

THERMAL AND OXIDATIVE DEGRADATION OF AN
AROMATIC POLYAMIDE.

by

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Submitted in accordance with the requirement for the degree of Doctor of Philosophy under the supervision of Professor J.E. McIntyre and Dr. S.A. Sills.

The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to work of others.

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ABSTRACT.

The thermal oxidation of an aromatic polyamide fibre, namely poly(m-xylylene adipamide) has been investigated. The volatile and non-volatile products of oxidation identified using T.L.C., H.P.L.C. and G.C.-M.S. include homologous series of monocarboxylic acids, dicarboxylic acids, n-alkyl amines, diamines and aldehydes. Furthermore, several aromatics, ketones and amides were also identified. Mechanisms for their derivation have been proposed which are based on oxidation reactions already established in polymer chemistry. These include a mechanism of β scission by an alkoxy radical thought to be responsible for the creation of the homologous series.

MXD,6 fibres were also spun incorporating 100, 200 and 400ppm of a cobalt catalyst and the effect of the metal ions on the oxygen uptake of the fibres was investigated. The results show a consistent increase in the rate of oxygen uptake as the concentration of the cobalt is increased. Furthermore, T.G.A. oxidative degradation studies, conducted at isothermal temperatures in the solid state, show decreases in the activation energies associated with fibre oxidation with increased cobalt concentrations, implying the cobalt is a catalyst for oxidation.

A mechanism for the behaviour of the catalyst in the fibre has been proposed and it is thought the cobalt works predominantly as a catalyst for the initiation of radicals whilst in the melt stage of polymer spinning, then to a lesser extent as a catalyst for radical propagation whilst in the solid phase.

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LIST OF ABBREVIATIONS AND SYMBOLS.

A.E.G.	Amine End Group Concentration.
C.E.G.	Carboxyl End Group Concentration.
D.P.M.S.	Direct Pyrolysis Mass Spectroscopy.
D.S.C.	Differential Scanning Calorimetry.
E _a	Activation Energy.
F.I.M.S.	Field Ionization Mass Spectroscopy.
G.C.-M.S.	Gas Chromatography - Mass Spectroscopy.
H.P.L.C.	High Performance Liquid Chromatography.
I.R.	Infrared.
I.V.	Intrinsic Viscosity.
K _h	Huggins Constant.
K _k	Kraemer Constant.
k	Rate Constant.
MXD	m-Xylylene diamine.
MXD,6	Poly(m-xylylene adipamide).
R _f	Relative Front Value.
R _v	Retention Volume Value.
P.E.T.	Poly(ethylene terephthalate).
P _n	Degree of Polymerization.
ppms	Parts Per Million.
PXD,6	Poly(p-xylylene adipamide).
R	Gas Constant.
T _c	Crystallization temperature.
T.C.D.	Thermal Conducting Detector.
t _g	Gel Formation Time.
T _g	Glass transition temperature.
T.G.A.	Thermogravimetric Analysis.
T.H.F.	Tetrahydrofuran.
T.L.C.	Thin Layer Chromatography.
T _m	Melting temperature.
U.V.	Ultra Violet.
Δ	Thermal Energy.
hν	Photon of Light
[η]	Intrinsic Viscosity
η _{rel}	Relative Viscosity
η _{sp}	Specific Viscosity

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*"If I have seen further it is by standing on the
shoulders of Giants."*

Isaac Newton (1642-1727).

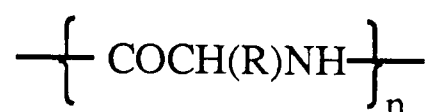
This dissertation is dedicated to Snai.

My guide and inspiration.

CHAPTER ONE :- INTRODUCTION.

1.1 HISTORY OF POLYAMIDES.

Hetero-chain polymers, such as polyamides, are widely represented in nature. A macromolecule of such polyamides is built up of individual units containing the characteristic amide group and the hydrocarbon residue with various substituents :-



They are various proteins and numerous other organic compounds of biological importance which are found among the constituents of the animal and plant kingdoms.

Synthetic polyamides however were only recognised in the late nineteenth century. The first synthetic polyamide was obtained by Harbort in 1862 [1]. Working with m-aminobenzoic acid he was able to isolate a grey powder when subjecting the acid to the action of hydrogen chloride at 200°C. This product was found to be virtually insoluble in all organic solvents, but would readily dissolve in concentrated sulphuric acid, from which it would reprecipitate on addition of water. This was poly(m-benzamide), the first representative of the synthetic polyamides.

During the following fifty years, a number of polyamides were identified and reported. Michler and Zimmermann [2] in 1881 were able to obtain poly(m-phenyleneurea) from a solution of m-phenylenediamine in chloroform with phosgene and later Lüdy [3] synthesized polyamides known as the carbamide or urea-formaldehyde resins by the polycondensation of urea with formaldehyde. These later products soon became of considerable practical importance, in that the carbamide resins were the first industrially important polyamides produced. The same year saw the introduction of poly-ε-caproamide to the polymer world. In 1899, Gabriel and Mass [4] obtained this polymer more commonly referred to as poly(caprolactam), from the polycondensation of ε-aminocaproic acid. They also made the very important

observation that heating of this acid resulted in the formation of a low molecular cyclic product known as ϵ -caprolactam.

However, the major developments of polyamides were largely due to the work of W.H. Carothers and his colleagues at E.I. DuPont de Nemours & Co. (Inc.) [5]. Carothers synthesized many polyamides including probably the most popular polyamide today, poly(hexamethylene adipamide), commonly referred to as nylon 6,6, from the polycondensation of hexamethylene diamine with adipic acid. This classic piece of research led to the commercial production of this polymer for the subsequent conversion into the first synthetic fibres.

In an attempt to circumvent the DuPont patents, German scientists at I.G. Farben investigated a wide range of synthetic fibre forming polymers. Success finally came in 1938 when Schlack [6][7] capitalized on the earlier discovery of ϵ -caprolactam by actually polymerizing this by-product formed from an earlier polymerization to form a high molecular weight fibre forming polymer designated "Perlon" and more commonly referred to as nylon 6.

Both these companies continued to prepare many more polyamides from various diamines and dicarboxylic acids which in turn encouraged polyamide development in other countries also. In the Soviet Union also nylon 7 (Enanth) and nylon 9 (Pelargone) were investigated. Others included nylon 11, nylon 12 and nylon 6,12, however these polymers do not match up to the total annual productions of nylon 6 and nylon 6,6, which account for nearly all of the polyamides produced for fibre applications today. Consumption of nylon plastics in the Western World was estimated at about 650,000 tonnes per annum in the late 1980s, which was about 15-20% of the total production of nylon materials. Virtually all of the rest went into fibres, where the market was shared roughly equally by nylons 6 and 6,6.

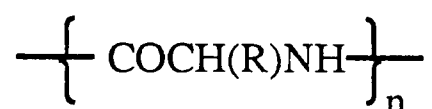
In the meantime, aromatic polyamides were slow in their development. While during the early 1960s the aliphatic polyamide development was thriving, only a few aromatic polyamides were commercially available. However, a small number of aromatic-aromatic, aromatic-aliphatic and aliphatic-aromatic polyamides were reported in the early literature [8]. Korshak and Frunze reported a number of aromatic polyamides in the late 1960s [9]. Manecke and Gauger were also interested in this field of polyamides and synthesized many poly(1,3-squaramides) from 1,2-dihydroxycyclobutane-3,4-dione (squaric acid) with diamines. Polyalkene(1,3-phthalamides), such as nylon 4,I [10] and nylon 6,I [11] were also produced by either melt or low temperature polycondensation techniques as interesting engineering plastics. Polyalkene(1,4-phthalamides) such as nylon 4,T have been synthesized not only via low temperature interfacial or solution methods, but also by a two-step process i.e. prepolymerization followed by post-condensation in the solid state. Gaymans [12] prepared prepolymer by the nylon salt method, ester polymerization method as well as low temperature interfacial and solution methods and compared their post condensation products.

However, it was only during the 1970s and 1980s that several other aromatics of more regular structure became important as fibres because of their exceptional physical and mechanical properties.

1.2 TERMINOLOGY AND NOMENCLATURE.

POLYAMIDES are polymers that contain recurring amide groups, $-\text{NHCO}-$, as integral parts of the main polymer chains [13].

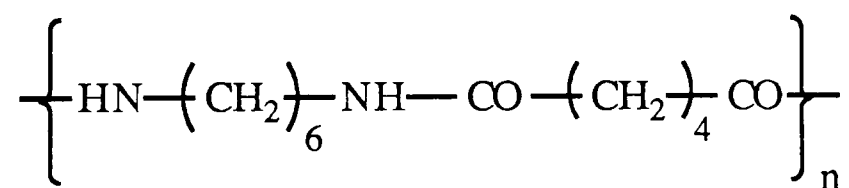
Proteins are biopolymer polyamides and are polymers of α -amino acids with repeating units of general structure :-



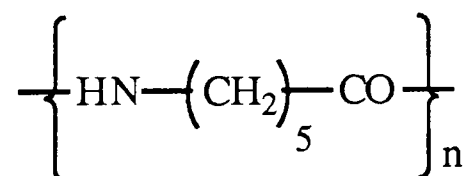
where R is any of about 30 different substituents. Proteins are copolymers and usually contain about 20 different amino acid units in each molecule.

However, the synthetic polyamides of greatest technological importance are the NYLONS. Nylons, according to the International Organization for Standardization [14], are members of the family of polyamides which are defined as "*synthetic linear macromolecule having in the chain recurring amide linkages, at least 85% of which are joined to aliphatic or cycloaliphatic groups.*".

e.g. Poly(hexamethylene adipamide) :-



Poly(caproamide) :-



Thus wholly aromatic polyamides are not referred to as nylons, although aliphatic–aromatic polyamides such as poly(m–xylylene adipamide) and poly(hexamethylene terephthalamide) are.

A nylon may be named either on the basis of the monomer(s) from which it has been derived or as a polyamide e.g. for nylon 6 either polycaprolactam or poly(caproamide) may be employed. For diadic nylons however the latter method is more commonly used e.g. for nylon 6,6, poly(hexamethylene adipamide), which is also indexed in 'Chemical Abstracts' as

Poly(imino{1,6-dioxo-1,6-hexanediyl}imino-1,6-hexanediyl) [15],

the former being used more commonly for convenience.

Frequently used are the abbreviated forms of polyamide names, of the types nylon 'z', (nylon 6) or nylon 'x,y', (nylon 6,6) for the monadic and diadic types respectively. The values of the numbers 'x' and 'y' are the numbers of carbon atoms in the monomer(s) from which the polymer was derived, 'x' referring to the diamine carbons and 'y' the diacid carbons. For monadic type polyamides the number 'z' refers to the number of carbon atoms on the amino acid backbone unit e.g. nylon 11 is derived from the eleven carbon amino–undecanoic acid.

For nylons derived from other common monomers, especially aromatic ones, appropriate abbreviations are sometimes used instead of the full name :-

'T' for terephthalic acid as in nylon 6,T {poly(hexamethylene terephthalamide)}

'I' for isophthalic acid as in nylon 10,I {poly(decamethylene isophthalamide)}

'MXD' for m–xylylene diamine as in nylon MXD,6 {poly(m–xylylene adipamide)}

1.3 PREPARATIVE METHODS FOR POLYAMIDES.

Polyamides can be synthesized by many methods, which have been adapted from the preparation of N-substituted carboxylic acid amides [16].

However, only three routes have gained commercial significance :-

- (1) Melt Polycondensation,
- (2) Ring Opening Polymerization,
- (3) Low Temperature Polycondensation.

The two principal pillars of polyamide synthesis, melt polycondensation and ring opening polymerization were joined in 1957 by a third, low temperature (interfacial and solution) polycondensation. This ingenious technique presented by Morgan [17], DuPont, made it possible to circumvent the difficulties of melt polycondensation in preparing high melting or heat sensitive polyamides.

1.3.1 Melt Polycondensation.

The technique of melt polycondensation is probably the most commonly applied method in polymerization. Being a simple procedure, it may be carried out using basic apparatus common to most chemistry laboratories. It is because of the ease by which polymer could be synthesized that Carothers [5] first employed this method for the synthesis of the first polyamides.

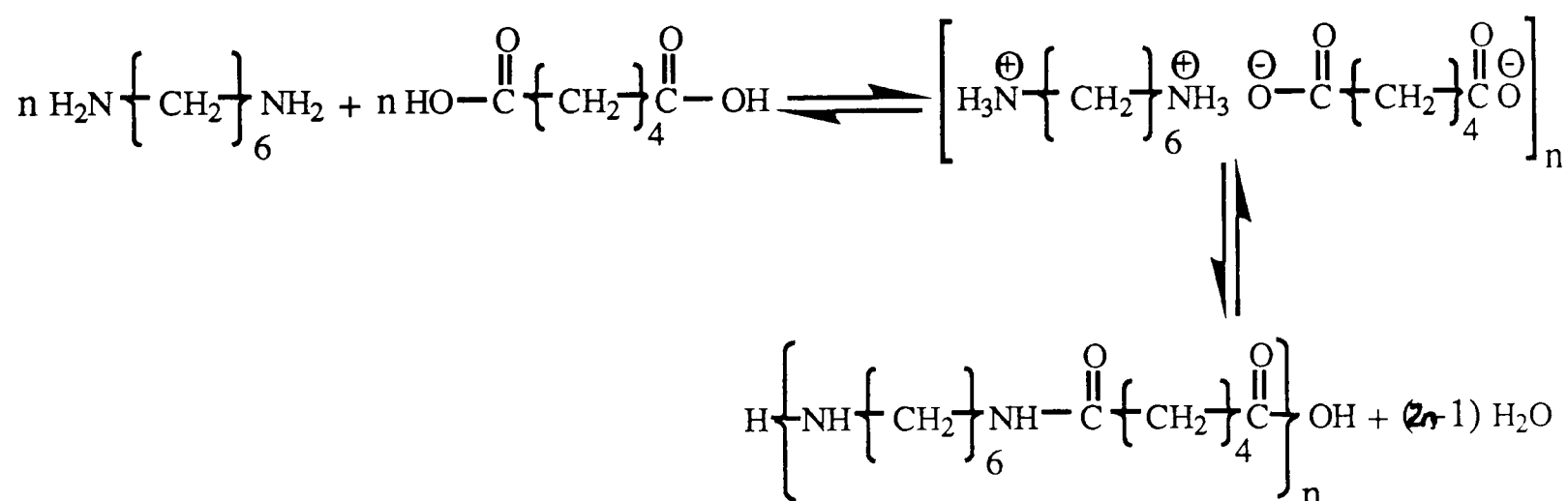
Carothers used 'Direct Amidation,' (Scheme 1.1) a synthetic route conducted by melt polycondensation, to prepare a whole range of novel polyamides including the world renowned nylon 6,6. In many of his patents on behalf of E.I. DuPont de Nemours & Co. (Inc.), Carothers disclosed fibre-forming polyamide made by reacting diamines with dibasic acids via direct condensation. As an advantageous way of making

these polyamides, he also included among the methods described the formation of the diamine-dibasic acid salt as an intermediate step between the reaction of the initial ingredients and the production there from of the desired polyamide [5].

For nylon 6,6, Carothers's first patent employed a mixture of 144 parts hexamethylene diamine, 174 parts adipic acid, 1300 parts 95% ethyl alcohol and 210 parts water which was heated until a complete solution resulted. The mixture was cooled and the precipitated hexamethylene diammonium adipate (nylon salt) filtered and recrystallized from alcohol.

Subsequently, the salt was used to charge a polymerization vessel, often an autoclave and melt polymerized under an inert atmosphere for up to 10 hours at a temperature ranging between 250-290°C.

Scheme 1.1:- Preparation of Nylon 6,6 via Direct Amidation.

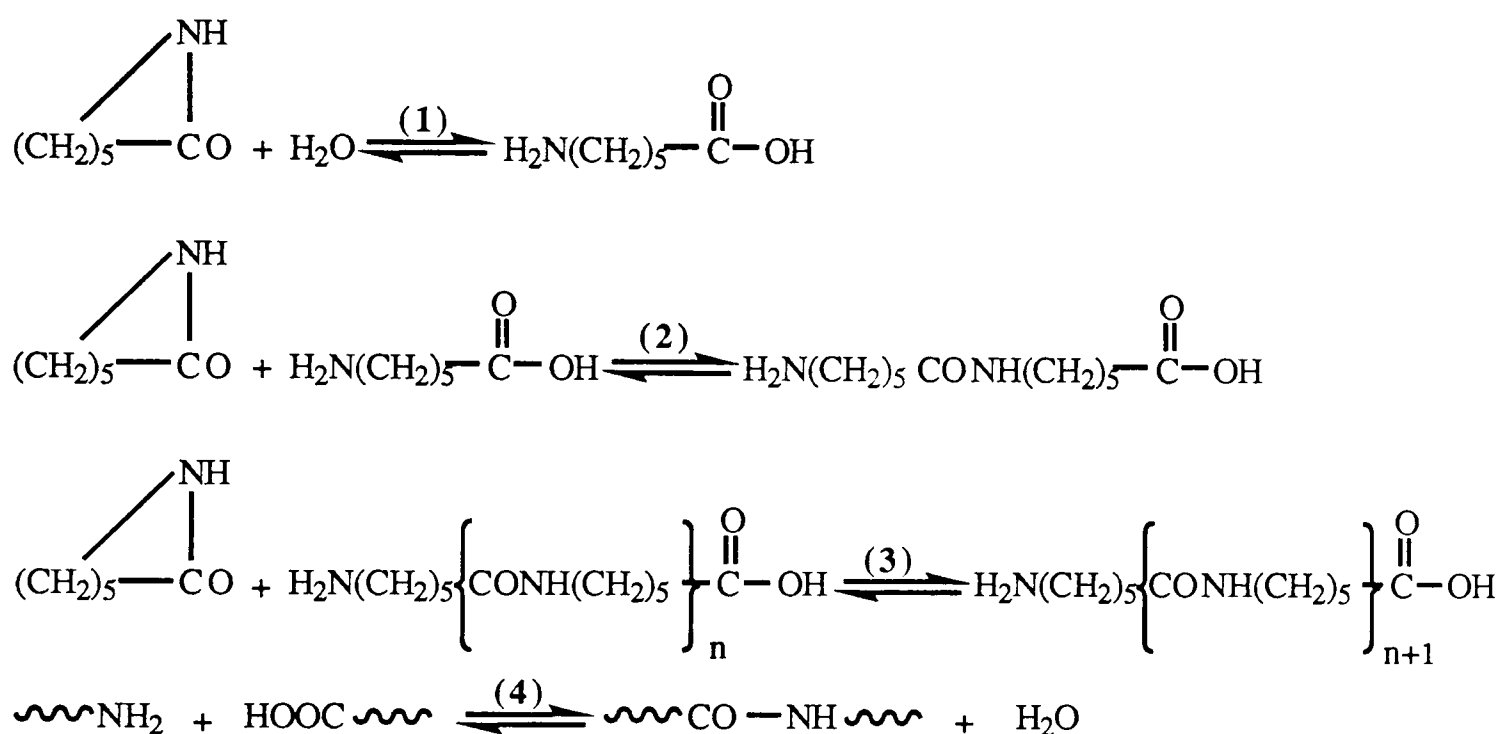


1.3.2 Ring Opening Polymerization.

Of the many polyamides prepared from ring opening polymerization techniques, nylon 6 is by far the most popular. Developed in Germany by Schlack [6][7] at I.G. Farben, it is now well known that the synthesis of nylon 6 for fibres from ε-caprolactam proceeds mainly via an initial stage of lactam hydrolysis, followed by the direct addition of cyclic caprolactam entities to the amino group of the aminocaproic acid

initially formed and then to the amino group of the growing polyamide chain. (Scheme 1.2) On formation, the resultant polyamide takes part in the normal polyamidation equilibrium which is greatly influenced by the presence of water, amino acids, or amine carboxylates (nylon 6,6 salt), which behave as initiators to the initial ring opening. Caprolactam is normally polymerized this way using water as the initiator. In comparison, pure dry caprolactam with no initiator, will not form nylon 6, even when heated at temperatures up to 270°C for periods in excess of 200 hours [18].

Scheme 1.2 :- Polymerization Mechanism for Nylon 6.



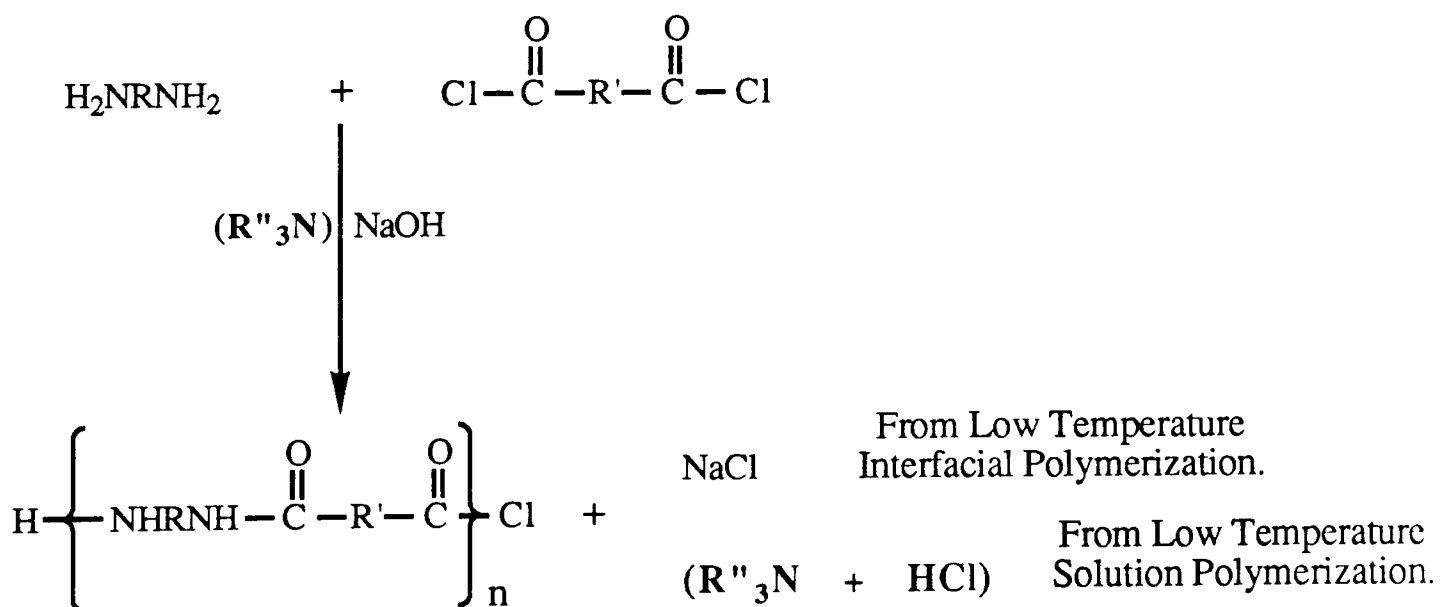
However, at temperatures between 230-270°C, the reaction also involves, but to a less extent, the self-condensation of the aminocaproic acid hydrolysate. Reaction (3) is recognized to be the predominant mechanism, but reactions (1) and (4) are considered to be more important as far as the over-all rate of polymerization is concerned. The final degree of polymerization is determined by the polyamide equilibrium (4) and the rate of attainment of the equilibrium is promoted by the generation of the carboxyl groups of reaction (1). Water in the system has two competing roles in this reaction and therefore the optimum water concentration varies during the course of the technical manufacture of nylon 6 by the hydrolytic polymerization of caprolactam [6].

1.3.3 Low Temperature Polycondensation.

Frequently employed for the synthesis of wholly aromatic "aramids", is the low temperature polycondensation of diamines with diacid chlorides. High melting point polyamides such as poly(m-phenylene isophthalamide), marketed as Nomex and poly(p-phenylene terephthalamide), recognised as Kevlar, are produced by such routes, as they normally decompose if prepared at high temperatures in the melt [17].

Of the low temperature polycondensation techniques, two methods have been significantly studied - low temperature interfacial polymerization and low temperature solution polymerization. In low temperature interfacial polymerization the diacid chloride is added in a water-immiscible solvent, to an aqueous solution of diamine, surface active agent and inorganic base. The latter reacts with the hydrogen chloride produced when the acid chlorides are the acylating species. Polymerization takes place in the organic layer of the interface, hence the name. Temperatures are held between 0-10°C, as at higher temperatures the acid chloride ends are readily hydrolysed, which consequently results in a lower molecular weight polymer. In low temperature solution polymerization only one solvent is present which is inert to both monomers. Generally, an organic base is also employed as an acid acceptor (Scheme 1.3).

Scheme 1.3 :- Low Temperature Polycondensation Routes.



In both the interfacial and solution methods high molecular weight polymers are achieved rapidly at low temperatures.

1.4 AROMATIC POLYAMIDES.

Until the early 1960s, the aromatic and cycloaliphatic polyamides were largely laboratory curiosities. By 1980 they were still only of minor importance with respect to the polymer industry, but of rapid expanding interest as fibre forming materials.

The main problem with aromatic polyamides was that they could not be prepared as easily as the conventional aliphatic polyamides. The slow development of these materials was generally ascribed to the slow amidation reactions, the inability of many of the polymers to melt without decomposition and the tendency to colour during polymerization [19].

In recent years however, the commercial importance of aromatic polyamides has grown considerably. With the aid of more sophisticated techniques and novel monomers, polyamides with exceptional properties have been developed.

These aromatic polyamides may be classified into three groups : –

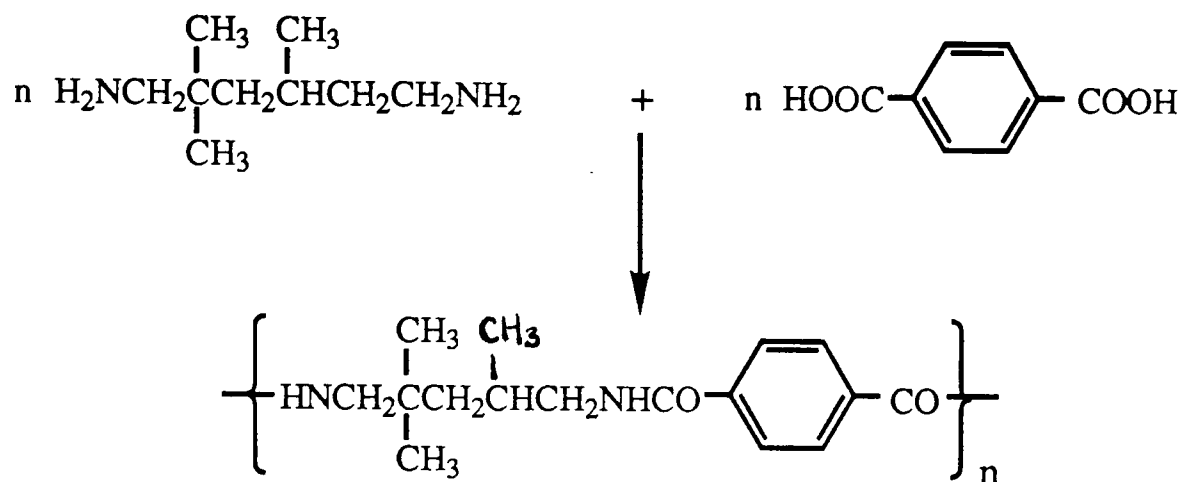
- (1) Amorphous glass-clear polyamides,
- (2) Crystalline wholly aromatic polyamides,
- (3) Crystalline aliphatic-aromatic polyamides.

1.4.1 Amorphous Glass-Clear Aromatic Polyamides.

These are the oldest of the aromatic polyamides and include the first commercially available aromatic polyamide, poly(trimethylhexamethylene terephthalamide), marketed by Dyamit Nobel in the mid 1960s as Trogamid T [20] (Scheme 1.4). It was Doffin, Pungs and Gabler who first synthesized this polyamide and found its remarkable physical and chemical properties. Later, Dietze [21] utilized the transparent nature of the polymer

by developing glass windshields for motor vehicles, which were coated with Trogamid T, rendering the glass scratch resistant.

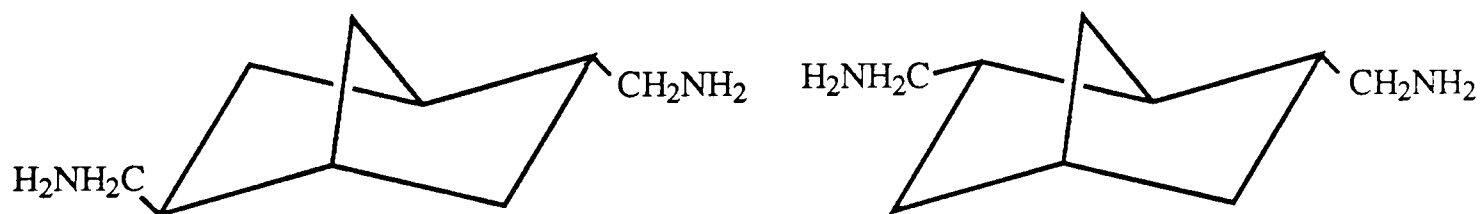
Scheme 1.4 :- Trogamid T.



However, it was Doffin et al who patented Trogamid T as a condensation product of trimethylhexamethylene diamine and terephthalic acid (or its dimethyl ester) and in practice, a 1:1 mixture of 2,2,4- and 2,4,4 trimethyl diamines was used; the former is shown above.

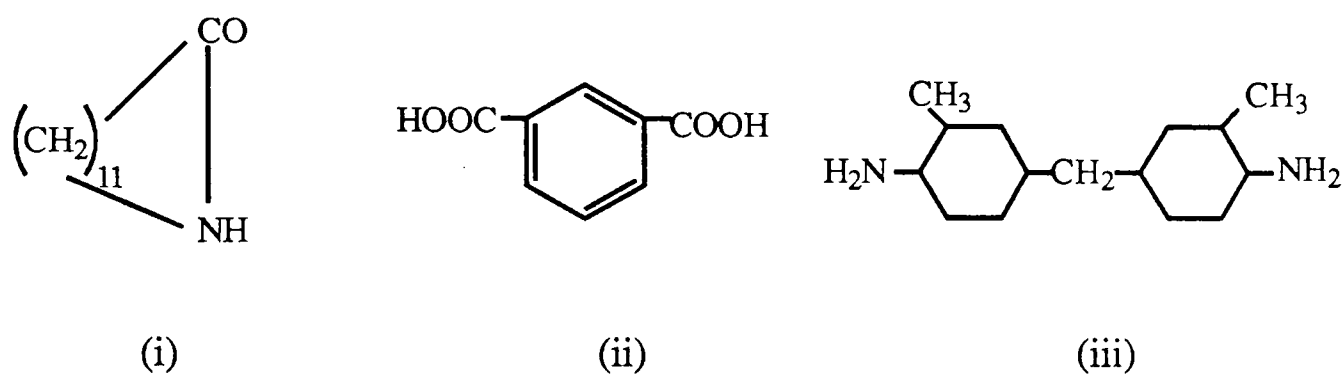
Soon after, another glass-clear polyamide was made available by Hoechst who announced Hostamid LP700 in 1976. Mano Runo [22] developed this polymer but was reluctant to disclose the true identity of it and merely patented that the Hostamids were copolyamides of a mixture of isomeric bisaminomethylnorbornanes (Figure 1.1), with aliphatic cycloaliphatic dicarboxylic acids with 7-20 carbon atoms as well as diamines, aminoacids or lactams. It may be because of the mystery behind the polymer that it never succeeded as an industrially developed polyamide and soon became redundant.

Figure 1.1 :- The Isomeric Bisaminomethylnorbornanes.



A third more successful transparent amorphous polyamide was Grilamid TR55 developed by Emser Werke [23]. As with Trogamid T and the Hostamids, it is a copolymer and was synthesized by reacting lauryllactam (i) with the salt of isophthalic acid (ii) and the diamine bis-(4-amino-3-methylcyclohexyl) methane (iii) (Figure 1.2). As with Trogamid T, it had the benefit of being clear, but had the added advantage of being chemically and stress crack resistant. Schaat and Hagen [24] utilized these properties together with the ability of the polymer to be molded to produce plastic pieces, especially for the eye glass frame industry.

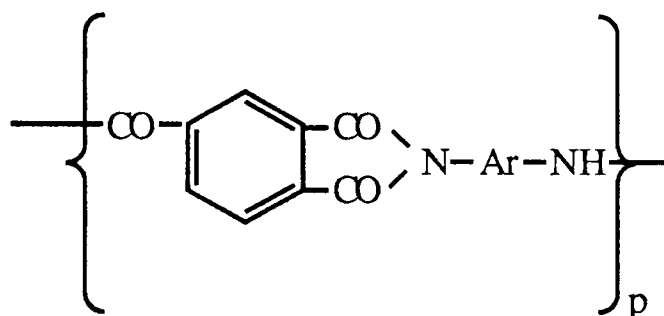
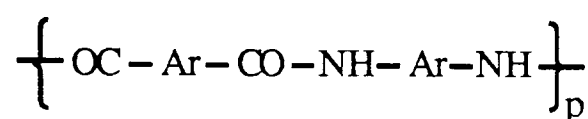
Figure 1.2 :- Grilamid TR55.



In general the glass-clear aromatic polyamides tend to have better properties in the form of the resin than many of the aliphatic polyamide resins. They will generally show a greater rigidity and hardness, lower water absorption, lower temperature co-efficient of expansion, better electrical insulation properties, particularly under hot damp conditions, and of course transparency. For these reasons these polymers are commonly employed as flow meter parts, transparent housing for electrical equipment, and containers for solvents.

1.4.2 Crystalline Wholly Aromatic Polyamides.

In recent years there has been considerable interest in wholly aromatic polyamide fibres, better known as ARAMID fibres. These are defined by the International Organization for Standardization, (ISO), as "*synthetic linear macromolecules made from aromatic groups joined by amide linkages, in which at least 85% of the amide linkages are joined directly to two aromatic rings and in which imide groups may be substituted for up to 50% of the amide groups.*" [25] e.g.

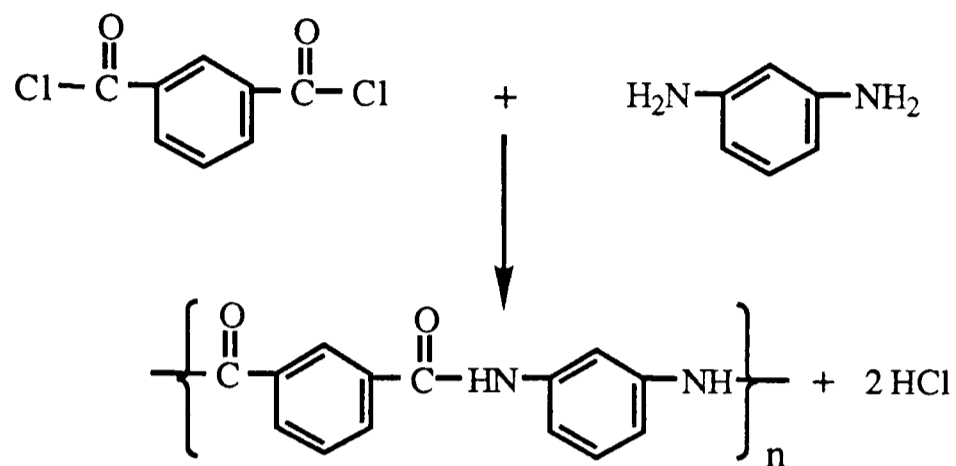


Where 'p' refers to the number of monomer units making up the polymer chain.
In each sample the aromatic radicals Ar may be alike or different.

It was not until the 1960s that the first synthetic material which could be defined as an aramid was developed. Prior to this date wholly aromatic polyamides had not been considered for large scale production because of high cost of intermediates, difficulty in fabrication, very high melting points and insolubility. It was DuPont [26] who first synthesized poly(m-phenylene isophthalamide) by the condensation of 1,3-phenylene diamine with a solution of isophthaloyl chloride (Scheme 1.5). It was known experimentally as HT-1 and later under the trademark of Nomex. The originally disclosed synthesis [27] involved low temperature interfacial polycondensation of the acid chloride in tetrahydrofuran (THF) with the diamine in aqueous sodium carbonate solution. The patent claimed an inherent viscosity of up to 1.65 for the resulting polymer. However, this process was quickly replaced by another method developed by Morgan et al [28]. Presently, Nomex is produced in dimethylacetamide or N-methylpyrrolidone (NMP).

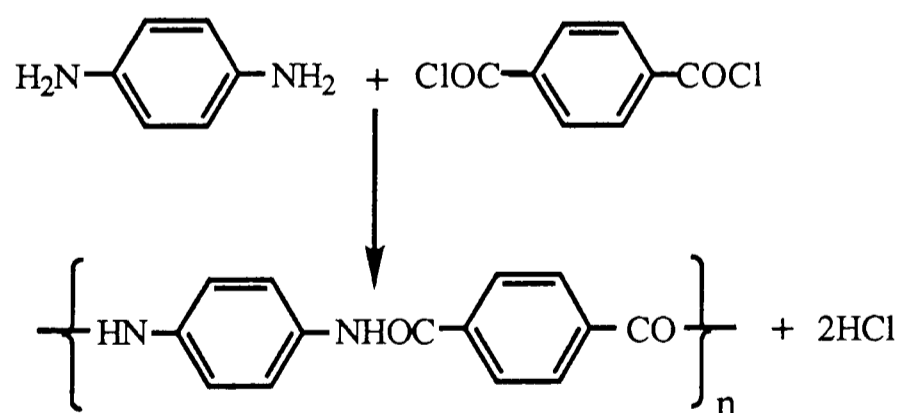
containing the acid acceptor calcium chloride, by a two step solution polycondensation technique [29]. Fibres are also spun from solution in dimethylacetamide containing 45% calcium chloride.

Scheme 1.5 :- Nomex Synthesis.



DuPont continued their research into aromatic polyamides and in 1973 introduced poly(p-phenylene terephthalamide) marketed as Kevlar [30]. It was prepared from the reaction of an aromatic diamine with an aromatic diacid chloride, specifically p-phenylenediamine with terephthalyl chloride in a mixture of hexamethylphosphoramide and N-methylpyrrolidone (2:1) at -10°C (Scheme 1.6). Fibres were spun from a liquid crystalline solution in concentrated sulphuric acid at temperatures below 90°C to minimise degradation.

Scheme 1.6 :- Kevlar Synthesis



The preparation of wholly aromatic polyamides, especially of Nomex and Kevlar has been reviewed in detail by Bair et al [31] who pointed out that the viscosity hence the molecular weight of such polyamides was dependent on such factors as the reaction temperature, stirring rate, solvent composition, stoichiometry and ingredient concentration.

1.4.3 Crystalline Aliphatic-Aromatic Polyamides.

Two of the most widely utilized man-made fibres today are nylon 6,6 {poly(hexamethylene adipamide)} and polyester 2GT {poly(ethylene terephthalate)}.

As expected, their properties vary greatly, which is mainly due to the considerable differences in their molecular structures. Nylon 6,6 has for example properties which include low density, versatility of dyeing and high resistance to alkali. Many of the desirable attributes of polyester 2GT are associated in large measure with the presence of the aromatic ring, which provides a considerable amount of polymer chain stiffness. For nylon 6,6, the desirable attributes as well as some of its limitations are due to the highly polar water sensitive amide linkage.

From these considerations, it is reasonable to expect that a polyamide containing both an aromatic ring and an aliphatic carbon chain might display many of the desirable properties of both nylon 6,6 and polyester 2GT, hence the reasoning for the development of the aliphatic-aromatic polyamides.

The incorporation of aromatic units such as the phenylene moiety into the polymer in place of aliphatic units affects the properties in quite complex ways. Usually, an increase in the glass transition temperature (T_g) is observed (Table 1.1); the polymers containing aromatic rings are accordingly more dimensionally stable at conventional use temperatures than aliphatic polyamides. However, the incorporation of an aromatic unit does not directly influence the melting point (T_m) of the polymer and in some cases can actually have a detrimental effect on the T_m while increasing the T_g (Table 1.1).

Another effect of the introduction of an aromatic unit in to a polyamide is to increase its modulus or stiffness, para-orientated aromatic units to a greater extent than meta-orientated aromatic units. The para-phenylene unit in the polymer chain permits much better molecular orientation than does either the meta or ortho-phenylene units, allowing improved intermolecular registration of aromatic groups for hydrogen bonding.

Table 1.1 :- The Influence of Incorporating an Aromatic Ring into the Polyamide Backbone on the Thermal Properties of the Polyamide.

NAME	STRUCTURE	Tg °C	Tm °C	Ref.
Nylon 6	$\left[\text{HN}-(\text{CH}_2)_5\text{CO} \right]_n$	75	220	6,7
Nylon 6,6	$\left[\text{HN}-(\text{CH}_2)_6\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO} \right]_n$	80	265	5
Poly(m-phenylene adipamide)	$\left[\text{HN}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO} \right]_n$	160	250	32
MXD,6	$\left[\text{HN}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO} \right]_n$	90	243	33, 34,35
PXD,6	$\left[\text{HN}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-\text{OC}-(\text{CH}_2)_4-\text{CO} \right]_n$	-	333	36
Nylon 6,T	$\left[\text{HN}-(\text{CH}_2)_6\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$	180	370	37
Nylon 6, I	$\left[\text{HN}-(\text{CH}_2)_6\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$	142	198	11

The conjugation of the amide linkage with the aromatic unit will also influence a polymer's properties. Consider the polymers poly(m-xylylene adipamide) and poly(hexamethylene isophthalamide), (nylon 6,I). Even though they are isomers, the former is more crystalline and has a higher melting and heat distortion temperature than the less crystalline polymer. This difference can be accounted for by the location of the methylene groups in the former polymer, which separate the amide groups from the aromatic rings. The amide groups are thus free to rotate and can hydrogen bond in all directions, which includes hydrogen bonding in directions perpendicular to the plane of the ring without hindrance from this bulky structure. Nylon 6,I on the other hand has its amide groups conjugated directly to the aromatic ring and hence held in a position essentially coplanar with it, by resonance forces. Hydrogen bonding in directions perpendicular to the plane of the ring is therefore difficult. This coupled with the hindrance caused by the bulky ring resulting from the unsymmetrical meta structure, prevents orderly hydrogen bonding. Also, with a conjugated system, a degree of colour formation is always inevitable.

Replacement of an aliphatic section of a polyamide by a cyclic segment, or an aromatic ring reduces chain flexibility. It also tends to increase the modulus and reduce solubility. This is observed with the drop in melting point of PXD,6 with flexible amide groups compared to the more rigid nylon 6,T. The melting point is far more influenced by the introduction of a symmetrical "stiff" aromatic ring than the flexible amide groups capable of hydrogen bonding in all directions.

With MXD,6 and nylon 6,I however, symmetry is lost due to the meta orientation of the aromatic ring, hence the influence of the hydrogen bonding is greater than the introduction of a "stiff" but unsymmetrical aromatic unit, resulting in the higher melting point for the former polymer.

With these considerations in mind, the development of crystalline aliphatic-aromatic polyamides commenced and although a number of nylons were spun, only two polymers were studied extensively, namely poly(hexamethylene terephthalamide) (nylon 6,T) fibres and fibres from poly(m-xylylene adipamide) (MXD,6).

During the late 1950s and early 1960s, research was conducted simultaneously on both these possible aliphatic-aromatic polyamides. In theory, the development of nylon 6,T was thought to be more easier of the two, since the monomers employed (hexamethylene diamine and terephthalic acid) were easily available in a pure form. MXD,6 on the other hand required m-xylylene diamine (MXD) as one of its monomers, which had to be used with great care not only due to the ease by which it could be oxidized but also because of the elaborate purification procedures which had to be conducted. In practice however, it was MXD,6 which was synthesized first and not the expected nylon 6,T. The latter's progress was hampered due to its high melting point (370°C) which made it impractical to process using a conventional condensation polymerization technique. It was not until 1961 that Allen Werner working for the Celanese Corporation of America [37] developed a more convenient solution polymerization method which allowed the synthesis of nylon 6,T for the subsequent spinning into fibre, using a wet spinning process, utilizing concentrated sulphuric acid as the solvent, rather than melt spinning, which would degrade the polymer prior to melting.

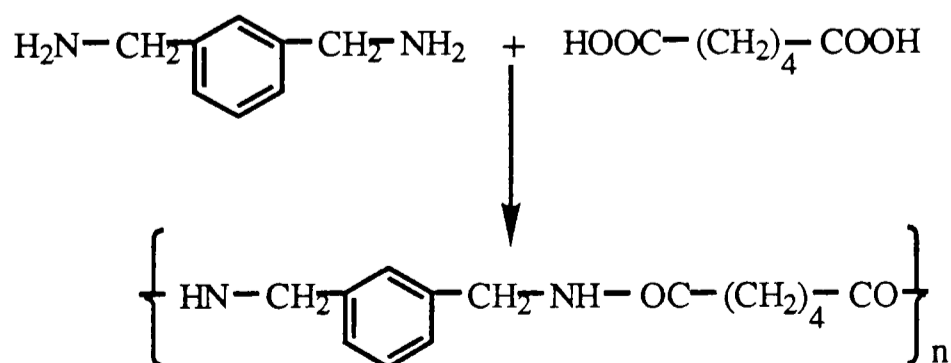
Producing high melting point fibres from nylon 6,T caused further problems in that the wet spinning apparatus employed had to be acid resistant and overall the production was uneconomical to run, even though the properties of the fibres produced were exceptional. For this reason, the melting point of the polymer had to be reduced by some means, so that spinning was more practical using a conventional melt spinning technique.

1.5 THE RISE AND FALL OF MXD,6.

1.5.1 MXD,6 Preparation.

In 1957, at the California Research Corporation, U.S.A., Lum and Carlson [33] recognised the problem associated with nylon 6,T prior to its development and concluded that decreasing the melting point of nylon 6,T could be achieved by introducing a meta-substituted aromatic unit into the backbone of the polymer chain instead of a para-orientated one. As the production cost of hexamethylene diamine was far greater than that of adipic acid, it was decided that the aromatic ring should be incorporated via the diamine instead of the acid. Meta-xylylene diamine was potentially available cheaply and in abundance at that time, so was the ideal candidate for polymerization with the as cheap adipic acid, resulting in the first development of the polymer *poly(m-xylylene adipamide)*. The polymer was produced from the condensation polymerization of MXD, with adipic acid (Scheme 1.7) and was later available commercially from Mitsubishi [38] as MXD,6 and is now marketed by Solvay and by Laporte as Ixef [19]. In contrast to nylon 6,T, MXD,6 was found to have a relatively low melting point (243°C) and a relatively high glass transition temperature (70-100°C). With a fibre forming polymer showing such thermal characteristics, Lum and his coworkers believed they had developed a synthetic fibre which was stable at the temperature of boiling water and other conventional laundering temperatures, yet not so high as to render the fibres unsuitable for conventional grid melt spinning [34].

Scheme 1.7 :- MXD,6 Preparation.



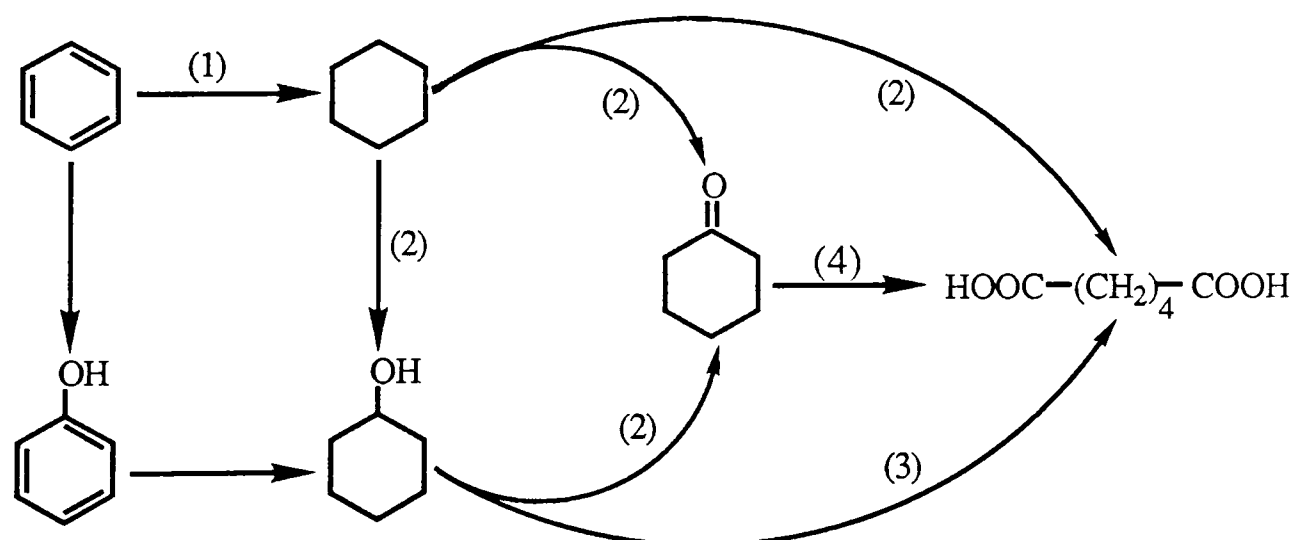
1.5.2 Intermediates for MXD,6.

1.5.2.1 Adipic Acid.

In theory, adipic acid can be manufactured from a number of starting materials, which generally tend to be cyclic in nature, although it has been obtained from linear starting material such as 1,6-hexanediol [19]. However, of all these potential production routes, the ones from cyclohexane, cyclohexanol and cyclohexanone only are of economical importance (Scheme 1.8).

Industrially, all these cyclics can be derived from either benzene or phenol. Benzene is generally hydrogenated at 340lb/in² pressure and 210°C using a Raney nickel catalyst to cyclohexane. After cooling and separating the catalyst, the cyclohexane is reheated and continuously oxidized in the liquid phase by air, using a trace of cobalt naphthenate as catalyst, from which a mixture of cyclohexanol and cyclohexanone can be produced. Either product may be oxidized using appropriate conditions to give adipic acid, however for convenience, the whole mixture (referred to as KA oil) is often oxidized using nitric acid ($\approx 60\%$) at 60-110°C in the presence of a mixed ammonium vandate catalyst. Yield is claimed to be over 90% with a very high conversion rate.

Scheme 1.8 :- Preparation of Adipic Acid from Benzene.



- 1) Raney nickel catalyst at 210°C and 340lb/in².
- 2) Air oxidation in the liquid phase using cobalt naphthenate.
- 3) 60% nitric acid at 60-110°C with a mixed ammonium vandate catalyst.
- 4) Air oxidation at 80-100°C using acetic acid and 0.1% manganese acetate or nitrate.

The oxidation of cyclohexanone is an alternative procedure but demands higher temperatures than with cyclohexanol when employing nitric acid as the oxidising agent. For this reason, the catalytic oxidation with oxygen or air, in the liquid phase is used. Acetic acid with 0.1% manganese acetate or nitrate is used at 80-100°C as the diluent, the cyclohexanone will readily oxidise to the adipic acid with a yield of up to 70% [39].

1.5.2.2 Meta-xylylenediamine [40].

During the 1950s, the xylene fraction of aromatic hydrocarbons obtained by reforming petroleum, was composed of ethylbenzene and ortho-, meta- and para-xylene, the ratios being approximately 5-10% ethylbenzene, 20-25% ortho-xylene, 45-50% meta-xylene and 20-25% para-xylene. While ethylbenzene, ortho-xylene and para-xylene were established as raw materials for styrene, phthalic anhydride and terephthalic acid respectively, meta-xylene had no such market.

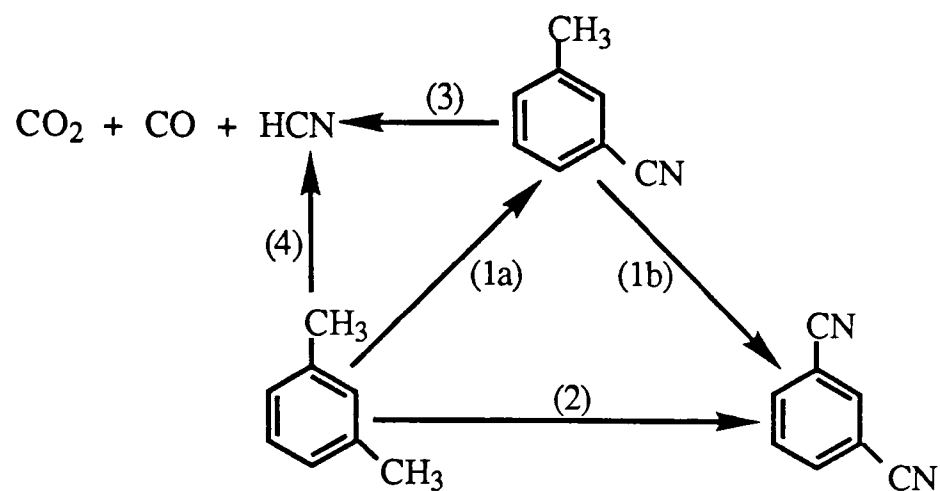
It was with a view to expand the use of this by-product that the Japanese company Showa Denko K.K. developed meta-xylylene diamine (MXD), from meta-xylene, the synthesis of which involved a two stage procedure :-

- (i) The ammoxidation of the meta-xylene to isophthalonitrile followed by,
- (ii) The reduction to meta-xylylene diamine.

(i) Ammoxidation.

The reaction scheme consists of four reactions, two reactions yielding the product isophthalonitrile and the other two producing the degradation products carbon dioxide, carbon monoxide and hydrogen cyanide (Scheme 1.9).

Scheme 1.9 :- Ammoxidation of Xylene to Isophthalonitrile.



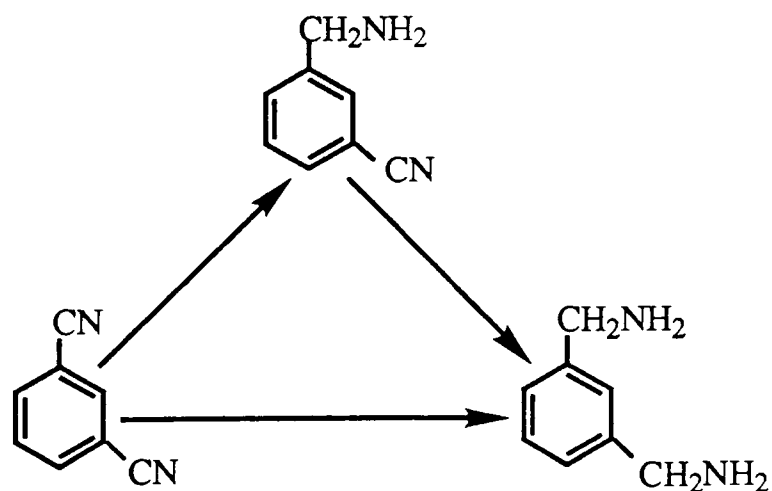
- Step 1 (a and b) Step by step ammoxidation of xylene to isophthalonitrile via tolunitrile.
 Step 2 Direct ammoxidation of xylene to dicyanobenzene.
 Step 3 Formation of CO_2 , CO and HCN via tolunitrile.
 Step 4 Direct formation of CO_2 , CO and HCN from xylene.

To aid in the production of isophthalonitrile, catalysts are employed which aid in preventing the production of degradation gases. Vanadium oxide mixed with oxides of either chromium, arsenic, selenium, sulphur and antimony, supported on ω -alumina are generally used [41].

(ii) Hydrogenation of Isophthalonitrile.

Hydrogenation of isophthalonitrile, also referred to as 1,3 dicyanobenzene, takes place in the liquid phase in the presence of a metal catalyst such as platinum or palladium. The reaction proceeds step wise, cyanobenzylamine being the intermediate (Scheme 1.10).

Scheme 1.10 :- Hydrogenation of Isophthalonitrile.

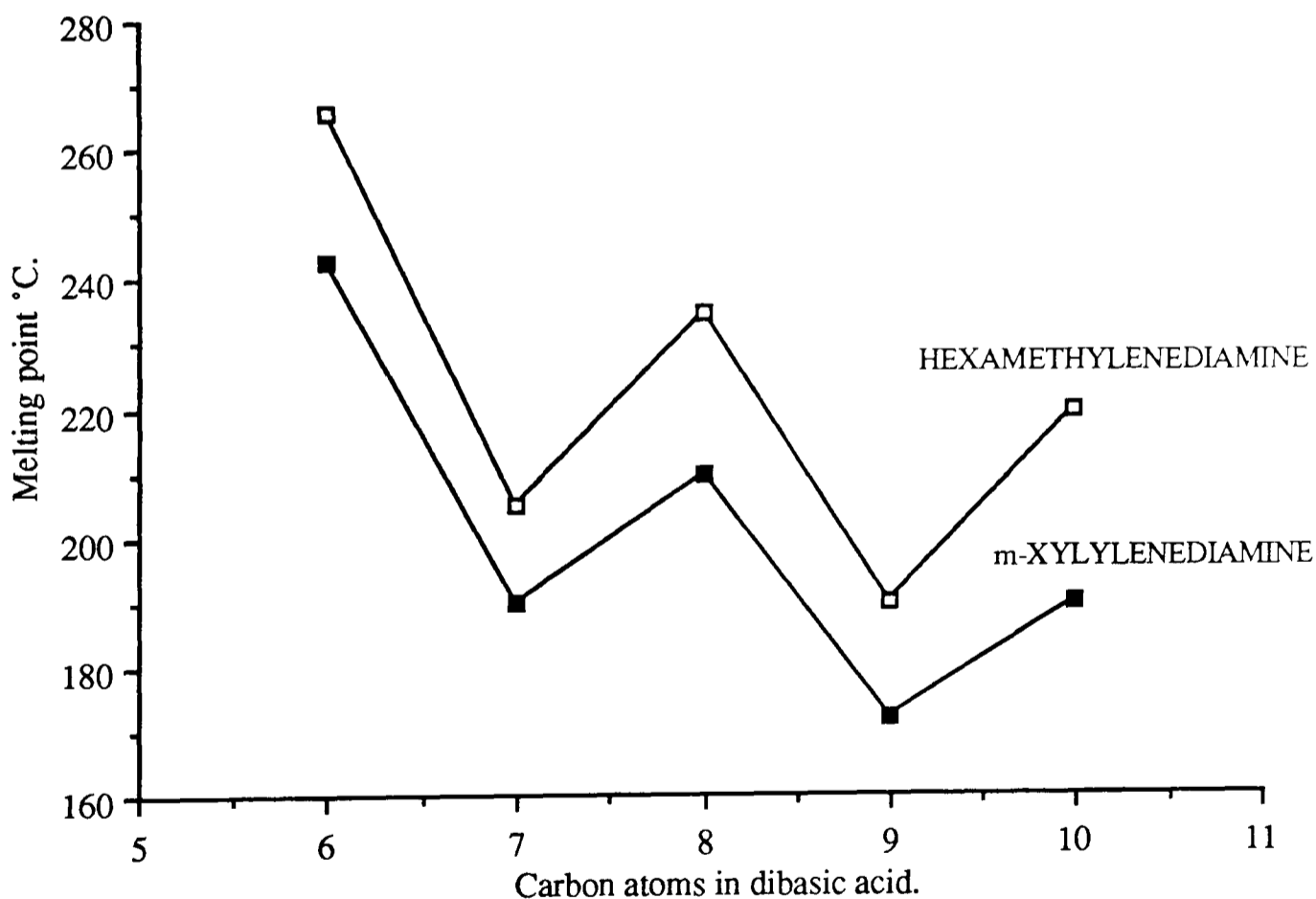


1.5.3 MXD,6...The Failed Fibre.

In the late 1960s, Carlston and Lum on behalf of the Californian Research Corporation [42] continued their research into the development of their 'superpolyamide', MXD,6. So much so that a series of polymers were synthesized with increasing carbon atoms in the dibasic acid [33].

Melting points were measured according to the method of Edgar and Ellery [43] and the data revealed that MXD formed crystalline polymers with the even number aliphatic acids, which formed a higher melting point series than the more amorphous polymers of the odd number acids (Figure 1.3).

Figure 1.3 :- Melting Points of Hexamethylene-and m-Xylylene Diamine Polyamide Resins.



