LIQUID CRYSTALLINE POLYMERS : STUDIES ON BISPHENOL, HYDROQUINONE AND 1,4-CYCLOHEXANEDIOL BASED THERMOTROPIC MAIN CHAIN LIQUID CRYSTALLINE POLYESTERS

by

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Abstract

Three types of Main Chain Moiety Liquid Crystal Polyesters, poly(phenylene-terephthalate) (PPT), poly(bisphenol-terephthalate) (PBA) and poly(1,4-cyclohexanediol-terephthalate) (PCY) were synthesised using acidolysis melt condensation method. In this project, PPT was used as a control for comparison.

The reactivity of hydroquinone (HQ), bisphenol A (BA) and 1,4-cycohexanediol (CY) towards terephthanoyl chloride (TCl) were analysed by Differential Scanning Calorimeter (DSC). It was found that the reaction of HQ and TCl was the fastest while BA was the slowest among the three diols.

In addition, a series of copolyesters with different ratio of HQ : BA were synthesised to study the effects of flexible BA content in PPT system. The properties of synthesised polyesters were characterised in terms of their solubility and thermal stability. Thermal and liquid crystalline properties were characterised by DSC and X-ray diffraction (XRD) method. Morphology of the crude and annealed (420°C) samples were observed by using Scanning Electron Microscope (SEM). Fourier Transform Infra-Red (FTIR) was done to confirm the presence of polyesters and the ratio of HQ/BA in the copolyesters.

PPT was insoluble in all of the organic solvents. PBA and PCY dissolved in chlorobenzene and mixture of phenol/*p*-chlorophenol /tetrachloromethane. The thermal stability and percentage of crystallinity of the homopolymers is in the sequence of PPT>PBA>PCY. PPT and PCY did not show any melting behaviour prior to polymer decomposition but PBA did. The crystallinity of PBA is thermodynamically unstable and dependent on its thermohistory. Combining DSC and XRD methods, PBA and PPT are expected to exhibit nematic mesophase. Non linearity of *cis*-1,4-cyclohexanediol prohibit the existence of mesophase in PCY.

As a whole, synthesised copolyesters can be divided into two groups, PPT rich copolyesters (PBA20 & PBA40) and PBA rich copolyesters (PBA60 & PBA80). PPT rich copolyesters exhibited properties of diffraction pattern, thermal stability profiles and solubility which are similar to PPT while those of PBA rich copolyesters are similar to PBA. PBA rich copolyesters exhibited anisotropic melt at temperature range of 301°C - 309°C but PPT rich copolyesters did not .

In conclusion, by replacing the rigid unit, HQ, with flexible unit, BA, has successfully depressed the anisotropic melt of the copolymers from >550°C to 329°C. This temperature was further decreased by using copolymerisation method. PBA60 showed the lowest anisotropic melt (301°C) among the synthesised polyesters.

Polymer Cecair Berhablur : Kajian Ke Atas Thermotropik Rantai Utama Polymer Cecair Berhablur polyester Berasaskan Bisfenol, Hydrokuinon dan 1,4-sikloheksadiol

Abstrak

Tiga jenis Poliester Cecair Berhablur Termotropik Rantai Utama, Poli(fenilina tereftalat) (PPT), poli(bisfenol A) (PBA) dan poli(1,4-sikloheksanadiol-tereftalat) (PCY) disintesiskan dengan mengunakan cara kondensasi leburan asidolisis. Dalam projek ini, PPT digunakan sebagai kawalan untuk perbandingan.

Kereaktifan hidrokuinon (HQ), bisfenol A (BA) dan 1,4-sikloheksanadiol (CY) terhadap tereftanoil klorida (TCl) dianalisis dengan menggunakan Kalorimeter Penskanan Diferensial (DSC). Didapati bahawa tindakbalas HQ dengan TCl adalah yang terpantas, manakala BA adalah paling lambat di antara ketiga-tiga diol.

Selain daripada itu, satu siri kopoliester dengan nisbah HQ : BA yang berlainan disintesiskan untuk mengkaji kesan kandungan BA lentur dalam sistem PPT. Sifat-sifat keterlarutan dan kestabilan termal poliester tersebut dicirikan. Sifat-sifat termal dan cecair berhablur dicirikan dengan menggunakan DSC dan Pembelauan Sinar (XRD). Morfologi sampel mentah dan sampel anneal (420°C) diperhatikan dibawah Mikroskop Penskanan Elektron (SEM). Fourier Transformasi Infra Merah (FTIR) dilakukan untuk menentukan kehadiran poliester dan juga kandungan nisbah HQ : BA dalam kopoliester.

PPT tidak larut dalam semua pelarut organik. PBA dan PCY larut dalam klorobenzena dan campuran fenol/*p*-klorofenol/tetraklorometana. Kestabilan termal dan peratusan kehabluran homopolimer adalah dalam siri PPT>PBA>PCY>. PBA lebur sebelum polimer terurai manakala PPT dan PCY tidak menunujukkan sifat tersebut. Sifat hablur PBA adalah termodinamik tak stabil dan ianya adalah bergantung kepada sejarah termalnya. Dengan gabungan cara DSC and XRD, didapati bahawa PBA dan PPT menunjukkan mesofasa nematik. Ketidaklurusan *sis*-1,4-sikloheksanadiol menghalang pembentukan mesofasa dalam PCY.

Secara keseluruhan, kopoliester boleh dibahagi kepada dua kumpulan, iaitu kopoliester kaya dengan PPT (PBA20 & PBA40) dan kopoliester kaya dengan PBA (PBA60 & PBA80). Kopoliester yang kaya dengan PPT menunjukkan corak belauan, profil kestabilan termal dan sifat kelarutan serupa dengan PPT, manakala kopoliester yang kaya dengan PBA adalah semirip dengan PBA. Kopoliester yang kaya dengan PBA menunjukkan leburan anisotropik pada suhu 301°C - 309°C tetapi kopoliester yang kaya dengan PPT tidak lebur.

