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December 2004 Yasemin YÜKSEL DURMAZ

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LIST of ABBREVIATIONS

THF	: Tetrahydrofuran
DMSO	: Dimethyl Sulfoxide
CFRP	: Conventional Free Radical Polymerization
GPC	: Gel Permeation Chromotography
^{1}HNMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
DSC	: Differential Scanning Calorimetry
POM	: Polarized Optical Microscopy
IR	: Infrared Spectroscopy
VAc	: Vinyl Acetate
LC	: Liquid Crystal
LCPs	: Liquid Crystal Polymers
MCLCPs	: Main-Chain Liquid Crystalline Polymer
SCLCPs	: Side-Chain Liquid Crystalline Polymer
LC6	: 6–(4–Cyanobiphenyl–4'–oxy)hexyl acrylate
LC11	: 11-(4-Cyanobiphenyl-4'-oxy) undecanyl acrylate
PLC6	: Poly (6–(4–Cyanobiphenyl–4'–oxy)hexyl acrylate)
PLC11	: Poly (11-(4-Cyanobiphenyl-4'-oxy) undecanyl acrylate)
AIBN	: 2, 2' – azobis(2- methylpropanenitrile)
TEA	: Triethylamine

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LIST of SYMBOLS

λ	**:** Wavelength
$h\upsilon$	**:** Radiation
$R^{\cdot}$	**:** Radical
I	**:** Initiator
M	**:** Monomer
M_n	**:** The Number Average Molecular Weight
M_w	**:** The Weight Average Molecular Weight
M_w/M_n	**:** The Molecular Weight Distribution
DP	**:** Degree of Polymerization
PDI	**:** Polydispersity
k_{tc}	**:** Rate Constant of Termination Step by Combination
k_{td}	**:** Rate Constant of Termination Step by Disproportionation
T_g	**:** The Glass Transition Temperature
T_{N-I}	**:** The Transition Temperature from Nematic to Isotropic
T_{g-SC}	**:** The Transition Temperature from Glass to Smectic C
T_{SC-SA}	**:** The Transition Temperaturte from Smectic C to Smectic A
T_{SA-I}	**:** The Transition Temperaturte from Smectic A to Isotropic
ΔH_{N-I}	**:** Enthalpy of Transition from Nematic to Isotropic of Copolymers
ΔH_{SA-I}	**:** Enthalpy of Transition from Smectic to Isotropic of Copolymers
SmA	**:** Smectic A Phase
SmC	**:** Smectic C Phase
N	**:** Nematic Phase
I	**:** Isotropic Liquid

SYNTHESIS OF SIDE CHAIN LIQUID CRYSTAL COPOLYMERS

SUMMARY

Since the introduction of side-chain liquid crystalline polymers (SCLCPs) much effort has been put in studying the effect of molecular architecture on their liquid crystalline properties. Because of their properties, SCLCPs were used in various advanced electro-optical technologies. SCLCPs can combine the unique properties of low-molar mass liquid crystals and polymers, which made it easier to form films during material processing.
This study consists of the investigation of new side chain liquid crystalline copolymers, which were synthesized from random copolymerization of vinyl acetate and liquid crystalline acrylate monomers possessing by different spacer length by free radical polymerization mechanism.

In the first step the related, liquid crystalline acrylate monomers were synthesized and their phase transitions studied. Secondly, copolymerisation of these monomers with vinyl acetate by conventional free radical polymerization using AIBN as initiator was performed to obtain side chain liquid crystal. Copolymer compositions were calculated in which its effect on transition temperature were observed. In addition, the influences of spacer length and copolymer composition on the transition temperatures were studied. The side chain liquid crystalline copolymers were characterized by gel permeation chromatography (GPC), ^{1}H-NMR, polarizing optical microscopy and differential scanning calorimetry (DSC).

YAN ZİNCİR SIVI KRİSTAL KOPOLİMER SENTEZİ

ÖZET

İlk yan zincir sıvı kristal polimerlerin (YZSKP) sentezinden bu yana, molekül yapısının, sıvı kristal özellikler üzerindeki etkilerini incelemek amacıyla bir çok çalışma gerçekleştirilmiştir. Yapılan bu çalışmalar, bu malzemelerin ileri elektro optik teknoloji alanında yaygın olarak kullanılmalarının bir sonucudur. YZSKP'ler düşük molekül ağırlıklı sıvı kristal bileşiklerin özellikleri ile polimerlerin özelliklerinin değişmeden bir araya getirildiği yapılardır. Polimer özelliklerinden dolayı bu malzemeler, malzeme olarak işlenmesi sırasında, düşük molekül ağırlıklı sıvı kristal malzemelerine kıyasla daha kolay film oluşturabilme özelliğine sahiptirler.

Bu çalışmasında; serbest radikal polimerizasyon yöntemi ile başlatıcı olarak AIBN varlığında farklı uzunlukta esnek gruplara sahip bifenil mesojenik birimler içeren akrilat monomerinin, vinil asetat monomeri ile kopolimerizasyonu yöntemi ile yan zincir sıvı kristal polimerler sentezlenerek sıvı kristal özellikleri incelenmiştir

Çalışmanın ilk aşamasında farklı uzunlukta esnek gruplar içeren akrilik sıvı kristal monomerler sentez edilerek yapıları ve sıvı kristal davranışları incelenmiştir. İkinci aşamada, sentezlenen sıvı kristal monomerlerin vinil asetat monomeri ile başlatıcı olarak AIBN varlığında serbest radikal polimerizasyon yöntemi ile yan zincir sıvı kristal kopolimerleri elde edilmiştir ve kopolimer bileşimleri hesaplanarak, geçiş sıcaklıklarına etkileri incelenmiştir. Ayrıca, farklı uzunluktaki esnek grupların da geçiş sıcaklıklarına ve polimerlerin sıvı kristal özelliklerine etkileri incelenmiştir. Polimerler, jel geçirgenlik kromatografisi (GPC), ^{1}H-NMR, polarize optik mikroskop ve diferansiyel taramalı kalorimetre (DSC) yöntemleri ile karakterize edilmiştir.

1. INTRODUCTION

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as important and comfortable as they are today. The advances in science and technology made in recent decades owe much to development of polymer science. The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and attempt to find interesting applications involving advanced structures and architectures, are in continuous development in the period of the polymer science.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.

Free radical polymerization is very important in the field of industrial polymer synthesis and is the preferred route to commercial polymers. It is very adaptable to many types of monomer under mild conditions. However, the preparation of well-defined polymers from unsaturated monomers has been limited by the technology available for conventional free radical polymerization. Certainly, such processes inherently do not allow to control over molar masses and give broad polydispersity since not all the polymeric chains are initiated at the same time because of a lack of control over chain-breaking reactions; i.e., both termination and the transfer steps greatly limit ability to polymer architecture.

Liquid crsytals (LCs) signifies a state of aggregation that is intermediate between the crystalline solid and the amourphous liquid. A substance in this state is strongly anisotropic in some of its properties as crystals and yet exhibits a certain degree of

fluidity like liquids. Polymer liquid crystals are a class of material that combine the properties of polymers with those of LCs. Liquid crystalline polymers are excellent structural materials for engineering applications because of their excellent chemical and heat resistance, high mechanical properties, high dimentional stability, low viscosity during processing, low thermal shrinkage, and electro optic and rheological properties.

This study contains two different mesogenic monomers, which polymerize thermally with AIBN by applying conventional free radical polymerization (CFRP) to form copolymers. Copolymerization is an effective way to disturb the regular structure of the polymer chain. The lack of periodicity along the chain inhibits crystallization and thus reduces the crystallity and depresses Tm (the transition temperature to form on LC phase) without necessarily leading to an additional loss of mesogennicity and Ti (the transition temp.from an LC phase to an isotropic phase).

2. THEORETICAL PART

2.1. Free Radical Polymerization (FRP)

Free-radical reactions are of importance in a wide variety of commercial applications. Polymers prepared by free-radical means are used in the manufacture of numerous products, such as fabrics, surface coatings and paints, plastics, packaging, spectacle and contact lenses and surgical devices. Free radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers.

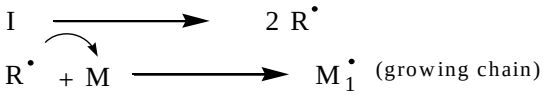
2.1.1. Steps of the Polymerization Process

A typical free-radical polymerization comprises four elementary steps [1-2]:

- initiation,
- propagation,
- chain transfer,
- termination.

The first step, *initiation* is decomposition of the initiator molecule into primary radicals $R^{\cdot}$. The actual initiation occurs when free radical react with a monomer (2.1a). The *propagation* or growth reaction consists of the rapid addition of monomer molecules to the radical species. In this step reaction is repeated many times (2.1b). Usually, it occurs in head-to-tail fashion, because the free radical formed is more stable. However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents.

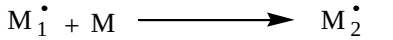
Initiation



(2.1a)

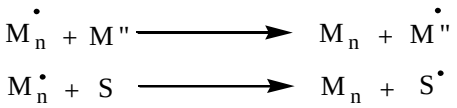
Propagation

(2.1b)



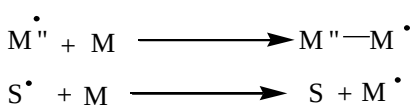
(2.1c)

Chain transfer to monomer or solvent



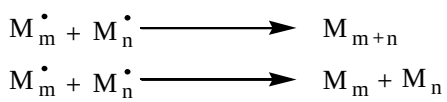
(2.1d)

Reinitiation by transfer radicals

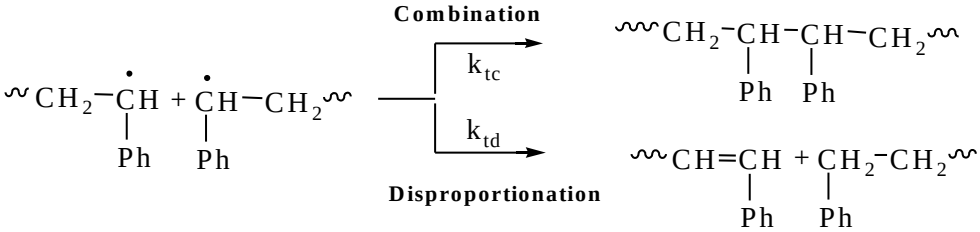


(2.1e)

Termination



In *termination*, growth of polymer chains is brought to an end by the destruction of propagating radicals (2.1e). Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals. These processes, analogous to those taking place with simple alkyl radicals, consist of radical combination or disproportionation (2.2).



(2.2)

Disproportionation leads to two polymer molecules, one saturated and one containing a terminal double bond. Many monomers show both types of termination: thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate preponderantly by combination (Table 2.1).

Table 2.1 Termination ratios of monomers.

Monomer	k_{td}/k_{tc}	Temparature
Styrene	0.07	20
Styrene	0.10	118
MMA	0.62	90

It is possible to make some generalizations:

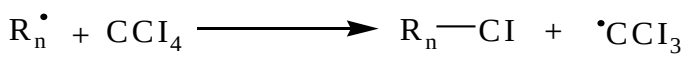
- Termination of polymerizations involving vinyl monomers involves predominantly combination.

- On the other hand, termination of polymerizations involving α – methylvinyl monomers always includes a measurable proportion of disproportionation.

- During disproportionation of radicals bearing an α – methyl substituent (for example, those derived from MMA), there is a strong preference for transfer of a hydrogen from the α – methyl group rather than the methylene group.

- Within a series of vinyl or α – methylvinyl monomers, k_{td} / k_{tc} appears to decrease according to the ability of the substituent to stabilize a radical center in the series Ph > CN >> CO_2R.

Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the *chain-transfer* process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate (2.1c and d). A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred. Transfer to to carbon tetrachloride is illustrated in 2.3.

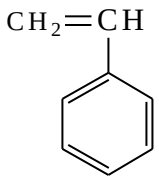


$$R_n^{\bullet} + CCl_4 \longrightarrow R_n{-}Cl + {}^{\bullet}CCl_3 \qquad (2.3)$$

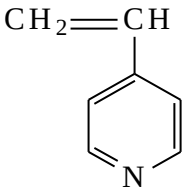
2.1.2. Monomers

Most of vinyl and diene monomers (2.4) can undergo free radical polymerization. Some potential monomers do not form polymers under usual free radical

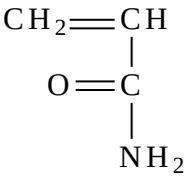
polymerization conditions. Such as α-methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature.



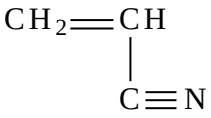
Styrene



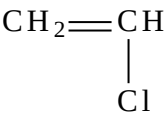
4-Vinyl Pyridiene



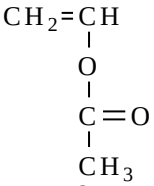
Acrylamide



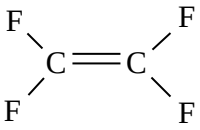
Acrylonitrile



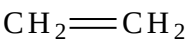
Vinyl Chloride



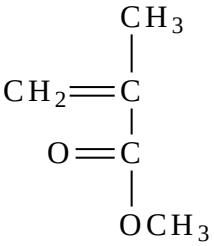
Vinyl Acetate (2.4)



Tetrafluoro Ethylene

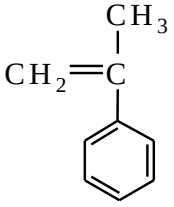


Ethylene

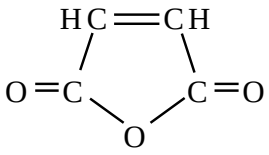


Methyl Methacrylate

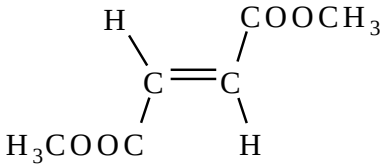
Maleic anhydride and dimetyl fumarate (2.5) are symmetrically substituted ethylenes therefore, they can not be polymerize by free radical polymerization.



α-Methyl Styrene



Maleic Anhydride



Dimetyl Fumarate (2.5)

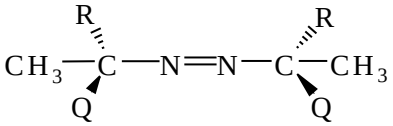
2.1.3. Initiator

Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commonest, but other processes such as use of γ-radiation or electron beams find applications.

2.1.3.1. Thermal Initiators

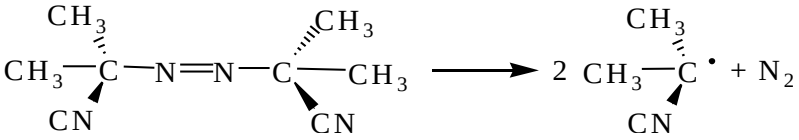
Azo Initiators

Most of the compounds are represented by the formula where R is an alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester) (2.6).



(2.6)

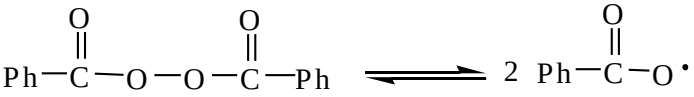
Azobisisobutyronitrile (AIBN) is very widely used initiator. Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction 2.7.



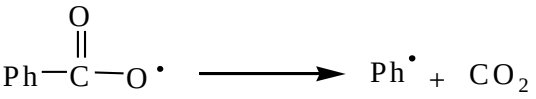
(2.7)

Peroxy Compounds

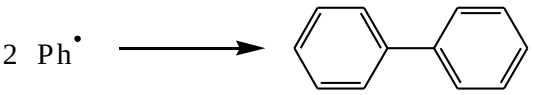
Benzoyl peroxide is a well-established initiator of polymerization. Like other peroxides, the primary step in the thermal decomposition is scission of the —O—O— bond to give two acyloxy radicals (2.8a). A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β-scission to phenyl radicals and carbon dioxide (2.8b). Further, recombination reactions giving biphenyl and phenyl benzoate may then occur (2.8c and d).



(2.8a)



(2.8b)

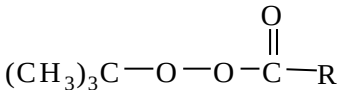


(2.8c)

(2.8d)

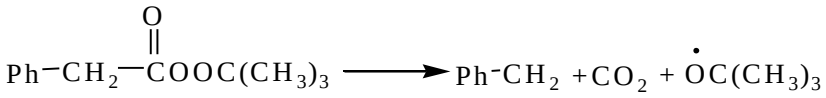
Peresters

The thermolysis of *t*-butyl peresters has received detailed attention [3-5].



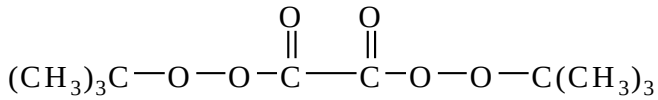
(2.9)

Evidence was adducted for the occurrence of concerted rupture of C — C and O — O bonds on thermolysis , for example with *t*-butyl phenylperacetate (2.10) [6].



(2.10)

Many of these peresters function as low-temperature initiators of free-radical polymerization. Although some of the stabilized radicals may not be effective initiators, the *t*-butoxy radical and its β-scission product, methyl, initiate readily (2.11). Di-*t*-butyl peroxyoxalate initiates well at 25°C. Di-isopropyl peroxydicarbonate is a familiar perester, which initiates well at moderate temperatures [7].



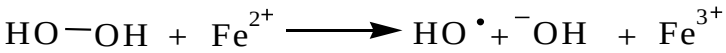
(2.11)

2.1.3.2. Redox Initiators

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred as *redox initiation, redox catalysis*, or r*edox activation.* A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50°C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [8].

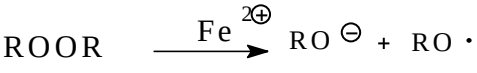
Types of Redox Initiators

1- Peroxides in combination with a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion (2.12).

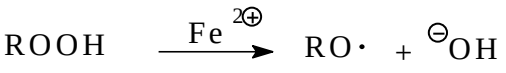


(2.12)

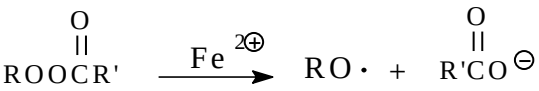
Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides (2.13).



(2.13a)



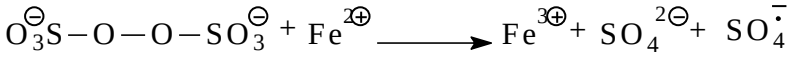
(2.13b)



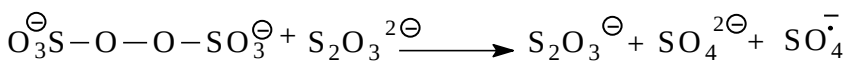
(2.13c)

Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, and Cu^{+} can be employed in place of ferrous ion in many instances.

