STUDIES IN SYNTHESES OF ISOCYANATES AND POLYMERS USING ISOCYANATES

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CONTENTS

Section I - SYNTHESIS OF DIISOCYANATES

Section II - THE REACTIVITIES OF DIISOCYANATES

PART II - ** POLYIMIDES

Section I - POLYARIMIDES

Section II - COPOLYIMIDES

....cont....

Section III- MODIFIED POLYIMIDES

Section IV- POLY(AMIDE-IMIDES)

PART III - STUDIES IN THE VULCANIZATION OF POLYURETHANE ELASTOMERS AND NATURAL RUBBER (NR)

Section I - POLYURETHANE VULCANIZATION

Section II - NATURAL RUBBER VULCANIZATION

PART-I

SYNTHESIS OF ISOCYANATES

GENERAL INTRODUCTION

The isocyanates (R-N=C=O) are a well known class of compounds in organic chemistry. The synthesis of an aliphatic isocyanate was first reported by Wurtz[1], in 1849, as compound resulting from the reaction of organic sulfate and alkali metal cyanate. Gautier[2] obtained isocyanates by oxidation of aliphatic isocyanides with mercuric oxide and confirmed the structure established by Wurtz. Hofmann[3] prepared the first aromatic isocyanate, phenyl isocyanate, by the pyrolysis of symmetrical diphenyl oxamide. The method developed by Hentschel[4] for the manufacture of isocyanates is still in use commercially, which consists of the treatment of amines and their salts with phosgene. Lussi[5] described the diisocyanates for the first time and Gattermann and Wrampelmeyer[6] were the first to report the phenylene diisocyanate. The exploratory work in the field of isocyanates was carried out by Prof. Otto Bayer and his coworkers[7,8], who, in 1937, developed polyurethane polymers to substitute polyamides developed by Carothers. He reacted a diisocyanate with a dihydroxy compound to form polyurethane by polyaddition mechanism. A polymer which contains significant number of urethane groups is called polyurethane, regardless of the nature of the rest of the molecule.

The polyurethanes can be tailor-made to any desired structure-property performance and were found to be suitable for a variety of applications such as elastomers, surface coatings, adhesives, resins, fibres, etc.

Isocyanates form the most essential starting materials in the polyurethane preparation. Several mono- and poly-functional isocyanates have been made commercially available in last 25 years to meet the demands of the fast expanding spectrum of isocyanate applications.

Methods of preparation of isocyanates

Among the methods reported for the preparation of isocyanates, the following are noteworthy:

(1) Phosgenation methods

(2) Curtis, Hofmann and Lossen rearrangements

(3) Double decomposition reactions

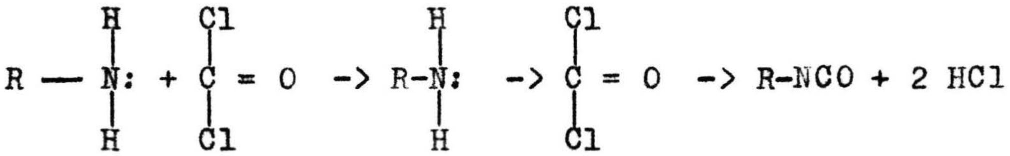
(4) Preparation from isocyanate derivatives

(5) Pyrolysis of N-t-butyl-N-alkyl carbomoyl chlorides

(6) Miscellaneous preparations.

(1) Phosgenation method

This is the only method which has been commercially exploited so far, for the manufacture of isocyanates. Hentschel[4] in 1884, described the formation of isocyanate from reaction between phosgene and a salt of a primary amine. Methyl isocyanate was obtained by modification of the above reaction by Gatterman and Schmidt[9]. The reaction between amine and phosgene can be described as below:



$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: + \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}=O \rightarrow R-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: \rightarrow \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}=O \rightarrow R\text{-}NCO + 2\,HCl$$

Amine hydrochlorides, carbomoyl chlorides and substituted ureas are also formed as by-products of the reaction. Shriener et al[10] described the preparation of high boiling isocyanates by reaction between phosgene and a refluxing slurry of amine hydrochloride in solvents, such as ethyl acetate, toluene and O-dichlorobenzene. The superiority of the carbamate salt over that of hydrochloride was shown in the preparation of hexamethylene diisocyanate[11] and was ascribed to the comparatively higher solubility of carbamate in the medium used.

$$H_2N(CH_2)_6NH_2 + CO_2 \rightarrow H_3\overset{+}{N}\,(CH_2)_6\,NHCO\overset{-}{O}$$
$$\big\downarrow\, 2\,COCl_2$$
$$OCN\,(CH_2)_6NCO + 4\,HCL + CO_2\uparrow$$

Experimental details of liquid phase phosgenation of amines and their salts on laboratory scale were described by Siefken[12].

Isocyanates were obtained in good yields and with faster rates by vapour phase reaction at 300°C [12,13].

As the commercial production gained importance, several modifications of the phosgenation method have been reported in the literature. A brief account of selected ones is given below.

(a) Initial phosgenation at sub zero and near zero temperatures[14]

The method comprises of bringing into intimate contact, with tertiary amine as catalyst, a primary amine and phosgene in the ratio of 1.0 to 0.5 mole, using temperature range of -40 to +10°C. The removal of unreacted phosgene and amine hydrochloride and dehydro chlorination gives isocyanate after decomposition of the carbomoyl chloride formed.

$$R'_3N + COCl_2 \rightarrow R'_3N.COCl_2$$

$$R'_3N.COCl_2 + RNH_2 \rightarrow \underset{\text{Carbomoyl chloride}}{RNHCOCl} + R'_3NHCl$$

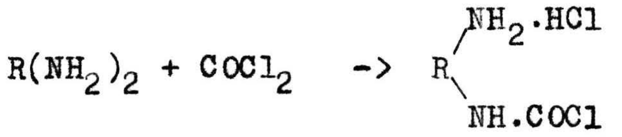
$$RNHCOCl \rightarrow RNCO + HCl.$$

(b) Operation under pressure[15]

This method is used for the preparation of polyisocyanates, e.g. triphenyl methane triisocyanate.

(c) Continuous operations[16-18]

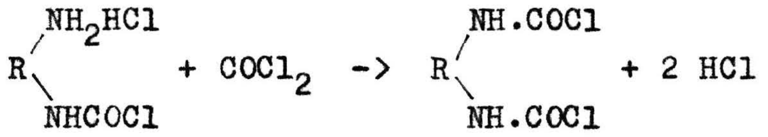
This method involves two steps. In the first, intermediate in the form of clear solution or slurry is obtained by the reaction of amine and phosgene at temperatures ranging from -20 and +60°C.



$$R(NH_2)_2 + COCl_2 \rightarrow R\genfrac{}{}{0pt}{}{\diagup NH_2\cdot HCl}{\diagdown NH\cdot COCl}$$

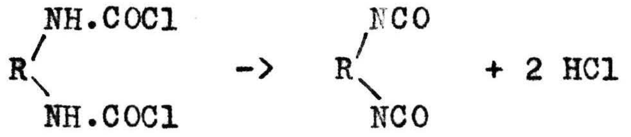
Intermediate

or



$$R\genfrac{}{}{0pt}{}{\diagup NH_2HCl}{\diagdown NHCOCl} + COCl_2 \rightarrow R\genfrac{}{}{0pt}{}{\diagup NH\cdot COCl}{\diagdown NH\cdot COCl} + 2\ HCl$$

In the second step, the intermediate, a carbomoyl chloride is heated to 80-320°C to get isocyanate and HCl gas.



$$R\genfrac{}{}{0pt}{}{\diagup NH\cdot COCl}{\diagdown NH\cdot COCl} \rightarrow R\genfrac{}{}{0pt}{}{\diagup NCO}{\diagdown NCO} + 2\ HCl$$

Isocyanate

A flow sheet of commercial diisocyanates, toluene diisocyanate and 4,4'-Methylenebis (phenyl isocyanate) is available in the literature[19].

Acyl isocyanates and sulfonyl isocyanates are obtained by reaction of phosgene with amides[20] and sulfonamides[21-23] respectively. The preparation of sulfonyl isocyanates and isocyanates was accomplished simultaneously by the reaction of 1-aryl sulfonyl-3-alkyl ureas $RSO_2NH\text{-}CO\text{-}NHR'$ with phosgene[22]. Recently, it has been reported that N-sulfinyl amines and N-sulfinyl sulfonamides react with phosgene to give corresponding isocyanates[25].

$$R\text{-}N{=}S{=}O + COCl_2 \rightarrow R\text{-}N{=}C{=}O + SOCl_2$$

This is useful in the preparation of both aliphatic as well as aromatic isocyanates.

Fluorinated isocyanates[26], a new class of isocyanates have also been reported in recent years.

$$\begin{tikzcd} C_nF_{2n+1}\,CH_2NH_2 + COCl_2 \arrow[d, "\text{Cold}"] \\ C_nF_{2n+1}\,CH_2NHCOCl \arrow[d, "\text{Heat}", "\text{excess } COCl_2"'] \\ C_nF_{2n+1}\,CH_2NCO \end{tikzcd}$$

(2) Curtis, Hofmann and Lossen rearrangements

A common intermediate appears to be formed in the Curtis rearrangement of acid azides, the Hofmann rearrangement of acid amides and Lossen rearrangement of hydroxamic acids, which later rearranges to isocyanate.

$$\begin{tikzcd} \text{Curtis} & RCON_3 \arrow[dr, "-N_2"] & & \\ \text{Hofmann} & RCONH_2 \arrow[r, "NaOBr"] & {[\ RCON\ ]} \arrow[r] & RNCO \\ \text{Lossen} & RCONHOH \arrow[ur, "-H_2O"'] & & \end{tikzcd}$$

Curtis rearrangement - Schroeter[27] prepared several isocyanates by treating an acid chloride with sodium azide and warming the resulting product in benzene solution. Curtis prepared substituted ethylene diisocyanate[28,29] by this method. Primarily short chain aliphatic diisocyanates, e.g. methylene diisocyanate[30] and unsaturated isocyanates e.g. vinyl isocyanate[31] are prepared by this method.

Hofmann rearrangement - Pyman[32] has pointed out the limitations of this method and has discussed the scope of reaction with numerous examples. This reaction was also discussed by Montagne and Guilmert[33], and Cagniant and Bru-Hoi[34].

Lossen rearrangement - Yale[35] has reviewed the chemistry of hydroxamic acids and nature of Lossen rearrangement. This is a less frequently used method. However, aliphatic diisocyanates have been prepared by this method.

(3) Double decomposition reaction

Alkyl isocyanates were obtained in good yields by this method in which organic halides or sulfates are reacted with salts of cyanic acid.

$$R_2SO_4 + KCNO \rightarrow RNCO$$

Wurtz[1], synthesized first alkyl isocyanate by this method and later Slotta and Lorenz[36] prepared ethyl isocyanate. Acyl isocyanates[37] and inorganic isocyanates[38-40] having NCO group attached to an element other than carbon are also prepared by this method.

(4) Preparation from isocyanate derivatives

Urethanes and ureas are formed by the addition of active hydrogen compounds to isocyanates. These reactions can be reversed under sufficiently vigorous conditions to obtain isocyanates back. This can be achieved either by heating the carbamates in the temperature range of 135 to 500°C [41] or by distilling the carbamate over phosphorous pentoxide[42,43].

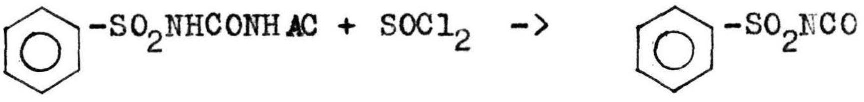
$$RNHCOOR' \xrightarrow{P_2O_5} RNCO$$

Urethanes derived from phenol rather than alcohol decompose much more easily.

Substituted low boiling alkyl isocyanates can be prepared by dissociation of corresponding ureas[12].

$$\begin{array}{l} Ar_2NCOCl + CH_3NH_2 \rightarrow CH_3NHCONAr_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \Delta \\ \qquad\qquad\qquad\qquad\quad CH_3NCO + Ar_2NH \end{array}$$

Sulfonyl isocyanates are obtained in 75-80% yield when substituted ureas are heated with thionyl chloride[45].



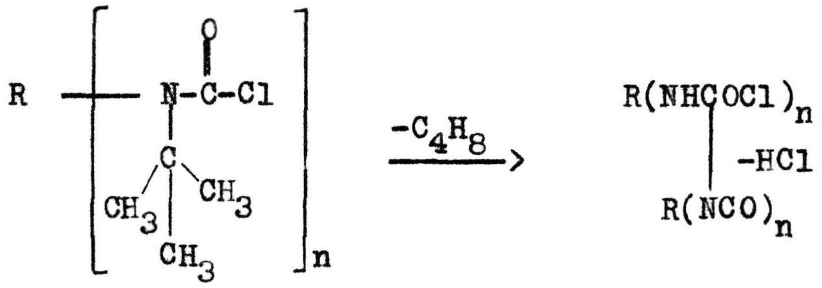
Sowa[46] has reported conversion of N-alkyl ureas into corresponding isocyanates by treatment of boron trifluoride

$$\begin{array}{c} (CH_3)_2CH{-}CH_2NH{-}CONH_2 + BF_3 \\ \downarrow \\ (CH_3)_2CH{-}CH_2{-}NCO + H_3N.BF_3 \end{array}$$

Sayigh et al[47] have utilised N,N'-dialkyl ureas in the synthesis of isocyanates.

(5) Pyrolysis of N-butyl-N-alkyl carbomoyl chloride

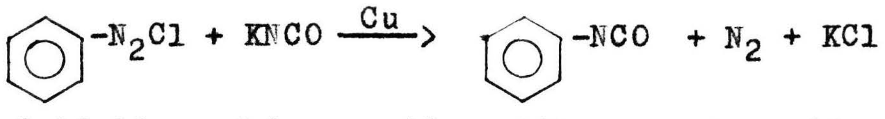
This method provides a synthetic approach to mono- and diisocyanates, some of which are not readily accessible by known synthetic methods. Using this new method, Sayigh and Tilley[48] prepared several N-t-butyl-N-alkyl carbomoyl chlorides by known methods and then decomposed the same with considerable ease at low temperatures with or without catalysis to the corresponding alkyl isocyanates in high yields.



(6) Miscellaneous preparations

A variety of other procedures are available for synthesis of isocyanates but they are of very little practical importance. However, a few interesting examples may be mentioned.

Diazonium chlorides , in the presence of copper react with potassium cyanate to give isocyanates[49,50].



Oxidation of isocyanides with mercuric oxide yields isocyanates[51].

$$RNC + HgO \longrightarrow RNCO$$

Fluorinated alkyl isocyanates have been prepared from nitriles and carbonyl difluoride[52].

$$CF_3CN + COF_2 \xrightarrow[300^{\circ}C]{CsF} CF_3CF_2NCO$$

An excellent review[53] on the preparation and chemistry of acyl isocyanates and acyl isothiocyanates (isocyanates and isothiocyanates of carboxylic, thiocarboxylic, carboximidic and sulfonic acids and acids of phosphorous etc.) has recently appeared.

In the case of amines, which are unstable or unreactive towards phosgene, their isocyanurates are pyrolyzed to corresponding isocyanate at temperature above 500°C. This is effective in both aliphatic and aromatic amino compounds[54].

Some attempts have also been made in the recent past to prepare isocyanates from organic nitro compounds and carbon monoxide, using various catalysts[55,56]. However, yields obtained by this route are not satisfactory.

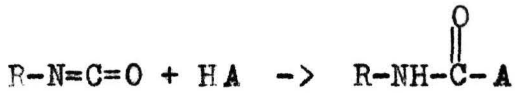
Reactions of isocyanates

The following possible resonance forms originate from the isocyanate electronic structure.

$$R-\overset{-}{\underset{\cdot\cdot}{N}}-\overset{+}{C}=O: \; \longleftrightarrow \; R-N=C=O: \; \longleftrightarrow \; R-N=\overset{+}{C}-\overset{-}{O}:$$

Due to the presence of high unsaturation in -N=C=O group which imparts high reactivity on isocyanates, this class of compounds has received considerable attention of the researchers. These compounds react with almost any compound containing active hydrogen atom i.e. one readily replaceable by sodium.

Thus, during the reaction of such compounds e.g. HA with isocyanate, the hydrogen becomes attached to the nitrogen of the isocyanate group while the remainder of the compound attacks as a nucleophile, the electrophilic carbonyl carbon.



$$R-N=C=O + HA \rightarrow R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-A$$

The addition product in many cases is stable. In those, where it is unstable it either dissociates to form the initial reactants or decomposes to some other products.

Reactivity of aromatic isocyanates is relatively higher than aliphatic isocyanates. This is due to the fact that the partial negative charge on the nitrogen of NCO group is shared by the unsaturation in the aromatic ring, making the carbonyl carbon more positive and hence highly susceptible to attack by nucleophiles. This suggests that the presence of electron withdrawing groups in the ring enhance the reactivity while electron donating groups reduce the reactivity of the isocyanate. Acids as well as bases catalyze these reactions. Certain metal compounds serve as catalysts. As in all other reactions, steric factors play considerable role in isocyanate reactions. Reaction medium too, affects the course of reaction, if the reaction is carried out in solvent. Some important reactions of isocyanates are given in Table-1.

Applications of isocyanates

Organic isocyanates have grown from the stage of obscure laboratory curiosities to commercial products in a short span of just 25-30 years. Their exploitation in the production of polyurethane polymers which can be tailor-made to suitable end uses, has given them so much of importance. Polyurethanes are utilised in the form of rigid or flexible foams[91,92], elastomer[93] and fibres[94,95] and also in surface coatings and adhesives. Recently they have found applications in high temperature polymer like polyimides and poly(amide-imides). A variety of isocyanate applications are given in Fig.I.

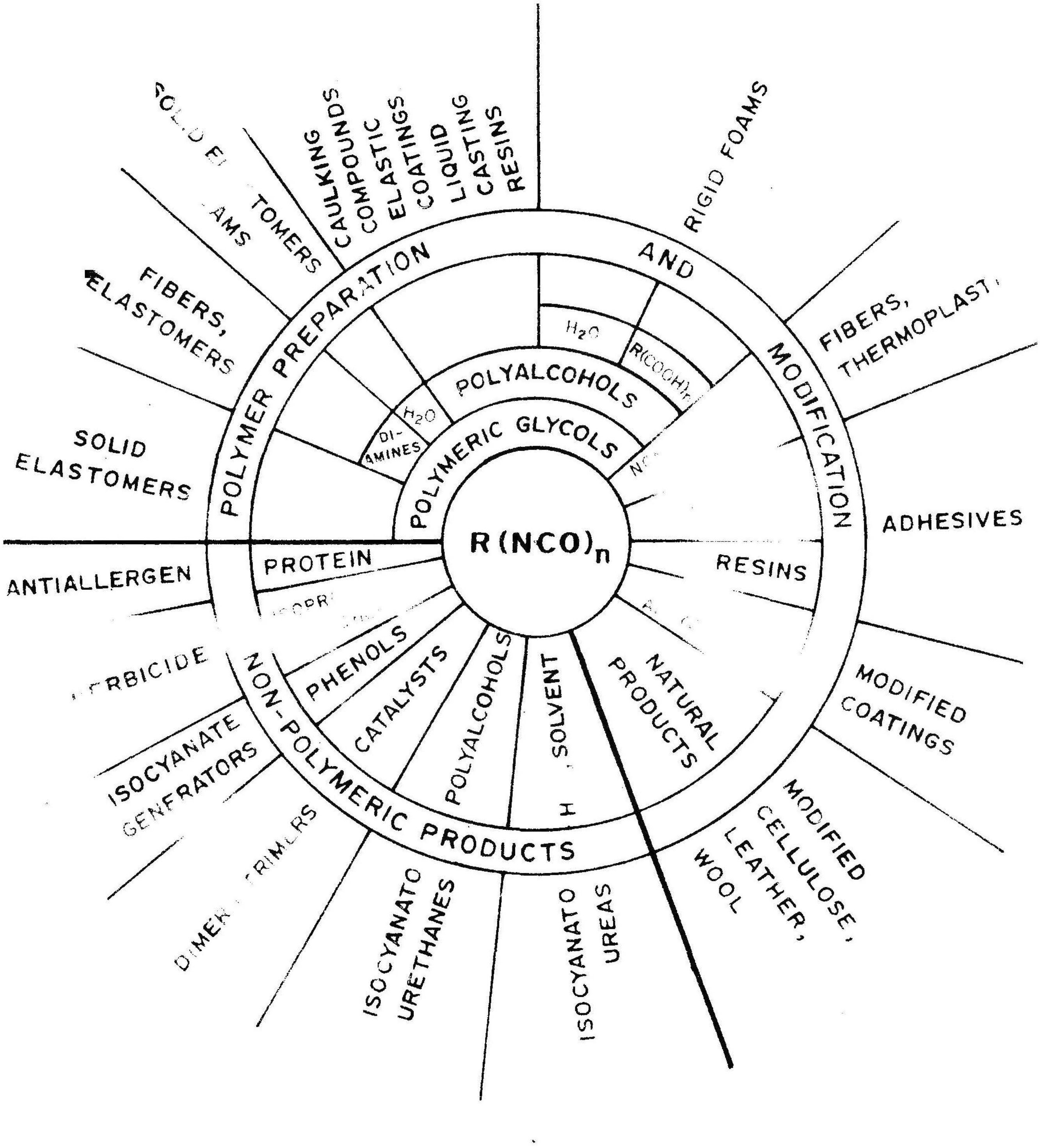
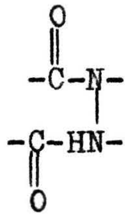
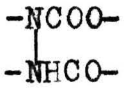
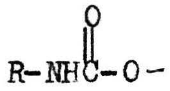
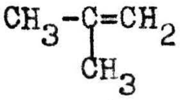
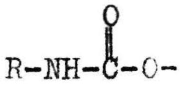


FIG. I ISOCYANATE APPLICATIONS

Table-1: Reactions of isocyanates with various functional groups and products obtained therefrom

No.	Group reacting with isocyanate	Product obtained		Ref.
1.	Amine (Primary, Secondary aliphatic, aromatic)	Disubstituted urea	R-NHCONHR	57,59
2.	Ammonia	Monosubstituted urea	$R-NHCONH_2$	60
3.	Hydrazines			61
4.	Hydroxyl amine			62
5.	Amides	Acyl ureas	 $-\overset{O}{\overset{\|}{C}}-\underset{\mid}{N}-$ $-\underset{\underset{O}{\|}}{C}-HN-$	63-66
6.	Urea	Biuret	 $R-\underset{\mid}{N}-CONHR$ $CONHR$	67
7.	Urethane	Allophanate	 $-\underset{\mid}{N}COO-$ $-NHCO-$	67
8.	Alcohol(Primary, Secondary)	Urethane	 $R-NH\overset{O}{\overset{\|}{C}}-O-$	68
9.	Alcohol tertiary	Disubstituted ureas and olefins	RNHCONHR  $CH_3-\underset{\underset{CH_3}{\mid}}{C}=CH_2$ type	68-70
10.	Phenol	Urethane	 $R-NH-\overset{O}{\overset{\|}{C}}-O-$	71
11.	Water	Disubstituted urea	RNHCOOCONHR	72,73

cont..

Table-1: (cont.)

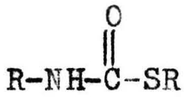
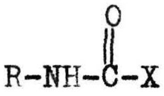
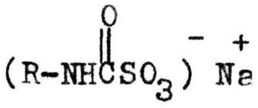
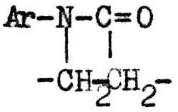
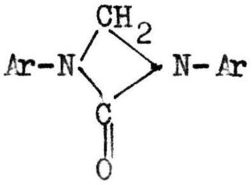
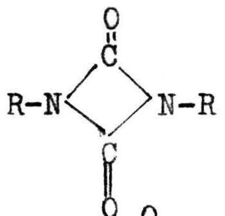
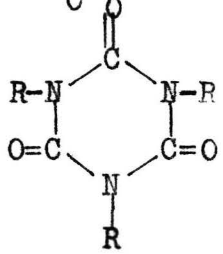
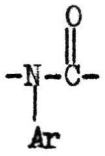
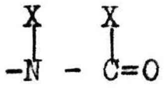
No.	Group reacting with isocyanate	Product obtained		Ref.
12.	Carboxylic acids	Amide	R-CONH-	74,75
13.	-CH	N-substituted amides	R-NHCO	58,76
14.	-SH	Thiourethanes	 $R-NH-\overset{\overset{O}{\|}}{C}-SR$	58
15.	Halogen halide	Carbomoyl halides	 $R-NH-\overset{\overset{O}{\|}}{C}-X$	77,78
16.	Aqueous sodium, potassium or ammonium bisulfite	Water soluble adducts	 $(R-NH\overset{\overset{O}{\|}}{C}SO_3)^{-}\ Na^{+}$	58
17.	Ketenes			
	a) Nitrobenzene		Ar-N=N-Ar	79
	b) Diazomethane	β-lactam, 1,Aryl-2-azetidinone		80
	c) Methylene aniline	1,3-Diphenyl uretidone		81
18.	-NCO	Dimer		82-85
		Trimer		

Table-1: (cont.)

No.	Group reacting with isocyanate	Product obtained		Ref.
19.	Aromatic isocyanate, self polymerization	N-substituted -1- nylons	 $-\underset{\displaystyle Ar}{\underset{\vert}{N}}-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	86
20.	-NCO	Carbodiphenyl imide	Ar-N=C=N-Ar	87
21.	Cl or Br	Dihalide	 $-\overset{\displaystyle X}{\overset{\vert}{N}}-\overset{\displaystyle X}{\overset{\vert}{C}}=O$	88,89
22.	Grignard reagent	Amide	RNHCOR'	90

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Section-I

SYNTHESIS OF DIISOCYANATES

INTRODUCTION

From the standpoint of synthetic polymers, only di- and polyisocyanates are of interest. Under proper conditions, they are reactive building units capable of forming high molecular weight materials. Aromatic diisocyanates having more reactivity, are receiving greatest interest.

The credit of exploring the use of diisocyanates in polymer synthesis goes to Prof. Otto Bayer and coworkers[1,2], who, in 1937, obtained polyurethanes by polymerizing hexamethylene diisocyanate with 1,4-butane diol. The use of hexamethylene diisocyanate to effect more rapid drying of alkyd resins was disclosed by Du Pont[3]. However, Lieser[4] obtained first U.S. patent on reaction of diisocyanates with dihydroxy compounds. Detailed study of reaction between diisocyanates and glycols was patented in 1942 by Catlin[5], who obtained the polymers in the form of fibres and flexible sheets.

With the advent of flexible urethane foam[6] of high strength at very low densities, the large scale commercial use of polyurethanes seemed established.

A variety of diisocyanates have been commercialised in last 3 decades. The oldest and the most widely used is toluene diisocyanate (TDI). This is available in the form of pure 2:4 isomer, 80/20 mixture of 2:4 and 2:6 isomers and 65/35 mixture of 2:4 and 2:6 isomers. Various investigators[7,8] have described the effect of different isomer ratio of 2,4- and 2,6-toluene diisocyanate, on flexible foam properties. Undistilled grade of mixed isomers of toluene diisocyanate has been recently tried successfully in the preparation of rigid foams[9].

In the manufacture of urethane elastomers too, TDI has been widely used either alone or in combination with other diisocyanates. Thus Chemigum SL (Neothane)[10,11] and Vulkollans[12] are the polyester based millable gums available from Goodyear Tire and Rubber Co. and I.G. Farbenindustrie A.G. respectively. Isocyanate terminated cast polymers, commercially known as 'Adiprene L' were described by Athey et al[13,14] of Du Pont and were based on poly(1,4-oxybutylene) glycol and TDI.

TDI has also found applications in the preparation of adhesives, coatings[15], fibres[16] etc. thereby indicating its versatality in applications.

The isocyanate which has gained considerable popularity in recent years is 4,4'-methylene bis(phenyl isocyanate) (4-MDI), commercially known as MDI. 4-MDI is used in the preparation of millable gums[19], thermoplastic elastomers, rigid foams[18,19], high temperature poly(amide-imide) polymers[20], films[16], fibres[22] etc.

The other commercially available diisocyanates are 1,5-naphthalene diisocyanate, 1,6-hexamethylene diisocyanate, 4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate (toluedine diisocyanate) etc. All of these diisocyanates have specific applications depending upon the nature of end uses of the polymeric products obtained from them.

PRESENT INVESTIGATION AND RESULTS

In India, Hindustan Organic Chemicals is engaged in producing m-aminophenol, in the production of which a step containing sulfonation of nitrobenzene is involved. Usually sulfonation of nitrobenzene is carried out with 65% oleum. If low percentage of oleum is used, the rate of reaction and also the sulfonated product obtained is considerably low. Therefore above mentioned higher oleum percentage is preferred. During this reaction about 3 to 4% of nitrobenzene gets converted into 3,3'-dinitrodiphenyl sulfone and contaminates the primary product, the sodium salt of m-nitrobenzene sulfonic acid. The former being insoluble in reaction mass unlike latter, comes out as white solid material. This is ultimately removed by filtration. The production of this by-product is about 60-70 tons per year. Its export figures for last 3 years are given in Table-2.

Table-2: Export figures of 3,3'-Dinitrodiphenyl sulfone from Hindustan Organic Chemicals, India

Year	Quantity in M.tons	Country to which exported	Value in US $
1973	20	Japan	5,600
1974	30	Japan	10,800
1975	-	No exports	-

Earlier it was exported in the form of wet cake, to

Japan where it was used in the reduced form (as amino compound) for curing of epoxy resins. Presently this by-product is dumped as waste because its applications have not yet been explored. In view of these facts, the present investigation was undertaken to study the possibilities of utilizing 3,3'-dinitrodiphenyl sulfone in different fields of polymer chemistry by converting it in suitable compounds like diamine and diisocyanate.

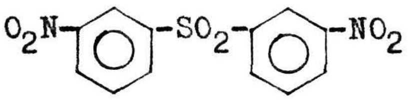
Thus, the commercially available by-product 3,3'-dinitrodiphenyl sulfone was used to synthesise the diisocyanate, 3,3'-sulfonylbis (phenyl isocyanate) (3-SDI). To observe the effect of substitution of sulfonyl group by a methylene group on the reactivity of diisocyanate, a compound 3,3-methylenebis (phenyl isocyanate) (3-MDI) was synthesised. The steps involved in the synthesis of these two diisocyanates are shown diagramatically in Fig.II.

The elemental analysis of all the compounds synthesised are given in the experimental section. The infra-red spectra of these compounds are given in the Appendix.

(a) Synthesis of 3,3'-sulfonylbis (phenyl isocyanate)(3-SDI)

3,3'-Dinitrodiphenyl sulfone

This compound, obtained in the form of wet cake, contained acidic impurities. It was washed several times with water to make it free of impurities and recrystallised from glacial acetic acid. m.p. 196°C.



3,3'-Dinitrodiphenyl sulfone.

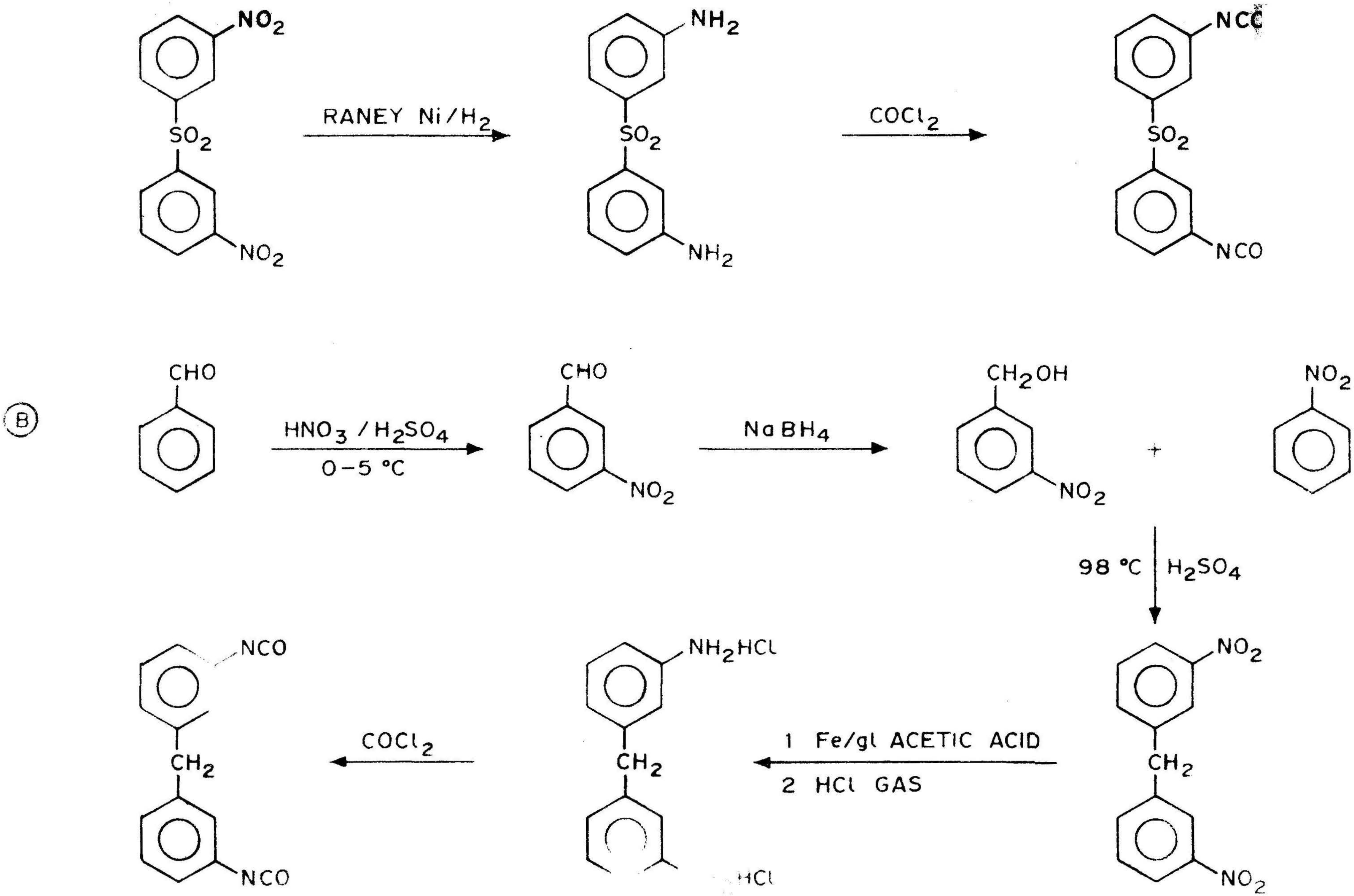
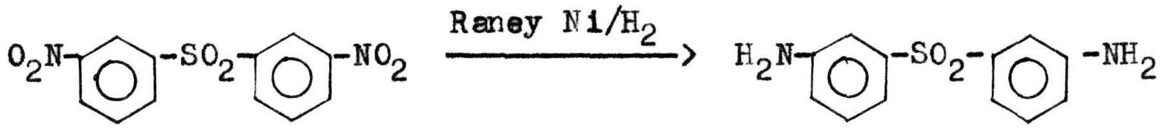


FIG. II SYNTHESIS OF DIISOCYANATES

3,3'-Diaminodiphenyl sulfone

3,3'-Dinitrodiphenyl sulfone was reduced in ethanol with Raney Nickel catalyst with 500 psi. hydrogen pressure at room temperature (25-30°C). The catalyst was removed and solvent distilled out. The residue obtained was recrystallised from alcohol-water mixture and gave white crystalline compound. m.p. 166°C.

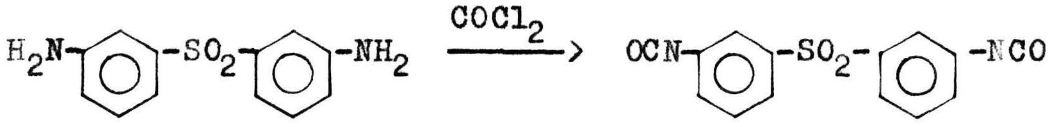


3,3'-Dinitrodiphenyl sulfone

3,3'-Diaminodiphenyl sulfone

3,3'-Sulfonyl bis (phenyl isocyanate) (3-SDI)

Phosgenation of 3,3'-diaminodiphenyl sulfone was carried out in o-dichlorobenzene using dry phosgene gas. The solvent from the clear reaction mass was removed and the residue obtained was distilled under reduced pressure. b.p. 360-380°C, bath temp./0.8 - 1.0 mm of Hg. m.p. 127°C.

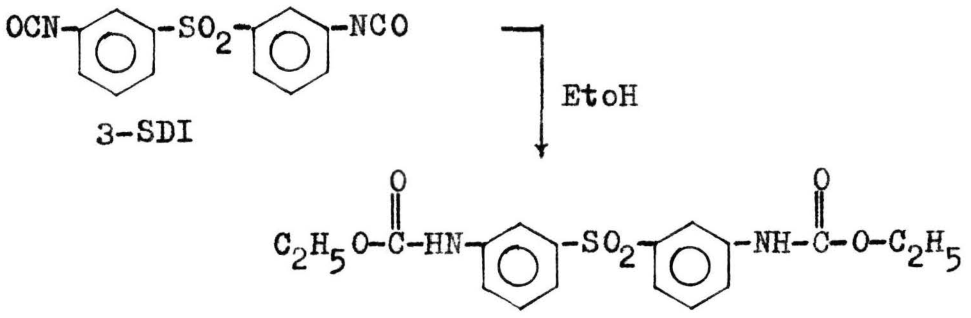


3,3'-Diaminodiphenyl sulfone

(3-SDI)

Ethyl urethane derivatives of 3-SDI

3-SDI was refluxed in ethanol and the resultant solution was filtered. This solution on concentration gave a crude derivative, which was then recrystallised from ethanol. m.p. 184°C.



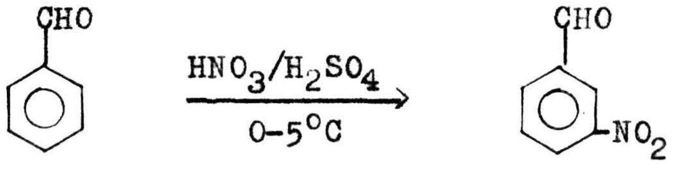
Ethylurethane of 3-SDI

(b) Synthesis of 3,3'-methylene bis(phenyl isocyanate)(3-MDI)

Dihydrochloride of 3,3'-diaminodiphenyl methane was synthesised using the method, in general, described by Lambert Thorp et al[22].

m-Nitrobenzaldehyde

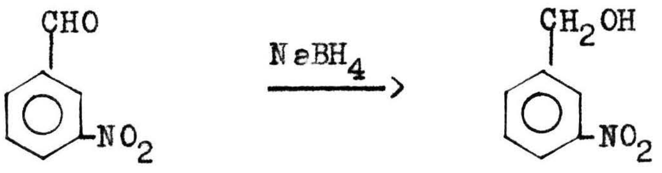
Benzaldehyde was nitrated at 0-5°C. The crude product obtained was distilled under reduced pressure and gave crystalline yellowish compound. b.p. 118°/1.2 mm. of Hg.



Benzaldehyde m-Nitrobenzaldehyde

m-Nitrobenzyl alcohol

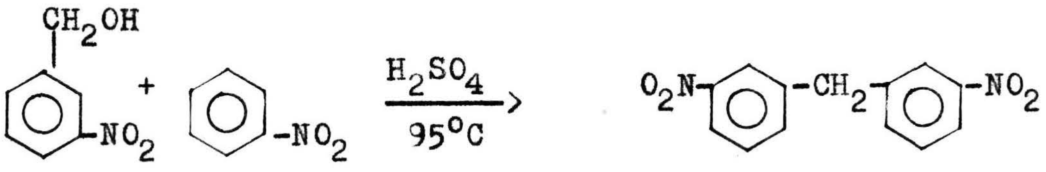
m-Nitrobenzaldehyde was reduced with sodium borohydride in methanol. After removal of methanol, the compound was taken in ether and washed several times with water. Ether layer was dried and the ether was removed. The crude m-nitrobenzyl alcohol, thus obtained, was distilled under reduced pressure. b.p. 220-230°C. bath temperature /1.0 mm of Hg.



m-Nitrobenzaldehyde m-Nitrobenzyl alcohol

3,3'-Dinitrodiphenyl methane

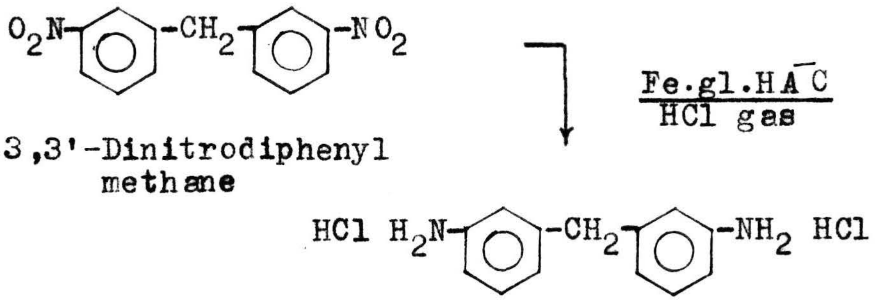
m-Nitrobenzyl alcohol was condensed with nitrobenzene in the presence of sulfuric acid at 95°C. The crude product obtained was recrystallised from glacial acetic acid and gave white crystalline solid. m.p. 174°C.



m-Nitrobenzyl alcohol Nitrobenzene 3,3'-Dinitrodiphenyl methane

Dihydrochloride of 3,3'-diaminodiphenyl methane

3,3'-Dinitrodiphenyl methane was reduced to 3,3'-diaminodiphenyl methane with iron and glacial acetic acid on a steam bath. The amino compound was extracted with ether and dry HCl gas was passed in ether when the dihydrochloride derivative precipitated out. It was filtered and dried. m.p. 205°C (decomposes).

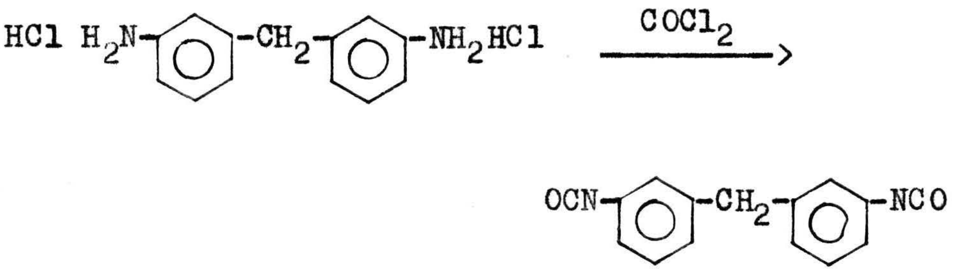


3,3'-Dinitrodiphenyl methane

Dihydrochloride of 3,3'-diaminodiphenyl methane

3,3'-Methylenebis (phenyl isocyanate)(3-MDI)

The phosgenation of dihydrochloride of 3,3'-diamino diphenyl methane was carried out in toluene with dry phosgene gas. The solvent was removed and the residue obtained was distilled under reduced pressure. b.p. 200-220°C. bath temp./ 0.5 mm. of Hg.

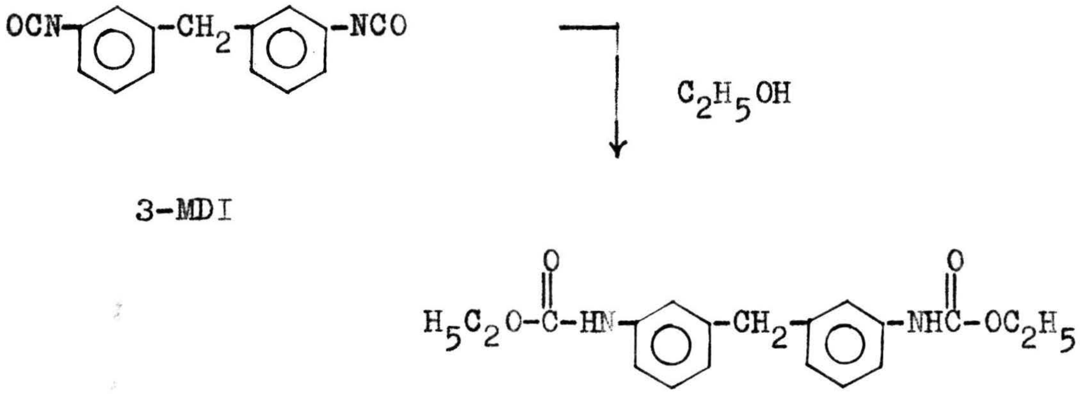


Dihydrochloride of 3,3'-diaminodiphenyl methane

3-MDI

Diurethane of 3-MDI

3-MDI was refluxed on a water bath with excess of ethanol and the resultant solution was filtered. The solution on concentration yielded a crude derivative which was then recrystallised from ethanol. m.p. 122°C.



