THE THERMAL DEGRADATION OF NYLON SIX, POLYETHYLENE TEREPHTHALATE AND POLYCARBONATE POLYMERS.

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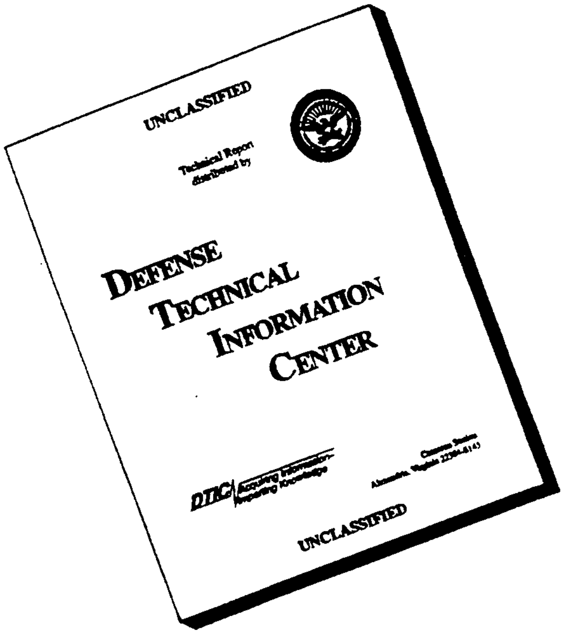

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THE THERMAL DEGRADATION OF NYLON SIX, POLYETHYLENE TEREPHTHALATE AND POLYCARBONATE POLYMERS

by

Nobuya Igarashi

A dissertation submitted to the faculty of The
University of Utah in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

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THE UNIVERSITY OF UTAH GRADUATE SCHOOL

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ABSTRACT

This study was designed to obtain a better understanding of the thermal decomposition processes pertaining to three different step-growth polymers (Nylon 6, polyethylene terephthalate (PET), and polycarbonate). An intensive analytical study of thermal degradation has been carried out on these step-growth polymers. Further studies were conducted on the Nylon 6 polymer containing non-reactive halogen-based fire retardants.

Prior to the degradation studies, each polymer was characterized by elemental analysis and infrared spectroscopy. Thermal analyses of samples were carried out using a Mettler Thermoanalyzer. The effects of heating rate and environment on the degradation processes of step-growth polymers were analyzed using thermal analysis techniques.

The polymeric samples were decomposed in both inert and oxidative environments. Low-boiling volatiles (gases) resulting from pyrolysis and oxidative degradation were identified and quantitated using a computerized gas chromatograph/mass spectrometer (GC/MS) system which provides both GC retention indices and mass spectra for each component. The evolution of carbon monoxide was determined by interfacing a non-dispersive infrared spectrometer to the pyrolysis apparatus.

The high-boiling volatiles (aerosols) which were often recovered in the form of a viscous oil were analyzed using high performance liquid chromatography (HPLC), elemental analysis and infrared spectroscopy. Solid residues which appeared as char, particulates and polymer

fragments were also characterized using elemental analysis and HPLC techniques.

Using the combined quantitative data from the analysis of low-boiling volatiles, high-boiling volatiles and solid residues, a material balance was obtained for the three different step-growth polymers during pyrolysis and oxidative degradation.

The study of the degradation products and the thermal behavior of Nylon 6, PET and polycarbonate polymers led to the development of proposed thermal degradation mechanisms. These mechanisms were found to be different for each basic polymer structure.

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TABLE OF CONTENTS

Page

CHAPTER

TABLE OF CONTENTS (Continued)

CHAPTER Page

TABLE OF CONTENTS (continued)

CHAPTER Page

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

LIST OF TABLES (continued)

NO. PAGE

LIST OF TABLES (continued)

LIST OF TABLES (continued)

CHAPTER I

INTRODUCTION

During the past few decades, polymeric materials have replaced many natural materials and become quite common in diversified market areas which include cellular plastics, reinforced composites, coatings, elastomers, fibers and textiles. An important class of polymers, known as step-growth or condensation polymers, have become commodity materials which are used in multibillion pound quantities on an annual basis. Among this important class of polymers, both Nylon and polyethylene terephthalate (PET) are used as fibers for wearing apparel and furnishings, while a newer polymer, polycarbonate, is finding increased utilization as an engineering plastic.

As the use of synthetic polymers has increased in commerce, there has been an increasingly greater number of reports pertaining to their involvement in unwanted fires. The performance of synthetic polymers during fire exposure may vary considerably from that of many natural materials which they have replaced. The linear step-growth polymers may often depolymerize rapidly when placed in contact with an ignition source. During such exposure these polymeric materials may propagate a flame more rapidly than natural materials. Some classes of polymers may release greater amounts of heat during thermal decomposition than more conventional natural materials. The decomposition process is often accompanied by the release of dense smoke and a wide variety of combustion products not frequently observed during the thermal degradation of natural materials.

An increasing public awareness concerning injury and losses due to fire has required raw material suppliers, plastics manufacturers,and fabricators to impart a higher degree of fire retardancy in their products than was previously necessary. The use of fire retardant additives has not always imparted the desired degree of improvement and to-date the success achieved via this route has been limited at best. Often the degree of improvement in the flammability characteristics of these polymeric materials has been marginally sufficient to meet current regulatory requirements. These fire standards, according to the author's opinion, are not sufficient to warrant this approach, inasmuch as many flame retarded polymeric materials still ignite and propagate rapidly. Many flame retardant polymeric materials produce a greater quantity of smoke and a higher concentration of potentially toxic decomposition products than do the non-retarded polymers. Recent studies have indicated the possible formation of highly toxic species during the combustion of fire retarded polymers.(1,2) Other studies have questioned the safety of utilizing many organophosphorous-based fire retardants without a proper pre-market toxicological screening to assure their safe use.(3)

Recent Federal Standards provided mandatory guidelines for the use of fabrics in children's sleepware,(4) carpeting,(5) automotive upholstery,(6) and mattresses.(7) Millions of square feet of fabric have been produced during the past several years which have met or exceeded these standards through the incorporation of a wide variety of fire retardants. It should be noted that, prior to the recent enactment of the Federal Toxic Substances Act, there were little, if any, regulations pertaining to toxicological evaluation of either the intermediate fire retardants or the fire-retarded products. In fact, there is no widely acceptable protocol available at this time which is used to evaluate the potential toxicity of fire retardants or fire-retarded products.

Blum and Ames(8) indicated that the use of the flame-retardant chemical tris(2,3-dibromopropxyl)phosphate used with blends of natural and step-growth polymeric fabrics created a potential carcinogenic threat to humans. As yet, incomplete studies conducted by the National Cancer Institute(9) have indicated that this fire retardant and a major contaminant (1,2-dibromo-3-chloropropane) were potent carcinogens. In view of these results, the Consumer Product Safety Commission has banned further use of this fire-retardant fabric system.

Insufficient data is available pertaining to the mechanism of thermal degradation and combustion of natural and synthetic materials. Even less information is available relating to the parameters affecting the thermal degradation mechanism, such as rate of heating, heat flux impingement and the effect of environment.

The purpose of this research program was to develop information pertaining to the thermal decomposition of selected step-growth polymers. The commercial importance of this class of polymers is obvious from the fact that 90% of the synthetic fabrics used world-wide are produced using Nylon 6, Nylon 66, PET, or acrylonitrile polymers. Three widely different step-growth polymers--Nylon 6, PET, and polycarbonate polymers--were selected for this study. A major objective of this investigation was to determine whether or not these different classes of step-growth polymers decompose via identical, similar, or different mechanisms.

In order to obtain detailed information on the thermal decomposition of these polymers, this study has been designed to utilize modern analytical techniques(10) to elucidate changes in the basic polymer structure and to analyze the decomposition products resulting from pyrolysis and oxidative degradation of these step-growth polymers. Specific emphasis has been directed toward the analysis of the low-boiling volatiles (gases), high-boiling volatiles (aerosols), and solid residues (particulates and chars) resulting from the decomposition process in order to obtain a material balance between the polymer and the composition of the combined decomposition products. A Mettler Thermoanalyzer Model I which was interfaced with a computerized gas chromatograph/mass spectrometer (GC/MS) system, has been widely used in this research to provide a controlled reproducible environment and rate of heating.

In order to present the results of this research in a logical fashion, this dissertation has been organized in the following manner:

(1) a review of the polymer chemistry of step-growth polymers, including Nylon 6, PET, and polycarbonate polymers;

(2) a general review pertaining to the thermal degradation of polymers;

(3) the results of an extensive literature survey;

(4) a description of the equipment and analytical methodology employed in this study;

(5) presentation of experimental results obtained during the study of the selected step-growth polymers;

(6) summary and conclusions resulting from this research program; and

(7) recommendations for further study.

The results of this research should offer new insights into the mechanism of polymer thermal degradation, as well as providing information useful in the design of more thermally-stable polymeric products.

CHAPTER II

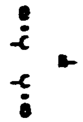
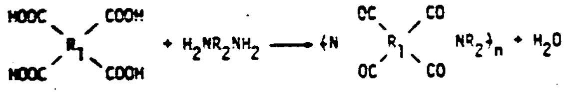
STEP-GROWTH POLYMERS (CONDENSATION POLYMERS)

A. Introduction

Nylon, polyethyleneterephthalate (PET), and polycarbonate polymers belong to the class of step-growth or condensation polymers. Carothers(11) defined "condensation" polymers as those in which the molecular formula of the repat unit of the polymer lacks certain atoms present in the monomers from which it is formed. This is a definition based on stoichiometry, for example, a linear polyester is formed by typical condensation reactions between dicarboxylic acids and diols with the elimination of water. The terms "step-growth" or "step-reactions" have recently replaced the older term "condensation." These names are based on a reaction mechanism, inasmuch as step-growth polymers can be defined as those which grow by a stepwise reaction mechanism without regard to loss of a small molecule (e.g., polyurethanes are formed by step-reaction polymerization) or type of interunit linkage (e.g., phenol-formaldehyde resins result from stepwise polymerization, even though they lack interunit functional groups).

Polyamides, polyesters, and polycarbonates are typical examples of the step-growth polymers, characterized by the linkages of $-\underset{\overset{\|}{O}}{C}NH-$, $-\underset{\overset{\|}{O}}{C}-O-$, and $-O-\underset{\overset{\|}{O}}{C}-O-$. Polyamide, polysiloxane, and polyurethane are other examples of step-growth polymers. Table 1 lists some representative structures of step-polymerization.

Table 1. Typical Step Growth Polymers

TYPE	INTERUNIT LINKAGE	EXAMPLES
POLYESTER	$-\overset{O}{C}-O-$	$HORCOOH \longrightarrow HO\{R-\overset{O}{C}-O\}_nH + H_2O$
		$HOR_1OH + HOOCR_2COOH \longrightarrow HO\{R_1O\overset{O}{C}R_2\overset{O}{C}O\}_nH + H_2O$
		$\begin{array}{l}CH_2OH\\ CHOH\\ CH_2OH\end{array} + HOOCRCOOH \longrightarrow$ Three dimensional network + H_2O
Polyanhydride	$-\overset{O}{C}-O-\overset{O}{C}-$	$HOOCRCOOH \longrightarrow HO\{OCRCOO\}_nH + H_2O$
Polyacetal	$-O-\overset{R}{C}H-O-$	$HOR_1OH + CH_2(OR_2)_2 \longrightarrow HO\{R_1OCH_2O\}_nR_1OH + R_2OH$
Polyamide	$-\overset{O}{C}-NH-$	$H_2NRCOOH \longrightarrow H\{HNRCO\}_nOH + H_2O$
		$H_2NR_1NH_2 + HOOCR_2COOH \longrightarrow H\{HNR_1NH\overset{O}{C}R_2\overset{O}{C}\}_nOH + H_2O$
Polyurethane	$-O-\overset{O}{C}-NH-$	$HOR_1OH + OCNR_2NCO \longrightarrow \{OR_1O\overset{O}{C}NHR_2NH\overset{O}{C}\}_n$
Polyimide		
Phenol-aldehyde	$-CH_2-$ $-CH_2OCH_2-$	 + $CH_2O \longrightarrow$ Three dimensional network with $-CH_2-$ and $-CH_2OCH_2-$ bridges
Polycarbonate	$-O\overset{O}{C}O-$	$HOROH + COCl_2 \longrightarrow \{R-O\overset{O}{C}O\}_n + HCl$
		$HOROH + CO(OR_2)_2 \longrightarrow \{R_1-O\overset{O}{C}O\}_n + R_2OH$
Polysiloxane	$-\overset{R}{\underset{R}{Si}}-O$	$HO-\overset{R}{\underset{R}{Si}}-OH \longrightarrow \{\overset{R}{\underset{R}{Si}}-O\}_n + H_2O$
		$HO-\overset{R}{\underset{R}{Si}}-OH + Si(OH)_4 \longrightarrow$ Three dimensional network + H_2O

B. Polymerization

The step-growth polymerization is distinguished from chain polymerization by its mechanism of formation. Chain polymerization commonly produces chain-reaction or addition-polymers. Some of the consequences of the difference in the mechanisms of step- and chain-polymerization are shown in Table 2.

Step-growth polymerization is also characterized by polyfunctional monomers. If each monomer possesses only two functional groups, linear polymers are produced. In the example of the polycondensation reaction involving a diol and a dibasic acid, the first stage in the reaction is the formation of a bifunctional dimer.

$$\underset{\text{Diol}}{HO\text{-}R_1\text{-}OH} + \underset{\text{Dibasic Acid}}{HOOC\text{-}R_2\text{-}COOH} \rightarrow \underset{\text{Dimer}}{HO\text{-}R_1\text{-}OOCR_2\text{-}COOH} + H_2O \qquad (1)$$

As the polymerization reaction proceeds with the elimination of water, a linear high molecular weight polymer forms as a result of esterification. On the other hand, a three-dimensional network structure is usually formed if the functionality of one or more of the reactants exceeds two. The formation of polyurethane and phenol-formaldehyde polymers are typical examples of polymers having a network structure resulting from the reaction of polyfunctional monomers.

C. General Properties of Step-Growth Polymers

Various kinds of monomers can be used for step polymerization (e.g., acids, acid-chlorides, amines, alcohols, phenols and isocyanates,

Table 2. Distinguishing Features of Step-Growth- and Chain-Polymerization Mechanisms

Step-growth Polymerization	Chain Polymerization
Any two molecular species present can react.	Only growth reaction adds repeating units one at a time to the chain.
Monomer disappears early in reaction: at DP 10, less than 1% monomer remains.	Monomer concentration decreases steadily throughout reaction.
Polymer molecular weight rises steadily throughout reaction.	High polymer is formed rapidly.
Long reaction times are essential to obtain high molecular weights.	Long reaction times give high yields but affect molecular weight little.
At any stage all molecular species are present in a calculable distribution.	Reaction mixture contains only monomer, high polymer and about 10^{-8} part of growing chains.

etc.) and numerous combinations of these monomers are possible. In other words, one can design polymers with desirable properties by selecting combinations of monomers based on structural configuration. The possibility of changing properties of step-growth polymers is much greater than that of addition polymers, which usually possess only carbon chain backbones. For example, so-called high-temperature polymers, such as aromatic polyamides, polyimides, and polybenzimidazoles, are produced by using the techniques of step-growth polymerization because the incorporation of heteroatoms or aromatic rings into the main chains of polymer can be easily carried out. By changing monomeric species, one can also design relatively unstable polymers (designed for certain uses) in which main chains easily degrade chemically or physically. The incorporation of specific monomers permits the design of polymer possessing a wide range of thermal, chemical or physical stability. This broad range of general properties makes it difficult to expect common behavior and mechanisms during the thermal degradation of the step-reaction polymers.

D. Utilization of Step-Growth Polymers

Table 3 contains a summary of the annual volume of major step-growth polymers in recent years. The use of addition polymers is also listed for comparison.

Table 3. Use of Major Plastics and Fibers in the United States

	Material	1975	1976
		1000 metric tons	
Addition Polymers	Alkyd	280	330
	Cellulosics	56	70
	Epoxy	85	110
	Nylon -- fiber	844	1032
	plastic	65	95
	Phenolic	465	600
	Polyester -- fiber	1361	1501
	plastic	11	14
	Polyurethane	614	738
	Polycarbonate	40	51
	Unsaturated polyester	350	430
	Urea and melamine	369	454
Step-growth Polymers	Acrylic -- fiber	239	285
	plastic	193	222
	Polyethylene -- high density	1048	1417
	low density	2148	2625
	Polypropylene	861	1178
	Polystyrene and copolymers	1875	2285
	Polyvinyl chloride & copolymers	1700	2103
	Other vinyls	320	390

CHAPTER III

THERMAL DEGRADATION

A. Introduction

The thermal degradation of polymeric materials is a very complex process; little fundamental information is available pertaining to the mechanisms of decomposition occurring at high temperatures. Degradation has been shown to occur via several concomitant reactions. Even a simple decomposition process that results in the evolution of low-molecular weight compounds into the gas phase will generally involve several independent reactions.

In the case of the thermal degradation of polymers, a variety of factors may lead to a perturbation of the decomposition process. Within a given generic class of polymers, degradation mechanisms may vary, depending upon the molecular weight, the molecular weight distribution, terminal groups, the degree of unsaturation, steric factors, crystallinity, etc. Environmental factors, such as oxygen concentration, temperature, heating rate, as well as size, orientation and configuration of the material undergoing decomposition can modify the decomposition process.

Numerous references may be found in the literature describing thermal decomposition reactions.(12-15) Einhorn(2,16,17) and Madorsky(18) have presented major reviews of polymer thermal decomposition mechanisms. Some of the principal processes involved in polymer thermal degradation will be covered within this chapter.

B. Modes of Thermal Degradation

Thermal degradation can occur under three different modes: pyrolysis, oxidative thermal degradation,and flaming combustion. Pyrolysis is defined as thermal degradation which proceeds in the absence of oxygen. Experimentally, pyrolysis may be carried out in an inert gas such as helium, nitrogen or argon, or under vacuum. Pyrolysis can occur in polymeric materials under conditions encountered in normal use. An example of such a process may be observed when interior surfaces of wire insulation decompose thermally in the absence of oxygen as might be encountered during a period of electrical overload. The mechanisms which govern pyrolysis are generally less complex than those encountered during thermal decomposition or flaming combustion.

Polymers usually decompose in the presence of air and/or oxidizing agents through oxidative thermal degradation at elevated temperatures. Thermal oxidative degradation is generally very complex, since it involves both thermal decomposition reactions and oxidation reactions. Thermal oxidative degradation may involve uncontrollable flaming combustion which complicates study of the polymer degradation mechanism.

C. Major Mechanisms of Thermal Degradation

The thermal decomposition reactions on polymeric materials can be classified into the following four categories: depolymerization, random chain scission, side chain reaction,and crosslinking. These reactions may occur individually or simultaneously, depending on the type of polymer, the temperature and the initiating processes.

1. Depolymerization

Depolymerization is a process in which monomer units are released from the polymer chain ends. Such a process can be viewed as a retrograde propagation step in an addition polymerization. Hence, it is frequently called an unzipping reaction. It should be realized the depolymerization does not necessarily require initiation at the chain ends of polymer molecules. Any weak linkage in a polymer's structure may serve as the focal point for initiation of degradation processes. The products, thus formed, are composed mainly of the monomer from which the polymer was produced. Depolymerization reactions are encountered most prevalently with vinyl polymers and polymers produced from cyclic monomers. Typical examples of the polymers which decompose thermally via a depolymerization process may be found in Table 4.(19) The conversion to monomer is nearly quantitative for polymethyl methacrylate and poly-α-methyl styrene. This indicates the degradation reaction for these polymers is depolymerization. The concentration of monomeric compound in degradation products can be used as a good indicator for distinguishing the degradation mechanisms.

2. Random Chain Scission

Random chain scission can be visualized as a reaction sequence approximating the reverse of polycondensation. Chain scission occurs at random points along the chain, leaving fragments of relatively high

Table 4. Thermal Decomposition Characteristics of Polymers Which Form Large Quantities of Monomer

Polymer	Approximate Temperature of Pyrolysis (°C)	Conversion to Monomer (%)
Polymethacrylonitrile	250	85
Polymethyl methacrylate	350	100
Polystyrene	350	65
Poly-α-methyl styrene	350	100
Polyisoprene	370	46
Poly-α-methyl styrene	390	44
Polyisobutylene	400	46
Polytetrafluoroethylene	600	86

molecular weight. This type of reaction is featured by the rapid decrease in the molecular weight, followed by the formation of a wide variety of compounds. The major primary products produced by random scissions are oligomers of varying molecular weights which further decompose via secondary reactions at higher temperatures to form volatile low-molecular weight compounds. The formation of monomers is usually low in random chain scission decomposition. Polyethylene, polypropylene and most step-growth polymers degrade thermally via random chain scission processes. Table 5 contains examples of polymers which degrade to yield little or no monomer via random chain scission reactions.(19)

3. Side Chain Reaction

In some types of polymers, such as polyvinyl chloride, polyvinyl acetate and polyvinyl alcohol, which have electronegative groups X (where X = Al, OAc and OH, respectively), the elimination of HX from side chains is more favored than the scission of main chains. Generally, hydrogens adjacent to X groups are eliminated almost quantitatively in this process, introducing conjugated double bonds systems (polyene structure) in the residual main chains. This polyene structure proceeds via crosslinking reactions and is converted to a char structure at high temperature.

Recent studies(20,21) have indicated that the polyene may rupture to form aromatic hydrocarbons, such as benzene or toluene. A branch structure in a polymer chain may be a weak site which is susceptible to thermal decomposition. Low density polyethylene is an example of such

Table 5. Thermal Decomposition Characteristics of Polymers Which Form Little or No Monomer

Polymer	Temperature of Complete Pyrolysis (°C)	Decomposition Products		Residue
		Low Boiling	High Boiling	
Polyvinyl Acetate	280 (Vac.)	Acetic Acid Hydrocarbons		Carbon
Polyacrylonitrile	350 (N_2)	NH_3, HCN	N-containing fractions	66%
Polypropylene	410 (Vac.)	Hydrocarbons	Paraffin Fraction 97% MW (200)	
Polyvinyl chloride	440 (N_2)	57.9% HCL, Unsat. Hydrocarbons	Unsat. Hydrocarbons	23% with 1.2% Cl_2
Polyvinylidene chloride	440 (N_2)	67.5% HCL		28% with 12.1% Cl_2
Polybutadiene	420 (Vac.)	Hydrocarbons	93% Fractions MW 666-784	Little
Polyethylene	475 (Vac.)	Hydrocarbons $C_3 - C_{15}$	Paraffin Fractions-96% MW 690	

a polymer.

4. Crosslinking

Some types of polymers undergo crosslinking reactions during the exposure to heat, which results in insoluble and infusible network structures. The formation of crosslinked structures during thermal degradation reactions can be attributed to many factors, such as the recombination of polymer radicals or the extensive reactions of multifunctional groups which were present in the original monomer and could not react due to steric factors.

In general, aliphatic gels which form during the initial stages of thermal degradation are weak and decompose completely to low-molecular compounds at elevated temperatures. Aliphatic polymers which have crosslinked structures originally, such as those found in rubbers and unsaturated polyester polymers, also tend to decompose completely at high temperatures. On the other hand, the so-called high-temperature polymers which often contain aromatic groups and/or heterocyclic rings in the chain structure, often form stable char structures. In the thermal degradation of these latter polymers, the crosslinking reactions are dominant over the chain scission reactions because of resonance stability and intermolecular bonding, such as $\pi\pi$ bonding.

D. Factors Affecting Thermal Degradation of Polymeric Materials

The factors which can affect thermal degradation are classified as either intrinsic or extrinsic. Intrinsic factors are those which are dictated by the inherent properties of polymers. These include cohesive energy densities, bond dissociation energies, hydrogen bonding, steric hindrance, specific heat, thermal conductivity, molecular weight, molecular weight distribution, and polymer morphology. Additives, such as pigments, reinforcing agents, plasticizers, colorants, anti-static agents and fire-retardants, may also affect the intrinsic properties of polymers. Extrinsic factors are those which are controlled by conditions of thermal degradation reactions. They are, for example, temperature, rate of heating, heating source, size and shape of samples, and oxygen concentration. The most significant factors will be discussed in depth in the following subsections.

1. Intrinsic Factors

Dissociation or bond energies. Dissociation or bond energy is defined as the energy required to rupture bonds. It is an important factor, since most thermal degradation processes are initiated by a thermally induced homolytic bond cleavage to form free radical species. Initiation will occur at the weakest point in a polymer structure. The bond energies of linkages commonly encountered in polymeric materials are presented in Table 6.(22) A review of the data shown in Table 6 clearly indicates that it is desirable, from the aspect of thermal stability, to incorporate functional groups which have high bond dissociation energies. Bond energies vary, depending on the nature of the chemical bond and nearby elements. For example, in the case of C-C bond, the bond energy for a tertiary alkyl branch is approximately 20 kcal/mole weaker than a normal C-C bond, since a tertiary alkyl radical resulting from a bond rupture is stabilized by hyperconjugation effects.

Table 6. Dissociation Energies of Chemical Bonds

Bonds	Dissociation Energy (kcal/mole)
C-N	49 - 60
C-C	59 - 70
C-O	70 - 75
N-h	84 - 97
C-H	87 - 94
O-H	101 - 110
C=C	100 - 125
C=O	142 - 166
C-Br	54
C-Cl	67

The bond energies of vinyl and phenyl groups, on the other hand, are approximately 10 kcal/mole higher than a normal C-C bond.

Cohesive energy. The cohesive energy pertains to secondary bond forces which lead to the aggregation of molecules in solid and liquid phases. It is the total energy necessary to remove a molecule from the liquid or solid material. Low cohesive energies permit the molecule to volatilize easily and thus fosters thermal decomposition. Cohesive energy is increased by the introduction of polar groups into the polymer structure. If the cohesive energy exceeds the primary bond energies, the polymer molecules will decompose before they volatilize. This decomposition may lead to char formation because the crosslinking would proceed faster than the evaporation of decomposition products. Cohesive energy values for chemical groups found in many polymers are given in Table 7.(22) A review of Table 7 indicates that the incorporation of ester, aromatic, amide, urethane and urea groups into the polymer will raise the cohesive energy and would be expected to improve the thermal stability of the material and increase char formation when thermally degraded.

Hydrogen bonding. Hydrogen bonding is defined as the secondary bonding between hydrogen and strongly electronegative atoms, such as oxygen. It has a tendency to raise the cohesive energy and the melting point of the polymer. For example, in Nylon and urethane polymers, an increase in hydrogen bonding leads to higher melting points which tend to favor thermal stability.

Steric hindrance in polymer structures. Some types of polymers are assumed to have unstable structures due to the steric hindrance by

Table 7. Molar Cohesive Energy Of Organic Groups

Group	Cohesive Energy, kcal./mole
--CH_2-- (Hydrocarbon)	0.68
--O-- (Ether)	1.00
--COO-- (Ester)	2.90
--C_6H_4-- (Aromatic)	3.90
--CONH-- (Amide)	8.50
--OCONH-- (Urethane)	8.74
--NHCONH-- (Urea)	10.64

substituents. This effect is typically recognized in α,α-disubstituted vinyl polymers. The bulkiness of two substituents attached on the same α carbon hinders the free rotation of C-C bond in a main chain, and the bond energy of the C-C bond for this type of polymer is weakened by the order of 5-8 kcal/mole, as compared to a C-C bond without bulky substituents.

Thus, a depolymerization reaction is quite dominant in the thermal degradation of α,α-disubstituted vinyl polymers, such as polymethyl methacrylate, methacrylonitrile, polyisobutylene, and poly-α-methyl styrene. As shown in Table 4, the principal products produced during the pyrolysis of these polymers are the monomers from which they were formed.(19)

The effect of the steric hindrance in the polymer structure was quantitatively explained by using the heat of polymerization.(23) Table 8 summarizes heats of polymerization ($-\Delta H_p$) for selected monomers.(24) A review of Table 8 indicates that heats of polymerization for α,α-disubstituted vinyl monomers is considerably lower than other non-substituted and monosubstituted vinyl monomers. The activation energy of depolymerization (ΔE_d) can be expressed as the sum of the activation energy of the chain growth reaction (ΔE_p) and the heat of polymerization ($-\Delta H_p$).

$$\Delta E_d = \Delta E_p - \Delta H_p \qquad (2)$$

Since ΔE_p for radical polymerization reactions ranges between 4 to 7 kcal/mole and is rather independent of monomeric species, the activation energy (ΔE_d) of α,α-disubstituted polymers and aldehyde polymers

Table 8. Heats of Polymerization $(-\Delta H_p)$ Of Selected Monomers

Type of Monomer	Monomers	Heats of Polymerization $(-\Delta H_p)$ kcal./mole
Monosubstituted Vinyl Monomer	Ethylene	21.2
	Vinyl Acetate	21.2
	Propylene	19.5
	Methylacrylate	18.5
	Acrylonitrile	18.4
	Styrene	16.7
Disubstituted Vinyl Monomer	Methylmetacrylate	13.3
	Methacrylonitrile	13.2
	Isobutylene	12.9
	α-Methyl Styrene	8.4
Diene Monomer	Isoprene	17.9
	Butadiene	17.6
Halogenated Vinyl Monomer	Tetrafluoreothylene	37.
	Vinyl Chloride	27.
	Vinylidene Chloride	18.
Aldehyde Monomer	Formaldehyde	7.4
	Isobutyl Aldehyde	3.8
	Chloral	4.7

can be estimated to be significantly low. In fact, a polymer which has a lower heat of polymerization than 13.3 kcal/mole tends to undergo rapid depolymerization to form 80-100 percent of monomeric units. The low $-\Delta H_p$ values for aldehyde-based polymers can be explained by the intrinsic instability of the ether linkage.

Polymer morphology. When thermoplastic polymers are heated, they generally soften or melt before degradation. Thus, one may expect that a crystalline polymer would require a larger amount of energy input to degrade thermally than amorphous polymers. This energy is consumed to overcome both strong intermolecular (Van der Waals) and intramolecular forces that lead to properties such as chain stiffening. An increase in polymer crystallinity also generally implies an increase in oxidative stability of solid polymers. This may be explained by the ease of penetration of oxygen into the polymer structure.

Some other intrinsic factors which may affect thermal degradation and combustion of polymeric materials are summarized in the following tables. Table 9 includes specific heat,(25) thermal conductivity,(19) and melting points of selected polymers. Table 10 summarizes the temperature of auto-ignition with pilot flame and the temperature of self-ignition for some polymers which were measured using a NBS electric furnace.(26) Both temperatures for polyethylene and rigid polyurethane foam are rather low, while the temperatures for melamine and fiber-reinforced polyester are high. The heat of combustion of polymeric materials varies, depending upon the polymeric structures. As is shown in Table 11,(27) the polymers formed

Table 9. Specific Heat, Thermal Conductivity, And Melting Point of Polymers

	Specific Heat (cal/g°C)	Thermal Conductivity 10^{-4}cal/sec.cm^2	Melting Point
Polyethylene	0.55	8.0-10.0	220
Polypropylene	0.46	2.8	214
Polytetrafluoreothylene	0.25	6.0	
Polyacetal	0.35	1.6-5.5	205-226
Nylon 6	0.38	5.9	228
Polycarbonate	0.30	4.6	220-230
Polyvinylidene chloride	0.32	3.0	212
Polyvinyl chloride	0.20-0.28	3.0-7.0	219$^{s.p.}$
Polystyrene	0.32	1.9-3.3	
Acrylonitrile-Butadiene-Styrene Terpolymer	0.30-0.40	4.5-8.0	313
Polymethylmethacrylate	0.35	4.0-6.0	
Cellulose acetate	0.30-0.50	4.0-8.0	
Phenol-formaldehyde resin	0.38-0.42	8.4	--
Epoxy resin	0.25	4-5	298$^{s.p.}$

Table 10. Flashing and Ignition Temperatures of Polymers

Material	Flashing Temperature (°C)	Ignition Temperature (°C)
Polystyrene	360	495
Polyethylene	340	350
Polymethylmethacrylate	338	486
Styrene acrylonitrile copolymer	366	455
Polyvinyl chloride	390	455
Polyurethane (rigid foam)	310	415
Phenolic Resin	---	429
Melamine	475	623
Paper (Newspaper)	230	230
Cotton	255	255
Pine Wood	260	260

Table 11. Heats of Combustion for Selected Polymers

Material	Heat of Combustion (cal/g)
Polyethylene (High Density)	11,140
Polyethylene (Low Density)	10,965
Polypropylene	10,506
Polystyrene	9,604
ABS	8,424
Polyamide	7,371
Polycarbonate	7,294
Polymethylmethacrylate	6,265
Polybutyrate	5,659
Polyester (unsaturated)	4,494
Polyvinyl chloride	4,315
Polyacetal (polyethylene oxide)	4,046
Polyisobutylene	3,833
Phenolic	3,219
Polytetrafluoroethylene	1,004

with hydrocarbons, such as polyethylene and polypropylene, have high values for heats of combustion.

2. Extrinsic Factors

Temperature. Organic polymers usually start to thermally degrade in the temperature range of 200-500°C, producing low molecular weight gases, aerosols,and solid residues. Secondary reactions occur at the elevated temperature ranging from 500 to 1000°C, which further decomposes the initial products into other compounds. If we use Equation (3) to define the rate constant of dissociation, k:

$$k = A \exp(-\Delta E/RT) \ , \qquad (3)$$

where A is a constant at the order of 10^{13} sec^{-1}, and ΔE is the activation energy (assumed to be close to the dissociation energy), an increase of ΔE by 5 kcal at approximately 300°C may decrease the rate of dissociation (k) by a factor of 10^{-2}.

Rate of heating. The rate of heating may alter the mechanisms of thermal degradation of polymers. At fast heating rates, high temperatures can be attained before low-temperature pyrolysis reactions proceed significantly. In this situation, high-temperature decomposition mechanisms can become dominant. At very high temperatures the chemical bonds, which were used to form polymers, can be broken down simultaneously, changing the nature and concentration of decomposition products.

Thermal analytical techniques, such as thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are generally employed to study the thermal degradation process of polymers.

Questions have been raised as to the validity of the use of thermogravimetric data to describe thermal degradation at high heating rates. In most TGA experiments the rates of temperature increase are on the order of 1°C to 30°C per minute, while in actual end-use applications rates of temperature rise may be several orders of magnitude higher. Although Melnick(28) has concluded that TGA data and kinetic parameters derived therefrom have no direct connection to the response of a material at high heating rates, Seader(29) and Einhorn *et al.*(30) believe that thermogravimetric analysis does provide a means for predicting thermal decomposition reactions in various environments which simulate actual degradation conditions that are encountered in use.

Oxygen concentration. In an oxidative environment, polymeric materials often degrade via a free radical initiation mechanism. The oxidative reaction is mostly the chemistry of the peroxy radical, RO_2, which is initiated generally from hydroperoxide molecules (R-O-O-H). During the course of the auto-oxidation reaction, polymer chains are broken and radical species are produced.

Thermal oxidative degradation in polymers may occur competitively with pyrolysis reactions. The nature of such reactions is dependent upon the oxygen concentration and the nature of polymeric structure. Oxygen concentration is, therefore, a controlling factor in the combustion of natural and synthetic polymeric materials. Also, there is a minimum level of oxygen necessary to sustain ignition and combustion. It should be noted that oxygen may permeate well below the surface of a polymer. Thus, a true pyrolysis reaction may not often be found under actual use conditions.

Fenimore and Martin(31) and Martin(32) designed a test procedure to measure the limiting oxygen concentration or minimum level of oxygen required to sustain ignition and combustion. This procedure (ASTM-28 63-70) is used as a method for measuring the concentration of oxygen required to maintain flaming decomposition of polymeric materials. Table 12 presents the limiting oxygen concentration, sometimes called limiting oxygen index, or LOI, for selected polymeric materials.(16)

Additives. Polymeric materials are modified by the incorporation of inorganic and organic additives. Such additives may tend to enhance thermal stability and combustion characteristics. However, improvement in polymer properties does not always result as a consequence of such modifications. For example, the incorporation of inert fillers, such as calcium carbonate and aluminum silicate, may dilute the quantity of polymeric material available to decompose under a given set of conditions, thus improving the apparent resistance to thermal degradation. On the other hand, the incorporation of glass fibers to a thermoplastic material, such as Nylon 6, may stabilize a flaming droplet and thus cause more rapid polymer decomposition via flaming combustion.

Organic additives, such as plasticizers and colorants, may act to soften polymers and facilitate the movement of polymer chains. This effect usually lowers the degradation temperature of polymers by reducing the intermolecular energies found in polymeric materials.

Fire retardants are also important additives, both organic and inorganic materials are used. Fire retardants, generally, decompose at

Table 12. Limiting Oxygen Index for Selected Materials

Polymer	$n\ O_2\ /\ (n\ O_2 + nN_2)^*$
Polyoxymethylene copolymer	0.148 - 0.149
Polyoxymethylene homopolymer	0.150
Polyethylene oxide	0.150
Polymethyl methacrylate	0.173
Polyethylene	0.174 - 0.175
Polypropylene	0.174
Polystyrene	0.181
Epoxide (conventional resin)	0.198
Epoxide (cycloaliphatic)	0.198
Chlorinated polyethylene	0.211
Polyvinyl alcohol	0.225
Polyvinyl fluoride	0.226
Chlorinated polyether	0.232
Polycarbonate	0.260 - 0.280
Polyphenylene oxide	0.280 - 0.290
Polyamide	0.290
Polyvinylidene fluoride	0.437
polyvinyl chloride	0.490
Polyvinylidene chloride	0.600
Polytetrafluoroethylene	0.950

*$n\ O_2$ = number of moles of oxygen present in mixture, and

$n\ N_2$ = number of moles of nitrogen present.

lower temperatures than non-fire-retarded polymers, which act to provide reactive species, such as free halogens and phosphoric acid. For further information consult books and reviews by Einhorn,(3,16,17) Kasen,(33) Lyons,(34) Cullis,(35) Kuryla and Papa,(36) Hilado,(37) and Konishi.(38)

CHAPTER IV

ANALYTICAL METHODOLOGY

A. Apparatus

The various instrumental systems used in this study are described in this chapter. They included a computerized interfaced gas chromatograph quadrupole mass spectrometer system, a thermoanalyzer, a grating infrared spectrophotometer, and a non-dispersive infrared spectrometer. A high-pressure liquid chromatograph and an elemental analyzer were also employed (carbon, hydrogen, nitrogen and oxygen).

1. Gas Chromatograph/Mass Spectrometer System

A major portion of the work described in this thesis was performed on a Model 5930A Hewlett-Packard dodecapole mass spectrometer system, which will be described only briefly; the reader is referred to a recently-published description of the apparatus for more details.(39)

The Hewlett-Packard mass spectrometer employs an electron impact ion source connected to a dodecapole mass filter with a mass range of 1 to 650 amu. Sensitivity for most organic compounds is in the nanogram to picogram level over the entire mass range. The dodecapole design incorporates all of the advantages of the well-known quadrupole mass filters, such as a linear mass output, fast scanning without hysteresis and efficient interfacing to a gas chromatograph (GC) and computer. Because this instrument does not need ion slits or aperatures, it may be tuned for high ion transmission efficiency, providing a high level of sensitivity. The Hewlett-Packard gas chromatograph/mass spectrometer (GC/MS) system also has a totally compatible data acquisition and retrieval system to facilitate routine analysis. A Hewlett-Packard Model 2100S Microprogrammable Systems Computer, equipped with 32K core of memory and a movable head disc, minimizes operator intercention for analysis and controls all mass spectrometer functions during data acquisition. Input/output devices for the computer are a high-speed paper tape reader and a Textronix Model 4012 Display Terminal (CRT). Several peripheral devices are available for data display: a digital x-y plotter, a line printer, or a Textronix hard-copy unit by way of the CRT terminal. The mass spectrometer itself contains an oscilloscope, a strip-chart recorder and a light beam oscilloscope for off-line display of the data. Two magnetic tape drives have been added recently for permanent storage of data files.

This data system is capable of recording mass spectral data at a rate of 365 amu/sec. It measures the detector output in 0.1 amu steps over the entire mass range and thus peak centroid determination is accurate to ± 0.2 amu. The peak intensity is based upon peak area, rather than peak height measurement. The fast scanning rate is extremely important when glass capillary columns are used in the GC and component peak share are extremely narrow. Operation of the GC/MS system is extremely simple. Once the operator answers some computer-generated dialogue on the CRT that allows him to choose instrument-operating parameters, the mass spectrometer is under computer control. The mass range, scan time and sensitivity are automatically set and the data stored on discs. The operator can monitor the total ion current and any specific mass ion simultaneously on the CRT as the GC run proceeds.

The data-handling option allows for rapid data storage, retrieval, and display. The tasks usually desired, such as background removal, comparison, or addition/subtraction of mass spectra, and display of the total ion current are provided in the data reduction package. Similarly, data can be conveniently displayed on the x-y recorder, the line printer, or the CRT hard-copy unit. For identification the mass spectrum of a specific compound can be compared to any spectra included in the Flammability Research Center's mass spectra file or the Aldermaston mass spectral file. The library search routine is based on a series of abbreviated spectra that are chosen by selecting the three most intense peaks in each 14-mass unit interval throughout the spectrum. Selecting peaks in consecutive regions of 14 amu units assures that the significant peaks belonging to a homologous series of ions are retained if they should happen to be relatively abundant. This technique assures that the molecular ion, if it is present in the complete spectrum, is not deleted from the abbreviated spectrum and that quadrupole mass discrimination effects are minimized. The actual computer search proceeds through a comparison of unknown spectra with the complete set of library spectra or some selected subset of these spectra. The selection of the library subset usually involves some prior knowledge about the characteristics of the unknown compound, such as molecular weight, retention indices, elemental content, or chemical groups contained in the compound.

Samples may be introduced into the mass spectrometer in various ways. Volatile compounds can be directly injected into an all-glass expansion bulb or introduced directly into a sampling loop which can utilize either molecular sieve, charcoal, or porous polymer traps for enrichment of the volatile components of gas samples. Solid samples and viscous liquids with significant vapor pressure below 350°C may be run via a direct insertion probe. In addition, the mass spectrometer is directly interfaced coupled to a Mettler Model 1 Thermoanalyzer for the identification of the volatile components from liquids or solids that result from the thermal degradation of polymeric materials.

The dodecapole mass spectrometer is also interfaced to a Hewlett-Packard Model 7626A research gas chromatograph, using a silicon membrane separator, a jet separator, or a direct capillary column interface. This is a "state-of-the-art" GC that permits the use of a variety of columns, injector accessories and detectors. The unit is equipped with a flame ionization detector (FID), a Nickel 63 electron capture detector (ECD), a flame photometric phosphorus detector (FPD), and a thermal conductivity detector (TCD). Any two of the detectors can be used simultaneously; GC traces are recorded on a dual pen strip chart recorder. A Hewlett-Packard Model 3352B Laboratory Data System was used to record relative peak areas.

Two other methods may be used for introducing samples into the gas chromatograph. The first technique employs flash pyrolysis of solids directly inside the GC injection port. Samples are placed on a resistively-heated platinum ribbon and heated from ambient temperature to as high as 1000°C in several hundred milliseconds. The second technique uses solid phase adsorbents to trap and concentrate volatile compounds in gas samples directly from the thermoanalyzer. Both of these sampling methods will be described in this chapter.

2. Thermoanalyzer

Thermal analysis studies were conducted using a Mettler Model 1 Thermoanalyzer. This instrument provides the capability for conducting simultaneous thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), differential thermal analysis (DTA), and effluent gas analysis (EGA) under controlled dynamic or isothermal heating conditions. The sample may be studied in vacuum (1×10^{-8} torr) or in a environment selected by the investigator. Two heaters are available: one capable of a maximum of 1000°C and the second capable of operation to 1600°C.

The thermoanalyzer has been interfaced with the computerized GC/MS system. Figure 1 is a schematic diagram of the thermoanalyzer showing the interface with the gas chromatograph. Figure 2 is a photograph of the TGA low-temperature furnace in place on the thermoanalyzer.

In this research two modes were used for analysis of thermal decomposition products: 1) the effluents produced in the thermal analyzer were transferred directly to the gas chromatograph; or 2) these degradation products were trapped and them desorbed into the GC.

3. Direct Probe Pyrolysis System

All direct probe pyrolysis studies were performed on a Chemical Data Systems Model 120 Pyroprobe that was inserted directly into the injection port of the GC. Samples were placed within the resistively-

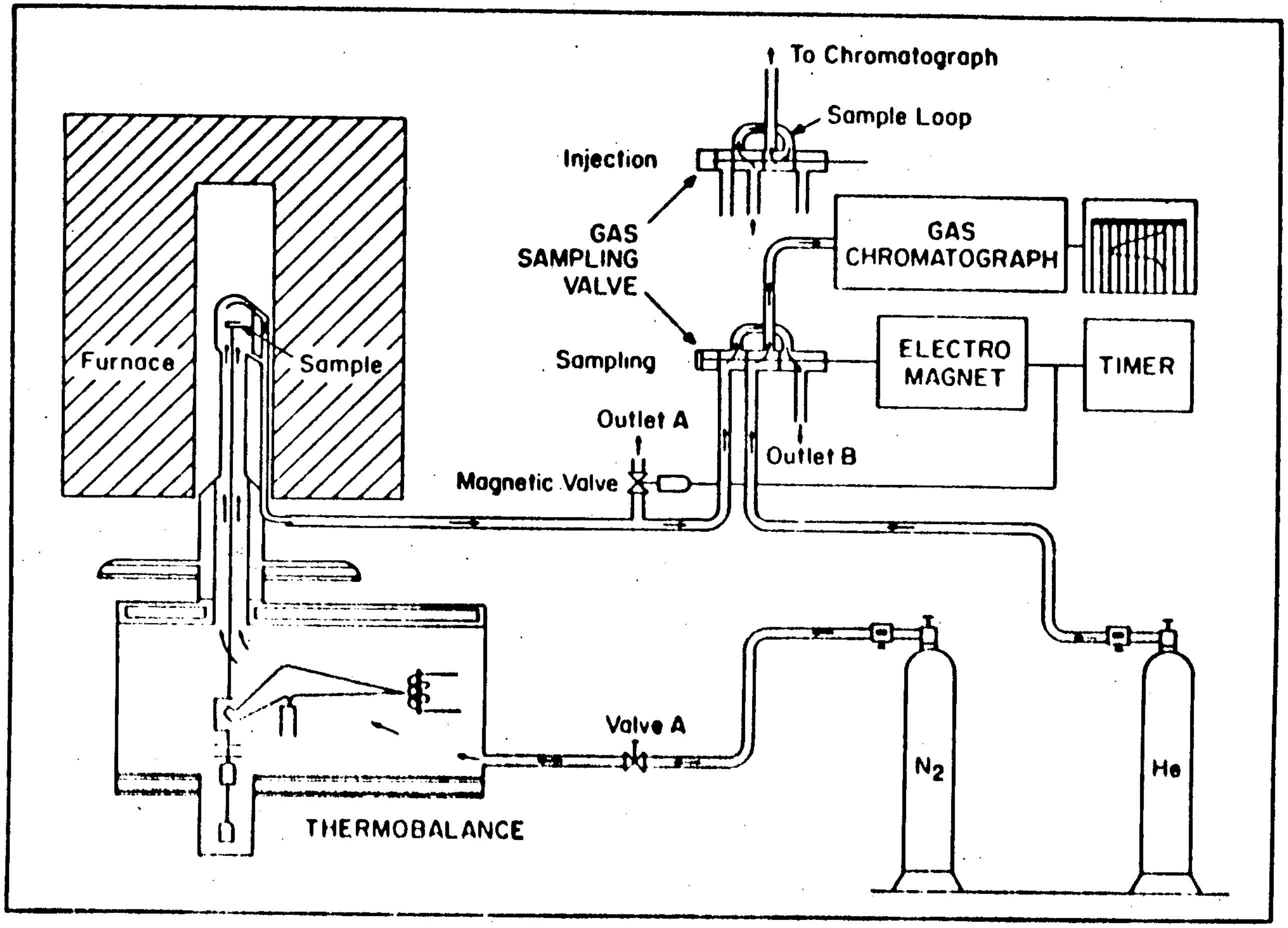


Figure 1. Schematic diagram of Mettler thermoanalyzer.

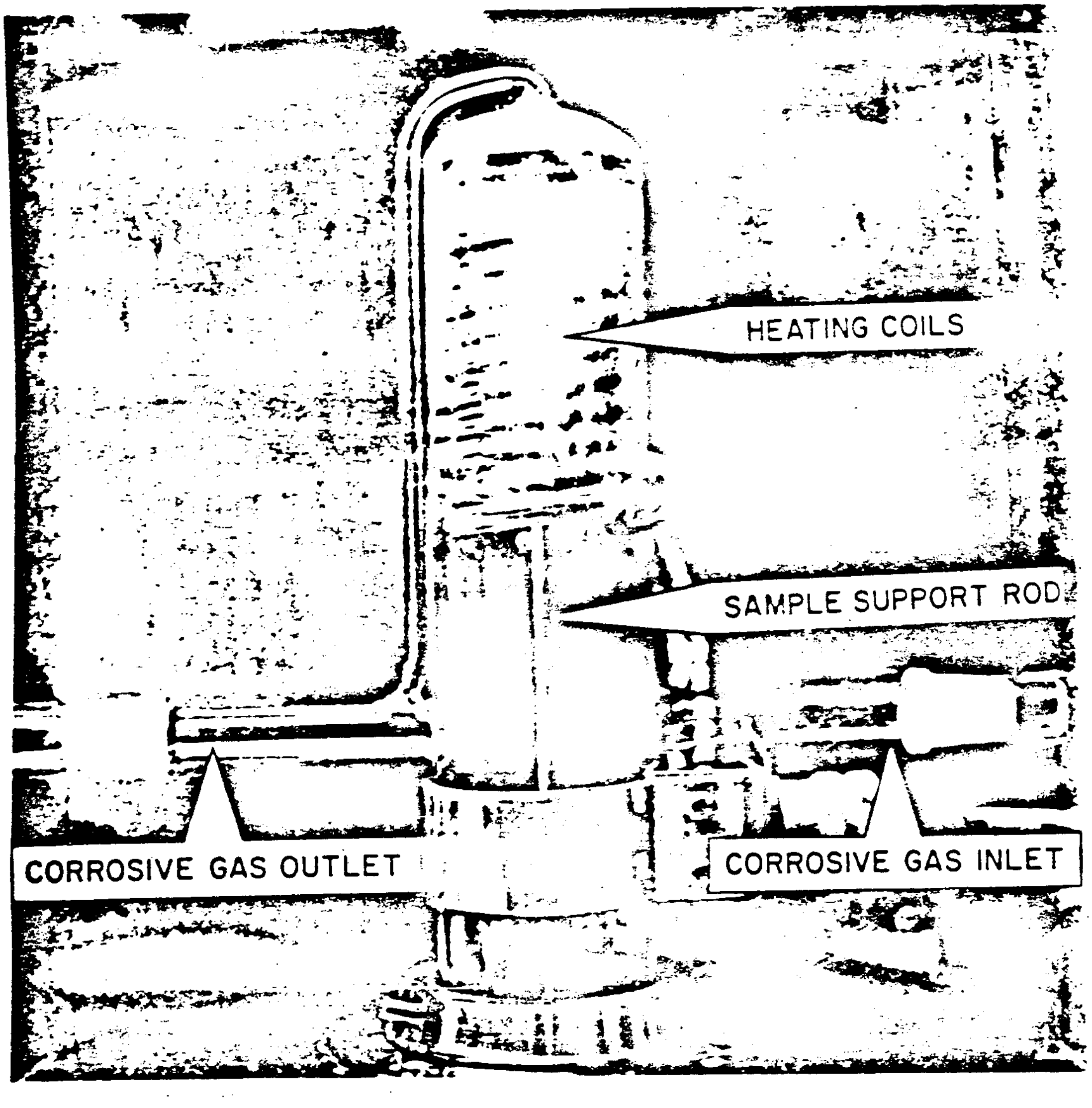


Figure 2. TGA low-temperature furnace.

heated tip of the probe and the temperature selected by varying the current supplied to the platinum ribbon heater. Typically, 3-5 mg of sample were inserted into the probe and pyrolyzed for 20 second.

4. Infrared spectrometers

A Perkin-Elmer Model 237 Grating Infrared Spectrometer, capable of covering in two scans the entire spectral region from 4000 to 250 cm^{-1} (2.5 to 16 microns), was used to characterize model polymers and char residues. Attachments were available for gas analysis and surface studies.

A Miran Model I infrared spectrometer, which has a cell path length of 20 meters, was used to determine the carbon monoxide content of the gaseous effluents resulting from the decomposition of polymers. This instrument has sufficient resolution to resolve the CO stretching frequency at 2160 cm^{-1} from all noticeable interferences.

5. High performance liquid chromatography

The analysis of low-boiling-point residues was conducted on a Perkin-Elmer Model 601 High Performance Liquid Chromatograph (HPLC). Both normal and reverse phase columns were available for use with this instrument. An ultraviolet (UV) detector was used for identification of compounds which elute from the HPLC. Samples were run in either a water/acetonitrile mixture (reverse phase) or hexane (normal phase).

6. Elemental analyzer

The elemental composition of polymers, residual compounds and chars were determined on a Perkin-Elmer Model 240 C,H and N Analyzer. Tests on compounds of known composition indicated that routine analyses were reliable to ± 0.1 percent for carbon, nitrogen and hydrogen. Oxygen determinations were measured either by difference or directly using a special column for oxygen analysis. In this case the accuracy is better than ± 0.2 percent.

B. Methodology

1. Analytical strategy

The general analytical scheme that has been used in the study of the thermal characteristics and degradation of Nylon 6, PET, and polycarbonate polymers is presented in Figure 3.(10) Polymer characterization was limited to the determination of the elemental analysis and the interpretation of the infrared spectrum of each polymer. An in-depth thermoanalytical study was used to examine the effect of oxygen and the dynamic heating rate upon polymer decomposition. This combined information was used to postulate the mechanism of the decomposition process. Finally, thermochemical studies were conducted under conditions of pyrolysis and oxidative degradation.

A detailed breakdown in the analytical scheme used to identify the products resulting from oxidative degradation and pyrolysis of Nylon 6, PET and polycarbonate polymers is presented in Figure 4.(10) An arbitrary division of the products from polymer degradation into "volatiles" and "residues" has been made. "Volatiles" (low and high boiling) are defined as those compounds that have significant vapor pressure under

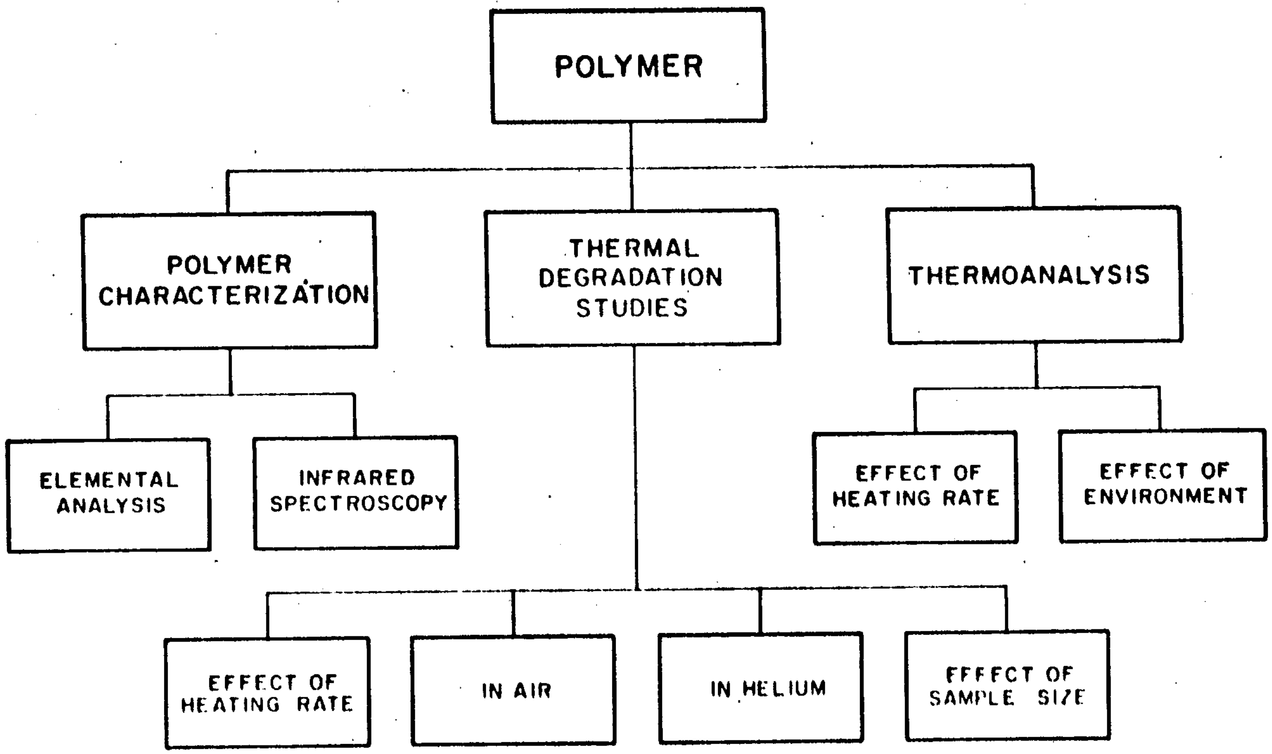


Figure 3. The analytical scheme for the study of Nylon 6, PET, and polycarbonate polymers.

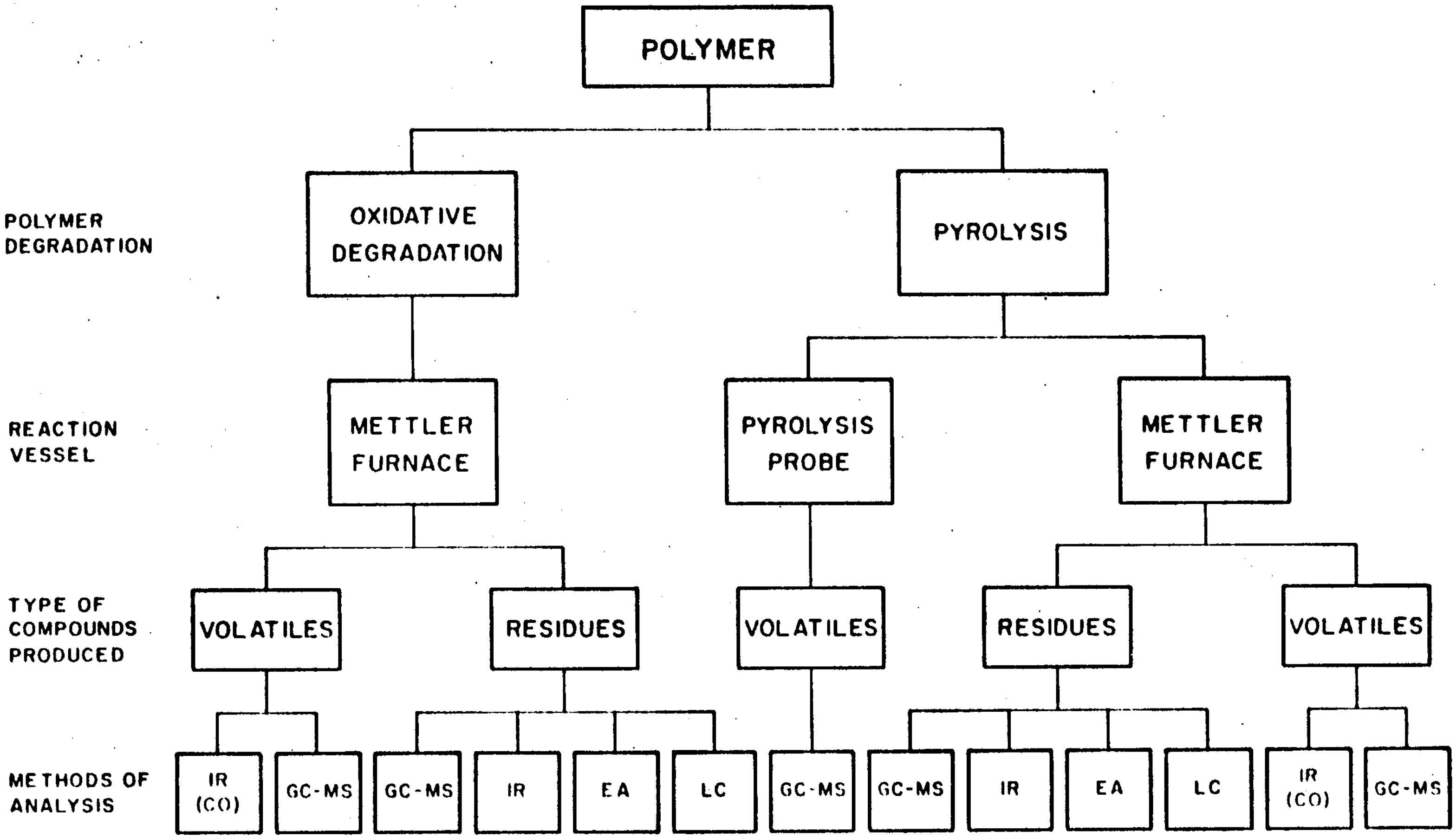


Figure 4. Analytical scheme for the analysis of decomposition products produced during polymer degradation.

the conditions imposed by the apparatus used to adsorb components (200°C), and solid "Residue" is the char that remains. Compounds that react with the quartz or stainless-steel surfaces of the apparatus are, of course, not trapped or detected and are not classified under either heading.

The methods of analysis are also summarized in Figure 4. The volatile products were identified using the GC/MS system. Carbon monoxide was monitored continuously using the non-dispersive infrared spectrometer interfaced to the outlet of the thermoanalyzer furnace. The low-boiling volatiles and residues were subjected to GC/MS, IR analysis, high pressure liquid chromatography and elemental analysis.

The following subsections present a more in-depth examination of the analytical methodology outlined in Figure 4. This includes direct probe pyrolysis, trapping techniques, the measurement of carbon monoxide, analysis of residues and the procedure for data reduction.

2. Thermoanalysis

The overall analytical scheme for the thermochemical study of Nylon 6, PET and polycarbonate polymers is presented in Figure 5. Studies were conducted to determine both the effect that oxygen and the effect that different dynamic heating rates had upon the polymer decomposition process. In addition, the elemental analysis of the chars produced at several different stages of degradation in helium and air atmospheres and the rate of carbon monixide evolution from the polymers have been included to help elucidate the mechanism of polymer decomposition.

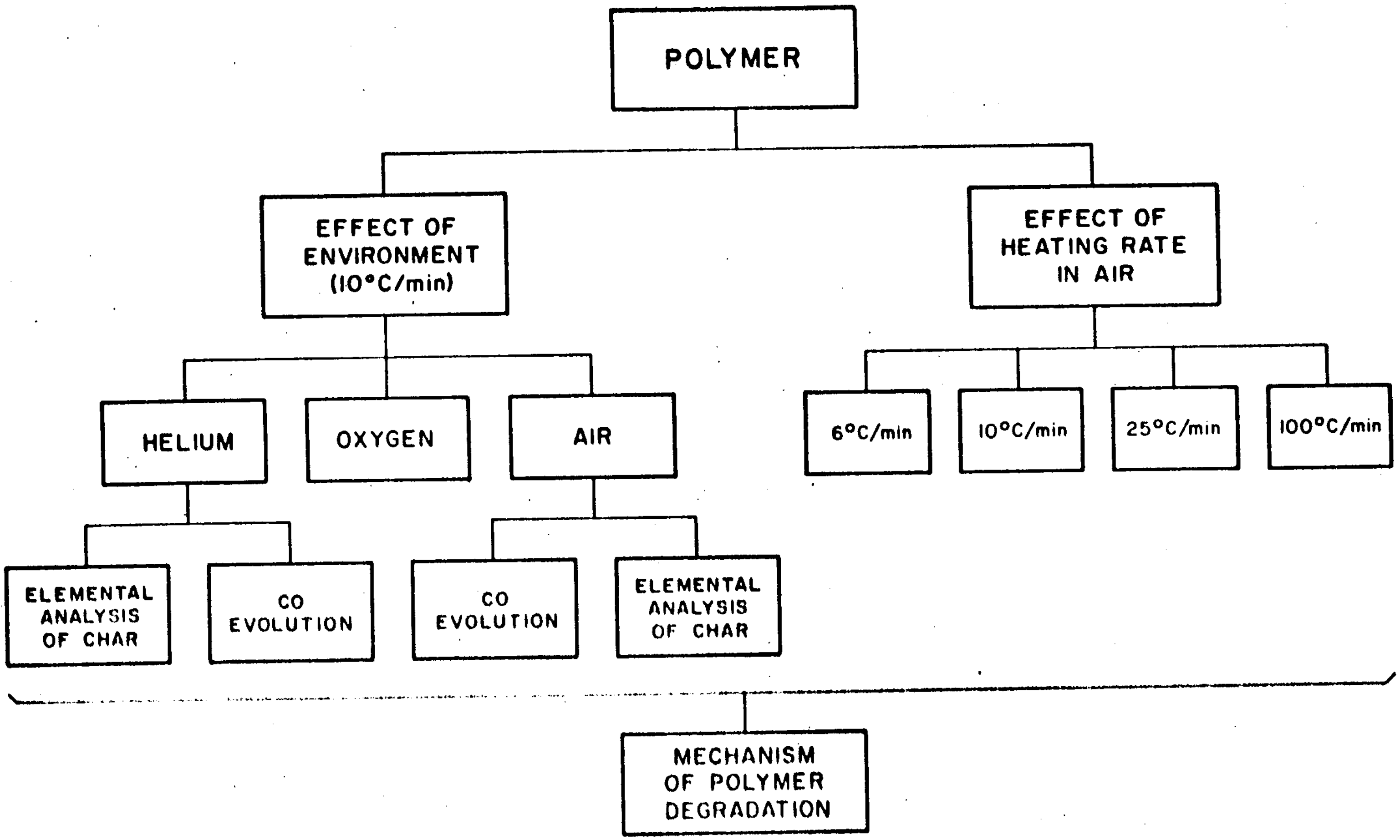


Figure 5. Analytical scheme used to determine the effect of variables on polymer thermal degradation.

