ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF SIDE CHAIN LIQUID CRYSTALLINE POLYURETHANES

M.Sc. THESIS

Deniz MEMİŞ

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JUNE 2019

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF SIDE CHAIN LIQUID CRYSTALLINE POLYURETHANES

M.Sc. THESIS

Deniz MEMİŞ
(515121045)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Yeşim GÜRSEL

JUNE 2019

ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YAN ZİNCİR SIVI KRİSTAL POLİÜRETAN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Deniz MEMİŞ
(515121045)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Yeşim GÜRSEL

HAZİRAN 2019

Deniz MEMİŞ, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515121045, successfully defended the thesis/dissertation entitled “SYNTHESIS AND CHARACTERIZATION OF SIDE CHAIN LIQUID CRYSTALLINE POLYURETHANES”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Yeşim GÜRSEL** ....
Istanbul Technical University

Jury Members : **Prof. Dr. Bahire Filiz ŞENKAL** ....
Istanbul Technical University

Assoc. Prof. Dr. Mustafa OKUTAN ....
Yıldız Technical University

Date of Submission : 02 May 2019
Date of Defense : 14 June 2019

To my family,

FOREWORD

I would like to express my sincere appreciation to Prof. Dr. Yeşim Gürsel, my dear advisor, for her kind support, scientific guidance and endless patience throughout this study. I would also like to thank Prof. Bahire Filiz Şenkal for her help and interest.

I owe special thanks to my family for their support and encouragement. They have always believed in me.

This thesis was financed by the BAP Unit of ITU Rectorate with the project number of TYL-2018-41166.

May 2019

Deniz MEMİŞ
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

LC : Liquid Crystal
LCP : Liquid Crystalline Polymer
MCLCP : Main-chain Liquid Crystalline Polymer
SCLCP : Side-chain Liquid Crystalline Polymer
MCSCLCP : Main-chain Side-chain Liquid Crystalline Polymer
LMMLC : Low Molecular Mass Liquid Crystals
LC6 : 1-Bromo-6-(4-cyanobiphenyl-4′-oxy)hexane
LC8 : 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane
LC6-diol : 6-(4-cyanobiphenyl-4′-oxy)hexyl-2,2bis(hydroxymethyl)propionate
LC8-diol : 8-(4-cyanobiphenyl-4′-oxy)octyl-2,2bis(hydroxymethyl)propionate
SCLCPU : Side-chain Liquid Crystalline Polyurethane
PULC6 : SCLCPU with the spacer of 6 methylene units
PULC8 : SCLCPU with the spacer of 8 methylene units
POM : Polarized Optical Microscopy
DSC : Differential Scanning Calorimetry
FT-IR : Fourier Transform Infrared Spectroscopy
NMR : Nuclear Magnetic Resonance Spectroscopy
p : pitch
Sm : Smectic
SmA : Smectic A
SmC : Smectic C
CMC : Critical Micelle Concentration
PU : Polyurethane
HMDI : Hexamethylene Diisocyanate
LCD : Liquid Crystal Display
LCE : Liquid Crystal Elastomer
MJLCP : Mesogen-jacketed Liquid Crystalline Polymer
DMF : Dimethylformamide
DBTDL : Dibutyl tin dilaurate

LIST OF TABLES

LIST OF FIGURES

Page

SIDE CHAIN LIQUID CRYSTALLINE POLYURETHANE SYNTHESIS AND CHARACTERIZATION

SUMMARY

Reinitzer, the botanist, he discovered birefringent liquid phase while investigating cholesteryl ester. Together with physicist Lehmann, they reported that this substance has two melting point and intermediate phase between melting points possesses optic characteristic like a crystal despite being fluid. These phases termed as mesophase differ thermodynamically from isotropic state. The molecules exhibiting these characteristics are called liquid crystals or mesogens.

SCLCPs can have optic features, provide classic polymer characteristics and respond to external stimulation like a mesogen by which LC and the polymer are combined. Owing to this combination, they have remarkable application potential in electro-optical technology. In such polymers, mesogens are connected as side-chain to the backbone of the polymer through an aliphatic spacer. SCLCPs are synthesized by homopolymerisation of monomer containing mesogen or copolymerization of diverse monomers containing mesogens. Mesogens promote order that is, LC behavior while the spacers decouple them to provide entropy to polymer. Both entropy and order are essential for properly combining LC behavior with polymer. Therefore, the balance between spacer and mesogen is significantly crucial to form LC phase in polymer.

In this study, polyurethanes that contain mesogenic unit in side-chain (SCLCPU) was synthesized. With the purpose of synthesis of SCLCPUs (PULC6 and PULC8), 4-cyano-4′-hydroxybiphenyl selected as mesogen was attached sequentially to the spacers and 2,2bis(hdyroxymethyl)propionic acid to obtain two-functional LC monomers (LC6-diol and LC8-diol). LC6-diol and LC8-diol was reacted separately with HMDI to polymerize.

Synthesized LC6 and LC8 precursors, LC6-diol and LC8-diol monomers and SCLCPUs was characterized and their presence was proved by NMR and FT-IR studies.

The investigation of thermal behavior of the products showed that both LC6 and LC8 display nematic microstructure, both of LC monomers display smectic mesophase and LC6-diol displays additionally nematic, PULC6 does not show LC behavior while PULC8 exhibits smectic. DSC results also corroborated behavior of the products under the POM.

Different behavior of SCLCPUs shows that SCLCPUs exhibiting more stable mesophase can be obtained when the number of the flexible methylene units increases in spacer.

YAN ZİNCİR SIVI KRİSTAL POLİÜRETAN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Sıvı kristaller, sıvı haldeyken çift kırınım özelliğine sahip organik bileşiklerdir. Çok önceden sabunların bu özelliğe sahip olduğu biliniyor olmasına rağmen keşfi 19. yüzyılın sonlarında gerçekleşmiştir.

1888 yılında bir bitki bilimci olan Reinizer havuçtan özütlediği kolesterol esterleri üzerinde çalışması esnasında sıra dışı faz geçişleri gözlemledi. Bu maddenin iki farklı erime noktası olduğunu fark etti ve bu erime noktaları arasında olağandışı renklenmeler gözlemledi. Farklı kolesteril esterleri üzerinde de benzer gözlemlere ulaşınca kristal izomerisi üzerine çalışan fizikçi Lehmann'a örnekleri gönderdi. Lehmann, gelişmiş polarizasyon mikroskobu sayesinde çok daha doğru gözlemler yapabildi ve örneklerin tıpkı bir sıvı gibi akışkan iken diğer yandan bu örneklerin bir kristal gibi optik özelliklere sahip olduğunu fark etti. Sonraki araştırmacılar bu gözlemlenen orta fazın maddenin izotropik sıvıdan farklı bir termodinamik halini temsil ettiğini kanıtladılar. İlk olarak "akan kristaller" şeklinde isimlendirilmesine rağmen daha sonra "sıvı kristaller" teriminde karar kılındı ve böylece yeni bir kavram ortaya çıkmış oldu.

Sıvı kristaller hem bir kristalin çift kırınım özelliğini hem de bir sıvının akışkanlığı gibi özelliklerini bir arada taşıdıkları için onlar düzenin ve hareketliliğin birleşimi olarak tanımlanabilir. Böyle bir sıvı fazda akışkanlığın sağlanması için yeteri kadar düzensizlik vardır ancak onlar aynı zamanda anizotropi de gösterir. Bu orta faz mezofaz olarak adlandırılmış, bu tip özellik gösteren maddelere de mezojen denilmiştir.

Mezofazlar genel olarak iki tip molekül tarafından oluşturulabilir. Disk tipi moleküller ki bunlara diskotikler denilir ve çubuksu moleküller bunlar da kalamitik olarak adlandırılır. Mezofaz sınıflandırılmasında molekül konformasyonunun moleküller arası etkileşimlerin rolü büyüktür. Kalamitikler taşıdığı polarize gruplar sayesinde sürekli bir dipol moment üretirler. Termal hareket kaynaklı hızlı rotasyonu sebebiyle aslında silindirik olmamalarına rağmen öyle de düşünmek pek de hatalı olmaz. Onların mezofaz oluşturabilmesi için bazı gereksinimleri karşılaması gerekir. Ekseriyetle sert esnemeyen bifenil gibi bir çekirdeğe ve esneyebilen hidrokarbon tipi bir kuyruğa sahiptirler.

Diskotiklerde de aynı şekilde bu gruplar vardır, bu tip moleküllerin genişliği kalınlığının yaklaşık beş katı büyüklüktedir ve sahip olduğu dallanmaları kabaca bir düzlem üzerindedir. Her iki molekül tipinde de sert ve esneyebilir bölümlerin dengesi çok önemlidir. Sert bölümler sıvı kristal davranışı lehinde çalışırken esnek bölümler düzensizliği arttırır. Fakat molekülün aşırı sert bölümlerden oluşması kristalleşme eğilimini arttırdığından dolayı mezofaz oluşumu gerçekleşmeden izotropik hale geçişe

sebebiyet verir. Bu sebeple esnek bölümlerde gereklidir ve molekül tasarımında bu husus üzerinde iyi düşünülmelidir.

Sıvı kristaller mezofazı oluşturan nedene göre ikiye ayrılır. Termotropik LC'ler hususi bir sıcaklığa göre mezofaz oluştururken lyotropik LC'ler ise özel çözgenlerin amfifilik moleküllerle karıştırılması sayesinde mezofaz oluşturabilir.

Sıvı kristal fazların bir çeşidi olan nematik fazlar hem kalamitik hem de diskotik mezojenlerde oluşabilirken ayrıca kalamitiklerde smektik fazlar, diskotiklerde ise kolumnar fazlar oluşabilir. Diskotik olmayan bazı moleküllerin de kolumnar fazlar oluşturduğu görülmüştür. Kalamitik moleküller tabakalar halinde toplanma eğiliminde iken diskotikler kolon oluşturarak düzene girerler.

Kalamitik bir mezojen kristal halden ısıtılırken smektik faza geçer. Smektik fazda kısmi bir düzen vardır, moleküller katmanlar halinde sıralanırlar ve bu katmanlar birbirleri üzerinde serbestçe kayabilirler. Burada moleküler oryantasyon ve molleküller arası konumsal bağlantılar vardır. Bu faz oluşumunda ve sınıflandırılmasında moleküller arası fiziksel bağların önemi çok büyüktür. Madde smektik halde viskoz yapıdadır. Smektik haldeki maddenin ısıtılmasıyla nematik mezofaz oluşumu meydana gelir. Nematik faz en düzensiz mezofaz şeklidir ve burada katmanlar yoktur. Maddenin viskozitesi azalır. Buradaki var olan moleküler oryantasyon da izotropik sıvı halde ortadan kaybolur. Diskotik bir mezojenin ısıtılmasında da safhalar benzerdir. Kristalden mezofaza döndüğünde moleküller kolonlar oluşturmak için üst üste istiflenme şeklinde düzene girer burada da smektikteki gibi kısmi bir düzen vardır. Madde daha da ısıtıldığında nematik kolumnar faz oluşur. Burada aslında kolonlar yoktur. Kalamitiklerin nematik fazı gibi en düzensiz mezofazdır ve en hareketlisidir. Daha sonra bir düzenin olmadığı izotropik noktaya ulaşılır.

Mezofazların diğer bir türü ve aslında ilk keşfedilen mezofaz olan kolesterikler kiral yapılı moleküllerden oluşur. Kiral olmaları hasebiyle optikçe aktiftirler ve bükümlü nematik fazları meydana getirirler. Kiral olmayan nematiklere kiral katkılar eklendiğinde de benzer fazların oluştuğu anlaşıldığından nematik fazların alt konusu olarak nitelendirilmiştir.

Amfifilik moleküllerin çözgenler ile karışımıyla elde edilen belirli sıcaklık ve konsantrasyonda benzer mezofazlar sergileyen diğer bir tür liyotropik LC'lerdir. Amfifillerin kendiliğinden düzenlenmesi onları termotropiklerden ayıran bir özelliğidir. Amfifiller hidrofobik ve hidrofilik olmak üzere iki kısımdan oluşur. Bu onun çözelti içerisinde miseller halinde toplanmasına neden olur. Yüksek konsantrasyonlarda bu moleküller çift kırınım özelliğine sahip iki katmanlı bir yapıda düzene girerler.

Bazı polimer çeşitlerinin mezofaz oluşturabileceğinin keşfiyle beraber mesojen içeren polimerler sentezlenmeye başlanmıştır. Ana zincirinde mezojen olan polimerlerin gelişimi De Gennes'in araştırmalarına atfedilir. LCP'ler sıvı kristallerin kendiliğinden karşılıklı düzenlenme özelliğinin yanı sıra bir polimerin klasik entropik davranışlarını da taşır. LCP'ler mezofaz oluşumunu tetikleyen duruma göre LMMLC'lerdeki gibi liyotropik ve termotropik olarak ikiye ayrılır. Termotropik LCP'ler mezojenlerin bağlanma şekli ve molekül geometrisine göre sınıflandırılır. Genel olarak mezojen bağlanma biçimine göre sınıflandırılması şu şekildedir; polimere yan zincir olarak bağlanan SCLCP'ler ve polimerlerin ana zinciri içerisinde bulunan MCLCP'ler.

MCLCP'ler polikondenzasyon veya farklı iki fonksiyonlu polimerlerin kopolimerleştirilmesiyle sentezlenir. Kalamitik moleküllerin uç uca esnek ayırıcı gruplar vasıtasıyla birbirine eklenmesi şeklinde meydana getirilir. Elde edilme şekli sadece polikatılma ile mümkün olmasından mütevellit MCLCP'lerin sentezi başlangıç maddelerinin yüksek saflığını ve yan ürün oluşturmayacak şekilde reaksiyon koşullarını gerektirir. SCLCP'lere kıyasla makul faz sıcaklığına sahip MCLCP'lerin sentezi oldukça zorlayıcıdır. MCLCP'ler esnek olmayan bölümlerden kaynaklı yüksek derecede izotropik sıcaklığa sahiptir ve kristalleşme eğilimindedir. Bu da onu birçok uygulama için elverişsiz yapar. Bu sorunu aşmak için kullanılan esnek ayırıcı gruplar ve bükümlü moleküller eklenmesi gibi çeşitli yöntemler vardır. Bu yöntemler LCP'lerin geometrisini ve düzenlenmesini değiştirerek faz sıcaklığını kontrol altına alır.

SCLCP'lerde mezojen kalamitik, diskotik veya amfifilik bir molekül olabilir. Burada mezojen ana zincir üzerine yan zincir olarak esnek bir ayırıcı grup vasıtasıyla bağlıdır. Bu polimerler mezojen içeren monomerlerin polimerleştirilmesiyle veya bu tip farklı monomerlerin kopolimerizasyonuyla hazırlanabilir. SCLCP'lerde ana zincir konformasyonu mezojenin bağlanma şekline göre değişkenlik gösterebilir. Bunlar mezojenin yan tarafından veya uç tarafından bağlandığı veyahut ayırıcı grubun bükülmüş olduğu yapılardır ve bunlara göre zincirin farklı konformasyonları vardır. Ayırıcı gruplar kristalleşme eğilimini ve mezojenlerin etkileşimini azalttığı için onların varlığı mesofaz türünü ve oluşumunu doğrudan etkiler ve mezojenler de düzen oluşturmayı desteklediğinden moleküle entropi kazandırmak için ayırıcı grup gereklidir. Mezofaz davranışı kimyasal yapının farklılaştırılmasıyla değiştirilebilir. Örneğin uzun ayırıcı gruba sahip bir yapı smektik faz gösterirken, ayırıcı grupların uzunluğunun kısalması nematik fazı oluşturma yönünde kabiliyeti arttırır.

Bu çalışmada yan zincirinde mezojenik birim bulunan poliüretanlar (SCLCPU) elde edilmiştir. Farklı ayırıcı grup uzunluklarına sahip SCLCPU'ların sentezlenmesi maksadıyla, öncelikle mezojenik birim ayırıcı gruplara bağlanmıştır daha sonra bu ara ürünlerin 2,2bis(hydroxymethyl)propionik asit ile tepkimesi sonucu çift fonksiyonlu LC8-diol ve LC6-diol monomerleri elde edilmiştir. En nihayetinde, LC8-diol ve LC6-diol monomerlerinin HMDI ile polikatılma (polyaddition) yöntemi sonucu bahsedilen SCLCPU'ların sentezi gerçekleşmiştir.

LC6 ve LC8 sırasıyla 1,6-dibromohekzan'ın ve 1,8-dibromooktan'ın, mezojen olarak seçilen 4-siyano-4′-hidroksibifenil ile baz katalizli (K_2CO_3) reaksiyonuyla hazırlandı. LC6'nın ve LC8'in 2,2bis(hidroksimetil)propionik asit ile baz katalizli (KOH) esterleşme tepkimeleri sonucu sırasıyla LC6-diol ve LC8-diol sentezlendi. LC6-diol'ün ve LC8-diol'ün HMDI ile DBTDL katalizörlüğündeki ve N_2 gazı altındaki tepkimeleriyle sırasıyla PULC6 ve PULC8 sentezlenmiştir. Her bir aşamada ürünlerin yapı tayinleri ve mevcudiyetlerinin kanıtlanması FT-IR ve ^{1}H-NMR ile yapılmıştır.

