

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Oxazole

Oxazoles are a class of five-membered ring, heteroaromatic compounds isoconjugate with the cyclopentadienyl anion and derived from this species by replacing two of the carbons with a nitrogen atom and an oxygen atom. Oxazoles are numbered around the ring starting at the oxygen atom and designated as 1,3-oxazoles to indicate the positions of heteroatom in the ring [12].

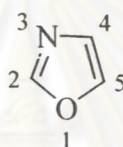
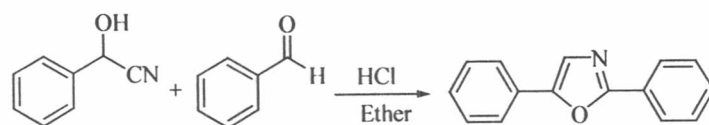


Figure 2.1: Structure of oxazole molecule

Many naturally occurring biologically active compounds contain one or more oxazole heterocyclic units. This has drawn much attention on the synthesis of such oxazole-containing natural products [13]. In addition, the discovery that 2,5-diphenyloxazole functioned as an efficient scintillation solute prompted the synthesis of a large number of 2,5-diphenyloxazole and related compounds [14].

2.2 Synthesis of 2,5-diphenyloxazole

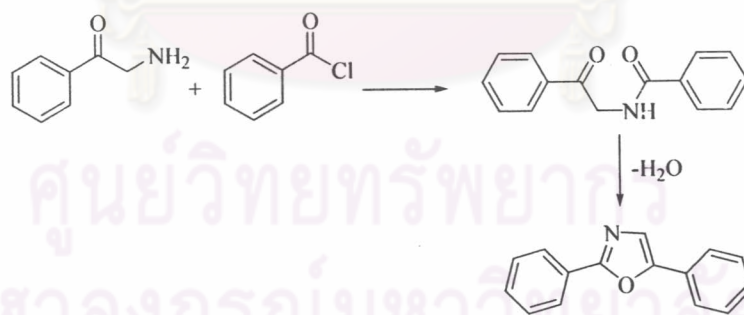
2,5-Diphenyloxazole is the most efficient fluorescent compound, which can be used as scintillator. The scintillator should be synthesized with absolute purity as even minute impurities can cause significant quenching of fluorescence emission. In general, 2,5-diphenyloxazole has been widely prepared by the Fischer synthesis [15] from the one step reaction between an aryl cyanohydrin and benzaldehyde in absolute ether at 0°C with dry hydrogen chloride.



Scheme 2.1: Synthesis of 2,5-diphenyloxazole by Fischer synthesis

The reaction always gives 2,5-diphenyloxazolid-4-one as the main byproduct together with other heterocyclic colored compound. The yield of this byproduct amounts to the 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 used for synthesizing 2,5-diphenyloxazole, is the condensation of an α -aminomethylketone with benzoyl halide, followed by cyclodehydration of the resulting α -aminomethylarylketone (Robinson-Gabriel synthesis) [16].

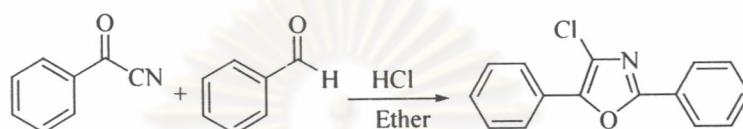


Scheme 2.2: Synthesis of 2,5-diphenyloxazole by Robinson-Gabriel synthesis

Concentrated sulfuric acid or phosphorus pentachloride is used as dehydrating agent to affect 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

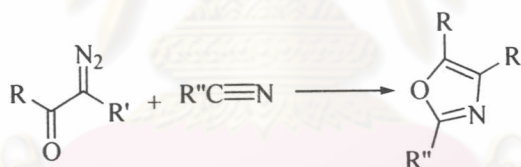
problem with this synthesis is the difficulty of obtaining the starting material, which often requires several synthetic steps.

In 1963, a modification of the Fischer synthesis [17] using a benzoyl cyanide instead of cyanohydrin had been developed which yielded 4-chloro-2,5-diphenyloxazole. This method leads to the oxazoles in high yields (typically twice the yield of the analogous Fischer method) without the formation of the corresponding oxazolid-4-ones.



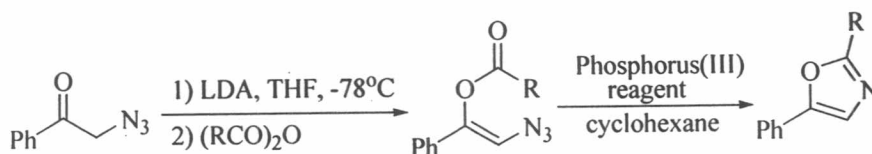
Scheme 2.3: Synthesis of 4-chloro-2,5-diphenyloxazole by modified Fischer synthesis

Doyle *et al.* [1980] reported that diazocarbonyl compounds react with nitriles under acidic condition to produce oxazoles [18].



