CHAPTER I

INTRODUCTION AND THEORY

A wide range of organic substances are known emitting luminescence when activated by different kinds of radiation. Depending on the types of excitation energy, a distinction can be made between *photoluminescence* (stimulated by ultraviolet radiation or by visible light of short wavelengths), *radioluminescence* (or scintillation, excited by radioactive substances), chemiluminescence and electrochemiluminescence, resulting from some chemical and electrochemical reactions. Substances exhibiting luminescence in response to various factors are known as *luminescent materials* or *luminophors*. Two basic kinds of luminophors include organic (organoluminophors) and inorganic (phosphors). The luminescence of the latter is determined by their lattice structure. On crystal break-down, their luminescence is altered or disappears altogether. In the case of the former, it is the structure of the individual molecule that is responsible for luminescence. Therefore, when such a substance passes from the solid crystalline state into a melt or vapor or its dissolved, its luminescence persists.

1.1 Excited State of Molecules

In the ground (unexcited) state of most molecules, the electrons occupy the same orbital have antiparallel spins.The resultant spin S of the electrons is zero, while the level of multiplicity, given by the quantity

$|2S|+1$, equals to unity. Such an energy state is referred to the *singlet* (S). If the transition to an excited state is accompanied by reversal of the spin of one of the electrons, the total spin will become unity and the multiplicity will equal three. Such an excited state is known as the *triplet state* (T). If absorption of a light quantum does not bring about any changes in multiplicity, the corresponding excited state will be the single state S^*. The singlet-singlet transition ($S_0 \rightarrow S^*$, the zero in the subscript correspondent to the ground state) associated with the absorption of light quantum may result from transfer of the valence π-electrons of molecule to the antibonding π^*-orbital ($S_0 \rightarrow S_{\pi\pi^*}$ transition) or from transfer to the same orbital of the n-electrons of a heteroatom, ($S_0 \rightarrow S_{n\pi^*}$ transition). A transition of the $S_0 \rightarrow S_{n\pi^*}$ type is possible if the molecule contains for examples C=C, -N=N-, C=N, $-NO_2$.

The energy of π-π^* transitions is substantially dependent on the size of the π-system. As the chain of conjugated bonds increases in length, for example, during annelation of the benzene rings in aromatic hydrocarbons or heterocycles, this energy decreases (the spectra shift toward longer wavelengths). The energy of n-π^* transitions does not decrease with the growth of the π-system, but may also become higher. This was demonstrated by Komarova and Plotnikov[1], who resorted to calculate using the semiempirical LCAO-MO method with a self-consistent field and to take into count the configuration interaction involving different molecules with C=O, C=S, NO_2, or NH groups.

The molecule passes from the excited state S^* either into the ground state S_0, having emitted a quantum of light, or to the triplet level T_1, having undergone intersystem crossing (transition between states with different multiplicities, Figure1.1).

