CHAPTER II

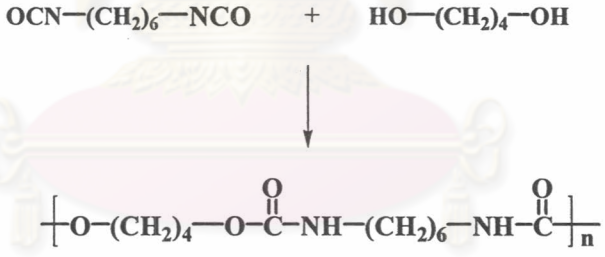
THEORY AND LITERATURE REVIEW

2.1 Polyurethanes

The basic reaction to obtain a urethane group is that of an isocyanate group with an alcohol group (Scheme 2.1). This reaction was originally conceived in 1937 by Otto Bayer [1].

Scheme 2.1 The basic reaction of polyurethane

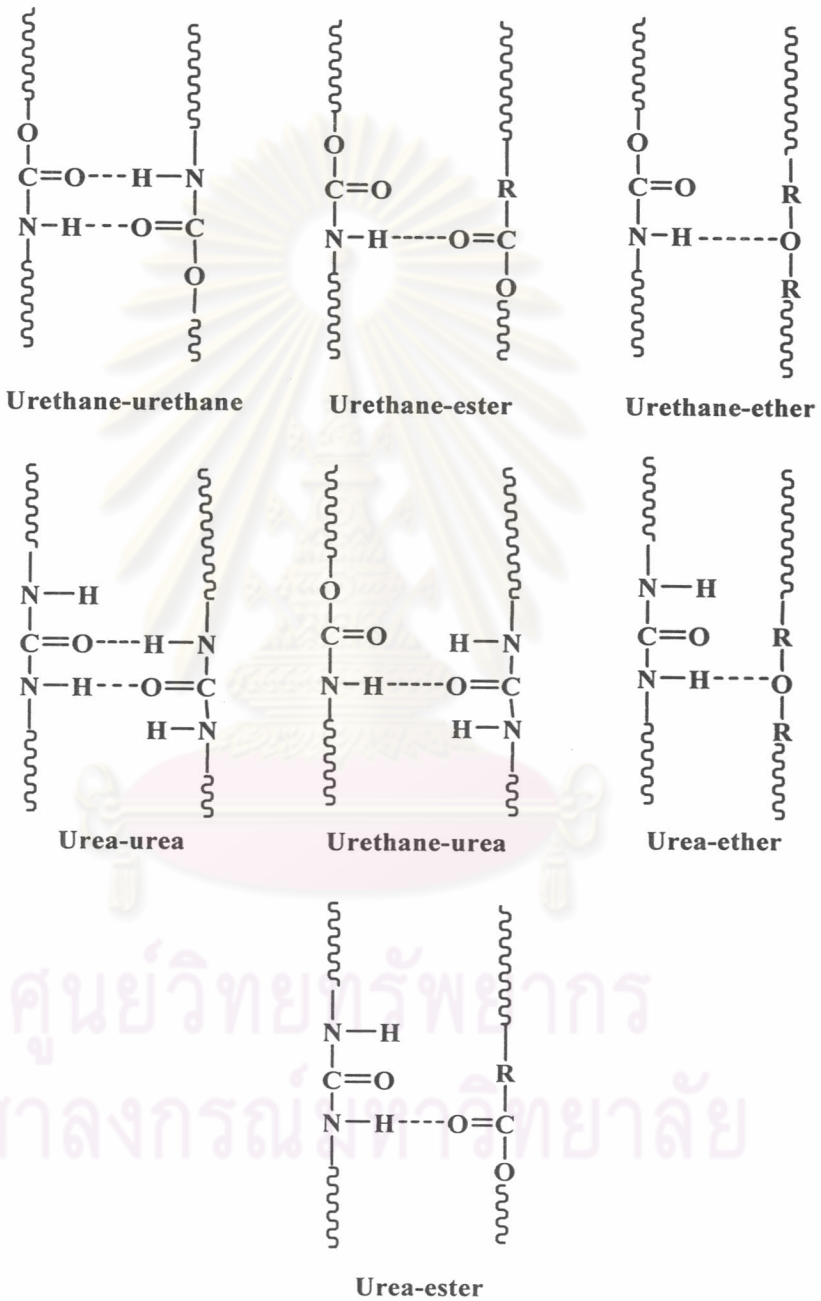
Because no small molecule is eliminated, this reaction is sometime named polyaddition. The first product was a fibre prepared from hexamethylene diisocyanate and 1,4-butanediol (Scheme 2.2) [2].



Scheme 2.2 Polyurethane fiber obtained from the reaction between hexamethylene diisocyanate and 1,4-butanediol.

The variety of reaction leads to various kinds of polyurethane products with a wide range of physical and mechanical properties. Polyurethane elastomers are thermoplastic copolymers of $(AB)_n$ type consisting of an alternating block of relatively long flexible "soft segment" and another block of highly polar, rather stiff chain or "hard segment". The soft segment is derived from a hydroxyl-terminated aliphatic polyester, polyether or polyalkene (MW 500 to 5,000), while the hard

segment is formed from the reaction of diisocyanates with low-molecular-weight diol or diamine chain extenders. Hydrogen bonding in polyurethanes occurs between the NH hydrogens in the hard segment and the carbonyl oxygens in the hard segment or between the carbonyl and ether oxygen in the soft segment (Scheme 2.3).



Scheme 2.3 Possible hydrogen bonding in polyurethanes

Polyurethane elastomers have high strength; extremely good abrasion resistance, good resistance to gas, greases, oils and hydrocarbons, and excellent resistance to oxygen and ozone. Polyurethanes are used in four principal types of products: foams, elastomers, fibers and coatings. In addition, polyurethane is a polymer of choice for a wide variety of biomedical applications [2].

Subsequently, polyurethane properties are improved by adding substituents to withstand extreme of temperature and can used in many areas. Examples of substituents added are diphenylsulfone [3], 4,4′-diphenylmethane [4], methyl-*p*-toluene sulfonate [5], metal complexes [6] and imides [7] .

