İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THE SYNTHESIS AND CHARACTERIZATION OF METHACRYLATE BASED HYDROGEN BONDED LIQUID CRYSTALLINE POLYMERS

M.Sc. Thesis by
Ceren Aytaç

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JUNE 2011

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JUNE 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

METAKRİLAT BAZLI HİDROJEN BAĞLI SIVI KRİSTAL POLİMERLERİN SENTEZ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ
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HAZİRAN 2011

FOREWORD

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Ceren Aytaç

Chemist

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ABBREVIATIONS

LCP	**:** Liquid crystal polymer
SCLCP	**:** Side chain liquid crystal polymer
MCLCP	**:** Main chain liquid crystal polymer
FT-IR	**:** Fourier transform infrared spectroscopy
^{1}H-NMR	**:** ^{1}H Nuclear magnetic resonance
POM	**:** Polarizing optical microscope
DTA	**:** Differential thermal analysis
DSC	**:** Differential scanning calorimetry
P1	**:** Diethylamine modified poly (glycidyl methacrylate)
P2	**:** Dibutylamine modified poly (glycidyl methacrylate)
P3	**:** Dioctylamine modified poly (glycidyl methacrylate)
PMAA	**:** Poly (methacrylic acid)
HBP	: Hydrogen bonded polymer
PGMA	**:** Poly (glycidyl methacrylate)

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SYNTHESIS AND CHARACTERIZATION OF METHACRYLATE BASED HYDROGEN BONDED LIQUID CRYSTALLINE POLYMERS

SUMMARY

In this present study side chain liquid crystalline polymers were prepared by using intermolecular hydrogen bonding concept. For this purpose, firstly H-bonded crystalline polymers were synthesized starting from tertiary amine containing methacrylate based polymers as H-bond acceptor and 4'-(-hydroxyalkoxy)-4-cyanobiphenyl derivatives as H-bond donor. Also other study, H-bonded liquid crystalline polymers were synthesized starting from poly (methacrylic acid) as H-bond donor and tertiary amine containing chalcone compound as H-bond acceptor.

-Synthesis of Hydrogen Bond Donors:

8-(4-Cyanobiphenyl-4'-oxy) octan-1-ol (LC8) and 11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol (LC11) were synthesized. The structure of the LC8 and LC11 were characterized by FT-IR and 1H-NMR spectroscopy.

-Preparation of Hydrogen Acceptor Polymers:

In this study, methacrylate based polymers was synthesized and modified with tertiary amine as a hydrogen acceptor. Therefore, poly (glycidyl methacrylate) (PGMA) was polymerized by radical polymerization method. PGMA was interacted with excess of (diethylamine or dibutylamine or dioctylamine**)** at room temperature for 24 h and at 80 ^{0}C for 2 h to obtained tertiary amine modified polymer. Modified polymer was characterized by FT-IR spectrum, and the amine content, determined titrimetricially.

-Preparation of methacrylate based liquid crystalline polymers: (HBP-LC)

Tertiary amine modified PGMA and 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 amine modified PGMA and hydroxyl group of the hydrogen donors is shown below:

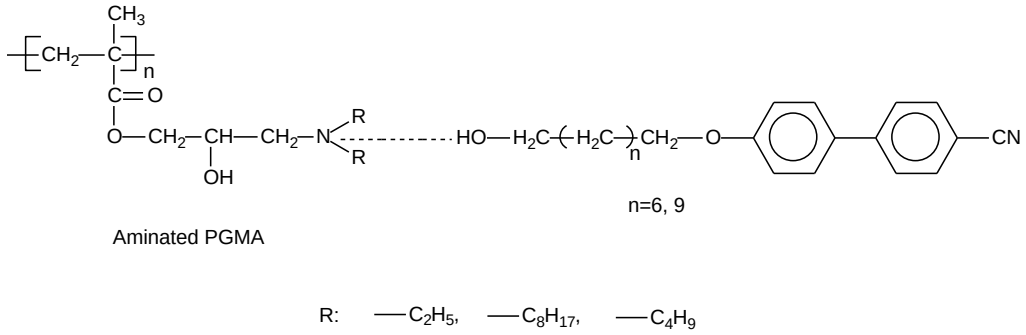


Figure 1: Preparation of methacrylate based hydrogen bonded liquid crystalline polymers.

The hydrogen bonded methacrylate based polymers were characterized by FT-IR spectroscopy, DTA and POM methods. According to the FT-IR spectra of the polymers hydrogen bonding donors and acceptors located so that intramolecular hydrogen bonding is favored, display slightly broadened O-H stretching absorption in the 3200 to 3500 cm^{-1} range.

-Preparation of a new chalcone compound:

The chalcone was prepared by reacting 4-Dimethylaminobenzaldehyde with 4'-(4-bromophenyl)acetophenone in ethanol in the presence of sodium hydroxide as base. The chemical structure of the compound was confirmed with FT-IR spectroscopic methods.

-Preparation of methacrylic acid based hydrogen-bonded side chain liquid crystalline polymer: (HBMAA-chalcone)

Chalcone was employed as a hydrogen bond acceptor and Poly(methacrylic acid) as a H-bond donor to yield hydrogen bonded liquid crystalline polymers. (Illustrated in figure 2)The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and UV-vis and FT-IR for spectroscopic characterization.

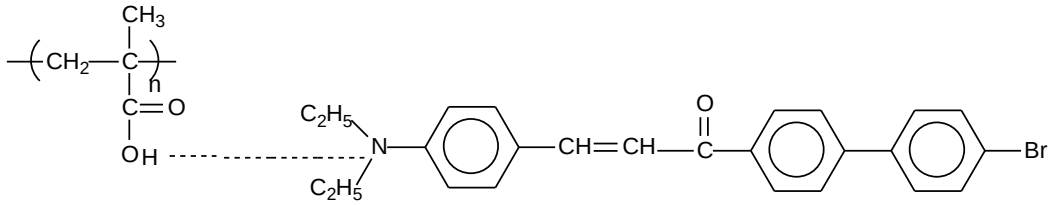


Figure 2: Preparation of PMAA based hydrogen-bonded side chain liquid crystalline polymer (HBMAA-chalcone)

HİDROJEN BAĞLI METAKRİLAT BAZLI SIVI KRİSTAL POLİMERLERİN SENTEZ VE KARAKTERİZASYONU

ÖZET

Bu çalışmada moleküller arası hidrojen bağı etkileşimi kullanılarak yan zincir sıvı kristal polimerler sentezlenmiştir. Bu amaçla ilk olarak, yapısında tersiyer amin grubu içeren içeren metakrilat bazlı polimerler Hidrojen bağı alıcı olarak ve 4'-(-hidroksialkoksi)-4-siyanobifenil türevleri de Hidrojen bağı verici olarak kullanılarak yan zincir sıvı kristal polimerler hazırlanmıştır. Diğer bir çalışmada ise, Hidrojen bağı vericisi poli metakrilik asit ve Hidrojen bağı alıcısı olarak amin grubuna sahip yeni bir kalgon bileşiği etkileştirilerek hidrojen bağlı sıvı kristal polimer sentezlenmiştir.

-Hidrojen Bağı Verici Molekülerin Sentezi:

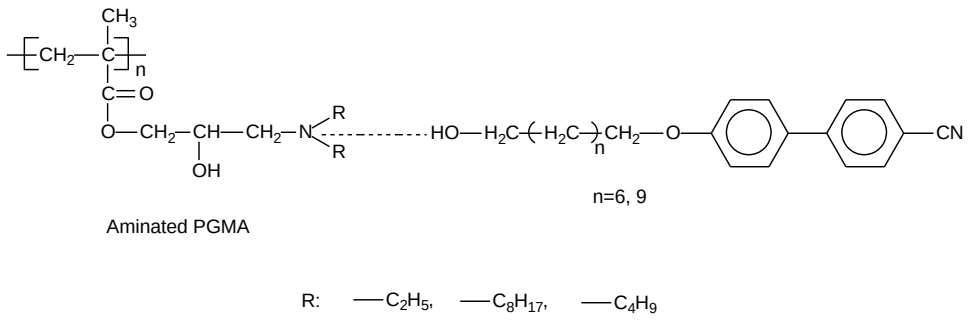
8-(4-siyanobifenil-4'-oksi) oktan-1-ol (LC8) and 11-(4-siyanobifenil-4'-oksi) undekan-1-ol (LC11) bileşikleri sentezlenmiştir. LC8 ve LC 11 FT-IR VE ^{1}H NMR spektroskopisiyle karakterize edilmiştir.

-Hidrojen Bağı Alıcı Polimerlerin Hazırlanması:

Bu deneysel çalışmada, metakrilat bazlı polimerler sentezlenip tersiyer aminle modifiye edilerek, polimerlere H bağı alıcı özellik kazandırılmıştır.Bunun için önce PGMA radikalik yolla polimerleştirilir. PGMA (dietilamin, dibütilamin ya da dioktilaminin) aşırısı ile oda sıcaklığında 24 saat, 80 °C de ise 2 saat tutularak etkileştirilmiştir. Modifiye edilmiş polimer FT-IR ile karakterize edilmiştir. Modifiye polimerin titrimetrik yöntemle amin tayini yapılmıştır.

Metakrilat Bazlı Sıvı Kristal Polimerlerin Hazırlanması:

Tersiyer aminle modifiye edilmiş PGMA Hidrojen bağı alıcısı olarak, LC8 ya da LC11 ile hidrojen bağı vericisi olarak etkileşime girerek hidrojen bağlı sıvı kristal polimerler elde edilmiştir. Amin grubu ile modifiye edilmiş PGMA' ın azot atomu ve hidrojen bağı verici moleküller arasındaki moleküller arası etkileşim aşağıdaki şekilde gösterilmiştir.



Şekil 1: HBP-LC

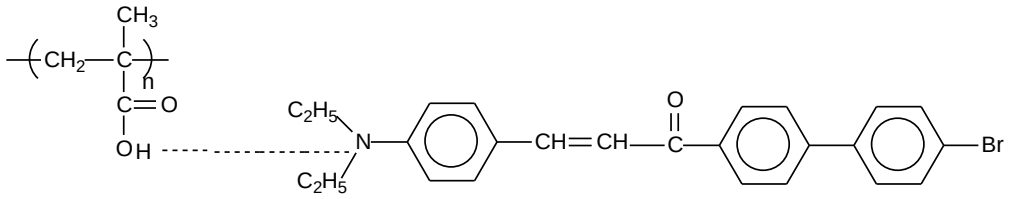
Hidrojen bağlı polimer FT-IR spektroskopisi, DTA ve POM ile karakterize edilmiştir. FT-IR spektrumuna göre OH gerilme absorpsiyonu 3200-3500 cm^{-1} bölgesine kayması hidrojen bağı oluşumunu kanıtlamaktadır.

-Yeni Kalgon Bileşiğinin Sentezi:

Kalgon bileşiği 4-aminobenzaldehitin 4'-(4-bromofenil)asetefenon ile NaOH varlığında etanolde reaksiyonundan elde edilir. Molekülün kimyaal yapısı FT-IR ile karakterize edilimiştir.

-Metakrilik asit bazlı hidrojen bağlı yan zincir sıvı kristal polimerlerin sentezi:

Sıvı kristal polimerlerin sentezinde kalgon, hidrojen bağı alıcısı olarak ve poli metakrilik asit ise H bağı vericisi olarak kullanılmıştır.Polimer sıvı kristal özelliklerini incelemek için POM, termal özellikler için DTA ve spektroskopik karakterizasyon içinse FT-IR kullanılmıştır.



Şekil 2: HBMAA-kalgon

1. INTRODUCTION

Side chain liquid crystal polymers combine properties characteristic of polymers with those low molar mass mesogens. Due to these two properties SCLCPs have potential applications in various fields, ranging from optical data storage, non-linear optics, to being the stationary phase in gas chromatography and high performance liquid chromatography. SCLCPs are generally prepared by covalently linking rigid mesogens through flexible spacers. In recent years, self-assembly through specific interactions, such as hydrogen bonding, ionic, ionic-dipolar and charge transfer interactions has been recognized as a new strategy for constructing SCLCPs. These supramolecular materials have some advantages over the covalently bonded systems as a dynamic function, environmental compatibility, and low energy processing.

Hydrogen bonding is one of the important non-covalent interactions in nature. Biopolymers such as nucleic acids, polypeptide, and cellulose have hydrogen bonding groups. The formation and dissociation of the hydrogen bonds for these polymers play an important role in many biological processes. Stable and dynamic molecular complexes can be prepared by simple molecular self-assembly processes using such hydrogen bonding. Carboxylic and benzoic acid groups were widely used as hydrogen-bond donors while pyridine and imidazole moieties were commonly used as hydrogen-bond acceptors.

In this present study side chain liquid crystalline polymers were prepared by using intermolecular hydrogen bonding concept. For this purpose, firstly H-bonded crystalline polymers were prepared starting from tertiary amine containing methacrylate based polymers as H-bond acceptor and 4'-(-hydroxyalkoxy)-4-cyanobiphenyl derivatives as H-bond donor. Also other study, H-bonded liquid crystalline polymers were synthesized starting from poly (methacrylic acid) as H-bond donor and tertiary amine containing chalcone compound as H-bond acceptor.

H-bonded crystalline polymers were characterized by using thermal analysis methods, FT-IR and POM studies.

2. THEORETICAL PART

2.1 Liquids Crystals

2.1.1 History of Liquid Crystals

Their discovery is generally dated back to the year 1888, when the Austrian botanist Friedrich Reinitzer reported on the observation of some esters of cholesterols with apparently two melting points[1]. Reinitzer was conducting experiments on a cholesterol based substance trying to figure out the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points [2]. At 145.5 °C cholesteryl benzoate melted from a solid to a cloudy liquid and at 178.5 °C it turned into a clear liquid. Some unusual colour behaviour was also observed upon cooling; first a pale blue colour appeared as the clear liquid turned cloudy and then a bright blue-violet colour as the cloudy liquid crystallised. He sent the samples to Otto Lehmann (German physicist). Lehmann observed the sample with his polarising microscope and he noted that they flow like liquids and exhibit optical properties like that of a crystal. The subsequent studies established that these observed intermediate phases represent a new thermodynamic state of matter. Lehmann first referred to them as flowing crystals and later used the term "liquid crystals" [3].

2.1.2 Fundamentals of Liquid Crystals

Liquid crystals are partially ordered, anisotropic fluids, thermodynamically located between the three dimensionally ordered solid state crystal and the isotropic liquid [1]. The difference between crystals and liquids is that the molecules in crystal are ordered whereas in a liquid they are not (figure 2.1) [3,4]. The existing order in a crystal is usually is usually both positional and orientational. The molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions. Contrary to it, the molecules in liquids diffuse randomly throughout the sample container with the molecular axes tumbling wildly. When a molecular material composed of anisotropic molecules is heated from the solid

phase, at the melting point, there is the possibility that the positional order either fully or partially disappears while some degree of orientational order is maintained. The phase thus derived is called as "liquid crystal" (LC). An other name in use which means intermediate phase is mesophase or mesomorphic phase. In this phase the unique axes of the molecules remain, on average, parallel to each other, leading to a preferred direction in space. It is convenient to describe the local direction of alignment by a unit vector n, the director, which gives at each point in a sample the direction of a preferred axis [3].

