

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Artificial Muscle

Artificial muscle is an upcoming actuation technology that offers great benefits in applications ranging from robotics to aerospace. An attempt to replace heavy electric motors and hydraulic actuators with something more muscle-like saw led to the introduction of shape memory alloys (SMAs) into the field of artificial muscle research. Despite their advantages, including high output-weight ratio and high volume-weight ratio, over other conventional actuator technologies at the time, a number of disadvantages also exist. Historically, the problem with SMAs has been their unpredictable movements, slow response, and suitability only for small-scale applications. Electroactive ceramics is another candidate material considered for artificial muscle development. While the response times of electroactive ceramics are superior to that of SMAs, the ceramic material is fragile and can only achieve actuation strains of less than 1% deeming them unsuitable for artificial muscle development thereby generating a need for an alternative approach. The emergence of a new class of material, electroactive polymers has led to the most recent approach to artificial muscle (Halloran and Malley, 2004).

##### 2.1.1 Electroactive Polymers (EAP)

Generally, Electroactive Polymers (EAP) can be categorized into two major classes (Bar-Cohen, 2004):

###### *2.1.1.1 Ionic Electroactive Polymers*

###### a) Ionic Gel (IGL)

Hydrogels are hydrophilic polymer networks that have a large capacity for adsorbing water, and are characterized by the presence of crosslinkages, crystalline and amorphous regions, entanglements, and rearrangements of the hydrophobic and hydrophilic domains. Hydrogels can reversibly change their volume and shape in response to external stimuli, such as

changes in pH, solvent composition, ionic strength, temperature, and electric field (Kim *et al.*, 2004)

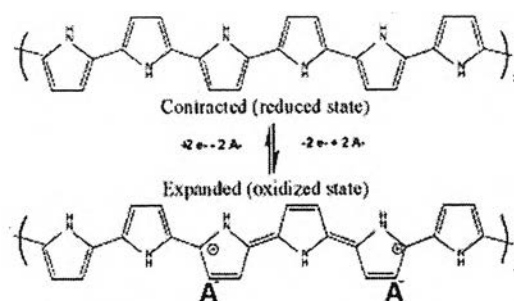
Application of voltage to ionic gels such as polyacrylic acid gel causes movement of hydrogen ions in or out of the gel, thus changing the environment from acid to alkaline causing the gel to become dense or swollen, accordingly (Moschou *et al.*, 2004).

#### b) Ionic Polymer Metal Composites (IPMC)

An IPMC consists of a polymeric electrolyte sandwiched between two layers of thin metal. An electric field induces a change in ion concentration, which attracts water molecules (or other solvents) to one side of the polymer. The nonuniform distribution of water produces swelling of one side of the actuator and contraction of the other, generating torque on the member and a bending motion (Madden *et al.*, 2004).

#### c) Conductive Polymers (CP)

Conducting polymers are electronically conducting organic materials featuring conjugated structures. Electrochemical changing oxidation state leads to the addition or removal of charge from the polymer backbone and a flux of ions to balance charge, as depicted in Figure 2.1.



**Figure 2.1** Conducting polymer actuators undergo dimensional changes in response to changes in oxidation state.

In the example shown polypyrrole expands as it is oxidized. Anions (A) enter to balance charge as electrons are removed. Expansion is generally correlated with net ion flux into the polymers (Pei *et al.*, 1992).

#### d) Carbon Nanotubes (CNT)

Carbon nanotubes (CNTs) are hollow cylinders consisting solely of carbon. Its surface area is important because actuation is associated with the charging of exposed nanotube surfaces. This is achieved by immersing nanotubes in an electrolyte and applying a potential between the nanotubes and a counter electrode. Ions are attracted to the nanotubes, leading to the accumulation of ionic charge at their surfaces, which is balanced by electronic charge within the tubes. (Madden *et al.*, 2004)

#### e) Electrorheological Fluids (ERF)

An electrorheological ER suspension is made from an insulating liquid medium embodying either a semi-conductive particulate material or a semi-conductive liquid material. The rheological properties (viscosity, yield stress, shear modulus, etc.) of an ER suspension could reversibly change by several orders of magnitude under an external electric field with the strength of several kilovolts per millimeter (Hao, 2002).

### 2.1.1.2 Electronic Electroactive Polymers

#### a) Ferroelectric Polymers

Ferroelectric materials are the electrostatic analogs of ferromagnets. The application of an electric field aligns polarized domains within the material. When the applied field is removed, a permanent polarization remains. Poly(vinylidene fluoride), also known as PVDF or PVF<sub>2</sub>, and its copolymers are the most widely exploited ferroelectric polymers (Bar-Cohen, 2004).

#### b) Electrostrictive Graft Elastomers (Relaxor Ferroelectric Polymer Actuators)

Electrostrictive graft elastomers are polymers that consist of two components, a flexible macromolecule backbone and a grafted polymer that can be produced in a crystalline form. The ferroelectric polymer most commonly used for actuation is poly(vinylidene fluoride-trifluoroethylene), abbreviated as PVDF-TrFE. (Madden *et al.*, 2004).

#### c) Electrostrictive Paper

Generally, the paper is composed of a multitude of discrete particles, which are mainly of a fibrous nature forming a network structure. An

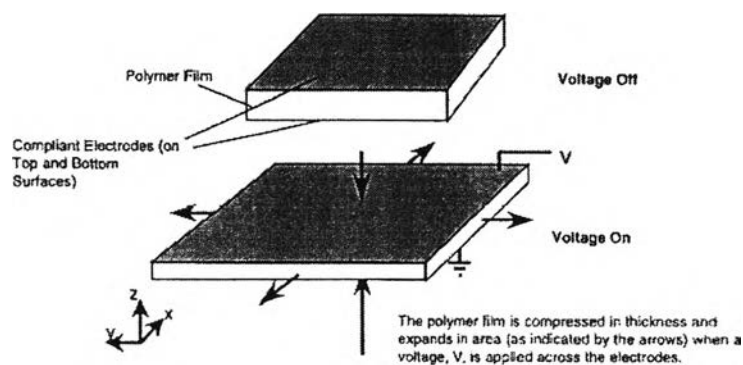
example of which is silver laminated paper whereby two silver laminated pieces of paper with silver electrodes are placed on the outside surfaces. Upon electric voltage being applied to the electrodes a bending displacement occurs (Bar-Cohen, 2004).