2.2 Metal-containing polymers

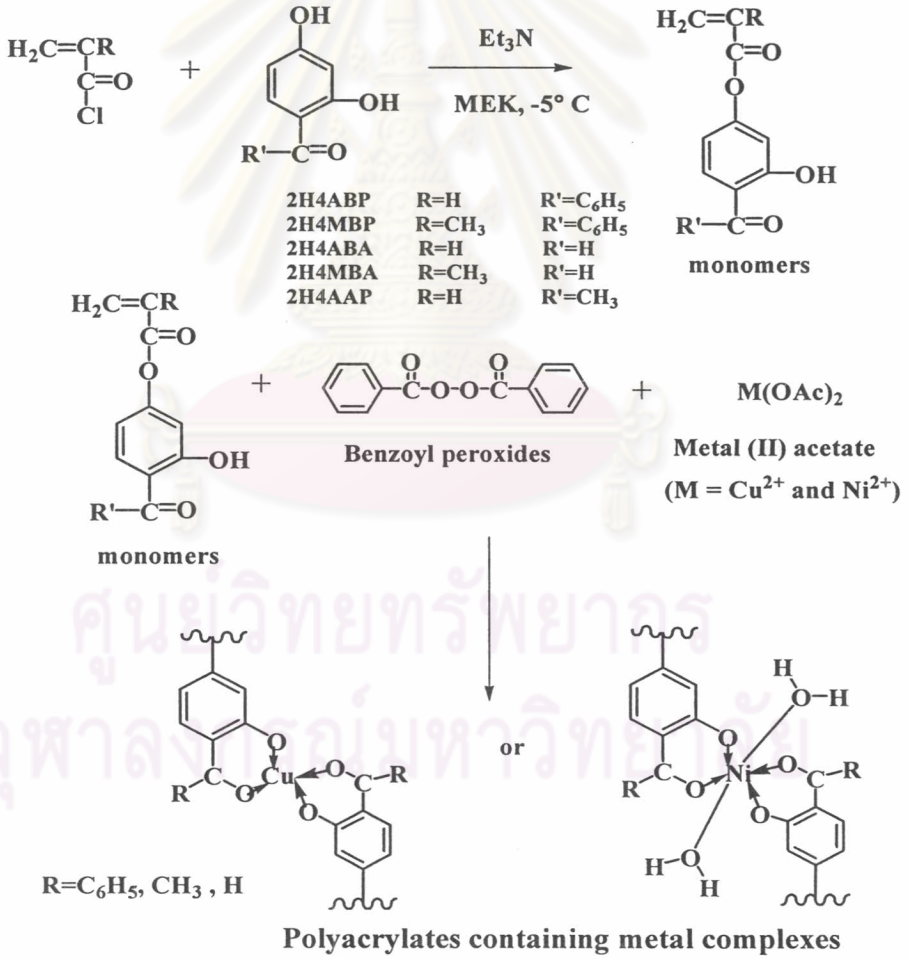
Metal-containing polymers are an important class of thermally stable or heat resistant polymers. This excellent property is widely investigated [8-9]. For a polymer to be considered as a thermally stable polymer, it should not decompose below 400 °C and should retain its useful service properties at temperature near the decomposition temperature [10].

Research on metal-containing polymers began three decades ago. These polymers have a wide range of applications such as for semiconductors, catalysts, biocides and adhesives.

2.3 Literature review

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

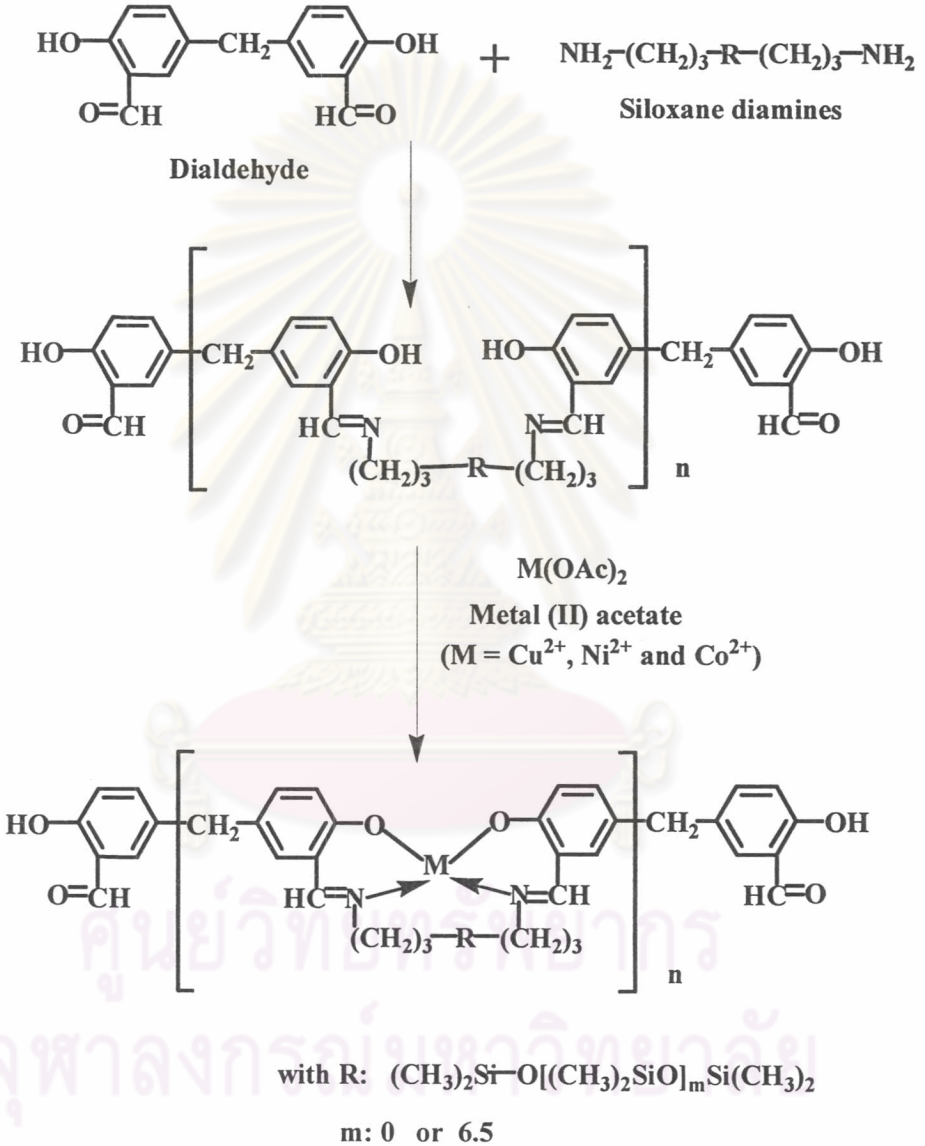
Kaliyappan and coworkers [11] synthesized polyacrylates pendant ligands containing divalent metal complexes by free radical polymerization reaction of an aqueous solution of metal ion [Cu(II) and Ni(II)], benzoyl peroxide as an initiator and monomers, namely, 2-hydroxy-4-acryloyloxybenzophenone (2H4ABP), 2-hydroxy-4-methacryloyloxybenzophenone (2H4MBP), 2-hydroxy-4-acryloyloxybenzaldehyde (2H4ABA), 2-hydroxy-4-methacryloyloxybenzaldehyde (2H4MBA). The monomers were prepared by reacting (meth)acryloyl chloride with 2,4 dihydroxybenzophenone, 2,4-dihydroxybenzaldehyde and 2,4-dihydroxyacetophenone as shown in Scheme 2.4.



