# 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 [31].
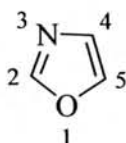
Figure 2.1: Structure of oxazole molecule.

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 [32,33,34,35]. 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 [36,37].
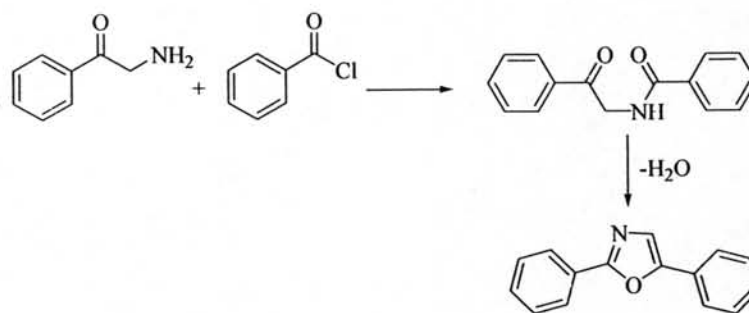
2.2 Synthesis of 2,5-diphenyloxazole

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 [38] from the one step reaction between an aryl cyanohydrin and benzadehyde in absolute ether at 0°C with dry hydrogen chloride.
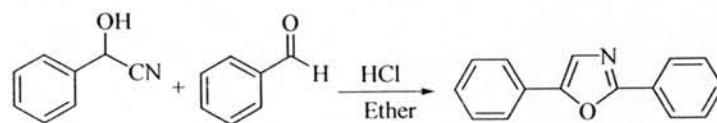
Scheme 2.1: Synthesis of 2,5-diphenyloxazole by Fischer synthesis.

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) [39].

**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 [40] 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.
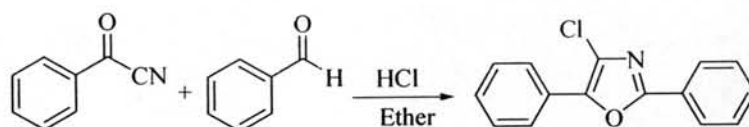
Scheme 2.3: Synthesis of 4-chloro-2,5-diphenyloxazole by modified Fischer synthesis.

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 Pd$_2$(dba)$_3$, tri(2-furyl)phosphine and NaO^{t}Bu. The reaction appears to proceed through a palladium-catalyzed coupling step followed by the in situ cyclization of the resultant coupling product [41].
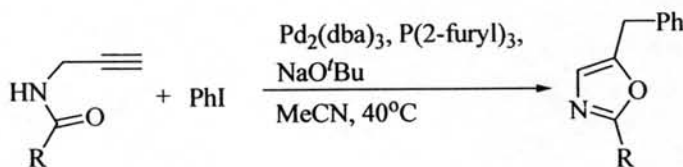
Scheme 2.4: Synthesis of oxazoles from *N*-propargylamides.

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 [42,43] 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.
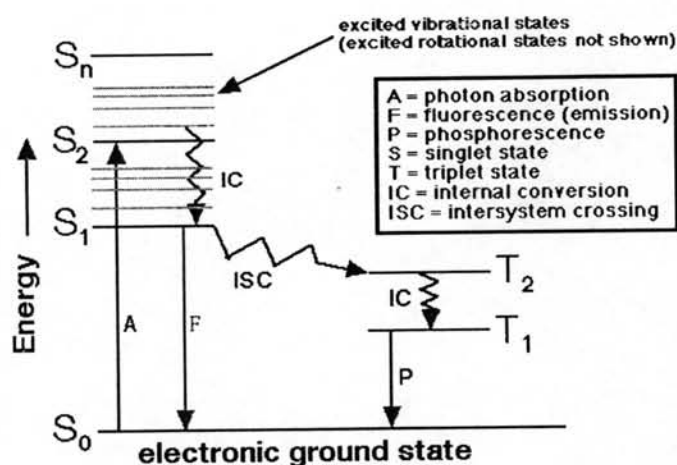
Figure 2.2: Jablonski state diagram of energy levels of organic molecules.

