

Liquid crystalline behavior of polymers: fundamentals, synthesis and characterizations

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Abstract

As it is well known that, materials that have liquid crystalline properties are early discovered long time ago. These type of materials can carry both type of different types of matter (conventional liquid and solid crystal). Upon inserting such properly to the backbone of any polymer structure. It can enhance its amazing properties to be considered as one of the most and effective smart materials in the last few decades. The current work presents a short summary about the historical overview and some important basic fundamentals of liquid crystalline materials and its different types of calcifications. In addition, a detailed study about liquid crystalline polymers (LCps) have been described classifications and synthetic method. Both types of these polymers were discussed including main chain or side chain polymers. The effects of mesogenic groups, structural unit, substituents and flexible spacers on the thermotropic properties were also displayed. Finally, a brief overview for the ethers, arylidenes, arylidene-ethers, azomethine-ethers, and hydrazone-ethers containing liquid crystalline polymers and their copolymers was illustrated.

Abbreviations

LC, Liquid crystal; LCP, Liquid crystalline polymer; N, Nematic; MCLCP, Main chain liquid crystalline polymer; SCLCP, Side chain liquid crystalline polymer; Sm, Smectic; N*, Cholesteric; 2-D, Two dimensions; TBAH, Tetrabutylammonium hydroxide; DHAB, 4,4'-Dihydroxyazobenzene; DN, 2,7-Dihydroxy naphthalene; DBP, 4,4'-Dihydroxybenzophenone; DPCH, 1,1'-Bis(4-hydroxyphenyl) cyclohexane; DMF, N,N-Dimethylformamide; TEA, Triethylamine; FT-IR, Fourier transform infrared spectroscopy; ¹H NMR, Proton nuclear magnetic resonance; ¹³C NMR, Carbon-13 nuclear magnetic resonance; FPAEK-LCP, Thermotropic liquid crystalline poly(aryl-ether-ketone) having 3-(trifluoromethyl)phenyl group; TMS, Tetramethylenesulphone; TBAB, Tetrabutylammonium bromide; TDAI, Tris(dioxa-3,6-heptyl)amine; ISFET, Ion sensitive field effect transistors; (EBr₂)_n α,α' -dibrominated diesters (n is the number of methylene groups); P388 and L1210; Murine leukemia cancer cells; TGA, Thermogravimetric analysis; POM, Polarized optical microscope; DSC, Differential scanning calorimetry; PDT, Polymer decomposition temperature; T_g, Glass transition temperature; T_i, Isotropization temperature; TEM, Transmission electron microscope; XRD, X-ray diffraction technique; DTG, Differential thermogravimetric analysis; DTA, Differential thermal analysis; TMA, Thermomechanical analysis; PI, Polyimide; PMDA, Pyromellitic dianhydride; PBA, Polybenzoxazine; UV-Vis, Ultraviolet-visible spectroscopy

Introduction

Liquid crystal is a unique state of matter that has properties between those of conventional liquid and those of solid crystal. In the crystalline solid state, the constituent molecules occupy specific sites in a three dimensional lattice (positional orders) and points their axes in fixed directions (orientational orders) as illustrated in Figure 1A.^{1,2} Liquid crystal phases which are considered as a true discrete state of matter, possess orientational order (tendency of the molecules to point along a common direction called the director n) and in some cases various degrees of positional molecular orderings³ in one or two dimensions as shown in Figure 1B & 1C. On the other hand, in the isotropic liquid state, the molecules move randomly and rotate freely about all possible directions 1(d)). Thus, liquid crystals (LCs) have been defined as “orientationally ordered liquids” or “positionally disordered crystals” that combine the properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states.⁴⁻⁷ This results in the anisotropy of the physical properties (the measured physical properties in different directions will not be the same), which have led to their widespread applications.^{8,9}

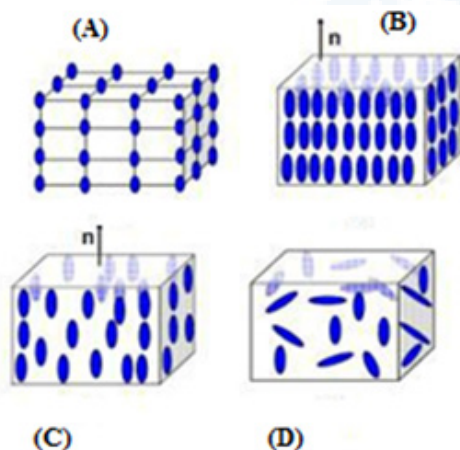


Figure 1 Schematic representation of molecular packing in the (A) crystals, (B) & (C) liquid crystals and (D) liquid state.

Historical overview

Liquid crystals were discovered since more than 100 years by the Austrian botanist Reinitzer (1888). He observed a peculiar thermal behavior of the crystalline cholesteryl benzoate ester^{10,11} where, it melted into a cloudy liquid at 145 °C and then as the temperature increased to 178 °C, suddenly became clear. This process was completely reversible and when cooling down, the substance transformed into an opaque liquid and finally became a white solid crystal. This strange behavior of the cholesteryl benzoate puzzled Reinitzer so, sent the sample to German physicist Otto Lemann, who later made detailed observations of this compound by using a polarizing microscope with a heating unit 2). Otto Lemann deduced that this compound must have a new state of matter in the indicated temperature range. A few years later, Lemann named this state of matter as “liquid crystal” (1900)¹² and this work was completed in a book published in 1921(Figure 2).¹³

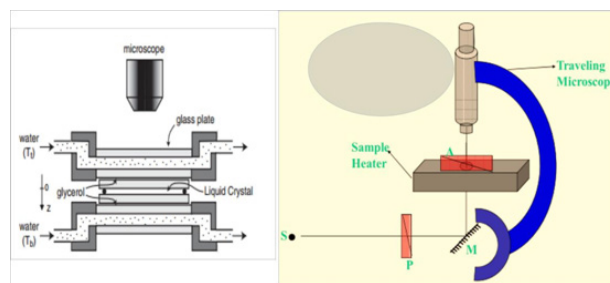


Figure 2 The proposed experimental setup of the used polarizing microscope.^{14,15}

At the beginning, the majority of researchers only interested in the theoretical study of the nature of the LC state, the study of their structural organization, elucidation of the relationship between the molecular constitution and physical properties of liquid crystals. After that, the unique properties of liquid crystals due to the high anisotropy and lability of the molecular structure encouraged them to find extensive areas of practical application. LC compounds have the ability to respond rapidly to changes in temperature, mechanical stress, electromagnetic radiation, and even chemical environment is now widely used for the construction of special thermo-indicators, devices for information recording in electro-nics, optoelectronics, display technology, and so on. LC televisions, LC monitors of personal computers, and large and small portable displays for mobile electronic equipment (telephones, games, video and photo apparatus, and personal productivity tools) are only a part of the technical devices based on liquid crystals. It can now be said without exaggeration that a number of branches of modern technologies would be unthinkable without the use of liquid crystals.¹⁶⁻²²



F.Reinitzer
1857-1927

O.Lemann
1855-1922

Classification of liquid crystals

Liquid crystalline materials are fundamentally divided into two categories, thermotropic and lyotropic mesophases.^{2,23-25} The term “mesophase” originates from the Greek word meso, meaning “in between” (the crystal and the liquid phases).²⁵

Thermotropic liquid crystal phases are obtained by temperature variation, thermodynamically stable mesophases which appear both on heating and cooling are termed enantiotropic, while the thermotropic mesophases that appear only on cooling are monotropic . On the other hand, lyotropic phases form by dissolving a compound in a suitable solvent under a given temperature and concentration. Most of lyotropic mesophases are mixtures, whereas many of the reported thermotropic liquid crystals are single compounds.^{15,23} Some mesogens may exhibit both lyotropic and thermotropic phases; these materials are named

amphotropic.^{23,25} To date, some 80000 different compounds, low molecular mass as well as polymeric materials, exhibiting liquid crystal properties have been reported. Most of these are collected in many literature Liquid Crystals: Stegemeyer,²⁷ Collings & Hird,⁷ Chandrasekhar,²⁸ De Gennes & Prost,²⁹ the Handbook of Liquid Crystals,³⁰ the monograph of Petrov.³¹ All terminological definitions which are related to liquid crystals and LC polymers are summarized in IUPAC document.³²

Lytropic liquid crystal

Compounds forming lyotropic mesophases are amphiphilic which consist of a flexible hydrophobic tail and a polar hydrophilic head group (Figure 3) within the same molecule.^{23,24} Tail is an alkyl chain with 6 to 20 methylene groups in most cases while, the head may be ionic or zwitterion or non-ionic group as shown in Figure 4.²³

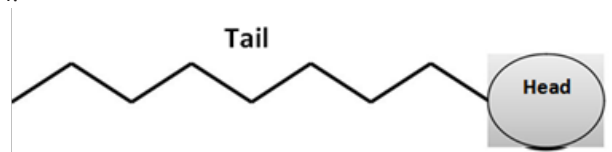


Figure 3 Graphical representation of an amphiphilic compound.²³

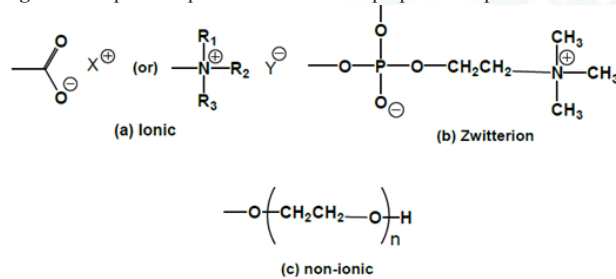


Figure 4 Examples for polar hydrophilic head group.²³

Different lyotropic mesophases can be obtained depending on the molecular structure, solvent, concentration and temperature. Their formation is caused by the separation of the two different parts (hydrophilic and hydrophobic) of the molecules. At low concentration, the added amphiphilic compounds into a polar solvent form a true molecular mixture because their molecules are dispersed randomly without any ordering. At higher concentration, the molecules are assembled spontaneously and the polar groups occupy the interface towards polar the solvent forming small aggregates with finite size called micelles or vesicles (Figure 5A). When the concentration of the amphiphilic molecules is further increased, the micelles can turn to disc-like, cylindrical (Figure 5B) and plate-like supramolecular aggregates which organize themselves forming different mesophases such as nematic, cubic, hexagonal columnar (Figure 5C) and lamellar (Figure 5D).^{24,33} Dissolution of soap in water is the typical example of a lyotropic phase.^{23,24}

Thermotropic liquid crystals

Thermotropic LCs has a relatively great attention because they are realized, handled and very important in fabricating display devices. Compounds which have thermotropic liquid crystalline properties do not loss of their long range positional and orientational orders on heating to transform into the isotropic

liquid phase spontaneously but rather exhibit a step-wise decay with increasing temperature of the long-range positional order in the first, second or third dimension and finally the long-range orientational order leading to an isotropic melt as shown in Figure 6. This indicate that such compounds do not show a single transition from solid to liquid but rather a series of transitions involving LC phases with the mechanical and symmetry properties intermediate between those of liquid and a crystal.²³

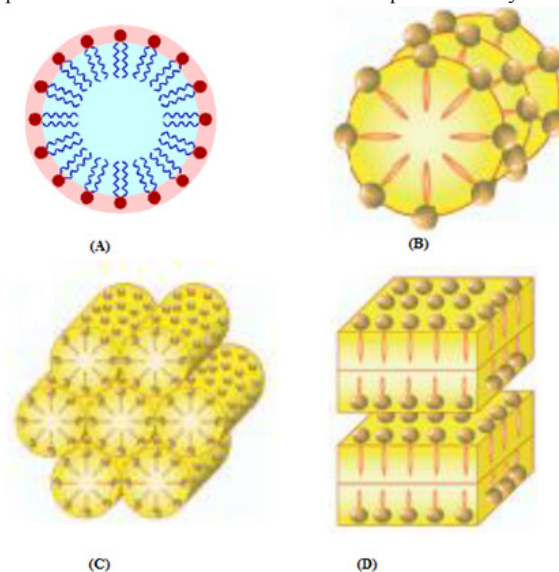


Figure 5 Some typical LC lyotropic structures formed by amphiphilic molecules in water solutions (A) micelle; (B) cylindrical micelle; (C) hexagonal packing of cylindrical micells; (D) lamellar liquid crystal.

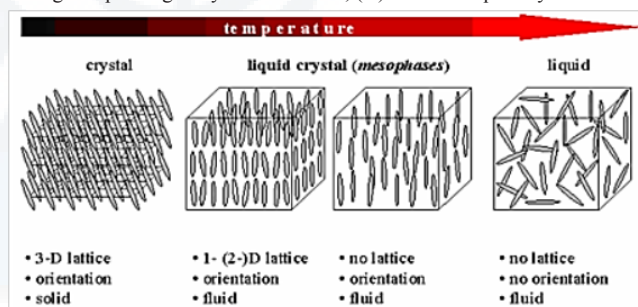


Figure 6 Transitions from solid to the liquid state by increasing the temperature.

Systematic investigations have proven that the LC property is existed only in those compounds whose molecules have a pronounced anisometric shape (having unequal axes). Changes in the conformation of these molecules should not substantially affect their anisometric shape; so, a relatively rigid molecular structure is required. This means that such compounds usually contain a rigid part (aromatic cores and some non-aromatic cores) in addition to flexible regions. These two parts are combined in a specific way to achieve an anisometric shape of the molecule giving what is known as the mesogenic group (Figure 7).^{23,34}

The thermotropic liquid crystals can be classified in different ways: in terms of their molecular size (as low and high molecular weight compounds), molecular shape of the constituent molecules (calamitic, discotic, sanidic and banana mesogens) and according

to the mesophase type (nematic, cholesteric, smectic, columnar, and cubic mesophase etc.).²³

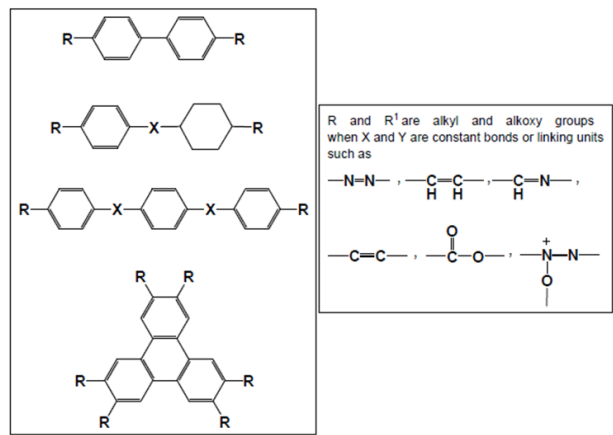


Figure 7 Examples of typical mesogenic groups.

Classification of thermotropic LC according to the molecular shape: Thermotropic LCs are generally classified with respect to the molecular shape of the constituent molecules, being called calamitic for rod-like, discotic for disk-like, sanidic for board- or lath-like and banana-shaped molecules which was discovered in this century (Figure 8).^{15,23,25,34}

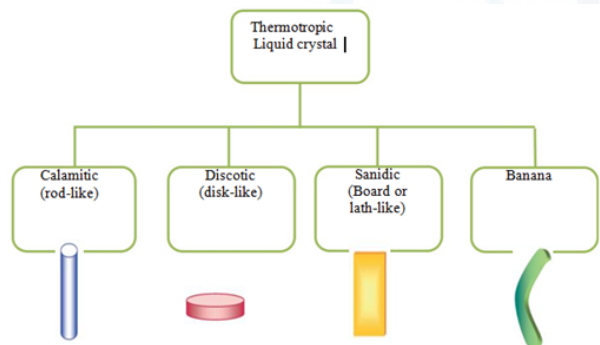


Figure 8 Classification of thermotropic LCs according to the molecular shape.

The structural feature of the majority of both rod-like and board-shaped LCs (Figure 9) is a relatively rigid core **RC1** and **RC2** which can be aromatic (one, two or even three benzene rings) or alicyclic rings chemically linked directly or via linking units **L** such as (CH=CH, CH=N, -NH-CO- and -COO-), in addition to two flexible end units **R** and **R'**, often alkyl or alkoxy chains [23–25, 34]. The terminal groups can also be polar (e. g., CN, F, N=CO, N=CS, NO₂, etc.). In some special cases, lateral units **X** and **Y** are incorporated in the main molecular structure such as (e. g., F, Cl, CN, CH₃, etc.).^{23,25} Examples of typical rod-shaped molecules are shown in Figure 10.

In discotic mesogens, four to eight terminal groups are attached to a rigid disk-like core with a suitable linkage.^{23–25} as shown in Figure 11. Banana mesogen consists of bent molecules, in which two mesogenic groups are linked through a semi-rigid group in such a way as not to be collinear^{25,27,35–38} as shown in Figure 12.