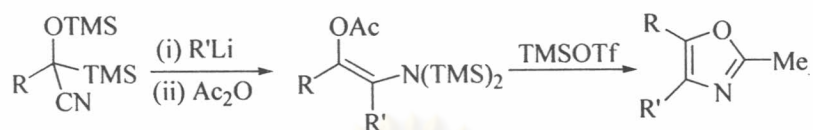
Scheme 2.4: Synthesis of oxazoles from diazocarbonyl compounds

Eguchi *et al.* [1989] described a synthetic method of oxazoles by an intramolecular aza-Wittig reaction. α -Azido ketones were initially converted to (*Z*)- β -(acyloxy)vinyl azides by selective enol acylation. These vinyl azides reacted with triethyl phosphate to afford the corresponding oxazole derivatives via the Staudinger reaction [19].



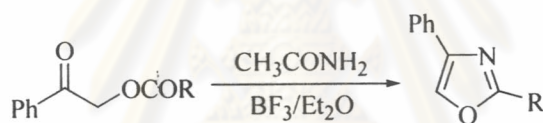
Scheme 2.5: Synthesis of oxazoles by intramolecular Aza-Wittig reaction

Cunico *et al.* [1992] had shown that sequential addition of organolithium reagents and acyl chloride to *o*-trimethylsilyl acyltrimethylsilane cyanohydrins affords β -(acyloxy)-*N,N*-bis(trimethylsilyl) enamines which cyclize to substituted oxazoles under thermolysis or treatment with trimethylsilyl trifluoromethanesulfonate [20].



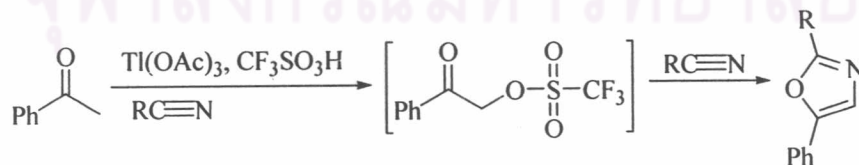
Scheme 2.6: Synthesis of oxazoles from cyanohydrin

Huang *et al.* [1996] described that acetamide was used as the nitrogen source to react with phenacyl benzoates in boiling xylene in the presence of $\text{BF}_3/\text{Et}_2\text{O}$ as the catalyst [21].



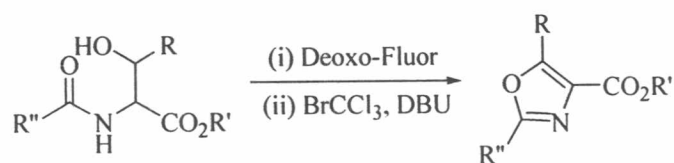
Scheme 2.7: Synthesis of oxazoles from acetamide and phenacyl benzoates

Lee *et al.* [1997] reported a direct method for conversion of aromatic α -methyl ketones to the corresponding oxazoles by use of the reaction of ketones with thallium(III) triflate (generated in situ by reaction of thallium(III) acetate with trifluoromethanesulfonic acid) in aliphatic nitrile [22].



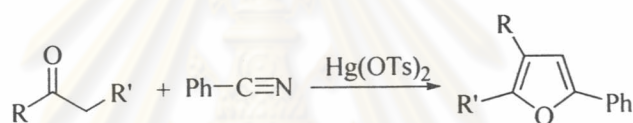
Scheme 2.8: Synthesis of oxazoles from aromatic α -methyl ketones

Williams *et al.* [2000] presented a one-pot protocol for the synthesis of oxazoles from β -hydroxy amides [23].



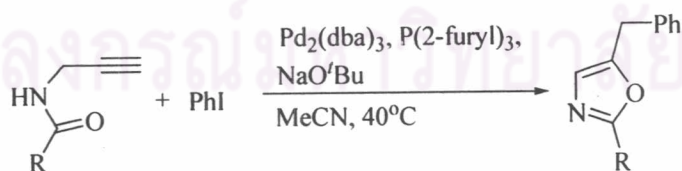
Scheme 2.9: Synthesis of oxazoles from β -hydroxy amides

Lee and Song reported a direct transformation of aromatic ketones into oxazoles in the presence of mercury(II) *p*-toluenesulfonate under microwave irradiation [24].