Ürünlerin POM ile incelenmesi sonucu, LC6 ısıtılırken 58ºC'de nematik faz sergilediği ve 68ºC'de izotropik noktaya ulaştığı, soğutmada ise 63ºC ve 33ºC arasında kristalleşmeye kadar nematik faz sergilediği görülmüştür. LC8'in ısıtma aşamasında mezofaz göstermediği ancak soğutma aşamasında 66ºC'dan 61,5ºC'de kristalleşmesine kadar nematik faz gösterdiği saptanmıştır. LC6-diol ısıtılması esnasında 36ºC'de smektik, 59,5ºC'de nematik ve 62.9ºC'de izotropik faz sergilerken soğutmada 61,5ºC'de nematik faz ve 58.7ºC'de smektik faz göstermiştir. LC8-diol'ün ısıtma aşamasında 35ºC'de smektik fazdan 54ºC'de izotropik sıvıya geçtiği görülmüştür. Soğutma aşamasında ise 53ºC'de smektik faz görülmüştür. PULC6 mezofaz sergilemezken, PULC8'in ısıtma ve soğutma boyunca smektik yapılar gösterdiği saptanmıştır. Bu davranış ayırıcı gruptaki esnek metilen zincir uzunluğu arttıkça daha kararlı sıvı kristal davranış sergileyen sıvı kristal poliüretan elde edilebileceğini göstermektedir. DSC sonuçlarıyla da örneklerin POM'daki davranışları teyit edilmiştir.

1. INTRODUCTION

A liquid crystal that is between liquid and solid state exhibits a different state of matter. LCs are anisotropic substances and form mesophases that have the characteristics of amorphous like a liquid and the ordered structure like a crystal. Polymers can form anisotropy by combining mesogenic compounds and thus the mesophase occurs.

LCPs contain mesogens which are bonded covalently to polymeric chain. They are able to display LC feature provided that mesogens are attached to flexible spacer. LCPs can be categorized as MCLCPs in which mesogens are linked into main chain of polymer, SCLCPs where mesogens are linked onto main chain through flexible compounds and MCSCLCPs that are combination of two species. Scientific investigations have concentrated on synthesis of LCPs by the development of these polymers that have special features.

SCLCPs can present the characteristics of both LC and polymers. They produce a way out by collaboration of them for troubles that LMMLC can not overcome all alone. Thanks to electro-optical features, SCLCPs are used in various applications such as electronic parts and optical display appliances. In SCLCPs, while designing molecules, the structure has to possess both adequately array for forming mesophase and flexibility for processability.

In this study, two SCLCPUs based cyanobiphenyl were prepared. While the backbone of polyurethanes was not changed, the flexible spacers having two distinct lengths, were used to attach onto backbone of polyurethane. For this purpose, spacers were bonded first to mesogens by using two distinct dihalidealkanes. In the latter stage, the products (LC6 and LC8) were added to a compounds with dihydroxl for the preparation of LC monomers required to polyaddition. SCLCPUs were then obtained by reaction of HMDI with LC monomers. Mesogens were linked thus onto main chain through spacers. POM and DSC studies indicated that the length of the flexible spacers affects LC and thermal charactacteristics of SCLCPUs and precursors of them. ^{1}H-NMR and FT-IR analysis also characterized the products exhibiting LC feature.

2. THEORETICAL PART

2.1 The Discovery of Liquid Crystals

LCs which have birefringence feature in liquid state are a kind of organic substances. Before the discovery of LCs, it was known that soaps possess this property. The myelinic figures formed by lecithins, were also observed in 1850. When the solution of these substances with water are prepared, the miscellaneous forms composed of concentric lamellar display [1]. LCs have been thought as the 4th state of matter. Although the concept of liquid crystallinity was found out in 19th century, it has attracted the scientists' attention in second half of 20th century [2].

It has ever been taught that three states of material are composed of solid, liquid and gas. Unlike liquids, a solid has not fluidity and tends to protect their form. In old times, it was thought that if we warm up a crystalline solid, it will be liquid, gas respectively. Due to these experiences, the earlier scientists have not managed to find presence of different phase. Contrary to all of these, Reinitzer, professor of botany, observed an unexpected series of phase transition.

In 1888, while the Professor investigated esters of cholesterol obtained by extraction of carrot, he found two melting points at 145.5°C and at 178.5°C of cholesteryl benzoate (Figure 2.1). It was blurry liquid between two temperatures. Above 178.5°C the phase turned into unclouded.

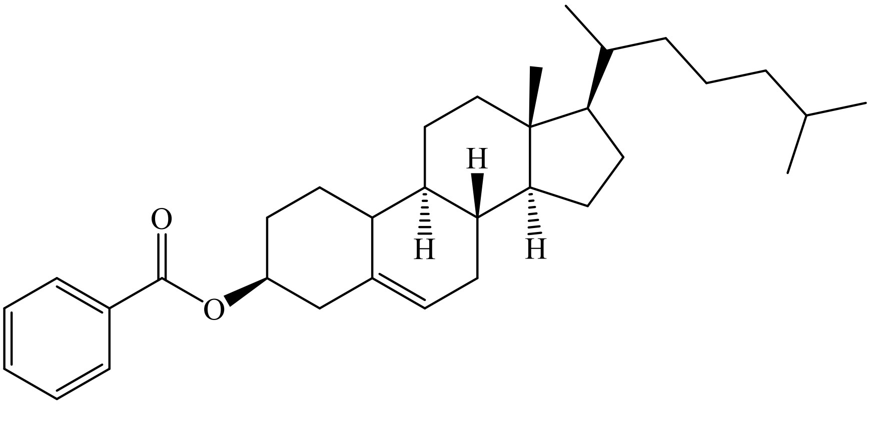


Figure 2.1 : Molecular formula of cholesteryl benzoate.

Under the polarizing light it displayed miscellaneous color upon cooling. While clear liquid was turning into turbidity, it displayed blue color and then violet appeared while turbidity was crystallizing. After observing similar behavior on cholesteryl acetate, Reinitzer contacted with Lehmann, the physicist, was experimenting about the isomerism of crystalline substances.

Lehmann's the polarizing microscope was more sophisticated. He managed to thus make more accurately investigations than observations of Reinitzer. Lehmann examined the samples which Reinitzer sent to him and observed that the samples have optic features like the crystals while in liquid state. The ensuing researches demonstrated that observed intermediate phases propound a new thermodynamic phase of matter that are different from the isotropic.

In 1889 the collaboration between two scientist revealed first publication about liquid crystals. Although they called firstly as "crystal that flow", then the term of "liquid crystals" was decided. Reinitzer is therefore known as the discoverer of LC. As for Lehmann, he is regarded as the builder of LC research [3,4].

2.2 Introduction to Liquid Crystals

LCs are organic substances exhibiting intermediate (meso) phases between liquid and solid phases. These phases are birefringent like a crystal and have the features of a liquid e.g fluidity [5]. Therefore, LCs can be described as the combining of array and mobility. The structure of LC phases is adequately disordered to provide fluidity depending on degree of arrangement. Therefore, depending on the features of reological, LCs can be thought as anisotropic liquids. This incorporation revealed the notion of mesophase (or mesomorphic phase) and the substances displaying this behavior are termed as mesogens [5,6].

2.2.1 Types of molecules forming mesophases

Mesophases are shortly derived from two types of molecules; rod-like molecules as shown in figure 2.2 and disc-like molecules.

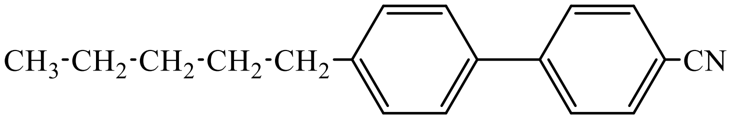


Figure 2.2 : A typical calamitic compound displaying nematic mesophase.

Rod-like (linear) structures define calamitic compounds whereas disc-like molecules represent discotics. In this classification of phases, the orientation of molecules, molecular conformation and intermolecular interaction (like hydrogen bonding) play a significant role [7].

2.2.1.1 Calamitics

In the calamitic molecules, like Pentyl-4-cyano-biphenyl (Figure 2.2), the molecular length is approximately five times of the diameter. They produce a constant dipole moment by having polarizability e.g. Nitrile. Althougth they are not actually cylindrical, when their behavior of physical is taken into consideration, due to rapid rotation resulted from thermal movement, they can be counted as a roller.

There are some necessities to behave as a LC; the rigid cores e.g. biphenyl and the flexible tails e.g. hydrocarbon chain. For example, if this molecule (Figure 2.2) had had wholly flexible structure, orientational order would never have been. If it had wholly consisted of rigid parts, it would have directly passed from crystal to liquid while heating. Therefore, in both cases mesophase is not observed. The rigid piece of molecules enhancing possibility of liquid crystallinity promote order whereas the piece that have flexibility raises disorder. Thanks to concord between flexible tails and rigid cores, they can behave as a LC.

2.2.1.2 Discotics

The molecules that are discotic (Figure 2.3) have flexible tails and a rigid core. Their branches are roughly on a plane. In discoid molecules, the diameter is approximately 5 times of their thickness.

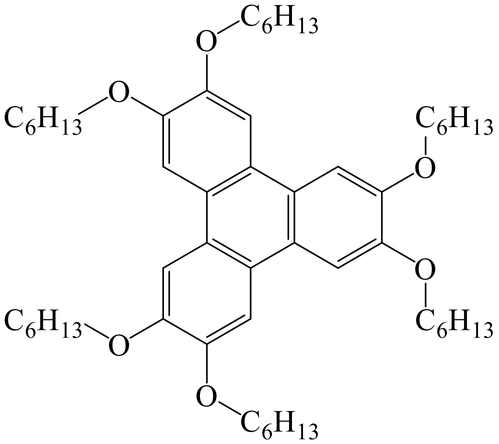


Figure 2.3 : A typical discotic compound displaying columnar mesophase.

If the structure has not polarizability perpendicular to molecules' the plane, they could be counted as discoidal owing to rapid spin about the vertical axis. If the structure has polarizability perpendicular to molecules' the plane, it is truer to imagine as a cup since the breaking begins in reflection symmetry and dipole interactions become in same direction. Hence, it is generated spontaneously polarization. If the tails possessing flexibility does not exist in the molecule, a crystalline phase occurs with positional order [8].

2.3 Types of Liquid Crystals

There are two ways to form mesogenic phase. In one, LCs exhibit mesogenic behavior in only specific temperature. This types are thermotropic LCs. The other is obtained by mixing particular solvents with a compound possessing high polarity. These types of LCs are called lyotropics [9].

2.3.1 Thermotropic LCs

Molecules having anisotropic shapes (calamitic or discotic mesogens) can form thermotropic mesophases. Both calamitics and discotics can display nematic phases but in discotics, the formation of nematic is uncommon. Also in calamitics, smectic phases appear and these phases possess a layered structure. Columnar phases possessing two-dimensional multi-layered are mostly formed by discotics. Nematics are most unstable mesophase beside the other. Polarizable groups, H bonding and ionic interactions are markedly influential in the formation of columnar and smectic mesophases [10]. The molecules of calamitic tend to assemble within the layers whereas the molecules of discotic tend to stack up for forming the columns [11].

The various mesophases generated by calamitic molecules are indicated in Figure 2.4. Initially, the substance is crystalline in which molecules is most ordered. When the temperature is increased, the substance turns up smectic mesophase where the molecules possess partial order and move round inside layers. The substance is viscous e.g. like a grease. When the temperature is increased further, the substance turns into the nematic where the molecules possess less order that does not exist any layer. The molecules are able to diffuse freely around. The viscosity of substances decreases in nematic phase. By increasing temperature, in the isotropic state, the viscosity of substances is not distinct from that of the nematic. In isotropic phase, the substance is most disordered.

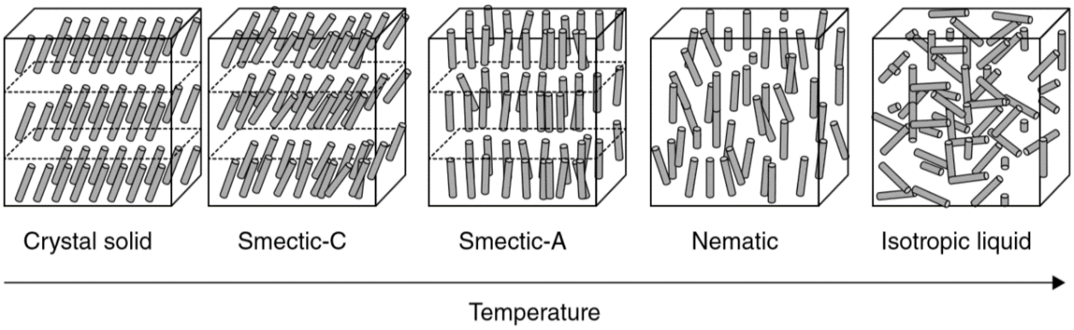


Figure 2.4 : Schematic arrangement of the mesophases formed by calamitics.

Some mesophases formed by discotics are indicated in Figure 2.5. Initially, the substance is crystalline in which there are the extended columns. When the temperature is increased, the substance turns into the columnar mesophase in which the molecules possess local order and stack up for forming the column. Inside the columns the substance is like a liquid without positional order. When the temperature is increased further, the substance turns up nematic mesophase in which the substance acts as a tidy liquid and has less order than the former. In isotropic phase, the substance has not any order [8].

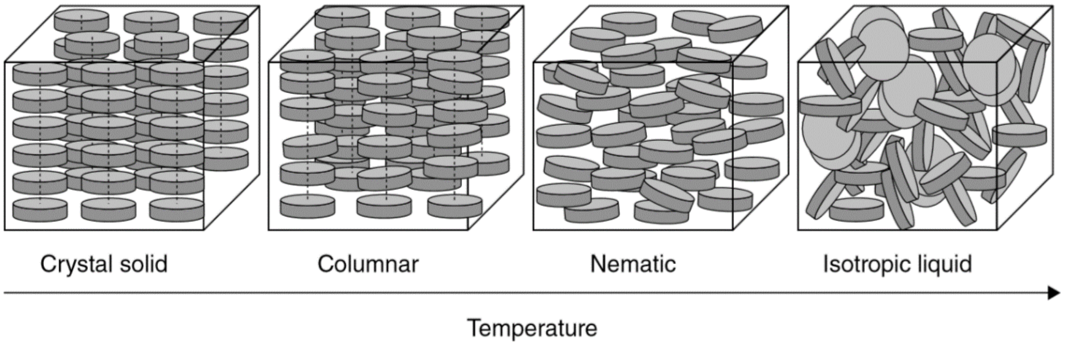


Figure 2.5 : Schematic arrangement of the mesophases formed by discotics.

2.3.1.1 Nematics

In nematics, the molecules, which is elongated (rod-like), have orientational order whereas it has not positional correlations. The long axis of one of these molecules are arranged parallel to the other throughout a preferential aspect. This orientation described as the director might change in any direction. Although among barycenter of this type of molecules does not exist any long-range alignment, there are 3D translational symmetry between the molecules. They move rotational on their long axis and are uniaxial substances having a center point of symmetry [5,12].

The nematic mesophases have both rotational freedom round single axis and translational freedom throughout 3 axes. This alignment, which is like a container of pens being swung, is depictured in figure 2.6.

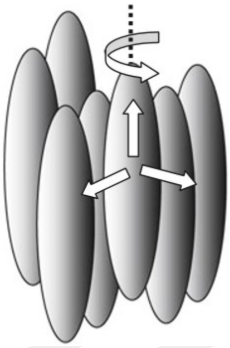


Figure 2.6 : Molecular alignment in nematic phase.

The term “Nematic” originated in the Greek means thread referring to the defects. These defects are termed disclinations. The nematic mesophases that is most common thermotropics have low viscosity. Their molecules have as fluidity as that of an isotropic. The first synthesized stable nematic substance is pentylcyanobiphenyl (Figure 2.2) [11].

When the pattern is examined with crossed polarizers, configuration of the director does not mostly idealize. a typical thread-shaped texture is shown in figure 2.7. The colors may vary according to thickness of sample [12].

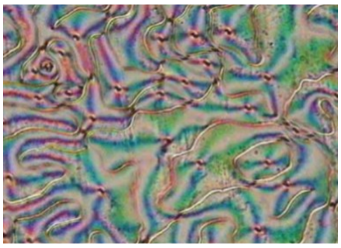


Figure 2.7 : A nematic texture.

2.3.1.2 Cholestrerics

The first discovered LC mesophase was cholesterics formed by cholestreyl esters. These steroid alcohols occurring naturally are chiral. Asymmerty of this molecules, which is optically active, leads to formation of the twisted nematic mesophases with iridescent colors. When small amounts of chiral compounds are added to non-chirals displaying nematic, similar mesophases also appear. Owing to this fact, cholesterics can be thought to be a subchapter of nematics. Cholesterics entitled twisted nematics are pointed out by a symbol with star (N*) [11].

