CHAPTER I

INTRODUCTION

1.1 Heat-resistance Polymers

One of the driving force in polymer synthesis is the search for polymer to replace metals since polymers are lightweight and easy to process into required shapes. One of the major synthetic efforts since the late 1950s is in the area of high-temperature polymers or heat-resistance polymers.[1-4]

Heat-resistance polymer are high-performance polymers that can be used at high temperatures. The need of such polymers is their potential utilization in many areas such as aircraft, spacecraft, automotive and electronic components, etc. Polymers with high strength, solvent and chemical resistance and stability at temperature higher than 250 °C would be very useful.

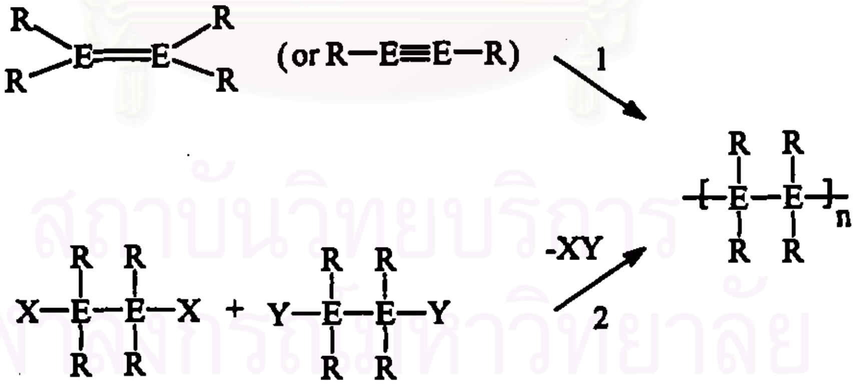
The most important factor that determines the heat resistance of polymers is bond strength in polymer structure. Breakage of these bonds in polymer chain lowers the molecular weight and causes a drop in mechanical strength. Therefore, introducing any functional groups with weak link into polymer chain should be avoided. Certain functional groups such as ether, sulfone, imide and amide are considered to be heat resistance substances.

Another factor that determines the heat resistance of polymers is the stiffness of polymer chains. Polymer chains with aromatic rings have both bond strength and stiffness. Strong secondary attractive forces such as dipole-dipole interactions also improve heat-resistance. High molecular weight and crosslinked polymers are also desirable.

One thing to consider about synthesis of heat-resistance polymer with rigid chains is the requirement of the polymer to have good processing properties. One approach is to introduce some flexible lingkages such as C=O and SO_2 groups into the polymer chain . These lingkages increase polymer processability by decreasing polymer chain rigidity. The other approach is to use oligomers which can then undergo polymerization reaction into high molecular weight polymer as starting material.

To date, the success is in the organic systems. Many polymers such as polycarbonate, polyamide and polyacrylate are among commercial polymers which can be utilized at high temperature.

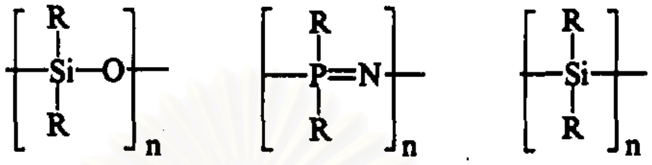
Another system that has been studied is inorganic and organometallic polymers.[5-6] Inorganic polymers offer a way to achieve new materials which have better properties than organic polymers. However, the traditional synthetic approach to organic polymers that involves a chain-growth mechanism such as addition polymerization (Sheme 1 pathway 1) is very difficult for synthesizing inorganic polymers since reactive but stable multiple bonds are difficult to prepare. Most of the early inorganic polymer syntheses focus on the use of polycondensation reactions
(Scheme 1 pathway 2).



E = inorganic element

Scheme 1. Synthesis of inorganic polymers.

However, synthesis of inorganic polymers is still not well established comparing to organic polymers mainly due to synthetic difficulties. Only a few inorganic polymers have been well-characterized : polysiloxanes(1), polyphosphazenes(2), and polysilane (3).

