were performed using an isotonic transducer and Young´s modulus and stress were measured with the servocontroller. The current was applied from a potentiostat-galvanostat. The PANI fibre acts as working electrode through a platinum strip mechanically clamped to the fibre. In the case of a dry actuator the reference and counter electrodes were short-circuited. When an electrolytic solution was used, a SCE electrode was taken as the reference electrode. The actuator was tested under potentials from -0.5 V to +0.8 V and current densities of $\pm$0.1 mA.

The results demonstrated that this actuator shows a linear relation between the strain and the exchanged charge density during the electrochemical reaction similar to other actuators based on CP. The strain values were low but the developed stress by the actuator was very interesting, around 3 MPa during cyclic voltametry. The typical relaxation-contraction time with square wave potentials was 100 s. The researchers suggested that response times could be reduced decreasing the fibre thickness. The exchanged charge density by the actuator in dry medium decreased almost 50% with respect to the wet medium due to the lower ionic conductivity in SPE.

Madden et al. demonstrated the operation of PPy linear actuators in air [39]. These actuators are capable of generating stresses exceeding those of mammalian skeletal muscles. They obtained PPy films galvanostatically on a glassy carbon substrate from a mixture of 0.06 M distilled pyrrole monomer and 0.05 M tetraethylammonium hexafluorophosphate in propylene carbonate. Deposition took place at -30°C in a nitrogen atmosphere at a current density of 1.25 A·m^{-2}. The resulting film was 35 mm long x 6 mm wide x 40 - 100 µm thick, it showed a density of 1.4 · 10^3 kg·m^{-3}, a conductivity in the range of 1 - 3 · 10^4 S·m^{-1}, a glassy modulus of 0.5 GPa (wet) and 1.0 GPa (dry), and a tensile strength > 25 MPa. A sketch of the cross-section of the constructed actuator is shown in Fig. 18.
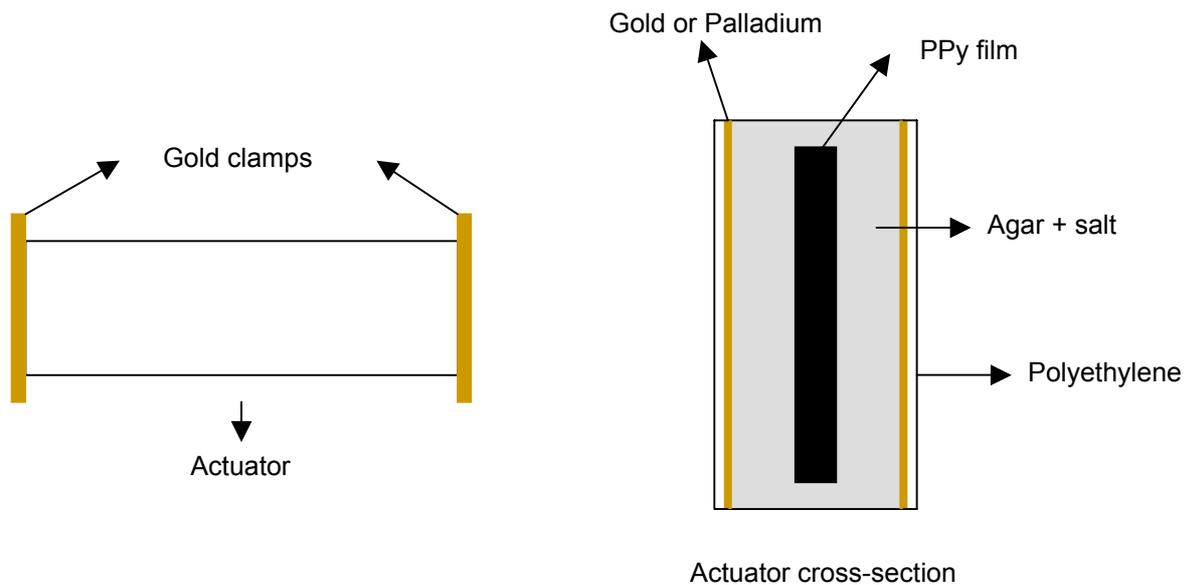
Fig.18. Sketch of the electric connections and cross-section of an encapsulated actuator