#### e) Liquid Crystal Elastomers (LCE)

LCEs are composite materials consisting of monodomain nematic liquid crystal elastomers and conductive polymers distributed within their network. Actuation is the result of changes in order and alignment of crystalline side chains, which generates stresses in the polymer backbone. Liquid crystalline elastomers (LCEs), have been shown to change dimensions under low stresses through phase transitions and retain network memory. Therefore, an ordered LCE with its anisotropic properties can provide an excellent framework to mimic muscular action. (Thomsen et al., 2001)

#### f) Dielectric EAPs

Dielectric elastomer actuators consist of a polymer film (elastomer) sandwiched between two compliant electrodes. A voltage difference is applied between the compliant electrodes, causing compression in thickness and stretching in area of the polymer film. Elastomers are sufficiently compliant that large strains are induced and there is efficient coupling between the electrical energy input and mechanical energy output. Pelrine et al. 2000 found that the performance of these materials was similar in many respects to the performance of natural muscle. For this reason, dielectric elastomer actuators can be regarded as a type of *artificial muscle*.



**Figure 2.2** Principle of operation of dielectric elastomers (Pelrine *et al.*, 2000).

The derivation of the electrostatic model of actuation was described by Pelrine et al., 1998. The effective actuation pressure,  $p$ , is given by

$$p = \epsilon \epsilon_0 E^2 = \epsilon \epsilon_0 (V/z)^2, \quad (1)$$

where  $E$  is the electric field strength,  $\epsilon$  is the dielectric constant,  $\epsilon_0$  is the permittivity of free space ( $\epsilon_0 = 8.85 \times 10^{-12}$  F/m),  $V$  is the voltage, and  $z$  is the polymer thickness.

Pelrine *et al.*, in 2000 briefly described three such actuators that illustrate the range of possible designs.

### 1. Unimorph and bimorph actuators

A unimorph actuator consists of an active electrode, polymer film and a ground electrode, forming a bilayer. Changing the polarity of the active electrode produces bending in the opposite direction. A bimorph actuator is fabricated by stacking an active electrode, a polymer film, a ground electrode, a polymer film and a second active electrode constituting a trilayer. Unimorph and bimorph actuators have application potential in low force robotic grippers.

### 2. Rolled actuators

Rolled actuators are an easy way to squeeze a large single layer of film into a compact shape.

### 3. Diaphragm actuators

Diaphragm dielectric elastomer actuators worked very well, because a diaphragm can easily exploit both directions of planar expansion of the film. Diaphragm motion with dielectric elastomers can easily be 10% or more of the diaphragm diameter.

An electromechanical actuation mechanism is a physical process whereby a mechanical system is activated by electricity. Two mechanisms, electrostriction and Maxwell's stress effect can be used to describe the electric actuation. Electrostriction is the direct coupling between electric polarization and mechanical strain response, while Maxwell stress is the attractive force between the opposite charges on the electrodes (Ma and Cross, 2004).

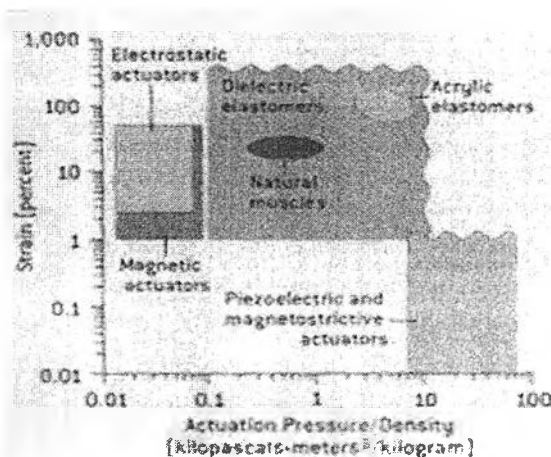
$$S_{\text{electrostriction}} = -Q\epsilon_0^2(\epsilon_r - 1)^2 E^2 \quad (2)$$

where  $S_{electrostriction}$  is the strain in the thickness direction of the film due to electrostriction,  $Q$  is the electrostrictive coefficient,  $\epsilon_0$  is the electrical permittivity of free space,  $\epsilon_r$  is the relative permittivity, and  $E$  is the applied electric field.

The Maxwell Stress Effect is a consequence of a change in electric field distribution inside the dielectric with strain.

$$S_{Maxwell} = -s\epsilon_0\epsilon_r E^2/2 \quad (3)$$

$S_{Maxwell}$  is the strain in the thickness direction of the film,  $s$  is the elastic compliance,  $\epsilon_0$  is the electrical permittivity of free space,  $\epsilon_r$  is the relative permittivity, and  $E$  is the electric field.



**Figure 2.3** Strain versus actuation pressure/density for various high-speed technologies (Ashley, 2003).

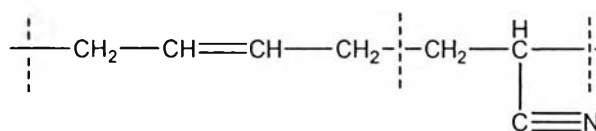
Figure 2.3 shows that Dielectric elastomers can generate more strain and force than other technologies (Ashley, 2003).

## 2.2 Acrylonitrile Butadiene Rubber, Nitrile Rubber (NBR)

The first polymerization of acrylonitrile and butadiene was carried out in 1930 by *E. Konral* and *E. Tschumkur* (Hofmann, 1989). It was produced with

different relative concentrations of the comonomers and its insulating material in the crude or in the vulcanized form (*Vallim et al.*, 2000).

The great number of NBR grades is produced, their acrylonitrile content ranging from 18 to 51 % by weight. The structural formula of NBR is as follows (*Hofmann*, 1989):



**Figure 2.4** The structural formula of NBR.

Acrylonitrile content; the glass transition temperatures of polyacrylonitrile at +90°C and of polybutadiene at -90 °C differ considerably, and therefore with an increasing amount of acrylonitrile in the polymer, the  $T_g$  temperature of NBR rises, together with its brittleness temperature. The elastic behaviour of NBR vulcanizates also becomes poorer as the concentration of bound acrylonitrile in NBR increases, but the same time the copolymer becomes more thermoplastic, which is advantageous regarding the processibility of compounds. The polarities of acrylonitrile and butadiene are very different, and the polarity of the copolymer becomes greater with increasing amount of acrylonitrile. The concentration of the acrylonitrile in the copolymer has therefore a considerable influence on the swell resistance of the vulcanizates in the non-polar solvents. The greater the acrylonitrile content, the less the swell in motor fuels, oils, fats, etc. However, the elasticity and the low temperature flexibility also become poorer. For the same reasons, the compatibility with the polar plasticizers (e.g. those based on esters or ethers) and polar plastics (e.g. PVC or phenolics) improves with increasing acrylonitrile concentrations in the NBR. The solubility of the polymers in non-polar solvents, and gas permeability of the vulcanizates become lower as the acrylonitrile concentration in the NBR becomes greater.

