ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF URETHANE BASED LIQUID CRYSTAL MATERIALS

M.Sc. THESIS

Sinem AĞTAŞ

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Thesis Advisor: Prof. Dr. Bahire Filiz ŞENKAL

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÜRETAN BAZLI SIVI KRİSTAL MALZEMELERİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Sinem AĞTAŞ
(509131047)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Bahire Filiz ŞENKAL

HAZİRAN 2018

Sinem Ağtaş, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 509131047, successfully defended the thesis entitled "SYNTHESIS AND CHARACTERIZATION OF URETHANE BASED LIQUID CRYSTAL MATERIALS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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

Date of Submission : 30th May 2018
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To my spouse and children,

Beloved family,

Friends and to The List,

FOREWORD

In this life, there are things that can change a person in a matter. This was my journey, and it changed me in a way that I can never thought of. First of all, I would love to thank my supervisor Prof. Dr. B. Filiz Şenkal for her absolute guidance, gracious support and understanding during the whole time. She was kind, cheerful and caring as well as inspiring, and she has the biggest heart I have ever known. Also, I would like to thank Prof. Dr. Yeşim Gürsel for her help through the research, for her ideas, perspectives and sympathy.

When it comes to friends, Burak Korkmaz was always with me and he was my true companion through this. He always gives me cheers and he made this study esthetically joyful. We have been in this together. I thank him for all.

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Very special thanks to my dear husband Taner Ağtaş. I feel him around me all the time even he is not. He gives me courage to accomplish everything and to believe in myself. My little bundle of joy, Lina, was so well-behaved and understanding. She amazes me and everytime I look in her eyes, she makes me a better person.

It was strange yet years, now it ends. But every ending has a new beginning.

May 2018

Sinem AĞTAŞ
(Chemist)

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ABBREVIATIONS

LC : Liquid crystal
LCP : Liquid crystal polymer
SmA : Smectic A
SmA* : Chiral smectic A
SmC : Smectic C
SmC* : Chiral smectic C
SCLCP : Side chain liquid crystal polymer
MCLCP : Main chain liquid crystal polymer
FT-IR : Fourier transform infrared spectroscopy
^{1}H-NMR : ^{1}H Nuclear magnetic resonance
POM : Polarizing optical microscope
DSC : Differential scanning calorimetry
NMP : *N*-Methyl-2-pyrrolidone
DMF : Dimethylformamide
LC8 : 8-(4-cyanobiphenyl-4'-oxy) octan-1-ol
LC11 : 11-(4-cyanobiphenyl-4'-oxy) undecan-1-ol
HBP : Hydrogen bonded polymer
PEG : Poly(ethylene glycol)
BI : Butyl isocyanate
PEG 500 : Polyethylene glycol monomethylether 500
TDI : Toluene diisocyanate
DEGME : Diethylene glycol monoethylether

SYMBOLS

S	**:** Order parameter
P	**:** Pitch
θ	**:** Angle
Tm	**:** Melting temperature
Ti	**:** Isotropic temperature

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SYNTHESIS AND CHARACTERIZATION OF URETHANE BASED LIQUID CRYSTAL MATERIALS

SUMMARY

Liquid crystalline polymers are usually synthesized by covalent linking of rigid mesogens and polymer backbones via flexible spacers. Side chain liquid crystalline polymers (SCLCPs) integrates low-molar mass liquid crystals and polymers' one of a kind characteristics. Since SCLCPs have appealing electrical and optical characteristics, they have been the object of intense researching mostly. Among these features they can be used in microelectronic devices in range of date storage and nonlinear optics. Liquid crystals which are the unique state of matter have a wide application area such as digital displays, sensors and LCD screens.

In this thesis, urethane compounds and their hydrogen bonded liquid crystal polymers were synthesized and optoelectronic properties are characterized. First, Polyethylene glycol 500 monomethyl ether (PEG 500) was reacted with butyl isocyanate (BI) and toluene diisocyanate (TDI) separately. Also, diethyleneglycol monomethyl ether (DEGME) was reacted with butyl isocyanate and toluene diisocyanate. Urethane based liquid crystalline polymers were prepared by using intermolecular hydrogen bonding concept. For this aim, hydrogen-bonded crystalline polymer was synthesized reacting urethane compounds with H-bond donors.

Synthesis of Hydrogen Bond Donors:

11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol (LC11) was synthesized as a bond donor. The structure of the LC11 was characterized by FT-IR and ^{1}H-NMR spectroscopy.

Preparation of urethane based liquid crystalline polymers:

Urethane based polymers were engaged as hydrogen bond acceptors and LC11 was employed as a hydrogen bond donor to yield hydrogen bonded PEG based liquid crystalline mesogen. Intermolecular H-bonding between nitrogen of amine of the polymer and hydroxyl groups of the hydrogen donors formed the structure of the side chain liquid crystalline polymers.

In characterization of hydrogen bonded urethane based polymers FT-IR (Fourier Transform Infra Red) spectroscopy, DSC (Differantial Scanning Calorimetry) and POM (Polarized Optic Microscope) methods were used. Hydrogen bonding donors and acceptors are positioned that intramolecular hydrogen bonding is favorable, displaying slightly broadened O-H stretching absorption band in the range of 3200 to 3500 cm^{-1}, according to FT-IR spectra of the polymers.

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

ÜRETAN BAZLI SIVI KRİSTALLERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Sıvı kristal polimerler, genellikle katı mezojenler ile polimer omurgalarının esnek bağlantılar aracılığıyla kovalent bağlanmasıyla sentezlenir. Yan zincir sıvı kristalin polimerler (SCLCP'ler), düşük molar kütleli sıvı kristallerin ve polimerlerin özelliklerini birleştirirler. SCLCP'ler, ilgi çekici elektriksel ve optik özelliklere sahip olduklarından, çoğunlukla yoğun araştırmanın hedefi olmuşlardır. Bu özellikler sayesinde, doğrusal olmayan optiklerde ve mikroelektronik cihazlarda kullanılabilirler. Maddenin eşsiz bir hali olan sıvı kristaller, dijital göstergeler, sensörler, LCD ekranlar gibi çok geniş bir uygulama alanına sahiptirler.

Bu tezde, üretan bileşikleri ve bunların hidrojen bağlı sıvı kristal polimerleri sentezlenmiş ve karakterize edilmiştir. Önce, polietilen glikol 500 monometil eter (PEG 500) butil izosiyanat (BI) ve toluen diizosiyanat (TDI) ile ayrı ayrı reaksiyona sokulmuştur. Ayrıca dietilenglikolmonometileter (DEGME) de BI ve TDI ile reaksiyona sokulmuştur. Üretan yan zincir sıvı kristal polimerler, molekül içi hidrojen bağlama konsepti kullanılarak hazırlanmıştır. Bu amaçla, H-bağlanmış kristal polimer, üretan bileşiklerinin H-bağ donörleri ile reaksiyona sokulması ile sentezlenmiştir.

Hidrojen Bağı Donörlerinin Sentezi:

11-(4-Siyanobifenil-4'-oksi) undekan-1-ol (LC11) sentezlenmiştir. LC11 yapısı, FT-IR ve ^{1}H-NMR spektropi yöntemleri kullanılarak karakterize edilmiştir.

Üretan Bazlı Malzemelerin Sentezi:

Üretan esaslı polimerler hidrojen bağı alıcıları olarak, LC11 ise hidrojen bağ donörü olarak kullanılmıştır ve buna göre hidrojen bağlı sıvı kristal polimerler sentezlenmiştir. Polimerin amin azotu ve hidrojen donörlerinin hidroksil grupları arasındaki moleküller arası H-bağlaması, sıvı kristal polimerlerin yapısını oluşturmuştur.

Hidrojen bağlı üretan bazlı polimerlerin karakterizasyonu için FT-IR (Fourier Transform Infra Red) spektroskopisi, DSC (Differantial Scanning Calorimetry) ve POM (Polarized Optic Microscope) yöntemleri kullanılmıştır. Hidrojen bağı donörleri ve alıcıları, molekül içi hidrojen bağını tercih ederek, polimerlerin FT-IR spektrumlarına göre 3200-3500 cm^{-1} aralığında hafifçe genişlemiş O-H gerilim bandı göstermişlerdir.

Hidrojen bağlı sıvı kristal polimerlerin faz davranışları, DSC ve POM yöntemleri kullanılarak incelenmiştir. DSC termogramları ikinci ısıtma devrelerinde elde edilmiştir. Numuneler N_2 atmosferi altında 10 °C/dakika tarama oranı ile ısıtılmıştır. POM (X200) analizi de DSC sonuçlarını ve faz geçişlerini doğrulamıştır.

1. INTRODUCTION

Liquid crystals are an intermediate phase between solid and liquid phases that can be observed in some materials. Liquid crystals are anisotropic and regular oriented liquids. Liquid crystal phase for each substance is not valid. Only materials that are suitable as molecular order show liquid crystal phase. For this reason, liquid crystals are not a phase such as solid, liquid, gas and plasma phases, it is an intermediate phase for some substances. This intermediate phase is called mesophase. Mesophase-indicating molecules are called mesogens.

Side chain liquid crystal polymers (SCLCPs) are generally prepared by covalent linking rigid mesogens with flexible spacers. Recently, hydrogen bonding, ionic, ionic-dipolar and charge transfer interactions has been recognized as a new strategy for constructing SCLCPs. SCLCPs integrate properties of polymers with low molar mass mesogens. Because of these features, SCLCPs have potential applications in different fields like optical data storage, non-linear optics, being stationary phase in gas chromatography and high performance liquid chromatography. These materials have some advantages over the covalently bonded systems like dynamic function, environmental compatibility and low energy processing.

One of the significant non-covalent interactions in nature is hydrogen bonding. Nucleic acids, polypeptide and cellulose are biopolymers that have hydrogen bonding groups. The formation and dissociation of the hydrogen bonds for these polymers play an important role in many biological processes. With this kind of hydrogen bonding, durable and dynamic complex molecules can be synthesized with basic molecular self-assembly processes. Carboxylic and benzoic acid groups are examples of hydrogen-bond donors while pyridine and imidazole moieties are widely used as hydrogen-bond acceptors.

In this study, by using intermolecular hydrogen bonding concept side chain liquid crystalline polymers were prepared. For this aim, urethane based polymers were prepared with reacting hydroxy group containing compounds and isocyanates. Second, H-bonded crystalline polymers were synthesized by starting from urethane

based polymers as H-bond acceptor and 4’-(-hydroxyalkoxy)-4-cyanobiphenyl derivatives as H-bond donor. All prepared polymers and H-bonded crystalline polymers were characterized by using thermal analysis methods (DSC), FT-IR and POM methods.

2. THEORETICAL PART

2.1 Liquid Crystals

2.1.1 History and development of liquid crystals

In 1850, Virchow, Mettenheimer, and Valentin observed in their work on the nerve fibers that the nerve fibers were fluid in water and behaved differently under polarized light. Virchow and his colleagues did not understand that it was a liquid crystal, but they were the first observers of this different phase. At the same time, W. Heintz observed that Stearin changed from solid to cloudy liquid at 52 ^{O}C, opaque at 58 ^{O}C and became completely liquid at 62,5 ^{O}C, but explained only as biological material behavior [14,15].

In 1888, Reinitzer, Austrian botanist and chemist, discovered the liquid crystalline (LC) phenomena. Reinitzer discovered the two melting points of cholesteryl benzoate, a cholesterol derivative extracted from the carrot (Figure 2.1). Reinitzer observed that cholesteryl benzoate turned from solid to cloudy liquid at 145,5 ^{O}C and remained in this state until 178,5 ^{O}C, and then became completely liquid. Reinitzer first thought that the situation was caused by impurity, but no change was observed in spite of all purification. Later, German physicist Lehmann affirmed the indicated information [1-3]. Material appears as liquid due to its mobility, while exhibits crystalline characteristics in terms of its optical properties.

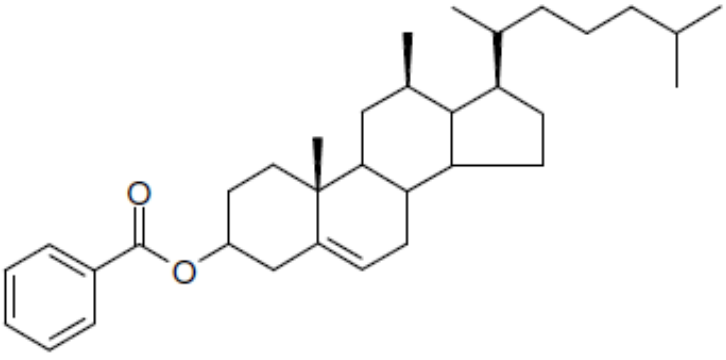

Figure 2.1 : Structure formula of cholesteryl benzoate [1].

