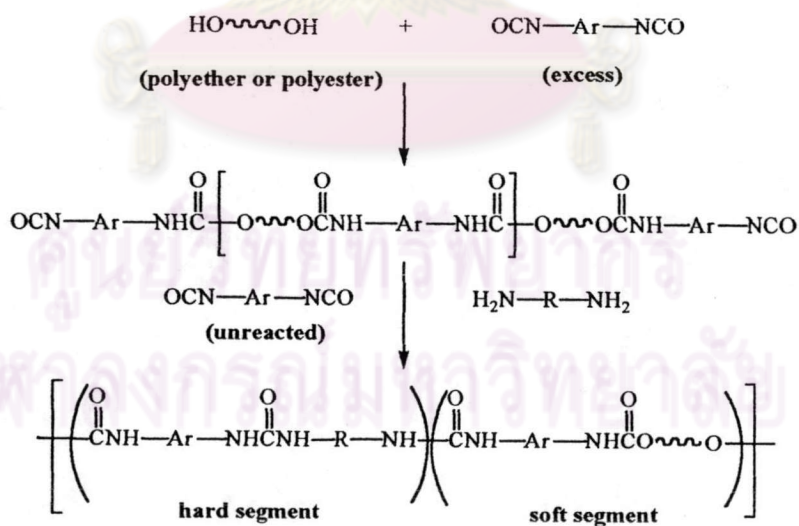


## CHAPTER I

### INTRODUCTION

#### 1.1 Polyurethanes

Polyurethanes are used in a wide variety of products, including fibers, elastomers, foams, coatings, and adhesives. The principal method of forming polyurethanes is the reaction of diisocyanates with dihydroxy compounds,<sup>1-2</sup> which has the advantage of no byproducts. The most important polyurethane fibers consist of elastomeric block copolymers alternating “soft” and “hard” segments. Typically, an aromatic diisocyanate is reacted in excess with hydroxy-terminated polyether or polyester having an average molecular weight of 2000 to 3000 to yield an isocyanate-terminated polymer that is, in turn, reacted with a diamine chain extender as shown in Scheme 1.1.



Scheme 1.1 Synthesis of an elastomeric polyurethane<sup>1</sup>

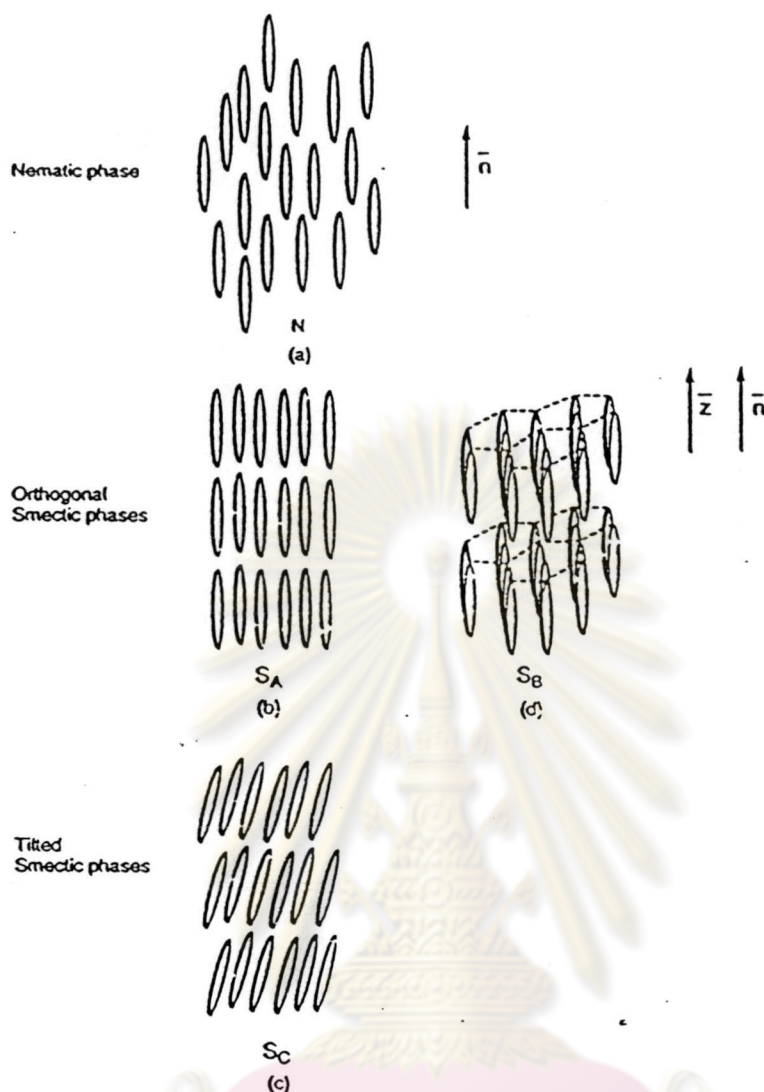
## 1.2 Liquid Crystalline Polymers

Liquid crystals or mesogens are materials which exhibit liquid crystalline behavior or mesomorphism.<sup>3</sup> This behavior appears under given conditions, where phases occur in which the molecular order is intermediate between that of an ordered solid crystal and a disordered liquid or solution; these intermediate phases are called *mesophases*. Liquid crystals have been defined as “orientationally ordered” liquids or “positionally disordered” crystals and combine properties of both the crystalline state (e.g. optical and electrical anisotropy) and the liquid state (molecular mobility and fluidity). There are two different ways in which a mesophase can be formed, and there give rise to the main classes of liquid crystals as follows:

a) Mesophases can be formed by pure compounds or mixtures of compounds by the influence of temperature. In this case, the liquid crystal is termed *thermotropic*. When the thermotropic mesophase appear both in the heating and the cooling process (i.e. when it is thermodynamically stable) it is called *enantiotropic*. Thermodynamically unstable mesophases, which only appear in the cooling process due to the hysteresis in the crystallization point, are referred to as *monotropic*.