Scheme 2.10: Synthesis of oxazoles from aromatic ketones

Cacchi *et al.* [2001] proposed that 2,5-disubstituted oxazoles have been prepared through the reaction of *N*-propargylamides with aryl iodides in the presence of $\text{Pd}_2(\text{dba})_3$, tri(2-furyl)phosphine and NaO^tBu . The reaction appears to proceed through a palladium-catalyzed coupling step followed by the in situ cyclization of the resultant coupling product [25].



Scheme 2.11: Synthesis of oxazoles from *N*-propargylamides

However, preparation of these reactive intermediates is not always straightforward to carry out because of various limitations involved, such as rare availability of starting materials, complicated procedures, low yields and harsh

reaction conditions. In this research we sought to further delineate the effect of substituents on benzene rings for the synthesis of several 4-chloro-2,5-diphenyloxazoles by the modification of the Fischer method. This method provides chlorine atom at 4 position of oxazole ring, which can react further.

2.3 Photophysical processes in polymers

The study of the photophysics of synthetic polymers [26] 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 Jablonski state diagram. There are three states, which play dominant roles in the photophysical process of organic molecules. They are the ground (unexcited) state with opposing spin, and the lowest excited singlet state, which is higher in energy than the corresponding triplet state. Molecular orbital 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.

2.3.1 Unimolecular pathway

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

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 diagram (**Figure 2.2**). The energy level indicated corresponds to energy differences.

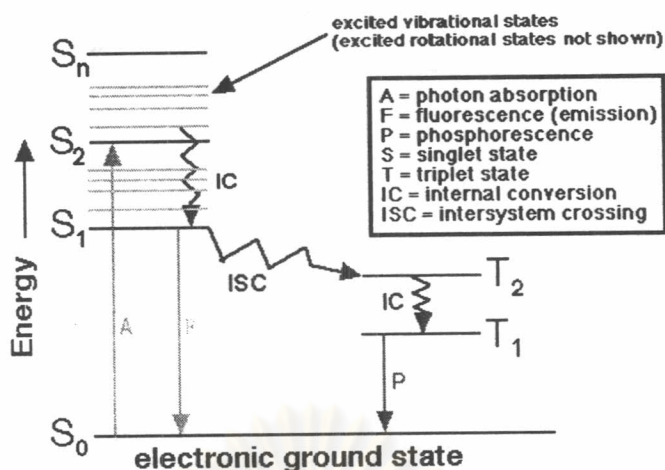


Figure 2.2: Jablonski state diagram of energy levels of organic molecules

- *Radiative processes*

Fluorescence is defined as the spin allowed emissive transition between vibrational states of identical multiplicity, usually from excitation of singlet to ground state. 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 vibration states of different multiplicity, generally from triplet state to ground state. Since the triplet state always lies below the excited singlet state, this band occurs at longer wavelengths than that of fluorescence. The lifetimes are relatively long, in the range of 10^{-4} -10 sec.

- *Nonradiative process*

There are two nonradiative processes. Internal conversion denotes a radiationless transition between two electronic states of the same multiplicity. Intersystem crossing is a similar radiationless transition connected with a change in multiplicity. 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. This occurs in condensed systems by energy transfer, i.e. transfer of vibrational energy to the surrounding medium.

2.3.2 Bimolecular pathway

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 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.



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. 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 or secondly, excitation localized on a sequence of chromophores may be transferred from one chromophore to the next by a hopping mechanism. This process is termed energy migration.

- *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.



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.

2.3.3 Quantum yield

When a fluorophore absorbs a photon of light, an energetically excited state is formed. The fate of this species is varied, depending upon the exact nature of the fluorophore and its surroundings, but the end result is deactivation (loss of energy) and return to the ground state. The main deactivation processes, which occur, are fluorescence (loss of energy by emission of a photon), internal conversion and vibration relaxation (non-radiative loss of energy as heat to the surroundings), and intersystem crossing to the triplet manifold and subsequent non-radiative deactivation.

The fluorescence quantum yield (ϕ_f) is the ratio of photons absorbed to photons emitted through fluorescence [27]. In other words the quantum yield gives the probability of the excited state being deactivated by fluorescence rather than by another, non-radiative mechanism. The quantum yield ranges from 0 to 1.

The most reliable method for recording ϕ_f is the comparative method, which involves the use of well-characterized standard samples with known ϕ_f values. Essentially, solutions of the standard and test samples with identical absorbance at the same excitation wavelength can be assumed to be absorbing the same number of photons. Hence, a simple ratio of the integrated fluorescence intensities of the two solutions (recorded under identical conditions) will yield the ratio of the quantum yield values. Since ϕ_f for the standard sample is known, it is trivial to calculate the ϕ_f for the test sample.

