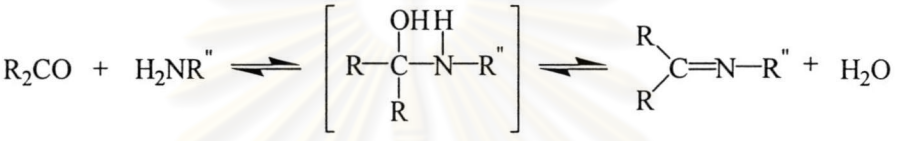
CHAPTER I

INTRODUCTION

1.1 Schiff base metal complexes

The most common method for preparing imines is the reaction of amines with aldehydes or ketones (Scheme 1.1). This reaction was first discovered by Schiff[1] and imines are often called Schiff bases.



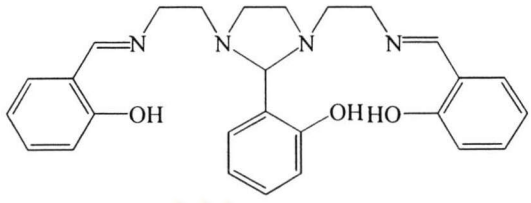
Scheme 1.1 Synthesis of imines

Schiff bases are widely used as ligands for synthesis of metal complexes. A large number of Schiff bases and their complexes have been studied because of their interesting and important properties, e.g. bis(salicylaldehyde)ethylenediiminato cobalt(II) complex which is able to bind oxygen in a reversible way. Metal complexes of Schiff bases derived from substituted salicylaldehyde and various amines have been widely investigated. There are numerous examples of the Schiff base complexes derived from amines and salicylaldehyde, substituted salicylaldehydes or β-diketones.[2-6] The metal complexes of these Schiff base ligands have been studied.

Pentadentate and hexadentate complexes are obtained when polyamines are used in the synthesis of ligands.[7-9] When the polyamine contains both primary and secondary amino groups, either Schiff bases, imidazolidines or Schiff bases containing additional imidazolidine ring are obtained,[10-12] eg. Bača and coworkers[13] synthesized 2,2′-[1,2-ethanediylbis(1,3-diazolidine-2-yl)]bis(1-oxopyridine) from the reaction of 2-pyridinecarboxaldehyde *N*-oxide with triethylenetetramine at the mole ratio of 2:1. The ligand formed as product was characterized by infrared spectroscopy, ^{13}C NMR spectroscopy, elemental analysis and X-ray structure analysis.[14-15]

Mukhopadhyay and coworkers[16] reported a new type of imidazolidine bridged heterodinuclear complex of copper(II)-zinc(II) [CuZn(OAc)(L)].$2H_2O$ which was synthesized from μ-bis(tetradentate) Schiff base ligand (**1**) (Figure 1.1) by employing

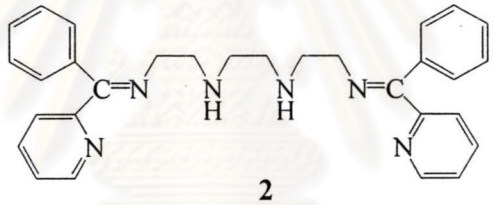
salicylaldehyde and triethylenetetramine as starting materials. They also reported a synthesis of dinuclear manganese(III/III) complexes of ligand **1**.[17]



H_3L, **1**

Figure 1.1 Structure of μ-bis(tetradentate) Schiff base ligand **1**

Chandra and coworkers[18] reported a new bis(μ-azido)nickel(II) complex which Schiff base ligand **2** which was prepared from the reaction of 2 moles of 2-benzoyl pyridine with 1 mole of triethylenetetramine.



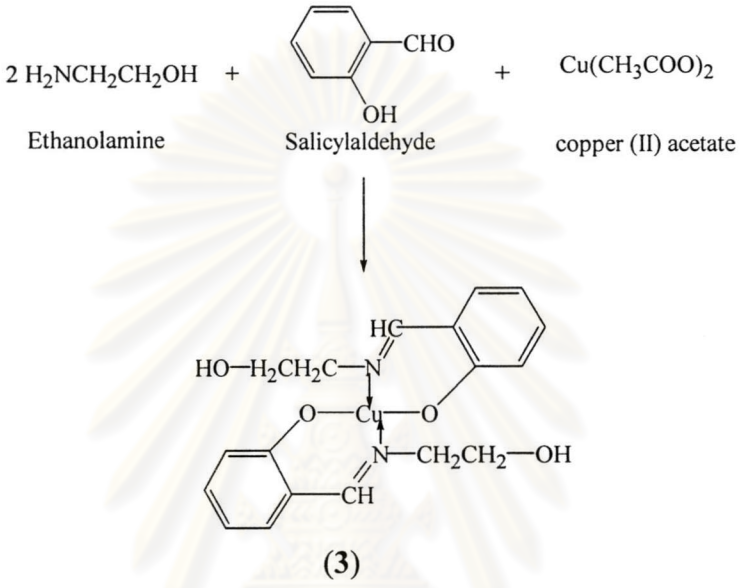
2

Figure 1.2 Structure of ligand **2**

Orvig and coworkers studied the coordination chemistry of Ga^{3+} and In^{3+} with a series of hexadentate[19-20] and heptadentate[21-22] amine phenol ligands, all of which possess amine nitrogen and phenolate oxygen donor atoms.

