

## Chapter 2

### Theory and literature review

Basic concepts regarding the modelling of three dimensional polymer networks were established by Carother, Flory and Stockmayer. The components of a simple network-forming polymer system are multiblock copolymers with an alternating sequence of hard and soft segments of HTPB and MDI

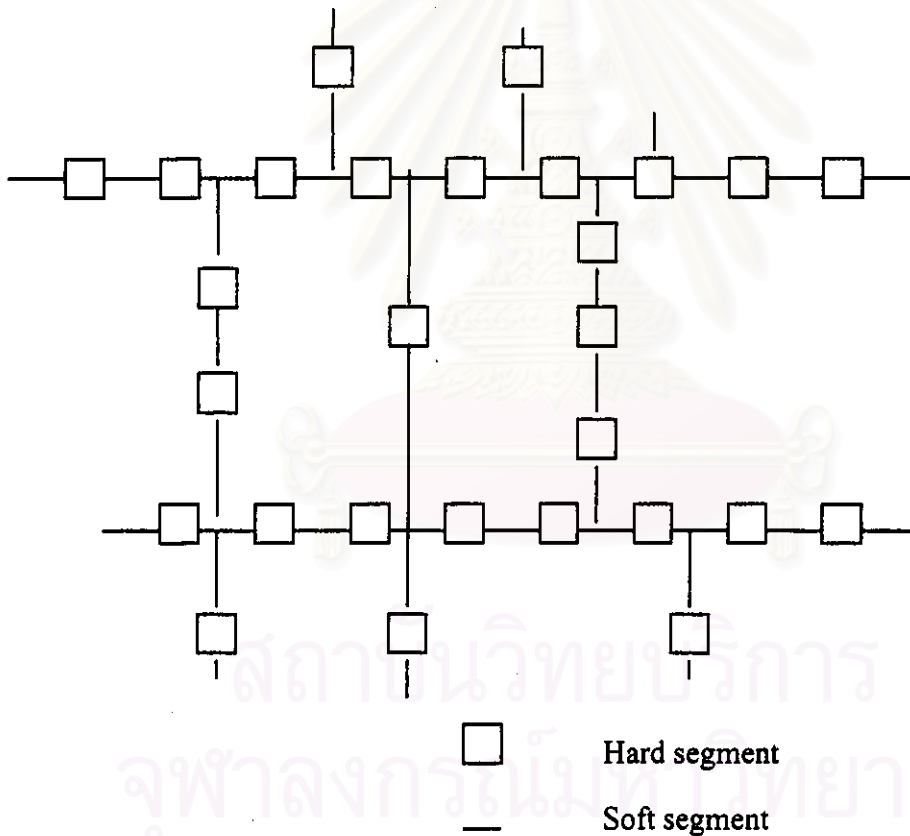


Figure 1 Schematic representation of the network structure. ( J.Appl.Polym.Sci., 42, 391,1991).

### **Hydroxy-terminated polybutadiene, HTPB**

Hydroxy-terminated polybutadiene prepolymers have gained considerable importance as polymeric fuel binders. Functionality, defined as the number of reactive functional groups (hydroxyl in this case) per molecule, is usually expressed as an average in the case of a polymer. However, the determination of average functionality of a prepolymer is not sufficient because it may consist of different proportions of mono-, di-, tri- and polyfunctional moieties. In the curing process the non-functional species do not contribute to the polymer network, the monofunctional species can terminate the growth of the network, the difunctional species contributes to polymer chain extension and hence flexibility, and the tri- or polyfunctional species result in the crosslinking and hence rigidity of the cured product.

The classical concept of determining the functionality distribution involved two steps separation of the polymer into fractions of different functionalities and estimation of each fraction in the terms of its functionality and quantity. Gel permeation chromatography (GPC) had been employed for the determination of molecular weight of the fractions. For determination of equivalent weights, sensitive spectrophotometric methods are generally used. Differences in the manufacture of these polymers and also batch-to-batch variability result in polymer varying in molecular weight distribution. These differences greatly affect the binders processibility, pot life, cure behaviour, mechanical properties. Three types of primary alcohol group were identified and correlate the functionality and molecular weight distribution with properties of the cured resins. Thus, HTPB may be considered to be a well-characterized polymer. However, studies on the relative distribution of the three types of hydroxyl functionalities in the polymer synthesized under varying conditions and also how these differences translate into the properties of the cured resin are lacking.

In this communication, HTPB can report on the functionality-type distribution of samples synthesized by free radical polymerization of 1,3-butadiene using hydrogen peroxide as initiator in an isopropanol-water solvent system. The relative amounts of butadiene,  $H_2O_2$ , water, and isopropanol were kept constant during the synthesis of the various polymers. The polymerization reactions can be summarized as follows:

### 1. Initiator decomposition

$H_2O_2$  is thermally cleaved to produce free radicals as show below;



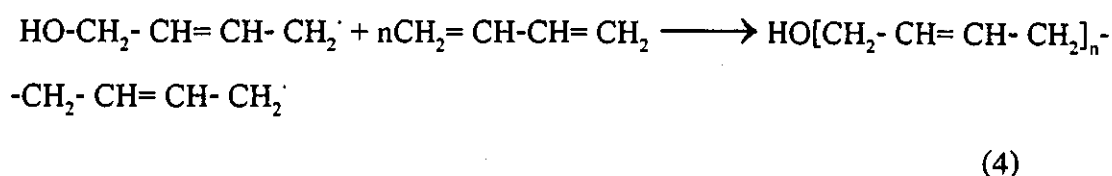
### Initiation

The free radicals formed initiate the polymerization reaction with butadiene :



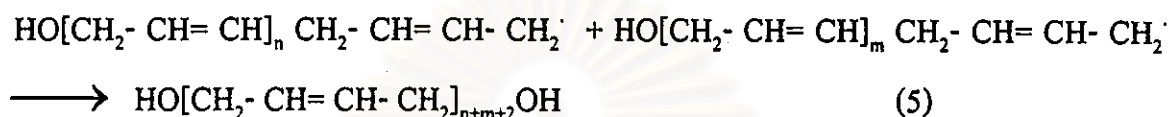
### Propagation

Further propagation of polymerization proceeds as follows :



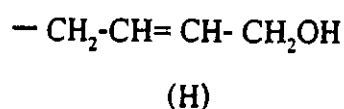
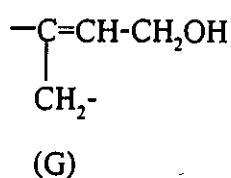
### Termination

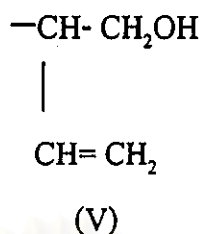
Polymer chain termination takes place by combination of two growing chains having free radicals.



In free radical polymerization, process parameters like reaction temperature, initiator-monomer ratio, and solvent ratio are the critical process parameters that affect the produce quantity. The quantity of initiator required in the reaction recipe is determined by the half-life period of the initiator. Keeping all other process parameters constant,  $\text{H}_2\text{O}_2$  content in the reaction recipe was increased gradually, and the resulting HTPB resins were used in the present study. With increase in  $\text{H}_2\text{O}_2$  content, due to the availability of more free radicals, the chance of collision increases, and this results in increased hydroxyl value and decreased molecular weight for the product. Average functionality, which is the ratio of molecular weight to equivalent weight, decrease with decreasing  $\text{H}_2\text{O}_2$  content.

The identified three types of primary hydroxyls, namely, (i) geraniol type (G), (ii) 2-hexane-1-ol type or hexenol type (H), and vinyl type (V) with the following structure units. The presence of secondary hydroxyls, if any was found to be small. The three structure of G,H, and V-type as follow:





The three hydroxyl function, G,H, and V-types, can be readily distinguished and their relative amounts estimated from their chemical shift differences in  $^1\text{H-NMR}$  spectra.

### Functionality-type distribution

G-type hydroxyl presents trifunctional component and the mole fraction of the hydroxyls on trifunctional chain can be readily obtained from  $^1\text{H-NMR}$  as show in figure 2 and table I give their concentration of the different OH groups as estimated from the  $^1\text{H-NMR}$ . Therefore, G-type is branched, whereas, H and V-types are terminals. Also, G-type contributes to crosslinking in the cured system, whereas, H and V-types act as chain extenders only. Consequently, the higher proportion of G-type in the polymer, the higher the tensile strength and lower the elongation of the cured polyurethane network. On the other hand, V-type gives rise to urethane linkages with a single bond at the  $\alpha$ -carbon, Whereas H-type gives rise to a linkages with a double bond at the  $\alpha$ -carbon atom ( $\text{ArNHCOOCH}_2\text{CH=CH-}$ ). Hence, V-type functionality is expected to contribute to higher elongation. Therefore, the net effect of the different types of functionality causes an increase in elongation and a decrease in tensile strength as the ratio of concentration of vinyl type to G-type, ( $[\text{V}]/[\text{G}]$ ). The excellent linearity demonstrates the influence of the functionality-type distribution on the sample stock properties. The functionality of HTPB lies in the range 1.85-2.25. Moreover, the functionality increase with increase in molecular weight. Therefore, the contribution of functionalities equal to or higher than 4 can be neglected, and the polymer can be approximated as having tri- and lower functionalities only.