Calculation of fluorescence quantum yields

The gradients of the graphs are proportional to the quantum yield of the different samples. Absolute values are calculated using the standard samples which have a fixed and known fluorescence quantum yield value, according to the following equation.

$$\phi_x = \phi_{ST} \frac{(\text{Grad}_x) \eta_x^2}{(\text{Grad}_{ST}) \eta_{ST}^2}$$

Where the subscripts ST and X denote standard and test respectively, ϕ is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity vs. absorbance and η is the refractive index of the solvent.

2.4 Thermal properties of polymers

2.4.1 Polymer glass transition

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature, T_g [28]. As the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner. As the temperature rises above the T_g , the polymer becomes more rubber-like. Thus, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers.

This behavior can be understood in terms of the structure of glassy materials, which are formed typically by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally such materials have a high viscosity in the liquid state. When rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too sluggish or the geometry too awkward to take up a crystalline conformation. Therefore the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. The term glassy has come to be synonymous with a persistent non-equilibrium state. In fact, a path to the state of lowest energy might not be available.

To become more quantitative about the characterization of the liquid-glass transition phenomenon and T_g , it should be noted that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, T_f . Instead, at the glass transition temperature, T_g , there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value

in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in **Figure 2.3**. Note that the intersections of the two straight-line segments of curve (2) define the quantity T_g .

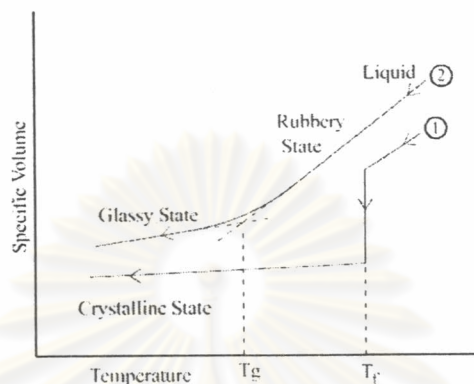


Figure 2.3: Curve of specific volume vs. temperature

The determination of T_g for amorphous materials, including polymers as mentioned above, by dilatometric methods (as well as by other methods) are found to be rate dependent. This is schematically illustrated in **Figure 2.4**, again representing an amorphous polymer, where the higher value, T_{g2} , is obtained with a substantially higher cooling rate than for T_{g1} .

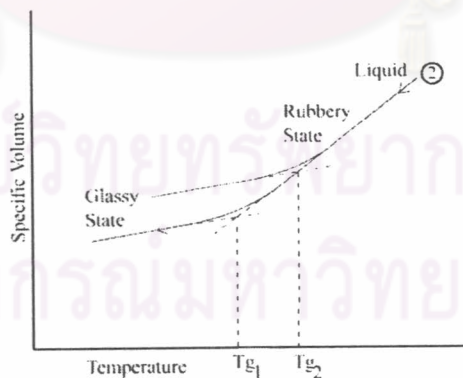


Figure 2.4: T_g for amorphous polymer

We can understand this rate dependence in terms of intermolecular relaxation processes. Since a glass is not an equilibrium phase, its properties will exhibit a time dependence, or physical aging. The primary portion of the relaxation behavior governing the glass transition in polymers can be related to their tangled chain

structure where cooperative molecular motion is required for internal readjustments. At temperatures well above T_g , 10 to 50 repeat units of the polymer backbone are relatively free to move in cooperative thermal motion to provide conformational rearrangement of the backbone. Below T_g , the motion of these individual chains segments becomes frozen with only small-scale molecular motion remaining, involving individual or small groups of atoms. Thus a rapid cooling rate or "quench" takes rubbery material into glassy behavior at higher temperatures (higher T_g).

Measurements of T_g are often made in a differential scanning calorimeter (DSC). In this instrument, the heat flow into or out of a small (10 – 20 mg) sample is measured as the sample is subjected to a programmed linear temperature change.

2.4.2 Differential scanning calorimetry

In differential scanning calorimetry (DSC), thermal properties of a sample are compared against a standard reference material, which has no transition in the temperature range of interest, such as powdered alumina. Each is contained in a small holder within an adiabatic enclosure as illustrated below.

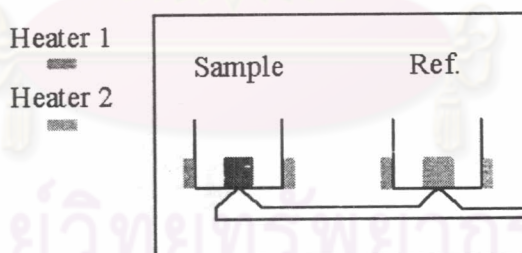


Figure 2.5: Differential scanning calorimetry (DSC) diagram

The temperature of each holder is monitored by a thermocouple and heat can be supplied electrically to each holder to keep the temperature of the two equal. A plot of the difference in energy supplied to the sample against the average temperature, as the latter is slowly increased through one or more thermal transitions of the sample yields important information about the transition, such as latent heat or a relatively abrupt change in heat capacity.

