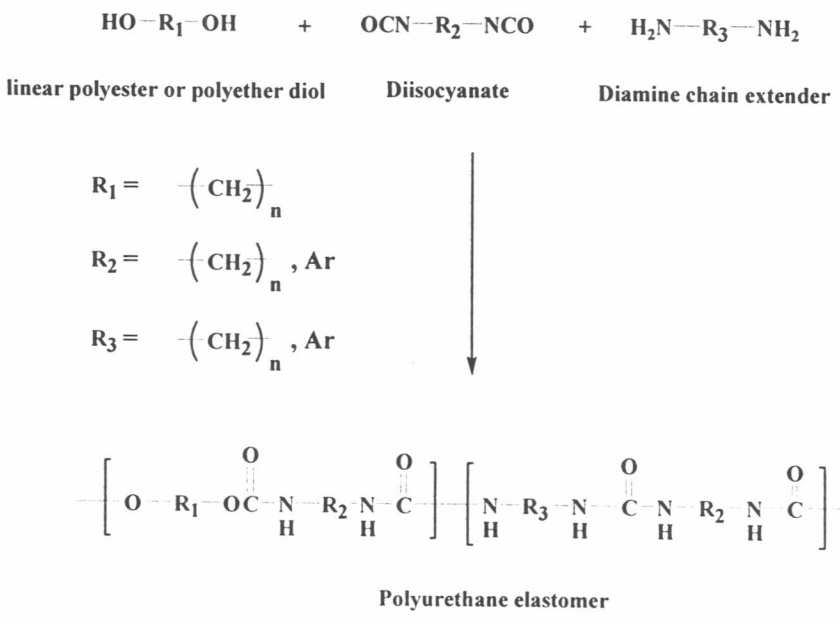
CHAPTER I

INTRODUCTION

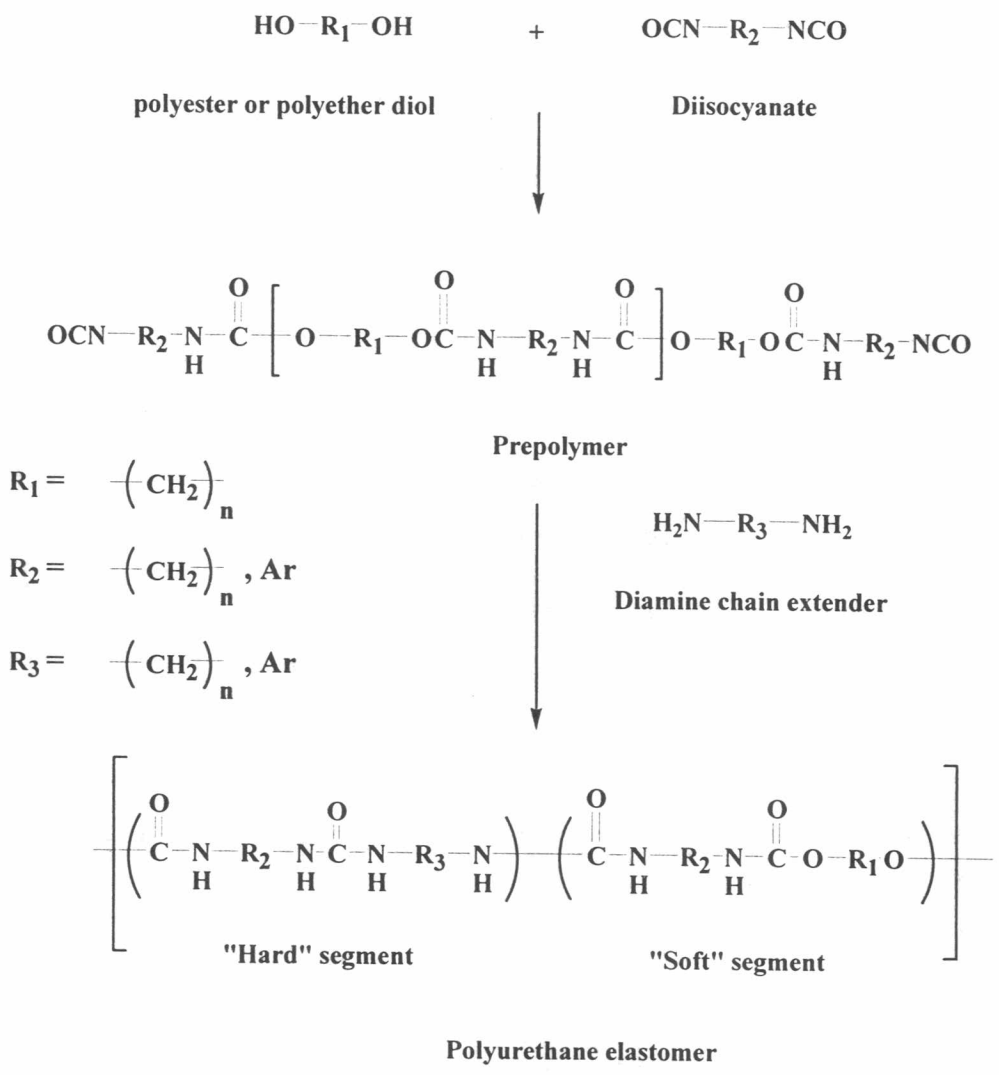
1.1 Polyurethanes

Polyurethanes are the polymers composed of urethane linkage (-NHCOO-) between the repeating units in molecules. The principal method of preparing polyurethane is the reaction of diisocyanates with dihydroxy compounds.[1] This polymerization reaction does not eliminate any by-products. One important polyurethane product is polyurethane elastomers. Polyurethane elastomers consist of elastomeric block copolymer alternating "hard" and "soft" segments, which contribute to the rigid and elastomeric properties. Polyurethane can be synthesized by two methods, one step (or one-shot) method and prepolymer method.[2] In the one step method, the polymer formation is carried out by simultaneous reaction of polyol, polyisocyanate and chain extender (Scheme 1.1).



