Chapter II
Theoretical Considerations

Photophysical processes in polymers [26-29]

The study of the photophysics of synthetic polymers can be simplified by considering them to have similar properties in photophysical terms like their small molecule analogues. These can be treated in the conventional way with reference to a state diagram, after Jablonski [26]. There are three states which play dominant roles in the photophysical process of organic molecules. They are the ground (unexcited) state (S_0) with opposing spins paired in molecular orbitals, the lowest triplet state (T_1) with parallel spins, and the lowest excited singlet state (S_1) which is higher in energy than the corresponding triplet state. Molecular orbitals can be classified as occupied or unoccupied. The highest occupied molecular orbital and the lowest unoccupied molecular orbitals are known as HOMO and LUMO, respectively. They are frequently referred to as frontier orbitals.

Absorption

The absorption of light (i.e. photons) by organic polymer molecules results in the excitation of π- and n-valence electrons including the additional excitation by molecular vibration. The absorption results in the promotion of the electron from the HOMO into the LUMO. Only the 0-0 transition occurs between the vibrational ground states of the electronic ground state (mostly S_0) and electronically excited states (S_n).

In the case of monomers the absorbing or emitting group is without measurable interaction with neighboring groups. In polymers, the absorbing or emitting group is either the entire macromolecule or part of it which might interact with other parts. Polymers therefore mostly show intense, structureless absorption bands which become narrower and show some structure at low temperature. Absorption processes are graphically presented by using **Jablonski state diagrams** (Figure 2.1) The energy level indicated corresponds to energy differences.
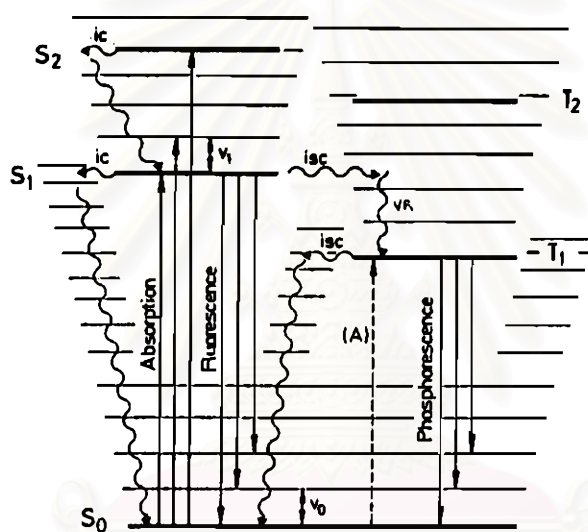

Figure 2.1 : Jablonski state diagram of energy levels of organic molecules

The processes are described by the Jablonski state diagrams in which states represented by horizontal lines are grouped into vertical columns according to their multiplicity. The individual processes are indicated by arrows (radiative process = straight arrow, non-radiative process = wavy arrows). The energy difference between the ground state (S_0), singlet states (S_1,S_0) and triplet (T_1,T_2) states are progressively lower at higher vibrational states. Each process is characterized by a rate constant (K_i); the sum of the reciprocal values of the deactivation rates of a vibrational state determines its lifetime (τ_i)

Unimolecular pathway

The reverse process to absorption, that is, the removal of the electron from the LUMO back to the HOMO, results in the emission of a photon. This process can occur via radiative transition which involves the spontaneous emission of a photon e.g. fluorescence and phosphorescence or radiationless transition e.g. internal conversion and intersystem crossing.

Radiative processes

Fluorescence is defined as the spin allowed emissive transition between vibrational states of identical multiplicity, usually from excitation of singlet S_1 to ground state S_0. The vibrational structure of fluorescence bands is a mirror image of the longer wavelength bands in the absorption spectrum, shifted to longer wavelengths. The emission from the longest absorbed and shortest emitted wavelength maximum usually corresponds to the 0-0 transition. Fluorescence is comparatively fast with lifetimes usually in the range of 10^{-6}-10^{-4} sec. Because of the relatively short lifetime of fluorescence, the emission can be used to probe for a variety of interesting characteristics of polymers.

Phosphorescence is the spin forbidden emission of radiation between vibrational states of different multiplicity, generally from the T_1 state to the S_0 state. Since the T_1 state always lies below the S_1 state, this band occurs at longer wavelengths than that of fluorescence. The lifetimes are relatively long; in the range of 10^{-4}-10 sec.

A typical energy relationship between absorption, fluorescence and phosphorescence spectra is shown in Figure 2.2. On the energy scale, fluorescence is often a mirror image of absorption, whereas

phosphorescence is of even lower-energy (red-shifted) emission with respect to the fluorescence reflecting the lower electronic level of the triplet state.
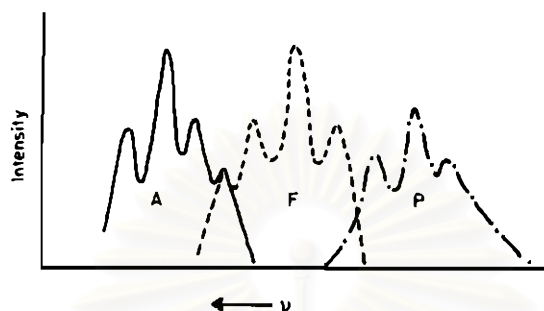

<u>Figure 2.2</u> : Energy relationship between absorption A, fluorescence F, and phosphorescence P.

