CHAPTER II
BACKGROUND AND LITERATURE REVIEWS

2.1 Polypyrrole

Conducting electroactive polymers (CEPs) have been intensively studied due to its wide applications. Polypyrrole is one example of CEPs. It could be formed by oxidation of pyrrole or substituted pyrrole monomers. In the vast majority of cases, these oxidations have been carried out by either electropolymerization at a conductive substrate (electrode) through the application of an external potential or chemical polymerization in solution by the use of a chemical oxidant. The idealized structure of polypyrrole and the mechanism for chemical and electrochemical preparation of polypyrrole via radical cation formation are shown in Figure 2.1 and Figure 2.2, respectively.
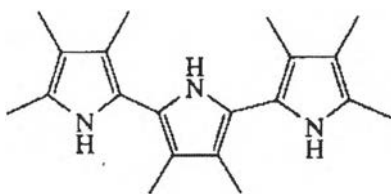

Figure 2.1 The idealized structure of polypyrrole.

Polypyrrole is very attractive CEP because it has good electrical, switching, optical, chemical and biochemical properties. However, it has some drawbacks in its properties, such as poor mechanical properties, weak processability and poor thermal stability which need to be improved to achieve a new function of polypyrrole.

Step 1. Monomer Oxidation

Resonance forms:

(I)   (II)   (III)
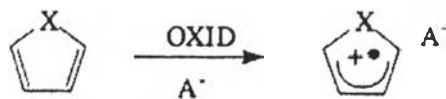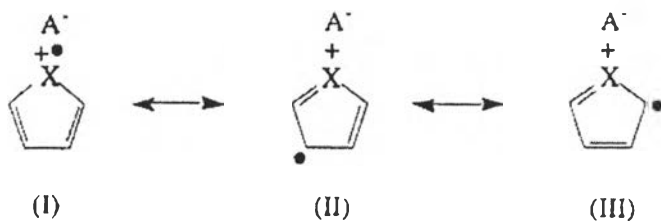
Step 2. Radical-Radical Coupling
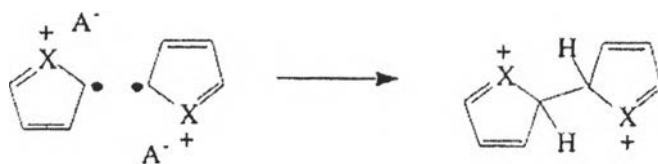
Step 3. Deprotonation/Re-Aromatization

(dimer)
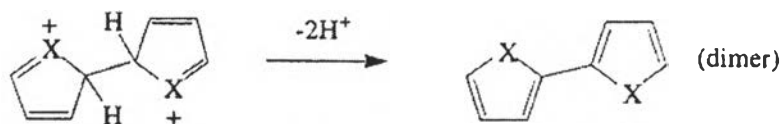
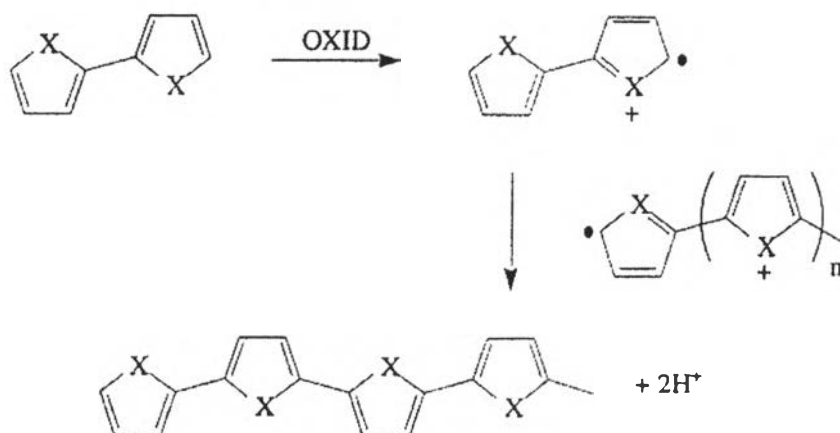**Step 4. Chain Propagation**

$+ 2H^+$

Figure 2.2 The mechanism for chemical and electrochemical preparation of polypyrrole via radical cation formation.

There are several research works on the preparation and characterization of electrically conductive polypyrrole to improve its shortcomings and to achieve the satisfactory applications.