Brewer and coworkers[23] prepared iron (III) complex from the Schiff base ligand which was obtained from of tris(2-aminoethyl)amine (tren) and 3 equivalents of 4-methyl-5-imidazolecarboxaldehyde.

Yu and coworkers[24] synthesized a Schiff base copper complex, *bis*[N-{(2-hydroxyphenyl)methylene}hydroxyl-ethyleneamino]copper(II) **3**, which was obtained from the reaction between ethanolamine, salicylaldehyde and copper (II) acetate as shown in Scheme 1.2. It was found that the complex **3** showed liquid crystalline property. Liquid crystalline polymers containing **3** in the main chain were prepared and characterized.



(3)

Scheme 1.2 Synthesis of *bis*[N-{(2-hydroxyphenyl)methylene}hydroxyl-ethylene-amino]copper(II) **3**

1.2 Metal-containing polymers

There is currently considerable interest in metal-containing polymers since they possess properties different from those of conventional organic polymer. The synthesis of metal-containing polymer of the transition elements has resulted in a tremendous variety because of their polymers provide the best properties of both organic and inorganic component, e.g. the flexibility of organic polymers coupled with the high thermal stability associated with inorganic species. Some of the coordination polymers are reported to have stability up to 500°C.

Polyureas and their related polymers, polyurethane-ureas, are widely used to obtain a variety of products including fiber, elastomer, foam, coating and adhesive. Polyureas are prepared by reacting isocyanates with amines. The common isocyanates used for preparing the polyureas are hexamethylene diisocyanate (HDI), toluene

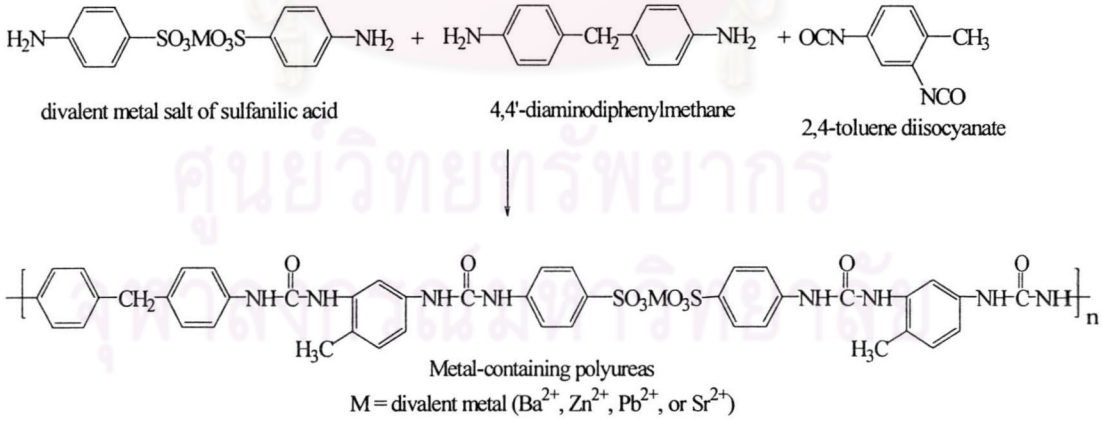
diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). Polyurethanes are obtained by the reaction between isocyanates, diols and amines. To improve the polymer properties for engineering applications such as high strength, solvent and chemical resistance, and especially high thermal stability, metal-containing polyureas and polyurethane-ureas have been studied.

1.3 Literature review

A number of polyureas and polyurethane-ureas containing metal in the polymer backbone have been studied. The synthesis and characterization of such polymers are described as follows:

Rausch and coworkers[25] reported a convenient method for the interfacial polycondensation of 1,1′-bis(β-aminoethyl)ferrocene with a variety of diacid chlorides and diisocyanates, leading to ferrocene-containing polyureas and polyamides. The polyamides showed negligible weight loss at 300°C in a nitrogen atmosphere.

