CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polyurethanes

The general structure or bond that forms the basis of this chemistry is the urethane linkage [1] shown in Figure 2.1.

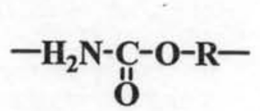
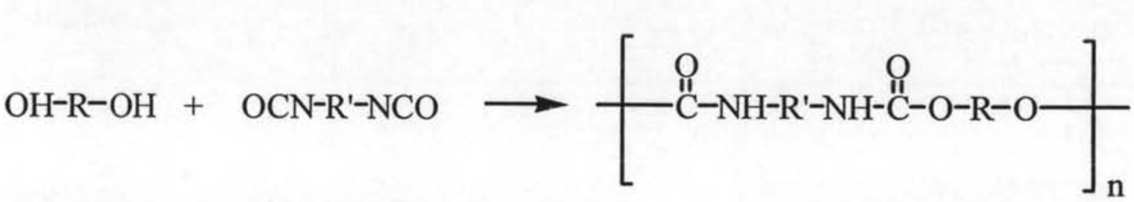


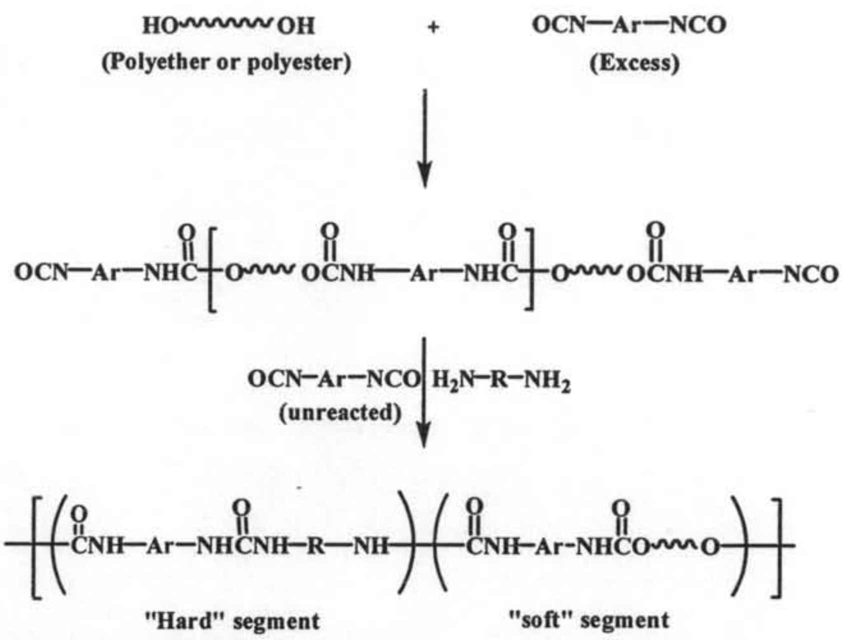
Figure 2.1 Urethane linkage

A urethane group is formed by the chemical reaction between an alcohol and an isocyanate. Polyurethanes [2-6] result from the reaction between alcohols with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate). This type of polymerization is called addition polymerization (Scheme 2.1). Polyurethane elastomers consist of elastomeric block copolymers containing alternating "hard" and "soft" segments. It has both urea and urethane linkages in its backbone (Scheme 2.2).



Polyol **Diisocyanate** **Polyurethane**

Scheme 2.1 Polyurethane addition reaction



Scheme 2.2 Synthesis of polyurethane elastomers

Polyurethanes were discovered by Otto Bayer *et al.* in the 1930s. Since then, they have found multitude of applications. Polyurethanes are therefore a whole family of specialty polymers that cover a wide range of physical and mechanical properties. The growth of science and technology of polyurethanes leads to the development of new materials with more desirable properties. Such materials include metal–containing polyurethanes [7], poly(urethane-urea)s [8], poly(urethane-ester)s [9], poly(urethane-ether)s [10], poly(azomethine urethane)s [11] and poly (urethane-imide)s [12] with different structural units combining the properties of enhanced thermal stability, fire retardancy, flexible and solubility.

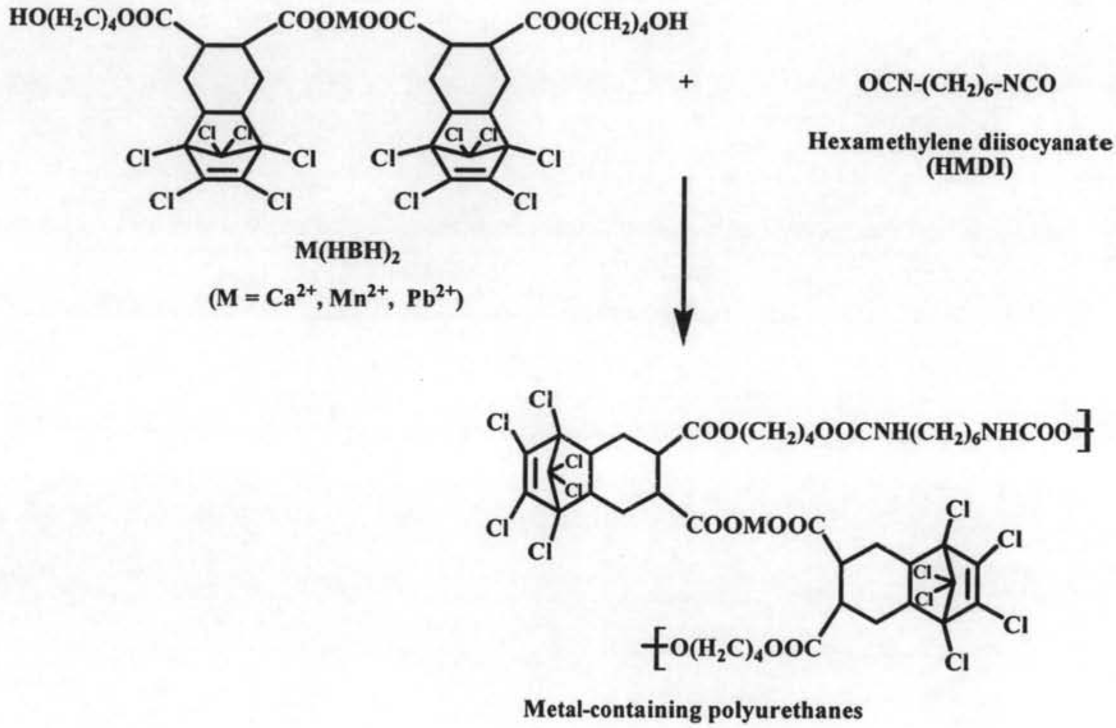
2.2 Metal-containing polymers

Metal-containing polymers are an important class of thermally stable or heat resistant polymers. This excellent property is widely investigated [13-16]. The introduction of metal into urethane-ureas backbone results in a considerable increase in thermal properties of polymer affected by the presence of metallic ions [17].

