

**SYNTHESIS AND CHARACTERIZATION OF HYDROGEN BONDED
SIDE CHAIN LIQUID CRYSTALLINE POLYMERS**

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**HİDROJEN BAĞLI YAN ZİNCİR SIVI KRİSTAL POLİMERLERİN
SENTEZİ VE KARAKTERİZASYONU**

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Esra ERBİL

Chemist

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ABBREVIATIONS

AIBN	: 2,2'-Azobis(2-methylpropionitrile)
DMF	: N,N-Dimethylformamide
DMSO	: Dimethylsulfoxid
DSC	: Differential Scanning Calorimeter
FT-IR	: Fourier Transform Infrared Spectroscopy
¹H-NMR	: Nuclear Magnetic Resonance Spectroscopy
HB-PLC	: Hydrogen Bonded Liquid Crystal Polymer
K₂CO₃	: Potassium Carbonate Anhydrous
LCs	: Liquid Crystals
LCPs	: Liquid Crystal Polymers
MCLCP	: Main Chain Liquid Crystal Polymer
NaOH	: Sodium Hydroxide
POM	: Polarized Optical Microscopy
PVI	: Poly(vinyl imidazole)
PVP	: Poly(4-vinyl pyridine)
PVPy	: Poly(4-vinyl pyrrolidone)
SCLCP	: Side Chain Liquid Crystal Polymer

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SYNTHESIS AND CHARACTERIZATION OF HYDROGEN BONDED SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

SUMMARY

Recently, the application of hydrogen bonding in the formation of new liquid crystalline materials, ie. supramolecular liquid crystals has been rapidly developed. Supramolecular liquid crystals are molecular complexes generated from complexation of molecular species through non-covalent intermolecular forces, e.g. hydrogen bonding. The mesogenic properties can be easily modified by several proton donors and proton acceptors, and new liquid crystalline properties, which are different from those of their original moieties, can be obtained by supramolecular structures. Hydrogen bonded liquid crystalline materials have various potential in the fields of display, biomaterials and materials for electro-optical applications.

This study describes the preparation of three different polymers as hydrogen bond acceptor and three different 4'-(hydroxyalkoxy)-4-cyanobiphenyl derivatives ($n=6,8,11$) as hydrogen bond donor. In the first step, poly(vinyl imidazole)(PVI) and poly(4-vinyl pyridine) (PVP) hydrogen bond acceptors were prepared by free radical polymerization of related monomers. Poly(vinyl pyrrolidone) was purchased commercially. The hydrogen bond donors were synthesized by the reaction of hydroxy halides having different number of methylene unit with hydroxy cyano biphenyl mesogens. In the second step, the hydrogen bond donors were attached to the proton acceptor polymers through H-bond interactions between the hydroxyl group of hydrogen bond donors and imidazole, pyrrolidone and pyridine groups of the hydrogen bond acceptors to yield the desired side chain liquid crystalline polymers. The formation of H-bond was confirmed by using FTIR spectroscopy. To confirm the liquid crystalline nature and to identify the phases of 4'-(hydroxyalkoxy)-4-cyanobiphenyl derivatives and corresponding H-bonded polymers, differential scanning calorimetry (DSC) and polarising optical microscopy (POM) were employed. The co-operation of hydrogen-bonding and dipolar interactions resulted in the formation of LC behaviour.

HİDROJEN BAĞLI YAN ZİNCİR SIVI KRİSTAL POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Son yıllarda, supramoleküler sıvı kristaller gibi, yeni sıvı kristal malzemelerin hazırlanmasında hidrojen bağı uygulamaları hızla gelişmektedir. Supramoleküler sıvı kristaller, moleküler türlerin, hidrojen bağları gibi kovalent olmayan moleküller arası kuvvetler vasıtasıyla oluşturdukları komplekslerdir. Mesojenik özellikler, çeşitli proton verici ve proton alıcı gruplarla kolayca değiştirilebilir ve başlangıç türlerinin özelliklerinden farklı yeni sıvı kristal özelliklere sahip supramoleküler yapılar elde edilebilirler. Hidrojen bağı sıvı kristal malzemeler, gösterge, biyomalzeme ve elektro-optik malzemeler için çeşitli uygulama potansiyeline sahiptirler.

Bu çalışma, hidrojen bağ alıcı olarak üç farklı polimerin ve hidrojen bağ verici olarak üç farklı 4'-(n-hidroksi alkoksi)-4-siyanobifenil türevlerinin ($n=6,8,11$) hazırlanarak, H-bağı yan zincir sıvı kristal polimer sentezinde kullanımlarını tanımlamaktadır. İlk aşamada, hidrojen bağı alıcı polimerler poli(vinil imidazol) ve poli(4-vinil piridin), monomerlerinin serbest radikal polimerizasyonu ile hazırlanmıştır. Poli(vinil pirolidon) ticari olarak elde edilmiştir. Hidrojen bağı verici bileşikler, farklı sayıda metilen grubu içeren hidroksi halojenürler ile hidroksi siyano bifenil mesojenlerinin reaksiyonu ile sentezlenmiştir. İkinci aşamada, hidrojen bağ verici bileşiklerin hidroksil grubu ile hidrojen bağ alıcı polimerlerin imidazol, pirolidon ve pridin grupları arasındaki H-bağı etkileşimleri vasıtasıyla istenilen H-bağı yan zincir sıvı kristal polimerler hazırlanmıştır.

Hidrojen bağı oluşumu FT-IR spektroskopisi yöntemiyle kanıtlanmıştır. Sıvı kristal özellikleri saptamak ve 4'-(n-hidroksi alkoksi)-4-siyanobifenil türevlerinin ve hidrojen bağı polimerlerinin sıvı kristal fazlarını belirlemek için, Diferansiyel Taramalı Kalorimetre (DSC) ve Polarize Optik Mikroskop (POM) kullanılmıştır. Hidrojen bağı ve dipolar etkileşiminin birleşimi sıvı kristal davranışların oluşumuna neden olmuştur.

1. INTRODUCTION

Liquid crystal technology has had a major effect many areas of science and engineering, as well as device technology. Liquid crystal polymers combines polymer-specific properties and specific properties of the liquid crystalline phase so that, this combination leads to a multitude of new prospectives; this has made possible a wide range of applications of liquid crystal polymers with excellent properties.

SCLCPs are generally prepared by covalently linking rigid mesogens to polymer backbones through flexible spacers. Recently, self-assembly through specific interactions, such as hydrogen-bonding, ionic, ioncdipolar, and charge transfer interactions, has been recognized as a new strategy for constructing SCLCPs. Hydrogen bonding is particularly attractive since there are many natural models for it. The formation and dissociation of the hydrogen bonds play an important role in many biological processes. Hydrogen-bonded systems are prepared using two suitably designed components that are commonly called H-bond donors and H-bond acceptors. The association between the ‘donor’ and ‘acceptor’ effectively induces hydrogen bonds that lead to a more stable structural organisation.

Hydrogen bonded liquid crystalline materials have various potential applications in the fields of display and electro optical devices which makes them good candidates for applications in microelectronic devices ranging from optical data storage and nonlinear optics.

In this study, three different polymers poly(vinyl imidazole)(PVI), Poly(vinyl pyrrolidon) (PVPy) and poly(4-vinyl pyridine) (PVP) as hydrogen bond acceptor and three different 4'-(hydroxyalkoxy)-4-cyanobiphenyl derivatives (LC6, LC8, LC11) as hydrogen bond donor were prepared. The hydrogen bond donors were then attached to the proton acceptor polymers through H-bond interactions between the hydroxyl group of hydrogen bond donors and imidazole, pyrrolidone and pyridine groups of the hydrogen bond acceptors to yield the desired side chain liquid crystalline polymers. The SCLCPs was characterised using differential scanning calorimetry (DSC), polarising optical microscopy (POM) to determine whether the

liquid crystalline and thermal properties of the supramolecular complexes. The structure analysis of the SCLCP was characterised by FT-IR spectroscopy.

2. THEORETICAL PART

2.1 . Liquid Crystals

2.1.1. Historical development of liquid crystals

The discovery of liquid crystals is usually attributed to an Austrian botanist by the name of Friedrich Reinitzer. In 1888, he experimented with a substance related to cholesterol and noted that it had two melting points. At 145.5°C it melted from a solid to a cloudy liquid and at 178.5°C it turned into a clear liquid. He also observed some unusual colour behaviour upon cooling; first a pale blue colour appeared as the clear liquid turned cloudy and second a bright blue-violet colour was present as the cloudy liquid crystallised [1]. The molecular structure of cholesteryl benzoate and its phase transition temperatures are shown in Figure 2.1 [2].

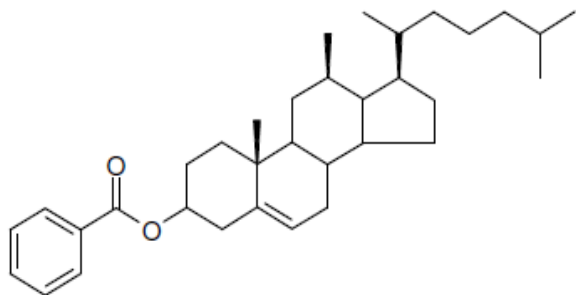


Figure 2.1: Structure formula of cholesteryl benzoate. Phase Transitions: K 150.5
N*182.6 Iso

Reinitzer sent samples of this substance to Otto Lehmann, a professor of natural physics in Germany. Lehmann was one of the people studying the crystallisation properties of various substances and first he called them soft crystals; later he used the term crystalline fluids because of their both solid and liquid properties [1].

In the early 1900s, Vorlander started systematic synthetic work. Under his direction, many new crystalline compounds were synthesized. Another early outstanding contribution to the liquid crystal field was made by George Friedel who gave the first

rational explanation for the patterns observed with liquid crystals in the polarizing microscope and deduced the molecular order of these liquid crystal textures [3].

Shortly before 1960, interest in liquid crystals awakened in the United States, Great Britain, and the Soviet Union. An American chemist, Glenn Brown, published a lengthy review article on liquid crystals. George Gray, a British chemist, published a full-length book on liquid crystals, and I. G. Chistyakov started a group working on liquid crystals in Moscow. Research on liquid crystals also began in Germany and France. Also during this time period the first room temperature, moderately stable liquid crystal was discovered [1].

Over the decade after Reinitzer's discovery, about 15 compounds became known to behave like liquid crystals (LC). By 1935, about 1100 liquid crystalline substances were synthesized. Today, more than 50,000 compounds and mixtures are known to possess liquid crystalline properties [4].

Liquid crystal technology has had a major effect many areas of science and engineering, as well as device technology. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems. The most common application of liquid crystal technology is liquid crystal displays (LCDs.), also they are using as thermometers, optical imaging and recording, medical applications. As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications [5].

2.1.2. General definition and classification of liquid crystals

Solids, liquids and gases are the most common phase of the matter. These three common states of matter are different from each other because the molecules in each state possess different amounts of order.

The solid state consists of a more or less rigid arrangement of molecules because each molecule occupies a certain place in the arrangement and remains there. And the molecules also oriented in a specific way. The molecules might vibrate a bit, but on average they constantly maintain this highly ordered arrangement. There are large

attractive forces holding the molecules of a solid in place, so solids are hard and difficult to deform.

The liquid state is quite different in that the molecules neither occupy a specific average position nor remain oriented in a particular way. The amount of order in a liquid much less than in a solid. Attractive forces still exist in a liquid but they are much weaker than the forces in solids. Liquids flow and will change its shape easily.

In the gas state, the amount of order is less than in liquids and the forces are not strong enough to hold the molecules close together. A gas can be deformed more easily.

The molecules in a solid are constrained to occupy only certain positions. To describe this condition saying the solid phase possesses positional order. In addition, the molecules in these specific positions are also constrained in the ways they orient themselves with respect to one another. So solid phase also possesses orientational order. When a solid melts to a liquid, both types of order are lost completely; the molecules move and tumble randomly. When a solid melts to liquid crystal, however, the positional order may be lost although some of the orientational order remains. The molecules in the liquid crystal phase are free to move about in much the same fashion as in a liquid; but as they do so they tend to remain oriented in a certain direction. Still this partial alignment does represent a degree of order not present in liquids and thus requires that to call this condition a new phase or state of matter. Scientist was described this new phase as liquid crystal phase or mesophase [6].

Liquid crystals are partially ordered, anisotropic fluids, thermodynamically located between the three dimensionally ordered solid state crystal and the isotropic liquid [7]. The average alignment of the molecules for each phase are shown in Figure 2.2 [5].

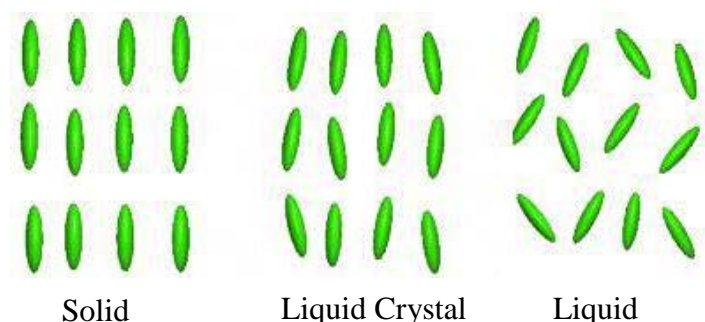


Figure 2.2 : The average alignment of the molecules for each phase

To quantify just how much order is present in a material, an *order parameter* (S) is defined. Traditionally, the order parameter is given as follows:

$$S = \frac{1}{2} (3 \cos^2 \theta - 1) \quad (2.1)$$

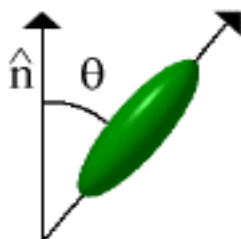


Figure 2.3 : Figural representation of the angle between director and long axis of molecules

θ is the angle between the director and the long axis of each molecule (Fig.2.3). In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9 [5] and highly dependent on the temperature of the sample. Typical order vs. temperature relationship are shown in Figure 2.4 [8].

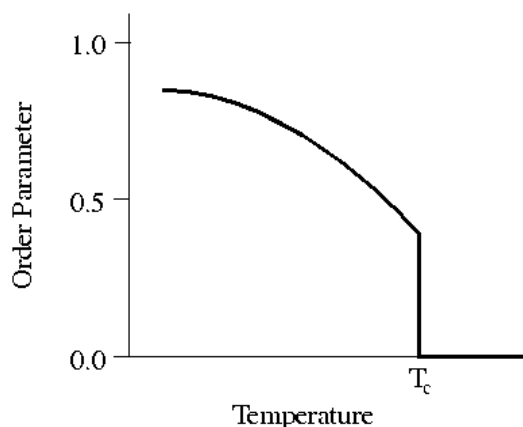


Figure 2.4 : Order vs. temperature for a typical liquid crystal

Liquid crystalline materials are generally divided into two categories the *thermotropic* and the *lyotropic* mesophases. The term “mesophase” originates from the Greek word *meso*, meaning “in between” (the crystal and the liquid phases). Thermotropic liquid crystal phases are observed by a change of temperature, while lyotropic phases form in the presence of a suitable (isotropic) solvent. An additional variable of state in the latter case is the concentration. Thus lyotropic mesophases are always mixtures, whereas many of the reported thermotropic liquid crystals are

single compounds. Some mesogens may exhibit both lyotropic and thermotropic phases; these materials are named *amphotropic* [7].

Lyotropic liquid crystal phases are frequently encountered in everyday life. For example, most surfactants in water form lyotropic liquid crystal phases; detergents and soaps are used with water, liquid crystal phases are generated. Of far greater importance, however, is occurrence lyotropic liquid crystal phases in biological membranes. The cell membranes in the body are a result of the lyotropic liquid crystal phase that is generated from the dissolution of phospholipids in water.

The types of molecular structure that generate lyotropic liquid crystal phases are amphiphilic. They combine a hydrophobic group at one end with a hydrophilic group at the other end, and possess both polar and non-polar region in the same molecule [1]. The two most important types of amphiphilic molecules are soaps and phospholipids [6]. Chemical structures and schematic representation of soaps and phospholipids are shown in Figure 2.5.

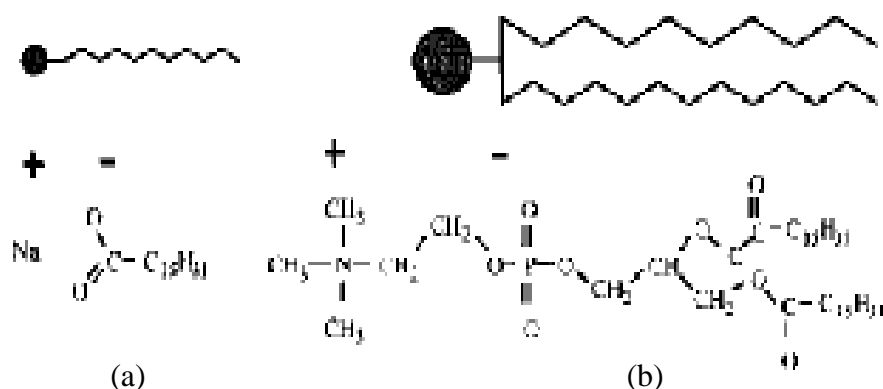


Figure 2.5 : Two lyotropic liquid crystals, (a) a soap, and (b) a phospholipid

While the molecules are arranged in thermotropic liquid crystals, micelles and vesicles are arranged in lyotropic liquid crystals as Figure 2.6 [1].