They evaluated as electrolytes both a PMMA-based gel and agar containing tetraethylammonium hexafluorophosphate salt. The best results were obtained with agar gel as electrolyte. The counter-electrode was formed by a PE film coated with a 400 nm thick gold or palladium layer. An approximately 100 µm thick layer of gel electrolyte was applied to each side of the PPy film. The counter electrode was wrapped around the gel-coated PPy with the metal contacting the gel. The electric contact of counter electrode and working electrode and the circuit were made with metallic strands and clamps.

In the test of this encapsulated actuator a force feedback was employed to maintain isotonic conditions and the resulting displacements were recorded. The total strain was just over 2% for an applied stress of 2 MPa related to the cross-sectional area in response to a ± 20 mA current. This corresponds to a volume change per charge of 2.2 · 10^{-28} m^3. The volume change was similar to identical PPy films activated in solution. That suggests that the gel´s stiffness doesn't offer significant mechanical impedance. The strain rate is higher than those reported for other actuators, around 0.03% Hz. The lifetime of the actuator is limited both by the drying of the agar gel and by bubble formation at the counter electrode. In response to the application of a ± 20 mA current, degradation is observed over five cycles. The authors suggest the opti-

mization of the encapsulation to avoid the stiffness of the actuator and increase the strain. They also consider both minimization of the salt-gel ratio to improve the force per cross-sectional area and the use of alternative gel/salt combinations that are not gas generating [39].

Lewis et al. fabricated an actuator that produces axial movement. The design consisted of a hydrogel electrolyte sandwiched between two PPy electrodes grown on a Pt-coated polyethylene layer. In order to produce axial movement each PPy film was doped with different counterions. One electrode was doped with large immobile PSS^- anions and the other with small mobile NO_3 anions. As electrolyte cross-linked polyacrylamide hydrogel containing 1 M $NaNO_3$ was used. When a potential difference was applied over the two films ($\pm$ 1.5 V), oxidising $PPy(PSS^-)$ and reducing $PPy(NO_3)$, both layers shrunk, de-inserting Na^+ and NO_3^-, respectively. When the polarity was altered the volume of both films was increased due to ion insertion. The result of this ion-movement was a longitudinal motion (Fig. 19) [135,136].

However, both the magnitudes of force and stress were quite low (0.002 N/mm per width and 0.18 MPa related to the thickness of PPy). These low values were attributed to clamping problems. Besides, the authors found that electrical resistance of the gel electrolyte also reduces actuator performance. The actuator could be optimized improving the electric contacts and reducing the thickness of the gel layer.
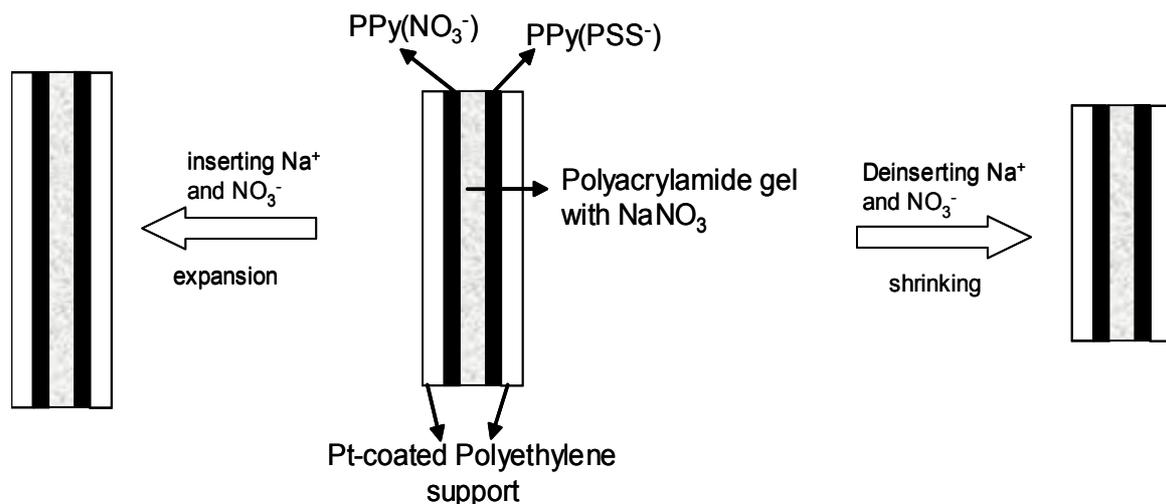
Fig. 19. Design and operation of a linear solid-state actuator: $PPy(NO_3^-)$ on Pt-coated PE layer/hydrogel/$PPy(PSS^-)$ on Pt-coated PE layer

