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SYNTHESIS OF DIISOCYANATES, POLYURETHANES AND THERMALLY STABLE POLYMERS

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA,
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

BY

C.V. AVADHANI, M.Sc.

DIVISION OF POLYMER CHEMISTRY,
NATIONAL CHEMICAL LABORATORY,
PUNE 411.008, INDIA

JUNE 1991

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TO
MY BELOVED
PARENTS

DECLARATION

Certified that the work incorporated in the Thesis entitled "Synthesis of Diisocyanates, Polyurethanes and Thermally Stable Polymers," submitted by Mr. C.V. Avadhani, was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged.

S.P. Vernekar

(Research Guide)

29 June 1991

ACKNOWLEDGEMENT

I take this opportunity to express my deep sense of gratitude to **Dr. S.P. Vernekar**, Scientist, Division of Polymer Chemistry, National Chemical Laboratory, Pune, for his inspiring guidance and encouragement during the course of this work.

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Thanks are due to all the Divisional staff members and all the Research Scholars for the willing cooperation extended to me at the various difficult stages of this work.

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C.V. Avadhani

29 June 1991.

C.V. Avadhani.

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ABSTRACT

ABSTRACT OF THE THESIS SUBMITTED TO THE UNIVERSITY OF POONA FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY.

The thesis entitled "**Synthesis of Diisocyanates, Polyurethanes, and Thermally Stable Polymers,**" is divided into five chapters.

Chapter I: Introduction to Diisocyanates

This chapter is an introduction to the diisocyanates - an interesting and fascinating class of monomers. Diisocyanates are unique in that they are highly reactive towards active hydrogen compounds. They find pervasive applications in agriculture, pharmaceuticals, and polymers.[1] This chapter gives an overview of the literature on methods of the preparation, reactions and applications of isocyanates in polymer chemistry.

Chapter II: Synthesis and Characterization of Diisocyanate

Diisocyanates can serve as backbone for a variety of polymers other than the conventional polyurethanes and polyureas. They are used for the preparation of a host of thermally stable polymers. Diisocyanates can be prepared by a variety of routes of which phosgenation of diamines and the Curtius reaction of the diacylazides are important.

This chapter is subdivided into four sections dealing with the synthesis (*via* the Weinstock modification of Curtius reaction) and characterization of the following functional group containing diisocyanates, viz.,

1. Ether group containing diisocyanates:
   α,ω-Bis(isocyanatophenoxy)alkanes and
   Bis[2-(isocyanatophenoxy)ethyl] ether,
2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
4. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides.

In all 28 diisocyanates were synthesized of which 22 are new compounds. The diisocyanates and intermediates involved in their synthesis were characterized by analytical and spectral methods.

Chapter III: Synthesis and Characterization of Diacylhydrazides.

Diacylhydrazides are an important class of condensation monomers, useful in the synthesis of polyhydrazides and poly(amide-imide)s.

This chapter describes the synthesis of four oxyethylene containing diacylhydrazides, viz.,

1. 1,2-Bis(3-hydrazinocarbonylphenoxy)ethane,
2. 1,2-Bis(4-hydrazinocarbonylphenoxy)ethane,
3. Bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether and
4. Bis[2-(4-hydrazinocarbonylphenoxy)ethyl] ether.

The diacylhydrazides were synthesized from the corresponding esters by reacting them with excess of hydrazine hydrate. These were characterized by elemental analysis, IR, NMR and mass spectroscopy.

Chapter IV: Synthesis and Characterization of Polyurethanes.

Important among the industrial polymers are the polyurethanes. These find applications in coatings, adhesives, sealants, binders, fibres, elastomers, foams, etc. These are prepared by the polyaddition reaction of diisocyanates with diols/polyols.[2,3]

In this chapter is described polyaddition reactions of formal, ester and imide group containing diisocyantes, viz.,

1. Ether group containing diisocyanates:
   α,ω-Bis(isocyanatophenoxy)alkanes and
   Bis[2-(isocyanatophenoxy)ethyl] ether,
2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
4. Imide group containing diisocyanates:
   N,N′-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and N,N′-Bis(isocyanatoalkyl)-3,3′,4,4′-benzo phenonetetracarboxylic-3,3′4,4′-diimides,

with aliphatic diols/polyols to obtain polyurethanes containing respective functional groups. These polyurethanes were characterized by viscosity measurements, IR spectra, X-ray diffractograms (XRD), and thermogravimetric analysis (TGA).

Chapter V: Thermally Stable Polymers.

Aerospace, aircraft, electrical and allied industries have given rise to the need for newer thermally stable polymers. Important among these are polyimides, polyamides and poly(amide-imide)s. They possess excellent thermal, mechanical and electrical properties. However, they are difficult to process by conventional techniques, thus restricting their use considerably. The extent to which their properties can be modified depends on the type of structural units incorporated. Of the various approaches adapted to improve upon their processing characteristics, the incorporation of flexibilizing groups, incorporation of meta- linkages and bulky pendant groups along the polymer backbone are important.[4-7]

Consequently, in this chapter the synthesis and characterization of thermally stable polymers with flexibilizing groups in the polymer backbone is discussed. This chapter is subdivided into two subsections.

1. Polyimides:

This section deals with the synthesis and characterization of polyimides containing ether, formal, ester and aliphatic spacers in the polymer backbone.

The following types of diisocyantes, viz.,

1. Ether group containing diisocyanates:

α,ω-Bis(isocyanatophenoxy)alkanes and

Bis[2-(isocyanatophenoxy)ethyl] ether,

2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
4. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides,

were polycondensed in dimethylacetamide (DMAC) with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) to obtain polyimides. These were characterized by viscosity measurements, IR, XRD and TGA.

2. Poly(amide-imide)s:

Poly(amide-imide)s are generally prepared by the reaction of a diamine with an anhydride acid chloride, or by the reaction of a diisocyante with an anhydride acid. These can also be prepared by the reaction of a diacylhydrazide with a dianhydride.

(1) via Diacyl Hydrazides:

Two diacyl hydrazides, viz.,

1,2-Bis(3-hydrazinocarbonylphenoxy)ethane and

Bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether

were polycondensed in DMAc with PMDA and BTDA to yield oxyethylene containing poly(amide-imide)s which were characterized by IR, XRD and TGA.

(2) Formal, ester and imide group containing diisocyantes, viz.,

1. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,

2. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
3. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides

were polycondensed in DMAc with trimellitic anhydride (TMA) to yield poly(amide-imide)s. These were characterized by viscosity measurements, IR, XRD and TGA.

GENERAL REMARKS

- All melting/boiling points are uncorrected.
- IR spectra were recorded on Perkin-Elmer Infra Red Spectrophotometer Model 683 B, as nujol mulls using sodium chloride optics.
- ^{1}H-NMR spectra were recorded using trimethylsilane as an internal standard on either Jeol T 60, Varian FT 80 or Brucker WH-90 spectrometers. All the chemical shift values are expressed in δ or ppm units.
- Mass spectra were recorded using a double focusing spectrometer using direct inlet system at 70 eV.
- Elemental analysis of compounds was carried out by micro-analytical procedure for carbon, hydrogen, and nitrogen.
- The list of references pertaining to a chapter are given at the end of that chapter.

CHAPTER 1

INTRODUCTION TO DIISOCYANATES

1. INTRODUCTION

1.1. HISTORICAL

Isocyanates **(R-N=C=O)** are a fascinating class of organic compounds known since the past hundred and forty years. These compounds are very versatile and are best known by their single largest family of polymers, the polyurethanes.

The first synthesis of an organic isocyanate was reported by Wurtz[1] in 1849, by the reaction of an organic sulfate with a metal cyanate. Later, Gautier[2] confirmed the structure of isocyanate proposed by Wurtz, by the synthesis of isocyanates by the oxidation of aliphatic isocyanides with mercuric oxide. By the pyrolysis of symmetrical diphenyl oxamide, Hofmann[3] prepared the first aromatic isocyanate - phenyl isocyanate. Shortly thereafter, Hentschel[4] developed an alternate route for the synthesis of isocyanates by the reaction of phosgene with the corresponding amines. This has remained a popular method for the commercial manufacture of isocyanates. Lussy[5] is credited for the synthesis of diisocyanates for the first time, while Gattermann and Wrampelmeyer[6] are known for the first synthesis of aromatic diisocyanates.

Isocyanates remained relatively unimportant reactive intermediates until the pioneering work of Staudinger and his coworkers[7], who emphasized the structural similarities of isocyanates and ketenes, and that like ketenes, isocyanates undergo reactions with certain unsaturated compounds.

The applications of isocyantes in synthetic polymer chemistry was not triggered off until the synthesis of polyamide

(Nylon) by Carothers. The initial exploratory and developmental work in the field of isocyanates and polyurethanes was carried out by Bayer and his coworkers[8], who in 1937, developed polyurethanes as a substitute for polyamides. Polyurethanes are prepared by the reaction of an organic diisocyanate with a diol. Polyurethanes can be tailor-made to any desired structure-property performance, and, since their first appearance, polyurethanes have revealed high versatility. Consequently, polyurethanes have one of the widest range of applications: in fibres, elastomers, foams, skins, adhesives and coatings. They also find applications in pharmaceutical and agricultural applications and formulations.

The synthesis of isocyanates[9-21] and the chemistry and technology of polyurethanes[13,22-32] has been a subject of several reviews.

1.2. PREPARATION OF ISOCYANATES

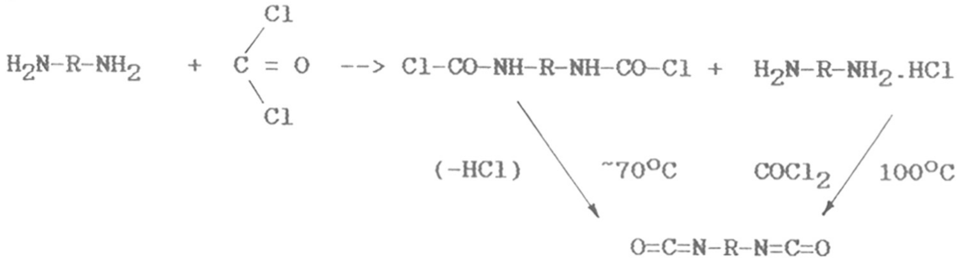
Amongst the several synthetic routes for the preparation of isocyanates, the following are important:

1. Phosgenation of amines,
2. Curtius, Hofmann and Lossen rearrangement,
3. Carbonylation,
4. Double decomposition.

There are some other miscellaneous methods for the synthesis of specific isocyanates.

1.2.1. Phosgenation of Amines

Hentschel´s[4] process of phosgenation of diamines to prepare a variety of diisocyanates is age old and is perhaps the most widely used process for the manufacture of diisocyanates. The method consists of reacting a diamine with a large excess of phosgene in solution below 20°C. A slurry consisting of carbamoyl chloride and hydrochloride of the diamine is obtained which, on heating, results in the formation of the corresponding diisocyanate.



$$H_2N\text{-}R\text{-}NH_2 \quad + \quad \overset{Cl}{\underset{Cl}{C}} = O \longrightarrow Cl\text{-}CO\text{-}NH\text{-}R\text{-}NH\text{-}CO\text{-}Cl \; + \; H_2N\text{-}R\text{-}NH_2.HCl$$

$$Cl\text{-}CO\text{-}NH\text{-}R\text{-}NH\text{-}CO\text{-}Cl \xrightarrow[\sim 70^{o}C]{(-HCl)} O{=}C{=}N\text{-}R\text{-}N{=}C{=}O \xleftarrow[100^{o}C]{COCl_2} H_2N\text{-}R\text{-}NH_2.HCl$$

The diamine may alternately be treated with carbon dioxide or hydrochloric acid to yield a dicarbamic acid or the dihydrochloride, respectively. This stage is followed by phosgenation above 100°C.

Benzene, toluene, xylene, dioxane, ethyl acetate, di- and trichlorobenzenes and nitrobenzene may be used as solvents. Polar solvents like dimethyl sulfoxide and dimethylacetamide are avoided owing to specific interaction these may have with phosgene.

Although phosgenation is by far the most widely used commercial process, it has the following demerits:

1. High toxicity and corrosive nature of phosgene gas and the necessity of energy intensive chlorine,
2. Phosgene itself is prepared from carbon monoxide and

chlorine, and

3. Expensive chlorine gas is involved while inexpensive hydrogen chloride gas is a byproduct.

Nonetheless, the work done on the phosgenation of diamines for the preparation of diisocyanates needs special mention.[9,18,33-40]

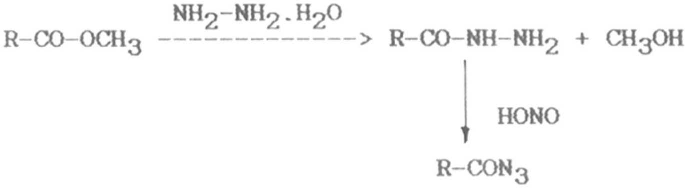
1.2.2. Curtius, Hoffmann and Lossen Rearrangement

A. Curtius Rearrangement

In this method the isocyanate is generated by the decomposition of an acid azide with the concurrent evolution of nigrogen gas in an inert solvent.[41] The method consists of treatment of an acid chloride with sodium azide to obtain the corresponding acylazide which on decomposition gives the respective isocyanate.

$$\text{R-COOH} \xrightarrow{PCl_5/SOCl_2} \text{R-COCl} \xrightarrow{NaN_3} \text{R-CON}_3 + \text{NaCl} \xrightarrow{\triangle} \text{R-N=C=O}$$

Pure acid chlorides are difficult to prepare from acids that are susceptible to either decomposition or undergo isomerization in the presence of mineral acids. In such cases the route, to overcome this difficulty by the conversion of the corresponding ester to the hydrazide and then converting that hydrazide to the azide by the treatment with nitrous oxide, emerges.

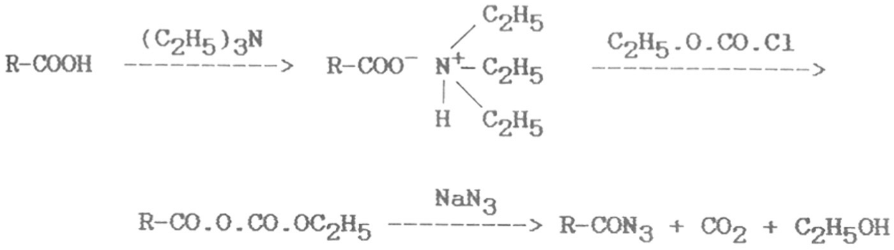


$$\begin{tikzcd} R\text{-}CO\text{-}OCH_3 \arrow[r, dashed, "NH_2\text{-}NH_2.H_2O"] & R\text{-}CO\text{-}NH\text{-}NH_2 + CH_3OH \arrow[d, "HONO"] \\ & R\text{-}CON_3 \end{tikzcd}$$

The route to azide *via* the hydrazide has been enumerated by Curtius[42] although the acid chloride-sodium azide method was known. There are several reviews[43-48] which indicate that acid chloride-sodium azide route is indeed preferable and satisfactory in many cases.

Short chain aliphatic isocyanates, eg., ethylene isocyanate,[49,50] methylene isocyanate[51] and vinyl isocyanate,[52] may all be prepared by the Curtius reaction. Ghatge et al[53,54] reported the synthesis of silicon containing diisocyanates. Smith[55] reviewed the Curtius reaction exhaustively and concluded that aliphatic, alicyclic, aromatic and heterocyclic acids and also saturated and unsaturated acids containing various functional groups undergo Curtius reaction. This method is suitable for many carboxylic acids and is a good method for the preparation of isocyanates.

The Curtius reaction was modified by Weinstock.[56] In essence, it is the reaction of a carboxylic-carbonic anhydride with sodium azide under mild conditions to form the acid azide in an excellent yield.



$$R\text{-}COOH \xrightarrow{(C_2H_5)_3N} R\text{-}COO^- \; \overset{+}{N}H(C_2H_5)_3 \xrightarrow{C_2H_5.O.CO.Cl}$$

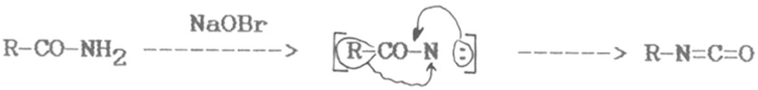
$$R\text{-}CO.O.CO.OC_2H_5 \xrightarrow{NaN_3} R\text{-}CON_3 + CO_2 + C_2H_5OH$$

The use of mixed carboxylic-carbonic anhydride in peptide synthesis and in place of acid chlorides for the preparation of amides and esters of sensitive acids was developed by Evans[57] and Johnson.[58]

Lago[59] claims the preparation of acylazides in high yields. Sulfonyl azides do not rearrange in the Curtius reaction and there are few acylazides that undergo anomolous rearrangement.[60-62]

B. Hofmann Rearrangement

This method consists of the treatment of an amide with sodium hypobromite when a nitrene intermediate is formed. This intermediate rearranges to the respective isocyanate. The only limitation is that this rearrangement is carried out in an aqueous medium.[63]



$$R\text{-}CO\text{-}NH_2 \xrightarrow{NaOBr} \left[R\text{-}CO\text{-}N\,\overset{\cdot\cdot}{}\right] \longrightarrow R\text{-}N{=}C{=}O$$

This is easily overcome by the use of tertiary butylhypochlorite in place of sodium hypobromite. Lead tetraacetate[64] has also been used for the generation of the nitrene intermediate.

C. Lossen Rearrangement

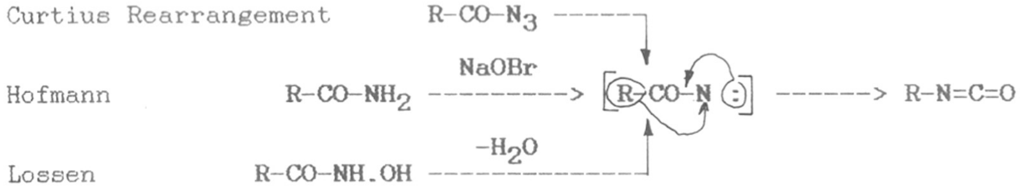
In this method an oxime generates the nitrene intermediate which rearranges to the isocyanate.

$$R-CO-NH.OH \dashrightarrow \left[R-CO-N\ :\right] \dashrightarrow R-N=C=O$$

$$R-CO-NH.CO.R \dashrightarrow \left[R-CO-N\ :\right] \dashrightarrow R-N=C=O$$

Yale[65] has studied the chemistry of hydroxamic acids and the nature of the Lossen rearrangement. Many aliphatic diisocyanates have been prepared by this method.

Briefly, in Curtius, Hofmann and Lossen rearrangements reactive nitrene intermediate is formed.



1.2.3. Carbonylation Method

Isocyanates can be prepared by the direct reaction of carbon monoxide with aromatic nitro compounds. Hardy[66] reported the first synthesis of phenyl isocyanate by this method. The reaction proceeds *via* the reactive nitrene intermediate, the trapping of which with excess of carbon monoxide produces an isocyanate.

By the carbonylation of nitrobenzene at 190°C and 500 atmospheres in presence of rhodium on carbon and $FeCl_3$ or other Lewis acids, phenyl isocyanate may be prepared. Literature[67-79] abounds with reports of the success of carbonylation of nitro compounds for the preparation of isocyanates. Toluene diisocyanate was prepared from dinitrotoluene in about 80% yield.

Full scale commercialization is yet to be achieved. Recovery of expensive catalysts and their recycle pose a challenging situation.

1.2.4. Double Decomposition

This method consists of the reaction of an organic sulfate or halide with a salt of isocyanic acid to yield an organic isocyanate. This method is of historical importance as the first alkyl isocyanate was synthesized by Wurtz[1] by this very method.

$$R_2SO_4 + 2\ KCNO \text{ ---------> } 2\ R{-}N{=}C{=}O + K_2SO_4$$

By this route, Lorenz[80] prepared ethyl isocyanate while Hill and Degnan[81] prepared acyl isocyanates. Inorganic and organometallic isocyanates with -NCO group attached to an element other than carbon have been synthesized employing this method by Anderson et al.[82-84]

1.2.5. Miscellaneous Methods

There are several methods other than those described above that are reported in the literature for the synthesis of isocyanates. Most of these methods are either too cumbersome or too expensive. Nevertheless, these are useful for the synthesis of specific isocyanates.

A. From Furan-N-Oxides or Furoxans

Furoxanes when heated generate the isocyanates[85] *via* the nitrile oxide followed by rearrangement.[86]

Furan-N-oxides may be prepared[87] by the reaction of N_2O_3 with olefins to form a pseudo-nitrosite which on heating rearranges to the furoxan.

Many fancy diisocyanates[88-90] can be prepared by this method. As in the case of blocked isocyanates, urethanes can be prepared at high temperatures without the evolution of by-products.

B. From Ureas

Ureas on phosgenation give isocyanates. This is useful for the synthesis of isocyanates that cannot be obtained by the direct phosgenation of diamines.[9,91-94] This method too would be unlikely to find general acceptance except in special and specific circumstances.

C. From Aminides

Aminides (eg., trimethylamine benzimide) decompose on heating to give isocyanates and tertiary amine.[95] The amine is a catalyst for further reaction and in case of aromatic isocyanates this promotes the trimer formation. Some of these find application in tyre-cord adhesives.[96]

$$C_6H_5\text{-CO-}N^-\text{-}N^+(CH_3)_3 \xrightarrow{\triangle} C_6H_5\text{-N=C=O} + (CH_3)_3N$$

D. From Hydroxamic Acid Halides

In this method an aromatic compound containing one or more methyl or chloromethyl groups is heated with nitrosylhalide using visible or UV radiations as an initiator.[97] Hydroxamic acid halide is formed which can be thermally decomposed to give the isocyanate.

$$\begin{tikzcd}
R\text{-}CH_3 \arrow[r, "NOCl"] & R\text{-}CH{=}N.OH \arrow[r, "Cl_2"] & R\text{-}CCl{=}N.OH \arrow[r, "180^{o}C", "(-HCl)"'] & R\text{-}N{=}C{=}O \\
R\text{-}CH_2Cl \arrow[urr, "h\nu\ /\ NOCl"] & & &
\end{tikzcd}$$

E . From Monothiocarbamates

Aliphatic amine when treated with carbonyl sulfide and triethylamine forms monothiocarbamate salt. The reaction of this salt with S-ethylchlorothioformate produces a product whose decomposition results in an isocyanate.[98]

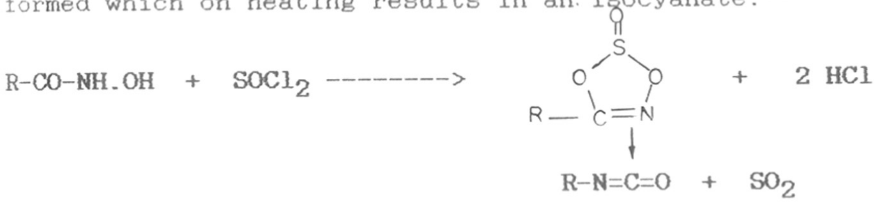
$$R\text{-}NH_2 + O{=}C{=}S + (C_2H_5)_3N \longrightarrow R\text{-}NH\text{-}CO{=}S\ (C_2H_5)_3N^+H$$

$$\xrightarrow{ClCO.S.C_2H_5} R\text{-}NH\text{-}CO\text{-}S\text{-}CO\text{-}S\text{-}C_2H_5 \longrightarrow$$

$$R\text{-}N{=}C{=}O + O{=}C{=}S + C_2H_5\text{-}SH$$

F. From Dioxathiazole S-Oxides

By the reaction of oxalyl chloride or thionyl chloride with hydroxamic acid, 1,3,2,4-dioxathiazole-S-oxide is formed which on heating results in an isocyanate.[99]

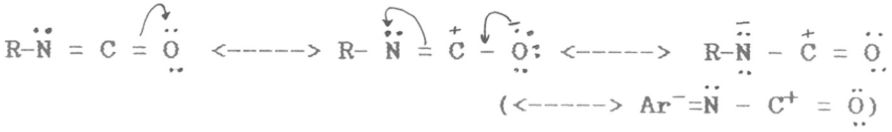


G. ADDITION AND INTERCHANGE REACTION

The addition of isocyanic acid and iodine to olefins affords isocyantes in low to good yields, depending on the reactivity of the olefin. Since isocyanic acid can be obtained from the pyrolysis of either cyanuric acid or urethanes, this reaction will be of importance provided high yields are obtainable.[18]

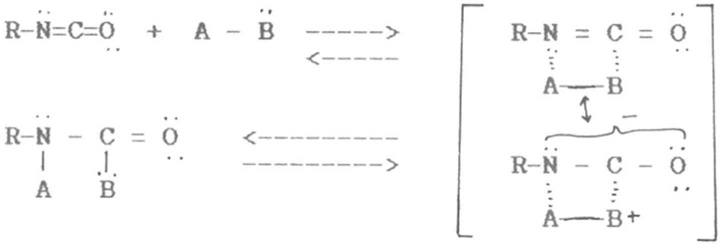
1.3. REACTIVITY OF DIISOCYANTES

Isocyanates belong to the class of heterocumulenes which are characterized by a high reactivity. The reactions of isocyanates arise mainly from the resonance hybrids of the -NCO group.

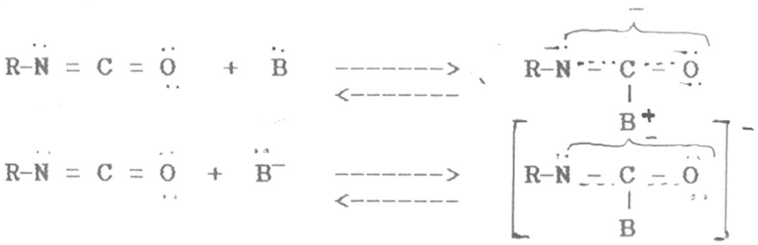


Consequently, there is a pronounced electrophilic character to the C atom of the -NCO group. This is further enhanced by conjugation with the aromatic ring (in case of aromatic isocyanates).

The isocyanate group is particularly prone to attack by nucleophilic agents. Most of the isocyanate reactions occur by the addition of nucleophilic reactants. The H-atom gets attached to the N-atom of the -NCO group while the remainder of the reactant to the carbonyl carbon.



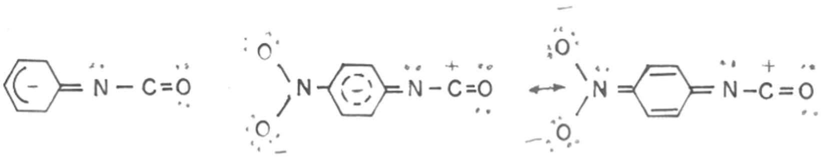
The isocyanate reactions are catalyzed (initiated) by Lewis base (anion) attack.



Catalysis by Lewis acids (protic acids) and metals may be expected by the interactions with nucleophilic N and O atoms. However, in practice, acids display feeble catalytic effect on the isocyanate reaction.

1.3.1 Effect Of Isocyanate Structure

The reactivity of isocyanates arise from the structure and the disposition of various substituent groups. Electron withdrawing (-Cl, NO_2) substituents bonded to an aromatic isocyanate enhance the electrophilicity of the C-atom, and thereby, the isocyanate reactivity both in addition of nucleophiles and in the base promoted processes. The partial positive charge on the C-atom developed makes the nucleophilic attack easier. On the other hand electron donating ($-OCH_3$, $-CH_3$) substituents act in an opposite way making the C-atom more electronegative. This reduces the ability of nucleophilic attack and the reactivity of the isocyanate.[100] Aromatic isocyanates are more reactive than aliphatic and aralkyl isocyanates.[101]



The general reactivity of isocyanates may be

chlorosulfonyl > p-nitrophenyl > phenyl > benzyl > n-alkyl > cyclohexyl > tert. butyl.

The Hammett equation[102] correlates the effect of ring substituents on aromatic isocyanate reactivity on the basis of the reaction rates of variously monosubstituted phenyl isocyanates with 2-ethyl hexanol.

The effect of the isocyanate structure on the reactivity has been studied. Ghatge et al[35,36,38,53,54,103,104] obtained kinetic data from the reaction of various diisocyanates with 2-ethyl hexanol by IR spectroscopy. The effect of the structure of isocyanate and the reactivity was also studied by others.[105-116]

Steric hindrance reduces the isocyanate reactivity. Primary alkyl isocyanates display faster kinetics than secondary which are faster than tertiary ones. Analogous effects are exerted by ortho- substituents in aromatic isocyanates. The combination of such electronic and steric effects can explain the difference of reactivities between two -NCO groups in diisocyanates, especially in aromatic diisocyanates, eg. toluene diisocyanate (TDI).

1.3.2. Effect of Structure of Nuclophilic Agent

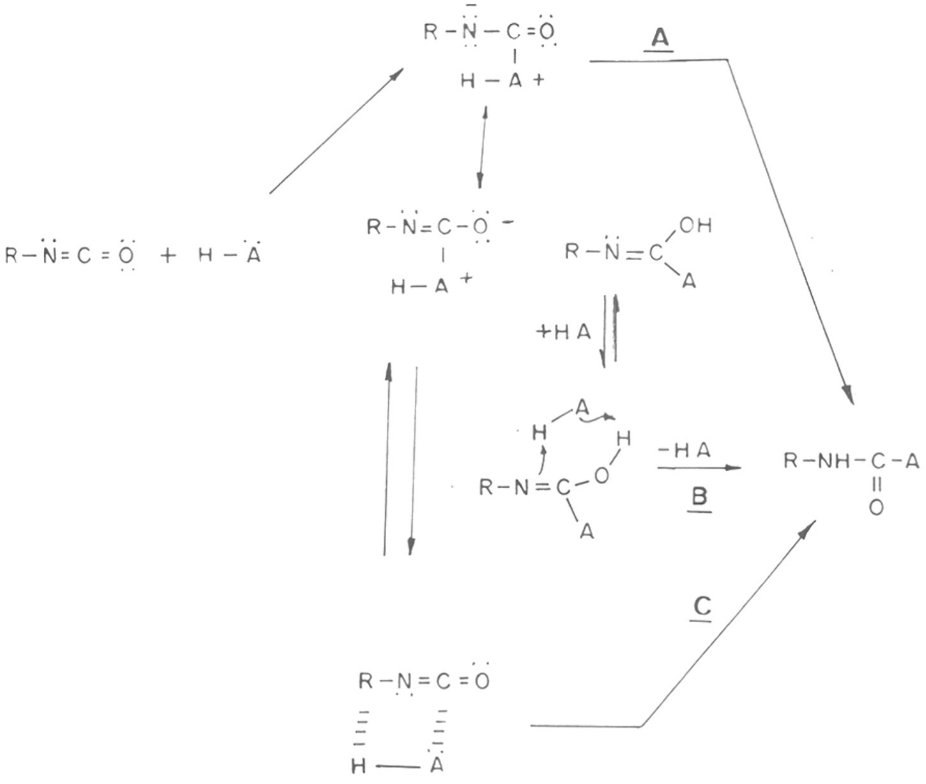
The structure of the nucleophile (eg. alcohol) influences the rate of the reaction.[39,108,109] The steric factors affect the reactivity of alcohol and also influence effectiveness of a catalyst in case of catalyzed reactions. The following order of reactivity[13] can be given:

primary alcohols > secondary alcohols > tertiary alcohols > phenols > thiophenols

The reactivity of an alcohol, unlike the isocyanate, is reduced by electron withdrawing substituents which reduce the basic character of oxygen of the hydroxyl group. Electron donating substituents increase the basic character of oxygen of the hydroxyl group making it more reactive. Hence all active hydrogen containing compounds are electron donors.

1.3.3 (A) Reaction of Protic Nuclephiles

Addition of protic nucleophiles belongs to the class of "insertion" reactions of isocyanates. An uncatalyzed addition follows alternative or coexisting mechanistic pathways (A, B, C):



A is the nuclophilic atom of the reactant.

A broad spectrum of active hydrogen containing nucleophiles, such as, OH (H_2O, ROH, phenols, acids, oximes), SH (H_2S, mercaptans, thiophenols), NH (amines, hydrazines, amides, ureas, urethane), acidic CH (enolizable compounds: malonic acid, acetoacetic ester, nitroalkanes, HCN), and PH (phosphines, hydrogen phosphites) react with isocyanates.

1.3.3 (B) Isocyanate - Alcohol Reaction.

This is perhaps the most studied reaction of isocyanates owing to its commercial importance. Studies on both mono- and diisocyanates show that mechanistically and kinetically, monoisocyanates are the simplest. The first qualitative study of NCO/OH reaction was undertaken by Davis and Farnum[110]. The uncatalyzed NCO/OH reaction has been studied extensively.[101,109-115]

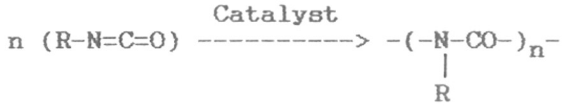
The NCO/OH reaction follows a second order kinetics (reaction rate = K[-NCO] [-OH]) which almost invariably increases during the process due to a moderate catalytic effect of the formed urethane which behaves as a weak base.

Recently, the NCO/OH reaction was monitored by high performance liquid chromatography by Caraculacu et al.[116]

1.4. CHEMISTRY OF ISOCYANATES AND THEIR REACTIONS.

Isocyanates are esters of isocyanic acids. These belong to the class of heterocumulenes,[117] ie., compounds containing cumulated double bonds between atoms one of which, at least, is an element other than carbon (N, O, S, P, etc.). (Examples of heterocumulene systems are ketenes, isothiocyanates, carbodiimides, etc.) The two double bonds on the carbon atom of the -NCO group presage a very reactive system. This unique and intrinsic feature of the isocyanate moiety offers a plethora of different reactions, such as, the high reactivity towards active hydrogen containing compounds, addition to unsaturated systems, Diels Alder reaction, etc., to mention only a few.[28-32] They also undergo a variety of polymerization reactions following either a chain-growth or step-growth mechanism. Some of the reactions are given below.

Mono- or polyisocyanates behave as a monomer in chain polymerization process. The homopolymerization of monoisocyanates[118] in presence of a catalyst gives rise to polyamides (nylon-1),



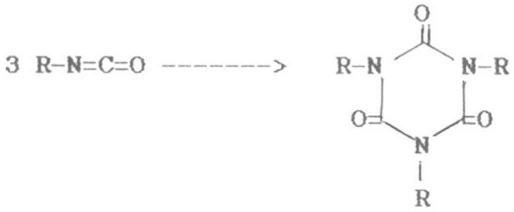
$$n\ (R{-}N{=}C{=}O) \xrightarrow{\text{Catalyst}} -(-\underset{\displaystyle R}{\underset{|}{N}}-CO-)_n-$$

while diisocyanates[119] yield cross linked polyisocyanates,

$$n\ (O{=}C{=}N{-}R{-}N{=}C{=}O) \xrightarrow{\text{Catalyst}} \text{Cross linked polyisocyanate}$$

Aromatic isocyanates easily undergo dimerization[10] at low temperatures in the presence of an acidic catalyst. This equilibrium reaction is easily reversed by heat.

Trimers may also be formed[10] at high temperatures in presence of acidic/basic catalysts.



Certain diisocyanates may undergo copolymerization with certain monomers to yield copolymers. For example, a diisocyante may react with

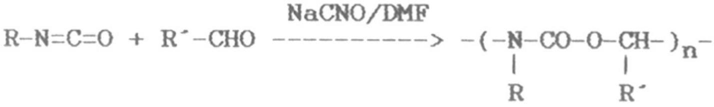
i. an olefin,[120]

$CH_2=CH_2$ + O=C=N-R-N=C=O ------> **NCO TERMINATED COPOLYMER**

ii. a ketene,[121]

$$R{-}N{=}C{=}O + R'_2{-}C{=}C{=}O \xrightarrow{NaCN/DMF} -({-}\underset{\displaystyle R}{\underset{|}{N}}{-}CO{-}O{-}\underset{\displaystyle CR'_2}{\underset{\|}{C}}{-})_n{-}$$

iii. an aldehyde,[122,123]

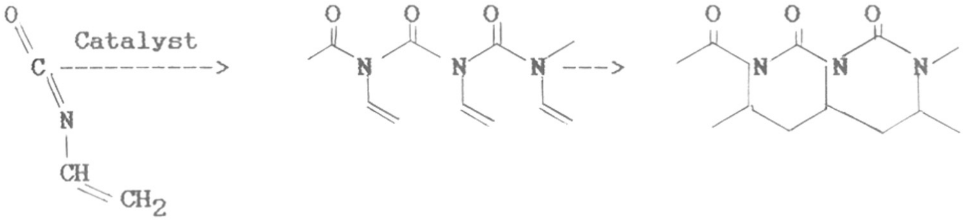


$$R{-}N{=}C{=}O + R'{-}CHO \xrightarrow{NaCNO/DMF} -({-}\underset{\displaystyle R}{\underset{|}{N}}{-}CO{-}O{-}\underset{\displaystyle R'}{\underset{|}{CH}}{-})_n{-}$$

iv. ethylene oxide,[124]

to yield a copolymer in each case.

Cyclopolymerization reactions[125,126] of certain diisocyanates in presence of a catalyst have been reported.



Diisocyanates undergo step-polymerization reaction. The reaction of diisocyanates with

i. Diols to yield polyurethanes,[127]

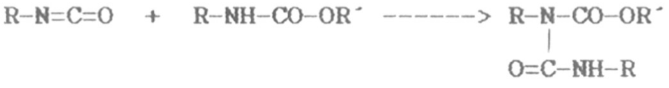
$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad HO{-}R'{-}OH \quad \text{----->} \quad -({-}CO{-}NH{-}R{-}NH{-}CO{-}O{-}R'{-}O{-})_n-$$

and with thiols to yield polythiourethanes.

$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad HS{-}R'SH \quad \text{------>} \quad -\ (CO{-}NH{-}R{-}NH{-}CO{-}S{-}R'{-}S{-})_n-$$

The isocyanate alcohol reaction may be accompanied by the formation of allophanate and biuret linkages, among others.

<u>ALLOPHANATE FORMATION</u>: The reaction of isocyanate with a urethane group forms an allophanate linkage. This leads to branching/crosslinking of the polyurethanes. This reaction can be avoided by the use of moderate temperatures.



$$R{-}N{=}C{=}O \quad + \quad R{-}NH{-}CO{-}OR' \quad \text{------>} \quad \begin{array}{l} R{-}N{-}CO{-}OR' \\ \quad | \\ O{=}C{-}NH{-}R \end{array}$$

<u>BIURET FORMATION</u>: When an isocyanate reacts with urea biuret is formed.

$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad H_2N{-}CO{-}NH_2 \quad {-}{-}{-}{-}{-}{>} \quad -(-R{-}NH{-}CO{-}NH{-}CO{-}NH{-})_n-$$

ii. Diamines to form polyureas,[128]

$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad H_2N{-}R'{-}NH_2 \quad {-}{-}{-}{-}{>} \quad -(-R{-}NH{-}CO{-}NH{-}R'{-})_n-$$

iii. hydrazine hydrate fo form polyurylene,[128]

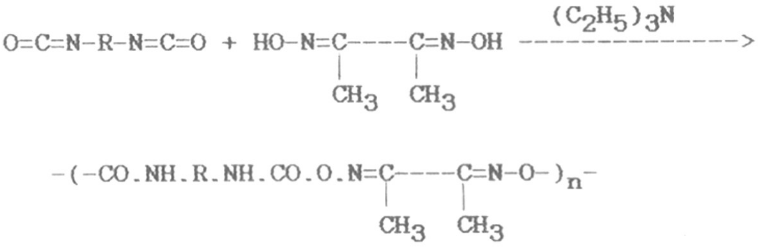
$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad H_2N{-}NH_2 \quad {-}{-}{-}{-}{>} \quad -(R{-}NH{-}CO{-}NH{-}NH{-}CO{-}NH{-})_n-$$

iv. dihydrazides, such as, oxaloyl hydrazide and isophthaloyl dihydrazide to form polysemicarbazides,[130]

$$O{=}C{=}N{-}R{-}N{=}C{=}O \quad + \quad H_2N{-}NH{-}CO{-}R'{-}CO{-}NH{-}NH_2 \quad {-}{-}{-}{-}{>}$$

$$-(R{-}NH{-}CO{-}NH{-}NH{-}CO{-}R'{-}CO{-}NH{-}NH{-}CO{-}NH{-})_n-$$

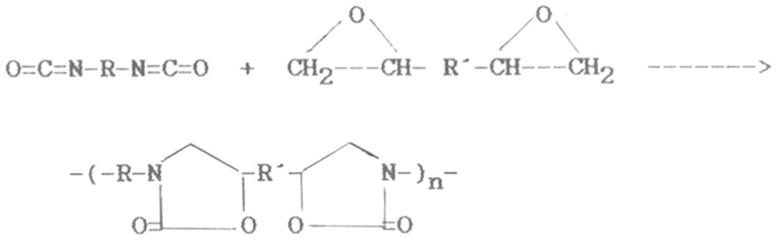
v. dioximes to form poly-o-acyloximes,[129]



$$O{=}C{=}N{-}R{-}N{=}C{=}O + HO{-}N{=}\underset{CH_3}{\underset{|}{C}}{-}{-}{-}{-}\underset{CH_3}{\underset{|}{C}}{=}N{-}OH \xrightarrow{(C_2H_5)_3N}$$

$$-(-CO.NH.R.NH.CO.O.N{=}\underset{CH_3}{\underset{|}{C}}{-}{-}{-}{-}\underset{CH_3}{\underset{|}{C}}{=}N{-}O{-})_n-$$

vi. diepoxides to result in polyoxazolidinones.[131]

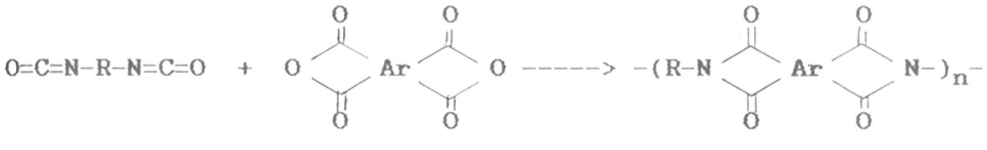


Diisocyanates can undergo step-polymerization reaction with

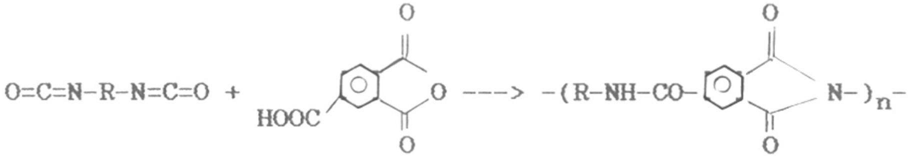
i. dicarboxylic acids[132] to result in polyamides,

$$O=C=N-R-N=C=O \quad + \quad HOOC-R'-COOH \longrightarrow -(-NH-R-NH-CO-R'-CO-)_n-$$

ii. cyclic dianhydrides[133] to give polyimides,



and iii. an anhydride of tricarboxylic acid[134] (eg., trimellitic anhydride to give poly(amide-imide)

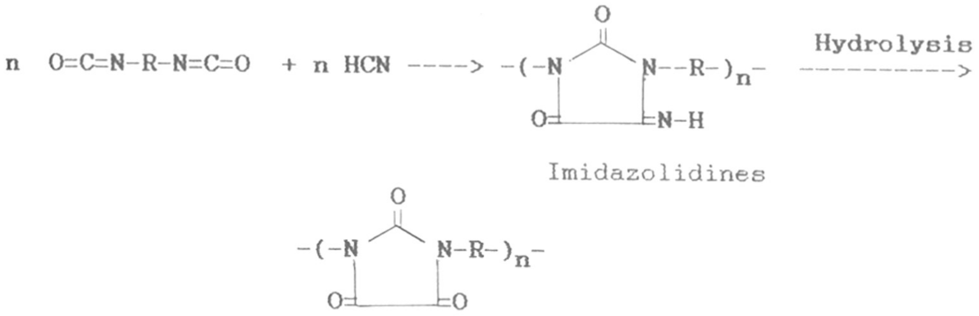


Diisocyanates may directly condense with each other in presence of a catalyst to result in poly(carbodiimide).[135]

$$O=C=N-R-N=C=O \xrightarrow[(-CO_2)]{\text{Catalyst}} -(-R-N=C=N-)_n-$$

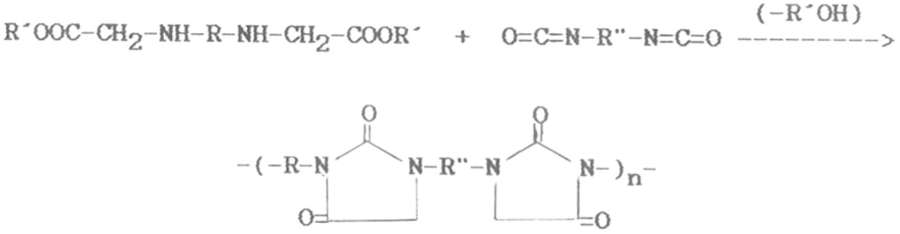
Diisocyanates are also capable of undergoing a two stage addition cyclization polymerization. By the reaction of diisocyanate with

i. hydrogen cyanide, to form polyparabanic acid[136]

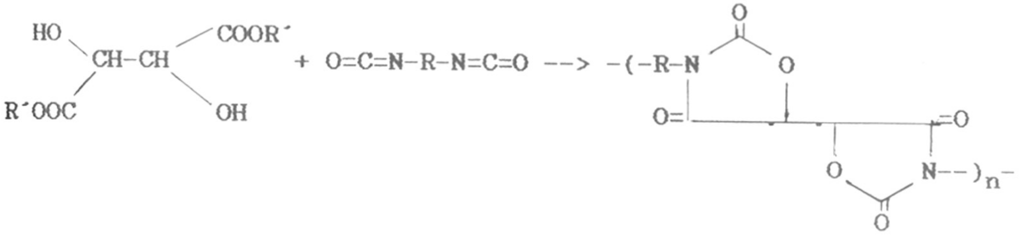


Imidazolidines

ii. bis glycine or di(glycine ester)s result in polyhydantoins,[137]



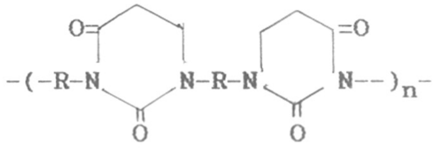
iii. bis(-hydroxy acids) or bis(-hydroxy acid esters), poly(oxazolidinedione)s[138] are formed,



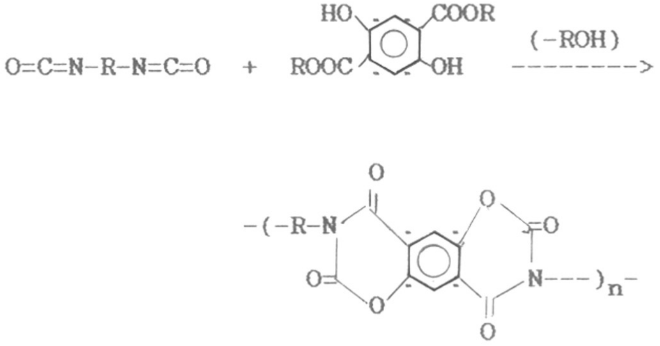
iv. bis(p-aminoether)s results in the formation of poly(hydrouracil)s,[139]

$$H_2N-R-NH_2 \quad + \quad 2\ CH_2=CH-COOR' \longrightarrow$$

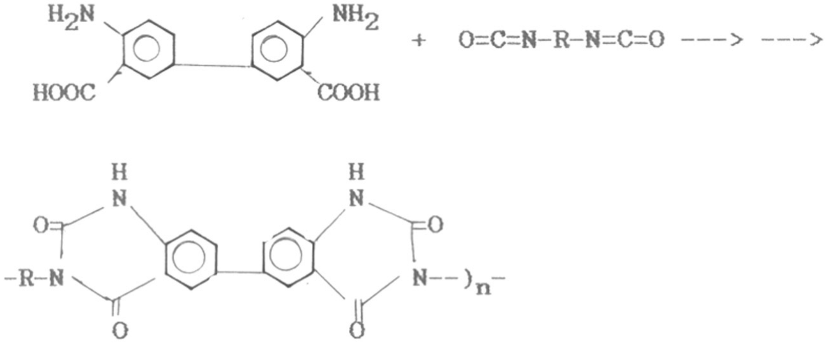
$$R'-O-CO-CH_2-CH_2-NH-R-NH-CH_2-CH_2-CO-OR' \xrightarrow{+\ O=C=N-R-N=C=O} \longrightarrow$$



v. o-Hydroxy acid esters give polybenzoxazinedione[140]



and vi. bis(anthranilic acid) yields polyquinazolinedione.[141]



1.5. APPLICATIONS OF ISOCYANATES

Isocyanates constitute an important segment in organic and polymer chemistry. These find applications in two broad areas: in polymer preparations and modifications and in non polymer applications.

