

CHAPTER II

LITERATURE SURVAY

2.1 Conductive Polymer

Conducting polymers or unique intrinsic conductivity of organic materials are long chain organic molecules in which successive carbon atoms along the axis of the chain are bound alternately by one shared electron pair (single, or σ -bond) and by two shared electron pairs (double, or π -bond). Therefore, the carbon chain is contained with heteroatoms such as N and S that arise uniquely from π -conjugation. Like most organic polymers, CP's are normally poor electrical conductors. By adding or removing electrons from the CP chains, and embedding positive or negative ions into the chains to maintain electrical neutrality. It is possible to make the locations of the δ -bonds less well defined (MacDiarmid, 2001).

Presently, there are several families of conducting polymer such as

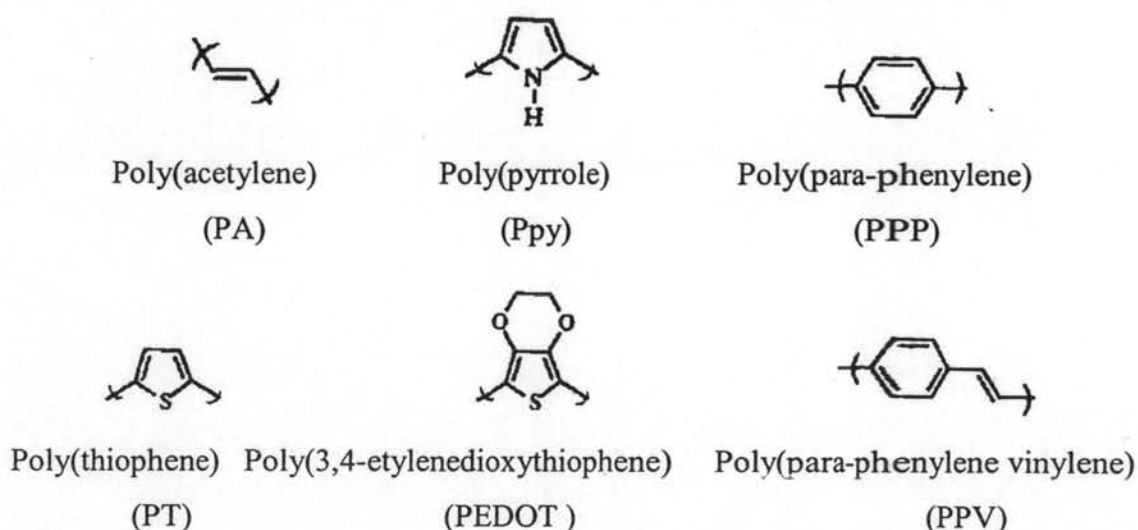


Figure 2.1 Schematic diagram of conjugated polymers in their neutral forms.

The conductive properties of these polymers arise from the doping process. This method allows some of the electrons more freedom to move from atom to atom,

increasing electrical conductivity. Through this process is known as redox doping. The conductivity of CP's can be varied continuously from insulating to semi-conducting and then metallic. Doping process of a polymer can be carried out electrochemically or by exposing polymer to a vapor or a solution that consisting of a dopant. There are 2 different routes in the doping process; a dopant accepts charges (*p*-type) or donates charges (*n*-type) onto the polymer

2.2 Conduction Mechanism

Materials in the world can be classified into three broad categories according to their room temperature conductivity properties: Insulators, Semiconductors and Conductors [9]. Conduction is the transport of charge from one point to the other and is governed by charge carriers that move through a specimen. In general, electrical conductivity, σ , [$\text{S}\cdot\text{cm}^{-1}$] is a function of the number of charge carriers, n , [cm^{-3}], the charge carried by the carrier, q , [A.s], and the mobility of the charge carriers, μ , [$\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$] as followed; [11].

$$\sigma = |q| n \mu \quad [\text{S}\cdot\text{cm}^{-1}] \quad (2.1)$$

Conduction in solids can be described with the band model which is shown in the schematic diagram of Figure 2.3. In this model, two molecular orbitals, both with half filled orbitals, are brought close enough to each other until overlapping occurs. The overlapping of individual molecular electronic states in all these materials produces electronic bands; valence electrons overlap to produce a valence band which is a low-energy band, while the electronic levels immediately above these levels also coalesce to produce a conduction band which is a high-energy band. The energy difference between the newly formed bands is called the energy gap. The extent of occupation of the energy bands and the energy gap between them determines the conductivity of a material. If the valence band is only partially filled by available electrons, or if the energy gap vanishes, an overlap between the valence and conduction bands occurs. When electrical potential is applied, some of electrons as charge carriers rise into empty levels where they can possess freedoms of movement ($\mu = \infty$). This leads to the metallic conduction. In semiconductor and

insulators, the valence band is completely filled ($\mu = 0$) and the conduction band is empty ($n = 0$); both bands are separated by an energy gap. Therefore, electrical conduction can only take place when charge carriers are excited from the valence band to the conduction band. For insulators, if the energy gap is too large it is difficult for charge carriers to be excited into the conduction band. If the energy gap for semiconductors becomes smaller charge carriers can be easily excited into the conduction band by means of thermal excitation, vibrational excitation, or excitation by photons (Kumar and Sharma, 1998; Chandrasekhar, 1999; Deependra *et al.*, 2004; Van Vught *et al.*, 2000).

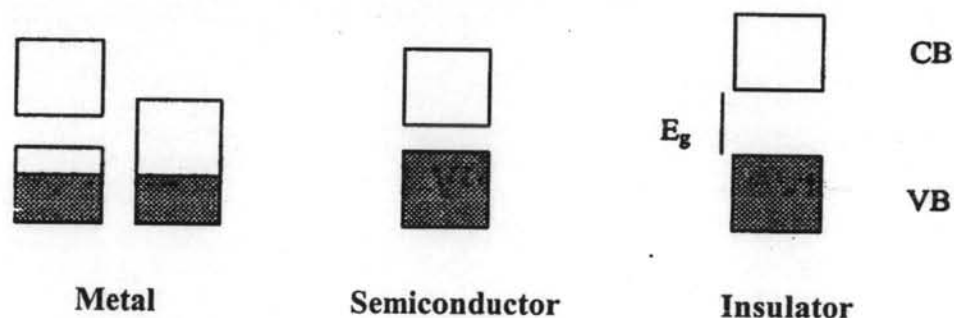
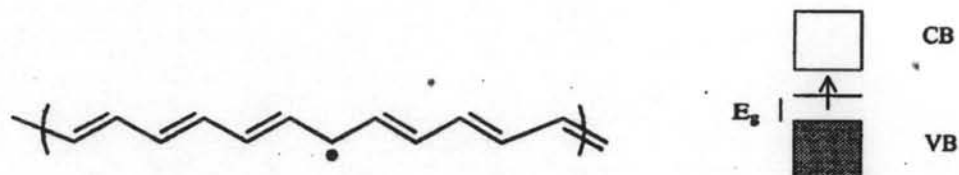


