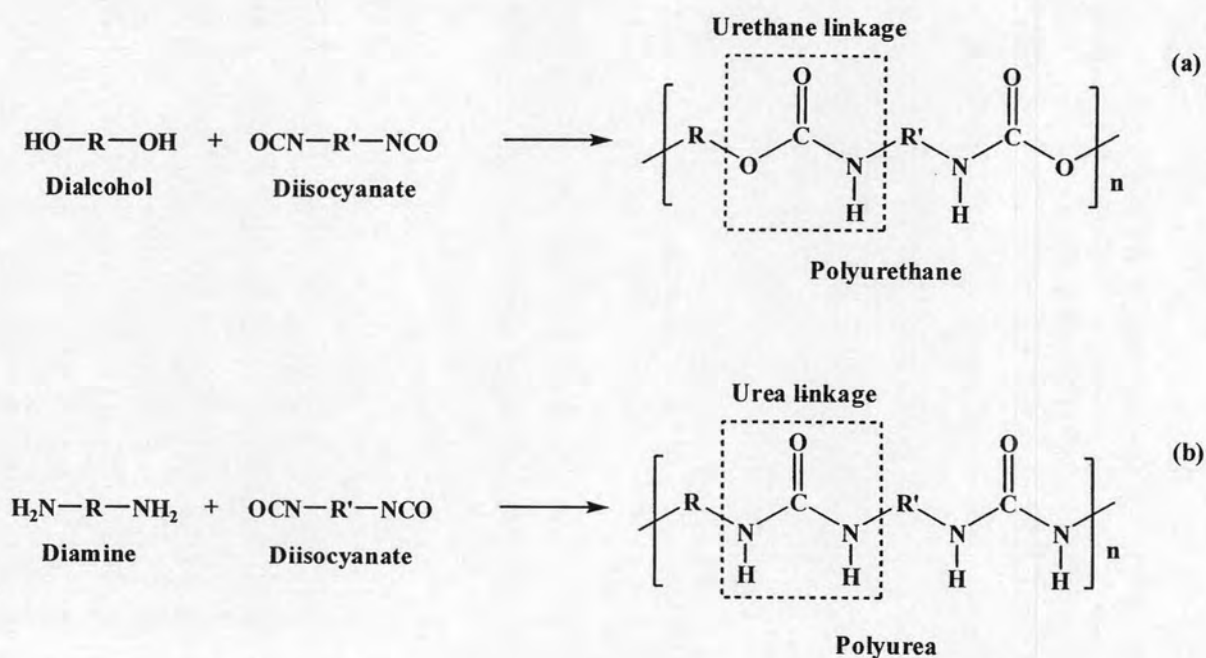


CHAPTER II

THEORY AND LITERATURE REVIEW

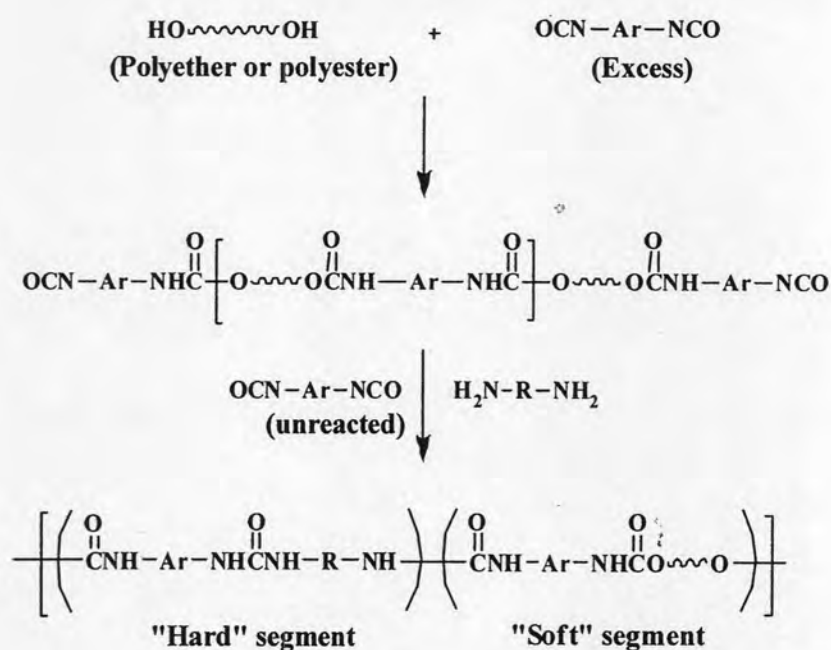
2.1 Polyurethanes

Polyurethane [1-7] is a polymer in which the repeating unit contains a urethane linkage. The urethane linkage results most through the reaction of an isocyanate with an alcohol (Scheme 2.1). Polyurethane can also contain a urea linkage and these are formed when an isocyanate reacts with an amine resulting in a poly(urethane-urea). Polyurea is prepared by the reaction between diisocyanates and diamines that formed urea linkage (Scheme 2.1).



Scheme 2.1 (a) The reaction between diisocyanate and dialcohol to give polyurethane; (b) the reaction between diisocyanate and diamine to give polyurea

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).

