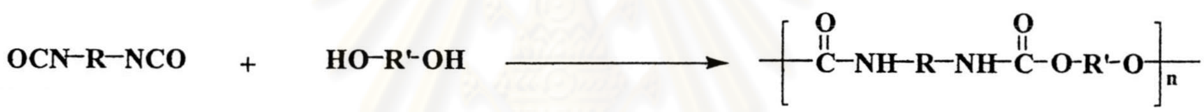
CHAPTER I

INTRODUCTION

1.1 Polyurethanes

The principal method of polyurethanes forming[1] that is important from the industrial perspective is the reaction of diisocyanate with dihydroxy compounds (Scheme 1.1).



Diisocyanate   Polyol   Polyurethane

Scheme 1.1 Principal method of polyurethane forming

Since the functionality of the polyol or the diisocyanate can be adjusted, a wide variety of branch or crosslinked polymers can be formed. The variety of reactants led to various kind of polyurethane products with a wide range of physical and mechanical properties. Polyurethane products include highly elastic foams (mattresses, cushions, car seats), rigid foams (insulation materials), rigid and flexible moldings with compact skins (window frames, housings). In addition, one of polyurethane products was polyurethane elastomer.

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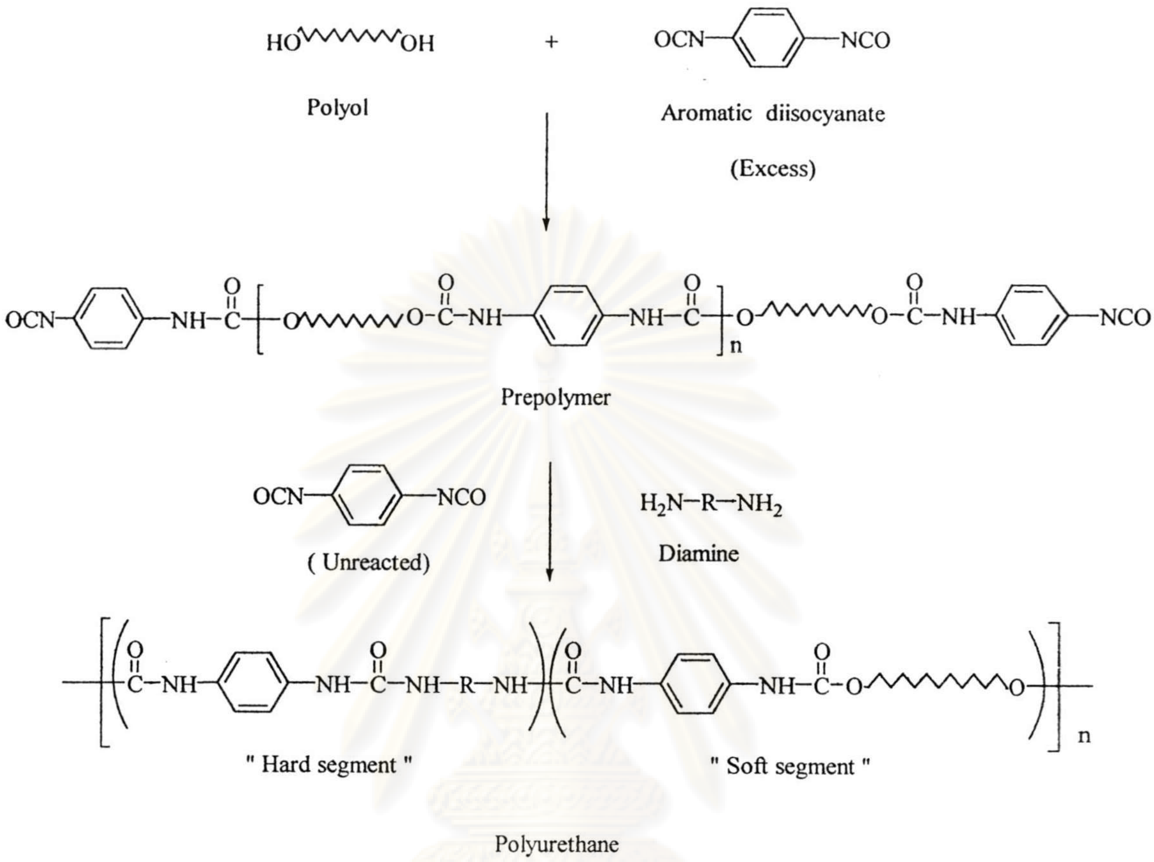
The most important polyurethane elastomer consists of elastomeric block copolymer containing alternative "soft" and "hard" segments. The sequence of the synthesis is shown in Scheme 1.2.



Scheme 1.2 Synthesis of an elastomeric polyurethane[2]

From a very wide range of properties that is available from chemical synthesis, polyurethane elastomers are used in a wide variety of products including membranes, seals, coating, woodworking industries such as protective edges for office furniture, adhesive and corrosion protection.