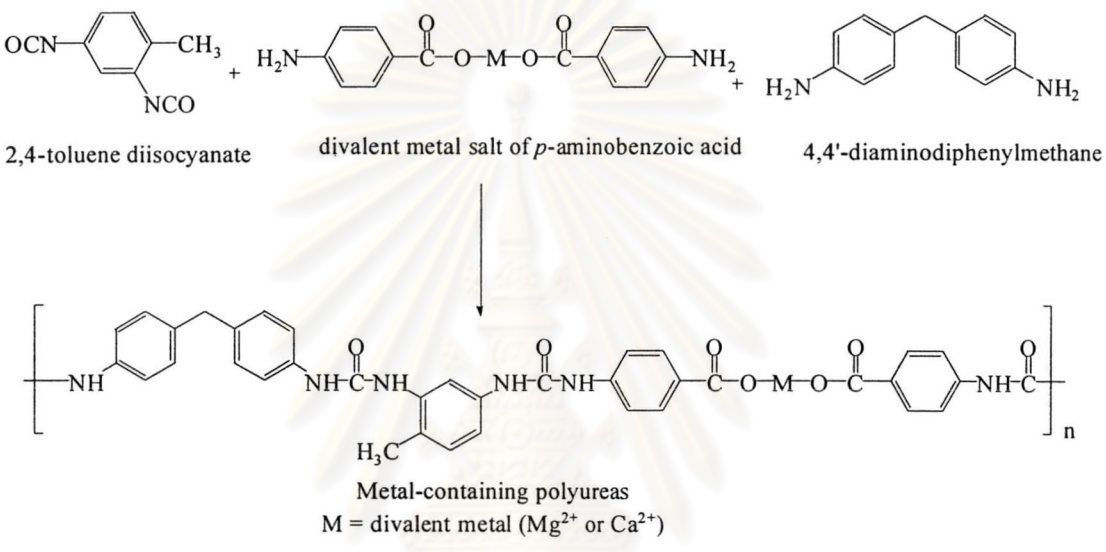
Wang and coworkers[26] prepared metal-containing polyureas from divalent metal salt of *p*-aniline sulfonic acid. The polymerization occurred *via* addition reaction of toluene diisocyanate (TDI), 4,4′-diaminodiphenylmethane and salts of *p*-aniline sulfonic acid (ASA) when the metals employed were Ba^{2+}, Sr^{2+}, Pb^{2+} and Zn^{2+} (Scheme 1.3).



Scheme 1.3 Synthesis of metal-containing polyureas from TDI, 4,4′-diaminodiphenylmethane and ASA

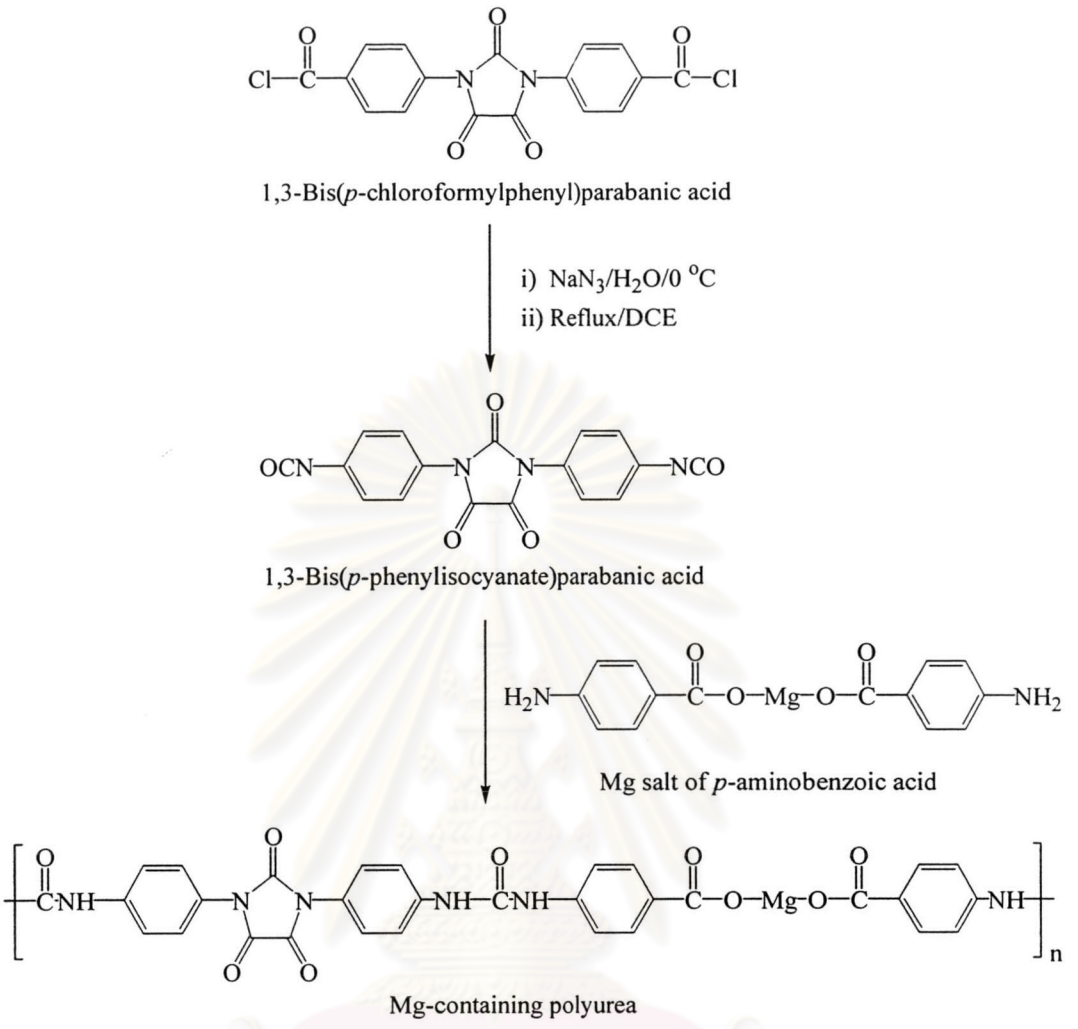
It was found that thermal stability of polyureas increased with the increase in feed ratio of ASA : 4,4′-diaminodiphenylmethane.