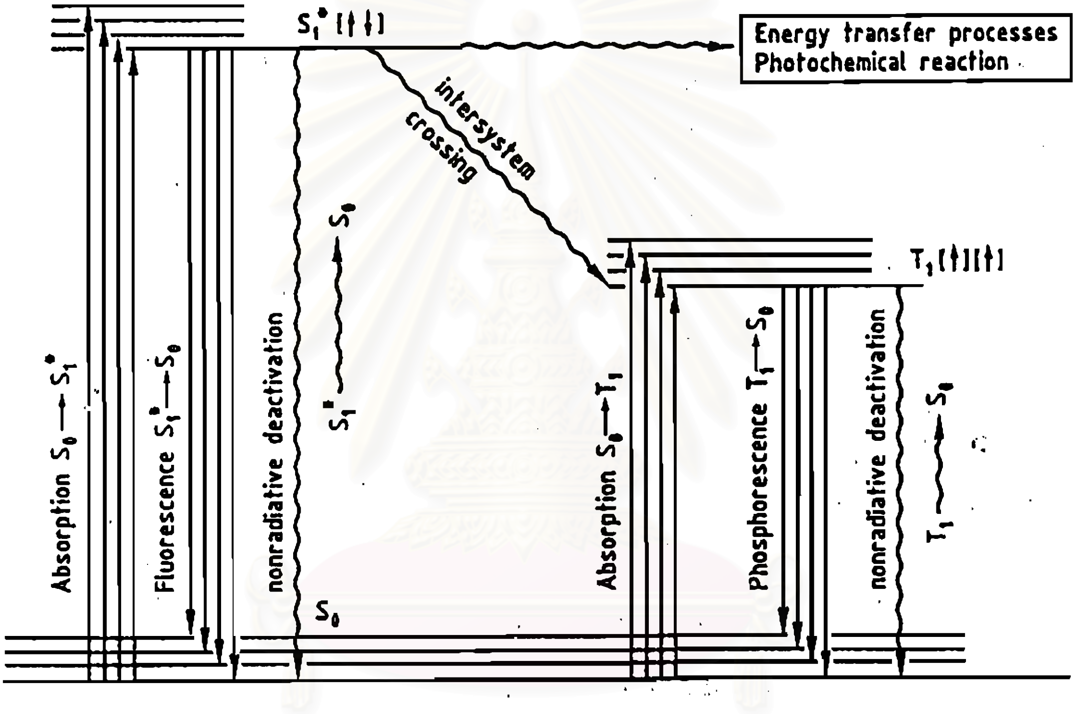


Figure 1.1 Electronic and vibrational levels in a polyatomic molecule, and paths of radiative (straight arrows) and nonradiative (wavy arrows) transitions.

Since the lifetime of an excited molecule in the triplet state is much longer than in the singlet (Table 1.1), the probability of nonradiative energy losses is much higher in the triplet state.

Table 1.1 Basic characteristics of photophysical processes.

Photophysical process	Notation	τ, s
Absorption	$S_O \rightarrow S^*$	10^{-15}
Fluorescence (singlet-singlet light emission)	$S^* \rightarrow S_O$	10^{-9}-10^{-7}
Phosphorescence (triplet-singlet light emission)	$T^* \rightarrow S_O$	10^{-4}-10^{2}
Intersystem crossing (non-radiative transition from the excited singlet to the excited triplet state with the same energy)	$S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$ $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$	10^{-11}
Internal conversion (nonradiative transition to a lower level of the same multiplicity and with the same energy)	$S_2 \rightsquigarrow S_1 \rightsquigarrow S_0$	10^{-2}-10
Vibrational-rotational relaxation from the excited vibrational sublevel usually to the zeroth vibrational level of the same state	$(S1)\upsilon_i \rightsquigarrow (S1)\upsilon_o$	10^{-14}-10^{-12}

It is a well established fact that the probability of intersystem crossing between electronic states of different types, i.e., $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ or $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$, is two or three orders of magnitude above the probability of the same process occurring between electronic states of the same type, i. e., $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ or $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$.

Nurmukhametov and coworkers [2] proposed a classification of organic molecules according to the relative arrangement of the excited-state levels. In accordance with this classification (Figure 1.2), the following five main types of molecules are possible, differing in their luminescence characteristics (the electronic states are given in the order of increasing energies):

1. S_0, $T_{n\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$
2. S_0, $T_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$
3. S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$
4. S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$, $S_{n\pi^*}$
5. S_0, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$