Selampinar *et al.* (1995) employed the electrochemical polymerization process to synthesize polypyrrole-polyamide (PPy-PA) composite films for use as a gas sensor. They reported that the response of the resulting material PPy-PA composite films to NH_3 and CO_2 gases was better than pristine conducting polymer in terms of both rapid and reversible responses. In the same year, composite films of poly(vinylidine fluoride)-polypyrrole (PVDF/PPy) were also prepared by electrochemical polymerization of pyrrole on a very thin PVDF matrix film in order to improve mechanical properties of polypyrrole by Bhat *et al.* (1995). They found that the resulting PVDF/PPy films showed a decrease in tensile strength as the PPy content decreased, while the conductivity remained more or less similar to that of pure PPy.

Two years later, the preparation process of highly electrically conductive polymer composites of poly(metyl methacrylate) and polypyrrole (PMMA/PPy) was studied by Osmastova *et al.* (1997). They took the view that the composites were prepared by a chemical modification method resulting in a network-like structure of PPy embedded in the insulating polymer matrix. The results obtained from x-ray photoelectron spectroscopy indicated that pyrrole was polymerized inside the PMMA particles. Furthermore, their electrical conductivity was enhanced by more than four orders of magnitude and depended on the concentration of PPy. Shortly after this study, Selampinar *et al.* (1997) tried to improve thermal stability of PPy by preparing it in the form of conducting polymer composites. Therefore, a new electrically conducting composite film from PPy and 4, 4'-(hexafluoroiso propylidine)- bis(phthalic anhydride)- based polyimide was prepared. They revealed that pyrrole and the dopant ion could easily penetrate through the polyimide substrate and electropolymerize on the platinum electrode due to the swelling of the polyimide on the metal electrode. Besides, it was shown that the PI/PPy composites showed a rather high thermal stability and high

electrical conductivity and electroactivity associated with stability to ambient conditions when compared with the pure polymer.

Jesus *et al.* (1998) prepared electrically conductive nanocomposites by a selective in situ polymerization of pyrrole within the lamellae ionomeric microdomains of sulfonated poly(styrene-*b*-(ethylene-*alt*-propylene)), SEP, diblock copolymers. They said that incorporation of PPy into the block copolymer did not affect the alternating lamellae microstructure of the block copolymer but helped to improve the modulus of the melt above T_g of the sulfonated polystyrene microdomains. Moreover, a conductivity of 10^{-3}-10^{-1} S/cm was achieved parallel to the film surface for PPy concentrations from 5-11 wt% of PPy.

2.2 Polymer-Clay Nanocomposites

Polymers have been successfully reinforced by glass fibers and other inorganic materials. In these reinforced composites, the polymer and additives are not homogeneously dispersed on a nanometer level. If nanometer dispersion is achieved, the mechanical properties will be further improved.

A clay mineral is a potential nanoscale additive because it comprises silicate layers in which the fundamental unit is 1 nm thick planar structure. On the basis of clay crystalline properties, silicate clays can be divided into three major groups, which are kaolinite, montmorillonite (MMT), and hydrous mica groups. Among these three groups of silicate layers, MMT has often been used and was used in this work. MMT is a hydrous alumina silicate mineral with counterions present between the clay layers whose lamellae are constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, as shown in Figure 2.3.
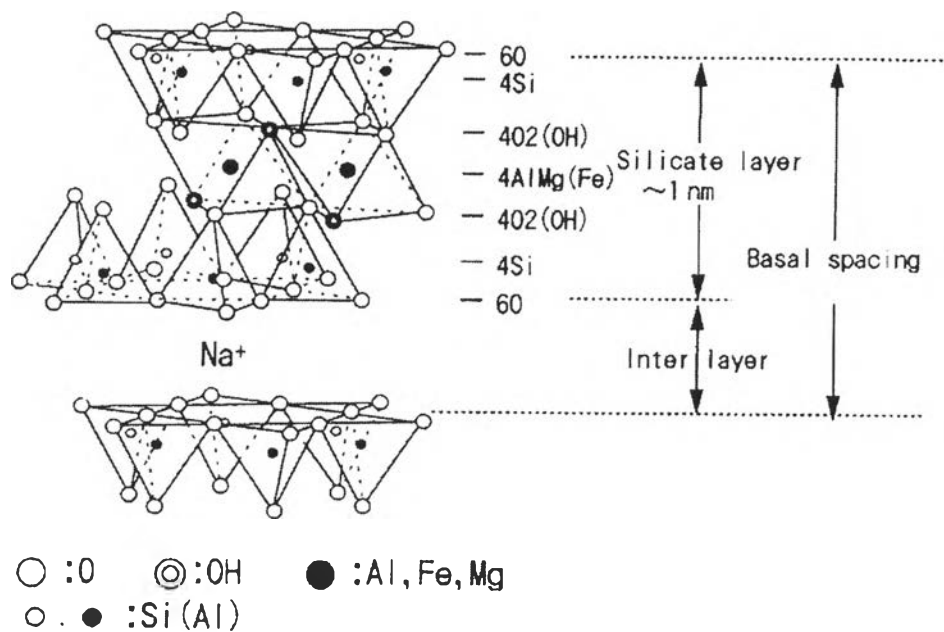
O :0 $\circledcirc$:OH $\bullet$:Al,Fe,Mg
o . $\bullet$:Si(Al)

