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**Conjugated Polymers as Actuators for Medical Devices and
Microsystems**

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Chapter 8. Conjugated Polymers as Actuators for Medical Devices and Microsystems

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Introduction

In conducting polymers ion transport occurs during the (electro-)chemical oxidation and reduction of the polymer. This redox change results in a change of material properties such as conductivity [1], electrochromism [2], and wettability [3, 4]. The ion transport during this redox switching has also been used in drug release applications [5-7]. This reversible intercalation motion of the ions also results in a volume change of conducting polymers. These materials were proposed as actuator materials by Baughman *et al.* for their large strains and low operating potentials [8]. The first such conducting polymer-based actuator was demonstrated in the early 90's by Pei and Inganäs [9]. The phenomenon was thereafter demonstrated by other laboratories [10-14] and the new field of conjugated polymer actuators emerged¹. Initial research was focused on understanding the physical principles behind the electrochemically induced actuation

¹ Conjugated polymers are also commonly referred to as electroactive polymers (EAP) when used as actuators. EAPs are commonly classified as electric or ionic, with conducting polymers being a subgroup within the latter. Other groups of ionic actuators are Ion Polymer Metal Composites (IPMCs), carbon nanotubes, and gels, but these fall beyond the scope of this chapter.

and exploring the limitations.

Actuation in Conjugated Polymers

As said, the electrochemical switching of conjugated polymers may result in a volume change of the material due to the insertion and extraction of counter ions into the polymer matrix.

Depending on the dopant used in the polymer, two different redox reactions (and accompanying ion flows) are possible [11, 15-17]. In a general sense, the ion flow and redox reactions can be describes as follows. For a polymer P doped with small, mobile anions (a^-) in contact with an electrolyte containing both mobile cations and anions the reaction is:

That is, when reducing the polymer to its neutral state, anions a^- are expelled and when oxidizing the polymer, anions are inserted into the polymer matrix in order to compensate for the charge imbalance. On the other hand, for a polymer P doped with large, immobile anions A^- in contact with an electrolyte containing small mobile cations M^+ the reaction is:

That is, cations M^+ are inserted when the polymer is reduced and expelled when the polymer is oxidized. In the former case, the volume typically expands in the *oxidized* state, *i.e.* when a positive potential is applied, and in the latter case the volume of the polymer expands in the *reduced* state, *i.e.* when a negative potential is applied. In the former case however, there may be two moving species because not only reaction (11.1) occurs, but reaction (11.2) may also occur,

which can lead to a “twitching” behaviour [16]. Thus it is preferable to have only one moving species. Therefore polypyrrole (PPy) doped with large immobile anions, such as dodecylbenzene sulfonate (DBS), has frequently been employed since it provides a smooth motion (with only cations as the moving species), stability, and long life time. In addition to the ion motion, osmotic flow of solvents due to the altered ion concentration inside the polymer matrix [18] and conformational changes and coulombic repulsion of the polymer chains may also contribute to the volume change [19, 20].

Initially, the volume change was estimated to be only a few percent [17]. The numbers were deduced by measuring the bending angle of a tri-layer device consisting of a polyethylene film, an evaporated Au layer, and an electrosynthesized PPy layer and using Timoshenko’s bending beam theory to calculate the volume change. However, it was shown that the volume change is highly anisotropic. *In situ* volume change measurements using Atomic Force Microscopy, showed that the reversible volume change in the perpendicular direction could be up to 30-40% for 0.8-1.5 μm films of PPy(DBS) [21, 22]. These large volume changes were later confirmed for “thick” PPy (40-55 μm thick), showing expansions ranging from 4-19 μm [23]. While the volume change is not bistable, intermediate states can be reached with the amount of bending depending on the charge added to or removed from the polymer [24-26].