#### 2.2.1 Acrylic Acid Terpolymer (X-NBR)

NBR grades; which are terpolymers of butadiene, acrylonitrile, and a diene monomer with carboxylic acid groups (e.g. one based on acrylic acid), are

particularly reactive because of the potential crosslinking site of the carboxylic acid site group (Hofmann, 1989).

Compounds of this rubber are largely used in the car industry for making fluid hoses due to its resistance to chemical attack, particularly from lubricants. Nitric rubber is also acid and alkali-resistant and in the vulcanized form, shows a low swelling degree with organic solvents (*Vallim et al.*, 2000). Typical uses are in static seals, O-rings and packagings for crank shafts and valves, in membranes, bellows for coupling, in hose, including high pressure hose, for hydraulic and pneumatic applications, in roll coverings, conveyor belts, friction coverings, linings, containers, work boots, shoe soling and heels, printing blankets, and stereo type plates. Because of the growing requirements by the automotive industry for high temperature and oil resistance, NBRs have been increasingly replaced in this market by more heat resistant rubbers. NBRs are also used in considerable quantities in products for the food industry (Hofmann, 1989).

### 2.3 Conductive Polymers

Conductive Polymers are a new class of polymers; they are organic materials that generally are comprised of C, H and simple hetero-atoms such as N and S and consist of unique  $\pi$ -conjugation electrons. These materials differ from typical organic polymer due to their unique  $\pi$ -conjugation electrons properties which impart higher electrical conductivity at room temperature on oxidation or reduction than ordinary polymers that are usually insulating materials relative to metals such as copper (Chandrasekhar, 1999; Deependra *et al.*, 2004).

The conductivity may occur through the movement of either electrons or ions. In general, electrical conductivity,  $\sigma$ , [ $\text{S}\cdot\text{cm}^{-1}$ ] is a function of the number of charge carriers,  $n$ , [ $\text{cm}^{-3}$ ], the charge carried by the carrier,  $q$ , [ $\text{A}\cdot\text{s}$ ], and the mobility of the charge carriers,  $\mu$ , [ $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ] as followed (Blythe and Bloor, 2005)

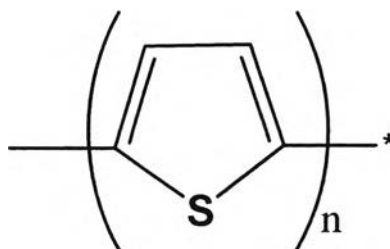
$$\sigma = |q| \cdot n \cdot \mu \quad [\text{S}\cdot\text{cm}^{-1}] \quad (4)$$



The naturally  $\pi$ -conjugated electrons systems on conductive polymer backbone are not sufficient to render them highly conductivity; trans-polyacetylene possesses only  $10^{-6}$  S.cm<sup>-1</sup>. The high electrical conductivity is achieved by the process called the “doping process”. This process was firstly discovered by Shirakawa and Ikeda (Kumar and Sharma, 1998) by doping of polyacetylene (PA) with iodine, and conductivity increases by 9-13 orders of magnitude. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent (dopant) in the gas or solution phase, or by electrochemical oxidation or reduction. Doping agents are either strong reducing agents or strong oxidizing agents. They may be natural molecules and compound or inorganic salts which can easily form ions, organic dopants and polymeric dopants (Kumar and Sharma, 1998).

## 2.4 Polythiophene

Polythiophene (PTs) is a one of the electronic conductive polymers, a heteroaromatic conductive polymer comprising of S atoms and the  $\pi$ -conjugated electron system as shown in the schematic structure of Figure. 2.5. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as electrical conductors, nonlinear optical devices, polymer LEDs, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and transistors ( McCullough *at al.*, 1998).



**Figure 2.5** Schematic structure of polythiophene.

#### 2.4.1 Synthesis of Poly(thiophenes)

Polythiophenes are essentially prepared by means of two main routes, i.e. the chemical and the electrochemical syntheses (Roncali, 1992).

##### 2.4.1.1 *Electrochemical Synthesis*

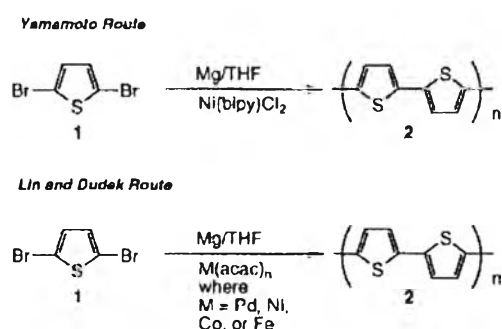
The electrochemical formation of conducting polymers is a unique process. Although it presents some similarities with the electrodeposition of metals since it proceeds via the nucleation and the phase-growth mechanism, the major difference lies in the fact that the charged species precursors of the deposited material must be initially produced by oxidation of the neutral monomer at the anode surface. The first electrochemical step (E) consists in the oxidation of the monomer to its radical cation. Since the electron transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce a dihydro dimer dication which leads to a dimer after loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step (C). Due to the applied potential, the dimer, which is more easily oxidized than the monomer, occurs in its radical form and undergoes a further coupling with a monomeric radical.

##### 2.4.1.2 *Chemical Synthesis*

One of the first chemical preparations of unsubstituted polythiophene (PT) was reported in 1980 by two groups. Both synthesized polythiophene by a metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene (Figure 2.6). Yamamoto's synthesis treats 2,5-dibromothiophene. The Mg reacts with either bromide to form either 2-bromo-5-

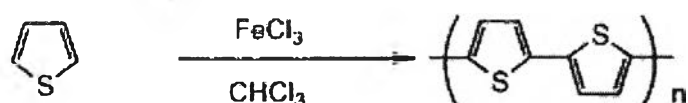
magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene, which is self-coupled with the NiII catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other.

This condensation reaction is propagated and eventually low molecular weight PT is formed (McCullough *et al.*, 1998).



**Figure 2.6** The first chemical syntheses of polythiophene.

Other methods have been reported. Sugimoto described the synthesis of PT by treating thiophene with  $\text{FeCl}_3$  (Figure 2.7) (McCullough *et al.*, 1998).