The twisted nematic phases, which is similar to nematic phase, have orientational order and positional order does not exist. The molecular orientation (the director) rotates along the range with regular frequency. That distinguishes them from nematics. The twisting of molecules arranged along the long axis around the other axis, constitutes the director dispersion. In aspect perpendicular to helix axis, preferential direction varies constantly (Figure 2.8).

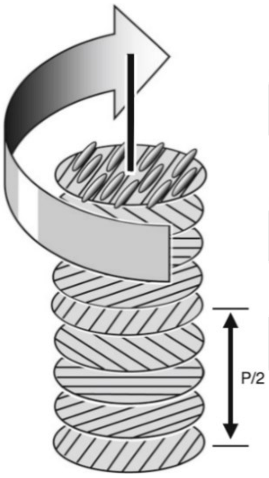


Figure 2.8 : Molecular arrangement in cholesteric mesophase.

When the director returns along a whole cycle, the range occurred along the helix axis is termed as the pitch of N* (p). The p is used for characterization of N*'s secondary structure. A nematic LC is cholesteric with infinite p. Consequently, between two mesophases, a phase transition does not exist. Nematics containing enantiomorphic substances are long cholesterics but with the finite p. The periodic spiral regulation is in charge of rotation strength and the typical colors of cholesterics. The p depends on chemical composition, temperature electrical fields. A cholesteric texture is exhibited in figure 2.9 [12].

Figure 2.9 : A cholesteric fingerprint texture.

2.3.1.3 Smectics

When nematic mesophases is cooled, arrangement's a new dimension turns up generally if a transition appears. This new order possesses a layered structure (smectic) becoming spontaneously [11]. The stratification of smectic that distinguishes them from nematics is unique property. the stratums glide freely over each other in smectic phase which molecules possess positional and orientational order. According to alignment of molecules into layers, there are several types of smectics [12]. To classify of smectics, a categorization is made in alignment between; orientational order of intermolecular bonds e.g. H bonds, correlations in orientations (3D) and positioning of molecules in the stratum plane. Figure 2.10 explains summarily smectics [13].

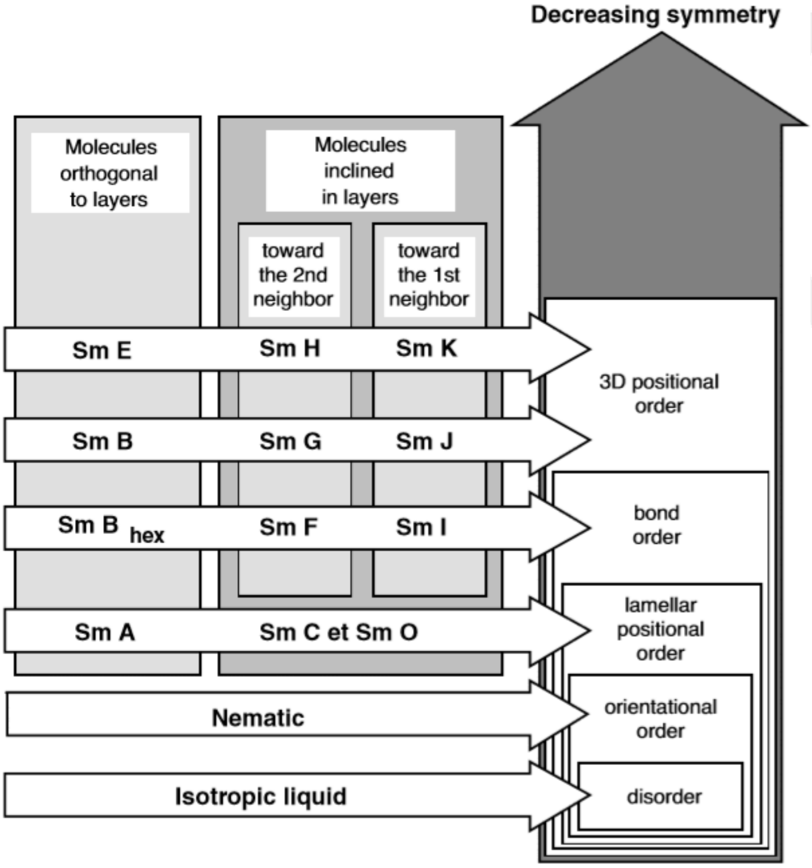


Figure 2.10 : Classification of smectics.

In SmA, which is the simplest of smectics, the symmetry of their is same as that of nematics, the molecules normal to director are perpendicular to the plane of the stratums and have rotatory freedom about z axis, so SmA is optically uniaxial. The translational freedom of molecules does not maintain thoughout z axis as they move freely inside stratums such as 2D fluids [14]. SmC mesophase is biaxial as molecules non-being perpendicular to stratum are inclined (Figure 2.11b) to the plane of stratum.

Figure 2.11a shows the molecules of SmA perpendicular to stratum. In SmC, mobile stratums are able to slip within one another like in SmA, so the translational symmetry of Sm mesophase is split at least one time.

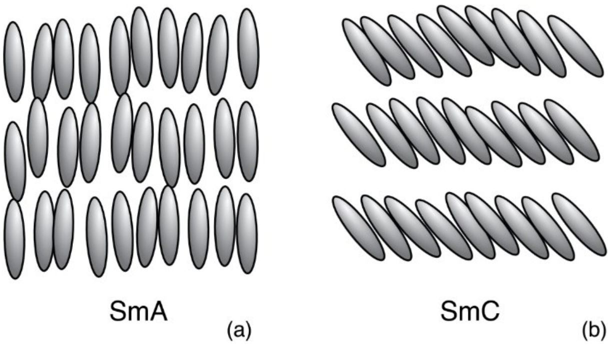


Figure 2.11 : Schematic representation of SmA and SmC.

Owing to this splitting of stratums, although thickness of smectics are constant, these stratums bring about peerless texture (Figure 2.12) shaped like focal conic when the sample is placed between glass sheets [13].

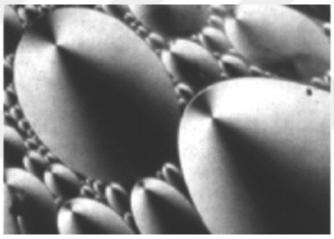


Figure 2.12 : Texture in a SmA.

2.3.1.4 Columnar mesophases

The columnar mesophases are usually generated by discotic molecules e.g. triphenylene derivatives (Figure 2.3). Recent studys has shown that non being discotic molecules are able to display a few columnar mesophase, so it is truer that they are classfied as columnar LCs. Columnar LCs are categorized according to packing system of the columns [12]. The plane of the molecules is parallel with one another and they can slip freely inside each other like a casket of coins being swung (Figure 2.13) [11].

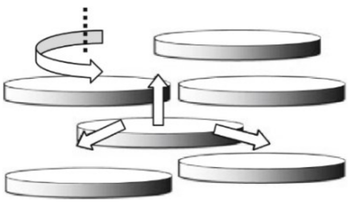


Figure 2.13 : A nematic columnar mesophase.

The structure of columnar mesophases is organized mainly in 2D lattices. However, in columnar nematics, the molecules are not actually composed of columns [12]. The columnar nematic mesophase has highest mobility and lowest order which is orientational and no positional. These possess similar features to nematic formed by calamitics and are uncommon beside the other columnar mesophases [8,11].

Columnar mesophase possesses orientational and positional array but inside a column, no positional order [8]. Also the correlation does not exist positionally between the columns. The molecules of discoid is either parallel to the axis of column or is inclined to the axis as shown in figure 2.14.

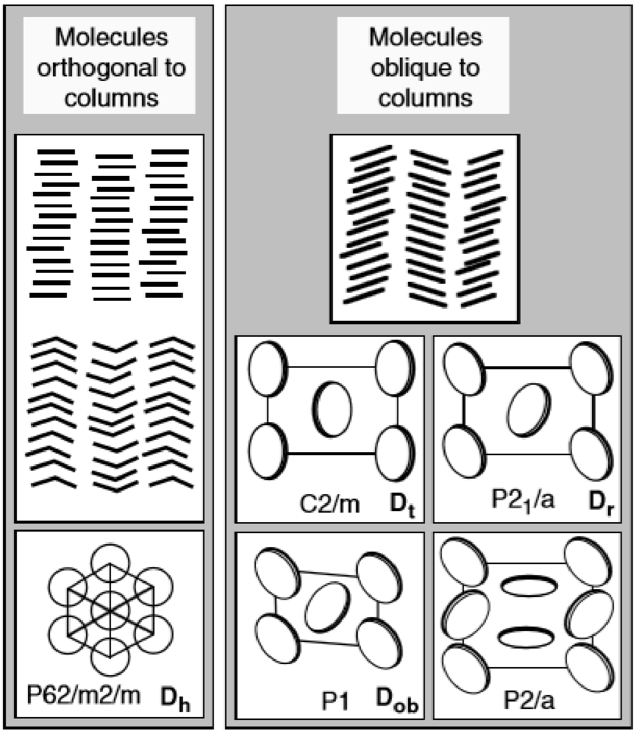


Figure 2.14 : The variety of columnar mesophases.

The correlations of positional between molecules throughout the columns are short distance. Although the piling up of molecules is very coordinated, this distance can vary at times throughout a column. However, these two phases can be thought as unidimensional but can not be distinguished from each other. The columns being parallel with each other constitute a bidimensional lattice. This lattice (Figure 2.14) can be oblique or hexagonal, rectangular. According to this, columnar mesophases are with 2D. In the hexagonal, the molecules can not be parallel to the axis of columns. hexagonal symmetry of the molecules is protected, provided that they freely revolve around the axis. A type of calamitic molecules termed as phasmids, have 6 aliphatic compounds, can also produce columnar phases [13].

Fan-shaped textures (Figure 2.15) are appeared in hexagonal phases. These textures are very similar to those of smectic A. Hence, while deciding whether a phase is columnar, its texture should not be merely observed [14].

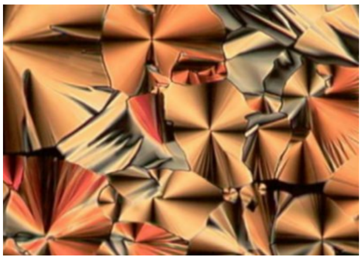


Figure 2.15 : Texture of a columnar mesophase.

2.3.2 Lyotropics LCs

Before the discovery of thermotropic LCs, LC phases have actually been found in aqueous solutions with amphiphiles. They are called nowadays lyotropic LCs [13]. Lyotropics, also termed lyomesophases, are obtained by mixing of amphiphilic molecules with solvent at certain temperature and specific concentration. Their LC features is affected with pressure, the ratio of concentrations of varied ingredients constituting the mixture and temperature. The self-assembling feature of amphiphilic materials distinguishes them from thermotropics [15].

In old times, scientists were investigating the samples extracted from animal and plant tissues under the polarized microscopy. In 1857, Mettenheimer extracted myelin from nerves and has observed with POM. Having put myelin into water, He saw the formation of tubular particle. Before the observations of Mettenheimer, in Buffon's studies, "writhing eels" obtained by disintegration of wheat in water have actually been mentioned. Apparently, it was myelin shapes constituted by lecithin or ergosterol in wheat. Myelins have been found out that possess phospholipids which are essential component of cell membranes.

When concentration increases in water, phospholipids are organized in bilayers. These bilayers are able to change forms e.g. concentric cylinders. These cylinders have the feature of birefringence and compose the structure of the myelin textures as shown in figure 2.16 [13].

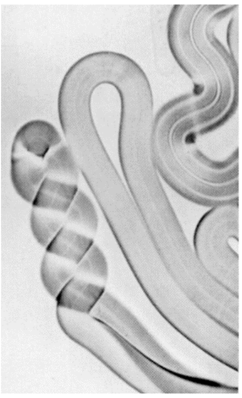


Figure 2.16 : A myelin texture.

The amphiphiles have two parts; hydrophobic and hydrophilic e.g. surfactants. This case leads to aggregation of molecules into micelles. The formation of micelles decreases relationship between water and hydrophobic groups. When a substance is dissolved in the solvent, the formation of micelles is shown in figure 2.17 [11].

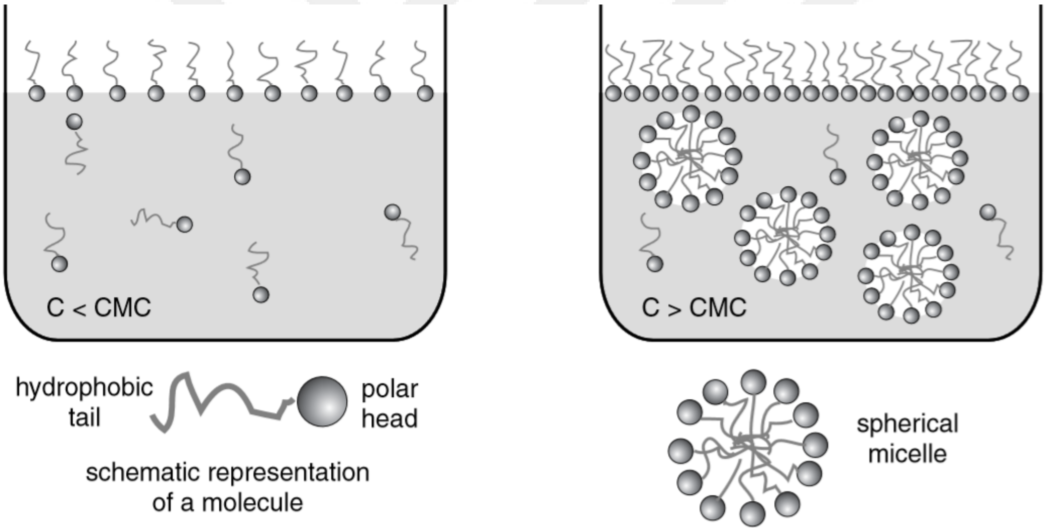


Figure 2.17 : Schematic formation of micelles.

At extreme low concentrations, the molecules constitute a film at the solution surface and are dispersed in solution. As the concentration increases, the surface tension decreases. The absorption of molecules is a consequence of the decreasing of this tension. When the concentration arrives the CMC, the surface tension does not decrease further, the saturation of the film happens at the solution surface, so this bring about aggregation of molecules by the adding of the molecules to the solutions. The aggregation structure of the simplest surfactants with single chain is spherical called micelles. Above the CMC, the formation of micelles occurs [13].

The CMC stage reveals crucial changes in the features of the solution. As hydrophobic regions are covered from the water, the system of micelles has high stability since it is more suitable for a molecule to be added to a micelle in terms of energetic. The pattern of dispersion of aggregation changes substantially because almost all of molecules are included in micelles. While the number of micelles ascending, micelles combine into cylinders that package in hexagonal alignment. While concentration increasing further, cylinders combine to yield extensive plate forming lamellar [11].

2.4 Liquid Crystalline Polymers

In LMMLC, the appearance of mesomorphic features is a consequence of a mutual array of anisodiametric compounds composed of approximate 105 molecules. As polymers that are substantially asymmetric have long chain, in macromolecules their existence pre-determines the probability of the formation of the mesogenic state. Besides the existence of polymers, some circumstances have to be supply for forming LC state. Researchers reported that the size of the areas of self-assembly fragments is too little to form anisotropy in most of flexible polymer without the effect of an exterior orienting domain. Despite this study, after the discovery of the probability of the forming of mesogenic state in polypropylene and polysiloxane derivatives, the synthesis of LC polymers was consciously performed by placing mesogens [16].

Polymers containing mesogens in main chain arose with the investigation of De Gennes. The study of him demonstrated that the potential capability to form a LC phase for such compounds due to its characteristics. Roviello and Sirigu deviated from the suggestion of a chain composed of solely mesogen and appointed the function of mesogenic units which are rigid to the molecules having flexibility. Two scientists permitted thus the mutual array of mesogenic units.

The mesogenic units are chosen wholly among LMMLC because LCPs should have both strong anisotropy and intermacromolecular interactions supplied with polarized units for probability of array [17].

LCPs possess specific LC ordering beside their polymer characteristics. They combine spontaneous orientation of LCs with entropically actuated behavior appeared in polymers. A LCPs must be design delicately; excessive chain rigidity that makes structure entropic spring prevents numerous configuration of a chain. Owing to rigid chain, it becomes like a rod even if a long chain. Excessive little rigidity, that is, too little mesogens induces an inadequate behavior for orienting and causes isotropic melting [18].

LCPs are like LMMLCs; they can be lyotropic or thermotropic according to the situation triggering the formation of mesophase. LCPs have been categorized depending on the style of mesogen linkage and macromolecular geometry. LCPs catergorize as MCLCPs and SCLCPs according to the point of mesogens bonding. There are also more complex LCPs such as the combined MCSCLCP, LC networks and LCE [19].

2.4.1 MCLCPs

This kind of LCPs are synthesized by polycondenzation or copolymerization of distinct two-functional polymers. MCLCPs typically consist of spacers having flexibility and anisotropic (Figure 2.18) segments [16].

