

Chapter 2

Basic Theoretical Concepts

Chapter 2

Basic Theoretical Concepts

2.1. The Electric Polarization:

Dielectrics may be broadly divided into 'non-polar materials' and 'polar materials'. In non-polar materials the molecules, which are usually diatomic and composed of two atoms of the same type, may be represented as positive nuclei of charge q surrounded by symmetrically distributed negative electron cloud of charge $-q$. In the absence of an applied field, the center of gravity of the positive and negative charge distributions coincide. When the molecules are placed in an external electric field the positive and negative charges experience electric forces tending to move them apart in the direction of the external field. The centers of positive and negative charges no longer coincide and the molecules are said to be polarized. Each molecule now forms a dipole whose moment is defined as ⁽⁴¹⁾

$$p = qdI \quad (2.1)$$

Where dI is the distance between the two centers of charge and is a vector pointing from the negative to the positive charge dipoles so formed are known as induced dipoles since when the field is removed the charges resume their normal distribution and the dipoles disappear.

There are several types of polarization:

2.1.1. Electronic Polarization ⁽⁴²⁾:

When an isolated neutral atom is placed in an electric field it acquires a dipole moment and is said to be polarized. In this case the relationship between the induced dipole moment and the electronic structure of the atom is a simple one:

$$p_{ind} = \alpha_e E \quad (2.2)$$

where the proportionality factor α_e is called the electronic polarizability of the atom.

2.1.2. Ionic Polarization:

As the name implies is only found in ionic substances (such as sodium chloride) whose molecules are formed of atoms having excess charge of opposite polarities. An electric field will tend to shift the relative position of the positive and negative ions of a molecule, thus inducing a dipole moment other than that induced by the distortion of the electronic charges around individual atoms. The ionic polarization is given by:

$$p_i = \alpha_i E \quad (2.3)$$

Where α_i is the ionic polarization of the molecules

2.1.3. Orientation Polarization ⁽⁴¹⁾:

It is associated with dipolar substance. Here the molecules or association of ions possess a dipole moment even in the absence of an

applied field. Such a moment is not normally observed macroscopically because as a result of thermal agitation the molecules are oriented at random so that the average moment over a physically small volume is zero. In the presence of an external field the dipoles experience a torque tending to orient them in the direction of the field so that the average moment is no longer zero. Finally, the average dipole moment per molecule is given by:

$$\mathbf{p} = \alpha \mathbf{E} \quad (2.4)$$

And the electric polarization by:

$$\mathbf{P} = N\alpha\mathbf{E} \quad (2.5)$$

Where N is the number of molecules per unit volume and α is the total polarizability ($\alpha_e + \alpha_i + \alpha_o$) and E is the electric field intensity acting on each molecule and is usually referred to as the local field or the internal field.

2.2. Electrical Properties of Polymers:

The basic properties of dielectrics are the permittivity (dielectric constant) and the dielectric loss.

2.2.1- Dielectric Constant:

The dielectric constant of a dielectric material can be defined as the ratio of capacity C of an electric capacitor filled with the dielectric substance to that of the vacuum at a definite external field (41) frequency:

$$\epsilon_r = \frac{C}{C_o} \quad (2.6)$$

Where ϵ_r is called the relative permittivity or dielectric constant of the medium.

The value of ϵ_r is a dimensionless parameter which characterizes a given dielectric material.

In the MKS system of units, the permittivity or the absolute dielectric constant of the medium is defined as ⁽⁴³⁾

$$\epsilon = \epsilon_o \epsilon_r \quad (2.7)$$

Where ϵ_o is so-called dielectric constant, which describes an electric field which doesn't interact with matter (permittivity of vacuum).

The dielectric constant ϵ_o is equal to $8.454 \cdot 10^{-12}$ F/m. The term (dielectric constant) is sometimes used for both ϵ & ϵ_r .

The dielectric constant ϵ of a material can also be defined in terms of the inverse square dependence of the distance (r) of the repulsive force (F) between like charges. Mathematically, this is expressed as ⁽³⁹⁾:

$$F = \frac{q_1 q_2}{\epsilon * r^2} \quad (2.8)$$

Where $q_1=q_2 =1$ electrostatic unit (ESU) of charge in vacuum. The magnitude of ϵ is always dimensionless & preserves its value irrespective of the selected system of units and the form of writing the equations. E is the force on 1 ESU of charge and is a vector quantity (oriented in the direction of r), for a unit charge.

$$E = \frac{q}{\epsilon * r^2} \quad (2.9)$$

2.2.2. Dielectric losses:

When an electric field acts on any matter the latter dissipates a certain quantity of electric energy that transforms into heat energy. This phenomena is commonly known as "the expense" or "loss" of the power. The loss of power in a specimen of a material is directly proportional to the square of the electric voltage applied to the specimen ⁽⁴³⁾.

$$P = V^2 / R \quad (2.10)$$

Where P is the loss of power in watts, V is the voltage in volts and R is the resistance in ohms. For dielectrics, under a given voltage, the dissipation of power depends on the voltage frequency; the expense of power at an alternating voltage is markedly higher than that at a direct voltage & rapidly grows with an increase in the frequency, voltage & capacitance and also depends on the material of the dielectric.