2.3 Literature review

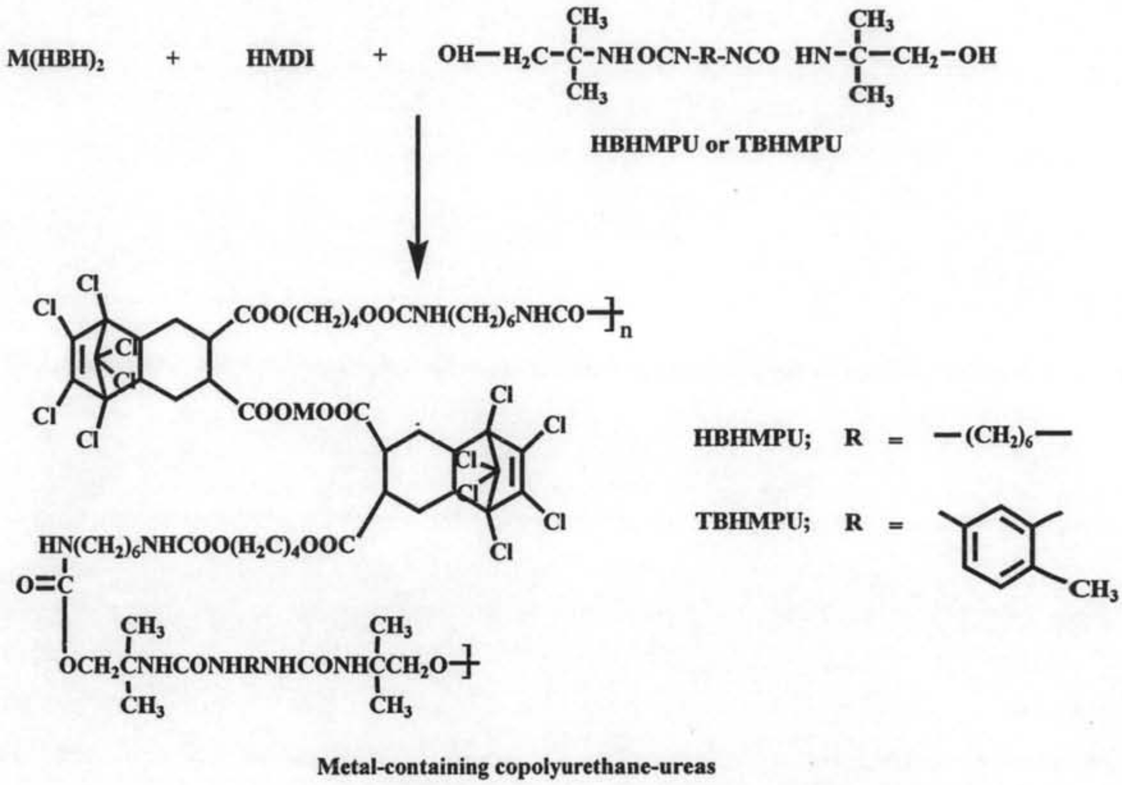
A number of research work concerning the preparation and physical properties of metal-containing polyureas, polyurethanes, polyurethane-ureas and other polymers containing metal in the polymer backbone have been reported as follows:

Nanjundan and coworkers [18] synthesized and characterized metal-containing polyurethanes and copolyurethane-ureas. Metal-containing polyurethanes were synthesized by the polyaddition reaction of hexamethylene diisocyanate (HMDI) with the divalent metal salts of mono(hydroxybutyl)hexolate [$M(HBH)_2$, M = Ca^{2+}, Mn^{2+}, Pb^{2+}] as shown in Scheme 2.3.



Scheme 2.3 Synthesis of metal-containing polyurethanes from $M(HBH)_2$ and HMDI

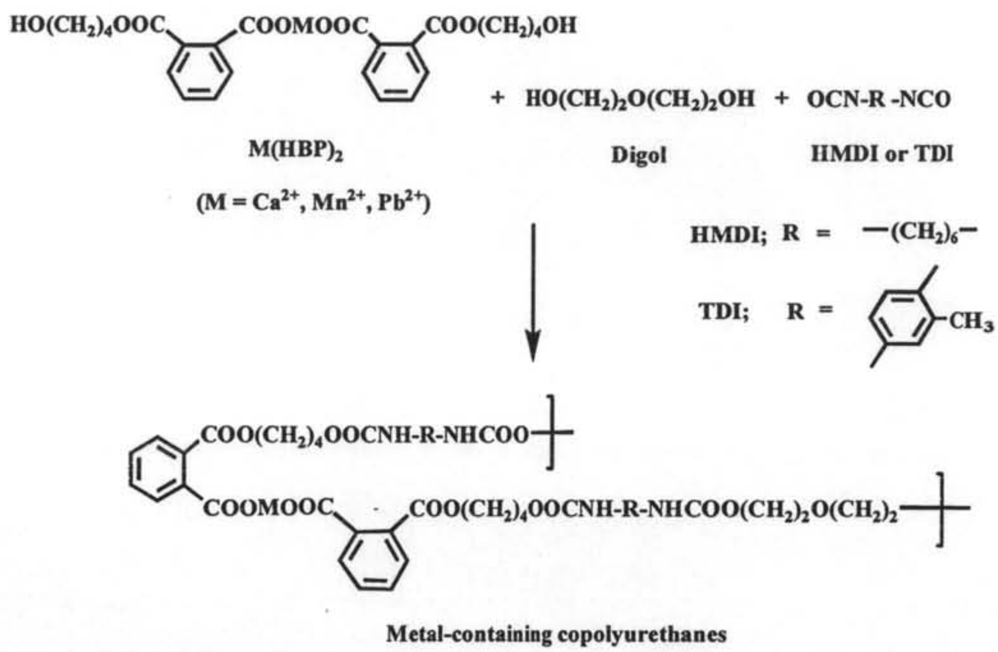
In addition, they synthesized copolyurethane-ureas by reacting HMDI with 1:1 mixture of $M(HBH)_2$ and hexamethylene bis[*N*′-(1-hydroxy-2-methyl-prop-2-yl)urea] (HBHMPU) or toluene 2,4-bis[*N*′-(1-hydroxy-2-methyl-prop-2-yl)urea] (TBHMPU) as shown in Scheme 2.4.