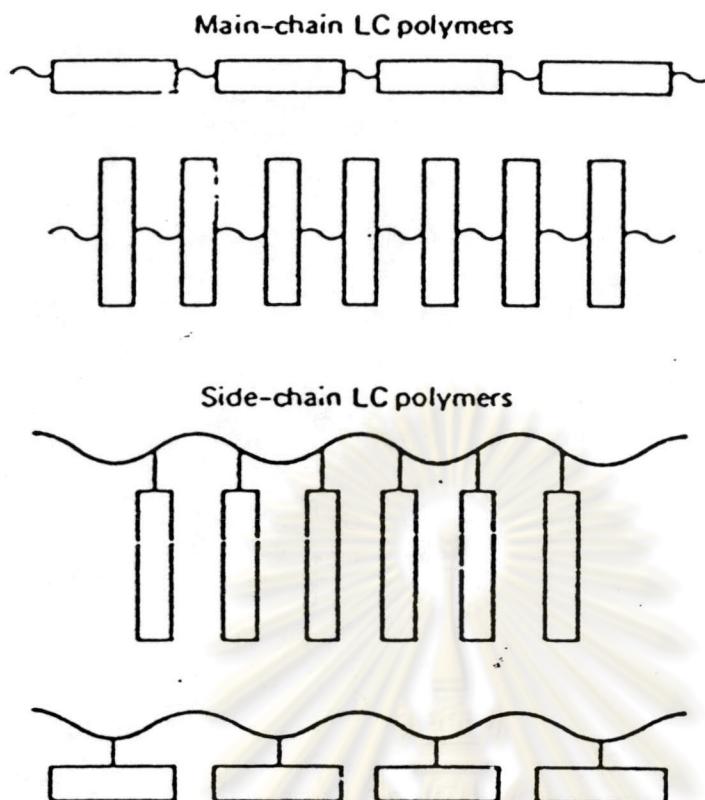
b) Mesophases can also be observed as a result of certain species (e.g. amphiphiles) forming anisotropic aggregates in the presence of a solvent (usually water). These mixtures are known as *lyotropic* liquid crystals.

A liquid crystal phase, often termed a mesophase, is an intermediate phase of matter between the ordered solid and disordered liquid phase which can exhibit certain physical properties of both these phases. Liquid crystal polymers are polymer that exhibit liquid crystal characteristics. Liquid crystal polymers show either smectic or nematic liquid crystal behavior (Figure 1.1), depending upon the amount of order in the material.



**Figure 1.1** Schematic representation of phases: (a) Nematic (b) Smectic A (c) Smectic B (d) Smectic C<sup>3</sup>

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 1.1. 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 1.2** Main-chain and side-chain liquid crystal polymers<sup>4</sup>

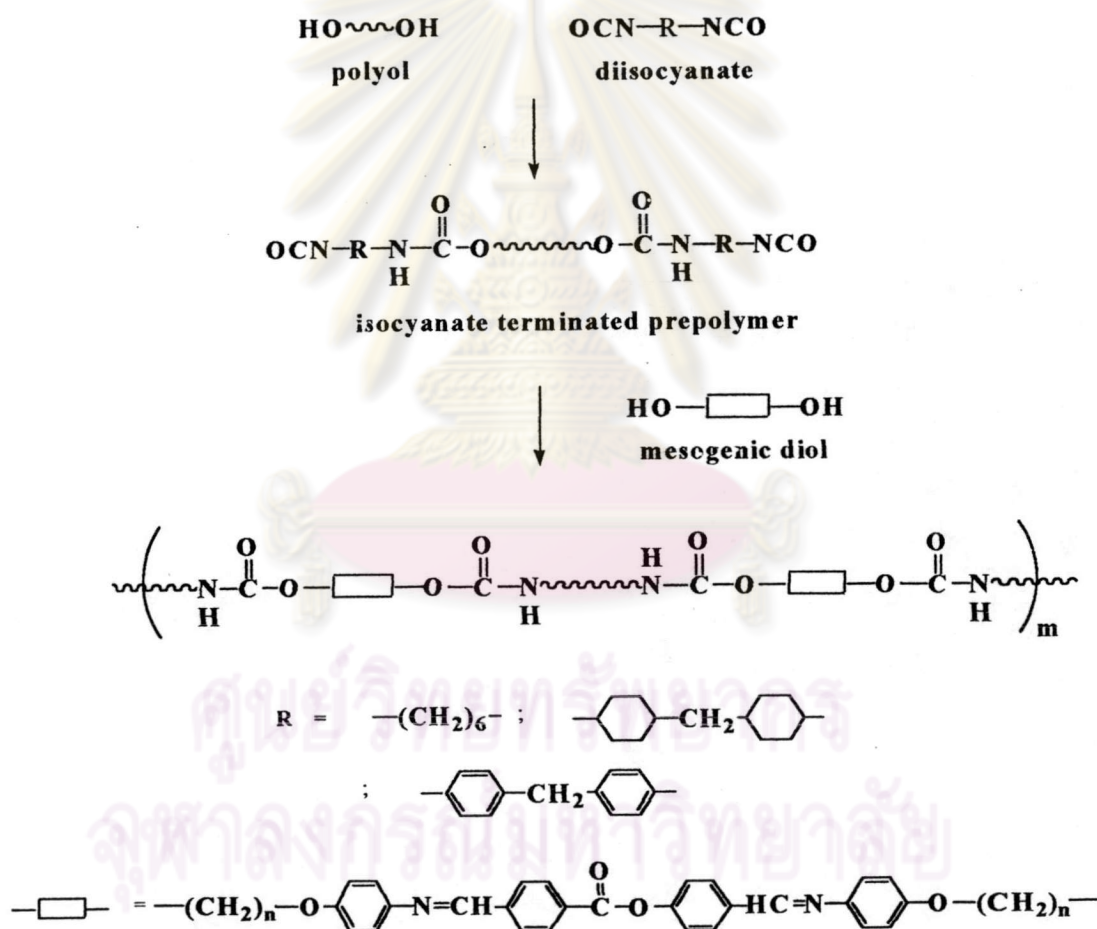
### 1.3 Metallomesogenic Polymers

Many metallomesogenic structures have also introduced into polymeric systems. Metallomesogenic polymers or metal-containing liquid crystalline 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 liquid crystalline order by polymerization).

The structure design of metallomesogenic polymers is essentially similar to that for conventional organic LCPs: metallomesogenic cores incorporated in the main-chain or side-chain of a polymeric structure. 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.

## 1.4 Liquid Crystalline Polyurethanes

A number of papers concerning the preparation and physical properties of thermotropic polyurethanes have been reported [5-7]. For example: Srinivasan and coworkers<sup>8</sup> synthesized main-chain liquid crystalline polyurethanes by using mesogenic diol (4-{{4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-benzoic acid 4-{{4-(6-hydroxyhexyloxy)-phenylimino]-methyl} phenyl ester) as a chain extender. PCL diol synthesized from soft segments of different number-average molecular weights (530,1250 or 2000) and different diisocyanates are shown in Scheme 1.2.