Lyotropic liquid crystals are used in the food industry as food emulsifiers and in medical applications for some drugs [6]. Also, in recent years, various nanostructures have been created using lyotropic liquid crystal (LLC) templates, such as nanowires, nanofilms, nanorods, nanotubes, nanofibers, mesoporous materials and molecular imprinted materials [9].

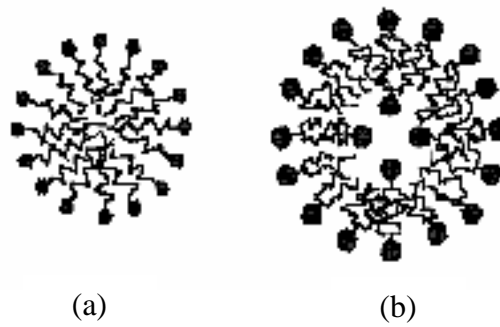


Figure 2.6 : Structures formed by amphiphilic molecules in a polar solvent
(a) micelle, (b) vesicle

Thermotropic liquid crystals form thermally activated mesogenic phases that extend from the crystal melting temperature, T_m , up to the clearing or isotropic temperature, T_i [3]. If thermotropic mesophase is formed by heating and cooling, it is called *enantiotropic* and it is a thermodynamically stable mesophase. If thermotropic phase is formed by cooling an isotropic liquid, it is called *monotropic*.

Thermotropic liquid crystals are generally further distinguished with respect to the molecular shape of the constituent molecules, being called *calamitic* for rodlike, *discotic* for disk-like, and *sanidic* for brick- or lath-like molecules (Figure 2.7) [7].

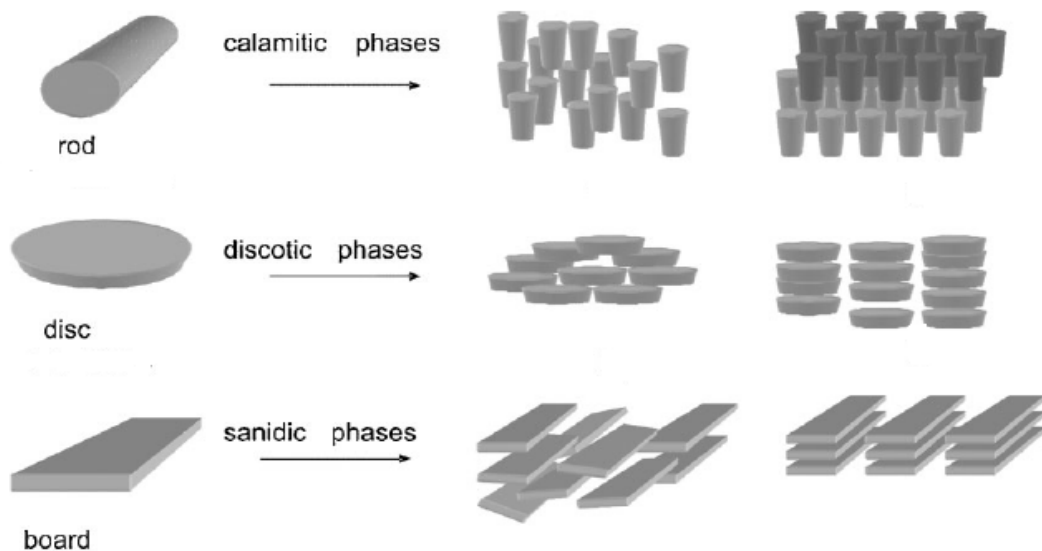


Figure 2.7: Different types of mesogens and the resulting calamitic, discotic and sanidic phases [10].

The last types of molecule that form liquid crystal phases are polymers. Liquid crystal polymers are obtained from its main chain or side chain arrangements (Figure 2.8).

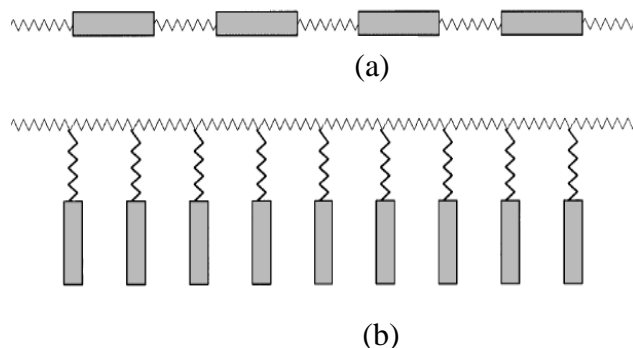


Figure 2.8 : Polymeric liquid crystals: (a) main chain, (b) side chain [11].

2.1.2.1 . Calamitic liquid crystals

The most common type of molecule that forms liquid crystal phases is a rod shaped molecule (one molecular axis is much longer than the other two). Such compounds are called calamitic liquid crystals and many different phases are possible [1]. A common structural feature of calamitic mesogens is a relatively rigid core, often incorporating phenyl and biphenyl groups, and two flexible endgroups, often alkyl or alkoxy chains [7]. A typical calamitic liquid crystal molecule and its molecular shape is shown in Figure 2.9 [12].

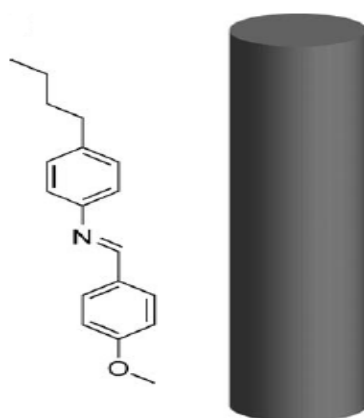


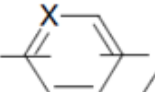

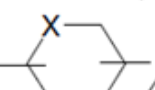
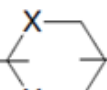
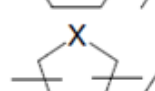
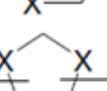


Figure 2.9 : A calamitic mesogen and its effective molecular shapes as rods.

Generally, calamitic mesogens are obtained from the structures such as given at Table 2.1

Table 2.1: General structure of calamitic liquid crystals

R— A —L— A —R'		
A	L	R/R'
	C=N	CN
	N=N	Alkyl
	COO	Alkoxy
	F/Cl/Br/I	Fluorinated alkyl
	COS	Fluorinated alkoxy
	C≡C	
	C≡C	
		

In this structure A is the core units, this core of the structure is usually provided by linearly linked ring systems that are most often aromatic but can be also alicyclic. The rings can be directly linked or they may be joined by a linking group (L) which maintains the linearity. And flexibility is provided by the terminal substituents R and R' which are usually straight alkyl or alkoxy chains. In general, calamitic liquid crystals show two different type of mesophase: Nematics and smectics [1,2].

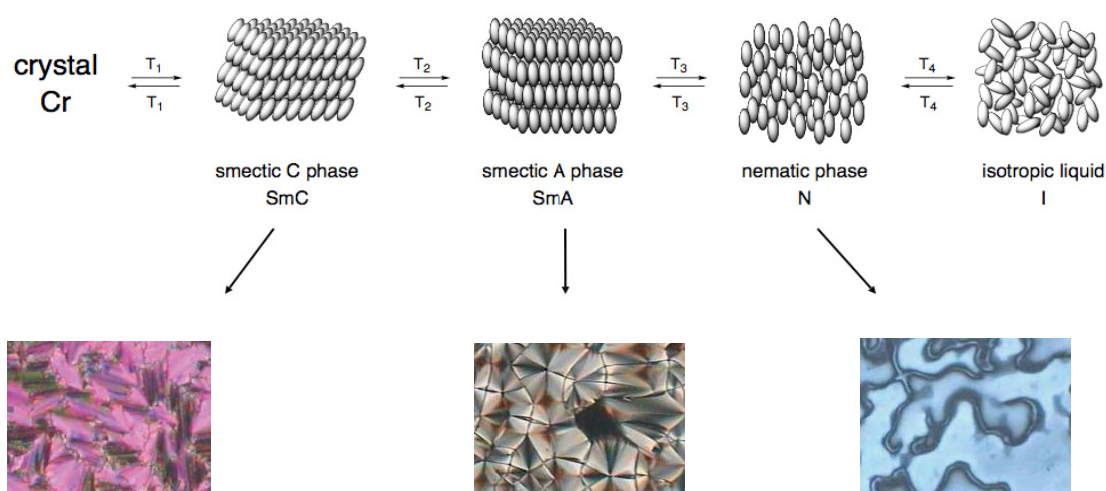


Figure 2.10 : Type of calamitic liquid crystal masophase [7,13].

Nematic Phase

The nematic phase of calamities is the simplest liquid crystal phase. In this phase the molecules maintain a preferred orientational direction as they diffuse throughout the sample. There exists no positional order (Figure 2.11). The nematic phase is the most commonly observed liquid crystalline phase. In this state, the intermolecular forces are very small, so molecules can easily pass by each other [3,14].

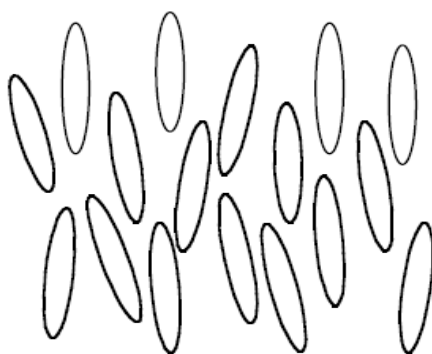


Figure 2.11: Nematic Phase

Smectic Phase

When the crystalline order is lost in two dimensions, one obtains stacks of two dimensional liquid. Such systems are called smectics. There is a number of symmetry variants exist in smectic phase. Smectic phases are characterized by layer structures, with additional order possible in each layer. Within the layers, the centers of molecules are arranged in equidistant planes. The planes are allowed to move perpendicular to the layers, and, within the layers, different arrangements of molecules are possible. The smectic modifications are labeled according to the arrangement of the molecules within the layers. The two most common smectic phases are smectic A and smectic C. The smectic A phase is the least ordered of all the smectic phases, with the molecules with their overall long axis perpendicular to the layer plane. In smectic C phase, the orientation axis of the molecules is tilted with respect to the layer phase. In the smectic B phase, the molecules are arranged with an even higher degree of order (Figure 2.12) they have two dimensional long-range order and positional order within the layer. Similar to smectic A, the molecules are perpendicular to the layer plane [3,1].

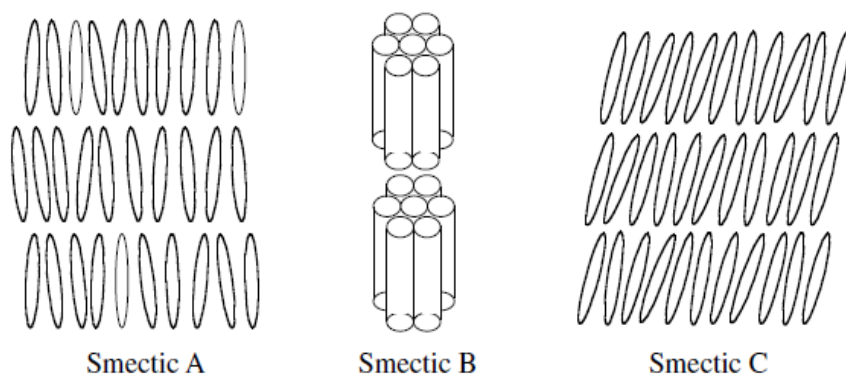


Figure 2.12: Smectic Phase

In the case of tilted smectic phases, there are several packing possibilities depending on the direction of the tilt and the positional ordering [3]. The molecular arrangement of smectic phases are shown in Figure 2.13 [15].

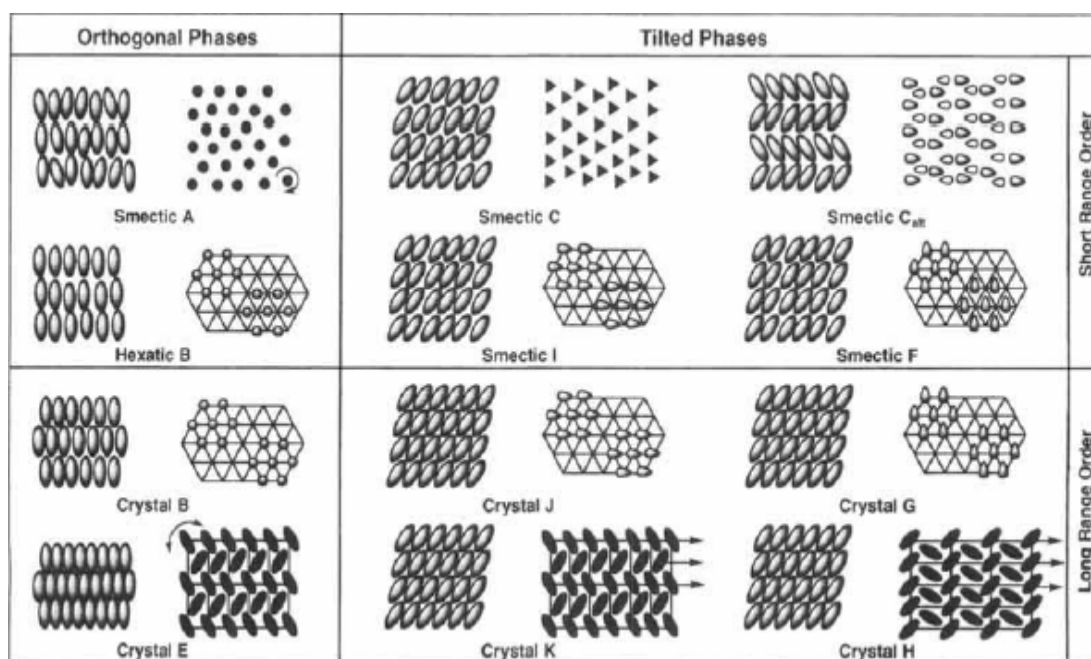


Figure 2.13 : The molecular arrangement presentation of smectic phases.

Chiral Phases

Chiral Nematic Phases: The structure of the chiral nematic phase (Figure 2.14) consists of liquid crystal molecules in a statistically parallel arrangement of the director. However, the asymmetry of the constituent molecules causes a slight and gradual rotation of the director. This gradual director change describes a helix which has a specific, temperature-dependent pitch; thus the chiral nematic phase has twist along one axis. The pitch length is temperature- dependent and hence so is the colour

of the reflected light. This is the basis behind the commercially-successful use of chiral nematic materials in thermochromic thermometer devices and other devices that change colour with temperature, such as, articles of clothing, inks and paints [1].

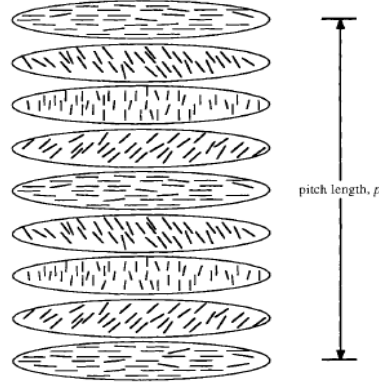


Figure 2.14: The structure of the chiral nematic phase [15].

Chiral Smectic Phases: There are many different types of chiral smectic liquid crystal phases and crystal smectic mesophases which could generate form chirality as a direct result of the molecular chirality of the constituent molecules. The form chirality of all of these chiral smectic mesophases takes the form of a helical structure, but the helix manifests itself in a different way from the helix in the chiral nematic phases. In addition to being substantially the most commonly exhibited of the tilted chiral smectic phases, the chiral smectic C phase is by far the most important (least ordered and least viscous) in this category. The structure of the smectic C phase (Figure 2.15) is lamellar and the molecules within the layers are tilted at a temperature-dependent angle from the layer normal.

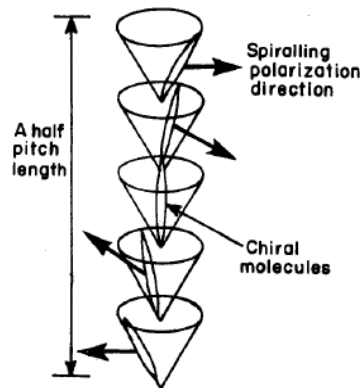


Figure 2.15: The structure of the chiral smectic C phase [14].

The chiral smectic C phase is employed in the ferroelectric display device [1].

2.1.2.2. Discotic liquid crystals

A typical discotic mesogen generally includes a central aromatic core functionalized with three to eight flexible chains (Figure 2.16) [16]. The existence of mesophases generated by disc-shaped molecules was theoretically predicted in 1970 and mesomorphism in discotic materials was first reported in 1977 by Chandrasekhar [1].

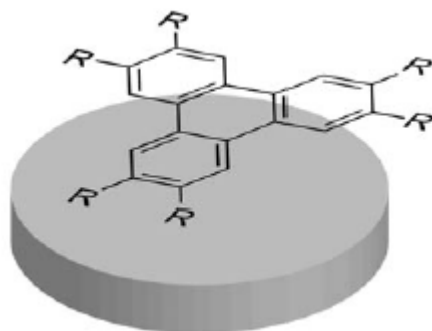


Figure 2.16 : A discotic mesogen and its effective molecular shapes as disks [12].

The two main types of mesophases DLCs form are nematic and columnar.