**Figure 2.7** Specific examples of the synthesis of polythiophene.

To improve the properties of polythiophene their derivatives were produced in many functional groups.

## 2.4.2 Poly( 3-substituted thiophenes)

### 2.4.2.1 Linear Alkyl Chains

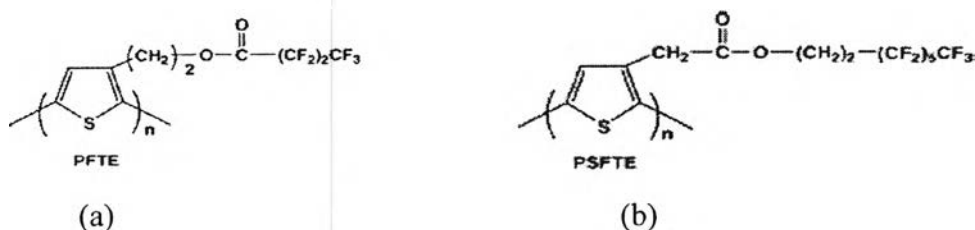
Poly(3-alkylthiophenes) (PATs) have attracted increasing interest, owing to the significant improvement of solubility and fusibility resulting from the grafting of flexible hydrocarbon chains on the conjugated PT backbone. The conductivity was found to decrease with the length of the alkyl chain but remained at a high level (Roncali, 1992). Poly(3-alkylthiophene)s with alkyl groups longer than butyl can readily be melt- or solution-processed into films, which, after oxidation, can exhibit reasonably high electrical conductivities of 1-5 S/cm (McCullough *et al.*, 1998).

### 2.4.2.2 Branched Alkyl Chains

In contrast to linear chains, branched alkyl groups drastically affect the effective conjugation of the PT backbone and in some cases the polymerizability of the monomer. Thus attempts to electropolymerize 3-isopropylthiophene were unsuccessful while 3-isobutyl- thiophene leads to a polymer considerably less conjugated and less conductive than its linear analog (Roncali, 1992).

### 2.4.2.3 Fluoroalkyl Chains

Fluoropolymers are generally known for their high thermal stability, chemical inertness, low coefficient of friction, and hydrophobicity. Fluorinated PTs had been prepared using the FeCl<sub>3</sub> method by Ganapathy *et al.*, 2006 figure 2.8.



**Figure 2.8** Structure of (a) poly(2-(3-Thienyl ethylperfluorobutyrate)) (PFTE), (b) Poly(2-(3-Thienyl) acetyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanate) (PSFTE).

#### 2.4.2.4 Aryl Groups

The direct grafting of a phenyl group on the thiophene ring is expected to induce an important steric hindrance to the coplanarity of the PT backbone, but the conjugation of the two cycles does not allow a clear distinction between the steric and electronic effects of the phenyl ring (Roncali, 1992).

#### 2.4.2.5 Ethers and Polyether Chains

Conjugated polymers substituted by polyether complexing groups are another class of potentially very promising electroactive materials. As a matter of fact, substitution of PT by oligo(oxyethylene) chains leads to interesting new properties such as solubility, hydrophilic character, and original electrochemical and optical behaviors (Roncali, 1992).

#### 2.4.2.6 Redox Groups

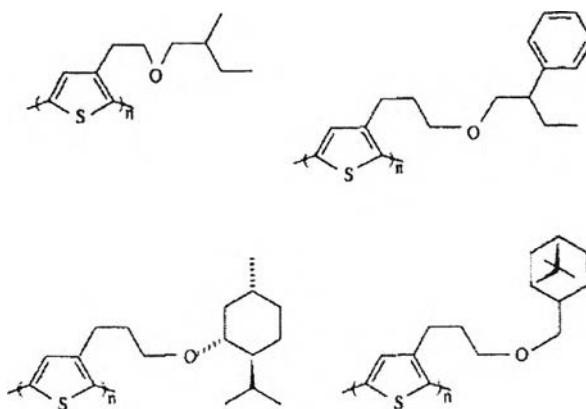
Only a few example of derivatization of PT by redox active groups have been described; PTs 3-substituted by bipyridyl, benzoquinone, ferrocene, and tetra-thiafulvalence. This situation is partly due to the much higher oxidation potential of thiophene ring which, in some cases, may lead to the degradation of the attached redox center during electrocopolymersization and also to the more drastic steric (Roncali, 1992).

#### 2.4.2.7 Self-Doped Poly(thiophenes)

The synthesis of poly(3-thiophene-3-ethanesulfonate) and poly(3-thiophene-6-buthanesulfonate). In these polymers, the charge-compensating anion is covalently bound to the polymeric backbone. Consequently, instead of anion incorporation, the charge compensation upon doping involves the expulsion of cationic species. Furthermore, the presence of the sulfonate group makes these polymers the first examples of water-soluble conductive polymers (Roncali, 1992).

#### 2.4.2.8 Chiral Poly(thiophenes)

Conjugated polymers substituted by optically active groups have potential technological applications as materials for enantioselective modified electrodes and membranes or for microwaves absorbers (figure 2.9) (Roncali, 1992).



**Figure 2.9** Chiral Poly(thiophenes).

### 2.4.3 Applications of Poly(thiophenes)

Applications can be divided into three main groups resorting to (i) the electrical properties of the doped conducting state, (ii) the electronic properties of the neutral semiconducting state, and (iii) the electrochemical reversibility of the transition between the doped and the undoped states.

#### **A. Applications of the Doped State**

The sensitivity of the conductivity of PTs toward gases was analyzed by exposing PT films to NO and NO<sub>2</sub> resulting in increases in electrical conductivity, whereas H<sub>2</sub>S and NH<sub>3</sub> had an opposite effect (Hanawa et al., 1989 and Roncali, 1992). These results have led to the proposal of PT-based gas sensors; however, the selectivity of such devices is rather poor.

#### **B. Applications of the Undoped State**

##### **1. Electronic Devices**

Photovoltaic cells based on electrogenerated PTs have been shown to present rather high quantum efficiencies under monochromatic illumination, but the overall conversion yield under polychromatic light remains low (Glenis et al., 1986). Recent developments in this field are oriented toward the synthesis of model molecules which could act as molecular or molecular rectifiers, or to the preparation of LB film (Roncali, 1992).

## 2. Nonlinear Optics

Experiments carried out on PT and on several of its substituted derivatives have shown that PTs present a large and very fast nonlinear optical response (Roncali, 1992).