2- The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example,



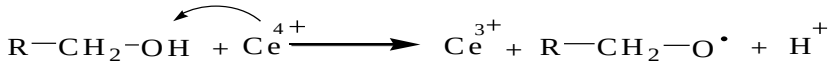
(2.14a)



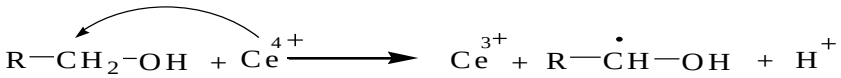
(2.14b)

Other redox systems include reductants such as HSO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_5^{2-}$ in combination with oxidants such as Ag^+, Cu^{2+}, Fe^{3+}, ClO_3^-, and H_2O_2.

3- Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+}or by V^{5+}, Cr^{6+}, Mn^{3+} (2.15a and b).



(2.15 a)



(2.15 b)

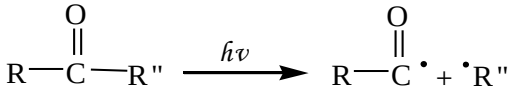
4- There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples include thiosulfate plus acrylamide or methacrylic acid and N, N-dimethylaniline plus methyl methacrylate.

2.1.3.3. Photoinitiators

Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

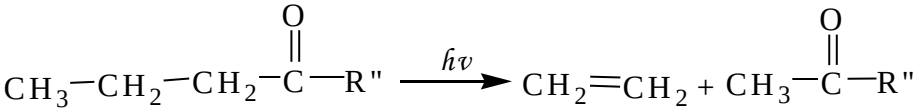
Photoinitiation by Intramolecular Bond Cleavage

Most peroxy initiators yield radicals on photolysis and benzoyl peroxide has frequently been used as a photoinitiator [9, 10]. They require shorter wavelengths than azo compounds (<300nm), a disadvantage since many monomers absorb in this region. The same remark applies to many simple ketones which photodissociate according to the Norrish type I mechanism (2.16) [11].



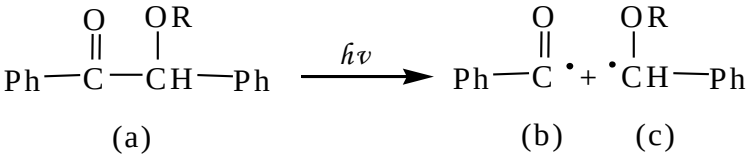
(2.16)

Ketones carrying alkyl chains three or more carbon atoms long may undergo the essentially nonradical Norrish type II fission (2.17):



(2.17)

Benzoin is a well-known photoinitiator [12, 13]. Benzoin ethers (a) which are much used in photocuring process undergo a type I photodissociation into two different radicals. It has been reported that both types of radicals can initiate the polymerization (2.18).

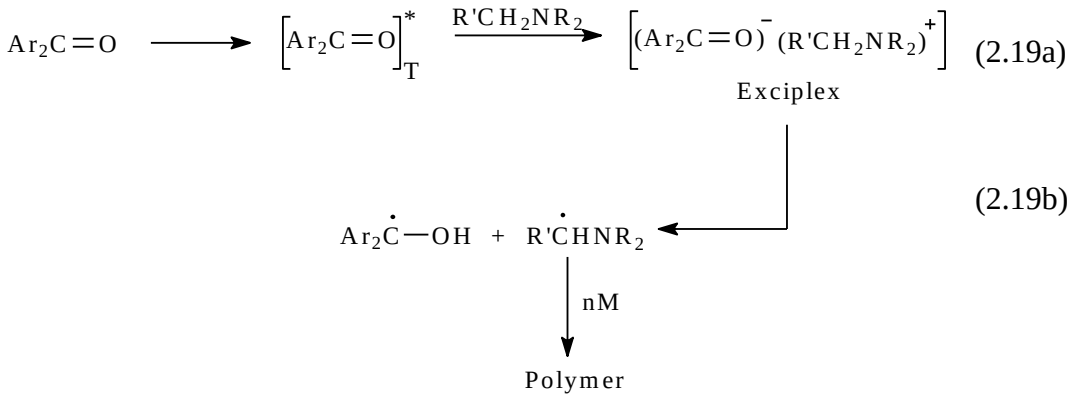


(2.18)

Photoinitiation by Hydrogen Abstraction

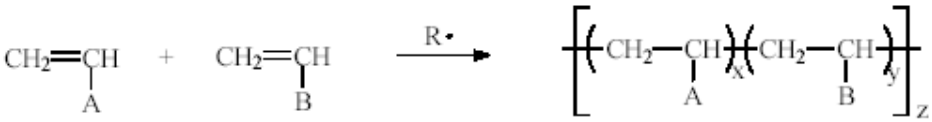
Photoinitiators of this type include benzophenone and derivatives such as Michler's ketone (14), thioxanthones, benzyl and quinones. In contrast to cleavage type photoinitiators, which are capable of generating radicals independently, this type of initiators must undergo a bimolecular reaction with hydrogen donors. Tertiary amines with abstractable hydrogen atoms are particularly effective H-donors for UV curing of acrylate monomers [14, 15].

The classical example is benzophenone, of which the photochemistry is well-known [16]. The lowest excited singlet (S_1) is of $n\rightarrow\pi^*$ character and yields by intersystem crossing the lowest excited triplet (T_1). In the presence of a hydrogen donor RH the following reaction occurs (2.19).



2.2 Free Radical Chain Copolymerization

The demand for new and improved materials often can be achieved as a result of altering the properties of existing polymeric materials. For example, the use of additives can incorporate desirable properties into an existing polymer material that is to be used for specialized applications. Common additives include plasticizers, stabilizers, flame retardants, fillers, colorants, processing aids, and impact modifiers [17]. Another approach is to combine the beneficial properties of different known polymer structures. One known technique to achieve this is to simply blend two individual polymers to give a material whose mechanical properties exceed those of the individual blend components (*i.e.*, synergism). A few advantages of blending include reducing the cost of expensive high performance polymers, improving the processability of a high temperature material, and improving impact resistance of materials. However, because few polymers are miscible, their blends form immiscible phase separated materials. These immiscible blends often have poor physical properties due to inadequate interfacial strength between the phases [18]. A desirable alternative is to copolymerize different monomer structures into a single polymeric material (2.20) [19]. Prime examples include the important commercial materials produced from vinyl chloride/vinyl acetate and styrene/butadiene copolymers. Careful consideration of such factors as the selection of the comonomers and the copolymerization reaction conditions allows one to precisely tailor the properties of the resulting copolymer and provides a useful method of synthesizing an almost unlimited number of polymeric structures with a wide range of properties and applications.



(2.20)

Copolymer structures can be described in a variety of ways. Different types of copolymers include statistical, alternating, block, and graft copolymers (Figure 2.1). Statistical copolymers result from a single process where the incorporation of the comonomers follow some statistical law that is due solely to kinetic factors [20]. Alternating copolymerization, which will be focused in the preceding sections, is an example of chain copolymerization where each of the monomers adds preferentially to the other and homopropagation is effectively nonexistent [21]. Block and graft copolymers differ in that they contain long sequences of each comonomer either along the backbone or as side chains (grafts) and are often the result of a multi-step process [22].

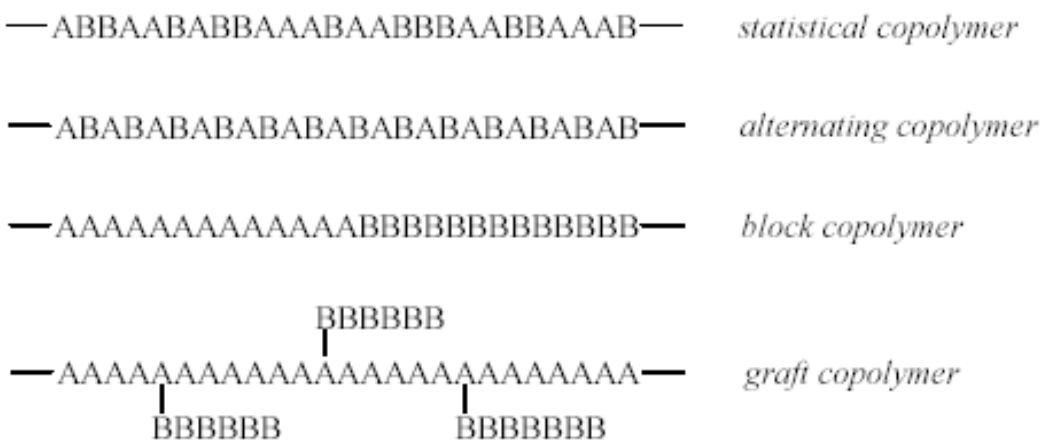


Figure 2.1 Types of copolymer topologies.

The manner in which comonomer repeat units are incorporated into the polymer backbone is determined from the reactivities of the monomers and radicals involved in the reaction. Reaction conditions such as solvent and temperature can also have a marked effect on the monomer reactivities and will contribute to the copolymer composition.

Therefore, in only a few select cases of chain copolymerization will the copolymer composition be directly proportionate to the monomer feed. More typically, both the

comonomer feed and instantaneous copolymer composition vary throughout the copolymerization, which results in heterogeneity.

2.2.1. Copolymerization Models

2.2.1.1. Terminal Model

The simplest quantitative statistical treatment for the determination of copolymerization composition, which is generally referred to as the terminal model, was first hypothesized by Dostal [23] in 1936 and later elucidated by others [24]. The terminal model is based upon the assumption that the chemical reactivity of a propagating polymer chain is independent of the size or composition of the chain and is only influenced by the active end group [25]. Though the terminal model is dependent on several assumptions and may not be the most accurate model to describe a copolymer process, it is relatively simple to apply and provides a facile starting point when evaluating copolymerizations of various monomer pairs. When two monomers, M_1 and M_2 are copolymerized by free radical methods, four reactions are feasible according to the terminal model:

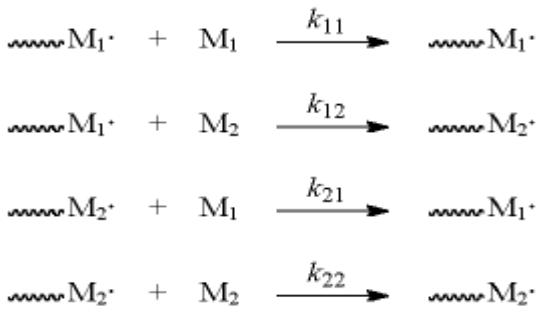


Figure 2.2 Terminal model of copolymerization.

Where k_{11} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_1, k_{12} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_2, and so on. The rate constants can then be expressed in terms of the monomer reactivity ratios, r_1 and r_2, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Monomer reactivity ratios may either be experimentally [26] determined or estimated [27] and for free radical polymerizations are generally independent of initiator and solvent with only slight temperature dependence. The different types of copolymerization behaviours can then be described based upon the values of the monomer reactivity ratios. “Random copolymerization” results when

$r_1 = r_2 = 1$ due to the equal reactivity of the monomers toward both types of propagating chain ends and the resulting copolymer composition will directly reflect the comonomer feed. When $r_1.r_2 = 1$, the two different types of propagating chain ends both add preferentially to one of the monomers, and is described as "ideal copolymerization". The case when r_1 and r_2 are much greater than one results in a tendency to form blocks of both monomers and is appropriately termed "block copolymerization". The copolymerization behaviours focused upon in this review, which describes the situation when $r_1 = r_2 = 0$, is referred to as "alternating copolymerization". The mechanism of most typical copolymerizations fall somewhere between the extremes of "ideal copolymerization" and "alternating copolymerization". The mechanism of becomes increasingly "alternating" as the r_1r_2 product decreases from one toward zero. For polymerizations where the r_1r_2 product lies somewhere between zero and one, the composition of the copolymer can be controlled to some extent by variation of the monomer feed ratio. However, as r_1r_2 approaches very close to zero, the "alternating" behaviour of the polymerization mechanism becomes the dominating factor and a 1:1 alternating copolymer can be formed independent of the monomer feed ratio. The terminal model also provides a useful means to approximate copolymer compositions that are dependent on such factors as the comonomer feed ratio and the reactivities of the comonomers according to the model. The Mayo-Lewis equation [24] , which is derived from the terminal model using the assumption of the steady-state radical approximation, can be used to describe the instantaneous copolymer composition(2.21):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \qquad (2.21)$$

Where r_1 and r_2 are the respective monomer reactivity ratios. $[M_1]$ and $[M_2]$ describe the beginning concentrations in the comonomer feed. The instantaneous mole fractions of the two repeating units in the copolymer is then defined as $d[M_1]/d[M_2]$. The terminal model, therefore, allows one to predict the instantaneous copolymer composition for a given comonomer feed simply on the basis of the comonomer reactivity ratios. Although the terminal model relies on several assumptions and may not be the most reliable model to describe of a copolymerization process, it is has the advantages of being simple to apply and very useful as a starting point to study a given copolymerization reaction.

2.2.1.2. Penultimate Model

It has been shown that the behaviour of the propagating species of some comonomer pairs is significantly influenced by the penultimate monomer unit [28]. The principal feature of the penultimate model is that the penultimate unit (Figure 2.3) in a propagating polymer chain will affect the reactivity of the terminal reactive radical. The exact nature of the penultimate unit of the propagating species will determine the magnitude of this effect. For example, Tirrell and coworkers have reported that in copolymerizations of styrene and acrylonitrile, there is little effect of the terminal radical reactivity when the penultimate units is styrene unit, but there is an appreciable effect when the penultimate unit is acrylonitrile [29].

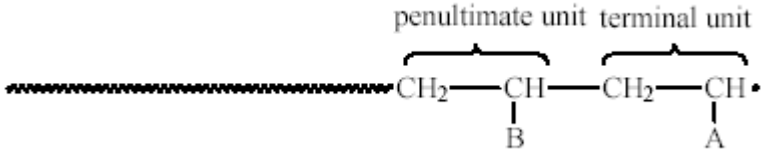


Figure 2.3 Penultimate and terminal units of propagating copolymer chain.

The effect of the penultimate unit on the kinetic of copolymerization was first reported by Merz et al. [30] and later by Ham [31] and Barb. [32] The mathematical model for the penultimate effect involves the use of eight propagating reactions (Figure 2.4) from which four reactivity ratios are defined (2.22):

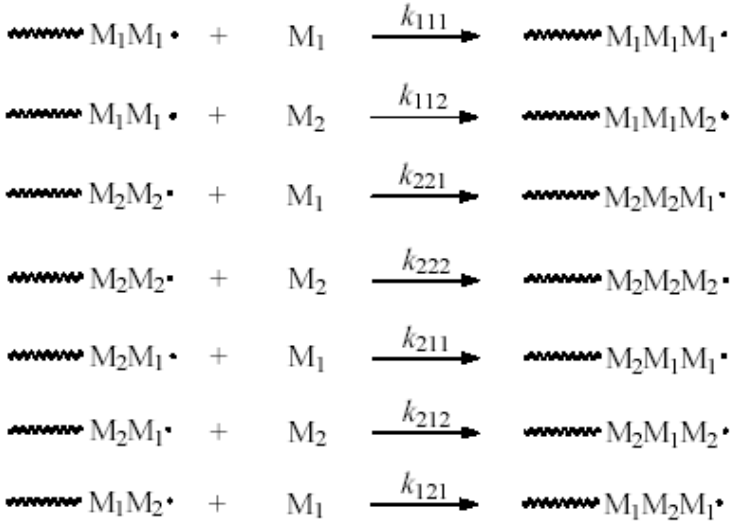


Figure 2.4 Penultimate kinetic models for copolymerization.

$$r_{11} = \frac{k_{111}}{k_{112}} \qquad r_{12} = \frac{k_{122}}{k_{121}} \qquad r_{22} = \frac{k_{222}}{k_{221}} \qquad r_{21} = \frac{k_{211}}{k_{212}} \tag{2.22}$$

Each monomer is thus characterized by two monomer reactivity ratios. One reactivity ratio (r_{11} and r_{22}) that represents the propagating species in which the penultimate and terminal monomer units are the same. The other represents the propagating species in which the penultimate and terminal units differ (r_{12} and r_{21}). Several copolymerization processes have been studied where the experimental data agreed better with the penultimate model that the terminal model. However, application of the penultimate model to study copolymerization behaviour is significantly more complicated and time consuming than application of the terminal model. Consequently, the study of copolymerizations has been primarily limited to analysis in terms of the terminal model. Comonomers that have been studied using the penultimate model include acrylonitrile, [33] butadiene,[34] maleic anhydride [35] and vinyl chloride [36].

2.2.2 Alternating Copolymerization

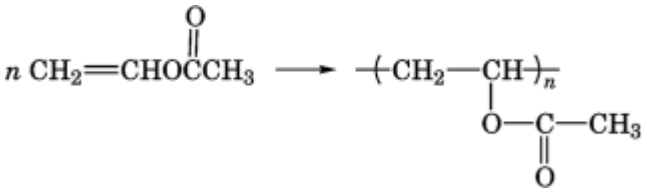
When two monomers are mixed together in the presence of an initiator there are several ways that the monomers may combine to form a copolymer. In general, the composition of the product rarely follows the monomer feed ratio. Furthermore, the composition resulting from a copolymerization reaction cannot directly be predicted from knowledge of the homopolymerization rates of the monomers [37]. Therefore, the factors that determine the incorporation of repeating units into a copolymer chain are not as trivial as those in homopolymerization reactions. Not only does the homopolymerization rate of the comonomers have an effect, but the rate at which comonomers react with each other is also a determining factor.

Alternating copolymerization is an example of chain copolymerization where each of the monomers adds preferentially to the other, which results in an alternating monomer sequence distribution along the backbone [38]. Monomers that are difficult to homopolymerize are often found to be capable of alternating copolymerization. For example, if a strong electron acceptor is added together with a strong electron donor, regular alternating copolymers may result from either spontaneous initiation or a free radical source [39].

2.2.2.1 Vinyl Acetate Polymers

Vinyl acetate (VAc), $CH_2{=}CHOOCCH_3$, the ethenyl ester of acetic acid, is primarily used for the manufacture of poly(vinyl acetate) (PVAc) and vinyl acetate copolymers. Poly(vinyl acetate) homo- and copolymers are found as components in coatings, paints and sealants, binders (adhesives, nonwovens, construction products, and carpet-backing), and miscellaneous uses such as chewing gum and tablet coatings.

The most important chemical reaction of vinyl acetate is free-radical polymerization [40, 41]. The reaction is summarized as follows:



(2.23)

Polymerization can be initiated by organic and inorganic peroxides, azo compounds, redox systems, light, and high energy radiation. Polymerization is inhibited or strongly retarded by aromatic hydroxyl, nitro or amine compounds, and by oxygen, quinone, crotonaldehyde, copper salts, sulfur, conjugated polyolefins, and enynes. Vinyl acetate has been polymerized by bulk, suspension, solution, and emulsion methods.

