ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF NEW CHOLESTEROL-FUNCTIONALIZED MESOGENS AND INVESTIGATION OF THEIR LIQUID CRYSTAL PROPERTIES

M.Sc. THESIS

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Department of Chemistry

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KOLESTERİL FONKSİYONLU YENİ MEZOJENLERİN SENTEZİ VE SIVI KRİSTAL ÖZELLİKLERİNİN İNCELENMESİ

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Dedicated to

my beloved family who have never deprived me of material and moral support throughout my life

and

my precious fiancé for his support, companionship and encouragement and for all of these years making me the person that I want to be.

FOREWORD

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ABBREVIATIONS

^{1}H-NMR : ^{1}H Nuclear Magnetic Resonance

Cho-BFCN : 4'-cyano-[1,1'-biphenyl]-4-yl ((3S,8S,9S,10R,14R,17R)-10-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate

Cho-LC8 : 8-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)octyl ((3S,8S,9S,10R,14R,17R)-10-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta-[a]phenanthren-3-yl) carbonate

Cr : Crystal Solid

DCM : Dichloromethane

DMSO : Dimethyl Sulfoxide

DSC : Differential Scanning Calorimetry

FT-IR : Fourier Transform Infrared Spectroscopy

I : Isotropic Phase

LC : Liquid Crystal

LC8 : 8-(4-cyanobiphenyl-4’-oxy) octan-1-ol

LCP : Liquid Crystal Polymer

MCLCP : Main Chain Liquid Crystal Polymer

n : Director

N : Nematic Phase

N^*_D : Chiral Discotic Nematic Liquid Crystal

N_D : Discotic Nematic Liquid Crystal

POM : Polarized Optical Microscope

Sm : Smectic Liquid Crystal

SCLCP : Side Chain Liquid Crystal Polymer

SmA : Smectic A Mesophase

SmB : Smectic B Mesophase

SmC : Smectic C Mesophase

TEA : Triethylamine

THF : Tetrahydrofuran

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SYNTHESIS OF NEW CHOLESTEROL-FUNCTIONALIZED MESOGENS AND INVESTIGATION OF THEIR LIQUID CRYSTAL PROPERTIES

SUMMARY

Since their incidental discovery in carrot roots, liquid crystals have been the focus of numerous sophisticated studies, and they remain a subject of active research. These molecules possess a broad range of applications, including their use as active components in technological devices such as watches, mobile phones, televisions, computer screens, projectors, and various other display devices. The integration of liquid crystals has led to significant advancements in the efficient presentation of information.

In order for a compound to exhibit liquid crystalline properties, it must possess a rigid and inflexible core that will assist in maintaining and organising the shape of the molecule, in conjunction with flexible side chains that will enable molecular movement. Compounds that exhibit liquid crystal properties are characterised by the presence of aromatic rings, side chains, terminal groups and binding groups within their structures.

Cholesterol and cyanobiphenyl-based liquid crystals remain the focus of scientific research because of their unique properties. Cholesterol-based liquid crystals are characterised by intricate structural complexity, a property that is intrinsic to their molecular composition. Their three-dimensional spiral structure enables them to modify the polarisation of light through the formation of chiral nematic phases. Cyanobiphenyl-based liquid crystals are typically analysed within the classification of nematic liquid crystals, as evidenced by their rod-shaped structures. Their molecular structure is characterised by a strong dipole moment, resulting in a polar molecular structure. These liquid crystals find application in numerous technological applications, including electronic displays, sensors, optical devices, and medical and biotechnology applications, owing to their molecular arrangements and physical properties.

The objective of this thesis is to synthesize and characterize cholesterol-based liquid crystalline mesogens. The synthesis of 8-(4-cyanobiphenyl-4'-oxy) octan-1-ol (LC8) was carried out according to the literature and characterized by FT-IR and ^{1}H-NMR. The cholesterol-based mesogen 8-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)octyl ((3S,8S,9S,10R,14R,17R)-10-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate (Cho-LC8) was prepared through a reaction between LC8 and cholesteryl chloroformate.

Another mesogen 4'-cyano-[1,1'-biphenyl]-4-yl ((3S,8S,9S,10R,14R,17R)-10-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate (Cho-BFCN) was synthesized using the same procedure, starting from a reaction with 4'-hydroxybiphenyl-4-carbonitrile and cholesteryl chloroformate.

The spectroscopic characterizations of the obtained mesogens (Cho-LC8 and Cho-BFCN) were studied by FT-IR and ^{1}H-NMR. Liquid crystalline images were obtained using polarized optical microscopy (POM) and thermal properties were investigated with differential scanning calorimetry (DSC).

The FT-IR spectrum of Cho-LC8 was analysed in comparison with that of LC8. This analysis revealed that the ester carbonyl peak at 1759 cm^{-1} in Cho-LC8 was not present in LC8. The aliphatic C-H stretching peaks ranging between 2855-2933 cm^{-1} and the characteristic CN peak at 2235 cm^{-1} were also observed. These results provide evidence that Cho-LC8 molecule was successfully synthesized. These findings provide substantial evidence that Cho-LC8 has been synthesized.

The ^{1}H-NMR spectrum of the Cho-LC8 showed that the chemical shifts of the molecule specify the presence of a cholesteryl group and aromatic protons between 0.70-2.0 ppm, and 7.0-7.70 ppm, respectively. Also, the signals at 3.6-4.0 ppm were attributed to CH_2-O protons.

In the FT-IR spectrum of Cho-BFCN, a characteristic ester carbonyl peak is observed at 1737 cm^{-1}. Furthermore, -OH stretching vibration peak disappeared in Cho-BFCN. Aliphatic C-H stretching peaks of cholesterol, ranging between 2866-2934 cm^{-1}, were also obtained. The presence of a CN peak at 2228 cm^{-1} in the FT-IR spectrum of Cho-BFCN confirming the synthesis of the molecule.

The ^{1}H-NMR spectrum of the Cho-BFCN reveal signals within the range of 0.63-2.1 ppm, which are indicative of cholesteryl group protons, and 4.5-5.3 ppm, which are attributable to CH_2-O protons. Additionally, the presence of aromatic protons is observed at a range of 7.2-7.63 ppm.

The phase properties and phase transition temperatures of Cho-LC8 were examined using POM and DSC, while the phase transition of Cho-BFCN was investigated through the use of POM. As depicted by POM images, both mesogens demonstrate nematic texture during both heating and cooling processes.

KOLESTERİL FONKSİYONLU YENİ MEZOJENLERİN SENTEZİ VE SIVI KRİSTAL ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Havuç köklerinde tesadüfen keşfedilmelerinden bu yana, sıvı kristaller çok sayıda çalışmanın odak noktası olmuştur ve araştırma konusu olmaya devam etmektedir. Bu moleküller, saatler, cep telefonları, televizyonlar, bilgisayar ekranları, projektörler ve diğer çeşitli görüntüleme cihazları gibi teknolojik cihazlarda aktif bileşenler olarak kullanımları da dahil olmak üzere geniş bir uygulama alanına sahiptir. Sıvı kristallerin uygulamaları, bilgi teknolojilerinde önemli gelişmelere yol açmıştır.

Bir bileşiğin sıvı kristal özellik gösterebilmesi için molekülün şeklinin korunmasına ve düzenlenmesine yardımcı olacak sert ve esnek olmayan bir çekirdeğe sahip olması, moleküllerin hareket etmesine olanak sağlayacak esnek yan zincirlere sahip olması gerekmektedir. Sıvı kristal özellik gösteren bileşiklerin yapılarında aromatik halkalar, yan zincirler, terminal grupları ve bağlayıcı gruplar bulunmaktadır.

Sıvı kristaller termotropik ve liyotropik sıvı kristaller olmak üzere iki grupta incelenmektedir.

Termotropik sıvı kristaller en düzenli hal olan kristal faz ile sıvı faz arasındaki belirli bir sıcaklık aralığında sıvı kristal davranış sergilemektedir. Sıvı kristal davranış gösterme eğilimi kristal yapının sıcaklığı artırıldığında ve sıvı fazın sıcaklığı azaltıldığında artmaktadır.

Liyotropik sıvı kristaller ise çözücünün belirli bir konsantrasyona ulaşmasıyla sıvı kristal davranış gösterir. Liyotropik sıvı kristaller su gibi elverişli çözücülerin kullanıldığı ve yüzey aktif maddeler (surfaktan) içeren çözeltilerle elde edilmektedir. En çok bilinen surfaktan örneklerinden biri olan sabun, su gibi bir çözücünün olduğu çözelti ortamına eklendiğinde misel yapıları oluşmaktadır. Sabun molekülünün hidrofobik kısmı yağ parçacıklarıyla etkileşerek çözünmelerini sağlarken hidrofilik kısmı suyla etkileşmektedir. Maddelerin temizlenmesi yağ veya kirin misellerin içine hapsolup su ile uzaklaştırılmasıyla sağlanmaktadır.

Termotropik sıvı kristaller moleküler geometrilerine bağlı olarak üç sınıfta incelenmektedir; kalamitik (çubuksu şekilli yapı), disk şeklinde yapı ve bükülmüş-çekirdek yapı (muz şekilli yapı).

Kalamitik sıvı kristaller ince, uzun ve çubuk şeklinde karakteristik yapılara sahiptir. Nematik, smektik ve kolesterik olmak üzere üç ayrı başlık altında incelenir.

Nematik sıvı kristaller çoğu kaynakta n ile temsil edilen yönlendirici yönünde doğrusal olarak hizalanma eğilimindedir. Her ne kadar düzenli bir yapıya sahip olsalar da sıcaklığın artmasıyla daha düzensiz hale gelerek sıvı gibi hareket edebilmektedir. Işığı polarizasyona uğratan nematik sıvı kristaller polarize optik mikroskop (POM) altında kolayca ayırt edilebilen ipliksi yapılarla karakterize edilmektedir.

Smektik sıvı kristaller katmanlar halinde düzenlenme eğilimindedir. Moleküller katmanlar arasında katman normaliyle yönlendiricinin birbirlerine yaptığı açıya göre düzenlenirler. Literatürde, bu düzenlenmeye dayalı olarak farklı smektik yapılar incelenmektedir. Ayrıca smektik sıvı kristaller katmanlı yapılarında yaptıkları açılar sebebiyle ışığı farklı şekillerde kırabilmektedirler. Bu özellikleriyle optik cihazlarda ve ekran teknolojilerindeki uygulamalarıyla kullanışlı hale gelmektedir. Smektik sıvı kristaller POM altında genellikle yelpaze şeklinde yapı göstermeleri ile karakterize edilmektedir.

Kolesterik sıvı kristaller moleküllerin birbirleriyle oluşturdukları farklı açılar sebebiyle heliks ya da spiral bir yapıda düzenlenme eğilimindedir. Bu heliks yapı sıcaklıkla değişerek molekülün renginde de değişimlere sebep olabilmektedir. Heliks yapı elektrik ve manyetik alana duyarlı olması nedeniyle molekülün düz bir hale gelmesine ya da yapının tamamen bozulmasına sebep olabilmektedir. Kolesterik sıvı kristaller POM altında genellikle parmak izi tekstürü ile karakterize edilmektedir.

Termotropik sıvı kristallerin bir başka sınıflandırılması olan disk şekilli sıvı kristaller düz ve geniş, halkasal veya disk formuna sahip olan yapılarıyla öne çıkmaktadır. Genellikle sert bir çekirdeğe ve esnek zincirlere sahiptirler. Çekirdek aromatik halkalardan oluşurken esnek zincirler uzun alkil zincirlerinden oluşmaktadır. Aromatik halkaların alkil zincirleriyle kurdukları bağ, molekülün disk şeklini almasına sebep olmaktadır. Alkil zincirlerinin farklılığı sebebiyle moleküllerin dizilimi ışığın farklı açılarda kırılarak yansımasına sebep olabilmektedir. Sahip oldukları optik özellikler nedeniyle ilgi çekmektedirler. Disk şekilli sıvı kristaller bu tezde diskotik nematik ve sütun şeklindeki yapı olmak üzere iki ayrı grupta incelenmiştir.

Diskotik nematik sıvı kristaller disk şeklindeki yapıların yönlendirici doğrultusunda sıralanmalarıyla karakterize edilir. Moleküler simetri sebebiyle kiral diskotik nematik mezofazlar az sayıda molekülde olsa da gözlemlenebilmektedir. Daha az düzenli olmaları sebebiyle nematik mezofazlarla karşılaştırıldığında daha akışkan oldukları görülmektedir.

Sütun şeklindeki (kolumnar) sıvı kristaller moleküllerin kolon ya da sütun şeklinde bir araya gelerek düzenlenmesiyle karakterize edilir. Moleküller birbirlerine paralel olarak kolon şeklinde düzenlenme eğilimindedir. Yapılar eğimli şekilde birbirlerine paralel hizalanarak bozulmuş bir görüntü oluşturabilmektedir.

Termotropik sıvı kristaller başlığında incelenen bükülmüş-çekirdek yapı, bükülen kısmı oluşturan merkez halkadan, bağlayıcı gruplardan ve terminal zincirlerinden oluşmaktadır. Bu yapı simetrik ya da asimetrik kollara sahip olabilmektedir. Genellikle asimetrik bir yapıya sahip olup bükülerek “muz” şeklini aldığı için literatürde bükülmüş-çekirdek yapıları tanımlamak amacıyla muz şekilli yapı terimi kullanılmaktadır.

Kolesterol ve siyanobifenil bazlı sıvı kristaller, sahip oldukları özelliklerle bilimsel araştırmalara konu olmaya devam etmektedirler. Kolesterol bazlı sıvı kristaller doğaları gereği karmaşık yapılara sahiptirler. Üç boyutlu spiral yapıya sahip olmaları sebebiyle kiral nematik fazlar oluşturarak ışığın polarizasyonunu değiştirebilmektedirler. Siyanobifenil bazlı sıvı kristaller ise genellikle çubuk şeklinde yapılar göstererek nematik sıvı kristaller başlığında incelenirler. Güçlü dipol momentleri sayesinde polar bir moleküler yapıya sahiptirler. Her iki tip sıvı kristal de moleküler düzenlenmeleri ve fiziksel özellikleri sayesinde elektronik ekranlar, sensörler, optik cihazlar, tıp ve biyoteknoloji uygulamaları başta olmak üzere birçok teknolojik uygulamada kullanılmaktadır.

Bu tezde kolesterol bazlı sıvı kristal mezojenlerin sentezi ve karakterizasyonu gerçekleştirilmiştir. 8-(4-siyanobifenil-4'-oksi) oktan-1-ol (LC8) sentezi literatüre göre gerçekleştirilmiş ve FT-IR ve ^{1}H-NMR ile karakterize edilmiştir. Ayrıca, LC8'in sıvı kristal özellikleri DSC kullanılarak incelenmiştir. Kolesterol bazlı mezojen 8-((4'-siyano-[1,1'-bifenil]-4-yl)oksi)oktil ((3S,8S,9S,10R,14R,17R)-10-metil-17-((R)-6-metilheptan-2-il)-2,3,4,7,8,9,10,11,12,13,14,15,16,17tetradekahidro-1H-siklopenta [a] fenantren-3-il) karbonat (Cho-LC8), LC8 ve kolesteril kloroformat arasındaki reaksiyonla sentezlenmiştir.

Bir diğer mezojen olan 4'-siyano-[1,1'-bifenil]-4-il ((3S,8S,9S,10R,14R,17R)-10-metil-17-((R)-6-metilheptan-2-il)-2,3,4,7,8,9,10,11,12,13,14,15,16,17tetradekahidro-1H-siklopenta[a]fenantren-3-il) karbonat (Cho-BFCN), 4'-hidroksibifenil-4-karbonitril ve kolesteril kloroformat reaksiyonundan başlayarak aynı prosedür kullanılarak sentezlenmiştir.

Elde edilen mezojenlerin (Cho-LC8 ve Cho-BFCN) spektroskopik karakterizasyonları FT-IR ve ^{1}H-NMR ile gerçekleştirilmiştir. Sıvı kristal görüntüleri polarize optik mikroskop (POM) kullanılarak elde edilmiş ve termal özellikleri diferansiyel taramalı kalorimetre (DSC) ile incelenmiştir.

Cho-LC8'in FT-IR spektrumu tezde LC8 ile karşılaştırılarak sunulmuştur. Cho-LC8’de 1704 cm^{-1}'de gözlemlenenen karakteristik ester karbonil piki LC8’de gözlemlenmemiştir. Cho-LC8’in FT-IR spektrumunda 2852- 2929 cm^{-1} arasında değişen alifatik C-H gerilme pikleri ve 2235 cm^{-1}'de karakteristik CN piki görülmektedir. Yapılan analiz Cho-LC8 molekülün sentezlendiğini kanıtlamaktadır.

Cho-LC8’in ^{1}H-NMR spektrumunda kimyasal kaymalar sırasıyla 0.70-2.0 ppm ve 7.0-7.70 ppm arasında bir kolesteril grubunun ve aromatik protonların varlığını göstermektedir. Ek olarak, 3.6-4.0 ppm'deki sinyaller ile CH_2-O protonlarının varlığı görülmektedir.

Cho-BFCN'nin FT-IR spektrumunda 1737 cm^{-1}'de karakteristik bir ester karbonil piki bulunmaktadır. -OH gerilme titreşim piki kaybolmuştur. Ayrıca, kolesterolün 2866-2934 cm^{-1} arasında değişen alifatik C-H gerilme pikleri ile 2228 cm^{-1} karakteristik CN piki görülmektedir. Yapılan analiz Cho-BFCN molekülünün sentezlendiğini kanıtlar niteliktedir.

Cho-BFCN'nin ^{1}H-NMR spektrumu incelendiğinde 0.63-2.1 ppm’de kolesteril grubu protonlarının varlığı ile 4.5-5.3 ppm aralığında CH_2-O protonlarının varlığını göstermektedir. Ek olarak, aromatik protonların 7.2-7.63 ppm'de olduğu görülmektedir.

Cho-LC8'in faz özellikleri ve faz geçiş sıcaklıkları POM ve DSC kullanılarak incelenirken, Cho-BFCN'nin faz geçişi POM kullanılarak belirlenmiştir. POM görüntülerinde gösterildiği gibi, her iki mezojen de hem ısıtma hem de soğutma sırasında nematik doku göstermektedir.

1. INTRODUCTION

The recent discovery of liquid crystals, which exhibit a unique molecular arrangement and orientation, has opened new avenues for research and technological development. These molecules, which are neither as regular as a solid nor as disordered as a liquid, offer distinct mesophases that can be illuminated through further study. These distinctive molecules, comprising aromatic rings, linkage groups, side chains, and terminal groups, can be classified as main and side chain molecules. They have found widespread applications in various fields, including LCD (liquid crystal display) screen technology, optical devices, biomedical applications such as biosensors, and wearable technologies like smartwatches. The historical development of liquid crystals, as evidenced by the findings of numerous scientific studies and industrial applications, commenced with the fortuitous discovery of cholesterol-based mesogens. These molecules, characterized by their helical structure, temperature-sensitive arrangement, and color changes, have garnered significant attention in scientific research and industrial applications due to their optical and chiral properties. In the present study, cholesteryl-based liquid crystals were synthesized, commencing with the acquisition of the LC molecule. The first mesogen was then prepared by treating cholesteryl chloroformate with a biphenyl-containing compound, and the second mesogen was obtained by treating the obtained LC molecule with cholesteryl chloroformate. The synthesized mesogens were characterized spectroscopically using FT-IR and ^{1}H-NMR, and thermal characterizations were carried out using DSC. Lastly, LC images were obtained using POM.

2. THEORY

2.1 Liquid Crystals

2.1.1 History of liquid crystals

The history of liquid crystals goes back to the Austrian botanist Friedrich Reinitzer [56].

During this period, Reinitzer continued his research with cholesterol, a substance that was more readily available and about which there was still insufficient knowledge [46]. In his article, Mitov emphasized that botanist Reinitzer had worked with crystals extracted from the carrot root [40].

The objective of his research was to determine the chemical formula and molecular weight of cholesterol in his studies with ester derivatives of cholesterol compounds such as cholesteryl acetate, cholesteryl benzoate and nitrocholesterin [46].

As Tyagi emphasized, Reinitzer observed that one of the substances he studied, cholesteryl benzoate, did not behave the same as the other substances and, unlike them, had two different melting points [56].

Reinitzer reported that in his work with cholesterol benzoate, despite prolonged cleaning procedures, he found the melting point to be 145.5°C and that the substance was completely liquid at this temperature. During the heating process to this temperature, the substance did not melt into a clear and transparent liquid, but instead became a cloudy and translucent liquid. However, when he heated the substance to higher temperatures (178.5°C), Reinitzer observed that the cloudiness abruptly vanished [46]. The point at which the cloudiness suddenly disappears and the material becomes transparent is referred to as the clearing point [40].

As demonstrated in Figure 2.1, the cholesterol benzoate substance, which was subjected to heating by Reinitzer from its initial room temperature state, is observed. When the cloudy sample was heated, he observed the formation of two phases, cloudy and transparent. However, when the sample was subjected to even higher temperatures, a sudden and complete transformation to transparency was observed [14].

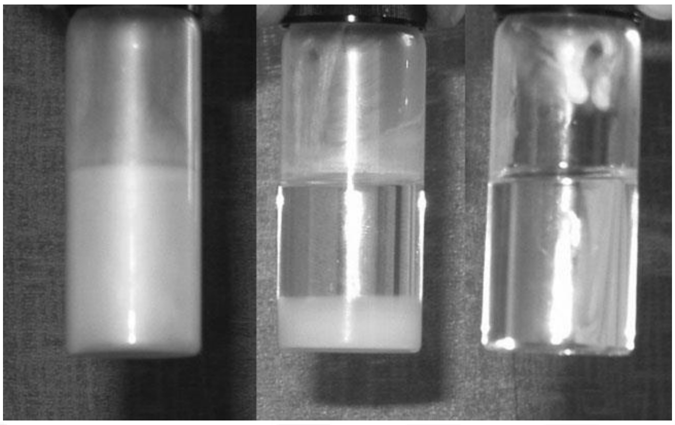


Figure 2.1 : The cholesterol benzoate substance observations.

Subsequent to the observation of this phenomenon in other substances with which he was working, he determined that a more thorough investigation was required [46].

Consequently, he submitted the substances under investigation to German physicist Otto Lehmann, an experienced crystallographer [40]. As Lehmann stated, in addition to the above information, Reinitzer reported to Lehmann that when he allowed the substance to cool, he first observed a violet and blue coloration, then these colors quickly disappeared and the milky white cloudy liquid remained. He also emphasized that as cooling continued, violet and blue coloration occurred again and immediately afterwards the substance turned into a white, crystalline structure [35].

According to Tyagi, while Reinitzer did not continue his work on liquid crystals, which he discovered by accident, Lehmann took his research even further and continued his crystallographic and microscopic studies with substances that exhibited the double-melting phenomenon [56]. As Singh emphasized, it was Lehmann who first referred to these flowing crystals as "liquid crystals" [49].

In the following period, liquid crystals have been developed through the work of various scientists and have continued to evolve up to the present day [56].

2.1.2 Fundamentals of liquid crystals

In the context of thermodynamics, intermediate phases that exhibit a greater degree of order relative to the isotropic liquid state, yet fewer order compared to a solid crystal, are designated as mesophases. These phases are distinguished by a smooth and continuous transition between the solid crystal and isotropic liquid phases, thereby combining the properties of both phases [17, 24]. According to Stegemeyer (1994), compounds that exhibit mesophases or mesomorphic properties are referred to as "mesogenic" (p. 4) [55]. In liquid crystals, the axial alignment of molecules is expressed by a unit vector, n, the director.

The term 'isotropic' is employed to denote the liquid phase, as its properties are independent of direction. In the liquid phase, molecules are randomly distributed and exhibit the same properties in all directions. On the other hand, a solid crystal is the most ordered state, exhibiting anisotropic properties due to the variation of its characteristics depending on the direction. In the solid phase, molecules are arranged at specific points according to a lattice structure, exhibiting both positional and orientational order. Liquid crystals, however, are not as disordered as liquids; they exhibit orientational order in a specific direction, and thus, they are more ordered internally. As with solids, liquid crystals exhibit anisotropic properties [8, 11, 16]. A summary of the similarities and differences between three states described in Table 2.1 [24].

Table 2.1 : A comparison of the similarities and differences between solid, liquid crystal, and liquid substances.

Solid	Liquid Crystal	Liquid
Anisotropic	Anisotropic	Isotropic
Rigidity	Fluidity	Fluidity
Ordered	Ordered	Disordered

The transformation of a material that exhibits a liquid crystalline intermediate phase is depicted schematically in Figure 2.2 below [29].

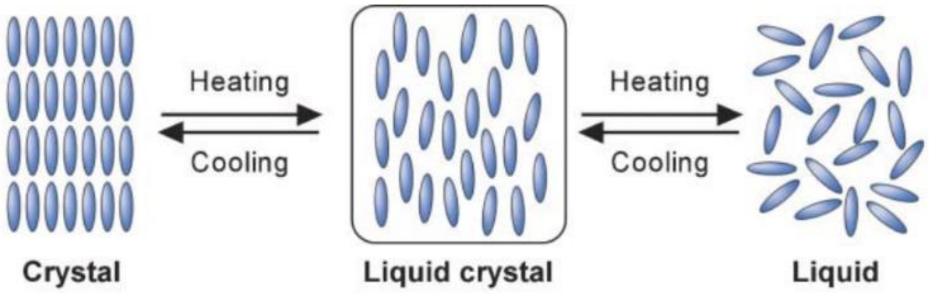


Figure 2.2 : Representation of the phase transformation and molecular order of a material that shows a liquid crystalline intermediate phase.

As demonstrated in Figure 2.2, the solid phase, which is characterised by the greatest degree of stability and order, exhibits a propensity to transition to the liquid crystalline intermediate phase upon application of heat. Conversely, when the liquid crystalline phase is subjected to heating, it undergoes a transition to the liquid phase. This transformation, which takes place by endothermic, is reversible and can be the opposite of what is described in the cooling process [11].

In the previous section, information regarding the clearing point was provided. To elaborate further, it should be emphasized that the point at which a solid phase directly transitions to the liquid phase is termed the melting point. In the absence of a direct transition temperature between the solid crystal phase and the liquid phase, the crystal phase will form a mesophase at the melting point. If the mesophase is subjected to further heating, it will transform into an isotropic liquid, and the point at which this transformation occurs is called the clearing point [8, 18].

2.1.3 Classification of liquid crystals

The classification of liquid crystals is shown in Figure 2.3 [31, 32, 50].

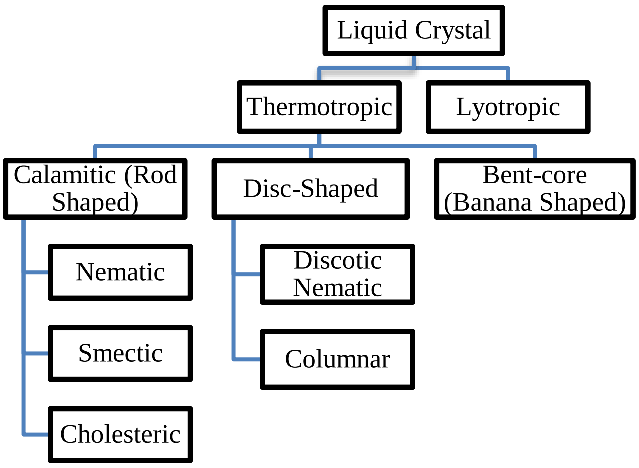


Figure 2.3 : Classification of liquid crystals.

2.1.3.1 Thermotropic liquid crystals

The fundamental principle of thermotropic liquid crystals lies in the crystalline structure melting within a specific temperature range during the heating process, turning into a cloudy liquid, and then transitioning into a clearer liquid state as heating continues [8, 51]. Instead of a single-step transition, as Priestly stated, multiple intermediate phases, or mesophases, form as a result of temperature effects [45]. The mesophases observed during the heating process for the transition from crystalline to isotropic liquid phase in thermotropic liquid crystals are shown in Figure 2.4 [1].

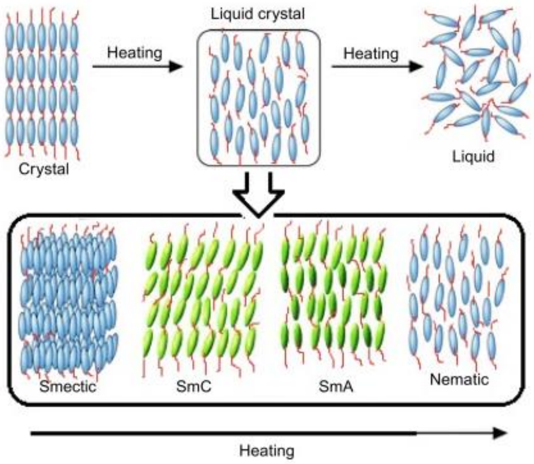


Figure 2.4 : Mesophases observed in thermotropic liquid crystals with the process of heating from the crystal phase to the isotropic liquid phase.

It has been established that the mesophases that form in thermotropic liquid crystals are reversible. These phases can be observed through various methods during the processes of heating and cooling [22, 50]. An enantiotropic mesophase, which is stable only under a specific temperature or pressure, can be directly observed by heating the solid phase. On the other hand, a monotropic mesophase can be observed when the isotropic liquid phase is cooled beneath its melting temperature [2, 6]. According to Binnemans & Görller-Warland (2002), “monotropic phases are thermodynamically unstable mesophases” (p. 3) [3].

As discussed in section 2.1.3, thermotropic liquid crystals are categorized into three distinct groups based on their molecular structures: calamitic (rod-shaped), disc-shaped, and bent-core (banana-shaped) [50].

Calamitic (rod shaped) liquid crystals

As stated by Demus et al. (1998), “The most common liquid crystal substances are those with an elongated, cylinder-like shape” (p. 39) [12].

As Khoo pointed out, the molecules of liquid crystals are constituted of aromatic rings (represented by A and A' in Figure 2.5), groups that link the aromatic rings (represented by X in Figure 2.5), side groups (represented by R in Figure 2.5), and terminal groups (represented by R' in Figure 2.5) [30].

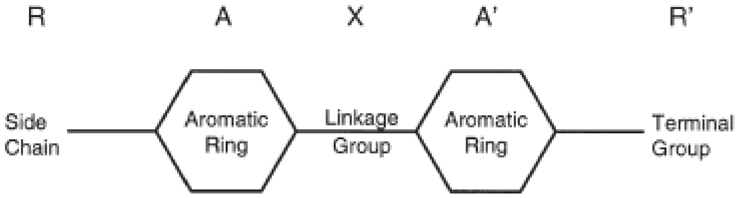


Figure 2.5 : General representation of the structure of liquid crystal molecules.

Nematic Liquid Crystals

In the context of nematic liquid crystals, there is only the presence of orientational order among the molecules is observed, while positional order is absent. This implies that the molecules have the ability to move in any direction. However, they generally tend to align parallel with long-range orientational order along the principal axis director (n) [48, 55, 58]. As illustrated in

Figure 2.6, the alignment of the nematic phase along the director n is shown [27]. In addition, it is important to note that at this point, the layer arrangement is no longer present [52].

In summary, as Dierking also stated (2003), "the nematic phase is the one with the least order and the highest symmetry" (p. 17) [13]. Furthermore, the nematic phase is a turbid phase and has much lower viscosity compared to the smectic phase, which will be discussed in the next section [52].

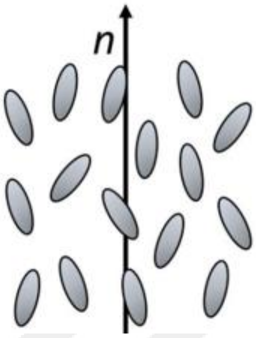
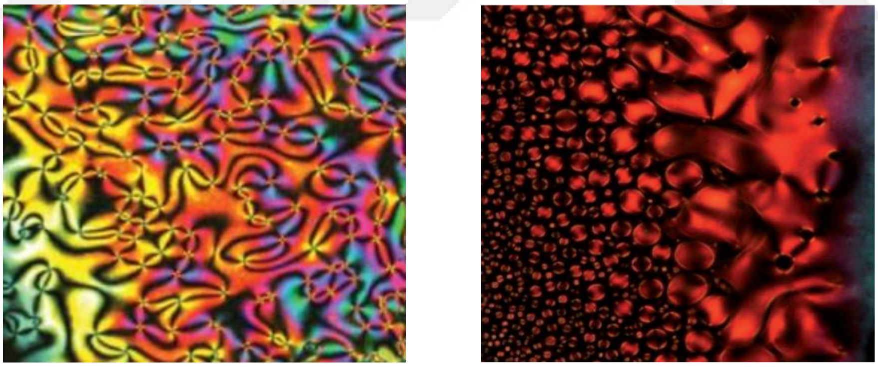


Figure 2.6 : Orientation of molecules in the nematic phase.

Additionally, Figure 2.7, depicts the schlieren texture (a) droplets of the nematic phase (b) that are observable with POM [7, 44].



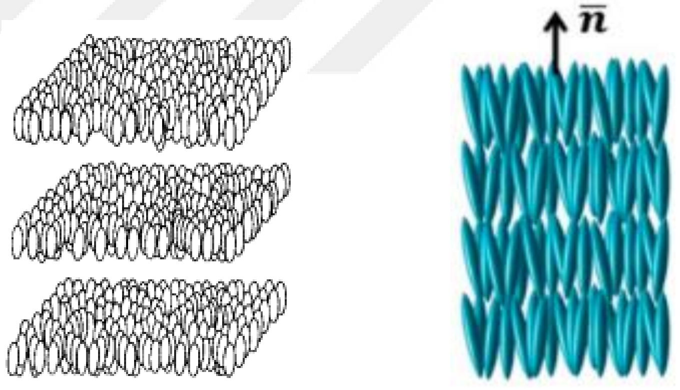
(a) (b)

Figure 2.7 : POM images of Schlieren texture (a) and nematic droplets (b).

Smectic Liquid Crystal

When the crystal structure is subjected to heating, the initial phase is SmC, and as the heating continues, SmA mesophases are formed. Consequently, this order is followed by N and I as the heating process continues. In other words, the smectic mesophase shows a higher degree of order than the nematic mesophase, thereby demonstrating a greater similarity to the crystal structure. Molecules that exhibit SmC and SmA mesophases are separated into vertical layers and are oriented in layers. The layers are parallel to each other and the molecules capable of movement within their own layers. However, there is no rotational movement between these layers, and thus no positional relationship is observed. As a result, they have lower viscosities and are more fluid compared to the nematic and cholesteric mesophases [8, 13, 48].

In the SmA mesophase, the long axis of the molecules is aligned parallel to the layer normal. This ensures that n and the layer normal, +n and -n, are equivalent (head-to-tail symmetry), thereby making SmA uniaxial. The layer thickness is equal to the molecular length, and the molecules exhibit relatively high mobility within the layers. It is significant to note that, as Stegemeyer stated (1994), “In many smectic A phases the layer thickness is smaller than the molecular length” (p. 14) [55]. There is no positional order in the layers. SmA liquid crystals are optically positive. Due to their layered texture in POM, they exhibit a fan-like texture [5, 8, 19, 57, 58]. As shown in Figure 2.8, the arrangement of layers and the molecular alignment of the SmA phase can be observed [26, 57].



(a) (b)

Figure 2.8 : The arrangement of layers in the SmA phase (a) and the molecular alignment of the SmA phase (b).

The fan-shaped texture of the SmA phase, which is also described above in relation to the POM image, is demonstrated in Figure 2.9 [13].

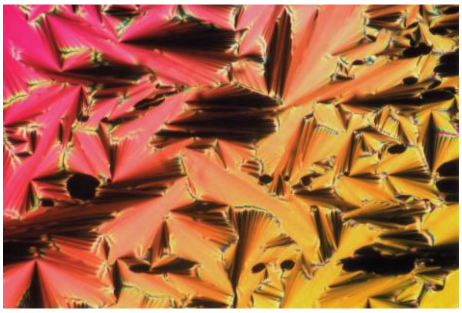


Figure 2.9 : Fan-shaped texture of the SmA phase.

In the SmB mesophase, the molecules align perpendicularly along the n direction and form layers with hexagonal packing. This arrangement gives rise to a more ordered structure in comparison to that of SmA. Furthermore, SmB is also characterized by head-to-tail symmetry [5, 8, 57]. The arrangement of in the SmB phase is illustrated in Figure 2.10 [57].

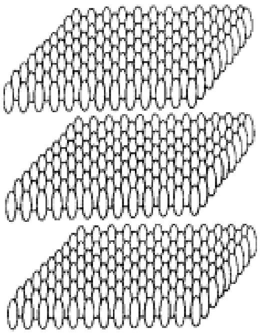


Figure 2.10 : The arrangement of layers in the SmB phase.

The POM image of the SmB phase is shown in Figure 2.11 [13].

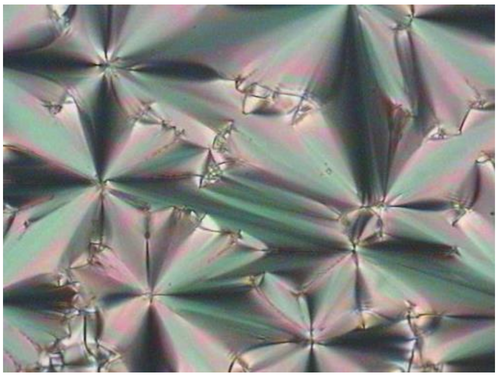
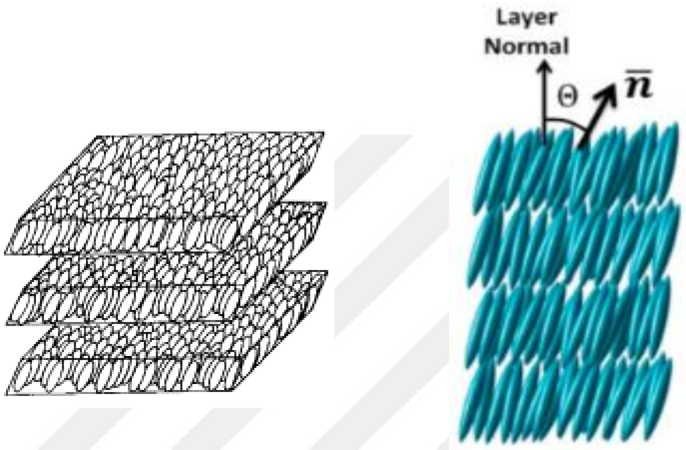


Figure 2.11 : POM image of the SmB phase.

Although the SmC mesophase is similar to the SmA phase, the long axes of the molecules tilt and form an angle with the layer plane. This angle is referred to as the “tilt angle”. In the SmC phase, the layer thickness is less than the molecular length. Unlike SmA, it is optically biaxial. Observations demonstrate that for certain materials, the tilt angle remains constant, while for others, it is temperature-dependent. The molecules rotate freely around their long axes, but their centers of mass are randomly ordered [49, 57, 58]. In Figure 2.12, the arrangement of layers and the molecular alignment of the SmC phase can be seen [26, 57].



(a) (b)

Figure 2.12 : The arrangement of layers in the SmC phase (a) and the molecular alignment of the SmC phase (b).

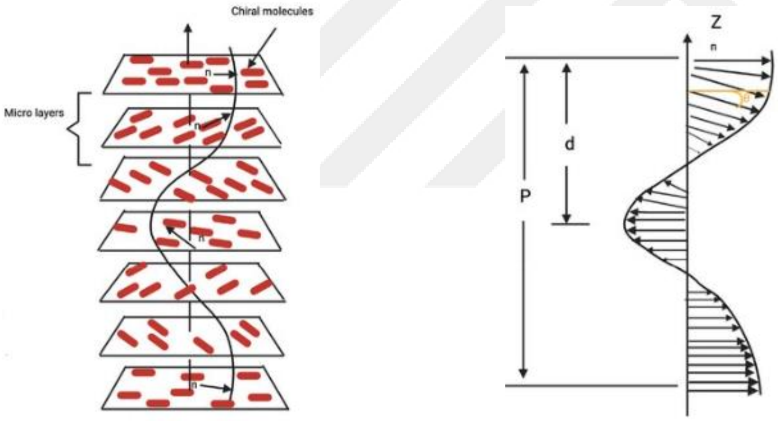
The broken fan-shaped textures of the SmC phase is shown in Figure 2.13 [5, 13].

Figure 2.13 : Broken fan-shaped structures of SmC phase.

Cholesteric liquid crystal

In general, the term “cholesteric mesophase” is named as such because many of the materials forming this phase are derived from cholesterol products [14]. The occurrence of the cholesteric phase is exclusive to optically active compounds. Despite the observation of a nematic arrangement, unlike in nematic liquid crystals, the director (n) is not fixed. Since n is different in each layer, and cholesteric liquid crystals have a helical structure [52].

Figure 2.14 (a) shows the helical structure of the cholesteric mesophase. It was previously mentioned that cholesteric liquid crystals with different layers are obtained by the molecules of the chiral nematic mesophase (N^*_D) arranging at a small angle relative to each other. This layered structure is chiral and the rotation of the helical structure can be either clockwise or counterclockwise. P in the Figure 2.14 (b) is the pitch, defined as the distance over which n completes one full rotation in the helix [41]. Also, d represents the distance during rotation over the period (P/2) and θ indicates the rotational (twisting) angle of the chiral centers [14, 41, 52].



(a) (b)

Figure 2.14 : The helical structure of the cholesteric mesophase (a) and orientation along n in the cholesteric phase, P, d, and θ (b).

Figure 2.15 shows the fingerprint texture of the cholesteric phase observed by POM [13].

Figure 2.15 : Fingerprint texture of the cholesteric mesophase.

Disc shaped liquid crystals

Disc-shaped molecules typically consist of a flat, rigid core (usually aromatic) and flexible peripheral chains. The peripheral chains surrounding the molecules lower the melting point and increase fluidity. The interactions between the rigid core and the peripheral chains facilitate the molecular ordering of discotic liquid crystals and assist in their columnar arrangement. Due to this arrangement, discotic liquid crystals are of great interest today for their potential applications in electronic devices [47, 50].

A schematic representation of disc-like liquid crystals is shown in Figure 2.16 [50].

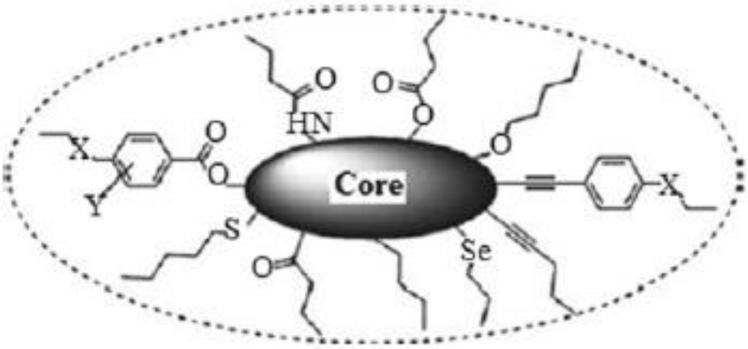


Figure 2.16 : Schematic illustration of disc-shaped liquid crystals.

Discotic nematic liquid crystal

In the subject of molecular symmetry, the alignment of the axes of disk-shaped molecules in a nematic mesophase-like arrangement gives rise to the formation of a discotic nematic mesophase and a chiral discotic nematic mesophase. However, in comparison to other nematic phases, the discotic nematic phase is less ordered and exhibits lower viscosity. In this phase, the disk-shaped molecules align their short axes parallel to each other and can rotate freely, aligning orientationally in a specific pattern. This means the phase exhibits short-range positional order and long-range orientational order. Additionally, it is also noteworthy that the number of disk-shaped molecules exhibiting the discotic nematic phase is low, and as Kumar & Varshney emphasized (2001), "Only a few derivatives of triphenylene, truxene, thiotruxene, naphthalene, alkynylbenzenes, etc., are known to show a stable N_D phase" (p. 2) [34]. Their appearance under POM is quite similar to that of the nematic phase [4, 34, 57].

In Figure 2.17, the molecular arrangements of N_D and N^*_D are shown [4].

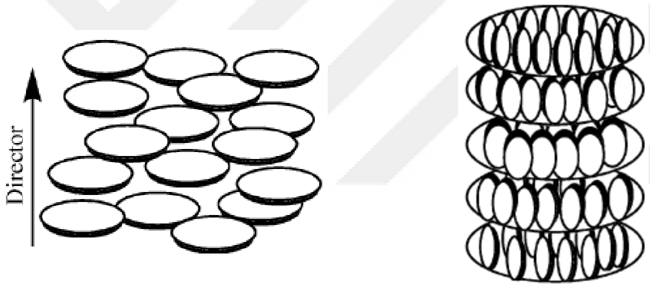


Figure 2.17 : Molecular arrangements of N_D (a) and N^*_D (b).

In Figure 2.18, The Schlieren texture of the discotic nematic phase, as observed by POM [4].

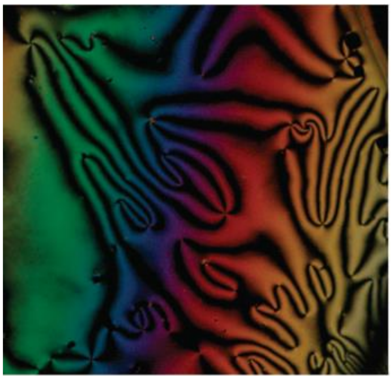


Figure 2.18 : The Schlieren texture of the discotic nematic liquid crystal.

Columnar liquid crystal

In columnar liquid crystals, the crystalline order is lost in one direction, and the core mesogen is surrounded by highly disordered side chains. In other words, disc-shaped molecules stack upon each other to form a structure where the columns are arranged in a two-dimensional hexagonal lattice. Along the axes of the columns, the molecules can be ordered or exhibit disorder on a long-range scale [13, 49, 54].

Figure 2.19 shows the structures of columnar mesophases depending on their molecular arrangement [13].

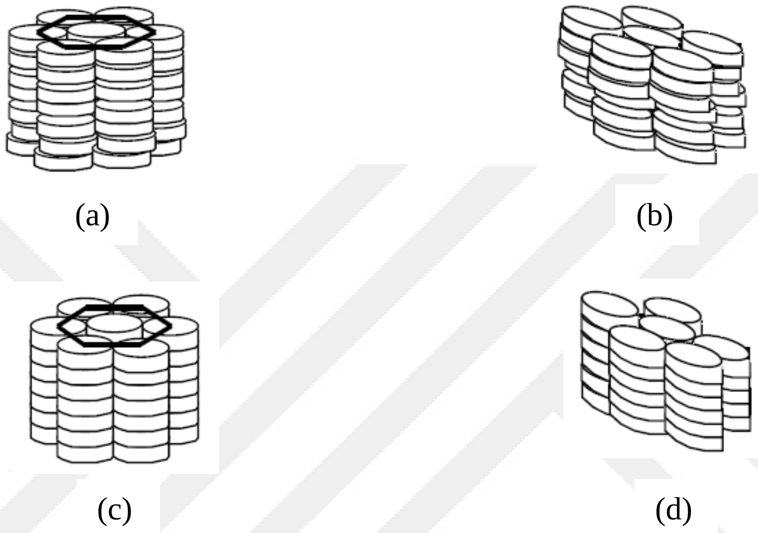


Figure 2.19 : Schematic representation of disordered columnar (a), tilted disordered columnar (b), ordered columnar (c) and tilted columnar mesophases (d).

Figure 2.20 shows the shapes formed by columnar mesophases in a top view [13].

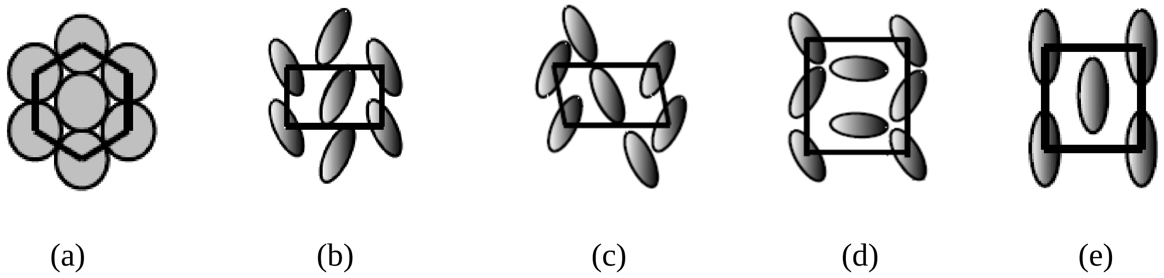


Figure 2.20 : Schematic representation of hexagonal (a), rectangular (b), oblique (c) and rectangular columnar mesophases (d, e).

As illustrated in Figure 2.21, the POM visualisation demonstrates the alterations in the material's structure during the processes of heating and cooling at varying temperatures [28].

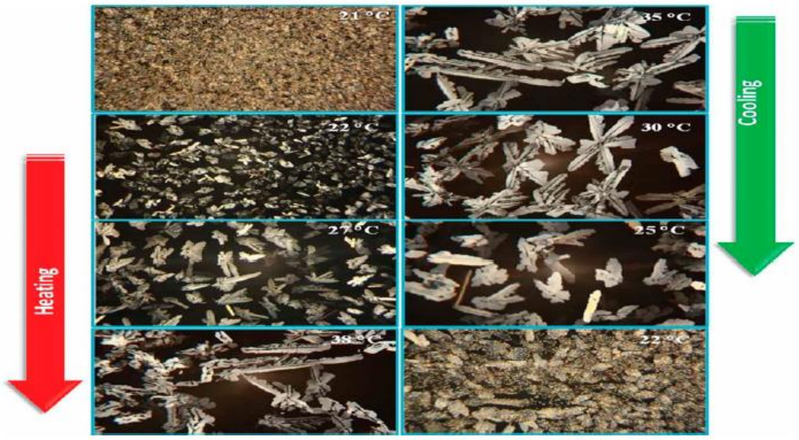


Figure 2.21 : POM images of columnar mesophases.

Bent-core (banana shaped) liquid crystals

Bent-core (banana shaped) molecules consist of a rigid core unit attached to two side groups, with lateral chains connected to these. The synthesis of bent-core molecules involves a minimization of the degree of curvature, resulting in a structure that is nearly rod-like. It should be added that, although bent-core core molecules are not chiral, they can become spontaneously chiral due to chiral symmetry breaking [23, 37, 25]. This phenomenon can be seen in Figure 2.22 [25].

(a) (b)

Figure 2.22 : Due to chiral symmetry breaking right-handed dimer (a) and left-handed dimer (b) observed in bent-core mesophases.

In Figure 2.23, the structure of bent-core molecules can be seen [50].

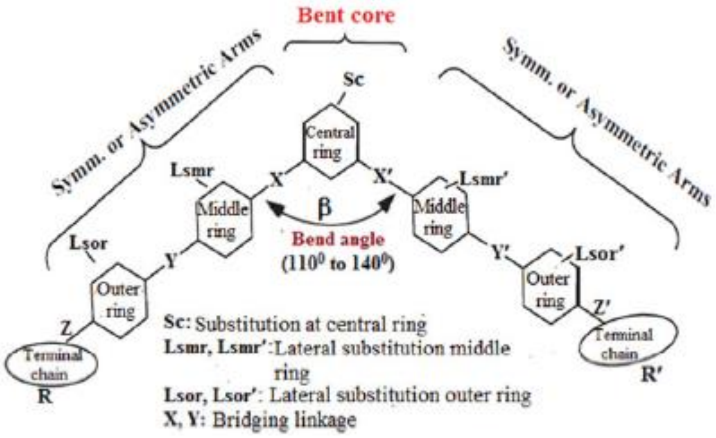


Figure 2.23 : Scheme of the structure of bent-core molecules.

2.1.3.2 Lyotropic liquid crystals

Liquid crystal types that exhibit liquid crystal properties in the environment where generally water is used as the solvent and show different structures and arrangements depending on the concentration of the solvent in which they are dissolved are called lyotropic liquid crystals [50, 58].

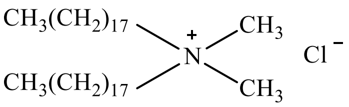
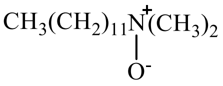
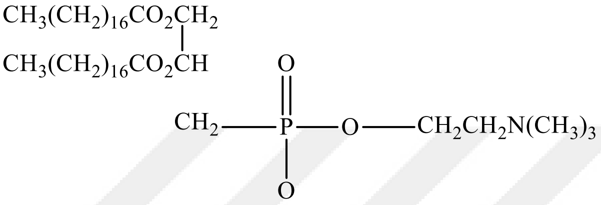
As Singh mentioned, lyotropic liquid crystals are formed by dissolving amphiphilic molecules, which exhibit both hydrophobic and hydrophilic properties, in a suitable solvent such as water [49].

According to Dunmur & Sluckin (2011), "The origins of surface science lie in the attributes of soap" (p. 134) [15]. Therefore, we encounter the concept of surfactants, which are molecules with a molecular structure consisting of a polar head group and a non-polar tail [8]. The following table (Table 2.2) summarize the surfactants type and their applications.

Table 2.2 : Surfactants type and applications.

Name	Structure	Application
Sodium dodecyl sulfate	$CH_3(CH_2)_{11}OSO_3Na$	Detergents, emulsifiers
Sodium dodecanoate (laurate)	$CH_3(CH_2)_{10}CO_2Na$	Soap Bars
Hexa-ethylene glycol monododecyl ether	$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$	Detergents, emulsifiers
1-octadecanoyl-sn-glycerol (monostearin)	$CH_3(CH_2)_{16}CO_2CH_2CH(OH)CH_2OH$	Food emulsifier

Table 2.2 (continued) : Surfactants type and applications.

Name	Structure	Application
Hexadecyltrimethyl ammonium chloride	$CH_3(CH_2)_{15}N^+(CH_3)_3Cl^-$	Hair conditioner
Dioctadecyldimethyl ammonium chloride		Fabric conditioner
Dodecyl dimethyl amine oxide	 $CH_3(CH_2)_{11}\underset{\underset{O^-}{\mid}}{\overset{+}{N}}(CH_3)_2$	Speciality surfactant
1,2-dioctadecyl-sn-glycero-3 phosphatidylcholine (distearoyl lecithin)		Food emulsifier, membrane lipid
Perfluorooctanoic acid	$CF_3(CF_2)CO_2H$	Speciality surfactant
Octaethylene glycol mono tri siloxyl propyl ether	$((CH_3)_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_8OH$	Cosmetics, wetting agent

An example of a surfactant, soap begins to form clusters known as micelles in water at low concentrations. The structures formed by this arrangement are referred to as spherical and cylindrical micelles. As the concentration increases, the molecules of the soap begin to organize themselves in a manner similar to liquid crystals [15, 30].

The representation of the hydrophobic and hydrophilic parts of the micelle structure formed by oil particles in an aqueous environment is shown in Figure 2.24 [36].

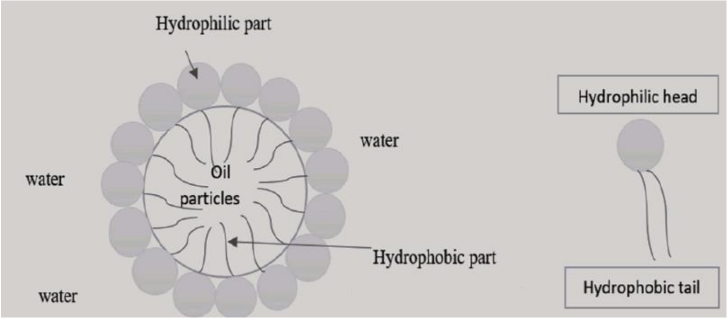
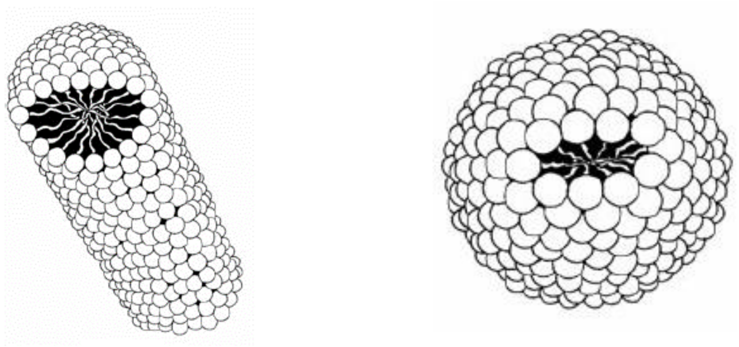


Figure 2.24 : General representation of the hydrophilic and hydrophobic parts of a micelle structure.

The structural arrangement of spherical and cylindrical micelles in water is shown in Figure 2.25 [14].



(a) (b)

Figure 2.25 : The structure of spherical micelles (a) and cylindirical micelles (b).

2.1.4 Polymeric liquid crystals

Polymeric liquid crystals (LCPs) are high molecular mass materials [39]. As stated by Srivastava & Das (2017), "LCPs consist of rigid segments on the main chain axis, interrupted by flexible spacers. " (p. 3) [53]. LCPs consist of main-chain (MCLCP) and side-chain (SCLCP) liquid crystals [50]. In both of these groups, the concepts of polymer backbone, mesogen, and spacer are encountered. In summary, the term "polymer backbone" refers to the main structure of a polymer formed by long, repeating monomer units [20]. The term "mesogen" is employed to denote molecules that demonstrate liquid crystalline behaviour and are responsible for the formation of the mesophase. "Spacers", on the other hand, are the elements that attach mesogens to the polymer backbone [53].

2.1.4.1 Main chain liquid crystals

In main-chain liquid crystal polymers (MCLCPs), LC mesogens are placed in the polymer backbone. Typically, the mesogens and the polymer backbone are separated by flexible spacers [5, 50]. Aliphatic groups, including alkyl groups found in the main chain, have been demonstrated to effectively reduce the melting point and processing temperatures of LCPs [53].

As Collings and Hird stated (2009), “The monomer unit must be anisotropic and bifunctional (one function at each end) to enable polymerization” (p. 96) [8].

Additionally, the following four methods can be employed to reduce the transition temperatures of MCLCPs for industrial processing and scientific research:

I. Introducing Flexible Bonds
II. Introducing Kinks or Bends
III. Lateral Substitution
IV. Adding Asymmetric Elements [9].

In Figure 2.26, how the mesogens are incorporated into the polymer backbone is shown [53].

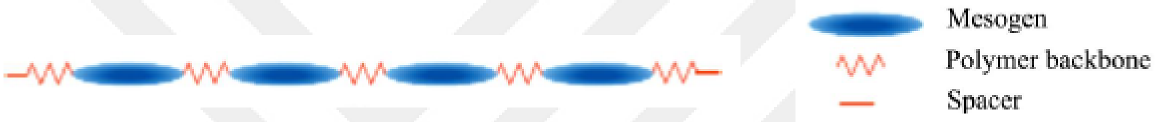


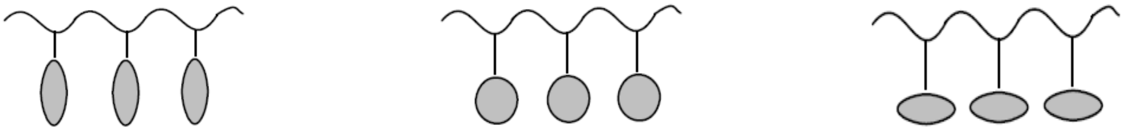
Figure 2.26 : Schematic illustration of MCLCPs.

2.1.4.2 Side chain liquid crystals

In certain sources, the term may also be referred to as "side chain (comb) types" [9]. As Noël and Navard stated (1991), “in SCLCP's the mesogenic groups are linked to an existing polymer backbone either directly or via flexible spacer units” (p. 95) [42]. The attachment of mesogens to the polymer backbone can be accomplished with either less or more flexible chains [5].

When mesogens are attached to the polymer backbone, they adopt an anisotropic arrangement. In fact, the polymer backbone is flexible and tends to remain in a free state. Since both situations cannot occur simultaneously, the polymer backbone dominates over the mesogenic groups, suppressing the mesomorphic behavior. This indicates that the choice of polymer backbone directly affects the mesomorphic properties of SCLCPs [8].

As can be seen in Figure 2.27, SDLCPs can be classified into three distinct categories: rod-like, disc-like, and rod-like lateral [21].



(a) (b) (c)

Figure 2.27 : Illustrations of possible structures of SCLCPs rod-like (a), disc-like (b), rod-like lateral (c).

In Figure 2.28, how the mesogens are attached to the polymer backbone is shown [53].

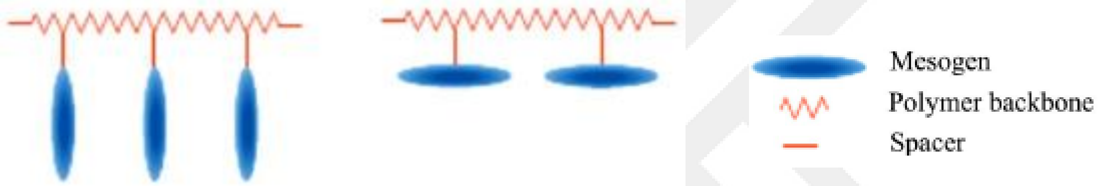


Figure 2.28 : Schematic illustration of SCLCPs.

2.1.5 Spacer length effect on mesomorphic behaviour

Spacers are generally composed of methylene (-CH_2) units, and a polymer's capability to form multiple subphases is directly proportional to the number of methylene units in the spacer. As Collyer stated, “spacer groups are typically comprised of 3-12 methylene units.” (p. 45) [9]. Polymers with short spacers and short terminal chains exhibit a nematic phase. An increase in spacer length occurs with polymerization, which leads to the transition from the nematic phase to the smectic phase. On the other hand, excessively short spacer lengths can also cause various effects on the clearing points of the polymers. In some systems, the presence of one more or one less unit in the spacer can lead to a higher clearing point in similar polymers [8, 50]. Changes in spacer length directly affect the freedom of mesogens in the polymer backbone and the length of the side chains [39].

2.1.6 Mesogenic unit effect on mesomorphic behaviour

Research has demonstrated a direct correlation between the increase in the aromatic ring and the enhancement of both the molecular length and the molecule's tendency to polarize. In such nematic polymers, it has been observed that the clearing point undergoes a substantial increase. As the length of the mesogens increases, polymers tend to transition to a crystalline state. As mentioned earlier, since the spacers are short, SCLCPs show a low tendency to form smectic phases. That is, although the polymer backbone may have long spacers, a nematic phase is observed. However, it should be noted that in this case, the glass transition temperature will be low. In circumstances where there is a discrepancy between the units responsible for connecting the spacer to the mesogenic unit, it is imperative to conduct a thorough investigation into the tendency to polarize. The glass transition temperature, a critical property in the study of amorphous materials, exhibits a dependence on the polarity of the spacer. Consequently, predictions about the mesophase of a molecule can be made in both instances [8].

2.1.7 Polymer backbone effect on mesomorphic behaviour

The polymer backbone has flexibility, and as its flexibility increases, the glass transition temperature decreases [39]. As Noël and Navard emphasized, “It has been demonstrated that the transition temperatures of mesogenic side groups of the same chemical structure are affected by the flexibility of the polymer backbone to which they are attached. In this case, the side groups are attached via flexible spacers of approximately the same length to different polymer backbones” (p. 45) [42].

2.1.8 Cholesterol and cyanobiphenyl compounds

2.1.8.1 Cholesterol compounds

As Yanagisawa et. all also emphasized (2022), “cholesterol is a lipid that is widely present in our body” (p. 1) [59]. Owing to the cholesterol compound having a membrane made of phospholipids, it has a hydrophobic structure. On the other hand, cholesterol-based liquid crystals tend to have a three-dimensional helical structure because of this hydrophobic nature and rigid skeleton. Due to their supramolecular helix structure, they can selectively reflect polarized light. Due to the fact that their optical properties are susceptible to variation depending on specific conditions, such as temperature, pressure, and electric field, they are utilized extensively in a variety of electronic techniques [43, 59]. Cholesterol-based liquid crystals, which are still being researched in many aspects today, can also be synthesized as dimers and trimers. Figure 2.29 and Figure 2.30 shows the dimesogen and trimesogen, respectively, quoted from an article [38].

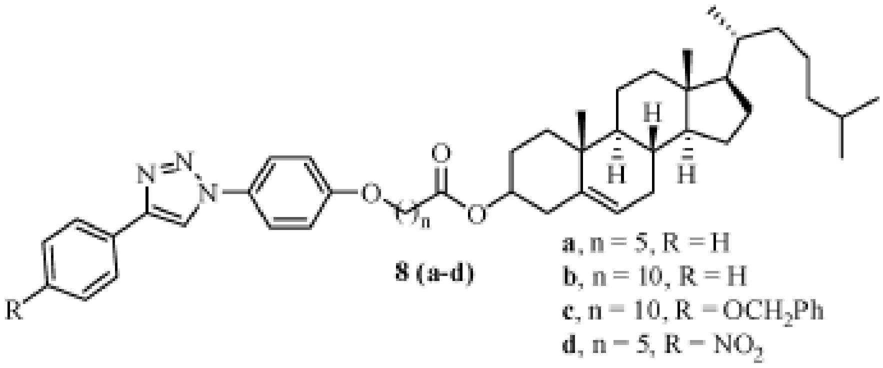


Figure 2.29 : Dimesogen synthesis.

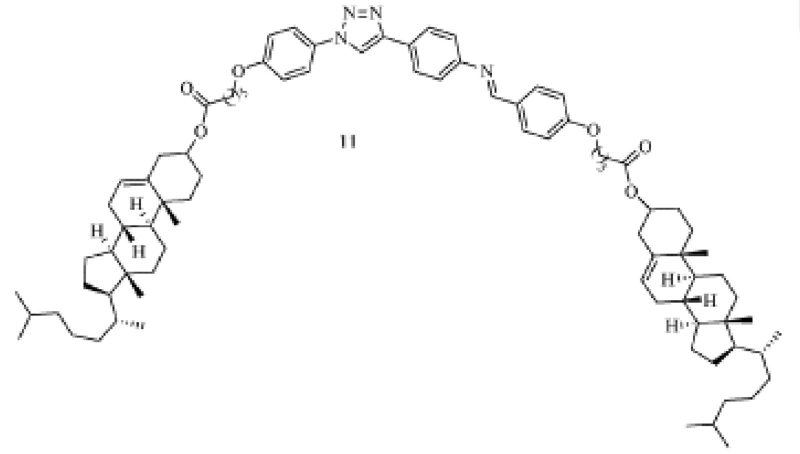


Figure 2.30 : Trimesogen synthesis starting from dimesogen.

2.1.8.2 Cyanobiphenyl compounds

George Gray, especially with his work on cyanobiphenyls, made a great contribution to the development of liquid crystals. He observed that the molecular lengths of nematic cyanobiphenyls increased by a factor of 1.5 with X-ray measurements, and although not at first, he later related this to dipole-dipole interactions. It was determined that these interactions contributed to the parallel arrangement of the molecules [14].

In the cyanobiphenyl compound synthesized by Gray, pentyl-cyanobiphenyl, the two surfaces are directly connected, allowing for a strong bond to be formed. Surprisingly, such a strong molecule exhibits liquid crystal properties. In Figure 2.31, the structure of the flexible alkyl chain attached to the cyanobiphenyl compound in Gray's synthesized molecule can be seen. Studies have determined that the synthesized compound exhibits liquid crystal properties at room temperature, maintaining a stable structure [14].

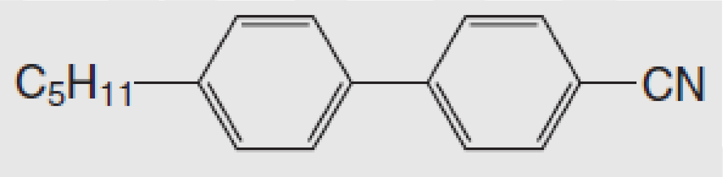


Figure 2.31 : Pentyl-cyanobiphenyl compound synthesized by Gray.

2.1.9 Mesophase characterization

The characterization of the mesophase can be carried out by means of the techniques described below.

2.1.9.1 Polarized optical microscope (POM)

Polarized optical microscope is utilised for the examination of the optical patterns and textures of liquid crystals under polarized light [10, 48].

With the employment of POM, we can observe textural changes in liquid crystal materials with different geometries, gaining information about various optical textures and classifying the mesophases [13, 49]. A detailed illustration of the commonly used POM is shown in Figure 2.32 [10].

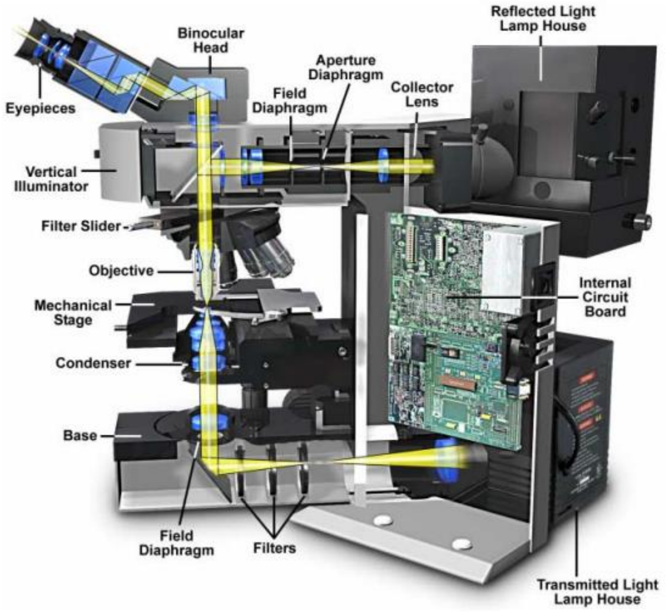


Figure 2.32 : Schematic representation of the components of the POM.

2.1.9.2 Differential scanning calorimeter (DSC)

DSC is used as a complementary tool for the observation of phase transitions in materials which have liquid crystal properties [49].

When a substance is subjected to heating and cooling over several cycles using DSC, the amount of energy absorbed or released is measured, and a graph of heat flow versus temperature or time can be generated [60].

With DSC, the phase transition temperatures, enthalpy changes, transition orders and purities of liquid crystals can be determined [13, 60].

3. EXPERIMENTAL PART

3.1 Materials

4’-hydroxybiphenyl-4-carbonitrile (Sigma Aldrich), 8-chloro-1-octanol (Sigma Aldrich), ethanol (Merck), cholesteryl chloroformate (Sigma Aldrich), dimethyl sulfoxide (DMSO) (Sigma Aldrich), anhydrous K_2CO_3 (Fluka), diethyl ether (Sigma Aldrich), dichloromethane (DCM) (Sigma Aldrich), triethylamine (TEA) (Sigma Aldrich), tetrahydrofuran (THF) (Sigma Aldrich) and NaOH pellets (Merck). All materials are commercially available and have been used as received.

3.2 Instruments

3.2.1 ^{1}H Nuclear magnetic resonance (^{1}H-NMR)

^{1}H-NMR analyses were performed on a Varian 500 MHz spectrometer.

3.2.2 Fourier transform infrared spectroscopy (FT-IR)

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

3.2.3 Polarized optical microscope (POM)

POM (Leica DM2500P with LTSE350 Liquid Crystal Prosystem TMS 94 Hot Stage) has been used for the determination of the LC behavior of the LC compounds.

3.2.4 Differential scanning calorimetry (DSC)

DSC is used to investigate thermal behaviour of the LC polymers. For this purpose, a nitrogen atmosphere on the TA instruments Q1000 series DSC apparatus was used in the thermal characterizations.

3.3 Preparation of the LC Molecules

In this study 4’-hydroxybiphenyl-4-carbonitrile and 8-(4-cyanobiphenyl-4’-oxy) octan-1-ol (LC8) were used to prepare LC mesogen.

3.3.1 Synthesis of LC8

LC8 was synthesized according to the literature [33].

A quantity of 3 g (15 mmol) of 4'-hydroxybiphenyl-4-carbonitrile was dissolved in 200 mL of DMSO. Subsequently, 2 g (14.5 mmol) of anhydrous K_2CO_3 was added to this solution as an acid scavenger. Subsequently, 3.4 milliliters of 8-chloro-1-octanol (20 mmol) was added dropwise to the reaction mixture, which was stirred with a magnetic stirrer under nitrogen atmosphere at 110 °C. The reaction was allowed to proceed at this temperature for a period of three hours. Upon completion of the reaction, the mixture was added dropwise to a 400 mL solution of NaOH (10%). Precipitated white crystalline product was filtered. The obtained product was dried at 40 °C under vacuum. The obtained LC8 was recrystallized from ethanol. Purified white crystalline product was dried under vacuum. The reaction yield was 52 % [33].

3.4 Preparation of Cholesterol-Based Mesogens

3.4.1 Synthesis of Cho-LC8

A quantity of 0.403 g (1.25 mmol) of LC8 was dissolved in 15 mL of THF, and 0.20 mL of TEA was subsequently added to this solution. Thereafter, 0.56 g (1.25 mmol) of cholesteryl chloroformate in 15 mL of THF solution was added slowly with a dropping funnel at 0 °C. Subsequently, the reaction was carried out at room temperature for a duration of 24 hours. Upon completion of the reaction, the reaction mixture was poured into iced water, and the precipitate obtained was filtered. The TEA product was then recrystallized using diethyl ether, resulting in the formation of a white crystalline substance that was dried under vacuum at room temperature. The yield obtained was 0.55 g (63%).

3.4.2 Synthesis of Cho-BFCN

A quantity of 0.43 g (2.20 mmol) of 4'-hydroxybiphenyl-4-carbonitrile was dissolved in 15 mL of THF. Subsequently, 0.35 mL of TEA was added into the solution as an acid scavenger. Then, 1 g (0.99 mmol) of cholesteryl chloroformate in 15 mL of THF solution was added slowly with a dropping funnel at 0 °C. Thereafter, the reaction was carried out at ambient temperature for a period of 24 hours. Subsequent to the termination of the reaction, the mixture was poured into iced water, and the precipitated mass was filtered. The obtained product recrystallized with DCM, dried under vacuum, and white crystals were obtained. The reaction yield was 1.20 g (88.9%).

3.5 Characterization of the mesogens

Spectroscopic characterization of the mesogens were performed with FT-IR and ^{1}H-NMR. Then, thermal characterization of Cho-LC8 mesogen was made with DSC. LC image of the mesogens were obtained with POM.

4. RESULTS AND DISCUSSION

In this study, cholesterol-based mesogens were synthesized and characterized.

4.1 Synthesis of LC8

8-(4-cyanobiphenyl-4’-oxy) octan-1-ol (LC8) was synthesized starting from 4’-hydroxybiphenyl-4-carbonitrile and 8-chloro-1-octanol in the presence of DMSO according to the literature [33].

4.2 Synthesis and Characterization of Cholesterol-Based Liquid Crystalline Mesogen of Cho-LC8

The synthetic process for Cho-LC8 involved the reaction of cholesteryl chloroformate and LC8 in the presence of triethylamine (TEA) as an acid scavenger at room temperature, as demonstrated in Figure 4.1.

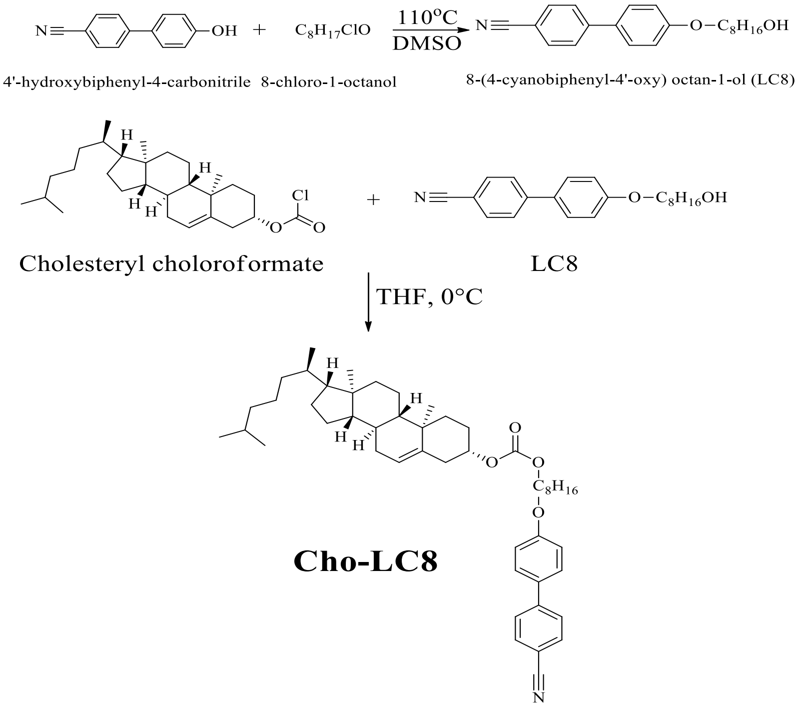


Figure 4.1 : Synthesis of the Cho-LC8.

The characterization of Cho-LC8 and Cho-BFCN was performed through spectrophotometric analysis, employing FT-IR and ^{1}H-NMR. The FT-IR spectrum of Cho-LC8 and Cho-BFCN (Figure 4.2) revealed a characteristic ester carbonyl peak at 1704 cm^{-1} and 1737 cm^{-1}, respectively. A comparison of the FT-IR spectrum of Cho-LC8 and Cho-BFCN with that of LC8 reveals a significant difference. The ester carbonyl peak observed at 1704 cm^{-1} in the Cho-LC8 spectrum and at 1737 cm^{-1} in the Cho-BFCN are absent in the LC8 spectrum. Furthermore, the aliphatic C-H stretching peaks of cholesterol, ranging from 2852 cm^{-1} to 2929 cm^{-1} in the Cho-LC8 spectrum and ranging from 2866 cm^{-1} and 2934 cm^{-1} in the Cho-BFCN spectrum, were also observed. The 2235 cm^{-1} and 2228 cm^{-1} peaks are attributed to the characteristic CN bond for Cho-LC8 and Cho-BFCN, respectively.

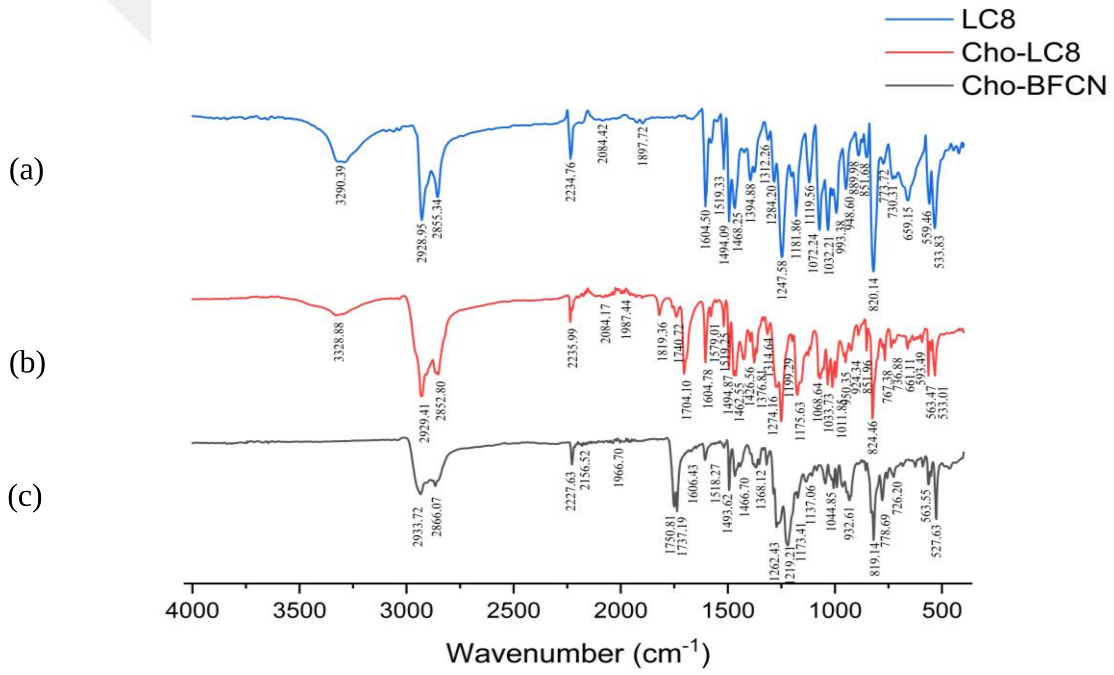


Figure 4.2 : FT-IR spectra of the LC8 (a), Cho-LC8 (b) and Cho-BFCN (c).

An additional characterization of Cho-LC8 was conducted using ^{1}H-NMR. The ^{1}H-NMR spectrum of Cho-LC8 (Figure 4.3) revealed that the chemical shifts of the molecule indicate the presence of a cholesteryl group and aromatic protons between 0.70-2.0 ppm, and 7.0–7.70 ppm, respectively. Additionally, the signals at 3.6–4.0 ppm were attributed to CH_2-O protons.

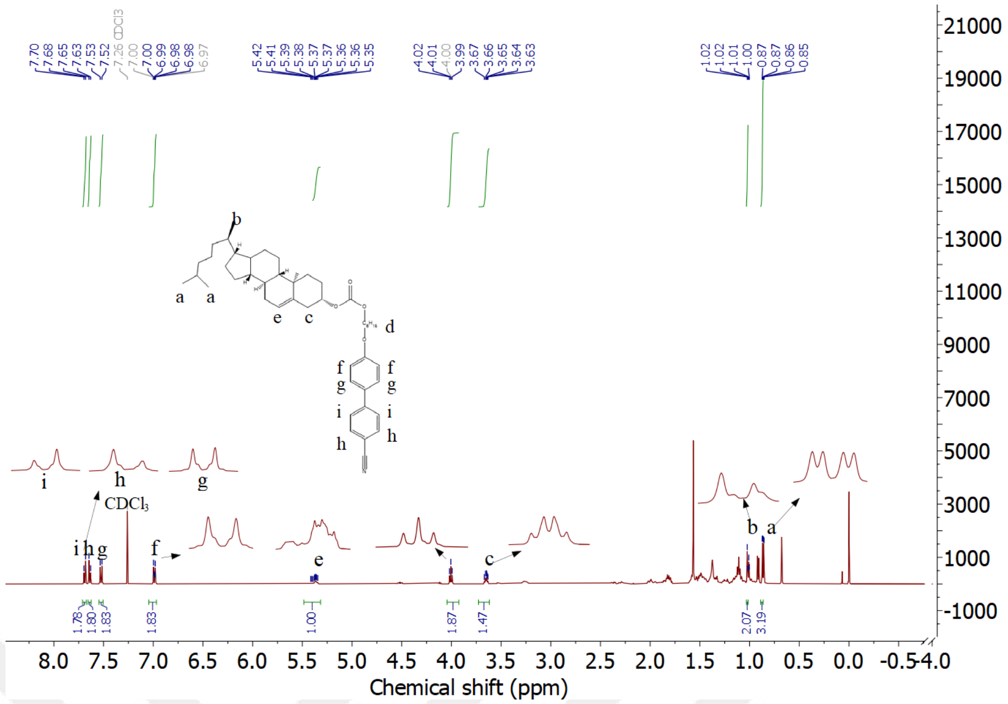


Figure 4.3 : ^{1}H-NMR spectrum of the Cho-LC8.

4.3 Synthesis and Characterization of Cholesterol-Based Liquid Crystalline Mesogen of Cho-BFCN

Cho-BFCN was prepared at room temperature using cholesteryl chloroformate and 4'-hydroxybiphenyl-4-carbonitrile in the presence of triethylamine (TEA) as an acid scavenger (Figure 4.4).

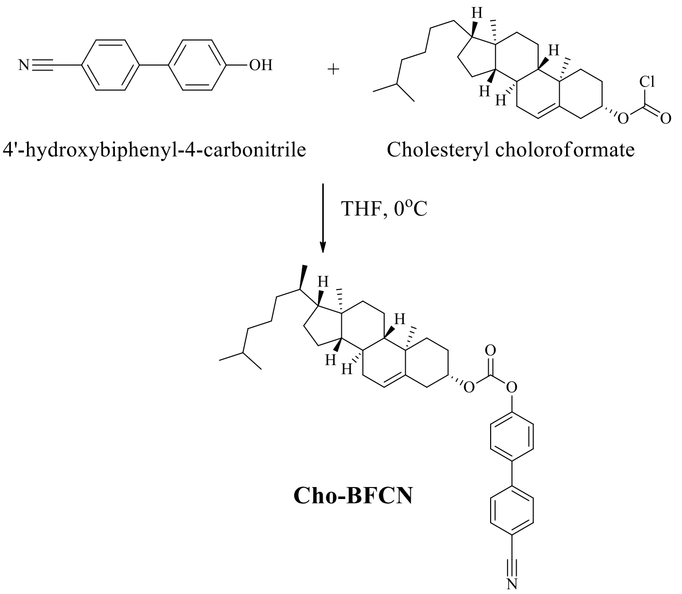


Figure 4.4 : Synthesis of the Cho-BFCN.

The obtained compound was characterized by FT-IR and ^{1}H-NMR Spectroscopy. As previously outlined in Figure 4.2, the FT-IR spectrum of Cho-BFCN was compared with those of LC8 and Cho-LC8.

The ^{1}H-NMR spectrum of the Cho-BFCN (Figure 4.5) exhibit signals within the range of 0.63-2.1 ppm, which are indicative of cholesteryl group protons, and 4.5-5.3 ppm, which are attributable to CH_2-O protons. Additionally, aromatic protons are discernible at 7.2–7.63 ppm.

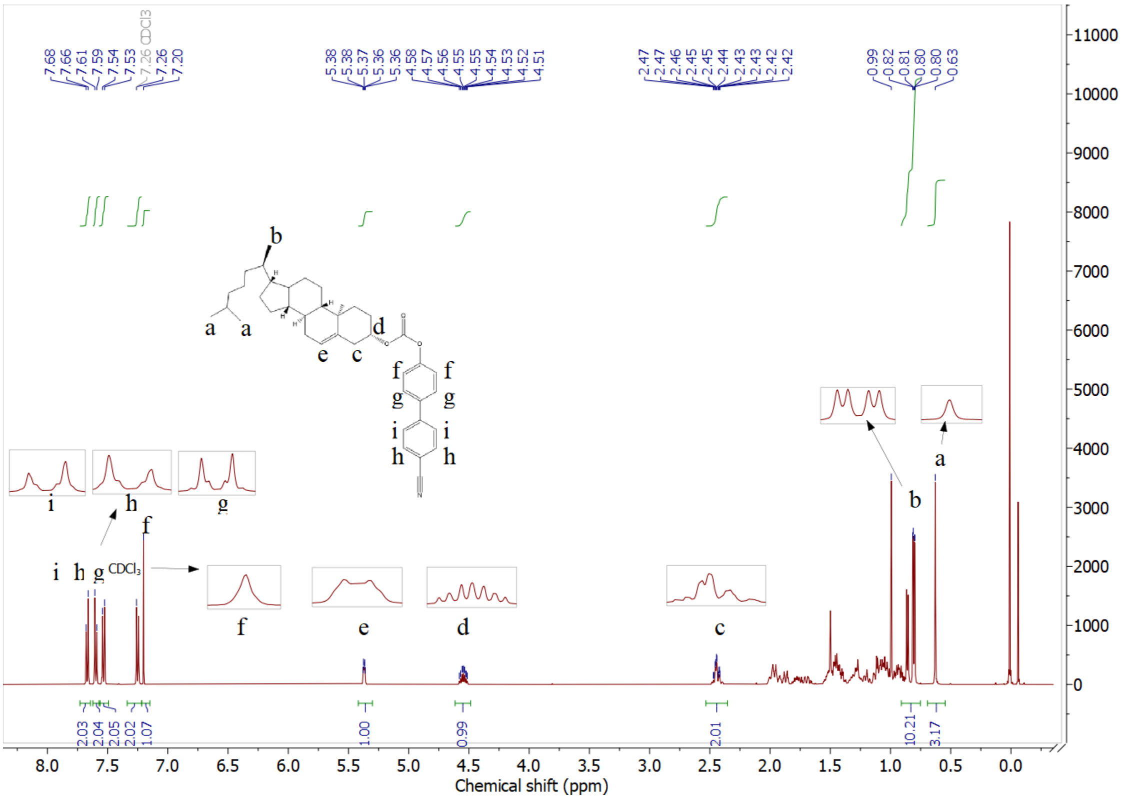


Figure 4.5 : ^{1}H-NMR spectrum of the Cho-BFCN.

4.4 Investigation of Thermal and Mesomorphic Properties of the Compounds

Thermal and mesomorphic properties of LC8 was described in the literature [33].
The phase behavior, phase transitions, and liquid crystalline structure of the compound were analyzed using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The transition temperatures and mesomorphic properties are summarized in Table 4.1 [33].

Table 4.1 : Phase properties of the synthesized compounds.

Compound	Phase Transition Temperature (°C)
LC8 [33]	Cr 90.7 → N 112.6 → I
Cho-LC8	Cr 66 → N 73 → I
Cho-BFCN	Cr 68 → N 110 → I

Cr= crystalline, N= nematic, I= isotropic

Figure 4.6 exhibits DSC heating and cooling curves of Cho-LC8.

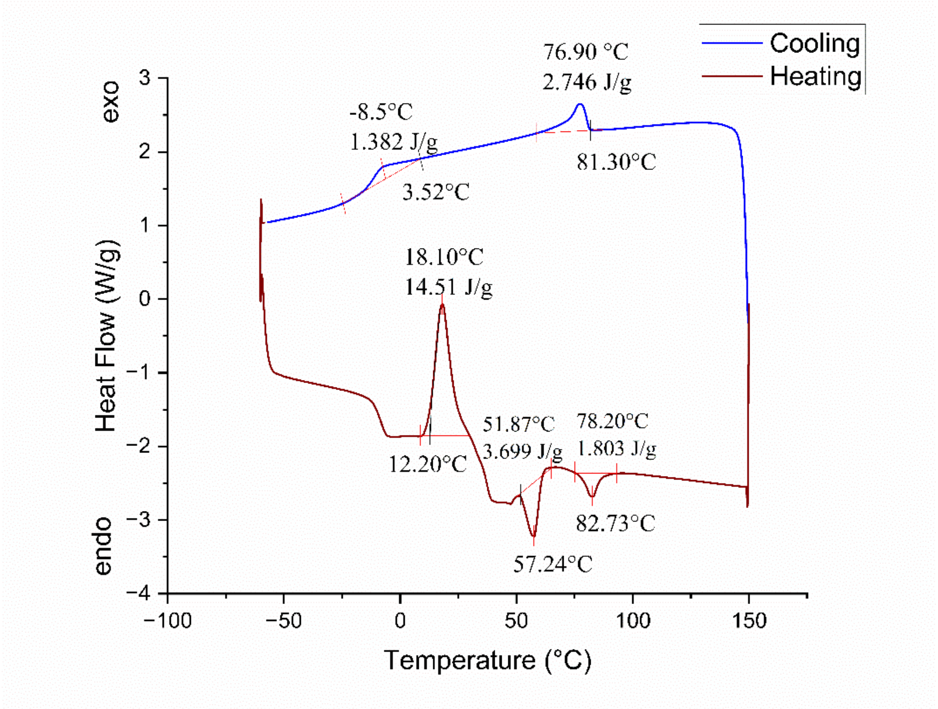
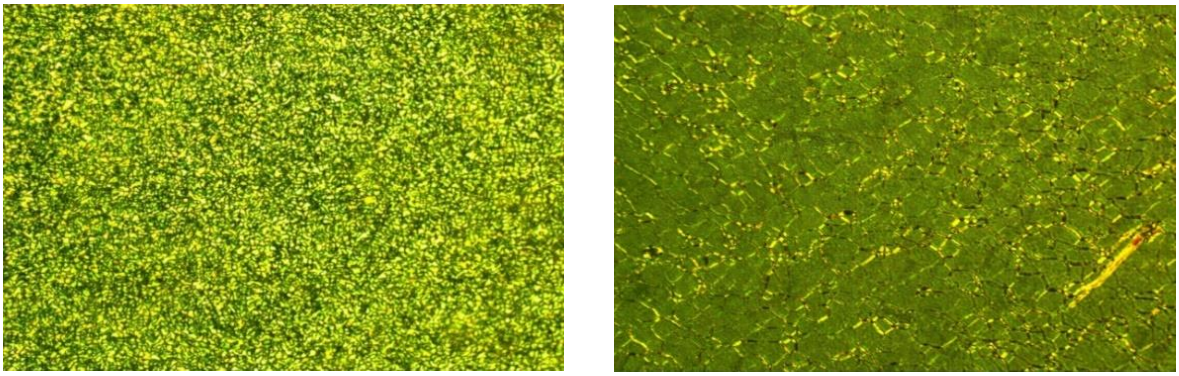


Figure 4.6 : DSC 2nd heating and cooling curves of the Cho-LC8.

The mesomorphic properties of the Cho-LC8 were investigated with POM by heating and cooling at 10 degrees per minute (Figure 4.7). Cho-LC8 mesogen shows enantiotropic nematic texture. During heating process (Figure 4.7a), Cho-LC8 gives nematic liquid crystalline phase at 73 °C and isotropic phase was observed at 79 °C. During the cooling process (Figure 4.7b), a nematic texture was seen at 66 °C. These results are consistent with the DSC thermogram.



(a) (b)

Figure 4.7 : POM textures of the Cho-LC8 (400x).

The mesomorphic properties of the Cho-BFCN were determined by heating and cooling at 10 degrees per minute using a POM (Figure 4.8). It was found that the Cho-BFCN mesogen has an enantiotropic–mesophase that exhibits nematic texture. The nematic liquid crystalline phase was observed at 110 °C during the heating process, while the isotropic phase was observed at 167 °C. In addition, a nematic texture was observed at 150 °C during cooling process.

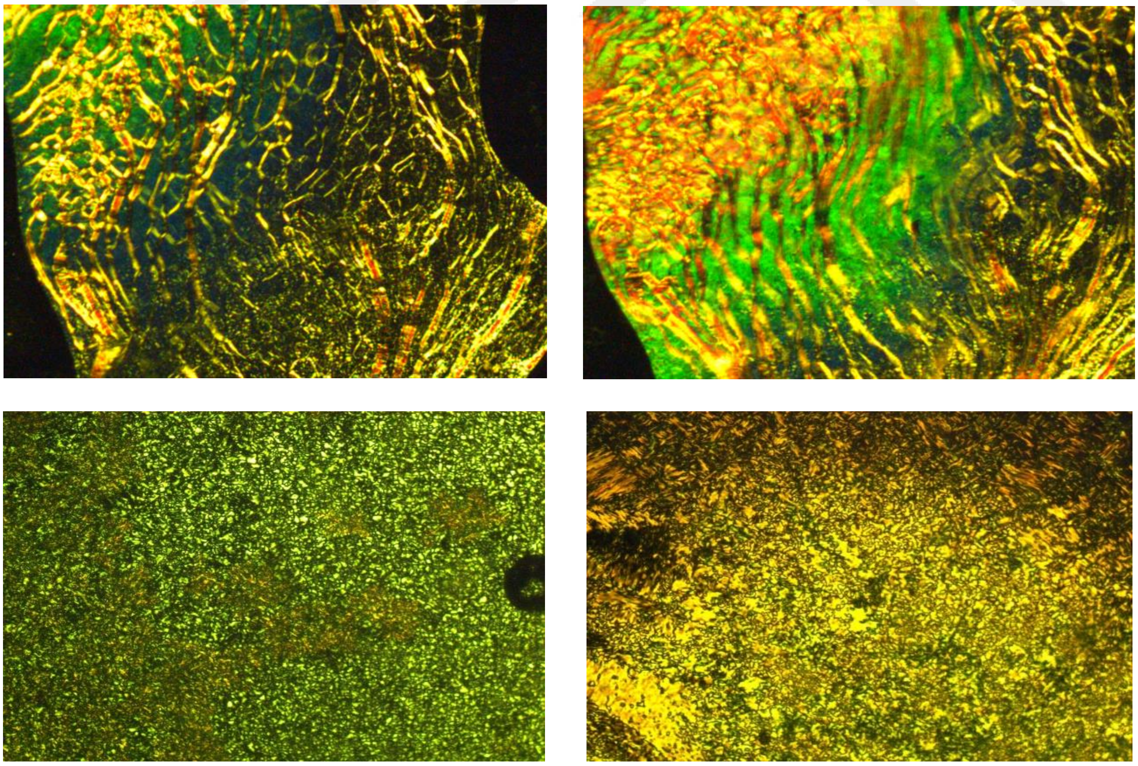


Figure 4.8 : POM textures of the Cho-BFCN (400x).

5. CONCLUSION

In this thesis, two cholesteryl-based compounds were synthesized and characterized spectroscopically using Fourier-transform infrared (FT-IR) spectroscopy and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The phase transitions of the liquid crystalline material, designated as Cho-LC8 and Cho-BFCN, were analyzed using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Notably, the phase transition temperatures were determined via POM. The POM images reveal that the compounds exhibit nematic phase transitions during both heating and cooling cycles.

According to the POM investigation, it was observed that the spacer group in Cho-LC8 adds flexibility to the substance and lowers the mesophase – isotropic transition temperature. Conversely, the absence of a spacer group in Cho-BFCN results in a rigid structure and a high nematic- isotropic transition temperature.

Furthermore, the optoelectronic properties of these materials will be investigated in subsequent studies.

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