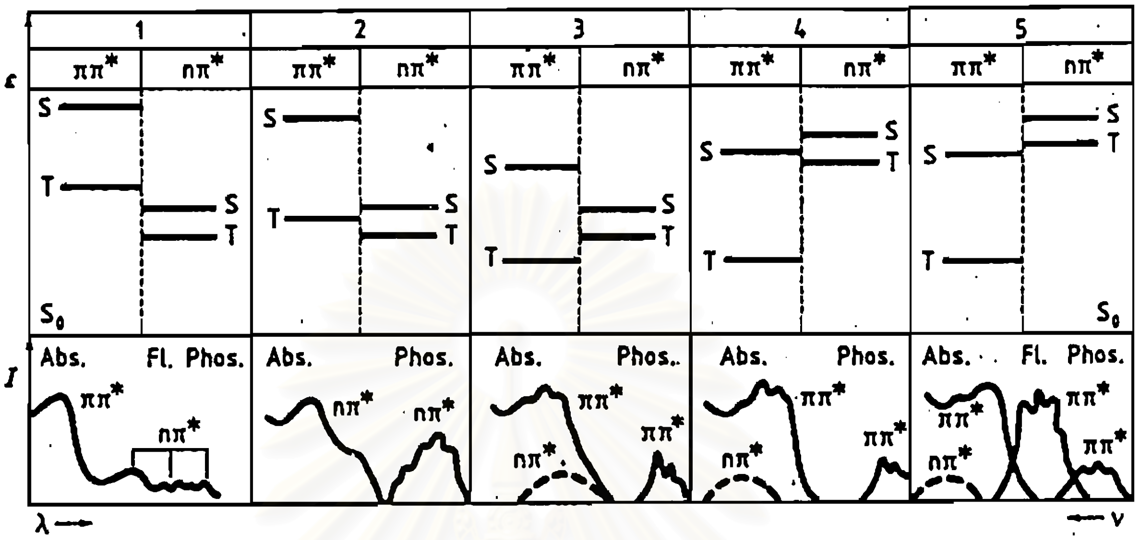


Figure 1.2 Relative arrangement of the singlet and triplet $n\pi^*$ and $\pi\pi^*$ levels in molecules of different types and the absorption (abs) and emission (fluorescence-fl, phosphorescence-phos) spectra corresponding to each type (1 to 5) [1].

Most of the currently used luminophors belong to type five. Their S_1^* and T states are of the same kind ($\pi\pi^*$).The energies of the $T_{n\pi^*}$ and $S_{n\pi^*}$ states are higher than that of the $S_{\pi\pi^*}$ state with the result that the probability of intersystem crossing is low. These compounds exhibit fluorescence and, in frozen solutions, persistent phosphorescence as well.

The above classification of molecules provides the theoretical basis for the empirical regularities established earlier in the search for new organic luminescent materials.

1.2 Organic Scintillators

Organic luminophors capable of emitting light when exposed to ionizing radiation may be used as scintillation media.Their contact with ionizing particle triggers flashes of light or, in other words, scintillation.

Scintillation is essentially a radioluminesence event comprising the following steps: (1) loss of energy by a fast charged particle in the scintillator, this energy being expanded in excitation of atoms and molecules as well as in formation of secondary free electrons which, in turn, cause ionization and excitation, (2) transfer of energy from excited or ionized particles to luminescence centres (molecules, ions, or more complex entities), and (3) emission of scintillation light by the luminescence centres.

Scintillators may be organic or inorganic luminescent substances, but not every luminophor (or its solution) is a scintillator. When liquid or solid solutions of organic luminophors are used as scintillators, it is imperative that the solvent should provide for effective transfer of excitation energy to the luminescence centres.

Scintillators are employed in scintillation counters to detect various types of radiation. A counter normally consists of a scintillator (scintillation detector), a sensor (usually a photomultiplier tube converting the light flash into electrical impulses), and an electronic device for counting these impulses. The impulse count is indicative of the ionizing flux density and, consequently, of the particle energy.

