

CHAPTER I

INTRODUCTION

1.1 Problem Statement

The role of polymers in the electronics industry has been traditionally associated with insulating properties, whether these are for isolating metallic conductors or for use in photoresist technology. From that starting point, it was the pioneering work of MacDiarmid, Heeger, and Shirakawa that inspired chemists and physicists to consider the opportunity of using polymers as conductors. In 1977, they discovered that the conductivity of polyacetylene increases significantly upon doping with various electron acceptors or electron donors. This discovery created an entirely new field of conducting polymers, which was recognized by the award of the 2000 Nobel Prize in Chemistry to these scientists (Service, 2000).

The development of light-emitting devices based on inorganic semiconductors and conjugated organic molecules has for decades been an active research area. Polymeric materials offer many advantages, including their versatility for fabrication, flexibility, low cost, low operating voltage, long term stability against morphological changes, and the ease with color tuning of light emission.

However, polymer used in light-emitting diodes (LEDs) is inherently susceptible to oxygen and moisture. Several researches have been concentrated on improving the stability of the devices. A possible solution of this problem has been found by a process combining polymer with organically modified clay. Polymer nanocomposites may be a class of very promising new light-emitting material for good color-tunability and environmental stability. In this work, nanostructured composite materials consisting of polymer and layered inorganic silicate are the focus of interest.

1.2 Background

1.2.1 Light-Emitting Diodes

A light-emitting diode (LED) is a semiconductor device that emits visible light when an electric current passes through it. The efficiency of LEDs and range of wavelengths has increased since the early 1960s (Sheats *et al.*, 1996). The first commercial GaAsP LEDs (Figure 1.1) were introduced in 1962. The breakthrough came in 1987 with the work of Tang and Van Slyke who produced multilayer devices using thin evaporated films of 8-hydroxyquinoline aluminum and voltages of about 10 V. The introduction of a multilayer structure effected a better luminous efficiency. Prospects for commercialization of organic electroluminescence (EL) devices brightened with the work of Friend *et al.* (1990), who fabricated devices based on poly(*p*-phenylene vinylene) (PPV) which could be formed by spin coating from solution and subsequent thermal treatment. Since the development of a PPV precursor which can be solution processed, there has been increased interest and hope for a simple LED fabrication from polymeric materials.

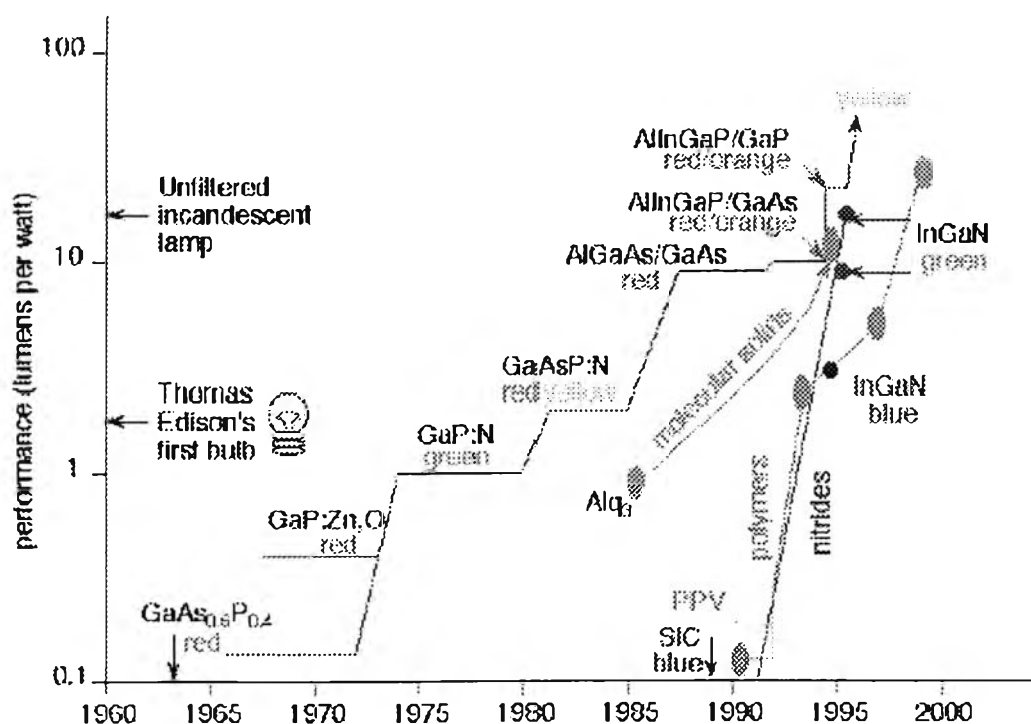


Figure 1.1 Evolution of LEDs performance.