So, the dielectric losses is defined as the amount of power losses "dissipated" in dielectric under the action of voltage applied to it.

Dielectric losses at a direct voltage can easily be found from the relation (2.10), where R stands for the resistance of insulation while the losses under an alternating voltage are determined by more complicated equations. When considering dielectric losses we usually mean the losses precisely under an alternating voltage.

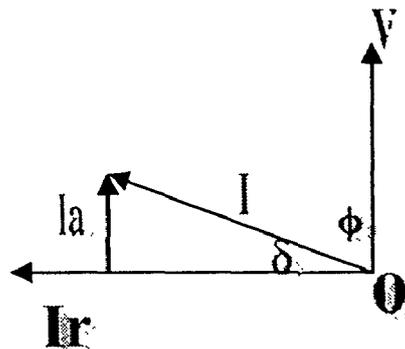
2.2.3. Dielectric Loss Angle:

Let us plot a phase diagram of current & voltage capacitor energized by an alternating voltage. If the power were not dissipated at all in the dielectric of the phasor of current I through the capacitor, would be a head of the phasor of voltage V precisely by 90° and the current would be purely reactive. In actual fact the phase angle ϕ is slightly less than 90° ; the total current I through the capacitor can be resolved into two components- active I_a & reactive I_r currents. Thus, the phase angle describes a capacitor from the viewpoint of losses in a dielectric. Since the phase angle is very close to 90° in a capacitor with a high- quality of dielectric, the angle δ is more descriptive parameter which when added to the angle ϕ , brings the angle ϕ to 90 ($\delta = 90^\circ - \phi$). The angle δ is called the dielectric loss angle, where the tangent of this angle is equal the ratio between the active & the reactive currents ⁽⁴³⁾:

$$\tan\delta = I_a/I_r \quad (2.11)$$

Or the ratio of the active power (power loss) P to the reactive power P_q :

$$\tan\delta = P/P_q \quad (2.12)$$



The dielectric loss angle is an important parameter both for the material of a dielectric and an insulated portion. All other conditions being equal, the dielectric losses grow with this angle. This parameter is usually described by the so-called loss tangent $\tan \delta$.

2.3. Frequency Dependence of the Dielectric Properties ⁽⁴³⁾:

- The dielectric constant:

The time required for electronic or ionic polarization to set in is very small as compared with the time of the voltage sign change (i.e. with the half-period of the alternating voltage) even for the highest frequencies. For this reason the dielectric constant of non polar dielectrics doesn't depend on the frequency when it changes within very broad limits.

When the frequency of alternating voltage increases the value of ϵ' of a polar dielectric at first remains invariable but beginning with a certain critical frequency f_0 when polarization fails to settle itself completely during one half period, ϵ' begins to drop approaching, at very high frequencies, the value typical of non polar dielectrics. As a general rule, an increase in the frequency may be attended by a practical independence of ϵ' on frequency or a drop in ϵ' , but never an increase of the latter.

By an analogy with the dispersion of light, the dependence of ϵ' on the frequency is known as dielectric dispersion.

- **The dielectric loss:**

Practically, the dependence of $\tan \delta$ or $\epsilon \tan \delta$ of an electrical insulating material on frequency shows different natures of dependence in the range of frequency change – an increase or decrease at a high frequency, or transition through the maximum or even through several maxima.

2.4. Temperature Dependence of Dielectric Properties⁽⁴³⁾:

- **The dielectric constant:**

In a non polar dielectric, the electronic polarizability of a molecule doesn't depend on temperature. However, due to thermal expansion of matter, the ratio of the number of molecules to the

effective length of the dielectric diminishes when the temperature increases, for this reason ϵ' should also diminish in this case. The nature of dependence of permittivity on temperature may be different in solid ionic dielectrics. In most cases an ionic mechanism of polarization increases ϵ' when the temperature grows. When the dependence of the permittivity are plotted versus two variable factors frequency & temperature, it can be seen that when the frequency increases the dipole maxima in the temperature trend of ϵ' are displaced towards higher temperature & become lower.