Scheme 2.4 Synthesis of polyacrylates containing metal complexes

The result found all polymer-metal complexes start to decompose around 310-400 °C. Around 700 °C the polymer-metal complexes lose 88-96% weight. The Cu(II) complexes are comparatively more stable than Ni(II) complexes

Maria and coworkers [12] synthesized a new metal-containing polyazomethines by polyaddition reaction of 5,5′-methylene-bissalicylaldehyde, siloxane diamines and divalent metals [Cu(II), Ni(II), Co(II)] as shown in Scheme 2.5.



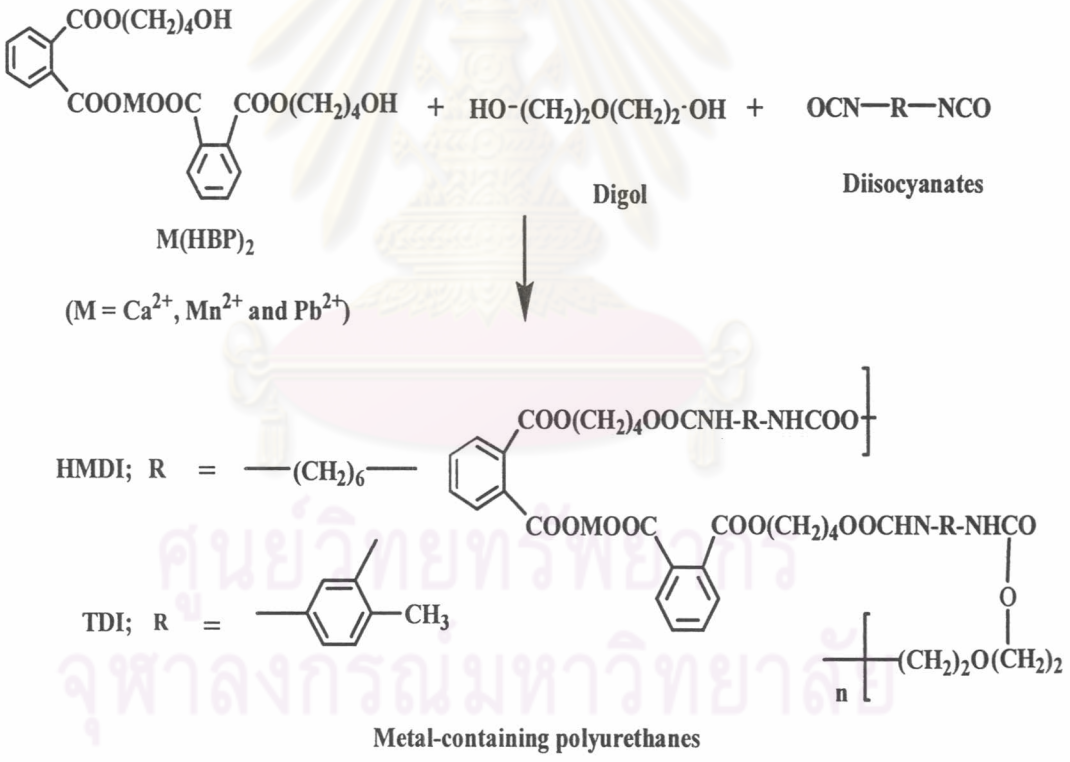
Scheme 2.5 Synthesis of metal-containing polyazomethines.

Thermogravimetric studies showed that the thermal stability decreased with chelation and increases in the siloxane segment length in the starting diamine. According to assumption, the metal ions in the polymers catalyze thermal decomposition.

From these above research works, it was revealed that the different metal-containing polymers showed both good and poor thermal stability.