- *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

$$D^* + A \longrightarrow D + A^*$$

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

$$D^* \longrightarrow D + h\nu$$
$$A + h\nu \longrightarrow A^*$$

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.

$$M + M^* \longrightarrow MM^*$$

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

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 [44]. 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.

$$\phi_x = \phi_{ST} \frac{(Grad_x) \, \eta_x^2}{(Grad_{ST}) \, \eta_{ST}^2}$$

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.
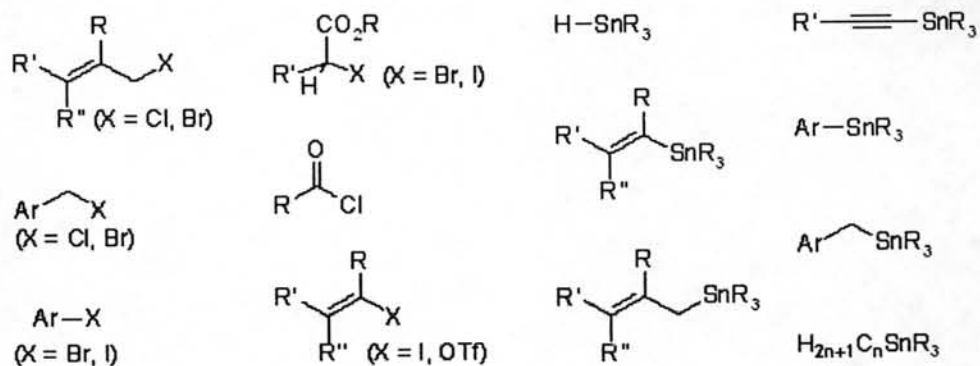
2.4 Stille coupling reactions

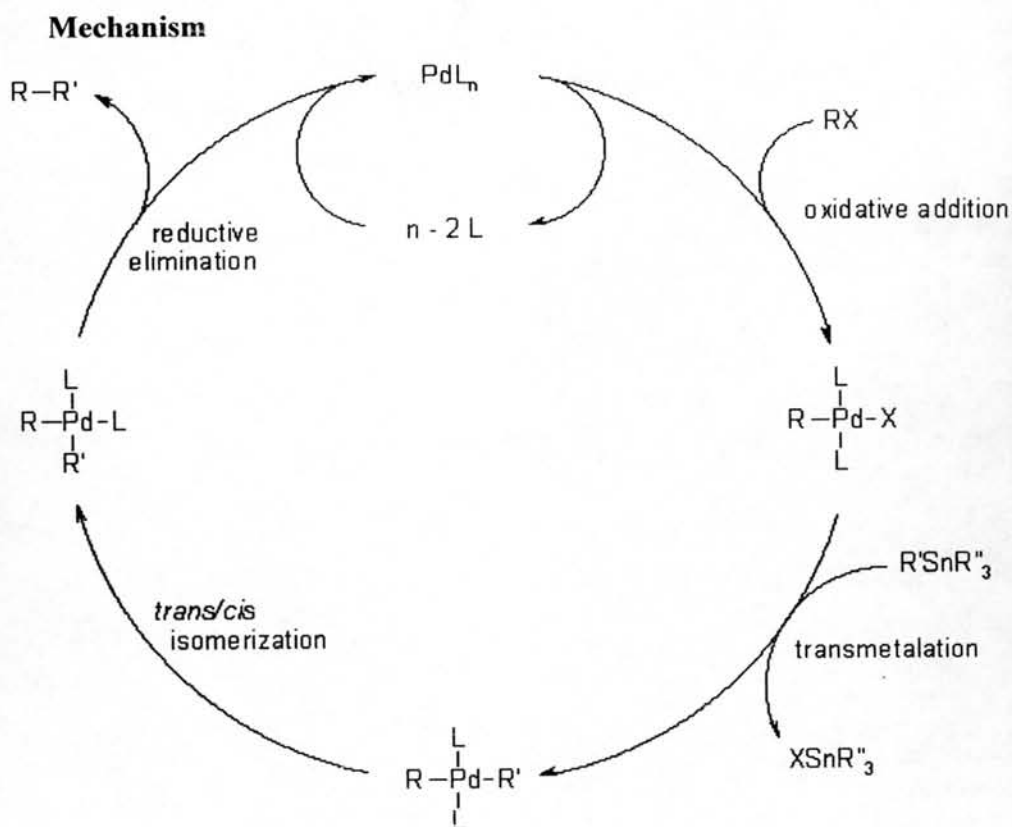$$R'-X \quad + \quad RSnBu_3 \quad \xrightarrow{\text{Pd-Cat}} \quad R'-R \quad + \quad XSnBu_3$$
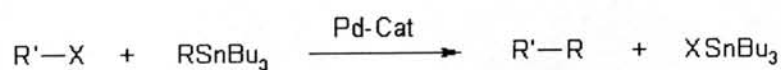
Scheme 2.5: Synthesis by Stille coupling reaction.