Conjugated polymers exhibiting this volume changing capacity can be used as an active material in actuators. This actuation can take a variety of forms (Fig. 11.1). The bulk expansion can be used as a piston-like actuator; the linear strain for linear actuators such as stripes and tubes; and the bending motion as a rolling sheet or hinge in bi- or multilayer devices. A variant of the

bending multilayer is a buckling configuration where at least two sides of the actuator sheet are clamped or attached.

Fig. 11.1 Different actuation modes used for conjugated polymer actuators, bulk expansion, linear strain, bending beam, and buckling sheet.

Materials and fabrication

The material properties are determined by the monomer(s) of which the conjugated polymer is constituted, the dopant ions trapped in the polymer, and synthesis conditions. Although most conjugated polymers are electrochemically active, only a few have been used as actuator materials (Fig. 11-2). Predominantly, PPy is used [9-11, 13] since it is easy to fabricate and actuate. However, polyaniline [14, 27, 28] and various polythiophenes [9, 29] have also been used in actuators. Bohn *et al.* have demonstrated that a substituted form of PPy, *i.e.* PEDOP, can actuate, although the performance was far less than that of ordinary PPy [30].

Fig. 11-2 The chemical structures of some common conjugated polymers used as actuator materials.

A film of conjugated polymers can be applied using several methods such as spin coating from a polymer solution, chemical polymerisation, and electrochemical polymerisation. For actuator applications, electrochemical polymerisation is most commonly utilized. Electrochemical polymerisation, a technique similar to electroplating, is a stable and well-reproducible synthetic method and one can rapidly synthesize materials with different properties by minor adjustment of the procedure. Typically, the polymer is synthesized from a solution containing the monomer and a salt (which becomes the dopant). Since the procedure relies on conduction/transfer of electrons, the conjugated polymer must be synthesized on a conducting surface, known as the working electrode (WE). This conducting surface can be a part of the actuator [9] or only be used during the synthesis. Otero *et al.* synthesize PPy on a stainless steel electrode, after which the PPy film is peeled off and laminated onto Scotch tape to form a bilayer or triple layer actuator [31]. The tube actuator as developed by the Wollongong group is synthesized on a solid Pt tube [32]. After PPy electrosynthesis, the Pt tube is removed and electrical contacts are added. To complete the electrochemical circuit of the synthetic “cell”, a counter or auxiliary electrode

(CE) and (most often) a reference electrode (RE) are used, all connected to a power supply, such as a potentiostat or galvanostat. In general, a constant current (galvanostatic method) or constant potential (potentiostatic method) is applied to synthesize the material, although more elaborate deposition methods have been reported, such as a sequence of potential steps [25]. Table 11-1 lists some commonly recipes used.

Table 11-1 Common PPy electrosynthesis procedures.

<i>WE</i>	<i>Electrolyte</i>	<i>Method</i>	<i>Time</i>	<i>Temperature</i>	<i>Ref.</i>
Pt	0.06 M pyrrole + 0.05 M TBA PF ₆ in propylene carbonate	Galvanostatic 0.15 mA/cm ²	6 h	-28 °C	[32]
Pt	0.2 M pyrrole + 0.1 M LiClO ₄ in acetonitrile + 2% water	Consecutive square waves of potential -500 mV (2 s) and 800 mV (10 s) vs Ag/AgCl		RT	[19]
Au	0.1 M pyrrole + 0.1 M NaDBS in water	Potentiostatic 0.5-0.6 V vs Ag/AgCl	10-30 min	RT	[33, 34]

TBA PF₆ : tetraethylammonium hexafluorophosphate

In some applications, it is either impractical or undesirable to synthesize the polymer on a conducting surface. In these cases, chemical synthesis can be employed. As an example, the actuator as developed by Vidal *et al.* could be mentioned [29]. PEDOT is chemically synthesised in a poly(ethylene oxide)-polycarbonate (PEO-PC) network, building a PEDOT gradient towards the centre, forming, in principle, a PEDOT-PEO-PC-PEDOT triple layer actuator. An additional fabrication option is solution casting, as has been used to fabricate PANi-based actuators [14, 28].

