

# Pyrolysis of Polyamides\*

Sidney Straus and Leo A. Wall

Thermal decompositions of various nylon samples having different molecular weights and composition were investigated by several procedures: (1) The rate of volatilization at temperatures between 310° and 380° C; (2) the analysis of the volatile products by mass spectrometry; and (3) a direct measurement of volatilizing material obtained by carrying out the pyrolysis within the ionization chamber of a mass spectrometer.

Activation energies based on the rates of volatilization for the various samples varied from 15 to 42 kilocalories. The rate behavior, i. e., the observation of maxima in the rate-versus-conversion plots, is close to that given by theory for random decomposition. The different activation energies appear to be the result of a hydrolytic mechanism which is sensitive to trace polymerization catalysts. Increases in rates were obtained when sulfuric and phosphoric acids were added to nylon. The fluctuations found in activation energies, and the production of CO<sub>2</sub> indicates that a hydrolytic decomposition mechanism may be contributing to the over-all process. It appears evident that, compared to a pure hydrocarbon chain, the polyamides are much more susceptible to thermal decomposition.

## 1. Introduction

Although there has been considerable work done on the thermal decomposition of nylon and related substances [1 to 4],<sup>1</sup> relatively little attention has been paid to the kinetics of the process. In previous studies, product identification and structural changes in the polymer comprised the major portion of the work.

The purpose of this present investigation was first to establish a better understanding of the thermal decomposition of linear high polymers. Prior work [5] on linear and branched polyethylene showed a striking difference between rates of volatilization behavior for linear and for branched polyethylene. This difference has not yet been quantitatively accounted for in terms of any mechanism hitherto treated [6]. It was, therefore, considered desirable to investigate some linear polymers that from previous product-analysis were suspected of decomposing more or less randomly. A second purpose was to establish the energetics so that a comparison could be made with polyethylene and the thermal stability of the peptide linkage determined.

The effects on the process of moisture, traces of polymerization catalyst, i. e., acids, a free radical inhibitor, and surface area were also studied to some degree in order to cast further light on the details of the mechanism of decomposition.

## 2. Materials

Nylon samples 4406, 4408, and 4409, used in the present work for rate of volatilization determinations, have been described previously [3]. The first two were made from a mixture of hexamethylenediamine-adipic acid and caprolactam, whereas the last one contains, in addition, some hexamethylenediamine-sebacic acid. The other nylons under study were nylon-6 samples made from caprolactam. They

were prepared by the National Aniline Co., Hopewell, Va.; one had a molecular weight of about 30,000 and the other about 60,000, as determined from viscosity measurements in formic acid. The relationship between the viscosity average of nylon in formic acid and the number average has been reported [7].

The Dacron sample used, a product of the E. I. du Pont de Nemours & Co., Inc., was in the form of bright threads with no delustrant added. The polyester had a 70-34 denier-filament structure.

## 3. Apparatus and Experimental Procedure

The experimental work consisted of (1) measuring rates of volatilization of the polymer in vacuum, and (2) identification of the various products of decomposition with the use of a mass spectrometer.

The apparatus and experimental procedure used in determining the rates of thermal degradation have been described previously [8, 9]. In brief, a 5- to 6-mg sample is placed in a glass crucible and suspended from a tungsten helical spring balance. It was determined that a Pyrex glass crucible gave a more accurate temperature measurement than a platinum crucible when the sample did not melt and flow freely on decomposition. This sample and weighing mechanism is enclosed in a Pyrex housing that could be evacuated to better than 10<sup>-5</sup> mm of Hg. A preheated electric furnace is then placed in position around the glass portion containing the crucible in suspension. The furnace is controlled by means of an electronic thermostat which is able to hold the temperature constant to about ±0.2° C.

There is a crossline on the tungsten spring that is observed during pyrolysis, and weight losses could be recorded at various time intervals. These data are then plotted as rate of volatilization in percent of original sample per minute versus percent volatilized. These curves exhibited very definite maxima in most cases. Activation energies were calculated from these maxima at 3 or 4 different temperatures.

The apparatus used to collect decomposition

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

products in the pyrolysis study is also described fully in a previous paper [10]. In brief, a 20 to 40-mg sample is placed in a small Pyrex tube enclosed in a larger glass housing. The system is evacuated and preheated at about 110° C to remove adsorbed gases and moisture. A tube furnace, preheated to the temperature of pyrolysis, is placed in position around the sample. Approximately 5 min are required for the sample to reach the temperature of pyrolysis and then the sample is heated for 30 min at 400° C. The heater is then removed from around the sample. During pyrolysis, some of the volatiles are condensed with liquid nitrogen.

