Chapter I

Introduction

Scintillation counting is a method of counting flashes of light emitted by fluorescent molecules when impacted by ionizing radiation, in order to establish the presence or amount of radioactivity. The lifetime of the light emission should be shorter than the frequency of the collisions of the particles with the scintillator molecules, since the accuracy of scintillation counting is controlled by the relaxation time of the electrons from their excited state. This technique is used in medical or biological laboratories, environmental science, nuclear physics, and in many other fields of science and technology.

The scintillator is defined as a flash emitter of light (pulse) which is a consequence of receiving excitation energy from the radiation source, i.e. a radioactively labeled organic chemical. The energy absorbed by the scintillator is converted into fluorescence emission of photons. The emitted photons are not usually counted directly. To increase the sensitivity and accuracy of measurement photomultipliers are commonly used. Modern instruments utilize charge coupled devices (CCD) to detect very low levels of photon emission. Because the lifetime of the emission is short, fast response is required to detect the fast photons. Figure 1.1 shows the principle of a photomultiplier/scintillation counter system. Characteristics to be considered in the selection of the scintillator are internal absorption of fluorescence, scintillation decay time, fluorescence quantum yield, and pulse height which is influenced by the sensitivity of the photomultiplier at the wavelengths of fluorescence emission of the particular scintillator [1]. Secondary effects, such as energy transfer, have to be considered.

Photodegradation could also occur in a solid scintillator system, since the high energy of particles might break up the molecule. These various considerations limit the number of practical scintillator compounds.

Historically, the first scintillators were single crystals such as antimony, sodium iodide, anthracene, naphthalene, *trans*-stibene. Pure liquids e.g. *p*-xylene and pure plastics e.g. polystyrene were also used. Unfortunately, they exhibit low fluorescence intensities so that their scintillation efficiency is too low for practical use.

A significant development has been the development of the binary system of liquid scintillators which contain one or more organic fluorescent compound(s) dissolved in an organic solvent system. The scintillator solutes are a select class of compounds with the property of losing energy from their excited states in the form of light emission.
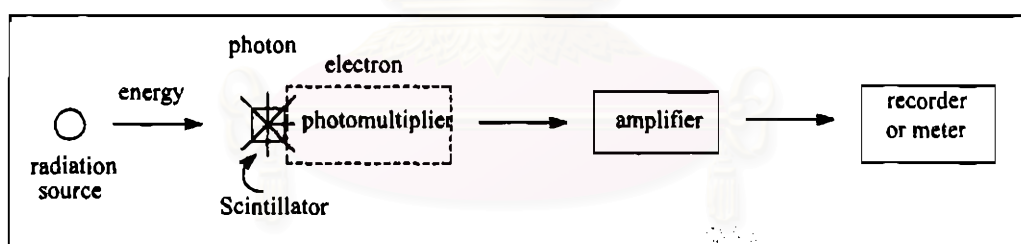

Figure 1.1 : The photomultiplier/scintillation counter system

A common feature of efficient organic scintillator solutes are aromatic rings linked in a manner to allow extended conjugation throughout the molecule. The aromatic ring systems which have been incorporated into scintillation solutes are phenyl, naphthyl, furan, pyrrole, oxazole, imidazole rings, etc.

Attemps to establish relationships between chemical structure and scintillation ability focus on the following requirements [2,3]:

- how to obtain fluorescence spectra at longer wavelengths.

- how to incorporate heterocyclic ring systems (such as oxazole) with better stability and sensitivity.

- Structure-activity relationships found that: methyl, fluoro and chloro substituent groups cause no difficulty and bromo, iodo and hydroxyl show undesirable heavy atom effects.