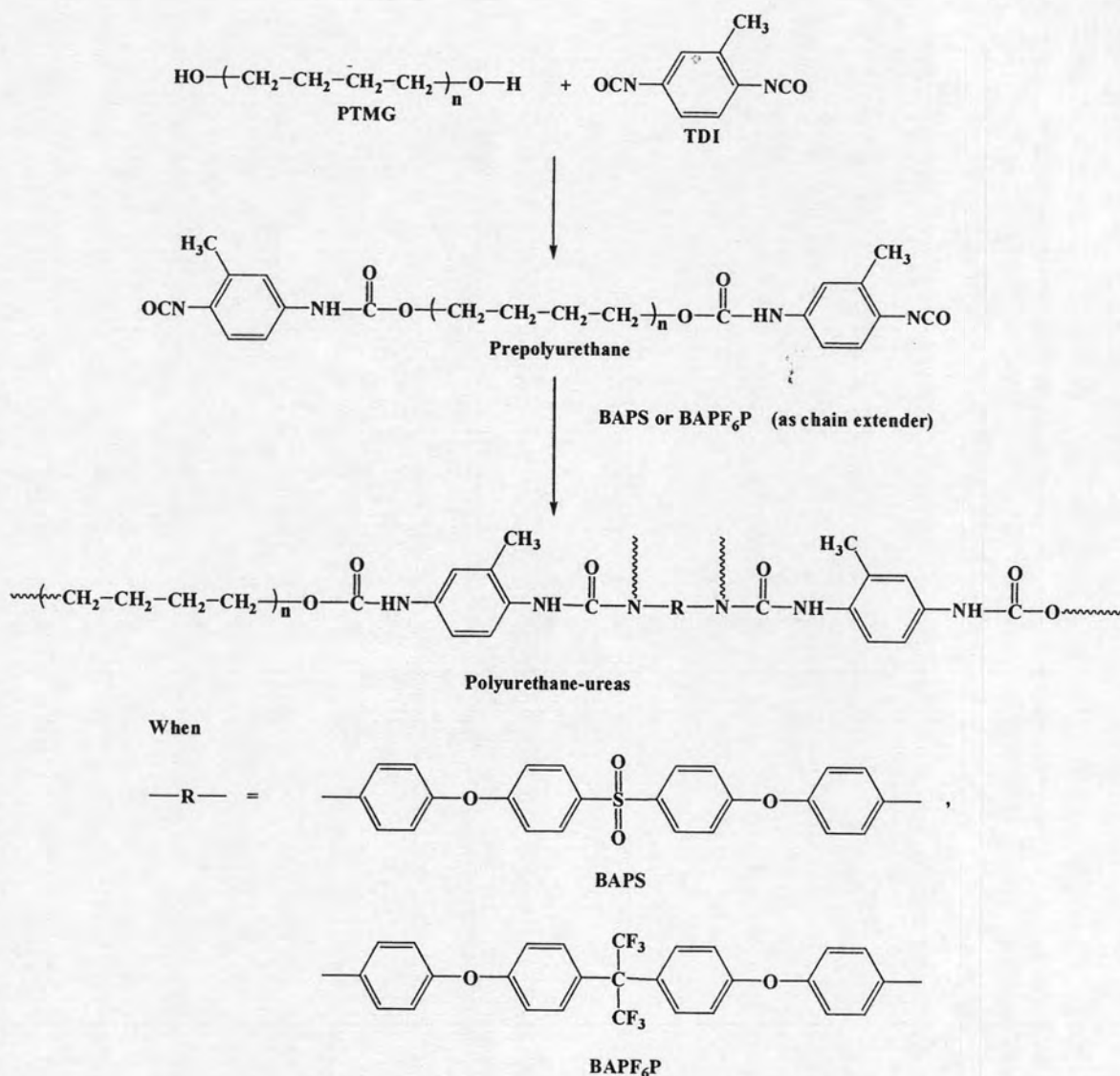


Scheme 2.2 Synthesis of polyurethane elastomers [32]

Polyurethanes were discovered by Otto Bayer *et al.* in the 1930s. Since then, they have found multitude of applications. Polyurethanes and polyureas can be found in products such as furniture, coatings, adhesives, constructional materials, fibers, padding, paints, elastomers and synthetic skins. Polyurethanes and polyureas are therefore a whole family of specialty polymers that cover a wide range of physical and mechanical properties. They exhibit excellent adhesion to many substances, abrasion resistance and resistance to degradation by water, oils and solvent. Although they are excellent polymers, they are found to be insoluble in common organic solvents that limited their applications due to difficulty in processing and they also exhibit low resistance to heat. In order to improve thermal stability, fire retardancy, flexibility and solubility of the polymers, chemical modification of their structure is used via e.g. the incorporation of flexible or bulky group [8, 9], imide group [10, 11], thermally stable heterocyclic or aromatic group [12-17].

Qin and coworkers [18, 19] synthesized fluorine-containing polyurethane-urea (FPU) and sulfone-containing polyurethane-urea (SPUU). FPU was prepared from the reaction between toluene diisocyanate (TDI), poly(tetramethylene glycol) (PTMG) and 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BAPF₆P). SPUU was prepared from the reaction between toluene diisocyanate (TDI), poly(tetramethylene

glycol) (PTMG) and bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS). The reactions were shown in Scheme 2.3.



Scheme 2.3 Preparation of polyurethane-ureas based on BAPS and BAPF₆P

The T_g of FPU and SPUU were -26.3°C and -34.2°C respectively. The polymers were soluble in polar organic solvent such as 1,4-dioxane, DMF, and DMSO. The TGA results showed that the temperature at weight loss 5% and 50% were $310\text{--}312^\circ\text{C}$ and $448\text{--}455^\circ\text{C}$, respectively.

The other method that can improve the thermal property of polymer is the incorporation of metal containing group into the polymer backbone.

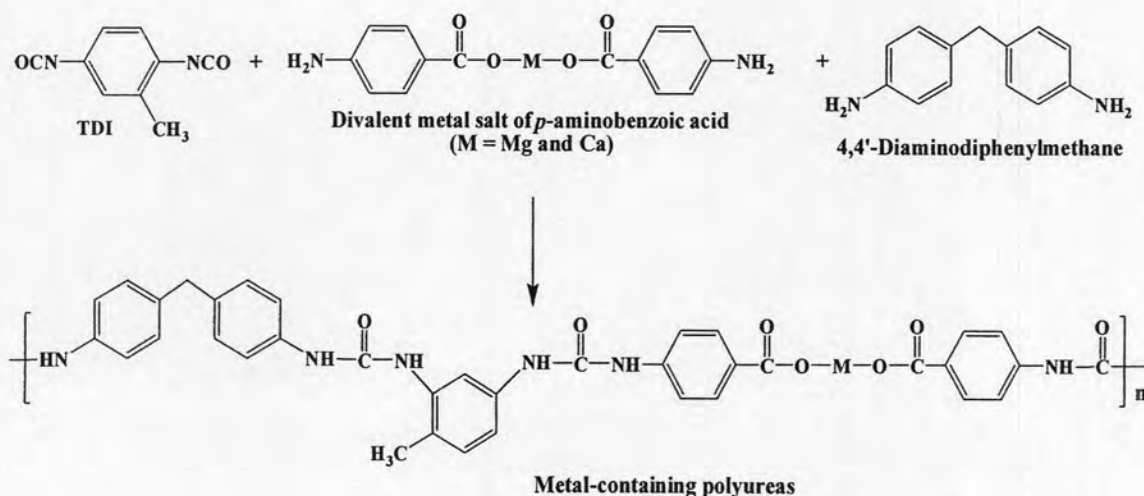
2.2 Metal-containing polymers

Metal-containing polymers are an important class of thermally stable or heat resistant polymers. This research area is widely investigated [20-31]. 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 [23].

2.3 Literature review

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

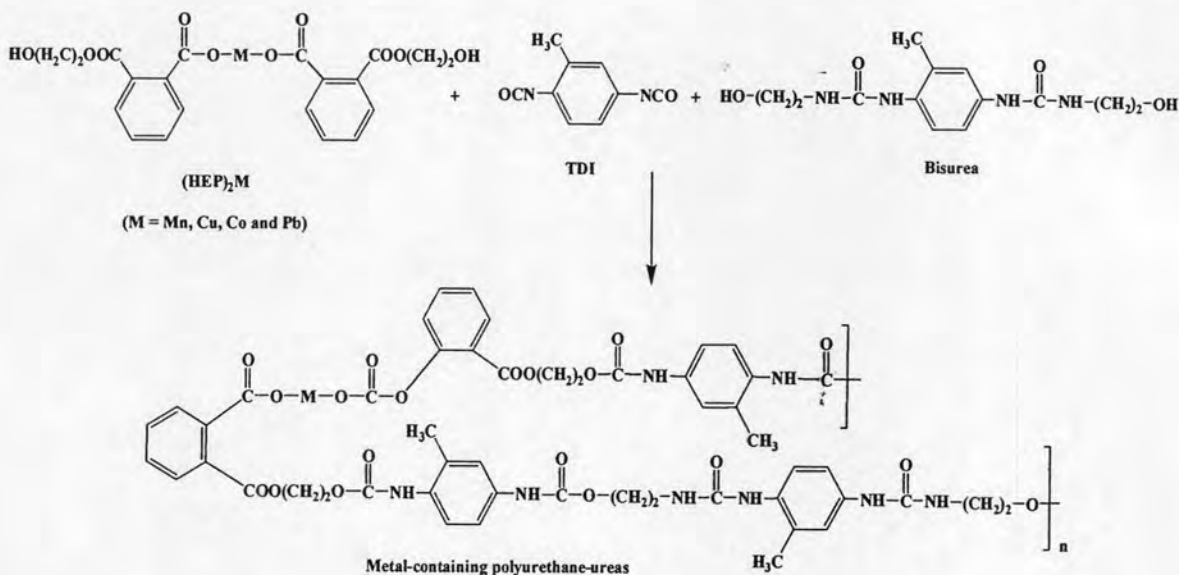
Matsuda and Takechi [24] synthesized metal-containing polyureas having ionic links in the main chain by polyaddition reaction of 2,4-toluene diisocyanate (TDI) with mixtures of divalent metal salts of *p*-aminobenzoic acid and 4,4'-diaminodiphenylmethane (Scheme 2.4). It was found that thermal stability of the polyureas increased markedly with an increase in metal content.