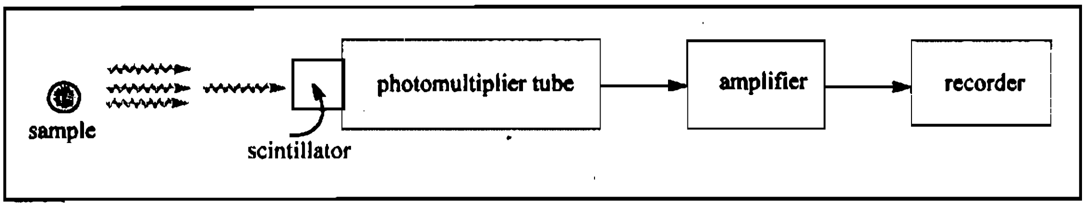


Figure 1.3 Scintillation counter system

The requirements for the scintillators vary, depending on their application. Measurement of small radiation fluxes calls for scintillators of a large surface area or volume, preferably as transparent to their own emission as possible. To measure weakly absorbable (indirectly ionizing) radiation, the scintillator should be a strong absorber of the incident particles and have a large volume. Those scintillators used to measure strong fluxes and those intended for use as "time markers" (to register the passage of particles) should produce the shortest light flashes possible. In some cases, scintillators must be selective - that is, permit detection of two (or more) type of radiation. In any event, their scintillation efficiency, (the ratio of the scintillation energy to that of the exciting particle), must be as high as possible. A high scintillation efficiency facilitates, for example, detection of low-energy radiation against the background of photomultiplier tube noise.

Organic scintillators are usually in the form of single crystals (namely, anthracene, anthraquinone, naphthalene, trans-stilbene, etc.), luminophor solutions in organic solvents (liquid scintillators), and solid solution in plastic (plastic scintillators). They are less effective than inorganic scintillators (scintillating phosphors) in detecting gamma rays and heavy particles, produce impulses of lower amplitudes, and have a poorer energy resolution. At the same time, they have the big advantage of producing light flashes of shorter duration (ca 10^{-9} s) , as compared to those produced by inorganic scintillators (ca 10^{-8} and more seconds). Organic scintillators are more transparent to their own fluorescence, and their wavelength lie near the maximum of the spectral response curve of the most widely used photomultiplier tube, which is why such a scintillator may have a rather large volume.

All this accounts for the great importance gained by organic scintillators in nuclear and space research, in geological prospecting, in biology, in medicine, and in other fields of science and technology. They have become instrumental in some major applications, primarily in the detection of low-energy beta particles. Owing to their high content of hydrogen atoms, they are highly effective in detecting the fast neutrons which knock out the protons responsible for light flashes. Addition of some organo-elemental substances to scintillators results in nuclear reactions triggered by the incident slow neutrons, which are also accompanied by scintillation.

Organic scintillators permit one to measure the delay times of unstable particles and to study the radiation of short-lived isotopes. They can be used, although less effectively, to detect alpha particles, heavy ions, gamma and X-rays.

1.3 Plastic Scintillators

Plastic scintillators are solid solutions of active additives in polymers and in many ways similar to liquid scintillators. They are also characterized by migration of the absorbed energy from the base to the activators, which is why the chemical structure of the polymer and the incorporated luminophor as well as their spectral characteristics are the major factors determining the scintillator properties.

Scintillating plastics are more stable under varying temperature conditions and can be used in a broader temperature range than can other organic scintillators. They can be machined into different shapes and sizes (plates, rods, cylinders, films, granules or capillaries). Polishing after machining reduces light losses due to reflection. These scintillators have light radiation stability, do not require special protection against environmental factors, and can be used inside evacuated devices.

Plastic scintillators can be prepared by polymerization of solutions of active additives in monomers or by introducing the additives into molten polymers [3]. The polymerization is conducted in special glass or metal ampoules. The temperature and time parameter of the polymerization and cooling (annealing) process are selected according to the scintillator size and its configuration.

The first plastic scintillators were produced on the basis of polystyrene and *p*-terphenyl in 1950 [4]. The purpose of further investigations was to increase the scintillation efficiency of plastic scintillators by suitable selection of the luminescent additives and the polymer base. A large number of organic luminophors such as polyphenyls, aromatic condensed ring compounds, phenyl substituted derivatives of ethylene and dienes, and heterocyclic compounds, namely derivatives of 1,3-oxazole, 1,3,4-oxadiazole, and Δ^2-pyrazoline, have been studied as luminescent additives.