At first, most of liquid crystal research was done in Germany and France. Directed by Vorlander, with systematic synthetic synthesis, new crystalline structure materials were synthesized and liquid crystal materials should be highly linear molecules, Vorlander exclaimed [1]. In addition to this, Friedel explained the textures observed by the polarized microscope and deduct the molecular order of liquid crystals [1,2]. Later, with van der Waals theories, Onsager, Maier and Saupe approaches was united as Onsager indicated repulsive forces in the order of crystals while Maier/Saupe pointed out dispersion forces based on statistics [1,4].

The years of 1945-1958, the post-World War II era, defined as silent years where no work has been done in the liquid crystal field. In 1958, American chemist Glenn Brown's article about liquid crystals published on "Chemical Reviews" magazine, and provided an international revival. Glenn Brown also established the Liquid Crystal Institute at Kent State University [19]. In 1960, Pierre-Gilles de Gennes, the theoretical physicist working on magnetism and superconductivity, began to become interested in liquid crystals, eventually noticing the astonishing resemblance between liquid crystals, superconductivity and magnetism, and taking the Nobel Prize in 1991 to revolutionize the liquid crystal world. Meanwhile, in 1969, Hans Kelker synthesized first liquid crystalline material at room temperature [20].

First big application of liquid crystals was found out in electro-optical display technology in middle of 1960s [1]. Later, this led to major increase in research on liquid crystals worldwide [1].

2.1.2 Classification and structure of liquid crystals

Liquid crystals are anisotropic and regular oriented liquids. The liquid crystal phase does not apply to each substance, only materials which are suitable as molecular order show liquid crystal phase. For this reason, liquid crystals are not a form of matter, but an intermediate phase. This intermediate phase is called mesophase, and mesophase-indicating molecules are called mesogens [23]. The transition temperature from the solid phase to the mesophase is called the melting point (MP), and the temperature from the mesophase to the isotropic liquid is called the clearing point (CP).

In the liquid crystal phase, not all molecules are in the same direcion as in the case of solids. Thus, only an average orientation and an orientation order can be mentioned.

In this way the molecule gains mobility. However, this is not as irregular as in liquids (Figure 2.2).

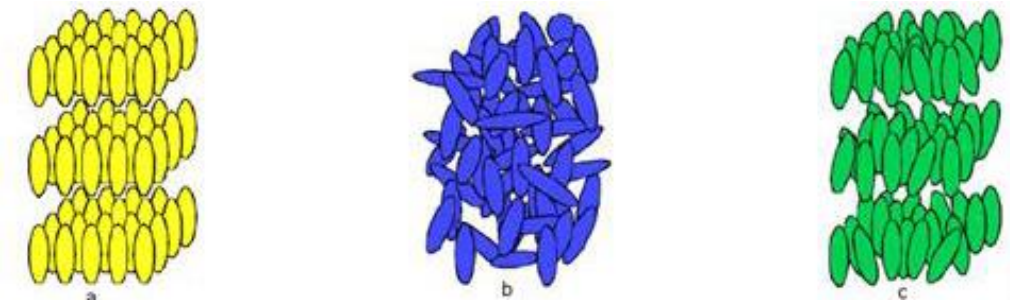

Figure 2.2 : Arrangements (a) in crystal (b) in a liquid (c) in a liquid crystal [26].

The most important difference between the crystal phase and the liquid crystal phase is that the crystals exhibit three-dimensionally tightly regulated structures in a large periodic area. In liquid crystals, this arrangement is not very tight, and this array has an angle. There are order parameters (S) used to find out how much a liquid crystal is regulated. The order parameter is shown in Equation 2.1 and the θ angle shown in Figure 2.3 [25].

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

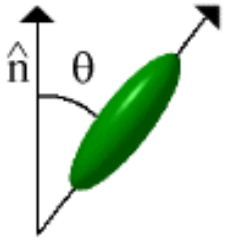

Figure 2.3 : Angle between director and long axis of molecule [25].

Liquid crystalline materials, according to their liquid crystalline state formation method (melting or in solution), can be identified as thermotropic or lyotropic [1,2].

The liquid crystal transition is thermally activated for thermotropic liquid crystals. In thermotropic LCs, thermally activated mesogenic phases are formed extending from the crystal melting temperature, T_m, to clearing or isotropic temperature, T_i. For example, when a liquid crystalline material is heated in solid state, the material becomes liquid crystal. If heating is continued, more than one liquid crystal phase is passed and material becomes liquid, i.e. isotropic. This substance is called polymorphomic compound. Thermodynamically stable mesophases that exhibit the

same liquid crystal phase when both heated and cooled are called enantiotropic mesophases. In liquid crystals, mesophase sometimes occurs during cooling, not during heating. These thermodynamically unstable mesophases are called monotropic mesophases [31]. Thermotropic LCs have a wide application area such as electro-optic displays [1,2].

For lyotropic LCs, solvents trigger the transition to the liquid crystal state. Lyotropic LCs show their transitions with adding or removing of the solvent [1,2]. The lyotropic liquid crystals are hydrophilic at one end and hydrophobic at another. The best examples are soap and phospholipids [27].

Molecules in which the liquid crystal phase is formed by both the effect of temperature and the effect of solvent is called amphotropic liquid crystals.

Liquid crystals can be divided into three types, according to increasing mesogenic order levels: nematic, smectic and cholesteric [1,2].

Nematic Mesophase

Generally observed liquid crystalline phase is the nematic phase. The “nematic” term means mesomorphic phase appearence between crossed polars. The molecule center is arranged randomly, therefore long-range order no longer exists in nematic phase [1,2]. Nevertheless, the axes of all molecules are specifically oriented in a direction, shown as in Figure 2.4. Molecules can pass by each other so easily due to very small intermolecular attractions in this state. The nematic phase is divided into several sub-phases. The most important of these are the unaxial and biaxial ones.

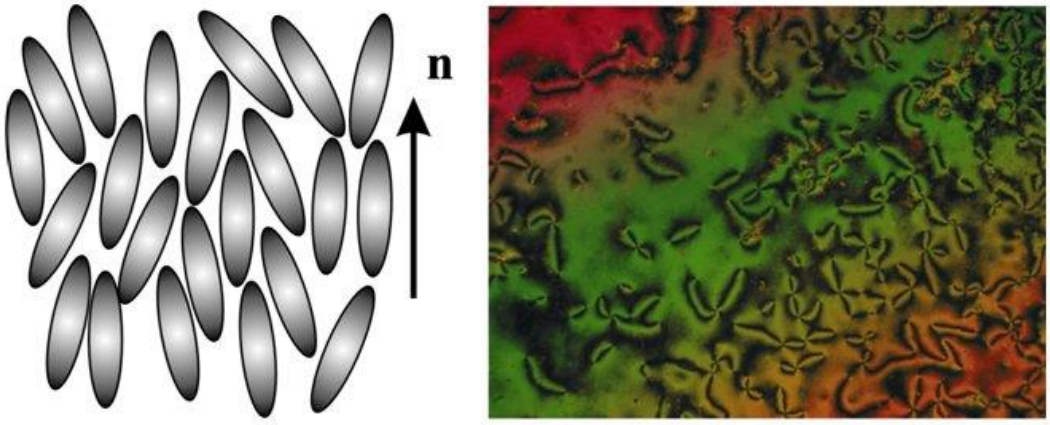

Figure 2.4 : Nematic phase [29].

Smectic Mesophase

Since a number of symmetry variants occur, the smectic phase is much more complex for describing. Also, the term “smectic” means “soap”. Smectic liquid crystals consist of layered structures and are both orientational and positional order. These are closer to the crystalline structure. The twelve different smectic liquid crystals types have been observed so far according to the structures in the layers [24]. The most commonly occurring phases are Smectic A, Smectic B and Smectic C mesophases (Figure 2.5).

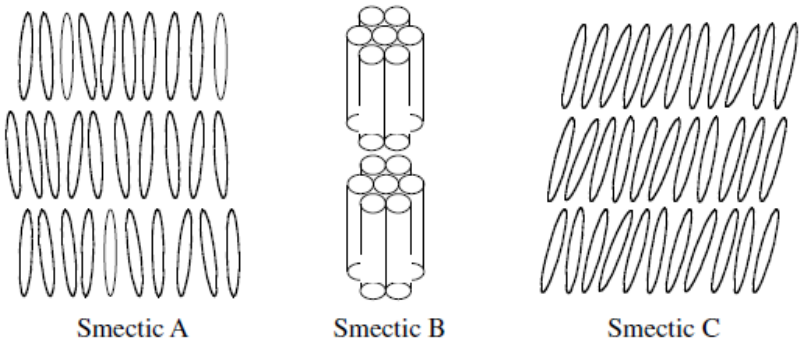

Figure 2.5 : Smectic phase [30].

From the smectic phases, A and C flow like liquids and have a random molecular order. The only difference between them is that while the Smectic A phase is at right angle, the Smectic C phase is obliquely arranged. Smectic B, F and I phases have hexate phase type. Their molecular configuration is hexagonal. The difference between them is caused by the gradient patterns. The Smectic B is perpendicular, the Smectic F is inclined to the edge, and the Smectic I is inclined to the top. The Smectic D phase has been observed to have the plastic phase type. The molecular configuration is micellar or rod-shaped. Smectic E, G, H, J, K and L have crystal phase type. Smectic E and L are perpendicular to the molecular order and others are inclined [35].

- *Smectic A Mesophase:* The classical Smectic A mesophase can be achieved from the nematic phase during cooling or by cooling the isotropic phase directly. Here the phase is periodic in one direction. As can be seen in Figure 2.6, the distance between each layer in the Smectic A is equal and denoted by d. Smectic A generally occurs in molecules in which the alkyl groups are

symmetrical groups. In general, the polarizing microscope has the appearance of a fan-shaped texture (Figure 2.6).

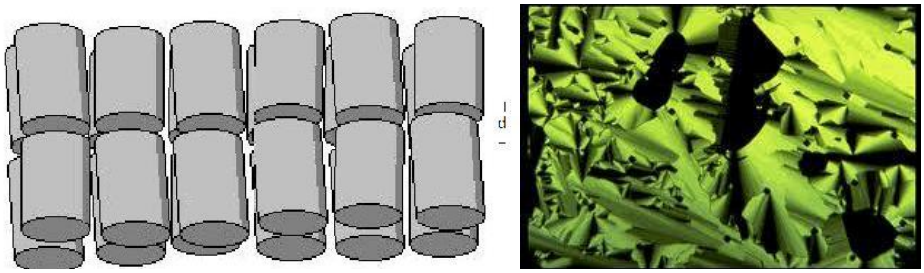

Figure 2.6 : Smectic A mesophase [32].

- *Smectic C Mesophase:* Smectic C mesophase is more irregular than the Smectic A mesophase. Switching between layers is possible. The longitudinal molecular axis is bent at an angle that is normal to the smectic plane.

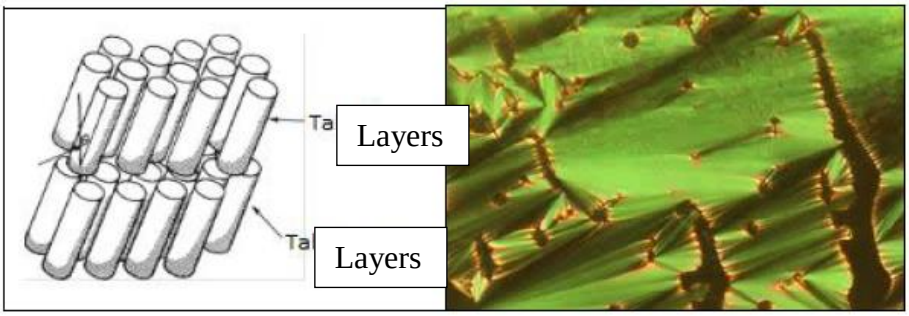

Figure 2.7 : Smectic C mesophase [32].

- *Smectic B Mesophase:* Nearly packed hexagonal layers in the Smectic B mesophase have a double stacking sequence. It is a phase where the molecules are inclined towards the top and sides of the hexagonal cage. The Smectic B phase shows mosaic textures. This phase consists of two analogues designated as Sm I and Sm F phases. In some structures, molecules change along their main axis due to periodically increasing spacing with increasing heat. A transition from the Sm B to the Sm H mesophase may occur when an additional settlement space is found [37].

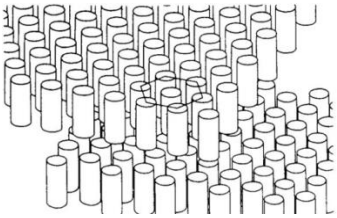

Figure 2.8 : Smectic B mesophase [37].

Cholesteric Mesophase

The cholesteric phase, also known as chiral nematic phase, was observed in the first liquid crystal found by Friedrich Reinitzer in 1888. The chiral asymmetry property of chiral molecules results in asymmetry of intramolecular interaction [28]. The liquid crystal molecules are arranged in a structure having an asymmetric helix shape. As the visible light passing through the liquid crystal molecule turns to the right or to the left, the light travels in a helix. The length of the cholesteric helix pitch, *P*, described as the interval over which the molecular director rotates by 2π ahead the helix axis. According to conformation of the molecule the twist is righ-handed or left-handed [1,2]. Rainbow-colored textures are characteristic in cholesteric phases (Figure 2.9).

