

Pyrolysis and Combustion of Nylon 6. I. Effect of Selected Brominated Flame Retardants

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Synopsis

The pyrolysis of nylon 6 has been shown to proceed by a first-order process to yield ϵ -caprolactam as the primary product. This degradation has an energy of activation of approximately 46 kcal/mole which would seem to indicate the involvement of a homolytic process. Inclusion of organobromine compounds such as hexabromobiphenyl and dodecabromopentacyclo [5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane catalyzed the pyrolysis but did not significantly alter the nature of the degradation products. Because of this, simple organobromine compounds are not good candidates for utilization as flame retardants for nylon 6.

INTRODUCTION

A considerable effort is currently being expended to impart flame-resistant characteristics to synthetic fibers. Although limited success has been achieved with some systems, fibers and fabrics composed of nylon 6 continue to pose a problem. Apparently, polyamides are not amenable to many of the approaches which have shown promise for other polymers. A few treatments have been reported to have some positive effect on nylons,¹ but most of these are not suitable for widespread commercial usage in textiles. They are generally based on aftertreatments in fabric form and often impair the physical and aesthetic properties. They also have the disadvantage of cost and frequently lack durability to laundering, dry cleaning, and abrasion. Thus, a better approach to the problem would seem to be that of developing a flame retardant that could be added directly to the polymer melt prior to spinning. For such purposes, a flame retardant should be effective at relatively low concentrations so that the physical properties of the fibers are not degraded.

In order to determine which compounds perform the most effectively as flame retardants, the decomposition mechanism of the polymer should be understood.

There is no clear understanding of the pyrolysis of nylon 6. Although several investigators²⁻⁸ have studied the thermal decomposition of polyamides, the different experimental procedures and instrumentation used have resulted in many conflicting decomposition mechanisms. Free-radical, ionic, and a combination of both mechanisms have been proposed.

Most early workers dealing with polyamides were concerned only with the analyses of the decomposition products. Decomposition mechanisms were based solely on the identification of compounds found among the pyrolysis products. Only one early study⁹ deals with the kinetics of the decomposition reaction. The method used for determining these kinetic parameters has since been improved.¹⁰⁻¹⁶ Energies of activation and orders of reaction can now be reproduced with great regularity; hence, the precision is improved. With this type of reproducibility, the kinetic data can be used to help deduce a decomposition mechanism.

The purpose of the present work was to investigate and characterize the kinetic parameters of the thermal decomposition of nylon 6 at 400° and 500°C and to show the effect of some brominated flame retardants on the decomposition. Analyses of the decomposition products and the studies of earlier workers were used in conjunction with the kinetics to investigate the decomposition reaction.

EXPERIMENTAL

The infrared spectra in this study were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. An F&M Model 500 programmed temperature instrument with a Model 1609 flame ionization attachment was used for the gas chromatography. Thermal analyses were made on the du Pont 950 thermogravimetric analyzer (TGA) and the 900 differential thermal analyzer (DTA). A General Electric time share computer was employed to obtain the least-squares plots of the kinetic data.

Polymer Samples

Samples of nylon 6 used throughout this work were obtained from American Enka Corporation of Enka, North Carolina. The polymer was obtained in chip form having a number-average molecular weight of approximately 15,000. The chains were capped with benzoic acid for molecular weight control. No delustrant was added to the polymer in order to minimize the number of variables in the system. Due to variations in the size of the nylon 6 chip and the need for uniformity in the experimentation, the polymer was ground into a fine powder in a mill with a rotary blade. The powder was conditioned at 75°C at atmospheric pressure for 5 hr and stored in a vacuum desiccator over phosphorus pentoxide prior to use.

Preparation of Nylon 6 Films Treated With Flame Retardants

In order to incorporate flame retardants into the polymer, the nylon 6 was dissolved in four parts by weight of trifluoroethanol with one part polymer, with continuous stirring for 3 hr. The flame retardant was added and the mixture was stirred for an additional 3 hr until a uniform mixture was obtained. A film was cast by pouring the mixture on a glass plate coated with tetrafluoroethylene which was seated on a water bath at 80°C. The film was air dried, removed from the plate, and placed in an oven at

85°C for 10 min and ground into a powder. In order to remove most of the remaining solvent, the powder was placed in the oven at 85°C at atmospheric pressure for 3 hr.