In polymer applications isocyanates are employed in the formation of elastomers (both solid and foams), caulks, coatings, rigid foams, adhesives, thermoplastics, synthetic cellulose, leather and wool. In the non polymer applications isocyanates find use in pharmaceutical and agricultural formulations.

1.6. SCOPE OF THE PRESENT WORK

Isocyanates form an important segment in both organic and polymer chemistry. To meet the challenges and satisfy the demands of isocyanate applications there is a constant quest for newer isocyanates. Many methods have been used to modify polymer properties. Their modifications *via* the diisocyanates attain special importance. Hence the need for the synthesis of newer diisocyanates. Various functional group containing diisocyanates have been synthesized and utilized in polymerizations.

In the present work the synthesis of different functional group containing diisocyanates was targeted with a view to utilize them for the synthesis of polyurethanes and polyurethaneimides, and thermally stable polymers, such as, polyimides, and polyamideimides.

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CHAPTER 2

SYNTHESIS OF DIISOCYANATES

2. SYNTHESIS AND CHARACTERIZATION OF DIISOCYANATES

2.1. INTRODUCTION

Isocyanates are a class of important organic compounds that have captured the imagination of organic and polymer chemists. The use of mono-, di-, and poly-isocyanates containing different functional groups or special structural features for the insertion of these groups or features into the polymers backbone has evinced interest. Thus, diisocyanates can serve as carriers of functional groups and can very conveniently be employed for the insertion of the respective functional groups into the backbone of conventional polyurethanes, polyureas and a host of thermally stable polymers.[1-3]

Mono-, di- and poly-isocyanates incorporating innumerable variations of the structual features can be visualized and synthesized from simple organic molecules by the various synthetic routes described in Chapter 1. These methods, of course, must be compatible with the functional groups to be incorporated.

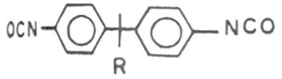
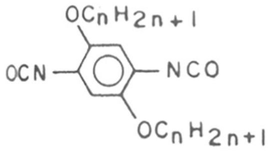
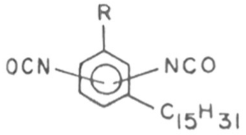
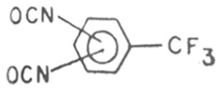
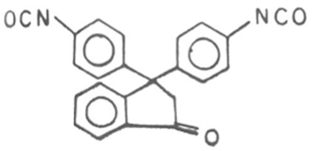
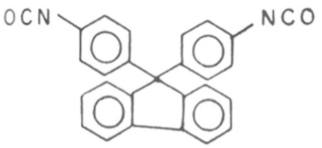
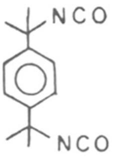
The functional groups or structural features impart characteristic attributes to the polymer into which these are introduced. These structural features influence such properties as, solubility, processability, thermal stability, mechanical and electrical properties, etc.

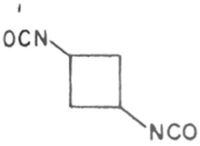
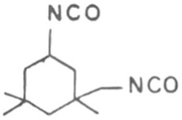
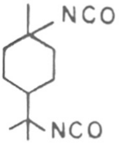
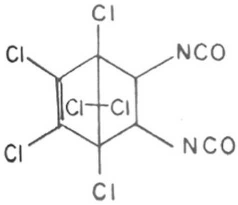
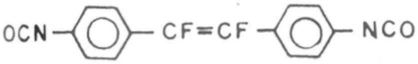
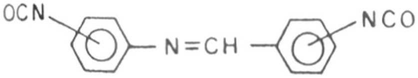
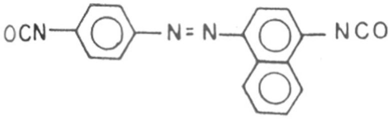
The most commonly used and commercially available diisocyanates are toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), xylylene diisocyanate (XDI), naphthalene-1,5-diisocyanate, hexamethylene diisocyanate, dicyclohexyl diisocyanate, isophorone diisocyanate (IPDI), etc.

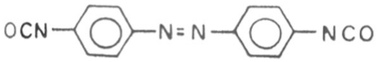
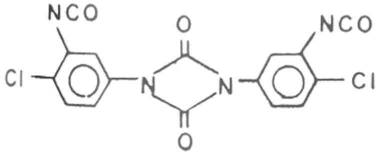
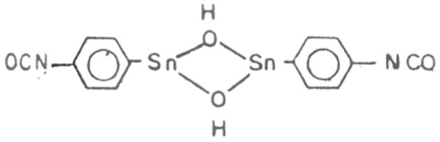
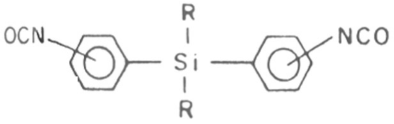
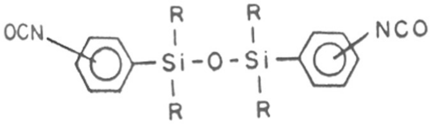
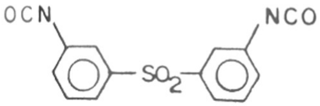
A survey of literature reveals the synthesis of numerous diisocyanates incorporating several structural feature variations. Cyclic (aromatic and saturated), acyclic (saturated and unsaturated), aliphatic (saturated and unsaturated), hetero-atom, heterocyclic, fused rings or bridged ring systems containing diisocyanates, etc., have been synthesized for use in the polymer forming reactions.[4] Table 1 lists a few of these diisocyanates. These are both important from the syntheses point of view as well as from the characteristic attribute that these structual features impart to the polymer.

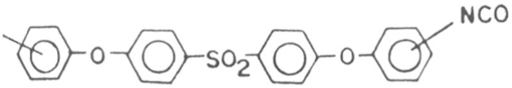
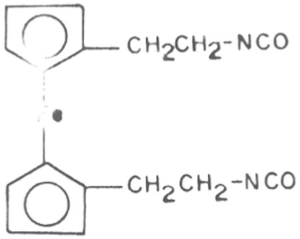
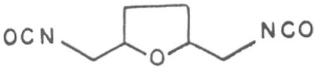
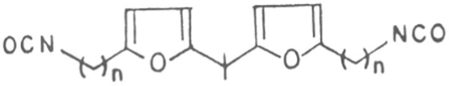
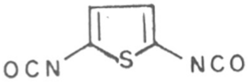
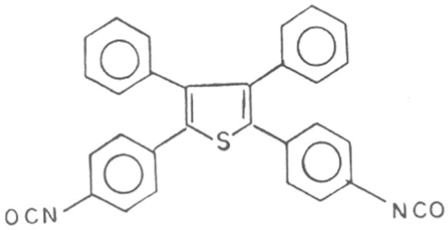
TABLE - I

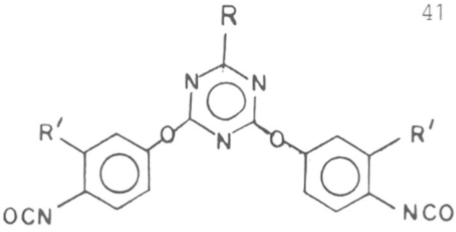
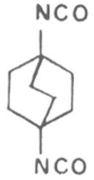
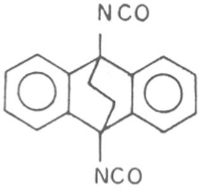
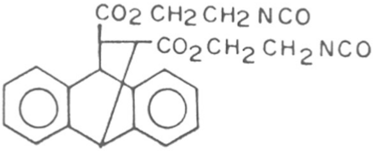
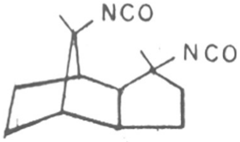
SOME INTERESTING DIISOCYANATES

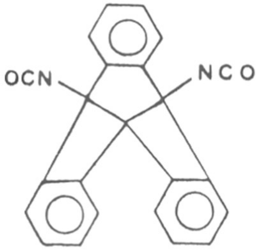
STRUCTURE	METHOD OF PREPARATION	REFERENCE
	A	5,6,7
	B	8
	A	9,10,11
	B	12
	A	13
	A	13
	D	14

	A	15
	A	16
	A	17, 18
	A	19
$OCN-(CF_2)_6-NCO$	B	5
	B	20
	B	21
	A	5

	A	22
	D	23
	C	24
	B	24
	A,B	26,27
	A	5
	A	28

	A	29
		30
	A	31
	A, B	32,33
	B	34
	A	35

	B	36, 38
	B	39
	A	40
	C	41
	A	2

	B	43
	A	44

A = PHOSGENATION METHOD

B = CURTIUS, HOFMANN & LOSSEN REARRANGEMENT REACTION.

C = DOUBLE DECOMPOSITION

D = ADDITION INTERCHANGE REACTION

2.2 SCOPE OF THE PRESENT WORK

The quest for the synthesis of new diisocyanates is an unceasing one. Being an important class of organic compounds, diisocyanates have been visualized as potential monomers for the delivery of certain functionalities into polymers. Consequently, α,ω-diisocyanates serve as vehicles to introduce a variety of functionalities or special structural features. Hence, the synthesis of diisocyanates with various functional groups, such as, oxyethylene, formal, ester and pre-formed imide groups has been visualized for use in the synthesis of polyurethanes, and thermally stable polymers, like polyimides and poly(amide-imide)s.

Functional group containing diisocyanates were synthesized from the corresponding dicarboxylic acids *via* the Curtius reaction or the Weinstock modification of the Curtius reaction in high purity and in excellent yields. The following four series of α,ω-diisocyanates were synthesized by the non-hazardous, non-phosgenation Curtius rearrangement reaction:

i. Oxyethylene containing (**OE**)
ii. Formal group containing (**F**)
iii. Ester group containing (**E**)
iv. Imide group containing (**I**) .

Hereafter, the dicarboxylic acids, the diacylchlorides, the diacylazides, and the diisocyanates containing (i) the oxyethylene moiety will be referred to as **OE 1, OE 2, OE 3** and **OE 4**, respectively and (ii) the pre-formed imide rings will be referred to as **I 1, I 2, I 3, and I 4**, respectively, while the diacids, diacylazides, and the diisocyanates containing (i) the formal group will be referred to as **F 1**, **F 2**, and **F 3**, respectively and (ii) the ester group will be abbreviated as **E 1**, **E 2**, and **E 3**, respectively.

A patent[46a] reports the preparation of five oxyethylene containing diisocyanates by the phosgenation of diamines.

However, the facile synthesis of these diisocyanates by the non-hazardous, non-phosgenation Curtius rearrangement of the corresponding diacylazides is being targeted for the first time.

Hence, in the present work the synthesis of a series of twelve oxyethylene containing diisocyanates, viz., α,ω-bis(3- and 4-isocyanatophenoxy)alkanes, **OE 4 a** – **OE 4 e**, and **OE 4 g** – **OE 4 k**, and bis[2-(3- and 4-isocyanatophenoxy)ethyl] ether, **OE 4 f** and **OE 4 l**; four new formal group containing diisocyanates viz., α,ω-bis(3- and 4-isocyanatophenoxy) methanes, **F 3 a** and **F 3 c**, and bis[2-(3- and 4- isocyanatophenoxy)ethyl] formals, **F 3 b** and **F 3 d**; four new ester group containig diisocyantes, viz., 3,3´- and 4,4´(glutaroyldioxy) diphenyl isocyanate, **E 3 a** and **E 3 c**, and 3,3´- and 4,4´-(adipoyldioxy)diphenyl isocyanate, **E 3 b** and **E 3 d**; and eight new pre-formed imide group containing diisocyantes, viz., N,N´-bis-(isocynatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides, **I 4 a** – **I 4 d** and N,N´-bis(isocyanatoalkyl)- 3,3´,4,4´-benzophenonetetracarboxylic-3,3: 4,4´-diimides, **I 4 e** – **I 4 h**, is being reported. These diisocyantes have been synthesized from the corresponding dicarboxylic acids. The detailed characterization of these 28 diisocyanates is given.

2.3. SYNTHESIS AND CHARACTERIZATION OF OXYETHYLENE CONTAINING DIISOCYANATES.

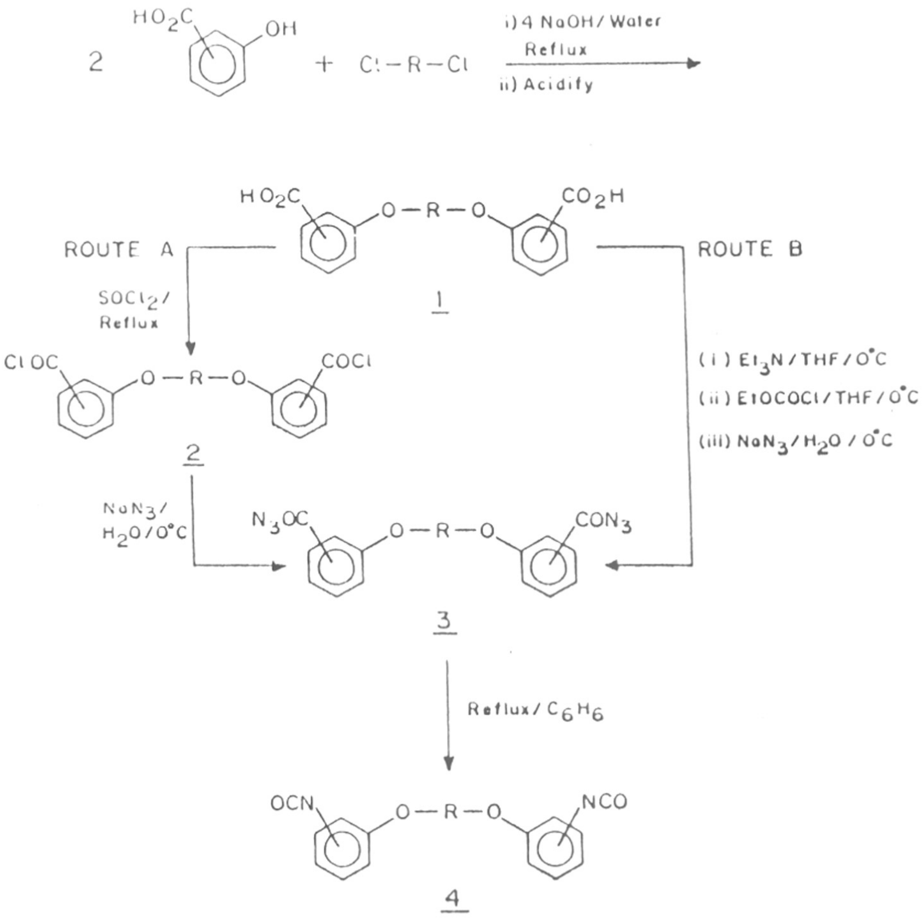
2.3.1 RESULTS AND DISCUSSION

A series of six meta- and six para- oriented oxyethylene containing diisocyanates (**OE 4 a - OE 4 l**) were synthesized by the non hazardous, non phosgention Curtius rearrangement reaction starting from the corresponding dicarboxylic acids (**OE 1 a - OE 1 l**) as illustrated in Scheme 1.

The oxyethylene containing dicarboxylic acids (**OE 1 a - OE 1 l**) were prepared by the Williamson ether synthesis.[45] (This method consists of the nucleophilic substitution of haloalkanes with alcohols/phenols. Although the formation of ether under neutral conditions is satisfactory, the use of alkoxide/phenoxide as a more reactive nuclophile is usually preferred.) Taking advantage of this fact, the disodium salts of 3- and 4-hydroxybenzoic acids (0. 01 mol) were reacted with appropriate α,ω-dihaloalkanes (0.005 mol) in aqueous sodium hydroxide solution to form a series of meta- and para-oriented α,ω-dicarboxylic acids containing oxyethylene groups in 55-60% yields.[46,47] (The phenoxide ion being more nucleophilic than the carboxylate ion, an ether is formed.[46,47])

The IR spectra of all the α,ω-dicarboxylic acids (**OE 1 a - OE 1 l**) showed characteristic bands at 1700 cm^{-1} (C=O) and 1230 cm^{-1} (C-O-C), both being stretching vibrations. Representative IR spectrum of dicarboxylic acid, **OE 1 l**, is shown in Figure 1 (a).

The α,ω-diacylazides (**OE 3 a - OE 3 L**) were prepared by two alternative pathways: the Curtius reaction and the Weinstock



R = $-(CH_2)_{2-6}-$; $-CH_2CH_2OCH_2CH_2-$

A B

SCHEME. 1 : SYNTHESIS OF 1,2-BIS(CARBOXYPHENOXY)ETHANES, OE 1a – OE 1e and OE 1g – OE 1k, and BIS [2-(CARBOXYPHENOXY) ETHYL] ETHERS, OE 1f and OE 1ℓ.

modification of the Curtius reaction. In the Curtius reaction, the dicarboxylic acids were converted into the diacid chlorides (**OE 2 a - OE 2 l**) by refluxing with excess of thionyl chloride.

The IR spectra of the diacylchlorides (**OE 2 a - OE 2 l**) showed the strong absorption bands at 1785-1790 cm^{-1} characteristic of the C=O of the acid chloride.

The acid chlorides (**OE 2 a - OE 2 L**) were subsequently converted into the diacylazides (**OE 3 a - OE 3 l**) by the treatment of the respective methylene chloride solution of the diacylchlorides with aqueous solutions of sodium azide at 0°C. The dichloromethane solution was concentrated under reduced pressure and poured into excess pet ether to precipitate the diacylazides (**OE 3 a - OE 4 l**).

In the other route, which is the Weinstock modification of the Curtius reaction, the diacylazides were synthesized under mild conditions. The diacids (**OE 1 a - OE 1 l**) were successively treated with triethylamine, ethyl chloroformate and sodium azide. The reaction of the diacids with triethylamine produces a salt which on treatment with ethyl chloroformate results in the formation of a mixed carboxylic-carbonic anhydride. When an aqueous solution of sodium azide is added, the azide ion attacks the more electrophilic carbonyl group of the mixed carboxylic-carbonic anhydride and results in the formation of the diacylazide (**OE 3 a - OE 3 l**). The reaction conditions employed are mild and there are apparently no side products formed in this \`one-pot´ reaction. The isolation of the intermediates is avoided

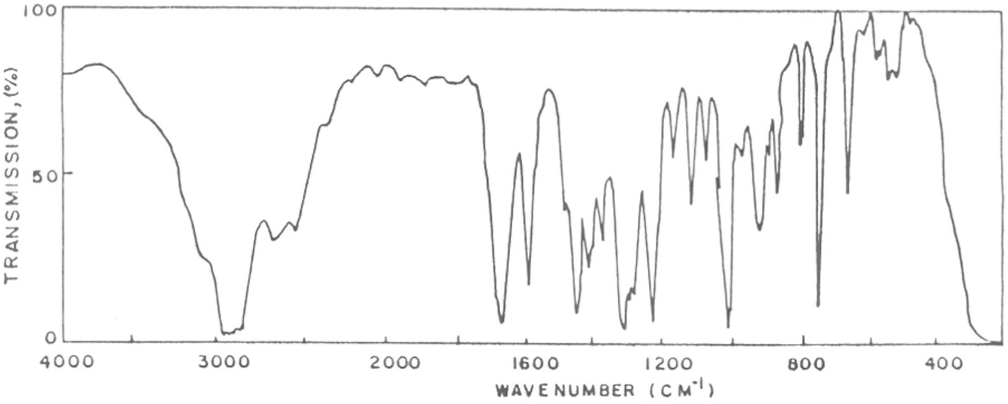


FIG. 1(a): IR(NUJOL MULL) SPECTRUM OF BIS [2-(4-CARBOXYPHENOXY) ETHYL] ETHER, OE 1ℓ.

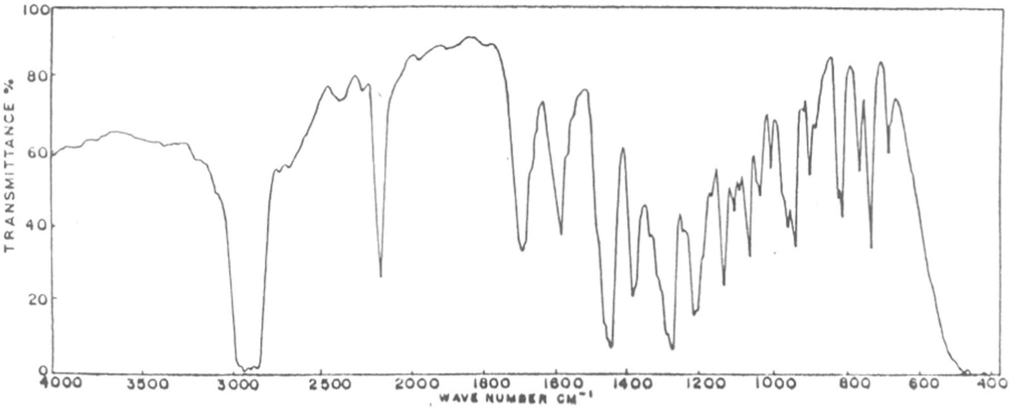


FIG 1(b) IR SPECTRUM OF BIS [2(3-AZIDOCARBONYLPHENOXY) ETHYL] ETHER, OE 3ℓ.

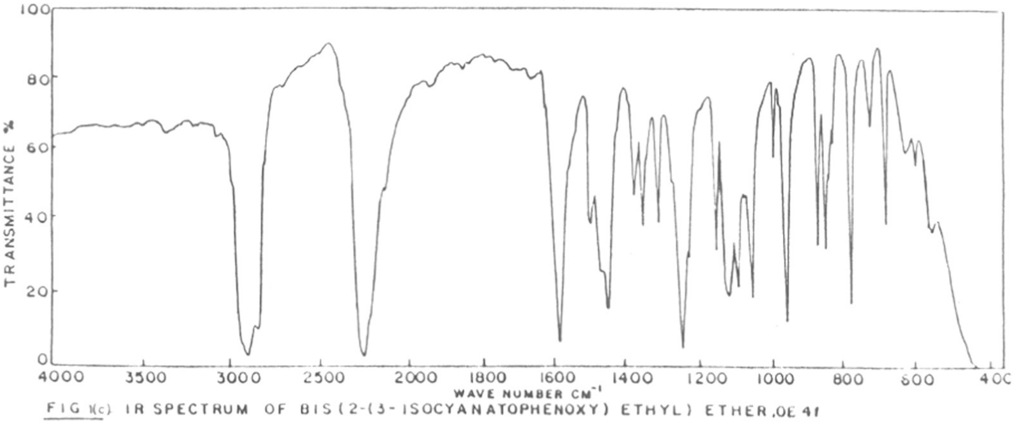


FIG 1(c) IR SPECTRUM OF BIS (2-(3-ISOCYANATOPHENOXY) ETHYL) ETHER, OE 4ℓ in this method and, hence, was preferred over the acid chloride-azide route.

The IR spectra of all the diacylazides (**OE 3 a - OE 3 1**) exhibited strong bands at 2130 cm^{-1}, 1680 cm^{-1}, 1230 cm^{-1}, corresponding to the asymmetric stretching vibration due to N_3, and stretching vibrations due to C=O and C-O-C, respectively. Figure 1 (b) is an illustration of the IR spectrum of diacylazide, **OE 3 1**. There was a splitting of the 2130 cm^{-1} N_3 asymmetric stretching bands in all the diacylazides. This splitting may be attributed to the Fermi interation with a combination tone involving the N_3 symmetric or the C-N stretching vibration and another low lying frequency.[48] The diacylazides were soluble in common solvents such as benzene, etc. The diacylazides could be handled safely without any explosion and could be stored at low temperaures in a refrigerator in a descicator for a resonable period of time.

The diacylazides (**OE 3 a - OE 3 1**) were decomposed to the diisocyanates (**OE 4 a - OE 4 1**) by refluxing in dry benzene for 12 h. The conversion of the diacylazides into the diisocyanates was smooth and uneventful.

In the IR spectra of the diisocyanates (**OE 4 a - OE 4 1**), strong absorption bands at 2260 cm^{-1} and 1230 cm^{-1} characteristic of N=C=O and C-O-C, respectively were observed. Figure 1 (c) is an illustration of the IR spectrum of the diisocyanate, **OE 4 1**.

In the ^1H-NMR spectrum of the diacylazide (**OE 3 1**) (Figure 2), the aliphatic protons H_a and H_b occur as multiplets centered at 3.85 δ and 4.12 δ, respectively. The multiplicity of

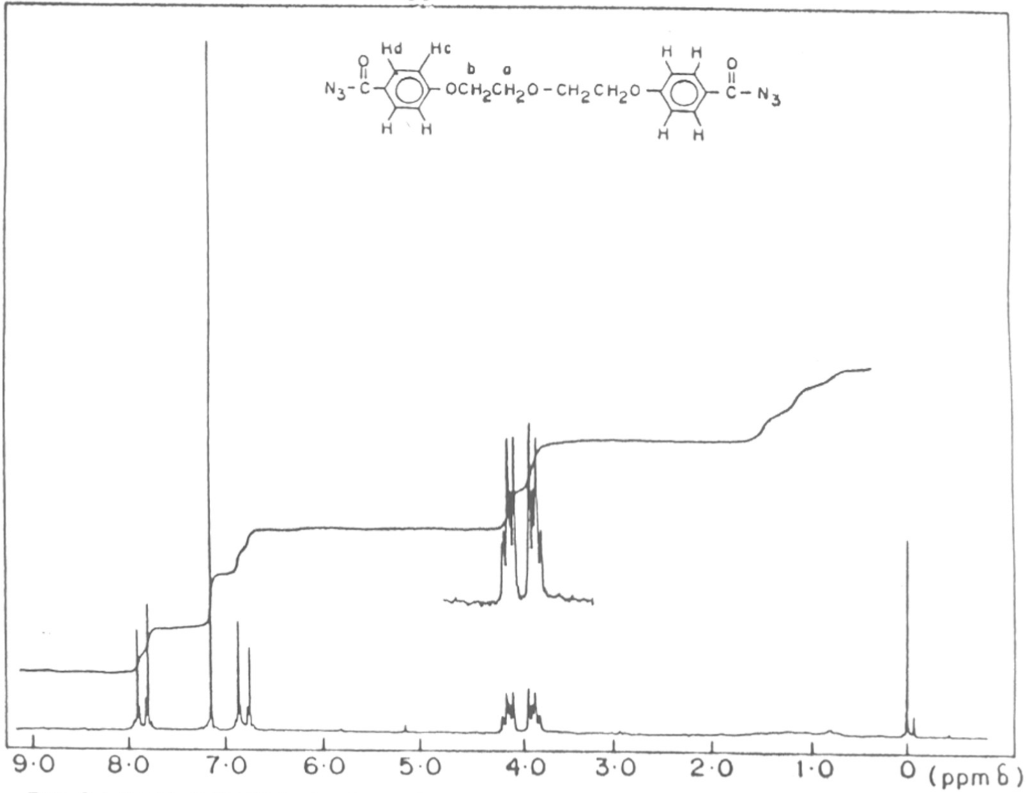


FIG.2 : NMR SPECTRUM OF BIS [2-(4-AZIDOCARBONYLPHENOXY) ETHYL] ETHER, OE 3ℓ.

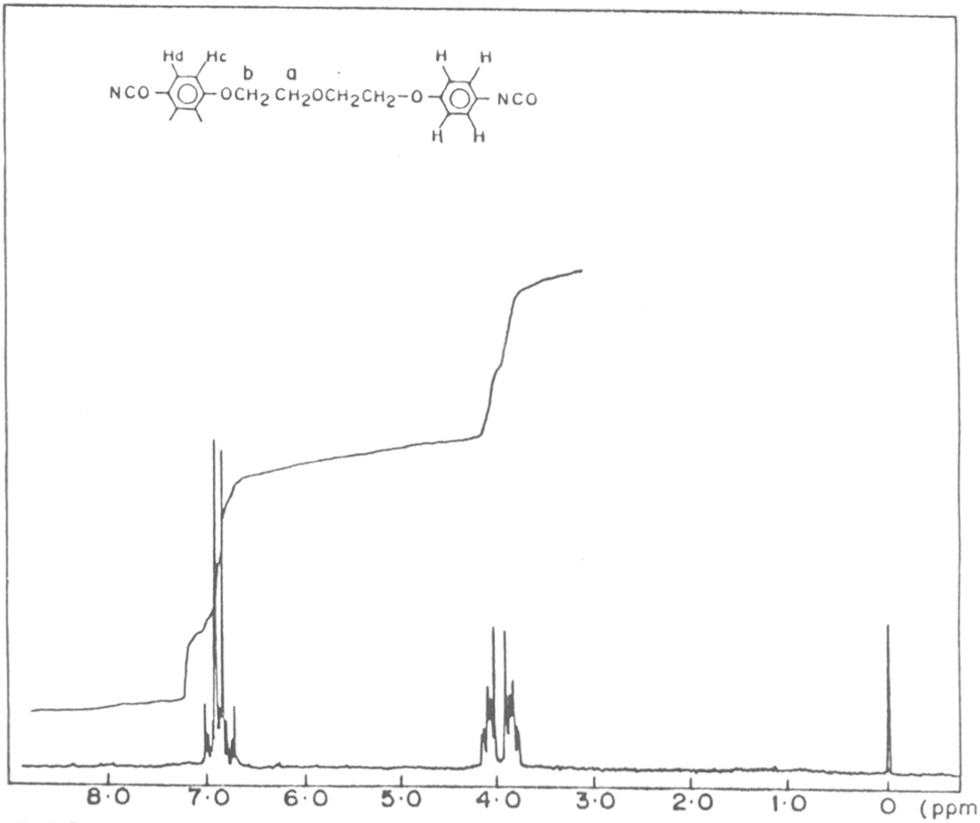


FIG.3 : NMR SPECTRUM OF BIS [2-(4-ISOCYANATOPHENOXY) ETHYL] ETHER OE 4L

signals arises due to the non equivalence of the methylene protons. Among the aromatic protons, the H_c protons occur as a doublet at 6.90 δ (J=8 Hz) while the H_d protons occur as a doublet at 7.80 δ (J=8 Hz). The downfield shift of H_d protons ortho- to the azidocarbonyl group is due to the strong electron withdrawing effect of the azidocarbonyl group. The protons H_c occur upfield due to the positive resonance effect of the ether linkage.

In the ^{1}H-NMR spectrum of the diisocyanate (**OE 4 l**) (Figure 3), the protons H_a and H_b occur as multiplets centered at 3.85 δ and 4.06 δ. The aromatic protons H_c occur as a doublet at 6.50 δ (J=8 Hz), while the protons H_d occur as a multiplet centered at 6.97 δ.

The ^{1}H-NMR spectra of all the diacylazides (**OE 3 a - OE 3 l**) and those of the diisocyanates (**OE 4 a - OE 4 l**) were taken in deuterated choroform solution and the spectra were in agreement with the structures proposed. The mass spectra and elemental analysis of the diisocyanates confirmed the structures assigned. The physical constants and spectral value of diacylazides and diisocyanates are incorporated in Tables 2 - 5.

TABLE 2

Physical and Spectral Characteristics of Oxyethylene Containing Diacylazides, **OE 3 a** – **OE 3 f**.

Product 3	R	Yield (%)	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ , ppm)
a	$-(CH_2)_2-$	86	105	4.44 (s, 4 H), 6.99 - 7.65 (m, 8 H),
b	$-(CH_2)_3-$	85	115	2.30 (quintet, 2 H), 4.22 (t, 4 H), 7.07 - 7.71 (m, 8 H)
c	$-(CH_2)_4-$	86	94	2.0 (quintet, 4 H), 4.09 (t, 4 H), 7.70 - 7.71 (m, 8 H),
d	$-(CH_2)_5-$	87	113	1.46 - 2.08 (m, 6 H), 4.02 (t, 4 H), 6.98 - 7.68 (m, 8 H)
e	$-(CH_2)_6-$	86	93	1.30 - 2.0 (m, 8 H), 3.94 (t, 4 H), 6.97 - 7.60 (m, 8 H)
f	$-(CH_2CH_2)_2O-$	87	100	3.73 - 4.02 (m, 4 H), 4.02 - 4.20 (m, 4 H), 6.99 - 7.6 (m, 8.H)

s = singlet, t = triplet, q = quintet, m = multiplet

TABLE 3

Physical and Spectral Characteristics of Oxyethylene Containing Diisocyanates, **OE 4 a** – **OE 4 f** .[a]

Product **4**	R	Yield (%)	m.p. ^{o}C	^1H-NMR ($CDCl_3$) (δ , ppm)	M^+ (70 eV)
a	$-(CH_2)_2-$	95	93	4.25 (s, 4 H), 6.57 – 6.76 (m, 6 H), 7.0 – 7.24 (m, 2 H)	296
b	$-(CH_2)_3-$	96	64	2.21 (quintet, 2 H), 4.09 (t, 4 H), 6.54 – 6.77 (m, 6 H), 7.0 – 7.28 (m, 2 H)	310
c	$-(CH_2)_4-$	97	84	1.98 (quintet, 4 H), 4.02 (t, 4 H), 6.6 – 6.82 (m, 6 H), 7.11 – 7.33 (m, 2 H)	324
d	$-(CH_2)_5-$	96	86	1.03 – 2.1 (m, 6 H), 4.0 (t, 4 H), 6.34 – 6.77 (m, 6 H), 6.93 – 7.24 (m, 2 H)	338
e	$-(CH_2)_6-$	95	74	1.26 – 2.09 (m, 8 H), 3.90 (t, 4 H), 6.5 – 6.73 (m, 6 H), 6.97 – 7.28 (m, 2 H)	352
f	$-(CH_2CH_2)_2O-$	97	74	3.62 – 3.82 (m, 4 H), 3.82 – 4.02 (m, 4 H), 6.40 – 6.60 (m, 4 H), 6.85 – 7.20 (m, 4 H)	340

[a] Satisfactory microanalyses obtained : C,±0.25 %, H,±0.20 %, N,±0.15 %

TABLE 4

Physical and Spectral Characteristics of Oxyethylene Containing Diacylazides, **OE 3 g** - **OE 3 l**.

Product 3	R	Yield (%)	m.p. °C	^{1}H-NMR (CDCl$_3$) (δ, ppm)
g	$-(CH_2)_2-$	86	112	4.44 (s, 4 H), 6.90 (d, J=8 Hz, 4 H) 7.90 (d, J=8 Hz, 4 H
h	$-(CH_2)_3-$	85	97	2.28 (quintet, 2 H), 4.21 (t, 4 H), 6.78 (d, J=8 Hz, 4 H), 7.97 (d, J=8 Hz, 4 H)
i	$-(CH_2)_4-$	85	113	2.02 (quintet, 4 H), 4.11 (t, 4 H), 6.92 (d, J=8 Hz, 4 H) 7.90 (d, J=8 Hz, 4 H)
J	$-(CH_2)_5-$	86	92	1.63 (m, 6 H), 4.02 (t, 4 H), 6.87 (d, J=8 Hz, 4 H), 7.80 (d, J=8 Hz, 4 H)
k	$-(CH_2)_6-$	86	102	1.70 (m, 8 H), 4.02 (t, 4 H), 6.80 (d, J=8 Hz, 4 H), 7.88 (d, J=8 Hz, 4 H)
l	$-(CH_2CH_2)_2O-$	86	126	3.84 (m, 4 H), 4.12 (m, 4 H), 6.90 (d, J=8 Hz, 4 H), 7.80 (d, J=8 Hz, 4 H)

TABLE 5

Physical and Spectral Characteistics of Oxyethylene Containing Diisocyanates, **OE 4 g** - **OE 4 l**. [a]

Product **4**	R	Yield (%)	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ, ppm)	M^+ (70 eV)
g	$-(CH_2)_2-$	95	102	6.30 (s, 4 H), 6.87 (d, 4 H), 7.05 (m, 4 H)	296
h	$-(CH_2)_3-$	97	84	2.24 (quintet, 2 H), 4.13 (t, 4 H), 6.80 (d, 4 H) 7.00 (m, 4 H)	310
i	$-(CH_2)_4-$	96	97	1.96 (quintet, 4 H), 3.98 (t, 4 H), 6.74 (d, 4 H), 7.00 (m, 4 H)	324
j	$-(CH_2)_5-$	97	84	1.73 (m, 6 H), 3.90 (t, 4 H), 6.79 (d, 4 H) 7.01 (m, 8H)	338
k	$-(CH_2)_6-$	95	94	1.50 (m, 8 H), 3.93 (t, 4 H), 6.77 (d, 4 H) 7.10 (m, 4 H)	352
l	$-(CH_2CH_2)_2O-$	96	110	3.85 (m, 4 H), 4.06 (m, 4 H), 6.50 (d, 4 H), 6.97 (m, 4 H)	340

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[a] Satisfactory microanalyses obtained:
C,±0.25 %, H,±0.20 %, N,±0.15 %.

2.3.2. EXPERIMENTAL

Materials:

α,ω-Dihaloalkanes, 2-chloroethyl ether, thionyl chloride, triethylamine, and ethyl chloroformate were all of reagent grade and were distilled prior to use.

Sodium azide was triturated with hydrazine hydrate, dissolved in water and reprecipitated with acetone. It was dried in vacuum at room temperature to obtain `activated´ sodium azide.

2.3.2.1. Synthesis of α,ω-Bis(carboxyphenoxy)alkanes (OE 1 a - OE 1 e, and OE 1 g - OE 1 k) and Bis[(carboxyphenoxy) ethyl] ether (OE 1 f and OE 1 l), the α,ω-Dicarboxylic acids. General Procedure.

In a three necked 250 mL flask equipped with an overhead stirrer, a reflux condenser and a dropping funnel, was placed a solution of 3- or 4-hydroxybenzoic acid (0.1 mol) and sodium hydroxide (0.2 mol) in 50 mL water. The solution was stirred and brought to reflux when α,ω-dihaloalkane (0.05 mol) was added dropwise over a period of 1 h. The reaction mixture was maintained in this condition for 10 h. Next, sodium hydroxide pellets (0.05 mol) were added and refluxed for a further period of 1 h. The reaction mixture was cooled, dissolved in water, filtered, and acidified with 10% hydrochloric acid to give the diacid (OE 1 a - OE 1 l) in about 55-60% yield. The crude diacid was redissolved in aqueous sodium carbonate solution and reprecipitated with 10% HCl. It was filtered and washed with excess of water and methanol before drying in vacuum at 70°C. The IR spectra of the confirmed the formation of diacids. The elemental analyses of the diacids were in agreement with the calculated values.

2.3.2.2. Synthesis of α,ω-Bis(azidocarbonylphenoxy)alkanes (OE 3 a – OE 3 e and OE 3 g – OE 3 k) and Bis[azidocarbonylphenoxy)ethyl] ether (OE 3 f and OE 3 l), the α,ω-Diacylazides. General Procecure.

<u>Route</u> A. The diacid (**OE 1 a – OE 1 l**) (0.01 mol) was heated at reflux with thionyl chloride (0.2 mol) for 2 h with a catalytic amount of pyridine. Removal of excess thionyl chloride under reduced pressure and recrystallization of the residue from benzene-pet ether mixture afforded the α,ω-diacylchloride (**OE 2 a – OE 2 l**) in yields about 95-97%.

To an ice-cold solution of 'activated' sodium azide solution (0.025 mol) in 20 mL water was added dropwise a solution of the diacylchloride (**OE 2 a – OE 2 l**) (0.01 mol) in 20 mL dichloromethane and the solution was stirred vigorously for 2 h at 0°C. The dichloromethane layer was separated and washed successively with water, 10% Na_2CO_3, and finally with water before it was separated and dried over anhydrous Na_2SO_4. Removal of the solvent at room temperature under reduced pressure gave the diacylazide (**OE 3 a – OE 3l**) in yields in the range 85-87%.

<u>Route</u> B: suspension of the diacid (**OE 1 a – OE 1 l**) (0.01 mol) in 15 mL THF-water (50/50 v/v) mixture was stirred at 0°C when triethylamine (0.022 mol) in 5 mL THF was added

dropwise over 30 min. To the clear solution formed was added ethyl chloroformate (0.022 mol) dropwise over a period of 30 min and stirred for 1 h and 30 min. `Activated´ sodium azide (0.025 mol) solution in 15 mL water was added dropwise over 30 min and the reaction mixture was stirred for 2 h at 0°C. Next, 100 mL water was added dropwise and the reaction mixture was allowed to attain ambient temperature. The solid that separated out was filtered, washed with water, and then dissolved in 25 mL dichloromethane. The dichloromethane layer was dried over anhydrous Na_2SO_4. The dichloromethane solution was concentrated under reduced pressure and poured into an excess of pet ether to precipitate the diacylazides (**OE 3 a - OE 3 l**)in pure form in about 85 - 87 % yield.

2.3.2.3. Synthesis of α,ω-Bis(isocyanatophenoxy)alkanes (OE 4 a - OE 4 e and OE 4 g - 4 k) and Bis[2-(isocyanatophenoxy)ethyl] ethers (OE 4 f and OE 4 l), the α,ω-Diisocyanates.

General Procedure.

The α,ω-diacylazide (**OE 3 a - OE 3 l**) (0.01 mol) was dissolved in 50 mL dry benzene and refluxed for 12 h. Evaporation of the solvent and recrystallization of the solid residue obtained from a mixture of benzene-pet ether gave the diisocyanate (**OE 4 a - OE 4 l**) in pure form and in yields ranging from 95-97%.

2.4. SYNTHESIS AND CHARACTERIZATION OF FORMAL GROUP CONTAINING DIISOCYANATES

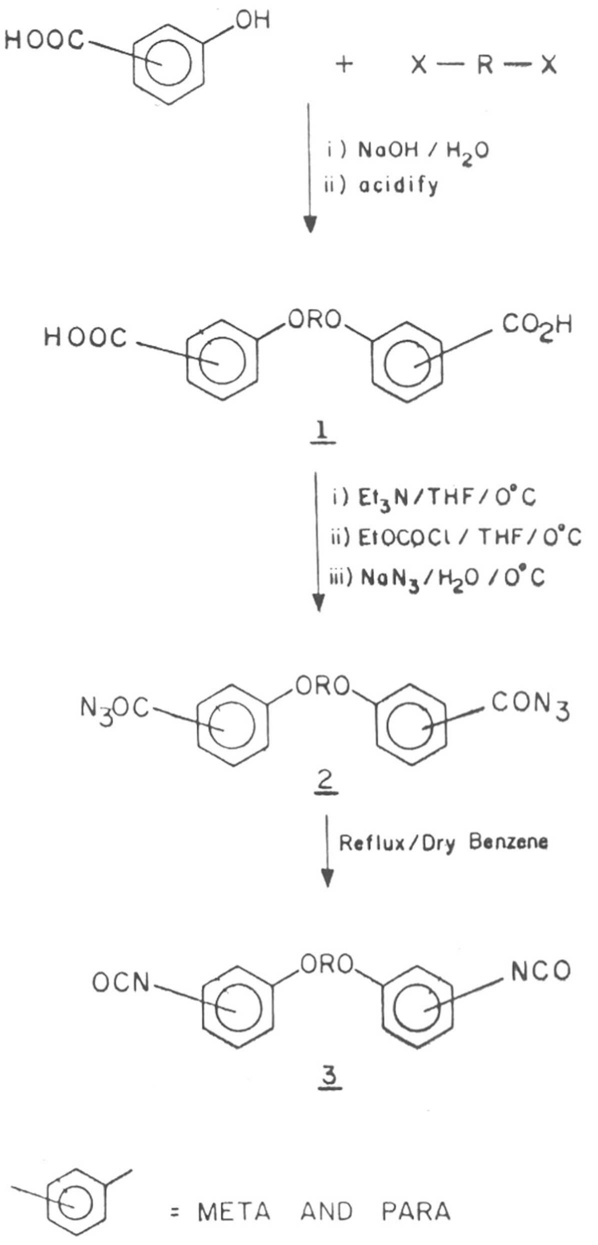
2.4.1. RESULTS AND DISCUSSION

The synthesis of new diisocyanates containing formal group (**F 4 a - F 4 d**) was carried out from the corresponding dicarboxylic acids (**F 1 a - F 1 d**) as depicted in Scheme 2.

The dicarboxylic acids (**F 1 a - F 1 d**) were synthesized by the condensation of dibromomethane and bis(2-chloroethyl) formal (or dichlorodiethyl formal) with 3- or 4-hydroxybenzoic acid in aqueous sodium hydroxide solution.[46,47]

α,ω-Diacylazides (**F 2 a - F 2 d**) were prepared from the α,ω-diacids by the elegant Weinstock modification of the Curtius reaction. These α,ω-diacylazides were dissolved in dry benzene and decomposed by heating at reflux to give the corresponding diisocyanates (**F 3 a - F 3 d**).

The IR spectra of the diacids (**F 1 a - F 1 d**) showed characteristic absorptions at 1700 cm^{-1} and 1230 cm^{-1} corresponding to C=O and C-O-C, stretching vibrations, respectively. Representative IR spectrum of the diacid (**F 1 b**) is given in Figure 4 (a). The IR spectra of all diacylazides (**F 2 a - F 2 d**) showed absorptions at 2130 cm^{-1}, 1660 cm^{-1}, and 1230 cm^{-1}, corresponding to N_3 asymmetric vibrations, C=O and C-O-C stretching vibrations, respectively. The IR spectra of the diisocyanates (**F 3 a - F 3 d**) showed bands at 2250 cm^{-1} and 1230 cm^{-1} corresponding to N=C=O and C-O-C, respectively. Representative IR spectra of the diacylazide (**F 2 b**) and diisocyanate (**F 3 b**) are depicted in Figures 4 (b) and 4 (c), respectively.



R = $-CH_2-$ AND $-CH_2CH_2OCH_2OCH_2CH_2-$

X = Br OR Cl

SCHEME 2 : SYNTHESIS OF FORMAL GROUP CONTAINING DIISOCYANATES, F 3a - F 3d

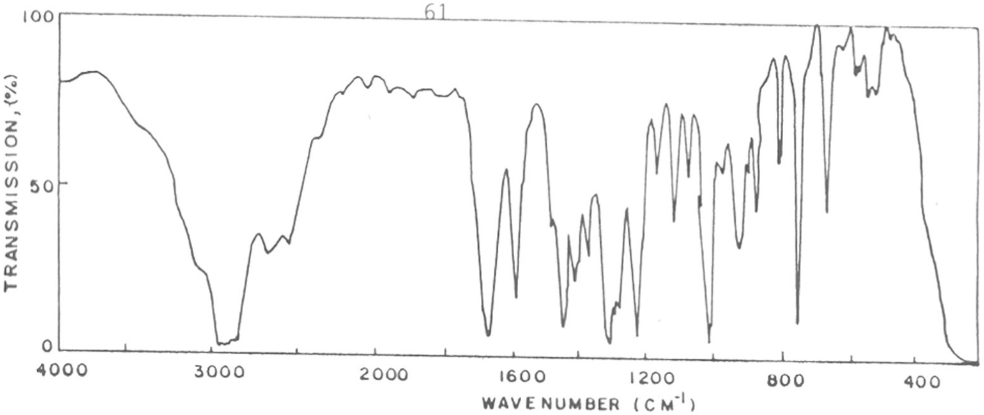


FIG.4(a) IR(NUJOL MULL) SPECTRUM OF BIS [2-(4-CARBOXYPHENOXY) ETHYL] FORMAL, F1b.