In efforts to improve upon the existing liquid scintillator counting and to provide data which would help to correlate chemical structure with the ability of various solutes to scintillate, a large number of organic compounds have been investigated [4,5]. *p*-Terphenyl in *p*-xylene was first proposed as a liquid scintillator in 1950 [3]. Other chemicals which are often used as scintillator solutes are naphthalene, pyrene, biphenyl, carbazole, 2,5-diphenyloxazole, anthracene, diphenylene oxide, etc. The solvent used in the system is usually aromatic such as benzene, toluene and p-xylene which also provide effective transfer of excitation energy to the scintillator solute. The energy transfer can occur in two ways; to an other fluorescent molecule or to the solvent. Therefore the emission and efficiency of the liquid scintillator is influenced by the concentration of the fluorescent solute, the temperature and the viscosity of the solvent.

The development of plastic scintillators was prompted by advances in physics and the needs for computerized three dimensional scintillation counting. The development of the two types have tended to follow each other. Plastic scintillators usually consist of an organic fluorescent compound mixed with a polymer. Plastic scintillators have the advantage of producing a short emission of light ($\sim 10^{-9}$ sec.) and can be used in a broader range of temperatures than liquid scintillators. Since the polymer has a

higher fluorescence quantum efficiency than the liquid solvent, there is an appreciable (10-20%) component of radiative transfer resulting in higher fluorescence intensity than that of the liquid scintillator. Moreover, the diffusion effect is not present in plastic systems. The efficiency of the plastic scintillator also depends on its mode of preparation as well as on its constituents. They can be made into a variety of sizes and shapes such as thin film, rod, plate or cylinder. The use of plastic scintillators as counting devices commenced in 1950, when they were first produced by Schorr and Torney on the basis of p-terphenyl with polystyrene [5]. Example use of plastic scintillator is whole body counting such as tomography. This counting technique is suitable to investigate tumor or cancer cells in the human body.

Plastic scintillators have been prepared by several techniques including [1]:

   -mixing of fluorescent compounds into molten plastic polymer.
   -molding of polymer and fluorescent mixtures under heat and
   pressure.
   -polymerization of liquid monomer in the presence of the fluorescent
   compound, commonly using free radical polymerization in bulk.

The last of these techniques appears to offer high purity and homogeneity of the scintillators. Benzoyl peroxide and azobisisobutyro-nitrile are widely used as initiators for radical polymerization, dependent on the temperature selected during polymerization. The polymerization carried out in a nitrogen atmosphere yields higher quantum yield than polymerization in air because oxygen can lead to quenching. Generally, polystyrene and polyvinyltoluene are most efficient as plastic solvents. Polymethylmethacrylate is normally an inefficient solvent but its high transparency and good mechanical properties are attractive.

The problem of plastic scintillators is the migration of the fluorescent compound to the plastic surface. Thus, the scintillator have lower efficiency with use. To solve this problem, the copolymerization of scintillator solute with an other monomer was carried out in order to bind it to the polymer.

2,5-Diphenyloxazole (PPO) as an organic scintillator

PPO is an efficient scintillator solute since it contains aromatic rings which allow resonance throughout the molecule and linked with a heterocyclic ring (oxazole), it has high fluorescence intensity and also emits at longer wavelengths. PPO has a solubility of 300 g/L in toluene at room temperature. Concentrations of about 3 g/L in toluene have been found to be suitable for scintillation counting standard [6]. It gives a broad fluorescence emission spectrum ranging from 340 to 460 nm, with maximum intensity at 380 nm.

Several experiments related to the energy transfer of liquid scintillators have appeared in the literature [7-10]. Solutions of PPO in different solvents were irradiated as a function of concentration. When the solution is exposed to either ionizing radiation (α, β and γ) or short wavelength ultraviolet radiation, the incident energy is primarily absorbed by the solvent molecule, then partially transferred to PPO, and subsequently emitted in part by the latter as fluorescent radiation in the visible part of the spectrum.

In 1960, Berlman [10] reported the energy transfer efficiency of PPO in *p*-xylene as a function of the solute concentration. Later, the efficiency of energy transfer from solvent to solute for solutions of 2,5-diphenyloxazole in benzene, toluene, cyclohexane and hexane were investigated by several groups [11-13] as a function of solute concentration and excitation wavelength.