The two flame retardants used in the study were dodecabromopentacyclo(5.3.0.0^{2,6}.0^{3,9}.0^{4,8}) decane (C₁₀Br₁₂) (obtained from Dow Chemical Co.) and hexabromobiphenyl (obtained from Michigan Chemical Co.). Samples were prepared such that they contained 10 percent bromine from C₁₀Br₁₂ and 16 percent bromine from hexabromobiphenyl. The bromine contents of the treated films were based on the weight of nylon in all cases.

Gas-Chromatographic Analyses of Pyrolyzate Solutions

Both isothermal and programmed modes of vapor-phase chromatography were used to analyze the pyrolyzate solutions and some known compounds considered to be possible decomposition products. A 6-ft silicone-gum rubber SE-52 column was used for the study.

The following conditions gave satisfactory separations for analyses:

Programmed: starting temperature, 90°C; temperature rate, 15°C/min; final temperature, 250°C; injection port, 305°C; detector block, 250°C; helium flow, 60 ml/min.

Isothermal: column temperature, 240°C; injection port, 305°C; detector block, 250°C; helium flow, 60 ml/min.

Determination of the Percentage of the Sample Trapped in the Pyrolyzate Solution

The percentage of the original sample trapped in the pyrolyzate solution was determined by weight difference. A weighed amount of carbon tetrachloride was placed in the trap attached to the TGA. The amount of polymer decomposed was calculated by subtracting the residue from the weight of the original sample. During decomposition, some of the products condensed on the walls of the oven cover and in the glass tubing leading to the trap. These were washed with solvent and added to the pyrolyzate solution. A known amount of the solution was added into a weighed beaker. The solvent was evaporated at 80°C at atmospheric pressure; the residue was cooled in a desiccator and reweighed. From the weight difference, the percentage of polymer trapped could be estimated. Approximately 80% of the original weight was trapped in the pyrolyzate solution.

RESULTS AND DISCUSSION

Samples of nylon 6 were decomposed isothermally at 400°C and 500°C and the pyrolyzates trapped in CCl₄ at 0°C. These solutions showed characteristic bands at 3200 cm⁻¹, 2930 cm⁻¹, and 1670 cm⁻¹ (Figs. 1 and 2). Since nylon 6 is a polyamide, a band in the 3200 cm⁻¹ to 3500 cm⁻¹ region would correspond to a nitrogen-hydrogen stretching frequency. A band at precisely 3200 cm⁻¹ could correspond to a dilute solution of a

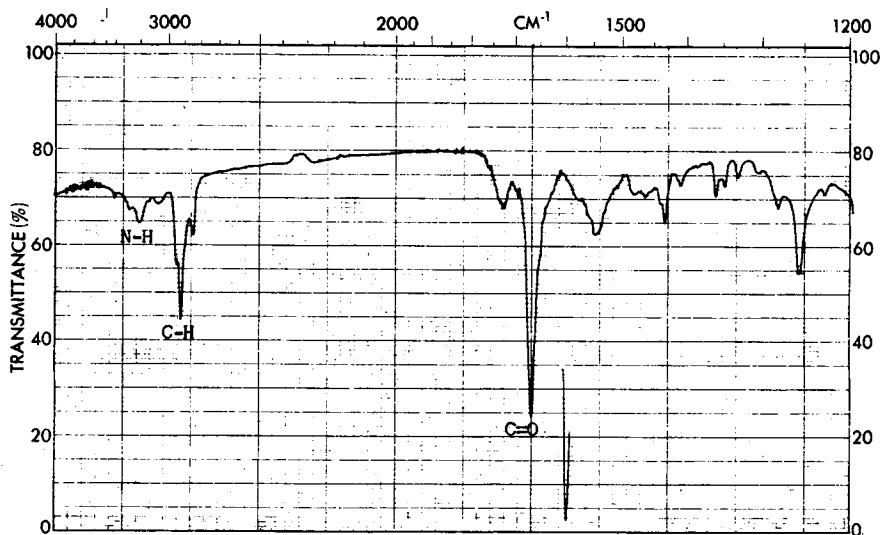


Fig. 1. Infrared spectrum of the pyrolyzate solution of Nylon 6 decomposed at 400°C.