3-MDI

Diurethane of 3-MDI

DISCUSSION

In the present investigation, two diisocyanates have been synthesized. The diisocyanates and the intermediate compounds were characterised on the basis of physical constants, elemental analysis and infra-red spectra. Derivatives of some compounds were also prepared in order to characterise them. For example, diurethanes were obtained by reacting diisocyanates with excess of ethanol. These derivatives were also studied for their elemental analysis, IR spectra and physical constants.

Earlier, Hart et al[23] have reported the synthesis of 3-SDI. However, they have used 3,3'-dinitrodiphenyl sulfone obtained by nitration of diphenyl sulfone, while in the present study, readily available compound has been utilised, which is a waste by-product of an industry. This dinitro compound, even when used without further purification, gave satisfactory results. A different method for reduction of 3,3'-dinitrodiphenyl sulfone has been used as compared to that of Hart et al[23]. Resultant amino compound has been obtained in good yields (70-75%) despite the poisoning of a catalyst. The reduction with Raney nickel and hydrogen was done at room temperature and it yielded 3,3'-diamino diphenyl sulfone in utmost pure form. The reduction was carried out in ethanol in which 3,3'-dinitrodiphenyl sulfone is insoluble and hence could be separated out, if any unreacted, by simple filtration, along with the catalyst. The reduced compound is soluble in reaction medium. Thus reduction with Raney Ni renders an easy separation of reaction product and unreacted reactants and also eliminates tedious recrystallization step as amine remains in the filtrate and is obtained in a pure form. The Raney Ni catalyst, could be reused only for the second time as its poisoning, probably due to the sulfonyl group in the 3,3'-dinitrodiphenyl sulfone, was observed. The reduced compound was characterized by its m.p. (167°C), elemental analysis and IR spectrum. The IR of reduced compound (Fig.2 in Appendix) showed single peak, instead of a doublet, at 3300 cm^{-1} corresponding to primary amine.

3,3'-Diaminodiphenyl sulfone was then converted into 3-SDI. The yields of as high as 70% were obtained in this conversion as against 40-50% obtained by Hart et al[23]. In this reaction more solvent was required to dissolve the diisocyanate that is formed during the reaction. And also it was necessary to bubble sufficient phosgene gas into the reaction mixture below 5°C to ensure complete conversion of amine to the corresponding carbomoyl chloride. For this reason, it was found advantageous to keep the reaction mixture at 0-25°C for 12-15 hours before decomposing the carbomoyl chloride to the diisocyanate at higher temperatures. This diisocyanate was reported to be accompanied by formation of considerable amount of urea, causing lower yields of the main product. However, it was observed during present work that if the amine used is dry and the conditions mentioned above are strictly followed, the urea formation can be completely avoided. Distillation of this diisocyanate was not attempted by earlier workers[23]. The boiling point of this diisocyanate is found to be 360-380°C. bath temp./ 0.8 -1.00 mm. of Hg.

The synthesis of 3-MDI was attempted following the method in general, described by Lambert Therp et al[22].

m-Nitrobenzaldehyde was obtained in good yields by nitration of benzaldehyde with HNO_3/H_2SO_4 mixture at 0-5°C. It was purified by distillation under reduced pressure. In the present study, m-nitro benzyl alcohol was obtained from reduction of m-nitrobenzaldehyde with sodium borohydride in preference to Becker's method[24]. As compared to Becker's method sodium borohydride reduction is easy and also gives excellent yields of the reduced compound. Reduction by sodium borohydride has also been described previously by Chaikin et al[25]. These authors obtained yields of m-nitro benzyl alcohol upto 82% as against 95% obtained in the present study. Two moles of sodium borohydride per mole of m-nitrobenzaldehyde have been used. The excess of sodium borohydride was removed by employing sufficient washings with water to the etheral solution of m-nitrobenzyl alcohol.

Condensation of m-nitrobenzyl alcohol with nitrobenzene was carried out in presence of large amount of sulfuric acid acting both as catalyst by donating proton to remove a mole of water from condensed product and as dehydrating agent by absorbing water that has been produced during condensation. The yields of 3,3'-dinitrodiphenyl methane, the condensed product, are very poor (15% based on m-nitrobenzyl alcohol) thereby making its large scale production very difficult. A large amount of black sludge was obtained during this condensation as has been reported by Lambert Thorp et al[22].

Reduction of 3,3'-dinitrodiphenyl methane was carried out by iron powder and glacial acetic acid, instead of $SnCl_2$ and HCl. The diamine obtained was extracted with ether and its hydrochloride derivatives was isolated. Phosgenation of this dihydrochloride in toluene yielded 3-MDI. This is an isomer of commercially available 4,4'-methylene bis(phenyl isocyanate) (4-MDI). The isocyanate group being placed at meta position with respect to the methylene bridge, in the present diisocyanate its reactivity may be expected to be comparatively less than its 4,4' isomer.

EXPERIMENTAL

Spectral measurements

The IR spectra were recorded on Perkin Elmer infracord 137 spectrophotometer. The spectra of solid compounds were taken in nujol mull while the spectra of liquids were taken as liquid films.

Preparations

3,3'-Dinitrodiphenyl sulfone

Commercially available 3,3'-dinitrodiphenyl sulfone (500 g) was taken in a 2 litre beaker and washed several times with ice-cold water, to remove the acidic impurities present in the compound, till nutral to a litmus paper. The white compound obtained after filtration was recrystallised from glacial acetic acid and was dried. It was also found that even unrecrystallised compound could be used for further reaction as the yields obtained are quite satisfactory.

Analysis: Found C 46.88%, H 2.59%, N 9.14%, S 10.17%

Calcd. for $C_{12}H_8O_6N_2S$: C 46.76%, H 2.59%, N 9.09%, S 10.39%.

3,3'-Diaminodiphenyl sulfone

In a medium pressure rocking type autoclave were placed 3,3'-dinitrodiphenyl sulfone (10 g), ethanol (100 ml) and Raney nickel catalyst (1.5 to 2.0 g). A hydrogen pressure of 500 lbs/sq.inch was filled in the autoclave and the mass was stirred for 8 hours at room temperature. The reaction mixture was filtered to remove the catalyst and the unreacted nitro compound, if any. The clear colourless filtrate was given norit treatment and the alcohol solution of amine thus obtained was concentrated to 50 ml and poured into 100 g of ice-cold water. The white crystalline compound precipitated out was 3,3'-diaminodiphenyl sulfone. yield 5.8 g (70%).

Analysis: Found C 58.28%, H 4.68%, N 11.20%, S 12.90%

Calcd. for $C_{12}H_{12}O_2N_2S$: C 58.06%, H 4.83%, N 11.29%, S 12.90%.

3,3'-Sulfonylbis (phenyl isocyanate) (3-SDI)

In one litre three necked round bottomed flask equipped with a mechanical stirrer, a reflux condenser and a thermowell were placed 3,3'-diaminodiphenyl sulfone (6.5 g) and o-dichlorobenzene (750 ml). The open end of the reflux condenser was joined to one end of the aspirator bottle containing potassium hydroxide solution. The other end of the aspirator bottle was connected to the exhaust. The flask was cooled to 0°C by ice-salt mixture and dry phosgene gas was bubbled into the suspension for about 4½ to 5 hours. The reaction mixture, which was in the form of white suspension, was kept at 0°C to 20°C for 12-15 hours (overnight) and then heated on a sand bath to the boiling temperature of the solvent (180°C) for 2 to 3 hours to get clear colourless solution. A stream of nitrogen gas was bubbled through the reaction mixture until no phosgene was detected in the gas outlet. The reaction mass was filtered and solvent removed completely. The yellowish white solid obtained was distilled under reduced pressure. yield 5.4 g. 70%.

Analysis: Found C 55.90%, H 2.77%, N 9.32%, S 10.70%

Calcd.for $C_{14}H_8O_4N_2S$: C 56.0%, H 2.66%, N 9.33%, S 10.66%.

Ethyl urethane derivative of 3-SDI

In a 100 ml round bottomed flask equipped with a water condenser 3-SDI (0.5 g) and ethanol (50 ml) were placed. The solution was refluxed on a boiling water bath for 1 hour. It was then filtered and concentrated. The crude product that separated out was filtered and crystallised from ethanol. yield 0.49 g 67%.

Analysis: Found C 55.33%, H 5.02%, N 7.34%, S 8.08%

Calcd.for $C_{18}H_{20}O_6N_2S$: C 55.11%, H 5.10%, N 7.34%, S 8.16%.

m-Nitrobenzaldehyde

In a 3 litre three necked round bottomed flask provided with a dropping funnel, a thermometer and an efficient mechanical stirrer was placed technical grade concentrated sulfuric acid (1.25 litres)(sp.gr. 1.84). To this, fuming nitric acid (167 ml)(sp.gr. 1.49 - 1.50) was added while efficient agitation of the sulfuric acid continued at a temperature of 5^oC to 10^oC. The mixture was maintained at this temperature with continuous stirring for a period of 2-3 hours during which addition of distilled benzaldehyde (213 g) was completed. Ice bath was removed at the end of addition and the mixture was allowed to stand overnight at room temperature. The mixture was then poured onto 3.25 kg. of crushed ice when yellowish m-nitrobenzaldehyde precipitated out. This was filtered, dried and was dissolved in benzene for removal of traces of water. Benzene solution of m-nitrobenzaldehyde was dried and benzene was removed completely. The crude compound obtained was distilled under reduced pressure to get yellowish white crystalline m-nitrobenzaldehyde. yield 220 g. 70%.

Analysis: Found C 55.63%, H 3.31%, N 9.27%

Calcd.for $C_7H_5O_3N$: C 56.06%, H 3.67%, N 9.82%.

m-Nitrobenzyl alcohol

In a 250 ml 3 necked round bottomed flask provided with a thermowell, a dropping funnel and an efficient mechanical stirrer were dissolved m-nitrobenzaldehyde (63.6 g) in dry and distilled methanol (150 ml). To this well stirred solution sodium borohydride (14.2 g) was added in instalments over a period of 25 to 30 minutes at 25-30°C. After the addition was over, the reaction mass, which had changed its colour from faint yellow to brown, was further stirred for 1 hour and methanol was completely removed. Thus, the dark brown liquid, m-nitrobenzyl alcohol, obtained was taken in ether and the ethereal solution was washed several times with water to assure the removal of excess of sodium borohydride. Ether solution was dried and ether was removed. The crude m-nitrobenzyl alcohol was purified by distillation to get 60.0 g of product. yield 95%.

Analysis: Found C 55.42%, H 4.53%, N 9.43%

Calcd. for $C_7H_7O_3N$: C 54.91%, H 4.57%, N 9.14%

3,3'-Dinitrodiphenyl methane

In a 500 ml three necked round bottomed flask equipped with a thermowell, a water condenser and a mechanical stirrer, were kept m-nitrobenzyl alcohol (20.35 g) and nitrobenzene (60.45 ml). To this, concentrated sulfuric acid (200 ml) was added and the solution was heated on a boiling water bath for 48 hours. The dark brown reaction mass was cooled and poured onto 1 kg. of crushed ice when yellowish white solid, 3,3'-dinitrodiphenyl methane precipitated out. This was filtered and recrystallised several times from glacial acetic acid to get white crystalline compound based on m-nitrobenzyl alcohol. yield 3 g. 15%.

Analysis: Found C 60.53%, H 4.0%, N 10.73%

Calcd. for $C_{13}H_{10}O_4N_2$: C 60.46%, H 3.87%, N 10.85%

Dihydrochloride of 3,3'-diaminodiphenyl methane

In an evaporating china clay dish were placed 3,3'-dinitrodiphenyl methane (4.2 g) and iron powder (9.0 g). To this glacial acetic acid (2 ml) was added and the mixture was heated on a boiling water bath with constant stirring. The white dinitro compound attained the colour of the iron powder in a few minutes. The solid mass was heated further on a water bath for ½ hour and extracted with dry distilled ether. The ethereal solution of diamine, thus obtained, was filtered and dried on KOH. It was further filtered and dry HCl gas was bubbled into it when white solid hydrochloride derivative of the diamine was obtained. This was filtered and dried. yield 1.9 g 73% based on 3,3'-dinitrodiphenyl methane.

Analysis: Found C 56.75%, H 6.32%, N 10.66%

Calcd.for $C_{13}H_{16}N_2Cl_2$: C 57.40%, H 5.92%, N 10.37%.

3,3'-Methylenebis (phenyl isocyanate) (3-MDI)

The hydrochloride of 3,3'-diaminodiphenyl methane (0.8 g) was suspended in dry, distilled toluene (50 ml) in a 100 ml 3 necked flask equipped with a mechanical stirrer, a water condenser and a thermowell. The open end of the condenser was joined to one of the aspirator bottle containing potassium hydroxide solution. The other end of the aspirator bottle was connected to exhaust. The flask was cooled to $0^{o}C$ with ice-salt mixture and dry phosgene gas was bubbled through it for 2 hours keeping the temperature at $0^{o}C$. The ice bath was removed and the reaction mass was kept overnight. It was then refluxed in an oil bath for 2 hours while phosgene was bubbled through it till a clear yellow solution was obtained. The phosgene was stopped and boiling continued for another hour. A stream of dry nitrogen gas was bubbled through the reaction mixture until no phosgene gas was detected in the gas outlet. From the reaction mixture which was clear yellow solution, solvent was completely removed. The residue obtained was distilled under reduced pressure. yield 0.45 g 66%.

Analysis: Found C 72.14%, H 3.98%, N 11.25%

Calcd.for $C_{15}H_{10}O_2N_2$: C 72.01%, H 4.00%, N 11.20%.

Ethyl urethane derivative of 3-MDI

In a 100 ml round bottomed flask equipped with a water condenser were placed 3-MDI (0.5 g) and ethanol (50 ml). The solution was refluxed on a boiling water bath for 2 hours. It was then filtered and concentrated. The crude product obtained was filtered and recrystallised from ethanol. yield 0.42 g 63%.

Analysis: Found C 66.95%, H 6.00%, N 8.19%

Calcd.for $C_{19}H_{22}N_2O_4$: C 66.67%, H 6.43%, N 8.18%.

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Section-II

THE REACTIVITIES OF DIISOCYANATES

INTRODUCTION

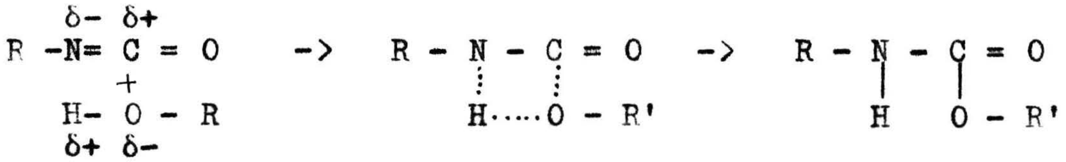
The structure of the isocyanate group:

$$\left[\; R{-}\overset{-}{N}{-}\overset{+}{C}{=}O: \quad \longleftrightarrow \quad R{-}N{=}C{=}O: \quad \longleftrightarrow \quad R{-}N{=}\overset{+}{C}{-}\overset{-}{O}: \;\right]$$

has unique features suggesting the possibility of ionic reactions, with electron donors attacking the carbonyl carbon and electron acceptors attacking the oxygen or nitrogen. As a result a variety of isocyanate reactions are observed. However, a few of these are of major interest, especially in the industrial applications of isocyanates. Kinetics and mechanism of the reactions of isocyanates with several functional groups have been studied but reaction of several isocyanates with different alcohols has been studied in greater detail because of its commercial importance. Kinetics of monoisocyanate reactions is the simplest and useful in the understanding of the structure and mechanism of the reactions. However, kinetics of diisocyanates is more involved than that of monoisocyanates.

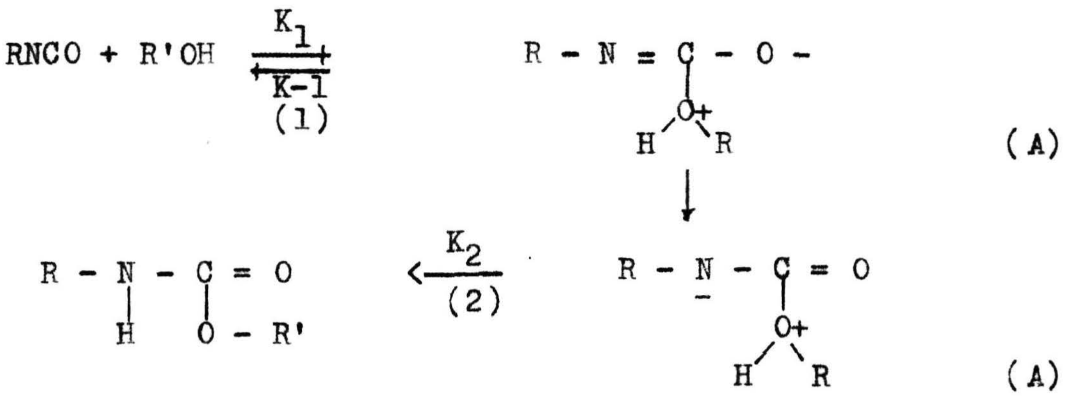
Davis and Farnum[1] were the first to study isocyanate-hydroxyl reaction quantitatively. These studies showed that the relative rates of reaction of isocyanate with aliphatic alcohols decrease in the order: primary > secondary > tertiary. This was found to be in accordance with the expected influence of steric hindrance due to the branching of the aliphatic chain close to the site of the reaction. Baker and coworkers[2-4] investigated the isocyanate-hydroxyl reactions in more details and provided a sound theoretical background for many of the later kinetics and mechanism studies made by others. The uncatalysed nucleophilic addition of an alcohol to an isocyanate can be visualised in several ways. These can be given as follows:

(i) Direct addition of R'OH to RNCO with the formation of a four membered activated complex[5].



Large negative entropies of activation[6] obtained during the uncatalysed reactions of isocyanates with alcohols support this mechanism.

(ii) An intermediate complex of ionic structure (A) is formed after preliminary reversible addition by the scheme accepted for the reactions of other carbonyl compounds[7], and its subsequent unimolecular conversions into urethane by prototropic rearrangement.



(iii) As in scheme (ii), an addition product (A) is formed in the first stage and is converted into the urethane by a bimolecular reaction with a second R'-OH molecule.

$$\text{R-NCO} + \text{R'OH} \overset{K_1}{\rightleftharpoons} (\text{A})$$

$$(\text{A}) + \text{R}_1\text{-OH} \xrightarrow{K_2} \text{RNH.COOR}_1 + \text{R'OH}$$

Baker and coworkers[3,4] suggested the third scheme.

Effect of the structure of isocyanate

Although isocyanates are considered to be reactive class of compounds, the reactivities vary according to their structures. For example, isocyanate reactivity is increased when an electron withdrawing substituent is present in the isocyanate nucleus as it helps in increasing partial positive charge on the carbon atom of the isocyanate group by moving the negative charge farther from the site of the reaction, thus making attack on the carbon by an electron donor easier. On the other hand, electron donating substituent decreases the partial positive charge on the carbonyl carbon atom of the isocyanate group, making attack at that point by an electron donor more difficult, thus reducing the rate of reaction. Experimental evidences have proved this theoretical proposition[3,4]. Thus substituent like $-NO_2$ group increases the reactivity while those like $-OCH_3$, $-CH_3$ decrease it. Aromatic isocyanates have been shown to be more reactive than aliphatic or aralkyl isocyanates[8]. Bailey and coworkers[9] and later Kaplan[10] have reported an additional data on the effect of isocyanate structure on reactivity. The relative effect of substituent groups was calculated from the observed rate data[9,11,12].

Brock[13] correlated the reaction of amyl isocyanates with alcohol by Hammett linear free energy relationship:

$$\log K/K_0 = \rho E \sigma$$

where:

ρ = reaction series constant

σ = the sum of the substituent constant

K_0 = rate constant for the reaction of phenyl isocyanate

K = rate constant for the substituent phenyl isocyanate in question.

The constant σ is a quantitative measure of the electronic effect of a given meta on para substituent relative to a hydrogen atom. A positive value of σ indicates an electron withdrawing effect, and negative value indicates an electron donating effect. The reaction, and conditions under which it occurs, influence the reaction constant ρ. Its positive value is characteristic of reaction enhanced by electron withdrawing substituent while negative value is characteristic of reactions which are promoted by electron donating groups. Based on limited data, ρ is calculated to be 1.69. Substituent constants (given in brackets) decrease in the order of:

P-NO_2(1.27) > m-NCO (0.43) > P-NCO (0.35) > p(-CH_2-C_6H_4NCO)

(0.04) > $p(CH_2-C_6H_4NHCOO-C_2H_5)$ (0.01) > $m-CH_3$ (-0.7) > $p.OCH_3$ (-0.27).

Effect of alcohol structure

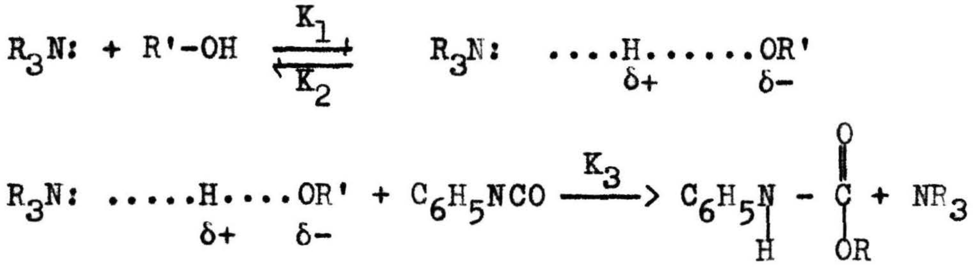
The structure of alcohol has also been shown to influence the reaction rates[1]. Dyer and coworkers[14] have reported a quantitative data on the effect, on the rate of reaction, of changes in the alcohol structure. As mentioned earlier primary alcohols have been shown to be more reactive than secondary alcohols. The steric factors, as one can expect, affect the reactivity of alcohol and also influence the effectiveness of catalyst in case of catalysed reactions. In contrast to the isocyanate reactivity, electron withdrawing groups decrease the reactivity of an alcohol by reducing basic character on oxygen atom while electron donating substituents increase the basicity of the alcohol making it more reactive. This suggests that the primary role of alcohol, as that of any active hydrogen compound, is not that of a hydrogen donor but electron donor.

Catalysis in isocyanate alcohol reaction

As catalysed reactions are utilised in the largest commercial applications of isocyanates, naturally the catalysis of the isocyanate-hydroxyl reaction has been extensively studied. Although a large number of catalysts have been described in the literature, the mechanism of catalysis has still remained a subject of thorough investigation. The catalysis of the isocyanate reactions and the reactions of certain carbonyl compounds have certain common features. Bases[15] have been shown to catalyse isocyanate reactions, while acids[16] act as mild catalysts in these reactions. If alcohol is present in large excess, the acids had little or no catalytic effect. Organometallic compounds have also been used as catalysts[17].

In earlier developmental period of isocyanate kinetics, a considerable amount of work has been done on amine type catalysts. Tertiary amines enhance the rate of alcohol addition to isocyanates[3,4,17,18].

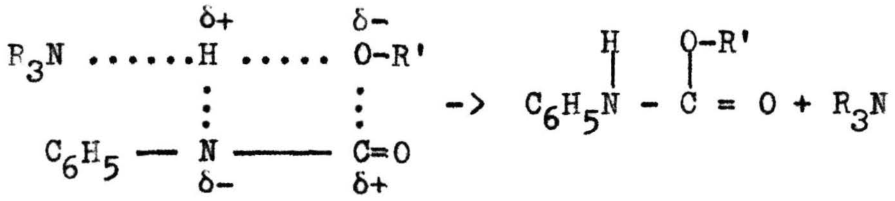
Recently, a mechanism that involves the formation of amine-alcohol complex[19] which then reacts slowly with the isocyanate, has been proposed for the formation of urethane.



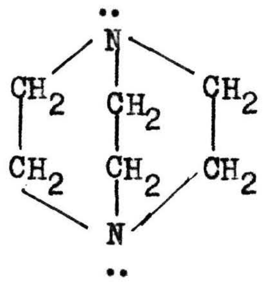
$$R_3N{:} + R'\text{-}OH \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R_3N{:}\;\cdots\underset{\delta+}{H}\cdots\cdots\underset{\delta-}{OR'}$$

$$R_3N{:}\;\cdots\cdots\underset{\delta+}{H}\cdots\cdots\underset{\delta-}{OR'} + C_6H_5NCO \xrightarrow{K_3} C_6H_5\underset{H}{\overset{}{N}} - \overset{O}{\underset{OR}{C}} + NR_3$$

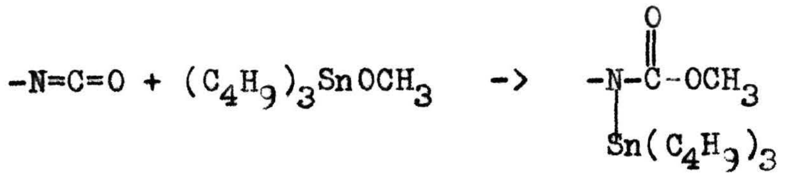
The above reaction may be assumed to proceed via four membered activated complex.



Flynn et al[20] have obtained a linear relationship between the rate constant for the reaction of phenyl isocyanate with 2-ethyl hexanol in benzene and pKa values of several amines. Recently, Anzuino et al[21,22] have reported a procedure to calculate rate constants for the primary and secondary reactions (urethane and allophanate formation respectively) between alcohols and isocyanate in both presence and absence of catalyst. It was confirmed[23] that tertiary amines which do not have strong steric hindrance, function as catalysts in direct proportion to their base strength. An exception to this is triethylene diamine[24] (1,4-diaza|2.2.2|bicyclooctane) which has been found to have powerful catalytic effect than would be predicted from its base strength.

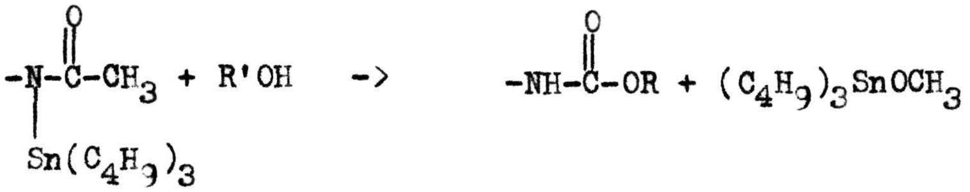


A complete absence of steric hindrance may be the reason for its high catalytic activity. On the contrary, diethylaniline having comparable basic strength is inactive due to the steric hindrance of bulky ethyl groups. Farkus et al[17] and Rabins[25] have analysed in details the published data on catalysis by metal compounds. Hostettler et al[24] and Wolfe[26] have studied the relative catalytic effect of several tin compounds. Bloodworth et al[27] indicated that tin containing carbamates are formed, on the addition of tin compounds, containing Sn-O bond to isocyanates and isothiocyanates.



$$-N{=}C{=}O + (C_4H_9)_3SnOCH_3 \rightarrow -\underset{\displaystyle Sn(C_4H_9)_3}{\underset{|}{N}}-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

This tin carmate readily reacts with alcohol or phenol to form urethane.



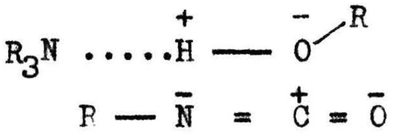
$$-\underset{\displaystyle Sn(C_4H_9)_3}{\underset{|}{N}}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + R'OH \rightarrow -NH-\overset{\overset{\displaystyle O}{\|}}{C}-OR + (C_4H_9)_3SnOCH_3$$

The observations have been made on the activating effect of a metal containing catalyst on alcohols[28,29]. It has been difficult to clarify the mechanism of acid-base catalysis due to the lack of quantitative data[31].

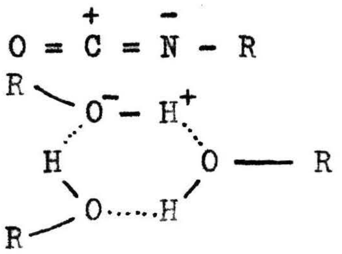
Effect of medium

The rate of the uncatalyzed urethane reaction is strongly effected by the reaction medium. For example, in 0.15 M solution, the phenylisocyanate-1 butanol reaction proceeds about 500 times faster in heptane than in dioxane. Since such a dominant role is played by solvent, it is not surprising that changes in reactant concentration have a more or less pronounced effect on the rate constant depending on the type of solvent in which the reaction is carried out. Ephraim and coworkers[32] correlated the solvent effect on rate of the reaction with its dielectric constant while deviations from second-order kinetics were attributed to hydrogen bonding between alcohol and solvent molecules. Although several investigators[32,33-35] felt that hydrogen bonding was responsible for deviations from predicted behaviour, none has conclusively proved this premise and obtained kinetic expressions which will include the hydrogen bonding between the alcohol and the solvent. However, Baker and coworkers[2] had studied this interaction in di-n-butyl ether and benzene solutions and concluded 'that the increased reaction velosity in benzene was mainly due to the presence of monomeric alcohol molecules which have much greater facility to attack the intermediate (alcohol-isocyanate) complex, than have the alcohol-ether solvated or associated (alcohol) molecules, exclusively present in the di-n-butyl ether'. Although this explanation appears quite convincing, it does not hold good in case of other solvent. For example, 0.15 M solution of alcohol in nitrobenzene shows a very high concentration of monomeric form, still the rate of urethane reaction is slightly slower in this solvent than in the dibutyl ether where monomeric alcohol is practically absent.

Recently, Oberth et al[36] have reported an exhaustive account of the effect of hydrogen bonding on the kinetics of the urethane reaction. They have shown that the rate of uncatalyzed urethane reaction depends essentially on the concentration of the polymeric (self associated) alcohol. A retardation of reaction rate is caused by solvent by breaking down the polymer and its magnitude is directly related to the hydrogen bonding power of the solvent. The polarization (weakening) of the O-H bond in the polymeric alcohol imparts high reactivity on it, the degree of polarization have been shown to be more pronounced in amine alcohol complexes, which accordingly are strong catalyst for the urethane reaction. This can be shown as below:



Polarization of O-H bond due to catalyst



Polarization of O-H bond due to polymeric form

Thus, Obert et al[36] have shed more lights on the role of hydrogen bonding as well as explained the complex kinetics of urethane reaction by taking this interaction into account.

Reactions of diisocyanates

As mentioned earlier, diisocyanates present a complicated reaction kinetics. The initial reactivity of an isocyanate can be compared to that of monoisocyanate substituted with an activating group whereas it can be compared with a monoisocyanate substituted with an urethane group as the reaction progresses. Although several complicated factors are involved in the diisocyanate reactions, their growing commercial importance has demanded more abundant information on the reactivities.

Bailey and coworkers[9] have reported reactions of several diisocyanates with large excess of 2-ethyl hexanol and hydroxyl terminated polyesters. Morton and coworkers[37,38] studied the reactions of 2,4-toluene diisocyanate and 4,4'-diphenyl methane diisocyanate with n-butanol in xylene and found that on increasing the alcohol/isocyanate ratio, the apparent reaction rate constants were increased as in the case of monoisocyanates. Tazuma and Latourette[39] reported similar experiments but using toluene as a solvent. A similar study of several diisocyanates in which triethylamine was used as a catalyst, was reported by Barkus and Eckert[12]. Kogan[40] obtained the kinetic data by following the rate of urethane formation using infra red absorption at 6750 cm^{-1}. Cunnigham and Mastin[41] threw an additional light on the relative reactivity of diisocyanate at higher temperatures. Case[42-45] showed the difference in reactivities of isocyanate groups in diisocyanates where strong steric hindrance existed on one group. Cooper et al[46] have reported the effect of structure of the hydroxyl compound on its reactivity towards phenyl isocyanate.

The present investigation was undertaken with a view to study the reactivities of two symmetrical diisocyanates in different solvents to obtain the kinetic data and find out the effect of solvent medium. The reactions carried out are uncatalyzed.

PRESENT INVESTIGATIONS AND RESULTS

Bailey and coworkers[9] have reported that the rate determination of a reaction between 4,4'-sulfonylbis (phenyl isocyanate)(4-SDI) and 2-ethyl hexanol in benzene solution was not possible due to the high reactivity of the diisocyanate. Hart et al[47] prepared 3-SDI an isomer of 4-SDI and attempted unsuccessfully to find out the rate of its reaction with 2-ethyl hexanol in benzene. In the present investigation efforts have been made to obtain the kinetic data on the uncatalyzed reactions between symmetrical aromatic diisocyanates (i) 3-SDI, (ii) 3-MDI, (iii)4-MDI and 2-ethyl hexanol in methyl ethyl ketone as well as in dioxane. In both of these solvents it was possible to follow the reaction between 3-SDI and 2-ethyl hexanol because of their higher hydrogen bonding power than benzene, which resulted in the reaction proceeding at slower rate. The reactivity of 3-MDI has not been described anywhere so far. The reactivity of 4-MDI was also studied under identical conditions and the data obtained was compared with that of its 3,3'-isomer.

The reactivities of all the three diisocyanates with 2-ethyl hexanol were studied by infra-red spectroscopic method. The intensity of the infra-red absorption caused by an isocyanate group at 2270 cm^{-1} was employed to follow the course of the reaction. 2-Ethyl hexanol was used in large excess and the pseudo first order rate constants were evaluated. Dioxane or methyl-ethyl-ketone solution of diisocyanate (0.03 M) with excess of (0.6 M) 2-ethyl hexanol was used for the spectroscopic measurements.

The absorbance At with respect to time t, for each of the diisocyanate in both the solvents as recorded by the instrument and the calculated quantities of unreacted isocyanate in respective cases are shown in Tables 3 to 8. The concentration of unreacted isocyanate is calculated according to the equation C = At/As x 0.03, where At is the absorbance after the lapse of time t and 'As' at the start of the reaction. From Tables 3-8, graphs of time in either seconds or minutes or hours against molar concentration of unreacted diisocyanates in respective cases were plotted and are shown in Figs. III-VIII The time values required for completion of 10%, 20% etc. of the reaction were found out from corresponding curves and are shown in Tables 9 and 10 along with the calculated values of the pseudo first order reaction rate constants for corresponding reactions. The pseudo first order reaction rate constants (K) for each reaction were obtained using the equation:

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

where t = time in seconds

a = initial molar concentration of isocyanate, and

a-x = molar concentration of isocyanate at time t.

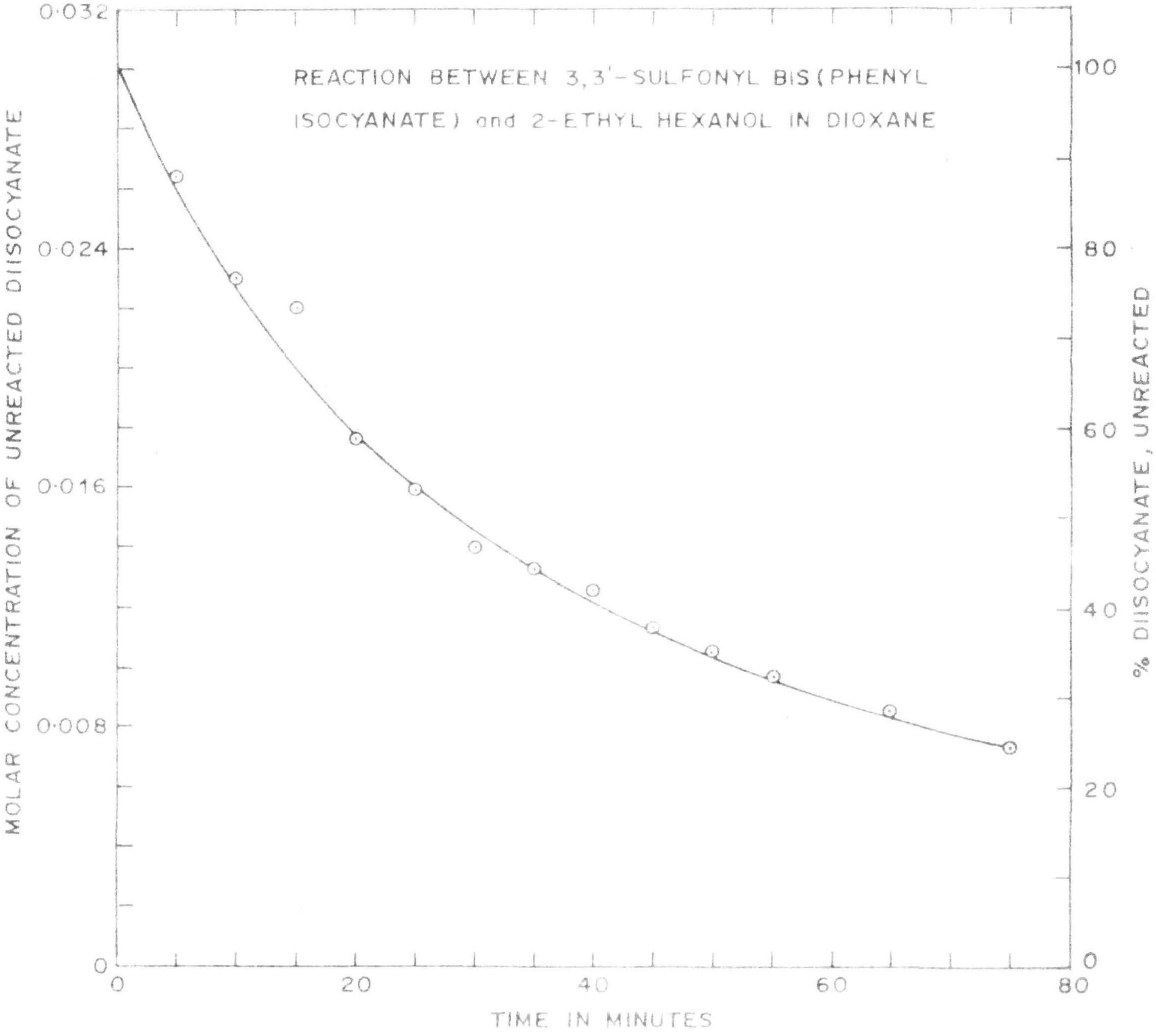


FIG. III PLOT OF TIME IN MINUTES AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

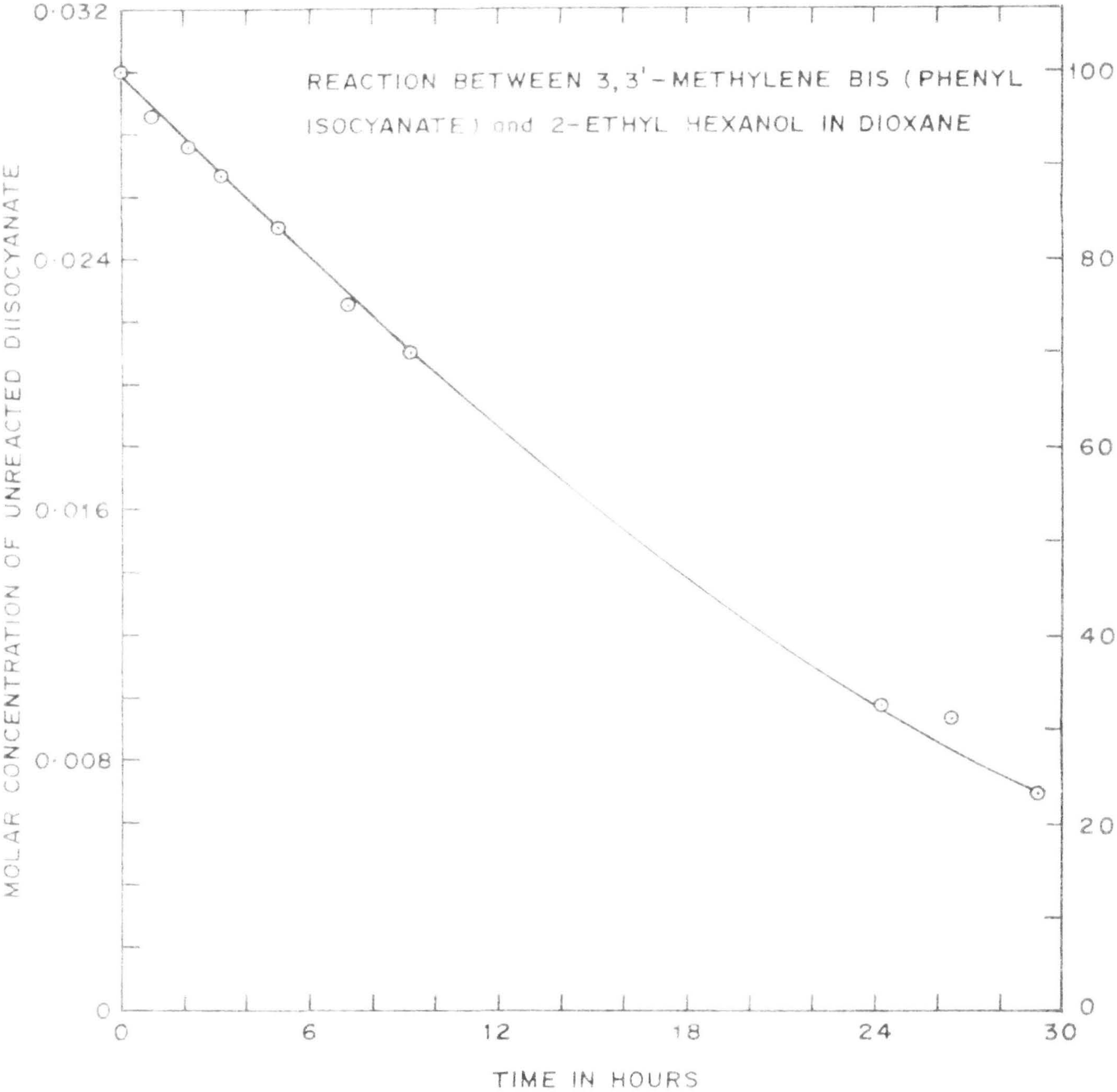


FIG. IV PLOT OF TIME IN HOURS AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

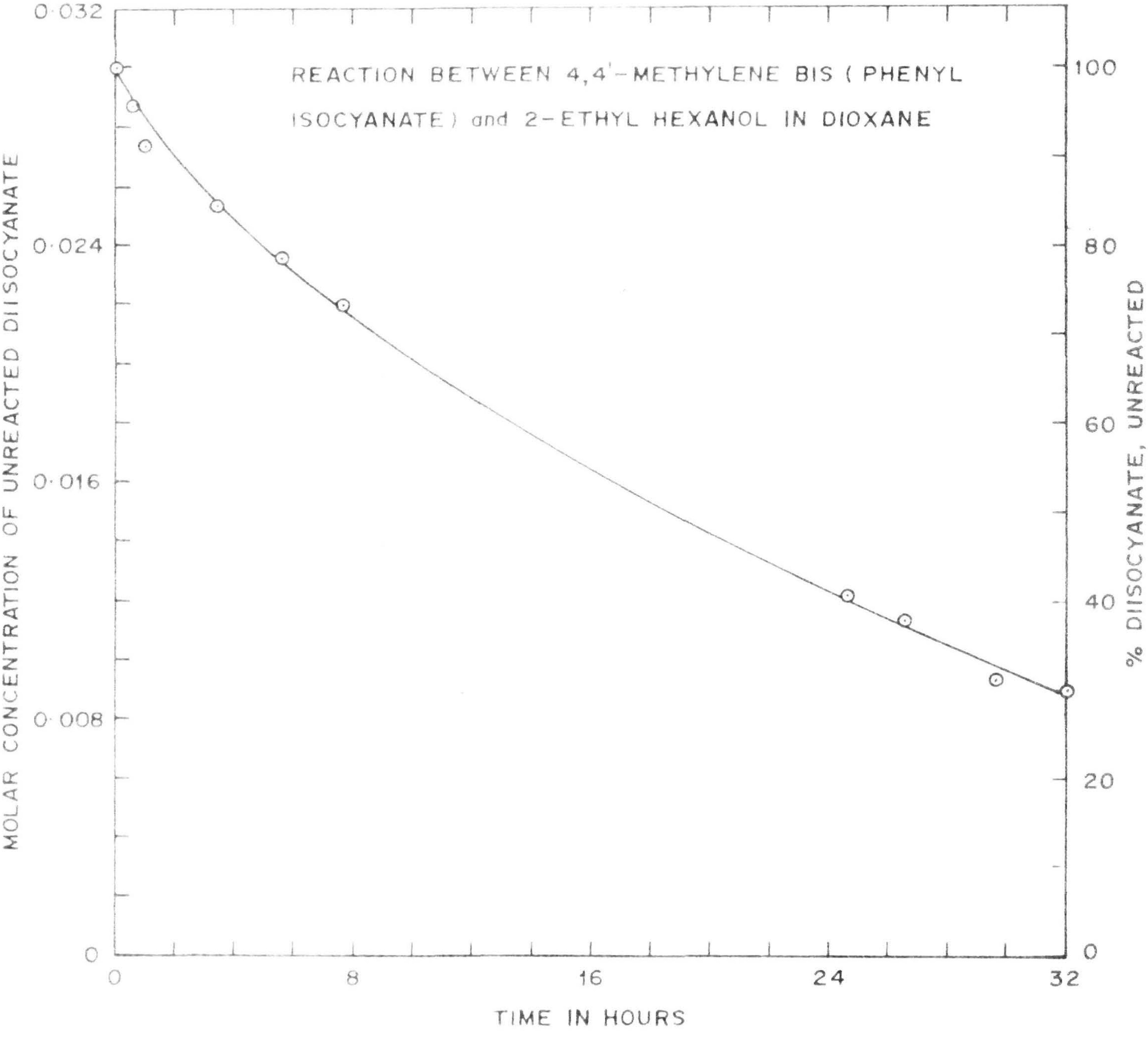


FIG. V PLOT OF TIME IN HOURS AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