### C. Electrochemical Applications

#### 1. Energy Storage

Initial works used PT- iodine conjunction with Zn or Li electrodes. Primary and secondary cells were constructed using chemically and electrochemically prepared PTs (Roncali, 1992).

#### 2. Electrochromic Devices

The considerable spectral changes in the visible region associated to the doping/undoping process of PTs have led to several proposals of electrooptical systems such as display devices or electrochromic windows.

#### 3. Electrochemical Sensors and Modified Electrodes

Selective modified electrodes and electrochemical devices appear as one of the most promising fields of application of PTs. Modified electrodes for electrocatalysis have been prepared from PMeP7 or PT-metal hybrid material (Roncali, 1992).

## 2.5 Acrylonitrile-butadiene Rubbers (NBR) and Blends of Acrylonitrile-butadiene Rubbers.

Ahn *et al.*, (2000) studied the effect of acrylonitrile (AN) repeating unit content in poly(butadiene-*co*-acrylonitrile) (NBR) on the miscibility, morphology, and physical properties of Poly(styrene-*co*-acrylonitrile) (SAN), of which the content of acrylonitrile (AN) repeating unit is 32 wt % (SAN32), was blended with NBR. They found that partial miscibility between SAN32 and NBR was enhanced as the AN content in NBR was increased. For the TEM photographs, all the blends showed NBR particles dispersed in SAN matrix; the size of dispersed NBR particles decreased as the AN content in NBR was increased. They found that SAN exhibited almost the Newtonian behavior at low shear rates showing zero shear viscosity. However, SAN/NBR blends showed the shear thinning behavior even at low shear

rate. This upturn of viscosity at low shear rate was frequently observed in heterogeneous polymer blends, and this observed behavior was explained in terms of an agglomeration or a three-dimensional association of dispersed phase.

Sau *et al.*, (2000) studied new conductive rubber composites based on ethylene–propylene–diene rubber, acrylonitrile butadiene rubber (NBR), and their 50/50 (weight ratio) blend filled with conductive carbon black. The effect of filler loading on the electrical and mechanical properties was studied in different conditions. The resistivity of the composites was only slightly different from that of the base polymer. However, beyond a certain critical filler loading a significant drop in resistivity was observed. The rate of change of resistivity with temperature decreased with the gradual increased of filler loadings against temperature. The activation energy of conduction for various blends decreased with increasing NBR concentration. The degree of reinforcement depended on the extent of polymer–filler interaction. They found that the degree of reinforcement was highest for vulcan-XC filled NBR composites followed by the blend and EPDM based composites.

Vallim *et al.*, (2000) blended Nitrilic rubbers containing 29 or 45% of acrylonitrile with polyaniline doped with different acids (chloridric, dodecylbenzenesulfonic, tetrapropylbenzenesulfonic, and *p*-toluenesulfonic acids). The blends were prepared by mechanical mixing in a roll-mill and vulcanized in a hot press. The results showed that increasing polyaniline content from 50 to 100 phr induced an increase in the electric conductivity from  $10^{-10}$  to  $10^{-8}$  S cm<sup>-1</sup>; however, the blends became harder and more brittle than the crude rubber. The results of the conductivities showed that the higher surface and volumetric conductivities for samples prepared with NBR29 occurred when they used PANi doped with PTSA, and for NBR45, this occurred with TBSA. Blends with NBR29 had lower surface conductivities compared to NBR45 blends with Pani doped with the same acid. The content of acrylonitrile affected the polarity of the rubber and increased the compatibility with the polar-doped PANi. The increase of acrylonitrile content produced harder and stiffer material due to the dipole– dipole interactions between these repeating units. For all blends containing PANi, they had the same flow tendency in the elastic region, confirming the hypothesis that the acid was an additional barrier to the crosslinking process. The different morphology indicated a



phase segregation between NBR29 blended with 50 phr of PANi. These results can be corroborated the DMA results, which indicated the phase segregation.

Ibarra *et al.*, (2002) studied the crosslinking of carboxylated nitrile rubber (XNBR) with a special preparation based on zinc oxide/zinc peroxide. Vulcanization was followed at different temperatures. In the integrated curves, the mathematical analysis made them split the rheometer curve into two contributions: a very fast plateau and a slower process. They proposed the first contribution was due to the reaction of zinc oxide with the carboxylic groups of the rubber to give ionic crosslinks, and the second contribution was due to the zinc oxide generated in the decomposition of the peroxide plus possibly additional covalent crosslinking produced by the radicals generated during the decomposition. They used Infrared and calorimetric analyses to find further evidences to support the separation crosslinking. From IR data, the carboxylic groups ( $1698\text{ cm}^{-1}$ ) disappeared and some other new peak appeared. From DSC data, a reaction exotherm which related to the heat evolved during zinc peroxide decomposition was found.

Varghese *et al.*, (2002) studied the effect of uncrosslinked (thermoplastic) and crosslinked (thermosetting) acrylonitrile butadiene rubber/poly(ethylene-*co*-vinyl acetate) (NBR/EVA) blends. The effects of blend ratio, crosslinking systems, frequency, and temperature were studied. Different crosslinked systems were prepared using peroxide (DCP), sulfur, and mixed crosslink systems. For Dynamic mechanical results, the damping properties of the blends increased with an increasing NBR content. On increasing the NBR content, the crystallinity was reduced. Therefore, the modulus of NBR-rich blends decreased much faster at higher temperatures. The damping peak height in the blend composition NBR/EVA; 50/50 %wt increased in the following crosslinking agent order: sulfur, and peroxide. This was in the increasing order of the crosslink density as obtained from swelling studies.

Lokander *et al.*, (2003) studied magnetorheological effect (MR) by using nitrile rubber with various acrylonitrile contents, where the polarisable particles were large and irregularly shaped were embedded in the matrix. These materials were compared with rubber materials filled with carbonyl iron. The magnetorheological effect was evaluated by measuring the dynamic shear modulus. They found that the MR effect of different matrix materials with approximately 28% of irregularly

shaped pure iron particles the matrix material did not influence the MR effect. For carbonyl iron, on the other hand, the MR effect for the materials with hard matrix materials was larger than for the materials with softer matrix. It was probably due to the fact that the particles were less well dispersed within the matrix when the viscosity was higher. Thereby aggregates, which acted like larger irregular particles, were present to a larger extent.

