

# CHAPTER I

## INTRODUCTION

Liquid crystals cover a wide range of chemical structures, including rod-like molecules, disk-like molecules, cellulose derivatives, steroids, glycolipids, etc. In general, they can be divided into two categories depending on their molecular mass: low molecular weight and high molecular weight or liquid crystal polymers [1]. In recent years considerable interest has developed on liquid crystal polymers. These materials are unique in their properties and uses. They show some advantages with respect to widely used thermoplastics for engineering applications such as chemical resistance, low flammability, excellent mechanical properties, low thermal expansion, high continuous use temperature and often unusual ease of processing. These properties make liquid crystal polymers of interest for numerous branches of industries that mainly use these materials as fibers, films or injection molding compounds.

### 1.1 Liquid Crystal Polymers

Liquid crystal polymers are polymers that exhibit liquid crystal characteristics. In general, solid (crystal) has three-dimensional, long-range ordering of molecules. The molecules are said to be ordered or oriented with respect to their centers of mass and their molecular axes. The physical properties (e.g., refractive index, electrical conductivity, coefficient of thermal expansion) of a wide variety of crystalline substances vary in different directions. Such substances are referred to as *anisotropic substances* [2]. Substances that have the same properties in all directions are referred

to as *isotropic substances*. For example, liquids that possess no long-range molecular order in any direction are described as isotropic.



**Figure 1.1** Molecular ordering comparison between solid, liquid crystal and liquid [3]

A liquid crystal phase, often termed a mesophase, is an intermediate phase of matter between the ordered solid and disordered liquid phases which can exhibit certain physical properties of both these phases, i.e. molecules can diffuse readily and viscous flow can occur as in liquid but also there is a degree of long range order as in solid. There are two different ways in which a mesophase can be formed [1]:

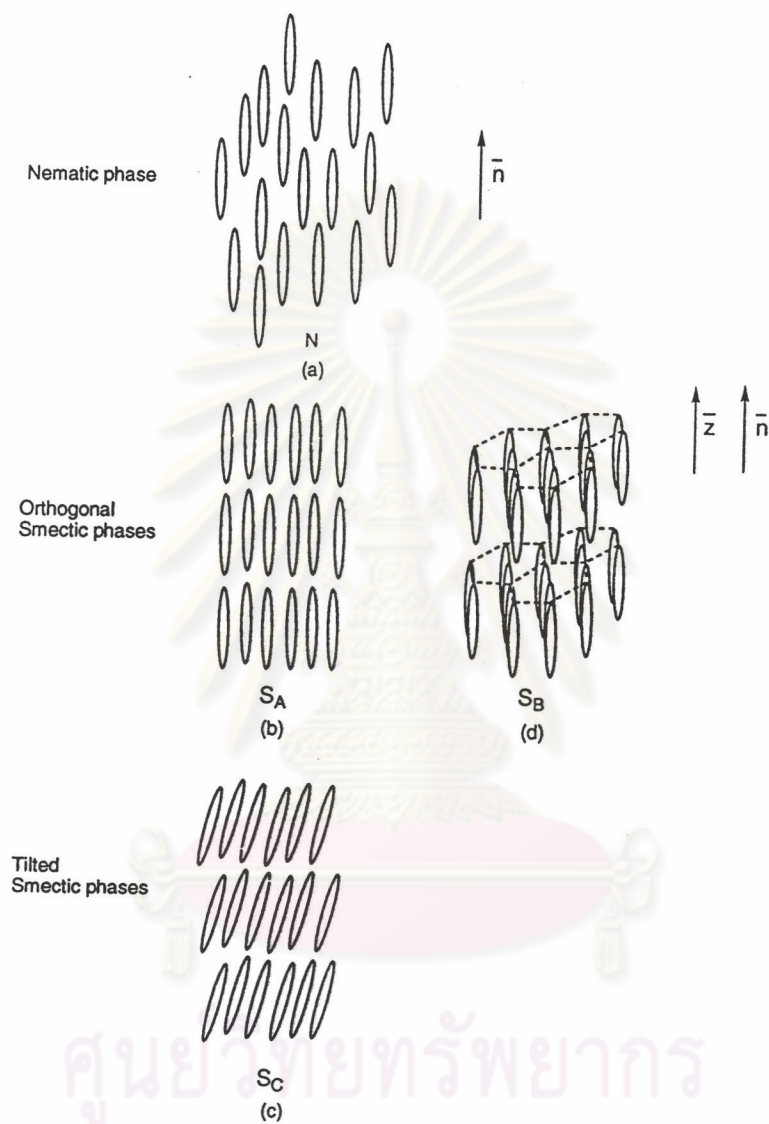
a) Mesophases can be formed by pure compounds (or mixture of compounds) by the influence of temperature between *melting temperature* ( $T_m$ ) and *isotropization temperature* ( $T_i$ ). In this case, the liquid crystal is termed *thermotropic*. When the thermotropic mesophase appears both in the heating ( $T_m$ - $T_i$ ) and the cooling process ( $T_i$ - $T_m$ ), it is called *enantiotropic*. Mesophase that appears only in the heating process is referred to as *monotropic*.

b) Mesophases can also be observed as a result of certain species forming anisotropic aggregates in the presence of solvent (usually water). These mixtures are known as *lyotropic* liquid crystals.

Thermotropic liquid crystals have gained a relevant place in the field of materials science, whereas lyotropic liquid crystals are of fundamental interest in life science.