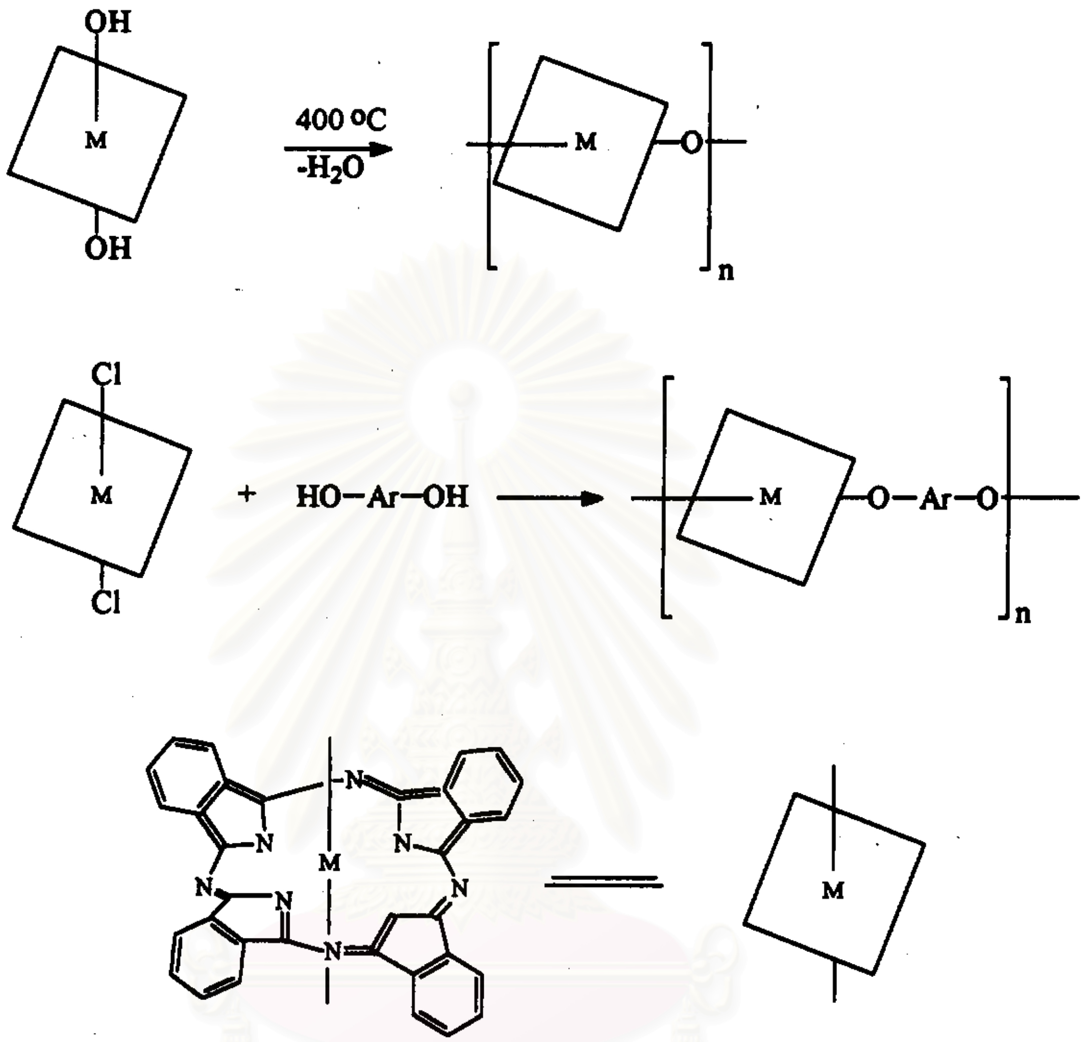


1 2 3

Structures of some inorganic polymers

Organometallic polymers, which process characters of both inorganic and organic substances, have been studied to develop heat-resistance polymers. The general synthetic method is the introdution of metal atoms into polymer chains by the linkage between metal atoms and heteroatoms in polymer chains. Organometallic polymers containing metal atoms bonded by coordination such as metal complex systems known as coordination polymers. Polymerization may involve metals as reaction centers or may not concern metal centers at all.