Sebagai kesimpulan, dengan menggantikan unit rigid, HQ, dengan unit lentur, BA, telah berjaya menurunkan suhu leburan anisotropik kopolimer dari >550°C ke 329°C. Suhu leburan ini boleh diturunkan lagi dengan menggunakan cara pengkopolimeran. PBA60 menunjukkan suhu leburan anisotropik (301°C) yang terendah sekali di antara poliester-poliester yang disintesiskan.

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CHAPTER 1 : INTRODUCTION

1.1 Introduction

Liquid crystals (LCs) have been known for more than a century. They were discovered by an Austrian botanist, Friedrich Reinitzer in 1888. Reinitzer observed two melting points of cholestryl benzoate. On its first melting point at 145°C, cholestryl benzoate formed an opaque liquid and upon heating to higher temperature at 179°C, it became a clear transparent isotropic liquid. This behaviour was further studied by Friedel and was classified as mesophase or liquid crystalline phase by Lethmann (Cowie, 1991; Varshney, 1986).

Although LCs have been known for many years, they only attracted major attention in the last thirty years. The recent rise in interest was mainly due to their tremendous potential application in various fields such as electronic display devices, temperature indicator, radiator sensor, temperature controller *etc*. LCs are very sensitive to external disturbance *e.g.* temperature, pressure, electrical field or foreign chemical vapour. The molecules of LC are well orientated along a particular direction; any external perturbation may change the orientation of these molecules and thus their optical properties. This sensitive characteristic has made them to be popular especially in electronic display.

As D. Volander suggested that macromolecule may also exhibit liquid crystalline phase (Kelker & Hatz, 1980) and this was found true later in the polymers which contain several mesogen groups. These polymers are termed as Liquid Crystal Polymers (LCPs).

In the last thirty years, LCPs have received a great deal of attention from both industries and academic laboratories throughout the world. A number of new LCPs had been synthesised, developed and many products and synthesis process had been patented. Some examples of the patented LCP are shown in Appendix 1.

The outstanding properties of LCPs is the main reason enabling them to be a highly interesting material researched by polymer chemists. High tensile strength, high modulus, high impact strength, high temperature capability, excellent chemical resistance, excellent dimension stability with low shrinkage and low thermal expansion are among the valuable inherent properties of LCPs which are comparable or even better than engineering plastic, thermoset plastic and ceramic (Thomas & Roth, 1990). Table 1.1 shows the typical properties of LCPs as a comparison to other engineering plastics.

Table 1.1: Key properties of LCPs and competitive high-temperature resins

	LCP		Other Engineering Resin			
	30%GR Vectra A130	GR Xydar	40%GR PPS	20%GR PES	30%GR PEI	30%GR PET
Specific Gravity	1.57	1.70	1.67	1.50	1.51	1.60
Water Absorption	0.02	0.01	0.05	0.35	0.90	0.05
Mold Shrinkage, in/in	0.001	0.001-0.004	0.002-0.004	0.002-0.004	0.002-0.009	0.002
Tensile Strength, 10^3lb/in^2	29.0	16.0	17.5	18.0	24.5	23.0
Elongation, lb/in^2	2.2	2.0	0.9	3.0	3.0	2.5
Flex. strength, 10^3lb/in^2	36	18	26	25	33	33
Flex. modulus, 10^3lb/in^2	2100	1800	1700	850	1200	1400
Notched Izod Impact ft-lb/in	2.5	1.9	1.3	1.5	2.0	1.6

Source : Dole (1987)

Note : GR = glass reinforced
PES = polyether sulfone
PET = polyethylene terephthalate
PPS = polyphenylene sulfide
PEI = polyetherimide

There are some LCPs available in the market, for instance, Xydar from Dart and Kraft, Vectra from Celanese Corporation, DuPont's HX200 *etc*.. Other plastic industries which are actively involved in this area are Eastman-Kodak, Imperial Chemical Industries (ICI) and Carborudum. Presently, the Kevlar fiber has replaced steel, fiberglass, asbestos and graphite for a variety of applications, including radial tires, armorplate, brake linings and composites. Similarly, the copolyester LCP synthesised by Eastman (under Trademark of "X7G") and Celanese's Vectra has good opportunity in the market (Chung, 1986). Tupperware, with their LCP-based Ultra 21, have dominated the field of house hold products especially in high temperature cookware (Dole, 1987). LCPs have penetrated various markets due to their development in highly specialised and performance oriented application. The key application of LCPs are as follows :

- Consumer and appliances
- Electrical and electronics
- Telecommunication
- Transportation
- Industrial
- Fiber optics
- Aircraft and aerospace
- Chemical and hostile environments
- Military and ordnance

According to Dole (1987), the growth of LCP usage in the market will be broad based and rapid from day to day, and is expected to reach 5 - 10 million pounds in mid 1990. Now it is classified as an advance material and can be termed as "the 20th century materials".

Nowadays, a lot of efforts has been put in to develop or produce the desired thermotropic LCP for various application by researchers compared with lyotropic system. This is mainly due to the predominant processing advantages of thermotropic LCPs. The main interest of the present study is to develop the thermotropic LCPs which are melt processable at accessible temperature.

1.2 Objective of The Project

In the present project, the main objectives are :

(i) to learn the technique to synthesise main chain liquid crystal polyesters (LCPEs) by melt condensation method.

(ii) to develop the lower melting thermotropic main chain LCPEs based on poly(phenylene terepthalate) (PPT) system by using flexible units, Bisphenol A (BA) and 1,4-cyclohexanediol (CY). Three types of main chain moieties of LCPEs were synthesised, PPT, poly(bisphenol terephthalate) (PBA) and poly(1,4-cyclohexanediol-terephthalate) (PCY).

