



CHAPTER I

INTRODUCTION

Interpenetrating Polymer Networks

Interpenetrating polymer networks are a novel type of polymer blend containing two or more network polymers.¹⁻³ They are held together predominantly by entanglement of two crosslinked networks. IPNs offer an advantage over typical mechanical polymer blends in improvement of mechanical properties since IPN combines two crosslinked polymers with limited phase separation. There are two basic techniques for producing IPNs. The first method is crosslinking of monomer B in a crosslinked network of polymer A. For example, Millar⁴ prepared a network of polystyrene crosslinked with divinylbenzene employing this method. Other such IPNs were prepared by Meyer^{5,6} and Sperling.⁷ They found that while the properties of IPNs such as in rubber modulus and swelling tendency improved, the glass transition temperature and the viscoelastic properties in the glass-to-rubber transition region were not much altered. The second method is simultaneous polymerization of monomer A and monomer B in the presence of each other. For example, Frisch and coworkers produced IPNs of polyurethane-poly(methyl methacrylate)⁸, polyurethane-epoxy resin⁹ and aliphatic polycarbonate-polystyrene¹⁰. The physical and mechanical properties of these IPNs showed interesting and remarkable trends. Figure 1 is a schematic representation of an ideal IPN.

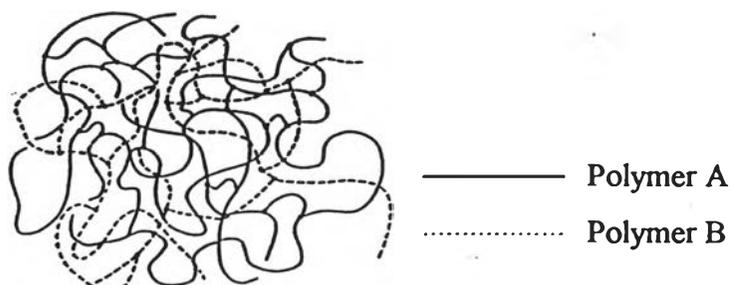


Figure 1. Ideal interpenetrating polymer network¹¹

IPN systems that have been studied are the IPN of polyurethane-polystyrene¹², polyurethane-poly(methyl methacrylate)⁸, polyurethane-polyunsaturated polyester resins⁹ since their solubility parameters are so different that phase separation occurs easily. The use of IPN is a route to combine these two polymers which results in enhancement of mechanical properties.

Polyurethane elastomers

Polyurethanes are polymers containing the urethane linkage (Figure 2).

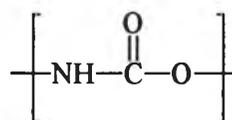


Figure 2. The urethane linkage¹³

The reaction of an isocyanate with an alcohol to form the urethane linkage was discovered by Wurtz in 1848.¹³ This reaction was used for urethane polymer formation by Otto Bayer and his co-workers at I.G. Farbenindustrie at Leverkusen, Germany in 1937.^{14, 15} The most familiar polyurethanes are prepared by reaction of diisocyanates with diols (Scheme 1).¹⁶

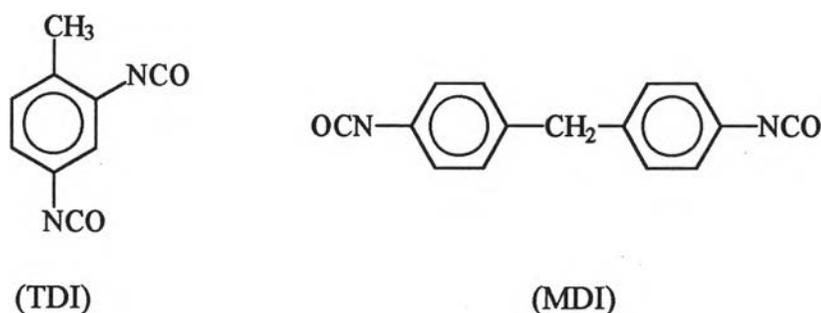


Scheme 1.