The choice of dopant species is of critical importance, determining both the actuation scheme (cf. eq 11.1 vs. eq 11.2) and amount of volume change. For instance, a study on the effect of the alkyl chain length in alkylbenzenesulfonate dopants showed that the medium sized octylbenzenesulfonate gave the largest strain [35]. By exchanging the dopant BF_4 for CF_3SO_3 the strain of PPy increased to 12% [36] and by switching to bis(trifluoromethanesulfonyl)imide as the dopant the strain increased further to 26% [37]. Apart from these more exotic ions, typical dopant ions used are DBS [9, 38, 39], PF_6 [32, 40], BF_4 [41], and ClO_4 [19].

The solvent used during synthesis is another factor which determines the performance of the material. Most commonly, water [9], acetonitrile [25], or propylene carbonate [40] have been used. Bay *et al.* added pentanol as a co-surfactant to water and were able to increase the strain from 2.5% to 5.6% [42]. Likewise, Hara and co-workers showed that using methyl benzoate as the solvent resulted in a strain of up to 12% [36].

One limiting factor is the decreased electrical conductivity in PPy and other conjugated polymers in the reduced state. This results in a so called IR drop in the material, *i.e.* the potential decreases in the polymer with distance from the conducting (metal) contact, resulting in only some of the material being redox active. For example, Della Santa *et al.* observed that only the first 30 mm closest to the electrical contact of a 90 mm PPy strip was active during cycling [43]. In order to overcome this issue, a conducting material can be added in close contact with the conducting polymer. In bending beam actuators, the polymer is often synthesized on a conducting layer that later forms a part of the actuator and functions as a current collector [9, 44, 45]. Hutchinson *et*

al. platinised a PPy strip and obtained greater force from the strip used as a linear actuator [46].

The tube actuator as developed by the Wollongong group has a helical metal wire embedded into the polymer to assure good electrical conductivity throughout the entire actuator [32]. In addition, the wire supplies mechanical support and endurance. Similar approaches have been taken by others including electropolymerizing PPy on a microfabricated meander-type electrode and on a spring [47].

Activation and control

Due to the nature of the actuating mechanism an ion source/sink is needed. In laboratory settings the actuator, a strip or bending beam is often submerged into a liquid electrolyte similar to that used during electrochemical synthesis, but without the monomer. However, in order to get a more functional device the actuator material, the electrolyte, and the counter electrode should be integrated into a single unit that can be operated under normal conditions. Several approaches have been taken. Bending beams are often sandwiched as multi layer devices comprising at least two electrodes on both sides of an electrolyte, and that may further include metallic layers for better electrical conduction and/or an encapsulation. The electrolyte may be a solid polymer electrolyte, a gel electrolyte, or a liquid electrolyte/ionic liquid soaked into a matrix such as paper or an ion exchange membrane [14, 29, 48-51]. Schemes involving an integrated electrolyte reservoir [32] or device encapsulation [40] have also been demonstrated. In biomedical applications, the surrounding fluids can be used as an electrolyte, making the devices less complicated since the electrolyte does not have to be integrated. Salt solutions, cell culture media, blood plasma and whole blood, urine, x-ray contrast media, all have been used as electrolytes [38].

In order to design an actuator unit many parameters have to be taken into account since they all influence the performance of the unit. A systems approach should be taken. The parameters include electrolyte (solvent type, composition, concentration, and pH) [23, 36, 52-54], electrodes (2 electrode vs 3 electrodes, position, and material) [23], signal (current, vs potential, shape, limits) [23, 26, 55-57], and temperature [36]. In addition, one must also take into account mechanical aspects such as number, thickness, and Young's modulus of the different layers of the active unit [24] and micropatterns to increase or direct the movement [58, 59]. Finally, adhesion between the different layers can be an issue, due to the large stresses that can occur between the various layers [26, 60, 61].