Table 2.2 Copolymerization Parameters of Vinyl Acetate (M_1) and Comonomers (M_2).

Comonomer (M_2)	**r_1**	**r_2**	Temperature ^oC
Acrylamide	0.07	7.5	50
Acrylic acid	0.01 ±0.0003	10.0 ± 1	70
n-Butyl acrylate	0.388	5.529	50
Ethylene	1.02±0.02	0.97 ± 0.02	120
Maleic anhydride	0.072	0.01	
Methyl acrylate	0.029 ± 0.011	6.7 ± 2.2	60
Styrene	0.01 ± 0.01	55 ± 10	60
Vinyl chloride	0.6 ± 0.2	1.8 ± 0.6	60

Poly (vinyl acetate) polymer and copolymer properties may be modified through the addition of plasticizers and fillers. Cross-linking agents react with copolymers of vinyl acetate containing a cross-linkable group. The material properties can be altered to allow improved flow, rigidity, and toughness.

2.2.3 Copolymers

Homopolymers are derived from one species of monomer whereas copolymers are composed of two or more monomer units. Copolymers form two, three, four species of monomers are called bipolymers, terpolymers, quarter polymers etc. Copolymers are subdivided into random, alternating, block, gradient, periodic, segmented and graft copolymers. Block copolymers are polymers, which consist of two or more monomers that are segregated into separate regions of the polymer chain, but covalently bound to each other. Gradient copolymers exhibit a compositional gradient along the chain: one end of a bipolymer is enriched in first monomer unit and the other end in second monomer unit. Random copolymers have no continuous change in instantaneous composition. In periodic copolymers, monomeric units are arranged in periodic sequences. Multiblock copolymers with short block lengths are known as segmented copolymers. In graft copolymers, the blocks are connected to the main chain as side-chains.

2.3 Liquid Crystals

Liquid crystals are a state of order between crystals and liquids (2.24). They can be fluid like a liquid and they can have anisotropic properties like crystals. The study of liquid crystals began in 1888 when an Austrian botanist named Friedrich Reinitzer observed that a material known as cholesteryl benzoate had two distinct melting points. Because of this early work, Reinitzer is often credited with discovering a new phase of matter - the liquid crystal phase [42].

$$\begin{array}{c} \text{HEATING} \rightarrow \\ \textbf{SOLIDS} \leftarrow\rightarrow \textbf{LIQUID CRYSTAL} \leftarrow\rightarrow \textbf{LIQUID} \\ \leftarrow \text{COOLING} \end{array} \qquad (2.24)$$

In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state (Figure 2.5). Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals [42].

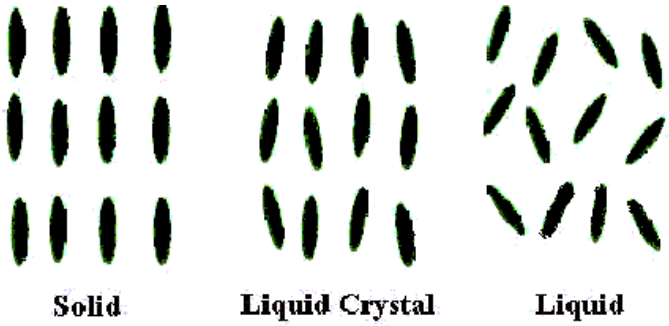
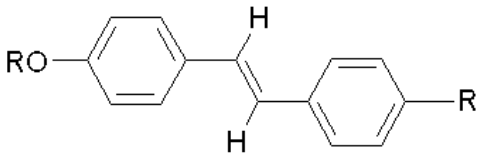


Figure 2.5 The illustration of the average alignment of the molecules for each phase.

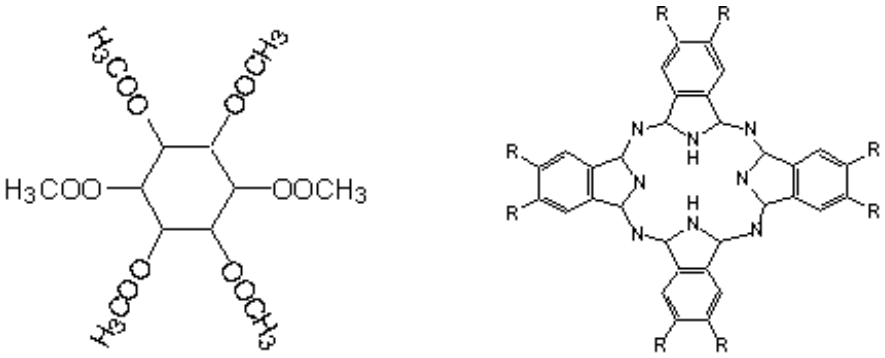
2.3.1 Classification of Liquid Crystals

The most common type of molecule that forms liquid crystal phases is a *rod-shaped (rod-like)* (2.25). In this type molecules, one molecular axis is much longer other two. Such compounds are called *calamitic liquid crystals* and many different phases are possible [43].



(2.25)

Disc-like molecules (2.26), namely molecules with one molecular axis much shorter than the other two, also form liquid crystal phases. Such compounds are called *discotic liquid crystals*



(2.26)

Both calamitic and discotic liquid crystals are also called *thermotropic liquid crystals* because the liquid crystal phase is stable for a certain temperature interval. There are two characteristic mesophases:

- *Enantiotropic mesophases* can be obtained from either lowering the temperature of a liquid or raising of the temperature of a solid.
- *Monotropic mesophases* can only obtained from either an increase in the temperature or a decrease in the temperature of a liquid [44].

There is another type of molecule, however, which liquid crystals phases only when mixed with a solvent of some kind. For these compounds, the concentration of the solution is just as important, if not more important, than the temperature in determining whether a liquid crystal phase is stable. These compounds have been given the name *lyotropic liquid crystals* [43].

The recipe of a lyotropic liquid crystal molecule is one which combines a hydrophobic group at one end with a hydrophilic group at the other end.. Such amphilic molecules form ordered structure in both polar and non-polar solvents. Good examples are the soaps and various phospholipids.

2.3.2 Chemical Structure of Liquid Crystals

2.3.2.1 Molecular Structure of Rod-like Liquid Crystals

Most liquid crystals molecules are highly anisotropic, and to a good approximation they can be regarded as rigid rods or ellipsoids of revolution with lengths *l* greater than their widths *d*.[45].

The basic structure of low molecular mass liquid crystals or monomers of liquid crystalline polymers is schematically shown Figure 2.6.

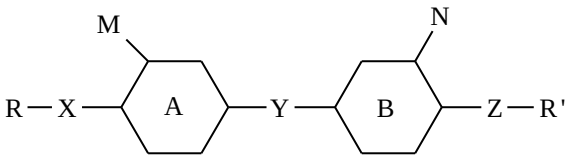
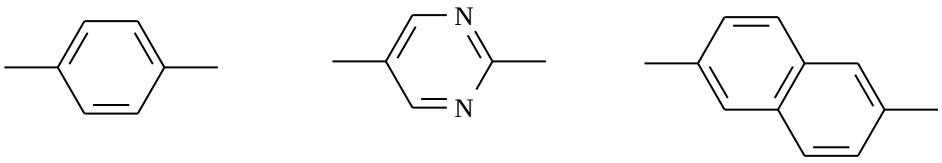


Figure 2.6 A general structural template for calamitic liquid crystals.

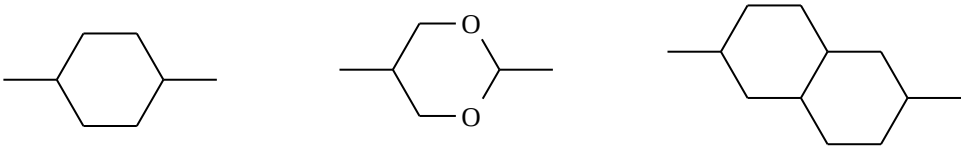
A and B are the core units which are sometimes linked by a linking group (Y) but more often a direct link is used. Similarly, the terminal chains (R and R') can be linked to the core with groups X and Z but usually the terminal chains are directly linked to the core. Lateral substituents (M and N) are often used to modify the mesophase morphology and physical properties of liquid crystals to generate enhanced properties for applications [43].

Aromatic Rings (The Core)

A certain rigidity is required to provide the anisotropic molecular structure; this core of the structure is usually provided by linearly linked ring systems (A and B) that are most often aromatic (2.27a) but can also be alyclic (2.27b). Usually, the longer the ring, the higher the melting temperature.



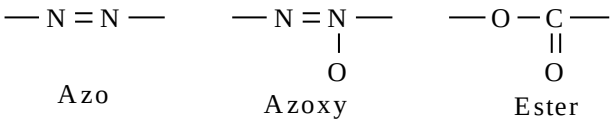
1,4-phenyl　　2,5-pyrimidinyl　　2,6-naphthyl　　(2.27a)



trans-1,4-cyclohexyl　　trans-2,5-dioxanyl　　trans-2,6-decalinyl　　(2.27b)

Linking Groups

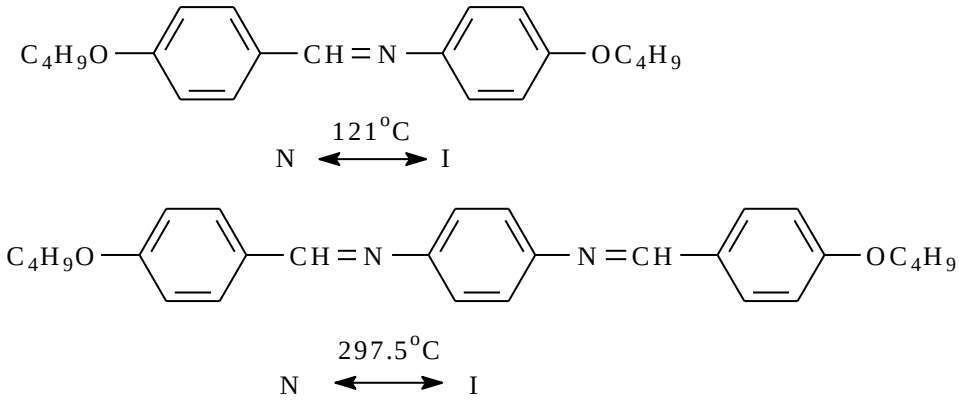
The linking group makes an important contribution to the phase transition and physical properties such as the birefringence. [45]. The rigid core alone is not usually sufficient to generate liquid crystal phases and a certain flexibility is required to ensure reasonably low melting points and to stabilise the molecular alignment within the mesophase structure. Saturated groups, such as ethylene, esters, unsaturated groups containing a double bond or a triple bond such as stilbene, azoxy, schiff base, acetylene and diacetylene are most uses linking groups (2.28).



Azo　　Azoxy　　Ester　　(2.28)

Olefin　　Acetylene

Most of the linkages are highly polarizable and strong the dipole, these properties of the linkages and conjugated structures (2.29) provide high thermal stabilities of the masophase [44].



(2.29)

Terminal Groups

The flexibility is provided by the terminal substituents R and R' which are usually straight alkyl group (C_nH_{2n+1}); alkoxy group ($C_nH_{2n+1}O$) and alkenyl (C_nH_{2n-1}) or alkenyloxy

($C_nH_{2n-1}O$), however, one terminal units is often a small polar substituent such as CN, F, NCS, NO_2 OCH_3.[41] [41] The length and flexibility of the chain affect the type of liquid crystal phases and phase transition. In general, for homologues, the compounds with small *n* show no mesogenic phase. As *n* increases, the monotropic liquid crystal phase appears. As *n* further increases the nematic phase occurs and thereafter smectic phases may appear. As *n* varies the even-odd alternation occurs: the compounds in odd carbon numbers in the side chains have the higher transition temperature whereas compounds in even numbers have lower transition temperatures [45].

Lateral Groups

By substituting the hydrogen in the 2-, 3-, or 4-, position of a phenyl ring by cyano, flluoro,or chloro, polar group, one can modify the physical properties of liquid crystals. In most cases, the lateral substitution will broaden the molecule, thus reducing lateral attractions and lowering the nematic and smectic phase stability. Not only do the nature and size of the substitution affect the liquid crystal properties, but also the position of the group can have a significant effect.[45] the fluoro substituent is the most useful because of its subtle combination of small size and high electronegativity.

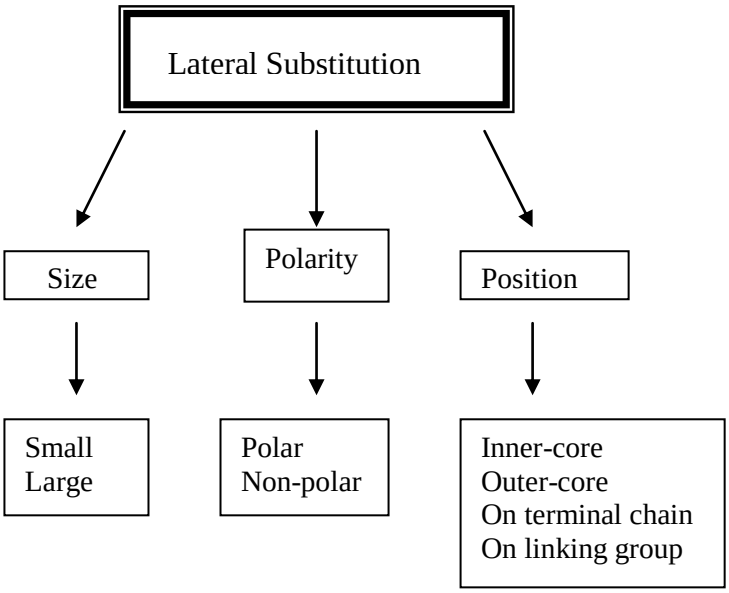


Figure 2.7 The important issues when considering lateral substitution.

2.3.3. Liquid Crystal Phases

Liquid crystals are generally classified according to their basic molecular organization. Three main types are widely recognized: ***smectic, nematic,*** and ***cholesteric***.

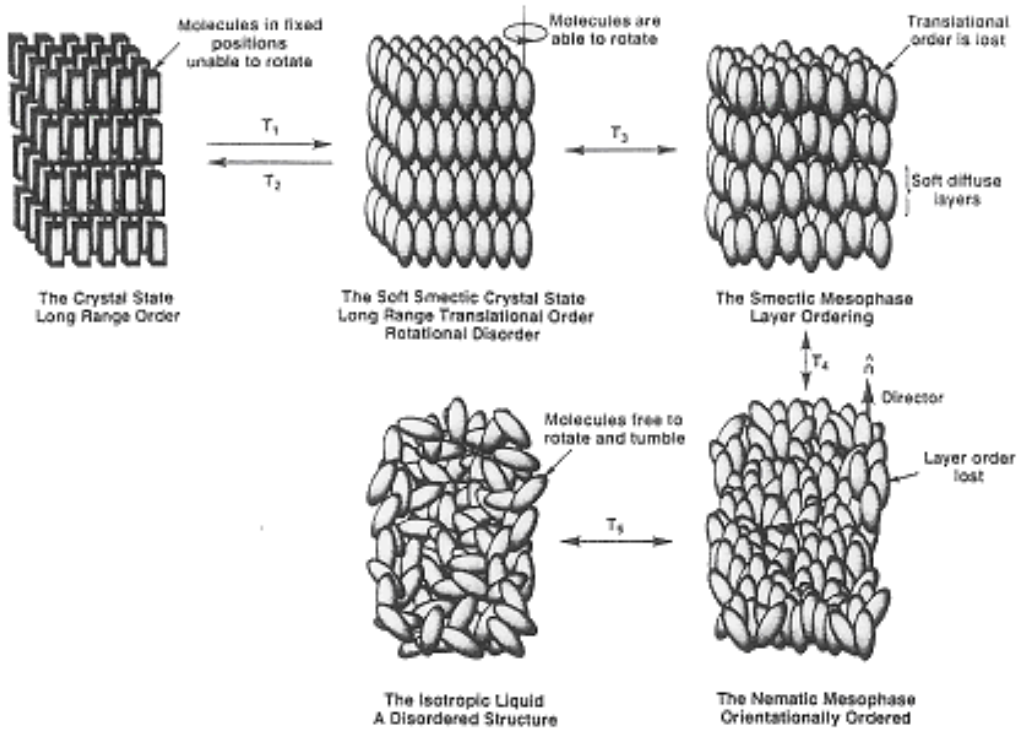


Figure 2.8 The melting process of a calamitic (rod-like) liquid crystalline material.

When thermotropic liquid crystals are heated some differences occur which are ;

i) initial beakdown in order with the molecules ossilating or rotating rapidly about one or more axes (simectic and smectic like crystals).

ii) a collapse of the long-range positional ordering of the molecules to give a state where the molecules have short-range positional order. (nematic phase)

iii) a disruption in the short-range and longe-range order to produce a completely disordered liquid. (isotropic liquid) (Figure 2.8) [43].

2.3.2.1 Nematic Phase

The nematic phase is essentially a one –dimensionally ordered elastic fluid in which the molecules are orientationally ordered, but where there is no long range positional order of the molecules. In this phase the rod-like molecule tend to align parallel to each other with their long axes all pointing roughly in the same direction.[46]. The average direction along which the molecules point is called the director of the phase, and is usually given the symbol *n* (Figure 2.9).

Figure 2.9 The structure of the nematic phase.

2.3.2.2 Smectic Phases

The lamelar smectic state is rapidly divided into four subgroups by considering first, the extent of the in-plane positional ordering of the constituent molecules, and second, the tilt orientational ordering of the long axes of the molecules relative to the layer planes (Figure 2.10) [47]. Two groups can be defined where the molecule has their long axes on average normal to the layers. These two groups are distinguished from each other by the extent of the positional ordering of the constituents molecules. For example, the smectic A and hexatic B phases are smectic liquid crystals in which molecules have only short-range positional order

[48], whereas the crystal B and crystal E phases are smectic-like soft crystal modification [49, 50] where the molecules have long-range positional ordering in three dimensions [51]. Two other classes can be distinguished where the molecules are tilted with respect to the layer planes. In the smectic C, smectic I, and smectic F phases the molecule have short-range positional ordering [52, 53], whereas in the crystal G, crystal H, crystal J,and crystal K phases the molecules have long-range positional ordering [48,52].