Liquid crystal behavior is due chiefly to molecular rigidity that excludes more than one molecule occupying a particular volume, rather than intermolecular attractive forces. The requirement for a substance to exhibit liquid crystal behavior is molecular shape anisotropy, which is not affected by conformational changes. The typical polymer liquid crystal is a rigid-rod molecule. The rigid groups are referred to as *mesogens* or *mesogenic groups*. The collection of mesogenic unit results in a rigid rod molecule with molecular shape anisotropy and liquid crystal behavior. Liquid crystal polymers show either *smectic* or *nematic* liquid crystal behavior, depending upon the amount of order in the material. There is a parallel arrangement of the long molecular axes in both nematic and smectic liquid crystals. Smectic liquid crystals are more ordered than nematic liquid crystals. In nematic phase, the molecules can move and rotate around the molecular long axis. The molecules are aligned in only one direction (Figure 1.1a), that is they possess orientational, but no positional order. In smectic phase, the molecules are organized into layers. Within a layer the molecules tend to align parallel to each other. Each smectic modification is denoted by a letter. The smectic A phase (Figure 1.1b) is a phase in which the molecules are aligned parallel to the layer normal without having positional order within the layer. Similarly, in the smectic B phase (Figure 1.1c), the molecules are arranged into a network of hexagonal within the layer. In the smectic C phase (Figure 1.1d), the molecules are arranged as in the smectic A phase, but the director is at a constant tilt angle measured normally to the smectic plane. Smectic A and smectic C phases are the least ordered smectic phases and are also commonly observed. Other types of smectic phases show three-dimensional order, restricted mobility and higher viscosities. In these phases, known as crystal smectic phases, the molecules show intralayer as well as interlayer positional order.





**Figure 1.2** Schematic representation of phases: (a) Nematic; (b) Smectic A; (c) Smectic B; (d) Smectic C [1]

Liquid crystal polymers are further divided into main-chain or side-chain depending on the location of the mesogenic units in relation to the polymer backbone as depicted in Figure 1.3. Main chain liquid crystal polymers are formed when rigid elements are incorporated into the backbone of normally flexible polymers. These stiff regions along the chain allow the polymer to orient in a manner similar to ordinary liquid crystal, and thus display liquid crystal characteristics. Side chain liquid crystal polymers are formed when rigid elements are connected as a side chain to the flexible polymers.

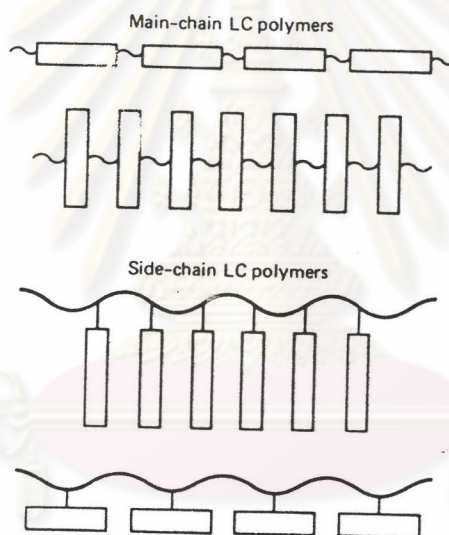
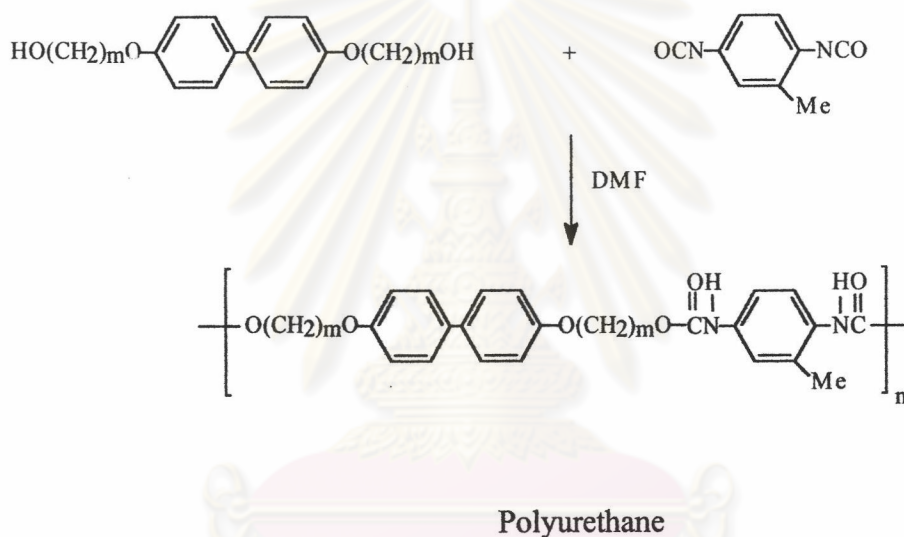


Figure 1.3 Main-chain and side-chain liquid crystal polymers [3]

