CHAPTER I

INTRODUCTION

1.1 Heat-resistant polymers

The investigation of thermally stable polymers or heat-resistant polymers has received great emphasis due to requests for high-performance materials that can be used at high temperature. The applications of heat-resistant polymers are in many areas such as electronic and aerospace industries, *etc.*[1-3]

For a polymer to be considered as thermally stable polymer or heat resistant polymer, it should not decompose below 250°C and should retain its properties at temperature near the decomposition temperature.

A wide variety of metal-containing polymers with good thermal stability has been developed. Metal-containing polyurethane, polyurethane-urea and polyurea are among the metal-containing polymers that have received much interest.

1.2 Metal-containing polyurethanes, polyurethane-ureas and polyureas

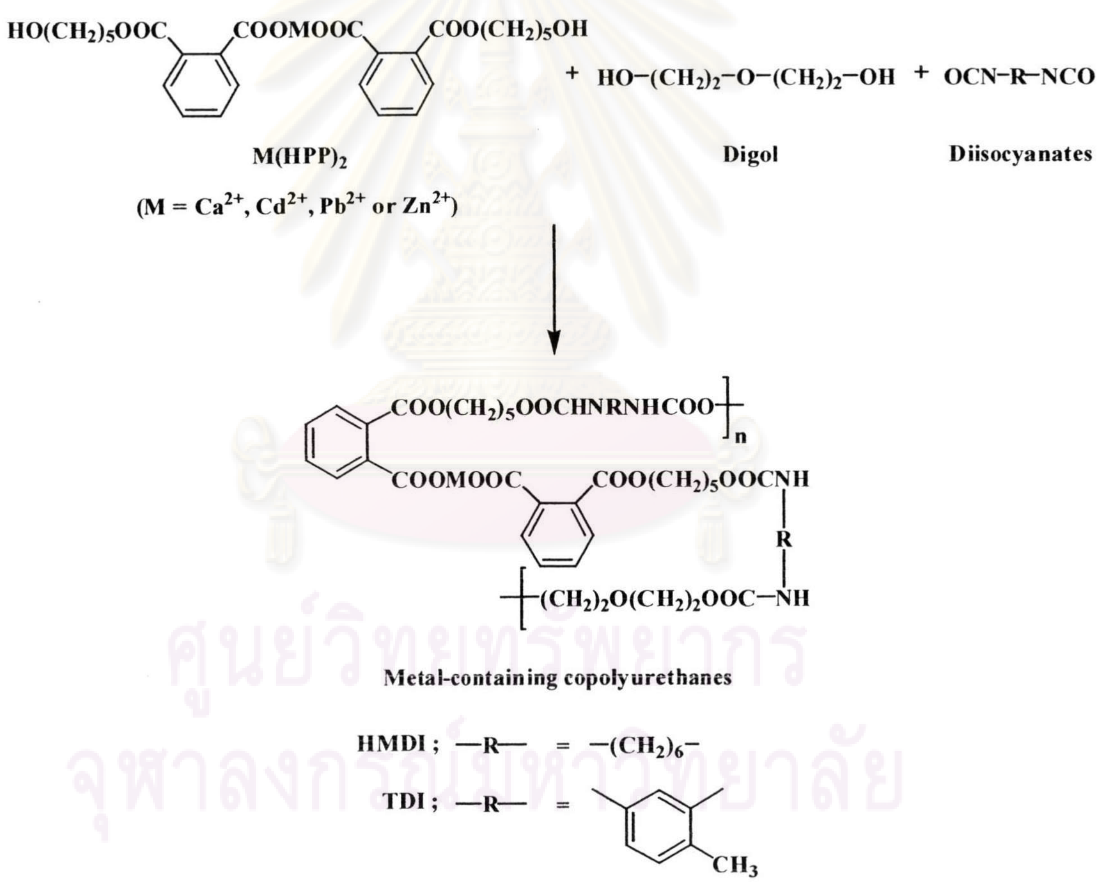
Incorporation of metal into the polymers has led to wide applications such as resins, catalysts, electronics, medicines and textile sizers because the interaction between polymers with coordinating groups and metallic ions gives them the numerous interesting properties such as high strength and thermal stability.

Metal-containing polyurethanes, polyurethane-ureas and polyureas having metal in the backbone result in useful interesting properties such as flame retardancy, high strength, solvent and chemical resistance and high thermal stability. Therefore, metal-containing polyurethanes, polyurethane-ureas and polyureas have been studied and developed for many applications.

