ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND INVESTIGATION OF A NEW CHALCONE BASED LIQUID CRYSTALINE POLYMER

M.Sc. THESIS

Burak KORKMAZ

Department of Chemistry

Chemistry Programme

MAY 2015

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND INVESTIGATION OF A NEW CHALCONE BASED LIQUID CRYSTALINE POLYMER

M.Sc. THESIS

Burak KORKMAZ
(509131004)

Department of Chemistry

Chemistry Programme

Thesis Advisor: Prof. Dr. Bahire Filiz ŞENKAL

MAY 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YENİ KALGON BAZLI SIVI KRİSTAL POLİMERİN SENTEZİ VE İNCELENMESİ

YÜKSEK LİSANS TEZİ

Burak KORKMAZ
(509131004)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Bahire Filiz ŞENKAL

MAYIS 2015

Burak Korkmaz, **a M.Sc.** student of ITU **Graduate School of Science, Engineering and Technology** student ID **509131004**, successfully defended the **thesis** entitled "**SYNTEHIS AND INVESTIGATION OF A NEW CHALCONE BASED LIQUID CRYSTALINE POLYMER**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Bahire Filiz ŞENKAL** İstanbul Technical University	.....
Jury Members :	**Prof.Dr. Yeşim HEPUZER GÜRSEL** Istanbul Technical University	.....
	Assoc. Prof. Dr. Mustafa OKUTAN Yıldız Technical University	.....

Date of Submission : 04th May 2015
Date of Defense : 25th May 2015

To my beloved family,

Irreplaceable friends

And to The List,

FOREWORD

After 2 years, here again I found myself writing a new foreword for another ending. Since every study can be considered as a journey, every study changes person, for better or worse. Firstly, of course I would love to thank my supervisor Prof. Dr. B. Filiz Şenkal for resolutely letting me in when I was confused and unwelcomed, and for her gracious support, encouragement and guidance during the whole study. She was kind, cheerful and caring as well as inspiring. I also thank to Prof. Dr. Yeşim Gürsel for her help through this research, for her ideas, directives and sympathy. She helped me from the point where I began. I thank to both Dr. Erdem Yavuz and Re. Ass. Gülçin Torunoğlu Turan for their help and support; they guided me and supported me even when they didn't have to. I would not be able finish this thesis without their guidance and help. Esma Ahlatçıoğlu was there as an experienced and kind-hearted friend who was never reluctant to help and share at unforgettable times, I also owe her my debt of gratitude. Re.Ass. Ufuk Saim Günay and Pınar sinem Omurtag was helping me while I was unable to see that change is not as hard as I thought and they helped me to let things go. I thank both of them, for their friendship and guidance.There were lots of things that aren't here right now but İrem Çokgez was always with me and she was my true companion through this. We have done everything together. Without her, these 2 years would have been boring as hell. I am so glad that I had her at my side. I thank her for all.

Apart from everything else one always requires someone to call, someone to help him escape from reality or to gossip with, basically to be friends with. For this, I want to thank İdil Melis Dinç for answering my calls, for helping me sneak out of boring stuff, for being a wonderful friend. I thank to Eren Kalem and Burcu Günay since they both are unique and are at my side as my friends. Every second I spend with these three awesome person, I find things that shouldn't and couldn't be described. They are my bespoken super heroes and irreplaceable by all means.I also thank to Sinem Yaşar for being around with her joyful nature and her friendship. Burcu Sıla Candan was a sweet light of my road, through this period, I thank her for being there. I must happily thank to Ayla Karlı, who made me fall in love with Chemistry in the blink of an eye.
My family is the sole reason of everything, that's why I can only thank God for having them.

It was strange but beautiful and pushing 2 years, now it ends. Still it is not endings that are sad but absence of people you once thought you don't want to be lack of. However, experiencing this absence becomes liberating.

May 2015

Burak KORKMAZ
(Chemist)

TABLE OF CONTENTS

Page

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
DSC	**:** Differential scanning calorimetry
NMP	**:** *N*-Methyl-2-pyrrolidone
DMF	**:** Dimethylformadie
LC8	**:** 8-(4-cyanobiphenyl-4'-oxy) octan-1-ol
LC11	**:**11-(4-cyanobiphenyl-4'-oxy) undecan-1-ol
Chalcone	**:** 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one
HBP	: Hydrogen bonded polymer

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYNTHESIS AND CHARACTERIZATION OF METHACRYLATE BASED HYDROGEN BONDED LIQUID CRYSTAL POLYMERS

SUMMARY

Side chain liquid crystalline polymers (SCLCPs), which combine the unique properties of low-molar mass liquid crystals and polymers, have been the subject of intensive research mainly due to their interesting electrical and optical properties which makes them good candidates for applications in microelectronic devices ranging from optical data storage and nonlinear optics. Side chain liquid-crystalline polymers (LCPs) are usually prepared by covalently linking rigid mesogens to a polymer backbone through flexible spacers.

In thesis, new chalcone compound and its methacrylate monomer were synthesized aand characterized. 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one as a chalcone compound was synthesized by using Claisen-Schmidt method. 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was reacted with methacryloyl chloride to obtain monomer. This chalcone based monomer was polymerized by using free radical polymerization method. Chalcone side chain liquid crystalline polymer was prepared by using intermolecular hydrogen bonding concept. For this purpose, firstly H-bonded crystalline polymer was synthesized starting from tertiary amine containing methacrylate based polymers as H-bond acceptor and 4'-(-hydroxyalkoxy)-4-cyanobiphenyl derivatives as H-bond donor.

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.

Chalcone based polymer 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 of the polymer and hydroxyl group of the hydrogen donors.

The hydrogen bonded methacrylate based polymers were characterized by FT-IR spectroscopy, DSC 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.

The phase behavior of all the hydrogen bonded liquid crystalline polymer was studied using a combination of DSC and POM. DSC thermograms were obtained in second heating cycles. The samples were heated with a scan rate of 10°C/min in an N_2 atmosphere. POM (X200) studies also confirmed DSC results along with the results of phase transitions.

Also, 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was interacted with LC8 and LC11 to compare with liquid crystaline polymers.

YENİ KALGON BAZLI SIVI KRİSTAL POLİMERLERİN SENTEZİ VE İNCELENMESİ

ÖZET

Sıvı kristallerin keşfi genel olarak 1888 yılına Avusturyalı botanist Friedrich Reinitzer'ın ilk raporlarına dayanmaktadır. Reinitzer'ın ilk çalışmaları klosterol temelli bir bileşik üzerineydi. Yapının molekül ağırlığını hesaplamaya çalışırken, erime noktasını da bulması gerekti ki yapının saflığından emin olabilsin. Erime noktası için gerekli çalışmalara başlamışken şaşırtıcı ve umut kırıcı bir şekilde iki tane faz değişim noktasının varlığını tespit etti. Kolesteril benzoat kristalleri 145.5 °C'da önce eriyip dumanlı bir sıvı halini alıyor ardından da 178.5 ºC'da billur bir sıvı halini alıyordu. Aynı şekilde bu yapıların geriye dönewrken, donarken de iki noktada değişim geçirdiğini gözlemledi. Bu açıklayamadığı ilginç fenomen sonucunda elindeki örnekleri incelemesi için Alman bir kimyager olan Otto Lehnmann'a yolladı.

Bu gelişmeler genel olarak sıvı kristaller mefhumunun doğmasıyla sonuçlanmıştır ve genel olarak sıvı kristaller katı ve sıvı fazlar arasında, belli moleküllerin gösterdiği ayrı bir faz olarak tanımlanmıştır. Bu faz ne katı gibi rijit ve düzenli bir özellik göstermektedir ne de sıvı gibi düzensiz ve dağınık düzenlenmektedir. Bu sebeple ikisinden de ayrı olarak tanımlanmaktadır.

Bir molekülün sıvı kristal özelllik gösterebilmesi için gerektirdiği özellikler vardır. Bu özellikler genel olarak bakıldığında aromatiklik şartlarını andırır. Molekülün düzlemsel olması gerekliliği, yapının üzerinde elektronların serbestçe hareket edebileceği bir konjugasyon hattının var olması,

Düşük molekül ağırlıklı sıvı kristallerin ve polimerlerin özgün özelliklerini bir araya getiren Yan Zincir Sıvı Kristal Polimerler, onları optik veri toplamadan tutun da doğrusal olmayan optik alanına kadar mikroelektronik cihaz uygulamalarında iyi adaylar olmalarını sağlayan ilgi çekici elektriksel ve optik özelliklerinden ötürü yoğun araştırmaların konusu olmaktalar. Yan Zincir Sıvı Kristal Polimerler genellikle rijid mezojenlerin polimer ana zincirine, bir ara yapı üzerinden kovalent bağ ile bağlanmasıyla elde edilir.

Bu tezde, yeni bir kalgon bileşiği ile metakrilat monomeri sentezlendi ve karakterize edildi. Kalgon bileşiği olarak 1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on, Claisen-Schmidt metodu kullanılarak sentezlendi. 1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on, metakriloil klorür ile reaksiyona sokularak bu monomer elde edildi. Bu kalgon temelli monomer serbest radikalik polimerizasyon kullanılarak polimerleştirildi. Kalgon Yan Zincir Sıvı Kristal Polimer, moleküller arası hidrojen bağı kurularak hazırlandı. Bu amaçla, ilk aşamada Hidrojen Bağlı Kristal Polimer, hidrojen akseptör olarak tersiyer amin taşıyan metakrilat temelli bir polimer ve

hidrojen donör olarak da 4'-(-hidroksialkoksi)-4-siyanobifenil türevleri kullanılarak hazırlandı.

1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on bileşiğinin sentezi şu şekildedir.

1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on, katalizör olarak NaOH ortamında Claisen-Schmidt metodu kullanılarak, p-hidroksi asetofenon ve 4-piridin karboksialdehit bileşiklerinden sentezlenmiştir. Bu reaksiyon klasik bir aldol kondenzasyonu reaksiyonudur. Elde edilen bileşik karakterize edilip varlığından emin olunması için FT-IR ile analiz edilmiştir. Bu analiz elde edilmiş olan bileşiğin hedeflenen bileşik olduğunu doğrulayacak sonuçlar vermiştir. 1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on'un FT-IR spektrumu, 2898 cm^{-1} bölgesinde (–CH_2–) piklerini ; 1658 cm^{-1} bölgesindeki ketonik yapıyı ispatlayan pikleri; 1587 cm^{-1} bölgesindeki olefinik -C=C konjuge kalgon piklerini; 1510,1418 ve 1462 cm^{-1} bölgesindeki de aromatik -C=C piklerini açıkça göstermektedir.

4-(3-(piridin-4-il)-akriloil)-fenil metakrilat bileşiğinin sentezi şu şekildedir.

1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on bileşiği metakriloil klorür bileşiği ile çözücü olarak THF'in kullanıldığı oratımında reaksiyona sokulmuştur. Bu reaksiyon esnasında açığa çıkan asidik yapıları tutması için trieti,l amin bileşiği asit-tutucu olarak kullanılmıştır. Reaksiyon sonucun açığa çıkan bileşiğin adı 4-(3-(piridin-4-il)-akriloil)-fenil metakrilat'tır.

4-(3-(piridin-4-il)-akriloil)-fenil metakrilat karakterize edilip varlığından emin olunması için FT-IR ve^{1}H-NMR ile analiz edilmiştir. Analiz sonuçlarındaki veriler yapıyı doğrular nitelikte elde edilmiştir. 1722 cm^{-1} bölgesind çıkan bant açıkça ester grubunun varlığını göstermektedir. Ayrıca 3000-3100 cm^{-1} bölgesindeki pikler de vinil grubuna ait olduğundan bu fonksionun da yapıdaki varlığı ispatlanmıştır.

4-(3-(piridin-4-il)-akriloil)-fenil metakrilat yapısı ayrıca ^{1}H-NMR ile karakterize edilmiştir. NMR spektrumundan elde edilen verilere göre, 8.72–7.27ppm aralığında 11H, Ar-H ve olefinik CH=CH pikleri bu fonksiyonların yapıdaki varlıklarını ispatlamaktadır. Ayrıca 6.40 (1H,CH2=), 5.83 (1H, CH2=), 2.08 (s, 3H, CH3) piklerini de bu yapıları kanıtlamaktadır.