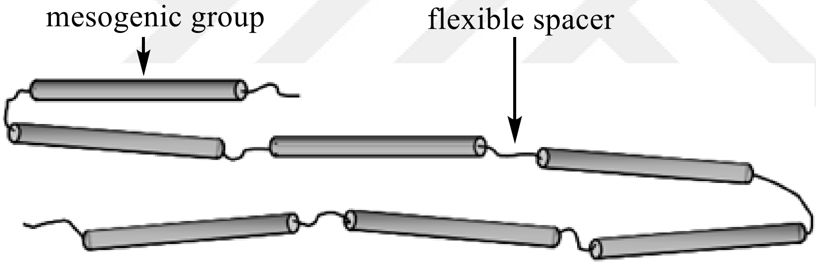


Figure 2.18 : Schematic representation of MCLCPs.

Rigid calamitics are organized in a head-to-tail style to form a MCLCP. Judicious selection of spacers between molecules of calamitic leads to adequate flexibility which provides therefore a random motion [18].

As MCLCPs are restricted with polyaddition and polycondensation, the synthesis of MCLCPs requests the greatest purity of the reactive substances and reaction conditions excluding by product. Compared to SCLCPs, the synthesis of MCLCPs with convenient temperatures is rather compelling. Most MCLCPs display much more clearing temperature owing to rigidity resulted from calamitic mesogens. They also tend to be crystalline and this makes unsuitable MCLCPs for applications [20].

The stability of mesophase, which can be represented by the LC-isotropic transition temperature, can be increased by enhancing the number of mesogens into the polymer. However, there is a crucial trouble; the melting temperature of the polymer also rises.

The LC-isotropic transition temperature usually rises more rapidly than that of the solid-LC transition, thus mesophase becomes more stable. However, in longer chain, the temperatures rise continually, the compound will be therefore inclined to decompose, a LC phase does not occur and processability will be gradually unfavorable [21]. Owing to array of mesogens throughout the main-chain of polymer, MCLCPs are inclined to form smectic or mesophases with high stability. Accordingly, particularly if nematic mesophase is desired, these troubles must be overcome [20]. So some strategies have been used for polymers containing mesogen. Firstly, the substances having additional flexibility is to design. A melting point less than 300°C is considered as the approachable range [21]. Some strategies used; kinked moieties combined with mesogens, laterally linked side chain which can behave as platicizers or spacers [20]. Some of kinks, lateral groups and flexible spacers are shown in figure 2.19. These structures modify alignment and geometry of LCPs and used for controlling phase temperatures [19].

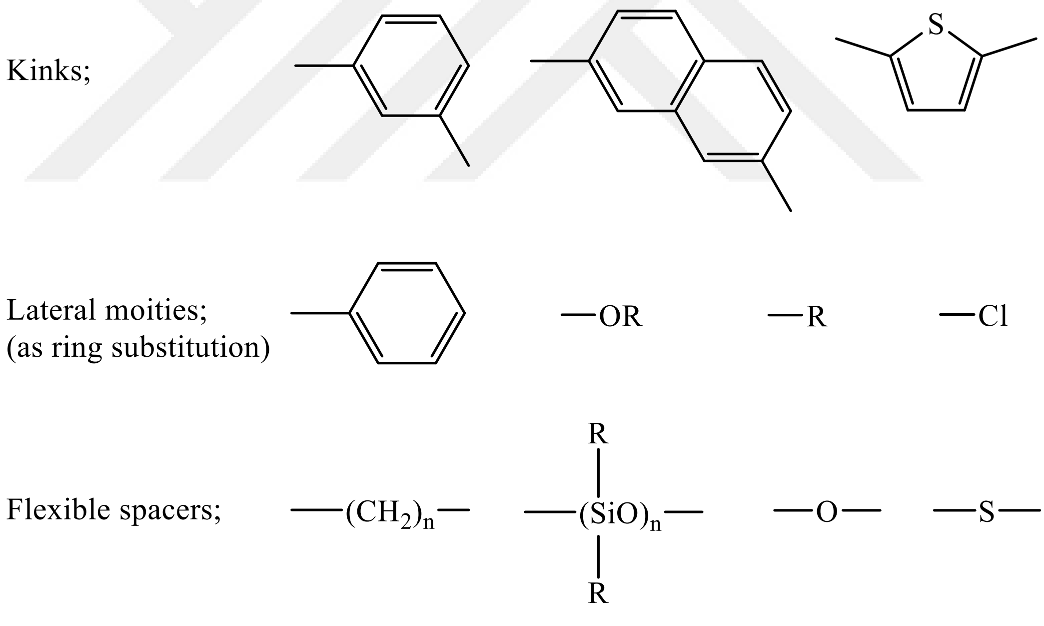


Figure 2.19 : The units used for modification of LCPs.

2.4.2 SCLCPs

In SCLCPs, the mesogenic units can be calamitic, discoid or amphiphilic. These molecules are linked as side segments to backbone of a polymer through a spacer that is aliphatic [20].

Comb-shaped SCLCPs are based on placement of calamitic molecules forming LC. Long branches assure what spacers make, which ensure adequate mobility of mesogens and spontaneous aligning. These make possible interaction of mesogens and thus the formation of mesophase. Such SCLCPs are obtained by homopolymerisation of diverse monomers containing mesogen, copolymerization of diverse monomers containing mesogen or copolymerization of monomers containing mesogen and not containing mesogen [22].

The backbone of SCLCPs may have distinct conformations for the same rating of ordering of mesogens. According to the manner of bonding mesogens to the main-chain, the conformation changes. In figure 2.20a, the 'side-on' manner extends the backbone along the director, it similar to those of MCLCPs but the extension is lesser. In the 'end-on' manner, spacer make the main-chain flatten in the plane normal to the director. That is called the oblate backbone as shown in figure 2.20b. In case of end-on, the spacer which is bent provides extension. The prolate backbone is as shown in figure 2.20c.

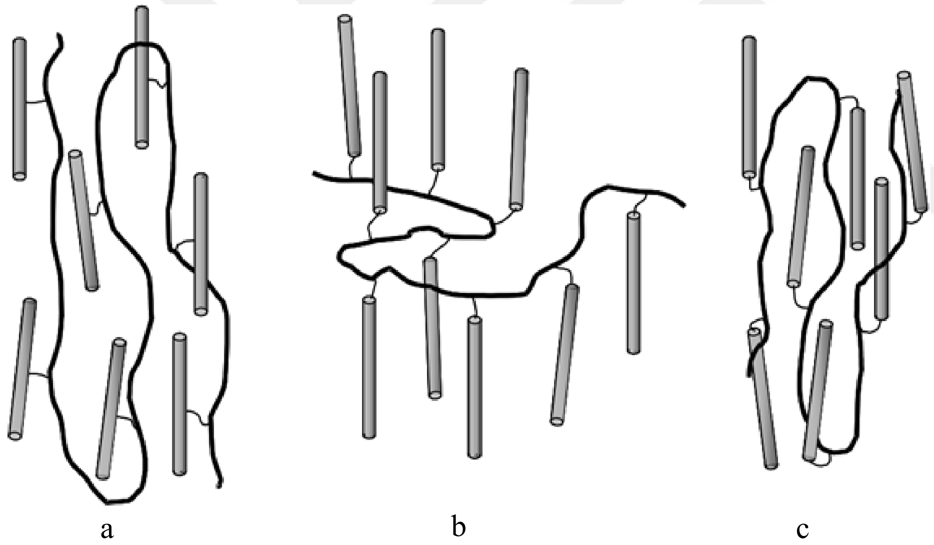


Figure 2.20 : Schematic representation of SCLCPs.

Although side-on SCLCPs exhibit lower anisotropy than MCLCPs, they have still significantly backbone aligning. In the varieties of end-on SCLCPs mesogens can be solely weakly attached to the backbone. The option between oblate and prolate array depends on the spacer selection [18].

Since the spacer reduces the inclination for crystallization and provides to decouple mesogens, the presence of them is crucial for the formation and the selection of mesophases. Decoupling is essential so that the polymer attains entropy while the mesogens promote order. Mesophase behavior can be change by modification of the chemical structure but crosslinking generally does not change mesophase behavior significantly. Calamitic mesogens usually consist of biphenyls that are linearly linked through bonds of ether or ester. If the spacers and tails of mesogens is short, SCLCPs displays nematic mesophases. Smectic mesophases become more stable as length of the spacer and tail increases. Mesogens with three phenyls display primarily nematic but transition temperature of them is very high [20]. When centres having chirality is attached to the structure, nematic order is bent and cholesteric phase appears [18].

2.4.3 LC polyurethanes

PU obtained from toluene diisocyanate and biphenyl mesogenic moiety displays LC features owing to its structure containing methyl into toluene diisocyanate, biphenyl moieties. In polyurethane, H bonding have solely secondary value to form mesophase but crucial to stability [23].

In the study of Jana, R.N. & Cho, J.W., Cholesteric SCLCPU that contains a two-step reaction of polycaprolactone diol, methylene diphenyl diisocyanate, glycerol and cholesterol, has been synthesized. PU composed of polycaprolactone diol, methylene diphenyl diisocyanate and glycerol was used as a main-chain with polycaprolactone diol, methylene diphenyl diisocyanate and glycerol. Cholesterol was attached to the polymer as a side-chain via methylene diphenyl diisocyanate. The investigation of thermal behavior showed that cholesteric SCLPU with a small amount of cholesterol exhibits a spherulite crystalline structure and melting temperature rises by increasing the weight percent of cholesterol [24].

In the study of Wen, Z. et al. SCLCPU networks was synthesized. 4’-hydroxy-4-biphenylcarbonitrile, mesogenic fragment, was attached sequentially to a spacer and diethanolamine to form a LC monomer with diol. This monomer was then reacted with HMDI for forming linear SCLCPU. Pentaerythritol was used for crosslinking to obtain SCLCPU network. Thermal behavior and thermomechanical properties of SCLCPU network was investigated. This SCLCPU network exhibits nematic mesophases [25].

2.5 LC Applications

LCs have exhibited an improvement on multipurpose applications such as electronics, metamaterials and photonics as LCs can simultaneously display some properties which are common to both crystals and liquids. The ability of changing themselves characteristics by external stimulant, e.g. temperature alteration, electrical or optical fields, makes LC materials attractive for developing of optical sensors and other appliances. Smartphone and notebook screen are examples of photonic appliances associated with designing of LCDs. The instability of both liquid and crystalline response of LCs is also appeared in the effects on these appliances. In the lack of geometrical restrictions and external stimulant, direction of the molecular orientation can freely change in any aspect but the orientation can be fixed in a direction by modification of LC substrates or mechanically. In visual appliances, optical contrast, vision angle, reaction time depend on LC alignment which is achieved by interplay between aligning stratum and LC. The technics used for the alignment of LC can also be applied in LCPs [26].

Cholesteric LCs can reflect light same wavelength as their pitch. Owing to sensitivity of the pitch to temperature alterations, the reflected light displays distinct color according to the temperature. The thermometers having cholesteric LCs determine the temperature by observing of variation in color. These thermometers can be also used for particular temperature ranges by mixing distinct substances [12].

MCLCPs are substantially sophisticated for molding applications by mechanical features. Owing to high orientation, they possess high strength and modulus. Their advanced mechanical characteristics, thermal capacitance, low water absorbing make them appealing for varied applications. The applications of MCLCPs are categorized as; molding applications used in micro electronics e.g. switches and carriers and extrusions used in chemical industry e.g. fibers and sheets.

MCLCP fibers with lightweight are used in military garments and helmets. MCLCP fibers are also used for protector gloves by perfect cut and tear resistance and thermal isolating property. MCLCP-carbon fiber composite is used for aerospace industry by their perfect chemical resistance and offering low viscosity. In aircraft, MCLCPs like Kevlar provide weight saving and have low flammability. MCLCP rods having low flexibility, high thermal resistance can also fulfill the function of steel ensuring strength in optical cable.

Most of MCLCPs applications comprise injection-molded components. Two of these types of MCLCPs are Vectra and Xydar that have good resistance against chemicals and solvents [19].

Contrary to MCLCPs, SCLCPs are able to easily dissolve in common solvent and their LC phase temperatures are lower than those of MCLCPs. SCLCPs is capable of forming sheet, fibres, properties of polymers, and respond to external stimulation like LMMLC. Thanks to these characteristics, SCLCPs have caught researcher's attention [26].

SCLCP has remarkable application potential for the developed electro-optic materials. They can successfully combine macromolecular features e.g. capability of easy processing, mechanical integrity with the electro-optic features of LMMLC. As chiral SCLCPs possess ferroelectric features, they have given a hope for potential applications [27]. One of the distinctive of structural features of SCLCPs is the ease to generate film during processing. Thus, this combination reveals distinct prospective applications since LMMLC has difficulty all alone in processing. There are numerous applications in SCLCPs e.g. chemical processing, telecommunication, optical appliances, medical appliances for diagnosis [2].

The improvements in SCLCPs contributed to LCEs used as actuators in micromechanical and propulsion systems e.g. artificial muscles, thermal and touch sensors, microfluidics. They are also another option to hydrogels and piezoelectrics. LCEs are prepared by reaction mesogenic monomers with non-being mesogenic crosslinking agent. Bent core SCLCPs, one of types of SCLCPs, are used for piezo and pyro electric appliances. The other type of SCLCPs is MJLCPs used in optical storage, optics, separation membranes. The popularity of SCLCPs continues to increase in the technology of LCP [20,26].

3. EXPERIMENTAL PART

3.1 Materials

4-cyano-4′-hydroxybiphenyl (TCI), N,N-dimethylformamide (Merck), Ethanol (Labor Teknik), Acetone (Hepak), potassium carbonate (Fluka), 1,6-dibromohexane (Fluka), 1,8-dibromooctane (Alfa Aesar), petroleum ether (Lab-Scan), dichloromethane (Merck), hexane (Zag Kimya), hexamethylene diisocyanate (Sigma Aldrich), methanol (Riedel de Haen), dibuthyltin diluarate (Sigma Aldrich), potassium hydoxyide (Riedel de Haen), 2,2 bis(hdyroxymethyl)propionic acid (Sigma Aldrich) were used.

3.2 Instruments

Fourier Transform Infrared Spectroscopy (FT-IR)

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

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a varian 500 MHz spectrometer in $CDCl_3$.

Differantial Scanning Calorimeter (DSC)

Thermal phase transitions of the molecules were determined by DSC Instrument (Perkin Elmer).

Polarized Optical Microscopy (POM)

Liquid crystalline behavior of the synthesized compounds and the polymers were investigated by POM using Leica DM2500P equipped with a LTSE350 Liquid Crystal Prosystem TMS 94 Hot Stage.

3.3 Synthesis of LC6 and LC8

3.3.1 Synthesis of 1-Bromo-6-(4-cyanobiphenyl-4′-oxy)hexane (LC6)

4-cyano-4′-hydroxybiphenyl (3,1g, 16 mmol) and K_2CO_3 (16 g, 120 mmol) were dissolved in dried acetone (250 ml) then 1,6-dibromohexane (25 ml, 160 mmol) was added to the solution. The reaction mixture was refluxed constantly stirred during 24 hours. After cooling to room temperature, the K_2CO_3 was removed by filtration and washed with acetone. The filtrates were concentrated by a rotary evaporator. The concentrated mixture was poured into cooled petroleum ether (150 ml). After a few hours, the consisted white precipitate was filtered and washed with petroleum ether. After drying, the obtained precipitate was crystallized with ethanol. (Yield: 50%)

3.3.2 Synthesis of 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane (LC8)

For synthesis of 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane, 4-cyano-4′-hydroxybiphenyl (2,1 g, 10 mmol), K_2CO_3 (10 g, 72 mmol) and 1,8-dibromooctane (20 ml, 108 mmol) were added to dried acetone (200 ml). The reaction mixture was refluxed constantly stirred during 24 hours. After cooling to room temperature, the K_2CO_3 was removed by filtration and washed with acetone. The filtrates were concentrated by a rotary evaporator. The concentrated mixture was poured into cooled petroleum ether (150 ml). After a few hours, the consisted yellowish precipitate was filtered and washed with petroleum ether. After drying, the obtained precipitate was purified by crystallization from ethanol. (Yield: 85%)

3.4 Synthesis of LC Monomers (LC6-diol and LC8-diol)

3.4.1 Synthesis of LC6-diol

2,2-bis(hdyroxymethyl)propionic acid (0,46 g, 3,4 mmol) and KOH (0,22 g, 4 mmol) were dissolved in DMF. The potassium salt occurred at 100˚C after 1 hour. 1-Bromo-6-(4-cyanobiphenyl-4′-oxy)hexane (1,5 g, 4 mmol) dissolved in DMF was then added by dropping funnel. The reaction mixture was refluxed with stirring for 15 hours at 100˚C. The mixture was separated by filtration. The residuary was washed with DMF. The filtrates were combined. DMF was removed at low pressure by a rotary evaporator. The concentrated mixture was dissolved in CH_2Cl_2 (100ml) then it was extracted with purified water (50 ml). The crude product was purified by crystallisation from CH_2Cl_2/Hexane (Yield: 74%)

3.4.2 Synthesis of LC8-diol

2,2bis(hdyroxymethyl)propionic acid (0,87 g, 6,4 mmol) and KOH (0,44 g, 7,7 mmol) were dissolved in DMF. The potassium salt occurred at 100˚C after 1 hour. 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane (3 g, 7,7 mmol) dissolved in DMF was then added by dropping funnel. The reaction mixture was refluxed with stirring for 15 hours at 100˚C. The mixture was separated by filtration and residue was washed with DMF. Filtrates was combined. DMF was removed at low pressure by a rotary evaporator. The concentrated mixture was dissolved in CH_2Cl_2 (100ml) then it was extracted with purified water (50 ml). The crude product was purified by crystallisation from CH_2Cl_2/Hexane (Yield: 94%)

3.5 Synthesis of Side Chain Liquid Crystalline Polyurethanes

3.5.1 Polyaddition of LC6-diol with hexamethylene diisocyanate (PULC6)

6-(4-cyanobiphenyl-4′-oxy)hexyl-2,2bis(hydroxymethyl)propionate (0,2 g, 0,5 mmol) was dissolved in CH_2Cl_2 (3 ml) then HMDI (0,09 ml, 0,6 mmol) was added under N_2 atmosphere. 3 drops DBTDL was then added as a catalyst. The reaction was carried out under N_2 atmosphere with mixing at room temperature in 6 hours. The polymer obtained was precipitated by pouring into methanol. PULC6 was separated by filtration and dried in vacuum. (Yield: 39%)

3.5.2 Polyaddition of LC8-diol with hexamethylene diisocyanate (PULC8)

8-(4-cyanobiphenyl-4′-oxy)octyl-2,2bis(hydroxymethyl)propionate (0,4 g, 0,9 mmol) was dissolved in CH_2Cl_2 (2-3 ml) then HMDI (0,172 ml, 1 mmol) was added under N_2 atmosphere. 3 drops DBTDL was then added. The polymerization reaction was carried out at room temperature in 24 hours. The polymer obtained was precipitated by pouring into methanol (200 ml). PULC8 was separated by filtration. (Yield: 65%)

4. RESULTS AND DISCUSSIONS

In this study, side chain liquid crystalline polyurethanes (SCLCPUs) containing cyanobiphenyl mesogens with two different lengths flexible spacers (PULC6 and PULC8), were prepared by polyaddition of a diol monomer that has mesogen with hexamethylene diisocyanate to combine the mechanical features of polyurethanes with anisotropic behavior of cyanobiphenyls. The mesomorphic properties of PULC6 was compared with those of PULC8 to find out the effect of diverse spacer lengths to LC properties.