Classification of thermotropic LC with respect to the type of mesophase: Depending on the degree of orientational and

positional order of the molecules, the mesophases can be divided into nematic, smectic, cholesteric, columnar, cubic and bent-core (banana) LC phases. Nematic, smectic and cholesteric are the most common mesophases.^{2,15,23,24}

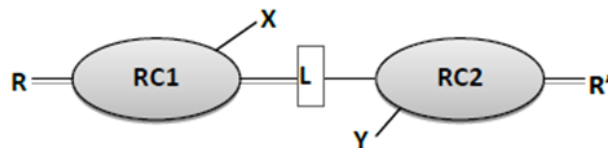


Figure 9 Graphical representation of rod-like and board-like structure.

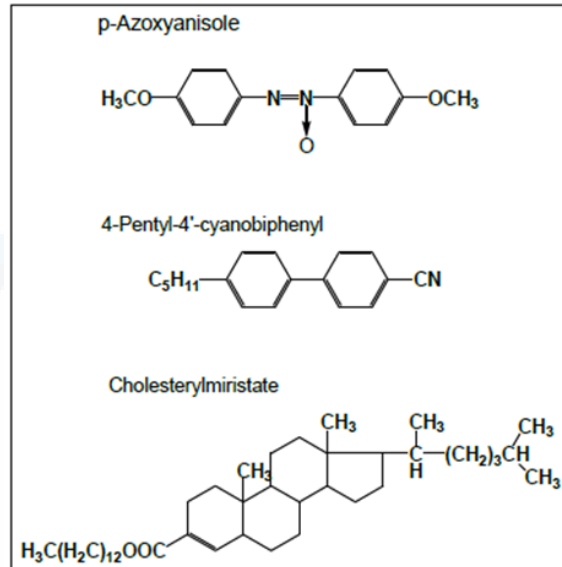


Figure 10 Examples of typical rod-like molecules.

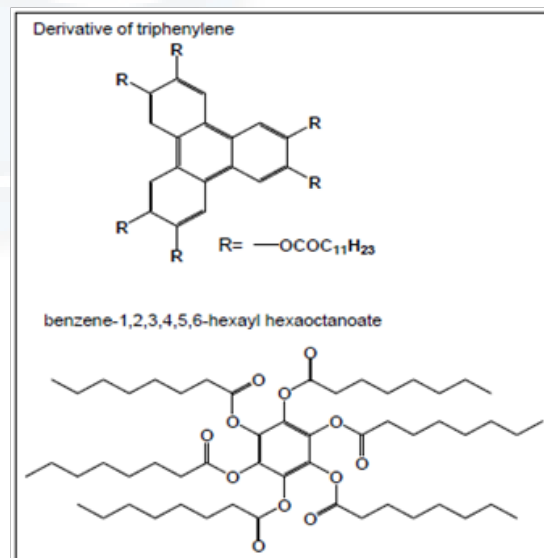


Figure 11 Examples of discotic molecules.

A. **Nematic (N) mesophase:** In the nematic phase, the molecules have no positional order but, they have long-range orientational order. These molecules are oriented about a particular direction called the director, **n** as displayed in Figure 13.^{2,24,25,39} The Nematic phase is seen as schlieren, marble and

pseudoisotropic textures.²⁵ This phase occurs just below the isotropic phase but more viscous.

B. Smectic (Sm) mesophase: In the smectic mesophases, the molecules are positionally ordered along one direction; therefore, they tend to align themselves in layers or planes. These layers can slide over one another in a manner similar to that of soap. The motion of molecules is restricted to within these planes.^{2,25,31} This mesophase has more order of molecules than that of the nematic phase so it can be called “solid-like”. There are many types of smectic mesophases which are characterized depending on the molecular arrangements within the layer, such as smectic A (SmA), smectic B (SmB), and smectic C (SmC).^{19,25} For example, In the SmA mesophase, the orientation of the molecules is parallel to the normal layer, while in the SmC mesophase it is tilted⁷ as shown in Figure 14.

C. Cholesteric (N*) mesophase: Cholesteric mesophase consists of nematic mesogenic molecules containing a chiral center; so, it is called as a chiral nematic phase. It can also be obtained by doping optically active molecules in the nematic LC. This type of liquid crystalline phases was first observed in cholesterol derivatives. In this system, the neighboring molecules tend to align at a slight angle at one another. This result in the formation of a structure which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted in a regular way with respect to those above and below forming a helix. The molecules are aligned perpendicular to the axis of the helix (Figure 15).^{2,25,36,39}

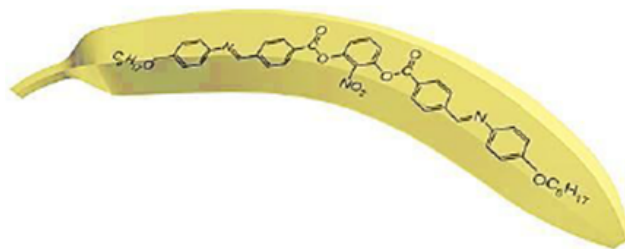


Figure 12 Graphical representation of banana-shaped mesogen.

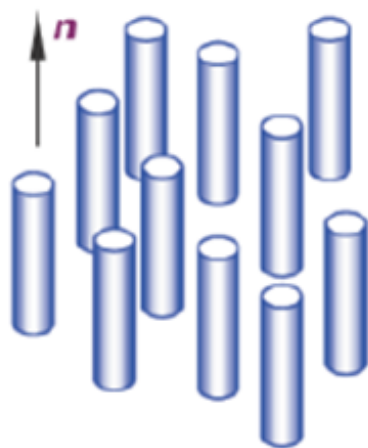


Figure 13 Schematic representation of the molecular order in the N phase of the calamitic LCs.

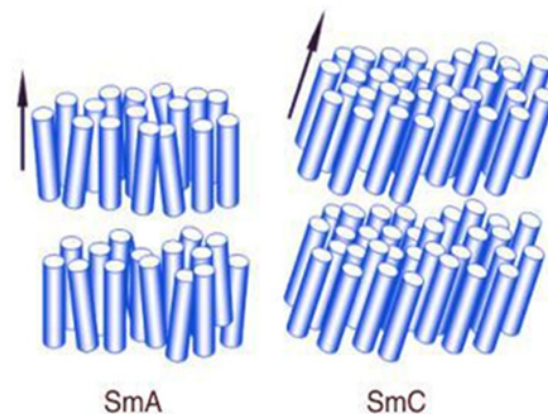


Figure 14 Schematic representation of the molecular order in both the SmA and SmC phases of the calamitic LCs.

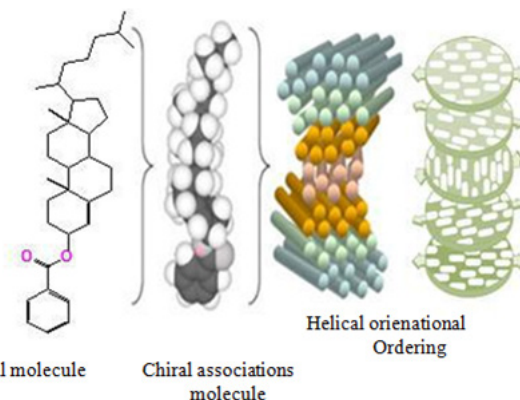


Figure 15 Graphical representation of cholesteric phase and helical structure.

Identification of thermotropic mesophases: Different techniques are required to be used in the precise characterization of LC phases because of the quite narrow structural differences between liquid crystal phases. The polarizing optical microscope (POM) is the most commonly used device to identify the LC phases which reveals the characteristic optical texture of a mesophase. The optical textures are usually observed in thin layers of the sample between two glass plates, pretreated for either homogeneous or homeotropic alignment of the molecules. Differential scanning calorimetry (DSC) is a complementary tool to microscopic studies to know the precise phase transition temperature and the enthalpy change associated with the transition.^{15,25} Diffraction studies such as X-ray, electron and neutron radiations^{15,25,40} can be used to obtain structural information such as relative molecular positions, the presence of long-range positional order, the quality of preferred molecular orientation, etc. for clear identification of mesophases. X-rays are probably the most suitable and widely used whereas electrons and neutrons have advantages in particular situations. Moreover, there are other experimental techniques such as electro-optic measurements, nuclear magnetic resonance (NMR) spectroscopy etc., which also may be used in the characterization of mesophase.

Liquid crystalline polymers

Liquid crystalline polymers (LCPs) are a class of materials that combine the properties of polymers with those of liquid crystals.

These “hybrids” (physico-chemical mixture) show the same mesophases characteristic of ordinary liquid crystals and still retain many of the useful and versatile properties of polymers.⁴¹ At the beginning, it was believed that the formation of these LC polymers is difficult to achieve because the polymer chains have a tendency to adopt in random coil conformations in a melt (easily change their conformations due to heat movement that are not favorable in LC formation), while LC-phases possess an orientational and/or a positional long-range order. In 1956, Paul Flory suggested the ability of forming such these polymeric materials which exist in liquid crystal state and still have a high degree of order from his studies of the thermodynamic properties of solutions of polymers.⁴² He received the Nobel Prize for chemistry in 1974 as a result of his studies on the relationships between polymer structure and properties. He predicted that the polymers which consist of rigid-rods molecules should form anisotropic ordered solutions depending on both the temperature and the axial ratio of the rod-like chain.⁴³ These theoretical predictions concerning the formation of anisotropic LC phases in polymer solutions were experimentally detected for the first time at the research laboratories of Courtaulds Ltd. in the UK in solutions of certain polypeptides.⁴⁴ Poly(γ -benzyl-L-glutamate) (Figure 16) has been the subject of the most studies of this class where the rod-like structures in solutions are formed by the stable helical conformation of the polymer molecules. As Flory predicted, the spontaneous packing of these stable helices leads to anisotropic liquid crystalline properties of their solutions. This kind of LC polymers is now known as “Lyotropic” which is different from those which form LC melts and are termed “Thermotropic”.^{44,45}

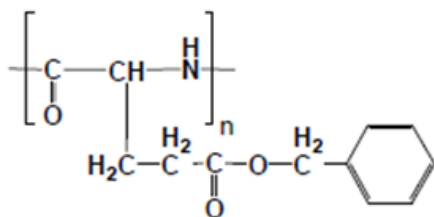


Figure 16 Structure of poly(γ -benzyl-L-glutamate).

As mentioned in the previous section, the main structural feature of low-molar-mass liquid crystals is predetermined by the existence of the anisometric mesogens or mesogenic groups. The molecular engineering has proven that the efficient way of producing LCPs with the desired properties can be carried out by introducing mesogenic units, such as rod-like or disc-like mesogens derived from low molecular weight compounds, into polymer chains as monomer units. The majority of such macromolecules that can easily form LC phase are rigid-rod polymers in which the length of the Kuhn segment of the chain, l , is much greater than the thickness (diameter) of the chain, d , (Figure 17) such as aromatic polyamide (poly(1,4-benzamide)). This type of macromolecules can be used only in forming lyotropic liquid crystals because they are characterized by high melting points close to the decomposition temperatures. In some cases, LC phases cannot be observed in spite of the presence of mesogenic groups in the polymer backbone. The tendency of the polymer to form random coil conformations will disrupt the alignment of the mesogens and effect on the LC behavior. After that, the researchers directed their attention to the creation

of thermotropic LCPs by the chemical bonding of both flexible and rigid-rod fragments in the same macromolecule. The flexible part may be long aliphatic or oxyaliphatic groups which reduce the rigidity of the macromolecules and so diminish their melting points. The flexible fragment which is known as “spacer”, provide the rigid mesogenic groups with sufficient mobility to their self-organization in the LC phase.^{24,34,46,47}

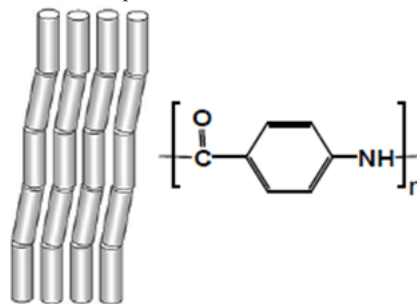


Figure 17 Rigid-rod LC polymer.

The study of LC polymers is of interest in its own right, motivated by the need to clarify the nature and specific features of LC state of macromolecular compounds.^{48,49} Moreover, the possibility of creating polymeric systems, combining the unique properties of low-molecular-mass liquid crystals and macromolecular compounds, making it feasible to produce films, fibers, and coatings with extraordinary features. For example, it is well known that the utilization of low-molecular-mass thermotropic liquid crystals requires special hermetic protective shells (electro-optical cells, microcapsules, etc.) that maintain their shape and protect LC compounds from external influences. On the other hand, thermotropic LC polymers do not need for such sandwich-like constructions, due to combining the properties of low-molecular-mass liquid crystals and the polymeric body in such single individual material. This resulted in new perspectives for their application.^{50,51} such as production of self-reinforced plastics based on LC polymers with main-chain mesogenic groups and the use of comb-shaped LC polymers as new photoactive materials for optics, optoelectronics, photonics, holography, display technology, telecommunications systems, and other no-less important areas of modern engineering.⁵²⁻⁵⁵ Many studies exclusively interested LC polymers, including dozens of monographs, thematic collections of articles, encyclopedias, and review papers and some of them are listed in references.⁵⁶⁻⁵⁸

Classification of liquid crystalline polymers (LCPs)

LC polymers can be classified in different ways: in terms of their structure (amphiphilic-lyotropic or non-amphiphilic-thermotropic), the phase as in the case of low-molecular-mass liquid crystals (nematic, smectic and chlosteric) and according to the mesogenic groups as proposed by Gray and Winsor.^{43,59}

According to the kind of mesogenic groups: The most widespread classification of these macromolecules depends on the strategy of incorporating the mesogenic units into the polymer chain. There are two fundamentally different types:

1. Main chain liquid crystalline polymer (MCLCP) in which the mesogenic groups are embedded into the backbone of a polymer chain (Figure 18A).

2. Side chain liquid crystalline polymer (SCLCP) or (comb-shaped LC polymers) where the mesogens are attached to the main chain as side groups (Figure 18B).^{24,34,60,61}

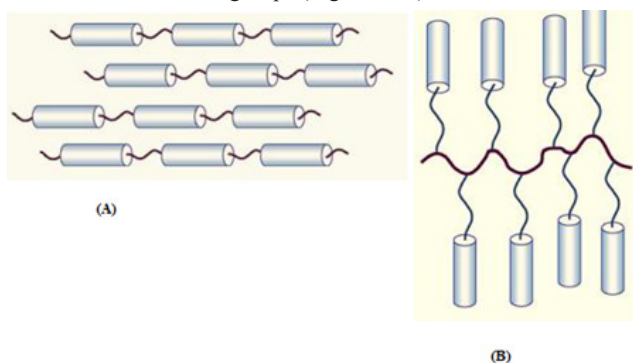


Figure 18 Schematic representation of macromolecules of LC polymers with (a) main-chain and (b) side-chain mesogenic groups (comb-shaped LC polymers). (1) mesogenic group, (2) spacer, and (3) main chain.

Moreover, the mesogens are linked to the polymer or the copolymer backbone in different positions; it can be either longitudinally or laterally attached into the polymeric system. This leads to MCLCPs with a longitudinal connection (end-on) of the mesogens are end-on MCLCPs and those with lateral connection (side-on) are called side-on MCLCPs. Similarly, for SCLCPs, there are also end-on SCLCPs and side-on SCLCPs, as displayed in Table 1.^{24,60,61} Later, the researchers directed their attention to the synthesis of polymer systems with a more complex architecture by introducing other moieties featuring their own functional properties with mesogenic groups into macromolecules⁶⁰ as shown below.

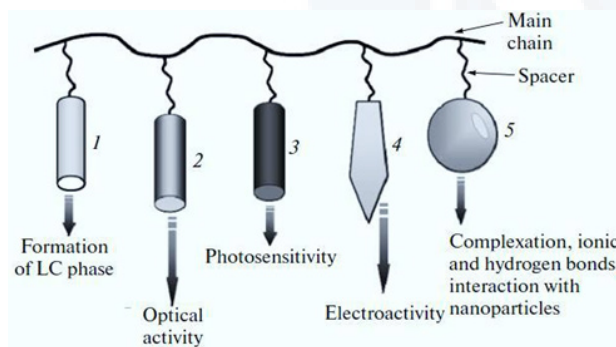


Table 1 Schematic illustration of structural models of liquid crystalline polymers

	Main-chain LCP	Side chain LCPs
End-on (longitudinally attached)		
Side-on (laterally attached)		

Main chain liquid crystalline polymers

These polymers are formed by incorporating mesogenic units only in the backbone of the polymer chain. A MCLCP is formed by linking together suitable relatively rigid units (mesogens)

directly such as poly(hydroxynaphthoic acid) (Figure 19A) or through appropriate functional groups (spacer) such as poly(p-phenyleneterephthalate) (Figure 19B).^{24,62}

The majority of macromolecules in the first type tend to be highly crystalline and have high melting points near to the decomposition temperature of the polymers. For example, the melting point of poly (hydroxynaphthoic acid) is 610°C which was measured by DSC (scan rate of 80°C/min to minimize degradation). So, such polymers can only form lyotropic liquid crystalline phases in a comparatively concentrated solution.^{24,63-66} This apparently led to an immediate search for synthesis of thermotropic LCs which can be used in manufacturing companies to form fibers with extraordinary mechanical properties. Roviello and Sirigu in 1975.⁶⁷

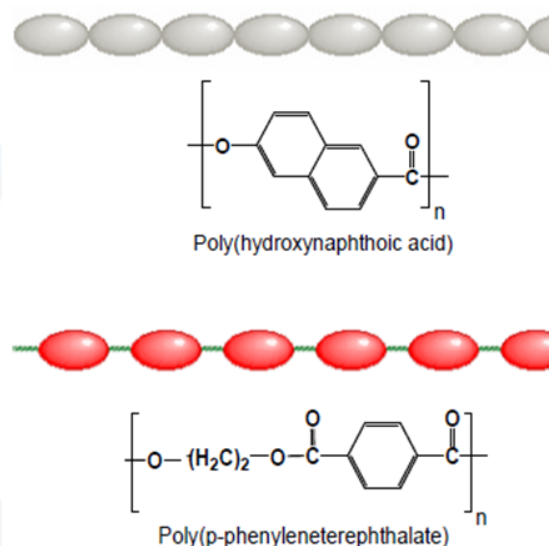


Figure 19 Schematic representation of main chain LCP consists of rigid units (a) directly linked and (b) linked through spacer.