The glass transition process is illustrated in the figure below for a glassy polymer, which does not crystallize and is being slowly heated from below T_g .

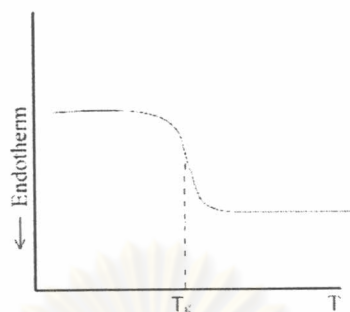


Figure 2.6: The glass transition process

Here, the drop marked T_g at its midpoint represents the increase in energy supplied to the sample to maintain it at the same temperature as the reference material, due to the relatively rapid increase in the heat capacity of the sample as its temperature is raised through T_g . The addition of heat energy corresponds to this endothermal direction.

A melting process is also illustrated below for the case of a highly crystalline polymer, which is slowly heated through its melting temperature.

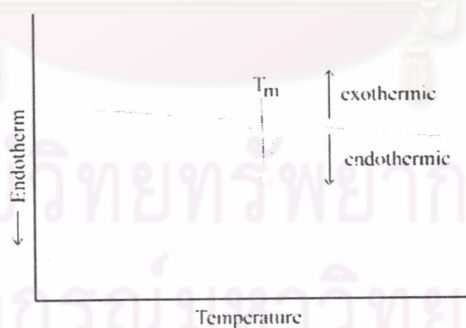


Figure 2.7: A melting process

Again, as the melting temperature is reached, an endothermal peak appears because heat must be preferentially added to the sample to continue this essentially constant temperature process. The peak breadth is primarily related to the size and degree of perfection of the polymer crystals.

Note that if the process were reversed so that the samples were being cooled from the melt, the plot would be inverted. In that case, as both are being cooled by ambient conditions, even less heat would need to be supplied to the sample than to the reference material, in order that crystals can form. This corresponds to an exothermal process.

Use of the DSC will be illustrated again in the section on liquid crystals in connection with the identification of their phase transitions. An interesting exercise for the reader would be to predict the general form of a DSC plot for a semicrystalline polymer, which has been rapidly quenched from the melt to a temperature below T_g . In the DSC plot, assume the temperature is slowly increased from this value below T_g to a value well above, thus allowing for significant increases in the chain mobility as temperatures above T_g are reached so that some crystallization can begin, well before the melting point is reached.

2.4.3 Factors affecting T_g

The magnitude of T_g varies over a wide temperature range for different polymers. As T_g depends largely on the amount of thermal energy required to keep the polymer chain moving, a number of factors which affect rotation about chain links, will also influence T_g .

Chain flexibility: The flexibility of the chain is undoubtedly the most important factor influencing T_g . It is a measure of the ability of a chain to rotate about the constituent chain bonds, hence a flexible chain has a low T_g whereas a rigid chain has a high T_g . The value of T_g is raised markedly by inserting groups which stiffen the chain by impeding rotation, so that more thermal energy is required to set the chain in motion.

Steric effects: The steric effects arise when bulky pendant groups hinder the rotation about the backbone and cause T_g to increase. The effect is accentuated by increasing the size of the side group. Superimposed on size factor are the effects of polarity and the intrinsic flexibility of the pendant group itself. An increase in the

lateral forces in the bulk state will hinder molecular motion and increase T_g . Thus polar groups tend to encourage a higher T_g than non-polar groups of similar size.

Configurational effect: Cis-trans isomerism in polydienes and tacticity variations in certain α -methyl substituted polymers alter chain flexibility and affect T_g .

Effect of crosslinks on T_g : When crosslinks are introduced into a polymer, the density of the sample is increased proportionally. As the density increases, the molecular motion in the sample is restricted and T_g rises. For a high crosslink density the transition is broad and ill-defined, but at lower values, T_g is found to increase linearly with the number of crosslinks.

2.5 Cyclic voltammetry

Cyclic voltammetry [29] is the most widely used technique for acquiring qualitative information about electrochemical reaction. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform (**Figure 2.8**). In this figure it is assumed that only the reduced form of the species is initially present. Thus, a positive potential scan is chosen for the first half cycle during which an anodic current is observed. Because the solution is quiescent, the product generated during the forward scan is available at the surface of the electrode for the reverse scan resulting in a cathodic current. Complex waveform composed of two isosceles triangles. The voltage is first held at the initial potential where no electrolysis occurs and hence no faradaic current flows. As the voltage is scanned in

the positive direction, so the reduced compound is oxidized at the electrode surface. At a particular set value, the scan direction is reversed and the material that was oxidized in the outward excursion is then reduced. Once the voltage is returned to the initial value, the experiment can be terminated. In this figure however a further voltage excursion takes place to more negative (more reducing) values. This may be useful in probing for other species present in the sample or for investigating any electroactive products formed as a result of the first voltage excursion.