Macro Devices

Development of conjugated polymer actuators has been primarily on linear actuation and bending beams. Strips [13], tubes [32], or fibers [46] as well several bending beams such as those in Ref. [9] have been made and characterized, but few devices have been fabricated.

Madden *et al.* have investigated the possibilities of CP actuators to deflect camber foils, *i.e.* the tail sections of propeller blades [62]. Both bending beams, *i.e.* bending the flaps directly, and linear strain actuation were evaluated. It was possible to actuate the foils on a small prototype, but scaling to full size will lead to issues with stacking of many thick layers and long actuation periods.

A Braille display has been developed by Ding *et al.* using the linear helical tube actuators mentioned previously [32]. The tube actuators, embedded in a single unit comprising an ionic liquid electrolyte, CE, and mechanical biasing spring, were able to drive a small pin up and

down. Each pin formed a single “pixel” of the Braille display. A movement of around 0.2-0.6 mm was achieved, within the right order of magnitude for the intended application.

Microactuators

In designing devices trade offs must be made between conflicting requirements such as force output (amount of material, *i.e.* thick PPy) and speed (thin PPy, since ion transport into the polymer layer is rate limiting). Microfabrication is an appealing route to increase device performance while avoiding cumbersome material development. In addition, the large strains and bending angles demonstrated by conjugated polymers are unmatched by the conventional actuator materials used in microsystems or MEMS devices, for example piezoelectrics [63] and shape memory alloys [64]. Therefore conjugated polymers are well suited to be employed as electro-active components in microsystems.

Using slightly adapted microfabrication methods, Smela *et al.* demonstrated the first conjugated polymer microactuators based on simple bending bilayers of Au and PPy(DBS) [44]. The complexity of the device was rapidly increased by adding additional elements such as rigid plates [65], multiple actuators [45], and sensors [66] leading to increased functionality.

Microfabrication

As mentioned previously, most of the technologies used in fabricating devices are standard microfabrication methods such as photolithography. However, they have been adapted to fit conjugated polymers. Especially, two critical processes have been adapted: patterning of the conjugated polymer material and release of the actuator or device.

Patterning of conjugated polymers has been achieved using a wide range of techniques including lift-off [67], etching [68], and microcontact printing [69]. However, only a limited number of methods are generally used in the development of PPy microactuators. One method is synthesis in photoresist openings: PPy is electrochemically synthesised in a pattern of openings in a layer of photoresist applied on a conducting surface. Patterning can also be achieved by synthesis on patterned electrodes. Also, PPy can be subtractively patterned using Reactive Ion Etching in an oxygen plasma. Even mechanical patterning methods have been developed. PPy and entire PPy based devices have been cut (out) using laser ablation and punching [70].

Initial release of the actuator from the fabrication substrate is often an issue in microsystem development. When a release step is required, such as for bending beam actuators, several methods have been developed over the years. One of the most common methods of release utilizes a property called differential adhesion [65] (Fig. 11-3a). This method is based on the poor adhesion between Au and Si (or SiO_2). An adhesive frame of Cr or Ti is patterned that surrounds the actuator, except for an anchoring point. Onto this patterned layer, a Au layer is deposited. The Au functions as both the passive structural layer in the bilayer actuator and as a current collector. Hereafter, further processing is performed including application of the patterned active PPy layer. Finally, the Au layer is etched. After the Au etching, the actuator is no longer attached to the adhesive frame. It is only attached to the substrate at the anchor point. Elsewhere, it is held onto the substrate only by the poor adhesive forces between the Si surface and Au layer. When the PPy microactuator is set in motion, it pulls itself free from the surface.

A limitation of the differential adhesion method is that it is restricted to a few combinations of

materials, such as Au and Si. Therefore, other methods have been developed. Sacrificial layer and bulk etching are standard methods in microsystem fabrication to release devices, such as actuators, from a surface and these methods have been adapted for PPy actuators as well (Fig. 11-3b and Fig. 11-3c) [24, 45]. This provides the opportunity to release more complex structures, such as individually actuated hinges or objects manufactured on Si wafers [71, 72].