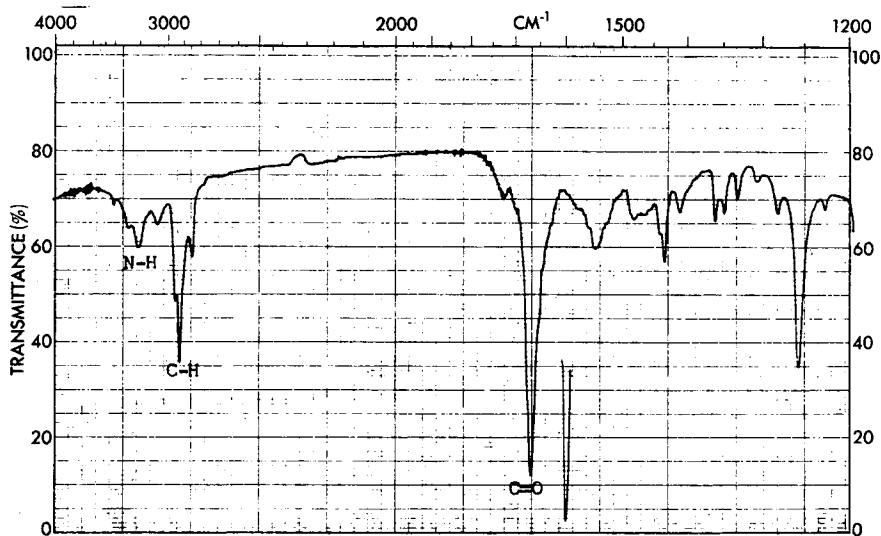


Fig. 2. Infrared spectrum of the pyrolyzate solution of Nylon 6 decomposed at 500°C.

secondary bonded amide. At 2930 cm^{-1} , the band represents the carbon-hydrogen stretching frequency of an alkane. The strong carbonyl stretching frequency at 1680 cm^{-1} in an amide system could indicate a cyclic lactam.

Identification of these functional groups in the pyrolyzate solutions led to a comparison with ϵ -caprolactam, the monomer of nylon 6. The infrared scan of a 1% solution of ϵ -caprolactam in carbon tetrachloride was quite similar to the scans of the pyrolyzate solutions of nylon 6 (Fig. 3).

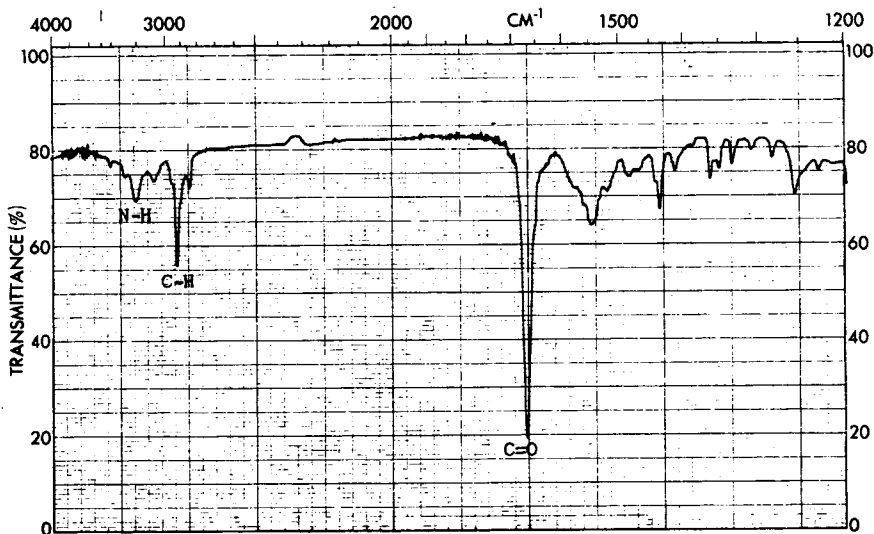


Fig. 3. Infrared spectrum of a 1% solution of ϵ -caprolactam in carbon tetrachloride.