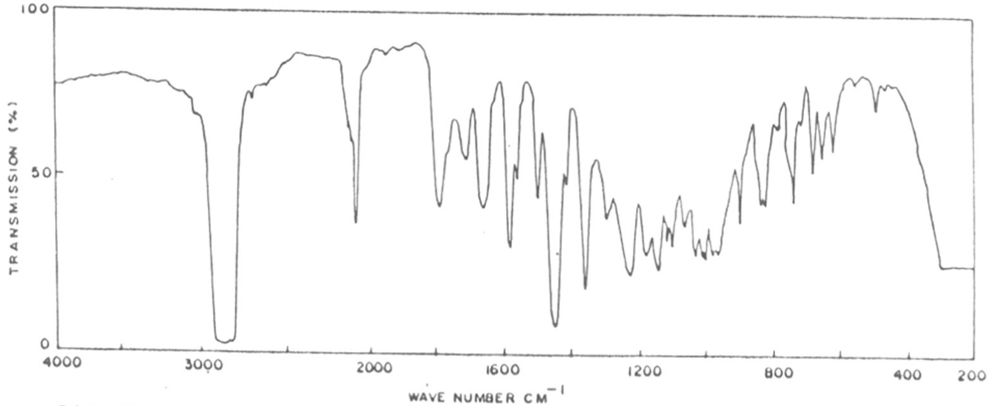


FIG 4b:IR(NUJOL MULL) SPECTRUM OF BIS [2(3-AZIDOCARBONYLPHENOXY) ETHYL] FORMAL, F2b.

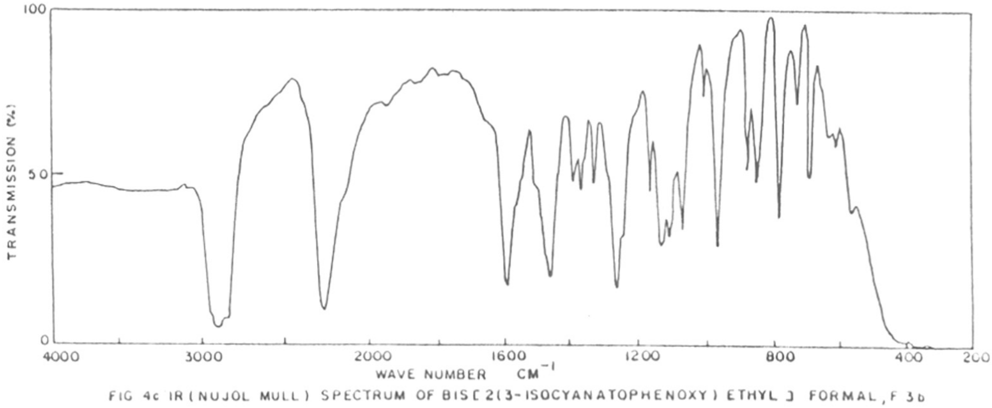


FIG 4c IR (NUJOL MULL) SPECTRUM OF BIS[2(3-ISOCYANATOPHENOXY) ETHYL] FORMAL, F3b

In the ^{1}H-NMR spectrum of the diacylazide, **F 2 d** (Figure 5), the aliphatic protons H_a that are flanked by two oxygen atoms occur as a singlet at 4.61δ. The aliphatic protons H_b and H_c occur as multiplets centered at 3.50δ and 4.12δ. The multiplicity of the signals arises due to the non equivalence of the methylene protons. Among the aromatic protons, protons H_d occur as a doublet at 6.77δ(J=8 Hz) while protons H_e occur as a doublet at 7.89δ(J=8 Hz). The downfield shift of the H_d protons ortho to the azidocarbonyl group is due to the strong electron withdrawing nature of that group. The protons H_e occur upfield due to the positive resonance effect of the ether linkage.

In the ^{1}H-NMR spectrum of the diisocyanate, **F 3 d** (Figure 6), the protons H_a occur as a singlet at 4.61δ. The protons H_b and H_c occur as multiplets centered at 3.56δ and 4.07δ, respectively. The aromatic protons, H_d occur as a doublet at 6.37δ (J=8 Hz) while protons H_e occur as a multiplet centered at 6.72δ.

Likewise, the ^{1}H-NMR spectra of all formal group containing diacylazides (**F 2 a** - **F 2 d**) and diisocyanates (**F 3 a** - **F 3 d**) were in agreement with the structures proposed. Mass spectra and elemental analysis of the diisocyanates confirmed the structures proposed. The physical constants and spectral values of the diacylazides and diisocyanates are incorporated in Tables 6 and 7.

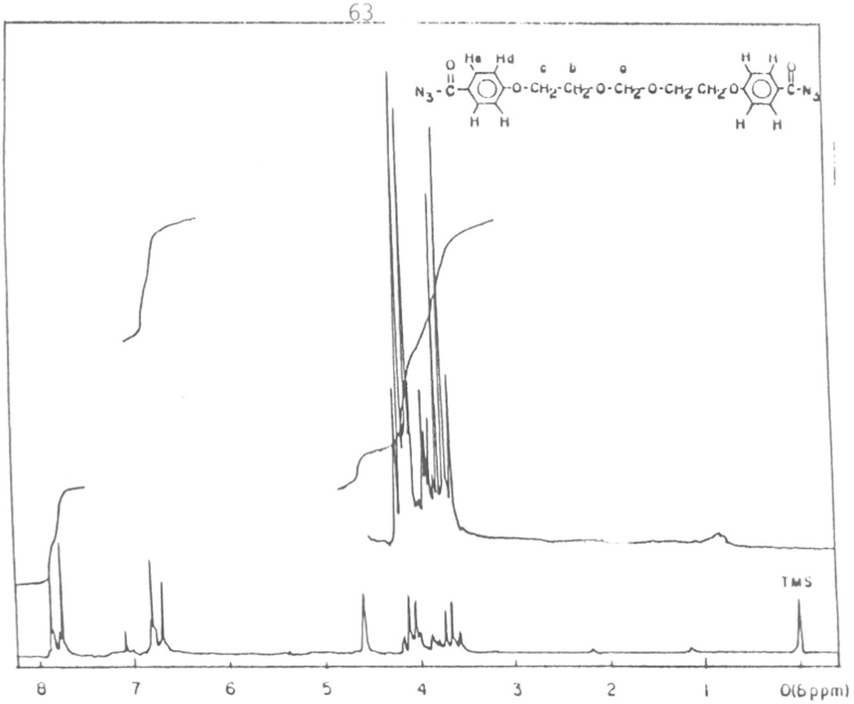


FIG. 5 : ^{1}H-NMR ($CDCl_3$) SPECTRUM OF BIS [2-(4-AZIDOCARBONYLPHENOXY) ETHYL] FORMAL, F 2d.

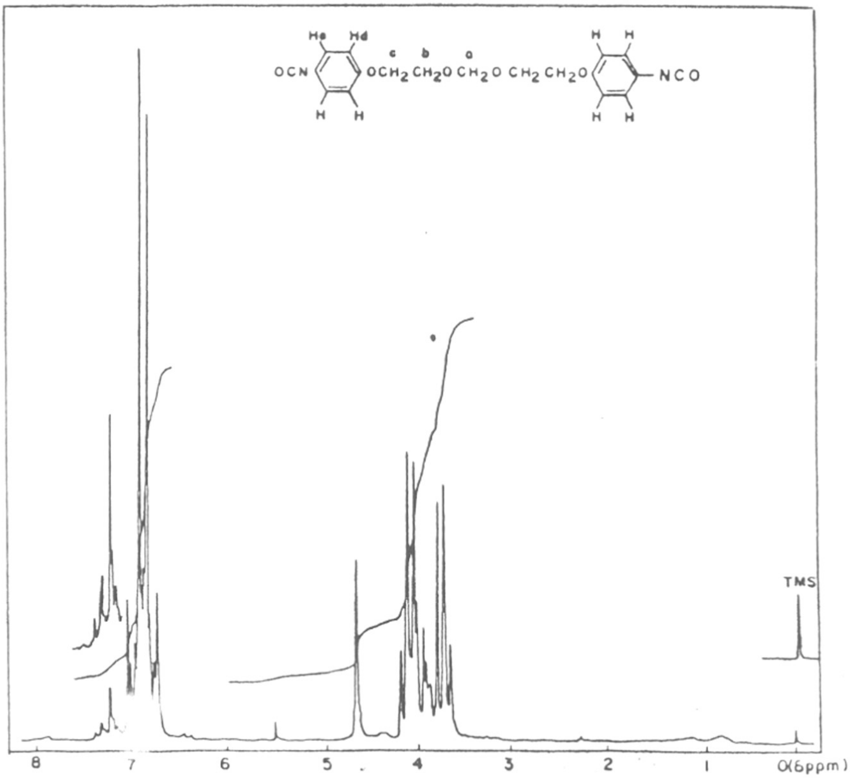


FIG.6: ^{1}H-NMR ($CDCl_3$) SPECTRUM OF BIS [2-(4-ISOCYANATOPHENOXY) ETHYL] FORMAL, F 3d.

Table 6

Physical and Spectral Data of Formal Group Containing Diacylazides (**F 2 a** - **F 2 d**).

Product[1] 2	R	Yield (%)	m.p °C	^{1}H-NMR / $CDCl_3$ (, ppm)
a	$-CH_2-$	85	98	5.75 (s, 2 H); 7.26-7.40 (m, 6 H); 7.60-7.76 (m, 2 H).
b	$-CH_2CH_2OCH_2OCH_2CH_2-$	87	83	3.89 (m, 4 H); 4.10 (m, 4 H); 4.77 (s, 2 H); 7.10 (m, 6 H); 7.60 (m, 2 H).
c	$-CH_2-$	88	112	5.79 (s, 2 H); 7.08 (d, 4 H); 7.95 (d, 4 H).
d	$-CH_2CH_2OCH_2OCH_2CH_2-$	87	103	3.53 (m, 4 H); 4.12 (m, 4 H); 4.61 (s, 2 H); 6.77 (d, 4 H); 7.89 (d, 4 H).

---

[1] a and b are meta- and c and d are para- substituted.

Table 7

Physical and Spectral Data of Formal Group Containig Diisocyanates (**F 3 a** – **F 3 d**).

Product[1] 3	R	Yield (%)	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ ,ppm)	M^+ (70 eV)
a	$-CH_2-$	95	85	5.75 (s, 2 H); 7.29-7.47 (m, 8 H).	282
b	$-CH_2CH_2OCH_2OCH_2CH_2-$	97	65	3.78 (m, 4 H); 4.22 (m, 4 H); 4.80 (s, 2 H); 6.50-6.77 (m, 6 H); 7.00-7.24 (m, 2 H).	370
c	$-CH_2-$	96	100	5.63 (s, 2 H); 6.77-7.24 (m, 8 H).	282
d	$-CH_2CH_2OCH_2OCH_2CH_2-$	97	97	3.56 (m, 4 H); 4.07 (m, 4 H); 4.61 (s, 2 H); 6.37 (d, 4 H). 6.72 (m, 4 H)	370

[1] a and b are meta- while, c and d are para- substituted.
Satisfactory microanalyses obtained:
C,±0.25 %, H,±0.20 %, N,±0.15 %.

2.4.2. EXPERIMENTAL

Materials:

Dibromomethane, bis(2-chloroethyl) formal, triethylamine, ethyl chloroformate and tetrahydrofuran were all of reagent grade and were distilled prior to use.

3- and 4-Hydroxybenzoic acids were recrystallized from water.

Sodium azide was `activated´ by trituration with hydrazine hydrate, followed by dissolution in water and precipitation with acetone. The product was filtered and dried in vacuum at room temperature.[49,50]

2.4.2.1. Synthesis of Bis(carboxyphenoxy)methanes (F 1 a and F 1 c) and Bis[2-(carboxyphenoxy)ethyl] formal (F 1 b and F 1 d), the Dicarboxylic acids. General Procedure.

To a stirred solution of 3- or 4-hydroxybenzoic acid (0.01 mol) and sodium hydroxide (0.02 mol) in 50 mL water under reflux, taken in a three necked flask equipped with an overhead stirrer, a reflux condenser and a dropping funnel, was added either dibromomethane or bis(2-chloroethyl) formal (0.005 mol) dropwise over 1 h. The reaction mixture was maintained in that condition for 10 h. Next, solid sodium hydroxide pellets (0.05 mol) were added and the reaction mixture refluxed further for 1 h. The reaction mixture was cooled, dissolved in water, filtered, and filtrate acidified with dilute hydrochloric acid to get the diacids (**F 1 a - F 1 d**). The diacids were purified by dissolving them in aqueous solution of sodium carbonate and reprecipitating with 10% HCl. The product was filtred, washed with water and methanol before drying at 70°C. The yields were about 55 - 60%. The IR spectrum spectra confirmed the formation of the diacids, and elemental analyses of the diacids were in agreement with the calculated values.

2.4.2.2. Synthesis of Bis(azidocarbonylphenoxy) methanes (F 2 a and F 2 c) and Bis[2-(azidocarbonylphenoxy)ethyl formals (F 2 b and F 2 d), the Diacylazides. General Procedure.

A suspension of the diacid (**F 1 a - F 1 d**) (0.01 mol) in 15 mL THF-water (1:1 v/v) mixture was stirred at 0°C when triethylamine (0.022 mol) in 5 mL THF was added dropwise over 30 min. To the clear solution formed was added ethyl chloroformate (0.022 mol) in 5 mL THF dropwise over 30 min and stirred for 2 h at 0°C. Next, sodium azide (0.025 mol) solution in 15 mL water was added dropwise over 30 min and the reaction mixture was stirred for 2 h at 0°C. Water (100 mL) was added dropwise and the reaction mixture was gradually allowed to attain ambient temperature. The solid that separated out was filtered, washed with water, and then dissolved in 25 mL dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure at room temperature afforded the corresponding diacylazide (**F 2 a - F 2 d**).

The crude product was dissolved in minimum amount of dichloromethane and poured into excess pet ether to obtain diacylazide (**F 2 a - F 2 d**) in pure form in yields in about 85 - 87 %.

2.4.2.3. Synthesis of Bis(diisocyanatophenoxy)methanes (F 3 a and F 3 c) and Bis[2-(isocyanatophenoxy)ethyl] formal (F 3 b and F 3 d), the Diisocyanates. General Procedure.

The diacylazide (**F 2 a - F 2 d**) (0.01 mol) was dissolved in 50 ml dry benzene and refluxed for 12 h. Evaporation of the solvent and recrystallization of the crude product from pet ether - benzene mixture gave the corresponding diisocyanate in pure form and in about 95-97% yields.

2.5. SYNTHESIS AND CHARACTERIZATION OF ESTER GROUP CONTAINING DIISOCYANATES

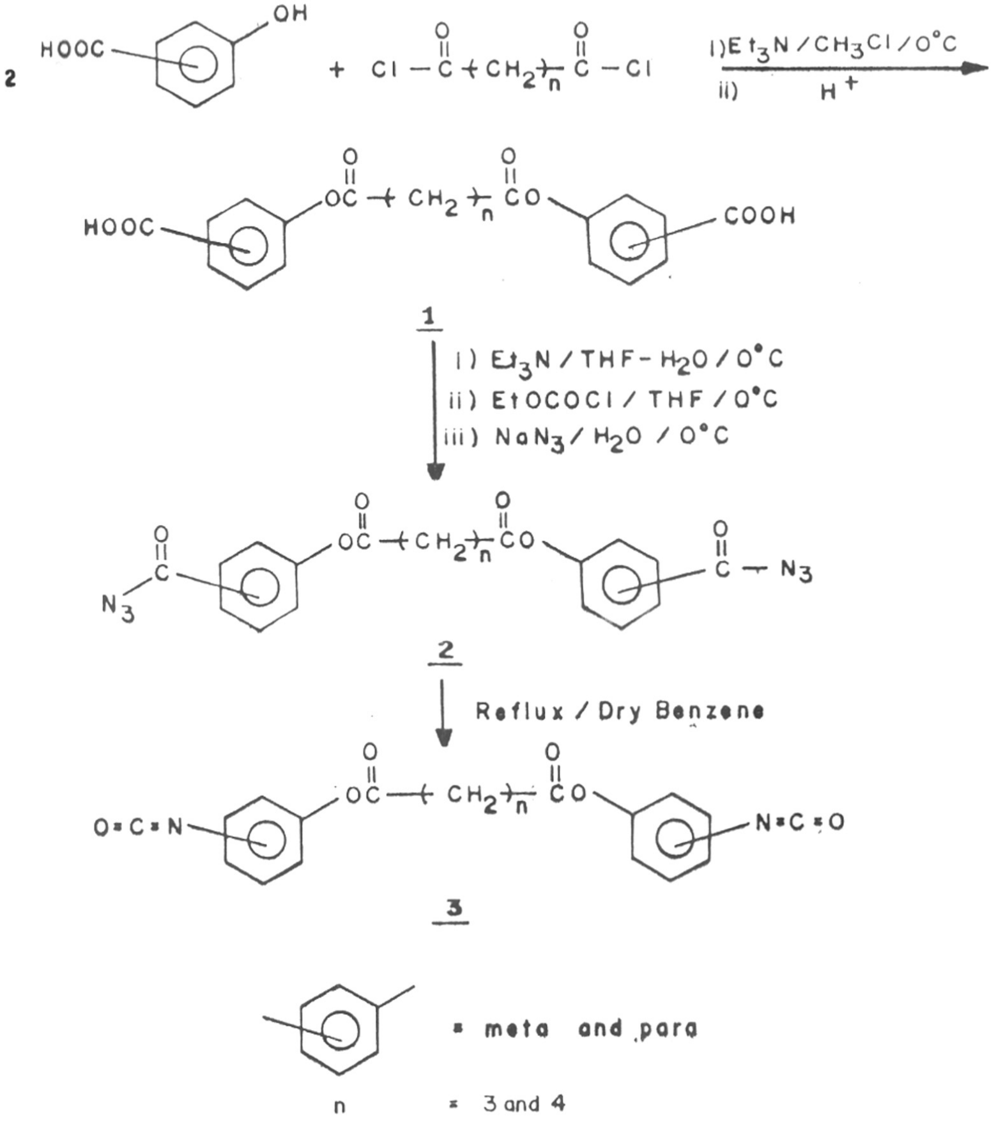
2.5.1. RESULTS AND DISCUSSION

By the non hazardous and non phosgenation Curtius rearrangement reaction, four new ester group containing diisocyanates were synthesized starting from the corresponding dicarboxylic acids as illustrated in Scheme 3.

The dicarboxylic acids (**E 1 a - E 1 d**) were prepared by the reaction of triethylamine salts of 3- or 4-hydroxybenzoic acids with alkanedioyldioxydichlorides (glutaroyl dichloride or adipoyl chloride) in yields ranging from 60-65% as detailed in the experimental section.

The diacylazides (**E 2 a - E 2 d**) were prepared from the dicarboxylic acids (**E 1 a - E 1 d**) by the elegant Weinstock modification of the Curtius reaction. The diacylazides were dissolved in dry benzene and decomposed by heating at reflux to yield the corresponding diisocyanates (**E 3 a - E 3 d**).

The IR spectra of the dicarboxylic acids (**E 1 a - E 1 d**) showed characteristic stretching absorptions at 1760 cm^{-1} (C=O of the ester group) and 1700 cm^{-1} (C=O of carboxylic acid). The IR spectra of the ester group containing diacylazides (**E 2 a - E 2 d**) exhibited characteristic stretching frequency bands at 2120 cm^{-1} (N_3), 1750 cm^{-1} (C=O of the ester group) and , 1700 cm^{-1} (C=O of the azidocarbonyl group). The IR spectra of the diisocyanates showed peaks at 2260 cm^{-1} (N=C=O) and 1750 cm^{-1} (C=O of the ester group).



SCHEME 3: SYNTHESIS OF (ALKANEDIOYLDIOXY) DIPHENYL DIISOCYANATES, E 3a-3d.

The IR spectra of dicarboxylic acid (**E 1 d**), diacyl azide (**E 2 d**), and diisocyanate (**E 3 d**) are shown in Figures 7 (a), 7 (b) and 7 (c), respectively.

In the ^{1}H-NMR spectrum of diacylazide, **E 2 d** (Figure 8), the aliphatic protons H_a occur as a quintet at 1.89δ . while protons H_b occur as a triplet at 2.68δ. Among the aromatic protons, protons H_c occur as a doublet (J=8 Hz) at 7.20δ, while protons H_d occur as a doublet (J=8 Hz) at 8.07δ. The downfield shift of H_d protons ortho to the azidocarbonyl group occurs due to the strong electron withdrawing nature of that group.

In the ^{1}H-NMR spectrum of the diisocyanate, **E 3 d** (Figure 9), the protons H_a occur as a quintet at 1.89 δ , while protons H_b occur as a triplet at 2.64δ . The aromatic protons (H_c and H_d) , occur as a multiplet centered at 7.60 δ.

The ^{1}H-NMR spectra of the diacylazides (**E 2 a – E 2 d**) and diisocyanates (**E 3 a – E 3 d**) were in accordance with the structures proposed. Mass spectra and elemental analysis of the diisocyanates confirmed the structures of the diisocyanates. The physical constants and spectral data of the diacylazides and diisocyanates are incorporated in Tables 8 and 9.

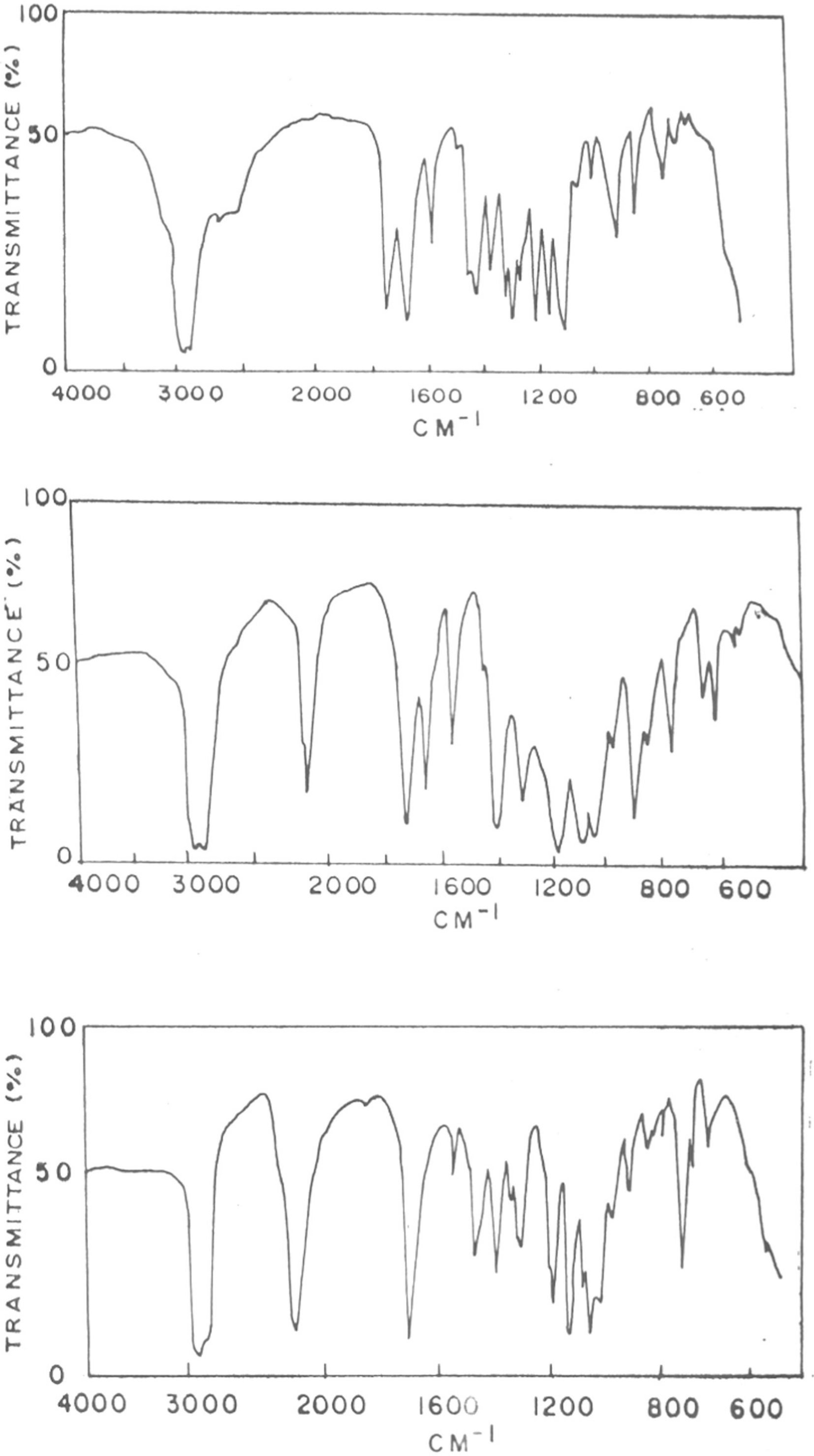


FIG. 7 : IR SPECTRUM OF(a) 4,4'-(ADIPOYL DIOXY) DIBENZOIC ACID, E 1d.
(b) 4,4'-(ADIPOYL DIOXY) DIBENZOYL DIAZIDE, - E 2d.
(c) 4,4'-(ADIPOYLDIOXY) DIPHENYL ISOCYANATE, E 3d.

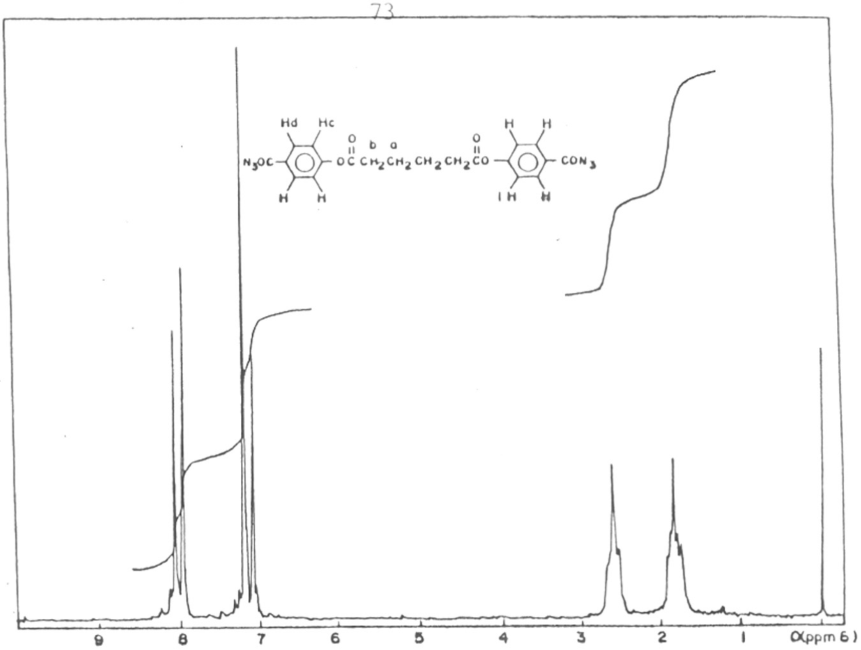


FIG.8: ^{1}H-NMR (CDCl$_3$) SPECTRUM OF 4,4'-(ADIPOYL DIOXY) DIPHENYL DIAZIDES, E 3d.

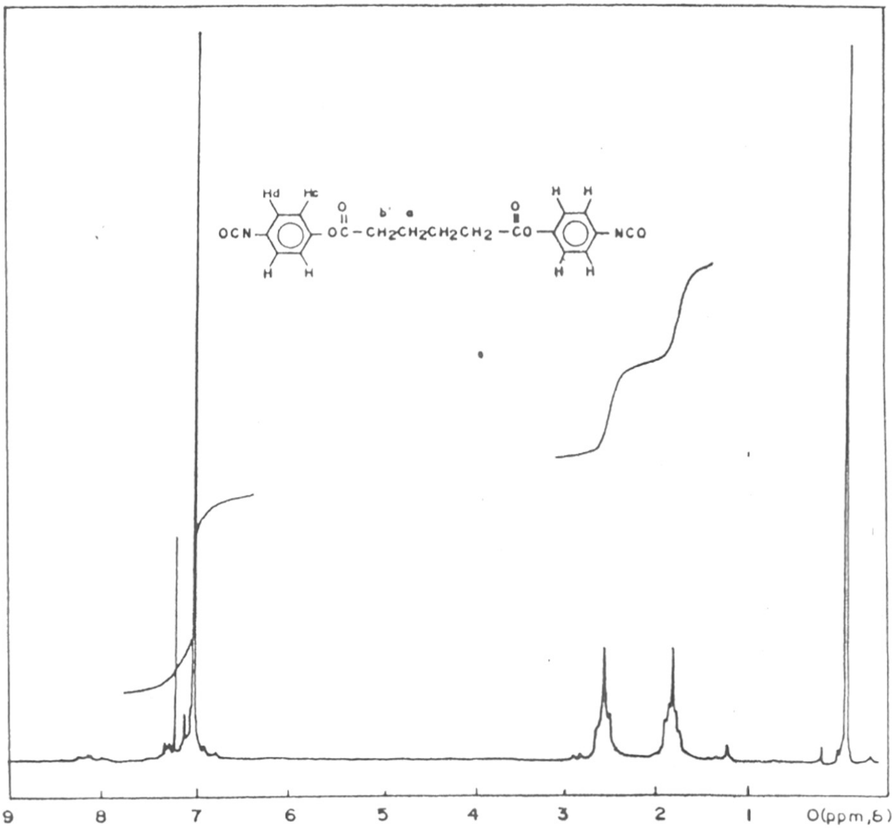
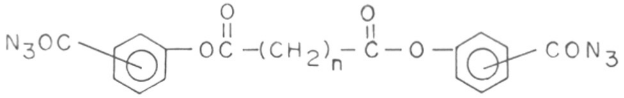


FIG.9 ^{1}H-NMR (CDCl$_3$) SPECTRUM OF 4,4'-(ADIPOYL DIOXY) DIPHENYL DIISOCYANATE, E 3d

TABLE 8

Physical and Spectral Data of (Alkanedioyldioxy)dibenzoyl Diazides (**E 2 a** – **E 2 d**).



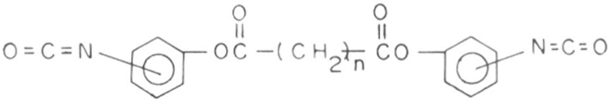
Product[1] **2**	n	Yield (%)	m.p °C	^{1}H-NMR ($CDCl_3$) (δ , ppm)
a	3	85	107	2.18 (quintet, 2 H), 2.68 (t, 4 H), 7.25 – 7.90 (m, 8 H)
b	4	86	98	1.89 (quintet, 4 H), 2.68 (t, 4 H), 6.81 – 7.48 (m, 8 H)
c	3	88	122	2.20 (quintet, 2 H), 2.76 (t, 4 H), 7.24 (d, 4 H), 8.11 (d, 4 H)
d	4	87	108	1.89 (quintet, 4 H), 2.68 (t, 4 H), 7.20 (d, 4 H), 8.07 (d, 4 H)

---

[1] a and b are meta- substituted, while c and d are para- substituted

TABLE 9

Physical and Spectral Data of (Alkanedioyldioxy)diphenyl Diisocyanates (**E 3 a** - **E 3 d**).



Product[1,2] **3**	n	Yield (%)	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ, ppm)	M^+ (70 ev)
a	3	95	71	2.18 (quintet, 2 H), 2.75 (t, 4 H), 6.95 (m, 8 H)	360
b	4	96	65	1.89 (quintet, 4 H), 2.68 (t, 4 H), 7.00 (m, H)	380
c	3	96	95	2.20 (quintet, 2 H), 2.77 (t, 4 H), 7.01 (m, 8 H)	366
d	4	97	88	1.89 (quintet, 4 H), 2.64 (t, 4 H), 7.60 (m, 8 H)	380

[1] a and b are meta- substituted, while c and d are para- substituted

[2] Satisfactory microanalyses obtained: C,±0.25 %, H,±0.20 %, N,±0.15 %.

2.5.2. EXPERIMENTAL

Materials:

. 3- and 4-Hydroxybenzoic acids were recrystallized from water.

. Glutaric acid and adipic acid were recrystallized from benzene and acetone-pet ether mixture, respectively.

. Sodium azide was first triturated with hydrazine hydrate and then dissolved in water before precipitation with acetone. It was dried in vacuum at room temperature to obtain `activated´ sodium azide.

. Tetrahydrofuran (THF), ethyl chloroformate, and triethylamine were all of reagent grade and were distilled prior to use.

. Glutaroyldichloride and adipoly chloride were prepared by refluxing the respective diacids with thionyl chloride in presence of a catalytic amount of pyridine. Removal of excess thionyl chloride and distillation of the crude product afforded glutaroyldichloride (bp 92°C/10 mm Hg) and adipoyl chloride (bp 112°C/10 mm Hg), respectively.[49,50]

2.5.2.1. Synthesis of 3,3´- and 4,4-(Glutaroyldioxy)dibenzoic acids (E 1 a and E 1 c) and 3,3´- and (Adipoyldioxy)dibenzoic acids (E 1 b and E 1 d), the Dicarboxylic acids.

General Procedure.

In a 100 mL three necked flask fitted with a dropping funnel, an overhead stirrer and a calcium chloride guard tube, was stirred a solution of 3- or 4-hydroxybenzoic acid (0.01 mol) in 50 mL chloroform at 0°C when triethylamine (0.022 mol) in 5 mL chloroform was added dropwise over 30 min . After stirring for 1 h and 30 min at 0°C, glutaroyldichloride or adipoyl chloride (0.005 mol) in 5 mL chloroform was added dropwise over 30 min and the reaction mixture was stirred overnight at ambient temperature.

Chloroform was removed under vacuum and the residue was dissolved in water, and acidified with dilute hydrochloric acid. The resulting dicarboxylic acids were filtered and washed with water and methanol before filtration and drying. The crude diacids were purified by dissolution in aqueous sodium carbonate solution followed by reprecipitation with 10% HCl. Filtration and washing with water and methanol followed by drying in an oven at 70°C afforded pure diacids in about 60 - 65% yields.

2.5.2.2. Synthesis of 3,3´- and 4,4´-(Glutaroyldioyldioxy)dibenzoyl diazides (E 2 a and E 2 c) and 3,3´ and 4,4´-(Adipoyldioyldioxy)dibenzoyl diazides (E 2 b and E 2 d), the Diacylazides. General Procedure.

To a well stirred suspension of the dicarboxylic acid (**E 1 a - E 1 d**) (0.01 mol) in 20 mL THF-Water (50/50 v/v) mixture maintained at 0°C was added triethylamine (0.022 mol) in 5 mL THF dropwise over 30 min and stirred for 1 h and 30 min. Ethyl chloroformate (0.025 mol) in 5 mL THF was added dropwise over 30 min and the reaction mixture was stirred for an additional hour at 0°C. Next, \`activated´ sodium azide (0.025 mol) solution in 20 mL water was added over 30 min and stirred for 1 1/2 h. Water (100 mL) was added dropwise and the reaction mixture was gradually allowed to attain ambient temperature.

The white solid that separated out was filtered at pump, washed with water and dissolved in 25 mL dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulphate. Evaporation of solvent at room temperature afforded a concentrated solution which when poured into excess of pet ether precipitated the respective diacylazide (**E 2 a** – **E 2 d**). The diacylazides were purified by pouring methylenechloride solutions into large excess of pet ether. Yields were in the region of 85-88%.

2.5.2.3. Synthesis of 3,3′- and 4,4′-(Glutaroyldioxy)diphenyl diisocyanates (E 3 a and E 3 c) and 3,3′- and 4,4′-(Adipoyldioxy) diphenyl diisocyanates (E 3 b and E 3 d), the Diisocyanates. General Procedure.

The diacylazide (**E 2 a** – **E 2 d**) (0.01 mol) was dissolved in 50 mL dry benzene and refluxed for 12 h. Evaporation of the solvent and recrystallization of the crude product from a mixture of pet ether-benzene afforded the corresponding diisocyanate (**E 3 a** – **E 3 d**) in pure form and in yields ranging from 95-97%.

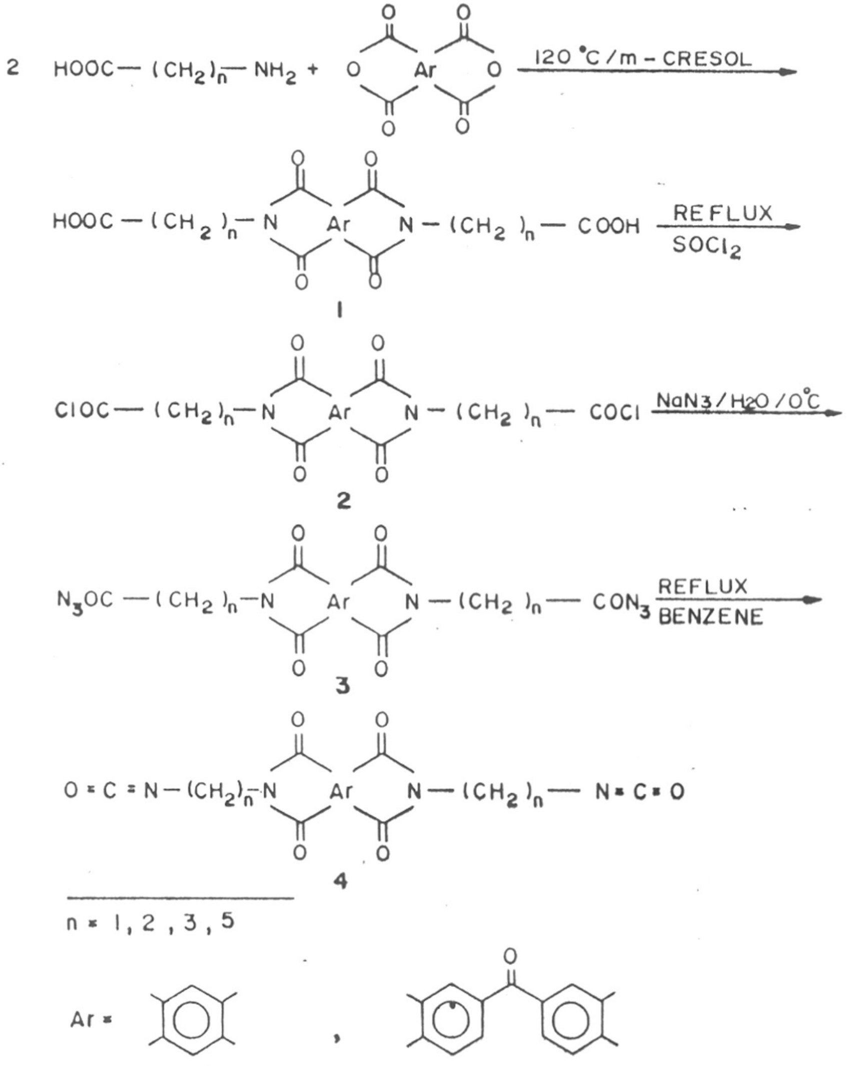
2.6. SYNTHESIS AND CHARACTERIZATION OF IMIDE GROUP CONTAINING DIISOCYANATES

2.6.1. RESULTS AND DISCUSSION

Imide group containing diisocyanates are considered to be useful intermediates for the synthesis of polymers containing imide groups. There are only a few reports in literature on the synthesis of pre-formed imide group containing diisocyanates. Matsuda[51] reacted pyromellitic dianhydride with toluene diisocyanate and obtained N,N′-bis(isocyanato)pyromellitimide. The product contained three possible stereoisomers and their isolation was difficult owing to their poor solubility. The synthesis of imide group containing diisocyanates was also reported by Masiulanis et al[52], who reacted pyromellitic dianhydride with excess diphenylmethane diisocyanate to obtain an imide containing diisocyanate and used it for the preparation of polyurethaneimides. However, in all the cases, it was difficult to isolate the pure imide containing diisocyanate in good yields. To our knowledge there was no report, on the synthesis of aliphatic diisocyanates containing pre-formed imide groups. Here the unequivocal synthesis of aliphatic diisocyanates containing pre-formed imide group *via* the Curtius rearrangement starting from the corresponding dicarboxylic acids was undertaken.

The synthesis of the pre-formed imide group containing diisocyanates (**I 4 a** – **I 4 h**) was carried out as shown in Scheme 4.

The parent dicarboxyolic acids (**I 1 a** – **I 1 h**) containing the



SCHEME. 4 : SYNTHESIS OF N,N-BIS(ISOCYANATO ALKYL)-1,2,4,5-BENZENETETRACARBOXYLIC-1,2:4,5-DIIMIDES, (I 4a-4d) and N,N-BIS(ISOCYANATO ALKYL)-3,3',4,4'-BENZOPHENONETETRACARBOXYLIC-3,3':4,4'-DIIMIDES, (I 4e-4h).

pre-formed imide rings were synthesized by the condensation of tetracarboxylic dianhydrides (0.1 mol), namely, pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) (0.1 mol) with the -aminoacids (namely, glycine, -alanine, 4-aminobutyric acid and 6-aminocaproic acid) (0.2 mol) in m-cresol in yields about 85-90% as detailed in the experimental section.[53]

These dicarboxylic acids (0.01 mol) were refluxed with excess thionyl chloride to form the diacylchlorides (**I 2 a** – **I 2 h**) which on treatment with sodium azide (0.025 mol) resulted in the formation of the respective diacylazides (**I 3 a** – **I 3 h**). The diacylazides were dissolved in benzene and refluxed to decompose into the corresponding diisocyanates (**I 4 a** – **I 4 h**). The diisocyanate was recrystallized from benzene-pet ether mixture.

The IR spectra of diacids (**I 1 a** – **I 1 h**) showed absorption bands at 1780 cm^{-1} and 1730 cm^{-i} (imide-I), 1700 cm^{-1} (C=O of the acid), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV).[54]

The IR spectra of the diacylchlorides (**I 2 a** – **I 2 h**) showed the absence of band at 1700 cm^{-1} (due to the C=O of the acid) and the appearance of a band at 1800 cm^{1} due to the C=O of the acid chloride, in addition to the above mentioned bands due to the cyclic imide structure.

The IR spectra of all imide containing diacylazides (**I 3 a** – **I 3 h**) exhibited characteristic peaks at 2130 cm^{-1} (N_3), 1780 cm^{-1} (imide-I), 1630 cm^{-1} (C=O of the acylazide), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV), while those of the diisocyanates (**I 4 a** – **I 4 h**) bearing the imide groups showed strong absorption at 2260 cm^{-1} (N=C=O) in addition to the above four bands due to the cyclic imide structure.

The IR spectra of the representative imide containing dicarboxylic acid (**I 1 h**), diacylazide (**I 3 h**), and diisocyanate (**I 4 h**) are shown in Figures 10 (a), 10 (b) and 10 (c), respectively.

In the ^1H-NMR spectrum of diacylazide, **I 3 h** (Figure 11), the aliphatic protons H_a occur as a triplet at 2.35δ, H_b protons occur as a multiplet centered at 1.57δ, and protons H_c occur as a triplet at 3.73δ. The aromatic protons H_d, H_e, and H_f occur as a multiplet centered at 8.13δ.

In the ^1H-NMR spectrum of the diisocyanate, **I 4 h** (Figure 12), the aliphatic protons H_a occur as a triplet at 3.31δ, H_b occur as a multiplet centered at 1.58δ, and H_c occur as a triplet at 3.74δ. The aromatic protons H_d, H_e, and H_f occur as a multiplet centered at 8.0δ.

^1H-NMR spectra of all the imide group containing diacylazides (**I 3 a** - **I 3 h**) and those of the diisocyanates (**I 4 a** - **I 4 h**) were in accordance with the structures proposed. Mass spectra and elemental analysis confirmed the structures assigned to the diisocyantes. The physical and spectral values of the diacylazides and diisocyanates are incorporated in Tables 10 and 11, respectively.

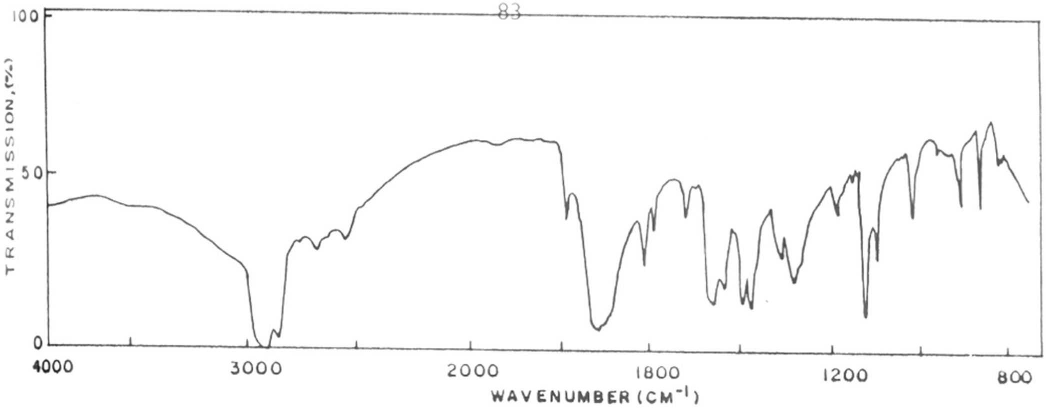


FIG.10(a): IR (NUJOL MULL) SPECTRUM OF N,N′- BIS (CARBOXYPENTYL) -3,3′,4,4′- BENZOPHENONETETRACARBOXYLIC 3,3′: 4,4′- DIIMIDE, I 1h.

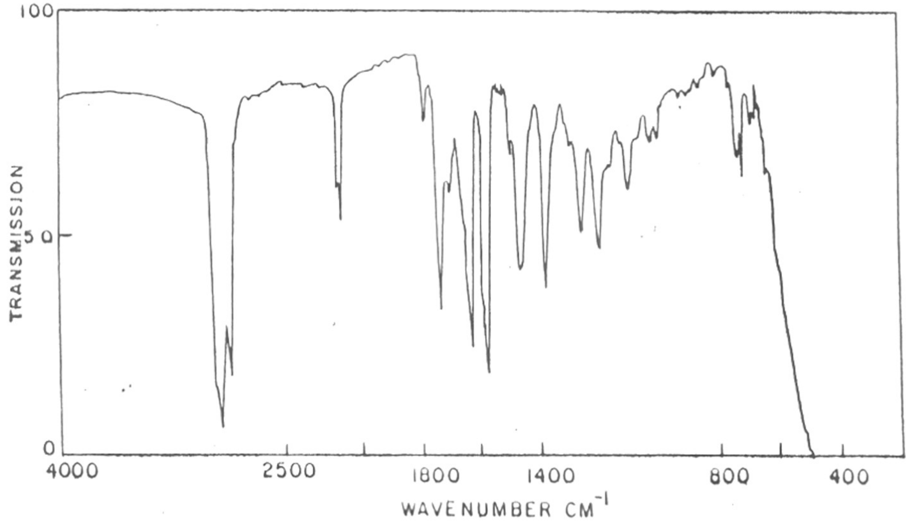


FIG 10 b IR(NUJOL MULL)SPECTRUM OF N,N′-BIS (AZIDOCARBONYL PENTYL) 3,3′,4,4′- BENZOPHENONETETRACARBOXYLIC-3,3′: 4,4′- DIIMIDE, I 3h.