Polymer LEDs have the potential to revolutionize display technology by enabling low cost, color flat panel displays with viewing properties comparable to conventional cathode ray tube. Polymer LEDs have been demonstrated with emission wavelengths throughout the visible spectrum, adequate luminous efficiency for large area displays and device operating lifetimes exceeding 7000 hours. In spite of these impressive results the intrinsic limits of polymer LED performance and operating lifetime have not yet been reached. It now appears that polymer LEDs will soon be utilized in a wide variety of display products.

The operating principles of polymer light-emitting diodes are fundamentally distinct from conventional inorganic semiconductor-based LEDs (Campbell *et al.*, 2002). The rectification and light-emitting properties of inorganic LEDs are due to the electrical junction between oppositely doped, p and n type regions of the inorganic semiconductor. In contrast, polymer LEDs are formed using an undoped, insulating polymer. The rectification and light-emitting properties of the polymer LEDs are caused by the use of asymmetric metal contacts.

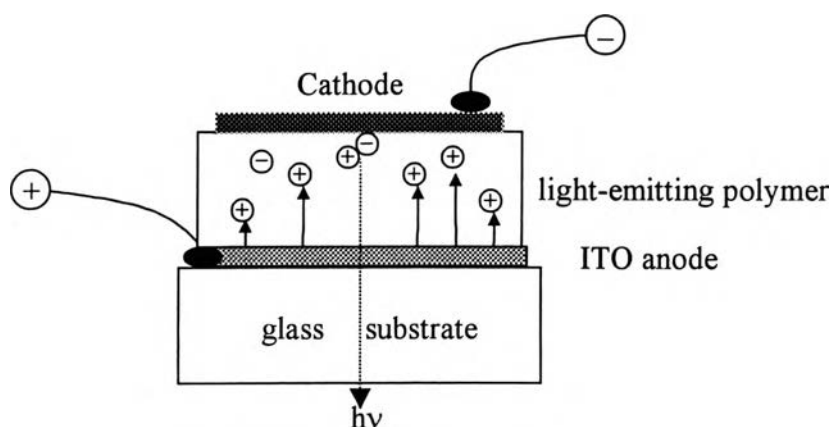


Figure 1.2 Schematic drawing of a single-layer electroluminescent device.

As illustrated by Figure 1.2, one metal contact is only able to inject electrons efficiently and the other contact only injects holes efficiently. The injected electrons and holes recombine in the undoped polymer emitting light. High work function metals inject holes more efficiently than electrons and, similarly, low work function metals inject electrons more efficiently than holes. Therefore, the high work function metal is the anode and the low work function metal is the cathode.

Formation of an electron-hole pair within the polymer may then result in the emission of light.

1.2.1.1 Poly(*p*-phenylene vinylene) (PPV)

Poly(*p*-phenylene vinylene) or PPV (Figure 1.3) is the most studied conjugated polymer for electroluminescence emission and serves as a useful system for elucidating the working principle for polymer light-emitting diodes.

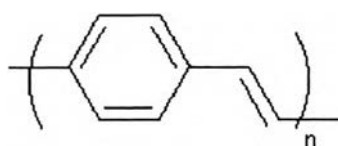


Figure 1.3 Chemical structure of poly(*p*-phenylene vinylene) (PPV).

The most common method to prepare PPV is illustrated in Figure 1.4 from the sulfonium precursor polymer. While PPV is an intractable material with a rigid-rod microcrystalline structure, the precursor polymer is solution processable and can be converted into the conjugated structure by thermal treatment.