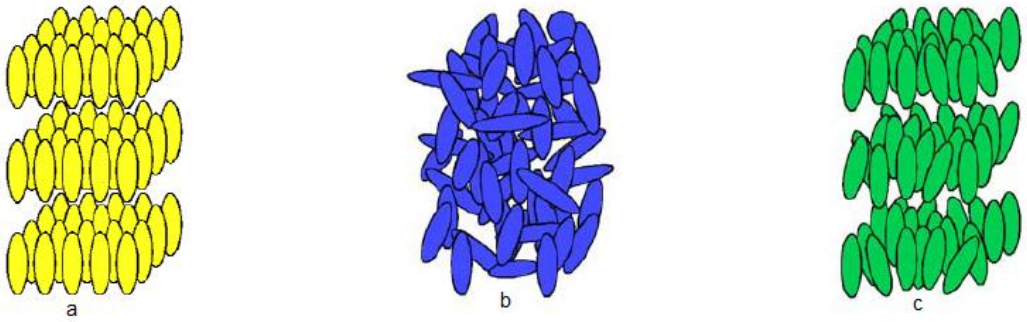


Figure 2.1: Arrangements of molecules (a) in crystal (b) in a liquid (c) in a liquid crystal.

The molecules in mesophases diffuse about much like the molecules of a liquid, but as they do so they maintain some degree of orientational order and sometimes some positional order also [5]. Liquid crystals are unique materials that combine dynamic nature with anisotropic structures [6].

To specify the amount of orientational order in such a liquid crystal phase, an order parameter (S) is defined. Traditionally, the order parameter is given as follows :

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

where theta is the angle between the director and the long axis of each molecule as can be seen in the figure 2.2. The brackets denote an average over all of the molecules in the sample. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero.

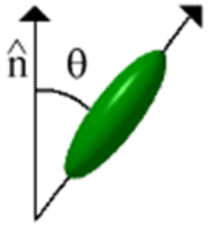


Figure 2.2: The scheme of angle between the director and the long axis of molecule.

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, with the exact value a function of temperature, as a result of kinetic molecular motion. This is illustrated below for a nematic liquid crystal material (figure 2.3) [5,7].

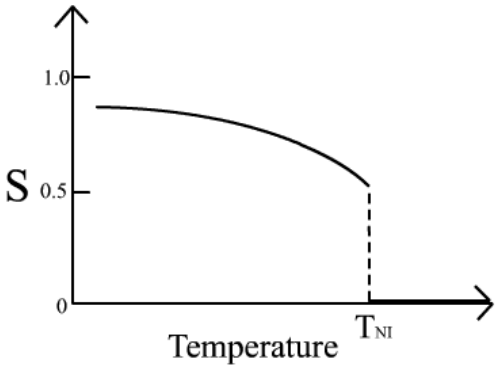


Figure 2.3 : Graphical representation of order parameter versus temperature for nematic liquid crystal.

The order parameter S can be measured in a number of ways. Usually a macroscopic property of the liquid crystal is measured, which then can be used to determine S if the molecular parameters that produce the macroscopic property are known. Diamagnetism, optical birefringence, nuclear magnetic resonance, and Raman scattering measurements are examples [5].

A compound that exhibits a mesophase (mesomorphic phase) is called a mesogenic compound [3]. Mesophases can be monotropic or enantiotropic. Monotropic mesophase is a metastable mesophase that can be formed by supercooling an isotropic liquid. Enantiotropic mesophase is a mesophase that is thermodynamically stable over a definite temperature or pressure range. The temperature at which the transition between the mesophase with the highest temperature range and the isotropic phase occurs is clearing point T_{cl} or T_i [8].

The optical, mechanical, electrical and magnetic properties of LC medium are defined by the orientation order of the constituent anisotropic molecules. Due to the anisotropy of the electrical and magnetic properties, the orientation of the LC molecules is effectively controlled by weak electric or magnetic fields. As a result, changing the LC molecules orientation, it is possible to change optical, mechanical properties of the medium. All of these are important to the functioning of devices based on LCs: digital watches, calculators, flat TV-displays, thermometers and LC displays are all examples of what LC technology can achieve [9].

2.1.3 Types of Liquid Crystals

Transitions to the mesophases may be brought about in two different ways; one by purely thermal processes and the other by the influence of solvents. The liquid crystals obtained by the first method are called "thermotropics" whereas those obtained by the second one are "lyotropics" [3].

Both calamitic (rod shaped molecules) and discotic (disk-like molecules) liquid crystals are thermotropic. Lyotropic liquid crystal molecule combines a hydrophobic group at one end with a hydrophilic group at the other end. Such amphiphilic molecules form ordered structures in both polar and non-polar solvents. Polymers also form liquid crystal phases. Sections of the polymer must be rigid in order for it to be liquid crystalline. In a main chain polymer rigid structural units ressemling, for example, calamitic liquid crystal molecules are separated by flexible hydrocarbon chains. In a side chain polymer, the rigid sections are attached to a long flexible polymer chain by short flexible hydrocarbon chains [5].

2.1.4 Lyotropic Liquid Crystals

The Lyotropic liquid crystals are always mixtures (or solutions) of unlike molecules in which one is a nonmesogenic liquid [3]. Generally, one of the components is formed by amphiphilic molecules and another is water. Amphiphilic molecules possess both polar and non-polar regions in the same molecule. Surfactans are amphiphilic materials whose constituent molecules have a molecular structure that includes a polar head group and a non-polar chain. Soaps such as sodium stearate have a polar head group made up of a carboxylate salt and a non-polar unit that is simply a long hydrocarbon chain [5].

When the concentration gets high enough, however, the molecules begin to arrange themselves in hollow spheres, rods, and disks called micelles (figure 2.4). As the concentration increases, the micelles begin to arrange themselves into loose patterns. These patterns are the actual liquid crystal aspects of the molecular behavior. Micelles take the place of individual atoms, ions, or molecules [10,11].

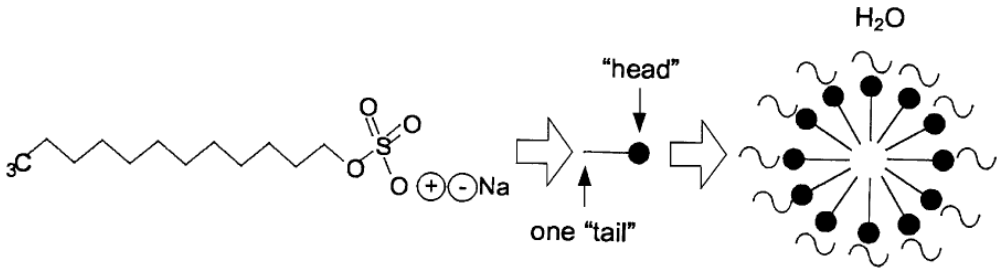


Figure 2.4 : Chemical structure and cartoon representation of sodium dodecylsulfate (soap) forming micelles.

There exist several different types of lyotropic liquid crystal phase. Structures each of these phases has a different arrangement of molecules within the solvent matrix. The concentration of the solute material in the solvent determines the kinds of lyotropic liquid crystal phase that is exhibited. However, at a given concentration, it is also possible to observe transitions between lyotropic mesophases by changing the temperature. On the basis of X-ray diffraction studies three different types of lyotropic liquid crystal phase structures have been identified - the lamellar, the hexagonal and the cubic phases (figure 2.5) [3,10].

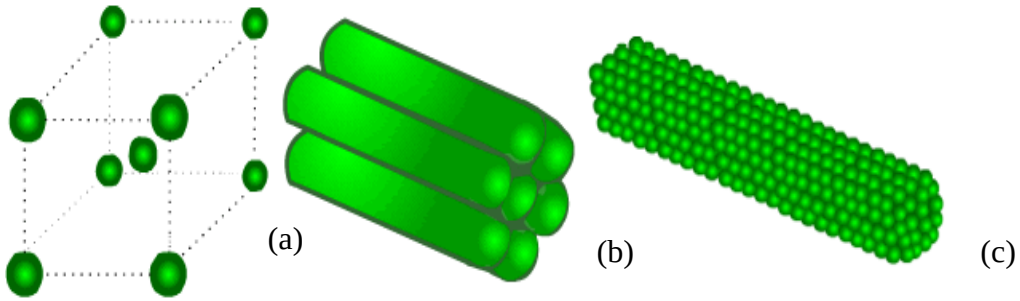


Figure 2.5 : (a) Cubic liquid crystal, (b) Hexagonal liquid crystal, (c) Rod micelle close-up.

2.1.5 Calamitic Liquid Crystals

Calamitic liquid crystals are rod shaped molecules. The molecule be fairly rigid for a least some portion of its length, since it must maintain an elongated shape in order to produce interactions that favour alignment [5]. In general aromatic liquid crystal molecules such those shown in figure 2.6 comprise a side chain R, two or more aromatic rings A and A' connected by a linkage group X Y and the other end connected to a terminal group R'. Examples of side chains and terminal groups are alkyl (CnH2n+1), alkoxy (CnH2n+1), others such as acyloxyl, alkylcarbonate, alkoxycarbonyl, and nitro and cyano groups. The Xs of linkage groups are simple bonds or groups such as stilbene (-CH=CH-), ester, tolane, azoxy, and Schiff base, acetylene, and diacetylene [11]. In figure 2.7 one example of calamitic liquid crystal has shown[1].

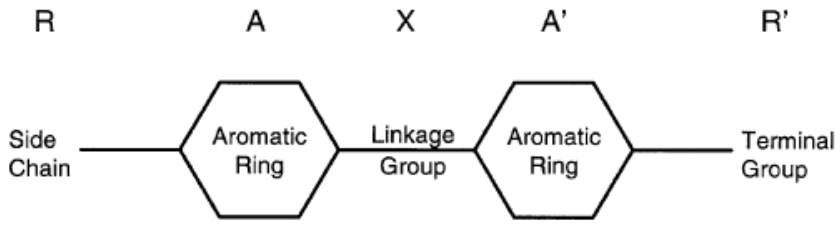
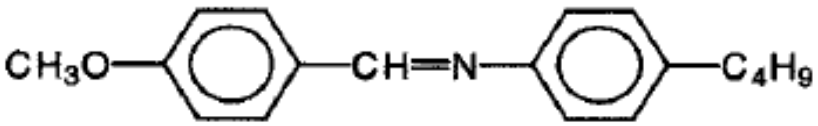


Figure 2.6 : Molecular structure of typical calamitic liquid crystal.



Cr 22 N 47 Iso

Figure 2.7 : Molecular structure of 4-butyl-N-[methoxy-benzylidene]-aniline (MBBA).

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 2.8 shows the nematic phases. Figure 2.9 give the schlieren texture and droplets of nematic phase seen at polarizing optical microscope [3,12]. In nematics, the long molecular axes are preferably

oriented in one direction, defined as the director n, and molecular dipoles are compensated, so in equilibrium this mesophase is electrically neutral. Both directions of director, +n and -n, are equivalent. The ordinary nematic structure shows an optically positive uniaxial behaviour with the optical axis parallel to the director n.

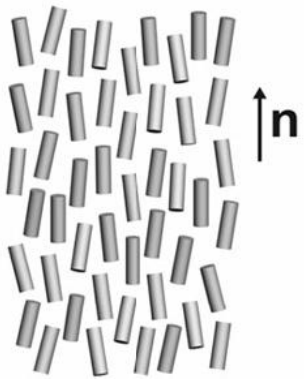


Figure 2.8 : Nematic phase.

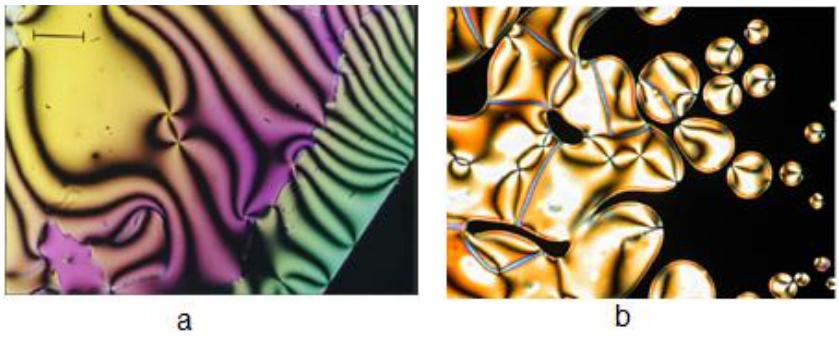


Figure 2.9 : (a) Schlieren texture, (b) droplets of nematic phase.

Nematic LCs possess a relatively low viscosity; they can be deformed by even small external forces. Considering only weak distortions, the nematic phase formally acts as an elastic medium, and the deformations can be treated by the continuum theory of nematics. An undeformed LC is one in which the director n points in the same direction throughout the LC. A deformed LC is one in which the director changes its direction from point to point [9].

The nematic (N) liquid crystal phase is technologically the most important of the many different types of liquid crystal phases. The nematic phase is the liquid crystal phase that is used in virtually all commercially available liquid crystal displays [5].

Smectic Mesophase

When the crystalline order is lost in two dimensions, one obtains stacks of two-dimensional liquid. Such systems are called smectics. Smectics have stratified structures, with a well-defined interlayer spacing. The molecules exhibit some correlations in their positions in addition to the orientational ordering. In most smectics the molecules are mobile in two directions and can rotate about one axis. The interlayer attractions are weak as compared to the lateral forces between the molecules and the layers are able to slide over one another relatively easily. This gives rise to the fluid property to the system having higher viscosity than nematics [3] In smectic A (SmA) phases, on average, the molecules are parallel to one another and are arranged in layers, with the long axes perpendicular to the layer plane (Figure 2.10). Within the layers, the centers of gravity of the molecules are ordered at random. Thus, smectics A possess the one-dimensional quasi long-range positional order and within the layers molecules show a relatively high mobility. The layer thickness is equal to the molecule length. SmA LCs are optically positive and uniaxial with the optic axis parallel to the molecular long axes [9,12]. The structure of the smectic C (SmC) liquid crystals is closely related to the structure of the SmA. The molecules are arranged in layers, but the long axes of the molecules are tilted to the layers planes (Figure 2.10). For some materials the tilt angle is constant but for others it is temperature dependent. The centers of gravity of the molecules are randomly ordered and the molecules are free to rotate around their long axes. SmC phases are optically biaxial [9] In figure 2.11 fan shaped structure of SmA and broken fan shaped structure of SmC are shown [1,12].