The results for benzene and toluene are similar but different from those for cyclohexane and hexane since benzene and toluene contain aromatic rings which have electrons delocalized through the molecule but the latter solvents are cyclic compounds which have localized electrons. For the first pair of solvents at normal solute concentrations (3-10 g/L) energy transfer takes place almost exclusively from the first excited level for all wavelengths of excitation and the relative scintillation efficiency of a solution is dependent on the particular solvent. The relative scintillation yields seem to follow the same general trend as the efficiency of internal conversion $S_3 \rightarrow S_1$ of the aromatic solvent. Moreover, transfer efficiency from the first excited state depends strongly on the electronic level which has been initially excited. Only for higher solute concentration (> 150 g/L) does the direct transfer from higher levels become noticeable. The relative scintillation efficiency of these solutions was independent of the particular aromatic solvent. The fluorescence was produced by a process which involved energy transfer before the $S_3 \rightarrow S_1$ internal conversion. A possible mechanism involves the transfer of energy from S_3 state of the solvent to an excited state of the solute, F_3. The relative scintillation efficiency of concentrated solutions would then be dependent on the internal conversion efficiency for the process $F_3 \rightarrow F_1$ of the solute. This mechanism leads to the lower efficiency of the scintillator. However, the major part of the transferred energy may still come from the first excited level.

Decay time measurements show that the time during which excitation energy is transferred from the solvent to the solute is very much shorter in cyclohexane than in toluene and benzene. It has been found that the fluorescence quantum yield of PPO (conc. 3 g/L) is higher by about 16% in cyclohexane and hexane than in benzene or toluene.

Energy transfer efficiency for deoxygenated and air saturated solutions shows a quenching effect which depends on the excitation wavelength. Oxygen quenching of the transfer process in benzene is mainly *dynamic*, as can be seen from the strong decrease of the quenching effect with increasing concentration of the PPO. The quenching effect in cyclohexane seems to be *static*, i.e. independent of solute concentration [11-12].

The three principal mechanisms of energy transfer from solvent to solute are: material diffusion, migration transfer and a single-step transfer [9]. In the solid state the first of these does not occur. Electronic excitation passing between solvent molecules until it reaches a solute molecule is the most likely process. Direct transfer of excitation from the solvent molecule, primarily affected over distances of several molecule diameter, to PPO molecule might occur, but only at higher concentrations. For solutions of PPO in benzene, toluene or p-xylene, it has been proposed that the migration is due to excimer formation and dissociation and that the energy transfer occurs by a diffusion/migration-controlled collisional process [14]. Dilution of the solvent decreases the migration, but increases the transfer distance, so that the transfer efficiency remains practically constant.

PPO as a plastic scintillator

In plastic scintillators, oxazole type agents are best used in concentrations of 0.5-1.0% in polystyrene [15]. The quantum yield of PPO in polystyrene as a quantum counter was 0.80 ± 0.05 [16]. The results of PPO in polystyrene and poly(methyl methacrylate) are discussed in term of the migration transfer and a single-step transfer with resonance (dipole-dipole) interaction [9]. A strong dependence of the fluorescence spectral distribution and the fluorescence quantum yield on the excitation wavelength was found.

The results were interpreted in terms of a competition between solvent-solvent and solvent-solute interactions.

Copolymer between PPO derivatives and styrene

In 1977, Mcinally et al. [17] synthesized 2-phenyl-5-(p-vinyl)phenyloxazole homopolymer and copolymer with styrene. The polymer in toluene solution exhibits excimer formation characterized through measurement of fluorescence decay time.
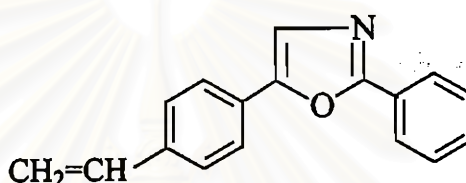