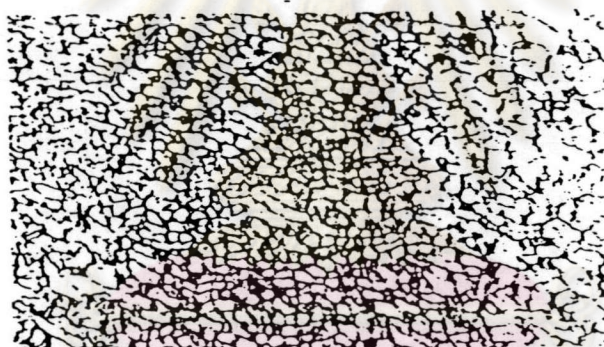


**Scheme 1.2** Synthesis of main-chain liquid crystalline polyurethanes by using (4-{{4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-benzoic acid 4-{{4-(6-hydroxyhexyloxy)-phenylimino]-methyl} phenyl ester) as a chain extender.

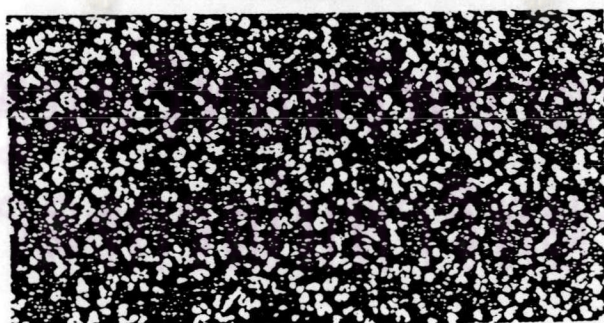
A 20% mesogen content was sufficient to impart a liquid crystalline property to all the polymers. Depending on the flexible spacer length and the mesogenic content, grained and threadlike textures were obtained for the 1,4-hexamethylene diisocyanate (Figure 1.3 (a)) and 4,4'-methylene bis(cyclohexyl isocyanate) series polymers (Figure 1.3 (b)), whereas the polyurethanes prepared from 4,4'-methylene bis(phenyl isocyanate) (Figure 1.3 (c)) showed only grained textures for all the compositions.



(a)



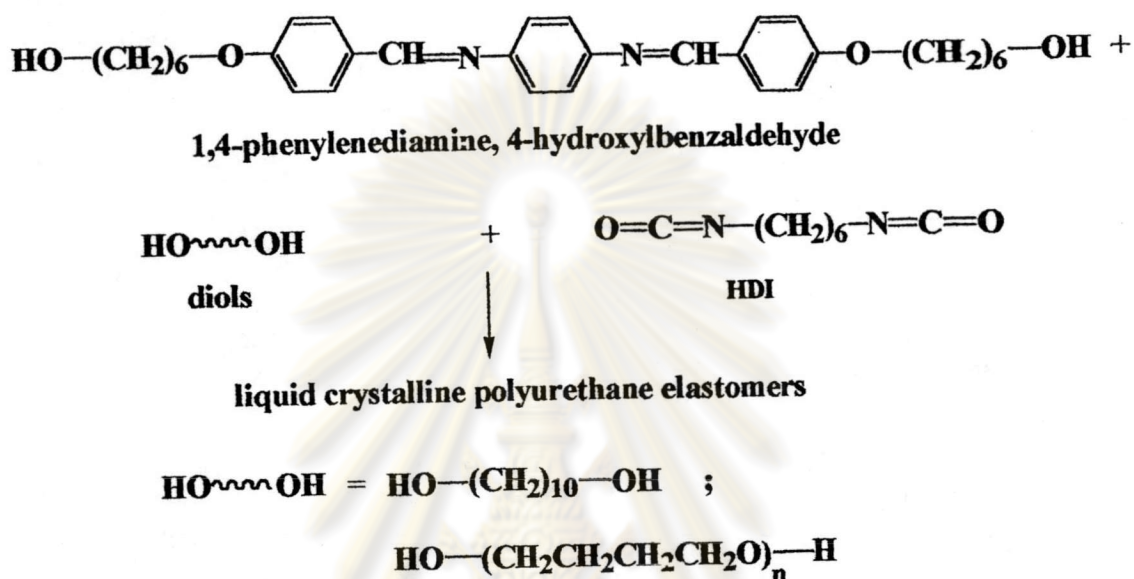
(b)



(c)

**Figure 1.3** Optical micrographs of the textures cooled from the melt: (a) 1,4-hexamethylene diisocyanate, temperature = 171°C, (b) 4,4'-methylene bis(cyclohexyl isocyanate), temperature = 154°C and (c) 4,4'-methylene bis(phenyl isocyanate), temperature = 175°C<sup>8</sup>

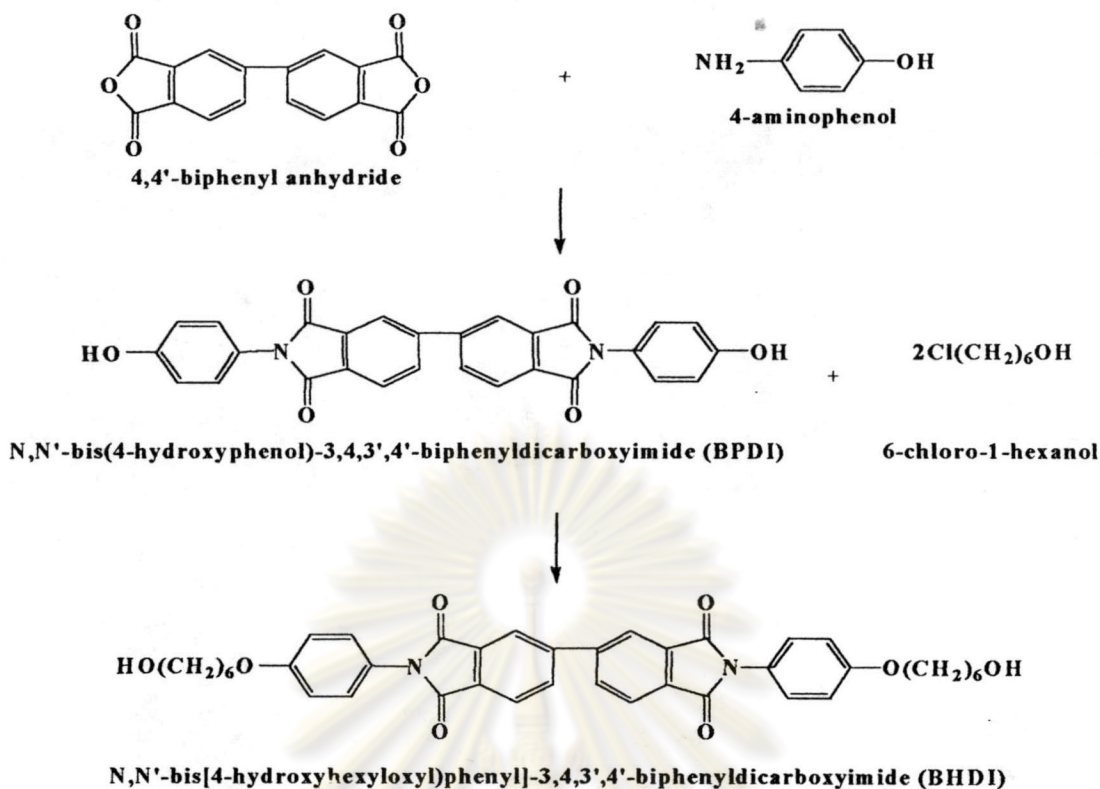
Chang and his coworkers<sup>9</sup> synthesized thermotropic liquid crystalline polyurethanes elastomers as shown in Scheme 1.3. Hard segments were the reaction of HDI with a mesogenic unit, benzene-1,4-di(4-iminophenoxy-*n*-hexanol), which also acted as chain extender. Two diols: 1,10 decanediol, poly(oxytetramethylene) glycol (PTMEG) were used as the soft segments.