Cho et al., (2006) presented the fabrication of dry type conducting polymer actuator. Nitrile rubber (NBR) was used as a base material of the solid polymer electrolyte by preparing to be thin films of NBR (150~200  $\mu\text{m}$ ). The conducting polymer, polypyrrole(PPy), was synthesized on the surface of NBR by chemical oxidation polymerization technique, and the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (BMITFSI) or in 0.5M LiClO<sub>4</sub> /propylene carbonate (PC) was introduced into the composite film. The film was studied from the cyclic voltammetry responses and the redox switching dynamics. The displacement of actuator was measured by laser beam radiation. Activation of PPy–NBR in BMITFSI resulted into very active displacement (4–5mm) with 2–3mm displacement in LiClO<sub>4</sub>/PC. Both the bending and bending rates observed in ionic liquids were greater than those observed in convention electrolyte systems. They measured a cycle life in excess of 200 cycles for PPy–NBR activated in BMITFSI. Neither chemical degradation nor any declination in the bending-displacement was observed.

Cho *et al.*, (2006) studied a conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), synthesized on the surface of the NBR layer by using a chemical oxidation polymerization technique, and room temperature ionic liquids (RTIL) based on imidazolium salts, e.g. 1-butyl-3-methyl imidazolium X [where X=BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], were absorbed into the composite film. This study determined the electrochemical actuation of several BMI ionic liquids. By examining the ionic liquid couples, the anion-size of the BMIX ionic liquids was found to influence the displacement of the actuator. the larger ion size cause higher displacement. DMA characterization of the original NBR and the NBR film swollen with ionic liquid was carried out. The results demonstrated the plasticizing effect of

the different ionic liquids. The loss tangent was 13–32 °C lower than that of the virgin NBR.

Soares *et al.*, (2006) prepared conductive elastomer blends based on polyaniline-dodecylbenzene sulfonic acid (PAni.DBSA/nitrile rubber (NBR) by polymerization of aniline in the presence of NBR, using a direct, one-step in situ emulsion polymerization method in which DBSA played both roles of surfactant and dopant. The preparation of these blends followed the same procedure as that used for the synthesis of PAni.DBSA, by using the NBR previously dissolved in toluene, in a fixed concentration of 10 wt.%, different NBR/Ani weight ratios were used to obtain blends with different amounts of PAni.DBSA. The comparisons of the surface conductivity and volume resistivity values were carried out for non-vulcanized blends prepared by both in situ emulsion polymerization and mechanical mixing. In all compositions studied, the emulsion-polymerized systems presented significantly lower volume resistivity values and higher surface conductivity values than the corresponding physical blends. Blends prepared by mechanical mixing are characterized by the presence of large agglomerates of PAni.DBSA heterogeneously dispersed and without great evidence of conducting pathways between them. The emulsion process resulted on the formation of PAni.DBSA as microtubules with relatively high aspect ratio and connected each other, producing conducting pathways. The blend prepared by in situ emulsion polymerization displayed significant higher viscosity values especially at low frequency, suggesting a reduction of chain mobility as a consequence of good interaction.

Yong *et al.*, (2006) studied electrically conductive blends produced by combining various grades of NBR with different amounts of PAni.DBSA by using solution blending technique. Their results showed that blends with high acrylonitrile (ACN) content, 48 wt%, had lowest electrical conductivity percolation thresholds, and were more conductive than previous thermally mixed blends. These results were suggested either that more compatible host material favored the formation of microscopic conductive pathways, or that the well dispersed PAni.DBSA species within the NBR-rich regions were assisting the process of bulk charge transport. FT-IR spectra and DSC were used to confirm molecular interactions between the polymers.

## 2.6 Dielectric Properties of NBR and NBR Blends

Ikada *et al.* (1972) studied dielectric constants and losses of four kinds of acrylonitrile-butadiene copolymers. They applied the Havriliak-Negami equation to study the dielectric relaxations of acrylonitrile-butadiene copolymers. The characteristic of the relaxations of polymers led to the conclusion that the relaxations of chain segments in the rubbery state may be governed by a similar motion. From results of the logarithm of the relaxation times against the reciprocal of absolute temperature, the relaxation times of NBR-4 which had a higher proportion of acrylonitrile were longer than those of NBR-3, since the dipole-dipole interaction was stronger.

George *et al.* (1999) investigated the dielectric properties of isotactic polypropylene/acrylonitrile-butadiene rubber blends as a function of frequency with special reference to the effect of blend ratio. The variation of the dielectric properties with blend composition was correlated with blend morphology and observed. The continuous nature of the NBR phase led to a better orientation of dipoles and resulting in a high dielectric constant. In the case of blends, due to the presence of two phases of NBR and PP with different conductivities, interfacial polarization occurred leading to an increase in dielectric constant. Because interfacial polarization decreased with an increase in frequency as the frequency increases to 100 Hz, the dielectric constant decreased considerably. The dielectric constant increased as the rubber content increased. This increase in  $\epsilon'$  with the incorporation of rubber was due to an increase in  $C\equiv N$  dipoles, which increased the orientation polarization and also due to the presence of interfacial polarization. The effects of various fillers on dielectric properties were also investigated. The dielectric constant increased on the addition of carbon black. The increase in  $\epsilon'$  value upon the addition of fillers was correlated with the presence of polar groups in the filler and interfacial polarization. For the effect of filler incorporation, in case of carbon black and silica, a further increase in the loading decreased the resistivity; whereas, in the case of cork, as the loading increases, the resistivity rather increased. The decrease in electrical

resistivity for silica and carbon black may arise from the presence of ionic groups present in silica and carbon black.

Eid *et al.* (2006) studied the effect of filling silica on dielectric and mechanical properties of ethylene propylene diene/acrylonitrile butadiene rubber EPDM/NBR blends with different compositions. In this work, polyvinyl chloride (PVC) was used as compatibilizer resulting an improvement in the electrical and mechanical properties of multiphase blend ethylene propylene diene/acrylonitrile butadiene rubber EPDM/NBR. The increase in  $\epsilon'$  with the incorporation of NBR was due to the increase in  $C\equiv N$  dipoles, which led to an increase in the orientation polarization and also to the presence of interfacial polarization.

## 2.7 Polythiophene and Derivatives

Kim *et al.* (1999) studied water-soluble poly(3-thiophene acetic acid) (P3TAA). The solution properties of these water-soluble polythiophene carboxylic acids were studied by potentiometric titration, viscosity measurements, and UV-vis spectroscopy. They found that titration curve showed an inflection of the slope around pH 5-6. The reduced viscosity and electronic spectra ( $\lambda_{max}$ ) of the P3TAA aqueous solution abruptly changed at this pH region. These pH-induced abrupt conformational changes occurred from the aggregated state to the extended state of the polymer main chain.