Fibres from MXD,6 also showed interesting properties compared to the other polyamides available at that time. The crystalline form of MXD,6 had a melting point of 243°C and an A.S.T.M. [44] heat distortion temperature (fibre stress of 66 pounds per square inch) of over 200°C. Compared to polyester 2GT, the presence of terminal amine groups aid in the dyeability of the polymer and compared to nylon 66, the presence of the aromatic ring provided a considerable amount of chain stiffness, hence good abrasion resistance.

For some time, this fibre appeared to be quite promising, but despite the several good points of MXD,6, wide use of it in textile applications was soon precluded. Further tests disclosed disturbing results from MXD,6 fibre, especially when conducted under hot, wet conditions [45].

The work conducted by Sprague and Singleton [34] in particular exposed these weaknesses and they provided sufficient evidence to bring about the downfall of MXD,6.

Specifically, the modulus-temperature relationship of MXD,6 fibre whilst dry (Figure 1.4) and then when wet (Figure 1.5) were considered. It was apparent that the modulus of the fibre underwent a marked reduction in the region of the glass temperature (80-100°C) and that in the presence of water a severe reduction in the modulus occurred at temperatures only slightly above room temperature.

Figure 1.4 :- Comparison of the Modulus-Temperature Characteristics of Nylon MXD,6, Nylon 6,6 and Polyester 2GT Fibres (dry).

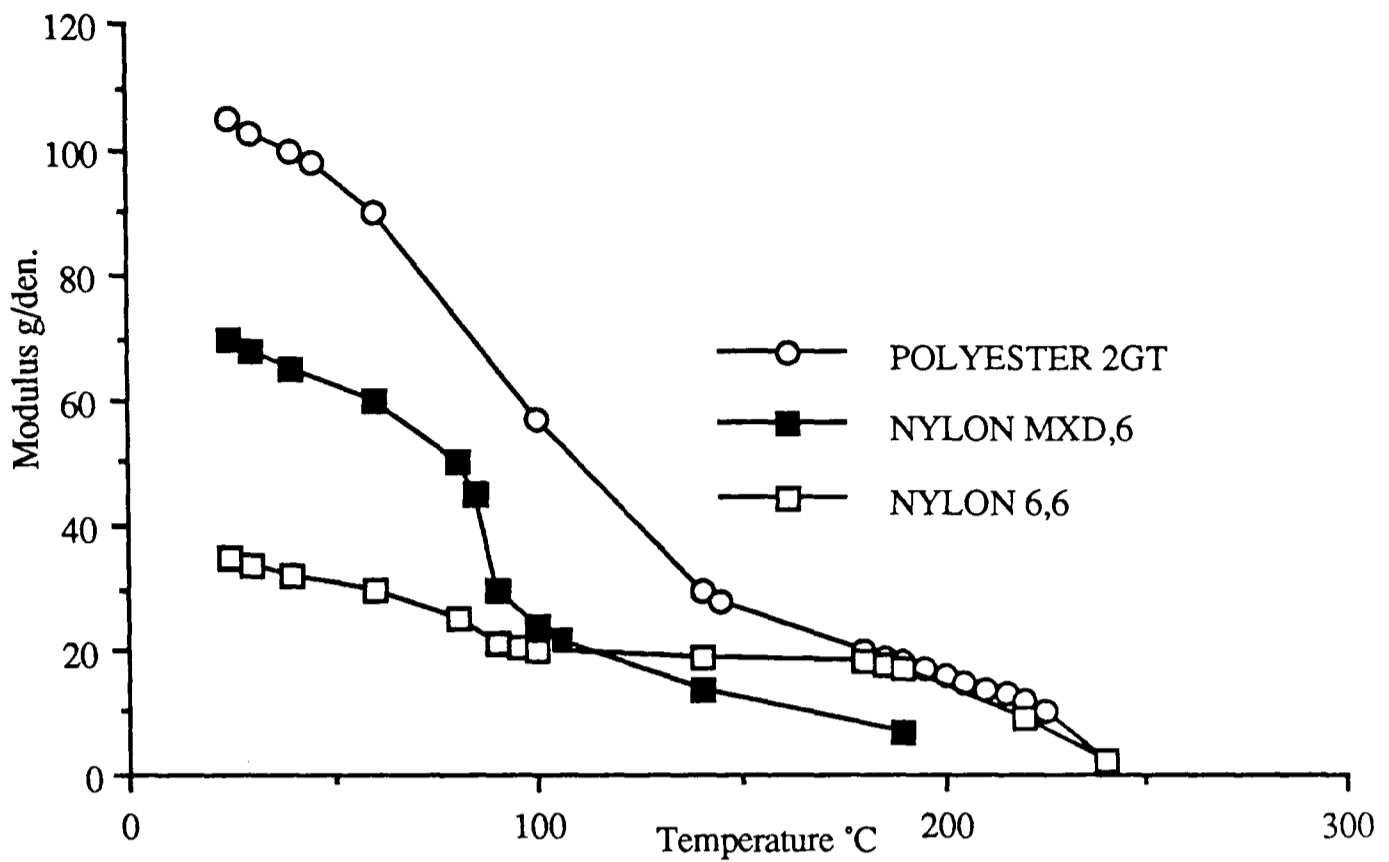
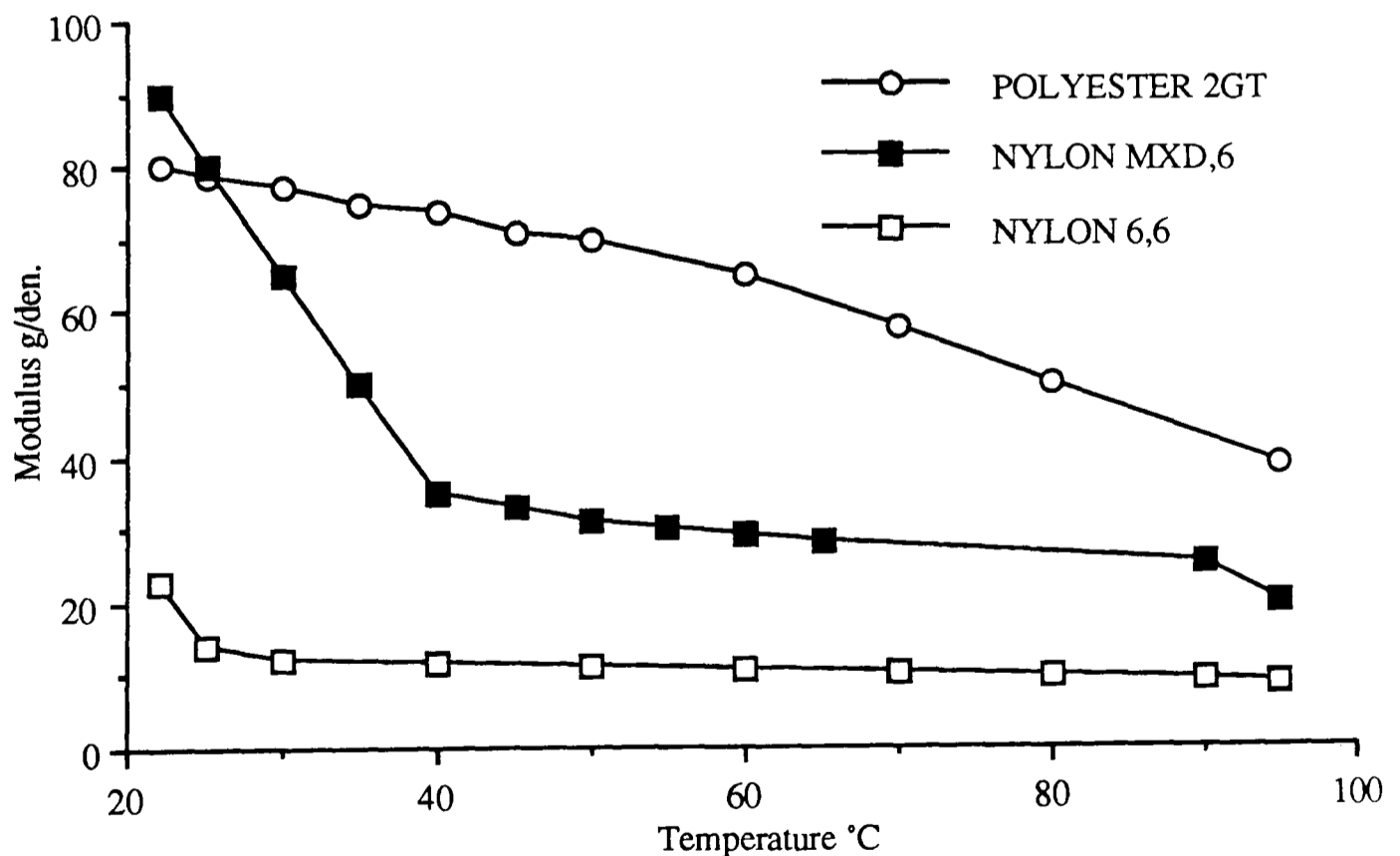
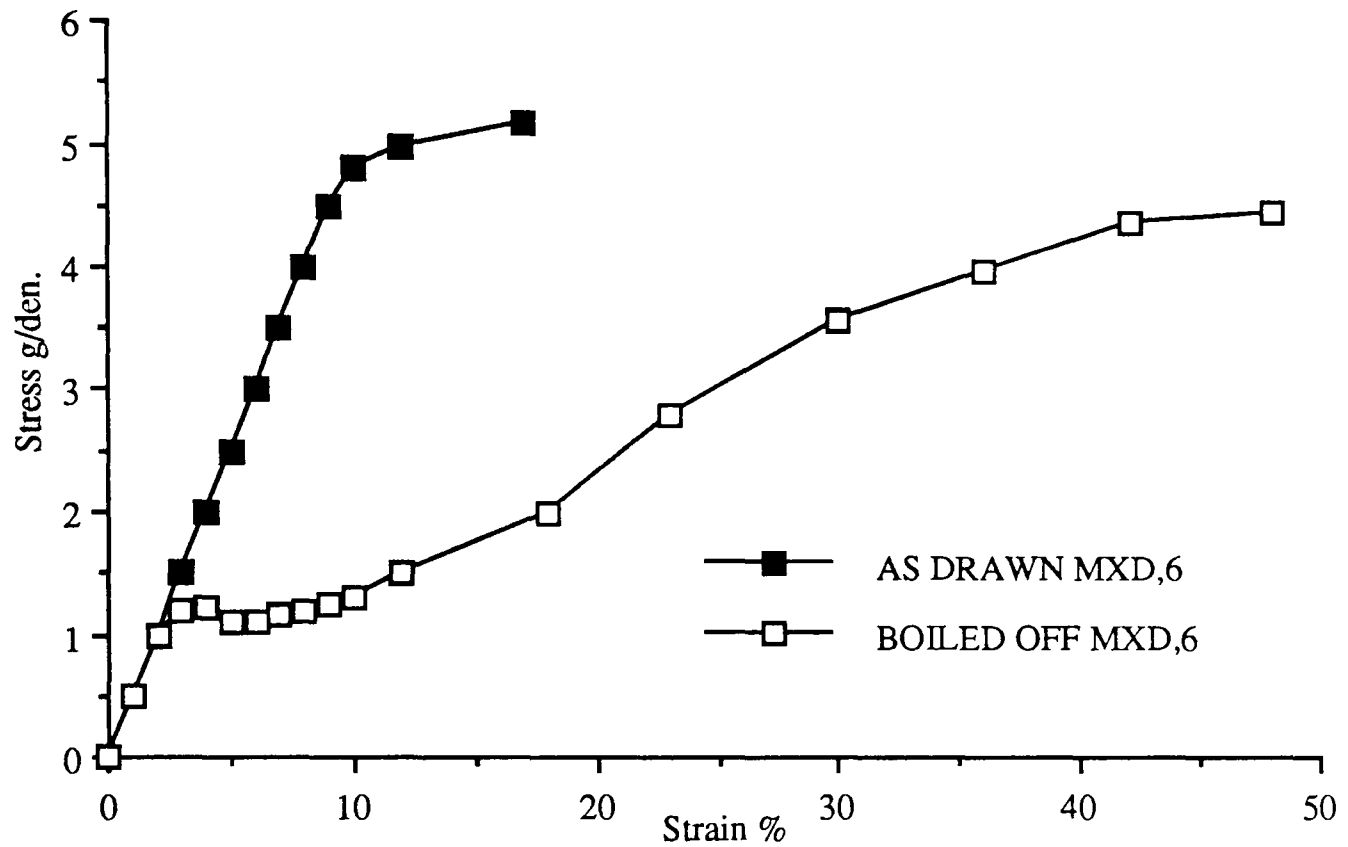


Figure 1.5 :- Comparison of the Modulus-Temperature Characteristics of Nylon MXD,6, Nylon 6,6 and Polyester 2GT Fibres (wet).



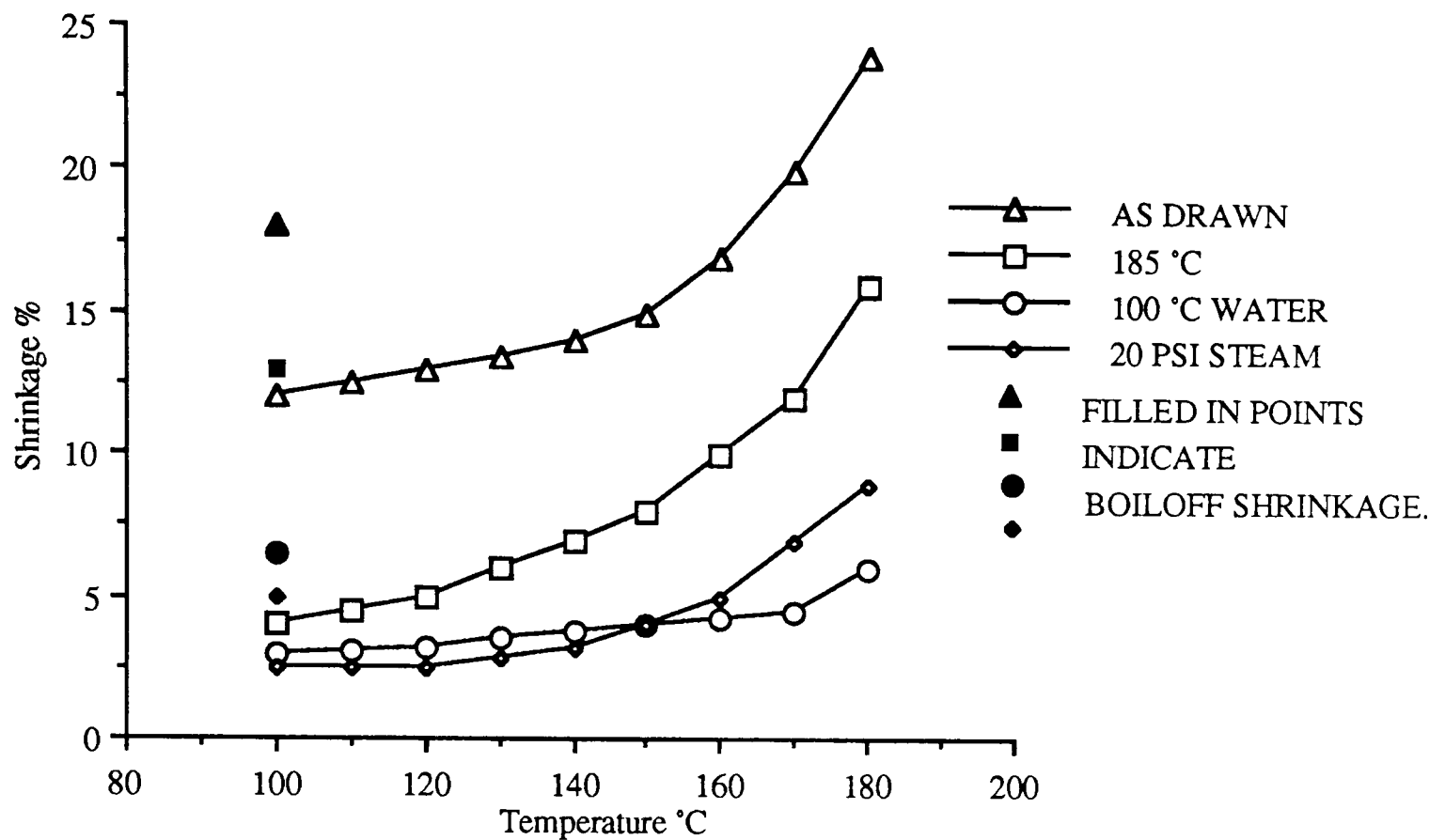
This sensitivity to moisture was also evident on stress strain behaviour after boil off (Figure 1.6).

Figure 1.6 :- Effect of Boil-off on the Stress-Strain Characteristics of Nylon MXD,6.



Surprisingly, even annealing the fibres at constant length in steam at 20lb/in² did not provide adequate stability to a subsequent boil off treatment, although the dry shrinkage of the fibre was considerably reduced (Figure 1.7).

Figure 1.7 :- Effect of Annealing at Constant Length on Shrinkage Behaviour of MXD,6.



According to Sprague and Singleton, this instability was due to the boiling water hydrating intermolecular secondary bonds, releasing significant numbers of chain segments, which then underwent entropic contraction. They showed that annealing fibres at high temperatures, or in boiling water, increased the crystallinity of the fibre when shrinkage was not allowed. However, further boil off without constraint resulted in considerable reduction in crystallite orientation, as chains were released and entropic contraction proceeded.

It was soon evident that MXD,6 would fail as a fibre for textile applications. What started as a possible alternative to nylon 6,6 and polyester 2GT, soon became virtually nonexistent in the textile and polymer industries.

1.5.4 MXD,6 Today.

Even though MXD,6 had been rejected as a textile fibre as early as the 1950s, it was clear to see that this polymer could not be laid to rest all together, as it still displayed some very useful properties unique to itself. However, it was obvious that it could only succeed in with other materials which could compensate for MXD,6's bad properties.

Today, the polymer is frequently utilized as one component of multilayered containers for the food industries. In particular, the Mitsubishi Gas Chemical Company, Japan, have concentrated a large area of their research into the development of plastic bottles which excel in gas barrier properties [46]. They are generally multilayered containers comprising a wall portion consisting of thermoplastic gas barrier resin (MXD,6) layers and thermoplastic resin (polyethylene terephthalate) layers. The wall portion is formed by alternately laminating the two resin layers in such a manner that there are at least two MXD,6 layers with the proviso that there is one more of the polyethylene terephthalate layers than the MXD,6 layers.

In addition, commercial grades of MXD,6 are also available with the inclusion of 30-50% glass fibre which brings the heat deflection temperature under load into the range 217-231°C, which is very close to the crystalline melting point. Glass fibre grades also have high tensile strength ($\approx 185\text{MPa}$) and flexural modulus ($\approx 10,000\text{MPa}$), hence are being looked at particularly as replacements for metals such as die-cast zinc alloys.

More recently, researchers have utilized the heat, water and fire resistant properties of MXD,6 composites [47]. Pellets extruded from a blend of MXD,6 (90 parts), nylon 6,6 (10 parts), glass fibre (60 parts), brominated polystyrene (12 parts), Sb_2O_3 (6 parts) and $\text{Ca}(\text{OH})_2$ (1 part) were used to prepare injection moulded test pieces with very good physical properties. Tests showed tensile impact strength of up to 117.5kgcm^{-2} and a heat distortion temperature of 220°C.

Alternatively, MXD,6 is commonly applied as a component for polymer blends which are used for electrical wire insulation, water pipes and pumps [48], as well as parts found in automobile engines, such as cylinder head covers and gear cases [49]. Composites have also been suggested for food containers with exceptional gas barrier properties. In particular, C.M.B. Technology Packaging, U.K., have developed a system whereby a container is prepared from a blend of 96% polyethylene terephthalate, referred to as the "non-oxidisable polymeric component", 4% MXD,6 referred to as the "oxidisable organic component" and a metal 'catalyst' which is thought to aid in the scavenging of oxygen [50]. Generally, Cobalt SiccatoI is used as the metal 'catalyst,' which is a solution of C₈-C₁₀ cobalt carboxylates in white spirit and is available from Akzo Chemie. The concentration of the cobalt as metal is 10% by weight relative to the solution. Using between 50-2000ppm of the cobalt metal in such a blend, containers prepared from these mixtures are found to have exceptional gas barrier properties. The oxidisable organic component (MXD,6) is thought to scavenge for oxygen in the container wall aided by the cobalt 'catalyst', reducing gas permeability dramatically.

CHAPTER TWO :- POLYMER DEGRADATION.

2.1 INTRODUCTION.

"POLYMER DEGRADATION", is the collective term given to various processes which depreciate the properties, or ruin the outward appearance of a polymer [51]. In a broad sense, polymer degradation leads to a decrease in molecular weight and tensile strength, the properties which make polymers commercially useful as fibres, plastics and rubbers [52].

The earliest reports of the deterioration of modern polymeric materials followed the discovery of rubber by European explorers in the Amazonian forests [53]. The product of *Hevea Brasiliensis* showed remarkable properties and its ability to rebound to its original configuration gave it an independent 'life' of its own. However, these properties soon degenerated when exposed to the atmosphere and it was only after Hoffmann reported in 1861 [54] that the degradation of natural rubber was accompanied by the absorption of oxygen, that the development of the art of stabilization into a science took place. His investigations showed that vulcanised rubber tended to 'age' better than raw rubber, which was later shown to be due to the formation of by-products from the 'curing' reaction which were identified as 'anti-oxidants'.

The term degradation is generally used to describe irreversible changes in the chemical structure of the polymer, as a result of exposure to external forces. A number of degradation routes have been understood which have been loosely classified into several categories, which include thermal degradation, oxidative degradation, radiation or photodegradation and mechanical degradation. These categories can be combined in numerous configurations which may or may not influence the final mechanism of degradation.

The degradation of polymers is of considerable importance from both practical and theoretical points of view. Knowledge of the extent of degradation of commercially available materials during use under various conditions is essential. However, a theoretical study can form the basis for the elucidation of the manner in which a material fails. Predictions of performance of substances exposed to environmental factors may often be assessed from such studies. Thus theory and practice are inseparable, particularly in thermal and oxidative degradation of polymers.

2.2 THERMAL DEGRADATION OF POLYAMIDES.

2.2.1 Introduction.

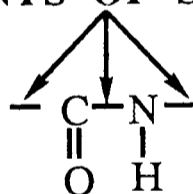
Early research into the degradation of polyamides was based on the the behaviour of polyamides at temperatures beyond their melting points. The elucidation of the chemistry of degradation is still a very controversial subject, as the mechanisms of thermal degradation are complex and cannot be determined by mere bond strengths alone.

Initial investigations were however based on model compounds of polyamides, where two dissimilar theories of amide bond scission were deliberated.

Goodman [55] believed decomposition involved fission of each bond in and adjacent to the amide group (Figure 2.1),

Figure 2.1 :- Amide Bond Fission According to Goodman.

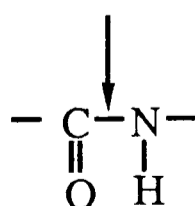
POINTS OF SCISSION



whereas Kamerbeek et al [56], then later Mortimer [57] asserted that the amide C-N bond alone was responsible for initial cleavage (Figure 2.2).

Figure 2.2 :- Amide Bond Fission According to Kamerbeek et al and Mortimer.

POINT OF SCISSION



Based on bond strengths alone, one would expect preferential scission of the amide C-N bond rather than the C-C bond as the former's dissociation energy is cited as 277kJmol^{-1} compared to the latter's of 336kJmol^{-1} [58].

However, research has shown that anticipating degradation mechanisms based on bond strengths alone can sometimes be more misleading than beneficial. For example, the C-C dissociation energy in propane is 344kJmol^{-1} whereas the C-N dissociation energy in the analogous dimethylamine is 353kJmol^{-1} . These higher than expected values suggest alternative factors influencing the processes during degradation of polymers. Scission of the main chain often gives rise to free radicals which can occur either at random in the chain, or at weak links resulting from, for example, anomalous structures as for poly- α -methylstyrene and polystyrene. Also, the chain ends often present labile structures suitable for initiation of thermal degradation. Formation of crosslinks sometimes occurs if the main chain contains double bonds. These and many other factors will influence the degradation of a polymer. If there is a mechanism whereby a suitable degradation reaction can proceed, then this will take preference to the bond dissociation mechanism.

2.2.2 Mechanisms in Polyamide Thermal Degradation.

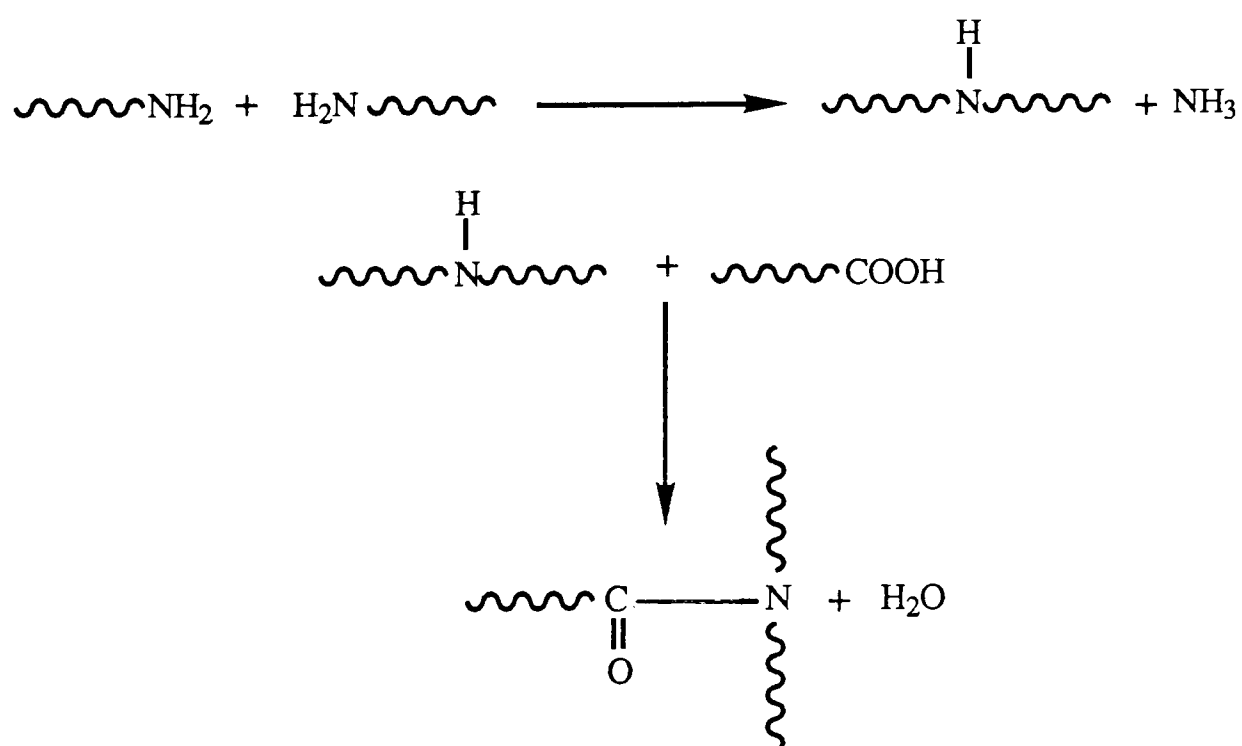
To obtain better insight into the chemistry of degradation, researchers have reported thermal degradation in many ways. Most commonly they have either recorded the weight loss at elevated temperatures, or they have analysed the products of degradation, volatiles as well as the residual polymer after degradation.

As early as the 1940s, Taylor [59] identified ammonia and carbon dioxide during the polycondensation of polyamides and assumed that these were evolved from side reactions working concurrently with the polymerization reaction.

Later, Achhammer et al [60] using mass spectrometry identified a wide range of degradation products for nylon 6 which included simple hydrocarbons, cyclopentanone, water, carbon monoxide, carbon dioxide as well as ammonia. This extensive investigation however could only give an insight into the mechanism of the degradation of polyamides and not the complete picture.

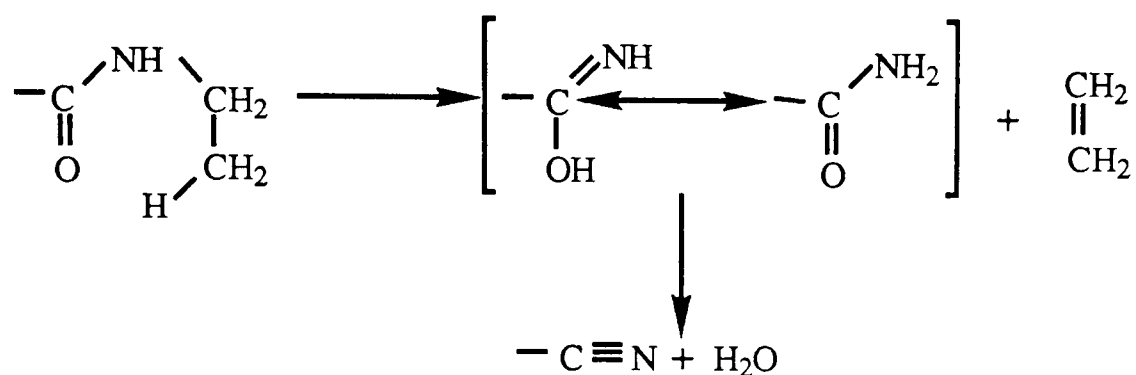
Korshak [61], on the other hand, was more interested in the influence of temperature on the molecular weight of the polymer. Using nylon 6,6, in an inert atmosphere, he found that the molecular weight was unaffected when heated at 270°C for up to 4 hours, but at 300°C, polymers with molecular weights of 18,000, 35,000, and 55,000 fell to approximately 9,000 within 2 hours of heating. Furthermore, gelation with some discolouration was reported at 330°C. This gelation was investigated by Kroes and then by Wiloth [62]. Kroes indicated that part of the gelation occurred from the dimerization of the hexamethylene diamine portion followed by amide formation (Scheme 2.1). Hence gelation was thought to be due to the reaction of a secondary amine formed between amine end groups, with a carboxyl end group, forming a branched structure.

Scheme 2.1 :- Branched Structure Formation According to Kroes.



Nitrile groups were also identified, which were attributed to the scission of the C-N of the amide forming primary amides. Bailey [63] suggested the mechanism of the C-N bond cleavage with the elimination of a gamma hydrogen (Scheme 2.2).

Scheme 2.2 :- Formation of Nitrile Groups According to Bailey.

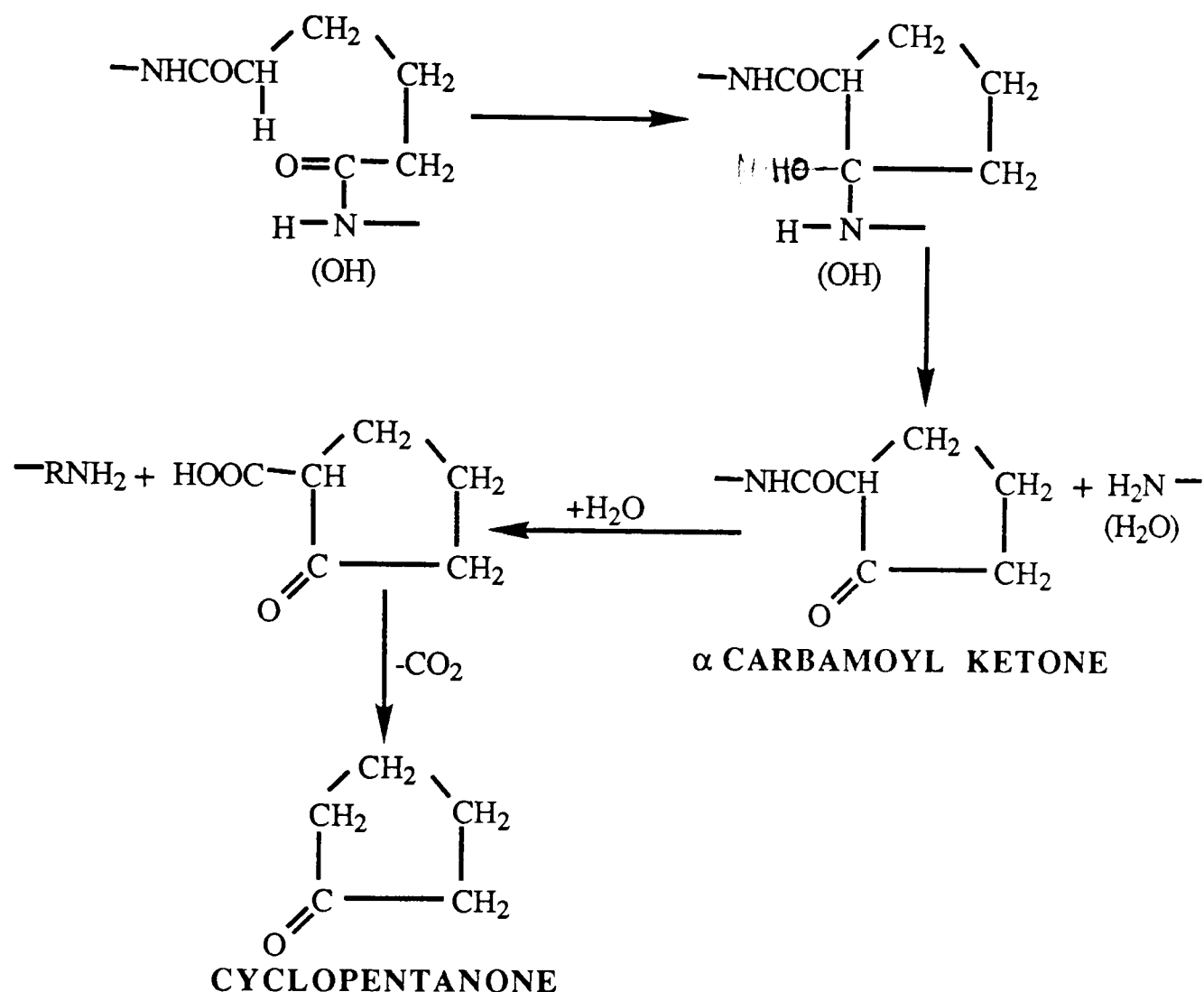


Wiloth worked with both nylon 6,6 and nylon 6,10 under different degradation conditions and assigned the considerably more pronounced instability of the former polymer to the ring closure tendencies of the adipic acid component, forming cyclopentanone and/or derivatives of cyclopentanone.

Goodman [55] also identified cyclopentanone derivatives as well as nitrogen containing rings when degrading polyamide model compounds. He found that model N-alkyl carbamides RCONHR' and N,N'-diacyl hexamethylene diamines $\text{RCONH}(\text{CH}_2)_6\text{NHCOR}$ showed very little degradation at temperatures up to 350°C, but bisamides of dibasic acids $\text{RNHCO}(\text{CH}_2)_n\text{CONHR}$, revealed significant decomposition giving primary amines, carbon monoxide, hydrocarbons and when n was at least 4, carbon dioxide. Unfortunately, a mechanism for cyclopentanone or the primary amines could not be suggested.

However, it was Edgar [64] who subsequently showed that the nitrogenous compounds could arise from the reaction of a carbonyl with a hydrogen activated by the carbonyl of the adipic acid moiety and also gave rise to cyclopentanone (Scheme 2.3).

Scheme 2.3 :- Formation of Nitrogenous Compounds and Cyclopentanone and its Derivatives According to Edgar.

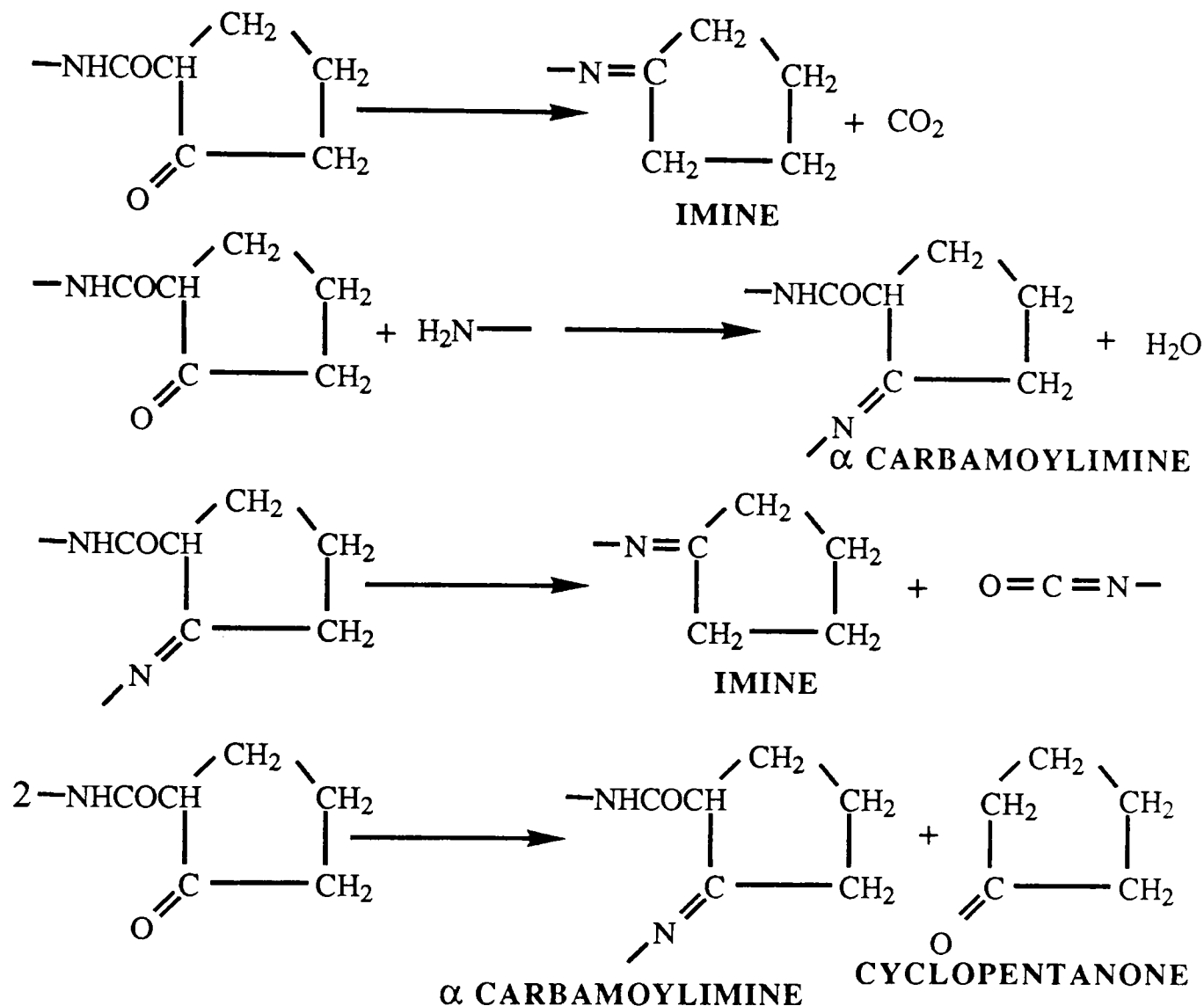


Also characterized has been the α -carbamoyl ketone whose reactive mechanisms have been determined. Beside cyclopentanone derivatives, a number of imines were thought to form concurrently (Scheme 2.4).

A large area of research in the thermal degradation of polyamides has concentrated on pyrolysis studies. Strauss and Wall [65] extended the earlier work conducted by Achhammer and his co-workers, carrying out pyrolysis of polyamides of varying composition and molecular weight at 400°C in vacuo. Using the ionization chamber of a mass spectrometer, rate curves were determined by plotting rate of volatilization against the percentage of polyamide volatilized. Mechanisms were postulated from the rate curves and a near random type breakdown was suggested.

Using mass spectrometry, the identification of carbon dioxide, water, ammonia, hexamethylene diamine and cyclopentanone and/or cyclopentanone derivatives was also possible.

Scheme 2.4 :- Mechanisms of Imine Formation According to Edgar.



More recently, Allen et al [66] have investigated many aspects of the decomposition of polyamides especially nylon 6,6. Included in this study is the influence of amine-carboxyl end group balance on luminescent species. Using many characterising techniques, including fluorescence and phosphorescence emission spectroscopy, viscosity number and end group balances, they found that polymer stability was markedly influenced by the final step of polymerization, under both steam and nitrogen atmospheres, the latter more detrimental. At lower degrees of polymerization, a higher concentration of amine end groups were observed, which in turn resulted in a more

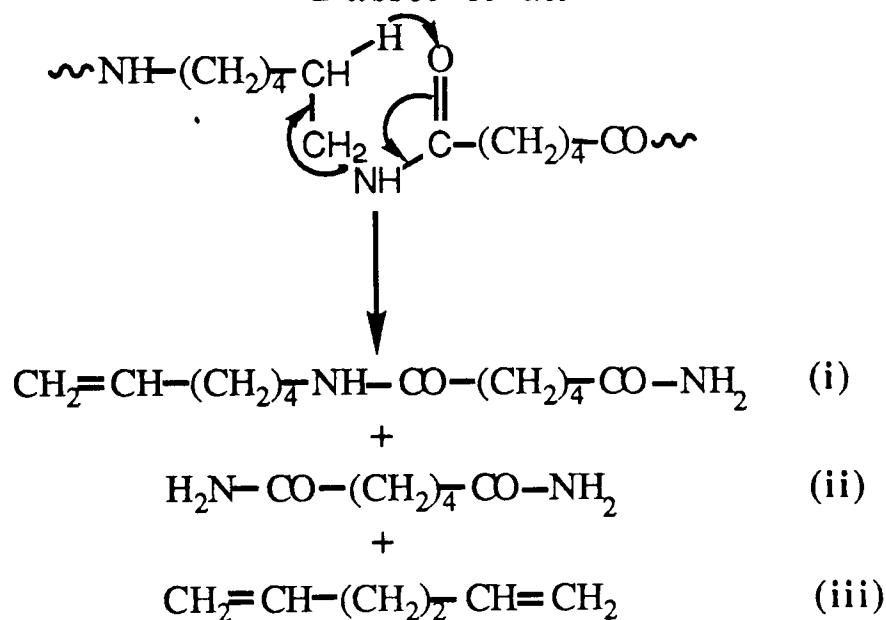
stable polymer, both thermally and photochemically. These results were confirmed to be associated with the radical/oxygen scavenging ability of the amine end groups, giving rise to the greater stability of the polymer.

At a similar time, Do et al [67] were more concerned with the F.T.-I.R. spectroscopic study on the thermal and thermo-oxidative degradation of nylons. They found that the effect of heat and oxygen on nylon film degradation caused an increase in crystallinity due to annealing and also an increase of non-hydrogen bonded amide groups, which seemed to entail mainly amide groups from the amorphous region. The intensities of the I.R. absorption bands related to the folded structure decreased as soon as heating started, whereas the intensities of I.R. spectra of carbonyl groups increased in the region of the spectra where carbonyl groups are frequently found.

With respect to the mechanisms of thermal decomposition of nylon 6,6, during the late 1980s, Ballistreri, Garozzo, Giuffrida and Montaudo [68] investigated this study using direct pyrolysis into a mass spectrometer. Several methods were employed to identify compounds present in the pyrolysis mixture including comparison of electron impact and chemical ionization spectra, accurate mass measurements, comparison with the mass spectra of authentic compounds and tandem mass spectrometry (daughter and parent ion spectra). They found that using Direct Pyrolysis Mass Spectrometry (D.P.M.S.) had the added advantage that pyrolysis was accomplished under high vacuum, therefore the thermal degradation products formed were volatilized and removed from the hot zone straight to the detection zone. Furthermore, fast detection and the low probability of molecular collision reduced to a great extent the occurrence of secondary reactions therefore almost all the volatiles detected were primary reaction fragments. Their results suggested that the thermal decomposition mechanism of nylon 6,6 occurred via an α C-H hydrogen transfer reaction rather than by a β hydrogen transfer reaction as suggested by Dussel et al [69] (Scheme 2.5) with the consequent formation of compounds bearing amine and ketoamide end groups.

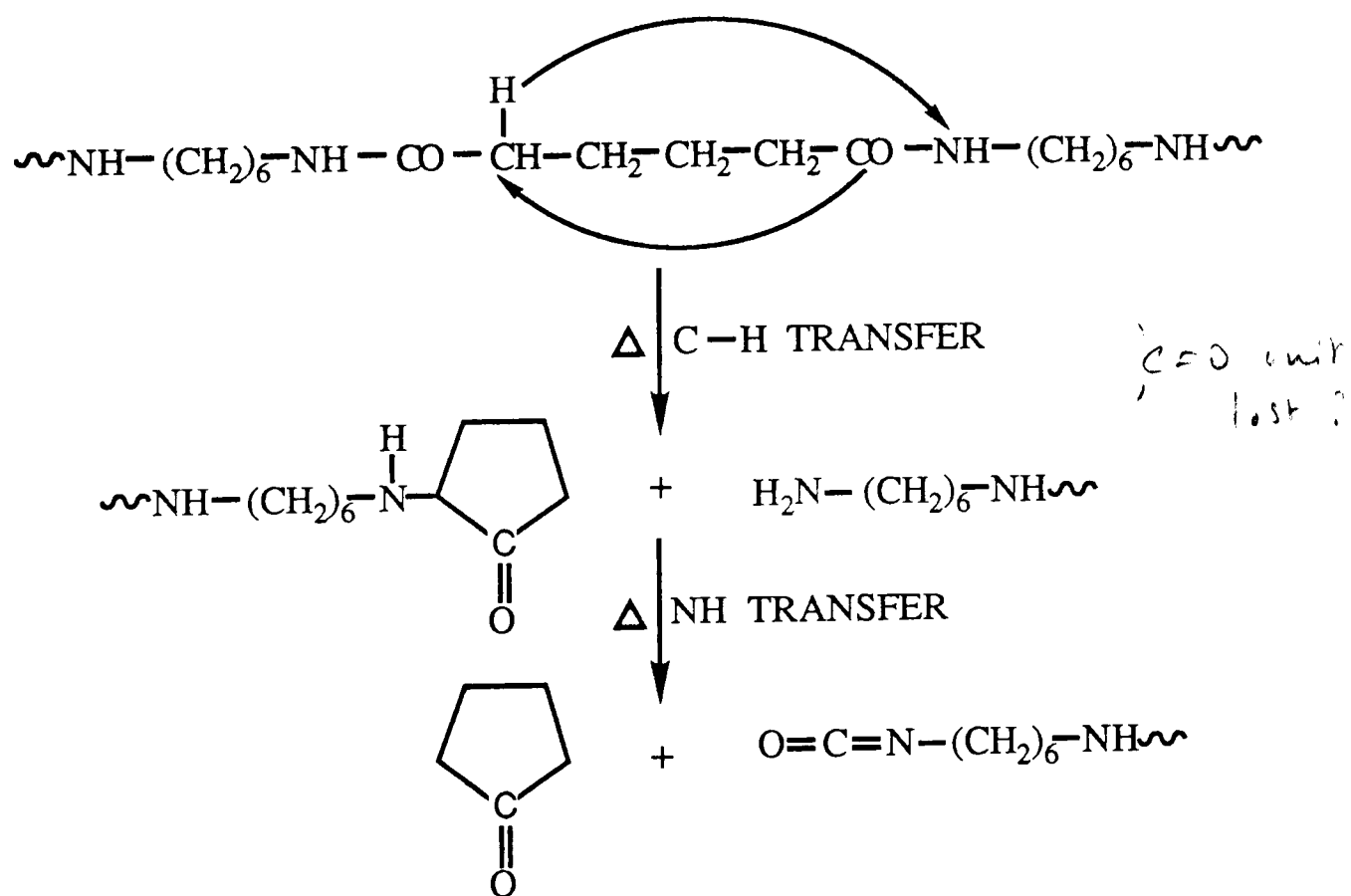
Dussel had employed Field Ionization Mass Spectrometry (FI-MS) to assign structure (i) to a peak at m/z 226, corresponding to the molecular weight of the repeating unit of the polymer, but could not assign peaks for compounds (ii) and (iii).

Scheme 2.5 :- β - Hydrogen Transfer Reaction as Suggested by Dussel et al.



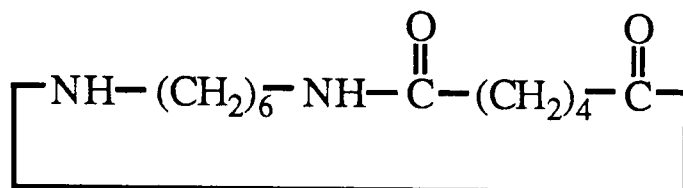
According to Ballistreri et al, the primary thermal products further decomposed or reacted with formation of cyclopentanone, aminohexamethylene isocyanate and compounds bearing amine and/or Schiff base groups (Scheme 2.6).

Scheme 2.6 :- Ballistreri's Degradation Mechanism for Nylon 6,6.



Ballistreri et al concluded that the presence of the peak at m/z 226 was due to cyclic monomer (Figure 2.3) formed during polymerization, as suggested by Peebles et al [70] and not during the degradation of nylon 6,6 via a β C-H hydrogen transfer process.

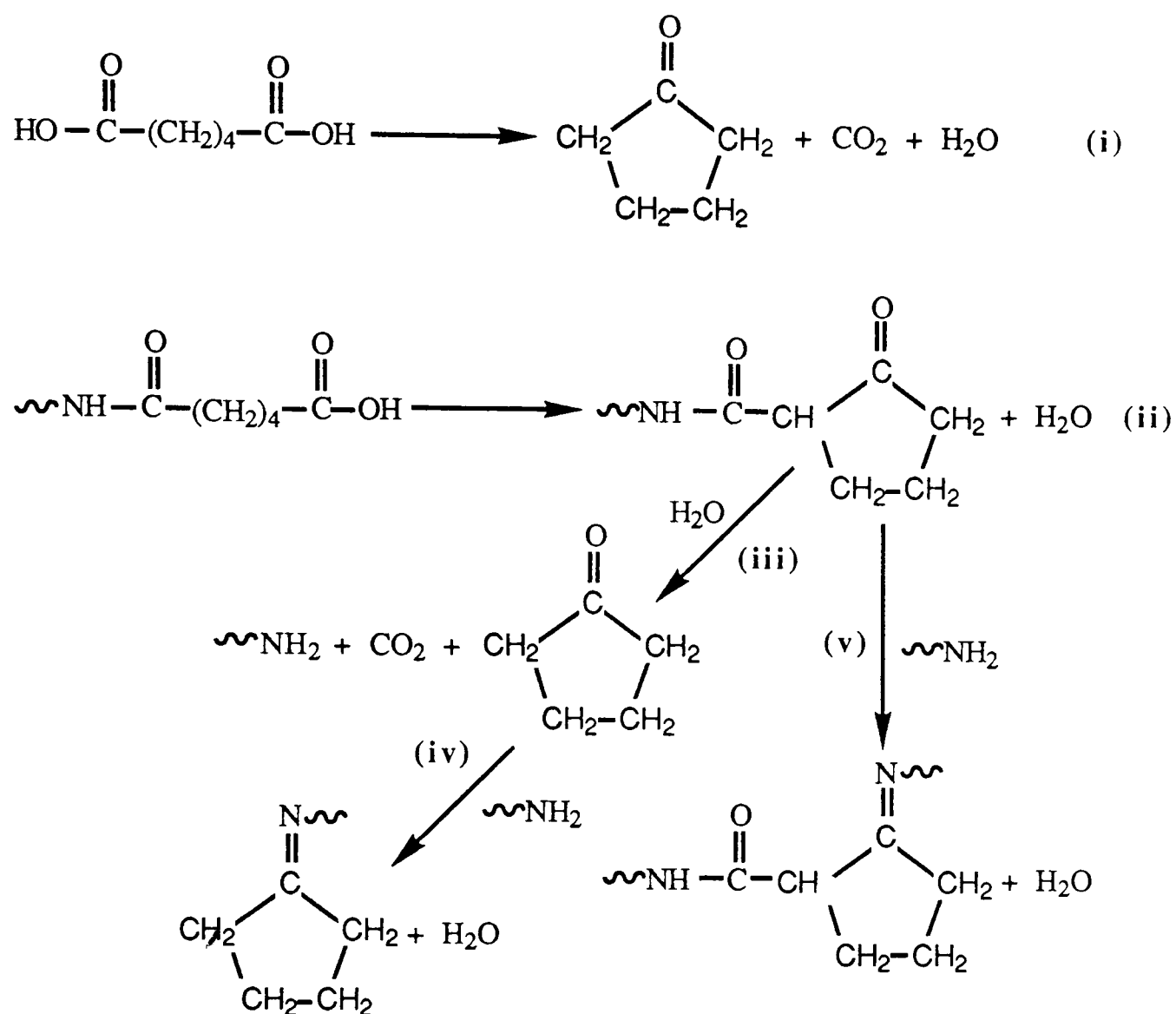
Figure 2.3 :- Cyclic Monomer of Nylon 6,6 Formed During Polymerization.



It is clear to see that over the last two decades or so there have been many suggestions for the degradation mechanism for polyamides. Most recently, a simplified reaction scheme (Scheme 2.7) for polyamide degradation, that is consistent with all chemically feasible reactions, was proposed by Steppan, Doherty and Malone [71].

Work spanning over 50 years was compiled to give a brief, but accurate account of the degradation mechanisms related to nylon 6,6. The initial investigations based on the cyclization of adipic acid [72], which lead to Sweeney and Zimmermans' [73] suggested analog of reaction (i) to give cyclopentanone derivatives as in reaction (ii), were followed by Achhammer, Reinhart and Klines' suggestion that the cyclopentyl chain end produced by reaction (ii) may continue to degrade to give rise to an amino end group, cyclopentanone and carbon dioxide as in reaction (iii). They continued their comprehensive review with Ballistreri et als' [68] confirmation of the formation of a Schiff base and water from the subsequent reaction of an amino end group with cyclopentanone as in reaction (iv), then Twilley's [74] suggestion of the same reaction, but from a cyclopentyl end group as in reaction (v).

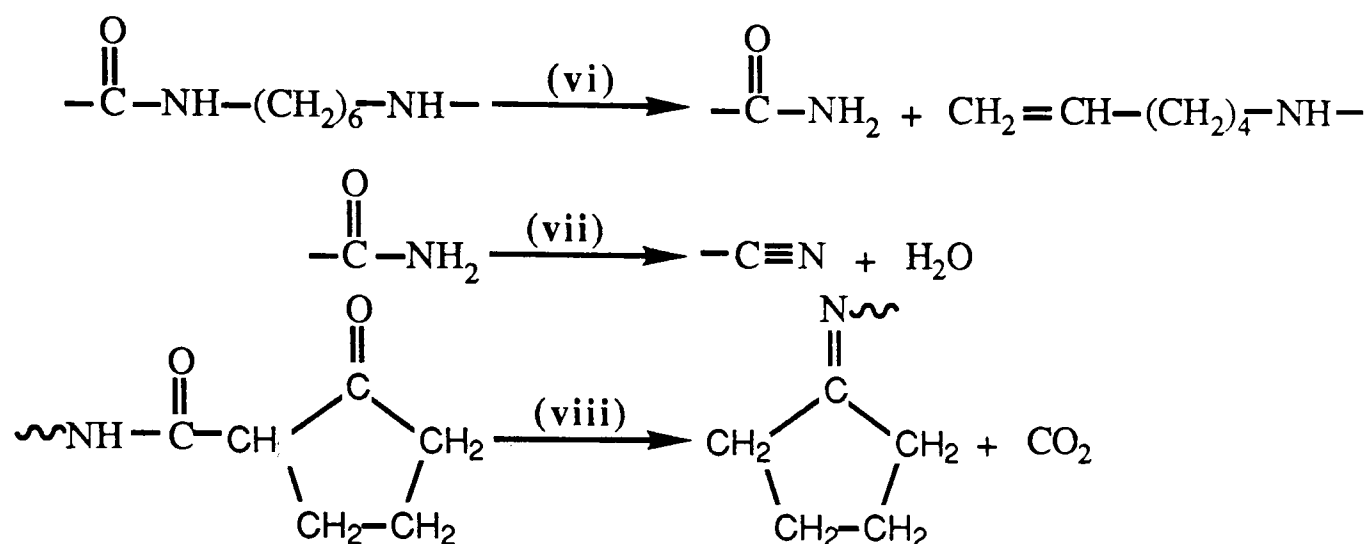
Scheme 2.7 :-Degradation Mechanisms for Nylon 6,6 Compiled by Steppan et al.



Also discussed are the reactions proposed by Kamerbeek [56] who suggested the weakest bond in the polyamide is broken at high temperature to form an olefinic end and a primary amide end. The latter is not stable and rapidly decomposes to give rise to a nitrile and water, as in reactions (vi) and (vii).

Wiloth and Schindlers' [75] mechanism is also discussed, which shows how carbon dioxide and a Schiff base may be produced by a unimolecular mechanism from a cyclopentyl end group produced from reaction (ii), as in reaction (viii) (Scheme 2.8).

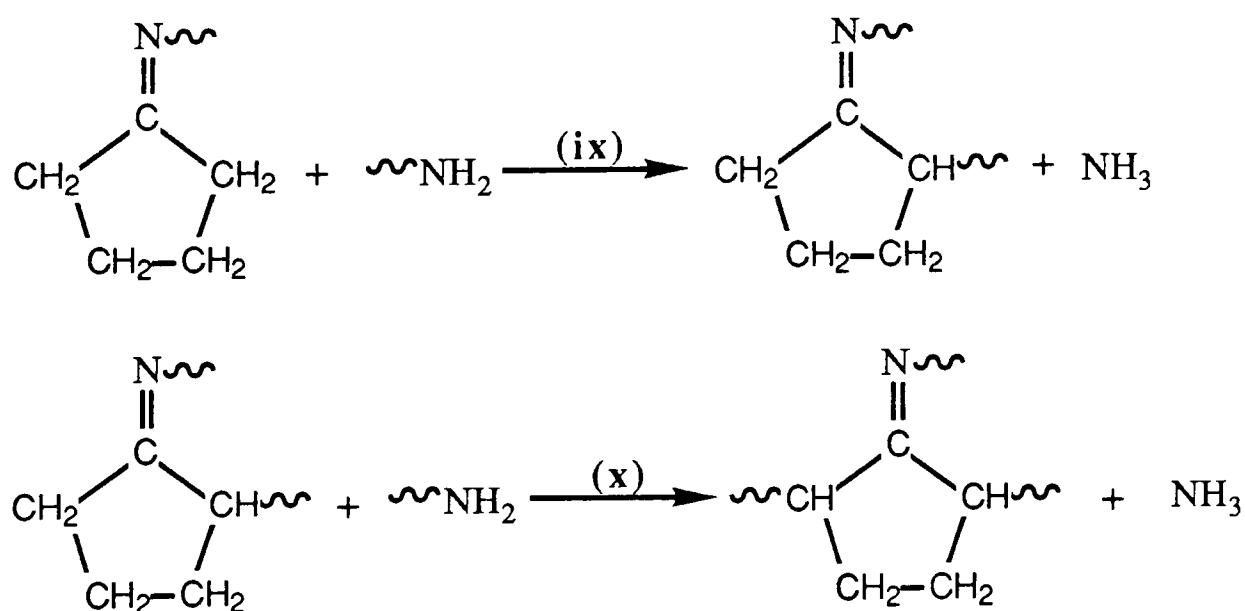
Scheme 2.8 :- Degradation Mechanisms Proposed by Kamerbeek and Wiloth et al.



With respect to crosslinking, two candidate crosslinking routes were reviewed. Ravens and Sisley [76] found that if a significant amount of water was present, there would be an appreciable amount of free amine and carboxyl groups from the reversible main amidation reaction. The amine end groups may combine and subsequently react with carboxyl end groups to form crosslinks.

Also Wiloth [75] reported that the Schiff base formed via reactions (iv), (v) and (viii) may subsequently react to form a variety of products including a crosslink (Scheme 2.9).

Scheme 2.9 :- Crosslinking Mechanisms as Proposed by Wiloth.



2.3 OXIDATIVE DEGRADATION OF POLYAMIDES.

2.3.1 Introduction.

All organic compounds are susceptible to attack by molecular oxygen, a process referred to as *Autoxidation*. In an oxygenated atmosphere, e.g. air, polymers, including polyamides, are oxidized, degraded to some extent and crosslinked. Often various low molecular weight products are evolved and groups containing oxygen (hydroxy, peroxide, carbonyl, aldehyde etc) are formed along the polymer chain or at the ends.