The Stille coupling is a versatile C-C bond forming reaction between stannanes and halides or pseudohalides, with very few limitations on the R-groups. Well-elaborated methods allow the preparation of different products from all of the combinations of halides and stannanes depicted below. The main drawback is the toxicity of the tin compounds used, and their low polarity, which makes them poorly soluble in water. Stannanes are stable, but boronic acids and their derivatives undergo much the same chemistry in what is known as the Suzuki coupling. Improvements in the Suzuki coupling may soon lead to the same versatility without the drawbacks of using tin compounds.

Convenient electrophiles and stannanes:

Figure 2.3: Structure of stannanes and halides or pseudohalides.

Mechanism

R—R' PdL$_n$ RX

reductive
elimination n - 2 L oxidative addition

L
|
R—Pd-L
|
R'

L
|
R—Pd-X
|
L

trans/cis
isomerization — R'SnR"$_3$

transmetalation

L
|
R—Pd-R'
|
L

XSnR"$_3$

Scheme 2.6: Mechanism of Stille coupling reaction.

2.5 Thermal properties of polymers

2.5.1 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 [45,46]. 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.

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 2.4**. Note that the intersections of the two straight-line segments of curve (2) define the quantity T_g.
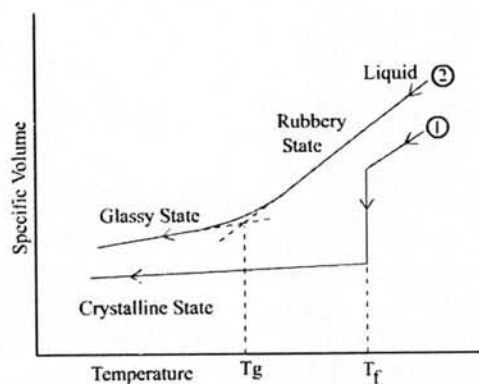
Figure 2.4: Curve of specific volume vs. temperature.

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 2.5**, again representing an amorphous polymer, where the higher value, T_{g2}, is obtained with a substantially higher cooling rate than for T_{g1}.
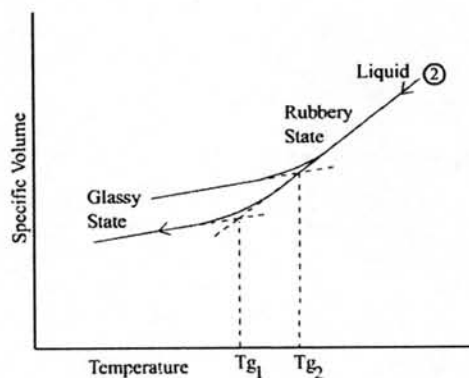

Figure 2.5: T_g for amorphous polymer.

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 Tg, 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 Tg, 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 Tg).

Measurements of Tg 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.

2.5.2 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.
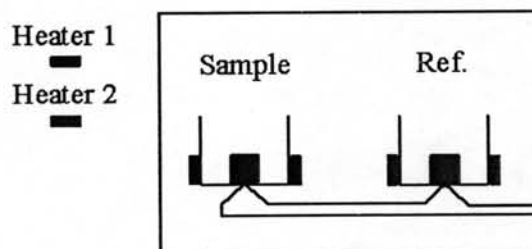

Figure 2.6: Differential scanning calorimetry (DSC) diagram.

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 Tg.
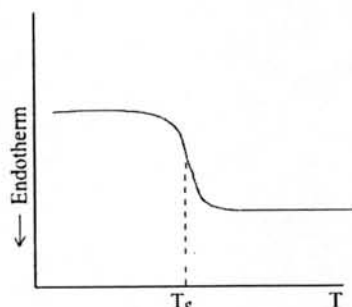
Figure 2.7: The glass transition process.

Here, the drop marked Tg 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 Tg. The addition of heat energy corresponds to this endothermal direction.

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 Tg. In the DSC plot, assume the temperature is slowly increased from this value below Tg to a value well above, thus allowing for significant increases in the chain mobility as temperatures above Tg are reached so that some crystallization can begin, well before the melting point is reached.

2.5.3 Factors affecting Tg

The magnitude of Tg varies over a wide temperature range for different polymers. As Tg 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 Tg.

Chain flexibility: The flexibility of the chain is undoubtedly the most important factor influencing Tg. It is a measure of the ability of a chain to rotate about the constituent chain bonds, hence a flexible chain has a low Tg whereas a rigid chain has a high Tg. The value of Tg 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 Tg 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 Tg. Thus polar groups tend to encourage a higher Tg than non-polar groups of similar size.

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

Effect of crosslinks on Tg: 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 Tg rised. For a high crosslink density the transition is broad and ill-defined, but at lower values, Tg is found to increase linearly with the number of crosslinks.