Hidrojen bağ donörlerinin sentezi şu şekildedir.

8-(4-Siyanobifenil-4'-oksi) oktan-1-ol (LC8) ve 11-(4-Siyanobifenil-4'-oksi) undekan-1-ol (LC11) sentezlendi. LC8 ve LC11 yapıları, FT-IR ve 1H-NMR spektropileri kullanılarak karakterize edildi.

3 g (15 mmol), 4'-hidroksi-4-bifenilkarbonitril, 200 mL DMSO içinde ve asit tutucu olarak görev alan 2 g (14.5 mmol) K_2CO_3 varlığında 8-kloro-1-oktanol ile tepkimeye sokulmuştur. 3.4 mL (20 mmol) 8-kloro-1-oktanol 110 °C derecede azot gazı varlığında damlatılarak karşımın üzerine ilave edilmiştir. . Reaksiyon karışımı 110 ° C derecede 3 saat boyunca karıştırılmıştır. Bu işlemden sonar karışım damlatılarak 400 mL, 10 % NaOH çözeltisine oda sıcaklığında ilave edilip süzülmüştür.. Sonuç ürün 40 °C derecede vakum altında kurutulmuştur. Ardından etanolda tekrar kristallendirilmiştir. Beyaz kristaller vakum altında elde edilmiştir.

8-(4-Siyanobifenil-4'-oksi) oktan-1-ol (LC8) bileşiği bu şekilde elde edilmiştir. 11-(4-Siyanobifenil-4'-oksi) undekan-1-ol (LC11) bileşiğinin sentezi de aynı şekilde gerçekleştirilmiştir. Bileşikler arasındaki tek fark yapılarındaki alkil zincirlerinin birinin diğerinden (LC11-LC8) 3 karbon daha uzun olmasıdır.

8-(4-Siyanobifenil-4'-oksi) oktan-1-ol (LC8) bileşiği ve 11-(4-Siyanobifenil-4'-oksi) undekan-1-ol (LC11) bileşiği diğer moleküller gibi FT-IR ve ^{1}H-NMR spektroskopileri ile karakterize edilmişlerdir. LC8 ve LC11 bileşiklerinden elde edilen FT-IR spektrumu göstermektedir ki 3300-3400 cm^{-1} bölgesindeki karakteristik –OH pikleri, 1250-1050 cm^{-1} bölgesindeki eter pikleri, 2200 cm^{-1} bölgesindeki CN pikleri, 2900 cm^{-1} bölgesindeki H-C-H pikleri yapının abeklendiği gibi ortaya çıktığını gösteriyor.
8-(4-Siyanobifenil-4'-oksi) oktan-1-ol (LC8) ve 11-(4-Siyanobifenil-4'-oksi) undekan-1-ol (LC11) bileşiklerinin aydınlatılmasında aynı zamanda ^{1}H-NMR spektroskopisinde verdikleri pikler de yapıların beklendiği gibi olduğunu göstermiştir. LC8 ve LC11 bileşikleri 2.01-2.1 ppm bölgesinde $–CH_2$ protonlarının; 3.6-4.0 ppm bölgesinde CH_2-O protonlarının ve 7-8 ppm aralığında da aromatik protonların piklerini göstermişlerdir ^{1}H-NMR spektrumunda

Kalgon temelli sıvı kristal polimerlerin sentezlenmesi şu şekildedir.

Kalgon temelli polimer ve LC8 ile LC11, hidrojen bağlı sıvı kristal oluşturmak üzere hidrojen bağı akseptörü ve donörü olarak görev aldılar. Yan zincir sıvı kristal polimer yapısı, moleküller arası hidrojen bağının, polimerdeki amin türevinin azot atomu ile hidrojen donörlerinin hidroksi grupları arasında kurulması ile oluştu

Hidrojen bağlı metakriklat temelli polimerler FT-IR spektroskopisi, DSC ve POM metodları ile karakterize edildi.The hydrogen bonded methacrylate based polymers were characterized by FT-IR spectroscopy, DSC and POM methods. Polimerlerin FT-IR spekrasına göre, hidrojen bağ donörleri ve akseptörleri molekülleri arası hidrojen bağının kurulmasına uygun şekilde düzenlendi, O-H gerilmesi 3200 ile 3500 cm^{-1} arasında hafifçe yayılmış pik ile görüldü.

Hidrojen bağlı sıvı kristal polimerlerin tüm faz geçişleri DSC ve POM ‘un birlikte kullanılması ile incelendi. DSC termogramları ikinci ısıtma döngülerinde elde edildi. Örnekler N_2 altında, 10°C/dak. hızında ısıtıldılar. POM (X200) çalışmaları ayrıca göstemektedir ki DSC sonuçları faz geçişleri ile uyumludur.

Ayrıca, 1-(4-hidroksifenil)-3-(piridin-4-il)prop-2-en-1-on da LC8 ve LC11 ile sıvı kristal polimerlele kıyaslamak amacı ile kıyaslandılar.

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 liquids cystals

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].

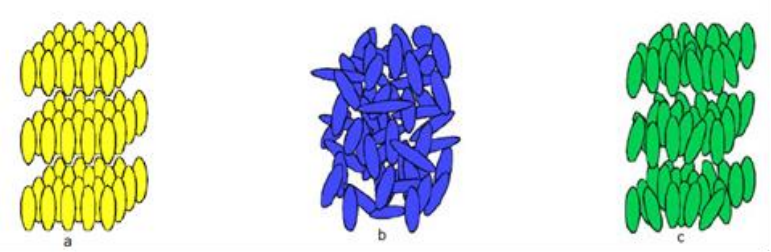


Figure 2.1 : Arrangements (a) in crystal (b) in a liquid (c) in a liquid crystal.

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].

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

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.

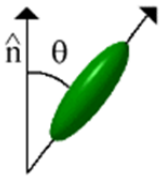


Figure 2.2 : Angle between director and long axis of molecule.

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].

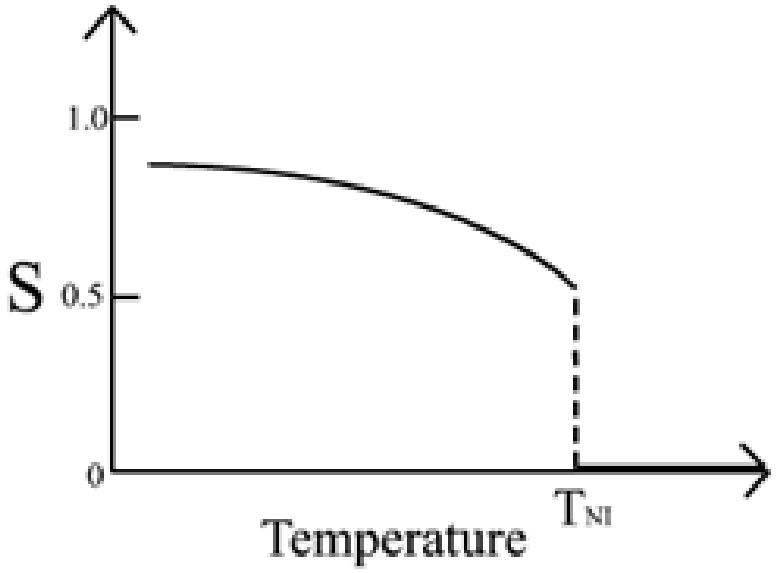


Figure 2.3 : Graphical representation of order parameter versus temperature.

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 Tcl or Ti [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].

2.1.3.1 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].

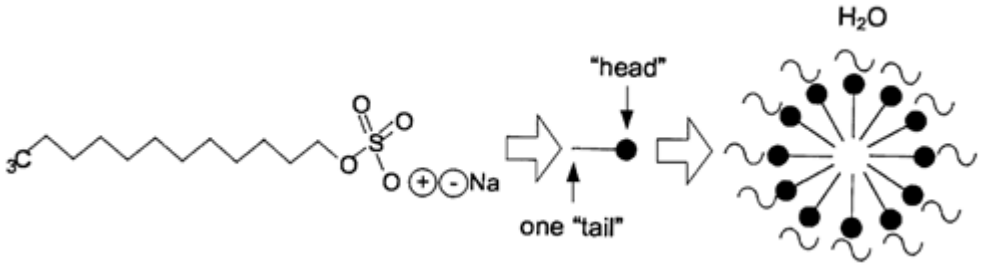


Figure 2.4 : Sodium dodecylsulfate (soap) forming micelles.

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 [3,10].

2.1.3.2 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 (C_nH_{2n}+1), alkoxy (C_nH_{2n}+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].

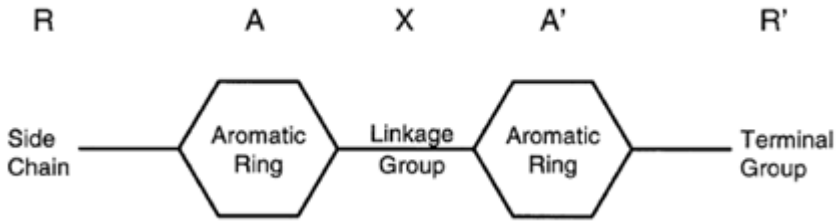


Figure 2.5 : Molecular structure of typical calamitic liquid crystal.

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 2.6 shows the nematic phases. Figure 2.7 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.

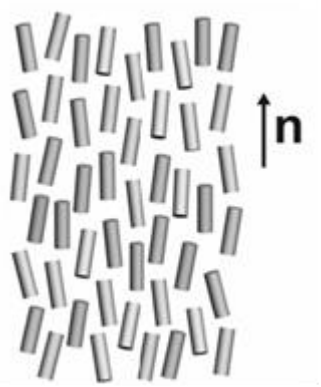


Figure 2.6 : Nematic phases.

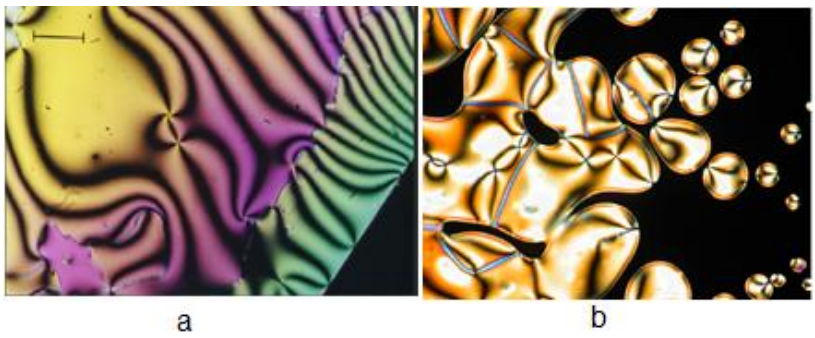


Figure 2.7 : (a) Schlieren Texture, (b) Droplets of Nematic Phases.

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 2.8). 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 2.8). 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 2.9 fan shaped structure of SmA and broken fan shaped structure of SmC are shown [1,12].

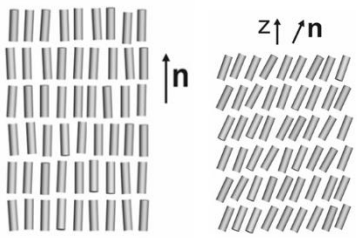


Figure 2.8 : (Left) Smectic A liquid crystal,(Right)SmC liquid crystal.

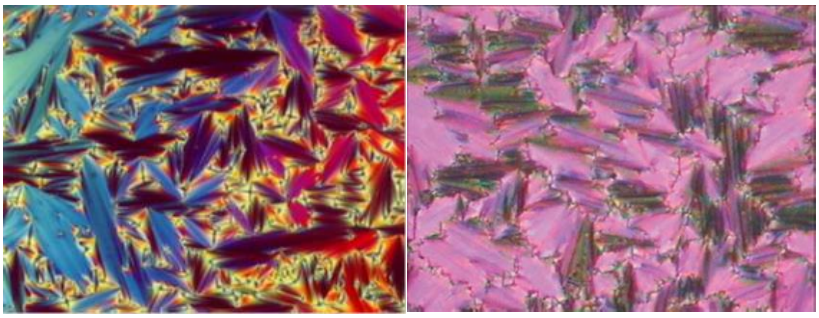


Figure 2.9 : (Left) Fan shaped SmA, (Right) broken fan shaped,SmC.