Non-radiative process

There are two non-radiative processes. The first or **internal conversion,** denotes a radiationless transition between two electronic states of the same multiplicity, usually $S_n{\rightarrow}S_{n-1}$ or $T_n{\rightarrow}T_{n-1}$. In the specific case being considered, this would be the ground electronic state, and the transition would be denoted $S_1{\rightarrow}S_0$. **Intersystem crossing** is a similar radiationless transition connected with a change in multiplicity (mostly $S_1{\rightarrow}$ T_1, or $T_1{\rightarrow}S_0$). Radiationless transitions are isoenergetic transitions to a vibrationally excited lower electronic state, and followed by very rapid **vibrational relaxation** which occurs from any vibrational state and represents a return to the thermal equilibrium of the vibrational ground state within the same electronic state, for instance $S^v{\rightarrow}S$ or $T^v{\rightarrow}T$. This occurs in condensed systems by energy transfer, i.e. transfer of vibrational energy to the surrounding medium.

All processes discussed above, except simple vibrational relaxation, are unimolecular which can be illustrated with simple kinetic schemes presented in Table 2.1.

Table 2.1 : Unimolecular pathways of photophysical process.

Process	reaction	rate	$k_i\,(S^{-1})$
Absorption or Excitation	$S_0 + h\nu \rightarrow S_1$	I_a	
Fluorescence	$S_1 \rightarrow S_0 + h\nu$	$k_f[S_1]$	$10^6 - 10^9$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu'$	$k_p[S_1]$	$10^{-2} - 10^{-3}$
Internal conversion	$S_1 \rightarrow S_0$	$k_{IC}[S_1]$	$10^7 - 10^{12}$
Intersystem crossing	$S_1 \rightarrow T$	$k_{ST}[S_1]$	$10^8 - 10^{11}$
	$T \rightarrow S_0$	$k_{TS}[S_1]$	$10^{-2} - 10^3$

Quantum Yield

The overall efficiency of an excited state process is usually described by its quantum yield (ϕ). The particular process (Table 2.2) maybe either photophysical or photochemical. The quantum yield ranges from 0 to 1.

$$\phi = \frac{\text{number of molecules undergoing a particular process}}{\text{number of quanta absorbed by the system}}$$

Table 2.2 : Quantum efficiency of the photophysical process

| Quantum yield	event	process
ϕ_{fl}	fluorescence	$S_1 \rightarrow S_0$
ϕ_p	phosphorescence	$T_1 \rightarrow T_0$
ϕ_{ic}	internal conversion	$S_n \rightarrow S_{n-1}$
		$T_n \rightarrow T_{n-1}$
ϕ_{isc}	intersystem crossing	$S_1 \rightarrow T_1$
		$T_1 \rightarrow S_0$

Bimolecular Pathways

In a polymer system the bimolecular pathway encounters will dominate, leading for example to electronic relaxation of the system, known as quenching. A typical bimolecular interaction between the excited singlet state and ground-state quenching process are energy transfer and excimer formation.

Energy Transfer is defined as the donation of excitation energy from one molecule to another or from one chromophore to another. One of the most general forms of electronic energy transfer can be represented by

$$D^* + A \rightarrow D + A^*$$

D represents a donor molecule, *A* represents an acceptor molecule and * denotes electronic excitation. The energy transfer process may involve two steps with intermediacy of a photon. This is known as radiative transfer, sometimes referred to as *trivial* process, with sequential emission of fluorescence or phosphorescence from the donor molecule D*, followed by desorption of the photons by the acceptor molecule A.

$$D^* \rightarrow D + h\nu$$
$$A + h\nu \rightarrow A^*$$
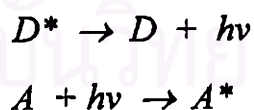
Polymer molecules can undergo at least two major types of energy transfer processes. The first of these involves the transfer of excitation from a small molecule to a large molecule, as shown in Figure 2.3a . For example, the excitation energy originally localized on a small molecule can be transferred to a large polymer chain. Alternatively, the excitation energy localized on a chromophore in a polymer chain can be transferred to a small