Kim *et al.* (2000) studied the environmental response of polythiophene hydrogels. They synthesized a chemically cross-linked and a water-swollen poly(3-thiopheneacetic acid) (P3TAA) gel. Its swelling and spectral changes associated with its ionization at certain pH were studied. They found that  $G''$  was much lower than  $G'$  in the measured frequency region, indicating that P3TAA gel occurred. For the swelling behavior, they found that the lower crosslinking density, the higher the degree of swelling and the sharper the transition. The pH-induced increase in the degree of swelling was associated with the electrostatic repulsion among the dissociated carboxylic groups of P3TAA; and the increase in  $\lambda_{max}$  which was the wavelength of UV-visible absorption spectra related to interchain length of

molecule was attributed to an enhanced effective electronic conjugation length of the polymer chain. Both cases were due to a backbone conformational transition from an aggregated state to an extended state in the network. But the dissociation of P3TAA gel was strongly suppressed due to the cross-linkage in the low-pH region. The gels prepared in the mixed solvents exhibited a higher  $\lambda_{\max}$  than those prepared in DMSO at any pH, confirming that the increase in the electronic conjugation structure of P3TAA chain. The electrical conductivities of doped water-swollen P3TAA gels with 60% $\text{HClO}_4$  were higher than that of undoped water-swollen gel.

Shiga and Okada (1996) directly measured the dynamic viscoelasticity of poly(3-hexylthiophene) doped with iodine or  $\text{FeCl}_3$  under an electric field. The result of storage modulus vs. time curves of iodine-doped P3HT showed that  $E'$  decreased by the action of a dc electric field and reached a constant value. They called this phenomenon the electroplastic effect. When the applied field was removed, the parameter recovered the starting value in the absence of an electric field. The response speed upon the applied field was almost equal to the reversing speed. When doped P3HT was measured by using X-ray diffraction patterns without electric fields, the peak positions were shifted to lower angles. Those were indicative of the expansion of interlayer spacing. When a dc electric field was applied, the expansion of the interlayer spacing was induced. They proposed two explanations for the electric field-induced peaks in the X-ray at wide angle. One was a conformational change in P3HT chains. The interaction between the interlayers led to a decrease in the elastic modulus. The other explanation was that the undoping process was produced by the electric field. It was well known that undoping induced a volumetric change of the conducting polymer and a decrease in  $E'$ .

Luzzati *et al.*, (1996) studied the polarized luminescence spectra of gel-processed blend: poly(3-octylthiophene) (POT) in ultra-high molecular weight polyethylene (PE). The films were oriented by tensile drawing to a draw ratio of 62. The spectrum of the blend exhibited a redistribution of the oscillator strength. In luminescence measurement, they found that at high concentration (above 1%) chains were aggregated. The spectral migration of the excitation to the lowest energy states was favored by three-dimensional interaction so that the emission spectra did not

shift with the excitation energy. Stretching induced the orientation of the aggregates while the isolated chains were non-oriented and segregated into the disordered amorphous part of PE.

Thermal degradation of conducting polymer composites of polythiophene and rubbers was studied by Hacaloğlu *et al.*, in 1997. They studied by using by direct and indirect pyrolysis mass spectrometry techniques. The samples were prepared by electrooxidation of polythiophene using natural rubber or synthetic rubber as the insulating matrix. The results showed that degradation mainly occurred in a narrow temperature range of 213 to 225°C, yielding principally 1-methylcyclopentene and 1-methylcyclohexene by cleavages followed by cyclization reactions. Indirect pyrolysis analysis of PTh/NR and PTh/SR showed very similar thermal behaviour, as in the case of direct pyrolysis results. The intensities of the characteristic peaks of NR and synthetic rubber (SR) not only decreased considerably but also started to appear in the spectra of the composites at lower temperatures compared to pure homopolymers NR and SR. From thermal characteristics of rubbers, the rubbers were totally disappeared in the composites indicating degradation of the rubbers during the electrooxidative polymerization.

Souza and Pereira (2001) described a method to prepare homogeneous aqueous solutions of PTAA, either in its salt form or in acid form, using PVA as surfactant agent to prevent macroscopic precipitation of the PTAA. The solutions were obtained by dissolving PVA in milli-Q purified water and adding PTAA salt form. For the preparation of the solution of PTAA in its acid form, diluted HCl was dropwise added until achieving pH 1.0. The color of PTAA salt±PVA solution changed from a brown-red to a yellow when the solution was acidified. This result indicated a significantly decrease of the band gap of PTAA salt in PVA solution. From the UV and luminescence measurements, the optical properties of PTAA in PVA solution were pH-dependent. They suggested that the photochemical behavior of PTAA in a PVA solution can be the result of the formation or the dissociation of hydrogen bonds occurring between the carboxyl groups of PTAA and the hydroxyl groups of PVA.

Puvanattvattana *et al.*, (2006) studied electrorheological properties of polyisoprene and polythiophene/polyisoprene blends. They investigated the effects of

of degree of crosslinking ratio, polythiophene particle concentration, and electric field strength on electrorheological properties.. For pure polyisoprene, they found that at degree of crosslink  $N_{DCP}/N_{PI} = 3$ ; (PI\_03), the materials had highest  $G'$   $G'$  sensitivity amongst the various systems studied. The effect of electric field strength on the rheological properties of polythiophene/polyisoprene blends (Pth\_U/PI) at various polythiophene particle concentrations was investigated in the range between 0 and 2 kV/mm. They found that blends Pth\_U20/PI\_03; 20% of polythiophene system attained a maximum  $G'$  sensitivity value. At very low concentrations, the distances between particles were too large to allow a significant particle interaction. At higher concentration than 20% of polythiophene, system became saturated at approximately the same value as that of Pth\_U20/PI\_03 system. Pure rubbers were studied for their temporal responses, the rubber with the degree of crosslink  $N_{DCP}/N_{PI} = 3$  (PI\_03) appeared to be a reversible system at 1 kV/mm. The Pth\_U20/PI\_03 was clearly an irreversible system due to hydrogen bonding between adjacent polythiophene particles, and the residual dipole moments inducing permanent interparticle interactions.

