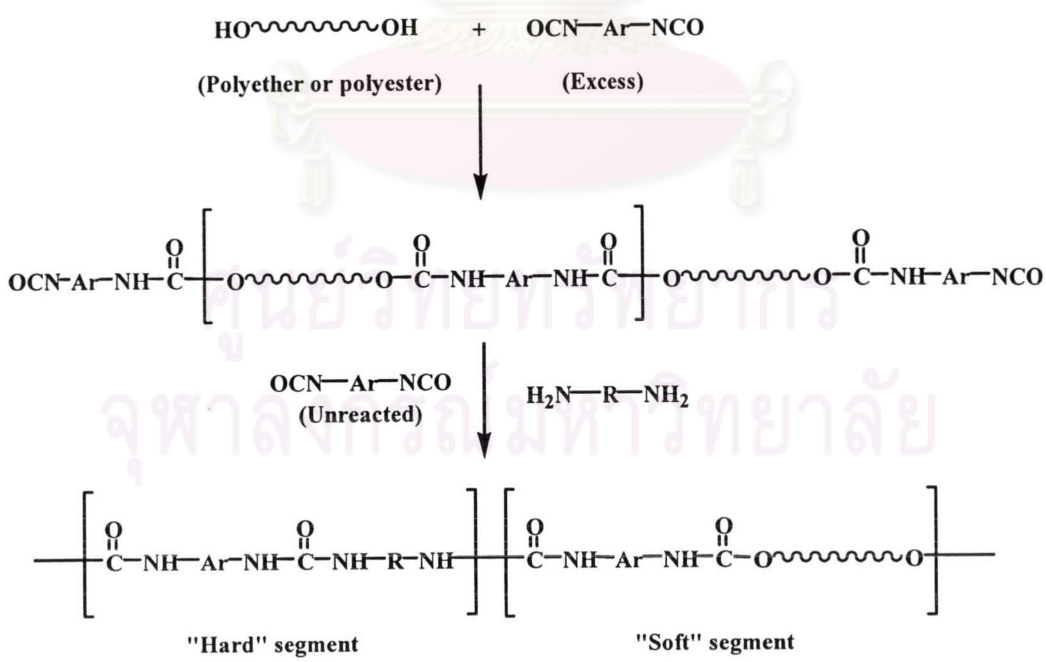
CHAPTER I

INTRODUCTION

1.1 Polyurethanes

Polyurethanes[1-3] can be tailor-made to have versatile applications. The synthesis of polyurethanes is usually presented as proceeding *via* the formation of urethane linkages by the reaction of isocyanates with alcohols (Scheme 1.1). The elastomeric polyurethane chains consist of alternating short sequences forming soft (flexible) and hard (rigid) segments. The soft segments, originated from the polyol, impart elastomeric characteristics to the polymer. The hard segments act as physical crosslink and as a consequence, the physical, mechanical and adhesive properties depend strongly on the degree of phase separation between hard and soft segments and interconnectivity of hard domains.



Scheme 1.1 Synthesis of a polyurethane elastomer[1]

Polyurethanes are used in a wide variety of products, including fibers, elastomers, foam, coatings and adhesives.