molecule, thus quenching a photophysical process. The intramolecular energy transfer can occur in a number of ways. For example, a quenching group on one part of the chain may react with an excited group on another part of the chain to change the position of the excitation energy (Figure 2.3b), or secondly, excitation localized on a sequence of chromophores maybe transferred from one chromophore to the next by a hopping mechanism (Figure 2.3c) . This process is termed energy migration.
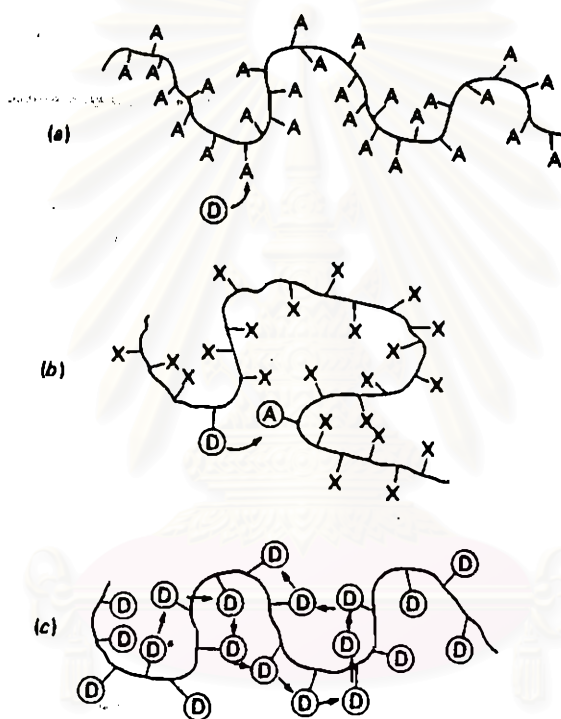

Figure 2.3 : (a) Energy transfer from small donor D, to polymer acceptor A

(b) Intramolecular energy transfer

(c) Energy migration

Since energy transfer from polystyrene to tetraphenylbutadiene was first observed by Birks and Kuchela [30], this polymer has been investigated by several workers. For instance, Jones *et al* [31]. Studied energy transfer from polystyrene to napthalene-d_8, p-terphenyl and

pyrene-d_{10}. Heisel and Lauustrait [32] studied the energy transfer from polystyrene to p-terphenyl, phenyl-2-p-biphenylyl-5-oxadiazole, phenyl-2-p-biphenylyl-5-oxadiazole.

Excimer formation

Fluorescence is often quenched by an increase in the solute concentration (self-quenching or concentration quenching). Simultaneously, a new structureless emission band, whose intensity is proportional to the concentration of the solutes, appears at longer wavelength. This new emission band is caused by the fluorescence of a bimolecular entity of definite stoichiometry (usually 1:1) that results from the collision of a molecule in the ground state with another molecule in the excited state.

$$M + M^* \rightarrow MM^*$$

The bimolecular entity mentioned above is a stable species . If it is only stable in only the excited state, and if, after transition to the ground state, it dissociates into its components, it is an *excimer* (*excited dimer*), assuming the two interacting components are identical. If they are different, an *exciplex* (*excited complex*) is formed. It is assumed that excimers and exciplexes are stabilized by transfer of the energy, with exciplexes stabilized by charge transfer as well.

Synthetic polymers prepared by free radical polymerization of vinyl monomers have a general structure of the form given below in which the substituents R are separated by three carbon atoms.
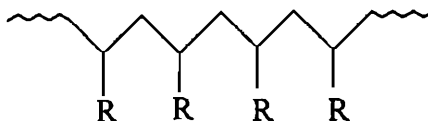
Links with two or four carbon atoms, due to head-to-head or tail-to-tail additions occur only as defects and are rarely observed in polymer systems. If the R groups are capable of forming excimers or exciplexes, then it is obvious that their structure is sufficiently flexible so that free rotation is possible about the carbon-carbon bonds and the aromatic rings are interacting with each other.

Polystyrene was one of the first excimer-forming polymers to be studied experimentally. The broad structureless emission band of atactic polystyrene at room temperature was first attributed by Basile [33] and Yaneri *et al* [34]. to excimer emission. In solid solution and in low temperature glasses, emission from polystyrene is primarily due to the monomeric emission, while in fluid solution, both monomeric and excimer fluorescences are observed. It is also obvious that the excimer emission is quenched more efficiently by oxygen than in monomer fluorescence. The excimer formation was due to intra- rather than intermolecular interactions. In PS it is now established that the excimers are formed between neighboring side groups. The quantum yield is lower than in the corresponding monomeric model compound. In the solid state the ratio of excimer to monomer fluorescence as a function of temperature for PS films cast at 295 K was independent of molecular weight. The absolute intensity of the monomer emission increases as the temperature decreases, which is attributed to a decrease in the rate of energy transfer to the excimer trap.

Excimer formation in polymers has been extensively studied because of its connection with energy migration and molecular mobility in polymer systems. Excimer fluorescence emissions of vinyl polymers [35-37] and copolymers which have been studied include polystyrene, poly(1-vinyl naphthalene), poly(2-vinylnaphthalene), poly(1-and(2-naphthyl methacrylate), polyvinyltoluene, poly(1-vinylpyrene) and poly (vinylcarbazole), styrene-acenapthylene copolymer [38] and styrene-methylmethacrylate copolymer [39].