Scheme 1.1 One step reaction for synthesis of polyurethane elastomer

In the prepolymer method, the polyisocyanate and polyol are reacted to form an intermediate polymer call "prepolymer". It is then polymerized into polyurethane elastomer by further reaction with diol or diamine chain extender. Chain extension occurs *via* urea rather than urethane linkage (Scheme 1.2).



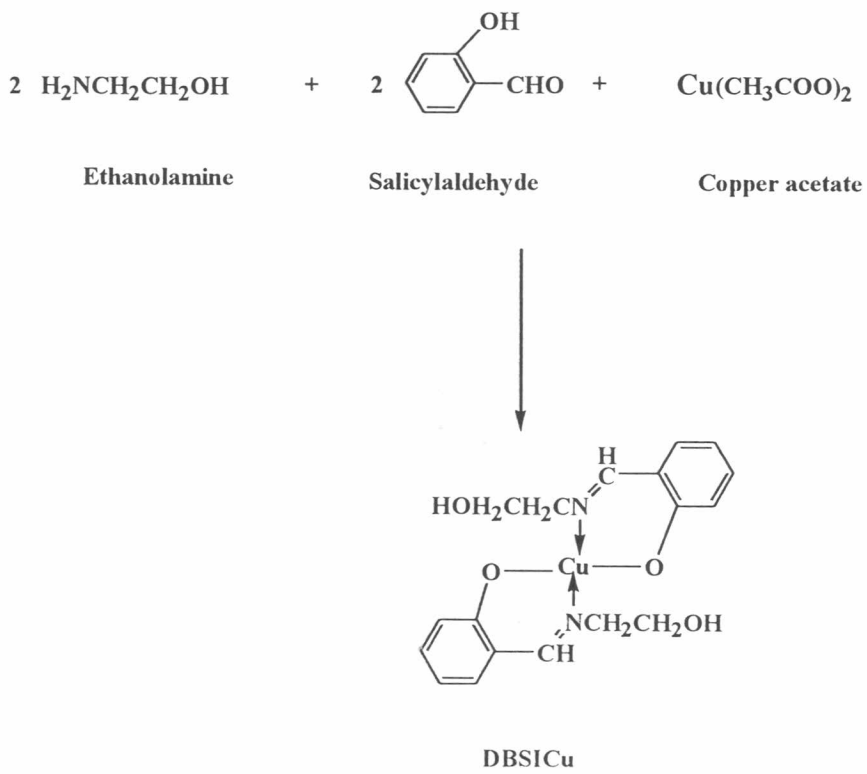
Scheme 1.2 Prepolymer method for synthesis of polyurethane elastomer

Since the properties of polyurethanes are depended on the ratio of hard and soft segments, polyurethanes are used in wide variety of products, such as rigid foams, elastic fibers, elastomers, coating and adhesives.

1.2 Metal-containing polyurethanes

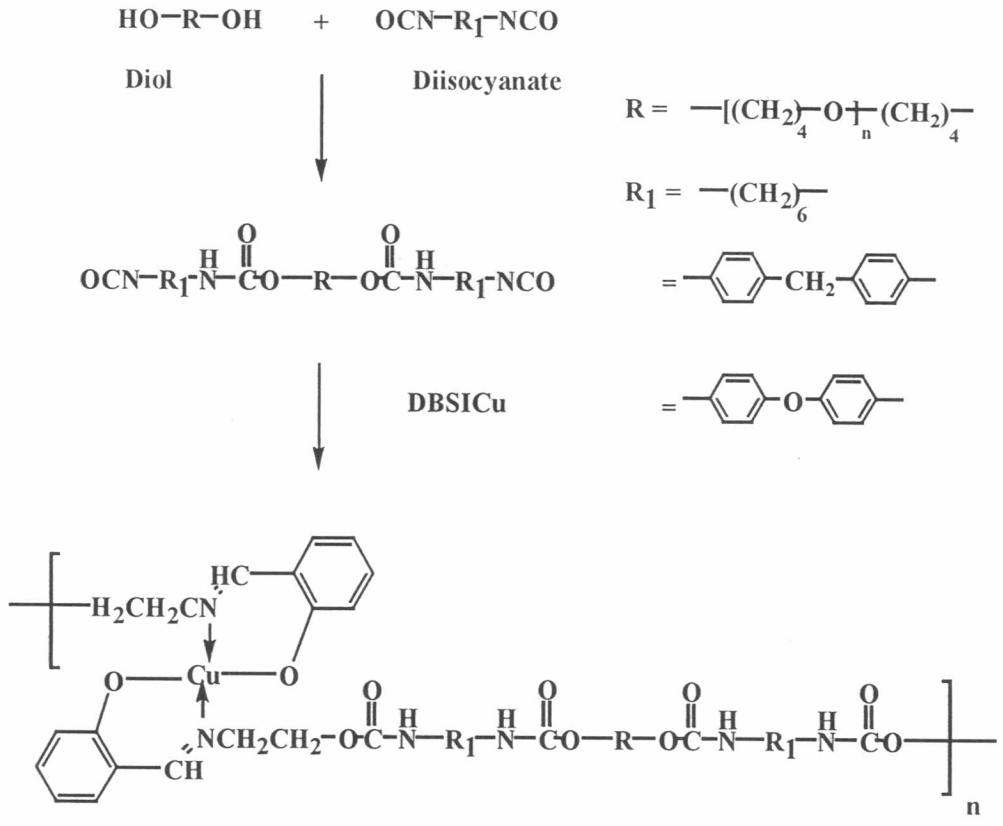
The interaction between polymers containing coordinating groups and metal ions is considerable interesting due to the large variety of new metal-containing polymer[3-4] that can be obtained, having a wide range of interesting properties and potential applications in diverse fields. It is known that the thermal properties of polymers can be influenced by the present of metal ion. A number of papers concerning the preparation and physical properties of metal containing polyurethane-ureas[5-7] have been reported as follows :