Introduced the first report in a scientific journal of the preparation and properties of a MCLCP and this paper followed shortly by large number of reports in this topic. Furthermore, they attempted to deduce the structural property relationship of this compounds.⁶⁸

In order to design thermotropic MCLCPs with lower melting point to a melt processable range without destroying LC formation, there are three possible ways:^{24,34,63,65,66,68-72} (1) introduction of flexible spacers between the mesogenic units into the polymer chain such as alkyl or alkoxy groups (Figure 20A). As the length of the flexible chain increases, the melting point of the polymer decrease and the tendency of mesogenic groups to order increase; (2) incorporation of substituents into the monomers (Figure 20B) or nonlinear aromatic units (benzene rings with ortho or meta substituents) acting as kinks (Figure 20C) leading to the disruption of the linear constitution of the main chain; and (3) combination of monomers (copolymerization) containing either different types of mesogenic units or of monomers with either two different types of flexible spacers or two different types of rigid molecular structures in which one of the monomers is mesogenic and the other is not because of its non-linear structure (Figure 20D). Moreover, the introduction of oxygen or sulfur atoms into the polymer chain (Figure 20E) is also a very effective method for making macromolecules more flexible.

A. Effects of mesogenic groups on thermotropic properties:

The mesogenic groups of polymers are responsible for their liquid crystallinity, determine within what range the transition temperature for a thermotropic polymer will occur and what type of mesophase can be formed.⁶⁹ Such mesogens of a liquid crystalline polymer may be aromatic (one, two or even three benzene rings), alicyclic rings or different heterocyclic fragments chemically linked directly such as biphenyl and terphenyl or via linking units such as imino, azo, azoxy, ester and trans vinylene groups in a linear array. It may also contain naphthalene rings such as 2,6-naphthalene. Substituents

such as F, Cl, Br, CH₃, OCH₃, phenyl or n-alkyl groups may be introduced into the mesogenic groups. In some cases, highly polar groups such as -CN and -NO₂ can be used as substituents in these rigid cores. Spacers have been used to separate these mesogenic groups in the polymer chain can be attached to through functional groups. The most commonly used functional groups are ester and ether groups in addition to amide, imine, urethane and carbonate groups which are recently used. The flexible spacer may be alkyl or alkoxy or siloxane groups such as polymethylene, poly (ethylene oxide) and polysiloxane spacers, respectively.^{63,69}

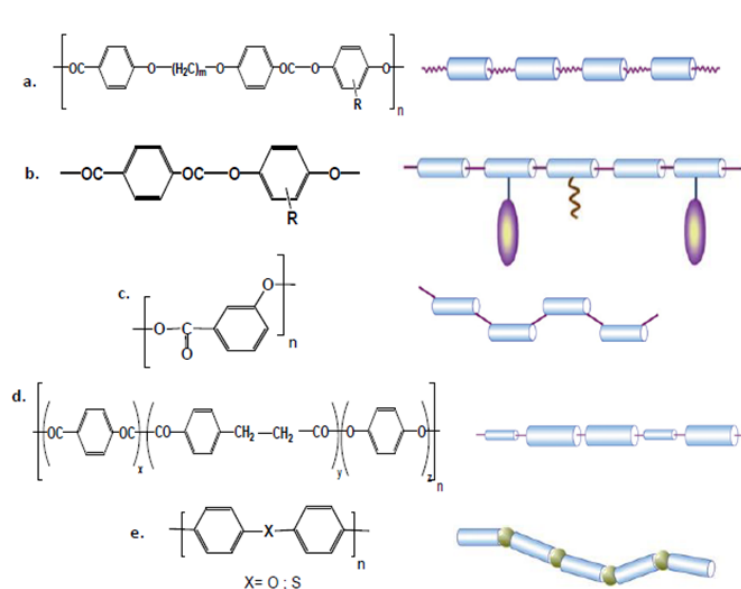


Figure 20 Some examples of chemical modifying to reducing rigidity of rod main chain polymers.

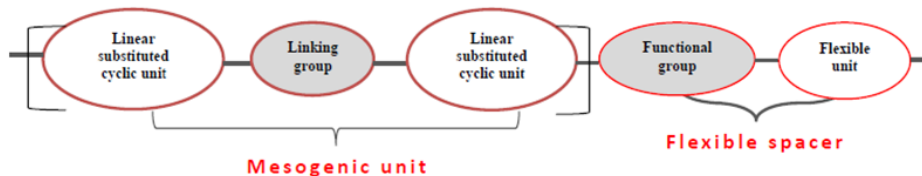


Figure 21 Schematic representation of the general structure of a liquid crystalline polymer having both a linear rigid mesogenic group and a flexible spacer in the main chain.

From a review of the results of studies, the effect of three different types of modifications of the chemical structure of mesogenic units on the liquid crystalline properties of thermotropic main chain polymers have been investigated using polyesters as example.^{68,69,73,74} They include changes in

- i. Structural units;
- ii. Length of mesogen and its aspect ratio (length to width ratio); and
- iii. The presence of lateral substituents. The researchers found that even a slight change in the chemical structure of mesogenic units can lead to a significant change in the thermal properties of the mesophase.^{68,73,75,76}

B. Effect of the structural unit: By comparing the clearing temperature T_i of a group of different but closely related aromatic esters connected through decamethylene spacer, small changes in the structure of mesogen result in profound changes in T_i . These observations can be briefed in (1) the

coplanar geometry of mesogenic units of polymer stabilizes the mesophase (higher T_i) because these mesogens have an effective molecular packing and alignment in the liquid crystal phase;⁷⁷ (2) increasing the length of the linear mesogenic group increases the thermal stability of the liquid crystal mesophase. This means that, mesophase behavior can be affected by modifying both rigidity and the length of the mesogen, which is generally described in terms of the length-to-width ratio of the molecular structure of the mesogen.^{75,78,79}

C. Effect of substituents: The presence of substituents in the mesogenic units effect on the thermal behavior of the mesophase of the main chain polymers. This effect depends on the size and the type of substituent and the mesogen involved. The earlier studies.^{24,65,68,69,74,76,78,80-85} deduced that (1) the introduction of substituents in the mesogens resulted in depression in both the melting point and the clearing temperature of the polymer; (2) increasing the size of the substituent decreases the value of T_i ; (3) there is additivity of substituent effect, when the presence

of two substituents of the same type, T_i lowers twice. These results can be attributed to the steric effects of the substituents which increase the separation of mesogenic groups in adjacent polymer chains. This in turn limits the molecular packing of mesogens and disrupts the regularity of the repeating units within the polymer. In case of substituted polymers with highly polar groups such as $-\text{CN}$ and $-\text{NO}_2$, the clearing temperatures are higher than those of the methyl-substituted polymers due to the dipolar interactions between neighboring polar substituents.⁶⁹

D. Effect of flexible spacers on thermotropic properties: The effects of the type and the length of the flexible spacers on the thermotropic properties of main chain polymers have been extensively investigated. These studies,^{24,61,68,72,75,76,86–99} documented that: (1) the transition temperatures decrease as the length of the spacer increase but for polymethylene spacers, this decrease is accompanied by an even–odd effect. That is, the transition temperatures of polymers with an even number of methylene units are higher than those with an odd number of the same series. This can be attributed to the decrease in the molecular rigidity; (2) the spacer plays an important role in determining the nature of the mesophase of LCP. For some types of mesogens, the increase of the spacer length is accompanied by change from nematic to smectic mesophase. The longer flexible spacers result in higher degree of freedom to the mesogenic units which permit their alignment to form smectic layers. All thermotropic main-chain LC polymers are obtained by polycondensation technique of different bifunctional compounds consisting of rigid (mesogenic) and flexible fragments (spacers).²⁴

E. Effect of copolymerization on thermotropic properties: From all previous studies,^{24,69,82,100} copolymerization of different types of mesogenic units or of monomers with either two different types of flexible spacers or two different types of rigid molecular structures in which one of the monomers is mesogenic and the other is not because of its non-linear structure results in depression the melting temperature. In addition, copolymers have wider temperature ranges of mesophase stability. This is due to the copolymerization cause frustrated chain packing. In case of copolymerization of mesogen with non mesogenic unit, polymer must not contain less than 50–60% mesogenic units to be able to form a stable thermotropic mesophase.

Side chain liquid crystalline polymers (comb-shaped)

In SCLCPs, the mesogenic units groups are linked to an existing polymer backbone either directly (Figure 22A) or via flexible spacer units Figure 22(B). The direct attachment of mesogens with the backbone,^{101,102} except in a few cases^{103,104} gives polymers with high glass transition temperatures. LC formation is suppressed because the coupling of steric interactions between the side groups, the tendency toward a statistical distribution of chain conformations hinders the ordered arrangement of the mesogens. Introduction of flexible spacers allows the main chain motion to occur without disturbance of the anisotropic arrangement of the side chains; in turn the polymer may exhibit LC properties. Typical spacer groups consist of between 3 and 12 methylene units. However, oligooxyethylene^{105–108} or oligosiloxane¹⁰⁶ units

may be used to enhance the degree of decoupling through a more flexible spacer. This type of liquid crystalline polymers is considered as functional thermotropic LC system.

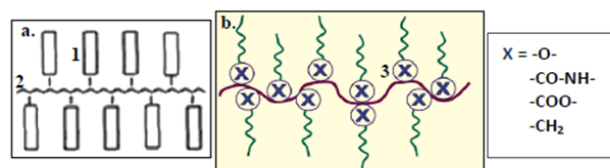
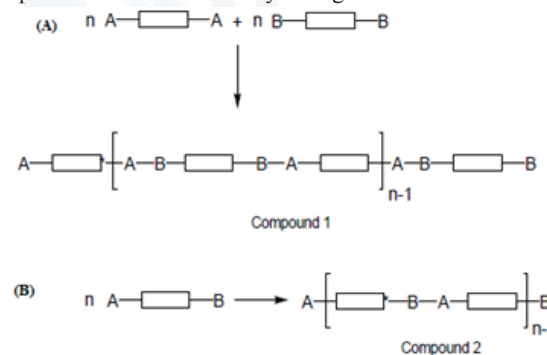


Figure 22 Schematic molecular structure of SCLCP 1- mesogenic group, 2- backbone and 3- spacer.

Synthesis of liquid crystalline polymers with flexible spacers in the polymers backbone

In initial studies, the researchers directed their attention to the synthesis of LC polymers by the development of various methods for incorporating only rod-like mesogenic groups, which are responsible for the formation of LC phase, into main and side branches of polymer chains. In most cases, they used already known low molar mass liquid crystals which are functionalized with groups able to undergo polycondensation (Scheme 1).³⁴ The most preferred reactions led to yielding



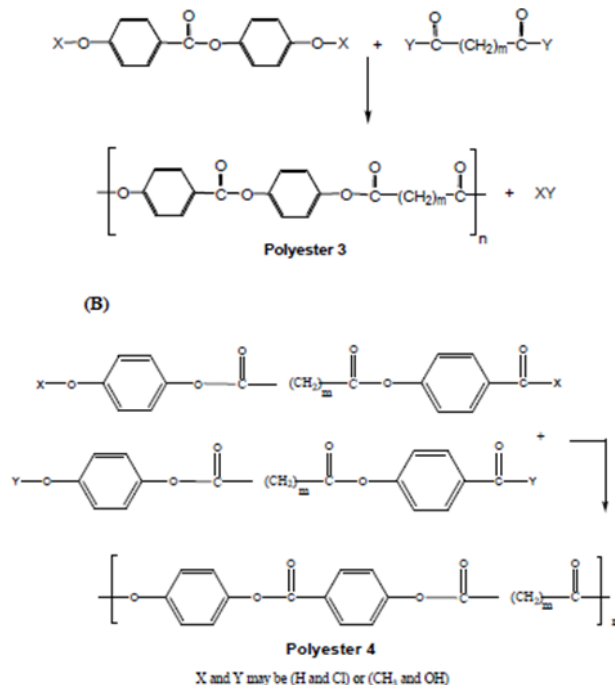
Scheme 1 Synthesis of compounds 1 (A) and 2 (B).

This direct, linear, rigid attachment of mesogenic groups leads to the formation of polymers with high anisometry of molecules, so, their liquid crystalline–isotropic phase transition temperatures are above their decomposition temperature. As a result, the liquid crystalline phase often cannot be reached even in the case of oligomers. In order to obtain the liquid crystalline state with these types of polymers, scientists began to modifying the rigid, rod-shaped basic structure to decrease the transition temperature. As mentioned above, the three ways of modification are introduction of flexible spacers between the mesogenic units, incorporation of substituents into the monomers and copolymerization.^{24,34,63,65,66,68–72} It should be noted that usually it is necessary to use a combination of at least two of these approaches to lower the melting point sufficiently for melt processability.⁶³ Later, macromolecules of these compounds contain, as a rule, flexible and rigid (mesogenic) fragments (in the form of rods, disks, and boards) chemically linked via different ways. There are two main basic approaches which result in the synthesis of liquid crystalline polymers containing mesogenic groups and flexible spacer in the main chain.⁶²

1. The polycondensation of two bifunctional compounds consisting of rigid (mesogenic) and flexible fragments

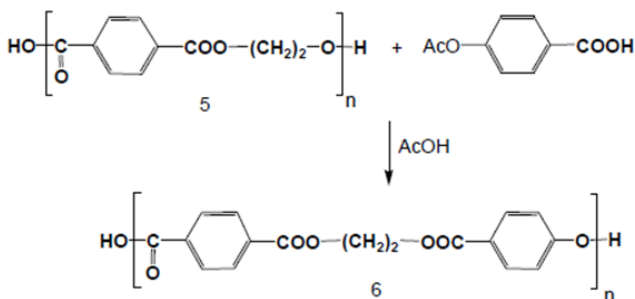
(spacers) (such as methylene, methylene oxide and dimethyl siloxane groups which decrease the melting point and enhance the thermal stability of mesophase) (Scheme 2A).

- ii. It involves the formation of mesogenic units as a result of polycondensation reaction of two different monomers containing no typical rigid mesogens (Scheme 2B).



Scheme 2 Synthesis of polyesters 3 (A) and 4 (B).

Sometimes a transification process is used to yield MCLCPs. For example, the copolymer was obtained by inserting inserting oxybenzoate units into poly(ethylene terephthalate) **5** (Scheme 3). Furthermore, copolymers consisting of rigid-rod fragments and felxible units can be prepared by copolycondensation reactions of different aromatic bifunctional compounds.²⁴



Scheme 3 Synthesis of polyester 6.

More than three decades have already passed since the appearance of the first publications devoted to the synthesis and study of thermotropic LC polymers containing mesogenic groups. A great quantity of studies devoted exclusively to the synthesis and investigation of main chain liquid crystalline polymers. These polymers including: polyesters, polyethers, polyamides, polyurethanes, polysiloxanes, polyamines, polythioether. In addition, the hybrid polymers like poly(ether-ester)s,

poly(amide-esters)s, poly(imid-ester)s, poly (azomethine-ether) s were synthesized.¹⁰⁹⁻¹¹⁷

Synthesis of liquid crystalline polyethers and copolyethers with flexible spacers in the main chain

Flory⁴² was the first one to introducing concept of the liquid crystalline polymers in 1956. He stated that the ability of the polymers which consist of rigid-rod molecules to form lyotropic liquid crystalline phase at a critical concentration. Another milestone in this field was passed in 1975 when de Genne¹¹⁸ suggested that thermotropic main chain LC polymers could be made by a combination of rigid and flexible units. At the same year, Roviello & Sirigu⁶⁷ introduced the first example of thermotropic LC main chain polymers, that is, polyalkanoates of p,p'-dihydroxy- α,α' -dimethylbenzalazine. This paper was shortly followed by the synthesis of several series of main chain liquid crystalline polymers and copolymers. MCLCPs of the ester type were the most widely synthesized because they can be prepared by the traditional methods of condensation polymerization. In addition, other MCLCPs have been synthesized such as polyazomethines,^{80,119} polyesteramides,¹²⁰⁻¹²² polyaminoesters,¹²³ polyetheresters,¹²⁴ polythioesters,¹²⁵ polyamides¹²⁶ and polyisocyanates.^{127,128} Since then, Percec et al.,¹²⁹ Jonsson et al.,¹³⁰ Keller¹³² actively engaged the sythesis of thermotropic polyethers containing rod-like mesogens. However, LC polyethers have been studied to a much lesser degree. Shaffer & Percec^{133,134} after performing extensive work on these polymers stated that the main advantages of LC polyethers over LC polyesters are lower melting temperatures, a broader mesophase stability range and higher solubility.