1.3 Literature review

A number of metal-containing polyurethanes, polyurethane-ureas and polyureas have been studied.[4-18] Examples of the preparation, characterization and physical properties of such polymers are reported as follows:

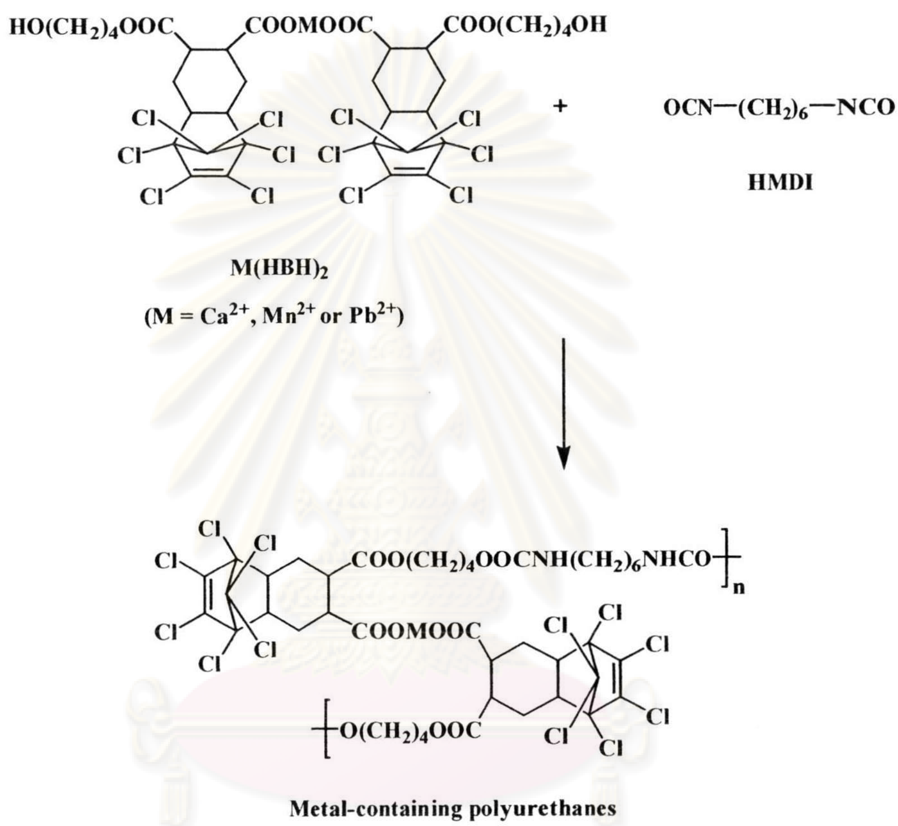
Nanjundan and coworkers[4] synthesized metal-containing copolyurethanes by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or 2,4-toluene diisocyanate (TDI) with 1:1 mixtures of divalent metal salts of mono(hydroxypentyl)phthalate [M(HPP)$_2$, where M = Ca^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}] and digol (Scheme 1.1).



Scheme 1.1 Synthesis of metal-containing copolyurethanes from M(HPP)$_2$, digol and diisocyanates

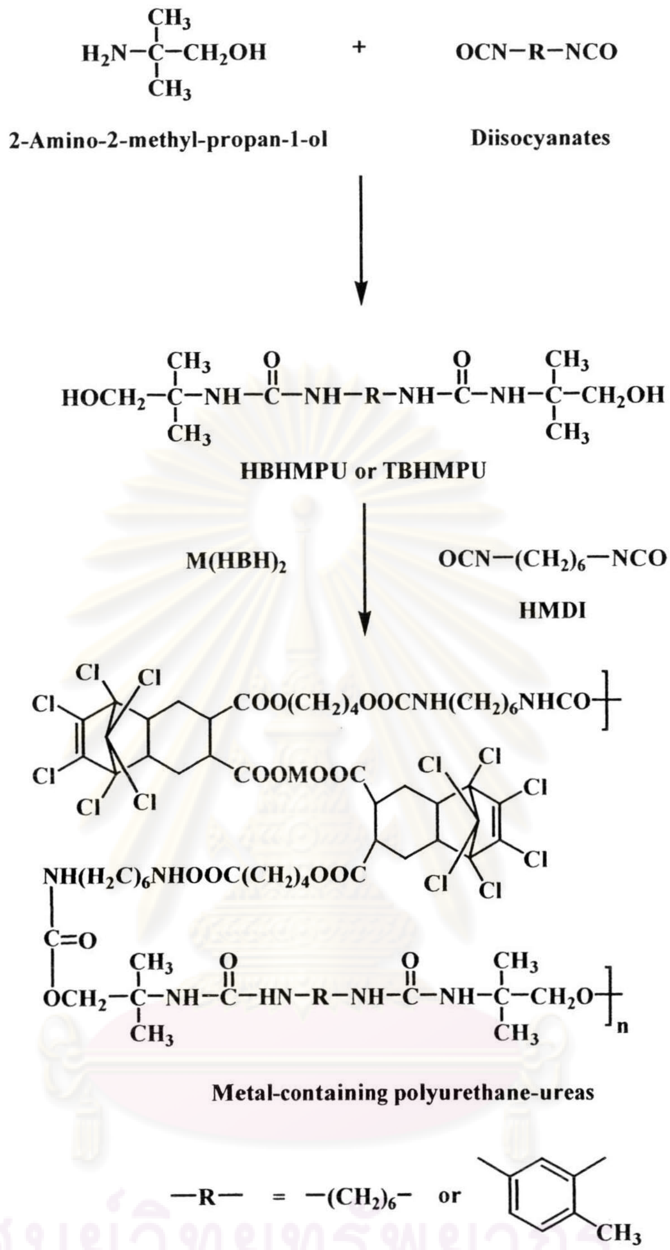
The results indicated that the TDI-based copolyurethanes showed higher thermal stability than HMDI-based copolyurethanes.