(iii) to study the effect of copolymerisation. A series of copolymer LCPEs from two types of diphenols, Hydroquinone (HQ) and Bisphenol A (BA) with Terephthanoyl Chloride (TCl) were synthesised. The percentage ratio of HQ : BA are as follows :

(a) 20 : 80

(b) 40 : 60

(c) 60 : 40

(d) 80 : 20

(iv) to characterise the LCPEs using Fourier Transform Infra-Red (FTIR), Thermal Analysis Instrument - Differential Scanning Calorimeter (DSC) and Thermal Gravimetry Analyser (TGA), X-ray Diffractometer, solubility testing and morphology study by Scanning Electron Microscope (SEM). A comparison among the LCPEs was carried out.

CHAPTER 2 : LITERATURE REVIEW

2.1 Liquid Crystals (LCs)

Conventionally, matter exists in one of three phases, *i.e.* solid state, liquid state or gaseous state. In solid state, all of the constituent molecules or atoms are fixed firmly in the lattice position where small vibration is allowed but no rotation; liquid state, where the components are allowed to have vibration and rotation, but is in the limited state. The amount of order in a liquid is in a much lesser degree than in solid, but there is no long range of order. In gaseous state, the molecules move freely through the entire volume without any constraint. LC is a compound which exhibits an additional phase between that of conventional liquid and solid. When LC melts, it forms a fluid in which some of the molecular order of the solid is retained. Although the positional order and center of gravity of the molecules in the parent solid may be lost substantially upon melting, molecular parallelism is retained. The fluid retain solid like properties at lower temperature and upon heating to higher temperature, orientation and individual alignment would be eventually destroyed when it passes the normal isotropic state. In short, LCs are the compounds which would simultaneously exhibit the feature of liquid (flow properties) and crystalline bodies (optical properties) during melting. This behaviour is exhibited in small molecules as well as macromolecules.

2.1.1 Structure Requirement to Form Liquid Crystalline Phase

In order to form liquid crystalline phase (mesophase), molecules should have the following features (Collings, 1990):

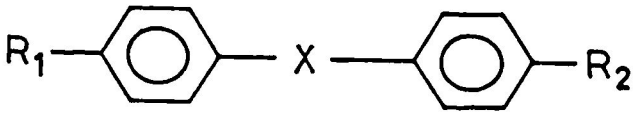
1) The molecules must be elongated in shape, that is, its length must be significantly longer than its width.

2) The molecules or part of the molecules should be rigid rod shape or disc shape structure which is called mesogen.

3) They should have aromatic structure in the system.

The molecules have advantages to form liquid crystalline phase if the ends of the molecules are flexible. This is because the flexible end structure would allow one molecule to position itself more easily between each other as they chaotically move about when they reach the transition state (anisotropic).

As shown in Figure 2.1, the basic structure of LC consists of two aromatic rings joined by a functional X linkage. Some of X linkages in LCs and the series name are listed in Table 2.1. The end groups at the *para* sites, R_1 and R_2 (Figure 2.1) may be alkyl, alkoxy or acyl, cyanide, cinnamate or halogens. This structure is the responsible group enabling the molecules to form liquid crystalline phase. They are called mesogens. Some of the typical examples of LCs are shown in Appendix II.



R_1, R_2 = alkyl, alkoxy, acyl, C≡N, cinnamate or halogens.

Figure 2.1 : General structure of a mesogen.

Table 2.1 : Some central linkages found in mesogen groups.

X	Series name
- CH = N-	Schiff bases
- N = N -	diazo compounds
- N = N(→O) -	azoxy compounds
- CH = N(→O) -	nitrones
- CH = CH-	stilbenes
- CH≡CH -	tolans
- OC(=O) -	esters
- (nothing)	biphenyls

Source : DuPre (1981)

2.2 Liquid Crystal Polymers (LCPs)

Liquid Crystal Polymers (LCPs) are high molecular weight materials in which the long chain of the molecules must contain several mesogen groups; but the introduction of mesogen groups into the polymer chains does not automatically generate the properties of liquid crystalline phase. One example is polycholesteryl acrylate, which is a typical amorphous polymer although the initial monomer unit has all the feature of LC substances (De Visser *et al.*, 1971). Like the LCs of low molecular weight, LCPs must have the tendency to maintain a high degree of crystalline order in the molten phase, either by heating or dissolving by solvents before they reach normal isotropic stage.

In general, LCPs can be divided into two main categories : a) those where liquid crystalline phases are obtained when introduced with a solvent are referred as lyotropic LCPs, and, b) those where liquid crystalline phases are formed on the application of heat are called thermotropic LCPs. Recently, liquid crystalline phase can also be brought out by pressure induction as reported by Hsio *et al.* (1988). It was defined as baratropic LCPs (Brostow, 1990). In lyotropic system, the liquid crystalline phase is obtained by dissolving the materials in certain concentration of solvent. They may exhibit lamellar, cylinder or spherical mesomorphics states as shown in Figure 2.2.

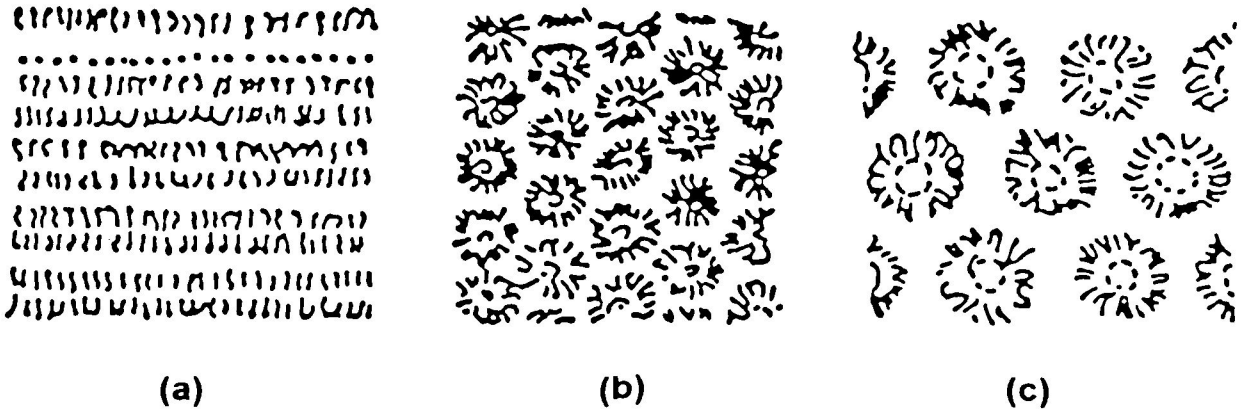


Figure 2.2 : Schematic presentation of molecular arrangements in lyotropic mesophases, (a) lamellar, (b) cyllindrical, and, (c) spherical forms.