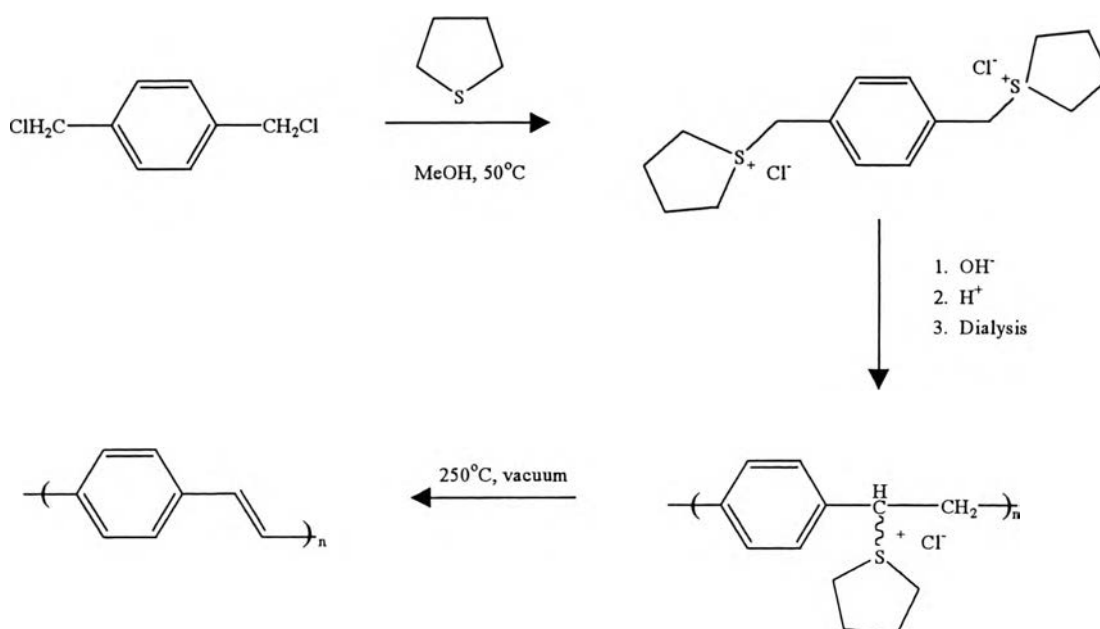


Figure 1.4 Synthetic route to PPV.

1.2.1.2 Protein Extracted from the Scales of Seabass

Seabass, *Lates calcarifer* (Bloch), also called giant sea perch (Table 1.1), is an economically important food fish in the tropical and subtropical regions of Asia and the Pacific (Figure 1.5). It is commercially cultivated in Thailand, Malaysia, Singapore, Indonesia, Hong Kong and Taiwan, in both brackishwater and freshwater ponds, as well as in cages in coastal waters. Because of its relatively high market value, it has become an attractive commodity of both large and small-scale aquaculture enterprises.

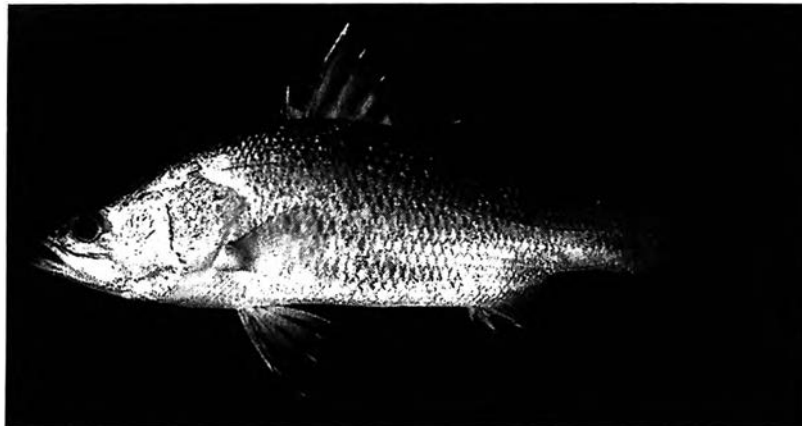


Figure 1.5 Seabass or giant sea perch.

Giant sea perch (called Pla Kapong Khao in Thailand) is famous for its beautiful fluorescent skin. Recently, Pramotethana *et al.* (2002) extracted protein from the skin of giant sea perch. They have successfully obtained the first observation of EL emission from biological materials. Therefore, this study also contributes utilization of natural resources. In future, polymeric materials for next generation displays in all over the world may be provided from Thailand sea.