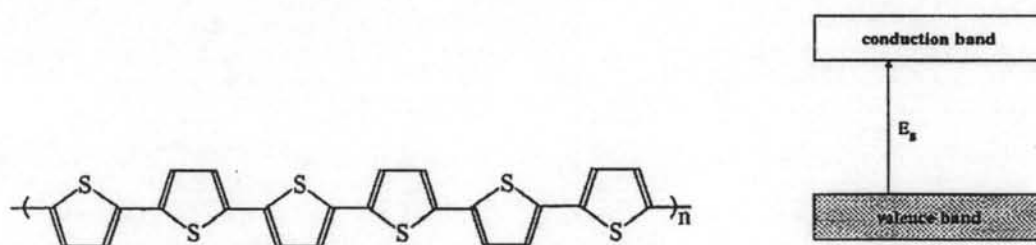
Figure 2.2 Schematic diagram of the band structure of metals, semiconductors, and insulators (E_g is the energy gap between the valence band (VB) and the conduction band (CB)).

The band model concepts can be used to describe conductive polymers behavior. A characteristic of all conductive polymers is the conjugated structure. The conjugation length is an important parameter influencing the conductivity due to the carrier mobility (which is related to conductivity); it increases with increasing conjugation length. The conduction mechanism of all conductive polymers is divided into two paths: charge carriers move along the extent of the π -conjugated system backbone (intrachain conductivity); or they move between the individual molecules (interchain conductivity). The conjugational defects or charge carriers are formed through solitons, polarons or bipolarons in the polymer chain when these conductive polymers are exposed to oxidation/reduction condition as shown in the schematic diagram of Figure 2.2. These defects or the charge carriers generate localized electronic states in the middle of the energy gap between the valence band

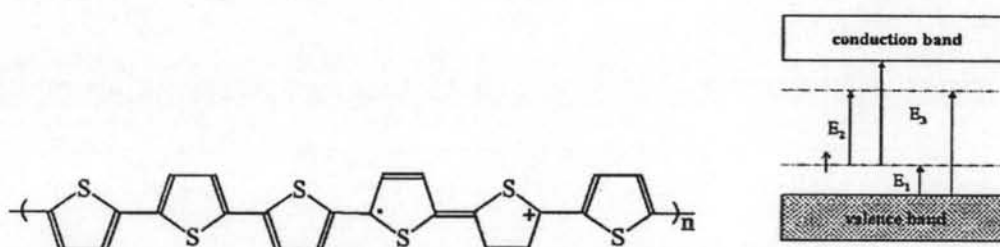
and the conduction band. This effectively reduces the energy gap and the charge carriers can jump into conduction band and electrical conductivity is enhanced (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).



Soliton in trans-polyacetylene (left) and electronic state induced between the VB and CB by the soliton (right)

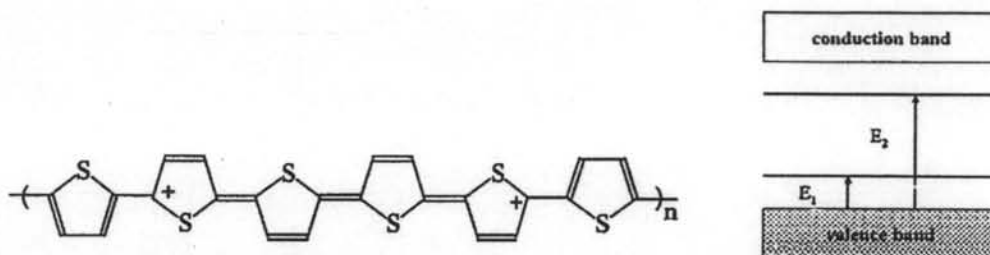


Neutral form of poly(thiophene) (left) and the electronic state of neutral form (right)



The oxidative doping of poly(thiophene) in form polaron (left) and electronic state induced between the VB and CB by the polaron (right)

Figure 2.3 Schematic diagram of soliton of polyacetylene, and polaron, bipolaron of poly(thiophene).



The oxidative doping of poly(thiophene) in the bipolaron form (left) and the electronic state induced between the VB and CB by the bipolaron (right)

Figure 2.3(cont.) Schematic diagram of soliton of polyacetylene, and polaron, bipolaron of poly(thiophene).

2.3 Ppy Synthesis

The conductive polymer polypyrrole were devised to two routes. The chemical and electrochemical routes for polymerization appear to be equally popular. In the chemical route, common oxidant such as FeCl_3 , may be used. The electrochemical route generally uses a non aqueous solvent medium such as acetonitrile, and graphite, steel or Pt electrode. (Chandrasekhar. P, 1999)

2.3.1 Chemical Polymerizations

In a typical synthesis, anhydrous FeCl_3 and pyrrole (pre-purified to remove chromophoric contaminants by passing through an alumina column) are taken in a 2.33:1 molar ratio (with 2.5 M FeCl_3 in MeOH solvent) and stirred at $0\text{ }^\circ\text{C}$ for ca.20 min next to that yield the polymer. The product is thoroughly washed with MeOH and dried in vacuum for ca. 12 h. The electrical conductivity of the Ppy so obtained has been claimed to be as high as 190 S/cm

2.3.2 Electrochemical Polymerization

Because of its simplicity and frequently higher polymer conductivity obtained, electrochemical polymerization of Ppy is many times preferred over chemical polymerization. Basically electrochemical synthesis, 0.01 to 1 M.

Monomer is taken with 0.1 to 2 M dopant/electrolyte (e.g. LiClO_4 , Et_4Ntos) in acetonitrile medium. Stainless steel, graphite or Pt is most commonly used as electrodes. A potentiostatic polymerization, at ca. + 0.8 V. vs. SCE, yields the best results, although potential sweeps are also routinely employed. A small water content in acetonitrile is found to be beneficial for the polymerization that yield slightly improved Ppy conductivity.