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 2.10). 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 2.11 shows the fingerprint texture of cholesteric phase seen at POM [12].

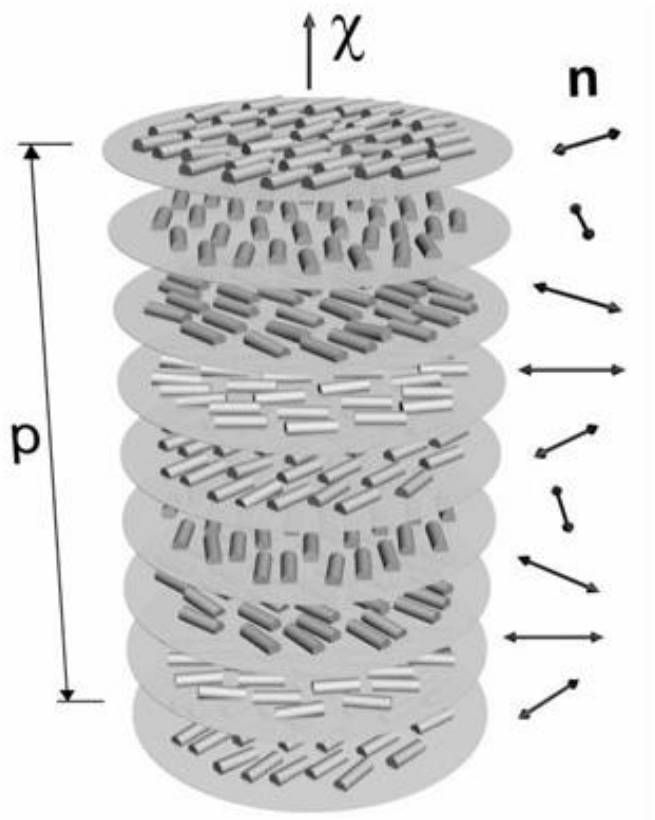


Figure 2.10 : Chiral nematic phase.

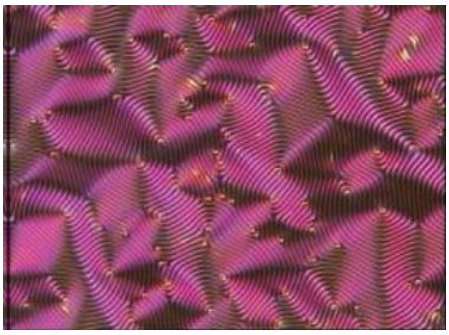


Figure 2.11 : Fingerprint texture of chiral nematic phase.

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 2.12 : Chiral SmC* phase.

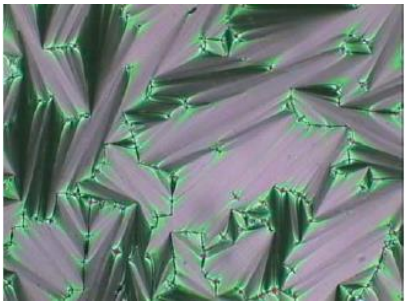


Figure 2.13 : Fan-shaped textures of the SmC*.

2.1.3.3 Discotic liqıid crystals

The key point of these kind of molecules is rigidity. 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 2.14 typical discotic mesogen can be seen [1].

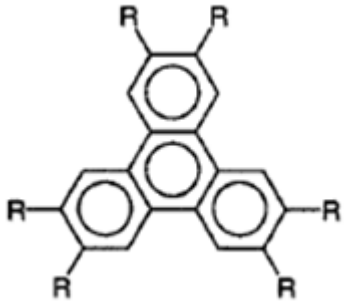


Figure 2.14 : Typical discotic mesogen.

Mesogens composed of disc-shape molecules exhibit two distinct classes of phases, the columnar and the discotic nematic phases. (Figure 2.15) [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].

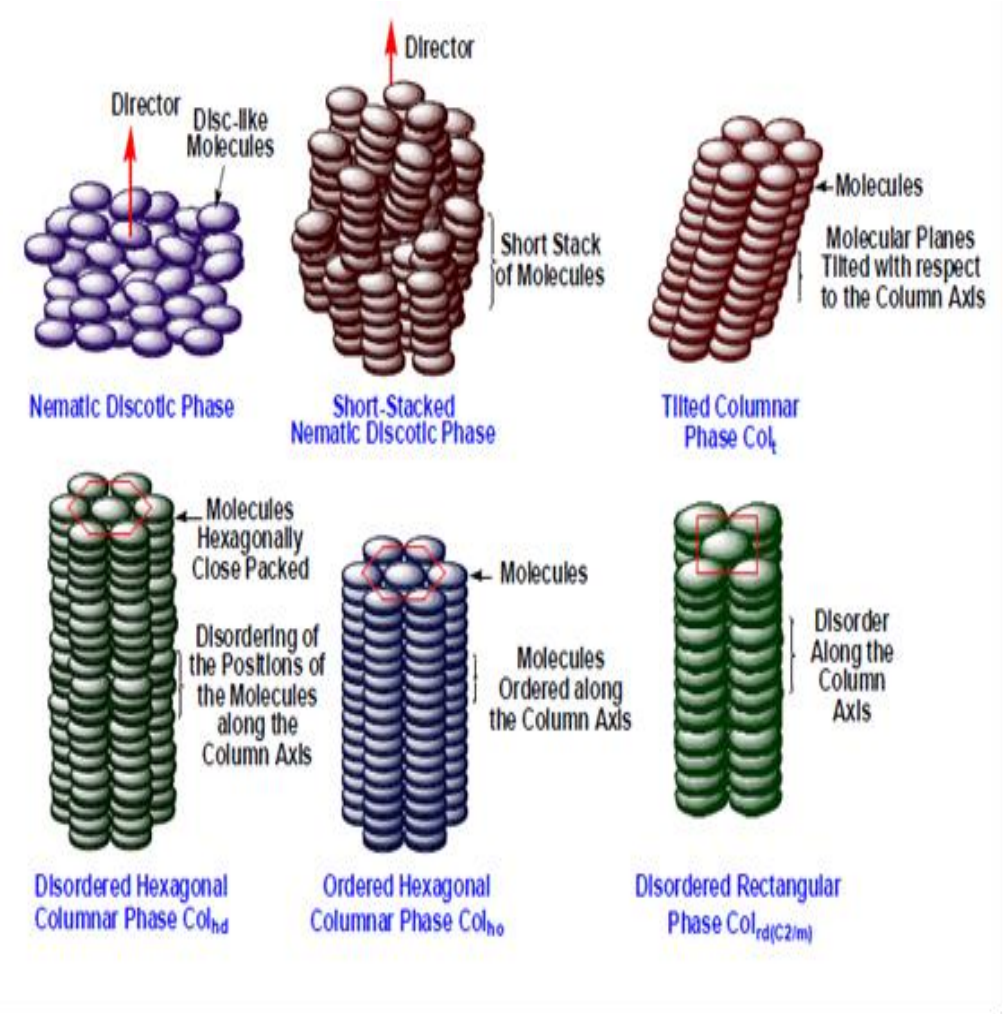


Figure 2.15 : Columnar and the discotic nematic phase.

2.1.4 Mesophase characterisation

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].

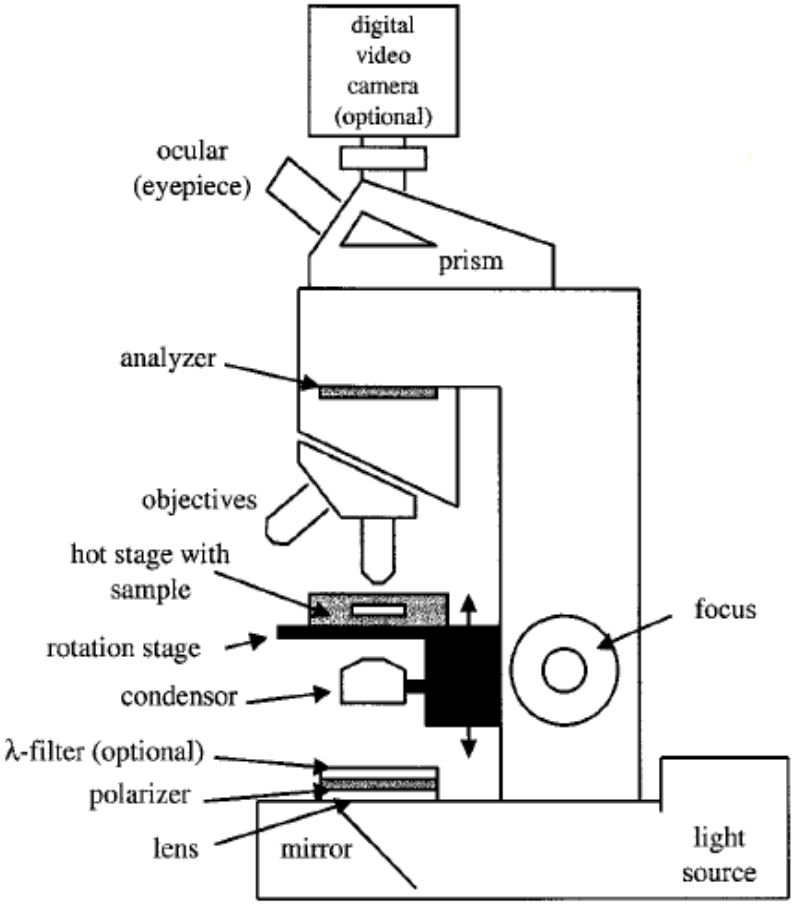


Figure 2.16 : Polarizing Optical Microscopy.

-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 2.17. 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].

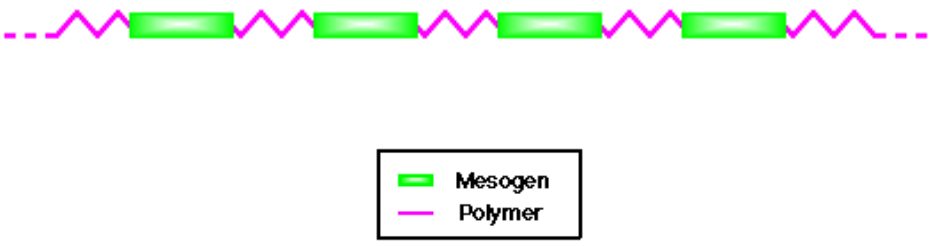


Figure 2.17 : Representation of main chain liquid crystal polymers.

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 long spacer units, which are usually several methylene units,

often with ester or ether units at the point of attachment [5]. In figure 2.18, the schematic representation of side chain liquid crystal polymers is given [10.].

Figure 2.18 : Representation of side chain liquid crystal polymers.

Liquid crystalline polymers combine characteristic properties of polymers with those 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 crystaline 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.

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 2.19) [15].

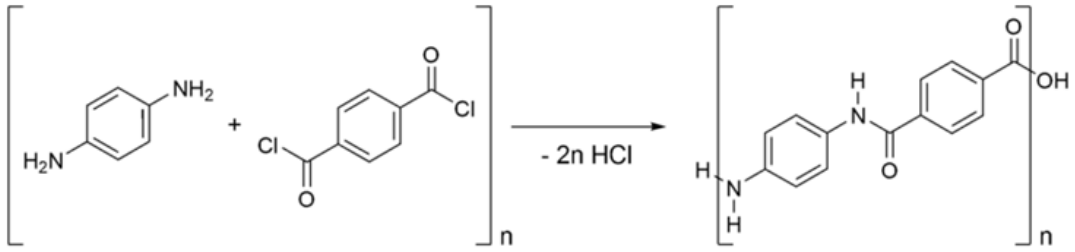


Figure 2.19 : Synthesis of Kevlar.

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:

I. Random copolymerization

II. Introducing kinks into the molecular backbone by using meta or ortho linkages

III. Introducing flexible linkages into the chain

IV. Incorporating bulky side groups onto the polymer chain [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 2.20 [6].