Nematic Discotic Phase: The most simple discotic phase is the discotic nematic; it is the least ordered and the least viscous, see Figure 2.17, There is no long-range positional correlation [14].

Columnar Discotic Phase: In the columnar phase the discs pile into columns (Figure 2.17) and are generally considered most useful for organic electronics applications. There are six different columnar DLC phases: hexagonal columnar, rectangular columnar, columnar oblique, columnar plastic, helical, and columnar lamellar [16].

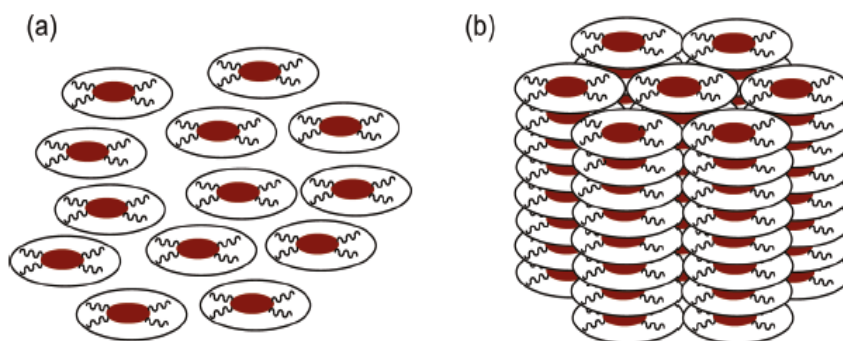


Figure 2.17: Schematic representations of (a) the discotic nematic and (b) the columnar phase.

There is several applications of discotic liquid crystals as a result of their orientation in the columnar mesophase, making them ideal candidates for molecular wires in various optical and electronic devices such as photocopiers, laser printers, photovoltaic cells, light-emitting diodes, field-effect transistors, and holographic data storage [12].

2.2. Liquid Crystal Polymers

2.2.1. General definition and classification of liquid crystal polymers

Polymers are long-chain molecules (or macromolecules) formed by the repetition of certain basic units or segments known as monomers. In liquid crystal polymers the low molar mass mesogens can be used as monomers. There are two aspects to the synthesis of macromolecule mesogens, the conventional synthesis to generate the monomeric unit(s) and then the polymerisation reaction that yields the desired liquid crystal polymer (LCP). It is the combination of polymer-specific properties, together with the properties specific to the liquid crystalline phase that has led to a multitude of new prospectives; this has made possible a wide range of applications of liquid crystal polymers with excellent properties.

On the basis of the location of mesogenic group, that is, depending on whether the mesogenic group is inserted within the main chain, or as side group, the LCPs can be divided mainly into two kinds: main -chain liquid crystal polymers (MCLCPs) and side-chain liquid crystal polymers (SCLCPs). A third kind can also be generated by inserting the mesogenic units both within the main-chain and as side groups; this class is known as combined liquid crystal polymers (CLCPs).

The mesogenic units used in the generation of LCPs can be rod-like, disc-like, amphiphilic, etc. In addition to linear polymer structure, polymers with many other architectures, such as, cyclic, hyperbranched, dendrimeric, crosslinked, etc., have also been synthesized [14].

2.2.1.1. Main chain liquid crystal polymers

The main chain liquid crystal polymers were found in 1956 that a polypeptide formed a mesophase in solution; however, systematic studies on main chain liquid crystal polymers did not begin until the 1970s [1].

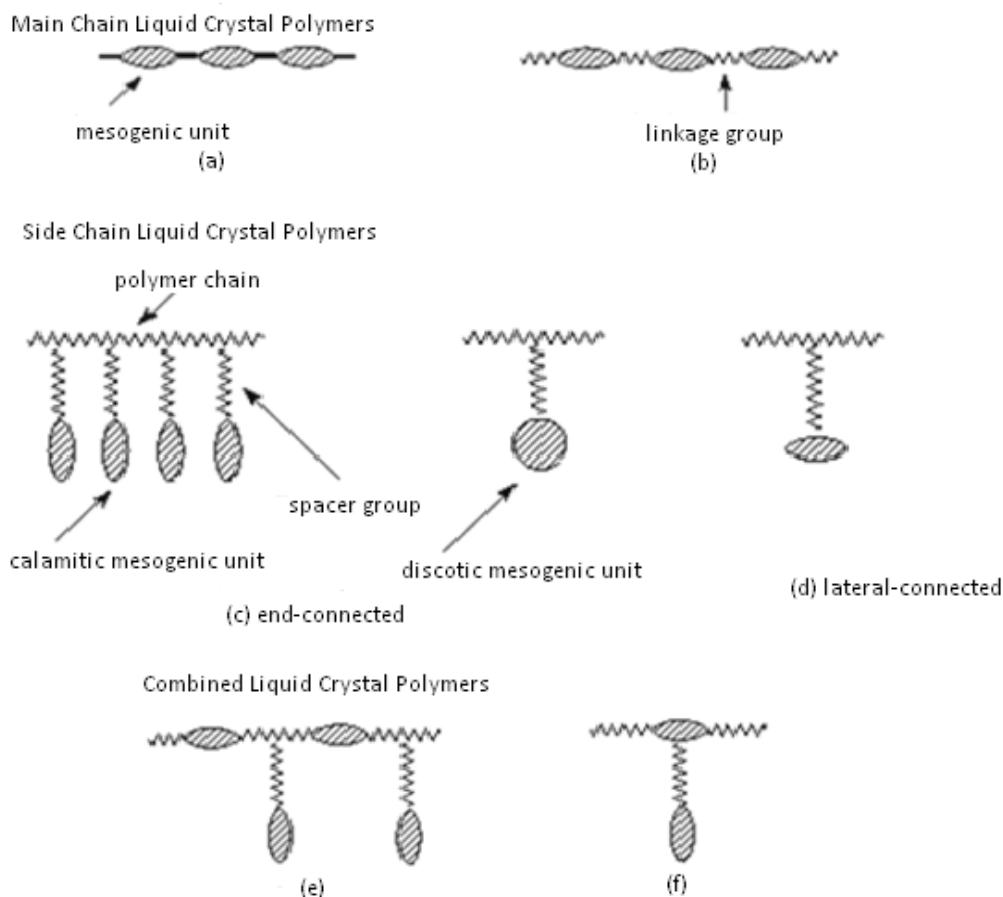


Figure 2.18: Schematic presentation of liquid crystal polymers [17].

Aromatic main chain liquid crystalline polymers consist of a sequence of directly connected aromatic moieties, namely, polyarylenes, or a sequence of aromatic moieties linked by an even number of atoms or heterocyclic units. Typical linkage groups in combination with aromatic moieties are, for example, ester and amid groups [18].

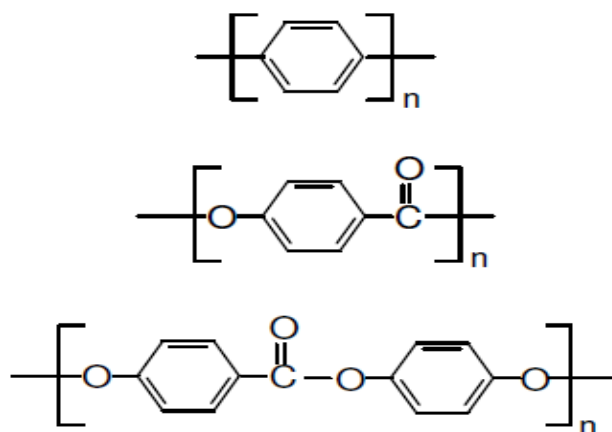


Figure 2.19 : General structure of main chain liquid crystal polymers [17].

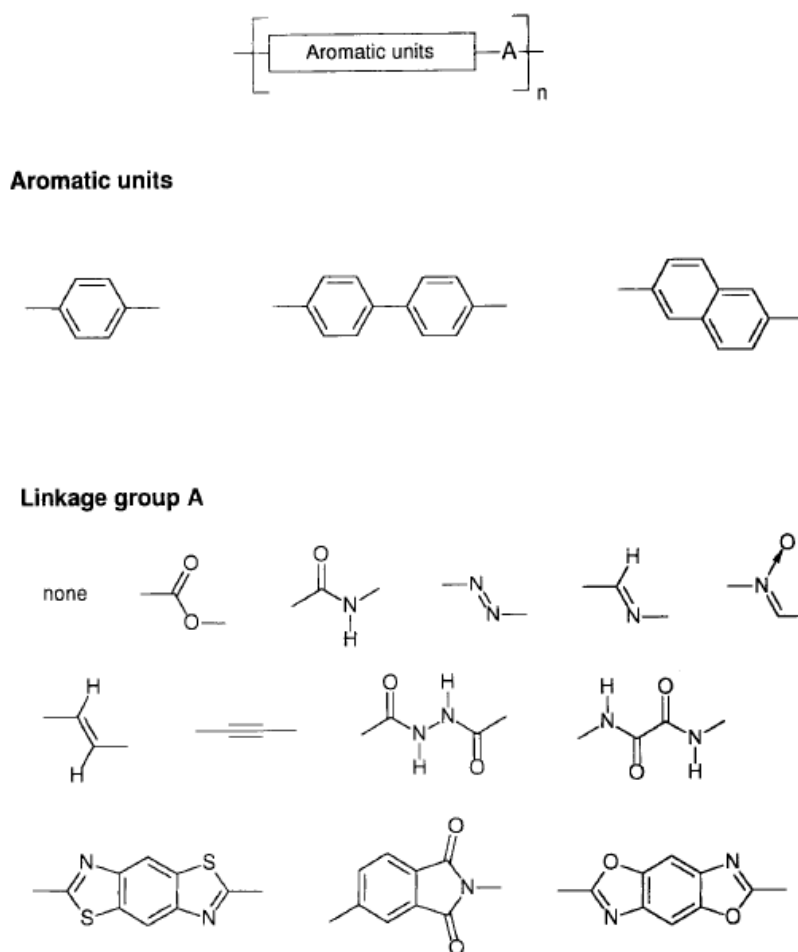


Figure 2.20: Typical aromatic units and linkage groups in main chain liquid crystalline polymers.

Main chain liquid crystal polymers can be divided in two groups; if the mesogenic units are directly linked (Figure 2.18a) then the polymer will be very rigid and intractable, if the mesogenic groups are connected via a flexible spacer (Figure 2.18b), the main chain becomes semiflexible [1,19].

The synthesis of LC main chain polymers normally follows step-growth reactions, such as polycondensation or polyaddition, where the reactants contain two monofunctional groups. The monomers can either be a suitably substituted mesogenic compound or a non-mesogenic substance. These monomers form the mesogenic segment of the polymer main chain by a polymerization reaction [19].

Kevlar (Figure 2.21) is a well-known polymer material is obtained by condensation reaction between terephthalic acid and 1,4-phenylenediamine. It is extremely strong and is used in bullet-proof vests and in construction and exhibits a nematic phase and when dissolved in sulfuric acid.

Many polymers are prepared by transesterification reaction also [1].

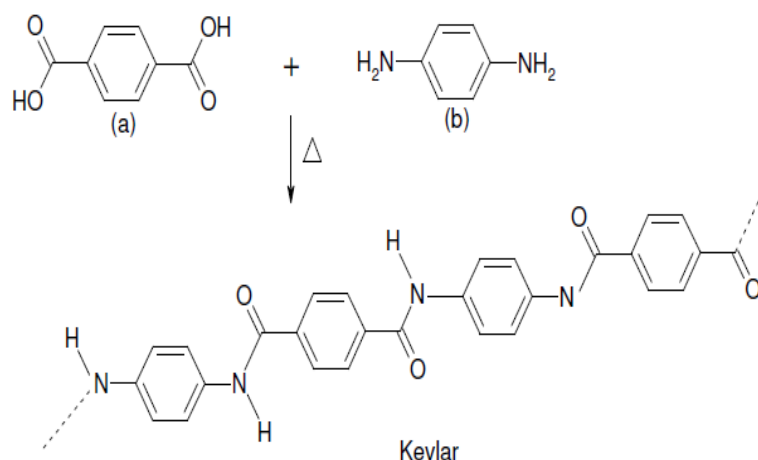


Figure 2.21: Kevlar

The main-chain thermotropic liquid crystalline polymers (MCLCPs) have still been attracting much attention owing to their scientific interests and numerous industrial applications. The aromatic main-chain liquid crystalline polymers usually exhibit insoluble properties and high melting temperatures because of their rigid and symmetrical conformation [20]. They have been intensively studied because of their potential applications as high performance materials. Among them, the wholly aromatic thermotropic polyesters have generally received a considerable interest for technological applications due to their high use temperatures, excellent chemical resistance, relatively high glass transition temperatures, T_g , in addition to excellent processing and mechanical properties [21].

2.2.1.2. Side chain liquid crystal polymers

Side-chain liquid-crystalline polymers (LCPs), which represent a combination of liquid crystalline behavior and polymeric properties, have been the subject of intensive research during the last decade. Systematic investigation of the synthesis of side-chain LCPs began only after Ringsdorf and co-worker proposed that a flexible spacer should be inserted between the polymeric backbones and mesogenic side groups to decouple the motions of the backbone and side groups in the liquid crystalline state (Figure 2.18 c,d). On the basis of the spacer model, a large number of side-chain LCPs containing rod-like or disk-like mesogens were synthesized. Different smectic, chiral smectic, nematic and cholesteric mesophases are exhibited

by these polymers that are based on different mesogenic groups and polymer backbones [22].

In SCLCPs the flexible polymer backbone has a strong tendency to adopt a random, coiled conformation. When mesogenic units are attached to the flexible polymer backbone, they will have a strong tendency to adopt an anisotropic arrangement. If the mesogenic groups are directly attached to the backbone, then the dynamics of the backbone usually dominate the tendency for the mesogenic groups to orient anisotropically; accordingly, mesomorphic behaviour is not usually generated [1].

SCLCPs can be synthesized three different methods; chain polymerization reactions, step-growth polymerization reaction and polymer homologous reactions (Figure 2.22). Monomers containing mesogenic groups are most frequently synthesized as methacrylates, acrylates, acrylamides, chloroacrylates and styrene derivatives. Therefore, the most convenient method to polymerize mesogenic monomers is by radical initiation [23]. In most cases, polymerization is performed in solution and initiated with common initiators such as AIBN or benzoylperoxide.

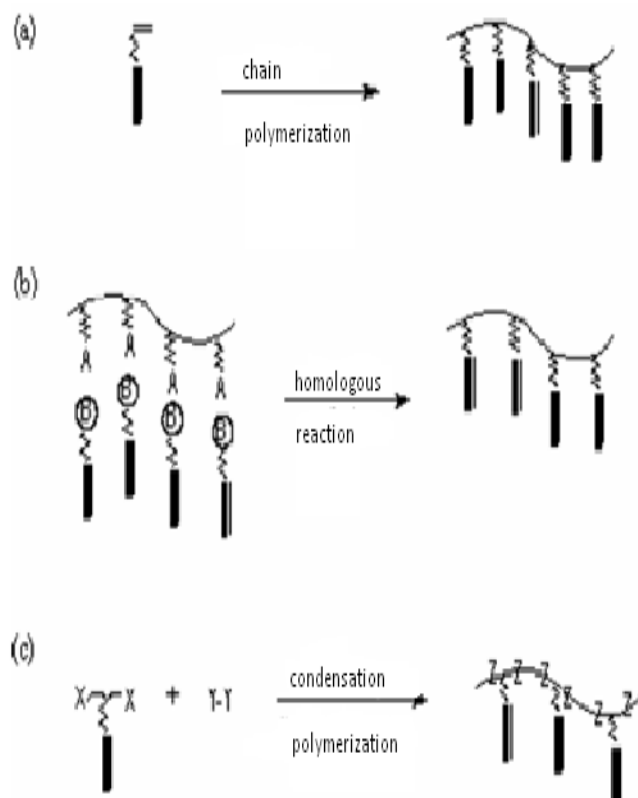


Figure 2.22: General synthesis method of side chain liquid crystal polymers [17].

If there is a functional groups on the mesogens, SCLCPs can be synthesized by condensation reactions [19]. The two organic reactions frequently used to synthesize side chain liquid crystalline polymers by polymer homologous reactions are nucleophilic displacement and hydrosilation [23].

There is some important effect on liquid crystal phase ordering of polymers; effect of mesogenic units, spacer length and polymer backbone.

2.2.2. Factors on mesomorphic behaviour of liquid crystal polymers

2.2.2.1. The effect of the mesogen

The mesogenic unit will have a great influence on the liquid crystal phases generated and the transition temperatures. The additional ordering on polymerization causes liquid crystal phases to be more ordered than for the monomeric analogue and transition temperatures and clearing points are higher. Generally, mesogenic units are formed by biphenyl units or connecting with two or more aromatic rings to each other by means of functional groups. The polymers become more crystalline as the mesogen length increases. Different terminal chains in SCLCPs have not been investigated; terminal cyano-substituted SCLCPs are very common and so are alkoxy-substituted analogues. A longer terminal chain results in an enhancement of the smectic tendency. Polar terminal units (CN, NO₂) tend to generate smectic phases, whereas non-polar terminal units (CH₃O, CH₃) favour the nematic phase. The increased polarisability and increased molecular length in going from two to four phenyl rings enhances the clearing points of polymers [1].