In thermotropic LCPs, three types of liquid crystalline phases can occur. They are, a) *Smectic*, b) *Nematic*, and, c) *Cholesteric*.

(a) Smectic

The mesogen groups which form the ordered structure are particularly arranged in one preferred direction of alignment which is called "director". They are well defined in inter layer spacing. The center of gravity of the mesogen groups are movable in two directions. The lateral force between the molecules in the smectic phase are stronger than the force between the layer. This phenomena would allow the slippage of one layer over another layer and thus provides the fluidity characteristics of the system without losing the order within each layer. About twenty types of smectic phases have been defined, depending on the orientation of the molecules and "director".

(b) Nematic

The molecules in nematic phase is less ordered than those in smectic phase. All the molecules are aligned along certain common director but no positional order. The center of gravity of the mesogen groups are movable in three directions.

(c) Cholesteric

The cholesteric phase is basically nematic phase, sometimes it is also called chiral nematic phase. The molecular arrangement is similar to nematic structure but the orientation of the director changes regularly from layer to layer, forming a helical arrangement of the directors in three dimensional state .

The schematic illustration of molecular arrangement in thermotropic mesophase is shown in Figure 2.3. Most thermotropic LCPs exhibit single liquid crystalline state upon heating to isotropic melt. However, some thermotropic LCPs may exhibit more than one type of liquid crystalline phase. This phenomenon is commonly observed in the smectic type. Generally when thermotropic LCP is heated, it would transform from one smectic to another smectic state, and perhaps nematic phase before it completely forms isotropic melt, *i.e.* from the most ordered to the least ordered phase. Figure 2.4 shows various transitions that LCPs undergo as temperature increases versus the volume. It indicated that both the volume and the enthalpy jumps through the several transitions are additive : that is equal to the sum of the changes directly from crystalline state to the isotropic melt (Frinkelmann & Rehage, 1984).

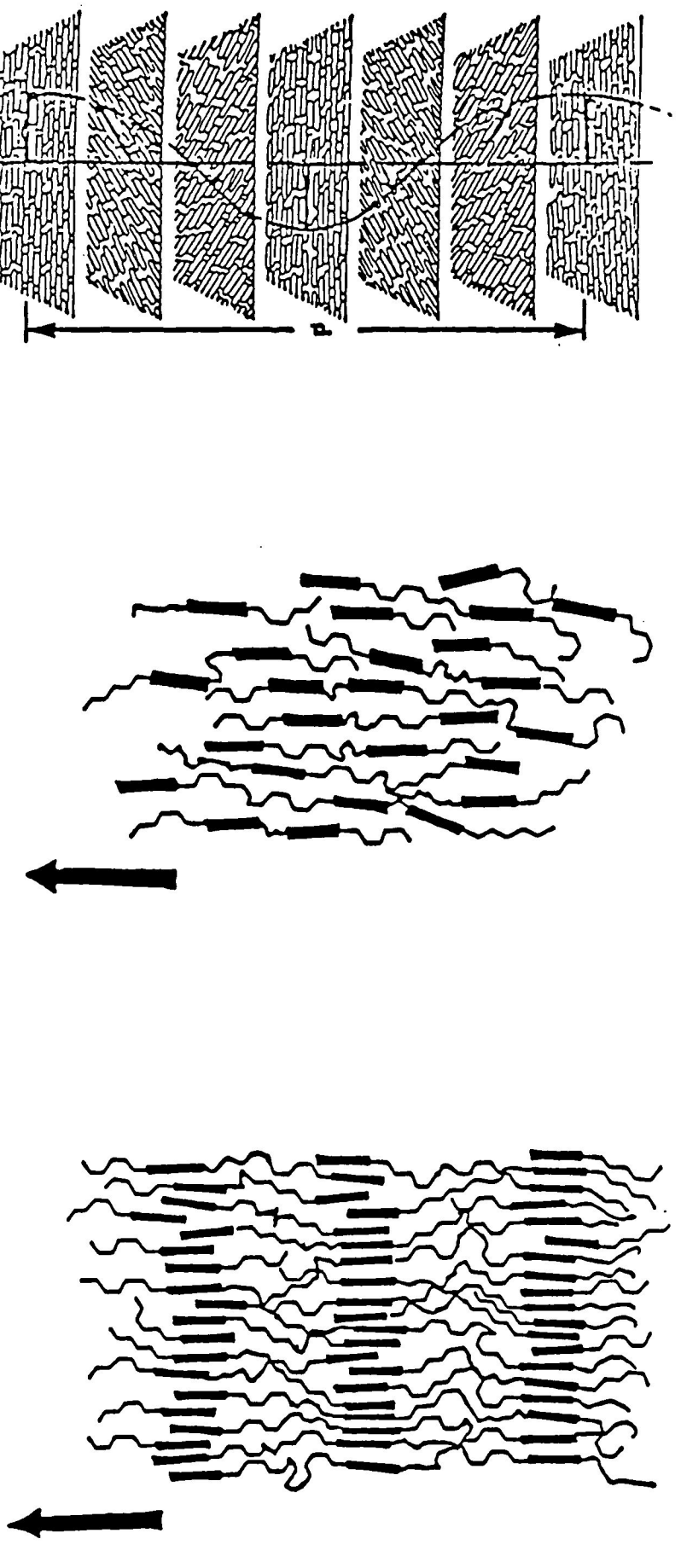


Figure 2.3 : Schematic presentation of molecular arrangements in thermotropic mesophases, (a) smectic, (b) nematic, and, (c) cholesteric phases.