Bending actuators

Kaneto et al. designed a shell-type actuator formed by two ES films (6 mm x 25 mm x 70 μm, 12 mg), a piece of one-sided cellophane tape (60 μm thickness) and a paper wetted with 1 M HCl aqueous solution between the ES films [77]. The piece of cellophane tape was used to cover the ES films. The electric contact was made with two Pt foils placed each one between an ES film and the intermediate paper (Fig. 20).

The shell-type actuator can be operated in air due to an intermediate paper wetted with 1 M HCl, which allows carrying out the electrochemical reaction and avoids electric contact between the PANI films. The actuator bent in a direction depending on polarity. This device can lift a mass of 1 g during a response time of several

seconds to reach the maximum bending. Similarly to the triple layers of PPy(ClO$_4^-$) reported by Otero and Cortés, this actuator maintained the position even after disconnection of the voltage, so, it is electrochemopositioning.
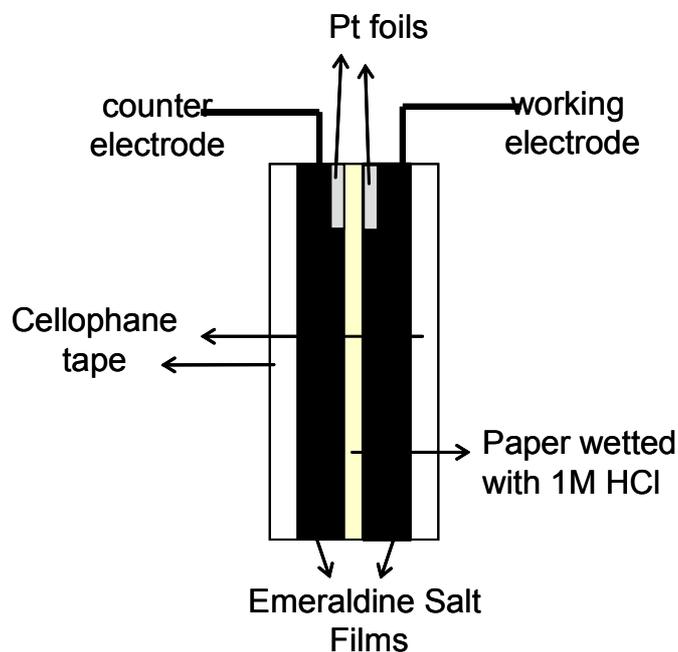
Fig. 20. Picture of a shell-type actuator based on PANI

Lu and Mattes fabricated a solid-state PANI bending actuator from PANI films covered with a gold layer. The PANI films were synthesized from emeraldine base dissolved in *N*-methyl-2-pyrrolidone and they were doped with CF$_3$SO$_3$H. The fabrication of the solid actuator was carried out from two identical metallised films. As electrolyte a polymer gel/LiClO$_4$ was sandwiched between the PANI films. The operation voltage of this actuator was typically 0.8 V and the bending was about 40° with a speed of 2.5°/s [129].