2.2.2.2. The effect of the spacer length

The actual flexible spacer is usually just a series of methylene (-CH₂-) units with the only variation being in the unit that joins the spacer to the backbone at one end and to the mesogenic unit at the other end. However, different spacers, such as oxyethylene and siloxane, are commonly employed. The glass transition temperature decreases with increasing spacer length. Where polymers without spacer units exhibit liquid crystalline phases, they are of the smectic type and formation of the liquid crystal phase is occurred high temperatures. However; a short spacer usually generates a nematic phase which gives way to smectic phases as the spacer length increases [1].

2.2.2.3. The effect of the polymer backbone

The backbone should not influence the mesomorphic properties of SCLCPs. However, decoupling is never perfect and the structural nature of the backbone has a considerable influence on mesomorphic properties of SCLCPs. The most important aspect of a polymer backbone when liquid crystallinity is being discussed is the flexibility. As flexibility of the polymer backbone increases, the glass transition temperature is reduced, leading to the generation of a wider liquid crystal phase range. However, the clearing points often fall with increased flexibility, but not too significantly and not in all cases. The most common backbones are employed in the synthesis of SCLCPs are the flexible acrylates and methacrylates. Siloxane backbones are also very common in SCLCPs and are even more flexible than acrylates [1].

Table 2.2: The effect of the polymer backbone structure on mesophase stability [17].

Polymer Chain		T_g/K	T_{N-I}	T_{SmA-I}	ΔT
$\left[\text{O}-\underset{\text{R}}{\overset{\text{CH}_3}{\text{Si}}} \right]_n$	$R = R_1$	287	-	443	156
	$R = R_2$	288	334	-	46
$\left[\text{CH}_2-\underset{\text{COOR}}{\text{CH}} \right]_n$	$R = R_1$	308	-	397	89
	$R = R_2$	320	350	-	30
$\left[\text{CH}_2-\underset{\text{COOR}}{\overset{\text{CH}_3}{\text{C}}} \right]_n$	$R = R_1$	333	-	393	60
	$R = R_2$	369	394	-	25
$R_1 = \text{---}(\text{CH}_2)_5\text{O---}\text{C}_6\text{H}_4\text{---}\text{C}_6\text{H}_4\text{---}\text{CN}$ $R_2 = \text{---}(\text{CH}_2)_2\text{O---}\text{C}_6\text{H}_4\text{---}\text{C}(=\text{O})\text{O---}\text{C}_6\text{H}_4\text{---}\text{OMe}$					

The application fields of SCLCPs are; optical data storage, non-linear optics, stationary phases for gas chromatography, supercritical-fluid chromatography and high-performance liquid chromatography, solid polymer electrolytes, separation membranes and display materials [22].

Another interesting type of liquid crystalline polymer is combined main-chain/side-chain liquid-crystalline polymer (MCSCSCLCP), which is consisted of a main-chain

liquid crystalline backbone and side-chain mesogenic groups, and can form versatile liquid crystalline phase. The main chain of MCSCLCPs (Figure 2.18 e,f) can be either of rigid nature without containing any flexible spacers or of nonrigid character containing some flexible spacers. The pendant side-chain mesogenic groups can join to the rigid mesogen or flexible spacers of the main chain via flexible spacers [24].

2.2.3. Synthesis of liquid crystal polymers via non-covalent interactions

A wide variety of self-organized molecular systems, such as liquid crystal, have attracted much attention because it has great potential as highly functional materials. Recently, new types of liquid-crystalline materials have been obtained by self-assembly through specific molecular interactions. The molecular association of two or more molecular species by intermolecular interactions results in the formation of mesomorphic molecular complexes. Such material design for liquid crystals based on noncovalent interaction is related to supramolecular chemistry, an area of great current interest [25].

Many polymeric liquid-crystalline structures have been produced using covalent bond chemistry. More recently, however, molecular recognition processes between different molecular species using noncovalent bonded interactions have been reported for their versatility in constructing dynamically functional LC molecules. These self-assembly strategies including hydrogen bonds , ionic interactions , and charge-transfer complexes have been used to construct liquid-crystalline polymers as “supramolecular” materials. Hydrogen bonding is particularly attractive since there are many natural models for it. The formation and dissociation of the hydrogen bonds play an important role in many biological processes. The use of hydrogen bonds has been demonstrated in building low-molecular weight liquid crystals as well as liquid-crystalline polymers of side-chain supramolecular assemblies , main-chain complexes, networks [26], and combined structures. Self-assembly of polymers and small molecules as shown in Figure 2.23 [27].

Hydrogen-bonded systems are prepared using two suitably designed components that are commonly called H-bond donors and H-bond acceptors. Hydrogen bonding is the strongest of the non-covalent interaction forces between two molecules. The association between the ‘donor’ and ‘acceptor’ effectively induces hydrogen bonds that lead to a more stable structural organisation [28].

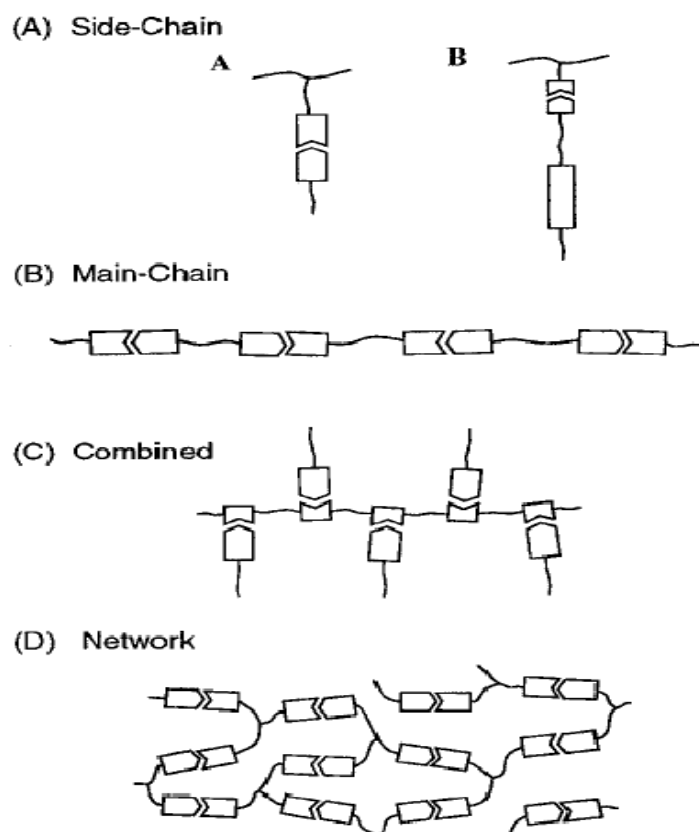


Figure 2.23 : Schematic illustration of supramolecular polymers:(A) side-chain-type, (B) main-chain-type, (C) combined type, and (D) network type.

SCLCPs are generally prepared by covalently linking rigid mesogens to polymer backbones through flexible spacers. The function of the spacer is to decouple the motions of the polymer backbone from the self-ordering tendencies of the mesogens [29]. The mesogens in supramolecular side-chain liquid crystalline polymers (SCLCP) are attached onto the polymer backbone directly or via a flexible spacer. In these systems, liquid crystallinity is induced through hydrogen bonding interactions between complementary binding sites on the polymer main-chain and low molar mass rigid mesogens. A number of supramolecular SCLCPs have been prepared, among which H-bonds between pyridyl and carboxylic acid functional groups are the most frequently used. Various synthetic strategies are used for the preparation of supramolecular hydrogen-bonded SCLP polymers. A mesogenic low molar mass compound can be attached to a pendant binding site on the polymer main chain or the side chain with the mesogenic unit can be bound to the polymer backbone through an H-bond connector. In both cases, a flexible spacer decouples the motion of the polymer main chain from the motion of the anisotropically oriented mesogenic side

chain [30]. Self-assembled SCLCPs have the advantage of being able to fine tune the liquid crystalline properties. Various molecular parameters, such as the nature of the rigid cores, the nature and the length of the terminal groups, and the spacer length, can be modified with relative ease compared with covalently bonded systems [29].

The combination of bifunctional hydrogen bonding components is expected to lead to the formation of supramolecular main-chain polymers. Liquid crystalline behavior can be induced by the association of bifunctional components through the formation of triple and single hydrogen bonds [27]. Main-chain hydrogen-bonded liquid crystalline polymers are mostly based on bipyridyl and dicarboxylic acid fragments [28].

2.2.4. Characterization of liquid crystal materials

Several analytical techniques are in use at present for the characterization and identification of phase structures. In some liquid crystal phases the classification is relatively simple and these phases can be identified by employing just one technique. Whenever minimal differences exist in the phase structures the precise classification often requires the use of several different techniques.

The structure is characterized by the arrangement and the conformation of the molecules and intermolecular interactions. The structural investigation is done mainly by X-rays supported by other methods like neutron scattering, nuclear magnetic resonance, infrared and Raman spectroscopy. The textures are pictures which are observed microscopically usually in polarised light and commonly in thin layers between glass plates. They are characterized by defects of the phase structure which are generated by the combined action of the phase structure and the surrounding glass plates. Depending upon the special experimental conditions for a given structure several different textures exist. This method allows a detailed classification of the mesophases. The textures are also known to exist in several phase types and with blurred pictures. Such textures do not allow the detailed classification of the phases. The miscibility properties have been used extensively by Halle liquid crystal group to classify the mesophases. In the course of their work they developed, as their main tool, the "miscibility rule" which states that the liquid crystals are of the same type if they are miscible in all proportions. As the miscibility studies can only give the probability [14].

Polarizing microscopy is one of the essential tools for the characterization of newly synthesized mesogenic materials, together with differential scanning calorimetry (DSC) and x-ray investigations. While DSC is easily and quickly carried out, it merely provides information on phase transition temperatures and the order of the transitions. X-ray investigations for actual structural evaluation, i. e. determination of the phase type, have to be performed on macroscopically well oriented samples, which is often time consuming and sometimes hard to realize. Therefore x-ray studies are often carried out on unoriented samples, while the results only allow limited characterization of the structural features. Polarizing microscopy on the other hand can provide a determination of both phase transition temperatures and phase type [7].

3. EXPERIMENTAL PART

3.1 . Materials and Chemicals

1-Vinylimidazole (Fluka) and 4-Vinylpyridine (Acros) were distilled under vacuum before using. Poly(vinylpyrrolidone)(Acros), 4'-Hydroxybiphenyl-4-carbonitrile (Merck,Aldrich), 6-Chloro-1-hexanol (Aldrich), 8-chloro-1-octanol (Aldrich), 11-bromo-1-undekanol (Acros), 2,2'-Azobis(2-methylpropionitrile) (Acros) were used as received. Benzene (J.T.Baker), Diethylether (Merck), Dioxane (Fluka), N,N-Dimethylformamide (Merck), Dimethylsulfid (Merck), Potassium carbonate anhydrous (Fluka), NaOH (Merck), Toluene (Riedel-de Haen), Acetone, Ethanol.

3.2 . Instruments

Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR analyses were recorded on a Bruker 250 MHz spectrometer in CDCl₃

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were recorded on Thermo Scientific Nicolet 380 Spectrometer

Polarized Optical Microscopy (POM)

LC behavior of the polymers was investigated by POM using Leica DM2500P equipped with a LTSE350 Liquid Crystal Prosystem TMS 94 Hot Stage (200x)

Differential Scanning Calorimeter (DSC)

Thermal transitions in the polymers was determined by a Thermal Analysis (TA) Instrument Q1000 at a heating rate of 5⁰C/min and 10⁰C/min from room temperature to 150⁰C under nitrogen atmosphere.

3.3 . Synthesis of Chemical Compounds

3.3.1. Synthesis of hydrogen bond acceptor polymers

3.3.1.1 . Synthesis of poly(N-vinylimidazole)

PVI was synthesized by free radical polymerization of N-vinylimidazole in the presence of AIBN as initiator. Distilled monomer (15 g, 160 mmol) was dissolved in 100 ml of DMF and polymerized at 70⁰C under a nitrogen atmosphere for 8 h with 1.3 g (5 mmol) of AIBN. The polymer was precipitated into acetone, filtered and dried under vacuum at room temperature (white powder). The inherent viscosity of the polymer was measured in 0.1 M NaCl as the solvent at 25⁰C [31].

3.3.1.2 . Synthesis of poly(vinylpyrrolidone)

Commercially obtained Poly(vinylpyrrolidone) was used.

3.3.1.3 . Synthesis of poly(4-vinylpyridine)

PVP was synthesized by free radical polymerization of 4-vinylpyridine in the presence of AIBN as initiator. Distilled monomer (8.92g, 38 mmol) was dissolved in 6 ml of Dioxane and polymerized at 80⁰C for 8 h with 0.1g (3 mmol) initiator. The polymer was precipitated into diethyl ether, filtered and dried under vacuum at room temperature (orange powder). The inherent viscosity of the polymer was measured in ethanol as solvent at 25⁰C [32].

3.3.2. Synthesis of hydrogen bond donor groups

3.3.2.1 . Synthesis of 6-(4-cyanobiphenyl-4'-oxy)hexan-1-ol

Under nitrogen atmosphere 6-Chloro-1-hexanol (20 mmol, 2.25 ml) was added drop wise to a stirring mixture of 4'-Hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3g) and anhydrous K₂CO₃ (15.5 mmol, 2g) in 200ml of anhydrous DMSO. The reaction mixture was heated at 110⁰C for 3 h. After this process, the reaction mixture was added drop wise to 400 ml of %10 NaOH solution at room temperature and filtered. The resultant was dried at 40⁰C in vacuum. It was recrystallized from benzene and dried under vacuum (Yield; %48, white crystals).

3.3.2.2 . Synthesis of 8-(4-cyanobiphenyl-4'-oxy)octan-1-ol

Under nitrogen atmosphere 8-Chloro-1-octanol (20 mmol, 3.4 ml) was added drop wise to a stirring mixture of 4'-Hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3g) and anhydrous K_2CO_3 (15.5 mmol, 2g) in 200 ml of anhydrous DMSO. The reaction mixture was heated at 110⁰C for 3 h. After this process, the reaction mixture was added drop wise to 400 ml of %10 NaOH solution at room temperature and filtered. The resultant was dried at 40⁰C in vacuum. It was recrystallized from ethanol and dried under vacuum (Yield; %52, white crystals).

3.3.2.3 . Synthesis of 11-(4-cyanobiphenyl-4'-oxy)undecan-1-ol

Under nitrogen atmosphere 11-bromo-1-undecanol (20 mmol, 2.25 ml) was added drop wise to a stirring mixture of 4'-hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3g) and anhydrous K_2CO_3 (15.5 mmol, 2g) in 200 ml of anhydrous DMSO. The reaction mixture was heated at 110⁰C for 3 h. After this process, the reaction mixture was added drop wise to 400 ml of %10 NaOH solution at room temperature and filtered. The resultant was dried at 40⁰C in vacuum. It was recrystallized from ethanol and dried under vacuum (Yield;%52, white crystals).

3.4. Preparation of Hydrogen-Bonded Side Chain Liquid Crystalline Polymers

3.4.1. General procedure

In a typical procedure to prepare H-bonded side chain liquid crystalline polymers, the slow evaporation technique is used. Solution of equimolar amount of H-bond donor (LC6, LC8 or LC11) in DMF was added to solution of H-bond acceptor polymer (PVI, PVPy or PVP) in DMF. This mixture was stirred about 12 h at room temperature. After evaporation of DMF, precipitated polymer was dried under vacuum.

4. RESULTS and DISCUSSION

Side chain liquid crystalline polymers were prepared by using intermolecular hydrogen bonding concept. This study involves the preparation of three different polymers as hydrogen bond acceptor and three different 4'-(hydroxyalkoxy)-4-cyanobiphenyl derivatives as hydrogen bond donor. First, poly(vinyl imidazole)(PVI), poly(4-vinyl pyrrolidone) (PVPy) and poly(4-vinyl pyridine) (PVP) hydrogen bond acceptors were prepared by free radical polymerization of related monomers.. The hydrogen bond donors were synthesized by the reaction of hydroxy halides having different number of methylene unit with hydroxy cyano biphenyl mesogens. The hydrogen bond donors were then attached to the proton acceptor polymers through H-bond interactions between the hydroxyl group of hydrogen bond donors and imidazole, pyrrolidone and pyridine groups of the hydrogen bond acceptors to yield the desired side chain liquid crystalline polymers. The details will be given below.

4.1 . Synthesis of Hydrogen Bond Donors

6-(4-Cyanobiphenyl-4'-oxy) hexane-1-ol (LC6), 8-(4-Cyanobiphenyl-4'-oxy) octan-1-ol (LC8) and 11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol (LC11) were synthesized according to the synthetic route illustrated in figure 4.1.

The structure of the LC6, LC8 and LC11 were characterized by FT-IR and ^1H -NMR spectroscopy. Figure 4.2 shows the FT-IR spectrum of LC6, LC8 and LC11. Characteristic absorbance bands for all the compounds were identified such as the O-H stretching at $3500\text{--}3224\text{ cm}^{-1}$, C-O-C stretching at $1248\text{--}1050\text{ cm}^{-1}$ CN stretching at $2231\text{--}2200\text{ cm}^{-1}$ and H-C-H stretching at 2900 cm^{-1} .