Scheme 2.4 Synthesis of metal-containing polyureas from 2,4-toluene diisocyanate, of *p*-aminobenzoic acid and 4,4'-diaminodiphenylmethane [24]

Rajalingam and Radhakrishnan [25] synthesized polyurethane-ureas from mono(hydroxyethyl)phthalate (HEP)₂M (where M = Mn, Cu, Co and Pb), toluene

diisocyanate (TDI) and a bisurea which was prepared from 2-aminoethanol and TDI as shown in Scheme 2.5.

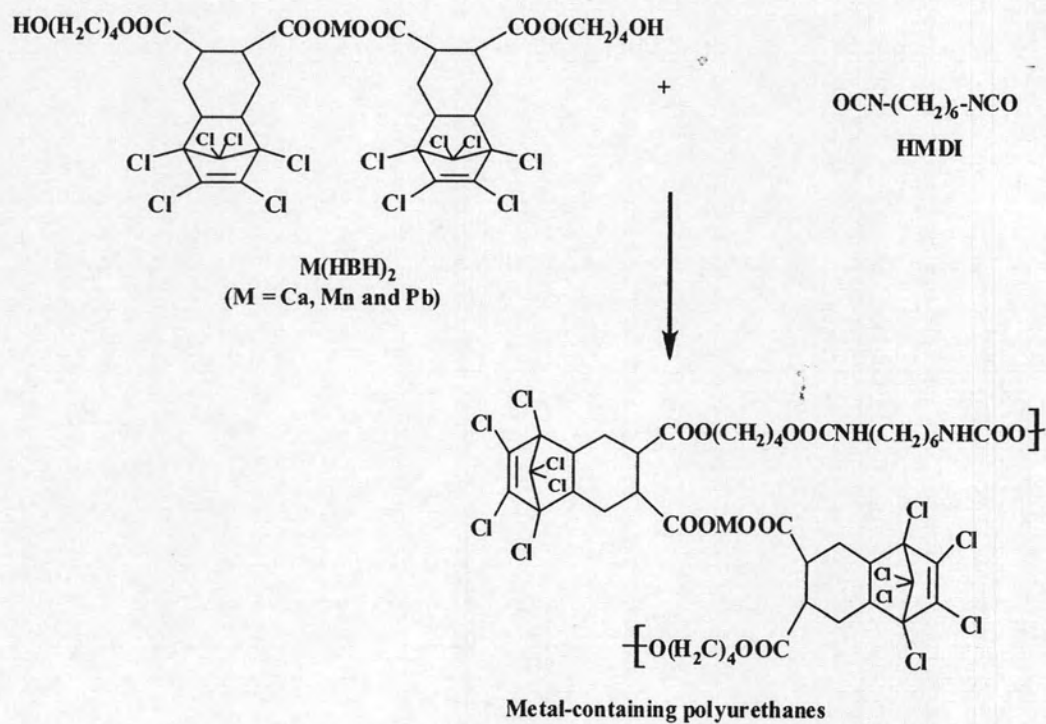


Scheme 2.5 Synthesis of metal-containing polyurethane-ureas from toluene diisocyanate, bisurea and mono(hydroxyethyl)phthalate (HEP)₂M (where M = Mn, Cu, Co and Pb) [25]

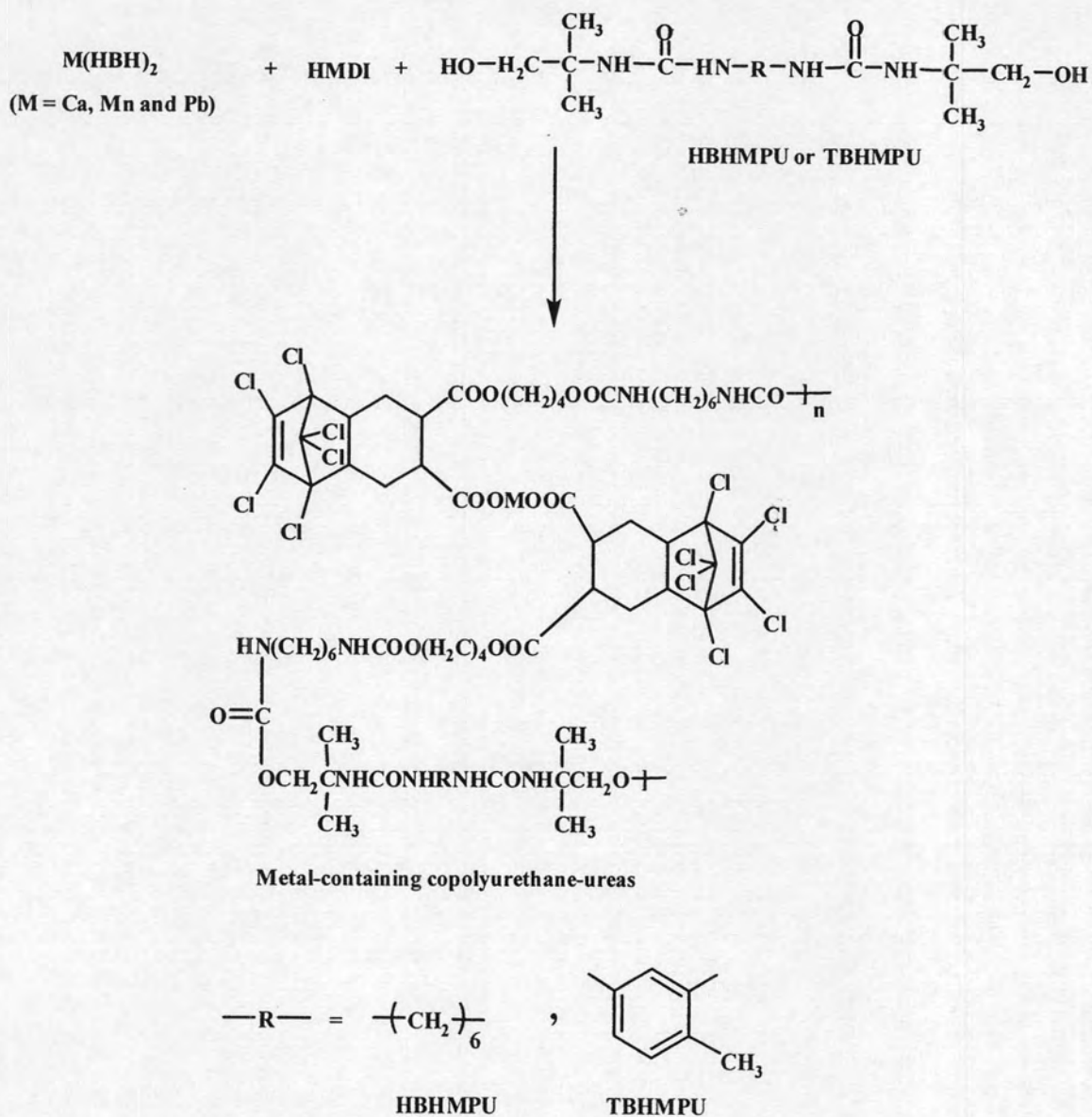
The initial 10% weight loss for all the polymers occurred in the temperature range 185-200°C. The thermal stability of the four metal-containing polyurethane-ureas was in the order Mn > Pb > Cu > Co because Mn-polyurethane-ureas had the highest activation energies and Mn²⁺ exhibits a thermally more stable ionic link in the backbone chain of polyurethane-urea by the support of the d⁵ orbital.