1.2 Metal-containing polyurethanes

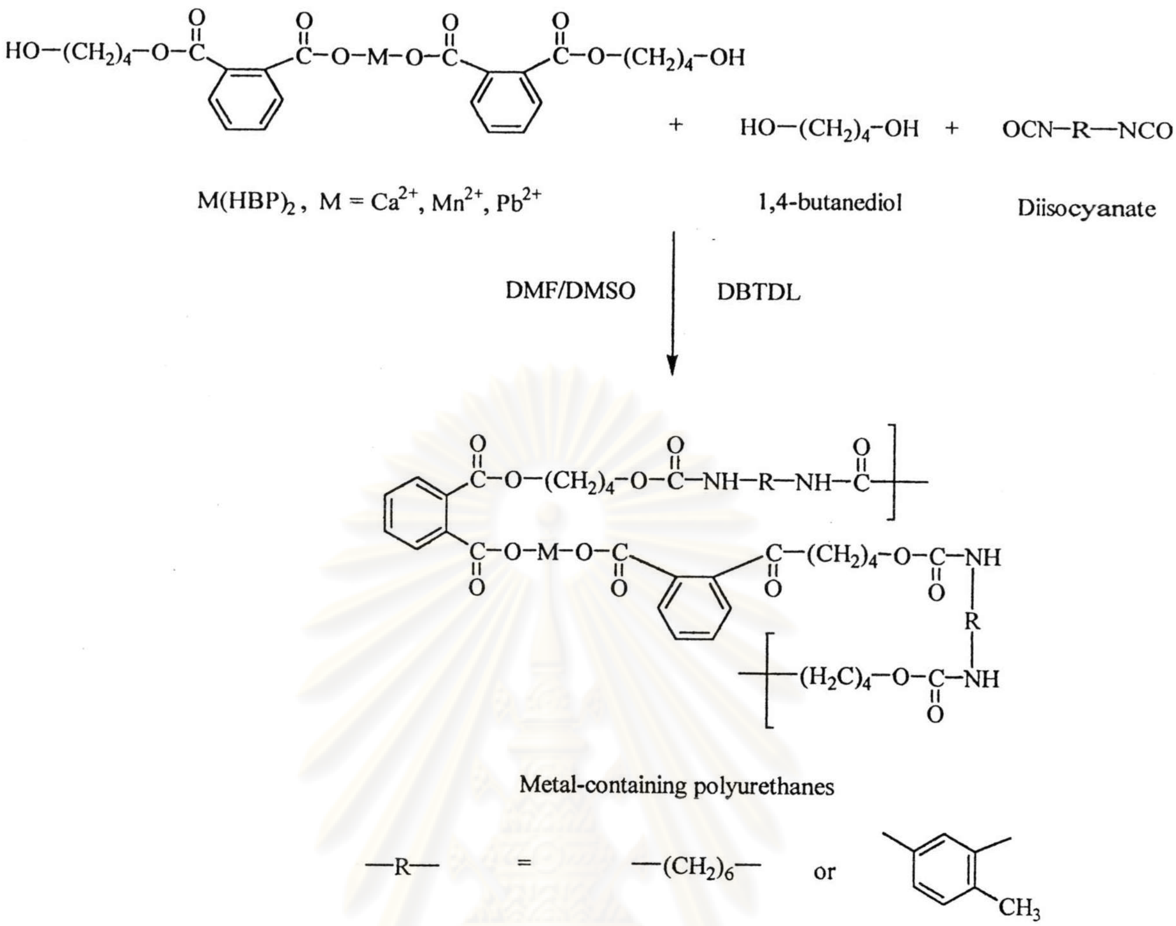
The metal-containing polymers have emerged in a large extent that poss a wide ranges of properties and used. These properties showed some advantage with respect to widely used thermoplastic elastomers for engineering applications such as high strength, solvent and chemical resistance, and especially high thermal stability. These properties make metal-containing polymer of interest for industries that mainly use these materials as aqueous thickness, textile sizers, adhesives, addition, resins, catalysts and in the field of medicine. Therefore organometallic polymers have been studied and characterized. One of them is metal-containing polyurethanes.

Polyurethanes are used in a wide variety of products including fibers, elastomer, foams, coating, and adhesive. The incorporation of metal into polyurethane give them superior properties, such as high strength and temperature stability, leading to a variety of applications. Metallo-polyurethane containing metal atom bound by coordinated such as metal complex system. Therefore, metal-containing polyurethane, polyurethane-ureas would possess ionic links and hence would be expected to have application in adhesives, coatings and biomedicine field.

1.3 Literature review

A number of metallo-polymers containing metal in the backbone of the polymer chain have been studied. The previous work from this laboratory was also synthesis and characterization of metal-containing polyurethanes and polyurethane-ureas.

Prasath and Nanjundan[3] synthesized metal-containing polyurethane containing ionic linkages in the main chain by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluene 2,4-diisocyanate with 1:1 mixture of divalent metal salts of mono(hydroxybutyl)phthalate [$M(HBP)_2$, M = Ca^{2+}, Mn^{2+} and Pb^{2+}], and 1,4-butanediol (Scheme 1.3). The structure and properties of metal-containing polyurethanes were studied.



Scheme 1.3 Synthesis of metal-containing polyurethanes from $M(HBP)_2$, 1,4 butanediol and diisocyanate

The TGA curves of 2,4-toluene diisocyanate (TDI)-based polyurethane indicated that the TDI-based polyurethane showed higher thermal stability than hexamethylene diisocyanate (HMDI)-based polyurethane because of the additional aromatic ring present in the polymer backbone.

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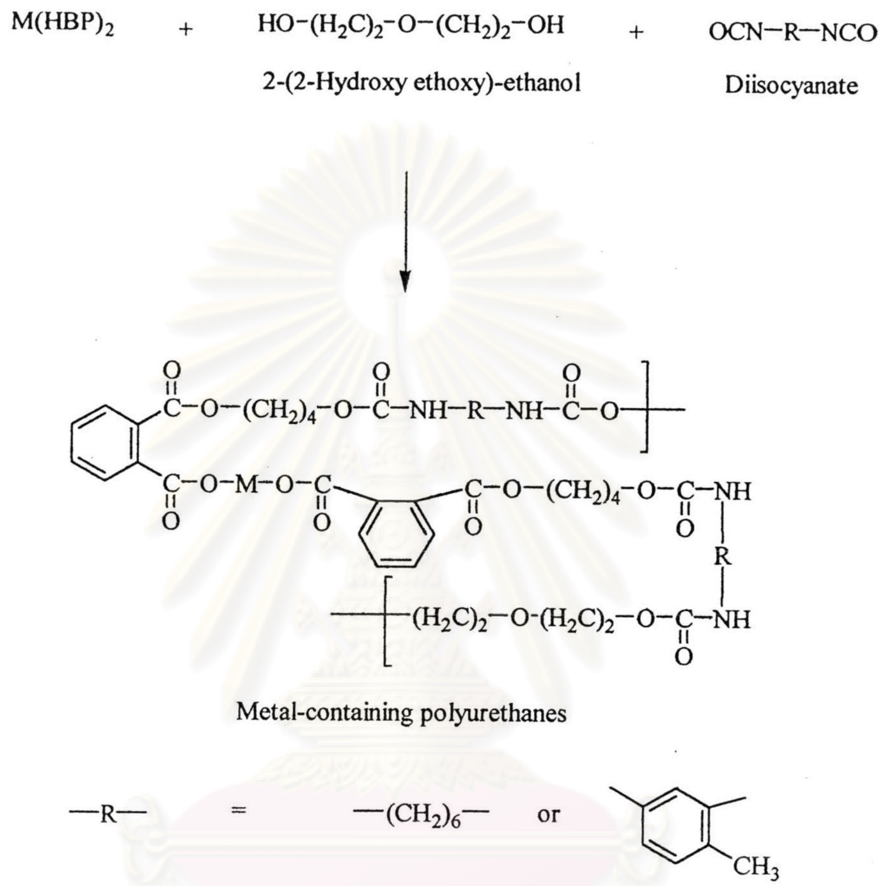
Another work of Prasath and Nanjundan[4] also involved the synthesis of metal-containing polyurethane by using different polyol. They use 2-(2-hydroxy ethoxy)-ethanol instead of 1,4-butanediol to synthesize polyurethanes containing ionic linkages in the main chain (Scheme 1.4).