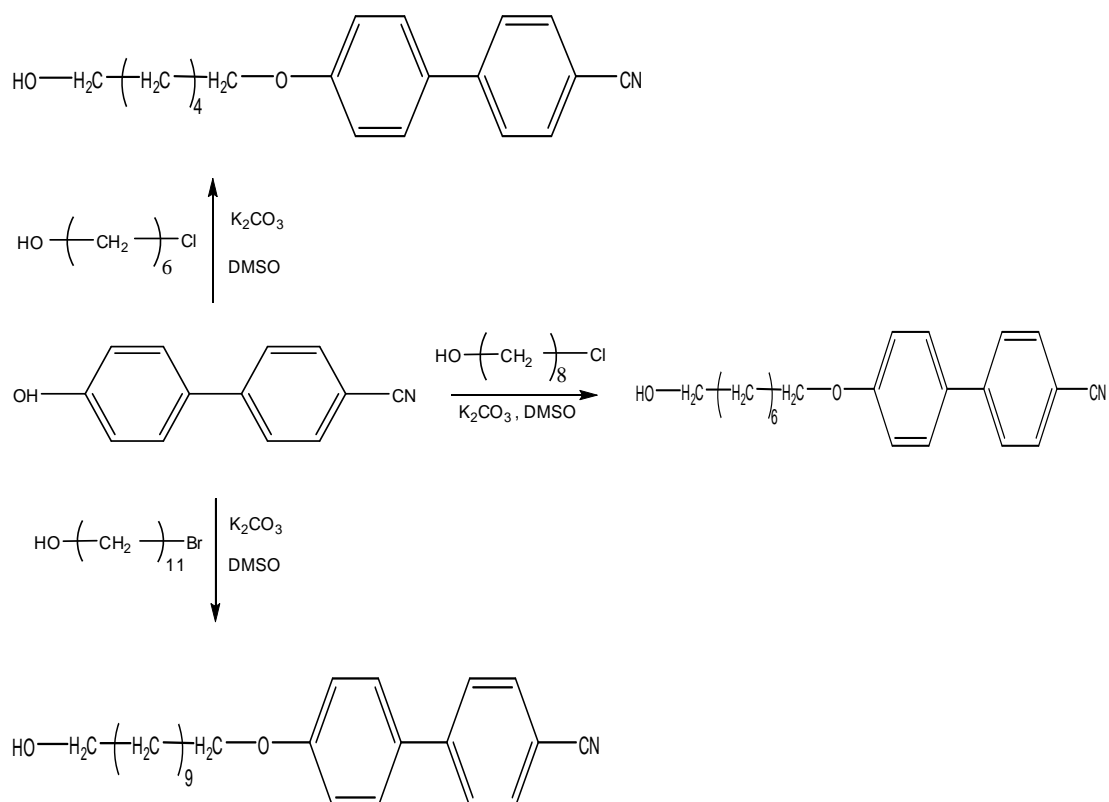


Figure 4.1: Synthesis and chemical structures of hydrogen bond donors

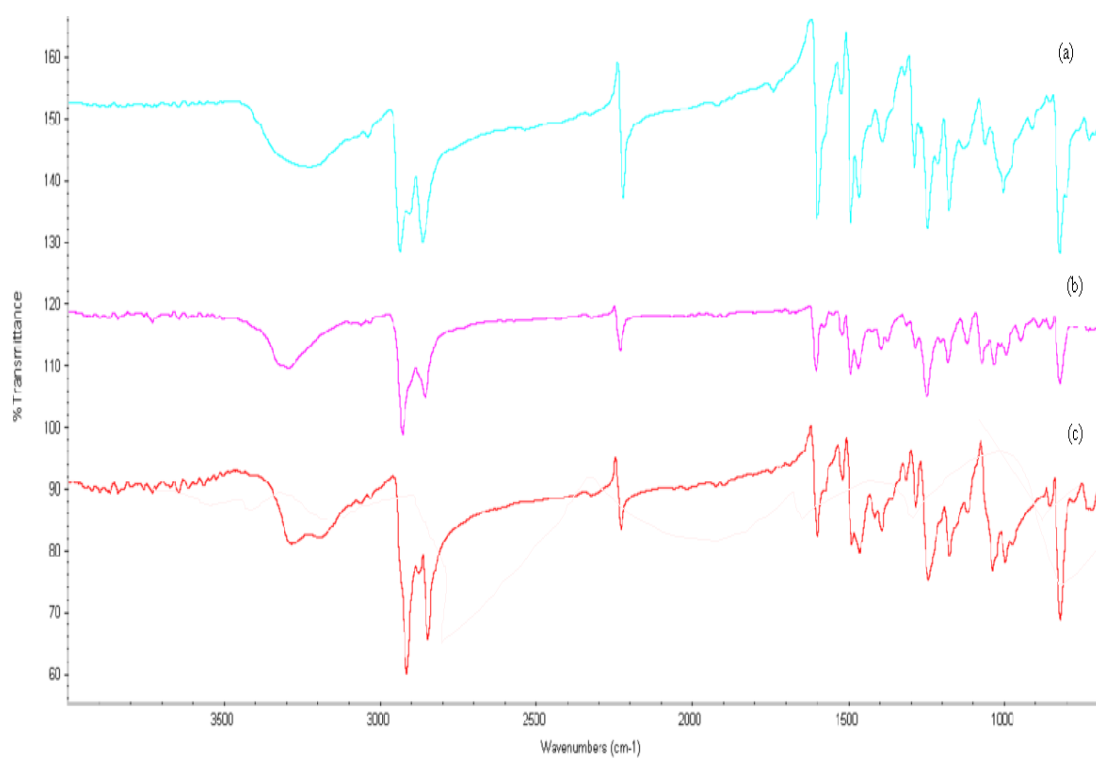


Figure 4.2 : FT-IR spectra of LC6 (a), LC8(b) and LC11(c)

^1H -NMR spectra of the LC6, LC8 and LC11 exhibit the signals in the range of 1.24-1.82 ppm corresponding to CH_2 protons, 3.5- 4.03 ppm corresponding to $\text{CH}_2\text{-O}$ protons and 6.9- 7.7 ppm corresponding to aromatic protons. The ^1H -NMR spectrum of the LC6 is given in the Figure 4.3.

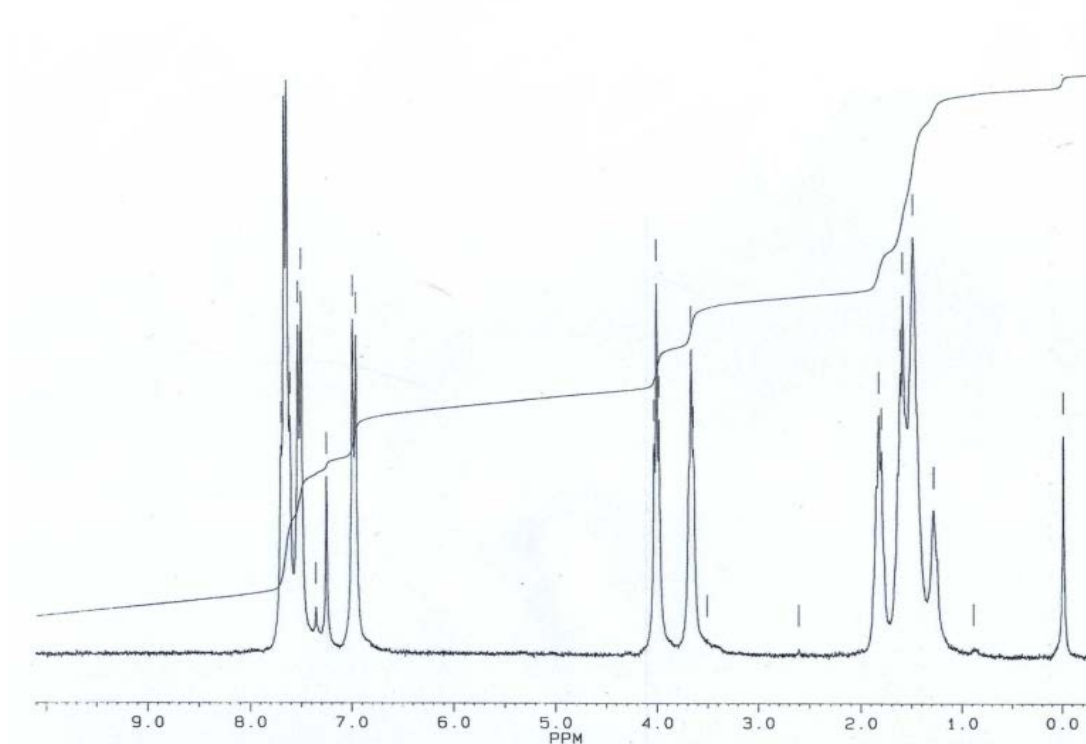


Figure 4.3 : ^1H -NMR spectra of the LC6

4.2. Synthesis of Hydrogen Bond Acceptors

PVI and PVP were prepared by free radical polymerization of related polymers as illustrated in Figure 4.4.

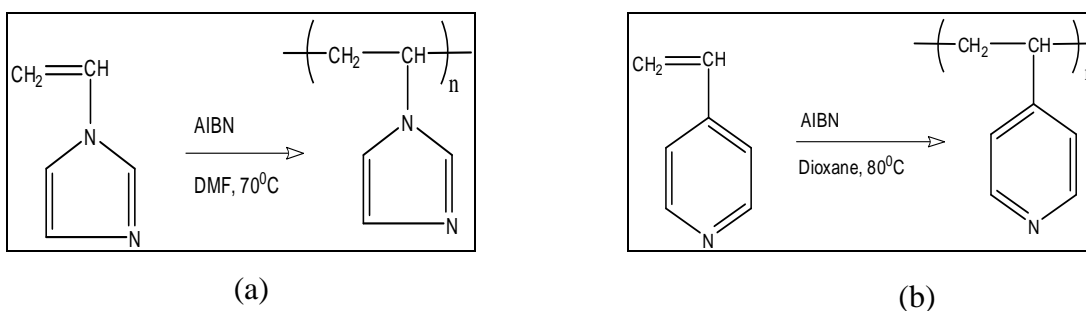


Figure 4.4 : Schematic presentation of PVI(a) and PVP(b) synthesis.

Polymerization conditions and the results are summarized in Table 4.1.

Table 4.1 : Conditions and the results of the polymerization reactions.

Code	Monomer (M)	Initiator (M)	Solvent	Temperature	%Conv	η_{inh}^a
PVI	1,6	AIBN (0,05)	DMF	70 ⁰ C	90	23,95
PVP	6,3	AIBN (0,05)	Dioxane	80 ⁰ C	88	21,54

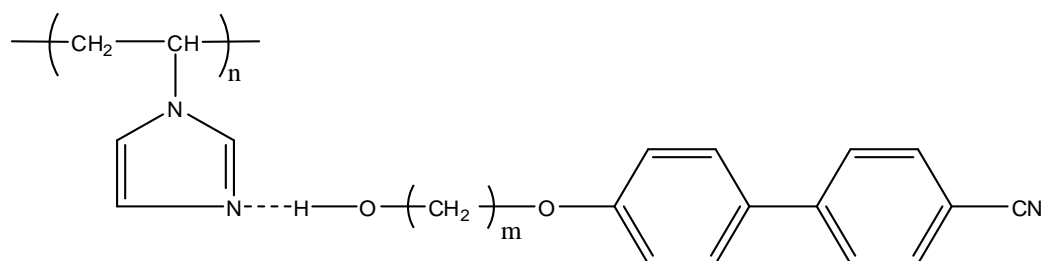
a: η_{inh} is the inherent viscosity value of polymers.

4.3. Preparation of Hydrogen-Bonded Side-Chain Liquid Crystalline Polymers

4.3.1. Poly(vinyl imidazole)-based liquid crystalline polymers (HPVI-LC)

PVI and LC6, LC8 or LC11 were employed as a hydrogen bond acceptor and a hydrogen bond donors, respectively to yield hydrogen bonded liquid crystalline polymers.

The structure of the side chain liquid crystalline polymers formed by intermolecular H-bonding between nitrogen of PVI and hydroxyl group of the hydrogen donors is shown below:



PVI-LC6 (m=6)
PVI-LC8 (m=8)
PVI-LC11 (m=11)

Figure 4.5 : Chemical structures of HPVI-LC

IR spectroscopy is used to investigate the hydrogen bonds in polymers. Figure 4.6(c) shows the FT-IR spectrum of the HPVI-LC6. The broad spectral shape in the O–H stretching region at 3234 cm⁻¹ should be an evidence for hydrogen-bond through the hydroxyl group on the LC6. Similar results were found for the other H-bonded polymers.

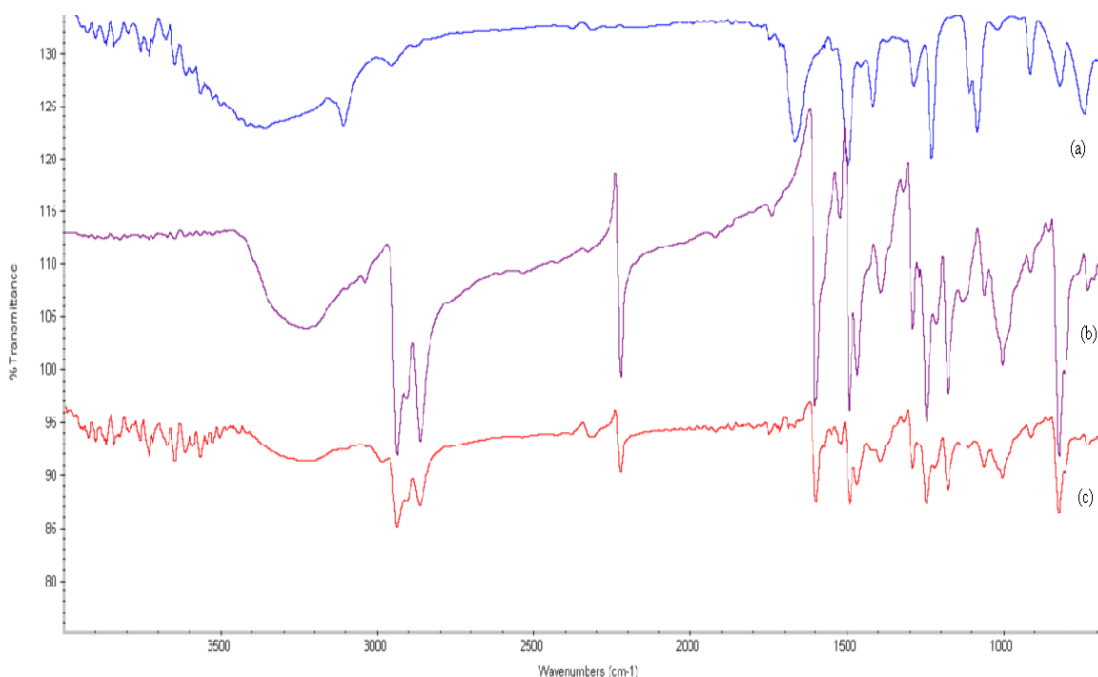
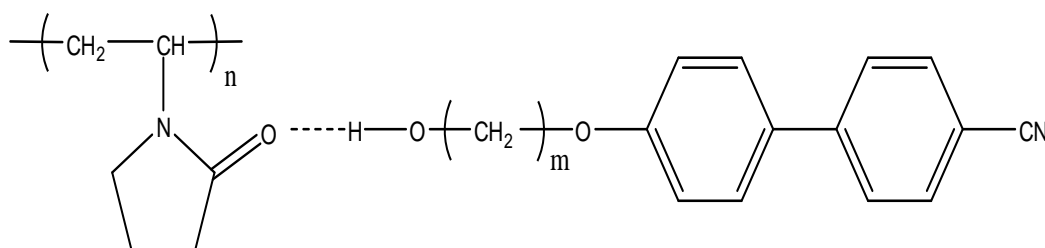


Figure 4. 6 : FT-IR spectra of PVI (a), LC6 (b) and HPVI-LC6 (c)

4.3.2. Poly(vinyl pyrrolidone) - based liquid crystalline polymers (HPVPy-LC)

Commercially obtained PVPy and LC6, LC8 or LC11 were employed as a hydrogen bond acceptor and a hydrogen bond donors, respectively to yield hydrogen bonded liquid crystalline polymers.

The structure of the side chain liquid crystalline polymers formed by intermolecular H-bonding between carboxyl group of PVPy and hydroxyl group of the hydrogen donors is shown below:



PVPy-LC6 (m=6)

PVPy-LC8 (m=8)

PVPy-LC11 (m=11)

Figure 4.7 : Chemical structures of HPVPy-LC

The formation of the hydrogen bond in polymers was investigated by FT-IR spectroscopy. Figure 4.8 (c) shows the FT-IR spectrum of the HPVPy-LC6. The broad spectral shape in the O–H stretching region at 3221 cm^{-1} should be an evidence

for hydrogen-bonds through the hydroxyl group on the LC6. Similar results were found for the other H-bonded polymers.