Table 1 Quantity of different hydroxyl groups and backbone microstructure of HTPB

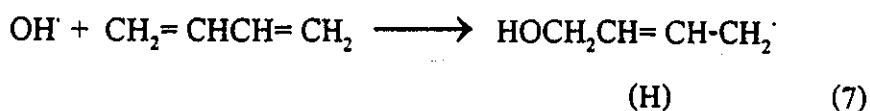
	HTPB (%)
<b>Peak and type of OH group</b>	
3.5 ppm (vinyl type)	40
4.0 ppm (hexenol type)	45
4.1 ppm (geraniol type)	15
<b>Microstructure</b>	
<i>cis</i> -	25
<i>trans</i> -	52
Vinyl-	23

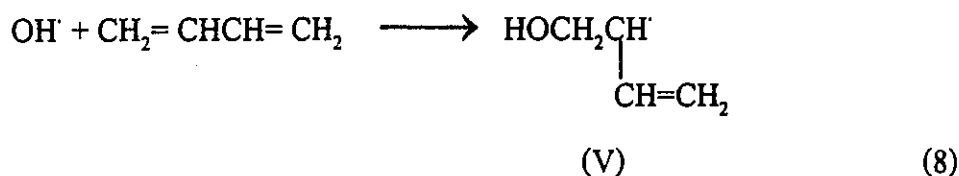
( J. Appl. Polym. Sci.,56,1797,1995)

**Molecular weight distribution**

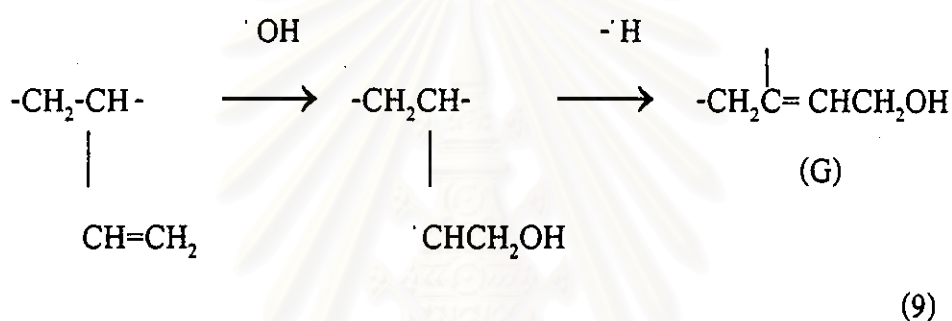
The molecular weight distribution of HTPB prepolymer was determined by size-exclusion chromatography, (SEC). A bimodal distribution of the molecular weight is clearly indicated. Attempts were then made to improve the resolution by reverse phase HPLC using a Shim-pack Prep-ODS column and THF as the eluente.

The bimodal distribution of HTPB prepolymers may be because two types of initiation reactions are occurring in the polymerization process, as is evident from the occurrence of H- and V-type hydroxyls in the polymer. H-type hydroxyls arise from the addition of OH radicals to a butadiene monomer in a 1,4- fashion, whereas the V-type hydroxyl arise from a 1,2-addition as was suggested by Pham:

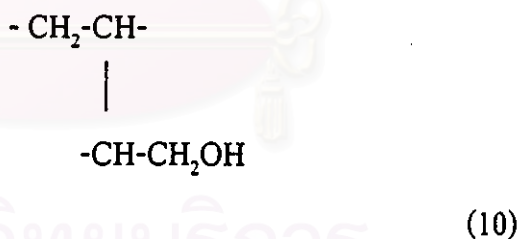




The G-type hydroxyl may arise from the addition of OH radical to a V-type double bond in a polymer chain and subsequent loss of a H-type radical;

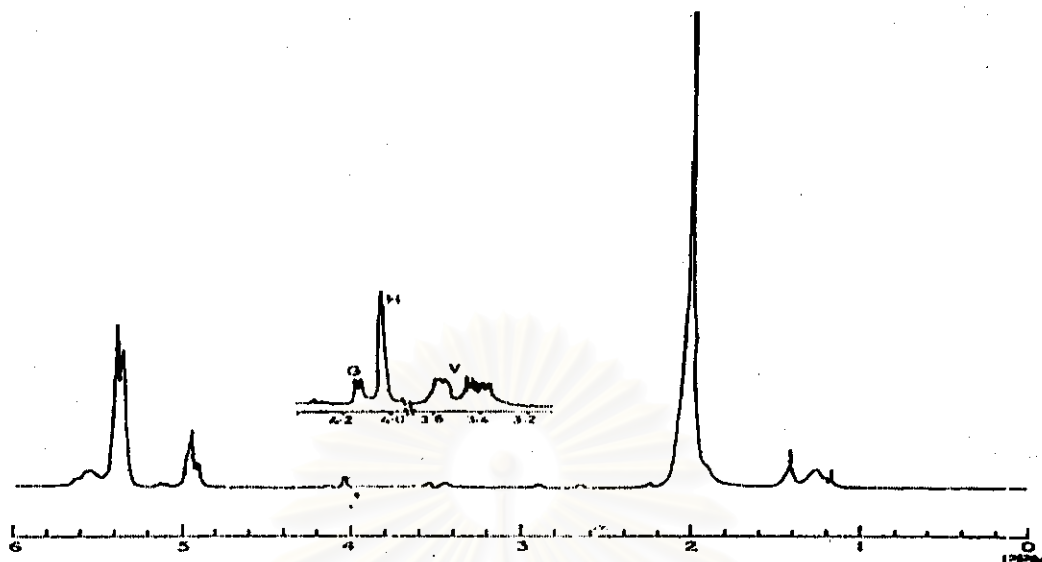


The absence of structural unit of type



in the polymers suggests that formation of G-type is not an initiation reaction. Thus, only reactions (7) and (8) can be considered as initiation reactions. The relative importance of the two initiation reaction (7) and (8) can be judged from the relative concentration of H- and V-type hydroxyls. The ratio ( $[\text{H}]/[\text{V}]$ ) can be contained from  $^{13}\text{C}$ -NMR as indicated earlier and values obtained for the various polymers are given in table 2. In the case of G-type, it is more reactive than H- and V-type hydroxyls and superior water-resistant properties to that of the conventional polyols used in polyurethane synthesis.





(J.Appl. Polym. sci.,56, 1797,1995)

Figure 2 The  $^1\text{H}$ -NMR spectra of free radical HTPB

The HTPB resins with lower hydroxyl values or higher molecular weights require a high polyfunctionality content to achieve a high tensile strength, and moderately high elongation.

Table 2 Functionality and Molecular weight distribution of HTPB prepolymers

Polymer	Functionality-type Distribution					MWD	
	[G]	[H]	[V]	[V]	[di]	$F_h$	[H]
	(%)	(%)	(%)	$\overline{[G]}$	$\overline{[tri]}$	(%)	$\overline{[V]}$
I	24.0	59.1	16.9	0.70	0.58	35.9	3.50
II	25.0	54.6	20.4	0.82	0.50	33.4	2.68
III	24.3	51.8	23.9	0.98	0.56	30.8	2.17
IV	23.1	51.7	25.2	1.09	0.67	29.2	2.05
V	21.5	53.2	25.2	1.17	0.83	23.8	2.11
VI	20.6	52.7	26.7	1.30	0.93	24.1	1.97
VII	17.4	57.6	25.0	1.44	1.37	23.8	2.30
VIII	18.2	54.5	27.3	1.50	1.25	24.6	2.00
IX	14.4	57.9	27.7	1.92	1.97	24.9	2.05



### **Degradation of HTPB**

Composition of binders generally consist of the double bond in the soft segment. Among the rubber-like binders are polyurethanes. Polyurethanes are prepared by the reaction of diisocyanate materials with polyols containing functional hydroxyl groups. The most commonly used polyglycols are the hydroxyl-terminated polybutadiene prepolymers. HTPB has some advantages over other binders, such as permitting a solid loading of up to 92 % in solid propellants while retaining the desired mechanical properties and the ability to cure at low temperatures. The mechanical properties of binders depend upon the properties of their components. Therefore, the chemical structure, functionality, viscosity and variations in these properties become important in the function of binders.

The necessity to obtain large quantities and their long-term storage may cause alternations in their properties. The mechanisms of these changes are not well understood and for that reason aging of binders is being investigated by many researchers. Among the changes due to aging are hardening caused by crosslinkage through the double bond present in the main chain of polyurethane and HTPB unreaction. A relationship between the changes in the chemical structure and the mechanical properties during aging was established. Depending on the aging temperature and duration complete curing and increase in crosslink density and a higher temperatures gel formation as a result of further reactions of urethanes with allophanate formations observed. Thermogravimetric analysis revealed that heating rate sample mass or the nature of the terminal groups did not affect the kinetic parameters. The activation energy for the thermal decomposition was found to be around 110 KJ/mol. From accelerated aging studies of researchers in the temperature more than 40 °C. Although various diisocyanates are used as curing agents for HTPB is care of the most commonly used. The details of curing reaction were examined and found to obey the second order rate equation. Since the mechanical properties are affected by the properties of the component used, their aging and lifetime gain importance.

The thermal aging of HTPB was examined at various temperatures and the alternations in chemical, physical and mechanical properties were measured from these changes.

#### 1. Viscosity

The effect of aging on the viscosity of the samples can be seen that an increasing in viscosity take place during aging at high temperatures. The increase in viscosity with aging can be explained by the formation of crosslinks between the double bonds of HTPB. Higher temperatures accelerate opening of the double bonds and the formation of crosslinks. The decrease in the amount of double bonds expected from the above explanation is also supported by the IR spectra.

#### 2. Molecular weight

The aging temperature and aging duration affect the molecular weight of HTPB increase in  $M_v$ . Higher temperature and storage longer periods case greater in  $M_v$ . For example, while the HTPB aged a 50 °C for 3 months showed about 25 % increase in  $M_v$ , the HTPB aged at 100 °C for three weeks demonstrated an 87 % increase. These also indicate that the rate of formation of crosslinks is higher than the rate of chain scission reactions.

#### 3. Functional groups

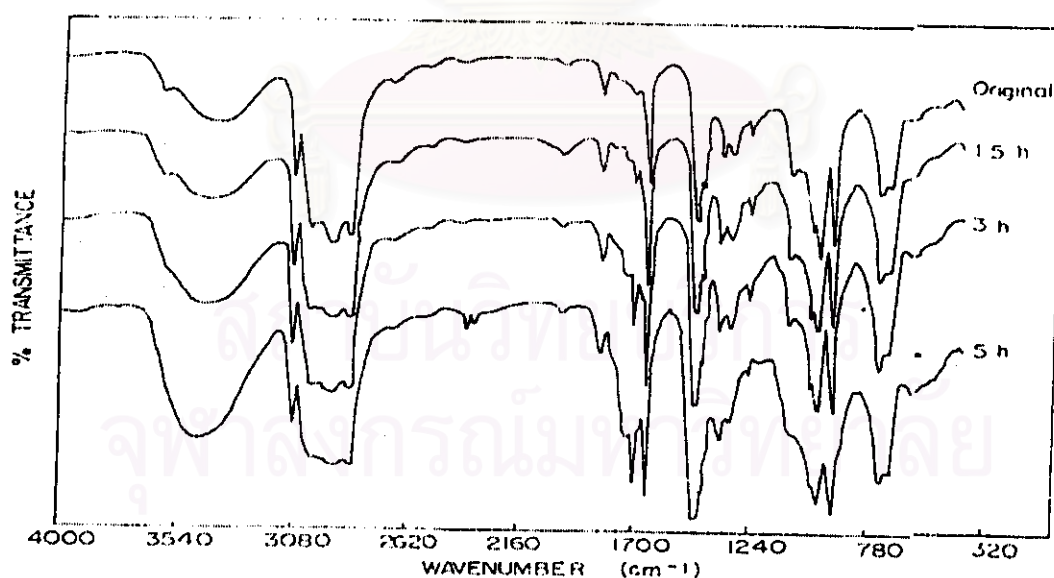
If the HTPB sample aged at 100 °C the hydroxyl value increased by 53 % after 35 days. This increase can be explained by the formation of radicals which are then converted to peroxides in the presence of oxygen. These peroxides may eventually lead to hydroxides or carboxyl compounds.