Matsuda and Takechi[27] synthesized metal-containing polyureas having ionic links in the main chain by polyaddition reaction of 2,4-toluene diisocyanate with mixtures of divalent metal salts of *p*-aminobenzoic acid and 4,4′-diaminodiphenylmethane (Scheme 1.4). It was found thermal stability of the polyureas increased markedly with an increase in metal content.



Scheme 1.4 Synthesis of metal-containing polyureas from 2,4-toluene diisocyanate, *p*-aminobenzoic acid and 4,4′-diaminodiphenylmethane

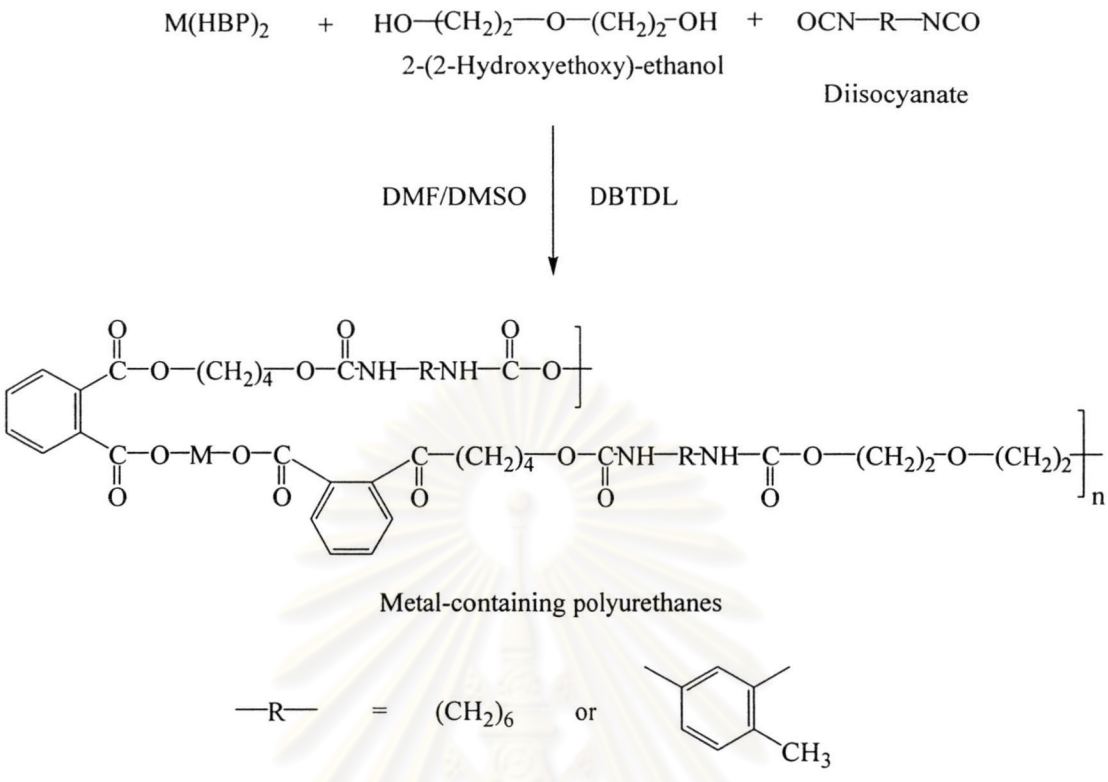
Caraculacu and coworkers[28] synthesized a new diisocyanate containing a parabanic ring [1,3-bis(isocyanatophenyl)]. The direct reaction of this diisocyanate with the Mg salt of *p*-aminobenzoic acid, or with a mixture of aromatic diamines gave ionic polyurea (Scheme 1.5). The detailed study of inherent viscosities of these polymers was achieved. The result showed that when the water content was increased, the inherent viscosity of Mg-containing polyurea was increased. This increased of viscosity can be attributed to the trend of molecules to adopt a linear shape, the interaction between the ionic groups of the polymers being diminished by polymer-water interaction.