The rate of oxidation of most polymers is usually very small without U.V. radiation at ambient temperature. Since the oxidative degradation of polymers is a radical reaction, under such conditions, the rate of production of initiating radicals is very small, resulting in the low rate of oxidation. The free radical chain reaction can however be initiated either thermally, photochemically, mechanically or by radiation from high energy sources such as γ rays. Also, small amounts of peroxide, oxygenated compounds and impurities incorporated into the polymer during the course of processing, may have a significant effect on the rate of initiation and overall rate of oxidation.

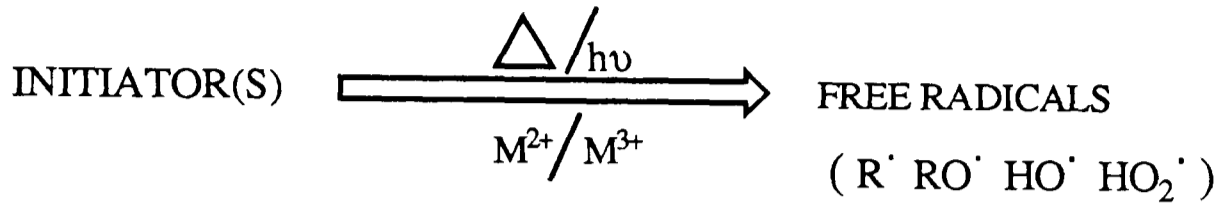
Thus, to obtain a better idea of the mechanisms involved with the oxidation of a polymer, accelerated experiments at elevated temperatures are often conducted, a process more commonly referred to as *Thermal Oxidation* or *Thermo-oxidation*.

2.3.2 Mechanisms in Polyamide Oxidation.

The oxidative degradation of polymers is a radical reaction and like other radical reactions it proceeds via a free radical chain mechanism consisting of three stages, initiation, propagation and termination. Included is an intermediate stage which may occur, referred to as branching. Of the suggested chain initiators, the hydroperoxide group is most likely to cause the greatest damage (Figure 2.4).

Figure 2.4 :- Mechanisms for the Thermo-oxidative and Photo-oxidative Degradation of Polymers.

CHAIN INITIATION :-

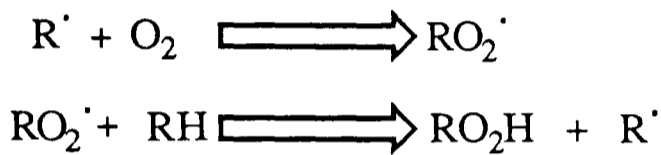


Δ = THERMAL ENERGY

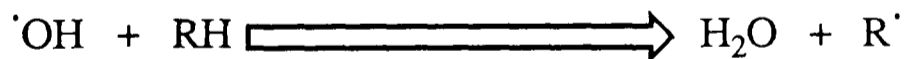
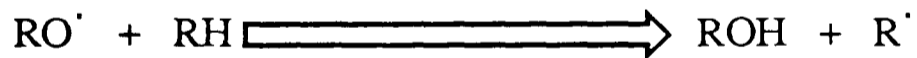
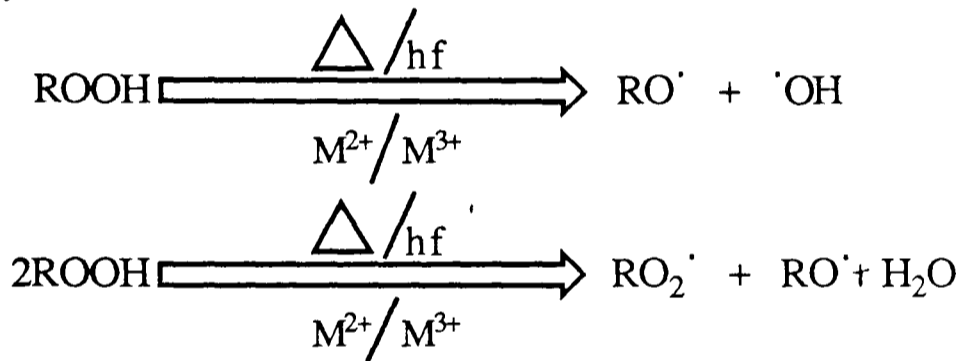
$h\nu$ = LIGHT ENERGY

$\text{M}^{2+}/\text{M}^{3+}$ = ONE ELECTRON CHANGE OF SUITABLE METAL ION
e.g. Fe^{2+} and Fe^{3+}

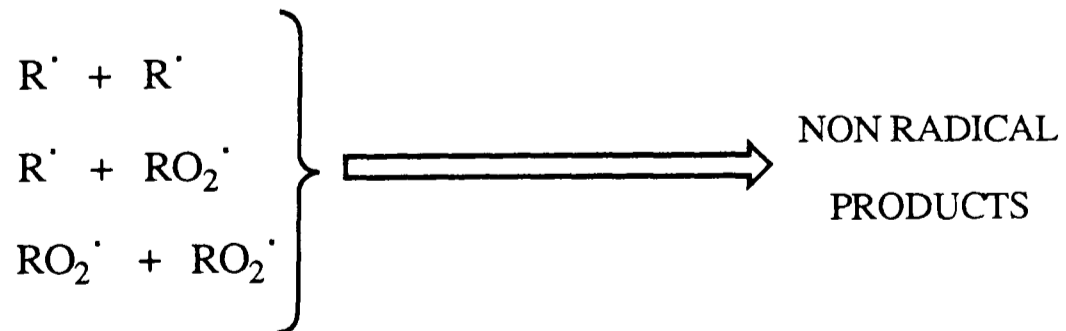
CHAIN PROPAGATION :-



CHAIN BRANCHING :-

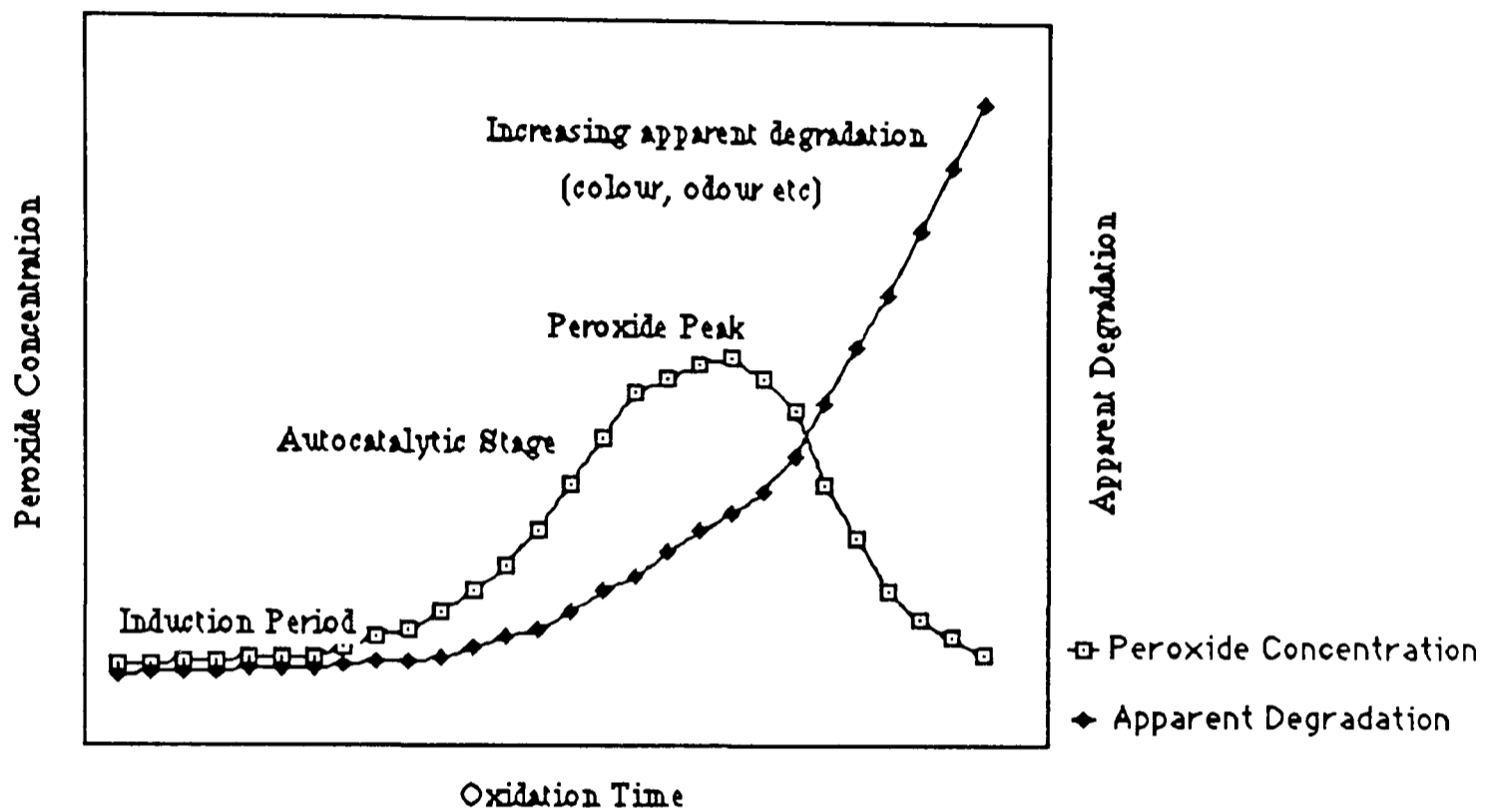


CHAIN TERMINATION :-



The exposure of a polymer to oxygen is characterized by an induction period, during which the polymer does not show any obvious changes and therefore there is no evidence of oxygen absorption (Figure 2.5).[77]

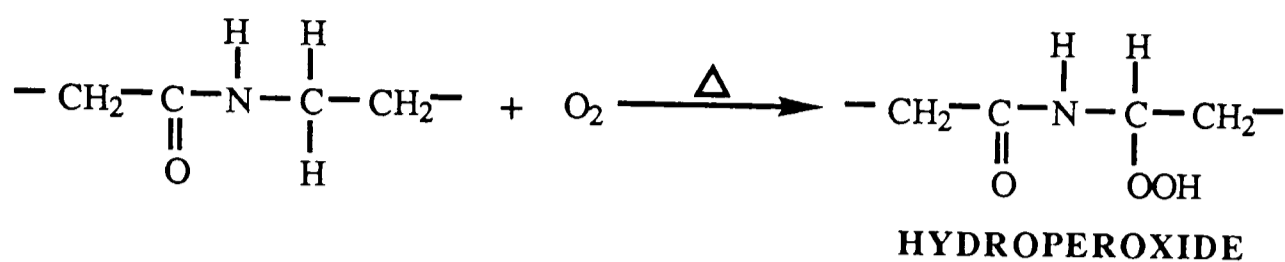
Figure 2.5 :- Schematic Diagram showing how the Concentration of Peroxide and Apparent Degradation Varies with Increased Oxidation.



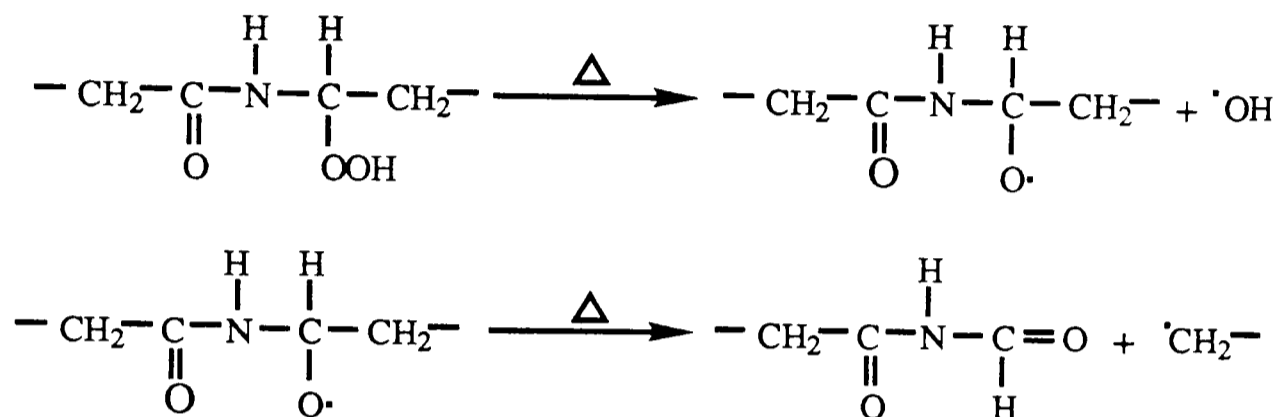
However, it is during this stage that small amounts of hydroperoxide are formed and initiate the subsequent rapid autoxidation of the polymer. If during processing the polymer has been thermally oxidized to some extent, then a significant quantity of hydroperoxide will be present in the polymer, resulting in a reduced induction period and accelerated autoxidation period. The appearance of impurities such as metal salt catalysts or carbonyl groups also catalyse oxidation and can sometimes cause oxidation to commence immediately without an induction period.

However, it was only when Sharkey and Mochel [78] conducted their work using C_{14} labelled model compounds that a realistic mechanism could be suggested to determine the position of attack on the polymer chain. The methylene group adjacent to the N-H of the amide group was considered the labile point of attack, more specifically the proton on this methylene group.

At elevated temperatures (>120°C) the following mechanism was thought to predominate :-



Decomposition of the hydroperoxide leads to the scission of the polymer chain.



Polymers which are in daily use, are often utilized in damp, oxidative conditions. It is therefore very important to gain a better understanding of the thermal degradative nature of the polymer in an environment relevant to the conditions it is most likely to encounter while in operation, as this way an idea of when and where the polymer fails can be concluded.

Studies into the thermo-oxidative degradation of polyamides, especially nylon 6,6 have been conducted in such conditions over the last 30 years or so. It was Schwenker [79] who first reported the influence of oxygen on the thermal degradation of nylon 6,6 using D.T.A. In air a sample of polyamide showed an initial weak endotherm at 100°C due to the loss of water, an exothermic reaction starting at 185°C, followed by an endotherm at 255°C due to the polymer melting. This exotherm was absent when conducted in an oxygen free atmosphere (N₂), suggesting this reaction was due to the oxidation of the polymer.

Following these initial observations, a vast number of polyamide oxidative investigations were reported. Valko et al [80] observed a drop in molecular weight when nylon 6,6 fibres were air oxidized at 130-215°C, although there was no change in the acid end groups and a decrease in amine end groups. However, an increase in molecular weight was noted when heating was conducted in an inert atmosphere, or in the presence of an anti-oxidant. They concluded that under these conditions chain linking (polymerization) predominated over thermal chain scission (depolymerization).

Later Valk [81], often mistaken for Valko, studied the thermal oxidation of nylon 6 fibres at 200°C for 3 hours. With his co-workers he was able to identify a series of monocarboxylic and dicarboxylic acids using a number of chromatography techniques after they had hydrolysed the degraded polyamide. Valeric and adipic acids were found to be the main constituents, which could have been attributed to the decomposition of the hydroperoxide formed by the attack of oxygen on the N-vicinal methylene group as earlier proposed by Sharkey and Mochel [78]. However, their suggested conclusions were not fully justified as a series of amines were also identified in the hydrolysis products, suggesting an alternative degradation mechanism running simultaneously with the mechanism suggested by Sharkey and Mochel.

Following on, Harding and MacNulty [82] carried out a number of experiments to determine the influence of moisture on the thermal oxidation of nylon 6,6 bars. Conducted in the dark to exclude photochemical effects, their results indicated that with the presence of moisture, there was a detrimental effect on the polymer's stability. Using the criterion of embrittlement (tensile strength loss of 80%) as an indication of the degree of oxidation, it was found that the embrittlement time for nylon 6,6 fell as either the temperature or moisture content was raised.

e.g. dry 70°C embrittlement time = 2 years
 wet 70°C embrittlement time = 8 weeks
 dry 100°C embrittlement time = 7 days

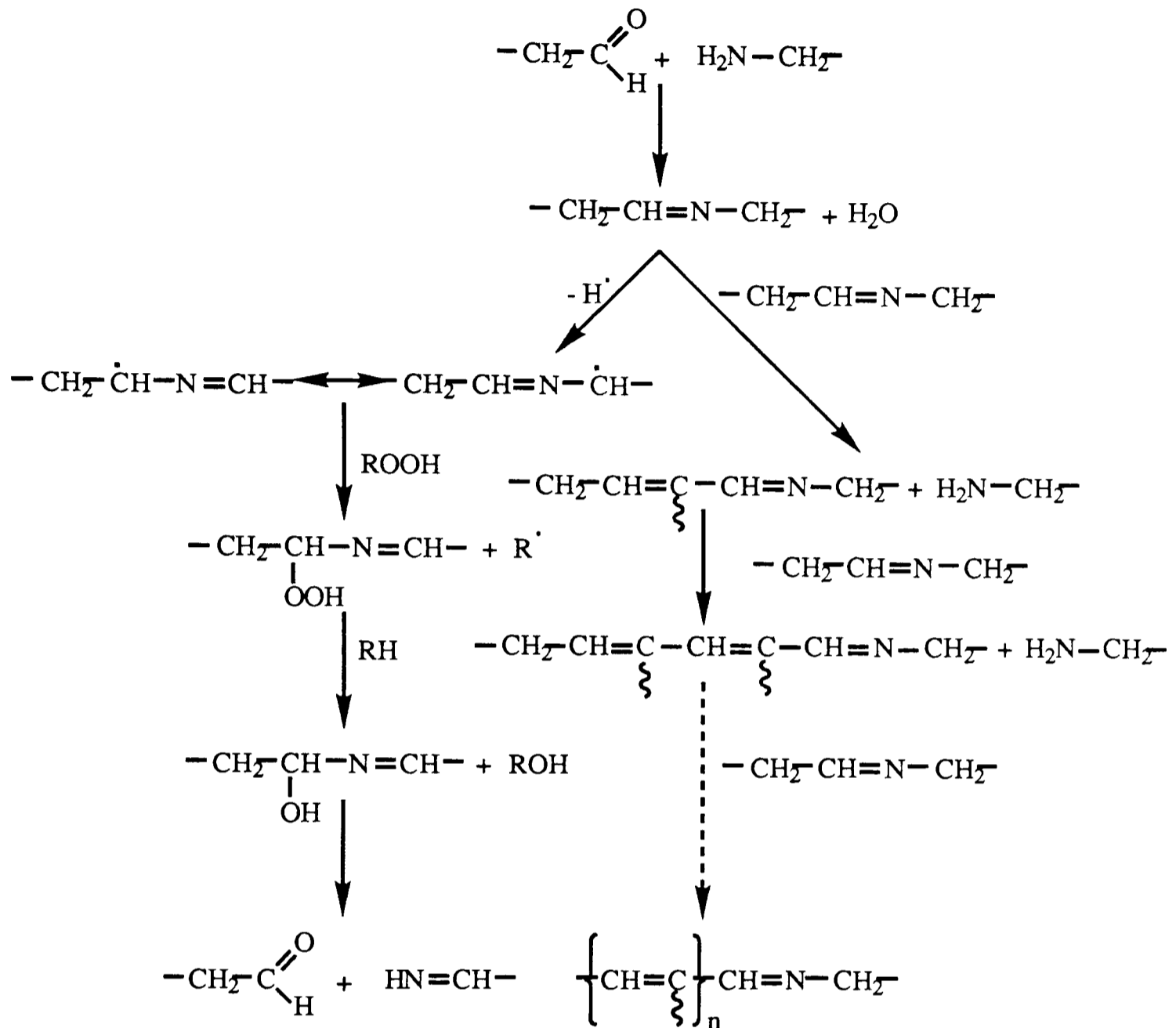
From these observations, an activation energy for oxidation of 93.2kJmol^{-1} was calculated which was not very similar to the one of 113kJmol^{-1} later reported by Sweeny [73].

Mikolajewski et al [83] continued their research in this field and found that the molecular weight of an oxidized polyamide bar was inconsistent throughout its cross section. On the surface they found a drop in molecular weight compared to the higher molecular weight for the core of the bar.

They postulated that the moisture facilitated the diffusion of the oxygen into the polymer bars by disrupting the hydrogen bonding in the amorphous region of the polymer, hence the lowering of the embrittlement time.

Most recently, in dedication to Professor Dr. H. Sinn, on the occasion of his 60th birthday, Ties Karstens and Volker Rossbach explored the thermo-oxidative degradation of polyamide 6 and polyamide 6,6, more specifically the kinetics [84] and structure, using U.V. spectroscopy [85] of the formation and inhibition of U.V./VIS.active chromophores. In their first paper, they suggested the formation of azomethine groups (Schiff's bases) (Scheme 2.10), which were formed as a result of the reaction of aldehyde and ketocarbonyl groups with amino end groups, from the thermal oxidation of polyamide 6 and polyamide 6,6.

Scheme 2.10 :- Azomethine Mechanism According to Karstens and Rossbach.



Karstens and Rossbach found that the Schiff's bases reacted with each other in an aldol-type condensation to give rise to conjugated unsaturated oligoimine structures that absorb in the U.V./VIS. range. They also concluded in their mechanism that during the aldol condensation, the amino end groups were regenerated allowing them to react once again with carbonyl groups, which were constantly being formed during the course of polymer degradation.

With the aid of a kinetic model, they calculated the concentration and sequence length distribution of the individual oligoimine structures and later found that these figures were in agreement with those found experimentally using U.V. spectroscopy.

2.4 PHOTODEGRADATION OF POLYAMIDES.

2.4.1 Introduction.

It has been apparent for many years that the phenomenon of photodegradation commences as soon as the polymer is processed. The problems caused by photodegradation are therefore at least as old as the discovery of the first polymer itself.

As the name implies, photodegradation refers to the detrimental effect on the properties of a polymer when subjected to light radiation. These often take the form of discolouration, cracking and loss of tensile properties to name a few.

Of the types of photodegradation possible, degradation caused by U.V. light has always been of greatest importance with regards to practical applications, as this source of light energy utilized in an oxygenated environment most resembles the conditions likely to be encountered in outdoor weathering. For this reason, degradation of this sort is commonly referred to as *Photo-oxidation*.

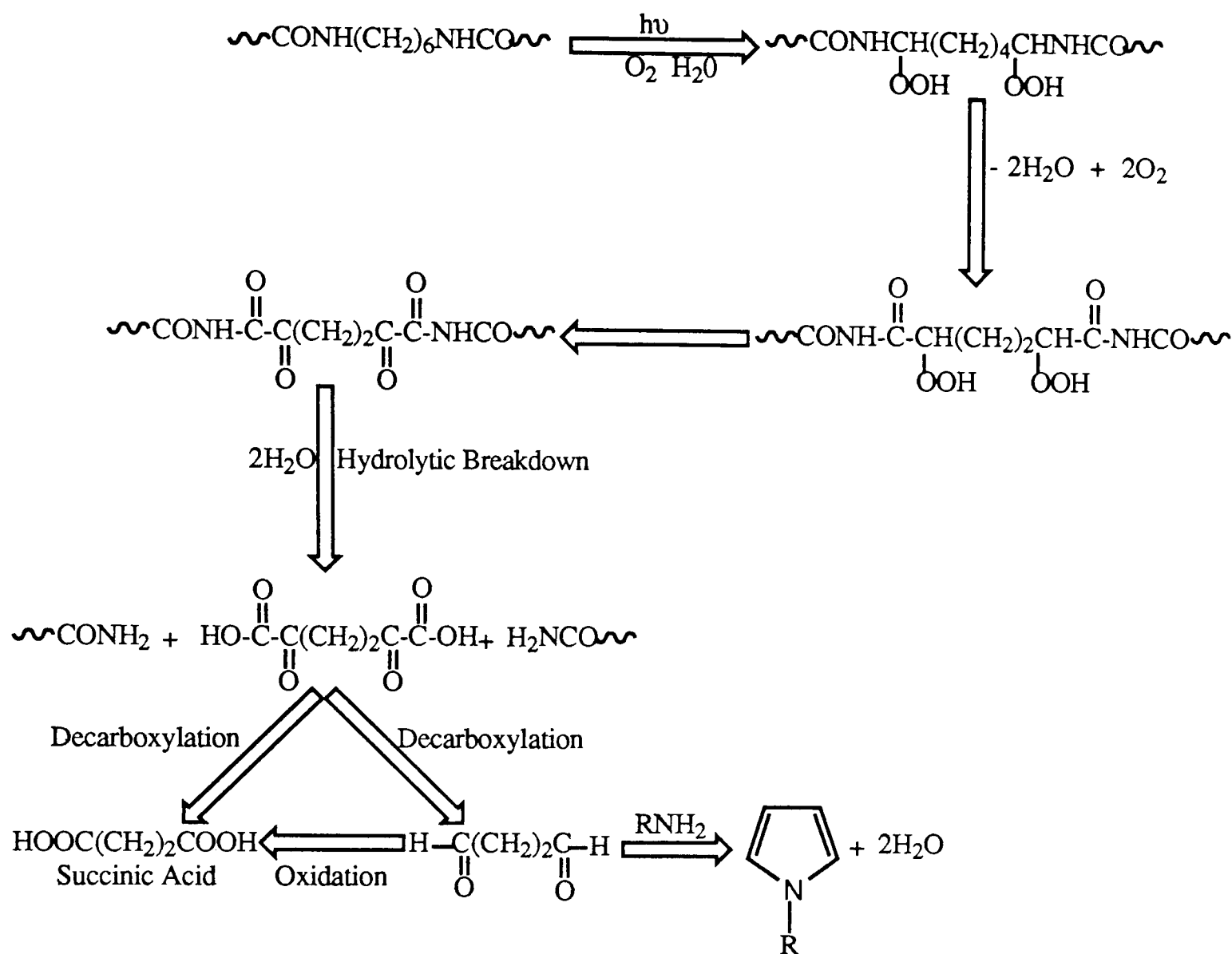
Many of the mechanisms encountered in the photo-oxidation of polymers are similar to those of thermal oxidation in that it is believed that both proceed via a free radical chain mechanism [86]. However, a number of differences have been identified, one being the dissimilarity in the length of the oxidative chains in the propagation phase; in thermal oxidation it is much shorter due to more complex reactions. Also, it is well known that with a photo-oxidized polymer, the influence of U.V. radiation is predominantly a surface phenomenon and does not ordinarily permeate through into the bulk of the polymer. With thermally oxidized polymers, degradation will continue throughout the whole of the polymer.

2.4.1.1 Yellowing.

Yellowing of polymers, including polyamides, is an important factor influencing their appearance. Exposure to light and heat more often than not results in discolouration, which is normally caused by the build up of degradation products. Light is absorbed by the polymer at the blue end of the visible spectrum which in turn gives the yellow appearance. For polyamides such as nylon 6,6, many nitrogen containing products such as imides, imines and pyrroles are formed which cause increased absorption in the blue part of the visible spectrum, hence the discolouration. It is therefore of vital importance to gain a better understanding into the reactions involved with polymer degradation especially photodegradation to try to eliminate these problems.

Of the many publications relating to the yellowing of polyamides, Marek and Lerch [87] attributed this phenomenon to the formation of pyrrole-type compounds. They suggested that the dialdehydes and diketones formed during degradation from hydroperoxide groups subsequently reacted with amine groups to give the pyrrole-type compounds (Scheme 2.11).

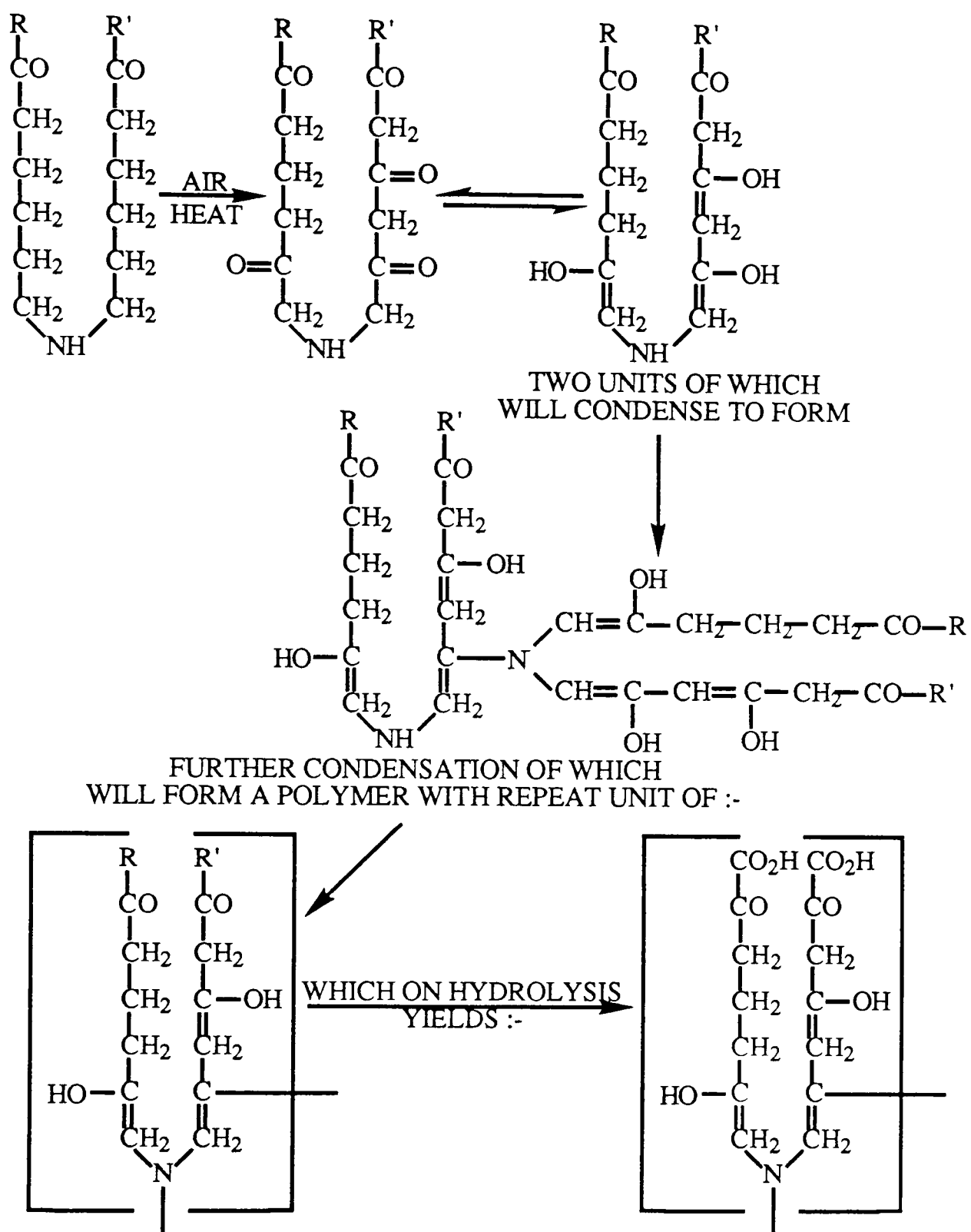
Scheme 2.11:- Pyrrole-Type Compounds Formed from the Photo-oxidation of Nylons.



However, East et al [88] later tentatively proposed that the yellowing of the polyamides was not necessarily based on the formation of derivatives of pyrrole and suggested an alternative concept whereby polymers of variable molecular weight containing chromophores of variable wavelength and of slight different chemical composition were formed.

Consequently, a number of mechanisms were suggested for their formation assuming that the chemical principles elucidated for the oxidation of pyrrolidine were valid for the oxidation of nylon (Figure 2.21).

Figure 2.12:- Yellowing Mechanisms Suggested by East et al.



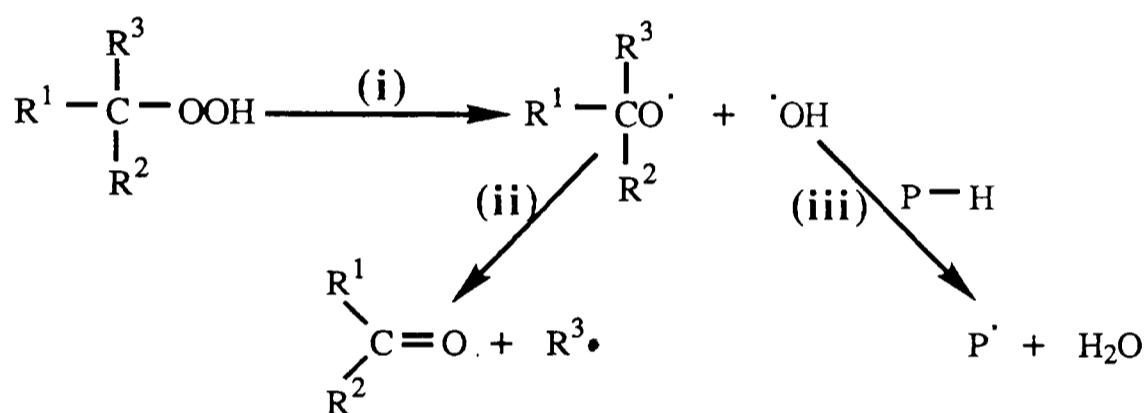
2.4.2 Mechanisms in Photo-oxidation.

The mechanisms involved with the photo-oxidation of polymers are conveniently subdivided into two types depending on the mode of U.V. absorption [89]. Firstly, there are, for example, most aliphatic polymers, which tend to absorb light through *Impurity Chromophores*, usually established during processing. Then there are, for example, aromatic polymers, which tend to absorb light directly via the aromatic units already making up the *Polymer Constitution*.

2.4.2.1 Impurity Chromophores.

Of the several impurity chromophores identified, the peroxide or hydroperoxide group is probably the one most studied. Incorporated into the polymer during manufacturing by the well demonstrated Bolland-Gee auto-oxidation mechanism [90], these impurities can absorb light up to 380nm in the near U.V. region, causing bond scission and producing alkoxy and hydroxy free radicals (i). These in turn start a free radical chain mechanism via hydrogen atom abstraction, giving rise to macroketones or aldehydes (ii) and water (iii) respectively, the former being formed by free radical β -scission (Scheme 2.13).

Scheme 2.13 - Formation and Reactions of Alkoxy and Hydroxy Free Radicals.



Of the many researchers who have worked in this field of study, Allen and his coworkers have been particularly productive in their investigations. Most recently, Allen reviewed all aspects of the photo-oxidation and stabilization of polymers, including his discussion of the role of the hydroperoxide groups during photo-oxidation of polymers. His results revealed that during the processing time of the polymer, an increase in hydroperoxide groups was observed with a consequent decrease in light stability [91]. Furthermore, extraction of these hydroperoxide groups gave rise to a vast improvement in light stability, suggesting these units were in some way responsible for the photo-oxidation of the polymer. Nevertheless, complete stabilization was not obtained, implying other chromophores present in the polymer continuing the photodegradation process.

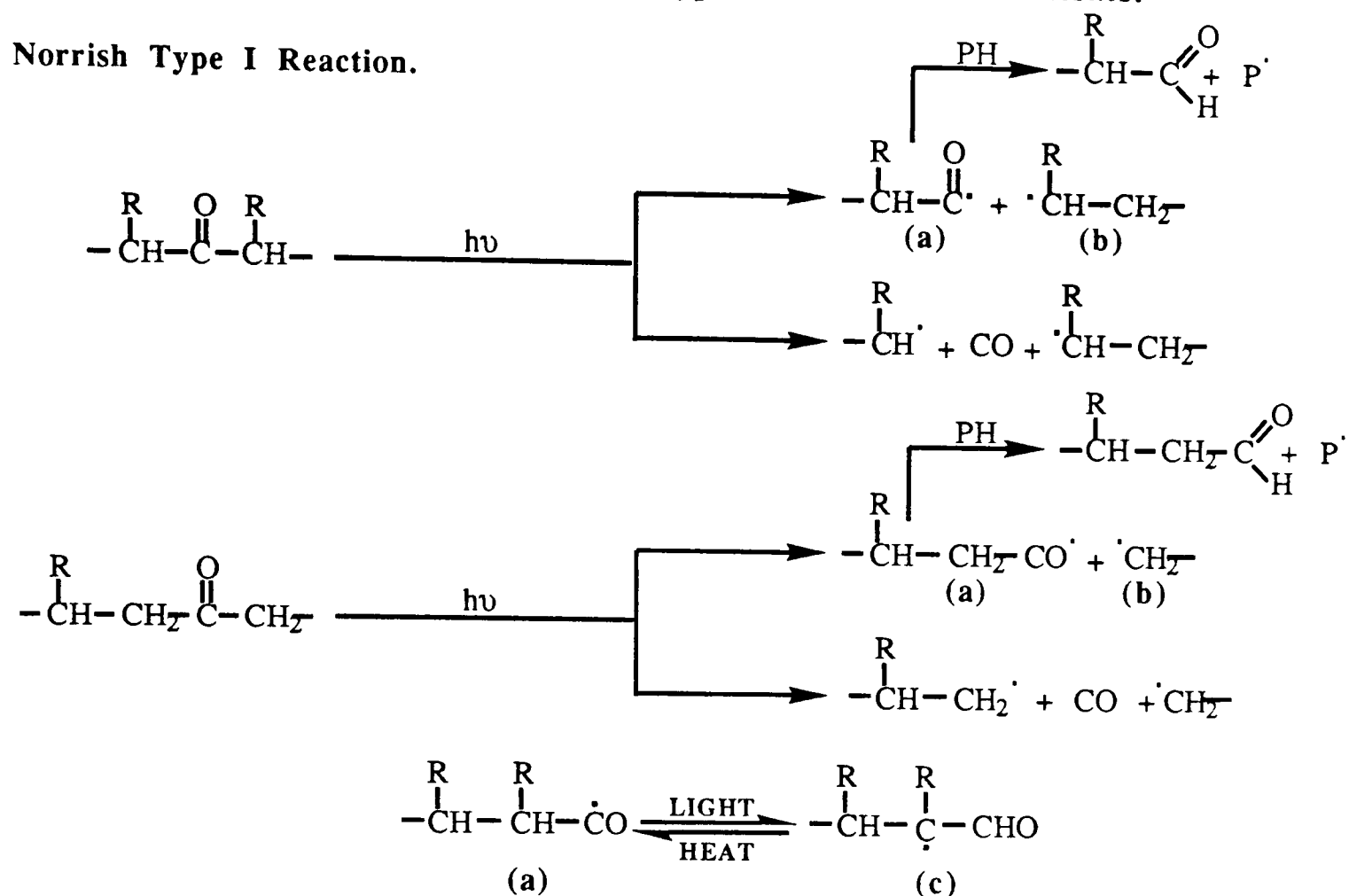
The carbonyl group was thought also to contribute as a photoinitiator towards the photolysis of many polymers. Based on the photochemical reactions of liquid-phase aliphatic ketones, investigated by Bamford and Norrish [92], Norrish Type I and Type II mechanisms were also suggested for polymeric systems. It was only when early investigators proposed mechanisms derived from ketone scission reactions, that a better understanding into the degradation routes associated with photo-oxidation were established (Scheme 2.13). By definition, Norrish reactions Type I and Type II are the photochemical reactions of the excited carbonyl group and in the case of polymers these give rise to degradation of the macromolecule [93].

With Type I reactions, homolytic cleavage occurs between the carbonyl carbon and an α -carbon, a process commonly called α -cleavage. It was Cicchetti [94] who showed that the precursors of this reaction were both the excited singlet and excited triplet state of ketones. Photolysis of ketones generates free radicals, hence chain scission via Type I reactions. Free radicals (a) and (b) are formed by U.V. radiation from carbonyl groups situated at chain ends or along the polymer chain and were identified by Hama et al [95] using ESR measurements. At a wavelength below 650nm another acyl radical was recognised. Derived from radical (a), the new radical (c) may either combine or disproportionate thereby causing no further damage, or combine with oxygen to give a peroxide radical [96].

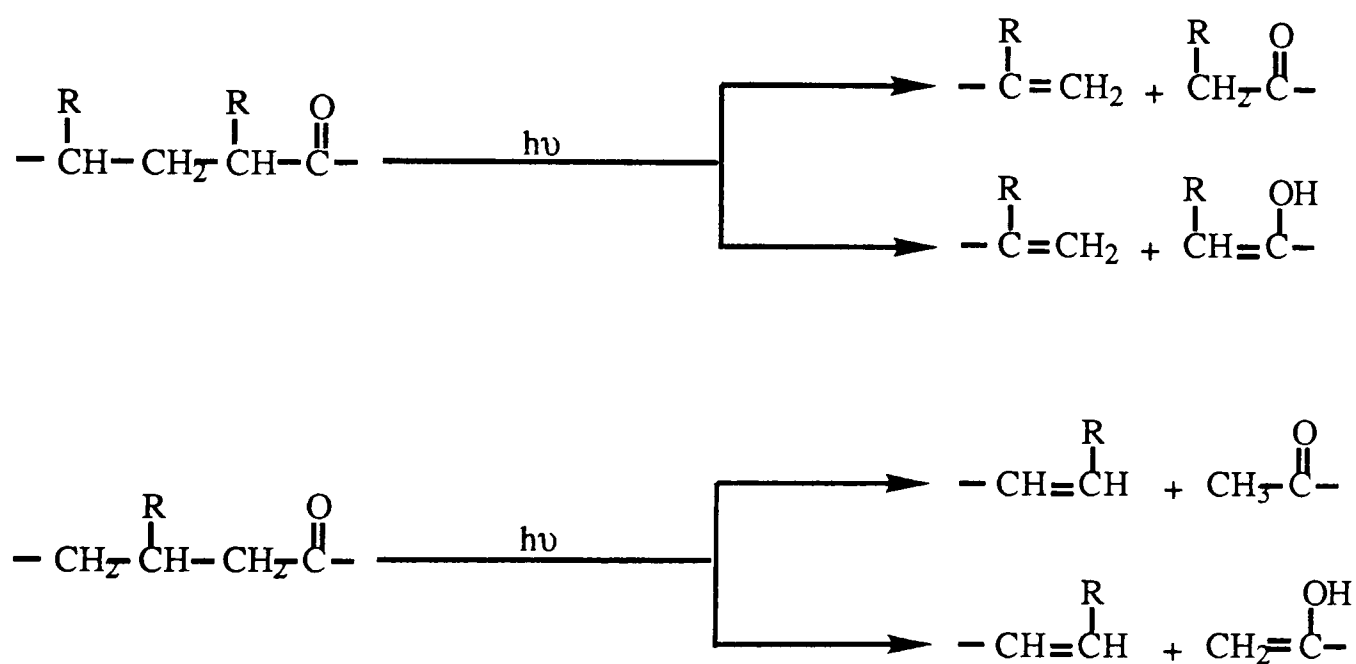
Norrish Type II reactions may occur if the ketone has at least one hydrogen atom on the carbon atom in the γ position relative to the carbonyl group and involves intramolecular hydrogen transfer, yielding an olefin and a ketone via an enol. In contrast to Type I reactions, it is noted that Type II reactions do not directly produce free radicals, hence are not as destructive as Type I, which can induce further degradation.

Scheme 2.14 :- Norrish Type I and II Mechanisms.

Norrish Type I Reaction.



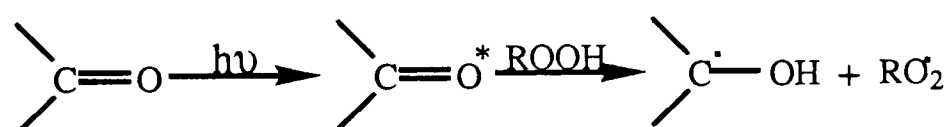
Norrish Type II Reaction.



Hartley and Guillet [97], using quantum yield studies, also proposed that a polymer having in its structure a hydrogen at a gamma carbon would favour a Norrish Type II reaction. If not, a Norrish Type I reaction would proceed, which was considered to be the case for polyethylene where carbonyl groups, thought to be present in the structure as impurities formed during processing, were the major sites for U.V. absorption and consequent chain scission. This would explain why polyethylene absorbs in the U.V. region and has rapid photo-oxidation.

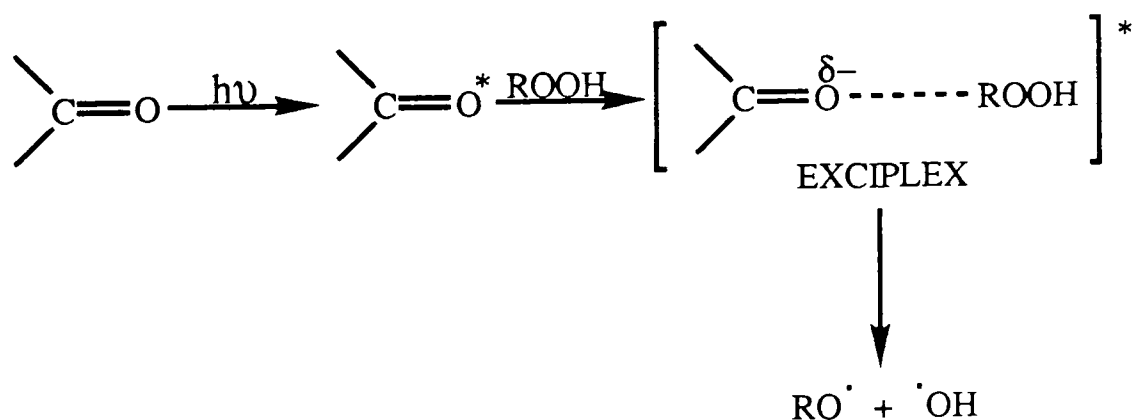
Nevertheless, dispute still reigned with respect to the relationship between hydroperoxide and carbonyl groups and in particular their participations in the photo-oxidation of polymers. Many scientists believed the hydroperoxide remained labile in the absence of carbonyl groups. Thus Stewart et al [98] proposed that primary light absorption was achieved via carbonyl groups, which in turn transferred this energy to the hydroperoxide groups activating them. Unfortunately, their mechanism was supported only from experimentation conducted on model compounds and not so much from solid phase polyolefins, causing more controversy. Instead, an alternative mechanism for polymers suggested photoexcited aliphatic ketones could abstract a hydrogen from the hydroperoxide group resulting in a peroxy free radical (Scheme 2.15).

Scheme 2.15 :- Peroxy Free Radical According to Stewart et al.



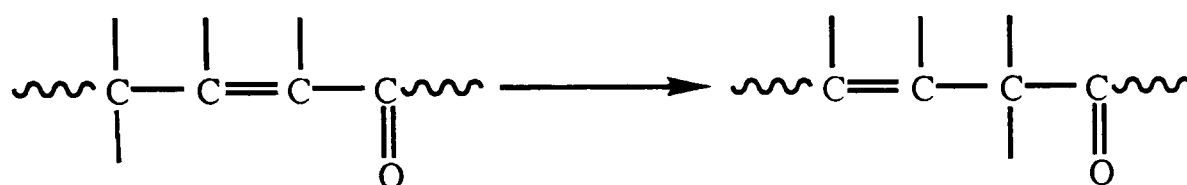
Alternatively, Ng and Guillet [99] suggested their "Exciplex Mechanism" formed from a carbonyl and hydroperoxide group. They claimed a mechanism whereby the resulting exciplex could dissociate more efficiently than the hydroperoxide alone (Scheme 2.16).

Scheme 2.16 :- Exciplex Mechanism as Proposed by Ng and Guillet.



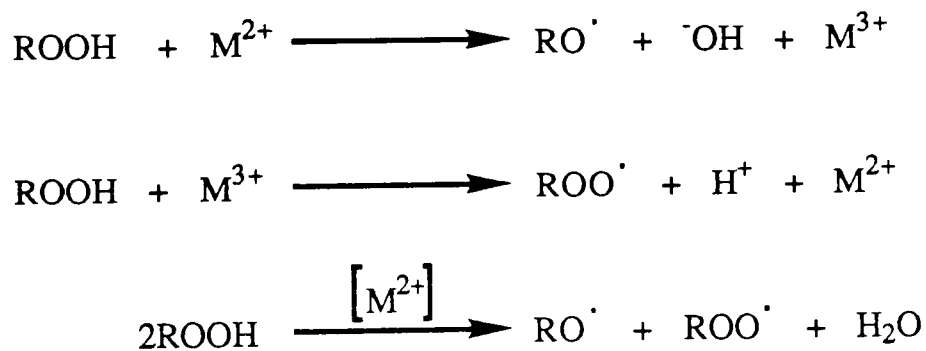
Of the many recent publications on the photoinitiators in the oxidative photolysis of polymers, Allen [100] has positively identified α,β -unsaturated carbonyl groups. It is now understood that the aliphatic α,β -unsaturated carbonyl groups initially rearrange to form β,γ -unsaturated carbonyl groups (Scheme 2.17), which can react further via Norrish Type I and II reactions resulting in non-luminescent products.

Scheme 2.17 :- Formation of β,γ -Unsaturated Carbonyl Group.



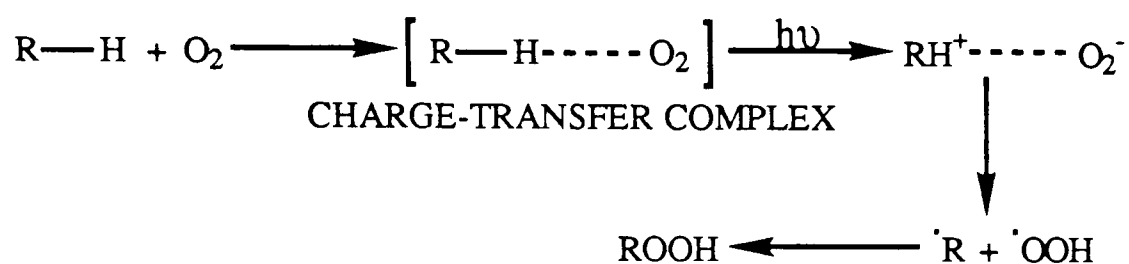
Other impurity chromophores of less importance include the incorporation of trace transition metals, which can absorb light and produce free radicals via an electron transfer process, or occasionally even catalyse the decomposition of hydroperoxides into alkoxy and peroxy radicals (Scheme 2.18).

Scheme 2.18 :- Formation of Alkoxy and Peroxy Radicals from the Decomposition of Hydroperoxide Groups Catalysed by Transition Metals.



Most recently, the polymer-oxygen charge transfer complex theory has been suggested as another chromophore for initiation. Based on work conducted by Chien [101], the mechanism entails the formation of a polymer-oxygen charge transfer complex when the polymer is saturated with oxygen gas. This complex subsequently forms a hydroperoxide group after absorption of a quantum of U.V. light (Scheme 2.19).

Scheme 2.19 :- Polymer-Oxygen Charge Transfer Complex Mechanism.



Guillet [102] reviewed the data responsible for some of the conflicting theories suggested and concluded that photolysis was initiated by free radicals formed after either a hydroperoxide or carbonyl group absorbed a quantum of U.V. energy. He proposed the reaction then continued by a radical initiated chain mechanism, being propagated by the decomposition of hydroperoxides, followed by the rapid formation of carbonyl groups. Carbonyl groups were found to absorb U.V. light much more efficiently than hydroperoxide groups, thus it appeared that these groups were responsible for primary U.V. energy absorption. The fact that the concentration of the hydroperoxide was very low in comparison to carbonyl groups suggested that the latter would be responsible for the induced decomposition of the former. Also, hydroperoxide sensitization by carbonyl groups supported a free radical chain mechanism similar to that of thermal oxidation, evidence in favour of the suggested mechanism.

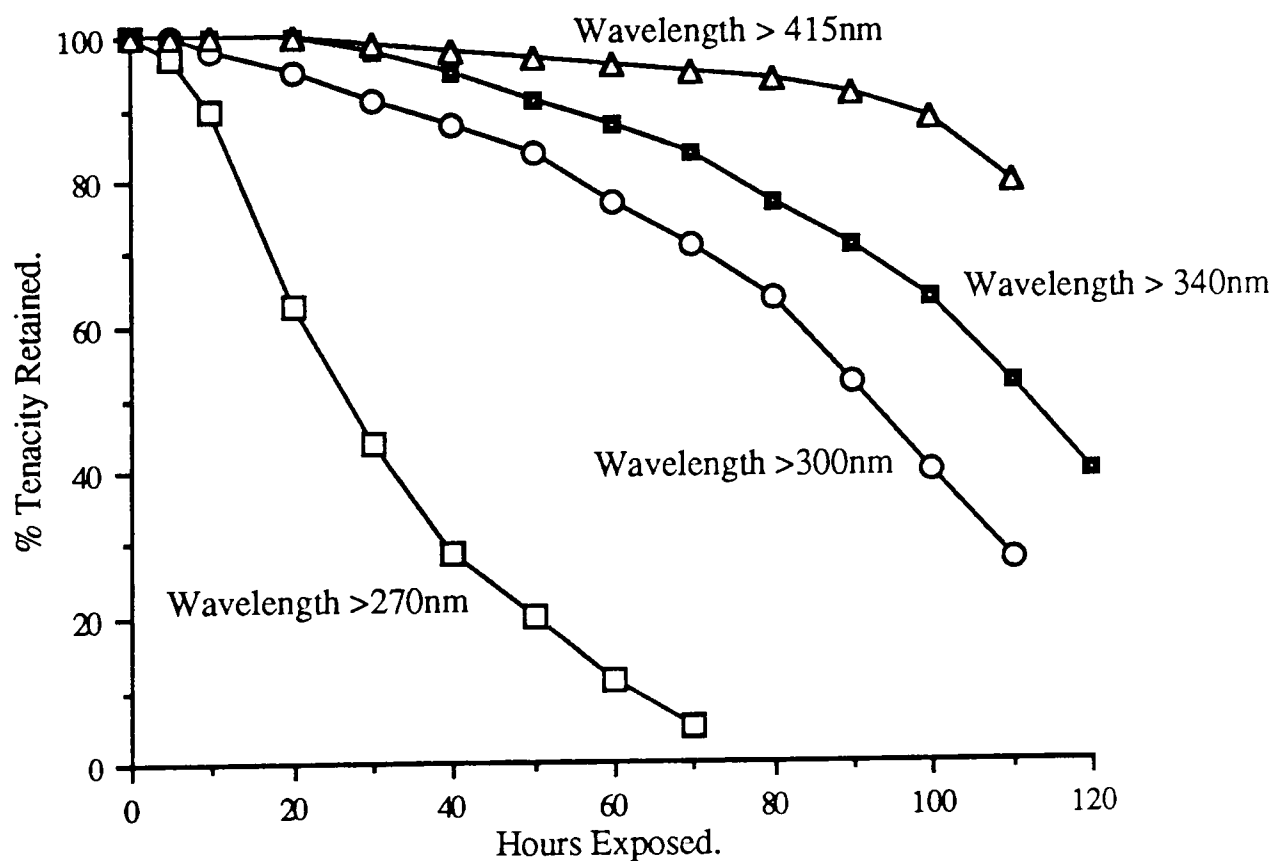
2.4.2.2 Polymer Constitution.

Of less importance, the second category by which a polymer may be photoexcited depends on the constitution of the polymer itself. The prior class was based on chromophores incorporated into the polymer during processing and manufacture. Alternatively, a number of polymers already have chromophoric units as part of the backbone of the polymer chain. More often than not, these are aromatic polymers, which absorb in the near U.V. region (300-350nm) causing photodegradative and photo-oxidative scission.

2.4.3 Photo-oxidation of Polyamides.

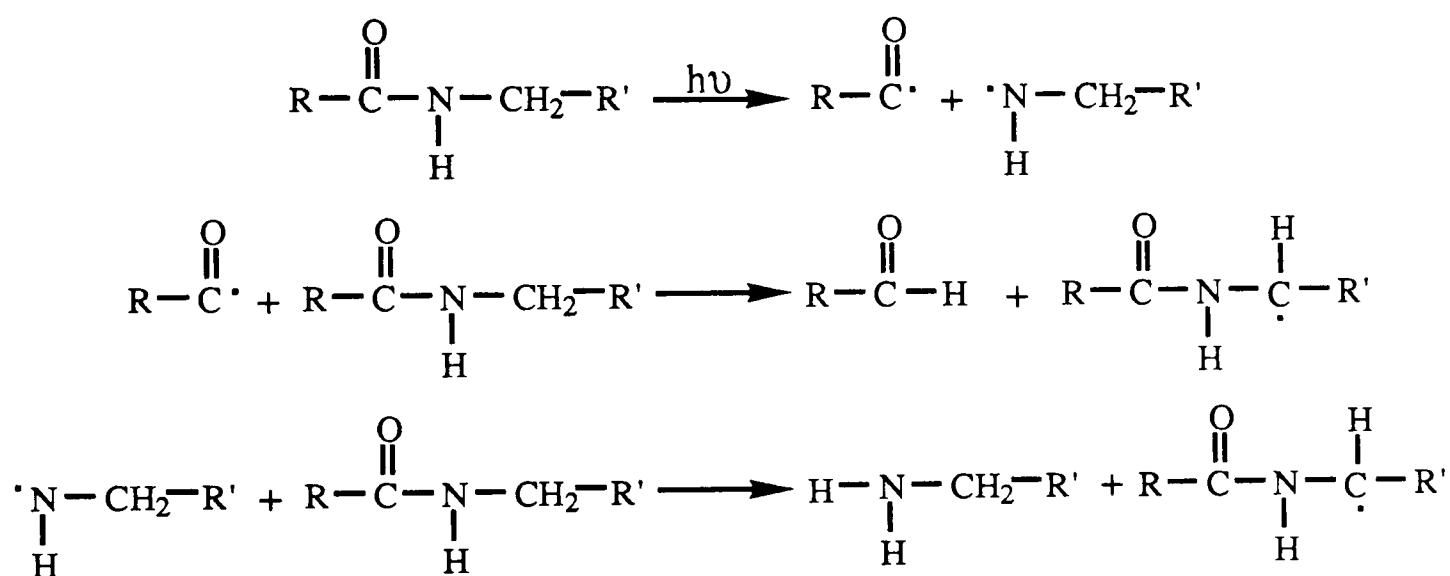
Over the last three decades or so, it has been a general acceptance that the main route of polyamide photodegradation is through the direct photolysis of the carbon-nitrogen bond of the amide group, especially when radiated with light of wavelength shorter than 300nm, as in theory, amide bonds should not absorb at wavelengths greater than 300nm. However, it was Anton [103] who disclosed that even at longer wavelengths, up to 415nm, some form of photodeterioration was still present, suggesting that other factors were also influential in U.V. light absorption, now recognised as hydroperoxide and carbonyl groups (Figure 2.6).

Figure 2.6:- Effect of Wavelength on the Photodegradation of Nylon 6,6.

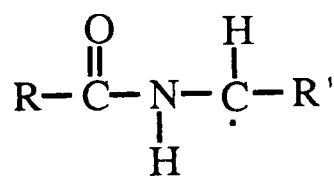


There have been a significant number of publications on the deterioration of polyamides as a consequence of photo-oxidation. In particular, Sharkey and Mochel [78] conducted extensive research on the photo-oxidation of model amides and concluded that the primary photochemical step in the photolysis of amides was the scission of the amide bond with formation of two free radicals, which in turn abstract hydrogen atoms from the methylene groups adjacent to the nitrogen (Scheme 2.20).

Scheme 2.20 :- Macroradical Formation According to Sharkey and Mochel.