#### 4. Chemical structure

The IR spectra of aged samples revealed an increase in the OH peaks at 3300  $\text{cm}^{-1}$  as show in figure 3. The reason for this increase in the hydroxide groups was explained previously. Also carboxyl absorption peaks, which were almost absent in

the original samples, were absenced after aging. This can be due to further reactions of peroxide bonds, the incipiente oxidation of the unsaturated bonds (observed as decrease in the peak at  $1080\text{ cm}^{-1}$ ) or as a combination of all these. A decrease in the vinyl absorption peak ( $966\text{ cm}^{-1}$ ) was observed, possibly as a result thermal breakage of double bonds and further reactions such as crosslinkings.

Christiansen studied the aging of HTPB and found that both tensile strength and gel content increased with aging time. He discribed this phenominon to the chemical reactions at the sites unsaturation in the polymer chain, Layton used iodimetric titration and NMR to determine the total unsaturation in the polymer and concluded that the double bonds were disappearing with aging and more rapidly at the elevated temperature. All the earlier studies showed that the HTPB was susceptible to  $\text{O}_2$  attack even at room



(Polymer J.,35,2568,1994)

Figure 3 The IR-spectra of HTPB aged at  $100\text{ }^{\circ}\text{C}$

temperature. Also, this reaction was accelerated by heat and UV radiation. In all studies, the absorbance in the OH and  $\text{C}=\text{O}$  region in the IR spectra increased and the double bond absorbance decreased. When aging at  $80\text{ }^{\circ}\text{C}$ , the IR spectra showed some changes.

The absorption bands at  $3400\text{-}3600\text{ cm}^{-1}$ , (OH) and  $1710\text{-}1750\text{ cm}^{-1}$ , (C=O) become broader with aging time. Also, the C=O absorbance was increasing at the lower wave number (around  $1700\text{ cm}^{-1}$ ), due to the thermal oxidation of HTPB, which would produce the hydroxyl and carbonyl groups. The probability of hydrogen bonding, thus, might have increased to some extent.

### 5. Lifetime prediction

Absorption of thermal energy and thermal aging trigger various reactions leading molecular chain degradation causing physical aging. On the other hand, an estimation in which the desired properties are retained. Generally a simplified form of an Arrhenius-type relation based on a time-temperature relation, is used for the prediction of lifetime. The time required for a 50 % deterioration in a physical property at various temperatures is used in this relation

$$t = t_0 \exp (E/RT)$$

Where  $t$  is the lifetime,  $t_0$  is the pre-exponential factor,  $E$  is the activation energy of the degradation process,  $T$  is the aging temperature and  $R$  is the gas constant. It is known that not all physical or mechanical properties deteriorate with aging or are sensitive to the thermal degradation. The variance of percentage elongation at break, which is sensitive to aging and shows a decrease, was chosen for the lifetime prediction. For the original sample, elongation at break was found to be 170 % it was assumed to have reached the limit of usage. The time required to reach this value for each temperature was obtained. The useful life of HTPB was predicted to be approximate 7 years from extrapolation to the normal storage temperature of  $20\text{ }^{\circ}\text{C}$ . It can be thus concluded that HTPB in this state which is used as binder, can be stored for 7 years at room temperature with its various properties maintained in the usable range.



### **Hazard of HTPB**

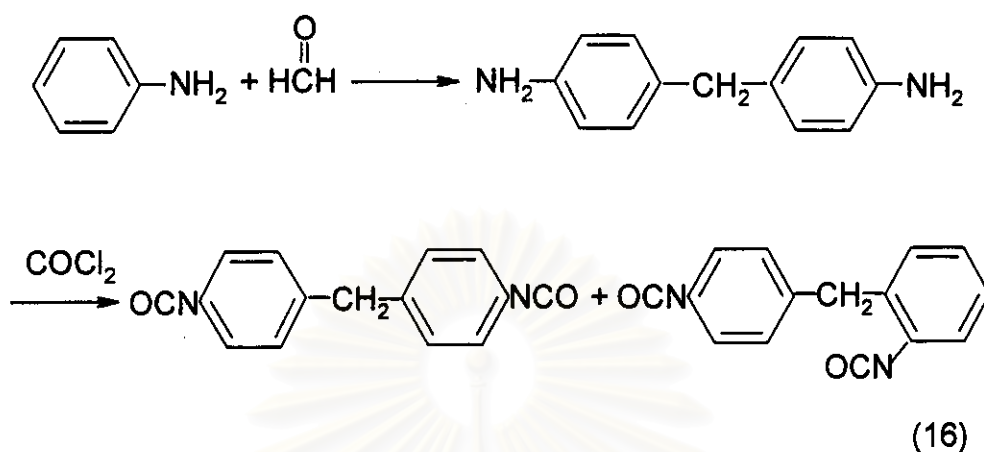
There are generally regarded as non hazardous, they do not vaporize at ambient temperatures and hence do not constitute an inhalation hazard. Oral consumption may result in serious injury or death.

### **4,4' diphenylmethane diisocyanate, MDI**

Only diisocyanates are interest for urethane polymer manufacture. Diisocyanates may by modified in many ways to give products with differing physical and chemical properties. Several aromatic and aliphatic diisocyanates are available, but about 95 % of all polyurethanes are based on two of them. These are toluene diisocyanate, (TDI), and MDI. Both materials are derived from readily available petrochemical intermediates and are manufactured by well understood and closely defined chemical processes. Some of the basic diisocyanates are converted on a commercial scale into derived products containing residual isocyanate groups such as polymerized diisocyanates of polyfunctional isocyanate to give low to non volatile products.

MDI is produced from aniline and formaldehyde, reacted together using hydrochloric acid as a catalyst. This condensation reaction produces a complex mixture of polyamines which are phosgenation to obtain a polyisocyanate mixture. The manufacturing route of MDI is follows in equation 16. Pure MDI is produced by separation from a polymeric MDI precursor. It can be used in its basic form or modified chemically to give a composition that is liquid at ambient temperatures. MDI is often used in the crude form. As would be expected from their chemical reactivity and substantial volatility, other diisocyanates can represent a serious toxic hazard in use, having a marked effect on the respiratory system and the skin, the care is very necessary in handing if damage to health is to be avoided.





On the other hand, the diisocyanate, MDI based on diaminodiphenylmethane is considerably safer to use, having a much lower volatility. There is, however, the disadvantage that it is less easily purified and consequently. According to the ratio of reactants and the extent of purification adopted, smaller amounts of higher molecular weight products, are also present and on phosgenation a mixed isocyanate of functionality greater than 2 results. For example, a typical crude MDI may contain 55 % of 4,4'- and 2,4'-diisocyanates and 20-25 % of the triisocyanates, the remainder being polyisocyanates. Such mixtures are conveniently liquid and available commercially in a wide range of variants, with a typical commercial series being illustrated in table 3. Purified 4,4'-diphenylmethane diisocyanate, a low melting point solid is also available and used in special applications, mainly elastomers and spandex fibers. When elastomers must process maximum strength it is preferable to use the pure form of solid MDI to obtain maximum linearity in the elastomer. Unfortunately pure MDI is not stable for long periods at ambient temperatures and hence needs to be transported and stored under refrigerated conditions (4 °C), otherwise a significant quantity of the dimerized MDI results in the originally pure MDI, rendering it unsuitable for elastomer production. For this reason many elastomers are manufactured from the liquid MDI isomer mixture with subsequent loss of strength.



Additionally in automatic machine processing, such as casting or reaction injection molding, the polyurethane intermediates must be processed as liquids, hence when pure MDI is used a heated storage facility is required that is unnecessary with the impure liquid MDI. Alternatively pure MDI may be stored and transported in a hot molten condition by tanker. Producers of isocyanate have developed processes for tailoring the MDI composition to the requirements of the end-product. The polyisocyanate mixtures are formulated to offer a range of differing functionalities. Functionality is defined as the average number of chemically reactive groups on each individual molecule present. Diisocyanate products are required for making elastomers, whilst high functionality MDI rich in polyisocyanates is desirable for the manufacture of rigid foams and binding materials. Within the latter groups, wide variation in molecular weight distribution and functionality are possible, giving considerable control over reactivity, viscosity, and application properties.



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

Table 3 Range of MDI variants

Average functionality	Product description	Polyurethane type
2.0	Pure MDI	High performance elastomers
2.01-2.1	Modified, liquid pure MDI	High performance elastomers. Micro-cellular elastomers
2.1-2.3	Liquid, low functionality polyisocyanates.	Flexible, semi-rigid foams.
2.5	Low viscosity liquid polyisocyanates.	High density flexible foams. Structural foams.
2.7	Low viscosity polymeric MDI.	Low density rigid foams. Semi-rigid foams. Particle binders.
2.8-3.1	High functionality polymeric MDI.	Rigid polyurethane and isocyanurate foams.

(The ICI Polyurethanes, George Woods, pp. 11)

Pure MDI is a white to pale yellow solid of melting point about 38-43 °C. It tends to form insoluble dimer when stored. The difficulty of handling solid pure MDI and its increased tendency to form dimer when stored as a liquid at over 40 °C, have led to the development of modified pure MDIs which are liquid at ordinary temperatures and have a reduced tendency to dimerize. Two main methods of depressing the melting point of pure MDI are used.

Both methods involve reacting part of the pure 4,4' diphenylmethane diisocyanate to form a derivative that is soluble in 4,4' diphenylmethane diisocyanate. One method is to react some of the isocyanate groups with an aliphatic diol having a low molecular weight or with mixture of such diols, to yield a solution of diurethanes having isocyanate end-groups in 4,4'-diphenylmethane diisocyanate.

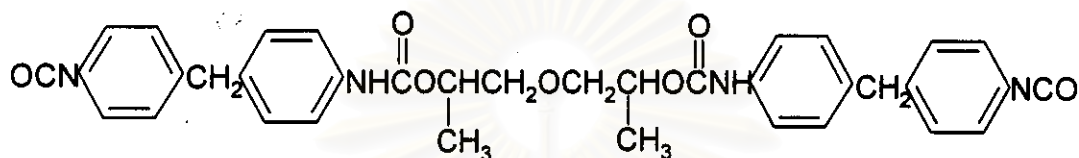


Figure 4 Modified pure MDI.

