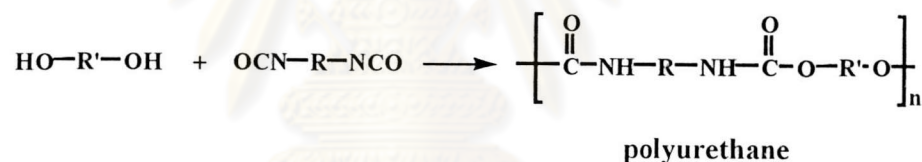


## CHAPTER I

### INTRODUCTION

#### 1.1 Polyurethanes

The urethane-producing reaction has been known since the nineteenth century. The commercial applications of polyurethanes are fiber, adhesive, coating and foam. A urethane group is formed by chemical reaction between an alcohol and an isocyanate.<sup>1-4</sup> Polyurethane results from the addition polymerization between diisocyanates or polydiisocyanates and diols or polyols (Figure 1.1).



**Figure 1.1** Synthesis of polyurethanes<sup>5</sup>

Since the functionality of the polyol or the isocyanate can be adjusted, a wide variety of branched or crosslinked polymers can be formed. The structure of polyfunctional isocyanates can be aromatic, aliphatic or polycyclic. The variety of reactants lead to various kinds of polyurethane products with a wide range of physical and mechanical properties. The most important applications of polyurethanes for fiber involves elastomeric [AB] block copolymers consisting soft and hard segment. The soft segment is typically a polyester- or polyether-diol. The hard segments normally includes the connection of a diisocyanate (aromatic or aliphatic) and a low molecular weight diol or diamine which is the chain extender. Diamine chain extenders are much more reactive than diol chain extender and give properties superior to those of similar polymers prepared with the equivalent diol chain extender.

This is because the hard segment (urea linkage) has a higher density of hydrogen bonding which results in a thermal stability. By varying the structure, molecular weight of the segment, and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained.

The various methods for producing segmented polyurethane elastomer can be differentiated according to the medium of preparation and the addition sequence of the reactants. However, the more common route of making polyurethane is *via* the prepolymer process (Figure 1.1).<sup>5</sup> In this method, the first step is to react the polyol with excess the diisocyanate to form a diisocyanate terminated intermediate oligomer. The second step is to convert this prepolymer to the final high molecular weight polyurethane by further reaction with a diol or diamine chain extender.

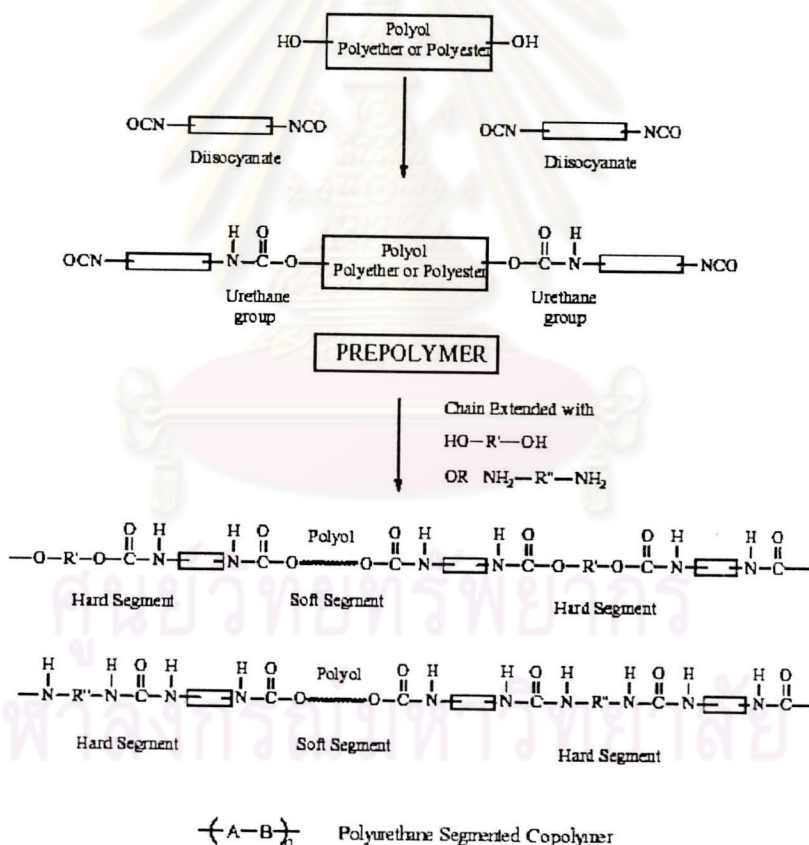


Figure 1.1 Two-step prepolymer technique for the synthesis of polyurethanes<sup>5</sup>

A polyurethane structure is made by the two-step method and tends to be more regular than the corresponding polyurethane made by the one-step method. Therefore, the polymer chain has a more regular hard-soft-hard sequence. This structural regularity may impart better mechanical properties to the polyurethane since the hard segments can easily aggregate or crystallize to form physical crosslink points.