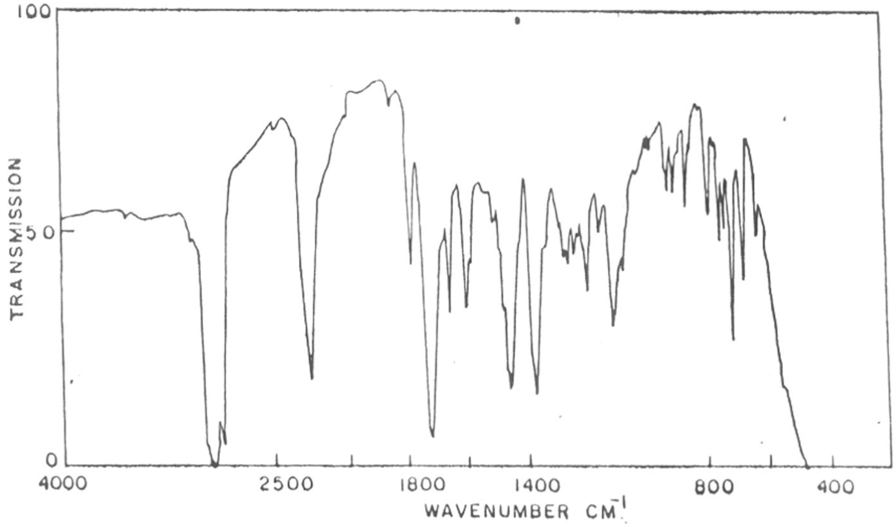


FIG.10c:IR (NUJOL MULL) SPECTRUM OF N, N′- BIS (ISOCYANATOPENTYL)—

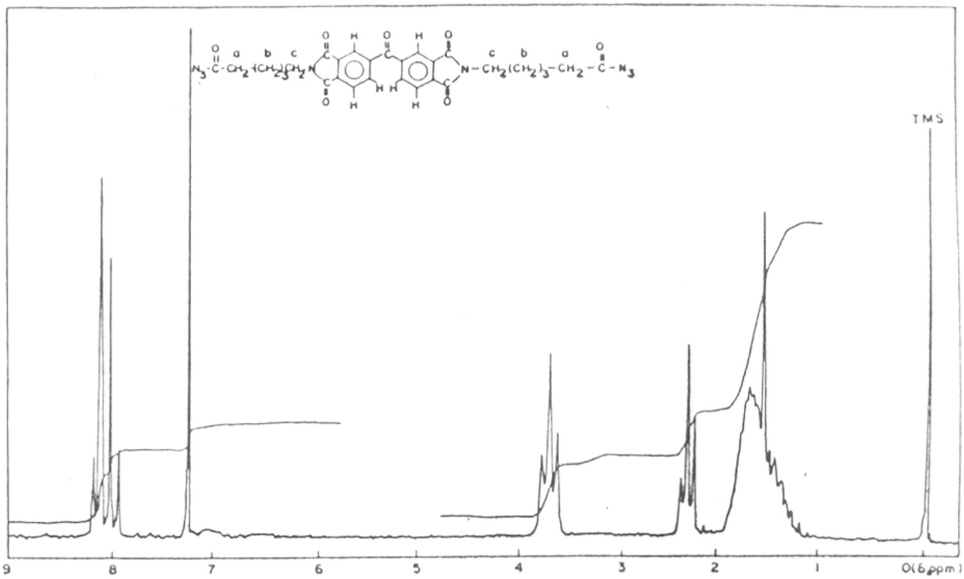


FIG. 11. ^{1}H-NMR ($CDCl_3$) SPECTRUM OF N,N′-BIS (AZIDOCARBONYLPENTYL)-3,3′,4,4′-BENZOPHENONE-TETRACARBOXYLIC-3,3′: 4,4′-DIIMIDE, 13h.

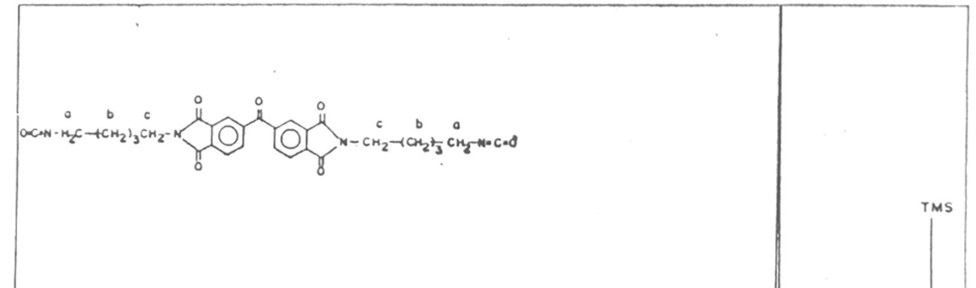
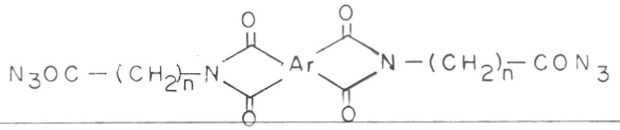


FIG. 12. ^{1}H-NMR ($CDCl_3$) SPECTRUM OF N,N′-BIS(ISOCYANATOPENTYL)-3,3′,4,4′-BENZOPHENONETETRACARBOXYLIC-3,3′:4,4′-DIIMIDE, 14h.

TABLE 10

Physical and Spectral Data of Imide Group Containing Diacylazides (I 3 a - 3h)



Product[1] 3	n	Yield (%)	m.p. °C	^{1}H-NMR ($CDCl_3$) (δ ppm)
a	1	85	129	4.48 (s, 4 H), 8.30 (s, 2 H)
b	2	88	125	2.79 (t, 4 H), 3.98 (t, 4 H), 8.27 (s, 2 H)
c	3	87	147	1.94 (m, 4 H), 2.56 (t, 4 H), 3.82 (t, 4 H), 8.23 (s, 2 H)
d	5	86	112	1.5 (m, 12 H), 2.32 (t,4 H), 3.72 (t, 4 H), 8.23 (s, 2 H)
e	1	85	120	4.48 (s, 4H), 8.01 (m, 6H)
f	2	86	152	2.80 (t, 4 H), 4.40 (t, 4 H), 7.99 (m, 6 H)
g	3	88	140	1.94 (m, 4 H), 2.62 (t, 4 H), 3.83 (t, 4 H), 8.00 (m, 6 H)
h	5	86	85	1.57 (m, 12 H), 2.35 (t, 4 H), 3.73 (t, 4 H), 8.13 (m. 6 H)

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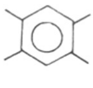
[1] I 4 a - I 4 d derived from PMDA while I 4 e - I 4 h derived from BTDA

Ar =



and

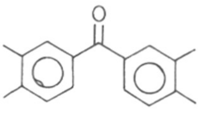
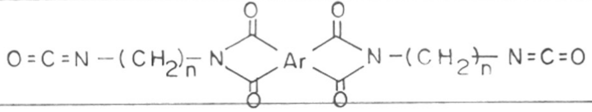


TABLE 11

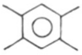
Physical and Spectral Data of Imide Group Containing Diisocyanates (**I 4 a** – **I 4 h**)



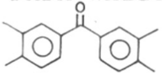
Product **4** [1]	n	Yield (%)	m.p. °C	^{1}H-NMR (CDCl$_3$) (δ, ppm)	M$^+$ (70 eV)
a	1	93	142	5.24 (s, 4 H), 8.37 (s, 2 H)	326
b	2	95	182	3.66 (t, 4 H), 3.99 (t, 4 H), 8.33 (s, 2 H)	354
c	3	95	162	1.84-2.20 (m, 4 H), 3.44 (t, 4 H), 3.89 (t, 4 H), 8.24 (s, 4 H)	382
d	5	96	158	1.23-1.84 (m, 12 H), 3.31 (t, 4 H), 3.73 (t, 4 H), 8.22 (s, 2 H)	438
e	1	96	145	5.20 (s, 2 H), 8.19 (m,6 H)	430
f	2	96	155	3.66 (t, 4 H), 4.07 (4 H), 8.20 (m, 6 H)	458
g	3	97	132	2.09 (m, 4 H), 3.42 (t, 4 H), 3.86 (t, 4 H), 8.00 (m, 6 H)	486
h	5	96	82	1.31 (m, 4 H), 3.31 (t, 4 H), 3.74 (t, 4 H), 8.00 (m, 6 H)	514

---

[1] Satisfactory elemental analysis obtained:
C, ± 0.25 %, H, ± 0.20 %, N, ± 0.15 %.
I 4 a – **I 4 d** derived from PMDA while **I 4 e** – **I 4 h** derived from BTDA. Ar =



and



2.6.2. EXPERIMENTAL

Materials:

- Glycine, β-alanine, 4-aminobutyric acid and 6-aminocaproic acid were of reagent grade and used as such.

- Thionyl chloride, triethylamine and m-cresol were distilled prior to use.

- Sodium azide was activated by trituration with hydrazine hydrate followed by dissolution in water and precipitation with acetone. It was finally dried in vacuum at room temperature.

- Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride and freshly sublimed in vacuum before use.[49,50]

2.6.2.1. Synthesis of N,N´-Bis(carboxyalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimide (I 1 a - I 1 d) and N,N´-Bis(carboxyalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´:4,4´-diimides (I 1 e - I 1 h), the Dicarboxylic acids. General Procedure.

Into a 100 mL three-necked flask were taken 50 mL m-cresol and the respective aminoacid (0.1 mol) and heated gently to 100°C with a magnetic stirring bar. To the solution was added the dianhydride (0.05 mol) in small portions. After heating the reaction mixture at 130 - 140°C for 3 h, the contents were poured into excess pet ether. The solid that separated out was filtered, washed with pet ether and methanol and heated in vacuum at 250°C for 3 h to achieve complete imidization. The yields of the imide containing dicarboxylic acids (I 1 a - I 1 h) were in the range 85-90%.

2.6.2.2. Synthesis of N,N´-Bis(azidocarbonylalkyl)-1,2,4,5-benenetetracarboxylic-1,2:4,5-diimides (I 3 a - I 3 d) and N,N´-Bis(azidocarbonylalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´:4,4´-diimides (I 3 e - I 3 h), the diacylazide .

General Procedure.

The diacid (I 1 a - I 1 h) (0.01 mol) was refluxed with thionyl chloride (0.2 mol) for 4 h with a catalytic amount of pyridine. Removal of thionyl chloride under reduced pressure and recrystallization of the residue from benzene-pet ether mixture gave the pure diacylchloride (I 2 a - I 2 h) in about 95-97% yield. The diacylchloride was recrystallized from pet ether-benzene mixture.

To an ice cold solution of sodium azide (0.025 mol) in 25 mL water was added the diacylchloride (I 2 a - I 2 h) (0.01 mol) solution in 20 mL dichloromethane dropwise and stirred vigourously for 2 h at 0°C. The dichloromethane layer was separated and washed successively with water, 5% Na_2CO_3, and water before it was dried over anhydrous Na_2SO_4. Removal of dichloromethane under reduced pressure at room temperature resulted in a concentrated solution of the diacylazide which when poured into excess of pet ether precipitated the azide in about 85 - 88 % yield.

2.6.2.3. Synthesis of N,N′-Bis(isocyanatoalkyl-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**I 4 a** - **I 4 d**) and N,N′-Bis(isocyanatoalkyl)-3,3′,4,4′-benzophenonetetracarboxylic-3,3′:4,4′-diimides (**I 4 e** - **I 4 h**), the Diisocyanates. General Procedure.

The diacylazide (**I 3 a** - **I 3 h**) (0.01 mol) were dissolved in 50 mL dry benzene and refluxed for 10 h. Evaporation of the solvent and recrystallization from a pet ether-benzene mixture gave the respective diisocyanates (**I 4 a** - **I 4 h**) in 93 - 97 % yields.

2.7. CONCLUSIONS

- A series of twelve oxyethylene containing, four formal group containig, four ester group containig, and eight pre-formed imide group containing diisocyantes have been synthesized by the non hazardous, non phosgenation Curtius reaction. The diisocyanates were characterized by IR, ^{1}H-NMR, mass spectroscopy and elemental analysis.
- These functional group containing diisocyanates have great potential for the utilization in the preparation of various polymers.

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CHAPTER 3

SYNTHESIS OF DIACYLHYDRAZIDES

3 SYNTHESIS AND CHARACTERIZATION OF DIACYLHYDRAZIDES

3.1 INTRODUCTION

Among the broad spectrum of active hydrogen containing nucleophiles are hydrazine (and substituted derivatives) and diacylhydrazides. These compounds are increasingly being sought after as monomers for the preparation of thermally stable and liquid crystalline polymers.[1,2]

Mono- and diacylhydrazides have been prepared by the reaction of carboxylic acids,[3] esters,[4] anhydrides,[4] or carbonyl chlorides,[5] with anhydrous hydrazine or carboxylic hydrazide, respectively. Amongst these, the reaction of esters with anhydrous hydrazine or 80% hydrazine hydrate is generally quantitative, while that with other acid derivatives, mixture of mono-, di-, tri-, and tetra- acylhydrazides[4,6-8] are formed.

Over the years, hydrazine and diacylhydrazides have been employed in the preparation of a wide variety of polymers. Campbell et al[9] described the preparation of polyurylene and polyacylsemicarbazide from the reaction of hydrazine and dihydrazides with diisocyanates, respectively.

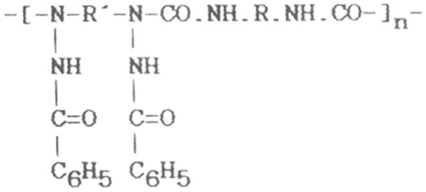
$$\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O} \; + \; \mathrm{H_2N{-}NH_2} \; \text{-------->} \; \mathrm{-[-NH.CO.NH{-}R{-}NH.CO.NH-]_n-}$$

$$\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O} \; + \; \mathrm{H_2N{-}NH.CO.R'.CO.NHNH_2} \; \text{----->}$$

$$\mathrm{-[-CO.NH{-}R{-}NH.CO.NH.NH.CO.R'.CO.NH.NH-]_n-}$$

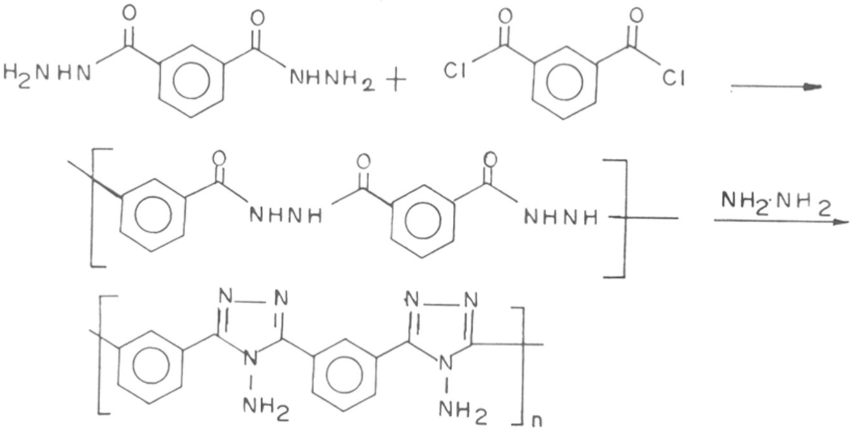
Takahashi[10] reports the preparation of new type of N-substituted polyureas and N-substituted polysemicarbazides, eg.,

$$C_6H_5\text{-CO.NH.NH-R}'\text{-NH.NH.CO-}C_6H_5 \quad + \quad O{=}C{=}N\text{-}R\text{-}N{=}C{=}O \quad \text{------->}$$



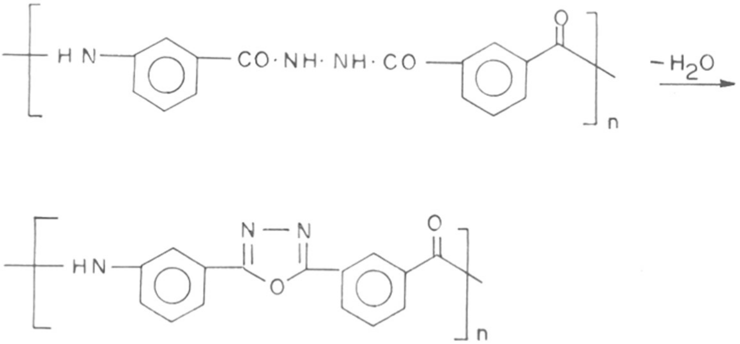
$$\text{-[-}\underset{\substack{|\\ \text{NH}\\ |\\ C{=}O\\ |\\ C_6H_5}}{\text{N}}\text{-R}'\text{-}\underset{\substack{|\\ \text{NH}\\ |\\ C{=}O\\ |\\ C_6H_5}}{\text{N}}\text{-CO.NH.R.NH.CO-]}_n\text{-}$$

From the reaction of two moles of hydrazine and one mole of dibasic acid at elevated temperature and pressure, Frazer,[11] and others,[12-14] obtained polyhydrazides and on further reaction with excess hydrazine, aminotriazoles were formed, eg.,



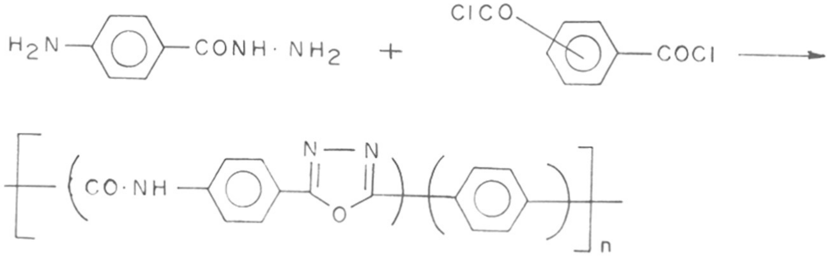
Polyhydrazides are polymers incorporating hydrazide linkages **-CO.NH.NH-** in the backbone. McFarlane and Miller[15] described the preparation of a series of polyhydrazides by the high temperature solution polymerization process. The preparation of aromatic polyhydrazides was detailed by Frazer and coworkers.[11,16]

Polyhydrazides are precursors of poly(1,3,4-oxadiazoles). The cyclodehydration of the polyhydrazides to the poly(1,3,4-oxadiazole) can be carried out either thermally near the glass transition temperature (Tg), or in solution using such dehydrating agents as acid chlorides, anhydrides, sulfuric acid, phosphorous oxychloride, polyphosphoric acid, etc.[1] By this method, Frazer et al[11], Iwakura[17], and Korshak,[18] and others,[19-23], obtained poly(1,3,4-oxadiazoles), eg.,



Polyoxadiazoles form fibers that have good strength and stiffness, good fatigue resistance and possess low density. Membranes can be prepared from polyoxadiazoles which have a high degree of permeability to water, and hence, these find application for reverse osmosis in sea water desalination. These polymers have salt rejection as high as 93% and this capacity depends on their structures.[24] Polyoxadiazoles form films, fibers, coatings, felts and laminates. Another application of these polymers is for the filtration of gases, and liquids at temperatures as high as 350°C.[25,26] Apart from finding use in adhesives, caulking compounds and channel sealants and fuel-tank liners, these polymers are used in thermal applications as they possess very good thermal and insulating properties.[27]

Preston and coworkers,[28] and Culberson and Murphy,[29] prepared poly(amide-hydrazides).



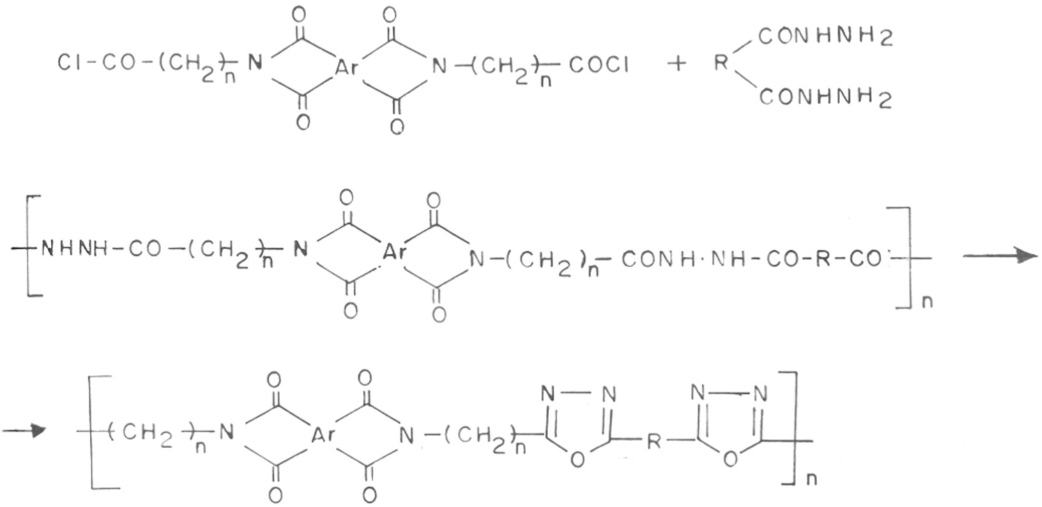
The preparation of poly(amide-hydrazides) by the phosphorylation technique was reported by Higashi[30,31] and Nanjan.[32]

The liquid crystalline nature of para-linked polyhydrazides and poly(amide-hydrazides) was studied by Morgan[2] and Hartzler.[33]

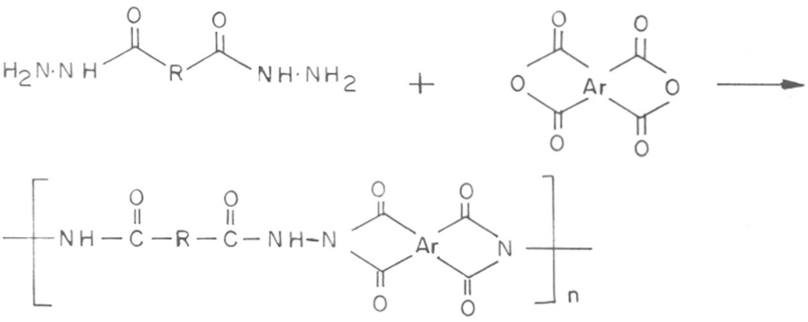
Poly(amide-hydrazides) possess excellent mechanical properties and are used in impact absorbing devices. Poly(amide-hydrazide) fibers find applications in fabric composites, tire-cord applications, etc.[28] Other areas of applications are as membranes for reverse osmosis.[34] Consequently, these films are employed for water pollution control, for the concentration of fruit juices,[35] and as semipermeable membranes for the desalination of sea water.[36]

The direct amidation of the acids by dihydrazides was achieved by the phosphorylation technique. The use of such systems as triphenylphosphite/pyridine/LiCl,[37] triphenylphosphite/LiCl,[30] or diphenylphosphite/pyridine/LiCl[31] has been made.

The low temperature solution polymerization of diacid chlorides containing preformed imide rings and diacylhydrazides[37-40] leads to the formation of poly(imide-hydrazides), as shown below.



Diacylhydrazides have also been employed in the preparation of poly(amide-imide)s. By the low temperature solution polycondensation of aliphatic or aromatic diacylhydrazides with tetracarboxylic dianhydrides, poly(amide-imide)s have been prepared.[41-46]



Highly polar solvents such as hexamethylphosphoramide (HMPA), N-methyl pyrrolidone (NMP), N,N-dimethylacetamide, etc., are normally employed for the polymerization reaction. Lithium chloride is often employed to dissolve the diacylhydrazide monomer (in case it is insoluble in the solvent).

Several structurally modified diacylhydrazides have been synthesized and employed in the preparation of various polymers. Table 12 incorporates a few of these diacylhydrazides.

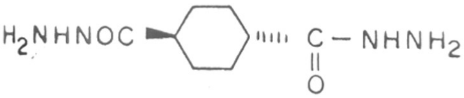
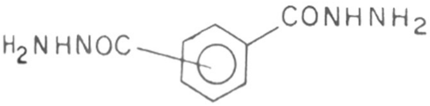
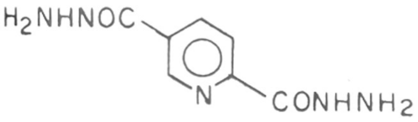
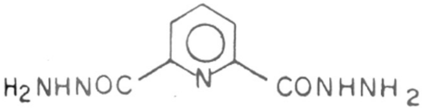
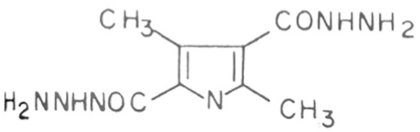
3.2 APPLICATIONS

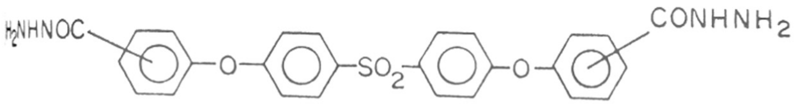
Diacylhydrazides are a useful class of condensation monomers that have been employed in the synthesis of various polymers. The polymers based on diacylhydrazides combine excellent thermooxadative stability with good mechanical strength. These polymers are versatile and they form fibers, films, membranes, coatings, etc.

The most important classes of polymers that can be derived from diacylhydrazides are : i. Polyureas, ii. polysemicarbazides, iii. Polyhydrazides, and Poly(1,3,4-oxadiazole)s, iv. Poly(amide-hydrazide)s, v. Poly(imide-hydrazide)s, and vi. Poly(amide-imide)s.

TABLE-12

SOME MONO-AND DIACYLHYDRAZIDES USED IN THE PREPARATION OF POLYMERS

HYDRAZIDE	REFERENCE
$H_2NHNOC{-}(CH_2)_n{-}CONHNH_2$	41,47,48
	41
	16,48
	16,21
	16
	41



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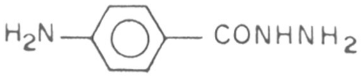
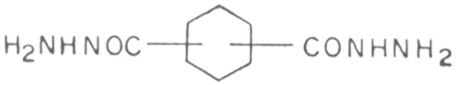


23, 29, 49



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17, 51

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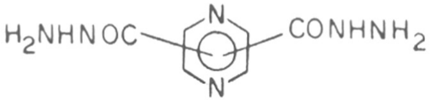


16

3.3 SCOPE OF THE PRESENT WORK

Diacylhydrazides are an important class of active hydrogen containing nucleophiles. These condensation monomers have been utilized for the preparation of various polymers, such as, polyurylenes, polyacylsemicarbazides, polyhydrazides, poly(1,3,4-oxadiazoles), poly(amide-hydrazide)s, poly(imide-hydrazides), poly(amide-imide)s, etc.

Oxyethylene group is a flexibilizing linkage. When incorporated into the backbone of rigid polymer chain, these groups would be expected to lower the glass transition temperature (Tg) and increase the solubility without significantly affecting the thermal and mechanical properties.

Hence, the synthesis and characterization of four oxyethylene group containing diacylhydrazides was targeted. These would lead to polymers containing oxyethylene linkages in the polymer backbone.

Towards this end, two non linear diacylhydrazides containing oxyethylene moiety, viz., 1,2-bis(3-hydrazinocarbonylphenoxy)ethane (**4 a**) bis[2-(3-hydrazinocarbonylphenoxy) ethyl] ether (**4 b**), and two linear diacylhydrazides, viz., 1,2-bis(4-hydrazinocarbonylphenoxy)ethane (**4 c**) and bis[2-(4-hydrazinocarbonylphenoxy)ethyl] ether (**4 d**), were synthesized and the former two diacylhydrazides were utilized for the preparation of oxyethylene containing poly(amide-imide)s.

3.4 RESULTS AND DISCUSSION

Oxyethylene group is a flexibilizing group and its incorporation into polymer backbone is reckoned to impart flexibility, and occasionally improved solubility to polymers without significantly affecting the thermal stability and other properties.

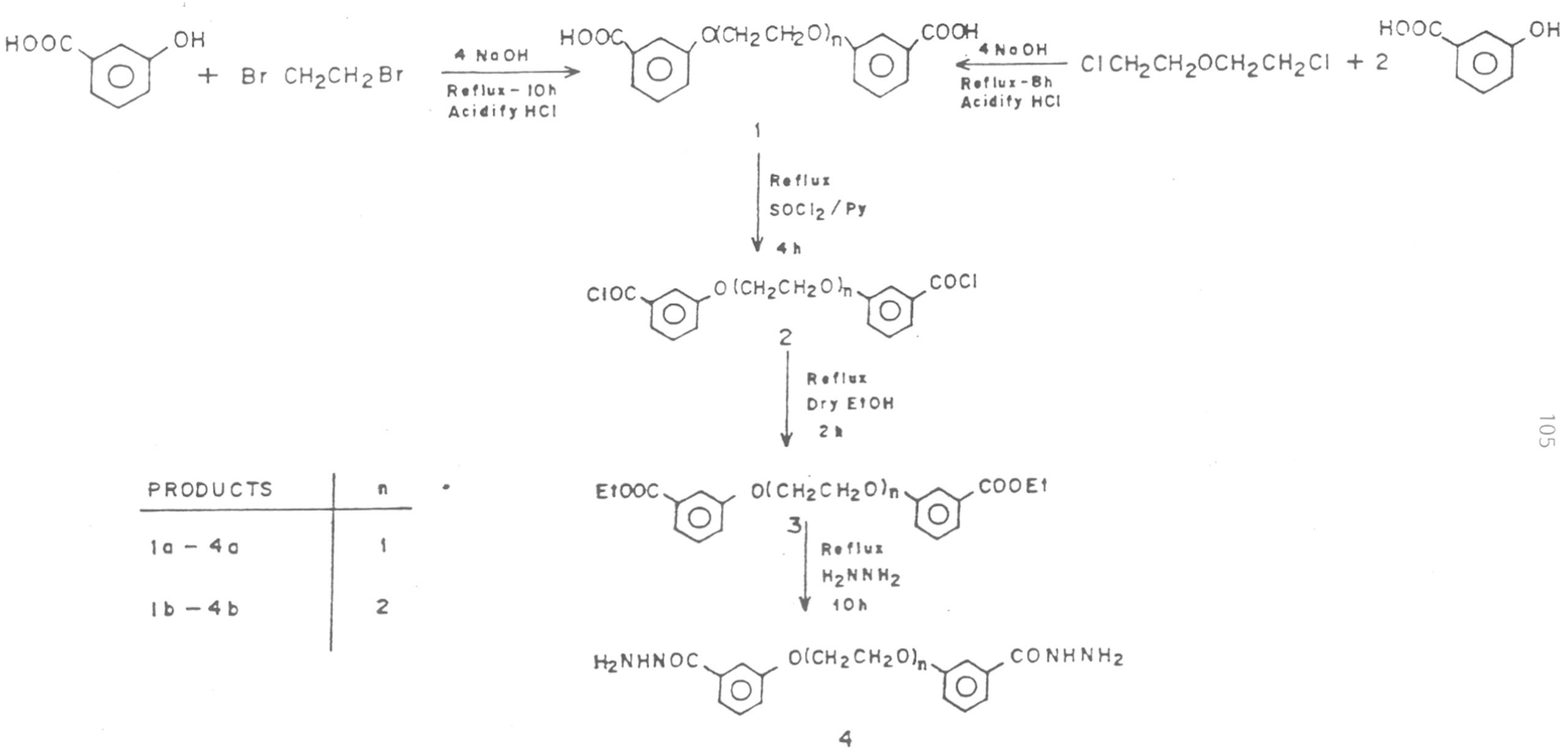
Two non-linear diacylhydrazides containing oxyethylene moiety, viz., 1,2-bis(3-hydrazinocarbonylphenoxy)ethane (**4 a**) and bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether (**4 b**), were synthesized by the facile and convenient acylation reaction of hydrazine hydrate with the corresponding aromatic diethylester,[52] as illustrated in Scheme 5.

Two linear diacylhydrazides, viz.,(1,2-Bis(4-hydrazinocarbonylphenoxy)ethane (**4 c**) and bis[2-(4-hydrazinocarbonylphenoxy) ethyl] ether (**4 d**), the *para*- analogs, were also prepared but owing to their poor solubilities, these were not pursued further.

The oxyethylene containing dicarboxylic acids (**1 a - 1 d**) were synthesized by the reaction of 2 mols of 3- or 4-hydroxybenzoic acid with 1.0 mol of either dibromoethane or 2-chloroethyl ether in aqueous sodium hydroxide solution.

The dicarboxylic acids were characterized by IR spectra, and elemental analysis (Chapter 2).

The preparation and characterization of diacylchlorides (**2 a - 2 d**) is described in Chapter 2 (Section 2.3.2.2 and Section 2.3.1, respectively).



PRODUCTS	n
1a – 4a	1
1b – 4b	2

SCHEME 5 : 1,2-BIS (HYDRAZINOCARBONYLPHENOXY) ETHANES, 4a and 4c, and BIS [2-(HYDRAZINOCARBONYLPHENOXY) ETHYL] ETHERS, 4b and 4d: SYNTHESIS.

The diacylchlorides were converted into the corresponding diethyl esters (**3 a** - **3 d**) by refluxing with excess of dry ethanol.

The IR spectra of the diethyl esters (**3 a** - **3 d**) showed charateristic bands at 1760 cm^{-1} (ester carbonyl) and 1240 cm^{-1} (C-O-C).

The diethyl esters (**3 a** - **3 d**) were refluxed with excess hydrazine hydrate in dry ethanol to yield the corresponding diacylhydrazides (**4 a** - **4 d**) in yields in the range 78-85%. The melting points of the diacylhydrazides are incorporated in Table 13.

The diacylhydrazides were characterized by IR, ^{13}C-NMR, mass spectroscopy and elemental analysis. The IR spectra of the diacylhydrazides showed absorption bands at 3260 cm^{-1} (N-H), 1650 cm^{-1} (C=O) and 1240 cm^{-1} (C-O-C). Representative IR spectra of the diacylhydrazide (**4 b**) is shown in Figure 13. The ^{13}C-NMR spectra of the meta- oriented diacylhydrazides (**4 a** and **4 b**) were obtained in $CDCl_3$. The chemical shifts for the respective carbon atoms of the diacylhydrazides (**4 a** and **4 b**) are incorporated in Table 14. The ^{13}C-NMR spctra of diacylhydrazides **4 a** and **4 b** are shown in Figures 14 and 15, respectively.

The mass spectra of the diacylhydrazides **4 a** and **4 b** showed molecular ion peaks at 330 and 374, respectively, indicating the agreement with the expected values. The elemental analyses for the diacylhydrazides (**4 a** - **4 d**) were in good agreement with the calculated values confirming the structures assigned for the diacylhydrazides.

TABLE 13

The Yields and Melting Points of Diacylhydrazides, **4 a - 4 d**.

Product[1] **4**	R	Yield (%)	m.p °C
a	$-CH_2CH_2-$	78	225
b	$-CH_2CH_2-O-CH_2CH_2-$	85	144-145
c	$-CH_2CH_2-$	83	235-237
d	$-CH_2CH_2-O-CH_2CH_2-$	84	195

[1] Satisfactory microanalytical results were obtained.
a and b are meta- oriented
c and d are para- oriented

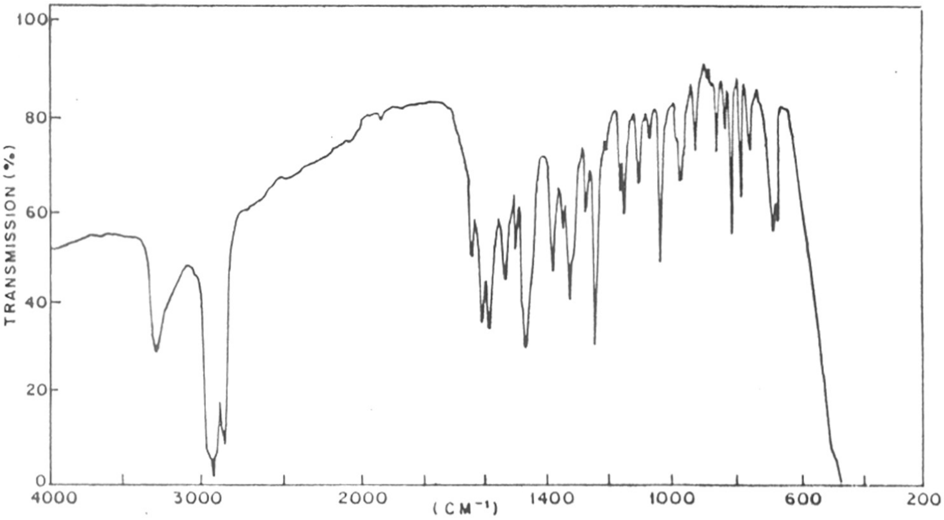
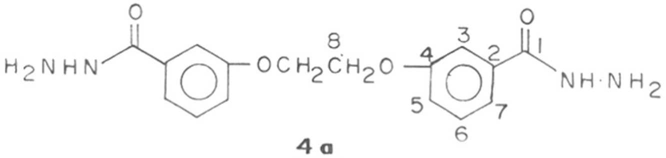


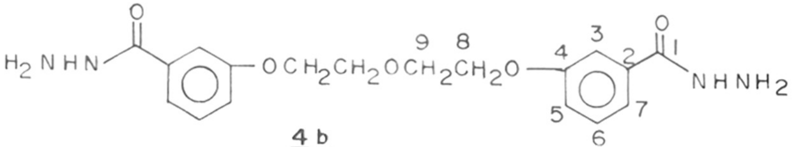
FIG. 13 : INFRARED SPECTRUM OF 1,2-BIS(3-HYDRAZINOCARBONYLPHENOXY) ETHANE

TABLE 14

^{13}C-NMR Chemical Shifts of Diacylhydrazides, **4 a** and **4 b**



4 a



4 b

Carbon No.	Diacylhydrazide 4 a ppm	Diacylhydrazide 4 b, ppm
1	165.61	166.91
2	134.87	135.00
3	129.48	130.39
4	158.33	159.12
5	112.90	113.56
6	117.65	118.50
7	119.60	120.06
8	66.57	68.13
9		69.62

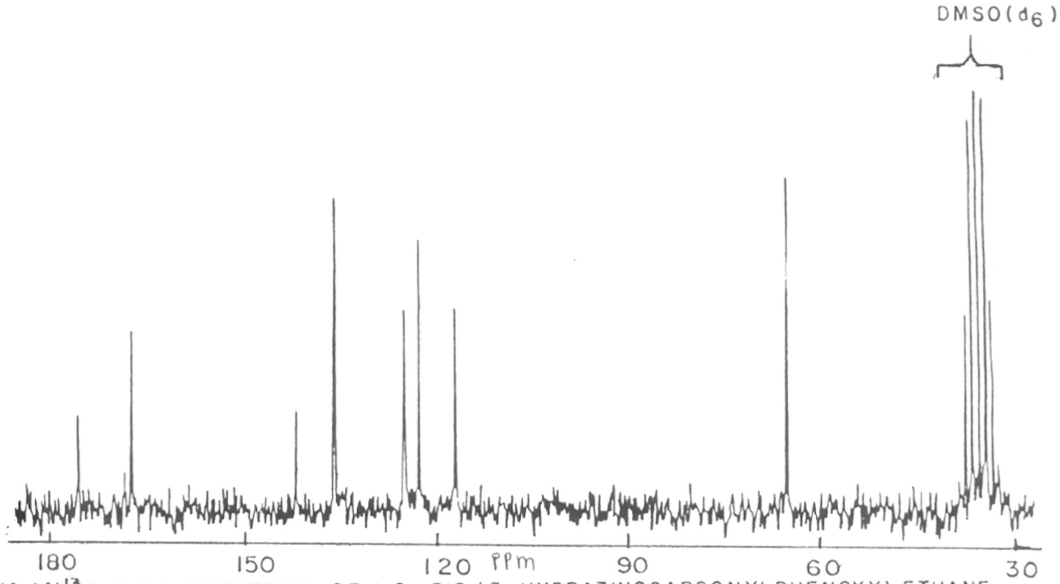


FIG. 14: ^{13}C-NMR SPECTRUM OF 1,2-BIS (3-HYDRAZINOCARBONYLPHENOXY) ETHANE

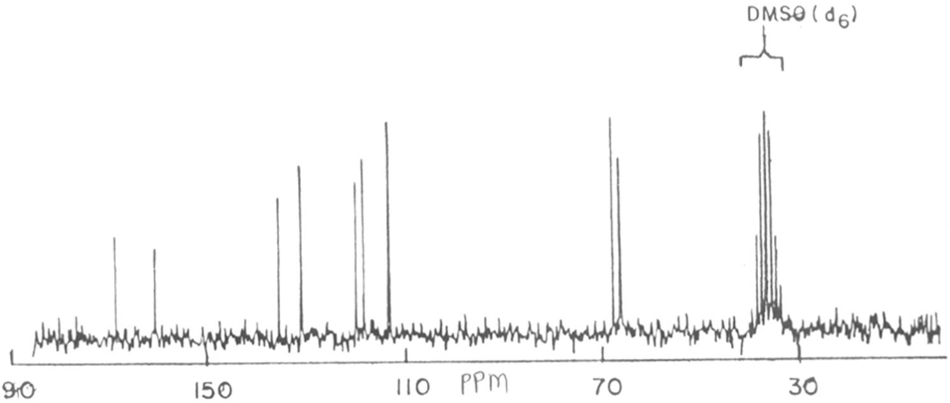


FIG. 15: ^{13}C-NMR SPECTRUM OF BIS [2-(3-HYDRAZINOCARBONYLPHENOXY) ETHYL] ETHER

3.5. CONCLUSIONS

. Two non-linear and two-linear diacylhydrazides, viz., 1,2-bis(3- and 4-hydrazinocarbonylphenoxy)ethane and bis[2-(3- and 4-hydrazinocarbonylphenoxy]ethyl ether, were prepared conveniently by the facile acylation of hydrazine hydrate with the corresponding diethyl esters.

. The diacylhydrazides were characterized in detail by IR, ^{13}C-NMR, mass spectroscopy and elemental analysis.

3.6 EXPERIMENTAL

Materials

- 1,2-Dibromoethane, 2-chloroethyl ether, and thionyl chloride were all distilled prior to use.[53]

- Hydrazine hydrate and all other chemicals were of reagent grade and were used as received.

3.6.1 Preparation of 1,2-Bis(carboxyphenoxy)ethanes (1 a and 1 c) and Bis[2-(carboxyphenoxy)ethyl] ethers, 1 b and 1 d), the dicarboxylic acid. General Procedure.

The dicarboxylic acids (**1 a** - **1 d**) were prepared as detailed in Chapter 2 (Section 2.3.2.1).

3.6.2 Preparation of 1,2-Bis(carbethoxyphenoxy)ethanes (3 a and 3 c) and Bis[2-(carboxyphenoxy)ethyl] ethers (3 b and 3 d), the diethyl esters. General Procedure.

The diacids (**1 a** - **1 d**) (0.01 mol) were reflexed with excess of thionyl chloride (0.2 mol) for 2 h. Excess thionyl chloride was distilled under reduced pressure. The crude product was recrystallized from a mixture of pet ether-benzene mixture to afford the corresponding diacylchlorides (**2 a** - **2 d**) in yields above 90 %).

The diethyl esters were prepared by refluxing (0.01 mol) the diacyl chloride (**2 a** - **2 d**) in 100 mL of dry ethanol. Removal of solvent and recrystallization of the crude product from pet ether gave the corresponding diethyl esters in pure form and in yields ranging from 90-97%.

3.6.3 Preparation of 1,2-Bis(hydrazinocarbonylyphenoxy) ethanes (4 a and 4 c) and Bis[2-(hydrazinocarbonylphenoxy) ethyl] ethers (4 b and 4 d), the diacylhydrazides. General Procedure.

To a solution of the diethyl ester (**3 a - 3 d**) (0.01 mol) in 100 mL ethanol was added hydrazine hydrate (0.04 mol) and refluxed for 10 h. The solid that separated out was filtered and recrystallized from water-dimethylacetamide mixture to give the corresponding diacylhydrazide (**4 a - 4 d**) in pure form and in yields in the range 78-85%.

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CHAPTER 4

POLYURETHANES

4. SYNTHESIS AND CHARACTERIZATION OF POLYURETHANES

4.1 INTRODUCTION

A new family of polymers, the polyurethanes were conceived and developed by O. Bayer[1] at Farbenfabriken Bayer by the polyaddition of organic diisocyanates and diols in the year 1937. The exceptional versatility of the isocyanate moiety has been exploited and an entire series of different polymers has arisen. Polyurethanes have revealed unusual versatility and consequently, they have the widest range of polymer applications: fibers, elastomers, foams, adhesives, coatings, etc.

Polyurethanes contain the **-NH-CO-O-** grouping along the polymer backbone. A polyurethane linkage may be considered as an ester of unstable carbamic acid or amide ester of carbonic acid. Polyurethanes are characterized by outstanding properties and find application in various specialized areas.

There are three processes for the preparation of solid polyurethanes - a widely utilized engineering material. These are i) castable process, ii) linear millable gums preparation, and iii) the injection molding and extrusion technique. In the casting process, the components are mixed in the liquid state and poured into a mold and cured in the mold itself. In the production of linear millable gums, the components are mixed with curing agents and crosslinked or vulcanized as with hydrocarbon rubbers. Thermoplastic polyurethanes are prepared by reaction injection molding and extrusion.

The various aspects of the synthesis, properties and applications of polyurethanes have been extensively reviewed.[2-4]

4.2 METHODS OF PREPARATION OF POLYURETHANES

Polyurethanes can be prepared by a variety of methods. The important synthetic routes are given blow.

4.2.1. Diol - Diisocyanate Reaction

This is the commonest and the most widely used method for the synthesis of polyurethanes.[5] Here the di- or poly-functional hydroxy compounds (commonly referred to as polyols) are reacted with di - or poly- functional isocyanates.

$$\mathrm{HO{-}R{-}OH} \;+\; \mathrm{O{=}C{=}N{-}R'{-}N{=}C{=}O} \;\mathrm{{-}{-}{-}{-}{>}}\; \mathrm{{-}({-}O{-}R{-}O{-}CO{-}NH{-}R'{-}NH{-}CO{-})_n{-}}$$

In an attempt to develop a polymer to rival the polyamide (Nylon) of Du Pont, Bayer utilized the above reaction scheme to prepare polyurethanes. He reacted 1,4-butane diol with 1,6-hexamethylene diisocyanate and obtained a polyurethane that could form bristles and fibres.

$$\mathrm{HO{-}(CH_2)_4{-}OH} \;+\; \mathrm{O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O} \;\mathrm{{-}{-}{-}{>}}$$
$$\mathrm{{-}[{-}O{-}(CH_2)_4{-}O{-}CO{-}NH{-}(CH_2)_6{-}NH{-}CO{-}]_n{-}}$$

Essentially, equivalent quantities of diisocyanates and diols are reacted to obtain high molecular weight, linear polyurethanes. Polar solvents, such as dimethylsulfoxide, dimethyl formamide, etc., may be employed for preparing polyurethanes.

The NCO - OH reaction is exothermic. Nonetheless, the temperature of the reaction is raised to 130 - 140°C and maintained for 2 h to effect complete reaction to allow high molecular weight polyurethanes to be formed.

Polyurethanes are often prepared by the reaction of a long chain diol with an excess of a diisocyanate to obtain an isocyanate terminated `prepolymer´. This prepolymer with reactive NCO groups react separately with diols or diamines to form high molecular weight polyurethanes.

The NCO-OH reaction is promoted by tertiary amines by the activation of both the reactants. An increase in basic strength of a catalyst is accompanied by an increased catalytic activity, except when steric hindrance interferes.[6] Some of the basic catalysts used for the isocyanate-alcohol reaction are N-methyl or ethyl morpholine, triethylamine, tetraethylene diamine, etc.

Metal compounds that are soluble in organic solvents (eg., metal acetylacetones, 2-ethylhexanoates, alkylmetal salts of fatty acids, etc.) exert a catalytic effect on the NCO-OH reaction. Other metal compounds that are used as catalysts are dibutyltin acetate, di-n-butyltin dilaurate, tributyltin acetate, tetrabutyltin, stannic chloride, etc.

The solvent employed may affect the rate and effectiveness of the catalyst. In general, the solvents that readily complex with the active hydrogen compound or the catalyst (eg. by hydrogen bonding or dipole moment interaction) provide a slower reaction rate than a solvent that can not easily associate with reactants and catalysts.

Most commercial applications utilize solvent-free system. By the judicious choice of the catalyst and temperature, the NCO-OH reaction can be forced in the desired direction. For linear polymers, low temperatures are desired to suppress the side reactions like biuret formation, the allophanate formation or the trimerization reaction, among other.