- **The dielectric loss:**

The dielectric losses caused by the dipole mechanism reach their maximum at a certain definite temperature. In actual fact, the rise in temperature and the resulting drop in viscosity exert a double effect on the amount of losses due to rotating dipoles; on one hand, the degree of the dipole orientation increases and on the other hand, there is a reduction in the energy required to overcome the resistance of the viscous medium internal friction of matter when the dipole rotates through a unit angle. The first factor increases P and therefore $\tan\delta$ and the second diminishes these magnitudes.

2.5. D.C Electrical Conductivity:

The electrical conductivity of polymers depends on the presence of free ions not connected chemically with the macromolecules. Materials are commonly classified according to their

conductivities into three categories of insulators, semiconductors & conductors or metals ⁽³⁹⁾

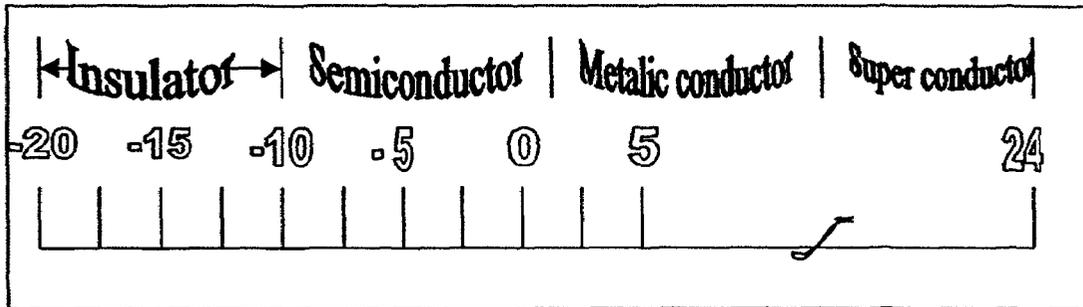


Figure (2.1): Conductivity ranges of various classes of materials at 300 K. Log scale units reciprocal of cm

The conductivity σ is related to the number of charge carriers' n , the mobility μ & the charge of the carrier e by the following relation ⁽⁴²⁾

$$\sigma \equiv \sum_{j=1}^j n_j \cdot e_j \cdot u_j \tag{2.13}$$

The molecular chain proper doesn't participate in the transfer of the electric charges. Therefore the conductivity of polymers depends largely on the presence of low- molecular impurities that can serve as sources of ions. The chemical constitution has only an indirect effect on the mobility of the ions.

In the glassy state, the conductivity of the polymers is approximately 10^{-3} to $10^{-19} \text{ohm}^{-1} \text{cm}^{-1}$ ⁽⁴⁾.

With increasing the temperature, the conductivity of polymers increases according to an exponential law:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{KT}\right) \quad (2.14)$$

K is Boltzman constant = $8.13 \cdot 10^{-15}$. σ_o is pre-exponential factor and inversely proportional to the temperature. E_a is the activation energy.

At temperature above the glass-transition temperature the ionic mobility increases owing to the considerable mobility of the chain units & the conductivity rises.

Experimentally, the conductivity is determined by measuring the current flow (I) at a given voltage (V). The resulting value is multiplied by the sample thickness & divided by the cross sectional area to eliminate geometrical consideration ⁽³⁹⁾.

$$\sigma = \frac{I}{V} \left(\frac{L}{A}\right) \quad (2.15)$$

$$\sigma = \frac{1}{R} \left(\frac{L}{A}\right) \quad (2.16)$$

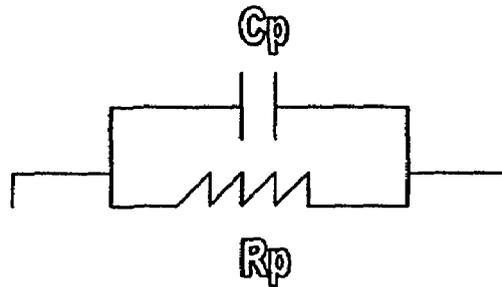
2.6. The A.C Electrical Conductivity:

For measuring the dielectric properties, a lumped circuit method ⁽⁴⁴⁾ always used at lower frequencies. The aim of this circuit is

to determine the equivalent electrical circuit of the specimen at a given frequency. Thus if the specimen is represented by a capacitance C_p connected in parallel with a resistance R_p , the total impedance "Z" will then be given by:

$$\frac{1}{Z} = \frac{1}{R_p} + j\omega C_p \quad (2.17)$$

where $\omega = 2\pi f$ and f is the frequency. The alternating voltage represented by the real part of $V = V_o e^{j\omega t}$ will produce a capacitive current I_c (imaginary part),



$$I_c = \left(\frac{V}{Z}\right) = j\omega C_p V \quad (2.18)$$

and a resistive current I_R (real part),

$$I_R = \left(\frac{V}{Z}\right) = \frac{V}{R_p} \quad (2.19)$$

It is convenient to express about the complex dielectric constant or relative permittivity as:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2.20)$$

The current I which flows in the external circuit after application of alternating voltage given by the real part of $V = V_0 e^{j\omega t}$ may be calculated as follow:

$$I = \varepsilon^* C_o \frac{dV}{dt} = j\omega \varepsilon^* C_o V \quad (2.21)$$

$$I = \omega C_o \varepsilon'' V + j\omega C_o \varepsilon' V \quad (2.22)$$

So, we have a capacitive component of the current,

$$I_c = j\omega C_o \varepsilon' V \quad (2.23)$$

which leads the voltage by an angle 90° , and a resistive component of the current,

$$I_R = \omega C_o \varepsilon'' V \quad (2.24)$$

which in phase with the voltage.

Comparing equations (2.18) and (2.19) with (2.23) and (2.24) respectively we have:

$$\varepsilon' = \frac{C_p}{C_o} \quad (2.25)$$

$$\varepsilon'' = \frac{1}{\omega R_p C_o} \quad (2.26)$$

From which:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{\omega R_p C_p} \quad (2.27)$$

The ac conductivity can be calculated from the dielectric loss at an angular frequency for the material in a parallel plate capacitor as follow:

$$R_p = \frac{1}{\sigma} \frac{d}{A} \quad (2.28)$$

Since,

$$C_o = \epsilon_o \frac{A}{d} \quad (2.29)$$

Equation (27) can be written as follow:

$$\epsilon'' = \frac{\sigma}{\epsilon_o \omega} \quad (2.30)$$

Thus:

$$\sigma = \epsilon_o \epsilon'' \omega \quad (2.31)$$

Therefore the dielectric constant, dielectric loss and conductivity of a material can be calculated from measured values of equivalent parallel circuit components of a specimen.

2.7. Activation Energy Determination:

The electrical conductivity of most of organic semiconductors is given by the relation ⁽⁴⁵⁾:

$$\sigma = \sigma_o \exp[-\Delta E_a / 2KT] \quad (2.32)$$

ΔE_a is the thermal activation energy (depends on the temperature) & may be associated with the excitation energy for thermal generation of carriers. The excitation mechanisms are as follow:

a) ΔE_a corresponds to the energy band gap for intrinsic conduction, or corresponds to the distance between the donor level & conduction band edge for n-type extrinsic conduction, or corresponds to the distance between the acceptor level & the valence band edge for p-type extrinsic conduction.

Extrinsic semiconductors usually exhibit an activation energy corresponding to the extrinsic conduction at low temperatures, & an activation energy corresponding to the intrinsic conduction at high temperatures.

b) ΔE_a corresponds to the depth of traps i.e. $(E_e - E_t)$ for electron traps & $(E_t - E_h)$ for hole traps, E_t being the trapping level. This implies that the conduction is dominated by thermal release of trapped carriers

c) ΔE_a may correspond to the energy required to raise the electrons from the ground state to an excited state so that they can tunnel the potential barrier efficiently to make a major contribution to electric conduction. Such a potential barrier is generally the barrier between molecules.

d) ΔE_a may correspond to the height of the potential barrier between the electrode & the solid specimen which must be overcome for carrier injection from the electrode.

It is clear from above mechanisms that ΔE_a is related to the structure of solid specimen. It was reported that ΔE_a which identified with the energy band gap, decreases with increasing the number of the π -electrons up to a limiting value, since the excitation process is strongly dependent on the position of π -electrons with the molecule and their delocalization. That ΔE_a tends to remain unchanged with the number of π -electrons for high molecular weight materials may be due to their unfavorable structure with respect to intermolecular overlapping.

In general the conductivity of organic semiconductors increases and their thermal activation energy decreases with increasing pressure. For organic semiconductors, particularly polymeric materials, the temperature & the pressure dependence of conductivity is partly due to the change of carrier mobility.

2.8 . Different Models of Conduction Mechanism:

Electrical conduction in polymers may occur through the movement of either electrons or ions. The basic equation which describes the conduction process is ⁽⁴⁶⁾:

$$\sigma = qn\mu \quad (2.33)$$

Where the electrical conductivity σ is resolved into three factors:

The charge q , the carrier concentration n and drift mobility μ of the carriers. Theories of conduction aim to explain how the concentration and drift mobility of the carriers are determined by molecular structure and how they depend on such factors as temperature and applied field.