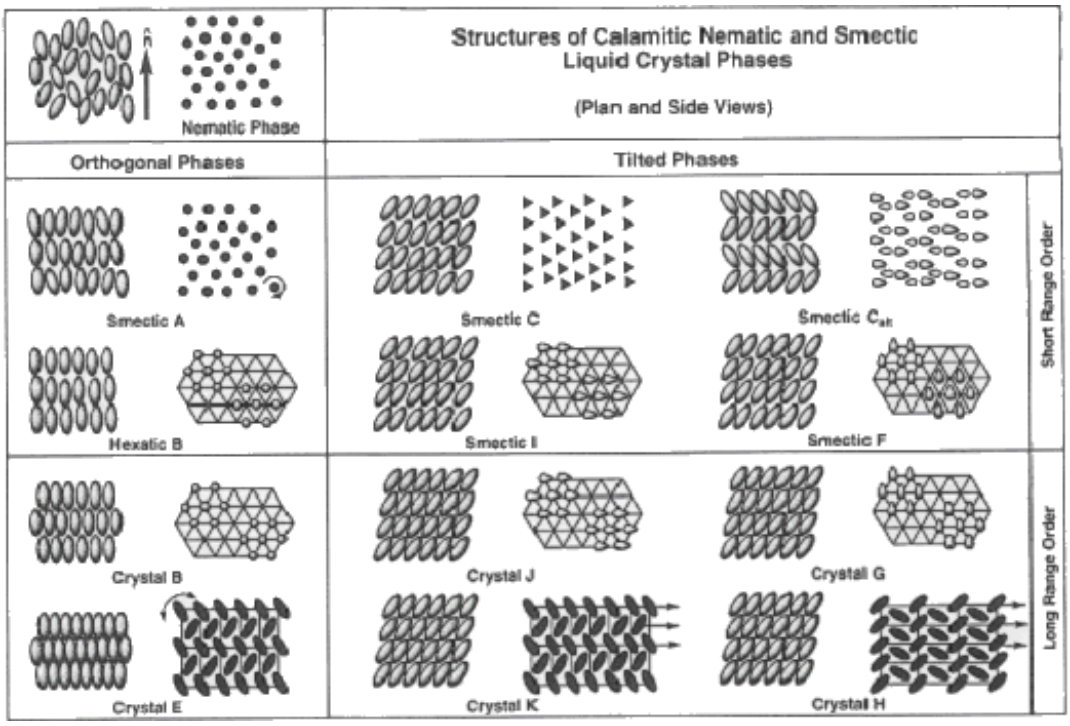


Figure 2.10 The plan and elevation structures of the smectic phases.

In both the smectic A and smectic C phases, the molecules randomly diffuse within each plane [54].

In the smectic A phase the molecules are arranged in layers so that their long axes are on average perpendicular to the layer plane.In the smectic C phase the constituent molecules are arranged in diffuse layers where the molecules are tilted at the layer planes (Figure 2.11).

Figure 2.11 The smectic A and C phases

2.3.3. Applications of Liquid Crystals

The best-known application of liquid crystals is the widely utilized liquid crystal display (**LCD**). Made practical in the 1960s by American scientist James Fergason, liquid crystal displays are based upon the interaction of liquid crystals with polarized light waves and an electric field. In its most basic form, the seven-segment LCD numerical display, which is widely used in watches, clocks, and similar items, this technology, is simple to understand. Placed in the middle of two polarizers oriented at right angles with respect to each other, a cholesteric liquid crystal is sandwiched between two glass plates that feature seven individually chargeable electrodes. When no current is applied to the electrodes, light entering through the first polarizer undergoes a 90 degree twist as it passes through the cholesteric liquid crystal between the glass plates due to the inherent molecular rotation characteristic of this phase of matter, enabling the light to successfully pass through the second polarizer. This light can then form one of the seven segments on the display. When current is applied to the electrodes, however, the liquid crystal aligns with the current and loses the cholesteric spiral pattern, effectively causing the light to be blocked by the second polarizer it encounters. Thus, by coordinating the voltage on the seven positive and negative electrodes, the display is capable of rendering the numbers 0 through 9.

In addition to the LCD, there are a number of other uses for liquid crystals and many more currently in development. For instance, the optical properties of cholesteric liquid crystals make them highly useful in a type of thermometer that changes colour as temperature fluctuates. The familiar novelty known as the "mood ring" is based on the same liquid crystal sensor technology, which is being investigated for its potential use in the medical field for temperature mapping of the body. Intense liquid crystal research is also being carried on in the optical imaging and recording industries, and early promise suggests that in the upcoming years new liquid crystal-based technologies could make drastic changes in these fields. Already on the market are "smart windows" that use liquid crystals and an electric current to turn windows from clear to translucent with the flip of a switch, readily providing a certain amount of privacy without sacrificing all incoming light. Liquid crystals have also been utilized for holography, stress testing of materials, and the

visualization of radio frequency waves, and will likely become even more important as the field of nanotechnology develops [55].

2.3.4 Liquid Crystalline Polymers (LCPs)

Under appropriate conditions, certain polymers may exhibit liquid crystalline behaviour. Liquid crystalline polymers (LCPs, for short) are composed of assemblies of rigid molecular chains or chain segments which exhibit long range orientational order either in solution or in the melt. DNA and certain cellulose fibers are some common examples of LCPs [40].

Basically, there are two types of liquid crystal polymers; main chain and side chain. Main chain liquid crystal polymers (MCLCPs) consist of repeating mesogenic (liquid crystal like) monomer units and this is illustrated in Figure 2.12. The monomer unit must be anisotropic and bifunctional (one function at each end) to enable polymerization and the generation of mesophases.

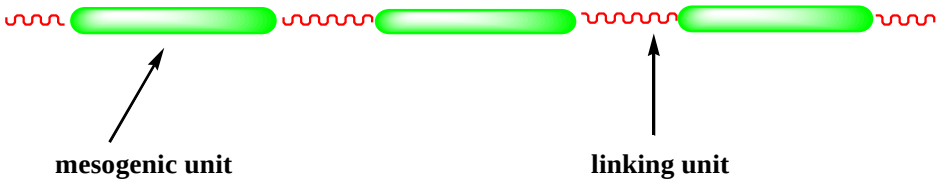


Figure 2.12 A general template for main chain liquid crystal polymers.

Side chain liquid crystal polymers (SCLCPs) consist of mesogenic structural moieties appended from a polymer backbone (Figure 2.13). The mesogenic units that have been used parallel those previously used for low molar mass liquid crystals, and the structural nature of the polymer backbone is widely variable. The mesogenic units (usually calamitic but many discotic types exist) are invariably separated from the polymer backbone by fairly long spacer units which are usually several methylene (-CH_2-) units, often with ester (-CO_2-) or ether (-O) units at the points of attachment. Attachment of the calamitic mesogenic units is usually at the terminal position (Figure 2.13a); however, a few polymers have their mesogenic units attached at a lateral position (Figure 2.13b).

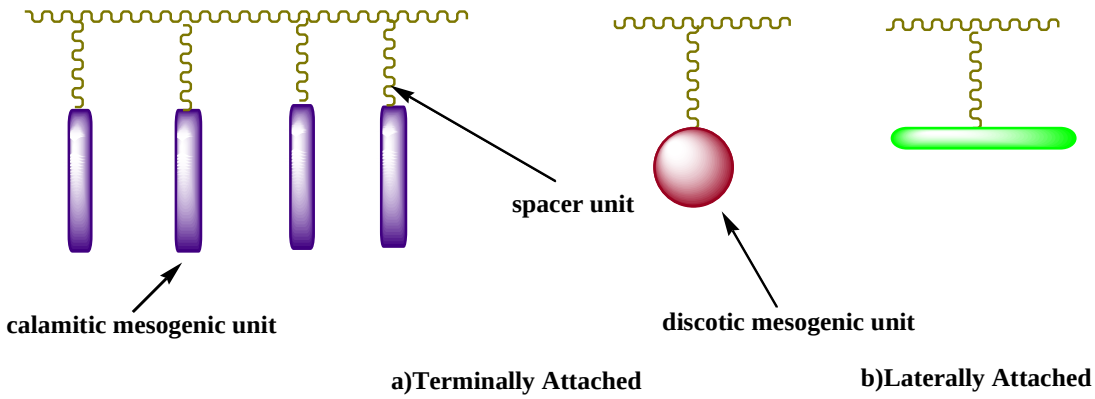


Figure2. 13 A general template for side chain liquid crystal polymers.

A third class of liquid crystal polymers is called combined liquid crystal polymers (Figure 2.14). These polymers, obviously enough, combine the features of MCLCPs and SCLCPs. Side chain mesogenic units can be attached, *via* a spacer unit, to a mesogenic main chain either at the linking unit (Figure 2.14a) or at the mesogenic unit (Figure 2.14b).

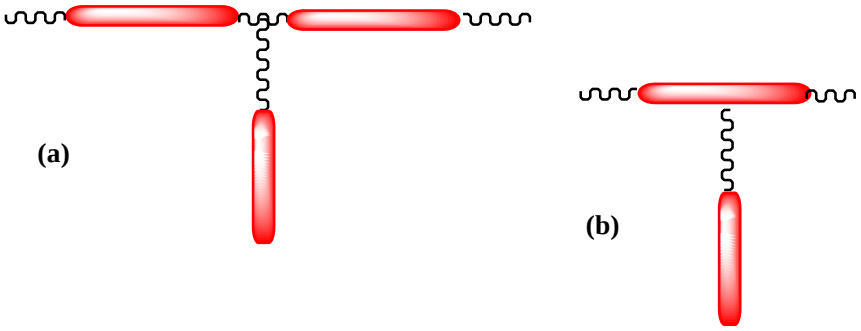


Figure 2. 14 A general template for combined liquid crystal polymers.

The synthesis and mesogenic behaviour of many liquid crystalline polymers has been published; however, in the vast majority of cases the molecular weights and polydispersities have not been determined. Accordingly, there are difficulties in truly relating mesogenic behaviour to polymer structure.

2.3.4.1 Main Chain Liquid Crystal Polymers (MCLCPs)

Main chain liquid crystal polymers have repeating mesogenic units that form a long chain (Figure 2.12). If the linking units are long and flexible, then a semi-flexible polymer results; however, if the mesogenic units are directly linked then the polymer will be very rigid and intractable. The degree of flexibility and the structural composition both determine the mesomorphic properties of MCLCPs. It was found in 1956 that a polypeptide formed a mesophase in solution; however,

systematic studies on main chain liquid crystal polymers did not begin until the 1970s.

MCLCPs are composed of chain units that vary in size. This distribution of chain sizes leads to wide ranges of melting to a liquid crystal phase and wide ranges over which the polymer clears to the isotropic liquid. Accordingly, biphasic regions are found to exist over wide temperature ranges. Nematic and smectic liquid crystal phases have been found in MCLCPs. Rigid polymers, of different chain sizes, have difficulty packing in a layer-like manner and so usually exhibit the nematic phase. However, polymers with flexible units between the mesogenic moieties can easily arrange in a layer-like arrangement. The flexible spacer tends to play the same role as the terminal chains in low molar mass liquid crystals and so the longer the spacer units the greater the smectic tendency. Overall, MCLCPs tend to be crystalline with very high melting points.

2.3.4.2 Side Chain Liquid Crystal Polymers (SCLCPs)

Side chain liquid crystal polymers were released in 1978 when Ringsdorf and coworkers inserted a flexible spacer unit between the rigid mesogenic unit and the polymer backbone (Figure 2.13). In SCLCPs the flexible polymer backbone has a strong tendency to adopt a random, coiled conformation. When mesogenic units are attached to the flexible polymer backbone, they will have a strong tendency to adopt an anisotropic arrangement. Clearly these two features are completely antagonistic, and where the mesogenic groups are directly attached to the backbone, then the dynamics of the backbone usually dominate the tendency for the mesogenic groups to orient anisotropically; accordingly, mesomorphic behaviour is not usually generated. However, if a flexible spacer moiety is employed to separate the mesogenic units from the backbone, then the two different tendencies of the mesogen (anisotropic orientation) and backbone (random arrangement) can be tolerated within the one polymeric system. If this theory is correct, the backbone should not influence the nature of the generated mesophases nor their thermal stabilities. However, the backbone does affect the mesomorphic properties of SCLCPs. The spacer moiety does not totally decouple the mesogenic unit from the backbone because the studies have shown that part of the spacer aligns with the mesogenic unit. However, enhanced decoupling is generated as the spacer moiety is lengthened. Spacer length influences the nature of the least ordered mesophase

exhibited and the overall thermal stability is influenced by the polymer backbone. Mesophases with a broad range tend to be favored by the use of flexible backbones (*e.g.*, polysiloxanes); a flexible backbone gives the mesogenic units more independence and so they can order more easily.

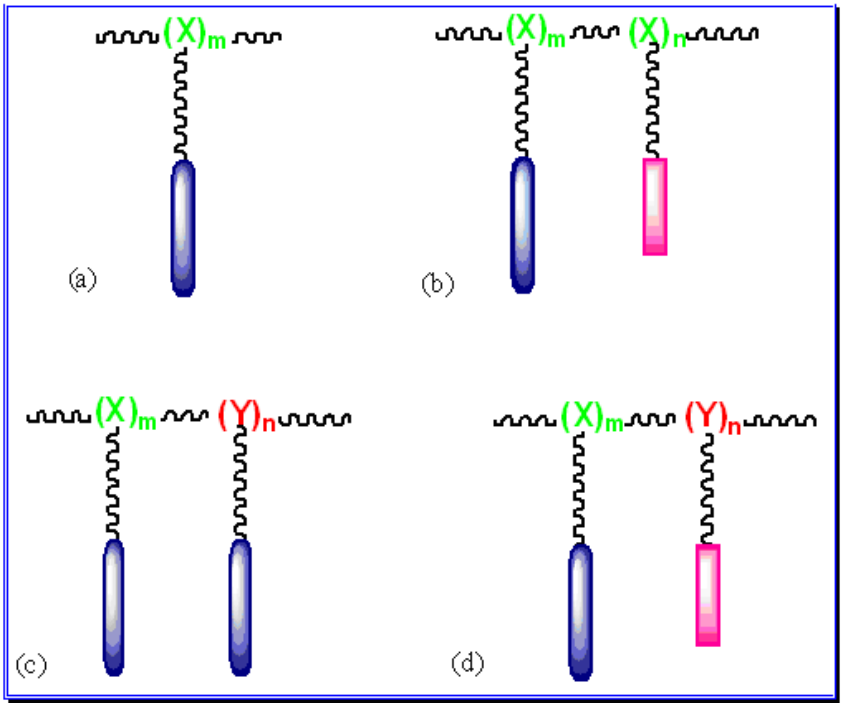


Figure 2.15 A range of different types of SCLCPs.

Many SCLCPs have been synthesized because of the combination of the vast number of mesogenic core units available from structure-property relationship evaluation of low molar mass liquid crystals and the many different backbone (BB) types possible (*e.g.*, siloxanes, acrylates, methacrylates, ethylenes, epoxides). Additionally, as shown in Figure 2.7, homopolymers (2.16a), SC copolymers (2.16b), BB copolymers (2.16c), and SC/BB copolymers (2.16d) considerably extend the scope of known and potential liquid crystal polymers.

2.3.5 The Applications of Side Chain Liquid Crystalline Polymers

- Application of side-chain LCPs in optical data storage
- Application of side-chain LCPs in non-linear optics
- Application of side-chain LCPs in display technology
- Side-chain LCPs used as stationary phases for gas chromatography, supercritical-fluid chromatography and high-performance liquid chromatography

- The application of side-chain LCPs as separation membranes
- The application of side-chain LCPs as solid polymer electrolytes
- Miscellaneous aspects for application of side-chain LCPs

3. EXPERIMENTAL PART

3.1. Materials and Chemicals

3.1.1 Monomer

Vinyl Acetate (Aldrich)

Distilled *in vacuo* and stored under nitrogen over calcium turnings at -4^{o}C.

3.1.2 Solvents

Methanol (Technical)

Methanol was used for the precipitation of polymers without further purification

Hexane (Aldrich)

Predried over magnesium sulfate and calcium hydride and then distilled over sodium immediately before use.

Tetrahydrofuran (THF) (J.T.Baker)

Predried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

Toluene (Merck)

Refluxed over CaH_2 for 24 hours, then distilled over sodium wire and benzophenone prior to use.

Ethanol (J.T.Baker)

Predried over magnesium sulfate and then distilled from calcium hydride before use.

Dimethyl Sulphoxide (DMSO) (Merck)

Distilled over CaH_2 before use.

Chloroform (J.T. Baker)

Shaken with several portions of conc. H_2SO_4 washed throughly with water and dried with $CaCl_2$ before filtering and distilling (61 ^{o}C / 760 mm Hg).

Benzene (Merck)

Purified by shaking with conc. H_2SO_4 then with water, dilute NaOH and water, followed by drying with $CaCl_2$ and distilled over sodium wire (80,1 ^oC / 760 mm Hg).

3.1.3 Other Chemicals and Reagents

2, 2'-Azobisisobutyronitrile (AIBN) (Aldrich)

2, 2'-Azobisisobutyronitrile was recrystallized from ethanol.

4'-Hydroxy-4-biphenylcarbonitrile (Across)

It was used without further purification

1-Chloro-6-hydroxyhexane (Across)

It was used without further purification

11-Bromo-1-undecanol (Across)

It was used without further purification.

Triethylamine (TEA) (J.T. Baker)

Distilled with fractionation under CaH_2.

Acryloyl Chloride (Aldrich)

It was used without further purification.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz Spectrometer.

3.2.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of an Waters 996 apparatus equipped with three Waters ultrastyragel columns (HR series 4,3,2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights of polymers were calculated with the aid of polystyrene standards.

3.2.3 Differential Scanning Calorimeter (DSC)

The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (TA DSC Q10) in a flowing nitrogen atmosphere at heating rate 5 and 10^0C / min.

3.2.4 Infrared Spectroscopy

IR spectra were recorded on Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.5 Polarized Optical Microscopoy (POM)

The structure and type of phase was determined by using Leitz Laborlux 12 POL S polarized microscopy,which has Mettler Toledo FP90 Central Processor and Mettler Toledo FP82HT Hot Stage.

3.3. Synthesis of Chemical Compounds

3.3.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy) hexyl acrylate (LC6)

3.3.1.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy) hexane-1-ol

Under nitrogen 6-chloro-1-hexanol (20 mmol, 2.25 ml) was added dropwise to a stirring mixture of 4'-hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3 g) and anhydrous K_2CO_3 (14.5 mmol, 2 g) in 200 ml of anhydrous DMSO. The reaction mixture was heated at 110^{o}C for 2 hours. After this process, the reaction mixture was added dropwise to 400 ml of 10% NaOH solution at room temperature and filtered. The resultant was dried at 40^{o}C in vacuum. It was recrystalized from benzene. White crystalline product was obtained and dried under vacuum (m.p= 90-92, yield 75%).