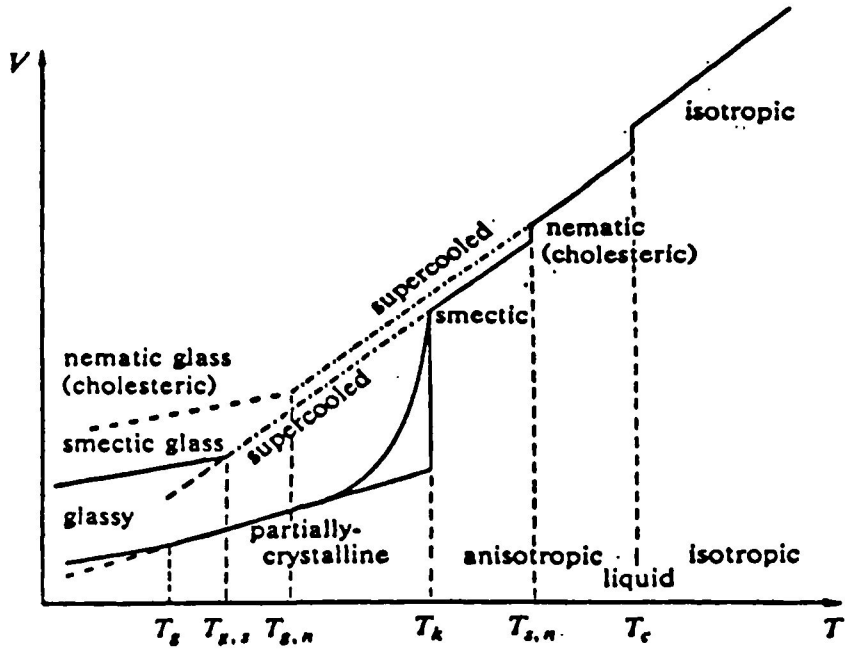


Figure 2.4 : Transition of LCP mesophase upon heating to isotropic melt.

2.3 Thermotropic LCPs

Thermotropic LCPs are mainly divided into 2 classes : a) main chain liquid crystal polymers (MC LCPs), b) side chain liquid crystal polymers (SC LCPs). In MC LCPs, the mesogen groups form the backbone of the molecular chain; whereas in the SC LCPs the mesogen groups link to a polymer backbone pendants in the side chain. The mesogen groups are attached directly or by flexible spacer to the main chain. A comprehensive review of SC LCPs has been published by McArdle in 1989. Reck and Ringsdorf had successfully combined the structure of MC LCP and SC LCP in 1985. Various possible way to link MC and SC were further developed by Reck *et al.* (1989).

In recent development, liquid crystalline phase is also noticed to be exhibited in setting network, which is classified as thermoset LCPs. MC LCPs and SC LCP functionalised with reactive groups would crosslink together or itself to form three dimensional network (Hsu *et al.*, 1993; Hoyt *et al.*, 1990; Zentel *et al.*, 1990; Peter & Ratzsch, 1990). The crosslink networks could be achieved through heating. Li *et al.* (1993a; 1993b) had synthesised LCPs which contained conjugated double bond and could be crosslinked in liquid crystalline phase with retention of the order in the final crosslinked solid. Recently Barclay *et al.* (1992) had synthesised the epoxy functionalised LCPs which the final network (smectic or nematic) was dependent on the molecular weight and polydispersity of the oligomer used. The architecture of the thermotropic LCPs is illustrated in Figure 2.5.

The mesogen groups in the LCPs are either rod-like or disk-like (Percec & Heck, 1990; Wenz, 1985; Kreuder & Ringsdorf, 1983; Kreuder *et al.*, 1985) as shown in Figure 2.5. The spacer between the mesogen groups and flexible units in both MC LCPs or SC LCPs are very important to determine the formation of liquid crystalline phase; leading to the properties of LCPs in all aspects.

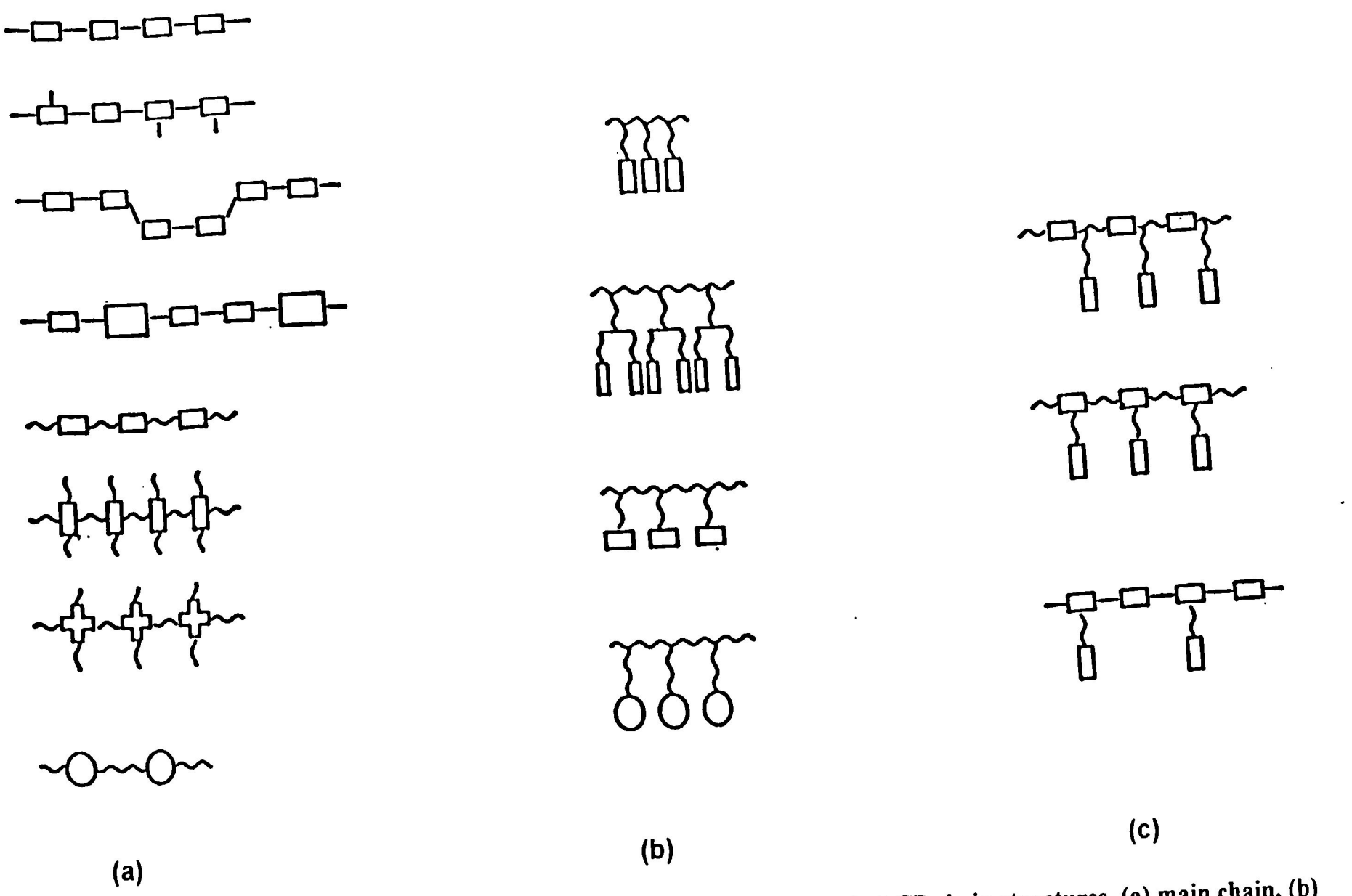


Figure 2.5 : Schematic representation of various possible arrangements of mesogens in LCP chain structures. (a) main chain, (b) side chain, and, (c) combination of main and side chain.

2.4 Identification of Liquid Crystalline Phases (mesophases) in Thermotropic LCPs

Basically, there are three possible ways to determine whether the synthetic polymer is an LCP. These are a) Differential Scanning Calorimeter (DSC), b) X-ray Diffraction (XD), and, c) Polarising microscope .

2.4.1 Differential Scanning Calorimeter (DSC)

DSC is the basic technique to study the thermal behaviour for most of the polymers. It is also not exceptional for LCPs and low molecular weight LCs. In fact, it is an extremely powerful technique to obtain rich information on the melt phase transition, mesophase transition, the transition from liquid-crystalline state to an isotropic melt, and relaxation transition in addition to T_g value. A typical DSC thermogram of LCP is shown in Figure 2.6 where the transitions between crystalline, liquid crystalline and isotropic melt are clearly visible on both heating and cooling traces with endothermic and exothermic peaks. For some LCPs, thermograms do not show the transition peaks as clear as low molecular weight LCs. It is attributed to a) high melt viscosity and polydispersity of the polymers, and, b) affected by appreciable undercooling. This phenomenon normally happens on MC LCPs where the phase behaviour, as shown by DSC thermograms, is generally less clear and informative, especially for LCPs which have rigid or semi rigid backbone. It is also common to obtain an almost "flat" DSC trace when studying a wholly aromatic LCPEs, copolyester or copolyesteramide. This

type of DSC traces would be observed on the LCPs which a) do not crystallise to an appreciable extent, b) shows no isotropic transition before major decomposition, and, c) has a very broad glass transition temperature (Magagnini, 1993).