## 1.2 Liquid Crystalline Polyurethanes

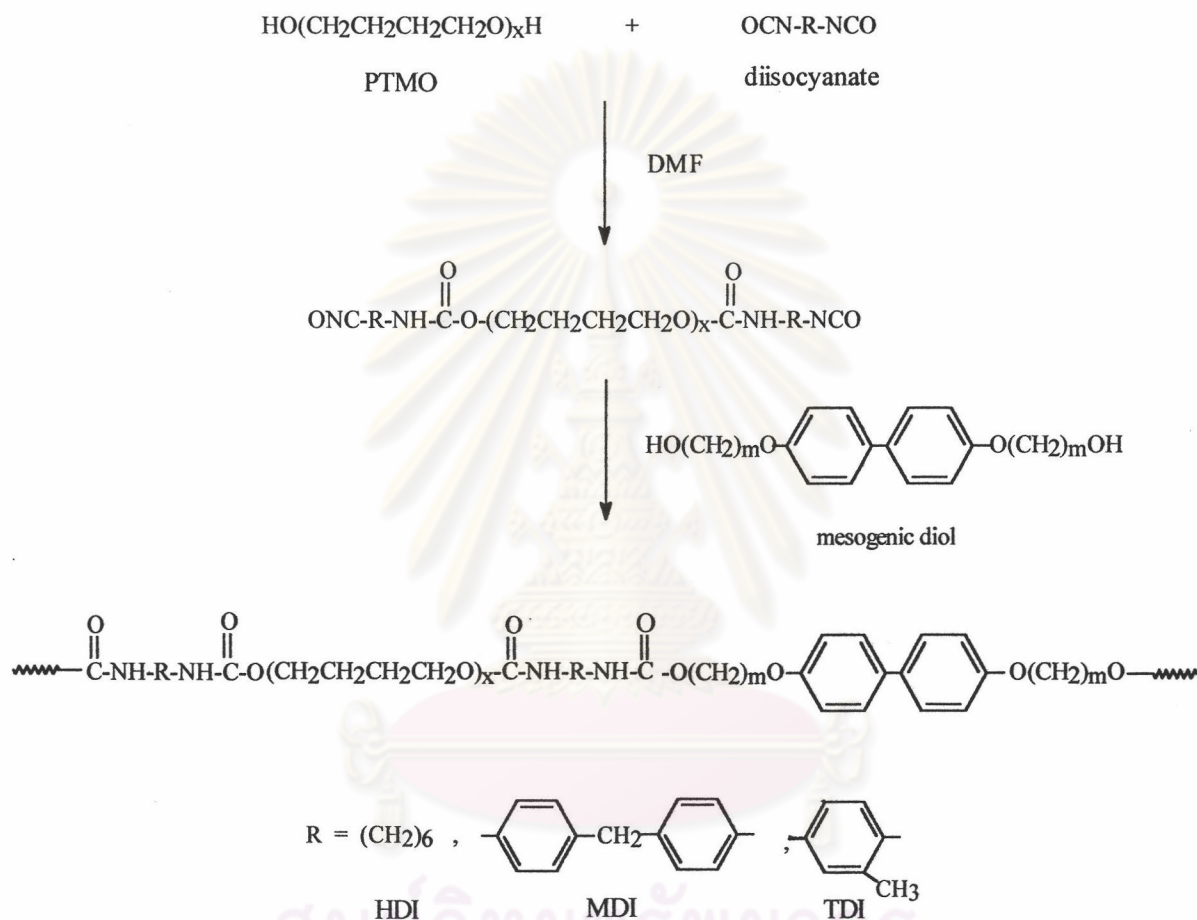
A number of papers concerning the preparation and physical properties of thermotropic polyurethanes have been reported [4-7]. For example: Uryu and his coworkers synthesized a new series of main chain thermotropic polyurethane from 2,5-tolylene diisocyanate (2,5-TDI) and 4,4'-bis(O-hydroxyalkoxy)biphenyls [4]. The polymer was prepared by solution polyaddition in DMF. Diol monomer contains a mesogenic biphenylene group and flexible spacers. Para-substituted monomer affords an overall linear structure of the polyurethane (Scheme 1.1).



**Scheme 1.1** Synthesis of the main chain thermotropic liquid crystalline polyurethane

The synthesized polyurethane exhibited mesomorphic properties. The incorporation of the para-type urethane linkage increased the melting temperature and contributed to liquid crystallinity.

Yu and coworkers synthesized liquid crystalline polyurethane elastomers by two-step block copolymerization reaction [8]. The main chain liquid crystalline polyurethanes were based on biphenyl mesogenic diol as a chain extender, poly(tetramethylene-oxide) (PTMO) soft segment and different types of diisocyanate (Scheme 1.2).



**Scheme 1.2** Synthesis of the liquid crystalline polyurethane elastomers

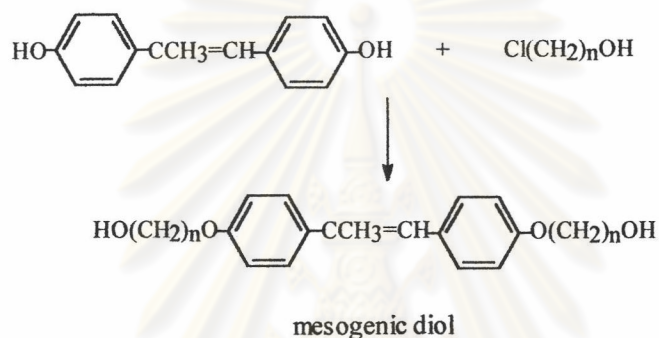
The melting point order for the synthesized polyurethane is MDI > HDI > TDI. This is due to the fact that hard segment of the TDI-based polyurethanes have lower order than HDI- and MDI-based polyurethanes. The better order of the rigid chain caused the higher melting temperature of MDI series polymers. Therefore, the liquid crystal properties strongly related to the interaction between the hard and soft segment of the polyurethane.

Jen-Feng and coworkers [9] synthesized new series of thermotropic liquid crystalline polyurethanes based on TDI and MDI. These polyurethanes contained 4,4'-bis(*o*-hydroxyalkoxy)- $\alpha$ -methylstilbene as a mesogenic core (Scheme 1.3).

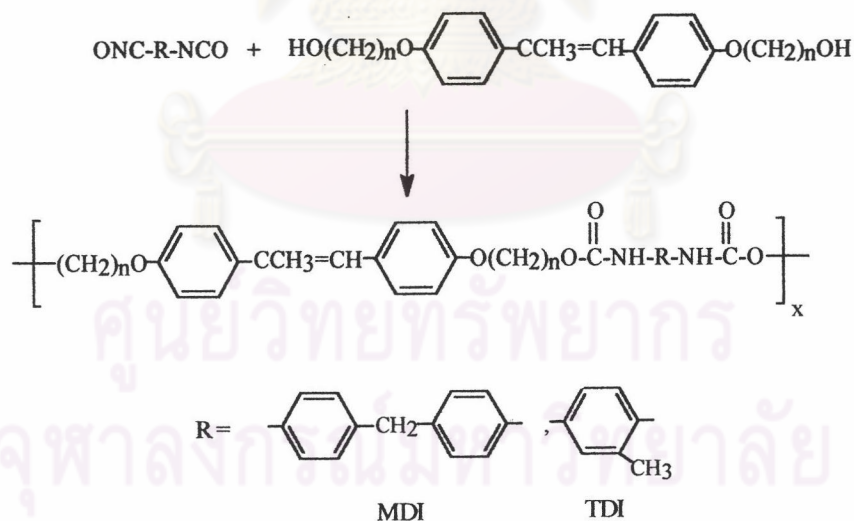
#### Synthesis of mesogen



#### Synthesis of mesogenic diol



#### Preparation of polyurethanes



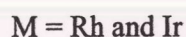
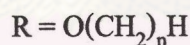
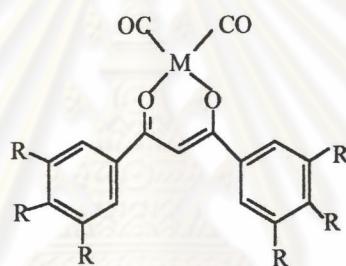
**Scheme 1.3** Synthesis of the thermotropic liquid crystalline polyurethanes based on different types of diisocyanates

The results showed that the transition temperature and the temperature ranges of mesophases changed with the length of alkoxy spacer and the type of diisocyanate.