Scheme 1.4 Synthesis of metal-containing polyurethanes from $M(HBP)_2$, 2-(2-hydroxy ethoxy)-ethanol and diisocyanate

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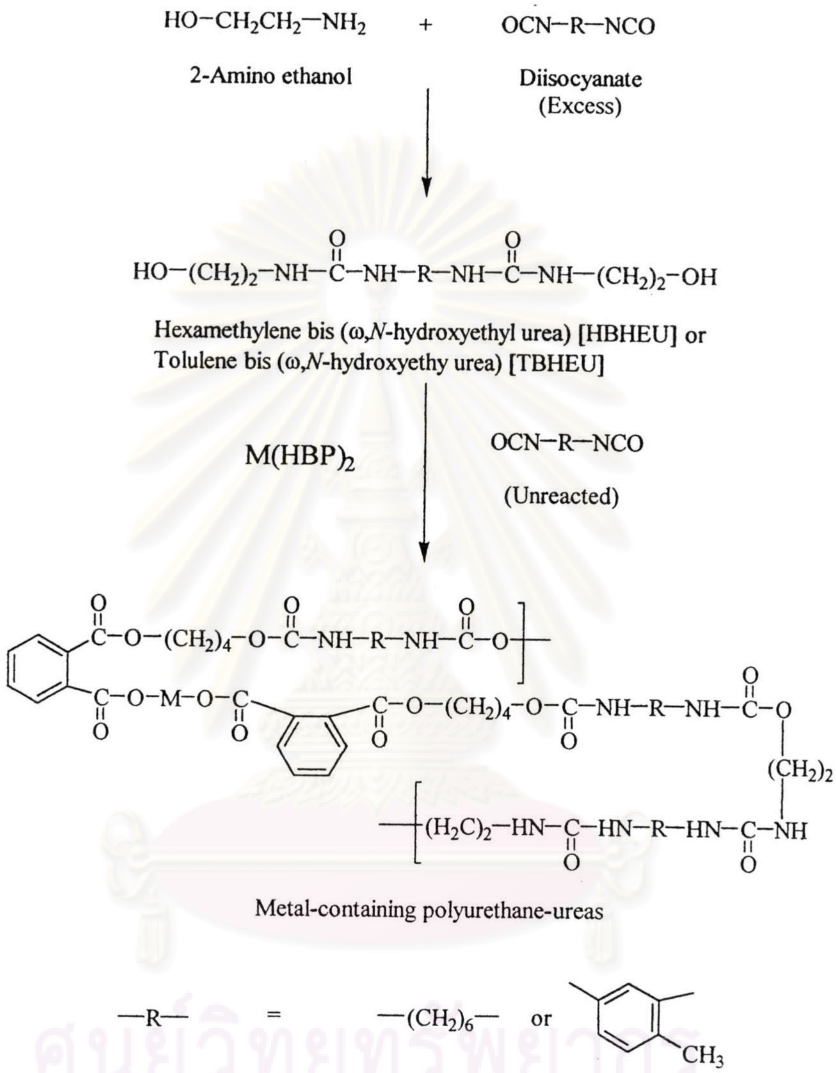
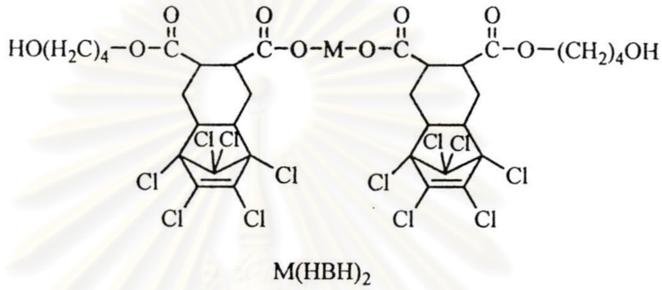
Furthermore, they synthesized polyurethane-ureas by reacting the diisocyanates with 1:1 mixture of hexamethylene bis(ω,*N*-hydroxyethylurea) (HBHEU) or toluene bis (ω,*N*–hydroxyethylurea) (TBHEU) and $M(HBP)_2$ (Scheme 1.5).



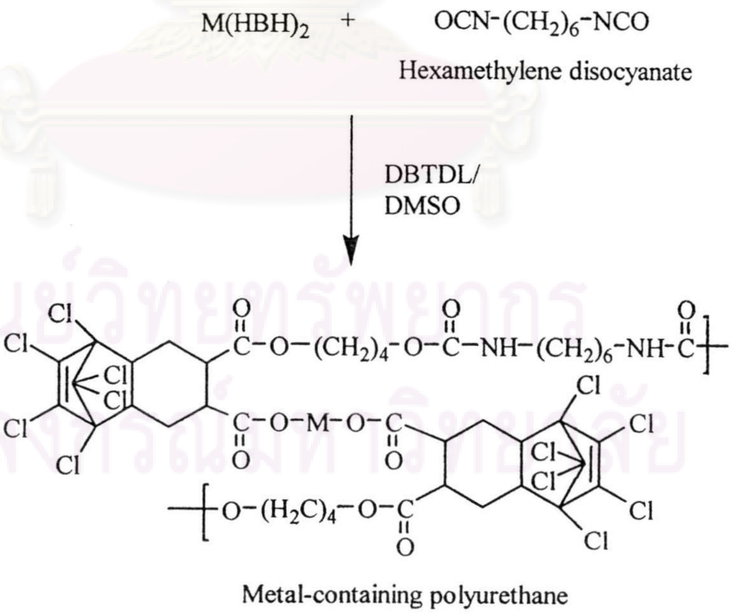
Scheme 1.5 Synthesis of metal-containing polyurethane-ureas from $M(HBP)_2$, hexamethylene bis (ω,*N*–hydroxyethyl urea) or toluene bis (ω,*N*–hydroxyethyl urea) and diisocyanate

It was observed that metal-containing polyurethanes had higher initial decomposition temperature than metal-containing polyurethane-urea. It may be explained based on probability that the prepared polyurethane copolymers were found to contain less metal than the prepared polyurethane-ureas. It had been reported that the existence of metal promoted the thermal decomposition of urethane-ureas and with increase in metal content of the polymers the stability decreased.