The type of liquid diisocyanate mixture has an effective functionality 2.0 and useful in the production of polyurethane elastomers of higher quality. The second common method of modifying pure 4,4'-diphenylmethane diisocyanate is by converting part of the diisocyanate to uretonimine-linked trifunctional and higher isocyanates.

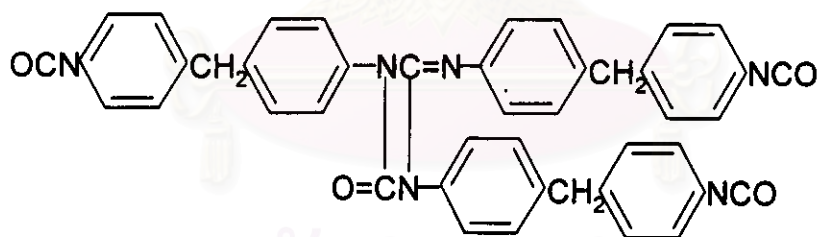


Figure 5 Modified pure MDI.

Uretonimine-modified pure MDI is a stable, low viscosity, liquid with a mean functionality usually approaching 2.2 . Mixture of uretonimine-modified and urethane-modified pure MDI are available with lower functionality. The melting point of pure 4,4'-diphenylmethane diisocyanate is also reduced by increasing the 2,4'-diphenylmethane diisocyanate content. Compositions containing high levels of 2,4'-diphenylmethane diisocyanate are not suitable for the production of polyurethane elastomers having a very high modulus but, for many applications,

adjustment of the 2,4'-diphenylmethane diisocyanate level is a useful method of increasing both the liquidity and the storage stability of pure MDI. 2,4'-diphenylmethane diisocyanate does not form dimer easily. Polymeric diphenylmethane diisocyanates are undistilled MDI compositions, made by the phogenesis of polyamine mixtures. Polymeric MDI compositions are available with effective mean functionalities from about 2.5 to over 3.0. A typical functionality distribution is illustrated diagrammatically in figure 6.

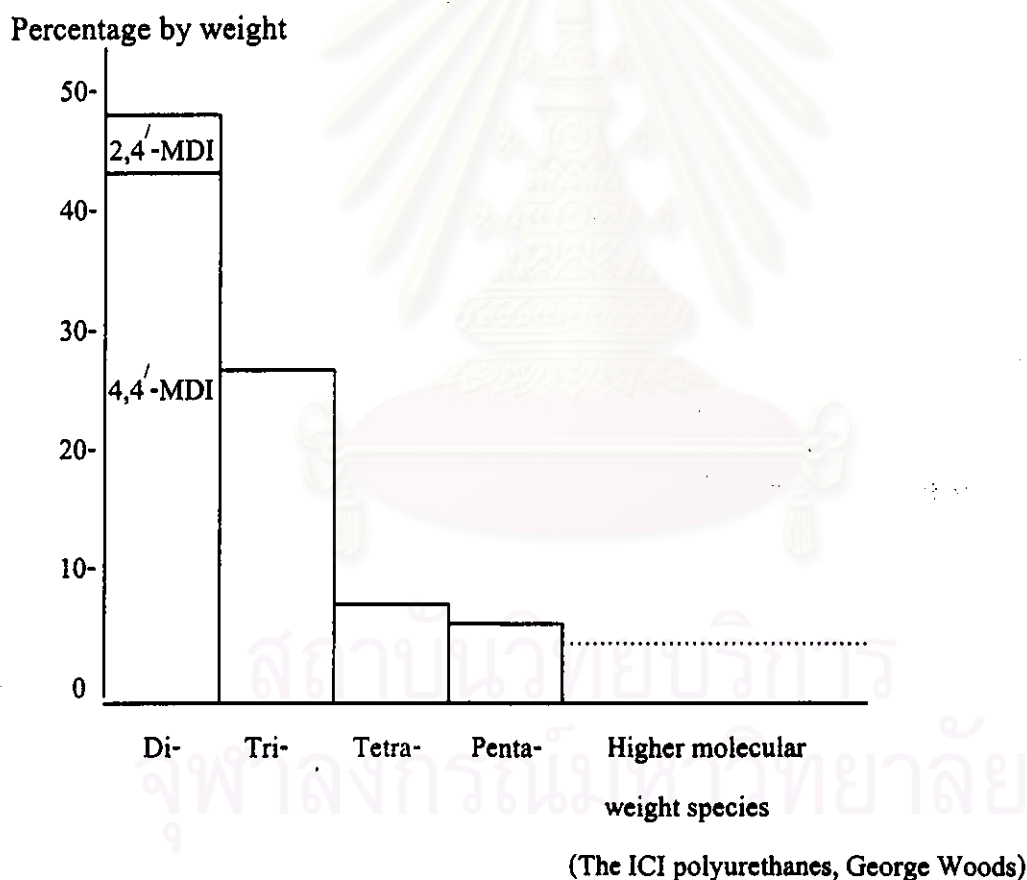


Figure 6 The functionality distribution of a typical polymeric MDI.

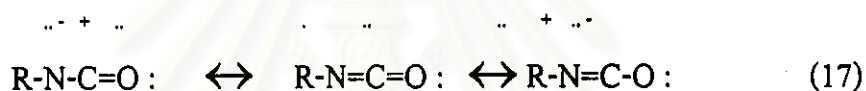
Polymeric MDI compositions are characterised by their viscosity and their content of reactive isocyanate groups. The viscosity increases with increasing mean molecular weight and polymeric isocyanate content.

Table 4 - Physical properties of 4,4'-diphenylmethane diisocyanate

Property	MDI	Polymeric MDI composition
Physical state at room temperature	Solid	Liquid
Color	White to pale yellow	Fawn to dark brown
Molecular weight	250.26	Typically about 450
Specific gravity		
at 15 °C	-	1.244
at 20 °C	-	1.242
at 25 °C	1.23 (solid)	1.239
at 40 °C	-	1.224
at 50 °C	1.19 (liquid)	-
Melting point (°C)	38 to 43	Varies with composition
Boiling point		
at 1 mm Hg, °C	170	-
at 760 mm Hg, °C	314	-
Viscosity		
mPas at 0 °C	-	6000 Typical values
mPas at 10 °C	-	1300 Typical values
mPas at 20 °C	-	400 Typical values
mPas at 25 °C	-	250 Typical values
mPas at 50 °C	4.7	- Typical values
Flash point (°C Cleveland open cup)	212 to 214	210 to 230
Fire point (°C Cleveland open cup)	-	220 to 250
Vapor pressure		
Pa at 25 °C	$6 \times 10^{-4}$	Less than $6 \times 10^{-4}$
Pa at 40 °C	$2.5 \times 10^{-3}$	Less than $2 \times 10^{-3}$
Pa at 70 °C	$1.3 \times 10^{-1}$	Less than $1 \times 10^{-1}$

## Reactions of MDI

The MDI, containing the highly unsaturated  $-N=C=O$  groups, are very reactive with a host of compounds, and may also react with themselves. Reaction can occur with almost any compound possessing a hydrogen atom that may be replaced by sodium and can occur with a few other compounds having hydrogen atoms not readily replaced by sodium. Some reactions may occur without involving a hydrogen transfer. Thus, it is not surprising that a tremendous number of references to MDI reactions. The electronic structure of the isocyanate group indicates that it should have the following resonance possibilities:



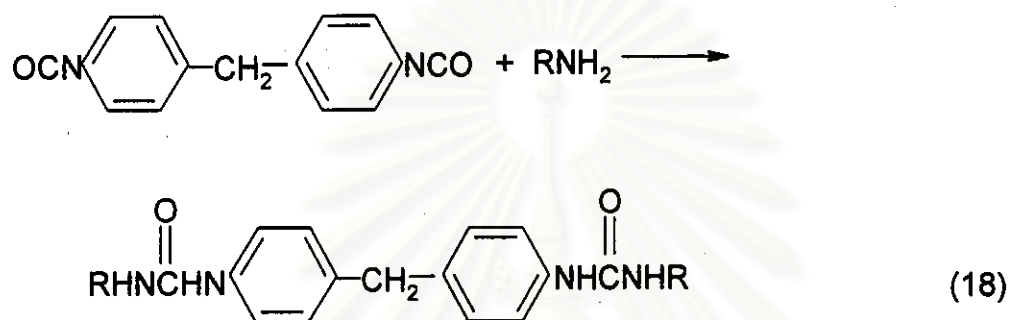
The thermal reaction ultimately provides addition to the carbon-nitrogen double bond. In the reaction with those compounds having an active hydrogen. In most reactions, especially with active hydrogen compounds, the aromatic isocyanates such as MDI, are more reactive than the aliphatic isocyanates. In addition, substitution of electronegative groups on the aromatic ring enhances the reactivity whereas electropositive groups reduce the reactivity of the isocyanate. As would be expected, steric hindrance on either the isocyanate or the active hydrogen compound will retard the reaction. All of the reactions are subject to catalysis by acids and, usually most strongly, by bases. Certain metal compounds are exceptionally powerful catalysts.

## Reactions with compound containing the N-H group

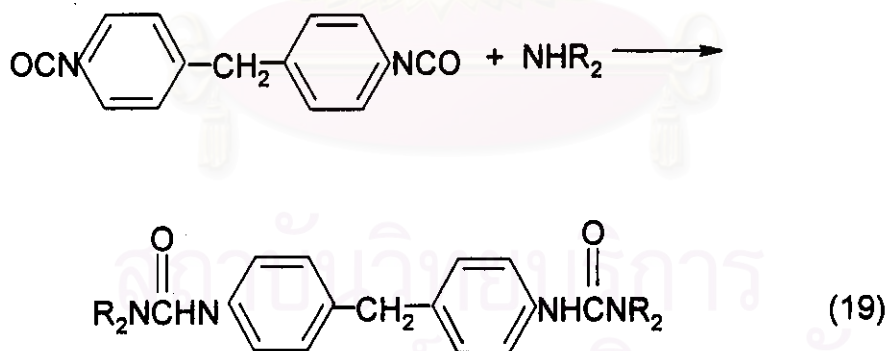
### 1. Amino-type compounds

All compounds containing the N-H groups are potentially reactive with isocyanates; the most basic are usually the most reactive unless steric hindrance is excessive.