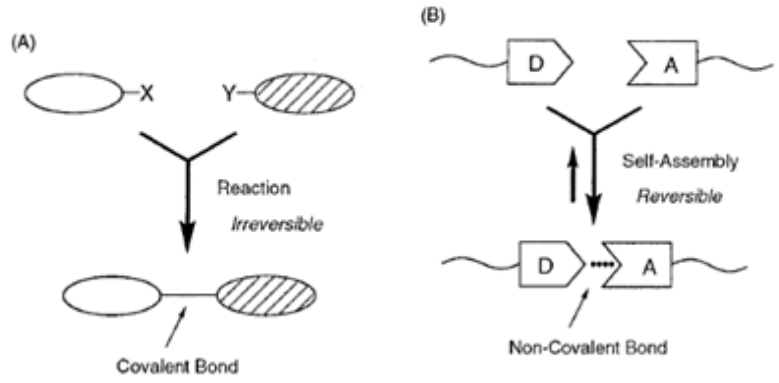


Figure 2.20 : Representation of (A) covalent bond, (B) non-covalent interaction.

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 [23] .

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 2.21 an example of H-bonded main chain liquid crystal polymer can be seen [6].

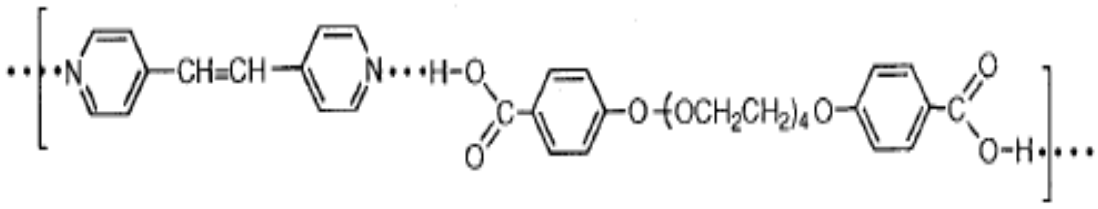


Figure 2.21 : Example of H-bonded main chain liquid crystal polymer.

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 2.22 [6].

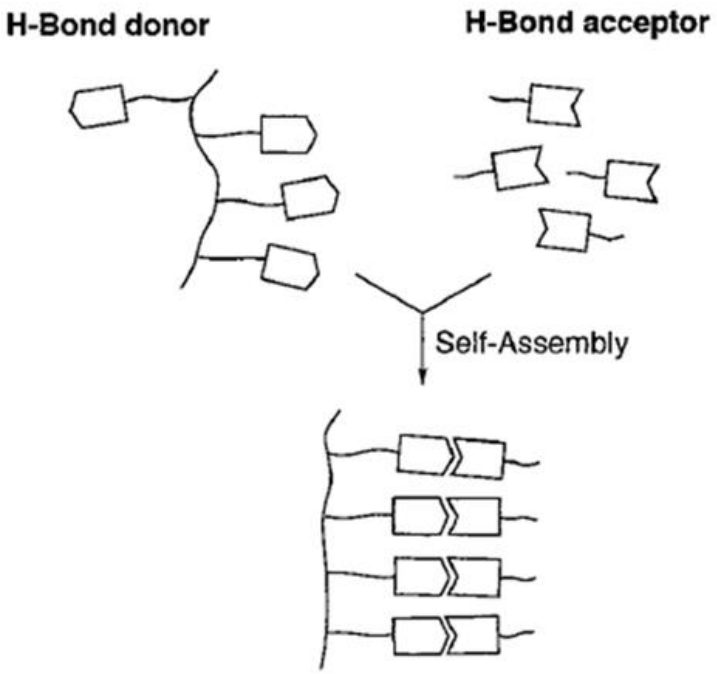


Figure 2.22 : Example of H-bonded side chain liquid crystal polymer.

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 2.23.

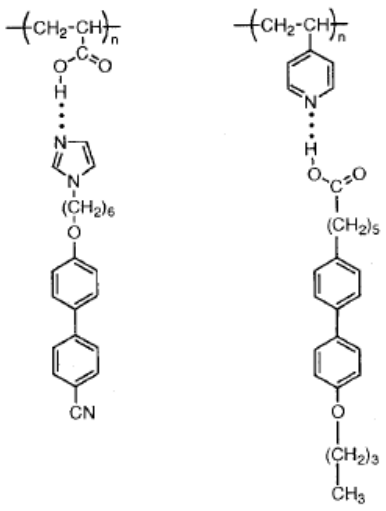


Figure 2.23 : Examples of H-bonded side chain liquid crystal polymers.

2.3 Chalcone Polymers

Chalcone is a compound consists of two aromatic rings linked by an unsaturated α, β-ketone. They contain many various substituents on these aromatic rings. Chalcone could be easily found in most of the plants naturally and is an intermediate precursor of flavonoids and isoflavonoids [20] .

They are essential chemical compounds and are being studied widely owing to their varied application area. In the fields of biology and biochemistry, they have been suggested to have a vital role in treatment of some inflammatory diseases, such as malaria. They may also have some important antitumor activity. It has been documented as well, that the chalcone possesses a notable nonlinear optical (NLO) property, which is a crucial element for optical communications devices [21]. Pendant chalcone groups on polymers have similar properties like pendant cinnamate groups, which have been used as photosensitive polymers for their excellent resolving power, high flexibility, and respectable resistance to solvents after exposure and good thermal stability [22]. 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 [24]. The technological applications of photosensitive polymers are applied in the fields of microlithography, photoconductors, nonlinear optical materials, energy exchange materials, liquid crystalline display etc. [25] .

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 [24] . In figure 2.24, one example of chalcone based side chain liquid crystal polymer is shown [26] .

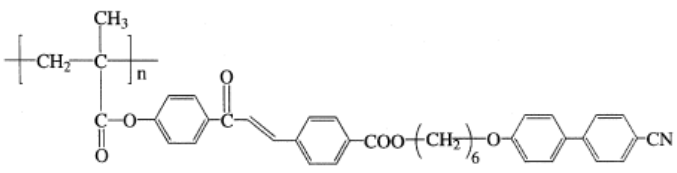


Figure 2.24 : Examples of H-bonded side chain liquid crystal polymers

3. EXPERIMENTAL PART

3.1 Materials

4-pyridine carboxaldehyde (Aldrich), p-hydroxy acetophenone (Aldrich), 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), N,N-dimethylformamide (DMF) (Merck), 1-methyl-2-pyrrolidone (NMP) (Merck), Tetrahyrofuran (THF) (Aldrich), Ethanol (Merck) were used.

3.2 Instruments

-Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a varian 500 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(PerkinElmer) Instrument.

These instryments have been used to characterize the structures and to determine the properities which these structures should have. NMR and FT-IR was used to enlighten the structure of molecules.

DSC and POM was used to determine the critical and important properities of structures that vital to enlighten the liquid crystals.

3.3 Preparation of Methacrylate Based Hydrogen Bonded Liquid Crystalline Polymer

3.3.1 Synthesis and characterization of 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one

1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was synthesized by using Claisen-Schmidt method. For this purpose, 4.56 g (0.0335 mol) of p-hydroxy acetophenone were dissolved in 20 mL of ethanol and 2.94 g of NaOH (2.2 mol) in 10 mL of distilled water. NaOH solution was added to the reaction mixture. Then 5 g (0.0335 mol) of 4-pyridine carboxaldehyde in 20 mL ethanol was added dropwise at 0 ^{0}C for 1 h. The mixture was stirred for 24 h at room temperature. The mixture was poured to distilled water. The precipitated yellow solid product was filtered, washed with excess of ice cold water, dried and re-crystallized from ethanol to get yellow crystals. 4.30 grams of product was synthesized. Yield %57.02

3.3.2 Preparation of the 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate

4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate (2.5 g, 9 mmol) and triethylamine (1.4 mL) were dissolved in 30 mL of dried THF in a 250 ml three necked flask and cooled to 0 ^{0}C. Methacryloyl chloride (1.4 mL) in 30 mL of THF was added to this mixture dropwise with constant stirring and at 0 ^{0}C. Stirring was continued for 2 h at 0 ^{0}C and for 12 h at room temperature. Then, the product was poured into ice cold water, filtered and washed with excess of cool water. The monomer was dried under vacuum at room temperature for 24 h. It was recrystallized from ethylacetate to get shining yellow crystals. Characterization of the monomer was carried out by using FT-IR and H-NMR.

3.3.3 Synthesis of polymer

4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate (1 g, 3.41 mmol) was dissolved in 10 mL of freshly distilled anhydrous Dioxane and 0.006 g (0.037 mmol) of AIBN as initiator was flushed with oxygen-free nitrogen for 10 min, and heated with stirring for 8 h at 70 0C.

The polymerization solution was cooled and poured on to 50 ml of stirred alcohol. The precipitated polymer was filtered off, washed with ether, and dried in vacuum, to

give 0.60 g of homopolymer. The characterization of the polymer was performed by DSC for thermal properties and FT-IR and ^{1}H-NMR for spectroscopic characterization.

3.4 Synthesis of Hydrogen Donor Reagents

3.4.1 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 K_2CO_3 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 %)

3.4.2 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) K_2CO_3 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%).

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

For this purpose, 0.162 g of LC8 (0.5 mmol) as a H-bond donor and 0.147 g the chalcone based polymer (0.5 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h. Also, 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was interacted with LC8 to obtain liquid crystaline compound.

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

For this purpose, 0.183 g of LC11 (0.5 mmol) as a H-bond donor and 0.147 g of chalcone based polymer (0.5 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h.

The characterization of the polymers were performed by using POM for observing liquid crystalline texture, DSC for thermal properties and FT-IR for spectroscopic characterizations.

Also, chalcone compound was interacted with LC8 and LC11 to obtain new hydrogen bounded liquid crystaline materials. These compounds were characterized by using POM and FT-IR.

4. RESULTS AND DISCUSSION

In this study, chalcone based hydrogen bonded side chain liquid crystalline polymers were synthesized and characterized.

4.1 Preparation of the 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one

1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was synthesized starting from p-hydroxy acetophenone and 4-pyridine carboxaldehyde in the presence of NaOH as catalyst by using Claisen-Schmidt method (Figure 4.1). The obtained compound was characterized with FT-IR spectroscopy (Fig.4.2a)