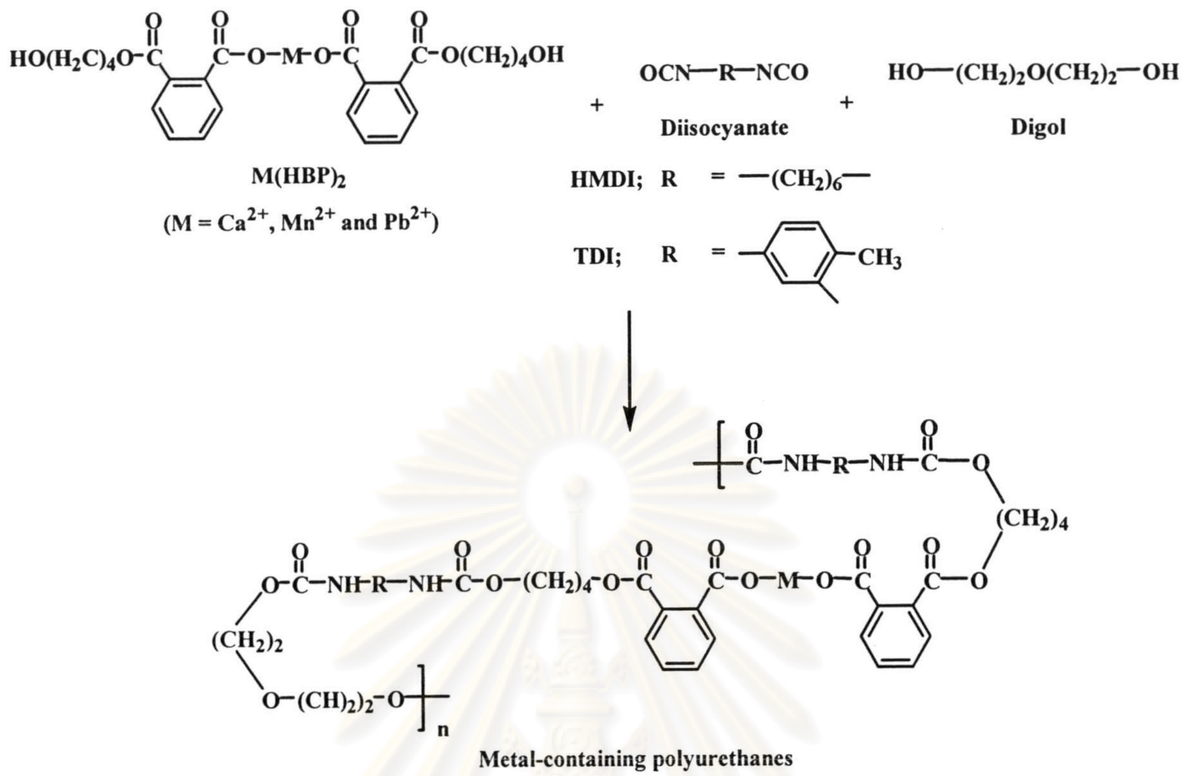
1.2 Thermally stable polymers

There have been continuing and strong efforts since the late 1950s to synthesize thermally stable polymers[3-4]. The advantage of these polymers is the weight saving in replacing metal items and the ease of processing polymeric materials into various configurations. Light weight polymers processing high strength, solvent and chemical resistance, and serviceability at temperatures in excess of 250°C would find a variety of potential uses, such as automotive and aircraft components, nonstick and decorative coating on cookware, structural components for aircraft, space vehicles, and electronic components.

The introduction of metal into a polyurethane backbone results in thermally stable properties. Many researchers have been studying metal-containing polyurethanes, polyureas and polyurethanes-ureas[5-20]. Examples of such works are as follows:

1.3 Literature review

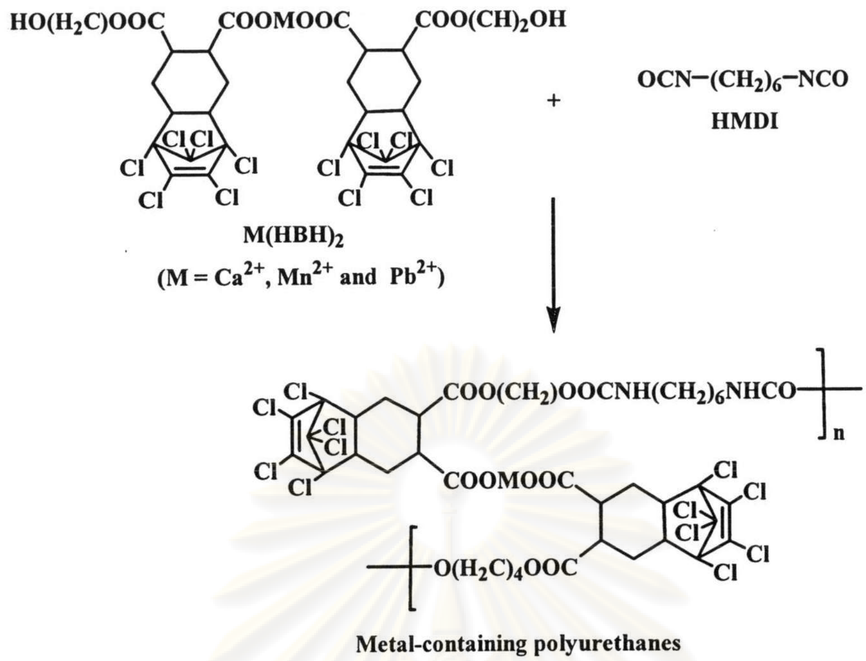
Nanjundan and Prasath[5] synthesized metal-containing polyurethanes from the reaction of hexamethylene diisocyanate (HMDI) or tolylene 2,4-diisocyanate (TDI) with 1 : 1 mixture of divalent metal salts of mono(hydroxybutyl)phthalate [$M(HBP)_2$] and digol (Scheme 1.2). They also synthesized polyurethane-ureas by reacting the isocyanates with 1 : 1 mixture of hexamethylene *bis*(*ω*,*N*-hydroxyethylurea) (HBHEU) and $M(HBP)_2$. Initial decomposition temperatures (IDTs) of polymers are found between 150 and 250°C. It was observed that metal-containing polyurethanes have higher IDTs than metal-containing polyurethane-ureas.



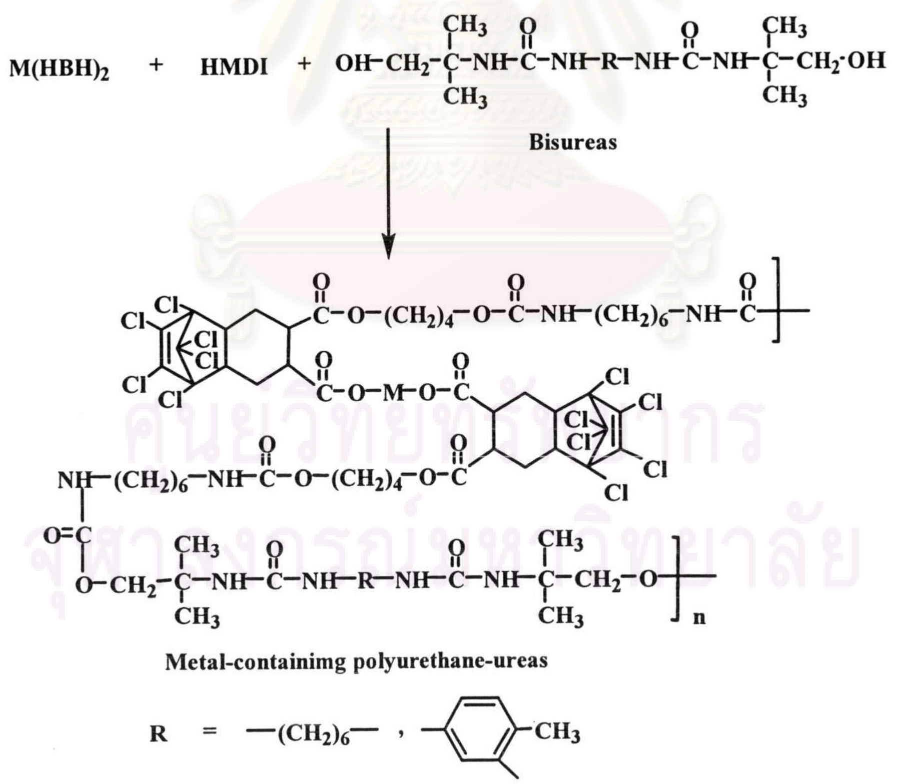
Scheme 1.2 Synthesis of metal-containing polyurethanes from $M(HBP)_2$, diisocyanate and digol