4.2.2. **Bischloroformate - Diamine Reaction**

By the reaction of bischloroformates with diamines, polyureathanes can conveniently be formed,[7] both by interfacial technique as well as solution polymerization technique.

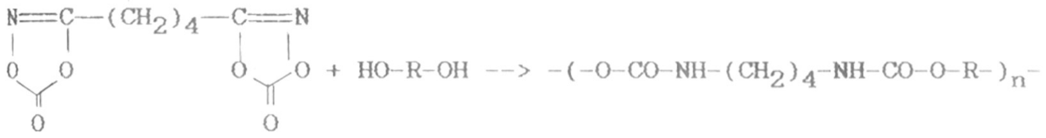
$$Cl\text{-}CO\text{-}O\text{-}R\text{-}O\text{-}CO\text{-}Cl \;+\; H_2N\text{-}R'\text{-}NH_2 \;\text{--->}\; \text{-}(\text{-}CO\text{-}O\text{-}R\text{-}O\text{-}CO\text{-}NH\text{-}R'\text{-}NH\text{-})_n\text{-}$$

A very convenient way of producing polyurethanes by the above route is *via* the interfacial polycondensation. The principle consists of the formation of a polymer at the interface of the two solvents that are immiscible. The diamine is dissolved in water while the bischloroformate is dissolved in an organic phase. The polymer formed dissolves in an organic solvent. The bischlorformate - diamine reaction lends itself to the preparation of a great variety of polyurethanes and copolymers, such as, poly(urethane-co-urea)s, poly(urethane-co-amide)s, poly(urethane-co-carbonate)s, etc., by the interfacial condensation.

The synthesis of polyurethanes and copolymers by interfacial condensation technique has been studied by Morgan.[8] Tanaka[9] reviewed the preparation of polyurethanes and copolymes by interfacial polycondensation.

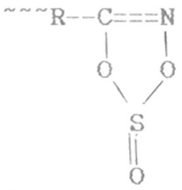
4.2.3. **Adiponitrile Carbonate - Diol Reaction.**

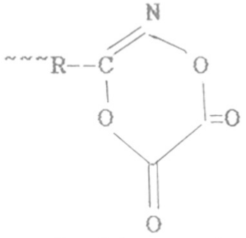
In an indirect method, polyurethanes may be prepared by the reaction of 3,3′-tetramethylenedi-(1,4,2-dioxadiazol-5-one) (adiponitrile carbonate, ADNC) with diols or polyols in presence of certain metal catalysts, eg., tin catalysts. The catalyst may be used alone or in combination with tertiary amine catalyst. The polyurethane is formed with the evolution of carbondioxide.[10-12]

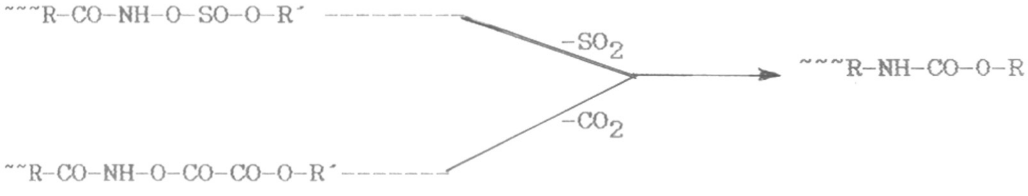


4.2.4. Cyclic Sulfites and Oxalates - Active Hydrogen Compounds Reaction

Burk and coworkers[11,12] demonstrated that cyclic sulfites and oxalates can also be used to form urethanes. These cyclic derivatives yield hydroxamates by the reaction with active hydrogen compounds. In the case of diols or polyols, these hydroxamates can be decomposed to yield polyurethanes in a manner similar to that for nitrile carbonates.


Cyclic sulfites

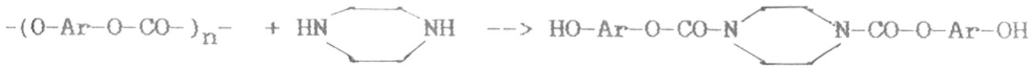

Cyclic oxalates



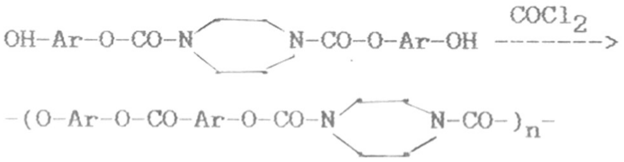
4.2.5. Miscellaneous Routes

A. In an indirect route to the preparation of polyurethanes, a urethane diphenol is formed first which on phosgenation results in the formation of alternating copolymers.[13]

Piperazine is reacted with an aromatic polycarbonate to yield a urethane diphenol.



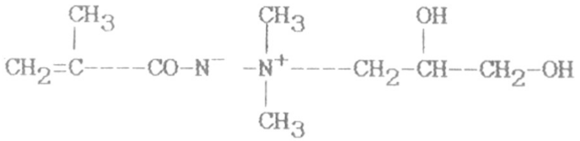
Urethane diphenol



Poly(carbonate-co-urethane)

B. From Aminides

Aminides containing two hydroxyl groups are formed by the reaction of an ester (eg. methyl methacrylate) with 1,1-dimethyl-hydrazine and 2-hydroxymethyl oxirane.[14]



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}{-}{-}{-}CO{-}N^- \; {-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}{-}{-}{-}{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}{-}CH_2{-}OH$$

The homopolymerization of this monomer with azobisisobutyronitrile (AIBN) in either water or methanol leads to the formation of a polymer which, on pyrolysis at 170°C for 2 h yields a cross-linked product containing urethane linkage.

4.3. APPLICATIONS

The application of polyurethanes are both numerous and varied. They are used as foams, elastomers and thermoplastic materials. Flexible foams are low density materials which are resilient and serve as protective and cushioning materials finding use in upholstery, etc. Stiffer high density foams are employed in the manufacture of instrument panels as well as tractor and motor cycle seats. They also find use in air filters, decorative linings and for high fidelity sound systems. Combustion modified polyurethane foams find use in cushions in aircrafts and in public transport systems. Rigid foams have excellent thermal insulations and are used for roofing, refrigerator, etc. Some of the speciality areas are flotation (body parts of ships and boats) and packaging applications.

Polyurethane elastomers find use in elevator wheels, brake diaphragms, gears, o-rings, sound dampeners, etc.

Thermoplastic polyurethanes form adhesives, conveyor drive belts, magnetic tape coatings, automobile parts, etc.

4.4. SCOPE OF THE PRESENT WORK

Polyurethanes are useful materials. The ease of processability along with good physical properties is the chief cause of their finding pervasive applications. Polyurethanes can be tailor made to any desired property requirement simply by varying the diol or the diisocyanate.

Incorporation of various functional groups in the polymer backbone results in properties being modified considerably. Thus, by the incorporation of various functional groups along the polymer backbone, the properties of polyurethanes have been studied. For instance, diisocyanates containing diphenylmethane,[15] thiophene,[16] tetraphenylthiophene,[17] isopropylidene,[18] s-triazine,[19] esters,[20] diesters,[21] sulfone ether,[22] have been synthesized and used in the preparation of polyurethanes.

In our quest for novel diisocyanates, we have synthesized diisocyanates containing oxyethylene (**OE 4 a - OE 4 l**), formal group (**F 3 a - F 3 d**), ester (**E 3 a - E 3 d**), and pre-formed imide (**I 4 a - I 4 h**) linkage (synthesis described in Chapter 2). The utility of these functional group containing diisocyanates was desired to be demonstrated by the preparation of polyurethanes containing the respective functional groups along the polymer backbone.

Consequently, 24 polyurethanes containing oxyethylene (**PU 1 - PU 8**), formal (**PU 9 - P U 16**), and ester (**PU 17 - PU 24**) group have been targeted based on the reaction of the above mentioned diisoyanates and aliphatic diols (eg. ethylene glycol and diethylene glycol. Both meta- and para- oriented diisocyanates have been utilized. Also, four polyurethanes containing imide linkages along the polymer backbone have been synthesized by the reaction of preformed imide group containing diisocyanate with a long chain diol, polytetramethylene glycol. Especially interesting is the premise that the presence of rigid imide groups in the polyurethane would help improve thermal stability.

The characterization of the polyurethanes thus prepared was done by viscosity measurements, solubility tests, IR spectroscopy, x-ray diffraction and thermogravimetric analysis.

4.5. RESULTS AND DISCUSSION

Polyurethanes can be tailor-made to any desired property simply by varying the diol or diisocyanate. The structure property relations in polyurethanes have been studied by Kwon et al[16], Maldar and Hosmane[17], and Suthar et al.[18]

The polyaddition reaction between a diisocyanate and a polyol is rapid. Nonetheless, the reaction is normally carried out for extended periods of up to 6 hours at moderately high temperatures to effect the completion of reaction.[23] Although the NCO-OH reaction rate is enhanced by the presence of catalyst, there are other competetive reactions that accompany the polyurethane formation. In presence of a catalyst and elevated temperatures, dimerization, trimerization, allophanate and biuret formation becomes a competitive reaction. By the proper choice of temperature and catalyst one can force the reaction to proceed in a desired direction with the avoidance of the formation of these side reactions.

Functional group containing diisocyanates, viz, oxyethylene (OE **4 a** - OE **4 l**), formal group (**F 3 a** - **F 3 d**) ester group (**E 3 a** - **E 3 d**) and pre-formed imide groups (**I 4 a** - **I 4 h**) were synthesized by the non hazardous, non phosgenation, Curtius rearrangement of the corresponding diacylazides (synthesis described in Chapter 2).

Preparation of Polyurethanes

The utility of the above diisocyanates was demonstrated by utilizing them in the formation of polyurethanes. Hence, 24 polyurethanes have been prepared by the reaction of diisocyanates containing oxyethylene (**OE 4 a** - **OE 4 l**), formal (**F 3 a** - **F 3 d**) and ester (**E a** - **E d**) gruop with ethylene glycol and diethylene glycol.

A set of four imide group containing polyurethanes were prepared by the solution polyaddition reaction of diisocyanates containing preformed imide groups (**I 4 a** - **I 4 h**) with long chain aliphatic diol, polytetramethylene glycol. The presence of imide groups in the backbone is expected to improve the thermal stability.

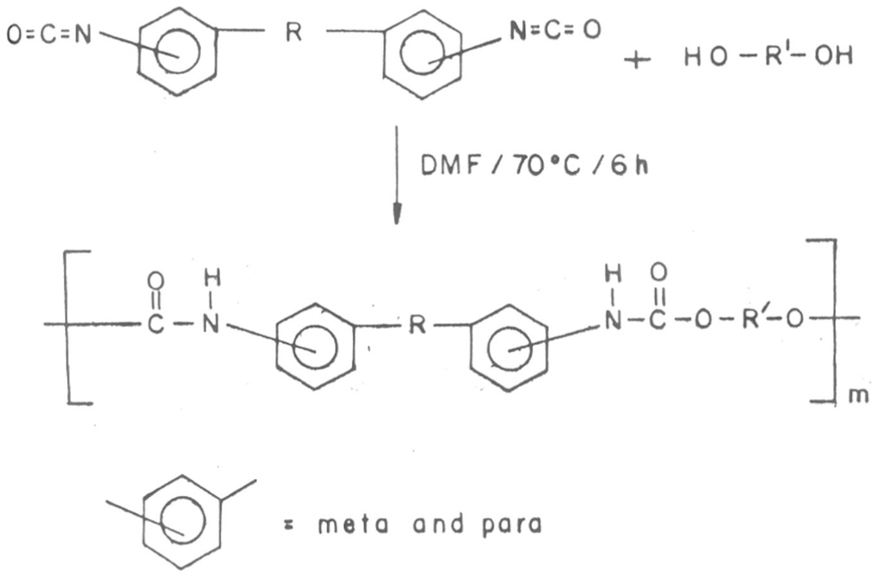
First Set

Twenty four functional group containing polyurethanes were prepared by the polyaddition reaction of diisocyanates containing oxyethylene, formal, and ester groups with ethylene glycol and diethylene glycol in dimethylformamide (Scheme 6, Tables 15 - 17), as detailed in experimental section. Both meta- and para-oriented diisocyanates have been used.

The polymers obtained were in pale yellow in colour.

Infra Red Spectra

The IR spectra of all the twenty four polyurethanes exhibited absorption bands at 3290 - 3320 cm^{-1} (-NH) and 1700 cm^{-1} (C=O). The IR spectra of oxyethylene and formal containing polyurethanes, (**PU 1** - **PU 8**) and (**PU 9** - **PU 16**), respectively, showed the presence of absorption at 1230 cm^{-1} (C-O-C), while those of the ester group containing polyurethanes (**PU 17** - **PU 24**) showed the presence of absorption band at 1725 cm^{-1} (C=O of the



R = $-OCH_2CH_2O$ and $-OCH_2CH_2OCH_2CH_2O-$

$-OCH_2O-$ and $-OCH_2CH_2OCH_2OCH_2CH_2O-$

$-O-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-O-$ and $-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-$

R' = $-CH_2CH_2-$ and $-CH_2CH_2OCH_2CH_2-$

SCHEME 6 - PREPARATION OF OXYETHYLENE (PU 1-PU 8), FORMAL (PU 9-PU 16) AND ESTER (PU 17-PU 24) GROUP CONTAINING POLYURETHANES.

TABLE 15

Preparation of Oxyethylene Containing Polyurethanes and Their Inherent Viscosities.

Polyurethane[1]	Diisocyanate[2] (0.01 mol)	Diol[3] (0.01 mol)	Yield (%)	$[\eta]_{inh}$,[4] dL/g
PU 1	OE 4 a	EG	98	0.18
PU 2	OE 4 a	DEG	98	0.22
PU 3	OE 4 f	EG	96	0.27
PU 4	OE 4 f	DEG	97	0.30
PU 5	OE 4 g	EG	96	0.23
PU 6	OE 4 g	DEG	98	0.26
PU 7	OE 4 l	EG	97	0.33
PU 8	OE 4 l	DEG	97	0.36

[1] Diisocyanates were synthesized as per Scheme 1 (Chapter 2)

[2] Solvent employed during the polyurethane formation was dimethylformamide; Temperature for the reaction was 70°C;

[3] Diol: EG = Ethylene glycol, DEG = Diethylene glycol

[4] Inherent viscosities were determined in dimethylformamide at a concentration of 0.5g/dL at a temperature of 30 ±0.01°C

TABLE 16

Preparation of Formal Group Containing Polyurethanes and Their Inherent Viscocieits.

Polyurethane[1]	Diisocyanate[2] (0.01 mol)	Diol[3] (0.01 mol)	Yield (%)	$[\eta]_{inh}$,[4] dL/g
PU 9	F 3 a	EG	96	0.15
PU 10	F 3 a	DEG	95	0.20
PU 11	F 3 b	EG	97	0.28
PU 12	F 3 b	DEG	96	0.33
PU 13	F 3 c	EG	95	0.20
PU 14	F 3 c	DEG	97	0.27
PU 15	F 3 d	EG	96	0.34
PU 16	F 3 d	DEG	97	0.38

---

[1] Diisocyanates were synthesized as per the Scheme 2 (Chapter 2)

[2] Solvent employed during the polyurethane formation was dimethylformamide; Temperature for the reaction was 70°C;

[3] Diol: EG = Ethylene glycol, DEG = Diethylene glycol

[4] Inherent viscosities were determined in dimethylformamide at a concentration of 0.5g/dL at a temperature of 30 ±0.01°C

TABLE 17

Preparation of Ester Group Containing Polyurethanes and Their Inherent Viscosities.

Polyurethane[1]	Diisocyanate[2] (0.01 mol)	Diol[3] (0.01 mol)	Yield (%)	$[\eta]_{inh}$,[4] dL/g
PU 17	E 3 a	EG	95	0.21
PU 18	E 3 a	DEG	96	0.26
PU 19	E 3 b	EG	97	0.26
PU 20	E 3 b	DEG	96	0.32
PU 21	E 3 c	EG	96	0.26
PU 22	E 3 c	DEG	97	0.30
PU 23	E 3 d	EG	96	0.30
PU 24	E 3 d	DEG	96	0.35

[1] Diisocyanates were synthesized as per Scheme 3 (Chapter 2)

[2] Solvent employed during the polyurethane formation was dimethylformamide; Temperature for the reaction was 70°C;

[3] Diol: EG = Ethylene glycol, DEG = Diethylene glycol

[4] Inherent viscosities were determined in dimethylformamide at a concentration of 0.5g/dL at a **temperature** of 30 ±0.01°C

ester grouping) in addition to a band at 3285 - 3330cm^{-1} (due to the -NH of the urethane linkage). No absorption band was observed at 2230 cm^{-1} in the spectra of all the polyurethanes indicating the absence of free diisocyanate.

The IR spectra of representative oxyethylene (**PU 8**) and ester group (**PU 16**) are illustrated in Figures 16 (a) and 16 (b), respectively. [The IR spectra of formal group containing polyurethanes (**PU 9** - **PU 18**) were identical to those of oxyethylene containing polyurethanes (**PU 1** - **PU 8**)].

Solubility

The solubility of polyurethanes was determined using a 3 % concentration of polymers in different solvents. They were found to be soluble in the following polar solvents: dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMAC), hexamethylphosphoramide (HMPA), N-methylpyrolidone (NMP), and m-cresol. However they were insoluble in benzene, petroleum ether, chloroform and acetone.

Viscosity Measurements

The inhetent viscosities of the functional group containing polyurethanes were determined in dimethylformamide at a concentration of 0.5 g/dL in an Ubbelohde viscometer at a temperature of 30±0.01°C.

The following equation was employed for the determination of inherent viscosities:

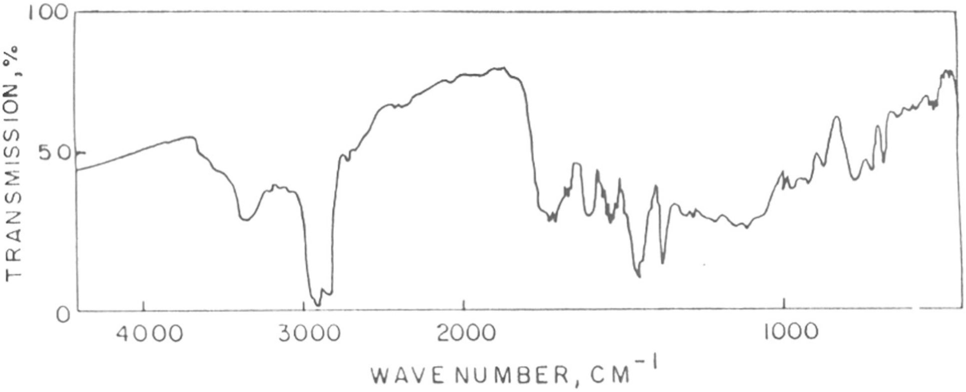


FIG. 16 (a). IR (NUJOL MULL) SPECTRUM OF POLYURETHANE CONTAINING OXYETHYLENE GROUP, PU 8

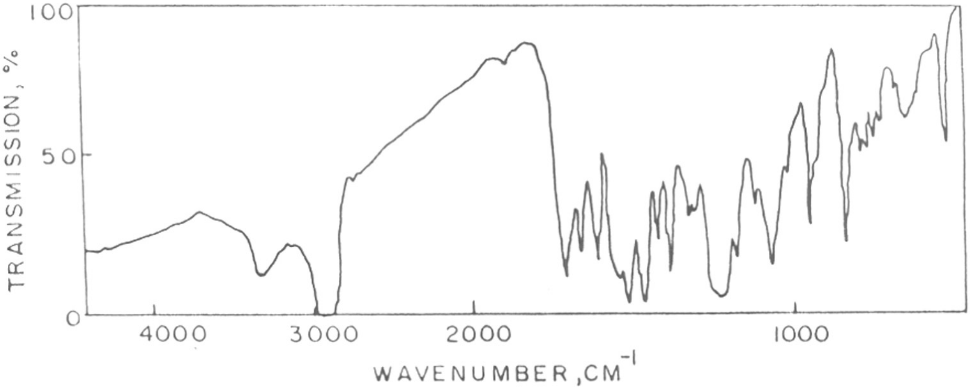


FIG. 16 (b). IR (NUJOL MULL) SPECTRUM OF POLYURETHANE CONTAINING ESTER GROUP, PU 16

$$\eta_{inh} \qquad \frac{2.303 \times \log t/to}{C}$$

where, t and t_o are flow rates of solution and solvent, respectively, and C is the concentration of the polymer (0.5 g/dl). The inherent viscosity value range for differet functional group containing polyurethanes are as follows: oxyethylene 0.18 - 0.36, formal 0.15 - 0.38, and for ester 0.21 - 0.35 dL/g. The inherent viscosity values are incorporated in Tables 15-17. The polyurethanes based on para-oriented diisocyanates exhibited a slightly higher viscosity value as compared to the polyurethanes based on the meta- oriented diisocyanate. Also, the polyurethanes based on ethylene glycol had lower viscosities than those based on diethylene glycol.

X-Ray Diffraction

The nature of polyurethanes, whether amorphous or semi-crystalline, was determined by wide angle X-ray diffraction studies. The X-ray diffractograms of the polyurethanes (**PU 1** - **PU 24**) were determined by the powder method using nickel-filtered CUK_α radiations on a Phillips Unit (Phillips Generator, PW 1730). The diffractograms indicated that the polyurethanes bearing oxyethylene, formal, and ester groups are amorphous in nature, as indicatd in Figures 17(a), 17 (b) and 17 (c), respectively.

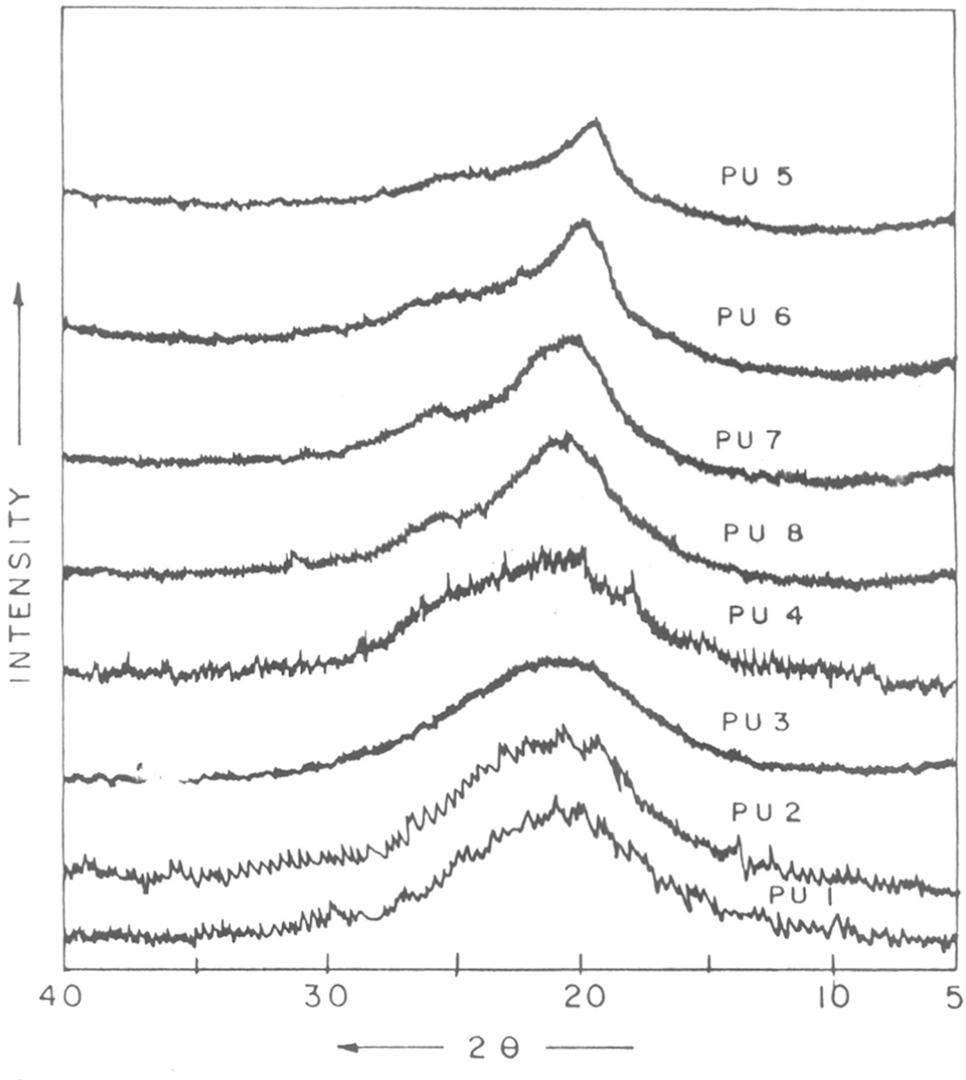


FIG. 17 (a): X-RAY DIFFRACTOGRAMS OF POLYURETHANES CONTAINING OXYETHYLENE GROUPS, (PU 1 - PU 8).

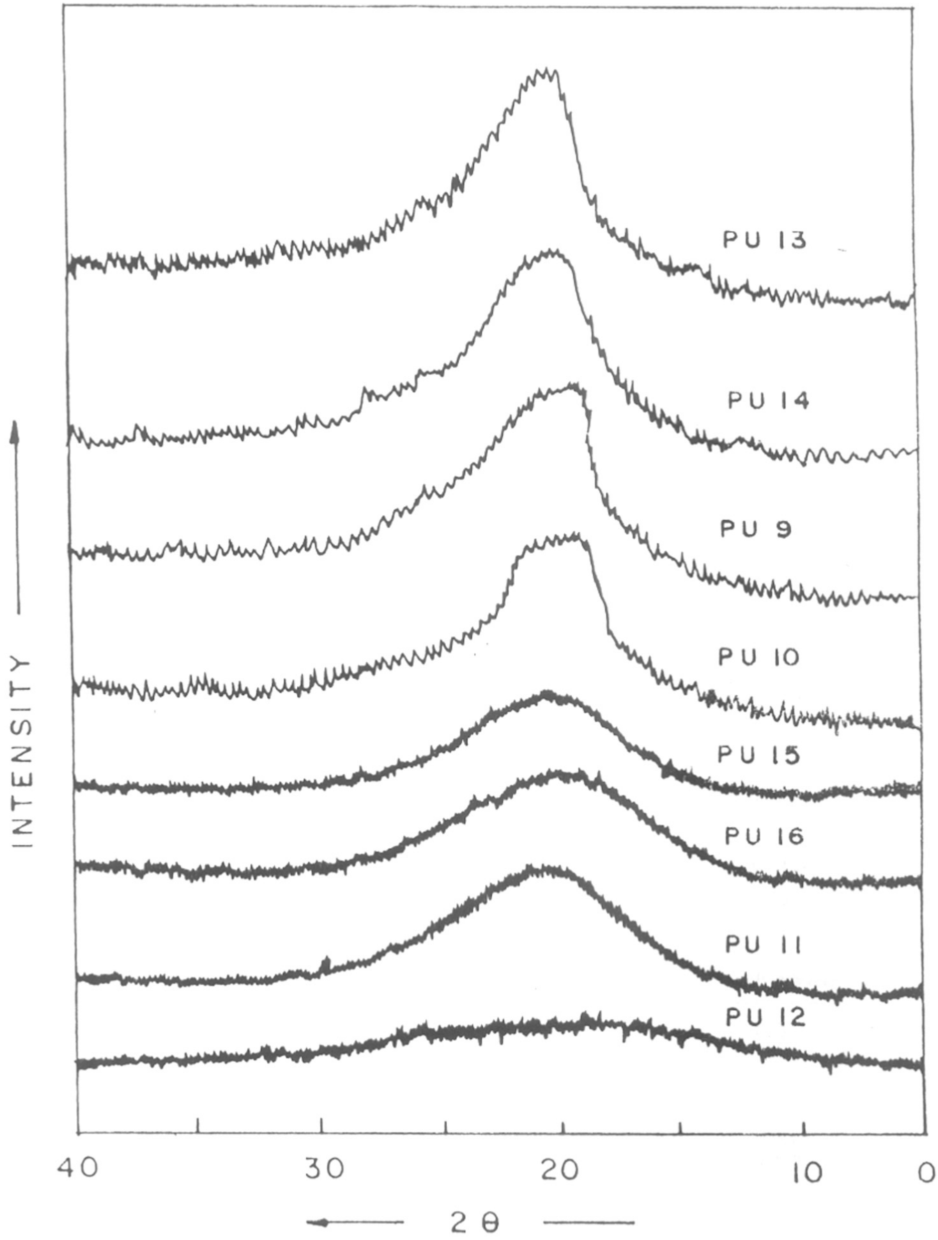


FIG. 17(b) : X-RAY DIFFRACTOGRAMS OF POLYURETHANES CONTAINING FORMAL GROUPS, (PU 9 - PU 16).

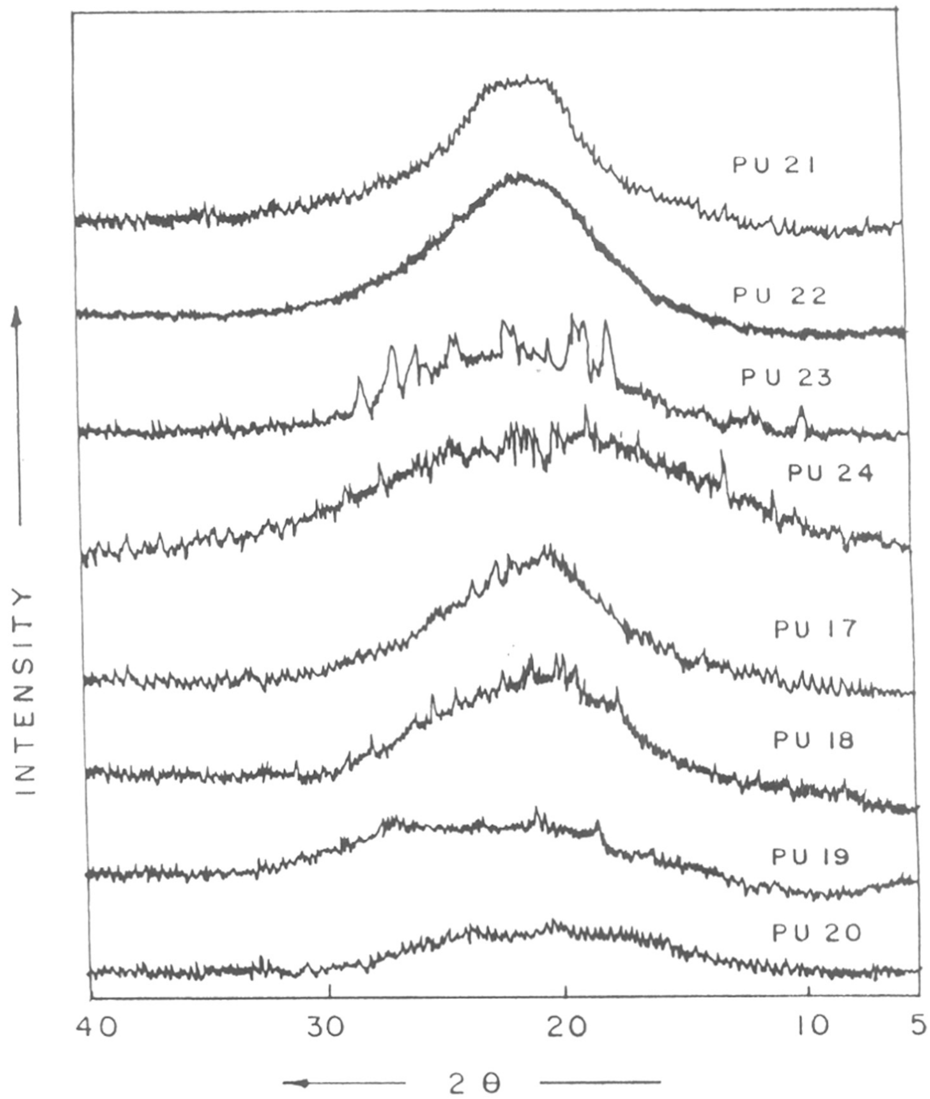


FIG.17(c) . X-RAY DIFFRACTOGRAMS OF POLYURETHANE CONTAINING ESTER GROUPS,(PU17 - PU 24).

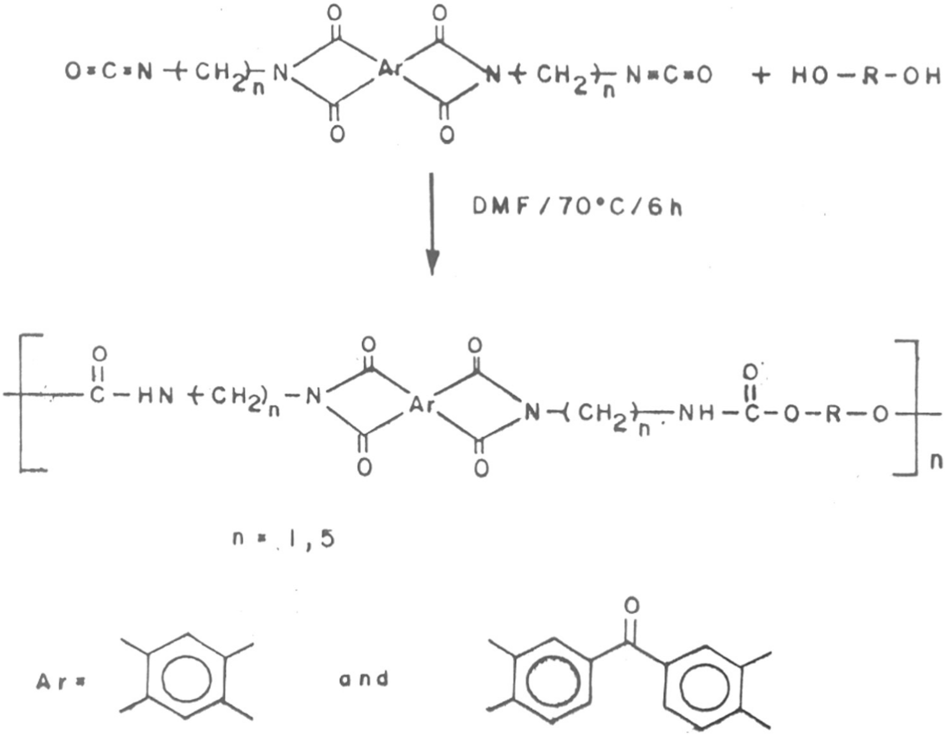
Second Set

Imide groups are known for the thermal stability and their presence in polymers improves their thermal properties. Moreover, our ability to synthesize preformed imide group containing diisocyantes led us to assume that imide groups may be introduced into the polyurethane backbone simply by the reaction with polyols. The resulting polyurethanes containing imide groups would be expected to have better thermal stablity than conventional polyurethanes. Conventional polyurethanes loose their mechanical properties above 90°C and undergo degradation at processing temperatures around 200°C. To improve upon their properties, heterocyclic imide groups may be introduced into the polymer backbone by reacting diisocyanates containing preformed imide groups with a suitable polyol.

Four imide group containing polyurethanes, poly(imide-urethene) (**PIU I - PIU IV**) were prepared by the polyaddition reaction of preformed imide group containing diisocyanates (**I 4 a, I 4 d, I 4 e, and I 4 h**) with polytetramethylene glycol in dimethylformamide (Scheme 7, Table 18, and as detailed in experimental section.) The polyurethanes were obtained in quantitative yield. The polyurethanes were yellowish in colour. These polyurethanes could be cast into films that were brittle.

Infra Red Spectra

The IR spectra of polyurethanes (**PIU I - PIU IV**) showed characteristic stretching absorption bands at 3320 cm^{-1} (-NH) and stretching band at 1710 cm^{-1} (C=O) in addition to the bands due



R = Polytetramethylene glycol (PTMG).

SCHEME 7: PREPARATIONS OF POLY (IMIDE-URETHANE)S, PIU I - PIU IV.

TABLE 18

Preparation of Pre-formed Imide Group Containing Polyurethanes and Their Inherent Viscosities.

Polyurethane[1]	Diisocyanate[2] (0.01 mol)	Diol[3] (0.01 mol)	Yield (%)	$[\eta]_{inh}$,[4] dL/g
PIU I	I 4 a	PTMG	96	0.56
PIU II	I 4 d	PTMG	97	0.83
PIU III	I 4 e	PTMG	96	0.36
PIU IV	I 4 h	PTMG	96	0.39

[1] Diisocyanates were synthesized as per the Scheme 4 (Chapter 2)

[2] Solvent employed during the polyurethane formation was dimethylformamide; Temperature for the reaction was 70°C;

[3] Diol: PTMG = Polytetramethylene glycol, Mol. Wt. 1000, OH No. 113.8

[4] Inherent viscosities were determined in m-Cresol at a concentration of 0.5g/dL at a temperature of 30 ±0.01°C

to the cyclic imide structure, viz., 1780 cm^{-1} (imide-I), 1370 cm^{-1}) imide-II, 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). The IR spectrum of a representative poly(imideurethane) (**PIU 4**) is shown in Figure 18.

Solubility.

The solubility of poly(imide-urethane)s was determined at a 3 % concentration in various solvents. All the poly(imide-urethane)s were soluble in polar solvents like, DMF, DMSO, DMAc, HMPA, NMP, and m-cresol. The solubility increases with the increase in the length of the aliphatic chain of the diisocyanate. The poly(imide-urethane)s derived from BTDA showed better solubility than those derived from PMDA.

Viscosity Measurements.

The inherent viscosities of the poly(imide-urethane)s were determinmed in m-cresol at a concentration of 0.5 g/dl in an Ubbelohde viscometer at 30$\pm$0.01°C, as described for polyurethanes in Set One. The viscosity values varied from 0.36 - 0.83 dL/g (Table 18). The polyimideurethanes based on BTDA showed lower viscosity values (0. 36 dL/g for **PIU III** and 0.39 dL/g for **PIU IV**) as compared to those based on PMDA (0.56 dL/g for **PIU I** and 0.83 dL/g for **PIU II**). The polymers based on diisocyanates derived from caproic acid showed a higher (0.83 dL/g for **PIU II** and 0.39 dL/g for **PIU IV**) viscosities than the polymers based on diisocyanates derived from glycine (0.56 dL/g for **PIU I** and 0.36 dL/g for **PIU III**).

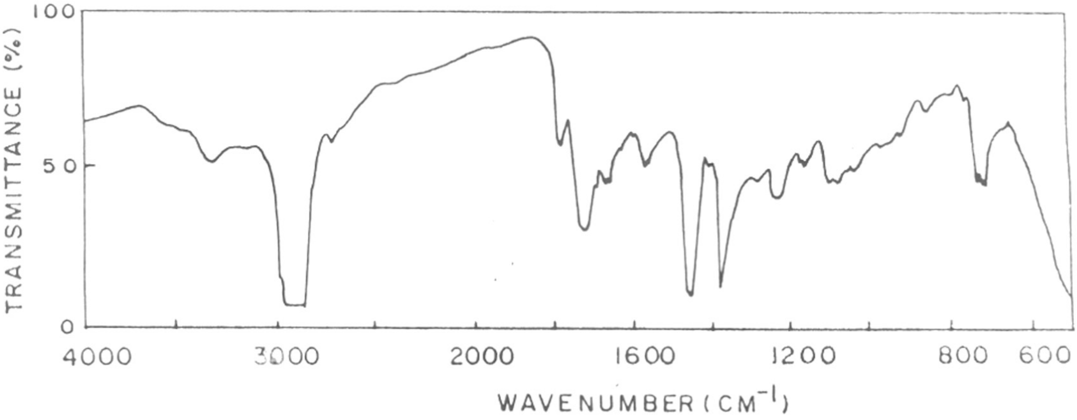


FIG. 18: IR(NUJOL MULL) SPECTRUM OF POLYIMIDEURETHANE, PIU IV.

X-Ray Diffraction.

X-Ray diffraction patterns (Fig. 19) of the poly(imide-urethanes (**PIU I** - **PIU IV**). These indicated that the poly(imide-urethane)s were semicrystalline in nature. The poly(imide-urethane)s, **PUI I** and **PIU II** (derived from diisocyanates based on PMDA), were more crystalline than poly(imide-urethane)s, **PIU III** and **PIU IV** (derived from diisocyanates based on BTDA).

Thermal Characterization.

Thermogravimetric analysis of the poly(imide-urethane)s was carried out on a Netzsch 409 Thermal Analyzer, by heating the polymer samples in air at a heating rate of 10°C/min. The TGA curves of all the polymers showed a two stage decomposition pattern without any weight loss below 215°C (Figure 20). The initial decomposition temperatures for the polymers was in the region 215 - 225°C. The first stage of decomposition may be attributed to the thermooxidative cleavage of the weak and labile linkages, while the second stage being that due to the cleavage of the stable imide linkage. Polyimideurethanes based on diisocyanates derived from PMDA showed higher thermal stability than thosed based on diisocyanates derived from BTDA. Also the caproic acid based diisocyanates result in lower thermal stability as compared to those derived from glycine. Thermal characteristics such as, initial decomposition temperature (IDT), T_{10}, T_{30}, T_{50}, and T_{max}, ie., temperatures at 10%, 30%, 50%, and maximum decomposition, respectively, are incorporated in Table 19. T_{max} was determined from the DTG curve.

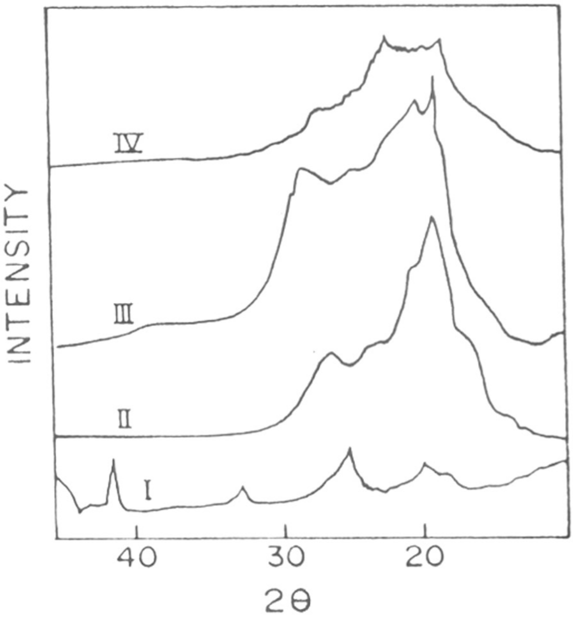


Fig. 19. X-Ray Diffractograms of Polyimideurethanes, PU I - PU IV

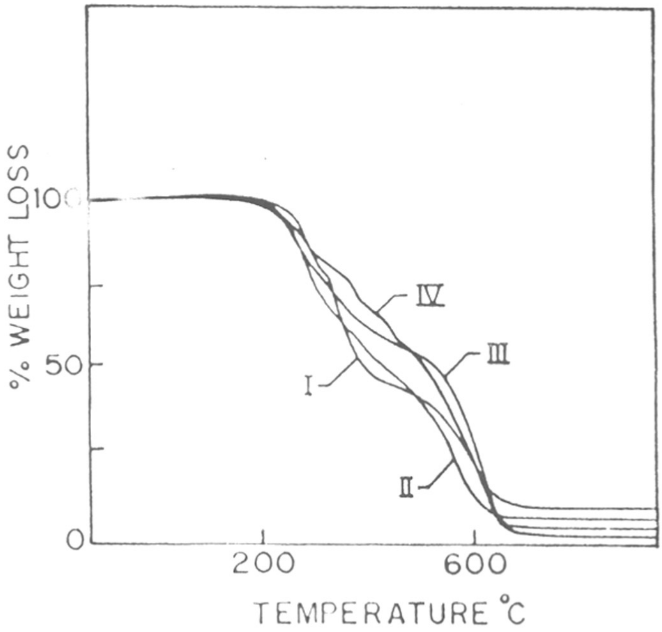


Fig. 20. TGA Curves of Polyimideurethanes, PU I - PU IV

TABLE 19

Thermal Characteristics of Poly(Imide-Urethane)s.

Polymer ->	PIU I	PIU II	PIU III	PIU IV
IDT	215	217	219	216
T_{10}	290	289	291	306
T_{30}	350	341	382	410
T_{50}	397	444	583	512
T_{max}	580	558	610	593

[a] All temperatures in °C
IDT - Initial Decomposition temperature
T_{10}, T_{30}, T_{50}, and T_{max} are temperatures at T_{10} %, T_{30} %, T_{50} %, and maximum decomposition, respectively.

5.6 CONCLUSIONS

. Polyurethanes containing functional groups, such as, oxyethylene, formal, ester, and imide, may be conveniently prepared by the polyaddition reaction of the respective diisocyanate with a diol/polyol.

. By the polyaddition reaction of preformed imide group containing diisocyanates with polytetramethylene glycol, poly(imide-urethane)s may be conveniently prepared. These poly(imide-urethane)s are soluble in many polar solvents and have showed reasonably good thermal stability.

4.7. EXPERIMENTAL

Materials:

- Functional group containing diisocyanaes, viz., oxyethylene (**OE 4 a, OE 4 f, OE 4 g,** and **OE 4 h**), formal (**F 3 a** - **F 3 d**), ester (**E 3 a** - **E 3 d**), and imide (**I 4 a, I 4 d, I 4 e,** and **I 4 h**) were synthesized as per the Schemes 1 - 4, described in Chapter 2.
- Ethylene glycol (EG), diethylene glycol (DEG) were of reagent grade and were distilled and stored over Linde Type 4 A Molecular seives. Polytetramethylene glycol (PTMG) (TERACOL, Dupont, USA), (Mol. wt. 1000, Hydroxyl number 113.8) was dried till constant weight at 70°C in vacuum.
- Dimethylformamide (DMF) was purified by standard procedure[26].
- All other materials were of reagent grade and were used as such.

4.7.1 Preparation of Polyurethanes Containing Oxyethylene, Formal, Ester and Pre-formed Imide Groups. General Procedure.

In a dry 100 mL three-necked round bottom flask fitted with a thermowell, a nitrogen gas inlet, and a reflux condenser fitted with a calcium choride guard tube, was placed a solution of a diisocyanate (0.01 mol) in 15 mL of dry DMF. To this was added diol/polyol (0.01 mol). The reaction mixture was stirred with a magnetic stirring bar and the temperature gradually raised to 70°C. A slow stream of dry nitrogen was bubbled throughout the reaction. After stirring the reaction mixture for 6 h, the resulting viscous liquid was poured into large excess of methanol. The polymer that precipitated was filtered at pump and dried in vacuum at 100°C for 3 hours.

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CHAPTER 5

THERMALLY STABLE POLYMERS

5. THERMALLY STABLE POLYMERS

5.1 INTRODUCTION

The growing interest in the area of high temperature or thermally stable polymers has been evolutionary. Conventional heat resistant or thermally stable materials like clay, mica, glass, metals, etc., have been and are being replaced progressively by high performance polymers. The rapid development of the science of thermally stable materials spans about three decades. However, the need to replace the conventional heat resistant materials by high performance polymers is a continual one. Speciality applications like high temperature adhesive systems, organic insulators, preventive coatings, high modulus fibres, flame and heat resistant fibres, ablative systems and composites, etc., have put maximum demand for such polymers. The frontier areas of aerospace, microelectronics, medical, nuclear and related areas have always provided with the most conducive atmosphere for the development of new polymer systems to meet the specific requirements.

Consequently, the use of high performance/high temperature thermoplastics has increased significantly as these materials offer the potential for low cost of manufacturing and an attractive combination of chemical, mechanical and physical properties.[1]

In order to qualify as a high temperature or thermally stable polymer, it must possess certain structural attributes. Some of these are :

. a high molecular weight to provide strength, toughness and flexibility,

. a minimum of oxidizable hydrogen atoms, ie., resistance to oxidative degradation at elevated temperatures,

. a maximum of high temperature stable structural units,

. connecting linkages or groups that can resist the effect of heat, and

. resistance to mechanism by which the chain can readily undergo thermal degradation.