Thus, the primary aliphatic amines are extremely reactive at 0-25 °C, giving disubstituted ureas in high yield:

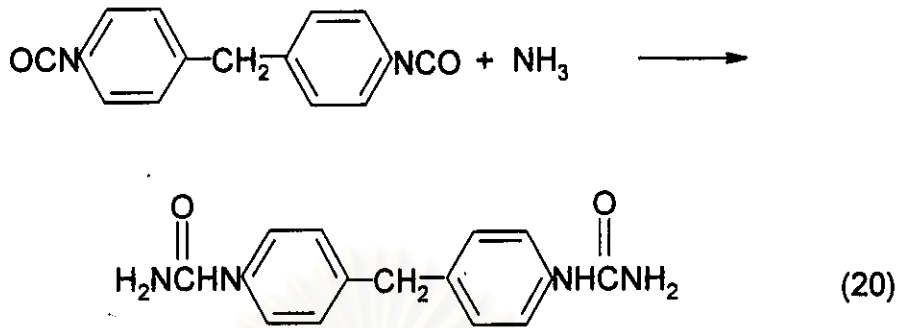


Secondary aliphatic amines, as well as primary aromatic amines, react similarly although not quite so readily. The secondary aromatic amines are still less reactive :

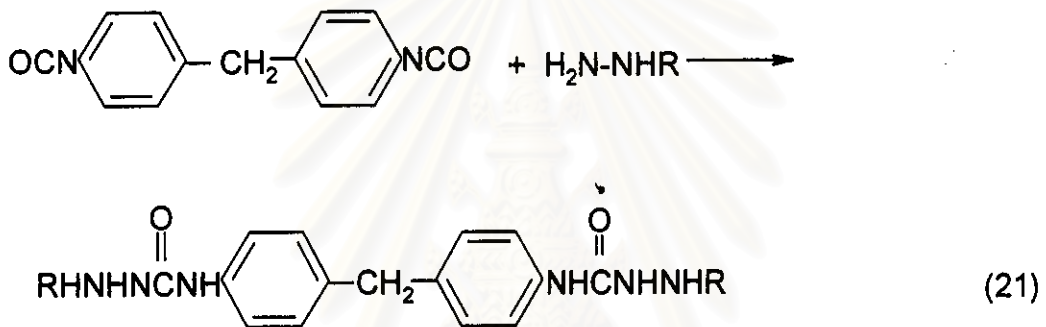


These reactions being inherently fast, are not strongly influenced by many compounds that are strong catalysts for other, slower, isocyanate reactions. Other nitrogen compounds having similar basicity react almost as readily as do the amines; for example, ammonia :

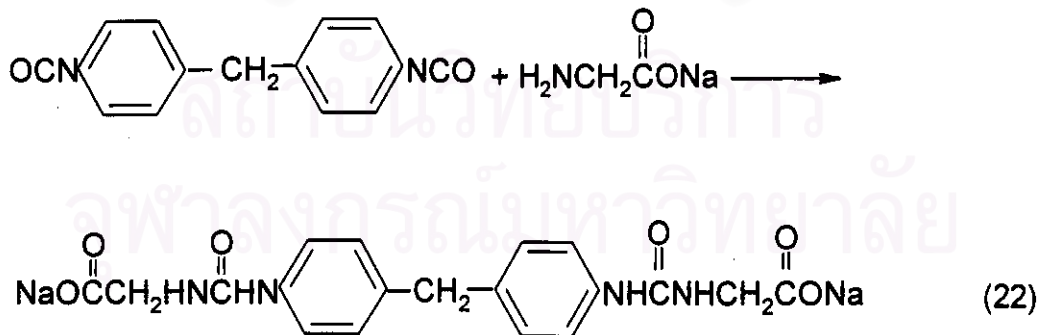




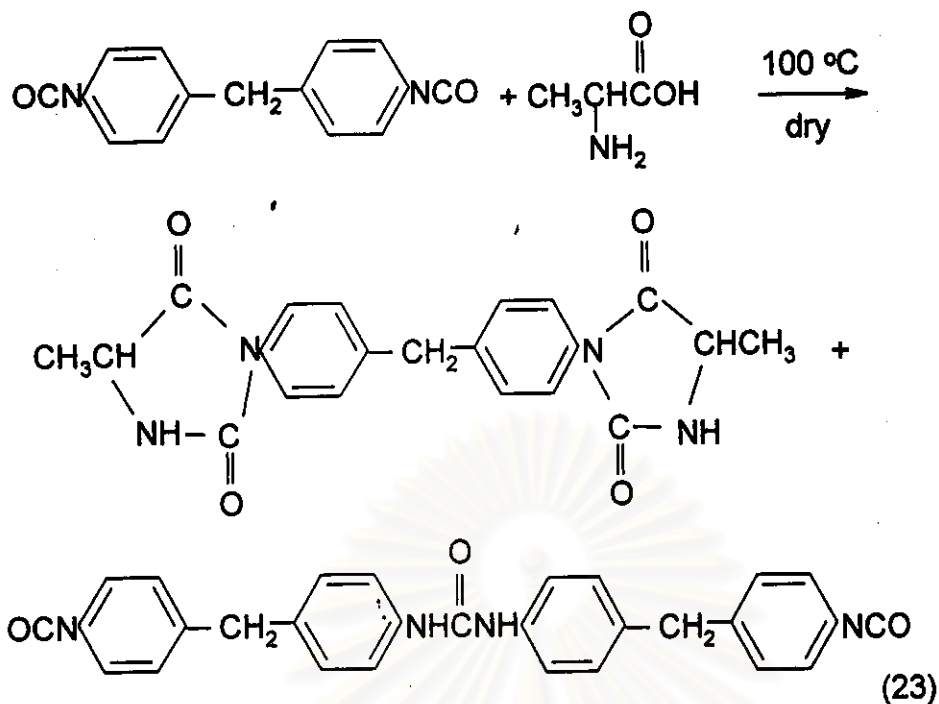
Hydrazines:



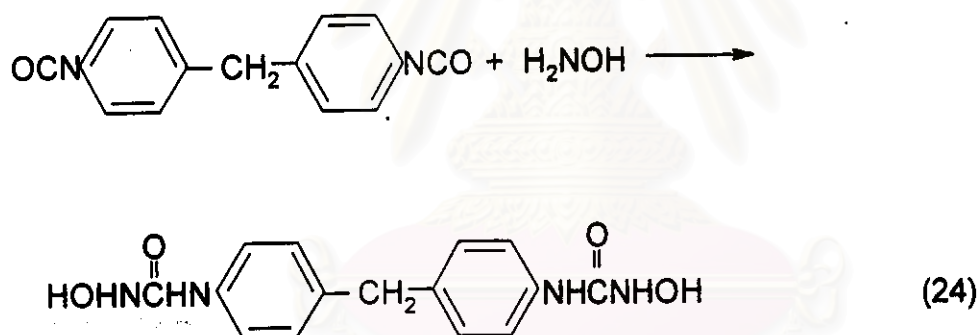
and sodium salts of amino acids. At temperatures sufficiently low so that the carboxyl group does not react or other side reactions occur, the basic salts of the amino acids give the expected urea derivative :



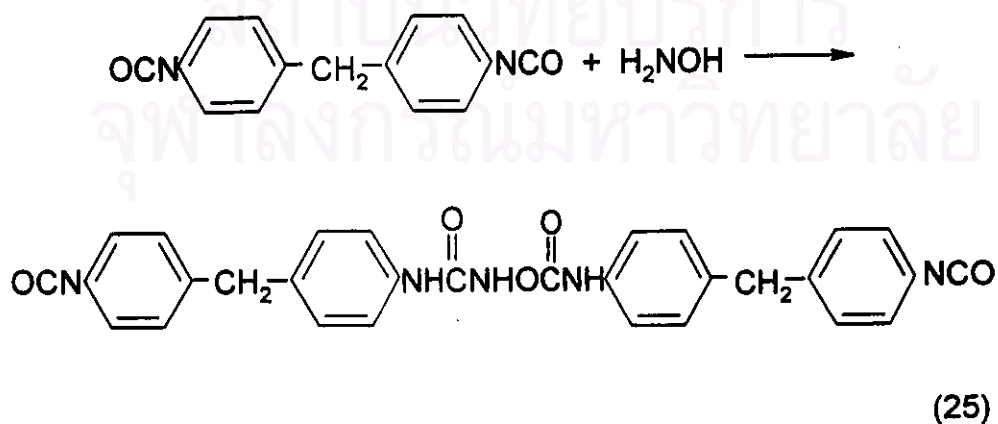
Reaction of MDI with amino compounds containing other functional groups may often be complicated by reactions of the other groups. Thus, at higher temperatures both carboxyl and amino groups in an amino acid may react, and ring closures may occur :



If the MDI is added dropwise to a large excess of cold hydroxylamine, forming the urea :