Sansiñena et al. fabricated a triple layer formed by PPy(ClO$_4^-$)/solid polymeric electrolyte (SPE)/ PPy(ClO$_4^-$) [49]. Epichlorohydrin-*co*-ethylene oxide [P(ECH-co-EO)] with LiClO$_4$ (thickness 3 μm) was used as SPE. This actuator works in air although it needs high environmental moisture for optimal operation. The PPy films were synthesized by the method reported by Otero et al. [5] The SPE layer was formed from a solution of [P(ECH-co-EO)]/LiClO$_4$ in tetrahydrofuran. The triple layer was constructed by dripping the electrolyte solution on two PPy films grown on two stainless steel electrodes followed by evaporation of the solvent. The evaporation of the solvent increases the viscosity and the adhesion of the films. The two electrodes covered by both the PPy film and SPE were put in contact. After 30 min the triple layer was peeled off the stainless steel electrodes. A PPy film was connected as working electrode and the other as counter electrode short-circuited with the reference electrode contact (Fig. 21). This actuator moved up to 360°; under a constant current of 20 mA the free end of the triple layer spent 5.4 s to cover 90°. As in the triple layer operating in liquid, in the solid triple layer the position is controlled by the electric charge consumed during the motion. The actuator consumed 36 mC per mg of PPy to cover 90°. The lifetime of this triple layer is limited by the

delamination of the PPy films. It is anticipated that improving the adherence between the PPy films and the SPE layer will increase the lifetime of the actuator.
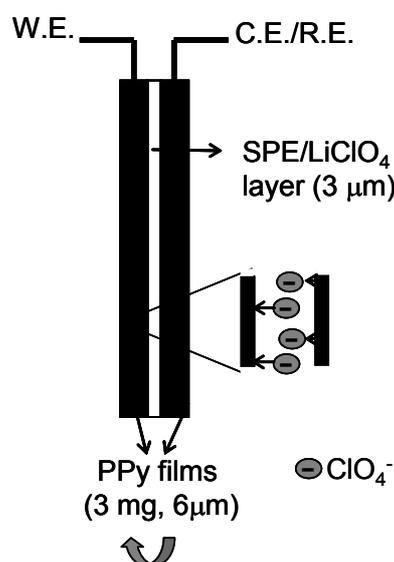
Fig. 21. Triple-layer actuator formed by PPy(ClO$_4^-$)/solid polymeric electrolyte (SPE)/ PPy(ClO$_4^-$). A PPy film acts as working electrode and another one as counter electrode short-circuited with the reference electrode contact. This actuator works in air

Summary of the evolution of artificial muscles based on conducting polymers

As mentioned before, Baughman was the first in proposing the application of CPs to the direct conversion of electrical energy into mechanical energy in 1991 [44]. The concept is the utilization of the dimensional changes, which occur upon electro-chemical doping of CPs. Such dimensional changes of CPs are much larger compared with piezoelectric polymers and used voltages are about an order of magnitude lower than required for electrostatic or piezoelectric actuators [44].