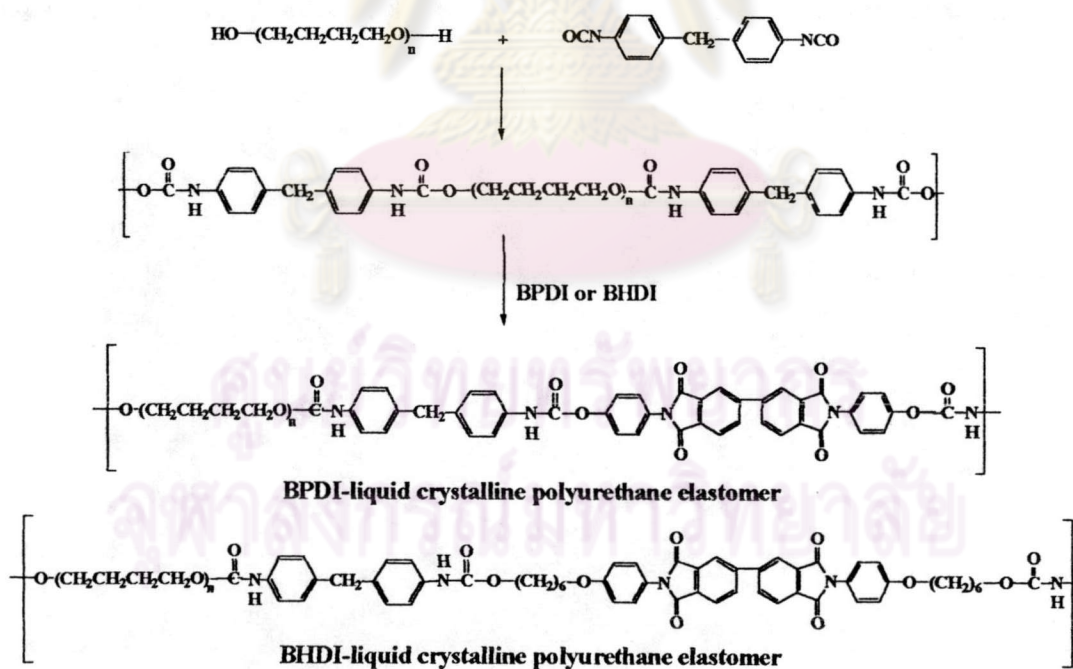
**Scheme 1.3** Synthesis of liquid crystalline polyurethane elastomers with benzene-1,4-di(4-iminophenoxy-*n*-hexanol) as a chain extender.

Polyurethane elastomers from HDI with 1,10-decanediol series (H1-A series) possessed better thermal stabilities than polyurethanes from HDI with PTMEG ( $M_w = 1000, 2000$ ) series (H2-A series). The polyurethane H2-A series showed less mesophase stability than H1-A series.

Lee and his coworkers<sup>10</sup> synthesized liquid crystalline polyurethane elastomers from *N, N'*-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboxyimide (BPDI) or *N, N'*-bis[4-hydroxyhexyloxy]phenyl]-3,4,3',4'-biphenyldicarboxyimide (BHDI) as a mesogenic chain extender as shown in Scheme 1.2, 4,4'-diphenyl-methane diisocyanate and poly(oxytetramethylene)glycol ( $M_n = 1000$ ) as a soft segment. The polymers were prepared by solution polyaddition in DMF as shown Scheme 1.5.



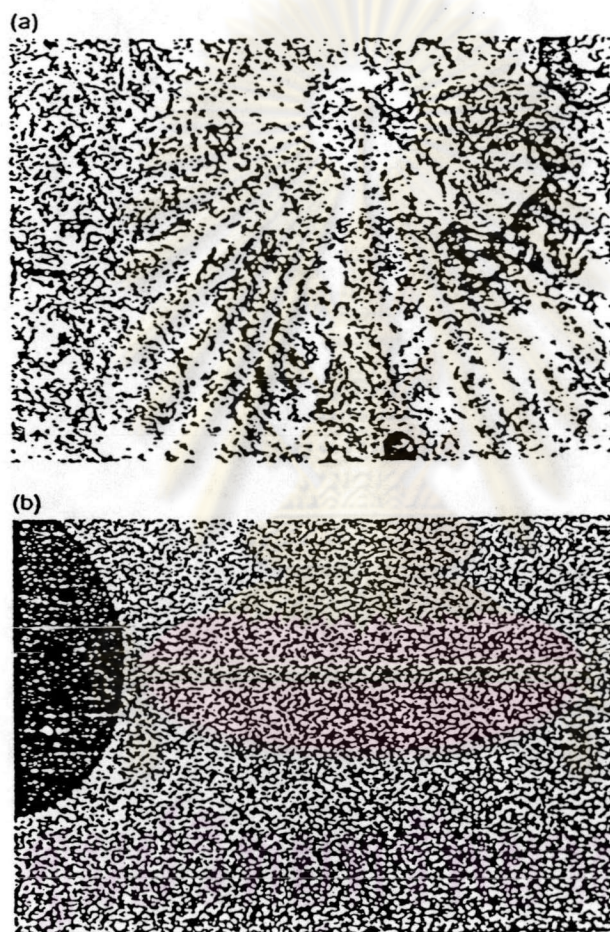
**Scheme 1.4** Synthesis of BPDI and BHDl



**Scheme 1.5** Synthesis of liquid crystalline polyurethane elastomers from 4,4'-diphenylmethane diisocyanate, poly(oxytetramethylene)glycol and BPDI or BHDl