Nanjundan and Prasath[6] also synthesized 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, $M(HBH)_2$, where metals were Ca^{2+}, Mn^{2+} and Pb^{2+} (Scheme 1.3).

Polyurethane-ureas were obtained from the reaction of $M(HBH)_2$ with HMDI and bisureas, hexamethylene *bis*[*N'*-(1-hydroxy-2-methyl-prop-2-yl)urea] (HBHMPU) or tolylene 2,4-*bis*[*N'*-(1-hydroxy-2-methyl-prop-2-yl)urea] (TBHMPU), as shown in Scheme 1.4.



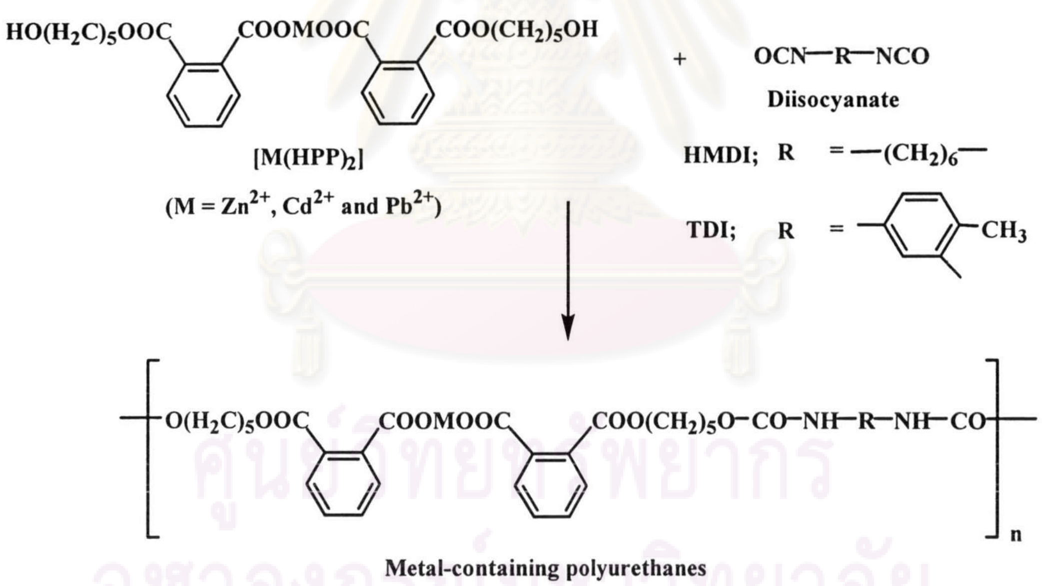
Scheme 1.3 Synthesis of metal-containing polyurethanes from $M(HBH)_2$ and HMDI



Scheme 1.4 Synthesis of metal-containing polyurethane-ureas from $M(HBH)_2$, HMDI and bisureas

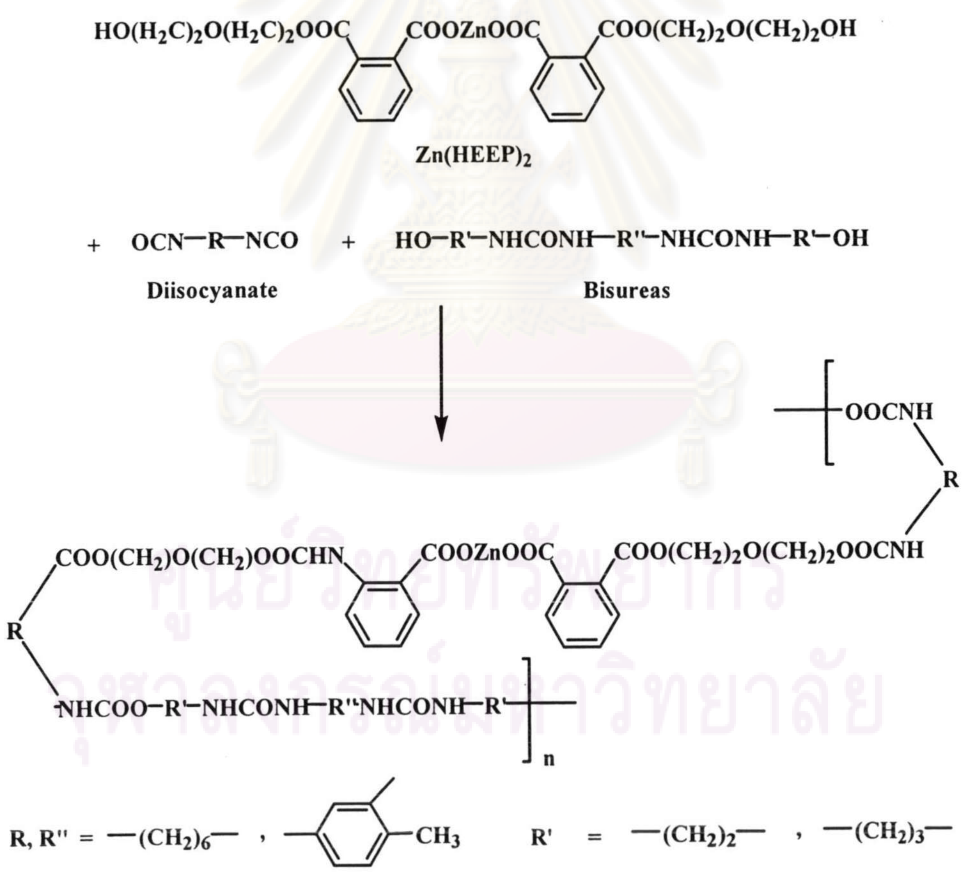
From TGA study, thermal stability of metal-containing polyurethanes was higher than that of metal-containing polyurethane-ureas. Among the polyurethane-ureas, TBHMPU-based polyurethane-ureas were slightly more thermally stable than HBHMPU-based polyurethane-ureas due to the presence of aromatic rings in the polymer chain. 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-ureas, the TBHMPU-based polyurethane-ureas were found to have higher flame retardancy.

