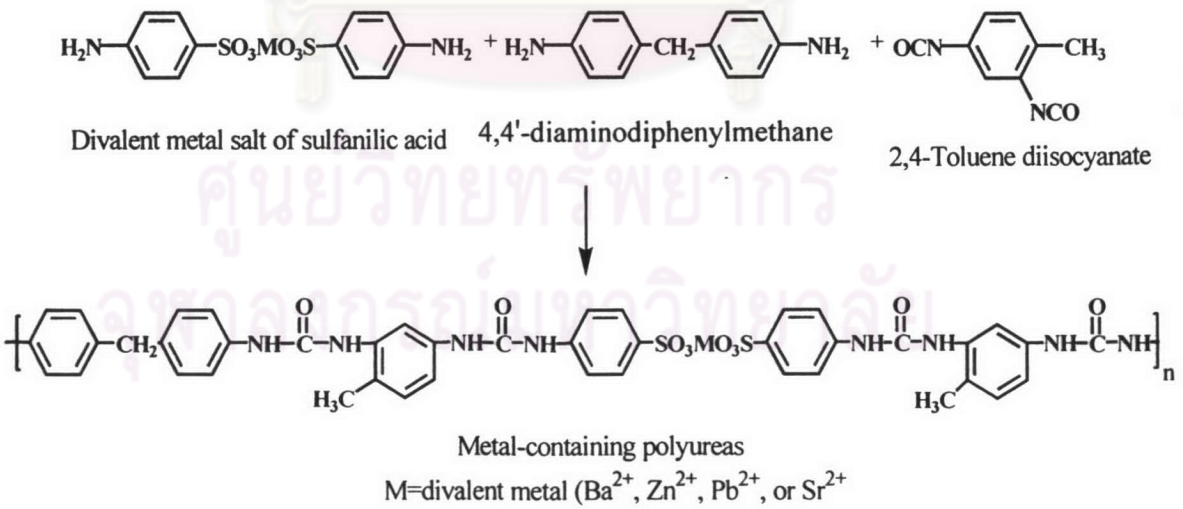
CHAPTER I

INTRODUCTION

Metal-containing polymers

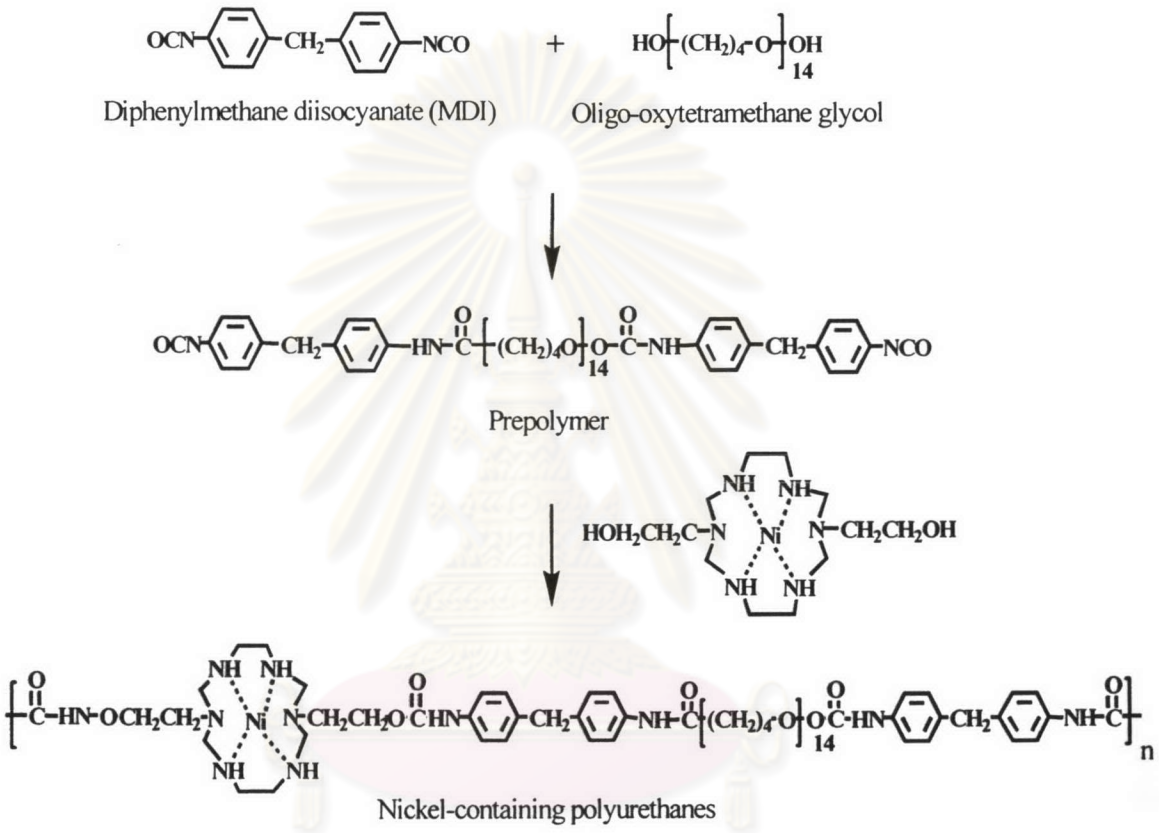
Metal-containing polymers have been widely investigated due to their excellent properties, especially thermal stability[1-5]. Metal-containing polyureas, polyurethane-ureas and polyurethanes are among the metal-containing polymers that have received attention since it was found that introduction of metal into the polymer structure resulted in the improvement of polymer properties. A number of research works concerning the preparation and physical properties of metal-containing polyureas, polyurethane-ureas and polyurethanes have been reported[6-7]. Examples of such works are as follows:

Wang and coworkers[8] reported the synthesis of metal-containing polyureas containing ionic linkages in the main chain that were obtained from the polyaddition reaction of 2,4-tolulenediisocyanate (TDI), divalent metal salts of sulfanilic acid (*p*-aniline sulfonic acid) (ASA) and 4,4'-diaminodiphenylmethane where Ba^{2+}, Zn^{2+}, Pb^{2+} and Sr^{2+} were used as divalent metal. The results indicated that introduction of the metal into polymer structure increased thermal stability of polymer.



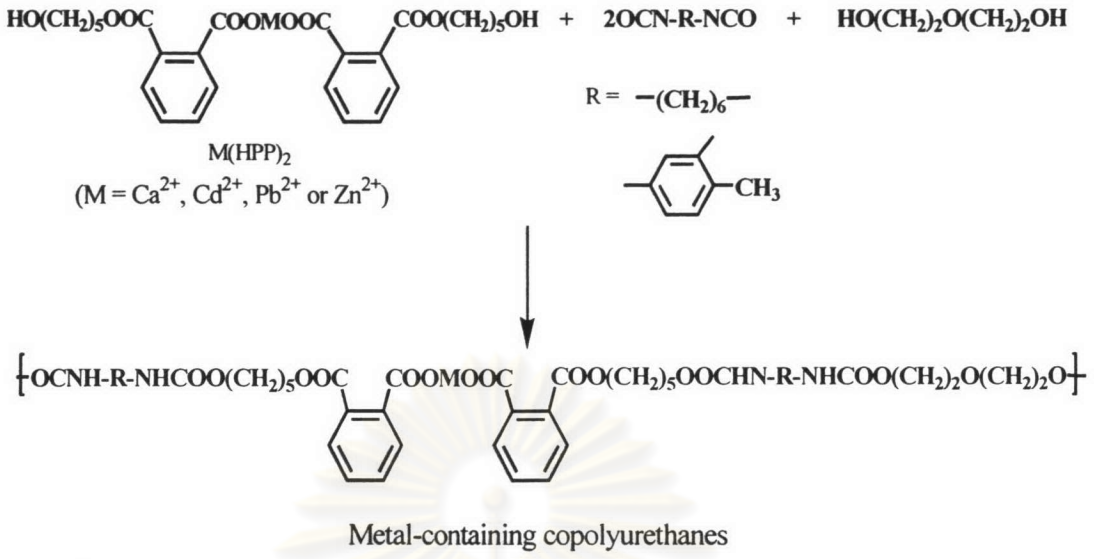
Scheme 1.1 Synthesis of metal-containing polyureas from TDI, 4,4'-diaminodiphenylmethane and ASA

Georgoussis and coworkers[9] synthesized nickel-containing polyurethanes.by a two-step reaction. First, prepolymer was prepared from the reaction between 4,4'-diphenylmethane diisocyanate (MDI) and oligooxytetramethyleneglycol and then aza-macrocyclic nickel complex were added to obtain the polymers as shown in Scheme 1.2. It was found that all polymers show good thermal stability.