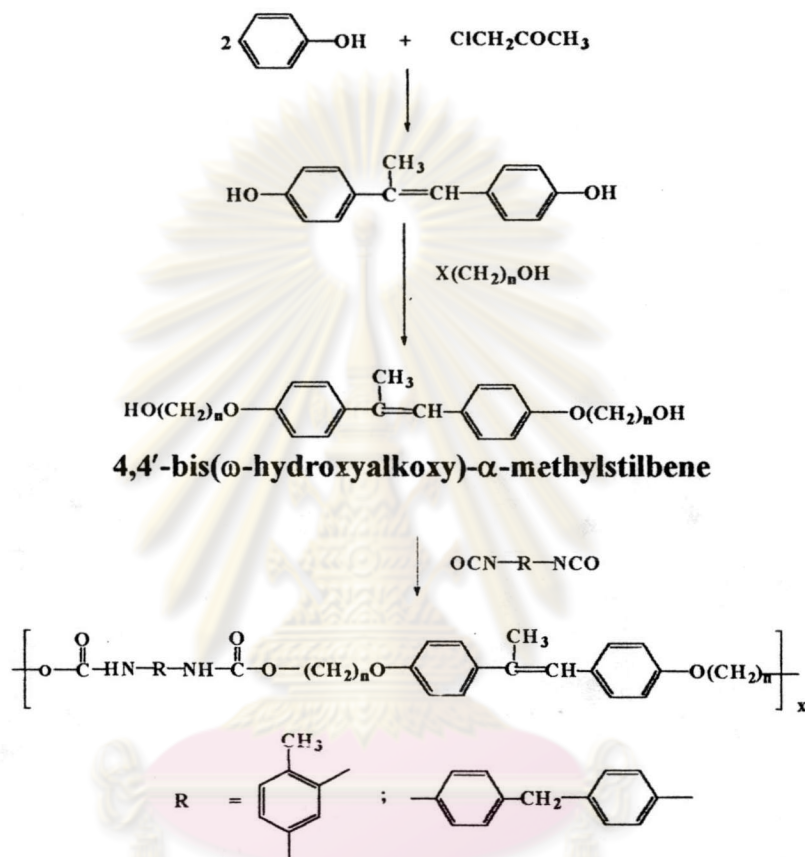


The melting behavior was not shown in the BPDI-based polyurethanes because of higher melting temperature than decomposition temperature. The BHDI-based polyurethanes containing 50 wt% and 65 wt% of hard segment content exhibited nematic liquid crystal behaviors as shown in Figure 1.4. As the hard segment content of the BHDI-based polyurethanes increased, the glass transition temperature ( $T_g$ ), strength, modulus, and the amount of hydrogen bonding increased.



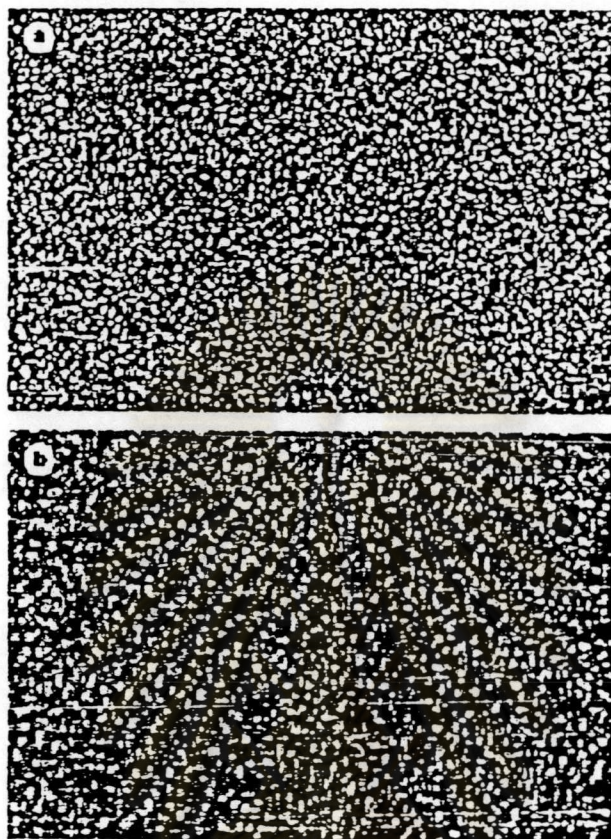
**Figure 1.4** Polarizing optical micrographs of the sample BHDI-based polyurethane (50% hard segment) (a) mesophase at 240°C on heating (b) at 206°C on cooling<sup>10</sup>

Kuo and coworkers<sup>11</sup> synthesized novel thermotropic liquid crystalline polyurethanes based on 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate. The thermotropic liquid crystalline polyurethanes containing the mesogenic core of 4,4'-bis( $\omega$ -hydroxyalkoxy)- $\alpha$ -methylstilbene are shown in Scheme 1.6.



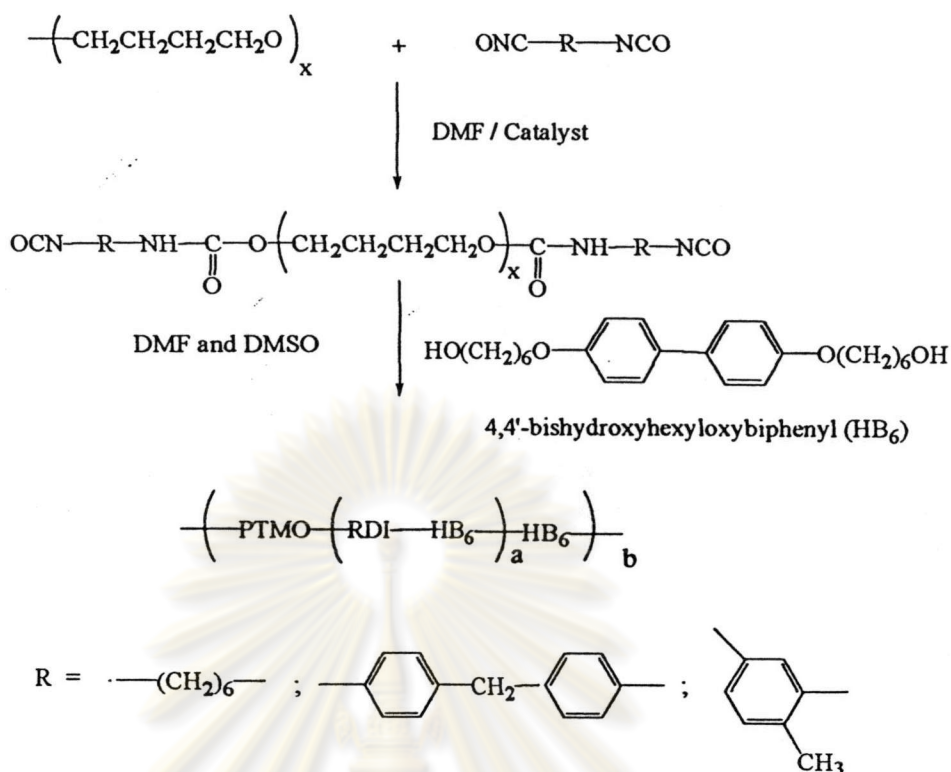
**Scheme 1.6** Preparation of liquid crystalline polyurethanes from 4,4'-bis( $\omega$ -hydroxyalkoxy)- $\alpha$ -methylstilbene and 4,4'-diphenylmethane diisocyanate or 2,4-toluene diisocyanate.