Prior to analysis all samples were dried at 60°C at 10^{-6} torr for several days under vacuum. All gases used in the thermoanalyzer were checked for purity using GC; the helium was Ultra High Purity grade from Matheson Gas Products and the oxygen was CP grade. Studies in an air environment used laboratory air that was dried by passing it through a calcium sulfate trap.

Figure 6 illustrates the principle of thermogravimetric analysis. This thermogram of hypothetical polymers shows weight change as a function of temperature. In Figure 6 polymer A stands for a thermoplastic polymer such as Nylon, polyester and polycarbonate that was heated in air at 10°C/min. High temperature polymers, including aromatic polyamides, polyimides and polybenzimidazole,and general thermosetting polymers, such as phenol-formaldehyde polymer, would produce thermograms such as illustrated by polymer B.

The thermograms of most polymers can be generally classified into three regions, as illustrated. Initial decomposition, or other changes, such as evolution of water, entrapped solvents, or other low-molecular weight species, may take place in the range of Region I and may be observed as deviation from the horizontal trace at the beginning of the thermogram. The color of the polymer samples generally darkens in this region.

Major decomposition reactions or depolymerization reactions occur in the area of Region II. Typically, the slope of the weight loss curve becomes greater as a rapid evolution of low-molecular weight volatile species takes place. For many polymer systems char formation occurs within this region of the TGA thermogram.

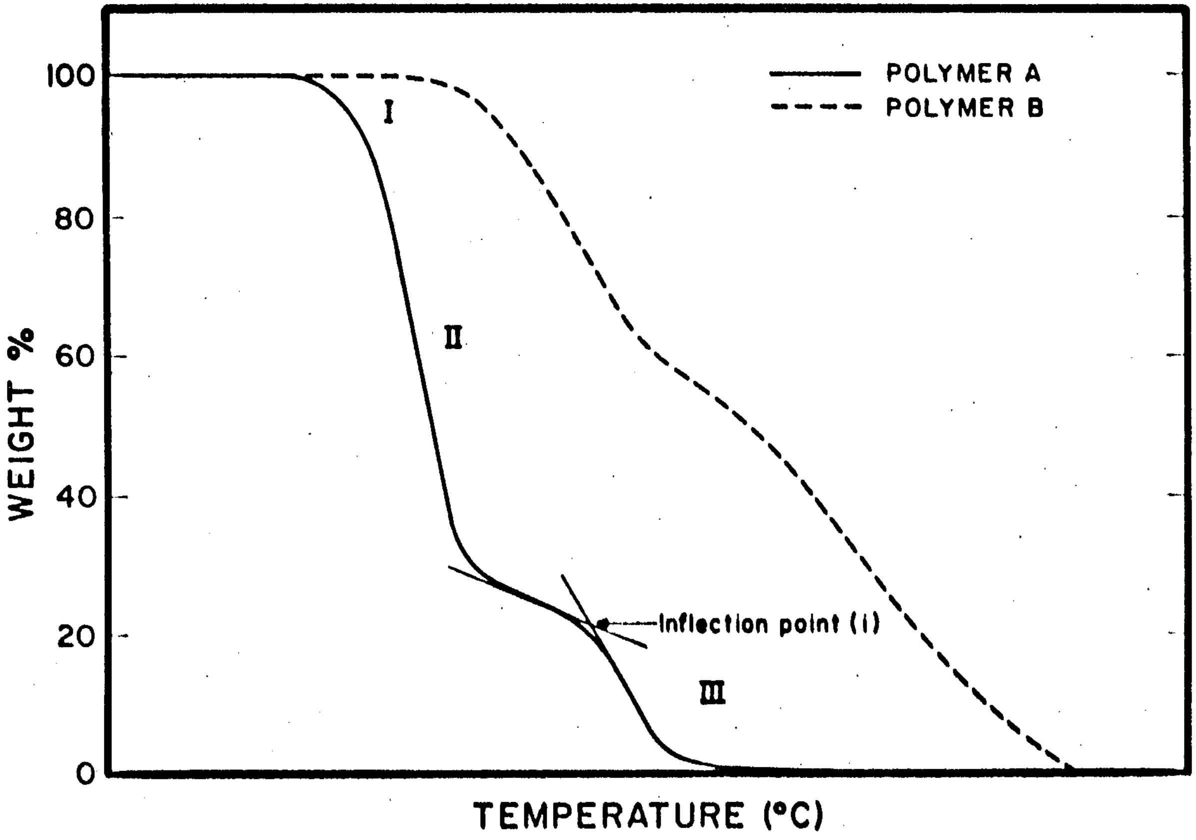


Figure 6. Thermograms of hypothetical polymers.

If the thermogram indicates the presence of Region III, it is usually attributed to a thermal sintering of the char or oxidative degradation of the char structure formed in Region II. Region III is seldom observed in an inert environment.

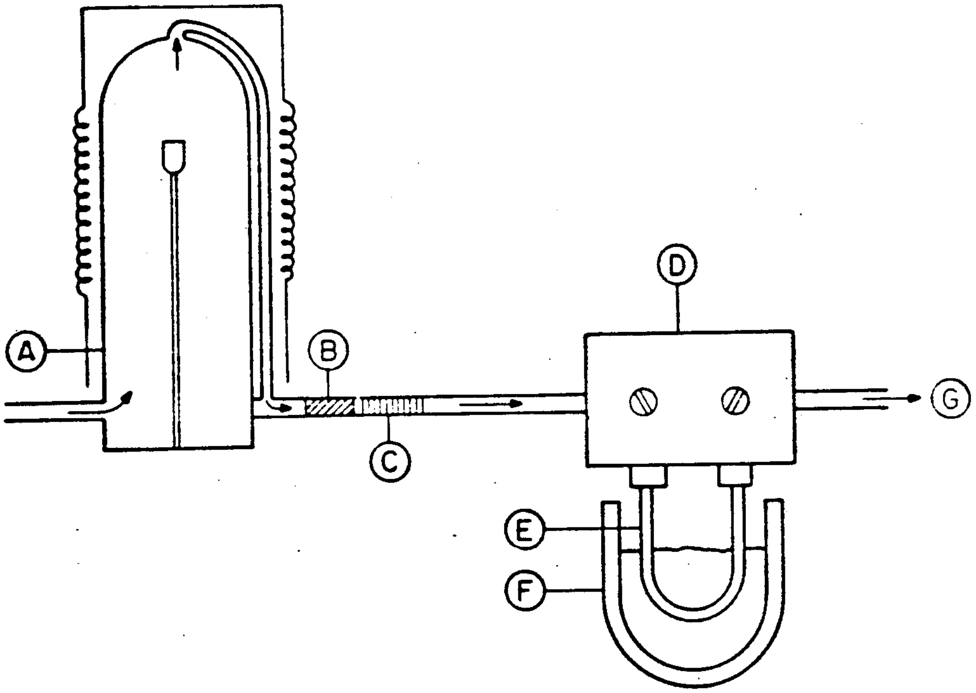
Polymers classified as Type B do not always show distinct regional separation, as observed during the thermal decomposition of polymers classed as Type A. However, the inflection point, "i", can often be observed in the region of low percent weight loss. It suggests that the char formation due to crosslinking reactions or recombination reactions is dominant in this type of polymer, rather than depolymerization reactions which result in rapid sample weight losses.

3. The trapping technique (analysis of low-boiling volatiles)

One of the major objectives of this study involved the quantitative determination of the volatile components resulting from polymer degradation. Since standard analytical techniques for this purpose have not been discussed widely in flammability or toxicologically-related literature, this section describes the procedures used for trapping and analyzing volatile compounds that have recently been developed in this laboratory. The methodology outlined here should be applicable to the analysis of volatile compounds from most sources.

The technique of direct-probe pyrolysis (see Direct Probe Pyrolysis) is a rapid straightforward method of introducing the degradation products from polymers into a GC/MS system. However, this technique suffers from several serious limitations, the most serious problem being the lack of reproducibility. The temperature of the resistively-heated platinum ribbon is sensitive to the nature and flow rate of the carrier gas used, the age of the ribbon and its exact location with respect to the walls of the injection port. These problems have been described by other workers.(40) Second, quantitation of the volatile products is extremely difficult, even under the most ideal conditions. Some polymers melt and drip away from the platinum ribbon during flash pyrolysis, while others may form a uniform surface char only in places where there is direct contact between the heater and sample, causing non-uniform heat transfer through the sample. In laboratory use one also discovers that the size of the injection port on the chromatograph imposes a limitation upon the size of the sample that may be pyrolyzed. Lastly, the gas chromatographic detectors are not designed to operate in an oxygen-containing atmosphere during polymer degradation, thus limiting thermal decomposition studies to the pyrolysis mode.

A comprehensive search of the literature encompassing modern analytical methods was conducted in an attempt to develop modified procedures applicable for the study of combustion processes. Techniques developed by food and flavor chemists, as well as scientists in the air pollution field, have used porous polymer adsorbents for the trapping of volatile components at cryogenic temperatures. The apparatus that has been constructed in this laboratory for the analysis of products produced during polymer degradation is shown in Figure 7. Gases are sampled directly from the quartz furnace of the thermoanalyzer A, which allows the temperature, the TGA, the DTG and the DTA to be monitored continuously during the degradation of the sample. Particulate matter and/or materials with high-boiling points generated



Ⓐ Furnace of thermoanalyzer
Ⓑ Glass or teflon wool to trap particulates and less volatile products
Ⓒ Optional trapping material
Ⓓ Interface housing valves
Ⓔ U-tube trap containing absorbing support
Ⓕ Coolant or heat source for absorption or desorption step
Ⓖ Effluent to additional stages of trapping

Figure 7. Apparatus for trapping gases from thermoanalyzer.

during pyrolysis or oxidative degradation are removed in the glass or Teflon fiber filter B and the volatile products are collected in trap E which is packed with a porous polymer material. An optional trap at C may be used to absorb water from the effluent to simplify the subsequent analysis. The carrier gas is finally bubbled through aqueous and non-aqueous solvent traps at G to insure that no products escape into the room. As shown in Figure 8, a heated aluminum block D contains two multiport high conductance valves that direct the carrier gas from the thermoanalyzer and the gas chromatograph through the trap. The three possible orientations of the valves are: 1) the GC and the thermoanalyzer operate independently of one another; 2) the thermoanalyzer vents through the trap; and 3) the GC carrier gas flows through the trap and sweeps the adsorbed volatile compounds into the injection port of the GC. In practice, products of polymer decomposition that are produced at any temperature are swept through the trap E which is held at subambient temperatures. After the gases are adsorbed, the interface valves are turned to direct the GC carrier gas through the trap. By applying heat from source F, most volatile components can be desorbed from the porous polymer packing in the trap in less than several seconds and swept into the gas chromatograph.

Although the trapping of effluents from the thermoanalyzer is clearly a more precise method of studying polymer degradation than the use of a pyrolysis probe, it does introduce an extra step of complexity to the problem of analysis. Besides the need to measure the absolute response of the gas chromatograph to each compound, one must also consider the efficiency of the porous polymer trap and the sample holdup

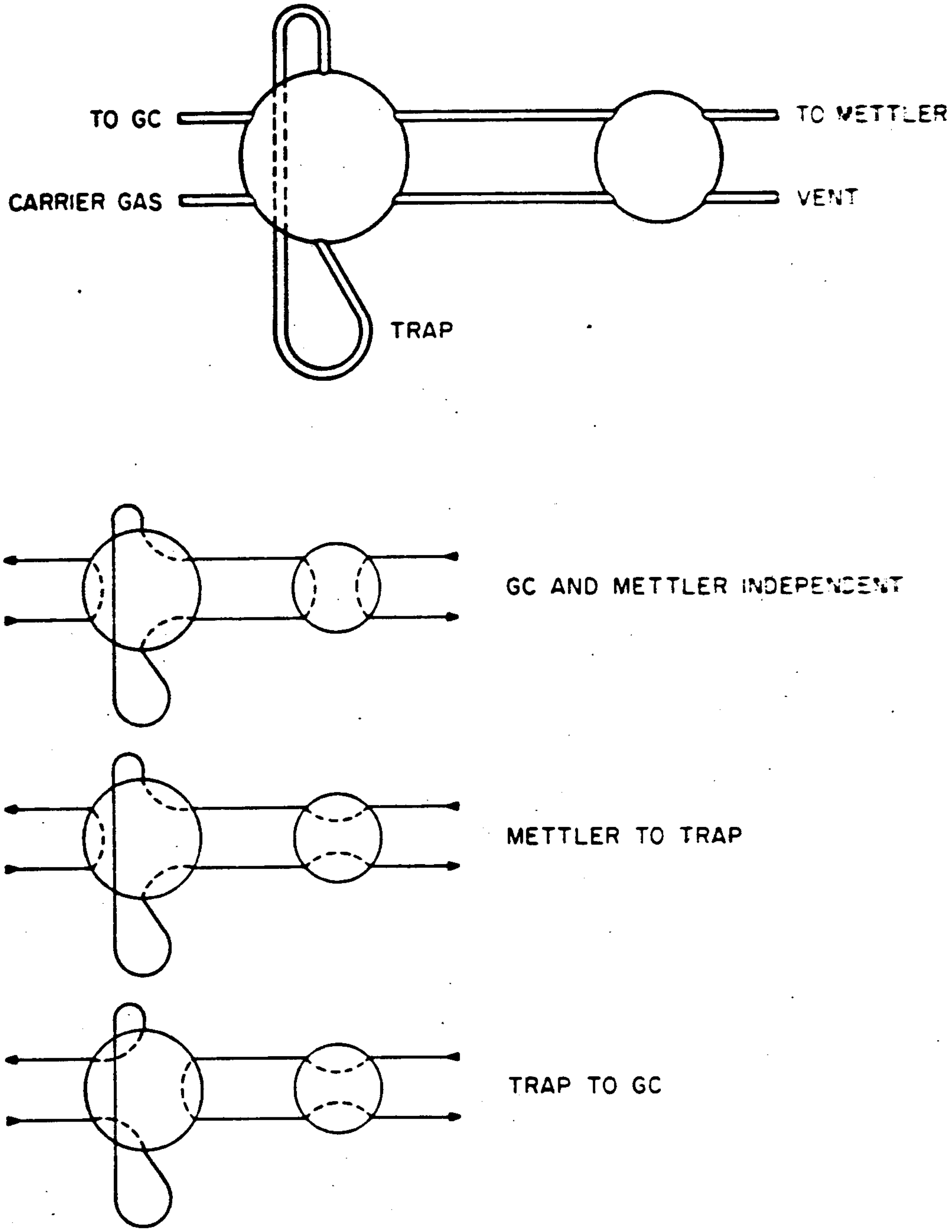


Figure 8. Thermoanalyzer interface trapping system.

in the heated inlet lines, the furnace, etc. The actual amount of a given compound, C_x, is dependent upon four variables, according to the expression:

$$C_x = \frac{S \cdot A(x)\ R.F.(x)}{T.E.(x)} \tag{4}$$

where

S = sensitivity of the GC, as determined by injection of a known compound as an internal standard,

A(x) = GC peak area of compound C_x,

R.F.(x) = relative GC detector response factor of compound C_x, and

T.E.(x) = relative trapping efficiency of C_x.

The factor S is determined by injecting known quantities of one or more compounds, usually benzene and ethane, directly into the GC and determining the instrument response per mg of sample. The GC peak area A(x) is automatically recorded on an electronic integrator for either the thermal conductivity or flame ionization detectors. Response factor R.F.(x) must be measured for each compound in the chromatogram, and some values do exist in the literature.(41) Trapping efficiency not only includes the relative trapping efficiency of the adsorbent material, but also the sample holdup in the furnace of the thermoanalyzer, the valves in the sampling loop and the heated tubing that connects the components.

To insure consistency in the data, all trapping experiments used a "standard" set of operating parameters, which included a trapping time of four minutes, an inlet line and trapping block temperature of 200°C and a carrier flow rate of 160 ml/min. The trap E, containing

0.25 grams of Porapak Q porous polymer, was cooled to -112°C using an ethanol/liquid N_2 slurry for the adsorption step, and heated to 200°C to desorb all materials for GC analysis.

To measure the trapping efficiencies of this interface, known compounds were introduced into the carrier gas stream exiting from the furnace on the thermoanalyzer. Known amounts of gases or liquids were injected directly into the effluent stream through a rubber septum mounted on the sidearm leading from the quartz furnace. The samples were trapped and desorbed under "standard" operating conditions and the resulting GC detector response compared to the response obtained when the same amount of material was injected directly into the GC.

Table 13 contains some examples of the trapping efficiencies and the thermal conductivity detector response factors that were measured for various compounds under "standard" operating conditions. In general, the trapping efficiencies of all compounds that have been measured in this laboratory, that contain two or more carbon atoms and possess boiling points below 200°C, are approximately equal to 0.9. The less than quantitative efficiency of the trapping system is believed to be the result of sample holdup in the heated transfer lines and the porous polymer trap. Other than strong acids and bases, no compounds have been observed to chemically react with the porous polymer adsorbent at 200°C. Lighter gases, such as methane, carbon monoxide and hydrogen, are too volatile at -112°C to be trapped effectively and are analyzed by other means, as will be described later in this chapter.

As an example of how the "raw data" is quantitated, consider that

Table 13. Trapping Efficiencies and Response Factors for Selected Compounds[a]

Compound	Trapping Efficiency[b]	Response Facot[c]
CO	<.01	.67
CO_2	.87	.92
H_2O	.82	.55
CH_4	.05	.45
CH_3OH	.99	.58
C_2H_6	.95	.59
n-Nonane	.90	.72
Benzene	.89	.78
Aniline	.96	.82

[a] Based on 2 to 25 mg samples on 0.25 Porapak Q absorbent at -110°C. Samples were flash desorbed at 160°C after trapping for a period of four minutes.

[b] Trapping efficienty = $\frac{\text{mg sample recovered}}{\text{mg sample injected}}$.

[c] Thermal conductivity detector response, where NO_2 = 1.00.

the peak areas for the products from a pyrolysis experiment have been recorded and that benzene and toluene are identified as two of the products. Immediately after the GC run a series of dilutions of benzene in a suitable solvent were injected into the GC and a "standard curve" constructed of integrator peak area versus microliters of benzene, such as is shown in Figure 9. Hence, if the area of the benzene peak from the pyrolysis experiment equals 2200, the absolute amount of benzene found is equal to 0.8 µl, or 0.703 mg. Solving Equation (5) for S, one gets:

$$S = \frac{C_x \ \text{T.E.}(x)}{A(x)\text{R.F.}(x)} \tag{5}$$

The T.E. and R.F. of benzene are 0.90 and 0.893 (FID), respectively, thus, S is equal to

$$S = \frac{0.703 \text{ mg } (0.90)}{2200 \ (0.893)} = 3.2 \times 10^{-4} \text{ mg/unit area} \tag{6}$$

Using this value of S, one may solve Equation (4) for any integrated GC peak. If, for example, the integrated peak area of toluene is 1500, one may solve for C_x, knowing T.E. (toluene) = 0.95 and R.F. (toluene) = 0.935:

$$C_{\text{toluene}} = \frac{(3.2 \times 10^{-4} \text{ mg}) \ (1500) \ (0.935)}{0.95} = 0.48 \text{ mg} \tag{7}$$

If the total weight loss of the polymer during pyrolysis was 12 mg, then the weight percent (wt.%) of toluene in the volatile products is

$$\text{wt.\% toluene} = 100\% \ \frac{0.48 \text{ mg}}{12 \text{ mg}} = 4.0\% \ . \tag{8}$$

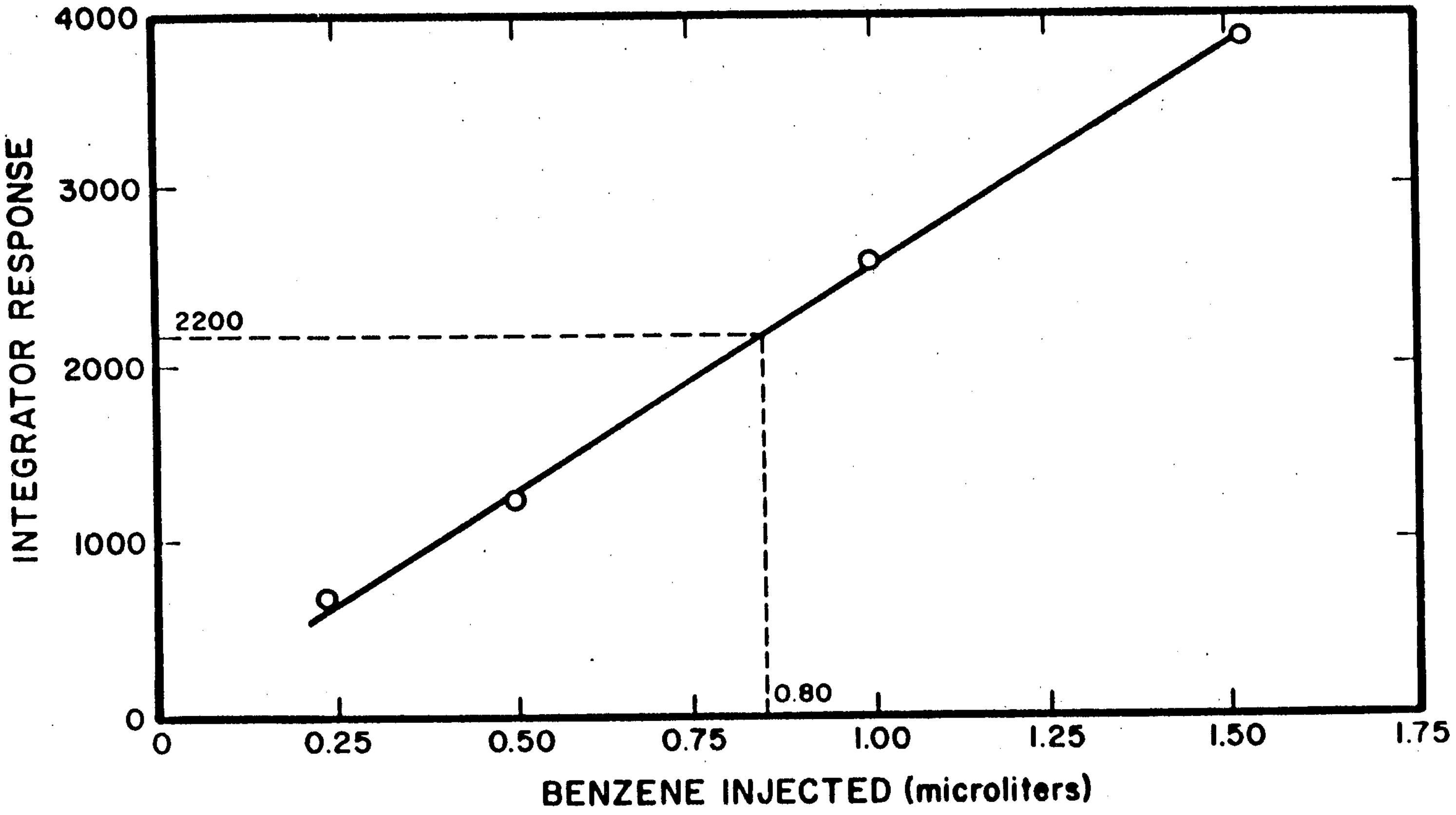


Figure 9. Construction of a "standard curve" for quantitative analysis.

4. Carbon monoxide analysis

Since carbon monoxide cannot be trapped efficiently using the techniques described previously, alternative means of detection were explored to meet our specific application. Since the use of non-dispersive infrared analyzers has become the method of choice in monitoring carbon monoxide levels in the atmosphere,(42) it was judged to be a reliable technique for this study. To remove any compounds that may interfere with the CO adsorption at 2160 cm^{-1}, the gas effluent from the thermoanalyzer was drawn through a trap containing Porapak Q adsorbent at -112°C before admitting the gases into the sample cell on the Miran I infrared spectrometer. A standard curve of concentration versus absorption at 2160 cm^{-1} was constructed by direct injection of known amounts of CO through a septum mounted just outside the furnace on the thermoanalyzer, and the absorptions of CO liberated from the polymer degradation experiment were directly compared to the standard curve.

An example of how the spectrometer responds to the CO generated as a polymer decomposed is illustrated in the strip-chart recording (Figure 10). Because of the limitations imposed by the finite volume of the gas sampling lines connecting the IR spectrometer to the furnace, there was a 17-second delay between the time of actual polymer decomposition and the response of the IR detector. The CO absorption initially increased and then leveled off as the gases entered the large sample cell of the spectrometer. Finally, there was a slow decrease in the CO absorption as the effluent enriched in CO was displaced from the sample cell by air containing a lower concentration of carbon

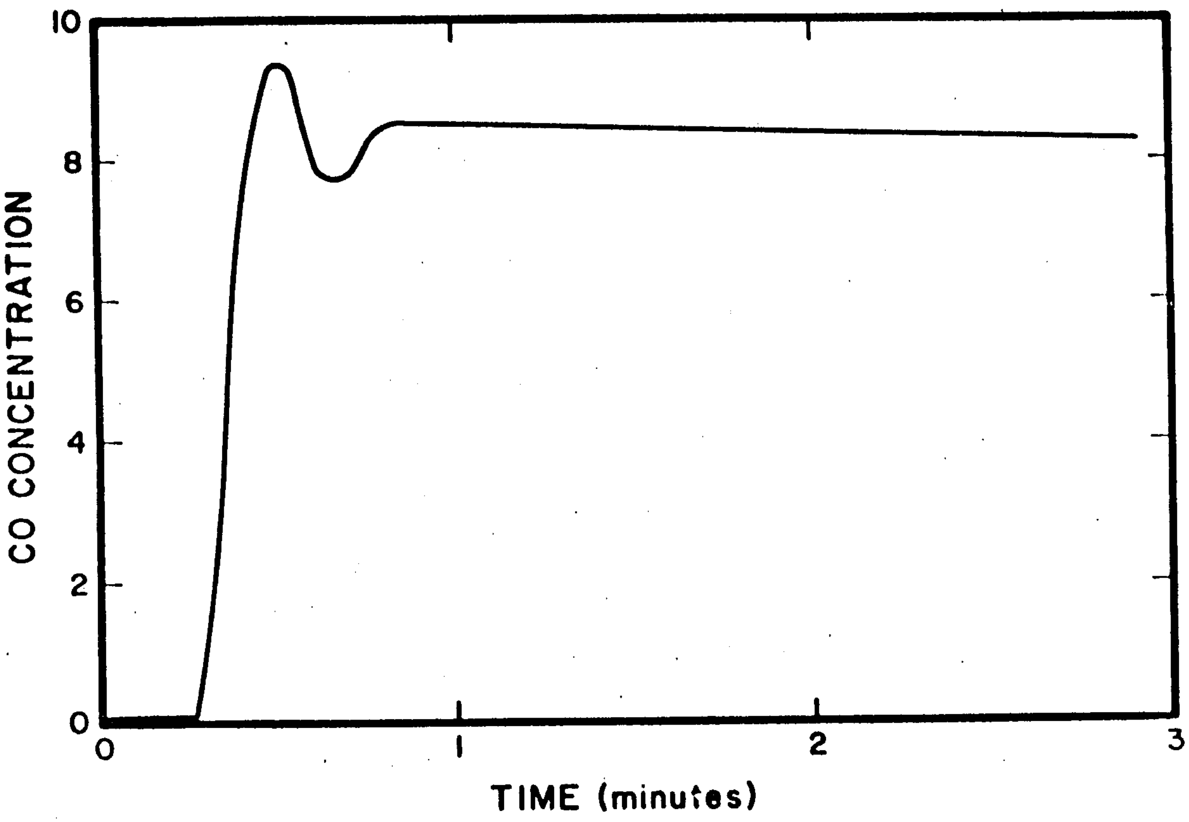


Figure 10. The recorder trace of carbon monoxide concentration as a function of time--non-dispersive infrared spectroscopy.

monoxide. The specificity and sensitivity of this technique was found to be excellent; sample weight losses as small as 0.01 percent of total polymer weight loss were easily quantitated.

5. Analysis of high-boiling volatiles

Using the trapping system decribed previously to collect products from polymer degradation, compounds that were produced which possessed low vapor pressures would condense as a residue in the colder regions of the furnace or the gas transfer lines. Likewise, any aerosols that may contain polymer oligomers would condense on the glass surfaces or the glass or Teflon fiber filter which is inserted in the transfer lines for the purpose of collecting these materials.

To aid in the identification of high-boiling volatiles that were formed during polymer decomposition, several techniques were employed: infrared spectroscopy, gas chromatograph/mass spectrometry, liquid chromatography,and elemental analysis.

When the materials deposited on the glass wool could be removed as a solid, the KBr pellet technique utilized for infrared analysis was employed. When the deposited residue consisted of fine particulate matter or a heavy oil, these compounds were extracted using solvents such as chloroform. The solvent was then removed by passing helium over the surface at room temperature. The remaining residue was spread uniformly between two sodium chloride plates and the IR spectrum recorded.

When GC/MS analyses of the residue was conducted, the residue was dissolved in solvents such as chloroform, acetone,and tetrahydrofuran

(THF), and the solution was injected into a GC equipped with high temperature columns (Dexil or OV-1). The analyses of separated compounds were performed employing the same methods which were used for the analysis of non-volatile products.

Further analysis of the high-boiling volatiles was conducted using liquid chromatography. The high-boiling volatiles were prepared for HPLC analysis by dissolving the sample in THF, acetone or acetonitrile, followed by filtration to remove the insoluble material. The solvent was removed by evaporation and the sample completely dried under vacuum. The samples were re-dissolved in THF prior to injection into the HPLC.

The samples were chromatographed using a reverse-phase column (Whatman, Portisil PSX 10/25 ODS) operated at 50°C. A mixture of acetonitrile and water (35:65, v:v) was used isocratically at a flow rate of 1.0 ml/min for the separations. The eluting compounds were detected using a detector monitoring the uv absorbance at 240 nm. Separated peaks in the chromatogram were identified by agreement in retention times with known compound standards.

6. Identification of unknown compounds

To insure the reliability of the qualitative and quantitative data, all experiments were performed a minimum of three times. In pyrolysis or oxidative degradation studies, a 50 mg sample size was generally used, since that sample size was found to be adequate for separation identification and the quantitation of components. Smaller sample sizes were used when difficulties were encountered in the identification of trace compounds. The use of large sample sizes introduced problems pertaining to sample homogeneity and uniformity of heating sample environment. The effect of sample size is discussed later. In the study of the initial phase of degradation much larger sample sizes (≃ 150 mg) were used to insure the additional sensitivity required for the analysis of small quantities of compounds produced during the initial degradation process. Several GC columns were used for separation and identification of the individual products resulting from polymer decomposition. Most of the experiments for quantitation of the volatile components utilized a 16 ft. x 1/8 in. O.D. Chromosorb 101 porous polymer column. Supplemental data were obtained using Chromosorb 103 and 104 columns (i.e., separation of nitrogen-containing compounds).

The identification of volatile products formed during the polymer degradation was carried out using the computerized Hewlett-Packard GC/MS system. Since the mass spectrum of a compound is usually a unique "fingerprint," the GC/MS system provides the most valuable information for correct identification of degradation products. To facilitate rapid handling of the enormous quantity of data that are gathered during a GC run, the mass spectra of the unknown compounds are compared to the FRC Mass Spectral File and the Aldelmaston Mass Spectral File which contains over 14,000 mass spectra in digital form. Information from a computer search, even if it does not uniquely identify the unknown compounds, provides valuable information about the most probable chemical structure, i.e., the molecular weight, empirical formula, functional groups present, the degree of substitution, etc.

As the resolved components that elute from the GC are analyzed by mass spectrometry, the retention times are recorded and peak areas are integrated simultaneously for either the FID or TC detectors. From the GC data, Retention Indices(43) are calculated for every compound that eluted from the column. The retention indices of over 400 compounds and many FID and TC response factors of compounds often encountered during polymer degradation studies have been measured on several porous GC supports in this laboratory to aid in the identification of unknown compounds. Since it is highly improbable that two different compounds have identical retention indices on two different types of GC columns, one can often identify the unknown compound solely on the gasis of retention time.

By measuring the FID to TC response factor ratio, one has access to another valuable parameter. The ion current measured at a flame detector is proportional to both the total number of carbon atoms and the specific oxidation state of any carbon atom in the molecule.(44) Similarly, a linear relationship exists between the relative thermal conductivity response and the number of carbon atoms in a homologous series of compounds.(45) Hence, the FID to TC response ratio is predictable for a wide range of molecules. In practice, one uses the measured FID to TC ratio to make educated guesses pertaining to the structure of compounds that are eluting from the GC column. For example, saturated and unsaturated hydrocarbons have FID to TC ratios larger than 0.90, but acids, alcohols and ketones have ratios below 0.80.

All of the GC and MS techniques discussed above have been utilized for unraveling chemical structures of the products produced during polymer degradation. The positive identification of a specific compound as a decomposition product requires a specific amount of internally consistent chemical evidence from the GC and MS data. The five possible combinations of GC and MS data and the conclusions that can be drawn from them are listed in Table 14.(10) In combination 1, where the GC retention time data does not support the mass spectral "fingerprint," one can only, at best, determine the molecular weight and functional groups present in the unknown compound. Similarly, the Retention Index for that particular compound from one type of GC column does not constitute sufficient data for positive identification. However, the combined evidence of a correct mass spectrum with the correct Retention Index from one or more types of GC columns is usually sufficient to identify the chemical structure.

In many cases compound identification has been made on a basis of mass spectrometric data combined with chemical intuition. The Retention Indices and the FID to TC ratios have not been measured in this laboratory for many of the degradation products from Nylon 6, Pet or polycarbonate polymers. However, relative retention times and Retention Indices can usually be predicted from data for other compounds of similar structure or other members of the same homologous series. A firm identification of chemical structure of many compounds found in polymer decompositions has been made on a basis of a correct mass spectrum and the predicted Retention Index on two different GC columns.

7. Quantification of data

As was described previously, several factors are involved in

Table 14. The Required Evidence for Compound Identification by GC/MS Techniques

Input Data[a]				Compound Identification[b].		
	MS	Kovats' Column #1	Kovats' Column #2	Yes	No	M.W. Only
1	X					X
2		X			X	
3		X	X	X		
4	X	X		X		
5	X	X	X	X		

[a] Experimental data in the form of mass spectral identification and the correct Kovats' Retention Index on Column #1 or Column #2.

[b] Conclusions concerning compound identity that can be made from the given input data. "M.W. Only" means that only the molecular weight of the unknown compound may be determined from the input data.

quantitating the GC results from a trapping experiment performed using the thermoanalyzer. The absolute sensitivity (S) of the GC, the relative trapping efficiency (T.E.) and the response factors (R.F.) for each compound that eluted from the chromatograph should, in principle, be measured. In practice, S is easily measured, but evaluating T.E. and R.F. for each individual compound is an extremely time-consuming task.

In this work the sensitivity, S, was measured after each individual trapping experiment. The deviation in S for both the FID and TC detectors was only several percent on a day-to-day basis and insignificantly small between individual experiments. A standard curve of concentration versus integrated peak areas (see Figure 9) was constructed for two compounds, ethylene and benzene, under GC conditions identical to those used in the actual pyrolysis experiment. The concentration of ethylene and benzene from polymer decomposition was then read from the standard plot. The use of two "internal standards" insured the reliability of the technique and compensated for errors caused during GC injections. Not all the response factors and trapping efficiency measurements for the porous polymer traps have been evaluated for each individual compound detected in this study. However, all general classes of compounds (e.g., aromatics, nitriles, alcohols, ketones, etc.) have been analyzed using Porapak Q porous adsorbents and trapping efficiencies are very high ($\geq$ 90 percent) for all nonreactive organic compounds. Moreover, as discussed in the previous section, response factors for most compounds can be estimated with certainty from structurally similar compounds.(46) For example, the FID response factors for the alkane series, hexane, heptane, octane, and nonane, are 0.971, 1,00, 1.03, and 1.02, respectively. The relative trapping efficiencies and response factors used are included in the final data and are marked with an asterisk to denote if the value is only an estimate.

A first approximation to the absolute error in the quantitative data can be made by considering the error in each variable in Equation (4) which is repeated below:

$$C_x = \frac{S\ A(x)\ R.F.(x)}{T.E.(x)} \tag{4}$$

where

$$S = \text{area }(x)/\text{mg}(x)$$

$$A(x) = \text{area }(x)$$

$$R.F.(x) = \frac{\text{area }(x)}{\text{area (standard)}} \times \frac{\text{mg (standard)}}{\text{mg }(x)}$$

$$T.E.(x) = \frac{\text{mg }(x)\text{ (from trap)}}{\text{mg }(x)\text{ (direct injection)}}$$

The "standard" is, in this data, the compound that is directly injected into the GC to determine the S term. When values for S, A(x), R.F.(x), and T.E.(x) are substituted into Equation (4), C_x is equal to:

$$C_x = \frac{\text{area}(x)^3}{\text{area}(x)} \times \frac{\text{mg}(x)}{\text{mg}(x)^2} \times \frac{\text{mg}(i)}{\text{mg}(t)} \tag{9}$$

where

$\text{mg}(s) = \text{mg(standard)}$,

$\text{mg}(i) = \text{mg}(x\text{, direct injection})$

$\text{mg}(t) = \text{mg}(x\text{, from trap})$, area(s) = area(standard).

The normalized standard deviation in C_x, $\sigma(C_x)/C_x$ can be written[47] as

$$\frac{(C_x)}{C_x} = 9\,\frac{\sigma(\mathrm{area}(x))^2}{\mathrm{area}(x)} + 4\,\frac{\sigma(\mathrm{mg}(x))^2}{\mathrm{mg}(x)} + \frac{\sigma(\mathrm{area}(x))^2}{\mathrm{area}(x)}$$

$$+ \frac{\sigma(\mathrm{mg}(s))^2}{\mathrm{mg}(s)} + \frac{\sigma(\mathrm{mg}(\ell))^2}{\mathrm{mg}(\ell)} + \frac{\sigma(\mathrm{mg}(t))^2}{\mathrm{mg}(t)}^{1/2} \qquad (10)$$

where the sigmas represent the standard deviation of the individual variables. Since all peak areas are measured with an integrator to better than ± 0.2 percent, the first and third terms can be neglected with respect to the error imposed by the sample injections into the GC or through the trapping system. Repetitive injections with a syringe are to within ± 5 percent in precision if one corrects for the dead volume in the needle. This 5 percent error in known sample volumes, hence in the known sample mass, is substituted into Equation (11) to obtain:

$$\frac{(C_x)}{C_x} = 4(5)^2 + (5)^2 + (5)^2{}^{1/2} = 12.3\% \qquad (11)$$

Therefore, neglecting possible errors due to sample inhomogeneity and sample handling, a safe upper limit to the standard deviation of the quantitative data is ± 12 percent.

The error in the carbon monoxide determinations is considerably more accurate than the data from the trapping experiments. Since the concentration of CO is read directly from a standard curve, the only significant error is in the injection of pure CO for calibration. The error imposed by multiple injections is most likely below ± 5 percent.

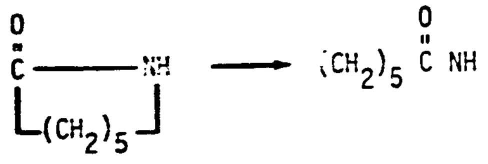
CHAPTER V

NYLON 6 POLYMER

A. Introduction

Nylon 6 is one of the most widely used polymeric materials in the area of synthetic fibers and plastics. Its production has been expanding continuously since 1939 when the first commercially produced Nylon 6 appeared on the market. The world consumption of Nylon fibers reached approximately 3.4 million tons in 1975 with a United States consumption of about one million tons.(48) In addition, over 83 thousand tons of molding grade resins were used in the United States in 1974.(49) Today Nylon 6 represents approximately 50% of the total polyamide volume used commercially. Although Nylon 6 has a lower melting point (215-220°C) than Nylon 66 (260°C), Nylon 6 has some advantages over the latter. First, the process used to produce Nylon 6 is relatively simple, inasmuch as the polymer can be produced by heating ε-caprolactam. Nylon 6 has better resistance to light degradation than Nylon 66, as well as possessing better dyeability, elastic recovery and fatigue resistance characteristics.

Nylon 6 is produced by the ring-opening reaction of ε-caprolactam. The ε-caprolactam monomer is usually synthesized from benzene, phenol, or cyclohexane. The synthesis of of Nylon 6 from ε-caprolactam proceeds without the formation of water.



(12)

ε-caprolactam Nylon 6

where n is about 200 for Nylon 6.

Nevertheless, in order to facilitate ring opening, water must be added to the reactor or autoclave in which the ε-caprolactam is undergoing polymerization. Water is removed in the course of the high-temperature reaction. The reaction proceeds to a point where the polymer is in equilibrium with about 10 percent of the monomer. The monomer, however, is easily stripped by washing the polymer with water.

Nylon 6, thus produced, is widely used in the form of fiber for production of fabrics used in apparel, tire cord, rope, monofilament fishing line and carpets. Molding grades of Nylon 6 polymer are also used in the manufacture of film, sheets, electrical,and automotive parts.

Like most of the other organic polymers, Nylon 6 is flammable when placed in contact with an ignition source. As the use of Nylon polymers has increased in commerce, there has been an increasingly greater demand for fire-retardant Nylon polymers. Numerous reports and patents have been issued pertaining to improved fire-retardancy of Nylon polymers, and some of these are summarized in Chapter 8. Little detailed information is available in the open literature pertaining to the basic mechanisms of the thermal degradation of Nylon polymers. One of the objectives of this study was the development of a better understanding of the thermal decomposition mechanisms of the thermal degradation of Nylon polymers.

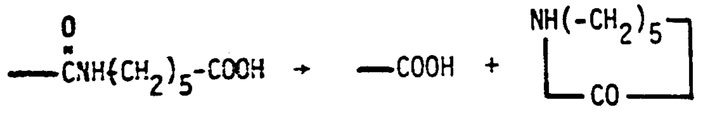
B. Literature Survey

Although several investigators have studied the thermal decomposition of aliphatic polyamides, their conclusions resulted in the presentation of conflicting decomposition mechanisms. The experimental procedures and the instrumentation used by these investigators did not furnish an accurate assessment of the thermal decomposition of these polyamide polymers.

1. Pyrolysis

Nylon 6 becomes reddish brown in color when it is heated in air between 225-245°C. When it is kept in a molten state for a long time, under nitrogen or under vacuum, a gel product is formed, which is insoluble in formic acid or hot phenol, but which swells in cresol and xylene.(50) This gel compound is thought to be formed by the catalysis of trace amounts of oxygen. A similar product can sometimes be found on the inside wall of reactors used to produce the polymers.

Tailor(51) observed that the viscosity of Nylon 66 polymer decreased sharply with the increase in the number of end-groups when the polymer solution was left in formic acid at high temperature. Several investigators(52,53) studied the equilibrium of Nylon 6 polymer in the molten state, and indicated the influence of the temperature and water on the depolymerization of the polymer. Smith(53) suggested the possibility of a back-biting reaction which forms monomeric lactam from molten Nylon 6:



$$-\overset{O}{\overset{\|}{C}}NH(CH_2)_5\text{-}COOH \rightarrow -COOH + \boxed{NH(\text{-}CH_2)_5 \; CO} \qquad (13)$$

This reaction was reported to be accelerated by water.

The formation of lactams from various polyamides during pyrolysis was also observed by Kricheldorf and Leppert.(54) They suggested the elimination of lactams could occur from the center of polymer chain through amide exchange reactions in molten polyamides.

The first precise study of the volatile products from polyamides was performed by Achhammer *et al.*(55,56) Nylon 6, 66, 66/6 and 610/6 were pyrolyzed at 420°C in high vacuum for 20 minutes. The degradation products found using mass spectrometric techniques were carbon dioxide, water, cyclopentanone, hydrocarbons containing less than seven carbons, and carbon monoxide. No nitrogen compounds were reported. From the nature of the products observed, they proposed that the polyamide chain breaks at C-N bond of the amide group.

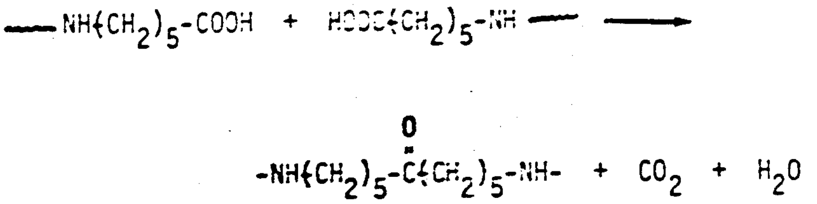
Hopff(51) reported that ammonia, cyclopentanone, and hexamethylenediamine were found in the thermal degradation product of Nylon 66, although no detailed experimental conditions and data were given.

Hasselstrom *et al.*(58) isothermally pyrolyzed Nylon 66 in a nitrogen atmosphere for 1 to 8 hours at 280-305°C. The base and acid present in the volatile products were collected by sulfuric acid and potassium hydroxide columns. The total amount of base and acid was measured by titration. Ammonia and ammonium carbonate were reported to be found in the volatile products from the pyrolysis, but no direct identification of these products was reported.

Straus and Wall(59) studied the pyrolysis of Nylon 6, 66, 610 and blends of these polyamides. Five different Nylon polymers were heated for 30 minutes at 400°C in a vacuum. Ten percent of weight of volatile products and 90 wt. percent of residual compound were recovered. The volatile products produced during thermal decomposition of Nylon 6 with a molecular weight of 60,000, were comprised of a mixture of carbon dioxide, water, and various hydrocarbons ranging from C_2 to C_8. No nitrogen-containing compounds were identified. Straus and Wall(59) also investigated the rates of thermal degradation of Nylon polymers in vacuum and found that the rate of volatilization observed during the isothermal pyrolysis of Nylon 6 in vacuum approached a maximum of 20-40 percent volatilization.

Kamerbeck *et al.*(60) carried out the pyrolysis study of Nylon 6 and 66 at 305°C in nitrogen. They postulated that primary and secondary reactions were involved in pyrolysis. Primary reactions, which take place at temperatures below 300°C, formed products which were mainly low-molecular weight volatiles, such as water, carbon dioxide, and ammonia. Secondary reactions, which take place at temperatures above 300°C, resulted in a high degree of crosslinking. Kamerbeck postulated the following reaction pathways to explain the formation of these light gases:

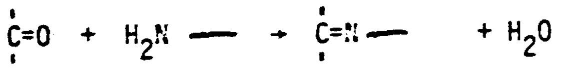
(a) Two carboxyl end groups might react as follows:



$$-NH(CH_2)_5-COOH + HOOC(CH_2)_5-NH- \longrightarrow -NH(CH_2)_5-\overset{O}{\overset{\|}{C}}(CH_2)_5-NH- + CO_2 + H_2O$$

(14)

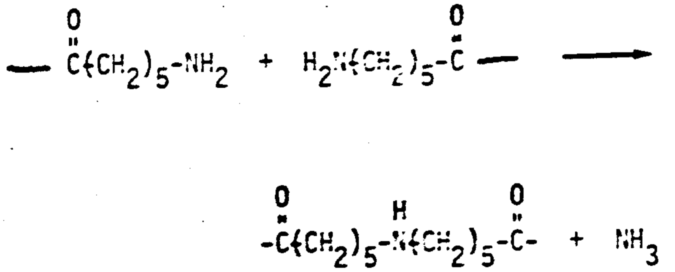
Also a carbonyl group can give rise to a branched structure:



$$\overset{|}{\underset{|}{C}}=O + H_2N- \rightarrow \overset{|}{\underset{|}{C}}=N- + H_2O$$

(15)

(b) Two amino end groups might react in the following way:



$$-\overset{O}{\overset{\|}{C}}(CH_2)_5-NH_2 + H_2N(CH_2)_5-\overset{O}{\overset{\|}{C}}- \longrightarrow -\overset{O}{\overset{\|}{C}}(CH_2)_5-\overset{H}{N}(CH_2)_5-\overset{O}{\overset{\|}{C}}- + NH_3$$

(16)

There was no explanation for the appearance of carbon monoxide in the work by Kamerbeck.

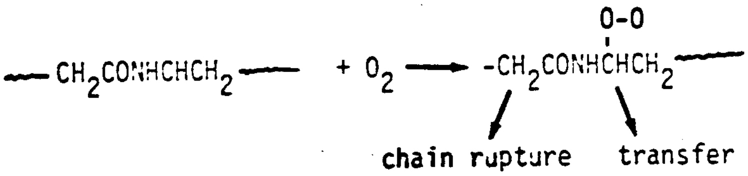
Several authors(61-63) reported in recent articles that the pyrolysis of Nylon resulted in depolymerization and not crosslinking of the aliphatic polymer chains. The overall decomposition process for Nylon was assumed to be typical of a random chain scission of linear chains similar to that reported for linear polyethylene.(64) This theory was based on the identification of ε-caprolactam and oligomeric units produced during the pyrolysis of Nylon 6 polymer. For example, Chelnokova and Rafikov(65) identified ammonia, carbon dioxide and cyclic monomer and oligomers during the pyrolysis of Nylon 6 and 66 at 350°C. Miunov *et al.*(66) indicated that the major products from the pyrolysis of Nylon was ε-caprolactam. Miunov also found that the amorphous region was more likely to be attacked by heat than the crystalline region. Similar observations were reported by Heuvel(67) and Goldstein(63) summarized their results and suggested that both free-radical and hydrolytic decomposition (caused by water tightly bound to the amide groups) occur simultaneously during the pyrolysis of Nylon polymers. Both the -C-N- and $-\overset{O}{\overset{\|}{C}}-CH_2-$ bonds were assumed to break during the thermal degradation.

2. Oxidative degradation

Levantovskaya *et al.*(68) determined the volatile products resulting from the oxidative degradation of polyamides and suggested a possible mechanism for the thermal oxidation of polyamides. The major products obtained from the thermal oxidation of Nylon 6 were water, carbon dioxide, and carbon monoxide. Methanol, formaldehyde, and acetaldehyde were formed in much smaller quantities. Levantovskaya assumed that the oxygen molecule initiates the chain process of oxidation in degradation. It has been suggested by the results of the photo-oxidation and irradiation of low-molecular-weight polyamides, that the most mobile hydrogen atom in the polyamide molecule may be on the carbon adjacent to the NH group.(69-71)

Levantovskaya, therefore, postulated the following mechanisms:

$$—CH_2NHCONHCH_2CH_2 \xrightarrow{O_2} —CH_2CONHCHCH_2— \quad + \; HO_2\cdot \qquad (17)$$



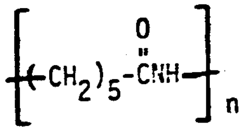
$$—CH_2CONHCHCH_2— + O_2 \longrightarrow -CH_2CONH\overset{O-O}{C}HCH_2— \qquad (18)$$

Sumi and Tsuchiya,(72) Woolley,(73) and Einhorn *et al.*(74) analyzed combustion products of polymeric materials containing nitrogen. In addition to carbon monoxide, carbon dioxide, and water, significant amounts of hydrogen cyanide were observed from the combustion of Nylon 6 polymer.

In addition to the literature quoted, there are a number of other references which are available for developing a better understanding of the thermal degradation of Nylon polymers. Three such references are by Madorsky,(18) Conley,(13) and Stepniczka.(75)

C. Experimental Program

The sample of Nylon 6 polymer used in this study was received through the courtesy of Teijin, Inc., Japan. The assumed structure of this Nylon 6 polymer is:



$$\left[(CH_2)_5-\overset{O}{\overset{\|}{C}}NH \right]_n$$

with a molecular weight of 113 per repeat unit.

1. Polymer characterization

The Nylon 6 sample was crushed into powder and dried at 10^{-6} torr pressure at 60°C for one week.

Elemental analysis. Carbon, hydrogen, nitrogen,and oxygen analysis was performed on the Nylon 6 polymer in this laboratory. A summary of the results of this elemental analysis is present in Table 15, together with the theoretical composition based upon the assumed monomeric unit. Excellent agreement was found between the experimental results and those obtained by theoretical calculation. According to the manufacturer's information, a slight amount of titanium oxide was added to the polymer as a pigment; this pigment may account for the slight difference between the actual and calculated elemental composition.

Table 15. Elemental Composition of Nylon 6 Polymer

Element	% Composition	
	Sample as received	Theoretical*
Carbon	63.82	63.69
Hydrogen	9.92	9.80
Nitrogen	12.41	12.38
Oxygen	13.85	14.13
Total percent	100.00	100.00

*Composition based upon the structure of the monomeric unit.

Infrared analysis. The infrared spectrum for the Nylon 6 polymer, shown in Figure 11, was obtained using a thin film prepared from polymer

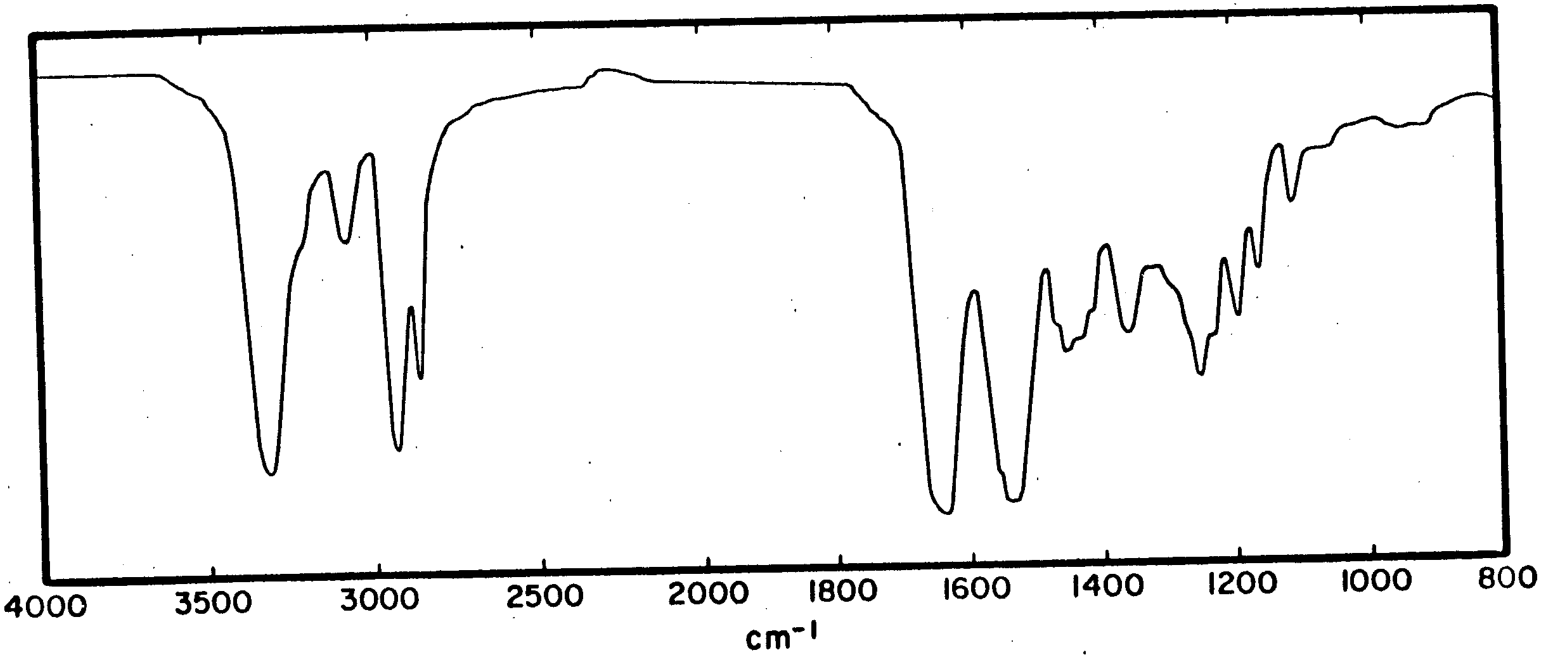


Figure 11. The infrared spectrum of Nylon 6.

melt. The spectrum is identical with a standard spectrum of Nylon 6 polymer. A summary of the band assignments for this spectrum is presented in Table 16.

2. Thermoanalytical studies

A series of experiments were conducted to determine the effects of dynamic heating rate and the oxygen content of the degradation environment on the decomposition of the Nylon 6 polymer. Simultaneous thermal analysis procedures (DTA, DTG and EGA) were used to follow the decomposition process.

Effect of heating rate on polymer degradation. Samples of Nylon 6 polymer, 10 ± 0.1 mg, were heated at 6, 10, 25,and 100°C/min. rates from ambient to 1000°C to determine the effect of heating rate on the decomposition process. Figure 12 is a composite drawing containing the averaged TGS (three runs per sample) spectra conducted in an air environment at the selected four heating rates. There was no noticeable weight loss at any of the four heating rates below 270°C in this environment. The samples lost weight gradually until a temperature of 350°C was reached. A marked increase in the rate of weight loss occurred at approximately 375°C; by 450°C approximately 90 percent weight loss had occurred in all samples heated at the pre-selected heating rates. During this degradation mode the sample was observed to turn color, first brown, then black. At approximately 415°C a yellow smoke appeared and clear liquid droplets were observed to form at the outlet tube of the quartz furnace. The major degradation step which occurred between 350° and 450°C was insensitive to the heating rate. The

Table 16. Infrared Analysis of Nylon 6 Polymer

Frequency (wave numbers)	Band Intensity	Assignment
3310	S	N-H stretch
3060	W	Amide II
2930	M	Asymmetric N-H stretch
2840	M	Symmetric N-H stretch
1640	S	C = O Stretch (Amide I)
1540	S	N-H Bend (Amide II)
1450	M	CH_2 bend
1250	M	Amide III
1190	W	Amide III
1160	W	Amide III

S = strong

M = medium

W = weak

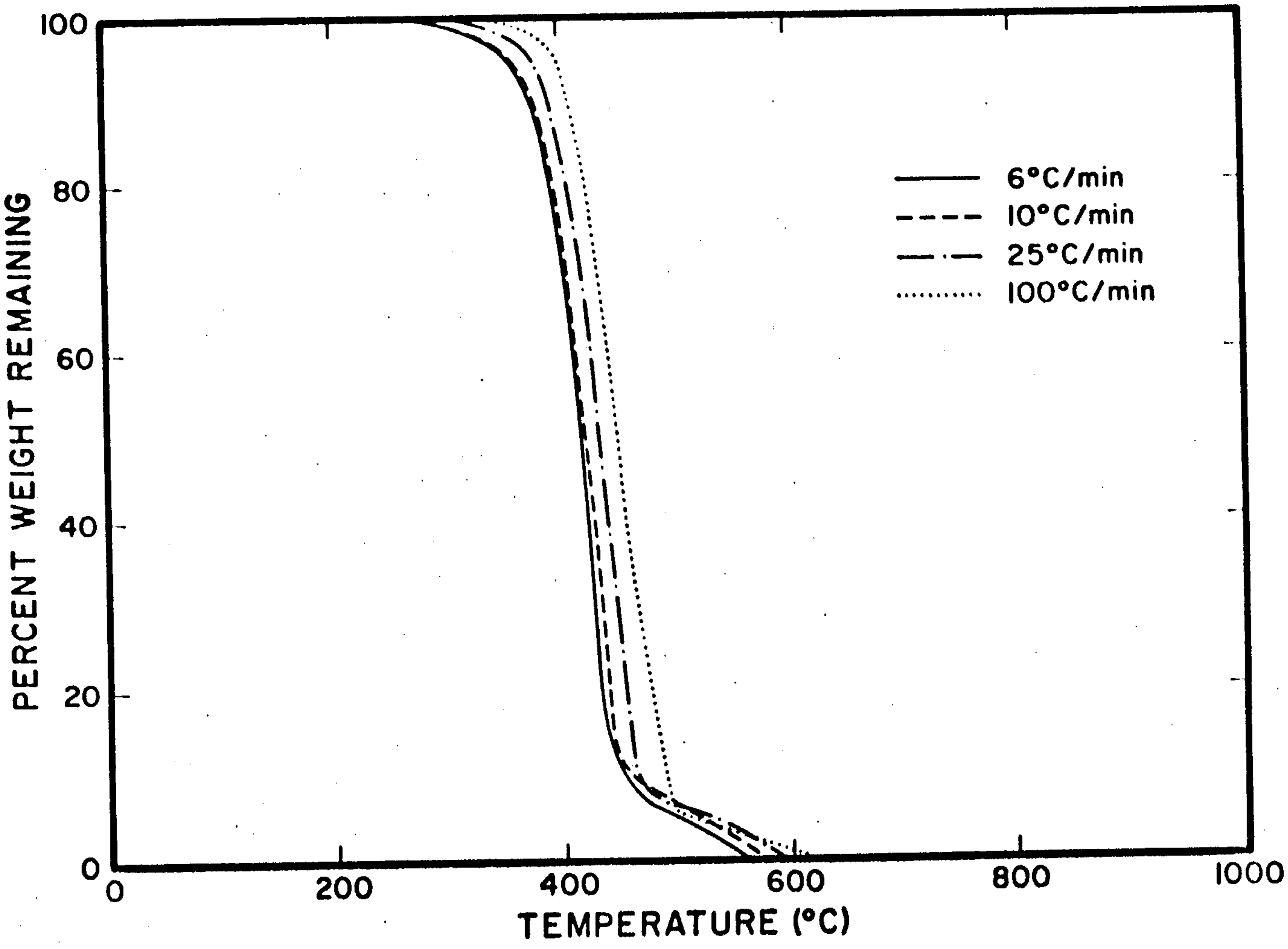


Figure 12. Effect of heating rate on sample weight loss for Nylon 6 in air.

polymer residue remaining above 500°C was observed to be in the form of a black char layer that degraded at an appreciably slower rate. The remaining char was decomposed by 560°C at the slowest heating rate and by 640°C at the heating rate of 100°C/min.

Effect of environment on polymer degradation. Little overall differences were observed when samples of the Nylon 6 polymer were decomposed in oxygen, air and helium environments. Figure 13 is a composite figure which contains the TGA spectra obtained during thermal decomposition of the Nylon 6 polymer in the three environments. The polymer ignited spontaneously at approximately 425°C in the oxygen environment, but in an air atmosphere it was observed to slowly form a black char without ignition. The polymer sample which was heated in the helium environment did not begin to discolor until approximately 265°C (25°C higher in temperature than was observed in samples in the oxidative environments). It should be noted that a char was not formed during the decomposition of the Nylon 6 polymer in the inert helium environment.

The simultaneously-generated DTA and DTG traces for the three environments under investigation for Nylon 6 polymer are presented in Figures 14 and 15, respectively. A heating rate of 10°C/min was used in all of these experiments. As indicated in Figure 14, the degradation process in helium was a slightly endothermic process. In both air and oxygen environments the decomposition process was highly exothermic.

The DTA curve corresponding to thermal decomposition in the air environment was composed primarily of a single peak with a maxima at

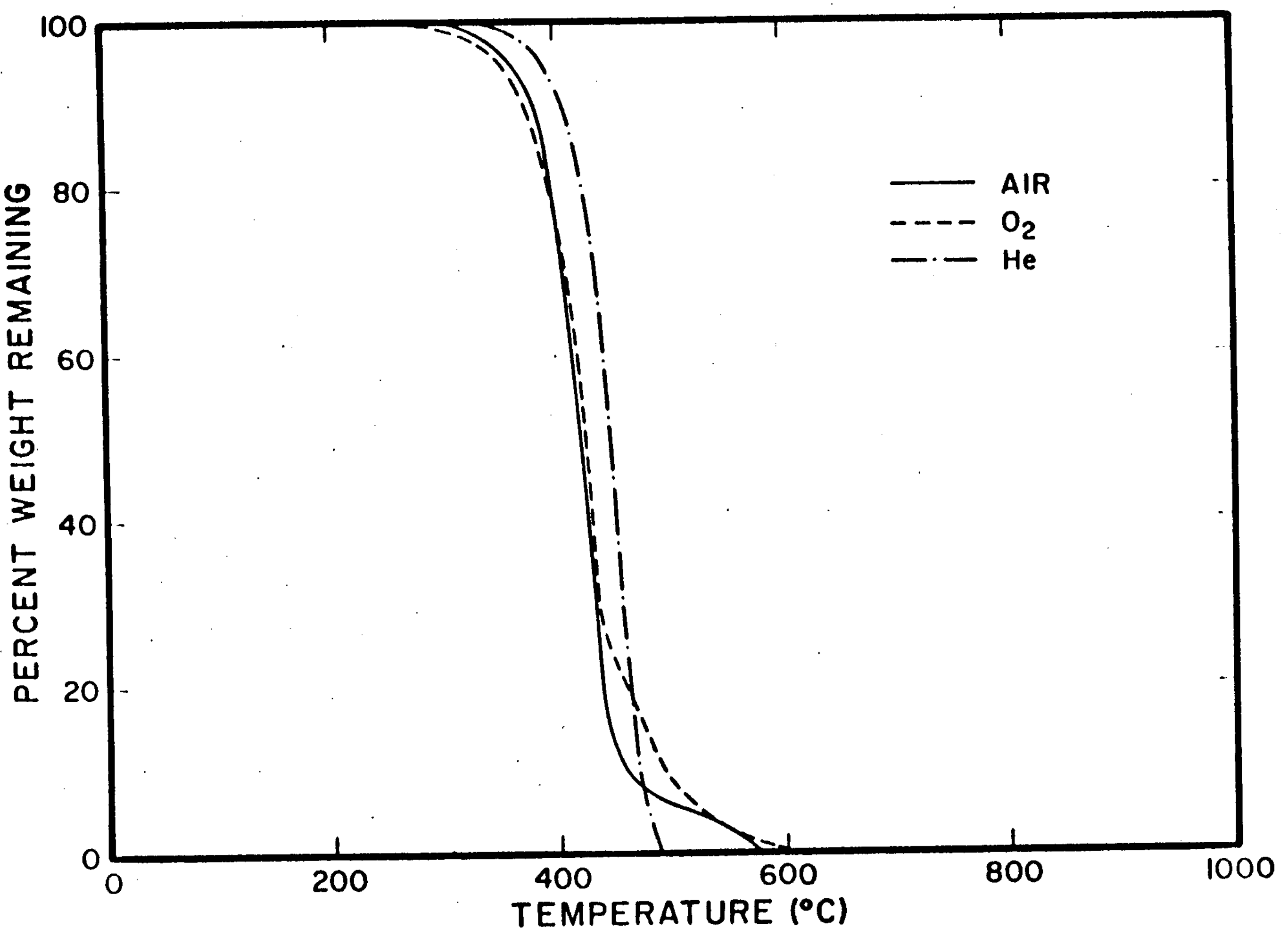


Figure 13. The effect of environment upon the weight loss of Nylon 6 at a heating rate of 10°C/min.