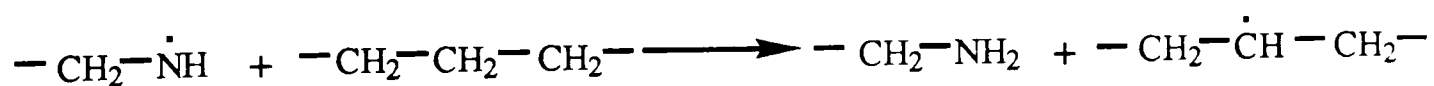


It is now well accepted that the result of photoinitiation is the generation of the macroradical :-



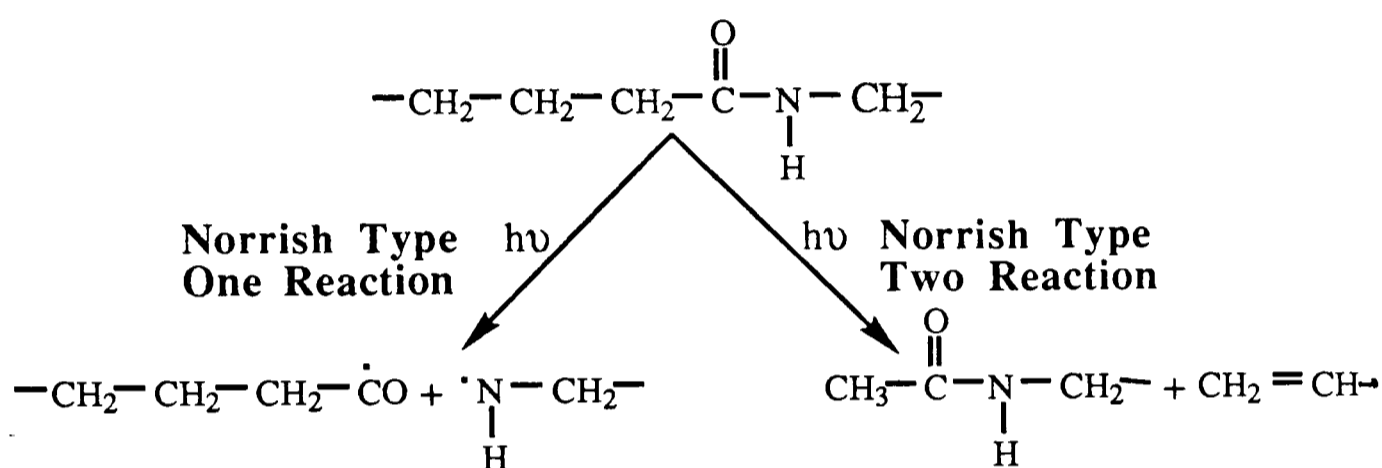
Following this work, several mechanisms for polyamide photo-oxidation were postulated. Heuvel et al [104], using electron spin resonance studies identified other radicals formed by the irradiation of nylon 6 with U.V. energy (Scheme 2.21).

Scheme 2.21 :- Heuvel et al Alternative Radicals.



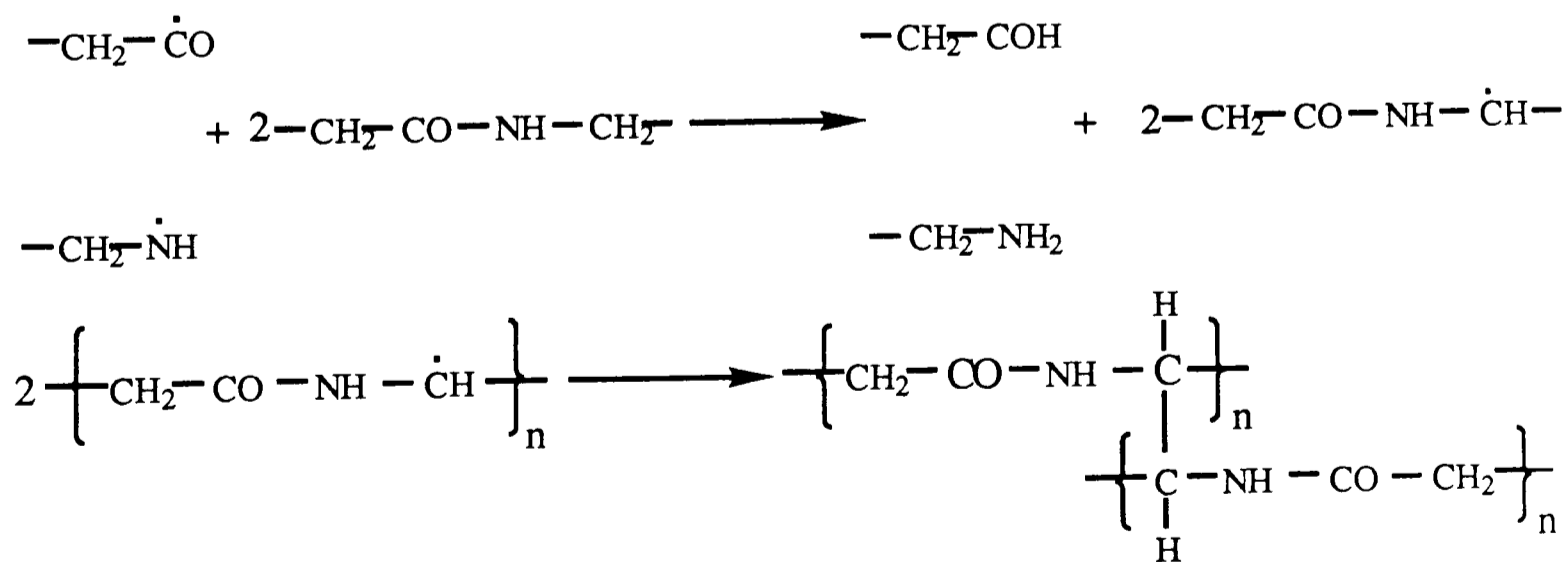
After analysing the products obtained from the hydrolysis of irradiated polyamides, Moore [105] also recognised the radicals formed from the rupture of the amide bond but also postulated simultaneous chain scission as well as crosslinking reactions. His results suggested, like those of Burgess, that chain scission was according to reactions similar to the Norrish Type I and Norrish Type II reactions, the former being preponderant (Scheme 2.22).

Scheme 2.22 :- Mechanism of Radical Formation According to Moore.



The radicals formed from the Norrish Type I reaction were thought to abstract a hydrogen atom from the methylene group adjacent to the nitrogen group, the resulting radicals formed thought to recombine resulting in crosslinking (Scheme 2.23).

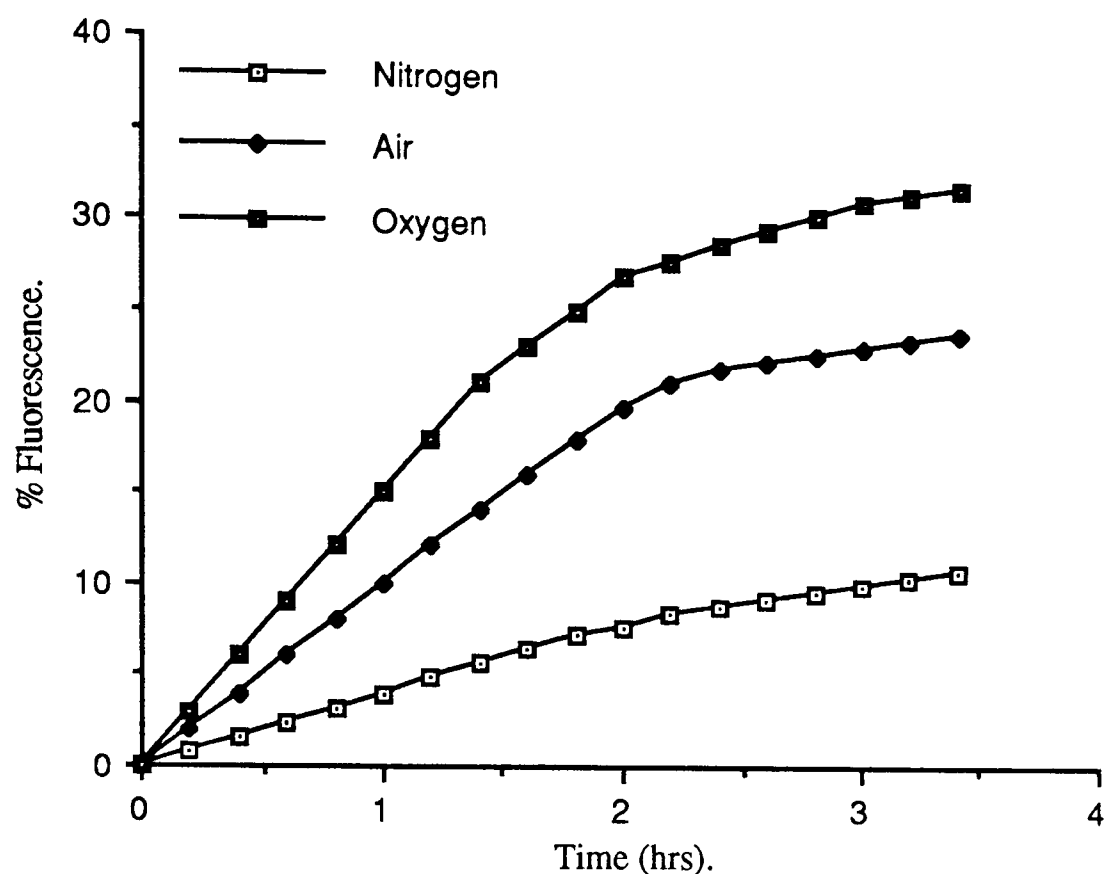
Scheme 2.23 :- Crosslinking Mechanism as Suggested by Moore.



Many of the early interpretations in the science of the photo-oxidation of polyamides were reviewed by Allen and McKellar [106] in the late 1970s and more recent publications by Allen have provided more information concerning this field of polymer degradation. In several of his initial studies, Allen employed luminescence spectroscopy for the identification of the fluorescent and phosphorescent species in polyamides, especially nylon 6,6. Working with both polymer [100] and model compounds such as N,N'-dicaproylhexamethylenediamine and N,N'-dibutyladipamide [107], he showed that the phosphorescence emission was mainly due to the presence of α,β -unsaturated carbonyl groups of the dienone or al-type, which act as photoinitiators, whilst the nature of the fluorescent species remained unidentified.

In more recent studies, Allen and Harrison [100] were able to identify both the fluorescent and phosphorescent species in nylon 6,6 polymer and concluded that they were due to aldol condensation products of cyclopentanone. Using 2-propanol, they extracted the main chromophoric species from nylon 6,6, with an excitation maximum at 290nm and corresponding emission maximum at 326nm. Furthermore, using T.L.C., they were able to separate the nylon 6,6 cyclic monomer from the chromophoric species, the latter now having a dual excitation maxima at 228 and 284nm, with emission maxima at 332 and 343nm respectively. Prior to these observations, many researchers believed that after extraction, the regeneration of the fluorescent species in many polyolefins was due to contamination from atmospheric naphthalene. Allen proved this theory wrong and showed that in actual fact regeneration occurred spontaneously in pure oxygen and was attributed to an oxidation process creating these chromophores (Figure 2.7) and not through the absorption of naphthalene.

Figure 2.7 :- Regeneration of Fluorescence of Nylon 6,6.

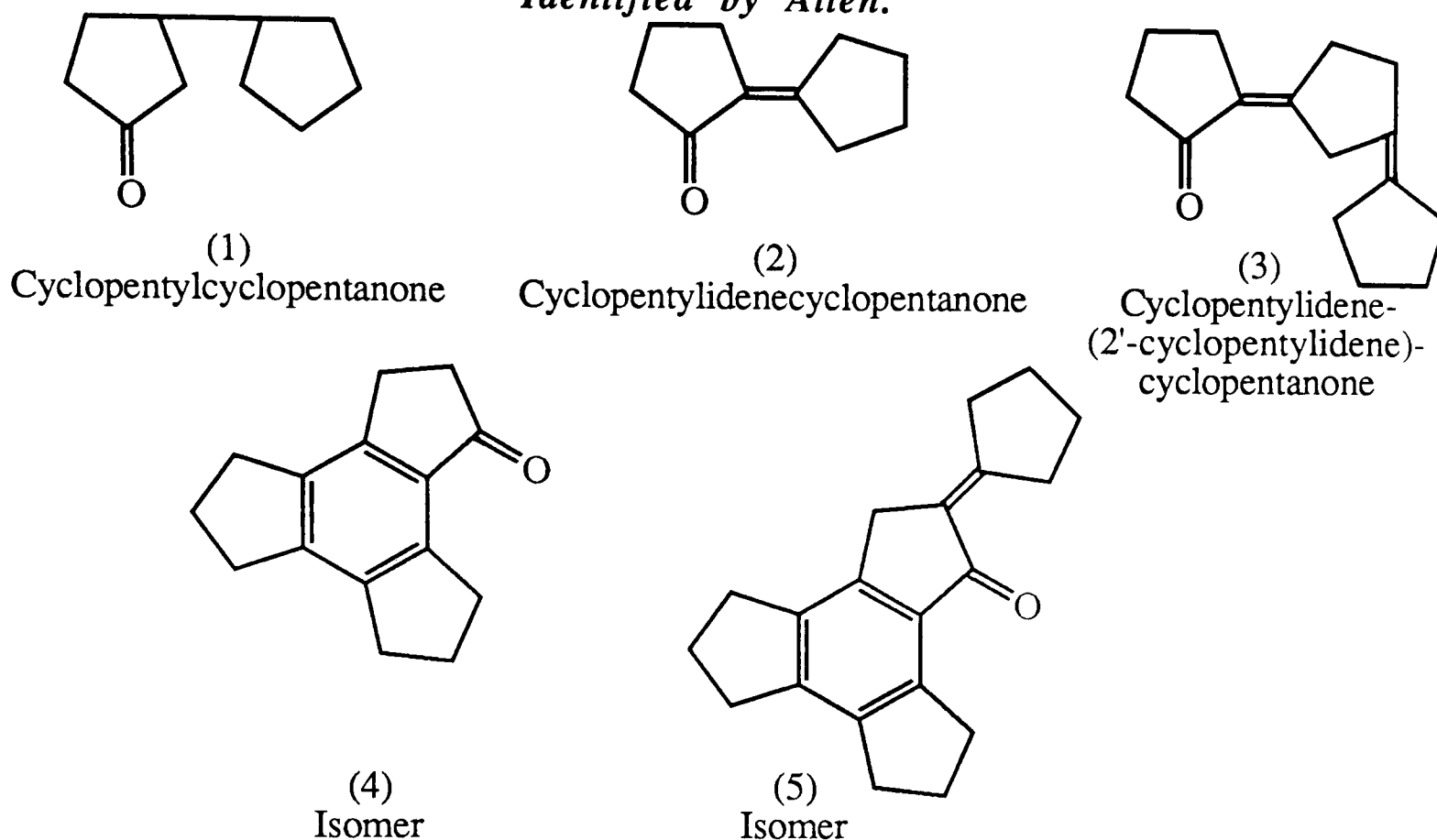


His theory was confirmed when the fluorescence excitation and emission spectra of naphthalene did not compare to that of the fluorescent species recovered from the T.L.C. extraction of the polymer. Using GC-mass spectrometry, Allen concluded his study by identifying the structure of many of the α,β -unsaturated carbonyl compounds studied (Figure 2.8).

Of the many structures named, structures (1) to (3) were thought to be more connected with the structured phosphorescence emission from nylon 6,6, whilst structures (4) and (5) were thought to be connected with the short wavelength fluorescence (excitation at 230 and 290nm) and phosphorescence emission at 407nm.

Figure 2.8 :- 'Aldol' Condensation Products of Cyclopentanone

Identified by Allen.



More recently, Roger suggested an alternative initiation mechanism which implied direct photolysis of the amide bond, without the aid of any impurities at wavelengths longer than 300nm (up to 340nm) [108]. This as well as the earlier suggested mechanism for photoinitiation via a impurity chromophore at wavelengths shorter than 300nm (254nm) [109] were studied extensively and it was claimed that at longer wavelengths, a dual initiation mechanism was involved, implying excitation of impurities as well as the direct excitation of the amide bond.

2.5 THE THERMAL DEGRADATION OF MXD,6.

In the early 1980s, Kaoru Furukawa and Chiaki Tsukamoto [110] investigated the kinetics of gel formation in molten MXD,6, which was one of a series of papers collectively referred to as "Studies on Thermal Degradation of Polyamides". This particular study was conducted for MXD,6 under various reaction conditions i.e. unbalanced monomer content as viscosity stabilizer (MXD or adipic acid), steam pressure and temperature.

Using the experimental equation :-

$$t_g = \frac{1}{kp_n - t_o}$$

where

p_n = degree of polymerization

t_g = gel formation time,

and based on Flory's theory of gelation [111], they showed that the crosslinking involved three reactions :-

- (i) the formation of a tertiary amide by the condensation reaction between a carboxylic end group and a secondary amine formed from two amino end groups,
- (ii) the formation of a tertiary amino group by the condensation reaction between a secondary amine and an amino end group,
- (iii) catalytic action of H^+ on these reactions

Utilizing these conditions, Furukawa and Tsukamoto calculated rate constants which indicated that for MXD,6, reaction (ii) was more important than reaction (i).

More recently, Shimasaki et al at the Faculty of Engineering, Toyama University, Japan have studied the thermal degradation of MXD,6 using D.T.A.-T.G., F.T.I.R., T.G.-G.C./M.S. and mass spectroscopy [112]. They found that the D.T.A.-T.G./D.T.A. results showed that the thermal decomposition of MXD,6 occurred via two stages. Initially MXD,6 melted at about 235°C and then decomposed to either the monomer or an oligomer with a total weight loss of 40% in the temperature region between 330 to 400°C. A T.G. effluent gas collected in a cold trap from the thermal decomposition of MXD,6 was injected into a G.C. for separation, followed by a M.S. for an unequivocal identification. From these results, ten effluent degradation products were identified (Table 2.1) and from these, they concluded that the main fragmentation mechanism by electron impact for MXD,6 involved two processes.

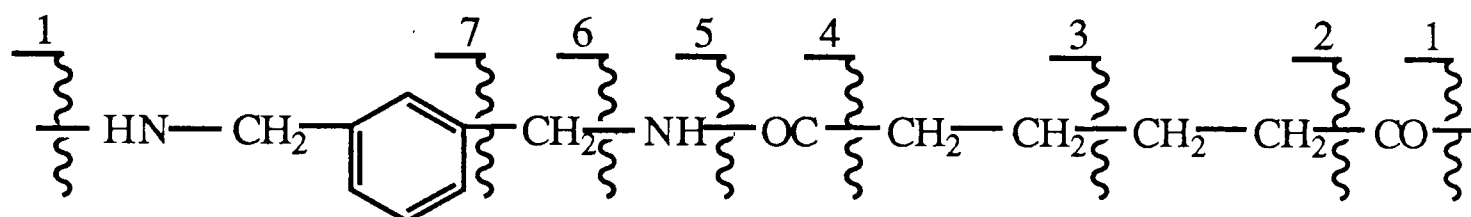
Table 2.1 :- Identification of Products from Mass Chromatogram for Degraded MXD,6.

m/z	Probable ion Composition	Comments
28	N ₂ or CO	} most intense
32	O ₂	
119	C ₈ H ₉ N ⁺	Apparent maximum mass number
106	(C ₇ H ₇ NH) ⁺	Tropylium ion
	↓	
105	(C ₇ H ₇ NH) ⁺	
91	(C ₇ H ₇) ⁺	
84	(C ₂ H ₄ CO) ⁺	
55	(C ₄ H ₇) ⁺	
	↓	
41	(C ₃ H ₅) ⁺	
	↓	
28	(C ₂ H ₄) ⁺	

The first was thought to proceed at temperatures below 300°C and involved dehydration, rearrangement, evolution of CO, CO₂, and the formation of carbonaceous residue. However, the second process was thought to proceed at a temperature in excess of 400°C and overshadowed the first at these temperatures. Shimasaki et al suggested this process involved the cleavage of the m-phenylenebis(methyleneimino) unit by intramolecular rearrangements, followed by the formation of a tar mixture and some randomly linked low molecular weight aliphatic derivatives which then evaporated.

M.S. results showed the ion of the largest intensity in the mass spectrum as being the C₈H₉N⁺ ion appearing at m/z 119 and referred to as the base peak. The spectrum also indicated that the maximum mass number was the (M-H₂O)⁺ of the monomer. A compound of MXD,6 after ionization of the (M-H₂O)⁺ produced cleavages to form fragments of m/z 100, 119, 134, 161, 189, 218 and 246 (Figure 2.9).

Figure 2.9 :- Main Fragment ions by Electron Impact for MXD,6.



Simple cleavages such as fragments 1,2,5 and 6 of an even electron ion produced another even electron ion and a neutral olefin or product. With fragment ions 3,4 and 7, the cleavage was thought to occur via the McLafferty rearrangement process [113].

Using T.G., the activation energy of the thermal decomposition was estimated to be 230kJmol⁻¹ during the first stage and 150kJmol⁻¹ during the second stage. Employing the calculated activation energy values, they were able to obtain the kinetic data for the degradation of MXD,6 and calculated that the first stage of the degradation process obeyed a first order reaction and that the second stage of the degradation process obeyed a half order rate law.

2.6 OBJECTIVE OF STUDY.

At C.M.B. Packaging Technology (formerly Metal Box), a novel polymeric system was discovered consisting of a blend of polyester, namely poly(ethylene terephthalate), with an aliphatic-aromatic polyamide, namely MXD,6 and between 50-2000ppm of a variable-valency metal ion, namely cobalt. Containers prepared from such a blend were found to exhibit exceptional oxygen barrier properties.

It was proposed that many of the extraordinary properties shown by the blend were due to the behaviour of the so called "oxidisable organic component", the MXD,6, which was thought to scavenge for oxygen in the walls of the container aided by the cobalt behaving as a catalyst and this work was directed at understanding the processes involved.

Initial studies were concentrated on the oxygen barrier properties of MXD,6 fibres spun with between 50-2000ppms cobalt. The effectiveness of the cobalt as a catalyst was assessed and from these results, the most efficient polymer blend for reduced gas permeability proposed.

Following these preliminary investigations, it was proposed that the oxidation of MXD,6 should also be studied to obtain a better understanding of the mechanisms involved with the oxygen barrier properties of the blend. Using a controlled oxidative degradation system at elevated temperatures, volatiles produced during oxidation could be collected and characterized using modern analytical techniques and these results consequently utilized to derive a feasible degradation mechanism for MXD,6. Analysis of the residue of degraded polymer itself was also carried out so as to give an overall picture of the oxidative degradation mechanism.



CHAPTER THREE :- EXPERIMENTAL.

3.1 MATERIALS.

During the course of this study, the following materials were utilized.

Acids.

Table 3.1 :- Acids utilized during the course of this study.

ACID	GRADE	SOURCE
Formic	96%	Aldrich
Acetic	Analar	B.D.H.
Propionic	99%	Aldrich
Butyric	99%	Aldrich
Valeric	99%	Aldrich
Caproic	99%	Aldrich
Oxalic	Analar	B.D.H.
Malonic	G.P.R.	B.D.H.
Succinic	Analar	B.D.H.
Glutaric	99%	Aldrich
Adipic	99%	Aldrich
Isophthalic	99%	Aldrich
Terephthalic	98%	Aldrich
Benzoic	99%	Aldrich
m-Hydroxybenzoic	99%	Aldrich
Dichloroacetic	99%	Lancaster Synthesis
Hydrochloric	1.0N solution in water	B.D.H.
Sulphuric	99%	B.D.H.

Amines.

Table 3.2 :- Amines utilized during the course of this study.

AMINES	GRADE	SOURCE
Methylamine	40% Aqueous Solution	B.D.H.
Ethylamine	70% Aqueous Solution	Aldrich
Propylamine	98%	Aldrich
Butylamine	97%	B.D.H.
Pentylamine	90%	B.D.H.
Diaminoethane	G.P.R.	B.D.H.
Diaminopropane	99%	Aldrich
Diaminobutane	99%	Aldrich
Benzylamine	99%	Aldrich
3-Methylbenzylamine	98%	Aldrich
m-Xylylene diamine	99%	Aldrich

Aldehydes and Ketones.

Table 3.3 :- Aldehydes and Ketones utilized during the course of this study.

ALDEHYDE / KETONE	GRADE	SOURCE
Formaldehyde	Analar	B.D.H.
Acetaldehyde	G.P.R.	B.D.H.
Propionaldehyde	97%	Aldrich
Butyraldehyde	99%	Aldrich
Valeraldehyde	99%	Aldrich
Acetone	Technical	B.D.H.
Butanone	Technical	B.D.H.
Cyclohexanone	99.8%	B.D.H.
Cyclopentanone	99%	Aldrich
Benzaldehyde	99%	Aldrich
2-Carboxybenzaldehyde	97%	Aldrich
4-Carboxybenzaldehyde	98%	Aldrich
Isophthalaldehyde	97%	Aldrich
Terephthalaldehyde	99%	Aldrich
Crotonaldehyde	99%	Aldrich

Bases.

Table 3.4 :- Bases utilized during the course of this study.

BASES	GRADE	SOURCE
Sodium hydroxide	G.P.R. Pellets	B.D.H.
Potassium hydroxide	G.P.R. Pellets	B.D.H.
Sodium bicarbonate	G.P.R.	B.D.H.

Catalysts.

Table 3.5 :- Catalysts utilized during the course of this study.

CATALYSTS	GRADE	SOURCE
Cobalt siccato	10% solution in white spirits	Akzo Chemie
Cobalt bromide	99%	Aldrich
Manganese bromide	99%	Aldrich

Alcohols.*Table 3.6 :- Alcohols utilized during the course of this study.*

ALCOHOL	GRADE	SOURCE
Methanol	HiPerSolv for H.P.L.C.	B.D.H.
Ethanol	90%	B.D.H.
Butanol	99.9%	B.D.H.
Benzyl alcohol	G.P.R.	B.D.H.
Phenol	99%	Aldrich
Ethylene glycol	99%	Aldrich
Hexafluoroisopropanol	99%	Lancaster Synthesis

Solvents.*Table 3.7 :- Solvents utilized during the course of this study.*

SOLVENTS	GRADE	SOURCE
Methyl acetate	97%	B.D.H.
Ethyl acetate	99.5%	Chromapak Vickers
Carbon tetrachloride	ARISTAR	B.D.H.
Ammonia	35% Analar	B.D.H.
Hexane	HiPerSol for H.P.L.C.	B.D.H.
Tetrahydrofuran	HiPerSol for H.P.L.C.	B.D.H.
Water	HiPerSol for H.P.L.C.	B.D.H.

Indicators.*Table 3.8 :- Indicators utilized during the course of this study.*

INDICATORS	GRADE	SOURCE
Bromocresol green	99% pH Indicator	Aldrich
Methylene red	99% pH Indicator	Aldrich
Ninydrin	0.5% solution in butanol spray	B.D.H.
Phenolphthalein	99% pH Indicator	Aldrich
Xylene cyanol	99% pH Indicator	B.D.H

Miscellaneous.*Table 3.9 :- Miscellaneous Chemicals utilized during the course of this study.*

MISCELLANEOUS	GRADE	SOURCE
Dansyl chloride	99%	Lancaster Synthesis
2,4-Dinitrophenylhydrazine	Analar	B.D.H.
m-Toluamide	99%	Aldrich
Monomethyl adipate	98%	Aldrich
Silica gel 60 F ₂₅₄ (20 × 20cm) TLC plates	MERCK	B.D.H.
Silica gel 60 (20 × 20cm) TLC plates	MERCK	B.D.H.

3.2 POLYMERIZATION TECHNIQUES.

During the course of this work, two different routes for the preparation of poly(m-xylylene adipamide), MXD,6, were evaluated. Both techniques were conducted on a small scale in the laboratory and the more efficient of the two applied on a larger scale for further study. Initially, polymers were prepared by orthodox polycondensation of polyamides with preparation of the polymer salt prior to its polymerization, a two stage procedure [5]. Subsequently, it was proposed that a direct polymer salt formation and polymerization technique, a one stage procedure, could be more efficient, as well as give a polymer of a higher molecular weight than the conventional method [38].

3.2.1 Two Stage Polycondensation.

3.2.1.1 Salt Formation.

73g (0.5mole) of adipic acid was dissolved in 500ml of methanol at room temperature and an equimolar quantity, 68g, of m-xylylene diamine, (MXD), was added dropwise. The white precipitate formed was filtered and washed in 200ml of methanol. The washed salt was then purified by dissolving in 200ml of distilled water and filtering to remove any insoluble impurities, followed by reprecipitation of the salt, using approximately 300ml of methanol.

3.2.1.2 Polymerization.

100g of the polymer salt was placed in a 750ml polymerization reaction vessel and sealed using a lid with an inlet for nitrogen and an outlet leading to a vacuum pump, via a cold trap.

The apparatus was purged with nitrogen five times, to ensure an inert atmosphere in the reaction vessel, after which the temperature of the vessel was gradually raised at 2°C/min. under a continuous flow of nitrogen, supplied at 100cm³/min.

Polymerization commenced at the melt temperature of the MXD,6 salt, (180-190°C), after which the temperature was again raised to 250°C, over a period of one hour, then held at that temperature for two hours. To ensure a high molecular weight polymer, during the last hour of polymerization the nitrogen was removed and vacuum finishing applied with at least a 0.03mm mercury vacuum.

Once the polymerization time had elapsed, the molten polymer was cooled under nitrogen and the solid polymer was ground down and dried in a vacuum oven at 60°C for 24 hours and stored in a desiccator containing silica gel, prior to use.

3.2.2 One Stage Direct Polycondensation.

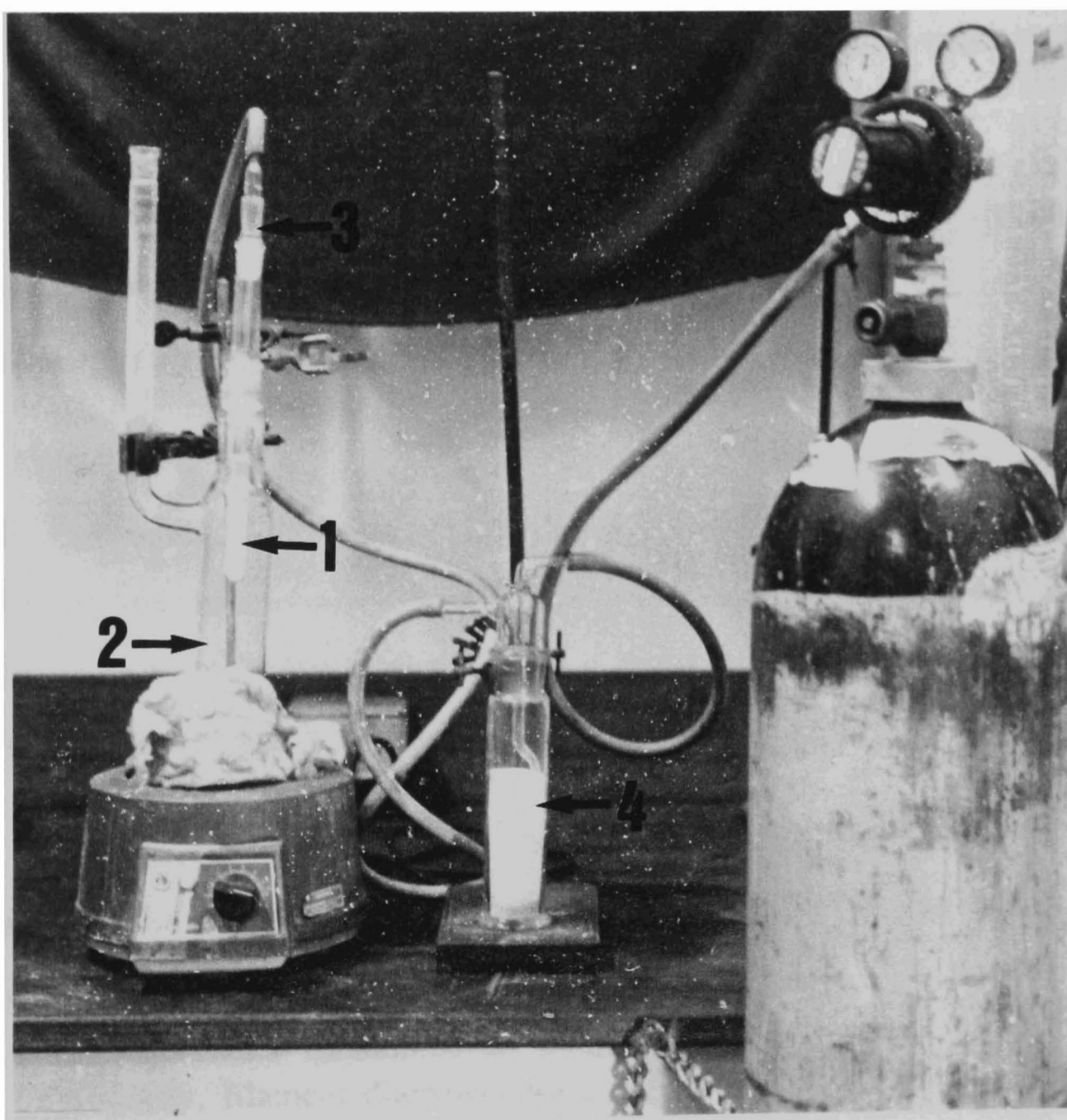
A polymerization vessel equipped with a stirrer, condenser, graduated funnel and nitrogen supply was charged with 73.1g, (0.5 mole), of adipic acid. A steady flow of nitrogen was introduced into the reaction vessel at 100ml/min. to provide an inert atmosphere, under which the adipic acid was melted by raising the temperature to 160°C (Figure 3.1).

To the molten monomer, 66.74g, (0.49 mole), of MXD was added dropwise from the graduated funnel with stirring, while the temperature was raised to 245°C over a period of 3.5 hours, and finally to 260°C in a further 3 hours. A further 1.36g, (0.01 mole), of MXD was added dropwise over a period of 50 minutes, after which the reaction was continued for another 60 minutes at 260°C.

Once the polymerization time had elapsed, the molten polymer was cooled under nitrogen, then finally ground down and dried in a vacuum oven at 60°C for 24 hours. The dried polymer was then stored in a vacuum desiccator containing silica gel, prior to use.

Throughout the reaction, the polymerization mixture remained in an uniformly fluid state, without any solidification and/or precipitation of the resulting oligoamide or polyamide.

Figure 3.1 :- Polymerization Apparatus Utilized in MXD,6 Polymerization.



- (1) Polymerization tube containing nylon salt.
- (2) Vapour bath.
- (3) Nitrogen supply.
- (4) Concentrated sulphuric acid tower for drying nitrogen.

3.3 FIBRE SPINNING.

Polymer decomposition experiments were predominantly conducted on fibres, as the increased surface area to volume, compared to that of polymer chip, enabled a more rapid rate of volatile production from the polymer, when subjected to high oxidative temperatures. Also, some samples of MXD,6 were prepared by blending with a cobalt salt which could influence the rate of degradation. To ensure a uniform distribution throughout the polymer, the polymer chips were initially coated with the required percentage of cobalt, followed by spinning into fibre on a Fourné melt extruder. The use of a cobalt salt in solution, namely cobalt siccato, made application and mixing easier.

Typically, 1Kg of commercial material was prepared for spinning by drying under vacuum at 150°C for 8-10 hours. Samples incorporating the catalyst were vigorously shaken with the required amount of the cobalt siccato before drying.

Once drying was completed, the drying tubes holding the polymer chips were sealed under nitrogen and fitted straight onto the melt extruder hopper without being exposed to the atmosphere. Polymer samples were spun using predetermined conditions and for MXD,6 with/without cobalt, the following conditions gave satisfactory fibres (Table 3.10).

Fibres of MXD,6 with/without cobalt were found to have similar diameters, hence the differences in the rate of degradation between them, if any, would only be accounted for by the different catalyst concentrations.

Ordinarily, filament diameters were measured and on average a value of $76.75 \pm 1.25\mu\text{m}$ was recorded for fibres spun under the conditions above.

Table 3.10 :- Typical Spinning Conditions used for MXD,6 Fibre Production.

SPINNING CONDITIONS.	SET CONDITIONS.	ACTUAL CONDITIONS.
HEATER TEMP. 1 °C	280	281
HEATER TEMP. 2 °C	302	305
HEATER TEMP. 3 °C	306	308
HEATER TEMP. 4 °C	308	316
HEATER TEMP. 5 °C	313	315
HEATER TEMP. 6 °C	315	314
PUMP SPEED r.p.m.	11.9	11.9
SCREW SPEED r.p.m.	95	95
SCREW PRESSURE bar	117	111
GODET SPEED m/min.	244	239
WINDUP SPEED m/min.	245	247

The temperatures recorded were the temperatures of the metal of the extruder and not the temperature of the polymer, which would have been lower than that ones quoted.

Degradation experiments were carried out on the fibres as spun, without any orientation by drawing. As soon as any fibres were spun, they were stored under an inert atmosphere in a vacuum desiccator and the whole assembly placed in a dark area prior to the fibres being utilized.

3.4 CHARACTERIZATION.

3.4.1 Chromatographic Techniques.

The principal characterization techniques used systematically for the detection of degradation products were thin layer chromatography, (T.L.C.), high performance liquid chromatography, (H.P.L.C.), and gas chromatography, (G.C.). All three methods were extensively used in this investigation for the qualitative and quantitative determination of carboxylic acids, aldehydes, ketones and amines.

3.4.1.1 Thin Layer Chromatography [114].

T.L.C. was found to be the simplest technique for the identification of degradation products. However, the method applied was heavily dependent on the type of organic species to be characterized. For this reason, a number of stationary phases as well as mobile phase conditions were employed in this investigation.

T.L.C. of Monocarboxylic acids [115].

A series of standard monocarboxylic acids ranging from nC_1 to nC_6 were chromatographed on silica gel 60 250nm (20 × 20cm) T.L.C. plates supplied by Merck, by a two development technique using methyl acetate:ammonia, 2.5% aqueous volume (95:5 v/v) as the eluent.

The chromatography tank was prepared 30 minutes prior to use and was filled with eluent 1cm in depth, with the walls of the tank lined with filter paper to aid in obtaining a saturated atmosphere.

20 μ g samples of each pure acid were spotted at a marked origin 2.0cm from the base of the chromatography plate.

Once the solvent front had reached its limit of travel, usually 15cm, the plate was removed and placed in an oven at 105°C for 2-3 minutes. After cooling, the plate was replaced in the tank and a second development conducted to the same distance, hence a two development procedure.

The acids were then located, the substrate being sprayed with a 0.1% alcoholic methyl red solution and dried in an oven at 105°C, until the acids appeared as dark red spots on an orange background. The relative front (R_f) values were calculated accordingly (Table 3.11).

The eluent was used with great care, as it was observed that the ammonia concentration would influence the degree of development dramatically if not used at the required concentration. If too high, the acids would remain close to the origin and if too low, the acids would streak towards the solvent front causing subsequent loss of resolution. For this reason, it was necessary to standardize the aqueous ammonia before use and to discard the eluent once employed for over 24 hours, as its effectiveness deteriorated thereafter.

Table 3.11 :- Relative Front Values for Monocarboxylic Acids.

MONOCARBOXYLIC ACID	R_f
FORMIC	0.06
ACETIC	0.12
PROPIONIC	0.28
n-BUTYRIC	0.40
n-PENTANOIC	0.49
n-HEXANOIC	0.59

T.L.C. of Dicarboxylic acids [116].

A series of standard dicarboxylic acids ranging from nC_2 to nC_6 were chromatographed on silica gel 60 250nm (20 × 20cm) T.L.C. plates supplied by Merck, using a solvent system comprising phenol:n-butanol:formic acid:water (5:2:1:2).

The chromatography tank as well as the chromatography plates were prepared as before and the solvent front allowed to reach its limit of travel, usually 15cm, after which the plates were sprayed with an alcoholic solution of bromocresol green and warmed at 110°C for one minute. Acids were visible as yellow spots on a blue background. The R_f values were calculated accordingly (Table 3.12).

Table 3.12 :- Relative Front Values for Dicarboxylic Acids.

DICARBOXYLIC ACID	R_f
OXALIC	0.30
MALONIC	0.48
SUCCINIC	0.59
GLUTARIC	0.68
ADIPIC	0.78

T.L.C. of Aromatic Acids [117].

A series of aromatic acids were spotted on silica gel 60 F₂₅₄ (20 × 20) T.L.C. plates supplied by Merck and chromatographed using a solvent system comprising chloroform:tetrahydrofuran (2:1). After the solvent front had travelled at least 10cm, the chromatograms were rendered visible by irradiating with U.V. light and the R_f values subsequently calculated accordingly (Table 3.13).

Table 3.13 :- Relative Front Values for Aromatic Acids.

AROMATIC ACID	R _f
ISOPHTHALIC	0.53
TEREPHTHALIC	0.50
BENZOIC	0.40
m-HYDROXYBENZOIC	0.35
ISOPHTHALAMIC	0.31

Furthermore, a novel type of T.L.C. referred to as Empore Thin Layer Chromatography was employed especially for aromatic acids. The stationary phase was a strip of 90% P.T.F.E. coated with a layer of 10% C₁₈ absorbant. Since the stationary phase is very similar to a C₁₈ reverse phase H.P.L.C. column, this type of T.L.C. is often used in conjunction with H.P.L.C. separation as a similar mobile phase may be utilized in both cases. Thus several aromatic acids were spotted on an C₁₈ Empore strip and chromatographed using a mobile phase of water:methanol (70:30), using phosphoric acid to adjust the pH to 3.5.

After chromatography, the chromatograms were located under U.V. light at 254nm wavelength and the separated spots cut from the Empore strips and mounted on a stage for F.T.I.R. analysis using a piece of fresh Empore strip as the background reading.

T.L.C. of Aldehydes and Ketones [118].

Identification and separation of aldehydes and ketones using T.L.C. was carried out in the form of their respective 2,4-dinitrophenylhydrazine, (D.N.P.H.), derivatives.

D.N.P.H. solution was prepared by gently warming 0.25g of the D.N.P.H. in 5ml of methanol and 0.5ml of concentrated sulphuric acid. The warm solution was clarified by filtration and then treated with 0.1g of the carbonyl compound, dissolved in a minimum volume of methanol or ether. The mixture was boiled for two minutes, then cooled to room temperature, which normally separated the D.N.P.H. derivative from the solution, however, if this was not the case, the solution was cautiously treated with dilute sulphuric acid dropwise [119]. The filtered and washed derivative was then recrystallised from ethanol, acetic acid or xylene.

A series of aldehyde 2,4-dinitrophenylhydrazone standards ranging from nC₁ to nC₅, as well as a variety of ketones and aromatic aldehydes, were spotted on silica gel 60 F₂₅₄, (20 × 20cm) T.L.C. plates supplied by Merck and chromatographed using a solvent system comprising of carbon tetrachloride:hexane:ethyl acetate (10:2:1).and the chromatograms rendered visible by irradiation with U.V. light. R_f values were calculated accordingly (Table 3.14).

Table 3.14 :- Relative Front Values for Aldehyde and Ketone Derivatives.

ALDEHYDE AND KETONE DERIVATIVE	R _f
2,4-DINITROPHENYLHYDRAZINE	0.00
FORMALDEHYDE	0.28
ACETALDEHYDE	0.32
PROPIONALDEHYDE	0.69
BUTYRALDEHYDE	0.71
VALERALDEHYDE	0.75
ACETONE	0.54
METHYLETHYL KETONE	0.54
CYCLOHEXANONE	0.56
CYCLOPENTANONE	0.47
BENZALDEHYDE	0.55
2-CARBOXYBENZALDEHYDE	0.36
4-CARBOXYBENZALDEHYDE	0.40
ISOPHTHALALDEHYDE	0.23
TEREPHTHALALDEHYDE	0.41
CROTONALDEHYDE	0.51

T.L.C. of Aliphatic and Aromatic Amines.

During the course of this study, amines formed from the degradation of MXD,6 were collected not only as the free volatile amines from headspace analysis but also as their respective hydrochlorides formed during the acid hydrolysis of the degraded polymer, which were isolated using steam distillation. Therefore, two techniques of T.L.C. separation were employed for amine identification.

(i) Free Amines.

Since a combination of aliphatic and aromatic amines would be expected as decomposition products from MXD,6, the system devised by Petromo and Russo for such separation was found to be ideal [120].

A series of standard monoamines, ranging from nC_1 to nC_5 were spotted along side a series of standard diamines, ranging from nC_2 to nC_4 and a number of typical aromatic amines on silica gel 60 F₂₅₄, (20 × 20cm) plates, using a solvent system comprising methanol:acetone (1:4).

After chromatography, the chromatograms were located by spraying the plate with a 2% solution of ninhydrin in ethanol and heated at 90°C for 15 minutes. Aromatic amines were also located under U.V. light at 254nm. The R_f values were calculated accordingly.

(ii) Amine Hydrochlorides.

Especially for this case, it was considered more effective if the hydrochlorides were converted to their respective dansyl derivatives using dansyl chloride for T.L.C. analysis.

A series of standard dansyl amines were spotted along-side a spot comprising a mixture of amine hydrochloride standards on a silica gel 60 F₂₅₄, (20 × 20cm) T.L.C. plate. The latter were then converted to the respective dansyl amine derivatives by overspotting the spot from the hydrochlorides with a saturated solution of dansyl chloride in acetone, followed by a saturated solution of aqueous sodium bicarbonate, the spot being allowed to evaporate between each application. Using a solvent system comprising of ether, chromatography was carried out, after which the chromatograms were located under U.V. light at 254nm. The R_f values were calculated accordingly.

Table 3.15 :- Relative Front Values for Amines.

AMINE	R _f *	R _f **
AMMONIA	0.10	0.81
METHYLAMINE	0.17	0.90
ETHYLAMINE	0.25	0.92
PROPYLAMINE	0.32	0.93
n-BUTYLAMINE	0.36	0.95
n-PENTYLAMINE	0.41	0.97
DIAMINOETHANE	0.00	0.60
DIAMINOPROPANE	0.00	0.62
DIAMINOBTANE	0.00	0.66
BENZYLAMINE	0.53	0.45
3-METHYL BENZYLAMINE	0.58	0.37
m-XYLYLENE DIAMINE	0.62	0.31

R_f * Solvent system comprising methanol:acetone (1:4).

R_f ** Solvent system comprising ether.

3.4.1.2 High Performance Liquid Chromatography (H.P.L.C.).

The technique of high performance liquid chromatography, variously called high speed and high pressure liquid chromatography, was used concurrently with other chromatographic methods for organic analysis. Especially in this study, H.P.L.C. was found to be the most effective chromatographic procedure, as it enabled trace constituents to be identified quantitatively.

As with T.L.C., the eluent employed was greatly dependent on the organic species to be characterized. However, in all cases, analyses were performed using a Pye Unicam LC-XPD pump and a Spherisorb ODS-2 (150 × 4.6mm) reverse phase column.

For convenience, the different types of chromatographic conditions utilized in this study have been tabulated (Table 3.16).

Table 3.16 :- Separation Conditions utilized on H.P.L.C.

IDENTIFICATION OF :-	ELUENT	U.V. (nm)	FLOWTIME ml/min.	REF.
ALIPHATIC MONOCARBOXYLIC ACIDS	WATER pH 2.5	210	1	*
ALIPHATIC DICARBOXYLIC ACIDS	WATER:METHANOL (98:2) pH 2.5	210	1	*
AROMATIC ACIDS	WATER:METHANOL (70:30) pH 3.5	254	1	*
ALDEHYDE AND KETONE DERIVATIVES	METHANOL:WATER (70:30) pH 3.5	360	1	122
AMINE DERIVATIVES	METHANOL:WATER (70:30)	254	1	123

* Many of the mobile phases utilized were derived especially for the H.P.L.C. system used in this study and may vary slightly depending on the condition and type of the H.P.L.C. system employed.

Monocarboxylic Acids.

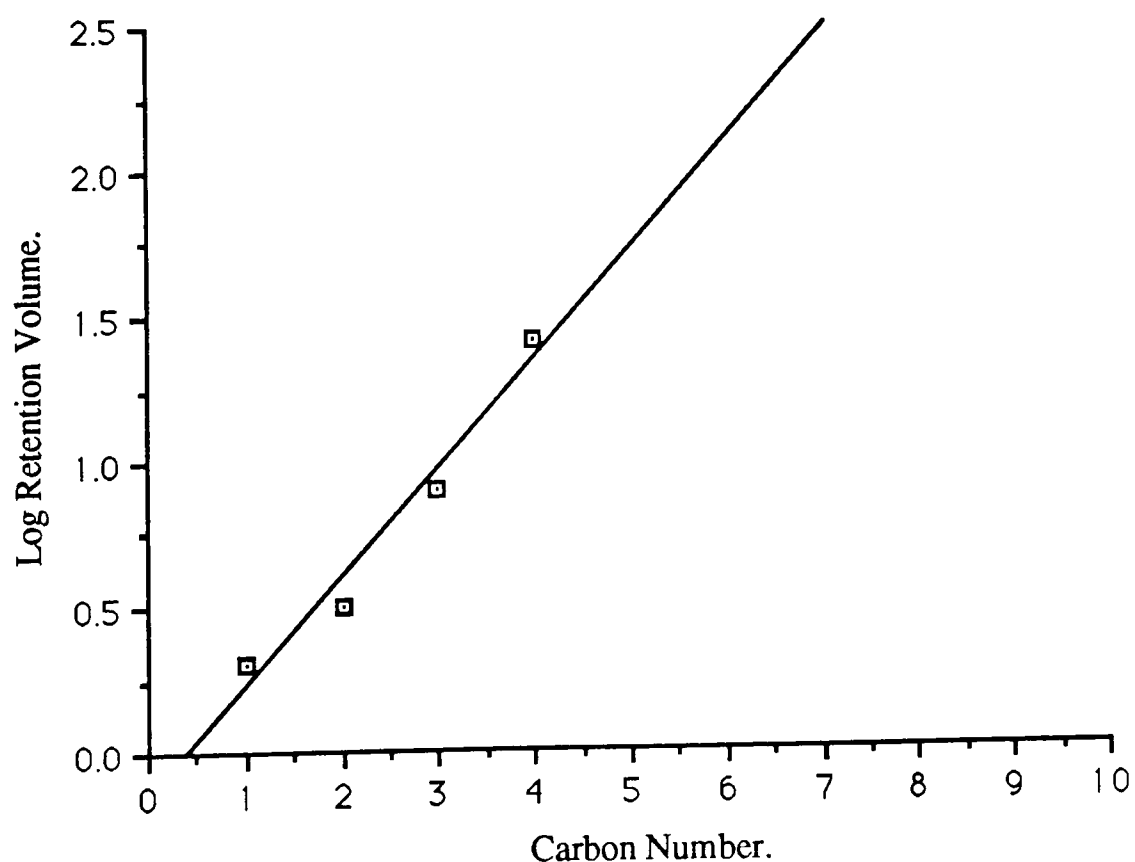
0.01% solutions of a series of monocarboxylic acids ranging from nC_1 to nC_6 were prepared in H.P.L.C. grade water and 1ml injected onto the column. The retention volume (R_V) values were calculated accordingly (Table 3.17).

Table 3.17 :- Retention Volumes Calculated for Monocarboxylic Acids.

MONOCARBOXYLIC ACID	R_V (ml)
FORMIC	2.0
ACETIC	3.2
PROPIONIC	8.0
n-BUTYRIC	26.0
n-PENTANOIC	56.2
n-HEXANOIC	151.4

Retention volumes for n-pentanoic and n-hexanoic acids were calculated by extrapolating on the log retention volume against carbon number relationship for a homologous aliphatic straight chain series (Figure 3.2). Such extrapolations may be carried out for most straight chain aliphatic homologous series.

Figure 3.2 :- Relationship between the Log Retention Volume and the Carbon Number for a Series of Monocarboxylic Acids.



Dicarboxylic Acids.

0.01% solutions of a series of dicarboxylic acids ranging from nC₂ to nC₆ were prepared in H.P.L.C. grade water and 1ml injected onto the column. The R_v values were calculated accordingly (Table 3.18).

Table 3.18 :- Retention Volumes Calculated for Dicarboxylic Acids.

DICARBOXYLIC ACID	R _v (ml)
OXALIC	1.3
MALONIC	2.2
SUCCINIC	4.0
GLUTARIC	8.2
ADIPIC	24.6

Aromatic Acids.

0.01% solutions of isophthalic, benzoic, m-hydroxybenzoic and isophthalamic acids were prepared in water : methanol, (60:40), at pH 3.5. 1ml of each was injected onto the column and the R_v values calculated accordingly (Table 3.19).

Table 3.19 :- Retention Volumes Calculated for Aromatic Acids.

AROMATIC ACIDS	R _v (ml)
ISOPHTHALAMIC	3.2
m-HYDROXYBENZOIC	5.8
ISOPHTHALIC	8.8
BENZOIC	15.4

Aldehydes and Ketones [121].

A simple method for the separation and quantitation of nanogram amounts of carbonyl compounds was used and entailed the precolumn derivatization of the aldehydes and ketones using 2,4-dinitrophenylhydrazine.

Table 3.20 :- Retention Volumes Calculated for Aldehyde/Ketone Derivatives.

ALDEHYDE AND KETONE DERIVATIVE	R _v (ml)
2,4-DINITROPHENYLHYDRAZINE	2.8
FORMALDEHYDE	4.2
ACETALDEHYDE	6.4
PROPIONALDEHYDE	8.2
BUTYRALDEHYDE	12.4
VALERALDEHYDE	17.8
ACETONE	11.6
METHYLETHYL KETONE	14.5
CYCLOHEXANONE	13.8
CYCLOPENTANONE	19.6
BENZALDEHYDE	18.4
2-CARBOXYBENZALDEHYDE	18.0
4-CARBOXYBENZALDEHYDE	16.6
ISOPHTHALALDEHYDE	16.2
TEREPHTHALALDEHYDE	14.8
CROTONALDEHYDE	8.6

0.01% solutions of a series of D.N.P.H. aldehyde derivative standards ranging from nC₁ to nC₅, as well as a variety of ketone and aromatic derivatives, were prepared in H.P.L.C. methanol solution. The R_v values were calculated accordingly (Table 3.20).

Amines [122].

Determination of amines was carried out through precolumn derivatization with dansyl chloride (5-dimethylamino-naphthalene-1-sulphonylchloride), which formed the corresponding amide characterized by high absorptivity, as well as fluorescence emission.

Derivatives were prepared by heating in a hermetically sealed vessel, 5.0ml of 0.25M sodium hydrogen carbonate solution with 1.0ml of 0.02M dansyl chloride solution, 0.5ml of each amine solution of the desired concentration and 10.5ml of acetone. Heating at 60°C for 20 minutes gave the best results.

A series of monoamine derivatives ranging from nC₁ to nC₅, diamine derivatives ranging from nC₂ to nC₄ and a number of aromatic amines were prepared and 1ml of each derivative solution was injected onto the column. The R_v values were calculated accordingly (Table 3.21).

Table 3.21 :- Retention Volumes Calculated for Amines.

AMINE	R _v (ml)
AMMONIA	2.6
METHYLAMINE	3.0
ETHYLAMINE	3.6
PROPYLAMINE	4.6
n-BUTYLAMINE	6.2
n-PENTYLAMINE	9.0
DIAMINOETHANE	8.8
DIAMINOPROPANE	9.5
DIAMINOBTANE	10.4
BENZYLAMINE	5.7
3-METHYL BENZYLAMINE	7.8
m-XYLYLENE DIAMINE	13.6

3.4.1.3 Gas Chromatography - Mass Spectroscopy (G.C.-M.S.).

G.C.-M.S. spectra were obtained courtesy of the Analytical Chemistry Department, C.M.B. Packaging Technology, Wantage, using a G.C. Hewlett Packard 5890 instrument.

A carrier gas of helium supplied at 10ml/min. was used through a G.C. capillary column 50 metres long and of $\frac{1}{8}$ of an inch in diameter.

The following column conditions were employed for the most effective detection of volatiles produced by the degradation of MXD,6.

- (i) Start at 35°C and hold for 2 minutes.
- (ii) Raise to 100°C at 20°C/min. and hold for 30 seconds.
- (iii) Raise to 220°C at 10°C/min.

Mass fragmentation spectra were obtained using a V.G. Masslab Trio-2 instrument attached directly after the G.C.

Samples of MXD,6 were degraded in sealed vials and immediately prior to analyses held in an oven at 50°C for 5 minutes, after which 5ml of the headspace gas was injected into the G.C.-M.S. Any volatilization product was detected using a Thermal Conducting Detector (T.C.D.).

3.4.2 Molecular Weight Measurement Techniques.

3.4.2.1 End Group Analysis [123].

3.4.2.1.1 Amine End Group Analysis (A.E.G.).

The method used for the determination of amine end groups was initially that devised by Waltz and Taylor [124]. However, the most effective solvent system for MXD,6 was found to be a mixture of phenol:methanol (80:20 w/w) rather than the suggested ratio of 70:30.

In principle, this is a simple acid/base titration where the end point can be detected potentiometrically, conductimetrically, or using a visual indicator. In this case a combination of potentiometric and visual detection was applied in determining the end point, using xylene cyanol as the indicator for the latter method. In both cases results tended to agree for a given sample.

Throughout the course of this study, A.E.G analysis was carried out with phenol : methanol as the solvent. Polymer solutions were prepared by accurately weighing approximately 0.5g of dry polymer in a 50ml conical flask and stirring vigorously, at room temperature, with 20ml of the freshly prepared solvent, using a magnetic stirrer and follower. After 15 minutes of mixing, the contents of the flask were gently refluxed, with stirring, for a further 15 minutes.

The cooled polymer solution was then titrated against a standard solution of 0.01M hydrochloric acid, using visual indicator when possible. When degraded samples coloured the polymer solutions, masking the end point, then potentiometric detection was applied.

The amount of standard acid required to neutralize a blank solvent solution was also determined and used subsequently in calculating the A.E.G. concentration.

Calculation of Amino End Group Concentration.

A polyamide solution comprising ' x^* ' grammes of polyamide in 20ml of solvent was prepared then titrated against ' w^* ' N HCl and ' V^* 'ml of acid was required for complete neutralization. If ' V_B^* 'ml of the same acid are required for the neutralization of 20ml of the blank solvent then ' $(V^*-V_B^*)$ 'ml of acid are required for the neutralization of the free amino groups in the polyamide sample.

$$\text{The number of moles of acid added} = \frac{(V^* - V_B^*) \times w^*}{1000}$$

$$\text{Hence, the number of moles of amine end groups} = \frac{(V^* - V_B^*) \times w^*}{1000}$$

However, the number of amine end groups are calculated in terms of equivalents per 10^6 g. Assuming there is one free amino end group per molecule then :-

$\text{The amino end group concentration of the polyamide} = \frac{(V^* - V_B^*) \times w^* \times 1000}{x^*}$
--

Measured in units of milliequivalents per kg.

In terms of the molecular weight,

$$\therefore \text{Molecular Weight} = \frac{1000 \times x^*}{(V^* - V_B^*) \times w^*}$$

In 10^6 g of polyamide, there are $\frac{10^6}{\text{Mol. Wt.}}$ equivalents of free amino groups. Assuming there is one free amino group per molecule then :-

$$\frac{10^6}{\text{Mol. Wt.}} = \frac{(V^* - V_B^*) \times w^* \times 1000}{x^*} \text{ equivalents}/10^6\text{g.}$$

$$\text{Mol. Wt.} = \frac{1000 \times x^*}{(V^* - V_B^*) \times w^*} \text{ equivalents}/10^6\text{g}$$

3.4.2.1.2 Carboxyl End Group Analysis (C.E.G.).

The most useful methods for the determination of carboxyl end groups are based on nonaqueous titrimetry, using an alkali soluble alcoholic solvent. Titration in hot benzyl alcohol, to a phenolphthalein end point, as proposed by Waltz and Taylor [124] was used.

The major source of error was from the oxidation of the solvent to benzoic acid, resulting in high and erratic blank titration values. Error also arose from the difficulty in detecting the end point. Due to the former reason, experiments were conducted as rapidly as possible under nitrogen.

The reagent used for dissolving the polymer was high grade pure benzyl alcohol (99%) and was only used when a 80ml test volume of solvent gave a blank titre of less than 0.15ml of 0.1M glycolic potassium hydroxide, using 0.3ml of a 1% solution of phenolphthalein in ethylene glycol as the indicator. The 0.1M glycolic potassium hydroxide solution was prepared by diluting 10ml of normal methanolic potassium hydroxide with 100ml of filtered ethylene glycol.

Approximately 0.1-0.2g of dry polymer was accurately weighed in a 25ml conical flask and 10ml of benzyl alcohol added. The polymer was dissolved under nitrogen by gently refluxing at 180°C for 20 minutes, followed by titration at 180°C using 0.02M glycolic potassium hydroxide and 0.1ml of phenolphthalein as indicator, the end point being recorded at the first trace of a persistent pink colouration.

Blank titrations for 10ml of solvent alone were carried out at 180°C as a correction for the acidity of the benzyl alcohol and used later in calculating the C.E.G. concentration.

Calculation of Carboxyl End Group Concentration.