Scheme 1.5 Synthesis of Mg-containing polyureas

Archer and coworkers[29] prepared zirconium-containing polyurethane-ureas from bis[2,2′-[[4-[[[(3-isocyanato-4-methylphenyl)amino]carbonyl]amino]-1,2-phenylene]bis-(nitrilomethylideyne)]-bis[phenolato]zirconium(IV) and polytetrahydrofuran. It was found these polymers showed thermal stability in air up to 400°C.[30]

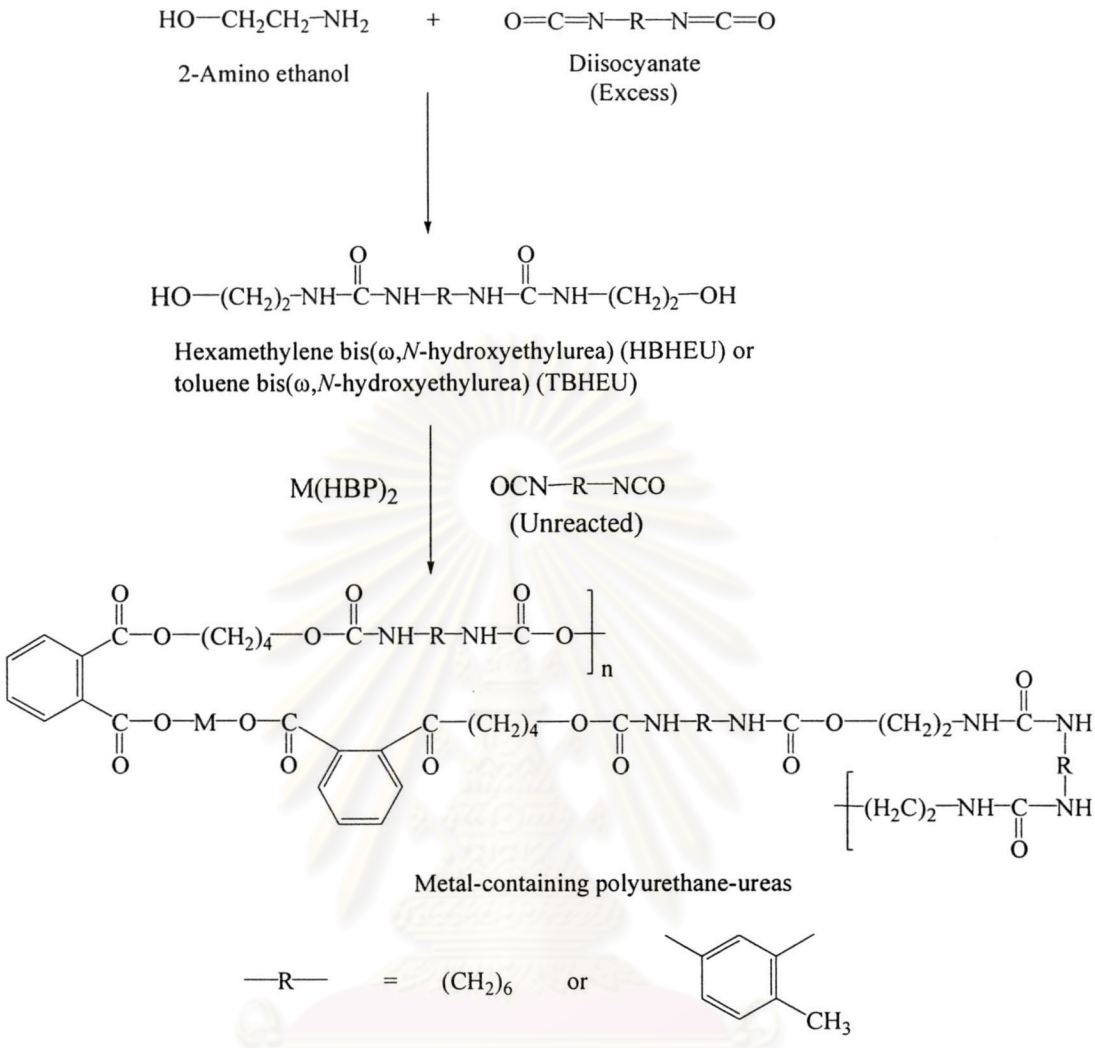
Prasath and Nanjundan[31] reported a synthesis of metal-containing polyurethanes containing ionic linkages in the main chain from metal complexes, 2-(2-hydroxy ethoxy)ethanol and diisocyanate. The metal complexes employed in the synthesis were mono(hydroxybutyl)phthalate [$M(HBP)_2$, M = Ca^{2+}, Mn^{2+} and Pb^{2+}] as shown in Scheme 1.6.



Scheme 1.6 Synthesis of metal-containing polyurethanes from $M(HBP)_2$, 2-(2-hydroxy ethoxy)-ethanol and diisocyanate

Furthermore, they synthesized polyurethane-ureas by reacting the diisocyanates with 1:1 mixture of hexamethylene bis(ω,*N*-hydroxyethylurea) (HBHEU) or toluene bis(ω,*N*-hydroxyethylurea) (TBHEU) and $M(HBP)_2$ (Scheme 1.7).