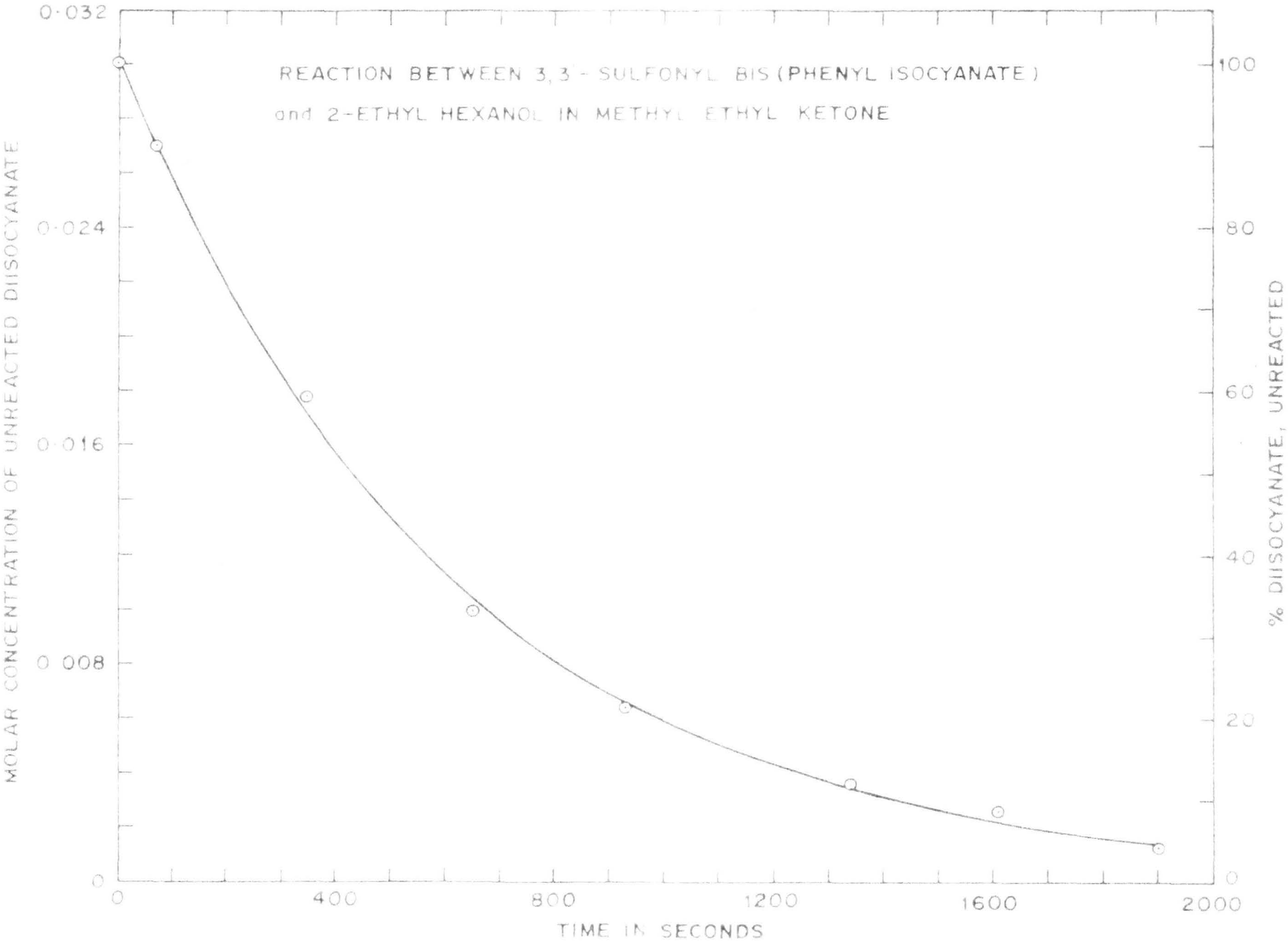


FIG. VI PLOT OF TIME IN SECONDS AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

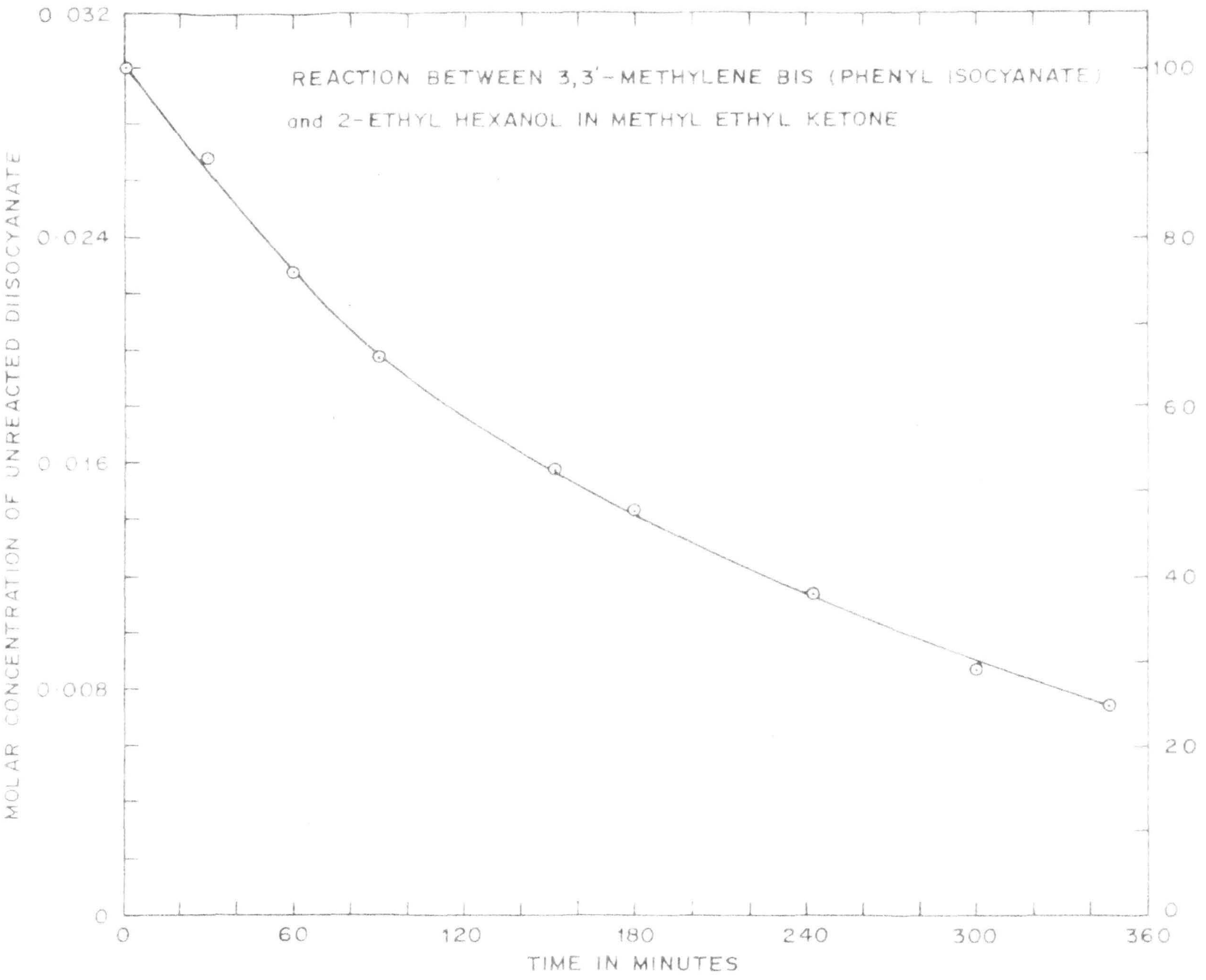


FIG. VII PLOT OF TIME IN MINUTES AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

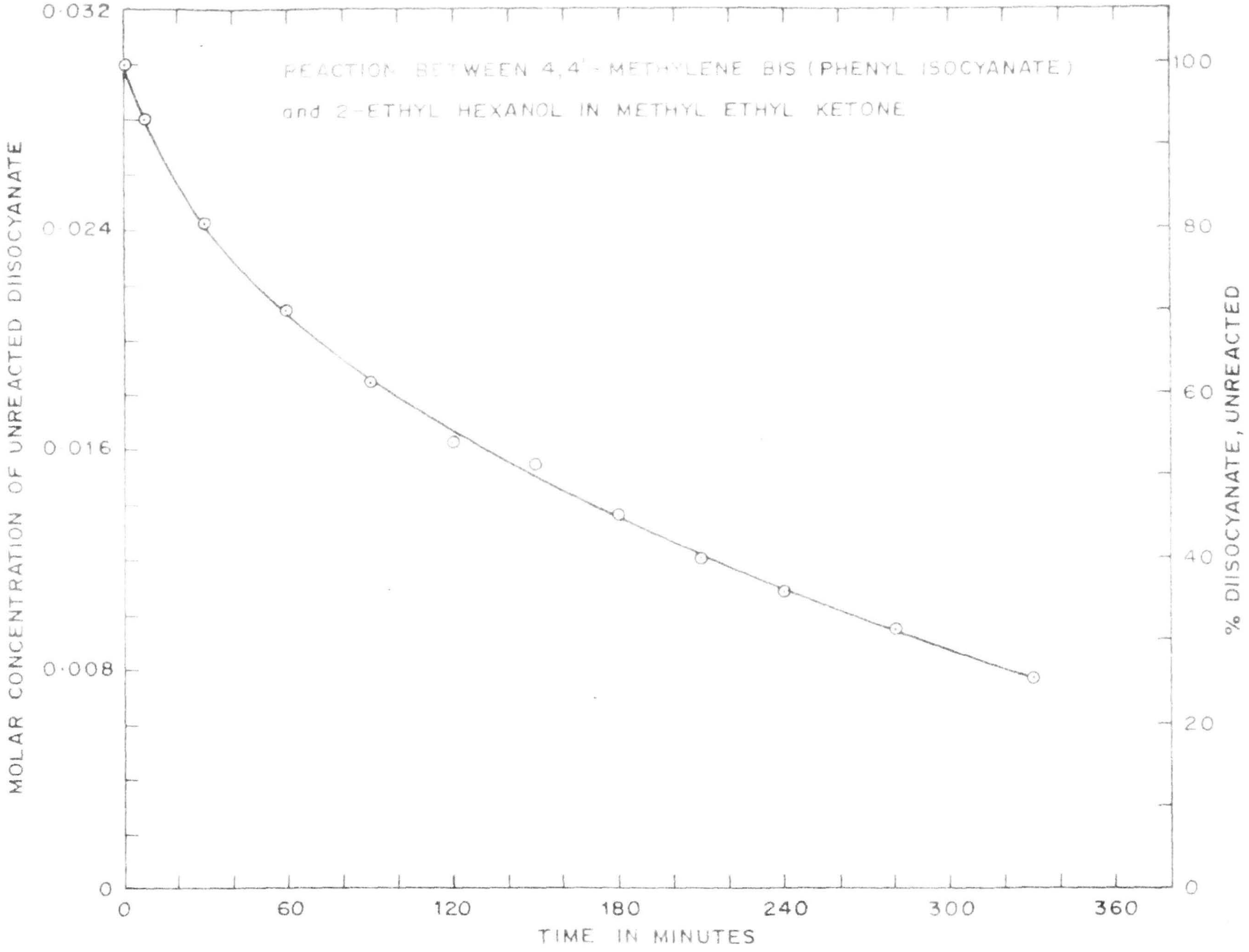


FIG. VIII PLOT OF TIME IN MINUTES AGAINST MOLAR CONCENTRATION OF DIISOCYANATE

Table-3: Absorbance of the mixture of 3,3'-sulfonylbis (phenyl isocyanate) and 2-ethyl hexanol in dioxane with respect to time

No	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0	0.7850	100.00
2	5	0.6900	86.66
3	10	0.6050	76.66
4	15	0.525	68.00
5	20	0.4625	60.66
6	25	0.4175	57.00
7	30	0.3900	50.00
8	35	0.3525	46.00
9	40	0.3300	42.00
10	45	0.3000	38.00
11	50	0.2775	37.66
12	55	0.2575	32.66
13	65	0.2275	27.33
14	75	0.195	26.00

Table-4: Absorbance of the mixture of 3,3'-methylenebis (phenyl isocyanate) and 2-ethyl hexanol in dioxane with respect to time

No	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0	0.5684	100.0
2	60	0.5400	95.33
3	130	0.5250	92.00
4	190	0.5050	89.33
5	320	0.4725	83.33
6	440	0.4275	76.00
7	565	0.3975	70.00
8	1470	0.1850	32.66
9	1580	0.170	28.00
10	1775	0.1350	26.00

Table-5: Absorbance of the mixture of 4,4'-methylenebis (phenyl isocyanate) and 2-ethyl hexanol in dioxane with respect to time

No.	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0	0.7150	100.00
2	30	0.6825	95.33
3	60	0.6550	91.33
4	90	0.6475	90.00
5	210	0.6075	84.66
6	330	0.5650	78.66
7	450	0.5250	73.33
8	1470	0.2900	40.33
9	1590	0.2700	38.00
10	1770	0.2225	31.33
11	1920	0.2140	30.00

Table-6: Absorbance of the mixture of 3,3'-sulfonylbis (phenyl isocyanate) and 2-ethyl hexanol in methyl ethyl ketone with respect to time

No.	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0.0	0.6475	100.00
2	5.45	0.3400	59.33
3	10.45	0.2100	32.66
4	15.25	0.1360	21.33
5	20.20	0.0790	12.00
6	26.45	0.0550	8.66
7	31.45	0.0250	4.00

Table-7: Absorbance of the mixture of 3,3'-methylenebis (phenyl isocyanate) and 2-ethyl hexanol in methyl ethyl ketone with respect to time

No.	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0.0	0.8295	100.00
2	30.45	0.7375	89.33
3	60.40	0.6300	76.00
4	90.40	0.5450	66.00
5	151.40	0.4375	52.66
6	180.40	0.3950	48.00
7	241.40	0.3050	38.00
8	300.40	0.2375	28.00
9	345.40	0.2025	24.66

Table-8: **Absorbance of the mixture of 4,4'-methylenebis (phenyl isocyanate) and 2-ethyl hexanol in methyl ethyl ketone with respect to time**

No.	Time in minutes	Absorbance At	Unreacted isocyanate %
1	0.0	0.7550	100.00
2	8.00	0.7050	93.33
3	30.00	0.6075	80.66
4	60.00	0.5300	70.00
5	89.00	0.4650	61.33
6	120.00	0.4100	54.00
7	151.00	0.3900	50.66
8	180.00	0.3450	45.33
9	210.00	0.3025	40.00
10	238.45	0.2725	36.33
11	279.00	0.2350	31.33

Table-9: Pseudo first order reaction constants for aromatic symmetrical diisocyanates at various degrees of reactions in dioxane at 24±1°C along with the time required for completion of reaction at those degrees

$K \times 10^4$ sec.$^{-1}$.

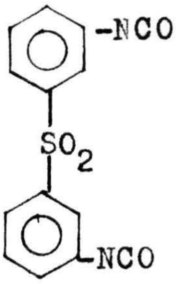
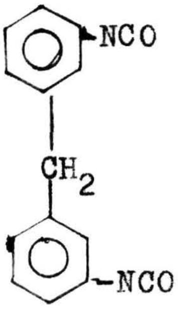
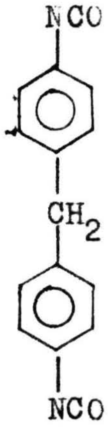
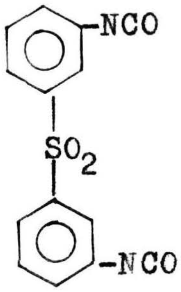
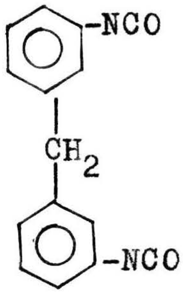
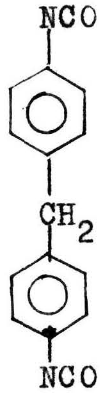
% Reaction						
	Time min.	K	Time min.	K	Time min.	K
10	3.30	12.18	180	0.23750	108	0.394490
20	8.30	5.6450	354	0.12450	306	0.15680
30	13.30	4.0640	540	0.10180	528	0.10390
40	20.30	3.1200	756	0.08482	780	0.08202
50	30.0	2.5590	987	0.07820	1116	0.06872
60	40.0	2.233	1242	0.07747	1488	0.06448

Table-10: Pseudo first order reaction constants for aromatic symmetrical diisocyanates at various degrees of reactions in methyl ethyl ketone at 24±1°C along with the time required for completion of reaction at these degrees

$K \times 10^4$ sec.$^{-1}$.

% Reaction						
	Time min.	K	Time min.	K	Time min.	K
10	1.10	36.5400	21	2.0330	12	3.5540
20	2.25	19.8600	46	1.0400	32	1.4990
30	3.50	14.3000	74	0.7418	60	0.9137
40	5.25	11.8100	112	0.5711	96	0.6878
50	7.15	10.6100	164	0.4687	150	0.5114
60	9.20	10.2800	224	0.4289	210	0.4568

DISCUSSION

Bailey et al[9] have reported that the reaction between 4-SDI and 2-ethyl hexanol in benzene was so fast that it was almost completed in 10 minutes and it was not possible to obtain adequate data for the calculation of reaction rate constant.

Similarly Hart et al[47] found it difficult to follow the reaction between 3-SDI and 2-ethyl hexanol in benzene as almost 50% of the reaction was over in 5 minutes and was practically complete in 30 minutes. Hence it was decided to study the reactivity of 3-SDI in solvents like methyl-ethyl-ketone and dioxane which differ substantially in their dielectric constants as well as in hydrogen bonding capacity. In view of obtaining kinetic data on the reactivity of symmetrical diisocyanates, two of which 3-SDI and 3-MDI are identical, differing only in the bridge that joins the two phenyl nuclei and two 3-MDI and 4-MDI are in their isomeric forms, the present study was undertaken.

Bailey et al[9] have studied the kinetics of several symmetrical diisocyanates, either substituted or non-substituted, with 2-ethyl hexanol in benzene as a solvent. Based on these studies, the relative effects of substituent groups on isocyanate reactivity have also been given. They are given in Table-11.

Table-11: Relative effects of substituent groups on isocyanate reactivity

Substituent group	Approximate relative effect
Sulfone (para)	> 50
Isocyanate (meta or para)	6
Phenyl isocyanate	1
4-MDI average	1.3

Thus, we can expect the sulfonyl group in meta position to isocyanate to be very effective in activating the -NCO group although to a lesser extent than in para position. It was indeed found to be true even in solvent like dioxane which has high hydrogen bonding capacity. It can clearly be seen from Table-9 and 10 that the reactivity of 3-SDI is very high as compared to that of 3-MDI in both methyl-ethyl-ketone and dioxane. This is understood in terms of the formation of a charge transfer through the sulfonyl bridge (unlike in the case of methylene bridge) and the electron withdrawing nature of the sulfonyl group that increases the reactivity of the isocyanate group positively polarising carbon atom of the isocyanate group and hence rendering attack by electron donor easier.

3-MDI reacted almost with a similar rate to that of its 4,4'-isomer, the latter being little faster. In dioxane only, the reaction rate in case of 3-MDI has been observed to be little faster than its 4,4'-isomer after nearly 50% of the reaction was completed.

The reactivity of all the three diisocyanates studied was faster in methyl-ethyl-ketone than in dioxane. The dielectric constant of methyl-ethyl-ketone is 18.4 and that of dioxane is 2.21. While concluding the studies on the effect of solvent on the reaction of an isocyanate with an alcohol, Ephraim et al[32] have reported that the reaction rate depends primarily upon the dielectric constant of the solvent. They attributed the deviations from second order kinetics to hydrogen bonding between alcohol and solvent molecules. However, an exhaustive study on the effect of hydrogen bonding on the kinetics of urethane reactions by Oberth et al[36], suggested the dependence of rates of these reactions completely on the hydrogen bonding power of the solvent. In the present study, this effect was observed in case of all the three diisocyanates.

When the reaction was carried out in dioxane, the yellowing of the reaction mixture was observed as the reaction proceeded, in all the three diisocyanates. This was in keeping with the observations of Obert et al[36] who attributed this yellowing of reaction mixture to the 'decomposition of dioxane in the presence of reactants'. These authors did not find noticeable decomposition of dioxane at higher concentrations of the reactants where the reactions proceed fast. In the present study, as described in the experimental section, the concentration of alcohol used was much higher that permited the reactions to proceed very fast as compared to that in which equivalent moles of reactants are used. The yellowing was, however, quite noticeable in case of all the three diisocyanates. Oberth et al[36] did not find such yellowing in other solvents. However, this yellowing of reaction mixture was observed in case of 4-MDI in methyl-ethyl-ketone while it was absent in case of 3-MDI and 3-SDI. This could not be attributed to the decomposition of methyl-ethyl-ketone as in case of dioxane as has been suggested by Oberth et al[36].

It was interesting to note during the studies in the reactivities of isocyanates by the absorbance measurements of the band at 2270 cm^{-1} in the infra-red spectra, that a band absent initially developed slowly at 2325 cm^{-1} - 2340 cm^{-1} (Fig. IX and X) reaching intensities comparable to 2270 cm^{-1} band, as the reaction proceeded. The intensity of this band varies with isocyanate and solvent. Even when the alcohol concentration was reduced to one-tenth of what was normally used (0.06 M), this band was still persisted. Every care was taken to avoid any side reaction taking place by drying all the solvents and reactants thoroughly as explained in the experimental section. It will not be appropriate to say that this band was due to carbon dioxide because the other band at 667 cm^{-1} due to CO_2 could not be seen clearly. However, if CO_2 was produced by the reaction of isocyanate with any of the components of the system,

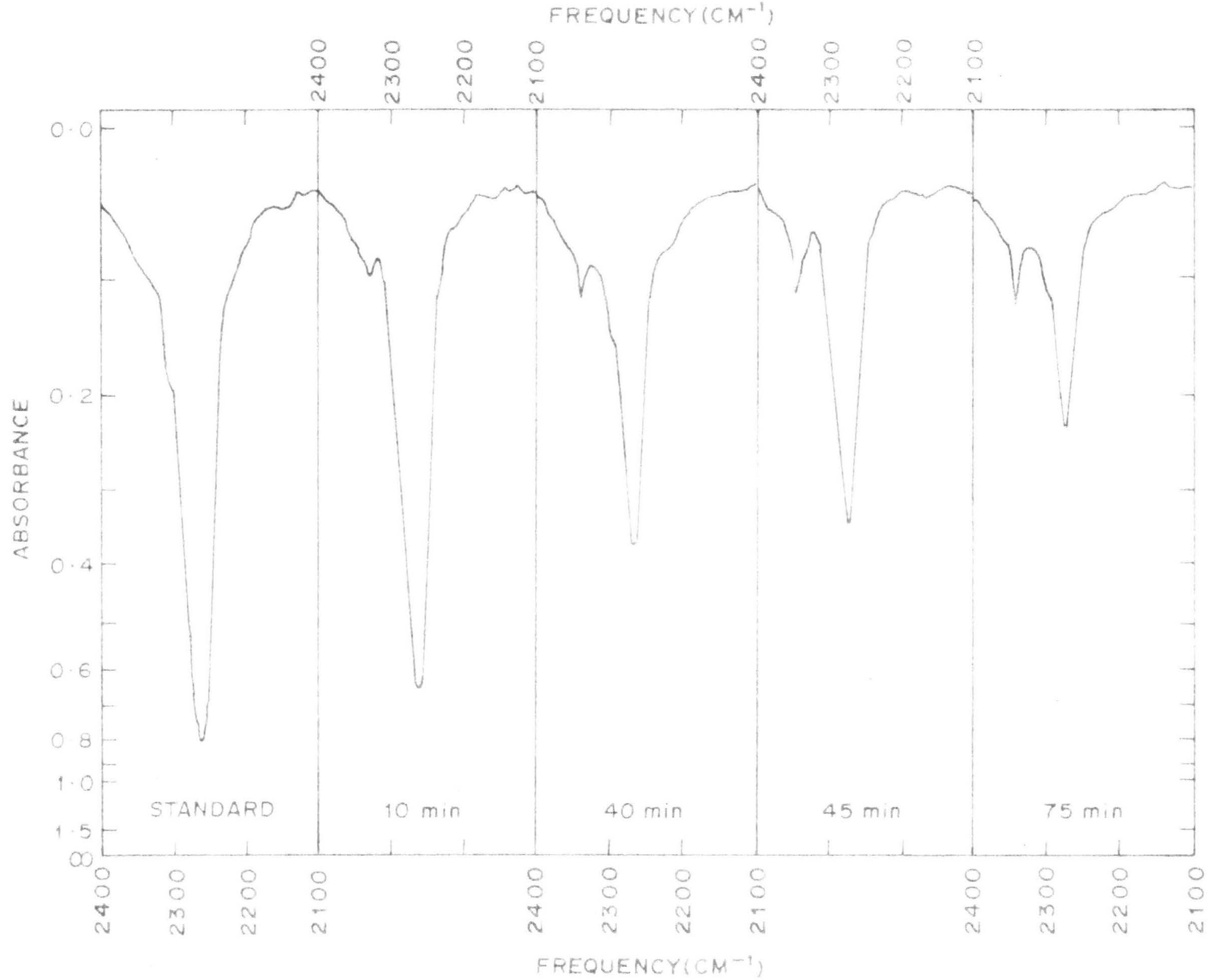


FIG. IX ISOCYANATE STRETCHING FREQUENCIES OF:
3,3'-SULFONYL BIS (PHENYL ISOCYANATE) IN DIOXANE

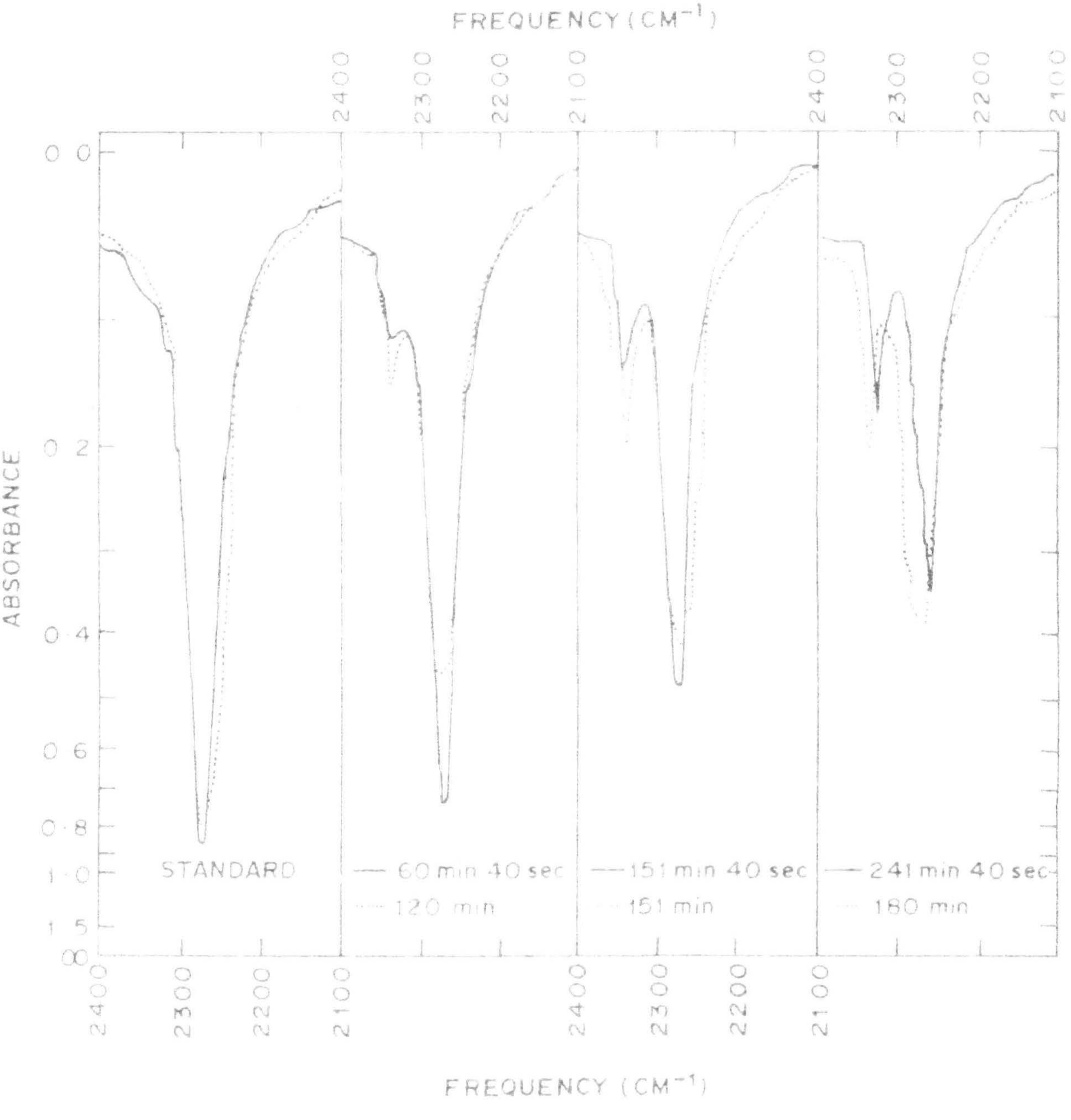


FIG. X ISOCYANATE STRETCHING FREQUENCIES OF
——— 3-MDI, ········ 4-MDI IN MEK

it would have developed immediately at the beginning of the reaction, which was not observed. Further, the amine which is also produced under such circumstances, would have catalyzed the urethane reaction, which was also not noticed. Therefore it is difficult to assign this band to any group or intermediate of the reaction. Investigation of this band in detail might help in understanding the mechanism for urethane reactions.

EXPERIMENTAL

Materials

(i) The dioxane was purified by refluxing over metallic sodium for several hours till the reaction was ceased and the sodium remained bright and then distilling from sodium using efficient reflux column. The boiling point of the solvent was 101°C. It was stored in contact with sodium.

(ii) Methyl ethyl ketone was purified by the method described by Mullar et al[48].

(iii) 2-Ethyl hexanol was distilled twice and the heart cut was used for the present work.

(iv) 4-MDI was obtained from M/s. Farbenfabriken Bayer AG Leverkusen, West Germany in the form of flakes. Freshly prepared 3-SDI and 3-MDI were used in this study. The methods for their preparation are given in Section I of this part. All the three diisocyanates were distilled under reduced pressure just before use.

Experimental method for the reaction

The intense absorption of infra-red radiation at 2270 cm^{-1} caused by the isocyanate group was used for plotting the course of the reaction. The infra-red spectra were recorded on a Perkin Elmer model 221 spectrophotometer equipped with sodium chloride cells. The instrument was previously calibrated with standard polystyrene film. All measurements were done at $24 \pm 1^{\circ}C$ with the same pair of cells (0.02 cm in thickness).

Reaction of 3-SDI

0.03 M dioxane or methyl-ethyl-ketone solution of 3-SDI was prepared by dissolving 90 mg of it in 10 ml solvent in a 10 ml capacity volumetric flask. It was used as standard solution. 90 mg of diisocyanate and 780 mg of 2-ethyl hexanol were dissolved in dioxane or methyl-ethyl-ketone and the solution was standardised to 10 ml in a 10 ml volumetric flask. This is the reaction mixture, 0.03 M with respect to diisocyanate and 0.6 M with respect to 2-ethyl hexanol. Absorbance As was recorded by scanning the infra-red spectrum of the standard solution which is filled in a cell. The reaction mixture was also run for infra-red spectrum in the cell and absorbance At at various times t were recorded. The reaction mixture, once introduced in the cell, was removed only after completion of the reaction. With the help of As and At values, the percentage of unreacted isocyanate was calculated.

Reaction of 3-MDI and 4-MDI

The same procedure as has been described above was used for the reaction of both of these isocyanates using appropriate quantities of isocyanates. As these two isocyanates are the isomeric forms of each other, quantities used in their reactions were the same. Thus, 0.03 M dioxane or methyl-ethyl-ketone solutions of diisocyanate (either of the two isomer) was prepared by dissolving 75 mg of it in either dioxane or methyl-ethyl-ketone in 10 ml volumetric flask. It was used as a standard solution. 75 mg of diisocyanate and 780 mg of 2-ethyl hexanol were dissolved in either dioxane or methyl-ethyl-ketone and volume of the solution was made up to 10 ml in a volumetric flask. This is the reaction mixture, 0.03 M with respect to diisocyanate and 0.06 M with respect to 2-ethyl hexanol.

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PART - II

POLYIMIDES

Section-I

POLYAMIDES

INTRODUCTION

Recent advances in space technology have produced a continuing and growing need for heat-resistant polymers i.e. polymers combining properties of temperature resistance and thermal stability. The former property is characterized by high melting and softening points i.e. the maximum temperature at which the polymer can still be utilized as solid, while the latter is characterized by the time of retention of the given value of mechanical strength and other properties at high temperatures, which is a measure of service temperature range. In order to achieve this goal, three pronged effort has been made in past several years.

(a) Improvement in existing polymers by the introduction of structural modifications

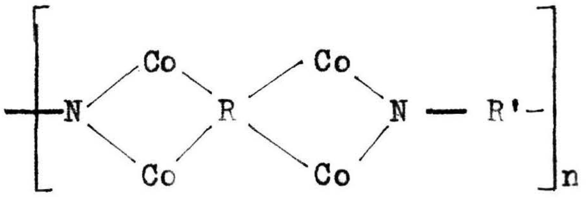
(b) Synthesis of newer class of inorganic or organic-inorganic polymers

(c) Tailor making of new organic systems capable of resisting heat effects.

In the first approach, the conventional, inherently flexible organic polymers were modified to raise the service temperature or inherently inflexible intractable polymers were modified into tractable forms. Phenyl groups were introduced in polymers like polyamides, polyesters etc. while in latter case methylene units or short chains of methylene units were introduced in polymers of poly-p-phenylene types.

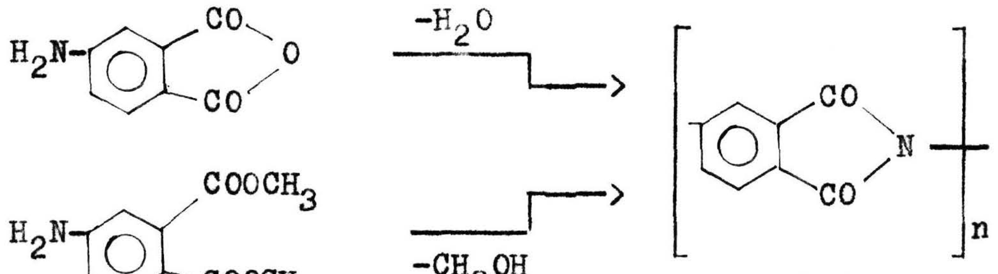
In the second approach, preparation of different inorganic and organic-inorganic (semi organic) polymers was the consideration. The fact that bonds stronger than carbon-carbon bond can be obtained as in silicones, led to the development of semi-organic polymers having inorganic chains framed by organic substituents.

Thirdly, a completely new generation of carbon-based polymers with inherently rigid chains has been developed. This involves the preparation of highly stable, rigid aromatic carbocyclic or heterocyclic ring systems directly incorporated into the polymer chain. The examples of this type are polybenzimidazoles, polybenzoxazole, polybenzthiazoles, aromatic polypyrazoles, aromatic polythiazoles, polyquinoxaline and polyimides etc. This forms the most important and useful approach. It may be unequivocally said that one of the most successful accomplishments in this respect was the synthesis of polyimides, which are ring-chain polymers of the structure:



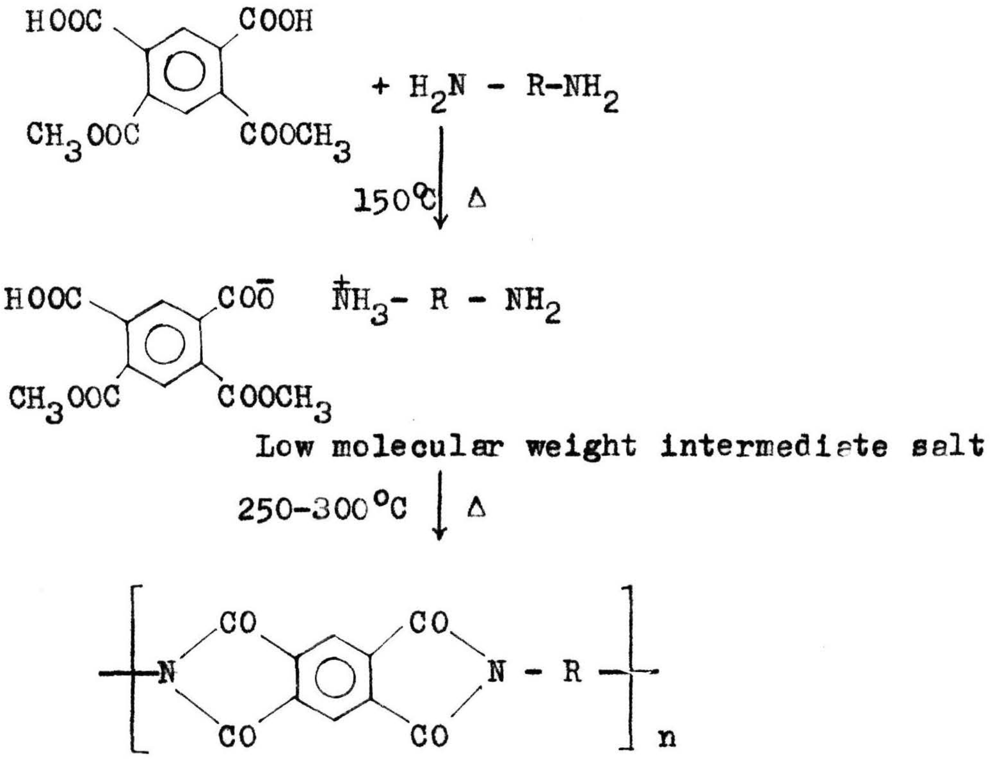
where R and R' are aromatic and other heat resistant groups.

Bogert and Renshaw[1] reported for the first time, the synthesis of a polyimide. It was formed when 4-aminophthalic anhydride or dimethyl 4-aminophthalate were heated.



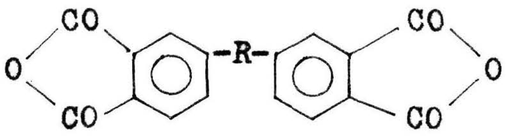
Polyimide

Edwards and Robinson[2] first reported the preparation of high molecular weight polyimides, by fusion of the salt from a diamine and tetracarboxylic acid or a diamine and a diacid/diester.



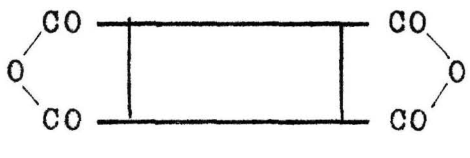
Polyimide

The necessary criterion for obtaining products with high molecular weight is that the melting point of the resulting polyimide must be below the reaction temperature so as to obtain molten reaction product during polycondensation. In a refinement of this method Edwards and Robinson[3] (a) heated the prepolymer at temperatures just below the melting point of the polymer, and (b) used mixtures of dianhydride and suitable diamines in aqueous ethanol at low temperatures to yield a prepolymer which was subsequently heated[4]. The success of all these processes was limited to the preparation of fusible polyimides. Using this technique however, polyimides capable of melting without decomposition were also prepared[5] from other anhydrides of the general formula:

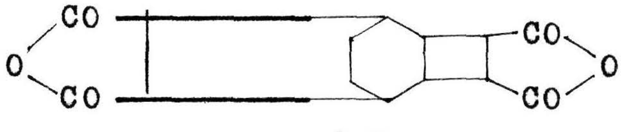


R= -O-, -CH$_2$-

and diamines with shorter chains, e.g. hexamethylene diamine, tetramethylene diamine. The following alicyclic tetracarboxylic acid dianhydrides were employed[6] in melt polycondensation with several aliphatic diamines and 4,4'-diaminodiphenyl methane.



Cyclobutane tetracarboxylic acid dianhydride



Dianhydride of tricyclo (4,2,2,$0^{2,5}$)-deca-10-ene-3,4,7,8-tetracarboxylic acid.

Hermans and Street[7] studied crosslinking in polypyromellitimides obtained by heating salts of pyromellitic acid and aliphatic diamines like hexamethylene diamine.

Aromatic polyimides are normally infusible and their preparation has been the subject of many publications[8-19]. Several methods have been developed for their preparation, a few of which are mentioned below:

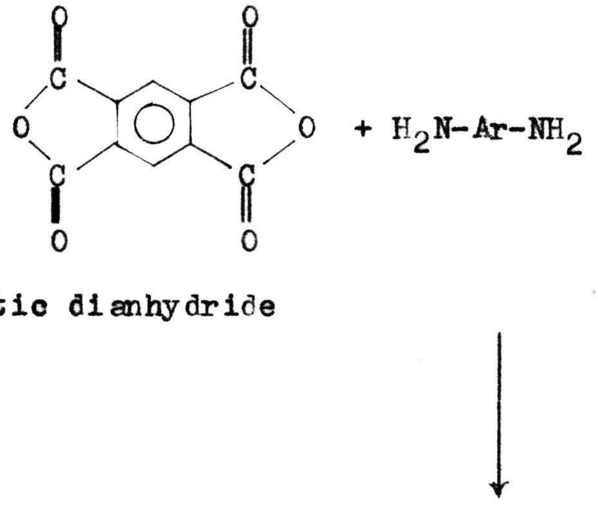
(1) Two step preparation of aromatic polyimides

(2) Polyimides from dihalides and aromatic diimides.

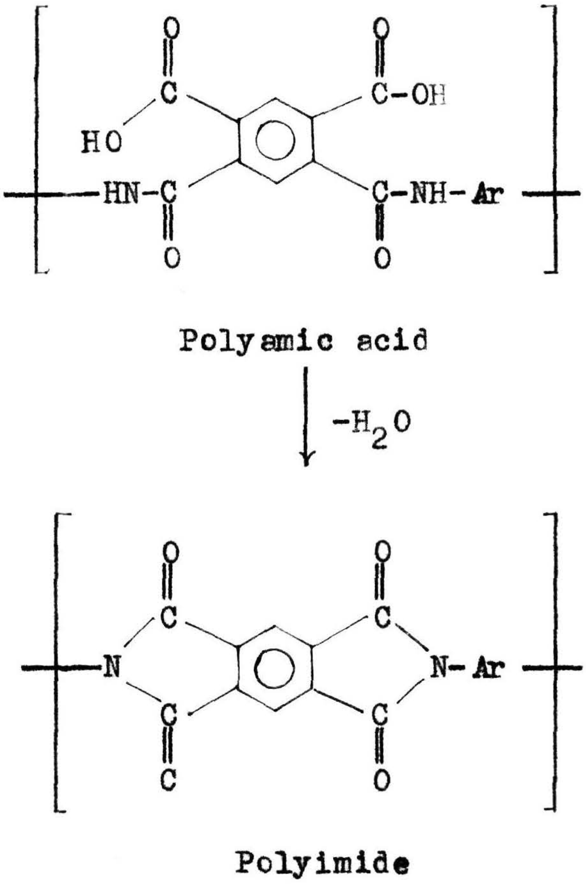
(3) Polyimides from diisocyanates.