A polyamide solution comprising 'x' grammes of polyamide in 20ml of solvent was prepared then titrated against 'w' N NaOH and 'V' ml of base was required for complete neutralization. If 'V_B' ml of the same base are required for the neutralization of 20ml of the blank solvent then '(V-V_B)' ml of base are required for the neutralization of the free carboxyl groups in the polyamide sample.

$$\text{The number of moles of base added} = \frac{(V-V_B) \times w}{1000}$$

$$\text{Hence, the number of moles of carboxyl end groups} = \frac{(V-V_B) \times w}{1000}$$

However, the number of carboxyl end groups are calculated in terms of equivalents per 10^6 g. Assuming there is one free carboxyl end group per molecule then

∴-

$\text{The carboxyl end group concentration of the polyamide} = \frac{(V-V_B) \times w \times 1000}{x}$

Measured in units of milliequivalents per kg

In terms of the molecular weight,

$$\therefore \text{Molecular Weight} = \frac{1000 \times x}{(V-V_B) \times w}$$

In 10^6 g of polyamide, there are $\frac{10^6}{\text{Mol. Wt.}}$ equivalents of free carboxyl groups.

Assuming there is one free carboxy group per molecule then ∴-

$$\frac{10^6}{\text{Mol. Wt.}} = \frac{(V-V_B) \times w \times 1000}{x} \text{ equivalents}/10^6\text{g.}$$

$$\text{Mol. Wt.} = \frac{1000 \times x}{(V-V_B) \times w} \text{ equivalents}/10^6\text{g}$$

3.4.2.2 Dilute Solution Viscometry.

The method applied for the determination of the average molecular weight of a polymer was that of dilute solution viscometry. Dilute solution viscometry is really a measure of the size or extension in space of a polymer molecule, but is also related empirically to the molecular weight for a linear molecule [125]. For this reason, it was considered a reliable method for the determination of the average molecular weight of the polymer employed in this work.

Dilute solution viscometry is commonly measured by using a capillary viscometer. In this case, an Ostwald viscometer was chosen preferentially for single-point measurements, as this type of analysis is less prone to the effects of degradation and tends to give more accurate values for intrinsic viscosity calculation [127].

The capillary size of the viscometer was chosen such that the flow time was above 100 seconds for the pure solvent, dichloroacetic acid, (D.C.A.), thereby eliminating density and kinetic energy corrections.

The following equation was used for the determination of the intrinsic viscosity :-

$$[\eta] = \frac{1}{C} \sqrt{2(\eta_{sp} - \ln \eta)}$$

However, this formula is only valid when the difference between the Huggins constant, K_h and the Kraemer constant, K_k is 0.5 i.e.

$$K_h - K_k = 0.5$$

the constants being derived from their respective equations :-

Huggins Equation :-

$$\frac{\eta_{sp}}{C} = [\eta] + K_h [\eta]^2 \times C$$

Kraemer Equation :-

$$\ln \frac{\eta_{rel.}}{C} = [\eta] + K_k [\eta]^2 \times C$$

In order to justify the calculation of the intrinsic viscosity from equation [127], an Ubbelohde viscometer was employed to measure a series of viscosities at different concentrations and from these results, $K_h - K_k$ was calculated to be in the region of 0.44 to 0.46, thereby allowing further solution viscometry work to be conducted using the said equation and the single-point measurement technique.

During the course of this work, a number of solvents were evaluated, however, D.C.A. was found to be the best solvent for this particular polymer. 1% (w/v) polymer solutions were prepared in D.C.A., flowtimes being recorded using an Ostwald viscometer, held in a thermostatted water bath at $25 \pm 0.005^\circ\text{C}$. The flowtimes for each sample were determined in triplicate, with measurements reproducible within 0.2 seconds.

3.4.3 Spectroscopic Techniques.

3.4.3.1 Fourier Transform Infrared Spectroscopy (F.T.I.R.).

Infrared spectra were obtained using a Perkin Elmer F.T.I.R. 1725X Spectrophotometer. Most of the samples were prepared in the form of potassium bromide discs. However, some spectra were also taken using thin films of the samples cast on sodium chloride cells, from a highly volatile solvent. In such cases, a solvent system of chloroform:hexafluoroisopropanol, (98:2), was used [128].

3.4.4 Thermal Analysis Techniques [129].

3.4.4.1 Differential Scanning Calorimetry (D.S.C.).

The studies on polymers using D.S.C. were performed on a DuPont 910 D.S.C. module, which was controlled by a DuPont 2000 Thermal Analyser. Information relating to the glass transition temperatures (T_g), the crystallization temperatures (T_c) and the melting temperatures (T_m) of the polymers was derived using D.S.C. Normally, 5-10mg samples were weighed in sealed aluminium pans and heated at $20^\circ\text{C}/\text{min}$. under a nitrogen atmosphere, supplied at 50ml/min., up to 320°C .

3.4.4.2 Thermogravimetric Analysis (T.G.A.).

Thermal degradation was investigated by T.G.A., using a DuPont 951 T.G.A. module controlled by a DuPont 2000 Thermal Analyser. Weight loss was monitored against isothermal temperatures, ($150\text{-}230^\circ\text{C}$) and the degree of degradation, if any, calculated. Similar sample sizes and heating up conditions to those of D.S.C. were employed for T.G.A.

3.5 OXYGEN PERMEATION MEASUREMENT.

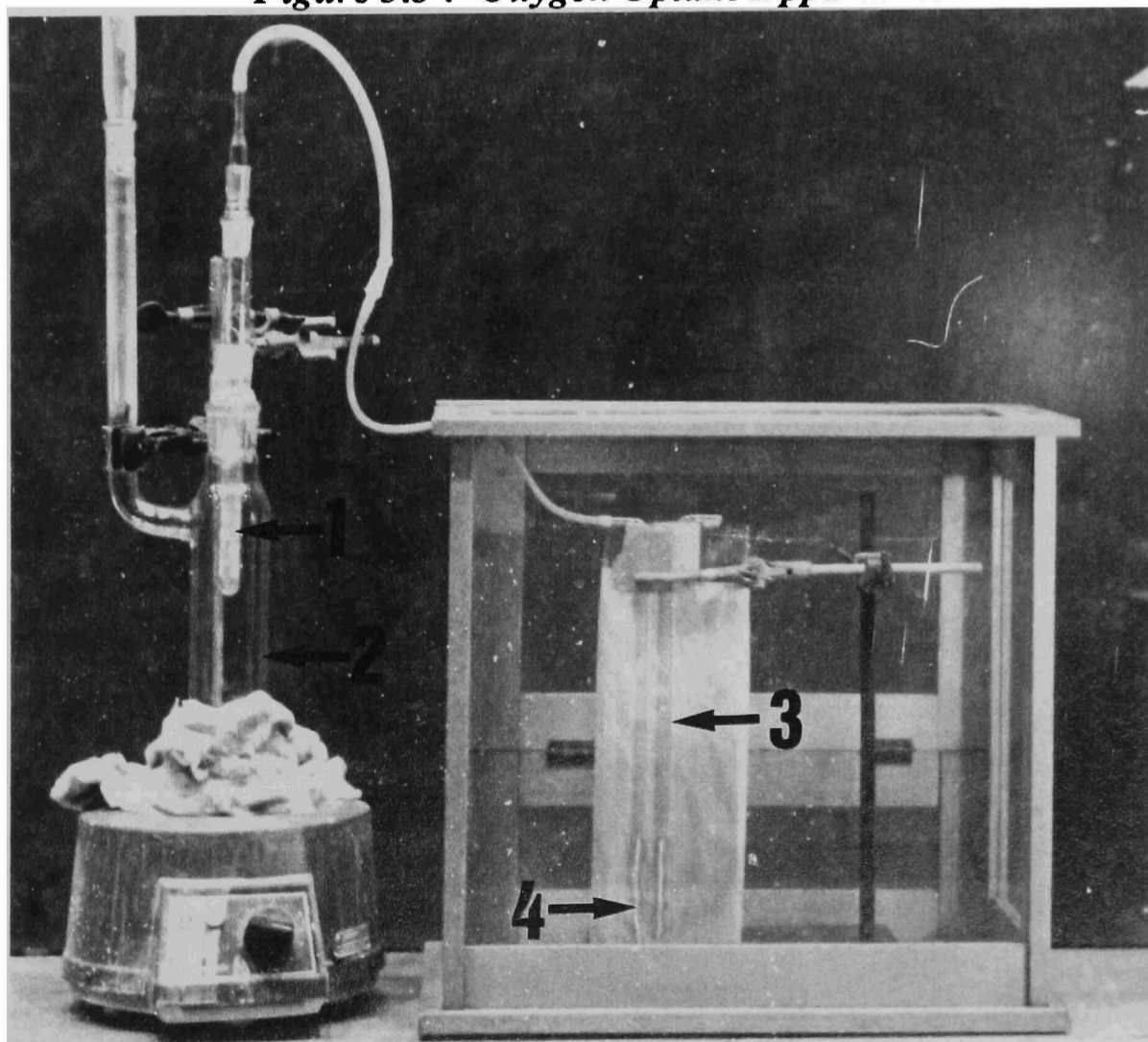
3.5.1 Introduction.

Early tests conducted to measure the rate of oxygenation of natural rubber are often used to measure the stability of polymers today. One such procedure was used to understand MXD,6 oxidation, spun with and without cobalt. Using typical oxygen uptake apparatus [86] (Figure 3.3), the influence of cobalt as a catalyst was established.

3.5.2 Method.

A polymerization tube containing 4g of fibre was placed in a vapour bath at 100°C, then connected to a manometer containing water. Normally, an immediate pressure build up was observed as a rise in the water level in the right arm of the manometer, which would returned back to atmospheric pressure over a recorded time period referred to as the Induction Period. Later, the polymer takes up oxygen seen as a rise in the water level in the left arm of the manometer. The rate of rise in the manometer was recorded for up to 60 minutes and was thought to be a satisfactory means by which the oxygen uptake of a polymer was evaluated.

Figure 3.3 :- Oxygen Uptake Apparatus.



(1) Fibre sample. (2) Vapour bath at 100°C. (3) Manometer. (4) Water level.

3.6 DEGRADATION.

In order to propose a feasible mechanism for the thermo-oxidative degradation of MXD,6, it was essential to identify the non-volatile and volatile products of degradation.

Initial investigations were conducted on the non-volatile fraction employing methods developed by East et al [88] and Mori et al [116]. Furthermore, analysis of the volatile fraction was also carried out using headspace analysis. This method involved using accurately weighed fibre samples sealed in small degradation vials, which were subsequently heated at an elevated temperature. Volatiles formed during the degradation were recovered from the headspace using a hot syringe and injected into a solvent, for later analysis.

3.6.1 Non-volatile Analysis.

Two dissimilar techniques were used for the detection of non-volatiles produced during the thermal oxidation of MXD,6 :-

Acid hydrolysis of degraded polymer followed by steam distillation according to East et al.

Acid hydrolysis of degraded polymer followed by evaporation according to Mori et al.

3.6.1.1 Analysis According to East et al.

Steam distillation of degraded polymer hydrolysed in acid, was also investigated by Kakar [130] and later by Lupton [131]. Kakar worked predominantly on nylon 6,6 thermal degradation whereas Lupton conducted a significant degree of research into the thermal degradation of nylon 6 as well as nylon 6,6 in the solid state.

Acids and bases could be separated by this method, by initially conducting the distillation at an acidic pH, for acids, then adjusting the pH to that of a strongly basic solution, for bases.

(i) Degradation.

12.5g of dried polymer fibre was degraded by heating in an oven at 180°C, in an open 500ml round bottomed flask for 12 hours, after which the flask was removed and stored in a vacuum desiccator over phosphorus pentoxide.

(ii) Hydrolysis.

Once cooled, the flask was fitted with a ground glass stopcock and the degraded polymer shaken with 250ml of 5M hydrochloric acid. The mixture was solidified at -78°C by placing the flask in a slurry of acetone and dry ice. The flask was evacuated for one minute using a vacuum pump and the stopcock closed hence providing a degassed atmosphere above the solid mixture. The mixture was allowed to liquefy at room temperature, after which the degassing procedure was repeated. After the vacuum pump was removed, the flask was sealed under vacuum and maintained at 110°C for 24 hours to complete hydrolysis.

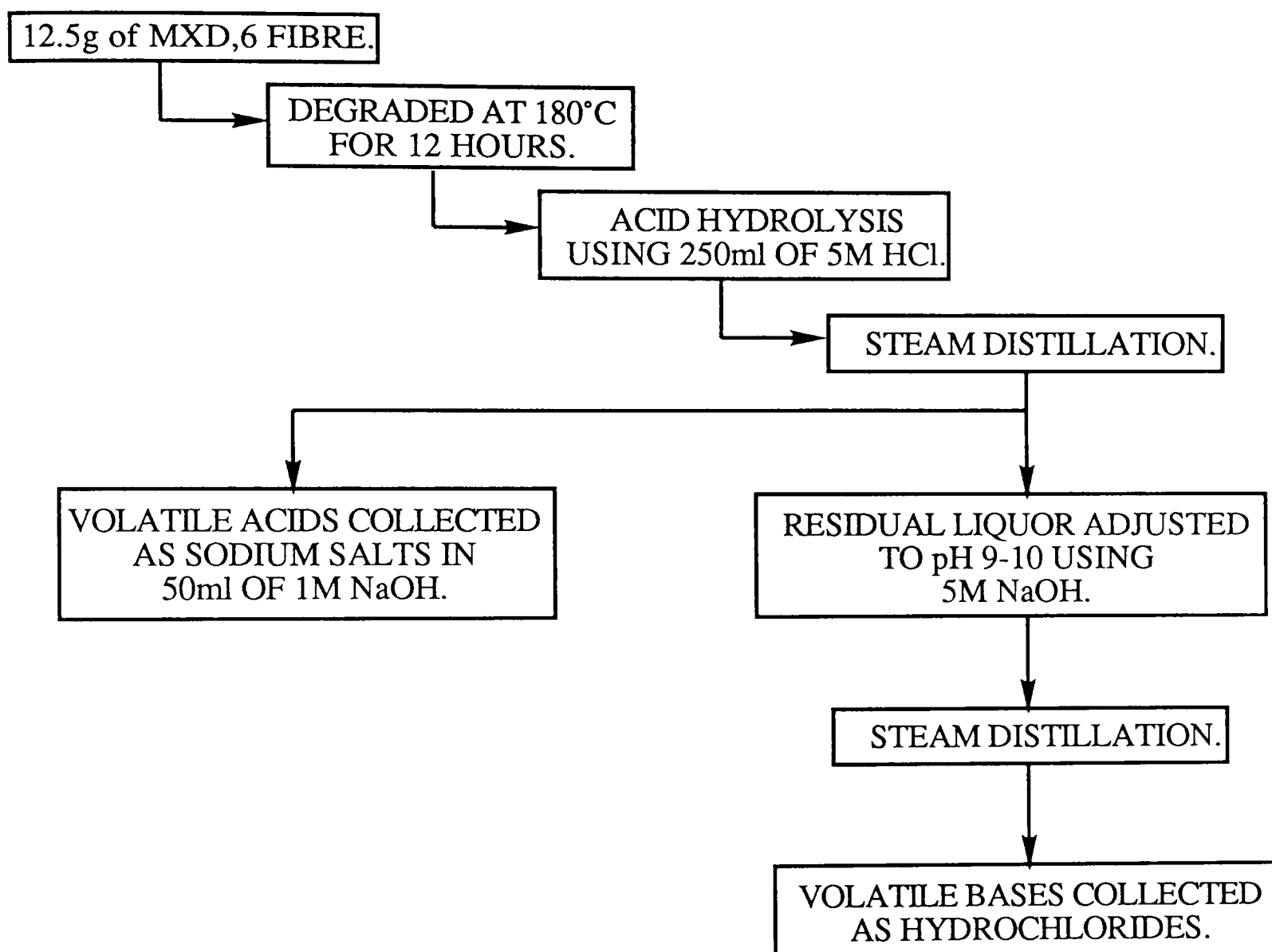
(iii) Fractionation of the Hydrolysate.

Fractionation of the hydrolysate was carried out according to the scheme shown (Figure 3.4).

The acids were initially separated by subjecting the acidic hydrolysate to steam distillation, the distillate being first collected as the free acids in solution and then trapped in 1M sodium hydroxide solution as the acid salts. Steam distillation was ceased once a pH of 6-7 was recorded for the distillate using indicator paper. The distilled acids were subsequently used for analysis using T.L.C. and H.P.L.C.

The residual liquor from the acid steam distillation was then adjusted to pH 9.0 with 5M sodium hydroxide solution and again subjected to steam distillation to separate any bases.

Figure 3.4 :- Fractionation of Hydrolysate.



3.6.1.2 Analysis According to Mori et al [116].

This form of characterization was conducted especially for dicarboxylic acids and diamines. The same procedure for acid hydrolysis was conducted for this method as for the technique suggested by East et al, however instead of steam distillation, the hydrolysate was evaporated to near complete dryness using a rotary evaporator, then dried completely in vacuo. The dried hydrolysate was dissolved in absolute alcohol to give a 1% solution which was spotted on a silica gel 60 F₂₅₄, (20 × 20cm) T.L.C. plate along side a series of standard diamine dihydrochlorides and dicarboxylic acids. Chromatography was carried out using a solvent system comprising phenol:n-butanol:formic acid:water (5:2:1:2). After the solvent front had reached approximately 15cm, the plate was dried after which it was sprayed with a 2% alcoholic solution of ninydrin and heated at 90°C for 15 minutes for positioning of the diamine dihydrochlorides. Once located the plate was then sprayed with an alcoholic solution of bromocresol green for dicarboxylic acid location. R_f value were subsequently calculated accordingly (Table 3.22).

Table 3.22 :- Relative Front Values for Diamine Hydrochlorides and Dicarboxylic Acids.

DIAMINE DIHYDROCHLORIDE OR DICARBOXYLIC ACID	R _f
DIAMINOETHANE	0.39
DIAMINOPROPANE	0.43
DIAMINOBTUTANE	0.46
OXALIC	0.29
MALONIC	0.44
SUCCINIC	0.55
GLUTARIC	0.67
ADIPIC	0.74

3.6.2 Volatile Analysis.

A novel system where by the volatiles produced during thermal oxidation of the polymer and released from the polymer was devised using headspace analysis. 2.00g of polymer fibre was sealed in a 25ml vial using a Teflon coated silicon septum and the whole assembly placed in an oven at 180°C for a predetermined period. Once the time had elapsed, 50ml of the headspace was drawn into a hot syringe and immediately injected into an appropriate solvent, the nature of which depended on what was to be analysed.

(i) Acid Analysis.

50ml of the headspace was injected into 10ml of ether, in a 10ml conical flask. The flask was sealed and kept cool prior to use.

(ii) Aldehyde and Ketone Analysis.

50ml of the headspace was injected into 10ml of a solution of 2,4-dinitrophenylhydrazine in order to prepare the 2,4-dinitrophenylhydrazone.

(iii) Amine Analysis.

50ml of the headspace was injected into 16.5ml of dansyl chloride solution in order to prepare the respective dansyl chloride derivative.

3.6.3 Melt Phase Thermal Degradation.

A number of MXD,6 samples were degraded in the melt using regulated conditions. Since temperatures above 250°C were employed, oxidation would occur rapidly in the presence of air causing accelerated gel and colour formation. For this reason, degradation was conducted under an inert atmosphere of nitrogen.

Ordinarily, several samples of polymer were degraded simultaneously in an oven at $280 \pm 5^\circ\text{C}$ and removed at regular intervals, for subsequent analysis. Any changes in molecular weight measured by solution viscometry during the course of heating, was recorded against the degradation time.

Typically, several identical 2g samples of polymer were weighed in aluminium trays and placed in an preheated oven supplied with nitrogen at 100ml/min.

Samples were methodically withdrawn every 30 minutes for the first 5 hours, then every hour thereafter up to 9 hours.

Samples recovered were analysed for A.E.G., C.E.G., and I.V.

3.7 SYNTHESIS OF EXPECTED DEGRADATION PRODUCTS.

To obtain a better understanding of the mechanisms associated with the decomposition of MXD,6, a number of unique compounds thought to be formed during the course of the polymers degradation were synthesized and subsequently utilized as standards for T.L.C. and H.P.L.C.

The behaviour of these compounds at elevated temperatures was also studied enabling mechanisms to be suggested capable of occurring in the polymer itself.

3.7.1 Isophthalamic Acid.

Based on research conducted by McIntyre [132] on the oxidation of alkyl substituted aromatic compounds to their corresponding aromatic carboxylic acids, it was thought that the air oxidation of m-toluamide could result in the formation of isophthalamic acid.

20g of m-toluamide was dissolved in 200ml of propionic acid, containing 0.195g cobalt bromide and 0.35g manganese bromide catalysts. Oxygen was bubbled through the vigorously stirred refluxing solution for 10 hours and the precipitated solid was filtered hot. The recovered acid was purified by refluxing in acetone for 30 minutes to remove any unreacted amide. After filtering hot, the solid was dried and finally recrystallized from boiling water.

The purity of the isophthalamic acid was confirmed by T.L.C., H.P.L.C., and D.S.C., the latter revealing a single melting point of 289.09°C. A yield of 86% was obtained.

3.7.2 Adipamic Acid.

The preparation of adipamic acid was conducted using the mono-methyl ester of the dicarboxylic acid.

16g of mono-methyl adipate was shaken up with 100ml of 35% ammonia for 5 hours. This resulted in the formation of the ammonium salt of the amide which was then acidified using dilute sulphuric acid to give the acid-amide. After recovery, the adipamic acid was purified by recrystallizing from water. A yield of 79% was obtained.

CHAPTER FOUR :- RESULTS AND DISCUSSION.

4.1 MXD,6 POLYMERIZATION.

Utilizing the two discussed techniques available for the polymerization of MXD,6, two batches of polymer of dissimilar properties were synthesized. Both polymers were characterized and the results compared to those of commercially available MXD,6 (Table 4.1).

Polymer prepared using the conventional two stage polymerization technique via the nylon salt was found to have a higher I.V. than that prepared via the one stage direct polymerization technique suggested by Miyamoto et al [38]. According to the Japanese researchers, their method of MXD,6 preparation was more economical and efficient than that of conventional polycondensation. They also implied that more heat was required for a longer time to polymerize MXD,6 using the two stage route which subsequently resulted in a polymer of low molecular weight and yield.

However, for reasons unknown, this was not the case during the course of this study. Employing the two stage procedure, polymer was prepared at 240-250°C. The direct polymerization method was conducted at 260°C as suggested by Miyamoto, a temperature at which the polymer will clearly be more susceptible to degradation.

Even though the two stage method did take a longer time to prepare the polymer, mainly due to the extra nylon salt preparation stage, it resulted in a polymer of higher quality. In comparison to the near white hard polymer obtained from the two stage procedure, a pale yellow brittle polymer resulted from the alternative method.

There may be a number of interpretations to suggest why the direct method resulted in a polymer of lower standard. Applying a volatile diamine (boiling point 139°C) to molten dicarboxylic acid at 153°C would probably result in the loss of diamine by evaporation. Miyamoto had suggested that addition of an excess of diamine would

compensate for this loss. Nevertheless, results tend to contradict his claims. Results show polymers with varying molecular weights from batch to batch. In order to prevent this loss, the reaction system could be kept under pressure with steam. Naturally, this would mean the apparatus employed for the polycondensation would have to withstand the applied pressure, complicating the apparatus and operation in general. On the other hand, preparing the nylon salt prior to polymerization will not lead to a significant loss in diamine and will consequently result in a polymer of higher molecular weight.

Table 4.1 :- Main Characteristics of the Synthesized Polyamides Compared to Commercially Available MXD,6.

POLYMERIZATION METHOD.	Tg (°C)	Tc (°C)	Tm (°C)	I.V.	DESCRIPTION OF POLYMER.
ONE STAGE DIRECT POLYCONDENSATION.	53.81	126.09	208.38	0.28	PALE YELLOW BRITTLE POLYMER.
TWO STAGE POLYCONDENSATION.	78.42	149.56	230.88	0.59	PALE CREAM HARD POLYMER.
COMMERCIAL MXD,6.	87.46	157.68	237.45	0.65	WHITE HARD POLYMER.

Secondly, direct polycondensation is conducted entirely at atmospheric pressure, whereas the two stage method requires vacuum finishing during the end of the reaction. This aids in removing the condensation by-products, pushing the equilibrium towards the polymer and so heading to a higher molecular weight polymer.

Miyamoto's direct polycondensation method may have been more successful if employed for a polyamide prepared from a more stable diamine. MXD is very sensitive to the presence of oxygen, especially at elevated temperatures and will readily colour even if stored in an inert atmosphere. Even though a very pure grade of MXD (99%) was used, impurity in the form of chromophores was still observed. An impure monomer will consequently lead to an impure polymer. However, during the two stage method, the nylon salt is purified prior to its polymerization therefore many of the initial impurities may be removed during this stage. Thus a polymer of higher grade will result from this procedure of polymerization in comparison to polymer prepared via Miyamoto's method where no monomer purification is suggested.

Thus the properties of the polymer prepared by the two stage technique are similar to those of the commercially available polymer. I.R. data of the polymer prepared this way also showed very little difference to the commercially available polymer. It was with the main intent to confirm that both polymers were of a similar nature that these investigations were initially carried out i.e. that the commercial polymer was genuinely that of pure MXD,6 and not of a lower grade with the possibility of the presence of impurities. Further study was therefore conducted on the readily available commercial MXD,6 rather than preparing a large quantity of the same polymer in the laboratory.

4.2 OXIDATION OF SPUN FIBRE.

4.2.1 Oxygen Uptake Experiments.

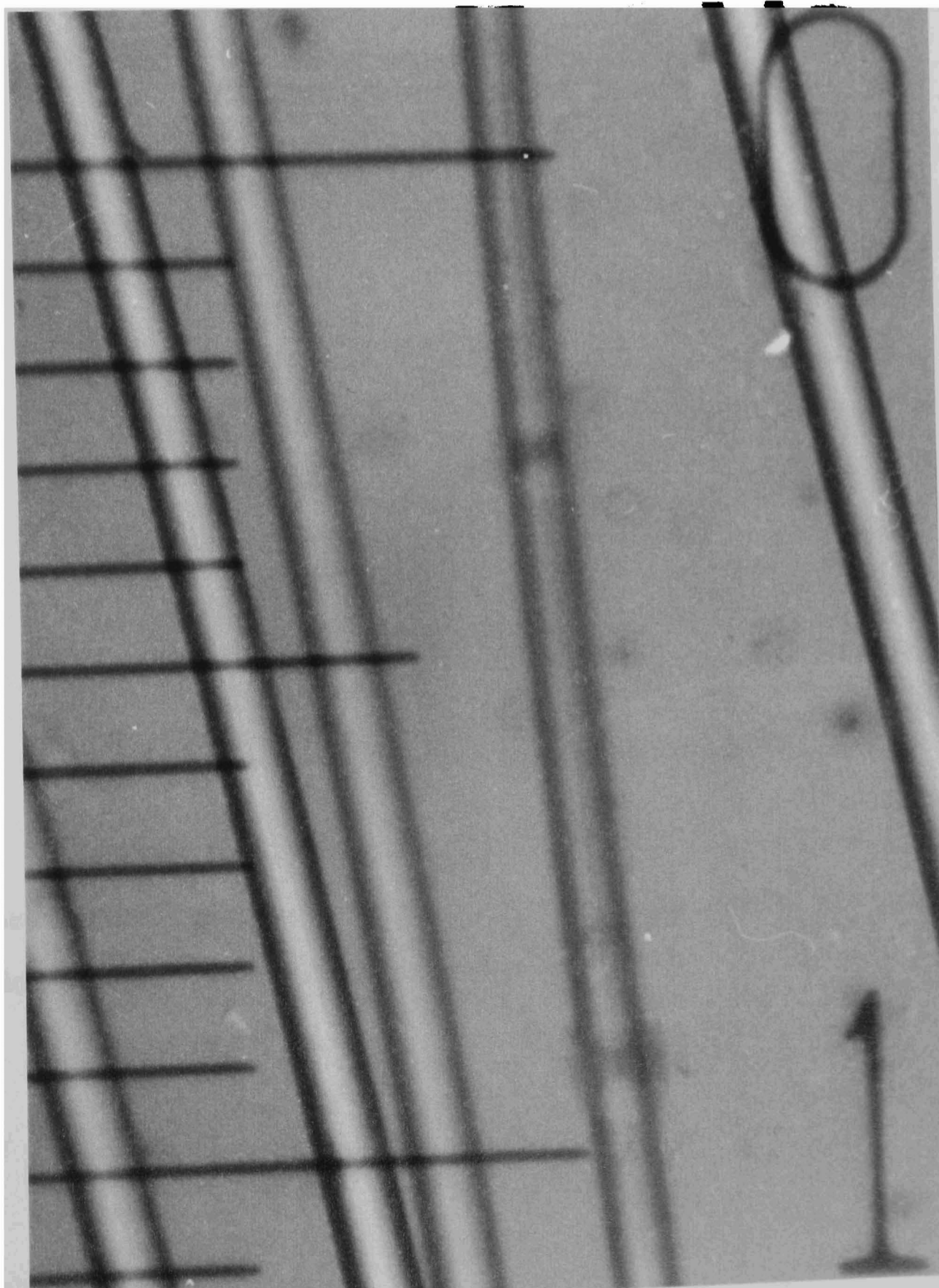
The method employed to determine the rate of thermal oxidation under accelerated conditions was simple, however it gave significant information to establish the effectiveness of cobalt as a catalyst for the polymer system.

Oxygen uptake measurements were conducted on not only MXD,6 fibre, but also on fibre from a blend consisting of MXD,6 and a polyester, namely poly(ethylene terephthalate). This was in order to reproduce composites similar to those utilized in the packaging industries, where such blends are commonly used to prepare containers, especially bottles, with improved capacity to withstand the passage of oxygen. In the C.M.B. patent claiming this type of product [50], a polymer composition comprising 96% polyethylene terephthalate and 4% MXD, 6 containing as an active component a metal compound having capacity to catalyse the scavenging of oxygen, had been reported. In this investigation, such a blend was prepared with 50, 100, 200 and 400ppm of cobalt and fibres spun from these mixtures were stored in an inert atmosphere, in the dark, prior to being used. Also spun were samples of MXD,6 with 50, 200, 400 and 2000ppm cobalt which were stored in a similar manner to the polyester-polyamide blended fibres.

To ensure all physical dimensions of the fibres were similar, so that comparisons could be made solely on the concentration of the catalyst, optical microscopic photographs were taken of the different fibre types, enabling diameters to be measured accurately (Figure 4.1). On the scale provide, 0 to 1 is \equiv 1cm. Total magnification is \approx 150 \times . On average a value of $76.75 \pm 1.25 \mu\text{m}$ was calculated for all samples.

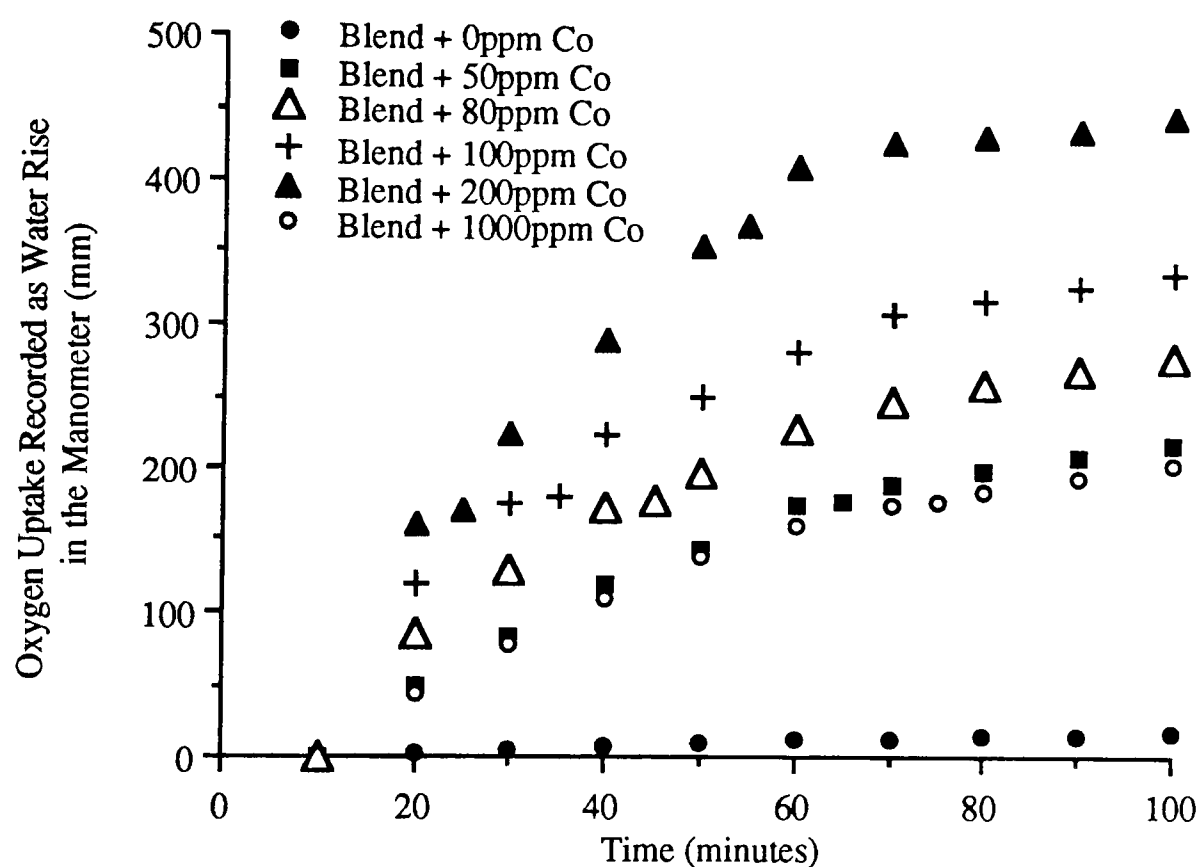
Curves relating the rate of oxygen uptake to the cobalt ion concentration were obtained and the influence of the metal ion as a catalyst for oxygen scavenging was assessed. The initial lack of oxygen uptake is referred to as the induction period. However, only the rate at which oxygen reacts with the blend was measured in these tests. The induction period was found not to be influenced consistently by the concentration of the catalyst and was found to range from 0 to 10 minutes for all samples studied.

Figure 4.1 :- Fibre Diameters Determined from Optical Microscopic Photographs.



Initial interpretations of the results for the blends reveal that the rate of oxidation rises with catalyst concentration until the catalyst concentration reaches a critical concentration where the most effective oxygen uptake results are recorded ($\approx 200\text{ppm}$). Thereafter further small increments in catalyst concentration result in the oxygen uptake rate suffering a catastrophic decline (Figure 4.2).

Figure 4.2 :- Curves relating the rate of Oxygen Uptake to the Concentration of Cobalt in a Blend of 96% Polyester and 4% MXD,6 at 100°C.



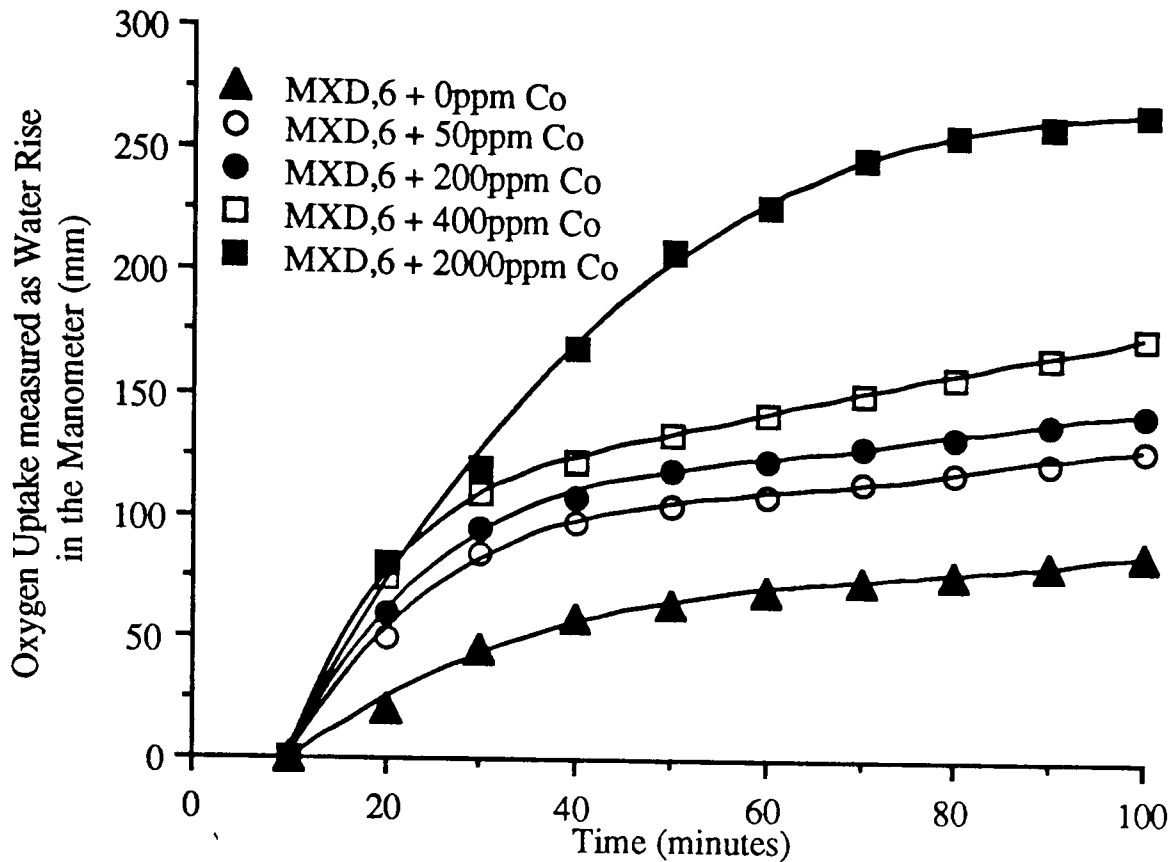
Note : The experiments were conducted on a batchwise exposure basis with renewal of the air at intervals, hence the intermittent nature of the graphs.

Furthermore, many other scientists including Kamiya and Ingold [133] have observed a similar decline in the rate of oxidation of polymers as the concentration of the transition metal ion is increased beyond a critical value.

Curves derived from these results clearly indicate a critical metal ion concentration in the region of 200ppm cobalt, at which levels optimum oxygen uptake properties are observed. Bottles and other containers prepared from such a blend also proved to be the most effective as a barrier to the passage of oxygen through the walls of the vessel. With respect to the general trends of these curves, it is suggested that by approximately 100 minutes of oxidation at 100°C, the active sites in the blend prepared with 200ppm cobalt became fully saturated (≈ 450 mm water rise on the manometer scale), hence the levelling off of the curve i.e. a decline in the rate of oxygen uptake. All other blends were observed to be still active during this stage of oxidation, (curves were still rising) which, given time, would also reach a stage of full saturation.

Furthermore, it was essential to vent the system regularly to the atmosphere in order to replenish the oxygen supply in the apparatus thereby allowing the continual measurement of oxygen uptake. Generally venting was conducted after approximately 175mm of water rise in the manometer. After venting, it was usual to find a decrease in the rate of oxygen uptake. Oxygen uptake measurements for MXD,6 fibres prepared with 50, 200, 400 and 2000ppm cobalt were also conducted. Similar plots to those obtained for the blend were derived (Figure 4.3).

Figure 4.3 :- Curves relating the rate of Oxygen Uptake to the Concentration of Cobalt in MXD,6 at 100°C.



The results revealed that a critical concentration greater than 2000ppm cobalt existed, compared to 200ppm for the 'ideal' blend. However, further concentrations of metal ion could not be incorporated into the unmodified MXD,6 as fibres spun from such a blend had inconsistent physical properties along their axis.

With these initial observations in mind, it was proposed that the cobalt ions complexed or were associated exclusively with the MXD,6 fraction of the blend. Since the most effective blend is 96% PET to 4% MXD,6 with 200ppm cobalt, then based on this assumption the concentration of metal ion with respect to the polyamide alone is 5000ppm cobalt. At such high concentrations of metal ion, the Fourné melt extruder was unable to spin fibres with similar dimensions to fibres prepared with lower concentrations, hence further analyses with these levels of catalyst were discontinued. Nevertheless, if this assumption is justified, then the oxygen uptake curve for a sample

of MXD,6 with 2000ppm cobalt, for example, should match that of the equivalent concentration of cobalt ion in an 96% PET, 4% MXD,6 blend i.e. 80ppm. Such a blend was not prepared for fibre spinning as this result was not then anticipated. However, a good estimation of the type of curve expected would be one in between the curves derived for 50 and 100ppm cobalt in the ideal blend (Figure 4.2). After 100 minutes of heating time had elapsed, the degree of oxidation recorded as oxygen uptake would be in the region of 250mm water rise. At a similar stage of the experiment, MXD,6 with 2000ppm cobalt gave an oxygen uptake value of approximately 220mm water rise in the manometer. These values are in good agreement and support the conclusion that the cobalt catalyst is exclusively associated with the MXD,6 and not the PET fraction of the blend.

4.2.2 Thermogravimetric Analysis of MXD,6 Fibres with and without Cobalt.

Thermogravimetric Analysis (T.G.A.) investigations were conducted on samples of MXD,6 with and without cobalt to obtain a better understanding not only of the mechanisms involved in the oxidation of the polyamide, but also of the role of the metal ion catalyst.

Samples of unmodified MXD,6, and MXD,6 with 100, 200 and 400ppm cobalt were heated isothermally in air at 200, 210 and 220°C for 15 hours. As the chemistry of the thermal oxidation of a polymer in the melt may differ from that conducted in the solid state, the temperatures employed in this study were all below the melting points of the polymers enabling comparisons to be made with oxygen uptake results.

Traces derived from isothermally heating these fibres gave trends revealing the action of temperature and cobalt catalyst concentration on the oxidation of MXD,6 (Figures 4.4 to 4.7). As expected, at higher temperatures the rate of weight loss was greater than at lower temperatures. In all cases, some degree of oxidation in the form of a weight gain was observed prior to any actual weight loss. D.S.C. traces of the same samples showed exotherms at similar times to the T.G.A. again suggesting oxidation. This exothermic weight gain was found to be dependent on both the temperature of oxidation and the concentration of catalyst in the polyamide. At high temperatures and low levels of cobalt ion, the weight gain was more apparent and concentrated over a shorter period of time. It appears that two reactions are associated with the oxidative degradation of the polymer. The initial weight gain is thought to be related to the oxygen up take of MXD,6. Polymer oxidation will result in the formation of, for example, hydroperoxide and carbonyl groups which decompose to form volatiles ejected from the polymer as, for example, carboxylic acids, aldehydes and ketones. Therefore the initial weight gain is thought to be caused by oxygen reacting with the polymer and the weight loss due to the emission of the oxidation by-products. These interpretations would explain the curvature of the T.G.A. traces obtained.

Furthermore the influence of 0, 100, 200 and 400ppm cobalt as a catalyst was investigated and their respective activation energies were calculated from the T.G.A traces.

Figure 4.4 :- T.G.A. Traces Obtained from the Isothermal Heating of MXD,6 at 200, 210 and 220°C in Air.

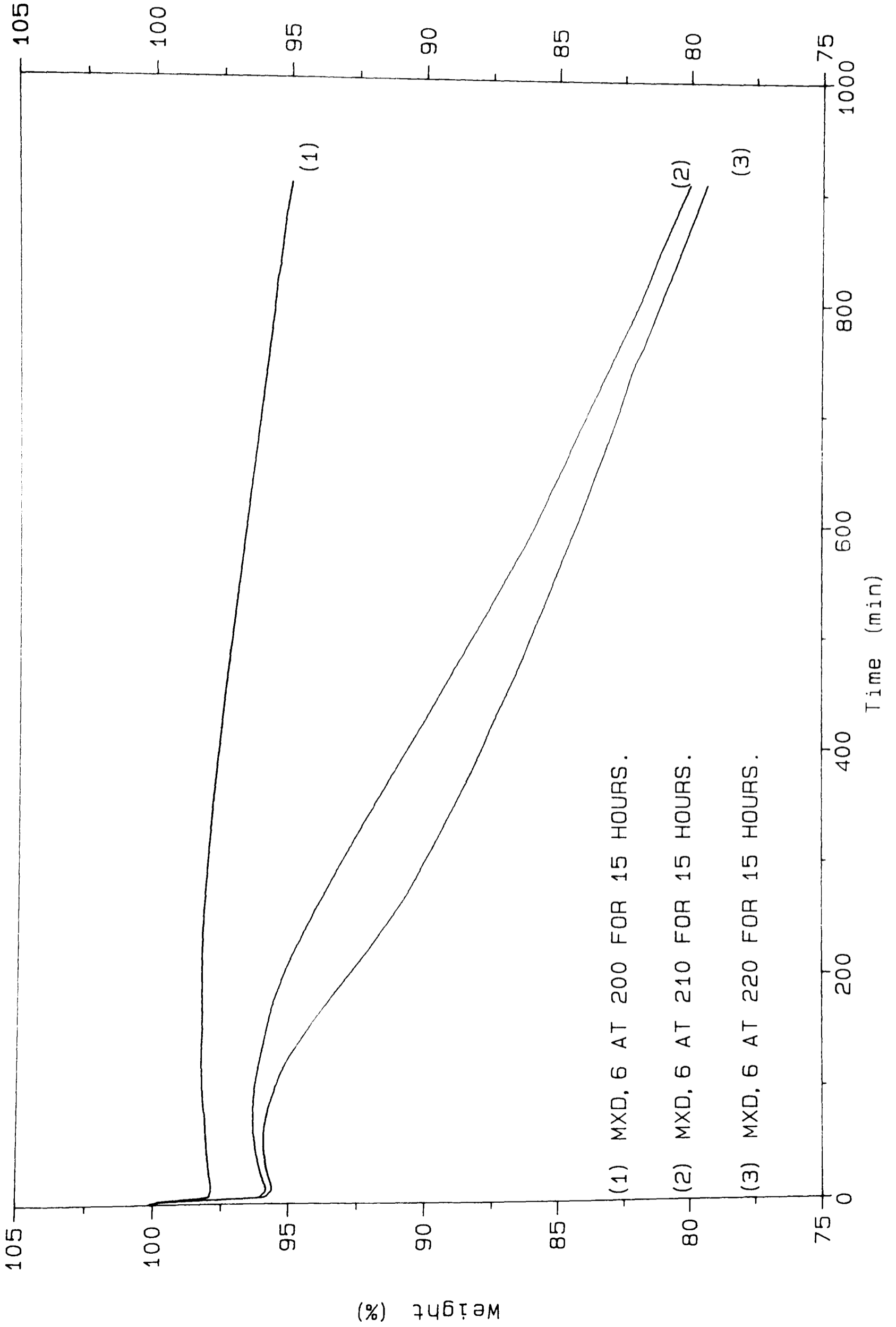


Figure 4.5 :- T.G.A. Traces Obtained from the Isothermal Heating of MXD,6 with 100ppm Cobalt at 200, 210 and 220°C in Air.

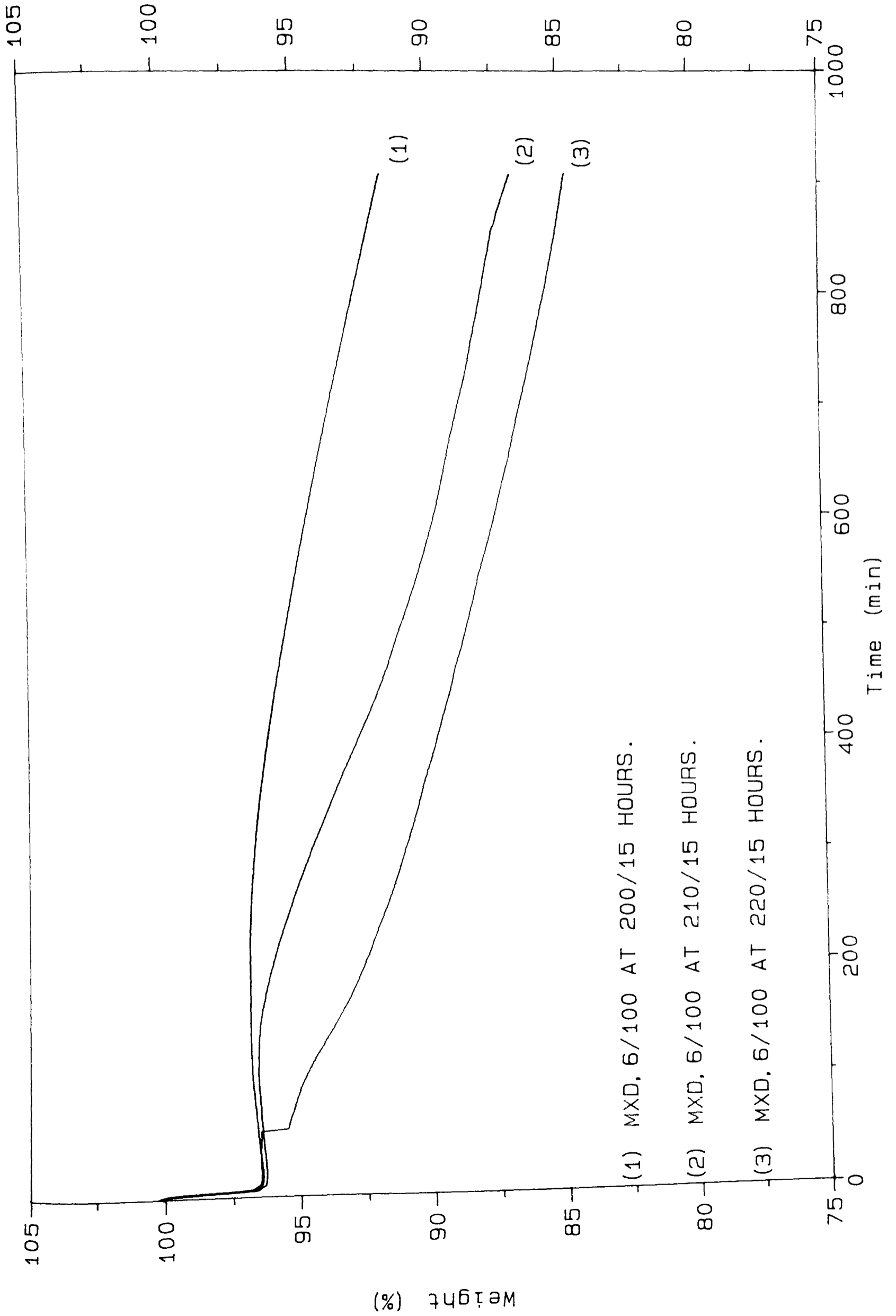


Figure 4.6 :- T.G.A. Traces Obtained from the Isothermal Heating of MXD,6 with 200ppm Cobalt at 200, 210 and 220°C in Air.

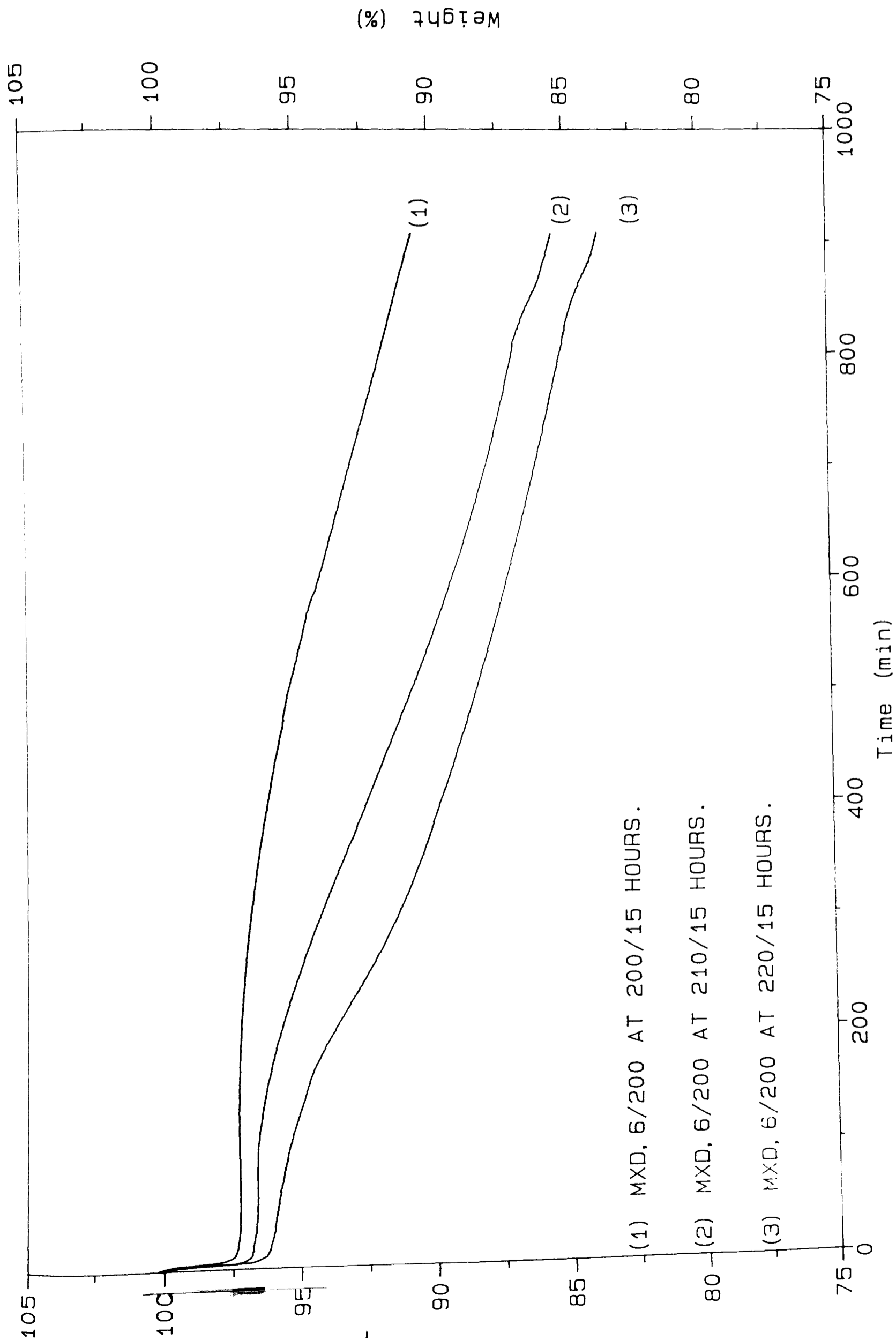
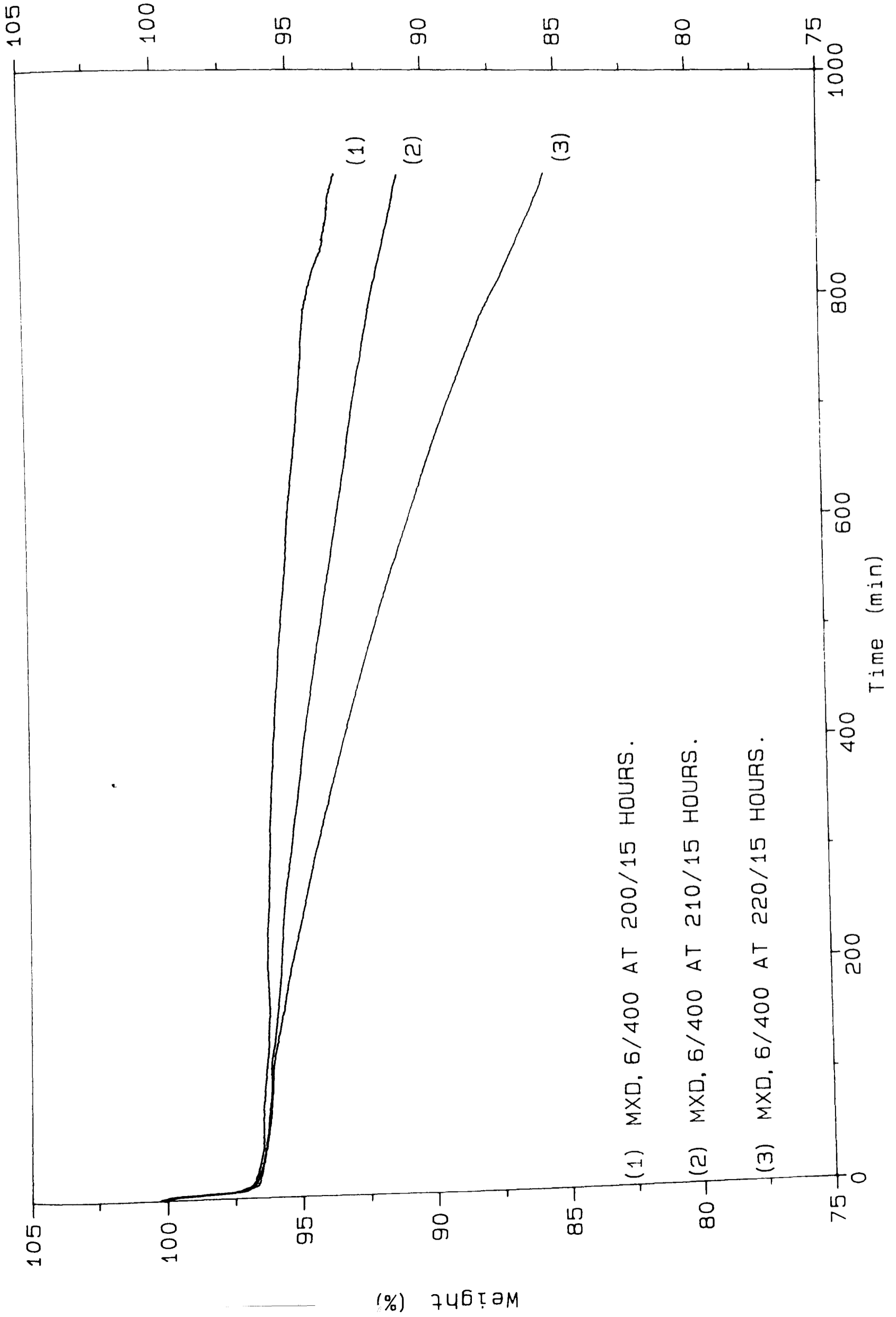


Figure 4.7 :- T.G.A. Traces Obtained from the Isothermal Heating of MXD,6 with 400ppm Cobalt at 200, 210 and 220°C in Air.



Based on first order kinetics, it was possible to estimate the activation energies associated with the oxidative weight loss (oxidative degradation) of MXD,6 with and without cobalt. The slopes of each trace were calculated directly after the onset of weight loss and recorded as rate constants 'k' (Table 4.2).

Table 4.2 :- Rate Constants Derived for the Thermal Oxidation of Samples of MXD,6 with and without Cobalt.