There are three ways to improve the thermal stability of a polymer: (i) increased crystallinity, (ii) increased crosslinks, and (iii) removal of thermooxidisable `weak links.´

When dealing with high temperature polymers, the thermal stress experienced by the polymer in terms of time and temperature must by addressed. An increase in either of these factors shortens the expected lifetime of the polymer; an increase in both, the life time is shortened logarithmically.

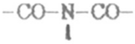
The thermal stability of a polymer is probably best defined as the temperature range that the polymer can withstand and still retain all the useful properties in a given application. More specifically, the total stress may be given as 260°C for 1000 hours, 350°C for 300 hours, 538°C for 1 hour or 816°C for 5 minutes.[2]

There are several classes of thermally stable polymers. The important ones are, polyimides, polyamides, polyamide-imides, polybenzimidazoles, aromatic polyesters, polycarbonates, and polyphenylene oxides, among others. Some of the other thermally stable polymers are polyhydantoins, polyhydrauracils, polycarbodiimides, polybenzoxazienediones, polyoxazolinedienediones, polyparabanic acid, polyquinazolinediones, poly-s-triazine, etc.

A plethora of research publications embodying the research findings in the development of high temperature polymers are available in the literature.$^{3-9}$

5.2 POLYIMIDES

Out of the extensive research efforts aimed towards the development of high temperature resistant polymers, aromatic polyimides have stood the test of time.

Polyimides are condensation polymers derived from a tetracarboxylic acid dianhydrides and primary diamines. They contain the imide structure  $-CO-\underset{|}{N}-CO-$ along the main chain of the polymer backbone. Aromatic polyimides possess a unique property combination: outstanding thermal stability (in addition to favourable properties like radiation and solvent resistance) coupled with excellent mechanical and electrical performance over a wide temperature range and have acquired major commercial and industrial importance.[10] These materials are replacing metals, glass, etc., in high performance applications throughout the electrical, electronics, automotive, aerospace and packaging industries. Polyimides are now commercially available in many forms: pellets, films, extruded sheets, raw stock and in solution. These possess outstanding high performance engineering and physical properties (including thermal stability) and hence may be placed above the commodity plastics like polyethylene and polystyrene.[11]

5.2.1 METHODS FOR THE PREPARATION OF POLYIMIDES

Bogert and Renshaw[12] were the first to synthesize polyimides by heating 4-aminophthalic anhydride or dimethyl-4-aminophthalate. The melt fusion method for the preparation of polyimides from the salts of diamine and tetracarboxylic acid or diamine and diacid/ester was reported by Edwards and Robinson.[13]

Today there are several methods for the preparation of polyimides. Some of the important methods are listed in Table 20. Amongst these methods the

1) diamine - tetracarboxylic dianhydride, and
2) diisocyanate - tetracarboxylic dianhydride reaction for the preparation of polyimides are the most important.

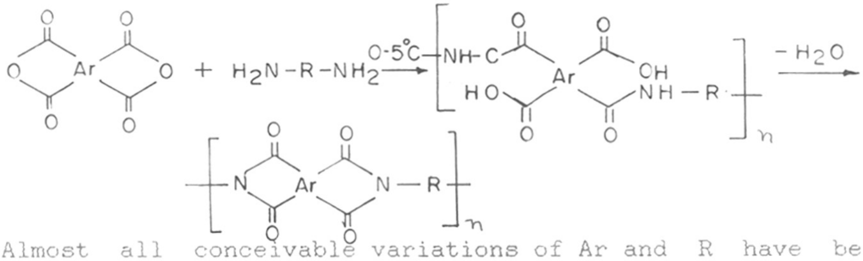
Table 20

Methods for the Preparation of Polyimides.

	Reactants	Product	Reference
-	Diamine + Dianhydride	Polyimide	14
-	Diisocyanate + Dianhydride	Polyimide	15
-	Addition polymerization of a bis(maleimide)	Polyimide	16
-	Bis(methylolimide) + Dinitrile	Copoly(amide-imide)	17
-	Bis(methylolimide) + Diamine	Copoly(amide-imide)	18
-	Bis(methylolimide) + Diisocyanate	Copoly(urethane-imide)	19
-	N,N´(Pyromellitoyl)di amino acetylchloride + Dihydrazide	Copoly(hydrazide-imide)	20
-	Bis(N-hydroxyimide) + Diacid chloride	Copoly(ester-imide)	21
-	Bis(carbethoxy)diimide + Diamine	Polyimide	22
-	Electrochemical condensation of aminophthalic acid	Polyimide	23

(i) Polyimides From Diamine - Dianhydride Reaction

The two step synthetic sequence of Bower and Frost[24] results in the polyimide being formed in the usable form. In this reaction scheme, the first step consists of the condensation reaction of a tetracarboxylic dianhydride with a diamine to form a polyamic-acid, which is either thermally or chemically cyclized to a polyimide in the second step. The advantage of this method is that the intermediate polyamic-acid formed is soluble in organic solvents and processable. At the same time, the polyamic-acid is corrosive and is unstable. The desired product conformation is developed at this stage. The cyclodehydration of this product results in the formation of a polyimide which is no more soluble. This is the most common and commercially important method for the preparation of polyimides.[25]



Almost all conceivable variations of Ar and R have been examined to date.

The mechanistic pathway for the diamine-dianhydride reaction has been studied.[26]

The polar solvents employed for the diamine-dianhydride reaction are dimethylacetamide (DMAc), dimethylformamide (DMF), N-methylpyrollidone (NMP), hexamethylphosphoramide (HMPA), etc. These solvents can be used alone or in combination with other solvents like benzene, toluene, xylene, benzonitrile, dioxane, etc.

Extremely pure monomers and rigorous exclusion of moisture lead to the formation of high molecular weight polyimides.[9] The diamine-dianhydride reaction is usually carried out below 50°C. The temperature limitation results from (i) the possible conversion to polyimide releasing water which would hydrolyze the polyamic acid, (ii) conversion to polyimide above 100°C which in addition to hydrolysis, results in the premature precipitation of low molecular weight polymer, and (iii) possible transamidation with the solvent.

The course of imidation was studied by ^{13}C-NMR studies.[27] It was found that the imide-acid ratio was zero at 0°C and virtually completely imidized at 300°. The onset of imidization is accepted to be 150°C and 300°C for near complete imidization to occur.[28] Imidization can be effected chemically by the use of acetic anhydride and pyridine at room temperature.[29]

Several factors govern the formation of high molecular weight polyimides. These are (i) effect of ratio of monomers,[29] (ii) order of monomer addition,[24, 30] and (iii) concentration[31] and purity[32] of monomers.

By this method Imai et al have synthesized novel polyimides from N,N´bis(ethoxycarbonyl)pyromellitimide,[33] N,N´-(bisphenylsulfonyl)pyromellitimide,[34] pyromellitic dithioanhydride[35] and aromatic diamines.

Phenylated dianhydrides were used to prepare soluble polyimides[36]. Polyimides containing phosphorous[37], perfluoroalkylene[38-40] linkages in the polymer backbone are reported. Diamines[41], such as, anilinefluorene, anilineanthrone, and anilinephthalein or bipyridyl diamines[42] have been employed for the polyimide preparation.

Using diamines and dianhydrides of different structural variations, Ghatge et al[43,44] have reported the synthesis of polyimides in our Laboratory.

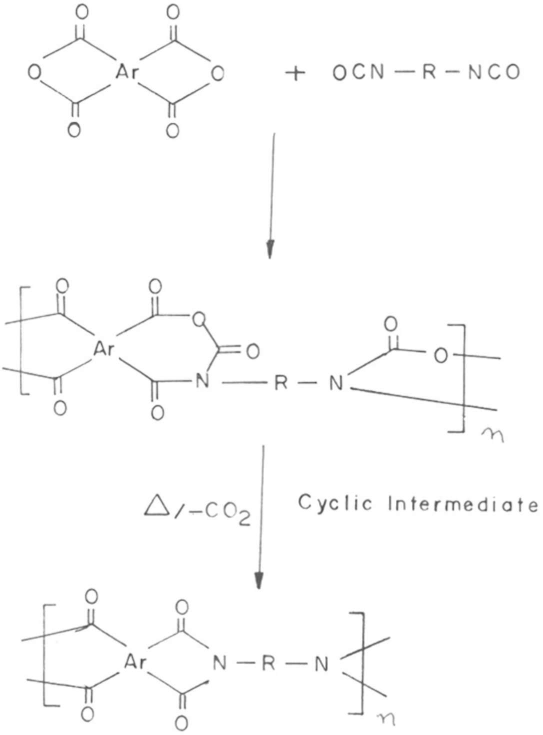
The incorporation of ethylene,[45] oxyethylene,[46] azo[47] ether,[48] carbonyl-ether,[49] thioether,[50] amide,[51] phosphorous,[52] fluorine,[53] silicone,[54] siloxane,[55] etc., moiety has been achieved by the use of either dianhydrides and diamines containing these functionalities.

(ii) Polyimides From Diisocyanates - Dianhydride Reaction

The discovery that acetic anhydride reacted with ethylisocyanate to form N-ethyl diacetamide by Wurtz[56] in 1854, remained unexploited for nearly a century until some preliminary work by Hurds and Prapas[57] and by Marton and Meisel-Agoston.[58,59] That the diisocyanate - tetracarboxylic acid or dianhydride reaction in polar solvents yields low molecular weight polyimide was revealed by a Dutch patent.[60] Polyimides can be prepared by the reaction of a diisocyanate and a diester of a tetracarboxylic acid.[61] Polyamic-acid ester is formed as an intemediate which on heating forms the polyimide with the liberation of water.

Using a tertiary amine as a catalyst Noya[62] prepared polyimides by the hydrogen transfer polymerization of pyromellitic acid diimide with diisocyanate in polar solvents.

A systematic study of the diisocyanate - dianhydride reaction was carried out by Meyers[15], both in polar solvents and under melt fusion condition. A possible mechanism that involves a seven-membered ring intermediate, which liberates carbon dioxide to give the polyimide was suggested by him.



POLYIMIDE

The diisocyanate - dianhydride reaction leading to the formation of imide is catalyzed by the presence of a trace amount of water.[63] The reaction takes place at a temperature lower than that required for the neat uncatalyzed reaction.

By the reaction of a diisocyanate and a mixture of dianhydrides and their acids in presence of a catalyst (tertiary amine), Alvino and Edelman[64] have prepared high molecular weight polyimides. They established that the purity of the reagents, the anhydride - acid ratio, temperature and the level of moisture determined the molecular weight of the resulting polyimide.

Alkali metal salts of alcohols or alkali metal lactamate were utilized as catalysts for the diisocyanate - dianhydride reaction by Onder.[65,66]

Block copolymers were prepared by Hergenrother[67] by the reaction of isocyanate terminated polybutadiene with benzophenone-tetracarboxylic dianhydride (BTDA).

Segmented copolyether-imides have been prepared by the condensatin of isocyanate terminated polyether with pyromellitic dianhydride (PMDA).[68]

Soluble polyimides have been prepared by Caraculacu et al[69] by the reaction between PMDA and N,N´-bis(3-isocyanato-4-methyl)phenyl parabanic acid. The structure-property relationship in polyimides resulting from the diisocyante - dianhydride reaction has been established by many researchers.[70-77]

Recently polyimides containing sulfone-ether [78] and s-triazine[79] groups in the polymer backbone have been synthesized in our Laboraory.

5.2.2. **Properties**

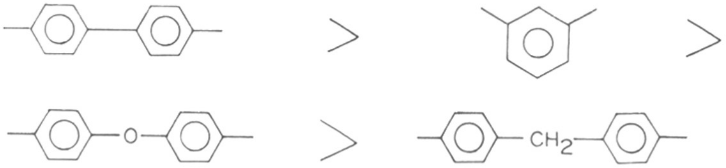
Polyamic-acid films are faintly coloured while polyimide films are yellowish. The density of polyimide is always higher than that of the polyamic-acid because the imide structure reduces the molar volume.

Polyimides are inert and are not usually affected by dilute acids but dissolve with degradation in strong acids like concentrated sulfuric and fuming nitric acids. This is manifested by the drop of the viscosity of the resulting polyimide solution.

<u>Thermal Properties</u>: Thermal and oxidative properties of polyimides are evaluated by thermogravimetric analysis (TGA), differential thermal analysis (DTA) or isothermal gravimetric analysis (IGA). The most widely used method for determining and comparing the thermal stabilities of the polyimides is the thermogravimetric analysis (TGA). This method gives the information on the threshold temperature at which fragmentation process occurs. In DTA, the polymer and a reference material are heated at some rate, and the differece in the absorption or evolution of heat between the sample and the reference material is recorded as a function of temperature. In TGA, the weight loss of a polymer is monitored as a function of temperature and recorded.

The mechanism of degradation of polyimides has been the subject of several research papers.[80-84]

Sroog et al[14] have studied the effect of the diamine structure on the thermal stability of the polyimides derived from pyromellitic dianhydride and concluded that pyromellitimides have the following order of stability relative to the structure of the diamine component.



The glass transition temperature (Tg) determines the method of processing and it is the maximum temperature at which a polymer can be used in a given application. Tg depends on the structure amongst other factors. Rigid and linear backbones afford polyimides with higher Tg. Flexible units along the polymer main chain, such as aliphatic carbon chains (eg, ether, thioethers, etc., afford an increased freedom of chain motion) tend to lower the Tg.

Solvent Resistance: Polyimides show good hydrolytic stability. Sroog et al[14] postulated that polyimides derived from aliphatic diamines and some electron-rich diamines, such as 4,4´-diaminophenyl ether, exhibit better hydrolytic stability than aromatic polyimides containing electron-withdrawing groups, eg. 4,4´-diaminophenylsulfone or 4,4´-diaminobenzophenone.

Polyimides are hydrolyticlly stable to acid or neutral aqueous environments. Almost all polyimides undergo hydrolytic degradation in the presence of strong aqueous alkali solutions. Nishizaki[85] studied the mechanism of hydrolysis of polyimides. Aromatic polypyromellitimides are insoluble in most organic solvents. Strong acids, such as sulfuric and nitric acids dissolve the polyimides.[86] Solvent resistance can be improved by cross-linking.

Mechanical and Electrical Properties: Polyimides are tough and stiff and exhibit high flexural modulus below their Tg. Tensile, flexural and compressive strengths are excellent and these mechanical properties can be enhanced by incorporating inert fillers.

The stability of polyimides to ultraviolet radiations is adequate for most ordinary applications. Polyimides undergo a deterioration on prolonged exposure to UV.[87] Polyimides are excellent insulators and can be used in electric, electronic applications for connectors and wire insulations.

5.2.3 APPLICATIONS

Polyimides and modified polyimides constitute a variety of commercially available materials. They possess high flexural modulus and compressive strength, and many under-the-hood applications are being developed for polyimides based on heat resistance and the ability to withstand high stress.

The outstanding dimensional stability under load and natural lubicating capacity of polyimides makes them excellent candidates for high temperature materials suitable for appliance construction, cookware and food packaging as they also combine chemical resistance to oils, greases and fats, microwave transparency and thermal resistance.

One of the recent uses for polyimides has been in the reverse osmosis membranes. The presence of polar methoxyl groups in these polyimides impart excellent stability towards hydroylytic stability and bacterial attack.[88]

The electrical properties are ideally suited for application in electrical and electronic industries. High heat connectors, switches, housings and controls employ polyimides in place of glass and ceramics. Polyimides are used in injection molded printed circuit boards as these are capable of withstanding vapour phase soldering.[89] Polyimide films are used as high temperature insulation materials and passivation layers in the fabrication of integrated circuits and flexible circuitry.

While conventional organic foams often burn with noxious and toxic odours, polyimide foams on the other hand tend to be self extinguishing. These foams are produced by the controlled reaction of a diisocyanate with a dianhydride to give a self blowing foam from the release of carbon dioxide.[90]

Several polyimides have been spun into fibres and are used in fire resistant fabrics, and thermally stable composites. Amide-imide composites with aliphatic backbone have been melt-spun.[91] Low smoke evolution and low flammability of polyimides provide halogen free flame resistant materials for aircraft interiors, etc.

The use of polyimides in integrated circuit technology has received attention.[92] Polyimide fibres are capable of replacing silicon dioxide or nitride layer in integrated circuit fabrication owing to their toughness, low conductivity and ease of processing.

5.2.4 SCOPE OF THE PRESENT WORK

Aromatic polyimides possess thermal stability of a very high order. They combine excellent mechanical and electrical properties with good chemical and solvent resistance. However, they have high glass transition temperatures and poor solubility in organic solvents and hence can not be processed easily. Most of the polyimides are processed in the polyamic acid stage. One of the demerit of polyamic-acid intermediate is that it is unstable and corrosive. This is subsequently imidized thermally or by chemical treatment, which restricts their use considerably.

The various approaches to improve the solubility and/or processability of polyimides without affecting significantly the thermal stability, like:

(i) introduction of large polar groups or non-polar substituents along the polymer backbone.

(ii) incorporation of flexibilizing or kinked groups that are known to be thermally stable.

(iii) disruption of symmetry or copolymerization,

have been attempted, and have met with some success.

As an attempt to obtain processable polyimides by the incorporation of functional groups, such as ether,[92] methylene,[93] oxyethylene,[46] carbonyl,[49] sulfone, arylether sulfone,[94] tetraphenyl thiophene,[95] fluorine,[96] silicone,[97] etc., several polyimides have been prepared.

Here, polyimides containing various flexibilizing linkages, such as, oxyethylene (**PI 1 - PI 8**), formal (**PI 9** **PI 16**), and ester (**PI 17 - PI 24**) groups have been targeted and synthesized starting from diisocyanates containing the corresponding moities.

In our pursuit to synthesize the above flexibilizing polyimides, new diisocyanates containing oxyethylene, formal, and ester groups have been synthesized. In the present work it is intended to introduce flexibilizing groups, such as oxyethylene, formal and ester, into the polyimide backbone by the reaction of the above functional group containing diisocyanates with tetracarboxylic dianhydrides, and to study their thermal and solubility behaviour.

Thus in the present work the synthesis of twenty four polyimides containing oxyethylene (**PI 1 - PI 8**), formal (**PI 9 - PI 16**), and ester (**PI 17 - 24**) groups has been achieved. The oxyethylene containing series of polyimides (**PI 1 - PI 8**) were based on the diisocyanates containing $-O-CH_2CH_2-O-$ and $-O-CH_2CH_2-O-CH_2CH_2-O-$ grouping. The formal group containing series of polyimides (**PI 9 - PI 16**) was derived from the diisocyantes containing $-O-CH_2-O-$ and $-O-CH_2CH_2-O-CH_2-O-CH_2CH_2-O-$ grouping, while the ester group containing series of polyimides (**PI 17 - PI 24**) was based on diisocyanates containing $-O-CO-(-CH_2-)_n-CO-O-$ ($n = 3$ and 4) linkages. Both *meta-* and *para-* oriented diisocyanates from the above three series were employed in the polycondensation reaction with BTDA and PMDA to form polyimides containing the respective flexibilizing group.

The polyimides were characterized by viscosity measurements, IR spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA). Some polyimides were characterized by differential scanning calorimetry (DSC).

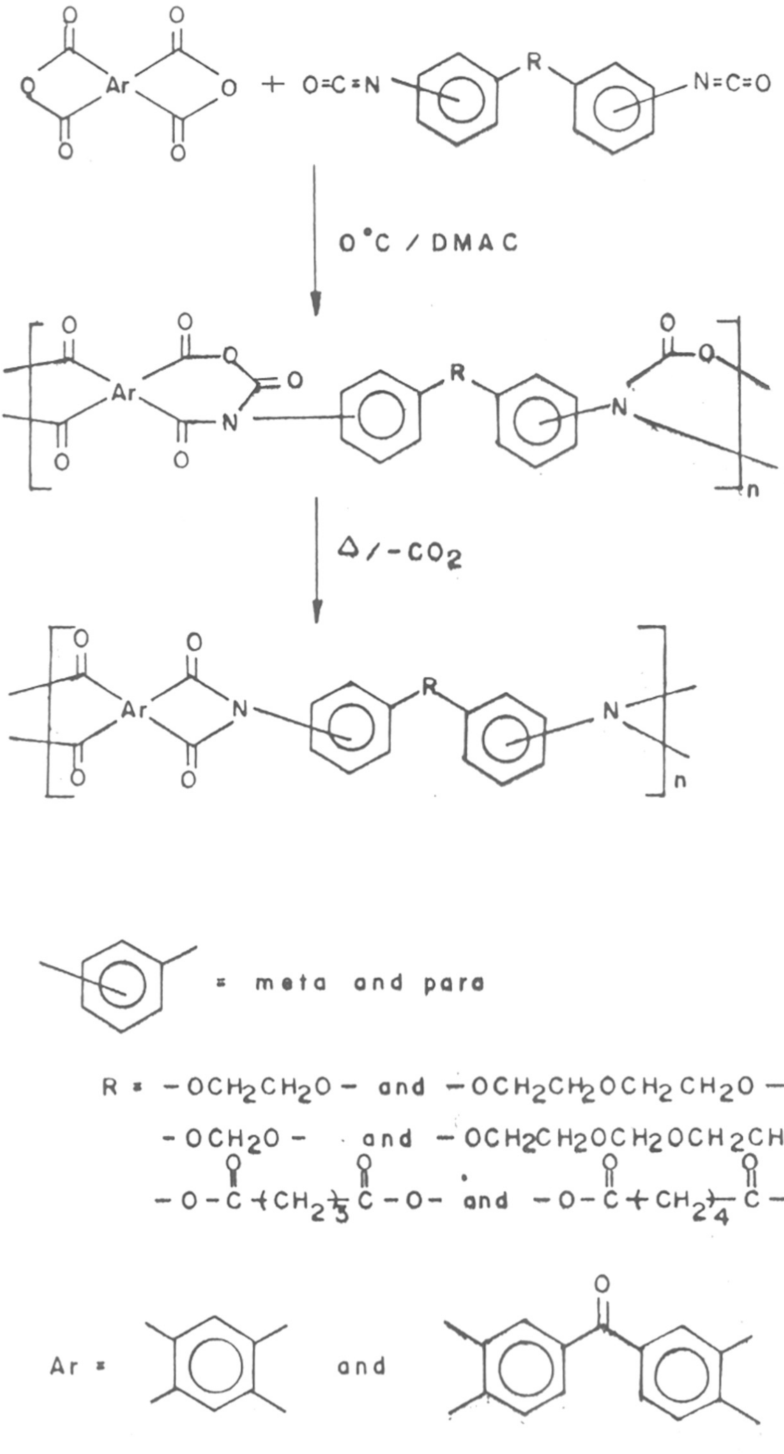
5.2.5. RESULTS AND DISCUSSION

Oxyethylene group is a flexibilizing group and its incorporation into the polyimide backbone is reckoned to impart solubility without much affecting the thermal properties. Likewise, formal groups in the aromatic formals are known to exhibit good thermal stability and yet have comparatively lower glass transition temperatures than most polyimides.

Consequently, three groups of polyimides, viz., oxyethylene containing (**PI 1** - **PI 8**), formal group containing (**PI 9** - **PI 16**), and ester group containing (**PI 17** - **PI 24**), have been prepared, by the solution polycondensation of the diisocyanate containing the respective functional group with dianhydrides (PMDA or BTDA) in DMAc.

Polyimides are formed by the addition of stoichiometric quantities of dianhydrides to well stirred solutions of the diisocyanates in DMAc, as per Scheme 8 and as described in the experimental section. The stoichiometric quantities of diisocyanates and dianhydrides for the formation of polyimides along with the polymer yields are listed in Tables 21, 22, and 23.

The formation of polyimides by the diisocyanate - dianhydride reaction is quantitative and the reaction proceeds *via* the formation of a seven-membered cyclic intermediate, which decomposes at elevated temperatures to form the polyimides with the evolution of carbon dioxide. Only polyimide **PI 4** could be cast into a film at the seven membered cyclic intermediate stage. However, all polyimides were yellowish coloured powders.



SCHEME 8 : PREPARATION OF POLYIMIDES CONTAINING OXYETHYLENE (PI 1 - PI 8), FORMAL (PI 9 - PI 16) AND ESTER (PI 17 - PI 24) GROUPS.

TABLE 21

Preparation of Oxyethylene Containing Polyimides and their Inherent Viscosities.[1]

Polyimide	Diisocyanate (0.01 mol)	Dianhydride (0.01 mol)	Yield (%)	Inherent Viscosity, [η], dL/g
PI 1	OE 4 a	PMDA	96	0.22
PI 2	OE 4 a	BTDA	96	0.23
PI 3	OE 4 f	PMDA	97	0.17
PI 4	OE 4 f	BTDA	96	0.25
PI 5	OE 4 g	PMDA	96	0.43
PI 6	OE 4 g	BTDA	96	0.36
PI 7	OE 4 1	PMDA	97	0.52
PI 8	OE 4 1	BTDA	96	0.56

[1] Measured at a concentration of 0.5 g/dL at 30 ± 0.01°C in concentrated sulfuric acid.

TABLE 22

Preparation of Formal Group Containing Polyimides and their Inherent Viscosities.[1]

Polyimide	Diisocyanate (0.01 mol)	Dianhydride (0.01 mol)	Yield (%)	Inherent Viscosity, [η], dL/g
PI 9	F 3 a	PMDA	95	0.23
PI 10	F 3 a	BTDA	96	0.28
PI 11	F 3 b	PMDA	96	0.43
PI 12	F 3 b	BTDA	96	0.48
PI 13	F 3 c	PMDA	96	0.31
PI 14	F 3 c	BTDA	95	0.35
PI 15	F 3 d	PMDA	96	0.36
PI 16	F 3 d	BTDA	97	0.65

[1] Measured at a concentration of 0.5 g/dL at 30 ± 0.01°C in concentrated sulfuric acid.

TABLE 23

Preparation of Ester Group Containing Polyimides[1]
and their Inherent Viscosities

Polyimide	Diisocyanate (0.01 mol)	Dianhydride (0.01 mol)	Yield (%)	Inherent Viscosity, $[\eta]$, dL/g
PI 17	E 3 a	PMDA	96	0.25
PI 18	E 3 a	BTDA	96	0.33
PI 19	E 3 b	PMDA	95	0.45
PI 20	E 3 b	BTDA	96	0.57
PI 21	E 3 c	PMDA	96	0.32
PI 22	E 3 c	BTDA	96	0.42
PI 23	E 3 d	PMDA	96	0.55
PI 24	E 3 d	BTDA	97	0.70

[1] Measured at a concentration of 0.5 g/dL at 30 ± 0.01°C in concentrated sulfuric acid.

Infra Red Spectra

The IR spectra of oxyethylene containing polyimides (**PI 1 - PI 8**) and formal group containing polyimides (**PI 9 - PI 16**) showed the characteristic stretching absorption band at 1230-1240 cm^{-1} due to C-O-C linkage, while those of the ester group containing polyimides (**PI 17 - PI 24**) exhibited a characteristic band at 1720 cm^{-1} due to C=O of the ester grouping. The spectra of all the polyimides exhibited the absorption bands at 1780 cm^{-1} and 1745 cm^{-1} (imide-I), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). The imide-I band is attributed to the stretching vibration of the two carbonyls which are weakly coupled. Imide-II, -III, and -IV bands are assigned to the axial, transverse and out- of-plane vibrations of the cyclic imide structure, respectively. The representative IR spectrum of polyimide containing oxyethylene (**PI 8**) and ester (**PI 24**) linkage is shown in Figures 21 (a) and 21 (b), respectively.

Solubility

The solubility of the three sets of polyimides was determined at a 3 % concentration of polymers in different solvents. Polyimides containing oxyethylene (**PI 1 - PI 8**), formal group (**PI 9 - PI 16**), and ester group (**PI 17 - PI 24**) were insoluble in organic solvents like DMAc, DMF, DMSO, HMPA, NMP, and m-cresol, except for formal group containing polyimide **PI 12** which was soluble in the above solvents. However, all polyimides dissolved in concentrated sulfuric acid.

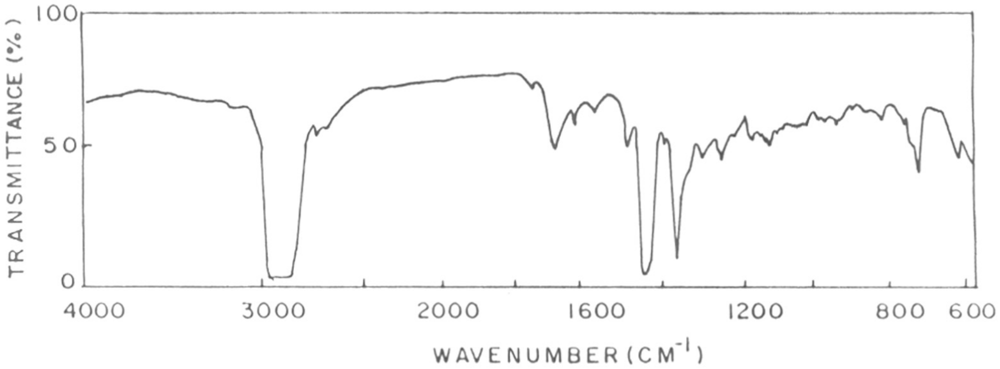


FIG. 21(a): IR (NUJOL MULL) SPECTRUM OF POLYIMIDE CONTAINING OXYETHYLENE GROUP, PI 8.

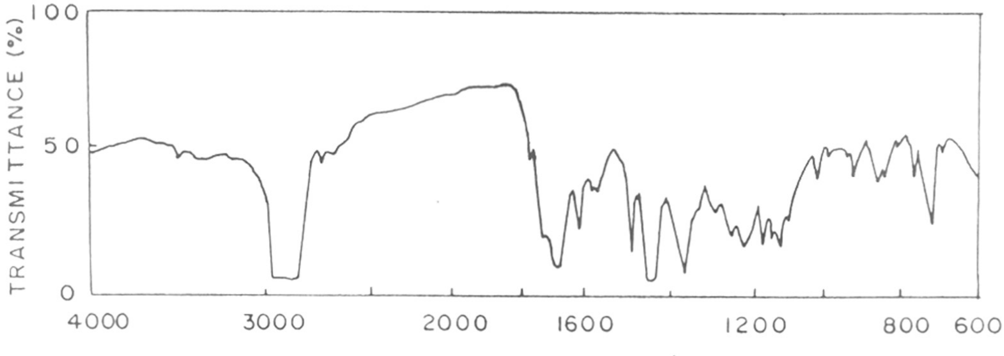


FIG. 21(b): IR (NUJOL MULL) SPECTRUM OF POLYIMIDE CONTAINING ESTER GROUP, PI 24.

Viscosity Measurements

The inherent viscosities of the three sets of polyimides were determined in sulfuric acid at a concentration of 0.5 g/dL at $30\pm0.01^{\circ}C$ with an Ubbelohde viscometer. The inherent viscosities were calculated using the equation

$$\eta_{inh} = \frac{2.303 \times \log t/to}{C}$$

where, t and to are flow times of polymer solution and pure solvent, respectively, and C is the concentration of the polymer solution (0.5 g/dL).

The viscosities ranged from 0.18 - 0.56 dL/g for the polyimides containing oxyethylene groups, 0.23 - 0.65 dL/g for the polyimides containing formal groups, and 0.25 - 0.70 dL/g for the polyimides containing ester groups. The inherent viscosities of the polyimides are incorporated in Tables 21, 22, and 23. It was observed that the polyimides based on BTDA had slightly higher inherent viscosity values than those based on PMDA.

X-Ray Diffraction

The crystallinity of the three groups of polyimides was studied by wide angle X-ray diffraction studies. X-Ray diffractograms of the polyimides were taken on powder samples using nickel-filtered CuK_{α} radiations on a Phillips X-Ray Unit (Phillips Generator, PW 1730). The X-ray diffractograms of polyimides containing oxyethylene group (**PI 1** - **PI 8**) indicated, all the polyimides are semicrystalline, except for polyimide **PI 4** (based on diisocyanate **OE 4 f** and BTDA), which was amorphous. The polyimides derived from PMDA were more crystalline than those derived from BTDA. The polyimides derived from para- oriented diisocyanates (**OE 4 g** and **OE 4 l**) were more crystalline than the meta- oriented diisocyanates (**OE 4 a** and **OE 4 f**). In the polyimides containing formal group (**PI 9** - **PI 16**), the polymers ranged from completely amorphous to semicrystalline, except for polyimide **PI 12** (derived from diisocyanate **F 3 b** and BTDA), which was amorphous. The polyimides derived from PMDA were more crystalline than those based on BTDA. The polyimides derived from para- oriented diisocyanates (**F 3 c** and **F 3 d**) were more crystalline than those based on meta- oriented diisocyanates (**F 3 a** and **F 3 b**). Also, the polyimides containing short (methylene) spacer were more crystalline than the polyimides containing long (bis[ethyl] formal) spacer.

In the ester group containing polyimides (**PI 17** - **PI 24**), all the polyimides were semicrystalline. The polyimides derived from para- oriented diisocyanates (**E 3 c** and **E 3 d**) were more crystalline than those based on meta- oriented diisocyanates (**E 3 a** and **E 3 b**). The polyimides based on PMDA are more crystalline than those based on BTDA.

The X-ray diffraction curves of polyimides containing oxyethylene (**PI 1** - **PI 8**), formal group (**PI 9** - **PI 16**), and ester group (**PI 17** - **PI 24**) are shown in Figures 22 (a), 22 (b), and 22 (c), respectively.

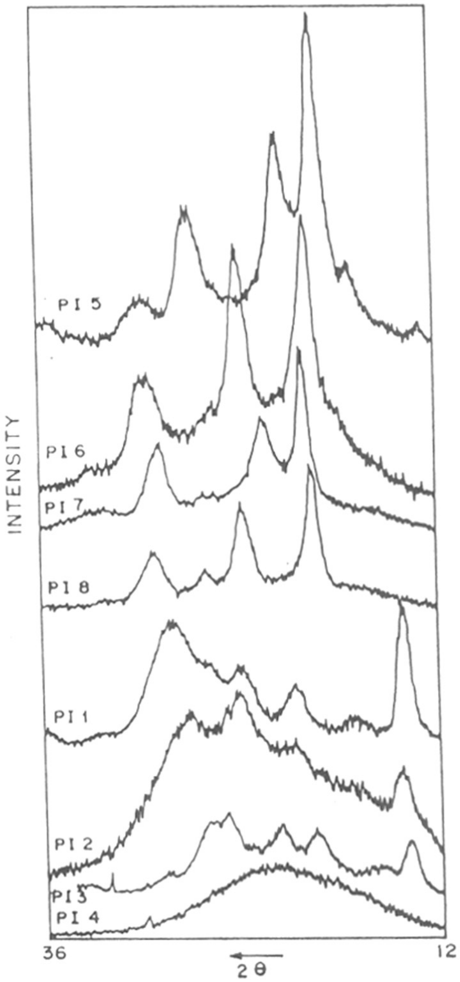


FIG.22(a) X-RAY DIFFRACTION CURVES OF POLYIMIDES, PI 1 - PI 8.

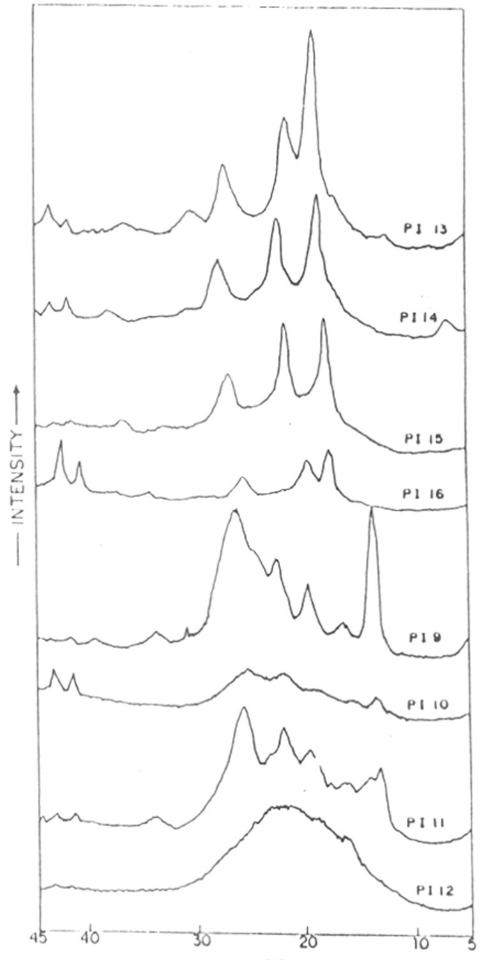


FIG 22(b) XRD CURVES OF FORMAL GROUP CONTAINING POLYIMIDES, PI 9 - PI 16.

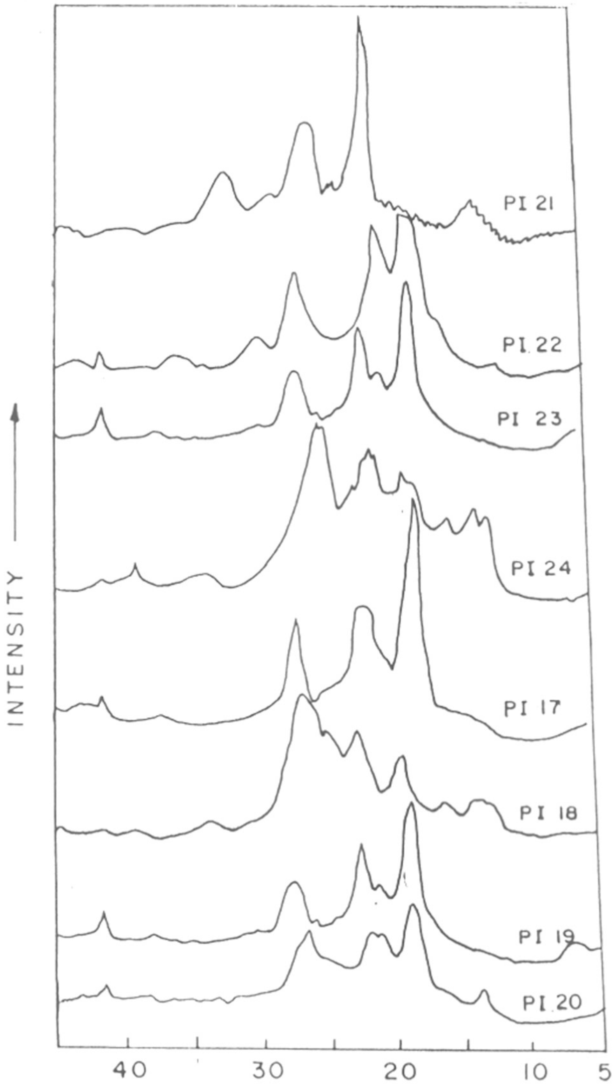


FIG. 22 (c) X-RAY DIFFRACTOGRAMS OF POLYIMIDES, PI 17- PI 24.

Thermal Characterization.

The thermal stability of polyimides was determined by thermogravimetric analysis. The thermogravimetric analysis (TGA) of the samples was carried out on a Netzsch 409 Thermal Analyzer, by heating the samples at a heating rate of 10°C/min in air. TGA, DTA and DTG were obtained simultaneously.

Polyimides containing oxyethylene (PI 1 - PI 8) and formal groups (PI 9 - PI 16) showed a two stage decomposition pattern as evidenced from the TG curves. The first stage of decomposition may be attributed to the weak oxyethylene linkage being cleaved while the second stage may be due to the cleavage of the stable imide linkage. The thermal characteristics, such as initial decomposition temperature (IDT), T_{10}, T_{30}, and T_{50}, i.e., temperatures at 10%, 30%, and 50%, respectively, were calculated from the original thermograms, and these values are incorporated in Tables 24, 25, and 26. T_{max} (temperature at maximum decomposition), was determined from the DTG curves.

It was observed that the T_{10} values for the oxyethylene containing polyimides ranged from 335 - 449°C, for the formal group containing polyimides the range was 357-465°C, and for the ester group containing polyimides it was 374-452°C, while the T_{max} values for the corresponding polyimides series ranged from 460-585°C, 532-582°C, and 548-588°C, respectively. When comparing the polyimides at a weight loss of 10 %, it was observed that longer the spacer, the lower is the temperature for decomposition, and shorter the spacer, higher is the temperature for this

TABLE 24

Thermal Characteristics of Oxyethylene Containing Polyimides I - VIII

Polymer-->	PI I	PI 2	PI 3	PI 4	PI 5	PI 6	PI 7	PI 8
IDT	360	397	360	394	355	370	308	318
T_{10}	432	449	401	449	423	437	335	380
T_{30}	531	535	491	515	498	513	425	522
T_{50}	558	565	516	533	520	541	440	544
T_{Max}	585	585	531	540	551	549	466	550

[a] All temperatures in °C
IDT - Initial Decomposition Temperature
T_{10}, T_{30}, T_{50}, and T_{Max} are temperatures at 10 %, 30 %, 50 %, and maximum rate of decomposition, respectively.

Table 25

Thermal Characteristics of Formal Group Containing Polyimides.[a]

Polyimide->	PI 9	PI 10	PI 11	PI 12	PI 13	PI 14	PI 15	PI 16
Tg	-	196	155	147	209	-	-	-
T_{10}	465	407	366	357	471	420	385	377
T_{30}	517	487	452	440	530	502	494	455
T_{50}	547	525	535	509	555	545	550	535
T_{max}	562	552	560	532	582	567	572	547

---

[a] All temperatures in °C.
T_{10} , T_{30}, T_{50}, and T_{max} the are temperatures corresponding to 10%, 30%, 50%, and maximum decompositions, respectively.

TABLE 26

Thermal Charactertistics of Ester Group Containing Polyimides,

Polyimides->	PI 17	PI 18	PI 19	PI 20	PI 21	PI 22	PI 23	PI 24
Tg	-	201	-	-	-	212	187	142
IDT	336	320	304	300	368	347	336	336
T_{10}	421	399	389	374	452	432	406	378
T_{max}	574	548	558	548	588	554	563	563

All temperatures in ^{o}C
IDT - Initial decomposition temperature, T
Tg - Glass transition temperature, T_{10} and T_{max} are temperatures at 10% and maximum rate of decomposition, respectively.

decomposition.

In general it was observed that polyimides obtained from PMDA were comparatively more thermally stable than those obtained from BTDA. Also, the polyimides based on short spacer containing diisocyanates were more thermally stable than those derived from long spacer containing diisocyanates. Polyimides based on para- oriented diisocyanates were more stable than the corresponding polyimides derived from the meta- oriented diisocyanates.

The TGA curves of representative polyimides containing oxyethylene (**PI 7** and **PI 8**), formal group (**PI 12** and **PI 13**), and ester group (**PI 17, PI 21, PI 23** and **PI 24**) are shown in Figures 23 (a), 23 (b), and 23 (c), respectively.

Differential Scanning Calorimetry.

The glass transition temperature (Tg) is a very important characteristic of polymers. It determines the temperature at which a polymer can be processed. The glass transition of some of the formal containing and ester group containing polyimides was determined on a Mettler DSC 30 S. The samples were scanned at heating rate of 20°C/min. The Tg values of some of the samples are incorporated in Tables 25 and 26.

Among the formal group containing polyimides whose Tg values were determined, the Tg values were higher for polyimides containing short (methylene) spacer as compared to the polyimides containing long (bis[ethy] formal) spacer. The polyimide **PI 11** derived from PMDA exhibited higher Tg value (155°C) as compared to

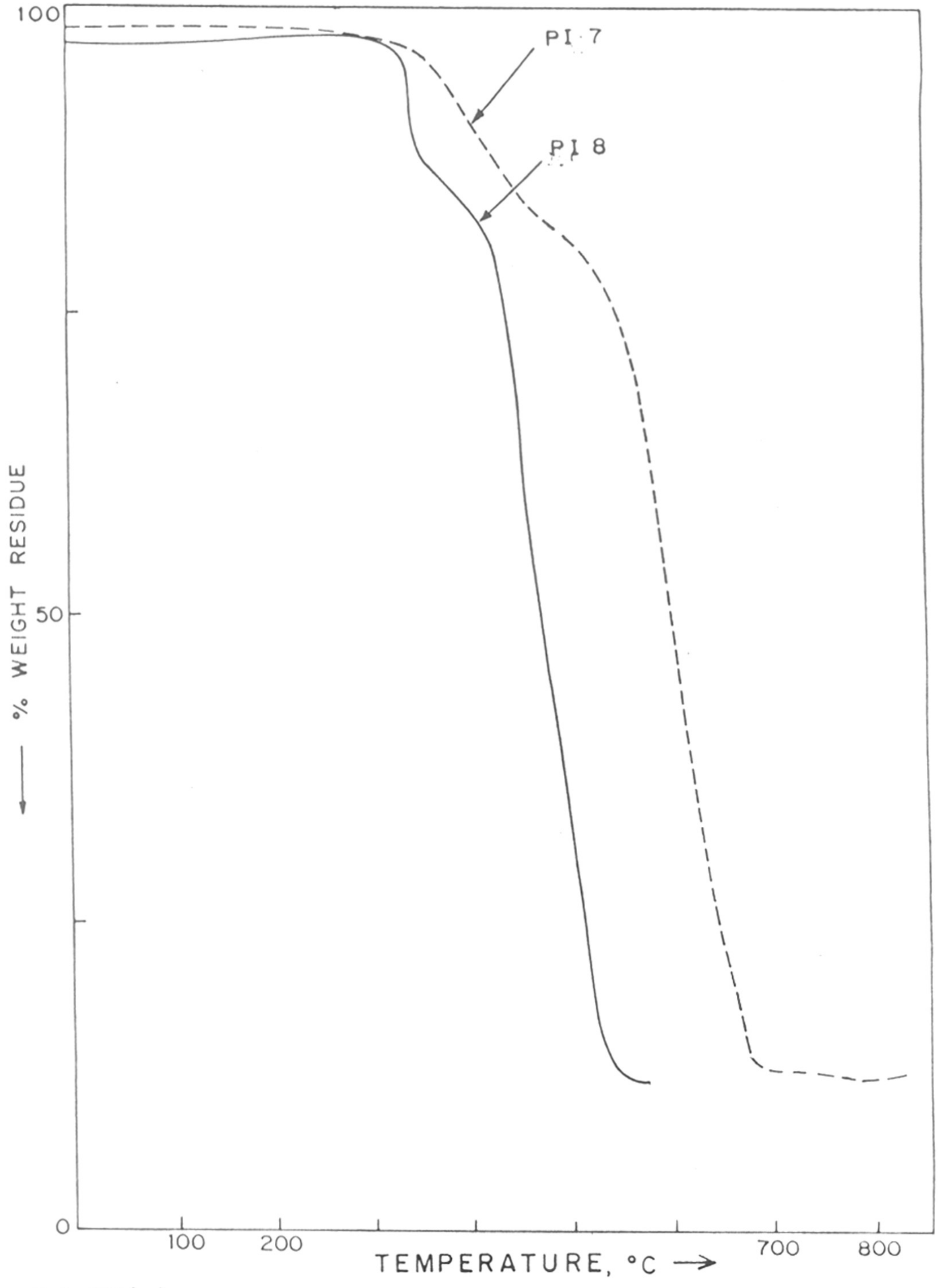


FIG.23(a). TG CURVES OF POLYIMIDES (PI 7 & PI 8) IN AIR AT A HEATING RATE OF 10° C/min.

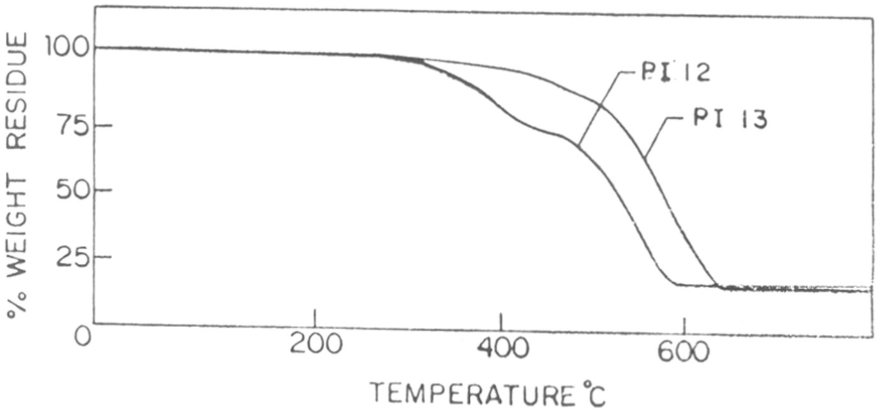


FIG.23(b) TGA CURVES OF FORMAL GROUP CONTAINING POLYIMIDES (12, 13).