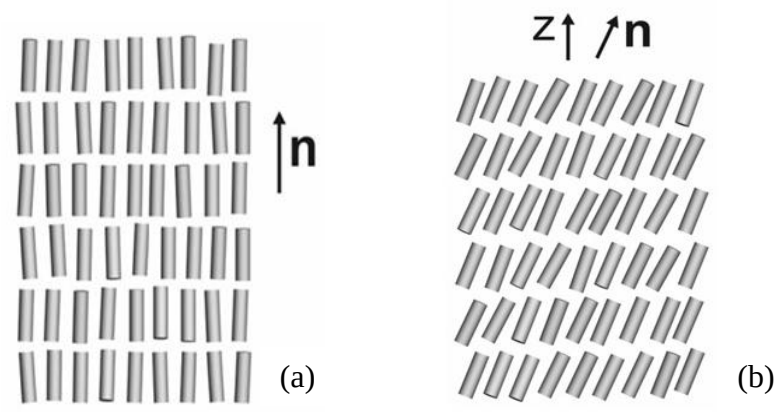
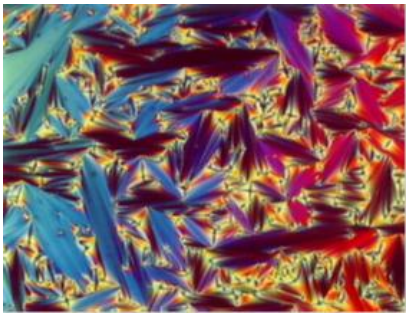
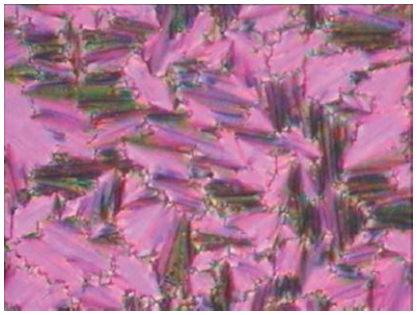


Figure 2.10 : (a) Structure of smectic A liquid crystal, (b) Structure of SmC liquid crystals (n is director; z is normal to layers).



(a)



(b)

Figure 2.11: (a) Fan shaped structure of SmA, (b) broken fan shaped structure of SmC.

Chiral Mesophases

Chiral molecules cause a twist in the nematic structure. Such a helical phase is called a cholesteric LC. Locally, the cholesterics are very similar to the nematic LCs. They consist of quasi-nematic layers, whose individual directors are turned by a fixed angle on proceeding from one layer to the next (Fig 2.12). The layers turned by an angle of 2π are equivalent; the distance between these two defines the pitch p of the helical structure [9]. Figure 2.13 shows the fingerprint texture of cholesteric phase seen at POM [12].

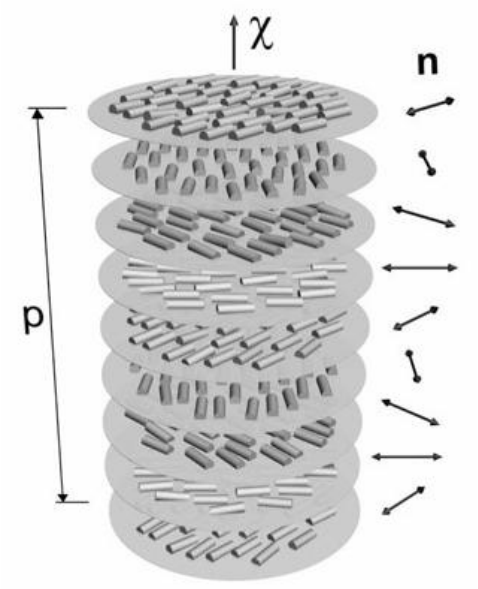


Figure 2.12 : Chiral nematic phase.

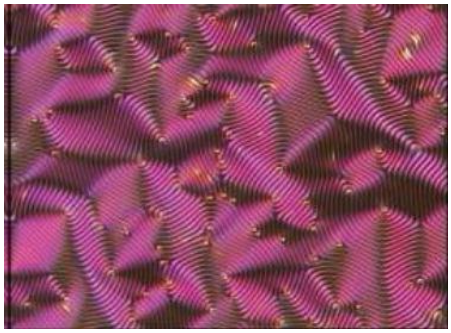


Figure 2.13 : Fingerprint texture of chiral nematic phase.

The Chiral Smectic C Phase

The SmC* phase is similar to the SmC phase but consists of the chiral molecules which rotate the direction of the director projection on the layer plane from one layer to the next. The twist axis of the SmC* is perpendicular to the layers. Therefore, these phases appear optically positive uniaxial, and show optical activity and selective reflection similar to the cholesterics. Figure 2.14 shows chiral smectic C phase [9]. At Figure 2.15 fan shaped texture of can be seen [1].

If the molecules in SmC* have the permanent dipole moments perpendicular to their long axes than such phase exhibits ferroelectric properties [9].

Figure 2.14 : Chiral SmC* phase.

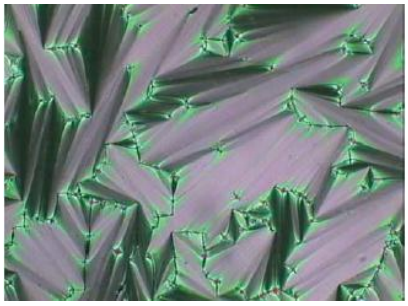


Figure 2.15 : Fan-shaped textures of the SmC*

2.1.6 Discotic liquid crystals

Rigidity in the central part of the molecule is essential. The core of a typical discotic liquid crystal molecule is based on benzene, triphenylene, or truxene, with or eight side chains, each resembling a typical calamitic liquid crystal molecule. [3] In figure 2.16 typical discotic mesogen can be seen [1].

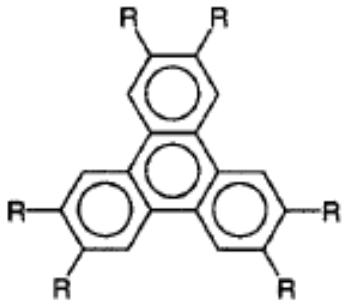


Figure 2.16 : Typical discotic mesogen.

Mesogens composed of disc-shape molecules exhibit two distinct classes of phases, the columnar and the discotic nematic phases. (Figure 2.17) [12,13].

When the crystalline order is lost in one direction (i.e. the system is melted in one dimension), one obtains a periodic stack of discs in columns; such systems are called columnar phases. The different columns constitute a regular 2D array and hence the structure has translational periodicity in two dimensions, but not in three. The discotic nematic phase, like its calamitic analogue, is the least ordered mesophase and the least viscous. In the columnar structures the molecules are stacked upon each other, building columns which may be arranged in hexagonal, tetragonal and tilted variants. Along the axes of the columns, long-range order or disorder of the molecules can exist [3].

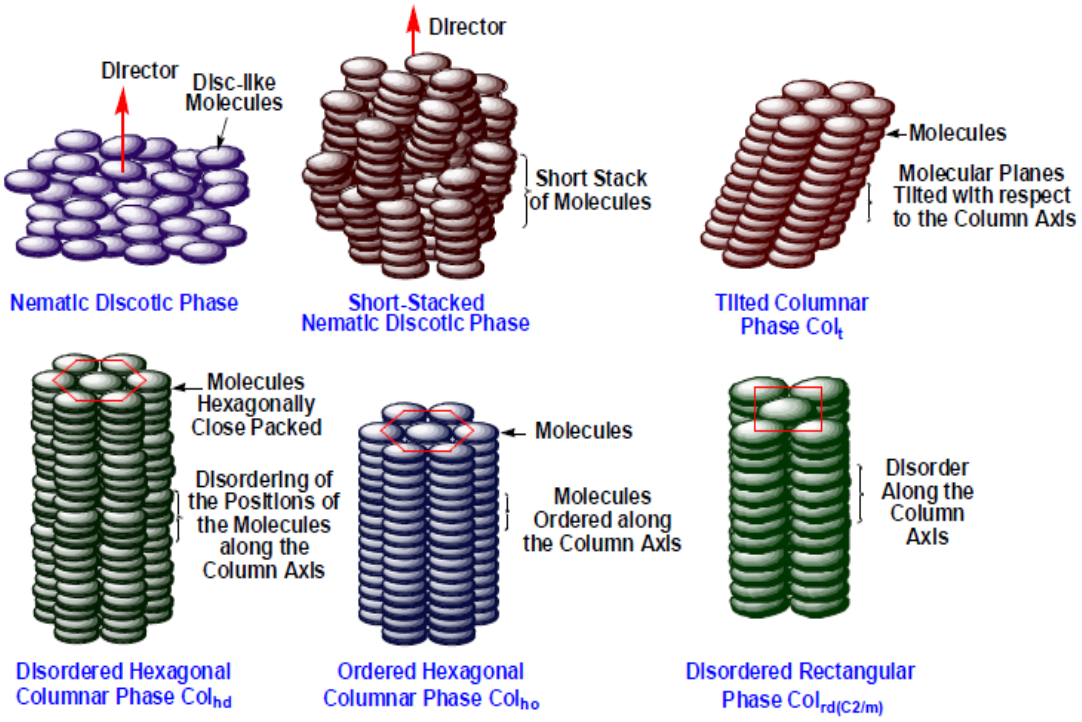


Figure 2.17 : Columnar and the discotic nematic phase.

2.1.7 Mesophases Characterization

The mesophase characterization can be done with following experimental techniques:

-Polarizing Optical Microscopy (POM)

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. Microscopy reveals that a distinct optical texture results from each different liquid crystalline phase [3]. In figure 2.3 Polarizing optical microscopy is illustrated [1].

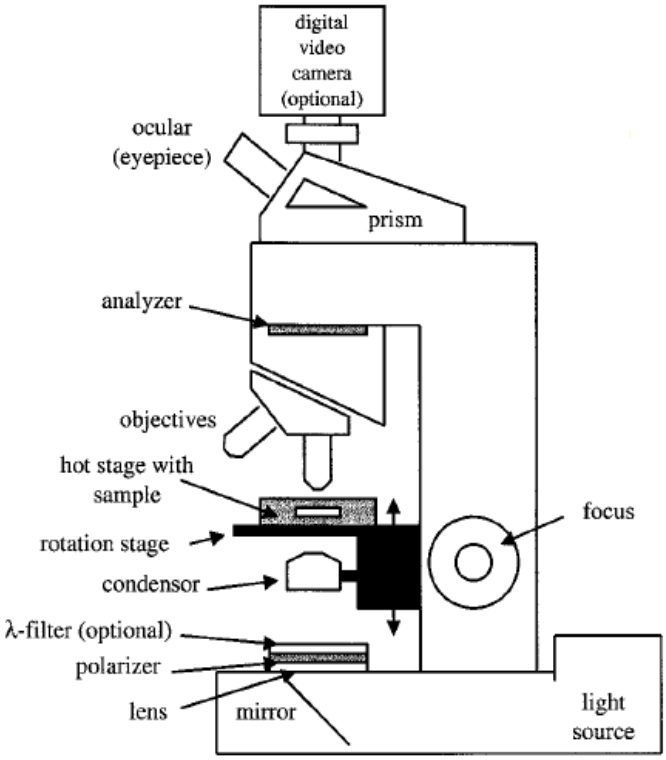


Figure 2.18 : Polarizing optical microscopy.

-Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is used as a complementary tool to optical microscopy. The DSC reveals the presence of mesophases and liquid crystal phases by detecting the enthalpy change associated with a phase transition.

-Miscibility Investigation

In the miscibility investigation, a material with unknown mesophases is mixed with a known mesogen of already identified phase types. If the two materials belong to the same symmetry group, they are completely miscible and it can be concluded that the phases of each compound are identical and belong to the same miscibility group. Strictly speaking this criterion of selective miscibility only applies if the two compounds possess the same molecular symmetry. Hence, when the two different compounds do not mix, this does not necessarily show a difference between the two phases. Some conclusions can only be derived from the miscibility of the two phases, and not from an observed lack of miscibility.

-X-ray diffraction (XRD)

The X-ray analysis is the final technique for the identification and classification of phase types. The X-ray diffraction provides direct information about the residual positional order in liquid crystals and hence determines the phase structure and classification to which the particular phase belongs [3].

2.2 Liquid Crystal Polymers

Basically, there are two types of liquid crystal polymers; main chain and side chain. Main chain liquid crystal polymers (MCLCP) consist of repeating mesogenic (liquid crystal like) monomer units. This is illustrated in figure 2.19. The monomer unit must be anisotropic and bifunctional to enable polymerization and the generation of mesophases. For example, one end of a long, lath-like mesogenic unit might be carboxylic acid and the other end might be an amine; condensation would sequentially link the mesogenic units together to give a liquid crystalline polyamide [5,10].

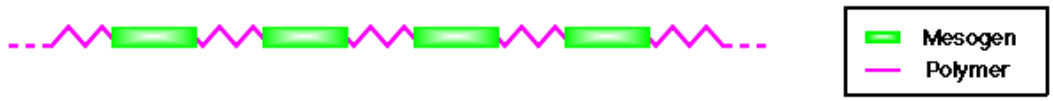


Figure 2.19 : Schematic representation of main chain liquid crystal polymers.

Side chain liquid crystal polymers (SCLCPs) consist of mesogenic structural moieties appended from a polymer backbone. The mesogenic units that have been used parallel those previously used for low molar mass liquid crystals, and the structural nature of the polymer backbone is widely variable. The mesogenic units (usually calamitic but many discotic types exist.) are invariably separated from the polymer backbone by fairly long spacer units which are usually several methylene units, often with ester or ether units at the point of attachment [5]. In figure 2.20 the schematic representation of side chain liquid crystal polymers is given [10.]

Figure 2.20: Schematic representation of side chain liquid crystal polymers.

Liquid crystalline polymers, combine properties characteristic of polymers with those of conventional low molar mass mesogens [14].

Liquid crystal polymers exhibit the same liquid crystalline phases and mesophases exhibited by low molar mass mesogens. However, the identification of the mesophases generated by polymers is usually far more difficult than for low molar mass materials [5].

2.2.1 Main Chain Liquid Crystal polymers

Main chain liquid crystal polymers have repeating mesogenic units that form a long chain. If the linking units are long and flexible, then a semi-flexible polymer results; however, if the mesogenic units are directly linked then the polymer be rigid and intractable. The most significant outcome was that the polymers of high tensile strength resulted when processed in the anisotropic mesophase. The degree of flexibility and the structural composition both determine the mesomorphic properties of MCLCPs.

Main chain liquid crystal polymers can be constructed from calamitic and discotic units by a condensation process [5]. Lyotropic liquid crystal Kevlar (poly (paraphenylene terephthalamide)) is synthesized in solution from the monomers 1,4-phenylene-diamine and terephthaloyl chloride in a condensation reaction yielding hydrochloric acid as a byproduct (Figure 2.21) [15].