Nanjundan and coworker[5] have also been interested in the metal-containing polyurethane-ureas. They synthesized the metal-containing flame-retardant polyurethane from the reaction between divalent metal salts of mono(hydroxybutyl) hexolate [$M(HBH)_2$] where metals were Ca^{2+}, Mn^{2+} or Pb^{2+}(Scheme 1.6) and hexamethylene diisocyanate (HMDI) (Scheme 1.7).

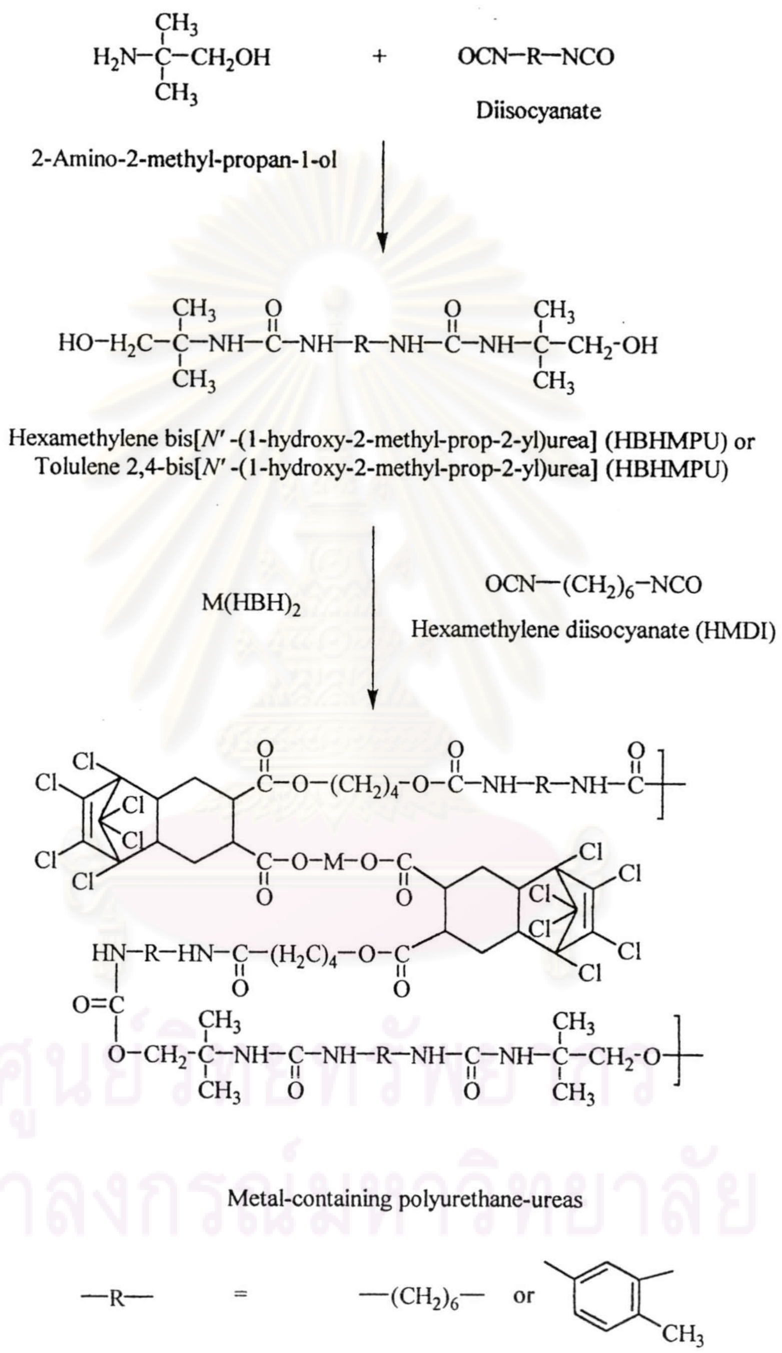


Scheme 1.6 Structure of mono(hydroxybutyl)hexolate [$M(HBH)_2$] $M = Ca^{2+}$, Mn^{2+} or Pb^{2+}



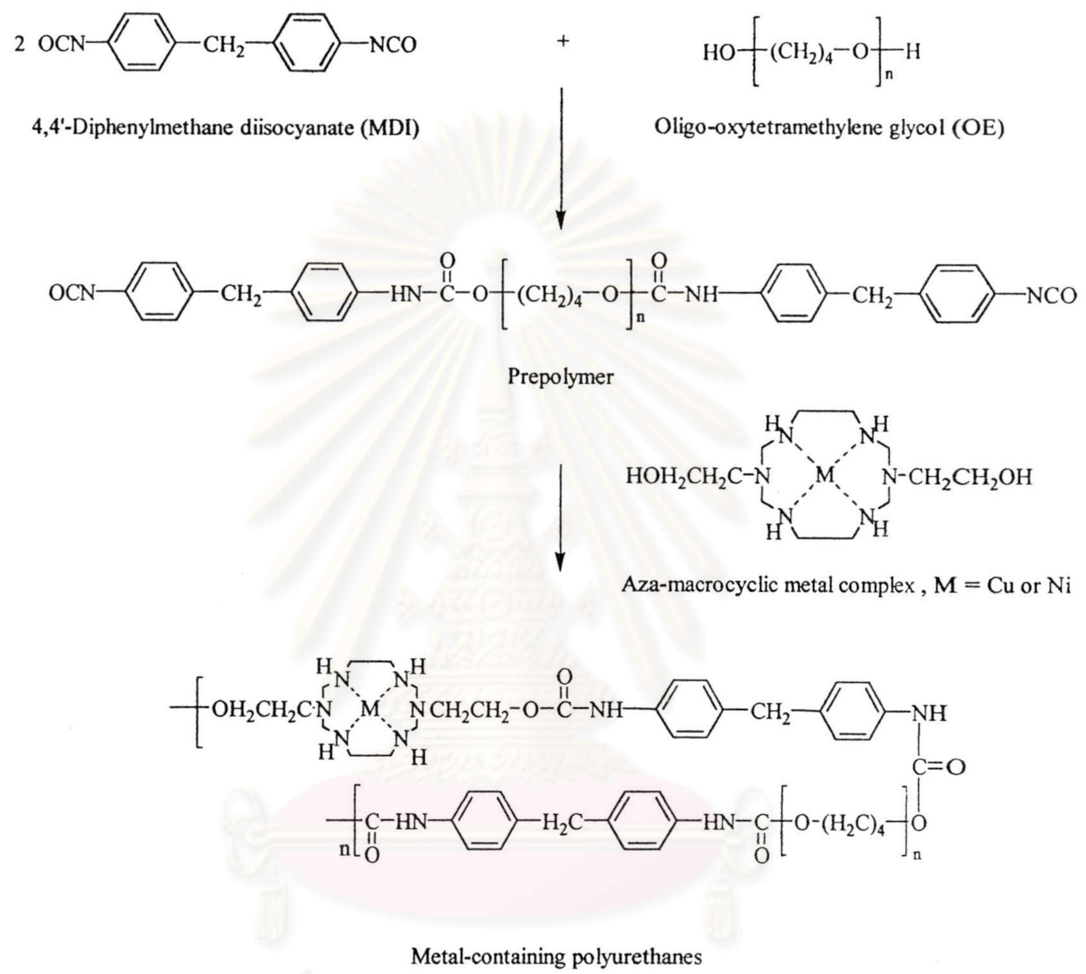
Scheme 1.7 Synthesis of metal-containing polyurethane from $M(HBH)_2$ and hexamethylene diisocyanate