Some metal-containing polyurethanes are liquid crystalline polymers. One example is the work of Yu and coworkers.[8] They synthesized polyurethane with organometallic complexes based on novel diol, *bis*[N-[[2-hydroxyphenyl] methylene] hydroxylethylene amino]-copper (II) (DBSICu). The metallic diol was synthesized by the reaction between ethanolamine, salicylaldehyde and copper (II) acetate as shown in Scheme 1.3.



Scheme 1.3 Synthesis of metallic diol (DBSICu) from ethanolamine, salicylaldehyde and metal acetate

In the polymerization reaction, poly(tetramethylene oxide) (PTMO) was reacted with *bis*(phenyloxide) diisocyanate (ODI) or (MDI) and DBSICu as a chain extender to obtain metal-containing polyurethanes as shown in Scheme 1.4.



Coordinated polyurethanes

Scheme 1.4 Synthesis of the coordination polyurethanes from the reaction of DBSICu with diol and diisocyanate

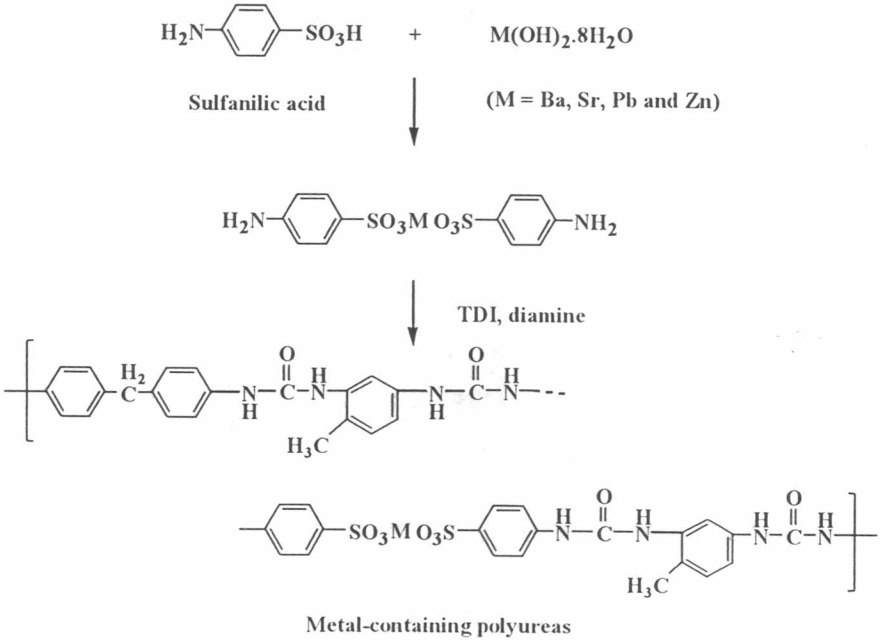
It was found that the obtained DBSICu showed liquid crystalline property. The sample was shown a band structure in 140°C under POM. When cooling to room temperature, this band structure could be preserved.

In the thermal stability study, DBSICu showed an endothermic peak that corresponded to the crystal-isotropic transition, (T_m = T_i). For the polymer, the isotropization temperature decrease with incorporating a polyether soft segment.

Thermal treatment has remarkable influence on the crystallinity of the hard segment. It was found that polymer based on MDI yielded a higher temperature mesophase than polymer based on ODI.