There are four fractions collected:

(1) *Residue*, left in the small Pyrex tube. A brown crust.

(2) *Wax-like fraction*, volatile at the temperature of pyrolysis but not at room temperature. This tan deposit collects immediately outside of the heater in the apparatus. It is soluble in warm ethanol.

(3) *"Condensed" fraction*, volatile at room temperature. Collected by means of liquid nitrogen and sealed for mass spectrometer analysis.

The weights of fractions 1, 2, and 3 are measured directly on a semimicro balance.

(4) *Gas fraction*, volatile gases not condensable at liquid nitrogen temperature. Collected in a gas sample holder, and also analyzed in the mass spectrometer. The weight of this fraction is calculated from the volume, pressure, and composition of the gas.

#### 4. Results

The rate data obtained in the volatilization of nylon samples 4406, 4408, and 4409 are shown in figures 1, 2, and 3. They all show maxima at about 30- to 40-percent volatilization. The temperatures in all three cases were at 310°, 315°, and 320° C. For nylon samples 4406 and 4408, the maxima in the curves are not too far apart for the three temperatures. This indicates a rather low activation energy.

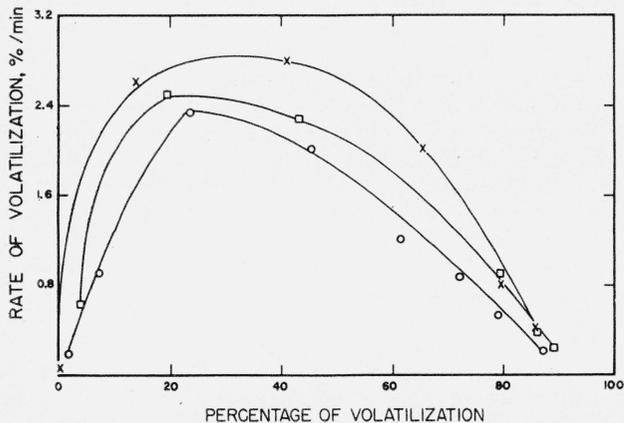


FIGURE 1. Rate of volatilization versus percent volatilized for nylon 66-6, sample 4406.

○, 310° C; □, 315° C; and ×, 320° C.

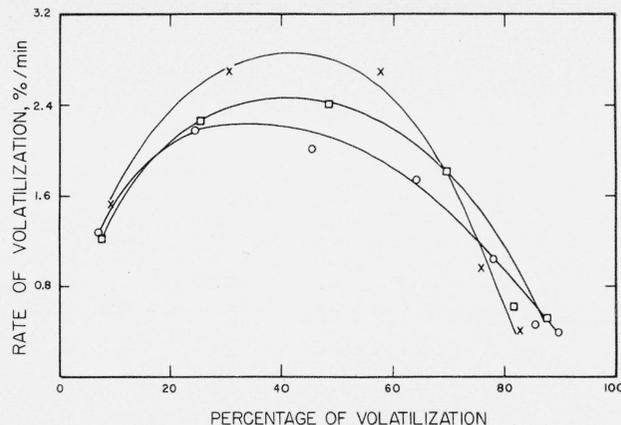


FIGURE 2. Rate of volatilization versus percent volatilized for nylon 66-6, sample 4408.

○, 310° C; □, 315° C; and ×, 320° C.

For nylon sample 4409, the rates at the maxima are further apart.

In figures 4 and 5, the rate of volatilization data were obtained on different molecular weights of the nylon-6 sample. The temperatures in all cases are higher than that used for the previous nylon copolymers. The lowest temperature is 340° C and the highest 380° C. Both figures show similar maxima curves, and the maximum volatilization rates are between 20 and 40 percent.

Finally, in figure 6, rate curves have been plotted for Dacron, a polyester of terephthalic acid and ethylene glycol. Four curves at temperatures 350°, 355°, 365°, and 370° C are shown; these have maxima somewhat different from the caprolactams with the maxima occurring at under 20-percent volatilization.