The transition temperatures and the temperature ranges of mesophases changed with the length of alkoxy spacer and the kind of diisocyanate. Both TDI and MDI exhibited a smectic phase as shown in Figure 1.5.



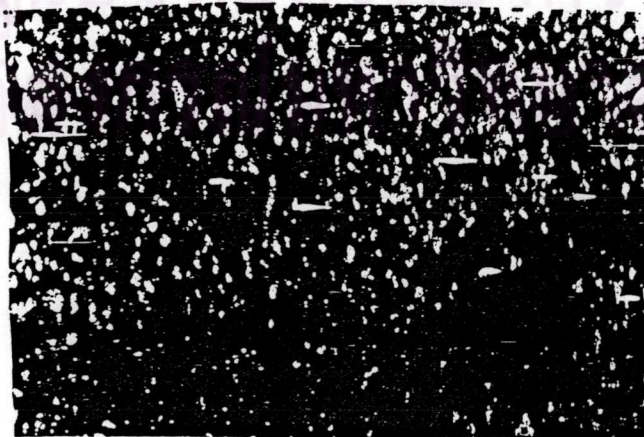
**Figure 1.5** Polarizing optical micrographs on cooling: (a) 2,4-toluene diisocyanate at 100°C (b) 4,4'-diphenylmethane diisocyanate at 165°C<sup>11</sup>

Yu and coworkers<sup>12</sup> synthesized liquid crystalline polyurethane elastomers by a two-step block copolymerization reaction. The main chain liquid crystalline polyurethanes were based on biphenyl mesogenic diol as a chain extender, a poly(tetramethylene oxide) (PTMO) soft segment and different diisocyanates, including 4,4'-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) as shown in Scheme 1.7.



**Scheme 1.7** Synthesis of liquid crystalline polyurethane elastomers with 4-4'-bishydroxyhexyloxybiphenyl as a mesogen

Figure 1.6 shows micrograph of the LC chain extenders (BH<sub>6</sub>), which shows nematic textures at 140°C. Most of the polyurethane samples exhibited nematic thermotropic liquid crystal behavior as shown in Figure 1.7. The liquid crystal properties are strongly related to the hard and soft segments of the polyurethane. The melting-point order is MDI>HDI>TDI.



**Figure 1.6** Textures of the nematic phase of 4,4'-bishydroxyhexyloxybiphenyl<sup>12</sup>

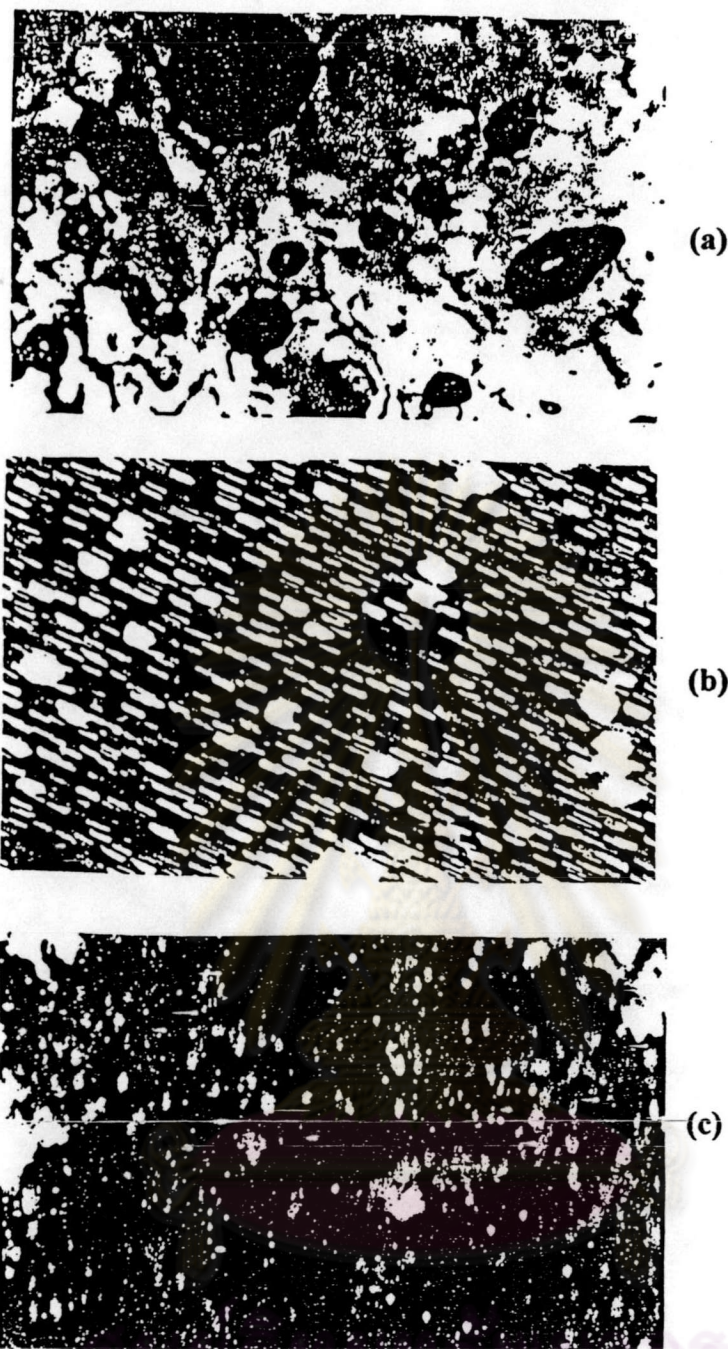
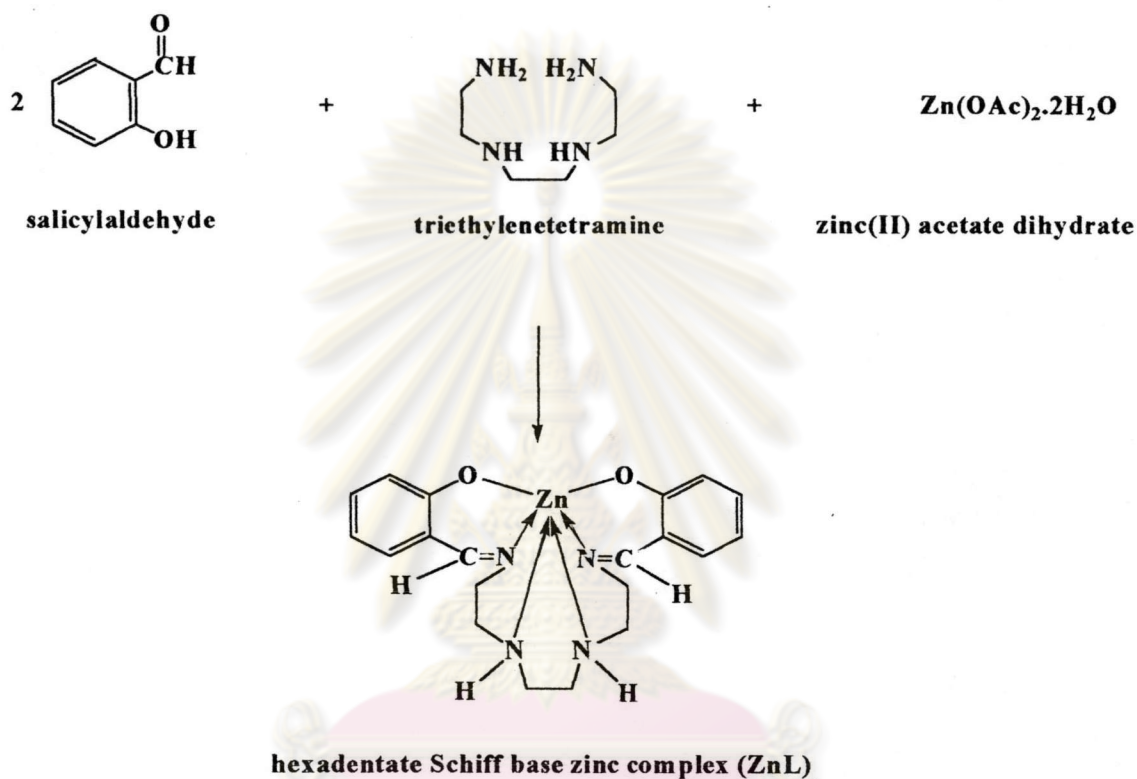