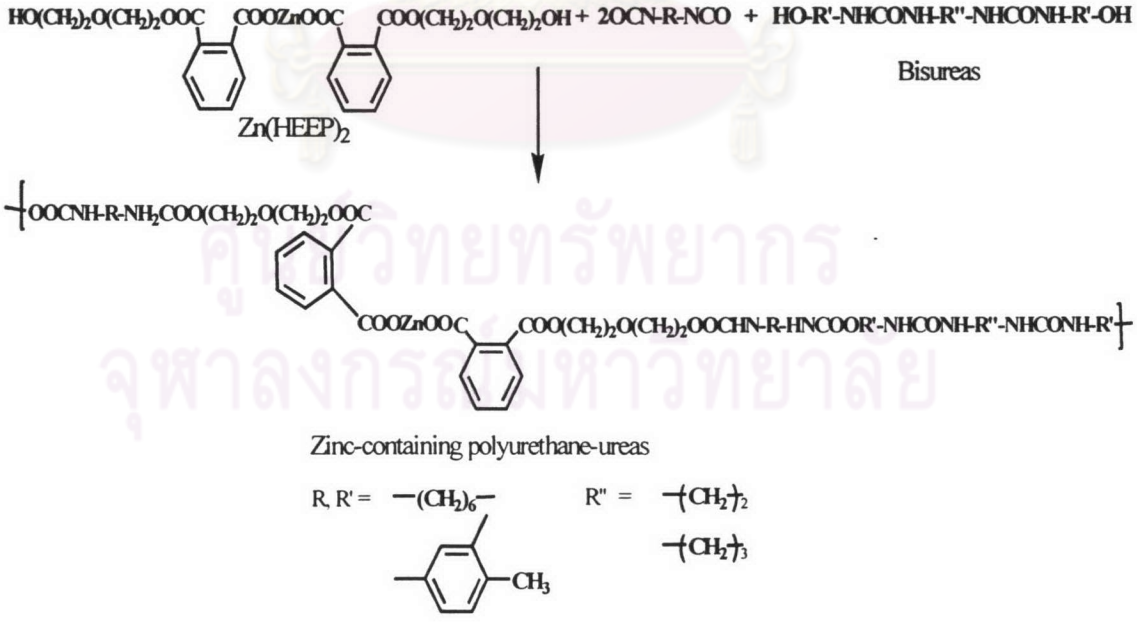
Scheme 1.2 Synthesis of Ni-containing polyurethane

Jayakumar and coworkers[10] reported metal-containing copolyurethanes having ionic linkages in the main chain which was prepared by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluene 2,4-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 diethylene glycol (Scheme 1.3). The TDI-based copolyurethanes showed higher thermal stability than HMDI-based copolyurethanes and all metal-containing copolyurethanes were found to exhibit antibacterial activities.



Scheme 1.3 Synthesis of metal containing copolyurethanes

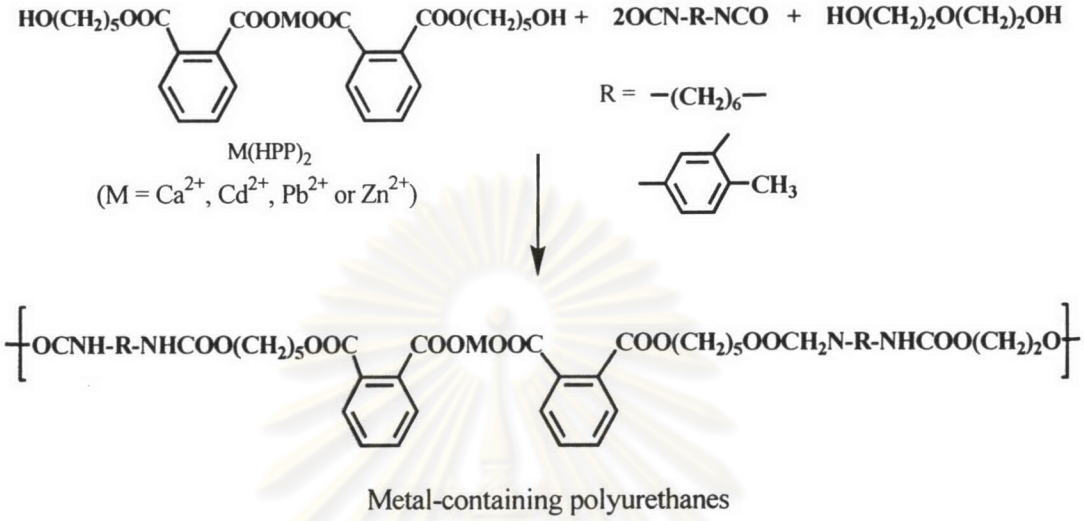
Zinc-containing polyurethane-ureas having ionic links in the main chain were synthesized[11] by the reaction of HMDI or TDI with 1:1 mixtures of zinc salts of mono(hydroxyethoxyethyl)phthalate $(ZnHEEP)_2$ and bisureas as shown in Scheme 1.4. The presence of ionic linkage in the polymers was confirmed by FT-IR spectra.