In order to determine the effect of catalysts on the volatilization rate, several catalysts that are commonly used for the polymerization of polyamides were added to the 60,000 molecular weight sample of the nylon-6 polymer. The effect of surface area on

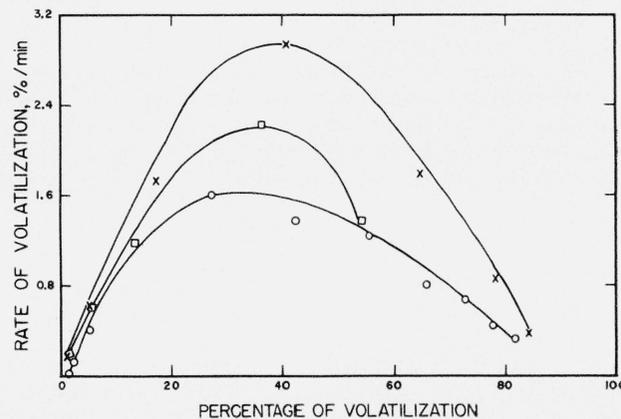


FIGURE 3. Rate of volatilization versus percent volatilized for nylon 66-610-6, sample 4409.

○, 310° C; □, 315° C; and ×, 320° C.

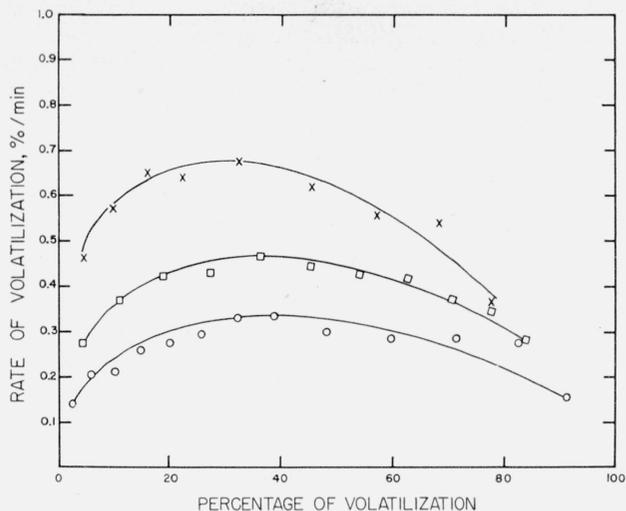


FIGURE 4. Rate of volatilization versus percent volatilized for nylon-6, 30,000 molecular weight.  
 ○, 345° C; □, 355° C; and ×, 365° C.

degradation was also studied. The results are shown in the curves in figure 7.

Curve A is the normal curve for this polymer at 345° C. To obtain curve B, double the amount of sample, 10 mg instead of 5 mg, was used. The small white crystals formed a somewhat thicker layer, but when the crystals began to degrade they flattened out to some extent. The crystals did not actually melt but rather flowed slightly. In using double the amount of sample, the rate of volatilization is slower at the beginning, but at about 25-percent volatilization, the two curves become one. This would indicate some surface effect.

Curve C indicates the result obtained on a thicker sample. A nylon sample was dissolved in a 90-percent formic acid solution, a portion transferred to a weighing bottle, and the viscous solution evacuated

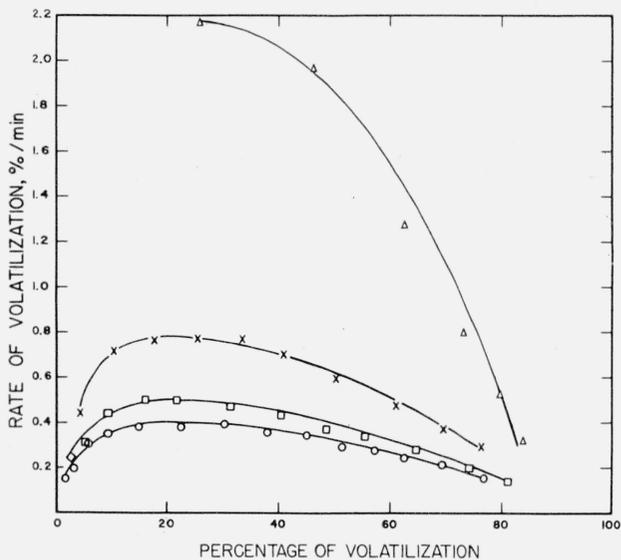


FIGURE 5. Rate of volatilization versus percent volatilized for nylon-6, 60,000 molecular weight.  
 ○, 340° C; □, 345° C; ×, 355° C; and △, 380° C.