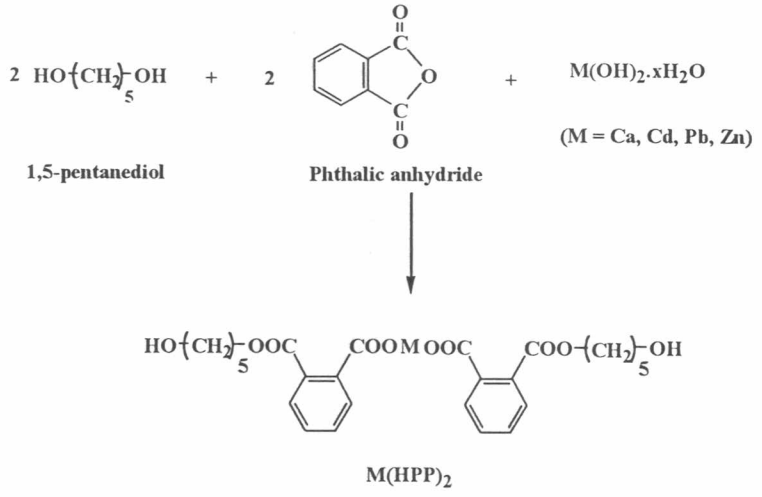
Wang and coworkers[9] prepared metal-containing polyureas from divalent metal salts of sulfanilic acid. The reaction occurred *via* polyaddition reaction of a diisocyanate, salts of *p*-aniline sulfonic acid (ASA) and diamine. The Ba, Sr, Pb and Zn was reacted with ASA to give ASA (Ba), ASA (Sr), ASA (Pb) and ASA (Zn) respectively. The obtained ASA(M) was reacted with diamine and TDI to give metal-containing polyureas (Scheme 1.5).

It was observed that the first stage of the thermal decomposition of metal-containing polyureas, at about 300°C, might be assumed to be due to the urea scission. When comparing decomposition temperature, it was found that the thermal stability of polyureas increased when the metal is introduced. Finally, it was observed that with an increase of content of ASA(Ba) in the feed diamine the thermal stability of metal-containing polyureas increases.

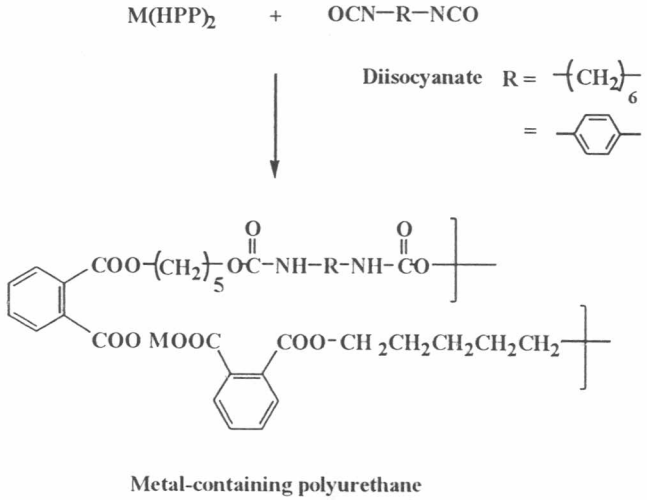


Scheme 1.5 Synthesis of metal-containing polyureas from sulfanilic acid, diamine and TDI with different metal salts

Nanjundan and coworkers[10] synthesized metal-containing polyurethanes with antibacterial activity. Metal salt of mono (hydroxypentyl) phthalate [$M(HPP)_2$ when M is Ca^{2+}, Cd^{2+}, Pb^{2+} or Zn^{2+}] were synthesized by the reaction of 1,5-pentanediol, phthalic anhydride, and metal acetate. The metal-containing polyurethanes were synthesized by the reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with the $M(HPP)_2$ salts. The route of metal salts $M(HPP)_2$ synthesis is shown in Scheme 1.6 and the polymerization of $M(HPP)_2$ with diisocyanates is shown in Scheme 1.7.



Scheme 1.6 Synthesis of metal salts ($M(HPP)_2$) from 1,5-pentanediol, phthalic anhydride with different metal salts

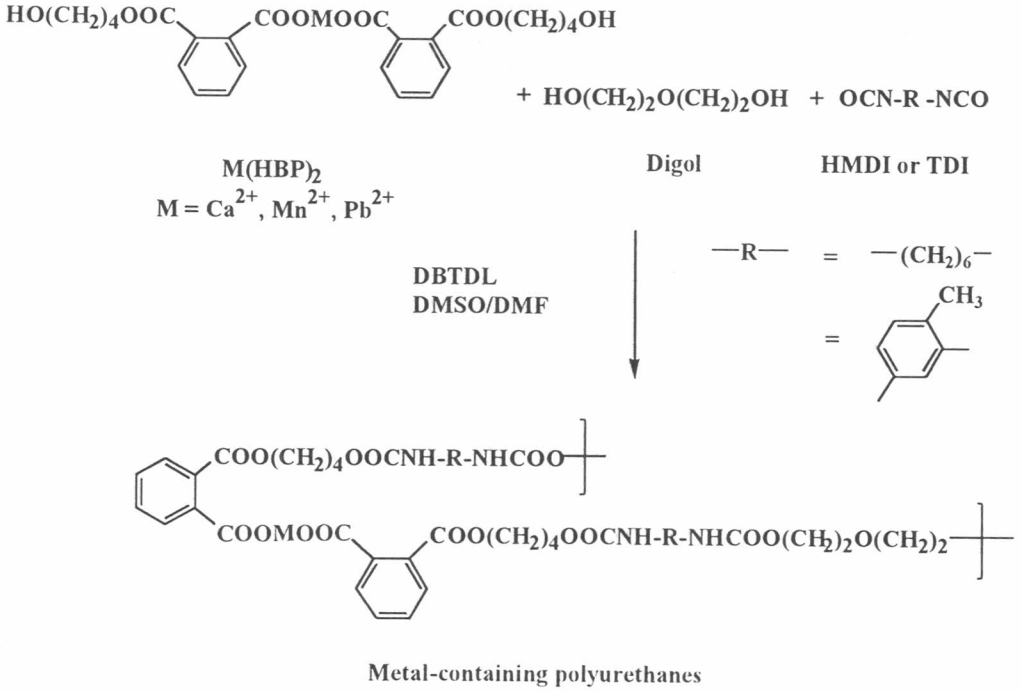


Scheme 1.7 Synthesis of metal-containing polyurethanes from $M(HPP)_2$ and HMDI or TDI

It was found that the TDI-based polymers showed higher thermal stability than the HMDI-based polymers because of the additional aromatic rings present in the polymer backbone.