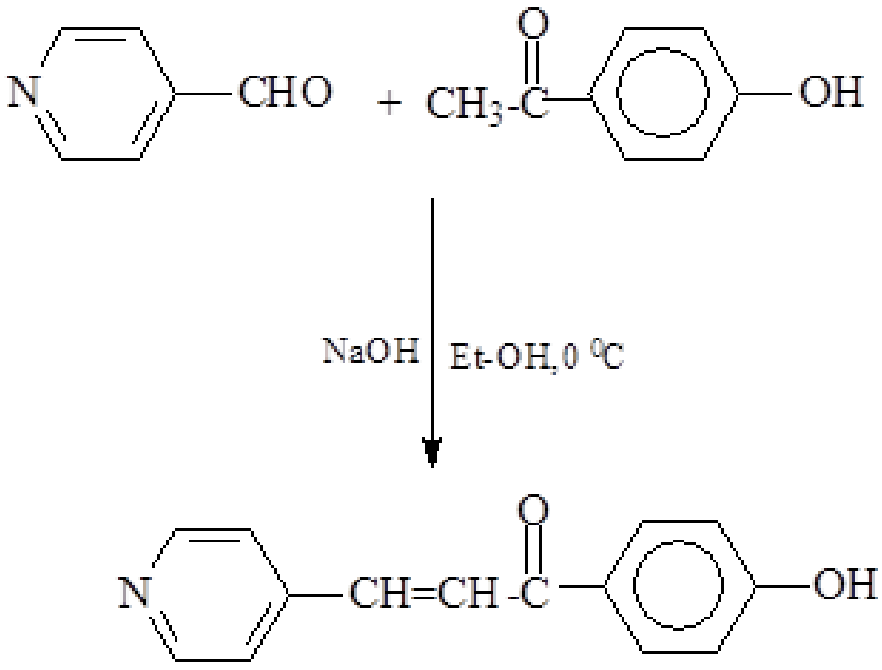


Figure 4.1 : 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one

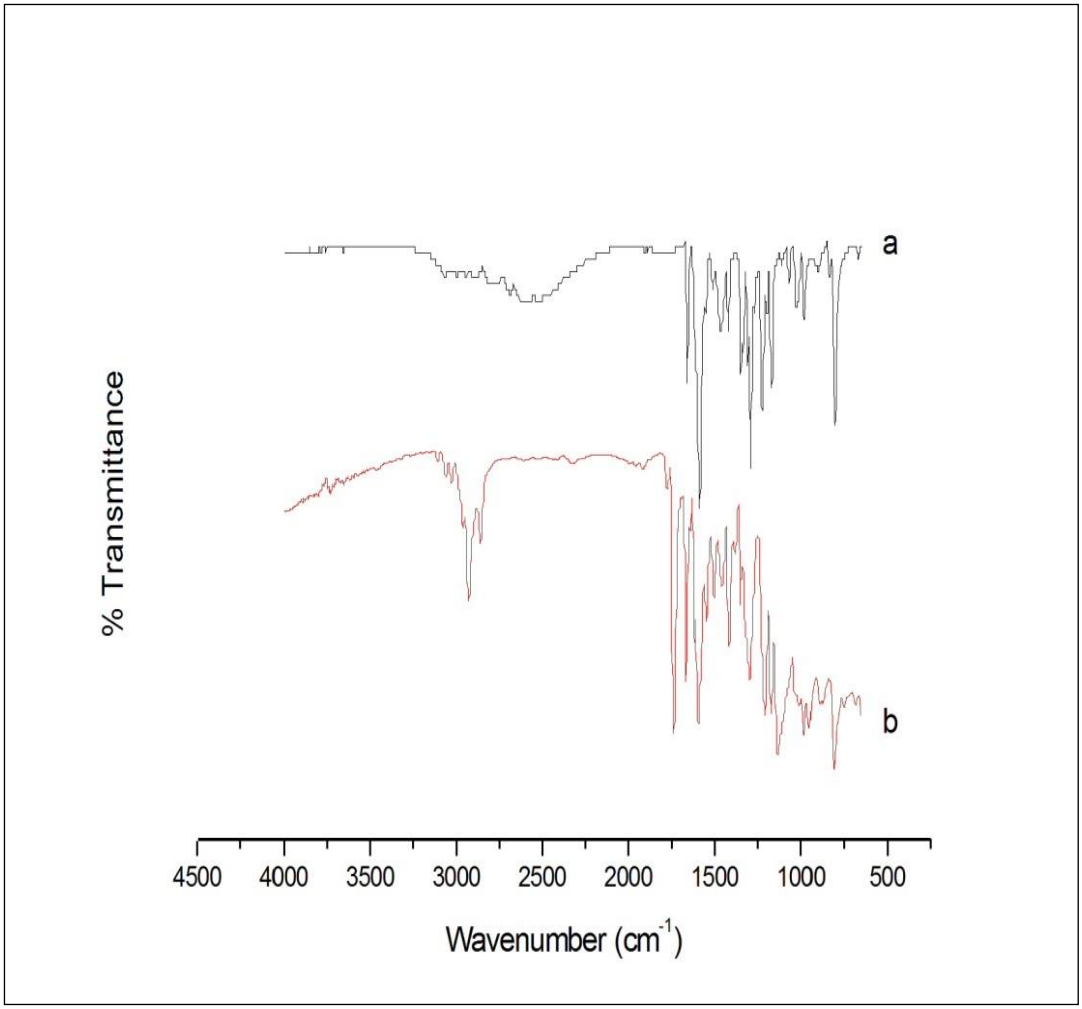


Figure 4.2 : FT-IR spectra of (a)chalcone and (b)monomer

The FT-IR spectrum of the 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one shows absorption bands at about 2898 cm^{-1} due to (–CH_2–) ; 1658 cm^{-1} which confirm ketonic group; at 1587 cm^{-1} due to (olefinic -C=C stretching) conjugated of the chalcone moiety; 1510,1418 and 1462 cm^{-1} (Ar, -C=C stretching).

4.2 Preparation of 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate and polymer

1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was reacted with methacryloyl chloride in the presence of THF as a solvent and triethyl amine as an acid scavenger.

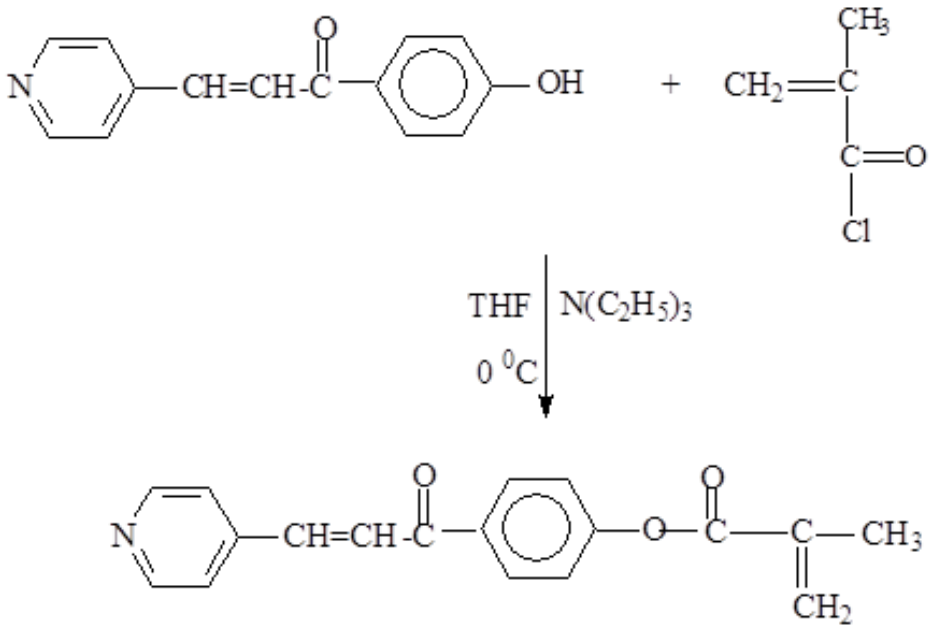


Figure 4.3 : Synthesis of the 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate

4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate was characterized by using FT-IR (Fig.4.2b) and ^{1}H-NMR (Fig.4.4). According to the Fig.2b, it can be observed band at 1722 cm^{-1} which confirm ester group.Also, the peaks of vinyl group was observed at 3000-3100 cm^{-1}.

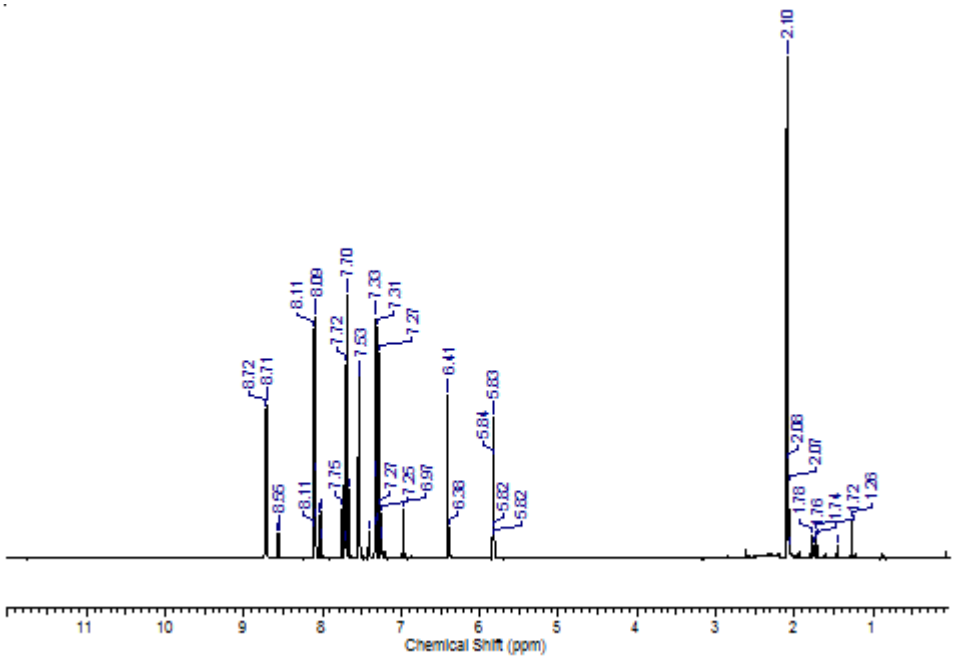


Figure 4.4 : ^{1}H-NMR of monomer

The structure of the 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate was identified by ^{1}H-NMR (Fig.4.4). According to the Figure 4.4, ($CDCl_3$, ppm): 8.72–7.27 (m, 11H, Ar–H and olephinic -CH=CH), 6.40 (1H,CH2=), 5.83 (1H, CH2=), 2.08 (s, 3H, CH3).

4.3 Polymerization of the 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate

The polymer was prepared by radical polymerization in a tube with 1.0 mol% AIBN in NMP as a solvent at 70 ^{0}C for 8 h. The polymer were obtained by precipitation with ethanol and were dissolved in NMP and re-precipitated. It was dried at room temperature under vacuum (Figure 4.5).

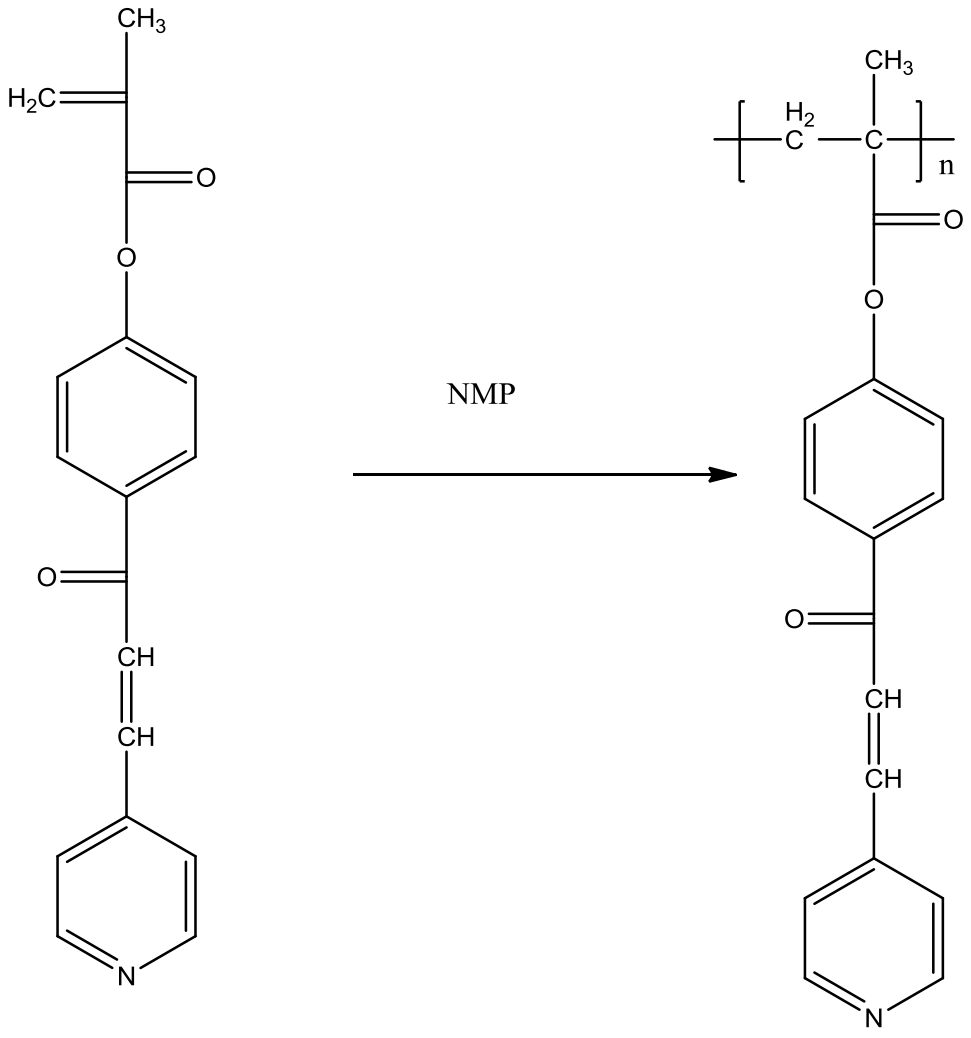


Figure 4.5 : Polymerization of 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate

Spectroscopic investigation of the polymer was carried out by FT-IR (Fig.3). The peaks at 3000-3100 cm^{-1} belong to vinyl group and dissappeare after polymerization.

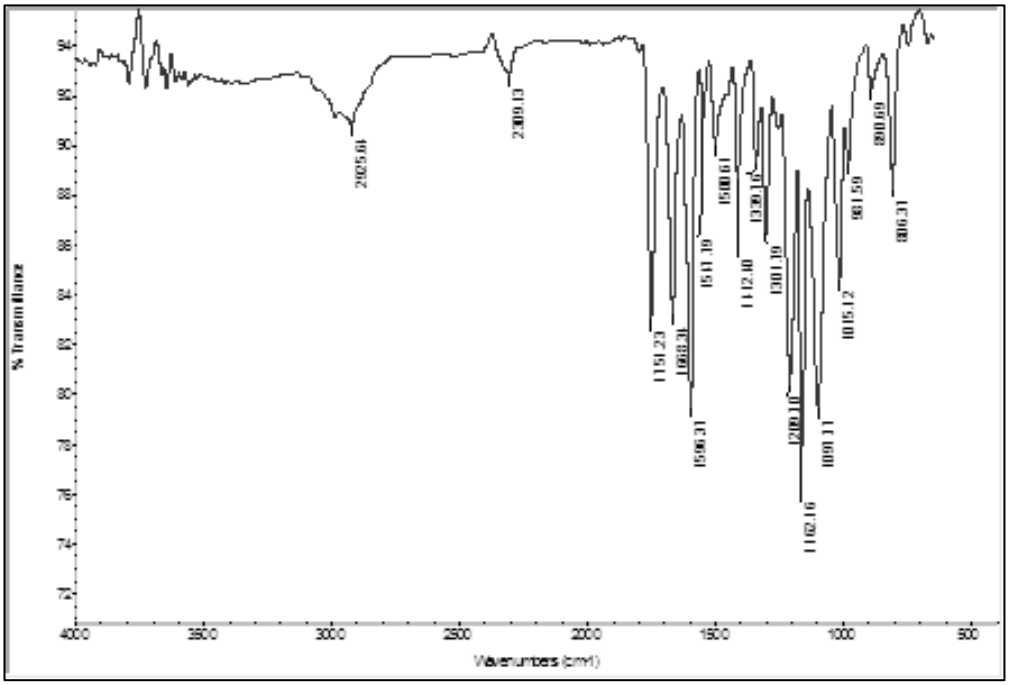


Figure 4.6 : FT-IR spectra of the polymer.

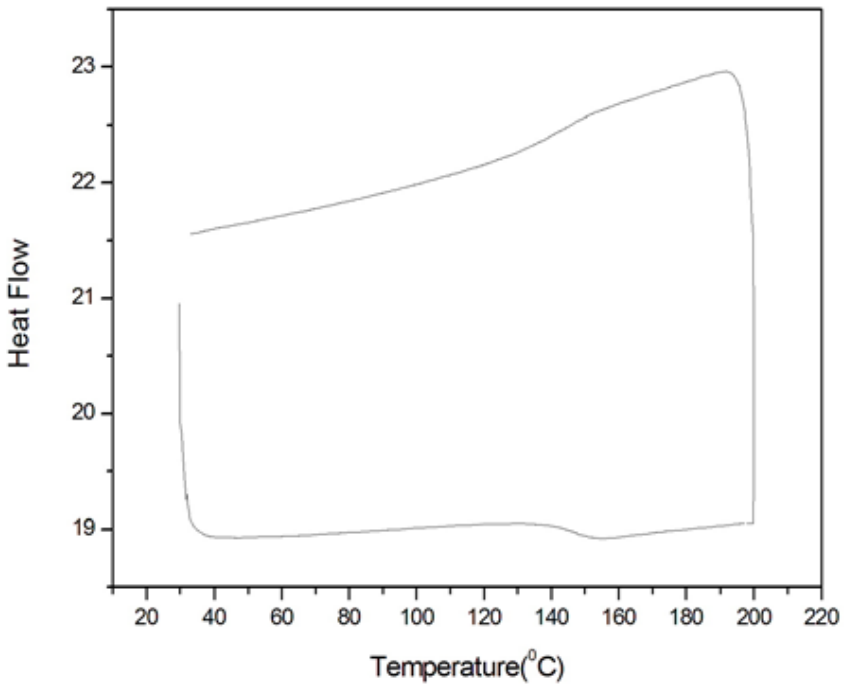


Figure 4.7 : DSC thermogram of the polymer.

According to the Fig.4.7, Tg of the homopolymer was found as about 144 ^{0}C.

4.4 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 4.8.

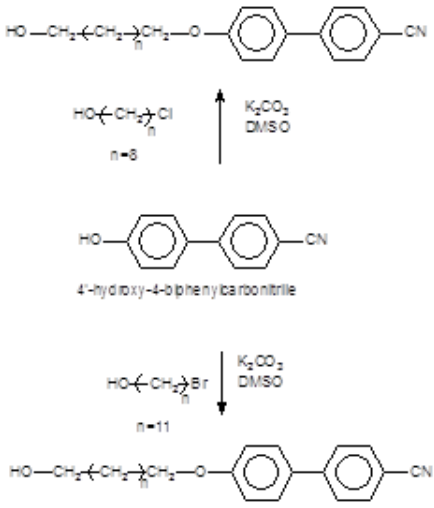


Figure 4.8 : Synthesis of hydrogen bond donors.

The structure of the LC8 and LC11 were characterized by FT-IR and ^{1}H-NMR spectroscopy. Figure 4.9 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 .

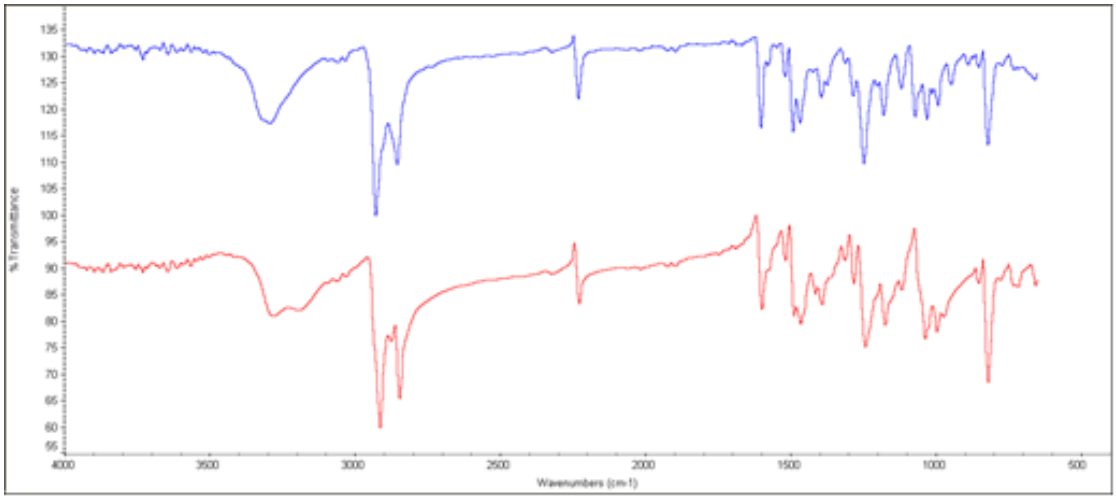


Figure 4.9 : FT-IR spectra of LC8 (a) and LC11(b).

^{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 4.10.

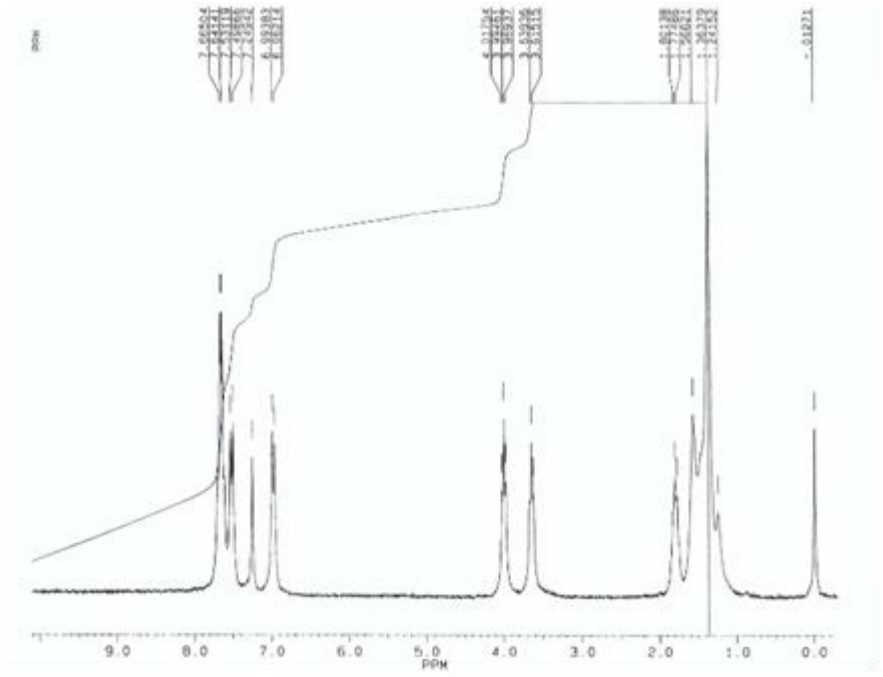


Figure 4.10 : ^{1}H-NMR spectrum of the LC8.

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 and mesomorphic properties were summarized in Table 4.1.

Table 4.1 : Thermal properties of LC8 and LC11a.

Code	Phase Transitions °C[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 4.11, 4.12 respectively.

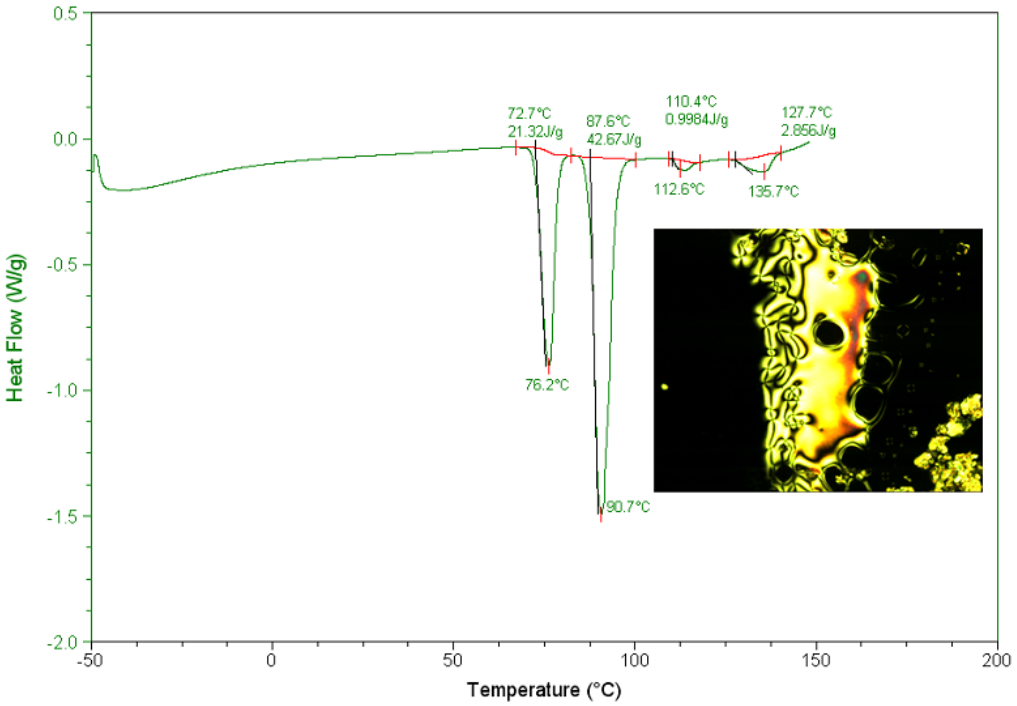


Figure 4.11 : DSC curve of the LC8.