Furthermore[5], they synthesized flame-retardant metal-containing polyurethanes by the solution polymerization of HMDI with divalent metal salts of mono(hydroxybutyl)hexolate [$M(HBH)_2$, M = Ca^{2+}, Mn^{2+} or Pb^{2+}] (Scheme 1.2).



Scheme 1.2 Synthesis of metal-containing polyurethanes from $M(HBH)_2$ and HMDI

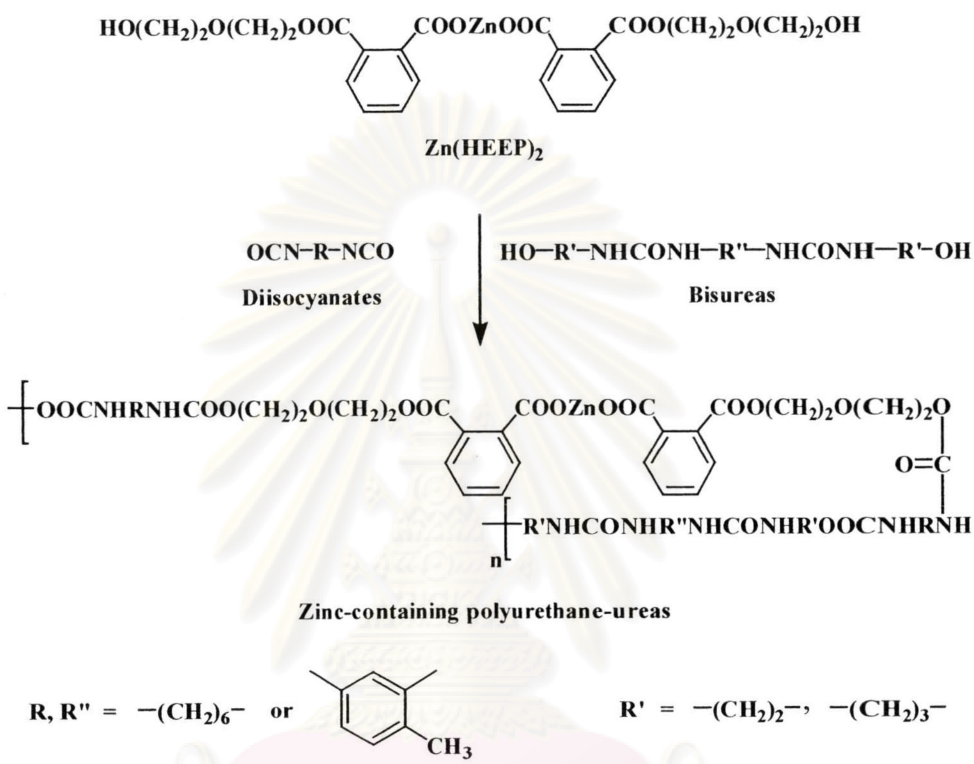
In addition, they synthesized polyurethane-ureas by reacting HMDI with 1:1 mixture of $M(HBH)_2$ and hexamethylene bis[*N*′-(1-hydroxy-2-methyl-prop-2-yl)urea] (HBHMPU) or toluene 2,4-bis[*N*′-(1-hydroxy-2-methyl-prop-2-yl)urea] (TBHMPU) (Scheme 1.3).



Scheme 1.3 Synthesis of metal-containing polyurethane-ureas from HBHMPU or TBHMPU, $M(HBH)_2$ and HMDI

Thermal analysis of the obtained polymers showed that the IDTs of polyurethanes were slightly higher than those of polyurethane-ureas. Among the polyurethane-ureas, TBHMPU-based polymers were found to have higher IDTs than HBHMPU-based polymers. In general, the thermal stability of the metal-containing polymers followed the order of Ca>Mn>Pb.

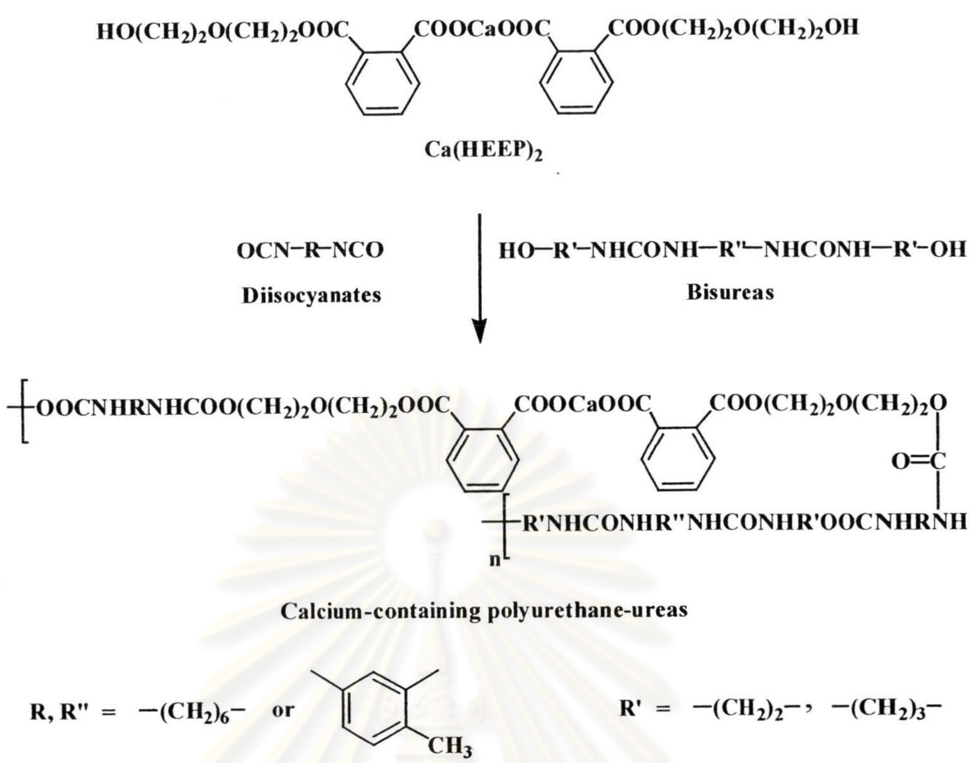
Moreover[6], they synthesized zinc-containing polyurethane-ureas having ionic links in the main chain by the reaction of HMDI or TDI with 1:1 mixture of zinc salt of mono(hydroxyethoxyethyl)phthalate [Zn(HEEP)$_2$] and each of bisureas (Scheme 1.4).



