

# CHAPTER I

## INTRODUCTION

### 1.1 Problem Statement

Conjugated polymers attract much interest because they combine the properties of organic macromolecules, such as good mechanical behavior and ease of fabrication, with semiconductor properties that arise from their particular electronic structure. Then conducting organic polymers are a novel class of synthetic metals. These advanced materials are potentially very interesting for use in photonic and electronic applications.

One of the major current research topics is light emission. Many conjugated polymer are highly fluorescent, which makes them suitable for use as laser dyes and active materials in light-emitting diodes.

A number of researches have interested in the photonic and electronic characteristic properties of conjugated polymers. Especially, poly(para-phenylene vinylene)(PPV) and its derivatives.

Poly(para-phenylenevinylene) PPV is the first conjugated polymer used in a light-emitting device but the polymer is not soluble in organic solvents and cannot be easily processed by the spin coating. Subsequently, soluble precursor polymers to PPV were developed. Alternatively, PPV derivatives, which are soluble in organic solvents, were synthesized by incorporation of flexible side groups. PPV and its derivatives usually emit lights in the range from green to red, depending on their chemical structures. Theoretically, it may be possible to obtain blue light-emitting PPV derivatives by interrupting the conjugation along the PPV main chain with chemical modification. PPVs are interesting in their easily modified properties and the well-defined phenylenevinylene-based chromophores because they can be covalently linked to polymer main chains or can be polymerized with nonconjugated segment-forming comonomers. Consequently, the physical properties of polymers such as thermal stability and film formability can be easily controlled by selecting proper main chain or nonconjugated segment.

There are many reasons for this attention that are the first; poly(para-phenylene vinylene) is easy synthesized in good purity and high molecular weight, the second, it is not only relatively stable and quite insoluble, but also it can be manipulated as a water-soluble precursor polymer to form films and fibers, and the optical band gap of  $\sim 2.6$  eV and bright yellow fluorescent make PPV a strong contender in applications such as light-emitting diodes and photovoltaic devices. Moreover, it can be readily doped to form electrically conductive materials, and its physical and electronic properties can be varied over a wide range by the inclusion of functional side groups. Even 30 years after its first synthesis, there is still much to learn about this interesting polymer.

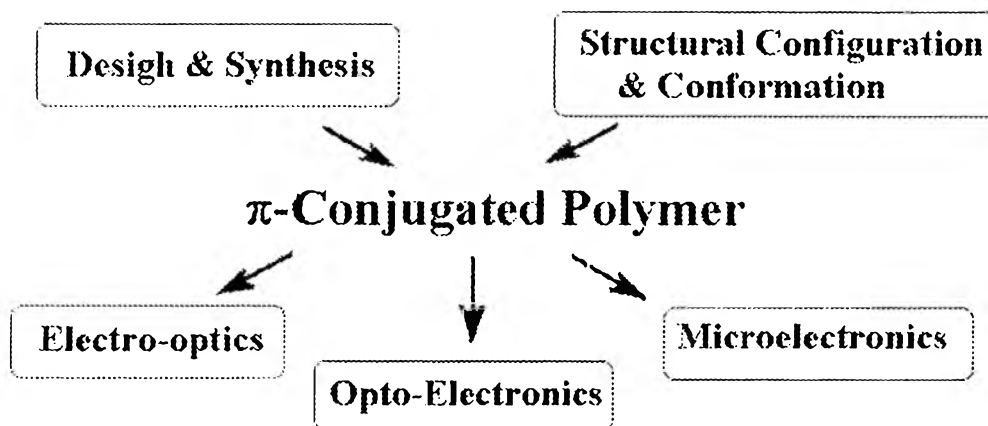
In recent years, PPV derivatives such as 1,4-bis-(R-cyano-stryryl)-benzenes (Kinami *et al.*, 2005), and 1,4-bis-(R-cyano-alkoxystyryl)-benzenes (Crenshaw *et al.*, 2003) are employed to blend with polymeric host materials such as poly (methylmethacrylate), polystyrene, polyethylene, and linear low density polyethylene. The interesting properties that came from the researches of PPV derivatives blending are the changed emission characteristics when they are under stress or strain and when the temperature is changed. Because of the dye molecules or PPV derivatives aggregation properties, it can be used as deformation or temperature sensor. Nevertheless, no one used natural rubber to be the host.