For this purpose, the synthesis of PULCs were achieved in three steps. The first step is addition stage of alkylenes to cyanobiphenyl. Dibromoalkanes were used for alkylation of cyanobipenyl mesogens. In the second stage, bromo alkyl cyanobiphenyls was reacted with 2,2-bis(hydroxymethyl)propionic acid for attaching to dihydroxl group. That was then used as a diol monomer for polyurethane synthesis. In the last stage, hexamethylene diisocyanate was reacted with diol monomer having cyanobiphenyl mesogen to obtain SCLCPUs.

4.1 Synthesis of LC6 and LC8

Two bromo alkyl cyanobiphenyl mesogens having different length methylene units (n=6, 8) were synthesized according to the synthetic route illustrated in figure 4.1.

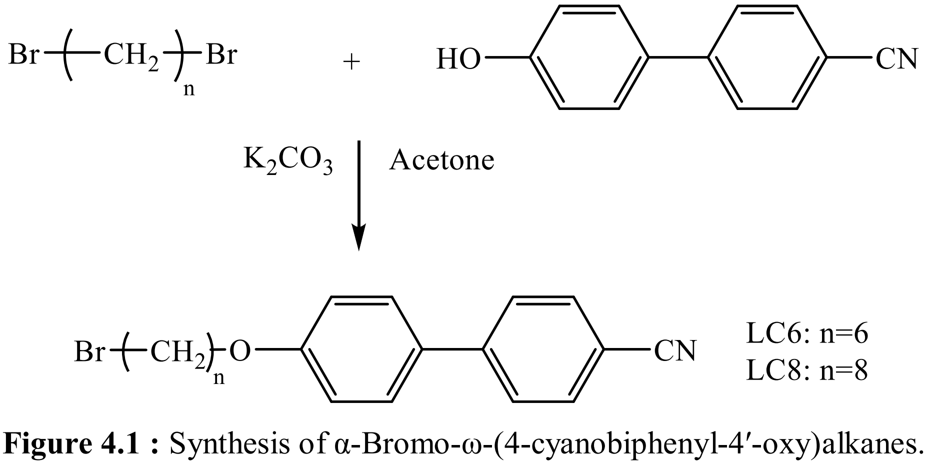


Figure 4.1 : Synthesis of α-Bromo-ω-(4-cyanobiphenyl-4′-oxy)alkanes.

4.1.1 Synthesis of 1-Bromo-6-(4-cyanobiphenyl-4′-oxy)hexane (LC6)

1,6-dibromohexane was reacted with 4-cyano-4′-hydroxybiphenyl by using a base catalyst (K_2CO_3).

The structure of LC6Br was characterized by FT-IR and ^{1}H-NMR spectroscopy.

Figure 4.2a shows the FT-IR of LC6. This spectrum indicates C-H stretching peak at 3045 cm^{-1} also bending vibrations at 811 cm^{-1} owing to aromatic phenyl rings. C-H of hexyl group gives stretching at 2919-2854 cm^{-1}. The appearance of Nitrile (C≡N) group’s stretching peak falls typically in 2220 cm^{-1}. Stretching vibration associated with C-Br bond is exhibited at 525 cm^{-1}. C-O strong stretching band at 1175 cm^{-1} show that exist ether group proving the reaction formation.

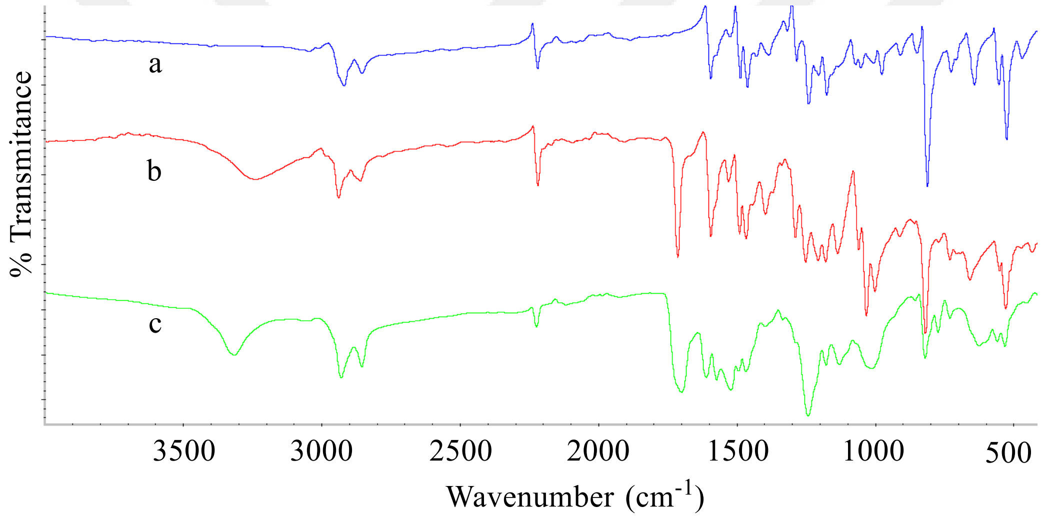


Figure 4.2 : FT-IR spectra of LC6 (a), LC6-diol (b), PUL C6 (c).

The ^{1}H-NMR spectrum of LC6 precursor is shown in figure 4.3.

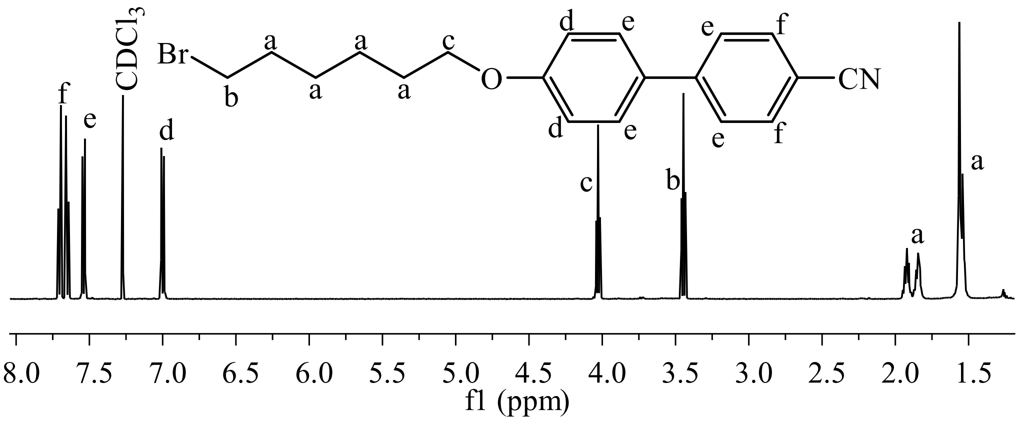


Figure 4.3 : ^{1}H-NMR spectrum of LC6.

^{1}H-NMR analysis of the LC6 indicates the peaks at 1.93-1.83 ppm (m, $-CH_2-$, 4H), 1.56-1.53 ppm (m, $-CH_2-$ 4H), 3.46-3.43 ppm (t, $-CH_2-Br$, 2H), 4.04-4.02 ppm (t, $-OCH_2-$, 2H). The typical shift of aromatic protons falls into 7.71-6.99 ppm; 6.99-7.00 ppm (d, aromatic CH=CH, 2H), 7.53-7.66 (overlapping d, aromatic CH=CH, 4H) and 7.69-7.71 (d, aromatic CH=CH, 2H).

4.1.2 Synthesis of 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane (LC8)

To prepare 1-Bromo-8-(4-cyanobiphenyl-4′-oxy)octane (LC8), the preparation steps of LC6 precursor was followed (Figure 4.1). 1,8-dibromooctane was reacted with 4-cyano-4′-hydroxybiphenyl in the presence of K_2CO_3.

The characterization of LC8 precursor and proof of its existence was carried out by using FT-IR and ^{1}H-NMR.

The FT-IR spectrum shown in figure 4.4a of LC8 indicates C-H stretching at 3051 cm^{-1} also bending vibrations at 817 cm^{-1} due to aromatic phenyl rings. Stretching C-H peaks belonging to octyl groups are observed at 2927-2853cm^{-1}. The typical peak of nitrile (C≡N) is observed at 2218 cm^{-1}. Stretching related to C-Br bond is at 529 cm^{-1}. The observed C-O stretching peak at 1176 cm^{-1} indicates that LC8 has occurred.

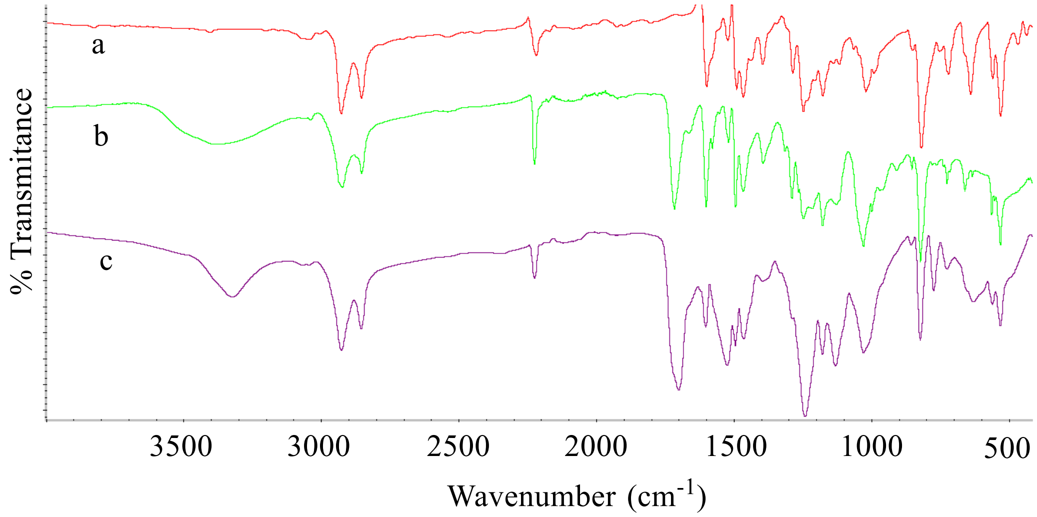


Figure 4.4 : FT-IR spectra of LC8 (a), LC8-diol (b), PULC8 (c).

^{1}H-NMR analysis of the LC8 indicates the peaks at 1.91-1.79 ppm (m, CH_2CH_2, 4H), 1.56-1.33 ppm (m, CH_2CH_2, 4H), 3.44-3.40 ppm (t, $Br-CH_2-$, 2H), 4.03-4.01 ppm (t,$-OCH_2$, 2H), 7.01-6.99 ppm (d, aromatic CH=CH, 2H), 7.53-7.66 ppm (overlapping d, aromatic CH=CH, 4H) and 7.69-7.71 ppm (d, aromatic CH=CH, 2H).

The ^{1}H-NMR spectrum of LC8 precursor is shown in figure 4.5.

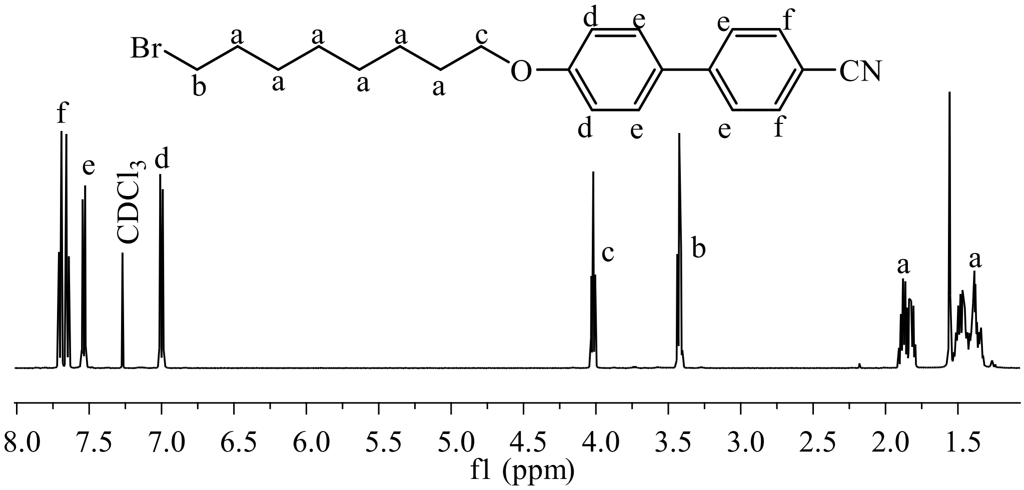


Figure 4.5 : ^{1}H-NMR spectrum of LC8.

4.2 Synthesis of LC Monomers (LC6-diol and LC8-diol)

4.2.1 Synthesis of LC6-diol

1-Bromo-6-(4-cyanobiphenyl-4′-oxy)hexane was reacted with 2,2bis(hydroxymethyl)propionic acid by base-catalyzed (KOH) esterification. Thus, the monomer that contains cyanobiphenyl mesogen with dihydroxyl groups required for polyaddition reaction of polyurethane, was synthesized. The synthetic route of LC6-diol was given in figure 4.6.

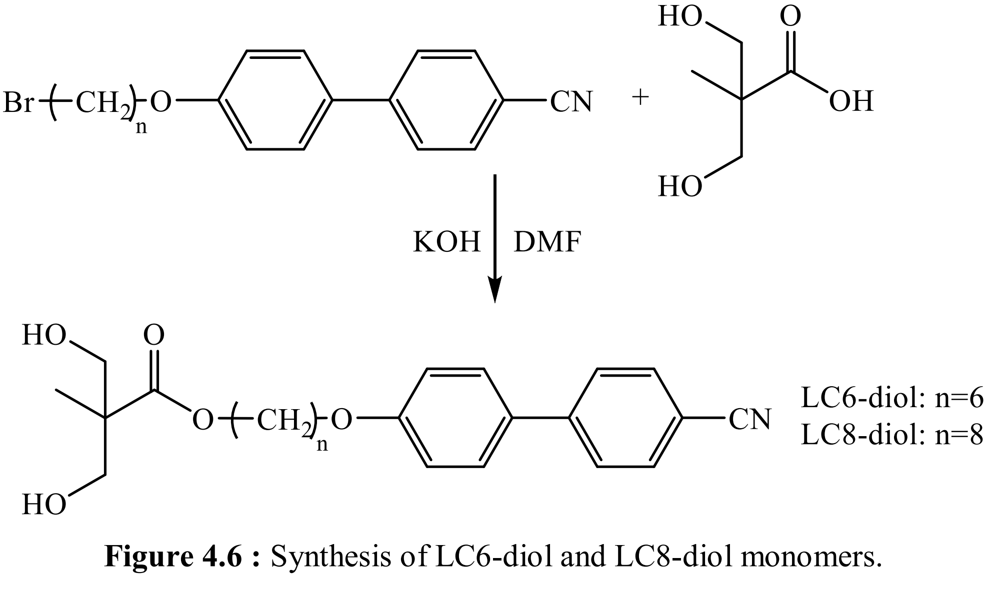


Figure 4.6 : Synthesis of LC6-diol and LC8-diol monomers.