Scheme 1.4 Synthesis of zinc-containing polyurethane-ureas from HMDI or TDI, Zn(HEEP)$_2$ and bisureas

Thermal properties of the obtained polymers showed that the TDI-based polymers were more stable than the respective HMDI-based polymers.

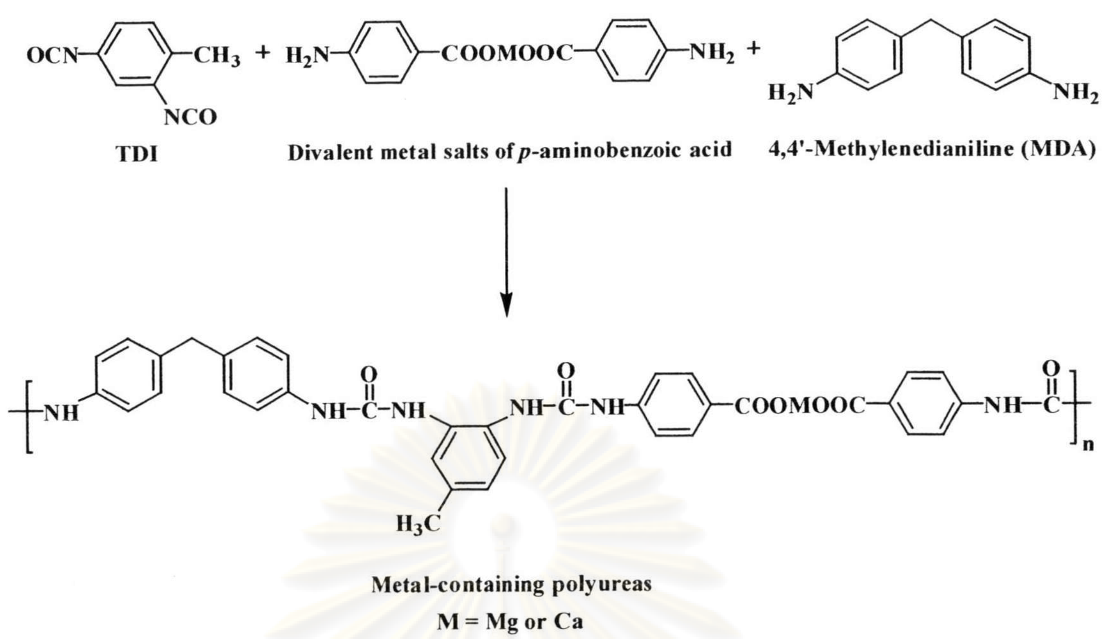
Another work of Nanjundan and coworkers[7] involved the synthesis of calcium-containing polyurethane-ureas by reacting HMDI or TDI with 1:1 mixtures of calcium salt of mono(hydroxyethoxyethyl)phthalate [Ca(HEEP)$_2$] and each of bisureas (Scheme 1.5).



Scheme 1.5 Synthesis of calcium-containing polyurethane-ureas from HMDI or TDI, $Ca(HEEP)_2$ and bisureas