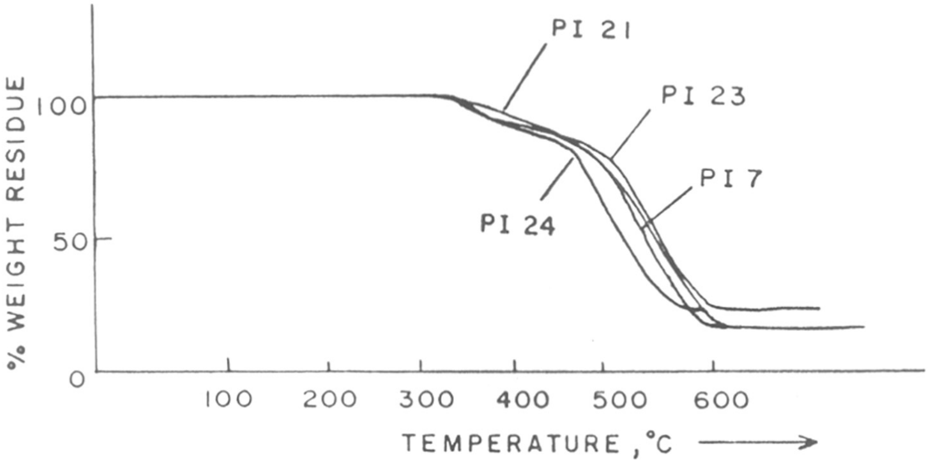


FIG. 23(c). TGA CURVES OF POLYIMIDES, PI 17, 21, 23 AND PI 24.

the polyimide **PI 12** (147°C) derived from BTDA.

Among the ester group containing polyimides whose Tg values were determined, the Tg values for polyimide **PI 18** based on meta-oriented diisocyanate (**E 3 a**) were lower (201°C) than polyimide **PI 22** (212°C) which was derived from para- oriented diisocyanate (**E 3 c**). The Tg value(187°C) for polyimide **PI 23** based on PMDA was higher than polyimide **PI 24** (142°C) based on BTDA.

5.2.6 CONCLUSIONS

- Functional group (oxyethylene, formal, and ester) containing polyimides can be conveniently synthesized by the solution polycondensation of the respective group containing diisocyanates with dianhydrides.

- The polyimides derived from (i) meta- oriented diisocyanates, or (ii) long spacers, or (iii) BTDA are less crystalline than those derived from (i) para- oriented diisocyanates, or (ii) short spacers, or (iii) PMDA which are more crystalline in nature.

- The polyimides containing oxyethylene, formal, and ester group along the polymer backbone are reasonably thermally stable.

- The polyimides derived from (i) meta- oriented diisocyanates, or (ii) long spacers, or (iii) BTDA are less thermally stable than the corresponding polyimides derived from (i) para- oriented diisocyanates, or (ii) shorter spacer, or (iii) PMDA which are more thermally stable.

- The polyimides derived from (i) diisocyanates with long spacers, or (ii) meta- oriented diisocyanates, or (iii) BTDA have lower Tg value than the corresponding polyimides derived from (i) diisocyanates with short spacers, or (ii) para- oriented diisocyanates, or (iii) PMDA which have a higher value of Tg.

5.2.7. EXPERIMENTAL

Materials:

- Diisocyanates containing functional groups, viz., oxyethylene (**OE 4 a, OE 4 f, OE 4 g,** and **OE 4 l**), formal (**F 3 a** - **F 3 d**), and ester (**E 3 a** - **E 3 d**) group, were synthesized as per reaction Schemes 1 - 3 described in Chapter 2.

- Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anydride and then sublimed *in vacuo* using a cold finger.

- N,N-Dimethylacetamide (DMAc) was dried over P_2O_5 for 24 h and then distilled under reduced pressure.

- All other chemicals were of reagent grade and were used as such.

5.2.7.1 Preparation of Polyimides Containing Oxyethylene (PI 1 - PI 8), Formal (PI 9 - PI 18), and Ester (PI 19 - PI 24) Groups Along the Polymer Backbone. General Procedure.

In a 100 mL three-necked flask fitted with a thermowell, a nitrogen gas inlet, and a reflux condenser fitted with a calcium chloride guard tube, was taken a solution of the corresponding diisocyanate (0.01 mol) in 10 mL DMAc. To this solution at 0°C was added the respective dianhydride (PMDA or BTDA) (0.01 mol) in small protions over 1 h. The reaction mixture was stirred at this temperature for 30 min and then heated gradually to 40°C at which temperature it was held for 2.5 h. Then the temperature was raised to 90°C. Finally the temperature of the reaction mixture was raised to 130-140°C and held for 24 h. A slow stream of dry nitrogen was bubbled throughout the reaction.

The reaction mixture was cooled and poured into a large excess of water. The polymer that precipitated was filtered at pump, washed with methanol and dried at 100° for 3 h in vacuum.

5.3. POLY(AMIDE-IMIDE)S

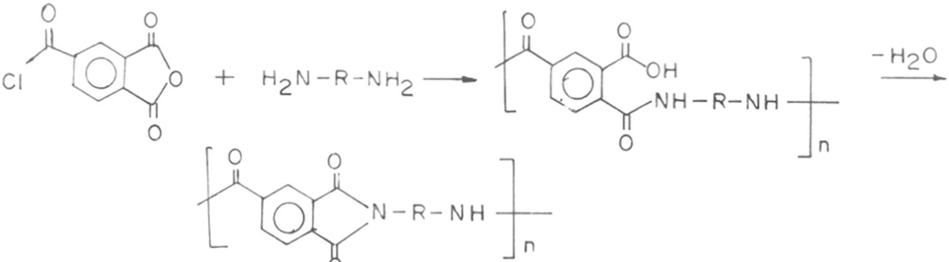
Another class of thermally stable polymers that has elicited interest among scientists working in the area of themally stable polymers is poly(amide-imide)s. These have gained commercial importantance as they combine the excellent thermal stabilities with the ease of processing and may be reckoned to be intermediate in properties between polyamides and polyimides.[8,98,99]

5.3.1. METHODS OF PREPARATION OF POLY(AMIDE - IMIDE)S

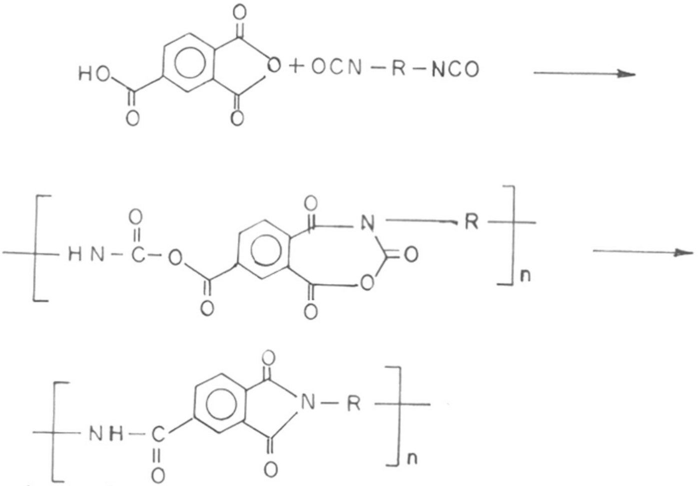
There are several methods for the preparation of poly(amide-imide)s. Listed below are some of the important methods:

1. By the reaction of excess diamine with tetracarboxylic dianhydride, say pyromellitic dianhydride (PMDA) or benzophenonetetracarboxylicdianhydride (BTDA), to form low molecular weight amine terminated polyamic-acid. This is then reacted with diacid chloride to form poly[amide(amic-acid)] which is then converted into the poly(amide-imide).
2. By the reaction of excess diamine with diacid chloride to form low molecular weight amine terminated polyamide, which is then treated with tetracarboxylic dianhydride in a suitable polar solvent to form a poly[amide(amic-acid)] that could be converted into poly(amide-imide).
3. By a reaction of anhydride acid (eg. trimellitic anhydride, TMA) or TMA derivative such as acid chloride with a diamine. The poly[amide(amic-acid)] formed is converted to the poly(amide-

imide)s.[100] The method for converting the poly[amide(amic-acid)] to the poly(amide-imide)s is similar to that described for polyimides (Sect. 5.2).



4. By the reaction of a diisocyante with an anhydride acid (eg. trimellitic anhydride, TMA).[101,102] The diisocyante reacts with both the carboxylic acid and the anhydride component of trimellitic anhydride. The reaction probably proceeds *via* the formation of a seven-membered cyclic intermediate, which on heating liberates carbon dioxide to yield the cyclic imide structure.



5. By the polycondensation reaction of a diacylhydrazide with a tetracarboxylic dianhydride (eg. PMDA and BTDA) in a suitable polar solvent. The reaction proceeds *via* the formation of poly[amide(hydrazide acid)], which on cyclodehydration, either

thermally or chemically, results in the formation of a poly(amide-imide).[103-106]

6. By the reactiion of preformed imide group containing diacid chloride with diamines[107] poly(amide-imide)s have been prepared. This reaction sequence was studied by Abajo et al.[108-110] Maiti et al[111-113] have prepared poly(amide-imide)s by the reaction of preformed imide group containing acids with aromatic diamines.

Yang et al[98,114] studied the formation of poly(amide-imide)s by the direct polycondensation of preformed imide group containing dicarboxylic acids with diamines (in the presence of triphenyl phosphite).

Poly(amide-imide)s may be prepared by other methods reported in literature.[115-125]

Poly(amide-imide)s containing various flexibilizing groups, such as, ether,[126], sulfone,[94,127] carbonyl,[128] ester,[129] silicon,[130] etc., have been synthesized and evaluated.

Poly(amide-imide)s are employed in a wide range of commercial applications due to their good thermal stability, strength, toughness, chemical resistance and due to the ease of processibility.

5.3.2. SCOPE OF THE PRESENT WORK

Poly(amide-imide)s are an interesting class of thermally stable polymers.

The synthesis of poly(amide-imide)s containing various functional groups continues to interest polymer chemists. These functional groups are reckoned to impart solubility, lend to the ease of processability without affecting the thermal stability to a large extent.

The incorporation of flexibilizing groups into the polymer backbone is known to improve solubility and/or processing characteristics. Oxyethylene group is one of such flexibilizing groups which improves the solubility and processability of thermally stable polymers without appreciably affecting the thermal stability.

Poly(amide-imide)s can be prepared by the various methods described above. In the present work the preparation of poly(amide-imide)s containing functional groups by the (i) diisocyanate - anhydride acid reaction and (ii) diacylhydrazide - tetracarboxylic anhydride reaction, was targeted.

In the present work the synthesis of twelve poly(amide-imide)s containing oxyethylene, fomal, ester and preformed imide groups along the polymer backbone is being reported. Specifically, by the solution polycondensation reaction of functional group containing diisocyanates with trimellitic anhydride (TMA) the formation of twelve new poly(amide-imide)s, **PAI 1 - PAI 12**, has been achieved. The synthesis of four new poly(amide-imide)s, **PAI A - PAI D**, by the reaction of oxyethylene containing diacylhydrazides with dianhydrides has also been acomplished.

These poly(amide-imide)s have been characterized by viscosity measurements, IR spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

5.3.3. RESULTS AND DISCUSSION

Polyimides are known for their high thermal stability and excellent mechanical properties. However, they have poor processability. Introduction of amide groups into the polyimides improves the processability without significantly affecting the thermal stability. Thus poly(amide-imide)s are intermediate between polyimides and polyamides in properties.

The introduction of amide linkages into the polyimides backbone leads to the formation poly(amide-imide)s having better solubility and/or processing characteristics than polyimides. Introduction of functional groups such as oxyethylene, formal or ester group in polyimides is expected to further improve processability of these polymers. Hence, preparation of poly(amide-imide)s with structural variations is gaining importance.

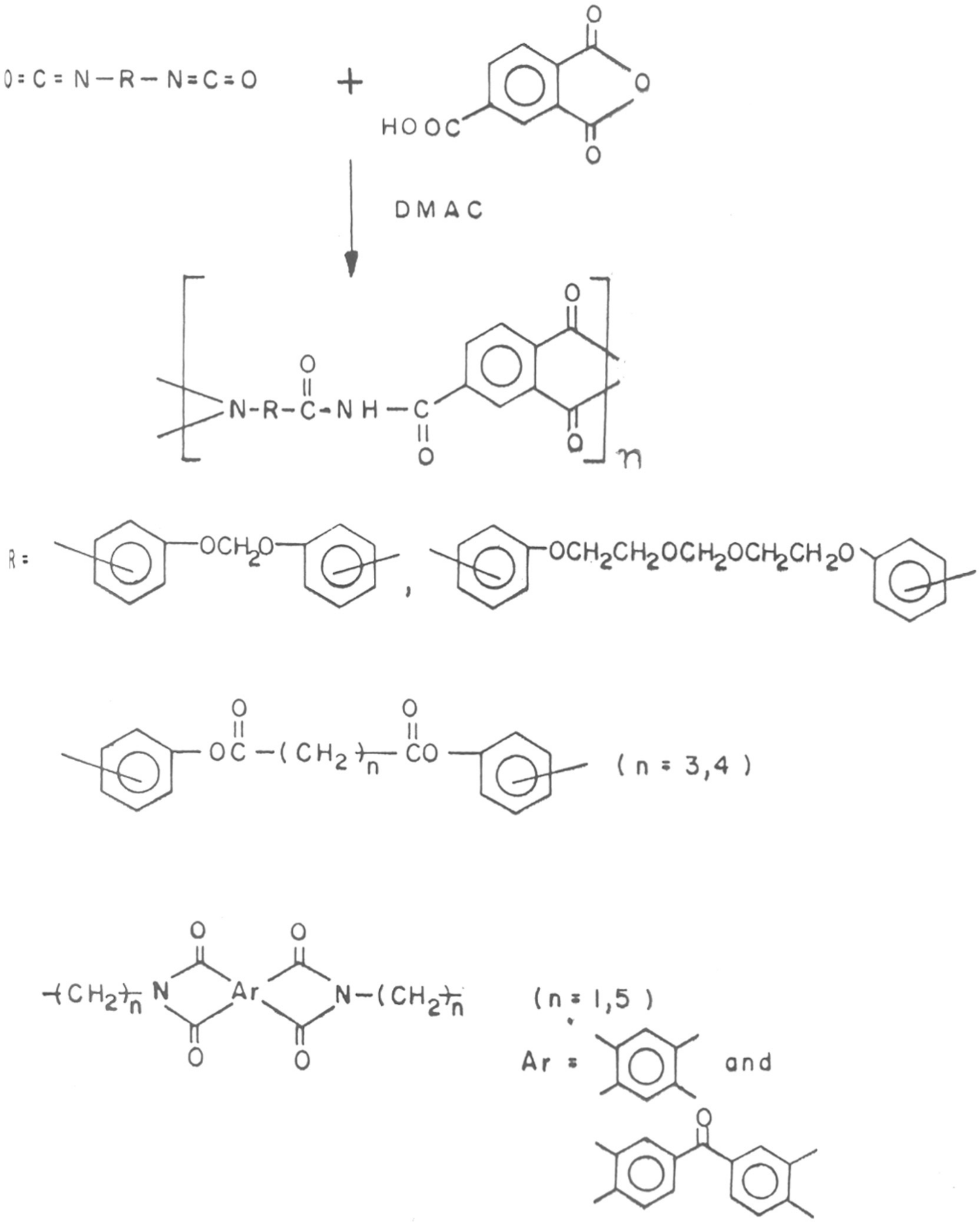
Generally, poly(amide-imide)s are prepared by the reaction of (i) diisocyanates with anhydride acid, and (ii) diacylhydrazide with tetracarboxylic dianhydride. Consequently, poly(amide-imide)s were prepared by both the methods, ie., (i) based on the diisocyanate - anhydride acid reaction and (ii) based on the diacylhydrazide - tetracarboxylic dianhydride route.

Preparation of Poly(amide-imide)s by the Diisocyanate - Anhydride Acid Reaction.

The method consists of the reaction of equimolar quantities diisocyanates containing various functional groups, viz., formal (**F 3 a - F 3 d**), ester (**E 3 a - E 3 d**), and preformed imide (**I 4 a, I 4 d, I 4 e,** and **I 4 h**), with trimellitic anhydride in DMAc (as shown in Scheme 9 and Tables 27 (a), (b), and (c). A slow stream of dry nitrogen was bubbled through the reaction medium throughout the reaction. Final imidization was carried out at 130°C. In all cases the polymers remained in solution. The polymers were precipitated by pouring the reaction mixture into excess methanol. The yields of the polymer were quantitative. The poly(amide - imide)s were pale yellow coloured powders. The polymers formed brittle films which crumbled into fine yellow powders.

Infra Red Spectra

The IR spectra of the poly(amide-imide)s **PAI 1 - PAI 12** showed characteristic absorbance at 3320 cm^{-1} (-NH-), at 1650 cm^{-1} (C=O of the amide linkage), and the absorption bands at 1795 cm^{-1} and 1745 cm^{-1} (imide-I), 1705 cm^{-1} (C=O of imide), 1380 cm^{-1} (imide-II), 1150 cm^{-1} (imide-III) and 720 cm^{-1} (imide-IV). Representative spectra of poly(amide-imide)s, **PAI 2** and **PAI 10** are shown in Figure 24 (a) and 24 (b), respectively.



SCHEME 9: PREPARATION OF POLY (AMIDE-IMIDE)S, PAI 1 - PAI 12.

TABLE 27

Preparation of Poly(Amide-Imide)s

a. Based on Formal Group containing Diisocyanates, **F 3 a – F 3 D**, and Their Inherent Viscosities

Polymers	Diisocyanates[a] (0.01 mol)	Anhydride (0.01 mol)	Yield (%)	$[\eta]_{inh}$ (dl/g)
PAI 1	**F 3 a**	TMA	96	0.32
PAI 2	**F 3 c**	TMA	95	0.35
PAI 3	**F 3 b**	TMA	97	0.40
PAI 4	**F 3 d**	TMA	95	0.42

b. Based on Ester Group Containing Diisocyanates, **E 3 a – E 3 d**, and Their Inherent Viscosities.

PAI 5	**E 3 a**	TMA	96	0.29
PAI 6	**E 3 c**	TMA	97	0.43
PAI 7	**E 3 b**	TMA	96	0.35
PAI 8	**E 3 d**	TMA	95	0.50

c. Based on Imide Group Containing Diisocyanates, **I 4 a – I 4 h**, and their Inherent Viscosities.

PAI 9	**I 4 a**	TMA	95	0.31
PAI 10	**I 4 e**	TMA	96	0.34
PAI 11	**I 4 d**	TMA	95	0.44
PAI 12	**I 4 h**	TMA	94	0.49

[a] The of diisocyanates were synthesized as reported in Chapter II.

[b] TMA = Trimellitic anhydride

[c] Measured at a concentration of 0.5 g/dL at 30 ± 0.01°C in m-Cresol

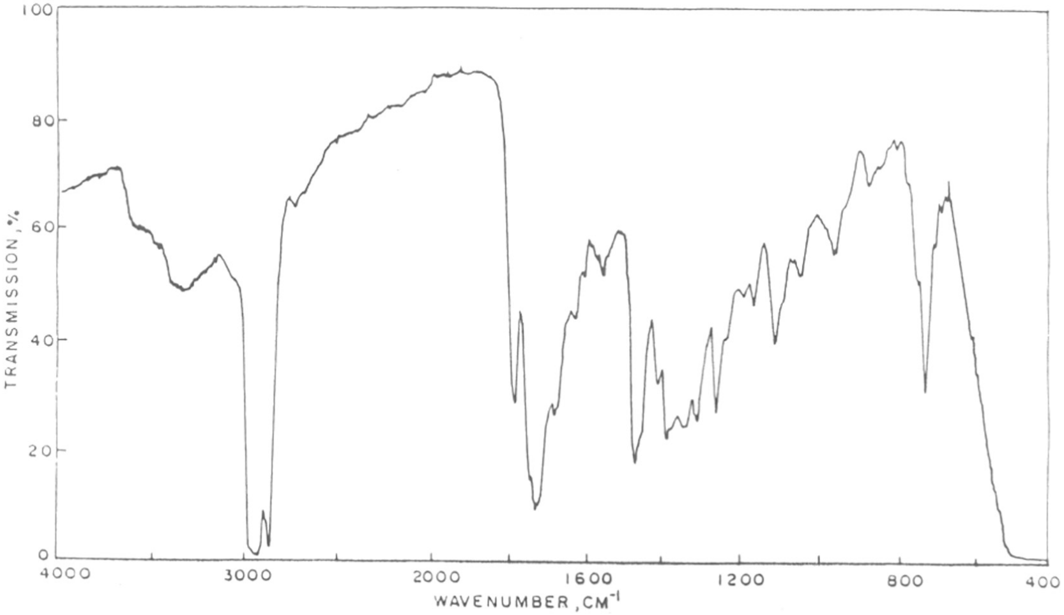


FIG 24 (a) IR (NUJOL MULL) SPECTRUM OF OXYETHYLENE CONTAINING POLY(AMIDE-IMIDE), PAI 2.

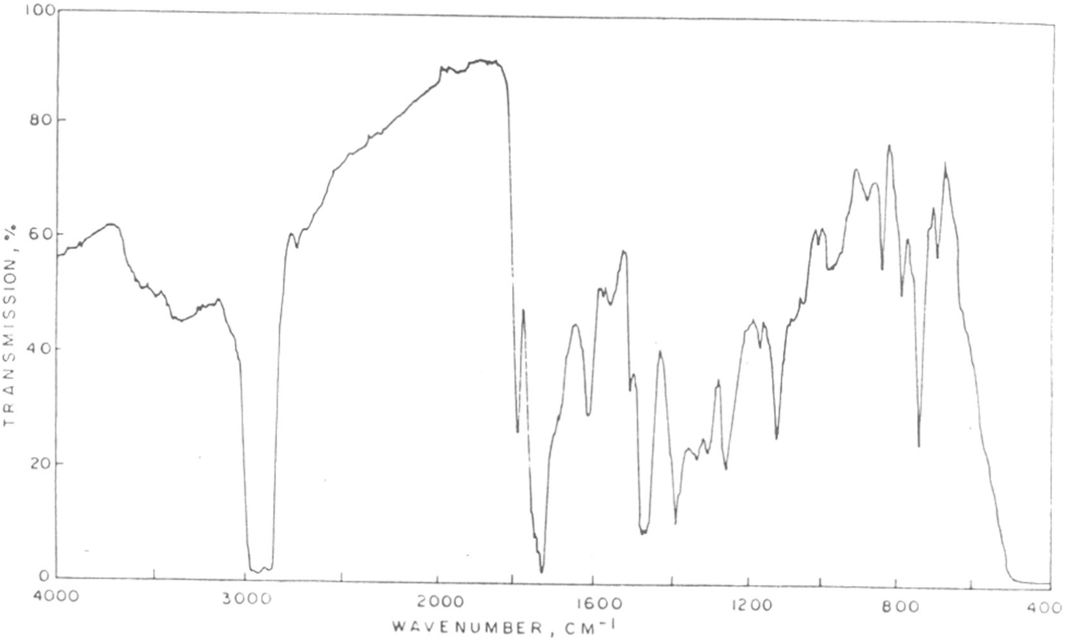


FIG 24 (b) IR (NUJOL MULL) SPECTRUM OF ESTER GROUP CONTAINING POLY (AMIDE-IMIDE), PAI 10

Solubility

The solubility of the poly(amide-imide)s was determined at 3 % concentration in polar solvents, like, DMF, DMAc, HMPA and m-cresol, and in concentrated sulfuric acid. The poly(amide-imide)s were soluble in most of the above solvents (Table 28). The poly(amide-imide)s based on meta-oriented diisocyanates were generally more soluble than the para- analogues. The polyimides containing long chain spacers, (**PAI 2, PAI 4, PAI 6, PAI 8, PAI 10 and PAI 12**) exhibited better solubility as compared the remaining polymers containig shorter spacers.

Viscosity Measurements

The inherent viscosities of the poly(amide-imide)s were determined in m-cresol at a concentration of 0.5 g/dL in at 30±0.01°C using an Ubbelohde viscometer. The viscocities ranges for polyimides containing the various functional groups are: 0.32 - 0.42 for formal 29 - 0.50 for ester and 0.31 - 0.49 dL/g for imide (Table 27 a, b, and c).

X-Ray Diffraction

The X-ray diffractograms of the poly(amide-imide)s, **PAI 1 - PAI 12**, indicated that the polymers derived from the formal and ester group containig diisocyanates were semicrystalline in nature while those derived from preformed imide containing diisocyanates were amorphous. The polymers based on para- oriented diisocyanates and TMA are more semicrystalline than those based on the meta-oriented diisocyanates. The polymers with longer spacers were more

TABLE 28

Solubility of Poly(Amide-Imide)s Containing Formal, Ester and Pre-formed Imide Groups, PAI 1 - PAI 12.

Solvent\Polymer	1	2	3	4	5	6	7	8	9	10	11	12
DMF	+	–	+	+	–	–	–	–	+	+	+	+
DMAc	+	+	+	+	+	+	+	+	+	+	+	+
HMPA	+	+	+	+	+	+	+	+	+	+	+	+
m-Cresol	+	+	+	+	+	+	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+	+	+	+	+	+	+

(+) Soluble (–) Insoluble

amorphous than those with shorter spaces. The polymers based on BTDA were more amouphous than those based on PMDA. X-Ray diffractograms of representative poly(amide-imide)s containing formal, ester and imide groups are shown in Figures 25 (a), 25 (b) and 25 (c), respectively.

Thermal Characterization.

The thermal stability of poly(amide-imide)s was determined on a Netzsch 409 Thermal Analyzer, by heating the samples in air at a heating rate of 10°C/min. Thermal characteristics, such as, initial decomposition temperature (IDT), T_{10}, T_{30}, T_{50}, and T_{max} corresponding to the temperatures at 10%, 30%, 50% and maximum decomposition were determined. The T_{max} values were determined from the DTG curves. The TGA curves (Figure 26 (a), 26 (b) and 26 (c)) of all polymers showed no weight loss below 277°C and the T_{max} ranged from 438 - 582°C, indicating that the poly(amide-imide)s are reasonably themally stable (Table 29 a, b, and c). A comparision of poly(amide-imide)s (**PAI 1** - **PAI 8**) at a 10 % weight loss, T_{10}, indicated that the polyimides derived from meta-oriented diisocyanates were less stable than those derived from para-oriented diisocyanates. The polyimides derived from diisocyanates containing long spacer were less thermally stable than those based on diisocyanates containing short spacer. The poly(amide-imide)s derived from diisocyanates based on PMDA were more stable than those derived from diisocyanates based on BTDA. The polyimides containing short spacer were more stable than those containing long spacer.

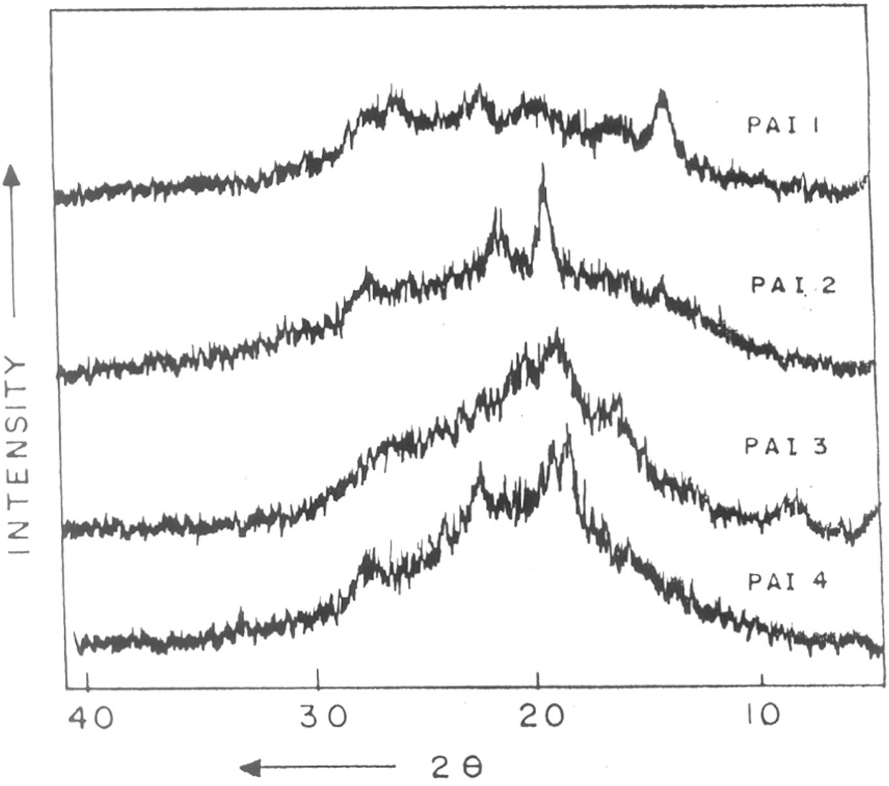


FIG. 25 (a). XRD CURVES OF POLY(AMIDE-IMIDE)S, PAI 1 - PAI 4.

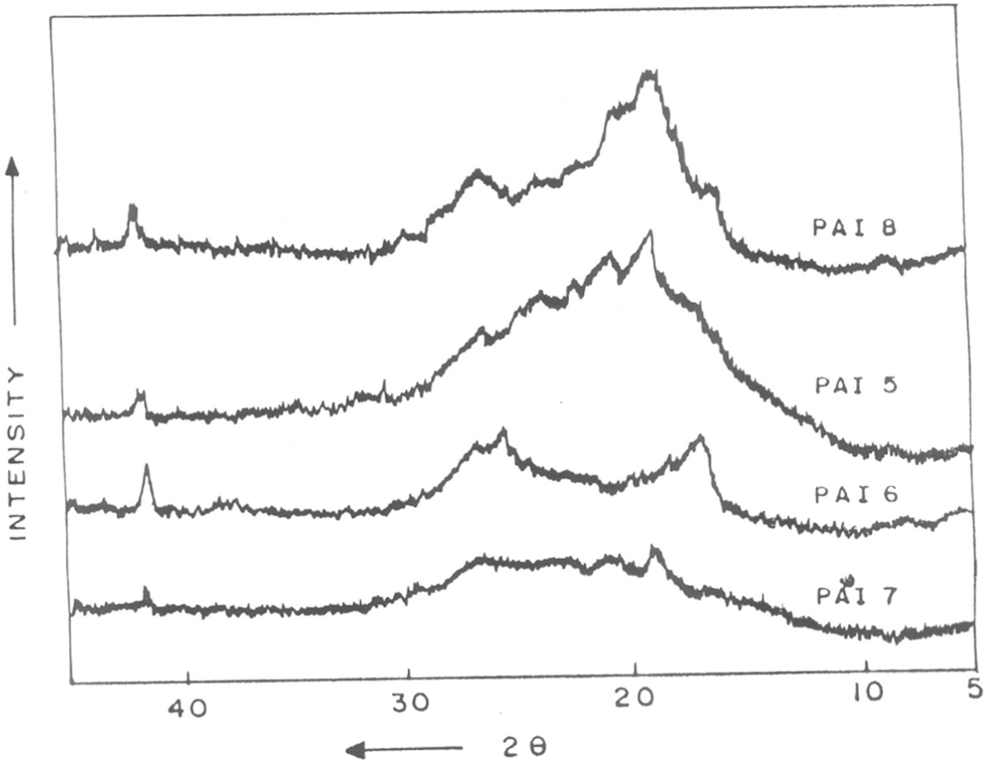


FIG. 25 (b). XRD CURVES OF POLY(AMIDE - IMIDE)S PAI 5 - PAI 8.

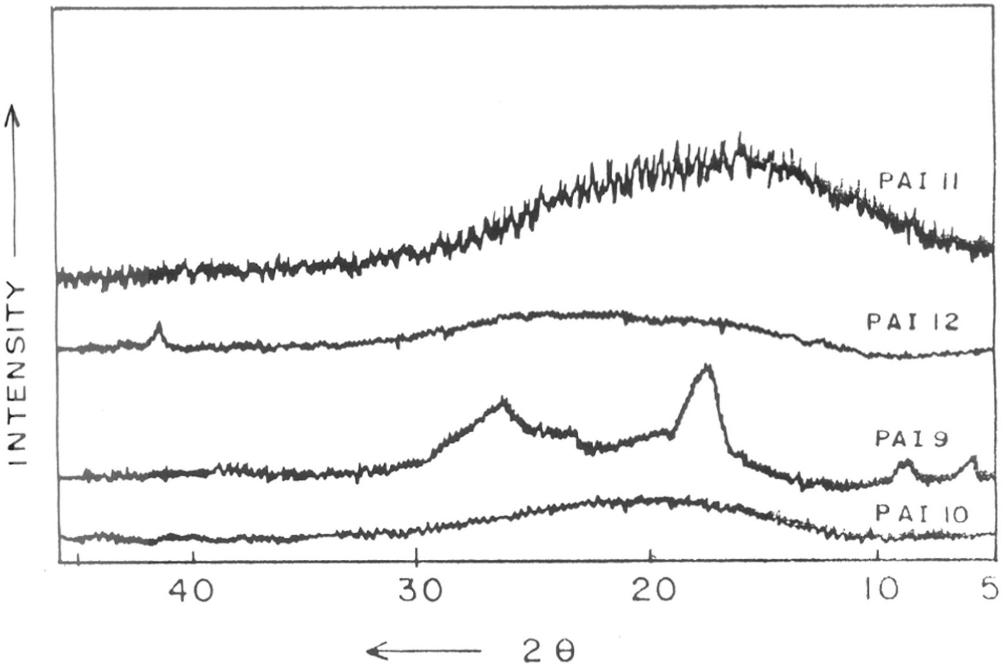


FIG. 25 (c). XRD CURVES OF POLY(AMIDE-IMIDE)S, PAI 9 – PAI 11.

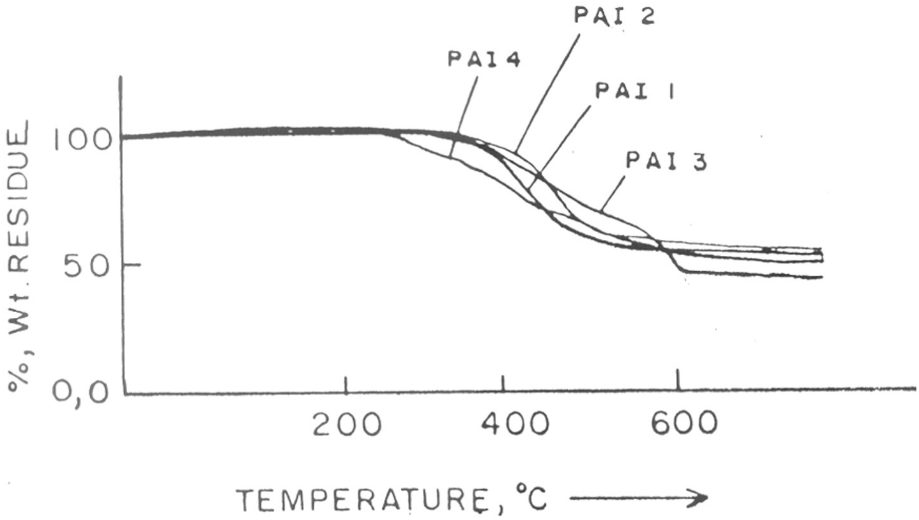


FIG. 26 (a). TGA CURVES OF POLY (AMIDE - IMIDE) S, PAI 1 - PAI 4.

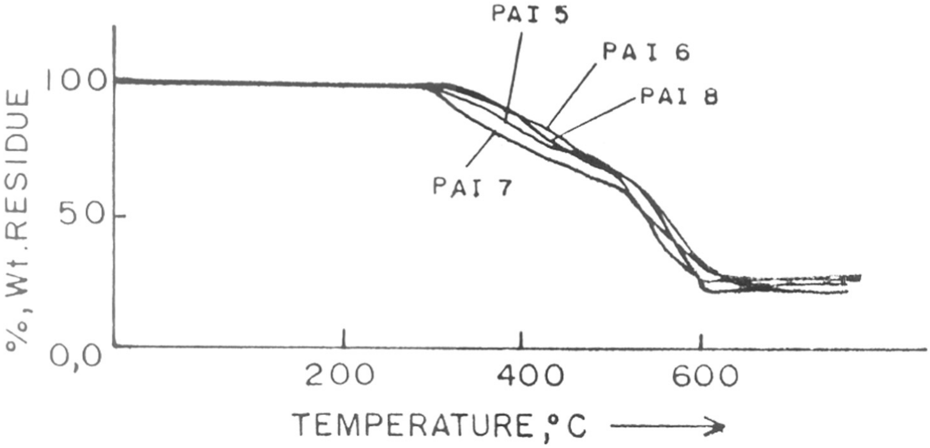


FIG. 26 (b). TGA CURVES OF POLY (AMIDE - IMIDE) S, PAI 5 - PAI 8.

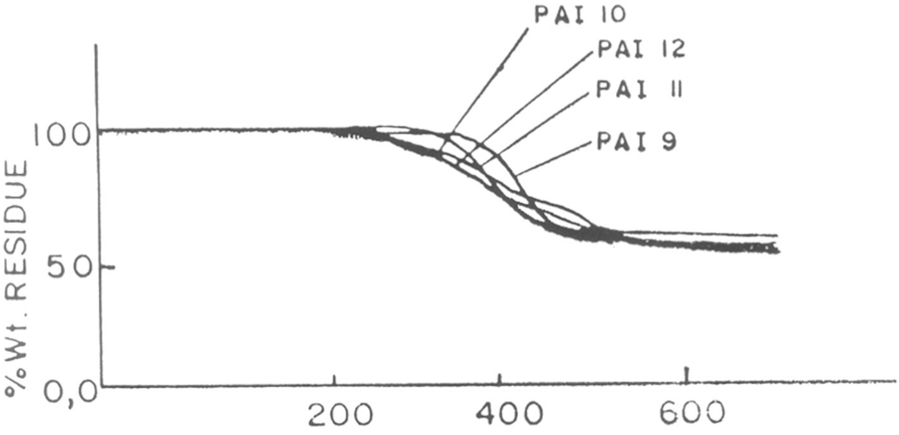


FIG. 26 (c) TGA CURVES OF POLY (AMIDE-IMIDE)S, PAI 9 - PAI 12.

TABLE 29

Thermal Characteristics of Poly(Amide-Imide)s

a. Based on Formal Group Containing Diisocyanates, **F 3 a - F 3 d.**

Polymer	IDT	T_{10}	T_{30}	T_{50}	T_{max}
PAI 1	352	423	495	517	551
PAI 2	365	432	513	541	567
PAI 3	299	357	440	509	532
PAI 4	291	366	462	535	560

b. Based on Ester Group Containig Diisocyanates, **E 3 a - E 3 d.**

PAI 5	281	361	447	529	559
PAI 6	306	380	477	553	582
PAI 7	277	314	400	510	549
PAI 8	293	379	447	538	568

c. Based on Imide Group Containing Diisocyanates, **I 4 a, I 4 d, I 4 e** and **I 4 h**

PAI 9	360	468	506	580	510
PAI 10	334	418	454	539	465
PAI 11	344	428	470	531	470
PAI 12	320	388	438	438	438

[a] . All temperatures in °C,

. Thermogravimetric analysis were carried out in air at a heating rate of 10°C/min.

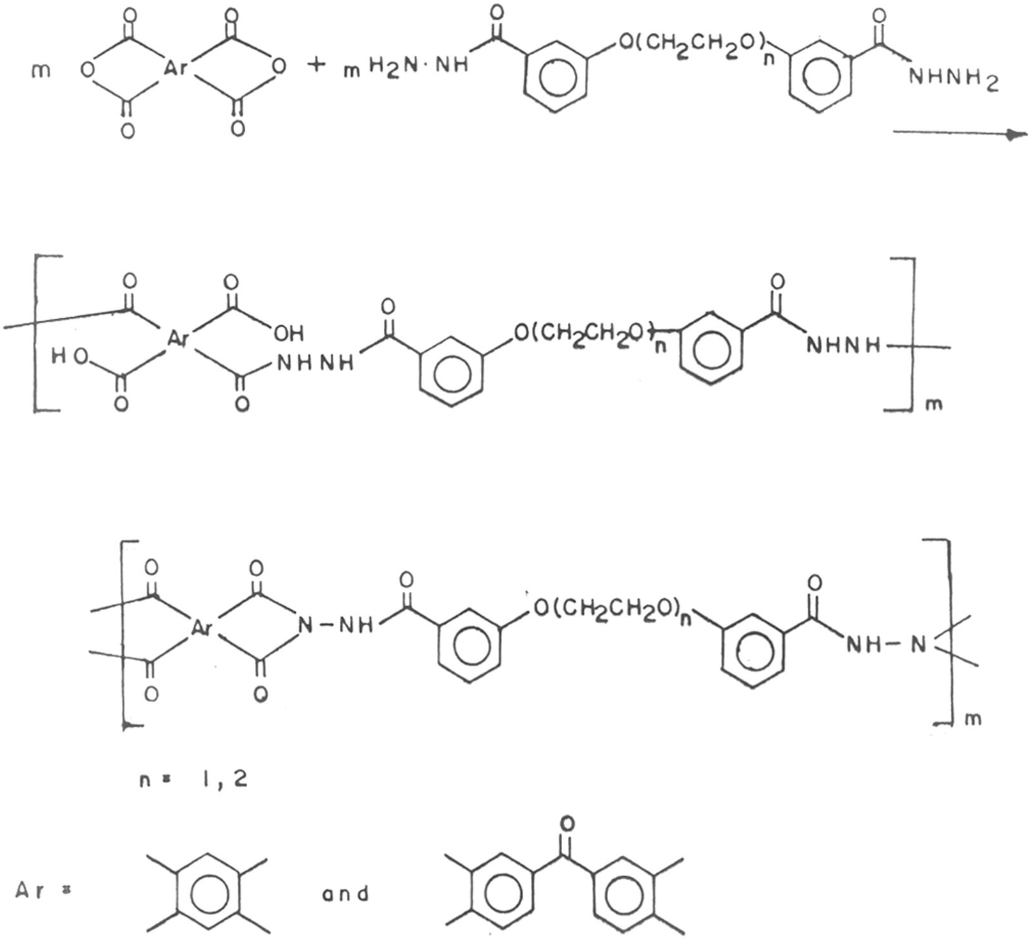
. IDT - Initial Decomposition Temperature, T_{10}, T_{30}, T_{50}, and T_{max} are temperatures at 10%, 30%, 50% and maximum rate of decomposition, respectively.

Preparation of Poly(amide-imide)s by the Diacylhydrazide - Tetracarboxylic Dianhydride Reaction.

The preparation of poly(amide-imide)s by the reaction of diacylhydrazide and dianhydride is a two stage process. The first stage is the low temperature ring opening polyaddition reaction of the dianhydride and the diacylhydrazide to form the poly(hydrazide-acid), **PHA**, while the second stage consists of the subsequent imidization of the poly(hydrazide-acid) to form the poly(amide-imide), as shown in Scheme 10 and Table 30. The ring opening polyaddition reaction of the dianhydride and the diacylhydrazide was conducted in a slow stream of dry nitrogen.

Diacylhydrazide, **4 b**, was soluble in DMAc. However, owing to its low solubility in DMAc, diacylhydrazide **4 a**, was dissolved in DMAc containing 5% LiCl. The diacylhydrazides in solutions were reacted with either PMDA or BTDA at 10°C to obtain respective poly(hydrazide-acid), **PHA A** - **PHA D**. The poly(hydrazide-acid) could be isolated by adding the solution into an excess of water. Alternately, tough, transparent films could be obtained by evaporation of solvent after casting.

The imidization of the poly(hydrazide-acid)s can be achieved chemically as well as thermally. In the present work both the methods were utilized. In the chemical cyclization, the DMAc solution of the poly(hydrazide-acid) was treated with acetic anhydride and pyridine when a yellow-coloured solution was obtained. Yellow flakes of the poly(amide-imide) were obtained by addition of methanol to the solution. In the thermal cyclization, the cast film of poly(hydrazide-acid) was heated in vacuum at



SCHEME 10: SYNTHESIS OF POLY (AMIDE-IMIDE)S, PAIA-PAID.

TABLE 30

Preparation of Poly(Amide-Imide)s Based on Oxyethylene Containing Diacylhydrazides, and their Inherent Viscosities.[1]

Polymer	Diacylhydrazide (0.01 mol)	Dianhydride (0.01 mol)	LiCl (g)	DMAc (mL)	Reaction condition		$[\eta]_{inh}$ (dL/g)
					°C	h	
PAI A	**4 a**	PMDA	0.5	10	10	2	0.85
PAI B	**4 a**	BTDA	0.5	10	10	2	0.81
PAI C	**4 b**	PMDA	---	10	10	1.5	0.84
PAI D	**4 b**	BTDA	---	10	10	1.5	0.65

[a] Measured at a concentration of 0.5 g/dL in DMAc at 30 ±0.01 °C Inherent viscosity was determined at the poly(hydrazide-acid) stage

$250^{o}C$ for 2 h to give a tough, pale yellow film.

The poly(hydrazide-acid)s were soluble in DMAc. But once the imidization occurred they were no more soluble in DMAc.

Infra Red Spectra

The IR spectra of poly(hydrazide-acid)s showed characteristic absorption bands at 3320 cm^{-1} (-NH- stretching), 1700 and 1660 cm^{-1} (for C=O of the acid and C=O of the amide, respectively), and 1230 cm^{-1} (C-O-C). The IR spectra of poly(amide-imide)s, on the other hand, showed charactistic absorptions at 1795 and 1745 cm^{-1} (imide-I), 1705 cm^{-1} (C=O of amide), 1380 cm^{-1} (imide-II), 1150 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). Representative IR spectrum of poly(hydrazide-acid) and poly(amide-imide) **(PAI C)** are shown in Figure 27.

Solubility

Poly(hydrazide-acid)s, **PHA A - PHA D**, were tested for solubility at a 3 % concentration in different solvents. These were found to be soluble in polar solvents like HMPA, NMP, DMAc and DMSO. The solubility of poly(amide-imide)s was tested at a 3 % concentration in different solvents. Poly(amide-imide)s were found to swell in NMP and HMPA and dissolved slightly on heating. Table 31 incorporates the solubility of poly(amide-imide)s in different solvents. However, in concentrated sulfuric acid, the poly(amide-imide)s dissolved with degradation.

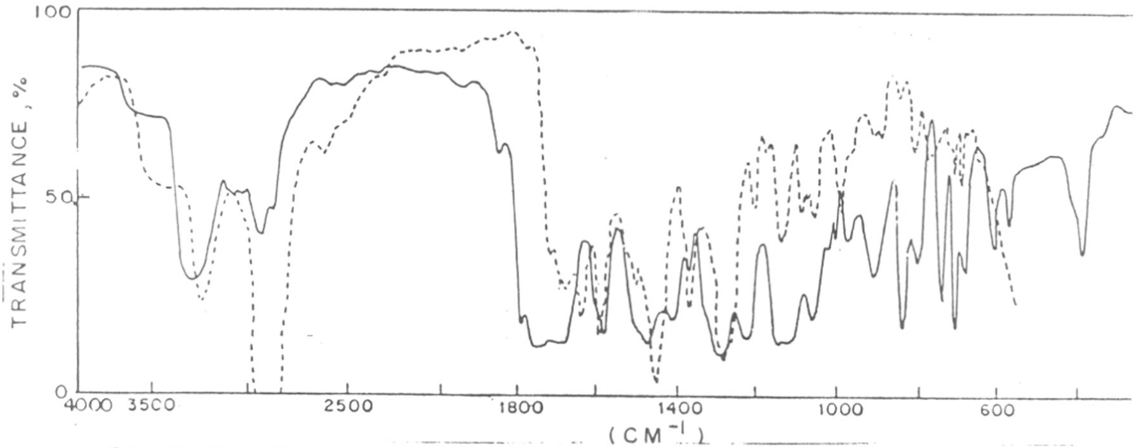


FIG. 27. IR SPECTRUM OF POLY (HYDRAZIDE-ACID) (-----) PHA AND POLY(AMIDE-IMIDE (——) PAI C.