(1) Two step preparation of aromatic polyimides

The general polymerization procedure involves (i) reaction of an aromatic dianhydride with an aromatic diamine in a suitable solvent to yield an intermediate of soluble precursor polymer, i.e. the polyamic acid (ii) which on subsequent cyclodehydration yielded the insoluble polyimide as shown in the following reaction.

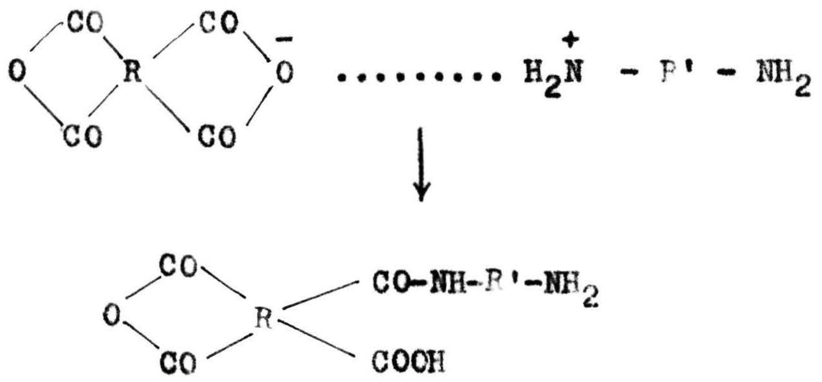


Pyromellitic dianhydride



Bowerr and Frost[16] investigated the effect of sequence of addition of the reagents on the molecular weight of the polyamic acid. Addition of dry dianhydride to the amine solution yielded highest molecular weights. Frost and Kesse[17] studied the effect of the ratio of the starting reagents on the variation in the viscosity of solutions of polyamic acids during their formation and also on prolonged standing. Zakoshchikova et al[20] observed that the specific viscosity of polyamic acids depend on the concentration of the reagents in the solvent. Wallach[21] determined molecular weights of several polyamic acids and studied the dependence of molecular weight and molecular weight distribution on the purity of the reagents.

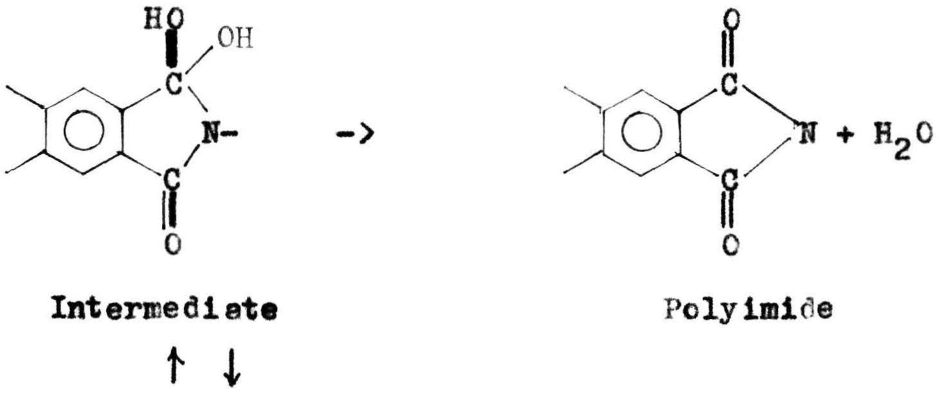
The synthesis of a polyamic acid is a bimolecular acylation of amines, consisting in a nucleophilic attack on the amino group accompanied by the opening of the anhydride ring (as shown below) and the formation of the polymer.

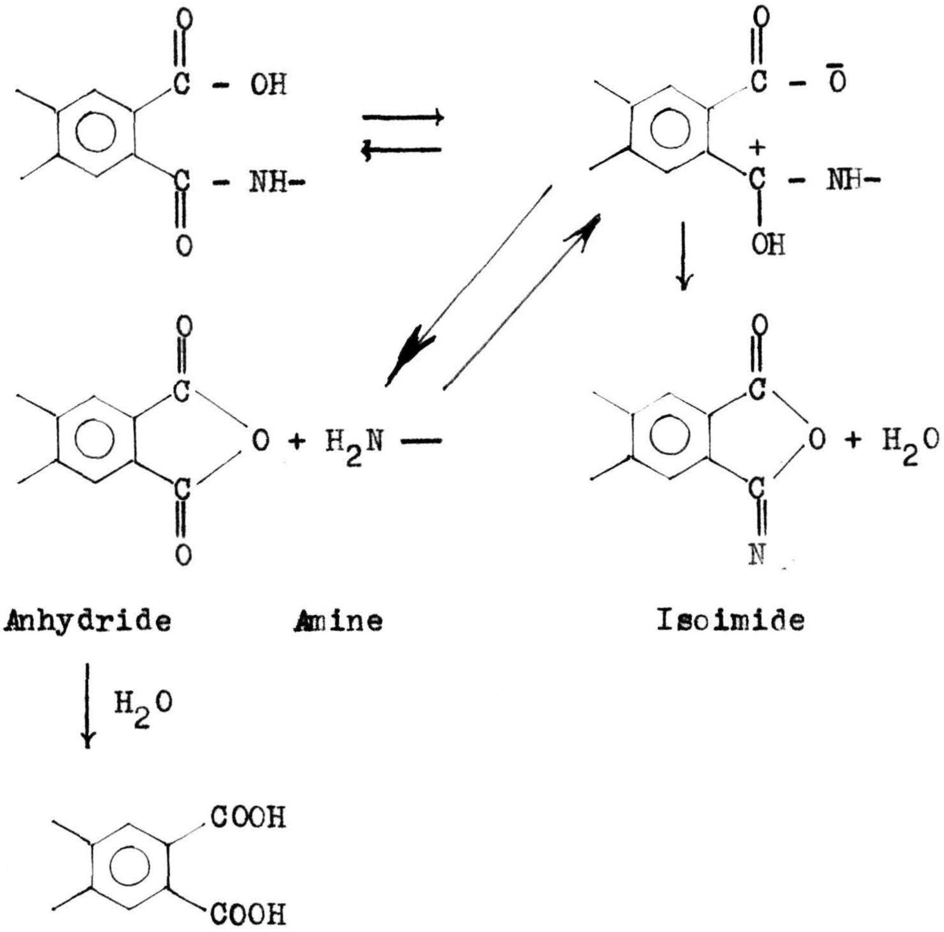


The complex formation is indicated by the intense colour formation on addition of dianhydride to the amine solution.

Wrasidlo et al[22] studied the mechanism and kinetics of reaction between pyromellitic dianhydride (PMDA) and m-phenylene diamine by IR spectroscopy.

Frost and Kesse[17] have suggested the following scheme for possible side reactions which may occur.





In addition to the factors mentioned so far, the course of polyamic acid formation depends also on the nature of reacting substances[23].

Conversion of polyamic acid to polyimide forms the second stage of the synthesis and is called either imidization or cyclodehydration. This can be accomplished in two ways, thermal and chemical.

In the thermal method[10,12a,16] of immidization the polyamic acid in the form of film, fibre etc. is partially dried to high solid content (65-70%) by gradual rise in the temperature and subsequently curing at higher temperatures (above 200°C) in either vacuo or inert atmosphere. The immidization can be followed by disappearance of -NH- band at 3247 cm^{-1} and appearance of characteristic imide bands at 1776 cm^{-1} and 725 cm^{-1} in the IR spectrum and also by following the evolution of water[22]. Individual polyimides may need different programmes of drying.

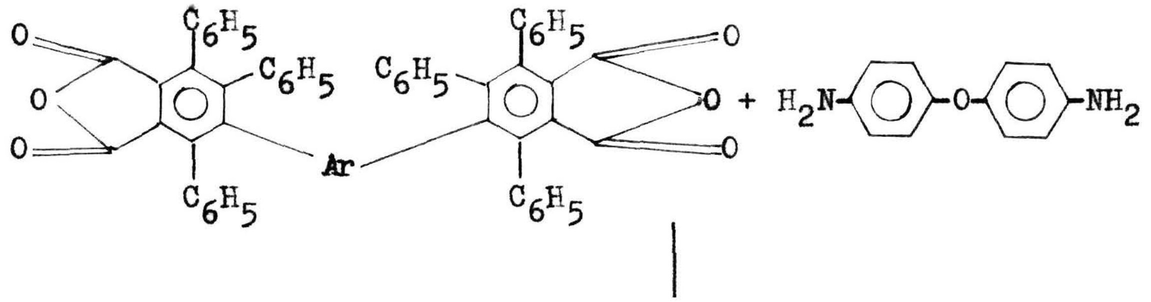
The chemical method of immidization[10,24] can be effected with the help of the dehydrating agents such as acid anhydrides and catalysts like tertiary amines.

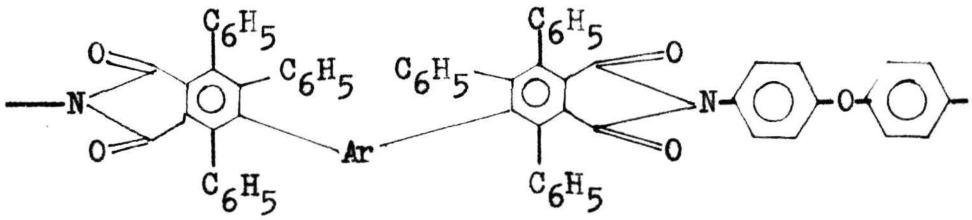
It has also been shown that aromatic polyamic acids can ~~also~~ be obtained in the absence of solvent by application of high pressure[25].

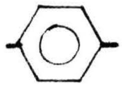
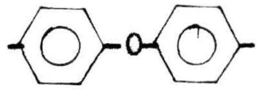
Recently, Dine-Hart and Wright[26] have made a systematic study of a large number of polyimides prepared from four tetracarboxylic acid dianhydrides and 21 different diamines.

Soluble aromatic polyimides were obtained by Japanese workers[27] from reactions of several dianhydrides with many diamines in m-cresol.

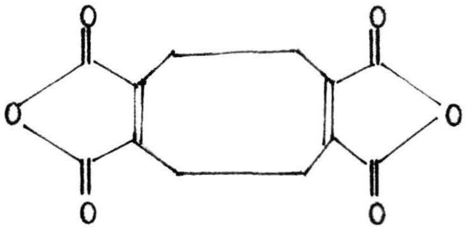
Harris et al[28] introduced pendent phenyl groups along the polymer backbone in order to achieve solubility to the polyimides. These researchers prepared soluble, high molecular weight polyimides from phenylated dianhydrides and aromatic diamine. The reaction can be represented as follows:





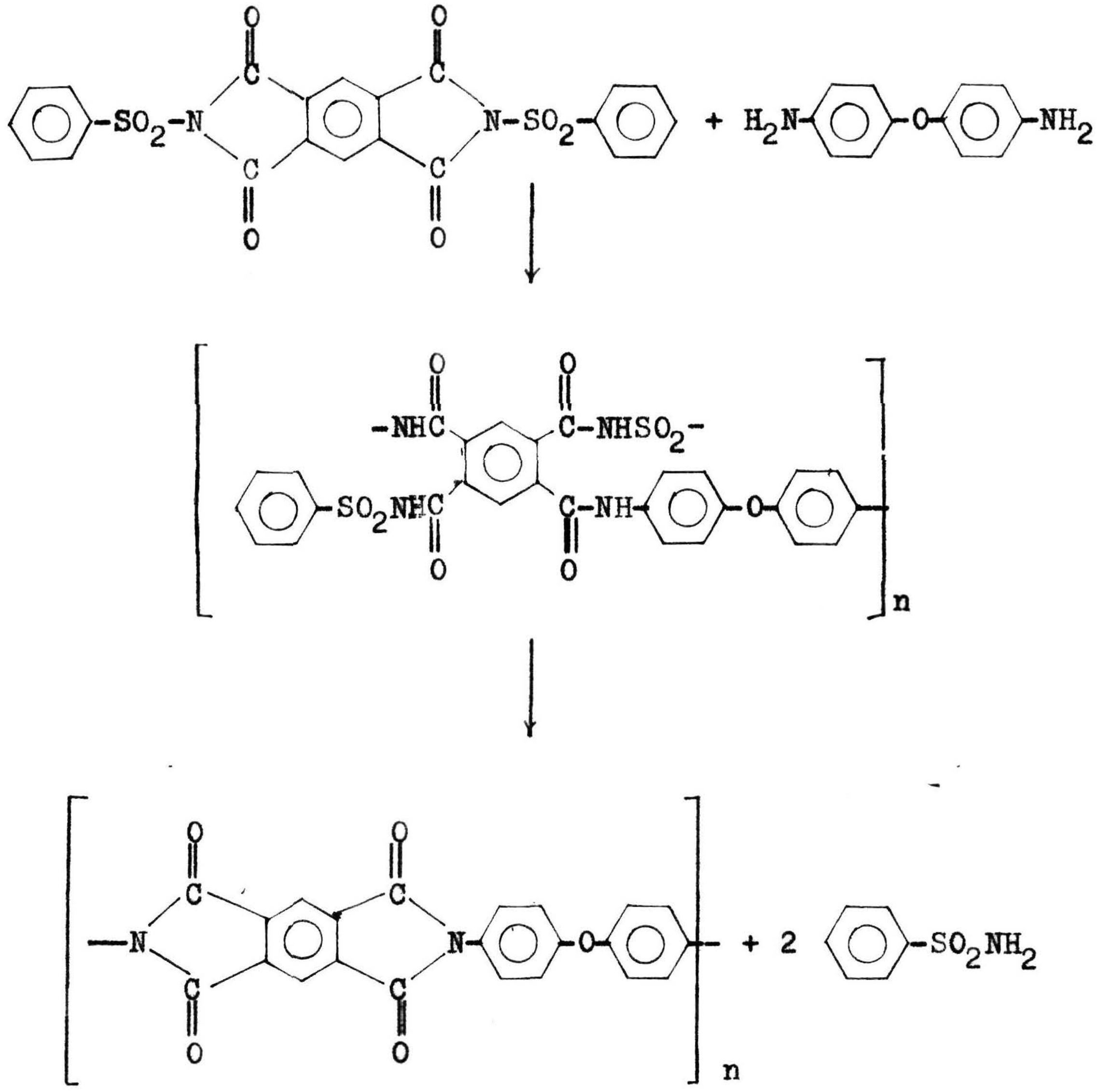
where Ar = i)  ii) 

High molecular weight polyimides soluble in m-cresol and tetrachloroethane were obtained by reacting 1,5-cyclooctadiene-1,2,5,6-tetracarboxylic acid dianhydride with diamines in m-cresol at 110°C[29].



1,5 Cyclooctadiene, -1,2,5,6-tetracarboxylic acid dianhydride

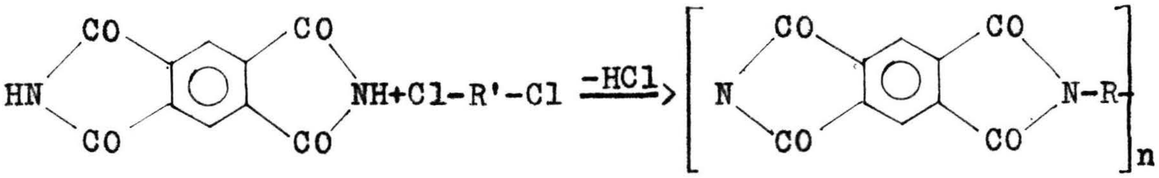
As the reaction between dianhydride and diamine is the most successful of all methods developed for polyimide preparation, an extensive work on it has been done and this reaction is still being explored to obtain newer polyimides. Recently Imai and Ishimori[29] have reported the synthesis of polypyromellitimides using N,N'-bis(phenyl sulfonyl) pyromellitimide and aromatic diamines. It can be represented as follows:



Using these general procedures, preparation of not only aromatic polyimides but also aromatic poly(amide imide) poly(hydrazide-imides), poly(amide-ester-imides) etc. has been accomplished.

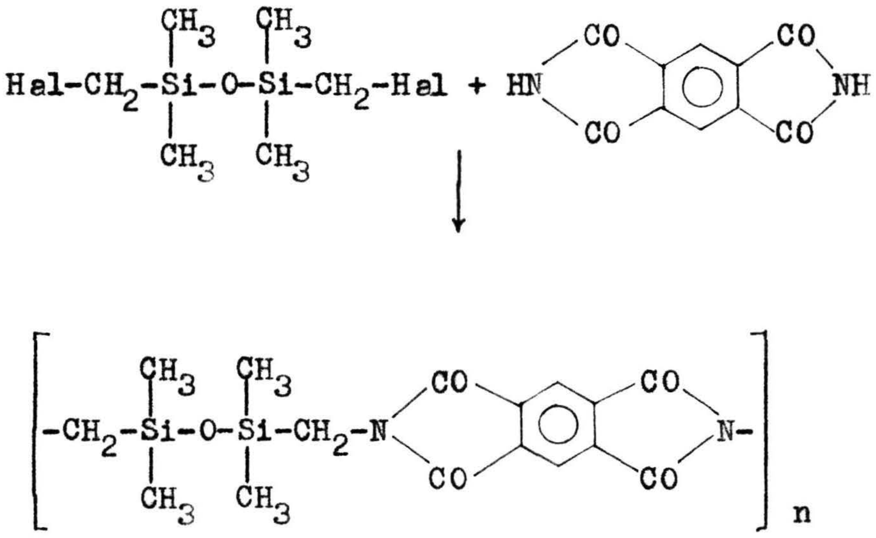
(ii) Polyimides from dihalides and aromatic diimides

Nishizaki and Fukami[30,31] prepared polyimides by polycondensation of pyromellitic acid diimides with different dihalides in a polar solvent. The reaction can be represented as follows:

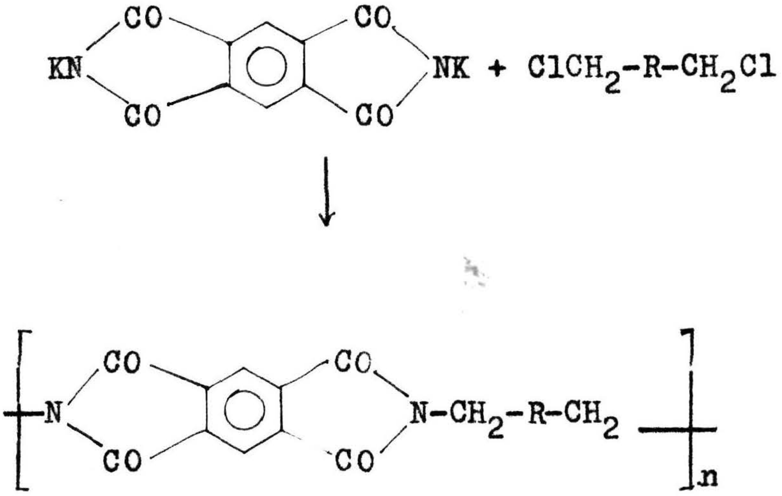


Tertiary amines and potassium carbonate catalyse the reaction. Aromatic dichlorides do not enter the reaction even after prolonged heating. Aromatic chloromethyl derivatives react in a manner similar to that of aliphatic dihalides. Polyimides obtained are insoluble and have low molecular weights.

Silicon containing polypyromellitic acid imides[30] soluble in aprotic polar solvents were also prepared by reaction between bishalomethyldisiloxanes and pyromellitic acid diimide. This can be shown as below:

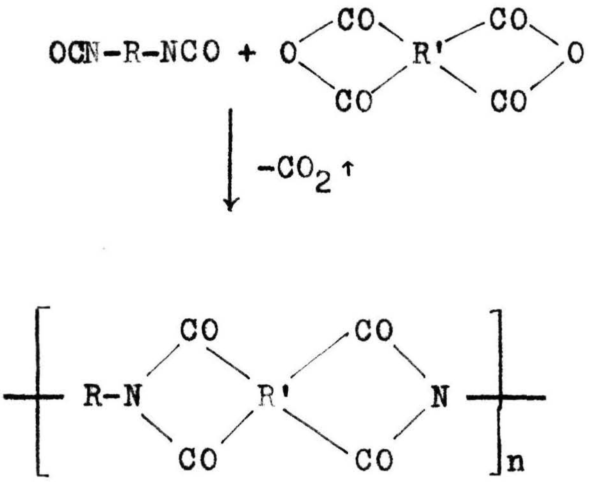


Potassium pyromellitic acid diimide when reacted with aromatic chloromethyl derivative, gives polyimide in good yields.



(iii) Polyimides from diisocyanates

A Netherlands' patent[32] disclosed the reaction of diisocyanate with tetracarboxylic acid and/or dianhydride in polar solvents to yield low molecular weight polyimides. It was, however, Mayers[33] who published a report describing this reaction and suggested a possible mechanism. The reaction can be represented as given below:



The reaction[34] of a diisocyanate with a diester of tetracarboxylic acid has been shown to give polyamic acid ester which on heating yields polyimide with the elimination of alcohol.

Yoda, Nasya[35] has reported the preparation of polyimides by H-transfer polymerization of cyclic diimides and diisocyanates in solvents like dimethyl acetamide. Tertiary amines were used as catalyst.

Recently, Carleton et al[36] have found that the presence of water, enhances the rate of imide formation during the reaction of isocyanates and anhydrides. According to them water hydrolyses the isocyanate to form urea which in turn reacts with anhydride to give corresponding imide. However, the presence of only catalytic amount of water has been found to be effective in obtaining desired product i.e. polyimide.

The polyimides prepared by isocyanate methods are of low molecular weights. Alvino and Edelman[37] have recently reported the synthesis of high molecular weight polyimides using diisocyanates and a mixture of dianhydrides and their acids in the presence of a tertiary amine catalyst.

Alberino and Farrissey[38] have prepared low molecular weight polyimides, soluble in aprotic polar solvents, by isocyanate method.

Thus, diisocyanate method, although has not yet gained commercial importance, has been the subject of wide research.

Properties of polyimides

(a) Thermal properties

The high thermal stability of polyimides offers advantage over other high polymers. Extensive and systematic studies have been done on the course and mechanism of decomposition of polyimides at high temperatures including both thermal degradation and pyrolysis[8,10,11,39-43]. Table-12 describes the thermal stability of several poly pyromellitimides, in inert atmosphere and in ambient air.

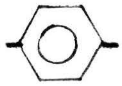
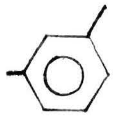
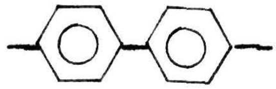
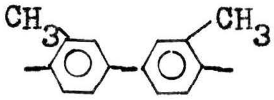
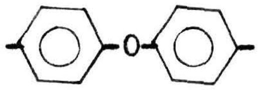
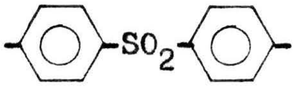
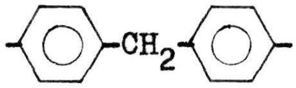
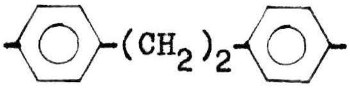
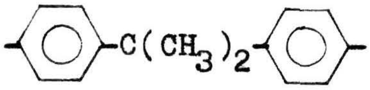
By means of differential thermal analysis (DTA) and dynamic thermogravimetric analysis (TGA) the thermal stabilities of several polyimides have been studied and the relationship between the chemical structure and thermal stability has been evaluated.

Similarly, the determination of isothermal weight loss[44] i.e. weight loss at a particular temperature, gives the service life of the polymer at that temperature.

Bruck[40-42,45] has studied the thermal stability of several polyimides in inert atmosphere as well as the thermoxidative stability.

Scala and Hickam[46] investigated the thermoxidative degradation of polypyromellitimide by varying gas composition (O_2,CO_2 and CO) of the atmosphere in which the samples were immersed. Based on the thermal analysis and mass spectrometric analysis of the decomposition of polyimide products, degradation mechanisms have been put forward[40,42,43].

Table-12: Thermal stability of polypyromellitimides by the DTA method[39]

No.	Diamine nucleus R'	In nitrogen		In air
		Incipient* decomposition temp. °C.	Peak temp. °C	Incipient oxidation temp. °C
1.		500	610	450
2.		460(540)	590	300
3.		510	615	410
4.		490	540	330
5.		490	595	400
6.		420	485	300
7.		480	550	230
8.		470	580	200
9.		400(450)	430(485)	320
10.	$-(CH_2)_6-$	370	430	290

* incipient heat absorption temperature

(b) Chemical properties

Most polyimides, particularly those highly thermostable aromatic products of commercial importance, are inert to organic solvents and oils. They are not particularly affected by dilute acids. However, they dissolve with degradation in strong acids like fuming nitric acid or concentrated hot sulfuric acid[10].

Polyimides show low resistance to alkalis and super heated steam, and the imide groups are hydrolysed by these agents.

Nishizaki[47] has thoroughly studied the mechanism of degradation of polyimides and has recorded the resulting changes in the external properties of the film, the solubility and the IR spectra.

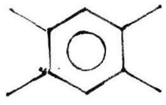
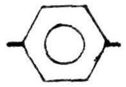
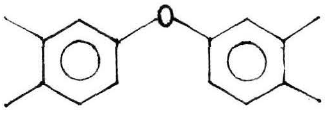
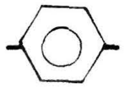
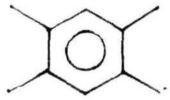
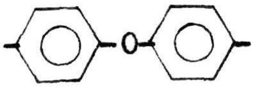
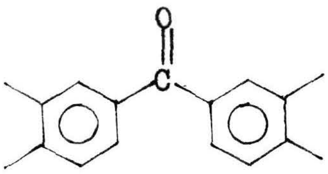
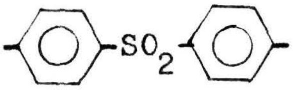
(c) Physical and mechanical properties

The densities of polyimides are always much higher than those of polyamic acids. Polyimide densities depend on the conditions of immidization. Thin films have lower densities due to nearly complete removal of solvent during the thermal treatment. On the contrary, presence of solvent is unavoidable in thick layers which ultimately reduces the imidization temperature and facilitates crystallization.

Formation of stable free radicals at high temperatures is a characteristic of polyimides[48,49]. The polymer chains consisting of phenyl ring, interlinked by means of five-membered imide rings and hetero atom groupings are responsible for numerous properties. The variation in the location of benzene rings relative to the imide rings and heteroatomic groups causes characteristic differences giving rise to different classes of polyimides based on structure-property relationship.

The polyimides can be subdivided into several groups. However, if the criterion for each group is considered to be the presence, in the monomeric units, of hinges consisting of heteroatoms like -S-, SO_2- , -CO-, etc. and their location with respect to imide rings, the polyimides can be arranged in four groups. They are given in Table-13, along with illustrations.

Table-13: Classification of polyimides

Group	Description	Illustrations	
		anhydride	amine
Group I.	Contain only aromatic rings, linked to each other directly or via imide rings i.e. no hetero atom		
Group II.	Presence of hetero atoms in anhydride component only		
Group III	Presence of hetero atom in amine component only		
Group IV.	Presence of hetero atom in both anhydride and amine component		

Effect of chemical structure on the physical properties of polyimides belonging to different groups

Group I polyimides display maximum thermal stability. Thermooxidative processes are minimum as compared to any polyimide belonging to other groups. The values of elasticity modulus are high at both room and elevated temperatures, which may be attributed to strong intramolecular and intermolecular forces. The effect of crosslinking on elasticity modulus is insignificant.

Group II polyimides resemble Group I polymers in properties. This is due to the fact that the hinge links of anhydride moiety although present in fairly large numbers, do not ensure marked ductility owing to the bulky nature of the contiguous flat-shaped anhydride nuclei. Density is also high. They do not soften. Thermooxidative degradation appears to be easier than group I polyimides.

In Group III polyimides intermolecular forces are much weaker than in group I and group II polyimides. Effect of high temperature crosslinking are considerable, especially if the polymer displays a marked tendency to softening. The retension of ductility at cryogenic temperatures[51] (upto the temperature of liquid helium) is an important feature of this group of polyimides.

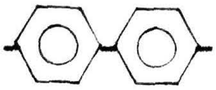
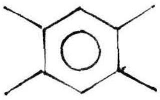
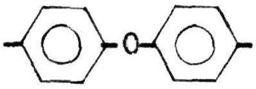
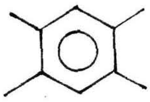
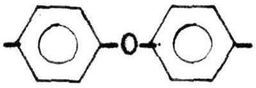
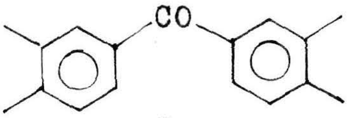
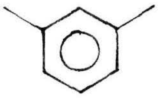
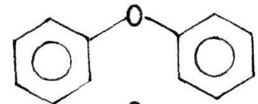
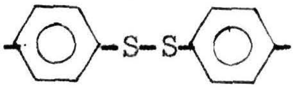
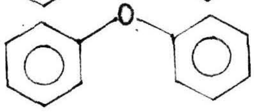
Group IV polyimides show high elasticity in a narrow temperature range and have a melting point. It is possible to work group IV polyimides into products of thermoplastic type due to their ready softening and melting character.

Crosslinking takes place in highly elastic states but the related changes in elasticity modulus are small. They are highly resistant to thermooxidative degradation if aliphatic links are absent.

(d) Electrical properties

Polyimides are medium frequency dielectrics. Their dielectric constant is 3 - 3.5 and does not vary much with either frequency or temperature. The specific volume resistance at room temperature is 10^{17} to 10^{18} ohm cm, while at 200°C, it is about 10^{14} ohms cm. Irrespective of the chain structure, the tangent of the dielectric loss angle tan δ at room temperature remains practically constant (Table-14)[50a] (exception polymer 5 in Table-14).

Table-14[50a] : Dielectric losses by polyimides at 23°C and a frequency of 5.10^5 hz.

No.	Amine ←	Polymer from → anhydride	$\tan\delta\ 10^3$
1.			1.1
2.			1.2
3.			0.9
4.			1.0
5.			0.6

It seems that in case of polyimides the polar CO groups are mainly responsible for dielectric losses and due to their symmetrical location, the losses are less. The tangent of the loss angle is 2-4 times lower than in polyesters of poly(ethylene terephthalate) in which CO groups form part of the chain.

Applications

Polyimides can be used to produce practically all types of technical materials in which polymers are used in the solid state. Thus they are used in electro insulating film preparation[53-58], enamel insulation[62-64] of coil ducts, adhesives, sealing compounds and glues. Fibres and plastic materials[60,61] are also being developed from polyimides. Recent applications include their use in the preparation of flame retardant foams[52,59].

PRESENT INVESTIGATION AND RESULTS

The synthesis of polyimides from diamines and dianhydrides and determination of their properties have been the subject of intensive research for last 15 years. However, research on the preparation of polyimides, via isocyanate route, is only a recent development. Mayers[33] in 1969, reported the formation of low molecular weight polyimides from pyromellitic dianhydride (PMDA) and 4,4'-methylenebis (phenyl isocyanate) (4-MDI) in aprotic polar solvent. Later several of the commercially available diisocyanates were used for the polyimide synthesis, but none could yield a high molecular weight polymer. Very recently, Alvino and Edelman[37] have reported for the first time, a synthesis of high molecular weight polyimides using diisocyanates. The resultant polyimides are capable of forming tough, flexible films having good properties like polyimide films obtained from the reaction of diamine and dianhydride. These authors have stated that in the preparation of above polymers, the use of tetracarboxylic acid along with the dianhydride and a tertiary amine catalyst, is a necessary condition to obtain high molecular weight polymers.

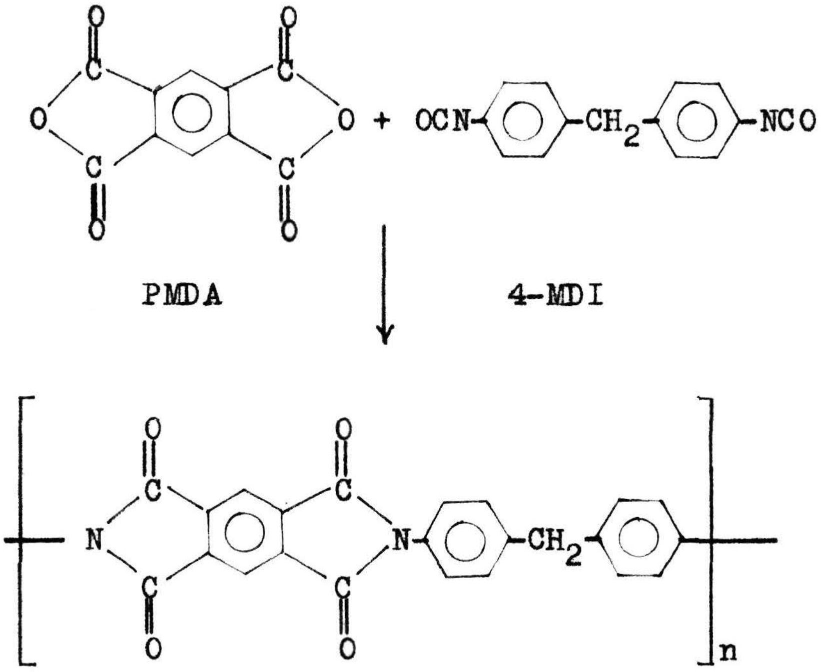
In the present investigation, polyimides have been prepared by reacting 3,3'-sulfonylbis (phenyl isocyanate)

(3-SDI) with PMDA and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BPTD). Although polyimides from 4-MDI have been synthesized earlier, they were prepared again for comparative study.

Viscosities and nitrogen analysis of polymers are given in Table-15. IR spectra of polymers are given in appendix.

Polyimide from PMDA and 4-MDI

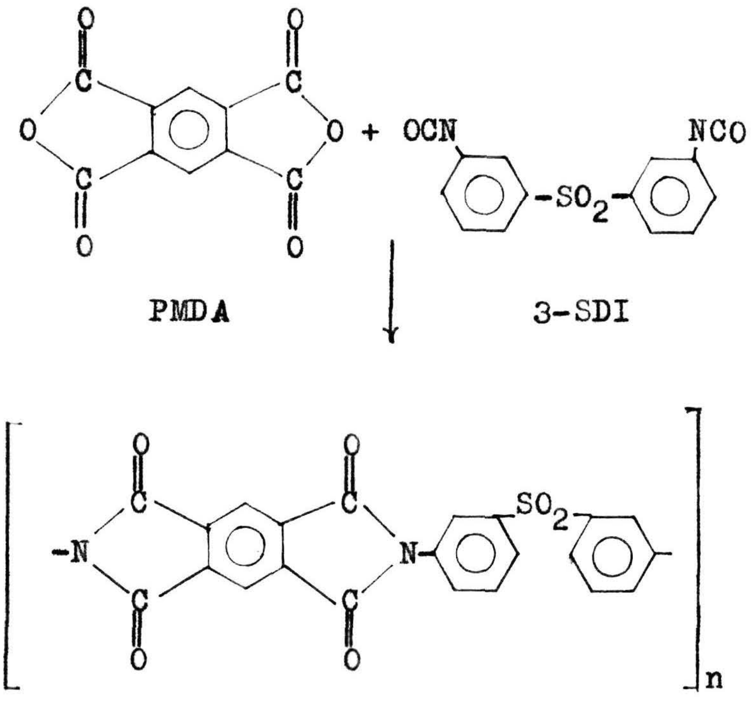
Dry PMDA and freshly distilled 4-MDI were placed in a round bottomed flask. A sufficient quantity of aprotic polar solvent was added to get clear yellow solution. The solution was steadily heated to 130°C. The polyimide separated out in the form of fine yellow powder at 90°C. The solid was filtered, washed several times with methanol to remove solvent and dried. yield 95%.



Polyimide

Polyimide from PMDA and 3-SDI

Dry PMDA and freshly distilled 3-SDI were placed in a round bottomed flask and were dissolved in sufficient quantity of aprotic polar solvent to obtain clear yellow solution. The reaction mixture was heated gradually to 130°C and maintained until polymer separated out. The polyimide that had separated out was filtered, washed with methanol and dried. yield 45-50%.

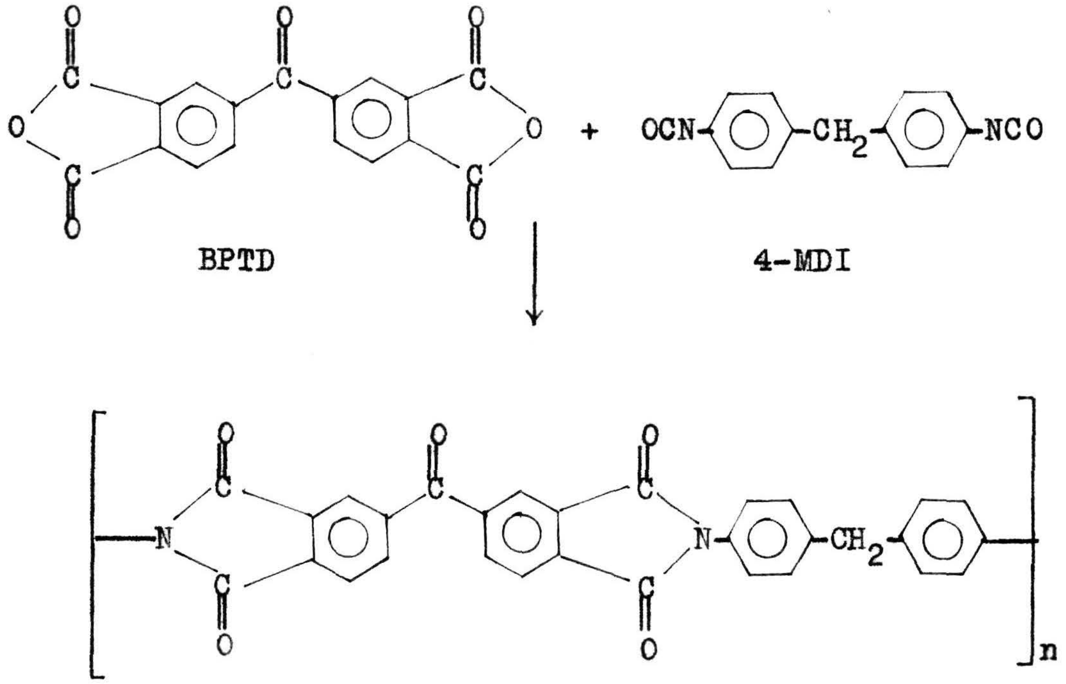


Polyimide

To the filtrate obtained after filtration of the above polyimide, was added sufficient quantity of water when solid precipitated out. This was considered to be the intermediate polymer, the structure of which is discussed in the discussion part.

Polyimide from BPTD and 4-MDI

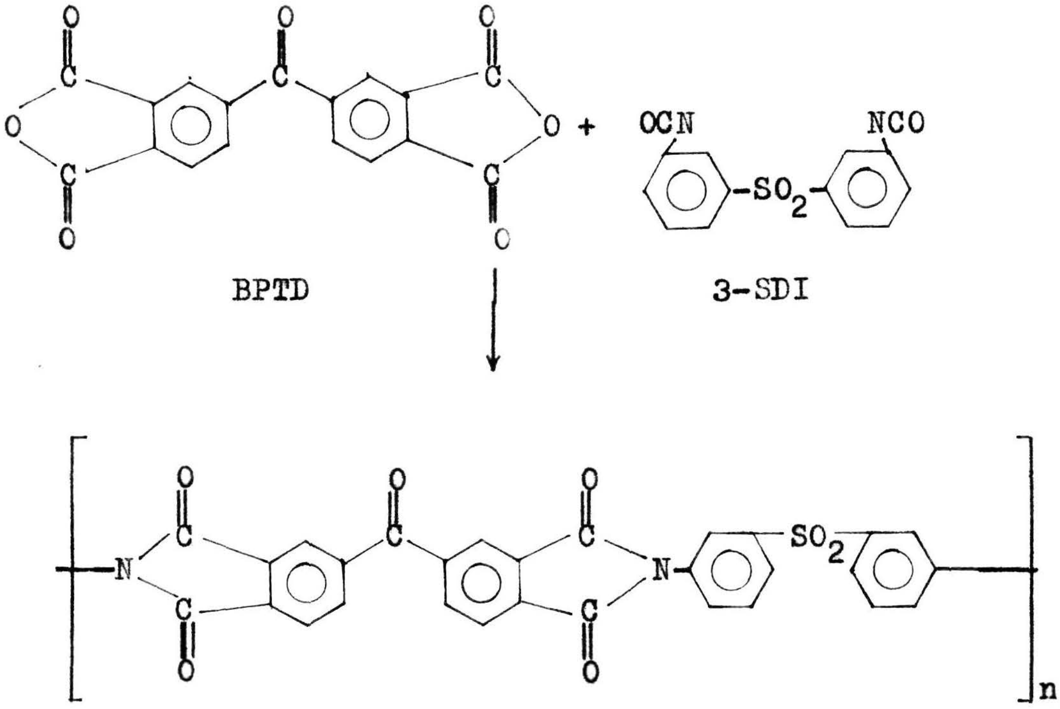
Dry BPTD and freshly distilled 4-MDI were dissolved in an aprotic polar solvent to get clear yellow solution. This was heated to 130°C in a stepwise manner. Yellow coloured solid of polyimide separated out at 90°C. The polymer was filtered, washed with methanol and dried. yield 90%.



Polyimide

Polyimide from BPTD and 3-SDI

Dry BPTD and freshly distilled 3-SDI were placed in a round bottomed flask and were dissolved in sufficient quantity of an aprotic polar solvent to yield a clear solution. This reaction mixture was heated gradually to 130°C and maintained at this temperature for several hours. As no polymer separated out, non-solvent, water was added to precipitate the polymer. This was then filtered, washed with methanol and dried. yield 80%.



Polyimide

This reaction was repeated in m-cresol, which yielded soluble, low molecular weight polyimide. The polyimide was precipitated with ether, washed with methanol and dried.

The reactions were carried out in Dimethyl formamide (DMF), Dimethyl acetamide (DMAC) and N-methyl-2-pyrrolidone (NMP). The reaction conditions, the nature of product obtained and their inherent viscosities are described in Table-15. Since the polyimides from 3-SDI are new, their nitrogen analysis is also given in Table-15.

Viscosities were determined in a constant temperature bath at 30°C using 0.5% solids polymer concentration and

Table-15: The reactants used, reaction conditions and properties of polyimides obtained

Polymer No.	Reactants	Solvent	Reaction time in hrs. at temp. °C			Comments	Inherent viscosity dl/g in D-DMF H conc. H_2SO_4
			40	90	130		
A	PMDA + 4-MDI	DMF	2.5	2	2	Polyimide precipitated out from solution. Yield 90-95% polyimide insoluble in all organic solvents	0.7074^H
B	PMDA + 3-SDI	DMF	2.5	2	25	Polyimide precipitated out from solution. Yield 40-45% Polyimide insoluble in all organic solvents	0.2598^H
C	BPTD + 4-MDI	DMF	2.5	2	2	Polyimide precipitated out from solution. Yield 90-95%. Polyimide insoluble in all organic solvents	0.6324^H
D	BPTD + 3-SDI	NMP	2.5	2	a.10	Polyimide remained in solution. It was precipitated out with non-solvent.	
					b.part heated for 50 hrs. at 200°C.	Polymer did not precipitate	0.2423^D

Nitrogen analysis for	B	and	D
Calcd.	6.51		5.24
Found	6.49		5.035

Ubelhode viscometer.

IR spectra were recorded on Perkin Elmer E 137 spectrophotometer.

Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) were made simultaneously with a Mom-Budapest derivatograph type OD 102 described by Pa~~l~~ulik et al[65] in air at heating rate of 9°C/min. Before the analysis, all the polymer samples were conditioned at 100-120°C under reduced pressure of 10^5 mm/Hg to remove the entrapped solvent and adsorbed moisture, if any.