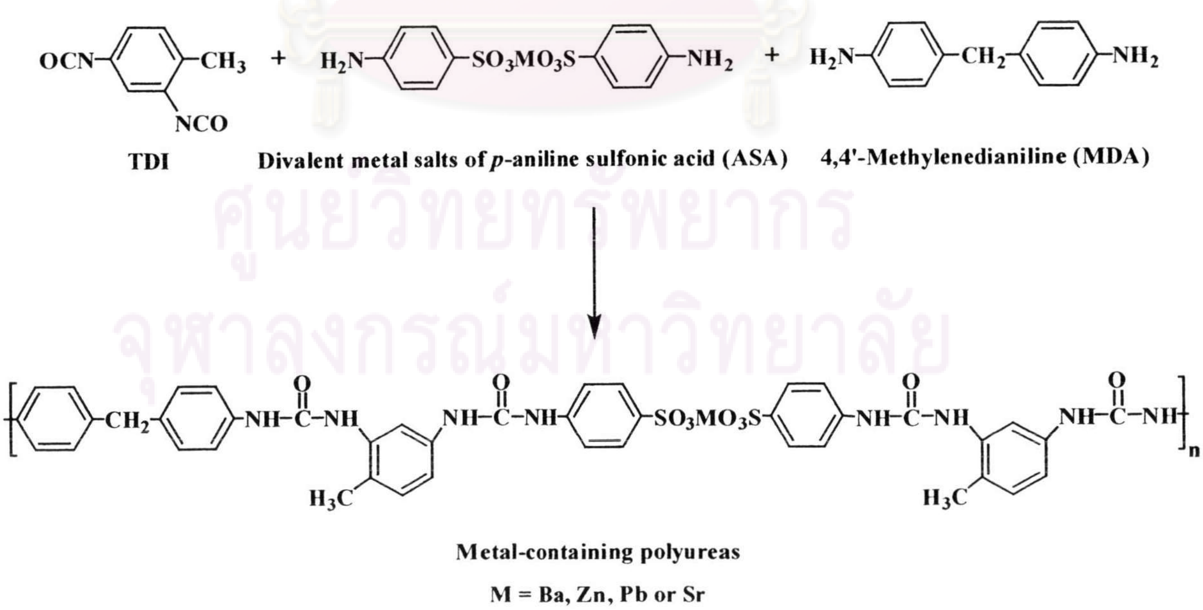
It was observed that the thermal stability of the TDI-based polymers was higher than those of HMDI-based polymers because of the presence of a rigid aromatic ring in the TDI-based polymers and the XRD studies of the polymers showed that the HMDI-based polymers are partially crystalline, whereas the TDI-based polymers are amorphous in nature.

Matsuda and Takechi[8] synthesized metal-containing polyureas having ionic links in the main chain by the polyaddition reactions of 2,4-toluene diisocyanate (TDI) with mixtures of divalent metal salts of *p*-aminobenzoic acid and 4,4′methylenedianiline (MDA) represented in Scheme 1.6. It was observed that glass transition temperature (T_g) of metal-containing polyureas increased with an increase in metal content but introducing the metals into the polyureas lowered the thermal properties as indicated by decreased decomposition temperatures.



Scheme 1.6 Synthesis of metal-containing polyureas from TDI, divalent metal salts of *p*-aminobenzoic acid and MDA

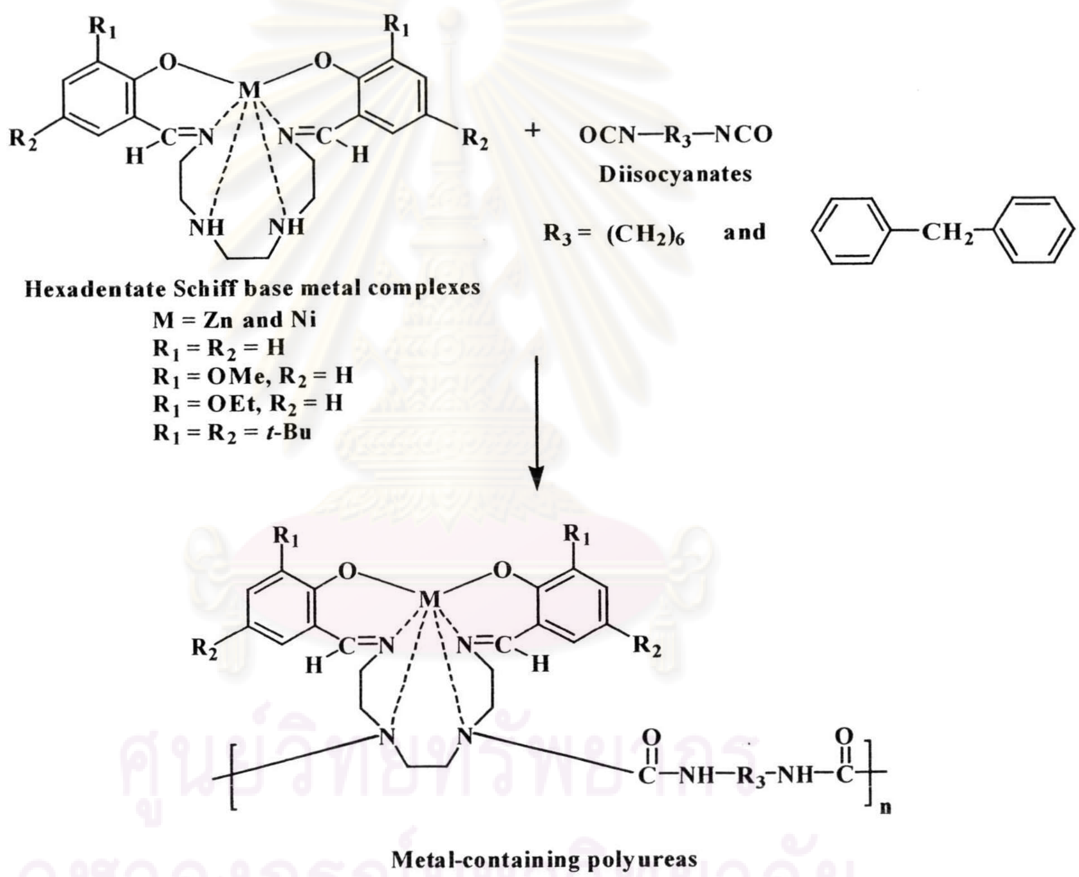
Wang and coworkers[9] prepared metal-containing polyureas having ionic links in the main chain by the polyaddition reactions of TDI with mixtures of divalent metal salts of *p*-aniline sulfonic acid (ASA) and MDA (Scheme 1.7).