In addition, they synthesized the polyurethane-ureas by reactting 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 1.8).



Scheme 1.8 Synthesis of metal-containing polyurethane-ureas from HBHMPU or TBHMPU, $M(HBH)_2$ and hexamethylene diisocyanate (HMDI)

Georgoussis[6] and coworkers investigated the relationship between structure and morphology and molecular mobility of the polyurethanes based on oligo-oxytetramethylene glycol with metal ions (Cu and Ni) incorporated in the chains (Scheme 1.9).

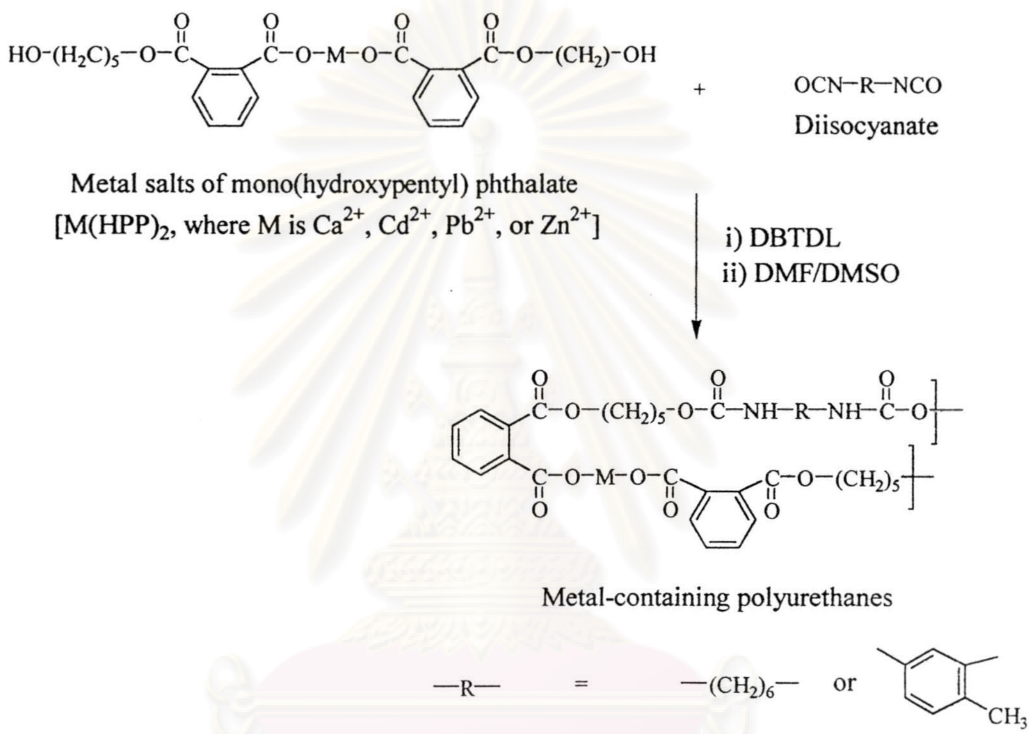


Scheme 1.9 Synthesis of metal-containing polyurethanes based on oligotetramethylene glycol and aza-macrocyclic metal complexes

The result were provided by the techniques employed for both the morphological and the molecule mobility studies that microphase separation is more pronounced for the system with Ni than with Cu ion. The different action of Cu^{2+} and Ni^{2+} cations on the structure formation in the SPU_2 studied might be due to the difference in their electronegativities.

Nanjundan[7] and coworkers synthesized a new series of metal-containing polyurethanes containing ionic links in the main chain by the reaction of hexamethylene diisocyanate or toluene 2,4-diisocyanate with the metal salts of mono (hydroxypentyl)phthalate [$M(HPP)_2$, where M is Ca^{2+}, Cd^{2+}, Pb^{2+}, or Zn^{2+}].

$M(HPP)_2$ were synthesized by the reaction of 1,5-pentanediol, phthalic anhydride, and metal acetate (Scheme 1.10). The antibacterial activity of these polyurethanes was investigated.