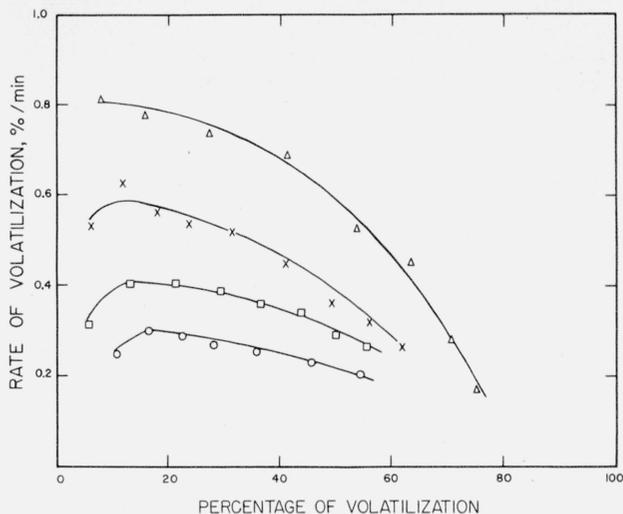


FIGURE 6. Rate of volatilization versus percent volatilized for Dacron.  
 ○, 350° C; □, 355° C; ×, 365° C; and △, 370° C.

for several hours. A small portion was then placed in a pyrolysis apparatus and heated to 110° C for 1 hr in a vacuum of about  $10^{-5}$  to  $10^{-6}$  mm of Hg. The heating was continued until constant weight was obtained. The resulting particle mass, free of the formic acid, was approximately 2-mm thick and about 3 to 4 mm in length. The original sample used in a rate experiment consisted of approximately 25 to 30 crystals, each piece covering a smaller area and less than one-half as thick as the sample used to obtain curve C. As indicated from curve C, the maximum rate of thermal decomposition of the thicker particle mass was reduced by about one-half.

The addition of 5 percent of  $H_2SO_4$  prior to

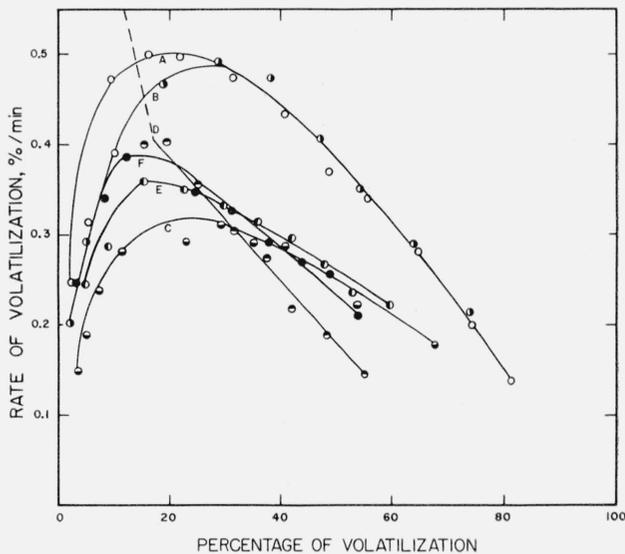


FIGURE 7. Effect of trace substances on pyrolysis of nylon-6, 60,000 molecular weight.

Temperature=345° C.

A—○, Original sample; B—●, double amount of sample; C—●, single thick specimen, specially prepared; D—●, plus 5.0%  $H_2SO_4$ ; E—●, plus 1.0% 1,5-diaminoanthraquinone; F—●, plus 1.0%  $H_3PO_4$ ; temperature=325° C.

pyrolysis had a considerable effect on the rate of volatilization of the nylon-6 sample at first, as can be seen in curve D. About 3 or 4 drops of dilute H<sub>2</sub>SO<sub>4</sub> solution was added to a weighed amount of sample, enough to cover it completely; no more than 5 mg are used in rate determinations. The water was evaporated by heating gently in an oven to constant weight. After the furnace is placed in position around the sample, about 15 percent of the sample volatilizes during the 15 min that it takes for the sample to reach the temperature of the furnace. In other words, the degradation proceeds rapidly, even prior to attaining the 345° C temperature level.

Curve F shows the effect of the addition of 1 percent of orthophosphoric acid to the nylon before pyrolyzing at 325° C. As in the previous case, a few drops of acid solution were added to the polymer, which was then dried. At 325° C the maximum rate would have been about 0.125 in the absence of the acid. Thus, the presence of the acid increases the maximum rate by a factor of three.

To determine whether traces of acid catalysts used in the preparation of the polymer were also catalyzing its thermal decomposition, the original sample was leached out. This was accomplished by soaking a small amount of nylon-6 sample in distilled H<sub>2</sub>O for 5 days. The water was then decanted and fresh water added for 5 more days. At the end of this period, the water was removed and the sample preheated to 120° to 130° C for 2 hr in a vacuum of about 10<sup>-5</sup> mm of Hg to constant weight.