3.3.1.2 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy) hexyl acrylate

Under nitrogen atmosphere acryloyl chloride (16.69 mmol, 1.36 ml) in 20 ml of dry THF was added to dropwise to a stirring mixture of triethylamine (21.03 mmol, 2.93 ml) and 6-(4-Cyanobiphenyl-4'-oxy) hexane-1-ol (10.12 mmol, 2.99 g) in 20 ml of dry THF at 0^{o}C. The reaction mixture was stirred for 15 hours at room temperature. Then it was added dropwise to 300 ml of 5% HCl solution. After neutralizing the mixture, it was filtered and dried in vacuum. The resulting product was recrystalized

from ethanol. White crystals were obtained and dried under vacuum (m.p = 72 ^{o}C, yield 75-80%) [56,57].

^{1}HNMR ($CDCl_3$): δ (ppm) : 1,2 – 2,0 (m, 8H, -$(CH_2)_4$), 3,9 – 4,1 (t, 2H, -OCH_2), 4,1 – 4,3 (t, 2H, ArO-$\underline{CH_2}$), 5,8 – 5,9 (d, 1H, =CH_2), 6,0 – 6,2 (m, 1H, =CH), 6,3 – 6,5 (d, 1H, =CH_2), 6,9 – 7,0 (d, 2H, 3' and 5' aromatic protons), 7,5 – 7,6 (d, 2H, 3 and 5 aromatic protons), 7,6 – 7,8 (q, 4H, 2, 6 and 2', 6' aromatic protons) (Figure 3.1).

3.3.2 Synthesis of 11-(4-Cyanobiphenyl-4'-oxy) undecanyl acrylate (LC11)

3.3.2.1 Synthesis of 11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol

Under nitrogen 11-Bromo-1-undecanol (20 mmol, 2.25 ml) was added dropwise to a stirring mixture of 4'-hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3 g) and anhydrous K_2CO_3 (14.5 mmol, 2 g) in 200 ml of anhydrous DMSO. The reaction mixture was heated at 110^{o}C for 3 hours. After this process, the reaction mixture was added dropwise to 400 ml of 10% NaOH solution at room temperature and filtered. The resultant was dried at 40^{o}C in vacuum. It was recrystalized from ethanol. White crystalline product was obtained and dried under vacuum (m.p= 90-92, yield 83%

3.3.2.1 Synthesis of 11-(4-Cyanobiphenyl-4'-oxy) undecanyl acrylate

Under nitrogen atmosphere acryloyl chloride (16.69 mmol, 1.36 ml) in 20 ml of dry THF was added to dropwise to a stirring mixture of triethylamine (21.03 mmol, 2.93 ml) and 11-(4-Cyanobiphenyl-4'-oxy) undecan-1-ol (10.12 mmol, 2.99 g) in 20 ml of dry THF at 0^{o}C. The reaction mixture was stirred for 18 hours at room temperature. Then it was added dropwise to 300 ml of 5% HCl solution. After neutralizing the mixture, it was filtered and dried in vacuum. The resulting product was recrystalized from ethanol. White crystals were obtained and dried under vacuum (m.p = 92-93 ^{o}C, yield 75-80%).

^{1}HNMR ($CDCl_3$): δ (ppm): 1,2 – 2,0 (m, 8H, -$(CH_2)_4$), 3,9 – 4,1 (t, 2H, -OCH_2), 4,1 – 4,3 (t, 2H, ArO-$\underline{CH_2}$), 5,8 – 5,9 (d, 1H, =CH_2), 6,0 – 6,2 (m, 1H, =CH), 6,3 – 6,5 (d, 1H, =CH_2), 6,9 – 7,0 (d, 2H, 3' and 5' aromatic protons), 7,5 – 7,6 (d, 2H, 3 and 5 aromatic protons), 7,6 – 7,8 (q, 4H, 2, 6 and 2', 6' aromatic protons)

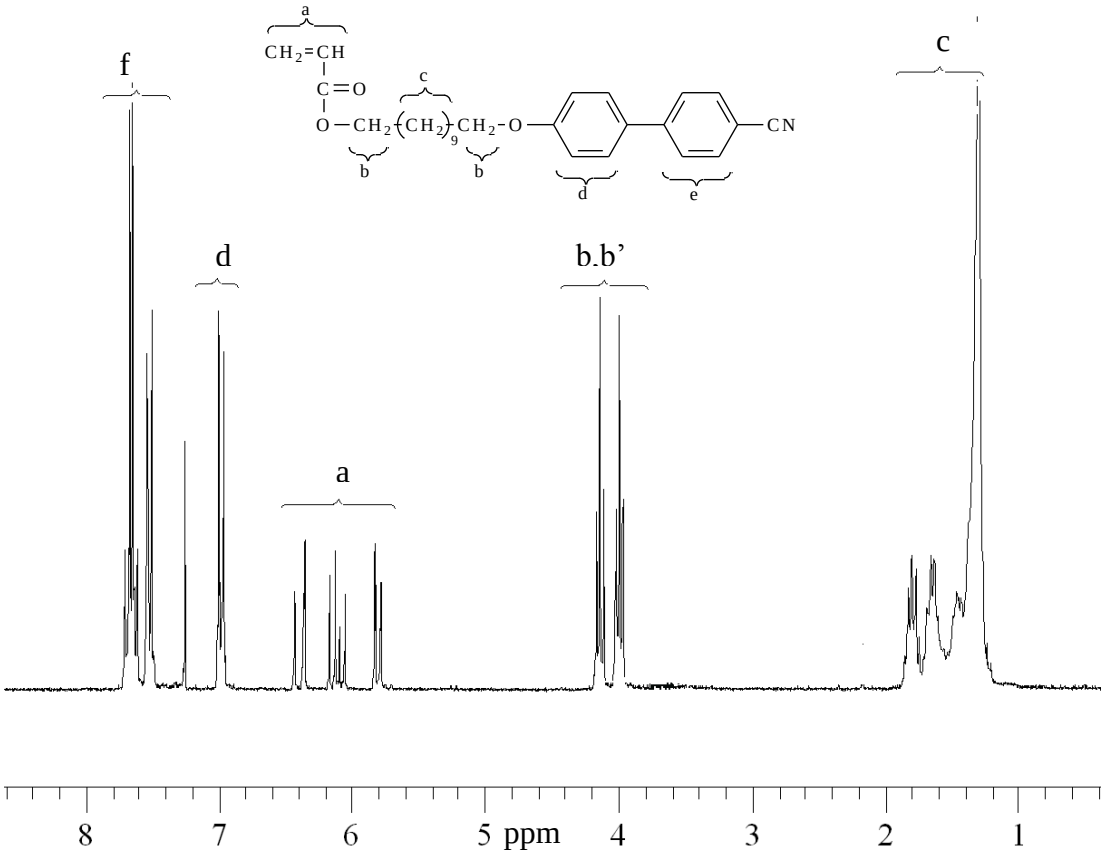


Figure 3.1 ^{1}H NMR spectrum of LC11 recorded in $CDCl_3$.

3.3.3 General Polymerization Procedure for CFRP of LC6 or LC11

In a typical polymerization reaction, predetermined quantities of monomer LC6 and initiator AIBN were dissolved in solvent (toluene or chloroform). The reaction mixture was introduced in a Pyrex glass tube, thoroughly freeze-thaw degassed and the sealed under vacuum. After reacting for variable time periods at 65^{o}C, the polymer was precipitated by addition of a ten-fold excess of methanol, filtered and purified by reprecipitation into methanol. The polymer was then dried in vacuo for 18 h.

3.3.4 General Polymerization Procedure for CFRP of VAc

A round bottom-flask equipped with magnetic stirrer was vacuumed and back-filled with dry nitrogen three times. Certain amounts of vinyl acetate, AIBN and toluene were introduced under inert atmosphere. The flask was placed in an oil bath and held for 24 h at 110 ^{o}C. After the polymerization completed, solvent was evaporated. The polymer was obtained by means of further drying in a vacuum oven for over night.

^{1}HNMR ($CDCl_3$): δ (ppm): 1,9 – 2,2 (t, 2H, -CH_2), 2.39 (3H, $OCOCH_3$), 5.03 (p, 1H, -CH)

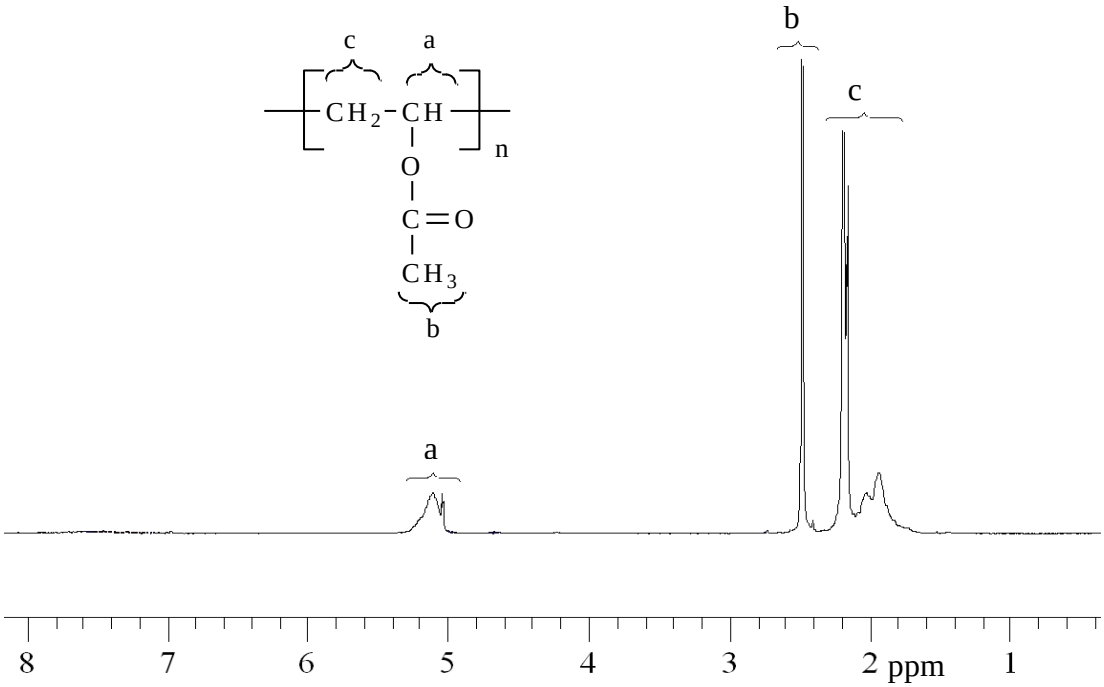


Figure 3.2 ^{1}HNMR spectrum of VAc recorded in $CDCl_3$.

3.3.5 General Copolymerization Procedure for CFRP of VAc and LC6 or LC11

Predetermined quantities of LC6 or LC11, VAc and AIBN were dissolved in toluene. In the case of the copolymerisation of VAc and LC11, chloroform was used as a solvent. The reaction mixture was introduced into a pyrex tube and sealed under nitrogen. The tube was immersed in an oil bath at 65 ^{o}C and held for 48h.The polymer was precipitated by addition of a ten-fold excess of methanol filtered and purified by reprecipitation into methanol. The polymer was then dried in vacuo for 18 h.

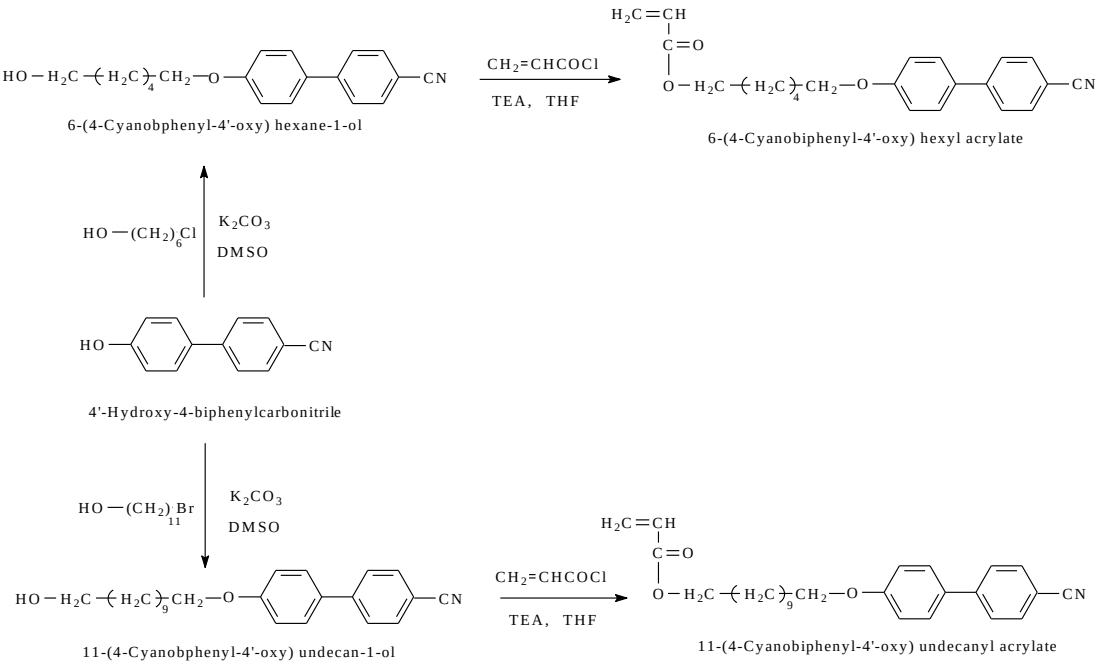
^{1}HNMR ($CDCl_3$): δ (ppm): 1,2 – 2,0 (m, 8H, -$(CH_2)_4$), 2.29 (3H, OCCH3 and 1H, -CH of LC6), 3,97 (t, 2H, -OCH_2), 4,85 (1H, -CH of VAc) 6,3 – 6,5 (d, 1H, =CH_2), 6,8 – 6,9 (d, 2H, 3’ and 5’ aromatic protons), 7,4 – 7,5 (d, 2H, 3 and 5 aromatic protons), 7,5 – 7,6 (q, 4H, 2, 6 and 2’, 6’ aromatic protons).

4. RESULTS AND DISCUSSION

4.1 Synthesis of Liquid Crystalline Acrylate Monomers

In this thesis, copolymers of VAc with liquid crystalline acrylate monomers were prepared by using AIBN as initiator at 65°C. In this purpose, liquid crystalline acrylate monomers with a different flexible group length were synthesized. By inserting flexible segments to separate the mesogenic units along the polymer chain, the chemical periodicity of the molecule preserved.

6-(4-Cyanobiphenyl-4'-oxy) hexyl acrylate (LC6) and 11-(4-Cyanobiphenyl-4'-oxy) undecanyl acrylate (LC11) were synthesized according to the synthetic route [55,56] illustrated in Scheme 4.1.



Scheme 4.1 Synthesis of liquid crystalline acrylate monomers (LC6 and LC11)

The structure of the monomers LC6 and LC11 were characterized by FT-IR and ^{1}H-NMR spectroscopy. Characteristic absorbance bands for both monomer were identified such as the C=C stretching at 3094, 3165 cm^{-1}, C = O stretching at 1699 cm^{-1} and CN stretching at 2224 cm^{-1}. Figure 4.1 shows the FT-IR spectrum of LC6.

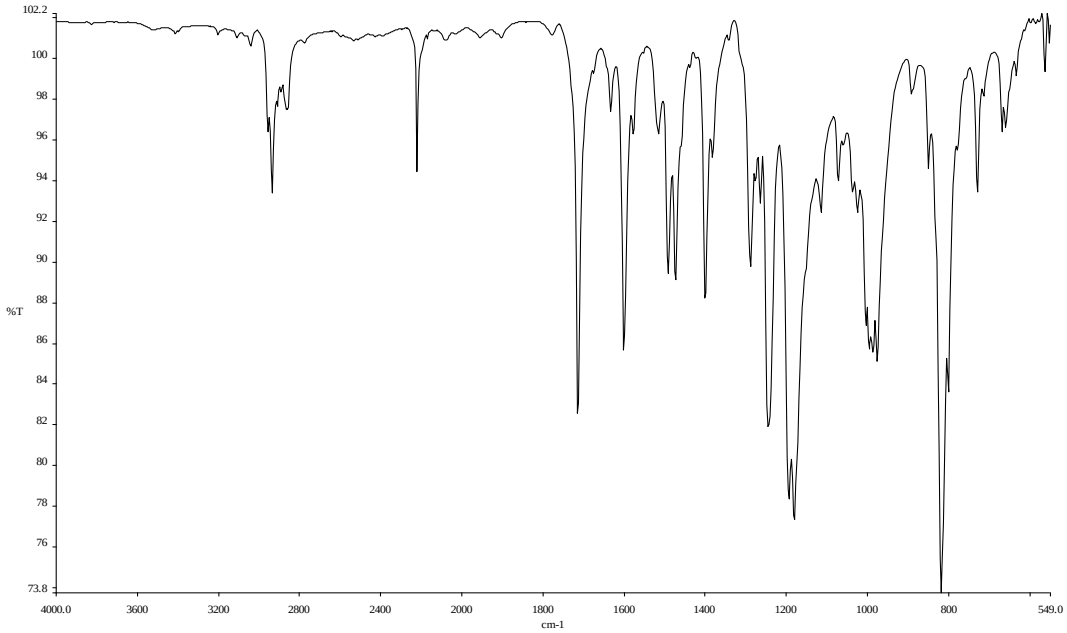


Figure 4.1 FT-IR Spectrum of LC6

^{1}H-NMR spectra of the monomers LC6 and LC11 exhibit the signals in the range of 2.0-1.2 ppm corresponding to CH_2 protons, 4.2-4.9 ppm corresponding to H_2C-O protons, 6.4-5.7 ppm corresponding to CH_2=CH protons and 7.7-6.9 ppm corresponding to aromatic protons. Figure 4.2 depicts the ^{1}H-NMR spectrum of LC6.