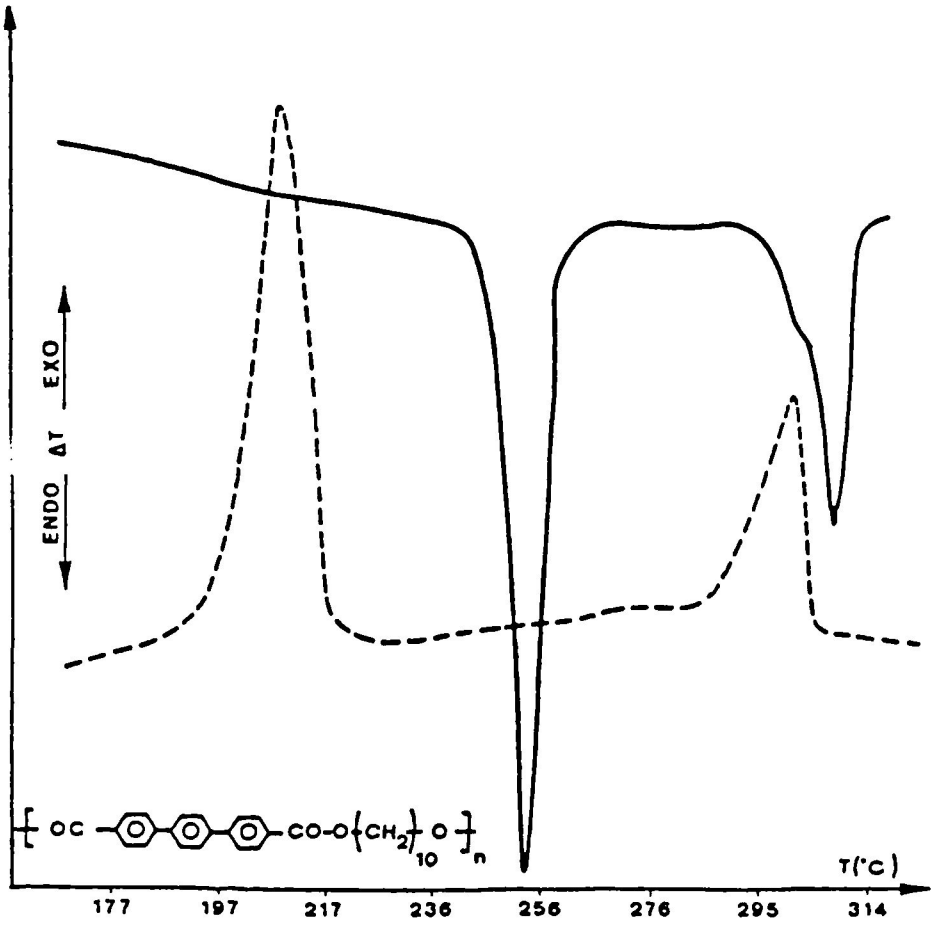


Figure 2.6 : DSC heating and cooling traces for ploy(terphenyl-4,4' dicarboxylate). — First heating run; ----- first cooling run (Noel, 1985).

2.4.2 X-ray Diffraction (XRD)

XRD analysis is the most important and reliable technique to study the structure of LCPs in both mesophase and solid state. It provides the information concerning the arrangement and mode of packing of molecules and types of order present in the mesophase. Wendorff (1978) has reviewed comprehensively the study of X-ray scattering of MC LCPs and SC LCPs. Blackwell and coworkers (Blackwell & Gutierrez (1982), Blackwell *et al.* (1984)), Noel *et al.* (1984) and Chivers *et al.* (1984) used X-ray diffraction method to characterise the orientation and molecular structure of MC LCPs in their work; while Tsukruk *et al.* (1983) and Friedzon *et al.* (1986) studied SC LCPs by using step by step scanning with the increase of temperature. Using this method, Tsukruk was able to study the structural changes of smectic phase of LCPs from the mesophase to isotropic phase.

2.4.2.1 X-ray Diffraction Pattern for Powder Samples (Unoriented Samples)

With the Debye-Scherrer powder technique, it is possible to identify liquid crystal from X-ray diffraction patterns of unoriented samples but it's limited for smectic A (S_A) and smectic C (S_C) orientation, because of their least ordered phases (Noel, 1985). The powder diagrams can, however, provide reliable information on the number of phases present (Cowie, 1991). The diffraction pattern of a powder can be divided into inner rings at small diffraction angles and outer rings at large angles. The inner rings are the indications of longer layer spacing and the outer rings corresponds to shorter

preferred spacing occurring in the lateral packing arrangement of the molecules. The appearance of a broad halo or sharp rings furnishes a qualitative indication of the degree of order (Noel, 1985).

The XRD pattern of various mesophases are described in the following statements (Wendorff, 1978) :

(a) Nematic Phase.

In the case of nematic phase, a weak diffuse inner ring is observed, which is related to the length of the molecules, and a strong diffused rings at outer rings, which is a measure of the distance between neighbouring molecules.

(b) Smectic Phase.

When the smectic phases are present, one or more sharp inner rings arise, indicating the more ordered lamellar structure in the molecules and one diffuse outer ring, which is due to the short range order within the layer.

(c) Cholesteric Phase.

The diffraction pattern of this phase is similar to that of the nematic phase. The intensity of inner rings increase if the cholesteric-smectic transition is approached.

2.4.2.2 X-ray Diffraction Patterns for Oriented Samples

More details and discriminating structural information can be obtained if the sample is in the oriented form (Watanabe & Hayashi, 1989). Oriented specimens can be prepared by cooling from the isotropic liquid phase under strong magnetic field. Least order of S_A and S_C may be very difficult to identify and the result depends on the preparation of the specimens and conditions. An alternative technique is to prepare the samples in the oriented fiber form or in single crystal by using melting method (Noel, 1985). Typical XRD patterns for the nematic, S_A and S_C phases are shown in Figure 2.7.

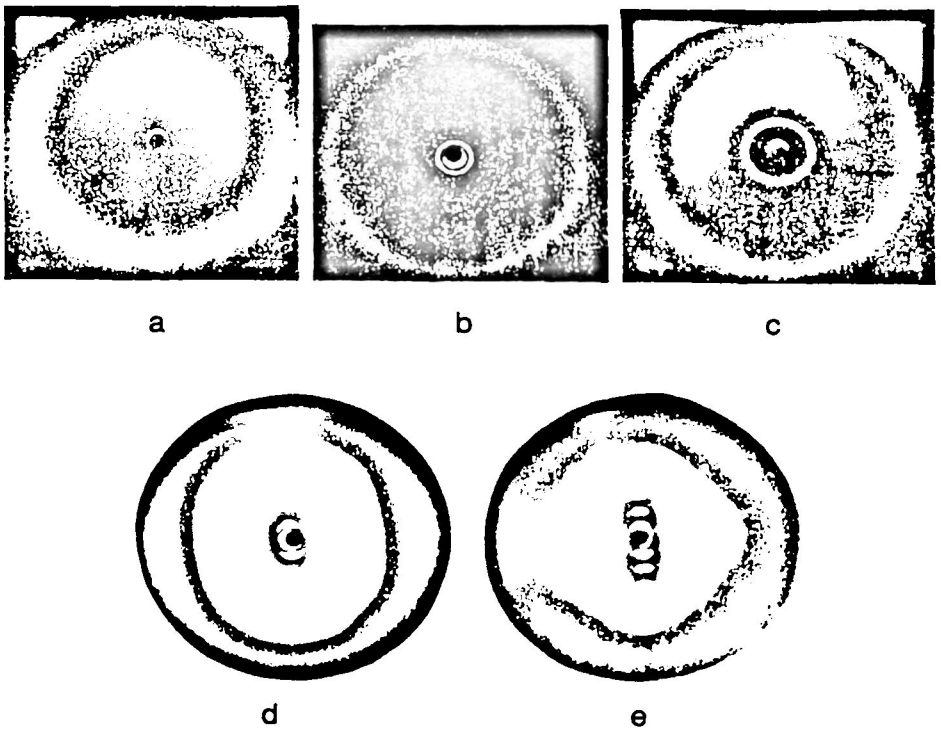


Figure 2.7 : Typical XRD pattern for unoriented (a) nematic, (b) smectic A, (c) smectic C, oriented (d) smectic A and (e) smectic C phases (Cowie, 1991).