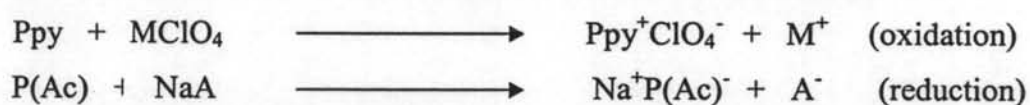
2.4 Concept of Doping

Commonly the conductive polymer comprises of a naturally π -conjugated electrons systems on backbone are not sufficient to render them highly conductivity; trans-polyacetylene possesses only $10^{-6} \text{ S.cm}^{-1}$. The high electrical conductivity is achieved by the process called the "doping process". This process was firstly discovered by Shirakawa and Ikeda by doping of polyacetylene (PA) with iodine, and conductivity increased by 9-13 orders of magnitude. (Kumar and Sharma, 1998)

Doping of pristine (undoped) conductive polymer can be accomplished by the chemical method of a direct exposure of the conjugated polymer to a charge transfer agent (called dopant) in a solution or in vapor phase, or by the electrochemical oxidation or reduction. Dopants are either strong reducing agents or strong oxidizing agents. They may be neutral molecules, compounds or inorganic salts, which can easily form ions. Organic dopants are, for example ClO_4^- or Na^+ . Polymeric dopants are poly (styrene sulfonic acid) or poly(vinyl sulfonic acid), for example. During the doping process, charge carriers can be generated by the oxidation or reduction of the polymer. The conductivity of either insulator or semiconductor (typically in the range of 10^{-10} to $10^{-5} \text{ S.cm}^{-1}$) is raised to the metallic conduction (typically in the range of 10^0 to 10^4 S.cm^{-1}) by controlling the doping level or the extent of oxidation/reduction. Increasing doping level leads to increasing conductivity, via the creation of more mobile charges carriers. The maximum doping levels achievable vary and depend on the conductive polymers and the dopants used.

Removal or addition of electrons may also be accomplished through the introduction of a dopant which imparts higher conductivity. If the oxidation in the

polymer occurs, it extracts electrons from the valence band (electrons from the polymer to the dopant), creating “holes” in the valence band, which is then known as “p-doping”. It generates a positively charged conductive polymer and an associated anion. When the reduction on the polymer occurs, it adds electrons to the conducting band (electrons from the dopants to the polymer), creating conducting electrons in this band, which is known as the “n-doping”. This generates a negatively charged conductive polymer with an associated cation. These processes are summarized in the schematic, where M and A are the cation and the anion, respectively:



In order to maintain charge neutrality, counter-ions (associated ions) are also incorporated. The interaction between counter-ions and the charge carriers on the conjugated polymer can influence the mobility of the charge carriers which is known as the pinning effect (Van Vught *et al.*, 2000). This effect becomes less when the size of counter-ions is larger and the degree of charge delocalization is stronger. This means that the stability of the conductivity can be affected by the size of the counter-ions.

Doping of a conductive polymer is resulted in the formation of new, neutral solutions, polarons or bipolarons in conjugated polymers. The doping with n-type dopants, anion conductive polymer is formed which is highly unstable in air and water. So, the conductivity which is generated by n-type dopants e.g. Na, Li is less stable than by p-type dopants e.g. I₂, AsF₅, FeCl₃, HClO₄. Therefore p-type dopants are more frequently used (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).

2.5 Polymer Actuator

The original focus was the feasibility of polymer based actuators for robotic applications. The project called “ARTMUS - Artificial Muscles” now aims at developing a novel class of electrically controlled actuators based on polymer materials (Peter Sommer-Larson 2002) Such an actuator must be based on low price

materials, act linearly with smooth movements that allow for integrated feedback and control and show a performance as required.

Polymer gels are crosslinked polymer chains swollen in a solvent. They often respond by a change in volume to changes in environmental parameters like temperature, solvent composition and electric fields (Peter Sommer-Larson 2002). Basically the equilibrium between gel and the solvent is disturbed by these changes. A drastic volume change in a polyelectrolyte gel in response to changes in pH is illustrated in Figure 2.4

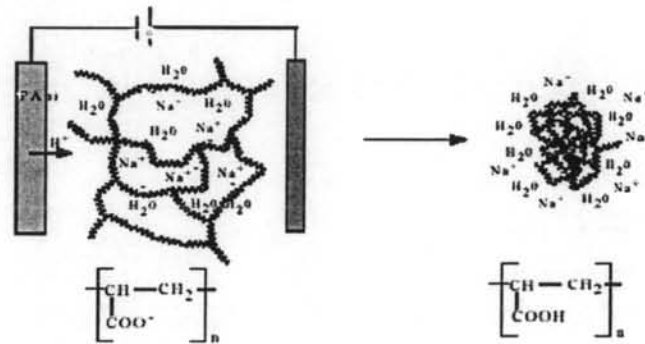


Figure 2.4 Polymeric system with actuator properties.

Partly ionized poly (acrylic acid) swollen in aqueous solution will contract strongly in an acidic solution. Flexible electrodes made from conducting polyaniline (PAni) may produce the necessary change in pH. Conducting polymers (e.g. polypyrrole and polyaniline) originally attracted attention because of their very large electronic conductivities (in special cases comparable with Cu). The polymers contain a conjugated, often one-dimensional, backbone, and their properties usually depend crucially on being oxidized or reduced by the introduction of anions or cations as dopants associated with the chain. (Peter Sommer-Larson, 2002)

The accommodation of ions in the polymer also has consequences for their mechanical properties (Peter Sommer-Larson, 2002). The creation of charged electronic species on the chain can change the stiffness and the length of the individual polymer chains and the incorporation of the sometimes bulky counter ions can increase the volume - especially when the ions are associated with co-

intercalating solvent molecules. This opens the possibility for the reversible control of mechanical properties by the application of a voltage, and is the foundation for the interest in conducting polymers as electromechanical actuators. The process is illustrated in Figure 2.5.