The traditional rigid rod-like mesogenic units are composed of linearly aromatic or cycloaliphatic rings connected by rigid linking groups, which provide a linear and eventually planar conformation to the resulting polyether compounds.¹³⁵ This rigid unit does not have to exhibit liquid crystallinity to be used as a mesogenic unit in LC polymers.¹³⁶ It must, however, contain an appreciable amount of rigidity, non-coplanar structure units,¹³⁷ asymmetrical shape¹³⁸ and even complex architectures.¹³⁹ In earlier publications, Percec et al.,^{140,141} discussed additional classes of rod-like main chain liquid crystalline polyethers containing mesogenic groups with and without flexible spacers based on conformational isomerization. Such a novel class of macromolecules was provided by hyperbranched and dendritic polyethers¹⁴³ which displayed liquid crystallinity. These types of LC polyethers of based on conformational isomerization were thoroughly reviewed in Percec publications.^{139,14-144}

The advancement of research in main chain liquid crystalline polyethers created an interest in macro cyclic¹⁴⁵ main chain liquid crystalline polymers. The first examples of cyclic main chain liquid crystalline oligomers¹⁴⁶ was synthesized from 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane with dibromoalkanes. Subsequently side chain liquid crystalline polyethers containing supramolecular quasi-rigid-rod-like mesogens,¹⁴⁷ monodisperse LC polyethers,¹⁴⁸ and LC crown ethers were also attained much attention. In addition to that, main chain polyethers of an elastomeric network also gained considerable interest.¹⁴⁹ These LC polyethers have been an important subject for fundamental and technological studies because of their unique anisotropic,

optical, electrical, and mechanical properties.¹⁵⁰ Thermotropic polyethers with photosensitive groups find wide applications in photoresists to make integrated circuits, printing plates, photocurable coatings, photorecorders photoconductors, energy-exchange materials, photosensitizers for organic synthesis, and liquid crystal displays. Photosensitivity, solubility, and thermal stability are the prime requirements for the applications of these polymers in the above mentioned field.¹⁵¹ Most of the studies of main chain LC polyethers to date have been concerned with materials in which the mesogenic groups are attached to a flexible polymer backbone. They classified into two major categories: (1) species with rigid mesogenic groups incorporated into the backbone structure (main chain liquid crystalline polyether); (2) polyethers with mesogenic units in the side-group structure (side chain liquid crystalline polyethers).¹⁵² The present work deals with polymers of the first type motivated by their theoretical and technological significance.¹⁵³ To obtain the mesophases of these polymers, introduction of flexible spacer groups between the rigid mesogens of polymer is necessary to provide the rigid mesogenic groups with sufficient mobility to their self-organization in the LC phase.^{24,34,46,47}

Percec & Yourd¹⁵⁴ presented the first series of experiments which prove that the synthesis of MCLCPs does not require rigid

rod-like mesogens. Mesophases can be obtained for polymers containing flexible structural units which exhibit conformational isomerism when their most stable conformer adopts an extended linear conformation. They prepared quasi-rigid polyethers and copolyethers based on methyl- and/or phenylhydroquinone 7 and trans and/or cis-1,4-bis((methylsulfonyl) methyl) cyclohexane 8 through phase-transfer-catalyzed polyetherification reaction. The methylene ether units inserted within the polyether backbone exhibit anti (extended) and gauche (kinked) as the two most thermodynamically stable conformers which are in dynamic equilibrium (Figure 23). The ratio between these two conformers allows the overall conformation of the polymers to be extended, and therefore they exhibit thermotropic liquid crystallinity (Scheme 4).

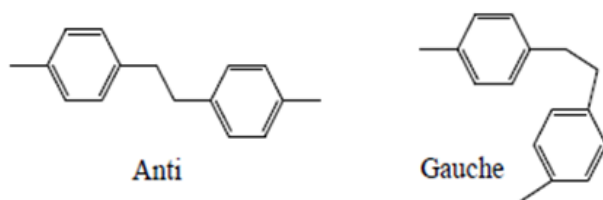
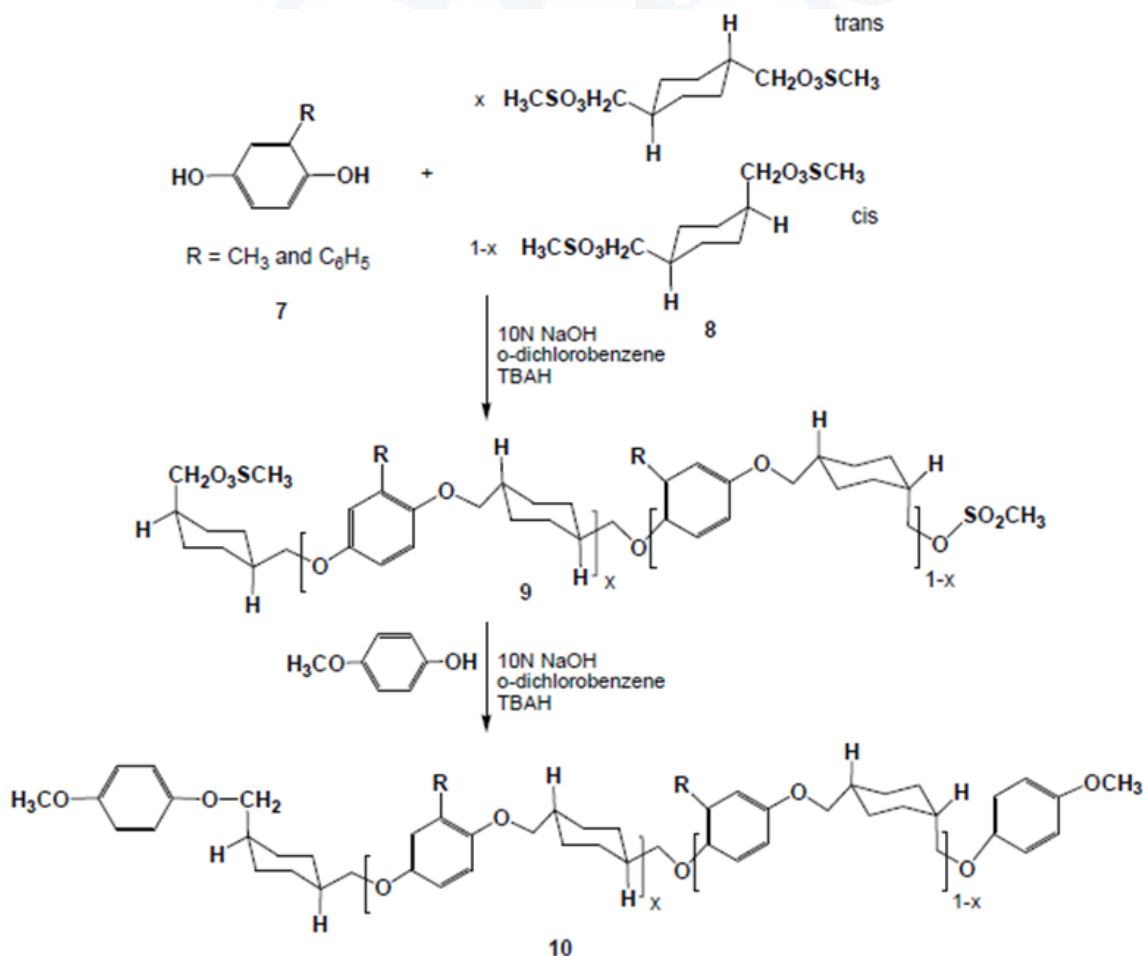
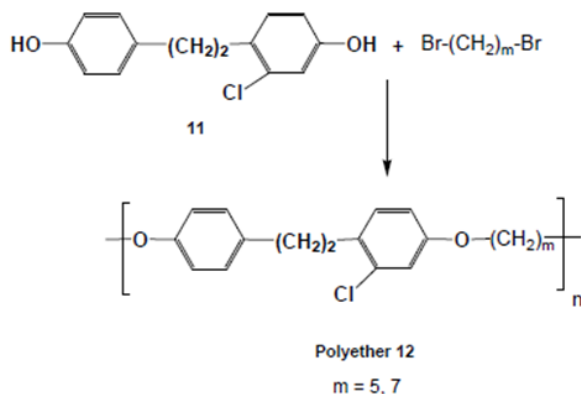


Figure 23 Structure of the anti and gauche conformers of the flexible mesogenic unit.

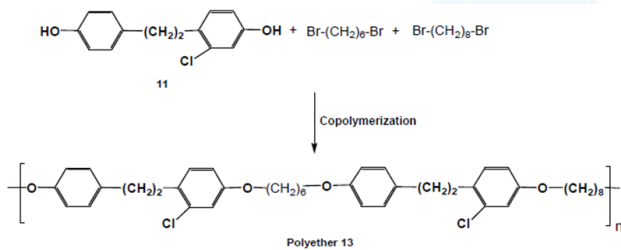


Scheme 4 Synthesis of polyether 9 and copolyether 10.

Zurber & Percec^{155,156} prepared and described a new series of main chain liquid crystal polyethers based on 1-(4-hydroxyphenyl)-2-(2'-chloro-4'-hydroxyphenyl) dioxyethane 11 through its polymerization with a series of 1,5; 1,6; 1,7; and 1,8-dibromoalkanes. In addition, the copolymer was synthesized (Schemes 5 & 6).



Scheme 5 Synthesis of polyethers 12.



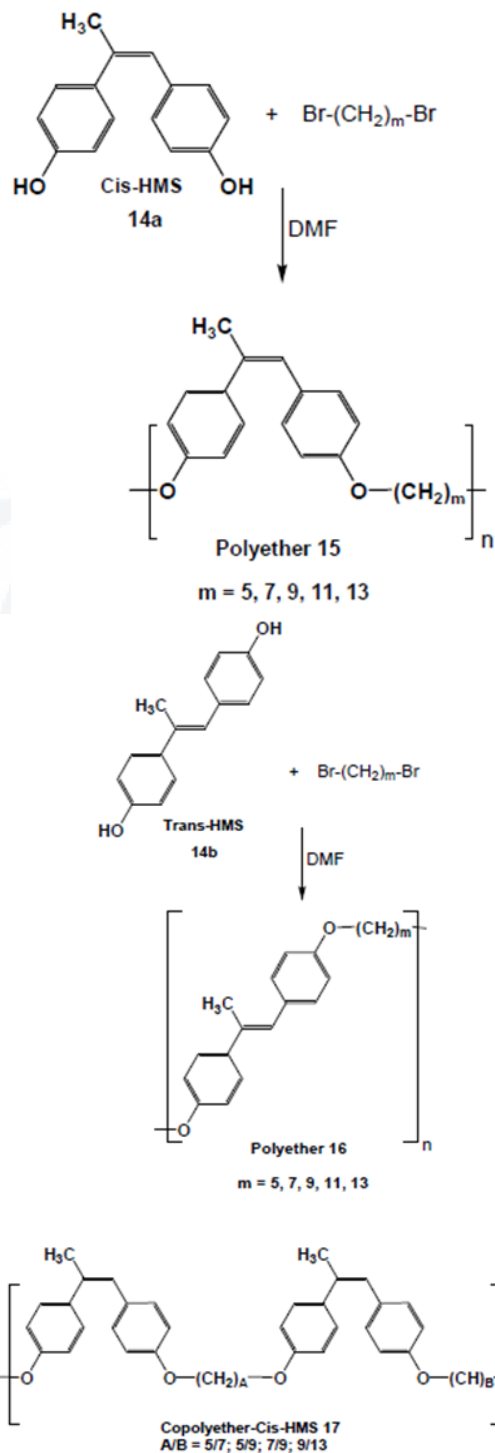
Scheme 6 Synthesis of polyether 13.

Percec et al.¹⁵⁷ synthesized a series of thermotropic polyethers and copolyethers based on 4,4'-dihydroxy- α -methylstilbene (HMS) by polymerization and copolymerization with flexible spacers containing odd number of methylene units [e.g. HMS-XY (AB)]. Where X is the number of methylene units in one of the spacer while, Y is the number of methylene units in the other spacer, and A/B refers to the molar ratio of the two spacers (Scheme 7).

Virgil Percec & Masaya Kawasumi¹³⁹ synthesized and described the first thermotropic liquid crystalline dendrimer exhibiting a nematic mesophase. This was carried out by using homopolymerization of the monomer 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD-b) followed by in situ alkylation of the phenol chain ends. This monomer represents a mesogenic unit based on conformational isomerism.^{135,140,141,158-160} The phase behavior of the resulting dendrimer with different chain ends (TPD-b-X, whose X indicates the structure of the chain end which may be Ph-CH₂- or methylene units) will be compared to that of its linear model compounds. This linear polymer was synthesized by the polyetherification of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (TPD) with α,ω -dibromoalkanes containing an X number of methylene units (TPD-X, where X = 6-10).

Catanescu et al.,¹⁶¹ synthesized a new series of polyethers based on bis (2-chloroethyl) ether and various bisphenols, by using phase transfer catalysis technique in liquid/liquid system. Only the polymers with azobenzene and biphenyl units exhibited

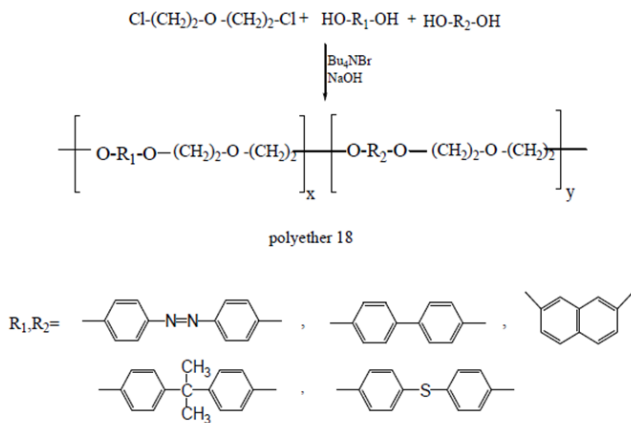
crystalline mesophases, the others displayed semi-crystalline or amorphous structures (Scheme 8).



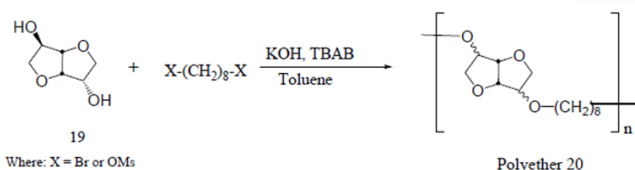
Scheme 7 Synthesis of polyethers 15,16,17.

The polymers were characterized by ¹H-NMR, DSC and optical microscopy in polarized light. The molecular weights of the samples were low, situated in the oligomer domain. Chatti et al.¹⁶² synthesized a new LC polyether by polycondensation of isosorbide 19 with 1,8-dibromo or dimesyl octane under phase

transfer catalysis with increased efficiency when performed under microwave activation (Scheme 9).

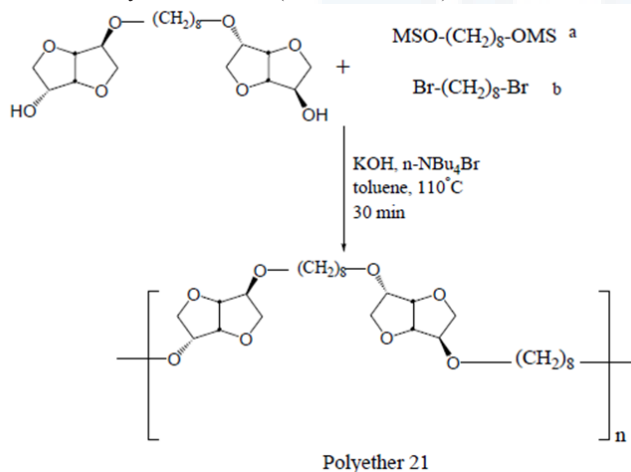


Scheme 8 Synthesis of polyethers 18.



Scheme 9 Synthesis of polyether 20.