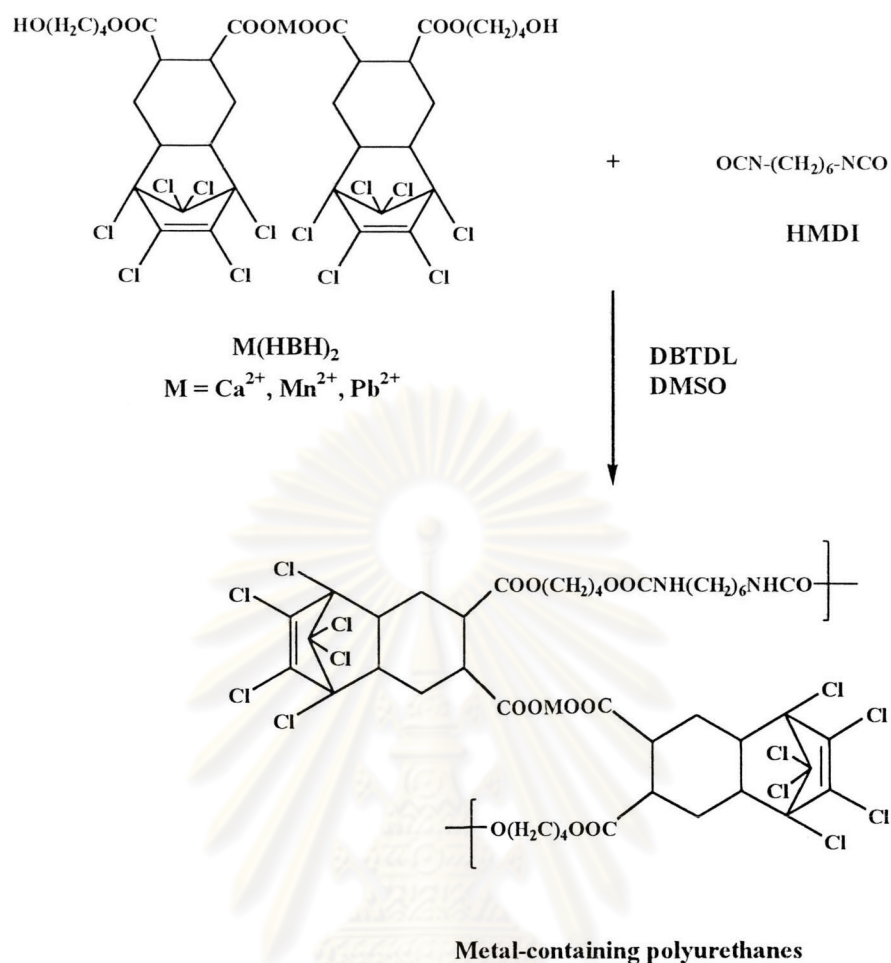
## 1.2 Metal-containing polyurethane-ureas

The polymers with coordinating groups and metallic ions are of great interest due to the numerous interesting properties and potential applications in many diverse fields such as catalysis, medicine and electronics. The interaction of metal into urethane-ureas backbone results in a considerable increase in the decomposition temperature and the thermal properties of polymer is affected by the presence of metallic ions.<sup>6-7</sup> Metal-containing polyurethane-ureas can be tailor-made with versatile applications and useful interesting properties such as flame retardancy, high thermal stability or resistance to chemicals. The incorporation of metal into the polymers gives them applications such as thickeners, adhesives and resins.

## 1.3 Literature review

A number of works concerning the preparation of polyureas, polyurethanes and polyurethane-ureas containing metal in the backbone of the polymer chain have been reported as follows:

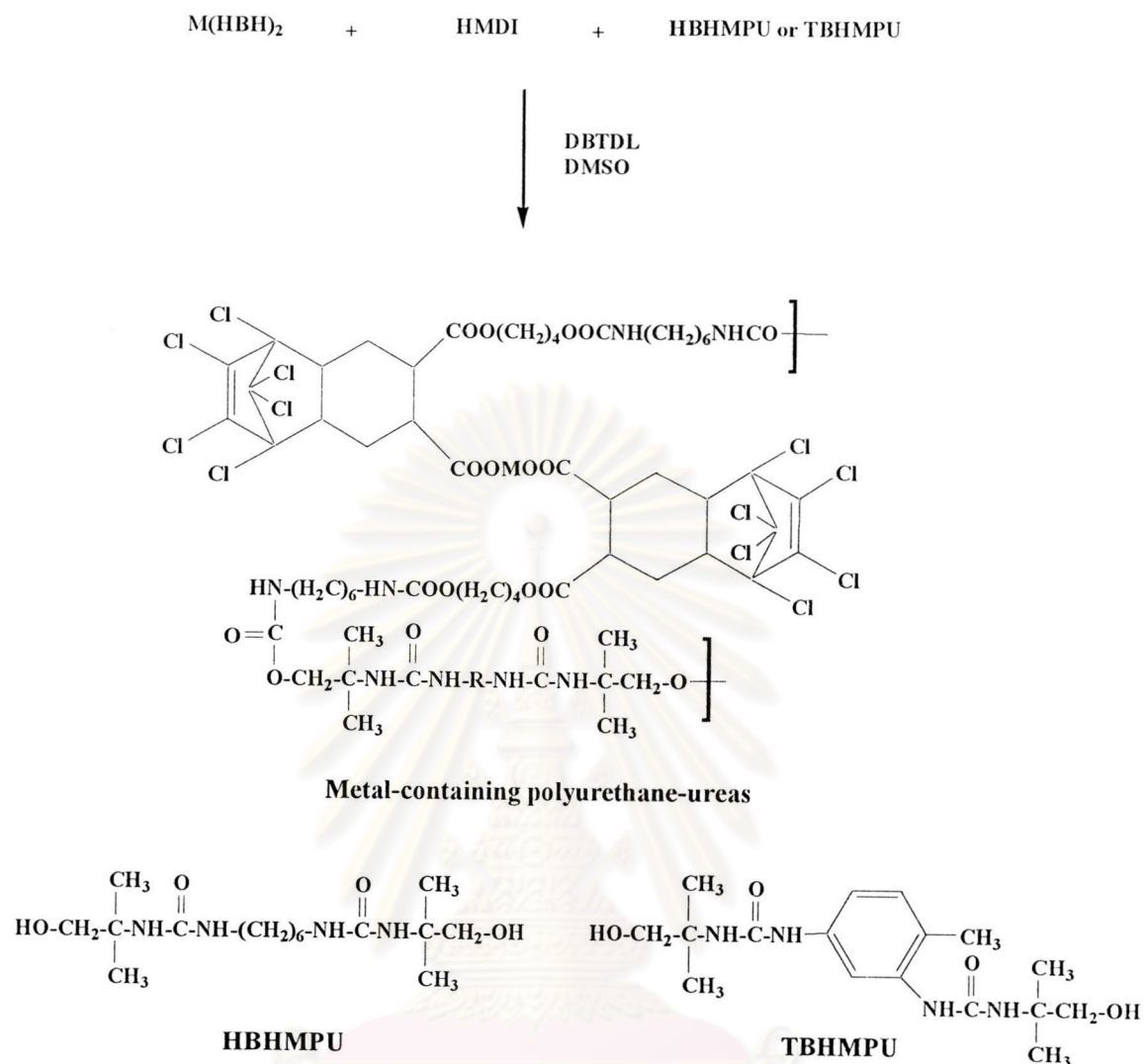
Nanjundan and Prasath<sup>8</sup> synthesized and characterized flame-retardant metal-containing polyurethanes and polyurethane-ureas. Metal-containing polyurethanes were synthesized by the polyaddition reaction of hexamethylene diisocyanate (HMDI) with the divalent metal salts of mono(hydroxybutyl)hexolate,  $M(\text{HBH})_2$ , where metals were  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Pb}^{2+}$  (Scheme 1.1).



**Scheme 1.1** Synthesis of metal-containing polyurethanes from  $M(HBH)_2$  and HMDI

Polyurethane-ureas were obtained from the reaction of  $M(HBH)_2$  with HMDI, hexamethylene *bis*[ $N'$ -(1-hydroxy-2-methyl-prop-2-yl)] (HBHMPU) or toluene 2,4-*bis* [ $N'$ -(1-hydroxy-2-methyl-prop-2-yl)urea] (TBHMPU) (Scheme 1.2).