The structure of LC6-diol was enlightened by FT-IR and ^{1}HNMR. FT-IR spectrum of LC6-diol (Figure 4.2b) shows strong OH stretching absorption at 3364 cm^{-1} , C-H stretching at 3051 cm^{-1} and bending vibrations at 817 cm^{-1} due to aromatic phenyl rings, it indicates also stretching C-H peaks of hexyl groups at 2939-2861 cm^{-1}, stretching C-O peak at 1179 cm^{-1} and carbonyl stretching absorption peak at 1714 cm^{-1}. The typical peak of nitrile ($C\equiv N$) is observed at 2219 cm^{-1} The absence of the stretching vibration band of C-Br, the appearance of the broad OH peak and carbonyl peak demonstrate that the reaction has occurred.

^{1}H-NMR analysis of the LC6-diol (Figure 4.7) indicates the peaks at 1.07 ppm (s, -CH_3, 3H), 1.87-1.46 ppm (m, CH_2CH_2, 8H), 3.91-3.72 ppm (s, CH_2OH, 4H), 4.01 ppm (t, -OCH_2, 2H), 4.22 ppm (t, -$OOCH_2$, 2H), 7.01-6.99 ppm (d, aromatic CH=CH, 2H), 7.53-7.66 ppm (overlapping d, aromatic CH=CH, 4H) and 7.69-7.71 ppm (d, aromatic CH=CH, 2H).

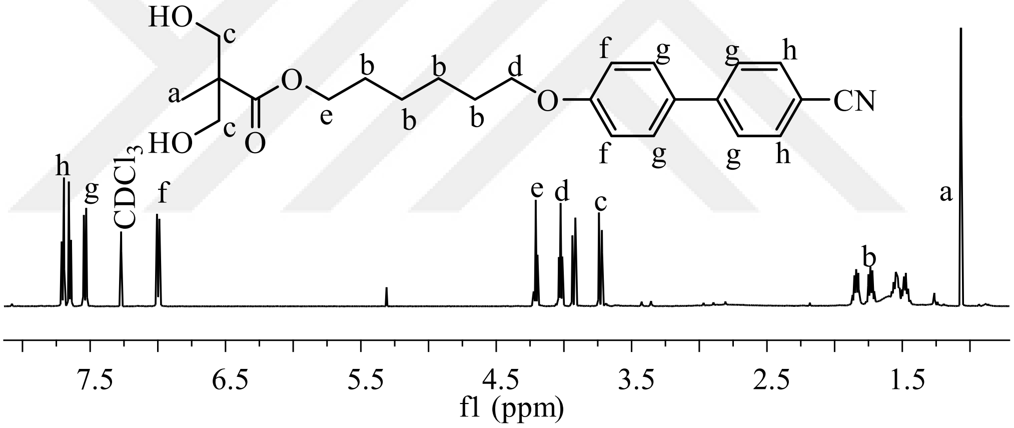


Figure 4.7 : ^{1}H-NMR spectrum of LC6-diol.

4.2.2 Synthesis of LC8-diol

LC8-diol monomer, was synthesized like the preparation of LC6-diol.

The structure identification of LC8-diol was achieved by FT-IR and ^{1}HNMR. The FT-IR spectrum of LC8-diol (Figure 4.4b) shows strong OH stretching absorption at 3364 cm^{-1}, C-H stretching at 3051 cm^{-1} and bending vibrations at 819 cm^{-1} due to aromatic phenyl rings. It points out stretching C-H peaks of octyl groups at 2926-2853 cm^{-1}, stretching C-O peak at 1179 cm^{-1} and carbonyl stretching absorption peak at 1715 cm^{-1}. The typical peak of nitrile ($C\equiv N$) is observed at 2223 cm^{-1} The absence of the stretching vibration band of C-Br and the appearance of the broad OH peak, carbonyl peak demonstrate that the reaction has occurred.

The structure of LC8-diol was enlightened by ^{1}HNMR. The chemical shifts of LC8-diol (Figure 4.8) indicates the peaks at 1.07 ppm (s,-CH_3, 3H), 1.26-1.83 ppm (m, -$CH_2CH_2CH_2$-, 12H), 3.91-3.72 ppm (s,-CH_2OH, 4H), 4 ppm (t, -$OOCH_2$-, 2H), 4.2 ppm (t -OCH_2-, 2H), 6.98-7.01 ppm (d, aromatic CH=CH, 2H), 7.53-7.66 ppm (d, aromatic CH=CH, 4H) 7.69-7.71 ppm (overlapping d, aromatic CH=CH, 2H).

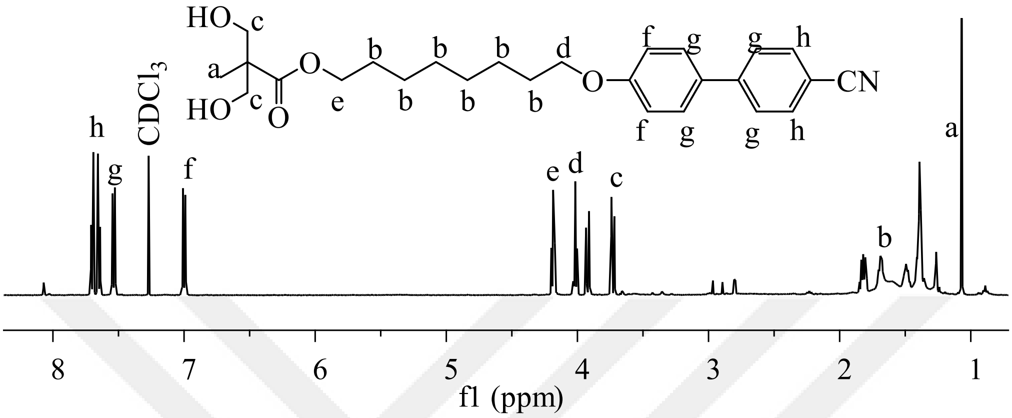


Figure 4.8 : ^{1}H-NMR spectrum of LC8-diol.

4.3 Synthesis of Side Chain Liquid Crystalline Polyurethanes (SCLCPUs)

4.3.1 Polyaddition reaction of LC8-diol with HMDI (PULC6)

Polyaddition reaction of LC6-diol with HMDI, was carried out via a catalyst (DBTDL). The synthetic route of PULC6 is as presented in figure 4.9.

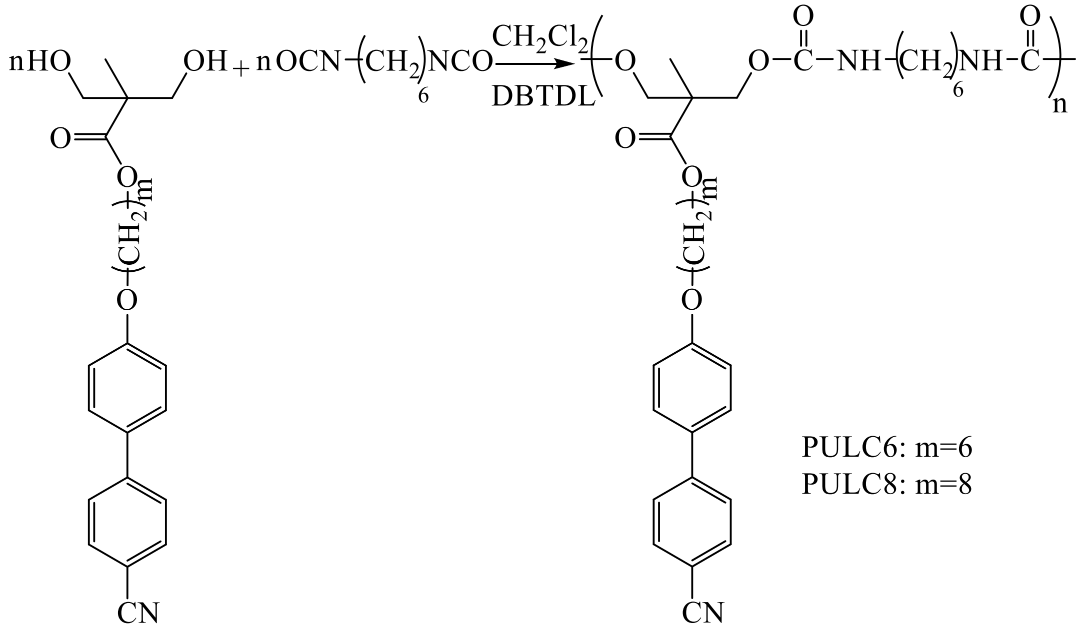


Figure 4.9 : Synthesis of side chain liquid crystalline polyurethanes.

The characterization of synthesized products is carried out by using FT-IR and ^{1}H-NMR. Figure 4.2c shows the FT-IR spectrum of the PULC6.

Narrow N-H peak shows repeating amide group of PULC6. The absence of strong OH stretching absorption at 3364 cm^{-1} proves that the polymerization reaction has occurred.

The FT-IR of PULC6 indicates the absortion bands at 3317 cm^{-1} (N-H stretching), at 3053 cm^{-1} (aromatic C-H, stretching), at 2930-2855 cm^{-1} (hexylene moiety C-H stretching) and 820 cm^{-1} (C-H bending), at 2224 cm^{-1} (C≡N, stretching), at 1702 cm^{-1} (C=O, stretching), at 1615 cm^{-1} (amide C=O, stretching), at 1178 cm^{-1} (C-O stretching).

The structure of PULC6 was proved by ^{1}H-NMR. Deshielding of hydrogens on C attached to nitrogen (3.14 ppm) indicates that PULC6 has occurred. The ^{1}H-NMR spectrum of PULC6 can be seen in figure 4.10.

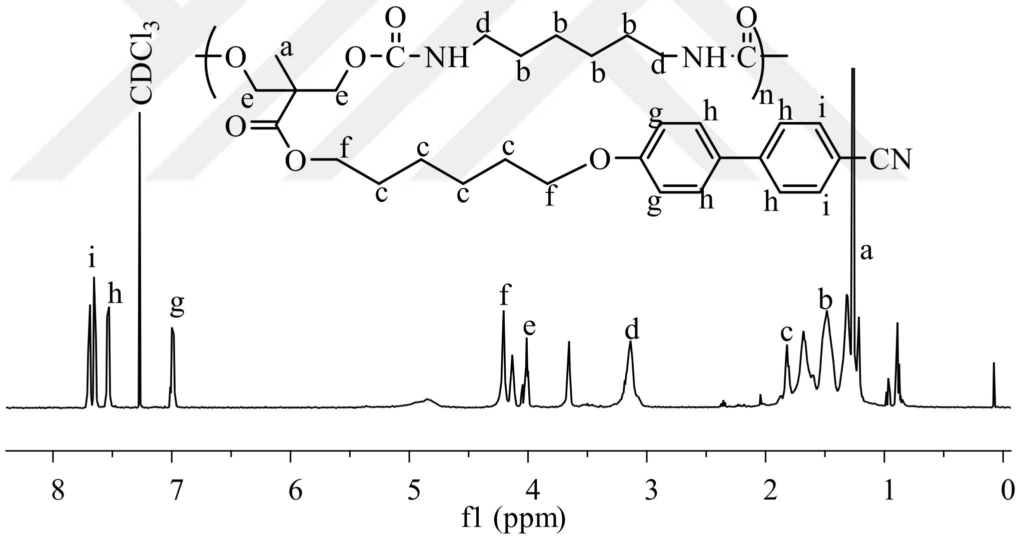


Figure 4.10 : ^{1}H-NMR spectrum of PULC6.

The chemical shifts of PULC6 indicates the peaks at 1.21 ppm (s,-CH_3, 3H), 1.48-1.32 ppm (m, -NHCC$\underline{H}_2$- on main chain, 8H), 1.82-1.68 ppm (m, -OCCH2- on side chain, 8H), 3.14 ppm (overlapping t, amide –CH_2NH-, 4H), 3.65-4 ppm (s, -OCH_2 on main chain, 4H), 4.21-4.12 ppm (overlapping t, -OCH_2-, -$OOCH_2$- on side chain, 4H), 6.98-7.00 ppm (d, aromatic CH=CH, 2H), 7.53-7.65 ppm (overlapping d, aromatic CH=CH, 4H) and 7.69-7.70 ppm (d, aromatic, 2H).

4.3.2 Polyaddition reaction of LC8-diol with HMDI (PULC8)

Polyaddition reaction of LC8-diol with HMDI, was carried out via a catalyst (DBTDL). The synthetic route of PULC8 is as presented in figure 4.9.

The structure determination and existence of PULC8 was achieved by FT-IR and ^{1}HNMR. As presented in Figure 4.4c, the disappearing of OH peak and appearing of narrower N-H peak explain presence of PULC8. The FT-IR of PULC8 points out absortion bands at 3323 cm^{-1} (N-H stretching), at 3051 (aromatic C-H, stretching), at 2927-2855 cm^{-1} (on hexylene C-H stretching) and 821 cm^{-1} (C-H bending), at 2225 cm^{-1} (C≡N, stretching), at 1700 cm^{-1} (C=O, stretching), at 1602 cm^{-1} (amide C=O on main chain, stretching), at 1241 cm^{-1} (C-O ester on main chain, stretching) and at 1178 cm^{-1} (C-O stretching),

The structure of PULC8 was proved by NMR. Deshielding of hydrogens on C attached to N (3.14 ppm) indicates that PULC8 has occurred. The chemical shifts of PULC8 (Figure 4.11) indicates the peaks at 1.65 ppm (s, $-CH_3$, 3H), 1.36-1.21 ppm (m, $-NHCCH_2-$ on main chain, 8H), 1.81-1.48 ppm (m, $-OCCH_2-$ on side chain, 12H), 3,14 ppm (overlapping t, amide $–CH_2NH-$, 4H), 3.65-4.01 ppm (s, $-OCH_2$ on main chain, 4H), 4.2-4.1 ppm (overlapping t, $-OCH_2-$, $-OOCH_2-$ on side chain, 4H), 7.00-6.98 ppm (d, aromatic CH=CH, 2H), 7.52-7.65 ppm (overlapping d, aromatic CH=CH, 4H), 7.68-7.00 ppm (d, aromatic CH=CH, 2H).

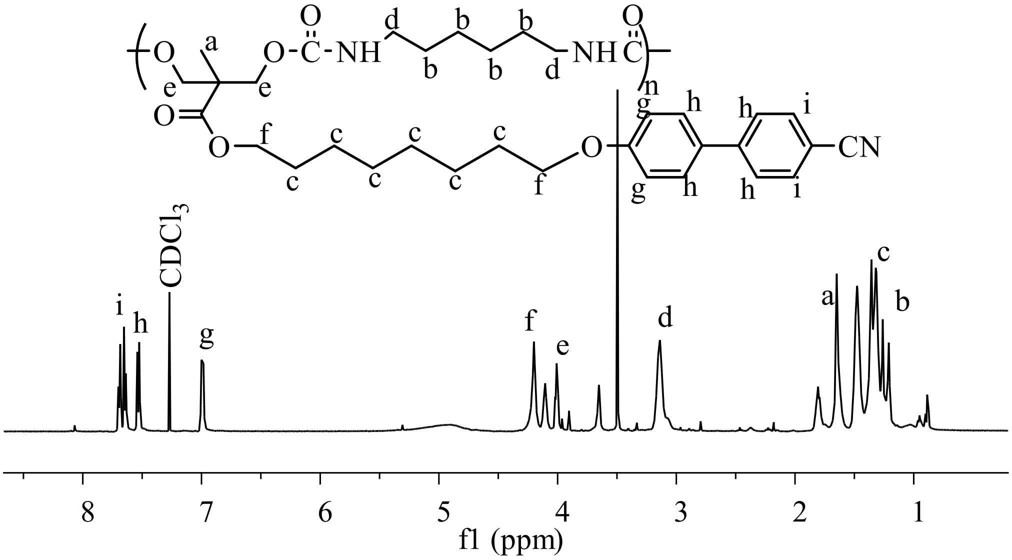


Figure 4.11 : ^{1}H-NMR spectrum of PULC8.

4.4 Investigation of Thermal and Mesomorphic Properties

To confirm the liquid crystalline nature and to identify the mesophases of the polyurethanes and precursors depending on the spacer length of side chain mesogens, differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) were employed.

4.4.1 Thermal and mesomorphic properties of LC6 and LC8

To observe mesophase behavior, LC6 and LC8 were investigated in POM. Polarized optical microscopy investigation of LC6 showed that on heating, the nematic phase was observed from 58ºC to 68ºC. During cooling, LC6 displayed nematic phase from 63ºC to 33ºC.

The POM investigation of LC8 showed that on heating, LC8 does not exhibit any mesophase and exhibits isotropic phase at 81ºC. while on cooling from isotropic phase, it exhibits nematic phase from 66ºC to 61.5ºC.