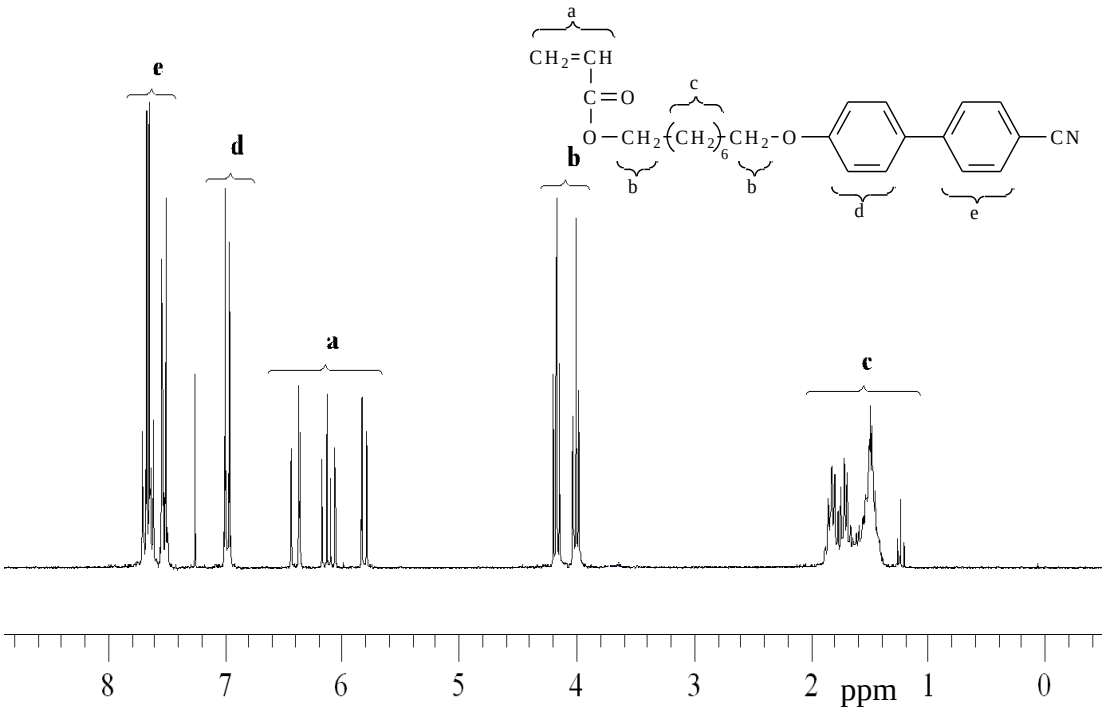


Figure 4.2 ^{1}H NMR spectrum of LC6 recorded in $CDCl_3$.

Thermal properties of the monomers LC6 and LC11 have been studied by DSC. The DSC thermogram of the monomer LC6 exhibits a sharp endothermic melting curve at 72^{o}C followed by an exothermic polymerization curve at 150^{o}C . As you can see Figure 4.3, monomer LC11 exhibits endothermic melting curve at 92^{o}C.

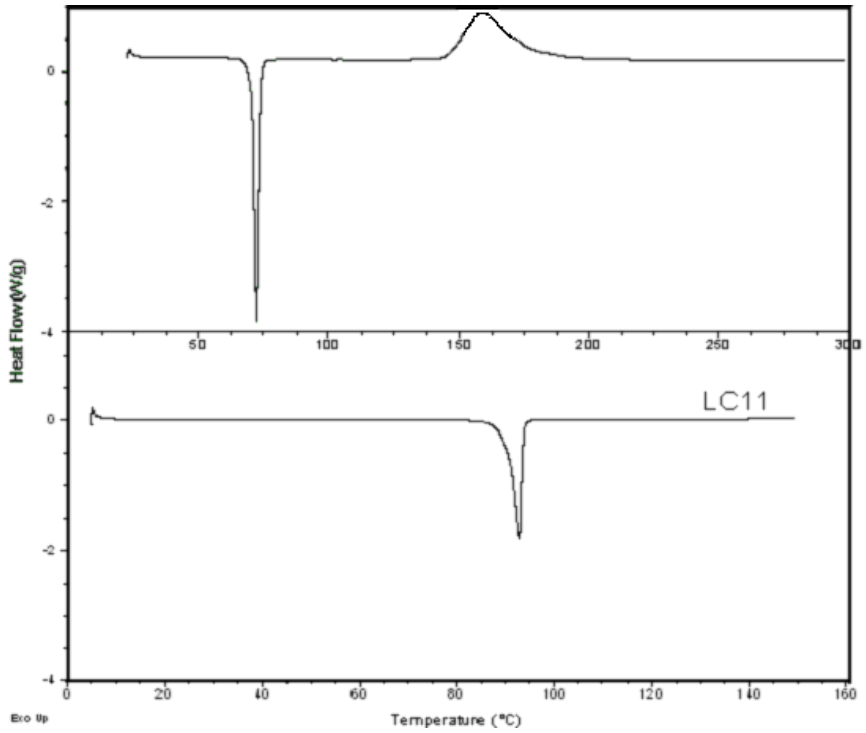
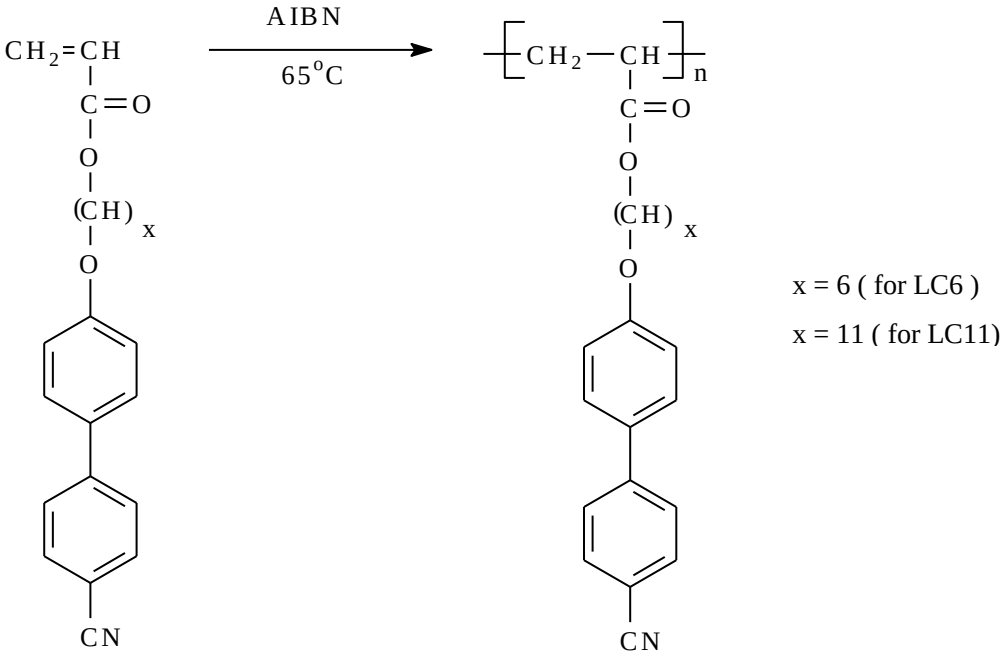


Figure 4.3 DSC curve for LC6 (second heating, 10^{o}C min^{-1}) and LC11 (second heating, 2^{o}Cmin^{-1})

4.2 Homopolymerization of LC6 and LC11

Homopolymers were synthesized via CFRP using AIBN as an initiator as illustrated in Scheme 4.2. The results of the polymerization reactions are summarized in Table 4.1.



Scheme 4.2 Synthesis of LC6 and LC11 homopolymers

The structures of homopolymers were defined by ^{1}H-NMR (Fig 4.4). The H-NMR spectrum show the signals at 2.0-1.2 ppm (CH_2), 2.26 ppm (C-H), 3.90 ppm (-OCH_2) and 7.5,6.5 ppm (Ar-H).

Table 4.1 CFRP of LC6 and LC11 [a]

Code	**Monomer (mol). 10^{-4}**	**AIBN (mol). 10^{-3}**	**Solvent**	**Time (h)**	**% Conv.**	**M_n [b]**	**M_w/M_n [b]**
PLC6	2	5	Toluene	8	21	7291	2.01
PLC11	3	5	$CHCl_3$	8	24	6679	1.39

[a] Temperature ; 65 °C

[b] Determined by GPC, based on PSt standarts

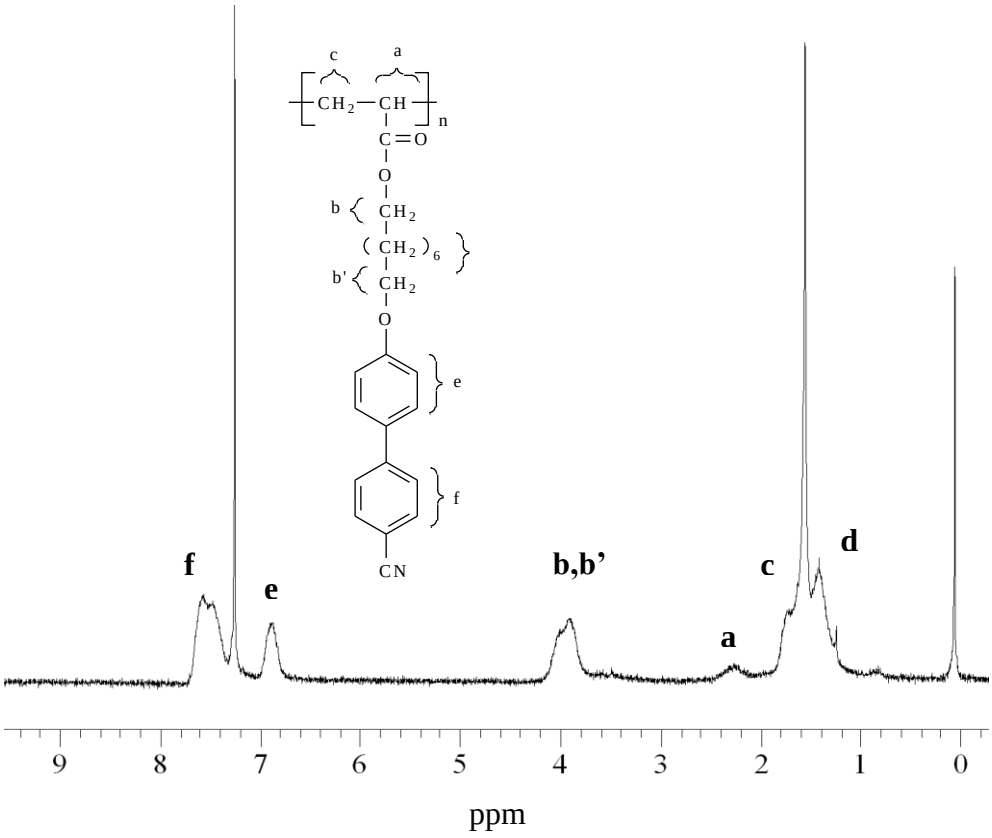


Figure 4.4 ^{1}H-NMR spectrum of PLC6 recorded in $CDCl_3$

The thermal and LC behaviours of the polymers prepared were investigated and considered as model polymers for the phase transition temperatures of the copolymers as measured by DSC measurements and polarizing microscopy analysis (POM). There are conflicting data in the literature for different polymer samples of LC6 and LC11 [45]. We found that PLC6 formed a nematic mesophase and PLC11 formed two different types of smectic phase structure S_A and S_c between their glass transition temperature (T_g) and the isotropization temperature (T_i). The DSC curves of homopolymers are shown in Figure 4.5.

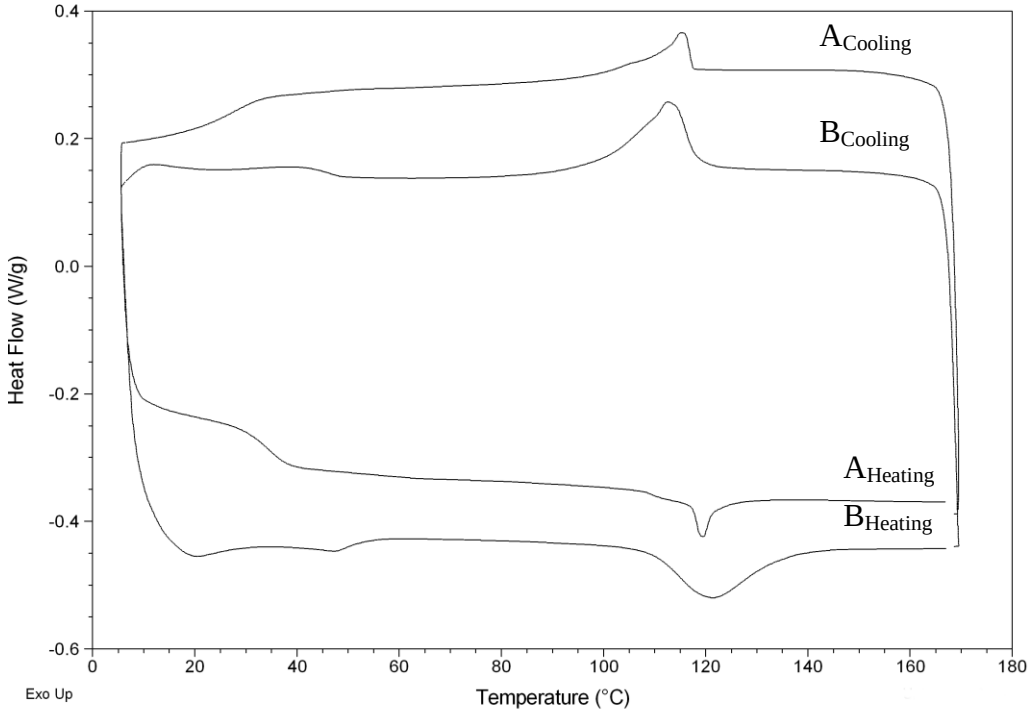


Figure 4.5 DSC curves for PLC6 (A) (first cooling, -10^{o}C min^{-1}; second heating, 10^{o}C min^{-1}) and PLC11 (B) (first cooling, -10^{o}C.min^{-1}; second heating, 10^{o}C.min^{-1})

Side chain polymer with longer spacer groups PLC11 tends to favour smectic mesomorfism , whereas polymer with shorter spacer units more frequently show a nematic order. Liquid crystalline properties of PLC6 and PLC11 were observed in DSC traces and in POM. Although monomers LC6 and LC11 do not exhibite the liquid crystalline properties, homopolymers of corresponding monomers PLC6 and PLC11 exhibites nematic phase and two different type smectic phase respectively, below the glass transition temperature [55]. Thermal properties of liquid crystalline acrylate polymers were given Table 4.2.

Table 4.2 Thermal Properties of LC6 and LC11 Homopolymers[a]

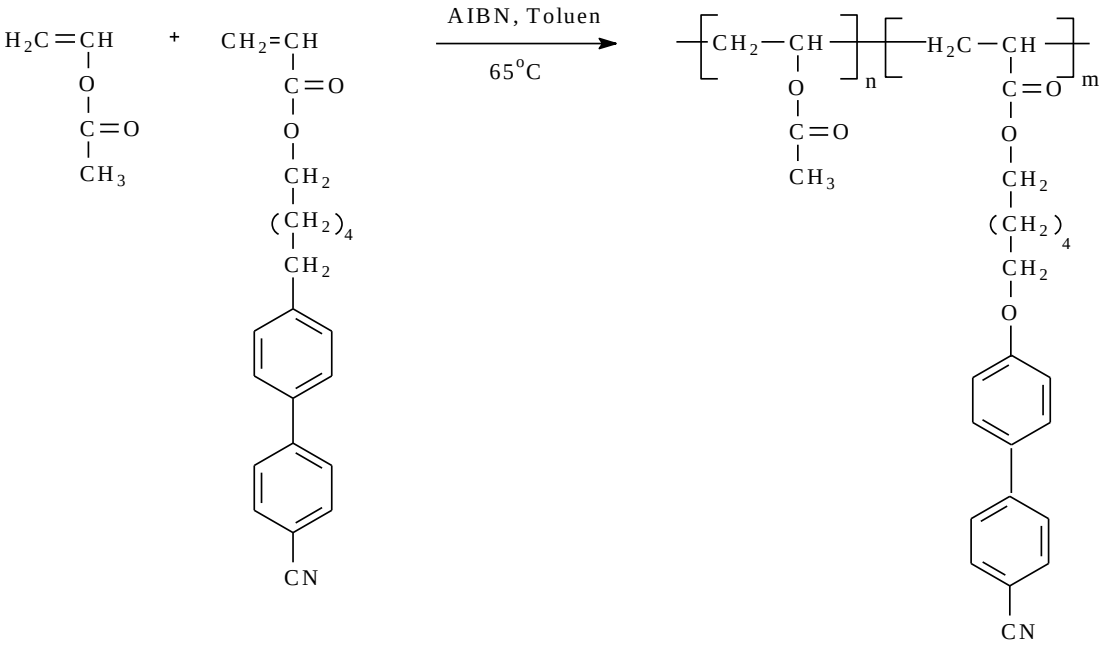
	T_g ^{o}C	$T_{g\text{-}SC}$ ^{o}C	$T_{SC\text{-}SA}$ ^{o}C	$T_{SA\text{-}I}$ ^{o}C	$T_{N\text{-}I}$ ^{o}C	$\Delta H_{N\text{-}I}$ J/g	$\Delta H_{SA\text{-}I}$ J/g
PLC6	34.63	-	-	-	119.54	0.83	-
PLC11	nd[b]	19.82	47.54	121.34	-	-	6.09

[a] By DSC
[b] Not dedected

4.3 Conventional Free Radical Copolymerization of LC6 and VAc

The addition of vinyl acetate to the basic liquid crystalline acrylate polymer structure results in modification of properties such as flexibility and optical properties etc. By varying the vinyl acetate content, different copolymers can be tailored to meet specific end use applications.

Copolymers were obtained from the conventional free radical copolymerization of 6-(4-Cyanobiphenyl-4'-oxy) hexyl acrylate and vinyl acetate using AIBN as an initiator according to Scheme 4.3. The results of the polymerization reactions and molecular weight and molecular weight distributions of the copolymers are given in Table 4.3.



Scheme 4.3 Synthesis of Copolymers of LC6 and VAc

The copolymer structures were assigned by means of ^{1}H-NMR spectral measurements (Fig 4.6). The spectrum of the copolymer (LC6-VAc) displays the signals in the range 2.0-1.2 ppm corresponding to CH_2 protons, 2.3 ppm corresponding to CH, CH_3 protons of the carbonyl groups, the characteristic peaks of LC6 appear at 3.92 ppm corresponding to O-CH_2 protons and 7.6-6.9 ppm corresponding to aromatic protons. Moreover the characteristic peak of vinyl acetate (O-CH) appears at 4.86 ppm. Figure 4.6 depicts the ^{1}H-NMR spectrum of LC6-VAc copolymer.