Table 1.1 Taxonomy Of Giant Sea Perch

Phylum	Chordata
Sub-phylum	Vertebrata
Class	Pisces
Sub-class	Teleostomi
Order	Percomorphi
Family	Centropomidae
Genus	Lates
Species	Lates calcarifer (Bloch)

1.2.2 Clay Filler

Clay or layered silicate is a specific material in soil which consists of many kinds of minerals. Several basic properties of clay minerals guide all of the study devoted to them. The most important is the capacity of certain clays to change volume by absorbing water molecules or other polar ions into their structure. This is called the swelling property. Clays are thus divided into swelling and non-swelling type materials. Swelling clays are called smectites. Small particles of other non-sheet silicate materials can have some of the properties of clays, forming gels or thixotropic states, but the swelling properties are unique to the clay mineral world.

There are many species of clays in a group of smectite clay minerals which consist of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers as list in Table 1.2

Table 1.2 The species in smectite clay group

Subgroup	Species	Ideal Formula
Saponites	Saponites	$\text{Na}_{0.6}[\text{Mg}_6(\text{Al}_{0.6}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$
	Hectorite	$\text{Li}_{0.6}[(\text{Li}_{1.6}\text{Mg}_{4.4})\text{Si}_8\text{O}_{20}(\text{OH})_4]$
	Fluorohectorite	$\text{Li}_{0.6}[(\text{Li}_{1.6}\text{Mg}_{4.4})\text{Si}_8\text{O}_{20}\text{F}_4]$
Montmorillonites	Montmorillonite	$\text{Na}_{0.6}[(\text{Mg}_{0.6}\text{Al}_{3.4})\text{Si}_8\text{O}_{20}(\text{OH})_4]$
	Beidellite	$\text{Na}_{0.6}[\text{Al}_4(\text{Al}_{0.9}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$

Montmorillonite is a group of smectic-clay minerals which consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Hofman *et al.*, 1933). The suggested crystallographic structure of montmorillonite is illustrated in Figure 1.6. Isomorphous substitutions of Si^{4+} for Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet cause an excess of negative charges are counterbalanced by cations such as Ca^{2+} and Na^+ situated between the layers. Due to the high hydrophilicity of the clay, water molecules are usually also present between the layers. Stacking of the layers leads to regular van der Waals gaps called interlayers or galleries.

The sum of the single layer thickness (9.6 Å) and the interlayer represents the repeat unit of the multilayer material, so called d-spacing or basal spacing, and is calculated from the (001) harmonics obtained from X-ray diffraction patterns. The d-spacing between the silica-alumina-silica units for a Na-montmorillonite varies from 9.6 Å for the clay in the collapsed state to 20 Å when the clay is dispersed in water solution (Mering, 1946).

Montmorillonite, and other layered silicate clays, are naturally hydrophilic. This makes them poorly suited to mixing and interacting with most polymer matrices. Moreover, the stacks of clay platelets are held tightly together by

electrostatic forces. For these reasons, the clay must be treated before it can be used to make nanocomposite. Its dispersibility can be improved to make it useful by ion exchanges with an organic cation molecule, such as cationic surfactant, onto the filler 's surface. The functions of organic cation molecules in organophilic-clay are to lower the surface free energy of the silicate layers and to improve the wettability behavior of hydrophilic polymer matrix. In addition, the organic cation may contain various functional groups that can react with the polymer molecule to improve the adhesion strength between the inorganic phase and the matrix as reported by Giannelis (1996).

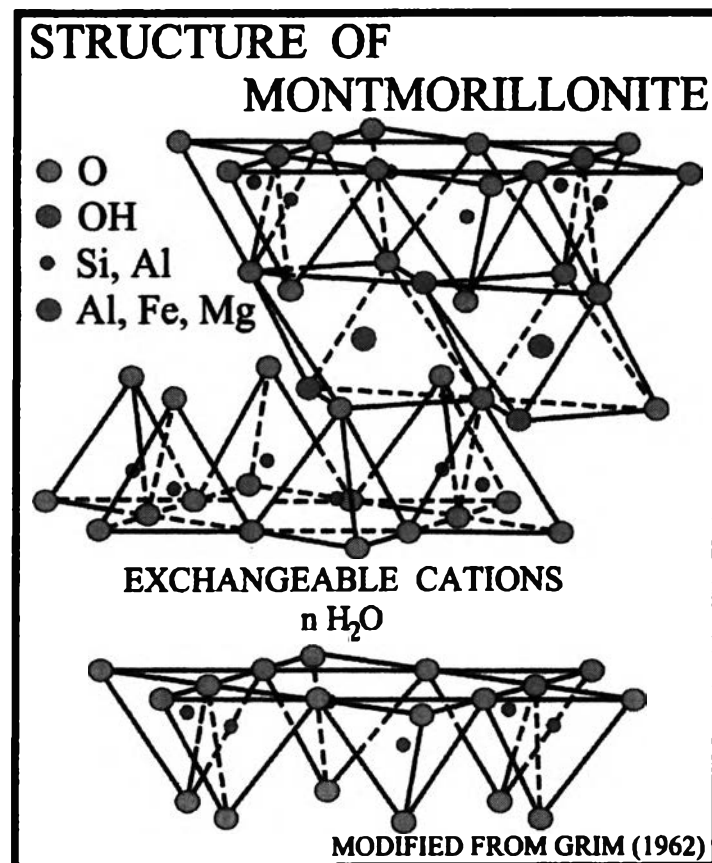


Figure 1.6 Model of 2:1 type clay montmorillonite.

1.2.3 Nanocomposites

The term “nanocomposite” describes a two-phase material where one of the phase is dispersed in the second one on a nanometer (10^{-9} m) level. Nanocomposites are a new class of minerals that exhibit ultrafine phase dimensions. Smectite clays and related layered silicates are the materials of choice for polymer nanocomposite designing for two principal reasons. Firstly, they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale. Secondly, they occur ubiquitously in nature and can be obtained in mineralogically pure form at low cost.

From a structural point of view, polymer-clay composite can be generally classified into conventional composite and nanocomposite. In a conventional composite, the registry of the clay nanolayers is retained when mixed with the polymer, but there is no intercalation of the polymer into the layered silicate

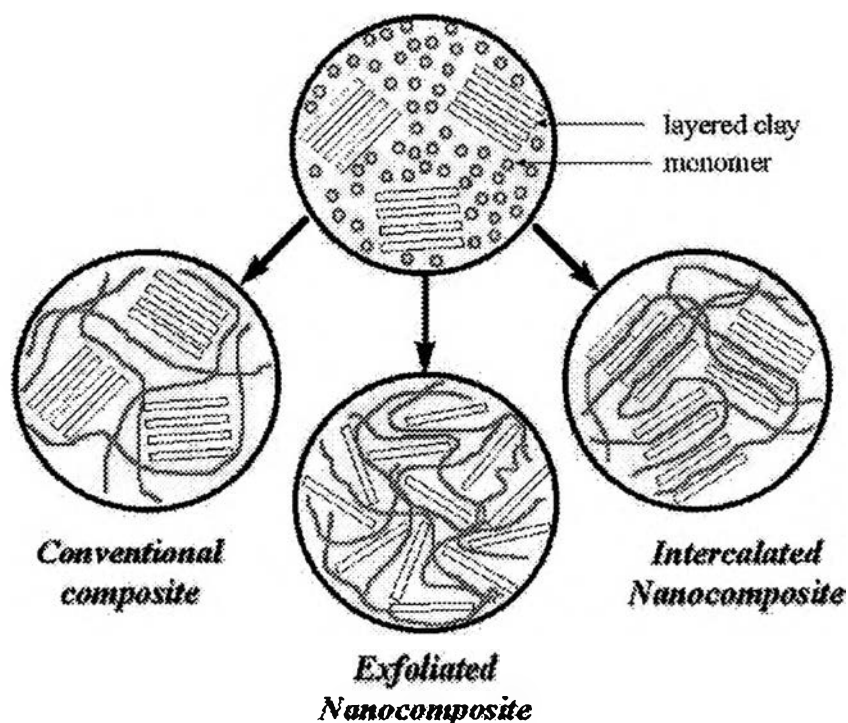


Figure 1.7 Schematic illustrations of the three possible types of polymer-clay composites.

structure (Figure 1.7). Consequently, the clay fraction in conventional clay composite plays little or no functional role and acts mainly as a filling agent for economic considerations.