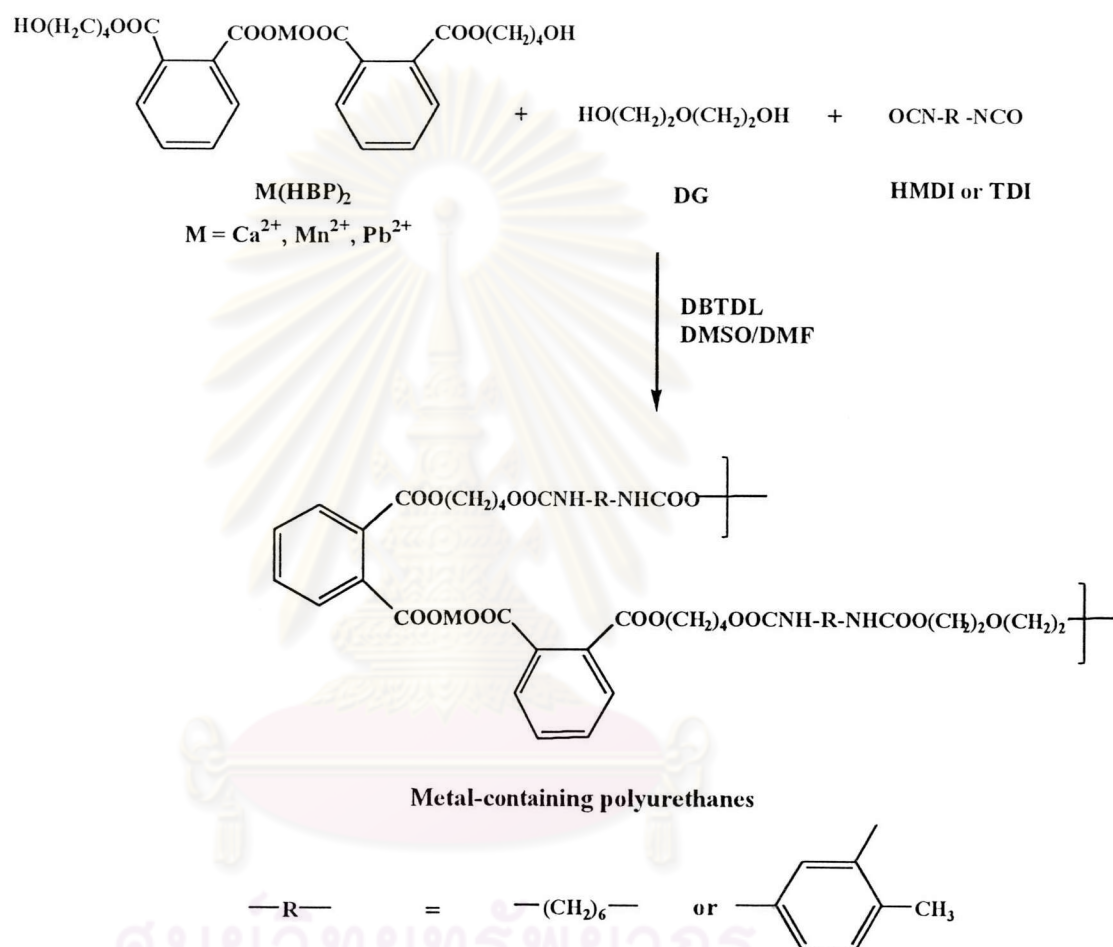
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**Scheme 1.2** Synthesis of metal-containing polyurethane-ureas from HMDI and HBHMPU or TBHMPU

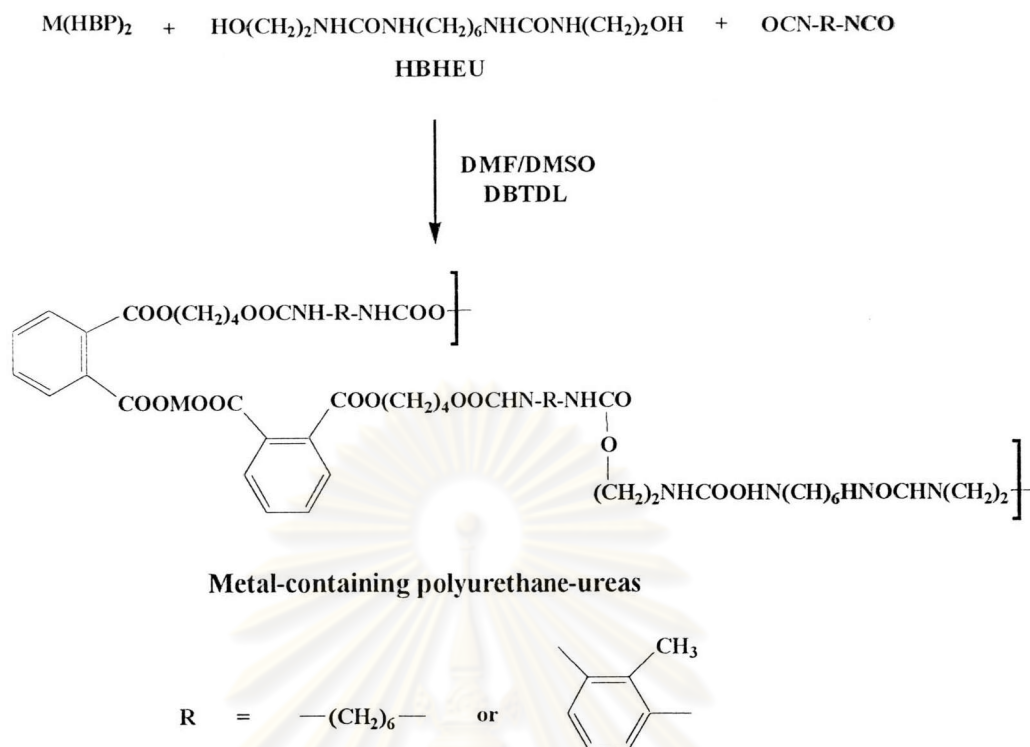
From TGA study, the thermal stability of metal-containing polyurethanes showed higher thermal stability than metal-containing polyurethane-ureas. Among the polyurethane-ureas, TBHMPU-based polyurethane-ureas were slightly more stable than HBHMPU-based polyurethane-ureas due to the presence of aromatic rings in the polymer chain. The thermal stability of metal-containing polymers followed the order  $Ca > Mn > Pb$ . Flame retardancy of polyurethanes was higher than that of polyurethane-ureas. Among the polyurethane-urea, the TBHMPU-based polyurethane-ureas were found to have higher flame retardancy.