There are different models which can be discussed in the following:

2.8.1. Tunneling Model⁽⁴⁶⁾:

This model assumes that an electron in a π -molecular orbital on one molecule, when excited to a higher energy level (e.g., to a singlet state), can tunnel through a potential barrier to a non-occupied state of a neighboring molecule with energy conserved in the tunneling process as shown in fig (2.2). An excited state of a molecule can be either a singlet or triplet, and the energy depends on the spin. The electron in the excited state may tunnel to its neighboring molecule or return to its ground state as in fig (2.2) but in general the probability for the former is much larger than that for the latter. The tunneling probability would be still higher if the excited electrons were in the long life triplet state.

2.8.2. The Band Model:

In the band model there is no explicit motion of potential barrier between molecules. However, it can be imagined that an

excited electron may tunnel over a distance of many molecules. Thus the tunneling model may be considered as a band model when the potential varies periodically and regularly throughout the crystal and the width of the potential barriers is much less than 10° A.

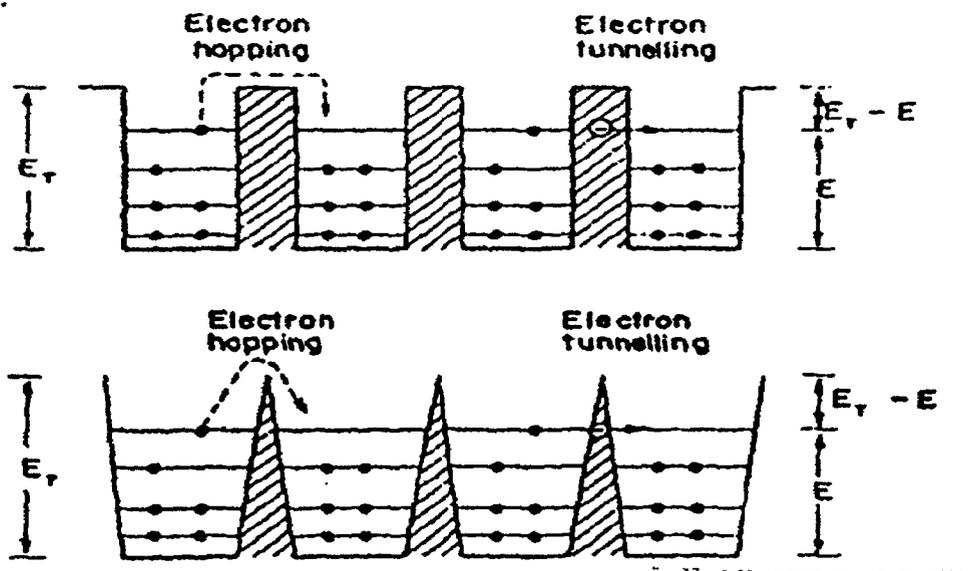


Figure (2.2): Schematic diagram illustrating the electron hopping across and the electron tunneling through square and a triangular potential barrier. The electron hopping or tunneling in one direction is equivalent to the hole hopping or tunneling in the opposite direction.

2.8.3. The Hopping Model:

A carrier can move from one molecule to another by jumping over the barrier via an excited state as shown in fig (2.2). In this case the electron motion is so rapid that in this case the vibration motion can be regarded as stationary and as perturbation to the motion of the electrons. The electron can be thought of as waves traveling over a several lattice sites before being scattered. This implies that during the time when the electron remains on the lattice site, the nuclei of the

molecule on the particular lattice site move to new equilibrium positions. This gives rise to the formation of a "polaron".

The interaction of the electrons and phonons in the lattice site may lead to a self-trapping in which the electrons polarize the molecules and are trapped in a self-induced potential well. This case may lead either to random hopping transport or to a coherent band transport.

2.8.4. Ionic Model:

Ionic conduction is observed in electrolytic conductors, whose molecules easily yield to electrolytic dissociation, i.e., they are split into two parts positively and negatively charged ions (cation & anion). Ionic conduction can also be observed in crystal dielectrics⁽⁴³⁾.

When ions move in an electric field there takes place electrolysis, i.e., a transfer of matter caused by the formation of new chemical substances near the electrodes.

During electrolysis the amount of substances carried with the current in electrolytic conductors is proportional to the quantity of electricity passed through a substance in conformity with Faraday's law. Under the effect of an external electric field the anions and cations move in opposite directions so that the total conductivity of matter is equal to the sum of anionic and cationic conductivities.