The purposes of this work are first is to synthesize poly(para-phenylene vinylene) (PPV) and oligo(phenylene vinylene)(OPV). The second is to compare the luminescent properties of PPV grafted on natural rubber as well as OPV grafting on the same host material. The third is to find the optimum amounts of PPV or OPV that is added in the host material to get the good strain sensitive photonic natural rubber from grafting method. The final is to study the properties when incorporated photoluminescent additive in to natural rubber that may be developed to be special material, which combine photoluminescent with elasticity and other important mechanical properties that are imported by the rubber matrix.

## 1.2 Background

Unique microelectronic and photonic applications are emerging in which  $\Pi$ -conjugated polymers and oligomers complement, or even replace, conventional inorganic and metallic component. The relationship between the chemical and physical properties has become a subject of intense study because of the potential impact on novel and existing technologies. For many of these applications, the effect of light on  $\Pi$ -conjugated polymers is critical issue which determines whether they are ever likely to play a significant role in specialized technical innovations such as optoelectronic and photoconduction display, electroluminescent displays, photovoltaic cells, photolithography, and electronically conducting polymer wires.

However, until recently very few studies existed in which chemical reactions resulting from the interaction of light with  $\Pi$ -conjugated polymer were investigated. A growing interest in photochemical processes of conjugated polymer has occurred since the emergence of polymer-based electroluminescent display technologies. For these devices to be commercially feasible, the polymer must be photochemically stable.



**Figure 1.1** Applications of  $\Pi$ -conjugated polymers (Nalwa *et al.*, 1997).

### 1.2.1 Photophysics

No photochemical reactions occur unless a photon of light is absorbed. For polymer, two types of chromophore are important: intrinsic chromophores, such as functional groups: and extrinsic chromophores are arising from impurities and additives. The principle laws governing the absorption of light by materials are Lambert's and Beer's laws. The first of these states that is the proportion of light absorbed by a transparent medium is independent of the intensity of the incident light and that each successive layer of the medium absorbs an equal fraction of the light passing through it. Mathematically; this leads to the expression.

$$\log_{10} \left[ \frac{I_0}{I} \right] = KI \quad 1.1$$

Where  $I_0$  and  $I$  are the intensity of the incident and transmitted light, respectively,  $I$  is the thickness of the absorbing material (cm), and  $K$  is the penetration defined as the distance over which the incident light attenuates  $e$  times. Beer's law incorporates a concentration variable, and states that 'the amount of light absorbed is proportional to the number of molecules of absorbing substance through which the light passes'. Defined mathematically as

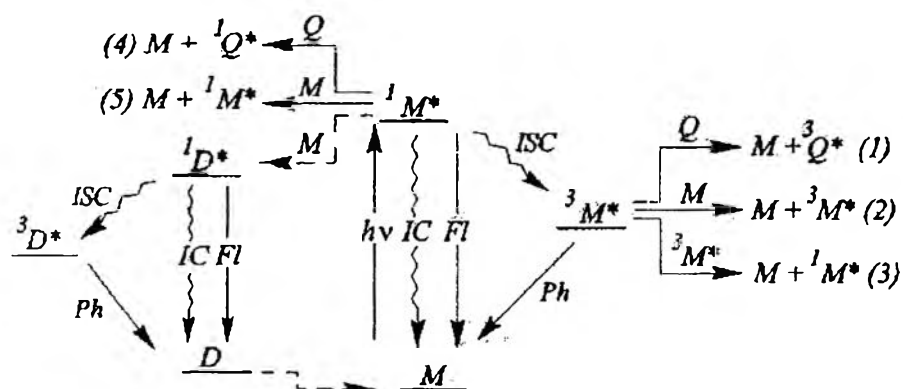
$$\log_{10} \left[ \frac{I_0}{I} \right] = \epsilon cl \quad 1.2$$

Where  $\epsilon$  is the molar extinction coefficient ( $\text{l mol}^{-1} \text{cm}^{-1}$ ), and  $c$  is the concentration of chromophore ( $\text{mol}^{-1}$ ). For convenience, the term  $\log_{10} (I/I_0)$  is usually replaced by absorbance,  $A$ .

Absorption of light creates an excited state analog of the ground state from which photochemical reaction can occur. Various photophysical routes for deactivation of the excited state are available. The rate of deactivate determines the inherent lifetime of the excited state and the time period over which photochemical reaction must process. Macromolecules share many fundamental photophysical processes with monomeric analogs but subtle differences exist due to the contiguous nature of polymer chains and the relatively high local concentration of

chromophores. For detailed account on photophysics of polymer, reader is referred to one of number of excellent monographs on the subjects.