Prasath and coworkers [26] prepared flame-retardant metal-containing polyurethanes and polyurethane-ureas by the polyaddition condensation of hexamethylene diisocyanate (HMDI) with the divalent metal salts of mono(hydroxybutyl)hexolate [M(HBH)₂] and the latter from HMDI with a 1:1 mixture of M(HBH)₂ and hexamethylene bis[N'-(1-hydroxy-2-methyl-pro-2-yl)urea] (HBHMPU) or tolyllene 2,4-bis[N'-(1-hydroxy-2-methyl-pro-2-yl)urea] (TBHMPU). The reactions were shown in Schemes 2.6 and 2.7. 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.

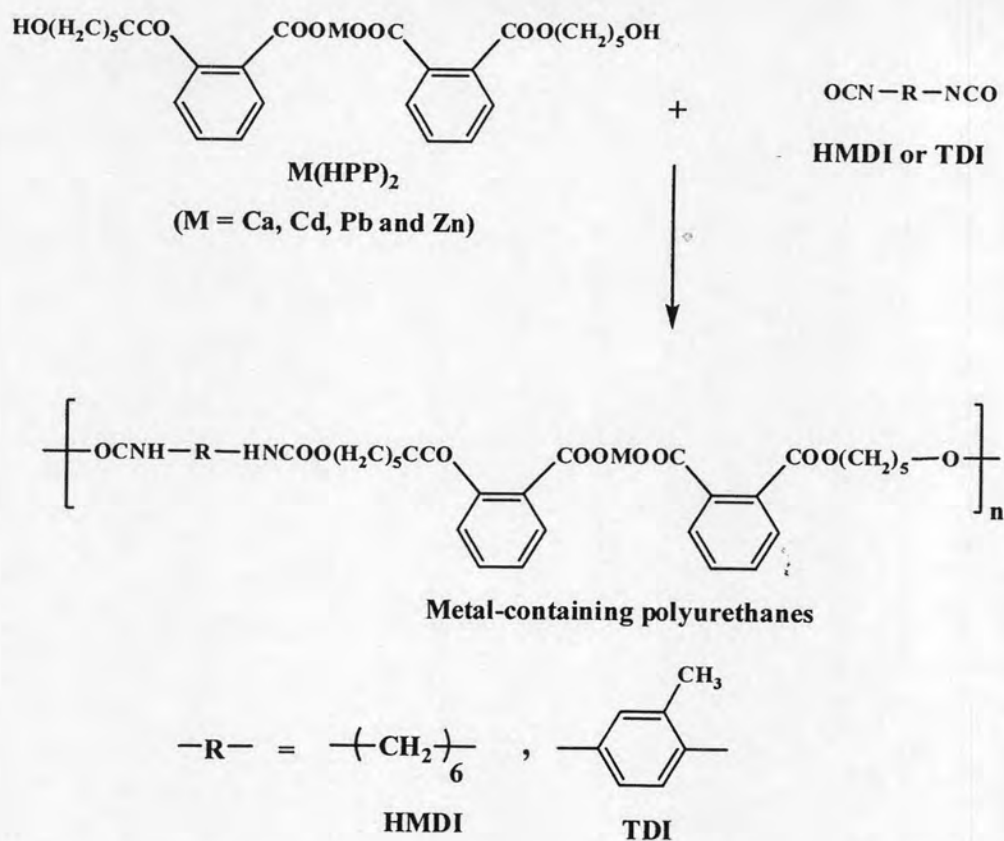


Scheme 2.6 Synthesis of metal-containing polyurethanes from M(HBH)_2 and HMDI [26]



Scheme 2.7 Synthesis of metal-containing polyurethane-ureas from HMDI with a 1:1 mixture of M(HBH)_2 and HBHMPU or TBHMPU [26]

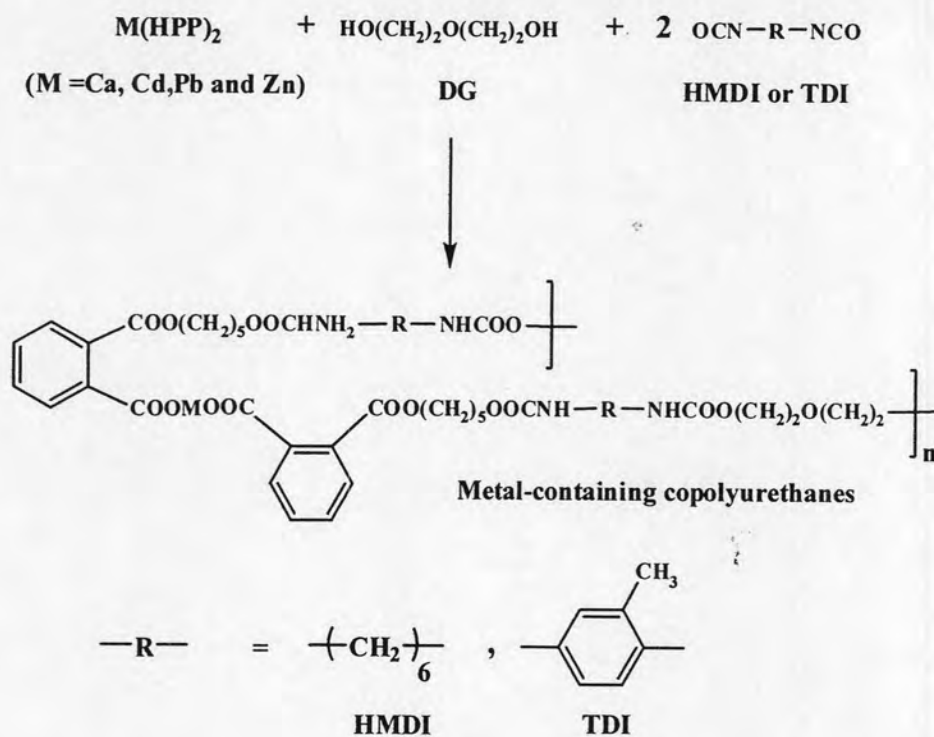
Jayakumar and coworkers [27] reported a synthesis of metal-containing polyurethanes by the reaction of HMDI or TDI with metal salts of mono (hydroxypentyl)phthalate [M(HPP)_2 , $\text{M} = \text{Ca, Cd, Pb and Zn}$] as shown in Scheme 2.8.