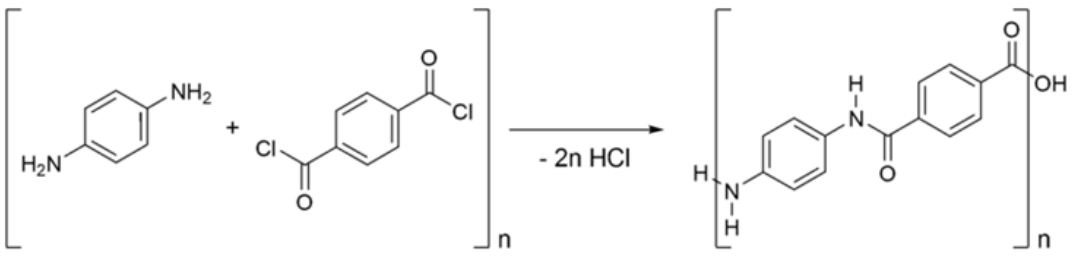


Figure 2.21 : Synthesis of Kevlar.

To be commercially viable, a thermotropic LCP must possess an LC transition temperature, Tm, lower than the polymer decomposition temperature, Td . However, aromatic para linked polyester homopolymers, for example, poly (p-hydroxybenzoate), Tm is above 500◦C while Td is around 400◦C. One of the main objectives in thermotropic LCP research has been to reduce the transition temperature to a temperature range that is suitable for conventional processing facilities, i.e., equal to or less than about 300 ◦C. Typical approaches to lower the mesogenic transition temperature are following:

1. random copolymerization

2. introducing kinks into the molecular backbone by using meta or ortho linkages

3. introducing flexible linkages into the chain

4. incorporating bulky side groups onto the polymer chain [16].

2.2.1.1 Applications of main-chain LCPs

Most applications of main-chain LCPs utilize the high mechanical properties of these materials. High modulus and high tensile strength are a result of the high molecular orientation characteristic of these polymers. LCP characteristics, such as high mechanical properties (strength, modulus), ease of processibility, excellent thermal resistance, low water absorption, and low gas permeability, make LCPs attractive for a wide range of applications. The applications of main-chain LCPs can be divided into several areas: extrudates (fibers, rods, sheets) used in the chemical and materials' industry, and moldings (chip carriers, connectors, switches) used in microelectronics. Fabrics of LCP fiber are used in ballistic protection garments, helmets, and military flak jackets. Excellent cut/tear resistance and good thermal insulation also make LCP fibers desirable for protective gloves and clothing [16].

2.2.2 Side Chain Liquid Crystal Polymers

Side chain liquid crystal polymers were realised in 1978 when Ringsdorf and co-workers inserted a flexible spacer unit between the rigid mesogenic unit and the polymer backbone. 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. These two features are completely antagonistic, where 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. However, if a flexible spacer moiety is employed to separate the mesogenic units from the backbone, then the two different tendencies of the mesogen (anisotropic orientation) and backbone (random arrangement) can be tolerated within the one polymeric system. If this theory is correct, the backbone should not influence the nature of the generated mesophases nor their thermal stabilities. However, the backbone does affect the mesomorphic properties of SCLCPs. The spacer moiety does not totally decouple the mesogenic unit from the backbone because studies shown that the part of spacer aligns with the mesogenic unit. However, enhanced decoupling is generated as the spacer moity is lengthened. Spacer length influences the nature of the least ordered mesophase exhibited and the overall thermal stability is influenced by the polymer backbone [5].

2.2.2.1 Effect of spacer length on mesomorphic behaviour

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. In general, the increased ordering generated on polymerization means that the smectic phases predominate and the nematic phase is only exhibited by polymers with a short spacer and short terminal chain [17].

The variation in spacer length affects both the freedom of the mesogenic unit from the polymer backbone and overall length of the side chain unit; accordingly, the variation in the mesomorphic behaviour with the spacer length is due to a combination of these factors [17].

2.2.2.2 Effect of polymer backbone on mesomorphic behaviour

The flexibility is the most important aspect of a polymer backbone when liquid crystallinity is being discussed. As flexibility of the polymer backbone increases, the Tg is reduced and wider liquid crystal phase range generates. However clearing points often fall with increased flexibility, but not too significantly and not in all cases. For this reason, the most common backbones of the general alkene type that are employed in synthesis of SCLCPs are the flexible acrylates and methacrylates

(less flexible). Comparisons of mesomorphic properties with respect to backbone flexibility are extremely difficult to rationalise because other structural aspects are often different. For example, there are cases of higher TN-I values generated from very flexible siloxane polymers when compared with the less flexible acrylates. The degree of polymerization (DP) and the polydispersity are also important aspects regarding the backbone [17].

2.2.2.3 Effect of mesogenic unit on mesomorphic behaviour

The mesogenic unit have a great influence on the liquid crystal phases and the transitions tempeatures. Cyanobipenyl units have incorporated into SCLCPs in order to generate polymers with a positive dielectric anisotropy. A longer terminal chain results in in enhancement of the smectic tendency. Polar terminal units tend to generate smectic phases, where as non-polar terminal chains favour the nematic phases [17].

2.2.2.4 Side Chain Liquid Crystal Polymers Applications

Side Chain Liquid Crystal Polymers applications are divided into two main classes: electro-thermo-optical application and separation and complexation applications [17].

1.Electro-thermo-optical application:

-Optical data storage: digital, analogue and holographic optical storage have been demonstrated using cholesteric,nematic and smectic side chain LCP’s

-Optical elements: Cholesteric side chain can be used in selective wavelength, notch and bandpass filters

-Non-linear optic: SCLCPs loaded with appropriate dyes or with inherently coloured mesogenic systems are under investigation.

-Electro-optic display: Side chain LCPs due to their high viscosity, are not practical display media. However they are used as dopants to advantageously modify the elastic constants of conventional LCs. SCLCPs are proposed as switchable alignments layers and polarizers in LCDs [14,17].

2. Separation and complexation application:

Side chain LCPs with oxyethylene spacers, can dissolve metal cations. Control of permeation of gases and simple drugs has been reported using side chain LCD membranes[5]. Another application of side chain LCPs is stationary phases in GC systems [14,17,18].

2.2.3 H-bonded Liquid Crystal Polymers

2.2.3.1 Non-covalent Interaction

Molecular recognition processes between different molecular species using noncovalent bonded interactions has been recognized as a new strategy for constructing liquid crystal polymers [19,20]. These self-assembly strategies including hydrogen bonds, ionic interactions and charge-transfer complexes have been used to construct liquid-crystalline polymers as "supramolecular" materials. Schematic representation of covalent bond and non-covalent interaction are shown in figure 2.22 [6].

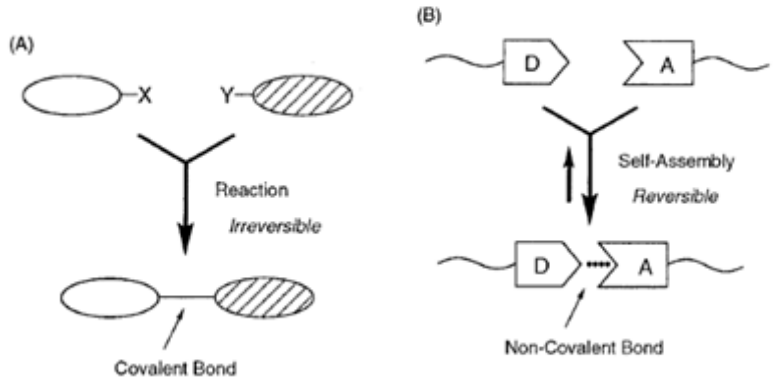


Figure 2.22 : Schematic representation of (A) covalent bond, (B) non-covalent interaction.

These supramolecular materials have some advantages over the covalently bonded systems as a dynamic function, environmental compatibility, and low energy processing [18]. For the covalent syntheses, very stable molecular structures are obtained, while non-covalent syntheses give less stable but dynamic molecular structures. Moreover, the simple mixing of two components results in the formation of functional molecular structures. This process needs less energy than covalent syntheses. Materials obtained from molecular self-assembly processes should have dynamic structures, which can respond to external stimuli and environment [6]. Self-assembled SCLCPs have also 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. Another advantage of self-assembled SCLCPs is the ease with which various 'copolymers' can be prepared through the simple mixing of the polymer and low molar mass mesogens [14].

2.2.3.2 Hydrogen Bonding

Hydrogen bonding is one of the important non-covalent interactions in nature [6] . Biopolymers such as nucleic acids, polypeptide, and cellulose have hydrogen bonding groups. The formation and dissociation of the hydrogen bonds for these polymers play an important role in many biological processes [15]. The bonding energies of normal hydrogen bonds are between 10 and 50 kJ/mol. These directional interactions can be expressed as -X…. H- Y- (X, Y = N, O,...). Stable and dynamic molecular complexes can be prepared by simple molecular self-assembly processes using such hydrogen bonding [6]. The use of hydrogen bonds has been demonstrated in building low-molecular-weight liquid crystals as well as liquid-crystalline polymers [20].

While conventional liquid crystalline polymers consist of only covalent bonds the supramolecular polymeric liquid crystalline complexes contain a hydrogen-bonding mesogenic core or a hydrogen-bonding linking moiety connecting the mesogenic molecule to the polymer. There are side chain and main chain type structures.

Main chain type: 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. In figure 2.23 one example of H-bonded main chain liquid crystal polymer can be seen [6].

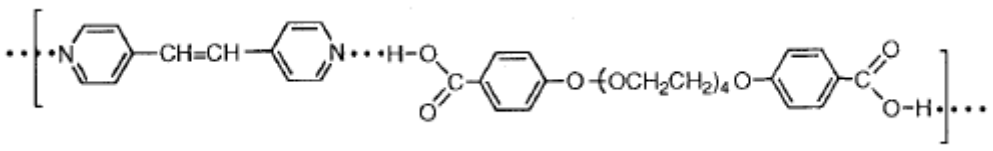


Figure 2.23 : Example of H-bonded main chain liquid crystal polymer.

Side chain type: The first example of supramolecular hydrogen-bonded liquid crystals (side chain) has been prepared by the complexation of a polyacrylate containing a benzoic acid moiety in the side chain with stilbazoles [6].

Well-defined molecular structures with liquid crystalline properties were obtained via a simple self-assembly process between hydrogen-bonding donor and acceptor moieties [19]. Schematic representation of H-bonded side chain liquid crystal polymers can be seen in figure 2.24 [6].

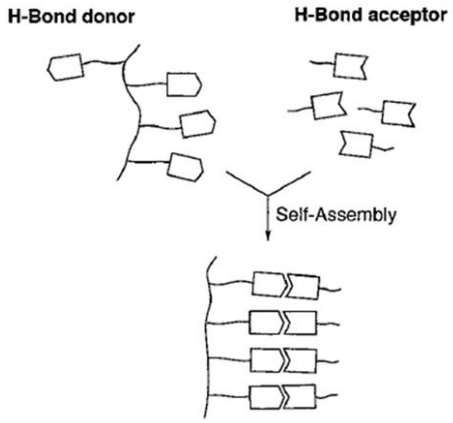


Figure 2.24 : Schematic representation of H-bonded side chain liquid crystal polymers.

Carboxylic and benzoic acid groups were widely used as hydrogen-bond donors while pyridine moieties were commonly used as hydrogen-bond acceptors. Imidazole derivatives are also useful as hydrogen-bonding components in connecting different molecular parts through the formation of stable hydrogen bonds [19]. Some examples of H-bonded side chain liquid crystal polymers can be seen in figure 2.25

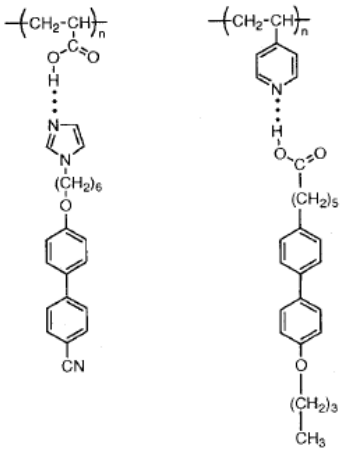


Figure 2.25: Some examples of H-bonded side chain liquid crystal polymers.

2.2.4 Chalcone Polymers

α,β unsaturated carbonyl group is a chalcone group and it has excellent photoreactivity. Polymers with chalcone or either in the backbone or side chain undergo crosslinking through [2π + 2π] cycloaddition of the carbon–carbon double bond upon irradiation with UV light and such polymers are regarded as negative-type photoresists. If polymer is less soluble in a solvent after exposure to UV, is named negative photoresist [21]. The technological applications of photosensitive polymers are applied in the fields of microlithography, photoconductors, nonlinear optical materials, energy exchange materials, liquid crystalline display etc. [22].

These polymers with the properties of high photosensitivity, the ability to form films, good solubility before irradiation, resistance towards solvents, plasmas and etching agents after crosslinking and good thermal stability are very important for commercial photoresist applications [21]. In figure 2.26 one example of chalcone based side chain liquid crystal polymer is shown [23].

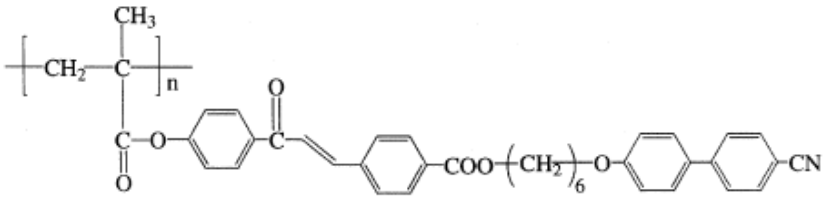


Figure 2.26 : Example of chalcone based side chain liquid crystal polymer.

3. EXPERIMENTAL PART

3.1 Materials and Instruments

3.1.1 Materials

Glycidyl methacrylate (Fluka), 4'-Hydroxybiphenyl-4-carbonitril (Merck), 8-Chloro-1-octanol 98 % (Aldrich), 11-bromo-1-undecanol (Across), Dimethyl sulfoxide (DMSO) (Merck), anhydrous K_2CO_3 (Fluka), NaOH pellets (Merck), , 2,2'-azobis(2-methyl propionitrile) (AIBN) (Acros Organics), 1,4-dioxane (Merck), N,N-dimethylformamide (DMF) (Merck), 1-methyl-2-pyrrolidone (NMP) (Merck), Dioctylamine (Fluka), Diethylamine, (Fluka), Dibutylamine (Aldrich), Ethanol (Merck), Methanol (Riedel-de Haen), phenolphthalein (Merck), HCl 35 % (Labkim), Methacrylic acid (Fluka), 4'-(4-Bromophenyl)acetophenone 97 % (Adrich), 4-Dimethylaminobenzaldehyde (Merck), Toluene (Riedel-de Haen) are used.

3.1.2 Instruments

-Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$.

-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.