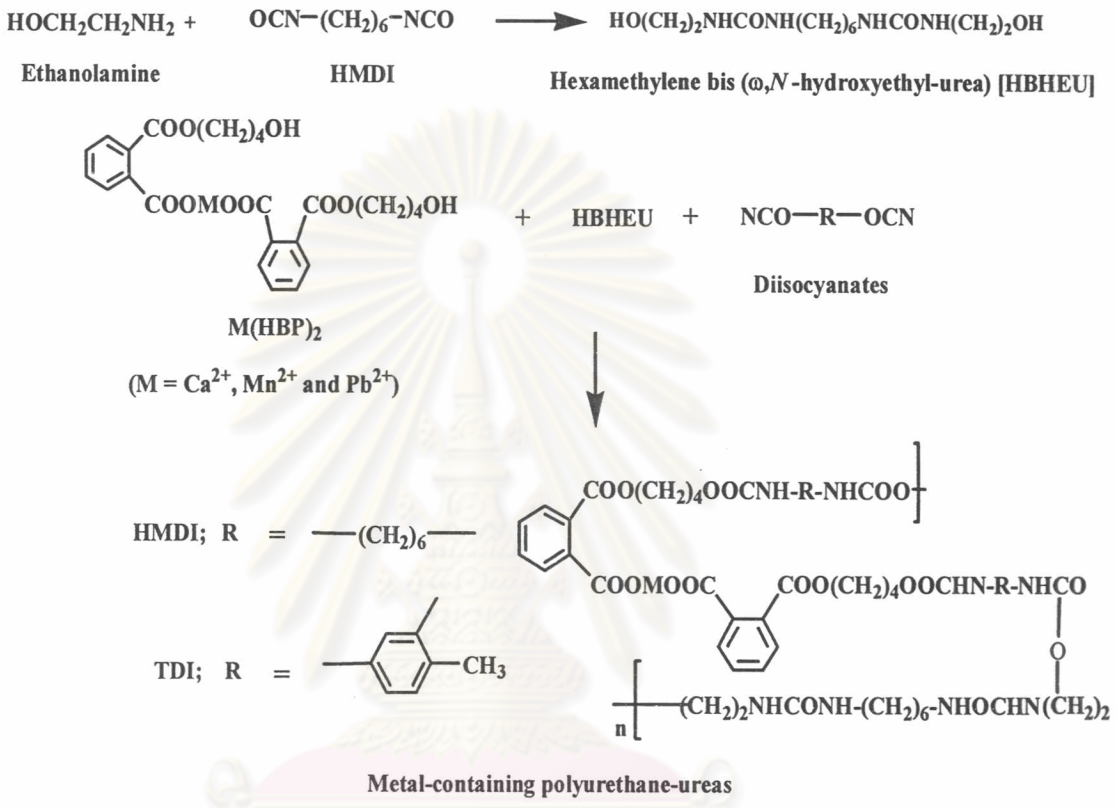
Other research works concerning metal-containing polymers are in the areas of metal-containing polyurethanes [13], polyurethane-ureas [14] and polyurethane-ethers [15-17]. Examples of such works are as follows:

Nanjandan and Prasath [18] synthesized metal-containing polyurethane by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanaye (TDI) with 1:1 mixtures of divalent metal salt of mono(hydroxybutyl)phthalate [$M(HBP)_2$, M = Ca^{2+}, Mn^{2+} and Pb^{2+}] and digol [DG] (Scheme 2.6).



Scheme 2.6 Synthesis of metal-containing polyurethane

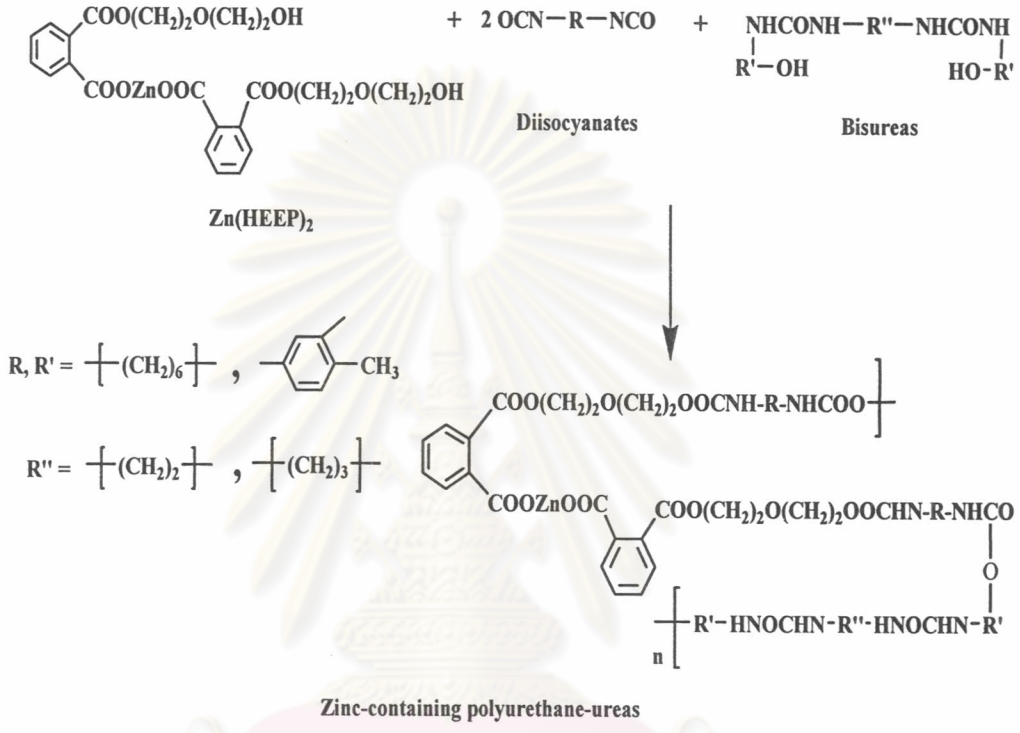
Moreover, they synthesized metal-containing polyurethane-ureas by the polyaddition reaction of the diisocyanates with 1:1 mixtures of hexamethylene *bis* (ω, *N*-hydroxyethyl-urea) [HBHEU] or toluene *bis* (ω, *N*-hydroxyethyl-urea) [TBHEU] and divalent metal salt of mono (hydroxybutyl) phthalate [$M(HBP)_2$] as shown in Scheme 2.7.



Scheme 2.7 Synthesis of metal-containing polyurethane-ureas

The result of thermal studies showed that the metal-containing polyurethanes have higher initial decomposition temperature (IDT) than metal-containing polyurethane-ureas. On the other hand, polyurethane-ureas are expected to be more stable than polyurethanes as the former is stabilized by more hydrogen bonding. Thermal stability of the metal-containing polymers is ordered as Pb>Mn>Ca. These polymers were soluble in DMF and DMSO.