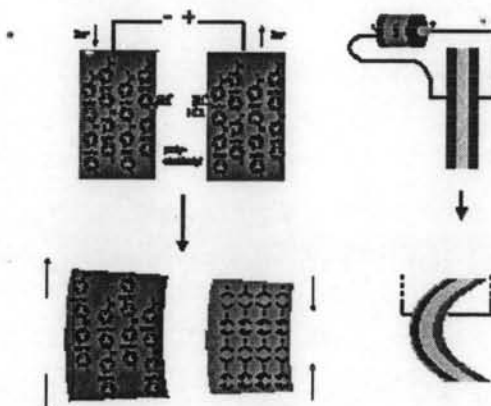


Figure 2.5 A bimorph based on the conducting polymer polyaniline (PAni).

Both the macroscopic and molecular changes during operation are illustrated. Two polyaniline films are sandwiched around an ion-conducting film. As current flows, one side of the sandwich is reduced and the other oxidized. Concurrently, ions are transferred between the two sides leading to an expansion of the first and a contraction of the second side. The overall effect is a bending of the bimorph (Peter Sommer-Larson, 2002).

Electrostatic contraction of an elastic polymer film has proven to be a genuinely new approach to polymer based actuators. From the phenomenological point of view, the actuators behave electrostrictive. Electrostriction is the second order term in the relation between strain and applied field. The first order term describes piezoelectricity. High electrostrictive coefficients have been measured in polymer gels and in certain rubbers, but the electrostatic actuator does not rely on materials showing electrostriction. The actuators are termed dielectric elastomer actuators, as illustrated in Figure 2.6

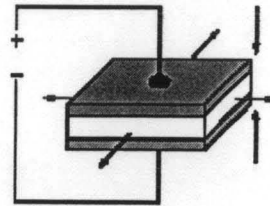


Figure 2.6 Dielectric elastomer actuator unit.

They are formed by an elastic thin film sandwiched between two compliant electrodes. At sufficiently high electric fields, the elastic film is compressed by the electrostatic forces between the electrodes. Simultaneously, the actuator expands in the plane of the electrodes. It is possible to get a macroscopic response in these directions even for a film thickness as small as 1 micron, for instance by rolling a tube from the film. (Peter Sommer-Larson, 2002)

2.6 Acrylic Elastomer (ACM)

Acrylic Elastomer is the one type of dielectric elastomer which can activate by electric field. Acrylic elastomer can use to made actuators which can change it size during apply electric field. (Study report by the University of Pisa *et al.*) The figure is shown below. (Figure 2.7)

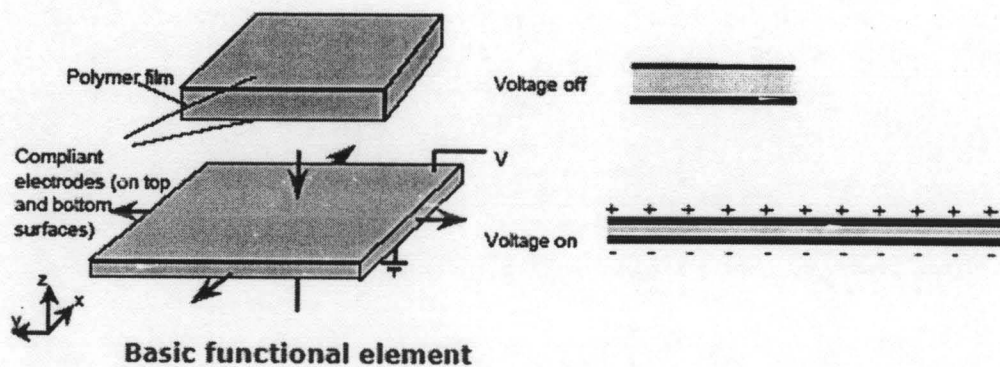


Figure 2.7 Electroactive respond of Acrylic Elastomer.

Polyacrylate rubber (ACM) is the one type of acrylic elastomer. ACM are saturated copolymers of monomeric acrylic esters and reactive cure site monomers. The first commercial products were based predominantly upon ethyl acrylate or butyl acrylate and in some grades, together with acrylic monomers of the alkoxyalkyl type such as methoxyethyl acrylate and ethoxyethyl acrylate. (Yang *et al.*, 1994) (shown in Figure 2.8)

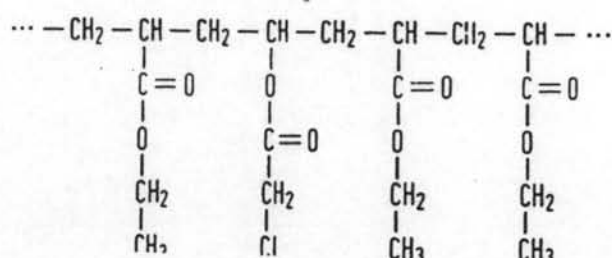


Figure 2.8 Structural Formula of a Chlorine-Containing ACM.

The more modern type of ACM rubber contain minor amount (less than 5% by weight) of cure site monomer with functional groups whose presence increase the cure rate and improve the vulcanizate properties. The cure site monomers can be divided in to two groups: one containing labile chlorine atom and the other chlorine-free. The names and chemical structure of the most widely used cure site monomers are given in Figure 2.9. The polymer chain of an ACM rubber with a chlorine-containing site monomer is shown in Figure 2.9 too.