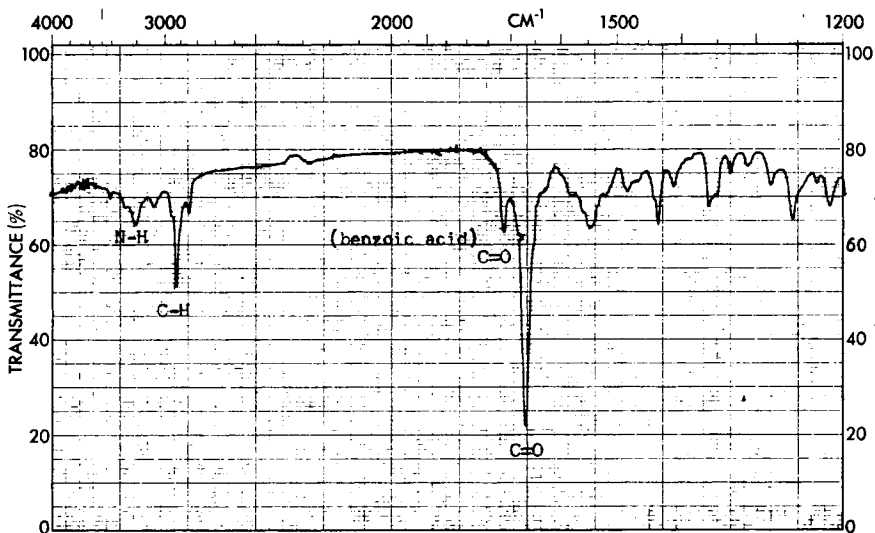


Fig. 4. Infrared spectrum of a 1% solution of ϵ -caprolactam in carbon tetrachloride to which benzoic acid has been added.

The characteristic bands on each of the spectra were almost superimposable. A small shoulder on the carbonyl peak at 1725 cm^{-1} is found in the spectra of the pyrolyzate solutions but not on the ϵ -caprolactam scan. This band was thought to be due to the presence of benzoic acid which is used to cap the polymer chains for molecular weight control. Some benzoic acid was added to the solution of ϵ -caprolactam, and the infrared scan did show a peak at 1720 cm^{-1} (Fig. 4). This substantiates the possibility that

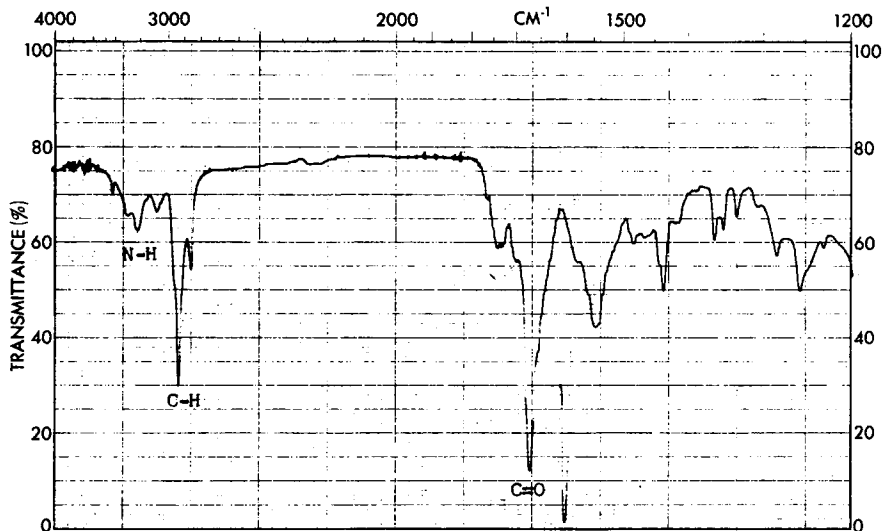


Fig. 5. Infrared spectrum of the pyrolyzate solution of Nylon 6 treated with hexabromobiphenyl decomposed at 400°C.

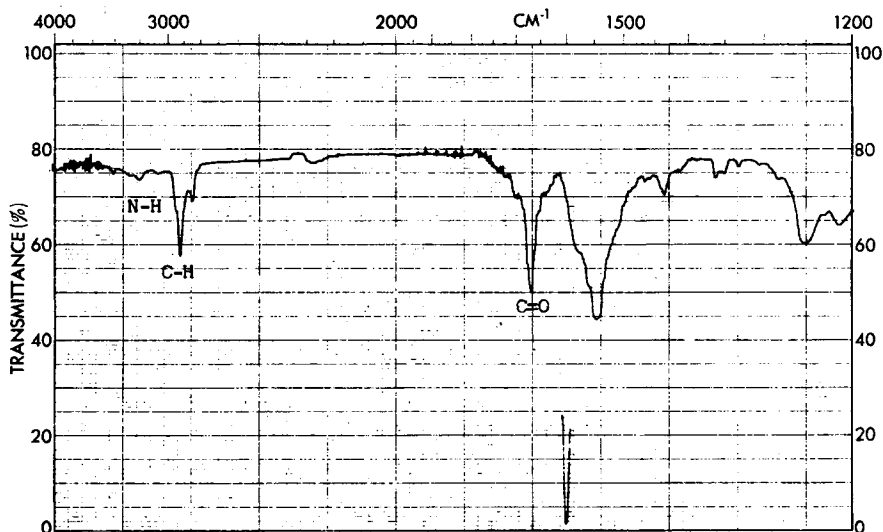


Fig. 6. Infrared spectrum of the pyrolyzate solution of Nylon 6 treated with $C_{10}Br_1$ decomposed at 400°C.

benzoic acid may be responsible for the shoulder in the carbonyl regions seen on the scans of the pyrolyzate solutions.