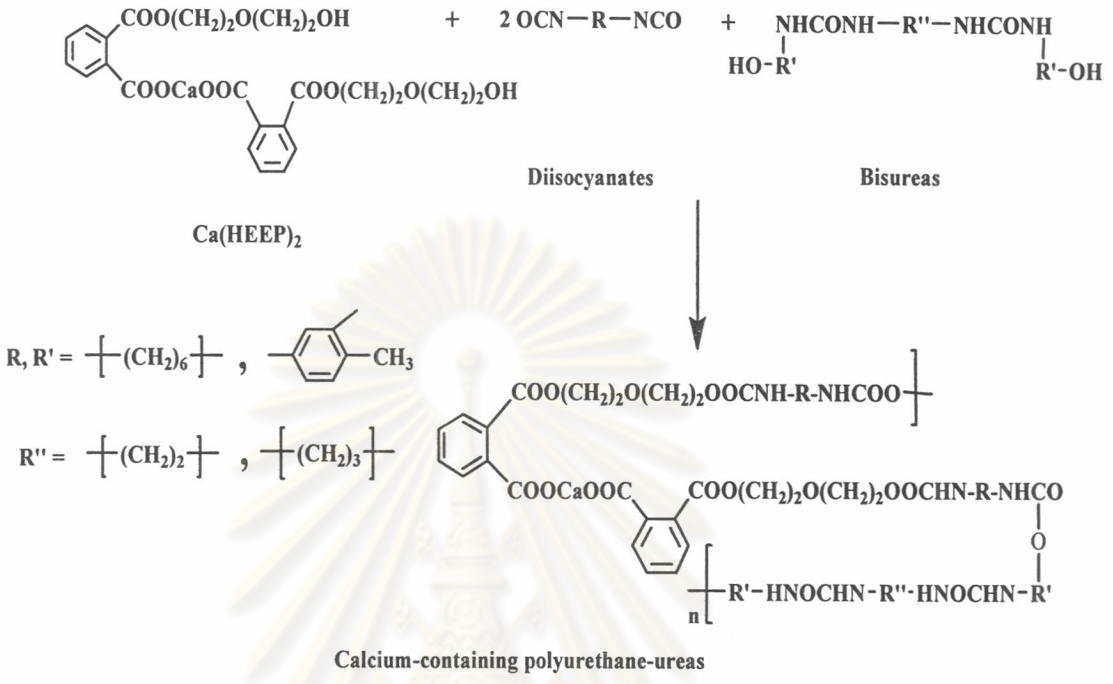
Jayakumar et al. [19] synthesized zinc-containing polyurethane-ureas by the reaction of HMDI or TDI with 1:1 mixture of zinc salt of mono(hydroxyethoxyethyl)phthalate [$Zn(HEEP)_2$] and each of the bisureas such as hexamethylene *bis* (ω, *N*-hydroxyethyl-urea) [HBHEU], toluene *bis* (ω, *N*-hydroxyethyl-urea) [TBHEU], hexamethylene *bis* (ω, *N*-hydroxypropyurea) [HBHPU] and toluene *bis* (ω, *N*-hydroxypropyurea) [TBHPU] (Scheme 2.8).



Scheme 2.8 Synthesis of zinc-containing polyurethane-ureas

Thermal properties showed that the IDT values are found between 233 ° and 272 °C. It was observed TDI–based polymers showed higher IDT than HMDI-based polymers. This may be due to the presence of stiff phenylene ring in the main chin. It was found that 50% weight loss occurred between 328 ° and 334 °C for HMDI-based polymers. In the case of TDI-based polymers, 50% weight loss occurred between 335° and 352 °C. These polymers were soluble in DMF, DMSO and DMAc.

They also synthesized calcium-containing polyurethane-ureas [20] by reacting HMDI or TDI with 1:1 mixtures of calcium salt of mono(hydroxyethoxyethyl)phthalate [$Ca(HEEP)_2$] and different bisureas (Scheme 2.9).

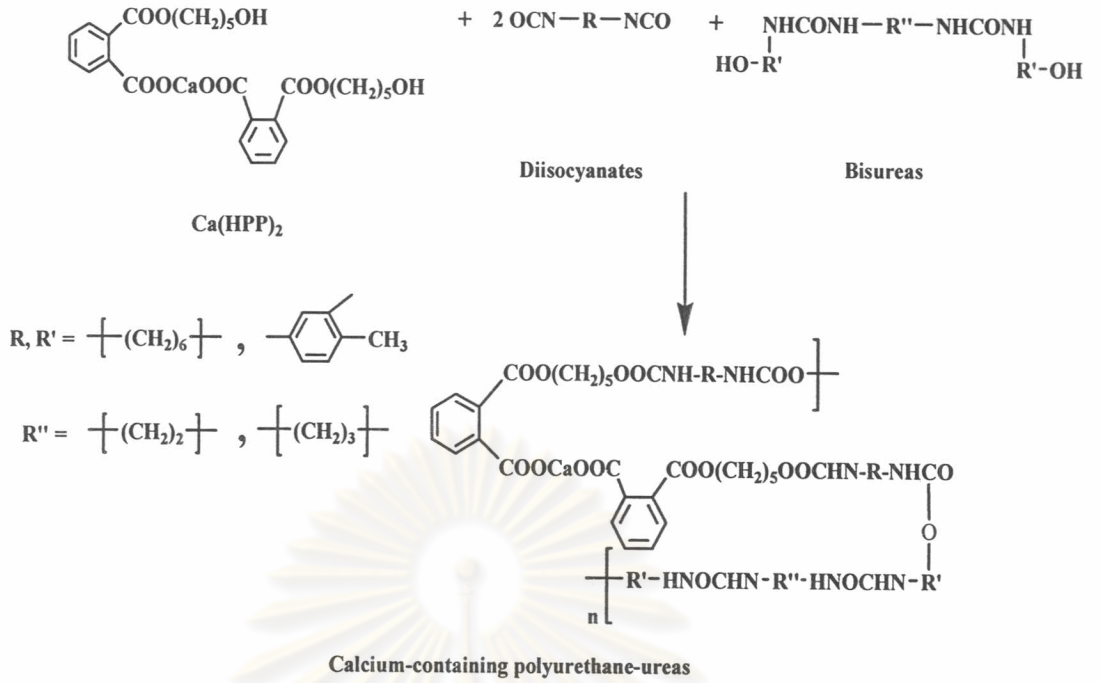


Scheme 2.9 Synthesis of calcium-containing polyurethane-ureas

The results of thermal properties of polymers are similar to that the thermal result of the former research work. That is, the IDT values were between 183 ° and 228 °C, the thermal stability of the TDI-based polymers were higher than that of HMDI-based polymers.