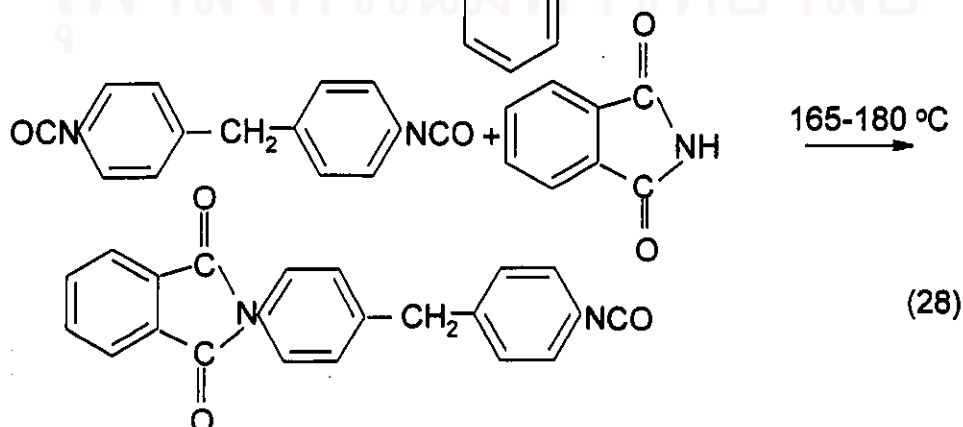
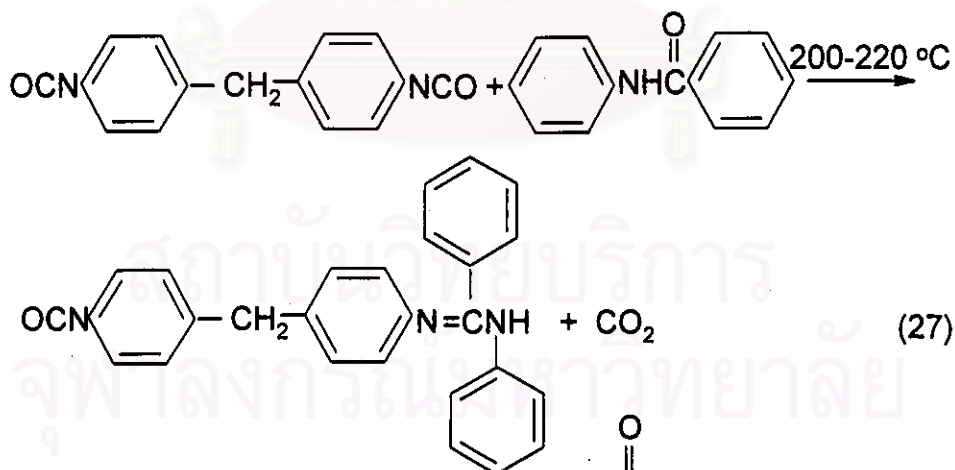
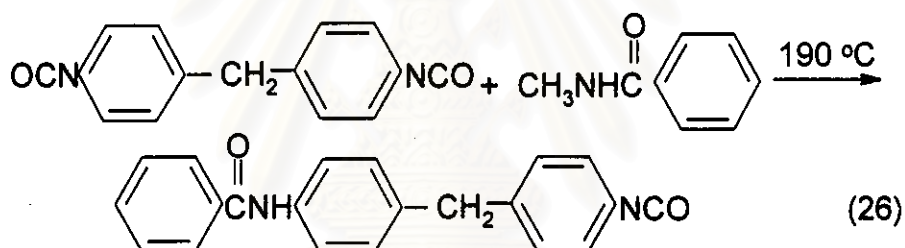
and



If the MDI is added dropwise to a large excess.

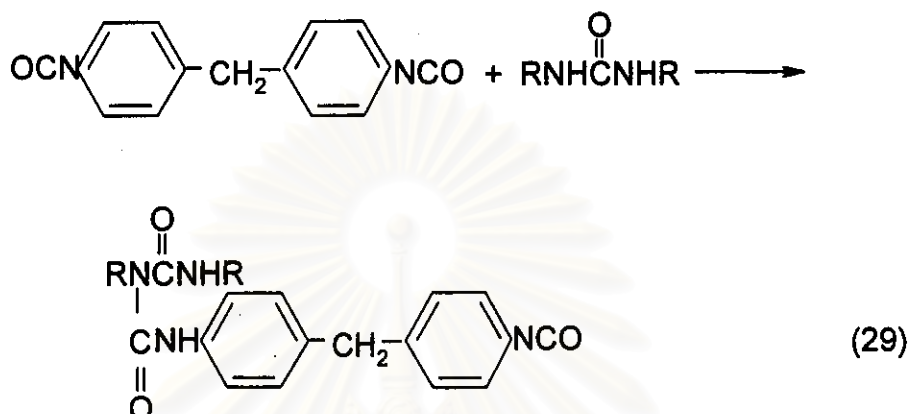
## 2. Amide

The substitution of an electronegative group on the nitrogen atom of the NH group usually reduces the rate of reaction with a MDI. Thus, amides react at moderate rate at about 100 °C, giving the urea. Wiley reported yields of 85-95 % for several examples when the reaction was run for 12-24 hours in refluxing benzene. He found that yield were lower when aluminum chloride or stannous chloride was present, and that triethylamine had no catalytic effect. The reaction of N-substituted amides under severe conditions show abnormal behavior, as show in equation 26-28



### 3. Ureas

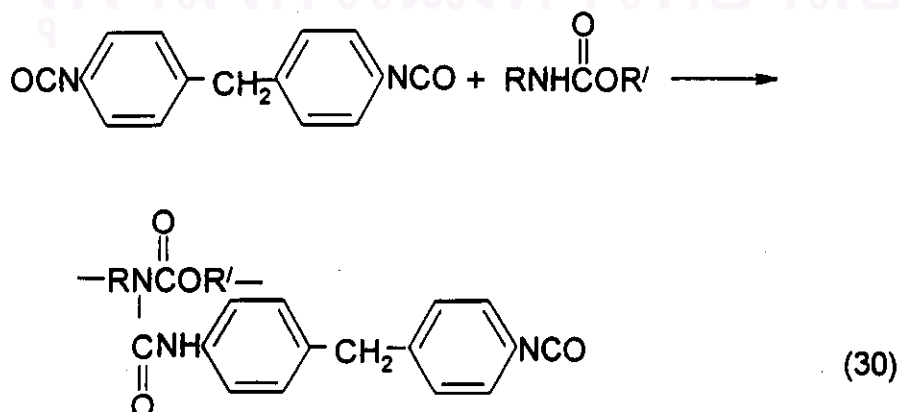
Ureas are important examples of other nitrogen compounds that are moderately reactive at elevated temperatures. The simple addition product is called a biuret :



Uncatalyzed reactions with ureas generally require temperatures of about 100 °C or higher to give a moderate rate. Most tertiary amides apparently are not very active catalysts for reactions of MDI with ureas, but stronger bases and certain metal compounds may be strongly catalytic.

### 4. Urethanes

Urethane generally less reactive toward isocyanates than are ureas. In uncatalyzed systems temperatures of approximately 120-140 °C are usually required to give a significance reaction rate. The initial product of the normal addition reaction is an allophanate :

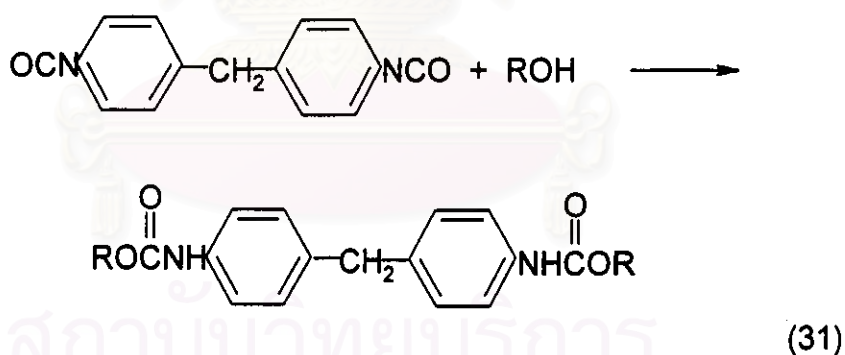


This reaction, like that of biuret formation, is not strongly catalyzed, if it is catalysed at all, by most tertiary amines, but it may be catalyzed by stronger bases and certain metal compounds.

### Reactions with compounds containing the OH group

#### 1. Alcohols

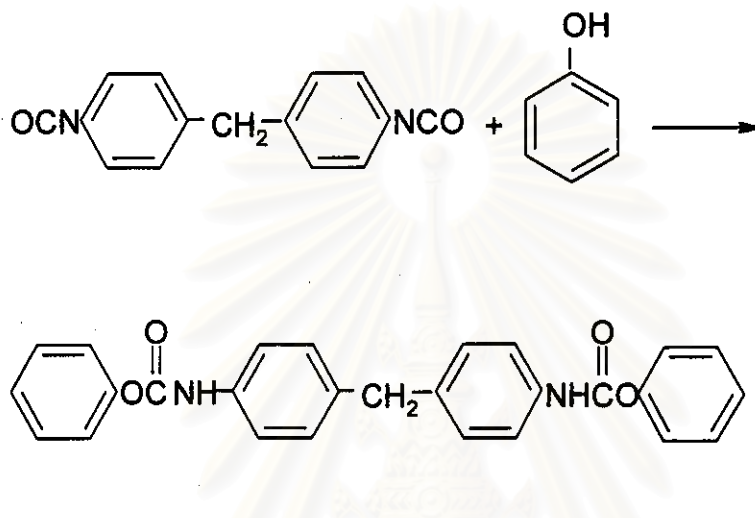
Essentially all compounds containing a hydrogen atom attached to oxygen will react under appropriate condition with the MDI. The most reactive class of such compounds is the family of alcohols with the alcohol, as with many other compounds, the effect of steric hindrance is pronounced, so that with primary alcohols react readily at 25-50 °C, secondary alcohols usually react only 0.3 as fast. Tertiary alcohols react much more slowly, approximately 0.005 as fast as the primary. The normal reaction of an alcohol with the MDI gives a urethane :



The reaction is readily catalyzed by mild, strong bases, many metals, and weakly by acids. This reaction with hydroxyl groups is perhaps the most familiar of the reactions of the isocyanates. Nearly all uses of the MDI, such as foam, elastomer, the other major compound of the system is normally a hydroxyl-containing resin. It is for this reason that most commercial polymers derived from isocyanates and other resins such as polyesters, polyethers, and castor oil are termed polyurethanes.

## 2. Phenols

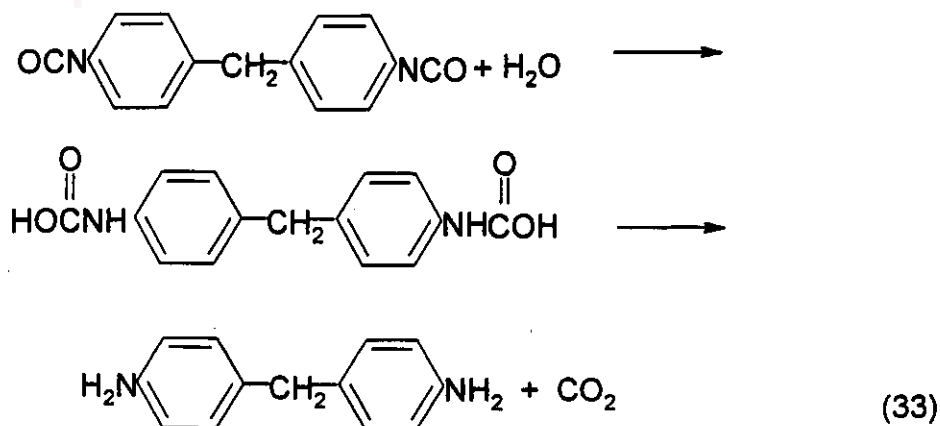
Phenols, being more acidic or less basic than the aliphatic alcohols, react more slowly with MDI than do the alcohols. The reaction of MDI with phenols is as so slow at 50-75 °C that one normally uses a catalyst such as a tertiary amine or aluminum chloride to promote this reaction



The presence of electronegative groups on the phenol nucleus retards the reaction with isocyanate, apparently because these groups reduce the basicity of the hydroxyl group still more.