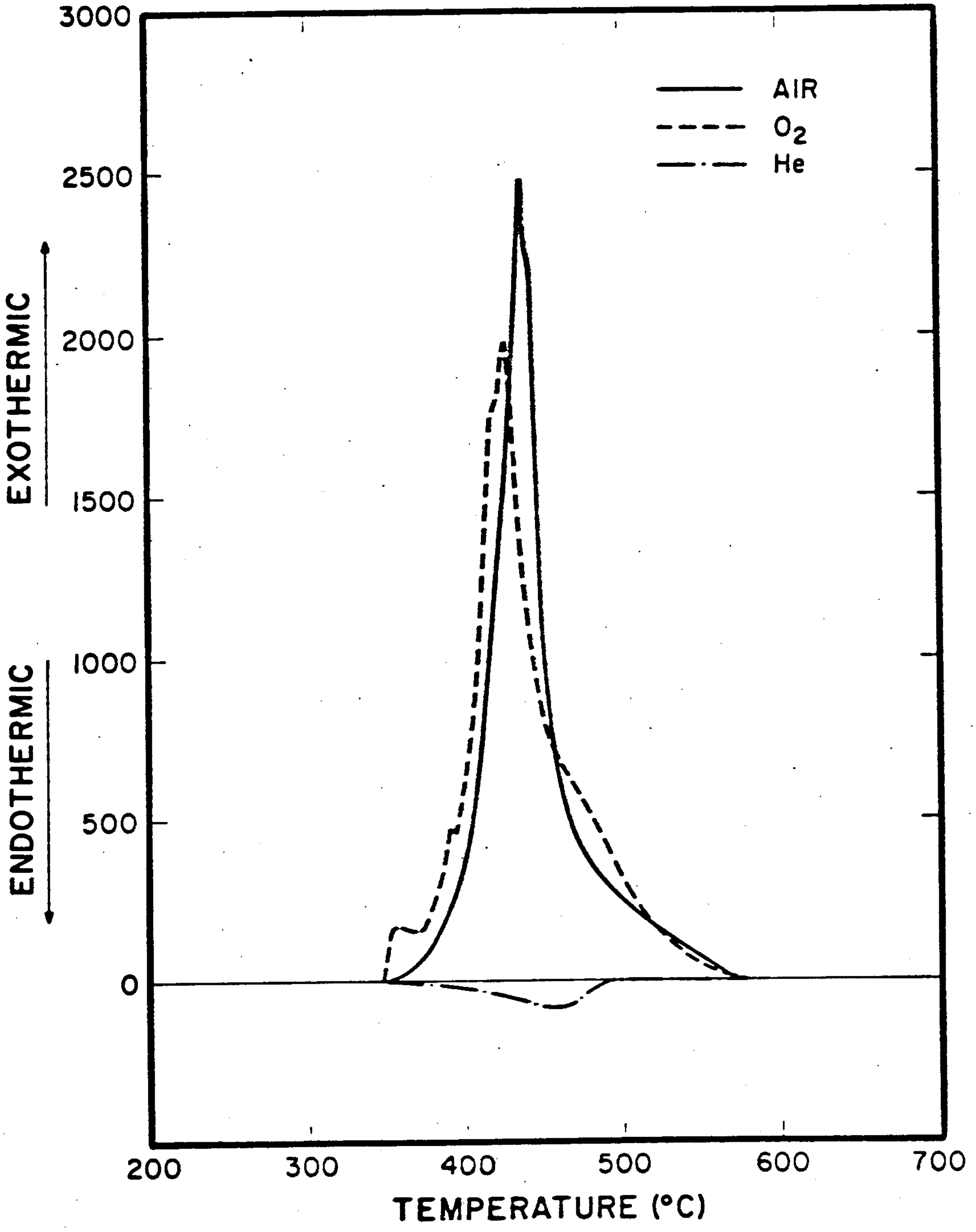


Figure 14. The DTA traces for Nylon 6 polymer in helium, air, and oxygen environments.

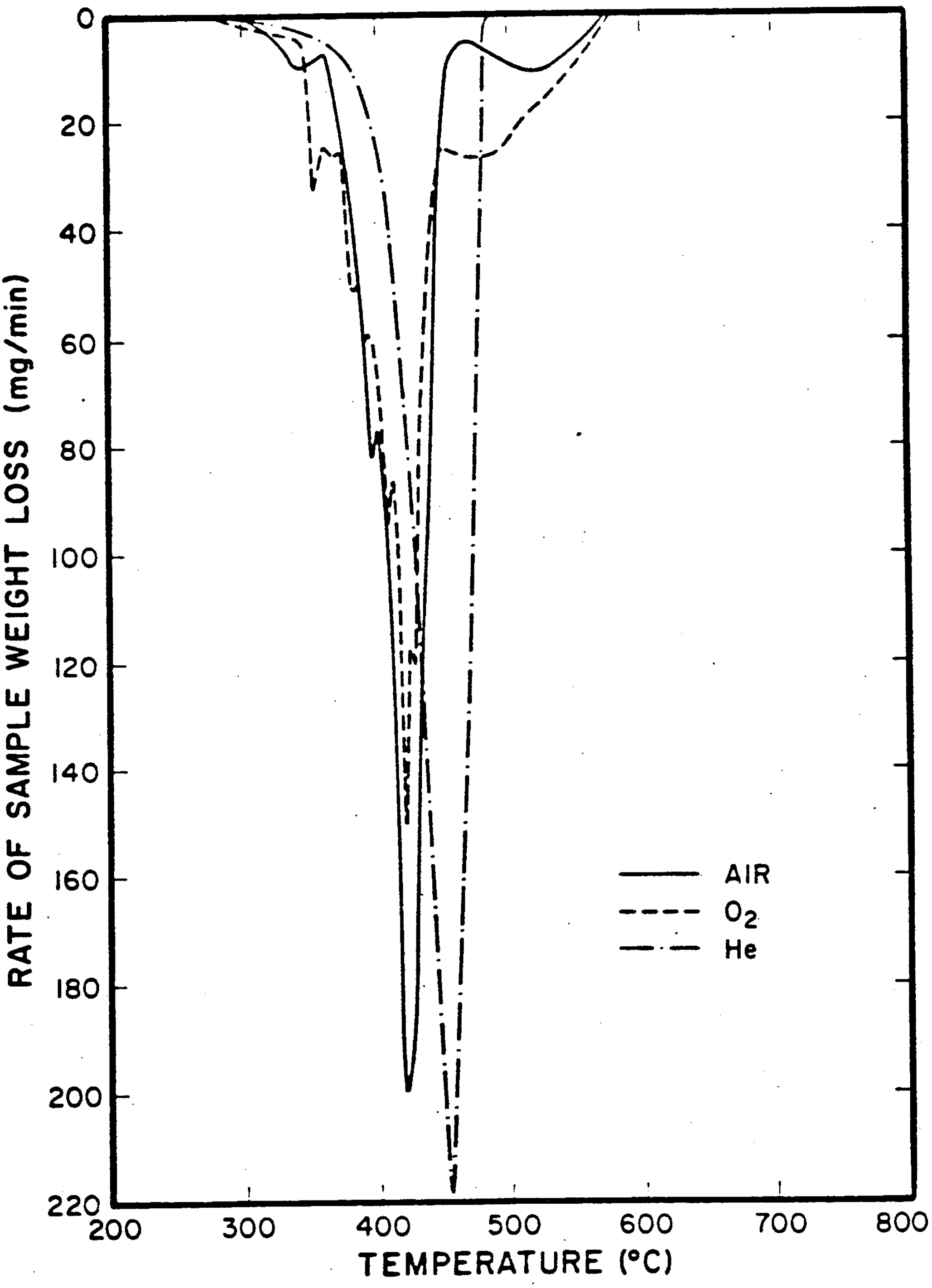


Figure 15. The DTG traces for Nylon 6 polymer in helium, air, and oxygen environments at 10°C/minute.

436°C. A slight tailing in the DTA curve at higher temperatures may be due to the decomposition of the char structure. In the oxygen environment the DTA curve was more complicated, exhibiting several peaks in addition to the main maxima observed at 428°C.

The DTG traces (Figure 15) exhibited more details of the decomposition process. In the helium environment there was an additional peak at 454°C. The curve is symmetric with the exception of the low temperature region, indicating that the degradation mechanism in helium is rather simple and may consist of a single decomposition process.

In both air and oxygen environments the DTG traces indicated that several decompositions take place. In air there was one major maxima at 425°C and several small maxima were observed at 341°C, 396°C and 525°C. The broad peak at 525°C corresponds to oxidative decomposition of the char structure.

In an oxygen environment more distinct maxima were found to appear in the DTG trace. The major weight losses occurred at 354°C, 421°C, 427°C and 490°C. In addition to these peaks, several additional minor peaks were observed.

Table 17 contains a summary of the more important features that were observed upon heating the Nylon 6 polymer in the helium, air, and oxygen environments. These include the temperature of the DTG maxima, the temperatures where 5, 50 and 90% of the sample was consumed, the reaction thermodynamics that were observed and the amount of residual chars remaining at "i point" (see Figure 6).

Table 17. The Effect Of Environment Upon The Degradation Of Nylon 6[a]

Environment	DTG Maxima[b]			Temperatures At Weight Loss Of			Overall Reaction Thermodynamics	% Char[c] at "i" Point
	1st	2nd	3rd	5%	50%	90%		
Helium	---	454	---	394	447	468	Slightly Endothermic	No Char
Air	341	425	525	377	421	475	Exothermic	8%
Oxygen	354	421	490	359	427	503	Exothermic	27%

[a] Data obtained from a programmed heating rate of 10°C/min from room temperature to 1000°C.

[b] Temperatures at which the derivative of the sample weight losses were at a maxima.

[c] Amount of Char remaining at "i" point.

3. Pyrolysis studies

Pyroprobe (fast heating) studies. The initial pyrolysis experiments were carried out using the direct probe pyrolysis unit that was inserted into the injection port of the GC. Pyrolysis experiments were performed with the probe temperature set at 1000°C. A fast-heating ramp was employed to reach the pre-selected temperatures as quickly as possible. The final probe temperature was maintained for 20 seconds to insure complete pyrolysis of the sample. A 3 to 4 mg sample of Nylon 6 was used for these experiments; pyrolysis resulted in approximately an 85 percent sample weight loss.

The pyrolysis of the Nylon 6 polymer was followed using three different GC columns for separation and identification of degradation products: 5 m long by 4 mm O.D. column packed with Chromosorb 101; a 3 m long by 4 mm O.D. column packed with Chromosorb 103; and a 5 m long by 4 mm O.D. column packed with Chromosorb 104. The temperature of the GC was raised at a rate of 10°C per minute from 0°C to 260°C in order to separate and identify the decomposition products.

Figure 16 is a composite figure containing the chromatograms obtained using the Chromosorb 101, 103 and 104 supports. The absolute amounts of each component were calculated from the integrated GC peak areas using internal standards and the technique described in Chapter IV. Almost all the volatile compounds were identified by the GC/MS techniques. About 43 percent (428.3 mg of volatile compounds per gram of the original sample) was accounted for by the degradation products listed in Table 18. This group of compounds accounts for approximately 97 percent of the volatile compounds produced, as indicated by the

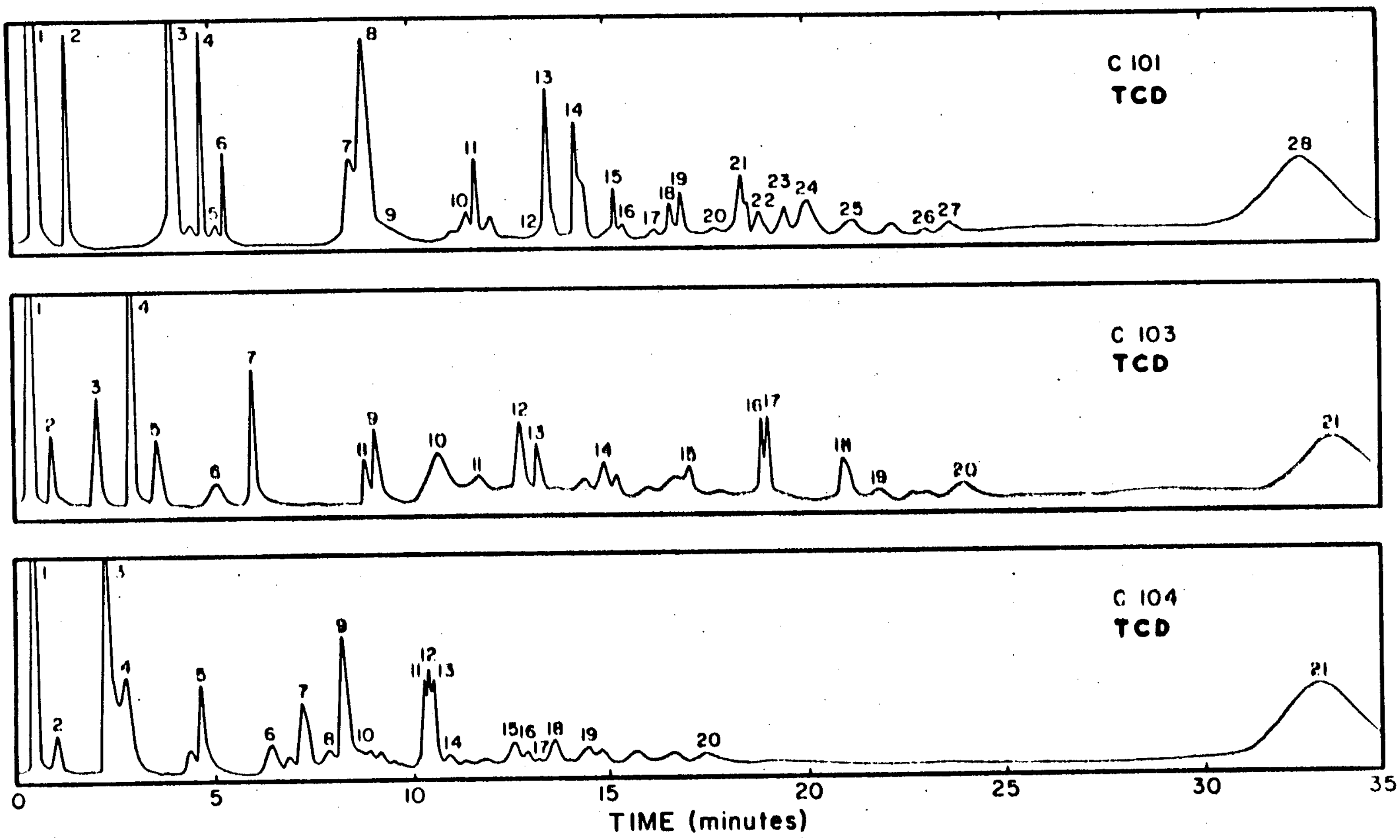


Figure 16. Low-boiling volatile products produced during the thermal decomposition (fast heating) of Nylon 6 at 1000°C.

Table 18. Low-Boiling Volatiles Produced During The Pyrolysis (Fast Heating)[a] of Nylon 6

Compound	Peak Number[c] (C101)	Peak Number[c] (C103)	Peak Number[c] (C104)	Quantity[b]
Low-boiling Volatiles				
Carbon monoxide	1	1	1	47.30
Methane	2	2	2	23.71
Carbon dioxide	3	3	3	18.79
Ethylene	4	4	4	63.23
Acetylene	5			Trace
Ethane	6	5		10.58
Ammonia[d]		6		14.35
Water	7	10	9	20.33
Propene	8	7	5	49.78
Hydrogen cyanide	9		10	Trace
1-Butene	10	8	6	7.66
1,3-Butadiene	11	9	7	14.10
1-Pentene	12	11	8	5.56
Acetonitrile	13	12	12	11.91
Propenenitrile	14	13	11	14.74
Propanenitrile	15	14	15	12.98
Methacrylonitrile	16		14	1.05
3-Butenenitrile	17			0.93
Benzene	18	15	13	2.51
Butanenitrile	19	17	17	6.41
Pyrrole	20			3.38
Toluene	21	16	16	7.57
Cyclopenatanone	22		18	1.57
Capronitrile	23	18	19	11.17
Hexenenitrile	24	19		4.57
Styrene	25			0.95
Phenol	26			0.84
Benzonitrile	27	20	2-	0.93
E-Caprolactam	28	21	21	71.38
Total (mg/g sample)				428.28

[a] Direct probe pyrolysis at 1000°C for 20 seconds using a 3.5 mg sample in a helium atmosphere.

[b] Milligrams of compound per gram of sample consumed during pyrolysis. Determined mostly on C-101.

[c] Correspond to peak numbers on Figure 16.

[d] Determined on C-103.

electronic integrator. The peak numbers refer to the peaks in the TC detector response curve found in Figure 16.

The major pyrolysis products produced during the decomposition of the Nylon 6 polymer (as indicated in Table 18) were carbon monoxide, ammonia, carbon dioxide, water, ε-caprolactam, and a series of aliphatic saturated and unsaturated hydrocarbons and nitriles, containing one to seven carbon atoms. Small concentrations of aromatic compounds, including benzene and toluene, were also found in the complex combustion products mixture. Another compound of toxicological importance, hydrogen cyanide, was identified in the mixture of pyrolysis products.

Inasmuch as only 43 percent of the original sample was accounted for during this analysis of the low-boiling volatiles, it was assumed that the remaining portion of the sample decomposed was in the form of high-boiling volatiles (aerosols) or tars which either condensed within the combustion/analytical system or were trapped irreversibly on the GC support columns. The large amount of ε-caprolactam identified in the mixture of combustion products suggests the possible degradation mechanism is a depolymerization process.

<u>Thermoanalyzer (slow-heating) studies</u>. Samples of the Nylon 6 polymer were pyrolyzed in a helium environment in the thermoanalyzer. The heating rate to which the polymer was exposed was 100°C/min. programmed from ambient to 1000°C. The polymer sample was virtually consumed by the time the temperature of the furnace reached 700°C. A sample size of 50 mg was found to be optimum for both the identification and quantification of the decomposition products.

The low-boiling volatiles produced during the pyrolysis of the

Nylon 6 polymer in a helium environment were collected using the trapping system described previously, desorbed from the porous polymer trap. and analyzed using the computerized GC/MS system.

A variety of GC columns, the same as employed for the analysis of volatile products produced during the fast-heating experiments, were used for positive identification of the individual decomposition products.

In these experiments the effluents from the thermoanalyzer were trapped for subsequent analysis, beginning at 250°C, which was a temperature level just below the range where the first major weight loss was encountered. Trapping of degradation products was continued for a five-minute period, after a temperature of 1000°C was attained, in order to collect products which remained in the furnace of the thermoanalyzer or in transfer lines.

A total of nine pyrolysis experiments were conducted. Five pyrolysis runs utilized a Chromosorb 101 support. The remaining experiments utilized Chromosorb 103 and 104 supports, in order to identify compounds which were not separated by Chromosorb 101 and to provide additional information necessary for positive identification of the decomposition products. Ammonia, for example, which was not identified on the Chromosorb 101 column, was separated and quantified on a Chromosorb 103 support. The chromatographic columns were programmed from -10°C to 260°C at a heating rate of 10°C/per minute. Typical FID and TC detector traces obtained using the Chromosorb 101, Chromosorb 103 and Chromosorb 104 supports are illustrated in Figures 17, 18 and 19, respectively. More than 25 degradation products, which were identified

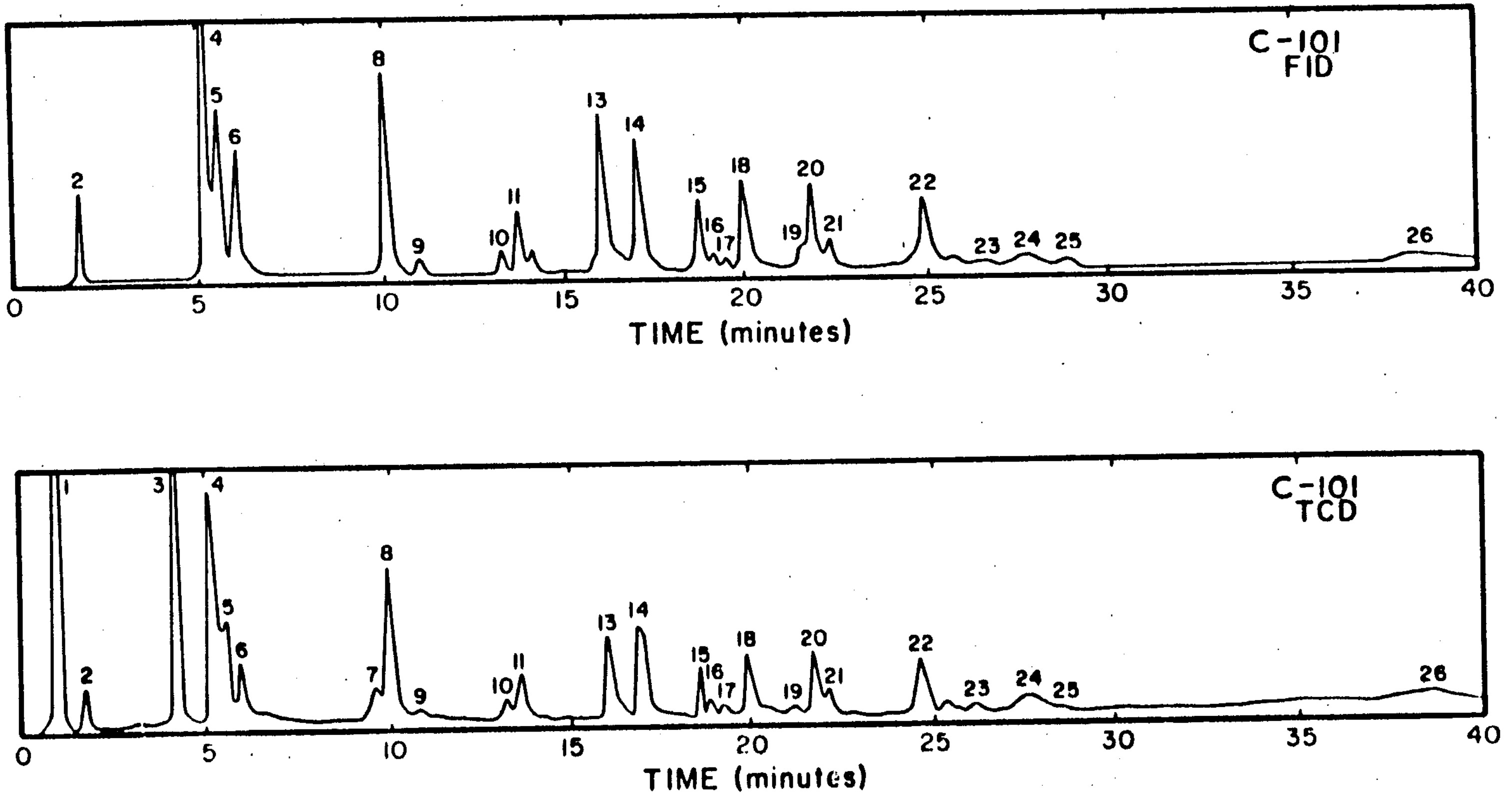


Figure 17. Low-boiling volatile products produced during the pyrolysis (slow heating) of Nylon 6 in helium.

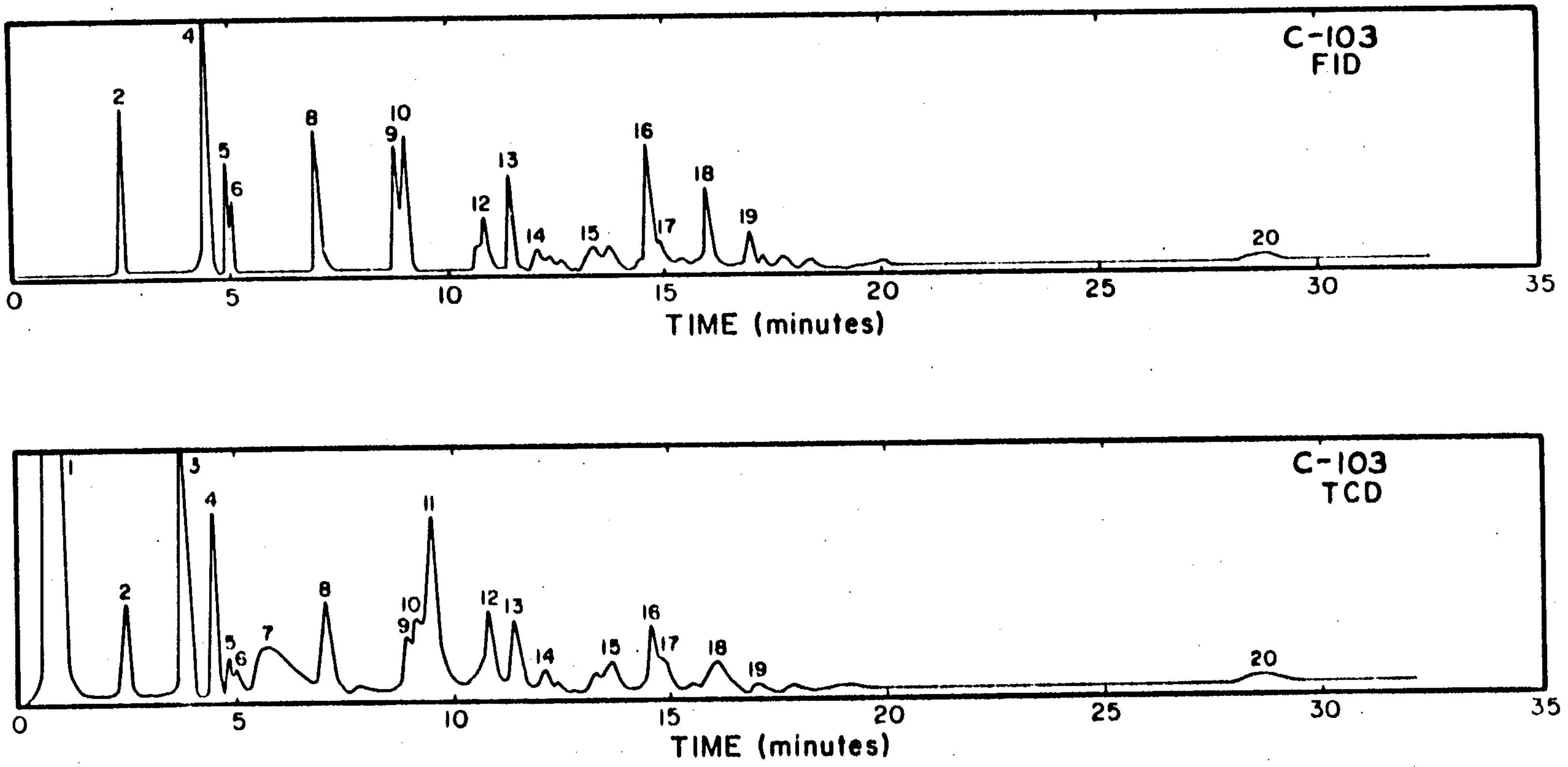


Figure 18. Low-boiling volatile products produced during the pyrolysis (slow heating) of Nylon 6 in helium.

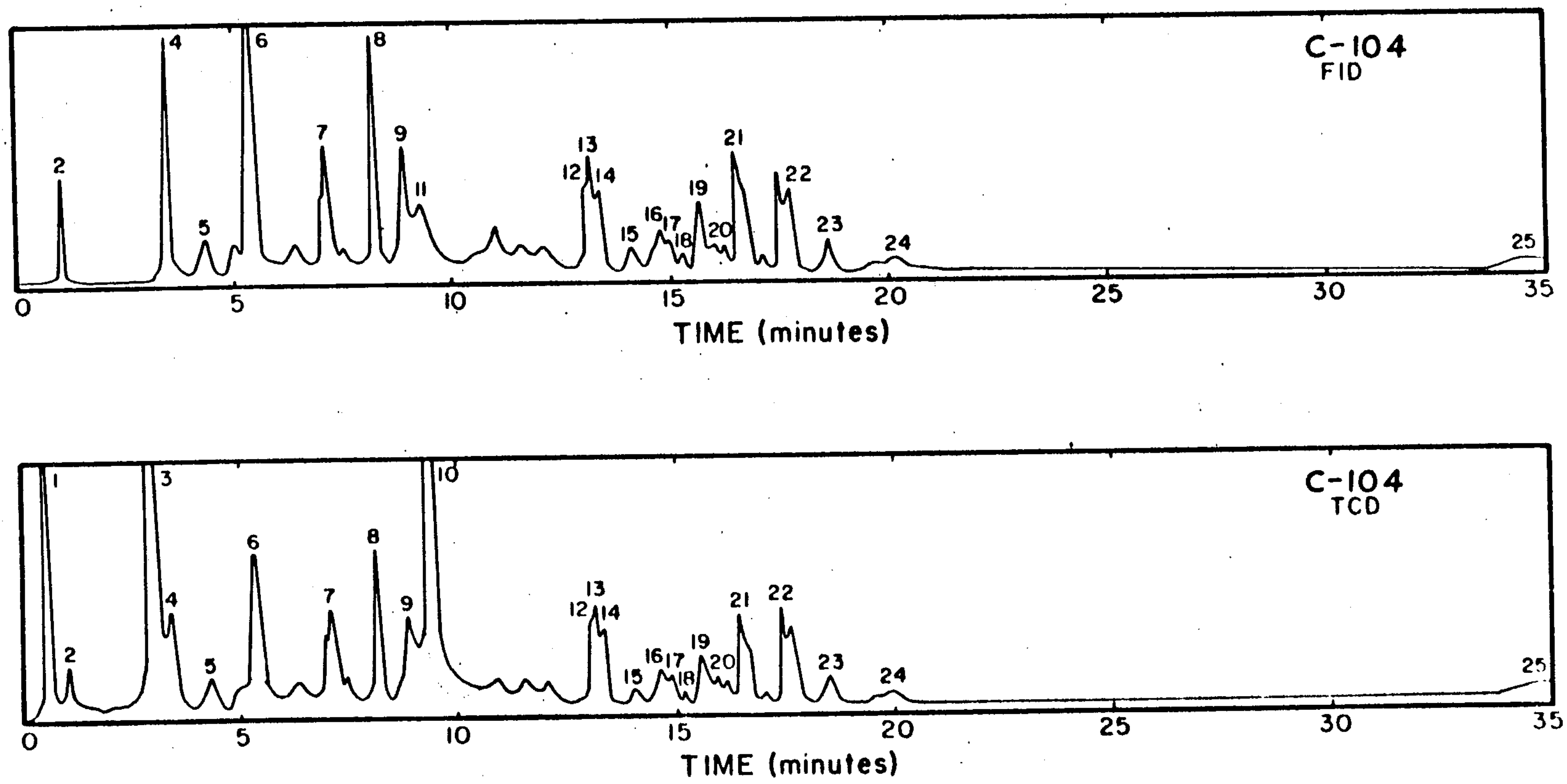


Figure 19. Low-boiling volatile products produced during the pyrolysis (slow heating) of Nylon 6 in helium.

and quantified in this phase of the research program are listed in Table 19.

The carbon monoxide fraction in the evolved gases, which was observed at a temperature of 280°C or higher, was quantified in a separate experiment using a non-dispersive infrared spectrometer. This carbon monoxide fraction accounted for 48 mg/gram of the original sample.

As indicated in Table 19, 32.31 mg/g of the original sample weight were identified and quantified as low-boiling volatile compounds that were liberated during the slow-heating pyrolysis experiments.

Samples of the high-boiling volatiles (aerosols) that condensed on the glass wool trap were extracted with acetone and analyzed by IR spectroscopy, GC/MS, HPLC,and elemental analysis.

The aerosol residue which was extracted from the glass wool by acetone and condensed by evaporation techniques was in the form of a viscous brown oil. This compound was spread on a sodium chloride plate and the infrared spectrum, illustrated in Figure 20, obtained. The IR spectrum closely resembled the spectrum of the original Nylon 6 polymer (see Figure 11).

Since this residue dissolved easily in ordinary solvents, such as acetone, dioxane,or toluene, this fraction was assumed to be composed of oligomers of Nylon 6.

A Chromosorb 101 column and an OV-1 column were used for separation of the aerosol residue. A considerable amount of ε-caprolactam and a small benzonitrile fraction were identified from the aerosol residue. Figure 21 illustrates the chromatogram of the residue

Table 19. Low-Boiling Volatiles Produced During The Pyrolysis (Slow Heating) of Nylon 6

Compounds	Peak Numbers[a]			T.E.[b]	R.F.[c]	Quantity[d]
	on C101	on C103	on C104			
Low-Boiling Volatiles						
Carbon monoxide	1	1	1	---	0.670	48.00
Methane	2	2	2	0.05	1.031	55.40
Carbon dioxide	3	3	3	0.97	0.915	18.76
Ethylene	4	4	4	0.96	0.980	39.29
Acetylene	5	5	5	0.96	0.930	4.36
Ethane	6	6		0.98	1.031	3.85
Ammonia		7	6	0.90	0.561	30.82
Water	7	11	10	0.82	0.550	18.85
Propene	8	8	6	0.98	0.652	46.92
Hydrogen cyanide	9		11	0.99	1.500*	5.43
1-Butene	10	9	7	0.97	0.697	2.41
1,3-Butadiene	11	10	8	0.97	0.674	5.16
1-Pentene	12		9	0.97	0.706	3.57
Acetonitrile	13	12	12	0.95	0.961	5.57
Propenenitrile	14	13	13	0.95	0.682	8.99
Propanenitrile	15	o4	16	0.95	0.650	3.27
Metacrylonitrile	16		15	0.95	0.682	0.98
3-Butenenitrile	17		18	0.95	0.727	0.70
Benzene	18	15	14	0.90	0.780	3.93
Butanenitrile		17	19	0.95	0.756	2.37
Pyrrole	19		20	0.90	0.727	0.66
Toluene	20	16	17	0.95	0.794	4.14
Cyclopenanone	21		21	0.90	0.827	0.60
Capronitrile	22	18	22	0.90	0.805	4.34
Hexenenitrile	23	19	23	0.90	0.785	2.11
Styrene			21	0.88	0.800	1.28
Phenol	24			0.88	1.105	0.25
Benzonitrile	25		24	0.88	0.895	1.10
E-Caprolactam	26	20	25	---	0.957	---
Total Low-Boiling Volatiles						323.11
High-Boiling Volatiles						
E-Caprolactam						129.80
Oligomer						519.00
Total High-Boiling Volatiles						648.80
Total (mg/g sample)						971.91

*Estimated

[a] Corresponds to peak numbers in Figure 17, 18, and 19 on Chromosorb 101, Chromosorb 103, and Chromosorb 104 respectively.

[b] Relative trapping efficiencies.

[c] Relative Response factors for the thermal conductivity detector.

[d] Milligrams of compound produced per gram of original polymer.

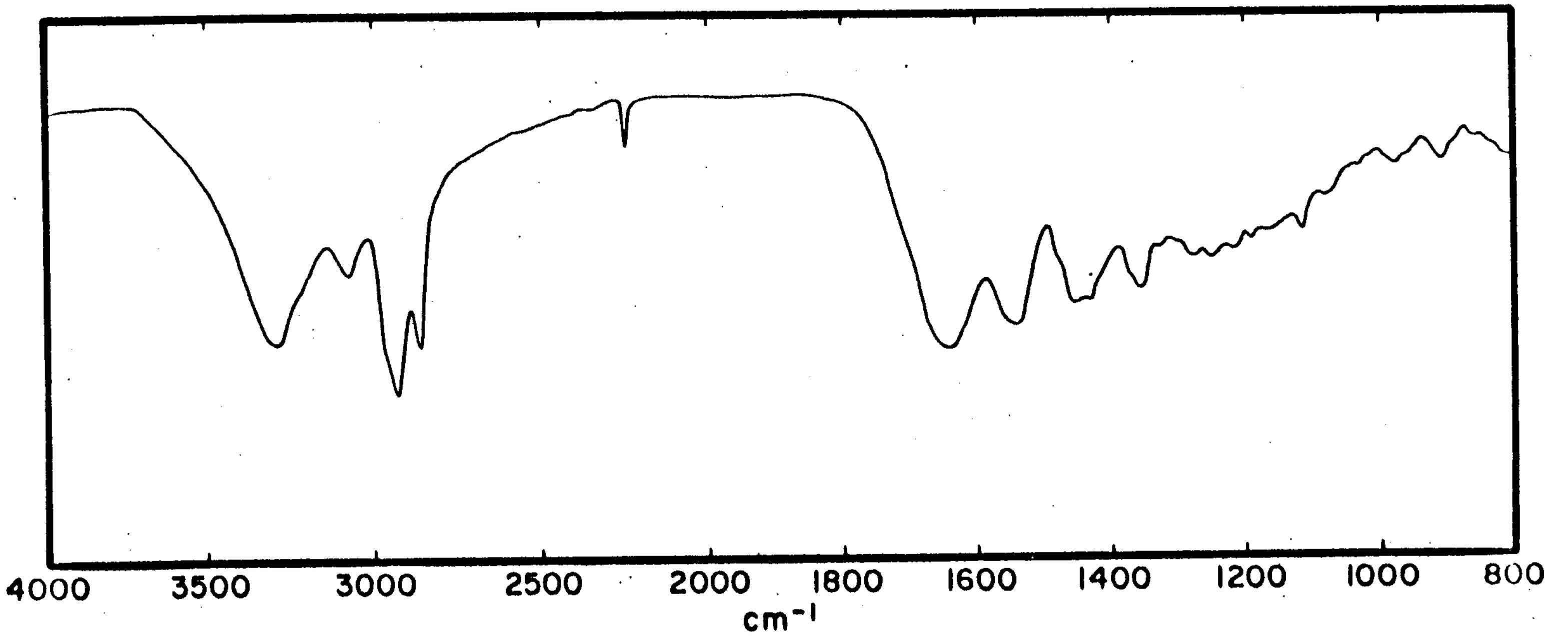


Figure 20. The infrared spectrum of the high-boiling volatiles produced during the pyrolysis (slow heating) of Nylon 6 in helium.

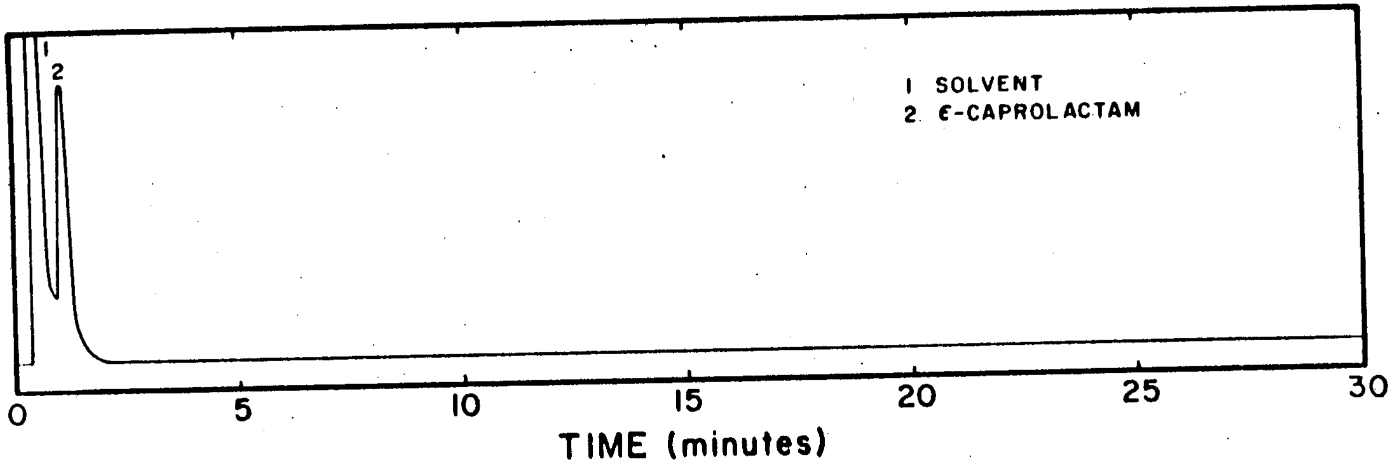


Figure 21. High-boiling volatiles produced during the pyrolysis (slow heating) of Nylon 6 in helium (On OV-1-3%).

obtained using an OV-1 column in the temperature range of 180°C to 220°C. The major peak is ε-caprolactam, which was determined to be approximately 20 percent of the aerosol residue. The insoluble component of the high-boiling volatile fraction was assumed to be composed of oligomers of Nylon 6.

The high-boiling volatiles were dissolved in acetonitrile and injected to the reverse-phase Whatman ODS column of the high performance liquid chromatograph, Perkin-Elmer Model 601 (Figure 22). A 35/65 mixture of CH_3CH/H_2O was used for mobile phase with a flow rate of 1.0 ml/min and the separated compounds were monitored by UV detector. The major peak (see Figure 22) was found to be ε-caprolactam; no other significant low molecular compounds were found.

The high-boiling volatiles were analyzed for carbon, hydrogen, nitrogen and oxygen content. The results of these duplicate analyses are listed in Table 20, together with the theoretical composition of Nylon 6 polymer and ε-caprolactam.

The composition of the residue was found to be similar to the theoretical values calculated for the Nylon 6 polymer and ε-caprolactam. These results indicate that the aerosol residue is composed of the mixture of ε-caprolactam and oligomers of the Nylon 6 polymer.

As indicated previously in Table 19, 37.31 mg/g of original sample was recovered in the form of low-boiling volatiles. 649 mg/g of original sample were recovered in the form of high-boiling aerosols. It is assumed that the unaccounted for weight loss was attributed to light gases, such as nitrogen or hydrogen, which were not trapped in the system used, plus additional compounds which condensed in the

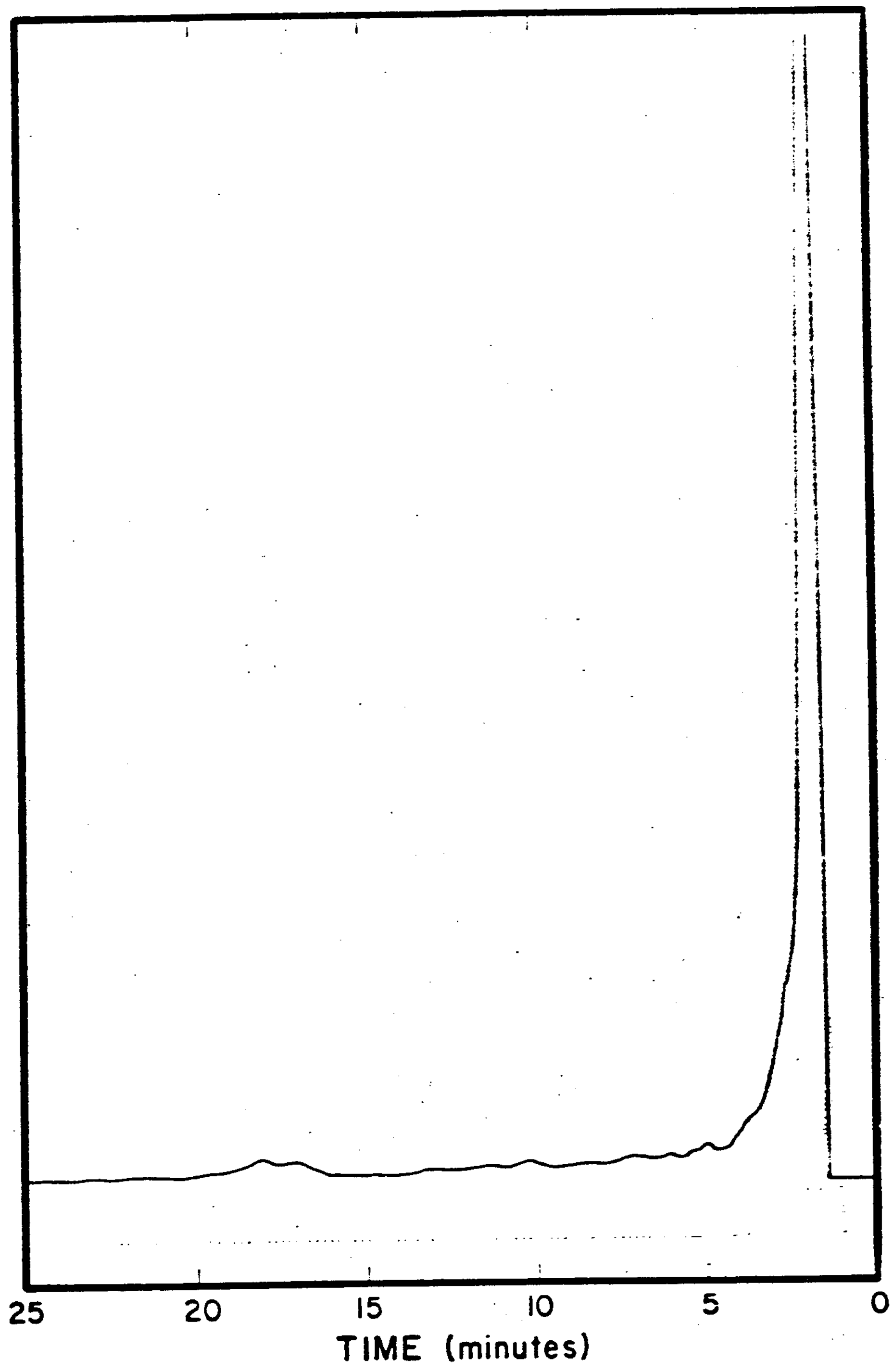


Figure 22. Liquid chromatogram of the high-boiling volatiles produced during the pyrolysis (slow heating) of Nylon 6 in helium.

Table 20. Elemental Composition Of The High-Boiling Volatiles Produced During the Pyrolysis (Slow Heating) Of Nylon 6

	% Composition				Total %
	Carbon	Hydrogen	Nitrogen	Oxygen	
Residue	62.98	10.13	11.16	15.73	100.00
Theoretical composition of E-caprolactam	63.72	9.73	12.39	14.16	100.00
Theoretical composition of nylon 6 polymer	63.72	9.73	12.39	14.16	100.00

combustion system and did not elute from the furnace or GC column.

As shown in Table 19, carbon monoxide, methane carbon dioxide, ethylene, ammonia, water, propane and ε-caprolactam comprised major products formed during the pyrolysis of Nylon 6. The ratio of content of these major products is similar to the product distribution that was found using the direct probe pyrolysis unit (see Table 18). A substantial amount of saturated or unstaturated hydrocarbons, aliphatic nitriles,and several aromatic compounds were also formed during the pyrolysis of the Nylon 6 polymer using the thermoanalyzer. The concentration of hydrogen cyanide was found to form in higher amounts during the slow heating experiments, as compared to the concentrations of this product formed during the direct probe pyrolysis studies.

No evidence of char structure was observed during these thermal degradation studies. This is consistent with previous studies reported in the literature as well as the thermoanalyzer traces obtained in the present work.

Materials Balance. The total quantity of pyrolysis products produced during the decomposition of the Nylon 6 polymer was 971.9 mg (97.2 percent)/gram of the original sample weight. Table 21 is a summary of the materials balance obtained after identification and quantification of decompositon products.

When the elemental composition of the identifiable materials were summed, 94.6 percent of the carbon, 100.8 percent of the hydrogen, 95.1 percent of the nitrogen and 108.2 percent of the oxygen that were present in the original sample are accounted for in the products identified and quantitated during these experiments.

Table 21. Materials Balance - Pyrolysis (Slow Heating) Of Nylon 6

	Weight (mg/g of Sample)					
	Total	Carbon	Hydrogen	Nitrogen	Oxygen	Total
Original polymer	1000	638.2	99.2	124.1	138.5	1000.0
Material recovered	971.9	604	100	118	149.9	971.9
Low-boiling volatiles	323.11	190	37.00	38.00	58.10	
High-boiling volatiles	648.80	414.00	63.00	80.00	91.80	
Solid Residue	0.00	0.00	0.00	0.00	0.00	
Percent polymer accountable in products	97.19	94.6	100.8	95.1	108.2	

4. Oxidative degradation (slow-heating) studies

Samples of Nylon 6 polymer were degraded under dynamic heating conditions from ambient temperatures to 1000°C. Heating rates of 10, 25, and 100°C/min were used to determine the effect of the heating rate on polymer degradation. The effect of the sample size was also investigated. Chemical analysis was conducted at intermediate stages of decomposition where 7, 50, 70 and 97 percent of the original polymer weight was lost.

In addition to the experiments conducted under dynamic heating conditions, several experiments were performed under isothermal conditions.

The low-boiling volatiles (excluding carbon monoxide and ε-caprolactam) have been identified and quantitated using the GC/MS techniques that were discussed earlier. The carbon monoxide concentration at selected temperatures was measured using an IR technique. The high-boiling volatiles, which were trapped at the outlet of the thermoanalyzer, were identified using IR and GC/MS techniques. The GC columns used to separate and quantitate the volatile products included Chromosorb 101, 103 and 104.

Analysis of Low-Boiling Volatile Products. More than 25 trapping experiments were performed to identify and quantitate the volatile products resulting from the thermal oxidative degradation of the polymer. Most of the experiments utilized a 50 mg sample size, which was determined to be most appropriate for the structural identification and the quantitation of degradation products. The sample was heated from ambient to 1000°C at the rate of 25°C/min. Chromatograms of the

GC-resolved products from the oxidative degradation of Nylon 6 polymer are presented in Figures 23, 24 and 25; both FID and TCD responses are illustrated.

A 16 ft. x 1/8 in. O.D. column containing Chromosorb 101, a 3 m x 4 mm O.D. column of Chromosorb 103 and a 16 ft. by 1/8 in. O.D. column with Chromosorb 104 were temperature-programmed from -10 to 260°C at 10°C/min to obtain separation and quantitation of the degradation products.

More than 30 components have been identified in the mixtures of low-boiling volatiles obtained during these experiments. Table 22 contains a summary of the compounds that have been identified. The peak numbers in the table correspond to the GC peaks in Figures 23, 24 and 25 and the T.E. and R.F. values that were used in the calculation of the quantities of each component are also included. The sum of all the volatile compounds that were determined by analytical technique is 1609 mg per gram of the original sample. It should be noted that a summary of the volatile products identified total approximately 60 percent higher than the weight of the sample used. This increase in weight was due to the interaction with oxygen in the sample's environment and resulted in increases in the amounts of carbon monoxide, carbon dioxide and water produced, compared to that measured during prior pyrolysis studies. It should also be noted that ammonia, which was identified in the degradation in the inert environment, was not found to be produced in the oxidative environment. As noticed during the thermal decomposition of other nitrogen-containing polymers, the concentration of hydrogen cyanide produced in the oxidative environment

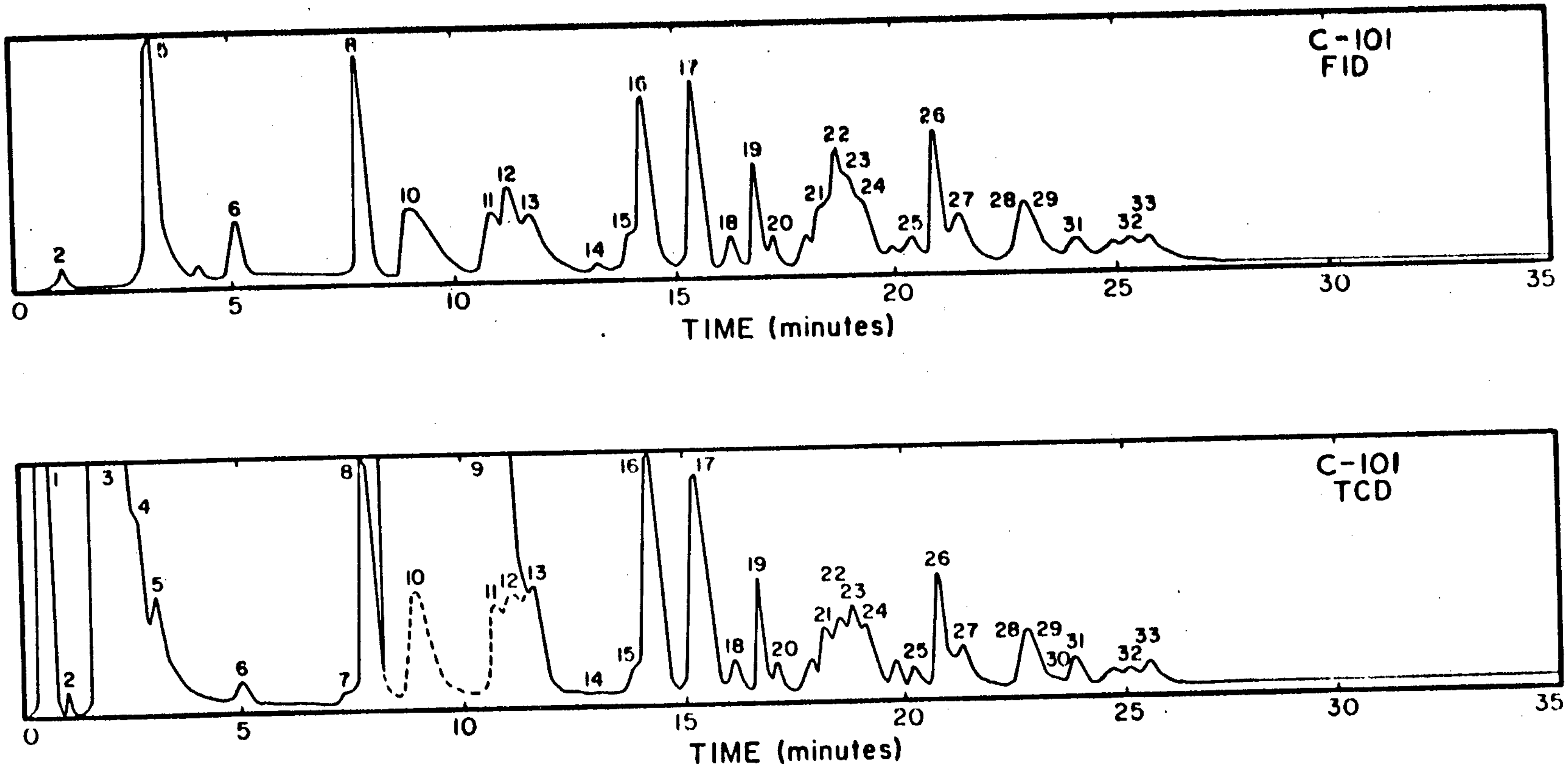


Figure 23. Low-boiling volatiles produced during the oxidative degradation (slow heating) of Nylon 6 in air.

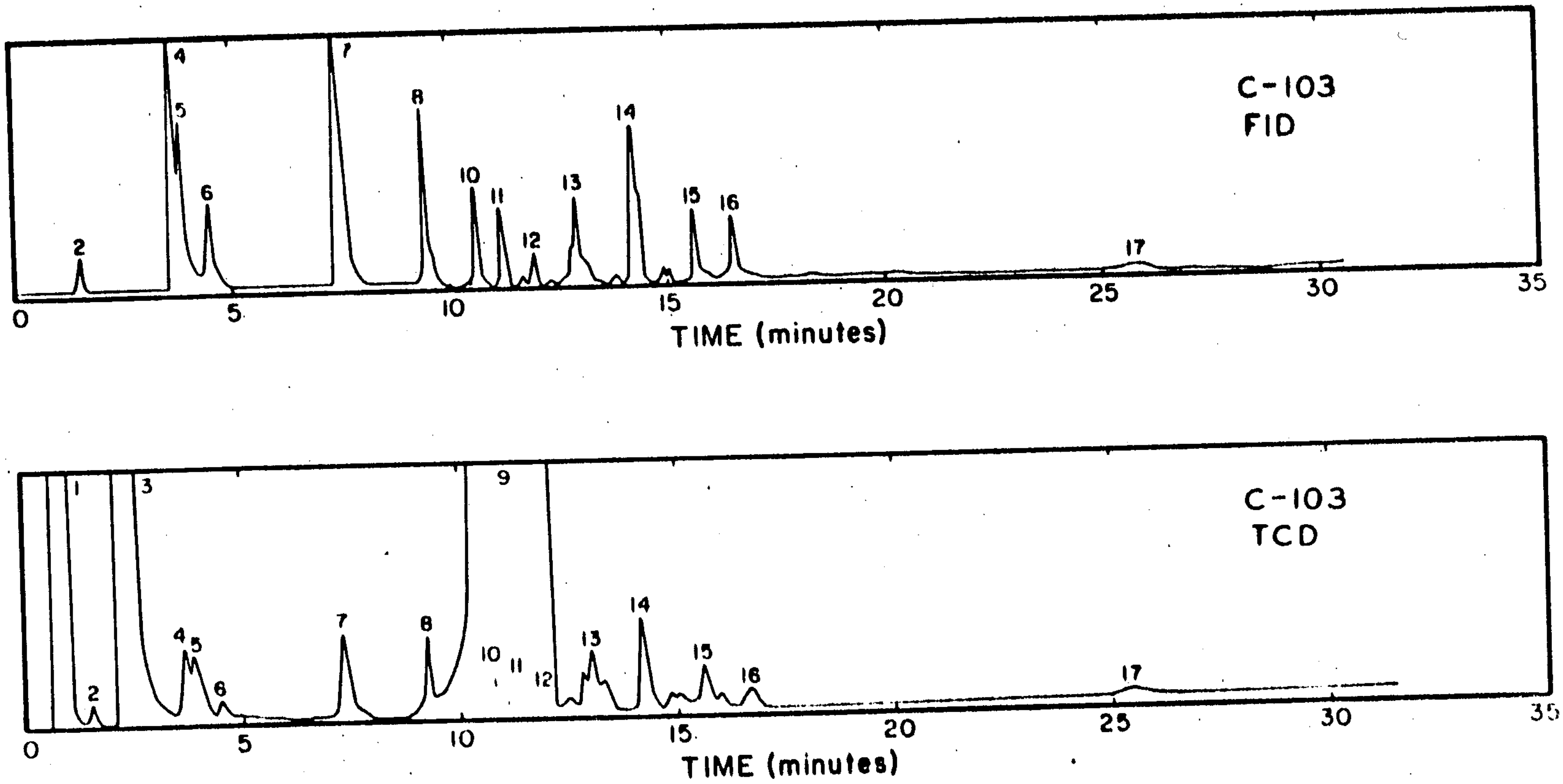


Figure 24. Low-boiling volatiles produced during the oxidative degradation (slow heating) of Nylon 6 in air.

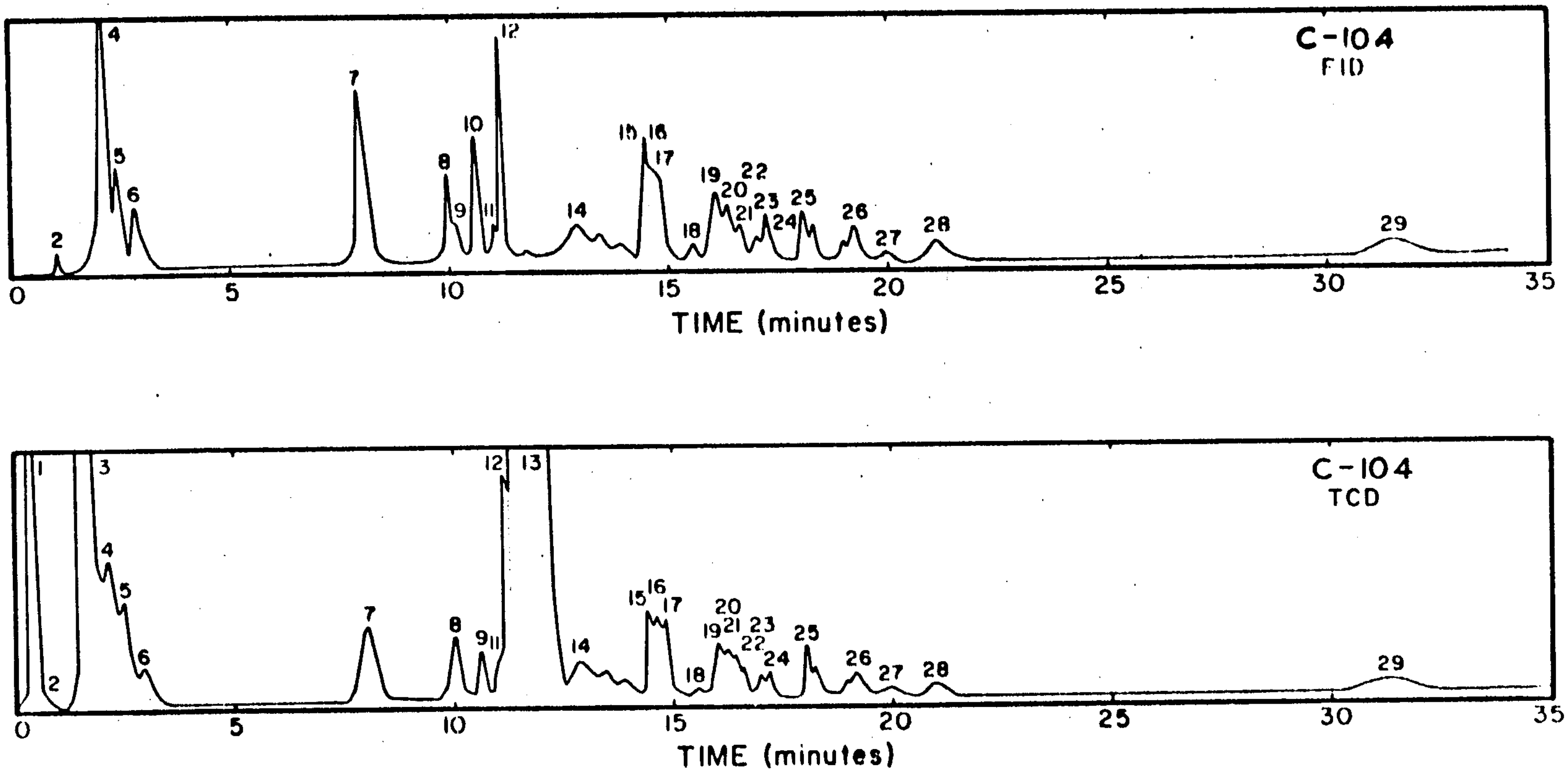


Figure 25. Low-boiling volatiles produced during the oxidative degradation (slow heating) of Nylon 6 in air.

Table 22. Low-Boiling Volatiles Produced During the Oxidative (Slow Heating) Degradation Of Nylon 6

Compounds	Peak Number on^b			T.E.^{c}	R.F.^{d}	Quantity^e
	C-101	C-103	C-104			
Low-Boiling Volatiles						
Carbon monoxide	1	1	1	---	0.670	470.00
Methane	2	2	2	0.05	1.031	73.80
Carbon dioxide	3	3	3	0.97	0.915	526.00
Nitrous oxide	4			1.00	0.890	3.28
Ethylene	5	4	4	0.96	0.980	14.37
Acetylene		5	5	0.96	0.930	0.19
Ethane	6	6	6	0.98	1.031	4.22
Cyanogen	7			0.44	1.5	Trace
Water	9	9	13	0.82	0.550	410.00
Propene	8	7	7	0.98	0.652	15.23
Hydrogen cyanide	10		12	0.99	1.5*	13.77
Methanol	11		9	0.75	4.348	4.34
Acetaldehyde	12			0.90	1.8*	3.39
Butene		8	8	0.97	0.895	4.37
1,3-Butadiene	13		10	0.97	0.870	5.85
Ethanol	14		14	0.85	0.640	0.80
1-Pentene	15		11	0.97	0.660	1.07
Acetonitrile	17	10	16	0.95	0.967	14.21
Propenenitrile	16	11	15	0.95	0.682	15.03
Nitromethane	18		20	0.95	2.0	0.60
Propanenitrile	19	12	19	0.95	0.650	4.34
Metacrylonitrile	20		18	0.95	0.727	0.63
3-Butenenitrile	21		22	0.95	0.727	1.31
Benzene	22	13	17	0.90	0.750	3.21
Butanenitrile	23		23	0.95	0.660	3.07
Pyrrole	24		24	0.95	0.671	0.24
Pentanenitrile	25			0.95	0.692	Trace
Toluene	26	14	21	0.95	0.794	3.18
Cyclopentanone	27		25	0.95	0.827	1.55
Xylene	28			0.90	0.818	0.05
Capronitrile	29	15	26	0.90	0.805	8.37
Styrene	30			0.88	0.800	0.08
Hexenenitrile	31	16	27	0.90	0.785	2.15
Phenol	32			0.88	1.105	0.30
Benzonitrile	33		28	0.88	0.895	0.30
E-Caprolactam	34	17	29		0.957	---
Total Low-Boiling Volatiles						1609.03
High-Boiling Volatiles						
E-Caprolactam Oligomers^g						161.00 69.00
Sub-total High-Boiling Volatiles						230.00
Total (Mg/g Sample)						1839.03

*Estimated

[a] The oxidative degradation of four samples with a sample size of 50.0 mg. from ambient to 1000°C at the heating rate of 25°C/min using the Mettler thermoanalyzer.

