

## CHAPTER III

### THEORY

#### 3.1 Poly(bisphenol A carbonate), PC

Carbonate (-O-CO-O-) linkages may be produced by the reaction of polyhydroxy compounds with a carbonic acid derivative. The polymer is being referred to as polycarbonate.

Polycarbonate was first prepared by Einhorn in 1898 by reacting the dihydroxybenzenes, hydroquinone and resorcinol with phosgene in solution in pyridine. The general chemical structure is shown in Figure 3-1.

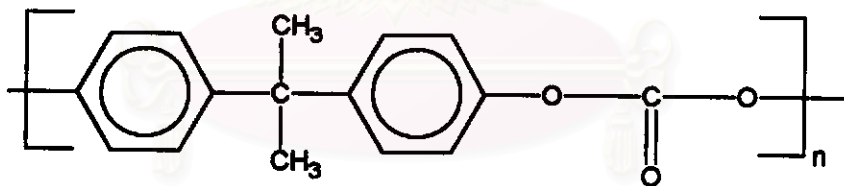


Figure 3-1 The general chemical structure of polycarbonate

In 1930 Carothers and Natta [1] prepared a number of aliphatic polycarbonates using ester-interchange reactions. These materials had a low melting point, were easily hydrolyzed and did not achieve commercial significance.

General Electric Company in America carried out in search of thermally and hydrolytically stable thermosetting resins. From this work, polycarbonate also produced as a by-product from bis-phenol A.

Today about 75% of the market is held by General Electric and Bayer with their products Lexan and Makrolon respectively. Other manufacturers are ANIC (Italy), Taijin Chemical Co., Mitsubishi Edogawa and Idemitsu Kasei in Japan and, since 1985, Dow (USA) and Policarbonatos do Brasil (Brazil).

### 3.1.1 structure and properties

A study of the molecular structures of bis-phenol polycarbonates enables one to make accurate predictions of the bulk properties of the polymer. The rigid molecular backbone of the bis-phenol A polycarbonates leads to a high melting temperature ( $T_m=225-250\text{ }^\circ\text{C}$ ) and glass transition temperature ( $T_g=145\text{ }^\circ\text{C}$ ).

It is found that observed values of  $T_g$  for the bis-phenol A polycarbonate are somewhat higher than estimated from  $T_m$  data by the general rule-of thumb relation;

$$T_g = 2/3 T_m$$

The range of polycarbonates commercially available has increased greatly in recent years. The main differences between these grades are due to:

1. Differences in Molecular weight
2. The presence or otherwise of a second polyhydroxy compound.
3. Differences in additives.

The conventional bis-phenol A polycarbonate has a lower heat distortion temperature (deflection temperature under load) than some of the aromatic thermoplastics such as the polysulphones. This has led to attempts to produce a polycarbonate of such a higher distortion temperature.

Although somewhat more expensive than the general-purpose thermoplastics, polycarbonates have a number of applications.

The desirable features of the polymer may be listed as follows:

1. Rigidity up to 140 °C.
2. Toughness up to 140 °C.
3. Transparency.
4. Very good electrical insulation characteristics.
5. Virtually self-extinguishing.
6. Physiological inertness.

The principle disadvantages may be listed as:

1. More expensive than polyethylene, polystyrene and PVC.
2. Special care required in processing.
3. Pale yellow color
4. Limited resistance to chemicals and ultra-violet light.
5. Notch sensitivity and susceptibility to crazing under strain.

The polycarbonates have a high volume resistivity and because of the low water absorption the values obtained are little affected by humidity. The very low water absorption of bis-phenol A polycarbonates contributes to a high order of dimension stability. Polycarbonates are good light absorber.

Unmodified polycarbonates are usually rated as slow burning with an oxygen index of 26 and an UL-94 V-2 rating.

### 3.1.2 Processing characteristics

The melt viscosity of the resin is very high and processing equipment should be rugged. The effect of increasing temperature on viscosity is less marked with polycarbonates than with other polymers. The apparent melt viscosity is also less dependent of the rate of shear than usual thermoplastics.

Processing temperatures are high and fall between the melting point, ( $\sim 230^\circ\text{C}$ ) and  $300^\circ\text{C}$ , at which temperature degradation occurs quite rapidly.

There is little crystallization on cooling and after-crystallization has not been observed. Mould shrinkage is of the order of 0.006-0.008 cm/cm and is the same both along and across the flow. In case of glass-filled polymer, mold shrinkage is lower.

### 3.1.3 Applications

Polycarbonates have now displaced polyacetals and become second to the nylons among engineering thermoplastics in terms of tonnage. Major consumption areas are the United States 45%, Western Europe 30% and Japan 15%. Such success arises from the advantages of toughness, rigidity, transparency, self-extinguishing characteristics, and good electrical insulation characteristics and heat resistance. The main factors retarding growth are cost, special cares needed in processing, limitations in chemical

and ultra-violet light resistance, moderate electrical tracking resistance and notch sensitivity.

Other polymers are as rigid, others are as transparent, others even both more rigid and as transparent, but the bis-phenol A polycarbonate is the only material that can provide such a combination of properties, at least at such a reasonable cost.

The largest application in electronics and electrical engineering comprises around 55% of the market. The applications cover for time switches, batteries, relays, because of the good electrical insulation characteristic. The polymer is widely used in making coil former. Polycarbonate molding have also been made for computers, calculating machines and magnetic disc pack housing, terminal, contact strips. Polycarbonate films of high molecular weight are used in the manufacture of capacitors.

The polymers are extensively used in telecommunications equipment, a major use being in telephone switching mechanisms. Polycarbonates now dominate the audio compact disc market, where material of very high purity is required.

## 3.2 Liquid crystal

### 3.2.1 The nature of Liquid Crystals

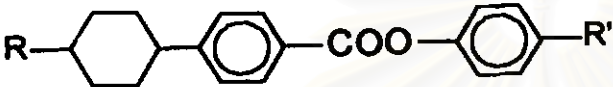
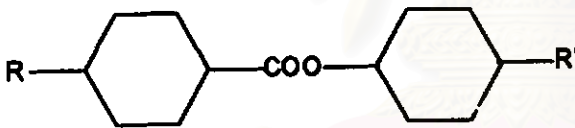
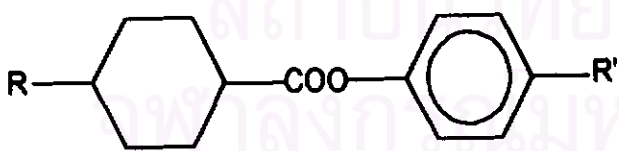
Liquid crystals were discovered over a hundred years ago. They are defined as materials which are characterized by a high degree of anisotropy, but have the properties of liquids. One of the important manifestation of LCs is their melting or softening behavior. When heating a crystalline solid that is not mesomorphic, it changes from the solid phase directly into an isotropic liquid phase at its melting point  $T_m$ . In liquid crystalline materials, several different mesophases may form before the isotropic melt phase occurs at the clearing temperature. The properties of liquid crystals are a consequence of groups characterized by a rigid geometry. Such groups are called mesogens. Mesogens may be components of low molecular compounds. They may be arranged along the main polymer chain or on side branches.

Many natural materials can exist in the liquid crystal state. Examples of common materials include DNA, cholesterol and tobacco mosaic virus. Probably the best known synthetic liquid crystals are those used in liquid crystal displays.

Both small molecules and polymers may exist in the liquid crystalline state, but generally special chemical structures are required. The chemical structure composed of a central core comprising aromatic or cycloaliphatic units joined by rigid links. And it has either polar or flexible alkyl and alkoxy terminal groups. Some typical examples of possible small molecule structures

that form liquid crystalline state are shown in Table 3-1 and these units are called "mesogens".

Table 3-1 The examples of mesogens [Merck, 1985].

Mesogen	R-group
	$R = -C_3H_7$ ; $R' = -C_3H_7$ $= -C_3H_7$ ; $= -C_5H_{11}$ $= -C_5H_{11}$ ; $= -C_3H_7$ $= -C_2H_5$ ; $= -CN$ $= -C_5H_{11}$ ; $= -CN$
	$R = -C_3H_7$ ; $R' = -C_3H_7$ $= -C_3H_7$ ; $= -C_5H_{11}$ $= -C_4H_9$ ; $= -C_4H_9$ $= -C_5H_{11}$ ; $= -C_3H_7$ $= -C_5H_{11}$ ; $= -C_5H_{11}$
	$R = -C_5H_{11}$ ; $R' = -C_5H_{11}$ $= -C_3H_7$ ; $= -OCH_3$ $= -C_3H_7$ ; $= -OC_2H_5$ $= -C_3H_7$ ; $= -OC_4H_9$ $= -C_4H_9$ ; $= -OCH_3$ $= -C_4H_9$ ; $= -OC_2H_5$ $= -C_5H_{11}$ ; $= -OC_4H_9$



The mesophase may exist in a solution - lyotropic liquid crystals, or in a melt - thermotropic liquid crystals. A crystal can become a random liquid in two ways: by melting or dissolving. If the phase change from crystal to liquid by heating, it is called thermotropic. If the phase change by dissolution, in which case it is called lyotropic. The ability of a polymer to form lyotropic or thermotropic liquid crystalline mesophases depends of the chemical structure of the molecules.

The formation of a lyotropic liquid crystalline mesophase will be present alone or in equilibrium with an isotropic liquid phase. At higher polymer concentrations the liquid crystalline mesophase can be present in equilibrium with crystalline solid.

The presence of mesogenic groups is important for the formation of liquid crystals in solutions and melts, but the occurrence of liquid crystals also depends on many other factors. One of these is temperature. Liquid crystals form only in a certain temperature range which lies between the melting point,  $T_m$  and the so called upper transition temperature at which a liquid crystalline phase changes into an isotropic liquid,  $T_i$ . This temperature is called the temperature of isotropisation or the solution point. If the material being tested does not crystallize, liquid crystals are formed between the glass transition temperature,  $T_g$ , and the temperature of isotropisation  $T_i$ .

In order to use liquid crystals, it is important that the mesophase covers a fairly wide temperature range. It should be in a range where the material being tested is thermally stable. However, compounds containing a mesophase, particularly polymers, have a melting point. And the melting point is often a limiting factor, since the region of liquid crystalline transitions is



located in the range of thermal decomposition. With increase in the length and rigidity of the mesogenic groups there is an increase in the melting point of the crystals, and an even faster increase in the range of the liquid crystalline phase.

The mesophases are differentiated from each other by the different ways in which the molecules pack. This may give rise at the clearing temperature to a disordering of the molecules. There are many different types of liquid crystals. There are three main classifications as recognized by Friedel: nematic, smectic and cholesteric.

### 3.2.2 Structure of Liquid Crystals

There are many different types of liquid crystal. But there are three main classifications by Friedel: nematic, smectic and cholesteric.

#### a. *Nematic structure*

The molecular organization in a nematic mesophase involves molecular alignment without a special regularity. Molecules remain parallel to one another in the nematic structure (Figure 3-2). But the positions of their centers of gravity are disorganized. Molecules of nematic liquid crystals can be oriented. Their mobility can be reduced by adhesion to supporting surfaces. For example, nematic molecules tend to lie parallel to the rough surface of a glass slide. A bright satinlike texture is observed when nematic liquid crystals are viewed between crossed polaroids. Characteristic dark threads appear at lines of optical discontinuity. These wavering filaments give the mesophase its name, taken from the Greek word *nematos*, meaning fiber.

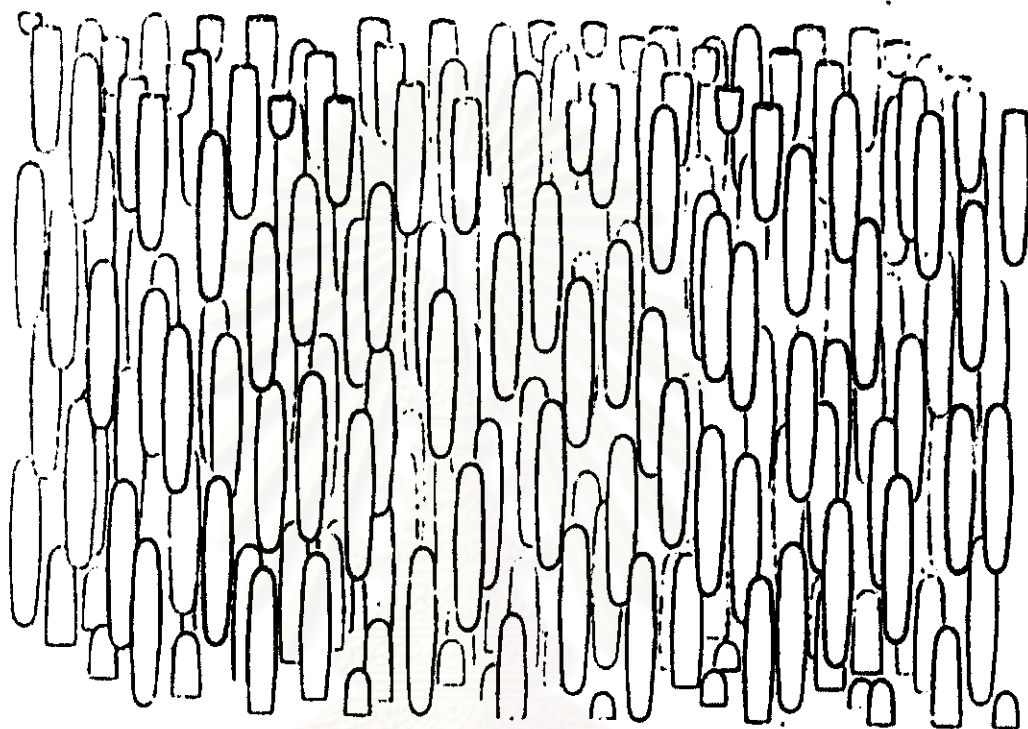


Figure 3-2 Nematic structure

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

### b. *Smectic structure*

In the smectic structure long molecules are arranged side by side in layers much like those in soap films. The term smectic (soaplike) is, derived from the Greek word for grease or slime. The layers are not strictly rigid but flexible. Two dimensional molecular sheets can slide past one another (Figure 3-3). Molecular motion is rather slow, and smectic mesophases are quite viscous.

Optically smectic layers behave as uniaxial, birefringent crystals. The velocity of light transmitted parallel to the molecular layers is greater than that transmitted perpendicularly. The temperature dependence of this birefringence indicates that very little change of internal order occurs over the smectic interval. The smectic mesophase is the most solidlike of all the liquid crystal modifications.

### c. *Cholesteric structure*

The cholesteric structure is the third type of liquid crystal modification. It is so named because many compounds that form this mesophase are derivatives of cholesterol. A cholesteric structure (Figure 3-4) is the shape of a nematic phase which is periodically wrapped around the axis. When chiral groups are present, the basic structure is helicoidal.

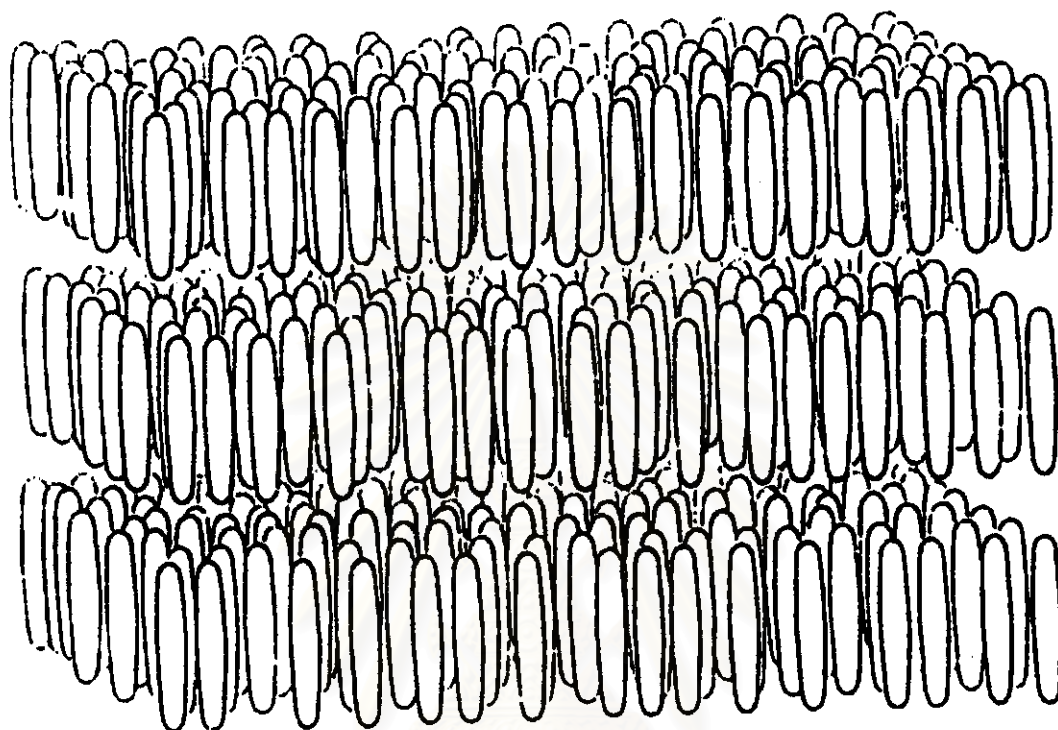
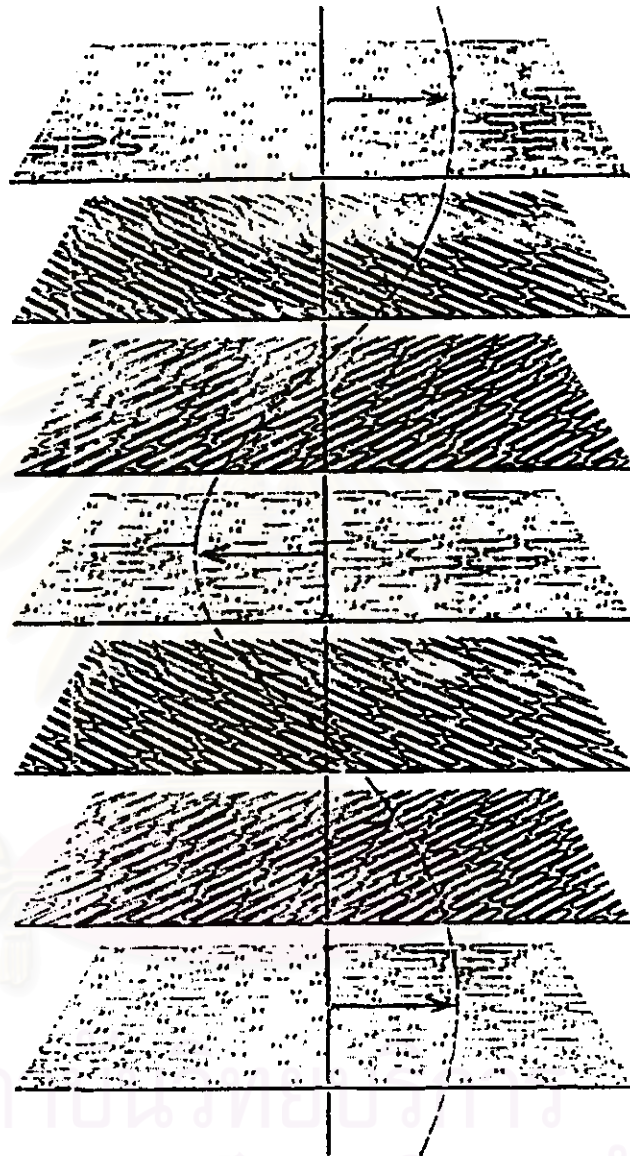


Figure 3-3 Smectic Structure

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

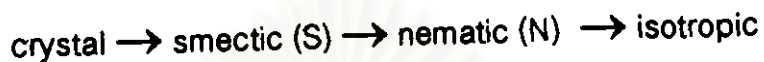


สถาบันวิจัยและพัฒนา  
จุฬาลงกรณ์มหาวิทยาลัย

Figure 3-4 Cholesteric structure

### 3.2.3 Mesophasic Transition Temperature

The various transitions that liquid crystals undergo as the temperature increases from the most ordered to the least ordered states, can be shown:



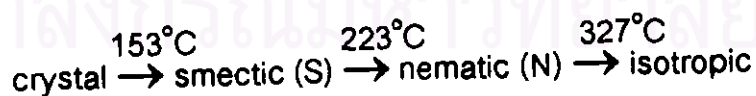
The temperature at which liquid crystal changes from crystal to the first liquid crystalline phase is called "crystalline melting temperature".

The temperature at which liquid crystal changes from smectic phase to nematic phase is call "S→N transition temperature".

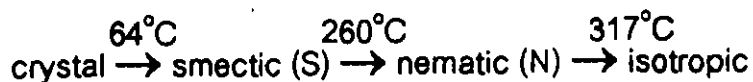
The temperature at which the last (or only) liquid crystalline phase gives way to the isotropic melt or solution is called "clearing temperature".

The examples of mesophasic transition temperature of low molar mass liquid crystals used in this study are shown below:

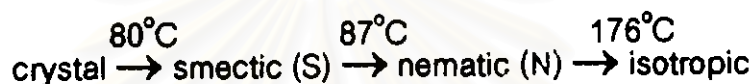
1. CBC33 exhibits a crystalline melting transition at 153 °C and the S→N transition temperature at 223 °C. CBC33 exhibits the state change from the nematic to isotropic (clearing temperature) at 327 °C [Merck, 1996].



2. *CBC53* exhibits a crystalline melting transition at 64 °C and the S→N transition temperature at 260 °C. *CBC33* exhibits the state change from the nematic to isotropic (clearing temperature) at 317°C [Merck, 1996].



3. *HP35* exhibits a crystalline melting transition at 80 °C and the S→N transition temperature at 87 °C. *HP35* exhibits the state change from the nematic to isotropic (clearing temperature) at 176°C [Merck, 1996].



4. *HP5N* exhibits a crystalline melting transition at 111°C and becomes an isotropic liquid (clearing temperature) at 226°C [Merck, 1996].



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย



### 3.2.4 Physical properties

#### a. Viscosity

In the nematic structure, the motion of liquid crystal molecules is similar to that in the normal, isotropic liquid phase. On the other hand, cholesteric and smectic liquid crystal are typically quite viscous.

Experiments on nematic liquid crystal indicate that the molecules of this structure readily orient themselves with their long axes more or less parallel to the direction of flow. This results in a viscosity lower than that of the isotropic liquid.

The viscosity of cholesteric mesophase is much higher than that of the corresponding isotropic liquid and is strongly dependent on shear rate. A more complicated flow process for cholesteric liquid crystal is evident.

#### b. Liquid Crystals in Electric and Magnetic Fields

It is a characteristic of liquid crystals that their physical properties are influenced by electric and magnetic fields ( as well as surfaces).

Liquid crystals are easily and rapidly oriented in electric and magnetic fields of even small intensity. X-ray studies show that strong magnetic fields have little effects on the orientation of individual molecules. The alignment of small volume elements containing large numbers of molecules. Almost complete alignment was achieved in a magnetic field of only 500 G. Thin

layers of p-azoxyanisole and other nematic liquid crystals have several electrical properties that are characteristic of ferroelectric crystals.

#### c. Heat and Volume Changes at Liquid-Crystal Phase Transitions

Transitions from solid to mesophase from mesophase to isotropic liquid and between multiple mesophase structures are of the first order. However, pre-transition and post-transition effects are observed to occur as the volume begins changing within a few degrees of transition temperature.

#### d. X-ray Diffraction in Liquid Crystals

X-ray diffraction studies of mesomorphic compounds give information about molecular arrangement in the liquid crystal. The order present in some of the fluid mesomorphic states makes it possible to obtain detailed information about typical spacing between molecules.

### 3.2.5 Practical Uses of Liquid Crystals

Some of the unusual physical and optical properties of liquid crystals have been put to practical application.

The temperature-dependent variation in the color of cholesteric liquid crystals has led to the use of these substances in the measurement of temperature and temperature gradients. A cholesteric substance or a mixture of cholesteric substances is found to always exhibit the same color at the same temperature. Liquid crystals can be color-temperature calibrated and serve as optical registers of absolute temperatures and temperature gradients.

Temperature variations of less than  $0.1\text{ }^{\circ}\text{C}$  can be visually observed with liquid crystal temperature sensors. In medicine cholesteric liquid crystal substances applied to the surface of the skin have been used to locate veins, arteries and tumors, which are warmer than the surrounding tissue.

Electrical response characteristics of nematic liquid crystal are examined as the engineering basis of new electrical display devices. When a thin film of a transparent nematic fluid is placed between two conductive glass plates, the substance is observed to turn rapidly opaque at any point where voltage is applied. The opaque areas will in turn reflect incident light and appear bright. If voltages are applied to the liquid crystal film in some pattern, an image will result. Many technological applications of this effect are electro-optical light shutters, automatic dimming window, alphanumeric displays, clocks with no moving parts, and thin, wall-mounted television screens. The display of information in direct sunlight becomes feasible. This capability will undoubtedly open up frightening new possibilities to the billboard and television industries.

Nematic liquid crystals have become useful research tools in the field of nematic resonance. Molecules dissolved in such solvents experience an anisotropic environment and give a very highly resolved NMR spectrum. They exhibit intermolecular dipole-dipole fine structure. Analysis of the spectra of molecules in liquid crystal solvent leads to information on the anisotropy of chemical shifts, direct magnetic dipole-dipole interactions, indirect spin-spin couplings, and bond angles and bond lengths. This new kind of high resolution NMR spectroscopy on partially oriented molecules has not only contributed to the understanding of NMR spectroscopy. But they have also

provided a new method of determining molecular structure, partially for small organic molecules.

Finally some liquid crystals have been used to separate *meta-para* isomers of organic compounds. The chromatographic effect apparently is due to the preferential retention of one geometric isomer over the other in the anisotropic matrix formed by the liquid crystal molecules.

### 3.2.6 Liquid crystal polymer

The term "liquid crystal" has been used by many workers to describe supramolecular arrangements in amorphous and semicrystalline polymers. A liquid crystal polymer is a polymer that exhibits one of the above liquid crystal structures. There are two main ways that anisotropic building blocks can form a polymer. They can either be joined end to end to form a main chain LCP or they can dangle off the side of a normal polymer chain to form a side chain LCP. Anisotropic aromatic building blocks can very usefully be copolymerized with traditional flexible monomers. If these flexible units are placed within the main chain they can be used to control the melting point and glass transition temperature of the LCP. Flexible units can also be placed between a normal polymer backbone and the liquid crystal group from the main chain.

The most important LCPs for blending with bulk polymer are thermotropic main chain LCPs. The LCPs that exhibit a liquid crystal phase within processing window of the bulk polymer but which then solidify on cooling to room temperature. As with any polymer a LCP can either crystallize on cooling or go through a glass transition temperature. Hence, at room

temperature, the structure of the LCP is that of an ordered glass or a semi crystalline polymer.

As LCPs are often formed from highly aromatic stiff monomers. It is hardly surprising that they can form very stiff polymers. Kevlar fibers, for example, have a specific modulus considerably in excess of steel. Carbon fibers with moduli up to 700 GPa can be produced from a liquid crystal pitch. The advantage that the liquid crystal brings is that processing from a naturally ordered fluid gives rise to a more perfect final structure than processing a normal chaotic fluid. These highly aromatic LCPs are also very brittle, have very low failure strains, but can be very strong.

The mechanical properties of LCPs are highly anisotropic. This does not a problem in LCP fiber applications. But this is a serious problem for most other applications. For example, injection molded specimens can show anisotropies in modulus of up to 20. There is also a strong skin core effect which makes the properties at the surface very different to the bulk. In general, the industry has not responded well to the challenge of harnessing the inherent anisotropy that results from LCPs. In stead, the much effort has been put into producing homogeneous, isotropic components, which in some cases have proved successful. The most useful properties of LCPs moldings is their very low thermal expansion coefficients. This results in low mould shrinkage. Hence, very high tolerance components can be molded. Another property of LCPs that is particularly important when considering their use in blends is their viscosity.

### 3.3 Rheology

At the beginning of this century, the developments of the chemical industry followed by the advent of large-scale synthetic polymer production, resulted in a host of new material with "strange" flow behavior. In 1920 the study of such materials prompted a chemistry professor at Lehigh University, Eugene Bingham, to create a new word, rheology. It comes from the Greek verb, to flow. Thus rheology means the science of flow and deformation of materials, whether in liquid, melt, or solid form. For many simple fluids, the viscosity depends primarily upon temperatures and hydrostatic pressure. However, the rheology of polymers is much more complex because polymer fluids show nonideal behavior.

Rheology :

- studies the deformation and flow of materials
- measures the material elasticity and viscosity

#### 3.3.1 Rheological behavior

The rheological behavior of polymers involves several widely different phenomena, which can be related to some extent to different molecular mechanisms, as follows.

- Rubberlike Elasticity*, where the local freedom of motion associated with small-scale movement of chain segments are retained, but large-scale movement (flow) is prevented by the restrain of a diffuse network structure.



Elasticity is the ability of a material to store deformation energy, and can be viewed simply as the capacity of a material to regain its original shape after being deformed.

b. *Viscoelasticity*, where the deformation of the polymer specimen is reversible but time dependent and associated (as in rubber elasticity) with the distortion of polymer chains from their equilibrium conformation through activated segment motion involving rotation around chemical bonds.

Materials respond to an applied force or displacement by exhibiting either elastic or viscous behavior, or through a combination of these, called *viscoelastic* behavior. Most polymeric materials are viscoelastic because their mechanical properties showing a marked time and temperature dependence.

c. *Viscous flow*, the irreversible bulk deformation of polymeric material, associated with irreversible slippage of molecular chains past other adjacent molecules.

Viscosity is a measure of a material's resistance to flow and reflects the material's rate of dissipation of deformation energy through flow.

d. *Hookean elasticity*, where the motion of chain segments is drastically restricted and probably involves only bond stretching and bond angle deformation: The material behaves like a glass.



### Hooke's law

Hooke's law describes the mechanical behavior of an ideal solid, relating the applied strain to the resultant stress through a proportionality factor called the modulus. Thus,

$$\sigma = E \epsilon$$

or

$$\tau = G \dot{\gamma} \text{ (shear)}$$

The modulus is a measure of the material's stiffness ( i. e., its ability to resist deformation). The linear region in which the modulus does not change when the strain is changed is called the *Hookean region* of the material.

### 3.3.2 Viscous flow

If the force per unit area causes a layer of liquid at a distance  $x$  from a fixed boundary wall to move with a velocity  $v$ , the viscosity  $\eta$  is defined as the ratio between the shear stress  $\tau$  and the velocity gradient  $\partial v / \partial x$  or rate of shear

#### Newton's law

Newton developed a relationship similar to Hooke's law for ideal viscous fluids, linearly relating the stress to the shear rate. Thus,

$$\tau = \eta \partial v / \partial x = \eta \dot{\gamma}$$

Here the proportionality factor  $\eta$  is the coefficient of viscosity. A fluid is Newtonian if the viscosity is independent of the shear rate. The viscosity of a non-Newtonian fluid changes with the shear rate. Polymer solutions and melts are usually non-Newtonian: their viscosity decreases when the shear rate increases. This is called *shear thinning* or *pseudoplasticity*. Less common is *shear thickening* or *dilatancy*, in which the viscosity increases with increasing shear rate. The molecular basis for shear thinning behavior is the effect of shear on entanglements. At low shear rates, the entanglements impede shear flow and, therefore, viscosity is high.

As the shear rate increases, chains begin to orient in the flow direction and disentangle from one another- the viscosity begins to drop. Finally, the molecules become fully oriented in the flow direction at very high shear rate.

Newtonian fluids give linear range in a stress-strain plot and viscosity does not change when changing the strain rate.

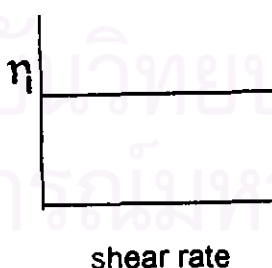


Figure 3-5 Viscosity of Newtonian fluid as a function of shear rate.

Most fluids is non-Newtonian. Viscosity changes with changes in shear rate.

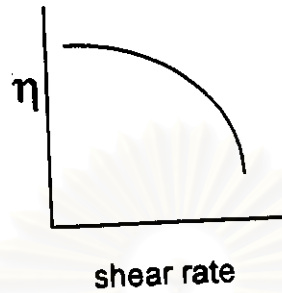


Figure 3-6 Viscosity of non-Newtonian fluid as a function of shear rate.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

### 3.3.3 Capillary Rheometry

Rheometry is the study of the flow of liquids. Polymer melts are 'liquids' so for our purpose we can think of rheometry as being the study of polymer melt flow.

A very popular type of instrument for studying the rheological behavior of molten polymers is a capillary rheometer. The capillary rheometer is somewhat like a "melt flow indexer", i.e. both units consist of a heated barrel having a central bore and a small die at the end. A piston is used to force the molten specimen out through the die. But whereas a melt flow indexer gives a 'single point' result (good for quality control), the capillary rheometer gives 'multiple point' results and can therefore provide us with a whole range of rheological properties such as melt viscosity, shear stress and shear rate at various temperatures. Thus, the test results can simulate the conditions usually found in the common plastics processing method, e.g. injection molding, blowing molding, extrusion, etc.

A liquid polymer is forced by a piston or by pressure from a reservoir through a capillary. The quantity of polymer coming from the capillary per unit of time at a given pressure drop is the basic measurement used to calculate the viscosity.

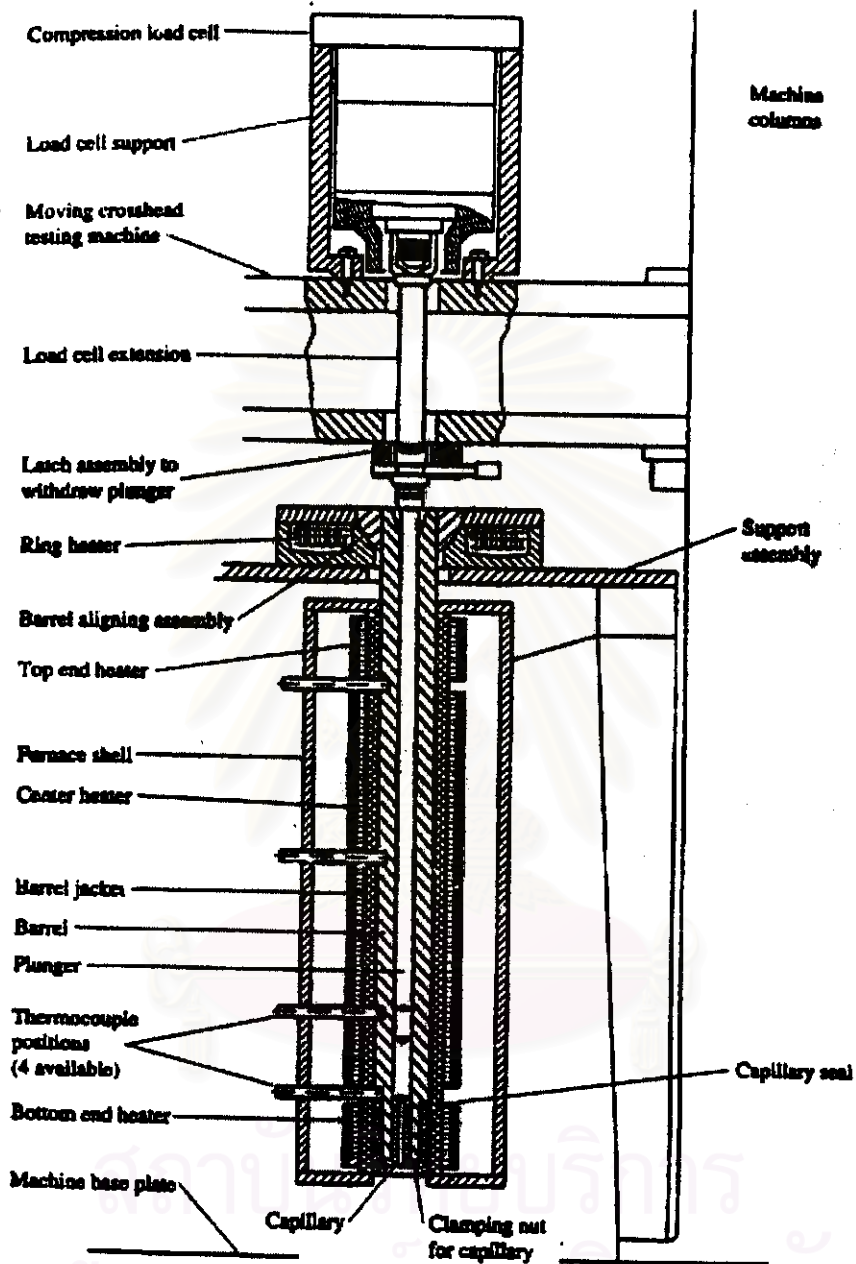


Figure 3-7 Capillary Rheometer

The capillary rheometer has a number of advantages. Firstly, the instrument is easy to fill. This is an important consideration since most polymer melts are too viscous to pour readily even at high temperatures. The test temperature and rate of shear are varied readily. The shear rates and flow geometry are similar to the conditions actually found in extrusion and in injection molding.

The main disadvantage of the capillary viscometer is that the rate of shear is not constant but varies across the capillary. Another disadvantage is the necessity of making a number of corrections in order to get accurate viscosity values.

Consider the steady laminar flow of polymer in capillary of length  $L$  and radius  $R$ . We can derive equations for the flow of liquids through a capillary,

$$\text{shear stress } (\tau) = PR/2L = Fr/(2\pi R^2 L) \quad (1)$$

$$\text{shear rate } (\dot{\gamma}) = 4Q/\pi R^3 = 4V/\pi R^3 t \quad (2)$$

$$\text{viscosity } (\eta) = \pi R^4 P/8LQ = FR^4 t/8R^2 LV \quad (3)$$

where:  $P$  = pressure applied to the capillary

$F$  = force applied to the capillary

$R$  = radius of the capillary

$L$  = length of the capillary

$Q$  = flow rate of melt through the capillary

Two corrections are commonly applied to capillary data in order to obtain the correct viscosity of polymeric fluids. The Rabinowitsch equation corrects the rate of shear at the wall for non-Newtonian liquids. It changes equation (2) to

$$\dot{\gamma} = [4Q/(\pi R^3)]^{3n+1}/(4n)$$

$$n = d \log \tau / d \log \dot{\gamma}$$

The factor  $n$  equals 1.0 for Newtonian liquids, and it is a constant for non-Newtonian fluids if the liquids follows the power law in which the shear stress depends upon  $\dot{\gamma}$  to the  $n^{\text{th}}$  power. Otherwise,  $n$  is a function of the shear rate.

The Bagley correction takes care of non-ideality arising from viscous and elastic effects at the entrance to the capillary. The shear stress at the wall of equation 1 becomes

$$\tau = PR/[2(L+eR)] = P/[2(L/R + e)] = (P-P_0)/(2L/R)$$

The Bagley correction factor  $e$  should be independent of capillary length, but in general it does vary somewhat with  $L/R$  because of elasticity of polymer melts. The Bagley correction is determined by measuring the pressure drop  $\Delta P$  at constant rate of shear for several capillary lengths and extrapolating to zero pressure drop as shown in Fig 3-8. In equation  $P_0$  is the pressure drop corresponding to a capillary of zero length for a given rate of shear.



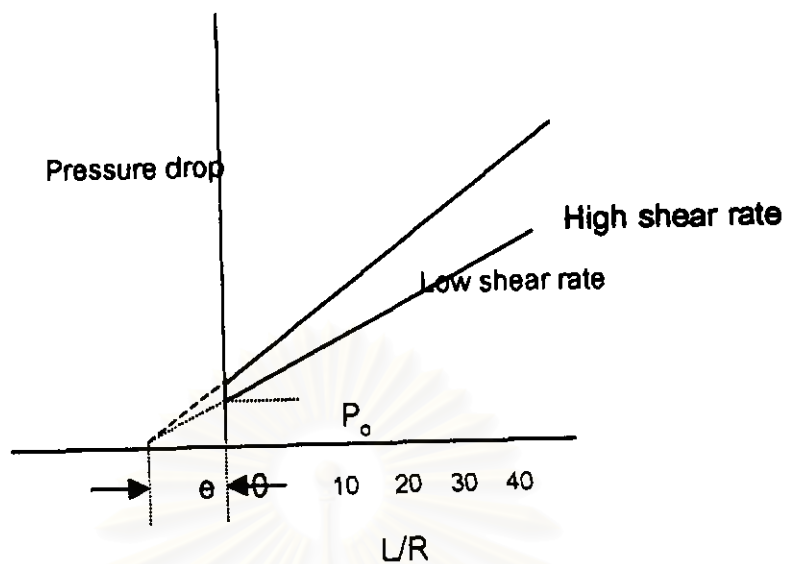


Figure 3-8 The bagley correction for capillary rheometers

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

### 3.3.4 Dilute solution viscosity

Measurements of solution viscosity are usually made by comparing the efflux time ( $t$ ) required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time  $t_0$  of the solvent. From  $t$ ,  $t_0$ , and the solute concentration are derived several quantities whose defining equations and names are given in Table 3-2. Two sets of nomenclature are in use for these quantities; one [Cragg, 1946] has had long and widespread application, the other [International Union, 1952] was proposed for greater clarity and precision. In this system the concentration  $c$  is expressed in grams per deciliter (g/dl or g/100 ml).

Table 3-2 Nomenclature of Solution viscosity

Common name	Recommended Name	Symbol and Define equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta / \eta_0 = t / t_0$
Specific viscosity	-	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp} / c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r) / c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp} / c)_{c=0} = [(\ln \eta_r) / c]_{c=0}$

The intrinsic viscosity  $[\eta]$  is independent of concentration by virtue of extrapolation to  $c=0$ , but is a function of the solvent used. The inherent viscosity at a specified concentration, usually 0.5 g/dl, is sometimes used as an approximation to  $[\eta]$ .

Dilute –solution viscosity is usually measured in capillary viscometers of the Ostwald-Fenske or Ubbelohde type. The latter has the advantage. The measurement is independent of the amount of solution in the viscometer, measurements at a series of concentrations can easily be made by successive dilutions.

Viscosity data as a function of concentration are extrapolated to infinite dilution by means of Huggins [1942] equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

where  $k'$  is a constant for a series of polymers of different molecular weights in a given solvent. The alternative definition of the intrinsic viscosity leads to the equation [Kraemer, 1938]

$$(\ln \eta_r)/c = [\eta] + k''[\eta]^2c$$

where  $k' - k'' = 1/2$ .

Staudinger's prediction in 1930 that the reduced viscosity of a polymer solution is proportional to its molecular weight has needed only slight modification: The intrinsic viscosity has been substituted for the reduced viscosity. And it has been recognized that the proportionality is to a power of the molecular weight somewhat less than 1. The relation is expressed in the equation.

$$[\eta] = K'M^a$$

where  $K'$  and  $a$  are constants determined from a double logarithmic plot of intrinsic viscosity and molecular weight.