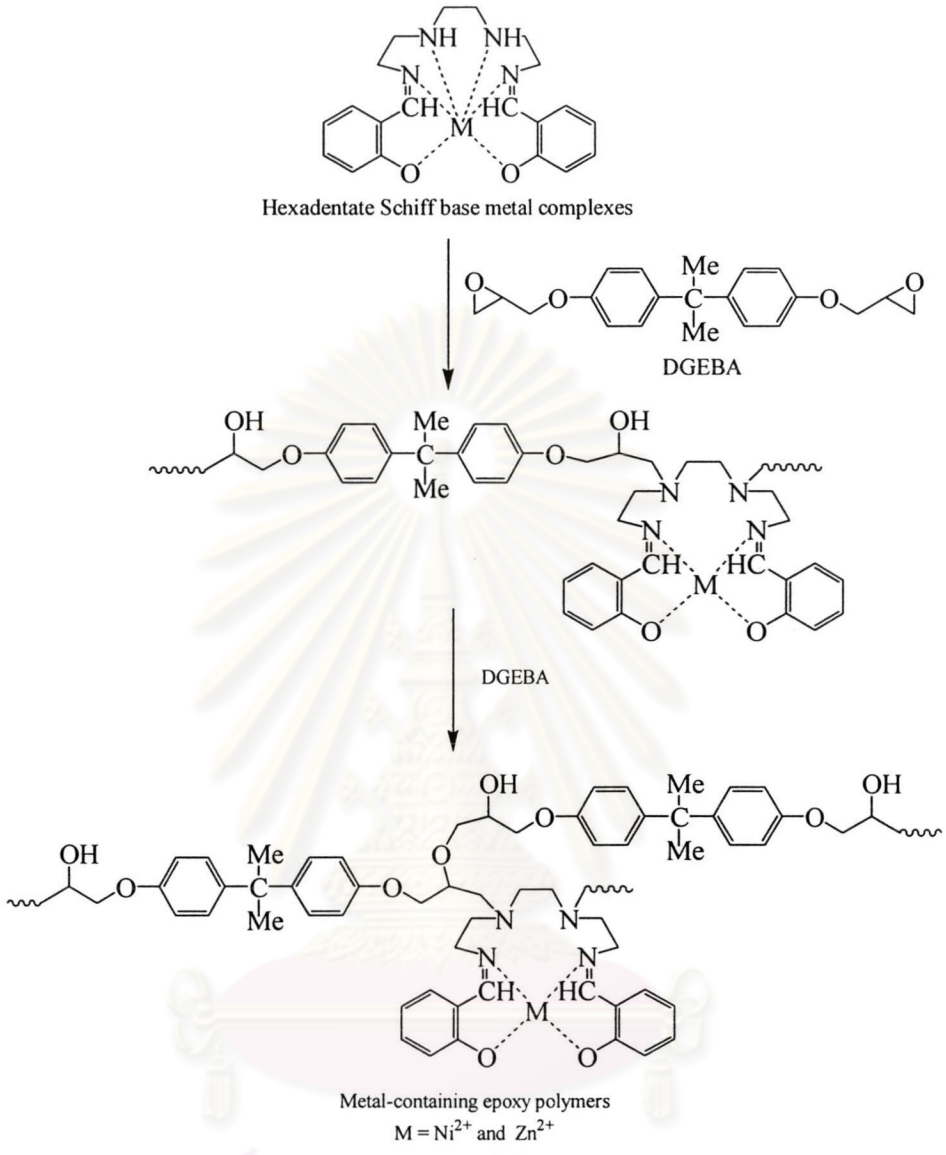
It was observed that metal-containing polyurethanes had higher initial decomposition temperature than metal-containing polyurethane-urea. It may be explained based on probability that the prepared polyurethane copolymers were found to contain less metal than the prepared polyurethane-ureas.



Scheme 1.7 Synthesis of metal-containing polyurethane-ureas from $M(HBP)_2$, hexamethylene bis(ω,*N*-hydroxyethylurea) or toluene bis(ω,*N*-hydroxyethyl urea) and diisocyanate

The TGA curves of 2,4-toluene diisocyanate (TDI)-base polyurethane indicated that the TDI-based polyurethane showed higher thermal stability than hexamethylene diisocyanate (HMDI)-based polyurethane because of the additional aromatic ring present in the polymer backbone.

Form the previous work in our research group, Chanma[32] reported the synthesis and characterization of hexadentate Schiff base metal complexes and their use as crosslinking agents for DGEBA to obtain metal-containing polymers (Scheme 1.11). These metal complexes were chosen because of their good stability, good solubility in organic solvents and availability of their starting materials.

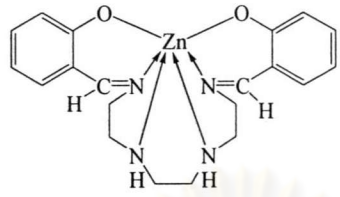


Scheme 1.8 Proposed crosslinking mechanism of DGEBA with Schiff base metal complexes.