Scheme 2.8 Synthesis of metal-containing polyurethanes from M(HPP)_2 and diisocyanates [27]

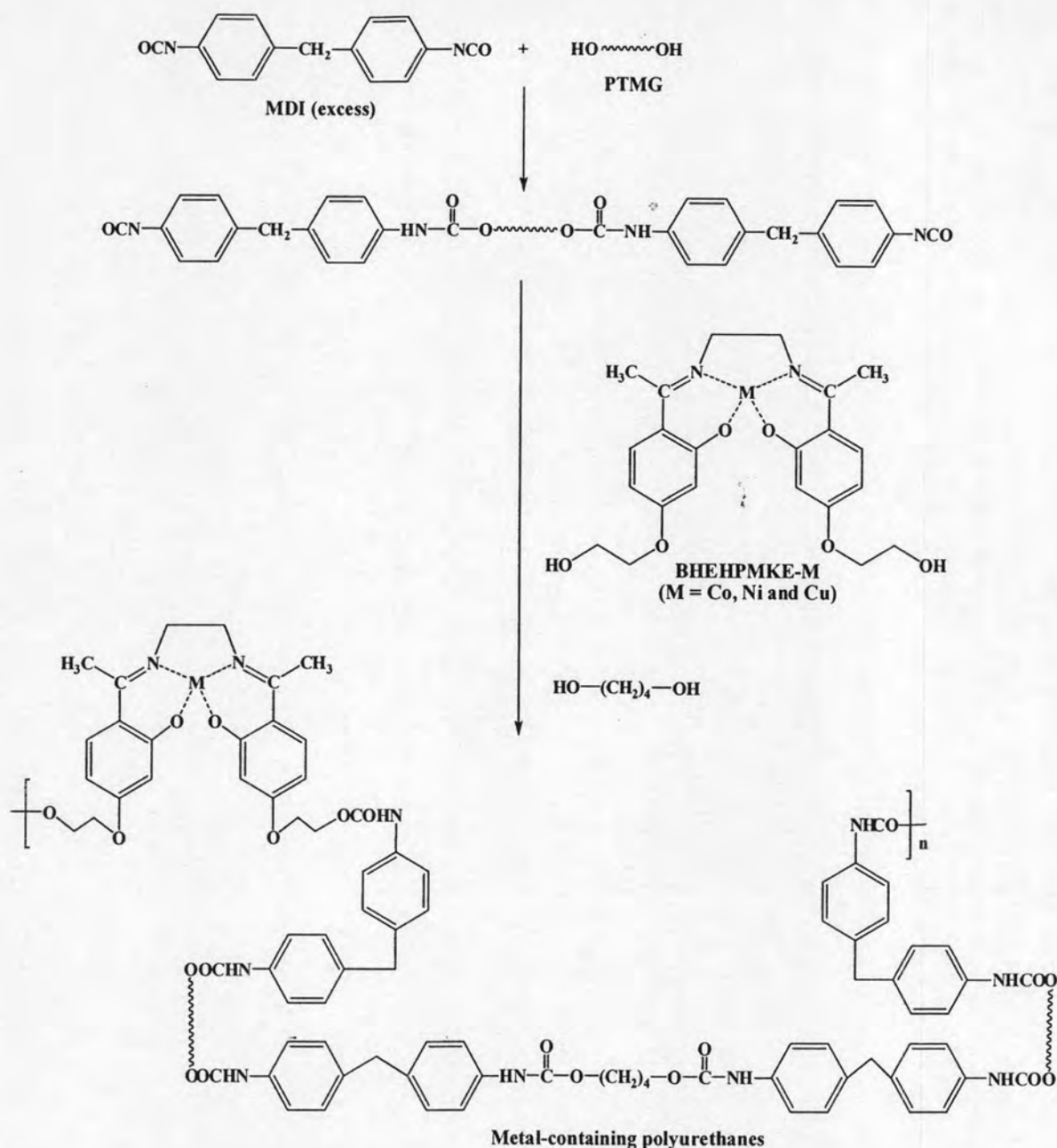
Furthermore, their work also involved the synthesis of copolyurethanes by reacting the diisocyanates with 1:1 mixtures of M(HPP)_2 and diethylene glycol (DG) (Scheme 2.9) [28]. It was observed that T_g values of the TDI-based copolyurethanes were slightly higher than those of the HMDI-based polymers, due to partial crystalline nature of HMDI-based polymers. In both series, the T_g values of the metal-containing polyurethanes follow the order $\text{Ca} > \text{Zn} > \text{Cd} > \text{Pb}$. This order may be attributed to the fact that with an increase in the size of the metal atom, the free volume of the polymer increased and the T_g value decreased.

The TGA curves of TDI-based polyurethanes indicated that the TDI-based polyurethane showed higher thermal stability than HMDI-based polyurethane because of the additional aromatic ring present in the polymer backbone.



Scheme 2.9 Synthesis of metal-containing polyurethanes from M(HPP)_2 , diethylene glycol and diisocyanates [28]