Scheme 2.4 Synthesis of metal-containing copolyurethane-ureas from $M(HBH)_2$, HMDI and HBHMPU or TBHMPU

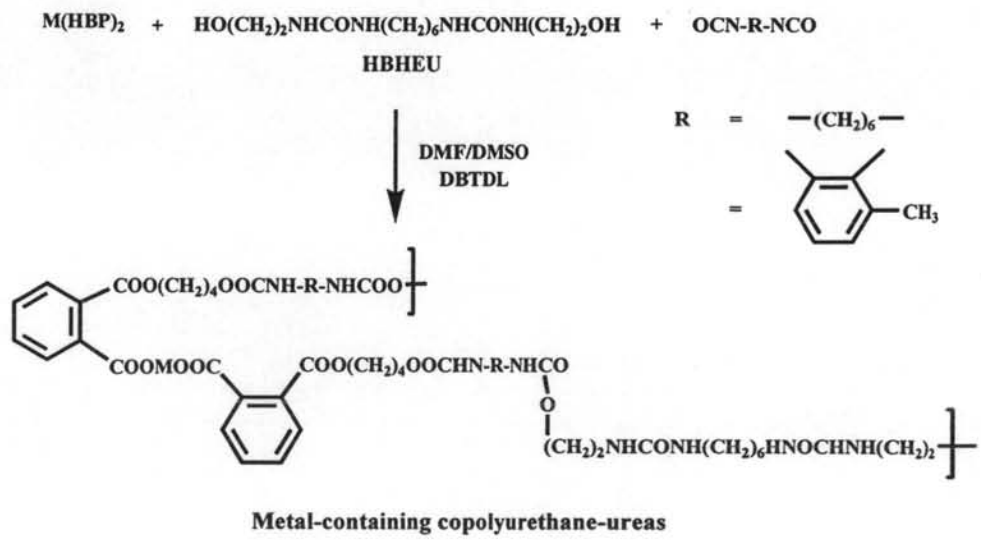
Thermal stability of metal-containing polyurethanes was higher than that of metal-containing copolyurethane-ureas. Among the copolyurethane-ureas, TBHMPU-based polyurethane-ureas were slightly more stable than HBHMPU-based copolyurethane-ureas due to the presence of aromatic ring in the polymer chain. Flame retardancy of polyurethanes was higher than that of copolyurethane-ureas.

Another work of Nanjundan and coworkers [19] also involved the synthesis and characterization of metal-containing copolyurethanes and copolyurethane-ureas by polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with 1:1 mixtures of divalent metal salts of mono (hydroxybutyl)phthalate [$M(HBP)_2$, M = Ca^{2+}, Mn^{2+} and Pb^{2+}] and digol as shown in Scheme 2.5.



Scheme 2.5 Synthesis of metal-containing copolyurethanes from $M(HBP)_2$, digol and HMDI or TDI

Furthermore, they synthesized copolyurethane-ureas by reacting the diisocyanate with 1:1 mixture 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 2.6.

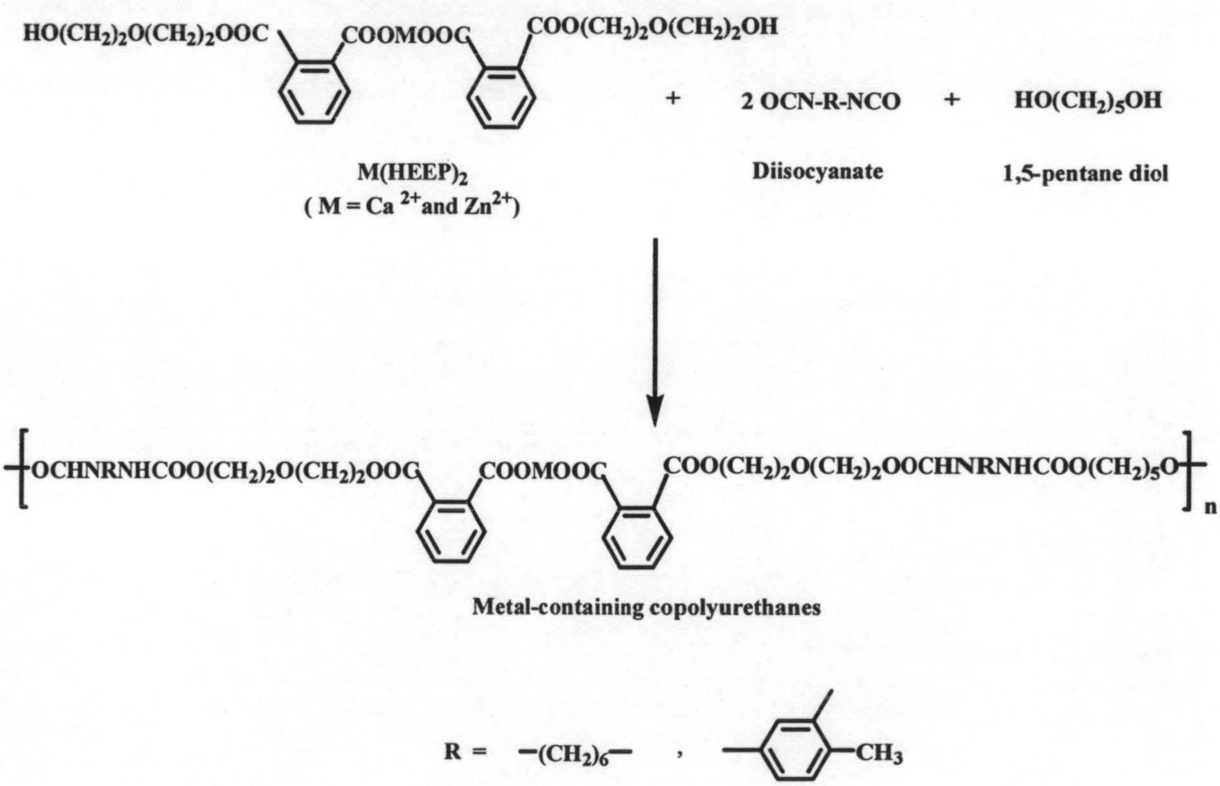


Scheme 2.6 Synthesis of metal-containing copolyurethane-ureas from $M(HBP)_2$, HBHEU and HMDI or TDI