All of the previous methods are based on bottom up fabrication, *i.e.* layers are added successively onto the substrate thus building the actuator or device. However, certain applications (*e.g.* medical) require a fabrication method that gives access to both sides of the actuator during fabrication in order to minimize contamination with different processing solutions. This resulted in the development of a fourth fabrication path (Fig. 11-3d) [70]. In this method, a Au membrane, the passive structural layer and current collector of the PPy actuator, is first made by bulk etching the substrate. Next, this membrane can be accessed from both sides to apply, for example, both the PPy active layer and a polyurethane blood-compatible polymer on opposing sides. Finally, the device can be cut out of the frame.

Fig. 11-3 Schematic overview of different fabrication methods: A) Differential adhesion, B) sacrificial layer, C) bulk etching, and D) membrane fabrication. A1 Deposition and patterning of the adhesion layer (e.g. Cr) on the substrate (e.g. Si). A2 Deposition of Au layer. A3 Deposition and patterning of the PPy layer. A4 Patterning and etching of the final PPy microactuator structure. The PPy microactuator will be released by actuation due to the poor Au-Si adhesion. B1 Deposition and patterning of sacrificial layer (e.g. Ti) on the substrate. B2 Deposition of the adhesion and Au layers. B3 Deposition and patterning of the PPy layer. B4 Patterning and etching of the final PPy microactuator structure and etching of the sacrificial layer, resulting in a free hanging PPy microactuator. C1 Deposition of the adhesion and Au layers. C2 Deposition and patterning of the PPy layer. C3 Patterning and etching of the final PPy microactuator structure. C4 Bulk etching of the substrate in order to release the PPy microactuator. D1 Deposition of Au layer on substrate. D2 Bulk etching of the substrate, resulting in a Au membrane. D3 Deposition of PPy on bottom side and polyurethane layer on top side. D4 Cutting out the PPy actuator from the substrate frame.

Microsystem devices

Hinges

The basic actuator devices are PPy/Au bending bilayers [27, 44, 73]. These were then combined with other microfabricated elements such as rigid plates made of an inert, photopatternable polymer. The bending bilayers functioned as microhinges 30 μm by 30 μm in dimension [65].

The moving plates were used to create an active surface, the properties of which could be changed by flipping the 90 μm by 90 μm plates. In addition, multiple plates were connected together using multiple hinges. When the hinges were activated, the plates self-assembled into a cube of 300 μm by 300 μm by 300 μm . By reversing the applied potential the cubes could be unfolded. The bending bilayers can also be used to grab micro-scale objects [38].

Microrobot

A more complex device that uses the PPy actuators as hinges is a microrobot. The microrobot was designed as an arm, having two hinges as an “elbow joint”, two hinges as a “wrist”, and three hinges as fingers of a “hand”, all interconnected by rigid elements of SU8 [45]. The joints were individually controlled. Using this arm a 100 μm bead could be moved over a surface (Fig.

11-4). By actuating the two hinges of the elbow joint in counter phase, *i.e.* bending one and stretching the other, the arm could even rotate somewhat.

In order to fabricate this complex device, a sacrificial layer release method was developed (Fig. 11-3b). The robotic arm was $670\text{ }\mu\text{m}$ long and $250\text{ }\mu\text{m}$ wide. The robot elegantly illustrates the capabilities of the PPy actuator technology.

Fig. 11-4 A sequence of pictures (left) showing the grabbing and lifting of a $100\text{ }\mu\text{m}$ glass bead by a PPy actuated microrobotic arm. A schematic drawing of the sequence is shown to the right. The robot arm has an “elbow”, a “wrist” and 3 “fingers” placed 120° from each other. The pictures do not show the fact that the bead is actually lifted from the surface before it is placed at the base of the robot arm. We have illustrated this in grey in the second sketch to the right. Reproduced with permission from [45].