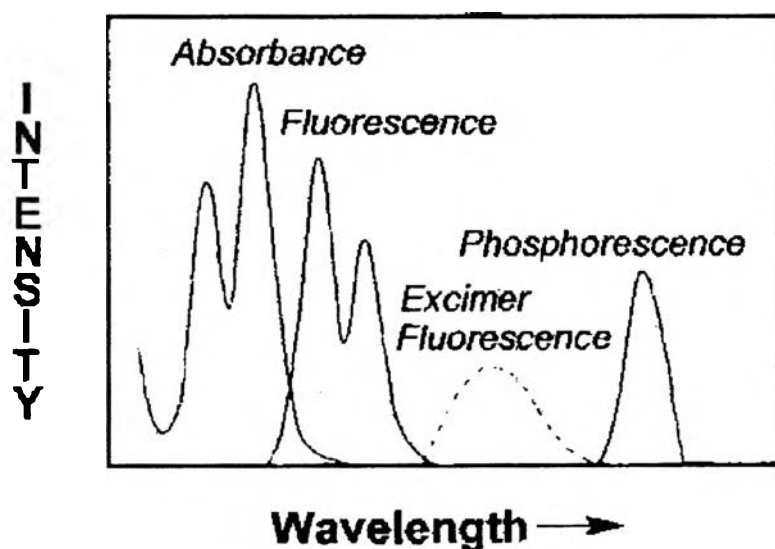
Key photophysical processes related to polymers are shown in Figure 1.2. Absorption of a photon promotes an electron from ground state ( $M$ ) to a higher energy state, usually singlet in nature ( $M^*$ ). Fluorescent transition (FI) occurs following excitation between states of the same multiplicity occurs on a much longer lifetime ( $\tau \sim 10^{-6}$ - $10^{-12}$ s). Non-radiative transitions of internal conversion (IC) and inter-system crossing (ISC) compete with radiative processes. IC is relatively fast ( $\tau \sim 10^{-12}$  s) and occur via vibronic coupling between an upper excited state to the lowest excited or ground state. Inter-system crossing is spin-forbidden radiationless transition ( $\tau \sim 10^{-11}$ - $10^{-6}$  s) by which triplet state are usually populated.



**Figure 1.2** Photophysical processes of polymers (Nalwa *et al.*, 1997).

The nature and local concentrations of the chromophore determine whether deactivation occurs unimolecularly or bimolecularly. When the local density of chromophores is high, such as in the case of  $\Pi$ -conjugated polymers, interaction can exist between the excited species and its nearest ground state neighbors. When this interaction occurs within the lifetime of the excited state, bimolecular mechanisms dominate deactivation processes. Quenching (Figure 1.2 paths 1 and annihilation (path 3) are bimolecular processes. Annihilation is rare for singlet state and can interact with ground state molecule of the same species to yield an excimer ( $D^*$ ), characterized by a broad, structureless fluorescence, which is red-shifted with

respect to monomer fluorescence. Many excimers have very low quantum yields of luminescence. The ground state dimer (D) is unstable and readily dissociates. Complex formation between excited state species and ground state or the difference molecules, gives rise to an exciplex. Emission characteristics are similar to those associated with excimers. Typical emission characteristics of lumiphore-bearing polymers are shown in Figure 1.3.

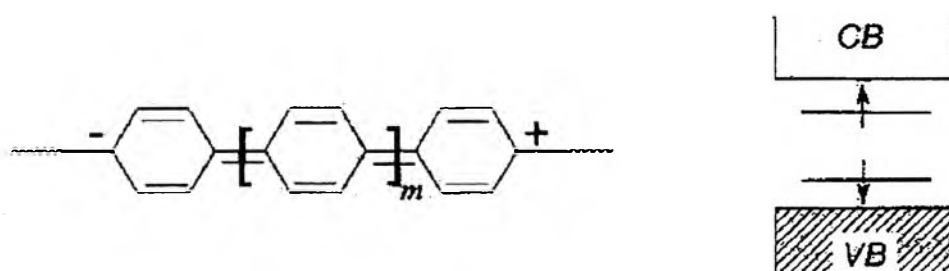


**Figure 1.3** Emission characteristics of luminescent polymer (Nalwa *et al.*, 1997).

Both radiative and internal conversion processes, whether originating from individual excited state molecules or excited complexes, generally serve to deactivate the excited state respect to the photochemical reaction. However, in some instances, non radiative processes can enhance photochemical reaction. In the first instance, energy transfer, as defined as the donation of excitation energy from one molecule to another, can serve to funnel excitation energy into a reactive center. The 'antennae effect' has been well documented for lumiphore-bearing polymer. Secondly, oxygen is efficient quencher of both singlet and triplet excited states, forming singlet oxygen ( $O_2$ ) in the processes. Singlet oxygen has a sufficiently long lifetime and is sufficiently reactive to initiate reactions with most unsaturated hydrocarbon.