## 3. Water

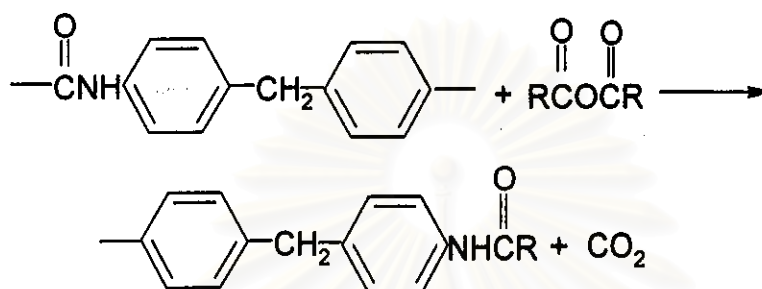
Water is usually similar to the secondary alcohols in its reactivity with MDI if both are soluble in the reaction medium. The reaction is not as simple as the formation of a urethane, however the first addition product is not stable, losing carbon dioxide :







At 160 °C the acid anhydride and urea may also react to give an amide and carbon dioxide

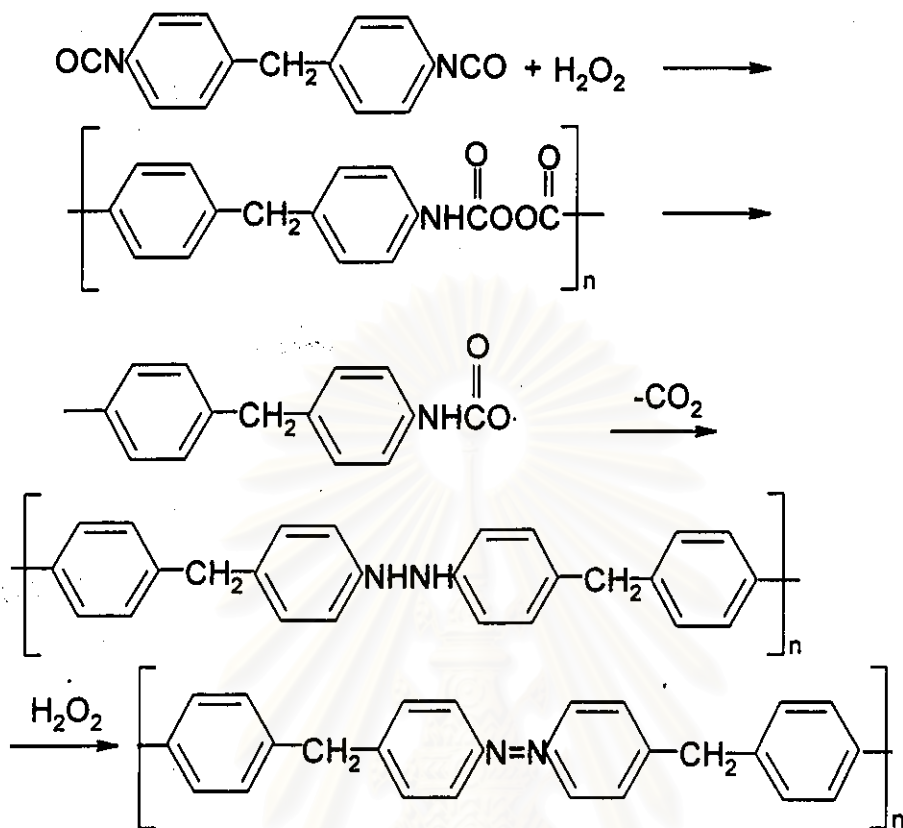


(36)

The mixed anhydrides of aromatic isocyanates and several acids have been isolated and are fairly stable at room temperature, but decompose slowly at room temperature to carbanilide and the acid anhydride, and more rapidly at 70-100 °C. The mixed anhydrides of phenyl isocyanate and aliphatic acids have been reacted with water, alcohols, and ammonia to give the aliphatic acid plus carbanilide, the urethane, and the urea, respectively.

### 5. Hydroperoxides

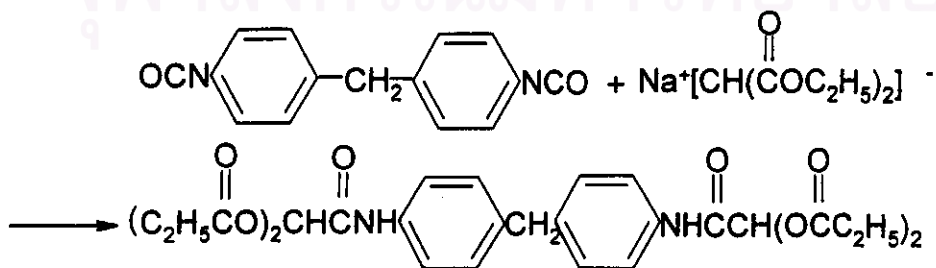
Hydroperoxides add to MDI and other isocyanates, giving peroxyurethanes. These compounds may decompose by a first order, free radical mechanism. The hydrogen peroxide gives a low yield of an azine, the reaction sequence is as follows :



(37)

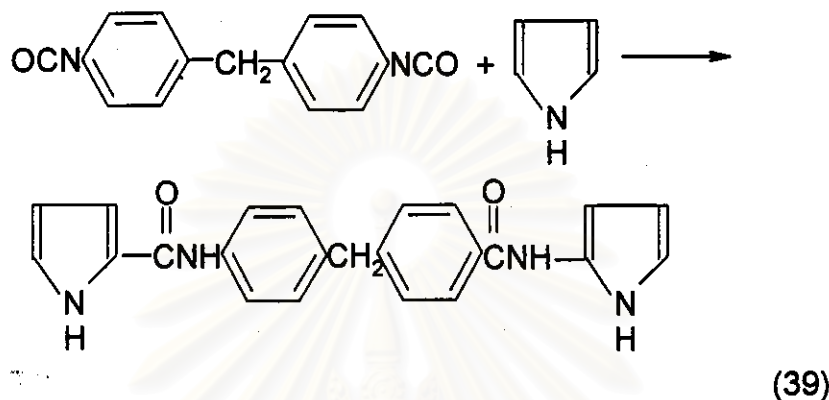
### Reactions with compounds containing the C-H group

Compounds containing C-H bond in which the hydrogen may readily be replaced by sodium may react with isocyanates to give substituted amides. Such compounds include malonic esters, nitroalkanes, acetoacetic esters, and acetylacetone.

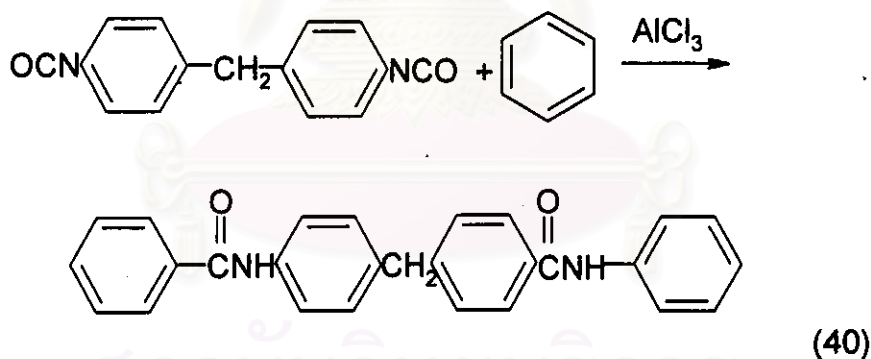


(38)

A variety of closely analogous methylene compounds containing activating groups also react similarly. The alpha position of pyrrole and the methylene group of N-alkyl-2-methylene dihydropyridine and related compounds may react similarly



MDI may be used as acylating agent in the usual Friedel-Crafts technique, giving aryl amides. At elevated temperatures, such as 130-160 °C

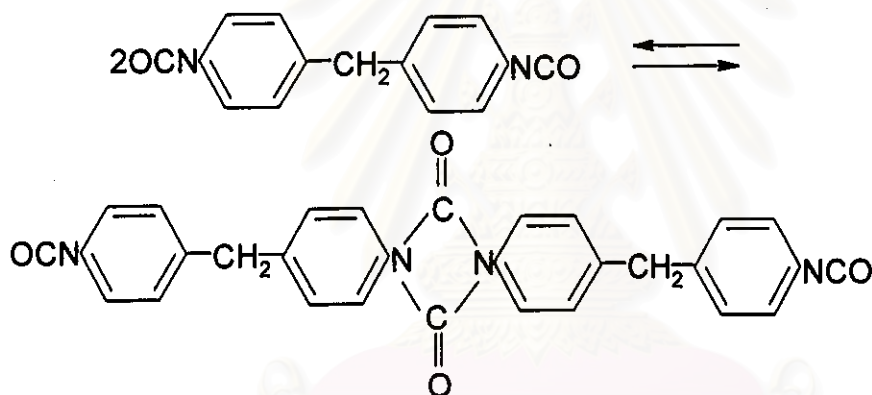


## 5. Self polymerization

### 5.1 Dimerization

As a special case of the reaction with unsaturated compounds, aromatic isocyanates, such as MDI, may react with themselves to form dimers, uretidined. The reaction also is analogous to the dimerization of ketenes. Dimerization is catalyzed vigorously by trialkylphosphines, and more mildly by tertiary amines such as pyridine. MDI dimerize slowly on standing, even without catalysts. The rate of dimerization of many other of isocyanates is greatly retarded if an ortho substituent is present.