It was found that the initial decomposition temperatures (IDT) of copolymers are found between 150-250 °C. The metal-containing copolyurethanes have higher IDT than copolyurethane-ureas. It may be explained based on probability that the copolyurethane prepared were found to contain less metal than the prepared copolyurethane-ureas. Thermal stability of the metal-containing polymers can be ordered as Pb>Mn>Ca. These polymers were soluble in DMF and DMSO.

Jayakumar and Nanjundan [20-21] synthesized metal-containing copolyurethanes by the polyaddition reaction of diisocyanate with divalent metal salts of mono (hydroxyethoxyethyl)phthalate [$M(HEEP)_2$] or mono(hydroxypentyl)phthalate [$M(HPP)_2$] and diol. Examples of the metal-containing copolyurethanes are as follows:

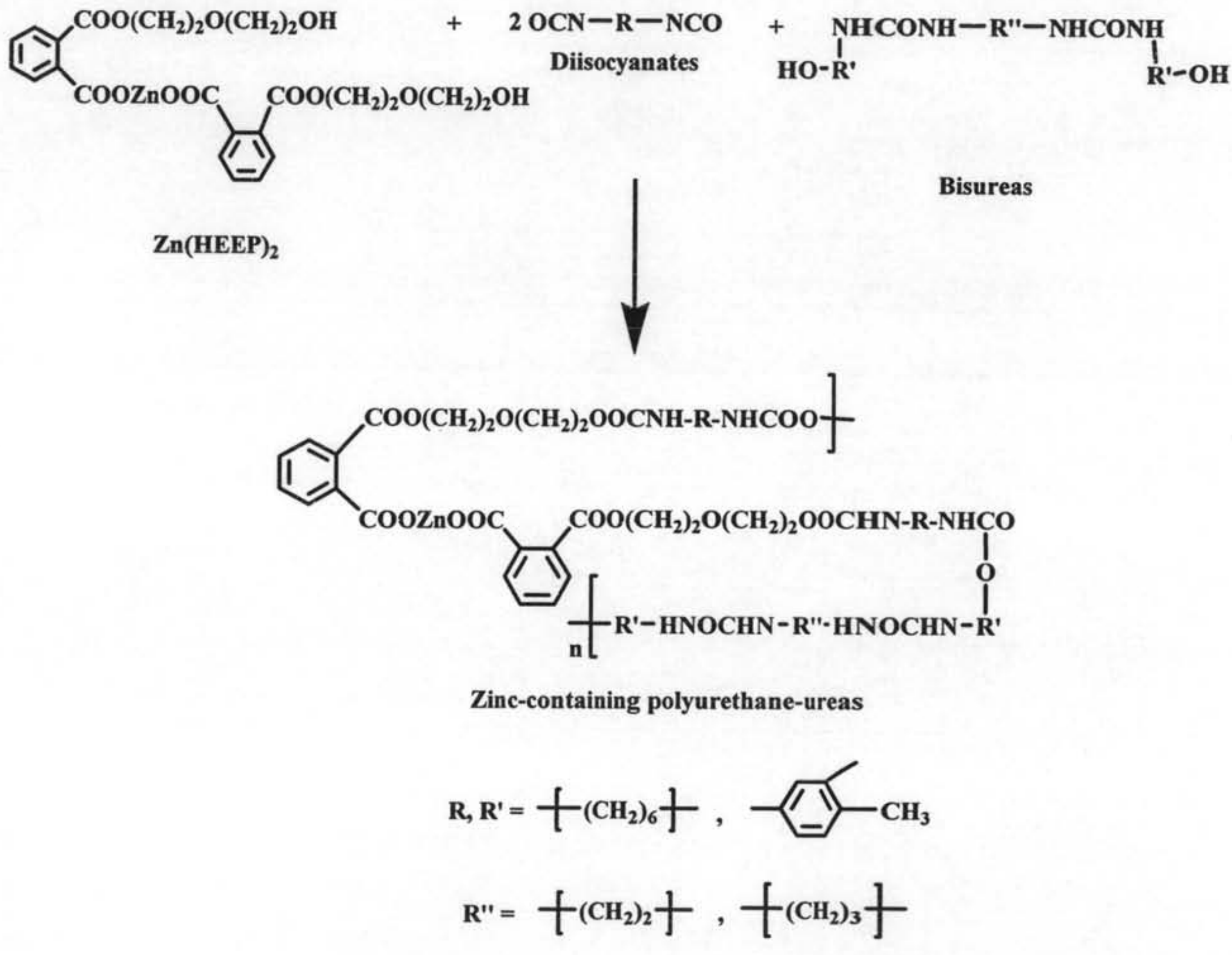
Metal-containing copolyurethanes were synthesized by the polyaddition reaction of hexamethylene diisocyanate or tolylene 2,4-diisocyanate with 1:1 mixture of [$M(HEEP)_2$, M = Ca^{2+} and Zn^{2+}] and 1,5-pentane diol using DBTDL as a catalyst (Scheme 2.7).



Schemes 2.7 Synthesis of metal-containing copolyurethanes from $M(HEEP)_2$, diisocyanate and 1,5-pentane diol

The result showed that the initial decomposition temperatures (IDT) of the copolyurethanes were found to be in the range of 188-207 °C. The TDI-based copolymers showed higher IDT than the HMDI-based copolymers. The blank polymers showed slightly higher IDT than metal-containing copolymers. These polymers were soluble in DMF, DMSO and DMAc.