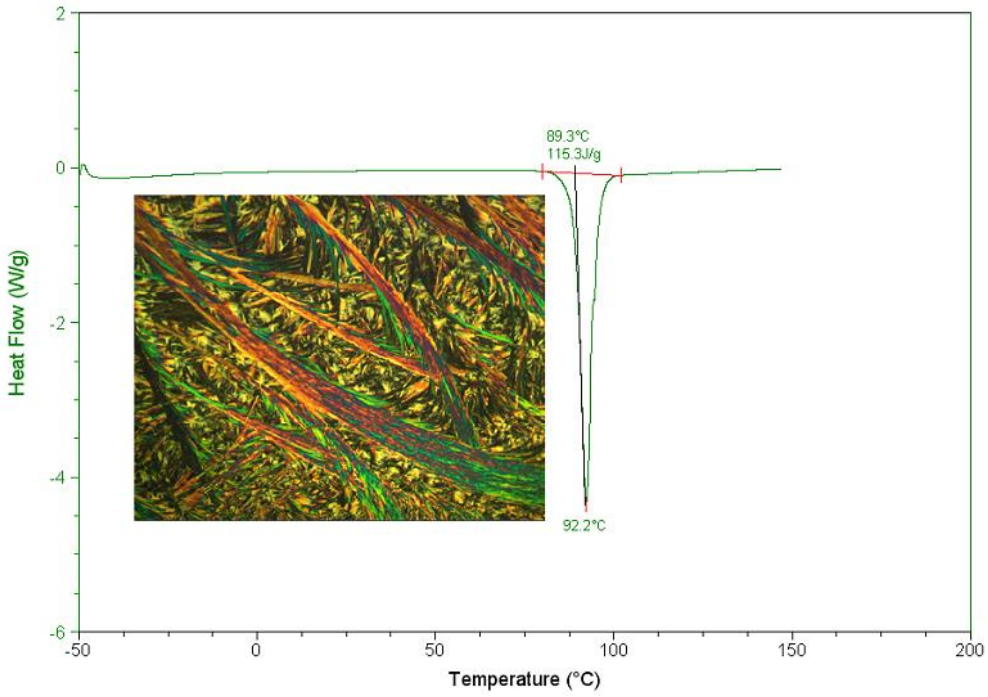


Figure 4.12 : DSC curve of the LC11.

As can be seen from the figure 4.8, 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 [27] .

4.5.2 Interaction of hydrogen bond donors with 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one and chalcone based polymer to obtain H-bonded Side-chain liquid crystalline polymer and liquid crystalline chalcone based material

Chalcone and it's based polymers show liquide crystaline properties as described in literatures (23).Pyridine containing chalcone compound and polymer were interacted with LC8 and LC11 in DMF to obtain liquid crystaline compound (Scheme 4.13 and 4.15).

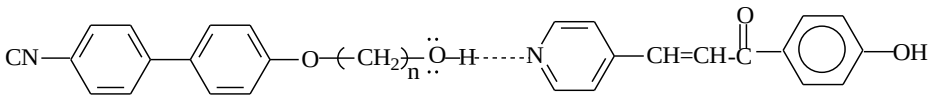


Figure 4.13 : Interaction of Hydrogen bond donors with chalcone.

LC8 and 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one gives nematic structure. (From left to right temparature;71°C,96°C, 102°C,113,3°C) (Fig.4.13)

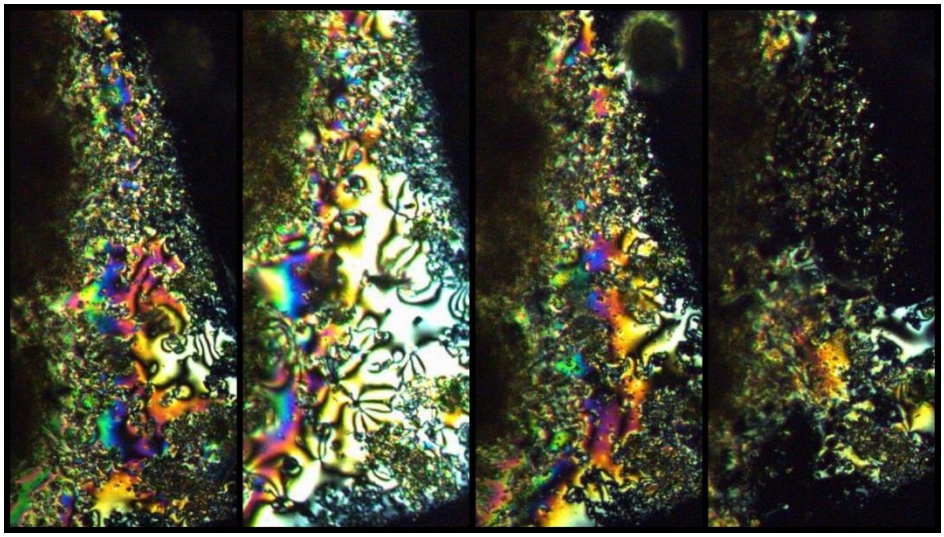
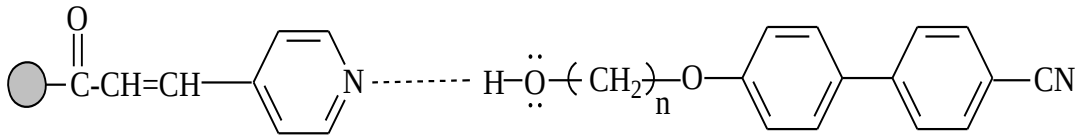


Figure 4.14 : Chalcone –LC8 POM images.

Polymer of 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate was also interacted with LC8 and LC11 to obtain H-bonded side chain liquid crystalline polymers (scheme 4.15).



n= 8,11

Figure 4.15 : Interaction of Hydrogen bond donors with polymer.

Spectroscopis characterization of the liquid crystaline polymers and chalcone based compound was performed by using FT-IR spectra.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 disseappered (Figure 4.16 and Figure 4.17) .

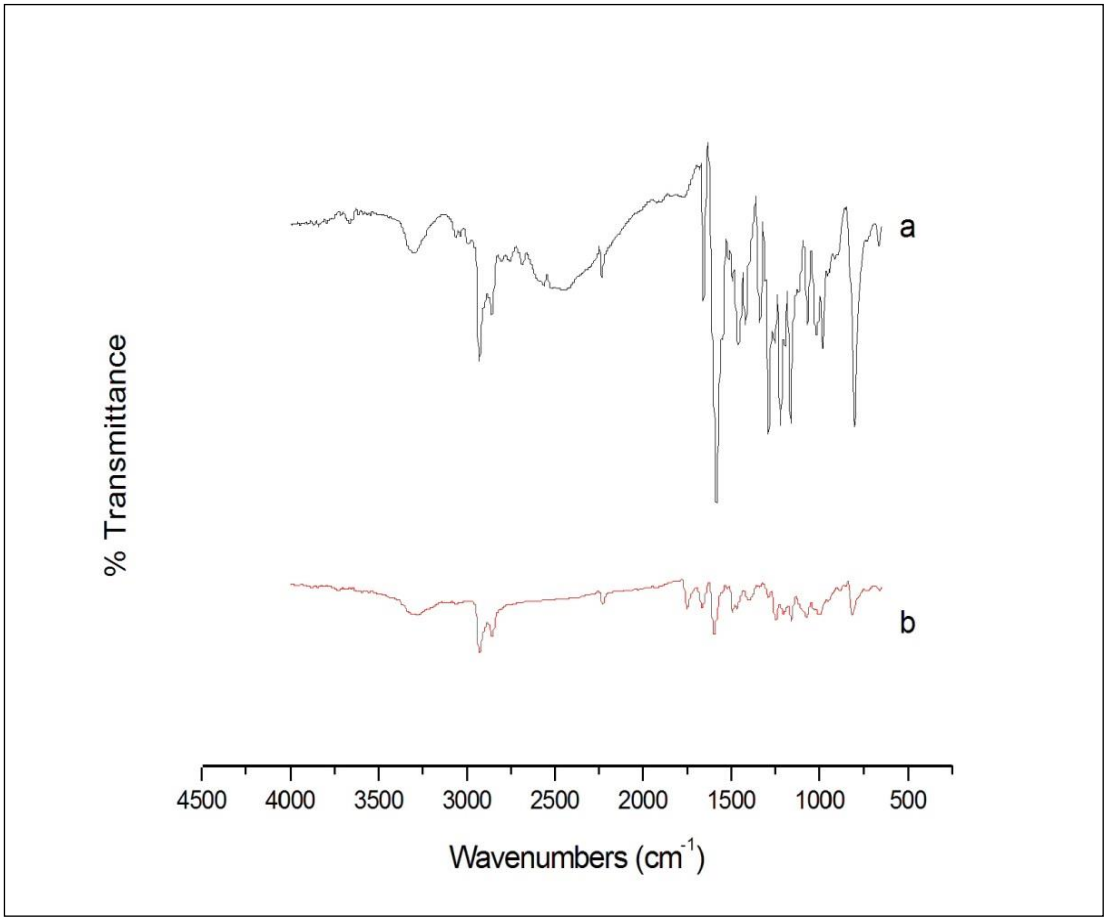


Figure 4.16 : (a) LC8-Chalcone H-bond intraction, (b) LC8-Polymer H-bond.

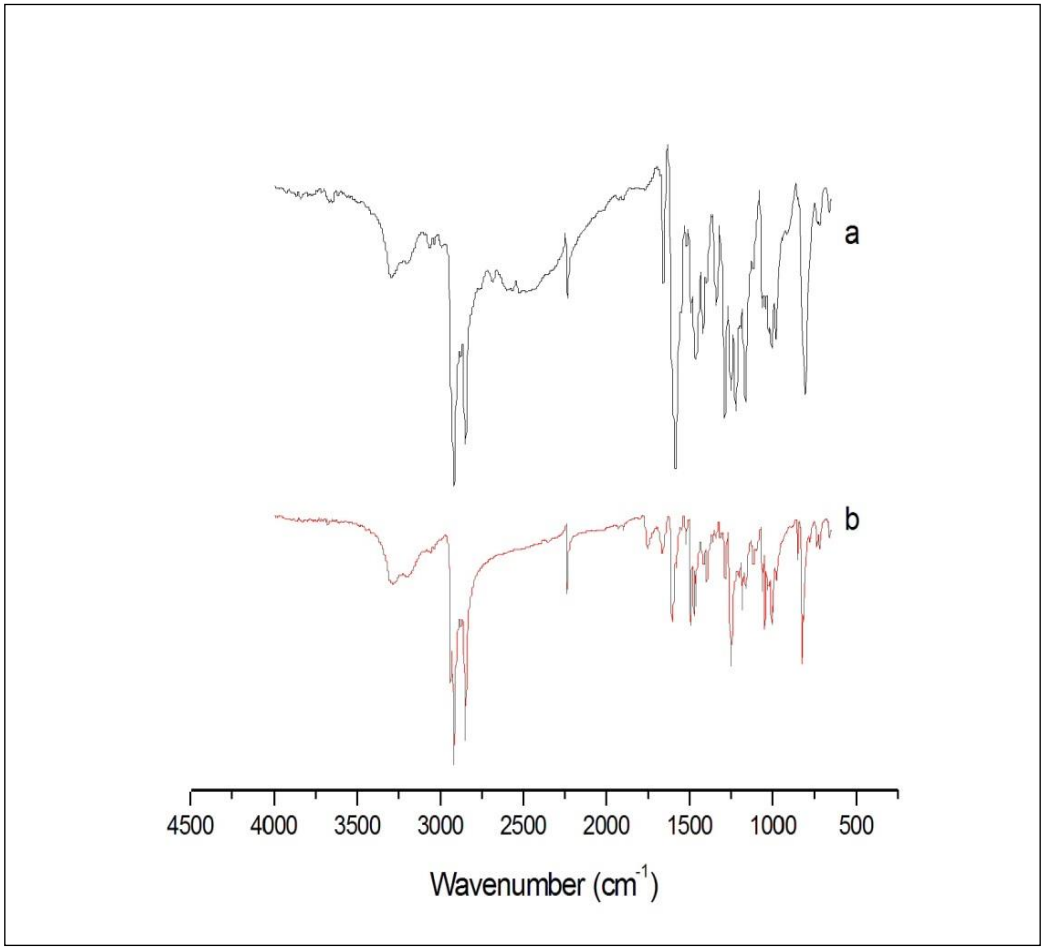


Figure 4.17 : (a) LC11-Chalcone, (b) LC11-Polymer .