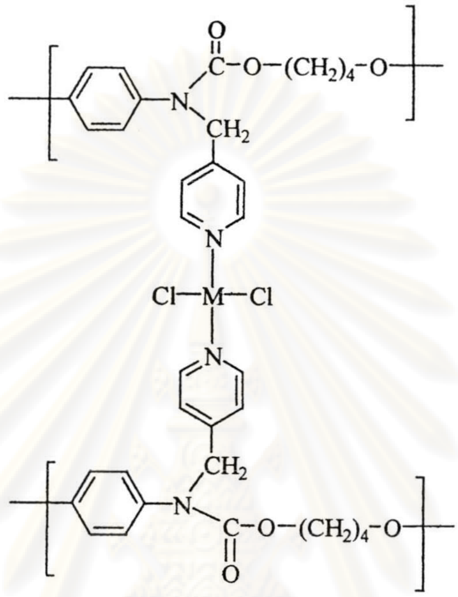


Scheme 1.10 Synthesis of metal-containing polyurethanes from $M(HPP)_2$ and hexamethylene diisocyanate or toluene 2,4-diisocyanate

The results indicated that the TDI-based on polymers showed higher thermal stability than HMDI-based polymers. The antibacterial activities of different test compounds indicated that Pb-and Cd-containing polyurethanes had strong inhibitory effects on all bacteria and that the polyurethanes containing other metals had various antibacterial activities depending on the bacterium. The antibacterial activity of all the polymers may not be entirely due to the metal alone. It may also be due to the residual isocyanate groups in the polymers.

Shen[8] and Yang synthesized *N*-Picolyl polyurethanes (PUPY) by nucleophilic substitution and blended these polyurethanes with several transition metal chlorides (coblat (II), nickel (II), and copper (II)) (Scheme 1.11).

They found that the coordination strength of pyridine with Ni^{2+} was stronger than Co^{2+} and Cu^{2+}.

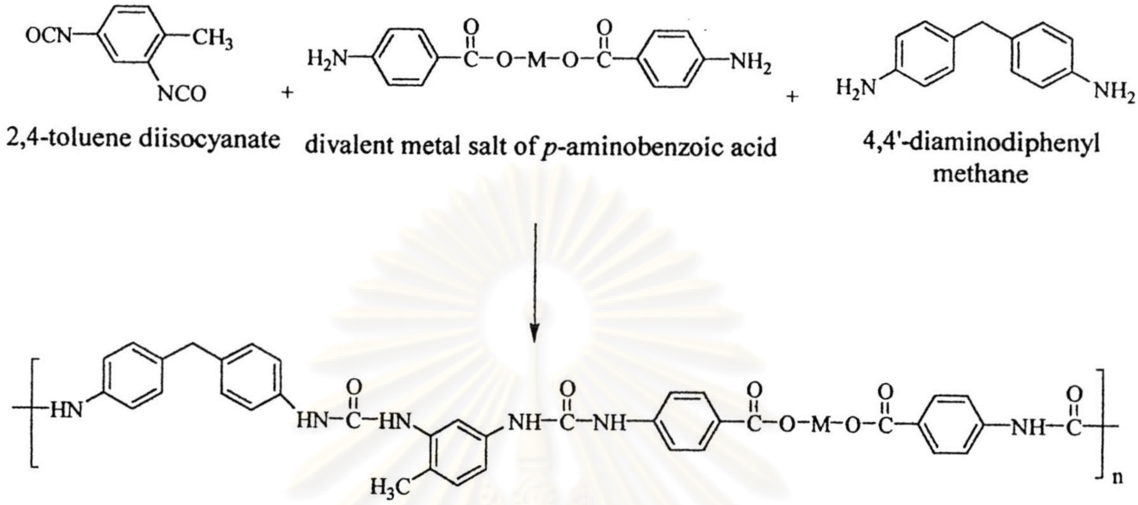


Transition metal complexes of *N*-Picolyl polyurethane
$M = Ni^{2+}$, Co^{2+}, and Cu^{2+}

Scheme 1.11 Structure of polyurethane metal complex

According to considerable interest in polyurethanes containing metal-ligand interactions, polyurethane metal complexes might be expected to possess properties different from those of conventional polyurethanes. Ligands can have pendent groups as part of chain extenders and introduced into polyurethane by condensation polymerization[9-11]. Then coordination polyurethane was prepared by blending polyurethane with metal ion. Polyurethanes containing Schiff base complexes[12], divalent metal-salts[13], and the influence of incorporated metal in the main chain on the properties of polyurethane[14] have also been reported.

Matsuda and Takechi[15] synthesized metal-containing polyureas having ionic links in the main chain by the polyaddition reaction of 2,4-toluene diisocyanate with mixtures of divalent metal salts of *p*-aminobenzoic acid and 4,4′-diaminodiphenylmethane (4,4′-methylenedianiline) (Scheme 1.12).



Metal-containing polyureas

M = divalent metal (Mg or Ca)

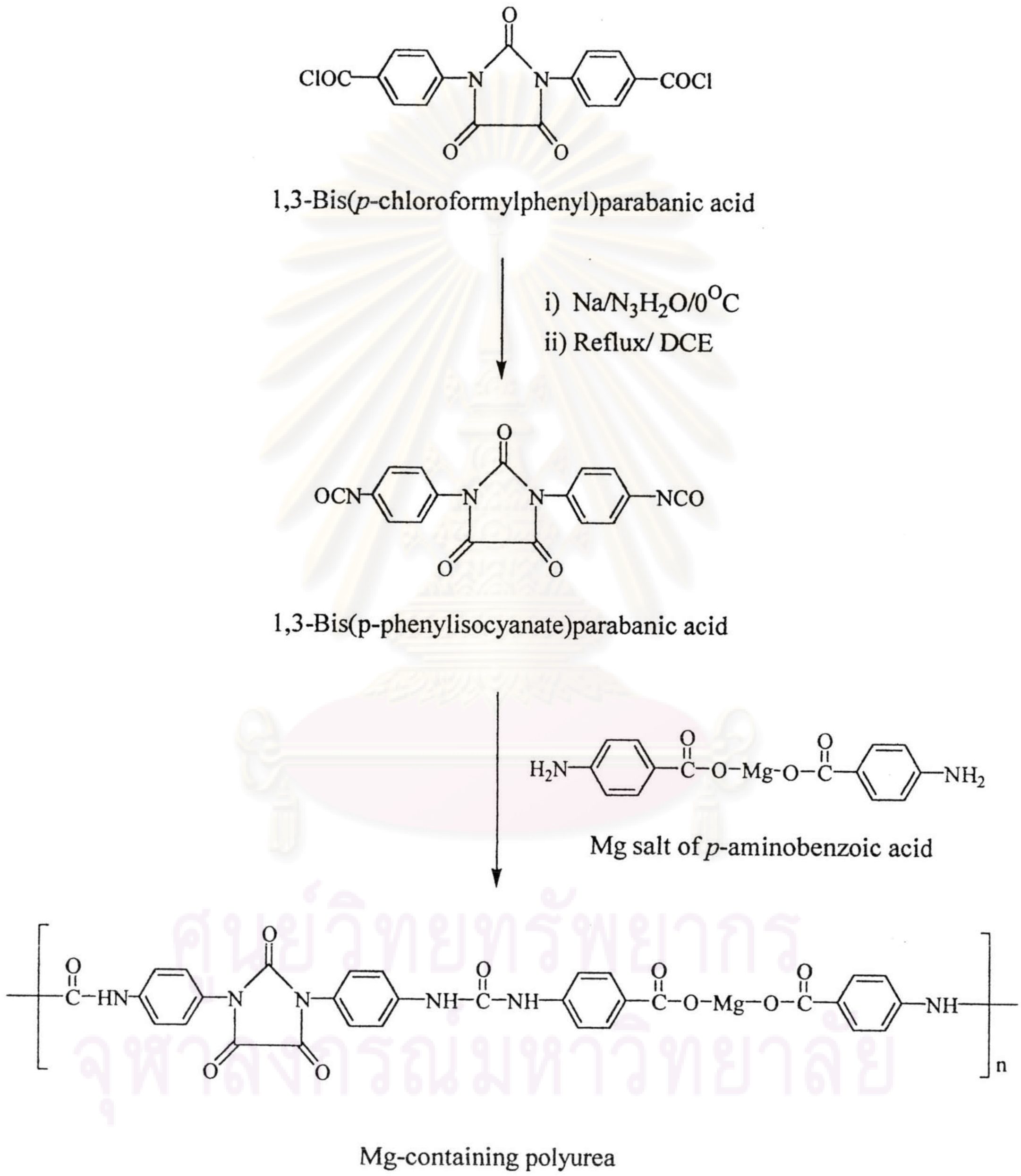
Scheme 1.12 Synthesis of metal-containing polyureas from 2,4-toluene diisocyanate, *p*-aminobenzoic acid and 4,4′-diaminodipheny methane