Moreover, they synthesized metal-containing copolyurethane-ureas [22-24] by the reaction of HMDI or TDI with 1:1 metal salts of mono (hydroxyethoxyethyl)phthalate $[M(HEEP)_2]$ or mono(hydroxypentyl)phthalate $[M(HPP)_2]$ and each of the bisureas. Example of such work is shown in Scheme 2.8.

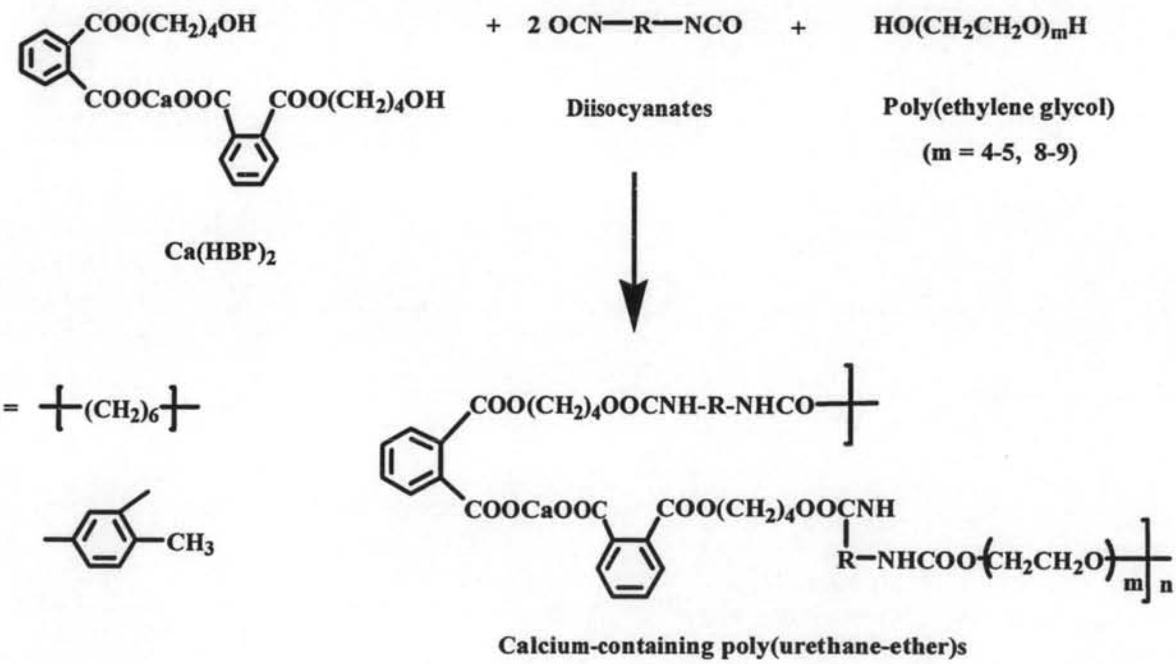


Scheme 2.8 Synthesis of zinc-containing copolyurethane-ureas from $Zn(HEEP)_2$, diisocyanates and bisureas

The result of thermal studies showed that the IDT values of the polymers were found between 233-272 °C. It was observed TDI-based polymers showed higher IDT than HMDI-based polymers. Thermal stability of the TDI-based polymers was higher than that of HMDI-based polymers. The IDT of polymers was increased by introducing bisureas into the polymers, this may due to the presence of a higher degree of hydrogen bonding in the polyurethane-ureas.

In addition [25-27], they synthesized Ca and Zn-containing poly(urethane-ether)s. Example of the metal-containing poly(urethane-ether)s is as follows:

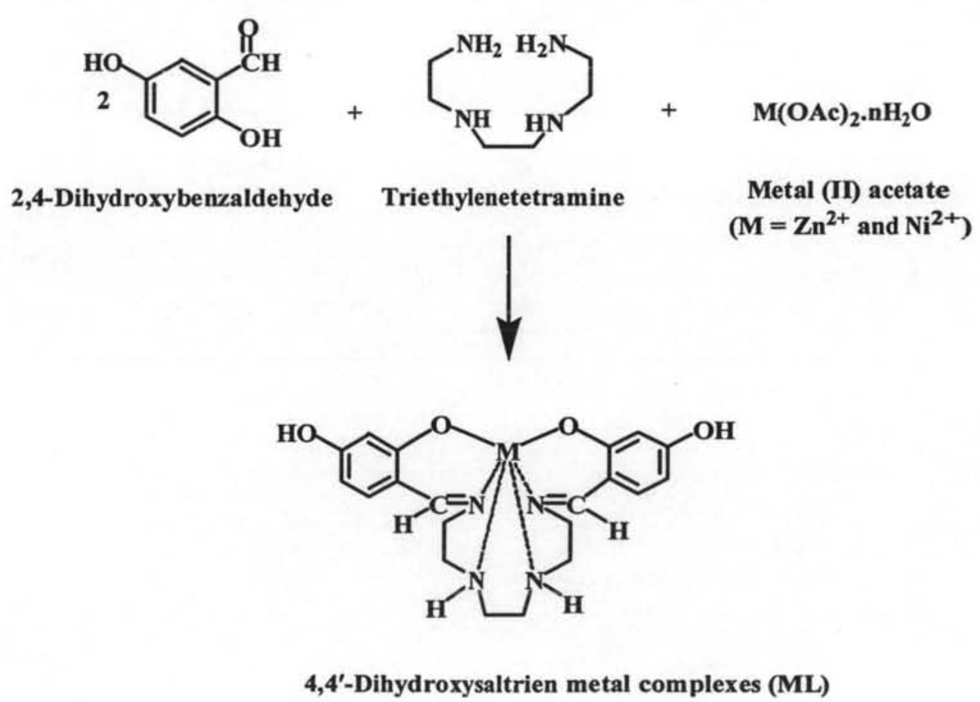
Calcium-containing poly(urethane-ether)s were synthesized by the reaction of calcium salt of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$] with polyethylene glycol (PEG_{200} or PEG_{400}) and diisocyanates (HMDI or TDI) (Scheme 2.9) using the mole ratios of $Ca(HBP)_2$:PEG:diisocyanate as 3:1:4, 2:2:4 and 1:3:4 to study the effect of calcium content on the properties of the copolymers. Blank poly(urethane-ether)s without a calcium-containing ionic diol were also prepared by the reaction of PEG_{200} or PEG_{400} with HMDI or TDI.