The dried sample was treated in a rate experiment at 355° C, similar to the previous experiment at the same temperature. The maximum rate was reduced by a little more than one-half in the experiment. Apparently the leaching-out process with water is effective in increasing the thermal stability.

Finally, in curve E, we see the effect of the addition of 1 percent of 1,5-diaminoanthraquinone, an inhibitor, to the sample prior to pyrolysis. This, too, was added in the form of a water solution until the additive was well dispersed throughout the sample. The rate of volatilization of the nylon is slowed from 0.5 percent per minute at its maximum to about 0.35 percent per minute at 345° C, which is about a 6° C decrease for equivalent volatilization rate.

Prior to the decomposition of the nylons to obtain the volatile products, each of the various samples were preheated to 110° C for 1 hr in a vacuum of better than 10<sup>-5</sup> mm of Hg. They each lost a small amount of volatile matter which was most probably H<sub>2</sub>O. The losses were in the order of the following percentages: Nylon sample 4406—2.3 percent; sample 4408—2.5 percent; sample 4409—2.2 percent; nylon-6 (60,000 mol wt)—1.3 percent; nylon-6 (30,000 mol wt)—0.6 percent; and polypyrrolidone—4.8 percent. These percentages were subtracted from the weights of the original samples prior to calculations, both in the rate work and in the collection of the decomposition products. (Polypyrrolidone is a nylon-4 sample of low molecular weight having the following repeating unit [—NH—(CH<sub>2</sub>)<sub>3</sub>CO—].)

The mass spectrometer analysis of the fraction volatile at room temperature is shown in table 1, in mole percent. The amount of this fraction in percent of total pyrolyzed part is generally small for nylon breakdown and is shown on the bottom line. The analyses of the degradation products of nylon samples 4407 and 4409, shown in the first two columns, were determined about 5 yr ago at the Bureau in a somewhat similar pyrolysis apparatus [3]. Nylon sample 4407 is the same as the 4408 sample used in the present work for rate determinations. The compositions were the same; only the thickness of the samples was slightly different. This would make no difference in product determinations.

Previously [3] the water obtained in the mass spectrometer analysis was excluded from the volatile products. Water is unlikely as a product of the thermal decomposition unless hydroperoxides have been formed in the material; however, it is concluded in this work that it is very tightly adsorbed by nylons. Consequently, the previous data [3] have been recalculated to include water since it appears to have a significant effect on the rate of decomposition.

In nylon sample 4407 the major breakdown products in the fraction volatile at room temperature are CO<sub>2</sub> and H<sub>2</sub>O in approximately equal amounts. The other constituents are small amounts of hydrocarbons, saturated, unsaturated, and cyclic compounds. Somewhat outstanding is the yield of cyclopentanone as compared to the other hydrocarbons. This is most probably a breakdown product of the adipic acid constituent. Hopff [11] also detected cyclopentanone on nylon decomposition.

TABLE 1. Mass spectrometer analysis of fractions volatile at room temperature

Components	Nylon 4407	Nylon 4409	Nylon-6, mol wt		Nylon-4
			30,000	60,000	
	<i>Mole %</i>	<i>Mole %</i>	<i>Mole %</i>	<i>Mole %</i>	<i>Mole %</i>
CO <sub>2</sub> .....	43.7	92.3	55.8	59.4	64.3
H <sub>2</sub> O.....	47.8	4.5	35.4	35.6	16.3
Ethylene.....	0.4	0.5	0.4	0.3	-----
Ethane.....	.3	.5	-----	.2	-----
Propadiene.....	-----	-----	-----	.1	-----
Propylene.....	.5	-----	.4	.7	-----
Propane.....	.2	-----	-----	-----	-----
Butadiene.....	-----	-----	.2	.4	-----
Butene.....	.2	-----	.2	.6	-----
Butane.....	.1	-----	.3	.5	-----
Isoprene.....	-----	-----	.3	.2	-----
Cyclopentene.....	.1	-----	-----	-----	-----
Cyclopentadiene.....	-----	.1	-----	-----	-----
Cyclopentanone.....	5.8	1.1	-----	-----	-----
Pentadiene.....	0.1	0.2	-----	-----	-----
Pentene.....	.2	.2	.1	.3	-----
Pentane.....	-----	.1	.1	.1	-----
Benzene.....	.4	.2	5.8	.1	13.3
Cyclohexene.....	.1	.1	-----	-----	-----
Hexadiene.....	.1	.2	0.3	.7	6.1
Hexene.....	-----	-----	.4	.2	-----
Hexane.....	-----	-----	.1	.2	-----
Toluene.....	-----	-----	.1	.1	-----
Dimethylbenzene.....	-----	-----	-----	.1	-----
Heptadiene.....	-----	-----	.1	.2	-----
Total.....	100.0	100.0	100.0	100.0	100.0
Fraction of pyrolyzed material.....%	5	5	5	10	1 to 2