Two types of polymer-clay nanocomposites are possible. Intercalated nanocomposites are formed when one or a few molecular layers of polymer are inserted into the clay galleries with fixed interlayer spacings. Exfoliated nanocomposites are formed when the silicate nanolayers are individually dispersed in the polymer matrix, the average distance between the segregated layers being dependent on the clay loading. The separation between the exfoliated nanolayers may be uniform (regular) or variable (disordered). Exfoliated nanocomposites show greater phase homogeneity than intercalated nanocomposites. More importantly, each nanolayer in an exfoliated nanocomposite contributes fully to interfacial interactions with the matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective in improving the reinforcement and other performance properties of clay composite materials.

1.2.4 Properties of Polymer-Clay Nanocomposites

Today's nanocomposites typically demonstrate unique improvement in material properties. The increasing interest devoted to polymer-clay nanocomposites arises from the fact that clay gives the possibility to modify drastically not only the mechanical properties of the polymer but also some of its physical properties. For LEDs application, the characteristic changes of polymer brought by the nanocomposites structure are described.

1.2.4.1 Color Tunability

The color tuning is one of the important advantages of inorganic over inorganic LEDs. The length of the conjugation sets certain characteristics of the molecule. The length defines the length where the electron is free to move within. Naturally, small molecules tend to have short conjugation length, while longer conjugated molecules may have a longer conjugation length resulting in a smaller bandgap. If the conjugation length of a molecule increases to affinity, the bandgap is closely to zero, which could be compared to the conductivity

for a metal structure. This may be done by doping, i.e. introducing ions to the conjugated molecule, or by changing the side chains of the conjugated molecule. Moreover, the introduction of clay nanoparticles into polymer matrix is a new choice to adjust the conjugation length.

1.2.4.2 Environmental Stability

Efforts have focused on improving the lifetimes of light-emitting devices. One of the primary degradation mechanisms is photo-oxidation (Hale *et al.*, 1997). In photo-oxidation, oxygen undergoes reaction across the double bond which cleaves to form two terminal aldehydes as shown in Figure 1.8.

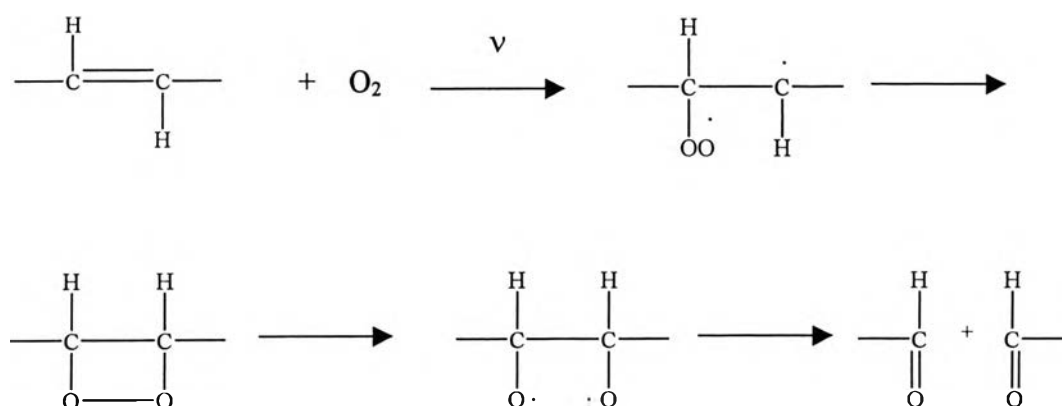


Figure 1.8 Photodegradation mechanism.

The reaction occurs chain scission which causes consequent shortening of the conjugation length. The result indicates that oxygen-sensitive polymer can be degraded by its own emitted light in an oxygen environment. This photodegradation of conjugated polymer may seriously effect the performance of devices. It is important to keep the devices from oxygen. Consequently, the constraint brought by the nanocomposites structure to the polymer chains is the essential factor contributing to the decrease of oxygen permeability.

1.3 Objectives

The objectives of this research work are:

1.3.1 To synthesize poly(*p*-phenylene vinylene) (PPV) and prepare protein extracted from the scales of seabass used as light-emitting polymers.

1.3.2 To study poly(*p*-phenylene vinylene) (PPV), protein extracted from the scales of seabass, and their nanocomposites for color tunability and environmental stability.