Infrared spectra were made of the pyrolyzate solutions from the nylon 6 samples treated with hexabromobiphenyl and $C_{10}Br_{12}$. Characteristic bands again appeared at 3200 cm^{-1} , 2930 cm^{-1} , and 1670 cm^{-1} . These were the same as for the untreated nylon 6 and the 1% solution of ϵ -capro-

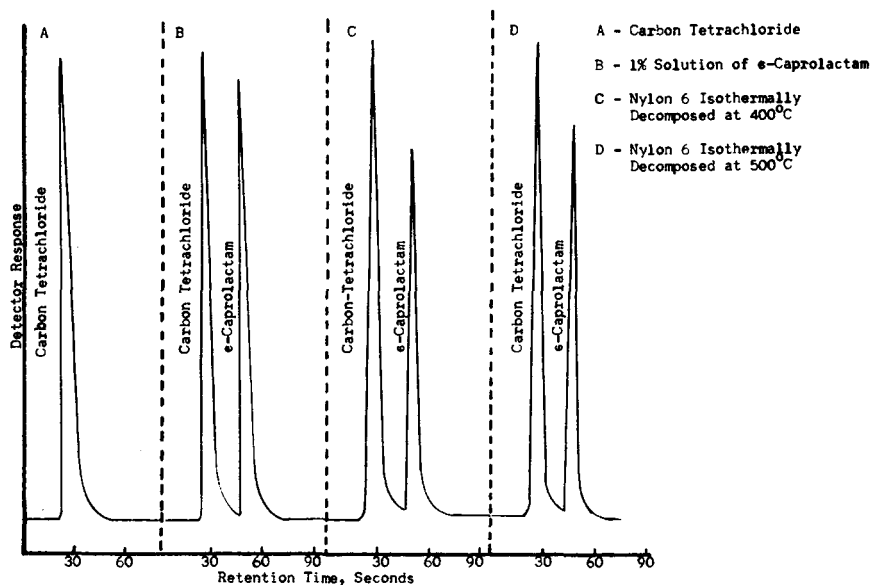


Fig. 7. Gas chromatographs of Nylon 6 pyrolyzate solutions compared to a 1% solution of ϵ -caprolactam in carbon tetrachloride.

lactam. The results indicate that ϵ -caprolactam is the major decomposition product for both the untreated nylon 6 and the nylon 6 treated with brominated flame retardants.

The pyrolyzate solutions of the nylon 6 samples were further analyzed by means of isothermal gas chromatography. Based on the findings of the infrared analyses, a 1% solution of ϵ -caprolactam was also included in the study. Two major peaks appeared for each of the samples (Fig. 5, A to D). The first peak was the solvent, carbon tetrachloride, and the second peak was identified as ϵ -caprolactam. The retention times for the nylon 6 pyrolyzate solutions and the one percent ϵ -caprolactam were the same.

In order to further substantiate these findings, the samples were again compared using programmed gas chromatography. In this study, both the treated and untreated nylon 6 samples were analyzed. For each of the samples, two major peaks appeared (Figs. 6–8). These again were the carbon tetrachloride and ϵ -caprolactam. Some minor peaks appeared in the scans of the pyrolyzate solutions. These components had greater retention times than that of ϵ -caprolactam. Although these peaks could not be positively identified, it is believed that they may be cyclic oligomers of ϵ -caprolactam. Preliminary investigations made by mass spectrometry showed significant quantities of cyclic dimers and trimers among the decomposition products.

Gas chromatography further substantiates the findings of the infrared study, namely, that ϵ -caprolactam is the main product of the thermal decomposition of nylon 6, for both the treated and untreated polymer.

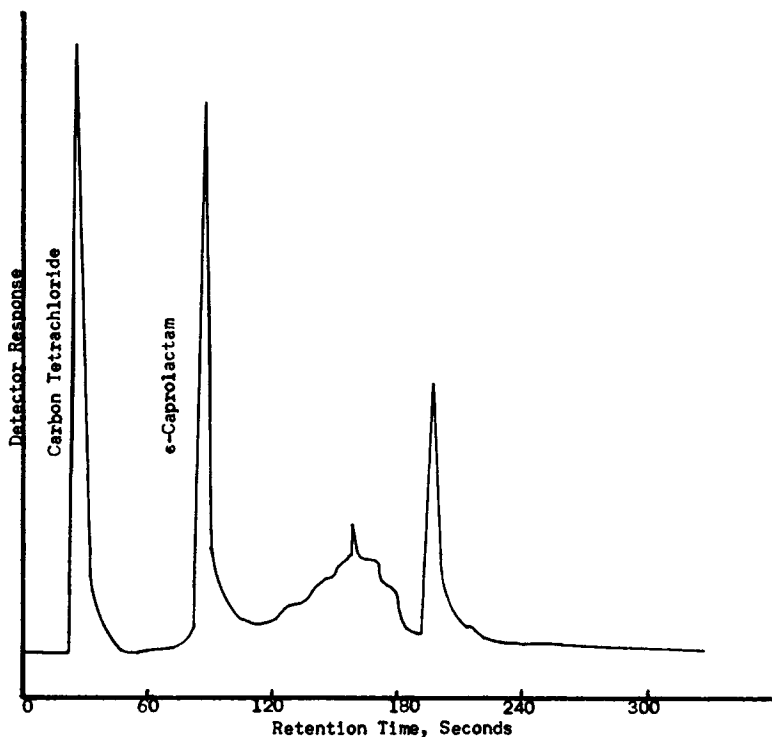


Fig. 8. Gas chromatograph of pyrolyzate solution of Nylon 6 programmed at 15°/min from 90°C to 250°C.

This indicates that these flame retardants do not alter the pathway of the nylon pyrolysis in a manner analogous to the way many flame retardants act in cellulose.¹¹ However, this cannot be taken as an indication of a complete lack of condensed phase activity on the part of these reagents.

A better technique to detect condensed phase activity would be through the use of thermal analysis; thus, DTA and TGA scans of both treated and untreated nylon 6 were made and analyzed to determine the effect of the bromo compounds on the thermal decomposition of the polymer.

A comparison of the TGA scans of the untreated sample and the sample treated with hexabromobiphenyl shows the treated sample exhibiting a decrease in decomposition temperature of 50°C in relation to the untreated nylon 6 (Fig. 9). The DTA curves of the same two samples further illustrate the change in decomposition temperature by the presence of a large endotherm at 355°C on the scan of the treated sample (Fig. 10). The endotherm indicates that a condensed phase reaction is taking place between the flame retardant and the polymer. This reaction, although it does not alter the decomposition products, has a marked effect on the decomposition temperature.

The effect of C₁₀Br₁₂ on the nylon 6 was quite similar to that of the hexabromobiphenyl. The decomposition temperature is lowered by 150°C

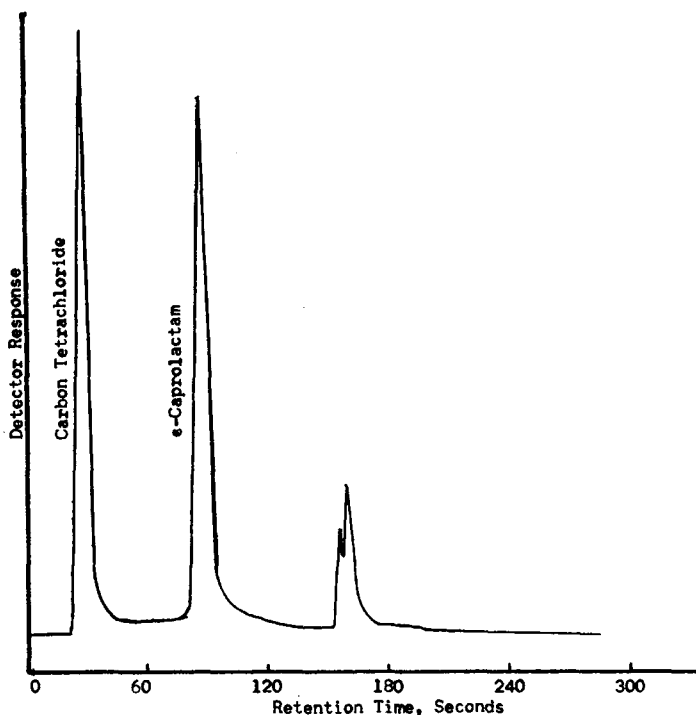


Fig. 9. Gas chromatograph of Nylon 6 treated with hexabromobiphenyl programmed a $15^{\circ}/\text{min}$ from 90°C to 250°C .

owing to the presence of the brominated flame retardant (Fig. 11). An endotherm appears in the DTA scan of the treated sample at approximately 280°C , again indicating that a condensed phase reaction is accompanying the decrease in decomposition temperature (Fig. 12).