Figure 2.3 Montmorillonite clay structure.

In general, the dispersion of the clay particles in a polymer matrix can be classified into three general types of composite materials which are shown in Figure 2.4.
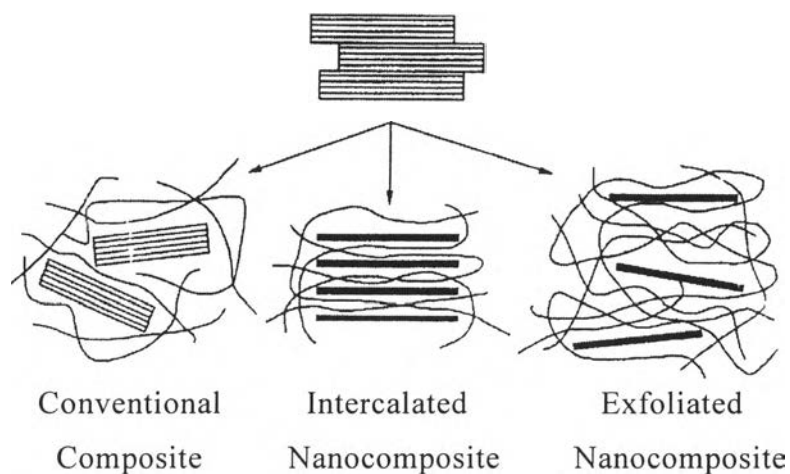

Conventional   Intercalated   Exfoliated
Composite   Nanocomposite   Nanocomposite

Figure 2.4 Schematic illustration of the three possible types of polymer-clay nanocomposites.

Conventional composites contain clay tactoids with the layers aggregated in unintercalated face-face form. The clay tactoids are simply dispersed as a segregated phase. Intercalated clay nanocomposites are intercalation compounds of definite structure formed by the insertion of one or more molecular layers of polymer into the clay host galleries and the properties usually resemble those of ceramic host. In contrast, exfoliated polymer-clay nanocomposites have low clay content, a monolithic structure, a separation between layers that depends on the polymer content of nanocomposites, and properties that reflect those of the nano-confined polymer.

Many research works involving in the preparation and characterization of polymer-clay nanocomposites have been vigorously investigated in order to overcome some drawbacks of the polymer interested.

A new polymer-ceramic nanocomposite consisting of well-dispersed, two-dimensional layers of an organically mica-type silicate (MTS) within a degradable poly(ε-caprolactone) matrix has been synthesized by Messersmith *et al.* (1995). A protonated amino acid derivative of MTS was used to promote delamination/dispersion of the host layers and initiate ring-opening polymerization of ε-caprolactone monomer, resulting in poly(ε-caprolactone) chains that were ionically bound to the silicate layers. It was found that permeability of water through these composite films containing modest amounts of silicate was dramatically reduced due to dispersion of impermeable high aspect ratio silicate layers within the polymer matrix. Two years later, Biswas *et al.* (1997) synthesized poly(N-vinylcarbazole)-montmorillonite nanocomposites via solution polymerization of N-vinylcarbazole (NVC) in the presence of MMT as a heterophase catalyst. From the results of TGA, it indicated that PNVC stability was much enhanced upon intercalation confirming formation of intimately associated microaggregates of PNVC and MMT. Conductivity of PNVC/MMT composite was also 10^{10} times greater than that for PNVC. After that, montmorillonite-based nanocomposites of polypyrrole were prepared through the polymerization of pyrrole with MMT

and FeCl$_3$-impregnated MMT in bulk medium by Sinharay *et al.* (1999). The XRD analyses revealed no change in d$_{001}$ spacing in MMT, suggesting no intercalation of PPy into MMT lamellae. They reported that the bulk conductivity of the composites was in the range of 1.3 to 26 x 10^{-5} S/cm, depending on the FeCl$_3$-impregnation level and on the PPy loading in the composites.