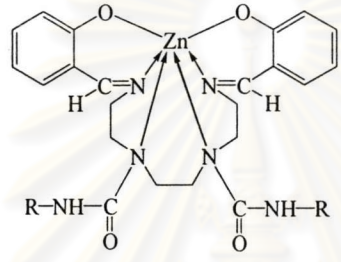
It was found that these metal complexes underwent crosslinking reactions with DGEBA to afford Ni- and Zn-containing epoxy polymers. The crosslinking reaction can be accelerated by use of tetrabutylammonium hydroxide. The obtained epoxy polymers have good thermal properties compared to the known thermally stable DGEBA/maleic anhydride system.

Batiya[33] synthesized derivatives of $Zn(Sal)_2$trien namely $Zn(Sal)_2$trien $urea_1$ and $Zn(Sal)_2$trien $urea_2$ (Scheme 1.12) and found that $Zn(Sal)_2$trien and $Zn(Sal)_2$trien

urea showed birefringence in the temperature range of 120-200°C and 145-200°C, respectively, which suggested that these metal complexes are liquid crystalline materials.



$Zn(Sal)_2trien$



$Zn(Sal)_2trien$ urea

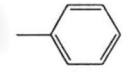
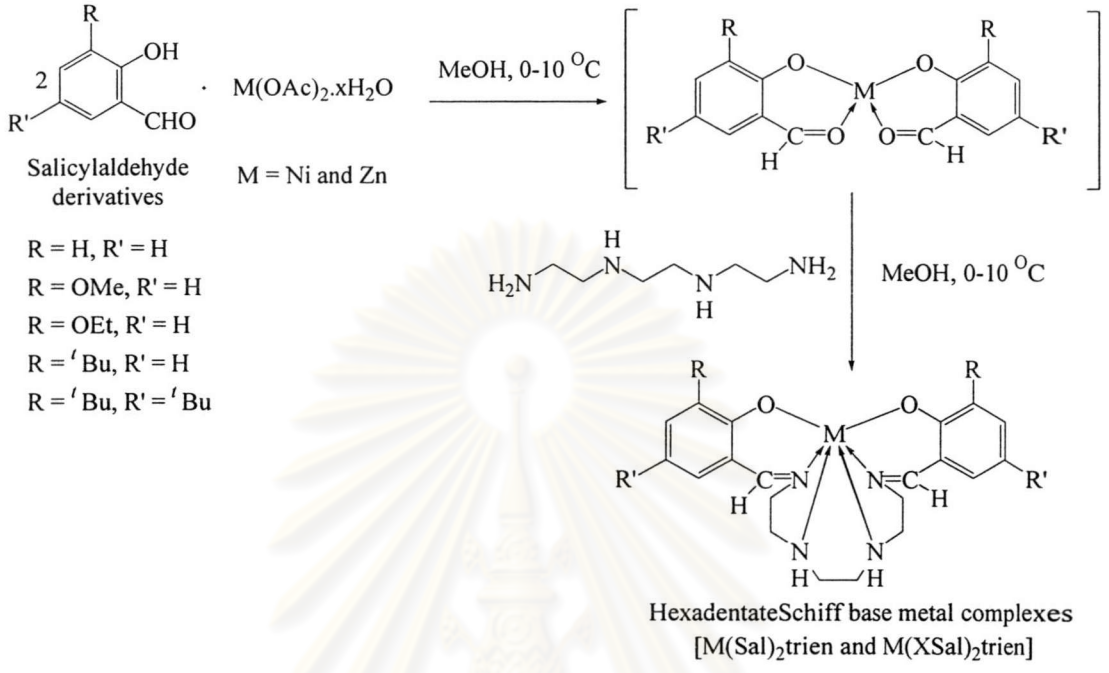
R = $-(CH_2)_5-CH_3$ and 

Figure 1.3 Structure of $Zn(Sal)_2trien$ and $Zn(Sal)_2trien$ urea

1.4 Objective and Scope of the Research

In our work, hexadentate Schiff base nickel and zinc complexes were synthesized and characterized. Attempts were made to synthesize urea derivatives of these metal complexes. It was found that the metal complexes and their derivatives did not show liquid crystalline property. The metal complexes are stable at high temperature and therefore they were used in the synthesis of thermally stable metal-containing polyureas.