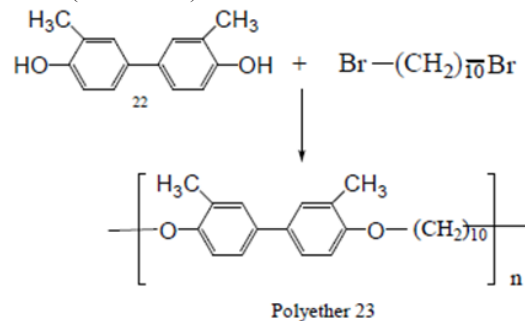
In 2004 Chatti et al.,¹⁶³ synthesized different new LC polyethers from numerous polycondensations of aliphatic diol of isosorbide and 1,8-dimesyl octane or other aliphatic dibromo and disulphonated alkylating agent that was performed under phase transfer catalytic conditions (Schemes 10&11).



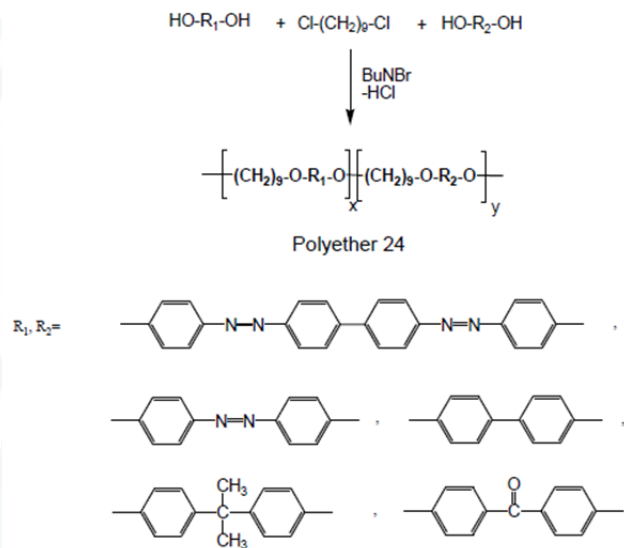
Scheme 10 Synthesis of polyether 21.

Murakami et al.,¹⁶⁴ prepared a new type of main chain thermotropic LC polyether EBMB-10 which is composed of 3,3'-dimethyl-4,4'-biphenyl units as mesogen and 10 methylene sequences as spacer. This polymer was synthesized by the polymerization of 3,3'-dimethyl-4,4'-dihydroxybiphenyl (22) and 1,10-dibromodecane in a two phase system containing each monomer in each phase using a phase transfer catalyst (Scheme 12). This polymer has a glassy phase, which was investigated by using DSC, Wide angle X-ray diffractometry, and solid-state ¹³C NMR spectroscopy.

Alazaroaie et al.,¹⁶⁵ investigated the relationship between the structure of macromolecular chain and its ability to generate a mesophase, when mesogens with an azobenzene structure are implied. They synthesized a series of polymers by phase transfer catalysis starting from 1,9-dichlorononane and different bisphenols (Scheme 12).



Scheme 11 Synthesis of polyether 23.



Scheme 12 Synthesis of polyethers 24.

The resulting polymers had been characterized by ¹H NMR spectroscopy, DSC, polarized optical microscopy and thermogravimetric analysis. Theoretical conformational studies, using molecular simulations had also been performed. Due to the particular geometry of bis(azobenzene) units, they are better mesogenic groups as compared with the azobenzene ones.

In 2005 Nicolae et al.,¹⁶⁶ studied the thermal stability of some aromatic copolyethers containing a propylenic spacer. The copolymers were prepared by using phase transfer catalysis technique starting from 1,3-dibromopropan and various bisphenols such as 4,4'-dihydroxyazobenzene (DHAB); 2,7-dihydroxynaphthalene

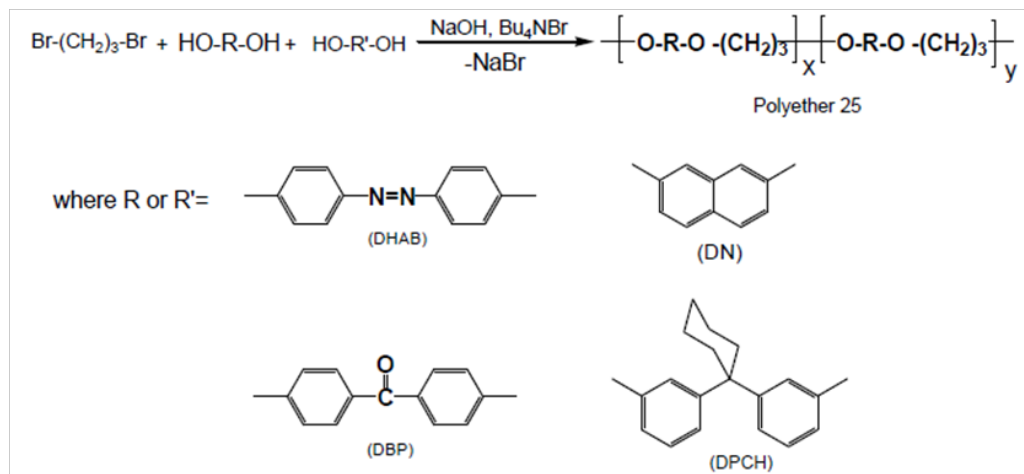
(DN); 4,4'-dihydroxy (benzophenone) (DBP) and 1,1'-bis(4-hydroxyphenyl)cyclohexane (DPCH) (Scheme 13).

Alazaroaie & Nicolae¹⁶⁷ studied the relationship between the structure and supramolecular ordering of some aromatic polyethers containing flexible spacer. These polymers were synthesized using a phase transfer catalysis technique, in a liquid=liquid system, starting from 1,4-dichlorobutane or 1,5-dichloropentane

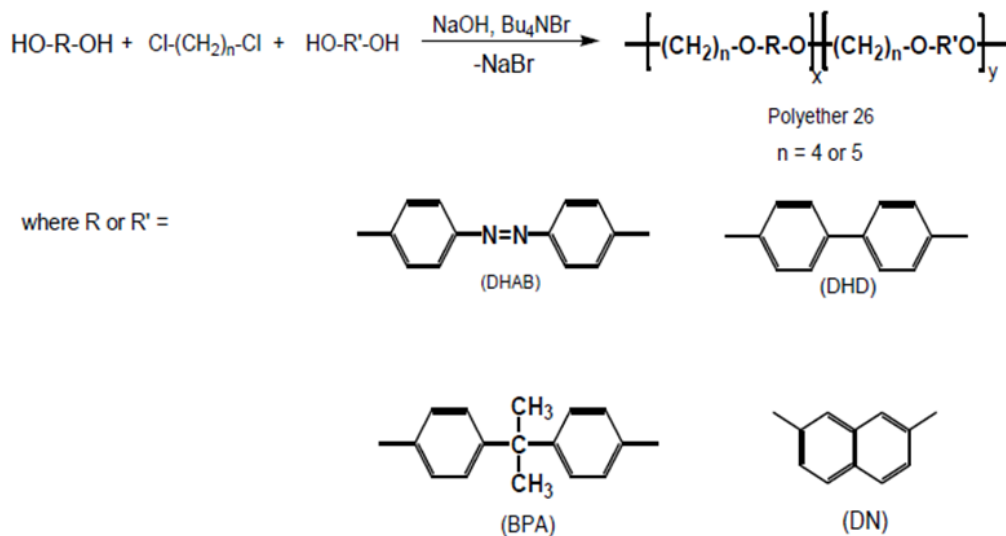
and various bisphenols such as 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), bisphenol A (BPA), and 2,7-dihydroxynaphthyl (DN) (Scheme 14).

All these polymers were investigated by using ^1H NMR, DSC, and optical microscopy in polarized light. Some samples containing azobenzene moieties showed LC properties, while the majority of them resulted as semi-crystalline compounds. If a bent bisphenol was used (BPA) to obtain homopolymers or copolymers, only amorphous products were obtained. The low thermal stability of the LC compounds led to some difficulties

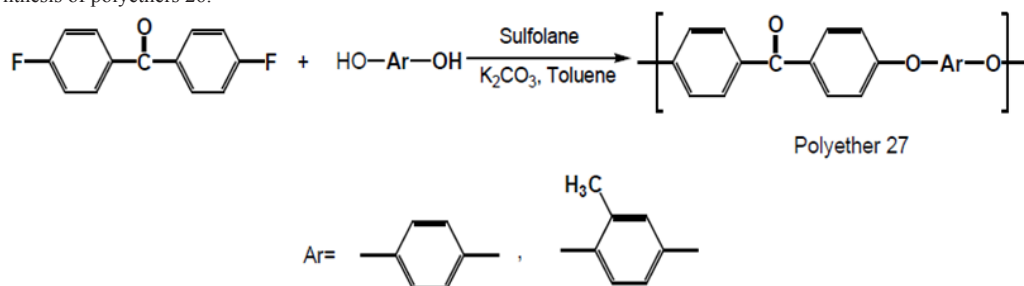
regarding the characterization of the mesophase. Generally, the copolymerization reaction influenced only the crystalline melting points, the isotropization temperature of the LC polymers being situated near their thermal degradation limit. Rao & Sabeena¹⁶⁸ prepared and described a series of polyether ether ketone and polyether ether ketone copolymers. These polymers were prepared by the nucleophilic substitution reaction of 4,4'-difluorobenzophenone with various mole proportions of both hydroquinone and methyl hydroquinone hydroquinone using sulfolane solvent in the presence of anhydrous K_2CO_3 (Scheme 16).³⁸



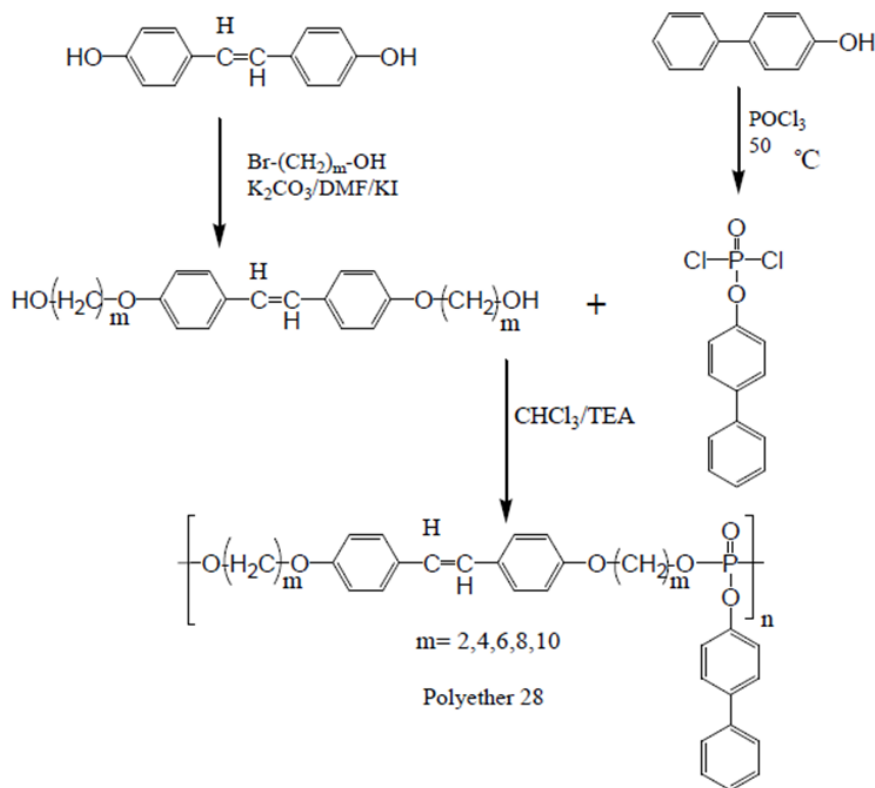
Scheme 13 Synthesis of polyethers 25.



Scheme 14 Synthesis of polyethers 26.



Scheme 15 Synthesis of polyethers 27.

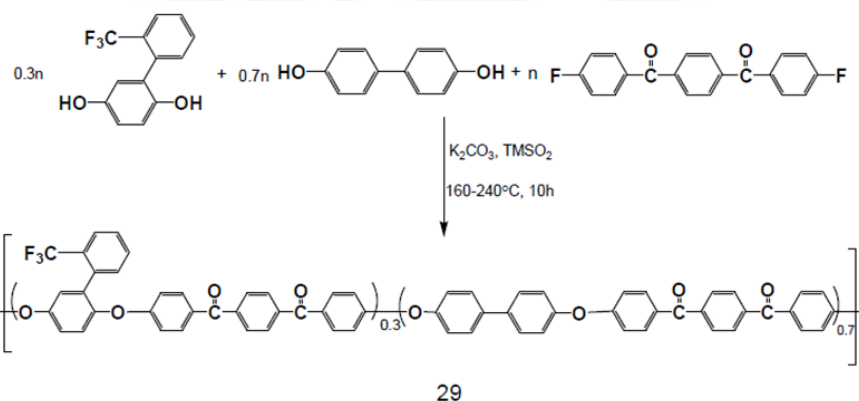


Scheme 16 Synthesis of polyethers 28.

Ravikrishnan et al.,¹⁶⁹ synthesized a series of liquid crystalline and photoactive polymers from biphenylphosphorodichloridate with various 4,4'-bis(m-hydroxyalkoxy)stilbenes (m = 2, 4, 6, 8, 10) in chloroform by solution polycondensation method using an acid scavenger (Scheme 17).

The resultant polymers were characterized by inherent viscosity,

FT-IR, ¹H, ¹³C and ³¹P NMR spectroscopies. The liquid crystalline (LC) properties were investigated using both POM and DSC and it was documented that only polymers which contain higher methylene chain (m = 6, 8, 10) of the five synthesized polymers exhibited LC properties. They also studied the thermal stability and the photochemical properties of these polymers using UV and fluorescence spectroscopy for these polymers.

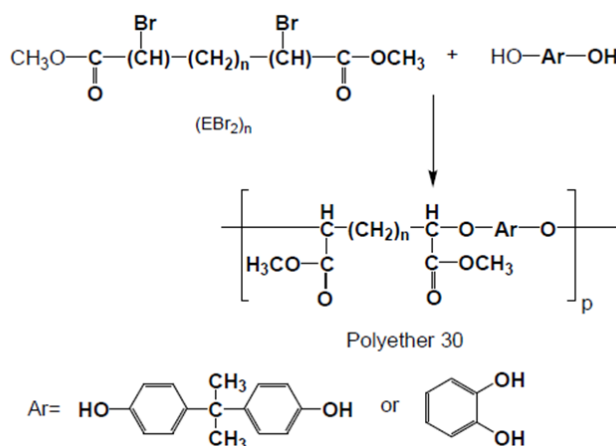


Scheme 17 The synthetic route of FPAEKLCP 29.

Jiashuang et al.,¹⁷⁰ was motivated to synthesize poly(ether ether ketone) (PEEK) because it is one of the most types of high-performance engineering thermoplastics. In addition, it has extensive applications in the aviation, automotive, medical, and electrical industries owing to the excellent mechanical performance, good thermal stability, and chemical resistance.¹⁷⁰ Therefore, PEEK fibers have a unique combination of mechanical properties that are stable under extreme environmental conditions.

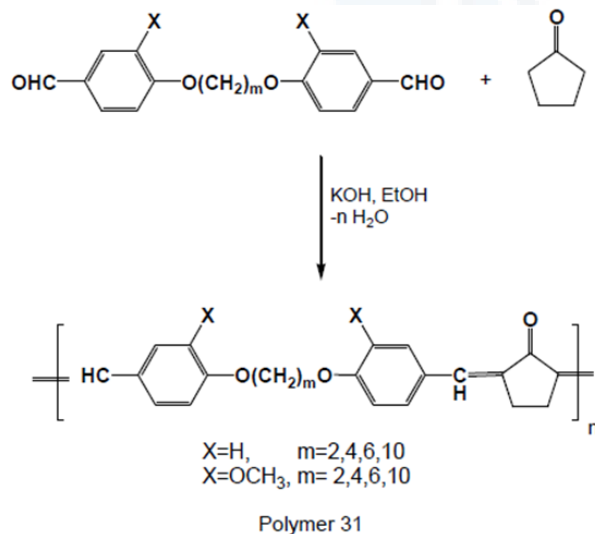
In the past few decades, numerous efforts have been devoted to improving their mechanical properties by the changes of processing parameters. They found drawbacks associated with their processing and applications such as high melting temperature and high melt viscosity.¹⁷¹⁻¹⁷⁴ Thermotropic liquid crystalline poly(aryl ether ketone) copolymers (FPAEKLCP) (Scheme 18) are excellent candidates for the processing aids due to the unique rod-like molecule, anisotropy, low melt viscosity, a high degree

of order in the melt under shear and elongational flow fields.¹⁷⁵⁻¹⁷⁸ Moreover, the matched processing temperature and the similar structure with PEEK resin, but also decreases the melt viscosity of PEEK, thereby improves the spinnability and the quality of as-spun fibers to obtain a high-performance PEEK fiber.