-Differantial Scanning Calorimeter (DSC)

Thermal transitions in the polymers was determined by DSC TA Instrument Q1000

-Differential thermal analysis (DTA)

Thermal transitions in the polymers was determined by SII EXSTAR TG/ DTA 6300

-UV–vis spectrophotometer

Perkin Elmer lamda 25 UV–vis spectrophotometer was used .

3.2 Preparation of Liquid Crystalline Reagents

3.2.1 Synthesis of 8-(4-cyanobiphenyl-4'-oxy) octan-1-ol (LC8)

3 g (15 mmol) of 4'-hydroxy-4-biphenylcarbonitrile was in 200 mL of DMSO in the presence of 2 g (14.5 mmol) of K2CO3 anhydrous as acid scavenger. 3.4 mL of (20 mmol) 8-chloro-1-octanol was added drop wise to a stirring mixture under nitrogen at 110 °C. The reaction mixture was heated at 110 ° C for 3 hours. 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 40 °C in vacuum. It was re-crystallized from ethanol. White crystalline product was obtained and dried under vacuum. (Yield: 52 %)

3.2.2 Synthesis of 11-(4-cyanobiphenyl-4'-oxy) undecan-1-ol (LC11)

4'-hydroxy-4-biphenylcarbonitrile (3 g, 15 mmol) was in 200 mL of a DMSO in the presence of (2g, 14.5 mmol) K2CO3 anhydrous as acid scavenger.11-bromo-1-undecanol (3.4 ml, 20 mmol) was added drop wise to a stirring mixture under nitrogen at 110 °C. The reaction mixture was heated at 110° C for 3 hours. 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 40 °C in vacuum. It was re-crystallized from ethanol. White crystalline product was obtained and dried under vacuum (Yield: 52%)

3.3 Preparation of Methacrylate Based Hydrogen Bonded Liquid Crystalline Polymers

3.3.1 Synthesis of the Poly (glycidyl methacrylate) (PGMA)

PGMA was synthesized by the polymerization of glycidyl methacrylate with azobis isobutyronitrile (AIBN) as the initiator. 10 ml (0.075 mol) of glycidyl methacrylate was dissolved in 40 mL of 1,4-dioxane in the presence of 0.165 g (0.001 mol) of AIBN as initiator. The polymerization was carried out at 65 °C under a nitrogen atmosphere for 6 h. After chilling the viscous polymer solution was poured into 200 mL of ethanol.

The polymer was precipitated as a white powder. The solid was collected by filtration and was dried under vacuum at room temperature. (70 % conversion)

3.3.1.1 Modification of PGMA with dioctylamine

0.5649 g (4 mmol) of PGMA was dissolved in 10 ml of NMP and 2.87 g (12 mmol) of dioctylamine was added to the solution. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 80 °C in a termostated oil bath for 1 h. After chilling the mixture was poured into 50 mL of distilled water. The modified polymer was precipitated. The waxy solid was collected by filtration and was washed with water and ethanol respectively. It was dried under vacuum. The yield was 0.76 g.

3.3.1.2 Determination of amine content

For determination of the amine content, 0.0768 g of the polymer sample was left in contact with 10 mL of HCl (0.1 M) for 24 h. After filtration, 2 mL of the filtrate was taken and the acid content of the solution was determined by titration with 0.1 M NaOH solution in the presence of phenolphthalein color indicator. A total amine content of the polymer was calculated as 0.7 mmol g^{-1} polymer.

3.3.1.3 Preparation of hydrogen-bonded side chain liquid crystalline polymer with LC8

The evaporation technique was used for preparing hydrogen-bonded side chain liquid crystalline polymer (HBP3-LC8). For this purpose, 0.22 g of LC8 (0.7 mmol) as a H-bond donor and 0.26 g (0.7 mmol) of dioctylamine modified PGMA as a H-acceptor polymer were dissolved in the NMP. Slow solvent evaporation at room temperature causes phase separation of HB-PLC. The resulting solid was dried under vacuum for 24 h. The white solid product was obtained. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR for spectroscopic characterization.

3.3.2 Modification of PGMA with diethylamine

(1 g, 7mmol) PGMA was dissolved in 10 mL of NMP and 4 mL of diethylamine (35 mmol) is added to that solution. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 80 ° C in a termostated oil bath for 1 h. After chilling the mixture was poured into 50 mL of distilled water. The modified polymer was precipitated.

The product was collected by filtration and was washed with water and ethanol respectively. It was dried under vacuum. The yield was 0.79 g.

3.3.2.1 Determination of amine content

For determination of the amine content, 0.1261 g of the polymer sample was left in contact with 10 mL of HCl (0.1 M) for 24 h. After filtration, 1 mL of the filtrate was taken and the acid content of the solution was determined by titration with 0.01 M NaOH solution in the presence of phenolphthalein color indicator. A total amine content of the polymer was calculated as 3.9 mmol g-1 polymer.

3.3.2.2 Preparation of hydrogen-bonded side chain liquid crystalline polymer with LC8

For this purpose,0.23 g (0.7 mmol) of LC8 as a H-bond donor and 0.15 g (0.7 mmol) of diethylamine modified PGMA as a H-acceptor polymer were dissolved in the DMF. Slow solvent evaporation at room temperature causes phase separation of HBP1-LC8. The resulting solid was dried under vacuum for 24 h. The white solid product was obtained. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR and 1H NMR for spectroscopic characterization.

3.3.2.3 Preparation of hydrogen-bonded side chain liquid crystalline polymer with LC11

For this purpose 0.21 g of LC11 (0.6 mmol) as a H-bond donor and 0.12 g (0.6 mmol) of diethylamine modified PGMA as a H-acceptor polymer were dissolved in the DMF. Slow solvent evaporation at room temperature causes phase separation of HBP1-LC11. The resulting solid was dried under vacuum for 24 h. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR and 1H NMR for spectroscopic characterization.

3.3.3 Modification of PGMA with dibutylamine

1 g of PGMA (7 mmol) was dissolved in 10 ml of NMP and (6 mL, 35 mmol) dibutylamine is added to that solution. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 80 °C in a termostated oil bath for 1 h. After chilling the mixture was poured into 50 mL of distilled cold water and this

mixture was storage in a refrigerator. Solid polymer particles were decantated from water. It was dried under vacuum. The yield was 0.6 g.

3.3.3.1 Determination of amine content

For determination of the amine content, 0.1211 g of the polymer sample was left in contact with 10 mL of HCl (0.1 M) for 24 h. After filtration, 1 mL of the filtrate was taken and the acid content of the solution was determined by titration with 0.01 M NaOH solution in the presence of phenolphatalein color indicator. A total amine content of the polymer was calculated as 3.3 mmol g^{-1} polymer.

3.3.3.2 Preparation of hydrogen-bonded side chain liquid crystalline polymer with LC8

For this purpose, 0.14 g of LC8 (0.45 mmol) as a H-bond donor and 0.12 g of dibutylamine modified PGMA (0.45 mmol) as a H-acceptor polymer were dissolved in the DMF. Slow solvent evaporation at room temperature causes phase separation of HBP2-LC8. The resulting solid was dried under vacuum for 24 h. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR and 1H NMR for spectroscopic characterization.

3.3.3.3 Preparation of hydrogen-bonded side chain liquid crystalline polymer with LC11

For this purpose, 0.15 g of LC11 (0.41 mmol) as a H-bond donor and 0.11 g of dibutylamine modified PGMA (0.41 mmol) as a H-acceptor polymer were dissolved in the DMF. Slow solvent evaporation at room temperature causes phase separation of HBP2-LC11. The resulting solid was dried under vacuum for 24 h. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR and 1H NMR for spectroscopic characterization.

3.4 Preparation of Methacrylic Acid Based Hydrogen Bonded Liquid Crystalline Polymers

3.4.1 Synthesis of Poly (methacrylic acid)

Poly (methacrylic acid) was synthesized by the polymerization of methacrylic acid with azobis (isobutyronitrile) (AIBN) as the initiator. 5 g (58 mmol) of methacrylic acid was dissolved in 15 mL of toluene in the presence of 0.1 g (0.6 mmol) of AIBN

as initiator. The polymerization was carried out at 65 °C under a nitrogen atmosphere for 4 h. The polymer was precipitated in toluene. The solid was collected by filtration and was dried under vacuum at room temperature (conversion 80 %).

3.4.2 Synthesis of chalcone compound

3 g (0.01 mol) of 4'-(4-Bromophenyl)acetophenone was dissolved in ethanol in presence of 0.523 g (0.01 mol) of NaOH. 1.65 g (0.01 mol) of 4-Dimethylaminobenzaldehyde was dissolved in ethanol and it was added drop wise to a stirring solution at 0 °C. The reaction mixture was stirred at room temperature for 24 h. The mixture was poured to distilled water. The solid collected by filtration and re-crystallized from ethanol. The yellow crystalline product was obtained and dried under vacuum (yield 65 %).

3.4.3 Preparation of hydrogen-bonded side chain liquid crystalline polymer

0.032 g (mmol) of Poly(methacrylic acid) as a H-bond donor polymer and 0.145 g (0.37 mmol) of as a H-acceptor were dissolved in NMP. Slow solvent evaporation at room temperature causes phase separation of HB-PLC. The resulting solid was dried under vacuum for 24 h. The characterization of the polymer was performed by using POM for observing liquid crystalline texture, DTA for thermal properties and FT-IR for spectroscopic characterization.

3.5 UV-Visible Characterizations

UV-Visible measurements of chalcone and hydrogen bonded chalcone liquid crystalline polymers were performed in NMP at room temperature.

3.6 Viscosity Measurements

The intrinsic viscosity and inherent viscosity of the polymers were measured on methanol for PMAA and NMP for PGMA solutions with an Ubbelohde viscometer at 25 °C.

4. RESULTS AND DISCUSSION

In this study, hydrogen bonded side chain liquid crystalline polymers were synthesized and characterized properly. Firstly, tertiary amine modified methacrylate based polymers as a hydrogen bond acceptor and two different 4'-(n-hydroxyalkoxy)-4-cyanobiphenyl derivatives as a hydrogen bond donor were prepared. The hydrogen bond donors were synthesized by the reaction of hydroxy halides having different number of methylene unit with hydroxy cyano biphenyl mesogens. The other study, a new chalcone compound as a hydrogen bond acceptor was synthesized. Then, poly (methacrylic acid) was prepared by radical polymerization method. This polymer was used as hydrogen bond donor. The hydrogen bond donors were then attached to the proton acceptors through H-bond interactions between the hydroxyl group of hydrogen bond donors and nitrogen atoms of the hydrogen bond acceptors.

4.1 Synthesis of Hydrogen Bond Donors

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.

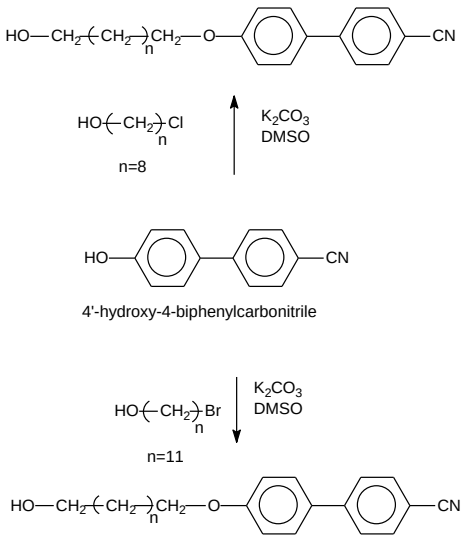


Figure 4.1 : Synthesis of hydrogen bond donors.

The structure of the LC8 and LC11 were characterized by FT-IR and ^{1}H-NMR spectroscopy. Figure 4.2. shows the FT-IR spectrum of LC8 and LC11. Characteristic absorbance bands for all the compounds were identified such as the O-H streching at 3300-3400 cm-1, C-O-C streching at 1250-1050 cm-1 CN streching at about 2200 cm-1 and H-C-H streching at 2900 cm-1 .

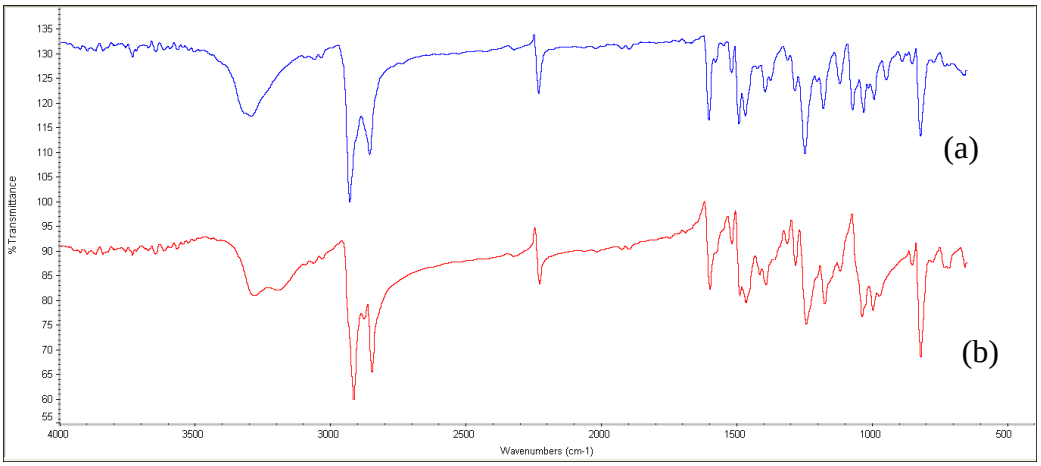


Figure 4.2 : FT-IR spectra of LC8 (a) and LC11(b).

^{1}H-NMR spectra of the LC8 and LC11 exhibit the signals in the range of 2.0-2.1 ppm corresponding to CH_2 protons, 3.6-4.0 ppm corresponding to CH_2-O protons and 7-8 ppm corresponding to aromatic protons. The ^{1}H-NMR spectra of the compounds were given in the Figure 4.3.

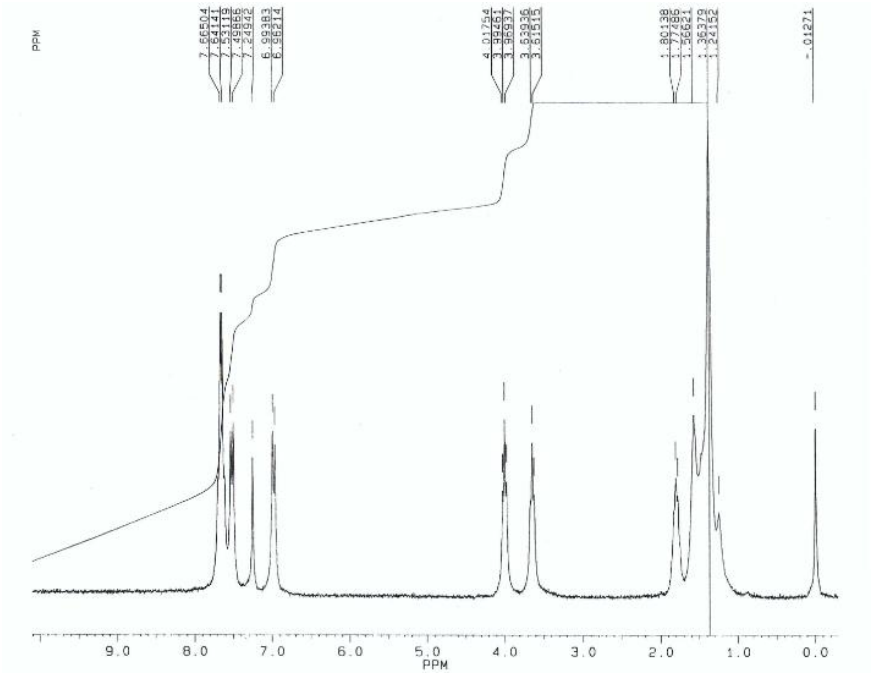


Figure 4. 3: ^{1}H-NMR spectrum of the LC8

4.2 Preparation of hydrogen acceptor polymers

In this study, methacrylate based polymers was synthesized and modified with tertiary amine as a hydrogen acceptor. Preparations and modifications of polymers were given as detailed below.