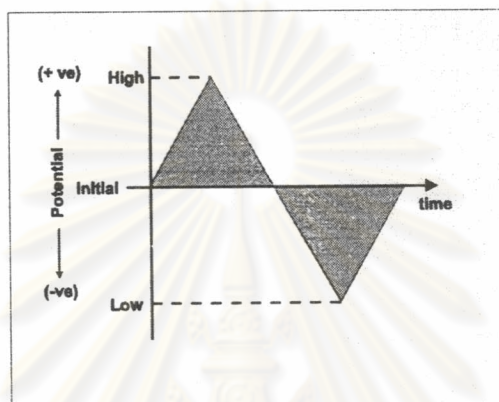


Figure 2.8: Potential-time excitation signal in cyclic voltammetric experiment

The basic shape of the current response for a cyclic voltammetry experiment is shown in **Figure 2.9**. At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidized form (point A). As the redox potential is approached, there is a net anodic current, which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidized to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence is qt resulting in any asymmetric peak shape. Upon reversal of the scan (point C), the current continues to decay with a qt until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current, which eventually produces a peak shape response (point D).

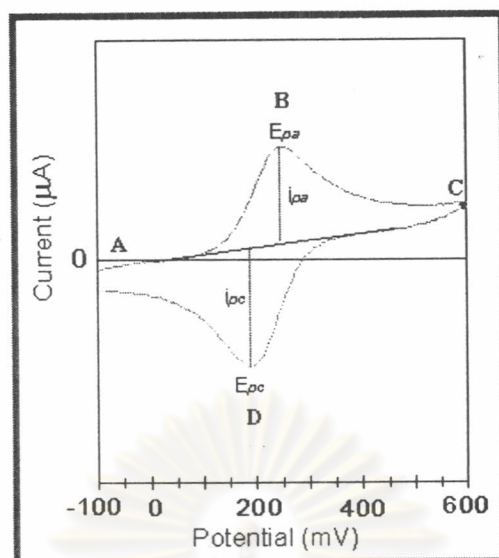


Figure 2.9: Typical cyclic voltammogram

If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst equation. The situation is very different when the redox reaction is not reversible, when chemical reactions are coupled to the redox process or when adsorption of either reactant or products occurs.

Electrochemical cell and electrodes used in cyclic voltammetry experiments

An electrochemical cell must consist of at least two electrodes and one electrolyte. An electrode may be considered to be an interface at which the mechanism of charge transfer changes between electronic (movement of electrons) and ionic movement of ions. An electrolyte is a medium through which charge transfer can take place by the movement of ions.

In a cell used for electroanalytical measurements there are always three electrode functions (**Figure 2.10**). The first of the three electrodes is the indicating electrode also known as the working electrode. This is the electrode at which the electrochemical phenomena being investigated take place. The second functional electrode is the reference electrode. This is the electrode whose potential is constant enough that it can be taken as the reference standard against which the potentials of the other electrodes present in the cell can be measured. The final functional electrode is the counter or auxiliary electrode, which serves as a source or sinks for electrons so that current can be passed from the external circuit through the cell. In general, neither its true potential nor current is ever measured or known.

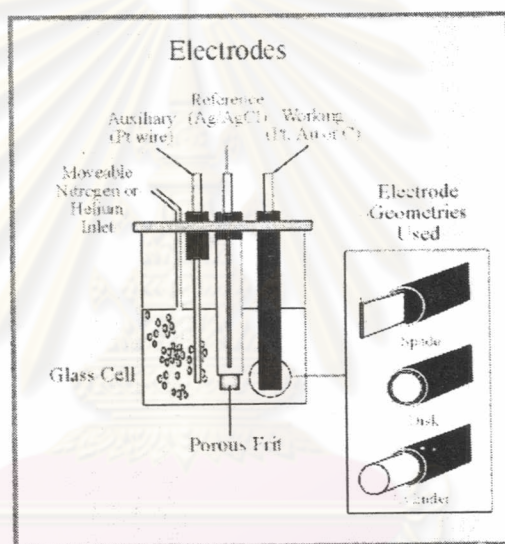


Figure 2.10: Electrochemical cell and electrodes

2.6 Electrospinning

A schematic diagram to interpret electrospinning [30] of polymer nanofibers is shown in **Figure 2.11**. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidified, and is collected as an interconnected web of small fibers. One electrode is placed into the spinning solution/melt and the other attached to the collector. In most cases, the

collector is simply grounded. The electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the concentration of the surface charges to the counter electrode cause a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. Further increasing the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In case of melting the discharged jet solidifies when it travels in the air.