Scheme 1.4 Synthesis of zinc-containing polyurethane-ureas

In addition, They synthesized calcium-containing polyurethane-ureas by the reaction of HMDI or TDI with 1:1 mixtures of $Ca(HEEP)_2$ and each of the bisureas

[12]. Moreover, They synthesized a new series of metal-containing polyurethanes by the reaction of HMDI or TDI with metal salt of mono(hydroxypentyl)phthalate ($M(HPP)_2$, where M is Ca^{2+}, Cd^{2+}, Pb^{2+} or Zn^{2+})[13] as shown in Scheme 1.5.

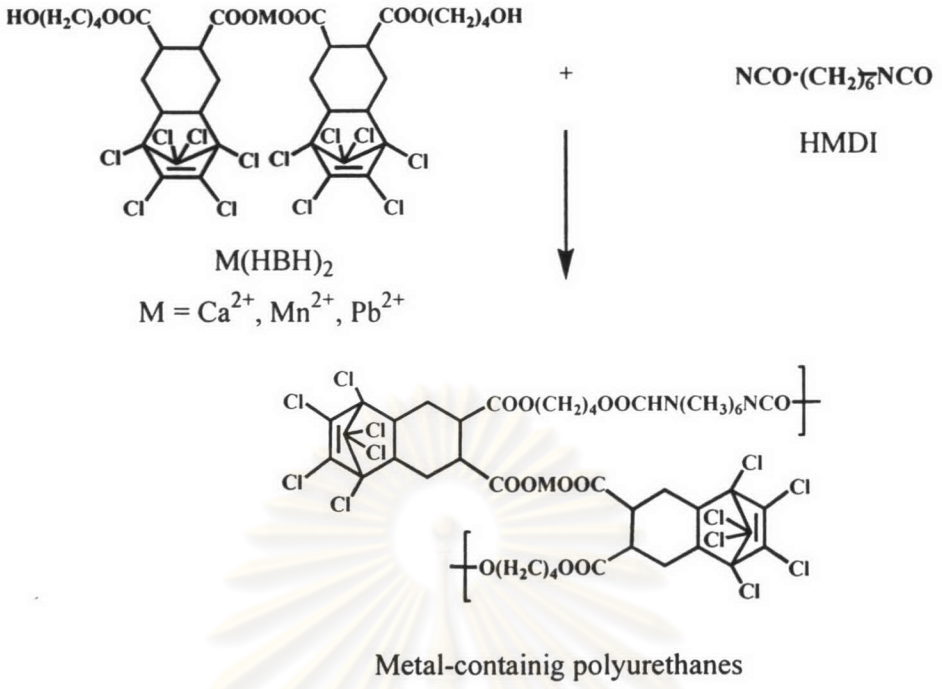


Scheme 1.5 Synthesis of metal containing copolyurethanes from $M(HPP)_2$ and HMDI or TDI.