4.2.1 Preparation of Poly (glycidyl methacrylate) (PGMA)

Glycidyl methacrylate was polymerized by radical polymerization method.This is illustrated in Figure 4.4. Inherent viscosity of the polymer was found as 31.48 cm^3. g^{-1}.

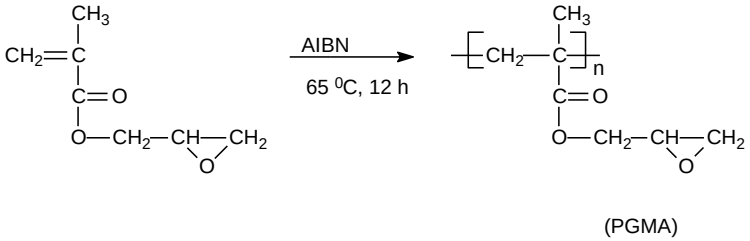


Figure 4.4 : Synthesis of Poly (glycidyl methacrylate).

4.2.1.1 Modification of PGMA with Diethylamine (P1)

PGMA was interacted with excess of diethyl amine at room temperature for 24 h and at 80 °C for 2 h to obtained tertiary amine modified polymer. Synthesis of methacrylate based hydrogen acceptor polymers are given in the Figure 4.5.

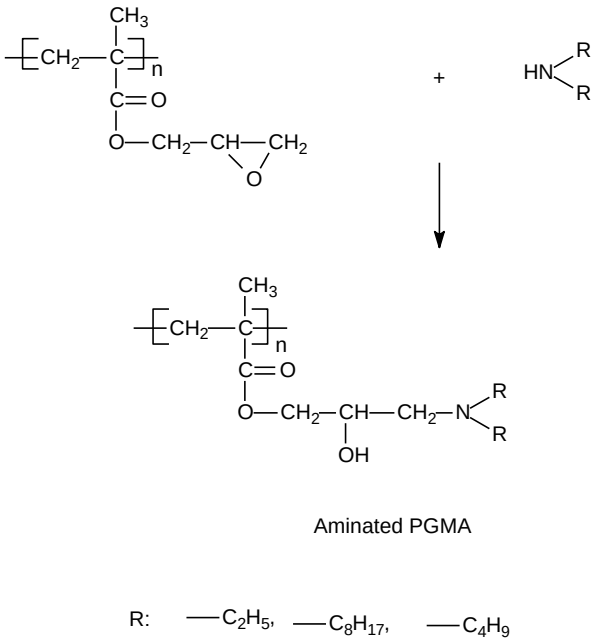


Figure 4.5 : Synthesis of aminated PGMA.

Modified polymer was characterized by FT-IR spectrum. The amine content, determined titrimetricially and was found found as 3.9 mmol.g^{-1}. The FT-IR spectrum of the PGMA (figure 4.6) shows symmetric and asymmetric vibrations of the epoxy rings observed at 1253 and 904 cm^{-1} ,respectively and strong C–O stretching vibrations at 1732 cm^{-1} belongs to carbonyl group. The FT-IR spectra of amine functionalized polymers have absorption bands different from that of the PGMA (Fig 4.7) at 1210–1150 cm^{-1} corresponding to the C–N stretching vibration.

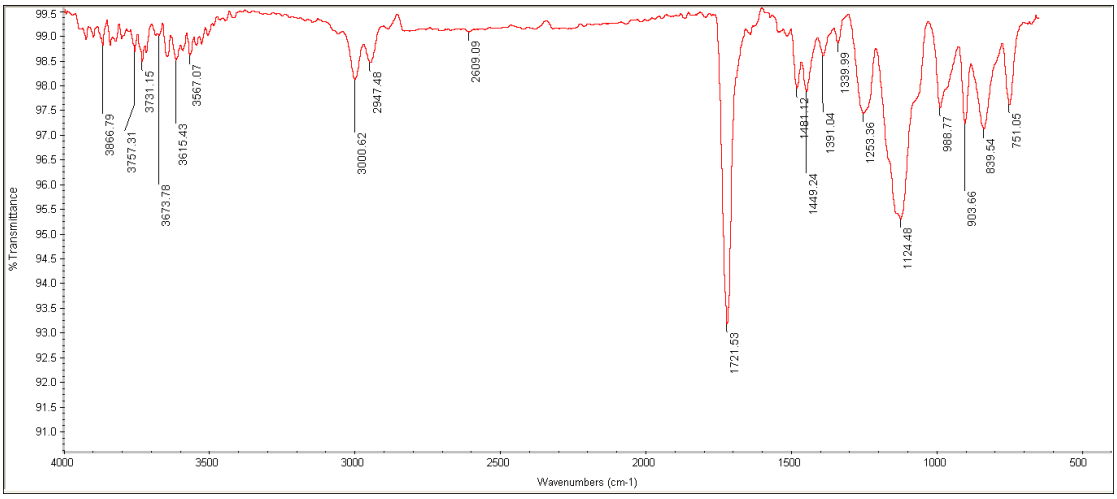


Figure 4.6 : FT-IR spectrum of the PGMA

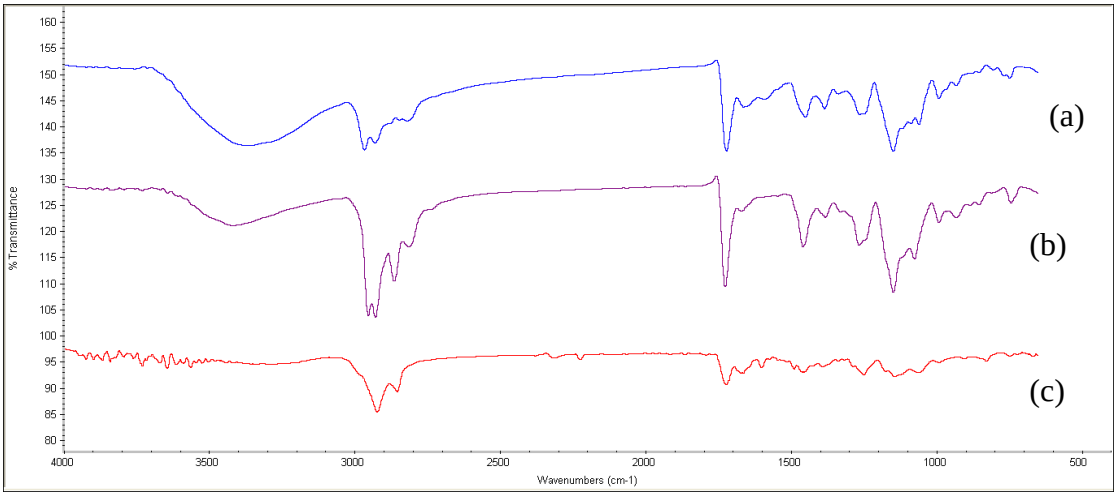


Figure 4.7: FT-IR spectra of (a) P1, (b) P2, (c) P3.

4.2.1.2 Modification of PGMA with Dibutylamine (P2)

PGMA was reacted with excess of dibutyl amine at room temperature for 24 h and at 80 ^{0}C for 3 h to obtained tertiary amine modified polymer.

Modified polymer was characterized by FT-IR spectroscop. The amine content, determined titrimetricially and was found as 3.3 mmol g $^{-1}$ polymer

Also, FT-IR spectrum of dibutyl containing tertiary amine functionalized polymer has absorption bands different from that of the PGMA (Fig 4.7) at 1260–1150 cm^{-1} corresponding to the C–N stretching vibration.

4.2.1.3 Modification of PGMA with Dioctylamine (P3)

PGMA was modified with dioctylamine according to the procedure described above. Modified polymer was characterized by FT-IR spectrum. The amine content, determined titrimetricially and was found as 0.7 mmol g^{-1} polymer.

Also, FT-IR spectrum of dibutyl containing tertiary amine functionalized polymer has absorption bands different from that of the PGMA (Fig 4.4) at 1260–1150 cm^{-1} corresponding to the C–N stretching vibration.

4.2.2 Synthesis of a new chalcone compound as a Hydrogen Bond Acceptor

The chalcone was prepared by reacting N,N-dimethyl benzaldehyde with 4,4'-bromobiphenyl acetophenone (Figure 4.8.)

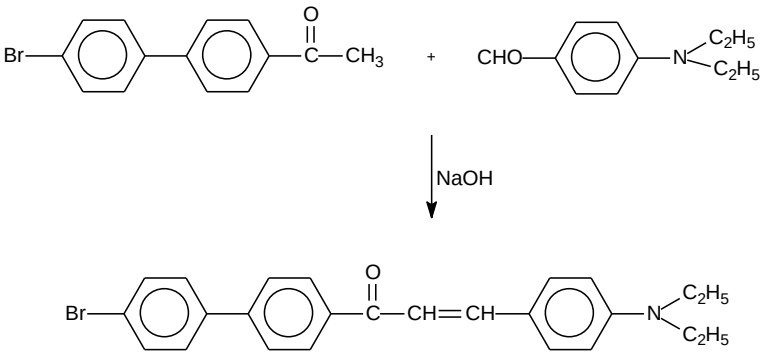


Figure 4.8 : Synthesis of chalcone.

The chemical structures of the polymer was confirmed with FT-IR spectroscopic methods and showed that the appearing peaks corresponded to the structure. The FT-IR spectra of the chalcone compound showed absorption band at 1519 cm^{-1} due to C=C conjugate group of the chalcone moiety Figure 4.9).

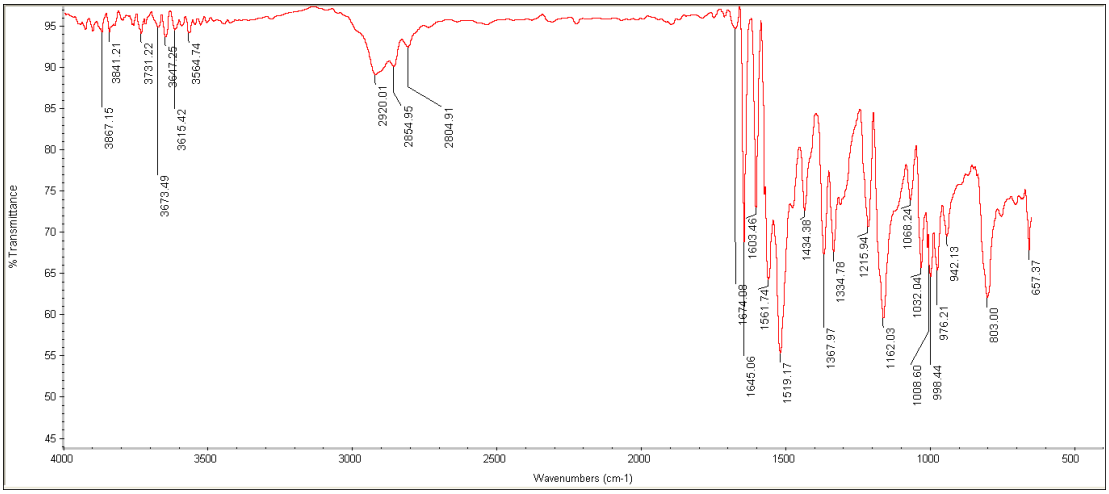


Figure 4.9 : FTIR spectrum of chalcone.

4.3 Preparation of hydrogen bond donor polymer

Poly (metacrylic acid) was used as hydrogen bond donor. Poly (methacrylic acid) was obtained by radical polymerization of methacrylic acid in the presence of AIBN as an initiator and toluene as a solvent. Synthesis of Poly (metacrylic acid) is given below at figure 4.10.

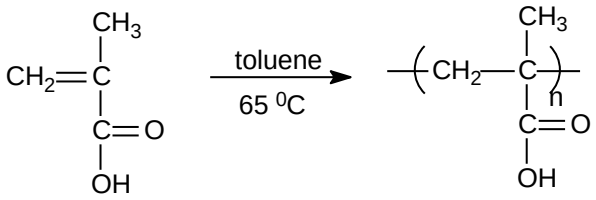


Figure 4.10 : Synthesis of Poly (metacrylic acid).

Mv's of polymer was determined by capillary intrinsic viscometer using an Ubbelohde-type viscometer in methanol solvent at 25 ^{0}C. Mark–Houwink equation is,

$$[\eta] = KM^a \qquad \textbf{(4.1)}$$

Mark–Houwink constant values of the poly (methacrylic acid): k = 2.42 × 10-3 dL g-1, α = 0.51). The plot of ηcp / C versus C was given Figure 4.11. [η] value was obtained from the intercept of figure.

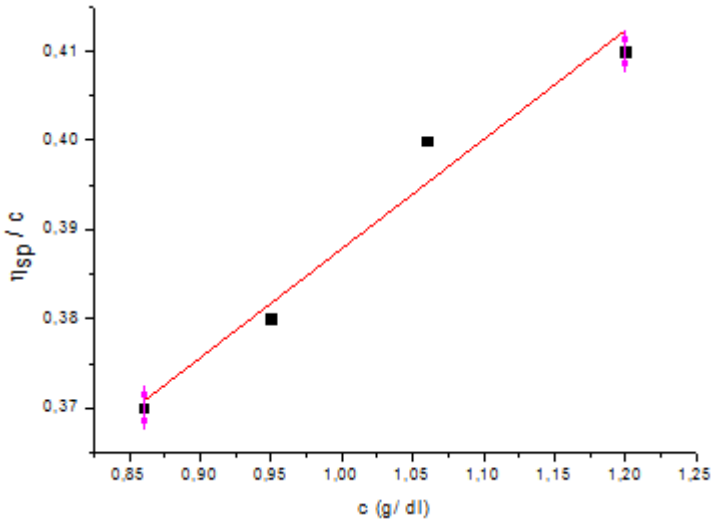


Figure 4.11 : The plot of η_{cp} / C versus C.