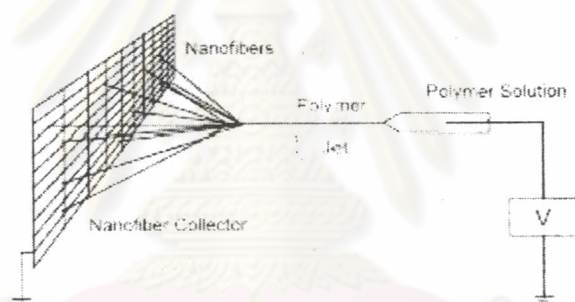


Figure 2.11: Schematic of the electro spinning process

Many parameters can influence the transformation of polymer solutions into nanofibers through electrospinning. These parameters include (a) the solution properties such as viscosity, elasticity, conductivity, and surface tension, (b) governing variables such as hydrostatic pressure in the capillary tube, electric potential at the capillary tip, and the gap (distance between the tip and the collecting screen), and (c) ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber.

As long as a polymer can be electrospun into nanofibers, ideal targets would be in that: (1) the diameters of the fibers are consistent and controllable, (2) the fiber surface is defect-free or defect-controllable, and (3) continuous single nanofibers be

collectable. However, researches so far have shown that their three targets are by no means easily achievable.

2.7 Scintillator

Scintillation counting [31] 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 collision of the particles with the scintillation molecules, since the accuracy of scintillation counting is controlled by the relaxation time of the electrons from their excitation state. This technique is used in medical or biological laboratories, environmental science, nuclear physics, and in many other fields of science and technology.

Scintillation is essentially a radioluminescence event comprising of the following steps: (1) loss of energy by a flash charged particle in the scintillator, this energy being extended 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 centers (molecules, ions, or more complex entities); and (3) emission of scintillation light by the luminescence centers.

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 flashes into electrical impulses), and an electronic device for counting these impulses. The impulse count is indicative of the ionizing flux density and, consequently, particle energy.

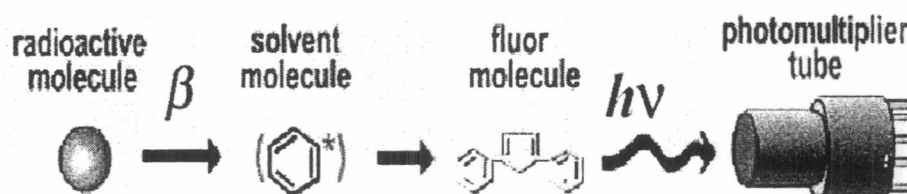


Figure 2.12: The photomultiplier/scintillation counter system

The requirements for 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 marker (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) types of radiation. In any event, their scintillation efficiency must be as high as possible. 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, luminophore solutions in organic solvents (liquid scintillators), and solid solutions in plastics (plastic scintillator). They are less effective than inorganic scintillators (scintillating phosphors) in detecting gamma rays and heavy particles, produce impulses of lower amplitude, 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 near the maximum of the spectral response curve of the most widely used photomultiplier tubes, this is why such a scintillator may have a rather large volume.

A large category of practical organic scintillators is based on organic molecules with certain symmetry properties, which give rise to what is known as a π -electron structure. The π -electronic energy levels of such a molecule are illustrated in Jablonski state diagram (**Figure 2.2**). For molecules of interest as organic scintillators, the energy spacing between S_0 and S_1 is 3 or 4 eV, whereas spacing between higher-lying state is usually somewhat smaller.

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 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 decay 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, and gamma and X rays.

2.7.1 Liquid scintillators

The efficiency of liquid scintillators is lower than in the best crystal ones, yet it may be as high as 60, 70 or more percent of the scintillation efficiency of anthracene single crystals. Liquid scintillators feature a number of advantages, which make them useful in various applications, especially where crystal scintillators cannot be used.

The best liquid scintillators are characterized by a short flash duration which is $(3-5) \times 10^{-9}$ s and less; the transparency to their own emission is greater than in the necessary and easily given any shape to correspond with that of the detector; the source of radiation can be accommodated inside the detector. By introducing appropriate luminophores and by increasing or decreasing their concentration one can drastically change the scintillator properties.

Liquid scintillators are easier to make than crystal and plastic ones. The cost of scintillating solution is determined by that of the solvent (base) and luminophores (activated additives). They are used in the detection of alpha and beta particles, gamma and neutron radiation, and ^{14}C and tritium in various objects, including biological substrates. Liquid scintillators are sometimes instrumental in measuring low-level gamma activity in living organisms. The possibility of extending the surface area of liquid scintillators is of great importance in cosmic radiation measurements.