Scheme 2.9 Synthesis of calcium-containing poly(urethane-ether)s from $Ca(HBP)_2$, diisocyanates and poly(ethylene glycol)

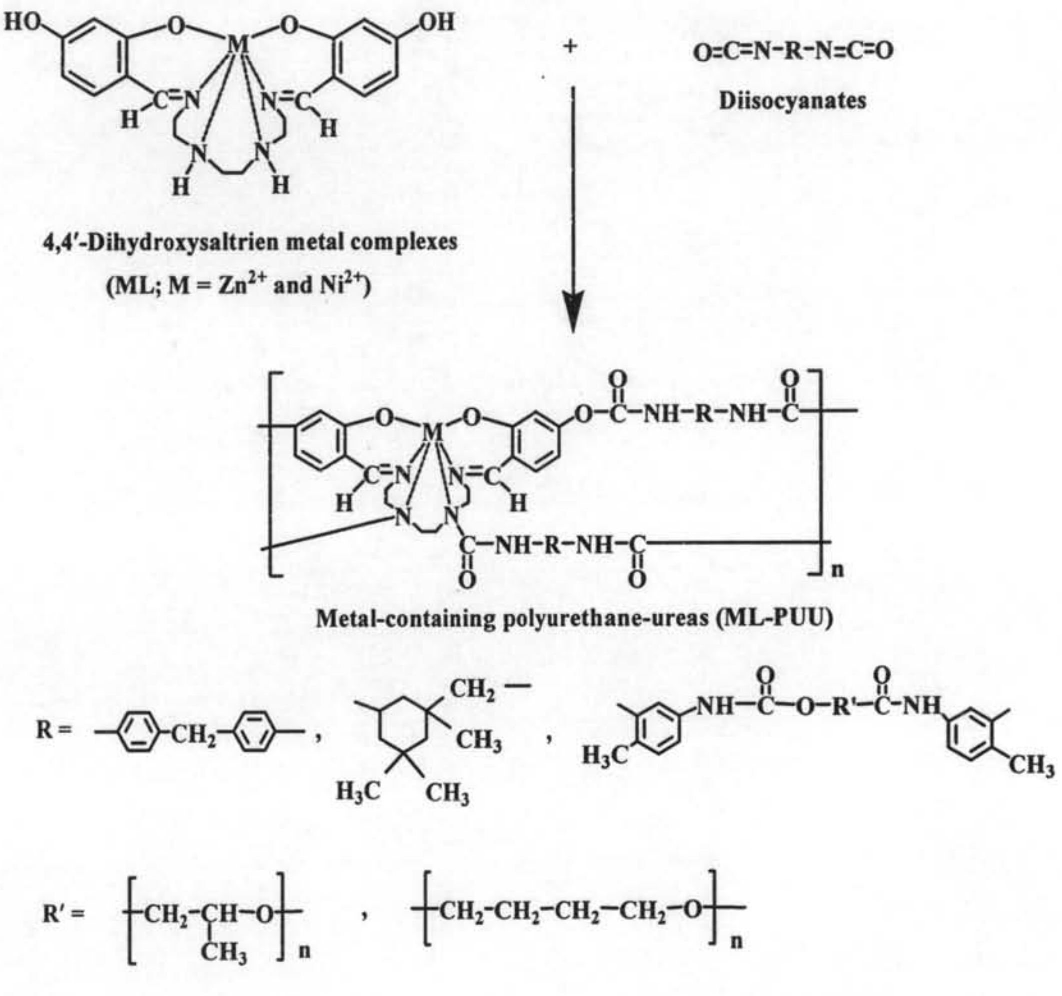
The result showed that the IDT of poly(urethane-ether)s found between 179-258°C. The IDT of the poly(urethane-ether)s decreased with increasing amount of calcium into the polymer but the rate of decomposition of these polymers decreased with increasing amount of calcium. This may be due to the fact that the metal catalyses the first stages decomposition and retards the further stages of decompositions. The blank poly(urethane-ether)s showed slightly higher IDT than calcium-containing poly(urethane-ether)s, but their rate of decomposition were higher than that of the calcium-containing poly(urethane-ether)s. The TDI-based poly(urethane-ether)s showed higher decomposition temperature than HMDI-based poly(urethane-ether)s due to the presence of stiff phenyl group in the backbone of the polymer. X-ray diffraction pattern of the polymers showed that the HMDI based polymers were partially crystalline and TDI based polymers were amorphous in nature.

From the previous works in our research group [28], 4,4′-dihydroxysaltrien metal complexes (ML) were synthesized from the reaction between 2,4-dihydroxybenzal dehyde, triethylenetetramine and metal acetates where the metals employed were Zn^{2+} and Ni^{2+} (Scheme 2.10).