Nylon sample 4409 has considerably less H<sub>2</sub>O in this fraction and more CO<sub>2</sub>. The yield of cyclopentanone is also lower than in sample 4407. The former has the sebacic acid salt as part of its makeup in addition to the adipic acid salt, and this would certainly have the effect of decreasing cyclopentanone formation. The different amounts of water found in the 4407 and 4409 samples may be related to the lower peptide-link content of the 4409 material compared to the 4407.

Columns 3 and 4 indicate the mass spectra patterns of the two caprolactams of different molecular weight. The breakdown of the light volatile fractions are quite similar, mostly yielding CO<sub>2</sub> and H<sub>2</sub>O. The high benzene figure in the 30,000-molecular weight nylon is most probably background in the mass spectrometer. The yield of monomer fraction for the nylon-4 sample is quite small, only 1 to 2 percent of the total volatilized part. The H<sub>2</sub>O and CO<sub>2</sub> findings are actually very small.

The gas sample collected showed small amounts of H<sub>2</sub>, CH<sub>4</sub>, and CO. It was calculated that this fraction was less than 0.1 percent of the total volatilized part.

The heavier volatiles, which comprised approximately 95 percent of the total volatiles, were weighed after recovery from a warm ethanol solution. No attempt was made to analyze this waxlike fraction.

The products of decomposition were determined by mass spectrometry by another technique [12]. Small samples of nylons 4406, 4408, and 4409 were placed in a tube furnace and the degradation products evaporated directly into the ionization chamber of a Nier-type mass spectrometer. The samples began to degrade at about 240° C with the evolution of gases. Degradation was complete at 400° C.

Mass spectra were obtained from mass 28 to 452 in nylon sample 4406 and from 28 to 360, in nylons 4408 and 4409. The mass spectra were complicated with no recurring patterns. There were indications of cyclopentanone formation and also alkyl amines. The hexamethylenediamine-adipic acid salt has a molecular weight of 226, and this may explain a relatively large observed peak at 226. The molecular weight of the caprolactam is 113, and this also gave a relatively large peak. The 452 peak in nylon 4406 may be the dimer of the adipic acid salt. Quantitative data could not be accurately obtained for the actual amounts of the various molecules. In general, the pyrolysis products were of relatively low mass containing one basic unit or less. This is rather small compared with other polymers [13] such as polymethylene, polypropylene, polyisobutylene, etc., which have average molecular weights over 500 in the heavy waxlike fraction.

## 5. Discussion

On the basis of the rate curves and the product analysis, a random or nearly random type of breakdown is indicated for the nylon decomposition. There are really no outstanding individual volatile compounds with the possible exception of CO<sub>2</sub>, but

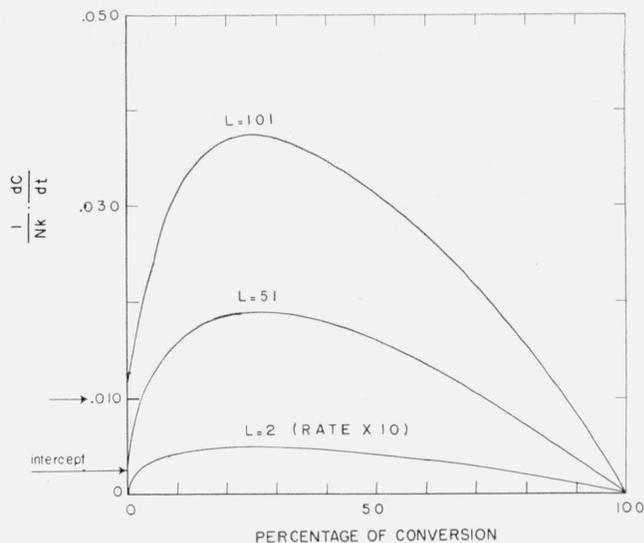


FIGURE 8. Theoretical curves for random decomposition showing effect of critical size for evaporation,  $L$ , on rate of volatilization [14].

Arrows indicate initial rates.

as the polymer decomposes, a large number of different compounds are produced.