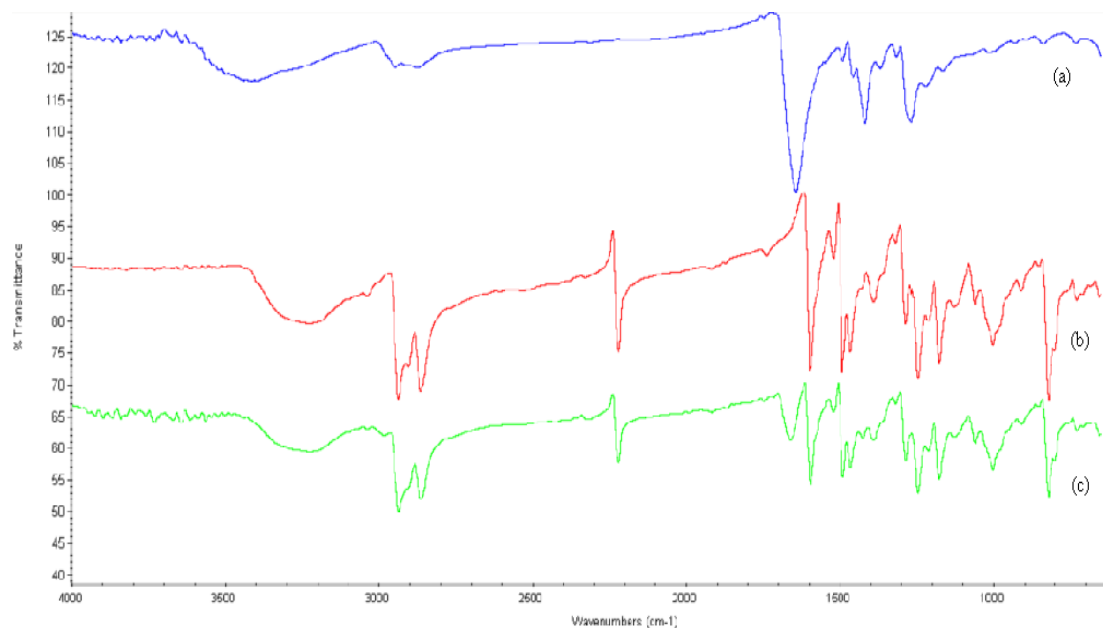


Figure 4.8 : FT-IR spectra of PVPy (a), LC6 (b) and HPVPy-LC6 (c)

4.3.3. Poly(vinyl pyridine) - based liquid crystalline polymers (HPVP-LC)

PVP and LC6, LC8 or LC11 were employed as a hydrogen bond acceptor and a hydrogen bond donors, respectively to yield hydrogen bonded liquid crystalline polymers.

The structure of the side chain liquid crystalline polymers formed by intermolecular H-bonding between nitrogen of PVP and hydroxyl group of the hydrogen donors is shown below:

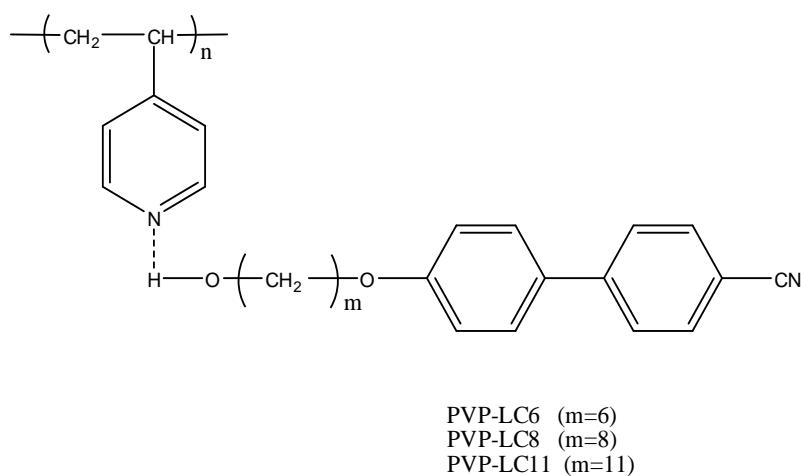


Figure 4.9 : Chemical structures of HPVP-LC

The formation of intermolecular hydrogen bond was shown in figure 4.10 (c). FT-IR spectrum of the HPVP-LC6 shows the broad spectral shape in the O–H stretching region at 3234 cm^{-1} should be an evidence for hydrogen-bonds through the hydroxyl group on the LC6. Similar results were found for the other H-bonded polymers.

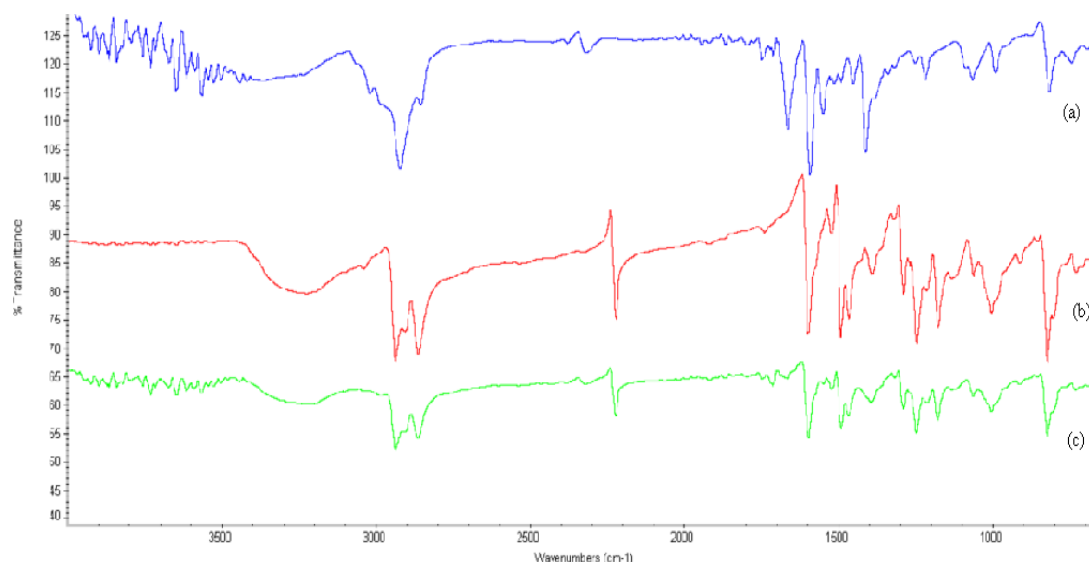


Figure 4. 10 : FT-IR spectra of PVP (a), LC6 (b) and HPVP-LC6 (c)

4.4. Investigation of Thermal and Mesomorphic Properties

4.4.1. Thermal and mesomorphic properties of H-bond donors

To confirm the liquid crystalline nature and to identify the phases of 4'-(n-hydroxyalkoxy)-4-cyanobiphenyl derivatives LC6, LC8, LC11, differential scanning calorimetry (DSC) and polarising optical microscopy (POM) were employed. The DSC transition temperatures, associated enthalpy change (ΔH) and mesomorphic properties were summarized in Table 4.2.

Table 4. 2 : Thermal properties of LC6, LC8 and LC11

Phase Transitions °C(Corresponding Enthalpy Change Jg^{-1}) ^a		
LC6	Cr 97.7 (50.78)	N 111.4 (3.199) I
LC8	Cr 76.2 (21.32)	Cr 90.7 N 112.6 (0.9984) I
LC11	Cr 92.2 (115.3)	I

^a Determined by DSC

^b Cr= crystalline, N= nematic, I= clearing temperature

Polarized optical microscopy studies show that LC6 and LC8 exhibit monotropic nematic schlieren textures on cooling from isotropic phase and enantiotropic

schlieren nematic textures, respectively. LC11 do not exhibit liquid crystalline phase. DSC curves and mesophases of LC6, LC8 and LC11 are shown in Figure 4.11, 4.12 and 4.13, respectively.

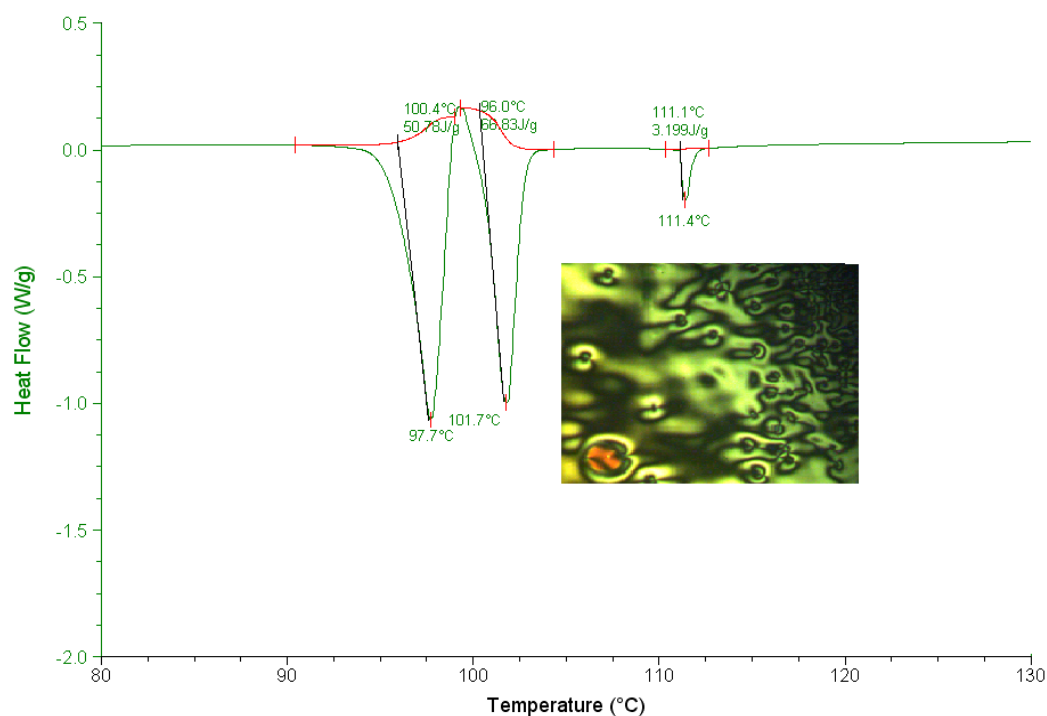


Figure 4.11 : DSC curve (second heating) and mesophase of LC6

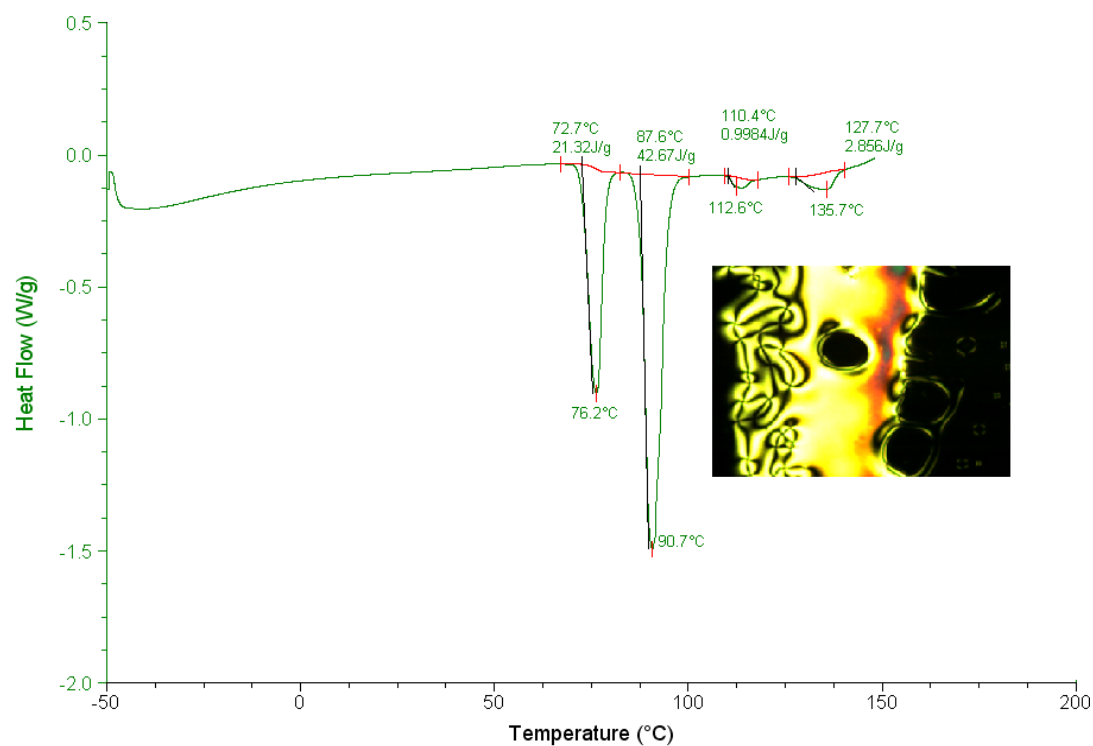


Figure 4.12 : DSC curve (second heating) and mesophase of LC8

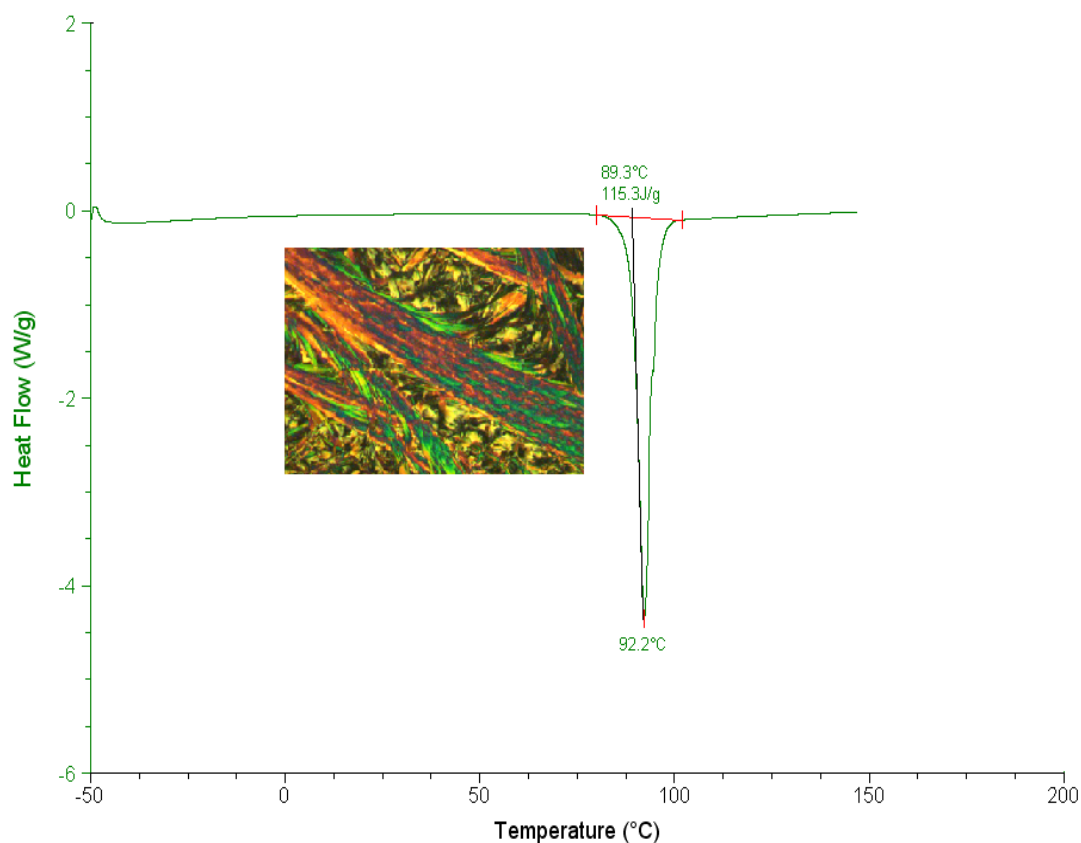


Figure 4.13 : DSC curve (second heating) and crystal structure of LC11

As can be seen from the Figure 4.12 LC8 exhibits polymorphic crystalline forms. Polymorphic crystalline forms result from a subtle balance of intermolecular interactions. For most alkoxy cyanobiphenyls it was observed that slow or delayed cooling gave rise to a lower melting crystalline polymorphic form, which then slowly converted into the higher melting stable crystalline structure [33]. For LC8 polymorphism has been reported up to now only during slow evaporation of solvents from acetone–water or diethyl ether–methanol solutions [34]. In this case four different crystalline phases were found [35]: square plate, parallelepiped and needle crystal forms which are metastable, and the most stable crystalline phase that can be found in commercial powder specimens.

4.4.2. Thermal and mesomorphic properties of H-bonded side chain liquid crystalline polymers

The phase behaviour of all the hydrogen bonded liquid crystalline polymers was studied using a combination of POM and DSC. DSC thermograms were obtained in second heating cycles. The samples were heated with a scan rate of 5°C/min and 10°C/min in an N₂ atmosphere. POM studies also confirmed these DSC results along

with the results of phase transitions. The polymers exhibited enantiotropic mesomorphic behaviour.

4.4.2.1 . Poly(vinyl imidazole) - based liquid crystalline polymers (HPVI-LC)

Figure 4.14, 4.15 and 4.16 shows the DSC curves for the HPVI-LC6, HPVI-LC8, HPVI-LC11 respectively. The DSC curves of the polymers exhibit endothermic transitions centered at between 90 - 110 C° due to the nematic-isotropic transition of the polymers. Glass transitions of the polymers can not detected. The DSC results are summarised in Table 4.3.