Mom-Budapest Derivatograph

The samples were placed in a platinum crusible of special shape which had an indenture at the bottom so that the thermocouple placed in it measured the temperature at the centre of the crusible. A similar platinum crusible filled with Al_2O_3 was used as the inert standard. The sample and the inert reference were heated at a programmed rate in a resistance furnace, and the change in weight of the sample was recorded on a photosensitive paper by means of a light beam reflected from a mirror attached to the pointer of the balance. The rate of change of weight (DTG) was also measured at the same time by the aid of a solenoid fixed on the balance beam and moving in the field of force of a permanent magnet. The current induced in the moving solenoid coil was proportional and was measured by a galvanometer connected to the poles of the solenoid. A beam of light reflected from this galvanometer, therefore, recorded the derivative of the thermogravimetric curve (DTG). The specimen temperature (T) was measured by means of a thermocouple inserted into the sample. A differential thermocouple inserted in the sample and the reference yields the temperature difference which is recorded as a thermogram.

DISCUSSION

The Table-15 summarizes the preparation and molecular weight index (viscosity) of the four polyimides synthesized in the present work. The nitrogen analysis for polyimides B and C is also given.

It can be seen from Table-15 that in spite of the higher polymerization time for 3-SDI dianhydride reactions the polymers obtained were of only low molecular weight as compared to those obtained in 4-MDI-dianhydride reactions. It is reported[50b] that polyimides with $-SO_2-$ groups in the chain have comparatively low molecular weights, although they are obtained by reacting diamine with dianhydride. In the present case, it is interesting to note that the build up of higher molecular weight appears to be difficult in 3-SDI dianhydride reactions, although 3-SDI is more reactive than 4-MDI. This may probably be due to the placement of -NCO groups at 3 positions in 3-SDI as compared to the 4th in 4-MDI.

Mayers[33] has shown that the reaction of a diisocyanate with a dianhydride proceeds according to the scheme, shown in Fig. XI.

Thus, a seven membered ring polymeric intermediate is formed as a result of the reaction between a diisocyanate and a dianhydride which in turn loses CO_2 to yield polyimide. The polymeric intermediate, according to

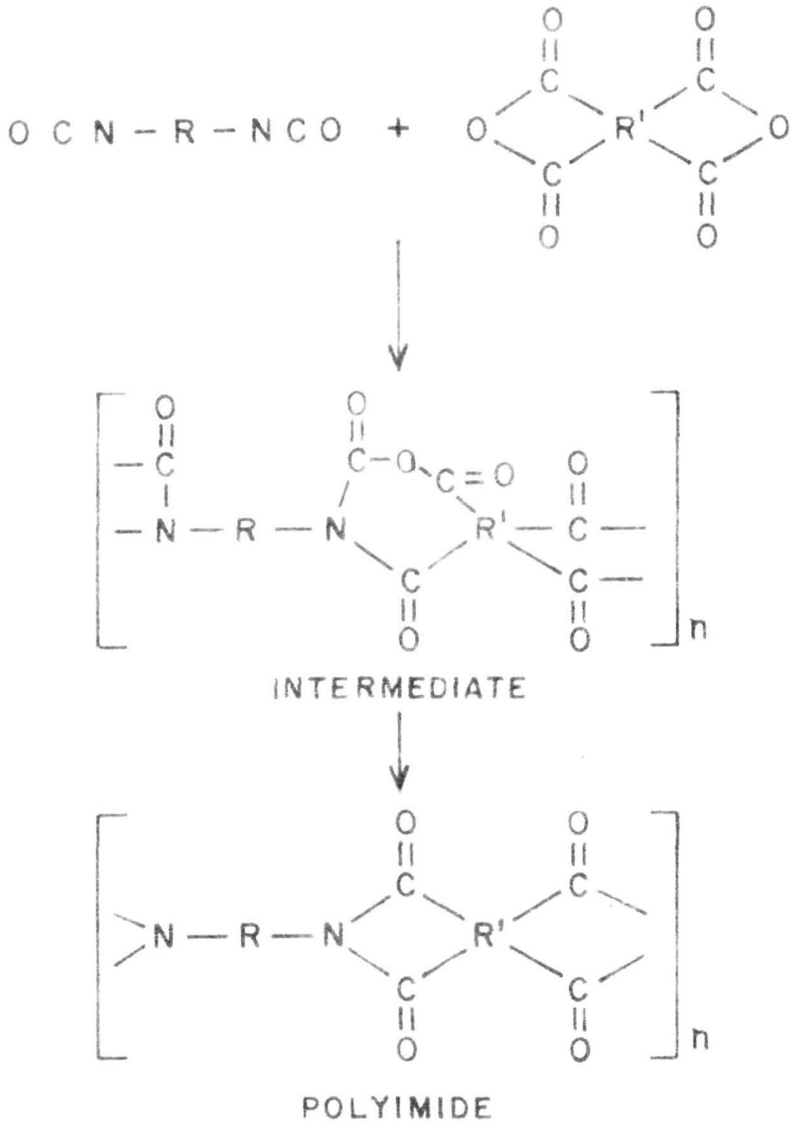


FIG. XI SCHEME FOR POLYIMIDE SYNTHESIS

Mayers[33], is soluble in polar solvents like DMF, DMAC etc. while the polyimide, like authentic sample, is insoluble in all organic solvents. This phenomenon was observed in the present study in case of polyimides A, B and C (Table-15) while in case of polyimide D, always low molecular weight polymer was obtained.

As has been postulated by Mayers[33], the seven membered ring polymeric intermediate shown in Fig.11 gives IR spectrum identical to that of respective polyimide except that the 1660 cm^{-1} peak is intense in case of the intermediate due to the presence of an additional amide carbonyl of the seven membered ring. The intensity of this peak decreases considerably when polyimide is formed after the loss of CO_2 from polymeric intermediate.

IR spectra of polymer A and B

Mayers' postulation mentioned above, holds good in case of polymer A and B obtained from PMDA-diisocyanate reactions. Fig.10 and 11 illustrate the IR spectra of polyimides A and B while Fig.12 showing IR is illustrative of the intermediate obtained in case of PMDA-3-SDI reaction. In this reaction the polyimide that had separated out from the solution was filtered out and the intermediate was isolated from the filtrate by precipitation with water, as explained in the experimental section.

IR spectra of polymer C and D

In case of polyimides obtained from BPTD-diisocyanate reactions, a peak of considerable intensity is seen at 1670-75 cm^{-1} (Fig.13 and 14) which may be assigned to the benzophenonic carbonyl group. An absorption at this frequency is also observed in the IR spectrum of BPTD (Fig.15). In polymers C and D, this absorption was present (Fig.13 and 14 respectively) irrespective of whether the polymer has been precipitated out or has remained in solution. Hence, it may be suggested that the presence of 1660 cm^{-1} band cannot be the criterian to differentiate between an intermediate and a polyimide.

Structure of polymer D

On the grounds (i) that the polyimide separates out, as it is formed, from the reaction mixture of diisocyanate and dianhydride in a polar solvent and (ii) the 1660 cm^{-1} band criterian, it was difficult to understand whether polymer D was an intermediate or a polyimide - the final product. However, the presence of imide band (at 1780, 1730 and 730 cm^{-1}) in IR spectrum of polymer D and confirmation of evolution of stoichiometric amount of CO_2 gas during its formation suggests that the BPTD-3-SDI reaction has yielded a polyimide (polymer D) soluble in polar solvents. The low molecular weight of the polymer may be one of the reasons for its solubility. Moreover, benzophenonic dianhydride has been shown earlier to give soluble polyimides[38] with some diisocyanates. Alberino[38] has reported the synthesis of soluble polyimides from BPTD and 2,4 or 2,6 toluene diisocyanate or mixture of

2,4 and 2,6 toluene diisocyanate.

Thermogravimetric analysis data

TGA curves obtained for all the four polyimides A, B and C, D are given in Fig.XII and XIII respectively. Table-16 shows the loss of weight at different temperatures for each polymer and these were calculated from the respective TGA curves. It is important to note that the conditioning of polymers, i.e. heating at 100-120°C under reduced pressure of 10^{-5} mm/Hg for 2 to 3 hours was found to be very essential, because it removed the entraped solvents and adsorbed moisture. This was reflected in the TGA curves as they showed considerable increase in thermal stability after conditioning.

Polyimides A and B belong to III group (Table-13) i.e. they have 'hinge' group in diisocyanate structure. Polyimide A exhibits TGA curve similar to that of the authentic sample described by Mayers[33]. It can clearly be seen from Table-16 that polyimide B starts losing weight at lower temperatures as compared to polyimide A, thus indicating its lower thermooxidative stability. This may be due to two factors. The first being the incorporation of $-SO_2-$ groups in the polyimide chain which have already been shown[50c] to affect the thermal stability of the polymer. Secondly, the low molecular weight of the polymer. It is a fact[66] that while polymer itself has a fairly stable structure, much of its instability arises from the end groups which are highly reactive than the rest of the

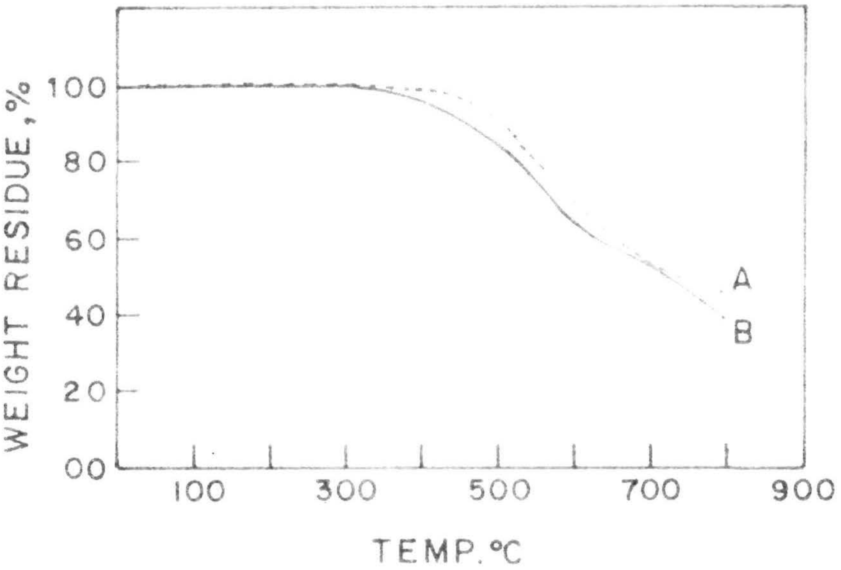


FIG. XII TGA CURVES IN AIR AT 9°C/MIN. FOR POLYIMIDE A AND

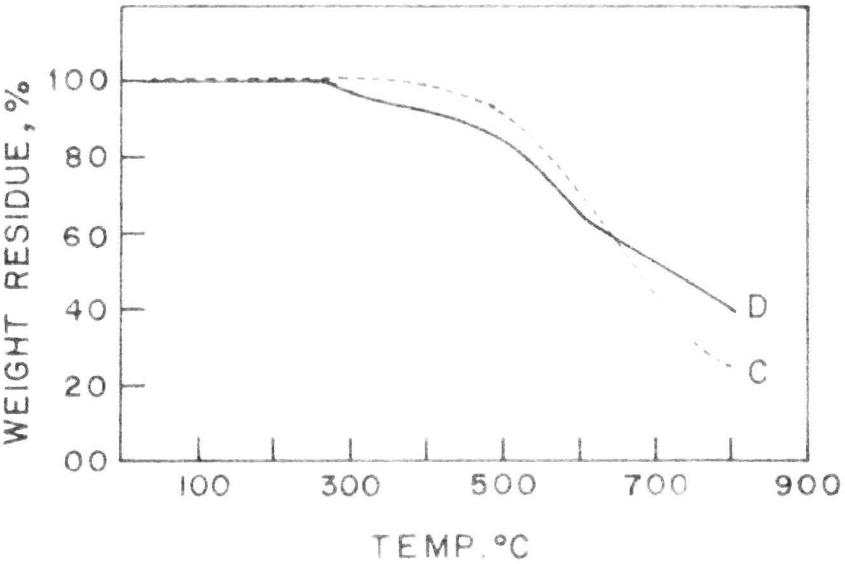


FIG. XIII TGA CURVES IN AIR AT 9°C/MIN. FOR POLYIMIDE C AN

Table-16: % weight loss at different temperature for polyimides A, B, C and D.

Temp. °C	Polyimide			
	A	B	C	D
100	0.25	1.0	1.0	0.5
200	0.5	1.5	1.0	1.0
300	2.0	4.0	2.2	5.0
400	2.0	6.7	2.5	8.0
500	9.0	14.5	9.0	15.0
600	31.5	37.0	31.5	36.0
700	47.0	56.0	58.5	56.0
800	53.0	72.0	76.0	61.0

polymer molecule and consequently showing the direct dependence of the thermal stability on the molecular weight. In addition to the above two factors, benzene rings in meta position, might also be responsible in markedly reducing the temperature of oxidative degradation.

Polyimides C and D belong to the IV group (Table-13) i.e. they have 'hinge' groups in the structures of both of the reactants. In such cases, polyimides are expected to possess higher resistance to thermooxidative degradation. In the present study, however, polymer C appears to be more stable than polymer D. This can be explained on the similar grounds as in case of the low thermal stability of polymer B.

Polyimides obtained from 4-MDI and either PMDA or BPTD (polymer A and C) show similar stability towards thermooxidative degradation. The same is true with the polyimides prepared from 3-SDI and either PMDA or BPTD (polymer B and D). This indicates that the presence of 'hinge' group like -CO- in dianhydride component does not make significant difference in thermooxidative degradation properties of polyimides when they are prepared by using either 4-MDI or 3-SDI.

DTA and DTG were also recorded simultaneously with TGA and they confirmed the weight losses shown by TGA. It could also be noted from Table-16 that loses at higher temperature were quite comparable.

These four polyimides were obtained also by using other solvents e.g. dimethyl acetamide, N-methyl-2-pyrrolidone etc. and showed similar behaviour as regards the progress of the reaction was concerned. They also exhibited identical properties as have been reported in Table-15 and 16.

Hence, it can be concluded that irrespective of isocyanate reactivity in uncatalyzed dianhydride-3-SDI reactions, only low molecular weight polymers (polymer B and D) were obtained as compared to those obtained from uncatalyzed dianhydride-4-MDI reactions, which are of relatively higher molecular weight.

EXPERIMENTAL

Materials

(1) PMDA was obtained from Koch Light Industries, England, in the form of white powder. It was used as such (on sublimation, no residue remained behind showing its good purity).

(2) BPTD was obtained from Gulf Oil Co. in the form of yellowish powder. This too, gave no residue on sublimation and hence was used as such.

(3) 3-SDI was prepared in this Laboratory as described in Part I. It was distilled just before use.

(4) 4-MDI was obtained in the form of flakes from Farbenfabriken Bayer, A.G. West Germany. It was distilled just before use.

(5) All solvents were dried and distilled by following standard procedures. DMF, DMAC, NMP and m-cresol were used in the preparation of polymers.

Preparation of polyimide from PMDA and 4-MDI

In a 200 ml 3 necked round bottomed flask equipped with a thermometer, a stopper, a gas outlet connected to barium hydroxide test solution and a magnetic stirrer, were placed 4-MDI (2.5 g 0.01 mole) and PMDA 2.86 g (0.01 mole). DMF (30 ml) was added to obtain a clear yellow solution which was heated to 40°C and maintained for 2½ hours.

The temperature was then slowly raised to 90°C. At 75°C, CO_2 gas evolution was visible and at 90°C the yellow polymer separated out. The temperature was further raised to 130°C at which it was kept for 2 hours. This was to confirm the completion of reaction. Polymer thus obtained was filtered, washed several times with methanol to ensure complete removal of solvent and then dried at 60°C in an oven to get 5.0 g polyimide.

Preparation of polyimide from PMDA and 3-SDI

PMDA 2.86 g (0.01 mole) and 3-SDI 3.0 g (0.01 mole) were placed in a 100 ml 3 necked round bottomed flask equipped with a thermometer, a stopper and a gas exit connected to barium hydroxide test solution and a magnetic stirrer. DMF (30 ml) was added to get clear yellow solution, which was kept at 40°C for 2½ hours. The temperature was gradually raised to 90°C in about 1 hour. CO_2 gas evolution was observed although it was not brisk. Polymer had not separated out. The temperature was then raised to 130°C at which it was maintained for 25 hours. After 19 to 20 hours of heating, polymer started separating out and after 25 hours of heating no further polymer separation could be noted. The polymer was filtered, washed with methanol to remove the solvent and dried at 60°C. yield 2.6 g.

The filtrate obtained after filtration of the polyimide, was treated with sufficient water to get yellowish white solid. This was filtered, washed with methanol and dried.

2.0 g. This was proposed to be the intermediate polymer on the basis of its IR spectrum.

Preparation of polyimide from BPTD and 4-MDI

4-MDI 2.5 g (0.01 mole) and BPTD 3.22 g (0.01 mole) were placed in a 100 ml 3 necked round bottomed flask equipped with a magnetic stirrer, a thermometer, a stopper and a gas exit connected to barium hydroxide test solution. To this mixture, DMF (30 ml) was added to get a clear yellowish solution which was maintained at 40°C for 2½ hours and then gradually heated to 90°C in 1 hour. Above 75°C, the CO_2 gas evolution was visible and at 90-95°C the polymer precipitated out as yellow solid. To ensure the completion of reaction~~s~~, the reaction mixture was heated to 130°C and kept at this temperature for 2 hours. The polymer was then filtered, washed with methanol till free from solvent and then dried. yield 5.1 g.

Preparation of polyimide from BPTD and 3-SDI

In a 100 ml 3 necked round bottomed flask equipped with a magnetic stirrer, a thermometer, a reflux condenser with a guard tube and a gas exit connected to barium hydroxide test solution, were placed 3-SDI 3.0 g (0.01 mole) and BPTD 3.22 g (0.01 mole). To this mixture NMP (30 ml) was added to get clear yellow solution. The reaction mixture after keeping at 40°C for 2½ hours, was gradually heated to 90°C in 1 hour. As the temperature reached 90°C, CO_2 gas evolution was observed although it was not so brisk. No polymer had separated out. Therefore the temperature was further raised to 130°C at which it was maintained for about 10 hours. Still no polymer separation was observed. In another set of experiment, even after heating the polymer further to the boiling temperature of the solvent (195-200°C) polymer did not separate out. Polymer was then precipitated out with non solvent, water, filtered and washed with methanol to remove solvent and dried at 60°C. yield 4.95 g.

An experiment was run to measure the amount of carbon dioxide evolved during this reaction. Equipment was set as described above except that the gas exit was connected to a U tube filled with soda asbestos. The U tube was equipped with stopcocks on both sides which enabled to connect the tube to the reaction flask while the reaction was in progress and to protect it from contact with air all other time. The U tube was weighed accurately before starting the experiment (84.0066 g). The quantities of reactants mentioned above were used in this experiment. Reaction was carried out in nitrogen atmosphere which also served as carrier gas for CO_2. Heating schedule was 2½ hours at 40°C, 1 hour at 90°C, 3 hours at 130°C.

After the reaction was over, the soda asbestos in U tube showed change in colour from black to white indicating absorption of CO_2 gas. The U tube, after the experiment, weighed (84.8820 g) showing increase in weight by 0.8754 g due to CO_2 absorption, thus indicating the evolution of nearly stoichiometric amount of CO_2 (0.88 g).

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Section-II

CORCIYIMIDES

PRELIMINARY WORK

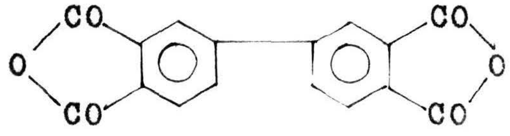
Copolycondensation is a well known procedure for regulating the molecular structure and properties of polyimides. Copolyimides (copolymers of polyimides) are prepared by condensation of more than one diamine with one dianhydride or more than one dianhydride with one diamine. Similarly, they can also be prepared by condensation of more than one dianhydride with a diisocyanate or more than one diisocyanate with a dianhydride. The preparation of copolyimides using amines has been described in patent literature. A Netherland patent[1] discloses the preparation of a copolyimide using 4,4'-diaminodiphenyl ether and a mixture of pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BPTD). The polymer obtained had good properties and could be used in the preparation of films and adhesive tapes. Similarly, a British patent[2] has described the preparation of copolyimides by reacting 3,4'-dicarboxy-1,2,3,4-tetrahydro-1-naphthalene succinic dianhydride and a different dianhydride or mixture of dianhydrides with diamino diphenyl ether. The copolyimides could be compression moulded at higher temperature to give tough, flexible molded articles. Copolyimides of dianhydrides and diamines yielding polyarimides of group I, II and III (classification of polymides as described in Table-13) show properties similar to the corresponding homopolymers.

Several property changes achieved by modification by copolymerization of polyimides have been reported in the literature[3]. Some of them have been briefed here.

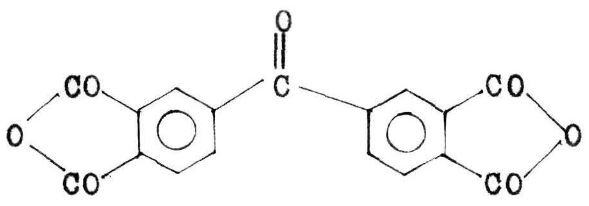
As a result of copolymerization, if a dianhydride forms group IV polyimide with one diamine and group II polyimide with the other, the copolyimide obtained displays properties which are intermediate between the two respective homopolymers.

If a given dianhydride gives crystallizing, softening group IV polyimides with each of the two diamines seperately, the softening temperature of the copolymer will be somewhat lower than the softening point of either homopolyimide.

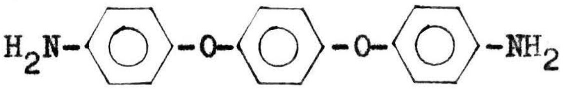
Many copolyimides display a better adhesion to glass and metals than do the corresponding homopolyimides. In certain cases, substantial improvement in the parameters of the final product may be brought about by copolycondensation. For example, the elasticity of copolyimide of the mixture of following two dianhydrides and the diamine is higher than either of two homopolymers.



3,3',4,4'-Biphenyl tetracarboxylic dianhydride



3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BPTD



Saluti et al[4] have reported the preparation of thermosetting polyimides by copolymerization of teralin dianhydride, maleic anhydride and 4,4'-methylene di-aniline.

Vollkommer et al[5] synthesized chlorine containing polyimides by copolymerizing bis-(4-amino phenyl ether), tetrachloro-p-xylene diamine and pyromellitic dianhydride.

Etsuo et al[6] synthesized copolyimide by using BPTD, 4,4'-diamino-3,3'-dimethyl-diphenyl methane and 3,3',4,4'-tetraamino diphenyl methane.

Copolyimide fibres and threads were obtained by Farrissey et al[7] by utilizing a mixture of toluene diisocyanate (TDI) and 4,4'-methylenebis (phenyl isocyanate)(4-MDI) along with BPTD.

Alberino[8] has reported copolycondensation of BPTD and mixtures in various proportions of 4-MDI and TDI (2,4- or 2,6 isomer or mixtures thereof). All the copolyimides obtained by Alberino were useful in the preparation of high temperature resistant materials and in various applications for which polyimides are known to be especially adopted.

In the present study, copolyimides of BPTD and mixtures in various proportions of 4-MDI and 3,3'-sulfonylbis (phenyl isocyanate) (3-SDI) were prepared.

PRESENT INVESTIGATION AND DISCUSSION

As has been observed in Section I of this part, BPTD when reacted with 3-SDI in aprotic polar solvent, gives a soluble polyimide. On the contrary, with 4-MDI it gives insoluble solid polyimides.

Alberino[8] while studying copolycondensation of mixture of 4-MDI and TDI with BPTD, noted similar type of observations. For example, when TDI was used as a major component, the copolyimides obtained were soluble in polar solvent. This prompted us to study the effect of copolycondensation of BPTD with mixtures in various proportions, of 4-MDI and 3-SDI, on the nature and the properties of the resulting copolyimides. The reaction of copolymerisation is given in Fig.XIV.

The procedure as described by Mayers[9] for the preparation of polyimides was adopted in the synthesis of all copolyimides. In a typical synthesis of a copolyimide, BPTD and mixture of diisocyanate (4-MDI: 3-SDI ratio varying) were mixed in 1:1 molar proportion and were dissolved in dimethyl formamide (DMF). A clear yellow solution resulted. This was heated gradually to 130°C at which it was kept for 2 hours. The polymer that precipitated was filtered, washed with methanol to remove solvents and dried. If the polymer did not separate out, it was precipitated by adding a non-solvent i.e. water, filtered, washed with methanol and then dried. The

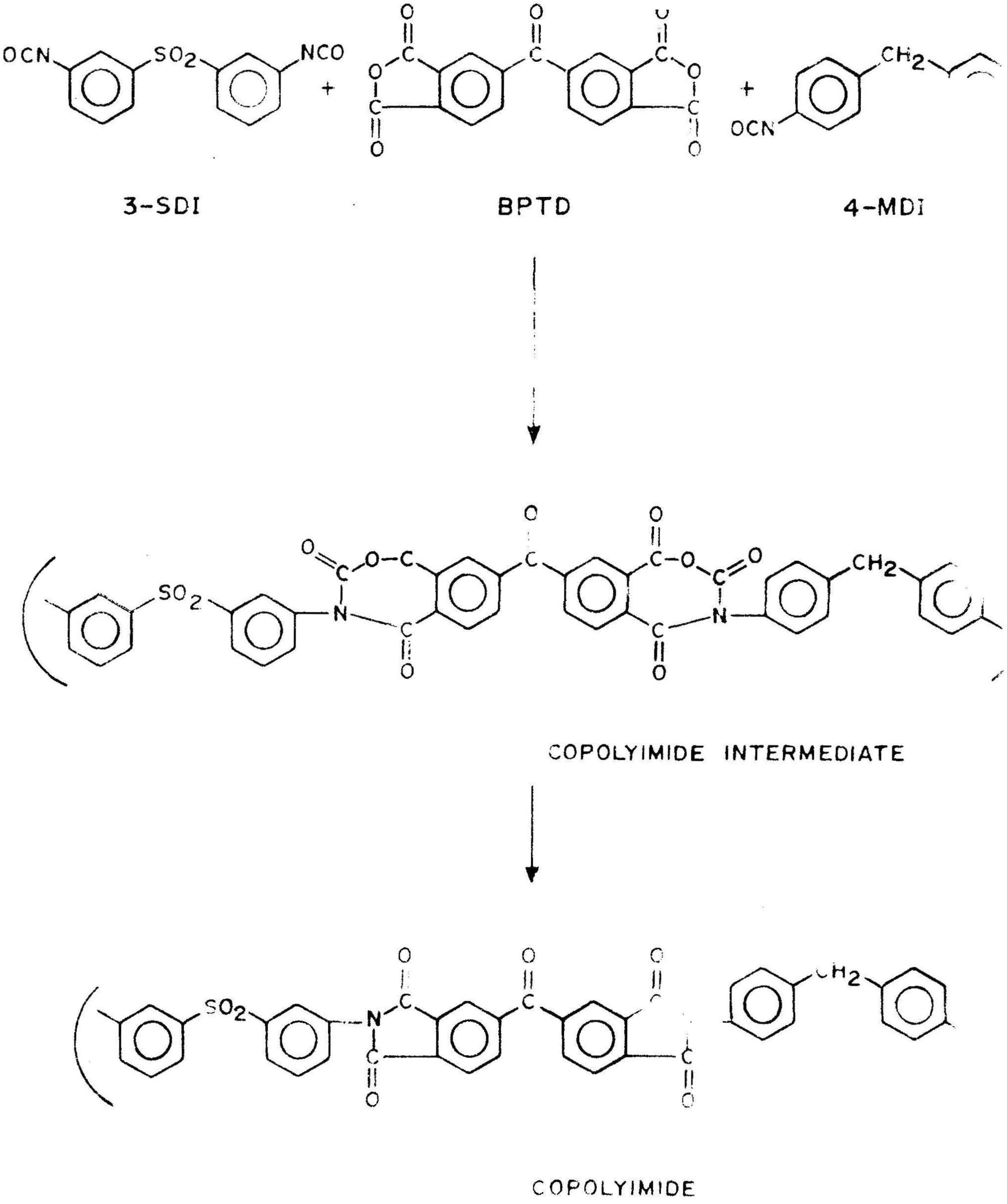


FIG. XIV SYNTHESIS OF COPOLYIMIDE

reactions carried out are listed in Table-17, which also describes the reaction conditions and properties of the product obtained in each reaction. The viscosity of the polymers, which are soluble in organic solvents, has been determined in DMF, while those which are insoluble has been measured in concentrated H_2SO_4.

The thermo-oxidative stability of the copolymers has also been studied. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) were obtained simultaneously on a Mom-Budapest-Derivatograph type OD-102 described by Paulik et al[10] in air at a heating rate of 9°C/minute. The working of this derivatograph is described in Section 1 of this part.

The infra-red spectra of polymers were recorded on Perkin Elmer E 137 spectrophotometer in nujol mulls.

It is evident from the nature of the copolymers obtained in various copolycondensations (Table-17) that the structure of isocyanate plays an important role in these reactions. It has already been observed (Part II - Section 1) that pure 4-MDI (i.e. in the absence of 3-SDI) when reacted with BPTD gives insoluble solid polyimide while 3-SDI (in the absence of 4-MDI) renders only low molecular weight soluble polyimide. From the data in Table-17, it could be noted that when 3-SDI forms a major component in copolymerization reactions, the copolyimides obtained are soluble in polar organic solvents, while 4-MDI when used as a major component, insoluble copolyimides are obtained. This supports the

Table-17: **Reactants used, their proportions and properties of resultant copolyimides**

Polymer No.	Diisocyanate proportion 3-SDI:4-MDI	Total molar proportion of BPTD: diisocyanate	Solvent	Polymer	Inherent viscosity dl/g D= in DMF H= in H_2SO_4	Sulfur content %
I.	10:90	1:1	DMF	Yellow polymer separated out. *yield 45%	0.5771^H	2.40
II.	50:50	1:1	DMF	Reaction mixture remained in yellow turbid form. No polymer separation was observed. Therefore polymer precipitated with water. *yield 42%	0.1939^H	4.78
III.	75:25	1:1	DMF	Reaction mixture remained in yellow turbid form. No polymer separation was observed. Therefore polymer was precipitated out with water. *yield 43%	0.1659^H	6.17
IV.	80:20	1:1	DMF	Clear reddish yellow solution was obtained at the end of reaction. Polymer was precipitated out with water. *yield 44%	0.1825^D	6.48
V.	90:10	1:1	DMF	Clear reddish yellow solution was obtained at the end of reaction. Polymer was precipitated out with water. *yield 50%	0.2335^D	9.40

* yield based on total amounts of reactants used.

conclusion drawn in the Section 1 of this part that 3-SDI-BPTD reaction gives polyimide soluble in aprotic polar organic solvents. The yields obtained in case of all copolyimides, however, were in the range of 40 to 50% based on the total amount of reactants used. It is apparent from the viscosity data (Table-17) that high molecular weights were not built up in any of the copolyimides at any of the molar concentration of either of the diisocyanate in the reaction recipe. However, when 4-MDI was used as a major component, the viscosity of the copolymer increased noticeably.

The infra-red spectra of all copolyimides were recorded. As an illustration, IR spectrum of copolymer II (Table-17) has been given in Fig.16. Imide bands at 1780, 1725 and 730 cm^{-1} were present. A band at 1660-1670 cm^{-1} was also observed, which may be assigned to the benzophenonic carbonyl group. The two medium intensity bands in the range of 1160-70 cm^{-1} and 1300-1310 cm^{-1} can be assigned to the presence of sulfone linkage in diphenyl sulfone nucleus.

Table-17 also shows the sulfur contents of all copolyimides. Although, random copolymerization may be expected to occur, the percentage of sulfur in the copolymer was found to increase, as expected, with increase in the proportion of 3-SDI in the reactants used.

Figs. XV and XVI show the thermogravimetric analysis (TGA) curves obtained for different copolymers. Table-18 describes the loss of weight at different temperatures for

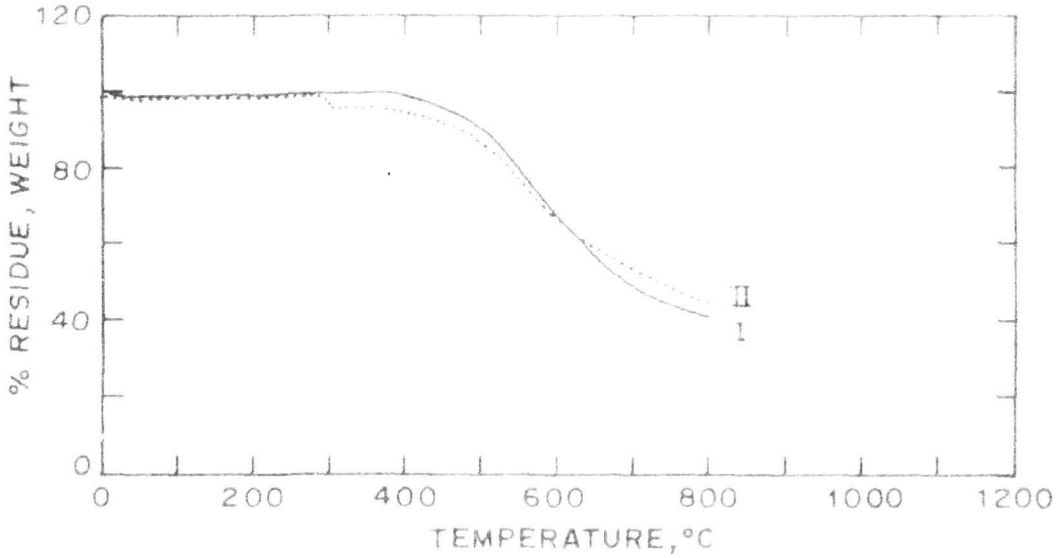


FIG.XV TGA CURVES IN AIR AT 9 °C/MINUTE FOR POLYMER I and II

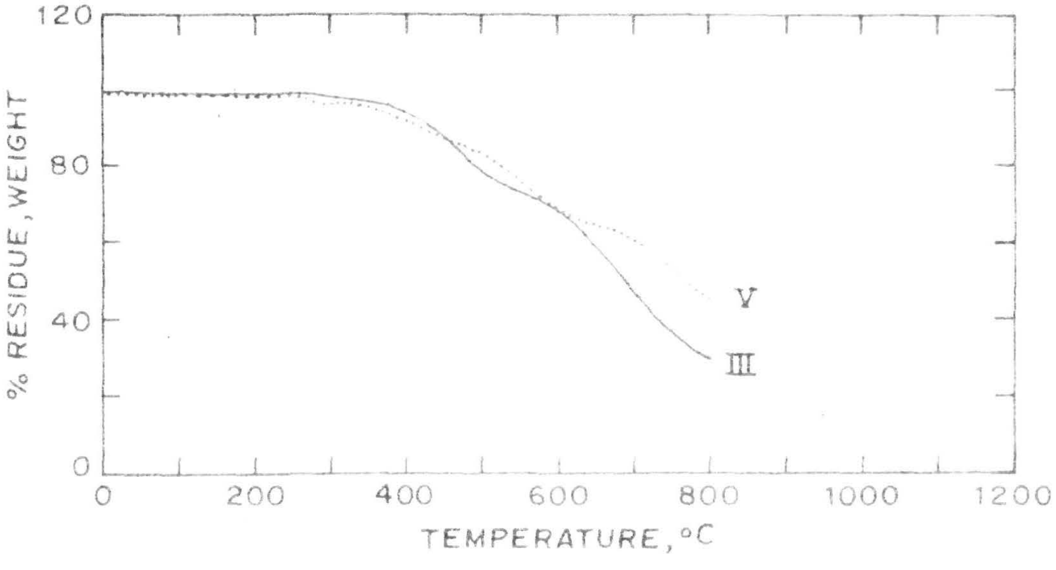


FIG.XVI TGA CURVES IN AIR AT 9 °C/MINUTE FOR POLYMER III and V

Table-18: % Weight loss at different temperatures for copolyimides I,II,III and V in air at 9°C/min.

Temperature	Polymer			
	I	II	III	V
100	0.5	0.5	0.5	1.0
200	1.0	0.5	0.1	1.0
300	1.0	4.0	2.5	2.0
400	1.0	5.5	5.0	7.0
500	8.0	13.0	10.5	14.0
600	31.5	33.0	30.5	30.0
700	49.0	46.0	54.0	58.0
800	58.0	55.0	69.0	73.0

a given polymer and these were calculated from the respective TGA curves.

It has been shown earlier (Section I part II) that the polyimide obtained from 4-MDI-BPTD reaction is more stable as compared to the polyimide obtained from 3-SDI-BPTD reaction. The incorporation of various proportions of 3-SDI in 4-MDI-BPTD reaction affects the thermal stability of the resultant polyimides in the expected direction, as can be seen in Table-18. As the proportion of 3-SDI in the copolymer increases, its thermo-oxidative stability is decreased. For example, the weight loss at 400°C in polymer I (Table-18) having 4-MDI as a major component, is minimum, while in case of polymer V, having 3-SDI as a major component, it is the highest. However, between 400°C and 600°C the losses are quite comparable. The maximum weight loss is attained by polymer V, which again is derived from the reactants in which 3-SDI is a major component. DTA and DTG were also recorded simultaneously with TGA and they confirmed the weight losses shown by TGA. The temperature at which the polymers exhibited maximum rates of decomposition have been given in Table-19. These were derived from the respective DTG curves. These polymers did not show complete degradation even upto 800°C. In general, the thermal stability of all these copolymers falls nearly between that of the two parent homopolymers and changes in a regular fashion with the copolymer composition.

Table-19: Temperatures at which decomposition rate is at highest

Polymer	Temperature °C
I	580
II	560
III	605
V	610

EXPERIMENTAL

Materials

(1) BPTD was obtained from Gulf Chemicals Corporation. It was used without further purification as no change in purity was noted after its sublimation.

(2) 3-SDI was prepared as given in Part I. It was distilled just before use.

(3) 4-MDI was obtained from Farbenfabriken Bayer A.G. West Germany in the form of solid flakes and was distilled just before use.

(4) Dimethyl formamide was used after distillation over efficient column.

The following procedure was used in general for the preparation of copolyimides.

In a 100 ml three necked round bottomed flask equipped with a thermowell, a gas exit, a stopper and a magnetic stirrer, were placed a mixture of diisocyanate (3-SDI:4-MDI proportion varying in each experiment) and BPTD in 1:1 molar ratio. The quantities of all the reactants used in individual experiments are given in Table-20.

The reactants were dissolved in dimethyl formamide (30 ml). The clear yellow solution was heated to 40°C and maintained at this temperature for 2½ hours. The temperature was then raised to 75°C in 1 hour and to

Table-20: The quantities of reactants used in copolycondensation

No.	3-SDI (g)	4-MDI (g)	BPTD (g)
1.	0.09	0.675	0.966
2.	0.45	0.375	0.966
3.	0.675	0.187	0.966
4.	0.72	0.15	0.966
5.	0.81	0.075	0.966

90°C in another 20-25 minutes. Further increase in temperature to 130°C was accomplished in 1 hour and it was maintained for 2 hours. The polymer was obtained in solid form. It was, however, precipitated out in certain cases where it remained soluble in the reaction medium at the end of the reaction. It was filtered, washed with methanol to remove solvent and dried at 100°C at 10^{-5} mm/Hg to remove entraped solvent and absorbed moisture. This was then used for characterization.

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Section-III

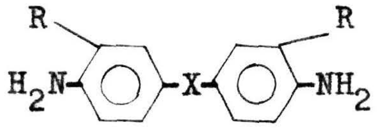
MODIFIED POLYIMIDES

PRESENT INVESTIGATIONS AND DISCUSSION

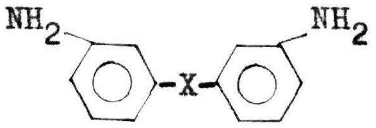
Modified polyimides can also be termed as copolyimides. Modifications in the preparation and properties of polyimides can be achieved by using a variety of reactants and their relative amounts. In the present work, isocyanate modified polyimides have been prepared and evaluated.

The diamines react with dianhydrides to give polyamic acids which can be cast and subsequently converted into insoluble polyimide films. The diisocyanates, on the contrary, have been reported by Mayers[1] to react with dianhydrides yielding insoluble low molecular weight polyimides, incapable of forming films due to their insolubility, in any organic solvent. However, it has been shown earlier in the present dessertation that 3,3'-sulfonylbis (phenyl isocyanate) (3-SDI), when reacted with BPTD in aprotic polar solvent, gave soluble low molecular weight polyimide. The same reactants also gave soluble low molecular weight polyimides in m-cresol. Several diamines have been reported[2] to give high molecular weight soluble polyimides when reacted with a number of dianhydrides in m-cresol. The structures of diamines and dianhydrides used are given below:

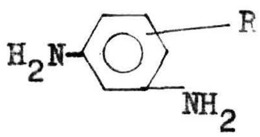
Diamines



I



II

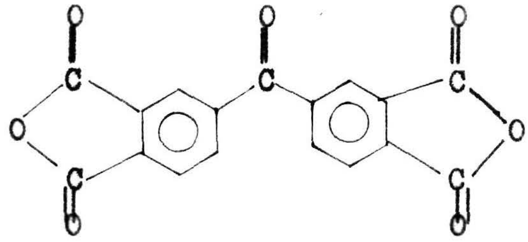


III

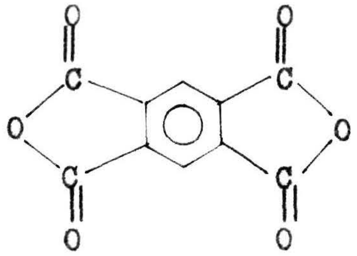
where R = OMe, OEt, COOH, OR or SO_3H

and X = CH_2, O, S, SO_2 or CMe_2

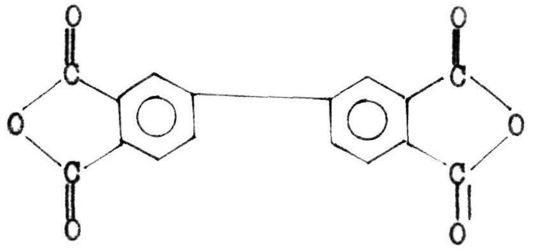
Dianhydrides



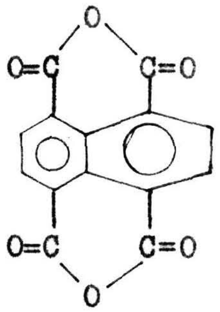
BPTD



PMDA



3,3',4,4'-Bisphenyl dianhydride

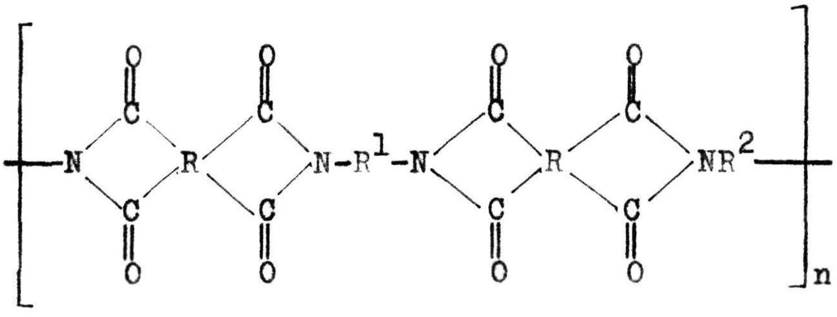


2,3,6,7-Naphthalene dianhydride

In view of the foregoing facts and in order to achieve polyimide films of improved properties, a reaction of the dianhydride with a mixture of half mole of diisocyanate and half mole of the diamine was investigated. Tackao et al[3] have reported such reaction in which they had reacted one mole of PMDA with half mole of methylene dianiline and half mole of 4-MDI in an aprotic polar solvent to get poly (amic acid imide). This, on heating yielded polyimide. Similarly, Takashi et al^4 have synthesized 4-MDI modified polyimide from 1,2,3,4-butane tetracarboxylic acid and 4,4'-diaminodiphenyl methane.

The reactions carried out and the nature of the resulting polymer in the present work, are summarized in Table-21.

Reactions I and II (Table-21) were carried out in m-cresol. BPTD when reacted with either of the two diamines (Table-21) or SDI in m-cresol, yielded soluble polyimides. The advantage of this fact was taken in the reactions I and II to obtain soluble modified polyimides directly. Polyimide solutions in m-cresol were used in the preparation of films. A part of the solution was precipitated with non-solvent, ether to get solid polyimide, which was used for IR spectral investigations. The structure of the polyimide can be represented as follows:



where R = BPTD nucleus, R^1 = Arylene diamine nucleus
R^2 = 3-SDI nucleus.