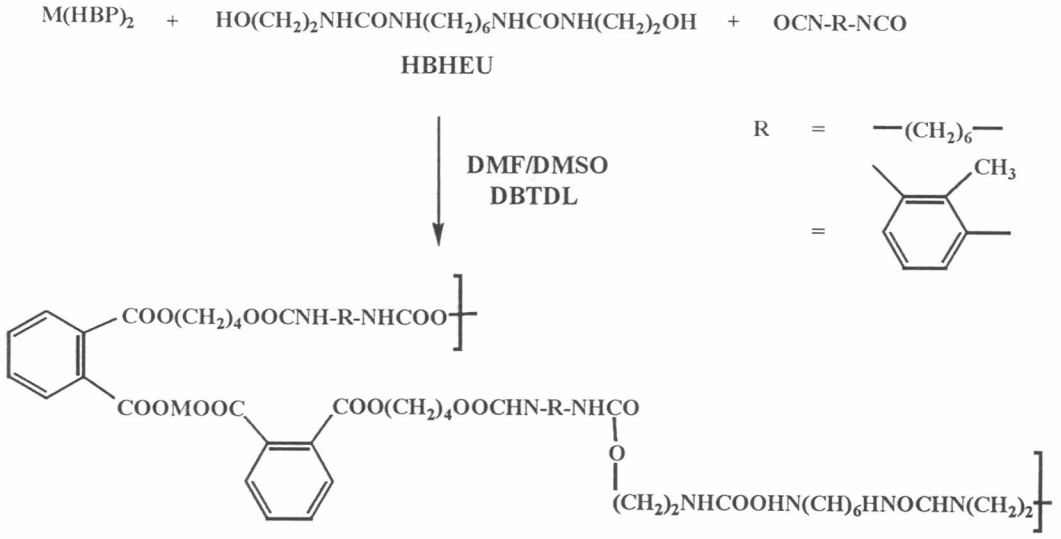
The glass-transition temperature (Tg) followed the order Ca > Zn > Cd > Pb. This order may be attributed to the fact that with an increase in the size of the metal atom, the free volume of the polymer increased and the Tg volume decreased. The HMDI-based polyurethanes have much lower Tg value than the TDI-based polyurethanes on the basis of their main-chain structure. This may be due to HMDI-based polyurethanes generally have higher crystallinity than TDI-based polyurethanes.

Nanjundan and Prasath[11] synthesized the divalent metal-containing polyurethanes and polyurethan-ureas. The reaction occurred *via* polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with 1 : 1 mixtures of divalent metal salts of mono (hydroxybutyl) phthalate [$M(HBP)_2$] and digol (DG). The route of synthesis is shown in Scheme 1.8.



Scheme 1.8 Synthesis of metal-containing polyurethane from $M(HBP)_2$, digol and HMDI or TDI

Similarly, the polyurethane-ureas were synthesized by reacting $M(HBP)_2$ with hexamethylene*bis*(N-hydroxyethyl-urea) (HBHEU) and HMDI or TDI. The route of synthesis is shown in Scheme 1.9.