Table 4.3 : Thermal properties of poly(vinyl imidazole) - based liquid crystalline polymers

Code	Phase Transitions °C(Corresponding Enthalpy Change Jg ⁻¹) ^a			
HPVI-LC6	G nd	N 108.2	(1.681)	I
HPVI-LC8	G nd	N 102.33	(2.781)	I
HPVI-LC11	G nd	N 91.38	(103.83)	I

^a The transition temperatures determined by DSC.

^b Cr= crystalline, N= nematic, I= clearing temperature

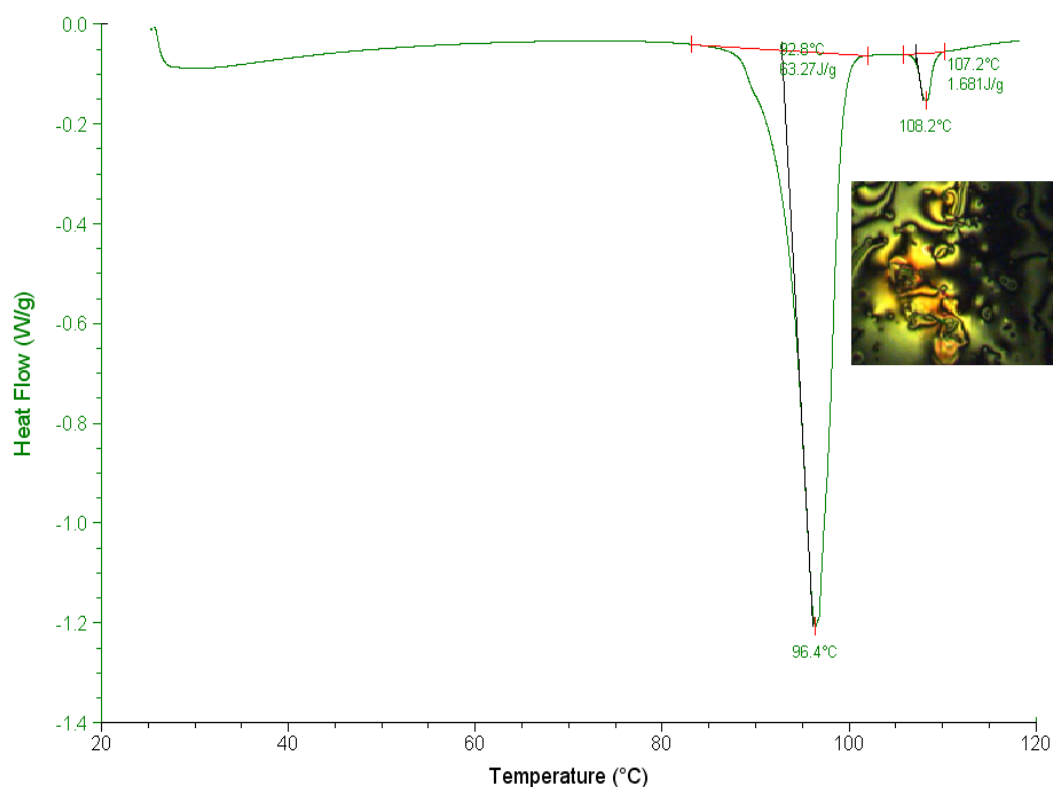


Figure 4 .14 : DSC curve (second heating) and mesophase of HPVI-LC6

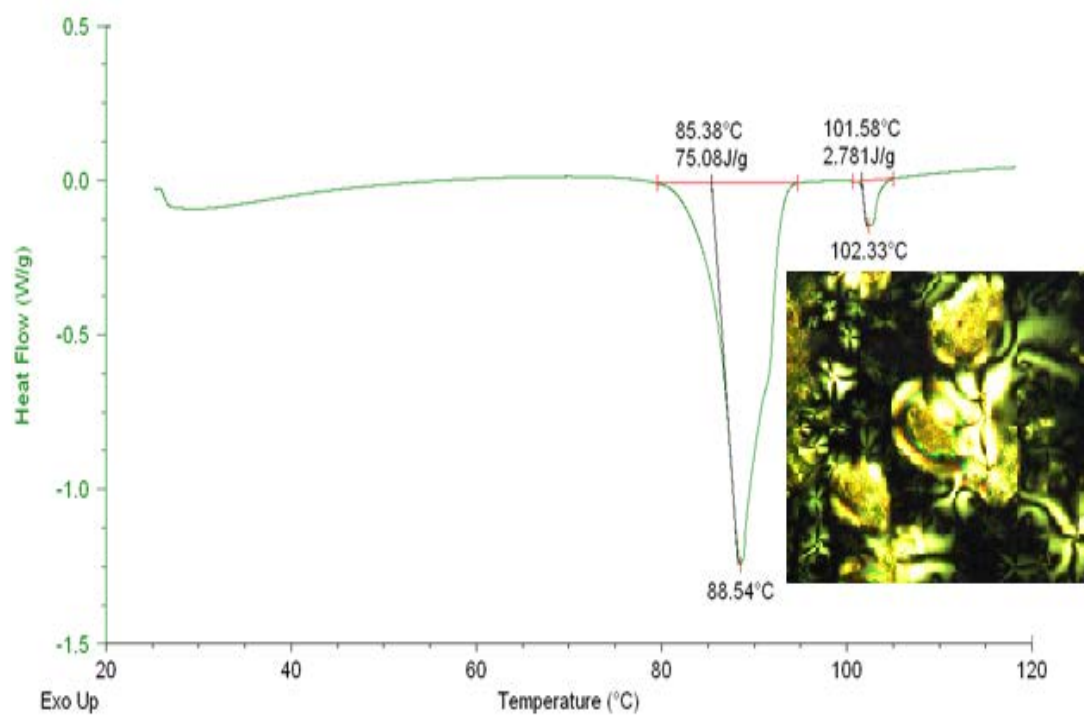


Figure 4 .15 : DSC curve (second heating) and mesophase of HPVI-LC8

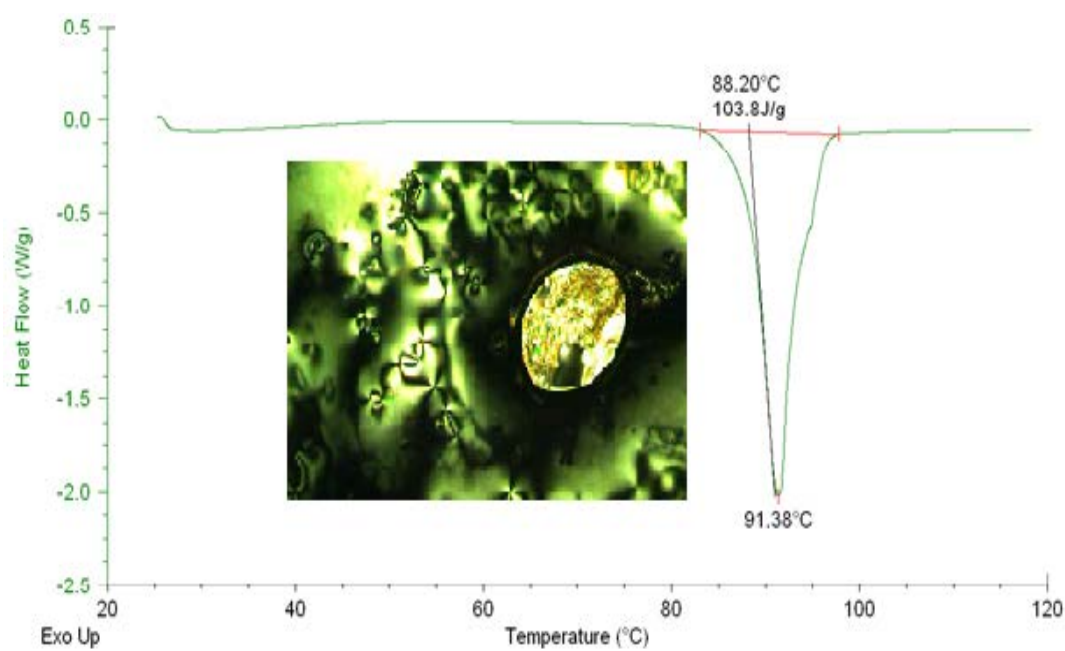


Figure 4 .16 : DSC curve (second heating) and mesophase of HPVI-LC11

It was observed with a polarizing microscope that all the HPVI-LC polymers show an enantiotropic nematic phases. An isotropic-nematic phase separation was observed in the polymers.

4.4.2.2 . Poly(vinyl pyrrolidone) - based liquid crystalline polymers (HPVPy-LC)

Differential scanning calorimetry (DSC) of the HPVPy-LC6 (Fig 4.17) and HPVPy-LC8(Fig 4.18) show endothermic peak corresponding clearing temperature at 94.48 °C and 84.54°C, respectively. DSC curve of the HPVPy-LC11 (Fig.4.19) exhibits endothermic peaks due to the polymorphic crystalline forms of LC11 mesogenic units. The DSC results are summarised in Table 4.4.

Table 4.4 : Thermal properties of poly(4-vinyl pyrrolidone) - based liquid crystalline polymers

Code	Phase Transitions °C(Corresponding Enthalpy Change Jg ⁻¹) ^a				
HPVPy-LC6	G	nd	N	94.48 (46.05)	I
HPVPy-LC8	G	nd	N	84.54 (37.26)	I
HPVPy-LC11	G	nd	N	97.20 (3.071)	I

^a The transition temperatures determined by DSC.

^b Cr= crystalline, N= nematic, I= clearing temperature

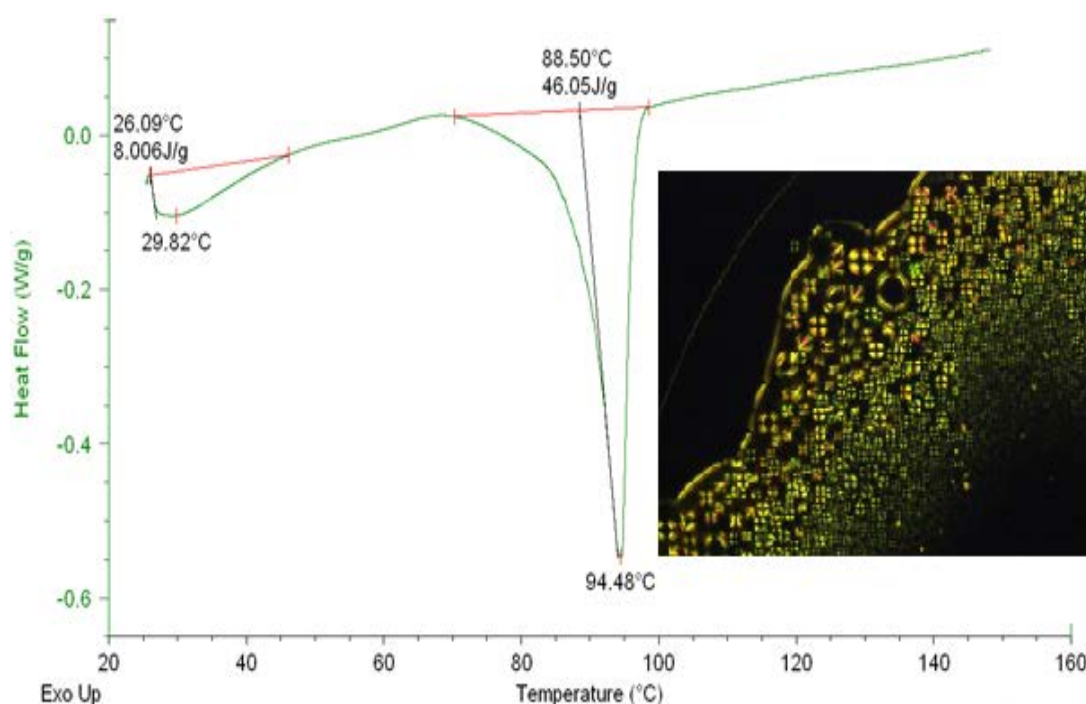


Figure 4 .17 : DSC curve (second heating) and mesophase of HPVPy-LC6

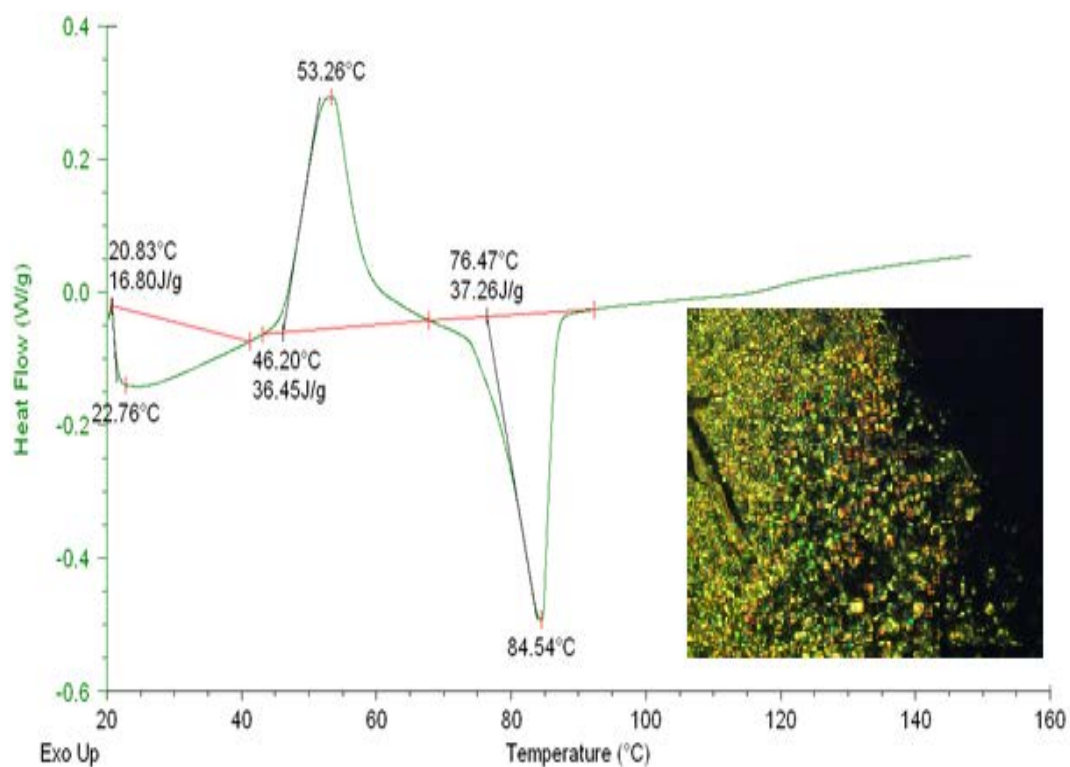


Figure 4 .18 : DSC curve (second heating) and POM images of HPVPy-LC8

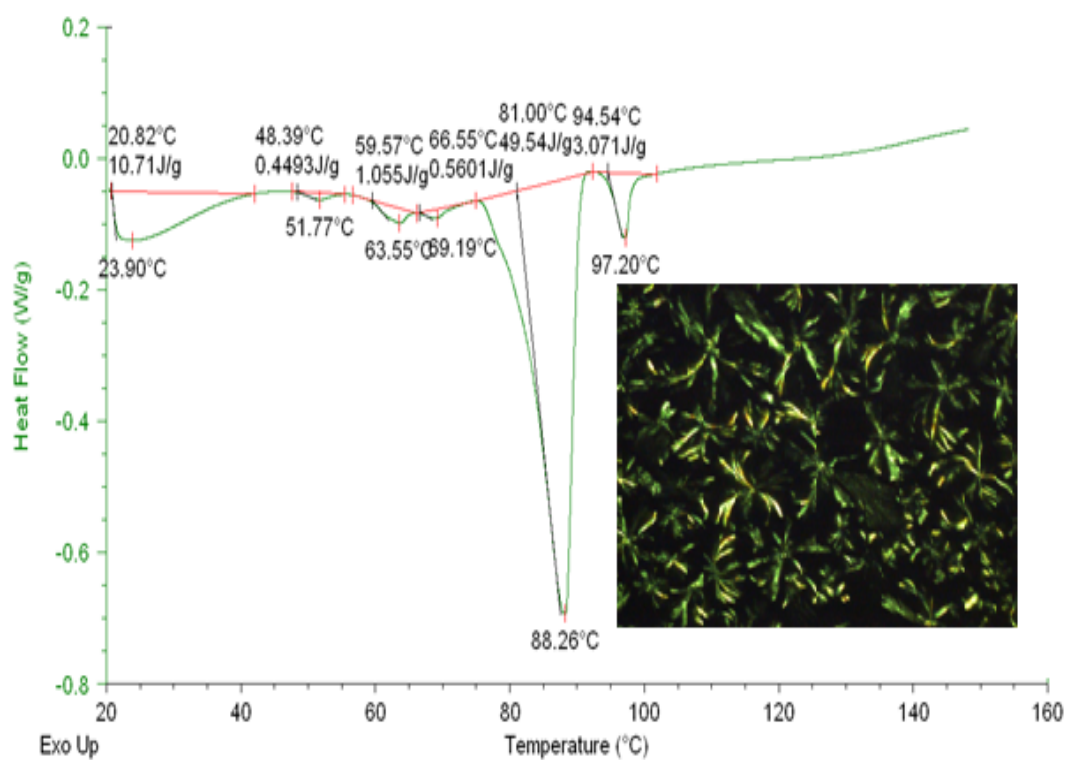


Figure 4 .19 : DSC curve (second heating) and POM images of HPVPy-LC11

The polymers was examined by polarizing optical microscopy. Upon cooling from the isotropic liquid, nematic droplets were observed for HPVPy-LC6. An isotropic-nematic phase separation was observed in the HPVPy-LC6. Liquid crystalline phase transition was not observed for HPVPy-LC8 and HPVPy-LC11.