A set of typical theoretical curves for a decomposition in which scissions can occur with equal probability at any link in the chain is shown in figure 8 [14]. These curves show the effect of size of the volatilizing fragments on the rate of volatilization,  $L$  being the number of basic units in the smallest chain that does not evaporate without degradation. Thus,  $L-1$  is the D. P. of the largest fragment that can vaporize without further decomposition. In these curves, the maximum occurs at about 26-percent conversion, at which point  $dC/dt \approx Lk/e$ , where  $k$  is the over-all rate constant for the random decomposition, and  $e$  is the base of the natural logarithms, 2.7. The rate at zero time, i. e., the intercept at zero conversion in figure 8, is given by  $dC/dt \approx L^2k/N$ . These relationships hold only when the initial degree of polymerization,  $N$ , is much larger than  $L$ . This condition is always fulfilled by the materials herein discussed. The curves in figure 8 show that the maximum rates are the more dependable quantities to use for the estimation of the rate constants because experimental initial rates would require very precise measurement at less than 1-percent conversion to be of any significance. Unfortunately, quantitative utilization of the maximum values also requires a determination of  $L$ . Nevertheless, an Arrhenius plot of the maximum rates should give dependable values for the activation energy.

The activation energies for the polymers studied are listed in table 2. The most striking aspect of the data is the large variation in the energies for the nylons. The low value of 14 kcal may be at least partially due to the low molecular weight of the first two materials. If the vaporization, and not the decomposition, process is rate determining,

TABLE 2. Activation energies based on rates of decomposition

Polymer	Molecular weight	Activation energy	Preexponential factor
		<i>kcal</i>	<i>L</i> = 5
Nylon 4406	Low < 10,000	14	3.6 × 10
Nylon 4408	Low < 10,000	14	3.6 × 10
Nylon 4409	13,000	42	5.8 × 10 <sup>11</sup>
Nylon-6	30,000	27	1.03 × 10 <sup>5</sup>
Nylon-6	60,000	34	4.1 × 10 <sup>7</sup>
Dacron	~10 <sup>4</sup>	38	5.1 × 10 <sup>8</sup>
			<i>L</i> = 72
Polymethylene (linear polyethylene).	5 × 10 <sup>6</sup>	68	1.9 × 10 <sup>15</sup>

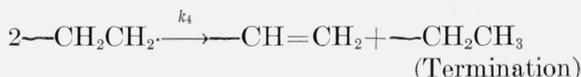
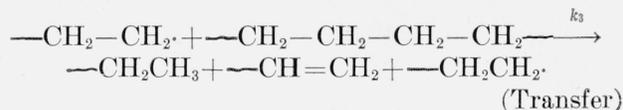
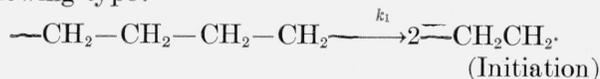
then a value of 14 kcal is reasonable for the activation energy, provided the volatilizing compounds have a molecular weight in the region of 200. Other factors such as the presence of some trace catalysts may, of course, be a contributing influence to the low activation energy.

In figure 7, it is seen that various acids of the type often used in the preparation of polyamides and polyesters produce considerable effect on the rate of decomposition. It is also seen in table 1 that the amount of water found in the pyrolysis products is least for the material that gave the highest activation energy. These observations suggest that the decomposition is complicated by an ionic mechanism, the contribution of which to the overall decomposition is dependent on the amounts of trace catalysts, i. e., acid and adsorbed water. Ionic mechanisms are fairly rare in degradation processes; however, they have been suggested by other workers in the case of polyvinyl ethers [15]. The effect of the diaminoanthraquinone suggests free-radical intermediates. Evaporation or dehydration of both the catalysts and traces of water, as well as the inhibitor, at the pyrolytic temperature may explain the smallness of the observed effects. At these temperatures it would be expected that free-radical mechanisms are most important. It is of importance and somewhat surprising that lingering traces of moisture and acid appear to have pronounced effects, presumably by inducing, to a relatively small degree, ionic processes in the overall decomposition mechanism.

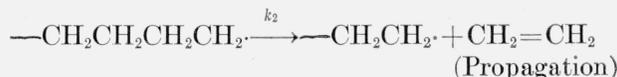
In general, the nylon materials showed a somewhat erratic behavior. From the data so far obtained (see table 2) the highest value of the activation energies, 42 kcal, is considered to be most representative for a free-radical mechanism of thermal decomposition.

The value of 38 kcal for the one sample of Dacron studied is seen to be quite close to the higher nylon values. Comparison with the result for polyethylene shows that the peptide and the ester linkage introduce, at least in the structures studied, a very large degree of thermal instability.