Sample Type	Degradation Temp. (°C)	Rate Constant 'k' (s ⁻¹)	ln 'k'
Unmodified MXD,6	200	- 1.27 × 10 ⁻⁵	- 11.275
Unmodified MXD,6	210	- 3.27 × 10 ⁻⁵	- 10.329
Unmodified MXD,6	220	- 6.44 × 10 ⁻⁵	- 9.651
MXD,6+100ppm Co	200	- 1.38 × 10 ⁻⁵	- 11.195
MXD,6+100ppm Co	210	- 2.75 × 10 ⁻⁵	- 10.501
MXD,6+100ppm Co	220	- 4.78 × 10 ⁻⁵	- 9.948
MXD,6+200ppm Co	200	- 1.48 × 10 ⁻⁵	- 11.123
MXD,6+200ppm Co	210	- 2.68 × 10 ⁻⁵	- 10.526
MXD,6+200ppm Co	220	- 4.28 × 10 ⁻⁵	- 10.058
MXD,6+400ppm Co	200	- 6.97 × 10 ⁻⁶	- 11.874
MXD,6+400ppm Co	210	- 1.03 × 10 ⁻⁵	- 11.485
MXD,6+400ppm Co	220	- 1.64 × 10 ⁻⁵	- 11.018

Thus using the Arrhenius expression, the activation energy for each run was calculated :-

$$k = A \exp(-E_a/RT)$$

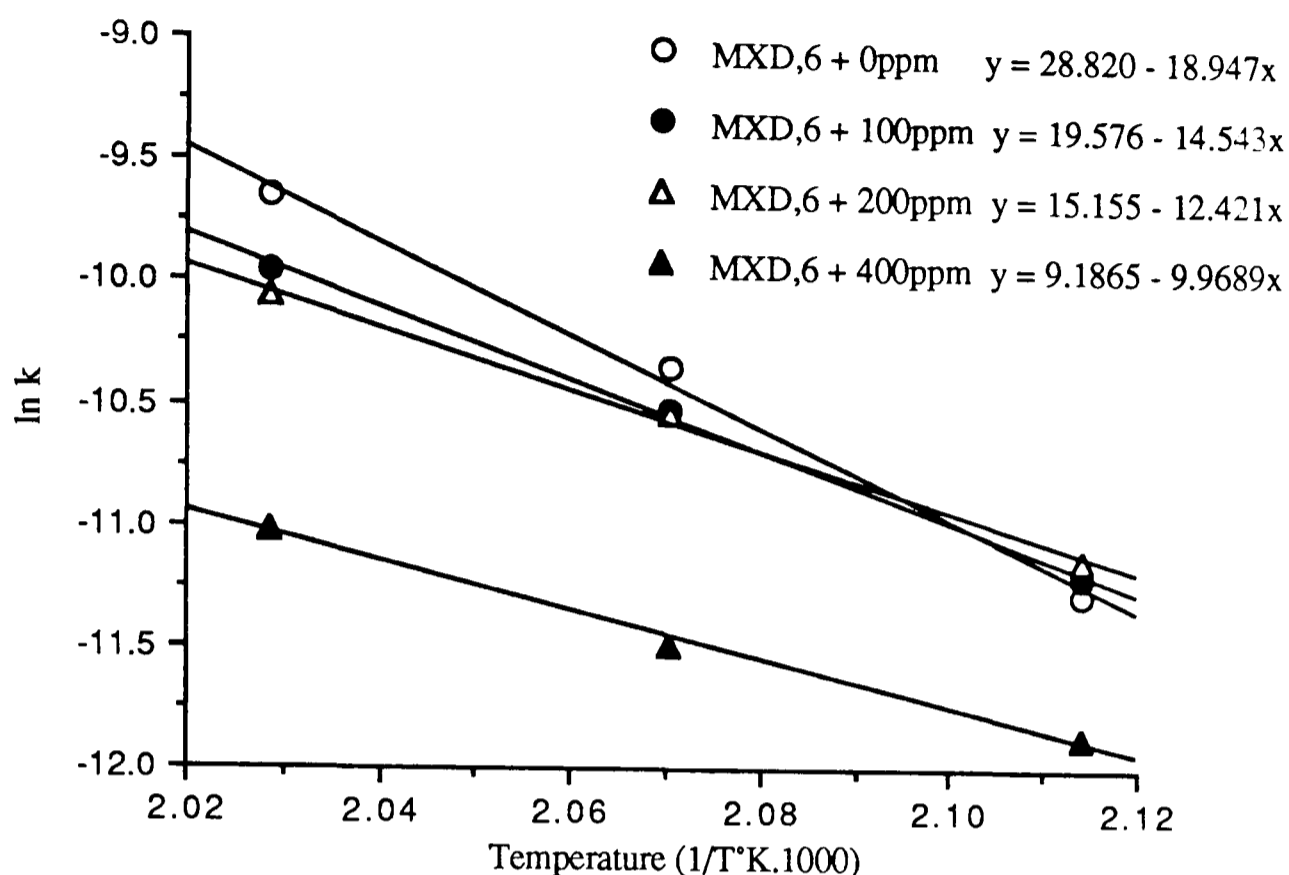
$$\therefore \ln k = \ln A - \frac{E_a}{RT}$$

From plots of the logarithms of the rate constants versus the reciprocal of the absolute temperatures at which the T.G.A.s were conducted, the activation energies were obtained by the slope of the straight line (Figure 4.8).

$$\therefore \text{Slope of the straight line} = \frac{-E_a}{R} \quad \text{where } E_a = \text{Activation energy in J mol}^{-1}$$

and R = Gas constant 8.314 J mol⁻¹

Figure 4.8 :- Determination of Activation Energies for the Thermal Oxidation of Samples of MXD,6 with and without Cobalt.



∴ Activation energy calculated for the oxidative degradation of MXD,6 = 157 kJ mol^{-1}
 and for MXD,6 with 100ppm cobalt = 120 kJ mol^{-1}
 and for MXD,6 with 200ppm cobalt = 103 kJ mol^{-1}
 and for MXD,6 with 400ppm cobalt = 83 kJ mol^{-1}

Shimasaki et al [112] have already proposed that there are two processes involved in the oxidative degradation of MXD,6. They claimed the former was due to oxidative decomposition while the latter resulted from a thermal decomposition reaction. In terms of thermal analysis according to the Ozawa method [134], they determined average activation energies of 150 and 230 kJ mol^{-1} for the first and second stages of the process respectively. The activation energy value of 157 kJ mol^{-1} for MXD,6 unmodified calculated in this study is consistent with the oxidation figure proposed by Shimasaki et al even though quite different techniques of derivation were employed. Inoue and Sumoto [135] obtained an activation energy for the oxidation of nylon 6,6 in the region of 155 kJ mol^{-1} which is again in accordance with results determined in this study even though the polyamides are very dissimilar.

The influence of the cobalt ions in the polyamide mixture was also assessed. It is apparent that the metal ion behaves as a catalyst for polyamide oxidation, reducing the activation energy for the oxidative degradation of MXD,6 with increasing concentrations. At higher levels of cobalt, the weight gain was observed to become less apparent. It is proposed that at such high concentrations of cobalt, the metal ion catalyses the oxidative degradation of the polyamide rapidly, hence as oxygen complexes with sites in the polymer, aided by the cobalt, oxidation proceeds immediately, producing volatiles which are emitted as soon as they are formed. MXD,6 with no cobalt possesses the most apparent weight gain, implying that oxygen forms hydroperoxide and carbonyl groups on the polyamide without immediate volatilization, hence an initial build up of oxygen on the polymer. This in turn is recorded on the T.G.A. trace as the greatest initial weight gain of the polymer samples investigated.

4.3 MXD,6 FIBRE DEGRADATION STUDIES.

In order to propose a feasible mechanism for the thermo-oxidative degradation of MXD,6, analyses of both the non-volatile and volatile components of decomposition were conducted using various analytical techniques.

Characterization of the degradation products from MXD,6 at 180°C in air was carried out according to the schematic diagram shown (Figure 4.9).

4.3.1 Non-volatile Acid Hydrolysis Studies.

Degraded polymer fibre was subjected to acid hydrolysis using 5M HCl at 110°C for 24 hours, after which half of the hydrolysate was used for steam distillation and the remainder evaporated to dryness and stored in vacuo prior to use.

4.3.1.1 Degradation Product Characterization via Steam Distillation.

Based on investigations conducted by East et al [88] on the decomposition of aliphatic nylons in the solid state, a similar procedure of study was carried out on MXD,6.

Degradation products were fractionated by steam distillation from acidic solution to yield volatile acids, which were first collected as sodium salts in 1M NaOH and then as free carboxylic acids in solution. Acid salts were used for analysis by T.L.C. and free carboxylic acids in solution for H.P.L.C. analysis.

On completion of acid steam distillation, volatile bases were isolated by steam distillation from basic solution. The residual hydrolysate liquor pH was adjusted to pH 9-10 using 5M NaOH and distillation continued. Volatile bases in the form of their respective hydrochlorides were collected and subsequently used for T.L.C. analysis.

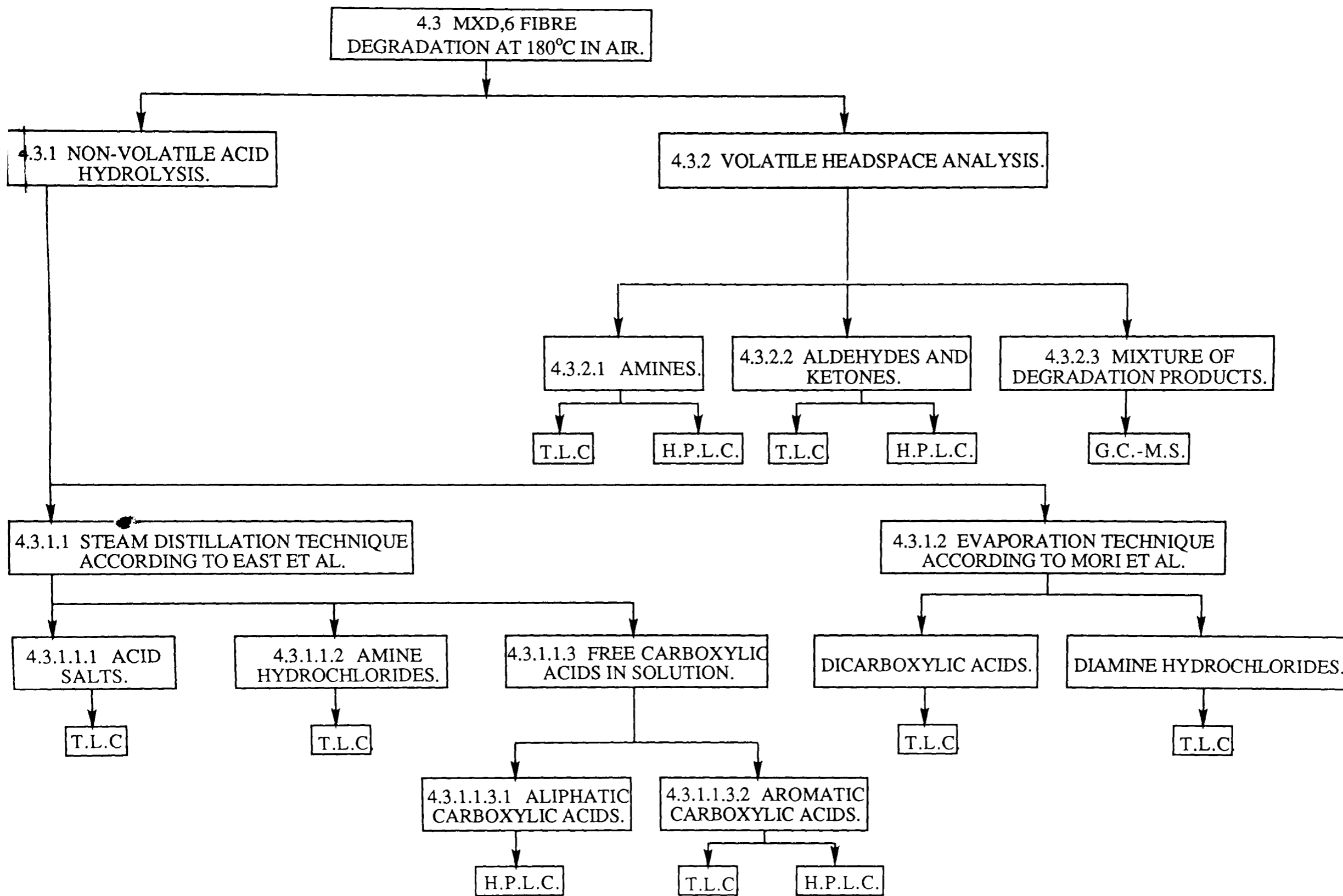


Figure 4.9 :- Schematic Diagram Representing the Characterization Route Taken for the Identification of MXD,6 Degradation Products.

4.3.1.1.1 Analysis of Carboxylic Acid Salts.

T.L.C. of Monocarboxylic Acid Salts.

A sample of acidic distillate collected in the form of the sodium salt was chromatographed against a series of standard monocarboxylic acids using the conditions described in chapter 3.4.1.1.

Figure 4.10 shows the composition of the monocarboxylic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C. Using the 0.1% alcoholic methyl red spray showed very faint red spots on an orange background. However, if the sprayed plate was then placed under a U.V. source, the monocarboxylic acids were rendered visible more easily.

T.L.C. of Dicarboxylic Acid Salts.

A sample of acidic distillate collected in the form of the sodium salt was chromatographed against a series of standard dicarboxylic acids using the conditions described in chapter 3.4.1.1.

Figure 4.11 shows the composition of the dicarboxylic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C. As with the monocarboxylic acids, the detection of the dicarboxylic acids was not very clear using the alcoholic bromocresol green spray, however, these spots were also located with ease when observed under a U.V. source.

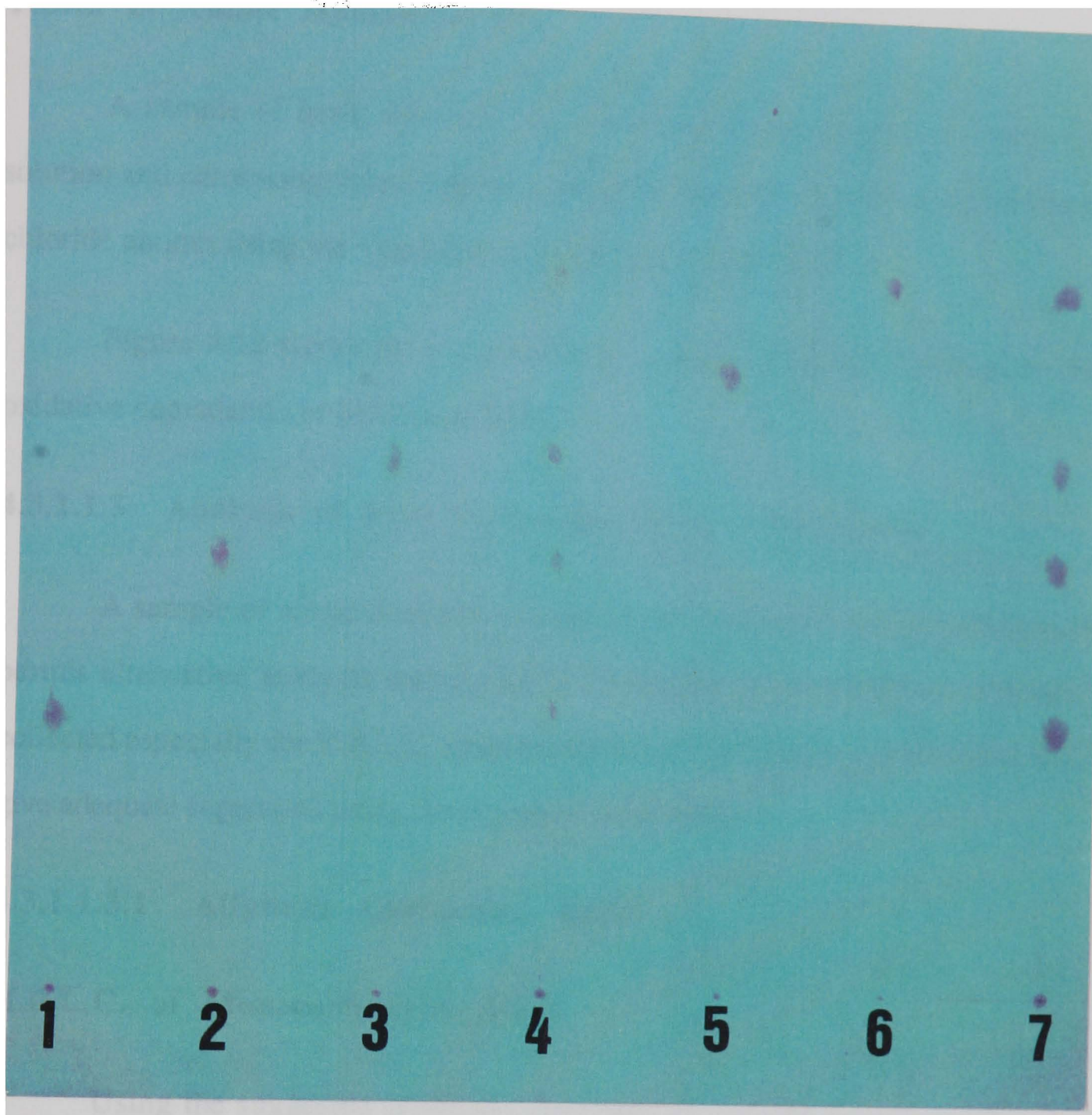
Figure 4.10 :- T.L.C. of Monocarboxylic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- | | |
|--------------------------|--------------------------|
| (1) Degradation mixture. | (6) n-Butyric acid. |
| (2) Formic acid. | (7) n- Pentanoic acid. |
| (3) Acetic acid. | (8) n-Hexanoic acid. |
| (4) Propionic acid. | (9) Degradation mixture. |
| (5) Degradation mixture. | |

Conditions :- Methyl acetate:ammonia 2.5% aqueous volume (95:5 v/v).
Development :- 0.1% alcoholic methyl red and U.V. light at 254nm.

Figure 4.11 :- T.L.C. of Dicarboxylic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- | | |
|--------------------------|--------------------------|
| (1) Oxalic acid. | (5) Glutaric acid. |
| (2) Malonic acid. | (6) Adipic acid. |
| (3) Succinic acid. | (7) Degradation mixture. |
| (4) Degradation mixture. | |

Conditions :- Phenol:n-butanol:formic acid:water (5:2:1:2).

Development : 0.1% alcoholic bromocresol green and U.V. light at 254nm.

4.3.1.1.2 Analysis of Amines.

T.L.C. of Amine Hydrochlorides.

A sample of basic distillate was converted to the respective dansyl chloride solution and chromatographed against a series of standard aliphatic and aromatic dansyl chloride amines using the conditions described in chapter 3.4.1.1.

Figure 4.12 shows the composition of the amines formed during the thermo-oxidative degradation of MXD,6 at 180°C.

4.3.1.1.3 Analysis of Free Carboxylic Acids in Solution.

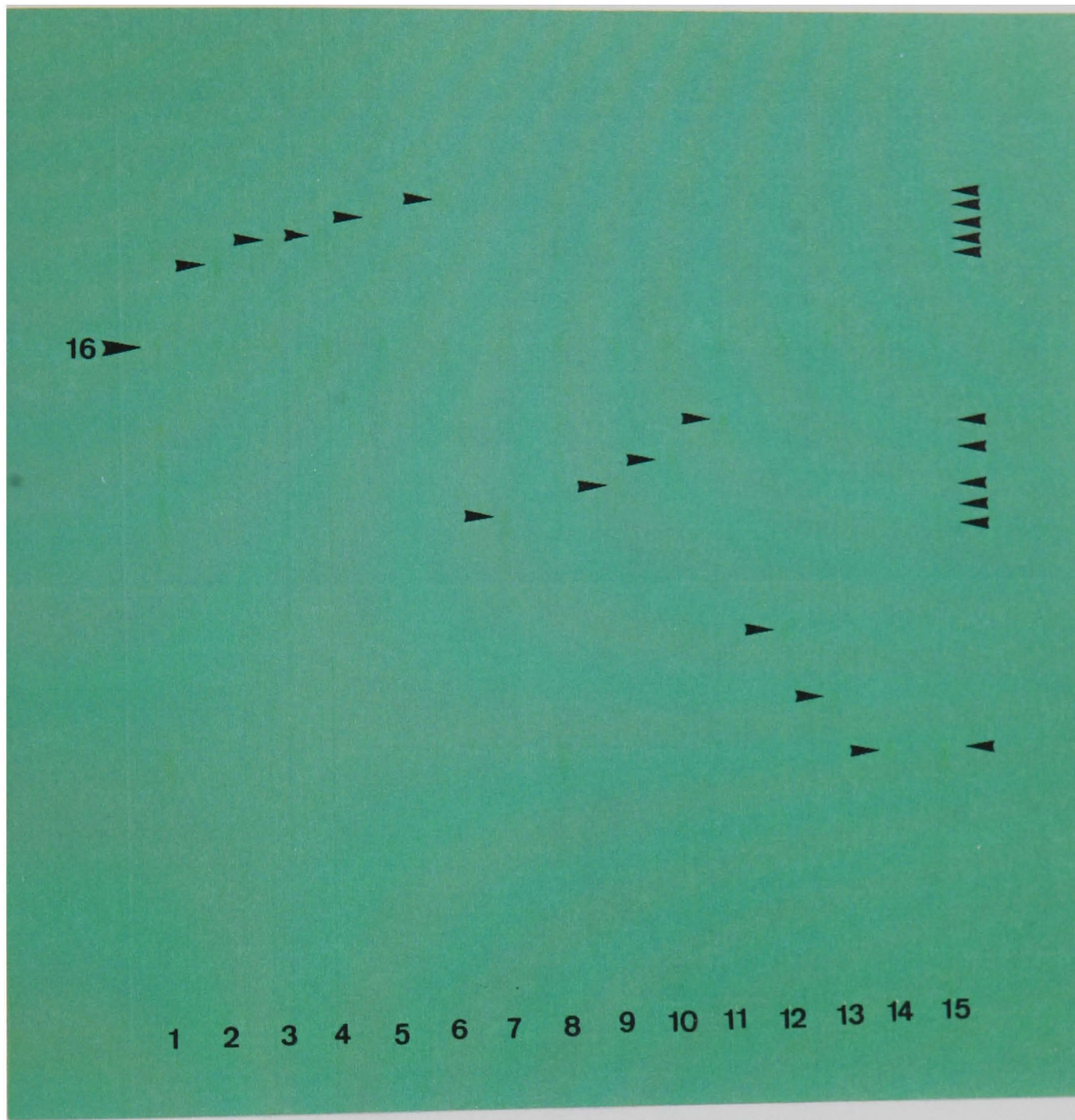
A sample of acidic distillate was collected in solution without salt formation to permit alternative analysis techniques to be employed. Free acids in solution were collected especially for H.P.L.C. characterization as their respective acid salts would not give adequate separation using the suggested conditions.

4.3.1.1.3.1 Aliphatic Carboxylic Acids.

H.P.L.C. of Monocarboxylic Acids.

Using the suggested conditions described in chapter 3.4.1.2, a H.P.L.C. trace for a series of standard monocarboxylic acids was obtained which was utilized in identifying the composition of the monocarboxylic acids. Figure 4.13 shows the composition of the monocarboxylic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C.

Figure 4.12 :- T.L.C. of Amines formed during the Thermal Oxidation of MXD,6 at 180°C.

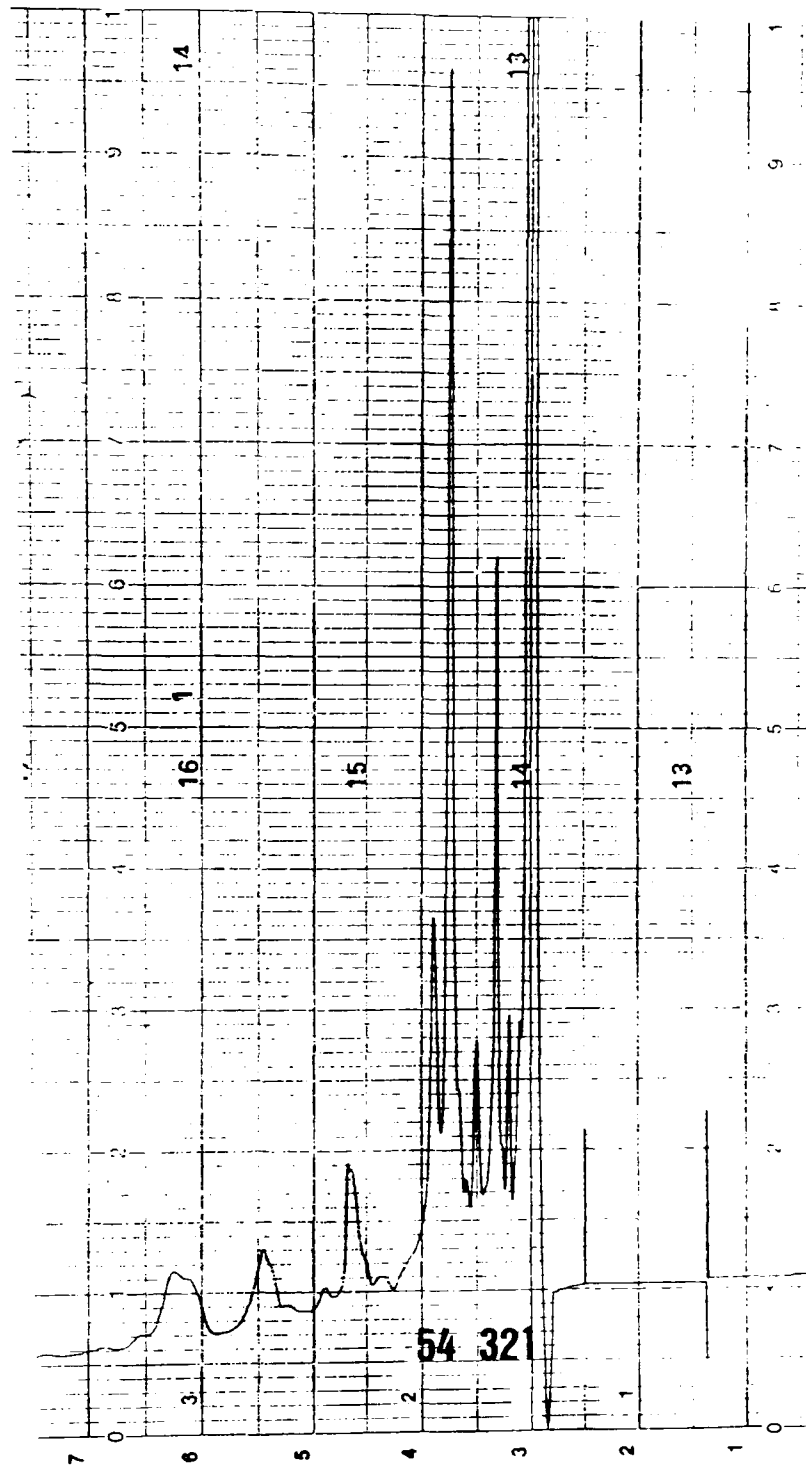


- | | |
|--------------------------|----------------------------|
| (1) Degradation mixture. | (9) Diaminopropane. |
| (2) Methylamine. | (10) Diaminobutane. |
| (3) Ethylamine. | (11) Diaminopentane. |
| (4) Propylamine. | (12) Benzylamine. |
| (5) n-Butylamine. | (13) 3-Methyl benzylamine. |
| (6) n-Pentylamine. | (14) m-Xylylene diamine. |
| (7) Diaminoethane. | (15) Degradation mixture. |
| (8) Degradation mixture. | (16) Ammonia. |

Conditions :- Ether.

Development :- U.V. light at 254nm.

Figure 4.13 :- H.P.L.C. Trace of Monocarboxylic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- (1) Formic acid.
- (2) Acetic acid.
- (3) Propionic acid.
- (4) n-Butyric acid.
- (5) n-Pentanoic acid.

Conditions :- Water at pH 2.5.
U.V. source :- 210nm.

H.P.L.C. of Dicarboxylic Acids.

Using the suggested conditions described in chapter 3.4.1.2, a H.P.L.C. trace for a series of standard dicarboxylic acids was obtained which was utilized in identifying the composition of the dicarboxylic acids.

Figure 4.14 shows the composition of the dicarboxylic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C.

4.3.1.1.3.2 Aromatic Carboxylic Acids.

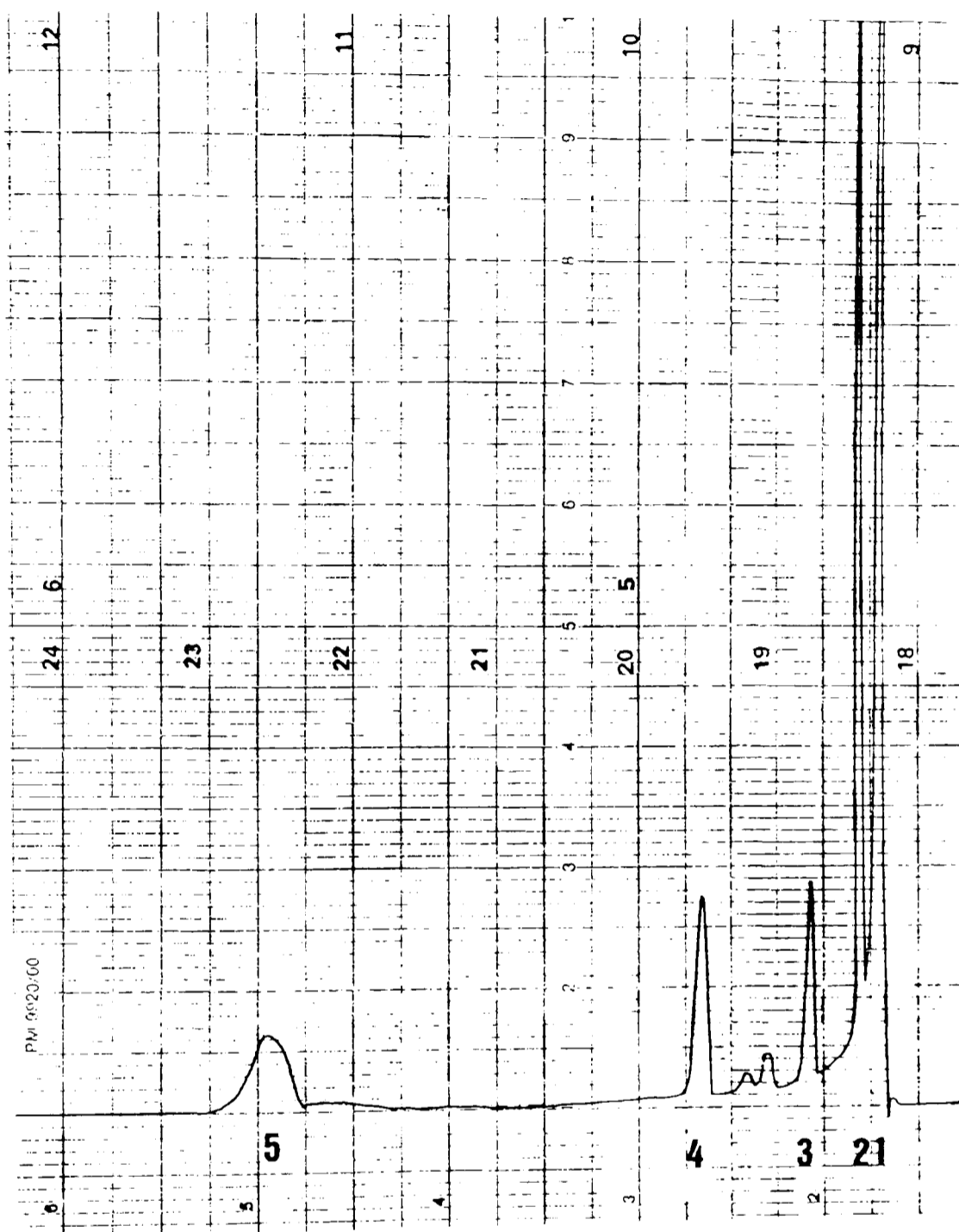
T.L.C. of Aromatic Carboxylic Acids.

The free acids in solution obtained from steam distillation were also used to identify aromatic acids using T.L.C. Using the conditions described in chapter 3.4.1.1, the composition of the by-products of the oxidative degradation of MXD,6 at 180°C were determined (Figure 4.15).

Also used, especially for aromatic acids, was a T.L.C. technique employing Empore Strips. A sample of acid distillate was ether extracted. The latter was spotted on a 90% C₁₈ absorbant to 10% PTFE with fluorescent indicator strip and chromatographed according to conditions described in chapter 3.4.1.1.

Figure 4.16 shows the composition of the aromatic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C using Empore strips.

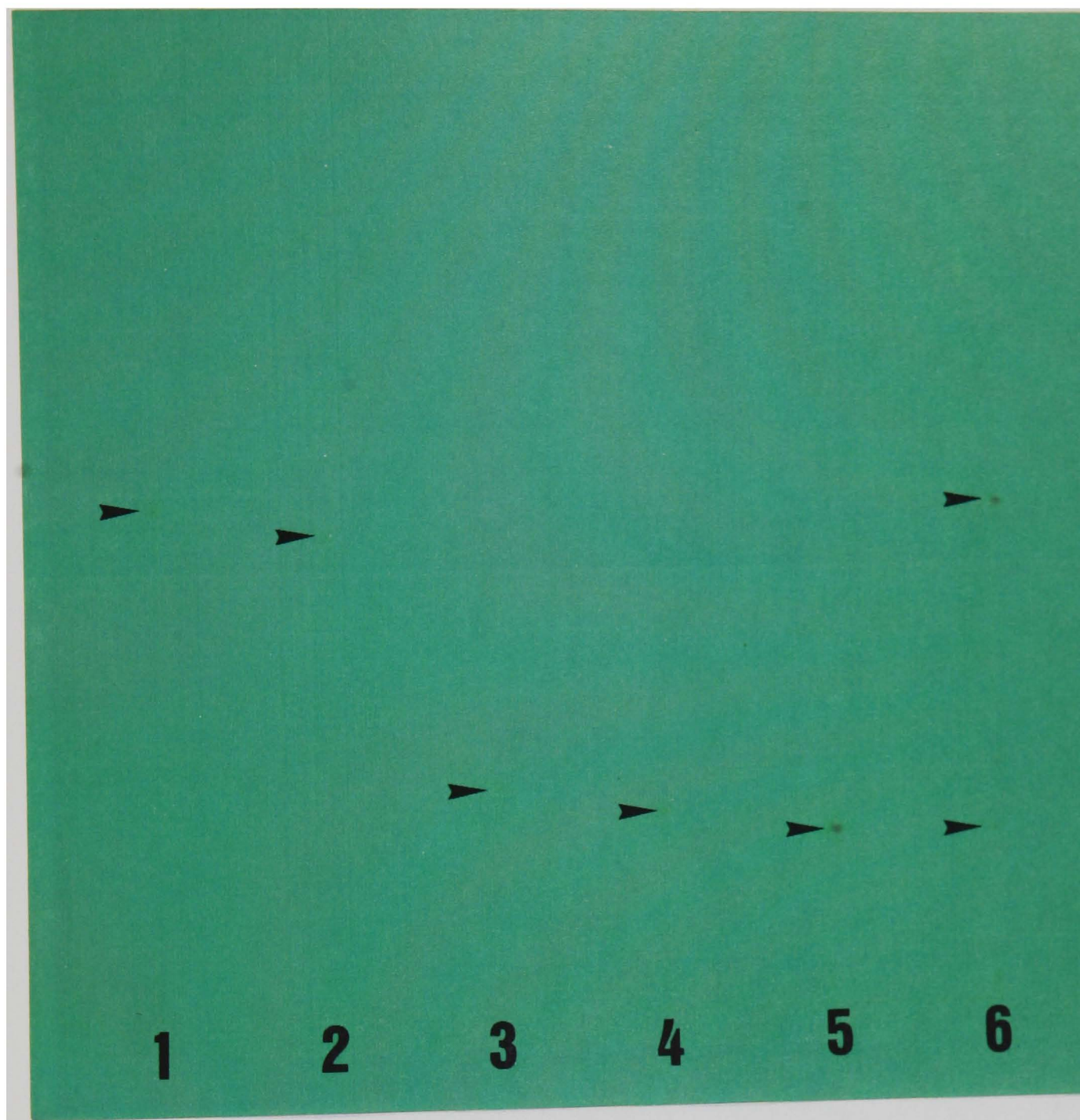
Figure 4.14 :- H.P.L.C. Trace of Dicarboxylic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- (1) Oxalic acid.
- (2) Malonic acid.
- (3) Succinic acid.
- (4) Glutaric acid.
- (5) Adipic acid.

Conditions :- Water:methanol (98:2) at pH 2.5.
U.V. source :- 210nm.

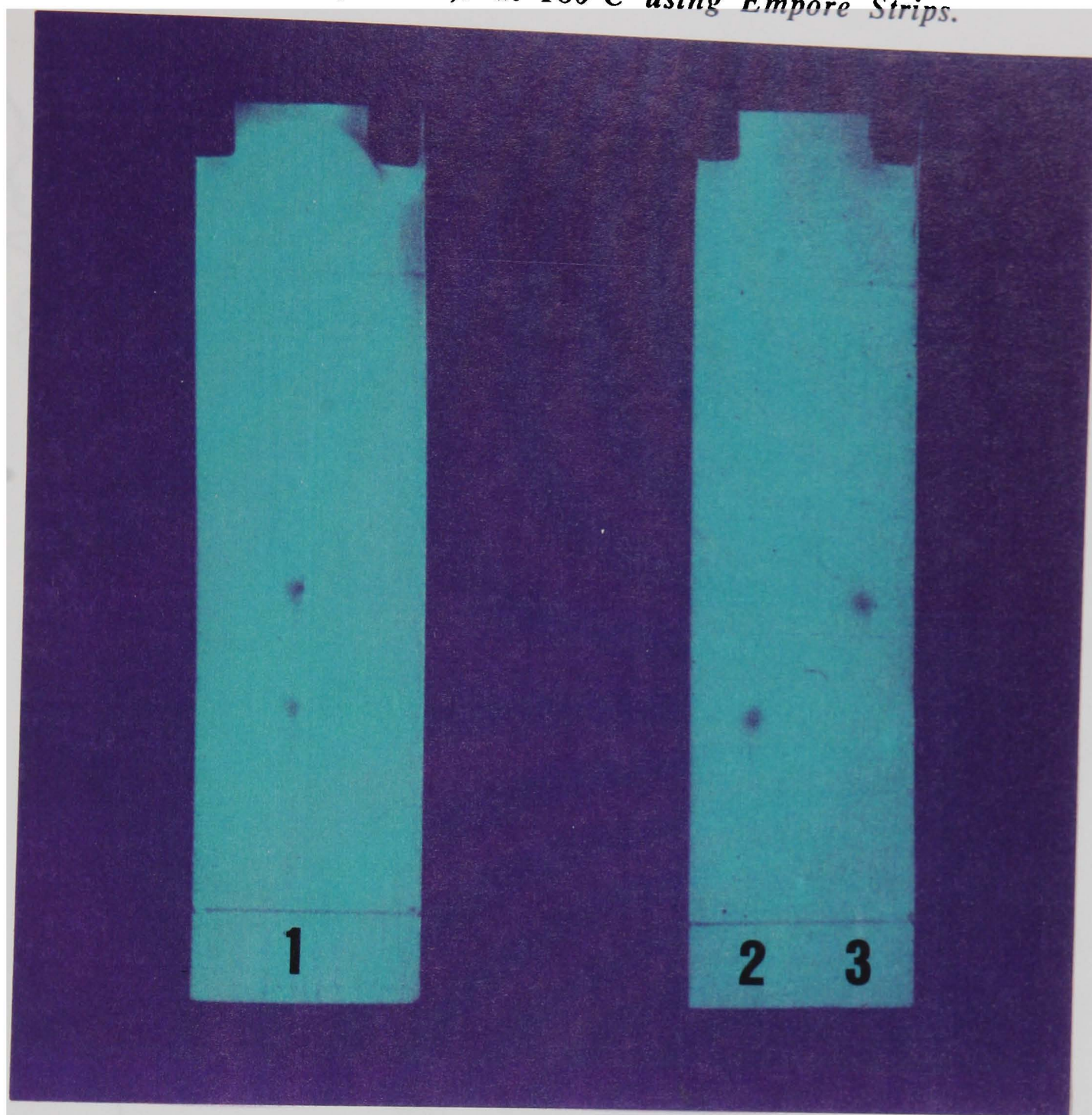
Figure 4.15 :- T.L.C. of Aromatic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- (1) Isophthalic acid.
- (2) Terephthalic acid.
- (3) Benzoic acid.
- (4) m-Hydroxybenzoic acid.
- (5) Isophthalamide.
- (6) Degradation mixture.

Conditions :- Chloroform:tetrahydrofuran (2:1).
Development :- U.V. light at 254nm.

Figure 4.16 :- T.L.C. of Aromatic Acids formed during the Thermal Oxidation of MXD,6 at 180°C using Empore Strips.



- (1) Degradation mixture.
- (2) Isophthalamic acid.
- (3) Isophthalic acid

Conditions :- Water:methanol (70:30) at pH 3.5.
Development :- U.V. light at 254nm.

In conjunction with the latter technique, I.R. spectra of the spots were conducted using a PTFE background. Standard aromatic acids on Empore Strips were also carried out and used for comparison. Figures 4.17 and 4.18 show the I R. spectra of isophthalic acid, isophthalamic acid unknown spot (i) and unknown spot (ii).

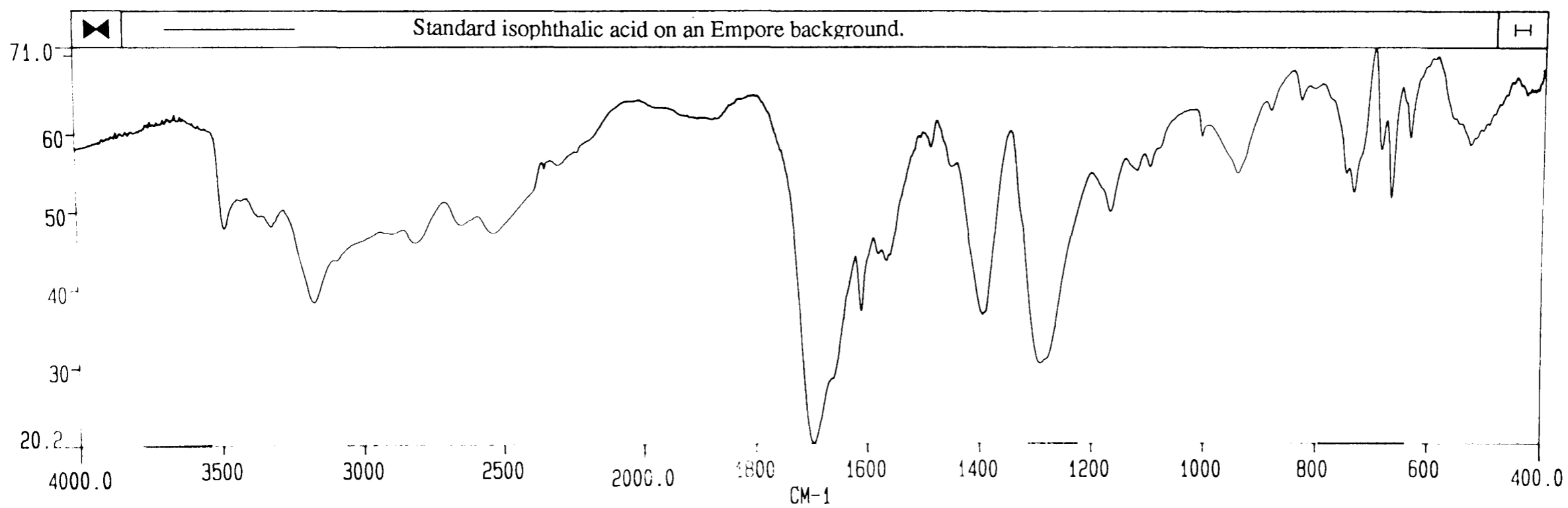
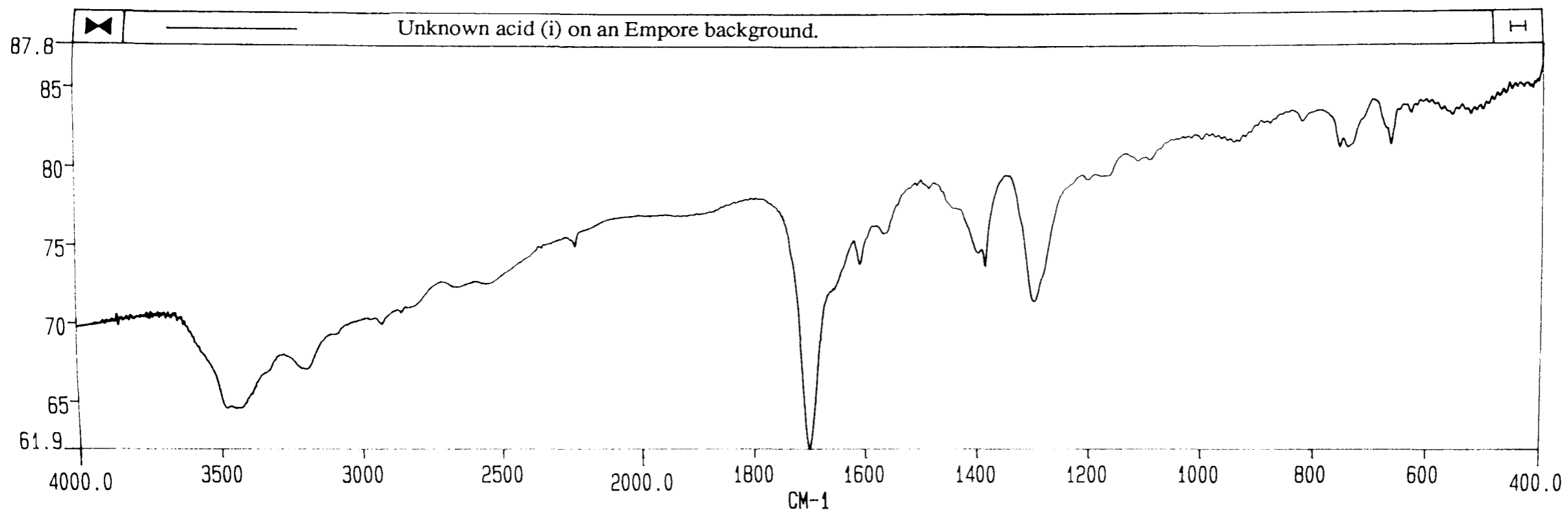


Figure 4.17 :- IR. Spectra of Isophthalic Acid and unknown acid (i).

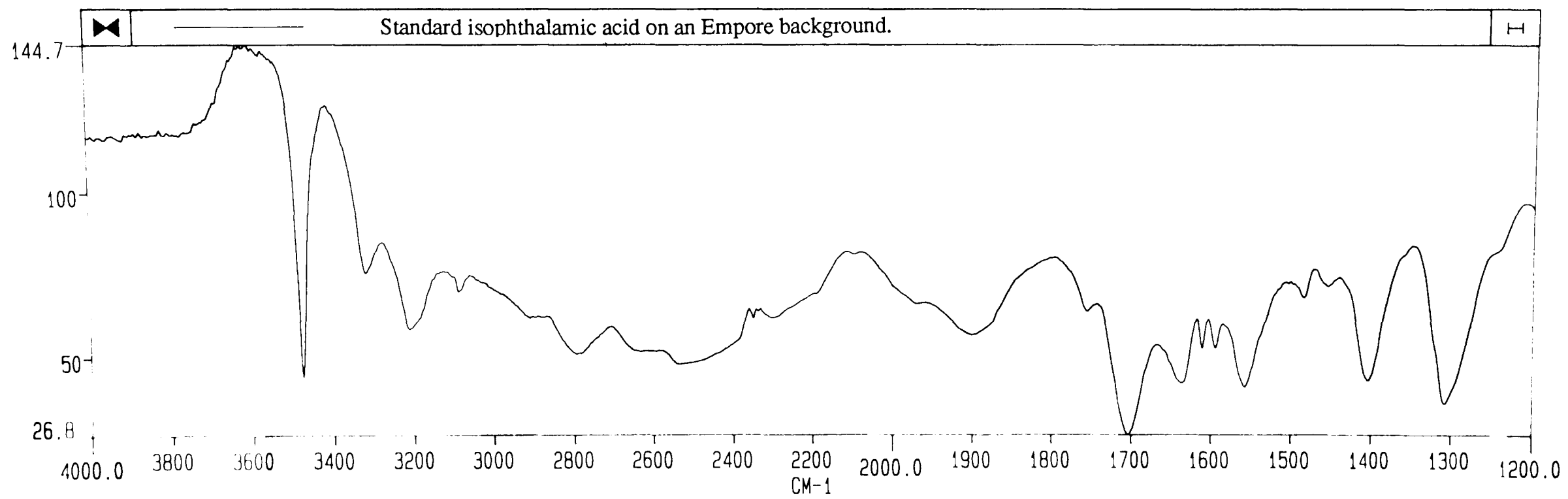
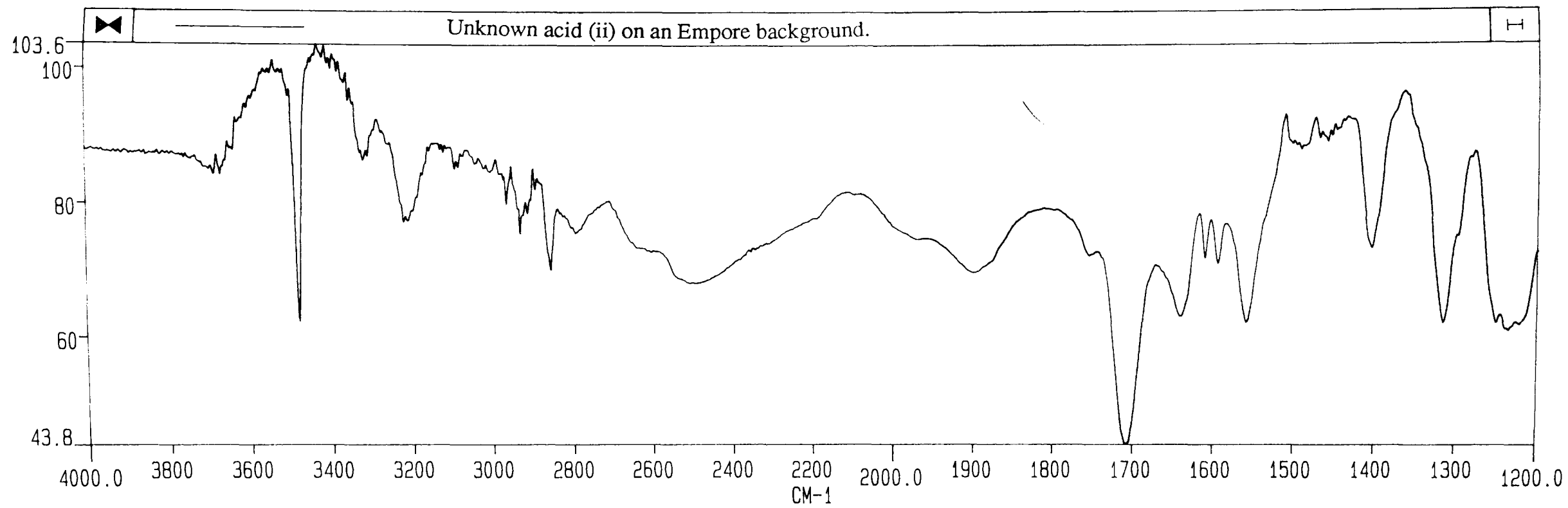
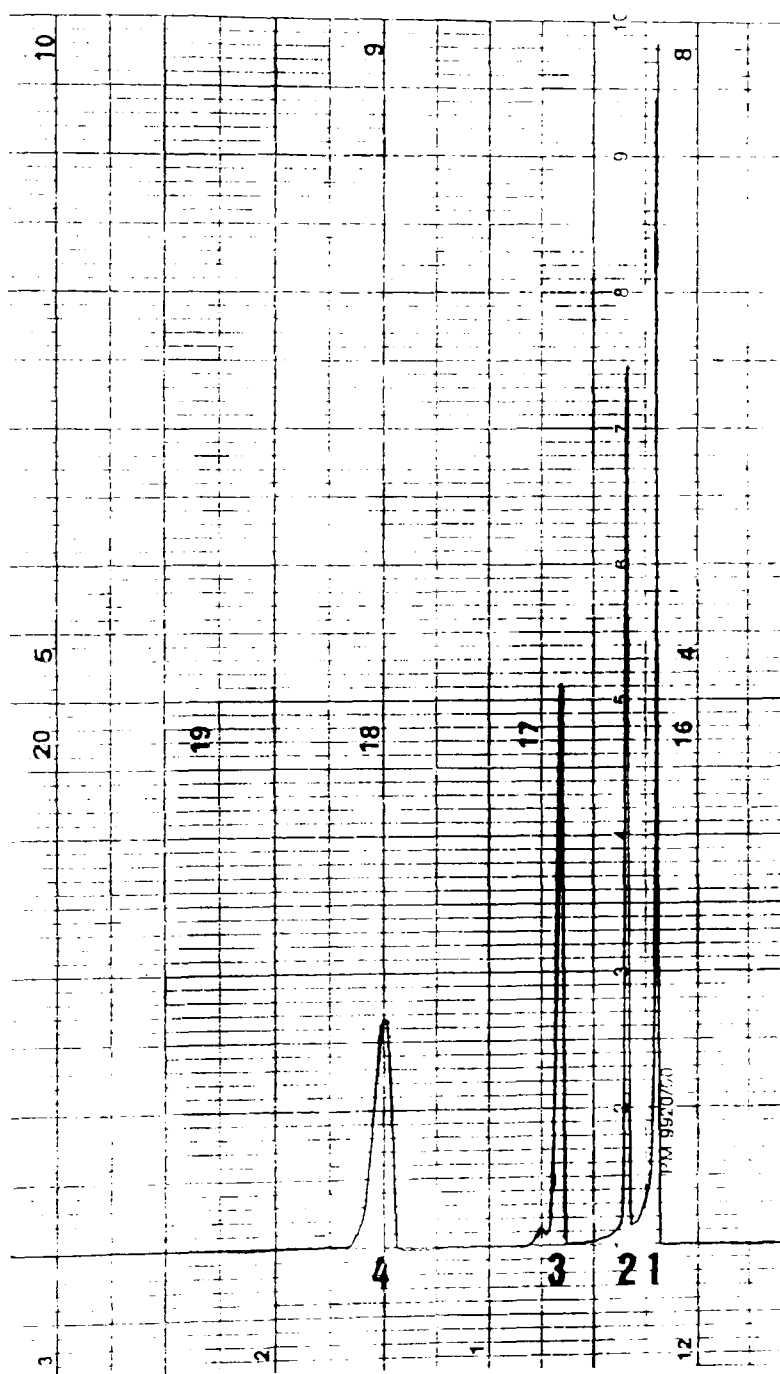


Figure 4.18 :- I.R. Spectra of Isophthalamic Acid and unknown acid (ii).

H.P.L.C. of Aromatic Acids.

Using the suggested conditions described in chapter 3.4.1.2, a H.P.L.C. trace for several standard aromatic acids was obtained which was utilized in identifying the composition of the aromatic acids. Figure 4.19 shows the composition of the aromatic acids formed during the thermo-oxidative degradation of MXD,6 at 180°C.

Figure 4.19 :- H.P.L.C. Trace of Aromatic Acids formed during the Thermal Oxidation of MXD,6 at 180°C.



- (1) Isophthalamic acid.
- (2) Isophthalic acid.
- (3) m-Hydroxybenzoic acid.
- (4) Benzoic acid.

Conditions :- Water:methanol (70:30) at pH 3.5.
U.V. source :- 254nm.

4.3.1.2 Evaporation Technique.

Based on investigations conducted by Mori and Takeuchi [116] on the analysis of diamines, dicarboxylic acids and ω amino acids with respect to copolyamide degradation, a similar procedure of study was carried out on MXD,6.

A sample of polymer was degraded and acid hydrolysed, followed by T.L.C. analysis using the conditions described chapter 3.6.1.2.

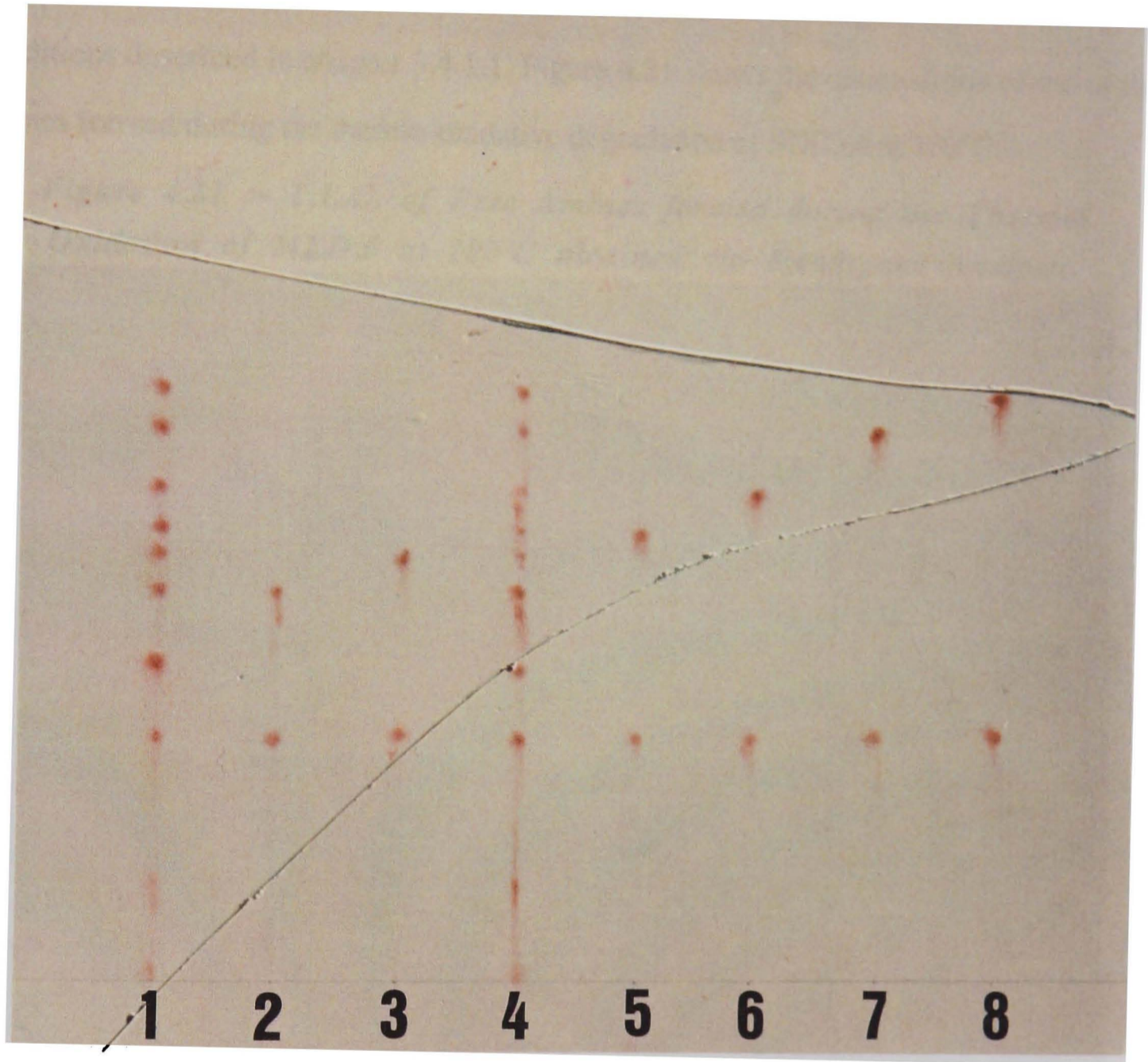
Figure 4.20 shows the composition of the of the diamine hydrochlorides formed during the thermo-oxidative degradation of MXD,6 at 180°C. However, even though Mori and Takeuchi claimed that the identification of both diamines and dicarboxylic acids were possible, the latter were not detected in this study.

4.3.2 Volatile Headspace Analysis.

In previous work [130] [131], investigations into the volatiles emitted during the thermal oxidation of polyamides have not been conducted. In this study, a novel method was devised for the analysis of such volatiles produced from degradation.

Carboxylic acids detected earlier from the polymer hydrolysis technique were also detected using the headspace technique. However, a group of volatiles which could not be detected or were difficult to isolate using the polymer hydrolysis technique, were obtained from the headspace method and identified using both T.L.C. and/or H.P.L.C.

Figure 4.20 :- T.L.C. of Diamine Hydrochlorides formed during the Thermal Oxidation of MXD,6 at 180°C Analysed according to Mori and Takeuchi.



- | | |
|--------------------------|--------------------------|
| (1) Degradation mixture. | (5) Diaminobutane. |
| (2) Diaminoethane. | (6) Diaminopentane. |
| (3) Diaminopropane. | (7) m-Phenylene diamine. |
| (4) Degradation mixture. | (8) m-Xylylene diamine. |

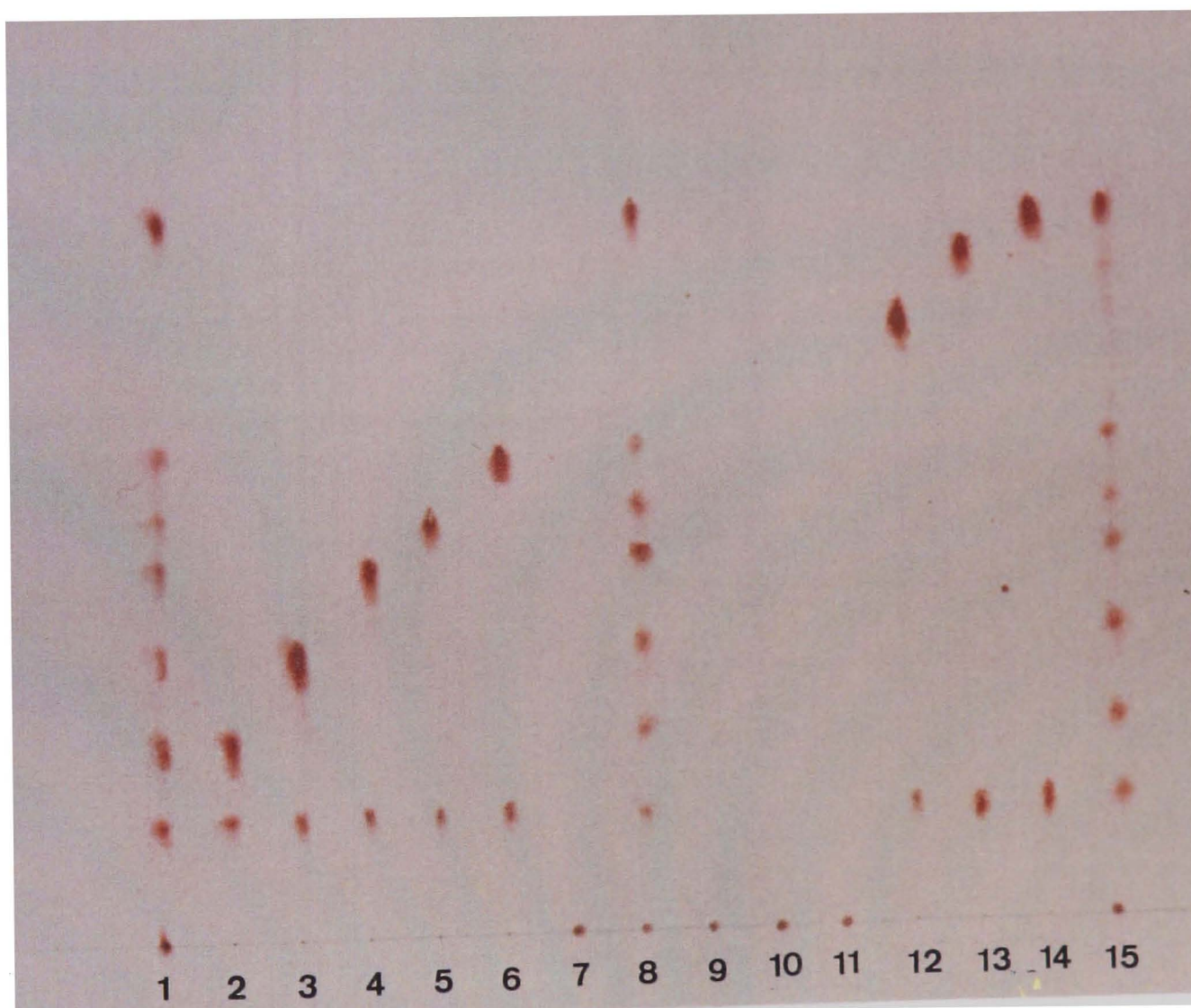
Conditions :- Phenol:n-butanol:formic acid:water (5:2:1:2).
Development :- 2% alcoholic solution of ninhydrin

4.3.2.1 Headspace Analysis of Amines.

T.L.C. of Amines.

A sample of headspace was prepared in an alcoholic solution in the form of the respective dansyl chloride derivative and spotted on a T.L.C. plate with a number of standard amine dansyl chloride derivatives then chromatographed according to conditions described in chapter 3.4.1.1. Figure 4.21 shows the composition of the of the amines formed during the thermo-oxidative degradation of MXD,6 at 180°C.

Figure 4.21 :- T.L.C. of Free Amines formed during the Thermal Oxidation of MXD,6 at 180°C obtained via Headspace Analysis.



- (1) Degradation mixture.
- (2) Methylamine.
- (3) Ethylamine.
- (4) Propylamine.
- (5) n-Butylamine.

- (6) n-Pentylamine.
- (7) Diaminoethane.
- (8) Degradation mixture.
- (9) Diaminopropane.
- (10) Diaminobutane.

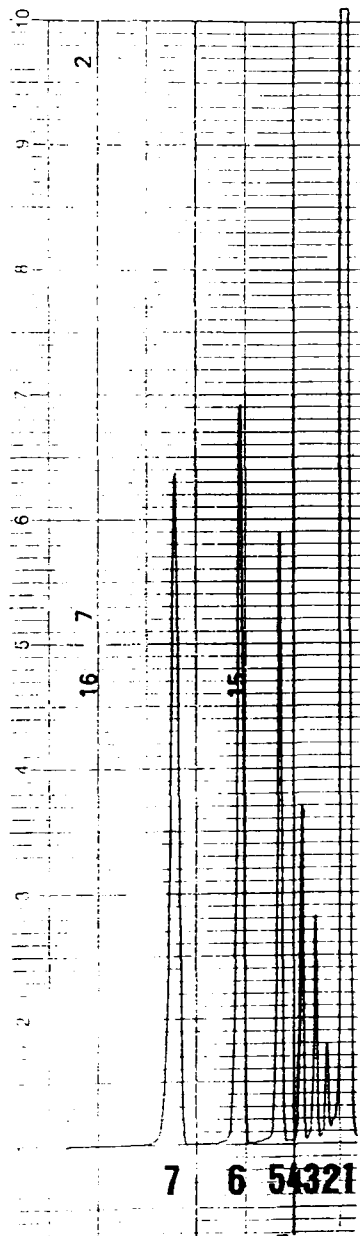
- (11) Diaminopentane.
- (12) Benzylamine.
- (13) 3-Methyl benzylamine.
- (14) m-Xylylene diamine.
- (15) Degradation mixture.

Conditions :- Methanol:acetone.
Development :- 2% alcoholic solution of ninhydrin

H.P.L.C. Free Amines.

As with T.L.C. analysis, a sample of headspace and number of standard amines were converted to their respective dansyl chloride derivatives and prepared for H.P.L.C. analysis using conditions described in chapter 3.4.1.2. Figure 4.22 shows the composition of the of the amines formed during the thermo-oxidative degradation of MXD,6 at 180°C.

Figure 4.22 :- H.P.L.C. Trace of Free Amines formed during the Thermal Oxidation of MXD,6 at 180°C and obtained via Headspace Analysis.



- | | |
|----------------------|--------------------|
| (1) Dansyl chloride. | (5) Propylamine. |
| (2) Ammonia. | (6) n-Butylamine. |
| (3) Methylamine. | (7) n-Pentylamine. |
| (4) Ethylamine. | |

Conditions :- Methanol:water (70:30).
U.V. source :- 254nm.

4.3.2.2 Headspace Analysis of Aldehydes and Ketones.

T.L.C. of Aldehydes and Ketones.

A sample of headspace and number of standard aldehydes and ketones were converted to their respective 2,4-dinitrophenylhydrazine derivatives and prepared for T.L.C. analysis using conditions described in chapter 3.4.1.1.

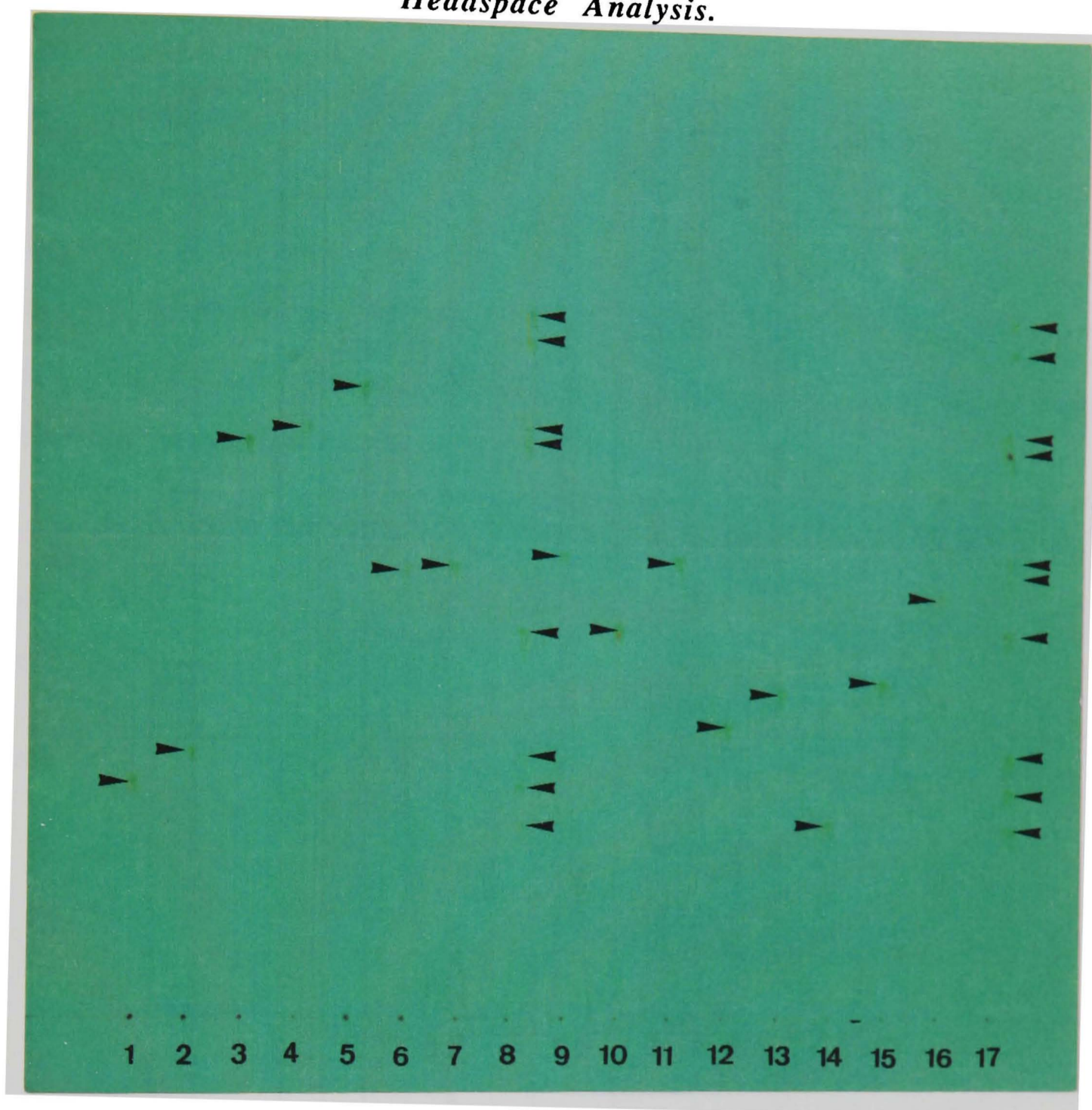
Figure 4.23 shows the composition of the of the aldehydes and ketones formed during the thermo-oxidative degradation of MXD,6 at 180°C.

H.P.L.C. of Aldehydes and Ketones.

As with T.L.C. analysis, a sample of headspace and number of standard aldehydes and ketones were converted to their respective 2,4-dinitrophenylhydrazine derivatives and prepared for H.P.L.C. analysis using conditions described in chapter 3.4.1.2.

Figure 4.24 shows the composition of the of the aldehydes and ketones formed during the thermo-oxidative degradation of MXD,6 at 180°C.

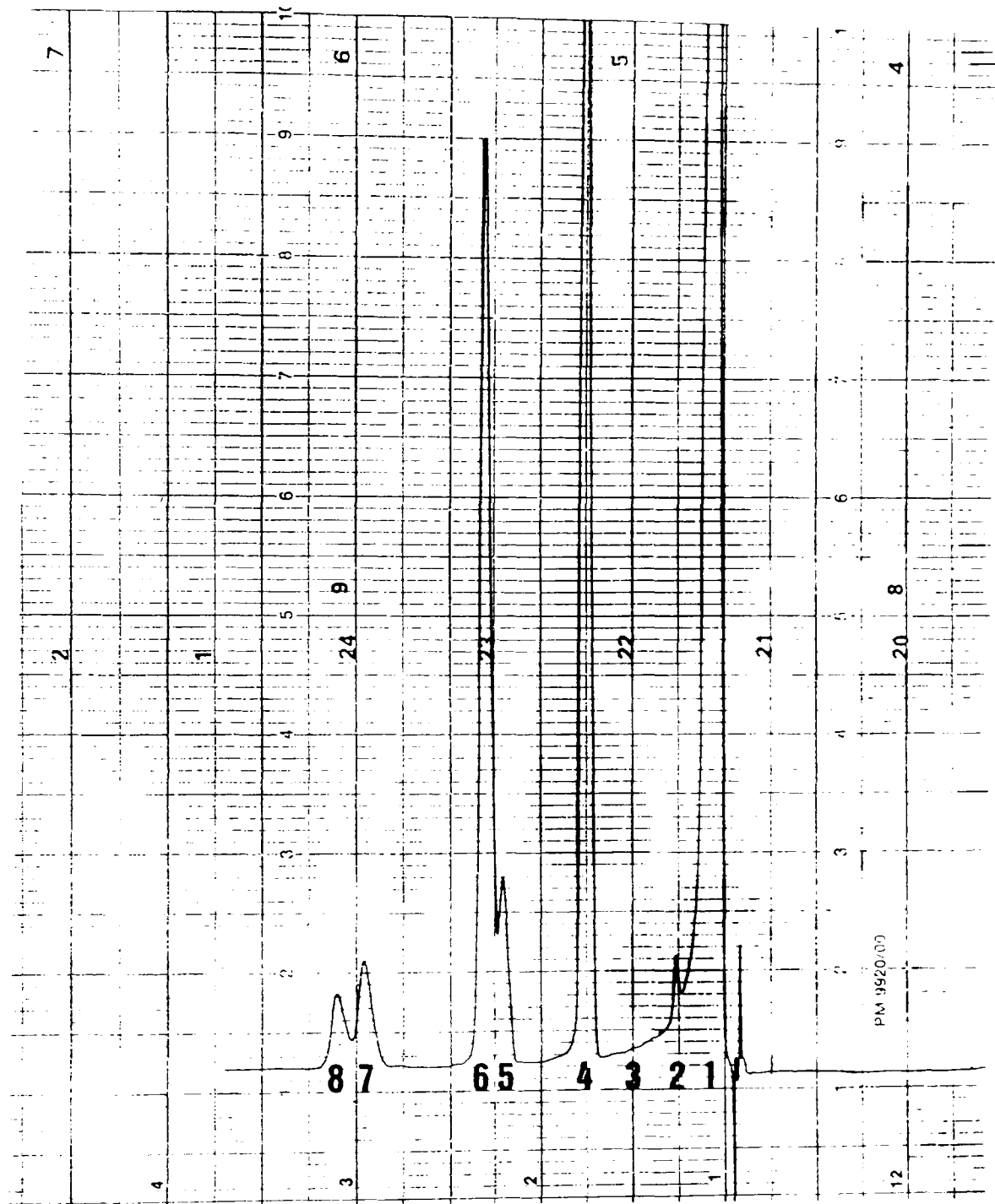
Figure 4.23 :- T.L.C. of Free Aldehydes and Ketones formed during the Thermal Oxidation of MXD,6 at 180°C and obtained via Headspace Analysis.



- | | |
|--------------------------|-----------------------------|
| (1) Formaldehyde. | (10) Cyclopentanone. |
| (2) Acetaldehyde. | (11) Benzaldehyde. |
| (3) Propionaldehyde. | (12) 2-Carboxybenzaldehyde. |
| (4) Butyraldehyde. | (13) 4-Carboxybenzaldehyde. |
| (5) Valeraldehyde. | (14) Isophthalaldehyde. |
| (6) Acetone. | (15) Terephthalaldehyde. |
| (7) Butanone. | (16) Crotonaldehyde. |
| (8) Degradation mixture. | (17) Degradation mixture. |
| (9) Cyclohexanone. | |

Conditions :- Carbon tetrachloride:hexane:ethyl acetate (10:2:1).
Development :- U.V. light at 254nm.

Figure 4.24 :- H.P.L.C. Trace of Aldehydes and Ketones formed during the Thermal Oxidation of MXD,6 at 180°C and obtained via Headspace Analysis.



- | | |
|---------------------------------|---------------------|
| (1) 2,4-Dinitrophenylhydrazine. | (5) Acetone. |
| (2) Formaldehyde. | (6) Butyraldehyde. |
| (3) Acetaldehyde. | (7) Butanone. |
| (4) Propionaldehyde. | (8) Cyclopentanone. |

Conditions :- Methanol:water (70:30) at pH 3.5.
U.V. source :- 360nm.

4.3.2.3 Headspace Analysis using G.C.-M.S.

Many of the volatiles recognised using T.L.C. and H.P.L.C. were also identified using G.C.-M.S., which had the added advantage in that all the volatiles produced during headspace degradation could be investigated simultaneously without the need for pre-column derivatization. However, the conditions employed were not satisfactory for identification of low molecular weight volatiles, which were not retained on the column and were expelled virtually immediately. For this reason, most straight chain aliphatic volatiles (C₁ to C₆) were not recorded. Nevertheless, several aromatics and cyclics were observed as degradation products from the oxidation of MXD,6.

Figure 4.25 in conjunction with the values from Table 4.3 reveal the identity of most of the major peaks obtained from injecting 50ml of headspace derived from a sample of MXD,6 fibre degraded in a vial in air at 180°C for 5 hours.

Table 4.3 :- Retention Times for the Major Peaks for MXD,6 Degradation and their Respective Interpretations using G.C.-M.S.

Retention Time of Major Peaks (mins.).	Identity of Peaks according to G.C.-M.S. Library.
10.83	Cyclopentanone
13.97	Benzaldehyde
17.55	3,5,5-Trimethylhexanoic acid
18.03	3,5-Dimethylbenzaldehyde
19.05	2,5-Dimethylbenzaldehyde
20.69	Isophthalaldehyde
21.78	Pentamide
21.82	Isophthalic Acid
22.21	Hexanedinitrile
22.55	Isophthalamic Acid

Analytical Chemistry CMB Packaging Technology plc
Sample: Decanted soluble extract of MXD6 with 400ppm Co in Methanol.....

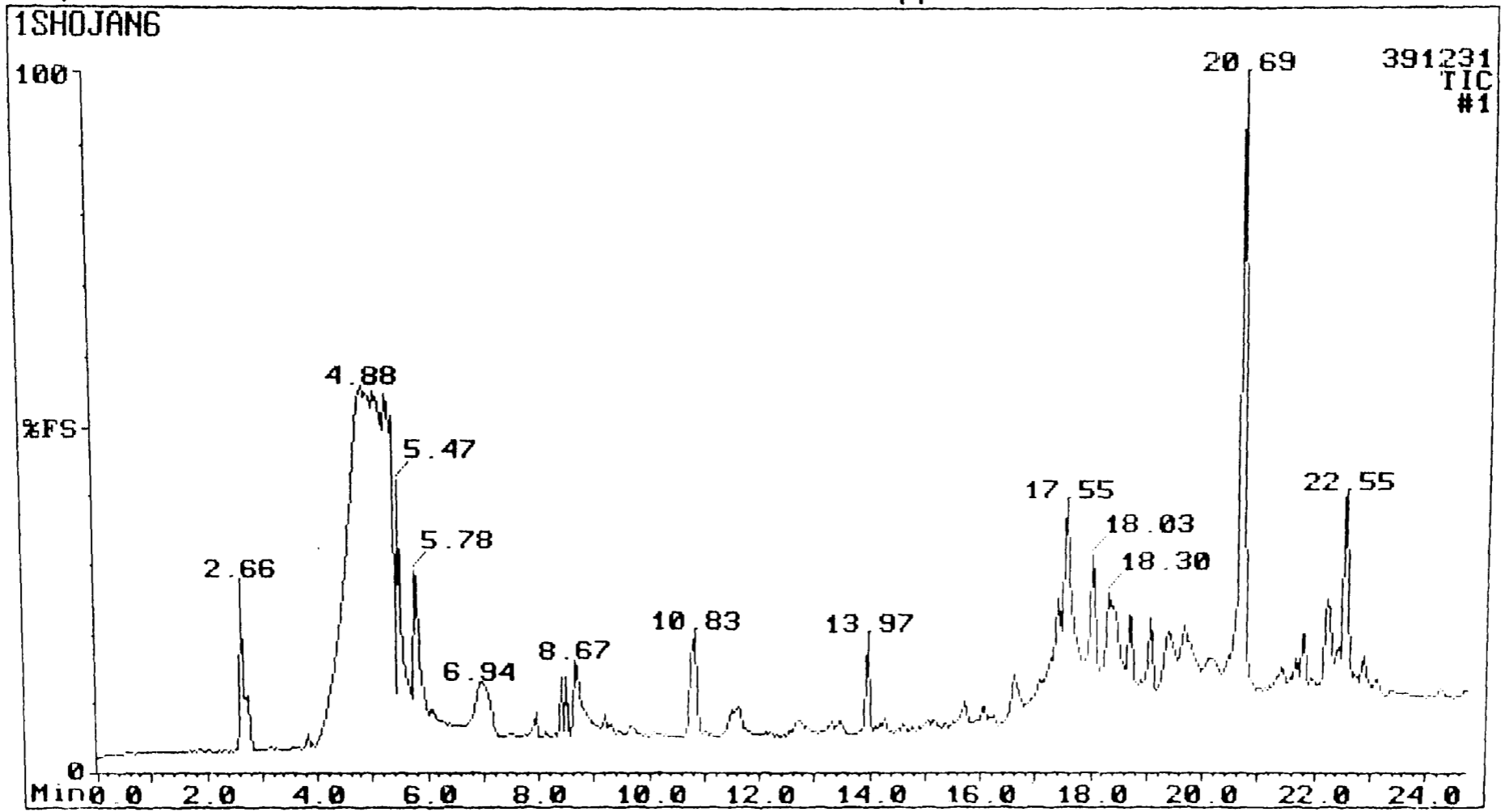


Figure 4.25 :- Degradation Products Identified using G.C.-M.S.

4.3.3 Analysis of Polymer Residue after Degradation.

A number of investigations were also conducted on the residual MXD,6 after thermal oxidation in order to gain a more complete picture of the mechanisms involved in the degradation of the polymer.

The influence of isothermal temperature on the average molecular weight of the polymer was deduced by monitoring the changes in intrinsic viscosity and end group concentrations over a period of degradation.

Almost all of this study was conducted on the thermal oxidation of MXD,6 fibre rather than of the polymer chip. This was not only to aid in accelerating polymer degradation but also because many of the polymer samples employed did not already contain a cobalt catalyst. Spinning the polymer was a simple means of incorporating the catalyst evenly.

However, at the high temperatures encountered during the spinning process, the molten MXD,6 was expected to participate in chemical reactions. Therefore, it was essential to understand these reactions related to the polymer melt prior to studying the effect of thermal oxidation of MXD,6 fibre in the solid state.

Several identical samples of MXD,6 were simultaneously degraded at 180°C in air in a preheated oven and one was removed every 30 minutes for subsequent analysis. Furthermore, a similar experiment was also conducted at 280°C in an inert atmosphere simulating conditions likely to be encountered by the polymer during melt spinning (chapter 3.6.3).

4.3.3.1 Analysis of Degraded MXD,6 by Intrinsic Viscosity.

In order to identify the influence of the heating on the average molecular weight of the polymer, each of the samples of MXD,6 degraded at 180 and 280°C were analysed using solution viscometry. Tables 4.4 with 4.5 and Figures 4.26 with 4.27 show this relationship over a period of 24 hours for both temperatures employed.

Peebles and Huffman [70] described nylon 6,6 as a “nonequilibrium” product as the average molecular weight tends to increase upon spinning. The same can be said for MXD,6 which has an initial polymer I.V. of 0.65 measured as a 1% solution in D.C.A., increasing to at least 0.8 during the course of spinning. Figure 4.26 shows the effect of heating MXD,6 chip over a period of time at 280°C in an inert atmosphere. This simulates conditions encountered during melt spinning. I.V. results show that the material tends to polymerize due to the unreacted ends present in the polymer, reaching a maximum value (≈ 1.1) whilst in the melt. Following the maximum, the I.V. drops to a minimum value. Peebles and Huffman also described a subsequent reaction where if degraded longer the I.V. climbs steeply towards an infinite molecular weight due to cross-linking reactions.

Figure 4.26 :- Plots of A.E.G., C.E.G. and I.V. against Degradation Time for MXD,6 Chip Degradation at 280°C for 24 Hours.

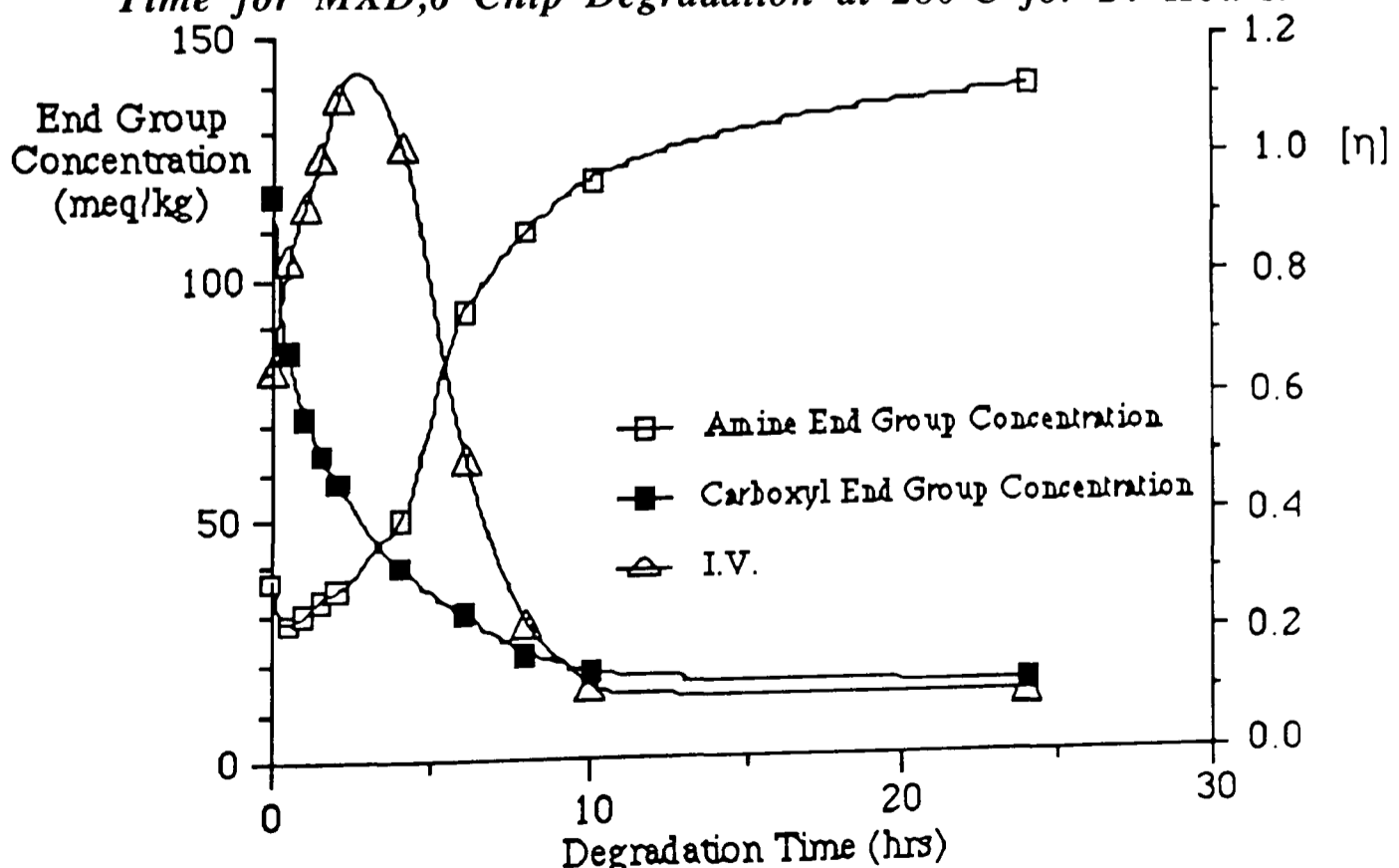


Table 4.4:- Results of End Group Analysis and Intrinsic Viscosity for MXD,6 Chip Degradation at 280°C.

Degradation Time (hrs)	[A.E.G.] (meq/kg)	[C.E.G.] (meq/kg)	[η]
0	37	118	0.65
0.5	28	85	0.83
1.0	30	72	0.92
1.5	33	64	1.00
2.0	35	58	1.10
4.0	50	40	1.02
6.0	93	30	0.50
8.0	115	22	0.21
10.0	121	18	0.15
24.0	140	15	0.12

Figure 4.27 shows the trend in I.V. for MXD,6 fibre oxidized at 180°C for 24 hours. Whereas this MXD,6 chip has an initial I.V. of 0.65, the fibre starts with an I.V. of 0.8, suggesting polymerization during the course of spinning. On Figure 4.26, a value of 0.8 is recorded at ≈ 10 minutes of heating and again at ≈ 5 hours of heating of the MXD,6 chip at 280°C. After ≈ 10 minutes of degradation of polymer chip at 280°C the polymer has a similar I.V. to that of freshly spun MXD,6, in agreement with the expectation that the residence time in the melt during spinning will be of that order.

Figure 4.27 :- Plots of A.E.G., C.E.G. and I.V. against Degradation Time for MXD,6 Fibre Degradation at 180°C for 24 Hours in air.

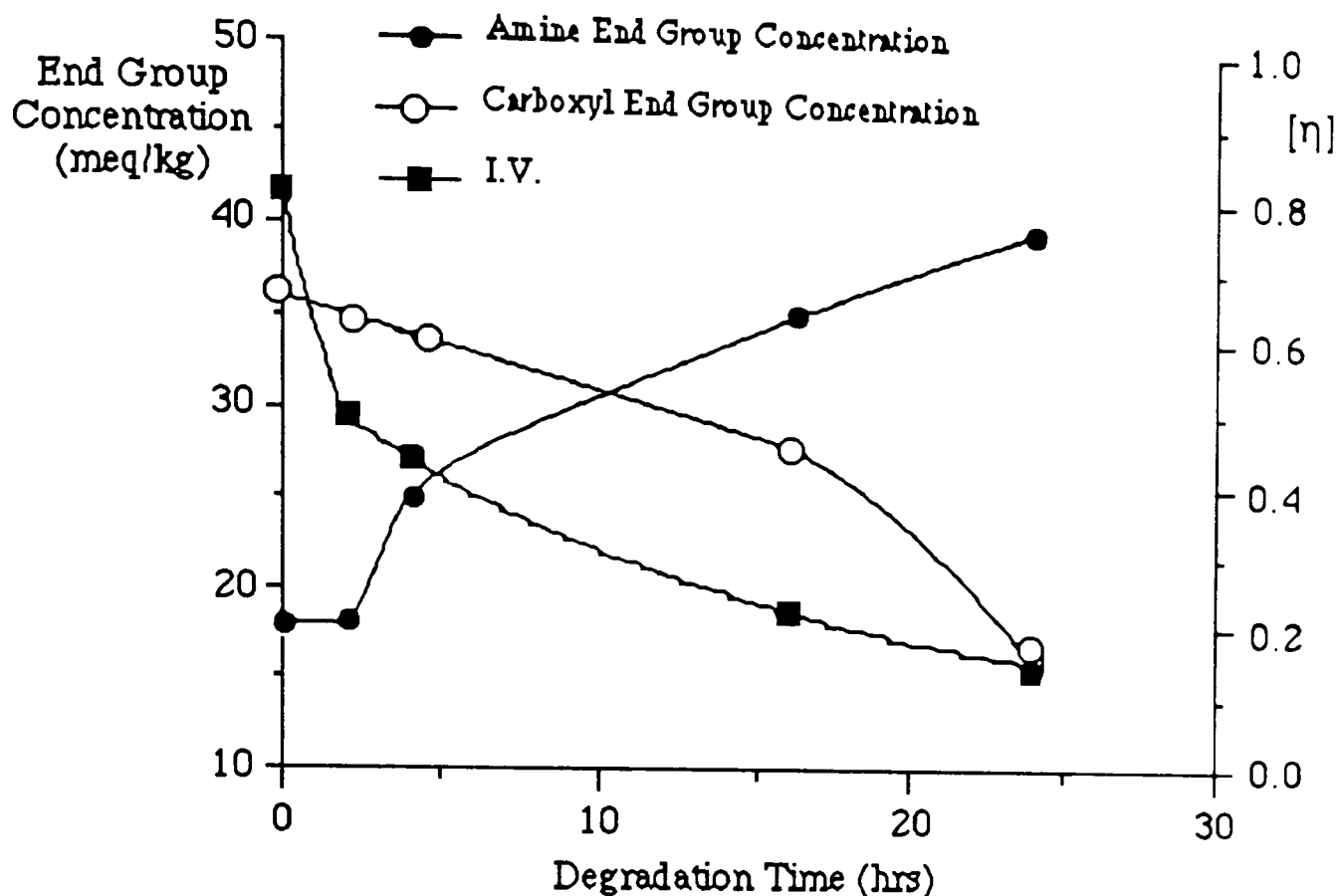


Table 4.5 :- Results of End Group Analysis and Intrinsic Viscosity for MXD,6 Fibre Oxidative Degradation at 180°C.

Degradation Time (hrs)	[A.E.G.] (meq/kg)	[C.E.G.] (meq/kg)	[η]
0	18	36	0.8
1.0	18	36	0.6
2.0	18	35	0.49
4.0	25	34	0.43
16.0	35	28	0.22
24.0	40	16	0.15

After this point, the reactions are different. Whereas the I.V. trend for the polymer chip at 280°C proceeds towards a higher value, the I.V. trend for the polymer fibre at 180°C goes down. The former trend is thought to be due to polymerization as explained earlier. However MXD,6 fibre at 180°C in air will be thermo-oxidatively degraded, hence the drop in I.V. over the 24 hour period.

4.3.3.2 Analysis of Degraded MXD,6 by End Group Analysis (E.G.A).

Samples of MXD,6 fibre degraded for I.V. measurement were retained for subsequent analysis by E.G.A., more specifically Amine End Groups (A.E.G.) and Carboxy End Groups (C.E.G.). Tables 4.4 with 4.5 and Figures 4.26 with 4.27 show this relationship over a period of 24 hours for both temperatures employed.

With respect to the A.E.G.concentration, whilst being spun, it is expected that the concentration of these basic groups will initially decrease because of polymerization, then increase markedly due to thermal degradation. If monitored for a longer period, the A.E.G. concentration would become very large at about the point of incipient gelation, then return to a small value in the gelled material [70]. On the other hand, with respect to the C.E.G. concentration, amide formation tended to be the main reaction mechanism involved with these acidic groups throughout the course of degradation, with a consistent loss in C.E.G. concentration over the 24 hour period, which is the expected behaviour for most polyamides degraded in this manner [70].

At 280°C, for MXD,6 chip, a similar trend in both end groups to that of other polyamides was measured over the 24 hour heating period. A brief period of polymerization was measured during the first 30 minutes of heating as the A.E.G concentration dropped to a minimum value. Also during this period, the I.V. value was seen to increase, again suggesting polymerization. Furthermore, the C.E.G. concentration was recorded as a consistent loss over the time period as expected.

During the course of spinning, a drop of 19meq/kg has occurred from 37 to 18meq/kg. This implies a stage of polymerization in the melt whilst being spun. The C.E.G. concentration also has a very large drop again probably due to amide formation. Further thermal oxidation of the fibre at 180°C shows a steady increase in A.E.G. concentration and a steady decrease in C.E.G. concentration, trends which are related to degradation.

4.4 INFLUENCE OF COBALT IONS ON THE OXIDATION OF MXD,6.

In many polymer processes metal ion catalysts, including transition metal ions, are used to enhance polymerization. This inevitably results in a small amount remaining in the polymer in the form of chelates which are too difficult to remove. Trace amounts of transition metal ion will have a profound effect on the rate of autoxidation [136]. Many workers have investigated the influence of trace metal ions on autoxidation. In this study also, the influence of cobalt ions on the oxidation of MXD,6 has been investigated. The activation energies for the oxidation of the polymer with and without cobalt have been calculated (chapter 4.2.2) and show the catalytic nature of the metal on the oxidation of the polymer. As an example of recently published work, Osawa [137] has already reported that the rate of oxidative degradation of polypropylene, evaluated by measuring the oxygen uptake from a closed system, was the greatest for a sample of polymer containing cobalt ions followed by manganese, copper and iron. Furthermore, catalytic decomposition of t-butyl hydroperoxide by metal salts gave a similar trend, which led to an apparent correlation between the catalytic activity of metallic salts in the oxidation of the polymer and the decomposition of the hydroperoxide. However, the role of the metal ion may not exclusively be as a hydroperoxide decomposer and in some cases it may be more important as a reaction initiator. Many factors will influence the behaviour of the catalyst. With cobalt the initial oxidation state is important as well as the ligands to which it is bonded.

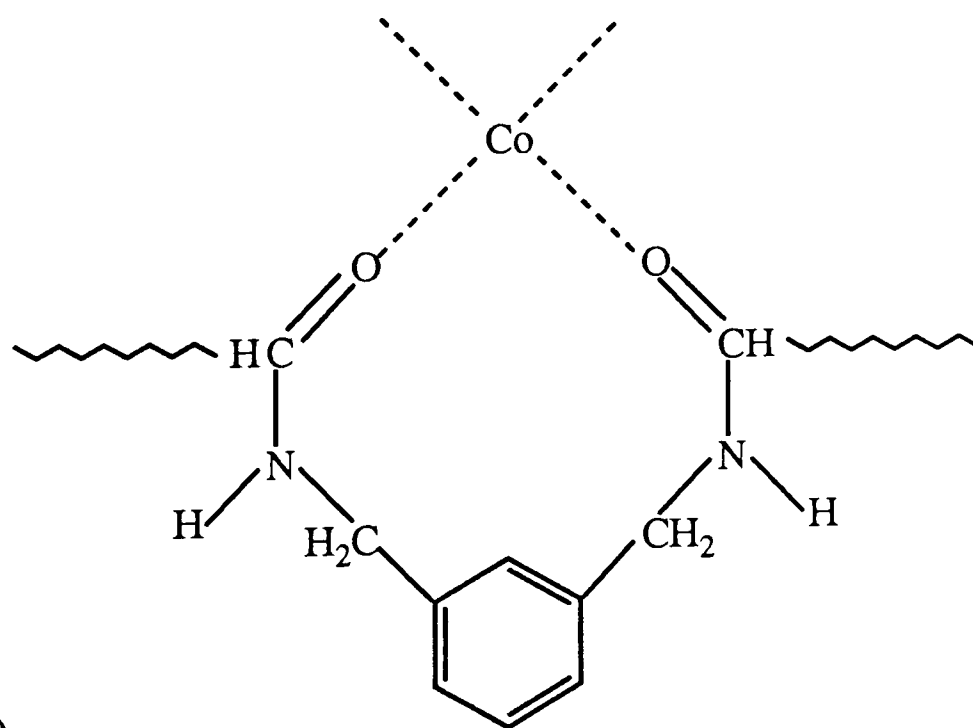
The mechanisms proposed for the catalytic autoxidation of MXD,6 using cobalt ions have been based on accepted mechanisms for other autoxidations [138] together with evidence obtained from this study and from concurrent research conducted at C.M.B. Packaging Technology Wantage.

4.4.1 The Role of Cobalt Ions in the Initiation Reactions.

Initiation is believed to involve the creation of sufficient free radicals to sustain the oxidation reactions. It is generally understood that a critical concentration of free radicals is required in order to do this. The critical concentration will be determined by the balance between the relative rates of the propagation and termination reactions. If the former reaction dominates, then oxidation will be sustained. If the reverse occurs, then termination reactions will dominate and oxidation will not continue.

It is proposed here that during the melt processing of the polymer, complex formation occurs between the cobalt and the MXD,6 chains and this has an enhancing effect on the uptake of oxygen in an autoxidative environment. To explain this complex formation, it is suggested that the carbonyl groups of the polyamide donate a lone pair of electrons to the cobalt in preference to electron pair donation via the N-H groups (Figure 4.28).

Figure 4.28 :- Proposed Complex Formation Between MXD,6 and Cobalt.



This species has been designated $L_2Co(II)$ where L is the electron donating ligand.

Evidence in favour of this complex formation has been found by C.M.B. Packaging Technology, in that other MXD,_n homologues prepared in a similar manner with 200ppm cobalt show varying oxygen scavenging. Polyamides that do exhibit an effect are capable of forming a relatively unstrained bidentate complex with the metal catalyst, as with MXD,₆. Polyamides with either a small (MXD,₂) or large (MXD,₁₀) number of carbon atoms in the carboxylic acid part of the chain show no evidence of oxygen scavenging. This is believed to be because the chelate ring cannot form due to steric hindrance associated with a short or a very long carbon chain.

There is no need to assume that (I) is the only structure formed, although this may be the thermodynamically stable structure on entropy considerations, relative to, for example the complex being formed through the more flexible aliphatic segment of the polymer chain. Once in the solid state, the complex is thought to activate the oxygen present thus creating a superoxide radical anion (II) which may be a very reactive centre (Figure 4.29) i.e.

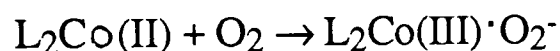
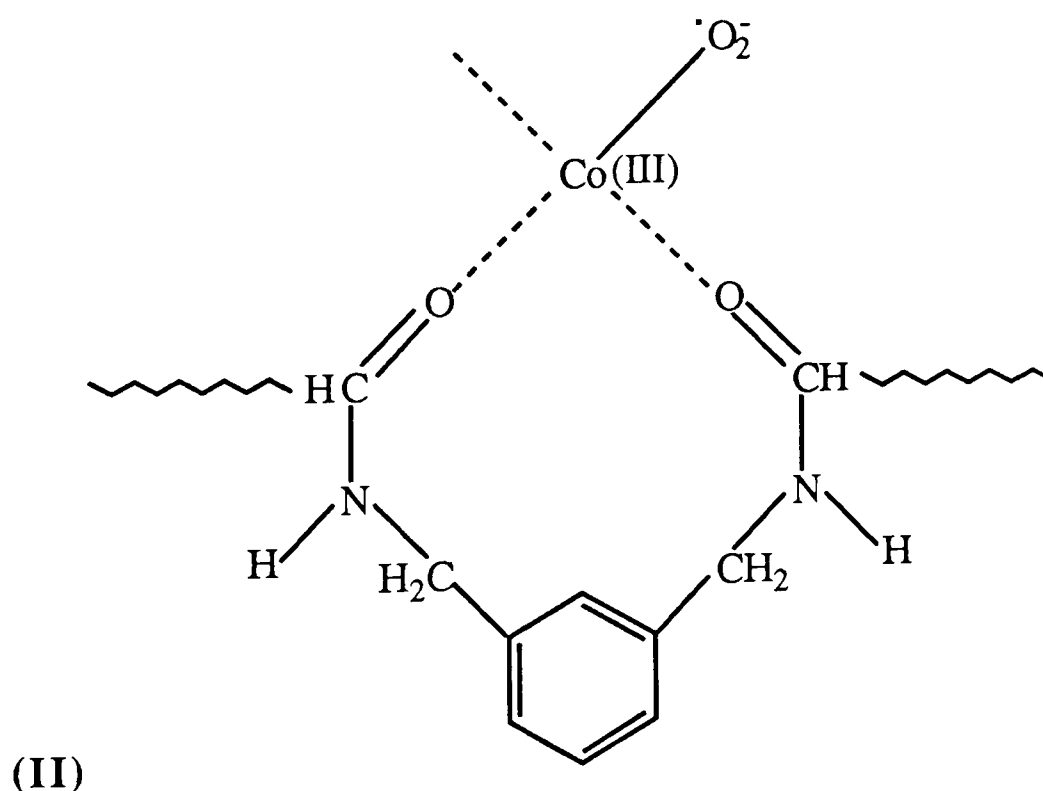


Figure 4.29 :- Superoxide Radical Anion Formation.



which in turn may abstract the most readily available hydrogen atom (III) from a neighbouring polymer chain i.e. in the α position to the N-H group (Figure 4.30) i.e.

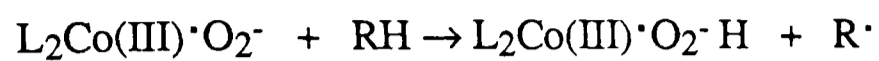
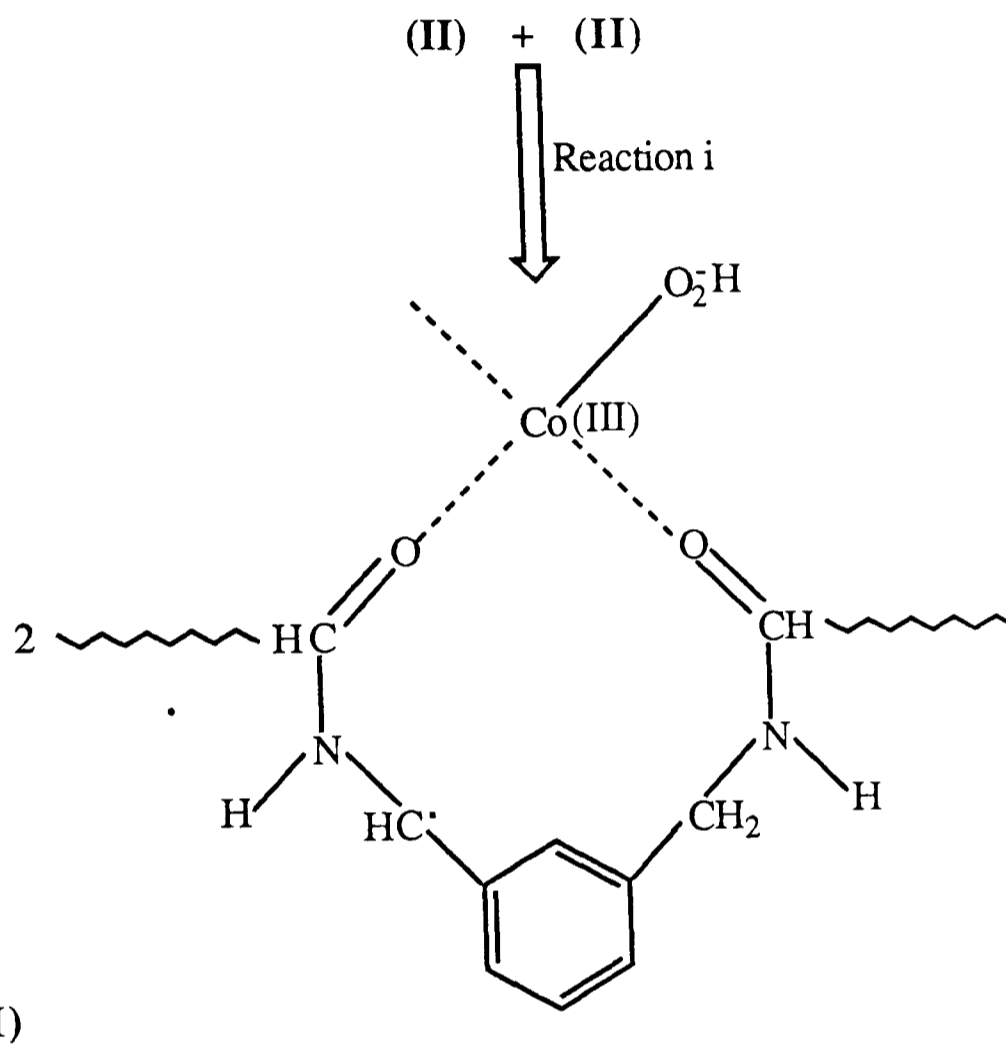


Figure 4.30 :- Proposed Hydrogen Abstraction Mechanism.



Disproportionation of the latter leads to a conjugated species having a high degree of resonance stabilization (Figure 4.31) i.e.

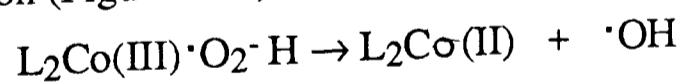
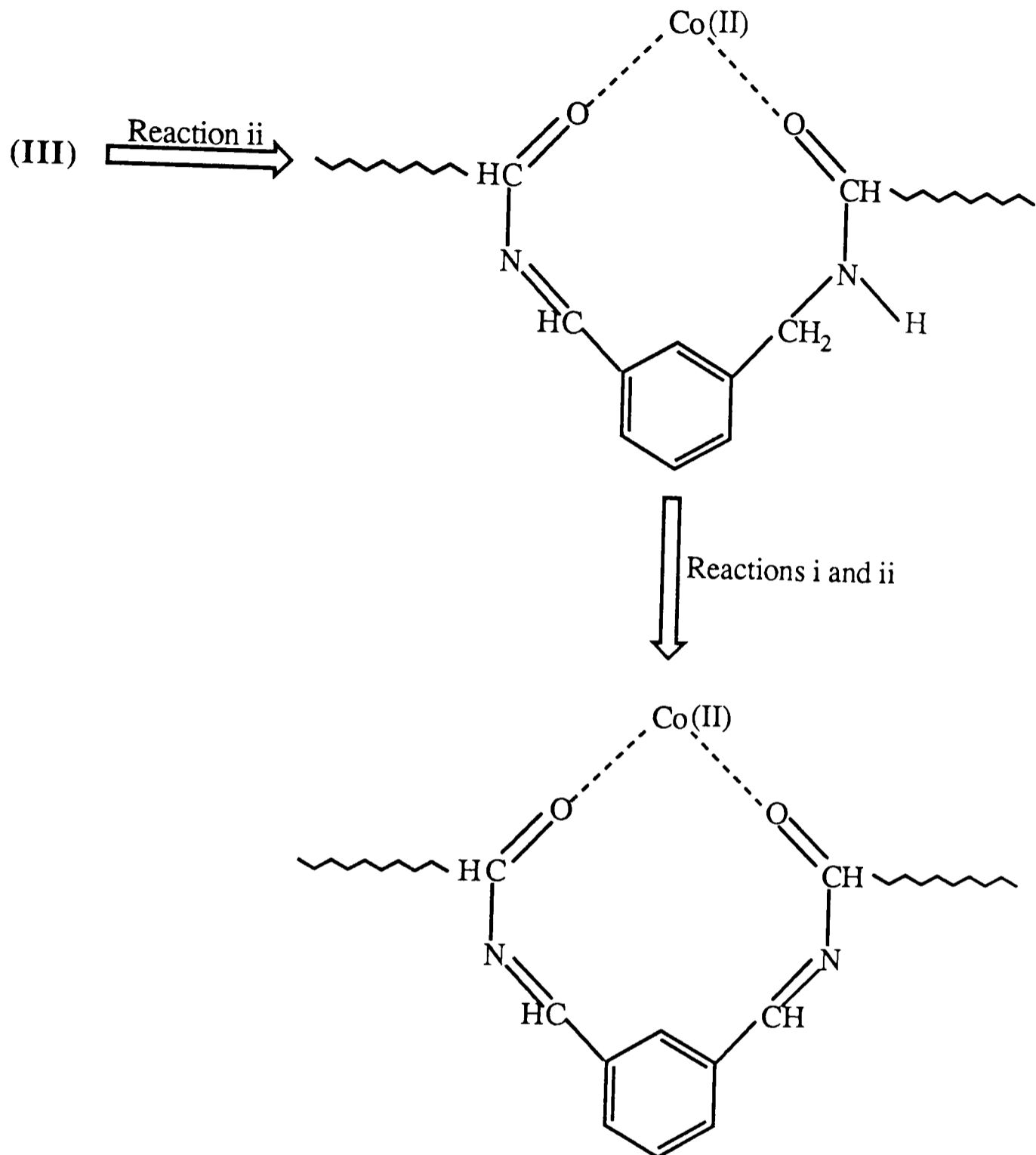


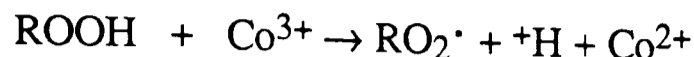
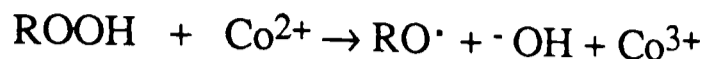
Figure 4.31 :- Proposed Disproportionation Mechanism.



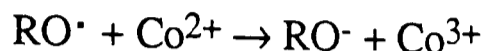
Thus during the course of initiation, the radicals R^\cdot , $\cdot O_2H$ and $\cdot OH$ have been formed. The $\cdot O_2H$ and $\cdot OH$ radicals would be expected to be mobile in the solid phase and would probably have diffusion constants similar to that of molecular oxygen. It is therefore postulated that these radicals are responsible for the latter stages of oxidative propagation in the solid phase. This therefore does not necessitate that the cobalt play any further part in the oxidation process and implies that it acts principally but perhaps not exclusively as a reaction initiator. Thus mobility of the cobalt in the solid state is not a pre-requisite of the proposed mechanistic pathway.

4.4.2 The Role of Cobalt ions in the Propagation Reactions.

In solution cobalt is known to aid in the decomposition of hydroperoxides [139].

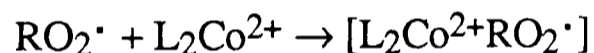


Furthermore, it is also known that the metal ion can deactivate alkoxy radicals :-



Where the concentration of the alkoxy radicals is less than the metal ion concentration, the antioxidation effect will predominate. When the concentration of the alkoxy radicals is greater than that of the metal ion concentration then the rate of oxidation increases.

In the solid phase, cobalt ions are believed to be essentially immobile. Extraction studies have shown that the cobalt is not readily removed from the polymer, supporting the earlier proposal that the cobalt is strongly bound to the solid polymer. Hence cobalt cannot fully participate in hydroperoxide decomposition or alkoxy deactivation. However, a further property of transition metal ions including cobalt is that they can stabilise peroxy radicals [139]. Thus :-



It is proposed that the influence of the cobalt in the polymer melt is to stabilise the peroxy radicals, preventing termination of the chain reaction. These radicals may undergo further reaction, forming other radicals which can participate in oxygen scavenging when in autoxidative conditions. Thus it is believed that the overall effect of the cobalt with MXD,6 is to catalyse the generation of free radicals in the melt, which scavenge oxygen in the solid phase. A large number of radicals are formed during initiation and some are stabilized by the cobalt ions. Fibre spun from such a composition will show a large increase in the rate of oxidative degradation, (evaluated by measuring the oxygen uptake) due to the radicals already created. Also, it is proposed that the metal ion cannot fully participate in any other propagation reactions once in the solid state due to the lack of mobility and that the role of the cobalt is primarily that of an initiation catalyst.

4.5 DISCUSSION.

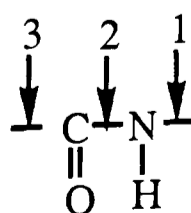
The solid state thermal oxidation of MXD,6 has been investigated. In order to postulate a feasible mechanism for the degradation of the polymer, several general principles have to be initially explained. Primarily, the rate of formation of a macro-radical depends on the chemical structure of the polymer, or more precisely on the dissociation energies of the particular bonds between the atoms forming the polymer in proportion to the value of $\exp(-E/RT)$ where E is the appropriate bond energy. Furthermore, as this study concentrates on solid state thermal oxidation, the molecular motion of the consequent macro-radicals is severely restricted, making their reactions more likely to occur with their immediate neighbours.

Even though the mechanisms of degradation are complex, a reasonable understanding of this subject may be obtained by investigating the bond energies associated with the polymer. Kamerbeek et al [56], then later Mortimer [57] asserted that the CH₂-NH bond was responsible for initial polyamide cleavage. Their arguments were based on the assumption that the weakest bond would break more easily than the stronger bonds. Table 4.6 shows the energies of bonds of the types present in nylon. Furthermore, the probabilities of their fission at 180°C relative to the probability of fission of the weakest polyamide bond, the CH₂-NH bond, have been calculated [131].

Table 4.6 :- Bond Energies and their Respective Probabilities of Fission at 180°C Relative to the CH₂-NH bond.

Bond.	Bond Energy (Kcal.mol ⁻¹).	Relative Probability.
CH ₂ -NH	62	1.0
CH ₃ -CO	71	4.6 × 10 ⁻⁵
CH ₂ -CH ₂	80	2.1 × 10 ⁻⁹
OC-NH	83	7.4 × 10 ⁻¹¹
N-H	84	2.5 × 10 ⁻¹¹
C-H	98	3.5 × 10 ⁻¹⁸
C=O	173	3.5 × 10 ⁻⁸⁴

With these probabilities in mind, it is reasonable to conclude that a near random fission of every bond in the polyamide chain, as suggested by Derminot et al [140], is highly unlikely. However, as already discussed in chapter 2.2, it is unsafe to base a mechanism of polymer degradation entirely on bond energies, as this can be sometimes more misleading than beneficial. Kakar [130] found he could not assign all the products of nylon 6,6 thermal oxidation to the fission of the CH₂-NH bond alone and proposed that a second bond on nylon 6,6 was also being broken. For polyamides, the next theoretically weak bond is the CH₂-CO bond. However, even though the probability of fission of this bond is very low, it is reasonable to propose that the quoted bond strength gives a false impression of the actual bond strength and that the true value for the fission of that bond would be largely dependent on other factors which may include the influence of its neighbouring groups. If this is the case then it may be accepted that amide bond fission according to Goodman may have justification i.e. fission of each bond in and adjacent to the amide bond must occur :-



Fission of bonds (1) and (3) has been accounted for. For polyamides, direct photolysis of the CO-NH bond, (2), of the amide unit is the dominant process of polymer deterioration. Thus Goodman's theory of polyamide bond fission may be valid. However, in this study, the probability of any type of photodegradation was low as most of the degradation was conducted in the dark.

Thus the most probable bonds, (1) and (3), to be broken have been established, hence the consequence of their respectively formed radicals must now be discussed. In order to do so, mechanisms where by these radicals are initiated, propagated and terminated must be proposed

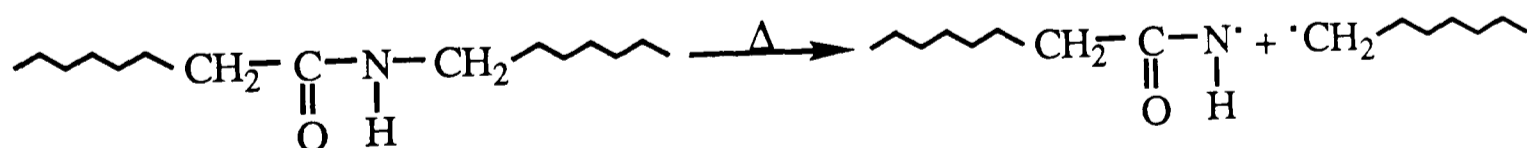
These postulates will be explored for the autoxidation of polyamides in general at 180°C.

4.5.1 Radicals Formed from the Fission of the CH₂-NH and CH₂-CO Bonds and their consequent Reactions.

4.5.1.1 Polyamide Initiation.

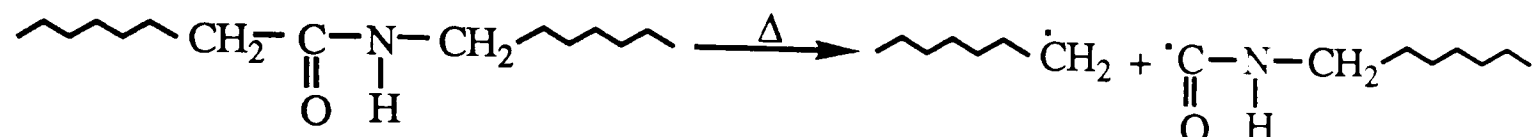
At 180°C initiation occurs causing dissociation of the CH₂-NH bond which will generate an amido and an alkyl radical (Scheme 4.1).

Scheme 4.1 :- Radicals formed from the dissociation of the CH₂-NH Bond.



On the other hand, under similar conditions, the CH₂-CO bond will dissociate to generate an alkyl radical and a hydroisocyanate radical (Scheme 4.2).

Scheme 4.2 :- Radicals formed from the dissociation of the CH₂-CO Bond.