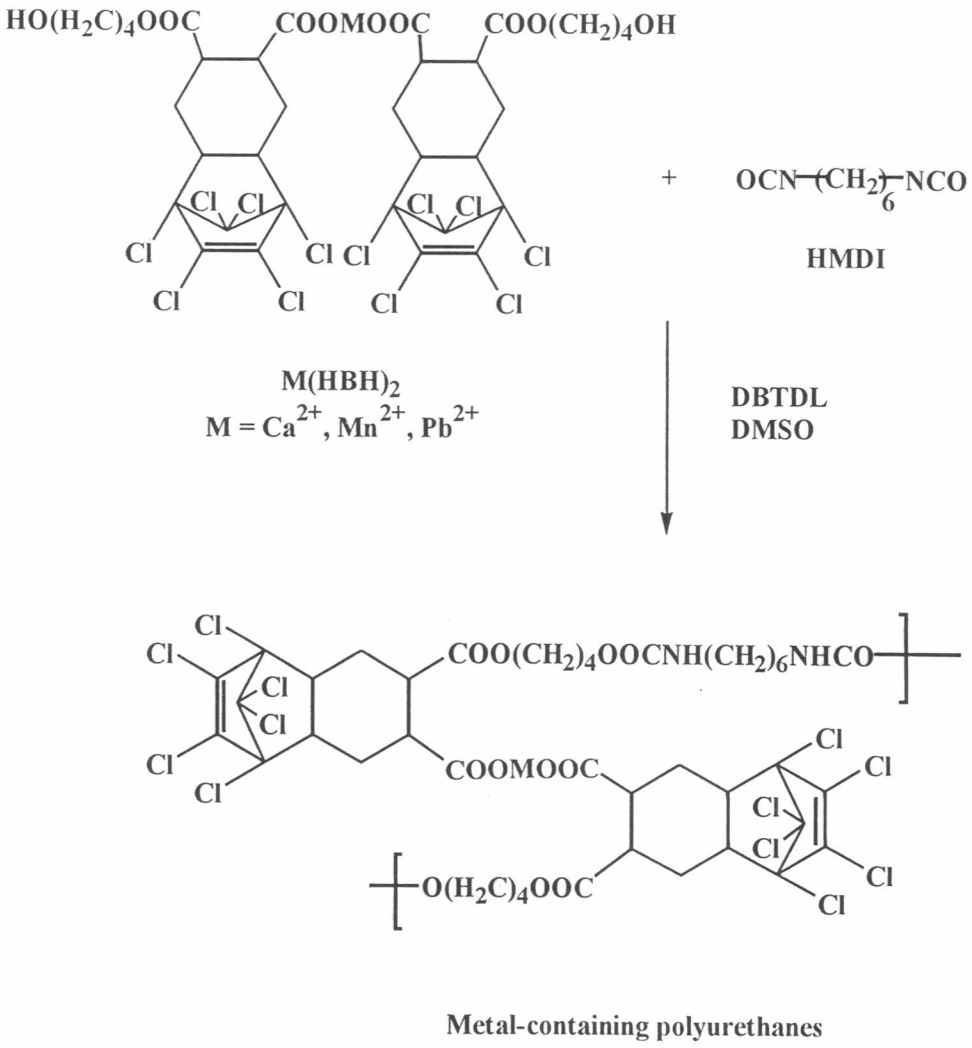


Metal-containing polyurethane-ureas

Scheme 1.9 Synthesis of metal-containing polyurethane-ureas from $M(HBP)_2$, HBHEU and HMDI or TDI

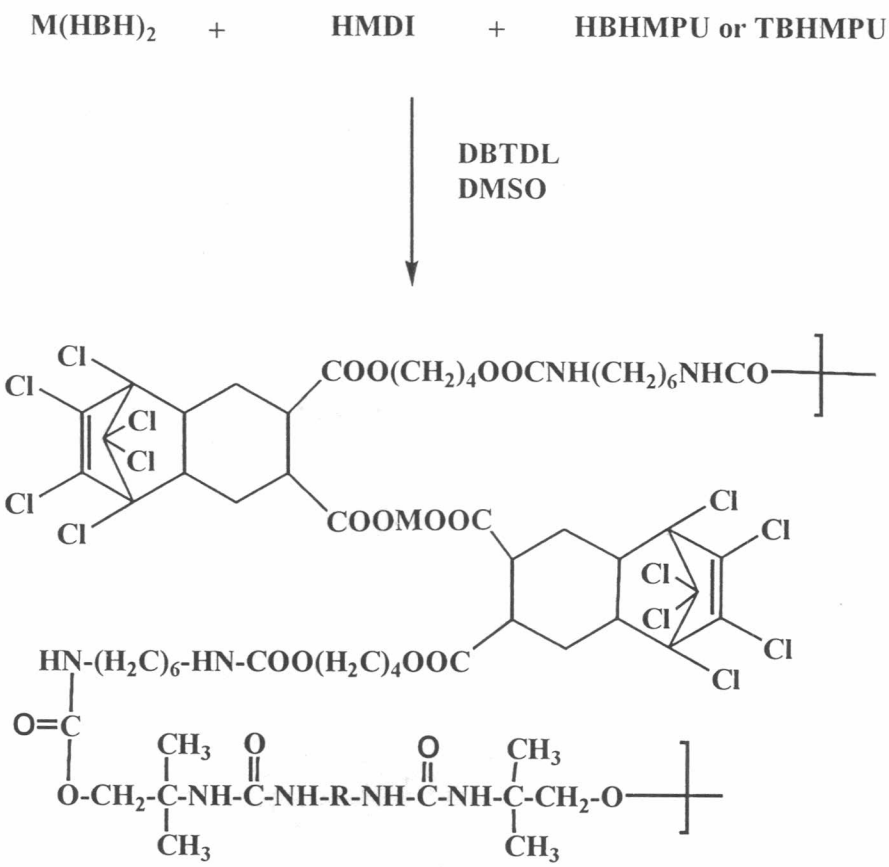
In the study of thermal properties, it was observed that metal-containing polyurethanes had higher IDT than metal-containing polyurethane-ureas. Thermal stability of the metal-containing polymers can be ordered as Pb > Mn > Ca.

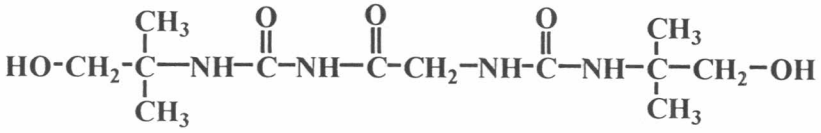
Another work of Nanjundan and Prasath[12] involved the synthesis of polyurethanes and polyurethane-ureas using divalent metal salts of mono (hydroxybutyl)hexolate [$M(HBH)_2$, M = Ca^{2+}, Mn^{2+}, or Pb^{2+}]. The reaction occurred *via* the polyaddition reaction of hexamethylene diisocyanate (HMDI) with $M(HBH)_2$ (Scheme 1.10).