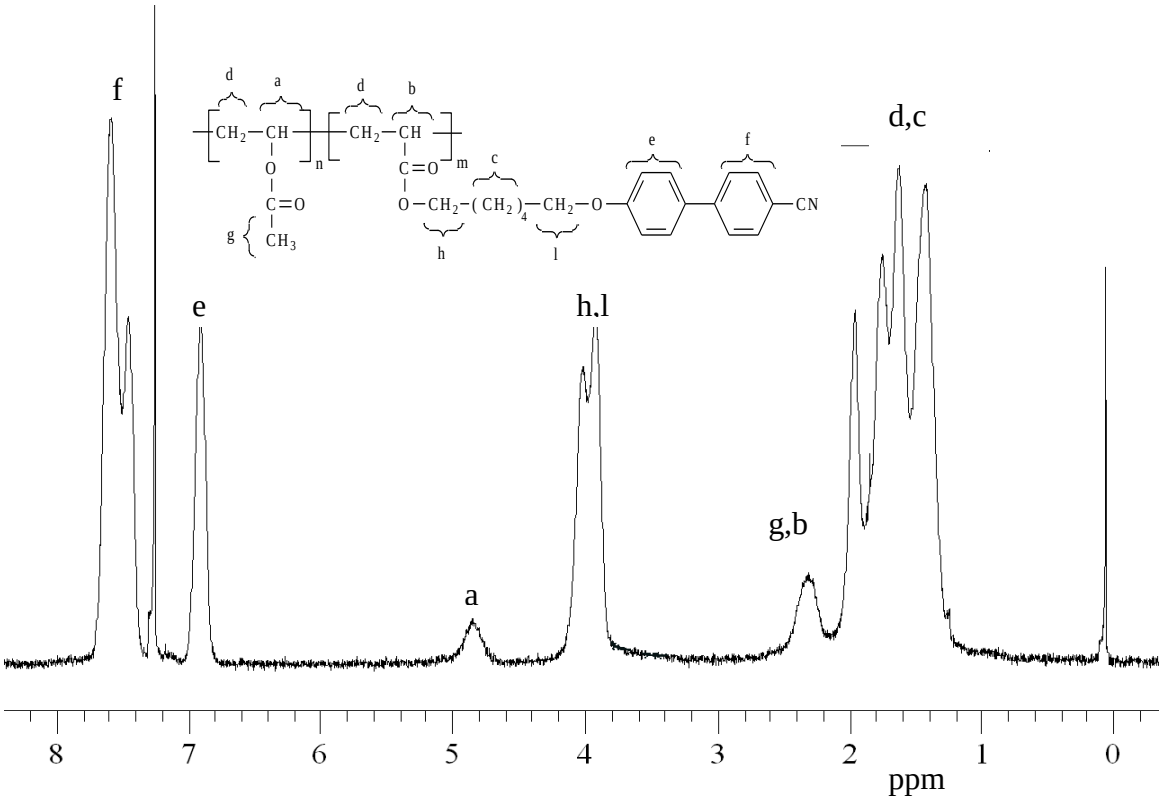


Figure 4.6 ^{1}H NMR spectrum of Copolymer **(**LC6-VAc**)** recorded in $CDCl_3$.

Table 4.3 Conventional Free Radical Copolymerization of LC6 and VAc by using AIBN[a]

Run	LC6 (mol)10^{-4}	VAc (mol)10^{-4}	Copolymer Composition[b](mol,%) LC6	VAc	Conv. %	M_n[c]	M_w/M_n[c]
1	10	90	15	85	24	19163	2.01
2	20	80	44	56	24	12419	1.99
3	30	70	53	47	18	17444	2.99
4	40	60	57	43	19	17748	2.35
5	50	50	49	51	18	25162	2.05
6	60	40	60	40	56	21260	2.60
7	70	30	63	37	83	18257	2.77
8	80	20	73	27	74	34975	2.19
9	90	10	49	51	83	27011	2.60

[a]Reaction Conditions : Temperature;65^{o}C , Solvent ; Toluen, Time; 48h
[b]Copolymer composition determined by^{1}H-NMR
[c] Determined by GPC, based on PSt standards

Mol fraction of the monomer units in the copolymer was determined by the integral areas in the ^{1}H-NMR spectrum and using the following formula [58].

$(8F_1 + 0) / (15 F_1 + 6F_2) = A_1/A_2$

$F_1 + F_2 = 1$

$F_1 = 6A_1 / 8A_2\text{-}9A_2$

A_1 = Area of aromatic protons
A_2 = Area of aliphatic protons

F_1 = Copolymer composition of LC6
F_2 = Copolymer composition of VAc

Terminal-model reactivity ratios of the LC6-VAc copolymers were calculated by the well-known extended Kelen–Tüdos (Ex. K-T) method from the composition of the monomer feed and that of the instantaneously formed copolymer.[59].

Extended Kelen–Tüdos method considers possible drift in composition of the copolymer as a result of considerable monomer conversions. This method essentially uses the equation (4.1)

$$\eta = (r_1 + r_2/\alpha) \xi - r_2/\alpha \quad (4.1)$$

where η and ξ are functions of both feed and copolymer compositions defined as,

$$\eta = G / (H + \alpha) \quad (4.2)$$

$$\xi = H / (H + \alpha) \quad (4.3)$$

H and G are defined using a conversion-dependent constant Z, which is expressed as,

$$Z = \log (1 - \xi_1) / \log (1 - \xi_2) \quad (4.4)$$

ξ_1 and ξ_2 are respectively the partial molar conversions in monomers M_1 and M_2 and given as,

$$\xi_1 = \xi_2 \cdot (Y / X) \quad (4.5)$$

$$\xi_2 = [w(\mu + X)] / (\mu + Y) \quad (4.6)$$

where,

$$Y = f1 / f2 \quad (4.7)$$

$$X = F_1 / F_2 \quad (4.8)$$

$$\mu = \mu_2 / \mu_1 \quad (4.9)$$

μ_2 and μ_1 represent the molecular weights of monomer 1 and 2, respectively, and w is the total fractional conversion. Thus, the H and G values are defined,

$$H = Y / Z^2 \quad (4.10)$$

$$G = (Y-1) / Z \quad (4.11)$$

and α is an arbitrary parameter, usually taken as,

$$\alpha = (H_{max} \cdot H_{min})^{1/2} \quad (4.12)$$

As can be seen in the Table 4.4, the parameters required for Extended Kelen Tüdös Method were calculated. Extended Kelen Tüdös Method provides reliable reactivity ratios up to ~ 60 % [59]. So, new low conversion copolymers were obtained under 60 %.

Table 4.4 Parameters Required to Construct the η vs. ξ Plot of the Extended Kelen-Tüdös Method for LC6 copolymers

Run	F_1[a] (%)	f_1[b] (%)	% Conv.	X	Y	G	H	η	ξ
1	20	51	10	0.25	1.04	0.009	0.055	0.023	0.143
2	40	51	29	0.66	1.04	0.024	0.371	0.034	0.529
3	60	55	25	1.5	1.22	0.282	2.005	0.120	0.858
4	70	70	48	1	1	0	1	0	0.75

[a]Mol fraction of LC6 monomer in feed
[b]Mol fraction of LC6 monomer in copolymer

η vs. ξ Plot of the Extended Kelen-Tüdös Method was drawn and obtained plot equation. The graphical plots for the VAc and LC6 copolymers are given in Figure 4.7. As can be seen from the Fig 4.7, the plots were linear indicating that copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit. α value was calculated by using equation (4.12) as 0.33 for LC6 copolymers. r_1 and r_2 correspond to reactivity ratios of LC6 and VAc, respectively.

$$\eta = (r_1 + r_2 / \alpha)\,\xi - r2 / \alpha$$

$$y = 0.078x - 0.0002$$

$$r_1 = 0.078$$

$$r_2 = 0.0000$$

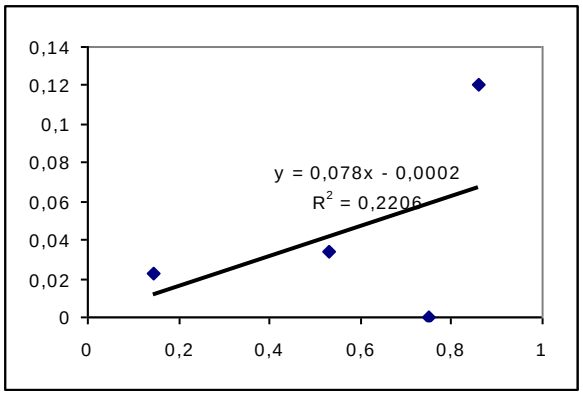


Figure 4.7 Plot of the Extended Kelen-Tüdös Method for the VAc and LC6 copolymers

The r_1 and r_2 values obtained by the Extended Kelen-Tüdös Method are 0.078 and 0.0000 respectively. The $r_1 . r_2$ value calculated as 0.0000 indicating that copolymers of VAc and LC6 are alternating.

The thermal and the LC behaviors of the copolymers prepared were investigated by DSC measurements and polarizing microscopy observations. The phase transition temperatures and enthalpies are summerized in Table 4.5.

Table 4.5 Thermal Analysis of LC6 Copolymers

Run	**% F_1[a]**	**Mn[b]**	**Tg_{exp} °C[c]**	**Tg °C[d]**	**Transition Temperature[e]**	**ΔH_{N-I} J/g[f]**
1	15	19163	32,25	nd	G 70,8 S 144,6 N 156,9 I	0,07
2	44	12419	38,28	39,64	G 77,1 S nd N 100 I	nd
3	53	17444	36,36	40,37	G 88,6 S nd N 103,2 I	nd
4	57	17748	36,84	39,40	G nd S nd N 102,4 I	0,93
5	49	25162	35,88	38,23	G 53,9 S nd N 105,5 I	1,10
6	60	21260	37,20	37,64	G nd S 100 N 118,8 I	1,25
7	63	18257	37,56	38,01	G nd S nd N 119,3 I	1,35
8	73	34975	38,76	37,70	G nd S nd N 122,1 I	1,45
9	49	27011	36,12	36,97	G nd S nd N 125,5 I	1,93

[a] Mol fraction of LC6 monomer in the copolymer, determined by ^1H NMR spectra.
[b] Determined by GPC, based on PSt standards
[c] Tg_{exp} calculated from $Tg_{exp} = F_1.Tg_{LC6} + F_2.Tg_{VAc}$ [61].
[d] The glass transition temperature of copolymers determined by DSC thermogram.
[e] The transition temperatures determined by DSC
[f] Enthalpy of transition from nematic to isotropic of copolymers.

As can be seen from the Table 4.5 the increase in T_i originates from a higher degree of decoupling between the motions of the mesogen and the polymer backbone. This is probably from the fact that the increase in composition of VAc unit in copolymer structure, results in the increase of the flexibility polymer backbone.

The thermal properties of the copolymers are influenced by their chemical structure, composition, and monomer sequence distributions. Several relationships have been employed to describe the effect of these parameters on the glass transition temperature of the copolymers [60].

The theoretical glass transition temperatures of the copolymers were calculated by using the following equation.

$$Tg_{exp} = F_1.Tg_{LC6} + F_2.Tg_{VAc} \quad (4.13)$$

The simplest equation describing the effect of composition on T_g is the Gibbs-Di Marzio equation [61].

As can be seen from the Table 4.5, the experimental T_g values of the copolymers are very close to the theoretical values. The DSC curves of copolymers (2-8) are shown in Figure 4.8

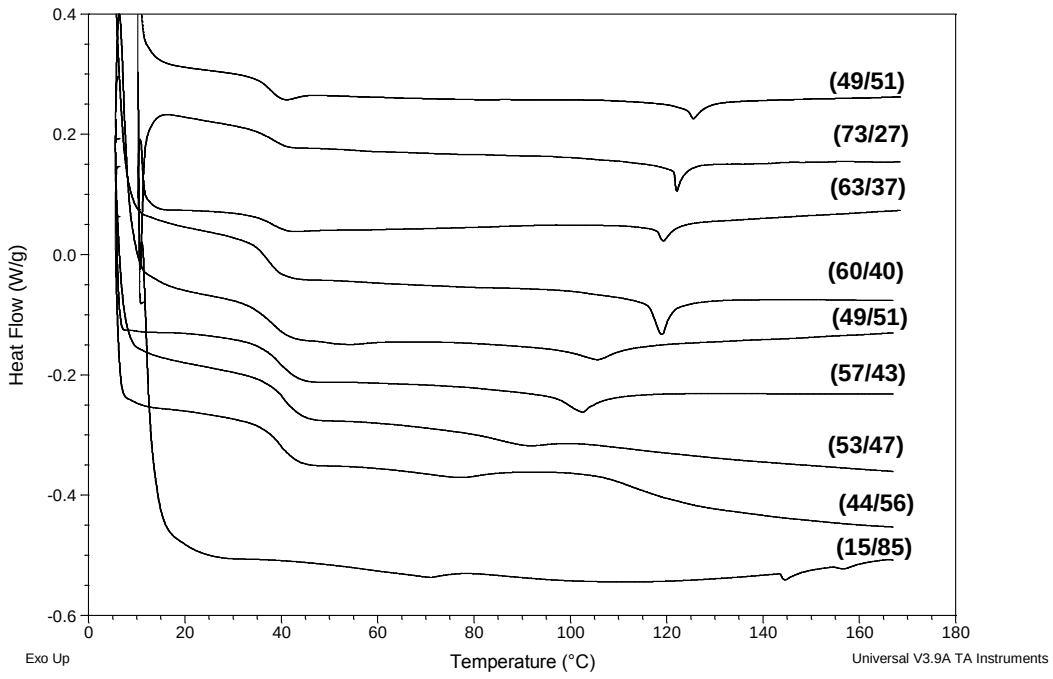


Figure 4.8 DSC thermogram of the copolymer with different composition (LC6/VAc)

The DSC curves of copolymers exhibit endothermic transitions centered at between 76-125°C due to the nematic-isotropic transition of the liquid crystalline copolymers. The glass transitions appear as a step at between 36-38°C.

The assignment of the mesophase type was made on the basis of the textures observed by polarizing optical microscopy as all LC6-VAc copolymers of the mesophases display the typical marbeled textures for nematic (N) and smectic phases.

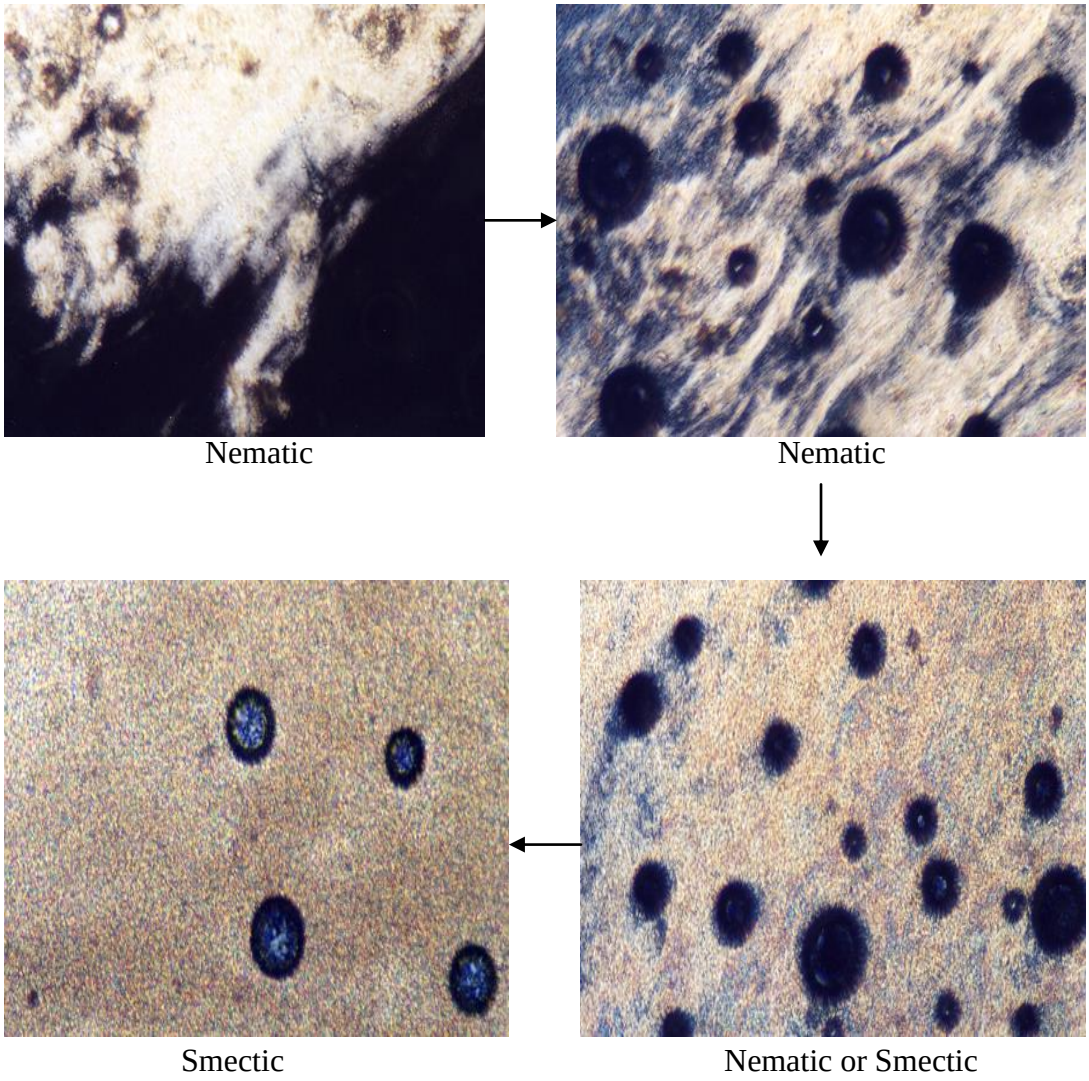
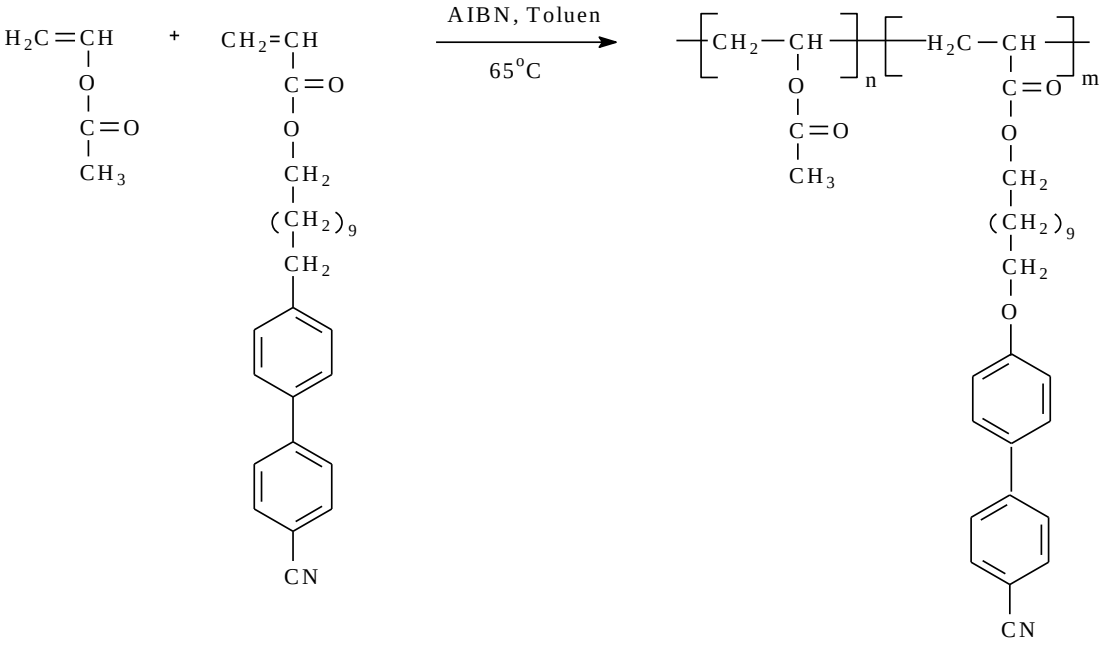


Figure 4.9 Textures observed under polarized optical microscopy for LC6-VAc copolymers (on cooling, x200)

4.4 Conventional Free Radical Copolymerization of LC11 and VAc

Copolymers were synthesized via CFRP by the same route used for the synthesis VAc and LC6 copolymers according to Scheme 4.3. Reaction conditions, molecular weight and molecular weight distributions of the copolymers are given in Table 4.6.