### 1.3 Metallomesogens

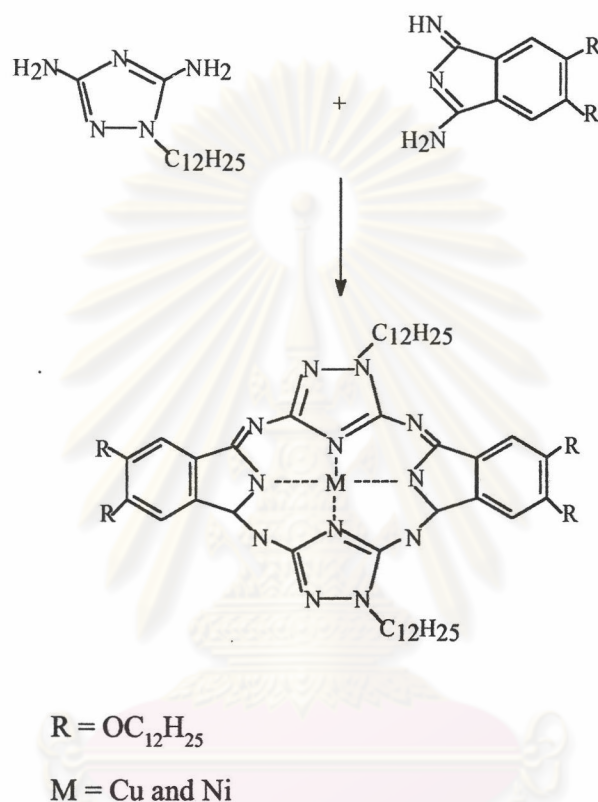
In recent years, an increasing number of research groups have turned their attention to metal containing liquid crystals or metallomesogens. The interesting properties derived from the presence of metal atoms in ordered fluid phases have given rise to expectations of new applications of liquid crystals based on metallomesogens. Metallomesogens combine the physical characteristics exhibited by metal coordination complexes with those of the organic molecules that give liquid crystal. For example: Swager and coworkers synthesized a series of non-discoid rhodium and iridium dicarbonyl  $\beta$ -diketonate complexes that organize in columnar liquid crystal phases (Figure 1.4) [10].



**Figure 1.4** Nondiscoid-shaped molecule of dicarbonyl  $\beta$ -diketonate metal complexes

Both rhodium and iridium dicarbonyl acetylacetonates have been reported to crystallize in a strict antiparallel pairwise arrangements that positions the metal centers on the top of each other to produce a one dimensional chain structure.

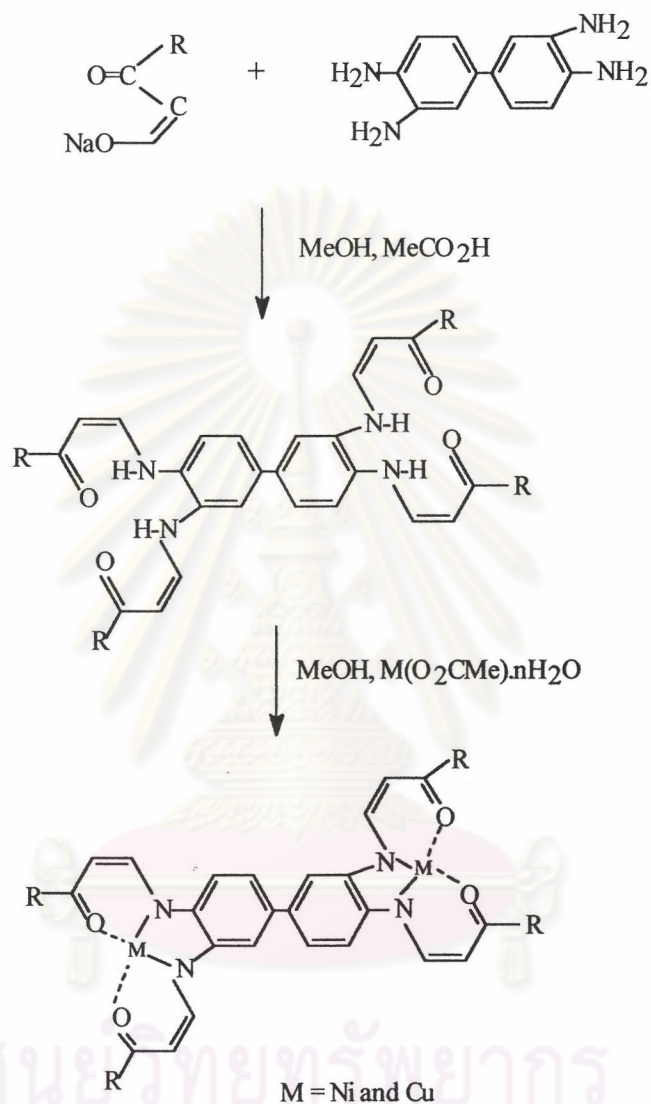
Fernandez and his coworkers synthesized a series of new discotic molecules based on the triazolehemiporphyrzine core [22]. This central unit has been attached to six lipophilic chains, two dodecyl groups on the triazole ring and four dodecyloxy on the isoindole moiety, and metallic complexes (Cu and Ni) have been prepared as shown in Scheme 1.4.