[b] Corresponds to peak numbers in Figure 23, 24 and 25 on Chromosorb 101, Chromosorb 103 and Chromosorb 104 respectively.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as measured by analytical techniques.

[f] Relative response factors for the flame ionization detector.

[g] Quantiatated by the residue analysis techniques (See Chapter IV).

was greater than that observed to be produced in the inert environment.

The quantity of carbon monoxide produced during the thermal decomposition of the Nylon 6 polymer in the oxidative environment was determined in separate experiments using the infrared techniques outlined in Chapter IV. The carbon monoxide values obtained are included in Table 22.

Analysis of high-boiling volatile products. The IR spectrum of this condensed fragment is shown in Figure 26. This spectrum closely resembles the spectra of ε-caprolactam is shown in Figure 27 for comparison purposes.

The condensed high-boiling volatile fragment was dissolved in acetone and injected onto an OV-1 volumn at 180°C. The temperature of the column was programmed at a rate of 10°C/min from 180°C to 230°C. The major peak found was identified as ε-caprolactam which comprised approximately 70 percent of the aerosol residue.

The high-performance liquid chromatograph (HPLC), Perkin-Elmer Model 601, was used for the analysis of the aerosol residue. The sample was dissolved in acetronitrile and injected to the reverse phase Whatman ODS column. A 35/65 mixture of CH_3CH/H_2P was used for mobile phase monitored by UV detector. The chromatogram obtained with the condensed high-boiling fragment was almost identical to the chromatogram obtained for the condensed fragment from the Nylon 6 polymer during pyrolysis. The major peak was identified as ε-caprolactam by the retention time.

The elemental composition of the aerosol residue was determined. The results from the duplicate analysis are presented in Table 23,

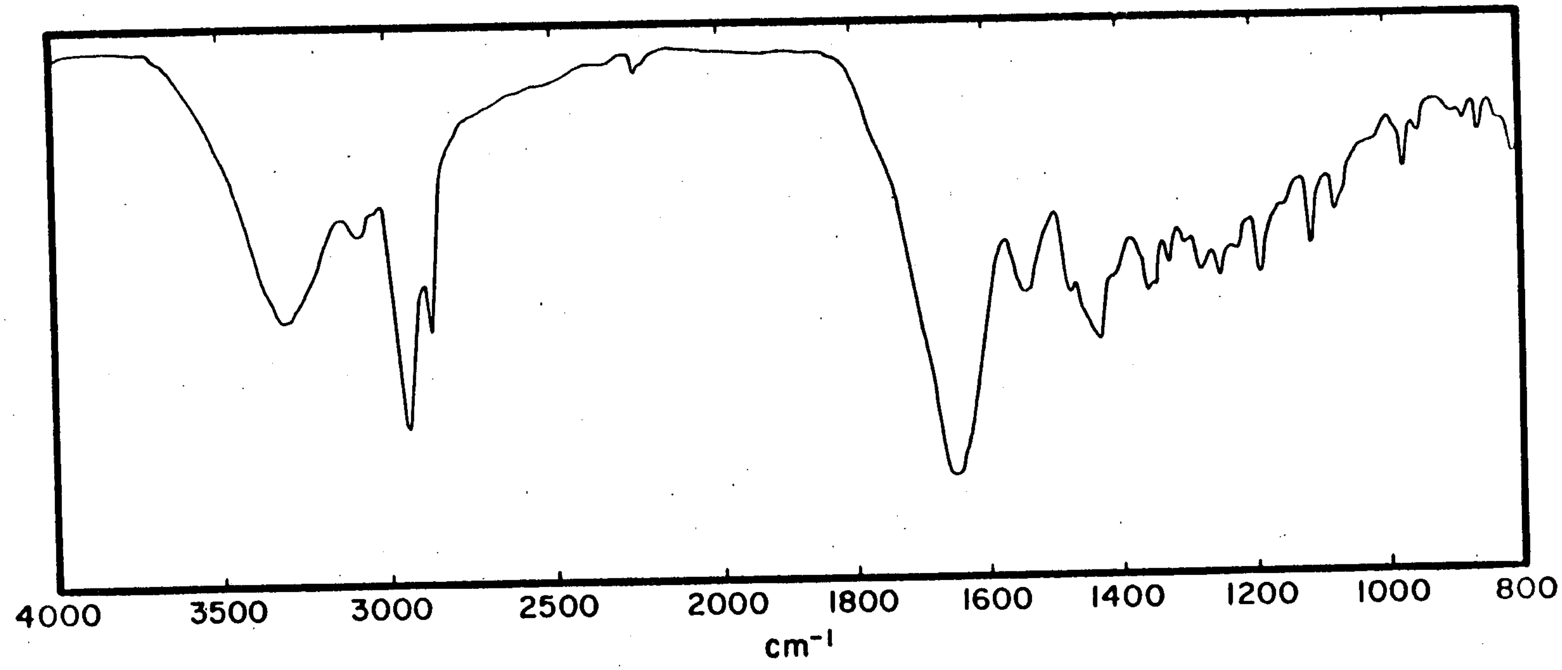


Figure 26. The infrared spectrum of the high-boiling volatiles produced during oxidative degradation (slow heating) of Nylon 6 in air.

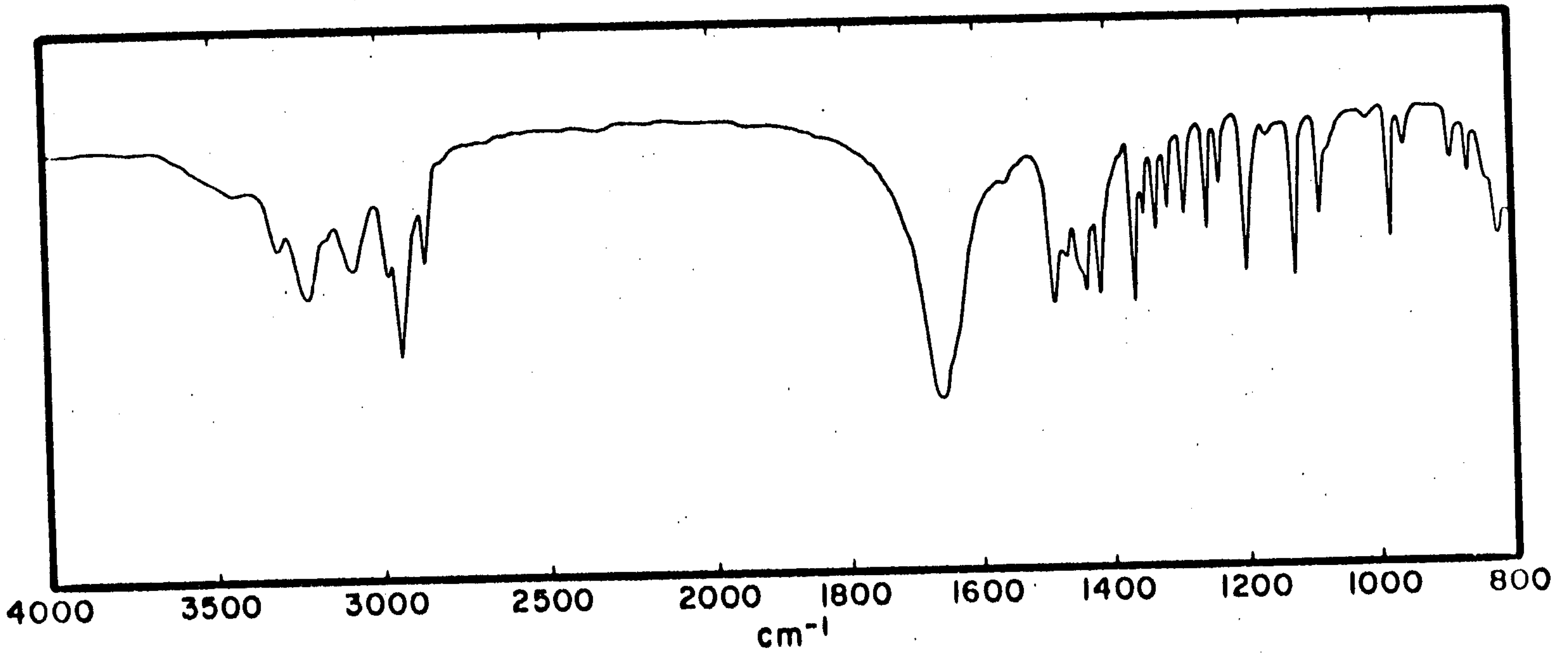


Figure 27. The infrared spectrum of ε-caprolactam.

Table 23. Elemental Composition of Residue Produced During Oxidative (Slow Heating) Degradation of Nylon 6

	% Composition			
	Carbon	Hydrogen	Nitrogen	Oxygen
Mixed Residue	64.23	9.02	13.30	13.45
Theoretical composition of ε-caprolactam	63.72	9.73	12.39	14.16
Theoretical composition of Nylon 6 polymer	63.72	9.73	12.39	14.16

along with the theoretical composition of Nylon 6 polymer and ε-caprolactam. It can be seen that the composition obtained closely resembled that of polymer and ε-caprolactam. Using the results of this analysis it is concluded that the aerosol residue was composed of approximately 70 percent of ε-caprolactam and 30 percent of oligomers of the Nylon 6 polymer. The calculated concentrations of ε-caprolactam and oligomers are listed in Table 23.

Materials Balance. One can calculate the material balance for nitrogen, carbon, hydrogen, and oxygen using the quantitative data presented in earlier sections on the low-boiling volatile products and the high-boiling volatiles produced during the thermal decomposition of the Nylon 6 polymer in an air environment. Table 24 contains a summary of the material balance that was obtained from this experimental study of Nylon 6. When the elemental composition of the identified

Table 24. Materials Balance - Oxidative (Slow Heating) Degradation Of Nylon 6[a]

	Weight (mg/gram sample)			
	Total	Carbon	Hydrogen	Nitrogen
Original polymer	1000	638.2	99.2	124.1
Material recovered	1839.03	638.0	99.0	50
Low-boiling volatiles	1604.03	491.0	77.0	22
High-boiling volatiles (aerosols)	230.00	147.0	22.0	28
Solid residue (char)	0.00	0.0	0.0	0
Percent of polymer accountable in decomposition products				

[a] Sample size was 50 mg, and the heating rate was 25°C/min.

decomposition products is summed, 100.0 percent of the carbon, 99.8 percent of the hydrogen and 40.3 percent of the nitrogen that were present in the original sample are accountable in the products observed.

Since almost all of the nitrogen present in higher boiling compounds was identified, it is assumed that the bulk of the nitrogen missing was in the form of N_2 or NO. More reliable techniques are being developed to permit trapping of these low-molecular weight gases. It is not possible to obtain an actual materials balance for oxygen since the sample reacts with the oxygen in its environment during the degradation process. Considerable increases in the concentrations of carbon monoxide, carbon dioxide and water were measured, as compared to prior pyrolysis studies.

Several sample sizes, ranging from 10 mg to 50 mg, were employed to find an appropriate sample size, both for the quantitation and the structural identification and to investigate the effect of the sample size on the production of degradation products. Samples were heated from ambient to 1000°C at the rate of 25°C/min. The results of this experiment are presented in Table 25. The relative ratio in major products, such as CO, CO_2, and H_2O, was not affected by the sample size but the amount shows slightly decreasing tendency as the sample size increases. On the other hand, minor products with higher boiling temperatures and molecular weight became prominent with the increase in the sample size. The data can be explained as follows: The supply of oxygen necessary for complete oxidation of the sample would be greater when the sample size is smaller. The diffusion of oxygen from

Table 25. Effect of Sample Size On The Concentration Of Low-Boiling Volatiles Produced During The Oxidative (Slow Heating) Degradation Of Nylon 6

	Quantity (mg/g sample)[b]		
	Sample Size		
Compounds	10 mg	20 mg	50 mg
Carbon monoxide	543.00	531.00	470.0
Methane	94.50	85.90	73.8
Carbon dioxide	612.70	603.50	526.0
Nitrous oxide	6.10	5.45	3.28
Ethylene	3.80	6.65	14.37
Acetylene	Trace	Trace	0.19
Ethane	Trace	0.35	4.22
Cyanogen	Trace	Trace	Trace
Water	602.60	597.50	410.0
Propene	5.20	8.85	15.23
Hydrogen cyanide	1.00	4.75	13.71
Methanol	Trace	3.75	4.34
Acetaldehyde	2.00	1.80	3.39
Butene	Trace	1.70	4.31
1,3-Butadiene	Trace	0.45	5.85
Ethanol	Trace	0.25	0.80
1-Pentene	Trace	0.20	1.01
Acetonitrile	2.40	3.90	14.21
Propenenitrile	2.00	3.15	15.03
Nitromethane	0.30	0.45	0.60
Propanenitrile	0.40	0.6	4.34
Metacrylonitrile	Trace	Trace	0.63
3-Butenenitrile	Trace	0.50	1.31
Benzene	0.50	0.45	3.21
Butanenitrile	Trace	Trace	3.01
Pyrrole	Trace	0.20	0.24
Pentanenitrile	Trace	Trace	Trace
Toluene	0.3	1.50	3.18
Cyclopentanone	Trace	0.70	1.55
Xylene	Trace	Trace	0.05
Capronitrile	Trace	Trace	8.31
Styrene	Trace	Trace	0.08
Hexenenitrile	Trace	Trace	2.15
Phenol	Trace	Trace	0.30
Benzonitrile	Trace	Trace	0.30
TOTAL	1876.80	1863.55	1609.03

[a] The oxidative degradation of three samples from ambient to 1000°C at the rate of 25°C/min.

[b] Milligrams of compounds produced per gram of polymer as measured by analytical techniques.

the sample's surface to the sample's interior becomes more difficult when larger samples are used. The sample size of 50 mg would be adequate for most studies pertaining to the Nylon 6 polymer.

Samples of Nylon 6 polymer, 50 ± 0.1 mg, were heated at 10, 25 and 100°C/min rates from ambient to 1000°C to measure the changes in the composition of the pyrolysis products. An air flow rate of 60 ± 10 ml/min was provided in these experiments. Table 26 contains the results obtained from duplicate analyses in the air environment at the three heating rates. Only slight changes were observed in product distribution or concentration as a result of these studies. The use of heating rates in these studies "did not" markedly change the fundamental mechanisms of the oxidative degradation of the Nylon 6 polymer.

To obtain a better understanding of the oxidative degradation process, the volatile compounds that were produced from the Nylon 6 polymer were studied at several stages of degradation (50, 70 and 90 percent weight loss). Using the TGA trace in Figure 12 as a guideline. products were trapped from the thermoanalyzer at various temperature ranges. The temperature range at 423°C corresponds to the point at which 50 percent of the sample weight is lost when heated from ambient at a rate of 10°C/min. Similarly, 433°C was selected as the temperature corresponding to a 70 percent weight loss and 465°C which corresponds to the point where approximately 90 percent weight loss occurred.

In this series of experiments a 50 mg sample of Nylon 6 was temperature-programmed from ambient to the pre-selected temperature at a heating rate of 10°C/min. The products from the oxidative degradation process were trapped, beginning at 350°C, and the sampling period

Table 26. Effect Of Heating Rate On The Distribution Of Decomposition Products During The Oxidative Degradation Of Nylon 6

Compounds	Quantity[b] Heating Rate		
	10°C/min	25°C/min	100°C/min
Carbon monoxide	500.00	470.00	495.00
Methane	93.80	73.80	92.10
Carbon dioxide	556.40	526.00	513.00
Nitrous oxide	3.08	3.28	5.08
Ethylene	13.45	14.37	17.91
Acetylene	0.31	0.19	0.20
Ethane	4.35	4.22	3.32
Cyanogen	Trace	Trace	Trace
Water	435.00	410.00	395.00
Propene	16.78	15.23	17.21
Hydrogen cyanide	15.85	13.71	17.98
Methanol	3.72	4.34	3.02
Acetaldehyde	1.24	3.39	2.41
Butene	4.33	4.31	3.87
1,3-Butadiene	6.31	5.88	4.56
Ethanol	0.41	0.80	1.00
1-Pentene	0.67	1.01	0.98
Acetonitrile	11.66	14.21	17.21
Propenenitrile	13.21	15.03	16.85
Nitromethane	0.32	0.60	0.80
Propanenitrile	3.22	4.34	4.97
Methacrylonitrile	0.90	0.63	1.66
3-Butenenitrile	2.38	1.31	2.69
Benzene	4.11	3.21	4.59
Butanenitrile	3.67	3.01	1.71
Pyrrole	1.00	0.24	0.98
Pentanenitrile	Trace	Trace	Trace
Toluene	5.04	3.18	5.06
Cyclopentanone	2.08	1.55	2.90
Xylene	0.09	0.05	0.02
Capronitrile	7.35	8.31	9.85
Styrene	0.04	0.08	0.20
Hexenenitrile	2.11	2.15	3.17
Phenol	0.20	0.30	0.56
Benzonitrile	0.30	0.30	0.77
Caprolactam & Oligomers	220.5	230.0	258.0
Total	1933.88	1839.03	1904.63

*Estimated

[a] The oxidative degradation of three samples with a sample size of 50.0mg from ambient to 1000°C.

[b] Milligrams of compound produced per gram of polymer as measured by analytical techniques.

was extended at least for five minutes after the sample was held at the final selected temperature. Each experiment was conducted in triplicate.

A summary of the volatile compounds that have been identified and the quantity of each compound are listed in Table 27. Typical chromatograms for each stage of the degradation on Chromosorb 101 are shown in Figure 28. The same values for trapping efficiencies and response factors were used, as cited in Table 22.

It should be noted, both from Table 27 and Figure 28, that almost all the compounds which were identified at the final stage of decomposition were also identified during the intermediate degradation processes, although the amount of components measured at the intermediate stages were considerably smaller.

The product distribution and concentration were similar, between 50% weight loss and 70% weight loss. However, the quantity of carbon dioxide, water, and alkenes increased rapidly after 70% weight loss was reached. Most of the nitrile compounds, such as hydrogen cyanide, acetonitrile, acrylonitrile and capronitrile, and aromatic compounds, including benzene and toluene, were formed in the higher temperature region after 90 percent weight loss occurred. The formation of lactams and oligomers of Nylon 6 (high-boiling volatiles) was rather constant across the temperature range studied.

Some nitrogen compounds, such as nitrous oxide and nitro-methane, appeared during the earlier stage of the degradation; little variation in the concentrations of these compounds was observed as the samples were exposed to higher temperatures.

Table 27. Distribution Of Decomposition Products During Different Stages of the Oxidative Degradation (Slow Heating) Of Nylon 6

Compounds	Peak No.	Quantity[b]			
		Weight Loss			
		50%	70%	91%	100%
Carbon monoxide	1				500.00
Methane	2	4.72	19.88	81.57	93.80
Carbon dioxide	3	92.07	121.34	257.40	556.40
Nitrous oxide	4	2.38	3.54	3.23	3.08
Ethylene	5	1.97	4.57	18.20	13.45
Acetylene	6	Trace	Trace	0.28	0.31
Ethane	7	Trace	Trace	0.64	4.35
Water	8	95.10	150.00	367.10	435.00
Propene	9	1.54	3.65	19.79	16.78
Hydrogen cyanide	10	0.55	0.97	2.22	15.85
Methanol	11	0.45	3.88	2.50	3.72
Acetaldehyde	12	0.68	2.00	1.78	1.24
Butene	13	Trace	0.85	1.13	4.33
1,3-Butadiene	14	Trace	0.95	1.61	6.31
1-Pentene	15	Trace	Trace	Trace	0.68
Acetonitrile	16	0.83	2.32	5.23	11.66
Propenenitrile	17	0.55	1.91	4.79	13.21
Nitromethane	18	0.25	0.48	0.32	0.32
Propanenitrile	19	0.13	0.38	0.73	3.22
Methacrylonitrile	20	Trace	0.44	0.54	0.90
3-Butenenitrile	21	0.18	0.35	0.48	2.38
Benzene	22	0.11	0.23	0.75	4.11
Pyrole	23	Trace	0.11	0.49	1.00
Toluene	24	0.18	0.64	1.16	5.04
Cyclopentanone	25	0.11	0.54	0.99	2.08
Capronitrile	26	0.17	0.29	1.29	7.35
Hexenenitrile	27	0.03	0.06	0.55	2.11
Phenol	28	Trace	Trace	Trace	0.20
Benzonitrile	29	Trace	Trace	Trace	0.30
E-Capralactam and Oligomers		138.50	173.30	211.80	220.50
Total(mg/g sample)		340.50	492.68	986.57	1929.66

[a] Corresponds to peak numbers in Figure 28.

[b] Milligrams of compound produced per gram of polymer.

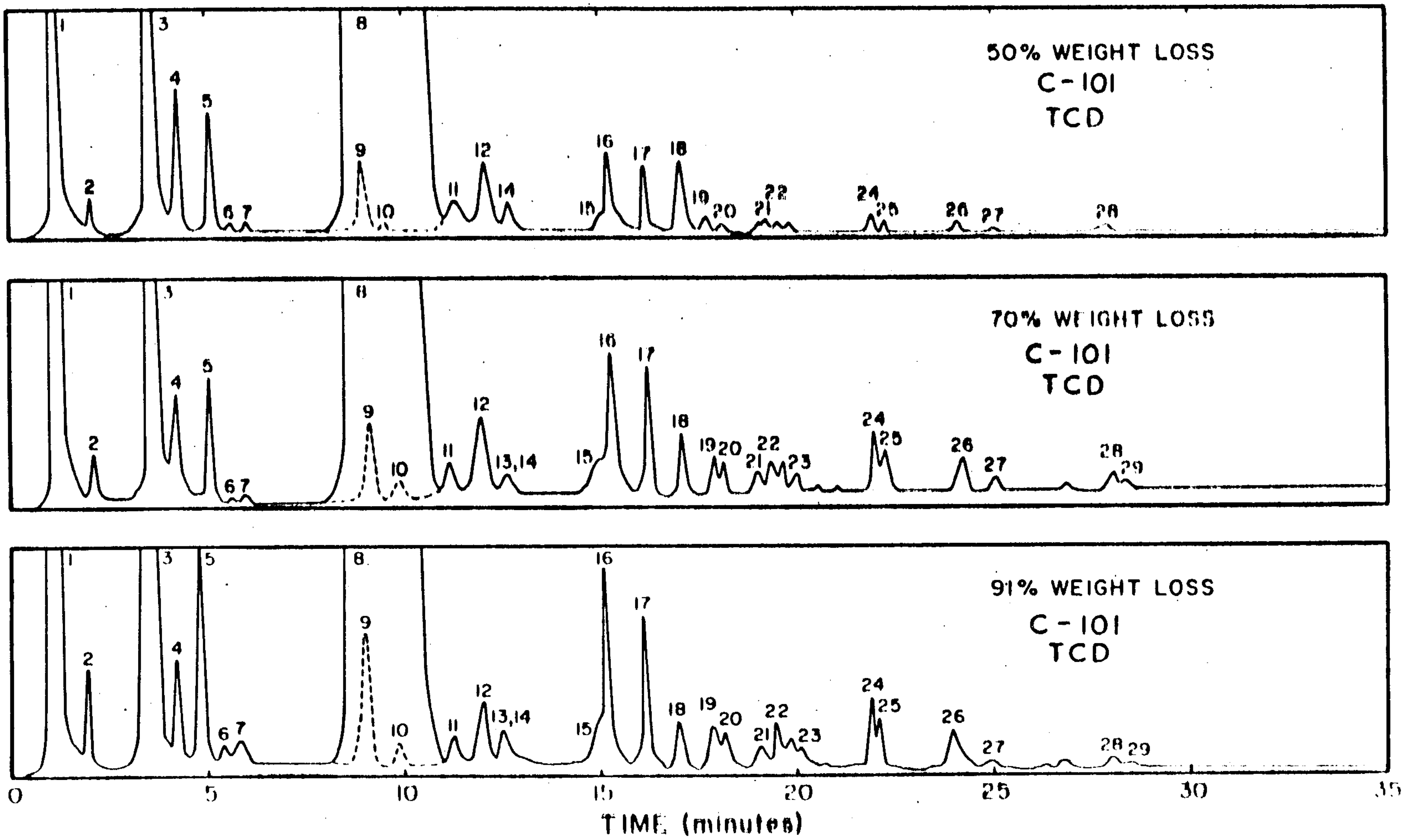


Figure 28. Low-boiling volatile products produced at different stages of the oxidative degradation (slow heating) of Nylon 6

These analytical results indicate the random chain scission and the depolymerization reaction which yields monomer and oligomers occur competitively.

The random chain scission, oxidation degradation induced will form low molecular weight compounds such as carbon monoxide, carbon dioxide, water, hydrocarbons and nitriles. The volatile products, monomers and low-molecular oligomers are continuously carried away by the flowing air and the remaining high-molecular oligomers and partially crosslinked chains are degraded, both oxidatively and thermally, at high temperatures, yielding highly decomposed simple fragments, such as methane, carbon monoxide, carbon dioxide, water, and nitrites.

Attempts were made to trace the change of the elemental composition of the samples which remained in the sample holder of the thermoanalyzer. The result of the elemental analysis of chars which were obtained at the several different stages of weight loss, including 50 percent, 70 percent and 90 percent, are summarized in Table 28.
It is interesting that the composition of the remaining sample does not change greatly between 0 percent weight loss and 70 percent weight loss.

A study was undertaken to evaluate the initial phase of polymer thermal degradation. In this experiment a 150 mg sample of Nylon 6 polymer was used in order to increase the sensitivity of determining degradation products. The sample was heated from ambient to 340°C at 10°C/min, after which the rate of heating was decreased to 4°C/min. The heating was stopped at 365°C where 7 ± 1 percent of weight loss was observed. The products from the oxidative degradation were trapped

Table 28. Elemental Composition of Nylon 6 Residual Chars At Various Stages Of Oxidative Degradation

% Weight Loss	Element			
	Carbon	Hydrogen	Nitrogen	Oxygen
0	63.93	10.02	12.41	13.64
50	66.45	9.40	11.30	12.84
70	68.44	9.18	10.79	11.59
91	78.86	3.01	7.51	10.63

beginning at 350°C and the sampling period was extended at least for five minutes after the 365°C was reached in order to collect all the products which might remain in the furnace and the trapping line. The flow rate of air was held at 160 ml/min throughout this experiment. These studies were conducted in triplicate. A jet separator was used to facilitate separation of trace compounds.

Typical chromatograms obtained using the Chromosorb 101 column are shown in Figure 29. A summary of the initial degradation products and the quantity of each product are listed in Table 29.

The amount of carbon monoxide and ε-caprolactam was obtained using the same techniques which have been described in Chapter IV.

It was surprising that some nitrile compounds, such as hydrogen cyanide, acetonitrile,and propenenitrile were produced during this low temperature range, since they were assumed to be products of secondary reactions at high temperatures.

Carbon monoxide, carbon dioxide, water,and ε-caprolactam were the major products produced during these low-temperature degradation studies.

In the isothermal degradation experiments a 50 mg sample was heated at the rate of 10°C/min to 340°C, then the rate was changed 4°C/min to 355°C, and finally 2°C/min was employed until 365°C was reached. The sample was held at 365°C for one hour. During the isothermal heating the sample weight decreased gradually. After one hour the rate of weight loss was very small. By the final stage of the isothermal heating, approximately 46 percent of the original weight was consumed. Trapping was started from 350°C and stopped at 5 minutes after the

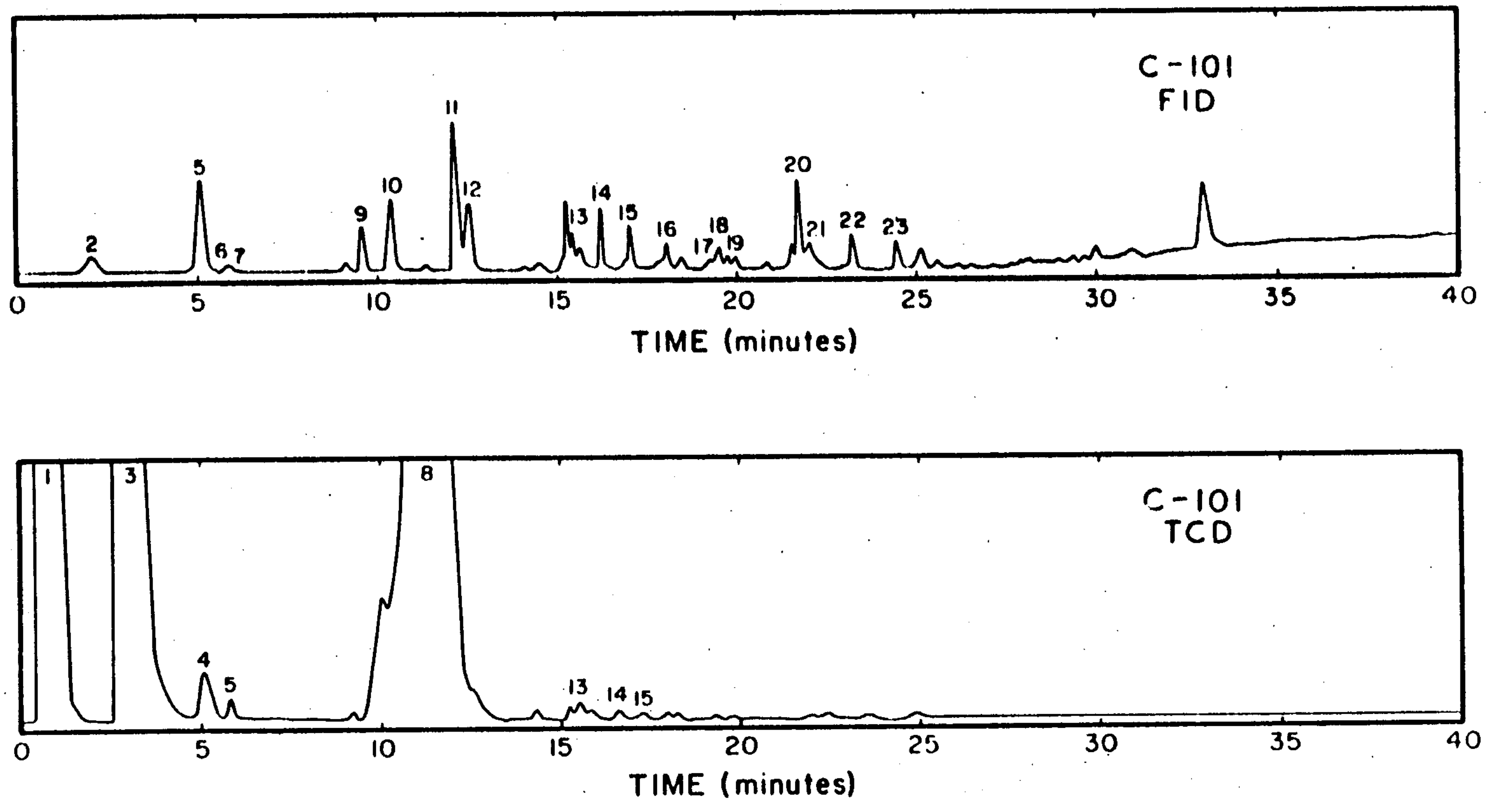


Figure 29. Initial low-boiling volatiles produced during the thermal oxidative (slow heating) of Nylon 6.

Table 29. Initial Decomposition Products Produced During The Oxidative Degradation Of Nylon 6[a]

	Peak[b] Numbers	T.E.[c]	R.F.[d]	Quantity[e]
Carbon monoxide	1		0.670[f]	73.00
Methane	2	0.05	1.031[f]	0.06
Carbon dioxide	3	0.97	0.915	54.00
Nitrous oxide	4	1.00	0.890[f]	0.22
Ethylene	5	0.96	0.980[f]	0.52
Acetylene	6	0.96	0.930[f]	T
Ethane	7	0.98	1.031[f]	T
Cyanogen		0.44*	1.5 [f]	N.D.
Water	8	0.82	0.550[f]	75.50
Propene	9	0.98	0.652[f]	0.45
Hydrogen cyanide	10	0.99	1.5* [f]	0.61
Methanol		0.75	4.348[f]	N.D.
Acetaldehyde	11	0.90	1.8* [f]	0.78
Butene		0.97	0.895[f]	N.D.
1,3-Butadiene	12	0.97	0.870	0.32
Ethanol		0.85	0.640	N.D.
1-Pentene		0.97	0.660[f]	N.D.
Acetonitrile	13	0.95	2.564[f]	0.30
Propenenitrile	14	0.95	1.679	0.44
Nitromethane	15	0.95	2.0	0.25
Propanenitrile	16	0.95	0.650	0.10
Methacrylonitrile	17	0.95	0.727	0.04
3-Butenenitrile		0.95	0.727	N.D.
Benzene	18	0.90	0.780	0.21
Butanenitrile		0.95	0.680	N.D.
Pyrrole	19	0.95	0.671	0.10
Pentanenitrile		0.95	0.692	N.D.
Toluene	20	0.95	0.794	0.30
Cyclopentanone	21	0.95	0.827	0.08
Xylene		0.90	0.818	N.D.
Capronitrile	22	0.90	0.805	0.34
Styrene		0.88	0.800	N.D.
Hexenenitrile	23	0.90	0.785	0.21
Phenol		0.88	1.105	N.D.
Benzonitrile		0.88	0.895	N.D.
Caprolactam			0.957	23.3
TOTAL				231.13

N.D. Not determined
T Trace
* Estimated

[a] The oxidative degradation of three samples with a sample size of 150 mg up to 365°C.

[b] Corresponds to peak numbers in Figure 29 on chromosorb 101.

[c] Relative trapping efficiencies.

[d] Relative response factors for thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as measured by analytical techniques

[f] Relative response by analysis of high-boiling volatiles residue.

heater was turned off.

Three experiments were performed for identification and quantification purposes. The chromatograms obtained on a Chromosorb 101 column using both TCD and FID detectors are presented in Figure 30. A summary of the degradation products that have been identified and the concentration of each of these products are listed in Table 30.

Comparison of the data with the results obtained during the oxidative degradation under a dynamic heating condition (10°C/min up to 423°C with a weight loss of 50 percent) indicated that the amount of water and carbon dioxide from the isothermal degradation is much higher than that obtained during the dynamic heating experiments.

Caprolactam and the oligomers produced during the isothermal experiments were much lower than observed during the dynamic heating studies. This indicates that the depolymerization reaction which results in monomer and oligomers and the oxidation reaction which forms carbon monoxide, carbon dioxide,and water are competitive and at higher temperatures depolymerization reactions are more likely to occur, while the oxidation is dominant at low temperatures.

D. Discussion

The comprehensive analysis of the decomposition products produced during the thermal degradation of the Nylon 6 polymer, including low-boiling volatiles, high-boiling volatiles (aerosols), and solid residues (chars), led to the development of a good materials balance.

In the inert helium environment, 97 percent of the polymer weight was recovered and analyzed. The materials balance on each element

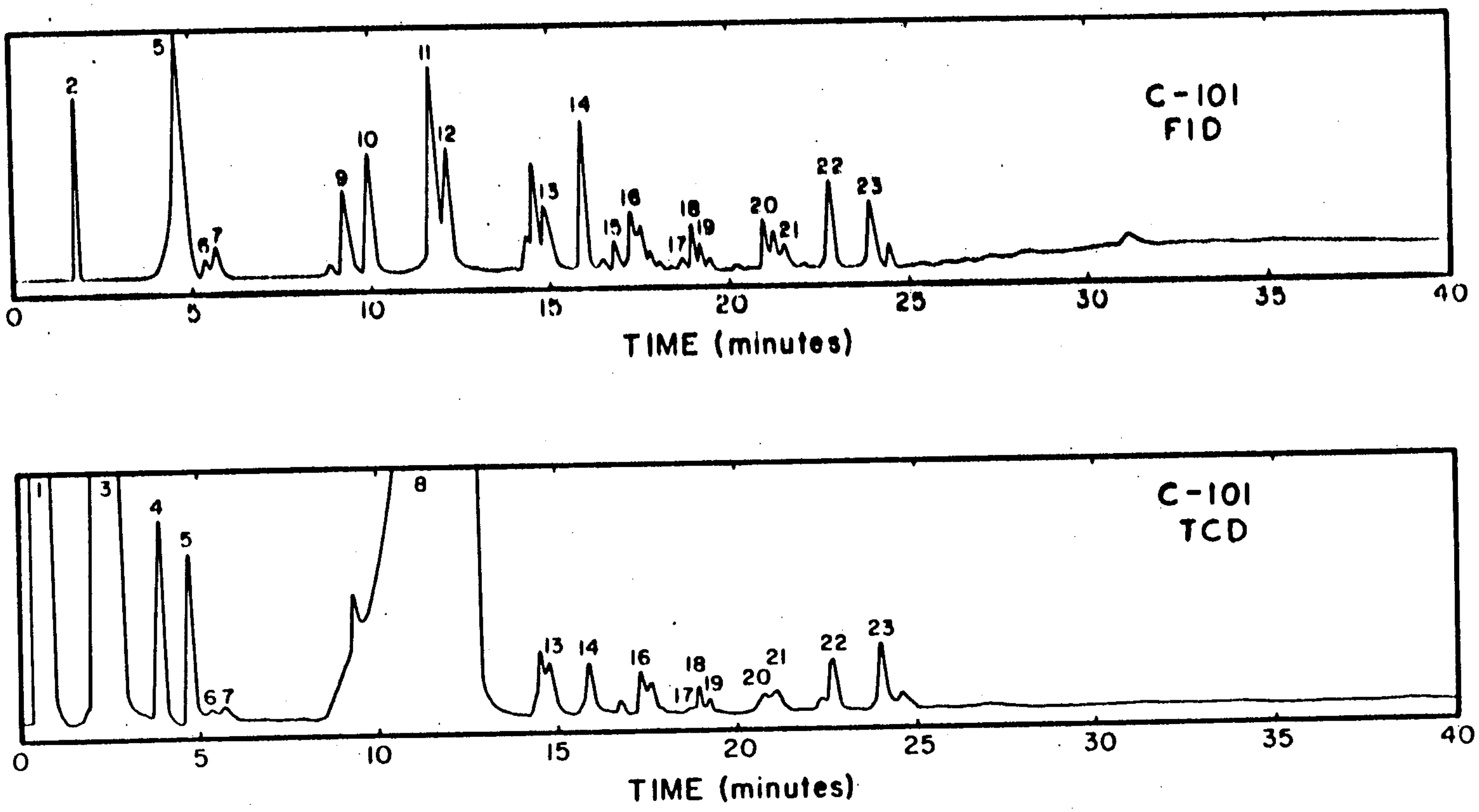


Figure 30. Low-boiling volatiles produced during the isothermal oxidative degradation of Nylon 6 at 365°C.

Table 30. Volatile Decomposition Products Produced During The Isothermal Oxidative Degradation Of Nylon 6 in Air At 635°C[a]

	Peak[b] Numbers	T.E.[c]	R.F.[d]	Quantity[e]
Carbon monoxide	1		0.670	N.D.
Methane	2	0.05	1.031	0.47
Carbon dioxide	3	0.97	0.915	120.00
Nitrous oxide	4	1.00	0.890[f]	1.16
Ethylene	5	0.96	0.980[f]	4.22
Acetylene	6	0.96	0.930[f]	0.07
Ethane	7	0.96	1.031[f]	0.14
Cyanogen		0.44*	1.5[f]	N.D.
Water	8	0.82	0.550[f]	228.00
Propene	9	0.98	0.650[f]	0.65
Hydrogen cyanide	10	0.99	1.5*[f]	0.84
Methanol		0.75	4.348[f]	N.D.
Acetaldehyde	11	0.90	1.8*[f]	1.13
Butene		0.97	0.895[f]	N.D.
1,3-Butadiene	12	0.97	0.870[f]	0.92
Ethanol		0.85	0.640	N.D.
1-Pentene		0.97	0.660[f]	N.D.
Acetonitrile	13	0.95	2.564[f]	0.44
Propenenitrile	14	0.95	1.679[f]	0.70
Nitromethane	15	0.95	2.0	T
Propanenitrile	16	0.95	0.650	0.14
Methacrylonitrile	17	0.95	0.727	0.06
3-Butenenitrile		0.95	0.727	T
Benzene	18	0.90	0.780	0.31
Butanenitrile		0.95	0.680	N.D.
Pyrrole	19	0.95	0.671	0.14
Pentanenitrile		0.95	0.692	N.D.
Toluene	20	0.95	0.794	0.51
Cyclopentanone	21	0.95	0.827	0.04
Xylene		0.90	0.818	N.D.
Capronitrile	22	0.90	0.805	0.33
Styrene		0.88	0.800	N.D.
Hexenenitrile	23	0.90	0.785	0.22
Phenol		0.88	1.105	N.D.
Benzonitrile		0.88	0.895	N.D.
Capralactam and Oligomers			0.957	52.8
TOTAL				413.29

N.D. Not determined.
T Trace
* Estimated

[a] The oxidative degradation of three samples with a sample size of 50.0 mg at 365°C for 1 hr using the Mettler Thermoanalyzer. The weight loss was 46 percent.

[b] Corresponds to peak numbers in Figure 30 on Chromosorb 101.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as measured by analytical techniques.

[f] Relative response factors for the flame ionization detector.

ranged from 93.5 percent to 108 percent. In the oxidative environment considerable interaction took place between the sample and its environment. Thus, the materials balance was calculated only for carbon, hydrogen,and nitrogen. The balances obtained for carbon and hydrogen were in excess of 99 percent. The balance for nitrogen was 40 percent. The bulk of the nitrogen not accounted for was believed lost in the form of nitrogen gas or amines. New analytical procedures have been developed to permit a better nitrogen balance, however, it was not possible to use these techniques within the scope of the research reported in this thesis.

Tables 31 and 32 summarize the major and minor products produced during the pyrolysis and the oxidative degradation of the Nylon 6 polymer. As indicated in these tables, the two major products produced during the pyrolysis process were ε-caprolactam and a variety of oligomers which resembled the initial polymer in chemical structure. The presence of amine was not observed in these studies.

The pyrolysis processes observed during the decomposition of the Nylon 6 polymer appeared to be rather simple. A single peak was recorded on the DTG trace. Little, if any, char structure was formed in the helium environment. These results suggest that the principal reaction which occurred during the pyrolysis of Nylon 6 was the formation of oligomers and monomers through back-biting reactions from the terminal groups on the polymer chains or through elimination of monomeric and polymeric units from the center of the chain, as was suggested by Smith(53) and Kricheldorf(54) (Equations (13), (19) and (20)).

Table 31. Major Decomposition Products Produced During The Thermal Decomposition (Slow Heating) Of Nylon 6

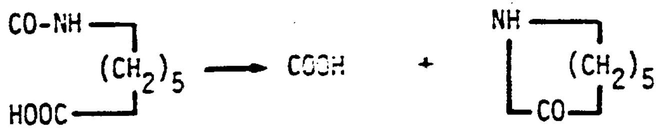
	Quantity[a]	
	In Helium	In Air
Low-Boiling Volatiles		
Carbon monoxide	48.00	470.00
Methane	55.40	73.80
Carbon dioxide	18.76	526.00
Ethylene	39.29	14.37
Ammonia	30.82	--
Water	18.85	410.00
Propene	46.92	15.23
Hydrogen cyanide	5.43	13.71
Acetonitrile	5.57	14.21
Propenenitrile	3.27	15.03
High-Boiling Volatiles		
ε-caprolactam	129.80	161.00
Oligomers	519.00	69.00

[a] Milligrams of compound per gram of sample.

Table 32. Minor Decomposition Products Produced During The Thermal Decomposition (Slow Heating) Of Nylon 6

	Quantity[a]	
	In Helium	In Air
Nitrous oxide	--	3.28
Acetylene	4.36	0.19
Ethane	3.85	4.22
Methanol	--	4.34
Acetaldehyde	--	3.39
Butene	2.41	4.31
1,3-Butadiene	5.16	5.88
Ethanol	--	0.80
1-Pentene	3.57	1.01
Nitromethane	--	0.60
Propanenitrile	3.27	4.34
Methacrylonitrile	0.98	0.63
3-Butenenitrile	0.70	1.31
Benzene	3.93	3.21
Butanenitrile	2.37	3.01
Pyrrole	0.66	0.24
Toluene	4.14	3.18
Cyclopentanone	0.60	1.55
Capronitrile	4.34	8.31
Hexenenitrile	2.11	2.15
Styrene	1.28	0.08
Phenol	0.25	0.30
Benzonitrile	1.10	0.30

[a] Milligram of compound per gram of sample.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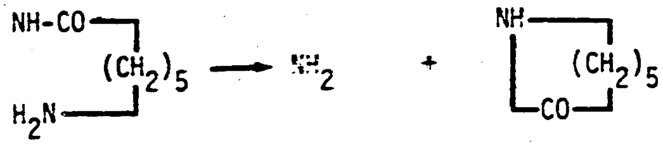
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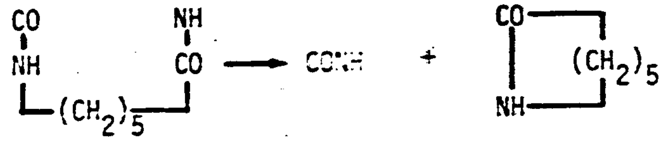

(20)

Equations (13) and (19) express so-called back-biting reactions and reaction (20) is an amide interchange reaction. Oligomers, most likely cyclic dimers and trimers, can also be obtained through any of the above three reactions.

Low-molecular-weight compounds, such as hydrocarbons containing 1 to 7 carbons and nitriles which were observed during the pyrolysis of the Nylon 6 polymer, were supposed to be formed via extensive breakdown of ε-caprolactam and oligomers. This is supported by the results of the pyrolysis of ε-caprolactam, oligomers and the Nylon 6 polymer, in which identical patterns of the pyrolysis products were obtained from those three materials. The fact that there was not much difference in the nature of the products between the pyroprobe experiments and the trapping studies suggested that most of the Nylon 6 sample was consumed by approximately 550°C, regardless of the heating conditions.

Most of the volatiles, including both light gases and heavy gases, are assumed to be produced at rather lower temperature ranges below 550°C. At the same time random chain scission may also take place at the weak bonds, such as $-CH_2-CO-$, $-CH_2-NH-$, and $-CO-NH-$. Such reactions have been proposed by Goldstein(63) and Staus and Wall.(59) This random chain scission may be responsible for the degradation of the viscosity and the formation of most of the volatile products. A proposed degradation process is presented in Figure 31. The branching reaction between carbonyl groups and the primary amines probably does not occur effectively under the conditions employed in this study, since there is no evidence for char formation. Pathway I (Figure 31) is of the greatest importance; the proposed pathways II and III probably occur to a much lesser degree. The random chain scission reaction which leads to the formation of volatile low-molecular species is accelerated at high temperatures. Large quantities of carbon monoxide, carbon dioxide,and water were formed during thermal degradation of the Nylon 6 polymer in an oxidative environment (see Table 31). The amount of high-boiling volatiles containing ε-caprolactam and low oligomers, decreased to almost one-third of the high-boiling volatiles obtained during the pyrolysis process. Ammonia was not detected among the oxidative degradation products. Hydrogen cyanide, nitrous oxide, alcohols,and several nitrile compounds were identified as products produced during degradation in the oxidative environment.

A slight amount of solid residue (char) which corresponds to 9 percent of the original polymer weight was formed during the oxidative degradation; this residue was completely decomposed at temperatures

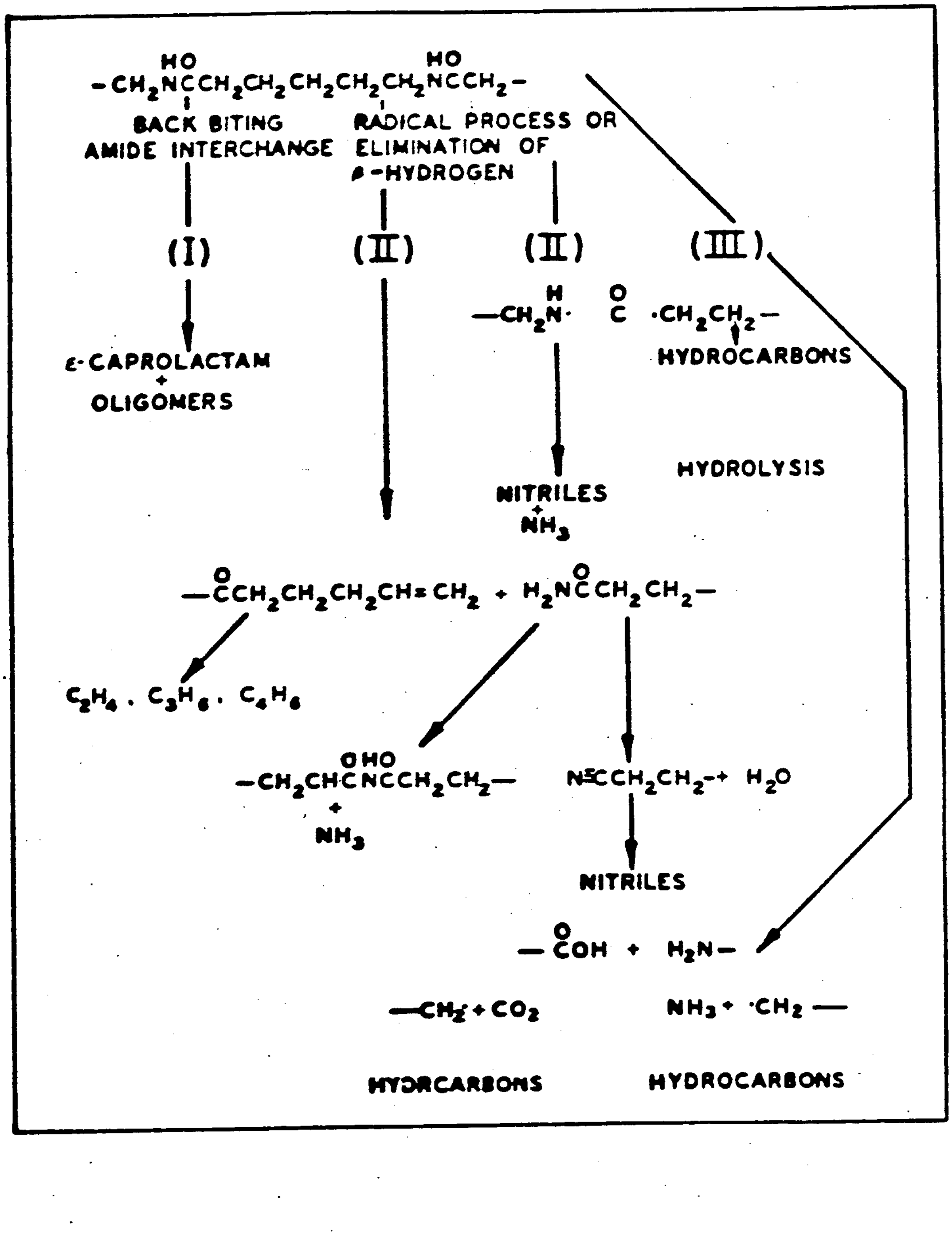


Figure 31. Proposed degradation mechanism for the thermal decomposition of Nylon 6.

in excess of 750°C.

The oxidative decomposition reactions were more complex than the inert pyrolysis reactions. The effect of the heating rate (10°C/min to 100°C/min) had limited effects on the degradation reaction (see Table 26). It should be noted, however, that the amount of carbon dioxide and water produced decreased while ε-caprolactam and oligomers increased, with an increase in heating rate. This suggests that the depolymerization reaction which led to the formation of caprolactam and oligomers, and the oxidation reaction are competitive in oxidative environments; the depolymerization reaction seemed to become slightly favored with the increase of the heating rate.

As the sample size was increased, major products such as carbon monoxide, carbon dioxide,and water decreased in amount, although the relative ratio of the three products was not affected. On the other hand, the other products with higher boiling points and higher molecular weights increased with the increase of the sample size. Since the diffusion of oxygen from the material surface to the sample's interior is expected to become more difficult as the sample size increases, the contribution of the oxidative degradation will become less as the sample size becomes larger.

Figure 32 illustrates the change in the concentration of major products on 7%, 50%, 70%, 91%,and 100% weight loss of the original sample weight during the oxidative degradation of Nylon 6. The different scales are used on the ordinate of this figure. The large scale (left ordinate) is for carbon monoxide, water, caprolactam and methane. The other compounds are plotted on the small scale (right ordinate).

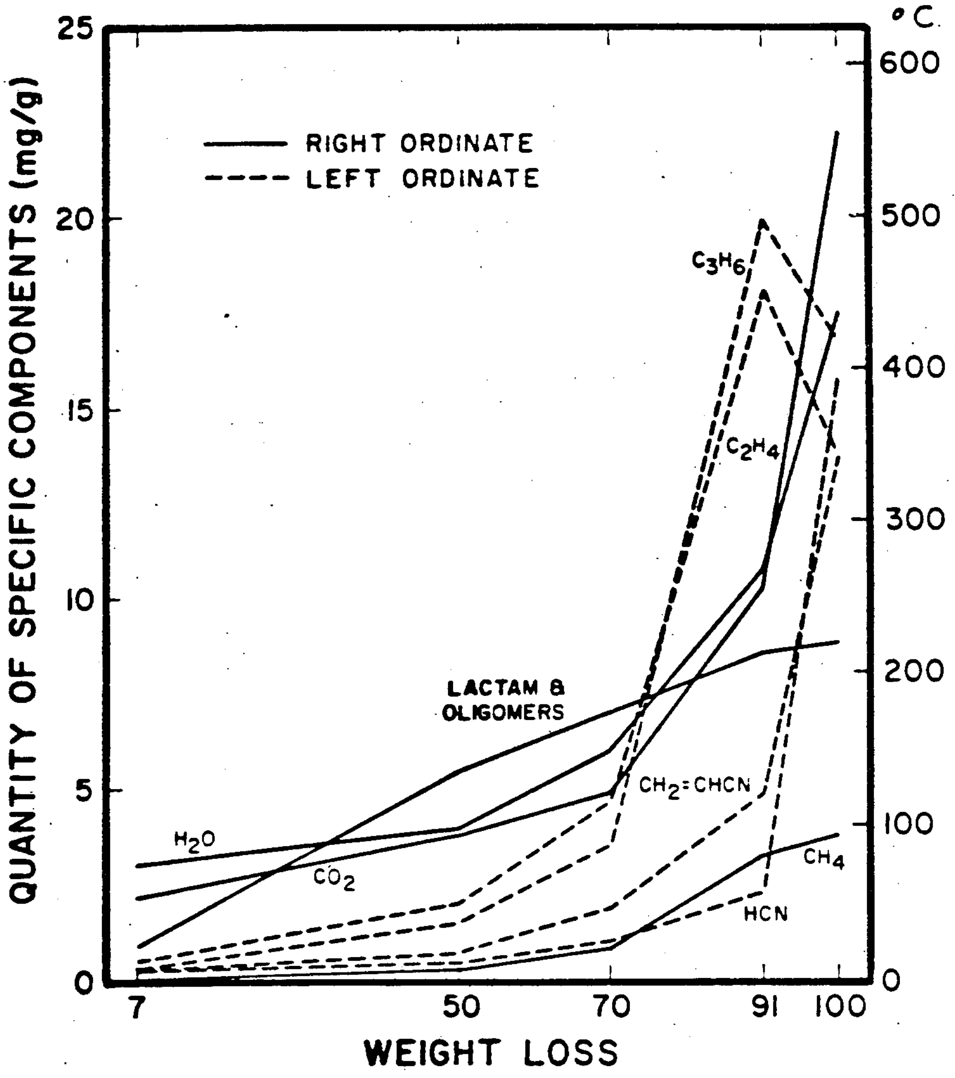


Figure 32. Observed concentrations of major low-boiling volatiles produced during the oxidation (slow heating) of Nylon 6.

As indicated in this figure, the relative ratio of volatile products does not change up to approximately 70 percent weight loss. The major contribution to weight loss up to this point is due to lactam and oligomers, water, carbon dioxide and probably carbon monoxide and nitrogen gas. The results of elemental analysis of the solid polymer and resin remaining in the crucible of the thermoanalyzer indicate that the overall composition does not change drastically until a level of 70 percent weight loss occurs (see Table 28). This can be explained by the elimination of oligomeric and monomeric units from polymer chains which will not change the elemental composition of residual solid compounds.

Random chain scission and oxidation may take place competitively, leading to the formation of small fragments such as carbon dioxide, water and hydrocarbons, along with a small amount of a crosslink structure which is responsible for the slight increase of carbon content in the residual solid.

At higher temperatures, where more than 70 percent weight loss was observed, the formation of low-boiling volatile products was accelerated. The residual char, present in the final 10 percent of sample weight, will virtually degrade to produce large amounts of carbon dioxide and water. The increase of nitriles during this phase of the degradation process can be explained by the oxidation or dehydrogenation of ammonia and amino compounds.

The results obtained during the isothermal degradation of Nylon 6 at 365°C indicate that much more water and carbon dioxide are produced than was observed during dynamic thermal processes while the formation of ε-caprolactam and oligomers are much less predominant that that observed during the dynamic heating experiments. The oxidative reaction is most likely to occur at this low temperature. As it was suggested by Levantovskaya,(68) the oxidation reaction may go through the hydroperoxide intermediate. Like the photo-oxidation, the methylene carbon next to the NH group is most susceptible to oxygen radicals. The breakdown of the hydroperoxide radical results in chain rupture.

The char will also be formed by the crosslinking between carbon radicals.

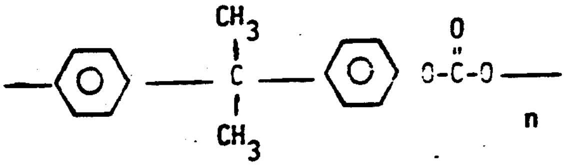
The basic degradation mechanisms of the Nylon 6 polymer may be mainly a depolymerization reaction which forms ε-caprolactam and oligomers. Further decomposition of the monomers and oligomers may take place at elevated temperatures to form low-molecular volatile compounds. Most of the original samples are consumed by 550°C, following the same degradation mechanism regardless of the heating conditions.

CHAPTER VI

POLYCARBONATE

A. Introduction

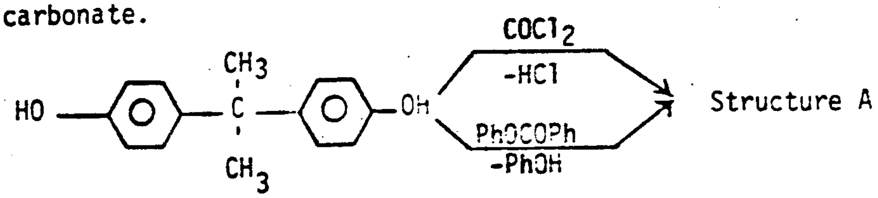
Although a wide range of aromatic polycarbonate polymers have been synthesized and examined,(76,77,78) the term polycarbonate usually refers to commercially available poly(2,2-propane bis (4-phenyl carbonate)), illustrated below:



Structure A

This form of polycarbonate polymer was used exclusively in this study.

Polycarbonate polymers can be synthesized by the reaction of Bisphenol-A (BPA) with phosgene or by ester interchange with disphenyl carbonate.



Bisphenol A

Polymerization by the ester interchange route is carried out as a melt polymerization in a two-stage process. In the first stage the reaction is carried out at a temperature of 180-200°C under a vacuum of 20-30 mm Hg to a conversion of approximately 80-90 percent. The temperature is then gradually raised to 290-300°C and the vacuum increased to below 1 mm Hg to complete the polymerization process. Polymerizations using the phosgene reaction are carried out in a basic solution. Organic solvents, such as pyridine or triethylamine, or mixtures of these with hydrocarbons, such as benzene, chlorobenzene, and chloroform, are most useful for this reaction. Polymerization can also be carried out using a stirred interfacial process. Bisphenol-A is dissolved in aqueous alkali, followed by the addition of an organic solvent and phosgene. The polycarbonate polymers thus formed possess a number of attractive mechanical properties, such as high impact strength, high elastic modulus, and good creep resistance. Polycarbonate polymers possess good stability against heat, light, and numerous chemicals. The two major deficiencies possessed by polycarbonate polymers are poor ultraviolet light resistance and poor abrasion resistance.

Due to these features, polycarbonates have been used widely as electric insulators, molded machinery parts, automotive parts, base for photographic films and substrates for magnetic tapes. The production of polycarbonates has been increasing on a yearly basis; world consumption of polycarbonates reached 51,000 tons in 1976 (see Table 3).

As the use of polycarbonate polymers has increased in commerce, there has been an increasingly greater necessity for a flame-retardant grade of polycarbonate. By 1974 approximately 10 percent of polycarbonate polymers produced were classified as fire retarded polymers; this level of fire retarded polymers is expected to grow continuously. A number of reports and patents have been issued covering methods used to impart flame-retardant characteristics to polycarbonate resins; however, very limited success has been achieved to date.

The gases and other volatile products that elute from the polycarbonate polymers during thermal decomposition processes and combustion processes have not been widely studied. The purpose of this phase of the present study has been directed toward developing better understanding of the thermal decomposition and combustion processes pertaining to polycarbonate polymers.

B. Literature Survey

In recent years several studies have been conducted by different investigators to determine the changes that occur during the thermal degradation of polycarbonate polymers. Polycarbonate polymers undergo little thermal decomposition below 250°C. Processing of polycarbonate polymers at higher temperature can, however, lead to thermal and thermo-oxidative breakdown accompanied by deterioration in mechanical properties. From an examination of processing conditions Kovarskaya(79) suggested that thermal degradation can lead to chain scission of the polymer. This has been confirmed by Davis and Golden,(80) who studied the breakdown of the polymer in a sealed evacuated system. Measurements of the intrinsic viscosity of a degraded polycarbonate have shown that the polymer undergoes random chain scission. Analysis of the molecular weight changes occurring during degradation at various temperatures showed that this process obeys first-order kinetics and can be expressed by the rate equation

$$k = 4.8 \times 10^{7} \exp(-39500/RT) \qquad (21)$$

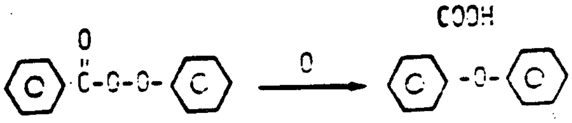
In contrast, when polycarbonate was degraded in a continuously evacuated system, it rapidly crosslinked to form an insoluble gel.(81,82)

The rate of gelation increased with a rise in temperature. The activation energy of the degradation process was calculated to be 27 Kcal/mol. The difference between degradation in a closed system and in a continuously evacuated system was explained by the competition between condensation and hydrolysis reactions.(81) It was assumed that branching and eventual gelation occur if the volatile products were removed during degradation, whereas chain scission predominates if they are retained in the system.

Davis and Golden(81,82,83) also pyrolyzed polycarbonates in a continuously evacuated system. The major products produced during the thermal decomposition of their polycarbonate polymers at 360°C were carbon dioxide, BPA, phenol, 2-(para-hydroxyphenyl)-2-phenyl propane, carbon monoxide, methane, and diphenyl carbonate.

In addition to the above named products, Lee(84) in another study, detected ethyl phenol, isopropenylphenol, isopropylphenol, and cresol. He suggested that the carbonate group undergoes appreciable decomposition below 400°C, whereas at higher temperatures the ispropylidene group is also prone to degradation.(85,86,87)

The mode of degradation of the carbonate group was elucidated by a detailed examination of the thermal decomposition of the model compound diphenyl carbonate.(86) The rearrangement of the carbonate was observed. This reaction resulted in the formation of 2-phenoxy benzoic acid.

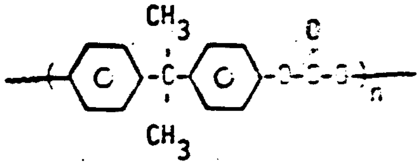

(22)

Kovarskaya(88) has shown, by measuring the rate of gas evolution, an autocatalytic thermo-oxidative process between 240 and 360°C. An activation energy of 36.5 Kcal/mole was calculated for this process. Lee(84) investigated the oxidative degradation of a polycarbonate polymer in an evacuated system. The major products at 475°C were BPA, carbon dioxide, water, acetone, benzene, toluene, phenol, cresol, ethylphenol,and isopropyl phenol. He suggested that at temperatures greater than 400°C the breakdown of more stable groups, such as isopropylidene groups, becomes the rate-controlling process. The wide range of volatiles identified indicates that extensive breakdown of both isopropylidene and carbonate groups actually occurs during thermal decomposition.

Kovarskaya et al.(79,88,89) studied the deterioration in mechanical properties of polycarbonate polymers induced by heat treatment (250-350°C) and recommended that both the time and temperature of processing should be minimized to reduce chain scission. Several investigators(79,89,90) reported that thermal degradation of polycarbonate polymers is accentuated by the presence of impurities and certain additives, e.g., unreacted Bisphenol A, sodium, some pigments,and zinc stearate.

C. Experimental Program

Samples of the polycarbonate polymer used in this study were provided by Teijin, Inc., Tokyo, Japan. The assumed structure of the polycarbonate with a molecular weight of 254 per repeat unit is shown below:



1. Polymer characterization

The polycarbonate sample was received as a powder which was dried at 10^{-6} torr pressure at 60°C for one week prior to use. The sample was then analyzed to determine its elemental composition. An infrared spectrum was prepared for additional identification.

Elemental analysis. Carbon, hydrogen and oxygen composition were determined. The results from these analyses are compared to the elemental composition of the assumed monomeric unit in Table 33. The results obtained by experimental analysis are in excellent agreement with those calculated using the assumed structure.

Infrared analysis. The infrared spectrum of the polycarbonate sample was obtained using a thin film made of polymer melt (Figure 33). The major absorptions and their band assignments are listed in Table 34. The spectrum was identical with a standard spectrum for polycarbonate polymers.

Table 33. Elemental Composition Of Polycarbonate

Element	% Composition	
	Sample as Received	Theoretical[a]
Carbon	75.66	75.59
Hydrogen	5.57	5.51
Oxygen	18.77	18.90

[a] Composition based upon the structure of the monomeric unit.

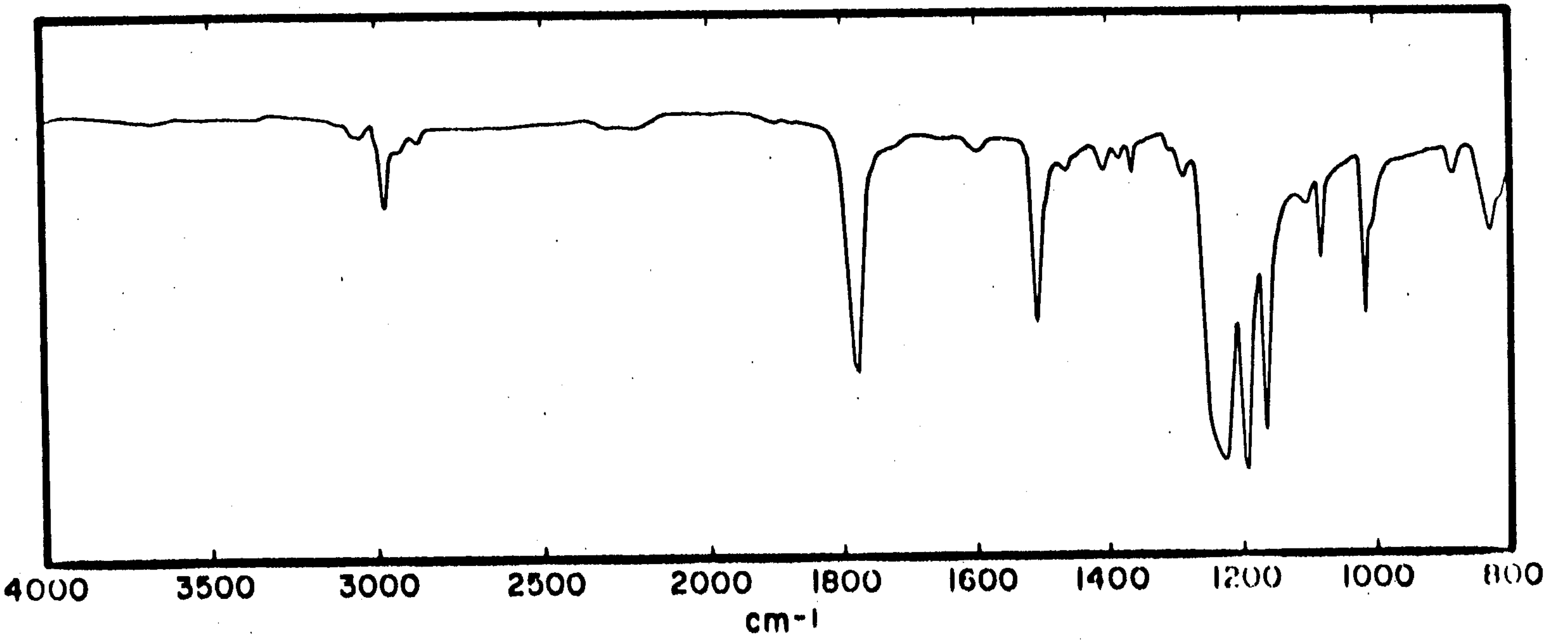


Figure 33. The infrared spectrum of polycarbonate polymer.

Table 34. Infrared Analysis Of Polycarbonate

Frequency (Wavenumbers)	Band Intensity	Assignment
2960	W	Aliphatic CH stretch
1775	S	C = O stretch
1590	W	aromatic C-C bend
1505	M	aromatic C-C bend
1225	S	C - O - C asymmetric stretch
1195	S	C - O - C stretch
1165	S	C - O stretch
1010	M	aromatic C-C bend
825	M	aromatic C-C bend

S = strong
M = medium
W = weak

2. Thermoanalytical studies

The thermal characteristics of the polycarbonate polymer were determined using the thermoanalyzer. The effect of rate of sample heating (6, 10, 25 and 100°C/min) and sample environments (air, helium, and oxygen) were determined.

Effect of heating rate on polymer degradation. Samples of polycarbonate (10 ± 0.1 mg) were heated in air at 6, 10, 25 and 100°C/min rates from ambient to 1000°C to determine the changes in sample weight loss as a function of the heating rate. The results of these experiments (conducted in triplicate) obtained in an air environment at the four selected heating rates are illustrated in Figure 34. There was no observable sample weight loss at any of the four heating rates below 375°C in air. Sample weight loss gradually increased between 375° and 450°C. The maximum weight loss, (T_{max}), occurred at approximately 490°C at the heating rates of 6 and 10°C/min; the temperatures at which T_{max} occurred at the faster heating rates was slightly higher than 490°C. A yellowish-white aerosol appeared at the outlet of the furnace as the temperature approached T_{max}. This aerosol was trapped on a glass fiber filter which was placed in the trapping line between the furnace and the cold trap. The sample lost approximately 65 percent of its original weight by 540°C. The sample remaining above 540°C was in the form of a black char layer which degraded at an appreciably slower rate than that portion of the sample observed to degrade within the lower temperature region. The remaining char disappeared by 620°C at the slowest heating rate and by 760°C at 100°C/min.

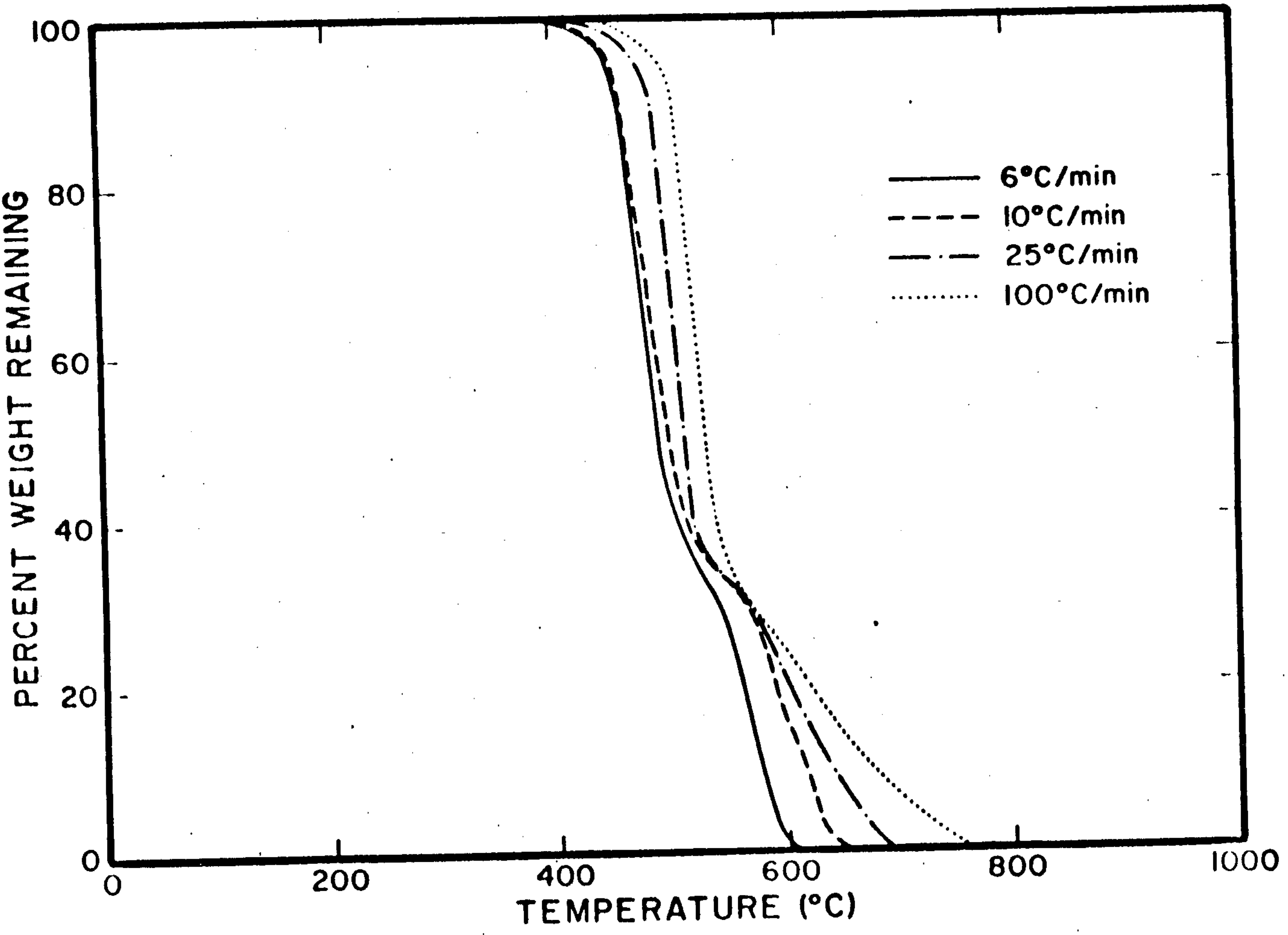


Figure 34. Effect of heating rate on sample weight loss for polycarbonate in air.

Effect of environment on polymer degradation. The effects of environment on sample weight loss for the polycarbonate polymer is illustrated in Figure 35. The first noticeable weight loss was observed when the polymer was heated to approximately 350°C in oxygen. The temperature at which the sample was first observed to lose weight in an air environment was 20°C higher than that which was observed in the oxygen atmosphere. Table 35 contains a summary of the information obtained during the thermoanalyzer experiments. The temperatures of the DTG maxima, the DTA maxima, the specific temperatures at which 5, 50, and 90 pe-cent of the original sample weight was lost, the nature of the overall degradation process, as well as the amount of char remaining at "i point" and at 1000°C, are compared for the three environments.

Figures 36 and 37 are composite thermograms illustrating the effect of environment on thermal transitions and rate of sample weight loss, respectively.

The results indicated in Figures 36 and 37 agree with the earlier studies by Telamini(91) and show that the mechanism and rate of polymer degradation is highly dependent upon the availability of oxygen to the sample. This dependence appears more pronounced in high-temperature resistant polymers such as the polyaromatic amides.

3. Pyrolysis studies

Pyroprobe (fast heating) studies. The volatile products produced during the pyrolysis of the polycarbonate polymer were separated, identified and quantitated as described in Chapter IV. Four experiments

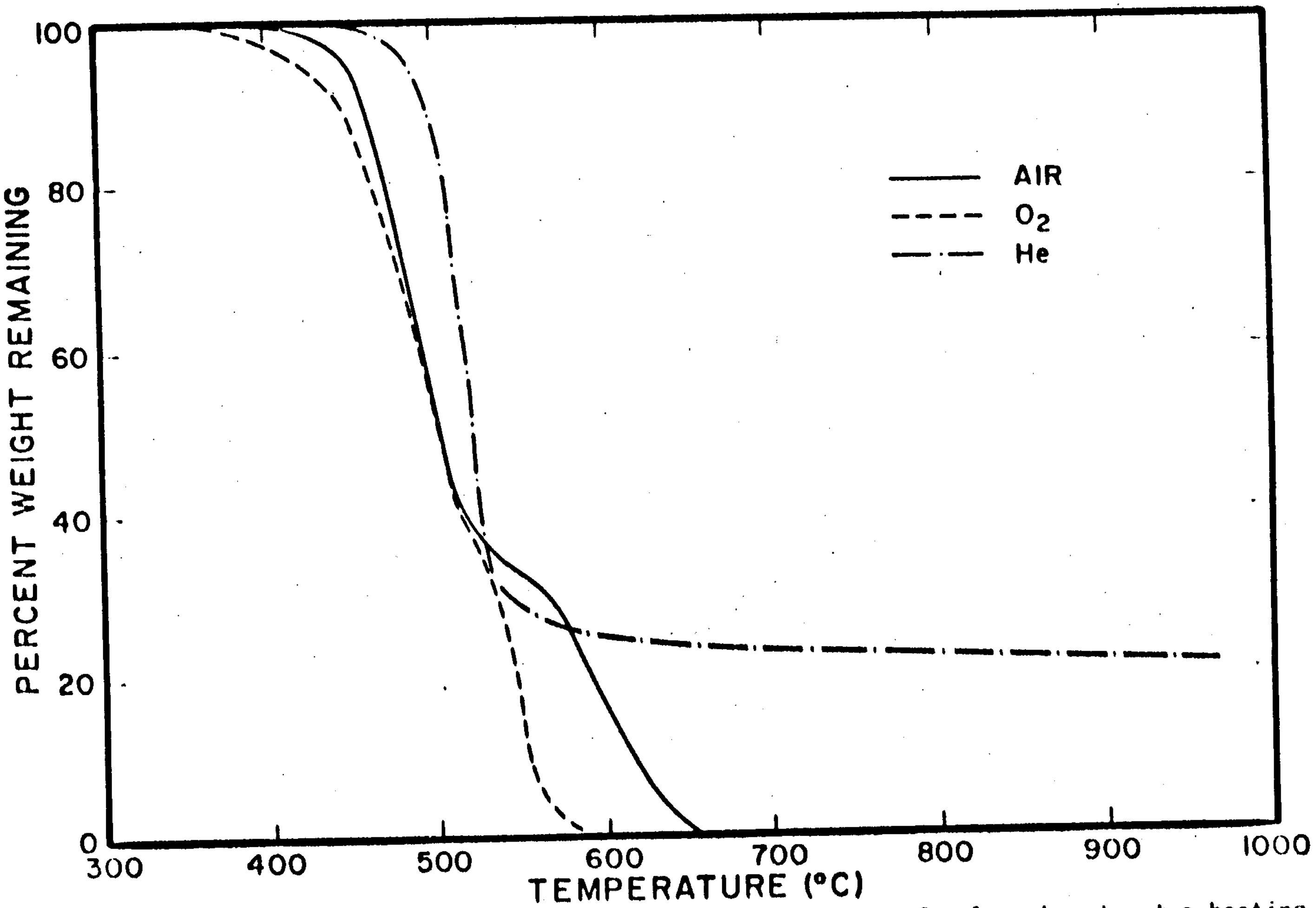


Figure 35. The effect of environment upon the weight loss of polycarbonate at a heating rate of 10°C/minute.

Table 35. The Effect of Environment upon the Degradation of Polycarbonate[a]

Environment	DTG Maxima[b]					DTA Maxima					Temperature at Weight Loss of			Nature of Degradation Process	% Char at	
	1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th	5th	5%	50%	90%		1 point	1000°C
Helium	521	-	-	-	-	515	-	-	-	-	495	522	-	Slightly Endothermic	30%	23%
Air	440	490	511	620	-	440	484	494	506	604	459	500	612	Exothermic	35%	0%
Oxygen	406	459	494	508	550	406	457	497	506	551	420	500	553	Exothermic	35%	0%

[a] Data obtained from a programmed heating rate of 10°C/min from ambient to 1000°C.

[b] Temperatures at which the derivative of the sample weight loss was at a maxima.

[c] The point where the TGA curve exhibits inflection. The degradation mode changes at this point.

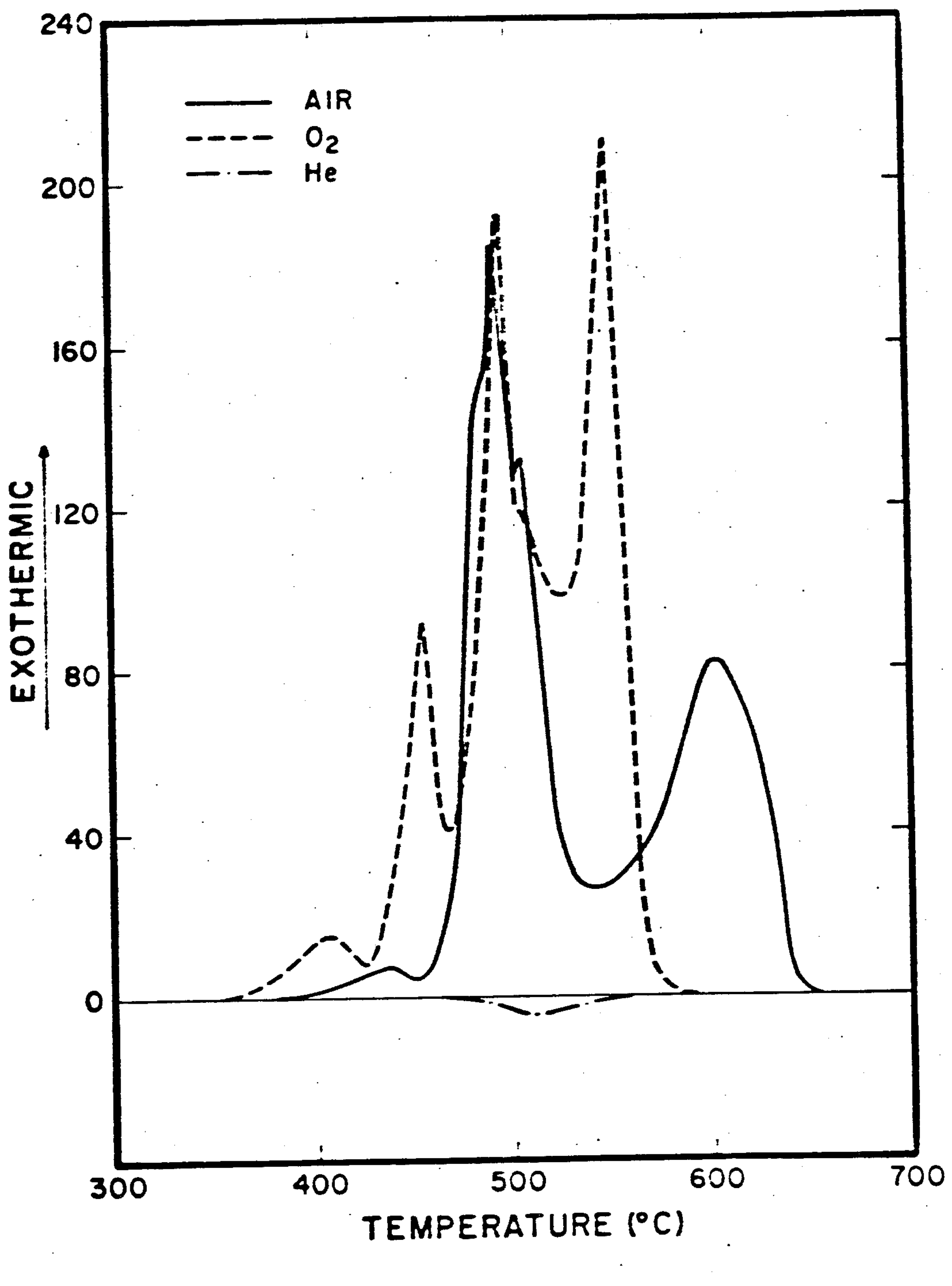


Figure 36. The DTA traces of polycarbonate in helium, air, and oxygen environments.

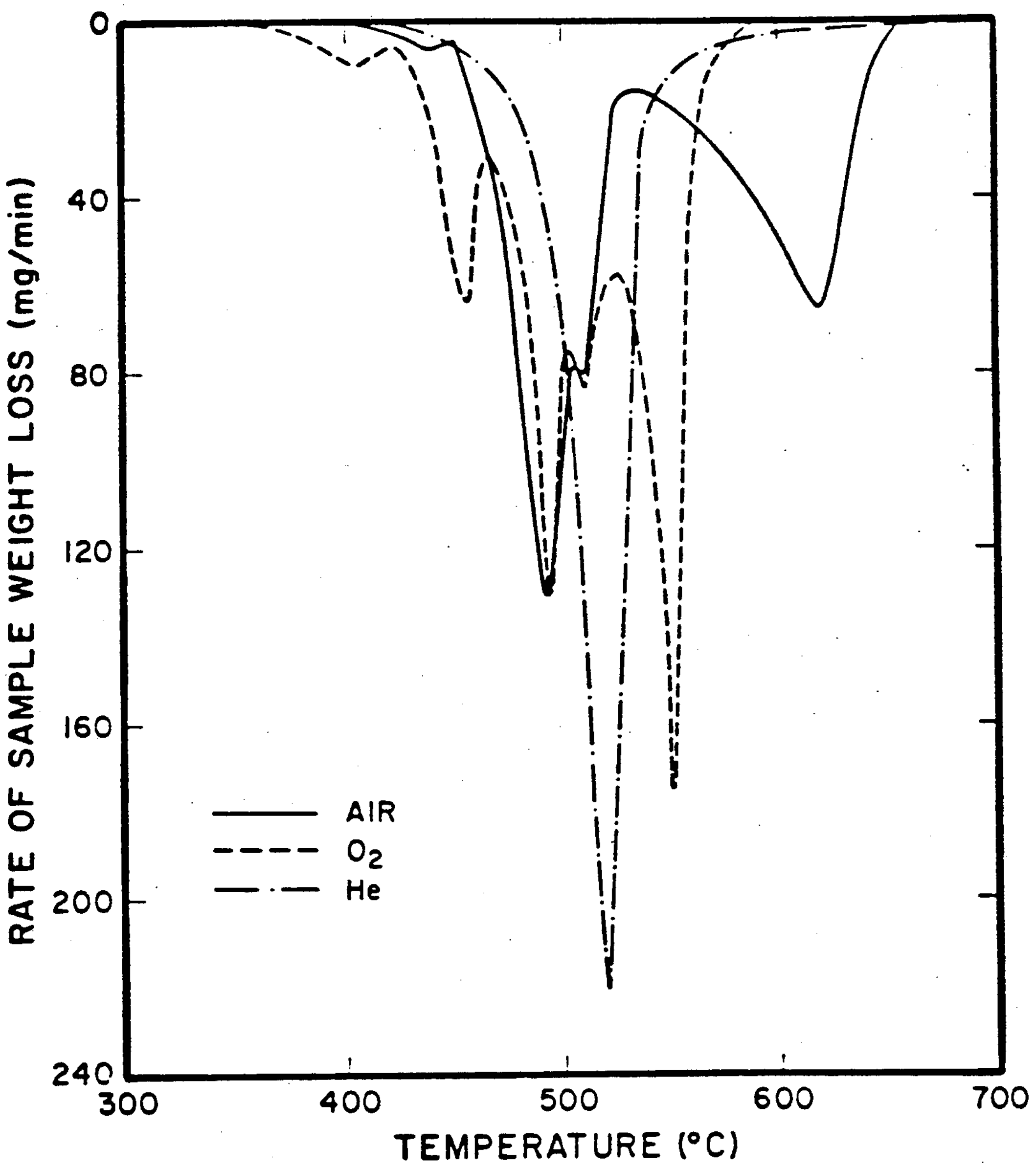


Figure 37. The DTG traces for polycarbonate in helium, air, and oxygen environments at 10°C/minute.

were conducted using samples of polycarbonate polymer (7-8 mg) wherein the sample was pyrolyzed at 1000°C for a period of 20 seconds. An average of 46.2 percent of the original low-boiling volatiles sample weight was lost during pyrolysis. A chromatogram of the low-boiling volatile products is shown in Figure 33 and the twenty compounds which were identified are listed in Table 36.

Approximately 21 percent of the original polymer weight was liberated in the form of low-boiling volatiles. Ninety-seven percent of this weight loss was identified and quantified as these specific compounds. The char residue recovered from the pyroprobe accounted for an additional 57 percent of the original sample weight. Thus, approximately 22 percent of the initial sample weight was converted to products which did not elute from the gas chromatograph.

As illustrated in Table 36, the major products obtained during the pyrolysis of the polycarbonate polymer at 1000°C were carbon dioxide, methane and carbon monoxide. Series of phenolic compounds, such as phenol, p-cresol, and ethyl phenol, were observed in significant quantities. Other products were, in order of decreasing concentration, naphthalene, water, toluene, benzene, ethane, xylene, propene, and ethylene.

Thermoanalyzer (slow heating) studies. Fifty million samples of polycarbonate powder were pyrolyzed in the thermoanalyzer in a helium environment. In all these experiments trapping of the effluents started at 400°C, which was below the temperature where the first weight loss occurred. The sampling of products was continued for a five-minute period after a temperature of 1000°C was attained, in order to collect

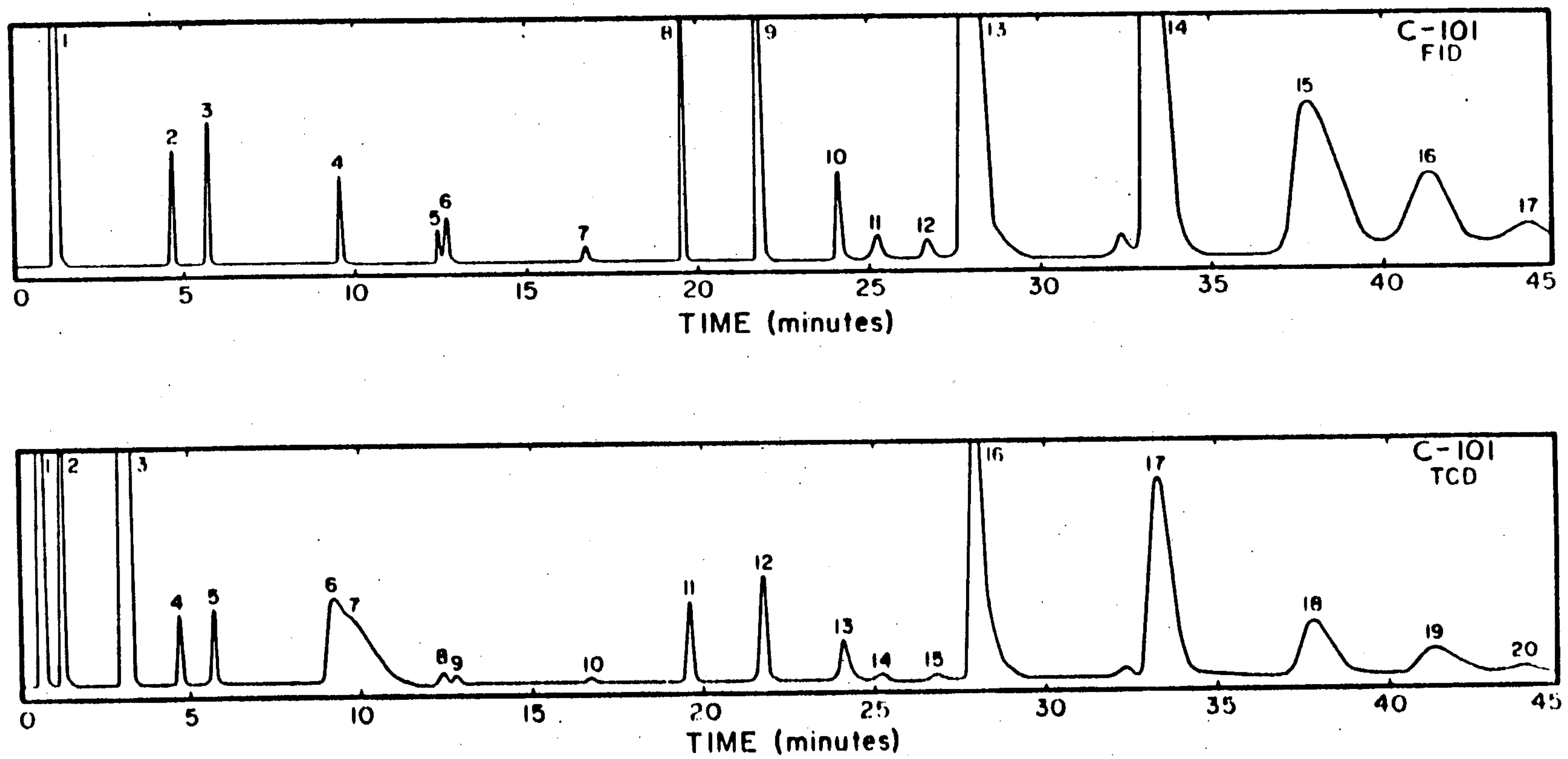


Figure 38. Low-boiling volatiles produced during the pyrolysis (pyroprobe) of polycarbonate at 1000°C.

Table 36. Low-Boiling Volatiles Produced During The Pyrolysis (Fast Heating) Of Polycarbonate[a]

Compound	Peak Number[b] (FID)	Peak Number[b] (TCD)	Quantity[c]
Carbon monoxide		1	82.01
Methane	1	2	120.16
Carbon Dioxide		3	119.36
Ethylene	2	4	2.60
Ethane	3	5	2.95
Water		6	7.77
Propene	4	7	2.66
Methanol	5	8	0.30
Acetaldehyde	6	9	0.25
Cyclopentadiene	7	10	Trace
Benzene	8	11	3.35
Toluene	9	12	5.40
Xylene	10	13	7.84
Styrene	11	14	Trace
Isopropylbenzene	12	15	Trace
Phenol	13	16	39.87
P-Cresol	14	17	57.90
Ethylphenol	15	18	17.00
Naphthalene	16	19	15.69
Biphenyl	17	20	Trace
Total			485.11

[a] Direct probe pyrolysis at 1000°C for 20 seconds using 7-8 mg sample in a helium environment.

[b] Peak numbers refer to Figure 38.

[c] Milligrams of compound per gram of consumed sample during pyrolysis.

all the residual materials which might remain in the furnace of the thermoanalyzer and inside the connecting transfer lines.

The low-boiling volatiles, which were identified from these experiments, are listed in Table 37 and the chromatograms are shown in Figure 39. A total of 330.54 mg per gram of original sample was recovered as low-boiling volatiles. As is indicated in Table 37, methane, carbon dioxide, carbon monoxide and water comprised the major products formed during pyrolysis. A substantial quantity of p-cresol, benzene, phenol,and toluene were also formed during pyrolysis.

The carbon monoxide that was produced by the polycarbonate polymer under conditions of pyrolysis in a helium atmosphere was measured by IR techniques. The CO absorption at 2160 cm^{-1} was monitored continuously as the temperature of the sample was increased at a rate of 100°C/min.

Carbon monoxide was liberated from the polymer beginning at an early stage of degradation; total carbon monoxide evolved represented 2.4 percent of the original sample weight. Thus, the value of 24 mg of carbon monoxide per gram of the original polymer has been added to Table 37, summarizing the volatile products formed in the pyrolysis experiments.

A heavy brown oil, which formed during pyrolysis, was trapped on the glass fiber filter. This oil, which was very viscous, accounted for 415 mg per gram of original sample. The analysis of this oil was performed as described below. In addition, the furnace was rinsed with dimenthyl formamide and dimenthysulfoxide several times after the furnace was cooled, but no significant amount of residue was recovered.

Table 37. Low-Boiling Volatile Products Produced During The Pyrolysis (Slow Heating) Of Polycarbonates[a]

	Peak Numbers[b]		T.E.[c]	R.F.[d]	Quantity[e]
	FID	TCD			
Carbon monoxide		1	0.00	0.670	24.00
Methane	1	2	0.05	0.340	97.00
Carbon Dioxide		3	0.97	0.915	95.00
Ethylene	2	4	0.96	0.585	5.73
Acetylene	3	5	0.96	0.580	2.04
Ethane	4	6	0.95	0.590	2.08
Water		7	0.82	0.550	25.00
Propene	5	8	0.93	0.970[f]	2.11
Propyne	6	9	0.98*	0.950	0.37
Cyclopentadiene	7	10	0.95	0.674	1.13
Hexatriene	8	11	0.95*	0.65*	0.13
Benzene	9	12	0.90	0.780	16.30
Toluene	10	13	0.95	0.794	10.80
Xylene	11	14	0.95	0.812	4.92
Styrene	12	15	0.95	0.800	1.35
Isopropylbenzene	13	16	0.95*	0.805	0.71
Phenol	14	17	0.88	1.105	14.02
P-Crosol	15	18	0.80	1.200	18.80
Ethylphenol	16	19	0.70*	1.3*	6.60
Naphthalene	17	20	0.50	1.050[f]	2.45
Biphenyl	18	21	0.40*	1.318	Trace
Total					330.54

*Estimated

[a] Average of five determinations, 50 mg sample size.

[b] Corresponds to peak numbers in Figure 3a.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as measured by analytical techniques.

[f] Relative response factors for the flame ionization detector.

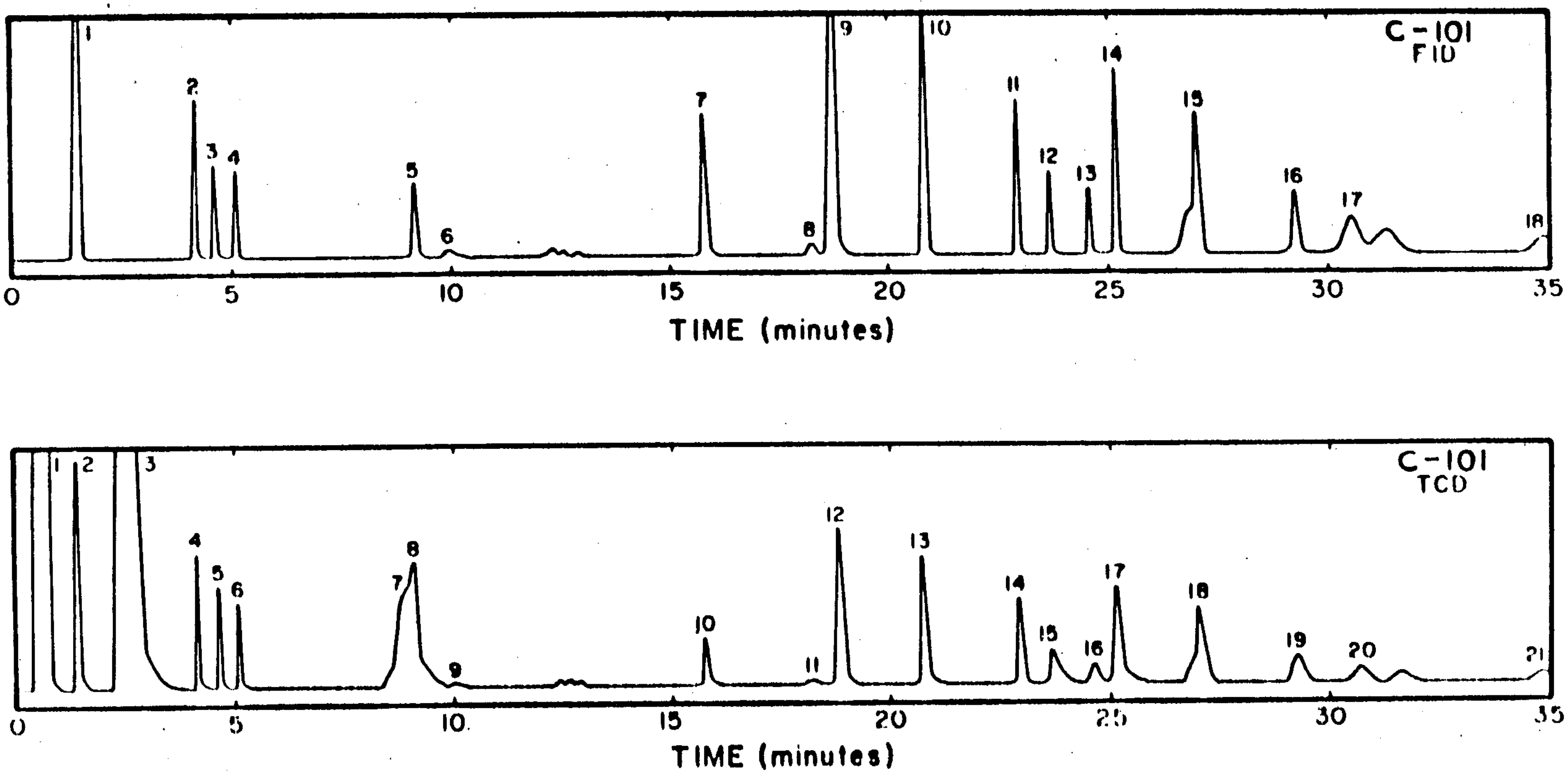


Figure 39. Low-boiling volatiles produced during the pyrolysis (slow heating) of polycarbonate to 1000°C.

The high-boiling volatiles that were formed in the pyrolysis of polycarbonate were spread on a sodium chloride plate and the infrared spectrum (shown in Figure 40) was obtained. The IR spectrum, thus obtained, resembles the Bisphenol-A used in the synthesis of polycarbonate polymers. An infrared spectrum of Bisphenol-A is shown in Fig. 41. Three small peaks were observed in the range of 1700-1800 cm^{-1} and one at 1790 cm^{-1} agrees with the carbonate C=O stretching band of polycarbonate. The other two peaks suggest the existence of small amounts of ester linkage of carboxylic acid.

The high-boiling volatiles dissolved in polar solvents, such as acetonitrile, acetone and THF, partly dissolved in benzene and toluene, and was not soluble in hexane and cyclohexane. This solubility indicates that the sample contained little Bisphenol-A (which is soluble in toluene) and that the major fractions of the sample were higher molecular weight species.

The HPLC chromatogram, illustrated in Figure 42, was obtained using the technique described in Chapter IV. More than 25 components were separated, however, no significant quantity of Bisphenol-A or p-cresol was found.

The elemental composition of the high-boiling volatiles were determined. The results from duplicate analyses of the high-boiling volatiles and theoretical values of Bisphenol-A, oligomers, and polycarbonates are shown in Table 38. It should be noticed that the calculated values of the tetramer are rather close to the observed values. From these results one can estimate the high-boiling volatiles

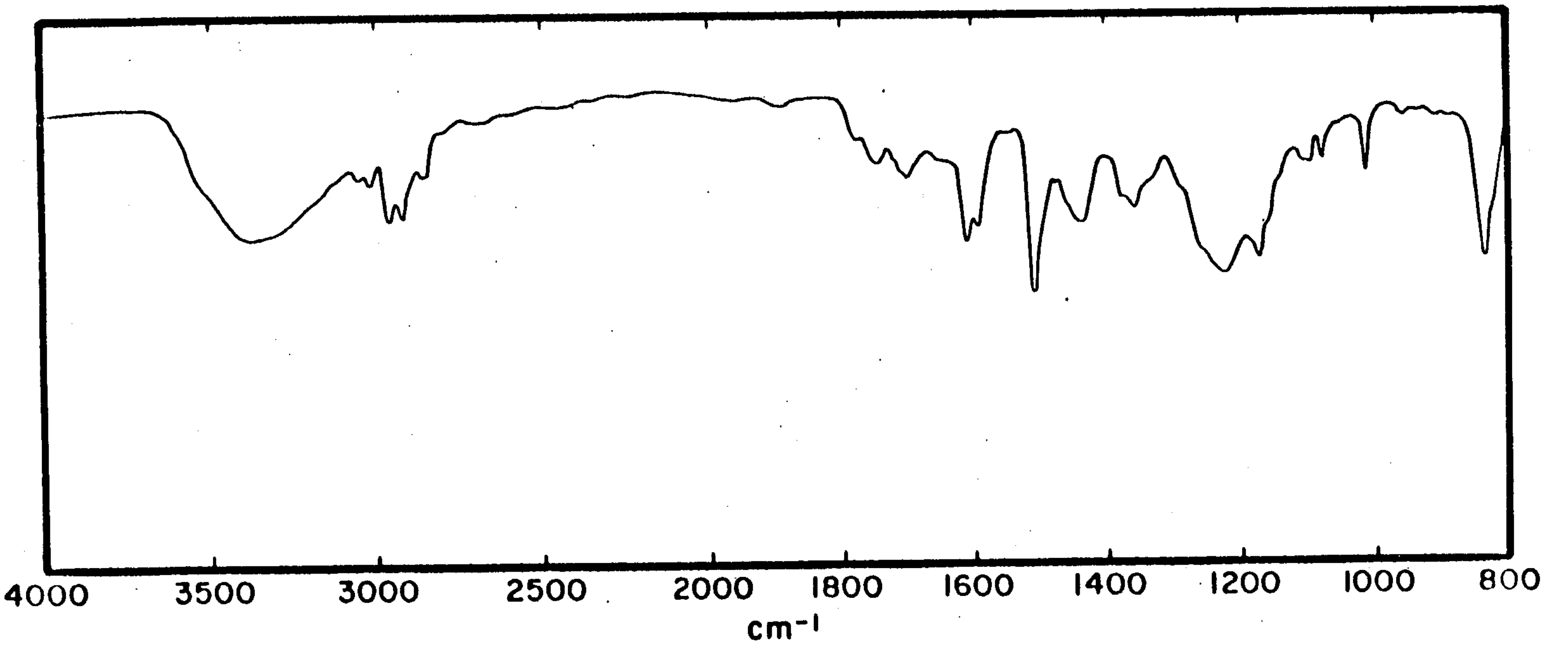


Figure 40. The infrared spectrum of high-boiling volatiles produced during the pyrolysis (slow heating) of the polycarbonate polymer.

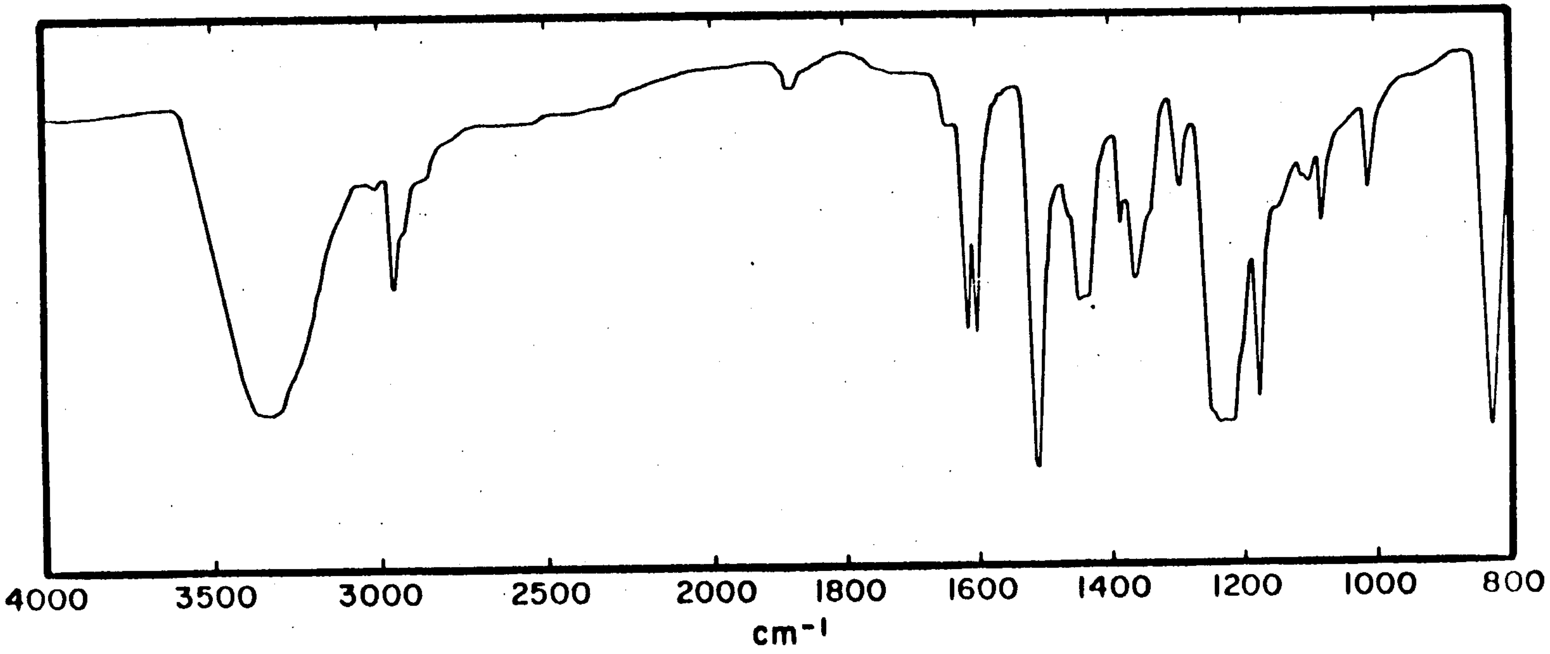


Figure 41. Infrared spectrum of bisphenol A.

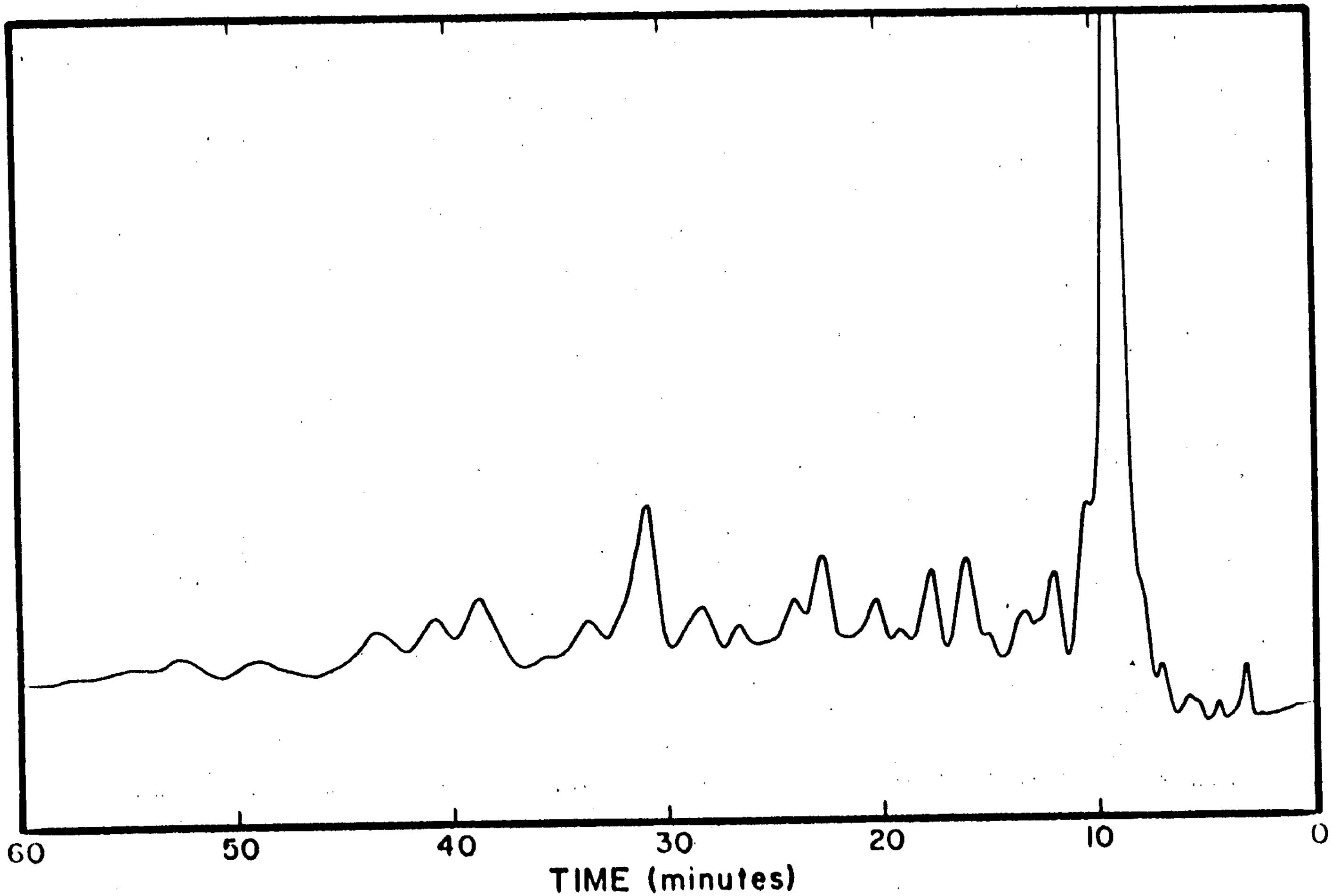


Figure 42. HPLC chromatogram of the high-boiling volatiles produced during the pyrolysis (slow heating) of the polycarbonate polymer.

Table 38. Elemental Composition of High-Boiling Residue Produced During the Pyrolysis (Slow Heating) Of Polycarbonate

	% Composition		
	Carbon	Hydrogen	Oxygen
Residue	75.78	7.05	17.17
Theoretical Bisphenol A	78.95	7.02	14.03
Theoretical Dimer	80.52	6.49	12.99
Theoretical Tetramer	76.36	5.86	17.78
Theoretical Polymer	75.59	5.51	18.90

trapped by the glass wool during pyrolysis may be a mixture of oligomers. It was surprising that no significant amount of Bisphenol-A was found under this condition of pyrolysis, as reported earlier by Davis.(87)

The char that remained in the platinum crucible of the thermoanalyzer after an exposure to 1000°C accounted for 23.0 percent of an original sample weight. This char was analyzed for carbon, hydrogen, and nitrogen content. The average values obtained were 96.65% C, 0.25% H, 0% N,and 3.10% O.

Materials Balance. The data obtained from the analysis of the low-boiling volatiles, the high-boiling volatiles (heavy oil residue) and the solid residue (char) were used to obtain a materials balance for carbon, hydrogen and oxygen contained in the polymer. The results of this material balance for the polycarbonate polymer are presented in Table 38. Of the 1000 mg of original sample, 330 mg was recovered as low-boiling volatile products (Table 37) and 415 mg was trapped by the glass wool as high-boiling volatiles (heavy oil). The char sample which remained in the platinum crucible after the pyrolysis was 230 mg per gram of sample. The total amount of materials recovered accounted for 97.6 percent of the original sample weight. The recoveries for carbon, hydrogen and oxygen were 96, 113,and 101 percent, respectively.

4. Oxidative degradation (slow heating) studies

Samples of polycarbonate were degraded in air under dynamic heating rates from ambient to 1000°C at a rate of 100°C/min. The high-boiling volatiles (heavy oil) that were formed in these experiments were examined by IR, HPLC chromatography and elemental analysis. Unlike the

Table 39. Materials Balance - Pyrolysis (Slow Heating) Of Polycarbonate in Helium[a]

	Weight (mg)[b]			
	Total	Carbon	Hydrogen	Oxygen
Original polymer	1000.0	755.6	55.6	187.7
Material recovered	975.6	722.8	63.2	189.5
Low-boiling volatiles	330.5	186.1	33.3	111.1
High-boiling volatiles (heavy oil residue)	415.0	314.4	29.3	71.3
Solid residue (char)	230.0	222.3	0.6	7.1
Percent of polymers accountable in products	97.6	95.7	113.7	101.0

[a] The sample with a sample size of 50 mg was heated from ambient to 1000°C at a rate of 100°C/min.

[b] Calculated on the basis of 1000 mg of the original poly.

[c] Based on the elemental analysis.

pyrolysis reactions conducted in a helium environment, no residual char was observed in the crucible of the thermoanalyzer after the oxidative degradation of polycarbonate samples was completed.

Analysis of the low-boiling volatiles. The apparatus described in Chapter IV was used to trap and to analyze the volatile components formed during the oxidative degradation of polycarbonate. Five trapping experiments were conducted using a 50 mg sample size for the identification and the quantitation of volatile compounds. Some additional experiments were conducted using a 100 mg sample size for the identification and the quantitation of volatile compounds. Other experiments were conducted with 10 to 20 mg sample sizes to obtain quantitative data of major products such as carbon dioxide and water. Separations were achieved using Chromosorb 101 column packing in a 16 ft. x 4 mm O.D. stainless-steel tubing.

Figure 43 contains chromatograms indicating the low-boiling volatile products produced during the oxidative degradation of the polycarbonate polymer. More than 24 distinct peaks have been resolved by temperature-programming the GC column from -10 to 265°C at 10°C/min. Table 40 contains a list of the products which have been identified and the amounts of each present in mg per gram of original material.

As may be observed in Table 40, 1702.7 mg per gram of the original polycarbonate sample were recovered as volatile products. Carbon dioxide, carbon monoxide and water comprise 95.4 percent of the total volatile products measured by analytical means. Other compounds that were found in greater than trace concentrations were methane, phenol and ethylene. All of the compounds which were identified in the

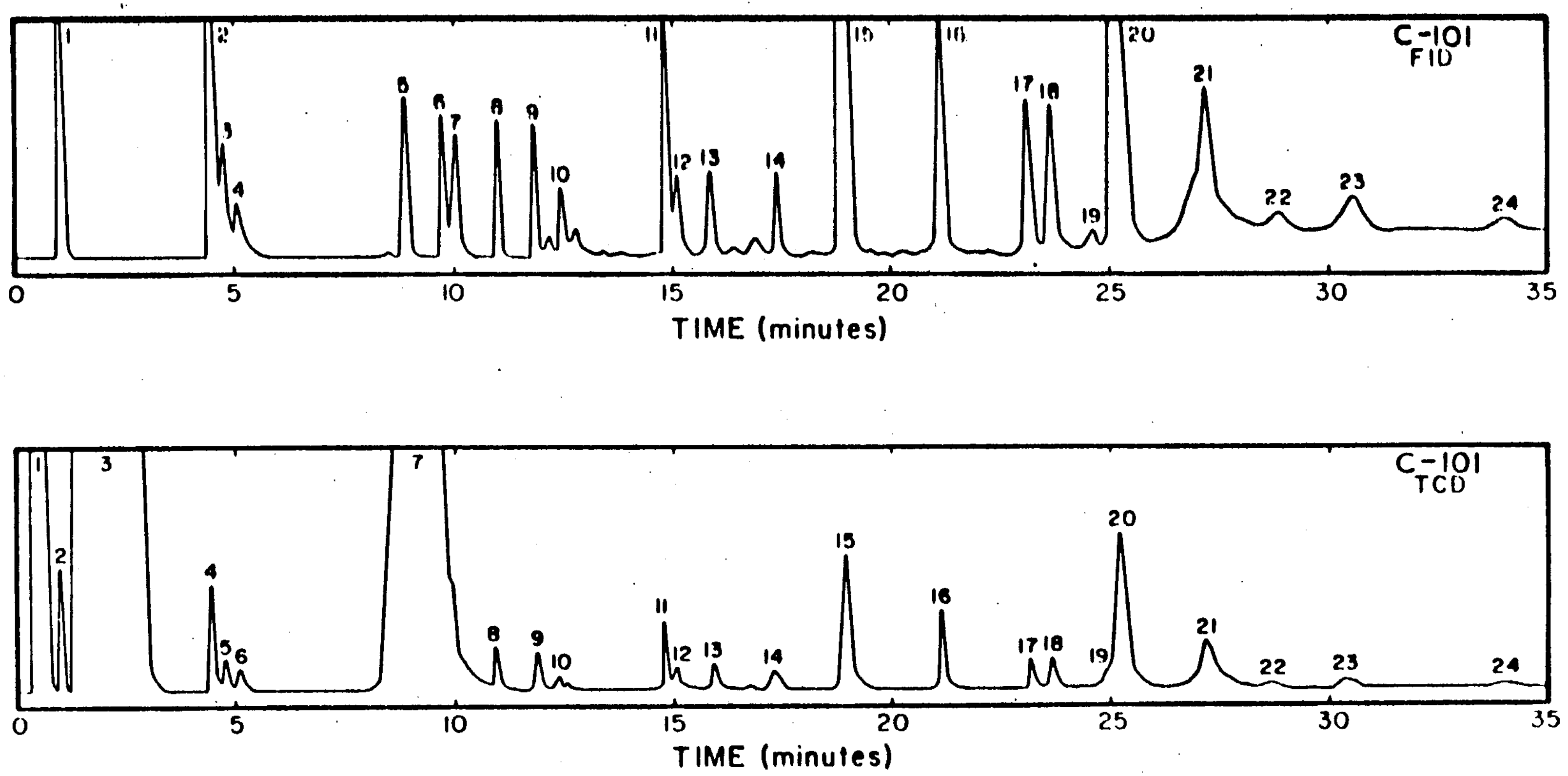


Figure 43. Low-boiling volatiles produced during the oxidative degradation (slow heating) of the polycarbonate polymer in air to 1000°C.

Table 40. Low-Boiling Volatiles Produced During Oxidative (Slow Heating) Degradation Of Polycarbonate[a]

Compounds	Peak TCD	Numbers[b] FID	T.E.[c]	R.F.[d]	Quantity[e]
Carbon monoxide		1	0.00	0.670	269.00
Methane	1	2	0.05	0.450	46.00
Carbon dioxide		3	0.97	0.915	1141.00
Ethylene	2	4	0.96	0.565	4.70
Acetylene	3	5	0.96	0.580	Trace
Ethane	4	6	0.98	0.590	0.28
Water		7	0.82	0.550[f]	215.00
Propene	5		0.98	0.970[f]	2.01
Propane	6		0.98	1.020[f]	1.42
Propyne	7		0.98*	0.950[f]	1.13
Methanol	8	8	0.75	0.580	1.59
Acetaldehyde	9	9	0.98	0.650	1.45
1,3-Butadiene	10	10	0.97	0.674	0.48
Acrolein	11	11	0.97*	0.66*	1.81
Acetone	12	12	0.97	0.680	0.36
Cyclopentadiene	13	13	0.95	0.674[f]	0.47
Butanal	14	14	0.95	1.613[f]	0.37
Benzene	15	15	0.90	0.780	3.00
Toluene	16	16	0.95	0.794	1.52
Xylene	17	17	0.95	0.812	0.89
Styrene	18	18	0.95	0.800	0.88
Isopropylbenzene	19	19	0.95*	0.805	0.07
Phenol	20	20	0.88	1.105	6.71
P-cresol	21	21	0.80	1.200	2.49
Ethylphenol	22	22	0.70*	1.3*[f]	0.09
Naphthalene	23	23	0.50	1.050[f]	Trace
Biphenyl	24	24	0.40*	1.319	Trace
TOTAL					1702.72

*Estimate

[a] Average of 5-50 mg samples heated from ambient to 1000°C at 100°C/min.

[b] Corresponds to peak numbers in Figure 43.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as determined by analytical methods.

[f] Relative response factors for the flame ionization detector.

pyrolysis experiment in a helium environment appeared in the product distributions that were produced in the oxidative degradation, although the amount of each compound is different. Some additional compounds such as methanol, acetaldehyde, acrolein, acetone, and butanol were identified as having been formed during the oxidative degradation. It should be noted that a weight increase of approximately 70 percent was observed during oxidative decomposition. This is attributed to the reaction of the sample with oxygen in its environment.

Analysis of high-boiling volatiles. During the oxidative degradation experiment a high-boiling volatile in the form of a dark-brown heavy oil deposited on the glass fiber trap which was inserted in the transfer line. This heavy oil residue, which accounted for 287 mg per gram of the original polymer was soluble in acetonitrile, acetone, THF, and dioxane, partly soluble in benzene and toluene, but insoluble in hexane. The analysis of the residue was performed utilizing IR techniques, high pressure liquid chromatograph (HPLC) and elemental analysis.

The heavy oil deposition, which was formed in the oxidative degradation of polycarbonate, was spread on a sodium chloride plate and the infrared spectrum, shown in Figure 44, obtained. This spectrum resembles that for the liquid fragment which was obtained from this polycarbonate polymer during pyrolysis. The infrared spectrum suggests that the sample contains considerable amounts of Bisphenol-A or its derivatives. Unlike the infrared spectrum of the sample exposed to pyrolysis, this sample shows stronger bands for the original polycarbonate sample at 1775 cm^{-1}, 1160 cm^{-1}, and 885 cm^{-1}.

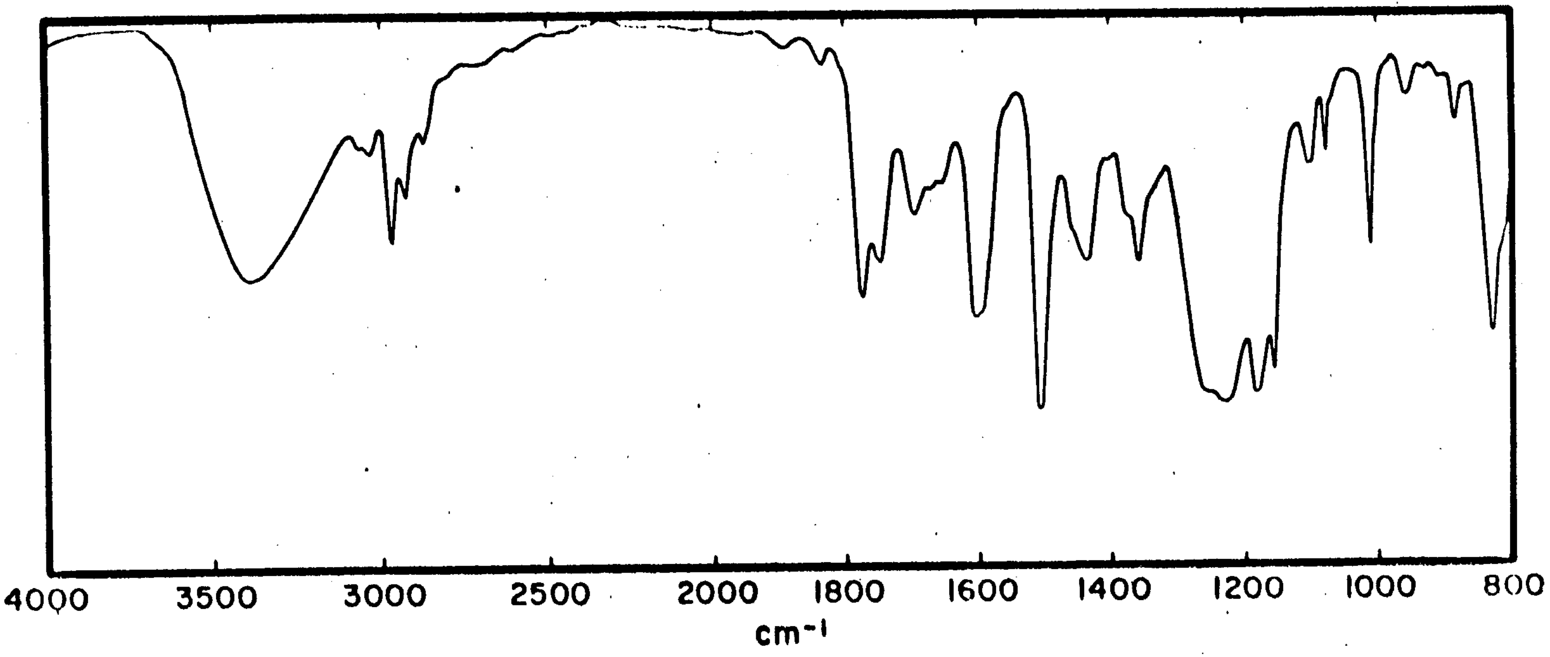


Figure 44. The infrared spectrum of high-boiling volatiles produced during the oxidative degradation (slow heating) of the polycarbonate polymer.

The heavy oil obtained during the oxidative degradation of the polycarbonate polymer was analyzed by HPLC techniques described in Chapter IV. The resulting chromatogram, shown in Figure 45, contained more than 20 compounds. The largest peak, with a retention time of 6.2 minutes, was found to be Bisphenol-A, a compound not present in the high-boiling volatiles produced during pyrolysis experiments.

Carbon, hydrogen, and oxygen analysis were performed on the high-boiling volatile residues produced during the decomposition of polycarbonate. A summary of these results is presented in Table 41, together with the analysis of the residue from the pyrolysis of polycarbonate. Theoretical compositions for Bisphenol-A, oligomers, and polycarbonate are also listed for reference. The elemental composition found for the sample can be explained as a mixture of Bisphenol-A and oligomers or polymer.

<u>Analysis of solid residue</u>. No char remained in the crucible of the thermoanalyzer after exposure of the sample in an oxidative environment to 1000°C. Attempts were made to follow the change of the elemental composition of the residual compounds remaining in the crucible during several stages of weight loss. The results of this study are summarized in Table 42.

<u>Materials Balance</u>. A materials balance was calculated using the information obtained from the analysis of the volatiles and the heavy oil residue (high-boiling volatiles). Since the reaction of the polymer with the oxygen accounted for a major increase in weight, as compared to the initial sample weight, a materials balance for oxygen was not calculated. Table 43 contains a summary of the materials balance

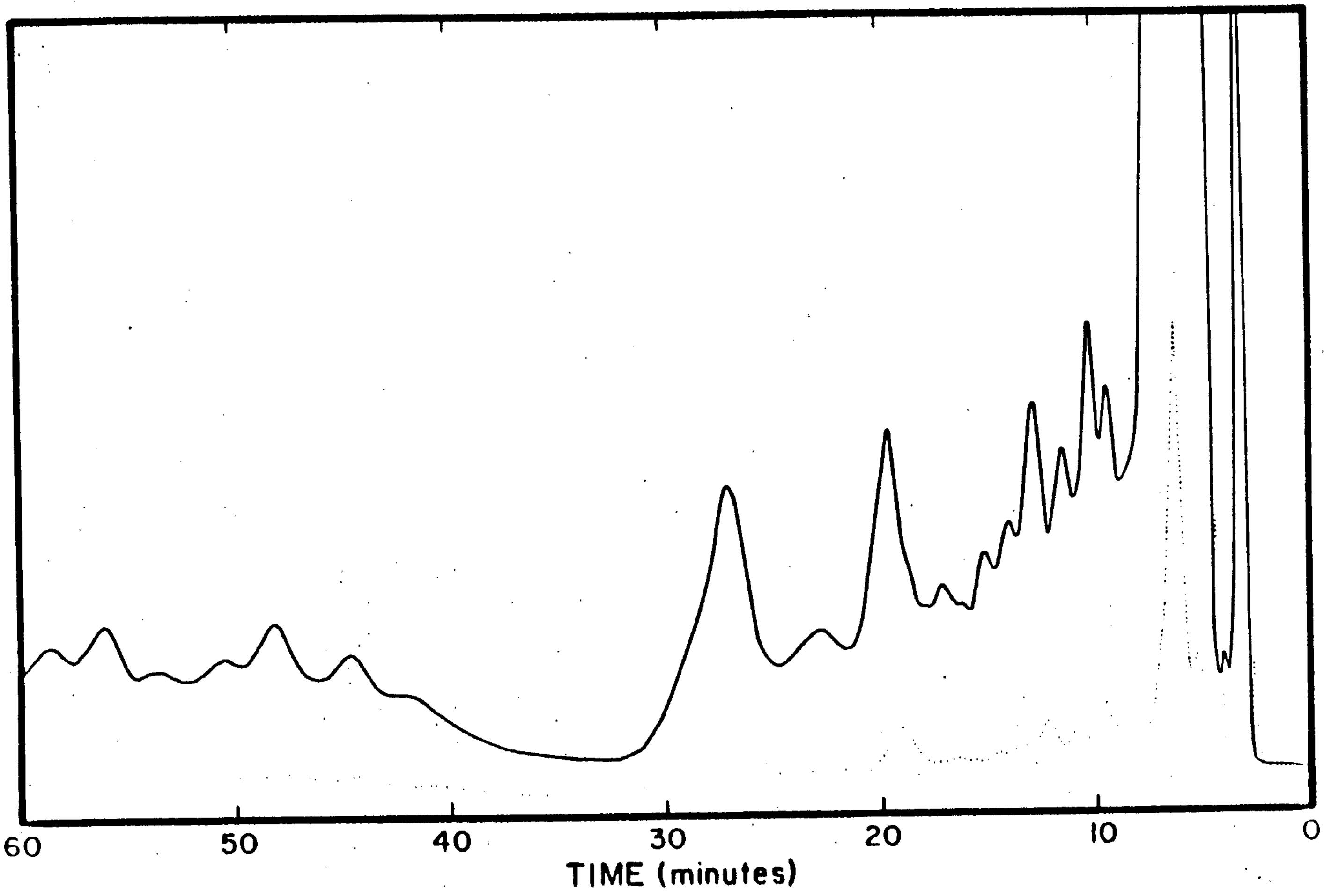


Figure 45. HPLC chromatogram of the high-boiling volatiles produced during the oxidative degradation (slow heating) of the polycarbonate polymer.

Table 41. Elemental Analysis of High-Boiling Residues Produced During The Thermal Decomposition (Slow Heating) Of Polycarbonate

	% Composition		
	Carbon	Hydrogen	Oxygen
High-Boiling Volatiles Produced During Oxidative Degradation	77.17	6.10	16.75
High-Boiling Volatiles Produced During Pyrolysis	75.78	6.10	16.76
Theoretical, Bisphenol-A	78.95	7.02	14.06
Theoretical, Dimer	80.52	6.49	12.99
Theoretical, Tetramer	76.36	5.86	17.78
Theoretical, Polymer	75.59	5.51	18.90

Table 42. Elemental Analysis Of Polycarbonate At Several Stages of Oxidative Degradation[a]

% Weight loss of the original sample	% Composition		
	Carbon	Hydrogen	Oxygen
0% (original sample)	75.66	5.56	18.77
50%	82.22	4.42	13.35
67%	86.58	2.96	10.46

[a] The heating rate of the sample was 10°C/min.

Table 43. Materials Balance - Oxidative Degradation (Slow Heating) Of Polycarbonate

	Weight (mg)[a]		
	Total	Carbon	Hydrogen
Original polymer	1000	756.6	55.6
Material Recovered	1989.7	706.8	56.1
Low-boiling volatiles	1702.7	485.3	38.6
High-boiling volatiles[b] (heavy oil residue)	287.0	221.5	17.5
Solid residue (char)	0	0	0
Percent of polymers accountable in products	199.0	93.4	100.9

[a] Calculated on the basis of 1000mg of the original polymer.

[b] Calculated from the result of elemental analysis.

that was obtained during these experiments with the polycarbonate polymer when a 50 mg sample was heated from ambient to 1000°C at a rate of 100°C/min in air. On the basis of 1000 mg of the original sample, 1702.7 mg of low-boiling volatiles, together with 287 mg of high-boiling volatiles, were recovered. No significant amount of char residue was recovered. The total amount of materialsrecovered was 1989.7 mg. Hence, the overall yield for this experiment was 199 percent, based on the original sample weight. The elemental composition of the volatile products was based upon the sum of carbon and hydrogen content of the individual products. The amount of each element in the high-boiling volatile fraction was based upon the result of the elemental analysis. When the elemental composition of the identified material is summed, 93.4 percent of the carbon and 100.9 percent of the hydrogen that were present in the original sample are accountable in the products observed.

D. Discussion

In the study of the pyrolysis and the oxidative degradation of the polycarbonate polymer virtually all the products (low-boiling volatiles, high-boiling volatiles and solid residues) were separated, analyzed and quantitated. These results were used to develop a materials balance specific for each mode of decomposition.

In the inert helium environment, approximately 98 percent of the sample weight was recovered. The materials balance for carbon, hydrogen, oxygen was 95.7, 113.7, and 101.0 percent, respectively.

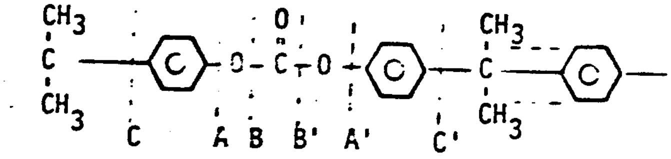
In an oxidative environment the materials balance was calculated only for carbon and hydrogen, since a considerable amount of oxygen was taken up from the environment during the oxidative degradation reaction. The balance for carbon and hydrogen was 93.4 and 100.9 percent. A significant amount of char was formed which accounted for approximately 23 percent of the original polymer weight. The degradation reaction commenced at lower temperatures than was observed during the pyrolysis in an inert helium environment. The oxidative degradation was multi-modal and thus more complex than was observed in the inert environment (see Figures 35, 36, 37). The char, which was observed to form during the oxidative degradation, decomposed completely at high temperatures. The products produced during the pyrolysis and oxidative degradation of the polycarbonate polymer are summarized in Tables 37 and 40. It is evident from the information presented in these tables that some differences exist between the product distributions that were observed in the inert and reactive environments.

In a helium environment oligomers were formed which accounted for 415 mg/gram of the original sample. These results are different from those reported by Davis and Golden.(86, 87) Davis and Golden reported the formation of a significant quantity of Bisphenol-A. It should be noted that their experiments were conducted in vacuum, thus the volatile products eluting from the sample were rapidly removed from the furnace and the potential for secondary reactions was substantially reduced. In the oxidative environment there was a major increase in the quantities of carbon monoxide, carbon dioxide and water produced as compared to the concentrations of these products produced during pyrolysis. In addition to the compounds which were identified during the pyrolysis experiments, a number of additional species were observed, including Bisphenol-A, during the oxidative decomposition of the polycarbonate polymer. In general, the quantities of most compounds, except of CO, CO_2, and H_2O decreased, as oxygen was added to the sample's environment.

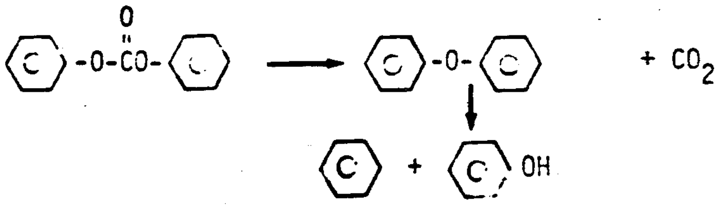
The elemental composition of the solid residue recovered during the oxidative degradation at 50 percent weight loss was significantly altered from that of the original polymer. Further increases in the carbon concentration accompanied by respective decreases in hydrogen and oxygen content of the char were observed at the point where 67 percent weight loss occurs. This is obviously different from the decompositions observed in the other polymers studied, such as Nylon 6 an PET. The rapid loss of oxygen in the oxidative environment should be noted. This information suggests that the elimination of carbon dioxide and the formation of char occurred at an earlier phase of the degradation of polycarbonate.

The formation of the major pyrolysis products can be explained in terms of simple cleavages of the carbon-carbon and carbon-oxygen atom bonds in the structure of the polycarbonate polymer.

The weak bonds in the polycarbonate structure are:

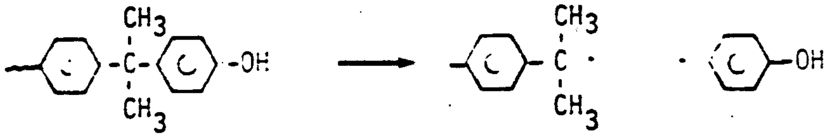


A, B, C and D, as illustrated. During the pyrolysis, consecutive cleavages at positions A and B' or B and A' could account for the formation of the most abundant species, carbon dioxide. Cleavage at D or D' is responsible for the formation of methane. Diphenyl carbonate will be formed by the scissions at C and C'. This compound will readily decompose to benzene, phenol and carbon dioxide by hydrogen abstraction:



(23)

Phenol and benzene can also be formed from terminal groups:



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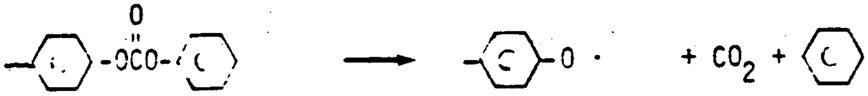
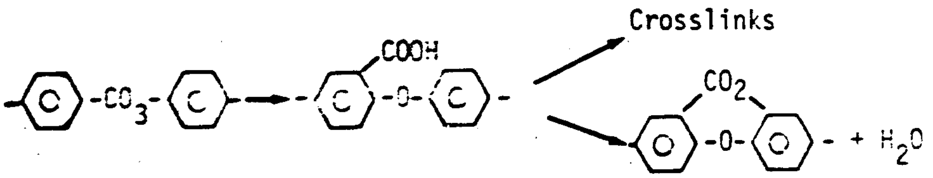


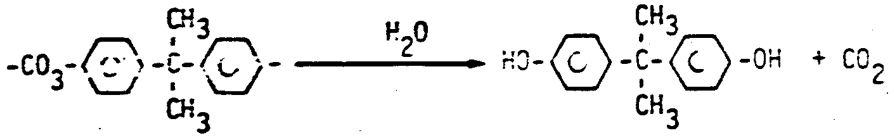
(25)

Using the hypothesis by Davis and Golden,(86) the formation of water and crosslink structure can be explained:



(26)

In the oxidative environment it is probable that the degradation of isopropylidene groups involves oxidation to hydroperoxides, followed by extensive chain scission.(84) This breakdown mechanism will be superimposed upon the normal thermal degradation of polycarbonate. Since a high concentration of water can be formed during the oxidative degradation process, hydrolysis may become an important reaction during the degradation in an air environment:



(27)

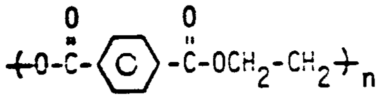
This reaction will result in the formation of carbon dioxide and Bisphenol-A, the latter not being observed in the products of pyrolysis.

CHAPTER VII

POLYETHYLENE TEREPHTHALATE POLYMER

A. Introduction

Polyethylene terephthalate (PET) is a polyester with a repeat unit of

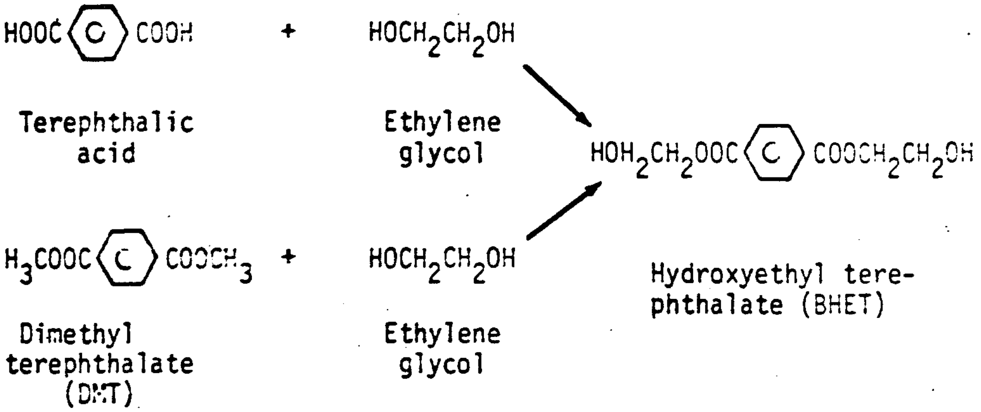


PET polymers are one of the most important classes of commercial polymers used in the manufacture of fibers and films where high strength is required. This polymer is widely used commercially in the manufacture of tire cord, as well as for the manufacture of motion-picture film and recording tapes. Polyethylene terephthalate was first synthesized by Whinfield and Dickson(92,93,94) and resulted directly from the earlier work of Carothers.(11,95,96) Whinfield and Dickson incorporated a stiff *p*-phenylene group into the polymer chain. Industrial production of PET polymers commenced in the early 1950's in England and the United States, and today the world consumption of PET in 1976 was estimated to be approximately 4.5 million tons with a United States consumption of nearly 1.5 million tons. Polyethylene terephthalate now completely outsells Nylon and it is the most widely used synthetic fabric material. Polyethylene terephthalate is produced worldwide and is sold under a variety of names which are listed below: Dacron (duPont); Mylar (duPont, film), Terylene (U.K.), Kodel (Eastman Kodak), Fortrel (Fiber Industries, Trevira (Hoechst), and Tetoron (Japan).

Polyethylene terephthalate possesses a high crystalline melting point, 265°C, and retains good mechanical properties at temperatures up to 150-175°C; its chemical and solvent resistance are good. Polyethylene terephthalate yarn blends well with other fibers, especially cotton, to provide easy-care and permanent press characteristics. The use of PET polymers in carpeting is expanding. Polyethylene terephthalate fiberfill is widely used for insulation applications. Due to its good mechanical properties and transparency, PET is used as a film base as well as a base for magnetic tapes where its thinning characteristics are required.

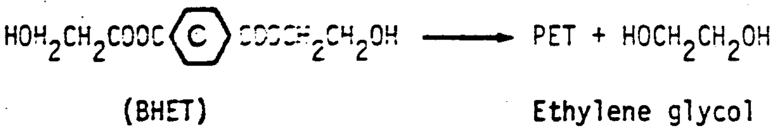
Polyethylene terephthalate is produced from terephthalic acid and ethylene glycol. Terephthalic acid is derived from p-xylene by an oxidation reaction and is frequently used in the form of the dimethyl ester--dimethyl terephthalate (DMT), since the latter is easier to purify and handle than terephthalic acid. Ethylene glycol is obtained commercially from ethylene via ethylene oxide.

Polymerization is carried out in two steps. The first step encompasses the reaction of terephthalic acid or DMT with ethylene glycol to form bis-(hydroxyethyl) terephthalate (BHET).



(28)

Calcium magnesium, or manganese, is used to catalyze this reaction. The first step is necessary to attain the exact stoichiometry between the carboxylic acid and the diol. The second step, during which the polymer is actually formed, is taken place in a temperature range of 230-285°C.



(29)

Since the equilibrium of this reaction is not favorable for the formation of polymer, it is necessary to remove ethylene glycol utilizing a high vacuum up to 0.5 mm Hg. Antimony trioxide, Sb_2O_3, is used to promote this condensation reaction. The polymer thus formed has molecular weight of 20,000-30,000, and an intrinsic viscosity of 0.40-0.50 as measured in o-chlorophenol solution.

As PET is widely used for apparel and home interior materials, such as carpets and curtains, good flame-retardancy is required. The

U.S. Sleepware Standard, the most stringent legislation in the world pertaining to flammability, has been in effect since 1972.(4) This regulatory legislation requires that sleepware in sizes 0 to 14X meet a required maximum burn length when exposed to a flame source in a vertical position. The PET polymer melts when exposed to a small ignition source and the flame often disappears in a flaming melt. It should be noted that the poor moisture regain characteristics of PET fabrics, similar to Nylon, makes it rather uncomfortable when used as a single fabric in clothing. Thus, other fibers, such as cotton, are used in the production of clothing. The cotton tends to stabilize the melt by forming a char and thus the PET fabric used in a blend burns more rapidly than when used alone. A number of patents have reported improved techniques for flame retarding PET fabrics. Basically, two methods are used: (1) the treatment of the textiles with fire-retardants containing phosphorus and/or halogen (chlorine or bromine); (2) the incorporation of flame-retardant elements or flame-retardants into PET polymer either by copolymerization or blending. Unfortunately, the incorporation of fire retardants into the PET polymer results in changes of the polymer's basic chemical, physical and mechanical properties.

Recently Blum and Ames (8) have stated that the fire retardant tris (2,3-dibromopropyl) phosphate, used in PET fabric, is carcinogenic. Early test results conducted by personnel of the National Cancer Institute(9) have confirmed these findings and the use of this particular fire retardant has been recently banned by the U.S. Consumer Products Safety Commission.

B. Literature Survey

Pohl(97) studied the relationship of chemical structure to the thermal stability in polyesters by measuring the rate of total gas evolution, the change in coloration and the formation of acid end groups in vacuum. These results inducated that the stability of the terephthalic acid polyesters decrease in the order of 2,2-dimethyl-propanediol-1,3>ethylene glycol>decamethyleneglycol>diethyleneglycol. Pohl attributed the order of thermal stability to the presence of the α-CH_2- group adjacent to the ether oxygen, since replacement of the β hydrogens by methyl groups increases the stability. The rate of polymer decomposition increases with an increase in the number of ether oxygens. Pohl also reported the formation of acetaldehyde, water, carbon dioxide and acid end groups as well as anhydride end groups as determined by infrared examination. These results were interpreted to indicate that random scissions occur during the degradation of PET polymers. Marshall and Todd(98) studied the kinetics of degradation of PET in an oxygen-free atmosphere, by measuring the change in melt viscosity as a function of time. The initial rate of degradation was calculated from the decrease in melt viscosity and was found to be in good agreement with that calculated using the standard equations for random chain scission. Scission was found to occur at the ester linkages to give one carboxyl group per chain scission. A radical mechanism was postulated for the thermal decomposition process, since the rate of degradation was accelerated by oxygen. The principal products of pyrolysis found, when the polymer was exposed at 280-320°C for 30 hours, were carbon dioxide, carbon monoxide and acetaldehyde. The sublimate consisted of terephthalic acid and an unidentified material, presumed to be a segment of the chain about the size of a monomer or dimer unit. The proportion of terephthalic acid and the unidentified material was found to increase by 300°C, while at 320°C the sublimate contained almost pure terephthalic acid.

Mikailov(99) studied PET fiber at temperatures around 200°C. He observed that deterioration of the mechanical properties of the fibers were accelerated by the presence of oxygen. Similar effects caused by oxygen were found in studies of the photo-degradation of PET polymers.

Ritchie(100) studied the mechanism of thermal degradation by pyrolyzing model compounds (simple carboxylic esters) in the vapor phase at 400-500°C. These studies indicated that initiation of thermal decomposition is a primary alkyl-oxygen scission of the type:

$$\mathrm{RCOOCCH} \rightarrow \mathrm{RCOOH} + {>}\mathrm{C{=}C}{<} \qquad (30)$$

with competing secondary scission such as alkenyl-o-scission

$$\mathrm{RCOOC{=}CH} \rightarrow \mathrm{RCOOH} + -\mathrm{C{\equiv}C}- \qquad (31)$$

Goodings(101) carried out degradation experiments of PET polymers in the liquid phase at 262-323°C in an oxygen-free atmosphere. He observed that PET decomposed slowly with an evolution of gaseous products, the formation of low-molecular weight products, the formation of different functional groups and the discoloration of the polymer. The concentration of hydroxyl end-groups decreases during degradation while the concentration of carboxyl groups tends to increase. These observations agree with the results obtained during analysis of actual production processes. Such studies have shown that the number of carboxylic end groups increase slowly, even in high vacuum, at temperatures above 285°C.

Goodings(101) studied the gaseous products produced during the pyrolysis of PET in the temperature range of 283-306°C by mass spectrometry. The observed products are listed in Table 44. He also analyzed a sublimate which contained naphthalene, low molecular-weight oligomers, and unsaturated esters. A number of compounds which were identified during the pyrolysis of PET are shown in Table 45. Pohl(97) and Goodings(101) suggested the color formation of PET during pyrolysis was attributed to the presence of ethylene linkages which remain in the main chain.

Table 44. Low-boiling Volatiles Produced During the Pyrolysis of Polyethylene Terephthalate at 288°C
(Data from Reference 101)

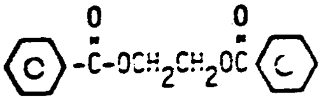
Constituent	% (mole percent of total gases)
CO	8.0
CO_2	8.7
H_2O	0.8
CH_3CHO	80.0
C_2H_4	2.0
2-Methyldioxolan	0.4
CH_4	0.4
C_6H_6	0.4

Table 45. Products Isolated from Extensively Pyrolyzed Polyethylene Terephthalate (Goodings, 1961)

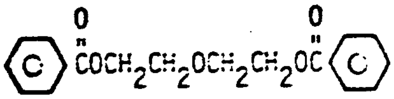
Product	Concentration in degraded polymer, Wt. %
$CH_3OOC-C_6H_4-C_6H_4-COOCH_3$	0.058
$CH_3OOC-C_6H_4-CH_2CH_2-C_6H_4-COOCH_3$	0.028
$C_6H_5-CO-C_6H_4-COOCH_3$	0.007
$CH_3-C_6H_4-COOCH_3$	0.085
$CH_3CH_2-C_6H_4-COOCH_3$	0.085
$C_6H_5-C_6H_4-COOCH_3$	0.005

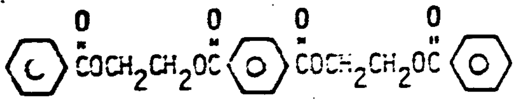
(Data from Reference 101)

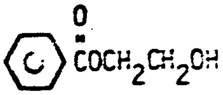
Due to the complexity of products obtained during the degradation of PET, both Ritchie(100) and Goodings(101) examined model compounds structurally related to PET. Both investigators studied the degradation of ethylene dibenzoate:

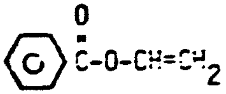


Ritchie also studied the following compounds:



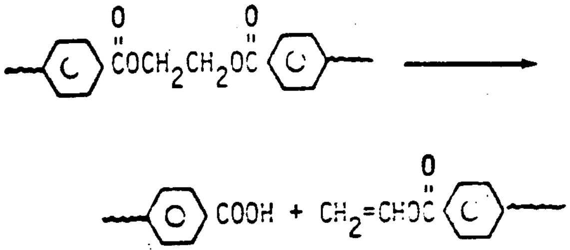






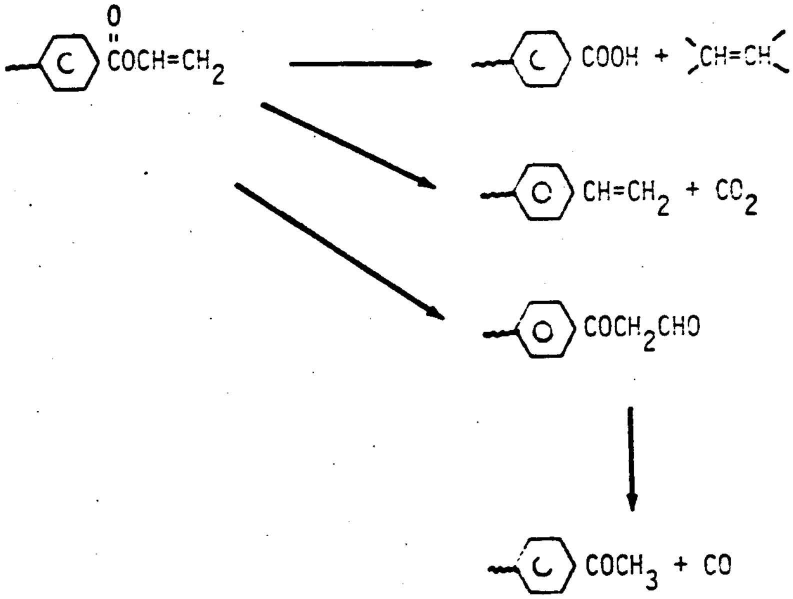
Comparison of the degradation of these compounds with that of PET led to the following conclusions:

(1) Initial random scission forms new carboxyl and vinyl ester end groups, as shown in Equation (33).



(32)

(2) The vinyl ester end groups are degraded in different ways, depending upon the temperature to which they are exposed and the residence time in the high temperature zone.

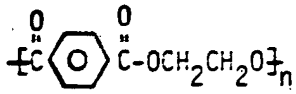


This series of reactions accounts for the formation of terephthalic acid, vinyl benzoate, acetylene, ketones, carbon monoxide and acetaldehyde. Another source of carbon monoxide could be the decomposition of acetaldehyde at temperatures above 400°C.

The activation energy for the pyrolysis of PET was calculated by Goodings(101) and Straus and Wall.(59) The results predict that the activation energy is in the range of 30-40 kcal/mole.

C. Experimental Program

A sample of PET polymer was provided by the Teijin, Inc., Tokyo, Japan. The assumed structure of the PET polymer (a polycondensate of terephthalic acid and ethylene glycol) is illustrated below:



with a molecular weight of 192 per repeat unit. The sample was supplied in the form of square chips.

1. Polymer characterization

The PET sample was crushed into a powder, dried at 10^{-6} torr at 60°C for 7 days, and analyzed for elemental composition. An infrared spectrum was also obtained using a thin film from the polymer melt.

Elemental analysis. A summary of the elemental analysis is presented in Table 46, together with the theoretical composition calculated on the basis of the assumed repeat unit. According to the manufacturer's information, a slight amount of titanium dioxide was contained in the sample as a pigment; however, this concentration of the pigment was negligible. The results obtained during actual elemental analysis shows an excellent agreement with the theoretical calculations.

Infrared analysis. Figure 46 is the infrared spectrum of PET

Table 46. Elemental Composition Of Polyethylene Terephthalate Polymer

	% Composition	
Element	Sample As Received	Theoretical[a]
Carbon	62.23	62.50
Hydrogen	4.03	4.17
Oxygen	33.74	33.33

[a] Composition based upon the structure of the monomeric unit.

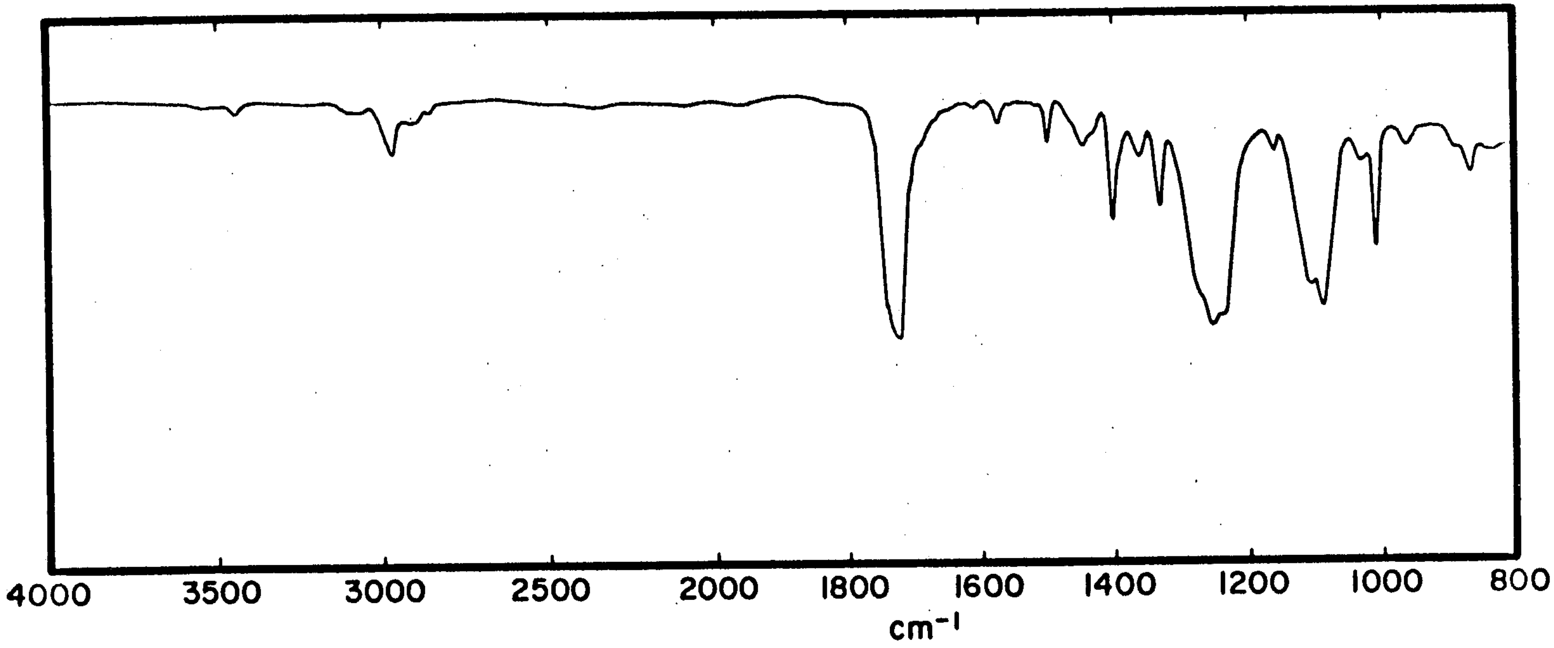


Figure 46. The infrared spectrum of polyethylene terephthalate.

polymer that was obtained from a thin film made from polymer melt. The infrared band assignments for this spectrum are summarized in Table 47. This spectrum supports the proposed structure of the PET polymer.

2. Thermoanalytical studies

Samples of the PET polymer which were evaluated using a thermoanalyzer were subjected to four dynamic heating rates and three different environments to ascertain what effect each variable had upon polymer degradation.

Effect of heating rate of polymer degradation. Samples of the PET polymer (10 ± 0.1 mg) were heated in air at 6, 10, 25,and 100°C/min from ambient to 1000°C. Figure 47 contains the data (triplicate analyses for each condition) that summarize the polymer weight loss characteristics at these four dynamic heating rates. There was no noticeable weight loss at any of the four heating rates below 295°C in the air environment. Above 350°C the samples lost weight rapidly between 350°C and 460°C at heating rates of 6 and 10°C/min in this environment.

Analysis of the TGA curves indicated a bimodal degradation process. The first phase of the degradation process, shown by the fairly steep linear range of the thermogram, corresponds to the depolymerization and the char-formation reactions. The second phase of the thermal decomposition process corresponds to oxidative degradation of the char structure.

The rate of heating had a moderate influence on sample weight loss; at the lower rates of heating no residues were observed above 575°C, while some residues were observed at temperatures above 700°C when the

Table 47. Infrared Analysis Of Polyethylene Terephthalate Polymer

Frequency (wave numbers)	Band Intensity	Assignment
3340	W	c = 0 overtone
3050	W	aromatic CH stretch
2955	W	aliphatic CH_2 stretch
2880	W	aliphatic CH_2 stretch
1725	S	C = 0 stretch
1570	W	aromatic C-C bend
1495	W	aromatic C-C bend
1440	W	CH_2 deformation
1400	M	aromatic C-C bend (in plane)
1360	W	CH_2 deformation
1330	M	CH_2 deformation
1250	S	unresolved triplet C-O-C
1110	S	C-O-C stretch
1090	S	C-O-C stretch
1010	M	aromatic C-C bend (in plane)
870	W	aromatic C-C bend (out of plane)
760	M	aromatic C-H bend (out of plane)

W = Weak band
M = Moderate band
S = Strong band

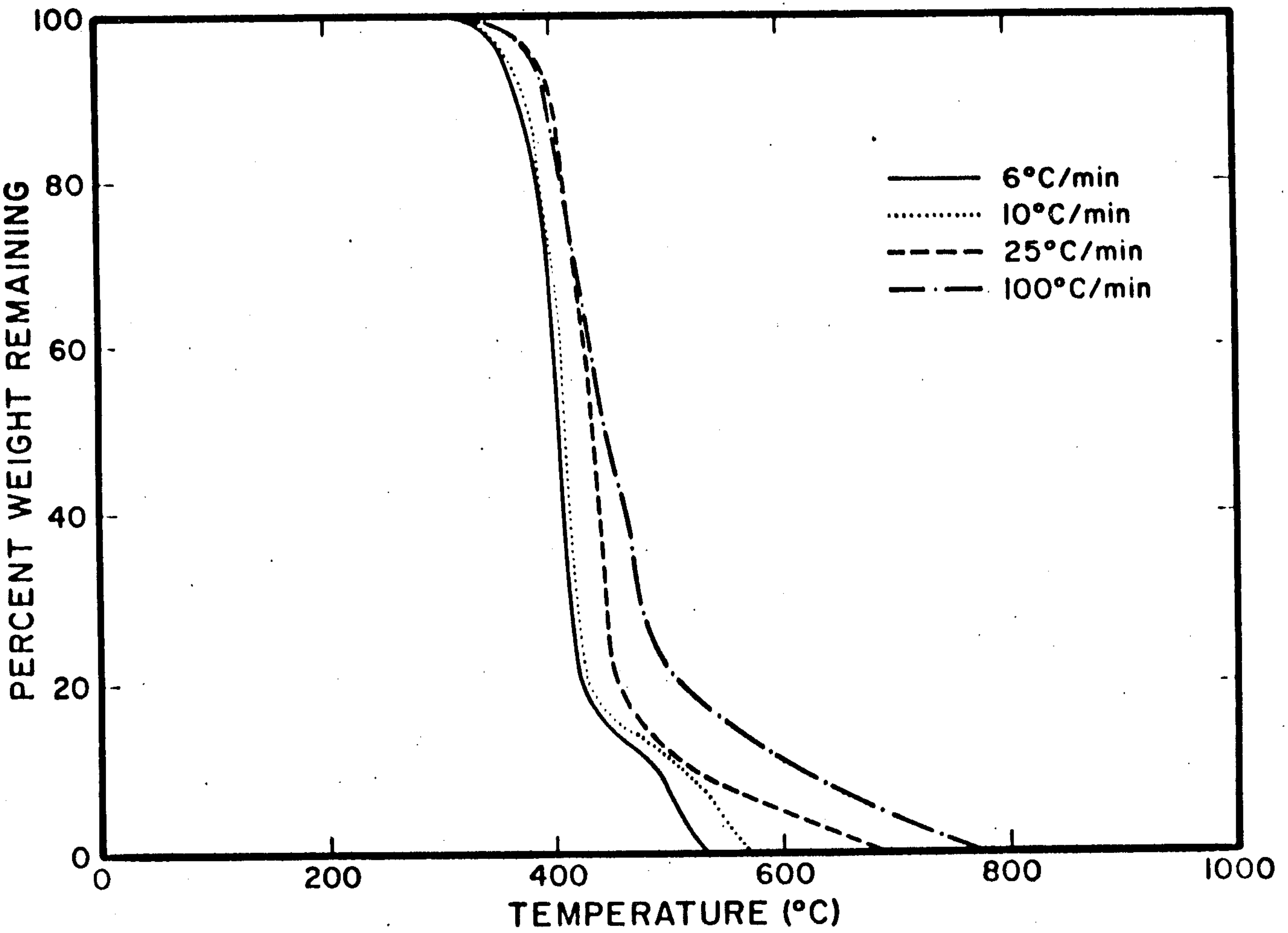


Figure 47. Effect of heating rate on sample weight loss for polyethylene terephthalate in air

sample was subjected to higher rates of heating. A dense white aerosol mist was generated when the weight loss of the PET polymer reached approximately 45-50 percent; this aerosol gradually disappeared as the temperature increased above 430°C.

Effect of environment on polymer degradation. It is generally accepted that the mechanism and the rate of polymer degradation is influenced by the concentration of oxygen present in the environment.(102) The thermograms presented in Figure 48 illustrate the effect of this phenomena. In pure oxygen the first major weight loss commenced at approximately 260°C, which is slightly higher than the melting point of the PET polymer. The sample was often observed to flow and self-ignite at approximately 420°C. The remaining char eroded slowly until the sample was totally consumed by 540°C.

Polymer weight loss in the air environment occurred at a slightly higher temperature than that which was observed in oxygen environment. The samples of polymer decomposed in the air environment did not exhibit evidence of flaming combustion, but continued to lose weight rapidly to a temperature of approximately 450°C when the formation of a black char was observed. Char formation occurred at an approximate weight loss of 87 percent. The char residue was consumed slowly and disappeared entirely by 575°C. A slight residue, in the form of a white powder, remained after the furnace was heated to 1000°C in the oxidative environments. This powder was later identified as the titanium dioxide pigment which was added to the polymer during processing.

The thermograms shown in Figure 48 indicate that the rate of weight loss by the PET polymer in the helium environment, although commencing

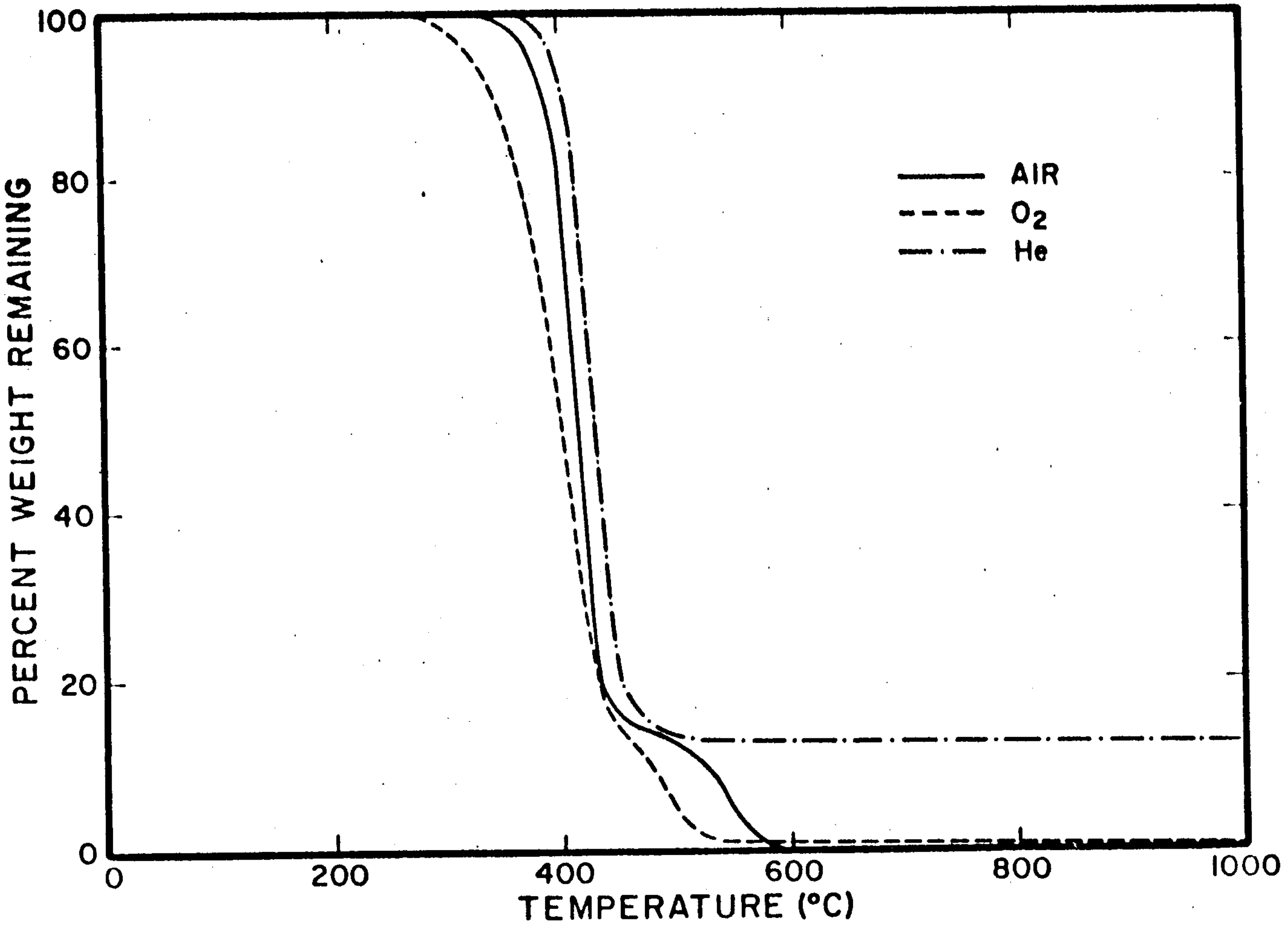


Figure 48. The effect of environment on the weight loss of polyethylene terephthalate.

at a higher temperature, was similar to that observed in the oxidative environments below 450°C. Little additional weight loss occurred in helium environments above 450°C and a black brittle char which comprised approximately 13 percent of the original sample weight, remained after exposure to 1000°C. The elemental analysis conducted on this residue indicated the char composition to be %C = 95.33; %H = 0.71; and % O = 3.96.

It is interesting to note that the formation of a stable char structure was not observed during the thermal decomposition of the aliphatic Nylon 6 polymer in the inert helium environment, as compared to the stable char structure remaining after exposure to 1000°C in the case of the PET polymer. Since both polymers were formed via a step-growth polymerization process, it is felt that the presence of aromatic rings in the polymer structure of the PET polymer served as a precursor for the formation of the rigid stable char structure.

Figures 49 and 50 are composites containing the DTA and DTG spectra obtained during the thermal degradation of the PET polymer in the three environments at a heating rate of 10°C/min. In helium the degradation process was observed to be slightly endothermic. In both air and oxygen environments the decomposition was observed to be highly exothermic and exhibited multiple maxima. In air two major maxima appeared in DTA traces at 420 and 546°C. The peak observed at the lower temperature region where the TGA curve is almost linear, while the latter peak corresponds to the oxidative decomposition of char structure which was formed during the early phase of polymer decomposition (as will be discussed later in this dissertation). The DTA data

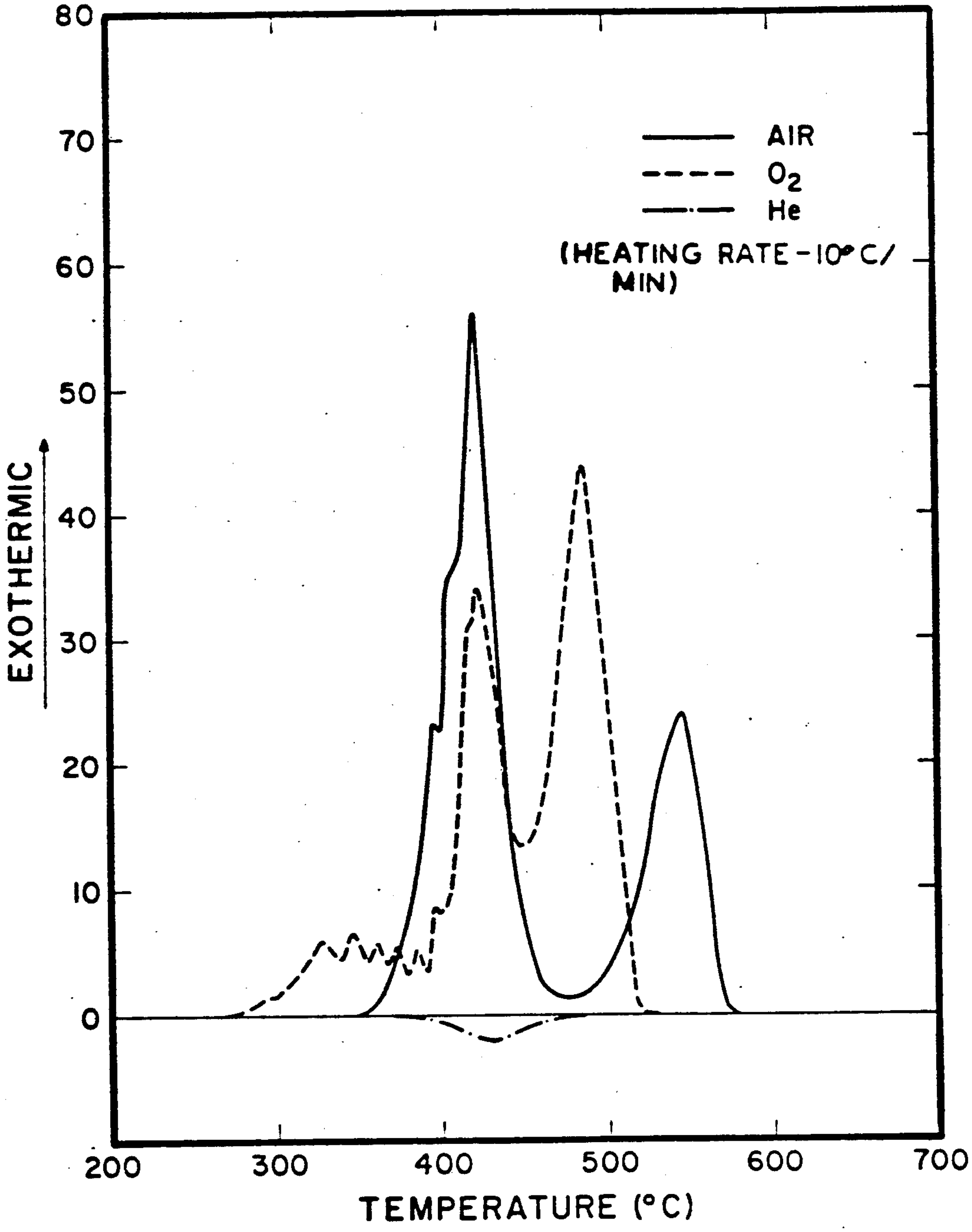


Figure 49. The DTA traces for polyethylene terephthalate polymer in helium, air and nitrogen environments.

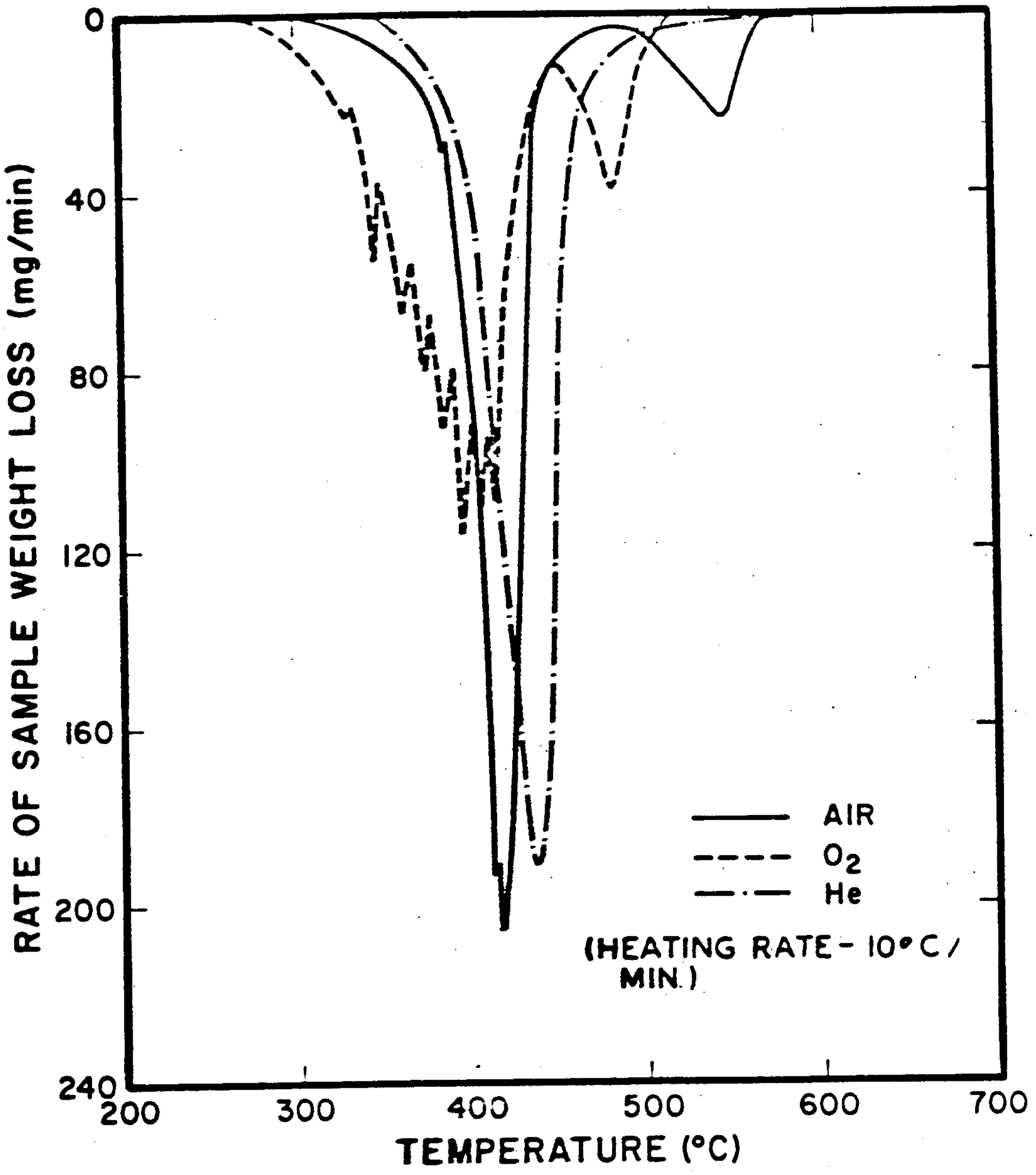


Figure 50. The DTG traces for polyethylene terephthalate polymer in helium, air and nitrogen environments.

recorded in an oxygen environment contained eight distinct maxima at 325, 345, 360, 375, 385, 395, 422 and 483°C, the last two peaks exhibiting a high degree of exothermicity.

The DTG traces (Figure 50) provided additional information pertaining to the thermal decomposition process. In the helium environment there was a single definite maximum which appeared at 437°C. In air and oxygen a good correspondence was observed between the DTG traces and the DTA traces. In oxygen, for exmple, there are eight or more peaks in DTG appearing at 330, 345, 361, 375, 385, 395, 405, 415,and 484°C, which correspond almost perfectly to those peaks observed in the DTA spectrum. Similar observations were observed in the DTG maxima obtained in the air environment which appeared at 417 and 546°C.

Table 48 summarizes some of the more important thermal characteristics that were observed during the thermal degradation of the PET polymer in helium, air and oxygen environments. The temperature of the DTG maxima, the DTA maxima and the specific temperature where 5, 50 and 90 percent of the original sample weight were lost, the nature of the overall degradation process, and the amount of chair remaining at "i point" and at 1000°C, are compared for the degradation processes which were observed under each condition of decomposition.

3. Pyrolysis studies

Pyrolysis studies of the PET polymer were conducted using the pyroprobe and the thermoanalyzer to simulate fast and slow heating rates, respectively.

Table 48. The Effect Of Environment Upon The Degradation Of Polyethylene Terephthalate[a]

Environment	DTG[b] Maxima		DTG Maxima		Temperature At Weight Loss Of			Overall Reaction Thermodynamics	% Char[c] at i point	% Char at 1000°C
	1st	2nd	1st	2nd	5%	50%	90%			
Helium	437	-	434	-	397	434	-	Slightly endothermic	13%	12 %
Air	417	546	420	546	373	417	526	Exothermic	10%	0.5%
Oxygen	d	484	422	483	324	401	480	Exothermic	7%	0.5%

[a] Heating rate of 10°C/min from ambient.

[c] Temperatures at which the derivative of the sample weight loss was at a maxima.

[c] Amount of a char remaining at the inflection of the TGA traces (i point).

[d] Eight maxima were observed between 330 and 415°C.

Pyroprobe (fast heating) studies. Preliminary experiments were carried out using the direct probe attachment for pyrolyzing samples directly into the GC injection port. Samples of the PET polymer were pyrolyzed at an indicated temperature of 1000°C; however, the actual temperature of the sample in the pyroprobe unit is not well-defined. Samples ranging in size from 3.2 to 5.6 mg were used during direct probe pyrolysis experiments. To insure complete pyrolysis, each sample was rapidly heated to a pre-selected temperature and held at this temperature for 20 seconds.

Figure 51 is typical of the chromatographs obtained using a 16 ft. x 1/8 in. O.D. column packed with Chromosorb 101 support that was temperature programmed from -10 to 260°C at a heating rate of 10°C/min. Twenty compounds, which were separated, identified and quantitated, are listed in Table 49.

The recovered low-boiling volatiles, listed in Table 49, accounted for 35.5 percent of the original sample. Approximately 57 percent of the weight of these volatiles was accounted for by the levels of carbon monoxide and carbon dioxide present. An additional 13.6 percent of the original sample weight was recovered in the form of a carbonaceous char. Thus, 49.1 percent of the original sample has been accounted for as degradation products, the remaining 50.9 percent were materials which did not elute from the GC column.

Thermoanalyzer (slow heating) studies. Samples of PET polymer were pyrolyzed in a helium environment using the thermoanalyzer and procedures outlined in Chapter IV. The pyrolysis temperature was programmed from ambient to 1000°C at the rate of approximately

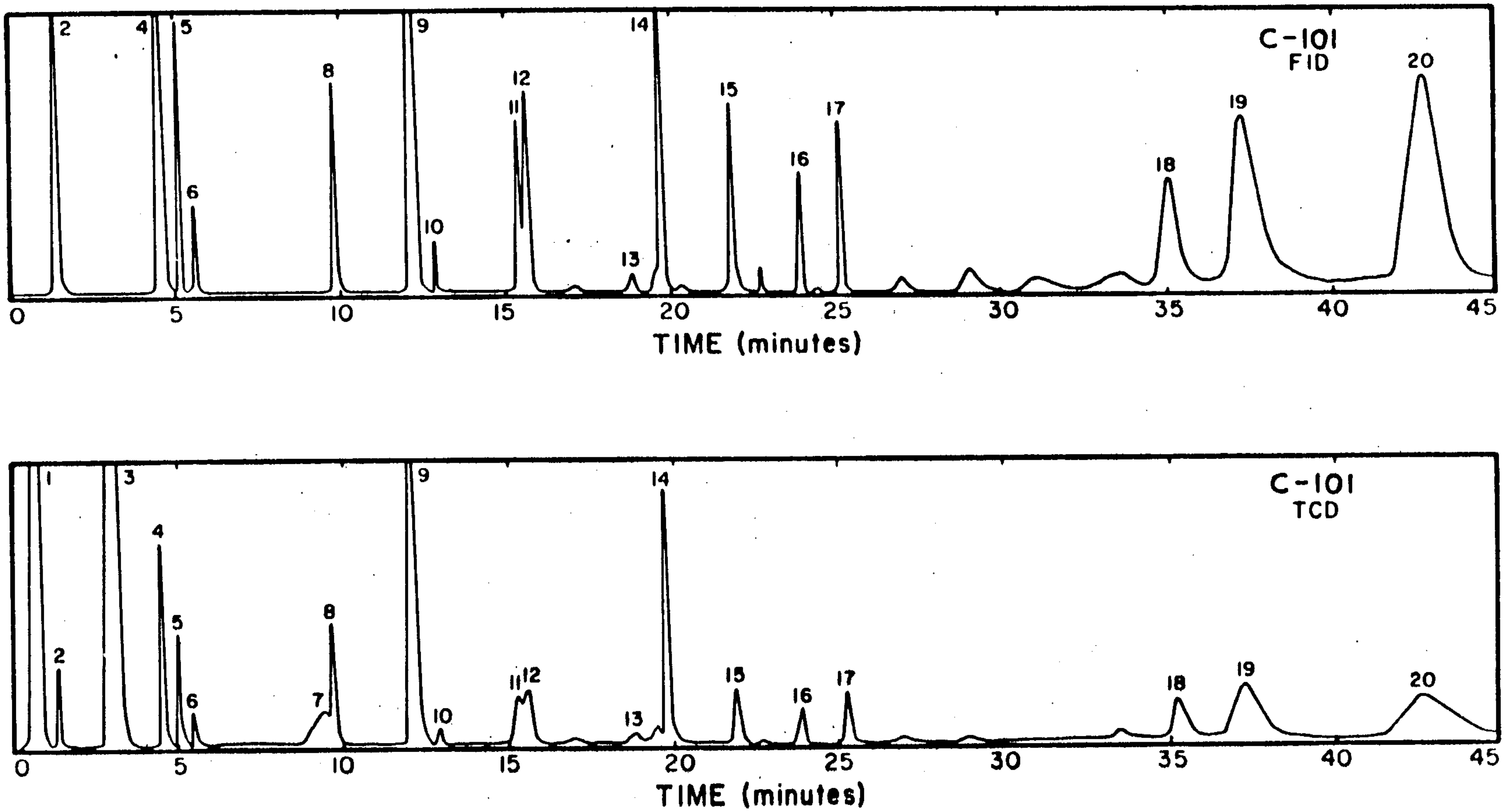


Figure 51. Low-boiling volatiles produced during the pyrolysis (fast heating) at 1000°C.

Table 49. Low-Boiling Volatiles Produced During The Pyrolysis (Fast Heating) Of Polyethylene Terephthalate[a]

Compound	Peak Number (FID)	Peak Number (TCD)	Quantity[b]
Carbon monoxide		1	113.20
Methane	2	2	7.54
Carbon dioxide		3	90.08
Ethylene	4	4	16.69
Acetylene	5	5	5.34
Ethane	6	6	0.49
Water		7	5.10
Propene	8	8	8.33
Acetaldehyde	9	9	43.17
1.3-Butadiene	10	10	0.46
Furan	11	11	Trace
Propanal	12	12	3.68
Acetic acid	13	13	0.92
Benzene	14	14	8.71
Toluene	15	15	2.44
Xylene	16	16	0.52
Styrene	17	17	1.56
Acetophenone	18	18	5.52
Ethylbenzoate	19	19	15.88
Benzoic acid	20	20	25.01
Total			354.64

[a] Direct probe pyrolysis at 1000°C for 20 seconds using 3.2 mg-5.6 mg samples.

[b] Average of four experiments. Milligrams of compound per gram of sample placed in the pyrolysis probe.

100°C/min. A sample size of 50 mg was found to be appropriate, both for the identification and quantification of the degradation products. Six pyrolysis runs were conducted under identical conditions. In all these experiments, trappings of the effluents was begun at 280°C, which is a temperature just before the first weight loss was encountered. The trapping continued for a five-minute period after a temperature of 1000°C was attained in order to collect materials which might have remained in the furnace or in the transfer lines.

The aerosols, particulates,and residues that condensed on the glass wool trap placed between the furnace and the cold trap were extracted using acetone and then analyzed. More polar solvents, such as dimethylformamide or dimethylsulfoxide, were also used to extract these condensates. The residual char that remained in the crucible at a temperature of 1000°C was analyzed to determine its elemental composition. Details of these analyses are presented in the following subsections.

Figure 52 represents the chromatographs that were obtained from the pyrolysis of the PET polymer at 1000°C using conditions described previously. A 16 ft. x 1/8 in. O.D. stainless steel column packed with Chromosorb 101 porous polymer was temperature programmed from -10 to 260°C at 10°C/min. to obtain this degree of resolution. More than 25 compounds were identified from these studies using the GC/MS techniques; these products are listed in Table 50. The peak numbers in Figure 52 and the trapping efficiencies and the response factors used in the calculation of the concentrations are included in this table for reference.

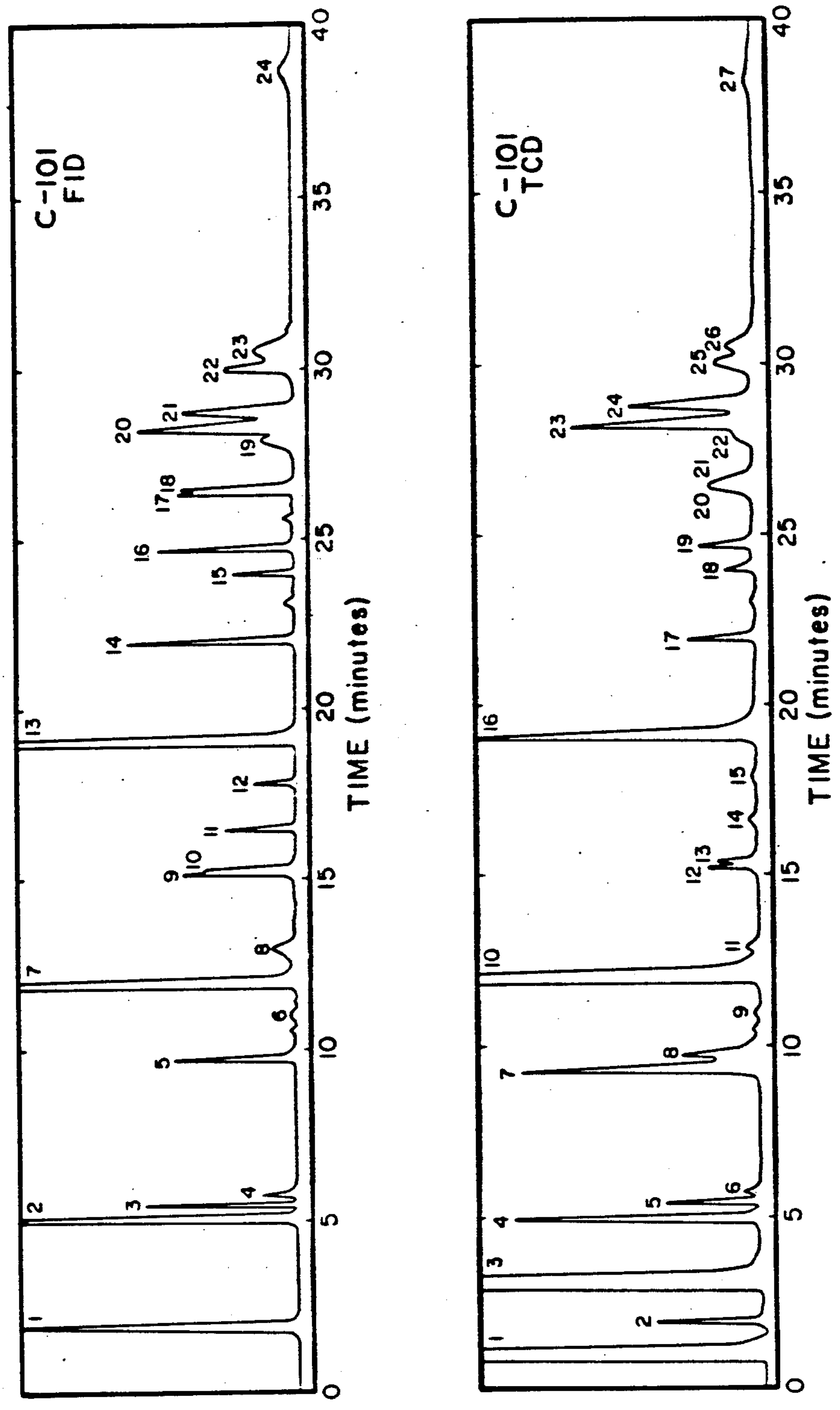


Figure 52. Low-boiling volatiles produced during the pyrolysis (slow heating) of polyethylene terephthalate in helium.

Table 50. Low-Boiling Volatiles Produced During The Pyrolysis (Slow Heating) Of Polyethylene Terephthalate[a]

Compounds	Peak Numbers[b]		T.E.[c]	R.F.[d]	Quantity[e]
	FID	TCD			
Carbon monoxide		1	0.00	0.670	94.00
Methane	1	2	0.05	0.450	46.00
Carbon dioxide		3	0.97	0.915	82.30
Ethylene	2	4	0.96	0.585	8.85
Acetylene	3	5	0.96	0.580	3.60
Ethane	4	6	0.98	0.590	Trace
Water		7	0.82	0.550	37.76
Propene	5	8	0.98	0.970[f]	5.60
Methanol	6	9	0.75	0.580	Trace
Acetaldehyde	7	10	0.98	0.650	67.01
1,3-Butadiene	8	11	0.97	0.674	3.25
Furan	9	12	0.97*	0.700*	0.33
Propanal	10	13	0.95	0.680	0.25
Cyclopentadiene	11	14	0.95	0.674	Trace
Acetic acid	12	15	0.80	4.167[f]	Trace
Benzene	13	16	0.90	0.780	23.36
Toluene	14	17	0.95	0.794	1.84
Xylene	15	18	0.95	0.812	0.49
Styrene	16	19	0.95	0.800	1.39
Phenol	17	20	0.88	1.105	0.93
Benzaldehyde	18	21	0.85	0.617	0.84
Indene	19	22	0.85*	1.020[f]	Trace
Acetophenone	20	23	0.70	0.651	8.62
Ethylbenzoate	21	24	0.70	0.980	7.89
Benzoic acid	22	25	0.35	1.590[f]	12.31
Naphthalene	23	26	0.50	1.050[f]	6.63
Biphenyl	24	27	0.40*	1.318	4.21
Total					417.46

*Estimated

[a] Average of six samples.

[b] Corresponds to peak numbers in Figure 52.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as determined by analytical methods.

The compounds listed in Table 50 constituted 41.7 percent of the original sample weight; it should be noted that 97 percent of the integrated GC peak areas have been identified and quantitated in these experiments.

The carbon monoxide that evolved from PET polymer under the conditions of pyrolysis in a helium atmosphere was measured by IR techniques. The CO absorption at 2160 cm^{-1} was monitored continuously as the temperature of the sample was increased at a rate of 100°C/min. Carbon monoxide liberated from the polymer reached a maximum value of 9.4 percent of the total sample weight at 445°C and stayed at the same level until 1000°C. Thus the value of 94 mg of CO per gram of the original polymer has been added to Table 50 that contains a summary of volatile products formed during the pyrolysis experiments.

During the thermal degradation experiments a yellowish-white powder was trapped by the glass wool filter. This high-boiling volatile fraction was determined gravimetrically to account for 40.4 percent of the original sample weight. This material was analyzed by IR and HPLC techniques that are described below.

The IR spectrum of the high-boiling volatiles obtained from a KBr pellet sample is shown in Figure 53. This spectrum contained characteristic bands similar to those found in both terephthalic acid (Figure 54) in the original polymer (Figure 46). Two carbonyl absorption bands can be observed at 1690 cm^{-1} and 1720 cm^{-1}, which correspond to carbonyl groups of terephthalic acid and PET, respectively. When the powder was dissolved in acetone, an insoluble fraction remained. This insoluble fraction was found to be almost pure terephthalic acid (as

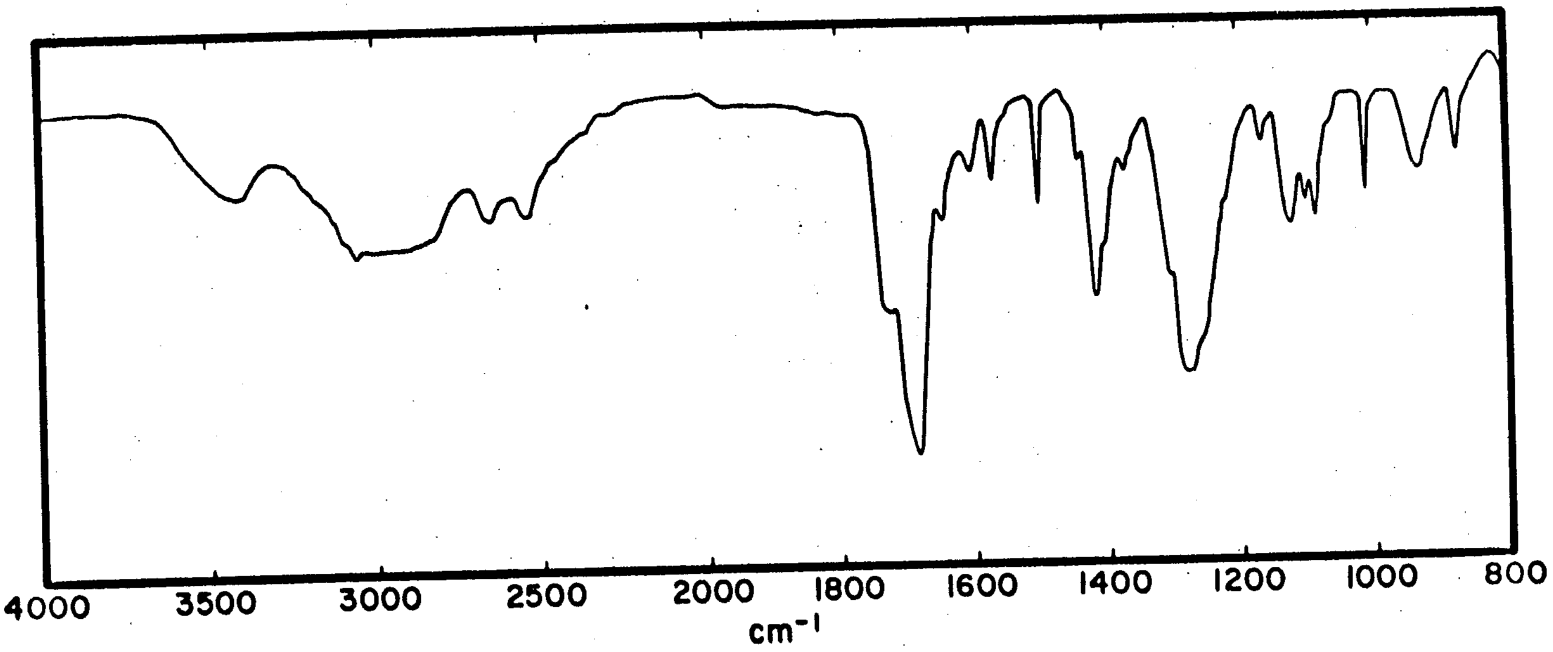


Figure 53. The infrared spectrum of the high-boiling volatiles produced during the pyrolysis (slow heating) of polyethylene terephthalate in helium.

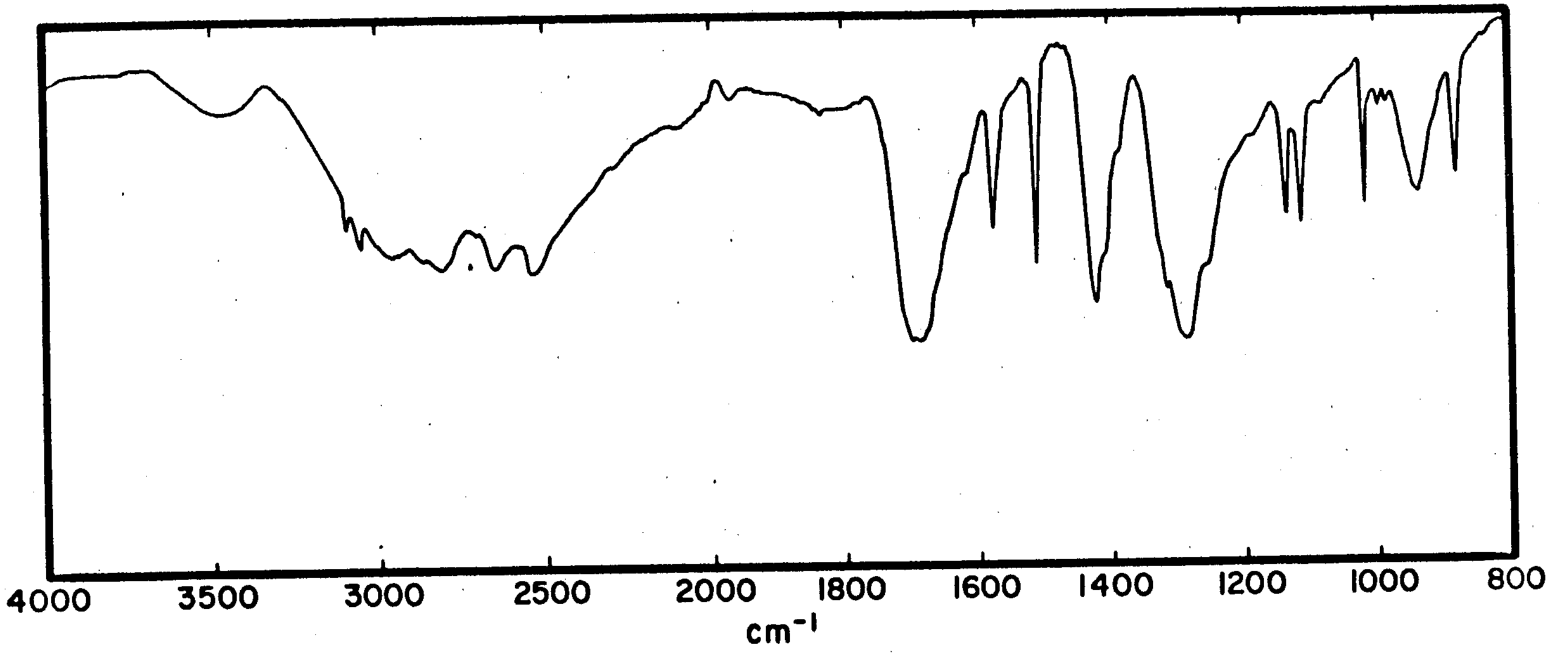
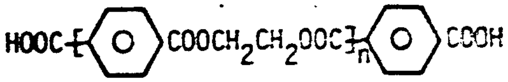


Figure 54. The infrared spectrum of terephthalic acid.

verified by IR and MS analysis). Terephthalic acid accounted for 11 weight percent of the powder residue. The soluble fraction was evaporated to dryness and redissolved in cyclohexane. The white powder which remained insoluble in cyclohexane had an infrared spectrum similar in nature to that of terephthalic acid, which suggests the structure of:



where n = 1 or 2.

The cyclohexane soluble fraction had an IR spectrum similar to that of the original polymer. The material was assumed to be comprised of oligomers of varying molecular weights.

The high-boiling volatiles were prepared for analysis using procedures described in Chapter IV. The HPLC chromatogram of the high-boiling volatiles produced during thermal decomposition of PET is shown in Figure 55. This chromatogram suggests that the high-boiling fraction contains more than 13 compounds. No further analysis of these eluting compounds was undertaken at this time.

The powder residue was analyzed for carbon, hydrogen and oxygen. These results are presented in Table 51. The values listed in Table 51 approximate the theoretical values obtained for a mixture with 89 percent of PET and 11 percent of terephthalic acid. This percentage agrees with the results that have been presented in previous sections.

The char that remained in the platinum crucible after the PET polymer was exposed to 1000°C at the rate of 100°C/min accounted for

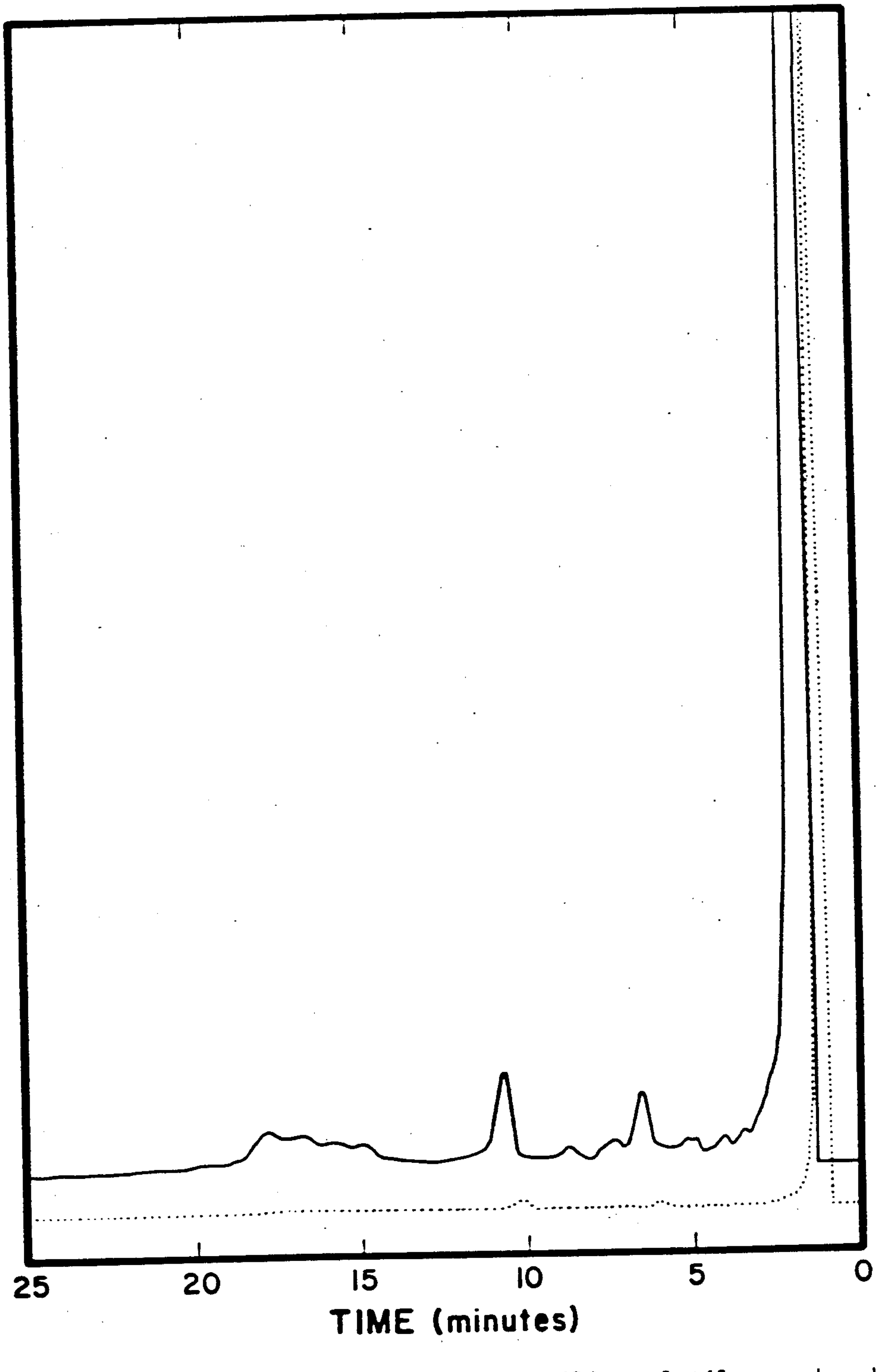


Figure 55. HPLC chromatogram of the high-boiling volatiles produced during the pyrolysis (slow heating) of the polyethylene polymer.

Table 51. Elemental Composition Of Solid Residue (Powder) Produced During The Pyrolysis (Slow Heating) Of Polyethylene Terephthalate

	% Composition		
Residue	Carbon	Hydrogen	Oxygen
	62.1	4.1	33.8
Theoretical value of terephthalic acid	57.8	3.6	38.6
Theoretical value of PET	62.5	4.2	33.3
Theoretical value of mixture[a]	62.0	4.1	33.9

[a] Calculated for the mixture with 89% of PET and 11% of terephthalic acid.

13.8 percent of an original sample weight. This char was analyzed for carbon, hydrogen,and oxygen content. The average values obtained from three determinations are listed in Table 52.

Table 52. Elemental Composition of Solid Residues Produced During Different Stages of Pyrolysis of Polyethylene Terephthalate

% Weight Loss	Element		
	Carbon	Hydrogen	Oxygen
0%	62.23	4.03	33.74
45%	68.43	3.90	27.67
60%	[illegible]	3.87	27.84
86% (residual char)	[illegible]	[illegible].71	3.96

A series of experimen [illegible] e progress of the char formation. The t [illegible] s were quenched after approximately 45 an [illegible] s. The residual char was removed from the thermoanalyz [illegible] e elemental composition was determined using the previously described techniques.

Materials balance. The data obtained from the analysis of the low-boiling volatile products, the high-boiling volatiles and the char residue was used to obtain a mass balance for carbon, hydrogen and oxygen content of the pyrolysis products at 1000°C. The results from the materials balance for PET are presented in Table 53. Of the original sample 41.8 percent was recovered as low-boiling volatile products

13.8 percent of an original sample weight. This char was analyzed for carbon, hydrogen, and oxygen content. The average values obtained from three determinations are listed in Table 52.

Table 52. Elemental Composition of Solid Residues Produced During Different Stages of Pyrolysis of Polyethylene Terephthalate

% Weight Loss	Element		
	Carbon	Hydrogen	Oxygen
0%	62.23	4.03	33.74
45%	68.43	3.90	27.67
60%	68.29	3.87	27.84
86% (residual char)	95.33	0.71	3.96

A series of experiments were carried out to follow the progress of the char formation. The thermal decomposition reactions were quenched after approximately 45 and 60 percent weight loss. The residual char was removed from the thermoanalyzer and the elemental composition was determined using the previously described techniques.

Materials balance. The data obtained from the analysis of the low-boiling volatile products, the high-boiling volatiles and the char residue was used to obtain a mass balance for carbon, hydrogen and oxygen content of the pyrolysis products at 1000°C. The results from the materials balance for PET are presented in Table 53. Of the original sample 41.8 percent was recovered as low-boiling volatile products

Table 53. Materials Balance - Pyrolysis (Slow Heating) Of Polyethylene Terephthalate

	Weight (mg)[a]			
	Total	Carbon	Hydrogen	Oxygen
Original Polymer	1000.0	622.3	40.3	337.4
Material Recovered	963.1	580.8	41.3	341.0
Low-Boiling Volatiles	417.5	212.0	23.9	181.6
Particulate Residue[b]	407.6	253.0	16.7	137.9
Char	138.0	115.8	0.7	21.5
Percent Polymer Accountable in Products	96.3	93.3	102.5	101.1

[a] Calculated on the basis of 1000 mg of the original PET polymer.

[b] The particulate residue is a mixture of terephthalic acid (11%) and oligomers (89%). Elemental composition was based on the elemental analysis.

(Table 50) and the 40.7 percent were trapped by the glass wool filter as high-boiling volatiles. The char that remained in the platinum crucible after the pyrolysis accounted for 13.8 percent of the original sample. The total amount of materials recovered accounted for 96.3 percent of the original sample weight.

The elemental composition of the volatile products was based upon the sum of the carbon, hydrogen,and oxygen content of the individual products. Thus, the materials balance accounted for 93.4 percent of the carbon, 104.3 percent of the hydrogen and 101.1 percent of the oxygen content that was in the original PET sample.

4. Oxidative degradation (slow heating) studies

Samples of PET were exposed to an oxidative (air) environment and heated at a rate of 100°C/min from ambient to a final temperature of 1000°C. The high-boiling volatiles and char residues that were formed in these experiments were examined by IR and MS techniques. Unlike the pyrolysis conducted in the helium environment, no residual char was observed in the crucible of the thermoanalyzer after the oxidative degradation of PET samples. These results are discussed in the following sections.

Analysis of the low-boiling volatiles. The trapping system that is described in Chapter IV has been used to collect the volatile products produced during the oxidative degradation of the PET polymer. Five individual trapping experiments were performed using a 50 mg sample size for each experiment. Several additional experiments were conducted using a 20 mg sample size to quantitate the major products such as carbon dioxide and water. Product separation was accomplished using a Chromosorb 101 column (16 ft long x 1/8 in. O.D. stainless-steel tubing). The quantitative data were obtained using both the FID and TC traces, as shown in Figure 56. Twenty-one components were resolved and positively identified by programming this column from -10 to 265°C at 10°Cmin. Table 54 lists the compounds identified and the quantities of each that were determined. The peak number for each compound in this table refers to the peak number in Figure 56. As shown in Table 54, 96.1 percent of the original sample of PET polymer was accountable as low-boiling volatiles, produced during the oxidative degradation experiments. It should be noted that considerable interaction takes place between the oxygen in the surrounding environment and the sample. This resulted in major increases in the concentrations of carbon monoxide, carbon dioxide,and water, as compared to results obtained during degradation under inert pyrolysis conditions. These three compounds account for 87 percent of the low-boiling volatile products in Table 54. Other compounds that were found in significant quantities were methane, ethylene, acetaldehyde and benzoic acid. These four compounds account for 8 percent of the volatile products identified during oxidation decomposition. Almost all of the compounds which were identified during this oxidative degradation were observed in previous pyrolysis experiments.

Analysis of the high-boiling volatiles. During the time that the trapping experiments of the low-boiling volatile products from PET were being performed with the thermoanalyzer, a yellow-white powder condensed on the glass fiber filter in the trapping line. The

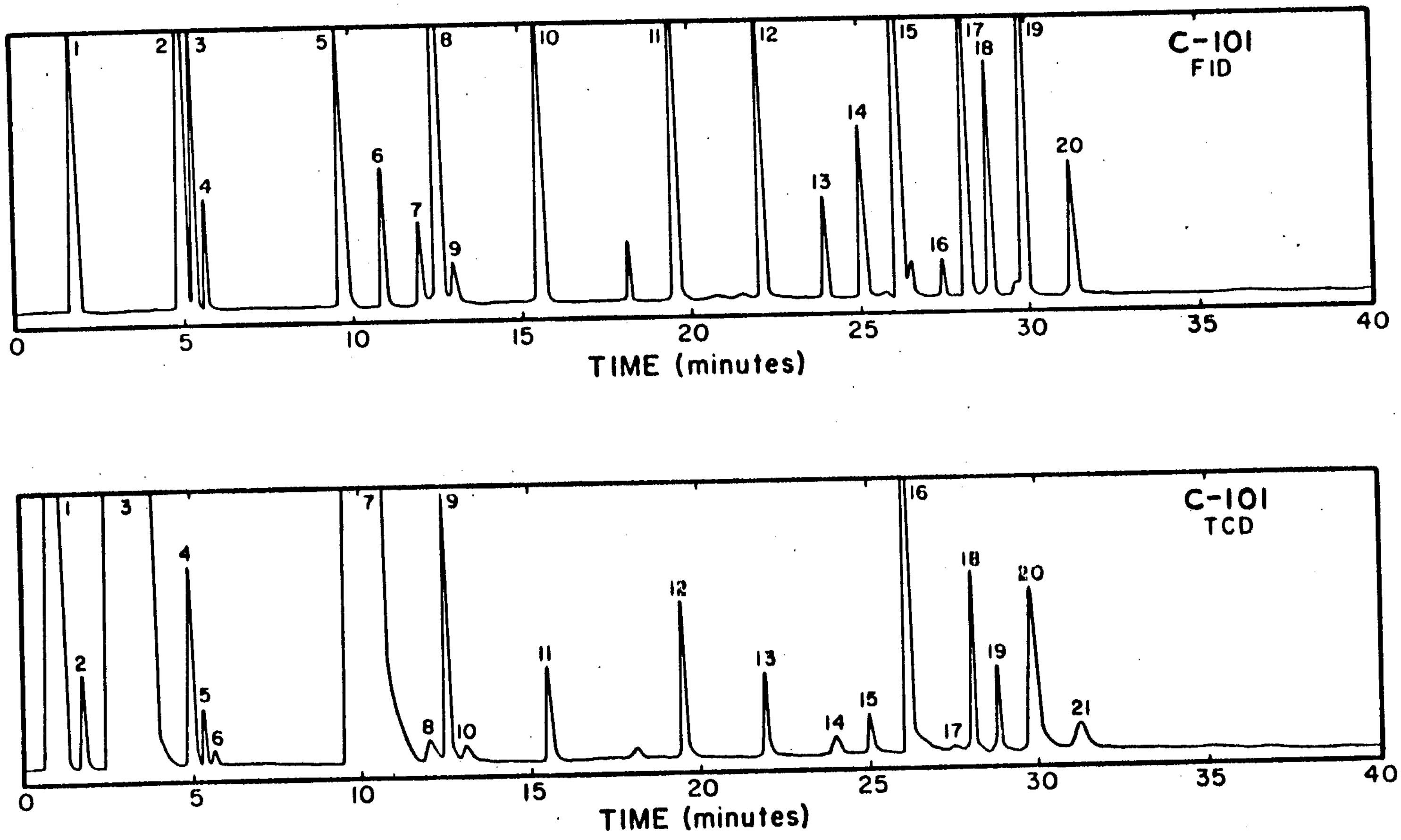


Figure 56. Low-boiling volatiles produced during the thermal oxidative degradation (slow heating) of the polyethylene terephthalate polymer in air.

Table 54. Low-Boiling Volatiles Produced During The Oxidative Degradation (Slow Heating) Of Polyethylene Terephthalate In Air[a]

Compounds	Peak Numbers[b]		T.E.[c]	R.F.[d]	Quantity[e]
	FID	TCD			
Carbon monoxide		1	0.00	0.670	253.00
Methane	1	2	0.05	0.450	28.40
Carbon dioxide		3	0.97	0.915	431.20
Ethylene	2	4	0.96	0.585	18.01
Acetylene	3	5	0.96	0.580	5.21
Ethane	4	6	0.98	0.590	Trace
Water		7	0.82	0.550	155.00
Propene	5		0.98	0.970[f]	3.59
Propyene	6		0.98	0.950[f]	0.96
Methanol	7	8	0.75	0.580	1.44
Acetaldehyde	8	9	0.98	0.650	15.35
1.3-Butadiene	9	10	0.97	0.674	Trace
Allylaldehyde	10	11	0.98*	0.640*	4.75
Benzene	11	12	0.90	0.780	5.30
Toluene	12	13	0.95	0.794	1.53
Xylene	13	14	0.95	0.812	0.80
Styrene	14	15	0.95	0.800	2.23
Phenol	15	16	0.88	1.105	7.08
p-cresol	16	17	0.80	1.200	Trace
Acetophenone	17	18	0.70	0.651	6.65
Ethylbenzoate	18	19	0.70	0.980	3.11
Benzoic acid	19	20	0.35	1.590[f]	14.81
Naphthalene	20	21	0.50	1.050[f]	2.15
Total					960.57

*Estimated

[a] Five samples - 50 mg.

[b] Corresponds to peak numbers in Figure 56.

[c] Relative trapping efficiencies.   thermal conductivity detector.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound per gram of original sample as determined by analytical methods.

[f] Response factors from the flame ionization detector.

condensate accounted for 30.7 percent of the original sample weight. After the oxidative degradation experiment the furnace and the trapping line were rinsed with a variety of solvents; however, no residue was found upon the evaporation of these solvents. The residue recovered from the glass filter was analyzed by IR, MS, HPLC and elemental analysis techniques.

The IR spectrum of this condensate resembled the spectrum obtained during the pyrolysis of PET (see Figure 46). The IR spectrum of the sample has group grequencies typical of both terephthalic acid and the original polymer. Since the powder was assumed to be a mixture of terephthalic acid and oligomers of PET, it was dissolved in acetone (a poor solvent for terephthalic acid) and the insoluble white powder was filtrated. Using IR and MS this powder was found to be almost pure terephthalic acid, which accounted for approximately 10 weight percent of the high-boiling volatile fraction.

The fraction soluble in acetone was examined by IR and HPLC techniques. The IR spectrum, which is illustrated in Figure 57, was similar to that of PET, but it contained a strong absorption for carboxylic acid. This material was estimated to be a mixture of PET oligomers having both ester groups and carboxylic terminal groups.

The HPLC techniques described previously were used for the analysis of the high-boiling volatile residues. Terephthalic acid was removed from the sample by filtration, evaporated to dryness and redissolved in THF. The HPLC chromatogram shown in Figure 58 contained more tha 14 peaks and was similar to that obtained during the pyrolysis study (see Figure 55).

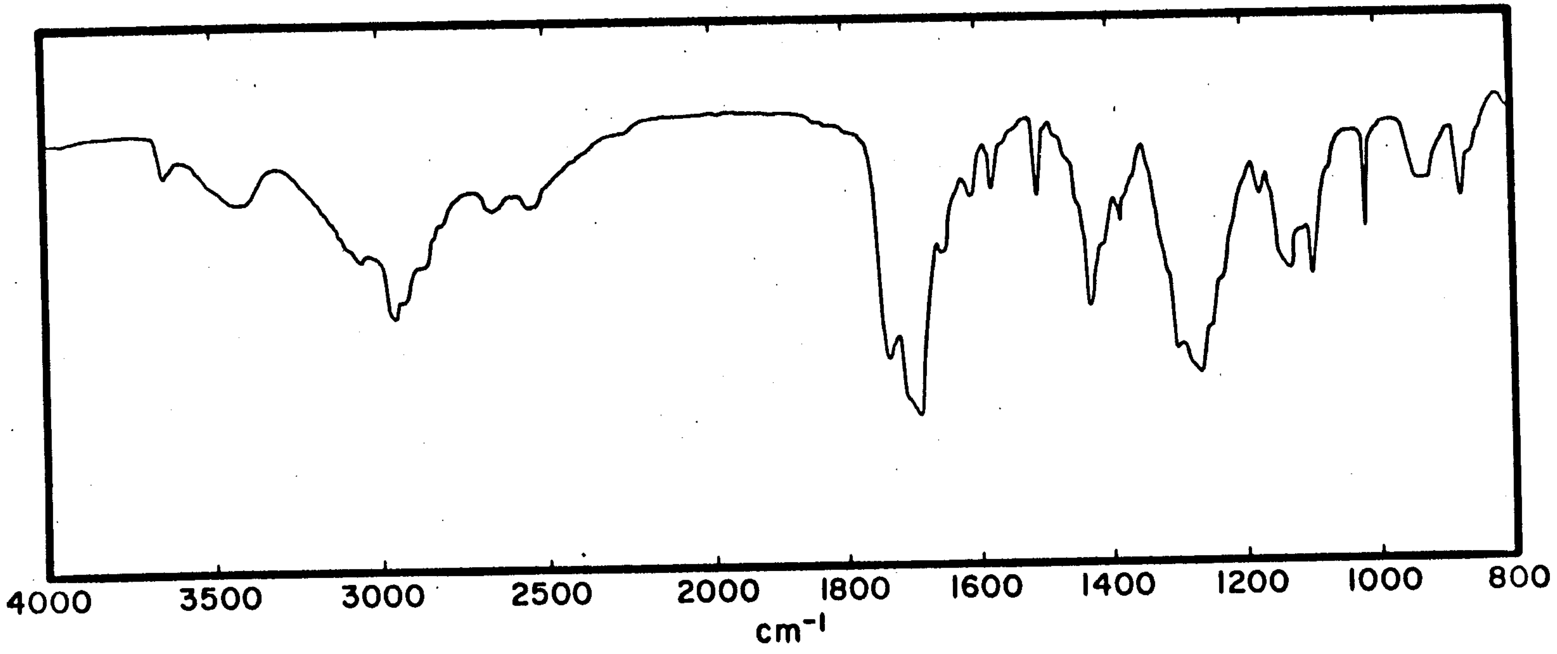


Figure 57. The infrared spectrum of the polyethylene terephthalate oligomers.

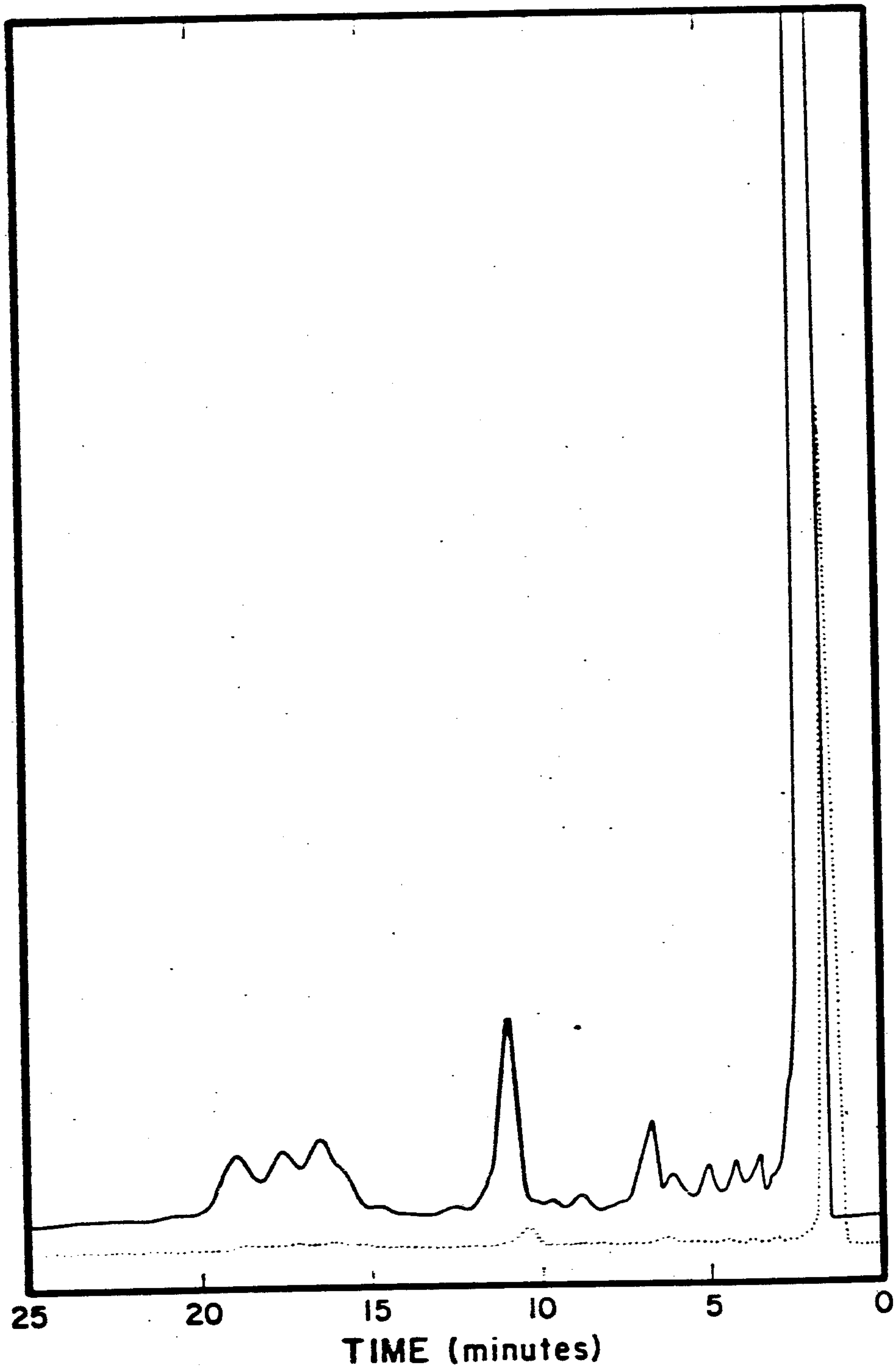


Figure 58. HPLC chromatogram of the high-boiling volatiles produced during the oxidative degradation (slow heating) of the polyethylene terephthalate polymer.

The condensate was analyzed for carbon, hydrogen,and oxygen. The results obtained are summarized in Table 55, along with the elemental composition of the residue from the pyrolysis in helium. Theoretical values for terephthalic acid, PET and the mixture of terephthalic acid (10%) and PET (90%) are also presented in Table 55.

It was concluded that the composition of the condensate produced from oxidative degradation was similar to that of the residue resulting from pyrolysis. This condensate was a mixture of approximately 10% terephthalic acid and 90% oligomers having a structure similar to the initial PET polymer.

Analysis of solid residue. During the thermal decomposition studies conducted in an oxidative environment, no char remained at the final temperature of 1000°C. However, in order to examine the compositional change of residual compound, the decomposition reactions were quenched at weight losses of 50 percent and 90 percent. Elemental analysis for carbon and hydrogen content was conducted and the results are presented in Table 56. Only slight changes in the concentrations of carbon, hydrogen and nitrogen occurred up to 50 percent weight loss. This can be attributed to the elimination of carbon monoxide, carbon dioxide and certain amounts of low molecular weight oligomers from PET in the earlier stage of the oxidative degradation. The residual char at 50 percent weight loss was black and brittle.

Materials balance. A materials balance was calculated using the results of the analysis of the low-boiling and high-boiling volatiles. The results for this balance for PET, shown in Table 57, indicate that 96.1 and 30.7 percent of the original sample weight were attributed to

Table 55. Elemental Composition Of High-Boiling Volatiles Produced During The Thermal Decomposition (Slow Heating) Of Polyethylene Terephthalate

	% Composition		
	Carbon	Hydrogen	Oxygen
High-Boiling Volatiles Produced During Oxidative Degradation	61.8	4.0	34.2
High-Boiling Volatiles Produced During Pyrolysis	62.1	4.1	33.8
Theoretical Valve Polyethylene Terephthalate	62.5	4.2	33.3
Theoretical Valve Terephthalic Acid	57.8	3.6	38.6
Theoretical Mixture[a]	61.9	4.0	34.1

[a] Calculated for a mixture of 89% PET and 11% terephthalic acid.

Table 56. Elemental Analysis Of Polyethylene Terephthalate Polymer At Several Stages Of Oxidative Degradation (Slow Heating)

% Weight loss of the original sample	% Composition		
	Carbon	Hydrogen	Oxygen
0% (original sample)	62.2	4.0	33.7
50%	67.2	3.7	29.1
90%	84.9	3.4	11.7

Table 57. Materials Balance - Oxidative Degradation (Slow Heating) Polyethylene Terephthalate

	Weight (mg)[a]		
	Total	Carbon	Hydrogen
Original Polymer	1000.0	622.3	40.3
Materials Recovered	1252.0	507.3	45.1
Low-Boiling Volatiles	950.6	317.8	32.7
High-Boiling Volatiles	307.4	189.5	12.4
Solid-Residue (char)	0	0	0
Percent Polymer Accountable in Products	125.2	81.5	111.9

[a] Calculated on the basis of 1000 mg of the original PET polymer.

the low-boiling and high-boiling volatiles, respectively. No significant amount of char residue was found during this phase of the study. The overall material balance was thus 126.8 percent of the original sample weight. The weight gain was due to the interaction of oxygen in the environment with the sample and the resulting large concentrations of carbon dioxide and water.

D. Discussion

The principal objective of this study was to determine whether the thermal degradation of PET polymer was similar to the degradation processes reported in the literature for other step-growth polymers. A second objective was to determine the inter-relationship between the basic polymer structure and its resistance to thermal oxidative degradation. To accomplish this goal the low-boiling volatiles, high-boiling volatiles, and char residues were qualitatively and quantitatively determined.

Pyrolysis studies of the PET polymer conducted in the helium environment proceeded via a process during which a char, representing approximately 13 percent of the original polymer weight, was formed. The pyrolysis of this step-growth polymer is somewhat different than that observed during the studies of the Nylon 6 polymer, where no substantial char formation was observed. This PET char contained approximately 95.3 percent of carbon.

In the oxidative environments, the thermal degradation reaction was bimodal, indicating the char sintering phase as contrasted to the relative stability of char structure observed during the degradation in the inert environment.

Elemental analysis was conducted on samples of char recovered during both the pyrolysis and oxidative decomposition studies at a stage where approximately 90 percent weight loss occurred. The char obtained during the pyrolysis experiments was stronger in physical structure than that obtained during the oxidative studies. Analysis of these chars indicated that the char formed under inert pyrolysis conditions had a greater carbon content and lower oxygen content that was observed in char recovered from oxidative environments. This clearly indicates the role of oxygen in the char sintering process.

Tables 50 and 54 represent a summary of the products produced during pyrolysis and oxidative degradation of polyethylene terephthalate polymer at 1000°C. Table 58 lists the major compounds found in both environments and Table 59 includes the compounds that were present in less abundant quantities.

As indicated in these tables, far greater concentrations of carbon monoxide, carbon dioxide, and water were formed when oxygen was present in the sample's environment during thermal decomposition. However, the composition of the mixture of oligomers and terephthalic acid trapped by the glass fiber filter was not affected by the oxidative reaction. The types and concentrations of the major low-boiling volatiles, with the exception of CO, CO_2, and H_2O, did not substantially change.

The elemental composition of the solid residue sample after approximately 50 percent weight loss in the oxidative environment was similar to that produced during the pyrolysis process after approximately the

Table 58. Major Decomposition Products Produced During The Pyrolysis And Oxidative Degradation (Slow Heating) Of Polyethylene Terephthalate

	Quantity[b]	
	In Helium	In Air
Carbon monoxide	94.00	253.00
Methane	46.00	28.40
Carbon dioxide	82.30	431.20
Water	37.76	155.00
Acetaldehyde	67.01	15.35
Benzene	23.36	5.30
Benzoic acid	12.31	14.81
Terephthalic acid	44.84	30.74
Oligomers	362.76	276.66

[a] Includes both volatile products and solid residues.

[b] Milligrams of compound per gram of sample.

[c] Calculated from the results of the residue analysis.

Table 59. Minor Decomposition Products Produced During The Pyrolysis And Oxidative Degradation (Slow Heating) Of Polyethylene Terephthalate

	Quantity[a]	
	In Helium	In Air
Ethylene	8.85	18.01
Acetylene	3.60	5.21
Ethane	T	T
Propene	5.60	3.59
Propyne	-	0.96
Methanol	T	1.44
1.3-Butadiene	3.25	T
Allylaldehyde	-	4.75
Propanal	0.25	-
Toluene	1.84	1.53
Xylene	0.49	0.80
Styrene	1.39	2.23
Phenol	0.93	7.08
P-Cresol	-	T
Acetophenone	8.62	6.65
Ethyl benzoate	7.89	3.11
Naphthalene	6.63	2.15
Biphenyl	4.21	-

T Trace

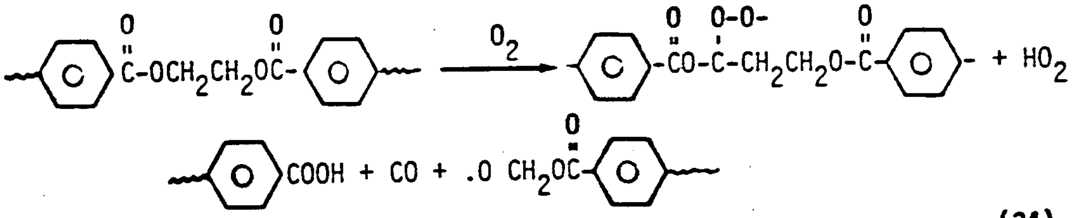
[a] Milligrams of compound per gram of sample.

same weight loss (see Tables 52 and 56). Thus, with all the results so far, it may be concluded that the basic degradation mechanism during the decomposition of PET is similar in both inert and oxidative environments. Figure 59 contains a proposed mechanism covering the thermal decomposition pathways which may be active during the degradation of PET polymers.

The pathway I was proposed by Ritchie.(100) This pathway assumes the decomposition process can successfully explain the formation of the major products identified during the pyrolysis studies. However, Processes II, III and IV, which involve a homolytic scission of C-C bond, may also occur.

Commercial PET usually contains 2-3 percent of diethylene glycol component in the polymer structure. The ether linkage in this component will also cleave readily. The char may be formed by the recombination of phenyl radicals. The aromatic polymer chains without weak aliphatic linkages will be formed first, then they will be condensed to a graphite-like structure, possibly by the elimination of aromatic hydrogens. The thermal stability of benzene rings aid in char-formation.

The presence of oxygen promotes chain rupture due to the attack by the oxygen radical on aliphatic carbon atoms as illustrated below:



(34)

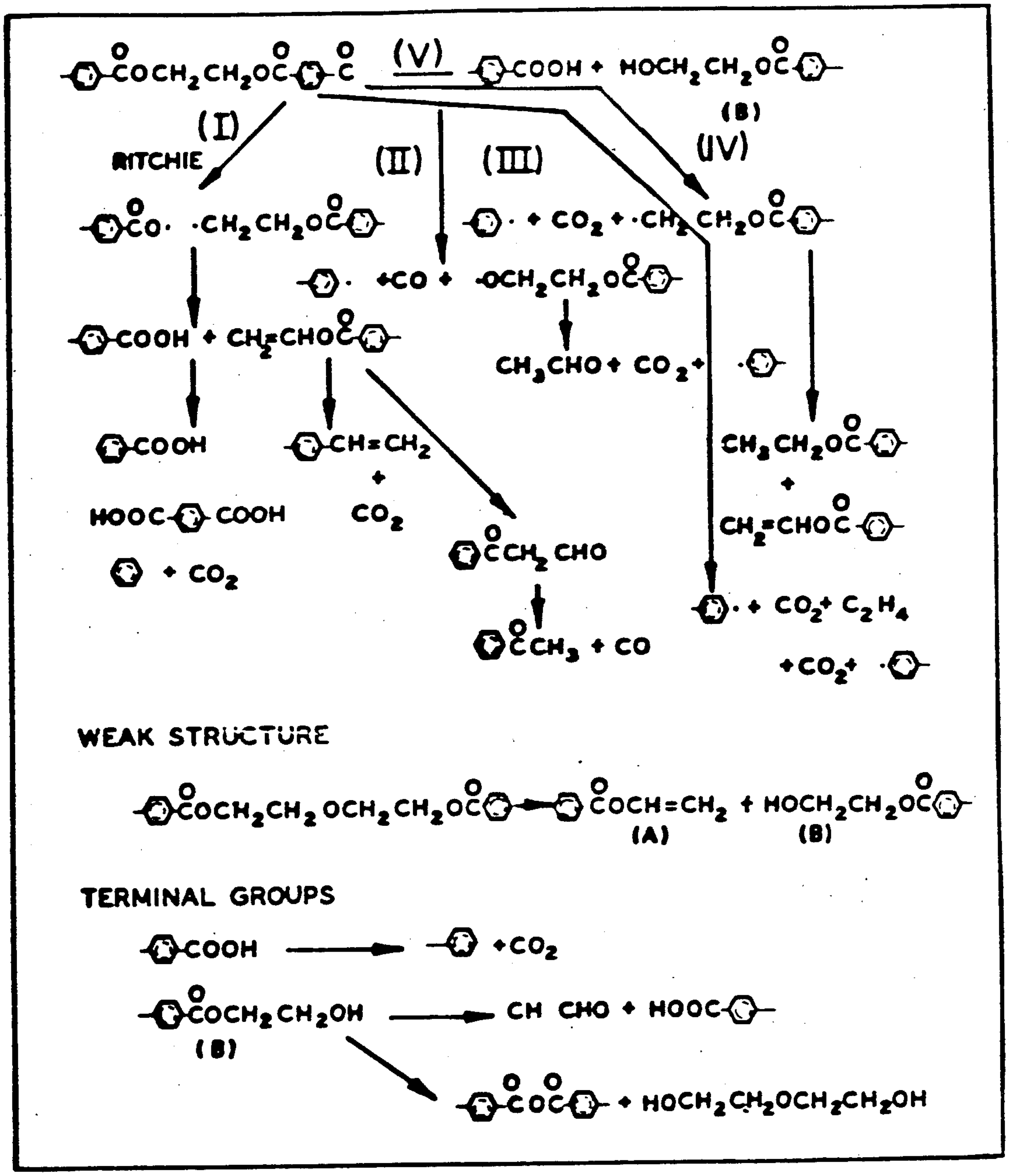


Figure 59. Proposed mechanism for the thermal decomposition of polyethylene terephthalate polymers.

Oxygen will induce the decomposition of aromatic groups at higher temperatures and thus lead to oxidative degradation of the rigid char structure.

CHAPTER VIII

FLAME-RETARDANT NYLON 6 POLYMER

A. Introduction

Since Nylons are one of the most popular polymeric material used in textile fabrics, an intense effort has been conducted to improve their flammability characteristics.

The most unfavorable feature of Nylon during exposure to an ignition source is its tendency to melt and drip. Since the heat generated during combustion is enough to melt the polymer, the molten polymer will retract from the ignition source in the form of a small globule. When tested in the vertical configuration, the cohesive energy is low and the molten Nylon tends to drip.

This phenomena often permits Nylon fabrics to pass flammability tests, such as the Vertical Flammability Test (AATCC 34-1966), because burning ceases due to the dripping of molten polymer which carries the flame away. However, this does not necessarily mean that Nylon is intrinsically non-burning or fire-resistant. For example, molded articles made of Nylon cannot be graded as self-extinguishing in many small-scale tests. Dyestuffs and other additives such as chrome dyes, coatings and the melamine resins used to obtain stiff Nylon nets considerably increase the polymer's flammability characteristics, because they can strengthen the fabric and support the burning material, thereby ensuring continued flame propagation.(103,104) Nylons blended with non-melting fibers, such as cotton, rayon and wool, will also burn rapidly. Kruse(105) termed this the "scaffolding effect" in which the non-melting fiber forms a carbonaceous grid under combustion, which holds the molten droplet in place, much as a wick holds the fuel in place when a candle is burned in a wick downward attitude.

Moreover, the molten droplets which are usually carried away with flame during the combustion of thermoplastic polymer, can often be a source of danger causing severe skin burns. Examination of "real fires" shows that thermoplastic materials, such as Nylon, used, for example, as curtains or drapes often propagate fire by dripping flaming polymer onto flammable materials, such as carpets.

Nylon is generally less flammable than polyethylene, polyoxymethylene, polymethyl methacrylate, and polystyrene and more flammable than polycarbonate, polyvinyl chloride, and polyvinylidene chloride.

B. Methods to Improve the Fire-Retardancy of Nylon Polymers

There have been numerous patents and reports published pertaining to fire-retarded Nylons. Most of these publications were directed toward applications for Nylon fabrics.

As usual, there are three basic approaches to render Nylon polymers flame retardant:

(1) finishing of materials with reactive or non-reactive fire retardants,

(2) the incorporation of fire-retarding additives into the polymer, and

(3) the development of intrinsically flame-retardant Nylons.

The fire retardants for Nylon can be divided into several main classes: halogen-containing compositions, organophosphorus fire retardants, nitrogen-based compounds, and miscellaneous fire retardants such as resins, polymers based on tin or silicone, and inorganic compounds.

The successful examples of imparting an improved degree of safety have been mostly achieved with the application of fire-retardant by the after-treatment of textile, since it is most convenient and less expensive. However, most of the treatments have the disadvantage of adversely affecting the durability and the hand of the products. Some attempts have been made to use reactive fire-retardants in Nylon polymers, but only a few successful cases have been reported.

Halogen compounds combined with Sb_2O_3 are generally used for after-treatment of Nylons. Polyvinyl chloride, chlorinated paraffins and urea resins are often used for coating or binder of fire-retardants. Some organophosphorus fire-retardants can also be used; a typical example is tetrakis (hydroxymethyl) phosphonium chloride (THPC).

The incorporation of fire-retardants by blending into the polymer is an alternative method for improved fire retardancy with less problems encountered in such areas as hand, appearance, change and fastness to washing. This method is particularly useful for molded articles, since finishing or treatment cannot apply effective amounts of fire retardants to molded materials which have smaller surface area than fabrics.

This approach, however, also has several serious drawbacks. Polyamides are generally fabricated at temperatures ranging from 200° to 280°C. Only a few fire retardants are sufficiently thermostable to be exposed to those temperatures without undergoing decomposition.

The carbonamide linkages in Nylons are considerably more reactive than many other polymer linkages, particularly at the high processing temperatures. Reactions between the polymer and potential flame retardants frequently occur, leading to polymer degradation. Phosphorus-containing fire retardants, especially phosphate esters, react at elevated temperatures with polyamides and cause a partial degradation or gellation of the polymer. Even traces of the decomposition products rapidly degrade the polymer and render it unsuitable for most applications.

Almost all fire retardants are effective only at rather large additive levels. This high amount of additive (up to 30%) impairs the polymer crystallinity, which is necessary for fiber fabrication. Therefore, many flame-retarded polyamide resins are useful only for moldings.

From the standpoint of chemistry, basically, two kinds of fire-retardants are blended with Nylons: halogen-containing systems with and without synergistic materials, such as antimony trioxide (Sb_2O_3) or organophosphorus compounds, mainly, low-molecular-weight polymers. Typically, polyhalogenated aromatic compounds are used with Sb_2O_3, and low-molecular-weight polyphosphorates are used to impart flame retardancy to Nylons.

So far, no successful example of incorporating fire retardants into the polymer structure by copolymerization has been reported. Such copolymers, if produced, would require fundamental changes in polymerization process and in manufacturing facilities. Several flame resistant fabrics have been developed based on aromatic polyamide precursors. These fabrics are presently too expensive to permit individual commercial utilization as commodity products.

C. Experimental Studies

1. Flame retardant Nylon 6 containing Dechlorane Plus 515

Introduction. Since there are limitations to the after-treatment of fabrics to impart fire retardancy, only a few fire retardants could meet the strict specifications outlined below:

1. The fire retardant must be thermally stable in the molten Nylon 6 polymer at elevated temperatures ranging from 200° to 225°C.
2. The fire retardant must not discolor the polymer, cause gellation, nor affect polymer viscosity.
3. The fire retardant must be dispersed homogeneously in the polymer, or be dissolved into polymer without any destruction of basic polymer's properties.
4. The fire retardant should not elute during processing and actual use of the fabric.
5. The fire retardant should not induce a toxic reaction during use nor produce skin irritation.

After many experiments, Dechlorane Plus 515 was found to meet the specifications established for fire retardants. Dechlorane Plus 515 is a product of Hooker Chemical Company and one of their Dechlorane series of fire-retardants. The result of analysis and chemical structure of this compound is reported in the following section.

Dechlorane Plus 515 does not dissolve in the polymer but can be mixed homogeneously without degrading the viscosity and the color of Nylon 6. The mixture can be molded easily without much problem.

The disadvantage was that the dispersed small particles of Dechlorane Plus 515 affected the crystallinity of Nylon 6 polymer and impaired its flexibility. Such dispersion systems cannot be used during fiber processing due to its particular size, compared to the diameter of fibers. Despite several limitations, this fire retardant has been used to produce fire-retardant Nylon polymers.

Processing of samples. Pure Nylon 6 chips were dried in a vacuum oven at 110°C for 24 hours to prevent hydrolysis and bubbling during fabrication at high temperatures. Dechlorane Plus 515 was used as received. Its particle size was 5-15 μ, according to the manufacturer's catalog. Antimony trioxide (Sb_2O_3), a catalytic grade, was used as a co-fire retardant. Its average particle size was 1-2 μ.

Nylon 6 chips, Dechlorane and Sb_2O_3 were mixed in a polyethylene bag by shaking and the mixture was loaded on a two-axis extruder in order to produce homogeneously mixed chips for fabrication. The ratios of components used in these experiments are listed in Table 60. The amount of Dechlorane Plus 515 was varied from 10 PHR (parts per hundred resins) to 50 PHR, and the ratio of Dechlorane Plus 515 and Sb_2O_3 based on PHR was also changed to three levels: 4,3, and 2. A total of 13 different grades of Fr-Nylon chips were produced. The heater of the two axis extruder was set to 255°C and the temperature of the Nylon polymer melt was maintained at 237 ± 2°C. Nitrogen gas was passed through the extruder to prevent thermal degradation of the polymer. The mixture of Nylon and fire retardants was extruded in the form of strands which were cooled in a water bath and cut into chips by a rotary cutter.

Table 60. Composition Of Fire-Retarded Nylon 6 Polymers

Sample Lot Number	Dechlorane PHR[a].	Sb_2O_3 PHR[a]	Dechlorane/ Sb_2O_3	Dechlorane[b] Wt. %	Cl[b] Wt. %	Sb_2O_3[b] Wt. %	Total Wt. %[b] Additives
1	10	2.5	4	8.89	5.78	2.22	11.11
2	10	3.3	3	8.82	5.73	2.94	11.76
3	10	5.0	2	8.70	5.66	4.35	13.05
4	20	5.0	4	16.00	10.40	4.00	20.00
5	20	6.7	3	15.79	10.27	5.27	21.06
6	20	10.0	2	15.38	10.00	7.69	23.07
7	30	7.5	4	21.82	14.19	5.45	27.27
8	30	10.0	3	21.43	13.93	7.14	28.57
9	30	15.0	2	20.69	13.45	10.34	31.03
10	40	10.0	4	26.67	17.34	6.67	33.34
11	40	13.13	3	26.09	16.96	8.69	34.78
12	40	20.0	2	25.00	16.25	12.50	37.50
13		16.7	3	30.00	19.50	10.00	40.00

[a] Parts per hundred resins.

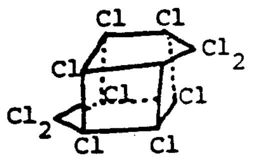
[b] Wt. % is calculated on the basis of total composites.

Sample specimens for use in the evaluation of the flammability characteristics of the fire-retardant polymers were produced by molding.

The FR-Nylon strand chips were dried in a vacuum oven for 4 hours before molding. The chips were loaded to an injection molding machine which was equipped with two dies. One die is of a size 1/4 x 1/4 x 5 in. which was used to produce specimens for the Limited Oxygen Index (LOI) test. Test pieces with a size of 1/2 x 5 x 1/16 in. were produced from another die; these samples were used for Underwriters Laboratory (UL) Test, Subject 94, a vertical flame test. The temperature of the cylinder of the injection molding machine was set to 250°C. A silicone mold release agent was used where necessary.

2. Analysis of fire retardants

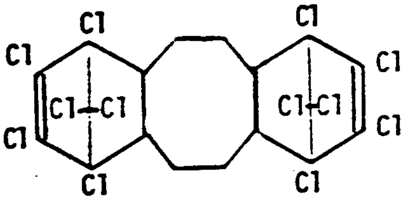
According to the manufacturer's information, Dechlorane Plus 515 (hereafter referred to as D-515) is a low volatile organic chlorinated compound, having a chlorine content of 65.1 percent. This fire retardant is insoluble in water and slightly soluble in organic solvents, such as methanol, benzene, and methyethylketone. This fire retardant is recommended to be used with Sb_2O_3 at a ratio of D-515/Sb_2O_3 = 2 on weight basis. No other information was available and it was generally believed to have a structure of



$(C_{10}Cl_{12})$

Declorane Plus 515

From chemical analyses conducted on this fire retardant, including elemental analysis and the mass-spectrometry studies, as well as from information available in the literature,(34) the structure of this compound was found to be 1, 2, 3, 4, 7, 8, 9, 10, 13, 13, 14, 14--dodecachloro--1.4, 4a, 5, 6, 6a, 7, 10, 10a, 11, 12, 12a--dodecahydro--1.4; 7.10--dimethanobenzo (a e) cyclooctane.



$(C_{18}H_{12}Cl_{12})$

The result of elemental analysis on the sample as tested in listed in Table 61. The data shows an excellent agreement with the theoretical values. The mass spectra of this compound had a molecular peak at m/e = 648 and the fragmentation pattern of m/2 = 648-672 agreed completely with the calculated peak ratio for a Cl_{12} compound.

A series of dechlorane compounds were analyzed using these same techniques and their chemical structures were identified. These structures are listed in Table 62 for reference.

3. Characteristics of flame-retarded nylon 6 polymer

Limited oxygen index (LOI) (ASTM D2863) test. As was illustrated previously, the Limiting Oxygen Index (LOI) is the minimum concentration of oxygen required to just sustain ignition and combustion of a test material. It should be noted that, although the test results obtained using the LOI procedure are very reproducible, this test does not measure the actual burning rate of a polymer.

Table 61. Elemental Composition Of Dechlorane Plus 515[R]

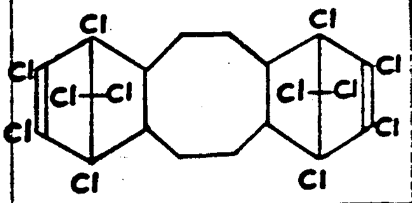
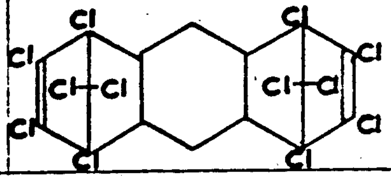
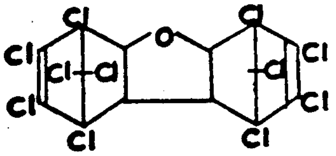
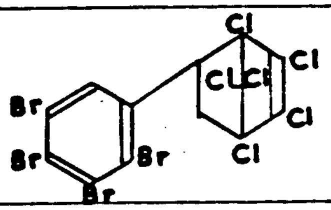
	% Composition			
	Carbon	Hydrogen	Nitrogen	Chlorine[b]
Dechlorane	33.07	1.85	0	65.01
Theoretical[a]	32.80	1.71	0	65.21

[R] Product of Hooker Chemical Corporation.

[a] Calculated on the basis of $C_{18}H_{12}Cl_{12}$.

[b] Obtained by titration method.

Table 62. Chemical Structures Of Dechlorane Series Fire Retardants[R]

Name	Chemical Structure		Wt. % of Halogens
Dechlorane plus 25 & plus 515		$C_{17}H_8Cl_{12}$	Cl: 65%
Dechlorane 603		$C_{17}H_8Cl_{12}$	Cl: 66.7%
Dechlorane 602		$C_{14}H_4OCl_{12}$	Cl: 69.3%
DeChlorane 604		$C_{13}H_4Cl_6Br_4$	Cl: 30.7% Br: 46.2%

[R] Products of Hooker Chemical Corporation.

Samples of FR-Nylon 6 used for the LOI test were rods with a size of 1/4 x 1/8 x 5 in., which were formed by injection molding. The results of LOI tests conducted on 14 FR-Nylon polymers which have different amounts of D-515 and Sb_2O_3 are summarized in Table 63.

Figures 60, 61 and 62 are LOI values plotted against total weight percent of fire retardants, including Dechlorane and Sb_2O_3, the amount of Dechlorane and the amojnt of Sb_2O_3. Analysis of these figures leads to the following conclusions:

1. There is an almost linear relationship between LOI and the amount of fire retardants utilized, although the effect of fire retardants is rather small when the weight of fire retardant is less than 10 percent.
2. The optimum ratio of Dechlorane to Sb_2O_3 is 3; further addition of Sb_2O_3 does not improve the flame retardancy of the polymer.
3. Dripping of Nylon resin was observed during burning of samples No. 0 through 6. Samples No. 4 through 6 formed char layers, although slight dripping was observed. Complete char formation was attained in samples No. 7 through 13, which burned sustaining their original rod form. The char layers formed on these samples prevented flame-propagation to the lower portion of the test specimens.

From the results obtained in this series of experiments, one can conclude that the more resistant FR-Nylon polymers require at least 30 PHR of the Dechlorane retardant plus the addition of Sb_2O_3. These formulations did not exhibit dripping and had a minimum LOI value of 30.

UL Subject 94 vertical flame test. The UL Subject 94 vertical flame test is a small-scale flame test developed by Underwriters Laboratory. Both vertical and horizontal tests are contained in this subject. In our experiments the vertical test, the test for "self-extinguishing materials," was used for the evaluation of FR-Nylon

Table 63. Limiting Oxygen Index (LOI) of Fire-Retarded Nylon 6 Polymers

Sample Lot Number	Dechlorane PHR[a]	Sb_2O_3 PHR	Dechlorane/ Sb_2O_3	LOI[b]
0	0	0	0	24.0
1	10	2.5	4	25.5
2	10	3.3	3	24.5
3	10	5.0	2	25.0
4	20	5.0	4	27.0
5	20	6.7	3	27.5
6	20	10.0	2	28.0
7	30	7.5	4	29.5
8	30	10.0	3	30.0
9	40	15.0	2	30.0
10	40	10.0	4	30.5
11	40	13.3	3	32.0
12	40	20.0	2	32.0
13	50	16.7	3	33.5

[a] parts per hundred resins.