Thus, the first actuator or artificial muscle based on a conjugated polymer was a bilayer PPy(ClO$_4^-$)/adherent which was reported by Otero in 1992 [5]. The increase of volume that this polymer showed during an oxidation reaction was about 50%. The microscopical changes were transformed to macroscopical motion through a bilayer system. The motion of this bilayer actuator (2 cm long x 1 cm wide) was an angular crossing over up to 180° under currents from 5 mA to 30 mA in LiClO$_4$ aqueous solution. A 90° angular motion of this device is equivalent to a displacement of 1 cm, the movement rates are from 0.3 to 0.6 rad/s. [4,71]. In spite of the high strains on this device its major disadvantage was the need of both additional counter electrode and reference electrode. To overcome this limitation, the same year Otero proposed a triple layer system which incorporated the three electrodes into one device: PPy(ClO$_4^-$)/adherent polymer/PPy(ClO$_4^-$). In this trilayer one PPy film could act as working electrode and the other as counter electrode/reference electrode. The first test of this device was made in 1992 and was reported in a video tape [4,137]. Also in 1992, Pei and Inganäs evaluated different conjugated polymers and different dopant ions as actuator materials [120]. For PANI, PPy and P$_3$OT were reported volume changes of 0.3 - 4%. These polymers were tested in bilayer systems, which were made using microfabrication techniques. The bilayers consisted of a conducting polymer layer glued to a polyethylene layer covered with a Au film (0.5 mm wide, 1.5

to 4 mm long), where the Au film acts as current collector. The motion of these bilayers was evaluated by the bending beam method and PPy(DBS$^-$) showed the best performance. The bending response was observed within several seconds [138].

From work initiated in 1992 by Pei and Inganäs, they reported a fabrication method for creating individually addressable and controllable polypyrrole-gold microactuators for liquid media in 1995 [123]. The manufacture and performance of the micro-actuators were based on differential adhesion. With these microactuators, the researchers fabricated paddles to self-assembling and disassembling cubes where the bilayers work as hinges to connect rigid plates to each other and to a silicon substrate. These hinges of CP can achieve folding of 180° at each joint.

In 1995 Gandhi et al. confirmed the ion flow in CP by testing freestanding films of PPy doped with different anions (pTS, PVS) and in different electrolytes. The authors demonstrated that the amount of volume change is influenced by the scan rate, electrolyte and dopants. These linear actuators showed strains from 1 to 3 mm [62]. Also in this year, the leap from the liquid media to air was given: the first actuator based on CP that worked in air was achieved. Kaneto et al. reported two types of artificial muscles based on PANI, 'backbone type' and 'shell type' actuators [77]. The backbone type actuator was a triple layer: emeraldine salt/tape/emeraldine salt, operated in HCl. The shell type actuator was formed by two emeraldine salt films insulated by a paper soaked with HCl or a solid polymer electrolyte (SPE); this triple layer was covered with a cellophane tape on one side. It can be operated in the air.

Della Santa et al. also reported the performance of PPy(BS$^-$) freestanding films in 1997 [81]. During the testing of this type of actuators the researchers observed dopant exchange (between BS$^-$ and Na$^+$) and 0.5 - 1.2% isotonic strain with typical cycling times in the order of one minute.

In 1997 Sansiñena et al. reported the first PPy actuator that worked in air: a triple layer PPy(ClO$_4^-$)/polyepichlorohydrin-co-ethylene oxide containing LiClO$_4$/ PPy(ClO$_4^-$), which showed 180° bending [49]. The optimal performance of this actuator depended on a high environmental humidity and its lifetime was limited by delaminating of the PPy films. During this same year, Lewis et al. made actuators of PPy doped with pTS and NaClO$_4$, which worked in air. The electrolyte was poly-acrylonitrile with ethylene carbonate, propylene carbonate and NaClO$_4$. In both cases, a bending of 90° was achieved [135].

During 1999, Lewis et al. reported the first solid-state actuator that showed a longi-tudinal motion [136]. They attained this by combining two oppositely doped PPy layers with a polyacrylamide hydrogel. Depending on the type of doping, when a potential was applied both layers shrank or swelled simultaneously. So, the result is a longitudinal motion, rather than bending. Also in 1999, Madden et al. presented an encapsulated device using agar or PMMA gel containing Et$_4$NPF$_6$ around a PPy(PF$_6$) layer and encapsulated with a PE/Au film [39]. The strains were about 2% and the typical actuation time was 3 min. Onoda et al. reported the features of actuators fabricated from a cylindrical PPy pipe and with a novel design [117]. This material shows anomalous behaviour with regard to its conductivity and bending. Both vary according to the PPy surface (if the polymer was in contact with the electrolyte when it was polymerized or not). In this actuator, the electrical connections were made so that the two faces of the polymer alternately act as working and counter electrode. So, bending up to 90° was shown in a strip of this polymer.