Nanjundan[7] synthesized metal-containing polyurethanes from metal salts of mono(hydroxypentyl)phthalate, $[M(HPP)_2]$ where M were Ca^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}, and HDI or TDI (Scheme 1.5). IDTs of the polymers are around 210 - 276°C. The T_g values of the metal-containing polyurethanes followed the order Ca > Zn > Cd > Pb.



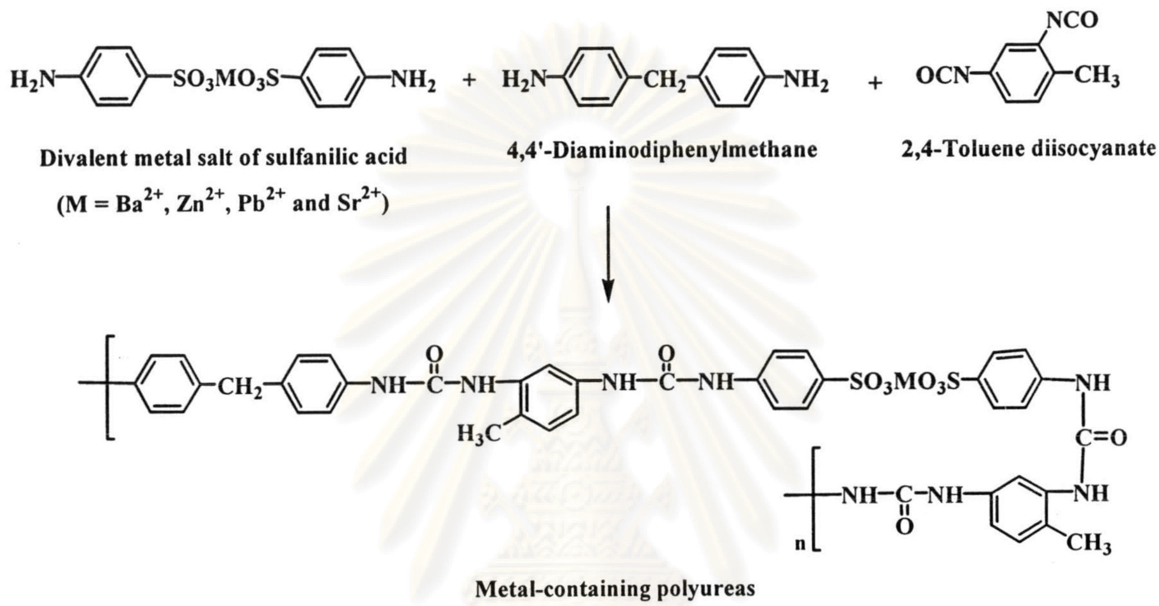
Scheme 1.5 Synthesis of metal-containing polyurethanes from $[M(HPP)_2]$ and diisocyanate

Nanjundan and Jayakumar[8] synthesized poly(urethane-urea)s based on zinc salt of mono[hydroxyethoxyethyl]phthalate [Zn(HEEP)$_2$] (Scheme 1.6). These polymers were synthesized by polyaddition reaction of HDI or TDI with 1 : 1 mixture of [Zn(HEEP)$_2$] and bisureas such as hexamethylene-*bis*(ω,*N*-hydroxyethylurea) [HBHEU], tolylene-2,4-*bis*(ω,*N*-hydroxyethylurea) [TBHEU], hexamethylene-*bis*(ω,*N*-hydroxypropylurea) [HBHPU] and tolylene-2,4-*bis*(ω,*N*-hydroxypropylurea) [TBHPU] by using dibutyltin dilaurate as a catalyst. All the metal-containing polymers were structurally similar but showed different thermal behavior. The IDTs values were found between 233 - 272°C. It was observed that TDI-based polymers show higher IDTs than HMDI-based polymers. This might be due to the presence of stiff phenylene rings in the main chain.