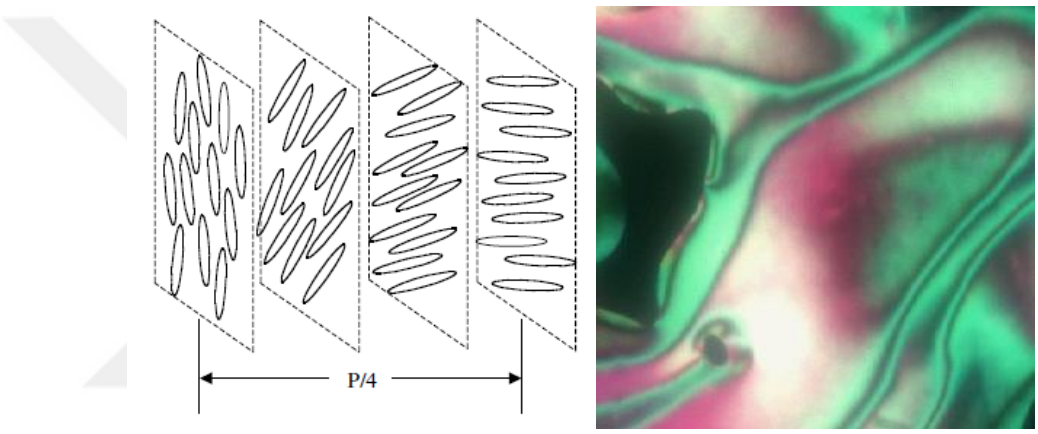

Figure 2.9 : Cholesteric phase [30].

It may suffice to add a chiral substance to a nematic substance to form the chiral nematic phase. Chiral material does not need to be liquid crystal.

The origin of liquid crystal phases is rooted in geometry of molecules. The most common shapes are: rod-like (calamitic), disc-like (discotic), banana-shaped and special geometries.

Calamitic Liquid Crystals

Calamitic mesogenes are liquid crystals arranged longitudinally and directionally in a three-dimensional structure in solid crystal state. Most of the mesogens synthesized in the liquid crystal field are calamitic liquid crystals. The specific chemical structure of mesogen is determinative for the emergence of calamitic mesophases (Figure 2.10). The geometrical structures of a single molecule or group of molecules play a significant role on mesomorphic properties. Thanks to the elongated structures with a positional and orientational arrangement, the interaction forces against the scattering

in the calamitic mesogen have reached a minimum and have a great anisotropy. Calamitic molecules usually show nematic and smectic mesophases.

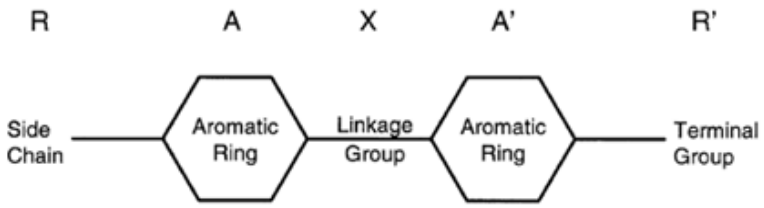

Figure 2.10 : Molecular structure of typical calamitic liquid crystal [11].

Examples of side chains and terminal groups are alkyl (C_nH_{2n+1}), alkoxy (C_nH_{2n+1}), others such as acyloxyl, alkylcarbonate, alkoxycarbonyl, nitro and cyano groups. The Xs of linkage groups are simple bonds or groups such as (-CH=CH-), ester, toluene, azoxy and Schiff base [11].

Discotic Liquid Crystals

By the 1970s, mesomorphism was only valid for rod-shaped materials. However, in 1977, a second major class of mesogenic structure compounds has been discovered. The first series are hexasubstitued benzene derivatives synthesized by S. Chandrasekhar. Discotic liquid crystals are generally described as aromatic molecules in the form of flat discs with a planar rigid core and generally four, six or eight long side chains around it [38,39,40].

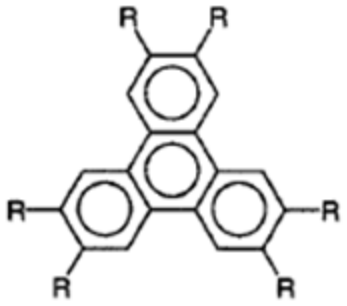

Figure 2.11 : Typical discotic mesogen [38].

Discotic liquid crystals usually exhibit columnar and nematic discotic mesophases.

- *Columnar Discotic Mesophase:* The columnar mesophase is quite regular. Each of the discrete molecules tends to stack upside down, forming a column. Mesophase has different names depending on the type of arrangement of these columns (Figure 2.12) [5].

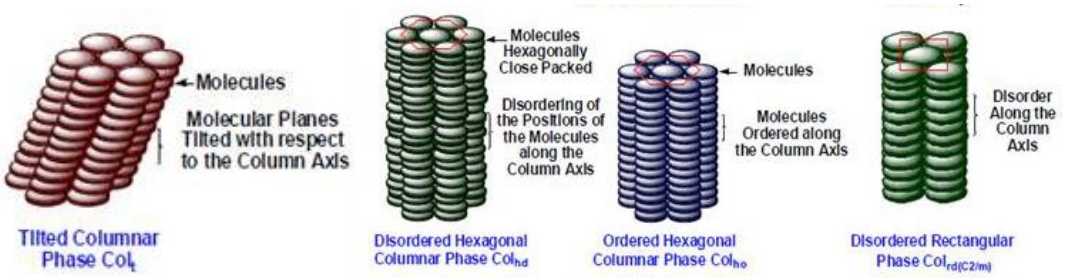

Figure 2.12 : Columnar discotic phases [5].

- *Nematic Discotic Mesophase:* The mesophase in which the molecules are oriented in the direction of the director and therefore only the orientational order is concerned. There is no spatial order (Figure 2.13).

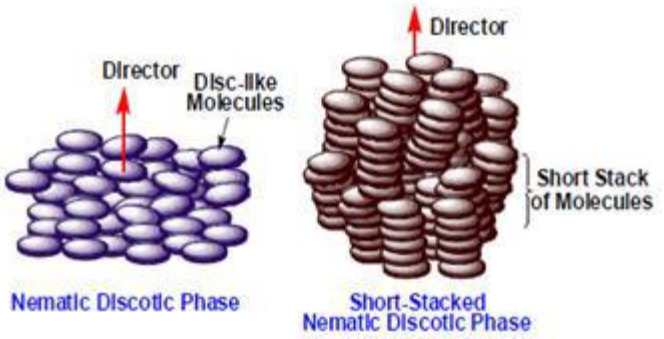

Figure 2.13 : Nematic discotic phases [5].

Banana-Shaped Liquid Crystals

Banana-shaped molecules were first discovered by Vorländer in the 1930s. Banana-shaped molecules contain hard core in bent form and obtained with different bulk substituents attached to the central core in the meta position (Figure 2.14).

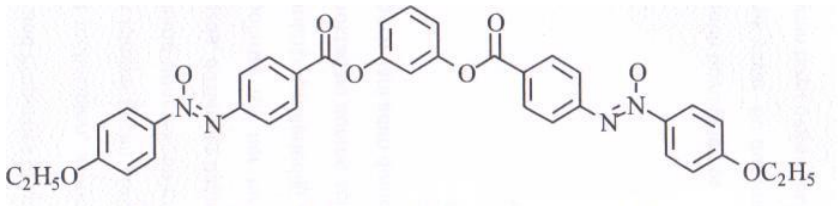

Figure 2.14 : Banana-shaped liquid crystal molecule [33].

Chiral Smectic Phases

The chiral smectic C mesophase (SmC*) is the most important of the chiral smectic phases. At this phase, the director rotates around the center by breaking at certain angles from each layer (Figure 2.15). If the molecules in SmC* phase have the permanent dipole moments perpendicular to their long axes, than such phase shows ferroelectric properties [6].

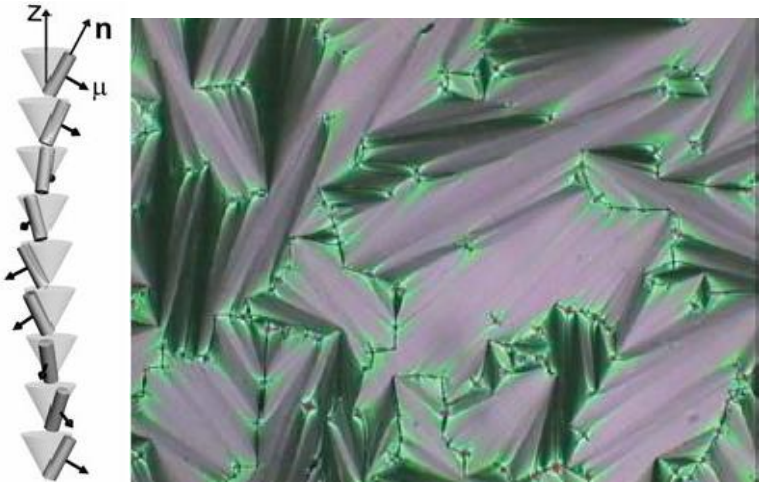

Figure 2.15 : Chiral smectic mesophase (SmC*) [6].

The chiral smectic A mesophase (SmA*) exhibits very similar properties to the non-chiral smectic A phase. For this reason, seperation of SmA and SmA* phases is difficult. Despite the frequent observation of non-chiral phase, chiral mesophase is a rarely encountered type of liquid crystal. The chiral smectic mesophase has transition temperatures close to the chiral smectic C phase. Chiral smectic A mesophase shows ferroelectric property [43].

2.2 Liquid Crystalline Polymers

2.2.1 Classification of liquid crystalline polymers

Liquid crystalline polymers (LCP) are thermotropic or lyotropic very much alike low molecular mass liquid crystals (LMMLC) due to crystal formation method [3,5-8]. According to geometry of molecules and mesogen attachment method, several division the LCPs into sub categories are purposed. Indicating the attachment of the mesogen nature into the polymer, LCPs are categorized into two main groups: main-chain LCPs (Figure 2.16) and side-chain LCPs (Figure 2.17).

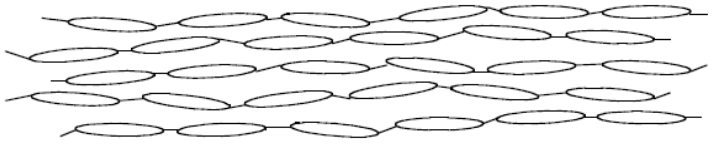

Figure 2.16 : Main-chain liquid crystalline polymer [30].

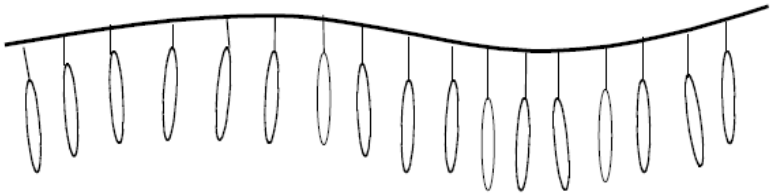

Figure 2.17 : Side-chain liquid crystalline polymer [30].

Generally, thermotropic and lyotropic liquid crystal polymers are synthesized by condensation method such as acidolysis, phenolysis, etc.

2.2.1.1 Main-chain liquid crystalline polymers

The main-chain LCPs structures are p-oriented cyclic, generally aromatic units, linking groups and modifying units consisting flexible spacers, commonly [7-9]. Generally used cyclic units are given below (Figure 2.18).

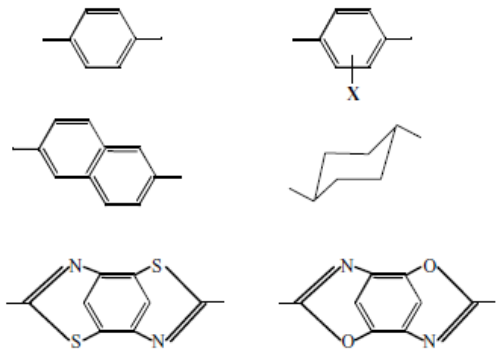

Figure 2.18 : Cyclic units [30].

Common linking groups are shown in Figure 2.19.

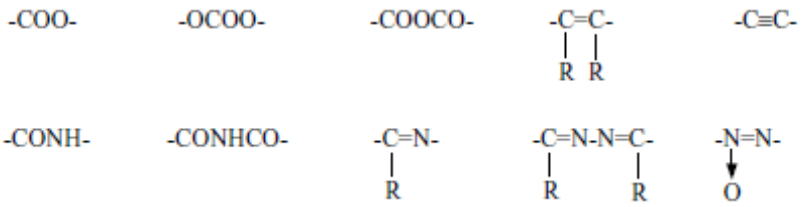

Figure 2.19 : Common linking groups [30].