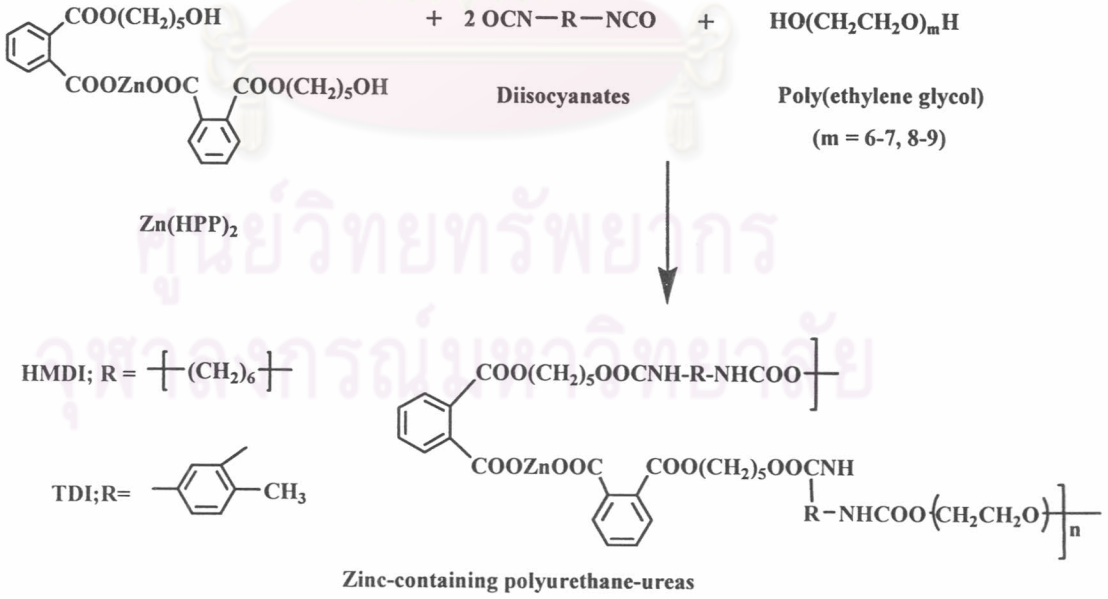
The observation from two research works describe above is that $Zn(HEEP)_2$ containing polyurethane-ureas show higher IDT than $Ca(HEEP)_2$ containing polyurethane-ureas. In addition, $Ca(HEEP)_2$ containing polyurethane-ureas have T_g and the temperature at 50 % weight loss higher than $Zn(HEEP)_2$ containing polyurethane-ureas.

In addition [21], Jayakuma and Nanjandan synthesized calcium-containing polyurethane-ureas by reacting HMDI or TDI with 1:1 mixtures of calcium salt of mono(hydroxypentyl)phthalate [$Ca(HPP)_2$] (Scheme 2.10) and each of the bisureas.



Scheme 2.10 Synthesis of calcium containing polyurethane-ureas

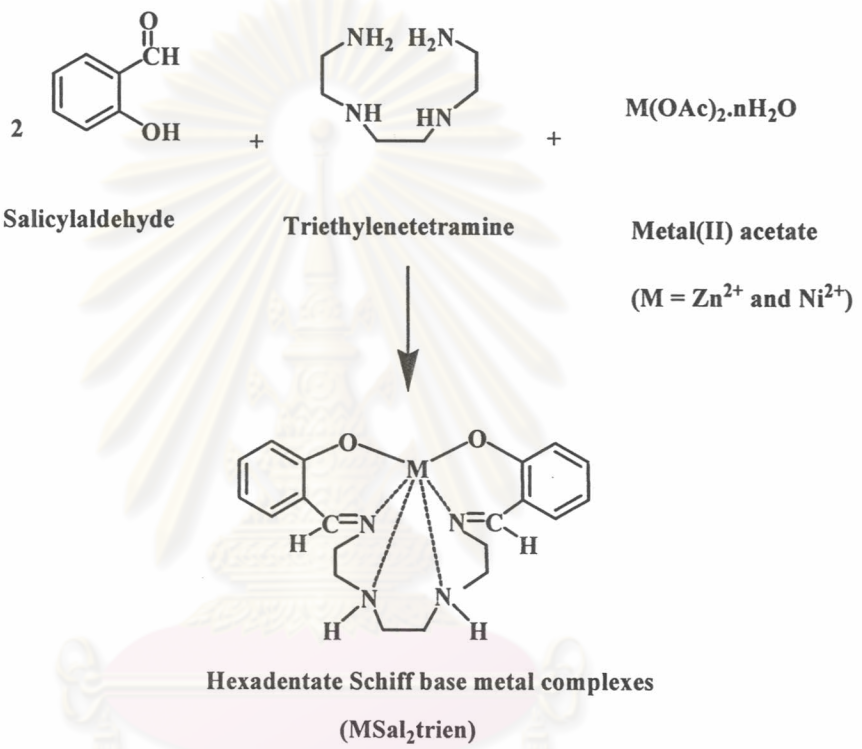
Moreover, they synthesized zinc-containing polyurethane-ethers [22] by the reaction of HMDI or TDI with a mixtures of zinc salt of mono (hydroxypentyl)phthalate [$Zn(HPP)_2$] and poly(ethylene glycol) (PEG_{300} or PEG_{400}) (Scheme 2.11).



Scheme 2.11 Synthesis of zinc-containing polyurethane-ethers

The result showed that the TDI-based polymers showed higher IDT than the HMDI-based polymers. These polymers were soluble in DMF, DMSO and DMAc.