Another work of Nanjundan and Prasath<sup>9</sup> also involved the synthesis of metal-containing polyurethanes by using different divalent metal salts. They used the divalent metal salts of mono(hydroxybutyl)phthalate,  $M(\text{HBP})_2$ , where metals were  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Pb}^{2+}$ , to synthesize polyurethanes by polyaddition with diethylene glycol (DG) and HMDI or TDI (Scheme 1.3).



**Scheme 1.3** Synthesis of metal-containing polyurethanes from  $M(\text{HBP})_2$ , digol and HMDI or TDI

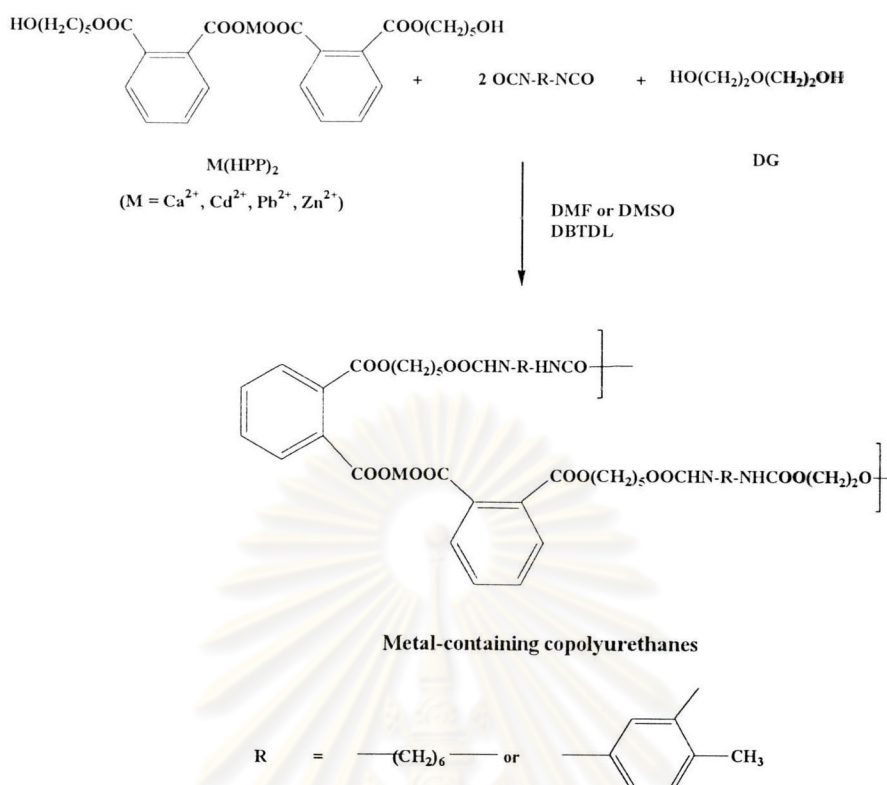
Furthermore, they synthesized polyurethane-ureas by reacting the diisocyanates with 1:1 mixtures of hexamethylene *bis*( $\omega$ , N-hydroxyethyl-urea) (HBHEU) and  $M(\text{HBP})_2$  as shown in Scheme 1.4.



**Scheme 1.4** Synthesis of metal-containing polyurethane-ureas from M(HBP)<sub>2</sub>, HBHEU and HMDI or TDI

It was found that the metal-containing polyurethanes have higher initial temperature decomposition (IDT) than metal-containing polyurethane-ureas. It may be explained based on probability that the polyurethane copolymers prepared were found to contain less metal than the prepared polyurethane-ureas. It has been reported that the existence of metal promoted the thermal decomposition of urethane and urea and with increase in the metal content of the polymers the stability decrease. Thermal stability of the metal-containing polymers can be ordered as Pb>Mn>Ca.