Using a similar design and fabrication, actuation in the same plane as the substrate was demonstrated [71]. Until that time, the bending bilayers only could move perpendicular to the substrate.

Cell clinic

A more application-based device is the so called cell clinic [66]. This device was designed to perform biological studies on single cells. It consisted of a microvial to contain a cell or cells, which could be opened with a lid actuated by PPy hinges, and an impedance sensor of two parallel Au microelectrodes on the bottom of the vial (Fig. 11-5). The PPy actuator hinges, lid, and electrodes were all monolithically fabricated on a common substrate. A thick, 20 μm layer of pattern SU8 formed the microvial on top of the patterned electrodes. This eliminated the need for complex fabrication and patterning techniques to form electrodes on the bottom of a microvial, which are generally made by etching cavities in a Si substrate [74, 75].

The lid was $150 \times 150 \mu\text{m}^2$, the hinges $100 \times 50 \mu\text{m}^2$, the microvial $100 \times 100 \mu\text{m}^2$, and the electrodes $10 \times 80 \mu\text{m}^2$. The lid could be opened and closed by activating the PPy hinges. *Xenopus laevis* melanophore cells were seeded in the vials (and on the device). These cells have pigment granules that aggregate and disperse upon (bio-)chemical stimulation. Impedance measurements by means of the microelectrodes on the bottom of the microvial were used to follow this intracellular event.

Fig. 11-5 Two cell-clinics in the (a) closed and (b) opened states. In the opened devices, two electrode pairs on the bottom of the transparent microvial are visible, as well as the PPy-microactuator hinges (black). (c) An illustration of the cell clinic. Reproduced with permission from [66].

The cell clinic has paved the way for further cell-based sensing [76]. The same scheme of fabricating the vials as a thick rim on top of a Si-based sensor system is employed. The device will also include an on-chip potentiostat [77] and on-chip CE and RE [78].

Microvalves

Microfluidics and drug delivery are another area where conjugated polymer microactuators may play a significant role. They have been demonstrated in a number of valve devices using different mechanical principles. Petterson *et al.* have constructed a microvalve based on a moving plate [79]. A PPy hinge rotated a rigid plate inside a PDMS microfluidic channel. By lifting the plate the flow was to be stopped. A similar type of valve has been developed by Madou and co-workers for their drug delivery capsule. The initial idea of using the bulk volume change of PPy to open and close a cavity proved unfeasible [80] and was replaced by a hinge and plate design similar to the cell clinic [81].

Another PPy valve was developed by HSG-IMIT and Micromuscle AB [82, 83]. This valve was developed to control the flow (on/off) of a drug delivery implant device called Intellidrug. The

implant was the size of two molar teeth and was intended to temporally control the release of a drug into the mucosal tissue in the mouth. Due to the application and the small size of the device, power consumption of the valve was an important design criterion. PPy actuators fulfilled the specifications best with regards to power consumption, size, and driving voltage [83]. The valve was designed as a buckling membrane valve over an orifice and was constructed as a normally closed valve for safety reasons. In the first devices the in- and outlets, PPy/Au membrane, CE, and RE were all integrated into a single Si chip. However, the membrane did not close perfectly in the off state. This was due to the irreversible volume change of PPy in the first cycle.

Therefore, in the second generation, a freestanding Au/PPy(DBS) bilayer membrane was made that was clamped between the fluidic circuitry comprising the orifice and the container that comprises the electrolyte and CE (Fig. 11-6a). The freestanding membrane was precycled and clamped after the irreversible volume change. A separate electrolyte (0.1 M NaDBS) was used in contact with the “back side” of the membrane, *i.e.* the PPy side, in order to separate the actuation from the liquid flow. Membrane deflection of $200 \pm 50 \mu\text{m}$ was achieved. Fig. 11-6b/c shows a flow profile of the valve. The on/off switching has a relatively large periodicity that fits the application.