Various aromatic vinyl polymers have been investigated as polymer bases. As a result of investigations of the scintillation efficiency and radiation resistance of plastic scintillators, the suggestion was made to classify polymeric scintillation compounds on the basis of the structure of the polymer repeat unit. Plastic scintillators are divided into four groups:

i) Scintillators based on polystyrene and its derivatives,

ii) Scintillators based on vinyl monomers with polyphenyl, condensed aromatic, and heterocyclic rings,

iii) Compositions with an inactive polymer base (π-conjugation is absent in the repeat unit) and a "secondary solvent" (a low molecular compound with aromatic rings), and

iv) Scintillators based on copolymers of various compositions.

Polystyrene and its ring-methylated derivative are most widely used as the plastic scintillator base. A relationship has been established between an increasing number of methyl groups, their location in the benzene ring, and the efficiency of polymer base [5]. The scintillation efficiency of polymeric systems is improved by increasing the number of methyl, phenyl groups and the size of alkyl groups in the styrene repeat unit.

The most useful combination is the application of the copolymer of given monomers either with styrene or methyl derivatives of styrene in the benzene ring or with methyl methacrylate. Of the inactive polymer bases, PMMA is the most popular owing to its good physical and mechanical properties and high transmission. However, because of the absence in the repeat unit of PMMA of π-conjugation, PMMA based scintillators have low scintillation efficiency, not exceeding 10% compared with that of polystyrene. The light yield of inactive bases is increased by introducing a secondary solvent. Satisfactory results are obtained with such the secondary solvents as naphthalene and phenanthrene. The scintillation efficiency of such the systems is determined by the amount of activator, the nature of the primary luminescent additive, and the presence of a spectrum mixer. This way can be achieved about 60% of the scintillation efficiency of polystyrene scintillators. However, being influenced by the sample transmission, the high yield of large scintillators based on PMMA is no less than that of polystyrene based scintillators.

The properties of scintillators based on MMA and dimethyl styrene , vinyldiphenyl, and *N*-vinylcarbazole have been described [6]. Of interest are scintillators made on the basis of styrene and methyl derivatives of styrene vinyl monomers with polyphenyl groups, and condensed aromatic rings [7], styrene, and 4′-vinyl-3-hydroxyflavone. The scintillators based on vinyldiphenyl, α-, β-vinylnaphthalene-styrene copolymers have higher light yield than the homopolymers of vinyldiphenyl and vinylnaphthalene [8]. To improve the heat resistance , of scintillators, the suggestion has been made to use crosslinked polymers as the base [9]. Thus the softening point of poly (2,4-dimethylstyrene) crosslinked with diisoprenylbenzene is 10-15^{0}C higher than that of linear chain, the light yield being unchanged.The light yield of scintillators is increased by copolymerization of styrene or 2,4-dimethylstyrene with aromatic vinyl monomers containing luminophor groups such as terphenyl, diphenyloxazole, and diphenyloxadiazole.

One of the advantages of polymeric scintillation materials over monocrystals, and to a certain degree, liquid scintillators, is the possibility of varying their compositions not only by using polymeric and luminescent additives of different types but also by adding to the polymer different organic and inorganic compounds to impart new properties to the ionizing radiation detectors.

The main problem has been, and still is, that the actual scintillator is, in effect, dissolved in the plastic medium, and therefore it will eventually, migrate to the outer surface, or alternatively form a crystalline precipitate within the matrix of the plastic medium. The consequence of either of these processes is a dramatic loss of scintillation counting efficiency.

1.4 Production of Plastic Scintillators

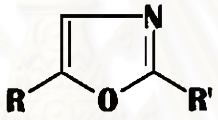
The main method for producing plastic scintillators is by dissolving the scintillator in the monomer or its solution, then bulk polymerizing the mixture. Plastic scintillators can be also obtained by dissolving the luminescent additive in the polymer melt, by pressure melt, by pressure melting the polymer-luminescent additive mixture at a high temperature, and by pressure moulding and extrusion.