## 2.8 Electroactive Polymers, EAPs

Shiga et al., (1993) they examined the electroviscoelastic effect of silicone elastomers having lightly doped conjugated polymer particles. The semiconducting polymers used experimentally were poly(*p*-phenylenes) lightly doped with  $CuCl_2$  or  $FeCl_3$  making PPP particles attained dc conductivities of  $10^{-10}$ - $10^{-7}$  S/cm. The increments of  $G'$  and of  $G''$  of the specimens which contained the particles content over 10.8% were induced by an electric field. They reported an effect of particle dispersion that the straight lines of particles aligned to electric fields were more effective in comparison with the random dispersion of particles, for a large electroviscoelastic effect to occur.

Gazotti *et al.*, (1999) studied the electrical, mechanical and thermal behaviours of a conductive polymer blend which was prepared by combining the elastomer poly(epichlorohydrin-co-ethylene oxide), which was of ionic conductivity



when containing  $\text{LiClO}_4$ , and a soluble derivative of polyaniline, poly(o-methoxyaniline) doped with p-toluene sulfonic acid. With an increase in concentration of the electronic conducting polymer up to 10% (w/w), the electrical conductivity of the elastomer increased by three orders of magnitude, with no changes in its mechanical properties. TGA results indicated that the presence of the rubber inhibited the degradation of the conducting polymer.

In 2000, Pelrine *et al.*, made electrical actuators from acrylic film coated on both sides with compliant electrode materials. This material demonstrated extraordinarily high strains. Actuated strains up to 215% were demonstrated with acrylic elastomers using biaxially and uniaxially prestrained films.

Carpi *et al.* (2003) studied an extension of electromechanical characterization of dielectric elastomer actuators. Planar actuators were realized with a 50  $\mu\text{m}$ -thick film of an acrylic elastomer coated with compliant electrodes. The isotonic transverse strain, the isometric transverse stress, and the driving current due to a 2 s high voltage impulse, were measured from four electrode materials (thickened electrolyte solution, graphite spray, carbon grease and graphite powder). Carbon grease, graphite powder and thickened electrolyte solution were smeared on the two sides of the strip, while graphite spray electrodes were realized as follows. They showed an electrode resistance per unit length; the graphite powder had the highest value, 50  $\Omega/\text{cm}$  by applying a certain voltage  $V$  across the definite thickness  $z_0$  of a prestretched actuator. The result showed electrostatic pressure generated a strain depending on the square of the applied electric field.

Kim *et al.*, (2004) prepared copolymer of poly(acrylic acid) and poly(vinyl sulfonic acid), PAAc/PVSA, to study swelling ratios at various temperatures and pH, and deformation ratio in an electrical field. Copolymer was prepared by sodium vinylsulfonate and *N,N'*-methylenebisacrylamide, crosslink agents, were dissolved in deionized water, then ammonium peroxydisulfate (APS) was added. The stored in a dry oven and heated at 50 °C for 2 days. Swelling properties of the PAAc/PVSA copolymer showed a temperature dependent swelling behavior in pure water and also pH-dependent swelling behavior. An applied electric field caused a contraction of the PAAc/PVSA copolymer hydrogels in the buffered

solutions at various pH. The contraction of the hydrogel in an applied dc electric field was due to the voltage-induced motion of ions, and the association state of the ionic groups within the polymer, which in turn, was due to the association/dissociation of the hydrogen bonds of the  $-\text{COO}^-$  groups of the PAAc and the  $-\text{SO}_3^-$  groups of the PVSA in the hydrogels.

Moschou *et al.*, (2004) prepared a novel artificial muscle material based on an acrylic acid/acrylamide hydrogel blended with a conductive polypyrrole/carbon black composite. After curing at 80 °C, the hydrogels were preconditioned in the NaCl test solution for at least 24 h. The material was optimized in terms of its electroactuation response by varying the acrylic acid content, the blending concentration of the conductive composite, and the intensity of the electric field. The higher the acrylic acid content, the higher the bending angle of the hydrogel was obtained. An additional parameter that was investigated when optimizing the artificial muscle composition was the incorporation of a conductive polymer such as polypyrrole on carbon black. They found that the hydrogel composed of 4% (w/w) carbon black alone presented a significantly lower response than its PPy/CB counterpart. The application of higher potentials (2 and 3 V) showed an expected improvement in the response of the material.

In 2004, Ma and Cross, studied electric field induced transverse-strain response in dielectric acrylic elastomer at 1 Hz. The strain was observed to be proportional to square of the electric field strength within the measurement range (0 to 2MV/m). Elastic compliance of the elastomer was measured as a function of frequency and was found to exhibit strong frequency dependence between 1 and 10 Hz. It was indicated that the field-induced-strain response in the acrylic elastomer originates primarily from the Maxwell stress effect.

Kyokane *et al.*, in 2005, studied the dielectric elastomer of polyurethane elastomer (PUE) doped by fullerene and carbon nanotube (CNT). They found that they could control the actuation under a low voltage when they put  $\text{C}_{60}$  or CNT derivatives into PUE. The force of actuation increased in proportional to the electric field. They found the large bending displacements were obtained by doping with fullerene due to the crosslinking density increase in the PUE films by combining with the hydroxyl groups of fullerene. The bending displacements of the CNT-

doped actuator were larger than those of fullerene doped actuator at the same concentration.

Moschoua *et al.*, (2005) improved response characteristics of the artificial muscle through optimization of the hydrogel material in terms of the electroactive constituents of the hydrogel precursor solution and the polymerization conditions. Hydrogels were prepared by mixing deionized water, the desired weight ratio of unsaturated aliphatic acids (acrylic, maleic or glutaric acid or mixtures of the above) and acrylamide based on a total monomer content of and polypyrrole composite with 20% (w/w) carbon black. After mixing, *N,N'*-methylenebisacrylamide (the crosslinking agents) was added, then the initiator–accelerator solution containing potassium persulfate and sodium metabisulfite, were dissolved in the monomer solution followed by the addition of *N,N,N',N'*-tetramethylethylenediamine. The polymerization was done at the desired curing temperatures (25, 45 or 60 °C) to form the artificial muscle samples. One way of increasing this ionic distribution in the hydrogel was to incorporate a monomer that has a higher content of charged groups per molecule. This research was accomplished by the introduction of a dicarboxylic aliphatic acid in the hydrogel precursor solution in the place of the monocarboxylic acid derivative. The responses of aliphatic acid content, maleic acid, and glutaric acid increased bending angles, but different value due to the difference in the molecular weights. When the temperature of polymerization of the hydrogel precursor solution was gradually increased to 45 °C and finally to 60 °C, the artificial muscle samples showed increased electroactuation responses. The crosslinking agent on the electroactuation had an effect on mechanical stability and the extent of hydrogen bonding taking place within the hydrogel network.