Figure 1.2 : Structure of 2-phenyl-5-(p-vinyl)phenyloxazole

Later, time-resolved fluorescence spectroscopy of a polystyrene labeled with 0.01% 2-phenyl-5-(p-vinyl)phenyloxazole in degassed dichloromethane solution was studied by Phillips et al. in 1983 [18]. The results showed three distinct emissions corresponding to luminescence from (i) polystyrene monomeric (*unassociated excited state phenyl chromophore*) (ii) polystyrene excimer and (iii) the oxazole label. The spectra provided unambiguous evidence for energy transfer from the polystyrene monomeric to the oxazole label. Singlet energy migration between near neighbor styrene moieties is involved and transfer of energy to PPO traps by intramolecular excimers of polystyrene has been suggested.

Gardettes et al. [19] also studied the polarization of the excimer fluorescence from styrene/2-phenyl-5-(p-vinyl)phenyloxazole copolymer in 1984. Excitation of the styrene moiety results in complete depolarization of all observable emission. By contrast, direct excitation of the PPO in

copolymer yields finite positive polarization. The time dependence of this process was also investigated.

Other plastic scintillators than 2-phenyl-5-(p-vinyl)phenyloxazole were also investigated. For instance [20]; Optical and scintillation characteristics of copolymers of styrene with 2-(p-vinylphenyl)-5-phenyloxazole, 2-(p-vinylphenyl)-5-(p-biphenylyl)loxazole, 2-(p-vinylphenyl)-5-(α-naphthyl) oxazole, 2-(p-vinylphenyl)-5-(β-naphthyl)oxazole. A long wavelength maxima observed was attributed to the formation of excimers, the number of which increase as the concentration of the luminophore in the copolymer increases. The presence of excimers has a negative effect on the scintillation activity. The extension of the conjugation chain in the aryl radical of the luminophore has a positive effect on the scintillation intensity. Film scintillators of styrene-substitued oxazole copolymers were less effected by the presence of excimers.

Synthesis of 2,5-diaryloxazole

2,5-diaryloxazoles, such as 2,5-diphenyloxazole (PPO) and 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP), are the most efficient fluorescent compounds which can be used as scintillators. The scintillators should be synthesized with absolute purity as even minute impurities can cause significant quenching of fluorescence emission.

POPOP   PPO
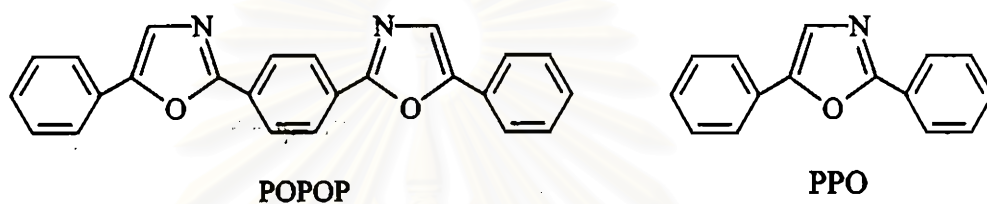
In general 2,5-diaryloxazoles, especially PPO, has been widely prepared by **the Fischer synthesis** from the one step reaction between an aryl cyanohydrin and an arylaldehyde in absolute ether at 0 °C with dry hydrogen chloride [21, 22].
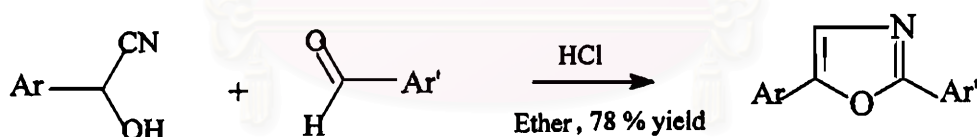
The reaction always gives 2,5-diaryl-oxazolid-4-one as the main byproduct together with other heterocyclic colored compound. The yield of this byproduct amounts to half of the yield of the oxazole under optimal conditions, while in the presence of even traces of water the yield of the oxazole drops rapidly with increased yield of the oxazolid-4-one. There is also a certain ambiguity in that the starting materials may exchange hydrogen cyanide, thus causing scrambling of the phenyl ring in the product if these bear different substituents.