4.4.2.3 . Poly(4-vinyl pyridine) - based liquid crystalline polymers (HPVP-LC)

The DSC heating traces of HPVP-LC6, HPVP-LC8 and HPVP-LC11 are reported in 4.20, 4.21 and 4.22 respectively. As can be seen from the Fig. 4.20, DSC curve of HPVP-LC6 exhibit an endothermic transition at 66.1 °C due to the nematic-isotropic transition. The glass transition appears as a step at -6.1 °C.

DSC curve of the HPVP-LC8 (Fig. 4.21) exhibits a glass transition at 23,2 °C and an endothermic peak at 86.7 °C corresponding to nematic-isotropic transition.

Figure 4.22 show the DSC curve of HPVP-LC11. The second heating scan of HPVP-LC11 shows an endothermic peak at 88.9 °C corresponding nematic-isotropic transition. Glass transition can not be detected.

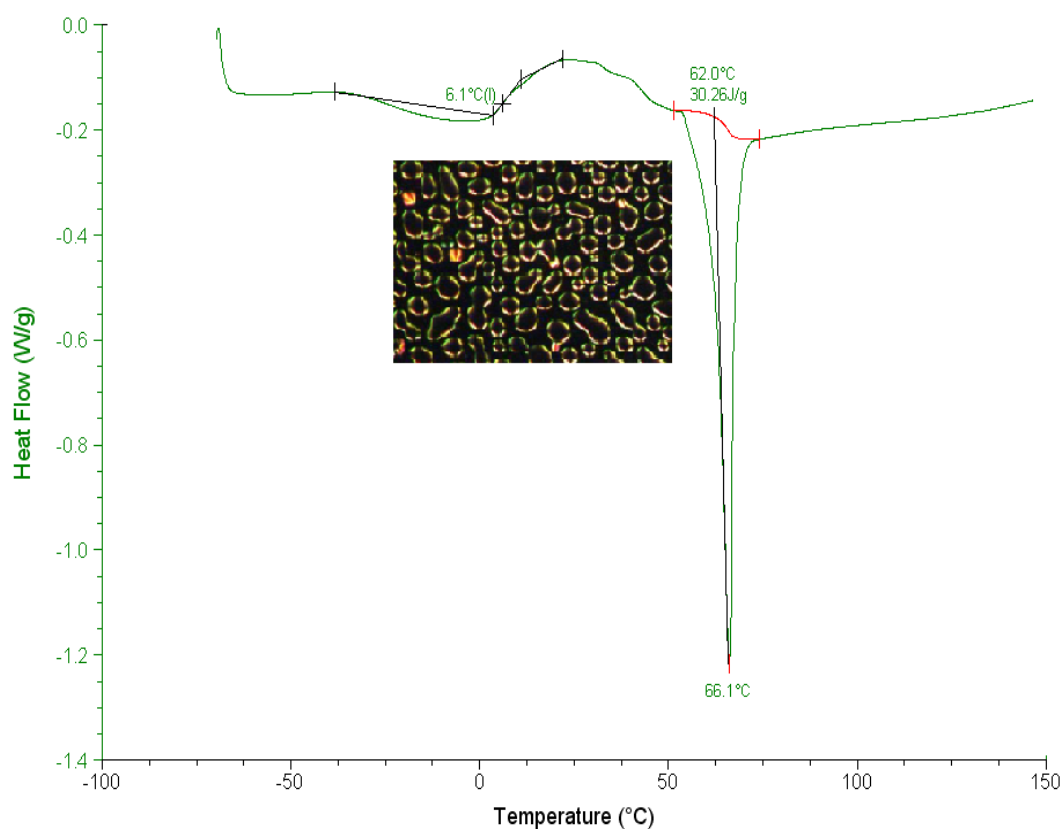


Figure 4 .20 : DSC curve (second heating) and mesophase of HPVP-LC6

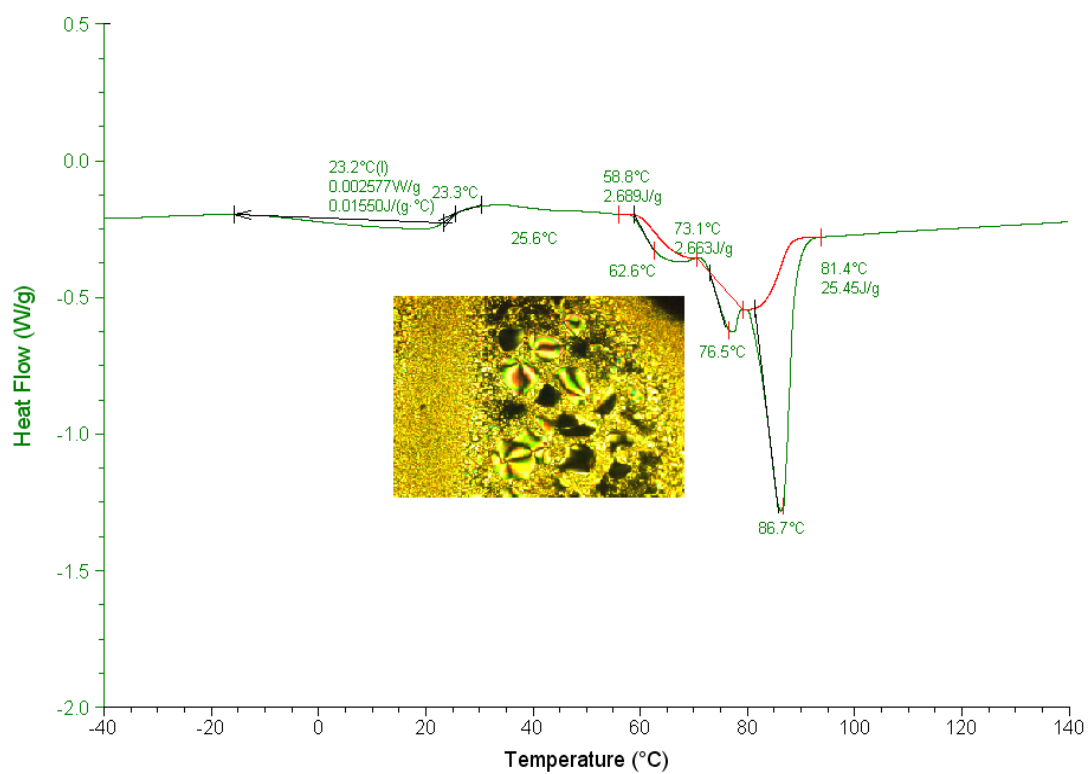


Figure 4 .21 : DSC curve (second heating) and mesophase of HPVP-LC8

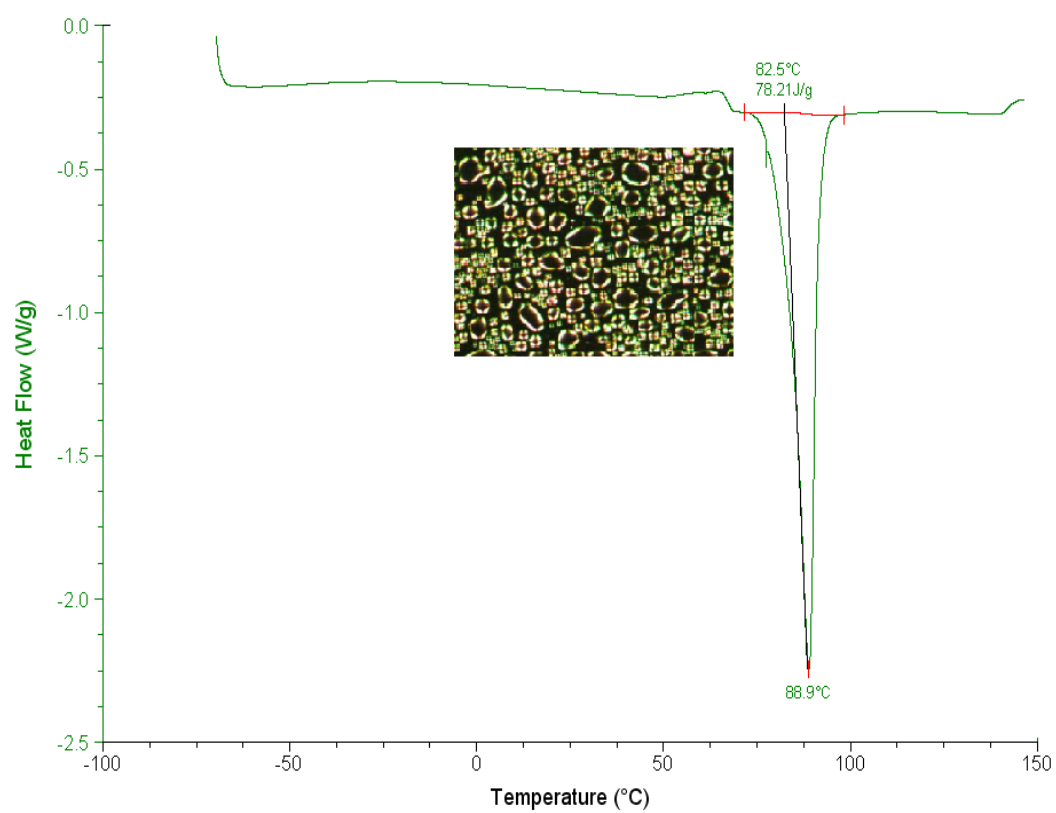


Figure 4 .22 : DSC curve (second heating) and mesophase of HPVP-LC11

Table 4. 5 : Thermal properties of poly(4-vinyl pyridine)-based liquid crystalline polymers

Code	Phase Transitions °C(Corresponding Enthalpy Change Jg ⁻¹) ^a				
HPVP-LC6	G	-6.1	N	66.1 (30.26)	I
HPVP-LC8	G	23.2	N	86.7 (25.45)	I
HPVP-LC11	G	nd	N	88.9 (78.21)	I

^a The transition temperatures determined by DSC.

^b Cr= crystalline, N= nematic, I= clearing temperature

Comparing the glass transition temperature of the poly(4-vinylpyridine), which exhibits a glass transition at 145°C [36], with the those of H-bonded side chain liquid crystalline polymers, glass transition temperature of the poly(4-vinylpyridine) decrease. This could be attributed to the plasticization of the polymer backbone by the flexible side groups.

The polymers was examined by polarizing optical microscopy. All the HPVP-LC polymers show an enantiotropic nematic phases. An isotropic-nematic phase separation was observed in the polymers.

5. CONCLUSION

The formation of H-bonding between the imidazole, pyrrolidon and pyridin groups of the poly(vinyl imidazole), poly(vinyl pyrrolidon) and poly(4-vinyl pyridine) respectively with hydroxyl groups in hydroxyalkoxycyanobiphenyl derivatives through hydrogen-bonding has been confirmed using FTIR, DSC and POM studies. The hydroxyalkoxycyanobiphenyl derivatives were attached to the polymer backbones through hydrogen-bonding yielding H-bonded liquid crystalline polymers.

The effect of spacer length on liquid crystalline properties is clearly observed in the PVI based H-bonded liquid crystalline polymers. The clearing temperature decreased and the temperature range of the LC phase increased with increasing spacer length.

In the PVPy based H-bonded liquid crystalline polymers, only HPVPy-LC6 has liquid crystalline properties and shows nematic mesophase, Liquid crystalline phase transition was not observed for HPVPy-LC8 and HPVPy-LC11.

All of the PVP based H-bonded liquid crystal polymers have liquid crystalline properties and show nematic mesophases. The clearing temperature increased with increasing spacer length.

REFERENCES

- [1] **Collings , P.J., Hird, M. ,** 2001 ; *Introduction to Liquid Crystals Chemistry and Physics*. Taylor & Francis Ltd, London
- [2] **Coşkun N.,** 2006 ; *Yeni Mesomorfik Bileşiklerin Sentezi ve Sıvı Kristal Özelliklerinin İncelenmesi*, Master Thesis, YTÜ, İstanbul
- [3] **Chung, T.S., Cheng, S.X., Jaffe, M.,** 2001; *Thermotropic Liquid Crystal Polymers: Thin Film Polymerization, Characterization, Blends and Applications; Introduction of Liquid Crystalline Materials*. CRC Press LLC, USA
- [4] **Url-1** <http://invsee.asu.edu/nmodules/liquid_mode/welcome.html> accessed at 28.03.2011
- [5] **Url-2** <<http://plc.cwru.edu/tutorial/enhanced/files/llc/intro/intro.htm>> accessed at 30.03.2011
- [6] **Collings, P. J.,** 1990; *Nature's Delicate Phase of Matter*. Princeton University Press, USA
- [7] **Dierking, I.,** 2003; *Textures of Liquid Crystals*. WILEY-VCH Verlag GmbH & Co. KGaA
- [8] **Url-3** <<http://web.media.mit.edu/~stefan/liquid-crystals/node1.html>> accessed at 03.04.2011
- [9] **Cui, J., He, W., Yue, Y., Zhao, H., Xia, X.,** 2010; *Inorganic Materials*, 46:1369-1374
- [10] **Pisula, W., Zorn, M., Chang, Y.J., Müllen, K., Zentel, R.,** 2009; *Macromol. Rapid Commun.* 30:1179-1202
- [11] **Url-4** <www.globalspec.com> accessed at 10.04.2011
- [12] **Laschat, S., Baro, A., Steinke, N., Giesselmann, F., Hagele, C., Scalia, G., Judele, R., Kapatsina, E., Sauer, S., Schreivogel, A., Tosoni, M.,** 2007; *Liquid Crystals*, 46:4832-4887
- [13] **Url-5** <www.chem.queensu.ca/people/faculty/lemieux/images> accessed at 12.04.2011
- [14] **Singh, S.,** 2002; *Liquid Crystals Fundamentals*, World Scientific Publishing Co. Pte. Ltd.
- [15] **Demus, D., Goodby, J., Gray, G. W., Spiess , H.W., Vill, V.,** 1998; *Handbook of Liquid Crystals 2A*, Weinheim
- [16] **Kaafarani, B. R.,** 2011; *Chemistry of Material Review*, 23:378-396
- [17] **Hepuzer, Y.,** 2000; *Sıvı Kristal Blok ve Graft Kopolimerler Sentezinde Yeni Yöntemler*, Doctorate Thesis, İTÜ

- [18] Demus, D., Goodby, J., Gray, G. W., Spiess, H.W., Vill, V., 1998; *Handbook of Liquid Crystals 3*, Weinhein
- [19] Finkelmann, H.,; *Thermotropic Liquid Crystals, Critical Reports on Applied Chemistry Volume;22, Liquid Crystal Polymers*
- [20] Qian, L., Zhi, J., Tong, B., Shi, J., Yang, F., Dong, Y., 2009; *Polymer* 50:4813-4820
- [21] Bagheri, M., Rad, R.Z., 2008; *Reactive and Functional Polymers* 68:613-622
- [22] Shu Hsu, C., 1997; *Prog. Polym. Sci*, 22: 829-871
- [23] McArdle, C.B., 1989; *Side Chain Liquid Crystal Polymers*, Blackie, Glaskow
- [24] Xie, H., Hu, T., Zhang, X., Zhang, H., Chen, E., Zhou, Q., 2008; *Journal of Polymer Science* 46:7310-7320
- [25] Kihara, H., Kato, T., Uryu, T., Frechet, J.M.J., 1996; *Chem. Mater.*, 8:961-968
- [26] Chao, C.Y., Li, X., Ober, K.C., 2004; *Pure Appl. Chem.*, 76:1337-1343
- [27] Kato, T., Mizoshita, N., Kanie, K., 2001; *Macromol. Rapid Commun.*, 22:797-814
- [28] Xu, X.Y., Zhang, B.Y., Wang, L.X., Gu, W.M., 2009; *Liquid Crystals*, 36:1365-1372
- [29] Hong Goh, S., Hing Lai, Y., Xue Cheng, S., 2001; *Liquid Crystals*, 28:1527-1538
- [30] Ambrozic, G., Zigon, M., 2005; *Acta. Chim. Slov.* 52:207-214
- [31] Öncül, A., Çoban, K., Sezer, E., Şenkal, B.F.: *Progress in Organic Coatings*, Inhibition of the corrosion of stainless steel by poly-N-vinylimidazole and N-vinylimidazole.
- [32] Choukchou-Braham, E., Benabadji, I., Mansri, A., Francois, J., 2003; *European Polymer Journal* 39: 297-303.
- [33] Hulme, D. S., and Raynes, E. P., 1974, *J. chem. Soc., chem. Commun.*, 98
- [34] Hori, K., and Wu, H., 1999, *Liq. Cryst.*, 26, 37
- [35] Hori, K., Kurosaki, M., Wu, H., and Itoh, K., 1996, *Acta Crystallogr.*, C52, 1751
- [36] Mccurdie, M. P., Belfiore, L. A., 1999; *Polymer* 40:2889-2902



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‘Synthesis of Poly (vinyl pyridine) Based Hydrogen Bonded Side Chain Liquid Crystalline Polymer’, *Advances in Applied Physics & Materials Science Congress, 12-15 May 2011, Antalya*