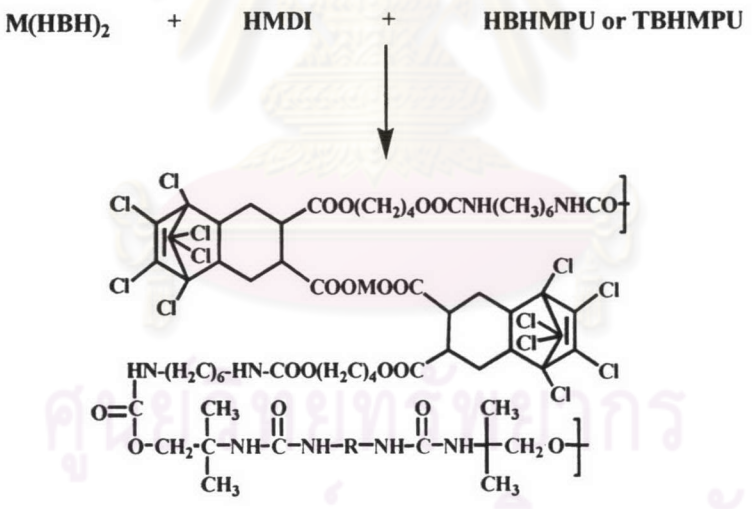
It was observed that metal-containing polyurethane-ureas showed higher stability than polyurethanes. That might be due to the higher number of hydrogen bonds and lower metal ions in polyurethane-ureas. However, TDI-based polymers showed higher thermal stability than HMDI-based polymers because of TDI-based polymers have the rigid aromatic ring in the polymer structure.

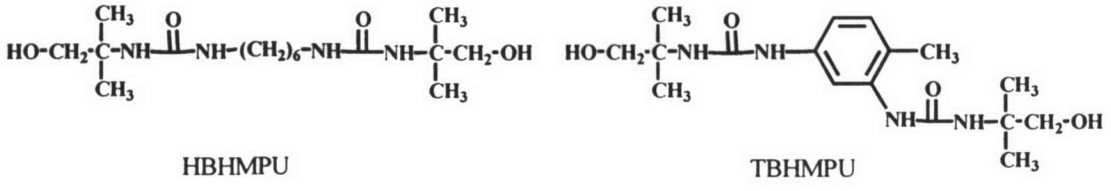
Nanjundan and coworker[14] synthesized metal-containing polyurethanes containing ionic linkages in the main chain by polyaddition reaction of hexamethylene diisocyanate (HMDI) with the divalent metal salt of mono(hydroxybutyl)hexolate $(MHBH)_2$ where metal were Ca^{2+}, Mn^{2+} and Pb^{2+} as shown in Scheme 1.6.

Polyurethane-ureas were prepared from the reaction of $M(HBH)_2$ with HMDI, hexamethylene *bis*[N'-(1-hydroxy-2-methyl-prop-yl](HBHMPU) or toluene 2,4-*bis* [N'-(1-hydroxy-2-methyl-prop-2-yl)urea] (TBHMPU) (Scheme 1.7).



Scheme 1.6 Synthesis of metal-containinig polyurethanes from $M(HBH)_2$ and HMDI



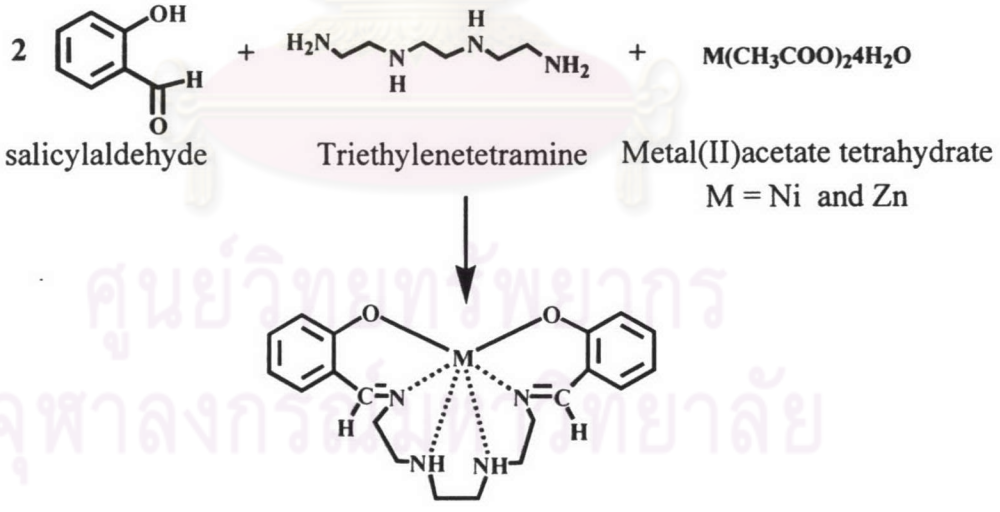


Scheme 1.7 Synthesis of metal-containing polyurethane-ureas from $M(HBH)_2$, HMDI and HBHMPU or TBHMPU

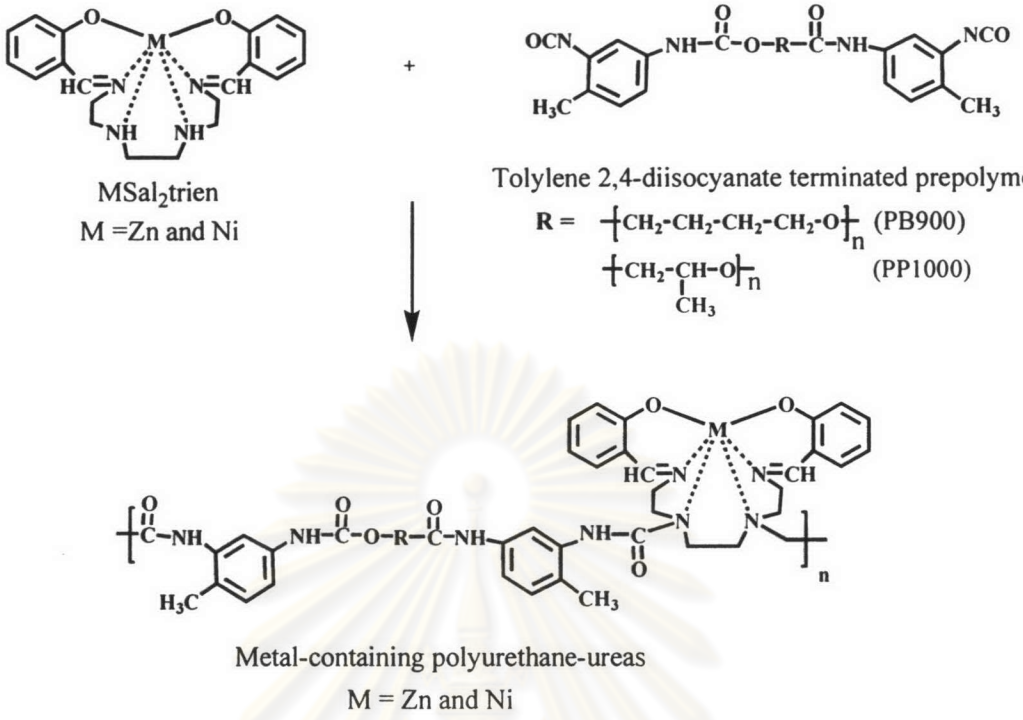
Thermal stability of metal-containing polyurethanes showed higher thermal stability than metal-containing polyurethane-ureas. TBHMPU-based polyurethane-ureas were slightly more stable than HBHMPU-based polyurethane-ureas due to the presence of aromatic rings in polymer chain.

In the same way, Caraculacu and coworker[15] reported a new diisocyanate containing a parabanic ring [1,3-bis(isocyanatophenyl)] by the reaction of diisocyanate with Mg salt of *p*-aminobenzoic acid, or with a mixture of aromatic diamines gave ionic polyureas. Matsuda[16-17] synthesized metal-containing polyureas and polyurethane-ureas based on 4-aminobenzoate salts.

From the previous works in our research group[18], metal-containing polyurethane-ureas were synthesized by the reaction of hexadentate Schiff base metal complexes and isocyanate-terminated polymers. The metal complexes were synthesized from the reaction between salicyaldehyde, triethylenetetramine and metal acetates as shown in Scheme 1.8. Polymerization of Schiff base metal complexes with the prepolymers yielded metal-containing polyurethane-ureas as shown in Scheme 1.9. It was found that the obtained polymers showed a good thermal stability.



Scheme 1.8 Synthesis hexadentate Schiff base metal complexes ($MSal_2trien$)

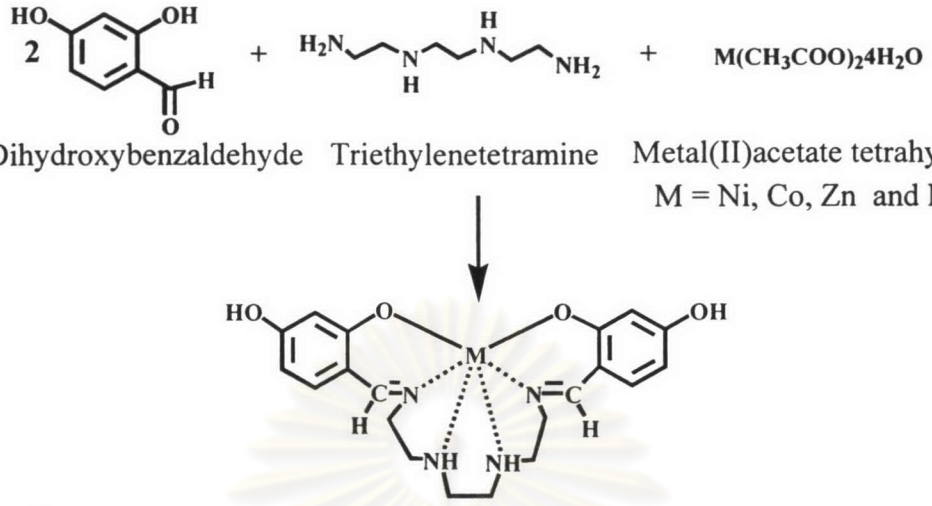


Scheme 1.9 Synthesis of metal-containing polyurethane-ureas from $MSal_2trien$ and PB or PP prepolymer

Objective and scope of the research

Since it was known that addition of hexadentate Schiff base metal complexes into the polymer structure could improve thermal property of the polymer. Therefore, the target of this research was to synthesize new hexadentate Schiff base metal complexes and used these complexes in the synthesis of metal-containing polyurethane-ureas. The metal complexes employed in this study were 4,4'-dihydroxysaltrien metal complexes, which contain two amino groups and two hydroxyl groups that can undergo polymerization reaction with diisocyanate compounds to yield metal-containing polyurethane-ureas with good thermal stability.

In the first step, 4,4'-dihydroxysaltrien metal complexes (ML) were synthesized from the reaction between 2,4-dihydroxybenzaldehyde, triethylenetetramine and metal acetates where the metals employed were Mn, Co, Ni and Zn as shown in Scheme 1.10.

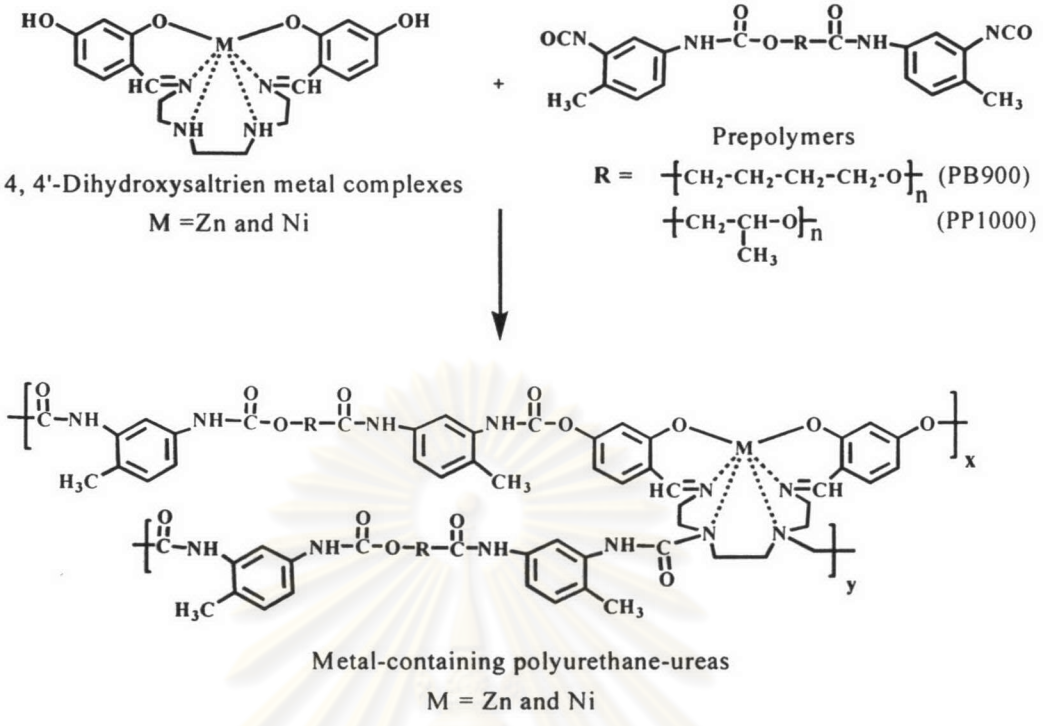


Scheme 1.10 Synthesis of hexadentate Schiff base metal complexes (ML)