In each case the thermal analysis data taken together with the infrared and gas-chromatographic data indicate that the decomposition products are not changed by the presence of the bromo compounds but that the decomposition reaction takes place at a lower temperature. These results show that the brominated flame retardants act as catalysts for the decomposition reaction. This should be most obviously reflected in the kinetics of the decomposition reaction, and kinetics would therefore seem to offer the best probe into the nature of the effect. Such studies can be quite easily carried out using TGA and the method of Mickelson and Einhorn.¹²

It was decided that the portion of the thermogram representing 80% to 20% undecomposed polymer would be studied. This area was chosen for several reasons. At the extremities of the thermogram where the curve is most pronounced, inaccuracies arise due to the measuring techniques. Also, with some polymers, initial weight loss is due to liberation of monomer which remains in the system after polymerization. This is the case with nylon 6, an equilibrium polymer, where ϵ -caprolactam is liberated

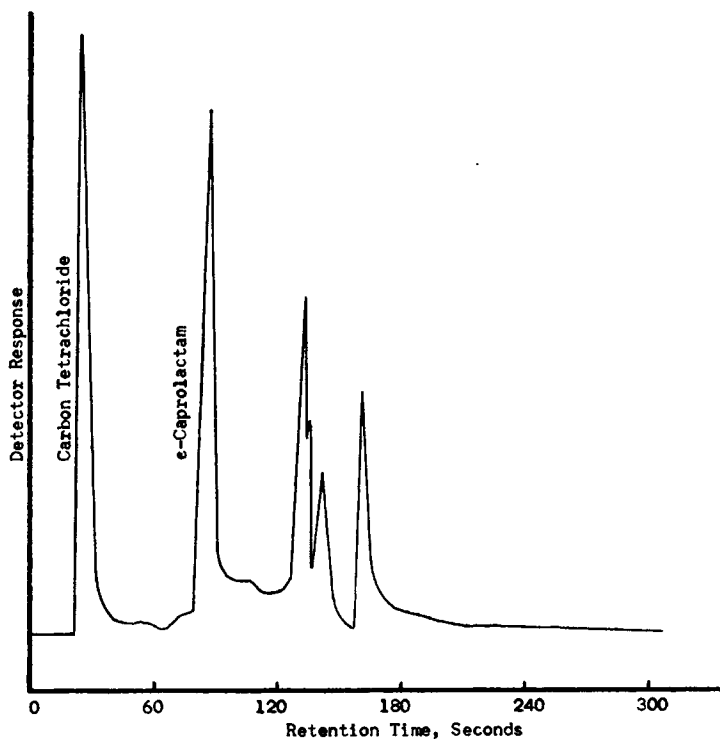


Fig. 10. Gas chromatograph of Nylon 6 treated with $C_{10}Br_{12}$ programmed at $15^\circ/\text{min}$ from 90°C to 250°C .