Detailed photophysical studies of  $\Pi$ -conjugated polymer began in the 1970s with poly (phenylacetylene) when it was realized that energy migration between pendent phenyl groups attached to polyconjugated chain was extremely efficient due to strong interactions between the chromophore and the unsaturated backbone. Photophysical studies have since been used to provide fundamental information regarding the electronic structure of  $\Pi$ -conjugated polymers. Their photophysical properties have also achieved significant technical interest because of potential applications in optoelectronics and electro-optics, particularly in the area of electroluminescence displays. Demonstration of lasting, photoconduction, photodegradation, and photoimaging of conjugated polymers also draws attention to the fate of excited states of these materials.

Many of this case of polymer fluoresce because of the delocalized  $\Pi$ -conjugated system. For  $\Pi$ -conjugated polymers other than the parent polyacetylene, two non-degenerate configurations are possible: the benzenoid and quinoid forms. Usually, the former has the lower ground state energy, but the reverse is the case in the excited state. Photoexcitation results in formation of polaron-exciton. There is a tendency for this excitation to become self-trapped and confined to the polymer chain because of the quasi-one dimensional nature of the chain. Dissociation of the excited state species results in photoconductivity and non-radiative decay whereas recombination can yield luminescence. The excited state configuration and the corresponding electronic energy diagram of a typically conjugated polymer, poly (p-phenylene), are illustrated in Figure 1.4.



**Figure 1.4** Excited state of poly(p-phenylene) (Nalwa *et al.*, 1997).

Of the conjugated polymers, photoluminescence of polyacetylene, poly(phenylene), poly(aryl vinylene)s and polythiophenes have been extensively examined. Many related polymers, including polypyrroles and polyaniline, are not considered photoluminescent because of competitive and efficient non-radiative processes. The photophysical properties of conjugated polymers are similarly because of their common  $\Pi$ -structure but variations exist in the color of emission, radiative lifetime and quantum efficiency of luminescence. These attributes are dependent on the molecular architecture which determines the band gap energy.  $\Pi$ - $\Pi^*$  transition energies (absorption and emission) decrease as the extent of conjugated increase according to the particle in a box theory. The photophysics also depend on the conformation of the polymer. In the solid state the polymer takes up a rod-like conformation which imparts a red shift to the fluorescence compared to the coil-like conformation adopted in solution. Thus, the wavelength of maximum emission exhibits a blue shift of up to 100 nm upon dissolution of the polymers due to interannular bond rotation. Similarly, the presence of the large bulky substituents attached to the conjugated backbone prevents the polymer from achieving a planar configuration and increase the  $\Pi$ - $\Pi^*$  transition energy. Noticeably, both absorption and emission spectra are broad due to the conformational statistics of the polymer coil which segmentalized  $\Pi$ -conjugated lengths into a range of persistence lengths. Stoke's shifts are usually large due to relaxation of the structure in the excited state.

The triplet state of conjugated polymers has not been studied in much detail, largely due to its very weak phosphorescence. As a result, there is considerable uncertainty about the role of triplet in the electronic structure of the ground and excited states of conjugated polymers. It appears that the triplet may be weakly populated which means that photochemistry is not likely to take place from this longer-lived state. A heavy-atom effect has also been employed to induce more efficient intersystem crossing due to enhanced spin-orbit coupling.

### 1.2.2 Photochemical processes relevant to conductive polymers

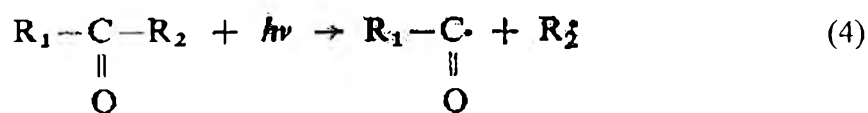
Photochemical reactions can originate from radical ions or excited states. If we concentrate the discussion on irradiation with light of photon energies smaller than the ionization potential, chemical changes can be initiated either by exciting molecules to repulsive states or by generating long-lived excited state which



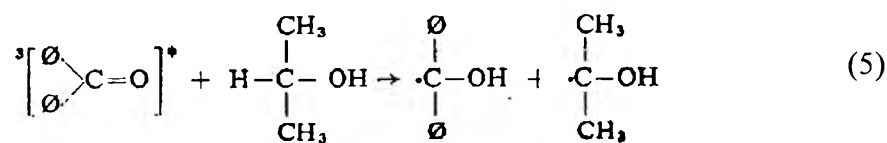
are capable of interacting chemically with other molecules. It was pointed out in the preceding section that radiative and radiationless i.e. physical deactivation routes are always competing with chemical routes. Quite seldom one observes quantum yields close to unity for chemical conversions. Usually, only a small portion of the total excited states deactivates via chemical routes. With respect to the initiation of photochemical reactions, it is appropriate to distinguish primary from secondary photochemical processes. In a primary process, the excited molecule dissociates into free radicals, for example:



A typical example pertains to  $\alpha$ -scission of ketones (also referred to as Norrish type I process).