The result was the inherent viscosity (at 0.5g/ml) of the polyureas decreased markedly with an increase in metal content.

Rajalingam and Radhakrishnan[16] synthesized a new series of metal-containing polyurethane-ureas containing ionic links in the main chain by reaction of toluene diisocyanate with Mn, Cu, Co and Pb salts of mono(hydroxyethyl)-phthalate and a bisurea

It was found that introduction of metal into the polyurethane-ureas produces some decrease in decomposition temperature. Furthermore, as metals represent in the main chain of polyurethane-ureas by ionic linkage, the thermal stability of the transition metals (Mn, Co and Cu) can be explained by the presence of odd electrons, in the outermost orbital, which probably enhances the ionic hold of the metal in the polymer chain. Hence Mn^{2+} exhibits a thermally more stable ionic link in the backbone chain of polyurethane-ureas by the support of the d^5 orbital.

Caraculacu[17] and coworkers synthesized a new diisocyanate containing a parabanic ring [1,3-bis (isocyanatophenyl)]. The direct reaction of this diisocyanate with the Mg salt of *p*-aminobenzoic acid, or with a mixture of aromatic diamines gave ionic polyureas (Scheme 1.13). The detailed study of inherent viscosities of these polymers was achieved.



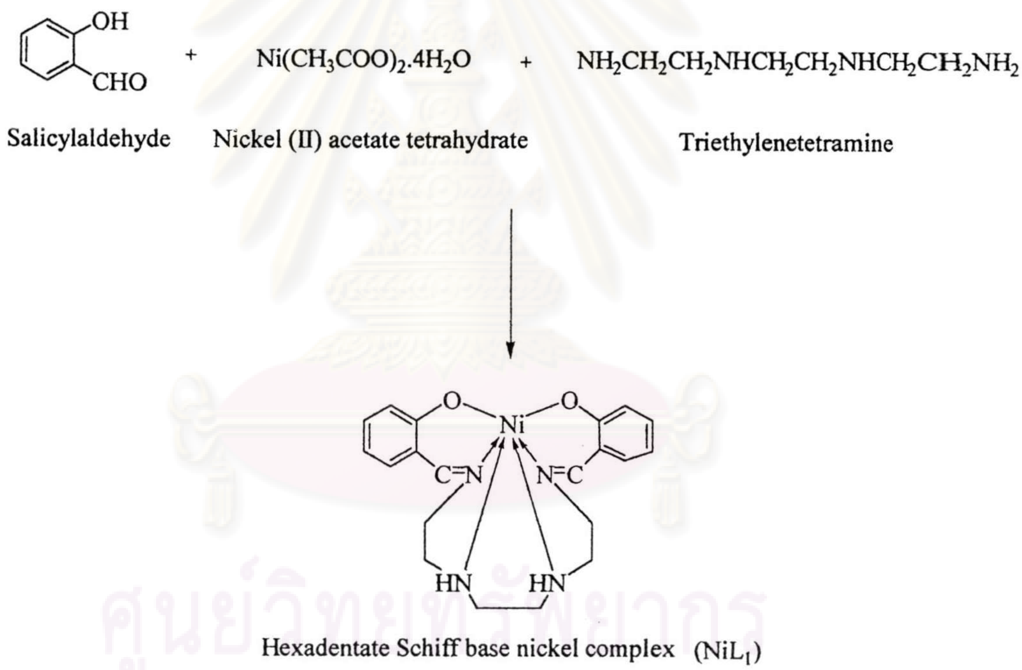
Scheme 1.13 Synthesis of Mg-containing polyurea

The result showed that when the water content was increased, the inherent viscosity of Mg-containing polyurea was increased. This increase of viscosity can be attributed to the trend of molecules to adopt a linear shape, the interaction between the ionic groups of the polymers being diminished by polymer-water interaction.

1.4 Objective and scope of the research

In our work, efforts were made to synthesize nickel-containing polyurethane. The optimum conditions for the polymerization were studied. The effects of the incorporation of nickel into the main chain of a series of polyurethane-urea on thermal properties were investigated.

The first step was the synthesis of hexadentate Schiff base nickel complex as shown in Scheme 1.14.