TABLE 31

Solubility of Poly(Amide-Imide)s Based on Oxyethylene Containing Diacylhydrazide and Dianhydrides, **PAI A – PAI D.**

Polymer\Solvent	DMAc	DMAc + 5% LiCl	DMF	DMSO	m-Cresol	HMPA	NMP	H_2SO_4
PAI A	–	+	–	–	–	+	+	++
PAI B	–	+	–	–	–	+	+	++
PAI C	+	+	–	–	–	+	+	++
PAI D	+	+	+	+	–	+	+	++

(++) Soluble, (+) Slightly soluble on heating, (–) Insoluble

Viscosity Measurement

The inherent viscosities of the polymer were determined at the poly(hydrazide-acid) stage at $30 \pm 0.01^{\circ}$C using an Ubbelohde viscometer. The viscosities ranged from 0.60 - 0.85 dL/g indicating formation of high molecular weight poly(hydrazide-acid)s (Table 30). The poly(hydrazide-acid)s (**PAH A** and **PAH C**) derived from PMDA showed a slightly higher viscosity than **PAH B** and **PAH D**).

X-Ray Diffraction.

The nature of poly(amide-imide)s, whether amorphous or crystalline was determined by the powder method using nickel-filtered CuK$_{\alpha}$ radiations on a Phillips X-Ray unit (Phillips Generator, PW 1730). The diffractograms of poly(amide-imide)s, **PAI A** - **PAI D**, indicate that these polymers are amorphous in nature (Figure 28).

Thermal Characterization

To evaluate the effect of the diacylhydrazde structure on the thermal stability, thermogravimetric analysis was carried out on a Netzsch 409 Thermal Analyzer, by heating the polymer samples in air at a heating rate of 10°C/min. A weight loss of 3% up to 300°C may be attributed to the adsorbed moisture (Fig. 29). The initial decomposition temperature ranged from 320 - 360°C. The poly(amide-imide)s based on BTDA showed a higher thermal stability as compared to those derived from PMDA. Thermal characteristics, like initial decomposition temperature (IDT), T_{10}, T_{20}, T_{30}, and T_{50} corresponding to 10%, 20%, 30%,and 50% weight loss were calcu-

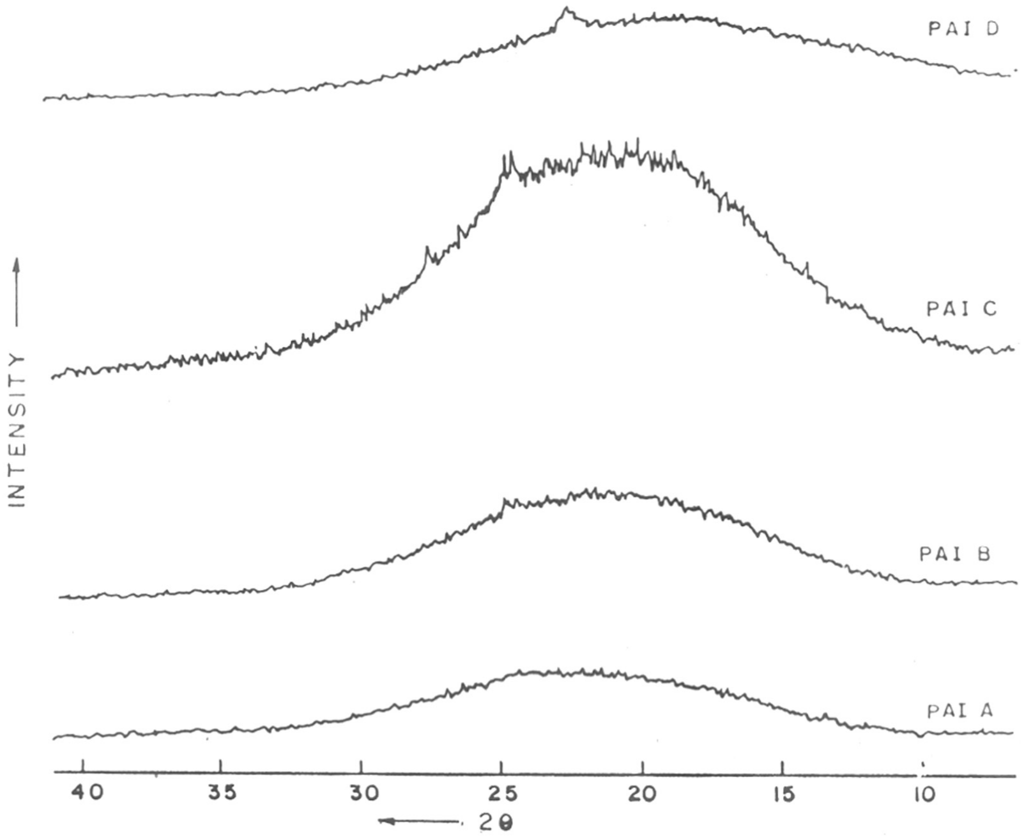


FIG.28. X-RAY DIFFRACTION PATTERNS OF POLY(AMIDE-IMIDE)S (PAI A – PAI D).

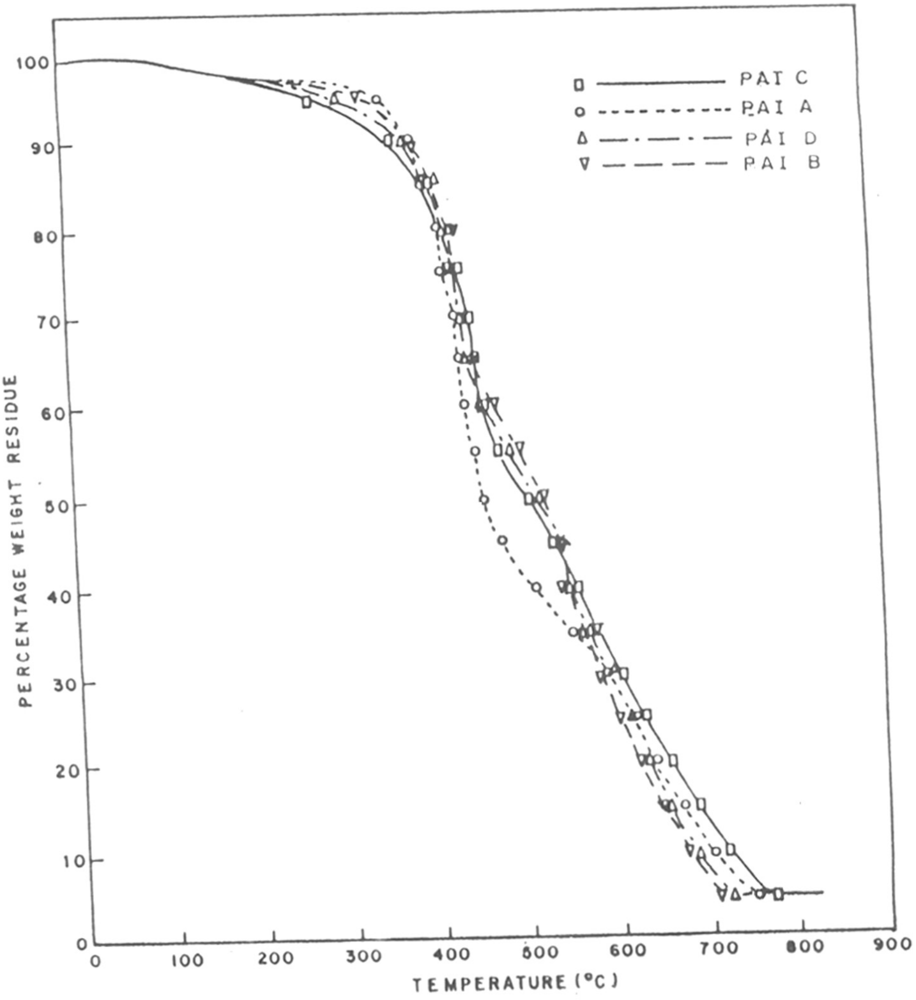


FIG.29.TGA CURVES OF POLY(AMIDE-IMIDE)S, PAI A-PAI D

lated from the original thermograms. These values are incorporated in Table 32.

TABLE 32

Thermal Characteristics of Poly(Amide-Imide)s Based on Oxyethylene Containing Diacylhydrazides[a]

Polymer	IDT	T_{10}	T_{20}	T_{30}	T_{50}
PAI A	340	365	395	415	445
PAI B	340	370	400	420	520
PAI C	320	335	380	405	480
PAI D	360	370	415	435	520

[a] All temperatures are in °C
Thermogravimetric analysis carried out in air at a heating rate of 10°C/min
IDT = Initial Decomposition Temperature
T_{10}, T_{20}, T_{30}, and T_{50} are temperatures at 10%, 20%, 30% and 50% rates of decomposition, respectively.

5.3.4 CONCLUSIONS

- Poly(amide-imide)s containing flexibilizing linkages have been prepared by the reaction of diisocyanates with trimellitic anhydride and by the reaction of diacylhydrazides with dianhydrides.
- Poly(amide-imide)s prepared by diisocyanate - anhydride acid route exhibited fairly good solubility.
- Poly(amide-imide)s exhibited reasonably good thermal stability.

5. 3.5. EXPERIMENTAL

Materials:

- Functional group containing diisocyanates, viz., formal (**F 3 a** - **F 3 d**), ester (**E 3 a** - **E 3 d**), and pre-formed imide (**I 4 a**, **I 4 d**, **I 4 e**, and **I 4 h**), were synthesized as per reaction Schemes 2 - 5 described in Chapter 2.

- Oxyethylene containing diacylhydrazides, viz., 1,2-bis(3-hydrazinocarbonylphenoxy)ethane (**4 a**) and bis[2-(3-hydrazino-carbonylphenoxy)ethyl] formal (**4 b**), were synthesized as per the reaction Scheme 5 described in Chapter 3.

- Trimellitic anhydride (TMA) was sublimed in vacuum by using a cold finger. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride and sublimed in vacuum using a cold finger prior to use.

- Dimethylacetamide (DMAc) was dried over P_2O_5 for 24 h and then distilled under reduced pressure.

- Other chemicals were of reagent grade and were used as received.

5.3.5.1. Preparation of Poly(Amide-Imide)s by the Diisocyanate - Anhydride Acid Reaction.

Preparation of Poly(Amide-Imide)s Based on Diisocyanates Containing Functional Groups, viz., Formal (F 3 a - F 3 d), Ester (E 3 a - E 3 d), and Pre-formed Imide (I 4 a, I 4 d, I 4 e, and I 4 h) and Trimellitic Anhydride.

In a 50 mL three-necked flask fitted with a thermowell, nitrogen gas inlet, a reflux condenser carrying a calcium chloride guard tube, was placed a solution of the respective diisocyanate (0.01 mol) in 10 ml DMAc and cooled to 0°C. TMA (0.01 mol) was added in small portions over a period of 45 min to the above solution with stirring. After the completion of addition, the reaction mixture was maintained at 0°C for 30 min, at 40°C for 30 min, and at 90°C for 30 min. Finally the temperature of the reaction mixture was raised to 130°C and held for 12 h. A slow stream of dry nitrogen was bubbled throughout the reaction.

The polymer was isolated by pouring the reaction mixture into large excess of methanol. The solid was filtered at pump and dried at 100°C for 3 h in vacuum.

5.3.5.2. Preparation of Poly(Amide-Imide)s by the Diacylhydrazide - Dianhydride Reaction.

Preparation of Poly(Amide-Imide)s Based Diacylhydrazides, viz., (1,2-Bis(3-hydrazinocarbonylphenoxy)ethane (4 a) and Bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether (4 b), and Dianhydrides (PMDA and BTDA). General Procedure.

I. Preparation of Poly(Hydrazide-Acid), PHA

In a 100 mL three-necked flask fitted with a thermowell, a nitrogen gas inlet, and a reflux condenser carrying a calcium chloride guard tube, was placed a mixture of the diacylhydrazide (0.01 mol) and 10 mL DMAc and then cooled to 10°C after dissolution. (In case of diacylhydrazide, **4 a**, which had poor solubility in DMAc, 0.5 g LiCl was added and the temperature raised to 90°C to effect complete dissolution.) To the clear solution maintained at 10°C, was added the respective dianhydride (either PMDA or BTDA) (0.01 mol) in small portions over a period of 1 h with constant stirring. The reaction mixture became viscous as the solid dissolved. It was kept in that condition for 2 h. A slow stream of dry nitrogen was bubbled throughout the reaction.

The reaction mixture contained the poly(hydrazide-acid), **PHA**, in DMAc solution. The inherent viscosity was determined at this stage at a temperature of 30+0.01°C. The viscosities ranged from 0.65 - 0.85 dL/g. The viscosity values of the four **PHA** are incorporated in Table 30.

The reaction mixture was divided into three portions. One portion was poured into large excess of water. The solid that precipitated out was filtered and dried in vacuum at room temperature, when white flakes of polymer were obtained.

II. Preparation of Poly(Amide-Imide)s, PAI, by Imidization Reaction.

Imidization was effected by two methods:

i. By Chemical Method.

To a portion of the solution of the poly(hydrazide-acid) solution in DMAc was added 2 mL of acetic anhydride and 2 mL of pyridine at room temperature and swirled for 5 min when the solution developed a yellow colour. Poly(amide-imide) formed in solution was isolated by precipitation by pouring this mixture into a large excess of methanol and filtered. It was further washed with methanol before drying in a vacuun oven for 3 h at 100°C.

ii. Thermal Cyclization.

The remaining part of the poly(hydrazide-acid) solution was poured onto a glass plate and the solvent was dried under vacuun. The tough, transparent film that was obtained was cyclized by heating in a vacuun oven at 250°C for 2 h.

Alternately, the poly(hydrazide-acid) flakes were heated at 250°C in a vacuum oven for 3 h.

5.4. COPOLYIMIDES

5.4.1 INTRODUCTION

Although polyimides have excellent high temperature resistance, they are extremely intractable, and insoluble in most organic solvents. The outstanding thermal, thermooxidative and chemical stability of polyimides are derived from the structural features of these polymers. A number of methods have been employed to overcome the problem of intractability while maintaining reasonably high temperature characteristics. These include incorporation of flexible, non symmetrical, and thermally stable linkages in the polymer backbone. Another method for improving the tractability of polymer is copolymerization technique.[131-133] Improvement of polymer processing characteristics has been achieved by the synthesis of copolymers of dianhydrides,[134] or different diamines.[135]

Copolymerization technique has been utilized to regulate molecular structure and properties of polyimides. The extent to which the properties could be modified depends upon the extent and type of structural unit incorporated.[136]

5.4.2 METHODS OF PREPARATION OF COPOLYIMIDES.

Copolyimides may be prepared by the condensation of

(i) a diamine with more than one dianhydride,

(ii) a dianhydride with more than one diamine,

(iii) a diisocyanate with more than one dianhydride, and

(iv) a dianhydride with more than one diisocyanate.

A Dutch patent[137] reveals the preparation of copolyimides by reacting 4,4´-diaminodiphenyl ether with a mixture of dianhydrides (PMDA and BTDA).

The preparation of copolyimides by the reaction of naphathalene dianhydride and another dianhydride with diaminodiphenyl ether, has been the disclosure of a British patent.[138]

Saluti et al[139] have prepared thermosetting copolyimides by the copolymerization of a mixture of tetralindianhydride, maleic anhydride and 4,4´-methylene dianiline.

Wollkommer et al[140] prepared chlorine containing copolyimides by the copolymerization of bis(4-aminophenyl ether), and tetrachloro-p-xylene diamine and PMDA.

By the copolymerization reaction of BTDA and 4,4-diamino-3,3-dimethyldiphenyl methane and 3,3´,4,4´-tetraaminodiphenyl methane, copolyimides have been prepared.[141] Farrissey et al[142] prepared copolyimide fibres and threads by the reaction of toluene diisocyanate (mixture of isomers) and MDI with BTDA.

Alberino and Farrissey[143] copolymerized various proportions of MDI, TDI and BTDA to prepare copolyimides that could be employed for the preparation of high temperature resistant materials.

Copolymerization improves the solubility and tractability of polyimides without much sacrifice in thermal characteristics. Thus copolymerization has become one of the important methods for the improvement of processability of polyimides.

5.4.3. SCOPE OF THE PRESENT WORK

Copolyimides have gained considerable importance because of their actual and potential applications in many fields. Copolyimides described in literature[132-134] have been synthesized by reacting a dianhydride with two diamines in different ratios or a diamine with two different dianhydrides. Both these routes invariably result in the formation of random copolyimides with little or no control over the sequence distribution. The properties of the copolyimides may be altered by controlling the sequence distribution. It is interesting to synthesize strictly alternating copolyimides and study their properties.

The reaction of a diisocyanate with a dianhydride yields a polyimide. A diisocyanate containing a preformed imide group provides a unique method for the synthesis of different strictly alternating copolyimides of two different dianhydrides.

Thus in the present work four homopolyimides and two strictly alternating copolyimides of BTDA and PMDA (separated by aliphatic spacers consisting of one methylene and five methylene groups) were synthesized by the reaction of diisocyanate (derived from either PMDA or BTDA) with PMDA or BTDA. The preformed imide group containing diisocyanates (**I 4 a** - **I 4 l**) were synthesized as described in Chapter 2. Diisocyanates containing preformed imide groups (**I 4 a, I 4 d, I 4 e,** and **I 4 h**) have been polycondensed with PMDA or BTDA to form homopolyimides and alternating copolyimides.

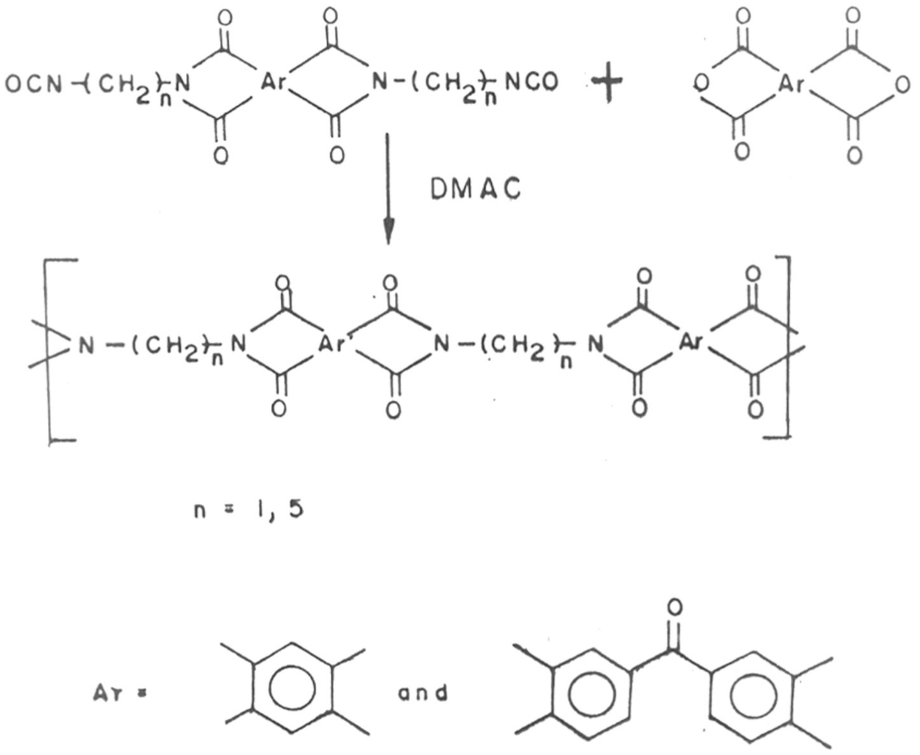
These homopolyimides and alternating copolyimides have been characterized by solubility tests, viscosity measurements, IR spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

5.4.4. RESULTS AND DISCUSSION

Copolyimides may be synthesized by the reaction of diisocyanates with dianhydrides (among other methods). The synthesis of homopolyimides and alternating copolyimides of PMDA and BTDA by the reaction of imide group containing diisocyanates with the same or different dianhydride may be achieved.

The facile synthesis of preformed imide group containing diisocyantes offers a unique method for the preparation of alternating copolyimides of two different dianhydrides, PMDA and BTDA, separated by aliphatic spacers. For example, a diisocyanate containing a preformed imide ring based on PMDA on reaction with BTDA gives a strictly alternating copolyimide of PMDA and BTDA. However, by the reaction of the diisocyanate based on PMDA with PMDA, a homopolyimide is formed.

The synthesis of homopolyimides and alternating copolyimides has been achieved as per Scheme 11, Table 33. Imide group containing aliphatic diisocyanates (based on either PMDA or BTDA) are taken in a polar solvent like DMAc and maintained at $0^{o}C$ when either PMDA or BTDA is added in small portions. The resulting polymer would be either homopolyimide and alternating copolyimide, with the benzene- or the benzophenone- moities being separated by aliphatic spacers. The length of the aliphatic spacer is determined by the aminoacid used for the diisocyanate synthesis. In the present work the diisocyanates based on glycine (spacer length $-(CH_2)-$ and 6-aminocaproic acid (spacer length $(CH_2)_5$ have been utilized for the synthesis of homopolyimides and alternating copolyimides. The structures of the resulting homopolyimides



SCHEME II: SYNTHESIS OF HOMOPOLYIMIDES AND ALTERNATING COPOLYIMIDES.

Table 33

Preparation of Homopolyimides and Alternating Copolyimides Containing Aliphatic Spacers and Their Inherent Viscosities.

Polyimides	Diisocyanates[1] (0.01 mol)	Dianhydrides[2] (0.01 mol)	Yield (%)	Inherent[3] viscositY [η], (dL/g)
PI A	I 4 a	PMDA	94	0.42
PI B	I 4 a OR I 4 e	BTDA OR PMDA	95	0.44
PI C	I 4 e	BTDA	96	0.29
PI D	I 4 d	PMDA	95	0.62
PI E	I 4 d OR I 4 h	BTDA OR PMDA	95	0.49
PI F	I 4 h	BTDA	96	0.36

---

[1] Diisocyanates were synthesized as per Scheme 4 (Chapter 2)

[2] PMDA = Pyromellitic dianhydride, BTDA = Benzophenonetetracarboxylic dianhydride

[3] Measured at a concentration of 0.5 g/dL in m-cresol at 30 ±0.01°C.

and alternating copolyimides are listed in Table 34. Equimolar amounts of pre-formed imide group containing diisocyanate were reacted with the same or different dianhydrides (different from the one used for the preparation of diisocyanate) in DMAc (as detailed in Experimental Section 5.4.4). The resulting polyimides were buff and pale yellow coloured powders.

Solubility

The solubility of homopolyimides and alternating copolyimides was determined at 3 % concentration. Unlike fully aromatic polyimides, these homopolyimides and alternating copolyimides showed comparatively better solubility in various solvents like DMF, DMSO, NMP, HMPA, m-cresol, etc., (Table 35). It was observed that the solubility increased with the increase in the length of the aliphatic spacer. Polyimides based on BTDA (**PI C** and **PI F**) showed better solubility than those derived from PMDA (**PI A** and **PI D**). Copolyimides, in general exhibited better solubility than homopolyimides.

Viscosity Measurements

Inherent viscosities of homopolyimides and alternating copolyimides (**PI A** – **PI F**) were determined in m-cresol using an Ubbelohde viscometer at a concentration of 0.5 g/100 mL at $30\pm0.01^{\circ}C$. The viscosity values varied from 0.25 – 0.68 dL/g (Table 33). The homopolyimide **PI A** showed a lower viscosity value (0. 42) than the copolyimide **PI B** (0.44). Homopolyimide **PI A** had a higher viscosity value as compared to homopolyimide

TABLE 34: STRUCTURES OF HOMOPOLYIMIDES (A,C,D and F) AND ALTERNATING COPOLYIMIDES (B and E)

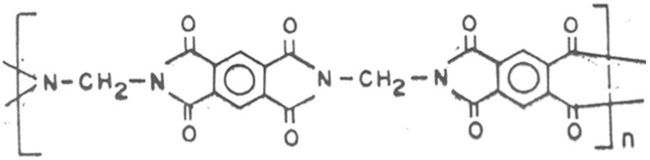
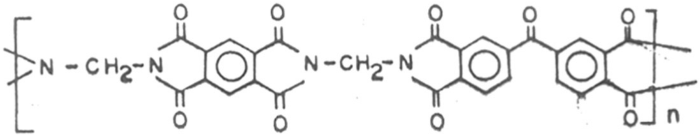
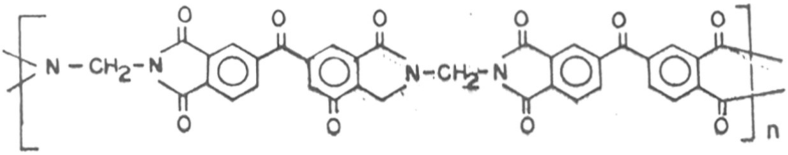
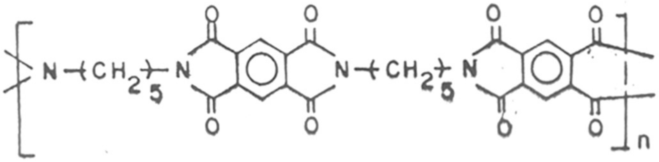
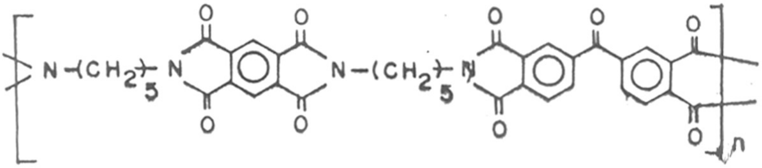
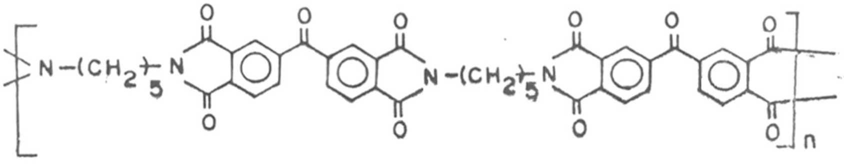
POLYIMIDES	REPEAT UNIT
A.	
B.	
C.	
D.	
E.	
F.	

TABLE 35

Solubility of Homopolyimides and Alternating Copolyimides Containing Aliphatic Spacers.

Polyimides	DMSO	DMF	DMAc	NMP	HMPA	m-cresol	H_2SO_4
PI A	–	–	+	–	–	+	++
PI B	+	+	+	+	+	+	++
PI C	+	+	+	+	+	+	++
PI D	+	+	+	+	+	+	++
PI E	+	+	+	+	+	+	++
PI F	+	+	+	+	+	+	++

++ Soluble; + Soluble on standing; – insoluble

PI C probably owing to the more rigid nature of the former. The homopolyimide **PIF** had the lowest inherent viscosity (0.36 dl/g). It contains a five methylene spacer and benzophenone moiety. The homopolyimide **PI D** had the highest viscosity (0.62 dL/g) probably due to the presence of rigid PMDA moiety. The alternating copolyimide **PI E** has a viscosity value of 0.49 dL/g and is intermediate between that of polyimide **PI D** (0.62) and **PI F** (0.36).

Infra Red spectra

The IR spectra of all the homopolyimides and alternating copolyimides showed characteristic absorption bands at 1780 cm^{-1} and 1745 cm^{-1} (imide-I), 1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). Illustrative IR spectrum of an alternating copolyimide (**PI E**) is shown in Fig. 30.

X-Ray Diffraction

The wide angle X-ray diffractograms (Fig. 31) of homopolyimides and alternating copolyimides (**PI A** - **PI F**) were taken by the powder method using nickel-filtered CUK α radiations on a Phillips PW 1730 unit. These indicate that the polyimides were semicrystalline in nature, except for polyimide **PI F**, which was amorphous. Polyimides derived from PMDA have higher crystallinity than those derived from BTDA. Crystallinity decreases with the increase in the length of the aliphatic spacer. Polyimide **PI A** was the most crystalline while polyimide **PI F** was amorphous. All other polyimides were intermediate in crystallinity.

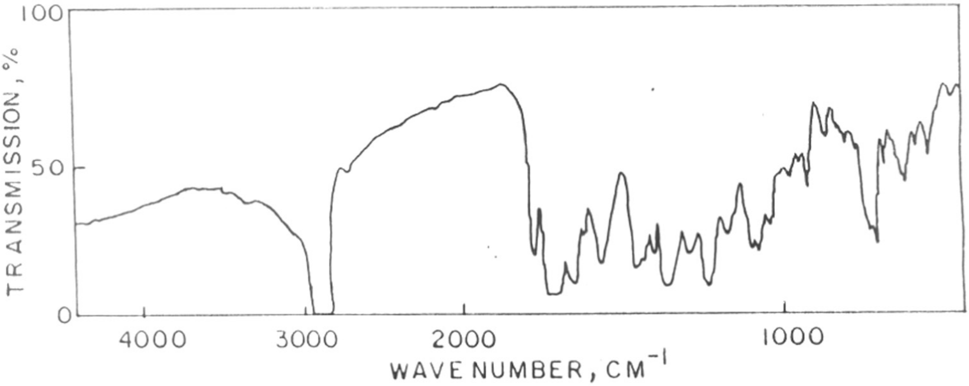


FIG. 30. IR(NUJOL MULL) SPECTRUM OF COPOLYIMIDE, PI E.

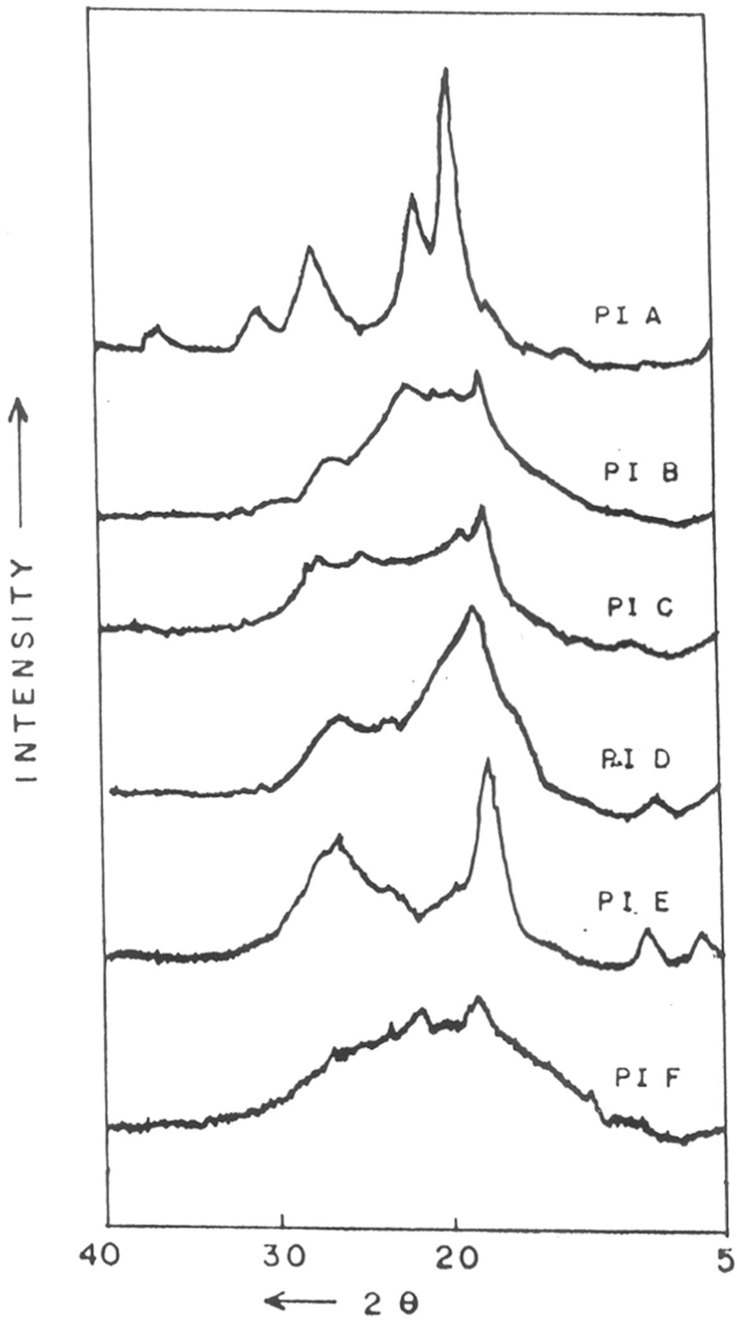


Fig.31. XRD CURVES OF POLYIMIDES, PI A - PI F.

Thermal Characterization

Thermogravimetric analysis (TGA) of polyimides was carried out on a Netzsch 409 Thermal Analyzer, in nitrogen at a heating rate of 10^{o}C/min. All the homopolyimides and alternating copolyimides showed similar patterns of decomposition without any weight loss below 335^{o}C. The TGA curves of representative polyimides are shown in Figure 32. The thermal characteristics, such as initial decomposition temperature (IDT), T_{10}, T_{30}, T_{50}, and T_{max} are temperatures at 10%, 30%, 50%, and maximum decomposition are given in Table 36. The temperature at maximum decomposition (T_{max}) was determined from the DTG curve. The IDT values for homopolyimides **PI A, PI C, PI D** and **PI F, PI a**, ranged from 335 - 371^{o}C. The IDT values for alternating copolyimides **PI B and PI E**, were 360 and 340^{o}, respectively. It is evident that the homopolyimides of PMDA (**PI A** and **PI D**) are more stable than the homopolyimides of BTDA (**PI C** and **PI F**). Also, the IDT of alternating copolyimides **PI B**, is intermediate between that of homopolyimide **PI A** and **PI C**, while that of copolyimide **PI E** is intermediate between that of homopolyimide **PI D** and **PI H**.

Differential Scanning Calorimetry

The glass transition temperature (Tg) of some of the homopolyimides and alternating copolyimides were determined on a Mettler DSC 30 S unit. The Tg values of some polyimides are incorporated in Table 36 and the thermograms shown in Fig 33. The Tg values ranged from 148 - 302^{o}C. It was observed that the Tg values were high for polyimide containing short aliphatic spacer.

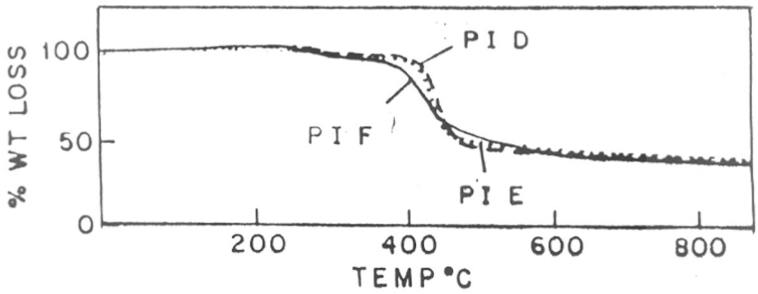


Fig. 32. TGA CURVES OF POLYIMIDES (PID, PIE, PIF) IN NITROGEN.

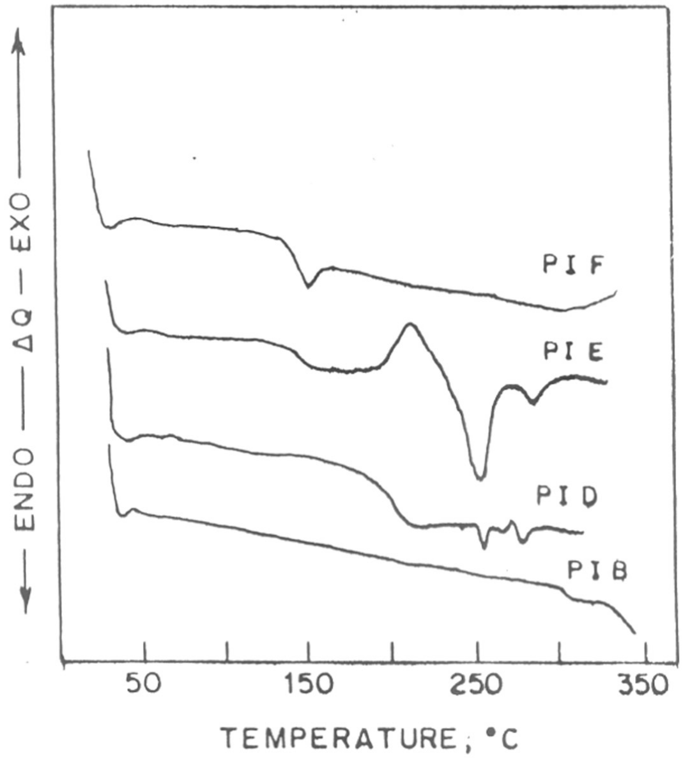


Fig. 33. DSC CURVES OF COPOLYIMIDES PI B, D, E AND F AT A HEATING RATE OF 20°C / min

Table 36

Thermal Characteristics of Homopolyimides and Alternating Copolyimides Containing Aliphatic Spacers.[a]

Polyimides ->	PI A	PI B	PI C	PI D	PI E	PI F
Tg	–	302	–	201	150	148
IDT	371	360	349	347	340	335
T_{10}	461	459	432	452	396	384
T_{30}	600	477	460	473	448	428
T_{50}		509	478	500	506	485
T_{Max}		490	473	483	460	423

[a] All temperatures in ^{o}C.
IDT - Initial decomposition temperature.
T_{10}, T_{30}, T_{50}, and T_{Max} are temperatures corresponding to 10 %, 30 %, 50 %, and maximum decomposition, respectively.

The polyimide derived from PMDA (**PI D**, Tg = 201^{o}C) exhibited higher Tg values than that derived from BTDA (**PI F**, Tg = 148^{o}C). The DSC curve of polyimide **PI E** showed probable existence of cold crystallization.

5.4.5 CONCLUSION

. Strictly alternating copolyimides of two different dianhydrides separated by aliphatic spacers were prepared by the reaction of imide group containing diisocyanate with a different dianhydride. This method may be extended to synthesize strictly alternating fully aromatic alternating copolyimides.

. These polyimides have good solubilities in polar solvents and have reasonably good thermal stability.

5.4.6. EXPERIMENTAL

Materials:

Diisocyanates containing pre-formed imide groups, viz.,

(i) N,N´-Bis(isocyanatomethyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimide (**I 4 a**),

(ii) N,N´-Bis(isocyanatomethyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´:4,4´-diimide (**I 4 e**),

(iii) N,N´-Bis(isocyanatopentyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-dimide (**I 4 f**), and

(iv) N,N´-Bis(isocyanatopentyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´:4,4´-diimide (**I 4 h**), were prepared as per the Scheme 4 (Chapter 2).

. The dianhydrides, pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA), were first recrystallized from acetic anhydride and then sublimed *in vacuo* prior to use.

. N,N-Dimethylacetamide was kept standing over P_2O_5 for 24 h before it was distilled under reduced pressure at the time of use.

. All other materials were of reagent grade and were used as received.

5.4.6.1 Preparation of Homopolyimides and Alternating Copolyimides

Homopolyimides and alternating copolyimides were prepared by the solution polycondensation of diisocyanates containing preformed imide groups with either PMDA or BTDA in dimethylacetamide, as per Scheme 11 and Table 33.

In a 100 mL three-necked flask equipped with a thermowell, a nitrogen gas inlet, a calcium chloride guard tube, was placed the solution of the respective diisocyanate (0.01 mol) in 10 mL DMAc. The solution was stirred with a magnetic bar at 0°C when the dianhydride (PMDA or BTDA) (0.01 mol) was added in small portions over 1 h. The reaction was maintained at this temperature for 30 min and then heated to 40°C, at which temperature it was held for 2.5 h. Then the temperature of the reaction mixture was gradually raised to 90°C and finally to 130-140°C and held for 24 h. A slow stream of dry nitrogen was bubbled throughout the reaction.

The reaction mixture was poured into a large excess of methanol to isolate the polyimide. The polymer that precipitated was filtered and washed with more methanol before drying *in vacuo* at 150°C for 3 h.

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SYNOPSIS

SYNOPSIS OF THE THESIS TO BE SUBMITTED TO THE UNIVERSITY OF POONA FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY.

Name of the Candidate: **Mr. C.V. Avadhani**

Name of the Research Guide: Dr. S.P. Vernekar

Title of the Thesis: Synthesis of Diisocyanates, Polyurethanes, and Thermally Stable Polymers.

Place where the work was carried out: Division of Polymer Chemistry,
National Chemical Laboratory,
Pune 411008.

Registration No. and date of registration: PGS / Ph.D / 16793, dt. 29-11-86 / 13-12-86

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Signature of Candidate

Dated: 28 Dec 90.

Signature of Guide

The thesis entitled "**Synthesis of Diisocyanates, Polyurethanes, and Thermally Stable Polymers,**" is divided into five chapters.

Chapter I

This chapter is an introduction to the diisocyanates - an interesting and fascinating class of monomers. Diisocyanates are unique in that they are highly reactive towards active hydrogen compounds. They find pervasive applications in agriculture, pharmaceuticals, and polymers.[1] This chapter includes methods of their preparation, reactions and applications in polymer chemistry.

Chapter II

Diisocyanates can serve as backbone for a variety of polymers other than the conventional polyurethanes and polyureas. They are used for the preparation of a host of thermally stable polymers. Diisocyanates can be prepared by a variety of routes of which phosgenation of diamines and the Curtius reaction of the diacylazides are important.

This chapter is subdivided into four sections dealing with the synthesis (<u>via</u> the Weinstock modification of Curtius reaction) and characterization of the following functional group containing diisocyanates, viz.,

1. Ether group containing diisocyanates:
   α,ω-Bis(isocyanatophenoxy)alkanes and
   Bis[2-(isocyanatophenoxy)ethyl] ether,
2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
4. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides.

In all 24 diisocyanates were synthesized of which 18 are new compounds. The diisocyanates and intermediates involved in their synthesis were characterized by analytical and spectral methods.

Chapter III

Diacylhydrazides are an important class of condensation monomers. They find applications in the synthesis of polyhydrazides and poly(amide-imide)s.

This chapter describes the synthesis of four oxyethylene containing diacylhydrazides, viz.,

1. 1,2-Bis(3-hydrazinocarbonylphenoxy)ethane,
2. 1,2-Bis(4-hydrazinocarbonylphenoxy)ethane,
3. Bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether and
4. Bis[2-(4-hydrazinocarbonylphenoxy)ethyl] ether.

The diacylhydrazides were synthesized from the corresponding esters by reacting them with excess of hydrazine hydrate. These were character ized by elemental analysis, IR, NMR and mass spectroscopy.

Chapter IV

Important among the industrial polymers are the polyurethanes. These find applications in coatings, adhesives, sealants, binders, fibres, elastomers, foams, etc. These are prepared by the reaction of polyfunctional diisocyanates with polyols.[2,3]

In this chapter ether, formal, ester and imide group containing diisocyantes, viz.,

1. Ether group containing diisocyanates:
   α,ω-Bis(isocyanatophenoxy)alkanes and
   Bis[2-(isocyanatophenoxy)ethyl] ether,
2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and

4. Imide group containing diisocyanates:

N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and

N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides,

were reacted with aliphatic diols/polyols to obtain polyurethanes. These polyurethanes were characterized by viscosity measurements, IR, XRD, and TGA.

Chapter V

Aerospace, aircraft, electrical and allied industries have given rise to the need for newer thermally stable polymers. Important among these are polyimides, polyamides and poly(amide-imide)s. These possess excellent thermal, mechanical and electrical properties. However, these are difficult to process, thus restricting their use considerably. The extent to which their properties can be modified depends on the type of structural units incorporated. Of the various approaches adapted to improve upon their processing characteristics, the incorporation of flexibilizing groups, incorporation of meta- linkages and bulky pendant groups along the polymer backbone are important.[4-7]

Consequently, in this chapter the synthesis and characterization of thermally stable polymers with flexibilizing groups in the polymer backbone is discussed. This chapter is subdivided into two subsections.

1. Polyimides:

This section deals with the synthesis and characterization of polyimides containing ether, formal, ester and aliphatic spacers in the polymer backbone.

The following types of diisocyantes, viz.,

1. Ether group containing diisocyanates:
   α,ω-Bis(isocyanatophenoxy)alkanes and
   Bis[2-(isocyanatophenoxy)ethyl] ether,
2. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
3. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
4. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides,

were polycondensed in dimethylacetamide (DMAC) with pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) to obtain polyimides. These were characterized by viscosity measurements, IR, XRD and TGA.

2. Poly(amide-imide)s:

Poly(amide-imide)s are generally prepared by the reaction of a diamine with an anhydride acid chloride, or by the reaction of a diisocyante with an anhydride acid. These can also be prepared by the reaction of a diacylhydrazide with a dianhydride.

(1) via Diacyl Hydrazides:

Two oxyethylene containing diacyl hydrazides, viz.,

1,2-Bis(3-hydrazinocarbonylphenoxy)ethane and
Bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether

were polycondensed in DMAc with PMDA and BTDA to yield poly(amide-imide)s which were characterized by IR, XRD and TGA.

(2) Formal, ester and imide group containing diisocyantes, viz.,

1. Formal group containing diisocyanates:
   Bis(isocyanatophenoxy)methanes and
   Bis[2-(isocyanatophenoxy)ethyl] formals,
2. Ester group containing diisocyanates:
   (Alkanedioyldioxy)diphenyl isocyanates, and
3. Imide group containing diisocyanates:
   N,N´-Bis(isocyanatoalkyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides and
   N,N´-Bis(isocyanatoalkyl)-3,3´,4,4´-benzophenonetetracarboxylic-3,3´4,4´-diimides

were polycondensed in DMAc with trimellitic anhydride (TMA) to yield poly(amide-imide)s. These were characterized by viscosity measurements, IR, XRD and TGA.

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LIST OF PUBLICATIONS

PUBLICATIONS

The following papers are based on the work incorporated in the thesis:

1. Synthesis and characterization of oxyethylene containing diisocyanates and polyimides therefrom
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar,
   J. Polym. Sci. A-1, **28**, 1681 (1990)

2. Synthesis and characterization of oxyethylene containing polyamide-imides
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar,
   J. Appl. Polym. Sci., **40**, 1325 (1990)

3. Synthesis and characterization of imide containing diisocyanates and poly(imide-urethane)s therefrom
   C.V. Avadhani, P.P. Wadgaonkar, R.S. Khisti, V.G. Gunjikar, and S.P. Vernekar, Polym. Bull. **23**, 163 (1990)

4. Synthesis and characterization of alternating copolyimides containing aliphatic spacers
   C.V. Avadhani and S.P. Vernekar, Polym. Bull. **24**(5), 481 (1990)

5. Synthesis and characterization of poly(amide-imide)s based on formal, ester, and imide group containing diisocyanates
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar, in "Polymer Science: Contemporary Themes", Tata McGraw-Hill Publishing Company, New Delhi, p. 21, 1990, Ed. S. Sivaram.

6. Synthesis and characterization of formal group containing diisocyanates and polyimides therefrom
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar.
   (Communicated to J. Appl. Polym. Sci.)

7. Synthesis and characterization of ester group containing diisocyanates and polyimides therefrom
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar.
   (Manuscript under preparation.)

8. Synthesis and characterization of polyurethanes based on ether, formal and ester group containing diisocyanates
   C.V. Avadhani, P.P. Wadgaonkar, and S.P. Vernekar.
   (Manuscript under preparation.)