Scheme 4.4 Synthesis of Copolymers of LC11 and VAc

The structure of the copolymers were characterized by H-NMR spectroscopy. H-NMR spectra of the copolymers (Figure 4.9) exhibit the signals in the range 2.0-1.2 ppm corresponding to CH_2 protons, 2.3 ppm corresponding to CH, CH_3 protons of the carbonyl groups, the characteristic peaks of LC11 appear at 3.9 ppm corresponding to O-CH_2 protons and 7.6-6.9 ppm corresponding to aromatic protons. Moreover the characteristic peak of vinyl acetate (O-CH) appears at 4.86 Figure 4.9 depicts the ^{1}H-NMR spectrum of LC11-VAc copolymers.

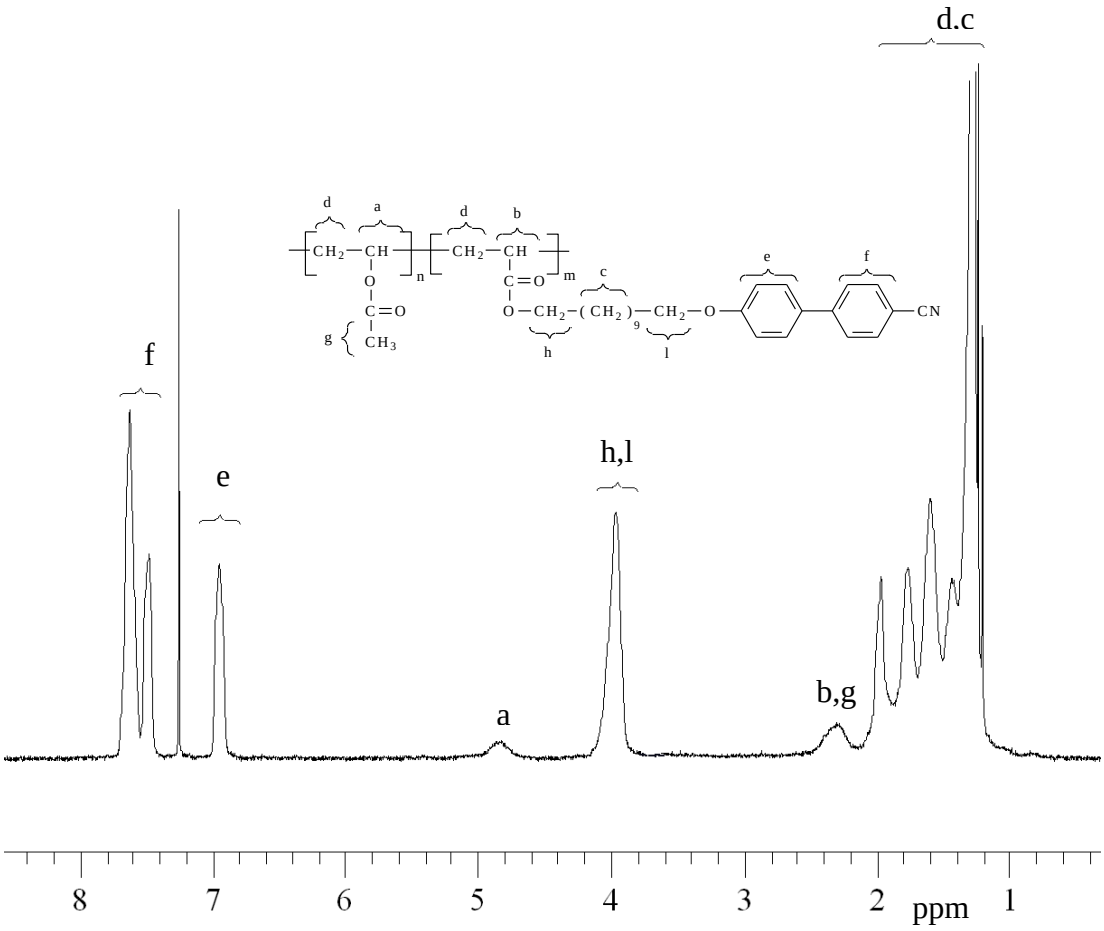


Figure 4.10 ^{1}H NMR spectrum of Copolymer **(**LC11-VAc**)** recorded in $CDCl_3$

Mol fractions of the monomer units in copolymer were also determined by the integral areas in the ^{1}H-NMR spectrum and using the same formula and the results are summarized in Table 4.6.

Table 4.6 Conventional Free Radical Copolymerization of LC11 and VAc using AIBN[a]

Run	LC11 (mol)10^{-4}	VAc (mol)10^{-4}	Copolymer Composition[b](mol,%) LC11	VAc	Conv. %	M_n[c]	M_w/M_n[c]
10	10	90	38	62	03	5251	1.49
11	20	80	34	66	35	7689	1.46
12	30	70	46	54	44	10113	1.52
13	40	60	28	72	24	10195	1.50
14	50	50	50	50	76	12698	1.52
15	60	40	27	73	77	13715	1.61
16	70	30	68	32	74	17950	1.60
17	80	20	60	40	81	17252	1.65
18	90	10	56	44	47	17378	1.78

[a] Reaction Conditions: Temperature ; 65°C, Solvent; Chloroform, Time; 48h
[b]Copolymer composition determined by ^{1}H-NMR Spectra.
[c]Determined by GPC, based on PSt standards

From the monomer feed ratios and the copolymer compositions, the reactivity ratios of VAc and LC11 were determined by the application of Ext K-T method.

Results from the analysis for Ext K-T are shown in Table 4.7. α was calculated as 0.23 by depending H_{min} and H_{max} values of LC11 copolymer series.

Table 4.7 Parameters Required to Construct the η vs. ξ Plot of the Extended Kelen-Tüdös Method for LC11 copolymers

Run	F_1[a] (%)	f_1[b] (%)	Conv. %	X	Y	G	H	η	ξ
1	20	30	30	0.25	0.43	-0.3	0,118	-0.86	0.34
2	40	80	17	0.66	4	0.455	0.092	1.41	0.28
3	60	89	42	1.5	8.09	1.024	0.168	2.57	0.42
4	70	87	37	2.33	6.69	1.68	0.58	1.44	0.72

[a]Mol fraction of LC11 in the feed.
[b]Mol fraction of LC11 in the copolymers.

The Ext K-T plots were shown in 4.10.

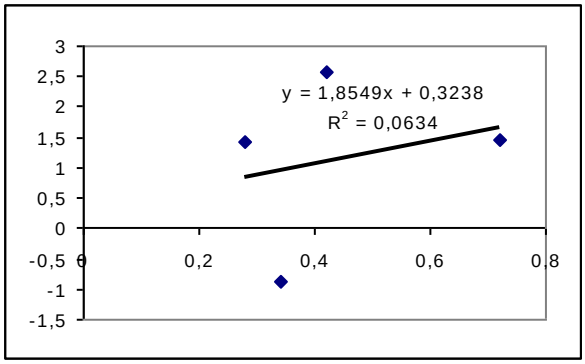


Figure 4.11 Plots of the Extended Kelen-Tüdös Method for LC11 copolymer

$$\eta = (r1 + r2 / \alpha)\,\xi - r2 / \alpha$$

$$y = 1.8549x + 0.3238$$

$$r_1 = 2{,}178$$

$$r_2 = -0.074$$

Although negative reactivity ratios of vinyl acetate for LC11 copolymers are absurd, its nearest rational values of $r_2 \approx 0$ and reactivity ratios of LC11 monomers, r_1 = 2.178. Random copolymerization can be suggested for LC11 and vinyl acetate system.

The value r_1 is greater than 1 and that of r_2 is less than 1, which indicates the presence of a larger proportion of LC11 units in the copolymer than in the feed.

The thermal behaviour of copolymers,10-18, was studied by DSC measurements and polarizing optical microscopy. The phase transition temperatures and relevant thermodynamic parameters are collected in Table 4.8.

Table 4.8 Thermal Analysis of LC11 Copolymers

	% F_1[a]	Mn	Tg_{exp} °C[b]	Tg °C[c]	Transition Temperature[d]	ΔH_{SAI} J/g[e]
10	38	5251	24,3	nd	G 54* S_C nd S_A 102 I	3,3
11	34	7689	24,9	12,38	G 64,5 S_C nd S_A 81 * I	4,75
12	46	10113	23,1	10,04	G nd S_C nd S_A 101 I	4,44
13	28	10195	25,8	11,53	G nd S_C nd S_A 114* I	4,01
14	50	12698	22,5	14,40	G nd S_C nd S_A 127* I	4,44
15	27	13715	25,9	16,21	G nd S_C 100 S_A 130* I	5,27
16	68	17950	22,2	16,91	G nd S_C nd S_A 135* I	5,39
17	60	17252	21	19,98	G nd S_C nd S_A 137* I	4,22
18	56	17378	21,6	10,73	G 43.9 S_C nd S_A 134* I	4,32

[a] Mol fraction of LC6 monomer in the copolymer, determined by ^{1}H NMR spectra.
[b] Tg_{exp} calculated from $Tg_{exp} = F_1.Tg_{LC6} + F_2.Tg_{VAc}$ [61].
[c] The glass transition temperature of copolymers determined by DSC thermogram.
[d] The transition temperature determined by DSC and POM
[e] Enthalpy of transition from smecticA to ısotropic of copolymers.
* The transition temperature determined by POM

As can be seen from the Table 4.8. increase in T_i originates from the increase in molecular weight of the copolymers. The S_c-S_A transitions of the copolymers, except 15 can not be detected by DSC. The experimental T_g values of the copolymers are very different from the theoretical values. The experimental T_g values are very close to the T_g value of homopolymer PLC11 indicating that the proportion of VAc units is very low or only homopolymer of LC11 occured.

Figure 4.11 shows the DSC heating curves of the copolymers, (10-18).

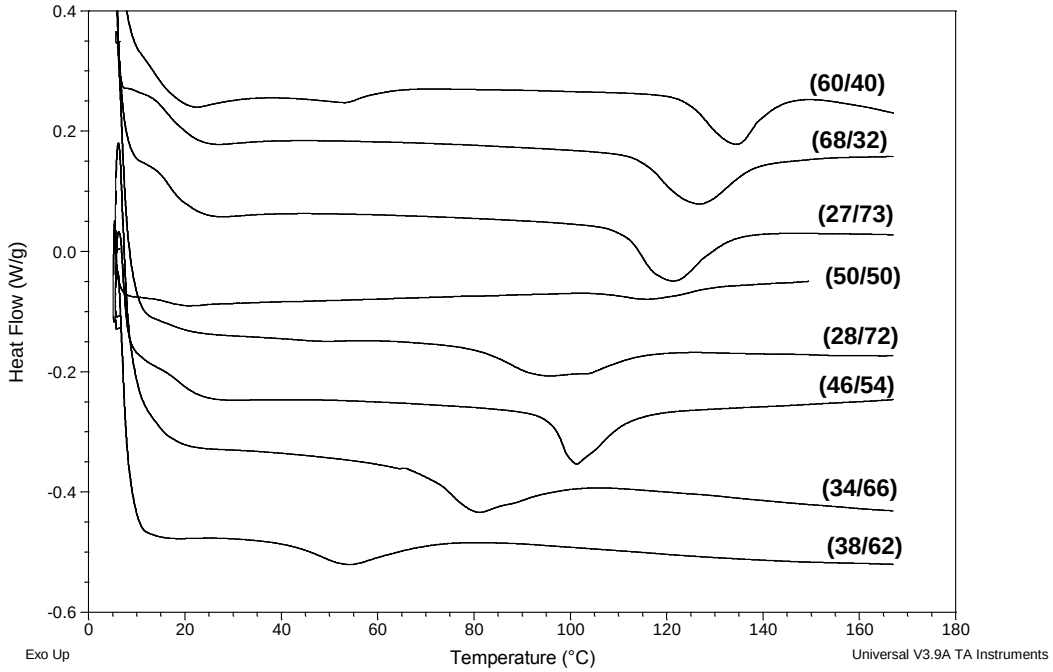
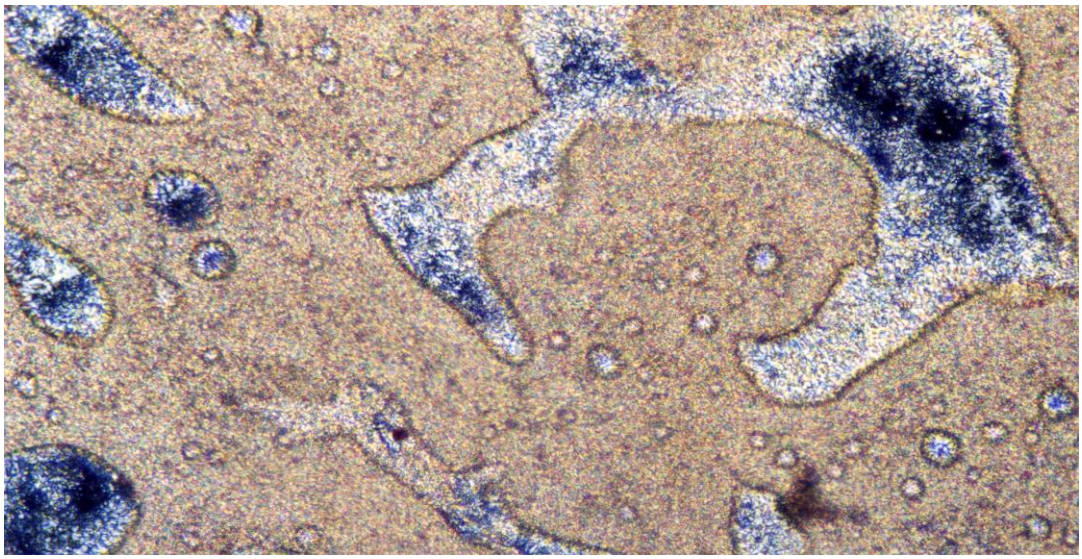
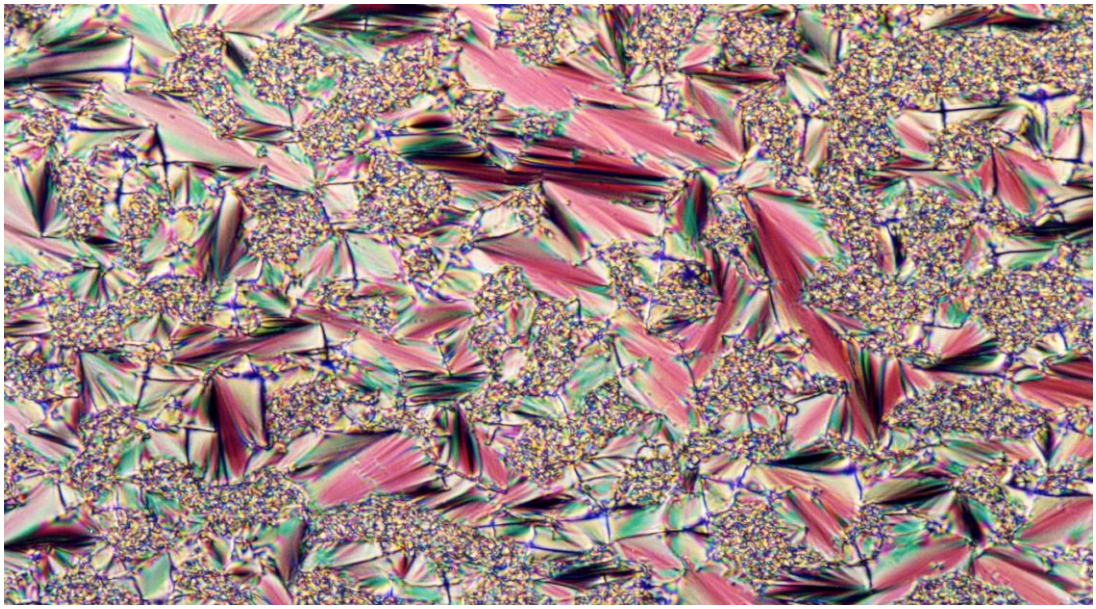


Figure 4.12 DSC thermogram of different copolymer composition (LC11/VAc).

Polarized optical microscopy studies showed that LC11 copolymer series, 14-18, have very similar mesomorphic behaviour in terms of transition temperetures and mesophase type as that of homopolymers. Figure 4.13 shows the S_A phase texture of copolymer 10 and copolymer 16.



(a)



(b)

Figure 4.13 S_A texture of copolymer 10 (a) (at 90^{o}C, x200) and copolymer 16 (b) (at 123^{o}C , x200).

5. CONCLUSIONS

In this study, the side chain liquid crystalline copolymers synthesized from copolymerization of vinyl acetate and methacrylic liquid crystalline monomers (LC6) and (LC11) with different spacer length by free radical polymerization mechanism.

The side chain liquid crystalline copolymers characterized by gel permeation chromatography (GPC), ^{1}H-NMR, polarizing optical microscopy and differential scanning calorimetry (DSC). Reactivity ratios of monomer were calculated by using Extended Kelen Tüdös Method. The $r_1.r_2$ values of monomers showed that VAc forms alternating copolymers with LC6 and random copolymers with LC11.

The thermal properties of copolymers are mainly influenced by their copolymer composition and monomer sequence distributions. Copolymers of VAc with LC6 and LC11 can show LC mesophase transitions according to their monomer contents.

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AUTOBIOGRAPHY

Yasemin Yüksel Durmaz was born in 1980 in Ordu. She graduated from Fatsa High School and attempted to the Chemistry Department of Yıldız Technical University in 1998. After graduating from YTU in 2003, accepted as a master student to İstanbul Technical University, Polymer Science and Technology Department of the Instıtute of Science and Technology in which she is about to graduate at the moment.