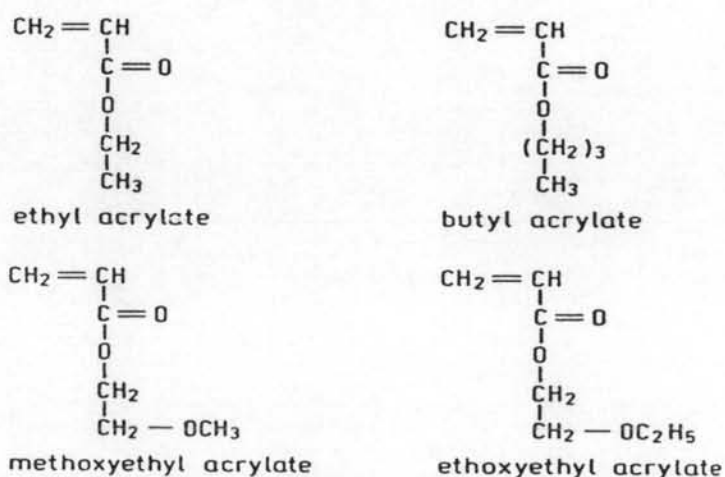
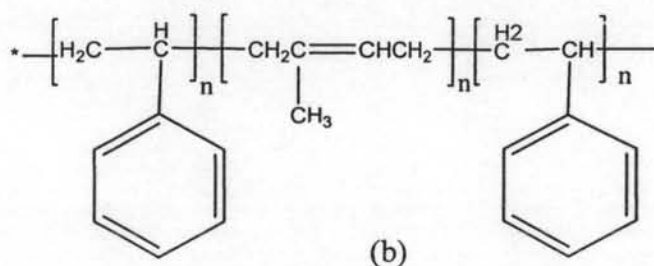
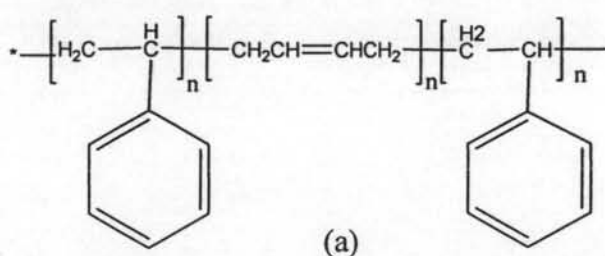


Figure 2.9 The monomer for Acrylic Elastomer.

The fully saturated backbone provides the excellent heat and ozone resistance of the vulcanizates and the polar side groups give the oil resistance. ACM grade based on ethyle acrylate have excellent oil resistance but poor low-temperature properties, whereas those based on butyl acrylate showed improved low-temperature flexibility but inferior oil resistance. (Yang *et al.*, 1994)

2.7 Styrenics

Styrene block copolymer are the most widely used thermoplastic elastomers (TPEs), accounting for close of the twentieth century. They are characterized by their molecular architecture, which has “hard” thermoplastic segment (block) and a “soft” elastomeric segment (block). (see Figure 2.9) Styrenic TPEs are usually styrene butadiene styrene (SBS), styrene ethylene/butadiene styrene (SEBS), and styrene isoprene styrene (SIS). Styrene TPEs usually have about 30 to 40 percent (wt) bound styrene; certain grades have a higher bound styrene content. The polystyrene end blocks create a network of reversible physical cross links that allow thermoplasticity for melt processing or salvation. With cooling or solvent evaporation, the polystyrene domains reform and harden, and the rubber network is fixed in position. (Harper, 2002)



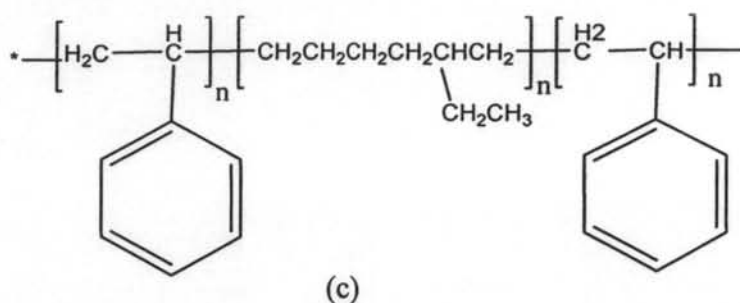


Figure 2.10 Structures of three common styrenic block copolymer TPEs a) poly(styrene butadiene styrene, SBS), b) poly (styrene isoprene styrene, SIS) and c) poly (styrene ethylene/butylene styrene, SEBS).

Principal styrenics TPE market are: molded shoe soles and other footwear; extruded film/sheet and wire/cable covering; pressure-sensitivity adhesives (PSA) and hot-melt adhesives; and viscosity index (VI) improver additives in lube oils, resin modifiers. They are also popular as grips (bike handles), kitchen utensils, clear medical products, and personal care products. Adhesive and sealants are the largest single market. Styrenics TPEs are useful in adhesive composition in web coating. (Harper, 2002)

Styrene block copolymer (SBC) thermoplastics elastomers were produced by Shell Chemical (KRATON[®]) and are available from Firestone Synthetic Rubber and Latex, Division of Bridgestone/Firestone (Stereon[®]), Dexco Polymers (Vector[®]), and EniChem Elastomers (Europrene[®]), SBC properties and processes are describes for these four SBCs. (Harper, 2002)

Styrenic TPEs have strength properties equal to those of vulcanized rubber, but they do not require vulcanization. Properties are determined by polymer type and formulation. There is wide latitude in compounding to meet a wide variety of application properties. According to application-driven formulations, KRATONS are compounded with a hardness range from Shore A 28 to 95 (Shore A 95 is approximately equal to Shore D 40), sp gr from 0.90 to 1.18, tensile strengths from 150 to 5000 lb/in (1.03 to 34.4 MPa), and flexibility down to -112 °F (80 °C). KRATONS are resistant to acids, alkalis, and water, but not long soaking in hydrocarbon solvents and oils deteriorates the polymer. (Harper, 2002)

2.8 Silicones (Polysiloxanes)

An interesting and commercially important class of polymers can be synthesized by the hydrolysis of suitably functionalized silicon derivatives. Note that leaving group (halides, alkoxides, carboxylates, or amines) attached to silicon reacts readily with water, and hydrolyze to silanols. These silicon-analogs of alcohols are also unstable, and in most cases quickly dimerize to produce siloxanes. Difunctional variations lead to linear polymers, as shown below for the polymerization of dimethyldimethoxy silane.

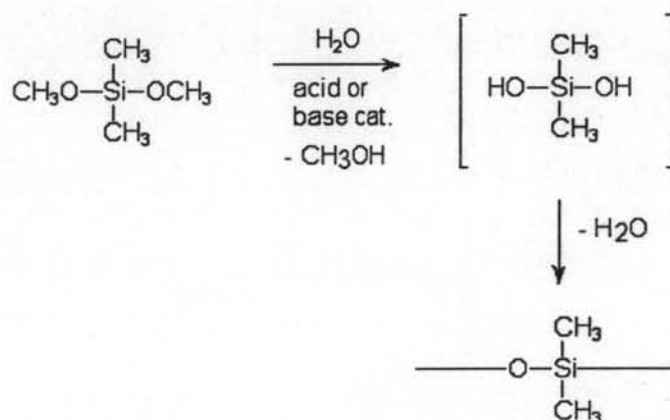


Figure 2.11 Polydimethylsiloxane synthesis.

The polymer shown above is polydimethylsiloxane (PDMS), better known as silicone oil. Note that there are no carbon atoms in the backbone; PDMS has an inorganic chain. The glass transition of PDMS is the lowest of all polymers, presumably because of the extremely flexible nature of the Si-O linkage. The linear polymer can also be made by ring-opening polymerization. Crosslinked PDMS versions are important rubbery sealants, caulking, coatings, and tubing materials. Because of their very low T_g , these materials remain flexible even when extremely cold. The above chemistry can be the basis for crosslinking, so that exposure to atmospheric moisture cures the material. Carboxylate is a common leaving group in silicone bathtub caulking that you can purchase in hardware-stores. As curing proceeds, one can smell acetic acid being liberated from the material. The name "silicone" is an artifact of early chemists, who wrongly presumed based on the

empirical formula that these compounds contained a silicone-oxygen double bond ($R-Si=O-R'$). It was thought that these compounds were the silicon analog of ketones, therefore the name silicone. We now know that silicone-oxygen double bonds are

2.9 Polypyrrole Synthesis

Lee, (1995) studied the chemically synthesizing of Polypyrrole by using dodecylbenzene sulfonic acid (DBSA) as the dopant and ammonium persulfate as the oxidant. The solution of the polymer in chloroform was cast to a film. The electrical conductivity of the film was 5 S/cm . The solubility of the polypyrrole powder was enhanced by adding an equal amount of DBSA to the polymer. The intrinsic viscosity of the polymer in *m*-cresol was 0.17 dl/g indicating low molecular weight. However, a stiff film was cast from the solution and elastic modulus and tensile strength were 1945 MPa and 17 MPa respectively while elongation at break was 0.9% . The film had a smooth surface and the electrochemical reactivity was sustained after 150 cycles of cyclic voltammetry.

Simmons (1995) described, for the first time, the use of tailor-made reactive polymeric stabilizers for the synthesis of polypyrrole colloids. Using a poly(2-(dimethylamino) ethylmethacrylate-stat-3-vinylthiophene)stabilizer, the polypyrrole particles had diameters of approximately 100 nm , contained $19 \text{ wt } \%$ stabilizer, and exhibited solid-state conductivities as high as 4 S cm^{-1}

Appel (1996) reported a method to deposit thin films of conductive polypyrrole powder on nonconductive substrates. Polypyrrole tosylate was synthesized by the chemical oxidation of pyrrole with ammonium persulfate in aqueous solution. They optimized the conductivity of polypyrrole through electrochemical by a variation of reaction conditions (concentration of pyrrole, time interval of oxidant addition, pyrrole/oxidant concentration and temperature). Then they produced a smooth film of polypyrrole and tested several methods of film deposition that was of high chemical stability, as can be seen from long time conductivity measurements

Fu (1997) investigated the use of SCCO_2 in the in-situ polymerization of pyrrole within a preformed polyurethane foam. They wanted to determine the

technical feasibility of replacing organic solvents with SCCO₂ through impregnating the oxidant into the foam and then, removing by products of the pyrrole polymerization reaction from the foams. It turned out that this method was less effective than using organic solvents for removing the reaction by products, presumably due to lower solubility of the products in SCCO₂ than in methanol.

Zhang (1997) investigated the plasma polymerization: the dense yellow film was deposited from pyrrole that can be detected by many methods. That shown the deposited plasma polymer still contains a certain amounts of pyrrole ring whose presence is important for doping of iodine and because of the chemical and structure disorder, the D.C. conductivity in the pristine film was very low but optical conductivity was considerably large.

Marco (1999) suggested the effects of oxidation and reduction to volume change of product on the basis of in-situ AFM experiments. They demonstrated that the morphology of Ppy at the initial stage of synthesis depended on the nature of the electrodes, the supporting electrolyte affects the kinetics of the synthesis process and after synthesis. The morphology of the Ppy film changed with time charge compensation during the early stages of Ppy redox reaction. That was probably accomplished by the cation transport rather than anion expulsion from the polymer matrix.

Reece (2002) investigated a new method to synthesize Ppy. Nitrate doped polypyrrole (Ppy) was coated onto polyurethane (PU) colloids using electro-hydro dynamic processing. Optimal yields for formation of the Ppy/NO₃/PU colloids were obtained using a polymerization potential of 0.60 V, a flow rate of 40 ml min.⁻¹ and a PU concentration of 4% w/v. Synthesis of Ppy/Tiron/PU colloids was accomplished using similar conditions to those used to prepare Ppy/NO₃/PU colloids. However, the reaction proceeded at a considerably faster rate (due to the fact that Tiron is an effective electro-catalyst for Ppy formation), giving a comparable yield of colloid in a shorter time. The UV-vis spectra of films cast from Ppy/Tiron/PU colloids were more typical of conducting Ppy than films obtained from Ppy/NO₃/PU colloids.

Song (2003) chemically synthesized Ppy powders by single-step polymerization at different oxidant concentrations, ranging from $[Mo]/[Ox] = 2.5$ to 15. As the ratio increased, the yield and conductivity decreased, while the solubility

of Ppy/DBSA in *m*-cresol was much higher above $[Mo]/[Ox] = 7.5$. FTIR study revealed that the poor conductivity at low oxidant concentration was related to the shorter conjugation length. When Ppy was doped with a series of alkylbenzenesulfonic acids (ABSAs) at $[Mo]/[Ox] = 7.5$, both doping level and yield increased while the conductivity decreased with increasing alkyl chain length in ABSA dopants. The controversy between doping level and conductivity might be attributed to the microstructure of Ppy. The high angle scattering peak at $2\theta \approx 26^\circ$ is relatively sharper with shorter chain length. Therefore, the shorter chain length of dopants resulted in higher conductivity due to short range ordering of polymer chains. UV/VIS/NIR results also confirmed the higher conductivity of shorter chain length systems by higher free carrier tail above 1000 nm.

2.10 Doping Ppy

Brie (1996) studied the action of ammonia on free-standing polypyrrole film doped with ClO_4^- and TsO^- . The gas sensitivity of conducting film of TsO^- doped polypyrrole films was different from that of film doped with ClO_4^- by the sensitivity to NH_3 was higher for the polypyrrole films with low initial conductivity. The responses of the polypyrrole films were identical for a long time interval, this result presented that free – standing polypyrrole films with relatively high conductivity are candidates for ammonia sensing

Li (1998) presented the effect of electrolyte concentration of the polymerization solution and temperature on the two doping structures. Conjugated chain doped with counter ion (1) and proton –acid doping structure (2) of polypyrrole nitrate film both were of high conductivity and of stronger mechanical property can be prepared from aqueous solutions at higher concentration and at low temperature. It was found that the doping degree of (1) increased with increasing $NaNO_3$ concentration in its polymerization solution and with decrease of temperature. Type (2) was easily formed in low electrolyte concentration and at high temperature.

Yfantis (1999) studied the effect of synthesis parameters as well as the structural changes of polypyrrole during aging. They varied chemical reagent to producing polypyrrole in aqueous solution doped. They were 3 fluoro-metal

complexes, fluorides and p-toluolsulfonates. All of them were incorporated and acted as counter ions within the polymers, their relative abundance depended on their relative size and concentration. That dopant contribution was found to increase when the size of the doping anion was decreasing. This was the main reason for the generally observed lower conductivity of polypyrrole prepared chemically. The result was the formation of the most stable fluoro-metal complexes with high coordination number. This process definitely led to a disorientation of the counter-ion and conductivity loss. Polypyrrole doped with fluoro-zirconate and with fluorotitanate both exhibited good stability on contrary to the polypyrrole doped with fluoro-aluminate which had poor stability due to the extended parallel incorporations of free fluoride and sulfate during doping.

2.11 Actuator or Artificial muscle

Shiga (1993) studied Dynamic viscoelasticity of immiscible polymer blends consisting of silicone elastomer and semiconducting polymer particles was studied under the influence of electric fields. The semiconducting polymers used experimentally were poly(p-phenylenes) lightly doped with CuCl_2 or FeCl_3 . The dc electric fields enhanced storage and loss shear moduli of the polymer blends (electroviscoelastic effect). The ac electric fields with frequencies of less than 1 kHz also induced the electroviscoelastic effect. The electroviscoelastic effect was observed in the rubbery state of the blends with many lines of adjacent particles spanning the space between electrodes. The electroviscoelastic behavior for the polymer blends with straight lines of adjacent particles aligned to electric fields was analyzed using a point-dipole approximation model for electrically polarized particles. The presented results provide insight into the relationship between mechanical properties of the blends and the cohesive forces between electrically polarized particles.

Kornbluh (2000) investigated the using of elastomeric dielectric materials with compliant electrodes as a means of actuation. When a voltage was applied to electrodes, the elastomeric films expanded in area and decreased its thickness. The strain response to applied electric fields was measured for a variety of elastomers. A

nonlinear, high-strain, Mooney–Rivlin model was used to determine the expected strain response for a given applied field. They determined the electrostatic forces between the free charges on the electrodes. Elastomeric polymers showed a promise as actuator materials when employed as a dielectric layer between compliant electrodes. Dielectric elastomer materials show excellent overall performance and appeared to be more attractive than many competitive actuators. Response was rapid, and the potential efficiency was high. Silicone polymers have produced the best combination of high strain and energy density

Onishi (2000) studied the induced bending motion in a perfluorinated polymer electrolyte by electric stimuli in water or saline solution by fabricate electrodes. A fluorocarboxylic acid membrane was soaked in Au (III) di-chloro phenanthroline complex solution and then any adsorbed Au (III) cation complex was reduced in aqueous sodium sulfate. Optimizing number of plating cycles (about 6-7) was reached beyond which little improvement in displacement occurred. A gradual loss in speed of response also occurred.

Fehér (2001) developed a new type of electric-field sensitive neutral polymer gels in a non-conductive medium. The main idea was to incorporate finely distributed colloidal particles into a swollen network responding to electric field. Since the particles cannot leave the gel matrix, thus all of the forces acting on the particles are directly transmitted to the polymer chains, resulting in either the locomotion or the deformation of the gel. Structural formation of TiO_2 particles dispersed in silicon oil and bending deformation of weakly crosslinked poly(dimethyl siloxane) gels containing finely distributed TiO_2 particles. The force for the non-contact mode of deformation derives from the interaction of the electric-field-induced charges with the external electric field. For application, the fast response, it is important to have large forces and a large displacement. The maximum charge before breakdown depends both on the voltage and the electric field. The lower limit is usually considered too weak to move macroscopic objects. A much higher value of the electric fields — which causes the breakdown in macroscopic cases — is typical of very small devices. It is the main reason why electrostatics tend to become more important in smaller scales

Madden (2001) found a model, system identification techniques are employed. Stress-strain tests were performed at constant applied potential to determine polypyrrole stiffness. They tested the important property of actuator such as the stress/strain relation and strain to charge relationship were combined to form a full description of polypyrrole electromechanical response. This description large increase in strain rate and power were obtained through miniaturization, yielding bandwidths in excess of 10 kHz. The modeling enables the designer to optimize actuator geometry for target loads, displacements, velocities, powers and geometries for their efficiencies applications

Patrick (2002) reported the synthesis of novel thiophene based conducting polymer molecular actuators. In this new class of materials, actuation was the result of conformational rearrangement of the polymer backbone at the molecular level due to ion intercalation in the bulk polymer chain upon electrochemical activation. Molecular actuation mechanisms resulted from π - π stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement which was expected to lead to surprising material properties such as electrically controllable porosity and large strains. They also assessed the mechanical properties.

Yan (2003) found factor that affected behavior of all-solid actuator by testing deformation of polyaniline (PANI) film and a solid polymer electrolyte (SPE) of poly(ethylene oxide) derivative (STO288). The PANI film and the SPE layer that showed the displacement and the response rate were mainly dependent on the applied voltage and the employed supporting salt. These experiments revealed that the influences of the humidity and temperature on the performance of the actuator were predominantly through the ionic conductivity of the SPE. From experiments they can concluded three factors concerning the the mechanism of the all-solid polyaniline actuators. 1) The redox changes, which are concerned with the accepting sites of the charged ions and conformation of the polyaniline molecules. 2) The direction and orientation of the molecular chains, which can affect the degree of displacement. 3) The amount of dopants in the polyaniline films, which is important for the degree and speed of the displacement in a similar way to that of general polymer gels.