Figure 1.7 Textures of the nematic phase (a) polymer based on TDI (b) polymer based on HDI (c) polymer based on MDI<sup>12</sup>

In other research,<sup>13-17</sup> there were many methods for preparing liquid crystalline polyurethane such as film, powder. There has been worldwide interest in the synthesis and properties of liquid crystalline polyurethanes in which the mesogenic diols are introduced into the backbone polymer chain or as pendants in to the polymer backbone.<sup>18</sup> Many studies have been devoted to decreasing the melting point and to improving the solubility without destroying the liquid crystal formation.

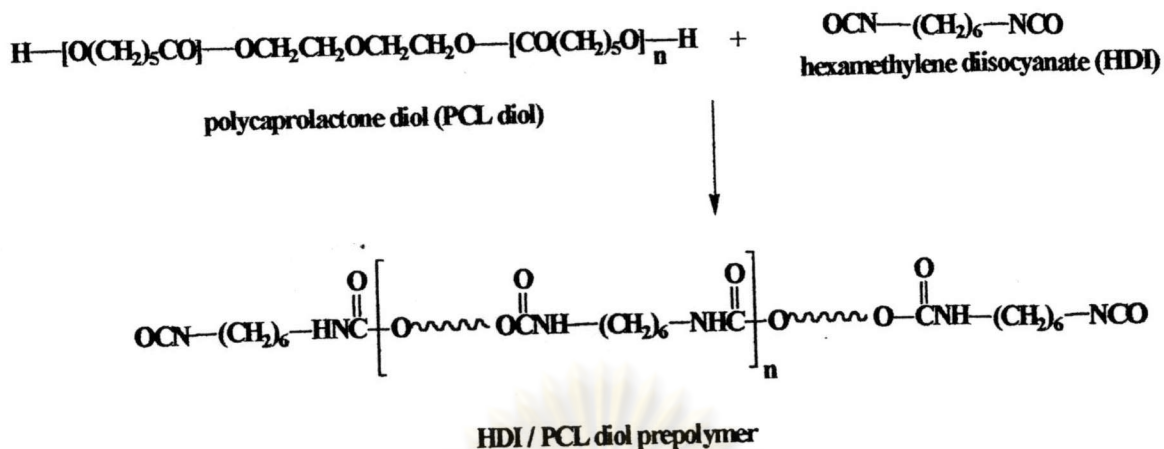
### 1.5 Objective and Scope of the Research

The target of this research is to synthesize liquid crystalline polyurethane elastomer from hexadentate Schiff base zinc complex (ZnL) as a mesogen. Firstly, zinc complex would be synthesized as shown in Scheme 1.8.