2.7.2 Plastic scintillators

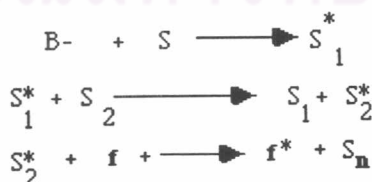
Plastic scintillators represent a complex system composed of a polymer (polymer base) and an organic luminescent compound (luminescent additive). The main characteristics of plastic scintillators are their scintillation efficiency and light yield.

The scintillation efficiency of a polymeric compound depends on the properties of both the luminescent additives and the polymer base. The use of polymers in scintillation compounds is determined by their ability to convert electronically excited energy into light energy, which happens because of the presence of the π -conjugated system in the macromolecule, and also by the transmission by polymers of the light of their natural luminescence and radiation of the luminescent additives.

The main requirements imposed on luminescent additives are high quantum yield and maximum overlap of the absorption and luminescence spectra of the polymer base. To increase the transmission of the whole system, another luminescent additive, the spectrum mixer, is introduced in the polymeric scintillation compound as a result of which the efficiency of light flash recording by the photomultiplier tube also increases.

2.7.3 Scintillation processes

In the first step of the scintillation process the beta particle excites the solvent molecule.



where: (B-) = energy of B

S = Solvent

* = excited state

In the second step of the scintillation process the excited solvent molecule transfers its energy to neighboring solvent molecules. This process continues until an excited solvent molecule transmits its energy to a fluor molecule, which is raised to a higher energy state. When the fluor returns to its ground state, it emits a photon of light ($h\nu$) at lower energy (longer wavelength) than it received. This radiation is detected by a photomultiplier tube and measured. A second fluor may be incorporated in the cocktail to shift the wavelength of light to a region in which the photomultiplier tube is more sensitive. Light flashed from the cocktail in the counting vial are detected and measured by the photomultiplier tube and associated electronics. The total number of atoms of the radionuclides present which spontaneously decay in a unit time is the absolute activity of that sample, usually expressed as disintegrations per minute DPM. Because factors in the environment, mainly substance in the cocktail, interfere with the energy transfer step outlined above, not every disintegration is detected by the photomultiplier tube. Since the counts per minute are always a fraction of the actual disintegration per minute, the efficiency of the LS Counting is expressed as shown:

$$\% \text{ efficiency} = \frac{\text{CPM}}{\text{DPM}} \times 100$$

Quenching [32] reduces scintillation counting efficiencies in two manners:

1. Quenching due to chemical or physical interference with the energy transmitted from the β -particle to the scintillator.

- a) When chemical agents compete with the scintillant molecules during the process of energy transfer, chemical quenching occurs. In other words, some energy is absorbed by an interfering substance and is dissipated as heat. Strong quenching agents include ketones, tertiary amines, thiols, iodides, oxygen, nitrosylated alkanes, and water.
- b) Analogous to chemical quenching, dilutional quenching prevents emitted energy from reaching and exciting the scintillant in solution. This typically occurs due to the diluting effect of aliphatic ether, esters, and alcohols on scintillation fluors.

- c) Lastly, physical quenching can reduce count efficiencies through self-absorption or surface adsorption.

Self-absorption is more pronounced with weak emitters such as ^3H and occurs when the radiolabeled material is incompletely dissolved or precipitate, resulting in a non-homogeneous mixture. In such a state, the weak energy is more likely in these cases to be absorbed by the compound itself rather than reaching solvent scintillant.

Surface adsorption reduces efficiencies by changing count conditions from 4π to 2π counting. When homogeneously dissolved, a radiolabelled compound is surrounded on all sides by the scintillation fluid, such that the solid angle subtended at the molecule surface is 4π . When adsorbed to other solid molecules or to the solid surface of the vial, the radiolabel surface is only in contact with fluid on one side, subtending a solid angle of 2π . In 2π counting, only half the β -energy is transmitted to the scintillation fluid, thus reducing counting efficiency by up to 50%.

2. Quenching due to interference with transmission of light from the scintillator to the counter's photomultiplier tube.

- a) Chemically, color quenching occurs when colored compounds are present in the sample and absorb or scatter some of the light emitted by the scintillator. Most colored compounds have absorption spectra, which overlap, to some extent with that of common scintillators. Red solution is the strongest and most common culprits of color quench and include heme-containing compounds as well as phenol red.
- b) Physically, the composition of the liquid scintillation vial is not as critical as many would believe. Though it is true that plastic or polyethylene tubes may reduce counting efficiencies of weaker emitters by a few percent as compared to clear glass, this impairment is typically improved by inclusion of secondary scintillators present in many common scintillation fluids.