The most generally employed method is radical bulk polymerization, which forms the basis for the commercial production of plastic scintillators. The advantages of this method are the most uniform distribution of the luminescent additive in the polymer base and the possibility of manufacturing scintillators of large sizes and different shapes. Promising methods for producing small (about 100 mL) scintillation detectors in the form of cylinders, hollow cylinders, glasses, etc., as well as scintillation films, fibres, capillary tubes, and thin plates, are transfer moulding extrusion.This method can be used for the manufacture of scintillators on the basis of thermoplastic polymers obtained solely by ionic polymerization. Initiators for radical polymerization usually significantly affect the light yield. Benzoyl peroxide is used heavily in the manufacture of plastic scintillators; however, the data on the effect of benzoyl peroxide on the light yield of the scintillator are rather contradictory. A number of studies established that benzoyl peroxide had a quenching effect, even at low concentrations.

However, it was shown in another studies [10] that low concentrations of this initiator had practically no effect on the light yield of the scintillator. Even at high concentration of azobisisobutyronitrile (AIBN), the light yield of plastic scintillators did not fall. It was noted [11] that during polymerization in air, the light yield of scintillators felled by 20-30%. A high light yield was attained in nitrogen or in vacuum. It followed that during the manufacture of plastic scintillators, it was important to exclude all processes which lead to the formation of compounds causing luminescence quenching or absorption.

1.5 Vinyl -Substituted 2,5-Diaryloxazole as Organic Scintillators

2,5-Diaryl oxazoles (1.1) are the most efficient organic luminophors which emit light in the violet or blue region. They have aroused a great deal of interest after they were introduced as the active additives in liquid and plastic scintillation counting. As oxazole derivatives have been used for scintillation counting in solution media, it is a reasonable suggestion to solve the problem of migration of the fluorescent solute by co-polymerizing it with the main monomer.



(1.1)

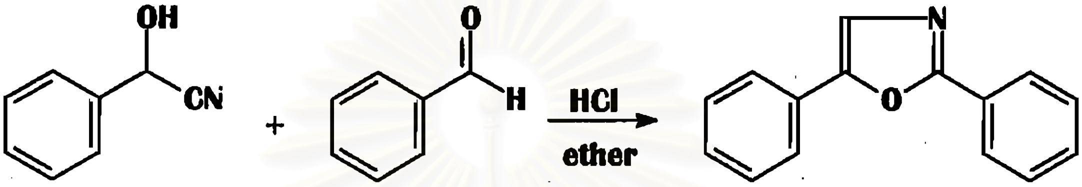
The effect of functional substituents on the spectral characteristics and luminescence intensity of diaryloxazoles has been studied in detail. The electron-donor and -acceptor substituents in the *para* position of the phenyl radicals of diphenyloxazole cause bathochromic and bathofluoric shifts in its spectra, which is the larger, the stronger the electronic effect of the substituent.

In term of quantum yield in toluene solution, *para*-substituted 2,5-diphenyloxazoles with both electron-donor and -acceptor, not counting the non-luminescent or weakly luminescing nitro- and iodo-substituted compounds, are generally closer to diphenyloxazole or emit more intense light [12]. The highest quantum yield (0.78) is found in the recently synthesized 2-(4-difluoromethylsulfophenyl)-5-phenyloxazole [13]. Intense fluorescence has been observed in substituted 2,5-diphenyl oxazoles contain a carboxyl, amide, or cyano group in the *para* position of the 2-phenyl group.

It can be concluded that the major structural factors responsible for the scintillation efficiency and the light yield include considerable lengthening of the conjugation chain the electron acceptor or donor behavior of the substituted aryl fragment, which interferes with the even distribution of electron density in 2,5-diphenyloxazoles.

1.6 Synthesis of 2,5-Disubstituted Oxazoles

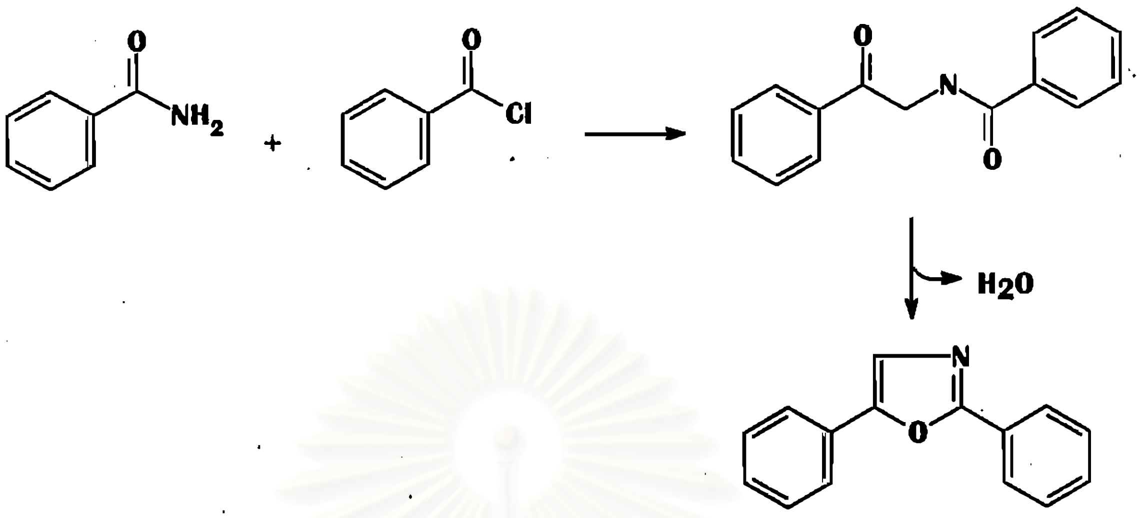
2,5-Diaryloxazoles and 2,5-diphenyloxazole (PPO) have been prepared using the Fischer synthesis [14] from the reaction between cyanohydrins and aldehydes.



Scheme 1.1

However, this synthesis is unsatisfactory as it suffers from three defects: (1) formation of 2,5-diphenyl-4-oxazolidonesas byproducts in high yields, (2) a certain ambiguity in that the starting materials may exchange hydrogen cyanide, thus causing “scrambling” of the phenyl rings in the product, and (3) the yield of the oxazole is low.

Another method for synthesizing 2,5-substituted oxazoles is condensation of an α-aminomethylarylketone with arocyl halide, followed by cyclodehydration of the resulting α-acylamino-methylarylketones (Robinson-Gabriel reaction) [15-18] as shown in Scheme 1.2.

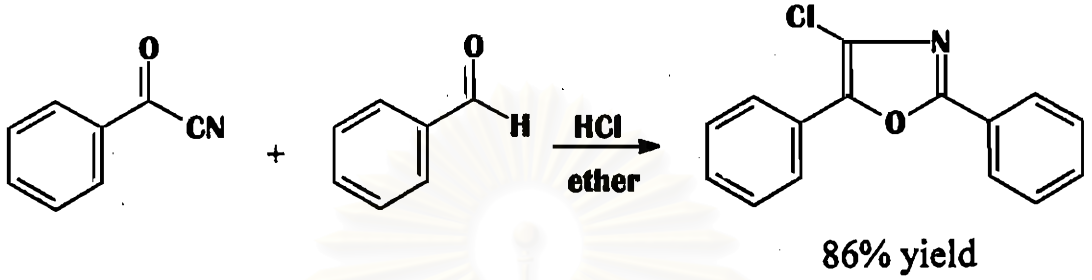


Scheme 1.2

This method has the advantage that it works with aliphatic substituents, while the Fischer synthesis fails with these, but the byproducts which form due to the presence of the cyclizing agents (H_3PO_4, Conc. H_2SO_4 etc.) are extremely difficult to remove. At any rate, aliphatic oxazole derivatives do not fluoresce. Concentrated sulfuric acid serves as the dehydrating agent in almost all cases, which results in the formation of decomposition products which cause strong quenching of the fluorescence. Their complete removal is difficult hence this method is not suitable for the production of scintillation grade oxazoles.