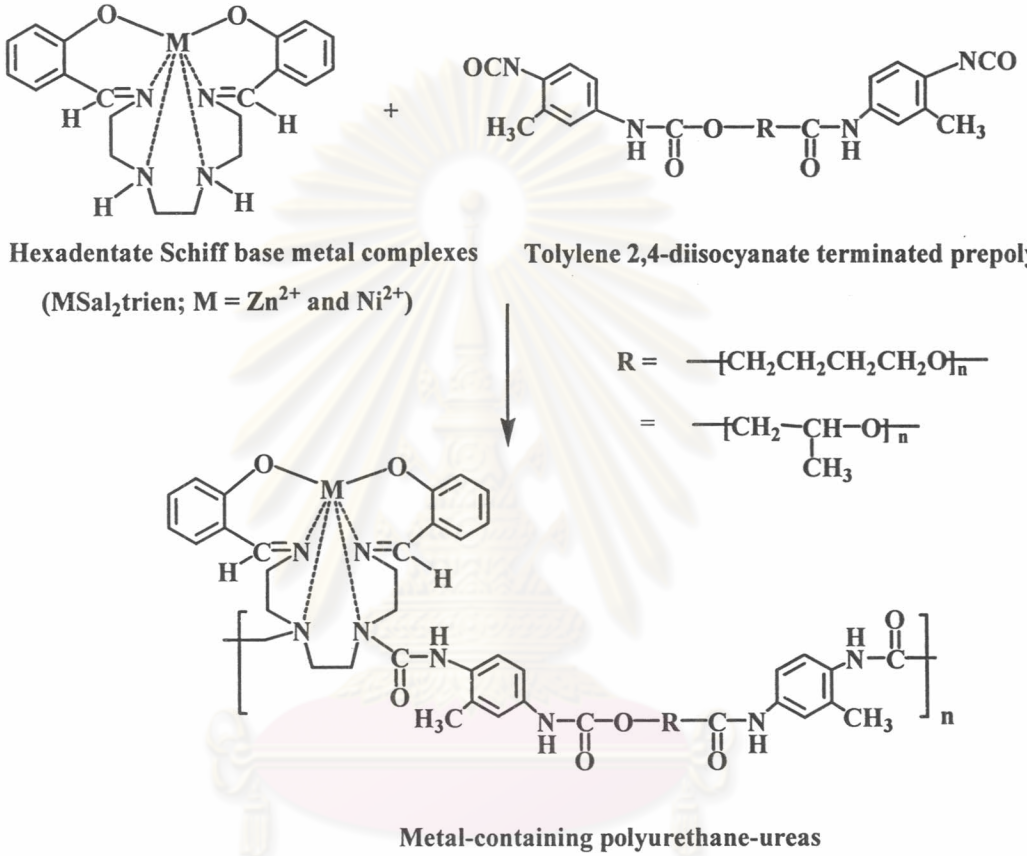
From the previous work in our research group [23], metal-containing polyurethane-ureas were synthesised by the reaction between hexadentate Schiff base metal complexes [$MSal_2trien$] and isocyanate terminated prepolymers. The metal complexes were prepared from the reaction between salicylaldehyde, triethylenetetramine and metal acetate as shown in Scheme 2.12.



Scheme 2.12 Synthesis of hexadentate Schiff base metal complexes

Ni- and Zn-containing polyurethane-ureas were prepared from isocyanate-terminated prepolymers and $NiSal_2trien$ or $ZnSal_2trien$ as shown in Scheme 2.13

The result of thermal studies was showed that IDT values were found between 187 ° and 237 °C. The weight of residue at 600 °C was between 14 and 21%. The polymers were soluble in polar solvent such as DMF and DMSO.

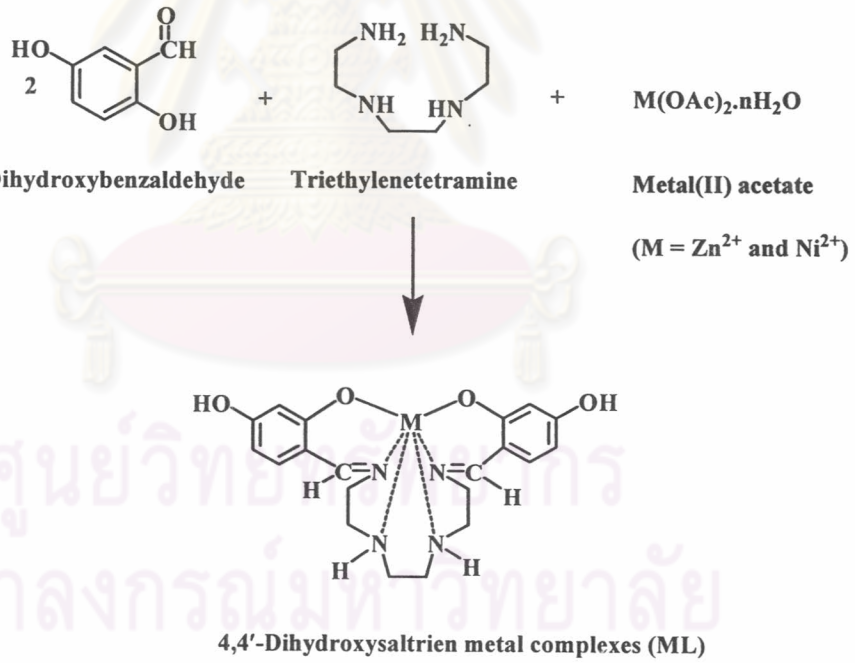


Scheme 2.13 Synthesis of metal-containing polyurethane-ureas from hexadentate Schiff base metal complexes and prepolymers