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

The phase behavior of all the hydrogen bonded liquid crystalline polymers and chalcone were 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 10°C/min in an N2 atmosphere (Figure 4.18 and Figure 4.19).

1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was interacted with LC11 as above , but any liquid crystaline texture was not observed in the POM.

POM (x200) studies also confirmed these DSC results along with the results of phase transitions (Table 4.2).

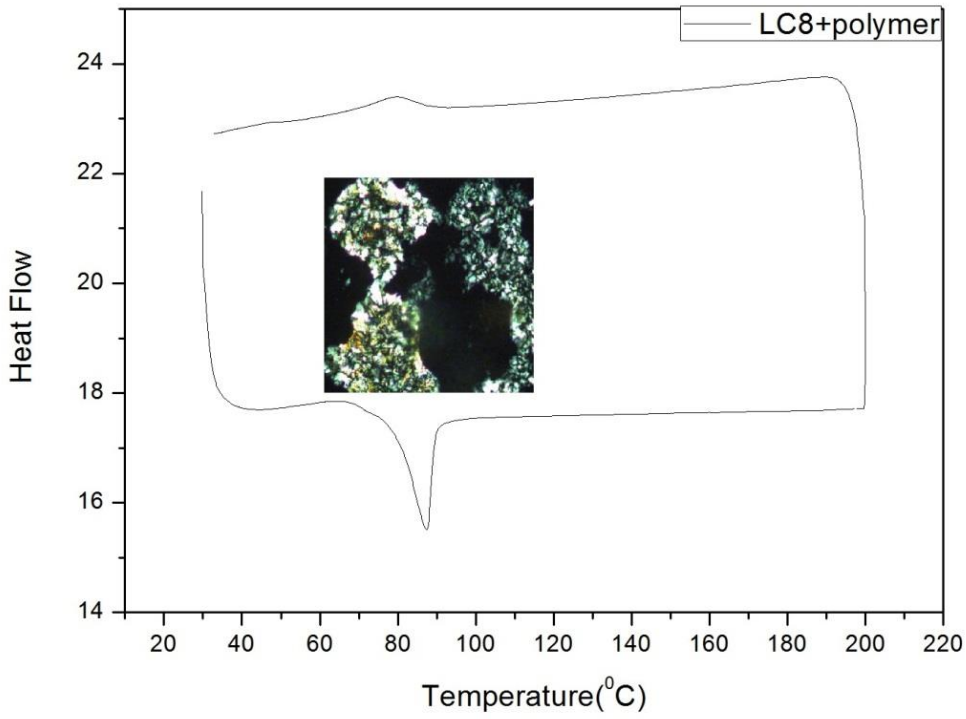


Figure 4.18 : DSC curve of the polymer-LC8.

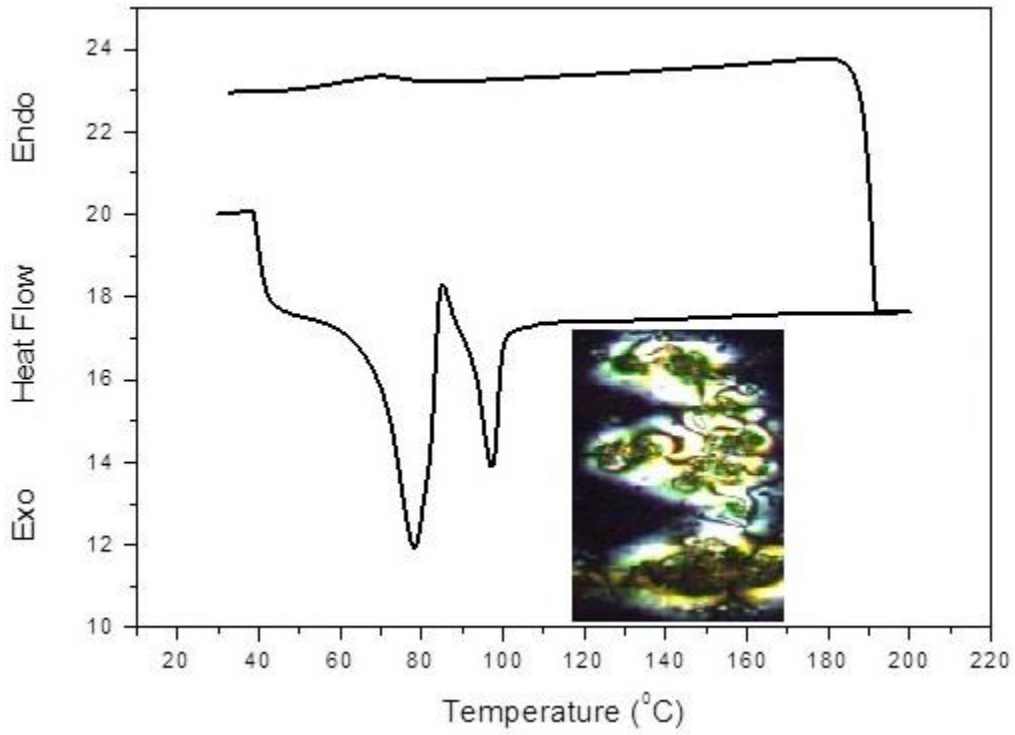


Figure 4.19 : DSC curve of the polymer-LC11.

Table 4.2 : Thermal properties of materials

Code	Phase Transition (°C) [b]
LC8-Chalcone	Cr: 62 °C, N: 100 °C (Heating) 101°C (Cooling), I:116 °C
LC8-Polymer	Cr: 36.5 °C, N: 88 °C (Cooling), I: 94 °C
LC11-Polymer	Cr: 71°C, N: 96 °C (Cooling), I: 111 °C

[a] Determined by DSC

[b] Cr= crystalline, N= nematic, I= isotropic

5. CONCLUSION

In this study, 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one was synthesized by Claisen-Schmidt method. 4-(3-(pyridin-4-yl)acryloyl)phenyl methacrylate monomer was obtained strating from 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one and methacryloyl chloride. Polymerization of the monomer was carried out by using free radical polymerization method. These chalcone based compound and polymer were H acceptor 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.

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

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

The DSC transition temperatures and mesomorphic properties were determined.

REFERENCES

[1] **Ingo Dierking, (**2003**).** Textures of Liquid Crystals, Weinheim.

[2] **Url-1** <*http://nobelprize.org/educational/physics/liquid_crystals/history/years*>, accessed

[3] **Shri Singh**, (2002). Liquid Crystal Fundemantals, Singapore.

[4] **Url-2** <*http://scifun.chem.wisc.edu/chemweek/pdf/liquid_crystals.pdf* > accessed at 28.04.2011

[5] **Peter J. Collings, Michael Hird**, (2001). Introduction to Liquid Crystals Chemistry and Physics, Philadelphia

[6] **Takashi Kato, Norihiro Mizoshita, Kiyoshi Kanie,** (2001). Hydrogen-Bonded Liquid Crystalline Materials: Supramolecular Polymeric Assembly and the Induction of Dynamic Function, *Macromolecular Rapid Communications 22*, pp 797-814

[7] **Url-3** <*https://plc.cwru.edu/tutorials/enhanced/files/lcc/intro.html*>, accessed at 28.04.2011

[8] **M. Barón, and R. F. t. Stepto,** (2002). Definıtıons of basıc terms relatıng to polymer liquid crystals, *Pure Appl. Chem., Vol. 74*, pp. 493–509.

[9] **Url-4 <***http://dept.kent.edu/spie/liquidcrystals/*>, accessed at 03.04.2011

[10] **Url-5** <*https://plc.cwru.edu/tutorials/enhanced/files/llcp/crphases/phases.html*>, accessed at 03.04.2011

[11] **Iam-Choon Khoo,** (2007). Liquid crystals, New Jersey.

[12] **Koen Binnemans,** Characterization of mesophases, retrieved April 13, 2010 from http://olla.ichf.edu.pl/lect/SS2005/Binnemans_lecture2.pdf

[13] **John W Goodby,** Liquid crystal phase transitions, retrieved April 13, 2010 from http://www.yorklc.com/docs/pdf/LCM.pdf

[14] **Goh, Suat Hong , Lai, Yee Hing and Cheng, Si Xue**, (2001). Supramolecular side chain liquid crystalline polymers assembled via hydrogen bonding between carboxylic acid-containing polysiloxane and azobenzene derivatives, *Liquid Crystals, 28: 10*, 1527 — 1538

[15] **Url-6** < *http://en.wikipedia.org/wiki/Kevlar*>, accessed at 28.04.2011

[16] **Tai-Shung Chung**, (2001). Thermotropic Liquid Crystal Polymers, Thin film Polymerization, Characterizations, Blends and Applications, Singapore

[17] **C.B. Mcardle,** (1989). Side Chain Liquid Crystal Polymers, Dublin

[18] **Yesim H. Gursel, Bahire Filiz Senkal, Mehmet Kandaz and Fahrettin Yakuphanoglu**, (2011). Poly (N-vinylimidazole) based hydrogen bonded side chain liquid crystalline polymer, *Polymers Advanced Technologies 22*, 90

[19] **Xiangen Han, Subing Zhang, Robert A. Shanks, Dumitru Pavel** (2008). Poly(4-vinylpyridine)-based hydrogen bonded side-chain liquid crystal polymers, *Reactive & Functional Polymers 68*,1097

[20] **S.T. Ha, Y.W. Low, (**2013). Synthesis and Phase Transition Behaviours of New Chalcone Derivatives, *Hindawi Publishing Corporation Journal of Chemistry Vol. 2013, Article ID 94372, 6 pp*

[21] **K. Kaniappan1, S. C. Murugavel, T. Daniel Thangadurai, (**2014). A Review on Photopolymers for Polymer Nanocomposite Applications, *J. Environ. Nanotechnol. Volume 3, No.3* pp. *01-15*

[22] **B. T. Thaker , D. M. Patel & J. B. Kanojiya**, (2009). New LiquidCrystalline Compounds Involving Ester-Chalcone Linkages Having 1,3,5-Trisubstituted Pyrazole as a Terminal Group, *Molecular Crystals and Liquid Crystals, 509:1, 145/[887]-164/[906]*

[23] **Chi-Yang Chao, Xuefa Li, and Christopher K. Ober, (**2004). Directing self-assembly in macromolecular systems: Hydrogen bonding in ordered polymers, *Pure and Applied Chemistry Vol. 76*, Nos. 7–8, pp, 1337

[24] P**. Selvam, S. Nanjundan**, 2005: Synthesis and characterization of new photoresponsive acrylamide polymers having pendant chalcone moieties, *Reactive & Functional Polymers 62*, 179–193

[25] **R. Balaji, S. Nanjundan,** (2001). Synthesis and characterization of photocrosslinkable functional polymer having pendant chalcone moiety, *Reactive & Functional Polymers 49,* 77–86

[26] **Mihara, T. , Tsutsumi, M. and Koide, N**.(2002): Synthesis and thermal properties of new chalcone-based side-chain polymers, *Molecular Crystals and Liquid Crystals*, 382: 1, 53 —64

[27] **Hulme, D. S., and Raynes, E. P.,** (1974). *J. chem. Soc., chem. Commun*., 98.

CURRICULUM VITAE

Name Surname:	Burak Korkmaz
Place and Date of Birth:	Istanbul/ 31.08.1990
E-Mail:	korkmaz0890@gmail.com
Education:	Gürlek Nakipoğlu Lisesi/Bakırköy/Istanbul
	Science (2004-2007)
	GPA: 80.62
B.Sc.:	Istanbul Technical University
	Faculty of Science and Letters
	Department of Chemistry (2008-2013)
	GPA: 2.86