Scheme 1.7 Synthesis of metal-containing polyureas from TDI, ASA and MDA

The results indicated that the thermal stability of polyureas increased when the metal was introduced and they also found that with an increase of ASA content in the feed diamine, the thermal stability of metal-containing polyureas increased.

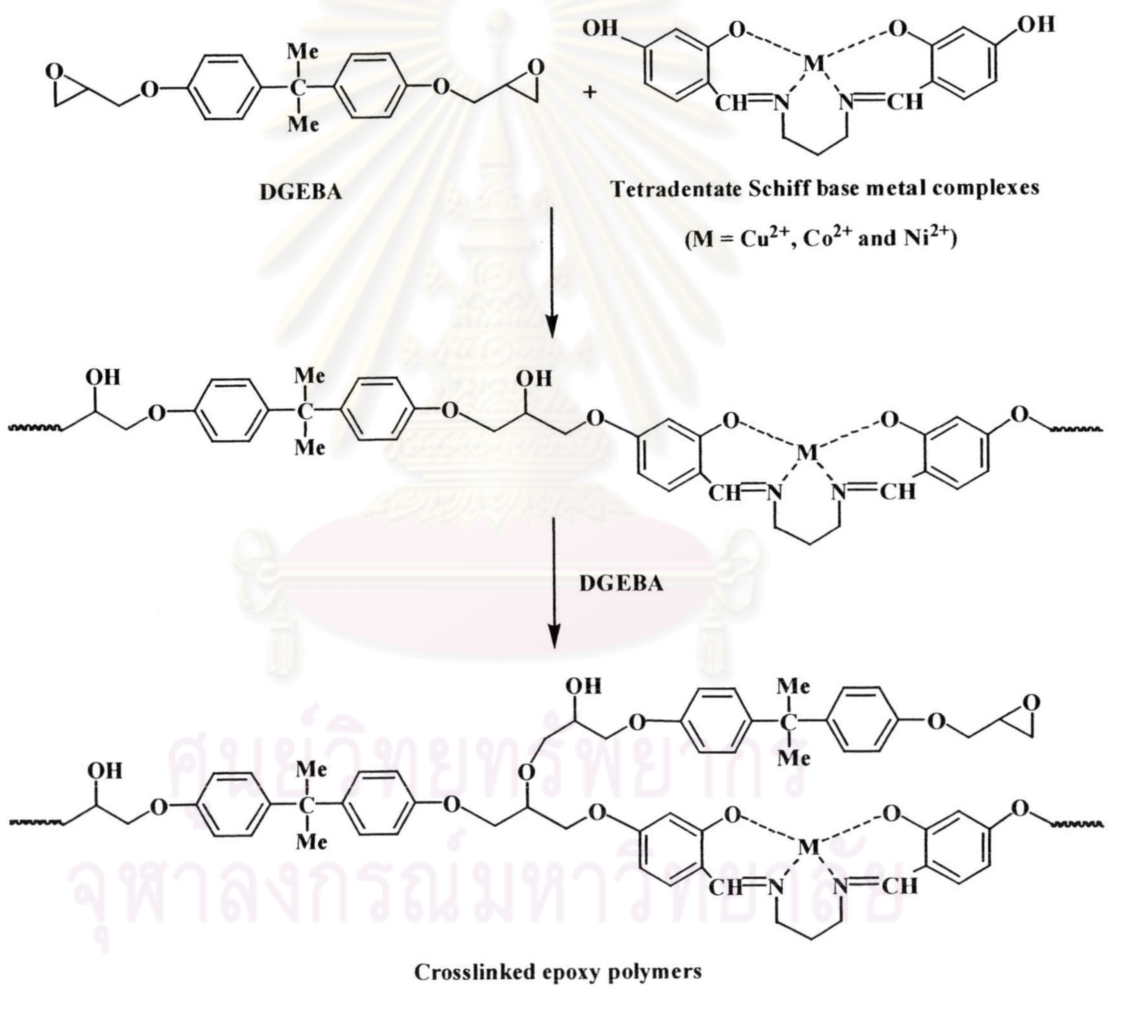
From the previous works in our research group, Chantarasiri and coworkers[19] synthesized nickel and zinc hexadentate Schiff base metal complexes and used these metal complexes in the preparation of metal-containing polyureas to improve the thermal stability by polycondensation reactions of the metal complexes with HMDI and 4,4′-diphenylmethane diisocyanate (MDI) (Scheme 1.8).



Scheme 1.8 Synthesis of metal-containing polyureas from the reaction between metal complexes and diisocyanates

The results showed that the obtained metal-containing polyureas had good thermal properties and MDI-based polyureas showed IDTs higher than HMDI-based polyureas but the solubility of these polymers in organic solvents was not good.