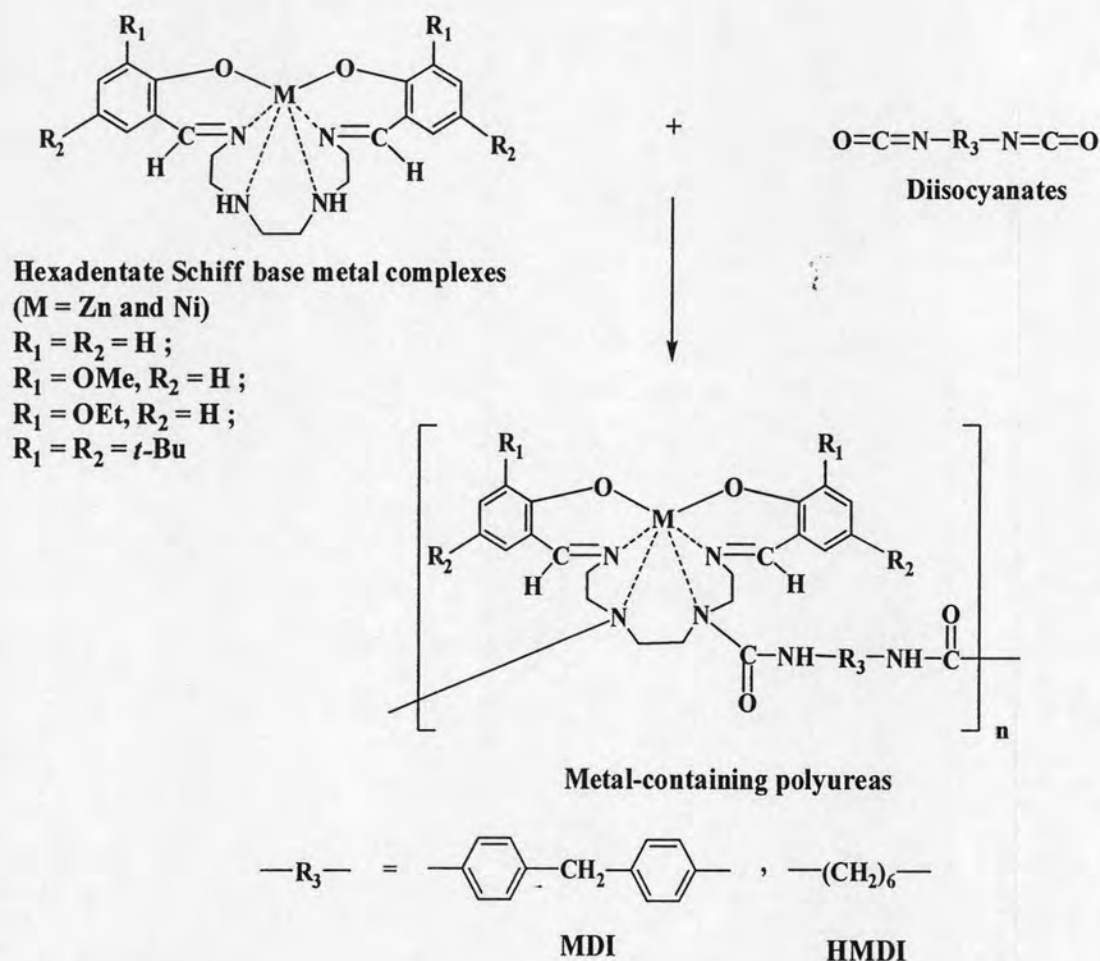
Senthikumar and coworkers [29] prepared metal-containing polyurethane elastomers by using tetradentate Schiff base metal complexes which is 1,2-bis[4-(2-hydroxy)ethoxy-2-hydroxyphenyl]methyl ketimino]ethane-metal (II) (BHEHPMKE-M; M = Co, Ni, Cu) and 1,4-butanediol as chain extenders for prepolymers based on poly(oxytetramethylene)glycol (PTMG) and MDI (Scheme 2.10). All the polyurethanes prepared with different metal-containing monomers show improved thermal stability compared to blank polyurethanes prepared using 1,4-butanediol and a Schiff base diol which does not contain metal. This improved thermal stability is due to the presence of heterocyclic ring structures in the metal-containing diol. The thermal stability of the polymer increased with increase in the amount of metal-containing diol. These polymers had the improved tensile strength compared to blank polymers and they were soluble in DMF and DMSO.



Scheme 2.10 Synthesis of metal-containing polyurethanes using metal coordinated tetradentate Schiff base diol [29]

From the previous works in our research group, Chantarasiri and coworkers [30] reported the synthesis and characterization polyureas from hexadentate Schiff base metal complexes and diisocyanates (Scheme 2.11). TGA results indicated that the polymers had high thermal stability. The initial decomposition temperatures (IDTs) and residual weights at 600 °C of the polymers were in the range 174-260 °C and 12-44%, respectively. When the polymers were obtained from the same metal complex, most MDI-based polymers exhibited higher IDTs than HDI-based polymers. This is

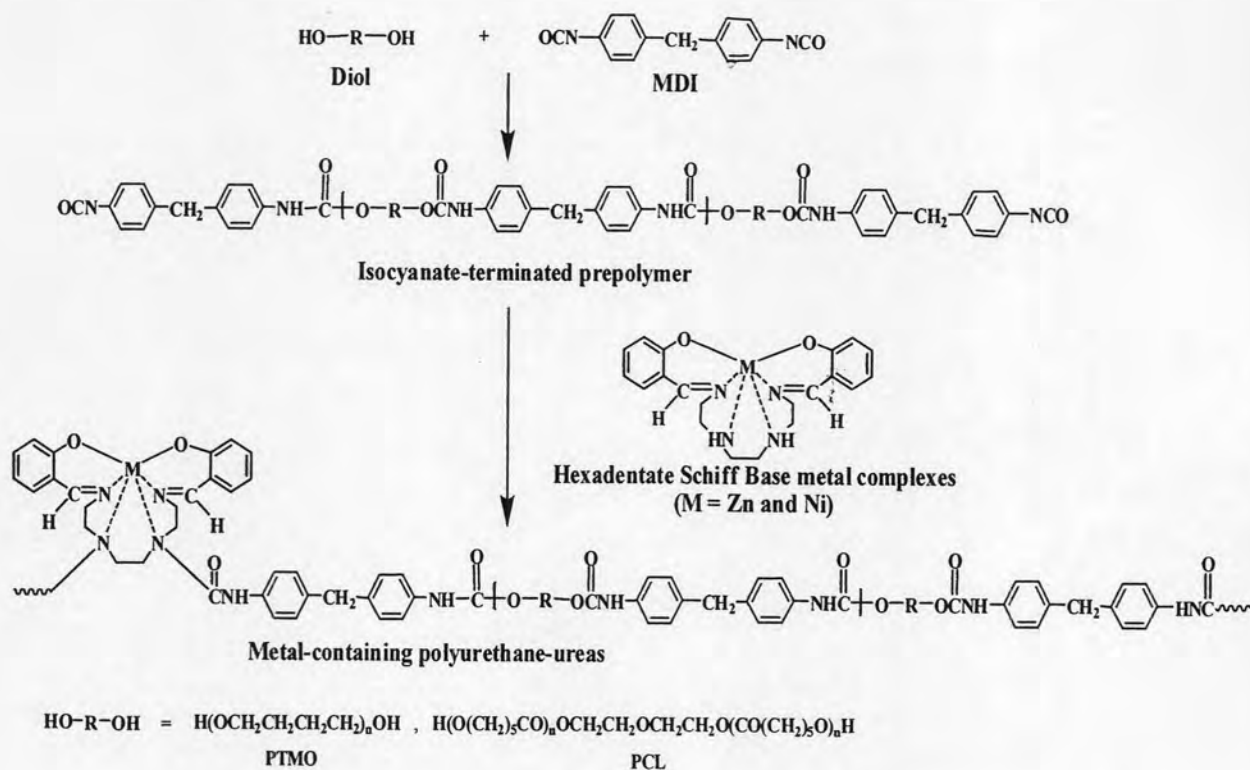
probably due to the presence of aromatic rings in the polymer chain. Most zinc-containing polyureas showed higher IDTs than nickel-containing polyureas. When $R_1 = \text{OMe}$ and $R_2 = \text{H}$, the metal-containing polyureas had the highest thermal stability. All the metal-containing polymers were soluble in DMSO.