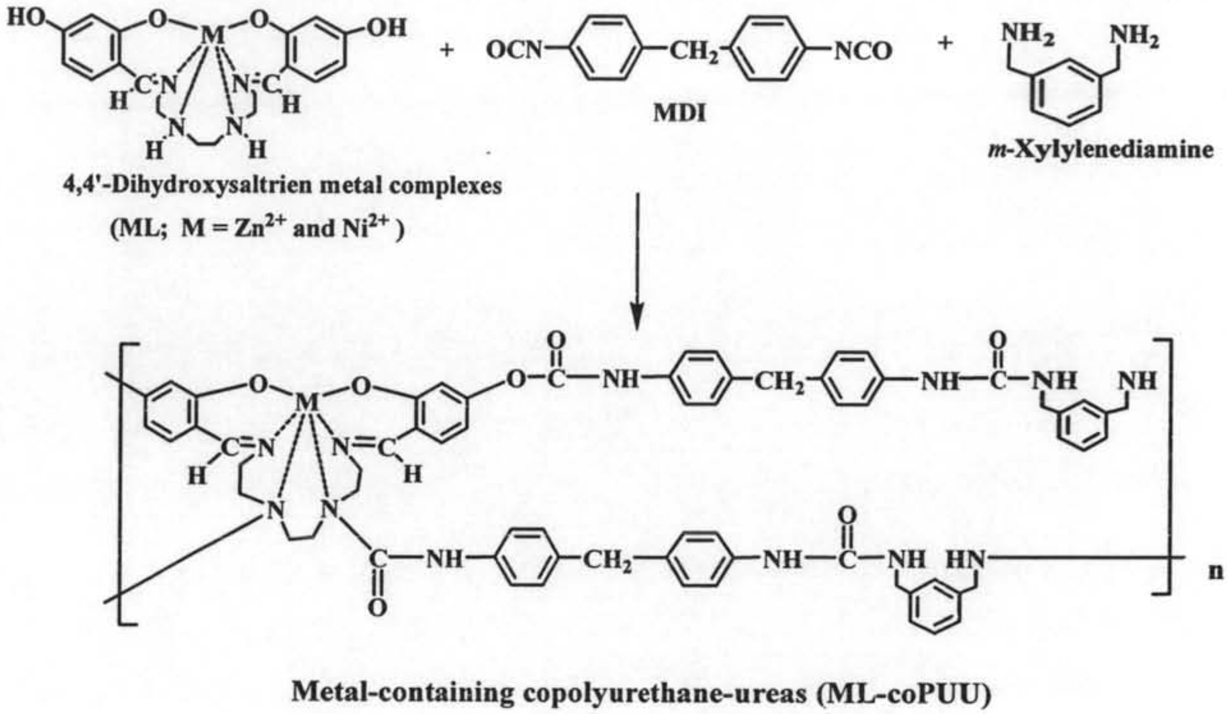
Scheme 2.10 Synthesis of 4,4′-dihydroxysaltrien metal complexes

It was found that 4,4′-dihydroxysaltrien metal complexes based on zinc and nickel had good thermal properties and stable in air. Then, metal-containing polyurethane-ureas (ML-PUUs) [29] were synthesized from the reaction between (ML, M = Zn^{2+} and Ni^{2+}) 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 2.11.



Scheme 2.11 Synthesis of metal-containing polyurethane-ureas from 4,4′-dihydroxysaltrien metal complexes and diisocyanates

The results showed that the MDI-based polyurethane-ureas had the most thermally stable polymers when compared to the polymer obtained from other diisocyanates. Then, the metal-containing copolyurethane-urea (ML-coPUU) were synthesized from the reaction between ML, 4,4′-diphenylmethane diisocyanate (MDI) and *m*-xylylenediamine as shown in Scheme 2.12.



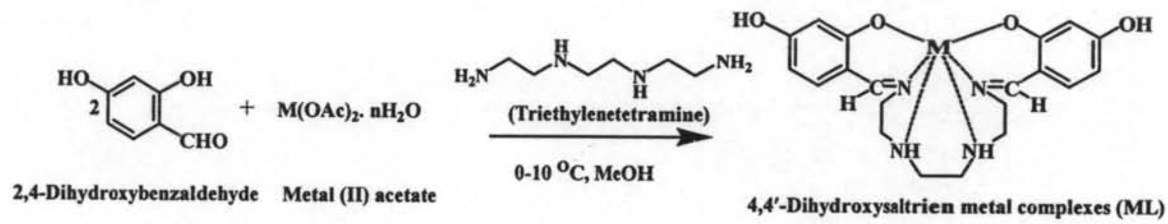
Scheme 2.12 Preparation of metal-containing copolyurethane-ureas

The result showed that the addition of *m*-xylylenediamine into the polymer structure could improve IDT of polymers. It was found that the IDT of metal-containing copolyurethane-ureas occurred in the temperature range 210-270 °C. The metal-containing copolyurethane-ureas obtained from ML with MDI and *m*-xylylenediamine showed good thermal stability.

2.4 Objectives and scope of the research

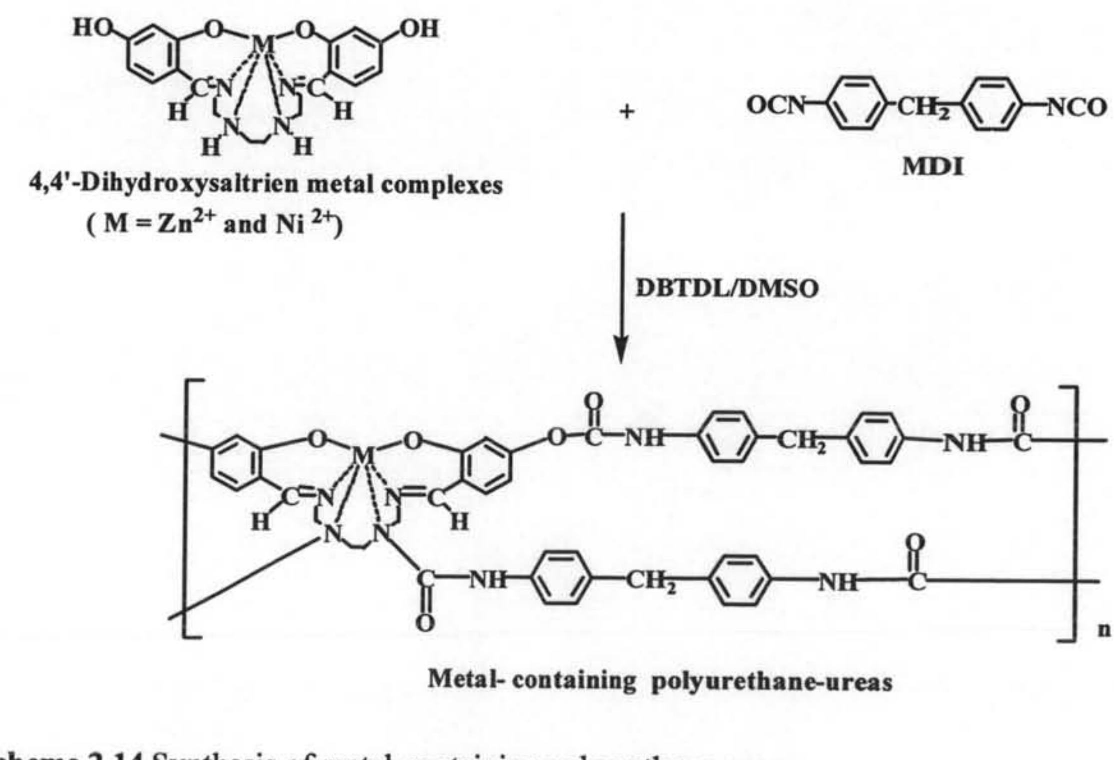
The target of this research is to synthesize metal-containing copolyurethane-ureas based on 4,4′-dihydroxysaltrien metal complexes (ML, M = Zn^{2+} and Ni^{2+}) with MDI and various diamines or dialcohols at different molar ratios. It was expected that these copolyurethane-ureas would show good thermal stability, good solubility and can be utilized at high temperature application.