Scheme 18 Synthesis of polyethers 30.

Ismail et al.,¹⁷⁹ synthesized new aromatic polyethers which were obtained with good yields by interfacial polycondensation of $(EBr_2)_n$ α, α' -dibrominated diesters (n being the number of methylene units) and bisphenol A (bis(4-hydroxyphenylether) or catechol (2-hydroxyphenol) with various catalysts [Aliquat (Tricaprylmethylammonium chloride), TBAB (tetrabutylammonium bromide), and TDA1 (Tris(dioxa-3,6-heptyl)amine)] (Scheme 19). These polymers can be used in many applications, for instance as tensioactives agents,¹⁸⁰ ion exchangers,¹⁸¹ and ion sensitive field effect transistors (ISFET).¹⁸²



Scheme 19 Synthesis of poly(arylidene-ether)s 31.

Liquid crystalline polymers and copolymers containing bisarylidene cycloalkanone moiety

In recent papers, the researchers have been directed their attention to the synthesis and investigating of new series of polymers and

copolymers containing bisarylidene cycloalkanone moiety. This is because the special features of polymers bearing this unit. The bisarylidene cycloalkanone mesogenic unit contributes to the LC properties and facilitates photochemical reactions of the polymer chains under the influence of UV irradiation.¹⁸³⁻¹⁸⁶ Furthermore; it was documented as medical therapy and chemotherapy. This has been resulted in potential applications of these polymers in biology, chemistry, materials science and technology.¹⁸⁷ Samdahl was the first one who synthesized the bis-arylidene cycloalkanone molecule in 1928.^{188,189} In 1969, Borden et al introduced this molecule into a macromolecular architecture.^{190,191}

The photosensitivity of such polymers or copolymers is based on the electron density of the photo-chromophores present in the polymer backbone. This mesogenic group has the ability to go in reversible or irreversible chemical transformations under irradiation with light. Such transformations may include (E/Z) isomerization reactions, cyclization, photo-crosslinking, photo-dimerization, photo-dissociation and photo-association of the polymer chains. Photoirradiation reactions in organic polymers are always accompanied by certain changes in physical and chemical properties.¹⁸³⁻¹⁸⁶ Many authors studied the synthesis and characterization of bisarylidene containing side-chain and main chain polymers with structural variations.

The list of architecture types includes polyesters,^{192,193} poly(phosphate esters),^{116,194-201} poly(azomethine-ethers),²⁰² polyphosphoramides,²⁰³⁻²⁰⁵ polysulfonates,¹⁸⁷ poly(siloxane ethers),²⁰⁶ and side chain methacrylate polymers.²⁰⁷⁻²¹⁵ The advantage of this class of mesogenic group is their high rigidity which enhance the thermal stability and possibility of facile structure modification.¹⁸⁷ Many application areas have appeared for utilization of this type of polymer. It was established to be utilized in the field of optical and electronic devices,²¹⁶ such as the development of polymer-based smart materials, reversible and irreversible information storage media, holographic applications and liquid crystalline display devices.^{217,218} The bisarylidene cycloalkanone molecules were discovered to be important in medicinal applications. Ramanan et al. documented that the bisarylidene molecule has anti-inflammatory effect. The continuous search for novel and cost effective drugs against diseases, bisarylidene cycloalkanone was found to have a promising cytotoxicity effect. Dimmock et al. reported that the bisarylidene cycloalkanone can be used as a potential cytotoxic analogue against human tumour cells especially towards colon cancer and leukemic cancer cells.^{219,220} They have synthesized a series of synthesized a series of 2,6-bisarylidene cycloalkanones and related compounds containing one or two substituents at the four position of the cyclohexyl ring. These compounds showed cytotoxic activity against murine P388 and L1210 cells as well as human Molt 4/C8 and CEM T-lymphocytes. About 25 times higher activity than the reference drug, namely carmustine, was observed to a number of human tumours in vitro, particularly towards human colon cancer and leukemic cells, for some representative compounds.

This class of compounds exerts their bioactivity by the reaction with cellular thiols. This can result in inhibition of protein syntheses and enzyme inactivation, eventually leading to cell death.²²¹ Researchers discovered that there is a structure-

bioactivity relationship. Previous work showed that the presence of electron attracting groups in the phenyl rings and substituents at position four of the cyclohexanone ring is the most structural features which influence the bioactivity of these compounds. Furthermore, the theory of sequential cytotoxicity, which states that successive chemical attacks of cellular constituents, may be highly deleterious to malignant cells. This means that the increase in the number of thiol alkylation sites, increase the potency of these compounds.

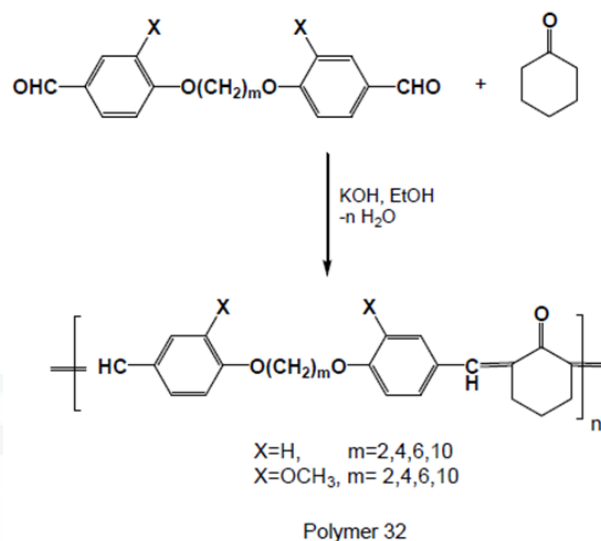
A range of polymers, bearing this moiety, were synthesized with backbone architectural variations and characterized for their liquid crystalline (LC) and other properties. These polymers can be classified as multifunctional materials.

Synthesis of liquid crystalline poly (arylidene-ether)s and copoly(arylidene-ether)s with flexible spacers in the polymers backbone

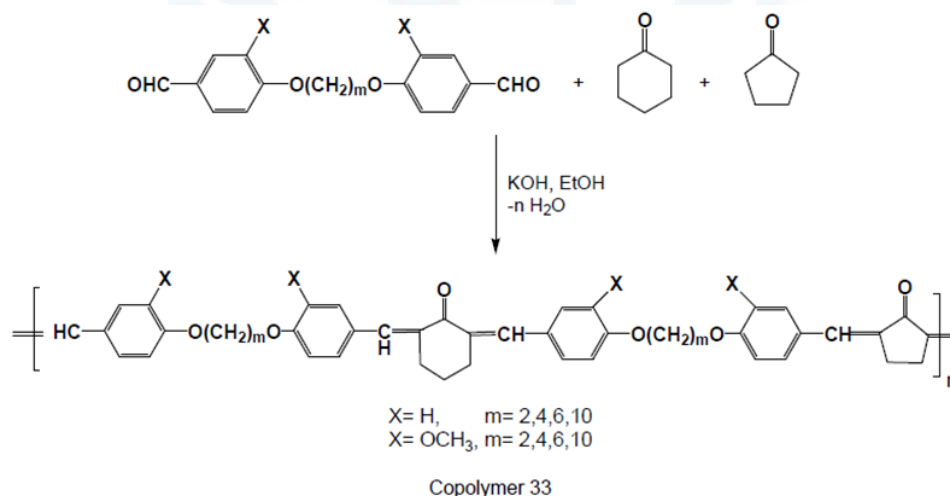
Aly & Hammam²²² synthesized a new series of poly(arylidene-ether)s containing cyclopentanone by polycondensation of 4,4'-diformyl- α,ω -diphenoxyalkane and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane with cyclopentanone (Schemes 19).

The thermotropic liquid crystalline properties of these polymers were examined by DSC, polarized optical microscopy using a heating unit, and thermogravimetric analyses. In addition, some

polymers showed some degree of crystallinity when examined by X-ray diffraction technique. Also, Aly²²³ prepared two novel series of poly(arylidene-ether)s and copoly(arylidene-ether)s via polycondensation of 4,4'-diformyl- α,ω -diphenoxyalkane and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane with cyclohexanone and/or cyclopentanone (Schemes 20 & 21).



Scheme 20 Synthesis of poly(arylidene-ether)s 32.



Scheme 21 Synthesis of copoly(arylidene-ether)s 33.

Aly & El-Kashef²²⁴ synthesized two novel series of poly(arylidene-ether)s and copoly(arylidene-ether)s from N-methylpiperidone and/or cyclohexanone, respectively. The first series (homopolymers) was derived from 4,4'-diformyl- α,ω -diphenoxyalkane or 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane with N-methylpiperidone. The second series (copolymers) was derived from the diphenoxyalkanes with N-methylpiperidone and cyclohexanone (Schemes 22 & 23).

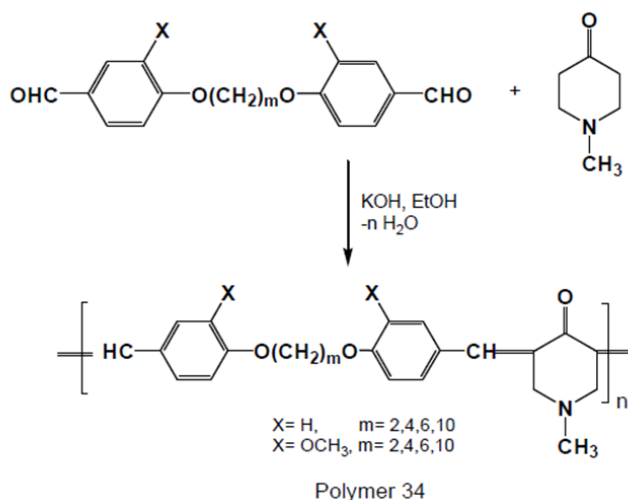
The polymers had been characterized by DSC measurements and microscopic observation under polarized light which demonstrated that all of the polymers and copolymers exhibited thermotropic liquid crystalline properties. Poly(arylidene-ether)s form nematic mesophase over a wide temperature range in

contrast to the corresponding copoly(arylidene-ether)s. Carmen et al.,²⁰⁶ synthesized new arylidene-siloxane polyethers by polycondensation reactions, starting from α,ω -bis(chloromethyl) polydimethylsiloxanes with different molecular weights and 2,6-bis(4-hydroxybenzylidene)cyclohexanone (Scheme 24).

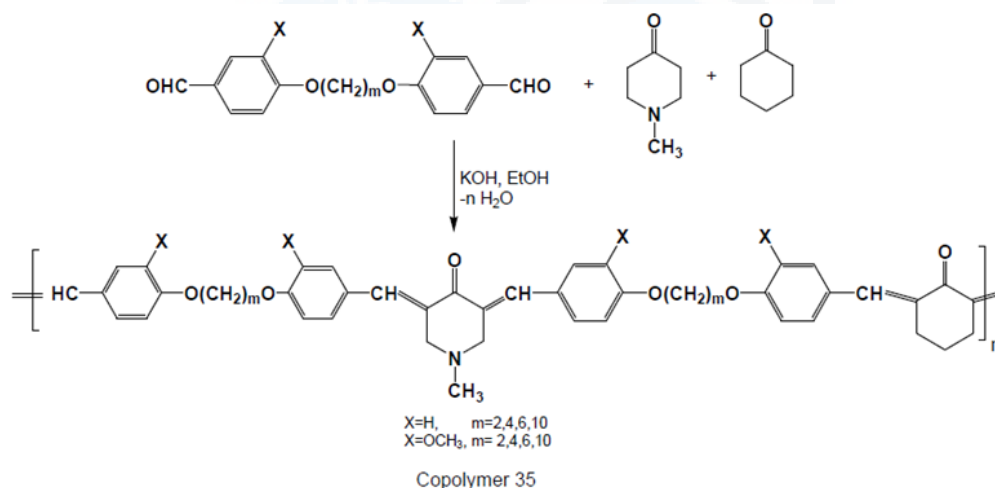
The structure of the resulting polymers was confirmed by IR and ¹H-NMR spectroscopy and their thermal properties and mesophase behavior were studied by TGA, DSC, and polarizing optical microscopy. Depending on the length of the siloxane spacer, some of the obtained compounds exhibited thermotropic liquid-crystalline properties. A decrease of the transition temperatures values was observed as the spacer length increased. The photochemical behavior of the siloxane polyethers was

studied by ultraviolet absorption spectroscopy. Srinivasa & Samui¹⁸³ synthesized a series of main chain photoactive liquid crystalline polyethers, containing rigid bisarylidene photoactive mesogen and flexible methylene spacers by polycondensation of bisarylidene diols and dibromoalkanes (Schemes 25).

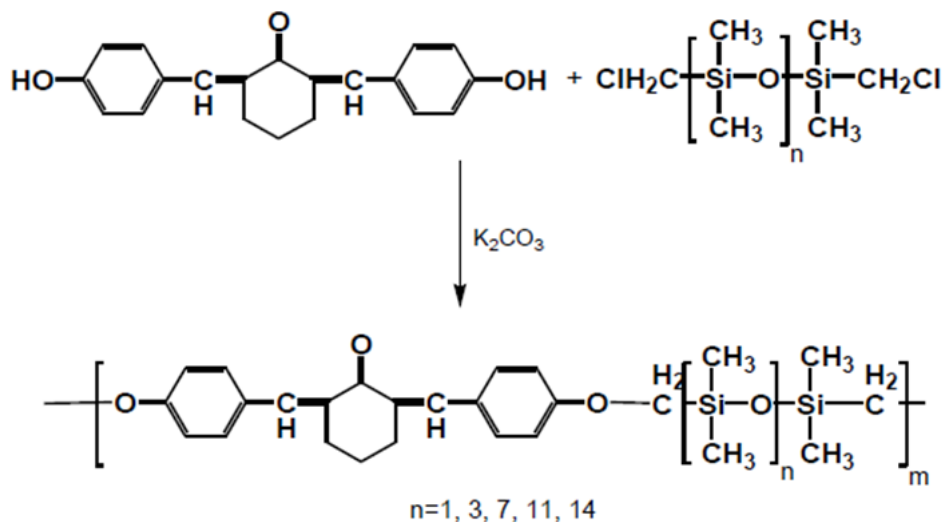
The polyethers were characterized with ¹H NMR, gel permeation chromatography (GPC), differential scanning calorimeter (DSC), thermo gravimetric analyzer (TGA), and polarized optical microscopy. Moreover, photoactive properties were investigated by using UV-vis spectroscopy. They found that steric hinderance caused by the substituents decreased the photoactivity as the number of substituents increased. Balaji & Murugavel²²⁵ synthesized two series of photosensitive main chain liquid crystalline poly(benzylidene-ethers) by Claisen-Schmidt polycondensation reaction of 4,4'-Diformyl- α,ω -diphenoxyalkanes (series 1) and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes (series 2) with acetone, cyclopentanone and cyclohexanone. The diformyl precursors were synthesized from 4-hydroxybenzaldehyde or and dibromoalkanes of varying spacer lengths.



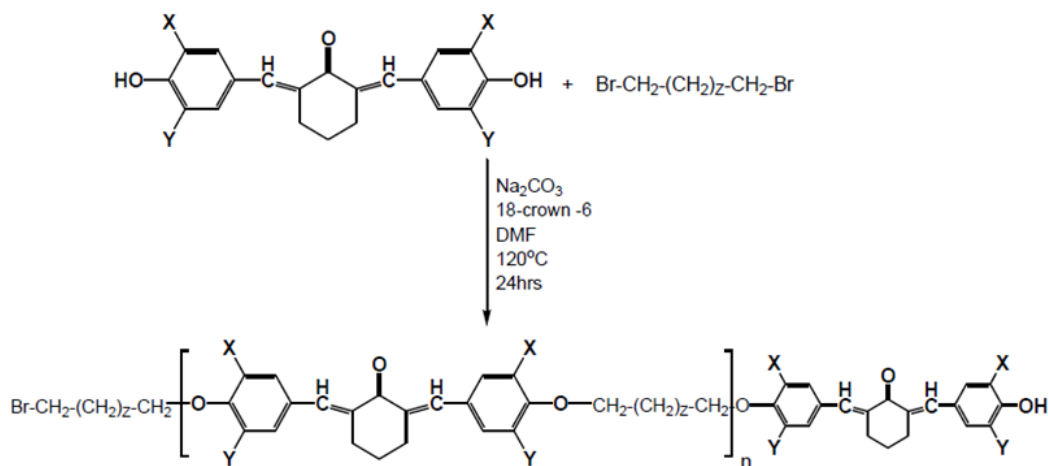
Scheme 22 Synthesis of poly(arylidene-ether)s 34.



Scheme 23 Synthesis of copoly(arylidene-ether)s 35.



Scheme 24 Synthesis of arylidene-siloxane polyethers 36.