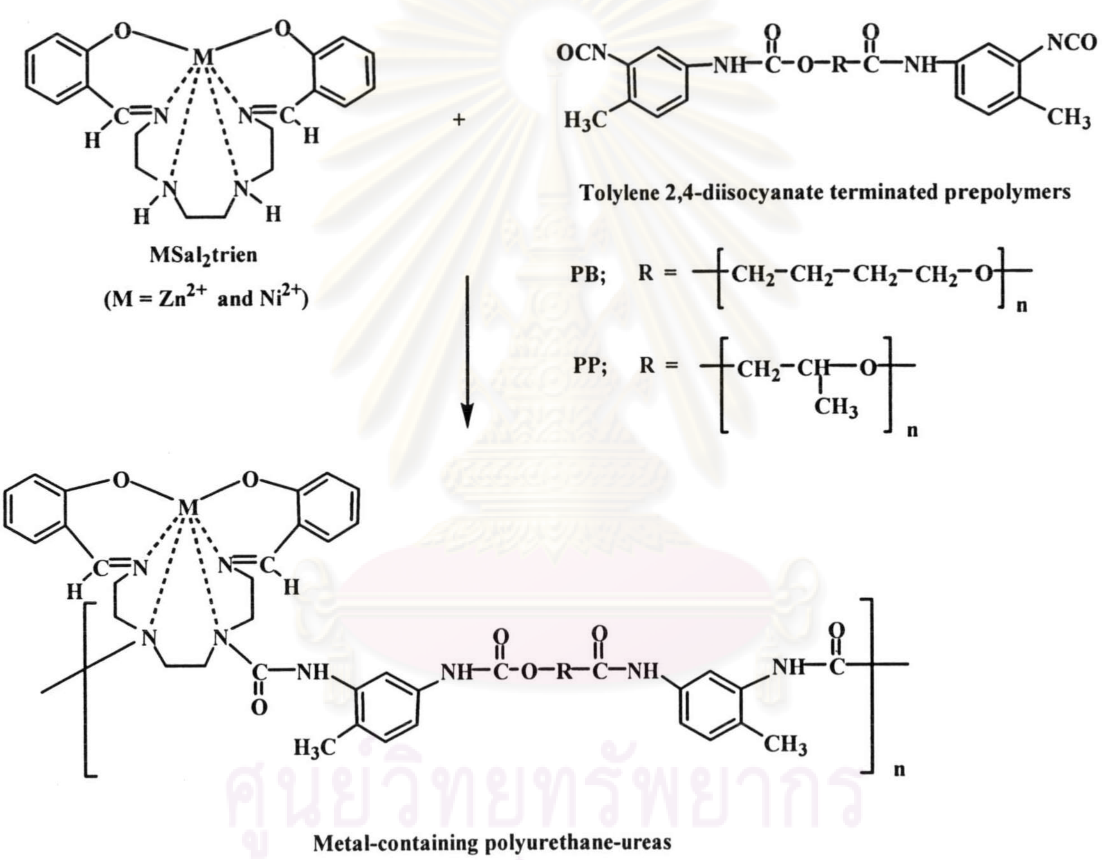
Scheme 1.6 Synthesis of poly(urethane-urea)s from HDI or TDI with 1 : 1 mixture of [Zn(HEEP)$_2$] and bisureas

Qiu and coworkers[9] synthesized metal-containing polyureas containing ionic linkages in the main chain by the polyaddition of TDI with 4,4′-diaminodiphenylmethane and the divalent metal salts of sulfanilic acid where metals were Ba^{2+}, Sr^{2+}, Pb^{2+} and Zn^{2+} (Scheme 1.7). It was found that introducing the metal into the polyurea increased the thermal stability.

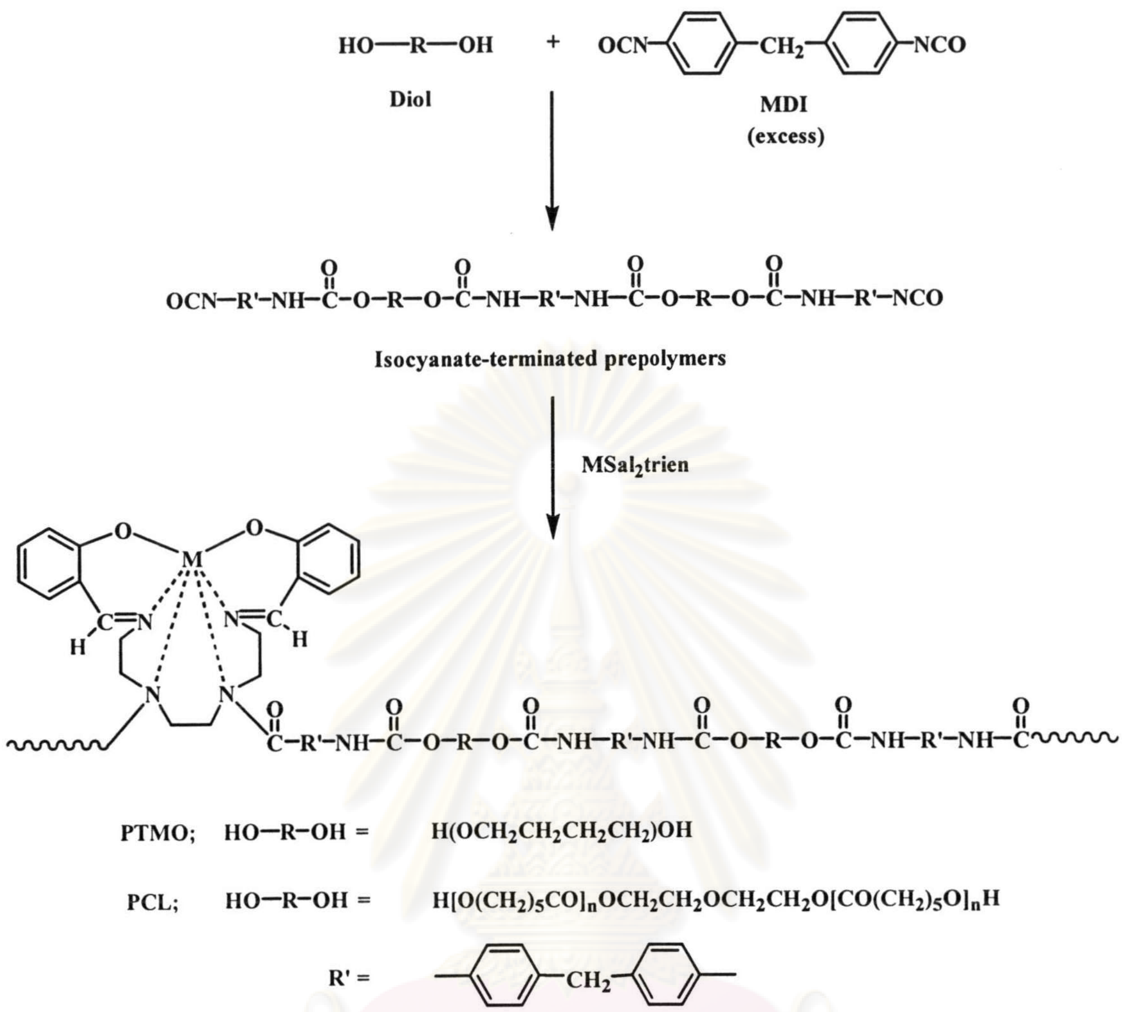


Scheme 1.7 Synthesis of metal-containing polyureas from TDI, 4,4′-diaminodiphenylmethane and divalent metal salts of sulfanilic acid

From the previous work in our group, metal-containing polyurethane-ureas (Scheme 1.8) and copolyurethane-ureas[10] (Scheme 1.9) were synthesized by the reaction between hexadentate Schiff base metal complexes and isocyanate-terminated prepolymers. The metal complexes employed were $MSal_2trien$ where M = Ni^{2+} and Zn^{2+}, Sal = salicylaldehyde and trien = triethylenetetramine. The NCO-terminated prepolymers used were tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) (PB) and tolylene 2,4-diisocyanate terminated poly(propylene glycol) (PP) prepolymers and the prepolymers synthesized from 4,4′-diphenylmethane diisocyanate (MDI) and diols. The diols employed were polycaprolactone diol (PCL) and poly(tetramethylene oxide) (PTMO). Copolyurethane-ureas were synthesized by the reaction between $MSal_2trien$, PB or PP prepolymers and MDI. It was found that the inherent viscosity of the polymers increased with increasing weight% of $MSal_2trien$ in the polymer, which indicated that $MSal_2trien$ did not dissociate in solvent. Metal-containing polymers show good stability compared to the polymers obtained without $MSal_2trien$ in the main chain and thermal stability increases with increasing weight% of $MSal_2trien$ in the polymers.



Scheme 1.8 Synthesis of metal-containing polyurethane-ureas from $MSal_2trien$ and isocyanate-terminated prepolymers



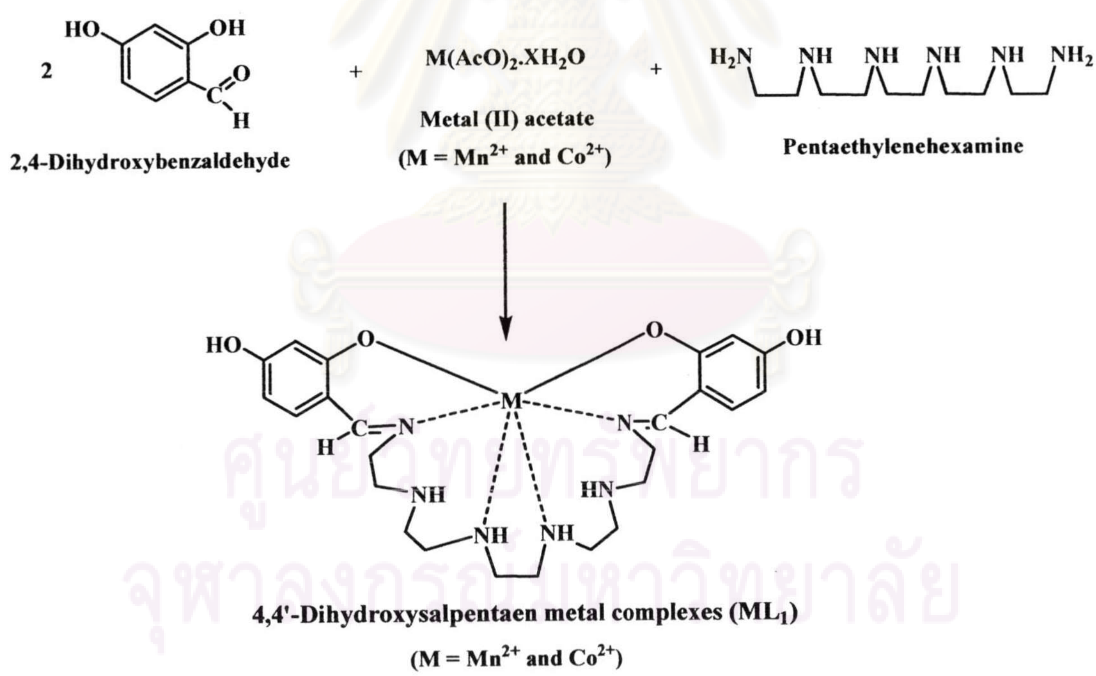
Scheme 1.9 Synthesis of metal-containing copolyurethane-ureas from MSal$_2$trien and isocyanate-terminated prepolymers

1.4 Objective and scope of the research

The objective of this research is to synthesize Schiff base metal-containing polyurethanes since it was known that addition of metals into the polymer chain could improve thermal properties of polymers.