In the first step, ML were synthesized from the reaction between 2,4-dihydroxybenzaldehyde, triethylenetetramine and metal (II) acetate (M = Zn^{2+} and Ni^{2+}) [28] (Scheme 2.13).



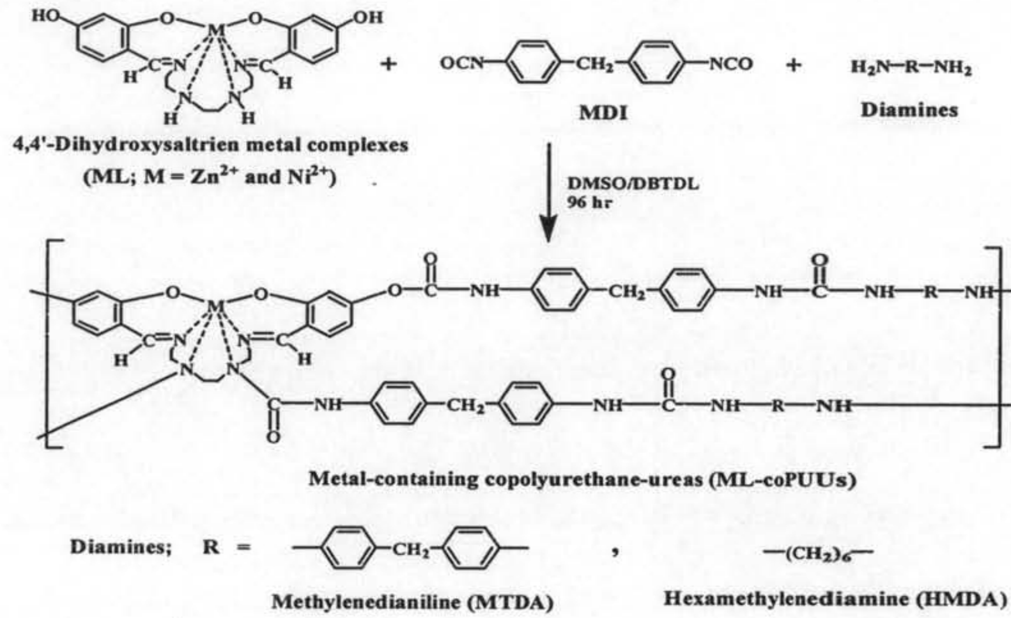
Scheme 2.13 Synthesis of 4,4′-dihydroxysaltrien metal complexes (ML)

In the next step, metal-containing polyurethane-ureas [29] were synthesized from the reaction between ML with MDI as shown in Scheme 2.14.

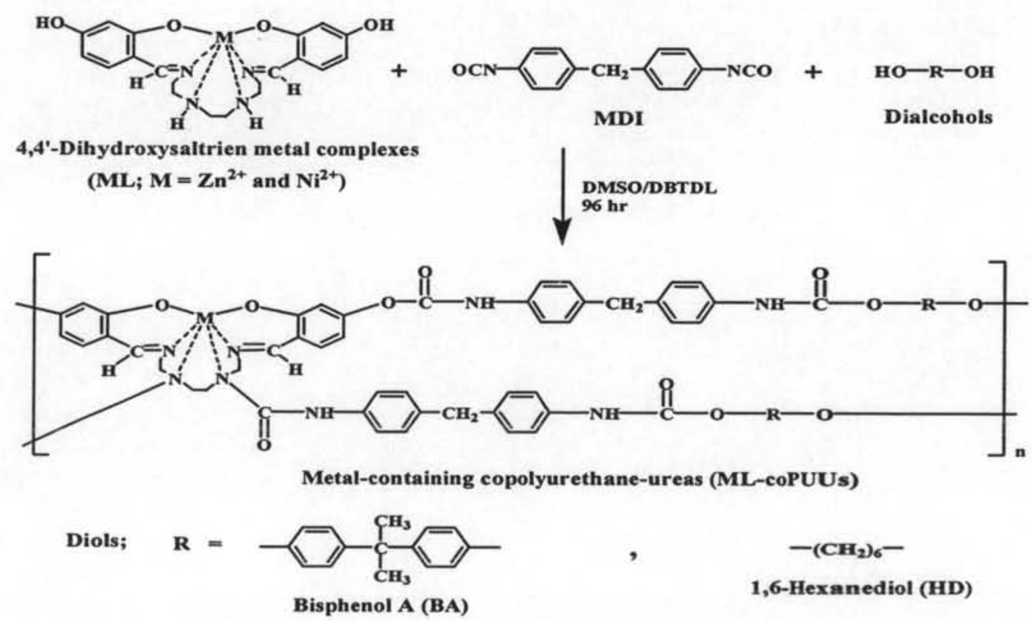


Scheme 2.14 Synthesis of metal-containing polyurethane-ureas

Then, metal-containing copolyurethane-ureas (ML-coPUUs) were prepared by the reaction between ML with MDI and diamines or dialcohols as shown in Schemes 2.15 and 2.16, respectively. Series of copolyurethane-ureas were synthesized with different compositions by taking the molar ratio of ML:MDI:diamine or dialcohol as 1:2:0, 0.5:3:1.5, 1.0:3:1.0, 1.5:3:0.5.



Scheme 2.15 Synthesis of metal-containing copolyurethane-ureas from ML, MDI and diamines



Scheme 2.16 Synthesis of metal-containing copolyurethane-ureas from ML, MDI and dialcohols

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