Polyurethanes have a wide range of commercial applications. They are useful in the production of different products such as foams, fibers, elastomers, and coating materials.^{15, 17} Polyurethanes have a specific structure which combines flexibility with strength. Their wide variety of uses is due to the ability to control their properties over a wide range from rigid materials to elastomers. The basic starting materials used in the preparation of polyurethanes are isocyanates, polyols and chain extenders or crosslinking agents.¹³

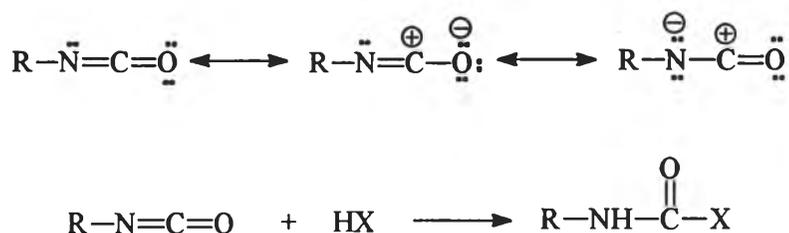
Isocyanates

Isocyanates are a major polyurethane component. Examples of common isocyanates used to prepare polyurethanes are toluene diisocyanate and 4,4'-diphenylmethane diisocyanate.¹⁸ (Scheme 2)



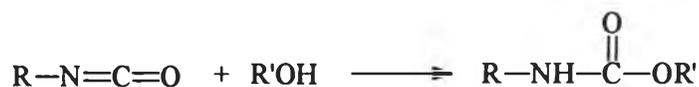
Scheme 2.

Isocyanates are very reactive compounds with many possible resonance structures. Any active nucleophile can add to the nitrogen-carbon bond as shown in Scheme 3.^{15, 19, 20}



Scheme 3.

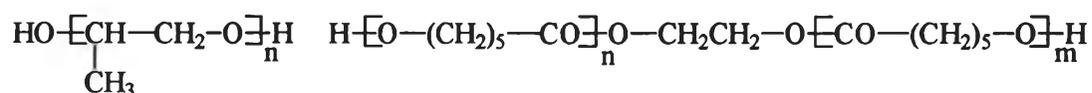
The decreasing order of reactivity of nucleophilic addition is : $\text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3 > \text{ArNH}_2 > \text{ROH} > \text{HOH} > \text{RCOOH}$.⁹ The order for hydroxyl group-containing compounds is primary alcohols > secondary alcohols > tertiary alcohol > phenols.^{15, 20} Tertiary alcohols and phenols can react with isocyanates when the reaction is catalyzed by acids or bases such as pyridines, triethylamine or aluminum chloride.²¹ The general reaction between an alcohol and an isocyanate is shown in Scheme 4.



Scheme 4.

Polyols

Polyols are an other important component for the formation of polyurethane. Polyols are polyethers or polyesters with long flexible chains terminated by at least two hydroxyl groups.¹³ Typical molecular weights are in the range of 1000-6000.^{17, 22} Typical examples of polyols are poly(oxypropylene) glycols and polycaprolactone ester (Scheme 5).¹³



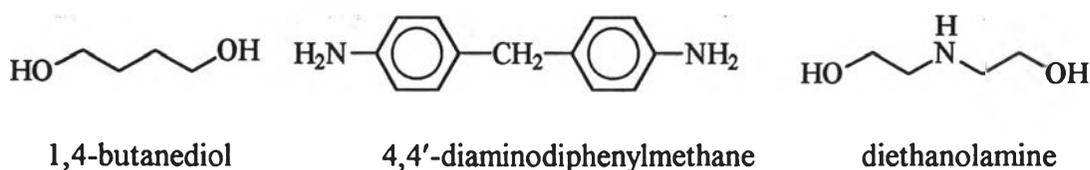
Poly(oxypropylene) glycols

Polycaprolactone esters

Scheme 5.

Chain-Extending Agents and Crosslinking agents

Chain-extending agents and crosslinking agents are necessary components for the preparation of polyurethanes. The main function of chain-extending agents is to increase the size and extend the polymeric chain. Crosslinking agents increase the size of polymeric chain and give network polymers. Examples of chain-extending agents and crosslinking agents are diols and diamines such as 1,4-butanediol, 4,4'-diaminodiphenylmethane and diethanolamine.^{13, 15} (Scheme 6)



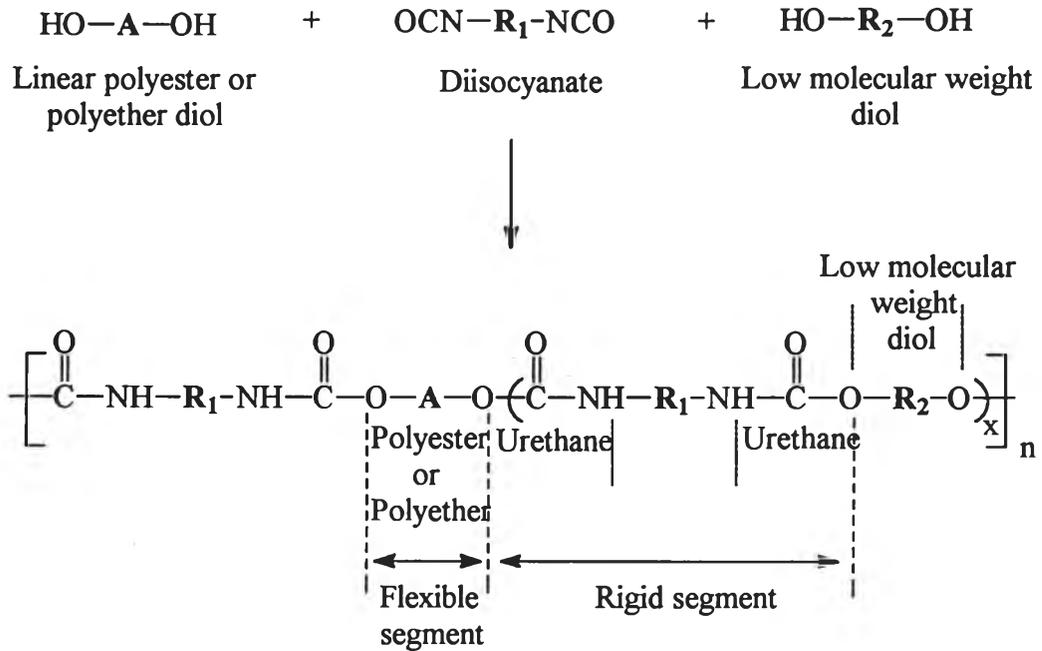
1,4-butanediol

4,4'-diaminodiphenylmethane

diethanolamine

Scheme 6.

Polyurethanes can be prepared by many routes. One of the methods is a one shot synthesis which is done by reaction between an isocyanate and a polyol in the presence of chain-extending agents or crosslinking agents as shown in Scheme 7.¹³

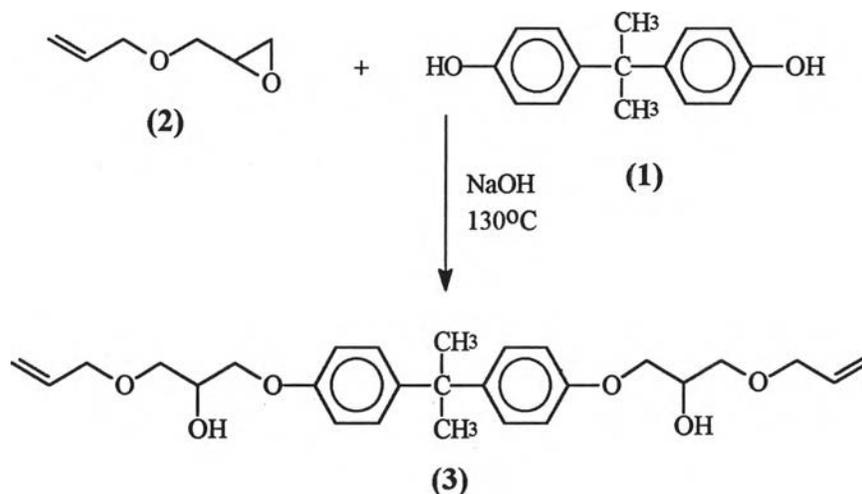


Scheme 7.

Objective and scope of the Research

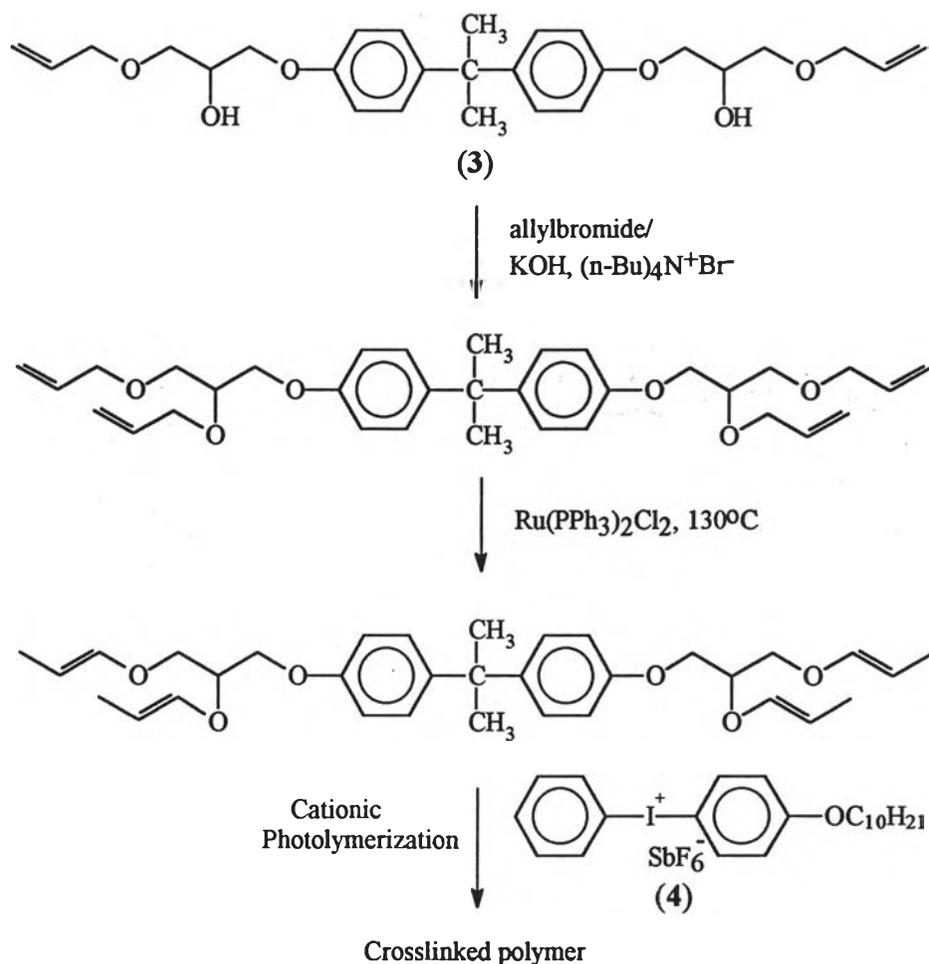
The objective of this research is to synthesize new crosslinking agents for polyurethane and investigate the possibility of using these crosslinking agents in the preparation of polyurethane elastomer.

In 1994, Crivello and Kim prepared bis-3-(allyloxy-2-hydroxy-1-propoxy) diphenoxypropane (**3**)²³, from allyl glycidyl ether (**2**) and bisphenol A (**1**) (Scheme 8). Compound (**3**) is a multifunctional compound which contains two hydroxy groups and two vinyl groups. It can be used as a crosslinking agent for poly(vinyl chloride) to improve thermal stability and low temperature resistance.²⁴



Scheme 8.

Another application of the multifunctional compound (**3**) is as a starting material for the synthesis of crosslinked polymers. Allylation of the secondary hydroxyl groups in (**3**) followed by isomerization of the allyl groups by a ruthenium catalyst yielded propenyl ether monomer which underwent cationic polymerization with (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**4**) as a photoinitiator²³ to give a crosslinked polymer (Scheme 9)



Scheme 9.

Since compound (3) has interesting applications, we chose to investigate the possibility of the use of (3) and related compounds as crosslinking agents in the preparation of polyurethane elastomers.

Four new compounds, (7), (9), (11), and (13) which are similar to (3) in having multiple hydroxy and vinyl groups, were synthesized^{23, 25} and characterized by spectroscopic techniques²⁶⁻²⁹ (Figure 3). A preliminary study of these multifunctional compounds as crosslinking agents for polyurethane was undertaken.

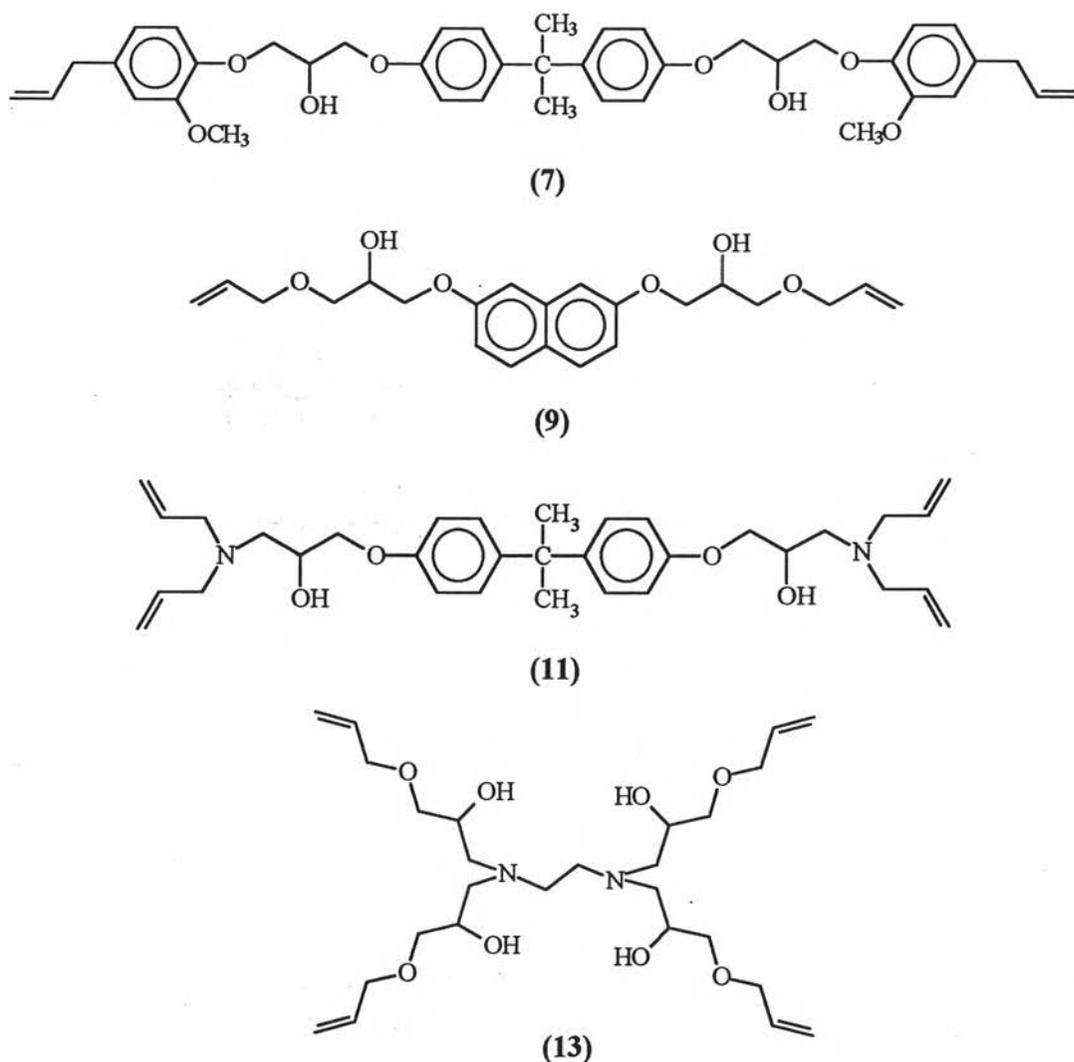


Figure 3. Representation of crosslinking agent

When compounds (3), (7), (9), (11), and (13) are used in the preparation of polyurethane elastomers, hydroxy groups of these compounds such as (3) should be able to react with the isocyanate groups of MDI to give urethane linkage, while the vinyl groups are expected to undergo free radical polymerization in the presence of a free radical initiator.(Scheme 10). The structure of the obtained polyurethane elastomer should be a semi-interpenetrating polymer network with improved physical properties due to the increased degree of crosslinking and the nature of the crosslinked polymer network.