The DSC heating trace of LC6 contains two endothermic peaks corresponding to the crystal-liquid crystalline phase transition and liquid crystalline-isotropic phase transition at 56.75°C and 69.42°C, respectively.

In the cooling trace of LC6, it contains an exothermic peak corresponding to the isotropic-liquid crystalline phase transition at 66.93ºC.

The DSC trace of LC8 contains and an endothermic and two exothermic peaks corresponding to the crystal-isotropic phase transition at 81.95ºC, isotropic-nematic transition and nematic-crystal transition at 65.24ºC and 59.19ºC, respectively.

Thermal properties of LC8 and LC6 are shown in Table 4.1.

Table 4.1 : Thermotropic behavior of LC6 and LC8 precursors.

Code	Phase Transitions (ºC) (enthalpy changes (ΔH $J.g^{-1}$))	
	Heating	Cooling
LC6	Cr 56.75 (-73.78) N 69.42 (-1.3) I	I 66.93 (1.15) N 33[a] Cr
LC8	Cr 81.95 (-89.14) I	I 65.24 N 59.19 (87.36) Cr

Determined by DSC.

[a]Observed by POM.

Cr: Crystalline, N: Nematic, I: Isotropic.

POM studies also confirm these DSC results of the transitions as shown in figure 4.12 and figure 4.13.

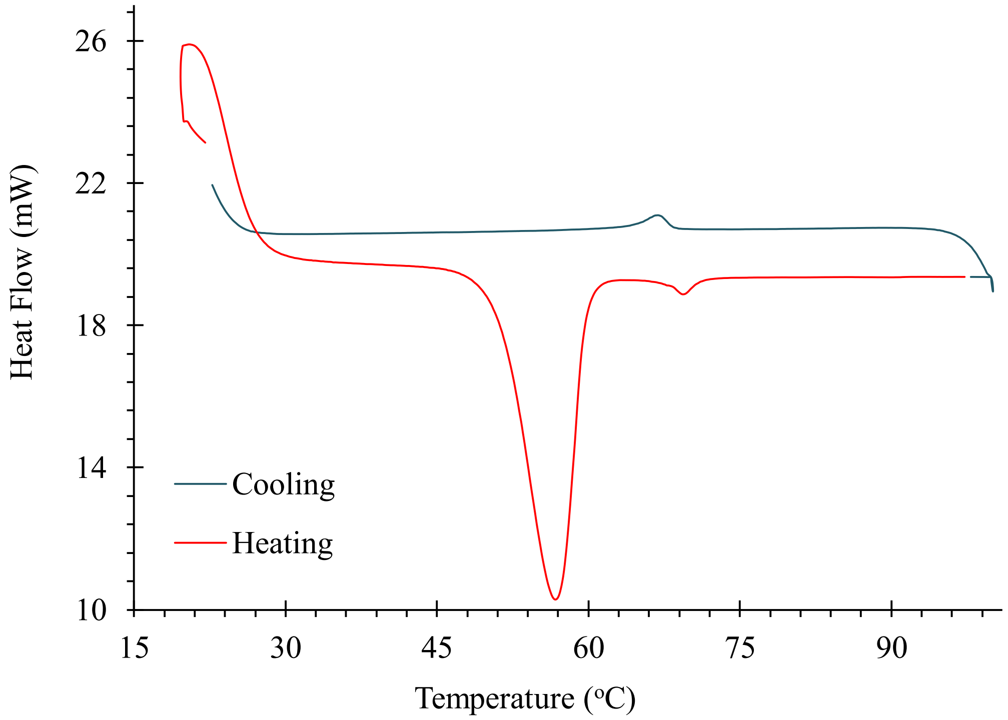


Figure 4.12 : DSC curve of LC6.

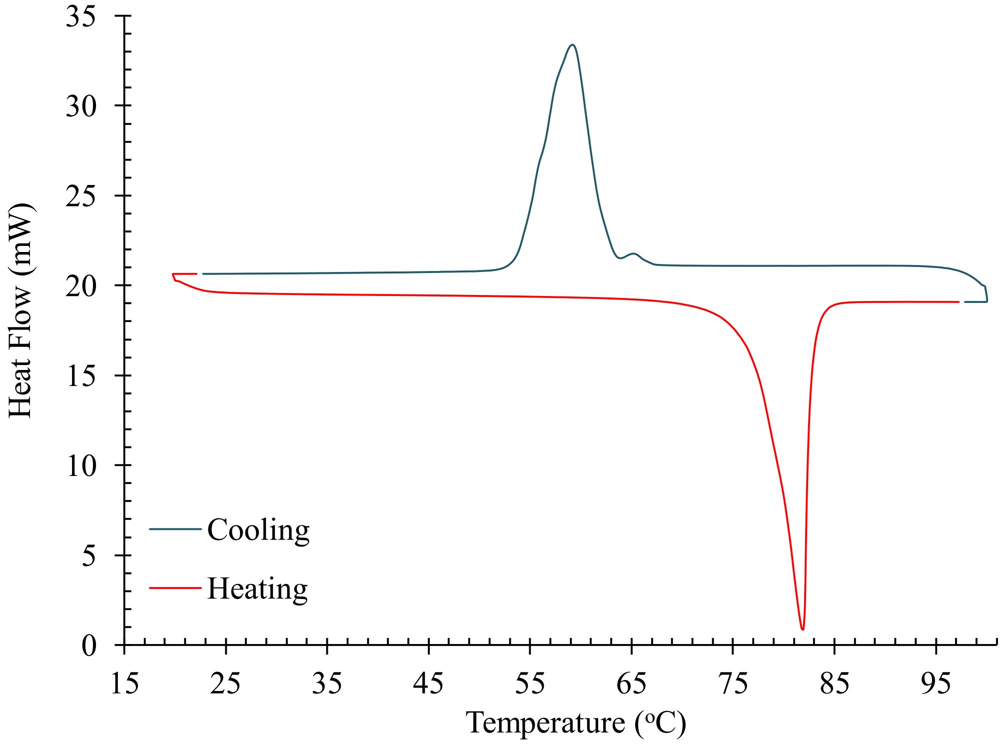
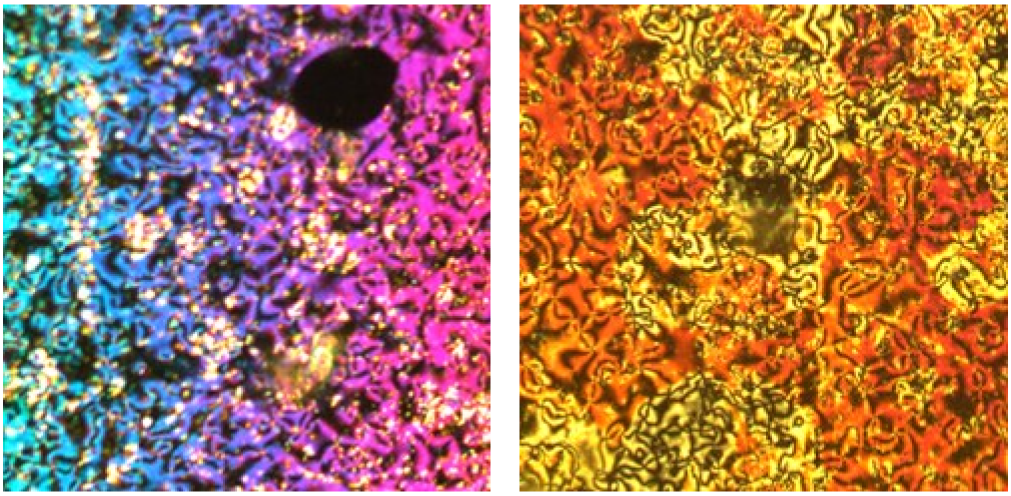


Figure 4.13 : DSC curve of LC8.

Polarized optical microscopic images of LC6 and LC8 were given in Figure 4.14.



(a) (b)

Figure 4.14 : Polarized optical micrographs of (a) LC6 and (b) LC8 taken during cooling from the isotropic phase at 63.2ºC and 65ºC respectively (x200).

4.4.2 Thermal and mesomorphic properties of LC6-diol and LC8-diol

Polarized optical microscopy studies showed that both LC6-diol and LC8-diol exhibited phase transition during heating and cooling stages.

The POM investigation of LC6-diol showed that LC6-diol exhibits smectic phase at 36ºC, nematic mesophase at 59,5ºC and isotropic phase at 62.9ºC during heating. While cooling from isotropic phase, the texture of LC6-diol shows nematic at 61.5ºC and smectic mesophases at 58.7ºC respectively. The crystallization of LC6-diol was not observed until the room temperature.

The POM investigation of LC8-diol showed that LC8-diol exhibits smectic phase at 35ºC and isotropic phase at 54ºC while heating. While cooling from isotropic phase, smectic mesophase appears at 53ºC. The crystallization of LC8-diol was not observed until the room temperature.

The DSC heating trace of LC6-diol contains four endothermic peaks corresponding to crystal-Sm_1 phase transition at -13.48ºC, Sm_1-Sm_2 phase transition at 35.89ºC, Sm_2-nematic phase at 56.9ºC and nematic-isotropic phase transition at 60.7ºC. In the cooling trace, it contains three exothermic peaks corresponding to isotropic-nematic phase transition at 58.44ºC, nematic-Sm phase transition at 54.9ºC and smectic-solid phase transition at -16.05ºC.

The DSC heating trace of LC8-diol contains three endothermic peaks corresponding to the crystal-Sm_1 phase transition at -24°C, Sm_1-Sm_2 phase transition at 34.88°C and Sm_2-isotropic phase transition at 50.94°C. In the cooling trace, there are two exothermic peaks corresponding to isotropic-Sm phase transition at 48,57°C and smectic-solid phase transition at -25°C.

Thermal properties of LC6-diol and LC8-diol are shown in Table 4.2.

Table 4.2 : Thermotropic behavior of LC monomers.

Code	Phase Transitions (°C) (enthalpy changes (ΔH $J.g^{-1}$))	
	Heating	Cooling
LC6-diol	Cr -13.48 (0.48[a]) Sm_1 35.89 (-0.92) Sm_2 56.9 (-0.5) N 60.7 (-0.55) I	I 58.44 (0.79)N 54.9 (0.29) Sm -16.05 (0.41[a]) Cr
LC8-diol	Cr -24 (0,77) Sm_1 34,88 (-28,5) Sm_2 50.94 (-4,02) I	I 48.57 (3.93) Sm -25 Cr

Determined by DSC

[a] ΔCp, Cr: Crystalline, Sm: Smectic, N: Nematic I: Isotropic

The observations with POM of the textures of LC8-diol and LC6-diol are compatible also with these DSC results shown in Figure 4.15 and Figure 4.16 of the transitions.

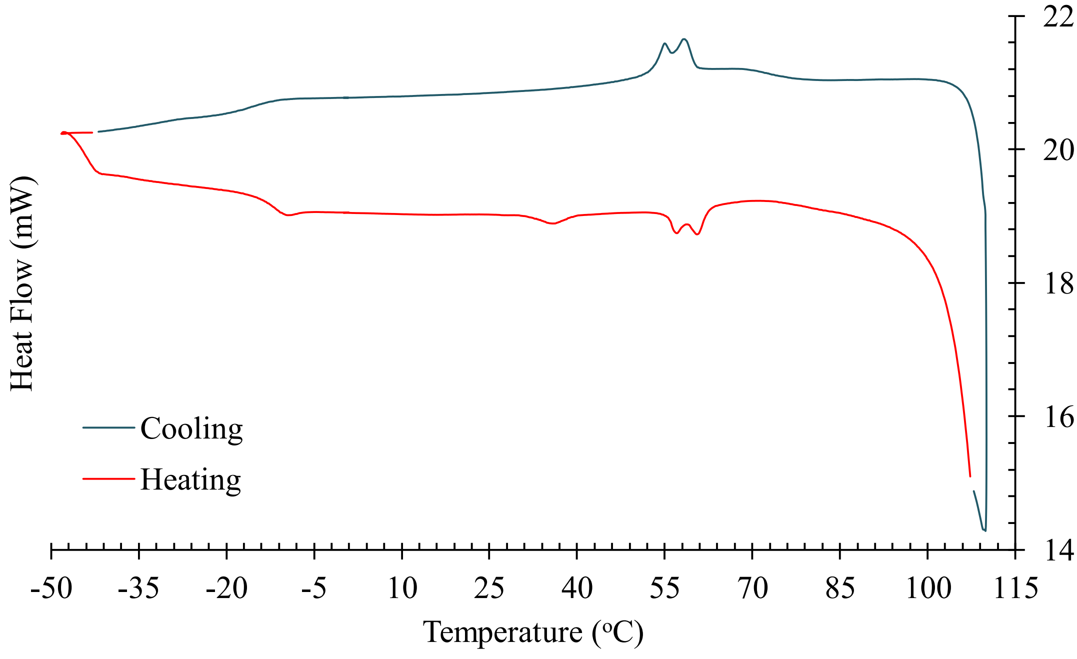


Figure 4.15 : DSC curve of LC6-diol.

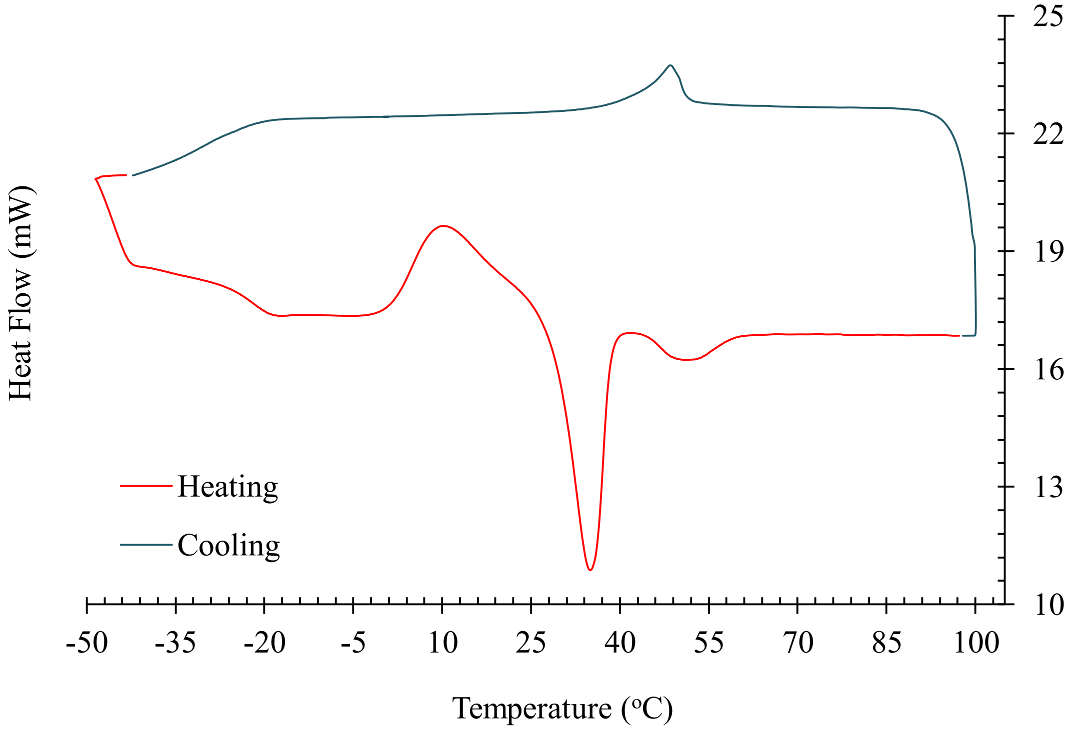


Figure 4.16 : DSC curve of LC8-diol.

Polarized optical microscopic images of LC6-diol and LC8-diol were given in Figure 4.17.

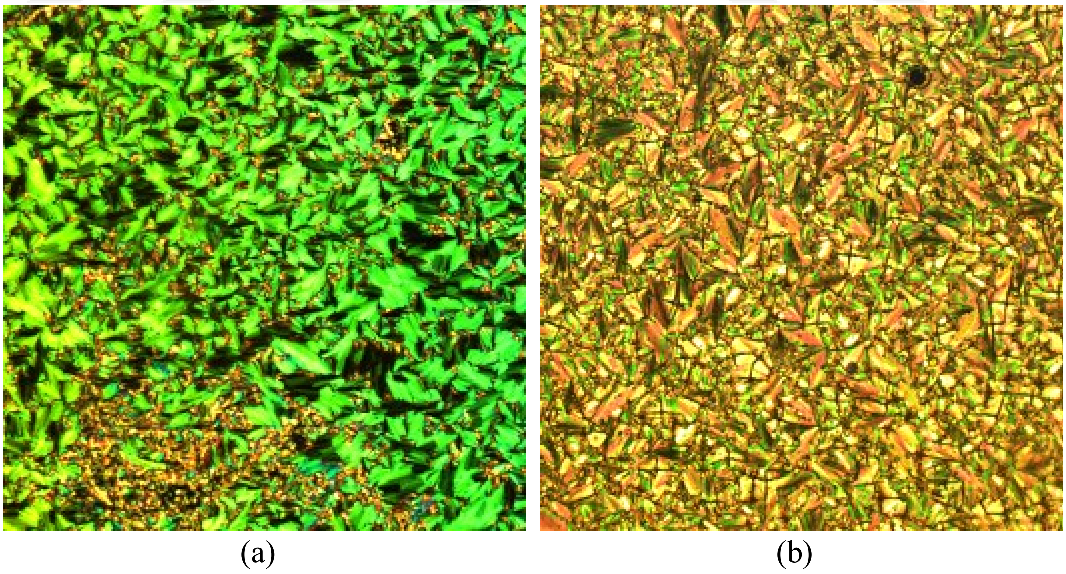

(a) (b)

Figure 4.17 : Polarized optical micrographs of (a) LC6-diol and (b) LC8-diol taken during cooling from the isotropic phase at 40.3°C and 33.4°C respectively (x200).