The aim of this work was to synthesize metal-containing polyurethane-ureas from 4,4′-dihydroxysaltetraen metal complexes (ML_1) which are hexadentate Schiff base metal complexes having OH groups in the structure to improve the solubility of polymers. Metal-containing polyurethanes were also synthesized from 4,4′-dihydroxysalcyclohexane metal complexes (ML_2) which are tetradentate Schiff base metal complexes having OH groups in the structure. It was found by Chantarasiri and coworkers that OH groups on ML_2 could react with isocyanate groups to give urethane linkage in thair metal-containing epoxy polymers (Scheme 1.9).



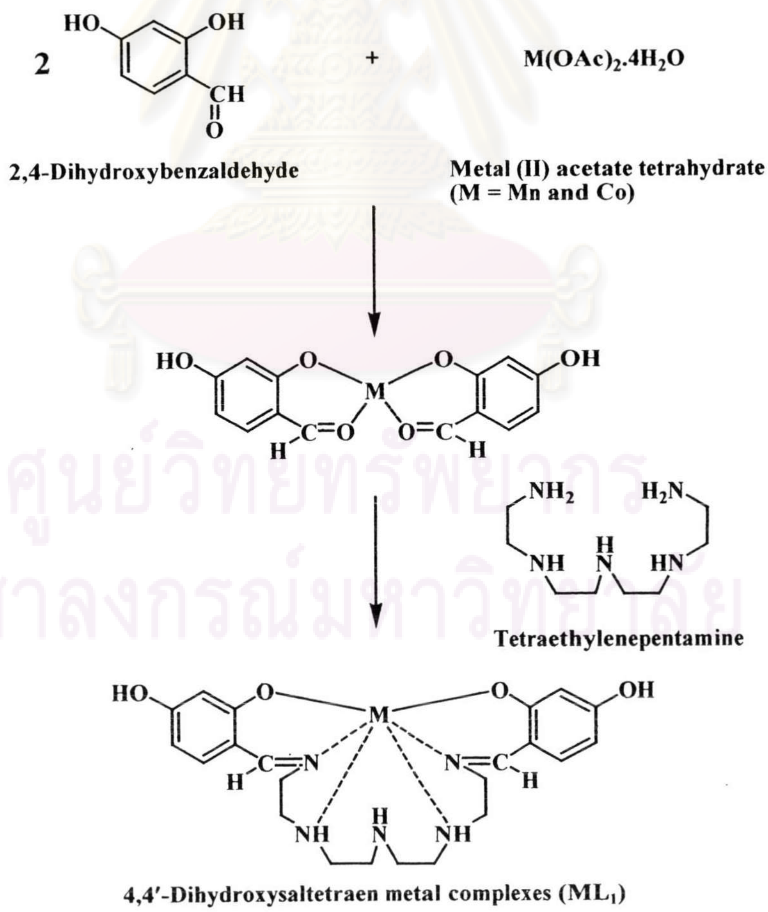
Scheme 1.9 Proposed crosslinking mechanism of DGEBA with tetradentate Schiff base metal complexes

It was found that introduction of tetradentate Schiff base metal complexes into the polymer matrix resulted in good thermal stability and tensile strength, especially in the case of the copper-containing epoxy polymer, which is comparable to the known epoxy-anhydride system.

1.4 Objective and scope of the research

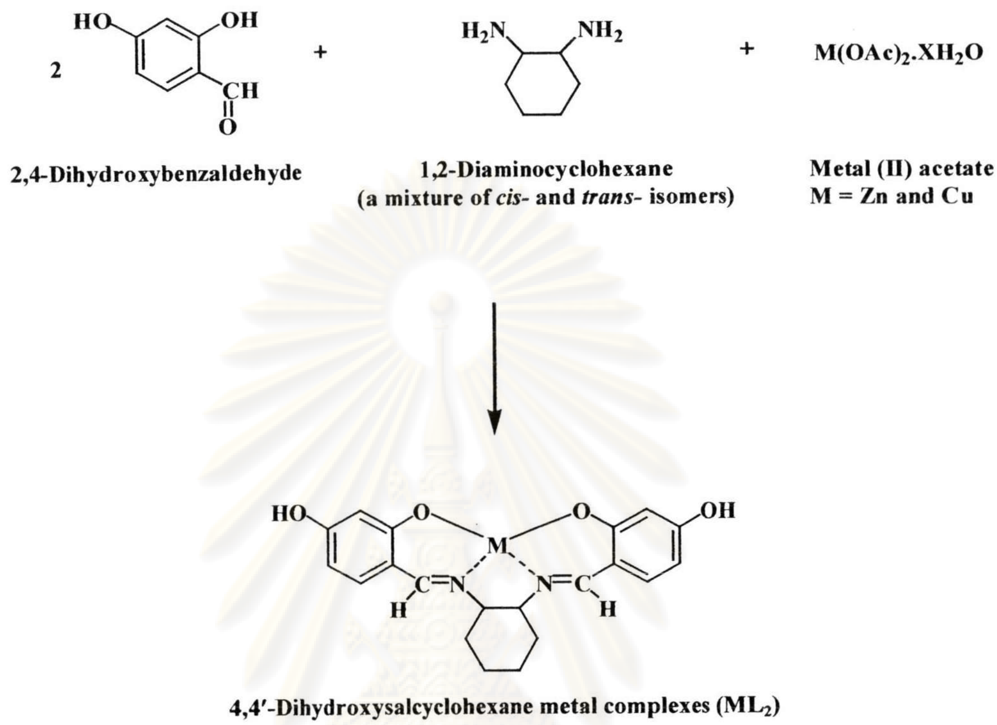
In our works, efforts were made to synthesize two types of metal complexes, 4,4′-dihydroxysaltetraen metal complexes (ML_1) and 4,4′-dihydroxysalcyclohexane metal complexes (ML_2) and used these metal complexes in the synthesis of metal-containing polymers to improve the thermal stability and solubility of the polymers.