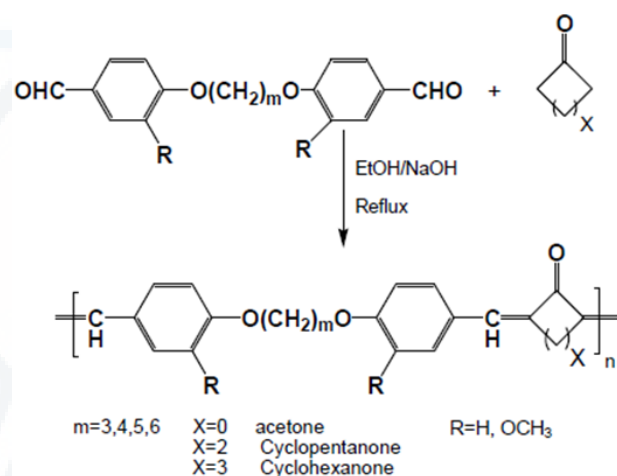


Scheme 25 Synthesis of polymers 37.

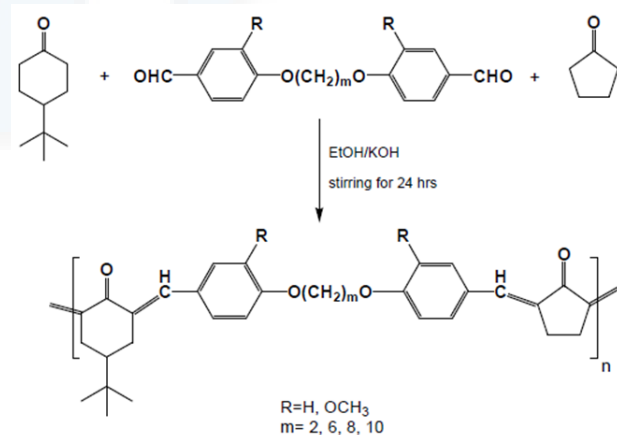
The formation of these poly(benzylidene-ether)s was confirmed by FTIR, ^1H NMR, and ^{13}C NMR spectral techniques. Their thermal and LC properties were investigated by using DSC, TGA, POM, and XRD techniques. The TGA results revealed that cyclopentanone containing polymers are more stable than acetone and cyclohexanone containing polymers, in addition, showed that series 1 polyethers displayed better stability when compared to series 2 polyethers. DSC analysis showed that the isotropic temperature decreases as the spacer length increases. The POM observations of some of these polymers exhibited schlieren nematic and nematic oily streak textures. Photoisomerization reaction was followed by UV-Visible spectrophotometer and found that E/Z isomerization is prevailed in the system. Fluorescence study showed that the polymers exhibit double emission in the visible region and proved that the methylene spacer have not influenced the photosensitive and photoluminescence properties of series 1, on contrary in series 2, fluorescence study proved that the methylene spacer have influenced the photosensitive and photoluminescence properties of the system and the length of spacers had a significant influence on their emission. Al-Muaikel & Aly²²⁶ synthesized a homologous series of thermotropic liquid crystalline copoly(arylidene-ether)s based on 4-tert-butylcyclohexanone moiety by solution polycondensation of 4,4'-diformyl- α,ω -diphenoxyalkanes or 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes with the 4-tert-butyl-cyclohexanone and cyclopentanone (Schemes 26 & 27).

Also Aly²²⁷ prepared a series of thermally stable thermotropic liquid crystalline poly(arylidene-ether)s and copoly(arylidene-ether)s by solution polycondensation of 4,4'-diformyl- α,ω -diphenoxyalkanes or 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes with 4-tertiary-butylcyclohexanone and/or 4-methyl cyclohexanone, respectively (Schemes 28-30).

Recently Kimura et al.,¹⁸⁵ synthesized a novel series of photoactive polymers containing 2,6-bis(benzylidene)-1-cyclohexanone in the main chain 43 and investigated as a photoalignment layer for polymerizable liquid crystals and liquid crystalline polymers. These polymers were easily prepared by thermal polymerization under mild conditions of the bis-azide and different diols diacrylate without the use of catalysts.



Scheme 26 Synthesis of polymers 38.

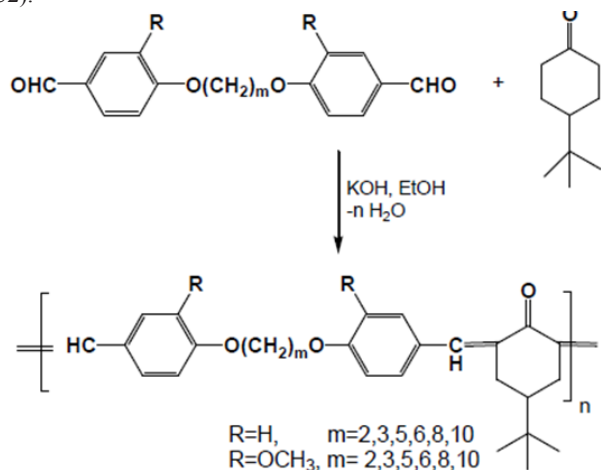


Scheme 27 Synthesis of polymers 39.

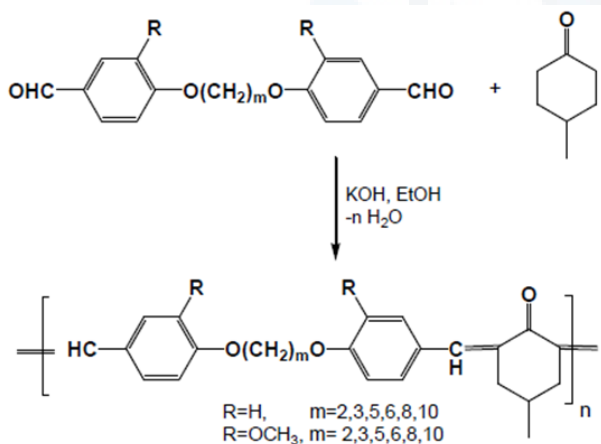
Synthesis of liquid crystalline poly(azomethine-ether)s with flexible spacers in the main chain

Polyazomethines belong to a class of materials that are known for their excellent thermal stability, good mechanical strength, and environmental resistance.²²⁸⁻²³⁰ and more particularly

as promising materials with optoelectronic and photonic applications.²³¹ Many of these polymers form mesomorphic phases on heating (thermotropic liquid crystalline polymers). However, their high melting points and low solubility usually make them inaccessible for processing by conventional methods. In order to improve their process ability, several approaches, such as the introduction into the main chain of flexible aliphatic segments or bulky lateral substituents have been attempted.^{232,233} Guillion and Skoulios²³⁴ prepared the first poly(azomethine-ether)s 44 from 4,4'-diformyl-1,10-diphenoxydecane and benzidine (Scheme 32).



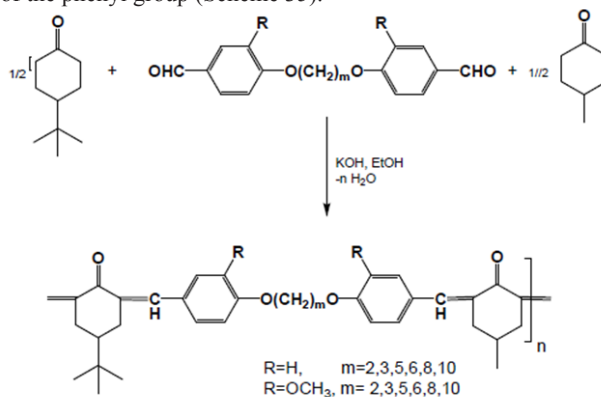
Scheme 28 Synthesis of polymers 40.



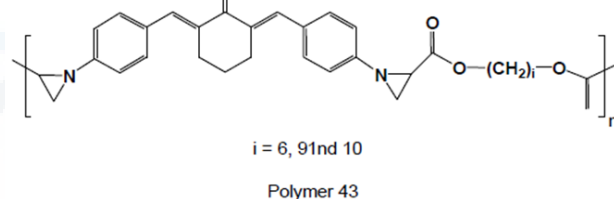
Scheme 29 Synthesis of polymers 41.

Also, terephthalaldehyde was reacted with 4,4'-diamino- α,ω -diphenoxyalkane to obtain poly(azomethine-ether)s 45 (Scheme 33). Poly(azomethine-ether)s 46 – 48 were also obtained from the polycondensation of 1,m-bis(4-amino-3-methylphenoxy) alkanes with terephthalaldehyde; 1,2-bis(4-formylphenoxy) ethane or 4,4'-biphenyldicarboxaldehyde (Scheme 34). The mesophoric properties were studied as a function of diphenoxyalkane spacers length. Analysis by DSC and optical polarized microscopy demonstrated that the poly(azomethine-ether)s form nematic mesophases over wide temperature ranges. Both the T_m and T_i values increased as the length of the flexible aliphatic spacers decreased; and also decreased with introduction of the methoxy group as a substituent in the polymer main chain. Li & Chang²³⁵ described the preparation of poly(azomethine-

ether)s 49 with rod-like segments connected by a short alkaline oxide spacers or insertion of methoxy group at the ortho position of the phenyl group (Scheme 35).



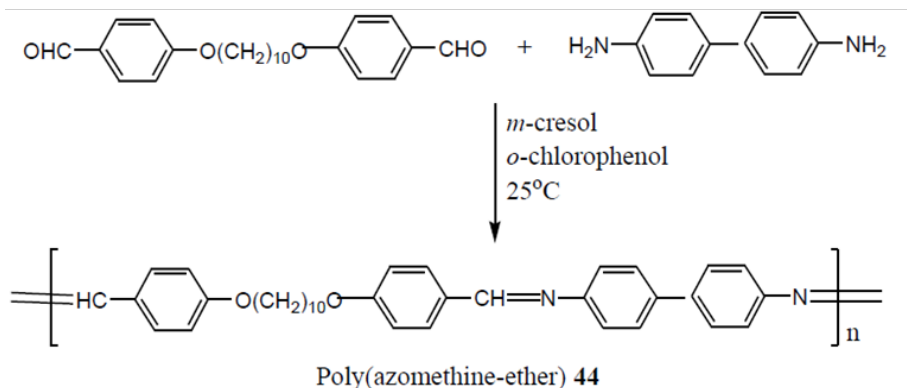
Scheme 30 Synthesis of copolymers 42.



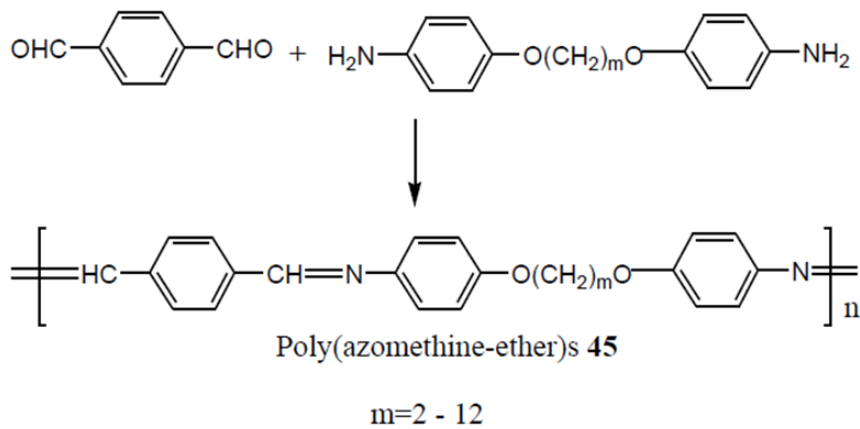
Scheme 31 photoactive polymers 43 containing 2,6-bis(benzylidene)-1-cyclohexanone.

The thermotropic liquid crystalline properties of the polymer were examined by DSC, OPM and TGA. Aly & Ahmed²³⁶ synthesized a series of polyazomethines 50 and 51 containing flexible spacers through polycondensation of diformyl- α,ω -diphenoxyalkanes with 2,5-bis(*m*-aminobenzylidene) cyclopentanone and 2,6-bis(*m*-aminobenzylidene) cyclohexanone (Scheme 36).

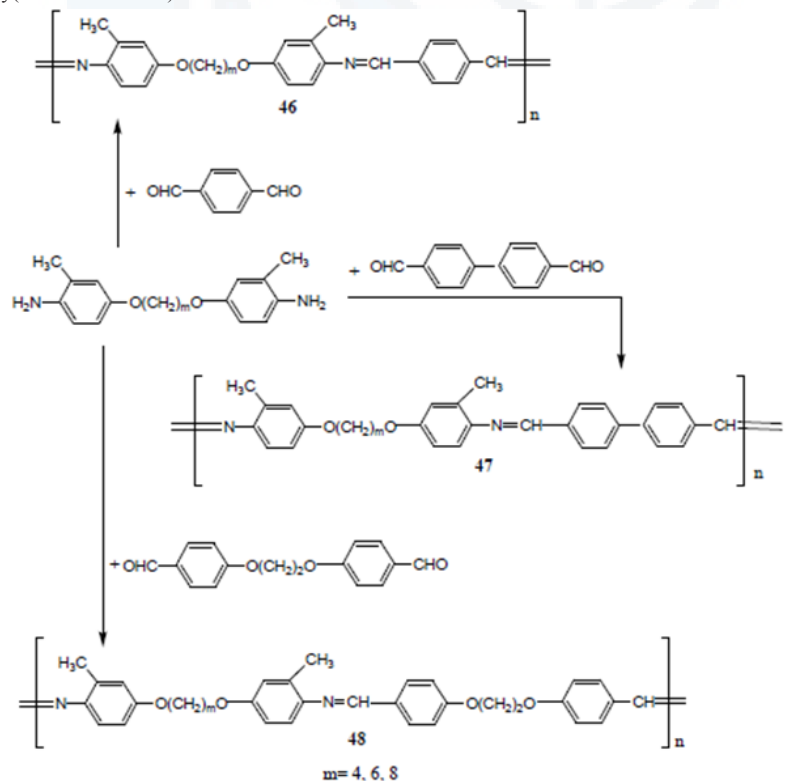
The polymers were characterized by IR spectroscopy, viscosity measurements, differential scanning calorimetry DSC and optical polarized microscopy OPM. The mesomorphic properties of these polymers were studied as a function of the diphenoxyalkanes space length. Analysis by differential scanning calorimetry and optical polarized microscopy demonstrated that the poly(azomethine-ether)s form nematic mesophases over wide temperature ranges. Jayanthi & Kishore²³⁷ synthesized a new hydroxy functionalized liquid crystalline poly(azomethine-ether)s 52 by solution polycondensation between dialdehyde and diamine (Scheme 37). An attempt was made to synthesize metal-containing liquid crystalline polymer networks 53 and 54 based on a new hydroxyl functionalized thermotropic polymer. This polymer exhibited nematic mesophase. DSC studies showed that the networks exhibited mesomorphic behavior up to 30 mol % of Cu(II). Similar networks were also formed by complexation of the polymer with various other metals like Co, Ni, Cd and Zn (Scheme 38). In 2003 Choi et al.,²³⁸ synthesized twelve azomethine polymers containing Banana-Shaped mesogen 55 as a repeating unit by polycondensation between different bisaldehyde and bisamine molecules (Scheme 39). The mesomorphic properties of these polymers were studied. The obtained polymers were characterized by FT/IR and NMR spectrophotometry, differential scanning calorimetry (DSC), optical microscopy and X-ray diffractometry.



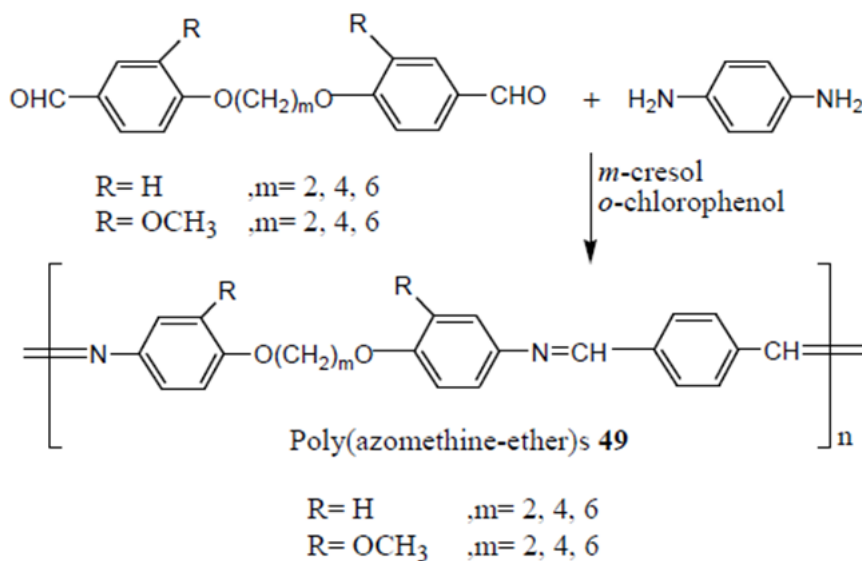
Scheme 32 Synthesis of poly (azomethine-ether)s 44.