Scheme 1.14 Synthesis of NiL_1

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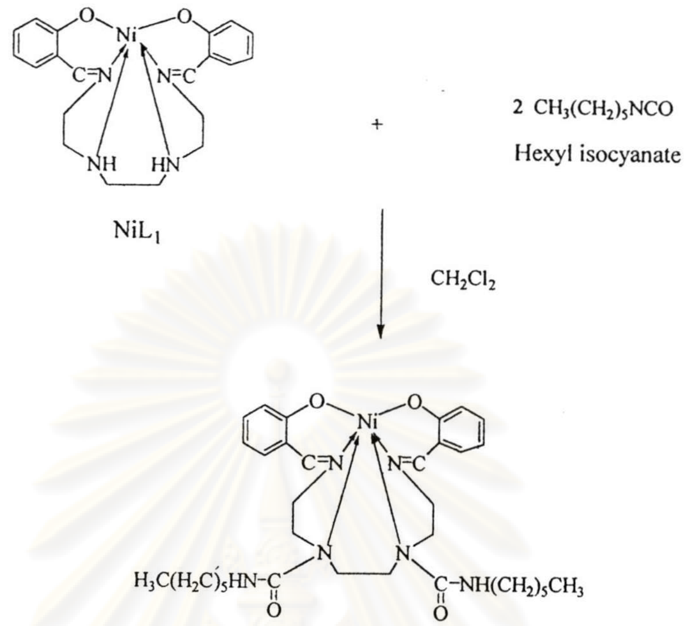
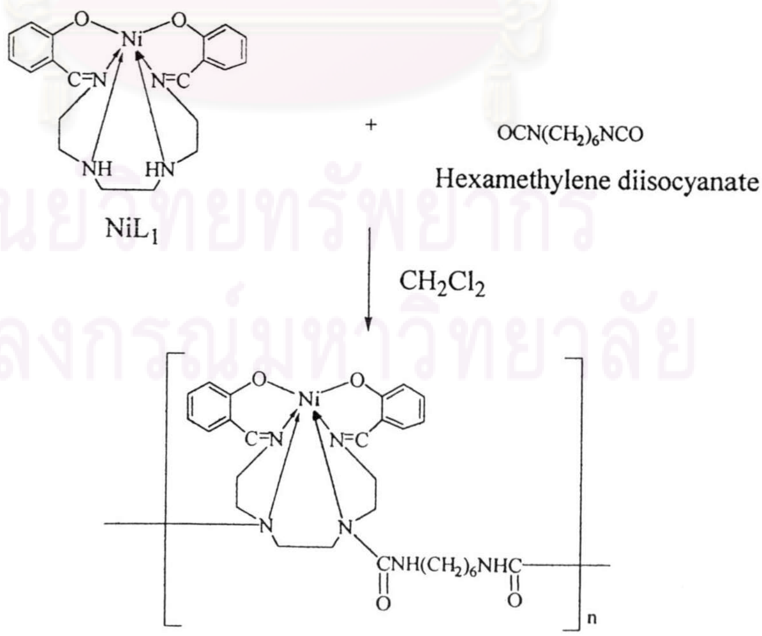
Secondly, NiL_1 urea (NiL_2) was synthesized from the reaction between NiL_1 and hexyl isocyanate (Scheme 1.15) to investigate the reactivity of the amine group in NiL_1 with isocyanate group.



NiL_1 urea (NiL_2)

Scheme 1.15 Synthesis of NiL_1 urea (NiL_2)

Finally, polymerization was performed in order to obtain polyurea (PU_1NiL_1) and polyurethane (PU_2NiL_1) (Schemes 1.16 and 1.17).



Nickel-containing polyurea (PU_1NiL_1)

Scheme 1.16 Synthesis of Nickel-containing polyurea (PU_1NiL_1)

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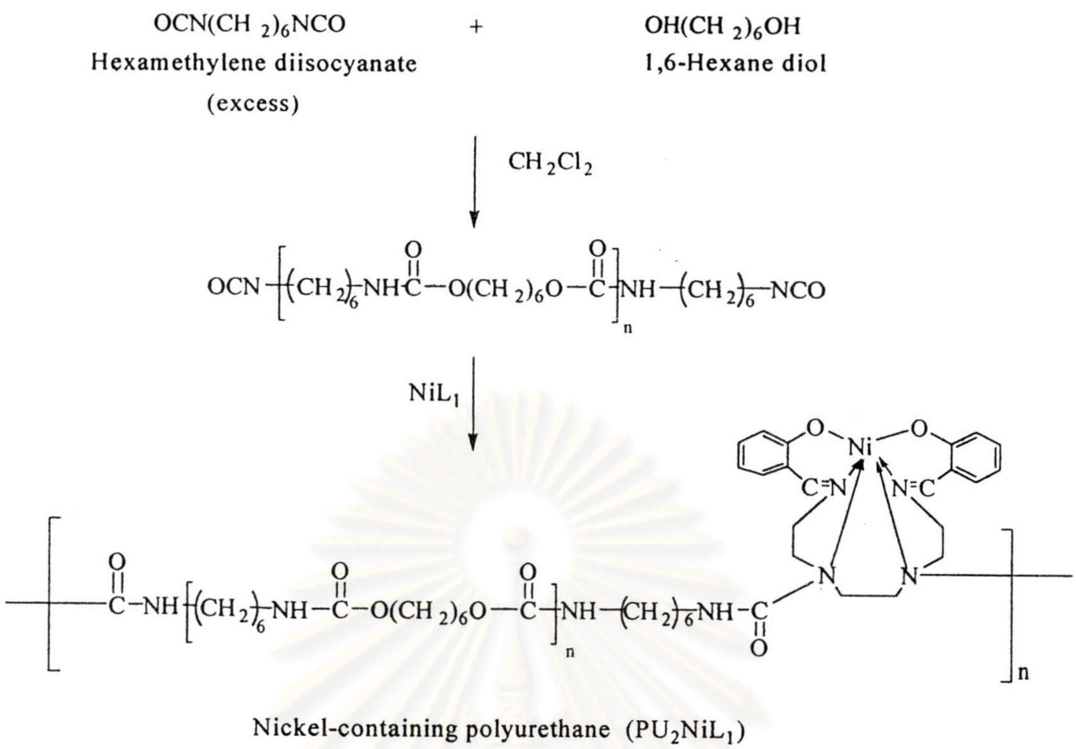

Scheme 1.17 Synthesis of Nickel-containing polyurethane (PU_2NiL_1)

The polymer structures were characterized by FTIR and elemental analysis (EA). Thermal properties were investigated by DSC and TGA.

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