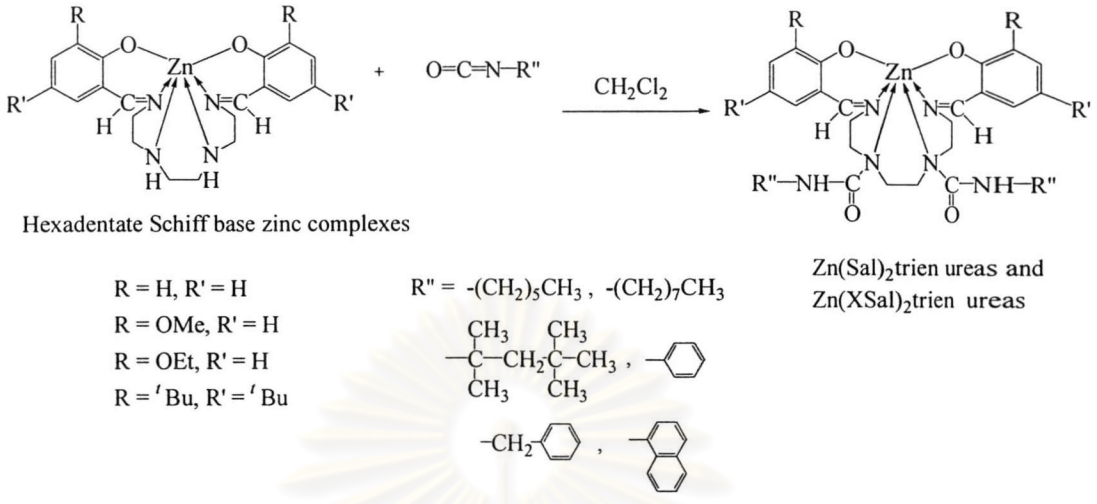
Firstly, hexadentate Schiff base zinc and nickel complexes were synthesized and characterized as described in Scheme 1.9.



Scheme 1.9 Synthesis of hexadentate Schiff base metal complexes [$M(Sal)_2$trien and $M(XSal)_2$trien]

The complexes were characterized by IR, NMR, elemental analysis, mass spectrometry and X-ray crystallography. Liquid crystalline property was investigated under differential scanning calorimetry (DSC) and thermal properties were investigated by thermogravimetric analysis (TGA).

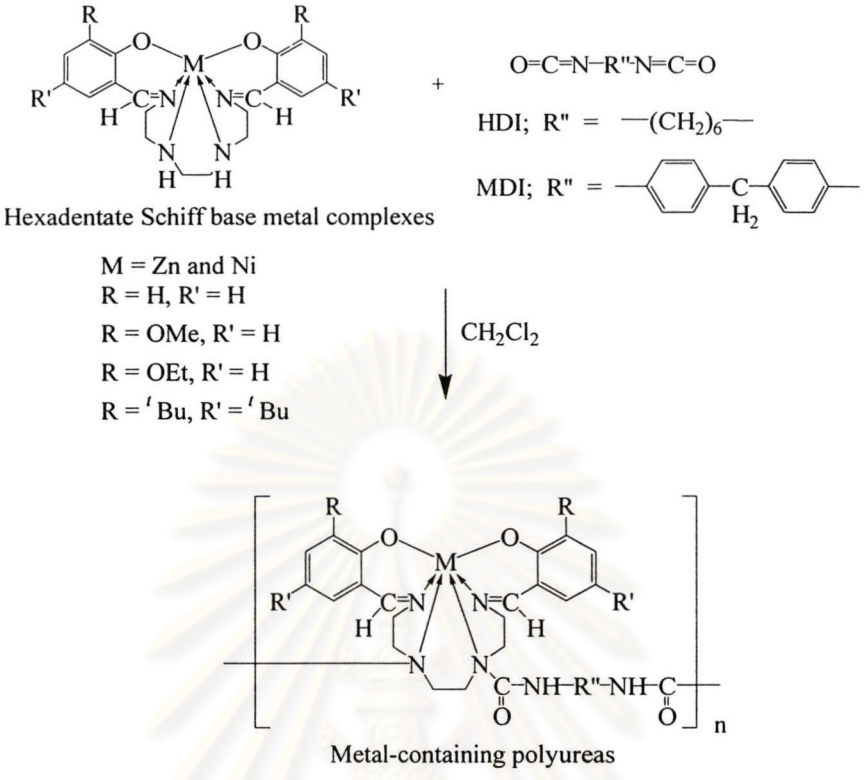
Secondly, $Zn(Sal)_2$trien, $Zn(XSal)_2$trien ureas were synthesized from the reaction between zinc complexes and isocyanates, namely hexyl isocyanate, phenyl isocyanate, benzyl isocyanate and 1-naphthyl isocyanate as shown in Scheme 1.10. This would give an information on the reactivity of the metal complexes towards isocyanate which could be applied in the synthesis of metal-containing polyureas.



Scheme 1.10 Synthesis of Zn(Sal)$_2$trien ureas and Zn(XSal)$_2$trien ureas

Zn(Sal)$_2$trien ureas and Zn(XSal)$_2$trien ureas were characterized by IR, NMR and elemental analysis. Liquid crystalline property was studied using DSC.

Finally, polymerization was performed to obtain zinc and nickel-containing polyureas as shown in Scheme 1.11. Polymerization was done by the reaction between M(XSal)$_2$trien and diisocyanates, namely hexamethylene diisocyanate (HDI) and 4,4′-diphenylmethane diisocyanate (MDI).



Scheme 1.11 Synthesis of metal-containing polyureas

Optimum conditions for the polymerization were studied. The polymer structures were characterized by IR, NMR, solubility, viscometry and elemental analysis. Flammability of the polymers was measured by limiting oxygen index (LOI) and thermal stability was investigated using TGA.