Table-21: Modified polyimides - The reactants used and nature of polymers obtained

Reaction No.	Diisocyanate	Dianhydride	Diamine	Solvent	Nature of polymer obtained	Abbreviation
I	3-SDI	BPTD	3,3'-diaminodiphenyl sulfone	m-cresol	Soluble polyimide	A
II	3-SDI	BPTD	4,4'-diaminodiphenyl methane	m-cresol	Soluble polyimide	B
III	3-SDI	PMDA	3,3'-diaminodiphenyl sulfone	m-cresol	Insoluble polyimide	C
IV	3-SDI	PMDA	3,3'-diaminodiphenyl sulfone	N-methyl -2-pyrrolidone	Soluble poly (amic acid imide)	D
V	3-SDI	PMDA	4,4'-diaminodiphenyl methane	N-methyl -2-pyrrolidone	Soluble poly (amic acid imide)	E

As an illustration, the IR spectrum of polymer A from reaction I is given in Fig.17. The IR spectrum showed the presence of imide bands at 1775, 1725 and 725 cm^{-1}. A small peak at 1665-70 cm^{-1} may be assigned to the benzophenonic carbonyl group. The medium intensity bands at 1300 and 1160-65 cm^{-1} show the presence of sulfonyl group.

In the third reaction (Table-21) a part of the polymer had separated out. It was filtered, washed with ether to remove solvent and dried. The IR spectrum of this sample (Fig.18) showed presence of imide bands at 1790, 1730 and 735 cm^{-1} indicating the formation of an insoluble polyimide in the reaction.

In order to obtain soluble, homogeneous solutions, reactions IV and V were carried out in N-methyl 2-pyrrolidone to get poly(amic acid imide) which was subsequently heated to remove solvent and water yielding polyimide. The reactions can be represented as given in Fig.XVII. In reactions IV and V (Table-21) the sequence of addition of the reactants has been changed as compared to that followed by Takao et al[3]. In their experiment, the dianhydride was initially reacted with a diamine followed by the reaction with a diisocyanate. In the present work, the dianhydride was initially reacted with the diisocyanate and this was followed by the reaction of the remaining dianhydride with a diamine, that was added later.

The solutions of polyimide A and B and poly(amic acid

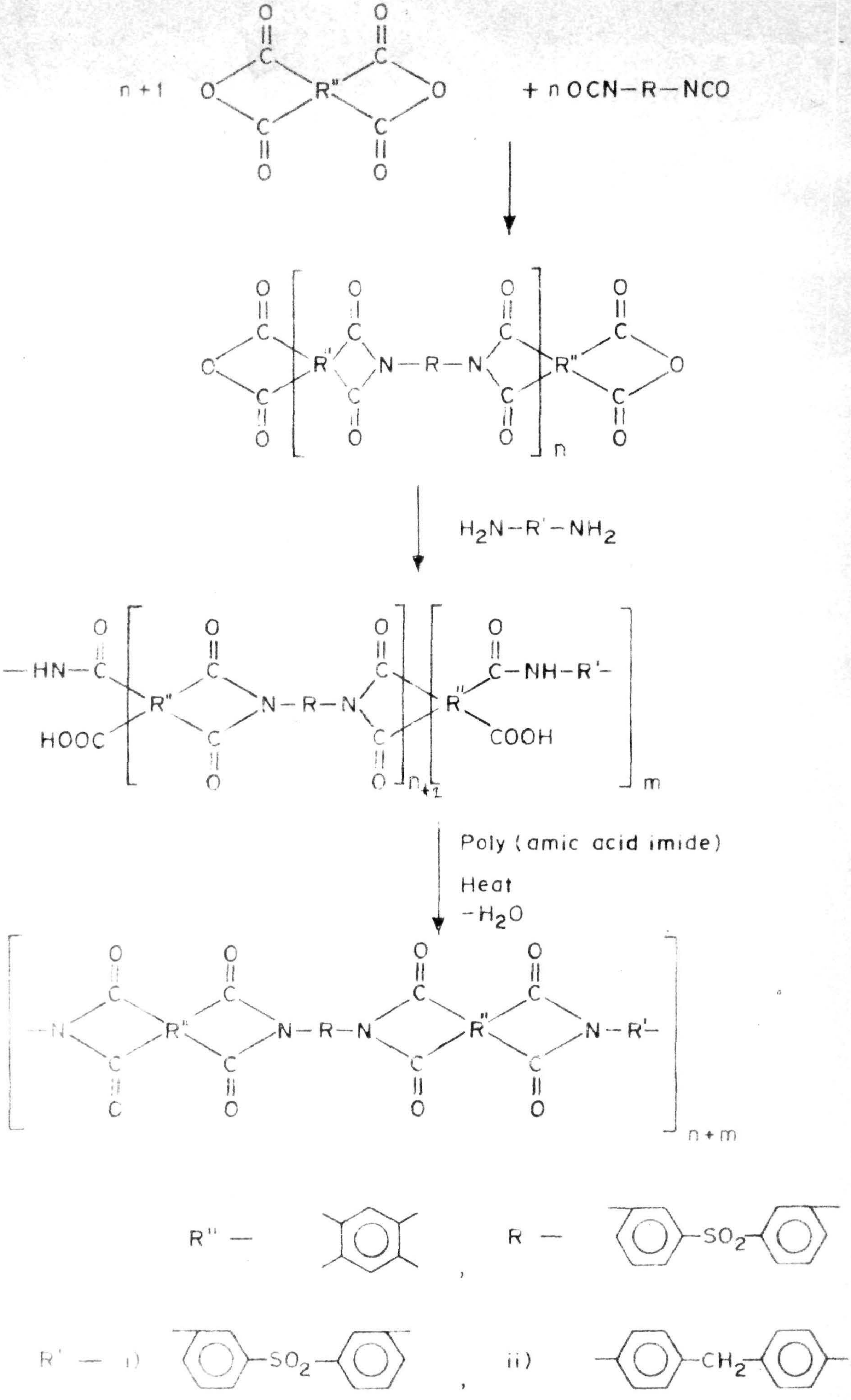


FIG. XVII
SYNTHESIS OF ISOCYANATE MODIFIED POLYIMIDES

imide) solutions of D and E (Table-21) were cast on brass dishes of 1.8 cm diameter. The following heating schedule was adopted to remove the solvent, and water resulting from immidization.

Temperature °C	Hours	Pressure mm/[illegible] Hg
60	1	2
80	1	2
100	1	2
125	2	2
150	2	2
180	2	2
200	1	7

In case of polymer D and E, the supported films (coatings) obtained were heated for an additional hour at 250°C to ensure maximum immidization, which was confirmed by the IR spectrum in nujol mull of crushed film. As an illustration, the IR spectrum of polyimide D is given in Fig.19. It shows absence of -NH band at 3200-3300 cm^{-1} and presence of imide bands at 1780, 1725 and 730 cm^{-1}. The medium intensity bands at 1300-10 cm^{-1} and 1140-1160 cm^{-1} can be assigned to the sulfonyl group from diamine and diisocyanate nuclei.

Electrical properties of these thin films (coatings) obtained on brass dishes were measured. They have been given in Table-22. All the polyimides displayed good volume resistivity which was of the order of either 10^{14}

or 10^{13} ohms.cm. The dielectric constant was in the range of 1.5 to 2.8 at an applied voltage of 10^3 Hz at 25°C. The dissipation factor or tan δ as has been expressed here, was better for all the four polyimides.

Table-22: Electrical properties of modified polyimides

Polymer No.	Volume resistivity ohms.cm at 25°C.	tan δ at 10^3 hz	Dielectric constant at 10^3 hz at 25°C
A	2.5×10^{14}	0.0015	2.81
B	5×10^{14}	0.0016	1.56
C	1.3×10^{13}	0.014	1.47
D	3×10^{13}	0.0093	2.093

EXPERIMENTAL

Preparation of modified polyimides A, B and C

In a 3 necked 100 ml round bottomed flask equipped with a magnetic stirrer, were placed a mixture of a dianhydride (0.002 mole) and the diisocyanate (3-SDI) (0.001 mole). To this m-cresol (30 ml) was added to get a turbid solution and the reaction mass was heated to 160°C. This temperature was maintained for 6 hours. During first 3 hours of heating, the reaction mass was turbid and later became clear. After 6 hours at 160°C, the clear reaction mass was cooled to 30°C and the diamine (0.001 mole) was added. The reaction mixture was kept at 160°C for 1 hour and cooled to get clear viscous brownish polyimide solution.

In case of reaction III (Table-21) only, a yellowish green polymer had separated out on the side walls of the reaction flask.

Preparation of modified polyimide D and E

In a 3 necked 100 ml round bottomed flask was kept a mixture of PMDA (0.002 mole) and the diisocyanate (3-SDI) (0.001 mole). This was dissolved in N-methyl-2-pyrrolidone (30 ml) to get a clear yellow solution. This was heated as given below:

Temperature °C.	Time hrs.
40	2½
75	1
90	1
130	2

After 2 hours at 130°C, the clear reddish yellow reaction mass was cooled to 30°C and a diamine (0.001 mole) was added. The clear solution was heated to 70°C for 10 minutes and cooled to give poly(amic acid imide polymer) which on further heating (see Discussion) yielded the polyimide.

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Section-IV

POLY(AMIDE-IMIDES)

PRESENT INVESTIGATIONS AND DISCUSSION

Poly(amide-imides) constitute a separate class of high temperature polymers. They contain in their repeating units, both amide as well as imide groups. An excellent review and bibliography on this subject is available in the literature[1,2]. Various methods of poly(amide-imide) synthesis are known, a few of which are of importance, have been mentioned below and the relevant reactions are given in Fig. XVIII.

(1) In the reaction of 4-chloroformyl phthalic anhydride with a diamine, HCl and water molecules are eliminated to give the poly(amide imide) polymer[3].

(2) By reacting a diacid, containing imide groups in its nucleus, with a diamine in the presence of tertiary amine catalyst[4], poly(amide-imide) is obtained.

(3) Reaction of an aromatic diamine with a mixture of pyromellitic anhydride and arenedicarboxylic acid halide gives brown coloured strong film of the poly(amide-imide)[5].

(4) A diisocyanate, when reacted[6] with trimellitic acid anhydride yields poly(amide-imide) by elimination of carbon dioxide.

Numerous articles[3,7-11] in the form of patents and papers have been reported in the literature in recent years.

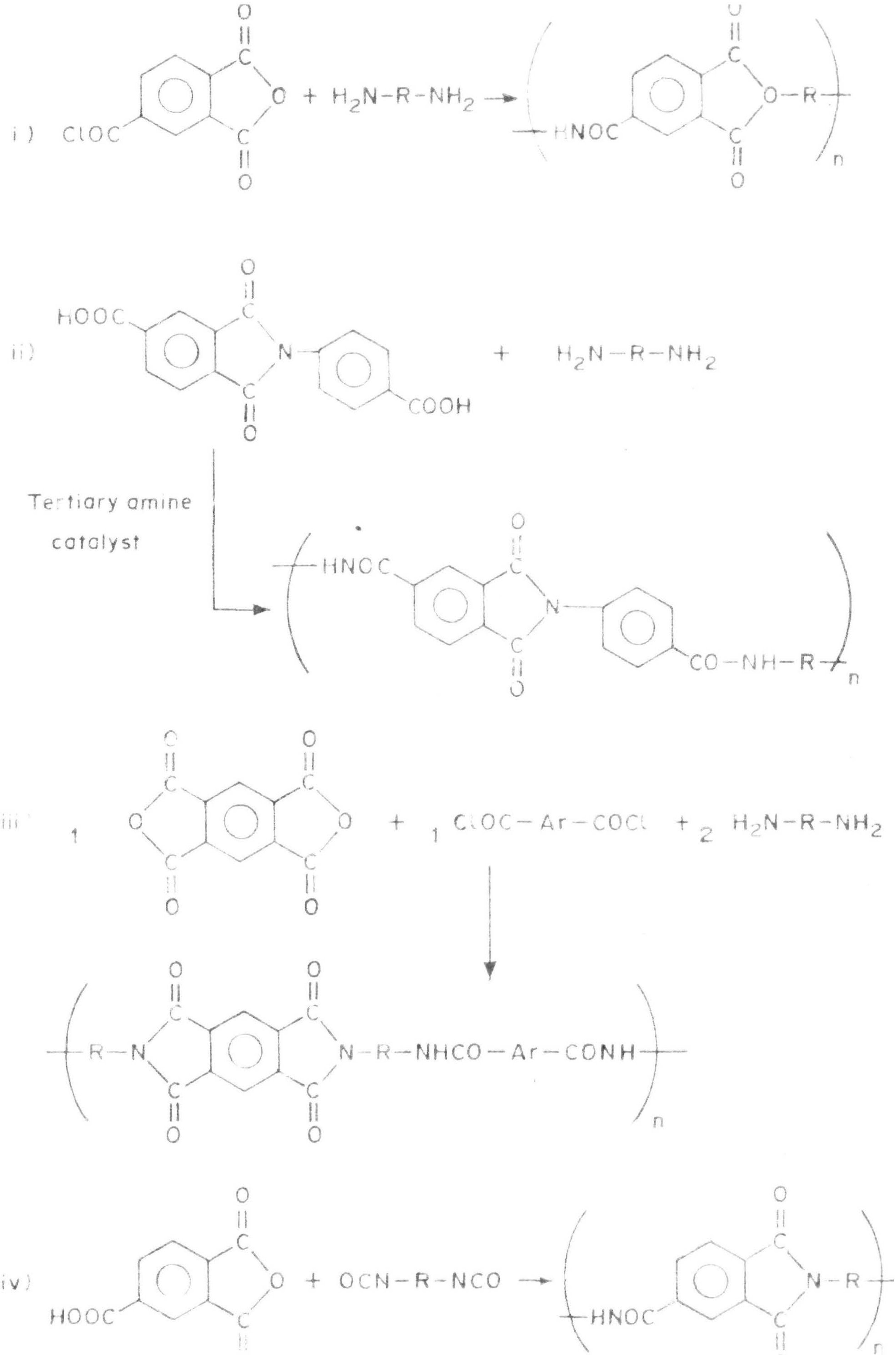
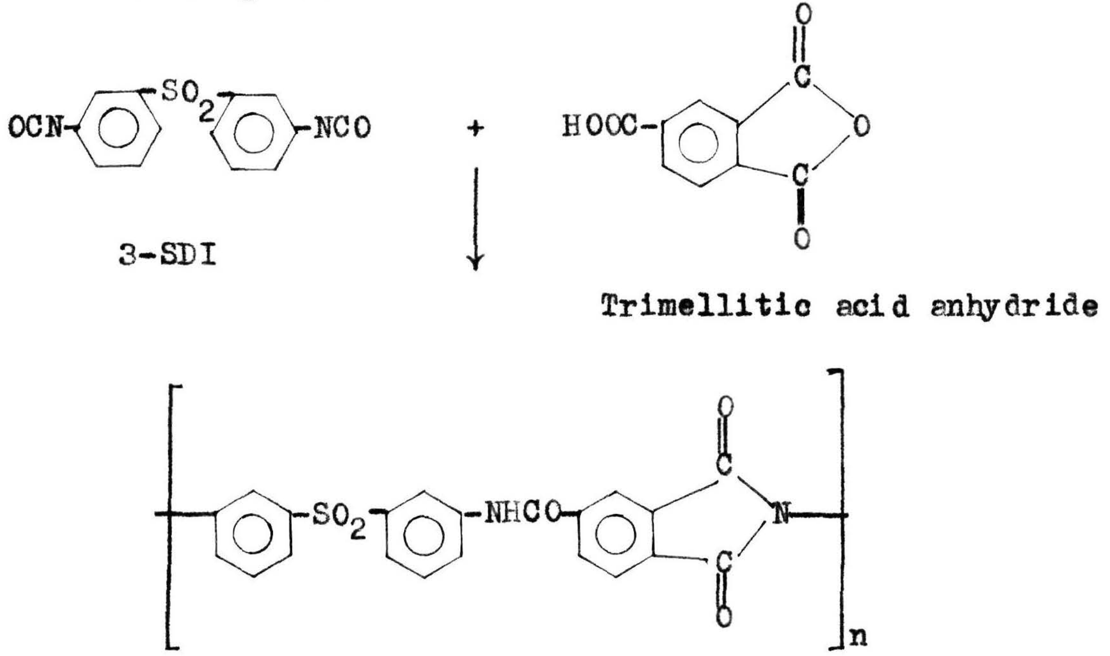


FIG. XVIII DIFFERENT METHODS FOR THE PREPARATION OF POLY (AMIDE-IMIDE) POLYMERS

In the present work, a poly(amide-imide) polymer was synthesised by reacting 3-SDI with trimellitic acid anhydride in dimethyl formamide (DMF) solution. The reaction can be represented as given below:



poly(amide-imide)

The poly(amide-imide) polymer, thus obtained, was soluble in polar aprotic solvent like DMF. The solution was cast on brass dishes of 1.8 cm diameter and solvent was removed by following the heating schedule as has been given in the preparation of modified polyimides (Part II, Section III).

The electrical properties of the coating (film) obtained on brass dishes were determined and are given in Table-23.

Table-23: Electrical properties of poly(amide-imide)

Volume resistivity	Dielectric constant at 10^3 hz. at 25^oC.	tan δ at 10^3 hz at 25^oC
7.2×10^{12}	3.6	0.0018

A part of poly(amide-imide) solution in dimethyl formamide was precipitated by non-solvent, water. The polymer was filtered, washed with methanol to remove solvent and dried under vacuum. The IR spectrum of this polymer sample has been given in Fig.20. It showed the presence of 3200 cm^{-1} peak corresponding to secondary amine from >CONH- group. The presence of bands at 1780, 1725 and 740 cm^{-1} confirmed the presence of imide groups in the polymer. The bands corresponding to the sulfonyl group from isocyanate nucleus can be seen at 1315 cm^{-1} and 1165 cm^{-1}.

EXPERIMENTAL

Preparation of poly(amide-imide) polymer

In a 3 necked round bottomed flask, equipped with a reflux condenser, a thermowell and a magnetic stirrer were placed trimellitic acid anhydride (1.3 g) and 3-SDI (2.52 g). To this, dimethyl formamide (30 ml) was added and the clear solution was slowly heated to 110°C at which it was maintained for 15 minutes. The temperature was further raised to the boiling point of solvent in about 25 to 30 minutes and the reaction mass was refluxed for 2 hours and cooled to get clear reddish solution. This poly(amide-imide) solution was used in the preparation of film.

Materials

Trimellitic acid anhydride was obtained from Koch-Light Laboratories Ltd., England.

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PART - III

STUDIES IN THE VULCANIZATION OF POLYURETHANE ELASTOMERS AND NATURAL RUBBER (NR)

Section-I

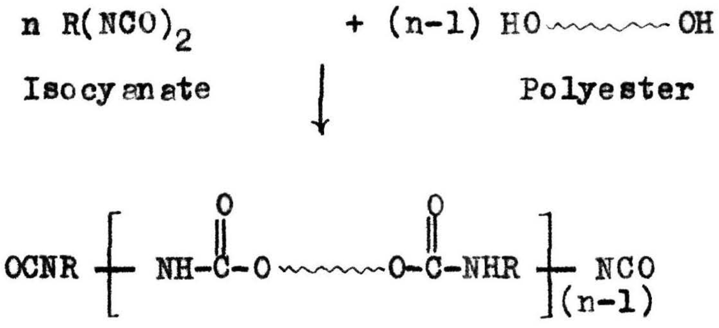
POLYURETHANE VULCANIZATION

INTRODUCTION

Urethane elastomers constitute a major field of applications of polyurethanes. The early developmental work in solid polyurethane elastomers started in the 1940's by German and English researchers independently. It was based on polyesters and diisocyanates. Linear polyesters were prepared for the first time by Hofmann[1], by using dicarboxylic acids and glycols. However, due to their low softening temperatures, with exception of poly (ethylene terephthalate)[2] they were of least practical significance. In 1940, Schlack[3] tried to increase the molecular weight of these polyesters by chain extension with diisocyanate but with a limited success. It is to Pinten[4] goes the credit of preparing highly elastic isocyanate rubbers (I rubbers) for the first time. Diisocyanates and polyesters were the raw materials for their preparation, while trimethylol propane was used as the crosslinking agent. These materials showed high tensile strength and abrasion resistance but poor tear resistance and had a tendency to harden upon storage.

Bayer and coworkers[5] prepared Vulcolans - the polyurethane elastomers.

In the first step a linear hydroxy terminated polyester is reacted with a diisocyanate to form a prepolymer.

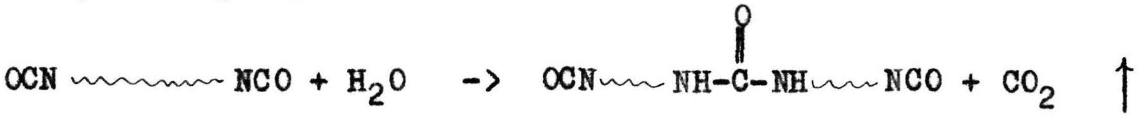


$$n\ R(NCO)_2 + (n-1)\ HO\sim\sim OH \longrightarrow OCNR\left[NH-\overset{O}{\overset{\|}{C}}-O\sim\sim O-\overset{O}{\overset{\|}{C}}-NHR\right]_{(n-1)}NCO$$

Isocyanate Polyester

Prepolymer

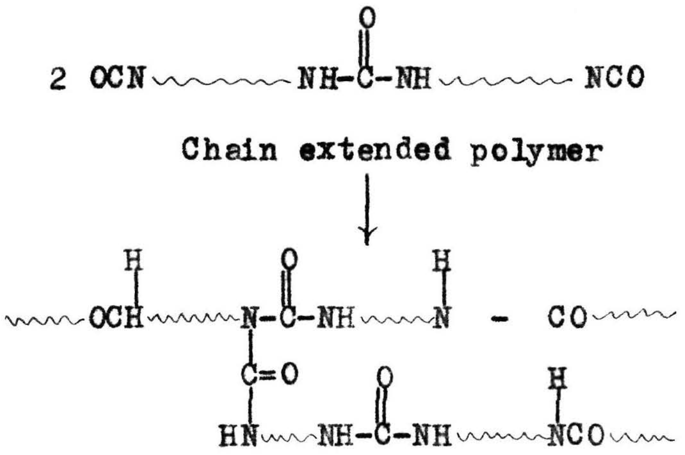
The chain extension of the prepolymer was achieved by formation of urea groups by the addition of controlled amount of water and thus leaving about 2-5% of unreacted isocyanate groups.



$$OCN\sim\sim NCO + H_2O \rightarrow OCN\sim NH-\overset{O}{\overset{\|}{C}}-NH\sim NCO + CO_2\uparrow$$

Prepolymer Water Chain extended polymer

At elevated temperatures (125-150°C) the excess isocyanate groups of the chain extended polymer react with active hydrogen of either urea or urethane groups of other chain to give crosslinks. The most favoured reaction being between the isocyanate and urea groups.



$$2\ OCN\sim\sim NH-\overset{O}{\overset{\|}{C}}-NH\sim\sim NCO$$

Chain extended polymer

Cross linked polymer.

Several modifications in vulcolan were reported and different chain extenders like diamines, aminoalcohols and glycols were tried.

The polyurethane elastomers were also developed in England and United States. Imperial Chemical Industries filed a patent[6] in 1941 describing the curing of a polyester-amide-diisocyanate adduct with formaldehyde and this material[7,8] was sold commercially in the form of a millable gum under the trade name, Vulcaprene. Data[9] on Chemigum SL, an isocyanate cured millable gum from Good Year, was published in 1953. Du Pont developed the polyurethane rubbers - Adiprenes - based on poly(oxytetramethylene) glycols rather than polyesters[10,11]. Adiprene B was another isocyanate cured millable gum. Formation of urethane-urea elastomers by one shot casting technique, comprising direct conversion of the raw materials into final polymer, was another landmark in the development of these elastomers[12]. Recently, thermoplastic urethane elastomers have been developed which can be processed on conventional rubber and plastic machines[13,14].

Urethane elastomers exhibit outstanding mechanical properties. They are well known for their general toughness, excellent wear and tear properties and good oil resistance. Due to these properties, solid polyurethane elastomers are now widely utilised as engineering materials.

Polyurethane elastomers are commercially available in the following 3 forms:

i) Castable
ii) Millable gum
iii) Thermoplastic

The castable elastomers are obtained by mixing the reactants in liquid state and pouring the liquid reaction mixture into a mould which is ultimately cured to a rubbery state. The millable gums are prepared as storage stable polymers having hydroxyl end groups. These are processed on a conventional rubber machinery and cured with either polyisocyanates or peroxide or sulfur curing systems. Thermoplastic urethane elastomers are obtained by a technique similar to that of millable gums. However, the molecular weights of thermoplastic materials are quite high due to the allophanate crosslinks that are present at ambient temperatures but break at higher temperatures. Moreover, they are soluble in common organic solvents.

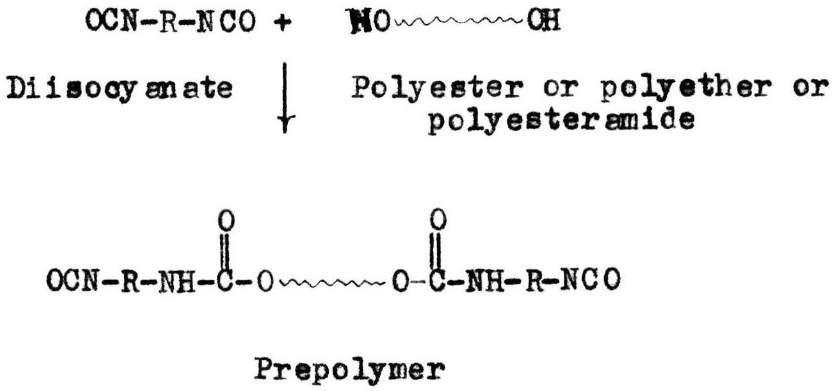
Use of polyurethane elastomers in engineering materials has steadily shot up in last few years.

Chemistry of urethane elastomers

Several reaction stages are involved in urethane elastomer preparation. They include the preparation of a low molecular weight prepolymer, chain extension to a higher molecular weight soluble polymer and crosslinking.

(i) Prepolymer formation

The reaction of a diisocyanate with a hydroxyl-terminated polyester or polyether or polyesteramide results in the formation of an isocyanate-terminated prepolymer.

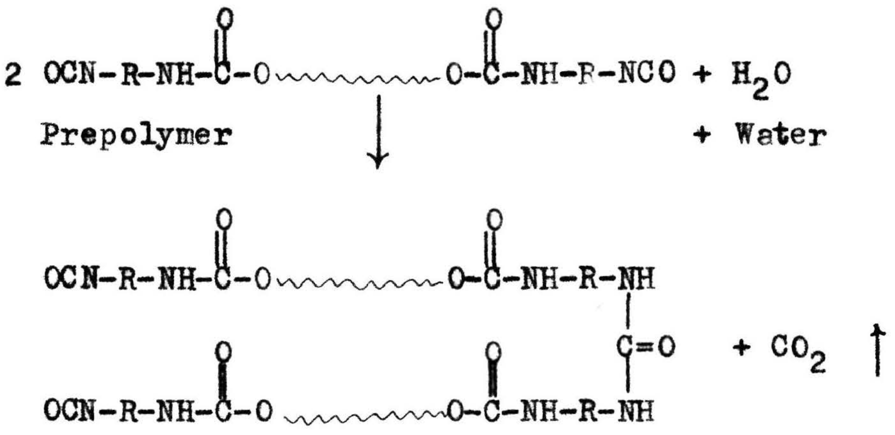


$$\underset{\text{Diisocyanate}}{OCN{-}R{-}NCO} + \underset{\text{Polyester or polyether or polyesteramide}}{HO\sim\sim\sim\sim OH} \longrightarrow \underset{\text{Prepolymer}}{OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O\sim\sim\sim\sim O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NCO}$$

(ii) <u>Chain extension</u>

Chain extension of the prepolymer with difunctional active hydrogen-containing compounds like water, diamines, glycols or aminoalcohols leads to the formation of a higher molecular weight soluble polymer.

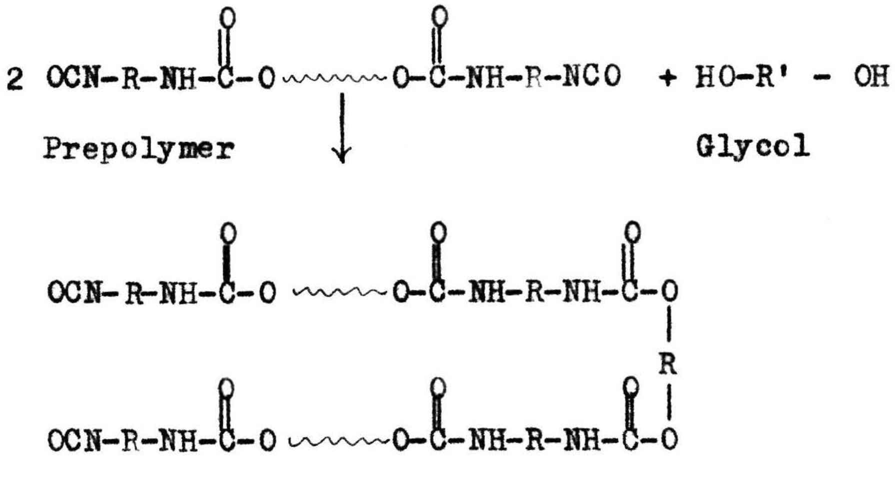
Substituted urea linkages are formed along with evolution of carbon dioxide as a result of chain extension with water.



$$\underset{\text{Prepolymer}}{2\ OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O\sim\sim\sim\sim O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NCO} + \underset{+\ \text{Water}}{H_2O} \longrightarrow \begin{array}{l} OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O\sim\sim\sim\sim O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C{=}O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O\sim\sim\sim\sim O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH \end{array} + CO_2 \uparrow$$

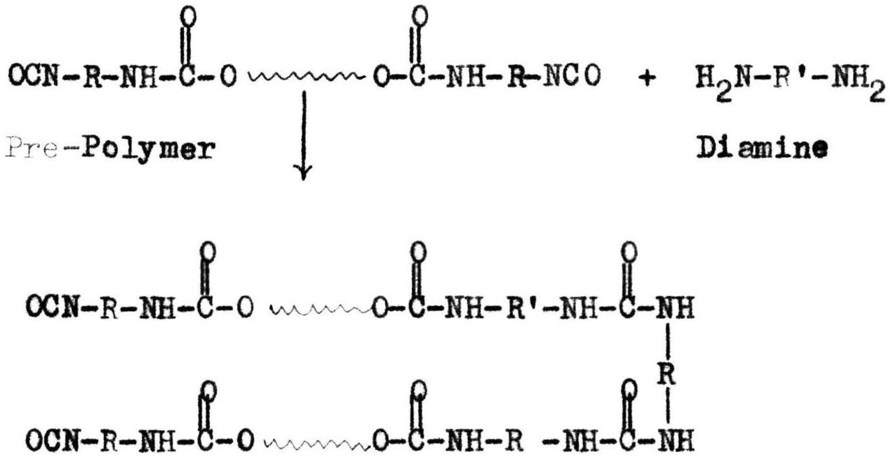
Substituted urea.

Chain extension with glycols takes place with the formation of urethane groups.



Urethane

Substituted urea type crosslinks are formed when diamines are used as chain extenders.



Substituted urea

Hydrogen sulfide, dithiols, dicarboxylic acids etc.[15] are also used as chain extenders.

In the above scheme, wherein an excess of isocyanate was used, a -NCO terminated polymer results. These polymers are not highly stable in spite of their high molecular weight because of the presence of reactive isocyanate groups.

Stable polymers with better solubility may be produced by using a slight excess of an active hydrogen compound, rather than an excess of isocyanate. For example, polyurethane with terminal hydroxyl groups would be formed if an excess of glycol is used.

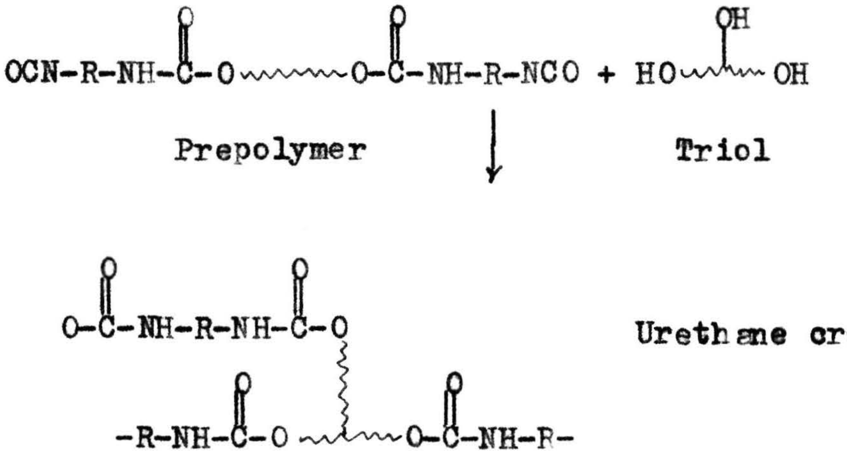
$$\underset{\text{Prepolymer}}{(n-1)\ \mathrm{OCN{-}R{-}NHOCO} \quad \mathrm{OCO{-}NH{-}R{-}NCO}} + \underset{\text{Glycol}}{n\ \mathrm{HO{-}R'{-}OH}} \;\downarrow$$

$$\mathrm{HO}\left[\mathrm{R'{-}OCONH{-}R{-}NH{-}OCO}\sim\sim\mathrm{OCO{-}NH{-}R{-}NH{-}OCO}\right]_{(n-1)}\mathrm{R'{-}OH}$$

Hydroxy terminated polyurethane.

(iii) Curing or crosslinking

(a) Urethane crosslinks are introduced by using triols such as trimethylolpropane, glycerol etc.



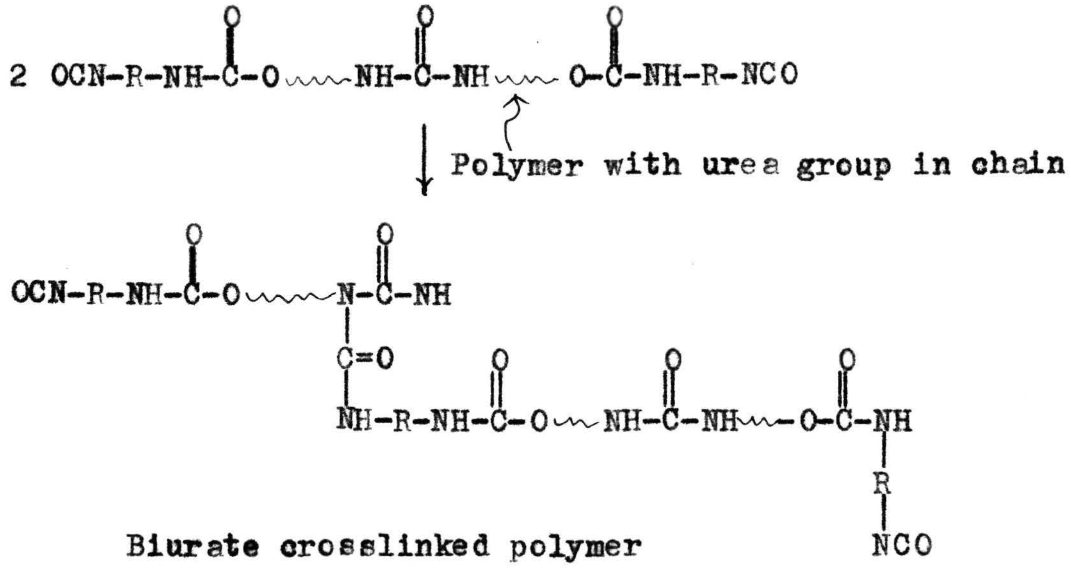
$$\underset{\text{Prepolymer}}{\mathrm{OCN{-}R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O}\sim\sim\mathrm{O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R{-}NCO}} + \underset{\text{Triol}}{\mathrm{HO}\sim\overset{\mathrm{OH}}{\sim}\sim\mathrm{OH}} \;\downarrow$$

$$\begin{array}{l}\mathrm{O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O} \\ \qquad\qquad\qquad\qquad\quad \wr \\ \mathrm{-R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O}\sim\sim\sim\mathrm{O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R{-}}\end{array}$$

Urethane crosslink.

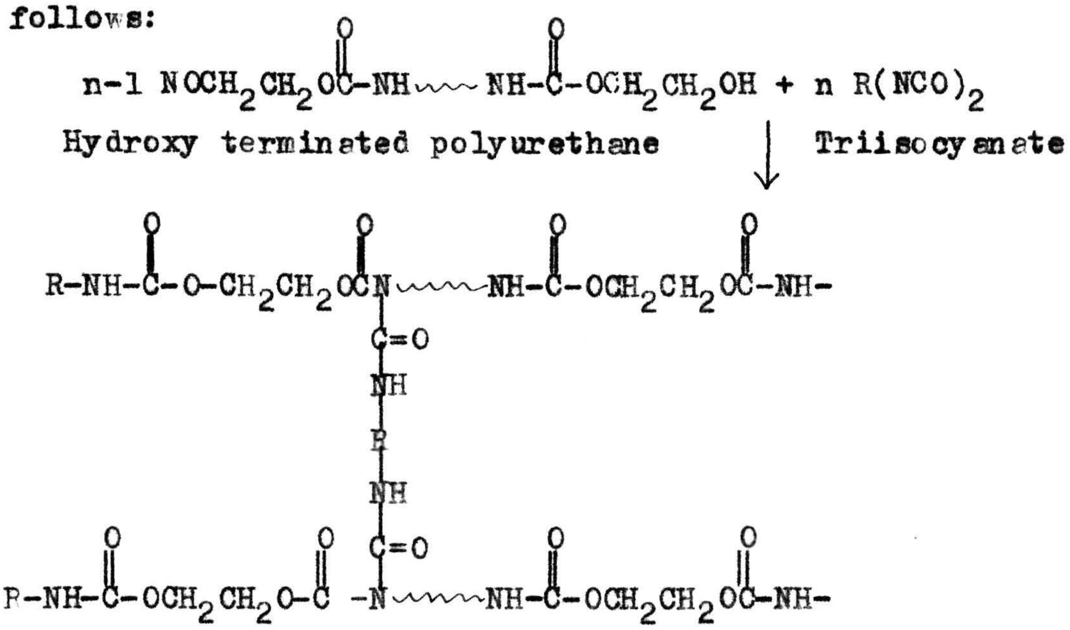
In case of isocyanate terminated polyurethane polymers, the isocyanate groups of polymer will react among themselves at elevated temperatures, to form allophanate crosslinks.

Similarly, the presence of urea and amide groups in polymer will yield biurate and acyl urea linkages respectively by reaction with isocyanate groups. This can be illustrated by heat cure of 'Vulcolan' at 125-150°C and can be represented as:



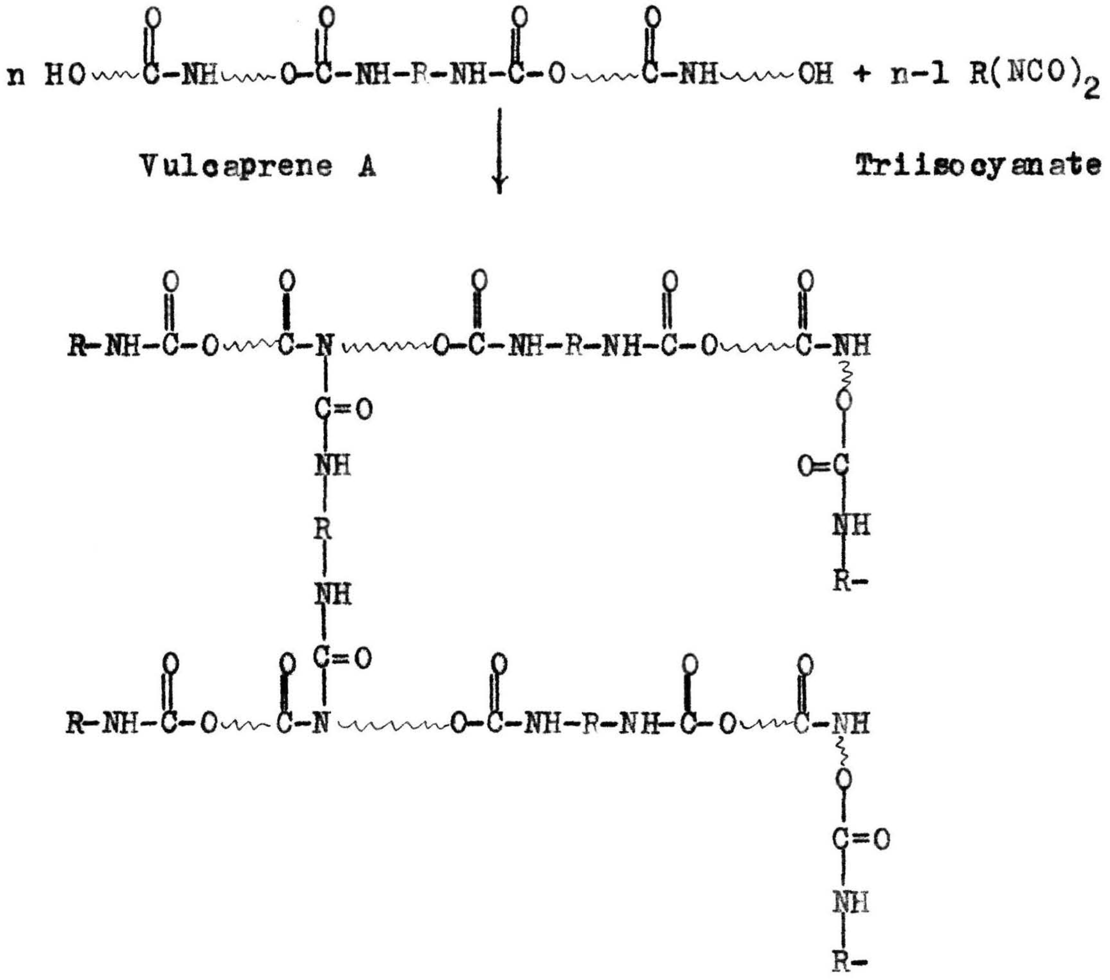
$$2\ OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O\sim\sim NH{-}\overset{O}{\overset{\|}{C}}{-}NH\sim\sim O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NCO$$

(b) Storage stable, hydroxyl terminated adducts can be cured by reaction with the excess diisocyanate or triisocyanate as follows:



$$n{-}1\ NOCH_2CH_2O\overset{O}{\overset{\|}{C}}{-}NH\sim\sim NH{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2OH + n\ R(NCO)_2$$

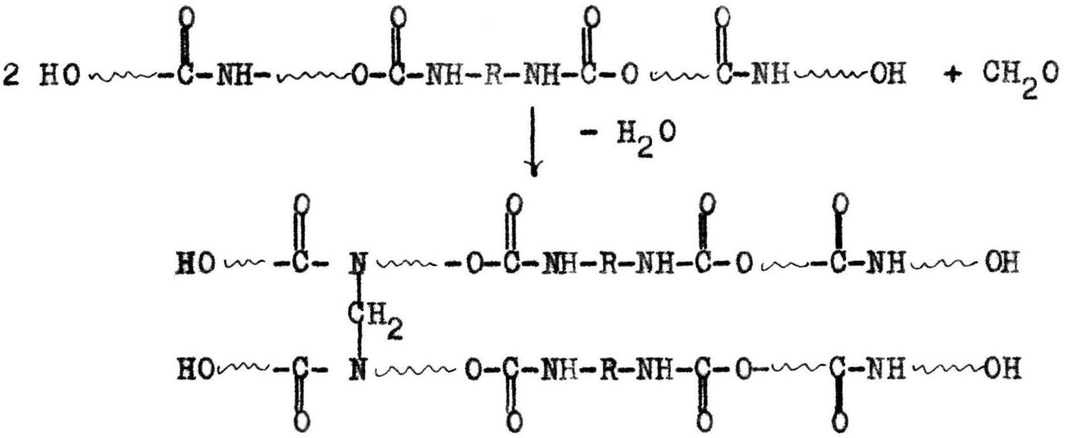
(c) Vulcaprene - a hydroxy terminated polyurethane elastomer prepared from diisocyanate and polyester-amide can be cured either with diisocyanate or with formaldehyde.



$$n\ HO\sim\overset{O}{\overset{\|}{C}}-NH\sim O-\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-O\sim\overset{O}{\overset{\|}{C}}-NH\sim OH + n-1\ R(NCO)_2$$

Isocyanate cured Vulcaprene

Urethane elastomers (Vulcaprene) can also be vulcanized by heating with formaldehyde-evolving substances and a small amount of acid (or acid forming compound)[16]. The source of formaldehyde may be paraformaldehyde or a product of condensation of amines with formaldehyde. The latter, first adds as to >NH groups of one chain with the formation of methylol groups, these methylol groups react with >NH units of another chain, forming methylene bridges.