Nanjundan and Lee<sup>10</sup> synthesized Ca-, Cd-, Pb- and Zn-containing copolyurethanes from the divalent metal salts of mono(hydroxypentyl)phthalate, M(HBP)<sub>2</sub>, where metals were Ca<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>, diethylene glycol (DG) and HMDI or TDI (Scheme 1.5).



**Scheme 1.5** Synthesis of metal-containing copolyurethanes from  $\text{M}(\text{HPP})_2$ , diethylene glycol and HMDI or TDI

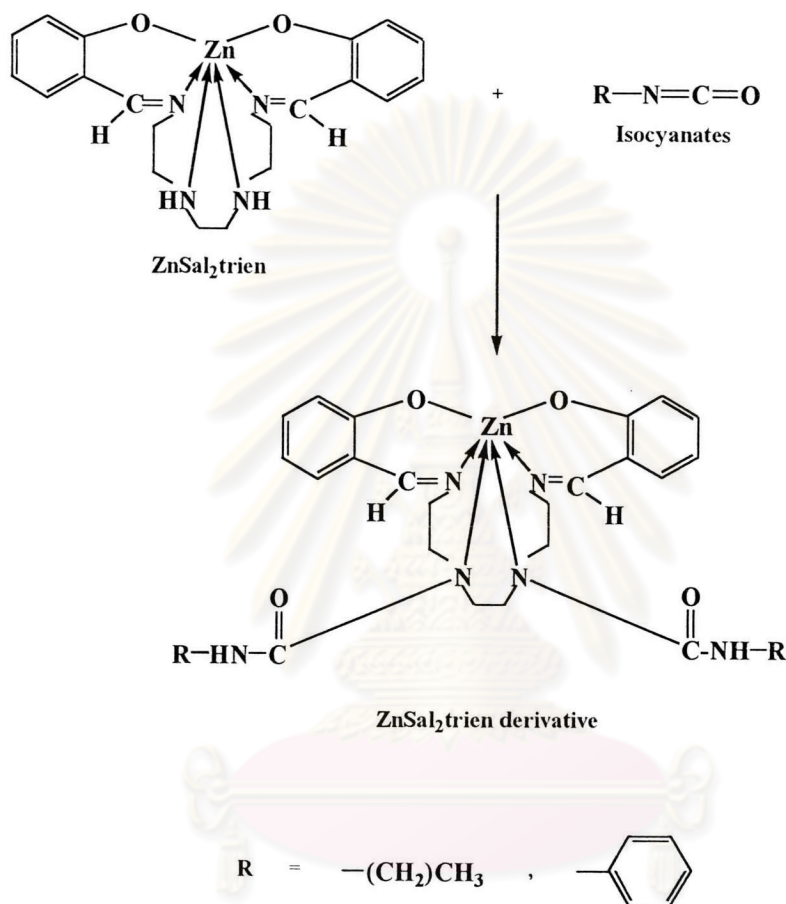
The result indicated that the TDI-based copolyurethanes showed higher thermal stability than the HMDI-based copolyurethanes. This may be due to the presence of stiff phenylene ring in the main chain of TDI-based polymers. In all cases of copolyurethanes, the residual weight at  $800^\circ\text{C}$  obtained from TGA corresponds to the amount of  $\text{CaO}$ ,  $\text{CdO}$ ,  $\text{PbO}$  and  $\text{ZnO}$  formed at this temperature. The metals act as catalyst and facilitate the first decomposition stage but retard the rate of decomposition of further stages. The copolyurethanes showed  $T_g$  values ranged between  $72.2$  and  $83.3^\circ\text{C}$ . The  $T_g$  values of the TDI-based copolyurethanes were slightly higher than those of the HMDI-based polymers.

Qiu and coworkers<sup>11</sup> synthesized metal-containing polyureas containing ionic linkages in the main chain by the polyaddition of TDI with the 4,4'-diaminodiphenylmethane (ASA) and the mixtures of divalent metal salts of sulfanilic



acid where metals were  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ . It was found that introducing the metal into the polyurea increased the thermal stability.

From the work in our research group,<sup>12</sup>  $\text{ZnSal}_2\text{trien}$  and  $\text{ZnSal}_2\text{trien}$  ureas were synthesized (Scheme 1.6).



**Scheme 1.6** Synthesis of  $\text{ZnSal}_2\text{trien}$  derivative

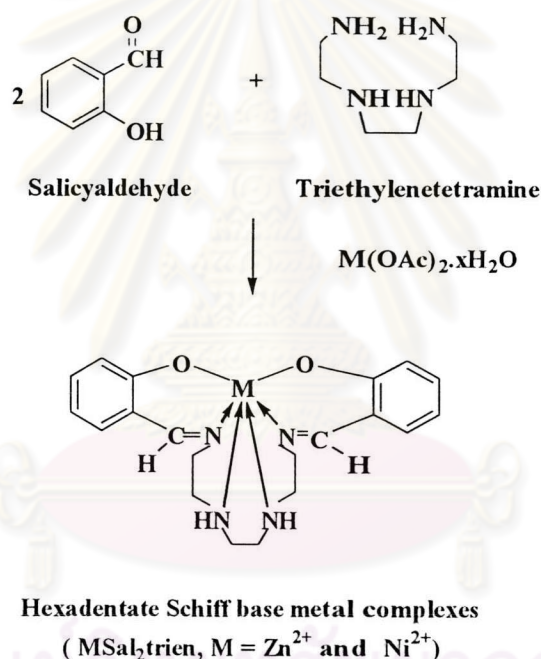
It was found that,  $\text{ZnSal}_2\text{trien}$  and  $\text{ZnSal}_2\text{trien}$  derivative showed birefringence under polarized optical microscope in the temperature range 120-200°C and 145-200°C, respectively. The results suggested that metal complexes are liquid crystals.

In this work,  $\text{MSal}_2\text{trien}$  ( $\text{M} = \text{Zn}$  and  $\text{Ni}$ ) will be incorporated into the polymer chain of polyureas and polyurethane-ureas. It was expected that the obtained polymers would exhibit liquid crystalline property and good thermal stability.

## 1.4 Objective and Scope of the Research

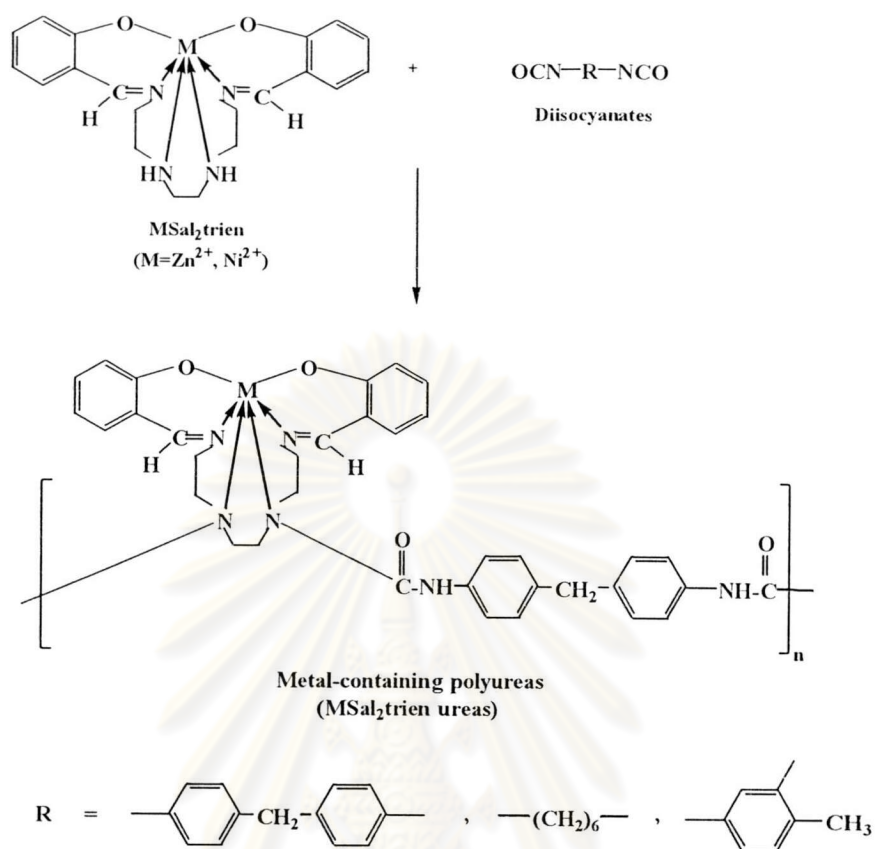
The target of this research is to synthesize zinc- and nickel-containing polyureas and polyurethane-ureas based on hexadentate Schiff base metal complexes. The optimum conditions for the polymerization were studied. The effects of the incorporation of zinc and nickel into the main chain of polyureas and polyurethane-ureas on thermal properties were investigated.

In the first step, hexadentate Schiff base metal complexes were synthesized as shown in Scheme 1.7.



**Scheme 1.7** Synthesis of ZnSal<sub>2</sub>trien and NiSal<sub>2</sub>trien

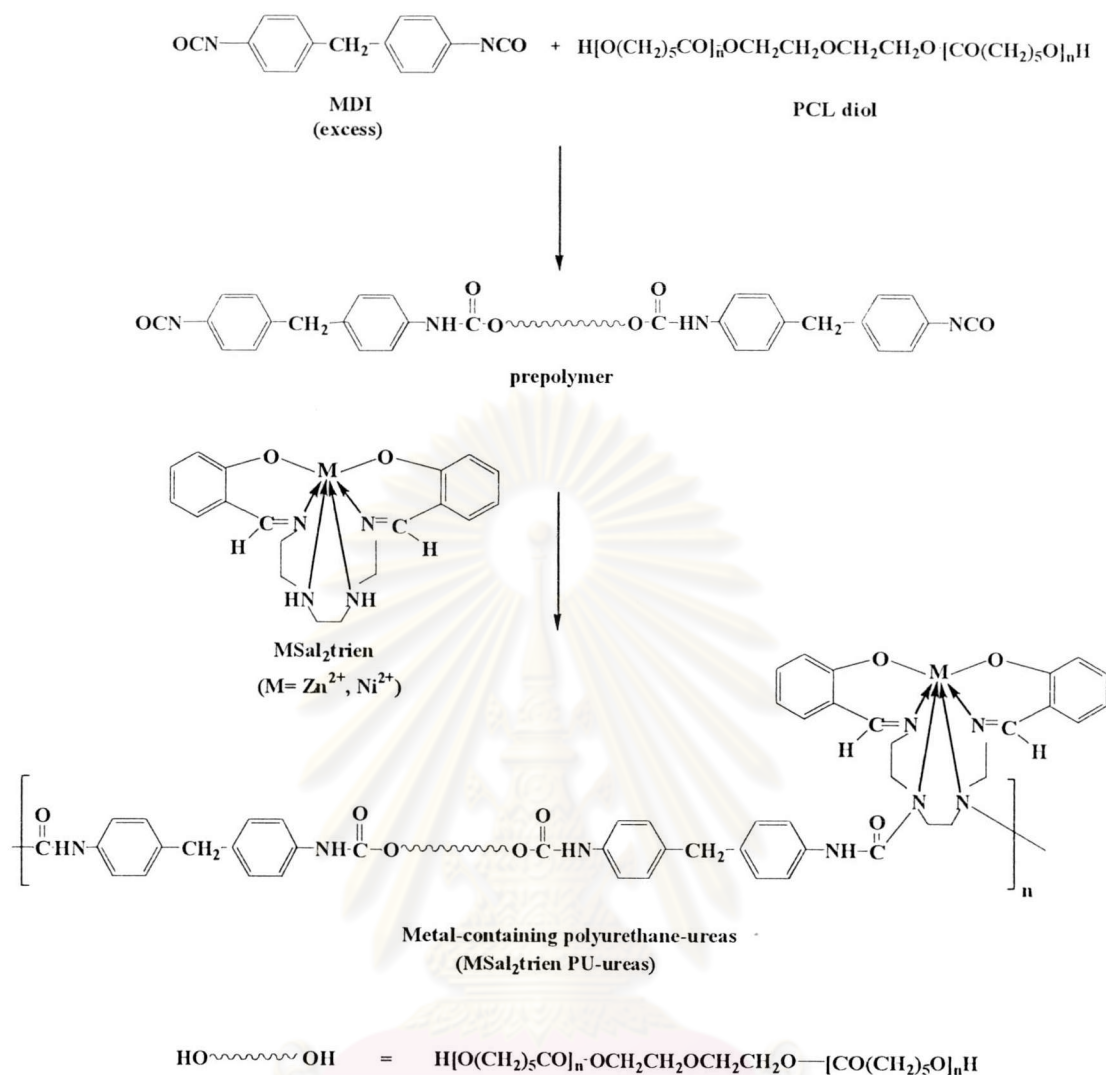
Secondly, metal-containing polyureas (MSal<sub>2</sub>trien ureas) were synthesized from the reaction between MSal<sub>2</sub>trien and different diisocyanates, including 4,4'-methylenebis(phenyl isocyanate) (MDI), hexamethylene diisocyanate (HMDI) and 2,4-toluene diisocyanate (TDI) (Scheme 1.8).



**Scheme 1.8** Synthesis of  $\text{MSal}_2\text{trien}$  ureas from  $\text{MSal}_2\text{trien}$  and diisocyanate compounds

Metal-containing polyurethane-ureas ( $\text{MSal}_2\text{trien}$  PU-ureas) were synthesized from the reaction between  $\text{MSal}_2\text{trien}$ , 4,4'-methylenebis(phenyl isocyanate) (MDI) and poly(caprolactone) diol (PCL diol) of different molecular weights (530, 1250 or 2000) (Scheme 1.9).

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**Scheme 1.9** Synthesis of MSal<sub>2</sub>trien PU-ureas from MSal<sub>2</sub>trien, MDI and PCL diol

Finally, Zn and Ni-containing polyureas and polyurethane-ureas were characterized by IR spectroscopy and elemental analysis. Solubility and viscosity were also determined. Liquid crystalline property was investigated under polarizing optical microscope. Flammability of the polymers was measured by limiting oxygen index (LOI) and char yield residue was obtained from thermogravimetric analysis (TGA).