2.2.1.2 Side-chain liquid crystalline polymers

Side-chain LCPs are combining liquid crystalline and polymeric properties. A flexible spacer is placed between the polymer backbone and mesogenic side groups to decouple the motions in the liquid crystalline state. Wide number of side-chain LCPs containing rod-like or disc-like mesogens was synthesized based on the space [22].

A random conformation is adopted in SCLCPs since the flexible polymer backbone has a distinct tendency. In the case of attachment of the mesogenic groups to the backbone directly, the backbone dynamics control the anisotropic orientation of the mesogenic groups, generally. According to this, mesomorphic behaviour is not usually created [27].

SCLCPs can be synthesized by chain polymerization, step-growth polymerization and polymer homologous reactions. Polymerization is performed in solution and initiators such as AIBN or benzoylperoxide are used in most cases.

2.2.2 Factors on mesomorphic behaviour of liquid crystal polymers

2.2.2.1 The effect of the mesogenic unit

The mesogenic unit has a big effect on the liquid crystal phases and the transition temperatures. The additional ordering on polymerization results in much more ordered liquid crystal than the monomeric analogue and higher transition temperatures and clearing points. Usually, mesogenic units are formed by biphenyl units or connection of two or more aromatic rings. Also, crystallinity increases with the mesogen length increase. Terminal cyano-substituted SCLCPs and alkoxy-substituted analogues are generally known. Much longer terminal chain causes augmentation of the smectic tendency. Polar terminal units (CN, NO_2) likely to create smectic phases, when in fact non-polar terminal units (CH_3O, CH_3) tend the nematic phase. The increase in polarisability and molecular length improves the polymer clearing points [27].

2.2.2.2 The effect of the spacer length

The actual flexible spacer is generally a series of methylene (-CH_2-) units with different joining points. Nevertheless, different spacers are generally used (oxyethylene, siloxane etc.). As the spacer length incease, the glass transition temperature decreases. Polymers without spacer units show smectic liquid crystalline phases and formation of the phase takes place at high temperatures. A short-length spacer generally generates a nematic phase which leads to smectic phases with the increase of the spacer length [27].

2.2.2.3 The effect of the polymer backbone

Since decoupling is never perfect, the structural nature of the polymer backbone has a important effect on mesomorphic properties of SCLCPs. Flexibility is the most important perspective to consider. With increasing flexibility of the backbone, the glass transition temperature is decreasing, which generates to a wider liquid crystal phase range. Nevertheless, as the flexibility increases, the clearing points decrease frequently. Mostly used backbones are flexible acrylates, methacrylates and siloxanes in the SCLCPs synthesis [27].

2.2.3 Synthesis of liquid crystal polymers

The new approach for designing liquid crystal polymers is to use non-covalent interactions between different molecules [12,13]. These self-assembly approaches include hydrogen bonds, ionic interactions and charge-transfer complexes. “Supramolecular” materials are constructed with the indicated methods. Covalent and non-covalent bond are represented in Figure 2.20 [10].

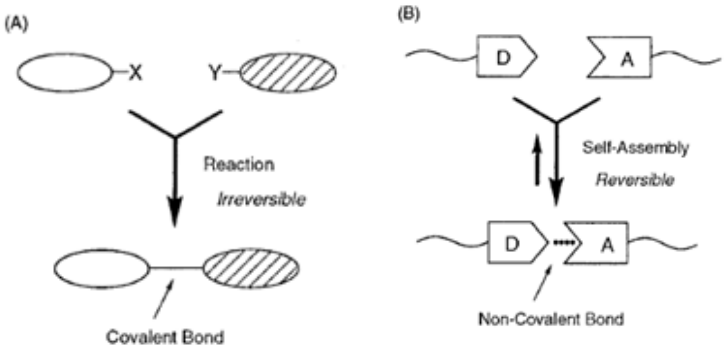

Figure 2.20 : Covalent (A) and non-covalent (B) interactions [10].

With the usage of this kind of hydrogen bonds, stable and dynamic molecular complexes can be synthesized with basic self-assembly processes [10].

Conventional liquid crystalline polymers include only covalent bonds. On the other hand, supramolecular polymeric liquid crystalline complexes consist of hydrogen-bonding mesogenic core or a hydrogen-bonding linking subdivision to connect mesogenic molecule to the polymer. There are two types of structures: main chain and side chain.

- Main chain type: The combination of bifunctional hydrogen bonding components is in favor to form supramolecular main-chain polymers. With

associating bifunctional components, liquid crystalline behavior can be activated through the formation of single and triple hydrogen bonds [10].

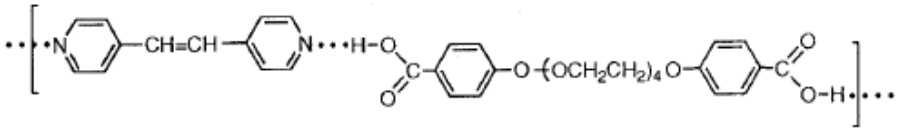

Figure 2.21 : A H-bonded main chain liquid crystal polymer [10].

- Side chain type: First example of side chain type hydrogen-bonded liquid crystals has been synthesized with polyacrylate containing a benzoic acid moiety in the side chain with stilbazoles complexation. Schematic representation of H-bonded side chain liquid crystal polymers shown in Figure 2.22 [10].

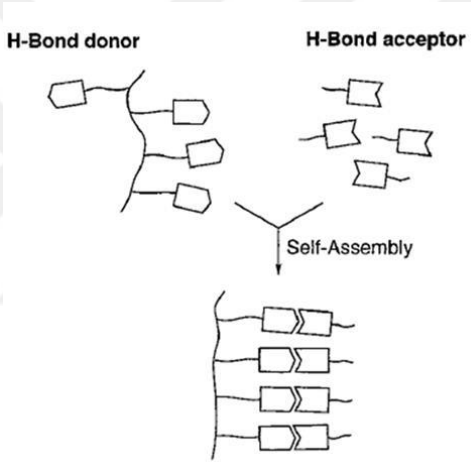

Figure 2.22 : H-bonded side chain liquid crystal polymers [10].

Carboxylic and benzoic acid groups are example of hydrogen-bond donors, and pyridine moieties are used as hydrogen-bond acceptors. Also, imidazole derivatives are beneficial as hydrogen-bonding components to connect different molecules [12].

2.3 Urethanes

In Leverkusen, West Germany, Otto Bayer and his colleagues were first the develop urethanes in the laboratories of the I. G. Farbenindustry. Urethanes are characterized by the linkage -NH-C(=O)-O-, and may consist ester, ether, urea, amide and other groups.

Figure 2.23 : Urethane formation [34].

There are several ways to synthesize urethane polymers, but the most important commercial route is the reaction between di- and polyfunctional hydroxyl compounds and di- or polyisocyanates [17]. Using difunctional reactants leads to linear polyurethane formation and the reaction can be represented as follows:

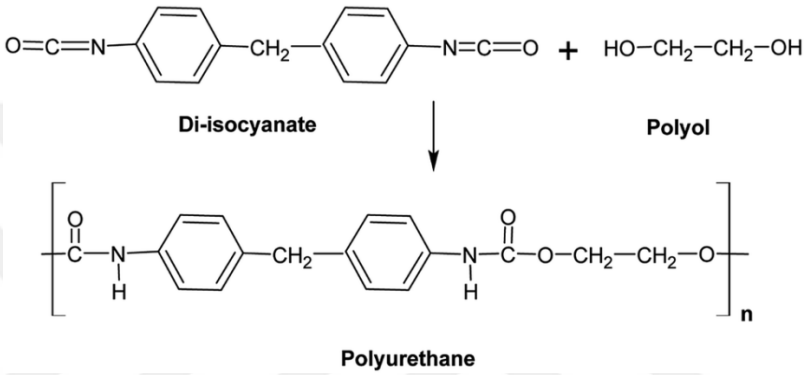

Figure 2.24 : Polyurethane formation reaction [36].

The increase of the functionality of the hydroxyl or isocyanate component branched or cross-linked polymers are formed [17].

2.4 Isocyanates

2.4.1 Isocyanate functionality

The isocyanate group is highly reactive and plays the main role in polyurethane chemistry [21]. Isocyanates are derivatives of isocyanic acid (H–N=C=O), where alkyl or aryl groups are directly attached to the N=C=O moiety with the nitrogen atom. Isocyanates (carbonic acid imides) are isomeric to cyanates, ROCN (carbonic acid nitrites) and nitrile oxides, RCN–O (carboxylic acid derivatives) [16].

The electronic structure of the isocyanate group indicates the following possible resonance structure:

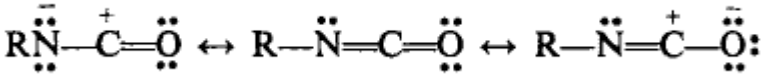

Figure 2.25 : Isocyanate resonance structure [16].

The isocyanate functionality [–N=C=O] is very reactive against proton-bearing nucleophiles. The inadequacy of electrons on carbon atom defines the isocyanate reactivity against nucleophilic attack and reactions occur mostly across the C=N bond as shown in the figure above [21]. With nucleophilic addition cross the carbon–nitrogen double bond, the reaction takes place. Aromatic isocyanates are usually more reactive than aliphatic isocyanates. The presence of electron-withdrawing substituents on the ring of aromatic isocyanates increases reactivity, where electron donors decrease reactivity. In addition to inductive effects, bulky substituents attached to isocyanate groups decrease reactivity according to steric hindrance. The reactions of isocyanates are catalyzed by acids and bases of both Bronsted and Lewis character [16].

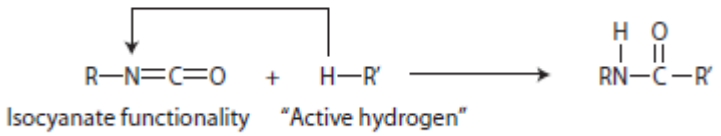

Figure 2.26 : Isocyanate functionality [16].

Mostly, the synthesis of monomeric and polymeric urethanes, semicarbazides and ureas includes isocyanates condensation reactions with alcohols, hydrazines or amines [18].

Examples of aromatic and aliphatic isocyanates are shown below (Figure 2.25, Figure 2.26).

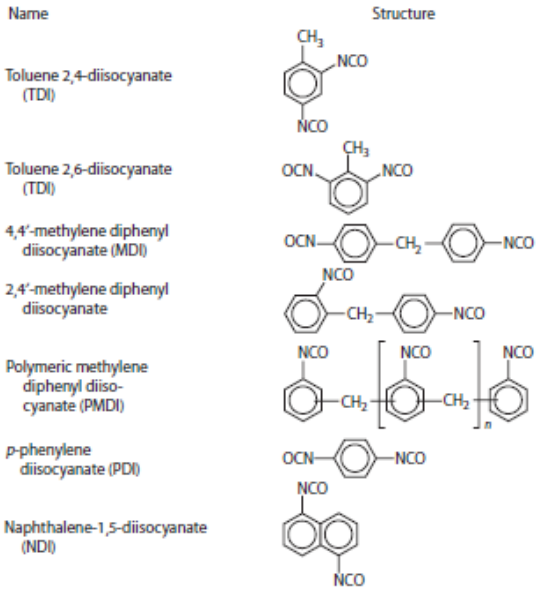

Figure 2.27 : Aromatic isocyanates [16].

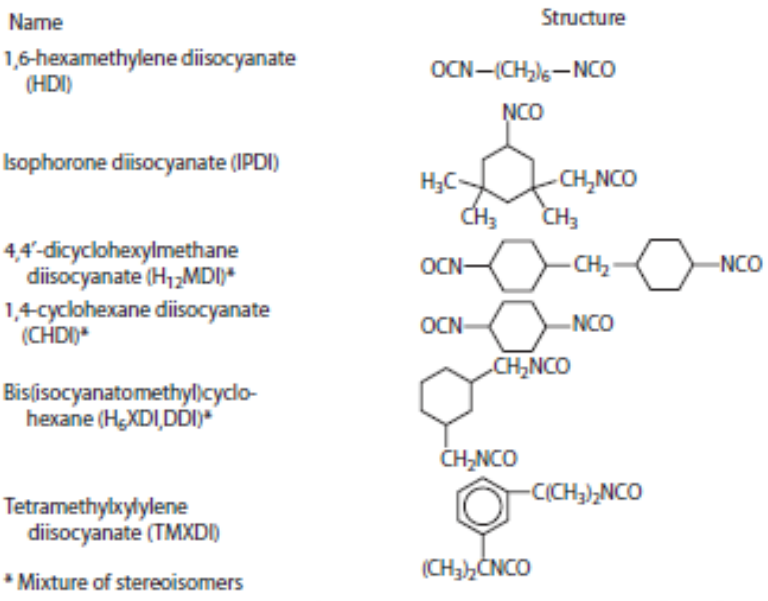

Figure 2.28 : Aliphatic isocyanates [16].