In the first step, 4,4′-dihydroxysaltetraen manganese and cobalt complexes (ML_1) were synthesized as shown in Scheme 1.10.



Scheme 1.10 Synthesis of 4,4′-dihydroxysaltetraen manganese and cobalt complexes

Purification of ML_1 was unsuccessful, therefore, the other 4,4′-dihydroxysalcyclohexane zinc and copper complexes (ML_2) were synthesized as shown in Scheme 1.11.

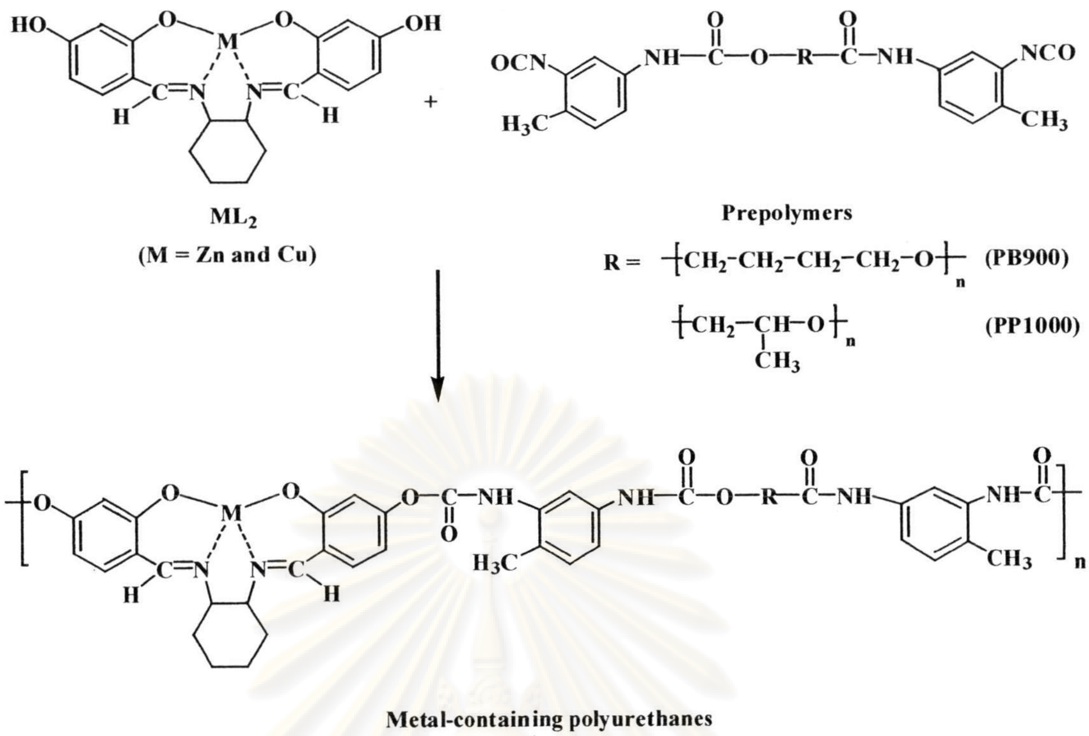


Scheme 1.11 Synthesis of 4,4′-dihydroxysalcyclohexane zinc and copper complexes

The results indicated that 4,4′-dihydroxysalcyclohexane metal complexes were suitable for use in the synthesis of metal-containing polyurethanes.

The next step was to investigate the polymerization reaction between 4,4′-dihydroxysalcyclohexane metal complexes (ML_2) and tolylene 2,4-diisocyanate terminated prepolymers (PB900 and PP1000) using differential scanning calorimetry (DSC) and IR spectroscopy. The reaction between ML_2 and prepolymers to yield metal-containing polyurethanes is shown in Scheme 1.12.

Finally, polyurethanes containing 4,4′-dihydroxysalcyclohexane metal complexes were synthesized from the reaction between 4,4′-dihydroxysalcyclohexane metal complexes (ML_2) and different prepolymers.



Scheme 1.12 Synthesis of polyurethanes containing 4,4′-dihydroxysalcyclohexane metal complexes from the reaction between ML_2 and prepolymers

To compare the properties of the obtained metal-containing polyurethanes, the polyurethane-ureas without metal in the main chain were synthesized from the reaction between *m*-xylylenediamine and prepolymers. Polyurethane-ureas with metal complexes in the main chain were also synthesized from the reaction between *m*-xylylenediamine, ML_2 and prepolymers.

All polymers were characterized by IR spectroscopy. Solubility and thermal stability of the polymers were also investigated.