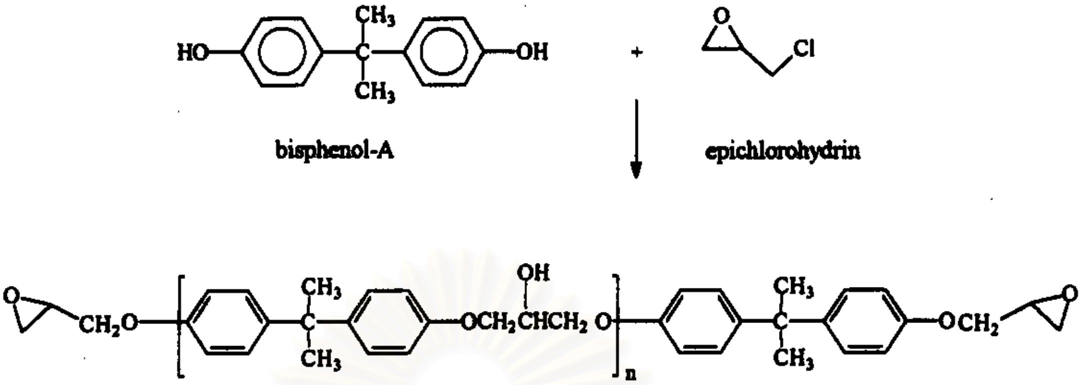
Incorporation of transition metals into polymer chains offers a possibility to access new useful materials which differ from organic materials. Transition metal complexes and metal-containing materials display many interesting properties such as redox and electrical properties. One example of recent development incorporates a phthalocyanine moiety into a polymer structure (Scheme 2).[7-8] The phthalocyanine-containing polymer has a potential application such as high temperature and electrical conducting materials.



Scheme 2. Synthesis of the phthalocyanine-containing polymer.[1]

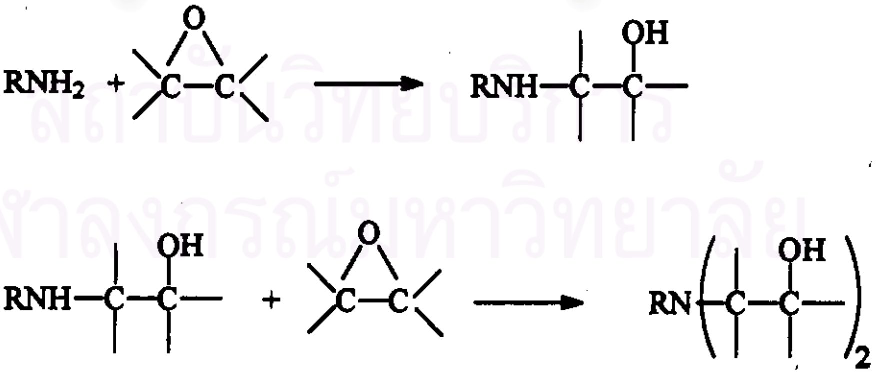
1.2 Epoxy Polymers

Epoxy resin is a molecule containing more than one epoxy group which is capable of being converted into a thermoset polymer. The first commercial epoxy resin was obtained from the reaction of bisphenol-A and epichlorohydrin in the presence of sodium hydroxide. The reaction first occurred by the formation of chlorohydrin followed by dehydrohalogenation (Scheme 3)



Scheme 3. Synthesis of epoxy resin.

This type of epoxy resins is referred as diglycidyl ether of bisphenol-A (DGEBA). The n of low-molecular weight liquid DGEBA is about 1 or less. When $n=0$, the resin is known as monomeric DGEBA. Upon mixing epoxy resin with proper crosslinking agent, the resin can be converted into a thermoset epoxy polymer. One of the most useful crosslinking agents is amines which undergo crosslinking reaction with DGEBA as shown in Scheme 4.

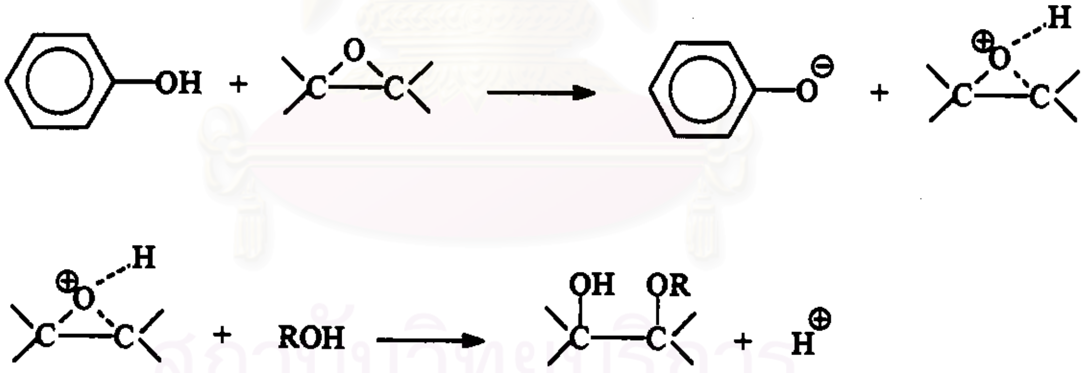


Scheme 4. Crosslinking reactions of DGEBA with amine.

Crosslinked epoxy polymers have unique useful properties such as low shrinkage, high adhesive strength, good mechanical properties, high electrical insulation, and good chemical resistance. Therefore, they offer wide applications in the areas of aircraft, automobile and coating industry.

1.2.1 Phenolic Crosslinking Agents

One type of crosslinking agents used industrially is phenolic compounds.[9-10] Diphenols such as biphenols A and diphenolic condensation products of diphenols are used, as curing agents in the present technology, most usually with the epoxidized olefin resins. Diphenols have been reacted with resins if elevated temperature are employed. They are generally used at a mole ratio of about 0.6/1 with diepoxides, and addition etherification is obtained. The exact mechanisms have not been elucidated, but it is likely that the reaction proceeds, in part, through the formation of an intermediate oxonium ion. The carbonium ion from the oxonium complex may react with a hydroxyl group, shown in Scheme 5.

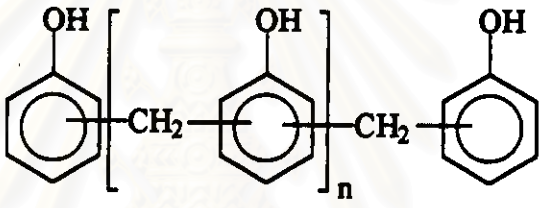


Scheme 5. Crosslinking reactions of DGEBA with phenol.

1.2.2 Phenol-Formaldehyde Crosslinking Agents

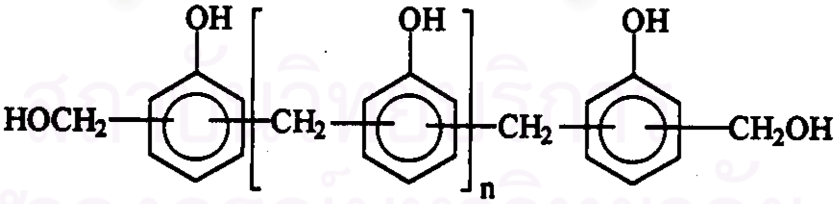
Phenolic resins from phenols or alkyl phenols and formaldehyde may be classified into two types, the resins and the resole resins. The novolac resins epresented by the structure A whereas the resoles are represented by the generalized structure B or by partially condensed products from the reaction of a phenol with excess formaldehyde, the monomeric compound containing more than two hydroxymethyl groups.

A



The idealized novolac

B



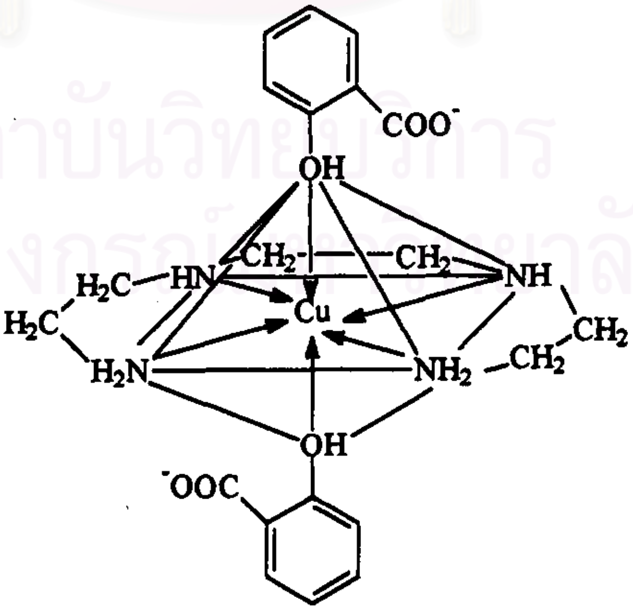
The idealized resole

Attempts have been made in order to improve physical and mechanical properties of epoxy polymers. Until now, metal-containing epoxy polymers[9] can be obtained by crosslinking of epoxy resin in the presence of metal complexes.

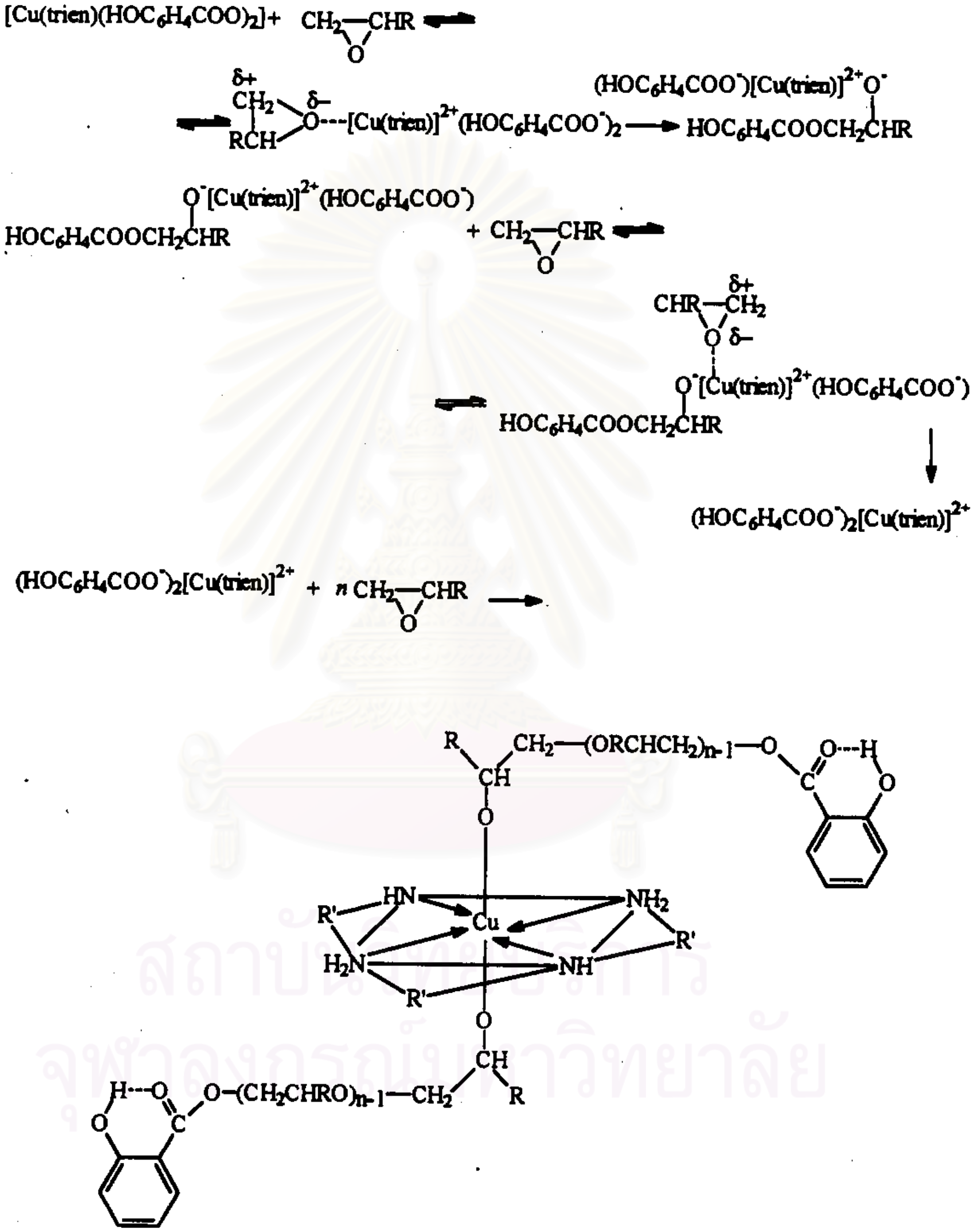
Anand and Srivastava[11] synthesized a new type of epoxy resins containing zinc, chromium, and copper by reaction of bisphenol-A with excess epichlorohydrin in the presence of metal acrylates. The obtained metal-containing epoxy resins were characterized by various techniques such as IR spectroscopy, NMR spectroscopy, and size exclusion chromatography, and the presence of metals in the resin was confirmed. Crosslinking of these epoxy resins with polyamide gave metal-containing resistance, and electrically conductive polymers as compared to conventional epoxy polymers without metals in their structures. The explanation for experimental results is the assumption that the metals form complexes with oxygen moieties in epoxy resin.

Lin, Shu, and Wey[12] investigated the toughtening effects of organotransition-metal complexes. Crosslinking of DGEBA was done by using diethylenetriamine in the presence of chromium or cobalt acetylacetonate as additives. Both complexes show catalytic effect in crosslinking reaction since crosslinking temperature decreases with increasing concentration of metal complexes. Results from size exclusion chromatography of a mixture between DGEBA and chromium acetylacetonate suggested that chromium acetylacetonate was able to interact with hydroxy groups in DGEBA and reinforcing the epoxy network. It was also believed that this interaction shortened the repeat distance of local ordered structure in crosslinked epoxy network.

Kurnokin[13-19] crosslinked DGEBA with hexadentate transition metal complexes. An example of metal complexes is shown in Figure 1.



One of the crosslinking mechanisms proposed was shown in Scheme 6. In fact, the crosslinking reactions of DGEBA with the above complex proceeded by many mechanisms and various structures of polymer matrixes were formed.

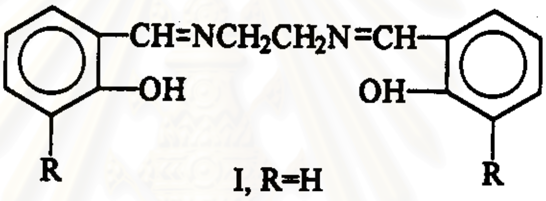


Scheme 6. Possible mechanisms of crosslinking reaction of DGEBA with a metal complex.

It was found that crosslinking reactions needed short cure time at not too high temperature. The obtained metal-containing epoxy polymers has good property, thermal stability, chemical resistance, and electrical resistance. Properties of metal-containing epoxy polymer on types of metals and ligands in metal complexes.

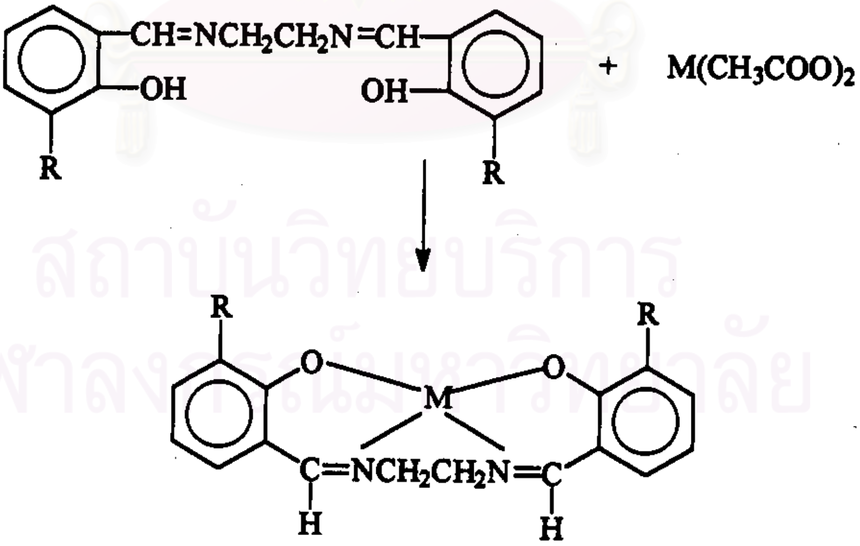
1.3 Tetradentate Schiff's base Complexes

This type of metal complexes has long been known since 1956. Marvel, Aspey and Dudley[20] synthesized Zn(II), Ni(II), Cu(II) and Fe(II) complexes of a variety of Schiff's bases prepared from hydroxy aromatic aldehydes and diamines have been prepared. An example of ligands in all Schiff's bases and the reaction can be occured as shown in Scheme 7.



I, R=H

II, R=CH_3



M = Zn, Ni, Cu and Fe

Scheme 7. The reaction of tetradentate Schiff' s bases ligands.

Many attempts have been made to synthesize organometallic polymers which structures held together by coordination bonding and employing oxygen or nitrogen as donor atoms. An example of organic ligands used in this way is Schiff's bases. Serrano and his coworkers [21] synthesized hydroxy-functionalized liquid-crystalline polyazomethines (Figure 2). Intrachain coordination leads to bending of polymer chains while interchain coordination leads to crosslinking of polymer chain.

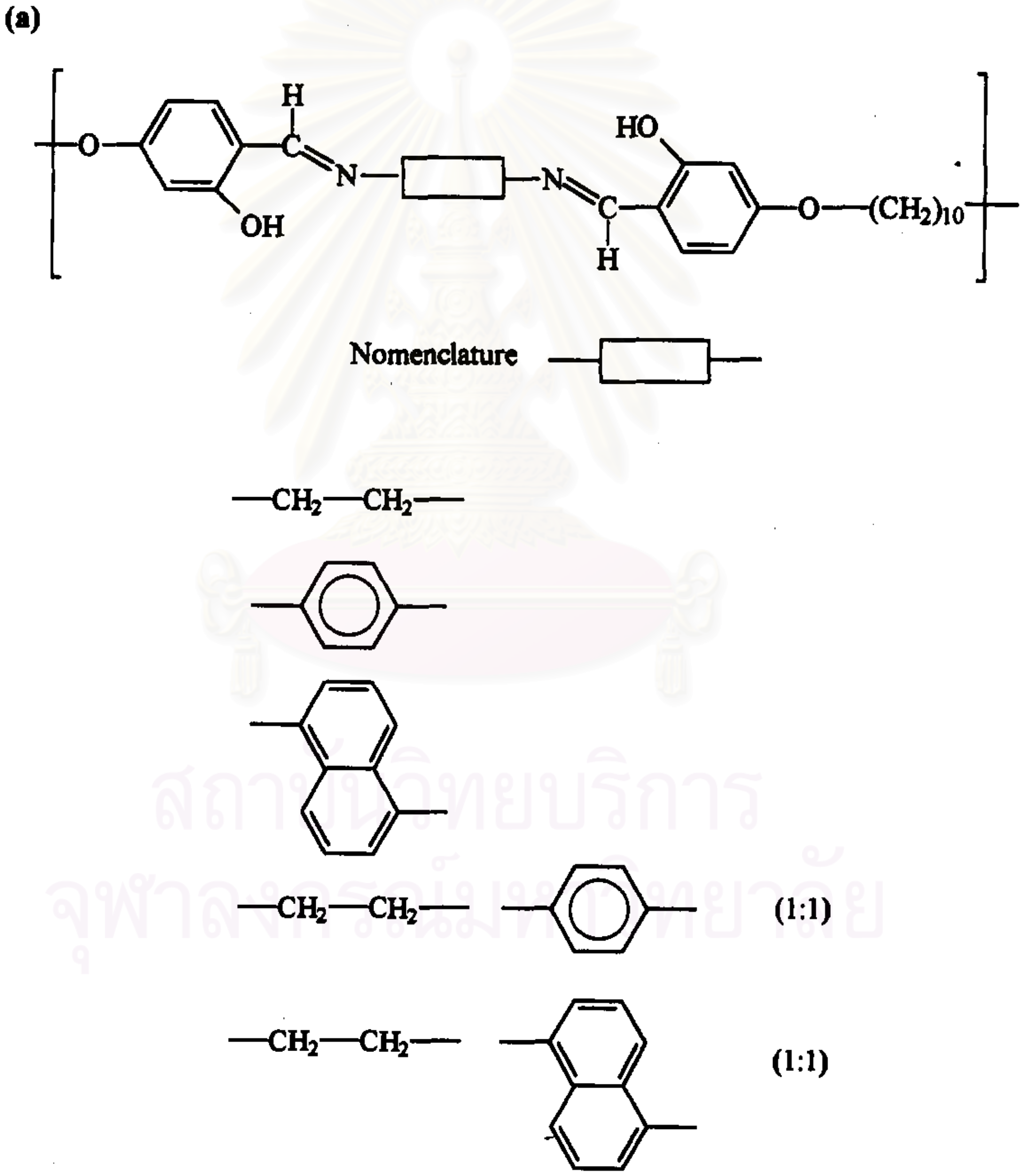
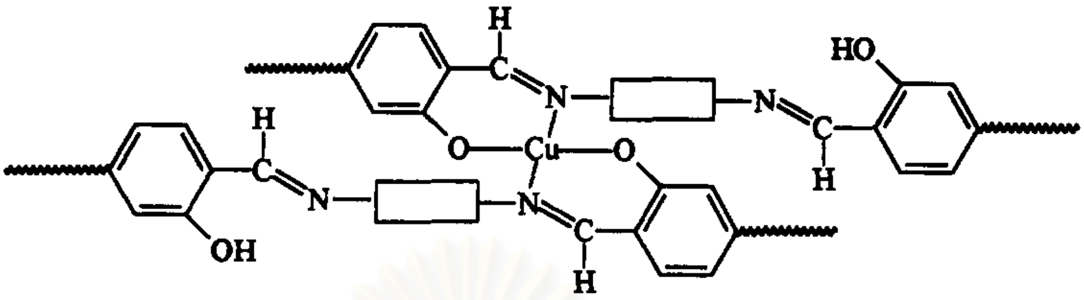
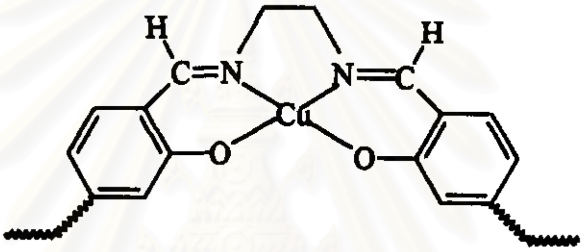


Figure 2a. Selected polyazomethines for their metal modification.

(b)



Interchain coordination

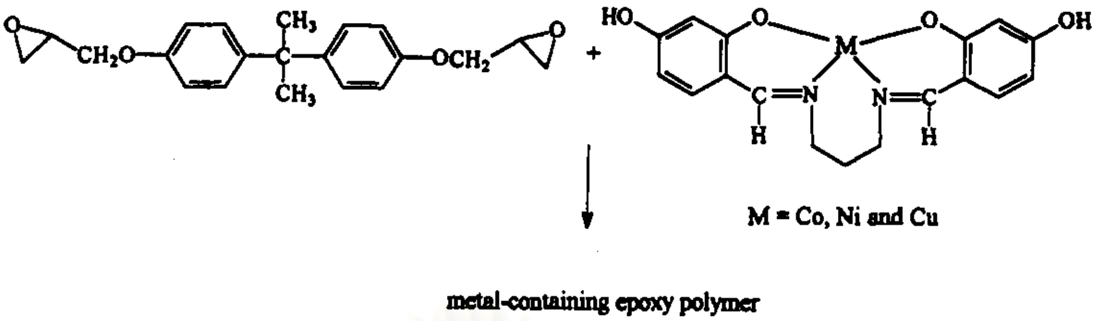


Intrachain coordination

Figure 2b. Structural modification introduced by metal depending on the geometry of the central core.

1.4 Objective and Scope of the Research

In this work efforts were made to synthesize metal-containing epoxy polymers since it was known that addition of metals into polymer frameworks improves thermal property of polymers. Crosslinking of DGEBA was done using tetradentate Schiff's base metal complexes as crosslinking agent (Scheme 8). These metal complex could be synthesized by a modification of the synthetic methods described by Marvell and Bottcher.[20,22] The optimum conditions for crosslinking process were studied and finally, thermal properties of the obtained metal-containing epoxy polymers were investigated.



Scheme 8. Syntheses of metal-containing epoxy polymers.