An elegant use of the bulk volume change in a microvalve has been shown by Berdichevski and Lo [84]. They mounted a microfluidic channel made in PDMS on top of an electrode covered with a thick layer of PPy. Upon activation, the volume of the PPy expanded and pushed against the thin bottom of the PDMS channel. The bottom then bulged upwards, pinching off the flow.

Fig. 11-6 a) A sketch of the buckling PPy membrane valve used in the Intellidrug device. b) The flow profile of the valve. Reproduced with permission from [83].

Other bulk expansion devices

Yet another device using the bulk volume change of PPy was a proposal for a device for tactile sensing. PPy was synthesized on comb-shaped microelectrodes and covered with a polyethylene glycol solid polymer electrolyte containing LiClO_4 as a salt. A $30\text{ }\mu\text{m}$ PPy layer expanded $2\text{ }\mu\text{m}$ in 30 s, which, according to the authors, should be enough to be sensed [85].

Wang and co-workers also used the bulk volume change to create a controlled wettability surface [86]. PPy was polymerised surrounding micropillars made of thick SU8, thus forming a PPy mesh. By activating the PPy mesh, the area between the pillars raised. This changed the surface from hydrophobic (a droplet was laying on the SU8 micropillars, fakir situation) to hydrophilic (the droplet was wetting the entire surface).

Medical applications

Since the actuation mechanism requires the presence of an electrolyte, applications involving the liquid environments common to cell biology, biotechnology, and medicine seem evident. Indeed, some of these applications have been addressed above in the discussion on microactuators.

One medical application that has seen significant progress is a PPy-based rotatable balloon seal developed in collaboration between Micromuscle AB and Boston Scientific. In bifurcation stenting, two stents are positioned around the bifurcation, one stent in the main artery and one in the side branch using a two-guidewire system. The first stent has an opening through which the second stent is to be placed. It is therefore important that the first stent is positioned correctly, with the opening over the side branch. For this purpose, a rotating balloon system has been developed [87]. When inflating the dilation balloon, the pivot points at both ends of the balloon have to be sealed in order to mechanically lock the balloon in place so that it cannot rotate and in order to be able to build up a liquid pressure to unfold the balloon and deploy the stent. A PPy valve has been developed for this seal (Fig. 11-7) [23, 88]. Inside a dilation balloon (nr. 216 in Fig. 11-7) a metal ring is mounted on a balloon shaft (nrs. 212, 214) onto which a thick (40-70 μm) layer of PPy is electrosynthesized (nrs. 230, 232). The counter electrode (nr. 257) is mounted on the same shaft, inside the balloon. The PPy seal was tested in a dilation balloon test system using a standard physiological saline solution. Activation of the PPy resulted in expansion up to 30% of the PPy layer. This expansion was sufficient to close the gap between the shaft (nr. 230 or 232) and balloon pivot point (nr. 220 or 222), locking the balloon in place and preventing rotation. In addition, the PPy ring was able to seal the balloon from leaking and to withstand inflation pressures up to 24 atm, exceeding the clinically used pressures of 12-20

atm.

It was also shown that standard ethylene oxide sterilization, as used in the medical device industry, did not affect the performance of the PPy seal. After the initial proof of concept, the PPy seal was optimized with respect to maximum expansion and speed [23]. After careful consideration of the synthesis conditions, dopants, temperature, applied potential, and electrolyte concentration and composition, the maximum expansion was increased to 15 μm for a 50 μm thick PPy ring activated at -1.3 V in 0.3 M LiCl at a temperature of 37°C. The expansion speed increased as well: an expansion of 11 μm was achieved in the first few seconds.

Fig. 11-7 Sketch of the rotating balloon system, comprising a PPy seal (230, 232). Reproduced from [88].