Zhou (2003) developed novel polymer-in-ionic liquid electrolytes (PILEs) for solid state electrochemical actuators based on polypyrrole. They tested properties

of the PILEs to have wider electrochemical windows than conventional liquid electrolytes. Cyclic voltammetric studies showed that the Ppy was stable and a strain of 9/2 % was observed when a potential of 9/2.0 V was applied. The shelf life of a Ppy/PF₆/Pt/ PVDF/PILE electromechanical actuators was at least several months and the system can be subjected to continuous pulsing for more than 3600 cycles without degradation.

Careem (2004) fabricated the form bilayer strips using an insulating polymer layer and polypyrrole (Ppy) conducting polymer film. He measured force produced by them during redox processes and studied the effects of anions in the polymerization electrolyte and cations in the cycling electrolyte on the force generated by such muscles. Higher forces can be obtained with large surfactant anions. Higher force can be obtained from Ppy/DBS artificial muscles when they were cycled in electrolytes containing smaller cations.

Mitsumata (2004) investigated storage moduli of silicone gels containing barium titanate in the presence of dc electric fields. It was found that the silicone/BaTiO₃ gels swollen by silicone oil exhibited the negative electrorheological effect under electric fields. Compared to the swollen gels, no electrorheological effects were observed in unswollen silicone/BaTiO₃ gels, suggesting the electric coupling of particles and oil played an important role. Change in storage modulus of the swollen gels was strongly affected by both cross-linking density and BaTiO₃ concentration. Swollen silicone gels showed a large positive change in modulus, oppositely, the unswollen silicone gels did not show any change in modulus under electric fields. Swollen silicone gels and silicone/BaTiO₃ gels without $C_{\text{BTO}} = 0.1$ obeyed empirical quadratic dependence in electric field strength. The electric conductivity of the BaTiO₃ particles and the silicone oil used in the present study were 10^{-10} S/cm and 1.6×10^{-9} S/cm, respectively. Although an apparent phase separation was not observed in the swollen silicone/BaTiO₃ gel, microscopic phase separation may occur in spite of each BaTiO₃ particles are completely embedded in the gel matrix.

2.12 Ppy Composites

OMASTOVÁ (1996) prepared Polypropylene particles 35 μm in diameter were chemically coated with polypyrrole. The content of polypyrrole varied from 1 to 10.4 wt%. Polypropylene/polypyrrole (PP/Ppy) composite films about 0.2 mm thick were prepared by compression molding of modified powders. The electrical conductivity of compression molded samples depended on the concentration of polypyrrole. That conductivity reached values from 4×10^{-10} to $5 \times 10^{-3} \text{ S cm}^{-1}$ which was about seven orders of magnitude higher than the conductivity in the blends prepared by mechanical mixing of PP and Ppy in the same Ppy concentration range. The PP/Ppy composites were characterized by elemental analysis, infrared spectroscopy, light microscopy, scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA). SEM pictures showed significant difference in coverage of the surface of the PP particles, while the concentration changing was within the range from 1.1 wt% to 8.9 wt% Ppy.

Fan (1999) investigated polypyrrole (Ppy) which was synthesized on carbon nanotubes (CNT) using in-situ polymerization method, then tested with TEM which showed a uniform tubular morphology with diameter less than 100 nm. They characterized CNT-Ppy composites compared their properties between pure Ppy and pure carbon nanotube.

Rupali (1999) reports the preparation of nano-composites in which colloidal ferric oxide particles have been combined with polypyrrole (Ppy). The colloid particles are entrapped or encapsulated in the core of the growing polymer chain, resulting in the formation of an inorganic-organic hybrid material. This is improved different physical properties of Ppy such as its compactness and mechanical property, morphology, DC electrical conductivity, thermal annealing and resistance towards ambient condition etc. The mechanism of electrical transport in these materials is revealed by their low temperature conductivity (DC and AC) and thermoelectric power data. However, the improvements made in different physical properties of the present nano-composites are expected to enhance the application potential of the polymer without hampering its chemical properties.

Kim (2002) studied effect of the conductive polymer on the PET fabric/Ppy composite with high electrical conductivity. It was prepared by polymerization of Ppy on PET fabric. Polymerization was carried out by both chemical and electrochemical oxidation of pyrrole monomer. As a result, the specific volume resistivity of the composite was as low as about $0.2 \Omega \text{ cm}$, giving rise to EMI SE of about 36 dB over the wide range of frequency, where 7% of the power of the incident wave was absorbed by the composite, therefore the PET fabric/Ppy composite is practically useful for many applications requiring not only a high EMI SE but EMI shielding by absorption of the wave.

Çakmak (2004) prepared the conductive and flexible carbon fiber (CF) reinforced polydimethylsiloxane (PDMS)/polypyrrole (Ppy) composites were synthesized electrochemically, they had superior such as conductivity, thermal stability and mechanical properties. SEM studies showed that CFs was coated by PDMS/Ppy matrix uniformly. Conductivities of composites were observed in the range of 2.2–4 S/cm. In mechanical tests, it has been observed that tensile strength of composites increased with increasing CF content. Higher percent elongation was achieved by the addition of PDMS. Highly flexible, foldable mechanically strong conductive composites were obtained and thermal analysis revealed that insertion of CF to the matrix increased the decomposition temperature and made the films more thermally stable as 63% weight remained at 1000 °C.

He (2004) tested the Polypyrrole (Ppy) composite powders doped with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ of variable mass were prepared by a way of in situ chemical polymerization. Electrochemical properties were investigated with cyclic voltammetry, charge-discharge tests and A.C. impedance spectroscopy in 1 M NaNO_3 . Morphology and crystalline structure of these Ru-doped PPY powders were examined by transmission electron microscopic (TEM). The Ppy/Ru composites electrodes showed much higher specific capacitance than pure Ppy electrode that are more promising for application in supercapacitor.

Ruangchuay (2004) studied in the sensor response toward acetone and toluene. The sensor polypyrrole was doped with α -naphthalene sulfonate. They used different insulating polymers PEO, PMMA, HDPE, PS and ABS mixed by three different methods dry mixing, solution mixing and coating. Blending of PS, ABS

and PMMA from solution mixing showed a significant improvement in sensitivity and temporal response to acetone and toluene by swelling effect. Moreover, the response to water (error detection) was successfully diminished. The PMMA coated was an ideal water insensitive sensing material.