Scheme 2.11 Synthesis of polyureas from the reaction between hexadentate Schiff base metal complexes and diisocyanates [30]

In addition, they synthesized polyurethane-ureas by reacting hexadentate Schiff base metal complexes ($R_1 = R_2 = \text{H}$) with MDI and polycaprolactone diol (PCL) or polytetramethylene oxide (PTMO) as shown in Scheme 2.12 [31]. The polymers were soluble in DMF and DMSO. The metal-containing polymers had higher thermal stability than metal free polymer and with an increase in the metal content, the thermal stability of the polymer increased. These polymers showed IDT in

the range 204 °C -271 °C, residual weights at 600 °C of the polymers were 18-32% and the decomposition temperature at weight loss 50% were 394-444 °C.

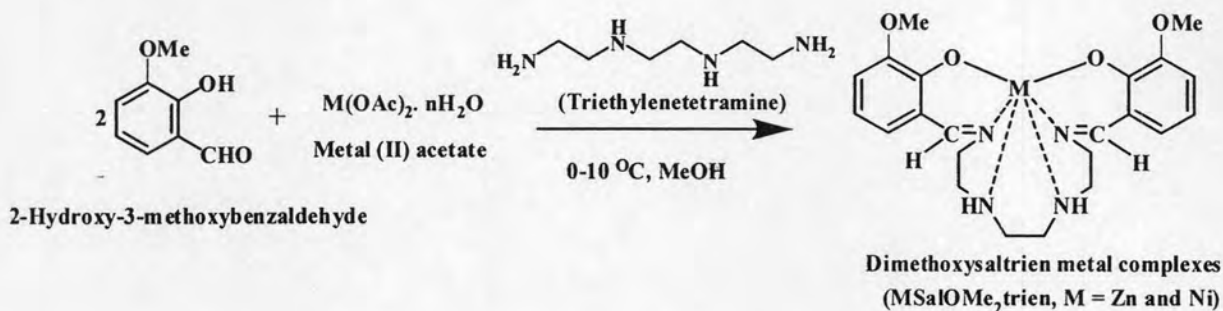


Scheme 2.12 Synthesis of metal-containing polyurethane-ureas from hexadentate Schiff base metal complex, PCL or PTMO and MDI [31]

2.4 Objectives and scope of the research

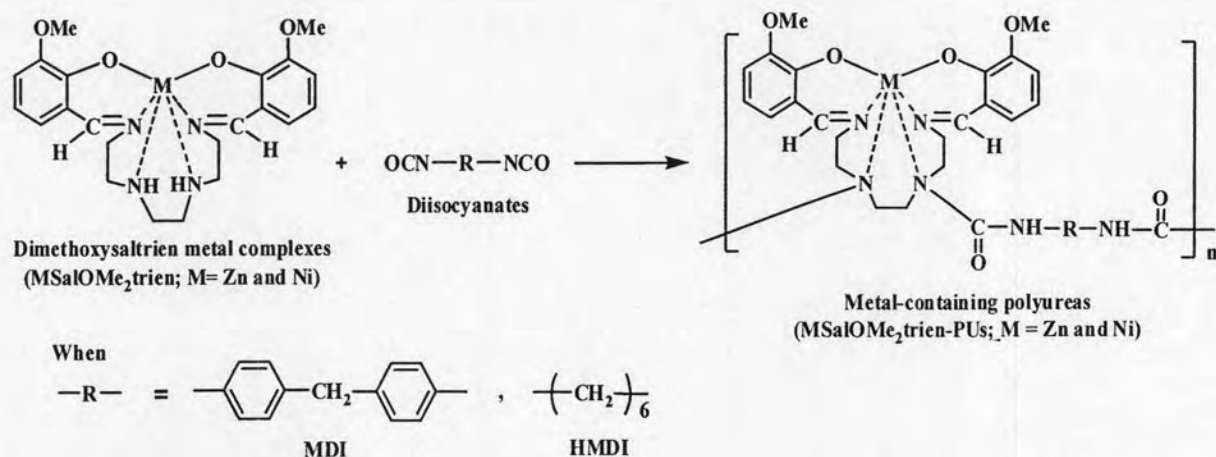
From the previous works in our research [30], the metal-containing polyureas based MSalOMe₂trien showed poor solubility in organic solvent but high thermal stability. The target of this research is to improve their solubility by synthesizing metal-containing polyurethane-ureas and copolyureas based on dimethoxysaltrien metal complexes (MSalOMe₂trien, M = Zn and Ni) with 4,4'-diphenylmethane diisocyanate (MDI) or hexamethylene diisocyanate (HMDI) and various dialcohols and diamines, respectively. It was expected that these polyurethane-ureas and copolyureas would show good thermal stability, good solubility and can be utilized at high temperature.

In the first step, MSalOMe₂trien were synthesized from the reaction between 2-hydroxy-3-methoxybenzaldehyde, triethylenetetramine and metal (II) acetate (M = Zn and Ni) [30] (Scheme 2.13).



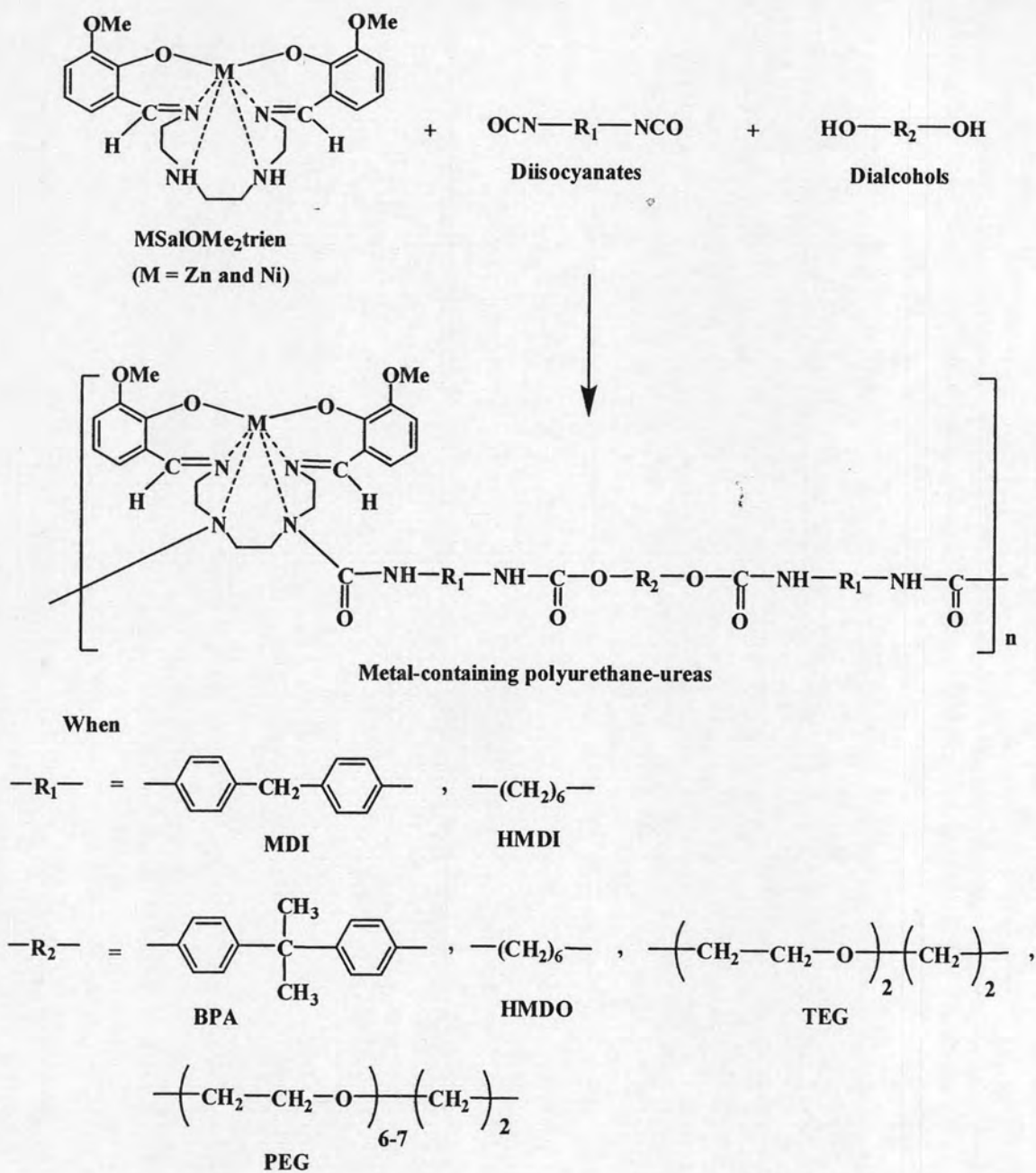
Scheme 2.13 Synthesis of hexadentate Schiff base metal complexes (MSalOMe₂trien, M = Zn and Ni) [30]