2.9. Differential Thermal Analysis and Calorimetry⁽²⁾:

Thermal analysis includes a group of analytical methods by which a physical property of a substance is measured as a function of temperature while the substance is subjected to controlled temperature regime. Thus, thermal analysis involves a physical measurement and not, strictly speaking, a chemical analysis.

The temperature changes occurring during these chemical or physical changes are detected by a differential method, such as illustrated in figure (2.3).

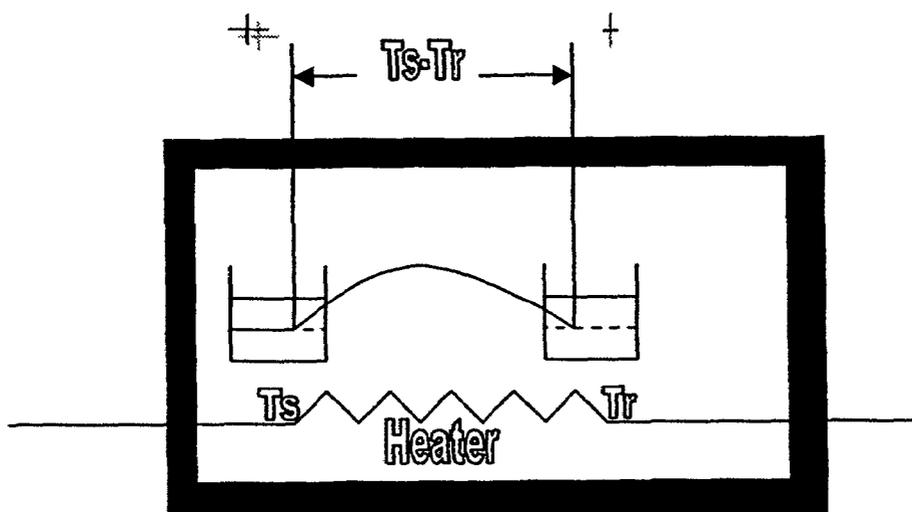


Figure (2.3): Basic DTA system.

Calorimetric methods record exo- and endothermic processes, e.g. melting, crystallization, liquid-crystalline phase transition, and chemical reaction, e.g. polymerization, depolymerization and

degradation. Second-order transition, e.g. glass transitions are readily revealed by the calorimetric methods.

Strictly speaking DTA measures the difference in temperature (ΔT) between sample and reference, but it is possible to convert ΔT into absorbed or evolved heat via a mathematical procedure. However a DTA which accurately measures calorimetric properties is referred to as a differential scanning calorimeter. The DSC instrument made by Perkin-Elmer shown in figure (2.4) is more 'true' calorimeter since it directly measures differences in heat between an inert reference and the sample.

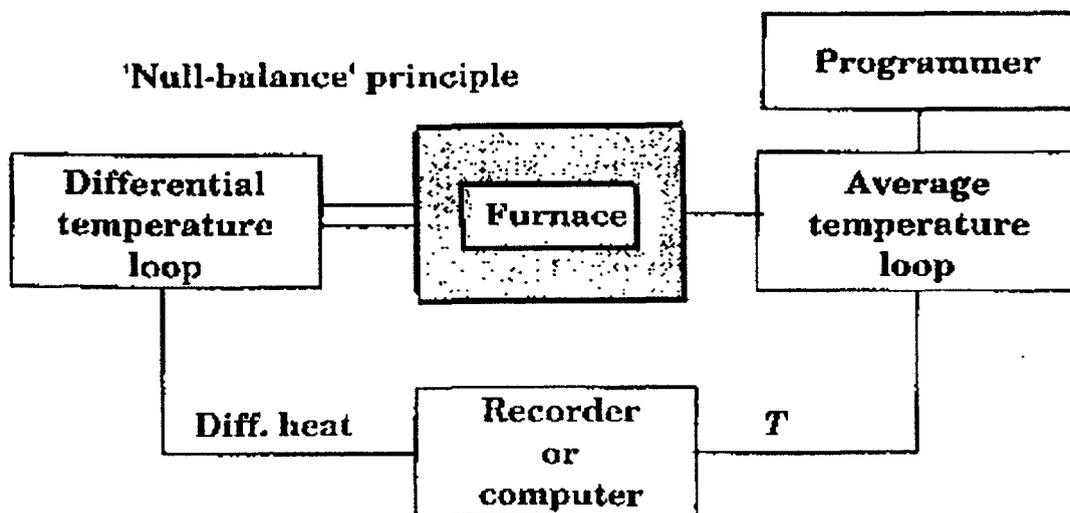


Figure (2.4): Principle of Perkin – Elimer DSC apparatus.