Another medical device developed by Micromuscle AB is a microanastomosis connector [89]. The device consists of a rolled-up tube, made of a triple layered sheet of blood-compatible polyurethane, Au, and PPy and further includes a Au micropattern that predetermines the bending direction [59]. It is intended to reconnect two ends of a small, 1-3 mm diameter blood

vessel, divided either by trauma or by a surgical procedure, as an alternative to extensive suturing (Fig. 11-8). By using a small potential the tube diameter is reduced by contracting, *i.e.* rolling up the sheet more tightly. The tube is then inserted in both ends of the divided vessel and the potential is disconnected. The tube diameter expands by unrolling the sheet and holds the two vessel ends together while the vessel can heal. The materials and device have passed basic biocompatibility testing, including cytotoxicity, irritation, acute systemic toxicity, and hemolysis. A small implantation study of the connector in a rat model has also been performed. After three months, the devices showed not to be causing blood clotting or other obstruction, indicating blood- and biocompatibility. Coagulation studies using a Chandler looping setup were also performed on both heparinized (in order to increase blood compatibility) and untreated, as fabricated PPy connectors. These studies indicated that there was little difference in coagulation between both the heparinized and unheparinized PPy connectors and commercial stents.

Fig 11-8. Ex vivo surgery using a microanastomosis connector. The microanastomosis connector is an implantable tubular device that is intended for reconnecting millimeter-sized blood vessels. Reproduced with permission from [34].

Conjugated polymer actuation has often been proposed as a mechanism to bend guidewires and catheters in order to increase the ease with which such devices are guided through the vascular system. One common design strategy has been to add strips or bending bilayers on four opposing

sides of the tubular device. In this way bending in both x and y direction, *i.e.* a 360° circular motion of the tip, should be achieved. This strategy was for instance used by Lee *et al.* [90]. They modified a standard 0.5 mm OD catheter by applying one or two opposing pairs of PPy electrodes on the tip. Upon activation in a (non physiological) 1 M NaPF₆ solution, bending curvatures up to 0.06 m⁻¹ were achieved. An alternative design concept has been presented by Micromuscle AB [91]. PPy is applied on one side of the coil that makes up the tip of a guidewire (Fig. 11-9). Due to asymmetric application of PPy, a volume expansion results in a bending motion of the tip. A full 360° circular motion of the tip can be achieved by rotating the guidewire or catheter shaft, as is common clinical practice using standard fixed curvature guidewires. This design makes electronic control and device fabrication extremely easy. Only one pair of electrodes (one of which is the PPy actuator) must be controlled, thus only two electrical leads have to be integrated into the guidewire. Fig. 11-9 shows how such a device can be manoeuvred through a mock-up vascular system by electroactively changing the tip curvature. The surrounding fluid, in this case a salt solution, was used as the electrolyte.

Fig 11-9. A PPy-activated guidewire for manoeuvring in vessels. a, b Demonstrated in a bench top set-up and c, d schematic drawing of the principle. a, c PPy is in the contracted state and the guide wire is straight. b, d PPy is in the expanded state and the guide wire tip bends. a, b Reproduced with permission from [34], c, d reproduced from [91].

The same issue of changing the curvature during a surgical procedure exists for cochlear implants. It would be advantageous if the curvature of electrodes for cochlear implants could be actively altered during the insertion procedure. Therefore, a cochlear electrode array that can electroactively bend using PPy has been developed by the University of Wollongong [92]. The active element was a PPy/Pt/PVDF/Pt/PPy multilayer actuator, with the PVDF pores filled with a propylene carbonate-based electrolyte. The multilayer actuator was mounted on the back of a standard cochlear electrode array. Bending of almost 180° could be achieved.

Conclusion

Since the first demonstration of conjugated polymer actuators, or artificial muscles, in the early 90's, the technology has made a huge progress, both in understanding the properties and improving performance such as strains and stresses. Several sophisticated device demonstrators and prototypes have been demonstrated. The development of the conjugated polymer actuator technology still continues and will pave the way for novel (commercial) applications.

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