In the second step, metal-containing polyureas [30] were synthesized from the reaction between MSalOMe₂trien with MDI or HMDI in DMF as shown in Scheme 2.14.



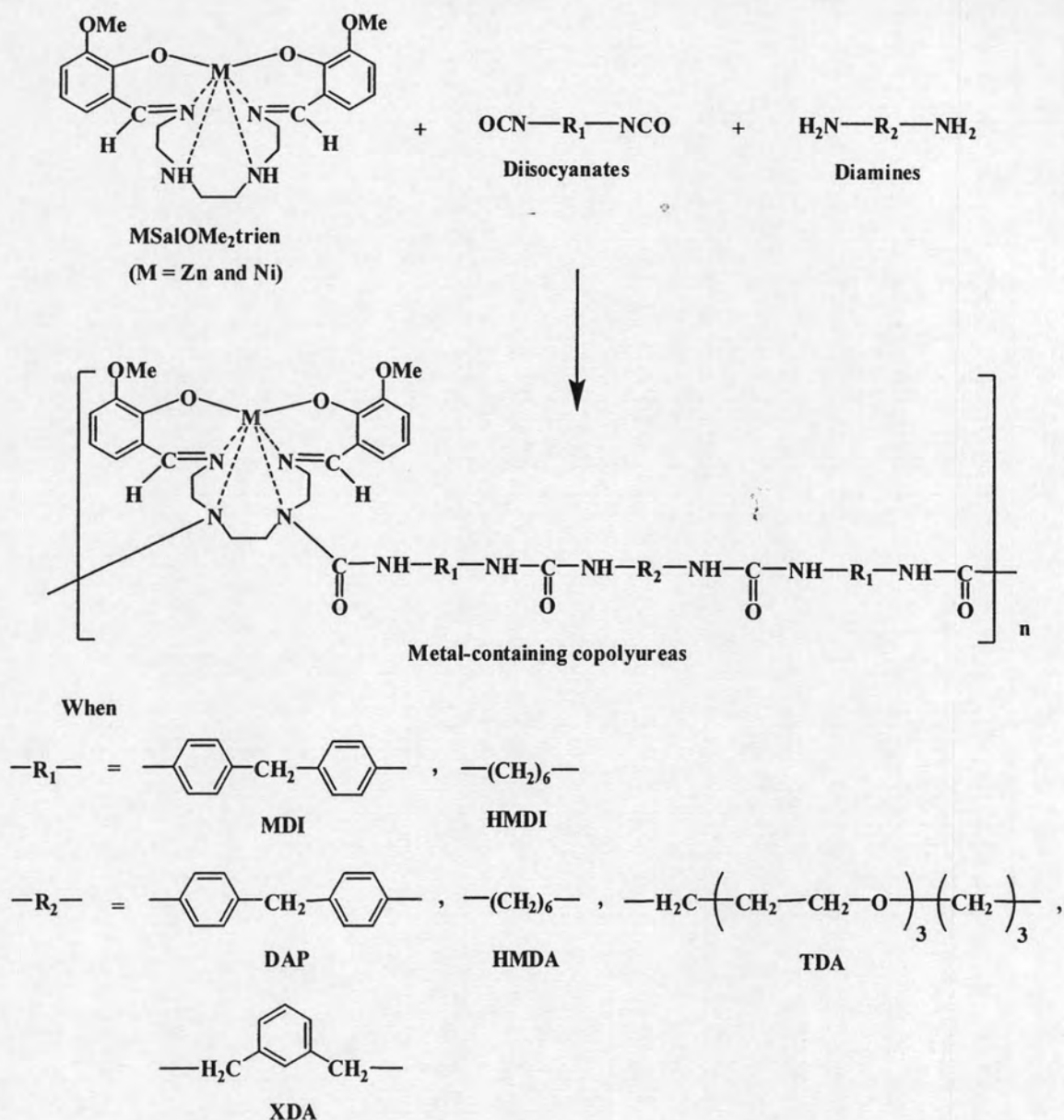
Scheme 2.14 Synthesis of metal-containing polyureas by reacting MSalOMe₂trien (M = Zn and Ni) with MDI or HMDI [30]

In the next step, metal-containing polyurethane-ureas [32] were synthesized from the reaction between MSalOMe₂trien with MDI or HMDI and dialcohols as shown in Scheme 2.15. The dialcohols used were bis(4-Hydroxyphenyl)propane (BPA), 1,6-hexanediol (HMDO), triethylene glycol (TEG), and polyethylene glycol (PEG, MW = 300).



Scheme 2.15 Synthesis of metal-containing polyurethane-ureas from MSalOMe₂trien (M = Zn and Ni), diisocyanates and dialcohols

Then metal-containing copolyureas were prepared by the reaction between MSalOMe₂trien with diisocyanates (MDI or HMDI) and diamines as shown in Scheme 2.16. The diamines used were hexamethylenediamines (HMDA), 4,4'-diaminodiphenylmethane (DAP), 4,7,10-trioxa-1,13-tridecanediamine (TDA), and *m*-xylylenediamine (XDA).



Scheme 2.16 Synthesis of metal-containing copolyureas from MSalOMe₂trien (M = Zn and Ni), diisocyanates and diamines

Finally, metal-containing polyureas, polyurethane-ureas and copolyureas were characterized by IR, ¹H-NMR, solubility and viscosity. Thermal properties of the polymers were investigated by TGA. Crystallinity was studied by XRD.