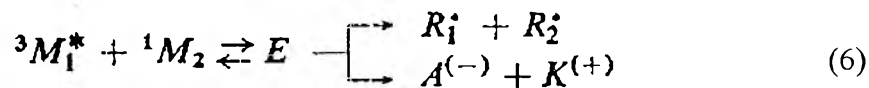


A typical secondary photochemical process is depicted in reaction (15):



In this case a rather long-lived triplet-excited ketone (benzophenone) reacts with a hydrogen donor (2-propanol) to form ketyl and 2-hydroxy-2-propyl radicals.

The generation of ions becomes under certain conditions, e.g., if triplet from exciplex E with ground state molecules of a second compound present in the system.



Exciplexes are complexes of excited chromophores and non-excited molecules of different chemical nature. Ions are formed if exciplexes dissociate according to reaction.

Moreover, ionic transient can be produced upon irradiation of charge transfer complexes with light of wave lengths corresponding to photon energies significantly smaller than the ionization energy of the constituents of the complex:



According to the definition given above, reaction should be classified as a primary process.

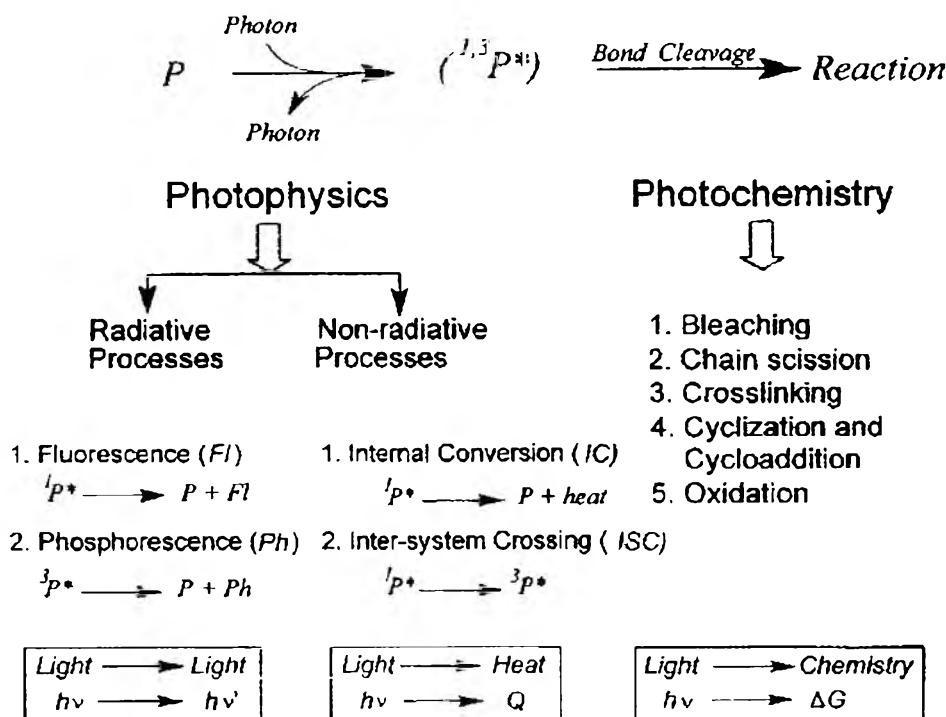


Figure 1.5 Photochemical processes of polymers (Nalwa *et al.*, 1997).

## **OBJECTIVES**

1. To synthesize poly(p-phenylene vinylene) and oligo(p-phenylene vinylene)
2. To study poly(p-phenylene vinylene) and oligo(p-phenylene vinylene) grafted on natural rubber for strain photonic sensor

## **SCOPE OF RESEARCH WORK**

The scope of this research work will cover:

1. The effect of amounts of PPV and OPV that are grafted to a hosting natural rubber in the range 0.5-4 %w of each dye on the luminescence property
2. Characterization of natural rubber that is grafted with PPV and OPV by chemical characterization, thermal property, tensile property, and morphology
3. The effect of stress or strain on the luminescent property of PPV and OPV grafted on natural rubber