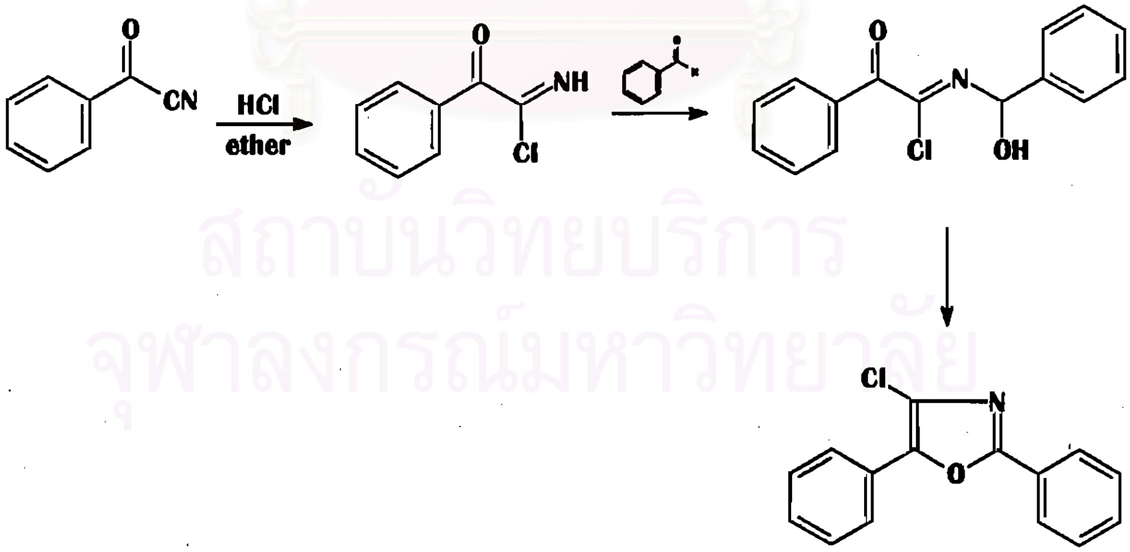
In 1963, a modification of the Fischer synthesis was developed using acyl cyanides instead of cyanohydrins. This affords 2,5-diaryl-4-chloro(or bromo)oxazoles [19] without byproducts and in high purity and yields (Scheme 1.3).

Since that time this was been the commercial method for the production of scintillation quality oxazoles and is known as the Ternai synthesis.



Scheme 1.3

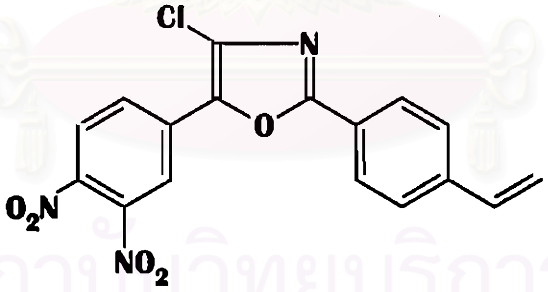
The mechanism of the reaction may involve an iminohalide intermediate as suggested by Cornforth [20] in his comments on the Fischer synthesis (see Scheme 1.4). The removal of the 4-halogen by reducing agents is quantitatively.



Scheme 1.4

It has been stated earlier that nitro substituted diphenyloxazoles do not show fluorescence [21]. However, this is not true, since the 2-phenyl-5-(4-nitrophenyl) oxazole [19] is fluorescent Inspection several electrochromic compounds show the presence of 3,4-dinitrophenyl groups, hence it was considered that incorporation of these substituents into the 2,5-diaryloxazole system might result in fluorescent / scintillator compounds with potential electrochromic properties

For this reason the target compound (1.2) of this work is 2,5-diphenyloxazole with nitro groups in the 3′ and 4′position and a vinyl group, as the active part for the copolymerization with other monomers such as styrene or methyl methacrylate monomers, in the 4-position.



(1.2)

In this thesis, the preparation of 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-vinylphenyl)oxazole is reported as a new monomer for the production of plastic scintillator.