Hutchison et al. reported the performance and the influence of a current collector on actuators with different designs in 2000 [104]. They tested unplatinised and platinised PPy linear actuators, bilayers of PPy/Pt-coated PVDF, axial solid state devices and bundled fibre actuators (bundled PPy on Pt-coated polyester fibres). The most interesting results showed that the bundled actuator provides maximum force and stress. This shows the higher efficiency of the bundled design compared to the others. The authors also studied the effect of the counterions on the actuation performance: they evaluated PPy/pTS and PPy/PVS films confirming that the volume change depends on the mobility of the ionic species present.

In this same year, Otero and Cortés reported the motion characterization of the triple layer (PPy(ClO_4^-)/adherent polymer/PPy(ClO_4^-)) in $LiClO_4$ aqueous solution [48]. In this actuator all electrodes are assembled (working, counter and reference electrode). So, it does not require additional electrodes. The testing showed that this actuator presents electrochemopositioning properties. This means that there is a perfect control of the motion by the magnitude and the sense of the current flow. The typical operation voltages are from 600 to 1500 mV and the movement rates about 0.5 rad/s.

During the year 2000, Jager et al. published several papers where they reported advances on the fabrication and utilization of the microactuators based on PPy-gold and which were initially developed by Pei and Inganäs [52,127]. Jager et al. utilized these microactuators to build more complex systems such as microrobots that manipulate micrometer-size objects in aqueous media. This microarm can pick up, lift, move, and place objects within an area of about 250 µm by 100 µm. In 2002, Jager presented the development of a cell clinic using microfabrication, which is a micromachined cavity that can be closed with a lid [126]. The lid is activated by two PPy/Au microactuators. They also showed the possibility of using impedance measurements to characterize intracellular processes through the microvial. A company that fabricates tools based on these microactuators was founded in 2000 [128]. They develop and commercialize products such as tubes, microgrippers, hinges and microrobots.

In 2002, Anquetil et al. reported the synthesis and fabrication of novel actuators based on thiophene oligomers integrated with calix[4]arene molecules [54]. In this type of actuator, the motion is the result of both the reversible π-π stacking of thiophene oligomers upon oxidation and of ion intercalation. The authors supported their actuation hypothesis by electrochemical data and demonstrated good strains in these actuators (55° bending).

The studies on the performance of the triple layer (PPy(ClO_4^-)/adherent polymer/ PPy(ClO_4^-)) continued and the influences of electrolyte concentration, temperature, lifted load and pushed load were reported in 2003 [51,132]. Otero et al. reported the sensing capability of the triple layer to determine electrolyte concentration, temperature of cell, lifted mass and pushed mass. The consumed energy changes proportionally to the variables mentioned. It is especially interesting to note that this device shows tactile sensing [51]. At the moment, some papers that present devices based on this triple layer are in review and writing. These devices develop more complex movements such as articulated fingers, opening and closing motions, like a hinge, like a gripper; these devices work in aqueous $LiClO_4$ solution.

Technological applications based on the actuation properties of conducting polymers

As we have seen during this review, CP actuators may lead to numerous technological applications because of:

- low operation voltages (around ± 1 V)

- large stress, higher than natural muscles

- large strain

- the possibility to fabricate actuators in different shapes (fibres, yarns, films, tubes, multilayers)

- Lu et al. achieved an important advance by increasing the lifetime of CP actuators using ionic liquids as electrolytes.

- good work density per cycle

- high degree of compliance

- electrochemopositioning.