Figure (2.5), showing the DSC thermogram of an undercooled, potentially semicrystalline polymer, illustrates the measurement principle. At low temperatures, the sample and reference is required in

order to maintain the two at the same temperature. The polymer crystallizes at a higher temperature and exothermal energy is evolved. The heat flow to the sample should in this temperature region be less than the heat flow to the reference. The integrated difference between the two, i.e. the area under the exothermal peak, is thus equal to the crystallization enthalpy. At further higher temperatures, melting which is an endothermal process occurs. The heat flow to the sample is higher than that to the reference and the peak points upwards. The area under the endothermal peak is thus proportional to the melting enthalpy.

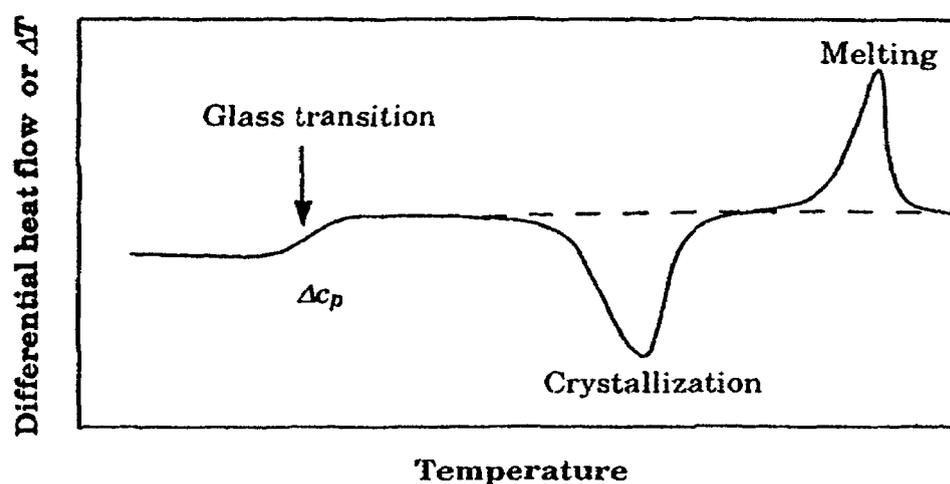


Figure (2.5): Schematic DSC traces showing three transition types.

There have been a number of different theories concerning the theoretical interpretation of the DTA curve. All the theories relate, in some manner, the area of the differential curve peak to the various parameters of the sample and the apparatus.

The first simple theory was developed by Speil⁽⁴⁷⁾ and modified by Kerr and Kulp⁽⁴⁸⁾, and leads to the equation:

$$M = \frac{g2\lambda}{\Delta H} \int_{t_1}^{t_2} \Delta T dt \quad (2.34)$$

Where M is the mass of reactant, g a geometrical shape constant for the apparatus, λ the thermal conductivity of the specimen, ΔH the difference in the heat content of 1gm of the specimen before and after the reaction and t_1 and t_2 are the integration limits of the differential curve. A somewhat similar equation derived by Yagfarov & Berg⁽⁴⁹⁾

$$M = \frac{2\pi l \lambda}{\Delta H \ln(d_2 / d_1)} \int_{t_1}^{t_2} \Delta T \quad (2.35)$$

Where l, d_2 and d_1 are the length and external and internal diameters of a cylindrical specimen and the other symbols have the same significance as in equation (2.34). This is essentially the Speil- Kerr-Kulp equation with the geometrical constant defined for a cylindrical specimen.

An equation analogous to eq. (2.34) can be obtained for the DSC system:

$$\text{Area} = \Delta H m / g k \quad (2.36)$$

There are a few significant differences between a DSC (Perkin-Elmer type) and DTA. The mass of the sample and reference holders in the

DSC apparatus is very low and the maximum cooling rate is greater in the typical (Perkin-Elmer) DSC apparatus than in DTA. The maximum measurement temperature for a DSC is only about 725 °C. The upper temperature limit for a number of DTA instruments is significantly greater. One obstacle to calorimetric operation remains unsolved for the DTA method: the factor converting the observed peak area to energy is temperature-dependent. This is particularly relevant for polymers which typically melt over a wide temperature range. The melting curve is asymmetric and requires the use of a complex conversion factor. The calibration constant in DSC is dependent of temperature and quantitative operation is inherently simpler than with DTA.

The accuracy in the determination of transition temperature by DSC/DTA is dependent on several factors:

- Standardized sample geometry and mass. The sample should be flat and have good thermal contact with the sample pan. Heat-conductive, thermally inert liquid media may be used to improve the thermal contact
- The pure gas and the sample pan material should be 'inert'
- Thermal lag (difference) between sample and thermometer may be corrected for by using the slope of the leading edge of the melting of highly pure indium (or similar metal)

2.10. Calculation of the Reactivity Ratio of the Monomers:

The copolymerization of two monomers can be expressed by the following equation:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (2.37)$$

Where M_1 and M_2 are the concentrations of the monomers, $r_1 = K_{11}/K_{12}$ and $r_2 = K_{22}/K_{21}$ are the monomer reactivity ratios.

At low conversions (< 10%) dM_1/dM_2 corresponds to the concentration ratio of the copolymer components. After introduction of:

$$M_1/M_2 = X \quad \text{and} \quad dM_1/dM_2 = Y,$$

The composition equation may be written as :

$$Y = X \cdot \frac{1 + r_1 X}{r_2 + X} \quad (2.38)$$

This equation was linearized by Fineman and Ross⁽⁵⁰⁾ as

$$G = r_1 F - r_2 \quad (2.39)$$

And/or

$$\frac{G}{F} = -r_2 \frac{1}{F} + r_1 \quad (2.40)$$

Where the transformed variables are:

$$F = X^2 / Y \quad \text{and} \quad G = X(Y - 1) / Y \quad (2.41)$$

Graphical plotting of Eq. (2.39) gives r_1 as the slope and $-r_2$ as the intercept, while the plot of Eq. (2.40) presents r_2 as the slope and r_1 as the intercept.

As pointed out by Tidwell and Mortimer⁽⁵¹⁾, the experimental data are unequally weighted by Fineman-Ross equations, the data obtained under extremes experimental conditions in Eq. (2.39) at rather low M_2 and Eq. (2.40) at very low M_1 co-monomer concentrations) have the greatest influence on the slope of a line calculated by the usual linear least-squares procedure, and accordingly, the calculated r_1 and r_2 values depend on arbitrary factors, such as which monomer is selected as M_1 . There is often considerable deviation between the corresponding values derived from Eq. (2.39) and (2.40).

Further disadvantage of the F-R method and other graphical procedures is that, it may happen, that the values calculated from the experimental data appear along the ordinate at growing intervals e.g., in the case of Eq. (2.41), F may take all positive values, (i.e., r_2 will be -ve value, or hard to calculate).

The above disadvantages may, however, be avoided by using the Kelen and Tüdös equations⁽⁵²⁾:

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha}\right) \bullet \frac{F}{\alpha + F} - \frac{r_2}{\alpha} \quad (2.42)$$

Where α denotes an arbitrary constant ($\alpha > 0$).

By introducing:

$$\zeta = \frac{F}{\alpha + F} \quad \text{And} \quad \eta = \frac{G}{\alpha + F} \quad (2.43)$$

Then Eq (2.42) may be written as:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\zeta - \frac{r_2}{\alpha} \quad (2.44)$$

and/or

$$\eta = r_1\zeta - \frac{r_2}{\alpha}(1 - \zeta) \quad (2.45)$$

The variable ζ cannot take any arbitrary positive value, only those in the interval (0-1). Thus plotting the η values calculated from the experimental data as a function of ζ , we obtain a straight line, which extrapolated to $\zeta = 0$ and $\zeta = 1$ gives $-r_2/\alpha$ and r_1 (both as intercepts).

This relationship is invariant to the inversion of data: re-indexing of the monomers and reactivity ratios does not change the calculated results. Uniform distribution of the experimental data in the interval (0-1) may be attained by proper choice of the α value. If the reactivity ratios are nearly identical ($r_1 \sim r_2$), the choice of $\alpha = 1$ is generally satisfactory : in the case of markedly different reactivity ratios or if the

choice of $\alpha = 1$ involves rather asymmetric data distribution along the interval (0-1), it is most feasible to choose the α value with the regard to the entire experimental range of composition for both the polymer and co-monomer of the F values calculated in Eq (2.41), if F_n stands for the lowest and F_M for the highest value, then the choice of α as the following relation:

$$\alpha = \sqrt{F_n F_M} \quad (2.46)$$

It will afford optimum distribution of the data, which ensures validity of the relationship between ζ_m related to the lowest F value and ζ_M related to the highest F value i.e.

$$\zeta_M = 1 - \zeta_m \quad (2.47)$$

Accordingly; the experimental data will be located symmetrically along the interval (0-1).