Another method which is use for synthesizing 2,5-diaryloxazoles, especially POPOP, is the condensation of an α-aminomethylarylketone with arocyl halide, followed by cyclodehydration of the resulting α-aminomethyl-arylketones **(Robinson-Gabriel synthesis)** [23,24].
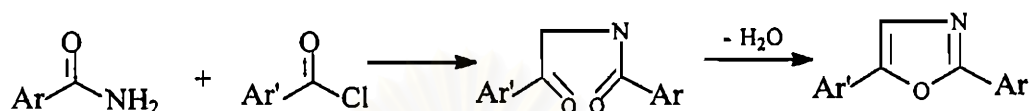

Concentrated sulfuric acid or phosphorus pentachloride is used as dehydrating agent effect the ring closure. However, the presence of the dehydrating agent leads to the formation of byproducts which are very difficult to remove. Thus this method is not suitable for obtaining the required purity of scintillator grade oxazoles. Another problem with this synthesis is the difficulty of obtaining the starting materials (either the α-aminocarbonyl compounds or their acrylate derivatives) which often require several synthetic steps.

In 1963, a modification of the Fischer synthesis using an aroyl cyanide instead of cyanohydrins have been developed which yields 2,5-diaryl-4-chloro(or bromo)oxazoles [25]. This method is known as **the Ternai synthesis**, which leads to the oxazoles in high yields (typically twice the yield of the analogue Fisher method) without the formation of the corresponding oxazolid-4-ones. The mechanism of the reaction may involve iminohalide intermediates (scheme1).
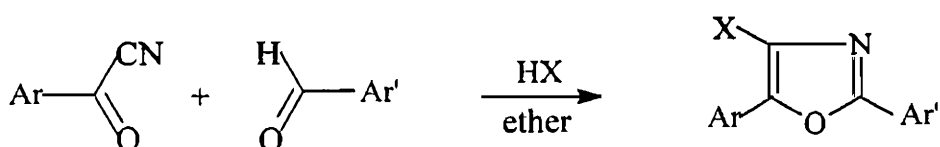
The halogen in the 4-position (Cl, Br or F) can be easily removed by reduction with Na amalgam in ethanol. Due to the convenience of using stable starting materials, easy purification of the product, obtained in high yield, this method is used almost exclusively for the commercial production oxazole based scintillators.

Generally, the fluorescence quantum yield of scintillators containing a halogen are generally low due to the "heavy atom" effect. However, it has been stated that the chloro group cause no difficulty in scintillation counting [2].
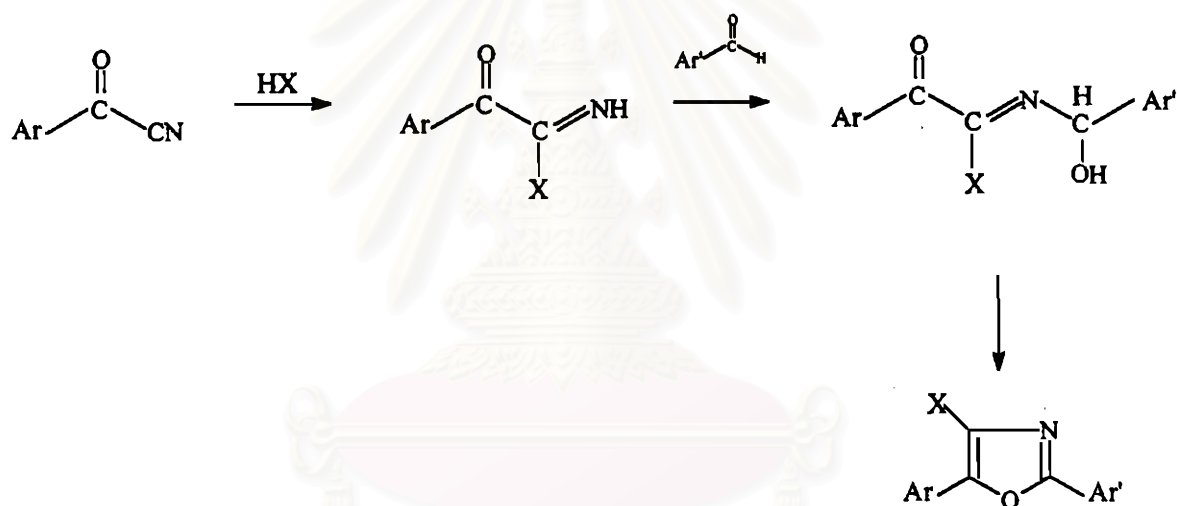
Scheme1