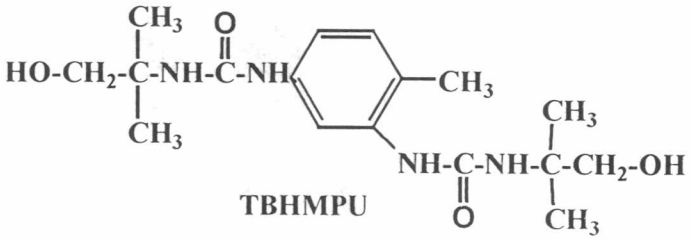
Scheme 1.10 Synthesis of metal-containing polyurethanes from $M(HBH)_2$ and MDI

The polyurethane-ureas were synthesized from $M(HBH)_2$ with HMDI 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 1.11).





HBHMPU



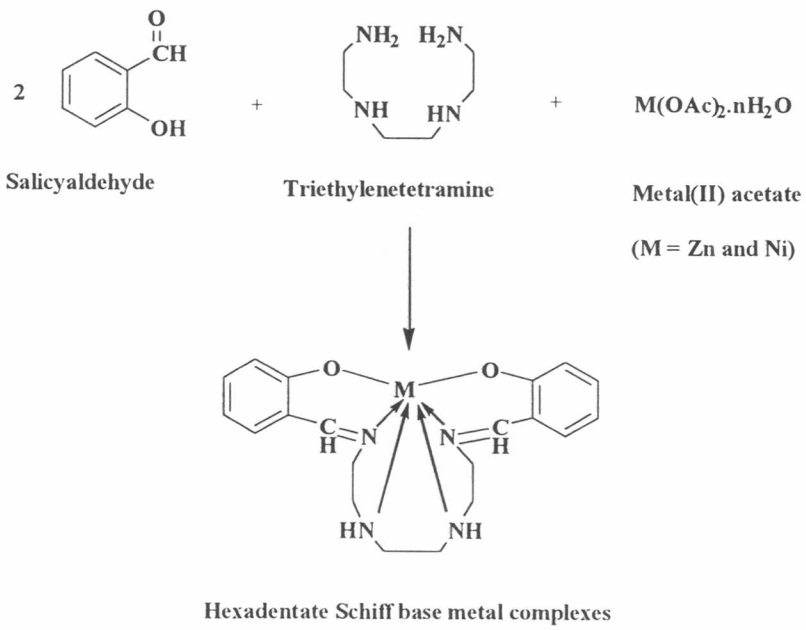
Scheme 1.11 Synthesis of metal-containing polyurethane-ureas from M(HBH)2, HMDI and HBHMPU or THBMPU

1.3 Objective and Scope of the Research

The target of this research is to synthesize hexadentate Schiff base metal complexes-containing polyurethane-urea elastomers based on zinc and nickel since it was known that the addition of metal into the polymer chain could improve thermal properties of the polymers. Batiya[13] synthesized hexadentate Schiff base zinc complex ($ZnSal_2trien$) which showed birefringence under polarizing optical microscope. This suggested that $ZnSal_2trien$ is a liquid crystal.

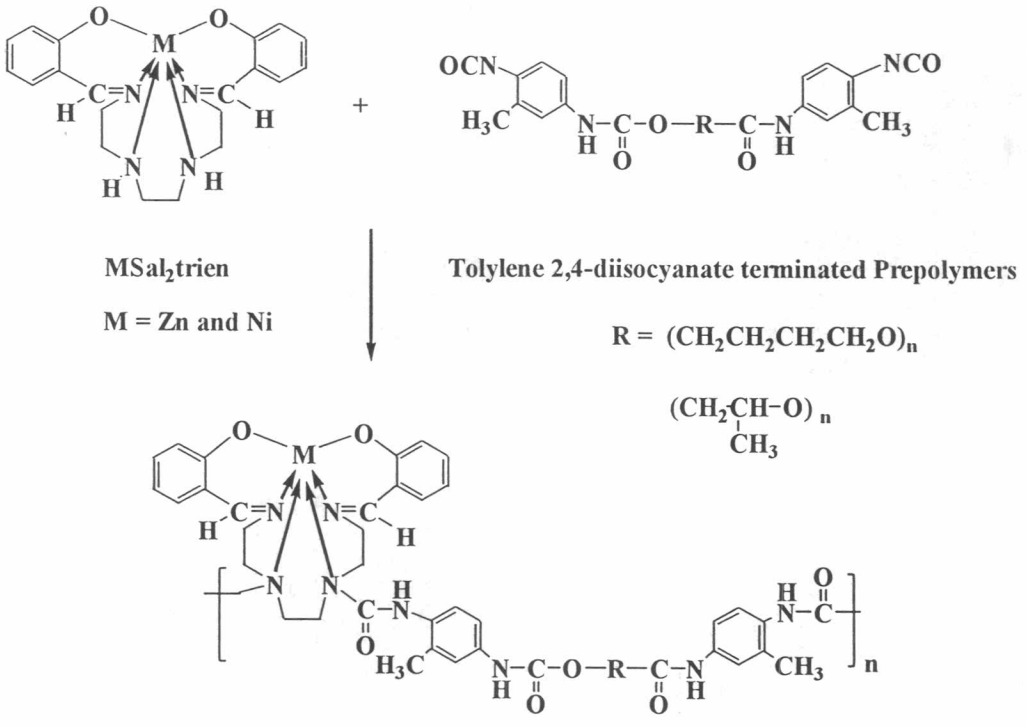
In this research, hexadentate Schiff base zinc and nickel complexes ($ZnSal_2trien$ and $NiSal_2trien$) would be synthesized. Then, both of $ZnSal_2trien$ and $NiSal_2trien$ were used as chain extender for the synthesis of metal-containing polyurethane-urea elastomers and metal-containing copolyurethane-urea elastomers. It was expected that the obtained polymers would show liquid crystalline property and good thermal stability.