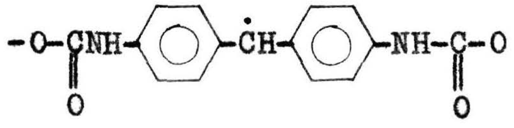


$$2\,HO\sim\overset{O}{\overset{\|}{C}}-NH-\sim O-\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-O\sim\overset{O}{\overset{\|}{C}}-NH\sim OH + CH_2O \xrightarrow{-H_2O}$$

$$\begin{array}{l} HO\sim-\overset{O}{\overset{\|}{C}}-N\sim-O-\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-O\sim-\overset{O}{\overset{\|}{C}}-NH\sim OH \\ \qquad\quad\;\; | \\ \qquad\quad CH_2 \\ \qquad\quad\;\; | \\ HO\sim-\underset{O}{\underset{\|}{C}}-N\sim O-\underset{O}{\underset{\|}{C}}-NH-R-NH-\underset{O}{\underset{\|}{C}}-O-\sim\underset{O}{\underset{\|}{C}}-NH\sim OH \end{array}$$

Formaldehyde cured Vulcaprene

(d) In case of elastomers prepared from 4,4'-methylenebis (phenyl isocyanate)(4-MDI) and either polyethers or polyesters, peroxides such as dicumyl peroxide can also be used for curing. Crosslinking takes place presumably through free radical formation at the methylene group of the diphenyl methane diisocyanate[17].



Free radical that participates in crosslinking

(e) In case of small amounts of unsaturation being present in urethane elastomer, conventional peroxide or sulfur curing systems generally used for unsaturated hydrocarbon rubbers, may be employed to effect the crosslinking.

PRESENT INVESTIGATIONS AND RESULTS

Numerous commercial organizations supply millable polyurethane gums (Table-24) under different trade names like Adiprene, Vulcaprene, Elastothane etc. and various curing systems are used in the vulcanization of these gums. Amongst the most widely used vulcanization systems are diisocyanates or polyisocyanates, peroxides and sulfur systems.

Finelli[37] has described the preparation of crosslinked soft polyurethane elastomers from poly(propylene) adipate and either 2,4-TDI or mixture of 80:20 2,4- and 2,6-TDI or 4-MDI. These polymers were crosslinked by either 3,3'-diamino diphenyl sulfone or 4,4'-diamino diphenyl sulfone and still remained soft. Such polyurethanes had good physical properties and were shown to have uses in making shock absorbers if fillers like cellulose were incorporated in the polymer.

By using 3,3'-dinitrodiphenyl sulfone as the starting material, a highly reactive diisocyanate, 3,3'-sulfonylbis (phenyl-isocyanate)(3-SDI) was synthesised. The reactivity of 3-SDI was found to be much higher (Part I, Section II) as compared to 4-MDI, which is generally used for crosslinking in polyurethane elastomers. Therefore it was thought that the use of 3-SDI might reduce the vulcanization

Table-24: **Commercially available polyurethane millable gums**

Commercial Name	Polyol	Diisocyanate	Chain extender	End group	Crosslinking agent	Ref.
Vulkollons	Adipate esters	MDI or 1,5-NDI	(1) Water (2) Glycol (3) Diamine (4) Amino alcohol	Either-NCO or -OH terminated polymer	Diisocyanate	5 15 15,18,19 15
Urepan	Adipate ester of diethylene glycol	TDI	Glycol	-OH terminated	Dimer of TDI or hydroquinone dioxyethyl ether	20,21
Urepan 601	Adipate ester of hexamediol	TDI	Glycol	-OH terminated	Dimer of TDI or hydroquinone dioxyethyl ether	22
Urepan 640	Adipate of mix of glycols	MDI	Glycol	-OH terminated	Peroxide	23
Chemigum SL	Adipate ester	TDI,MDI NDI,XDI	Glycol	-OH terminated	Diisocyanate	9,24,25
Vulcaprene A	Polyester amide		Glycol	-OH terminated	di-or triisocyanate or formaldehyde	8,26,27

cont...

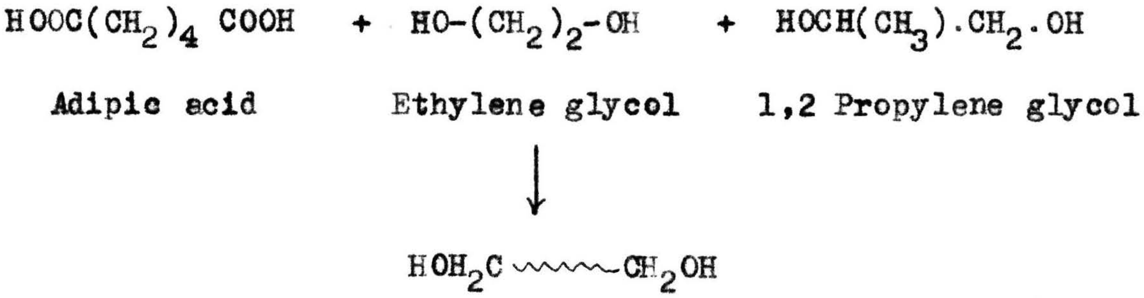
Table-24: (cont)

Commercial Name	Polyol	Diisocyanate	Chain extender	End group	Crosslinking agent	Ref.
Genthanes	Adipate polyester	MDI	Glycol	-OH terminated	Diisocyanate or peroxide	28
Vibrathane	Adipate polyester	MDI	Hexamethylene diamine	-OH terminated	Peroxide	29,30
Elastothane 455	Polyester	-	-	-	Sulfur	31,32,33
Cyanaprene	Polyester	TDI	Glycol	-OH terminated	Isocyanate	34
Adiprene C	Polyether		-	-	Sulfur; peroxide	35,36

time considerably, thereby increasing the efficiency of the process. The polyurethane elastomer used in the present work was a hydroxy terminated stable gum prepared from an adipate polyester based on a mixture of ethylene and propylene glycol, 4-MDI and ethylene glycol as a chain extender.

Preparation of polyester - polyethylene, polypropylene adipate (PEPA 55)

Polyethylene polypropylene adipate (PEPA 55) was prepared by the condensation of (80:20) molar mixture of ethylene glycol and 1,2-propylene glycol with adipic acid. It was a white waxy material with hydroxyl number 55 and the acid number less than 1.



$$\underset{\text{Adipic acid}}{HOOC(CH_2)_4\,COOH} + \underset{\text{Ethylene glycol}}{HO{-}(CH_2)_2{-}OH} + \underset{\text{1,2 Propylene glycol}}{HOCH(CH_3).CH_2.OH}$$

$$\downarrow$$

$$HOH_2C \sim\sim\sim CH_2OH$$

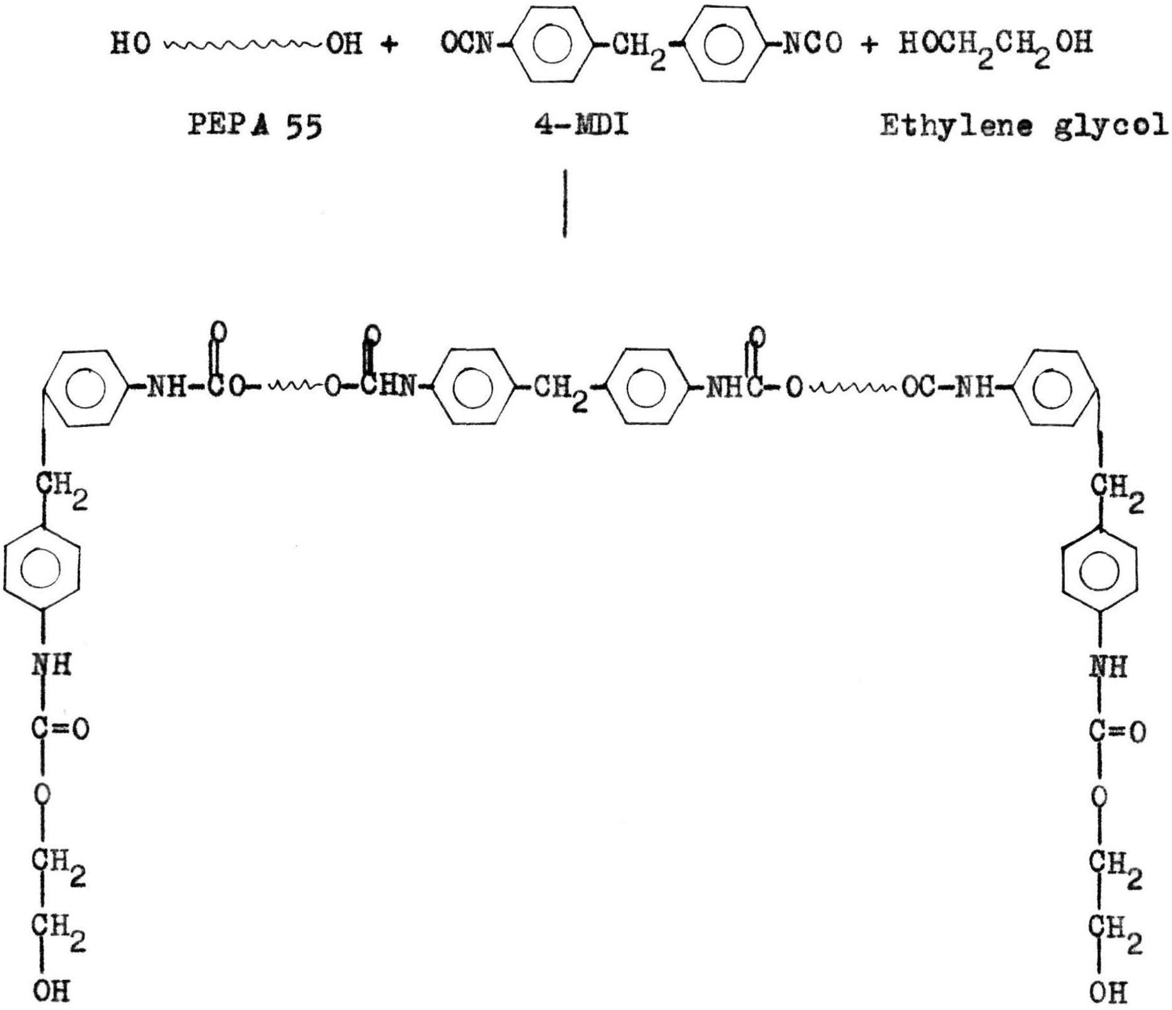
PEPA 55

4-MDI

This was obtained from Farbenfabriken Bayer A.G.(W.G.) in the form of flakes and was distilled just before use.

Preparation of urethane elastomer

The polymer was prepared by reacting 1 equivalent of PEPA 55 with 1.2 equivalent of MDI and 0.2 equivalent of ethylene glycol. The gum obtained was white, soft in the beginning and became hard after keeping it for some days at ambient temperature.



Polyurethane

Compounding of polymers

The polyurethane prepared was easy to process on a rubber mixing mill. The compounding recipes are given in Table-25.

Table-25: Compounding recipe

	Compound A	Compound B
Polymer	100	100
Stearic acid	0.5	0.5
SRF black	30.0	30.0
4-MDI	-	10.0
3-SDI	10.0	-

The compounds A and B were studied rheometrically. The description in brief, of rheometer used and its working is given in Section 2 of this part.

Vulcanization was carried out immediately after compounding and also after resting the compounded stocks for 24 hours at ambient temperatures. The temperatures used for vulcanization were 140°C and 160°C. The results obtained are given in Tables 26, 27, 28 and 29. These data were calculated from rheometric curves shown in Fig.XIX, XX XXI and XXII respectively. The meaning of each parameter in Tables 26, 27, 28 and 29 is given in Table-31.

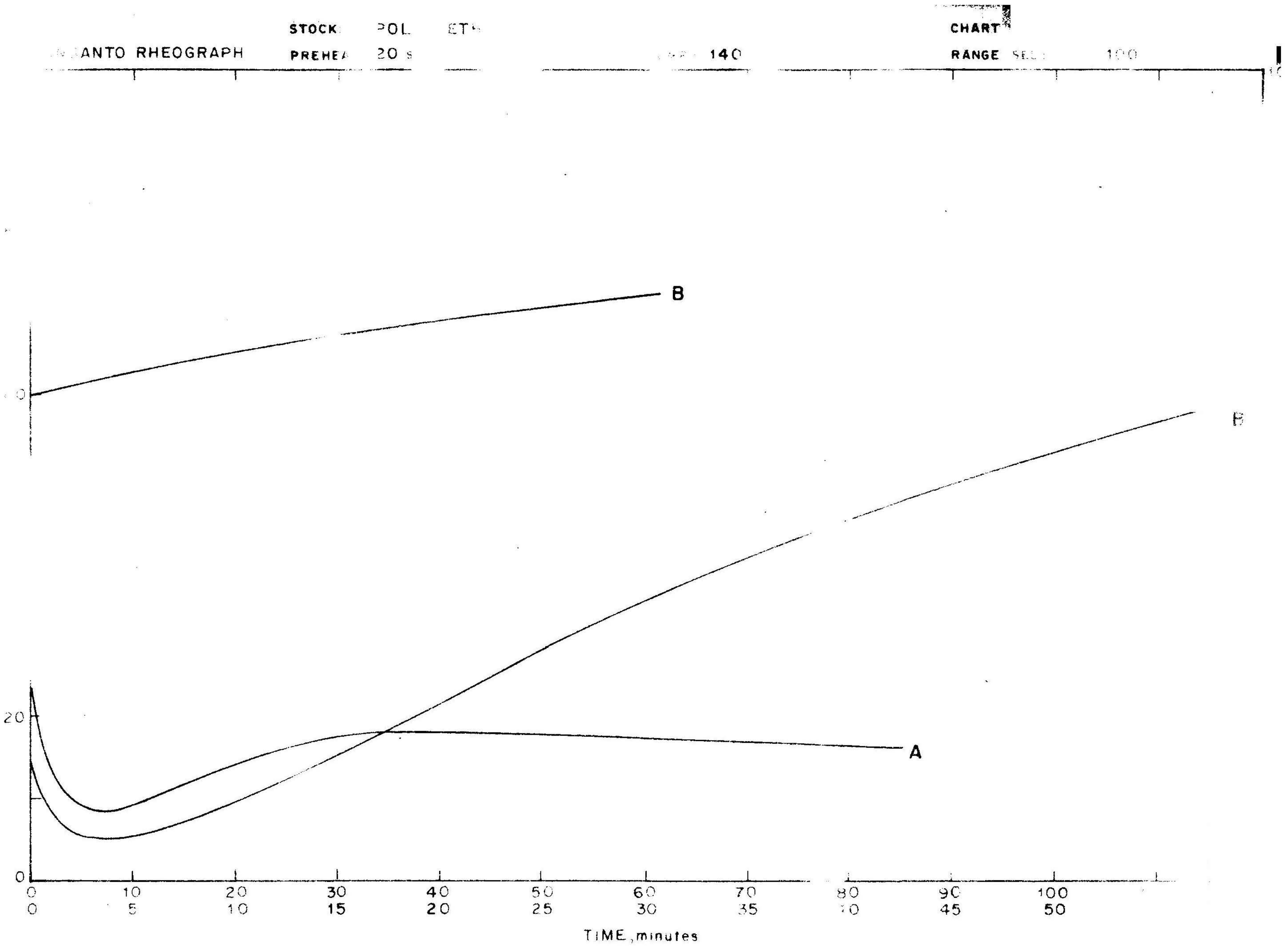


FIG. XIX. RHEOMETE CURVES FOR DIFFERENT POLYURETHANE COMPOUND
OBTAINED MEDIATELY AFTER MIXIN

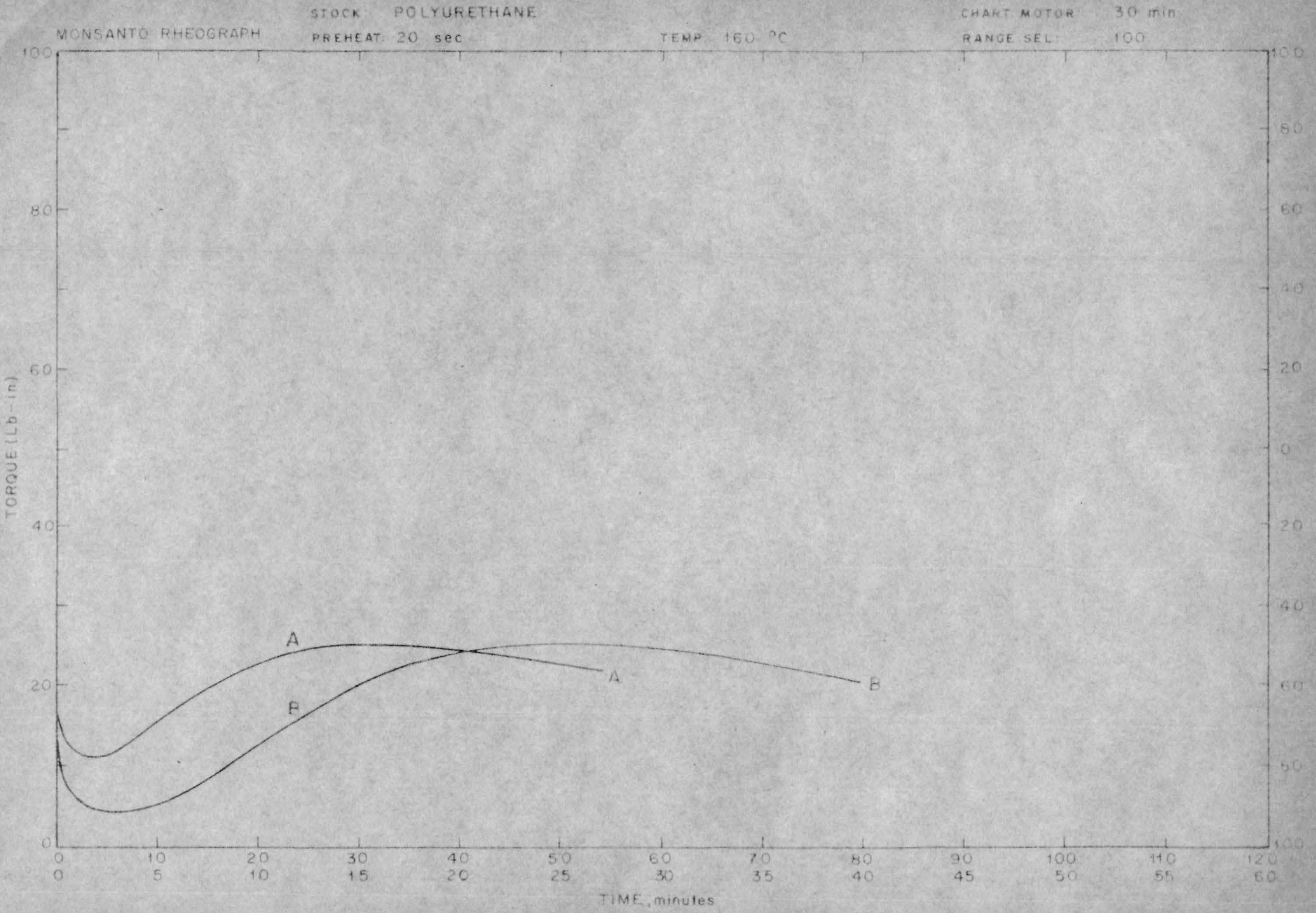


FIG. $\overline{XX}$ RHEOMETER CURVES FOR DIFFERENT POLYURETHANE COMPOUNDS OBTAINED IMMEDIATELY AFTER MIXING

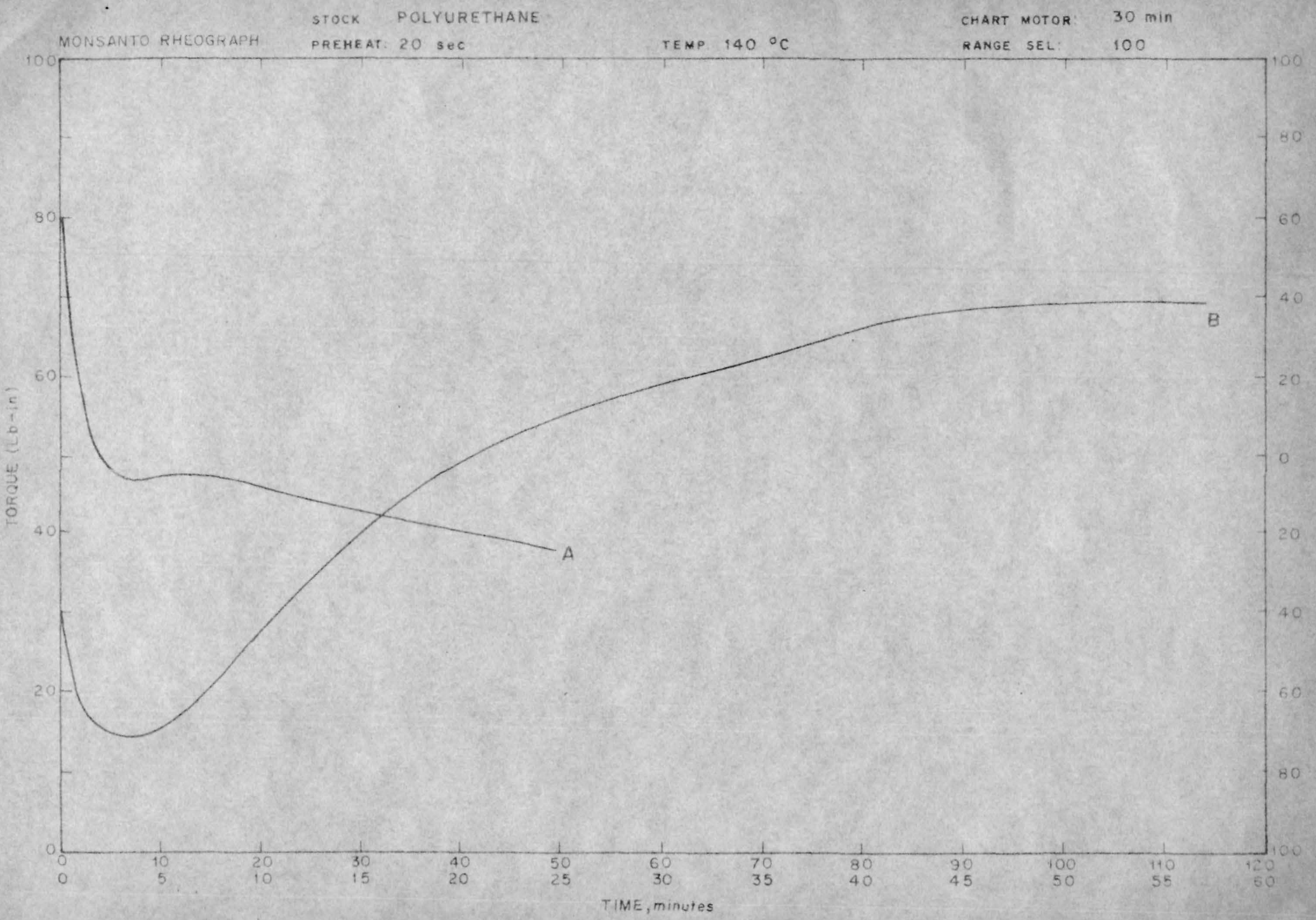


FIG. XXI RHEOMETER CURVES FOR DIFFERENT POLYURETHANE COMPOUNDS OBTAINED AFTER CONDITIONING FOR 24 HOURS AT ROOM TEMPERATURE

Table-26: Parameters obtained at 140°C vulcanization (immediately after compounding)

Stock	Polyurethane rubber compound
Preheat	20 seconds
Temperature	140°C
Chart Motor	30 minutes
Range Sel	100
Arc ±	3

			Compound	
			A	B
1.	Initial Viscosity	- Lo (lb.in)	25.90	14.60
2.	Minimum Viscosity	- Li (lb.in)	8.90	5.20
3.	Thermoplasticity	- Tp (Lo-Li)	15.00	9.40
4.	Induction time	- ti - time for one unit rise above Li (minutes)	2.60	2.90
5.	Scorch time	- t2 - time for two units rise above Li (minutes)	3.23	3.60
6.	Maximum cure	- Lf (lb.in)	18.10	58.80
7.	Optimum cure	- 0.9 (Lf-Li)+Li (lb.in)	17.18	53.44
8.	Optimum cure time	- t90 (minutes)	7.25	25.50
9.	Cure rate	- CR 100/T90-t2	24.87	4.56
10.	Reversion time	- RT - time to reach 98% LF after passing Lf(minutes)	13.75	-

Table-27: Parameters obtained at 160°C vulcanization (immediately after compounding)

Stock	Polyurethane rubber compounds
Preheat	20 seconds
Temperature	160°C
Chart Motor	30 minutes
Range Sel	100
Arc ±	3

			Compound	
			A	B
1.	Initial viscosity	- Lo (Lb.in)	23.00	12.00
2.	Minimum Viscosity	- Li (lb.in)	11.40	4.60
3.	Thermoplasticity	- Tp (Lo-Li)	11.60	7.40
4.	Induction time	- ti - time for one unit rise above Li (minutes)	1.50	2.50
5.	Scorch time	- t2 - time for two units rise above Li (minutes)	1.85	3.00
6.	Maximum cure	- Lf (lb.in)	25.20	25.20
7.	Optimum cure	- 0.9 (Lf-Li)+Li (lb.in)	23.82	23.14
8.	Optimum cure time	- t90 (minutes)	5.55	9.00
9.	Cure rate	- CR 100/T90-t2	27.02	16.66
10.	Reversion time	- RT -time to reach 98% LF after passing Lf(minutes)	10.00	15.60

Table-28: Parameters obtained at 140°C vulcanization (compounds rested for 24 hours at ambient temperature)

Stock	Polyurethane rubber compound
Preheat	20 seconds
Temperature	140°C
Chart Motor	30 minutes
Range Sel	100
Arc ±	3

			Compound	
			A	B
1.	Initial Viscosity	- Lo (lb.in)	Scorched	38.50
2.	Minimum Viscosity	- Li (lb.in)		15.00
3.	Thermoplasticity	- Tp (Lo-Li)		23.50
4.	Induction time	- ti - time for one unit rise above Li (minutes)		2.58
5.	Scorch time	- t2 - time for two units rise above Li (minutes)		2.85
6.	Maximum cure	- Lf (lb.in)		69.00
7.	Optimum cure	- 0.9 (Lf-Li)+Li (lb.in)		63.60
8.	Optimum cure time	- t90 (minutes)		19.00
9.	Cure rate	- CR 100/T90-t2		6.19
10.	Reversion time	- RT - time to reach 98% LF after passing Lf(minutes)		-

Table-29: Parameters obtained at 160°C vulcanization (compounds rested for 24 hours at ambient temperature)

Stock	Polyurethane rubber compound
Preheat	20 seconds
Temperature	160°C
Chart Motor	30 minutes
Range Sel	100
Arc ±	3

			Compound	
			A	B
1.	Initial Viscosity	- Lo (lb.in)	Scorched	19.80
2.	Minimum Viscosity	- Li (lb.in)		8.00
3.	Thermoplasticity	- Tp (Lo-Li)		11.80
4.	Induction time	- ti - time for one unit rise above Li (minutes)		2.00
5.	Scorch time	- t2 - time for two units rise above Li (minutes)		2.25
6.	Maximum cure	- Lf (lb.in)		24.80
7.	Optimum cure	- 0.9(Lf-Li)+Li (lb.in)		23.12
8.	Optimum cure time	- t90 (minutes)		5.35
9.	Cure rate	- CR 100/T90-t2		32.25
10.	Reversion time	- RT - time to reach 98% LF after passing Lf (minutes)		6.65

DISCUSSION

In the present study, the polyurethane gum was prepared using polyester (PEPA 55), 4-MDI and ethylene glycol. The diisocyanates used for crosslinking were 3-SDI and 4-MDI. The former has been used for the first time and the latter, a standard one, for the purpose of comparison. The reactivity of 3-SDI was found to be much faster than 4-MDI (Part I, Section II) and hence it would be expected to cure the elastomer at a higher rate than that with MDI. This was found to be the case when curing behaviour of both the diisocyanates was studied on rheometer.

After the preliminary study of vulcanization of urethane elastomer with 3-SDI, it was decided to cure the compound immediately after milling instead of allowing it to remain at ambient temperature for 24 hours before vulcanization. Subsequently, the compound of 4-MDI was also cured under similar conditions.

Compound A contains 3-SDI curing system while compound B contains that of 4-MDI. At curing temperature of 140°C, compound B displays overall superior properties (Table-27). Although initial viscosity and thermoplasticity in case of compound A were higher than compound B, scorch delay and maximum cure values for the latter were exceedingly good. The compound B did not show any reversion while compound A, although reverted, showed considerably good reversion time.

When the curing temperature was 160°C, both the compounds showed similar maximum cure properties. However, initial viscosity and thermoplasticity for compound A were superior to that of compound B. Scorch time for compound B was better than compound A. Although both compounds A and B showed reversion, the time required for reversion was 10 minutes for compound A and 15 minutes for compound B.

Vulcanization of compounds A and B was studied also after keeping them at ambient temperature for 24 hours before subjecting to curing in rheometer.

Both at 140°C and 160°C a scorching was observed in compound A and when it was further vulcanized, disintegration of crosslinks was observed (Fig.XXI and XXII). This showed that the diisocyanate had reacted completely, with a very high reaction velocity, with the active hydrogen groups in the urethane elastomer.

Compound B at curing temperature of 140°C, imparted better properties and improved processing conditions when it was kept at ambient temperature for 24 hours.

Initial viscosity and thermoplasticity were considerably increased showing better flow properties. Although scorch time was reduced to some extent, maximum level of cross-linking increased noticeably and optimum cure time also decreased considerably (comparison of compound B in Table-26 and Table-28).

In a similar fashion, initial viscosity and thermoplasticity increased when temperature of 160°C was used for curing (Table-27 and 29). However, no change was observed in the degree of maximum crosslinking. Optimum cure time was decreased but was accompanied by decrease in reversion time.

No rheometric data is found in the literature for comparison of the present data obtained for 3-SDI curing system, in vulcanization of polyurethane rubber.

Conclusion

It can be concluded that 3-SDI does not appear to be an useful curing agent for urethane elastomers when used alone. On the contrary, 4-MDI imparts overall better properties. The fast reactivity of 3-SDI could be made use of, in the speedy vulcanisation of urethane elastomers, if employed in proper combination with either 4-MDI or some other suitable diisocyanate.

EXPERIMENTAL

Preparation of polyethylene polypropylene adipate (PEPA 55)

In a 5 litre 4 necked round bottomed flask, equipped with a nitrogen inlet tube, a thermowell, a mercury sealed stirrer and a distillation condenser, were placed adipic acid (1401.6 ~~140.1~~ g) ethylene glycol (565.~~66~~44 g) and 1,2 propylene glycol (173.48 g). The reaction mixture was heated in a nitrogen atmosphere till the condensation was complete. The heating was done at 160°-170°C for 6 hours, 180°-90°C for 12 hours and 190°-200°C at 1 mm/Hg for 6 hours. The resultant polyester was soft, white, waxy material with hydroxyl number 55 and acid number less than 1.

Preparation of polyurethane elastomer

In a 2 litre enamel pot degassed polyester (495.0 g) was mixed with distilled 4-MDI (75.2 g) and the mixture was slowly heated to 100°C when a clear viscous liquid was obtained. The temperature was maintained at 100°C for 3 minutes and ethylene glycol (3.2 g) was added to the viscous prepolymer. After maintaining the temperature at 100°C for another 2 minutes, the highly viscous polymer was poured in silicon grease coated enamel tray and was cured at 90°-100°C for 17 hours. The white, solid, hydroxy terminated linear polyurethane, thus obtained, was utilised for crosslinking study.

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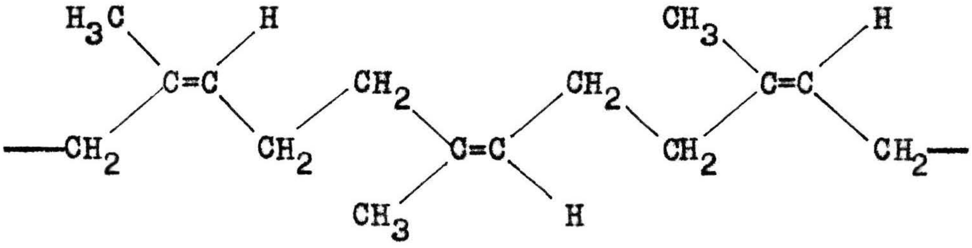
Section-II

NATURAL RUBBER VULCANIZATION

INTRODUCTION

The natural rubber (NR) is cis-polyisoprene:



The vulcanization of NR may be effected with the aid of sulfur, synthetic resins, organic peroxides, ionising radiation and other polyfunctional reagents, and diurethane derivative of a diisocyanate and p-nitrosophenol. Crosslinking of NR is caused by many factors including the opening of double bonds, splitting of labile hydrogen of the α-methylene groups, chain scission accompanied by the formation of polymeric radicals etc. The intermolecular crosslinks, thus, formed, have profound effect on the properties of vulcanizates.

Sulfur vulcanization

Sulfur vulcanization of NR has been reviewed in numerous publications[1-7]. Despite the development of many non-sulfur crosslinking systems for the vulcanization of NR, the sulfur vulcanization has remained the most preferred one for more than a century. Sulfur systems are effective in the presence of most other compounding ingredients like fillers, accelerators, coaccelerators, extending oils, antidegradents etc. Sulfur in the crosslinks may be present as monosulfide, disulfide or polysulfide (Fig.XXIII a) but it may also be present as pendent sulfides (Fig.XXIII b) or cyclic monosulfide or disulfide (Fig.XXIII c).

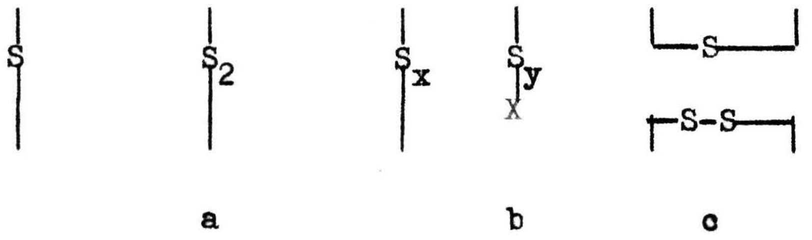


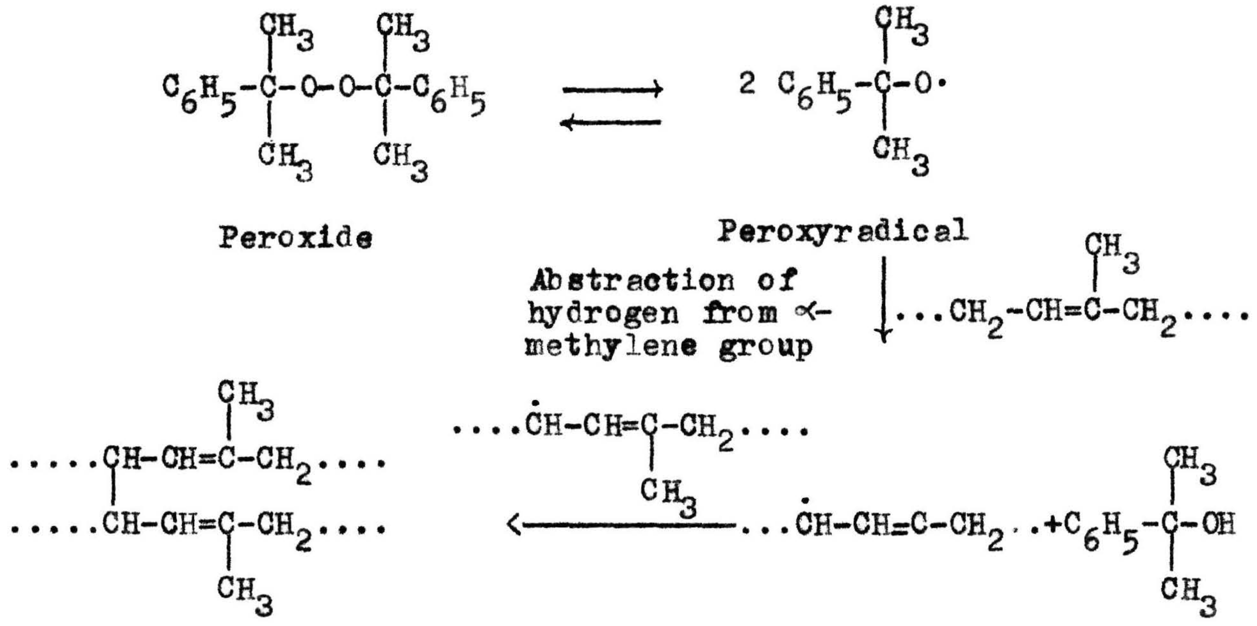
Fig.XXIII.

Vulcanization by synthetic resins

Vulcanization by synthetic resins has been reported in the literature[8-12]. The resins based on 2,6-di(bromomethyl)-4-methyl phenol, 2,6-di (bromomethyl)-3-bromo-4-methyl phenol etc. are vulcanizing agents while those, based on phenols like o-cresol, o-or p-aminophenol in which only one position (o - or p) is unsubstituted, are not useful in vulcanization. Vulcanization by resins reduces the unsaturation of rubber and eventually increases its heat resistance. The unreacted resin acts as antiaging agent by reacting with rubber peroxides that are formed at higher temperatures and thereby terminating the chain reaction of oxidative degradation.

Vulcanization by peroxides

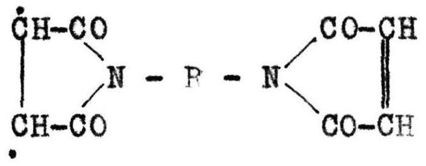
Peroxide crosslinking[13] can be explained by the following example:



Crosslinked polymer.

Vulcanization by ionizing radiation

Crosslinking of NR is also produced by ionizing radiation[14,15]. Radicals produced from bismaleimides of the type:



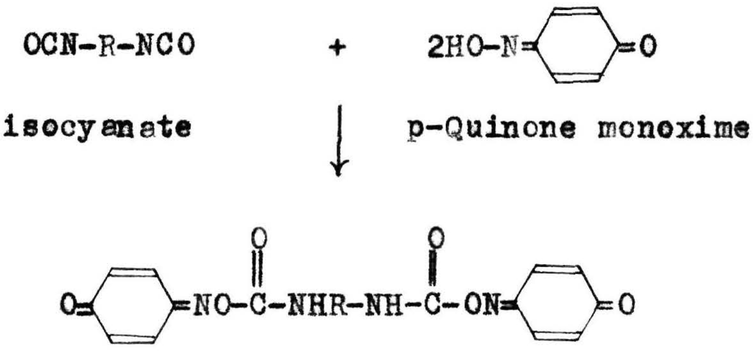
where R = phenylene, hexamethylene, ethylene.

accelerate the ionization induced vulcanization of NR. Bismaleimides, however, do not form homopolyimides in presence of radiation.

Other polyfunctional compounds used for the vulcanization of NR consist of polynitroso compounds, diazoaminobenzenes, bisthiols, bismaleimides, bisazodicarboxylates, and metal ions (for carboxylated NR).

New vulcanization reaction of NR

With the objective of developing newer types of crosslinks which impart excellent strength and dynamic properties with a high resistance to reversion and to changes in structure during service, Baker et al[16] in 1970 introduced a novel diurethane system for crosslinking of NR. They reacted p-nitrosophenol with an aliphatic or aromatic diisocyanate to get an addition compound termed as diurethane. The reaction can be represented as given below:



Diurethane

This system, however, has its limitations due to short scorch time and long cure time. The mechanism, as suggested by Baker et al[16] for the vulcanization of NR by this system is given in Fig.XXIV. It has three critical features:

(i) An oxime/isocyanate adduct 1 is thermally split into its components, quinone-monoxime (p-nitrosophenol)

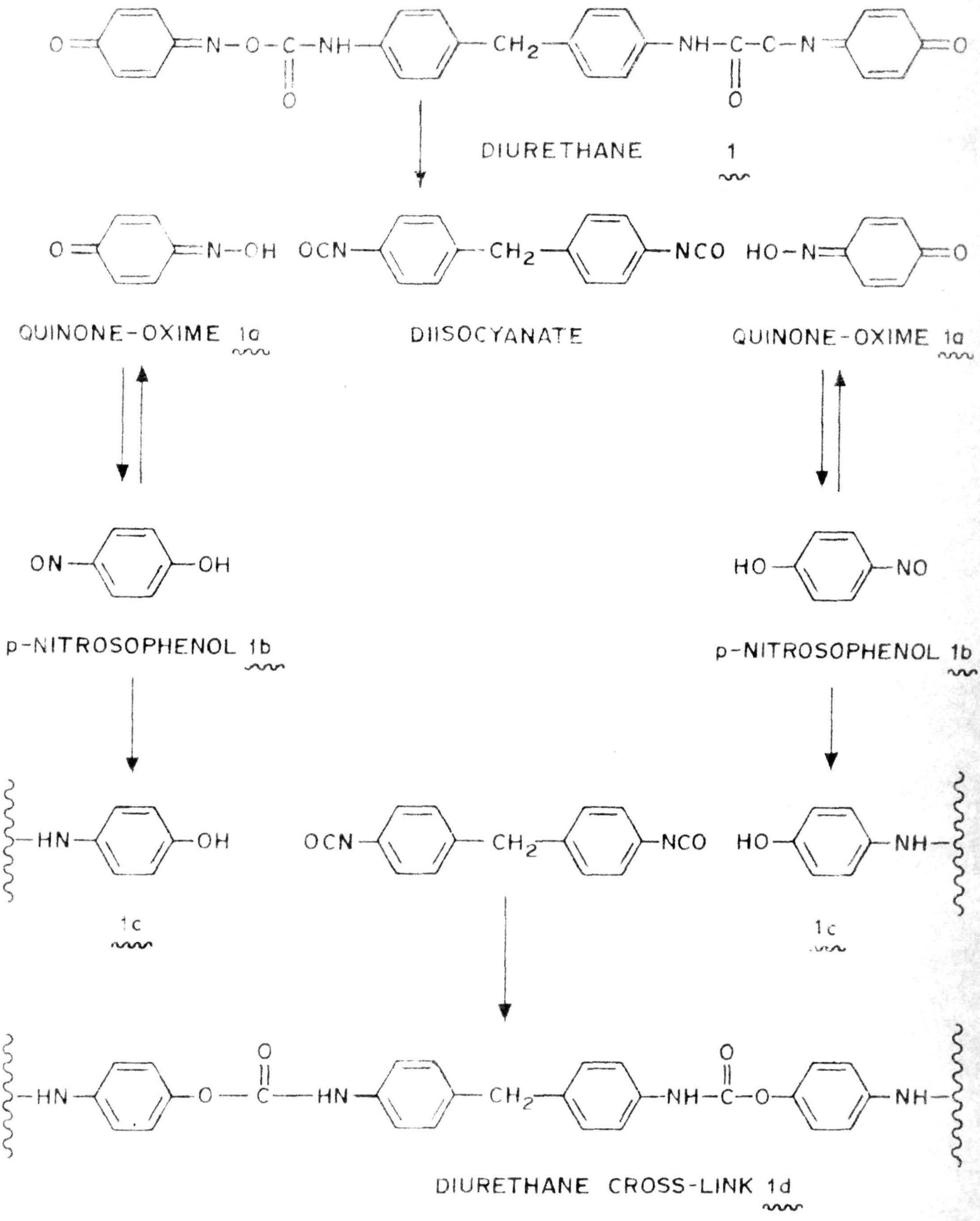


FIG. XXIV BAKER'S REACTION SCHEME FOR THE VULCANIZATION WITH NITROSOPHENOL/DIISOCYANATE ADDUCTS and diisocyanate.