**Scheme 1.4** Synthesis of disk-like metallomesogen: hexasubstituted triazolehemiporphyrzines

The result showed that the metallic complexes melt from the solid to liquid crystalline phase at relatively low temperatures and exhibit a hexagonal columnar mesophase in a large temperature range, up to 300 °C.

Szydłowska and coworkers synthesized nickel(II) and copper(II) cis-enaminoketone complexes with two chelating units linked by a biphenyl moiety which were found to form the rectangular columnar phase (Scheme 1.5) [11].



**Scheme 1.5** Synthesis of binuclear metal complexes

Both nickel and copper cis-enaminoketone complexes exhibited enantiotropic columnar mesophase by the disc-like assemblies of non-discoid molecules.



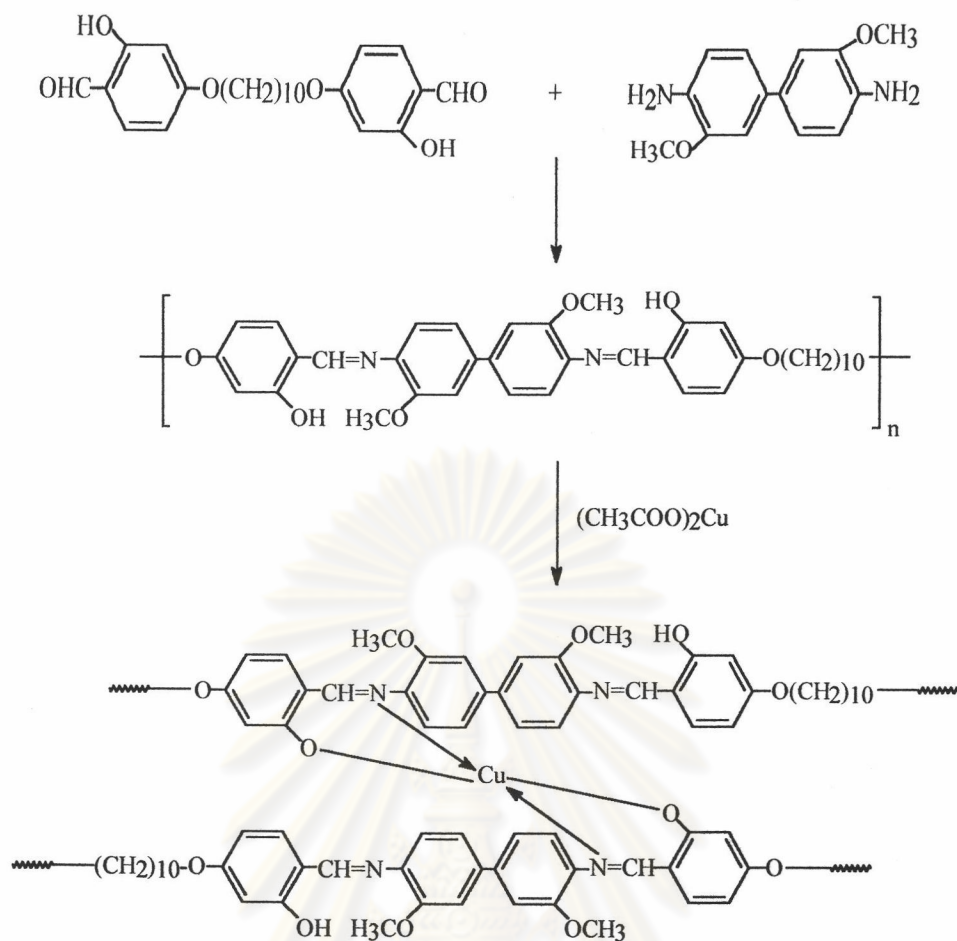


## 1.4 Metallomesogenic polymers

Many metallomesogenic structures have also introduced into polymeric systems. Metallomesogenic polymers can combine the promising properties of metallomesogens (physical properties of metal entities and molecular ordering of liquid crystals) with the advantageous properties of polymers (materials with good and easy processability or even the possibility of stabilization of the liquid crystalline order by polymerization) [1].

The molecular architecture of the metallomesogenic polymers reported usually corresponds to the two classical types depending on whether the mesogenic units are located on the main-chain or side-chain. In both cases calamitic (rod-like) and columnar (disk-like) metallomesogens can be used as core units. These compounds may be further classified according to the type of mesogenic behavior (lyotropic or thermotropic) and to the arrangement of the mesogenic units within the polymer structure. In this research, more emphasis was given to thermotropic metal containing liquid crystalline polymers. There are numerous examples of thermotropic metal containing liquid crystalline polymers.

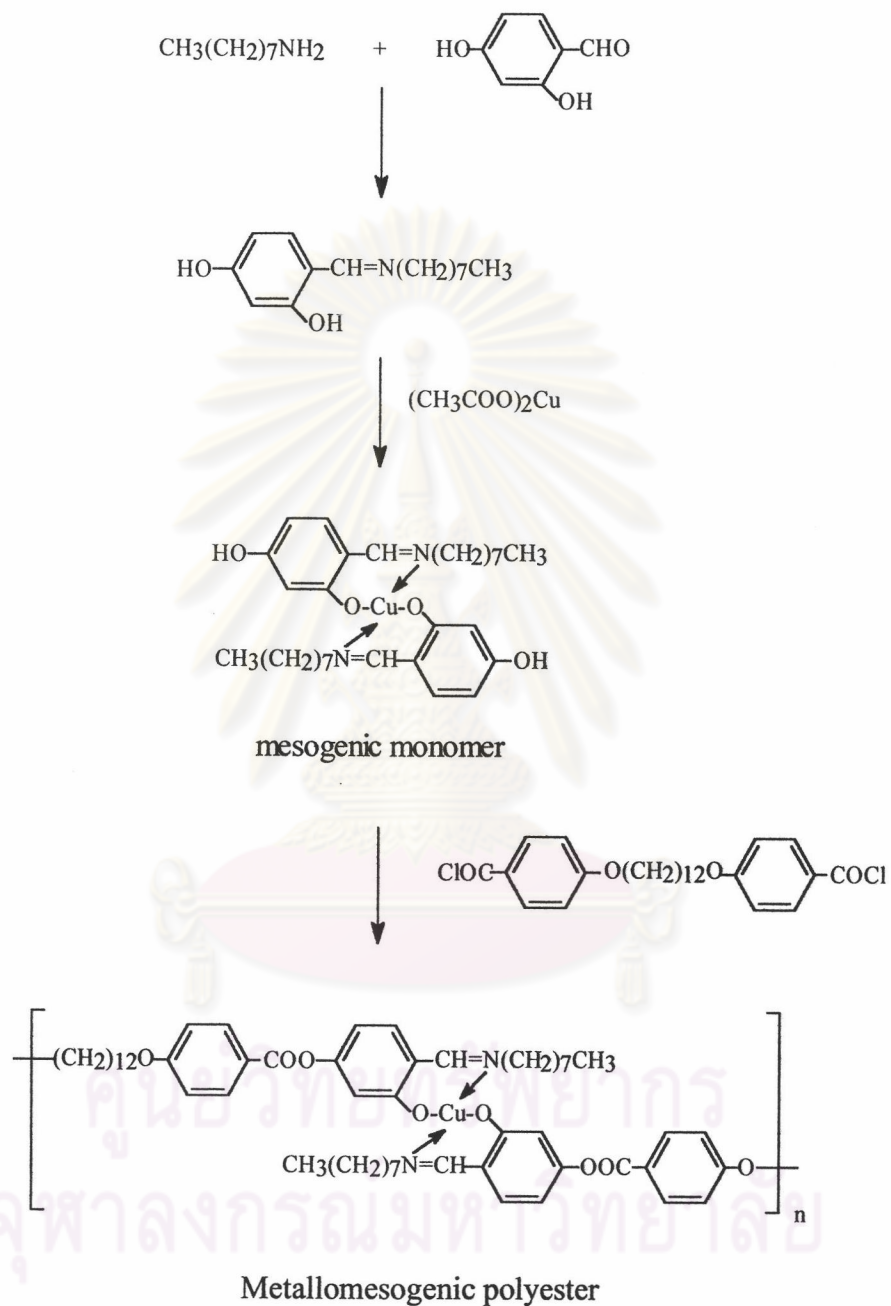
Serrano and coworkers [13] synthesized the metallomesogenic polymer by copper (II) complexation of a semiflexible main-chain liquid crystalline polyazomethine (Scheme 1.7). These metallomesogenic polymers are considered as hybrid materials which combine the anisotropic properties of liquid crystals, the physical properties of metal atoms, and the processing properties of polymers.



**Scheme 1.7** Synthesis of the metallomesogenic polymer by copper (II) complexation of a main-chain liquid crystalline polyazomethine

The metal complex acted as the cross-linker of the polymeric chain. It was found that the metal complex Schiff base polymer exhibited nematic texture as observed by polarizing optical microscope. However, annealing the sample at the mesophase temperature for several hours changed the nematic mesophase to smectic C mesophase [14].

Sirigu and coworkers synthesized a new type of metal containing polymer whose monomer unit was characterized by the presence of a square-planar coordinated Cu (II) atom (Scheme 1.8) [15].

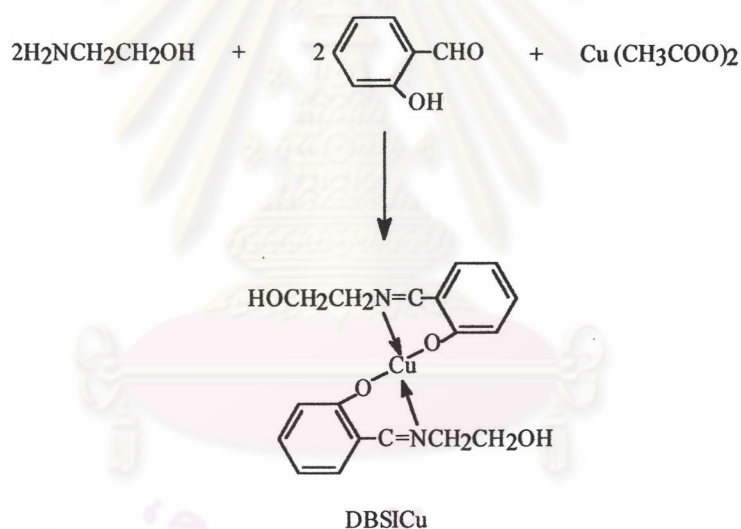


**Scheme 1.8** Synthesis of metal-containing liquid crystalline polyester

It was found that the synthesized metallomesogenic polyester exhibited mesophase behavior of nematic character.

Sirigu and coworkers have also synthesized liquid crystalline polymers containing other coordinated metal ions like Ni(II), Pd(II) or VO(II) instead of Cu(II) in the main chain [16]. The results showed that the difference in the liquid crystalline properties do connected to the nature of the coordinated metal atom which may be related to structural diversities in the coordination geometry. However, this relationship has not been demonstrated as yet.

Xuehai Yu and coworkers synthesized metal complex based on novel diols, bis[N-{(2-hydroxyphenyl)methylene}hydroxyethyleneamino]copper(II) (DBSICu) as a mesogen in order to import liquid crystalline properties to a polyurethane at room temperature. (Scheme 1.9) [17].



**Scheme 1.9** Synthesis of metallic diol

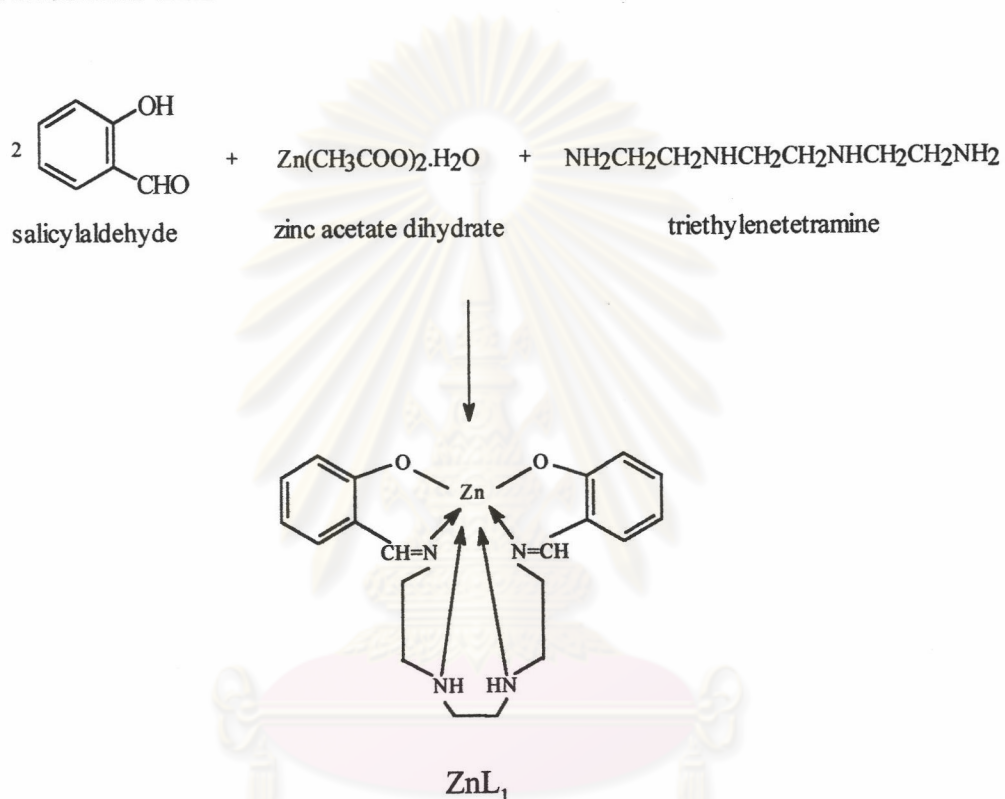
The DBSICu was found to be a perfect needle crystal structure at room temperature without any thermal treatment. Upon heating this diol to 140 °C, the needle crystal began to melt and a band structure appeared under POM. Further polymerization was carried out to give polyurethane (Scheme 1.10).





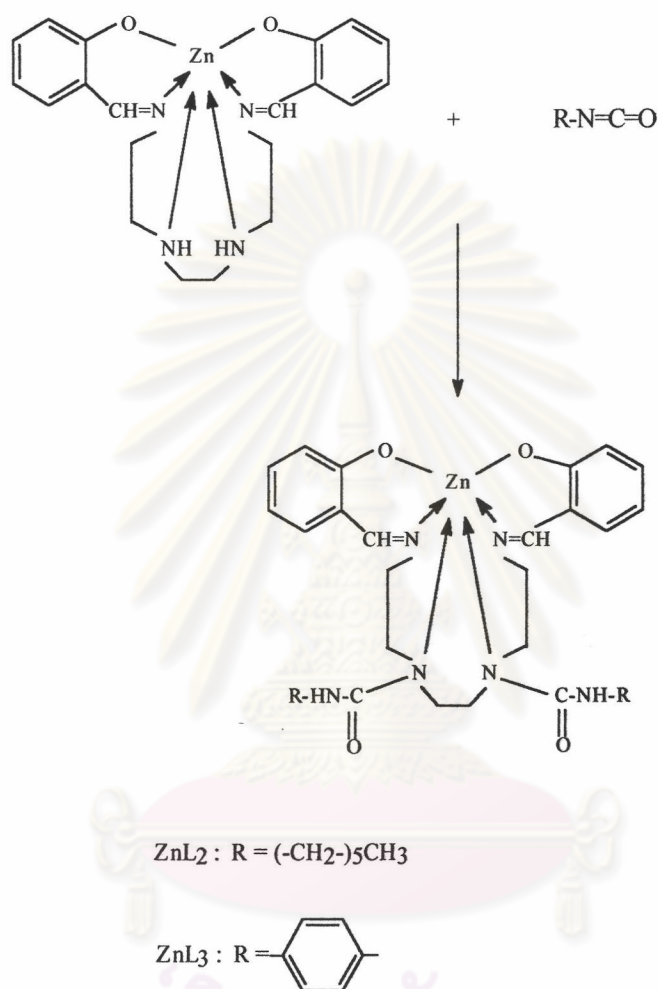
## 1.5 Objective and Scope of the Research

The target of this research is to synthesize liquid crystalline polyurethane based on the hexadentate Schiff base zinc complex ( $ZnL_1$ ) as a mesogen. Since it was known that an addition of metal containing liquid crystal into polymer chain could improve thermal properties of the polymer. Firstly,  $ZnL_1$  would be synthesized as shown in Scheme 1.11.



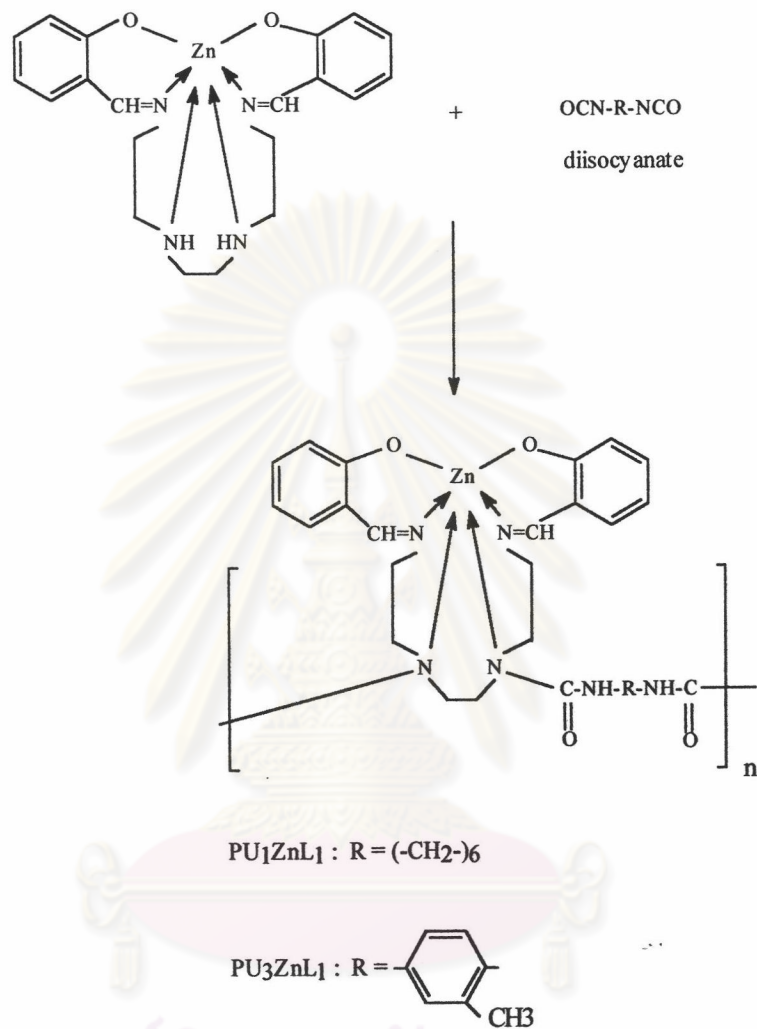
Scheme 1.11 Synthesis of  $ZnL_1$

Secondly, the derivatives of  $ZnL_1$ , namely  $ZnL_2$  and  $ZnL_3$  would be synthesized (Scheme 1.12) in order to compare their physical, thermal and liquid crystalline properties with  $ZnL_1$ .



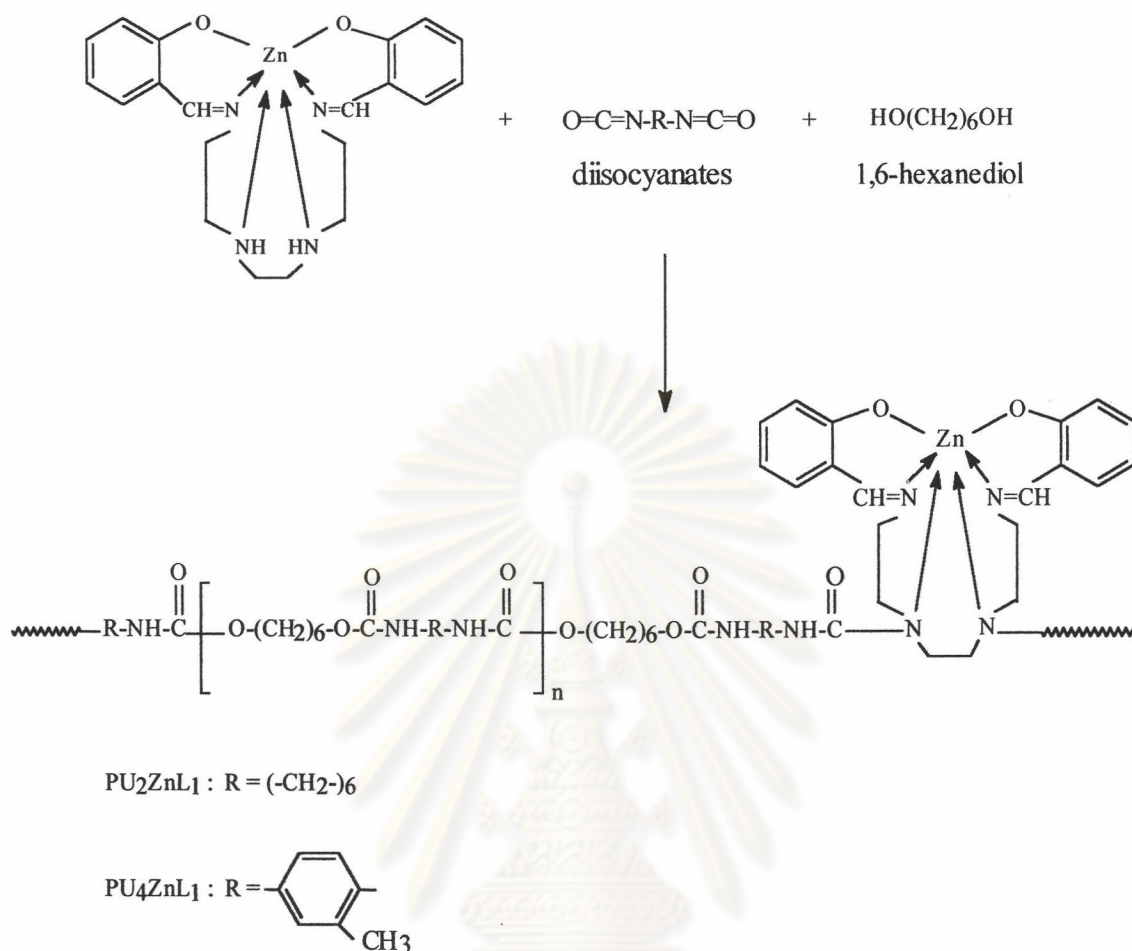
**Scheme 1.12** Synthesis of  $ZnL_2$  and  $ZnL_3$

Finally, polymerization would be performed in order to obtain polyurethanes, namely  $PU_1ZnL_1$ ,  $PU_2ZnL_1$ ,  $PU_3ZnL_1$  and  $PU_4ZnL_1$  (Scheme 1.13 and 1.14).



**Scheme 1.13** Synthesis of  $PU_1ZnL_1$  and  $PU_3ZnL_1$





**Scheme 1.14** Synthesis of PU<sub>2</sub>ZnL<sub>1</sub> and PU<sub>4</sub>ZnL<sub>1</sub>

The molecular structure of the synthesized metallomesogens and polyurethanes would be characterized by FTIR, NMR and elemental analysis. Thermal properties would be investigated by DSC and TGA. Liquid crystallinity would be examined by polarized optical microscope (POM).