In the first step, hexadentate Schiff base metal complexes ($MSal_2trien$) were synthesized as shown in Scheme 1.12.



Scheme 1.12 Synthesis of hexadentate Schiff base metal complexes ($MSal_2trien$)

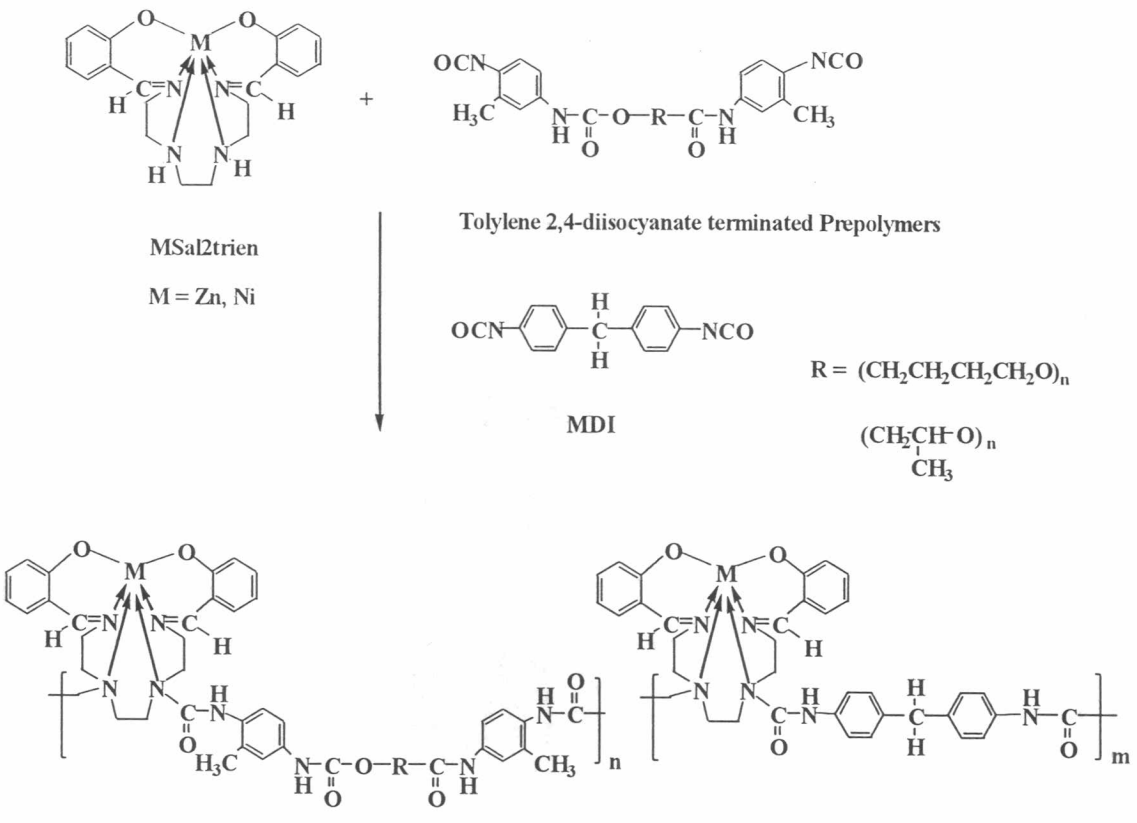
In the next step, the metal-containing polyurethane-ureas were synthesized from the reaction between metal complexes and tolylene 2,4- diisocyanate terminated poly(propylene glycol) prepolymer, molecular weight 1000 and 2300 (PP1000 and PP2300); tolylene 2,4- diisocyanate terminated poly(1,4-butanediol) prepolymer, molecular weight 900 and 1600 (PB900 and PB1600).



Metal-containing polyurethane-ureas

Scheme 1.13 Synthesis of metal-containing polyurethane-ureas

The metal-containing copolyurethane-ureas were synthesized from the reaction between $MSal_2trien$, 4,4′-methylene*bis*(phenyl isocyanate) (MDI) and tolylene 2,4- diisocyanate terminated poly(propylene glycol) prepolymer, molecular weight 1000 and 2300 (PP 1000 and PP 2300); tolylene 2,4- diisocyanate terminated poly(1,4-butanediol) prepolymer, molecular weight 900 and 1600 (PB 900 and PB 1600) (Scheme 1.14).



Scheme 1.14 Synthesis of metal-containing copolyurethane-ureas

Finally, metal-containing polyurethane-ureas and copolyurethane-ureas were characterized by IR and ^{1}H NMR spectroscopy, elemental analysis, solubility and viscosity. The thermal property of the polymers was investigate by thermogravimetric analysis (TGA). The flammability of the polymers was determined by measuring limiting oxygen index (LOI).