4.4.3 Thermal and mesomorphic properties of PULC6 and PULC8

The observations of the textures of PULC6 and PULC8 was achieved by POM. According to these observations, PULC6 does not exhibit any mesogenic phase.

isotropic phase appears at 155°C on heating. Isotropic-crystalline phase transition appears at 115°C on cooling.

The texture of PULC8 exhibits mesophase on both cooling and heating. The isotropic-liquid crystalline phase and liquid crystalline-isotropic phase transitions have not managed to be determined in POM. High heat causes decomposition of the substance without being isotropic liquid.

Thermal properties of PULC8 and PULC6 are shown in Table 4.3.

Table 4.3 : Thermotropic behavior of SCLCPUs.

Code	Phase Transitions °C (ΔCp $J.g^{-1}$)	
	Heating	Cooling
PULC6	G 98,23 (0,45) R 155[a] I	I 73,66 (0,11) G
PULC8	G 93,63 (0,48) R nd N nd I	I nd N nd G

Determined by DSC

[a]Observed by POM

G: Glassy, R: Rubbery N: Nematic, I: Isotropic, nd: not determined

The DSC heating and cooling traces of both PULC6 (Figure 4.18) and PULC8 (Figure 4.19) did not show any transition confirming POM results.

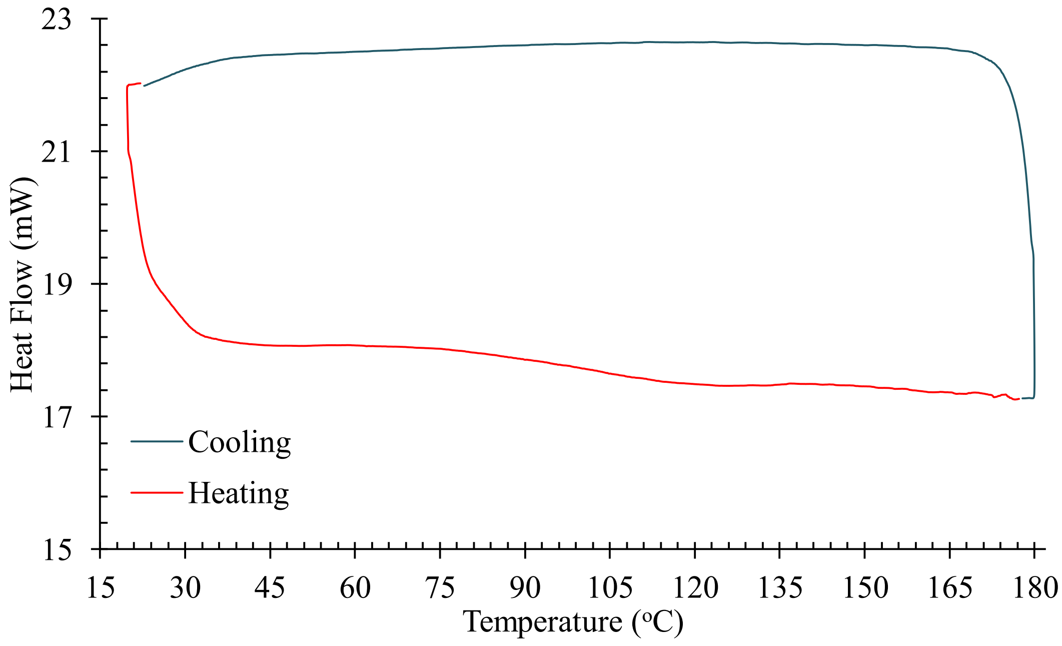


Figure 4.18 : DSC curve of PULC6.

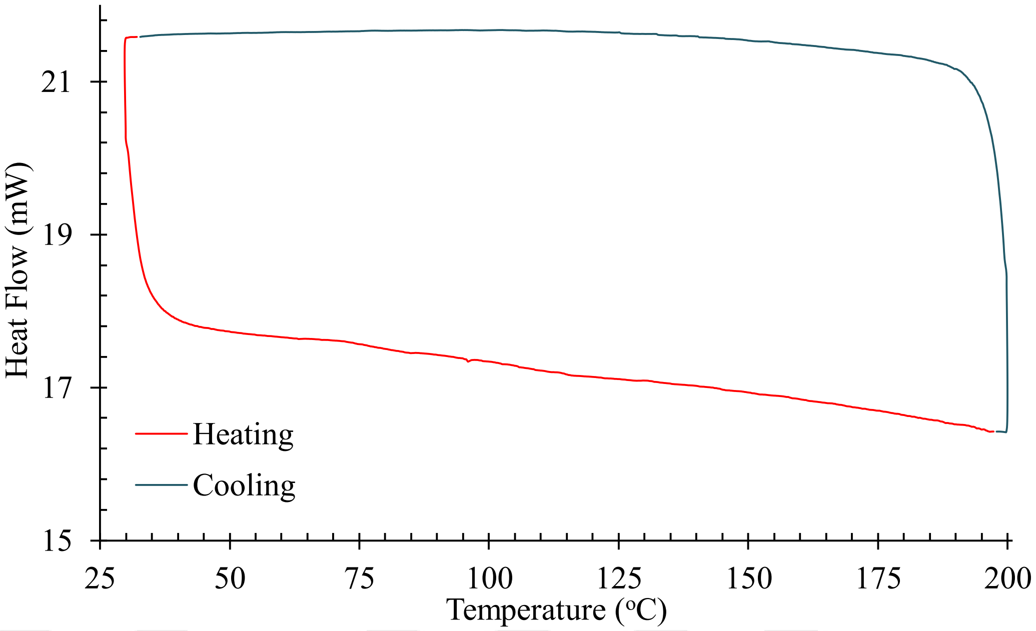
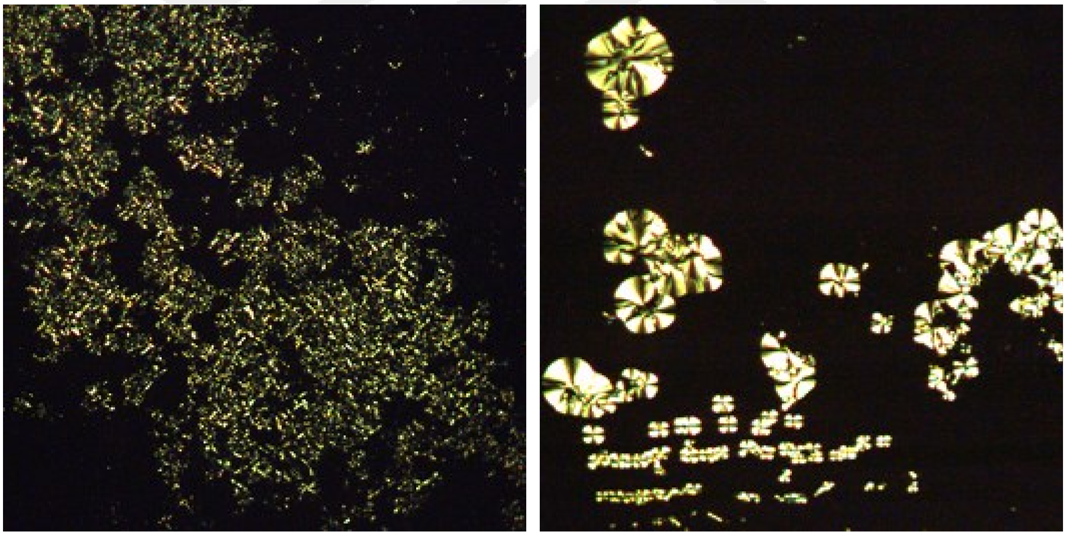


Figure 4.19 : DSC curve of PULC8.

Polarized optical microscopic images of PULC6 and PULC8 were given in figure 4.20.



(a) (b)

Figure 4.20 : Polarized optical micrographs of (a) PULC6 and (b) PULC8 taken during cooling at 68.2°C and 220°C respectively (x200).

5. CONCLUSIONS

SCLCPUs were synthesized successfully from 4-cyano-4′-hydroxybiphenyl, dibromoalkanes, 2,2bis(hydroxymethyl)propionic acid, HMDI respectively in three steps. After LC6 and LC8 precursors that consist of mesogenic moiety attached to spacer, were obtained, two-functional LC6-diol and LC8-diol monomers were synthesized in second step. SCLCPUs (PULC6 and PULC8) were obtained by polyaddition.

According to the observations of POM, LC6 is enantiotropic while LC8 is monotropic. LC6-diol and LC8-diol display smectic, this more stable phase is a consequence of the effect of H bonding.

While PULC6 does not exhibit mesophase, PULC8 exhibits smectic phase as the length of spacer increases. Contrast to PULC8, the spacer of PULC6 is not enough long for the formation of mesophase. This behavior shows that SCLCPUs exhibiting more stable mesophase can be obtained when the number of the flexible methylene units in spacer increases.

The DSC results show that glass transition temperature decreases in PULC8 as the spacer length increases. The phase transition temperatures of LC8-diol monomer are also lower than those of LC6-diol due to same reason.

REFERENCES

[1] **Bouligand, Y**. (1978). Liquid Crystals and Their Analogs in Biological Systems. In L. Liebert (Ed.), *Liquid Crystals* (pp 259-293). London: Academic Press Inc

[2] **Pavel, D**. (2016) Introduction to Liquid Crystalline Polymers. In V. K. Thakur & M. R. Kessler (Eds.), *Liquid Crystalline Polymers Volume 1-Structure and Chemistry* (pp 477-500). Cham, Heidelberg, New York, Dordrecht & London: Springer. doi: 10.1007/978-3-319-22894-5_16

[3] **Geelhaar, T., Griesar, K., & Reckmann, B.** (2013). 125 Years of Liquid Crystals-A Scientific Revolution in the Home, *Angew. Chem. Int. Ed., 52*, 8798–8809. doi: 10.1002/anie.201301457

[4] **Singh, S. & Dunmur D**. (2002). *Liquid Crystals, Fundamentals*. Singapore: World Scientific Publishing Co Pte Ltd.

[5] **Vertogen, G. & de Jeu W.H**. (1988). *Thermotropic Liquid Crystals, Fundamentals*. Berlin & Heidelberg: Springer-Verlag. doi: 10.1007/978-3-642-83133-1

[6] **Tschierske, C**. (2012). Fluorinated Liquid Crystals: Design of Soft Nanostructures and Increased Complexity of Self-Assembly by Perfluorinated Segments. In Tschierske C. (Ed.), *Liquid Crystals Materials Design and Self-Assembly*. Berlin & Heidelberg: Springer-Verlag

[7] **Qaddoura, M.A. & Belfield, K.D**. (2009). Synthesis, Characterization and Texture Observations of Calamitic Liquid Crystalline Compounds, Int. J. Mol. Sci, 10, 4772-4788. doi: 10.3390/ijms10114772

[8] **Yang, D.K. & Wu, S.T**. (2015). Fundamentals of Liquid Crystal Devices (2nd Ed.). Chichester: John Wiley & Sons.

[9] **Demus, D**. (1994). Phase Types, Structures, and Chemistry of Liquid Crystals. In H. Stegemeyer (Ed.), Liquid Crystals (pp 1-50). Darmstadt: Steinkopff & New York: Springer. doi: 10.1007/978-3-662-08393-2

[10] **Pelzl, G. & Weissflog, W**. (2007). Mesophase Behaviour at the Borderline between Calamitic and “Banana-shaped” Mesogen. In A. Ramamoorty (Ed.), Thermotropic Liquid Crystals Recent Advances. Dordrecht: Springer

[11] **Lydon, J.E**. (2013). Introduction to Liquid Crystalline Phases. In R. J. Bushby, S. M. Kelly & M. O’Neill (Eds.), *Liquid Crystalline Semiconductors Materials, Properties and Applications* (pp 1-38). Dordrecht, Heidelberg, New York & London: Springer. doi: 10.1007/978-90-481-2873-0_1

[12] **Andrienko, D**. (2018). Introduction to liquid crystals. *Journal of Molecular Liquids, 267*, 520-541. doi: 10.1016/j.molliq.2018.01.175

[13] **Oswald, P. & Pieranski, P**. (2005). *Nematic and Cholesteric Liquid Crystals Concepts and Physical Properties Illustrated by Experiments*. Florida: Taylor & Francis Group

[14] **Oswald, P. & Pieranski, P**. (2005). *Smectic and Columnar Liquid Crystals Concepts and Physical Properties Illustrated by Experiments*. Florida: Taylor & Francis Group

[15] **Neto, A.M.F. & Salinas, S.R.A**. (2005). *The Physics of Lyotropic Liquid Crystals: Phase Transitions and Structural Properties*. Sao Paulo: Oxford University Press Inc. doi: 10.1093/acprof:oso/9780198525509.003.0001

[16] **Plate, N.A. & Shibaev, V. P**. (1987). *Comb-Shaped Polymers and Liquid Crystals*. New York: Plenum Press (S. L. Schnur Trans.). doi: 10.1007/978-1-4613-1951-1

[17] **Skorokhodov, S.S**. (1993). Thermotropic Liquid Crystal Polymers with Mesogenic Groups in the Main Chain. In N. A. Plate (Ed.), *Liquid-Crystal Polymers* (pp 163-192) (S. L. Schnur Trans.). New York: Springer Science+Business Media. doi: 10.1007/978-1-4899-1103-2

[18] **Warner, M. & Terentjev, E.M**. (2003). *Liquid Crystal Elastomers*. New York: Oxford University Press Inc.

[19] **Chung, T.S, Cheng, S.X. & Jaffe M**. (2001).Introduction of Liquid Crystalline Material. In Chung, T.S (Ed.), *Thermotropic Liquid Crystal Polymers Thin-film Polymerization, Characterization, Blends and Application* (pp 1-20). Pennsylvania: Technomic Publishing Co. Inc.

[20] **Brömmel, F., Kramer, D. & Finkelmann, H**. (2012). Preparation of Liquid Crystalline Elastomers. *Adv Polym Sci, 250*, 1-48. doi: 10.1007/12_2012_168

[21] **Windle, A.H**. (1994). Structure of Thermotropic Main-Chain Polymers. In V.P. Shibaev & L. Lam (Eds.), *Liquid Crystalline and Mesomorphic Polymers* (pp 26-76). New York: Springer-Verlag. doi: 10.1007/978-1-4613-8333-8

[22] **Shibaev, V.P**. (2014). Liquid Crystalline Polymer Systems: From the Past to the Present. *Polymer Science, Ser. A 56*(6), 727–762. doi: 10.1134/S0965545X14060091

[23] **Jaisankar, S.N., Nelson, D.J. & Brammer, C.N.** (2009). New synthesis and characterization of ionic polyurethane-urea liquid crystals. *Polymer,50*, 4775-4780. doi: 10.1016/j.polymer.2009.07.049

[24] **Jana, R.N. & Cho, J.W**. (2009). Synthesis and Characterization of Polyurethane-based Side-chain Cholesteric Liquid Crystal Polymers. *Fibers and Polymers, 10*(5), 569-575. doi: 10.1007/s12221-010-0569-8

[25] **Wen, Z., Zhang, T., Hui, Y., Wang, W., Yang, K., Zhou, Q., et. al**. (2015). Elaborate fabrication of well-defined side-chain liquid crystalline polyurethane networks with triple-shape memory capacity. *J. Mater. Chem. A, 3*, 13435-13444. doi: 10.1039/c5ta02537k

[26] **Reddy, G.S.M., Jayaramudu, J., Ray, S.S., Varaprasad, K. & Sadiku, E.R**. (2015). Side Chain Liquid Crystalline Polymers: Advances and Applications. In V. K. Thakur & M. R. Kessler (Eds.), *Liquid Crystalline Polymers Volume 2-Processing and Applications* (pp. 389-416). Cham, Heidelberg, New York, Dordrecht & London: Springer. doi: 10.1007/978-3-319-20270-9_16

[27] **He, X.Z., Zhang, B.Y., Meng, F.B., Tian, M. & Mu, Q**. (2010). Synthesis and characterization of chiral liquid crystal polymers containing donor–acceptor group. *J Mater Sci, 45*, 201–208. doi: 10.1007/s10853-009-3919-4

CURRICULUM VITAE

Name Surname : Deniz MEMİŞ
E-mail : denizmemis@gmail.com

EDUCATION :

- **B.Sc.** : 2012, Trakya University, Faculty of Science and Letters, Department of Chemistry