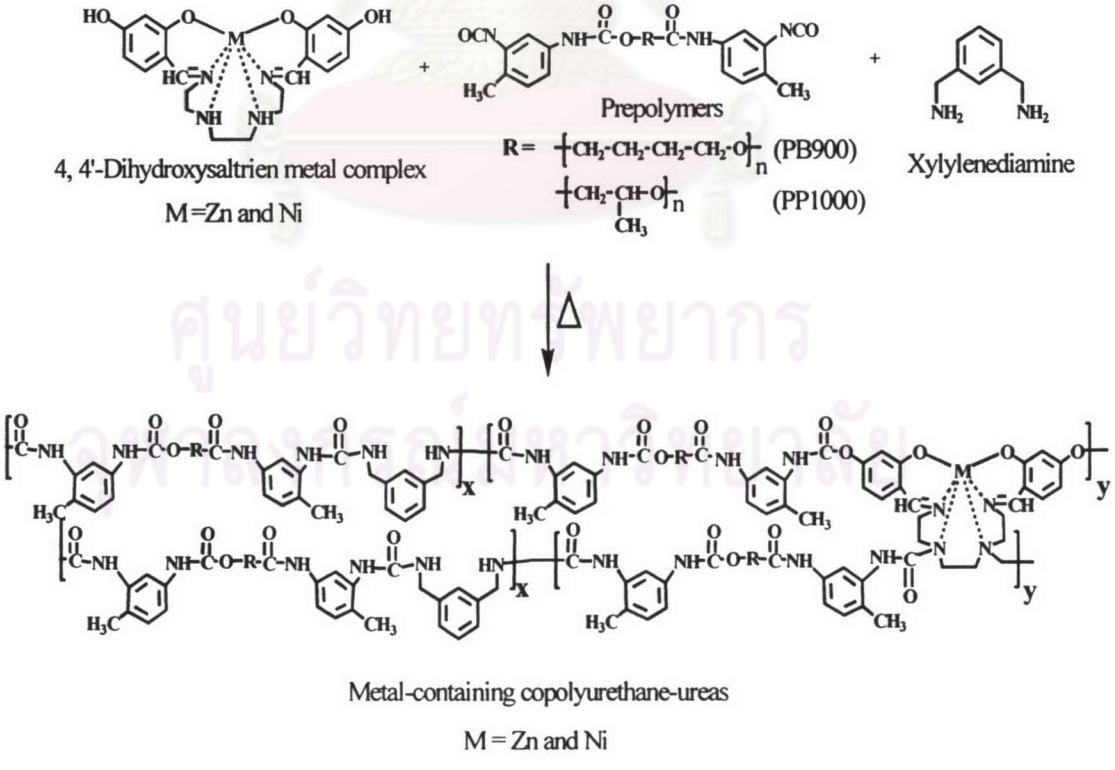
In the next step, polyurethane-ureas containing 4,4'-dihydroxysaltrien metal complexes in polymer chain have been synthesized from the reaction between 4,4'-dihyroxysaltrien metal complexes and prepolymers, namely tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer (PB900), MW 900 g/mol and tolylene 2,4-diisocyanate terminated poly(propylene glycol) (PP1000), MW 1000 g/mol (Scheme 1.11).

The metal-containing copolyurethane-ureas were synthesized from the reaction between ML, *m*-xylylenediamine and tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer (PB900), MW 900 g/mol and tolylene 2,4-diisocyanate terminated poly(propylene glycol) (PP1000), MW 1000 g/mol (Scheme 1.12).

Finally, metal-containing polyurethane-ureas and copolyurethane-ureas were characterized by IR spectroscopy. The polymer property investigated was their thermal stability which was determined using thermogravimetric analysis (TGA).



Scheme 1.11 Synthesis of metal-containing polyurethane-ureas



Scheme 1.12 Synthesis of metal-containing copolyurethane-ureas