(ii) The reaction of quinone monoxime 1a as its tautomer p-nitrosophenol 1b involves the nitroso group of 1b and introduces a phenol group into the polymer 1c.

(iii) The crosslinking reaction was originally assumed to be based on the reaction of diisocyanate with the phenol group, to give a urethane crosslink, 1d.

Recently, Lautenschlaeger et al[17] have discussed exhaustively the mechanism by which the diurethane participates in the vulcanization of NR. The mechanism proposed by these authors for splitting up of the urethane into different fragments are given in Figs. XXV and XXVI, while those suggested for the eventual crosslinking of unsaturated polymer by reaction with these fragments are given in Fig. XXVII and XXVIII.

Fig.XXV shows the decomposition of phenyl isocyanate adduct of p-nitrosophenol (i) by heating in p-xylene at 130°C. CO_2 gas was eliminated and isolation of diphenyl urea in 15% yield was possible. Diphenyl urea could arise via a cleavage of 1 at bond a, b and c. The resulting intermediate species 2 and 3 would be reactive towards unsaturated polymers. The remaining fragments 4 and 5 would combine to give diphenyl urea 6.

In a similar fashion, ionic splitting of the nitrosophenol/diisocyanate adduct 7 (Fig.XXVI) leads to the fragments 8, 9 and 10 to 12. 13 and 14 would be formed by elimination of

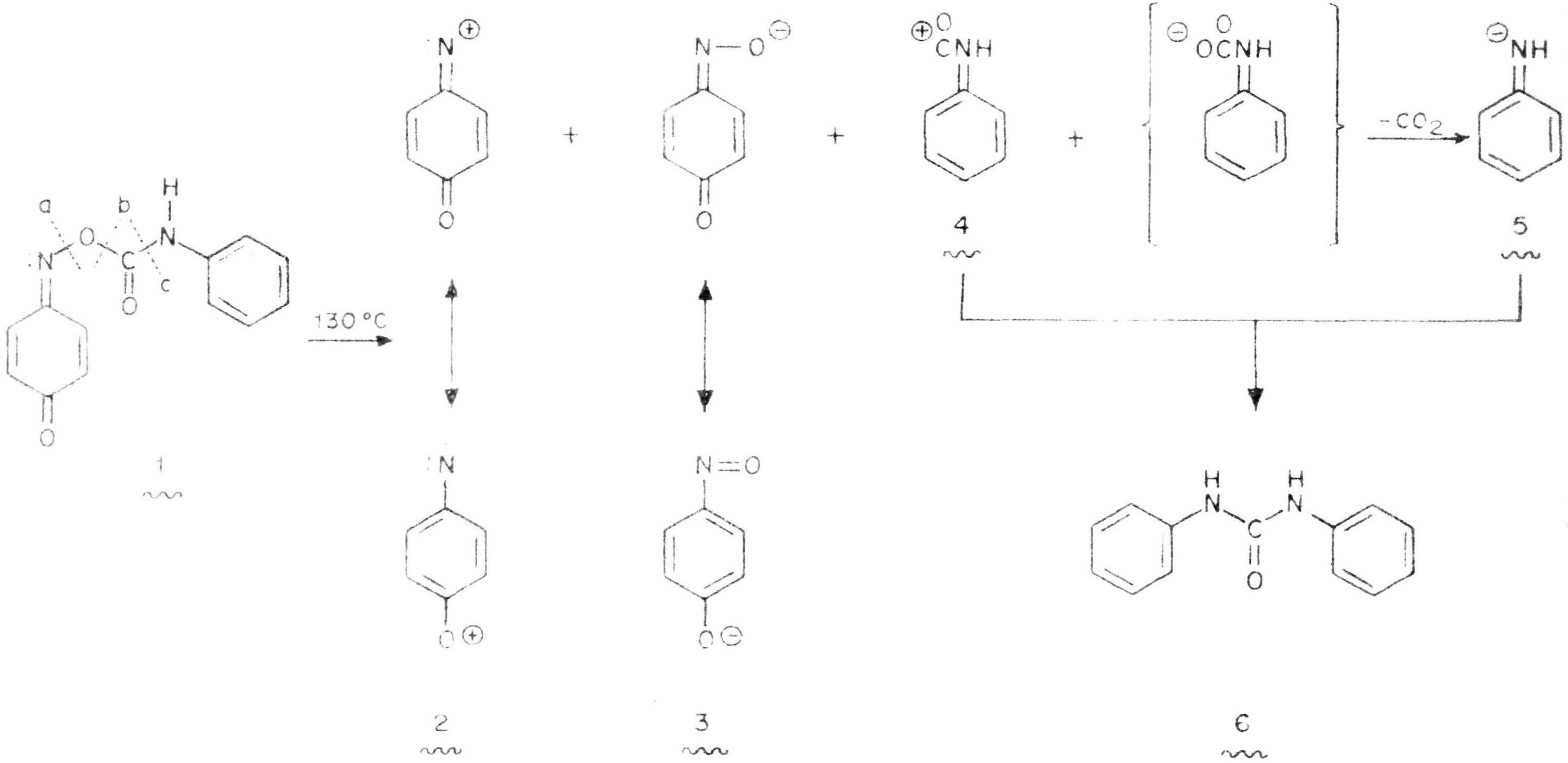


FIG. XXV POSTULATED THERMAL DECOMPOSITION OF AN ADDUCT OF QUINONE-MONOXIME AND PHENYL ISOCYANATE

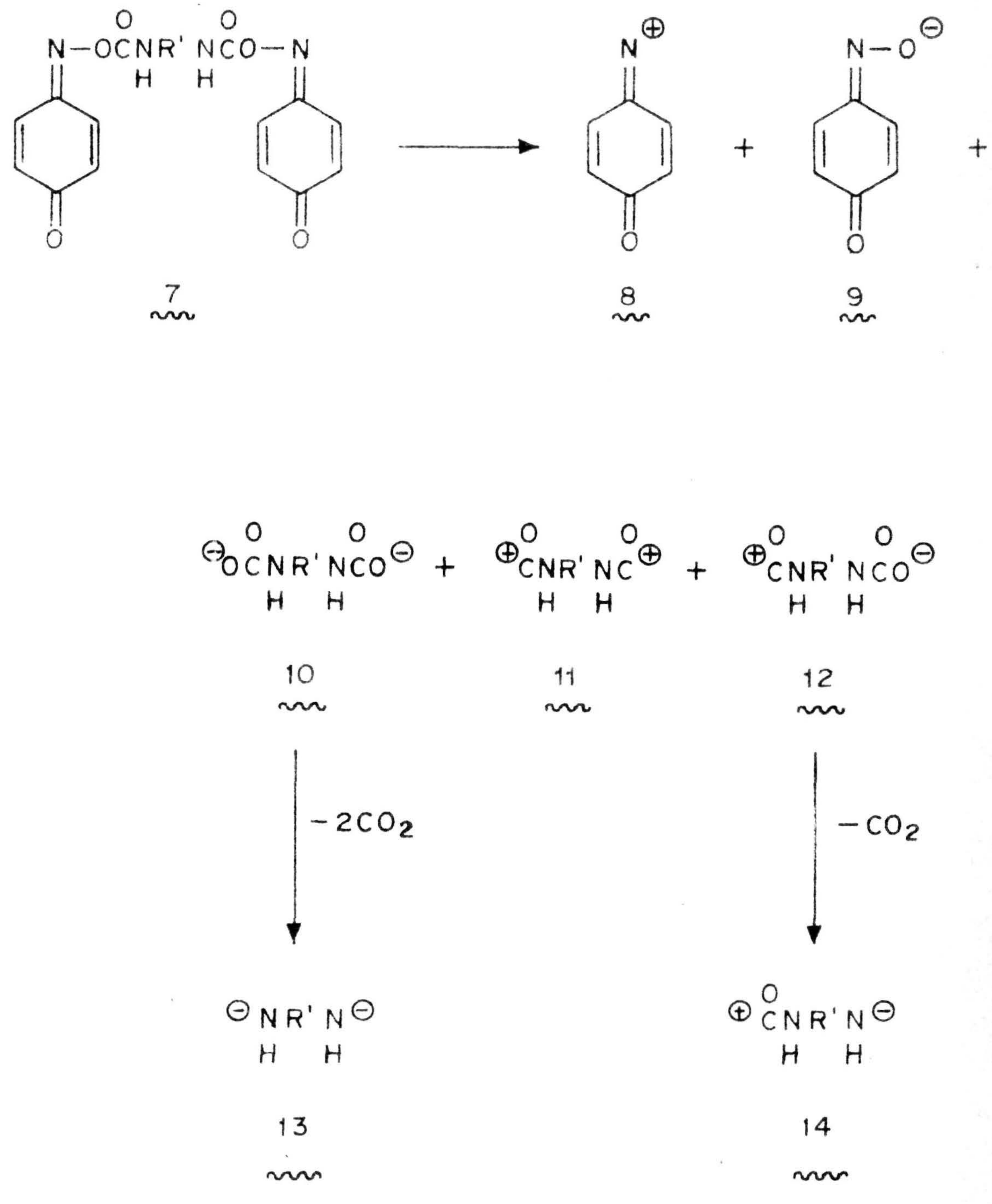


FIG. XXVI THE IONIC DECOMPOSITION OF ADDUCTS OF OXIMES AND ISOCYANATES

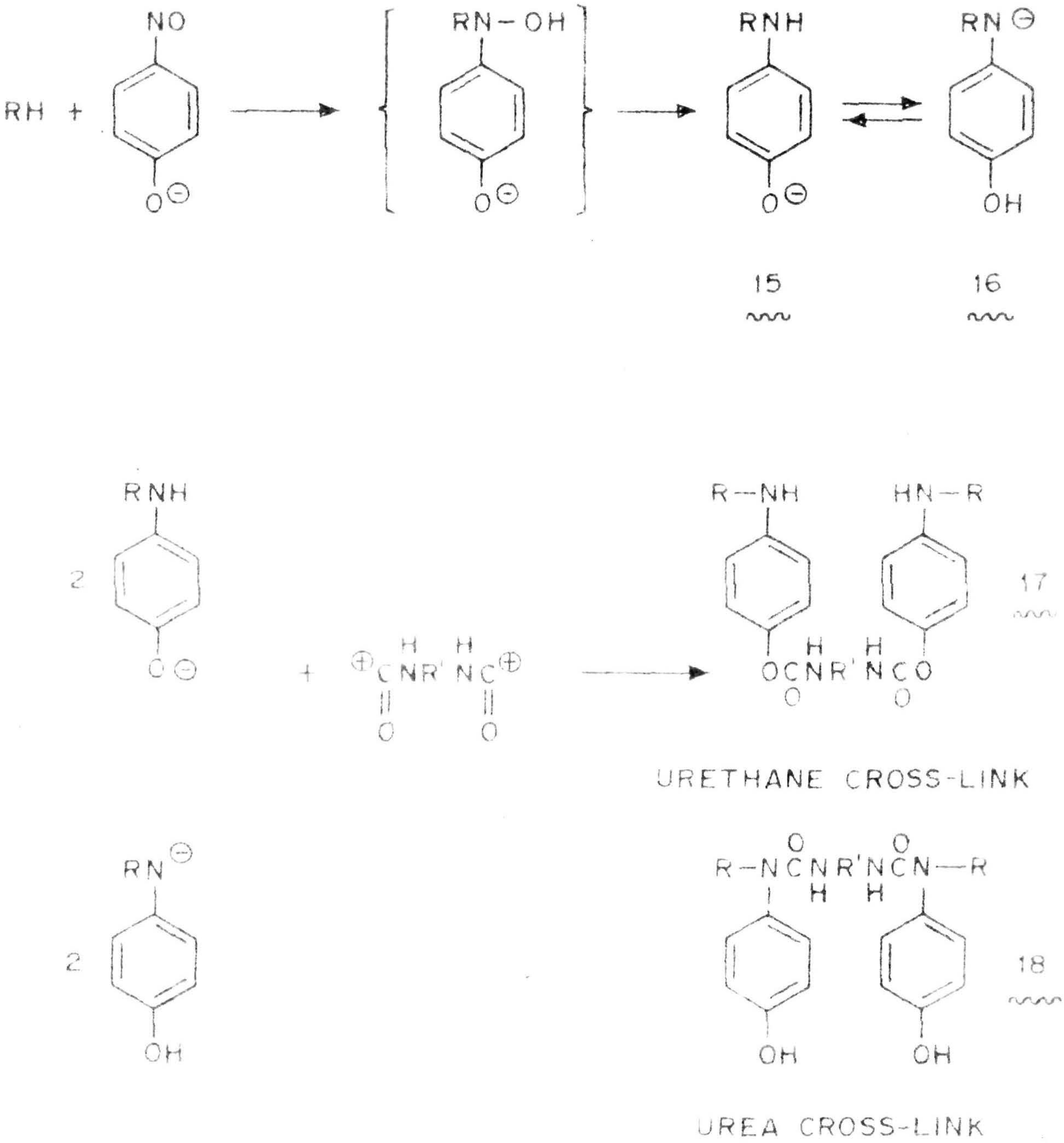


FIG. XXVII THE REACTION OF p-NITROSO PHENOXY ANION WITH UNSATURATED POLYMER

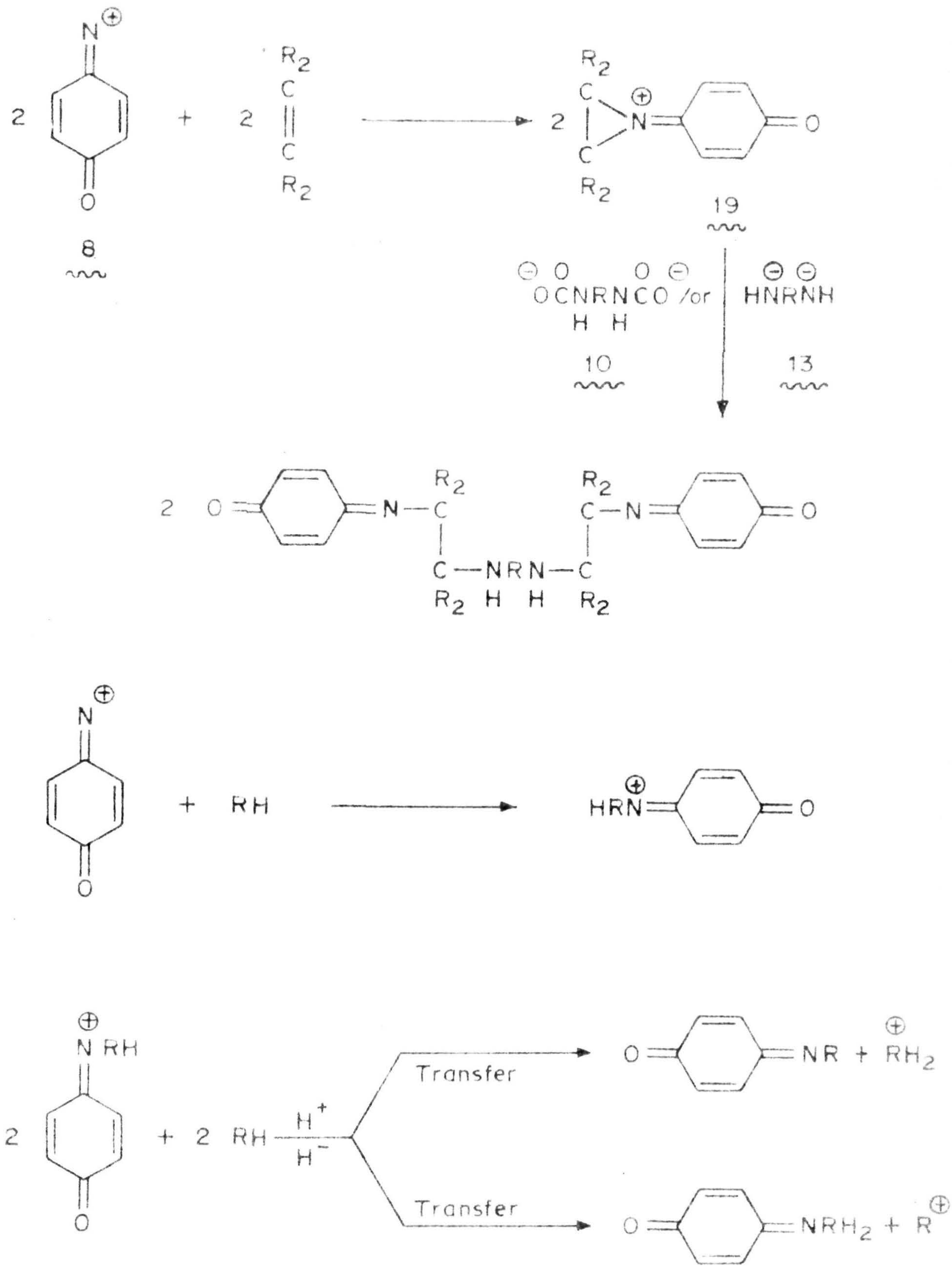


FIG XXVIII THE REACTION OF NITRENIUM ION WITH UNSATURATED POLYMERS

CO_2 gas. The actual proportions of 8 and 9 would depend on the relative stability of the N-O-C bonds in 7. The N-O bonds are assumed to be the weakest, favouring the formation of the electron-deficient species 8.

Fragment 9 can then undergo reaction with unsaturated compounds to give reaction products 15 and 16 (Fig. XXVII) which can combine with 11 to give either urethane 17 or urea 18 crosslink.

The nitrenium ion 8 would react with unsaturated polymer to form cyclic nitronium ion 19 and the overall nucleophilic addition would be completed by the addition of the fragments 10 and 13 to give an amino or urethane crosslink. Alternatively, proton or hydride transfer could lead to simple modification of the polymer by pendent iminoquinone groups accompanied by the formation of reactive polymer. The latter would undergo subsequent reaction with anionic fragments to form additional crosslinks (Fig.XXVIII).

Thus, based on the results obtained after exhaustive investigations, above mechanism proposed by Lautenschlaeger et al[17] set aside Baker's mechanism.

Barnard[17a] has recently reported that the urethane crosslinking systems are not only compatible with ordinary sulfur systems but are synergistic with them, giving more crosslinks than would be expected. Thus, combinations containing equal amounts of the two systems, or richer in urethane, give vulcanizates having very high proportion of thermally stable crosslinks and nearly approaches those of urethane vulcanizates proper. By varying proportions of urethane and sulfur systems, a good balance can be sought between the tailor-made properties of vulcanizates and the cost of the product.

Houghson Chemicals, Lord Corporation in USA, have been licensed by Malaysian Rubber Producers Research Association for world wide manufacture and sale of urethane vulcanizing agents. Houghson is now marketing three urethane reagents in USA and through its agents, in many parts of Europe and elsewhere[17b].

PRESENT INVESTIGATIONS AND DISCUSSION

Modern trends in the rubber industry are aimed at greater productivity and faster throughput by way of shorter curing cycles and higher curing temperatures. Such practice along with stringent conditions of service for resulting vulcanizates, has demanded reversion resistant high strength sulfur systems. As an alternative to the sulfur systems, the development of newer types of crosslinks has been necessitated.

In view of these facts Baker et al[16] and Lautenschlaeger et al[17] studied the vulcanization of NR with diurethanes of p-nitrosophenol with number of diisocyanates. The results of their investigations were encouraging showing the promising nature of the new crosslinking system.

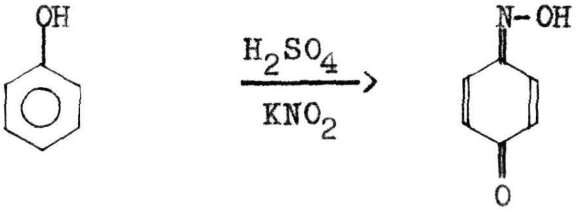
In the present investigation, a new diurethane was prepared from p-nitrosophenol and 3,3'-sulfonylbis (phenyl isocyanate) (3-SDI) and its performance was evaluated in the vulcanization of NR. Diurethane from p-nitrosophenol and 4,4'-methylenebis (phenyl isocyanate) (4-MDI) was also prepared and its vulcanizing action was studied in a similar manner.

IR spectra of the compounds prepared are given in Appendix and the elemental analysis in experimental section.

Synthesis of p-nitrosophenol

p-Nitrosophenol was prepared by the method described by Leonard and Curry[19].

Nitrosation of phenol was carried out both in presence and absence of sodium hydroxide. The product obtained in case of latter experiment was of better quality and the yields were good. The light brown crystalline precipitate which resulted was filtered, washed with water and dried to get p-quinone monoxime. yield 82-85%. m.p. 136°C.



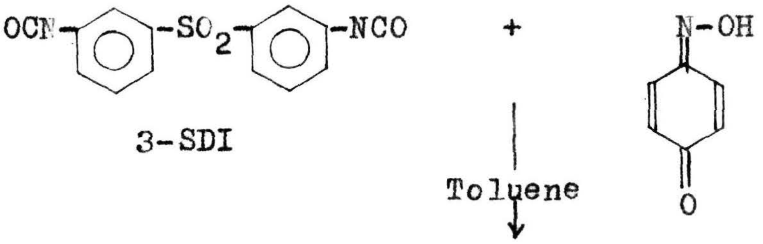
Phenol p-Quinone monoxime

Diurethane of 3-SDI with p-nitrosophenol

3-SDI was prepared according to the method described in Section I, part I.

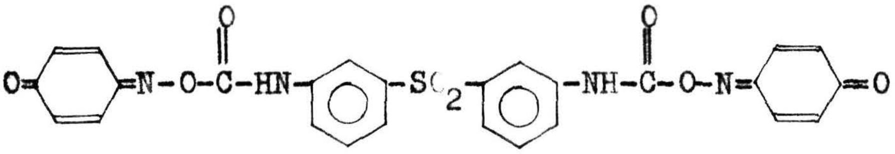
For the preparation of diurethane the procedure described by Baker et al[16] was followed.

p-Nitrosophenol and 3-SDI were reacted in toluene at 100°C to get a greenish yellow diurethane which was washed with toluene and dried. yield 80% m.p. 190°C (decomposed).



3-SDI

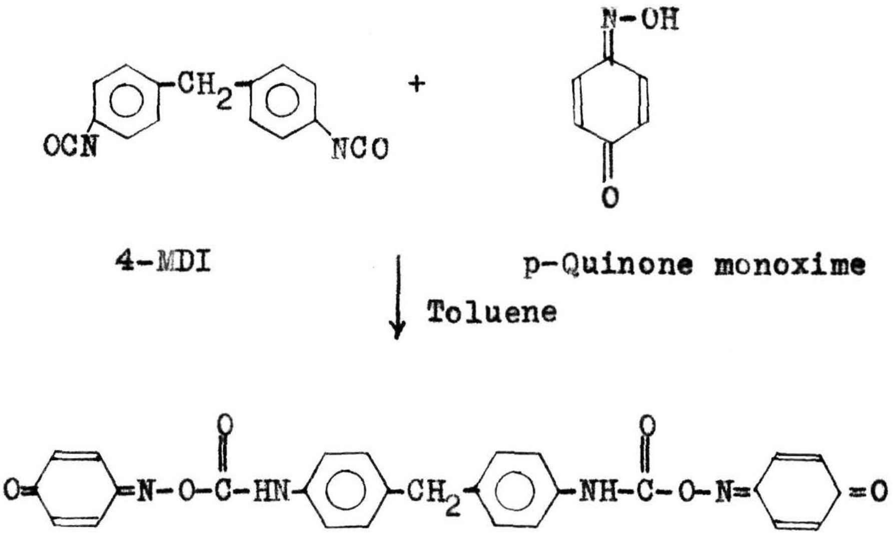
p-Quinone monoxime



Diurethane

Diurethane of 4-MDI with p-nitrosophenol

This was prepared by following Baker's[16] method. p-Nitrosophenol and MDI were reacted in toluene at 100°C to get a yellow diurethane which was washed with toluene and dried. yield 80% m.p. 177°C.



Diurethane

Monsanto Rheometer and evaluation of crosslinking agents

The Monsanto oscillating disc rheometer is a valuable tool for rubber compounding, quality control and research applications. The specifications about the use of this valuable apparatus have been published by American Society for Testing ~~and~~ Materials (A.S.T.M.)[20] and also described in Monsanto Technical bulletin[21]. Although Monsanto Rheometer resembles the Mooney viscometer superficially, it is an oversimplification of the latter.

A brief summary of the method of its operation is given below.

The rubber specimen is placed in a rectangular cavity and has embedded in it a biconical rotor which is oscillated sinusoidally by means of motor driven eccentric. Due to these oscillations a shear strain is exerted on the test specimen and the force (torque) required to oscillate the disc is proportional to the stiffness (shear modulus) of the rubber. The torque is recorded autographically as a function of time.

The stiffness of the rubber specimen increases as cure begins. A complete curve is obtained when the recorder torque either rises to an equilibrium value or to a maximum value. The time required to obtain a cure curve is a function of the test temperature and the curing characteristics of the rubber compound. The following measurements can be taken from a cure curve.

(a) Maximum torque

(b) Time required for incipient cure (scorch time)

(c) Time required for optimum cure or a percentage of full cure, and

(d) Maximum, equilibrium or highest torque attained by a particular cure curve.

The minimum torque is proportional to the stiffness or low shear rate viscosity of the uncured compound. The scorch time is a measure of processing safely. The time to optimum or some percentage of full cure is an inverse measure of cure rate while the fully cured torque is a measure of cured shear modulus or stiffness at the test temperature. The cure rate index is the average slope of the rising cure curves.

All these data are useful in formulating compounding recipe as per requirements of end use properties of the vulcanizates and also in establishing curing conditions.

Evaluation of crosslinking agents

The effect of various proportions of diurethanes per hundred parts of rubber (pphr) on vulcanization was studied. Table-30 describes the six compounds prepared on a laboratory type 6"x12" mixing mill. The compounds 1,2 and 3 contain diurethane of 3-SDI in 5, 10 and 15 parts per hundred parts of rubber while compounds 4,5 and 6 contain diurethane of 4-MDI in 5, 10 and 15 parts per hundred parts of rubber. The compounds 1 to 6 were cured using Monsanto Oscillating disc rheometer Model MPV-900 at temperatures of 150° and 180°C with a proper range selection and suitable chart motor. The curing behaviour of the different stocks were recorded graphically on a flat bed recorder attached to the rheometer[21].

The parameters 1 to 10 with full description of each in rheometric studies of rubber compounds have been given in Table-31.

Table-30: NR tyre tread compound having different proportions of diurethanes

Base stock@

Smoked sheet RMA-IX	100
HAF Black (Philblack)	50
Mineral oil	5
75% Dispersion of CaO in Mineral oil	5
ZDC	2

	SDI Diurethane			MDI Diurethane		
	1	2	3	4	5	6
Diurethane compound	5	10	15	5	10	15

@ Compounds mixed on laboratory type 6"x12" mill.

Table-31: The parameters and their meaning in Rheometer studies

Parameter	Meaning
Initial Viscosity, Lo(in/lb)	Effect of mastication- Time and procedure of milling. Effect of Peptizers
Minimum Viscosity Li(in/lb)	Joint effect of accelerator and processing; characterises flow properties in moulding.
Thermoplasticity, Tp(Lo-Li) (in/lb)	Plastic effect before chemical reaction starts
Induction time, t_1 - time for one unit rise above Li (min)	Time when chemical reaction starts.
Scorch time, t_2 - time for two units rise above Li(min)	Characterises processing safety.
Maximum cure, Lf (in/lb)	Highest crosslinking reached.
Optimum cure, 0.9 (Lf-Li) + Li(in/lb)	Level of cure at which most properties are satisfactory.
Optimum cure, t_{90} (min.)	Time to reach optimum cure level.
Cure rate, CR $100/(t_{90}-t_2)$ (min.)	Comparative value of cure activity.
Reversion time, RT - time to reach 98% LF after passing Lf(min.)	Time to reach noticeable fall in maximum vulcanization level i.e. chain scission

In the initial step, the temperature of vulcanization was chosen to be 150°C which is usually the conventional vulcanization temperature in industrial operations. The rheometric results - parameters of the compounds 1 to 6 at 150°C have been described in Table-32. They were obtained from Fig.XXIX.

From the calculated parameters in Table-32, it appeared that scorch time went on decreasing with increase in the concentration of diurethane compound, in general. Slightly longer scorch delay was observed in case of compounds 1 and 3 as compared to compounds 4 and 6 respectively. Scorch delay in case of compound 2 though less, compared to compound 5, was nearly the same. It was also observed that maximum cure level in case of compounds 2 and 3 was higher as compared to compounds 5 and 6 respectively and that of compound 1 was almost equal to compound 4.

The maximum cure level in 3-SDI-diurethane compounds was found to increase from 29 to 53.5 lb/in. with the increase in the concentration of diurethane from 5 to 10 pphr, while the similar increase in the concentration of 4-MDI-diurethane compounds increased the maximum cure level from 30 to 35 lb/in. only. This difference is quite noteworthy. Optimum cure time in case of both diurethanes increased with increase in concentration. Optimum cure time for compounds 1,2 and 3 was more than that for compounds 4 and 5 and 6 respectively.

In case of 3-SDI-diurethane, the thermoplasticity increased when concentration was increased from 5 to 10 pphr,

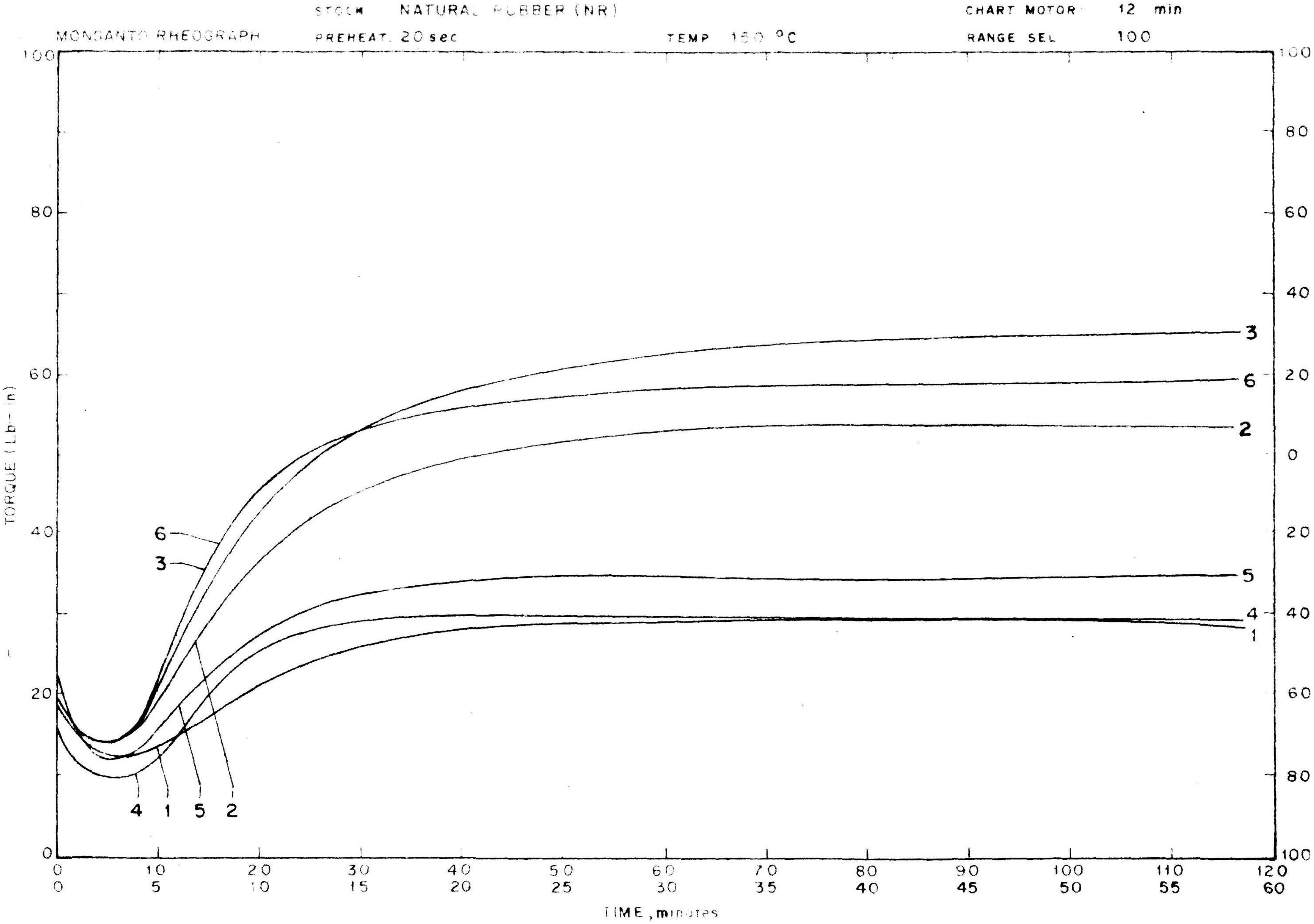


FIG. XXIX RHEOMETER CURVES FOR DIFFERENT NR COMPOUNDS OBTAINED AFTER CONDITIONING FOR 24 HOURS AT ROOM TEMPERATURE

Table-32: Parameters obtained at 150°C vulcanization

Stock	NR
Preheat	20 seconds
Temperature	$150^{\circ}C$
Chart Motor	30 minutes
Range Sel	100

	1.	2.	3.	4.	5.	6.
1. **Initial Viscosity** - Lo (lb.in)	19.80	23.00	22.5	18.0	19.5	20.50
2. **Minimum Viscosity** - Li (lb.in)	13.00	15.00	14.5	11.0	13.5	15.10
3. **Thermoplasticity** - **Tp** (Lo-Li)	6.80	8.00	8.0	7.0	6.0	5.40
4. **Induction time** - **ti - time for one unit rise** above **Li(minutes)**	2.75	1.93	1.75	2.25	1.9	1.70
5. Scorch time - **t2 - time for two units rise** above Li(minutes)	3.10	2.13	1.97	2.50	2.25	1.87
6. **Maximum cure** - Lf (lb.in)	29.00	53.5	64.5	30.00	35.0	59.00
7. **Optimum cure** - 0.9(**Lf-Li**)+**Li**(lb.in)	27.40	49.65	59.5	28.10	32.85	54.60
8. **Optimum cure time** - **t90 (minutes)**	9.25	10.4	11.62	6.20	7.75	8.55
9. **Cure rate** - CR 100/T90-t2	-	-	-	-	-	-
10. **Reversion time** - RT - **time** to **reach** 98% after passing Lf(minutes)	-	-	-	-	-	-

but remained constant even on further increase in the concentration to 15 pphr. However, the thermoplasticity was found to decrease with increase in concentration, in case of 4-MDI-diurethane.

No reversion was observed in all the compounds (1 to 6) at 150°C.

High temperature cures have been considered an attractive proposition. However, vulcanization of NR at higher temperatures imparts inferior qualities on the final product due to reversion. This aspect was studied by vulcanization at higher temperatures (i.e. 180°C).

The Rheometric results - parameters of the compounds 1 to 6, at 180°C obtained from Fig.XXX, have been given in Table-33.

No compound was found to be stable towards reversion at 180°C. The parameters in Table-33 indicate that the reversion time in case of compounds 1,2 and 3 was considerably good as compared to compounds 4,5 and 6 respectively. Although the scorch delay was better in all the six cases, compounds 1 and 3 showed little effectiveness in delaying scorch time over compounds 4 and 6 respectively.

Maximum cure was found to increase with increase in diurethane concentration, in general.

However, the maximum cure in compounds 1, 2 and 3 was higher than in compounds 4, 5 and 6 respectively. The maximum cure level in 3-SDI-diurethane compounds was found

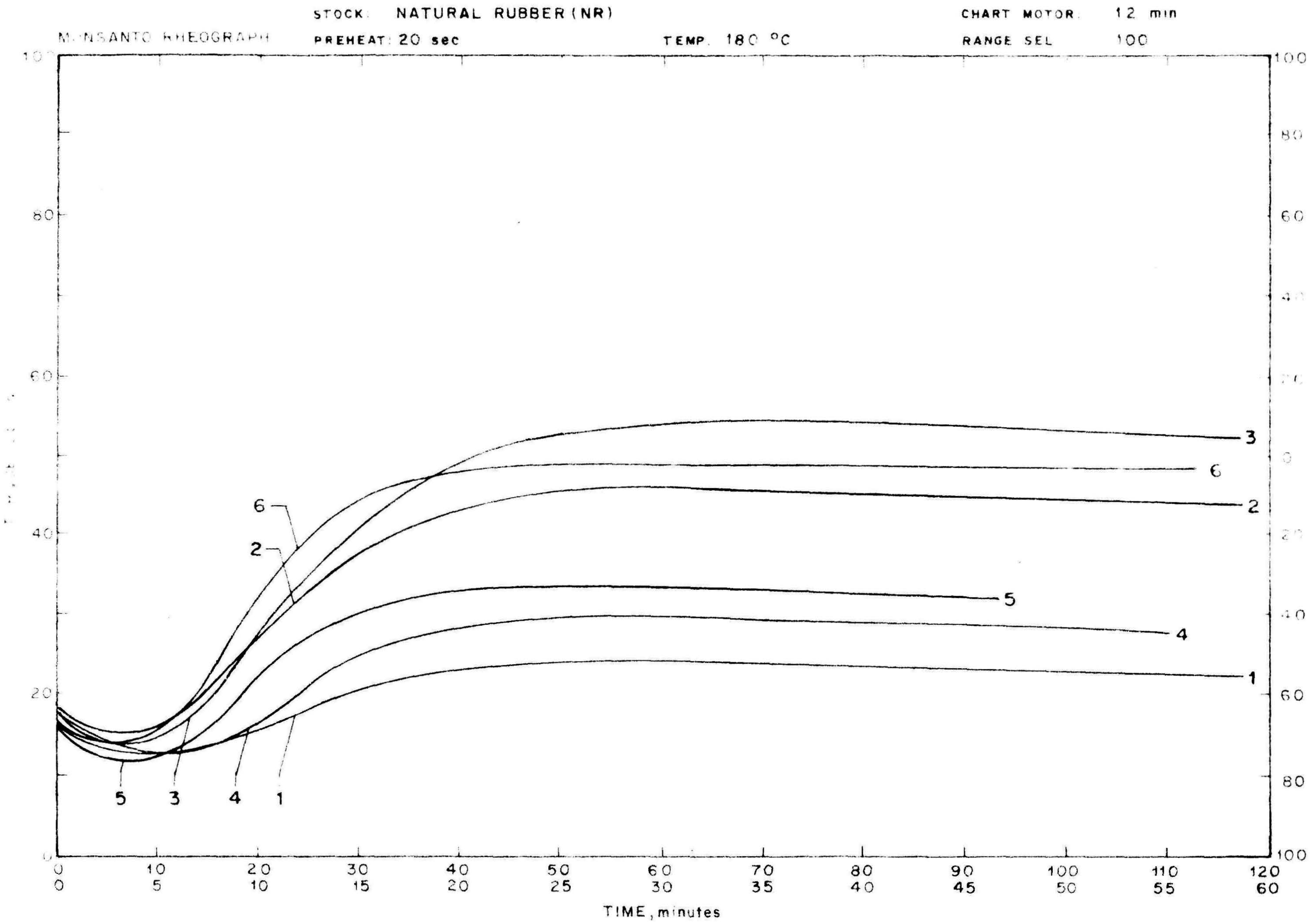


FIG: XXX RHEOMETER CURVES FOR DIFFERENT NR COMPOUNDS OBTAINED AFTER CONDITIONING FOR 24 HOURS AT ROOM TEMPERATURE

Table-33: Parameters obtained at 180°C vulcanization

Stock	NR
Preheat	20 seconds
Temperature	180°C
Chart Motor	12 minutes
Range Sel	100

	1.	2.	3.	4.	5.	6.
1. Initial Viscosity - Lo (lb.in)	19.00	20.20	20.00	18.10	17.50	20.40
2. Minimum Viscosity - Li (lb.in)	13.00	16.00	14.80	13.10	12.80	13.80
3. Thermoplasticity - Tp (Lo-Li)	6.00	4.20	5.20	5.00	4.70	6.20
4. Induction time - ti - time for one unit rise above Li (minutes)	1.60	1.10	1.08	1.60	1.17	1.00
5. Scorch time - t2 - time for two units rise above Li (minutes)	1.85	1.22	1.22	1.80	1.31	1.12
6. Maximum cure - Lf (lb.in)	24.70	46.00	54.00	29.10	33.10	48.20
7. Optimum cure - 0.9(Lf-Li)+Li(lb.in)	23.53	43.00	50.08	27.50	31.07	44.76
8. Optimum cure time - t90 (minutes)	3.84	3.85	4.10	3.68	3.20	3.16
9. Cure rate - CR 100/T90-t2	-	-	-	-	-	-
10. Reversion time - RT - time to reach 98% after passing Lf(minutes)	7.50	9.40	11.00	7.40	7.00	9.20

to increase from 24.7 to 46 lb/in. when the concentration of diurethane was increased from 5 to 10 pphr. while for increase of similar concentration in case of 4-MDI-diurethane, cure level was found to increase from 29 to 33 lb/in. only. This observation was similar to that noted in case of the compounds vulcanized at 150°C.

Optimum cure time for compounds 1, 2 and 3 was found to be little higher than compounds 4,5 and 6 respectively.

Conclusion

3-SDI-diurethane imparts overall better properties on the crosslinked NR as compared to 4-MDI-diurethane. It can also be said that the crosslinking agents used in the present work have characteristics of good reversion and aging resistance, at vulcanization temperature of 150°C.

EXPERIMENTAL

Synthesis of p-nitrosophenol (quinone-monoxime)

In a 3 litre three necked round bottomed flask equipped with a dropping funnel and an efficient mechanical stirrer were placed phenol (60.0 g), sodium hydroxide (27.0 g) and potassium nitrite (66.8 g). To this mixture 1.5 litres of water was added slowly and the clear solution thus obtained was cooled to -5°C. With efficient stirring of the above solution, concentrated sulfuric acid (150.0 g) in 400 ml water was slowly dropped into it at -5° to 0°C over a period of 2 hours. The stirring was continued for another 2 hours at -3° to 0°C and the solution was then filtered. The brownish crystalline precipitate obtained was washed with 100 to 200 ml of ice-cold water and air dried. yield 55 g.

In another experiment, the nitrosation was carried out following the procedure described above except that the use of sodium hydroxide was totally avoided. This gave the desired product in light yellow colour unlike brownish obtained in the above experiment. The yield obtained was 56 g.

Diurethane of 3-SDI with p-nitrosophenol (quinone-monoxime)

In a 3 necked 250 ml round bottomed flask equipped with a stopper and a mechanical stirrer were placed 3-SDI (3.0 g) and p-nitrosophenol (2.46 g). To this toluene (100 ml) was added and the suspension was heated in an oil bath at 100°C with constant stirring. The greenish yellow adduct, obtained after 20 minutes of heating, was filtered, washed with toluene and dried under vacuum. yield 4.8 g.

Analysis: Calcd.for $C_{26}H_{18}O_8N_4S$: C 57.75%, H 3.29%, N 10.26%
Found: C 57.77%, H 3.78%, N 9.83%

Diurethane of 4-MDI with p-nitrosophenol (quinone-monoxime)

In a 100 ml 3 necked round bottomed flask equipped with an efficient mechanical stirrer were placed 4-MDI (2.5 g) and p-nitrosphenol (2.46 g). To this mixture, 75 ml of toluene was added and the mixture was stirred at 100°C for 20-25 minutes till it gave a pale yellow fawn. This was filtered, washed with toluene and dried under vacuum. yield 4.3 g.

Analysis: Calcd.for $C_{27}H_{20}O_6N_4$: C 65.31%, H 4.03%, N 11.29%
Found: C 65.50%, H 3.86%, N 10.65%

Rubber compounding

The compounding ingredients were commercial grade rubber chemicals.

(1) High abrasion furnace black (Philblack)
(2) Mineral oil (processing oil)
(3) 75% Dispersion of calcium oxide in mineral oil
(4) Zinc dimethyl dithiocarmate

Mixing

All mixes given in Table-30 were prepared on a conventional laboratory size 6"x12" two roll rubber mixing mill. Rubber was masticated on a cold mill, immediately a band was formed. All the ingredients were then mixed according to the compounding recipes given in Table-30. The crosslinking agent was added at the end. The mix was cut thrice from either side and rolled six times through tight mill and sheeted out. The sheets were kept at ambient temperature for 24 hours before vulcanization.

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