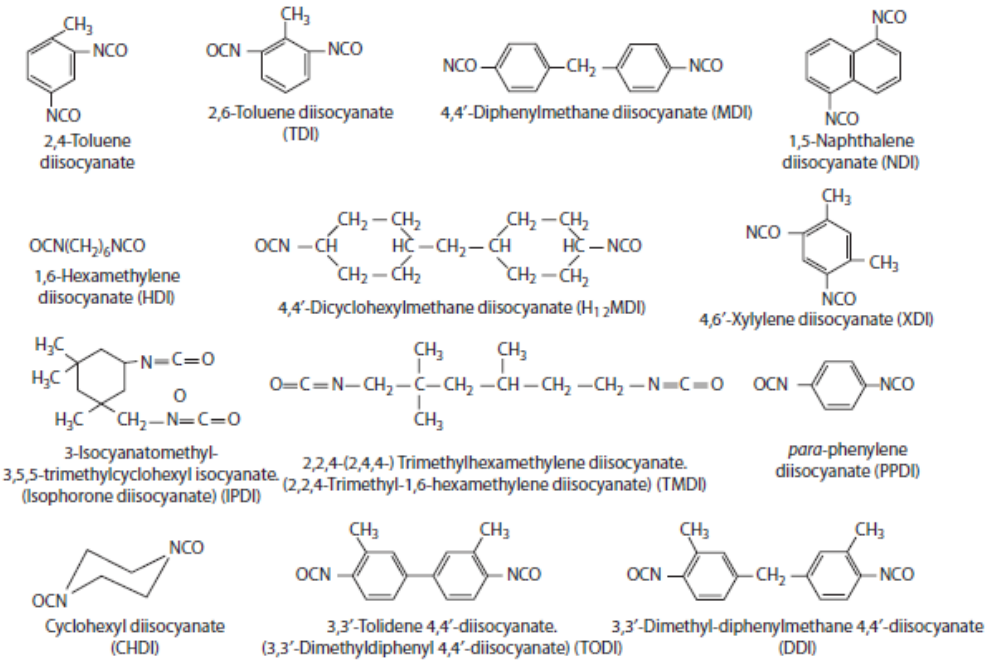

Figure 2.29 : Structures of important isocyanates [16].

2.4.2 Selected reactions of isocyanate

2.4.2.1 Reactions of isocyanates with [–OH] compounds

Primary alcohols react very quickly with isocyanates in order to form urethanes in quantitative yield. Because isocyanates are reacting fastly with water, especially with the impact of catalysts, the isocyanate reaction with water is very efficient and complex since an unstable carbamic acid intermediate is formed firstly, with the

contributing evolution of carbon dioxide. Then the carbamic acid disintegrates to form amine. Carboxylic acids are also a range of compounds that react with isocyanates and in comparison to amines, alcohols and water, the reaction is relatively mild [16].

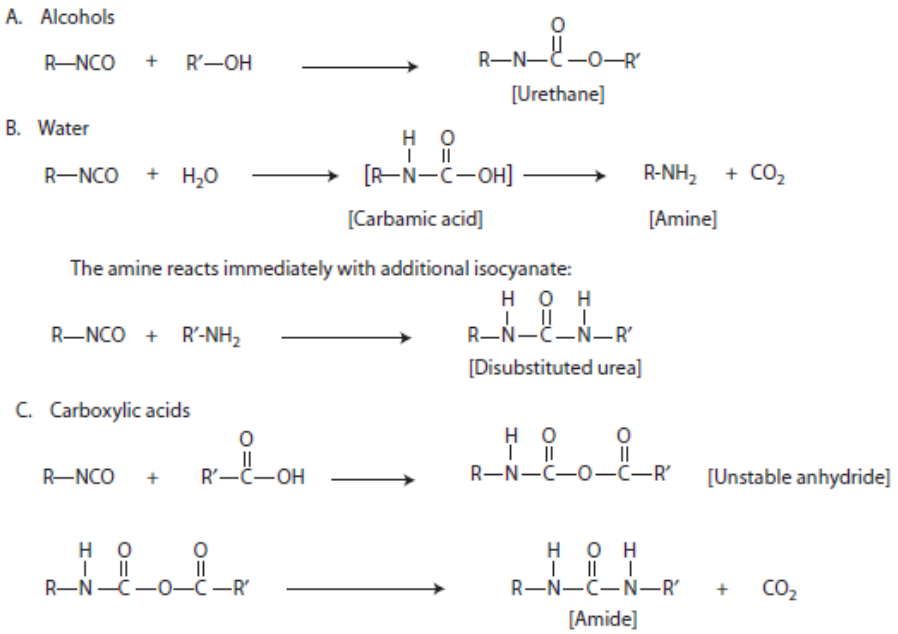

Figure 2.30 : Isocyanate reactions with -OH compounds [16].

2.4.2.2 Reactions of isocyanates with [–NH] compounds

Compounds that contain an N–H bond are very common and are almost consistently react with isocyanates. Primary and secondary amines give reaction fastly with isocyanates to form urea and substituted ureas. Aliphatic or aromatic amines are more reactive than the amide and substituted amides N–H protons because of the electron-withdrawing effect of the neigboring carbonyl group. The resulting products here are acyl ureas or substituted acyl ureas [16].

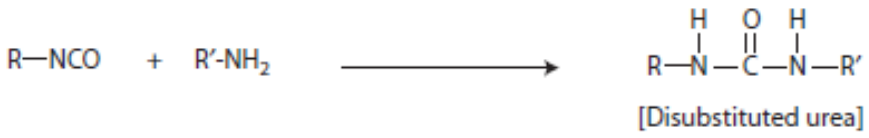

Figure 2.31 : Isocyanate reactions with -NH compounds [16].

2.4.2.3 Reactions of isocyanates with ureas and urethanes

The reaction between primary amines and isocyanates, ureas are formed that contain an Active H that can react with isocyanates to yield stable biuret cross-links. Like urea, the urethane groups include an N-H adjacent to a carbonyl group and an

electron donor (-O-). The urea proton is sufficiently reactive so that there is a significant amount of allophanate in the reaction under strong reaction conditions [16].

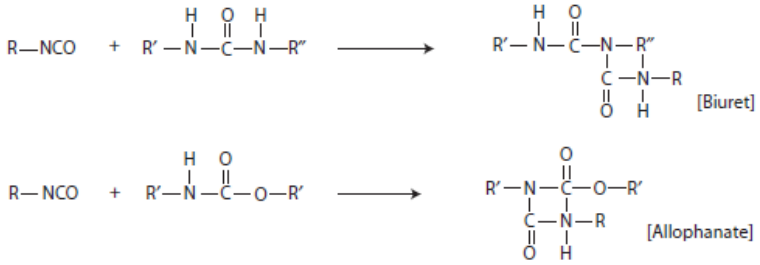

Figure 2.32 : Isocyanate reactions with -NH compounds [16].

2.5 Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is manufactured from ethylene oxide and water under catalyst, and has some characteristic qualifications usable for different applications such as biological, chemical and pharmaceutical. The synthesis rouse for Polyethylene glycol is the ethylene oxide anionic ring opening polymerization into a different molecular weights and end groups. As a result, PEG can be used in many research applications and when crosslinked into networks, can have a high water content, leading form hydrogels [41].

In the presence of air, Polyethylene glycol can oxidatively degrade. Degradation can be minimized by addition of an antioxidant, and/or limiting the exposure to elevated temperatures and oxygen. PEG is Polyethylene glycol is not compatible with phenol and can decrease the preservatives' antimicrobial action [42].

PEG can be dissolved in water and is miscible with another PEG grade in all proportions. Liquid forms of PEGs can be dissolved in acetone, alcohols, benzene, glycerin, and glycols. Solid forms of PEGs can be dissolved in acetone, dichloromethane, ethanol (95%), and methanol. PEGS can slightly dissolve in aliphatic hydrocarbons and ether but cannot be dissolved in fats, fixed oils and mineral oil [42].

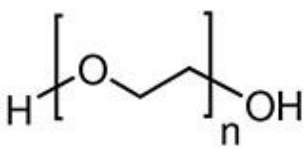

Figure 2.33 : Structure of Polyetylene glycol [41].

3. EXPERIMENTAL PART

3.1 Materials

Polyethyleneglycol 500 monomethyl ether (PEG 500), butyl isocyanate (BI), dibutyltinlaurate (DBTL), Toluene diisocyanate (TDI), hexane, Diethyleneglycolmonomethylether (DEGME) (Merck), ether, toluene, chloroform, 4'-hydroxy-biphenyl-4-carbonitrile (Merck), 11-bromo-1-undecanol (Across), Dimethyl sulfoxide (DMSO) (Merck), anhydrous K_2CO_3 (Fluka), NaOH pellets (Merck), N,N-dimethylformamide (DMF) (Merck), 1-methyl-2-pyrrolidone (NMP) (Merck), Tetrahyrofuran (THF) (Aldrich) were used as received.

3.2 Instruments

- **Nuclear Magnetic Resonance Spectroscopy (NMR)**

^{1}H-NMR analyses were recorded on a varian 500 MHz spectrometer in CDCl3.

- **Fourier Transform Infrared Spectroscopy (FT-IR)**

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

- **Polarized Optical Microscopy (POM)**

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

- **Differential Scanning Calorimeter (DSC)**

Thermal transitions in the polymers were determined by DSC (PerkinElmer) Instrument.

3.3 Preparation of Urethane Based Materials

3.3.1 Synthesis of urethane end group of PEG 500 with BI

5.0 g of Polyethyleneglycol 500 monomethylether (PEG 500) was reacted with 1.0 g of butyl isocyanate (BI) 1:1 molar ratio in DMF solution. 0.10 mL of

dibutyltinlaurate (DBTL) as a catalyst was added to the reaction medium and the mixture was heated at 60 ^{o}C for 24 h. Then, the reaction mixture was taken into hexane and phase seperation occurred in order to remove the unreacted isocyanates. The remainder mixture was separeted from separation funnel and dried under vacuum. ^{1}H-NMR ($CDCl_3$,δ in ppm): 3.4 (s, 3H, CH_3-O-), 3.5-4.23 (m, 8H, -O-CH_2CH_2-), 1.3-1.49 (m, 8H, -CH_2), 0.93 (s, 3H, -CH_3).

3.3.2 Synthesis of PEG - TDI polymer

20 g (0.04 mole) of PEG 500 was dissolved in 25 mL of DMF. 3.48 mL (0.02 mole) of TDI and catalytic amount of DBTL were added to the reaction mixture at room temperature and then the reaction was proceeded at 60 ^{0}C for 24 h. Then, yellow viscose liquid product was obtained and poured 100 mL of hexane to precipitate the PEG based urethane polymer. The obtained chain extended polymer was characterized by using FT-IR spectroscopy, GPC and HNMR.

3.3.3 Synthesis of DEGME and BI polymer

5.0 g of Diethyleneglycolmonomethylether (DEGME) was mixed with 1.0 g of butyl isocyanate (BI) about 1:1 molar ratio and dissolved in 25 mL of DMF. 3 drops of dibutyltinlaurate (DBTL) was added and the mixture was heated at 60 ^{o}C. Then the reaction mixture was taken into hexane and phase seperation occurred in order to remove the unreacted isocyanates. The remainder mixture dried and purified.

3.3.4 Synthesis of DEGME and TDI polymer

5.0 g of Diethyleneglycolmonomethylether (DEGME) was mixed with 0.871 g of toluene diisocyanate (TDI) about 2:1 molar ratio and dissolved in DMF. 3 drops of dibutyltinlaurate (DBTL) was added and the mixture was heated at 60 ^{o}C. The same purification procedure was applied described above.

3.4 Preparation of Liquid Crystalline Polymers

3.4.1 Synthesis of 11-(4-cyanobiphenyl-4’-oxy) undecan-1-ol (LC11)

11-(4-cyanobiphenyl-4’-oxy) undecan-1-ol (LC11) was sythesized as hydrogen donor reagent described before. Typical procedure is given below [44].

3 g (15 mmol) of 4’-hydroxy-4-biphenylcarbonitrile was dissolved in 200 mL of a DMSO in the presence of 2g (14.5 mmol) of anhydrous K_2CO_3 as an acid scavenger. 3.4 mL (20 mmol) of 11-bromo-1-undecanol was added dropwise to this mixture under nitrogen at 110 °C. The reaction was continued at 110° C for 3 hours. Then, the reaction mixture was added dropwise to 400 mL of 10% NaOH solution at room temperature for precipitation. The white powder product was filtered and washed with excess of water. The resultant was dried under vacuum at 40 °C. Obtained LC11 was crystallized from ethanol (Yield: 52%).

3.4.2 Preparation of LC11 with PEG 500 and BI

0.20 g of LC11 (0.5 mmol) as a H-bond donor and 0.1218 g the urethane based polymer (0.2 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h.