M_v value was calculated from equation (4.1) and was found as 10000 g. mol^{-1}

4.4 Preparation of H-bonded Side-chain Liquid Crystalline Polymers

4.4.1 Tertiary aminated methacrylate based side chain liquid crystalline polymers

Diethyl, dibutyl and dioctyl containing tertiary amine pendant methacrylate based polymers and 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 tertiary amine and hydroxyl group of the hydrogen donors is shown below: (figure 4.12)

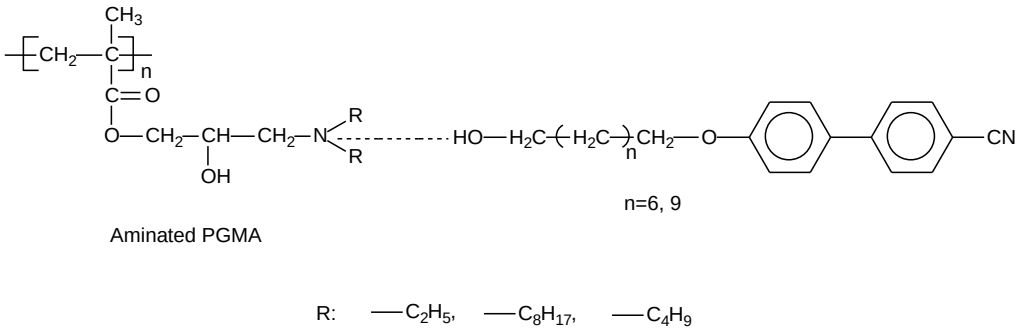


Figure 4.12 : Hydrogen bonding mechanism of HBP-LC.

IR spectroscopy is used to investigate the hydrogen bonds in polymers. Figure 4.13(c) shows the FT-IR spectrum of the polymers. Molecules having both hydrogen bonding donors and acceptors located so that intramolecular hydrogen bonding is favored, display slightly broadened O-H stretching absorption in the 3200 to 3500 cm^{-1} range.

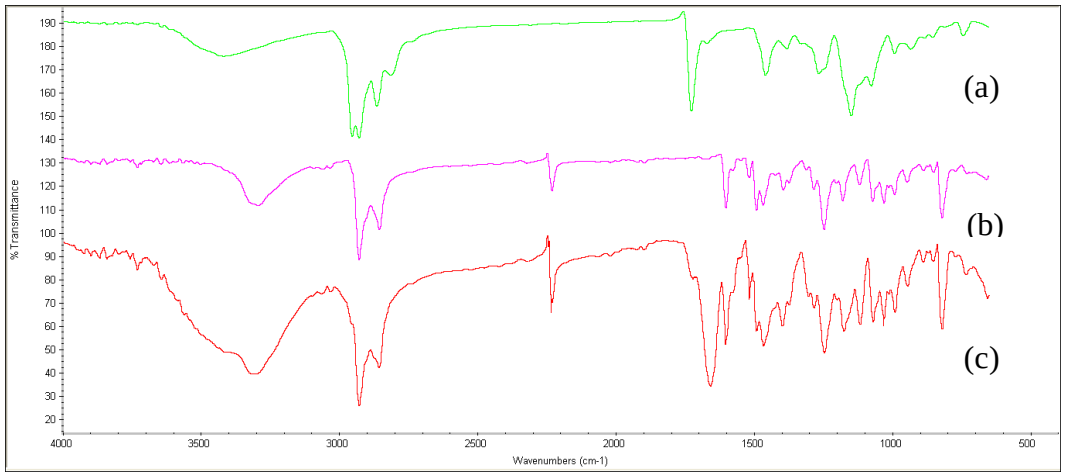


Figure 4.13 : FT-IR spectrum of the (a) P2, (b) LC8, (c) HBP2-LC8.

4.4.2 Interaction of chalcone compound and poly (methacrylic acid) to obtain H-bonded Side-chain Liquid Crystalline polymer

Chalcone based polymers show liquide crystaline properties as described in literatures (23).Tertiary amine containing chalcone compound was interacted with poly (methacrylic acid) in NMP. Structure of prepared H-bonded side-chain liquid crystalline polymer is illustrated in Figure 4.14.

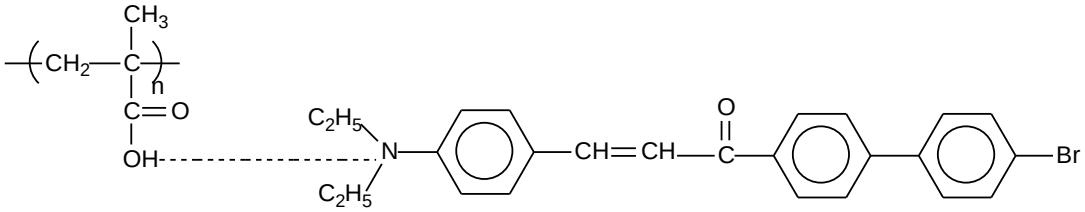


Figure 4.14 : HBMAA-chalcone.

Molecules having both hydrogen bonding donors and acceptors located so that intramolecular hydrogen bonding is favored, so O-H stretching absorption in the 3200 to 3300 cm^{-1} range disappeared (Figure 4.15) .

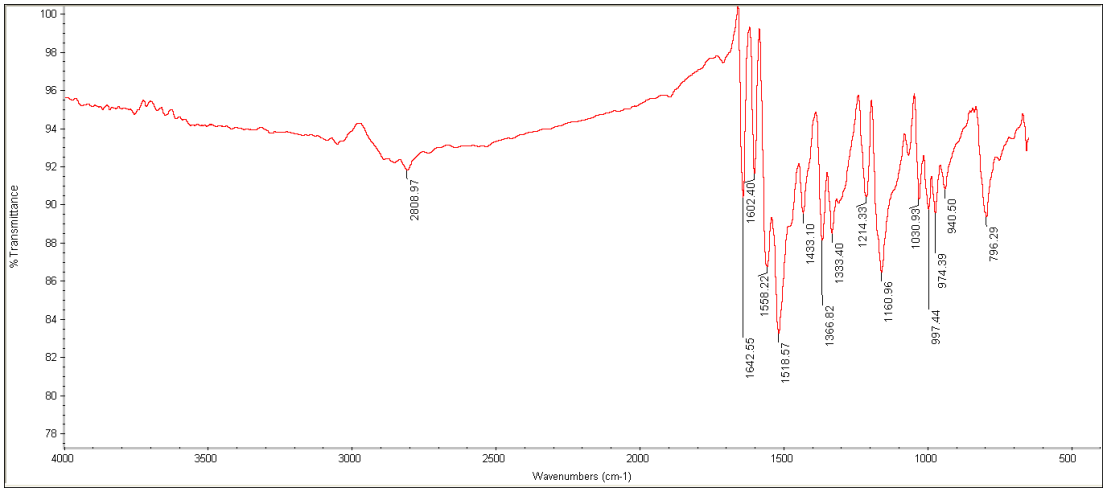


Figure 4.15 : FT-IR of HBMAA-chalcone.

In UV-VIS spectra of the PMA-chalcone and chalcone (Figure 4.16), shows two absorption peaks at 301 and 429 nm are observed due to π*-π transition related to >C=C< of the chalcone moieties

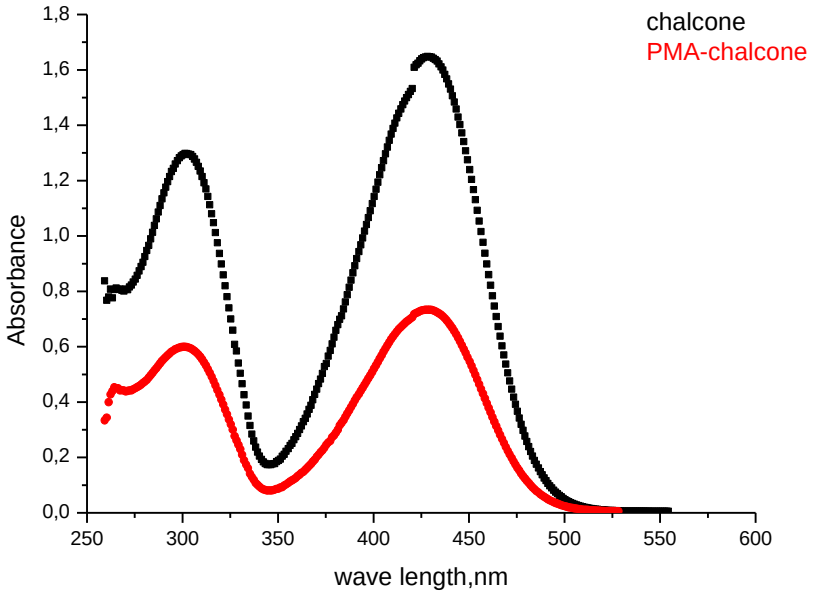


Figure 4.16 : UV-VIS spectrum of HBMAA- chalcone and chalcone.

4.5 Investigation of Thermal and Mesomorphic Properties

4.5.1 Thermal and mesomorphic properties of H-bond donors

To confirm the liquid crystalline nature and to identify the phases of 4'-(hydroxyalkoxy)-4-cyanobiphenyl derivatives (LC8 and LC11) differantial 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 4.1.

Table 4.1: Thermal properties of LC8 and LC11[a]

Code	Phase transitions °C(corresponding enthalpy change J.g-1)[b]
LC8	Cr 76.2 (21.32) Cr 90.7 (42.67) N 112.6 (0.99) I
LC11	Cr 93.3 (161.4) I

[a] Determined by DSC
[b] Cr= crystalline, N= nematic, I= isotropic

Polarized optical microscopy studies show that LC8 exhibit enantiotropic nematic schlieren textures. LC11 do not exhibit liquid crystalline phase. DSC curves and mesophases of LC8 and LC11 are shown in Figure 4.17, 4.18 respectively.

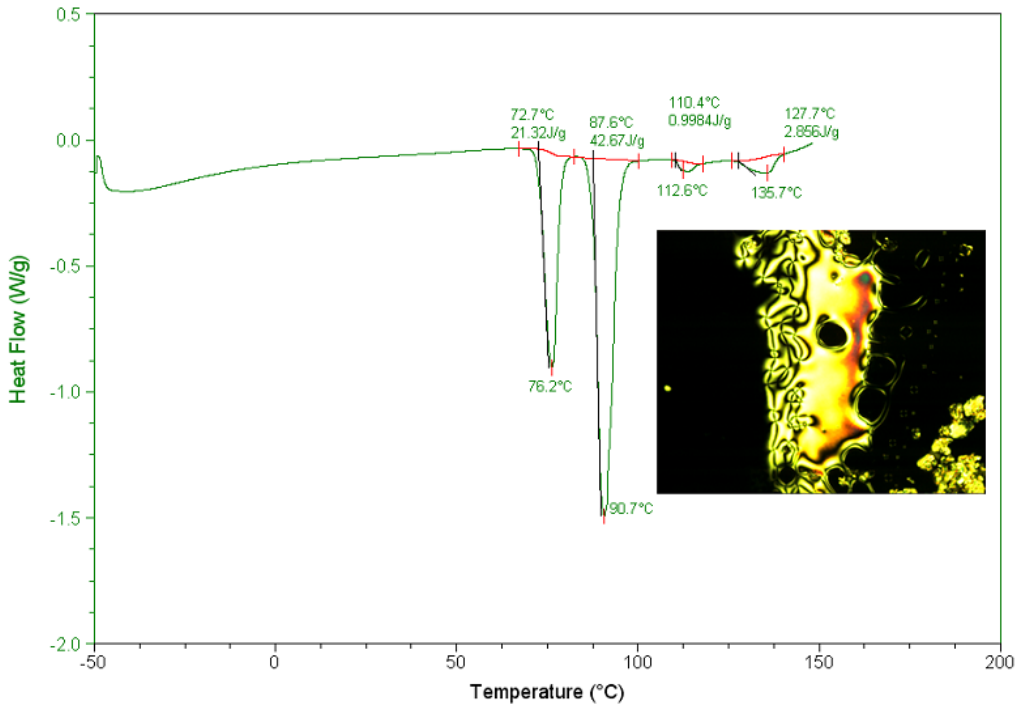


Figure 4.17 : DSC curve of LC8.

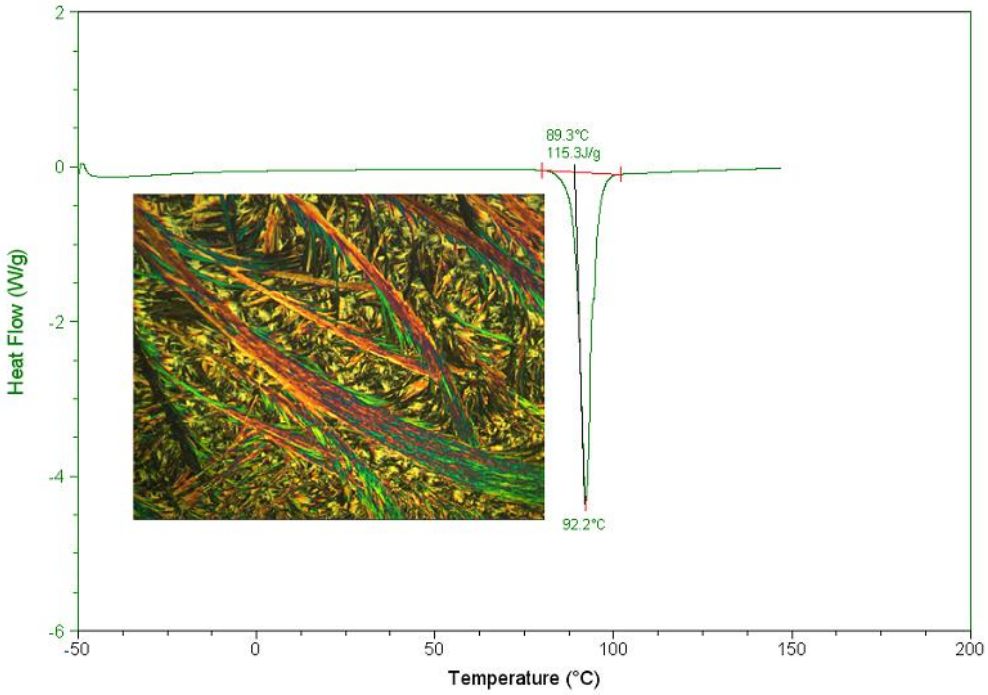


Figure 4.18 : DSC curve of the LC11.

As can be seen from the figure 4.17, LC8 exhibits polymorphic crystalline forms. Polymorphic crystalline forms result from a subtle balance of intermolecular interactions. For most alkoxycyanobiphenyls 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 [25]. For LC8 polymorphism has been reported up to now only during slow evaporation of solvents from acetone–water or diethyl ether–methanol solutions [26]. In this case four different crystalline phases were found [27]: square plate, parallelepiped and needle crystal forms which are metastable, and the most stable crystalline phase that can be found in commercial powder specimens.