Molecular weight measurements of phenyl isocyanate dimer are in the agreement with the dimer structure. These measurements were based on ebullioscopic method and observed molecular weights were somewhat lower than theoretical, suggesting some dissociation in the boiling solutions. The crystal structure has also been determined, and is in agreement with the symmetrical structure as indicated, when left standing at higher temperatures. The insoluble polymeric materials are formed as below :

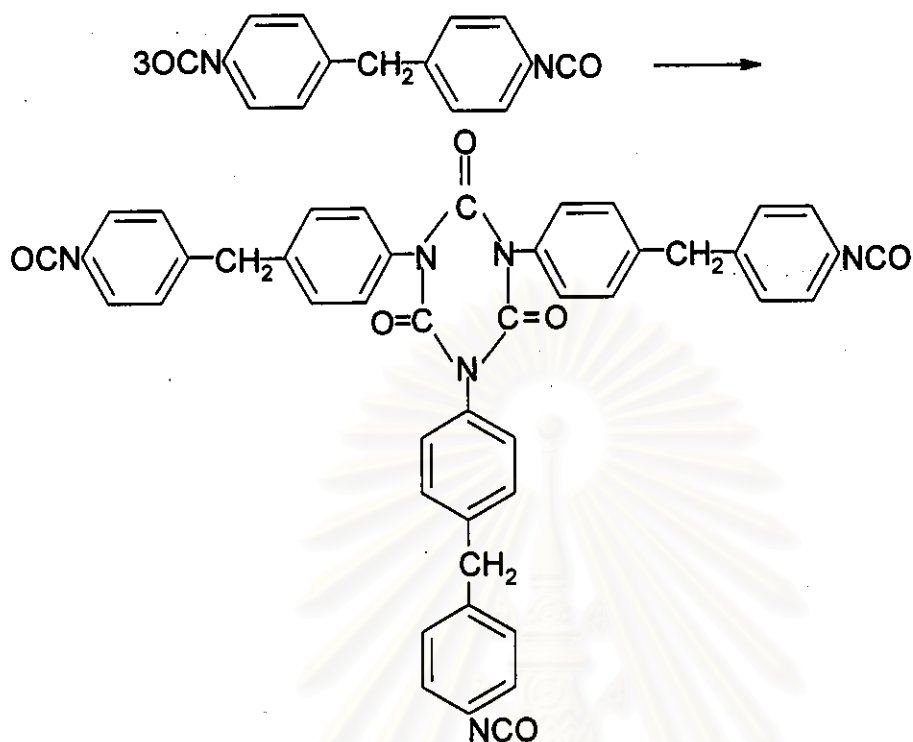


(41)

The reaction is accelerated by basic catalysts such as pyridine. It is most conveniently applied as the solvent medium for the reaction.

## 5.2. Trimerization

Aromatic isocyanates can form trimers. This reaction is another special example of a reaction of an isocyanate with an unsaturated compound (HTPB). Catalysts such as calcium acetate, potassium acetate, sodium carbonate, sodium benzoate in dimethylformamide that have been used to induce the trimerization of either aromatic isocyanates. The generally accepted structure for the trimer is that of a trisubstituted isocyanate as below :



This structure is called the 1,3,5-triazine or isocyanate ring. The isocyanates, normally called trimers, exhibit the characteristic spectra of the isocyanurate carbonyl groups in the infrared, the main band of which occurs at  $1709\text{-}1689\text{ cm}^{-1}$ . Other interesting and useful features of the isocyanates include their stability

(i) to form thermally labile adducts, (ii) to give higher molecular weight adducts in which some free isocyanate groups remain, and (iii) to give rise to cyclic dimers and trimers.

### Hazards and toxicities

Toxicity problems associated with MDI can be minimized by the use of good industrial hygiene, which is now obvious should constitute minimal exposure to vapor and skin contact. It has been established that exposure to low concentrations generally causes symptoms such as burning eyes, however, that those frequently exposed to the inhalation of MDI at lower concentrations after several years is more often affected by diseases of the upper respiratory tract.

The action of MDI over a period of several years at these levels of concentration, can lead to progressive impairment of pulmonary function with considerable shortness of breath which may produce cyanosis. Long-term exposure at levels below the established Threshold Limit Values (TLVs) have established for MDI that loss of pulmonary function does not occur compared with control groups. However, there is an important qualification to this generalization in that when respiratory sensitization to MDI has occurred, it is no longer safe to be exposed to even the TLV value and further contact with MDI must be avoided as a short instantaneous exposure will usually bring about an instantaneous asthmatic response. Individuals who suffer from constitutional respiratory problems or acquire hyperactivity of the bronchial system are always at greater risk from MDI exposure and should avoid its use.

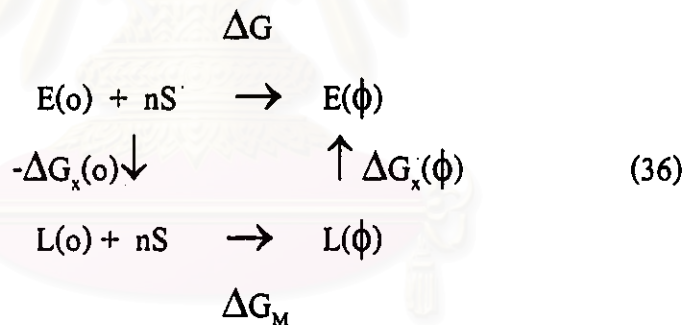
MDI has greater molecular weight, and this, together with a much lower vapor of less than  $10^{-4}$  mbar at 25 °C, 14 mbar at 40 °C and 550 mbar at 80 °C, make it a much safer material with respect to inhalation hazards. A single lethal dose for animals is found to be 31.6 grams per kilogram of body weight and small doses of 25 grams per kilogram over several days were not found to be fatal. As a generalization, the vapor pressure of MDI at ambient temperatures is considered sufficiently low for only a little hazard to exist. At higher temperatures, however, often used or generated in automatic processes, the MDI vapor pressure rises and it then does constitute a respiratory hazard. Also, droplets can be formed in spraying operations which also constitute respiratory hazard.

### Flory-Rehner theory

The theoretical treatment of the phenomenon of elastomeric swelling is based on the seminal work of Flory and Rehner with important contributions from Hermans. The essential assumption made in this theory is that the mixing and elastic free energies are separable and additive. Which allows one to write

$$\Delta G = \Delta G_M + \Delta G_{el} \quad (35)$$

Where  $\Delta G$  is the change in Gibbs free energy when the elastomer absorbs  $n$  moles of solvent.  $\Delta G_M$  is the mixing free energy to form an equivalent solution of linear, high molecular weight polymer, and  $\Delta G_{el}$  is elastic free energy that is incurred upon dilating the network. Flory made use of the following thermodynamic cycle to analyze the swelling behavior:



It is clear from this cycle that

$$\Delta G = \Delta G_M + [\Delta G_x(\phi) - \Delta G_x(o)] \quad (37)$$

and hence

$$\Delta G_{el} = \Delta G_x(\phi) - \Delta G_x(o) \quad (38)$$

The dry elastomer,  $E(o)$ , imbibes  $n$  moles of solvent,  $S$ , and swells to a solvent volume fraction  $\phi$  with the free energy change  $\Delta G$ . On the alternate path, the elastomer is uncrosslinked in the bulk with the free energy change  $-\Delta G_x(o)$  to form linear chains,  $L(o)$ , which then are dissolved in the solvent to form the solution  $L(\phi)$ . This process entails the mixing free energy  $\Delta G_M$ .



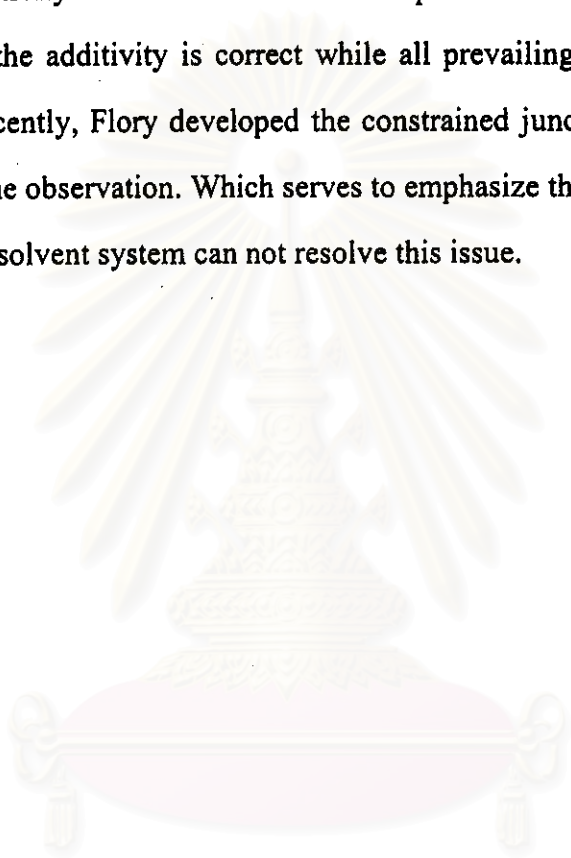
Finally, the linear change in the solution undergo and irreversible distortion to recover the same configurations as they have in the swollen elastomer, and then the crosslinks are formed. The free energy change accompanying the bond formation process is prersum to be the same in the bulk as in solution. so that only the distortional part of the free energy change for the last leg of the cycle,  $\Delta G_x(\phi)$  remains as  $\Delta G_{e1}$  in equation 38. When  $\Delta G_x(o)$  is subtraced from  $\Delta G_x(\phi)$  as required by the cycle. [if the network had been formed in the solution,  $\Delta G_x(\phi)$  would be reversible at the one particular solvent concentration that prevailed at the time of cure, but would be irreversible at all other concentration, including  $\phi = 0$ .]

Measurements of the difference  $\Delta G - \Delta G_M$  would, it prepare, yield  $\Delta G$  directly. And experiment to measure this difference, almost directly, was devised by Gee, Albert, and Roberts. They determined the different amounts of benzene that were absorbed by samples of crosslinked and uncrosslinked natural rubber, which samples were placed on the two pans of balance. These  $\Delta\phi$  VS. activity( $a_1$ ) data were then transformed into  $\Delta a_1$  VS.  $\phi$  so as the construct the elastic contribution to the solvent chemical potential. More precisely, differentiation of equation 38 with respect to the number of moles of solvent gives what. Gottlieb has called the dilation moldulus as

$$(RT\lambda/V_1) \ln (a_{1,c}/a_{1,u}) = (1/3\lambda V_0) (\partial\Delta G_{e1}/\partial n)_{T,P} \quad (39)$$

Where  $\lambda^3 = (V_0 + nV_1/V_0)$  :  $\lambda$  is the linear extention ratio,  $V_0$  is the volume of the dry elastomer, and  $V_1$  is the apparent molar volume of the solvent. The activities of solvent above the crosslinked,  $a_{1,c}$ , and uncrosslink,  $a_{1,u}$ , samples are derived from  $\Delta G$  and  $\Delta G_M$ , respectively.

Gee, Herbert and Roberts found that none of the theories of the elasticity that were known in 1965 were able to account for their data, and so they questioned whether the assumption of additivity was correct. Their one experiment could not settle this question, since it might be the additivity is correct while all prevailing theories of elasticity were incorrect. More recently, Flory developed the constrained junction theory to give a much better account of the observation. Which serves to emphasize the fact that measurements on a single elastomer-solvent system can not resolve this issue.



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย