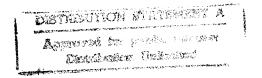
THERMAL DEGRADATION OF POLYAMIDES

PART I. ALIPHATIC POLYMERS

I. J. GOLDFARB
A. C. MEEKS



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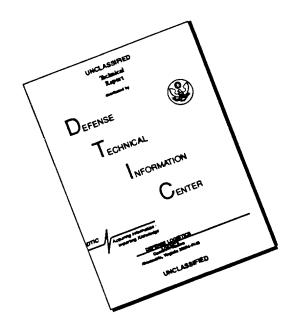
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." It was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. I. J. Goldfarb (MANP), Task Scientist.

The report covers work conducted from September 1966 to June 1968. It was submitted by the authors in November 1968.

The authors wish to thank Mr. W. Baltzell and Mr. R. R. Luthman, Jr., for their valuable assistance in the experimental work and in the calculations. Thanks are also due Dr. H. Friedman and Dr. H. Goldstein, General Electric Space Sciences Laboratory for the mass spectral analysis.

This technical report has been reviewed and is approved.

WILLIAM E. GIBBS

Chief, Polymer Branch

William E. Silles

Nonmetallic Materials Division Air Force Materials Laboratory

ABSTRACT

The thermal degradation of two aliphatic polyamides, polyhexamethylene adipamide (nylon 6.6) and polyhexamethylene sebacamide (nylon 6.10) have been studied. Molecular weight changes, weight loss, and volatile product analysis were used to help elucidate the reaction mechanisms.

The presence of low molecular weight material and polymerizable end groups in these polymers complicated the interpretation of molecular weight changes during degradation. The weight loss data obtained allowed the calculation of rate data. Nylon 6.6 degradation gave an activation energy of 45 kcal/mole while nylon 6.10 degradation was characterized by an activation energy of 55 kcal/mole. Both polymers gave evidence of random scission kinetics. The volatile products were consistent with the occurrence of further condensation, scission, and cross-linking reactions.

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SECTION I

INTRODUCTION

A wealth of information is available in the literature concerning the degradation of vinyl polymers (References 1 and 2) and in some cases complete analyses of mechanism are well established. However, there seems to be a deficit of similar information for polycondensates except perhaps for some polyesters (e.g., polyethylene terephthalate). In view of the considerable current interest in polymers of this type, this is somewhat surprising, especially since the more exotic polycondensates (e.g., polybenzimidazoles, poly(bis-benzimidazobenzo-phenanthroline) have shown considerable promise as thermally stable materials of improved useful service life.

A large number of polyamides containing the repeating unit

are available where R and R' range from short aliphatic hydrocarbon chains to aromatic and heterocyclic rings. Many of these polymers have useful physical and chemical properties and have achieved commercial importance as textiles and molding compounds.

One source of such a diversified range of structures has been the recent interest in increasing the useful life of polymeric materials at high temperature, particularly by the incorporation of aromatic rings into the backbone of the polymer. Russian research on polyamides has been particularly active (References 3 and 4) as has the work being carried out at Chemstrand Research Center (References 5 and 6).

Information is available on the composition of the evolved gases during degradation (Reference 7) but there has been relatively little interest in the rates of the various processes or the thermodynamic parameters which control the degradation of these compounds.

The work described here has been an attempt to correlate polyamide structure with the mechanism and kinetics of the degradation reactions. Early studies were devoted to molecular weight changes which were expected to take place at temperatures below those required for the onset of drastic weight loss of the polymer. Temperatures not far above the sample melting point were used but 1 to 2% weight loss was often evident. In this way, it was hoped to be able to follow molecular weight changes as a function of the exposure time, temperature, and polymer structure. Since undesirable changes in physical properties often accompany molecular weight changes, knowledge of the kinetics which govern molecular weight changes could be of use in predicting polymer lifetimes under various conditions. The main objective here, however, was a determination of the types of reaction (scission, etc.) responsible for molecular weight degradation.

The studies were extended to follow the kinetic laws involved in weight loss processes. This included evaluation of methods employed for the determination of kinetic parameters involved in weight loss processes (Reference 8). Measurements were made under both isothermal and linearly increasing temperature conditions, and machine methods for calculation of the results were devised (Reference 8 and 9). Some of the results of this work have been reported previously (Reference 10), but since a better method has been devised for the calculations they are repeated here.

This report is concerned with the weight loss, molecular weight changes, production of volatiles, etc., of poly(hexamethylene adipamide) and poly(hexamethylene sebacamide) designated as nylon 6.6 and nylon 6.10, respectively. The numbers represent, in order, the number of carbon atoms in the diamine and the diacid constituents of the polymer chain.

SECTION II PREVIOUS INVESTIGATIONS

In several of the early investigations into the degradation of polyamides (Reference 11), copolymers, e.g., of nylon 6.6 and nylon 6.10, were used. The use of such materials complicates the interpretation of the results of degradation particularly if the possibility of the formation of new structures by transamidation exists.

Achhammer, et al. (Reference 12) described a considerable amount of information on the degradation of a series of copolyamides. Changes in mechanical, electrical, and other properties were measured as a function of the time of exposure to artificial weather, etc. The gaseous products detected during exposure to high temperatures were water, carbon dioxide, carbon monoxide, hydrocarbons and ethanol (solvent). The source of water was suggested to be a cross-linking reaction and it was proposed that carbon monoxide and hydrocarbons were evolved during a series of scission reactions:

$$-NH-CO-(CH_2)_4-CO-NH \longrightarrow C-(CH_2)_4-C \longrightarrow 2CO + hydrocarbons$$

A significant quantity of cyclopentanone was detected in the pyrolysis gases, a possible mechanism for its formation being

$$-NH-CO-(CH_2)_4-CO-NH-\longrightarrow \cdot \overset{O}{C}-(CH_2)_4-\overset{O}{C}\cdot \longrightarrow \overset{O}{C}$$
and
$$-NH-CO-(CH_2)_4-COOH\longrightarrow \overset{O}{C}+CO_2$$

Sufficient CO and ${\rm CO}_2$ were present in the gaseous products to account for the formation of cyclopentanone by both of these mechanisms. When the polymer contained sebacic acid units, no CO was evolved and no cyclic hydrocarbons were detected. The 10 carbon cyclic ketone would not be stable under degradation conditions.

The quantity of ${\rm CO}_2$ produced was 10 times in excess of that expected on the basis of end groups alone, showing its source to be either absorbed ${\rm CO}_2$ or that produced by some unknown mechanism from parts of the polymer chain other than end groups.

Goodman (Reference 13) investigated the decomposition products of a series of N, N'-di-n-butylamides as model compounds for nylon polymers. Dibutyladip-amide decomposed almost completely giving n-butylamine, minor amounts of CO and hydrocarbons and substantial quantities of CO₂. No cyclic ketone was detected in conflict with expectations based on Achhammer's work (Reference 12). Goodman claimed to have established a unique reaction of N-substituted adipamides in which CO₂ is produced on heating without the formation of equivalent quantities of hydrocarbons. The composition of the residue was examined and shown to contain nitrogen. It was postulated that the nitrogen was present in a 5-membered heterocyclic ring. It was later shown (Reference 14) that residues from the degradation of both dibutyladipamide and nylon 6.6 contained 5- and 6-membered rings as well as a pyrrole derivative.

Kammerbeek, Kroes, and Grolle (Reference 15) published a considerable body of information on the gellation and the thermal degradation of nylon 6 and nylon 6.6 and postulated a series of possible reactions to account for the cross-linking and for the composition of the gaseous products. Some information on the changes in molecular weight during heat treatment were also presented. To back up the postulated mechanisms, authentic specimens of the residue structures were prepared and examined.

For nylon 6, the reactions suggested by these authors are given below.

(A) Primary Reaction

Scission of the bond in the $oldsymbol{eta}$ position to the carbonyl group.

$$-CO-NH-(CH2)4-CH2-CO-NH-CH2-(CH2)4-CO-NH····I$$

$$I \longrightarrow -CO-NH-CH2-(CH2)4-CO-NH2····II$$

$$+CH2 = CH-CH2-CH2-CH2-CO-NH-$$

The amide (II) may then split off water to leave the nitrile.

Also scission of the -NH-CH2- bond may occur:

I ---- - CO - NH -
$$(CH_2)_5$$
 - CO - $\overline{N}I$ + CH_3 - $(CH_2)_4$ - CO - NH -
Rearranges

- CO - NH - $(CH_2)_5$ - N = C = O

(B) Secondary Reactions

Chain end hydrolysis

Condensation

$$R-COOH + HOOC - R' \longrightarrow R - CO - R' + H_2O + CO_2$$

 $R-NH_2 + R'-NH_2 \longrightarrow R-NH-R' + NH_3$

Several other processes which modify the chain were also proposed.

Straus and Wall (Reference 11) examined the effects of the deliberate addition of impurities, e.g., phosphoric acid, to nylon 6. A threefold increase in the maximum rate of weight loss was observed with this acid, probably because of the greater importance of ionic processes. The same authors (Reference 16) also showed that purification of the polymer decreased the rates of degradation and of production of CO2 and increased the activation energy of the overall weight loss. Their sample of nylon 6 was extensively purified by extraction with solvents and dried well since it was claimed that the presence of moisture could cause hydrolytic decomposition, with the production of CO₂, which overshadows the normal free radical thermal decomposition. However, it was shown that the quantity of CO₂ evolved could never be reduced to that expected on the basis of end groups alone and it was suggested that even after being dried carefully the polymer still contained absorbed water capable of causing hydrolysis of the polymer. Cyclopentanone was detected in the gaseous products the quantity of which decreased after the polymer was treated with acid. Thus the production of the cyclic ketone is essentially a free radical process but not occurring at adipic end units.

The authors determined an activation energy of 43 kcal/mole for the weight loss of nylon 6.6 from the maximum rates of weight loss but suggested the true value for the pure free radical reaction with no hydrolysis component should be between 50 and 60 kcal/mole.

An early attempt at the determination of kinetic parameters for the pyrolysis of polyamides was made by Straus and Wall (Reference 11) using nylon 6 and mixtures of copolyamides. A wide range of activation energies (14 to 42 kcal/mole) was determined from isothermal weight losses but their highest value was considered to be more representative of the pure, free radical decomposition.

SECTION III

EXPERIMENTAL

1. PREPARATION OF POLYMERS

Nylon 6.6 and nylon 6.10 were received from Chemstrand Research Center in the form of fiber and chopped ribbon. Both materials were prepared from high purity intermediates without the addition of stabilizers or other additives (Reference 17). Both the polymers were reduced to a finely divided form by precipitation with water from formic acid solution following the procedure described in Reference 10. Traces of unreacted material and low molecular weight polymer were removed by extraction with hot water for a minimum of 8 hours.

2. INTRINSIC VISCOSITY MEASUREMENTS

All measurements were made using standard or Semi-Micro Cannon-Ubbelohde dilution viscometers. Formic acid solutions required a number 75 viscometer and a number 150 or 200 was used for m-cresol solutions.

3. END GROUP TITRATIONS

End group titrations were carried out on m-cresol solutions of the polymer using 0.01N alcoholic HCl and NaOH solutions. The polymer solution was contained in a small cell through which nitrogen could be passed to prevent oxidation of the solvent. The end point was determined by the inflection in the curve of conductivity versus volume of titrant added. Conductivity was measured using platinum electrodes and the Thomas SERFASS conductivity bridge Model RCM 15B1.

4. VAPOR PRESSURE OSMOMETRY (VPO)

Measurements of number average molecular weight were made using the Mechrolab Vapor Pressure Osmometer Model 302. The auxilliary high temperature chamber was used at 130°C for a limited number of measurements but normally 37°C and 65°C were used when fluoroalcohols were employed as

solvents. Early in this work, difficulty was encountered in obtaining reproducible results and the cause was traced to variations of sample drop size, a previously unreported phenomenon. References 18 and 19 describe in detail the techniques used for correction of time and drop size effects and Reference 20 describes the modification made to the instrument to permit recorder plotting of the VPO output.

5. WEIGHT LOSS MEASUREMENTS

Ainsworth Thermobalances, Models AV and RV, were used throughout this work, the former giving a full scale recorder pen deflection equivalent to a 100 mg weight change, the latter to a 10 mg change. A complete description of the apparatus and experimental technique is given in Reference 10.

SECTION IV

CHARACTERIZATION AND MOLECULAR WEIGHT DETERMINATION OF POLYAMIDES

1. SOLUBILITY

The literature is replete with descriptions of the determination of the molecular weight of polyamides, in most cases nylon 6.6. One of the major difficulties is the choice of a solvent suitable for the particular technique being employed.

Formic acid solution (85-97%) readily dissolves aliphatic polyamides but protonation of the NH group causes complications in the determination of viscosity (References 21 and 22). Meta cresol is a useful solvent but the solutions readily become colored by oxidation of the m-cresol. Purification of nylon by precipitation from m-cresol is not recommended since the color contaminates the precipitate.

Stronger acids, trifluoroacetic, sulfuric and methane-sulfonic, readily dissolve aromatic polyamides but the possibility exists for hydrolysis of aliphatic materials.

It has been reported (Reference 23) that a saturated solution of calcium chloride in methanol will dissolve some polyamides but nylon 6.10 is not included.

Recently several fluorinated alcohols have become readily available; they are especially useful in the determination of molecular weight by VPO (Reference 24) because of their compatibility with the materials of construction of the VPO and they have been used in the measurement of other solution properties (References 25 and 26). Nylon 6.10 dissolves readily in 2, 2, 2-trifluoroethanol on warming but at room temperature some solutions tend to be unstable (see Section IV.4).

No single solvent could be employed in this work since several different measuring techniques were used each having certain unique solvent requirements.

2. VISCOMETRY

The intrinsic viscosities (I.V.) of nylon 6.10 in m-cresol and in 85% formic acid have been measured using various samples of polymer. Identical I.V. values were obtained using several batches of purified polymer but material which had not received the water extraction process had a distinctly lower I.V. than extracted polymer. A composite of the viscosities of the extracted material is shown in Figure 1.

In formic acid, at concentrations between 0.2 and 0.8 g/dl, the data may be represented by a straight line which gives an intrinsic viscosity of 0.74 dl/g. It is well known that polyamides exhibit polyelectrolyte effect manifested by anomalously high values of $\eta_{\rm sp}/c$ at low concentrations (References 21 and 22) but this was not observed in the concentration range used here.

In m-cresol anomalously low values of $\eta_{\rm sp}/c$ were observed at concentrations below 0.1 g/dl. The intrinsic viscosity determined from the linear part of the curve is 1.15 dl/g. Viscosity data for nylon 6.6 (Reference 27) shows

 $[\eta]$ formic acid/ $[\eta]$ m-cresol = 0.9, but we find the ratio to be 0.64 for nylon 6.10.

In order to convert I.V. into viscosity average molecular weight, the constants K and α on the Mark Houwink equation $\left[\boldsymbol{\eta} \right] = \mathrm{KM}^{\alpha}$ are necessary. These apparently have not been determined for nylon 6.10 but data is available for nylon 6.6 (References 28 and 29). For nylon 6.6 in 90% formic acid (Reference 29), K = 11 x 10⁻⁴ and α = 0.72 in the molecular weight range between 5000 and 25,000. The value of K for nylon 6.10 should be larger because of the greater molecular size. Using these constants for the nylon 6.10 data gives an estimate for $\overline{\mathrm{M}}_{\mathrm{V}}$ of 8500.

For a mixed polyamide in m-cresol (Reference 30), K = 0.29 x 10^{-6} and α = 1.3. If $\left[\eta \right]$ = 1.15 then \overline{M}_{V} = 1.2 x 10^{5} .

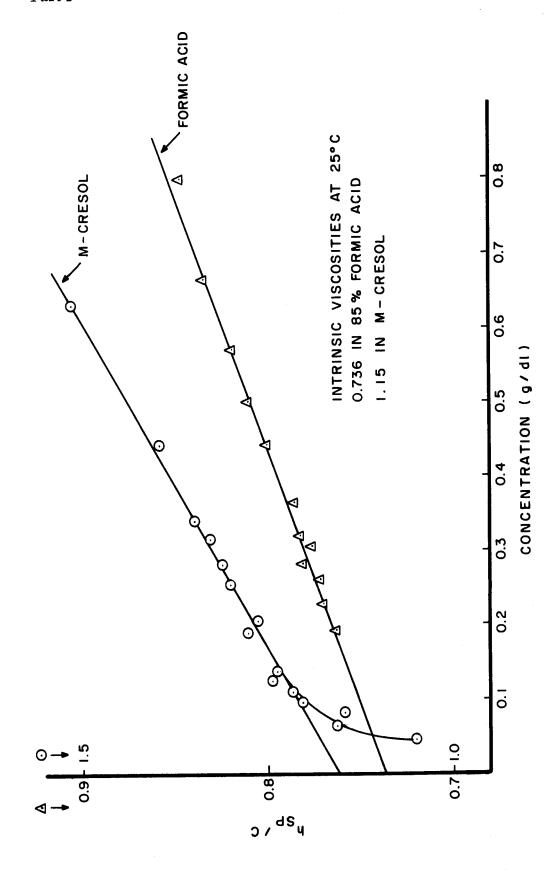


Figure 1. Intrinsic Viscosity Plots for Nylon 6, 10

Ohama and Ozawa (Reference 24) have quoted figures for several nylons: Nylon 6, $\overline{M}_V = 10,400 \left[\eta \right]^{1.61}$; Nylon 7, $\overline{M}_V = 17,000 \left[\eta \right]^{1.4}$ and Nylon 9, $\overline{M}_V = 18,600 \left[\eta \right]^{1.4}$ in m-cresol at 25°C. It has been shown that K and α are the same for nylon 6.6 and nylon 6 (Reference 31), so the constants seem to depend mainly on the number of carbon atoms in the chain. If this is so, the constants for nylon 6.10 might be similar to those for nylon 8. Using the relationship $M = 18,000 \left[\eta \right]^{1.4}$ interpolated from the nylon 6, 7, and 9 data, $\overline{M}_V = 21,900$ for the nylon 6.10 used here.

The nylon 6.6 used here has an intrinsic viscosity of 0.63 dl/g in m-cresol at 25°C. The molecular weight \overline{M}_V varies depending on which literature values of K and α are used.

Thus, it can be seen that no reliable estimate of the molecular weights of the starting polymers could be arrived at using published K and α data. Measurements of I.V. should still be a reliable indication of changes in molecular weight if it can be assumed that the reaction causing the molecular weight change does not alter the residue structure (e.g., degree of cross-linking) significantly. This implies that the constants K and α apply to both the starting material and the degraded polymer.

To test the effect of the purification procedure on the thermal behavior of nylon 6.10, several series of degradations were carried out at 289°C for varying times and intrinsic viscosities were measured. The results, plotted in Figure 2 show that considerable variations in I.V. of the degraded material are caused by batch changes. All batches were derived from the same original material.

Batches B and C had both been freeze dried and extracted with water in a Soxhlet but had slightly differing I.V.'s (1.15 and 1.17, respectively). Batch E was similarly prepared but was not extracted to remove low molecular weight materials. The I.V. of this batch was 0.92 which reflects the presence of low molecular weight components. The amount of material extracted during the Soxhlet treatment was only 1.3%. The thermal behavior of Batch E is in keeping with this. There is a rapid rise in I.V., probably due to continuation of polymerization but after 200 minutes exposure at 289°C, the I.V. falls as the importance of scission increases.

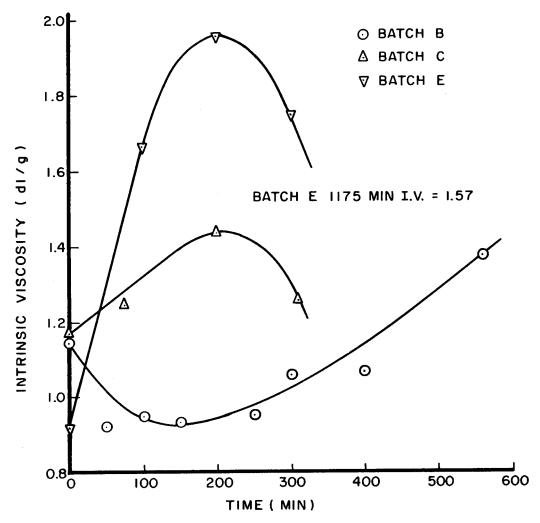


Figure 2. Intrinsic Viscosity Changes in Nylon 6.10 at 289 ± 1°C

Figure 3 shows the effects of exposure at a lower temperature, 280°C. In this case, the I.V. increases with time for all the batches. In 100 minutes, the I.V. of batch E increases to 1.41 as opposed to 1.67 at 289°C. It would seem that at the lower temperature and up to at least 300 minutes, further condensation is the predominant process, scission not occurring to any appreciable extent. The data shown in Figure 4 would seem to conflict with this however. Here, the variation of I.V. with time is shown for three temperatures for batch X, and in all cases the I.V.'s are significantly above their original values. A predrying cycle of 30 minutes at 220°C under high vacuum was carried out for all the experiments shown in Figure 4 in an attempt to remove the last traces of water from the polymer. No change in I.V. was noted for polymer subjected to this treatment alone.

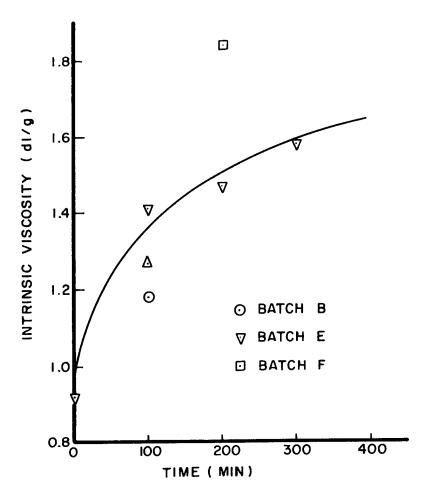


Figure 3. Viscosity Changes of Nylon 6.10 at 280°C

These data show, if nothing else, that it is essential to use a single standardized batch of polymer for all experiments in order to be able to compare results of viscosity studies. Further, the possible occurrence of further condensation, distillation of low molecular weight volatiles, branching and crosslinking will complicate interpretation of results.

3. END GROUP TITRATIONS ON NYLON 6.10

To determine unambiguously the molecular weight of a material a method which requires no calibration and which measures a colligative property is needed. End group titrations offer this possibility by counting, in the case of polyamides, the numbers of active-NH $_2$ and -COOH end groups. This method obviously requires that there be no end groups other than -COOH or -NH $_2$.

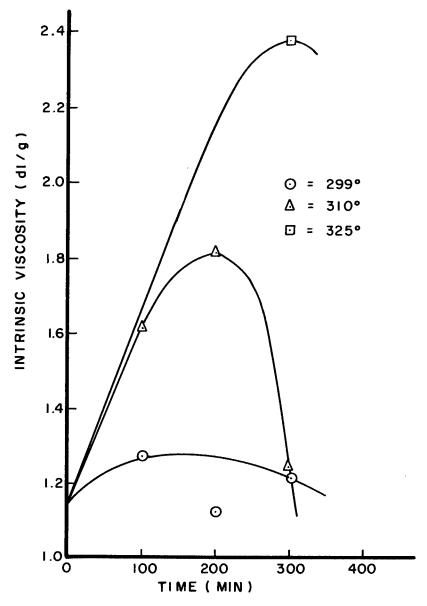


Figure 4. Viscosity Changes of Nylon 6.10

Since it was believed that the nylon 6.10 used here was prepared without the addition of end capping reagents (e.g., acetic acid) titration of m-cresol solutions of the polymer with dilute alcoholic HCl and NaOH solutions was attempted. The end point was determined by the break in the curve of conductivity against volume of titrant added. The results obtained were

$$\overline{M}_{n}$$
 (NH₂) = 18.6 and 19.2 x 10³ Average = 18.9 x 10³ \overline{M}_{n} (COOH) = 11.8 and 12.2 x 10³ Average = 12.0 x 10³

Differences in the numbers of each type of end group might be expected in low molecular weight polymers.

4. VAPOR PRESSURE OSMOMETRY

Several types of fluoroalcohols have been used for VPO measurements on polyamides (Reference 24). Both trifluoroethanol (TFE) and heptafluorobutanol were tried here and both were found to be suitable, the former at 37° and the latter at 65°C.

Meta-cresol was tried using the high temperature VPO chamber but the solvent attacked the insulation material around the chamber. It has been reported (Reference 32) that formic acid may be used if the chamber is gold plated.

Using TFE, solutions of nylon 6.10 up to a concentration of about 20 g/1 may be prepared and used. Solutions above this concentration may also be prepared but separation tends to occur after several hours producing gel-like material which readily clears on being heated.

Figure 5 shows a plot of the reduced resistance against the concentration for solutions of nylon 6.10 in TFE at 37°C. An upswing in the curve is apparent at low concentrations but the linear part of the curve, when extrapolated to zero concentration yields a number average molecular weight of 7100.

The molecular weight of the nylon 6.6 used (Figure 6) is 4900.

The number average molecular weights of the degraded polymers referred to in Figure 4 were measured in heptafluorobutanol at 65°C. The results are summarized in Table I.

Inspection of this data allows no apparent correlation between the I.V. and \overline{M}_n of the degraded materials; increases in I.V. are not always accompanied by increases in \overline{M}_n . If branching is taking place during degradation comparison of I.V.'s and \overline{M}_n would not be valid since a single relationship between the two (the Mark Houwink equation) would not apply. A clue to this is given by the fact

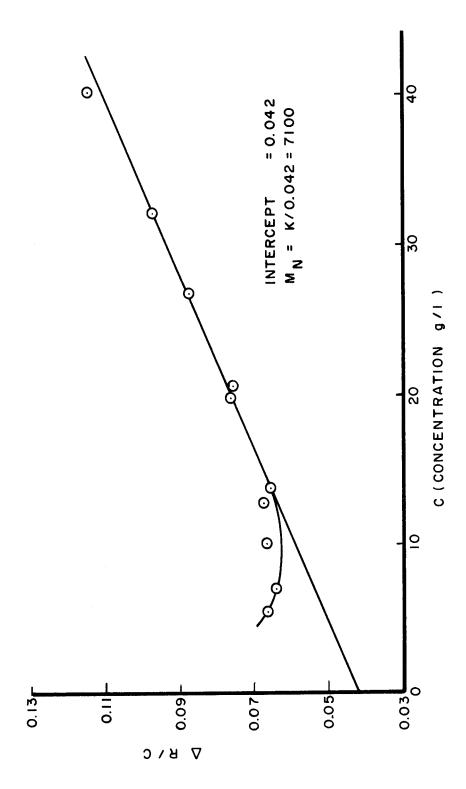


Figure 5. VPO Data for Nylon 6, 10 in Trifluoroethanol at 37°C

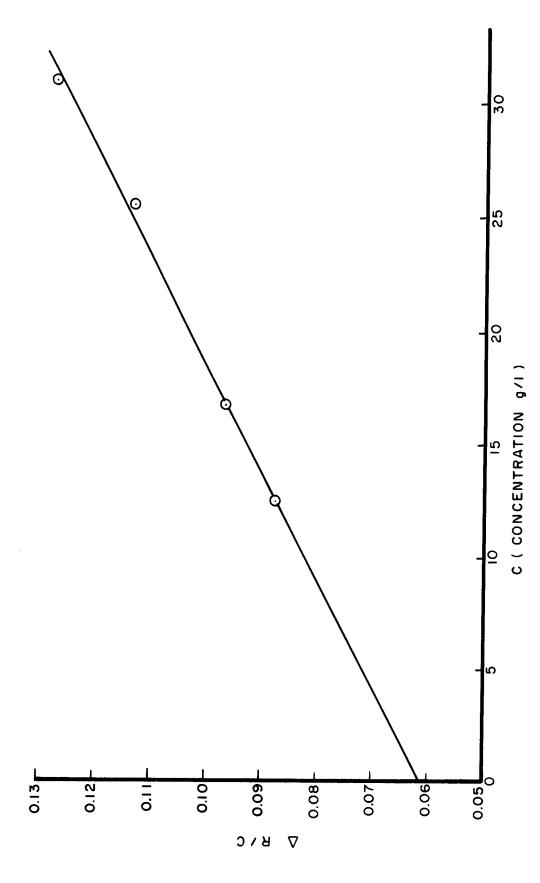


Figure 6. VPO Data for Nylon 6.6 in Trifluoroethanol at 37°C

TABLE I
INTRINSIC VISCOSITIES AND NUMBER AVERAGE
MOLECULAR WEIGHTS OF NYLON 6.10

Exposure Time (min)	Exposure Temperature (°C)	Intrinsic Viscosity (dl/g)	M _n by VPO (Heptafluorobutanol at 65°C)
Original Material		1.15	7100*
100	299	1.28	8900
200	299	1, 13	5600
300	299	1,22	10,700
100	310	1,62	5400
200	310	1.82	15,700
300	310	1.25	
300	325	2.38	9300

^{*} Determined in both heptafluorobutanol at 65 $^{\circ}$ and trifluoroethanol at 37 $^{\circ}\mathrm{C}$

that a plot of \log I.V. versus \log M $_n$ using the data given in Table I is extremely scattered so it is not possible to derive a Mark-Houwink equation to fit the data.

5. MOLECULAR WEIGHT DISTRIBUTION BY GEL PERMEATION CHROMATOGRAPHY

Measurements of molecular weight distribution by Gel Permeation Chromatography (GPC) were made at Battelle Memorial Institute using 2,2,2-trifluoroethanol as solvent (Reference 33). Initially three columns designated 10^5 , 10^4 , and 10^4 were used for the GPC analysis. Figure 7 shows the distribution curves obtained for nylon 6.10 both undegraded and after exposure at various temperatures for differing times. The curves for the undegraded and for several of the degraded polymers exhibit single maxima but the sample exposed at 317° C for 500 minutes shows a pronounced double peak. The sample exposed at 327° C for 100 minutes shows slight evidence for a binodal distribution.

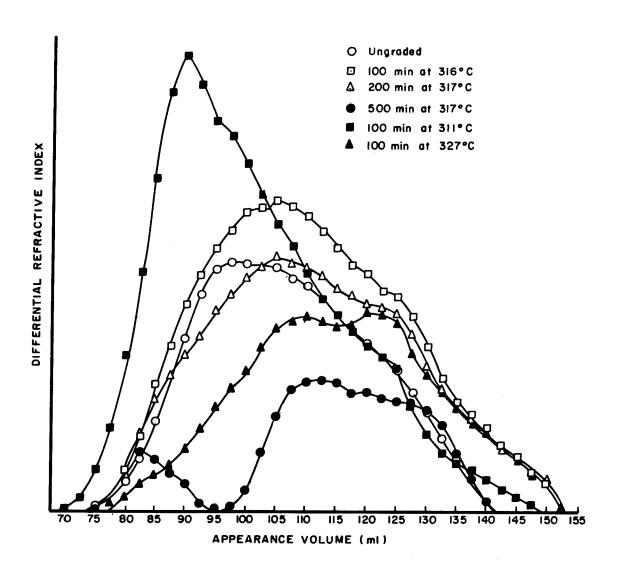


Figure 7. GPC Curves for Nylon 6.10

When nylon 6.10 was exposed to the mildest degradation (100 minutes at 311°C) there is a pronounced increase in the position and the height of the maximum. This may be attributed to either both sublimation of low molecular weight material, and further condensation of reactive end groups.

Similar data for nylon 6.6 is given in Figures 8 and 9. In Figure 8 the curve for the undegraded polymer is somewhat irregular and the various thermal exposures in all cases increase the molecular weight of the peak maximum.

The second series of distributions of nylon 6.6 (Figure 9) was conducted after one of the 10^4 GPC columns had been replaced by a 10^6 column. The undegraded material was then clearly demonstrated to be of binodal distribution. Exposure at 259° C for 100 minutes (polymer did not melt) caused a dramatic change in distribution. A single maximum was observed at $\overline{\mathrm{M}}_{\mathrm{n}} \cong 50,000$, the curve having a slight shoulder at a lower molecular weight. The distributions for samples held at 280° and 285° C for 100 minutes also had single maxima but at $\overline{\mathrm{M}}_{\mathrm{n}} \cong 19,000$.

Number average molecular weights of several of the nylon 6.6 polymers were measured by VPO in TFE solvent but there were inconsistencies between the values obtained and the positions of the maxima in the GPC traces.

The GPC data show that large changes in molecular weight distribution occur during thermal exposure of both nylon 6.6 and nylon 6.10 even under mild conditions. Normally an increase in the position of the maximum is evident but increased thermal exposure or higher temperatures cause gradual decreases in the molecular weight of the residues. The GPC data give a clue to the difficulties encountered in measuring number average molecular weights of degraded polymers especially using different batches of original polymer. Slight differences from batch to batch in the content of low molecular weight components will cause large differences in the molecular weight after thermal exposure.

Better removal of the low molecular weight material and end capping of residual reactive end groups from the original polymer is indicated for further studies of molecular weight changes.

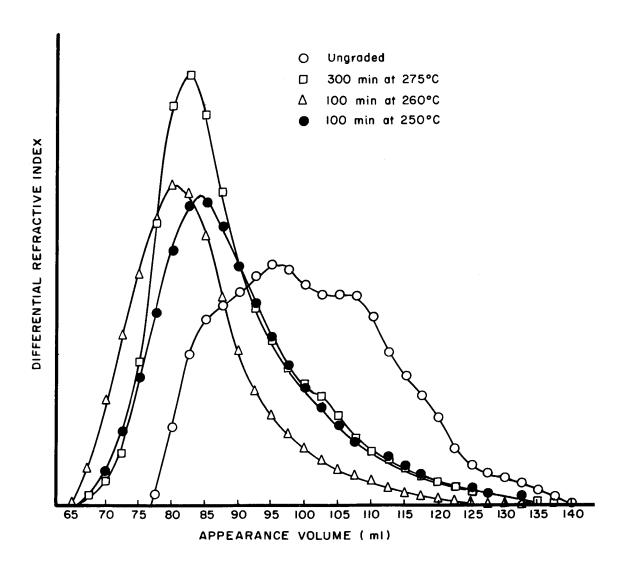


Figure 8. GPC Curves for Nylon 6.6

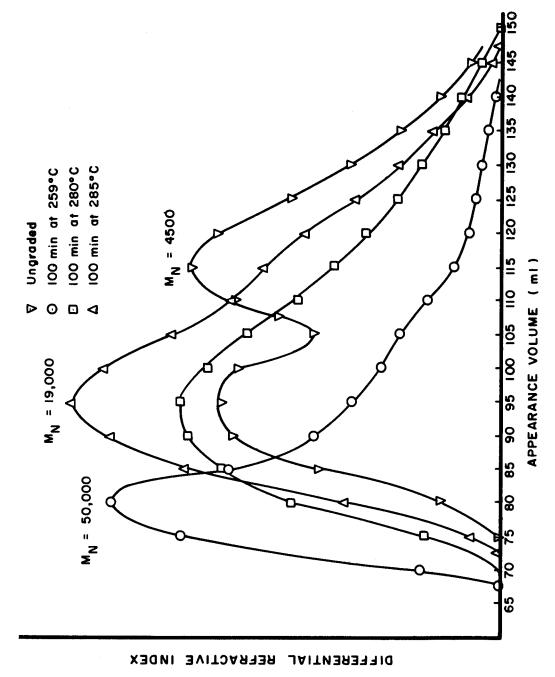


Figure 9. GPC Curves for Nylon 6.6

SECTION V

WEIGHT LOSS STUDIES

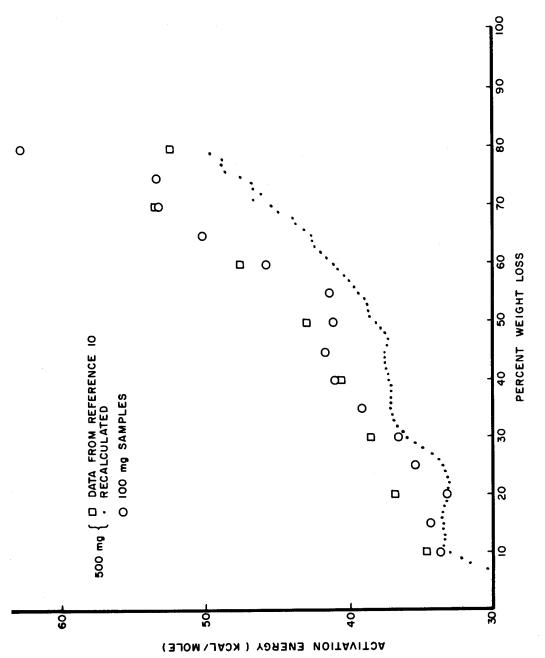
A previous report (Reference 10) describes determinations of the activation energy (E_a) for the thermal, vacuum weight loss of 500 mg samples of nylon 6.6 and nylon 6.10 under isothermal conditions. In our weight loss studies much importance has recently been placed on the determination of thermodynamic parameters from thermogravimetric experiments conducted under linearly increasing temperature profiles. It was deemed worthwhile, therefore, to compare the results obtained by the two methods. Since programmed temperature thermogravimetric experiments are more easily conducted (no temperature control problems such as those encountered in isothermal thermogravimetry), and since useful data may be obtained from the onset of degradation, it was hoped that the comparison would prove the worth of programmed thermogravimetry for the elucidation of mechanism and the determination of thermodynamic parameters involved in weight loss processes.

In other reports (References 8 and 9), we have described computer methods for the calculation of Arrhenius parameters from both isothermal and programmed temperature thermogravimetry data. The computational methods described were used for the results reported here.

To investigate the importance of diffusion controlled processes further isothermal experiments were carried out using various sample sizes.

1. NYLON 6.6

Some of the isothermal data presented in Reference 10 obtained using 500 mg samples has been recalculated using the computer method (Reference 9). The rate of weight loss data for this and other sample weights is collected in Appendix I. Figure 10 shows the variation of activation energy with percent weight loss using the recalculated 500 mg results. The original results quoted in Reference 10 are also shown for comparison. The differences may be attributed to the fact that only the higher temperature data was recalculated. Figure 10



Variation of Activation Energy With Conversion for Different Sample Sizes of Nylon 6.6 (Isothermal Experiments) Figure 10.

also shows results obtained using 100 mg samples. The differences between the E_a values for 100 mg and 500 mg samples are small indicating that diffusion controlled weight losses either are unimportant or do not have significant effect on the activation energy. There is a small dependence of rate of weight loss (% per minute) on sample size (Figure 11). The rates for the small samples are slightly higher so some diffusion is occurring.

Programmed temperature rates of weight loss of 100 mg samples of nylon 6.6 were measured using heating rates ranging from 75° /hr to 450° C/hr and E_{a} was again determined as a function of the percent weight loss. Some of the rate data is given in Figure 12 and in Appendix II. The activation energy results obtained are plotted in Figure 13 where the isothermal 100 mg data is replotted for comparison. There is excellent agreement between the two sets of data for most of the degradation range. The maximum difference is about 8 kcal/mole at 30% weight loss. It would be difficult to specify the cause of the differences observed but it is probable that the programmed temperature data is more representative of the "true" activation energy for the weight loss process since there are no temperature stabilization difficulties.

In a pure single step chemical reaction the activation energy for a chemical change should remain constant throughout the reaction. Any change in E_a during the reaction is indicative of a change in the mechanism of that reaction. The significant changes in E_a with extent of weight loss observed here must therefore give an insight into the mechanism of the weight loss process. Up to 25% conversion E_a rises slowly. It then remains approximately constant until about 60% weight loss, and then increases continuously until the end of the reaction.

The early rise is probably due to early weight loss from evaporation of water either absorbed in the polymer or produced during condensation of the reactive end groups on the polymer chains. As condensation continues and the temperature rises, the importance of a higher activation energy process, namely, random chain scission, increases with consequent increase in E_a . At about 25% weight loss, condensation has been completed and the weight loss is due solely to loss of low molecular weight units produced during scission. The activation energy then remains constant until the rate of a third reaction becomes

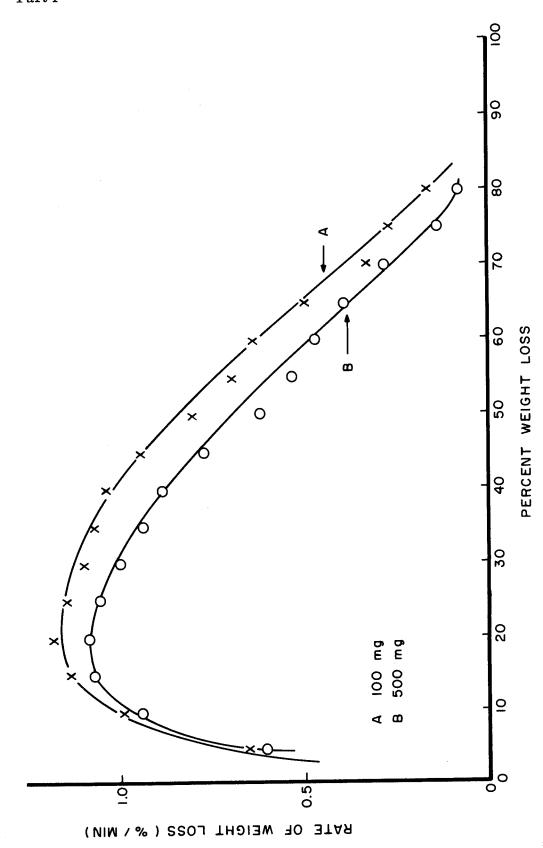


Figure 11. Variation of Rate of Weight Loss With Conversion for Two Sample Sizes of Nylon 6.6 at $380^{\circ}\mathrm{C}$

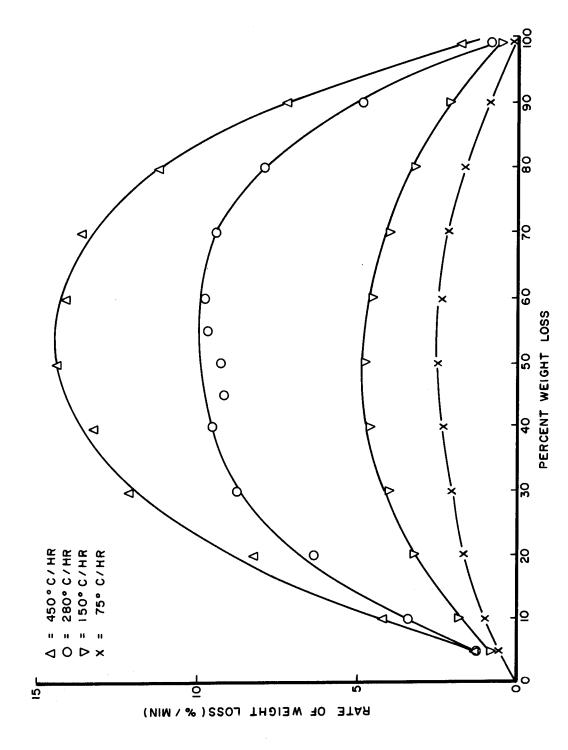


Figure 12. Variation of Rate of Weight Loss With Percent Weight Loss for Various Heating Rates for Nylon 6.6 (100 mg Samples)

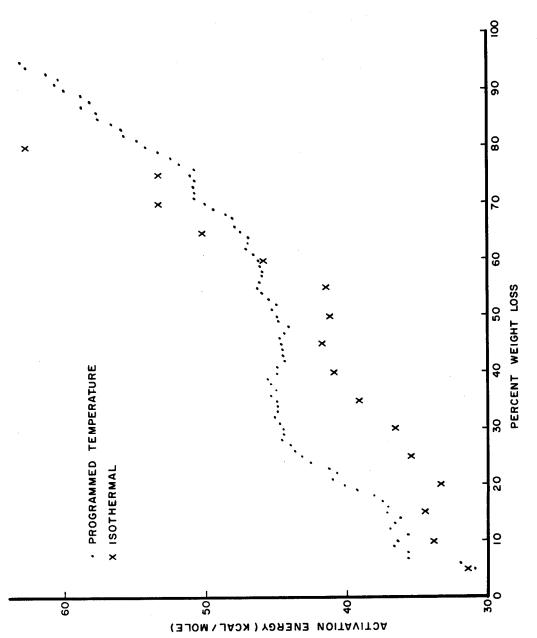


Figure 13. Activation Energy for Programmed Temperature Weight Loss of Nylon 6.6

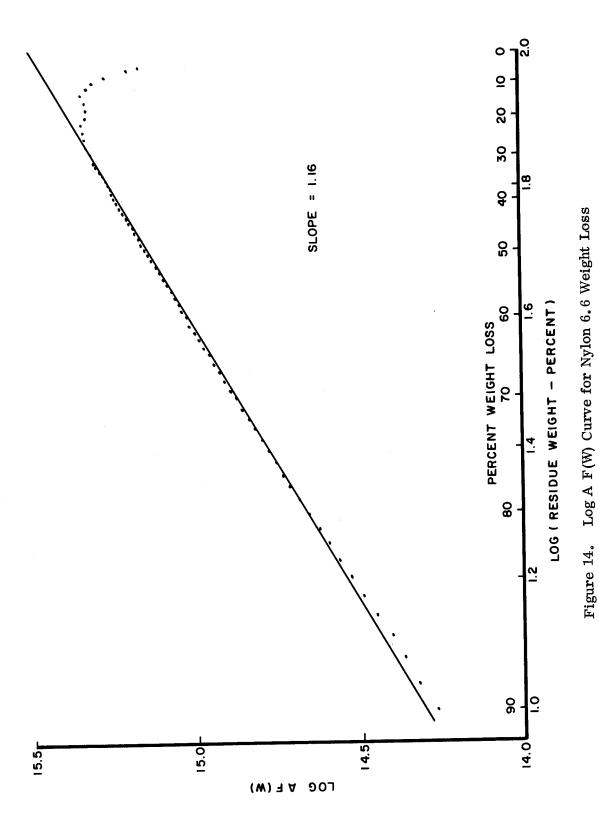
appreciable. During degradation, nylon 6.6 readily cross-links forming a dark insoluble material. The activation energy required to remove a small volatile unit from a cross-linked material will be greater than for the corresponding straight chain material. Thus \mathbf{E}_a would be expected to rise as the quantity of cross-linked polymer increases. This is shown up by the increase in \mathbf{E}_a from 46 to 67 kcal/mole for the last 40% of the weight loss reaction.

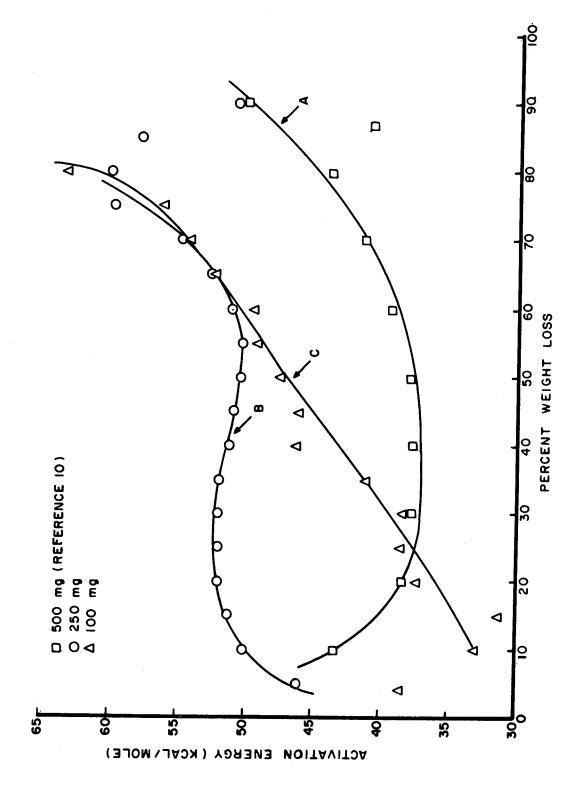
Besides a change in E_a, there exists the possibility for a change in the apparent order of reaction for the weight loss. In Reference 8, it has been stressed that apparent order of reaction may not be the same as "order of reaction" in its classical definition but the term will still be used here.

The computer technique used here allows the determination of order of reaction from the slope of a plot of log A F(W) against log (percent weight remaining). Such a plot for the programmed temperature TG data for nylon 6.6 is shown in Figure 14. A good straight line having a slope of 1.16 may be drawn through the data representing weight loss from 25% to 80%. Thus, there is no significant change in the weight functionality of the rate of weight loss. The slight drop in the curve at low conversions tends to indicate that the process obeys random rather than "order" type kinetics. It has already been shown that the weight loss of this polymer obeys random kinetics since a true maximum can be observed in the rate of weight loss against weight loss curve during low temperature isothermal weight loss. The maximum isothermal rate of weight loss occurs in the range 20 to 30% weight loss compared with 25% (depending on the chain length of the evaporating molecule) predicted for random kinetics (Reference 34).

2. NYLON 6.10

Figure 15 shows the variation of activation energy with conversion for the isothermal weight loss of nylon 6.10. Line A represents the data originally given in Reference 10 using 500 mg samples. Lines B and C show data obtained with 250 mg and 100 mg samples, respectively. Here there are rather large differences in the $\rm E_a$ values at any given conversion and there does not seem to be a smooth trend in the value of $\rm E_a$ with change in sample size. Activation





Variation of Activation Energy With Conversion for Different Sample Weights of Nylon 6, 10 (Isothermal Data) Figure 15.

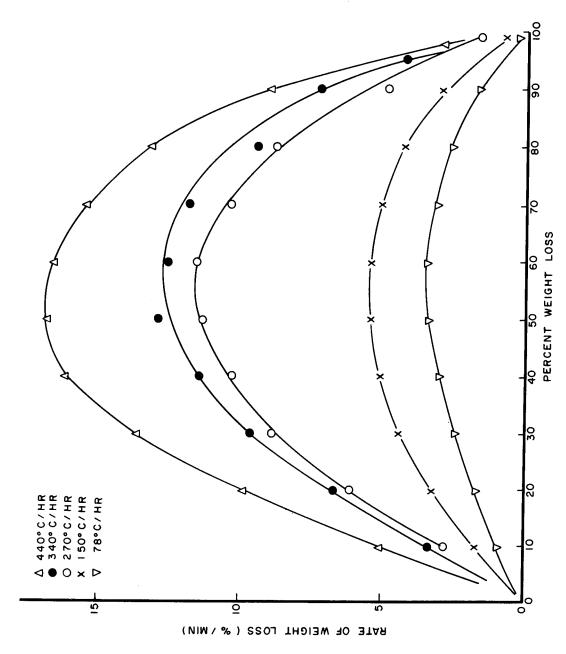
energies for the smaller samples agree reasonably well above 50% conversion. Any discrepancy in the low conversion region (up to about 20%) may be due to the failure to achieve temperature equilibrium until this amount of weight loss had occurred. The large differences between the 500 mg data and the smaller data show that diffusion controlled weight loss processes are taking place. For all further experiments with nylon 6.10, 100 mg was chosen as the standard sample size. For convenience the same weight of nylon 6.6 was also used.

Figure 16 shows the programmed temperature rate of weight loss data for 100 mg samples of nylon 6.10. The original data is given in Appendix II. The corresponding activation energies are given in Figure 17. Comparison with the isothermal data also shown in Figure 17 shows there are large differences between activation energies determined by the two different methods. The reasons for these differences are not known but they may be associated with the diffusion effects noted previously.

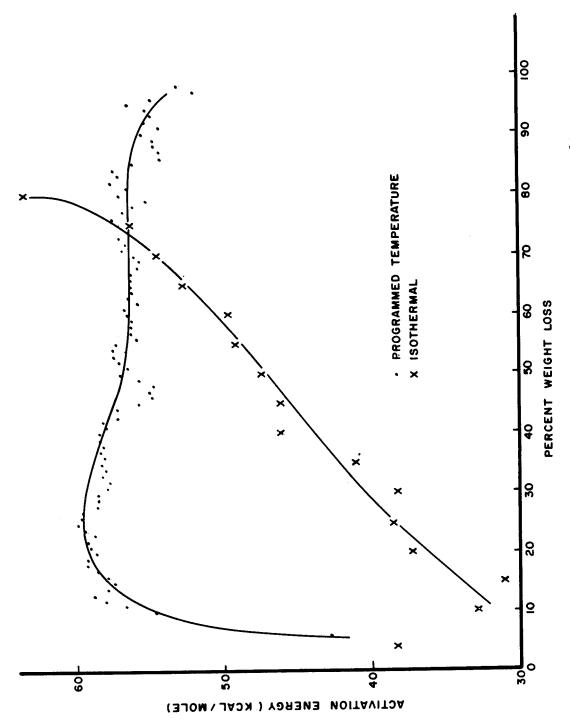
A further complication is that the programmed temperature data is gathered over a wider range of temperatures than is the isothermal data. This complication is inherent in the methods used and causes difficulties in interpretation of the results if the weight loss is not a simple process, e.g., if \mathbf{E}_a varies with conversion or with temperature.

Below 20% weight loss the programmed temperature E_a increases rapidly and it then remains fairly constant at about 57 kcal/mole until total weight loss has occurred. The isothermal E_a , however, increases continuously during weight loss. Significantly, nylon 6.10 cross-links less readily than does nylon 6.6 so any increase in E_a due to cross-linking might be delayed until high weight losses have taken place.

Figure 18 shows the log A F(W) curve for nylon 6.10. The data representing 20 to 80% weight loss is represented by a good straight line having a slope of 0.98. A slight drop in the curve at low conversions is apparent showing the reaction is probably a random weight loss process.



Variation of Rate of Weight Loss for Various Heating Rates for Nylon 6.10 (100 mg Samples) Figure 16.



Activation Energy for Programmed Temperature Weight Loss of Nylon 6. 10Figure 17.

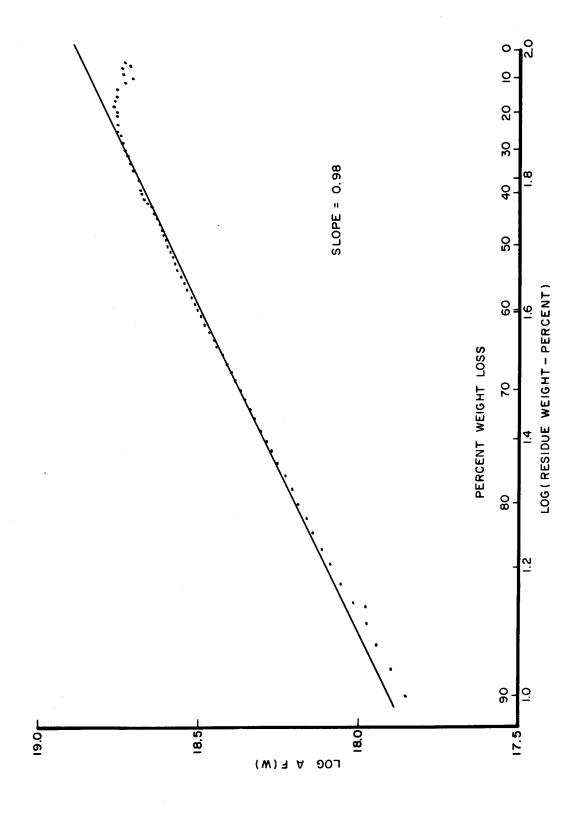


Figure 18. Log A F(W) Curve for Nylon 6.10 Weight Loss

SECTION VI

MASS SPECTROMETRIC THERMAL ANALYSIS

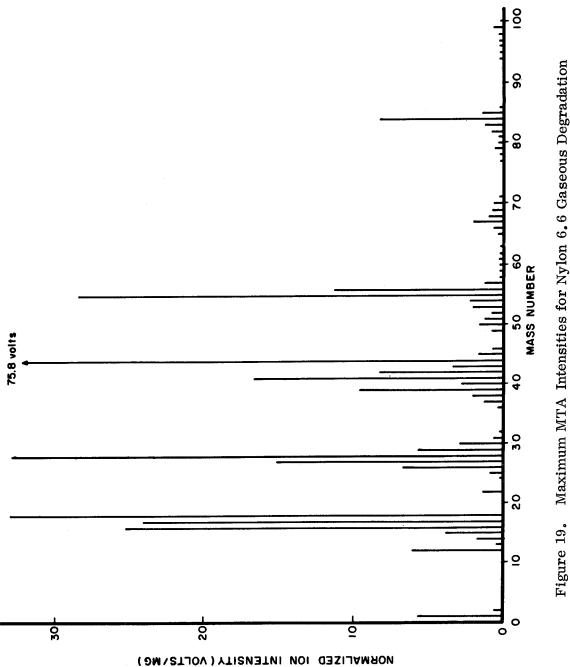
Small samples (usually about 1 mg) of both polymers were subjected to mass spectrometric thermal analysis (MTA) by the General Electric Company and a brief description of the results is given in Reference 35. A description of the experimental procedure is given in that reference. The method consists essentially of heating the sample from room temperature to 1000° C at a rate of 10° C per minute in a high vacuum. The effluent gases are pumped into the time-of-flight mass spectrometer and 200 preselected masses are scanned repetitively every 108 seconds. Computer data processing is used to obtain curves of ion intensity against temperature for each of the masses. It is hoped eventually, after suitable standard materials have been run, to be able to obtain complete quantitative analyses of the products of degradation.

1. NYLON 6.6

Examples of the original mass spectra are given in Reference 35. At about 425°C a peak is evident for many of the masses scanned and in most cases the peaks are well defined, dropping back rapidly to the base line. However, in some cases (e.g., mass 2, 13, 14, 24) a gradual increase in ion signal takes place above 600°C. At this temperature complete sample weight loss should have occurred so it is likely these are spurious signals caused by reevaporation of material which had condensed in the vacuum system, and can be ignored.

Figure 19 shows a bar graph of the peak intensities of all of the masses observed during MTA of Nylon 6.6. The compounds responsible for most of these peaks include NH₃, H₂O, CO, CO₂, cyclopentanone, and several hydrocarbons. It is difficult to obtain a quantitative analysis of all the compounds responsible for all of these peaks especially those present in small amounts.

Mass spectrometric data obtained from gases evolved from nylon 6.6 held isothermally were given in Reference 10. The same major components were present except for CO which was not trapped.



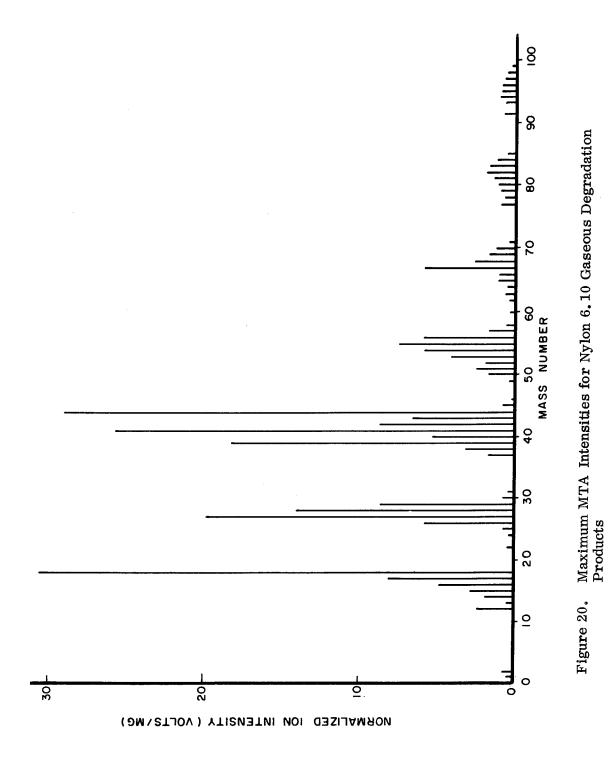
Maximum MTA Intensities for Nylon 6,6 Gaseous Degradation Products Figure 19.

2. NYLON 6.10

The bar graph for ion intensities of evolved gases is shown in Figure 20, and the major products were $\rm H_2O$, $\rm CO$, $\rm CO_2$, 1,5-hexadiene and other hydrocarbons. The temperature for the maximum intensity is $450^{\circ}\rm C$ for this polymer and there is no evidence for significant gaseous evolution at lower temperatures. In contrast with the nylon 6.6 gaseous products, no ammonia was produced from nylon 6.10.

An obvious feature of these results is the presence of large quantities of water and CO_2 and CO in the gaseous products from both polymers. It is well known that water is strongly held by polyamides (probably by hydrogen bonding); some of the water detected probably was due to this effect, but further condensation would also give rise to water evolution. The source of CO_2 is probably decarboxylation of acid end groups.

Hydrocarbon fragments are derived from the aliphatic CH_2 chains and often occur as unsaturated compounds. The presence of cyclic ketones in the MTA data has not been confirmed but quantitative analysis of the data has yet to be attempted.



SECTION VII

CONCLUSIONS

The molecular weight data presented in this report exemplify the difficulties in obtaining reproducible data from polyamides. The erratic behavior of polyamides has previously been attributed to the inability to obtain completely dry polymer samples (Reference 36). However, the present work indicates that the presence of low molecular weight material and polymerizable end groups in the polymer also contribute to the difficulties. The first of these has a profound effect on colligative solution properties of the polymers and the second complicates the interpretation of the molecular weight changes which take place during thermal exposure of these polymers, since polymerization takes place before scission or cross-linking. Attempts at removal of low molecular weight residues by extracting the polymer with solvents were evidently not successful. For further studies it would be desirable to employ narrow molecular weight range fractionated polyamides whose reactive end groups had been end capped.

These factors have, however, far less effect on the gathering of weight loss data. Obviously, polymers containing large amounts of low molecular weight fragments would not be desirable; small amounts would show up as slight early "bleeding" during weight loss experiments.

The removal of polymerizable end groups might also clarify some of the interpretation of mass spectral data, and could give further insight into the source or sources of water which is a major product. There are several possible sources for its production (desorption, further condensation, etc.) so removal of one of these would be useful.

The GPC data quoted demonstrates rather dramatically the large changes in molecular weight distribution of polymers which had been subjected even to mild thermal exposure.

The weight loss data obtained allows determinations of activation energy as a function of the amount of weight loss. This relationship combined with the A F(W) data permits mechanistic interpretation of the processes responsible for the overall weight loss.

Figure 13 which shows the activation energy data for nylon 6.6 weight loss indicates as explained previously, that E_a increases considerably during the weight loss but a plateau of 45 kcal/mole is evident in the range of weight loss from 30 to 60%. The early rise in E_a probably reflects further condensation of reactive end groups. The plateau region reflects the chain scission process which is apparent after the completion of further condensation. Finally the increase in E_a after 60% weight loss is caused by the various cross-linking reactions. These three processes may be summarized:

Further Condensation

$$R \cdots NH_2 + HOOC \cdots R' \longrightarrow R \cdots NHCO \cdots R' + H_2O$$
 (1)

$$R \cdots NH_2 + H_2N \cdots R' \longrightarrow R \cdots NH \cdots R' + NH_3$$
 (2)

$$R \cdot \cdot \cdot \cdot COOH + HOOC \cdot \cdot \cdot R' - R \cdot \cdot \cdot \cdot CO \cdot \cdot \cdot \cdot R' + H_2O + CO_2$$
 (3)

Scission Reactions

$$R \cdot \cdots \cdot CONH \cdot (CH_2)_6 \cdot \cdots \cdot R' \longrightarrow R \cdot \cdots \cdot CONH_2 + CH_2 = CH(CH_2)_4 \cdot \cdots \cdot R'$$
 (4)

$$R \cdots CONH_2 \longrightarrow R \cdots C \equiv N + H_2O \tag{5}$$

$$R \cdots CONH(CH_2)_6 \cdots R' \longrightarrow R \cdots CON + CH_3(CH_2)_5 \cdots R'$$

$$R \cdots N = C = O$$

$$\downarrow H_2O$$

Other reactions which break the hydrocarbon chains. (7)

Cross-Linking

All these reactions have been suggested by Kamerbeek, et al. (Reference 15) who also detected several of the suggested intermediates by infrared spectrophotometry. The present mass spectrometric data confirms the evolution of NH₃, CO₂, and H₂O. Carbon monoxide production can be explained on the basis of homolysis of polymer chains on either side of a carbonyl group. The free radical produced will readily split out the stable CO molecule leaving hydrocarbon fragments. The mass spectra of both nylons are rather complex, the peaks occurring in clusters. The various hydrocarbon fragments are mainly responsible for these clusters but the homologous series of aliphatic nitriles is probably also present. These compounds might be produced in reactions of the type:

$$2R CH_2CONH_2 \longrightarrow RCH_2COOH + NH_3 + RCH_2CN$$
 (Reference 37).

The mechanism of this reaction involves the formation of a six-centered intermediate.

The changes in chemical reactions which are responsible for the changes in E_a as weight loss of nylon 6.6 proceeds are not reflected in the log A F(W) curve (Figure 14). The weight loss appears to be a random process even up to about 80% weight loss.

In the case of nylon 6.10, similar reactions may be postulated; however, the absence of NH $_3$ in the MTA data, if real, would obviously rule out reaction (2). The programmed temperature activation energy data for nylon 6.10 (Figure 17) shows E_a remains fairly constant above 20% weight loss. The slope of the log A F(W) curve is 0.98 and the downward curvature at low conversion tends to indicate a random weight loss is taking place.

In some cases, the weight loss data obtained under isothermal and under programmed temperature conditions did not agree. This is attributed to the interference of diffusion controlled processes, particularly in the case of nylon 6.10, showing the importance of using small sample sizes for study. Difficulties in isothermal temperature control and rapid heating of the sample to the degradation temperature may also have been involved.

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APPENDIX I

ISOTHERMAL NYLON 6.6 AND 6.10 RATE OF WEIGHT LOSS DATA

NYLON 6,6 ISCTHERMAL WEIGHT LOSS 500 MG. RATE OF WT. LCSS IN PERCENT PER MINUTE

MT.LOSS 0.074 0.136 0.267 1.026 1.051 1.078 1.102 1.117 0.512 0.583 0.654 0.726 0.777 1507A .152 .154 .149 .142 0.871 0.957 106.0 986.0 380 MT.LOSS 0.218 0.330 0.426 0.521 0.610 0.775 0.836 0.836 0.983 1.013 0.959 0.948 0.937 0.929 0.916 4400 .083 .088 .083 • 084 .082 070 •056 .041 .047 .037 0.973 1510A 375 RATE OF WT.LOSS 0.219' 0.319 0.437 0.638 0.731 0.753 0.752 0.746 0.745 0.729 0.679 0.761 0.764 0.767 0.771 0.776 0.786 0.775 0.748 0.757 0.794 0.793 0.627 0.617 1503A 373 RATE OF WT.LOSS 0.207 0.301 0.387 0.578 0.658 0.722 0.774 0.811 0.849 0.848 0.848 0.773 0.772 0.772 0.769 0.766 0.759 0.753 0.744 0.736 0.728 0.790 0.774 969.0 0.682 0.781 1508A 367 RATE OF WT-LOSS 0.132 C.185 0.742 0.820 0.857 0.884 0.884 0.884 0.195 0.176 0.176 0.132 0.480 0.575 0.633 0.698 0.541 0.846 0.632 C.496 0.488 0.487 0.479 179.0 484 ISC6A 360 MT-LOSS 0.066 0.084 0.137 0.137 0.223 0.223 0.223 0.321 0.334 0.345 0.368 0.370 0.374 0.376 0.376 0.370 0.371 0.354 0.378 0.341 0.343 MT-LOSS 0.083 0.083 0.123 0.189 0.246 0.283 0.306 0.316 0.318 0.319 0.327 0.360 0.375 0.383 0.388 0.390 0.389 0.391 0.390 0.386 0.384 0.376 0.364 0.345 0.334 0.334 0.325 0.308 0.308 ISOZA 353 RATE OF WT.LCSS 0.209 0.369 0.451 0.511 0.566 0.566 0.585 0.620 0.619 0.558 0.555 0.618 0.622 0.622 809.0 0.616 0.619 119.0 0.626 0.503 0.492 0.449 ISCSA 347 RATE CF WT.LOSS 0.189 0.362 0.479 0.573 0.632 0.675 0.744 0.795 0.830 0.88C 0.886 0.885 0.868 0.857 0.783 0.777 0.729 0.878 969.0 0.807 0.865 0.669 RATE OF WT.LCSS 0.046 0.030 0.035 1517A 319 C.048 C.050 C.052 C.053 C.054 0.054 C.053 C.052 G.051 C.C50 C.049 C.048 0.046 C.044 C.043 C.040 C.038 C.035 0.032 C.031 C.040 0.044 C.054 C.054 C.054 0.046 240.3 0.054 C.045 C.041 0.047 WT.LOSS PERCENT 816 15 20

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ហ [.]	0.058 0.058	0.446	1.949	
6	C-1111	0.483	2.219	
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a co	0.129	0.541	2.653	
6	0.135	0.568	2.849	
0.7	C•139	0.590	3.032	
11	0.142	0.608	3.179	
12	C.145	0.625	3.297	
13	C-147	0.641	3.412	
14	C•145	0.652	3.505	
13	0.145	0.653	3.587	
9	C. 143	0.673	3.665	
17	C.141	0.677	3.703	
80 ·	0.139	0.683	3.750	
19	0.136	0.686	3.756	
) , V	C • 135	0 t	3.187	
21	0.133	0.685	3.807	
25	0.130	0.683	3.787	
23	C.128	0.681	3.784	
24	0.126	0.674	3.749	
25	0.123	0.668	14	
97	611.0	0.662	69	
27	C.116	0.654	3.650	
28	C.113	0.646	63	
53	0.111	0.637	533	
30	601.0	0.628	3.458	
31	0.106	0.619	3,377	
32	501.3	0.610	3.296	
33	C.103	0.601	3.216	
34	201.0	0.592	13	
en en	0.100	0.583	03	
36	850.3	0.572	46.	
37	C • 095	0.562	87	
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APPENDIX II

PROGRAMMED TEMPERATURE NYLON 6.6 AND 6.10 RATE OF WEIGHT LOSS DATA

NYLCN 6,10 100MG. SAMPLES H.R. = HEATING RATE IN DEGREES C PER HOLR RATE OF WT. LOSS IN PERCENT PER MINUTE

150	TEMP	DEG	331.6	358.4	372.9	381.7	386.9	391.2	393.6	396.	397.7	399.4	400.5	402.1	403.2	404.2	405.2	406.2	407.1	407.9	408.6	409.4	410.1	410.8	411.4	412.0	412.6	413.2	413.8	414.4	414.5	415.3	415.9	416.4	416.5	417.3	417.8	418.2	418.7	419.2	419.7	420.1	450.6	451.C	421.4	421.9	422.3	422.7	423.1	423.6	424.0	454.4
7 d 5 G	RATE OF 1	MT - LOSS	0.062	0.173	0.264	0.453	0.642	0.914	1.099	1.338	1.507	1.718	1.893	0.00	2.225	5.369	2.504	2.698	2.840	3.052	3.189	3,301	3.393	3.529	3.697	3.829	3.957	4.035	4.160	4.281	4.399	4.454	4.540	4.625	4.708	4.756	4.815	4.849	4.899	676.7	è	. O. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.	5.135	15	19	N	5.321	5.343	5.365	3	5.390	•
75	THE	DEG C	323.6	362.0	368.6	371.1	372.6	375.0	377.7	381.4	386.2	389.4	391.9	393.9	395.5	397.0	398.3	399.5	400.5	401.5	405.4	403.3	404.2	404.9	405.7	406.4	407.1	407.8	408.5	409.1	9.604	410.2	410.7	411.2	411.7	412.3	412.8	413.2	413.7	414.2	414.7	415.1	415.6	416.0	416.5	416.9	417.3	417.7	418.2	418.6	419.0	419.4
14P/	11	WT.LCSS	0.051	6.019	0.638	•	C.769	•	0.545	٠	0.461	0.603	0.758	0.874	1.001	1.114	1.214	1.319	1.402	1.524	1.607	1.685	1.753	1.827	1.908	1.981	2.052	2.143	2.218	2.291		2.406	2.406	2.459	2.501	2,539	2.576	2.633	2.661	2.689	2.756	2.783	2.809	2.810	2.834	2.858	2.880	2.896	2.892	2.912	2.932	2.951
78	TEMP	DEG C	343.4	362.1	371.8	376.5	381.1	385.0	387.9	390•3	392.1	393.6	395.1	396.3	397.4	398.5	366.4	4007	401.3	402.1	405.9	403.7	404.5	405.3	405.9	406.6	407.3	407.9	408.5	409.1	408.6	410-1	410.7	411.2	411.7	412.2	412.7	413.2	413.6	414.1	414.5	415.0	`.	•	416.2	•	417.0	417.4	417.8	418.2	418.5	418.9
039/	RATE OF	WT.LOSS	0.048	0.108	C.224	0.282	0.353	C-425	0.550	0.701	6.823	C.920	1.037	1.107	1.196	1.306	1,383	1.453	1.516	1.581	1.642	1.743	1.813	1.889	1.963	2.017	2.086	2.153	2.271	2.342	2,383	2.465	2.520	2.574	2.604	2.658	2.710	2,762	2.812	2.949	3°006	3.062	3.117	3.197	3.256	3.274	3.334	3,393	5	3.508	3.420	3.451
075	TEMP.	DEG	324.9	373.4	384.0	4C1.C	408.8	412.2	414.9	417.0	416.8	420.5	421.5	423.3	424.5	425.7	426.7	427.7	428.7	455.6	430.4	431.1	431.9	432.6	433.3	433.9	434.6	435.2	435.8	436.4	436.9	437.5	438.0	438.6	435.1	436.6	440.1	440.6	441.0	441.5	441.9	442.4	442.8	443.3	443.7	444.2	444.7	445.1	445.5	445.9	446.4	446.8
020	RATE OF TO	WT.LOSS	0.274	0.281	0.589	0.637	1.828	2.642	3.341	4.058	.57	5.030	5.511	6.016	•47	6.975	7.395	1.996	8.570	9.193	٠	9.841	16.309	10.549	10.945	11.571	12.056	12.391	12.749	13.093	13.286	13.589	13.790	14.138	14.478	14.811	14.850	15.125	15.277	15.503	16.058	16.175	24	32	7	16.408	16.541	29	16.623	16.644	•	16.794
270	TEMP.	DEG C	175.8	299.5	350.3	374.8	390.0	396.7	401.2	405.1	407.3	409.0	410.6	412.0	413.5	414.8	415.9	416.8	417.6	418.6	419.3	420.1	420.8	421.5	422.2	423.0	423.6	424.2	424.7	425.5	426.0	456.5	427.1	427.5	428.0	428.5	429.0	456.4	429.8	430.4	430.8	431.3	431.7	432.1	435.6	433.1	433.5	434.0	434.4	434.8	435.2	435.6
019/	RATE OF	WT.LOSS	0.116 17	٠ •	0.073	0.288	0.772	0.807	1.289	1.836	9	2.743	.13	n	83	-	• 73	5.237	5.215	5.771	6.123	6.118	6.593	6.804	7.009	6.972	7.366	7.715	7.785	8.056	8.525	8.876	9.213	9.257	9.385	9.541	9.694	6886	9.828	9.902	726.6				-:	Ξ.	_			11.205	11.209	11.361
I.C./F.R.		WT.LCSS		7	ĸ	4	n/ ^	0 I	- (2 0∵(6 (၁၂	11	12	57	14	51	16	11	œ :	6	26	21	22	23	24	25	26	27	28	58	30	31	32	33	34	3,5	36	37	80 G	39	٠ ٠	10	75	4	44	45	46	47	8 7	64	25

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.LCSS	WT.LOSS	DEG C	WT.LOSS	DEG C	WT.LOSS	DEG C	MT.LCSS	DEG C	WT.LOSS	DEGC
51	11.411	436.0	16.780	447.2	3.482	419.3	2.976	419.9	5.430	424 . B
52	11.463	436.4	16.765	447.6	3.513	419.6	3.002	420.3	5.390	425.3
53	11.514	436.8	16.900	448.0	3.544	420.0	3.029	420.7	5.406	425.7
54	11.366	437.1	16.834	448.5	3.574	450.4	3.017	421.0	5.423	426.1
55	11.304	437.6	16.767	448.9	3.483	420.7	3.021	421.4	5.439	426.5
56	11.375	438.0	16.717	449.3	3.612	421.0	3.073	421.7	5.459	426.9
57	11.305	438.3	16.653	445.B	3.585	421.3	3.062	422.1	5.450	427.3
58	11.275	438.8	16.588	450.2	3.558	421.7	3.052	422.5	5.440	427.7
59	11.682	439.1	16.524	450.7	3.531	422.1	3.042	422.9	5.431	428.1
90	11.600	439.5	16.613	451.1	3.504	422.5	3.049	423.3	5.443	428.5
61	11.276	436.6	16.549	451.5	3.476	422.8	3.042	423.6	5.411	428.5
62	11.105	440.3	16.484	452.0	3.517	423.1	3.035	424.0	5.379	429.4
63	11.039	440.7	16.271	452.4	3.470	423.5	3.014	454.4	5.347	429.8
49	10.972	441.1	16.186	452.8	3.423	423.9	3.004	424.8	5.316	430.2
65	10.807	441.5	16.099	453.3	3.375	424.3	2.995	425.1	5.266	430.6
99	10.684	441.9	16.013	453.7	3.304	424.7	2.972	425.5	5.215	431.1
29	10.559	445.4	15.926	454.2	3.267	425.1	2.949	425.8	5.209	431.
99	10.635	442.8	15.664	454.6	3.229	425.5	2.927	426.2	5,154	431.9
69	10.582	443.2	15,552	455.1	3.191	425.9	2.904	456.6	5.098	432.
70	10.407	443.6	15.440	455.5	3.157	426.3	2.881	427.0	5.041	432.
11	10,328	444.1	15.274	456.0	3.123	426.8	2.880	427.3	4.962	433
72	968.6	444.5	15.106	456.4	3,089	427.2	2.846	427.7	4.898	433.
13	906*6	444.9	14.936	456.9	3.046	427.6	2.811	428.1	4.834	434.
74	9,725	445.4	14.712	457.4	3.017	428.1	2.176	428.5	4.769	434.
75	9.427	445.9	14.520	451.9	2.988	428.5	2.732	428.9	4.703	435.2
76	9,365	446.4	14,325	458.3	5,869	428.9	2.688	429.3	4.659	435.
77	9,522	446.8	14.206	458.8	2.825	458.4	5.644	429.7	4.584	436.5
78	9.268	447.2	13.898	455.3	2.765	429.8	2,598	430.1	4.508	436.
46	9.056	447.7	13.535	459.8	2.708	430.5	2.546	430.5	4.420	437
80	8.794	448.2	13.185	460.3	2.614	430.7	2.495	430.9	4.299	437
81	8.376	448.7	12.825	460.8	2.557	431.3	2.419	431.4	4.200	438
82	7.937	449.2	12,535	461.4	2.465	431.8	2,363	431.8	4.099	438.
83	7.608	449.8	12.063	462.0	2-400	432.3	2.325	432.2	3.989	436
84	7.363	450.5	11.681	462.6	2,333	432.9	2.243	432.7	3.864	436
8	7.027	451.1	11.286	463.2	2.246	433.4	2.141	433.2	3.778	440
98	6.720	451.7	10.780	463.8	2.155	434.0	2.050	433.7	3.634	441.1
87	6.328	452.4	10.345	464.4	2.042	434.6	1.933	434.2	3.485	441.
88	5.975	453.1	9.892	465.1	1.934	435.3	1.842	434.8	3,368	442.
60	5.334	453.8	9.526	465.8	1.830	436.0	1.769	435.4	3.178	443.
06	4.897	454.7	8.599	466.6	1.707	436.7	1.659	436.0	2.975	443.
16	4.793	455.6	8.467	4.67.4	1.631	437.5	1.578	436.6	2.779	444
92	4.451	456.5	7.830	468.2	1.483	438.3	1.449	437.4	2,558	445.1
93	3.621	457.7	7.130	469.1	1.319	439.3	1.325	438.1	2.343	446.
94	3,381	459.0	6.478	470.1	1,201	440.4	1,189	439.0	2,198	447.
95	3.483	460.3	5.784	471.2	1.049	441.6	1.064	440.0	1.982	449.1
96	3,394	461.6	4.979	472.5	0.899	445.9	0.933	441.0	1.800	450.4
16	2.957	462.8	4.057	474.0	0.739	444.6	0.778	442.3	1.512	451.
86	2.930	464.0	2.920	476.0	0.556	446.7	0.634	443.9	7	453
			1 7.74	7 027	0 220	0 0 7 7	413		177	

.D./F.R.	. 06P	2	0797	50	
PERCENT	RATE OF	H C	RATE OF	TERP.	
1	1	350		362.1	
2	• 0	368	1.010	385.6	
m 、	•		1.071	399.5	
4 u	10.484	398	1.034	406-6	The second second of the second secon
n «c	2.467		104°7	4114	
7	2,152	409	3.641	417.1	The contract of the contract o
· 00	3.175	412	4.740	415°C	
6	3,313	414	3.380	421.3	AND ADMINISTRATION OF THE PROPERTY OF THE PROP
္	3.354	415	4.570	423.1	
11	3.779	417	6.297	424.7	Administratives of the control of th
12	4.489	418	7.215	425.9	The state of the s
13	4.939	419	8.352	427.0	
14	5.313	420	8.492	428.0	HEREN CHECKER COMMENTAL MANAGEMENT OF CHECKER AND A COMMENTAL OF CHECKER AND A COMMENTAL CONTRACT OF COMMENTAL CONTRACT OF CHECKER AND A COMMENTAL CONTRACT OF COMMENTAL CONTRAC
52	6.017	422	8.422	429.0	
9 !	6.377	422	986.8	430.0	WERNING CORPORATION CONTINUES OF THE PROPERTY
	6.490	423	066.6	431.0	
81	0.(30	474	11.030	431.8	A COMPANY OF THE PROPERTY OF T
7.0	0.383	463	11.93/	432.0	
21	7.187	427	12,427	0.46	The formal and the control of the co
22	7.463	428	13,239	434.6	
23	7.662	428	13.470	435.3	
24	8.191	459	13.870	435.9	The state of the common terms of the common terms of the common terms of the common of
25	8.697		14.401	436.5	
56	8.796	430	14.783	437.1	
72	9.026	431	15.387	437.7	
29	9.751	432	14.814	430.4	
30	9.616	433	15.583	4.064	
31	9.673	433	15.020	435.9	10. In the control of
32	9.874	434	15.328	440.5	
33	10.215	434	15.819	441.1	
34	10.464	435	15,661	441.6	
35	10.860	436	16.186	442.2	
30	10.897	430	16.469	442.1	The state of the common measurement of the case of the
- o	11.115	46.	16.796	449	
000	11 229	40.4	17 001	443.4	
4	11.455	438	18.255	7.777	
4.1	11.643	439	17.843	445.1	
42	11.952		9	445.6	
43	12,031	440	17.553	446.0	
44	12.086	4	17,838	446.5	
45	12.242	4	16.660	447.1	
46	12.328	4	16.011	•	
7 4	12.720	441.8	16.174		
04	12.764	1	17 100	448.	The state of the s

FTEMP	S DEG	8 450	9 450.	6 451.	1 451.	4 451.	9 452.	8 452.	2 453.	0 453.	9 454.	6 454.	4 454.	3 455.	4 455.	9 456.	456.	457.	45/	**************************************	100	4 200	459	3 460.	460.	6 461.	461.	2 462.	5 462.	1 463.	463.	1 464.3	***	100	466.	5 467	.894	469.	7 47C.	7 47C	471.	4 472.	5 473	. 474.	5 476.	5 477.	479.	. 482
RATE	WT.LO	18.9	20.0	20.7	21.3	20.5	20.0	20.2	26.1	20.0	20.3	20.5	19.5	19.9	19.6	19.7	19.5	19.3	6.81	10.	15.7	19.1	19.4	18.2	18.2	19.2	17.9	16.9	16.2	18.0	17.3	17.85	14.2	14.6	11.5	16.7	10.6	10.5	10.1	6.6	4.1	6.1	8.2	7.2	6.1	5.0	4.1	3.2
F TEMP	S DEG	6 443.	3 444.	7 444.	444.	9 445.	445	4 446.	446.	2 447.	6 447	1 448.	6 448.	449.	449	1 449.	450	• 600 • 600	451.	401	457	453	453.	1 454.	2 454.	4555	8 455.	7 456.	3 456.	2 457.	458	458	477.	460.	461.	1 461.	3 462.	1 463.	3 463.	9 464.	3 465.	. 466.	468.	.694	5 471.	5 472.	5 475.	5 479.
T RATE	2	ı,	4	٦,	٠,	'n	v,	₩,	ŝ	ď	٠,	٠,		•	ď.	4	9	•	٥	9 7	'n	4	4.	ŝ	3	9	'n.		۲.	4	<u>.</u>	00.0	•	2	2	6	m	ű		6	Ę.	ů	ď	~	ų	7	ò	6
ERCE	Ü	51	52	53	54	25	56	57	58	53	9	61	9	63	49	65	9	70	004	5 2	71	7.2	2	74	75	76	77	78	4	ခ	8	79	3 4	00	98	87	88	83	96	91	95	93	46	95	96		96	

NATE OF STATE OF STAT 2.532 2.532 2.501 2.47 046/150 NATE OF THE OF T 1.821 1.845 1.873 1.892 1.919 2.006 2.025 2.025 2.025 2.034 2.096 2.096 2.131 2.230 2.230 22.27 22.22 22.23 22.33 22.44 22.44 22.44 22.44 22.44 23.44 24.44 24.44 24.44 NYLON 6,6 100MG. SAMPLES H.R. = HEATING RATE IN DEGREES C PER HOLR RATE OF WT. LOSS IN PERCENT PER MINUTE TERP 9395000 9395000 9395000 9395000 9395000 9395000 9395000 9395000 939500 026/450 NT.LOSS DEC 0.354 255 0.279 339 016/280 05.S 05. 414.4 4115.0 4115.5 4115.0 4115.5 4116.9 4117.9 4117.9 4118.9 420.0 420.0 420.0 421.5 RATE OF WIT - LOSS OF SHIP - LOSS OF 9.448 I.C./K.R. PERCENT WT.LCSS

• L C C C C C C C C C C C C C C C C C C	2000	392.1	392.6	393.1	393.7	394.2	394•8	300	395 B	396.3	396°B	397.3	397.E	96E	398.8	399.4	399.9	400	401.0	401.6	402.1	405.1	403.3	404-0	404.6	405.2	405.5	406.5	407.1	D. 104	408. V. 000.	404	7 · O · V	410.9	412.7	413.6	414.7	415.7	416.8	417.8	419.1	450.4	421.5	423.0	425.5	427.6	2000	4364	437.2
TO 00 - 10	201. K	2.468	2.470	2.445	2.428	2.421	2.453	2.498	2.532	2.522	2.523	2.523	2,468	2.452	2.414	2.389	2.350	2.326	5.305	2.219	2.218	2.113	5.069	2.049	2.027	1.992	2.011	1.939	1.897	808.1	860.1	1.605	1.500	1.457	1,399	1,303	1.188	1.191	1.159	1.137	866.0	0.880	G-792	70/*0	0.646	0.584	0.504	0.367	0.206
- C	י ה ה ה	405.7	406.3	406.8	407.2	407.8	408.3	408.8	40604	409.8	410.4	410.9	411.5	412.1	412.6	413.2	413.8	414.3	414.9	415.5	416.2	416.8	417.4	418.1	418.8	419.4	420.1	420.8	421.5	422.2	422.9	423.6	4.44	423.0	426.8	427.7	428.6	429.6	430.6	431.8	432.9	434.1	435.4	436.9	438.5	440.3	442.2	444	447.5
TA TE	2010	4.791	4.786	4.781	4.714	4.688	4.657	4.619	4.581	4.605	4.549	4.491	4.433	4.441	4.385	4.328	4.271	4.187	4.122	4.060	3.994	3.927	3.858	3.753	3.691	3.628	3.553	3.484	3.414	3.343	3.279	3.191	3.100	3.00.0	2.828	2.683	2.554	2.444	2.310	2.163	2.031	1.936	1.754	1.578	1.438	1.273	1.101	0.928	0.587
- C	ביני	396.4	396.9	397.4	397.9	398.4	399.0	399.5	400.0	400.5	401.1	401.6	402.1	402.7	403.2	403.8	404.3	404.9	405.4	406.0	406.6	407.2	407.8	408.4	409.0	409.6	410.2	410.9	411.6	412.3	413.1	413.8	414.1	410.0	417.4	418-4	419.5	420.6	421.7	423.2	454.6	425.9	427.4	429.1	431.1	433,3	436.3	446.2	447.3
KAIE UF	MI-LUSS	2.470	2.460	2.475	2.449	2.437	2.412	2.380	2.371	2.382	2.388	2.374	2.353		2.310	2.288	2.265	2.243	2.227	2.205	2.136	2.126	2.106	2.079	2.039	1.994	1.934	1.866	1.790	1.725	1.652	1.593	1.502	1.434	1.241	1.229	1.132	1.103	1.016	0.854	0.865	0.892	0.807	0.711	0.597	0.487	0.361	0.280	0.013
- LE LO	0EG C	429.1	455.6	430.2	430.7	431.2	431.7	432.2	432.8	433.3	433.9	434.4	434.9	435.4	436.0	436.5	437.0	437.6	438.2	438.7	439.2	436.8	446.3	440.9	441.5	442.1	442.7	443.3	444.0	444.5	445.2	445.0	446.5	7-144	0 0 7 7	9.044	450.4	451.3	452.2	453.2	454.3	455.4	26	57.	459.4	461.1	462.9	465.7	0.594
RATE OF	MT.LOSS	14.281	14,187	14.265	14.114	14.206	14.026	13.933	14.000	14.061	14.057	14.053	14.011	13.684	13.607	13.517	13.437	13.415	13,316	13.400	13.559	13.275	12.984	12.721	12.471	12.488	12,193	12.038	11.901	11.500	11.136	10.941	10.604	10.237	7.673	8-861	8.413	8.029	7.625	7.198	6.745	6.259	5.883	5.417	4.726	4.414	3.607	2,791	1.739
TEMP.	DEG C	422.2	422.7	423.2	423.7	424.2	424.7	425.2	425.7	426.2	426.7	427.2	427.7	428.1	428.6	429.1	429.6	430.1	430.5	431.0	431.6	432.0	432.6	433.1	433.6	434.1	434.7	435.3	435.9	436.4	437.0	437.6	438.3	439.0	434.0	440.5	442.0	442.8	443.6	444.6	445.6	446.7	448.0	449.6	451.3	453,1	455.4	458.2	462.5
RATE OF	MT.LOSS	9.415	9.180	9.436	9.695	9.674	9.652	9.685	399.6	9.692	9.724	9.868	9.922	9.831	9.621	9.708	989*6	9.594	6.677	9.508	9.409	9.390	9.235	710.6	8 • 8 4 1	•	8.303	8.363	8.269	8.120	٠	7.435	7.258	7.046	4 7 7	6.226	5.594	5.366		4.844		3.978	•	•	2.579	œ	1.766	1.377	2.814
	- 1	21	52	53	54	55	56	57	58	59	9	61	62	63	. 64	65	99	19	6 8	69	20	7.1	72	73	74	75	16	7.7	78	4	96	16	82	m .	20 c	0 0 0	20	88	68	36	91	92	93	76	95	96	16	86	66

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	Wright-Pat	terson Air	Force Base, Ohio 45433
13. ABSTRACT			-
The thermal degradation of two aliphatic p	olyamides, p	olyhexamet	thylene adipamide
(nylon 6.6) and nolyhexamethylene sebacamide	(nylon 6.10)	have been	studied. Molecular
weight changes, weight loss, and volatile prod	uct analysis	were used t	o help elucidate the
reaction mechanisms.	•		_
reaction mechanisms.			
The presence of low molecular weight mat	erial and not	vmerizable	end groups in these
polymers complicated the interpretation of mo	leriar and poi	ot changes o	during degradation.
polymers complicated the interpretation of mo	lecular weigi	o doto Ny	ion 6 6 degradation gave
The weight loss data obtained allowed the calcu	liation of rav	e uata. Ny	characterized by an
an activation energy of 45 kcal/mole while nylo	on 6. 10 degra	tuation was	characterized by an
activation energy of 55 kcal/mole. Both polyn	ners gave evi	dence of ra	ndom scission kinetics.
The volatile products were consistent with the	occurrence o	or rurtner c	ondensation, scission,
and cross-linking reactions.			
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NET WORDS	ROLE	WT	ROLE	wr	ROLE	WТ
Thermal Degradation						
Polymer						
Polyamide						
Nylon						
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