Schiff base metal complexes are among the well known complexes since they are stable and have many applications[24]. Therefore, these metal complexes were chosen for this research. The metal complexes employed for this research were hexadentate and tetradentate Schiff base metal complexes. These complexes were expected to be stable since there are many bonds between ligand and metal ion.

From the previous work[10], the polymers containing Schiff base metal complexes showed good thermal stability, however, they had poor solubility in organic solvents. Therefore, 4,4′-dihydroxysalpentaen metal complexes (ML_1) containing two hydroxyl groups and four amine groups were chosen for the synthesis of metal-containing polymers. Two hydroxyl groups and two amine groups are expected to undergo the reaction with diisocyanate prepolymers to give metal-containing polyurethanes. It was expected that the polyurethanes containing ML_1 should have good solubility in organic solvents since there are more organic component in the polymer chain in comparison to the metal-containing polymers obtained from the previous work[10]. Scheme 1.10 shows the synthesis of 4,4′-dihydroxysalpentaen metal complexes.



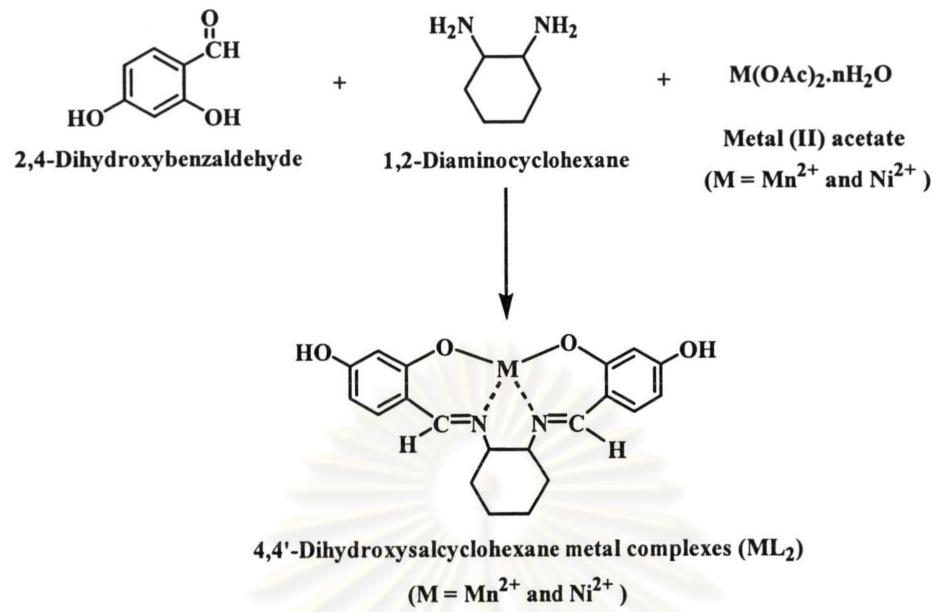
Scheme 1.10 Synthesis of 4,4′-dihydroxysalpentaen metal complexes (ML_1)

It was found that the purity of 4,4′-dihydroxysalpentaen metal complexes were not good. Therefore, a new metal complex was chosen as tetradentate Schiff base metal complexes.

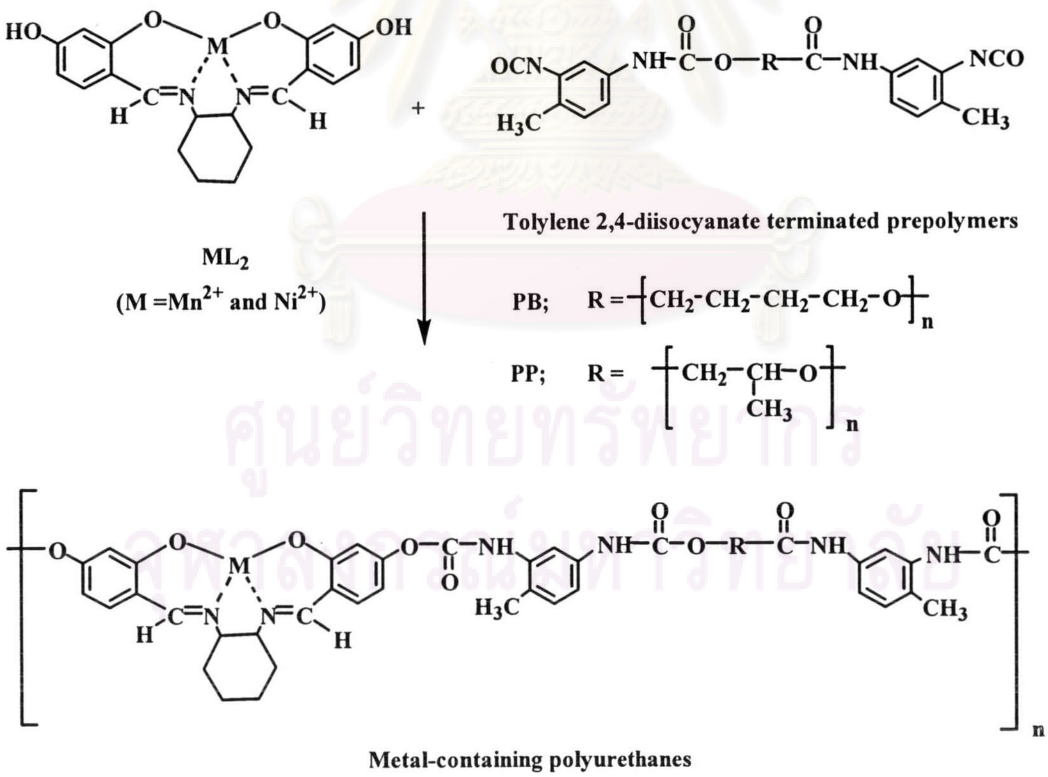
In the previous study[22-23], metal containing epoxy polymer containing tetradentate Schiff base metal complexes in the polymer chain have been studied. Polymerization of these metal complexes with diglycidyl ether of bisphenol A (DGEBA) epoxy resin gave polymer with good thermal stability. Therefore, we became interested in the application of Schiff base metal complexes in the preparation of metal-containing polyurethanes since it is expected that the polymers should also exhibit good thermal stability.