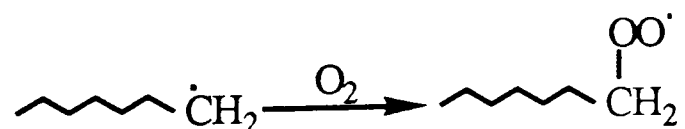
These radicals formed from either route will become stable entities via a number of different routes, which may or may not involve oxygen, as is discussed in the following sections.

4.5.1.2 Polyamide Propagation.

The radicals formed from the fission of either bond are reactive species which in an autoxidative environment will react with molecular oxygen. Alternatively, they may react with labile hydrogen available on the polyamide itself (hydrogen abstraction). This in turn would create further radicals in the polymer chain capable of either an oxidation or hydrogen abstraction reaction.

With respect to the oxidation reactions, it is still very unclear how the amido and hydroisocyanate radicals reacts with oxygen. As far as the alkyl radicals are concerned, the products of their oxidation are peroxy radicals (Scheme 4.3).

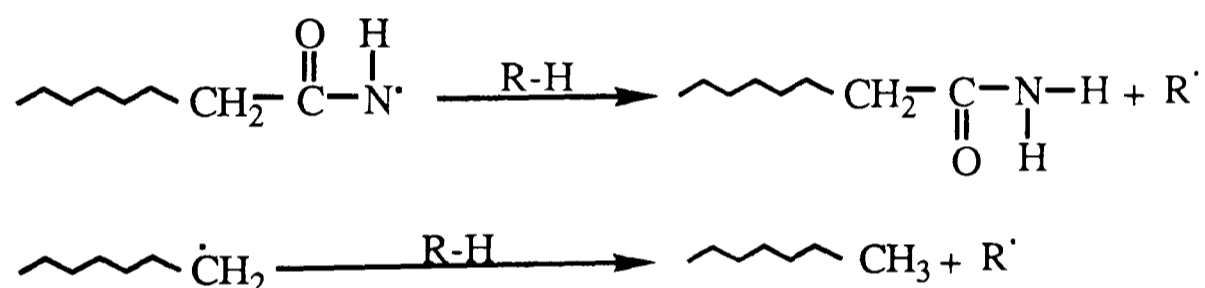
Scheme 4.3 :- Peroxy Radical Formation.



4.5.1.3 Polyamide Termination.

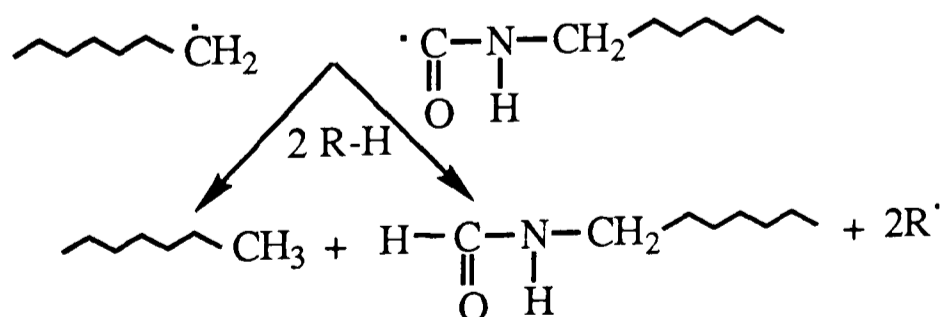
During the stages of initiation and propagation a large number of radicals are formed which react to become stable entities. If the parent radicals are first considered then as already mentioned, they may react with or without oxygen. Hydrogen abstraction reactions, although less likely, still have to be considered. With the radicals formed from the dissociation of the CH₂-NH bond, the amido radical would form an amide end group and the alkyl radical a methyl end group (Scheme 4.4). Other hydrogen abstraction mechanisms that have been discussed already [131], however, are of less importance in this study.

Scheme 4.4 :- Hydrogen Abstraction Reactions Associated with the Radicals formed from the Dissociation of the CH₂-NH Bond.



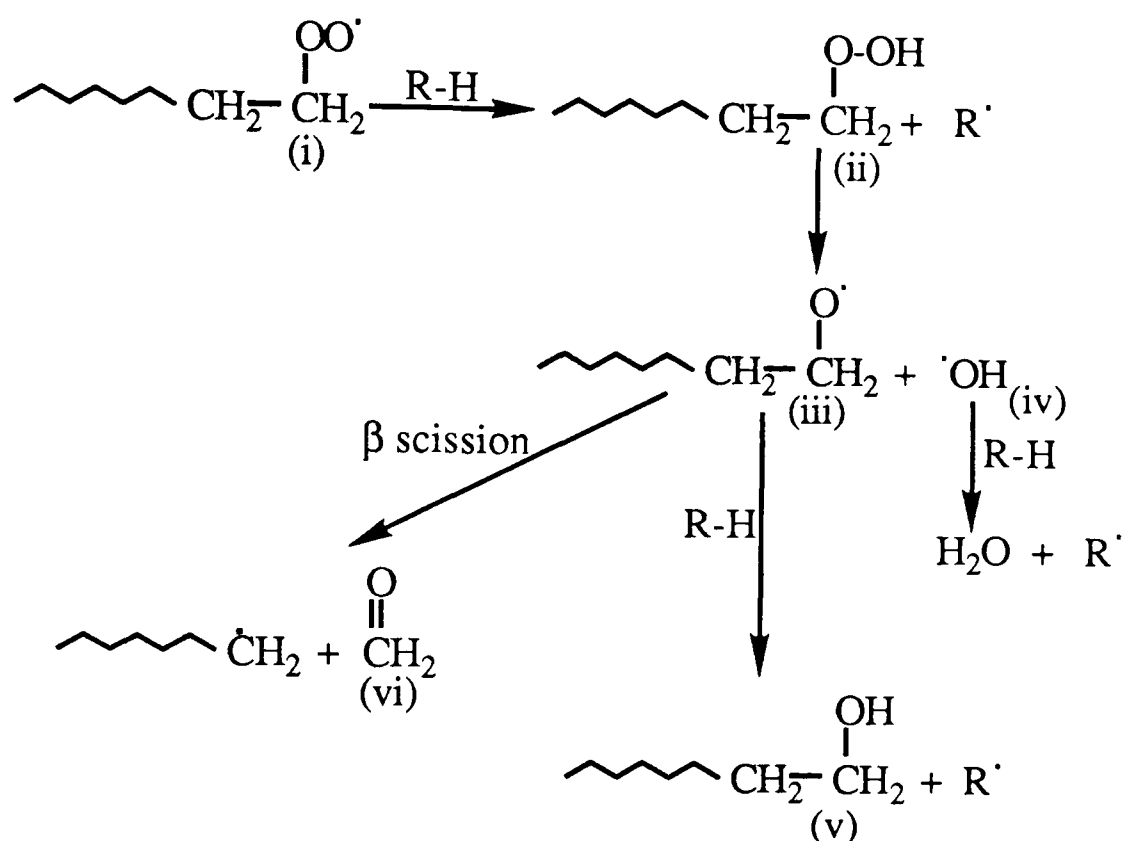
Furthermore, with the radicals formed from the dissociation of the CH₂-CO bond, the alkyl radical will again form a methyl end group, whereas the hydroisocyanate radical will form a formamide end group (Scheme 4.5).

Scheme 4.5 :- Hydrogen Abstraction Reactions Associated with the Radicals formed from the Dissociation of the CH₂-CO Bond.



The peroxy radical (i) terminations are of far more importance in this study and will be discussed more thoroughly (Scheme 4.6). Primarily, these radicals abstract labile hydrogen forming hydroperoxide groups (ii). However, these groups are not very stable, although less volatile than the peroxy radicals and will readily decompose to give alkoxy (iii) and hydroxy (iv) radicals.

Scheme 4.6 :- Peroxy Radical Terminations.



Hydroxy radicals tend to hydrogen abstract forming water as the stable entity, whereas the alkoxy radicals may undergo hydrogen abstraction giving rise to an alcohol (v). Alternatively, a reaction of β scission may proceed [51] which is a well established mechanism whereby main chain scission of the polymer chain occurs resulting in an aldehyde or ketone and another alkyl radical. However, it is also common to find further oxidation to occur with degradation products that will autoxidise. At high temperatures, alcohols will readily autoxidise to aldehyde and ketones, the former of which will also autoxidise via the established Baeyer-Villiger Oxidation mechanism to give rise to carboxylic acid groups [138].

Thus an idea of the oxidative mechanisms related to polyamides in general has been discussed. It is now possible to tackle the problem of autoxidation of MXD,6 and to propose mechanisms to explain the results derived earlier.

4.5.2 Mechanism of MXD,6 Oxidation.

Experimental evidence has shown that the thermal oxidation of MXD,6 at 180°C produces a variety of degradation products which have been identified using chromatographic and spectroscopic techniques. These include homologous series of monocarboxylic acids, dicarboxylic acids, aldehydes, ketones, n-alkylamines and diamines. Furthermore, a variety of aromatics were also detected and identified.

In order to continue with the proposition of how the polymer is oxidized, it is useful to postulate a mechanism whereby each of the homologous series is generated.

In this study, strong evidence indicated the sequential loss of one carbon at a time, presumably from an alkyl radical. It is a well established fact that β scission reactions are common to oxidation of many polymers. Alkoxy radicals, via the dissociation of hydroperoxide group, can form on the end methylene group of an alkyl radical. If hydrogen abstraction does not occur, then β scission will proceed, the effect of which formaldehyde is formed and a daughter alkyl radical, the latter of which may undergo further oxidation to form a peroxy radical or hydrogen abstraction to form a methyl end group.

For convenience, the mechanisms involved in the production of each homologous series will be considered separately using the thermal oxidation postulates already discussed for polyamides in general.

4.5.2.1 Aliphatic Monocarboxylic Acids.

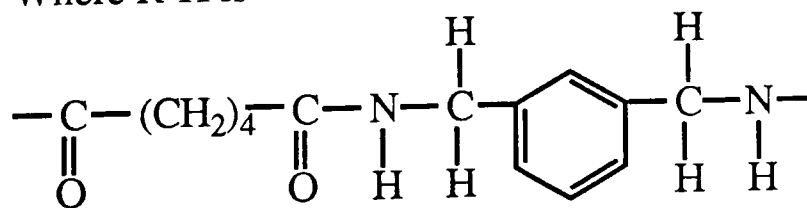
Since a homologous series of aliphatic monocarboxylic acids were derived from MXD,6 oxidation, it is essential to consider the possible routes whereby an alkyl radical may be formed.

If we first consider the rupture of the CH₂-NH bond, presumably the weakest polyamide bond, then the radicals formed will give rise to a convenient route to a homologous series of aliphatic monocarboxylic acids. However, fission of the CH₂-CO bond will also lead to radicals capable of transforming to a similar homologous series. The resultant alkyl radicals formed from the CH₂-NH and CH₂-CO bonds, will continue to react until stable entities are created. Hence the following mechanisms have been proposed (Scheme 4.7).

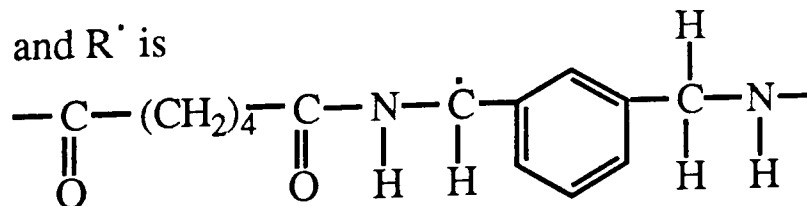
In all of the mechanisms concerned in this study, hydrogen abstraction will take place during some stage of termination. The most labile hydrogens available on the MXD,6 (R-H) polymer chain are the hydrogens on the methylene group attached to the aromatic ring (Figure 4.32). Thus after hydrogen abstraction, it is common to expect the resulting radical (R[•]) to undergo oxidation with the formation of oxidation products such as isophthalic acid.

Figure 4.32 :- Hydrogen Abstraction in MXD,6.

Where R-H is

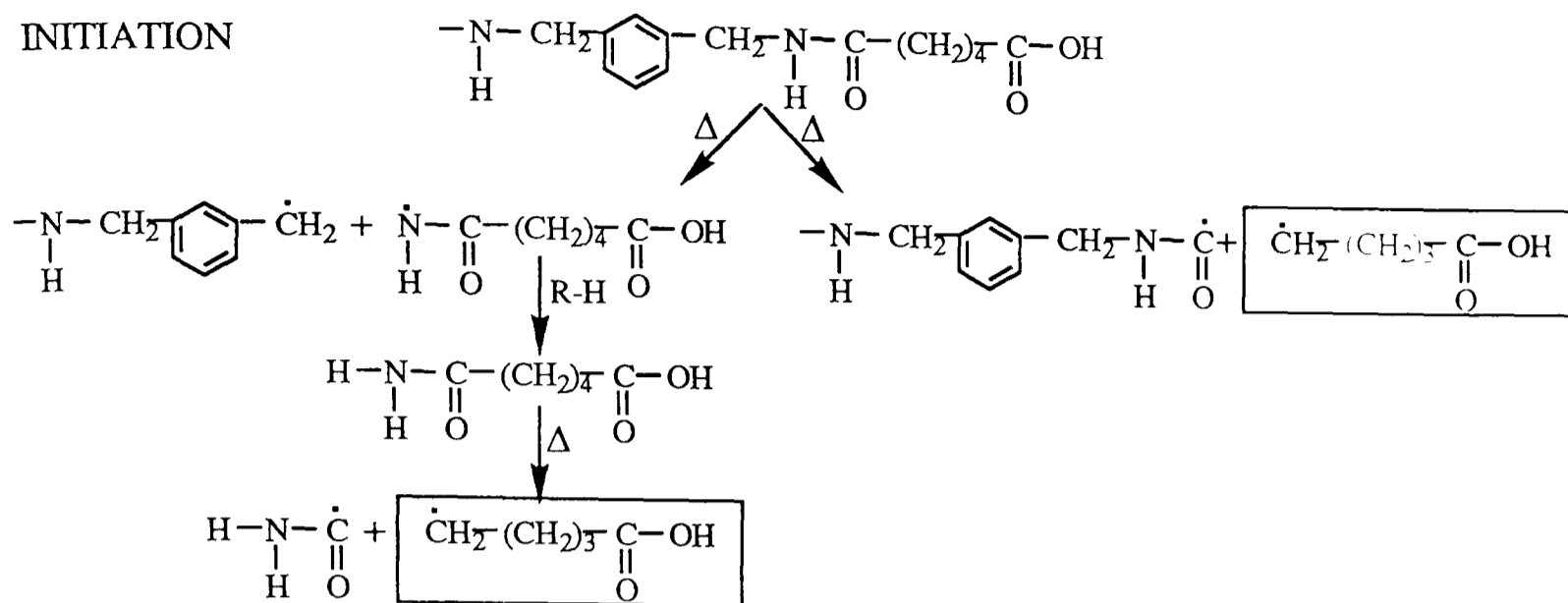


and R[•] is

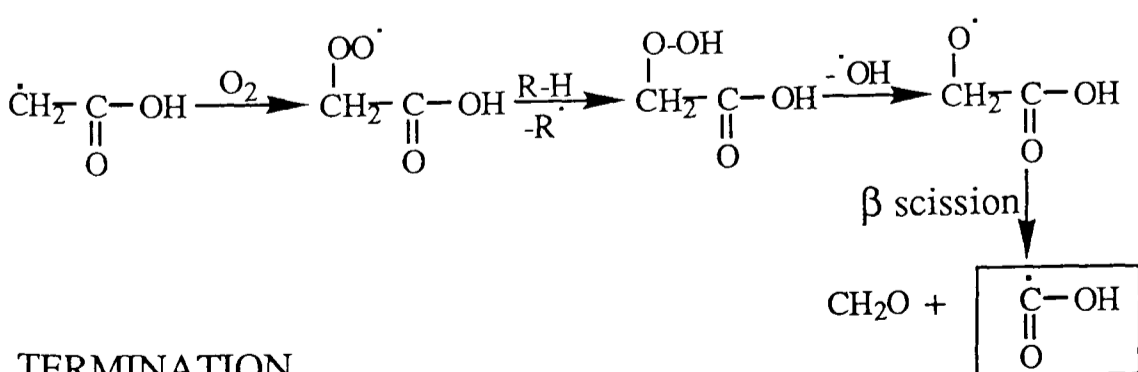
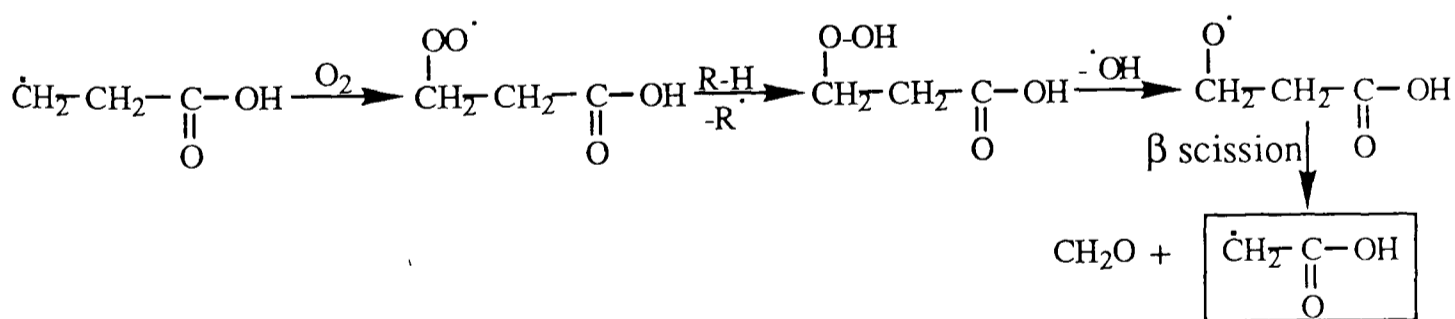
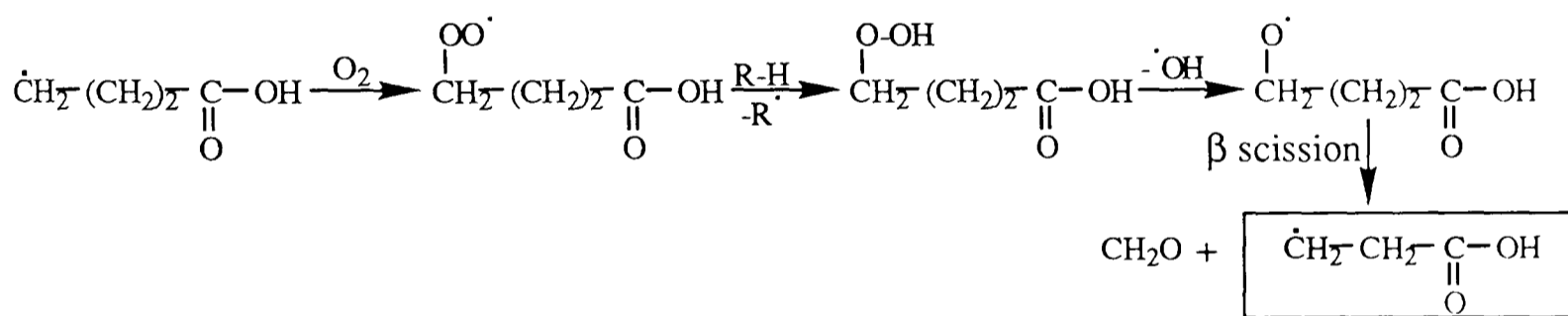
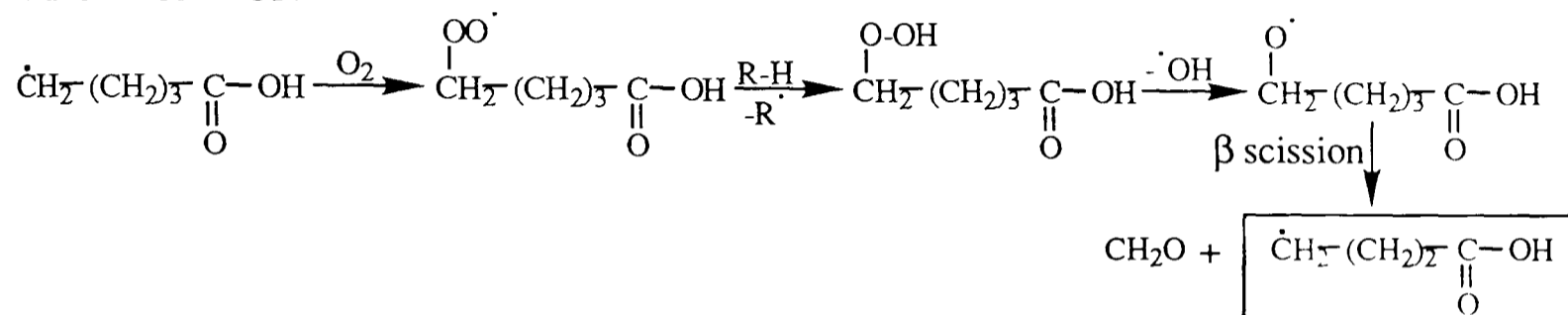


Scheme 4.7 :- Monocarboxylic Acids derived from MXD,6 Oxidation via an Alkyl Radical.

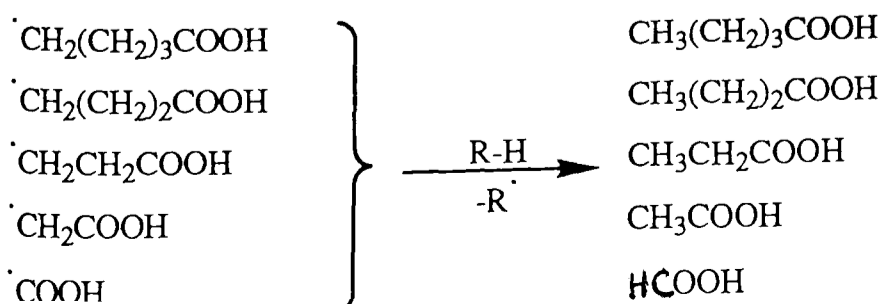
INITIATION



PROPAGATION



TERMINATION



For convenience, the carboxylic end groups have been considered so that their respective acidic degradation products can be readily recognised. However, these mechanisms do not apply specifically for the end groups only and may be employed for any of the carbonyl groups along the polymer chain. However, pentanoic acid was detected as a product which suggests that this mechanism does at some time take place at a carboxylic end group.

Thus from the alkyl radical, it is possible to derive a homologous series of monocarboxylic acids ranging from C₁ to C₅. This mechanism would account for the homologous series of monocarboxylic acids identified as degradation products from MXD,6 oxidation.

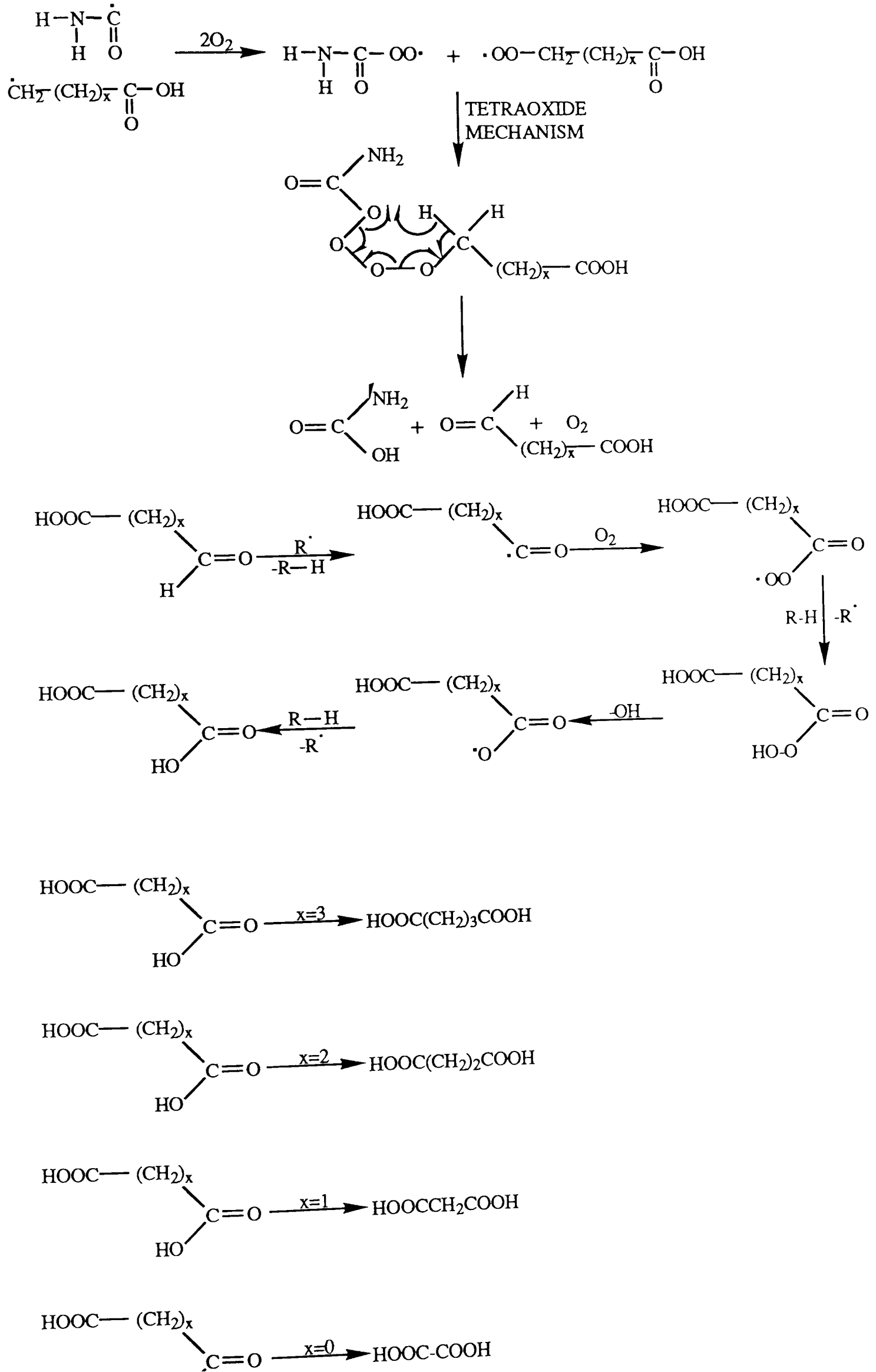
4.5.2.2 Aliphatic Dicarboxylic Acids.

As with the monocarboxylic acids, an homologous series of dicarboxylic acids was also identified. Hence it is assumed that they are also formed from a parent alkyl radical. Dissociation of the CH₂-NH bond will result in radicals most capable of transforming to the appropriate dicarboxylic acid.

With regards to the propagation reaction, the Tetraoxide Mechanism for the termination of peroxy radicals has been considered [141]. The reaction involves the reversible formation of a dimer which is formulated as a tetraoxide, which may break down in a concerted fashion to give equimolar amounts of alcohol and a carbonyl compound (Scheme 4.8)

Scheme 4.8 :- Dicarboxylic Acids derived from MXD,6 Oxidation via an Alkyl Radical continued.

TERMINATION



Thus from the alkyl radical, it is possible to derive a homologous series of dicarboxylic acids ranging from C₁ to C₄. However, adipic acid was also identified, which even though not formed due to the mechanism suggested can be accounted for as an original monomer. Therefore, this mechanism would account for the homologous series of dicarboxylic acids identified as degradation products from MXD,6 oxidation.

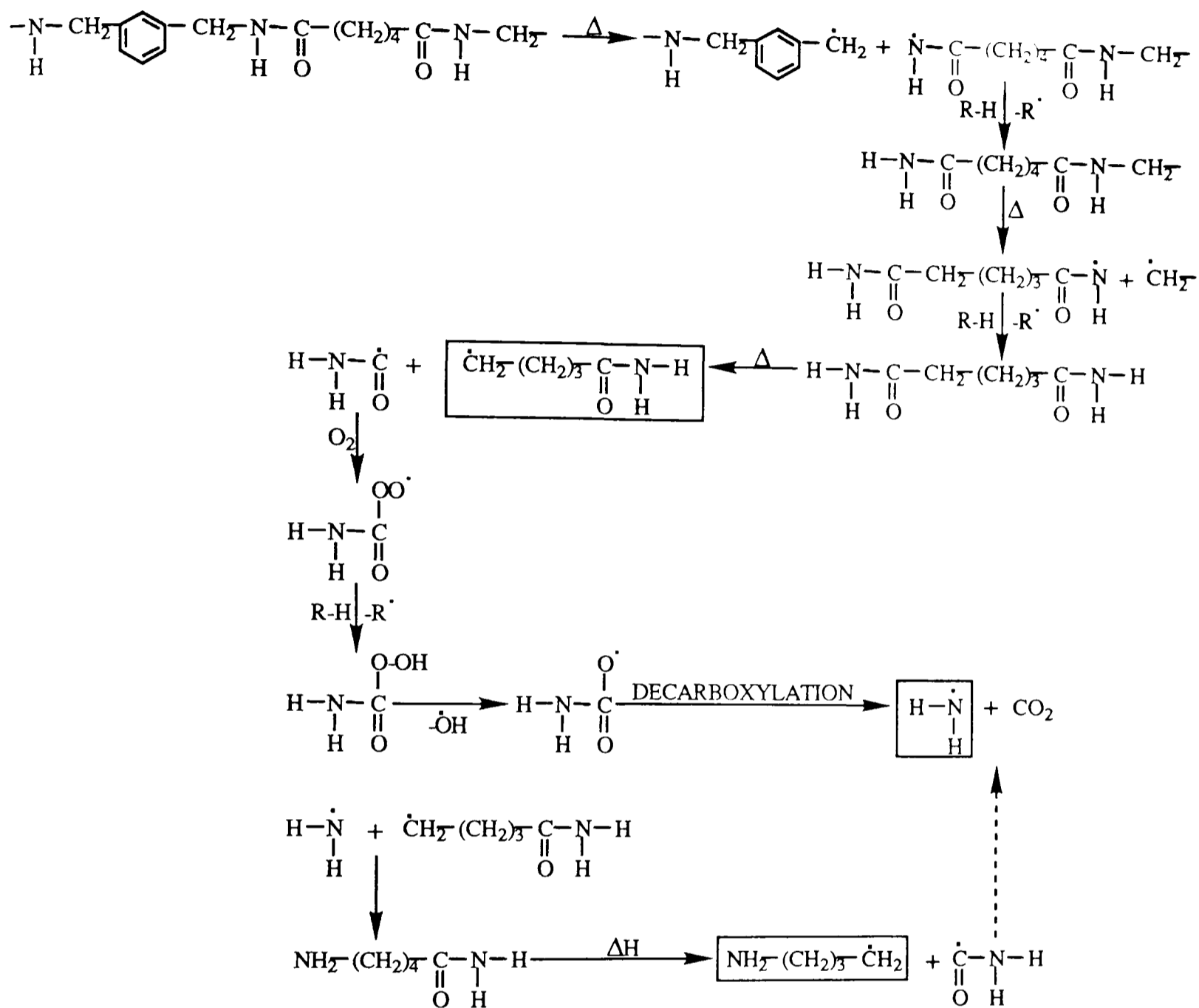
4.5.2.3 Aliphatic Mono- and Diamines.

Once again a homologous series of both mono- and diamines have been identified. These will originate from a parent alkyl radical. A mechanism which involves the formation of an amino radical has been derived, which explains the formation of both types of amine as well as the abundant amounts of ammonia and carbon dioxide also identified during this study (Scheme 4.9).

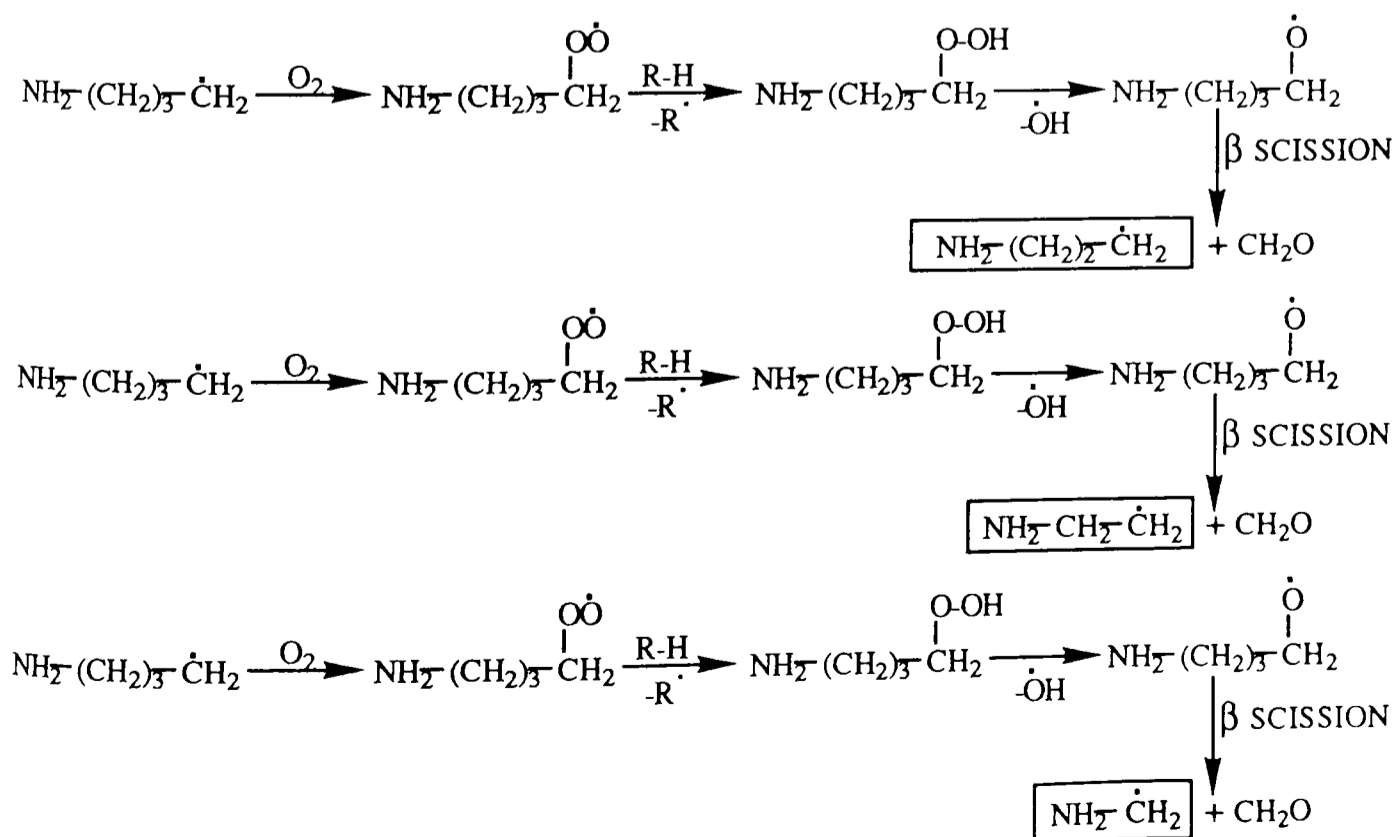
Thus from the alkyl radical, it is possible to derive a homologous series of monoamines as well as diamines ranging from C₁ to C₄. Furthermore, ammonia has also been accounted for which has already been established as a common degradation volatile derived from polyamides.

Scheme 4.9 :- Mono- and Diamines derived from MXD,6 Oxidation via an Alkyl Radical.

INITIATION

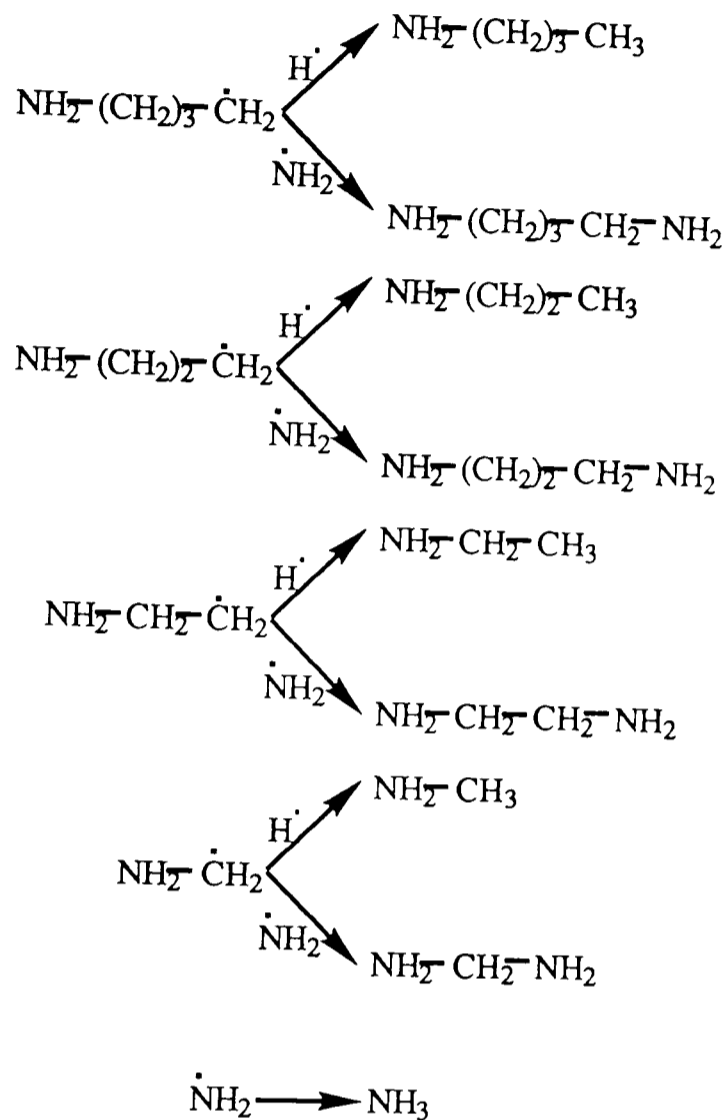


PROPAGATION



Scheme 4.9 :- Mono- and Diamines derived from MXD,6 Oxidation via an Alkyl Radical continued.

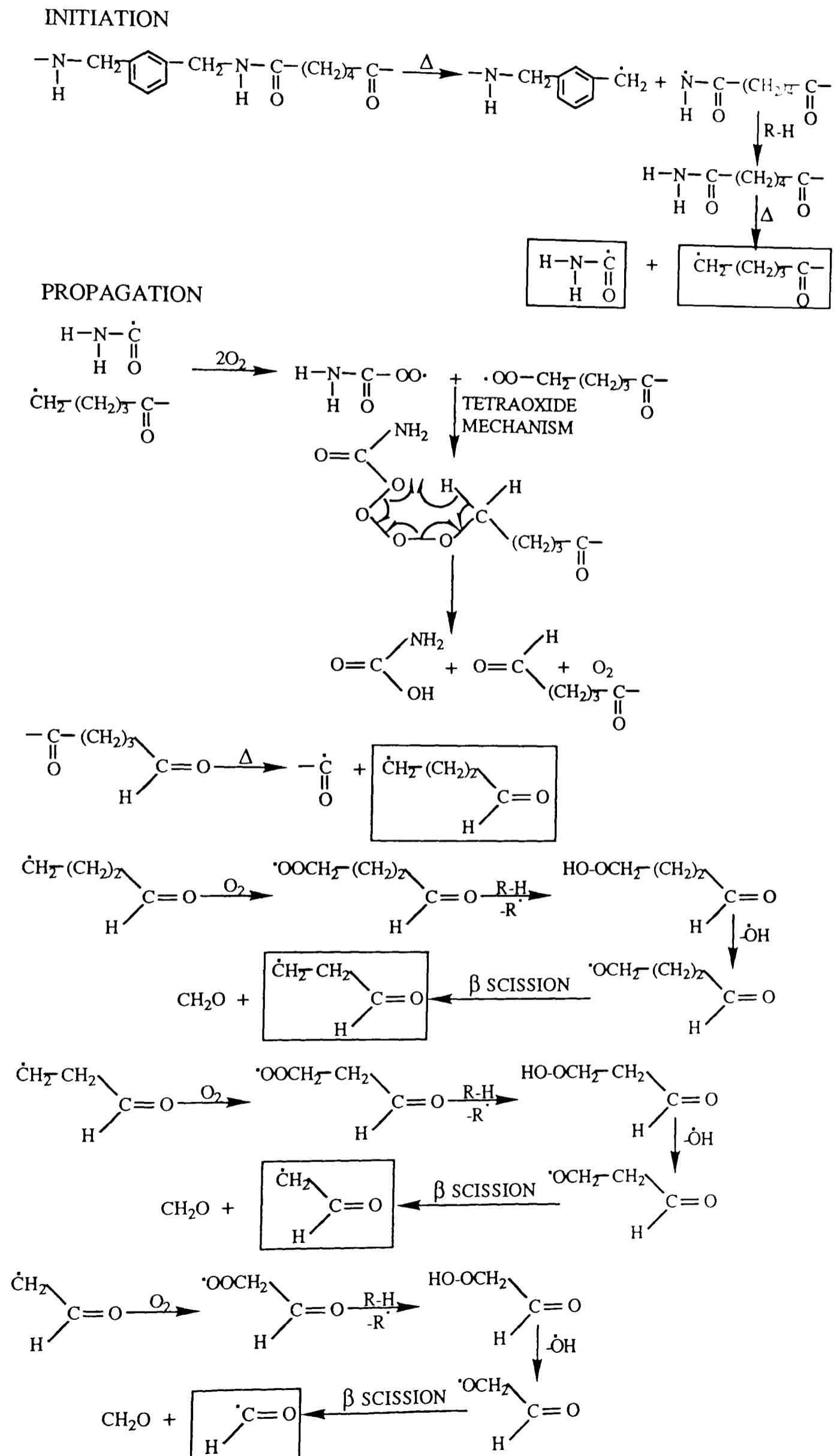
TERMINATION



4.5.2.4 Aldehydes and Ketones.

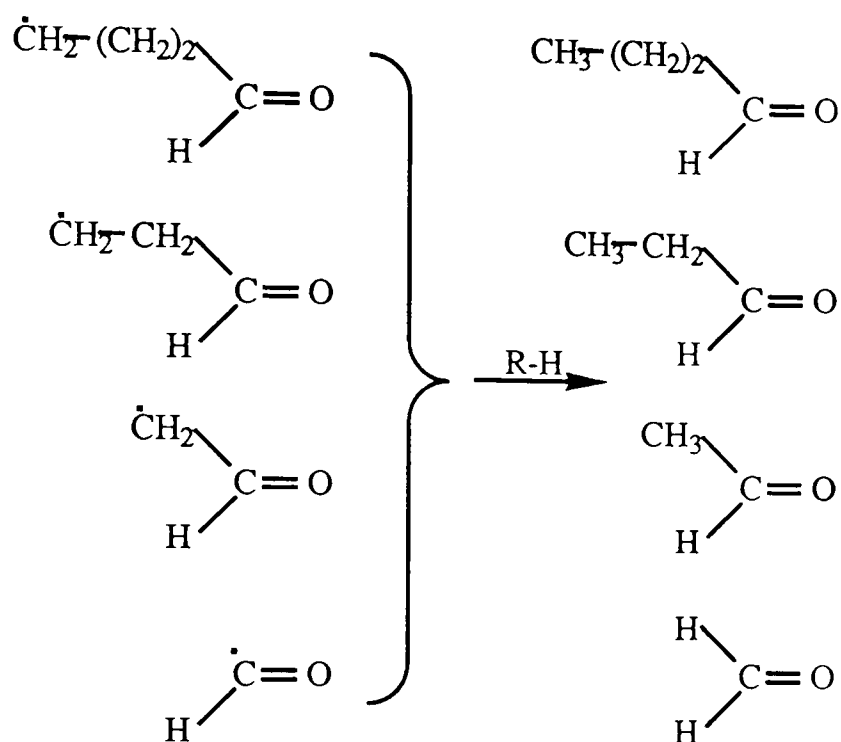
An homologous series of aldehydes was identified which can be derived from the fission of the CH₂-NH bond, resulting in an alkyl radical, which during the stages of propagation may undergo a tetraoxide reaction as shown (Scheme 4.10). Further scission, in particular the CO-CH₂ bond will result in an alkyl radical with a carbonyl end, which via β scission will give rise to several aldehydes.

Scheme 4.10 :- Aldehyde and Ketones derived from MXD,6 Oxidation via an Alkyl Radical.



Scheme 4.10 :- Aldehyde and Ketones derived from MXD,6 Oxidation via an Alkyl Radical continued.

TERMINATION



Thus from the alkyl radical, it is possible to derive a homologous series of aldehydes ranging from C₁ to C₄. However, acetone was also identified, which even though not formed due to the mechanism suggested is believed to be formed via alternative mechanisms which may involve crosslinking.

4.5.2.5 Aromatic Degradation Products.

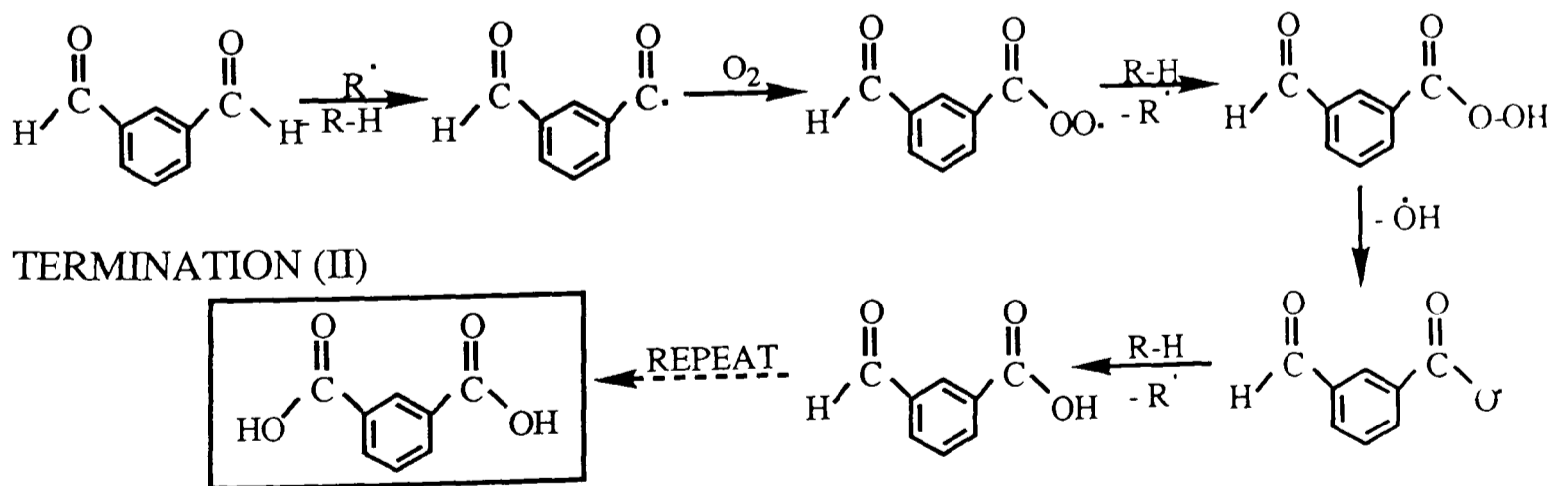
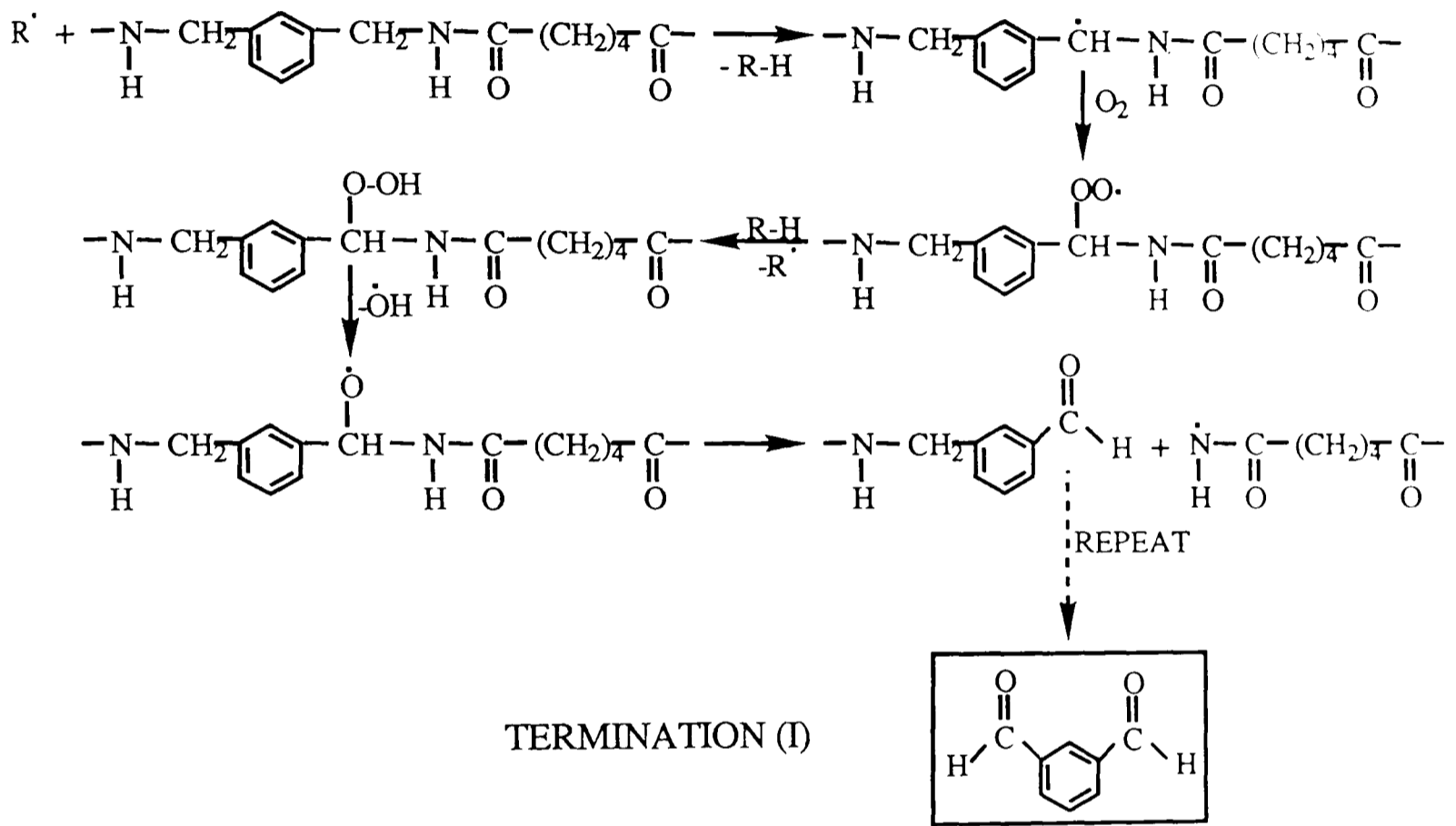
Aromatic degradation products from MXD,6 are without doubt derived from aromatic based radicals. Fission of the CH₂-NH bond will result in radicals most capable of transforming to the appropriate aromatics. In this study, a number of these compounds were identified including isophthalaldehyde, isophthalic and isophthalamic acids. The following mechanisms and discussion will try to establish routes whereby they are formed (Scheme 4.11).

Scheme 4.11 :- Aromatic Degradation Products derived from MXD,6 Oxidation.

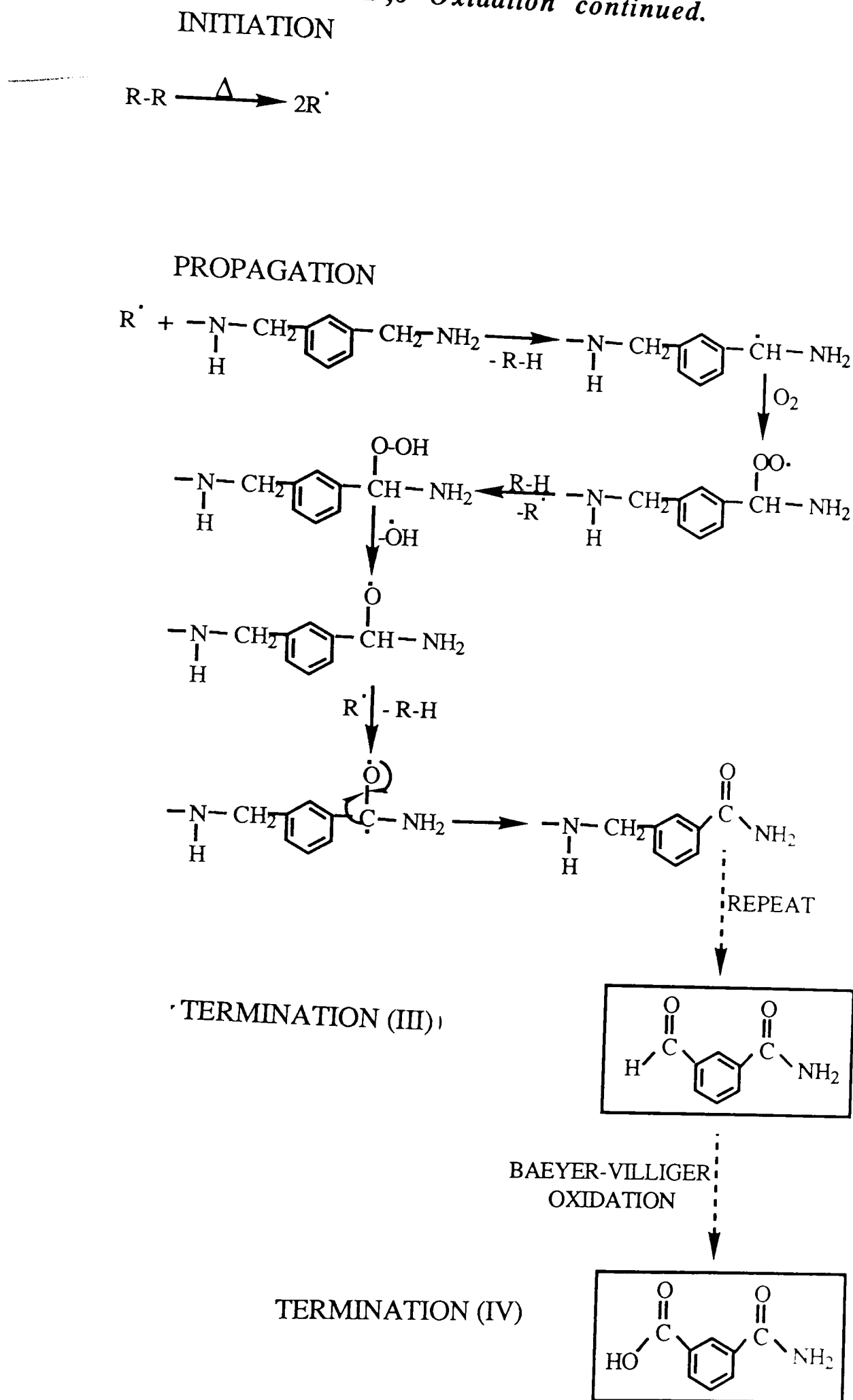
INITIATION



PROPAGATION



Scheme 4.11 :- Aromatic Degradation Products derived from MXD,6 Oxidation continued.



Thus via the mechanisms suggested isophthalaldehyde (Termination I), isophthalic acid (Termination II) and isophthalamic acid (Termination IV) have been accounted for.

CHAPTER FIVE :- CONCLUSION.

5.1 CONCLUSION AND GENERAL SUMMARY.

The main object of this study was to understand the mechanisms of MXD,6 oxidation at 180°C and to explain the influence of cobalt on the oxidation. In order to achieve these goals, a thorough investigation of the by-products derived from the degradation of the polymer was conducted. Table 5.1 summarises the main products of thermal oxidation of MXD,6 and their means of identification.

Mechanisms of oxidation based on established mechanisms of oxidation were derived from these results and led to the conclusion that random scission of the bonds was not the source of initiation. The mechanisms proposed are initiated by the fission of only two bonds, namely the CH₂-NH bond and the CH₂-CO bond. Also to account for the formation of several homologous series of products, a mechanism of sequential loss of a methylene group (in the form of formaldehyde) via β scission has been proposed. Thus employing already established mechanisms familiar in polymer oxidation in conjunction with mechanisms associated with oxidation reactions in organic chemistry, the products of MXD,6 oxidation have been accounted for.

As far as the influence of cobalt is concerned, evidence obtained from T.G.A. degradation studies shows that an increase in cobalt concentration causes a lowering in the activation energy for polymer oxidation, confirming the catalytic nature of the transition metal. Furthermore, a mechanism for its action has been proposed. Even though several alternative mechanisms may also be considered, using the evidence provided from this investigation a mechanism of complex formation between the cobalt and the polymer at specific sites seems to be the most convincing. Since this study has concentrated on the solid state oxidation of MXD,6 fibre, the mobility of the catalyst is highly restricted. It has therefore been proposed that a significant degree of radical formation has already occurred in the melt whilst the polymer was being processed and that the cobalt therefore behaves primarily as an initiation catalyst and to a lesser extent a propagation catalyst.

Table 5.1 :- Summary of Products from the Thermo-oxidative Degradation of MXD,6 fibre at 180°C.

SERIES	PRODUCTS	T.L.C.	H.P.L.C.	G.C.-M.S.
MONOCARBOXYLIC ACIDS.	FORMIC ACETIC PROPIONIC n-BUTYRIC n-PENTANOIC	√ √ √ √ √	√ √ √ √ √	√
DICARBOXYLIC ACIDS.	OXALIC MALONIC SUCCINIC GLUTARIC ADIPIC	√ √ √ √ √	√ √ √ √ √	√ √ √ √ √
AROMATIC ACIDS.	ISOPHTHALIC ISOPHTHALAMIC BENZOIC m-HYDROXYBENZOIC	√ √	√ √ √ √	√ √
ALDEHYDES.	FORMALDEHYDE ACETALDEHYDE PROPIONALDEHYDE BUTYRALDEHYDE	√ √ √ √	√ √ √ √	√
KETONES.	ACETONE BUTANONE		√ √	√
AROMATIC ALDEHYDES/KETONES.	BENZALDEHYDE ISOPHTHALALDEHYDE CYCLOPENTANONE	√	√ √ √	√ √ √
AMINES.	AMMONIA METHYLAMINE ETHYLAMINE PROPYLAMINE n-BUTYLAMINE	√ √ √ √ √	√ √ √ √ √	
DIAMINES.	DIAMINOMETHANE DIAMINOETHANE DIAMINOPROPANE DIAMINOBTANE	√ √ √ √		
AROMATIC AMINES.	m-XYLYLENE DIAMINE	√	√	√
MISCELLANEOUS	PENTANOIC AMIDE HEXANEDINITRILE			√ √

5.2 Recommendation for Future Study.

This study has examined the thermal oxidation of an aromatic polyamide, namely poly(m-xylylene adipamide). An intensive investigation of the oxidation products has been carried out and several homologous series identified. However, a few organic volatiles thought to be emitted during degradation according to the proposed mechanism of MXD,6 oxidation, were not identified. These include, for example, amino acids and alcohols, which are common to most polyamide oxidations. Several methods for the characterization of the former using chromatographic techniques e.g. H.P.L.C. have already been established, however, they require sophisticated mobile and stationary phases which are often not readily available. To investigate these other volatiles using common chromatographic conditions and standard equipment would not only further the understanding of the oxidation of the polymer but also benefit in the science of chromatography.

The study of the influence of cobalt as a catalyst for oxidation has also been investigated and a mechanism for its behaviour proposed. A similar study conducted using other transition metals which may have an adverse effect on the reaction would be interesting and could reveal information that may aid in confirming the catalysis mechanism proposed. Furthermore, a similar study conducted on poly(p-xylylene adipamide) (PXD,6), an isomer of MXD,6, would be most beneficial in furthering the knowledge of this research.

However, it was with the main intent to understand the extraordinary oxygen uptake of a blend of 96% poly(ethylene terephthalate) to 4% MXD,6 with 200ppm cobalt that this project was initially devised. Even though an insight into the oxidation of the oxidisable component (MXD,6) has been achieved, the mechanisms whereby such a small quantity of polymer can have such a proficient effect on the whole of the blend are uncertain and need to be investigated.

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