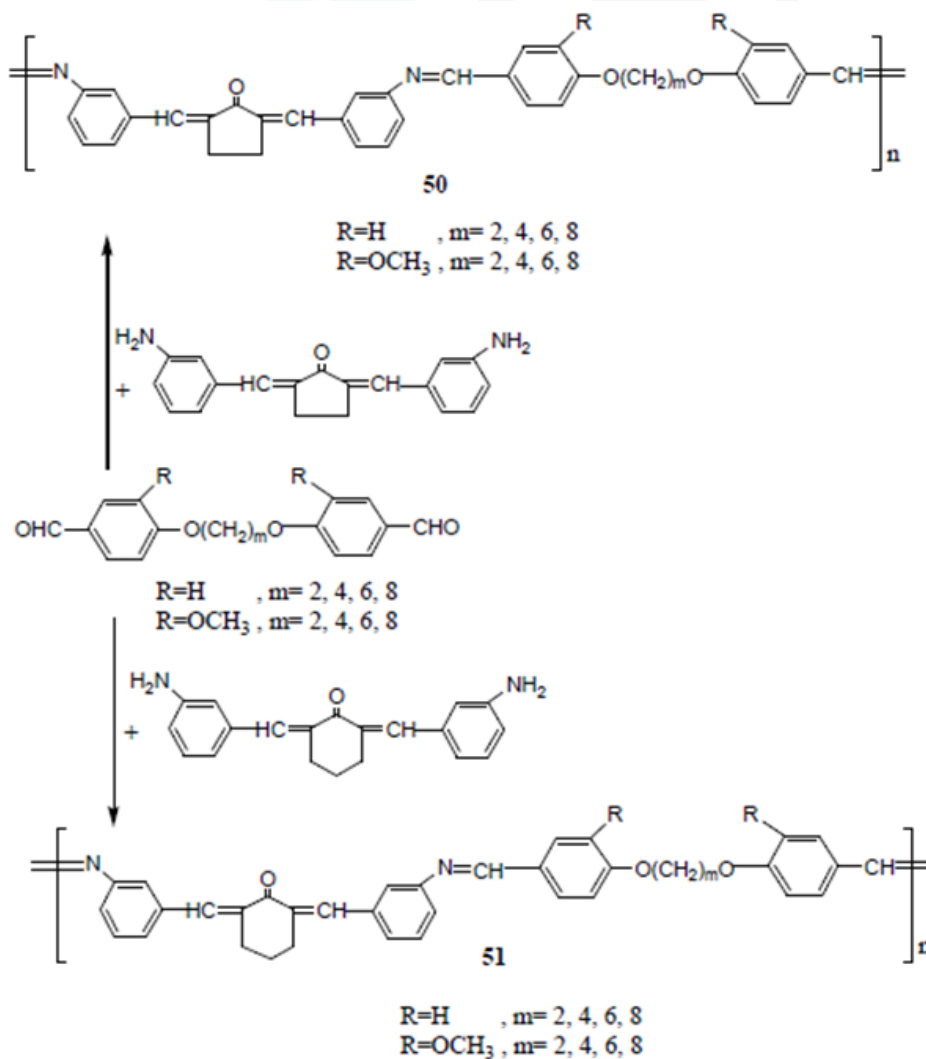
Scheme 33 Synthesis of poly(azomethine-ether)s 45.



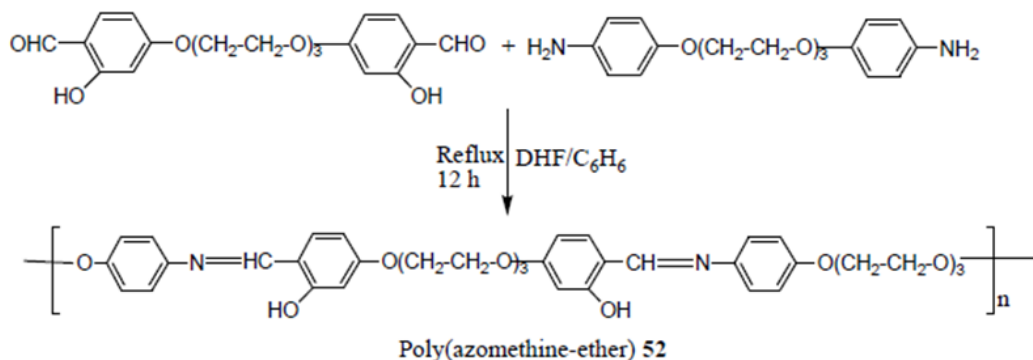
Scheme 34 Synthesis of poly(azomethine-ether)s 46-48.



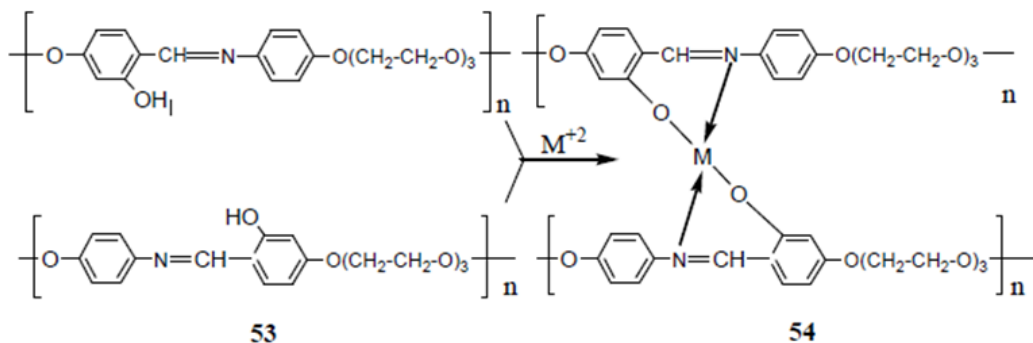
Scheme 35 Synthesis of poly(azomethine-ether)s 49.



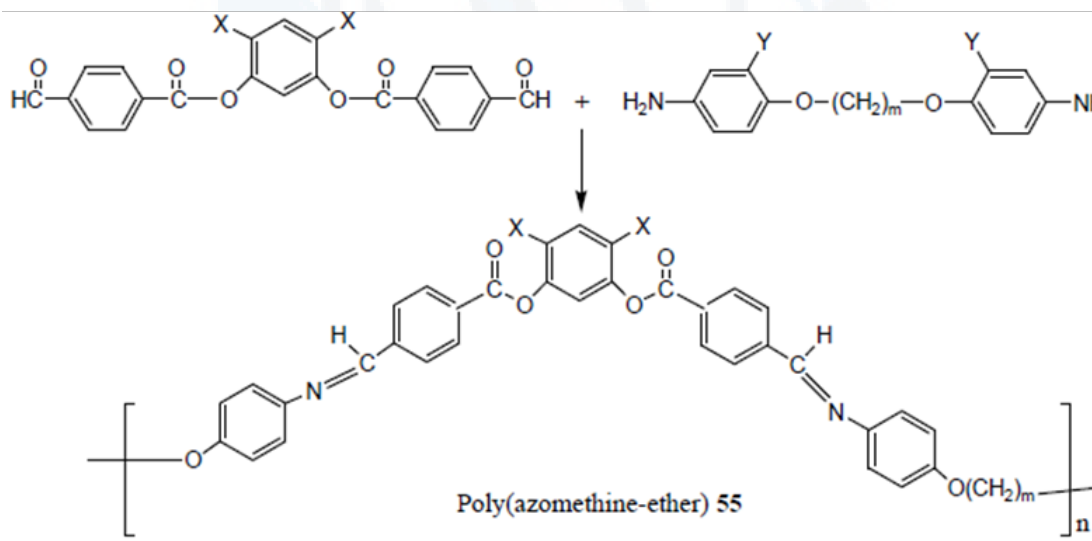
Scheme 36 Synthesis of poly(azomethine-ether)s 50, 51.



Scheme 37 Synthesis of hydroxy functionalized liquid crystalline poly(azomethine-ether)s 52.



Scheme 38 Synthesis of poly(azomethine-ether)s 53, 54.



Scheme 39 Synthesis of azomethine polymers containing Banana-Shaped mesogen

According to the importance of liquid crystalline poly(azomethine-ether)s, 56 Sauer et al.²³⁹ used temperature modulated differential scanning calorimetry (TMDSC), variable heating rate DSC, and trapping atomic force microscopy (AFM) to study thermal and morphological properties of liquid crystalline polymer including both polyester and azomethine groups. This polymer was prepared from terephthalaldehyde and 1,7-bis(4-amino-3-methylphenoxy)heptane as reported in (Scheme 40).²⁴⁰

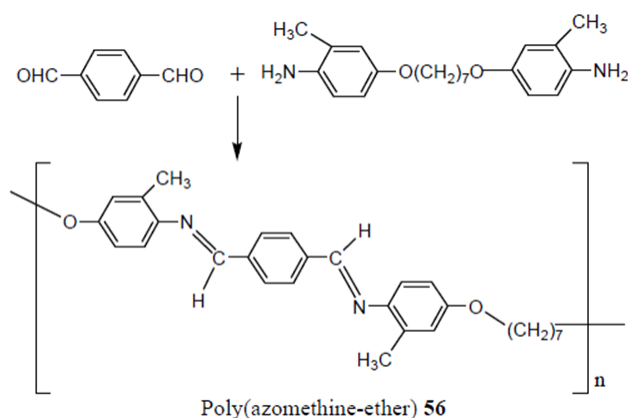
Synthesis of liquid crystalline poly(hydrazone-ether)s with flexible spacers in the main chain

Literature survey reveals that, a few authors are interested in the synthesis of liquid crystalline poly(hydrazone-ether)s. Troy & Stevens²⁴¹ synthesized poly(N, N-diacylhydrazones) from the reaction of pyromellitic dianhydride (PMDA) and benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) with terephthalaldehyde dihydrazone (TDH). In principle,

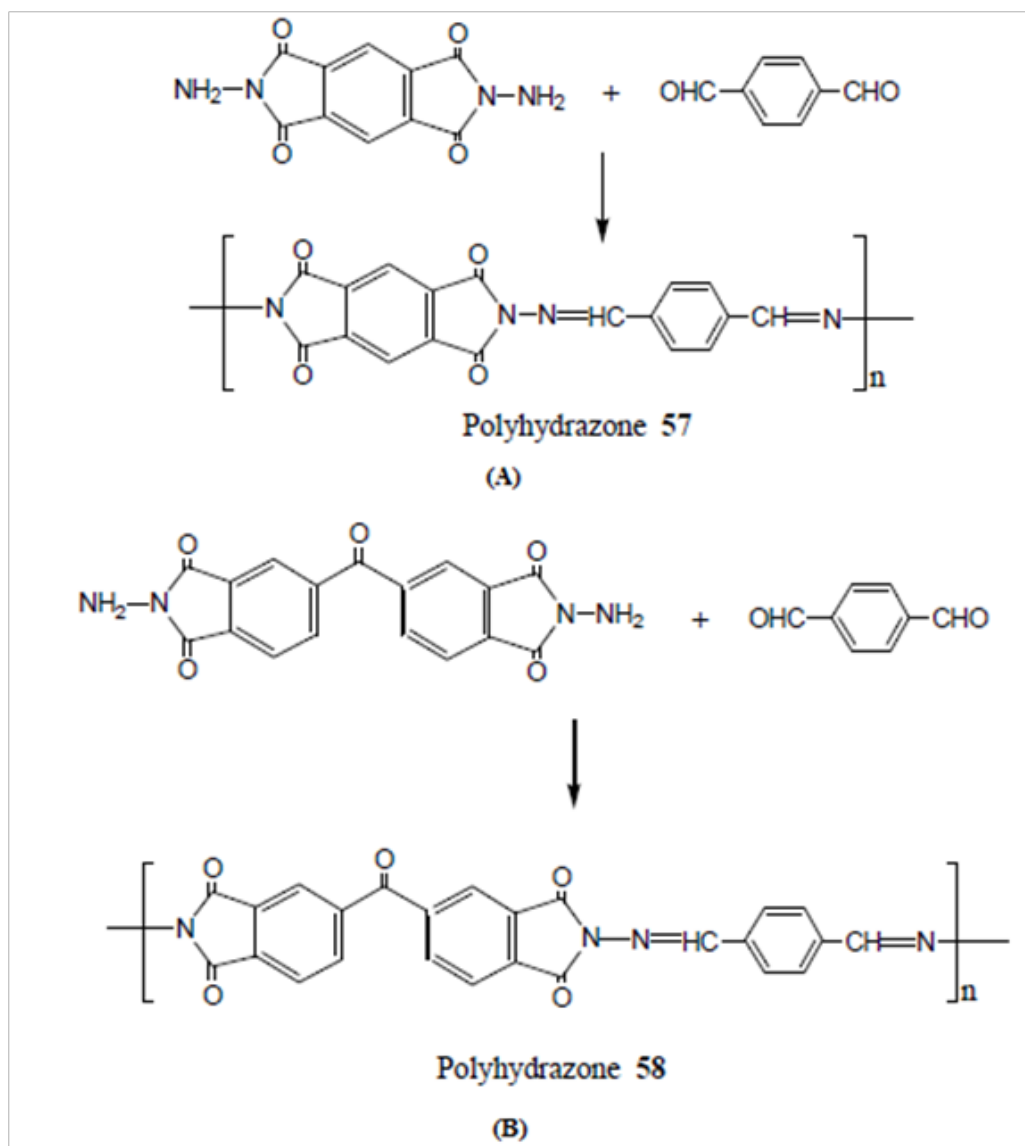
these polymers (57 and 58) can also be prepared from the corresponding *N,N*-diaminodiiimides of PMDA and BTDA with terephthalaldehyde (Scheme 41A,B).

The synthesis and characterisation of new liquid crystalline poly(hydrazone-ether)s 59 has been recently reported by Al-Muaiikel.²⁴¹ In this synthesis of new homologous series of thermotropic liquid crystalline poly(hydrazone-ether)s based on 1,3,4-thiadiazole moiety in the main chain, by solution polycondensation of various diformyl-diphenoxyalkanes with 2,5-bis(mercapto-acetichydrazide)-1,3,4-thiadiazole was reported (Scheme 42).

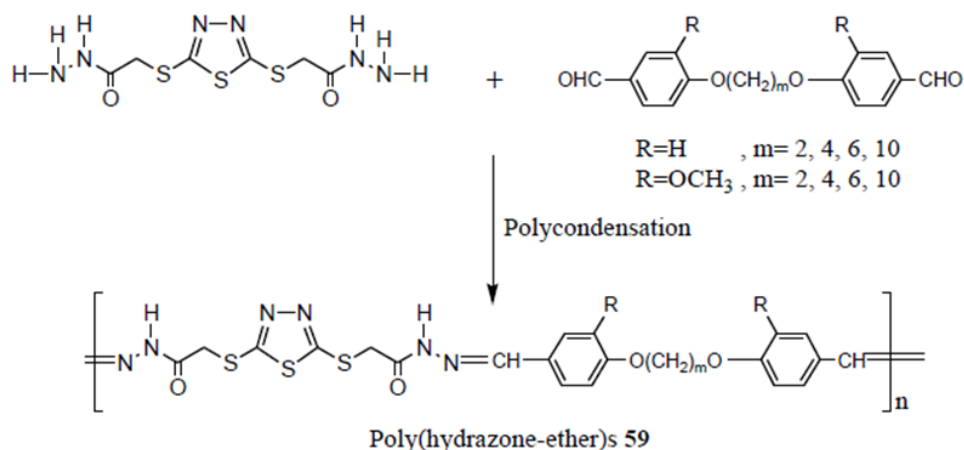
The phase behavior of these polymers was studied by differential scanning calorimetry (DSC), optical polarizing microscopy using a heated stage, and thermogravimetric analyses. Almost all the polymers exhibited thermotropic liquid crystalline properties.



Scheme 40 Synthesis of liquid crystalline poly (azomethine-ether)s 56.



Scheme 41A&B Synthesis of poly(*N, N*-diacylhydrazone)s 57 and 58.



Scheme 42 Synthesis of liquid crystalline poly(hydrazone-ether)s 59.

Conclusions

LCPs are highly appreciated to be synthesized as one of the most important smart materials in various fields of industrial applications. The polymer chains gain important behaviors upon carrying out LC properties. The important basic fundamentals about LC and LCPs have been displayed in this work; this includes variable types of classifications. The effects of mesogenic groups, structural unit, substituents and flexible spacers on the thermotropic properties also displayed. Moreover, the major synthetic methods for different types of LCPs were discussed in details including variable monomeric units with flexible spacers in the polymers main chains. This includes ethers linkage, bisarylidene cycloalkanone, arylidene-ethers, azomethine-ethers, and hydrazone-ethers moieties. All described LCPs show many important characters which can be used in a lot of industrial applications.

Acknowledgments

None.

Conflicts of interest

Authors declare there is no conflict of interest.

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