In 1977, The vinyl-substituted oxazole, was prepared in a six-stage synthesis involving the formation of 2-phenyl-5-(p-methyl)phenyloxazole, conversion of this compound to the corresponding Wittig salt, and subsequent conversion of the salt to the p-vinyl analog which was copolymerized with styrene as an efficient plastic scintillator (Scheme2). Experimental conditions for the various reactions within the synthetic scheme have been detailed elsewhere [19].
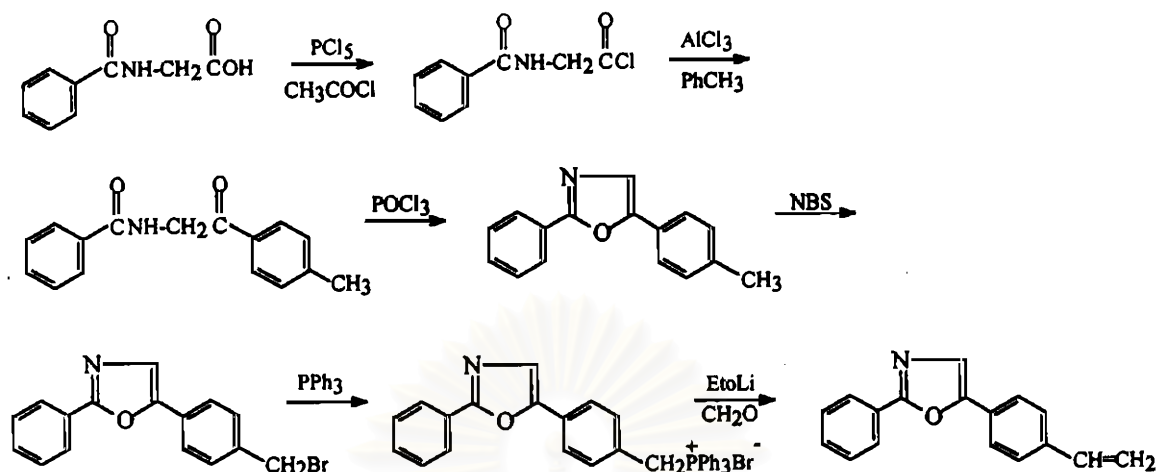
Scheme 2

This thesis reports the synthesis of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole using the Ternai method and its copolymer with styrene. The UV absorption, fluorescence spectra and the quantum yield has been obtained for, both the monomer and the copolymer.

Objectives of the research

The aim of this research is to synthesized a new copolymer of 4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole and styrene which can be used as an effective plastic scintillator. Moreover, the fluorescence emission properties of the copolymer are studied.

Scope of the research

1. Synthesis of 4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole.

   The reaction is shown in the following steps :

   1.1 Synthesis of 4-Chloro-2-(4′-ethylphenyl)-5-phenyloxazole

   1.2 Bromination of 4-Chloro-2-(4′-ethylphenyl)-5-phenyloxazole

   1.3 Dehydrobromination of 4-Chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazole

2. Preparation of poly(4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole -co-styrene) by varying the mol percent of the oxazole.

3. Investigation the copolymer's absorption and fluorescence emission properties.