3.4.3 Preparation of LC11 with PEG 500 and TDI

For this purpose, 0.2 g of LC11 (0.5 mmol) as a H-bond donor and 0.1244 g of urethane based polymer (0.5 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h.

3.4.4 Preparation of LC11 with DEGME-BI

For this purpose, 0.2 g of LC11 (0.5 mmol) as a H-bond donor and 0.3329 g of urethane based polymer (1.5 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h.

3.4.5 Preparation of LC11 with DEGME and TDI

For this purpose, 0.2 g of LC11 (0.5 mmol) as a H-bond donor and 0.3523 g of urethane based polymer (0.85 mmol) as a H-acceptor polymer were dissolved in the DMF. The resulting solid was dried under vacuum for 24 h.

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

4. RESULTS AND DISCUSSION

4.1 Characterization of PEG Based Urethane Modified Polymers

In this study, urethane based materials were synthesized and characterized by using physical and chemical methods. Firstly, PEG with terminal urethane group was synthesized by the reaction between PEG-500 and TDI and butyl isocyanate respectively in the presence of DBTL as catalyst and DMF as solvent at 60^0C (Figure 4.1).

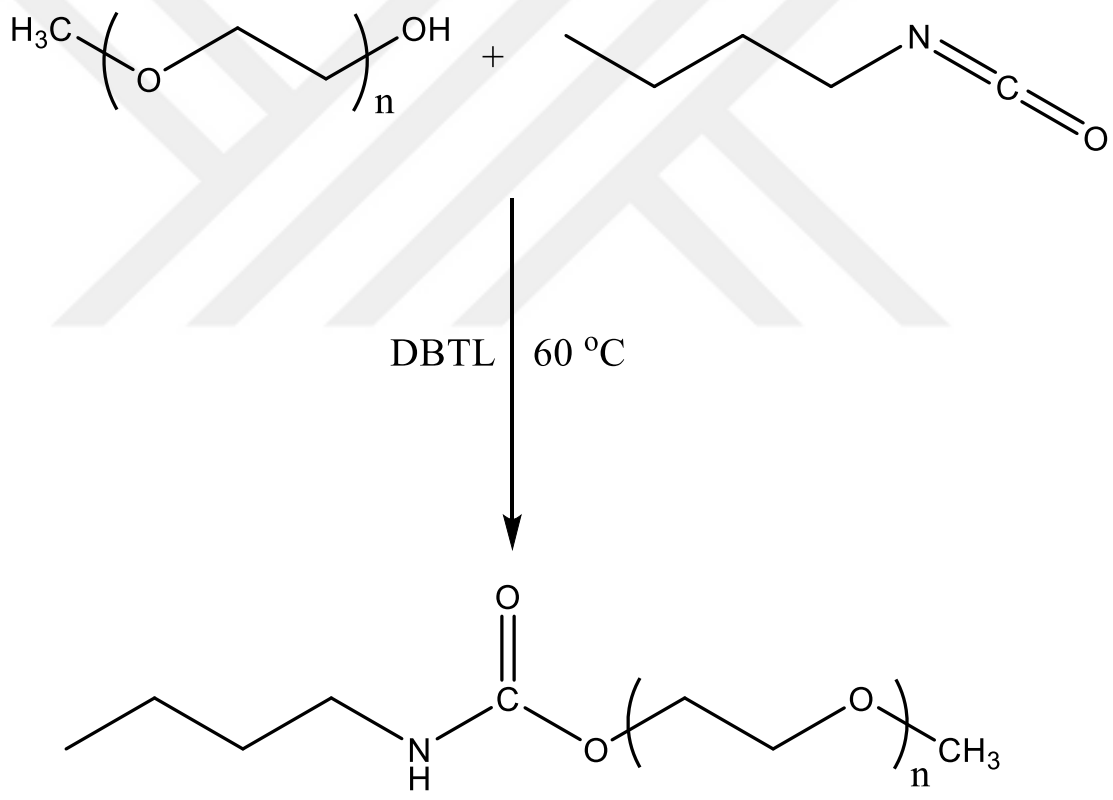

Figure 4.1 : Schematic reaction of PEG-500 and butyl isocyanate.

According to the FTIR spectra, characteristic carbonyl peak of the urethane was observed at 1711 cm^{-1}. The bending and C-N stretching vibration peaks appear at about 1535 cm^{-1} and 1248 cm^{-1} (Figure 4.2).

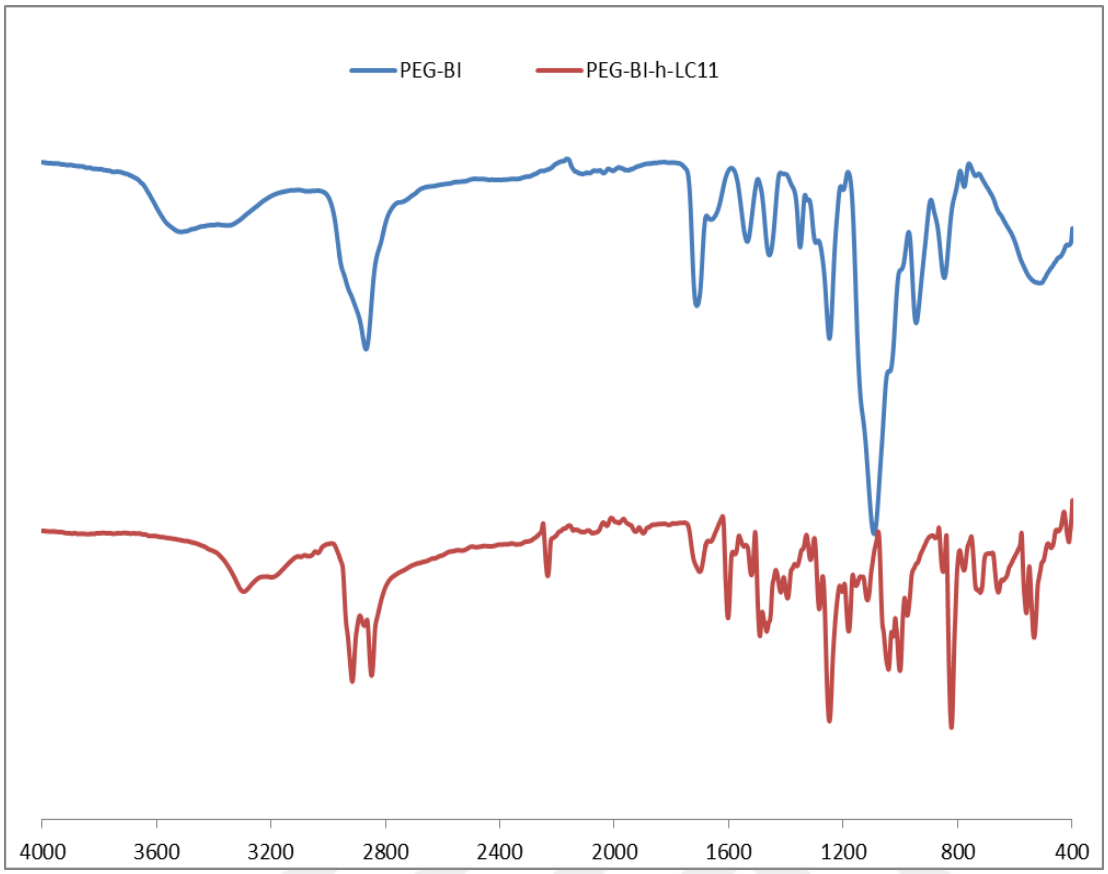

Figure 4.2 : FTIR spectra of PEG-500-BI and PEG500-BI-LC11.

Another PEG with terminal urethane group was synthesized starting from 2.0 mol PEG-500 and 1.0 mol TDI in the presence of DBTL using DMF as solvent at 60 ^{0}C for 24h. Molecular weight of the polymer was determined by GPC method and M_n and M_w values were found as 1100 Da, 1354 Da respectively. These results show that chain extension was occurred after urethane formation reaction.

Spectroscopic characterization of the material was carried out by FTIR. According to the FTIR spectra, characteristic carbonyl peak of urethane and C=C aromatic vibration peaks were observed at 1723 cm^{-1} and 1600 cm^{-1} respectively. The bending and C-N stretching vibration peaks appear at about 1535 $cm^{-1}$and 1228 cm^{-1}. After interaction with LC11 and urethane based polymer, we observed hydrogen bonding formation at 3290 cm^{-1} (Fig 4.4).

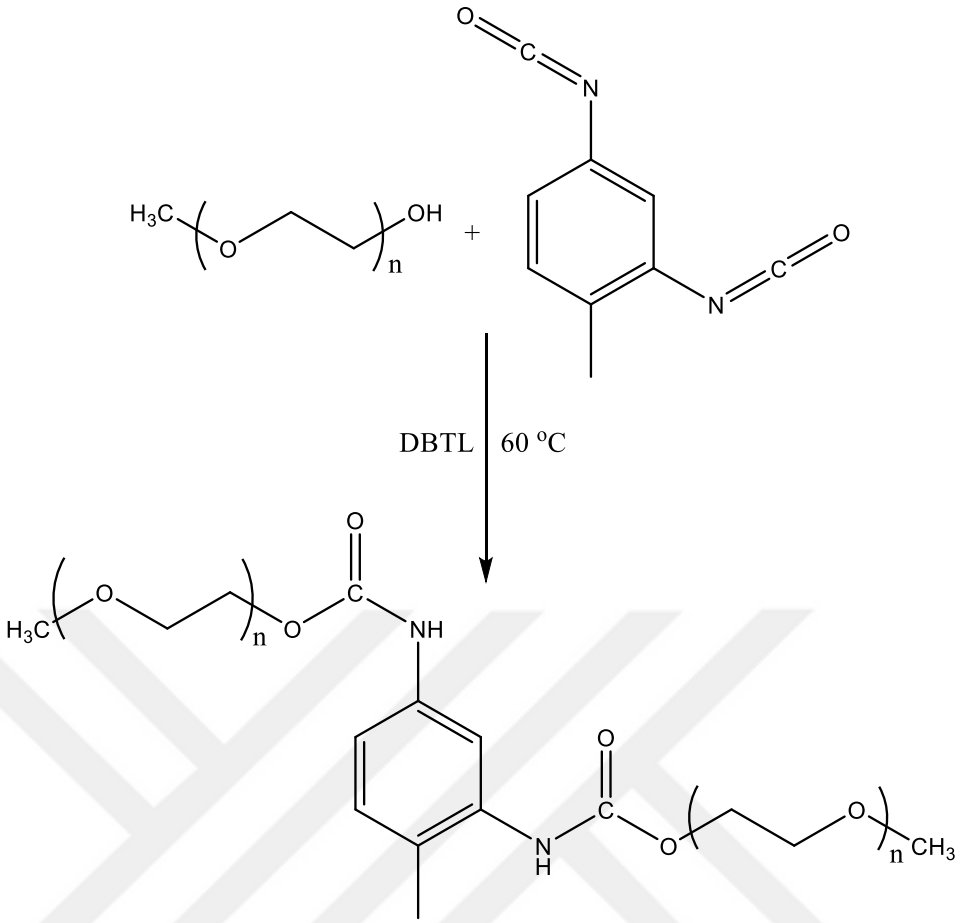

Figure 4.3 : Schematic reaction of PEG-500 and toluene diisocyanate.

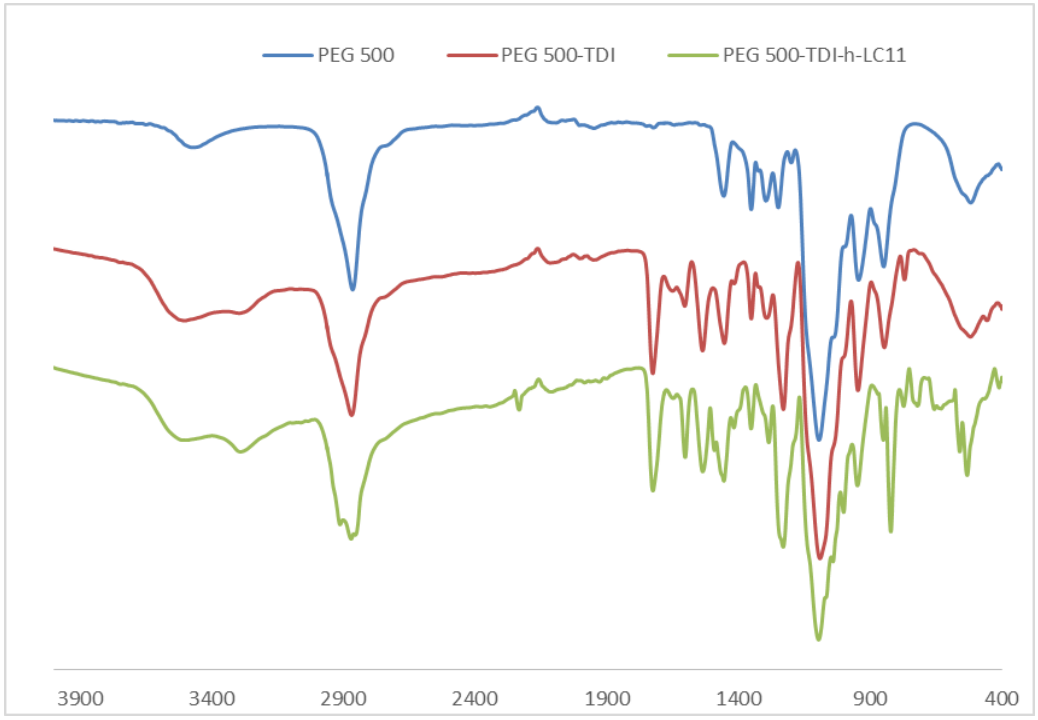

Figure 4.4 : Comparative FTIR spectra of PEG-500, PEG-500-TDI and PEG-500-TDI-LC11.

4.2 Characterization of DEGME Based Urethane Modified Materials

Liquid crystalline properties depending on molecular weight of urethane based materials are compared. Therefore, DEGME based urethane containing compounds were synthesized. Firstly, BI reacted with DEGME in the presence of DBTL at 60^{0C} in DMF for 24 h.

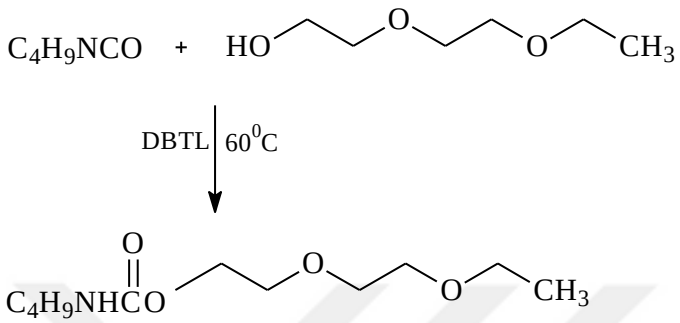

Figure 4.5 : Schematic reaction of DEGME and butyl isocyanate.

Spectroscopic characterization of the DEGME-BI was carried out by FTIR and HNMR. According to the FTIR spectra, characteristic urethane carbonyl peak and C=C aromatic vibration peaks were observed at 1697 cm^{-1} and 1605 cm^{-1} respectively. The bending and C-N stretching vibration peaks appear at about 1532 $cm^{-1}$and 1246 cm^{-1}.

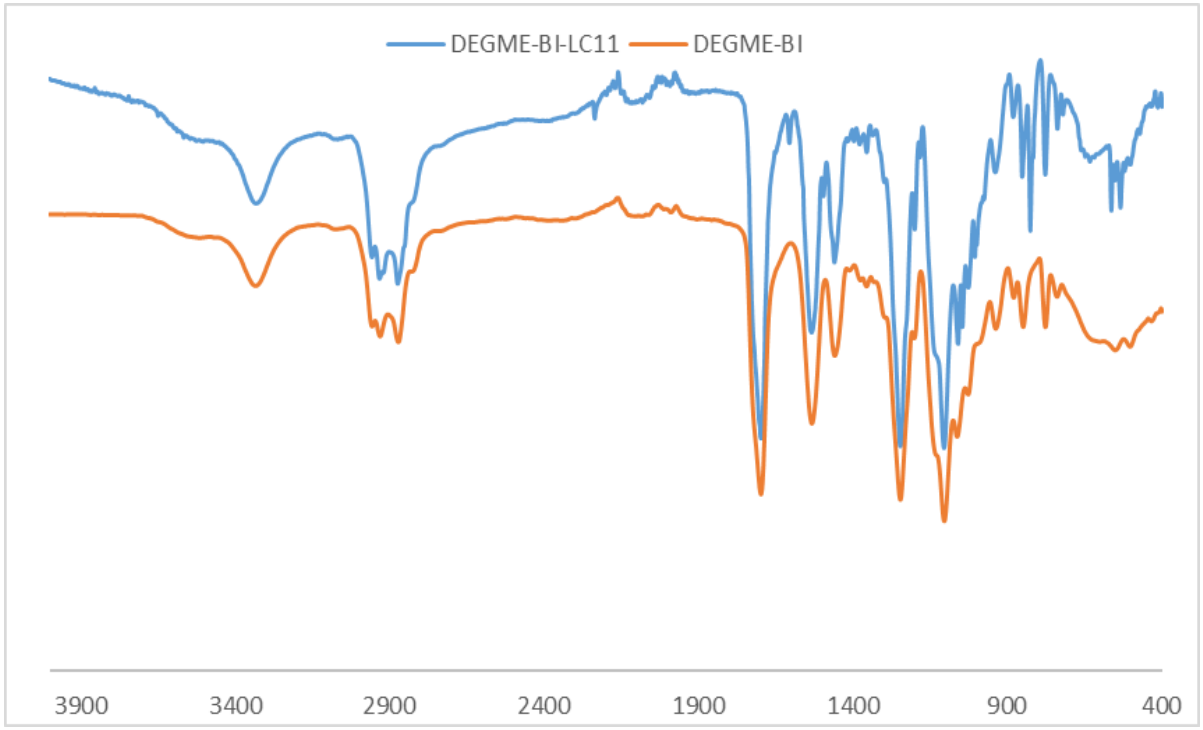

Figure 4.6 : FTIR spectra of DEGME-BI and DEGME-BI-LC11.

After interaction of LC11 with urethane based compound, strong OH stretching vibration was observed at 3290 cm^{-1} because of hydrogen bond formation and absorption at 2232 cm^{-1} corresponding to CN bond was observed, in the FTIR spectrum DEGME-BI-LC11 (Figure 4.6).

The structure of DEGME-BI was characterized by ^{1}H-NMR (Fig.4.7). In the HNMR spectra of the DEGME-BI, terminal methoxy group of the DEGME-BI was observed at 3.4 ppm. The proton signals of the DEGME (-O-CH_2-CH_2-), methylene groups of the butyl isocyanate (-CH_2) and terminal methyl group of butyl isocyanate (CH_3-) are detected at 3.5-4.23 ppm, 1.3-1.49ppm and 0.93 ppm, respectively.

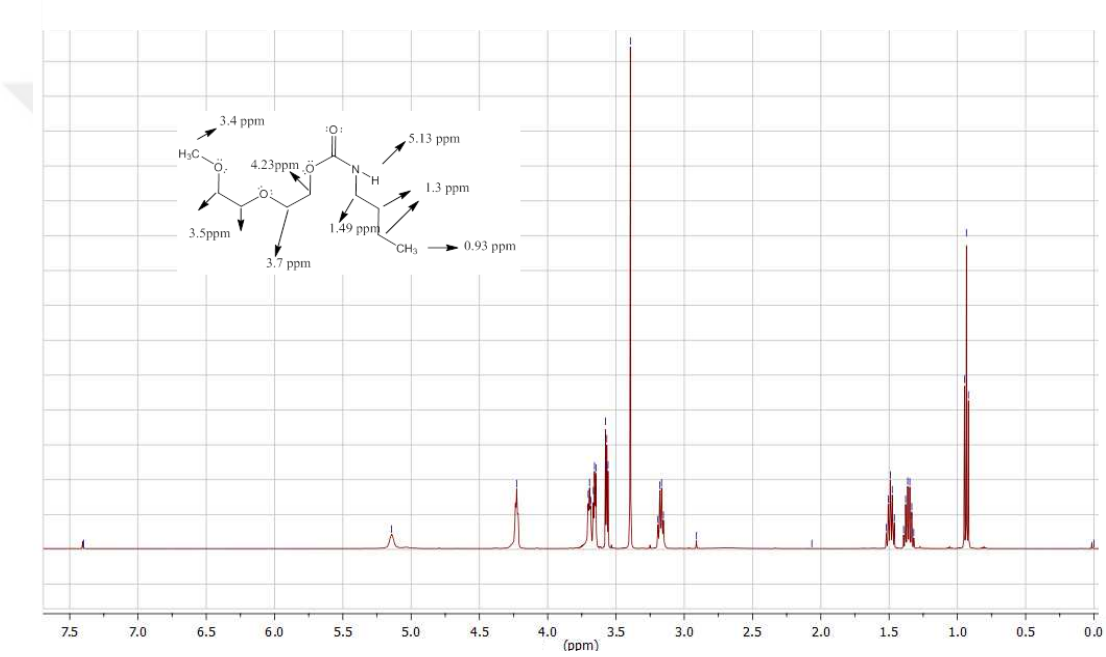

Figure 4.7 : HNMR spectrum of DEGME-BI

Another urethane based compound was synthesized reaction with 2.0 mol of DEGME and 1.0 mol of TDI and catalytic amount of DBTL at 60 ^{0}C in DMF for 24 h.

Chemical characterization of the DEGME-TDI was carried out by FTIR. According to the FTIR spectrum, urethane carbonyl peak and C=C aromatic vibration peaks were observed at 1706 cm^{-1} and 1600 cm^{-1} respectively. The bending and C-N stretching vibration peaks appear at about 1531 $cm^{-1}$and 1281 cm^{-1}.

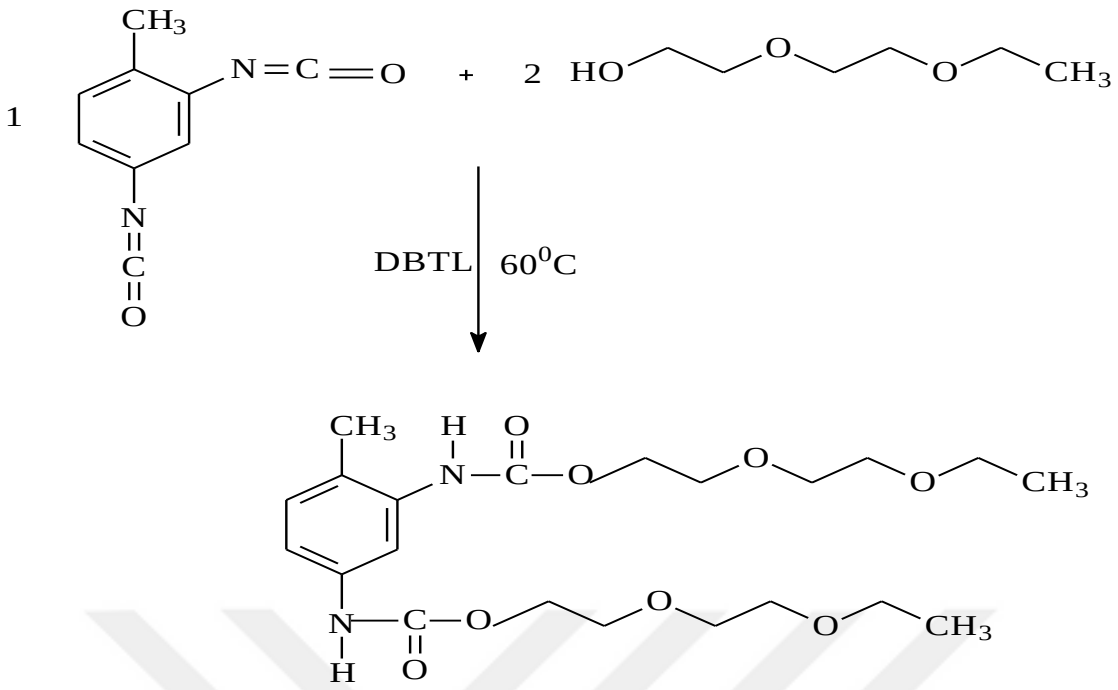

Figure 4.8 : Schematic reaction of DEGME and TDI.

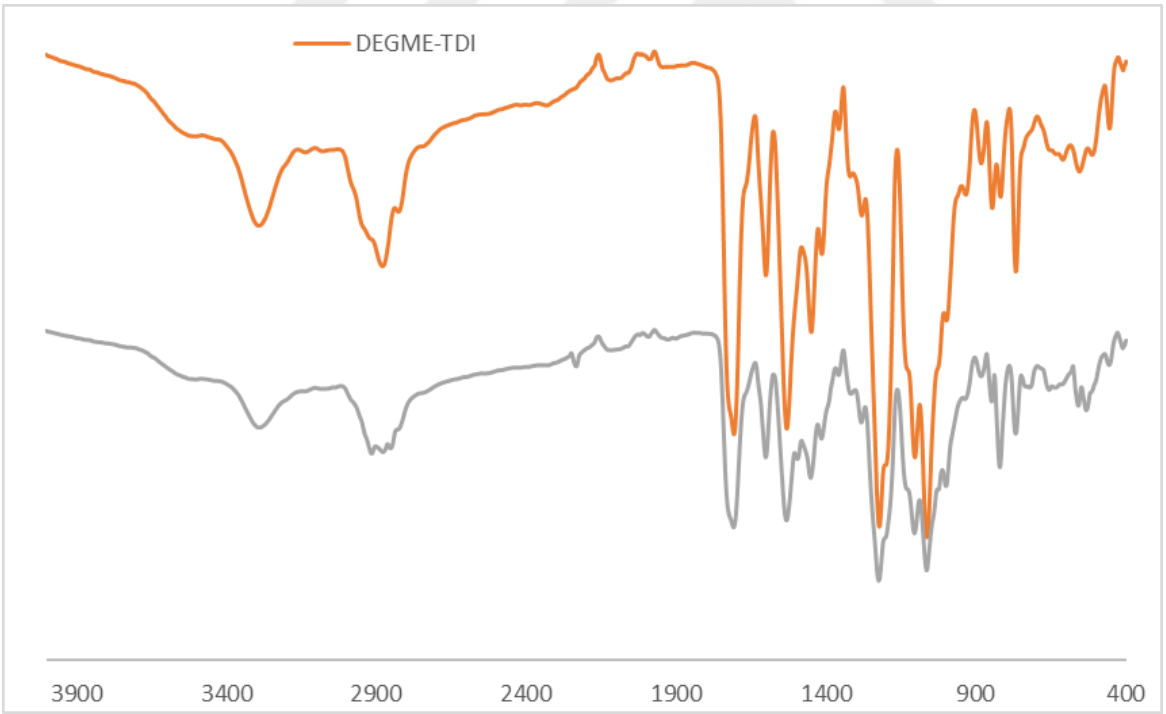

Figure 4.9 : FTIR spectra of DEGME-TDI and DEGME-TDI-LC11.

4.3 Liquid Crystalline Properties of Materials

In this study, four different urethane based materials were synthesized and investigated of the liquid crystalline properties. These materials were interacted with

LC11 in DMF to obtain hydrogen bonded liquid crystalline compounds. According to the DSC and POM results, PEG based materials have not shown liquid crystalline properties. On the other hand, DEGME which acts as a hydrogen bond acceptor were interacted with LC11 and they show liquid crystalline properties.

Two kinds of liquid crystalline materials were synthesized starting from DEGME with BI and TDI, respectively (Figure 4.9 and Figure 4.10).

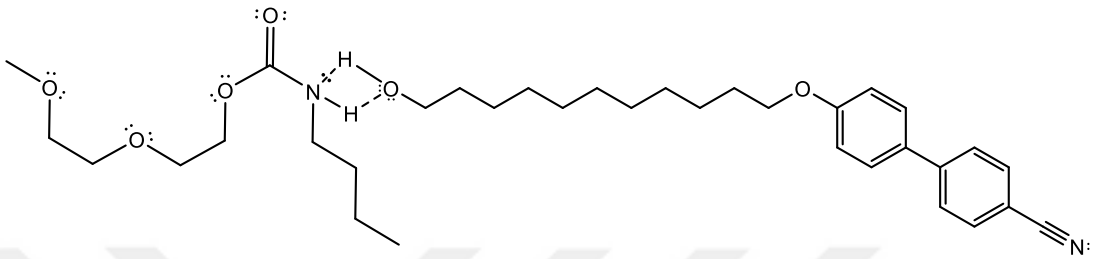

Figure 4.10 : Hydrogen bonding of DEGME-BI and LC11.

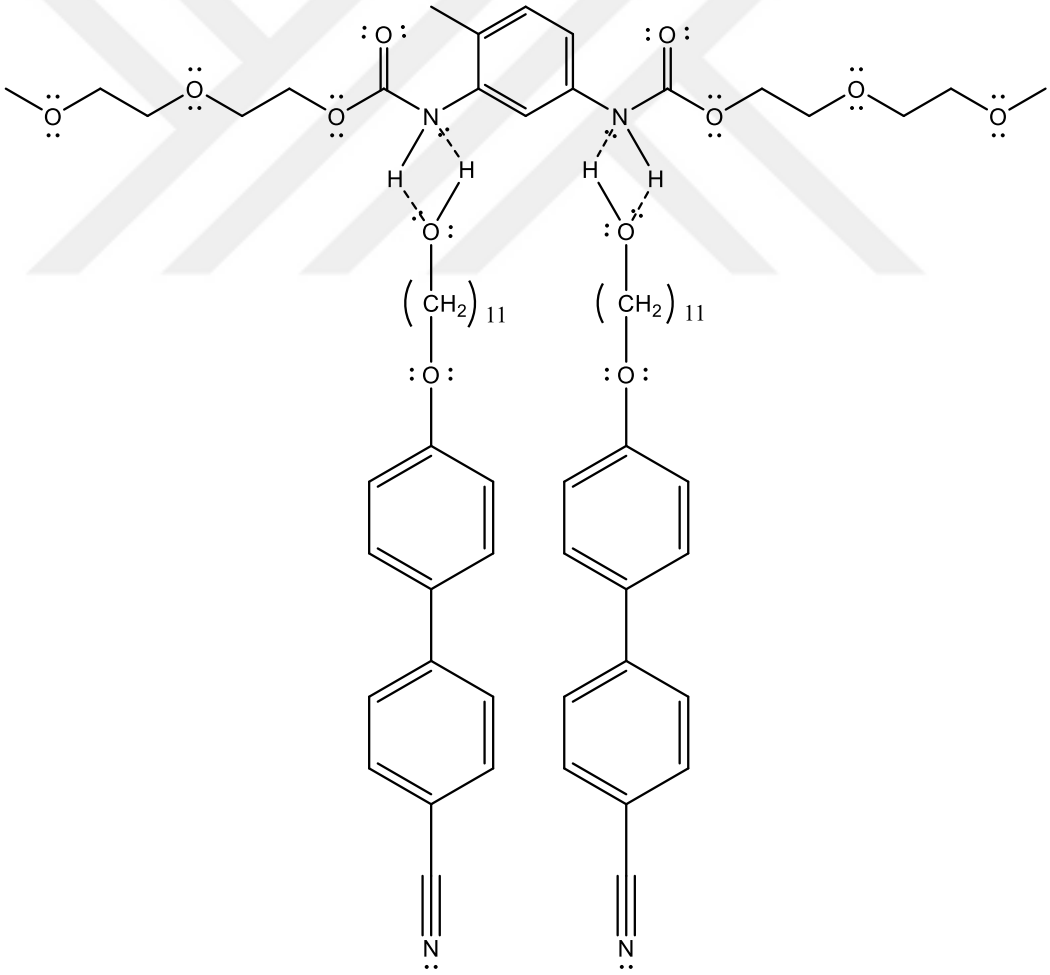

Figure 4.11 : Hydrogen bonding of DEGME-TDI and LC11.

The phase behaviors of the hydrogen bonded DEGME based liquid crystalline materials were investigated by using DSC and POM. DSC thermogram data were

obtained in second heating cycles with rate of 10°C/min in N_2 atmosphere (Figure 4.11 and Figure 4.12). According to the Figure 4.11, enantiotropic nematic phase of DEGME-BI-LC11 has been observed. DEGME-BI-LC11 shows nematic phase at 92 ^{0}C during heating. Nematic Schlieren texture was confirmed by POM results both during heating and cooling stage. Also while cooling, DEGME-BI-LC11 shows nematic phase at 96,2 ^{0}C and smectic phase (SmA) at 86 ^{0}C. DSC results are also compatible with POM (x200) studies which confirm these phase transition temparatures.

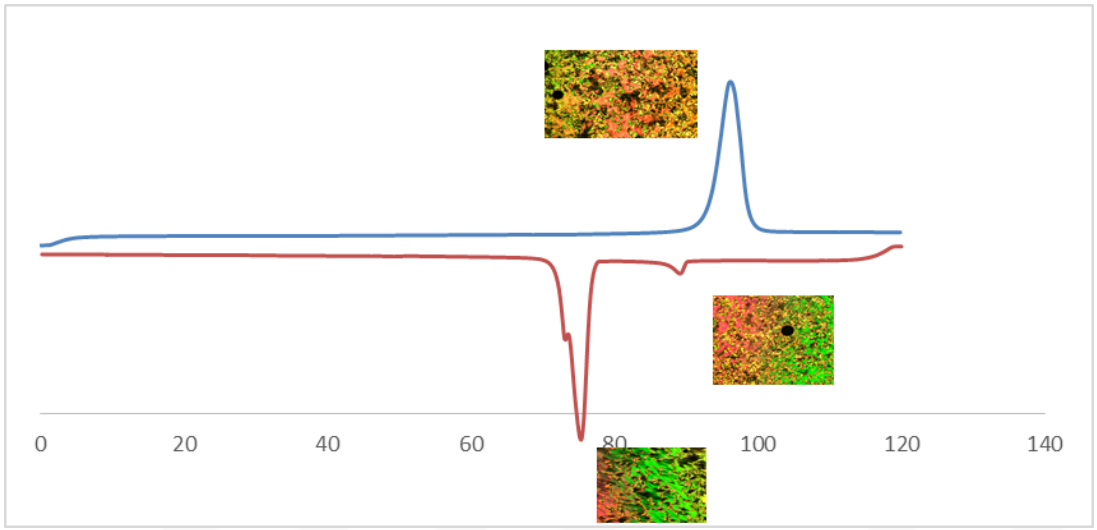

Figure 4.12 : DSC curve of DEGME-BI-LC11.

According to the Figure 4.12 DEGME-TDI-LC11, shows monotropic nematic phase at 82.6^{0}C during cooling.

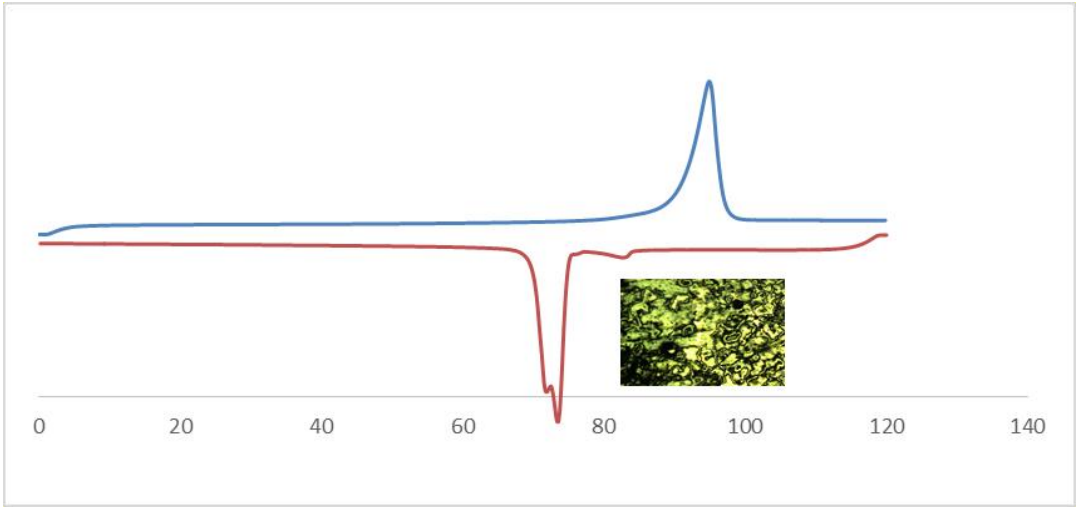

Figure 4.13 : DSC curve of DEGME-TDI-LC11.

The results were given in Table 4.1.

Table 4.1 : Thermal properties of DEGME based materials.

Compounds	Phase Transition (°C)
DEGME-BI-LC11	Cr 92 N 98 I (Heating), I 96,2 N 86 SmA 81 Cr (Cooling)
DEGME-TDI-LC11	I 88 N 82,6 Cr (Cooling)

5. CONCLUSION

In this study, four urethane based materials were synthesized starting from DEGME and PEG-500 with BI and TDI to obtain hydrogen bonded liquid crystalline material. All compounds were characterized by spectroscopic and thermal method and POM images. According to thermal and POM results, DEGME based materials give liquid crystaline properties.

It can be explained that liquid crystaline properties depend on molecular weight. Because, polymer based materials do not show liquid crystaline properties.

An interesting point, DEGME-BI-LC11 show both smectic and nematic phase transitions. While heating it also shows nematic phase. Generally, molecules give liquid crystalline structure during cooling. Also, this molecule gives both nematic and smectic phases during cooling.

Also, DEGME-TDI-LC11 gives only nematic phase during cooling. This phenomenon depends on molecular weight of the compounds.

LC11 generally shows nematic phase. By integrating DEGME-BI and DEGME-TDI into the LC11 chain, the behavior of the liquid crystalline molecule changed to the nematic, smectic and monotropic.

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CURRICULUM VITAE

Name Surname **:** Sinem AĞTAŞ

Place and Date of Birth **:** Bakırköy / 10.10.1990

E-Mail **:** yasarsinem@gmail.com

EDUCATION **:**

- **B.Sc.** **:** 2013, Istanbul Technical University, Faculty of Science and Letters, Chemistry

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2016 - Korozo Ambalaj / R&D Engineer
- 2013 – 2015 Poliser Polyurethane / R&D Engineer