2.4 Objectives and scope of the research

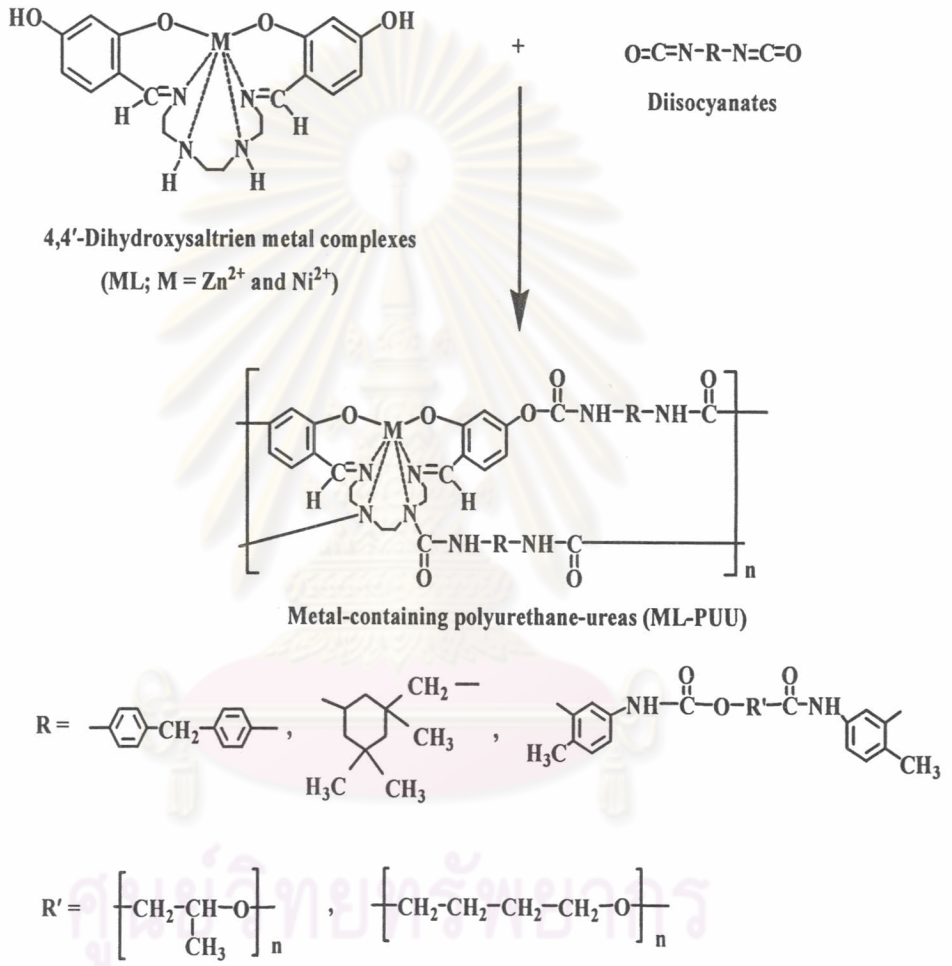
In this work, attempts were made to synthesize hexadentate Schiff base metal complexes, namely 4,4′-dihydroxysaltrien metal complexes (ML), and used these complexes in the synthesis of metal-containing polyurethane-ureas and metal-containing. The metal complexes contain two amino groups and two hydroxyl groups that can undergo polymerization reaction with diisocyanate, to give metal-containing polyurethane-ureas which have different structure from polyurethane-ureas containing $MSal_2trien$ in the polymer backbone (Schme 2.13). It was expected that the new metal-containing polyurethane-ureas would have better a good thermal stability than the former metal-containing polyurethane-ureas.

In the first step, two ML's were synthesized from the reaction between 2,4-dihydroxybenzaldehyde, triethylenetetramine and metal acetates ($M=Ni^{2+}$ and Zn^{2+}) as shown in Scheme 2.14 [24].



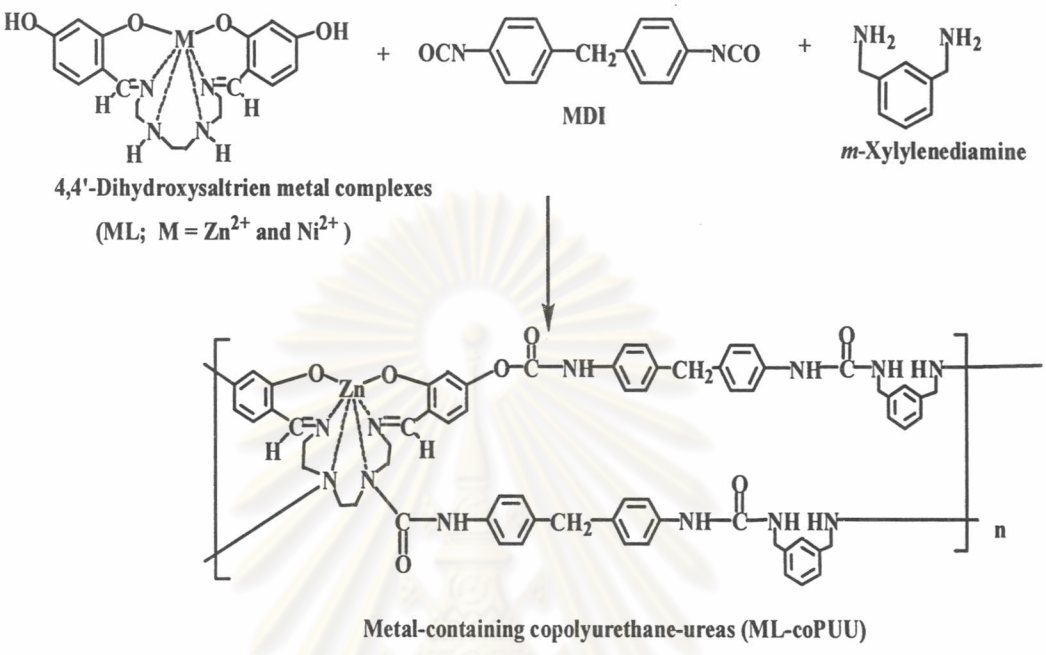
Scheme 2.14 Synthesis of 4,4′-dihydroxysaltrien metal complexes

In the next step, metal-containing polyurethane-ureas (ML-PUU) were synthesized from the reaction between ML and different diisocyanates, including 4,4′-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPD), tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer, molecular weight 1000 (PP1000), tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer, molecular weight 900 (PB900) as shown in Scheme 2.15.



Scheme 2.15 Synthesis of metal-containing polyurethane-ureas from 4,4′-dihydroxysaltrien metal complexes and diisocyanates

Then, metal-containing copolyurethane-ureas (ML-coPUU) were synthesized from the reaction between ML, 4,4′-methylene*bis* (phenyl isocyanate) (MDI), and *m*-xylylenediamine as shown in Scheme 2.16.



Scheme 2.16 Preparation of metal-containing copolyurethane-ureas

Finally, metal-containing polyurethane-ureas and copolyurethane-ureas were characterized by FT-IR, ^{1}H NMR, elemental analysis, solubility and viscosity. Thermal stability of the polymers was investigated by TGA. Flammability was studied by measuring limiting oxygen index value (LOI).