Tyan *et al.* (1999) studied the mechanical properties and thermal stability of clay/polyimide(pyromellitic dianhydride-4, 4'-oxydianiline, PMDA/ODA) nanocomposites. These nanocomposites were synthesized from the reactive organoclay formed by using p-phenylenediamine as a swelling agent for silicate layers of MMT and poly(amic acid). They found that the glass transition temperature and the thermal decomposition of these nanocomposites were higher than that of pure PMDA/PDA. In addition, both the maximum stress and the elongation at break of these clay/PMDA/ODA nanocomposites increased with the amount of organoclay.

The nanocomposite of polyaniline and Na-MMT was synthesized by Wu *et al.* (2000) in order to increase the conductivity of polyaniline. It was found that room temperature conductivity of the hybrid nanocomposite was 10^{-3} S/cm which had a relatively high conductivity in comparison with other PAn/inorganic host hybrids. This was due to the insertion of the conductive emeraldine salt form of PAn into the layers of MMT clay and a single chain with an extended chain conformation of PAn. They suggested that the extended PAn chains with high conjugation and small amount polymer bridges could enhance the conductivity of the hybrid nanocomposite. Shortly after this study, Liang *et al.* (2000) prepared a new thermosensitive polymer-clay nanocomposite with enhanced temperature response based on organically modified clay-poly(N-isopropylacrylamide) nanocomposites. They proposed that clay minerals in the nanocomposite were partially intercalated and partially exfoliated in the dried state and mostly exfoliated in the swollen state and reported that the interfacial chemistry between the clay minerals and the polymer in the new nanocomposite was modified through a coupling agent to favor a more efficient thermal transition. Furthermore, they showed that the

enhanced thermal response and increased release rate were desirable for a range of applications, including sensors, regulators, and controlled release devices.

Besides, Yeh *et al.* (2001) prepared polyaniline-organically modified MMT clay nanocomposites (PCN). They found that these nanocomposites in the form of coatings with low clay loading (e.g. 0.75 wt%) on cold-rolled steel were found much superior in corrosion protection and showed a better anticorrosion performance than those of conventional polyaniline. Moreover, the O_2 gas barrier of PCN materials exhibited a 400% reduction in permeability compared to conventional polyaniline. In this year, polystyrene-clay nanocomposites have been prepared using a bulk polymerization technique by Zhu *et al.* (2001). Three new onium salts have been used to prepare the nanocomposites, two were functionalized ammonium salts while the third was a phosphonium salt. Thermogravimetric analysis showed that thermal degradation of the nanocomposites occurred at a higher temperature than that of virgin polymer, especially the one with phosphonium clays. They reported that this may be useful when the polymer-clay mixture must be processed at the relatively high temperature. From cone calorimetry, it was found that the rate of heat release was significantly reduced by the formation of the nanocomposites. Shortly after this study, Hong *et al.* (2001) employed the direct one-step emulsion polymerization method to synthesize polypyrrole-montmorillonite nanocomposites by using DBSA as emulsifier and dopant. From the XRD patterns and the TEM photographs, they found the intercalation of PPy-DBSA between the clay layers in nanoscale. Moreover, the results from TGA showed that the thermal stability of PPy-DBSA/clay samples was improved due to the introduction of the clay.

Polypyrrole/caprolactam-modified montmorillonite clay composite was electropolymerized on a gold substrate by Liu *et al.* (2003). From the TGA results, it was clearly shown that the electropolymerized PPy/clay composite became more stable because at the ending temperature of 800°C, the weight loss of pure PPy reached 73.2% while that of the composite was just 44.0%. In addition, the SEM micrographs revealed that the film appeared

to be more densely packed for the PPy/clay composites; in contrast, pure PPy film showed a rougher and more porous surface morphology. Moreover, the conductivity of the composites was significantly enhanced from 26.4 S/cm for pure PPy to 322 S/cm and it could depress aging in comparison to pure PPy.