4,4′-Dihydroxysalcyclohexane metal complex (ML_2) was chosen in this work. ML_2 was synthesized from the mixture of *cis*- and *trans*-1,2-diaminocyclohexane and therefore ML_2 was expected to have good solubility in organic solvents since the structure of ML_2 was not highly ordered. Polymers synthesized from this metal complex were also expected to have good solubility. ML_2 was synthesized by reaction as shown in Scheme 1.11.

In the next step, the metal-containing polyurethanes were synthesized from the reaction between ML_2 and tolylene 2,4-diisocyanate terminated prepolymers. The prepolymers employed were tolylene 2,4-diisocyanate terminated poly(1,4-butanediol), molecular weight 900 (PB) and toluylene 2,4-diisocyanate terminated poly(propylene glycol), molecular weight 1000 (PP) (Scheme 1.12).

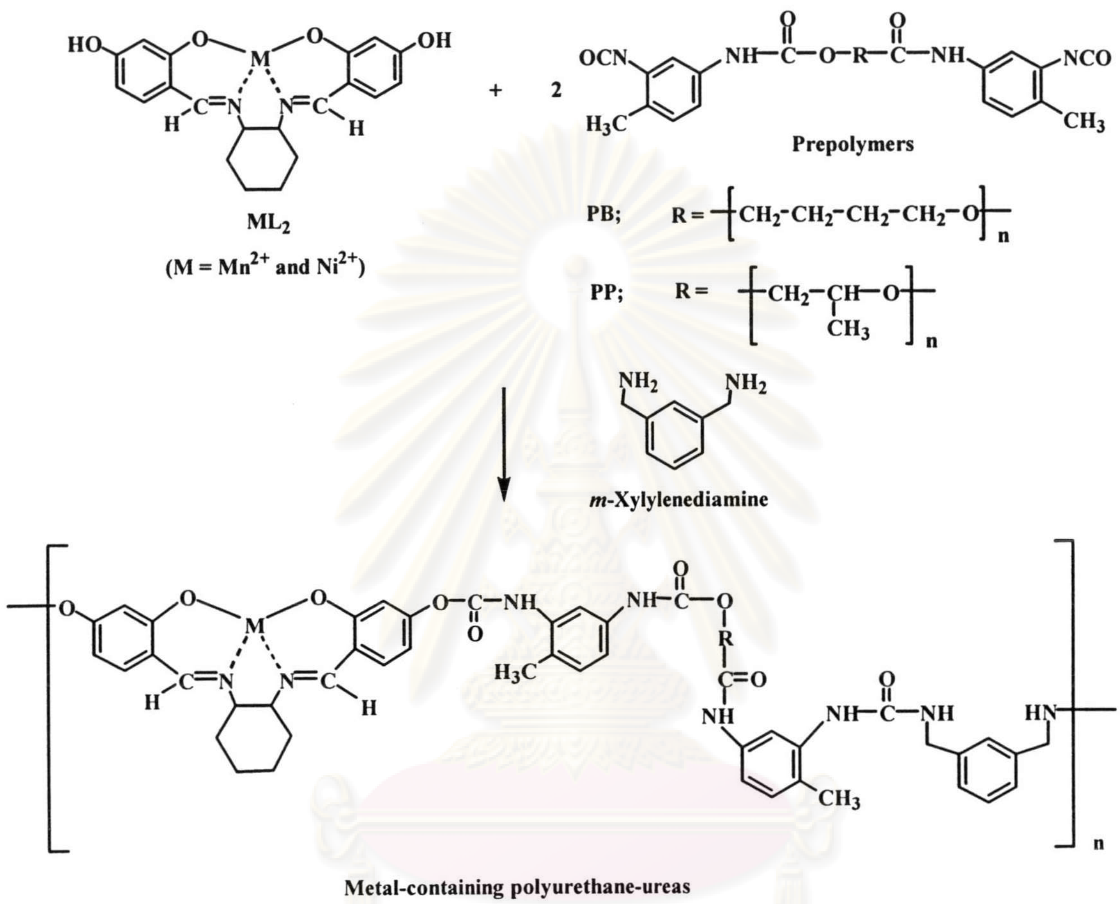


Scheme 1.11 Synthesis of 4,4′-dihydroxysalcyclohexane metal complexes (ML_2)



Scheme 1.12 Synthesis of metal-containing polyurethanes

Then, metal-containing polyurethane-ureas were synthesized from the reaction between ML_2, *m*-xylylenediamine and tolylene 2,4-diisocyanate terminated prepolymers, PB and PP (Scheme 1.13).



Scheme 1.13 Synthesis of metal-containing polyurethane-ureas

Finally, metal-containing polyurethanes and polyurethane-ureas were characterized by IR spectroscopy and solubility properties. Thermal property of polymers was investigated by thermogravimetric analysis (TGA).