The free-radical chain mechanism for the decomposition of polyethylene [5] is most likely of the following type:



The step:

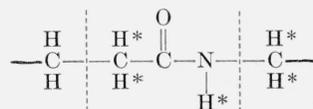


in polyethylene does not compete favorably with the transfer,  $k_3$  [5]. Thus, the  $k_3$  step, which is a composite of two elementary processes combined for the purpose of mathematical treatment [14, 16] of polymer decomposition, is the principal chain-carrying process. It would probably be more correct and descriptive to call this step, "propagation by transfer." The over-all constant for random decomposition by the above mechanisms is given by:

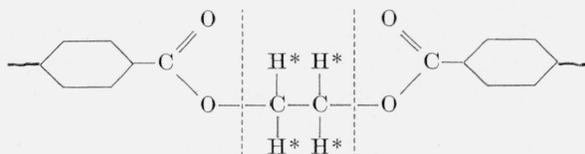
$$k = k_1 + k_3R \approx k_3R = k_3 (I/k_4)^{1/2}$$

where  $R$  is the total radical concentration and  $I$  is the rate of initiation of active centers. The term  $I$  includes  $k_1$ , a concentration term, and statistical factors depending on the exact mode of initiation. A considerable amount of further research would be required to determine the exact mode of initiation for the polymers discussed here. However, consideration of the structures shown below

*Polyamides (nylon)*



*Polyester (Dacron)*



suggests that initiation by homolytic scission at the linkages indicated by the vertical dashed lines is more probable than at a carbon-carbon bond in polyethylene. The C—N bond is known to be weaker than a C—C bond, the strength of the former being about 66 kcal, whereas the latter is about 80 kcal, depending, of course, on the structure in which it is located. The C—N bond alpha to the carbonyl is certainly stronger than that beta to the carbonyl. Hydrolytic scission of the peptide links, which our experiments indicate, would account for both the amines reported in the pyrolysis of polyamides [1, 2] and the CO<sub>2</sub> found by all workers in the field, the latter arising from the decomposition of the acid groups produced by hydrolytic scission.

The starred hydrogen atoms are more likely to be abstracted by a radical and hence facilitate transfer in polymers with the above structures, again compared to a linear paraffin material. The products of the pyrolyses, in general, support the above hypotheses, although the products listed in table 1 certainly suggest also that decomposition does not proceed exclusively at the points depicted in the structures by a free-radical mechanism.

In polyethylene, approximately 98 percent of the products of pyrolysis was in the form of a high-boiling wax with an average molecular weight near 700. In the polyamides, about 90 to 95 percent of the products was nonvolatile, but of much lower average molecular weight. Mass spectrometer studies of polyamide pyrolysis indicate that maximum size of the fragment is about 400 mass units. A rough estimate of the critical size for evaporation,  $L$ , is then about 5 caprolactam units. In table 2, preexponential factors are given. Notwithstanding the difference in  $L$  values between the polyethylene and other materials, it is seen that these values are hardly constant for the polyamides and are very much lower.

No such behavior has been found in pyrolysis studies of addition polymers. The low and fluctuating values suggest the presence of a concentration factor, probably of water or acid, in the preexponential factors. With  $L=5$ , the rate constants for the nylons and Dacron refer to the apparent breaking of peptide or polyester bonds, while with  $L=72$ , the constant for polyethylene refers to the breaking of any C—C bond in the chain.

## 6. Conclusions

The pyrolysis of polyamides shows a behavior incompatible with a pure free-radical mechanism. It seems evident that even at the pyrolytic temperatures of 300° to 400° C and with prior exhaustive drying at 100° to 130° C in a vacuum, enough water remains to provide a complicating effect in the decomposition reaction. The hypothesis that traces of water and polymerization catalysts influence the pyrolysis provides the simplest explanation of the more puzzling aspects of polyamide decomposition, including the production of appreciable quantities of CO<sub>2</sub>.

In the case of the 60,000 molecular weight nylon-6 material (see table 1), the amount of CO<sub>2</sub> produced would imply the hydrolytic scission of 15 percent of

the original peptide bonds. This implies the presence of about 2 percent of water at the pyrolysis temperature, presumably tightly bound to the peptide group, and that the decompositions studied here were about half hydrolytic and half free radical.

It is also clear that the over-all process for nylon is typical of a random decomposition of linear chains similar to that for linear polyethylene. The Dacron rate behavior, however, does not exhibit as decisive a result.

The activation energies for nylon and Dacron are probably considerably lower than those to be expected if the suggested hydrolytic process was completely suppressed or eliminated. In any case, the activation energies would be unlikely to approach that for polyethylene.

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