[b] $\frac{nO_2}{nO_2 + nN_2} \times 100.$

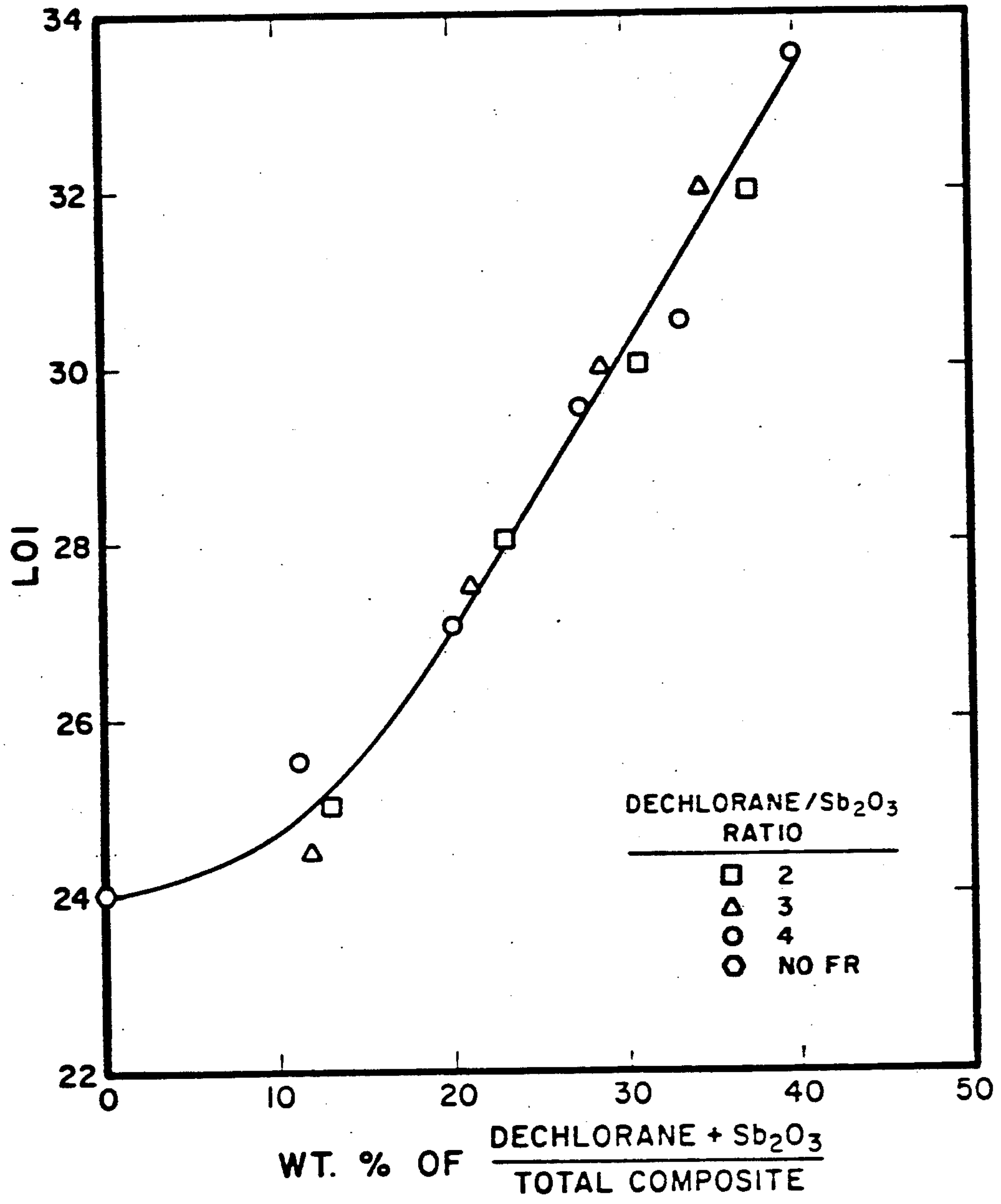


Figure 60. Effect of Dechlorane and Sb_2O_3 on LOI of Nylon 6 polymer

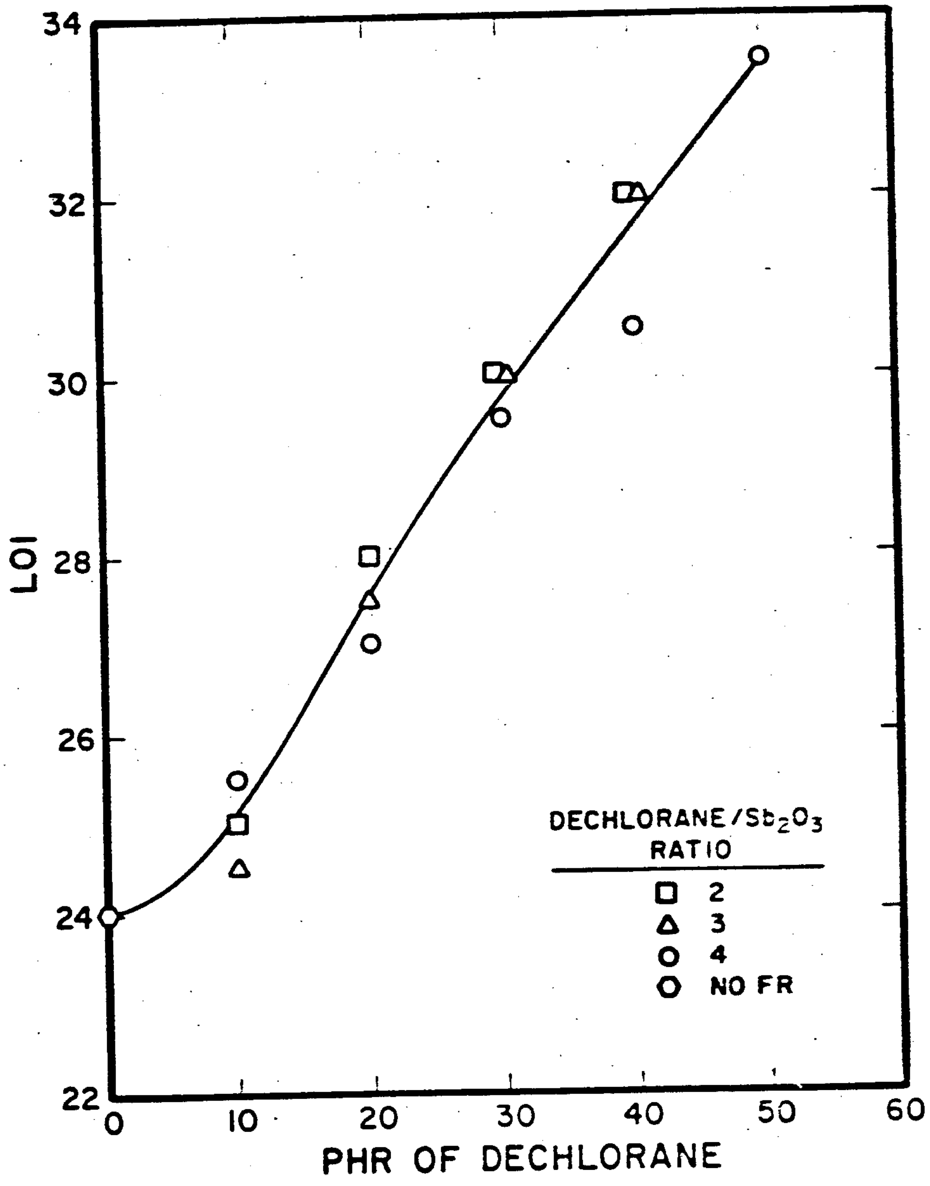


Figure 61. Effect of Dechlorane on LOI on Nylon 6 polymer.

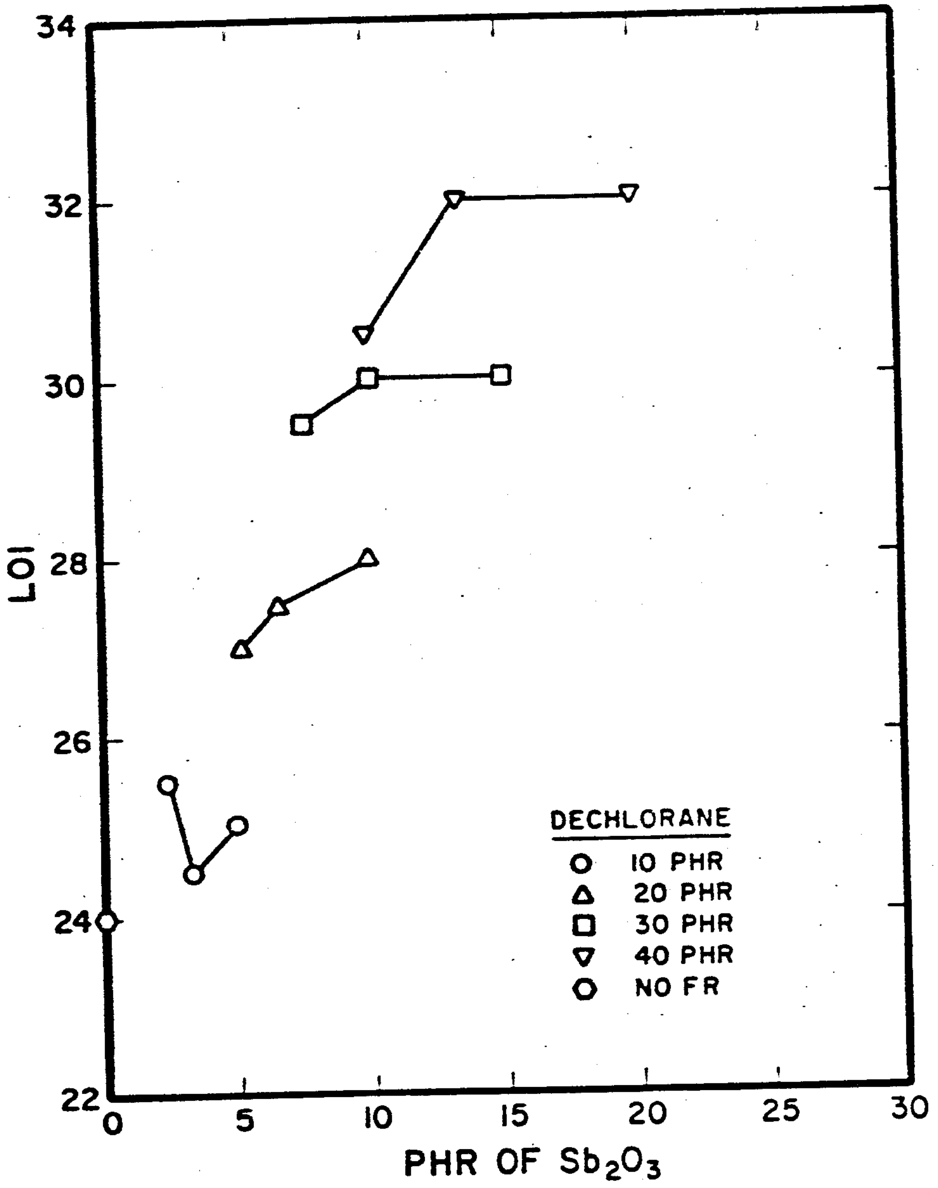


Figure 62. Effect of Sb_2O_3 on LOI of Nylon 6 polymer.

species, since the vertical test is much more severe than the horizontal one. It should be noted that this test procedure is used to obtain a laboratory comparison only, these results may not correlate to the materials in service performance in a fire.

Molded plates with a size of 5 x 1/2 x 1/8 in. were used. The specimens were dried in an air oven at 70°C for 168 hours and then held in a dessicator for 4 hours at room temperature. The UL-94 testing apparatus is illustrated in Figure 63.

The specimen is held by a clamp with 12-in. distance from its bottom end to ground, where a piece of cotton was placed. A Bunsen burner with I.E. of 3/8" is used as the flame source. A blue flame was controlled to 3/4" length and 3/8" of the flame was placed in contact with the bottom edge of the sample for 10 seconds. Then the burner was removed quickly and the time of the flaming combustion was measured. Immediately after the flaming was extinguished, the burner was put to the bottom end of the sample again for 10 seconds, and the time for the flaming and the glowing of the sample was measured. A wad of cotton placed beneath the test specimen was used for the measurement of fire spread by dripping (of flaming droplets).

Samples tested using the UL-94 test are usually classified into four grades in the order of the increasing fire retardancy: 94 HB < 94 V-2 < 94 V-1 < 94 V-0. The designation half-burning (HB) is applied to those materials which can pass UL-94 horizontal test, but cannot pass the vertical test due to a rapid flame propagation rate leading to complete combustion of the sample. The criteria of grading of UL-94 vertical test is summarized in Table 64. The results

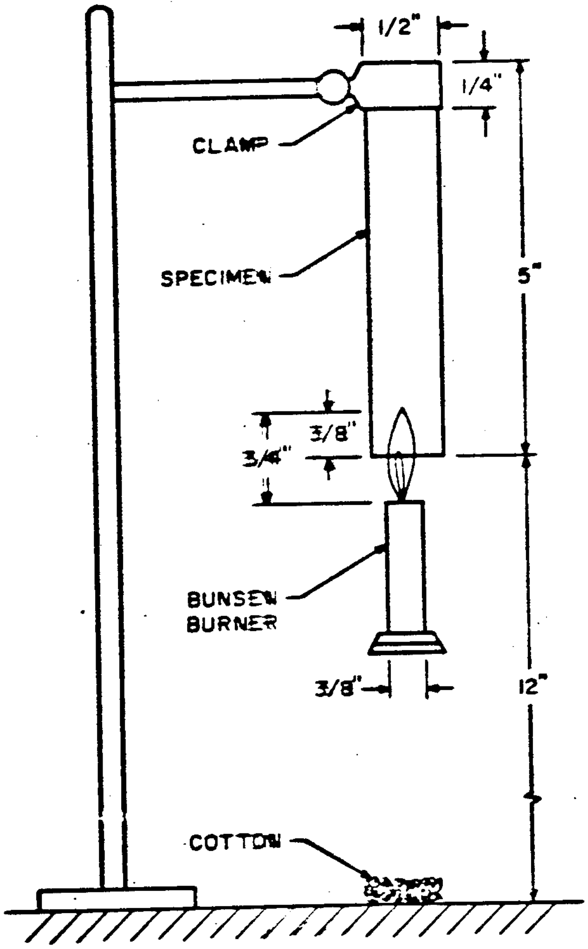


Figure 63. UL-94 vertical flame test.

Table 64. Criteria For Grading Fire Retardancy of Polymers By The Underwriters Laboratory UL-94 Test

Items	V-0	V-1	V-2
1. The time of flaming after the burner removed.	$\leqq$ 10 sec.	$\leqq$ 30 sec.	$\leqq$ 30 sec.
2. The total time of flaming of five specimens for ten times ignition by the burner.	$\leqq$ 50 sec.	$\leqq$ 250 sec.	$\leqq$ 250 sec.
3. Propagation of flame or glow up to the clamp (top end of the specimen).	No	No	No
4. Ignition of cotton by dripping.	No	No	Yes
5. Glowing time after the second ignition.	$\leqq$ 30 sec.	$\leqq$ 60 sec.	$\leqq$ 60 sec.

obtained from testing each of the fire-retarded Nylon polymers are summarized in Table 65. A level of 30 PHR of the Dechlorane fire retardant and 10 PHR of the co-fire-retardant Sb_2O_3 were required to achieve a rating of V-0. The atomic ratio of chlorine to antimony was 15:3.

4. Thermal analysis of flame-retardant Nylon 6 polymer

Effect of fire retardants on polymer decomposition. Samples of FR-Nylon were evaluated using the thermoanalyzer. The dried FR-Nylon chips were heated at 10°C/min rate from ambient to 1000°C in air. Figures 64, 65 and 66 contain the data that summarize the sample weight loss characteristics of FR-Nylons with different levels of fire retardants.

Samples of the Nylon polymers exhibited an initial loss of weight at lower temperatures as the concentration of fire retardants was increased.

The amount of char residues increased with the increased incorporation of fire retardants. Although the char residues contained a considerable portion of the Sb_2O_3 incorporated into the polymer the char-formation effect induced by this fire-retardant system was evident.

Dechlorane, Sb_2O_3 and the mixture of Dechlorane and Sb_2O_3, were examined by thermal analysis in air at a heating rate of 10°C/min. These results are summarized in Figures 6 and 68. Dechlorane started to lose weight at 255°C and it was totally consumed by 485°C, while there was not much weight loss shown by the Sb_2O_3 up to 900°C. The TGA trace of the mixture of Dechlorane and Sb_2O_3 is not the

Table 65. Evaluation of Fire-Retarded Nylon 6 Polymers (UL-94 Test)

Sample[a] Lot No.	Test Item Number						Grading[a]
	1 (sec)		2 (sec)	3	4	5 (sec)	
	First Ignition	Second Ignition					
0	4.4	39.9	221.5	pass	fail	0	HB
3	2.4	0.5	17.0	pass	fail	0	V-2
4	6.6	0	33.0	pass	fail	0	V-2
5	10.1	5.2	76.5	pass	fail	0	V-2
6	11.5	1.5	65.0	pass	fail	0	V-2
7	3.9	1.4	26.5	pass	pass	0	V-1
8	3.0	1.3	21.3	pass	pass	0	V-0
9	4.3	2.4	33.5	pass	pass	0	V-0

[a] See Table 64.

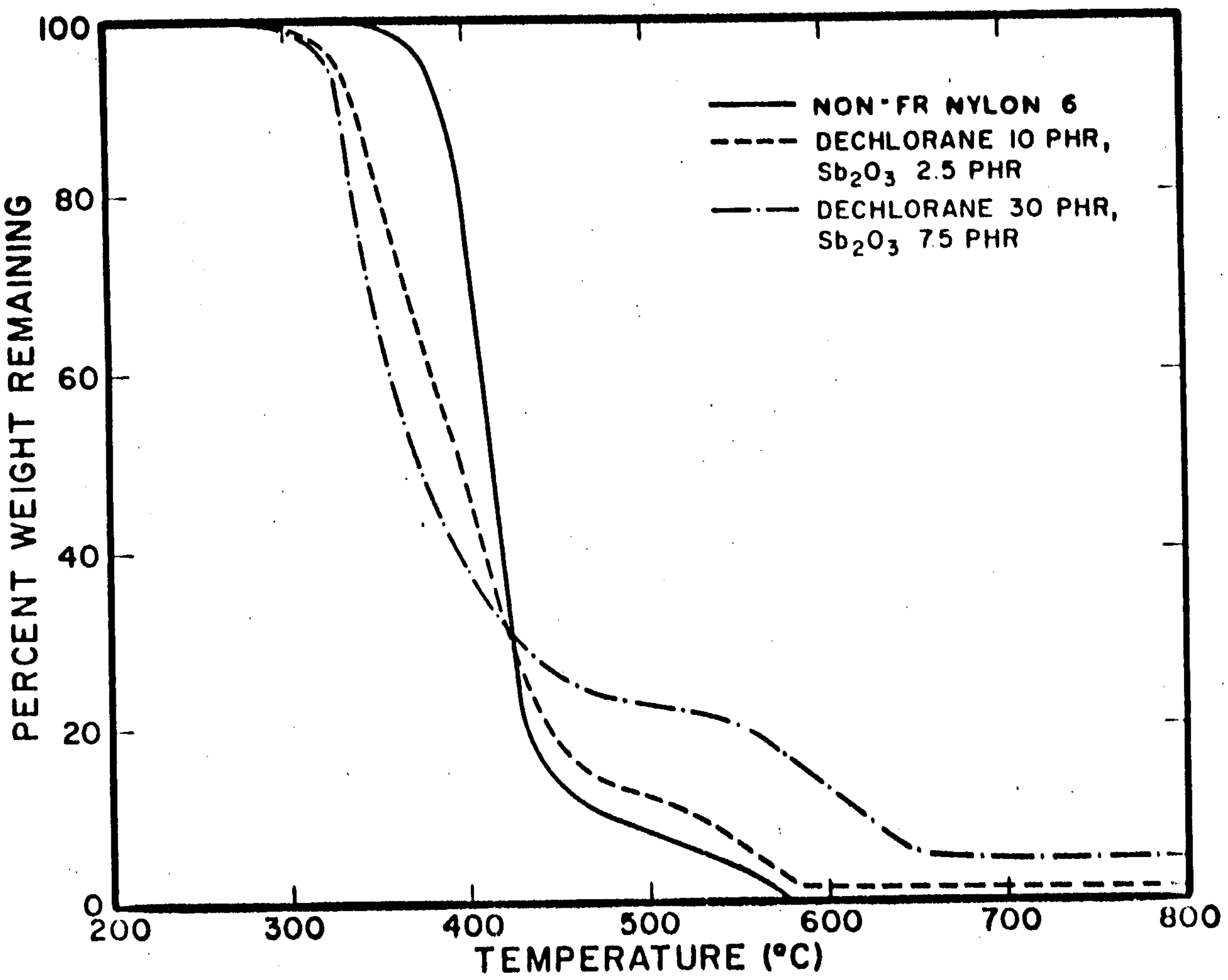


Figure 64. The effect of fire retardants upon the weight loss of Nylon 6 polymers in air at a heating rate of 10°C/min.

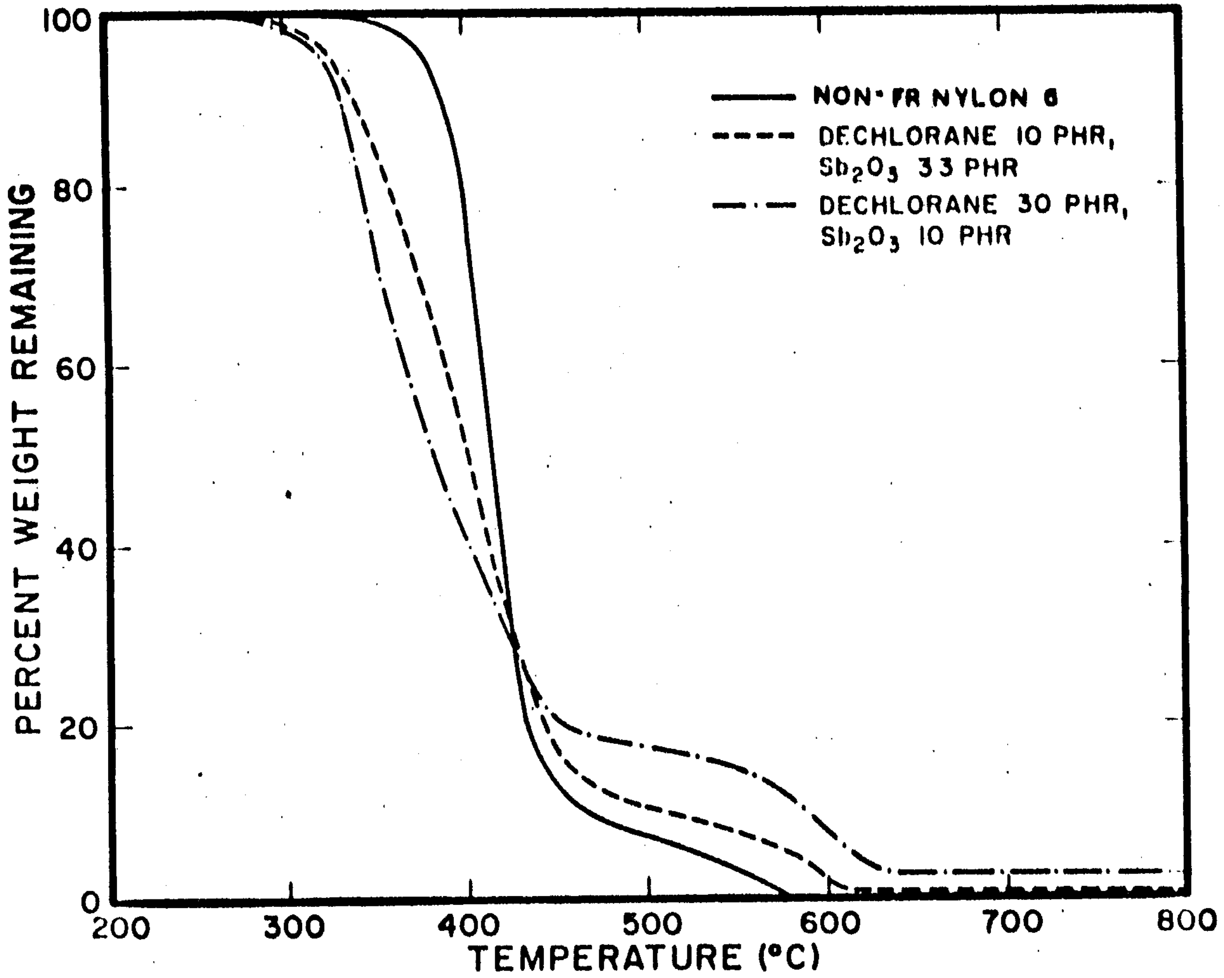


Figure 65. The effect of fire retardants upon the weight loss of Nylon 6 polymers in air at a heating rate of 10°C/min.

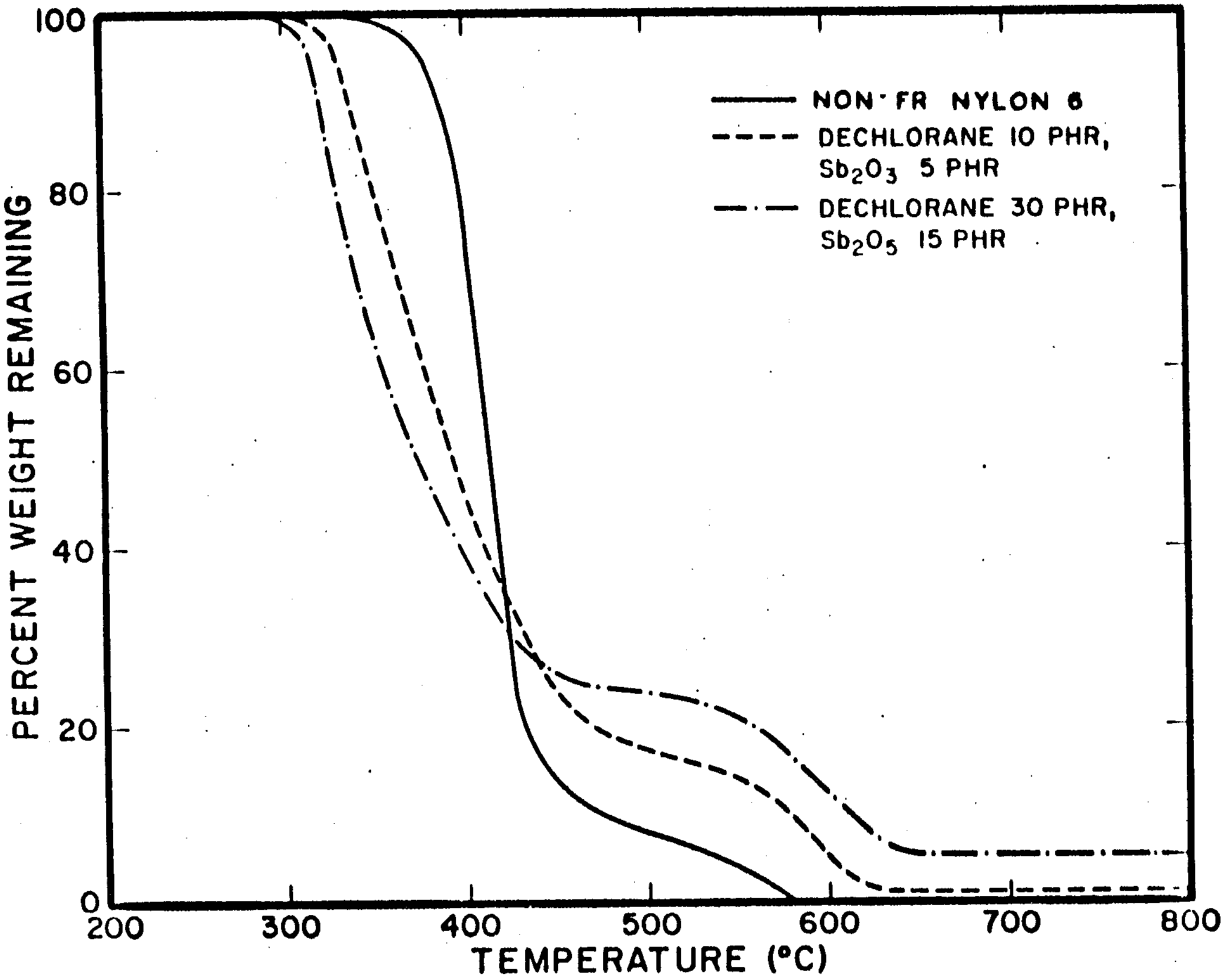


Figure 66. The effect of fire retardants upon the weight loss of Nylon 6 polymers in air at a heating rate of 10°C/min.

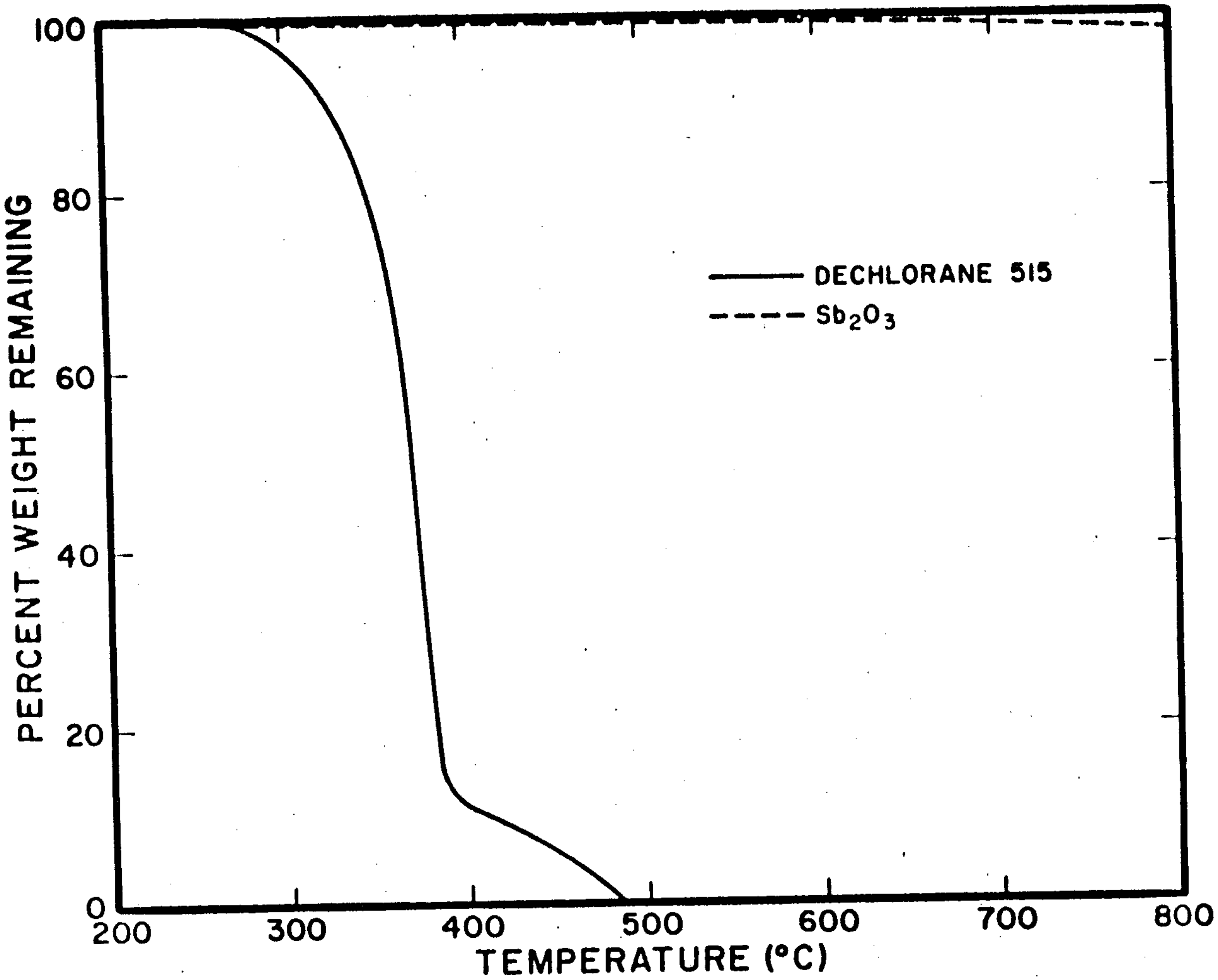


Figure 67. TGS traces for Dechlorane 515 and Sb_2O_3 at a heating rate of 10°C/min. in air.

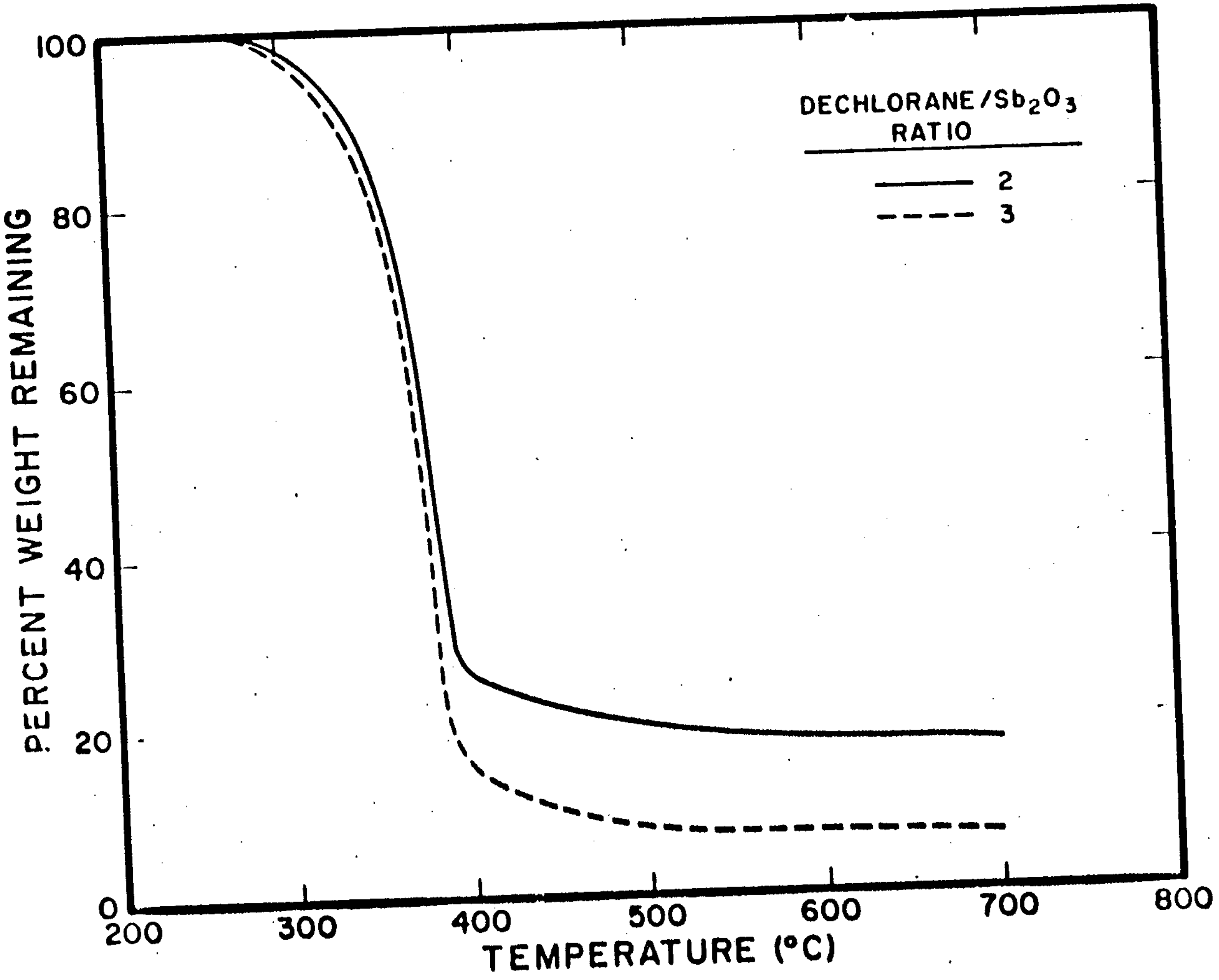


Figure 68. TGA traces for mixtures of Dechlorane and Sb_2O_3.

superimposition of two traces from individual components.

Effect of environment on the thermal degradation of Nylon 6 polymers. Figures 69, 70 and 71 illustrate the TGA thermograms of several FR-Nylons obtained in air and helium environments at a heating rate of 10°C/min. No weight loss occurred under 300°C; a rapid weight loss was observed to occur at approximately 320°C. Char formation did not occur during the inert thermal degradation; a slight amount of residue was observed above 500°C. This study suggests that the mode of the degradation of FR-Nylons is rather similar to that of the non-fire-retarded Nylon. The weight loss at low temperatures can be attributed to the loss of the Dechlorane fire retardant.

5. Analysis of low-boiling volatile products

Samples of FR-Nylon 6 polymers were exposed to an oxidative air environment and heated at a rate of 100°C/min from ambient to a final temperature of 1000°C. The volatile products from the oxidative degradation were collected using the trapping system that was described previously in Chapter IV. The experiments were performed with a 50 mg sample size for characterization and quantitation. Product separation was accomplished using Chromosorb 101 column packing in 16 ft. x 4 mm O.D. stainless-steel tubing which was temperature programmed -10 to 265°C at 10°C/min. Each experiment was conducted in duplicate; the quantitative data were obtained using both TCD and FID detectors.

Five samples with lot numbers 2, 5, 8, 10 and 11 (see Table 60 for composition) were analyzed. More than 35 volatile components were resolved, 32 compounds of which were identified. Typical chromatograms

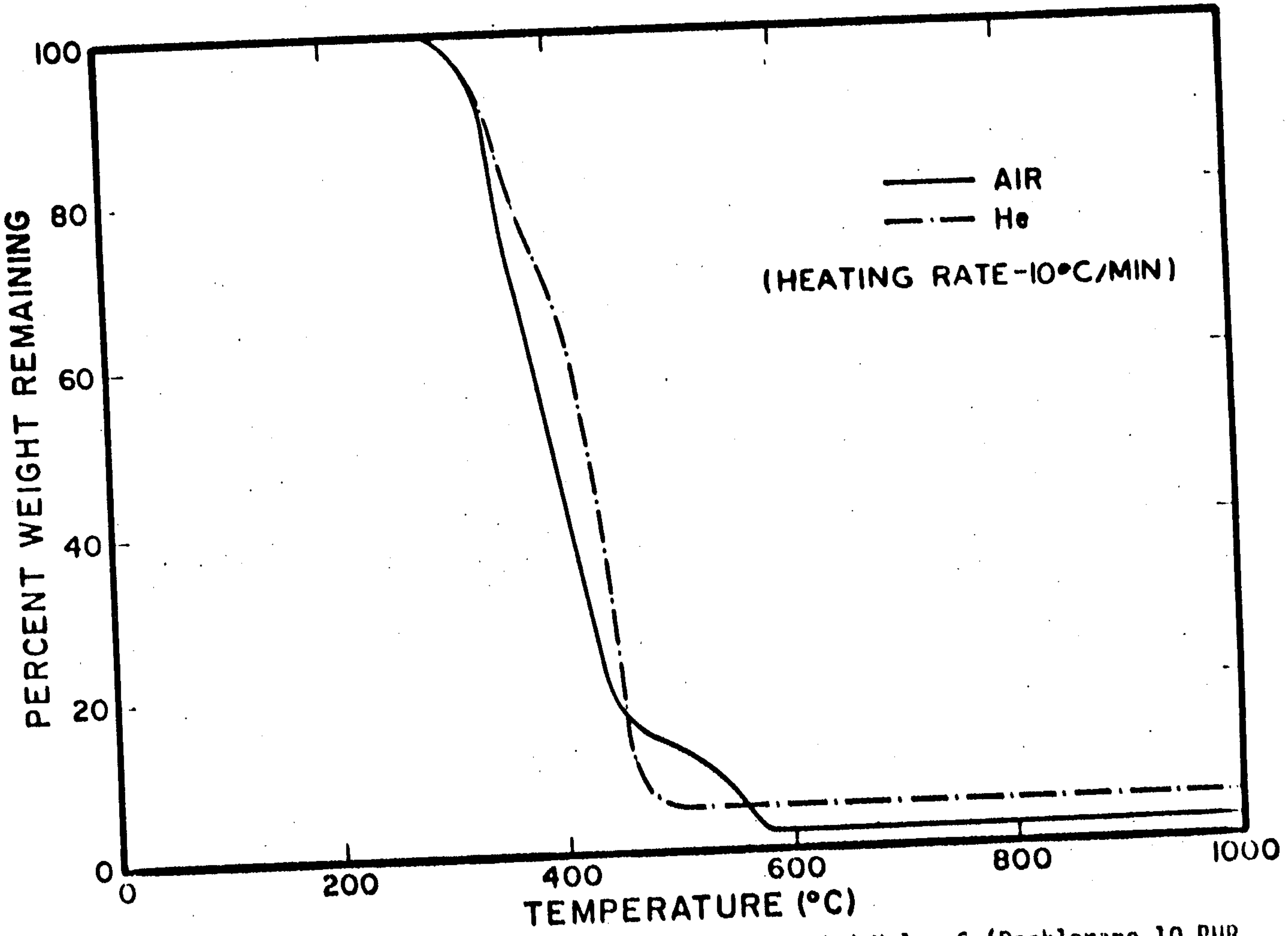


Figure 69. The effect of environment on fire retarded Nylon 6 (Dechlorane 10 PHR, Sb_2O_3 2.5 PHR).

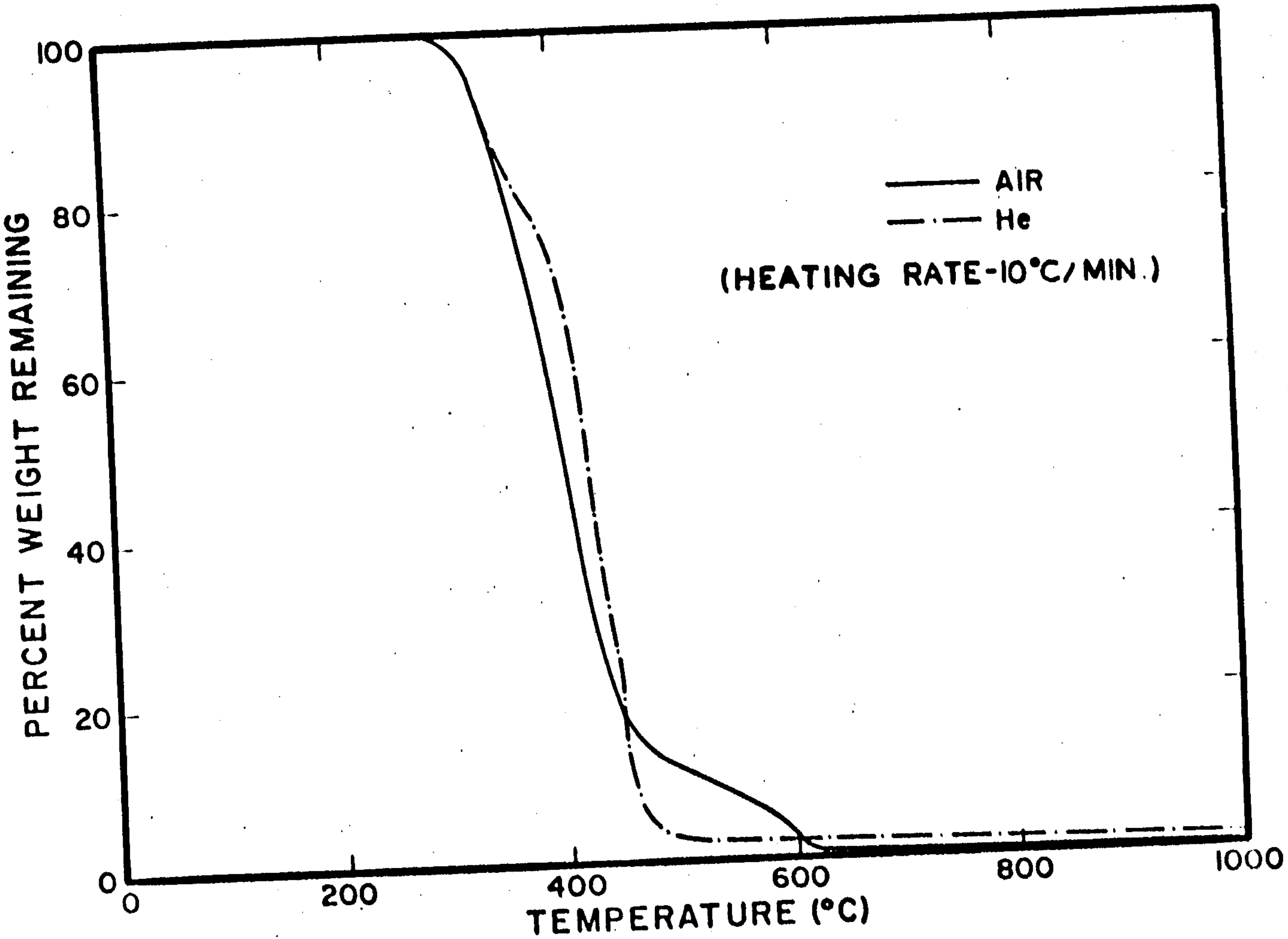


Figure 70. The effect of environment on fire retarded Nylon 6 (Dechlorane 10 PHR, Sb_2O_3 3.3 PHR).

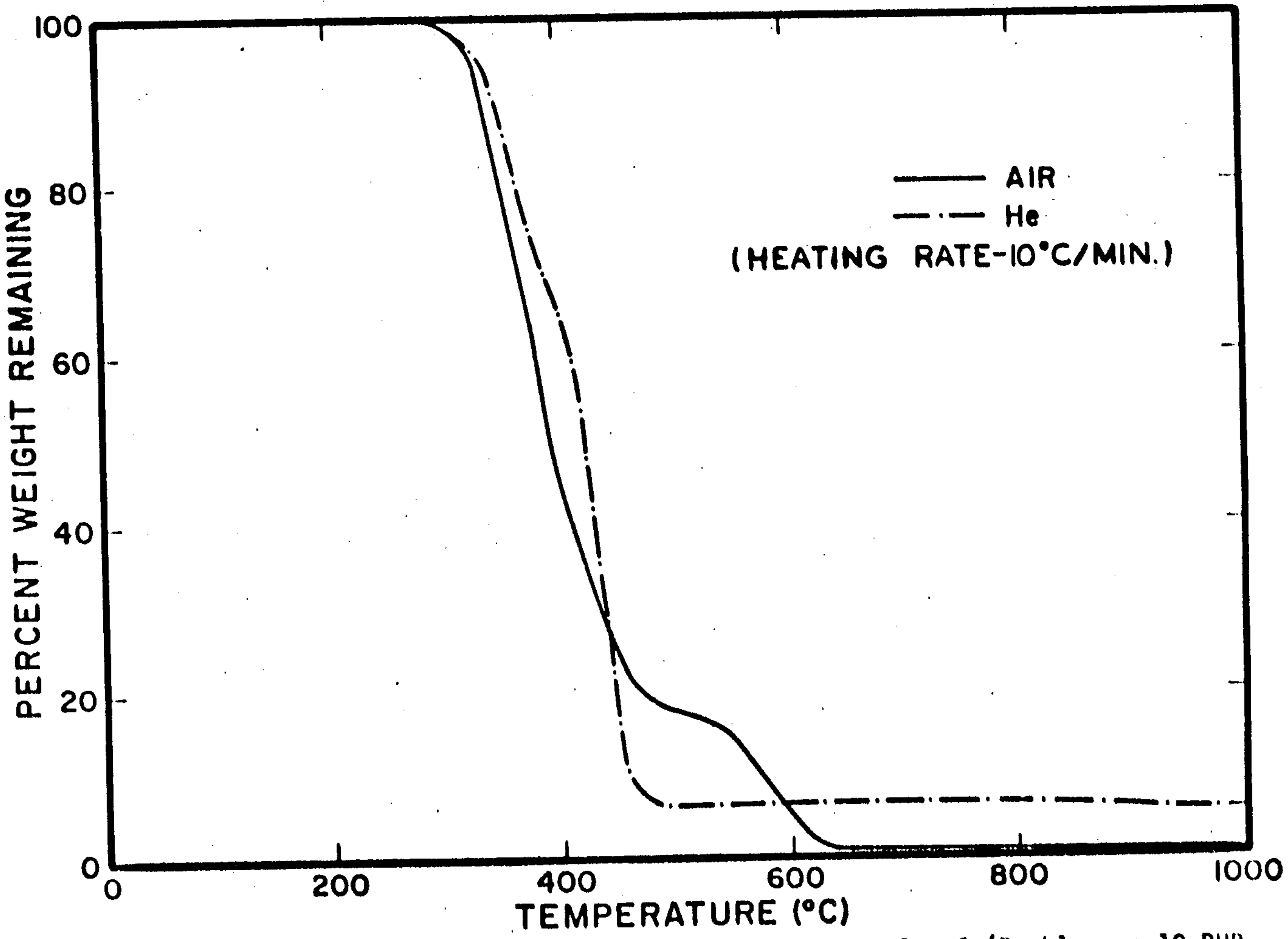


Figure 71. The effect of environment on fire retarded Nylon 6 (Dechlorane 10 PHR, Sb_2O_3 5 PHR).

obtained in this study are shown in Figure 72, the dotted lines illustrate peaks which are hidden by the large peak from water. Table 66 contains a summary of the low-boiling volatile products obtained during the oxidative degradation of the Nylon polymers.

An attempt was made to isolate hydrogen chloride from the volatile compounds, since no chlorine-containing compound was found in the volatile products. The exhaust gas from the thermoanalyzer furnace, containing the degradation products, was introduced directly to an aqueous solution of silver nitrate so that hydrogen chloride might be trapped as silver chloride; however, no precipitation of silver chloride was obtained in these experiments.

An analysis of the results of this series of experiments led to the following conclusions:

1. The nature and concentration of the volatile products produced during the oxidative degradation of Nylon didn't change substantially with the addition of fire retardants.
2. The quantity of organic volatiles decreased with the increased addition of fire retardants.
3. Hydrogen chloride was not found during polymer degradation.
4. No organic volatiles containing chlorine were isolated and identified utilizing the trapping techniques employed.

The results of these studies confirm the earlier studies of Reardon *et al.*(106) These investigators pyrolyzed Nylon 6 polymers which contained organobromine compounds, such as hexabromobiphenyl and dodecabromopentacyclodecane and reported the pyrolysis products were not altered by the incorporation of fire retardants. However, these studies do not necessarily imply the ineffectiveness of the halogen components as fire-retardants, as was claimed by Reardon.

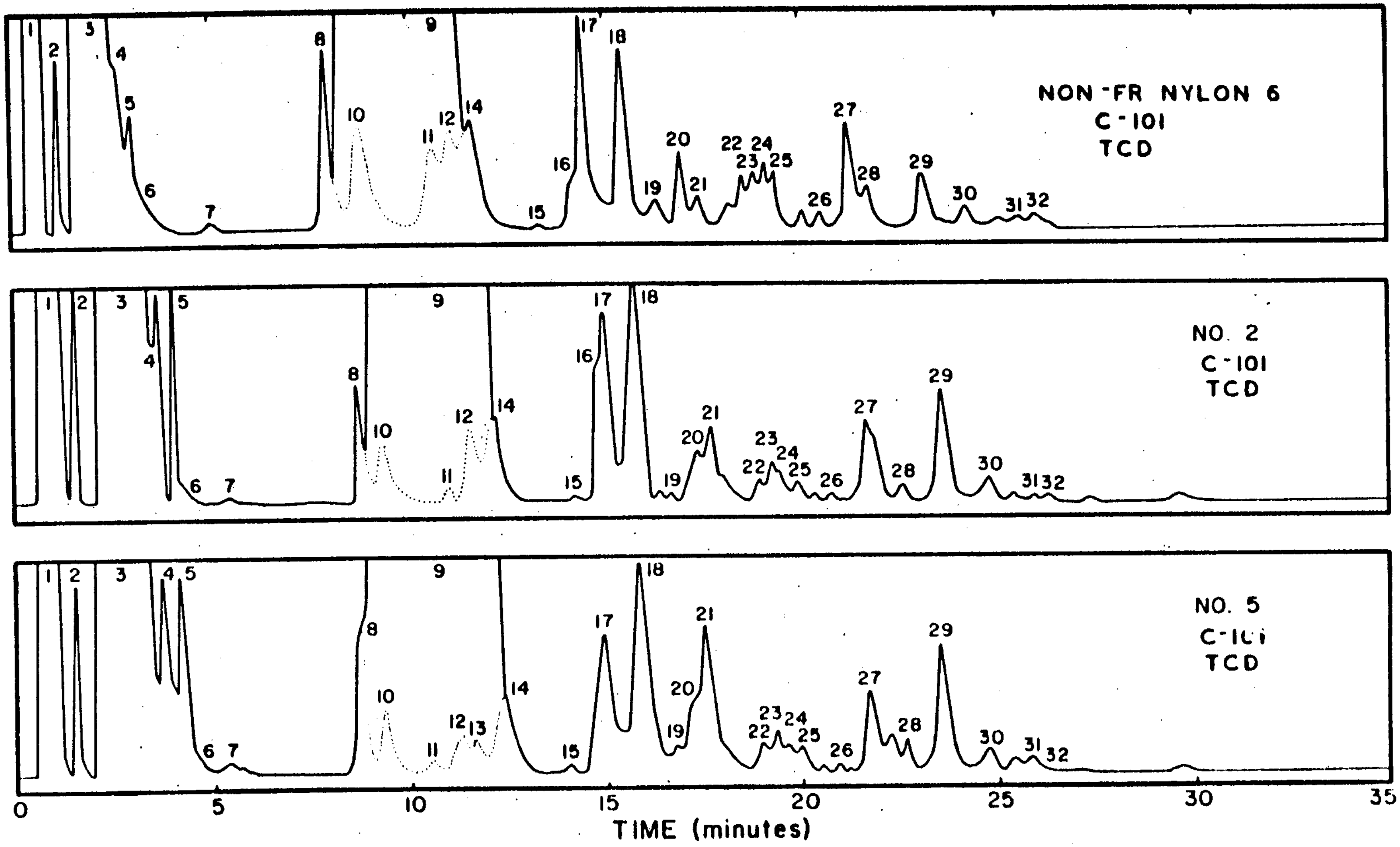


Figure 72. Low-boiling volatile products produced during the thermal oxidative degradation (slow heating) of fire-retarded Nylon 6 polymers in air.

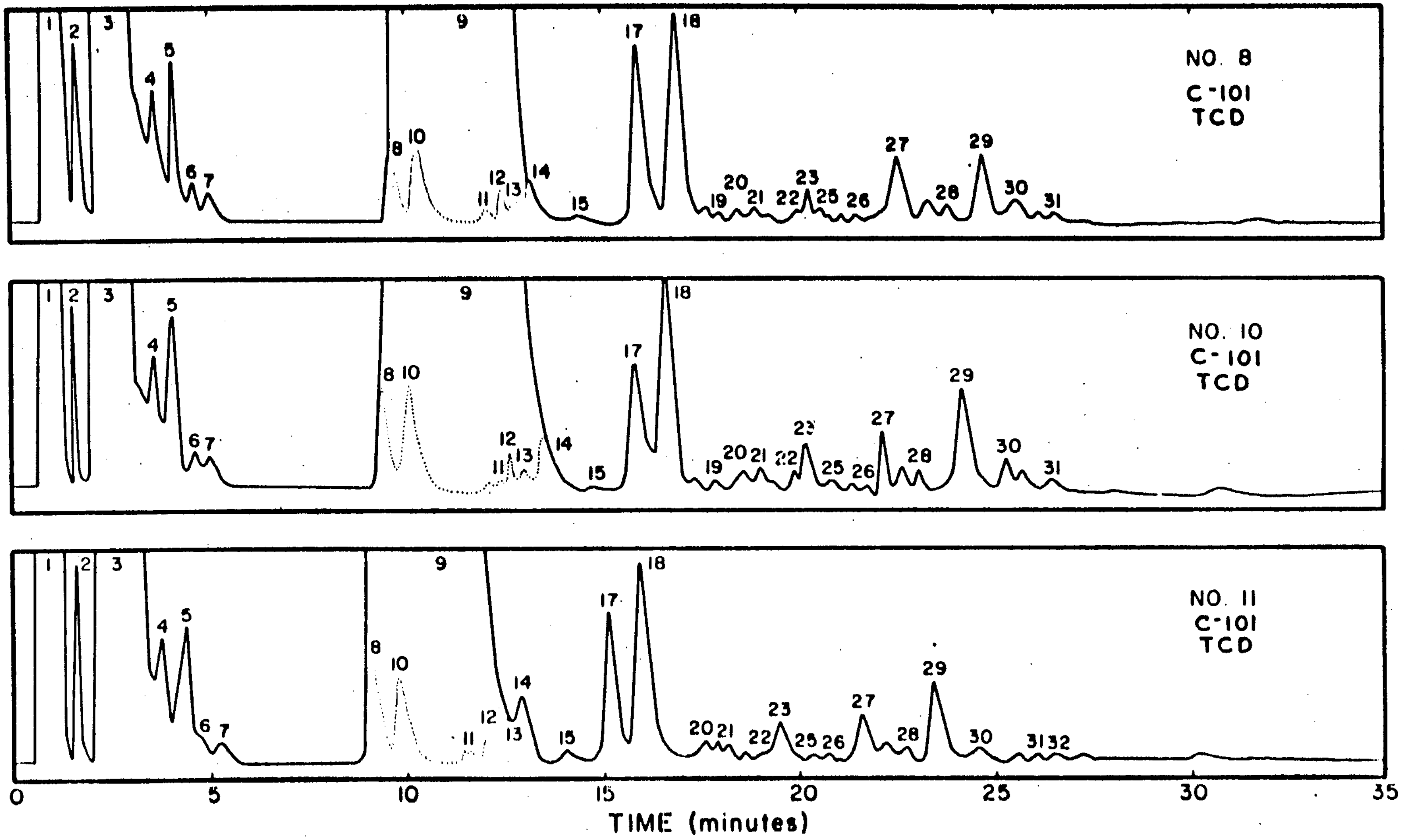


Figure 72 - continued.

Table 66. Low-Boiling Volatiles Produced During The Oxidative Degradation (Slow Heating) Of Non-Fire Retarded And Fire-Retarded Nylon 6 Polymers

Low-Boiling Volatiles	Peak Numbers[b]	T.E.[c]	R.F.[d]	Quantity[e]				
				Non-Fire Retarded Polymer	Fire-Retarded Polymers			
					#2	#5	#8	#11
Carbon monoxide	1	--	0.670	495	450	--	370	--
Niethane	2	0.05	1.231[f]	92.1	71.0	45.8	49.0	44.3
Carbon dioxide	3	0.97	0.915	513	493	490	423	399
Nitrous oxide	4	1.00	0.890	5.06	3.30	3.97	3.05	2.81
Ethylene	5	0.96	0.962[g]	17.91	12.50	10.34	11.02	9.37
Acetylene	6	0.96	0.932[g]	0.20	T	T	0.73	T
Ethane	7	0.98	1.231[f]	3.32	2.32	1.97	1.55	1.47
Cyanogen		0.44*	1.5[f]	T	--	--	--	--
Water	9	0.82	0.550	395	367	360	310	272
Propene	8	0.98	0.652[g]	17.21	12.10	12.53	11.21	8.31
Hydrogen cyanide	10	0.99	1.5*[f]	17.98	9.23	10.22	10.31	8.01
Methanol	11	0.75	4.348	3.02	0.63	0.88	0.41	0.30
Accloaldehyde	12	0.90	1.8*[f]	2.41	3.06	1.63	1.11	0.80
Butene	13	0.97	0.895[g]	3.87	--	1.01	0.70	0.66
1,3-Butadiene	14	0.97	0.870[g]	4.56	4.45	4.32	2.33	2.45
Ethanol	15	0.85	0.940	1.00	0.21	T	0.10	0.18
I-Pentene	16	0.97	0.660	0.98	2.03	--	--	--
Acetonitrile	17	0.95	0.961	17.21	11.49	6.93	2.94	4.28
Propenenitrile	18	0.95	0.582	10.85	16.75	9.95	4.53	4.30
Nitromethane	19	0.95	2.0	0.90	T	T	T	--
Propanenitrile	20	0.95	0.650	4.97	1.04	0.29	0.41	0.35
Metacrylonitrile	21	0.95	0.727	1.66	1.24	1.69	0.53	0.41
3-Butenenitrile	22	0.95	0.727	2.69	1.27	0.71	0.24	T
Benzene	23	0.90	0.790	4.59	3.34	1.52	0.57	0.34
Butanenitrile	24	0.95	0.680	1.71	0.85	1.07	--	--
Pyrrole	25	0.95	0.671	0.98	0.32	0.21	0.11	T
Pentanenitrile	26	0.95	0.692	T	T	T	T	T
Toluene	27	0.95	0.794	5.06	2.54	2.35	1.52	1.38
Cyclopentanone	28	0.95	0.827	2.90	0.89	1.10	0.56	0.75
Xylene		0.90	0.818	0.02	--	--	--	--
Capronitrile	29	0.90	0.805	9.85	7.57	6.12	4.00	3.92
Styrene		0.88	0.800	0.20	--	--	--	--
Hexenenitrile	30	0.90	0.785	3.17	1.63	1.24	1.00	0.52
Phenol	31	0.88	1.105	0.56	T	0.24	T	T
Benzonitrile	32	0.88	0.895	0.77	T	T	--	T

*Estimated

[a] The duplicated analysis of the oxidative degradation with a sample size of 50.0 mg from ambient to 1000°C.

[b] Corresponds to peak numbers in Figure 72.

[c] Relative trapping efficiencies.

[d] Relative response factors for the thermal conductivity detector.

[e] Milligrams of compound produced per gram of polymer as measured by analytical techniques.

[f] Non FR-sample that was degraded at the same conditions.

[g] Relative response factors for the flame ionization detector.

It should be remembered that hydrogen-containing fire retardants are expected to quench the chain propagation step in the vapor phase during combustion. In the pressure of Sb_2O_3 chlorine would form Sb_2Cl_3 or SbOCl, which act as very effective radical quenchers.

CHAPTER IX

SUMMARY AND CONCLUSIONS

In the study of the thermal degradation of Nylon 6, polyethylene terephthalate (PET), and polycarbonate polymers, most decomposition products including low-boiling volatiles (gases), high-boiling volatiles (aerosols, heavy oils), and solid residues (chars, particulates), were identified and quantitated. A good materials balance was obtained with these three different step-growth polymers, both for the pyrolysis and the oxidative degradation processes.

The study of the degradation products and the thermal behavior of Nylon 6, PET and polycarbonate polymers, led to the development of proposed thermal degradation mechanisms. The mechanisms were found to be different, depending upon the basic polymer structures.

The principal pyrolysis process for Nylon 6 in an inert environment was that of a rather simple depolymerization reaction which led to the formation of ε-caprolactam and oligomers resembling the structure of the original polymer. Secondary reactions occurred at higher temperatures which led to the decomposition of the monomer and oligomers. Homolytic random chain scission reactions may be responsible for the formation of methane, carbon monoxide, propene, ethylene, ammonia, carbon dioxide, water, hydrocarbons,and nitriles. No noticeable char formation was observed during the pyrolysis of Nylon 6.

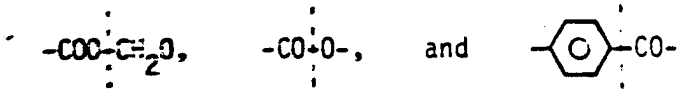
In an air environment the oxidative reaction was competitive with the pyrolysis reaction. The oxidation reaction products such as carbon monoxide, carbon dioxide, water, hydrogen cyanide, and nitriles, were dominant in the volatile product distribution. The total amount of ε-caprolactam and oligomers recovered from the oxidative degradation process decreased to approximately one-third that observed during the pyrolysis process.

The results of the analysis of volatiles, aerosols and non-volatile solid residues at several stages of the oxidative degradation of Nylon 6 suggest that the major degradation step occurring between 280-450°C is composed of the competitive reactions involving both pyrolysis and oxidative degradation.

A weak char structure was formed during the oxidative degradation of Nylon 6. This char was later decomposed to carbon monoxide, carbon dioxide,and water at elevated temperatures.

Under the conditions of high heating rates, when high temperatures are reached in a short time, the formation of ε-caprolactam and oligomers was favored. On the other hand, at low temperatures, the oxidative reaction is dominant, as was indicated by the results of the isothermal oxidative degradation.

Unlike the decomposition of Nylon 6 polymer, the principal thermal degradation process for the polyethylene terephthalate polymer appeared to be random scissions of polymer chains. Weak linkages in the PET structure, such as



$-COO-CH_2O$, $-CO-O-$, and

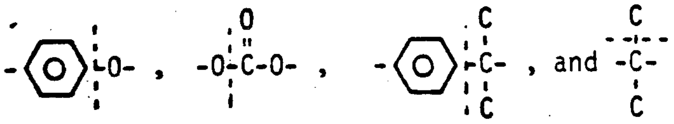
were broken under the dynamic heating conditions.

As contrasted to the formation of a weak char during thermal decomposition of the Nylon 6 polymer, a greater amount of a strong char was formed during the pyrolysis of PET. This char was stable at 1000°C in an inert environment and contained a high concentration of carbon. The stability of phenyl ring in the polymer structure may be responsible for the formation of this strong char structure.

It can be estimated that the weak aliphatic linkages are broken homolytically at lower temperatures, forming low-boiling volatile fragments and oligomers. These volatiles and some of the more volatile oligomers were carried away by the environmental gas stream, and the remaining polymer was then degraded at high temperatures to form a carbon-based char structure by stripping off low-molecular weight compounds.

The oxidation reaction is superimposed on the basic random chain scission mechanism. The oxidation accelerates the degradation of PET by attacking first the aliphatic part of the polymer structure. The aromatic part would be also decomposed by oxygen at elevated temperatures. Thus, the PET was completely consumed at 580°C in an air environment.

As observed in the degradation of the PET polymer, the principal degradation reaction of the polycarbonate polymer appeared to proceed through random chain scission reactions along the polymer chains. Any weak bonds, such as



ruptured under the dynamic heating conditions employed in this study.

The char formation reactions in polycarbonate can occur more readily than in PET. A large amount of char, which accounted for 23 percent of the original sample, was obtained during the pyrolysis of the polycarbonate polymer. The rapid char formation would be attained first by the elimination of carbon monoxide and carbon dioxide from the carbonate linkage followed by the decomposition of isopropylidene groups at higher temperatures.

In the oxidative environment it is probable that the degradation of isoproplyidene groups involved oxidation to hydroperoxides, followed by extensive chain scissions as was suggested by Lee.(84) The formation of Bisphenol-A which was identified only during the oxidative degradation can be explained by the hydrolysis of polymeric or oligomeric units contained in the polycarbonate polymer.

The fire retardant 1, 2, 3, 4, 7, 8, 9, 10, 13, 13, 14, 14 - dodecachloro- 1, 4, 4a, 5, 6, 6a, 7, 10, 10a, 11, 12, 12a - dodecahydro-1.4:7.10-dimethanobenzo [a.e.] cyclooctane (Dechlorane Plus 515 produced by Hooker Chemical Co.) in many was found to be an effective fire retardant for the Nylon 6 polymer. This fire retardant can be incorporated into the polymer without causing appreciable changes to the properties of the polymer. The optimum ratio of Dechlorane Plus 515 and antimony trioxide which was used as a co-fire-retardant was determined to be approximately 3. At least 30 PHR of Dechlorane Plus 515 and 10 PHR of antimony trioxide was needed in order to impart effective fire-retardancy to the Nylon 6 polymer.

The results of the analysis of the products from the oxidative degradation revealed that the nature of volatile products was not greatly affected by the inclusion of fire retardants, although the quantity of organic volatiles decreased with the increased addition of fire retardants.

As it is apparent from the results of this study, the patterns of thermal degradation reaction of three step-growth polymers are different, depending on their basic chemical structures. The classification of polymers in terms of their production routes cannot be applied to classify the pattern of the thermal degradation of polymers. Nylon 6 undergoes a depolymerization process, while PET and polycarbonate are degraded through random chain scissions. Nylon 6 tends to yield its original monomeric unit and form little char structure, while PET and polycarbonate mainly form oligomers and significant char formation was observed. The amount of char which can be an indicator to show the thermal stability of polymers, is roughly proportional to the aromatic carbon content in the original polymer structure.

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