2.4.3 Polarising Microscope

Perhaps Polarising Microscope is the most popular technique to be used for determining the occurrence of the mesophases of low molecular weight LCs with the aid of hot stage. The observation of a thin film on the hot stage under polarising microscope may provide sufficient information on the organisation of the LC molecules in mesophase and identify the transition between the various mesophases and its isotropic melt. In general, nematic, cholesteric, S_A and S_C mesophases are the most commonly observed mesophases in LCPs. Other types of higher order smectic mesophases are comparatively rare.

It is difficult for higher order of mesophases to have clear picture under polarising microscope attributing to the possibility of multiphase nature of polymers *i.e.* with the existence of a polycrystalline and /or of an amorphous phase in addition to the LC phase. Their polydispersity and /or high melt viscosity may also lead to the difficulty of observation and misleading for the identification of LCPs. It is even worse for the high molecular weight LCPs with clear microscopic texture are difficult to be observed. In order to obtain good result, special treatment is needed to be done before the polarising microscope is used, commonly, annealing the samples for a very long time is done (Magagnini, 1993). Lately, the details and systematic description of this method to study the structure of LCPs was described by Viney (1990).

In short, under polarising microscope, nematic phase shows threaded, schlieren or marbled texture when cooling from an isotropic melt. Cholesteric melt shows planar texture with oily streaks, moire fringes and/or Grandjean lines. It can also show strong reflection colour due to the pitch of the helical structure between the phase. Smectic phases show focal conic, fan shape, mosaic or broken focal conic texture. Example of each texture are shown in Appendix 3 (Cowie, 1991; Noel, 1985). Identification of mesophase can also be done by using the following equation :

$$|S| = \textbf{(number of brushes meeting) / 4}$$

where brushes is the extinction position of mesophases in schlieren texture and S is called disclination strength where at certain points, two or bark brushes meet together. If

S = ±1/2; ±1 Nematic Phase

S = ±1 Smectic Phase

Thus, nematic phase is indicated by mixture of two or four points disclinations, and smectic phase exhibits only four points disclinations (Sperling, 1993). The schematic diagram of molecular trajectories associated with various disclinations strength is shown in Figure 2.8 (Noel *et al.*, 1984).

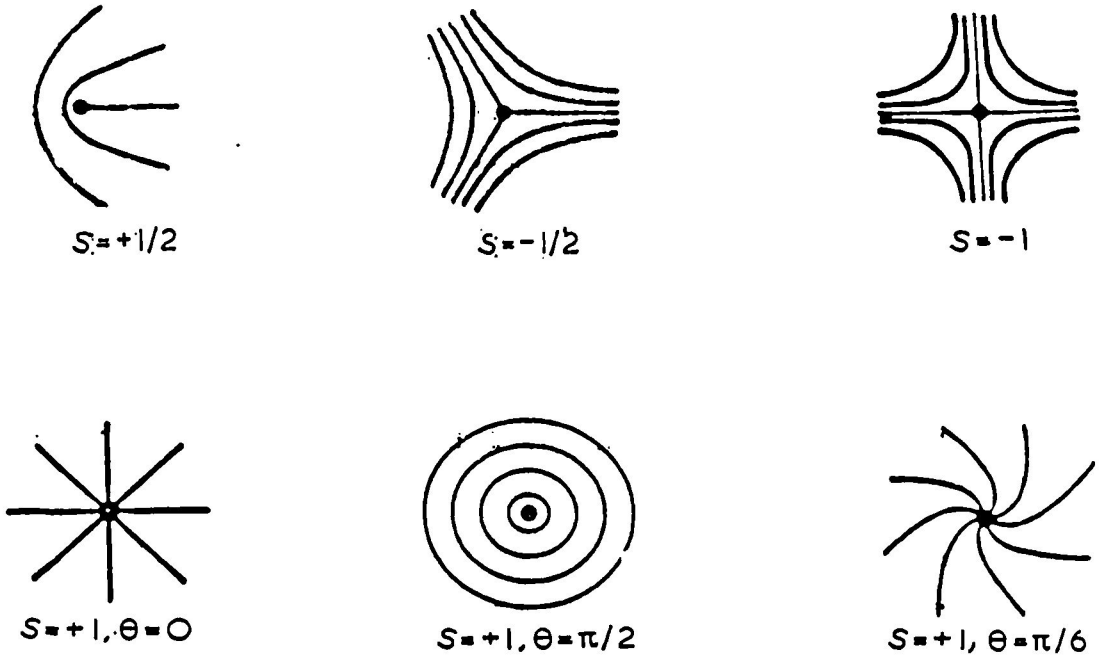


Figure 2.8 : Schematic diagram of the trajectories associated with different disclinations strength.

2.5 Thermotropic Main Chain Liquid Crystal Polymers (MC LCPs)

In general, thermotropic MC LCPs have both a linear rigid mesogen groups and a spacer (or flexible spacer) in the backbone. The mesogen groups must consist of at least two cyclic (aromatic or cycloaliphatic) units which are connected by a short central rigid bridging group. The bridging groups may be either imino, azo, ester, *trans*-vinylene groups or direct link between aromatic group such as biphenyl. The multiple bonds character in both central linking group and the spacer is very important in order to maintain polymer rigidity and linearity. Table 2.2 shows the representative structure of the rings and links combinations, as well as flexible spacers, which have been used as the basic for preparation of thermotropic LCPs (Ober *et al.*, 1984). Due to the inherent