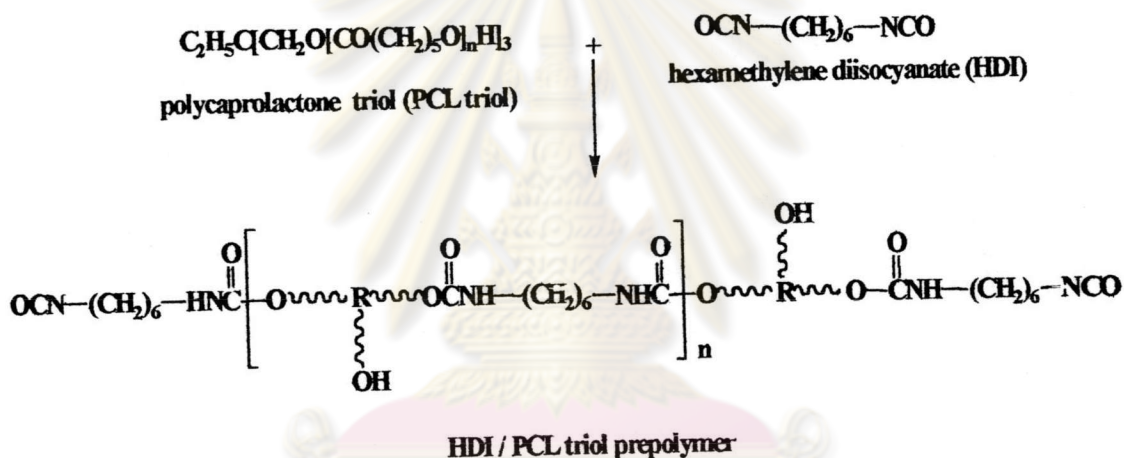


**Scheme 1.8** Synthesis of hexadentate Schiff base zinc complex.

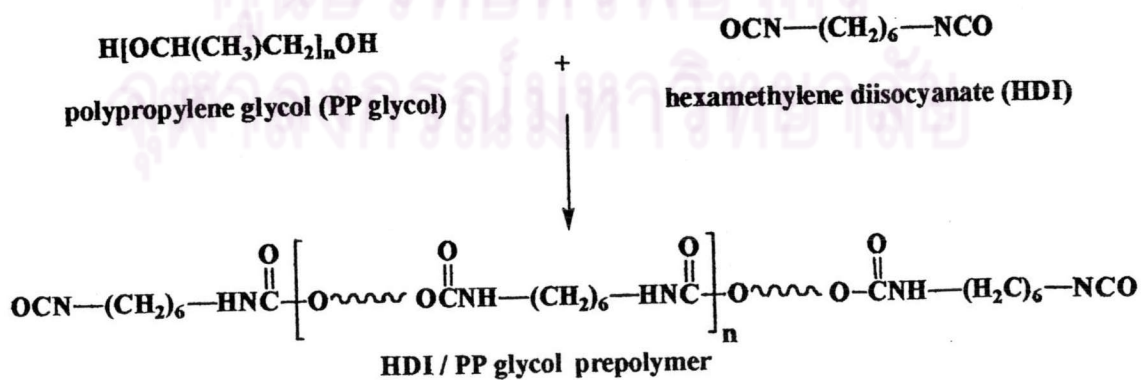
Secondly, the isocyanate terminated prepolymers, namely HDI / PCL diol prepolymer, HDI / PCL triol prepolymer and HDI / PP glycol prepolymer would be synthesized as shown in Schemes 1.9 a, 1.9b and 1.9c.



Scheme 1.9 a Synthesis of HDI / PCL diol prepolymer

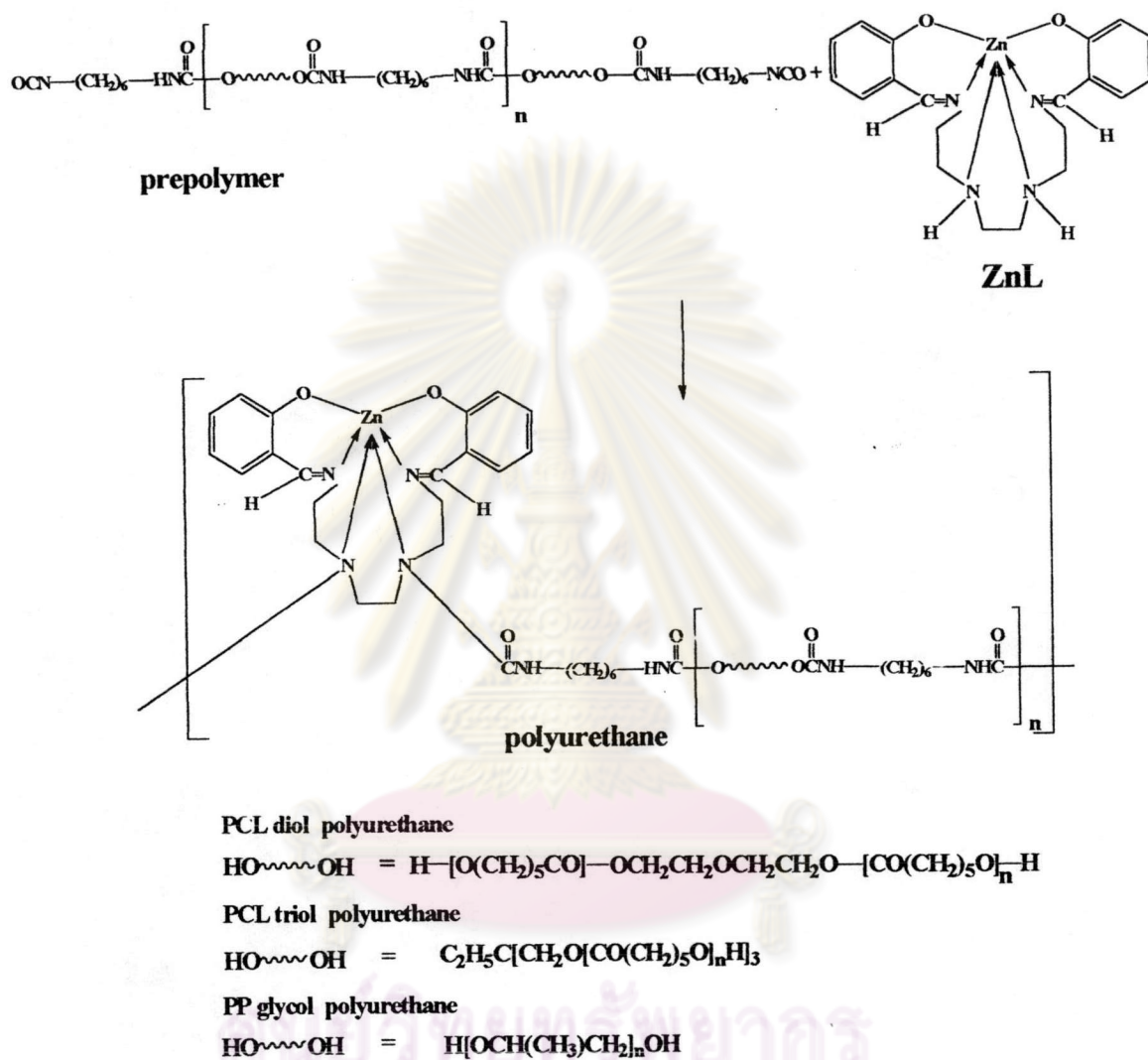


Scheme 1.9 b Synthesis of HDI / PCL triol prepolymer



Scheme 1.9 c Synthesis of HDI / PP glycol prepolymer

Finally, the polyurethanes elastomer of zinc complex, namely PCL diol polyurethane, PCL triol polyurethane and PP glycol polyurethane would be synthesized (Scheme 1.10).



**Scheme 1.10** Synthesis of PCL diol polyurethane, PCL triol polyurethane, PP glycol polyurethane.

The molecular structure of the polyurethanes elastomer would be characterized by FTIR. Liquid crystallinity and morphology of polymer would be examined by polarized optical microscope (POM) and scanning electron microscope (SEM) respectively.