4.5.2 Thermal and mesomorphic properties of H-bonded Side Chain Liquid Crystalline Polymers

The phase behavior of all the hydrogen bonded liquid crystalline polymers was studied using a combination of POM and DTA. DTA thermograms were obtained in first heating cycles. The samples were heated with a scan rate of 5°C/min in an N_2 atmosphere. POM (x200) studies also confirmed these DSC and DTA results along with the results of phase transitions.

4.5.2.1 Tertiary aminated methacrylate based side chain liquid crystalline polymers

DTA curve of the HBP1-LC11 (Fig 4.19) and HBP2-LC11 (Fig 4.20) show only one endothermic peak corresponding clearing temperature at 94 °C and 86 °C, respectively.

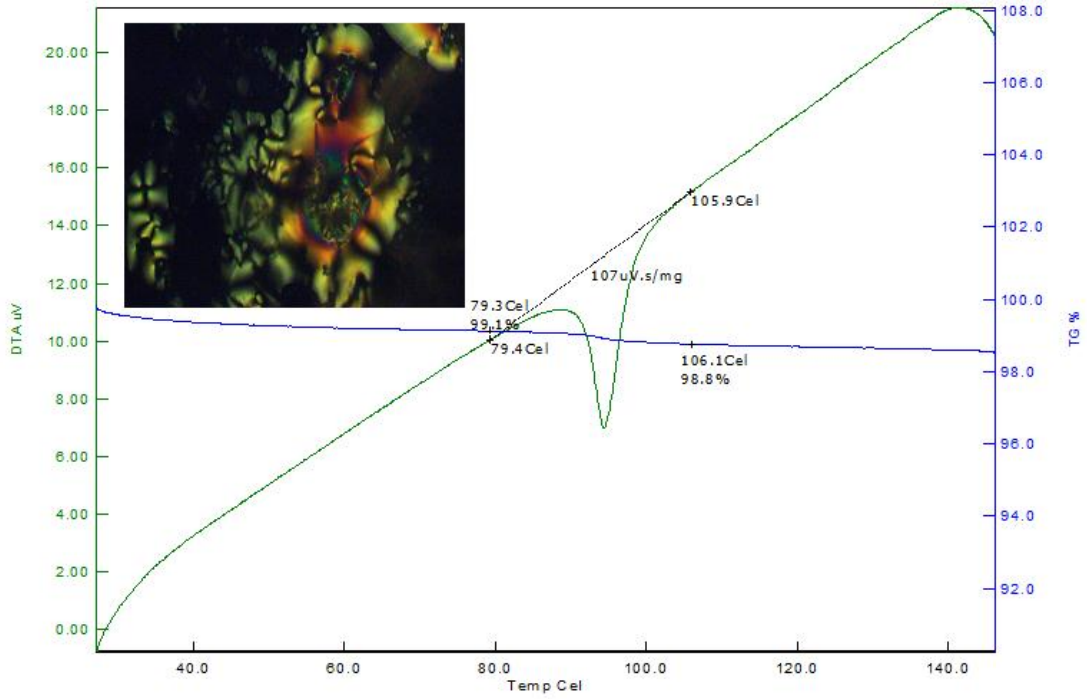


Figure 4.19 : DTA curve of the HBP1-LC11.

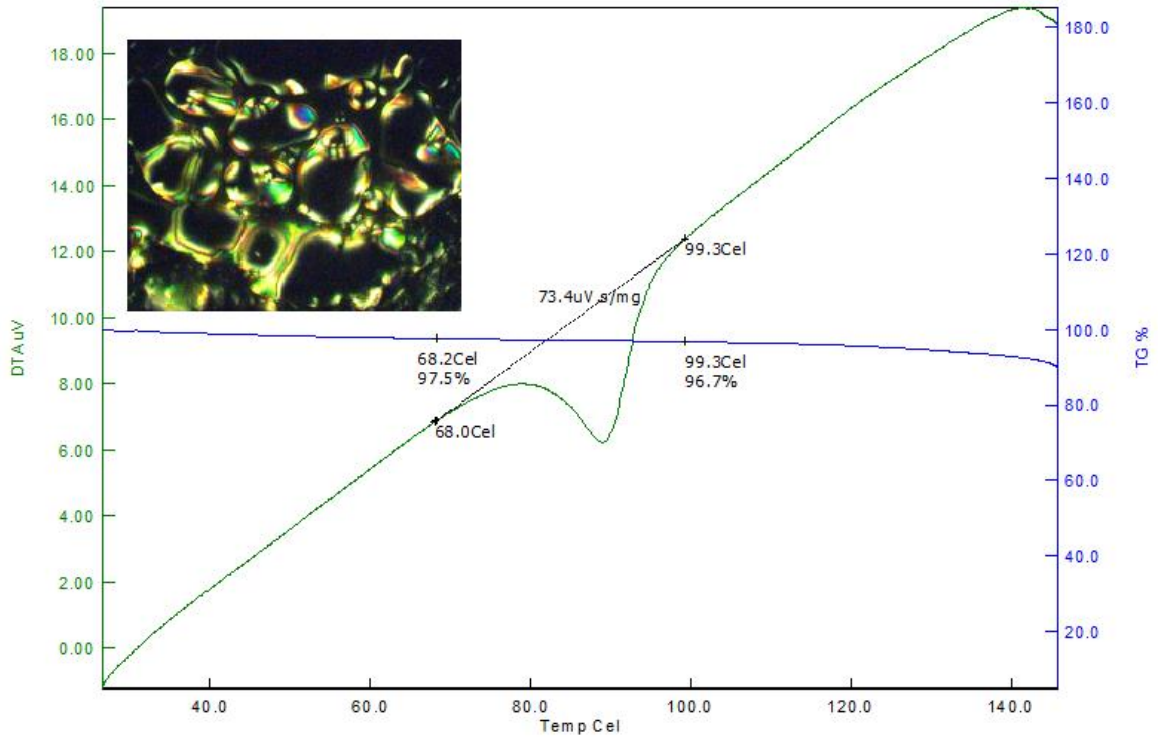


Figure 4.20 : A curve of the HBP2-LC11.

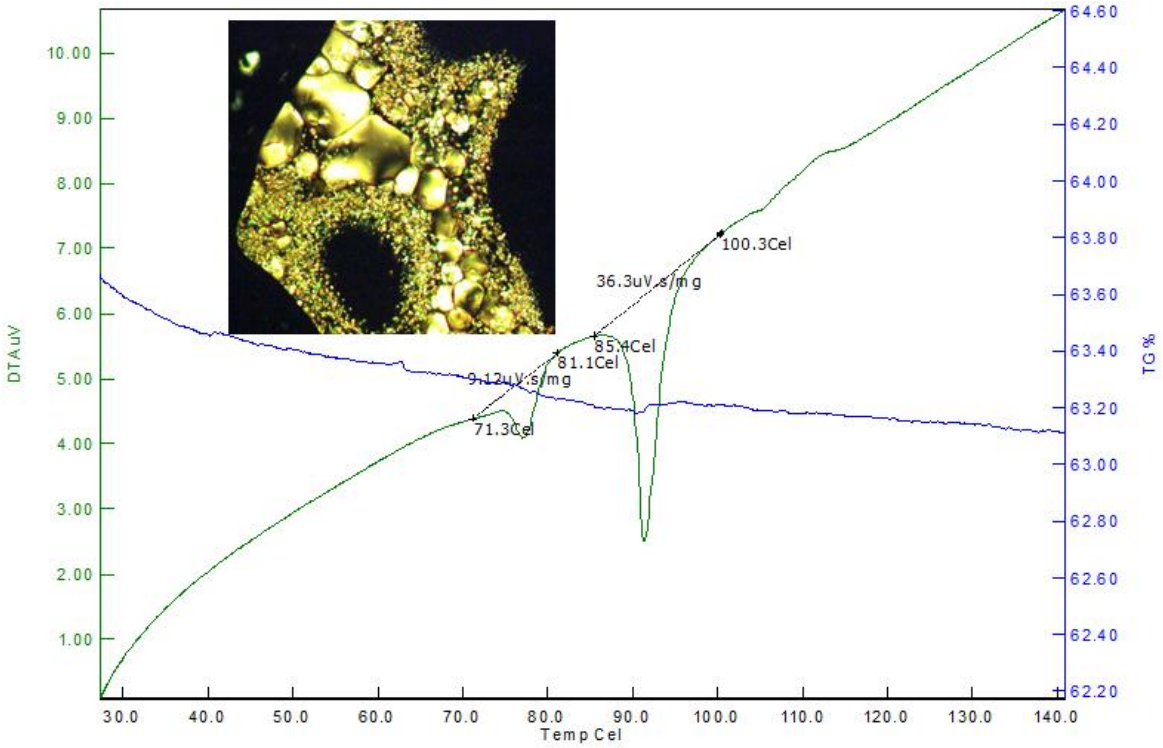


Figure 4.21 : DTA curve of HBP1-LC8.

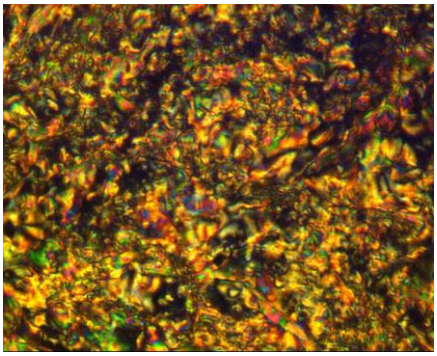
DTA curve of the HBP1-LC8 (Fig.4.21) exhibits two endothermic peak due to the polymorphic crystalline forms of LC8 mesogenic units. The DTA results are summarized in Table 2.

Table 4.2: Thermal properties of HBP-LC[a]

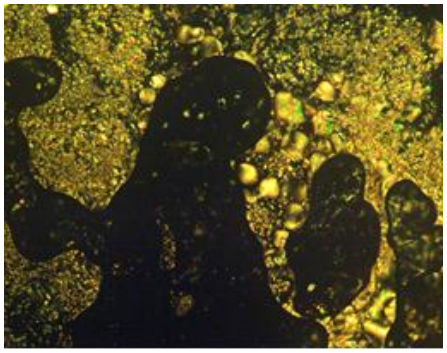
Code	Phase transitions °C(corresponding enthalpy change $KJ.g^{-1}$)[b]
HBP1-LC8	G nd N 105 (0.89) I
HBP1-LC11	G nd N 94 (107) I
HBP2-LC11	G nd N 86 (73.4) I

[a] The transition temperatures determined by DTA.

The polymers were examined by polarizing optical microscopy. All the HBP-LC polymers show enantiotropic nematic mesophases, except HBP2-LC11 which is monotropic (Figure 4.20). A phase separation was observed in the polymers during nematic-isotropic transition. The clearing temperature of HBP2-LC8 and HBP3-LC8 are respectively 90 °C and 105 °C (determined by POM) (Figure 4.22). Despite LC11 does not exhibit liquid crystalline texture, all HBP-LC11 show liquid crystalline mesophases. This proves the formation of hydrogen bonded side chain liquid crystalline polymers.



(a)



(b)

Figure 4.22 : (a) HBP3-LC8, (b) HBP2-LC8.

4.5.2.2 Poly methacrylic acid based side chain liquid crystalline polymers

DTA studies show that the HBMAA-chalcone exhibits only one endothermic peak corresponding to clearing temperature at 227 °C. Glass transition can not be detected (Figure 4.23).

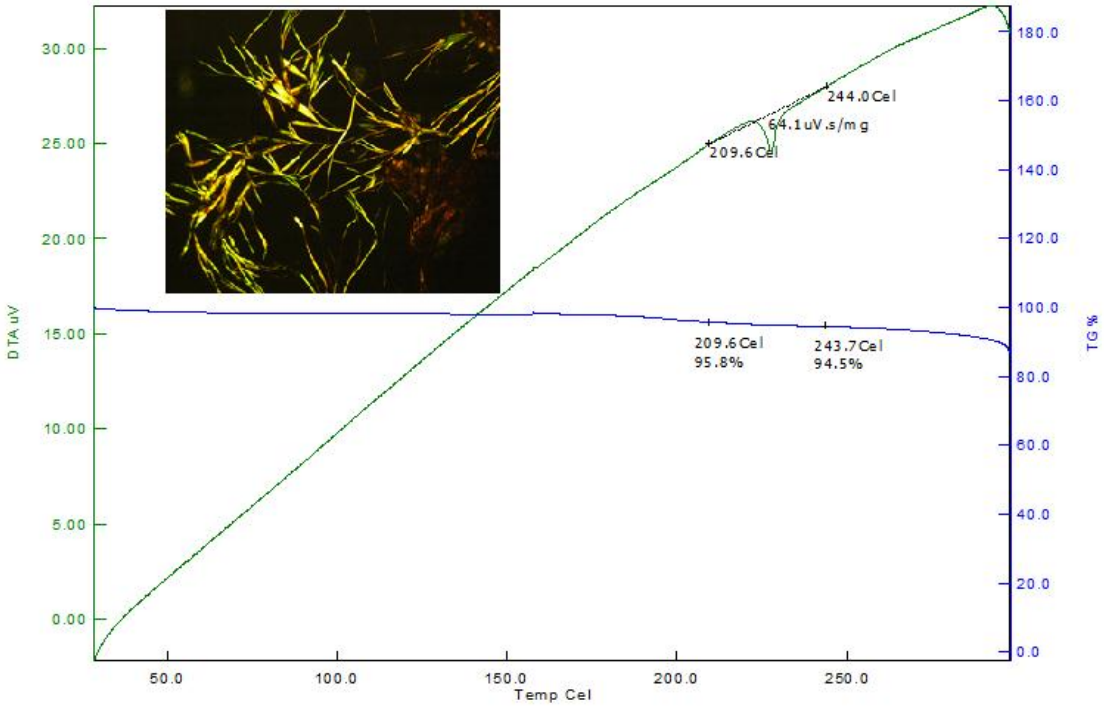


Figure 4.23 : DTA curve of the HBMAA-chalcone.

The polymer was examined by polarizing optical microscopy. It is considered that it has an enantiotropic filament texture.

5. CONCLUSION

In this study, poly (glycidyl methacrylate) was prepared and modified with diethylamine, dibutylamine and dioctylamine to obtain tertiary amine containing H acceptor pendant groups. 8-(4-Cyanobiphenyl-4'-oxy) octan-1-ol (LC8) and 11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol (LC11) were synthesized as hydrogen bond donors.

Also, tertiary amine containing a new chalcone compound was synthesized as H acceptor. Poly (methacrylic acid) was polymerized radical polymerization method. This polymer was used as H donor.

H bond donor and H bond acceptor groups were interacted to prepare H-bonding liquid crystalline polymers.

Obtained H bonding liquid crystalline polymers were characterized by thermal methods, FT-IR and POM measurements.

The DTA transition temperatures, associated enthalpy change (DH) and mesomorphic properties were determined.

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