However, breakthroughs are still needed to implement efficient and reliable devices. For example, some of the actuators with higher strain have a short life cycle due to adherence problems, in other actuators the response rates are much lower than for traditional actuators, and several actuators are still limited to work only in liquid media. Nevertheless, due to their attractive advantages a demand of this type of actuators in microrobotics, biomedics and bioengineering is expected.

The first commercialized actuators based on conjugated polymer are microactuators working in liquid media such as salt solutions, blood, urine, and cell culture media. These actuators are fabricated by Micromuscle Company [126]. They construct actuation devices from micrometers to millimeters size. The active part of these micromuscles is PPy doped with DBS^- and their design and operation are based on the work developed by Jager, Inganäs and Smela [47,52,53,73,74,116-125]. Devices have been developed such as tubes to be used to construct blood vessel sealers; microgrippers for handling objects from 30 µm until mm size; hinges for instance in a self-assembling cube or as joints in microrobots capable to manipulate single cells (Fig. 12). With these first commercial devices the real application of CPs as actuator materials has been demonstrated.

Remarks

Artificial muscles based on conducting polymers (CPs) are relatively new devices whose active material (CP) is generally synthesized as films by electrochemical polymerization. The actuation mechanism is based upon the motion of counterions (dopants) from and into the polymer in an electrolytic medium. This ion movement produces the volume change that is the basis of its performance. The amount of volume change is influenced by the scan rate, electrolyte and dopants. A great variety of conjugated conducting polymers have been studied as possible actuation materials. However, the CPs most utilized are polypyrrole (PPy), polyaniline (PANI), polythiophene (PT) and their derivatives. The electrochemical synthesis of these polymers had been widely studied in different solvents, with a variety of counter ions, with different materials as electrodes and with several electrochemical techniques. PPy is the polymer most tested due to the relatively low switching potentials, the facility of synthesis in various forms, its stability and considerable volume changes.

The performance of each actuator basically depends on electro-chemo-mechanical properties of the utilized CP and the design of the device. However, once understanding the role of the variables of synthesis, especially the counter ion, major advances have been presented in the structure, design and fabrication methods of the actuator devices.

The simpler devices are freestanding films, which produce linear motion being especially utilized to study the mechanism of ion motion. However, this was not the first design of an artificial muscle based on a CP. The first devices were bilayer structures formed by a CP layer and a flexible and insulating layer, which bend under an electric power. Sometimes a current collector was put between the two layers in order to improve the conductivity along the CP layer.

The bilayer was improved by a triple layer design (CP/insulating layer/CP), which integrates the three electrodes in a single system. To work in air, this triple layer should have an intermediate layer that allows ion motion without electric contact. Another design built to obtain actuators that work in air is the encapsulated device. In this type of design the triple layer is covered by a jacket containing the electrolyte. This device generally is limited by an increase of stiffness that decreases the performance capacity. Variations of the motion were obtained when the CP films as cathode and anode were doped with different counter ions. In this case, an axial motion of a triple layer device was obtained.

A more unusual design is a bundled fibre actuator, which showed higher, force and stress than actuators of other designs based on the same CP and which allows easy scaling. Also a cylindrical PPy pipe was prepared and evaluated as an artificial muscle. In this case, a PPy strip shows two surfaces with different conductivity depending on the surface in contact with the working electrode during polymerization. Thus, a polymer with an obvious anisotropy of its conductivity had been obtained.

Micromachining techniques have been introduced for the fabrication of PPy actuators. These methods open a new research field in microactuators focusing on biomedical applications. More complex actuators that seek to fulfil specific tasks have been built from bilayer and trilayer devices. However, such types of tools have been developed to work only in liquid media until now.

A new and very important property of CPs has been found in the last years. An actuator triple layer based on PPy and with sensing capacity was reported in 2003. This discovery opens interesting application possibilities for these materials, especially in the field of robotics.

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