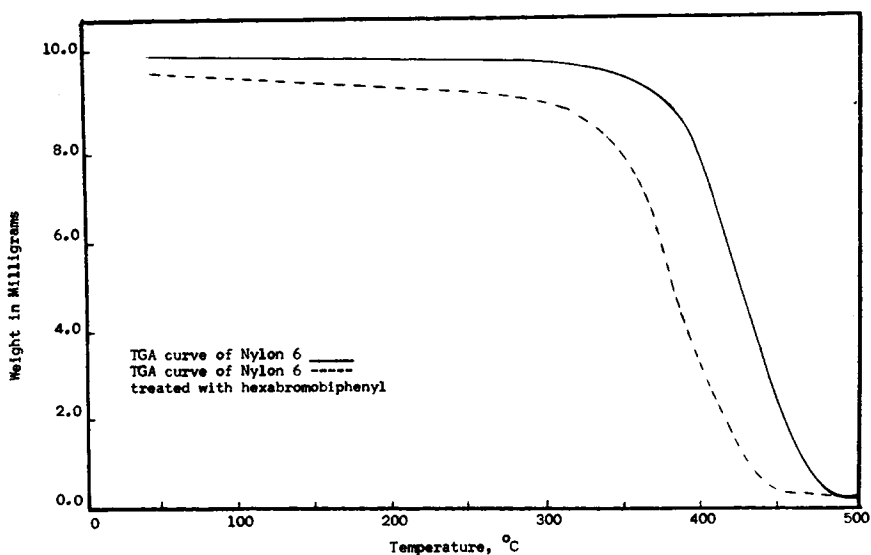


Fig. 11. Plot of the thermogravimetric analysis (TGA) curve of Nylon 6 compared to the TGA curve of Nylon 6 treated with hexabromobiphenyl. Samples were decomposed at a heating rate of $6^\circ\text{C}/\text{min}$.

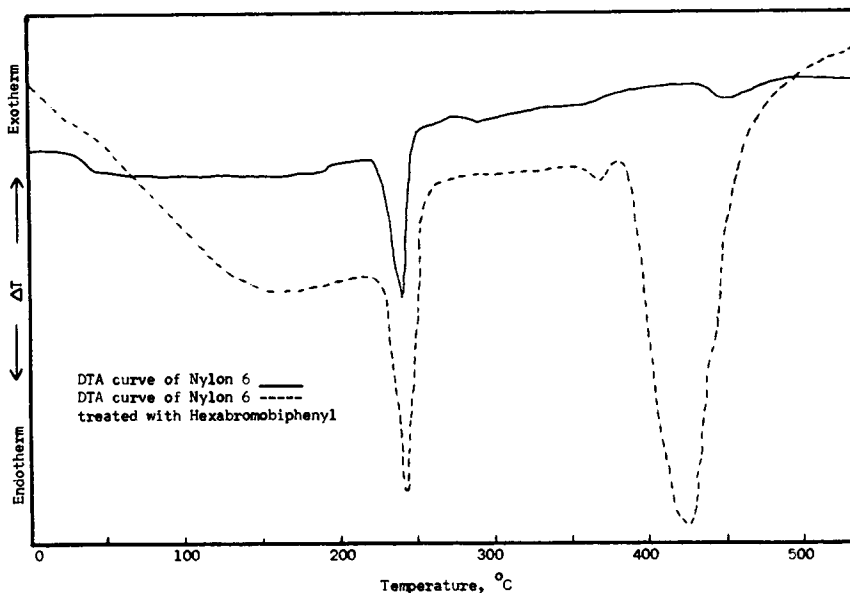


Fig. 12. Plot of the differential thermal analysis (DTA) curve of Nylon 6 compared to the DTA curve of Nylon 6 treated with hexabromobiphenyl.

and is thus partly responsible for initial weight loss. This evolution of ϵ -caprolactam was observed in some preliminary mass spectrometry studies. Another complication at the initial stages of decomposition was posed by Straus and Wall.² They hypothesized that two types of decomposition mechanisms were competing, both ionic and free radical. The ionic reaction is caused by the presence of absorbed water in the polymer which could attack the peptide links and cause hydrolytic scission. For a series of polyamide samples, they observed that the amount of water found in the pyrolysis products is least for the sample with the highest activation energy. The activation energies ranged from 42 kcal/mole for the sample with the least amount of water to 30 kcal/mole for the sample with the most water. The authors considered the value of 42 kcal/mole the most representative of a free-radical reaction, which, at pyrolytic temperatures, seems to be the most common mode of decomposition. Kamerbeek⁶ and Potemkina⁸ also support the theory of two different decomposition reactions, the ionic reaction being initiated by water. By disregarding the initial stages of decomposition, the effect of the water on the system will be minimized and the actual thermal decomposition of the polymer should be observed.

Flynn and Wall¹¹ in their review of kinetic determinations from thermogravimetric experiments stated that, in order to obtain reliable kinetic parameters, the polymer must be decomposed at several heating rates. In order to fulfill this requirement, samples of nylon 6 ranging from 10 to 12 mg were decomposed at three different heating rates, 6°C, 10°C,

TABLE I
Kinetic Parameters of Nylon 6 Determined by the Ratio Method at Various Heating Rates

Sample	Heating rate, °C/min	Reaction order	Activation energy, kcal/mole
Nylon 6	6	.93 ± .04	46 ± 3
Nylon 6	10	.96 ± .04	46 ± 3
Nylon 6	20	.94 ± .04	47 ± 3
Nylon 6 pre-heated to 275°C	6	.93 ± .04	45 ± 3

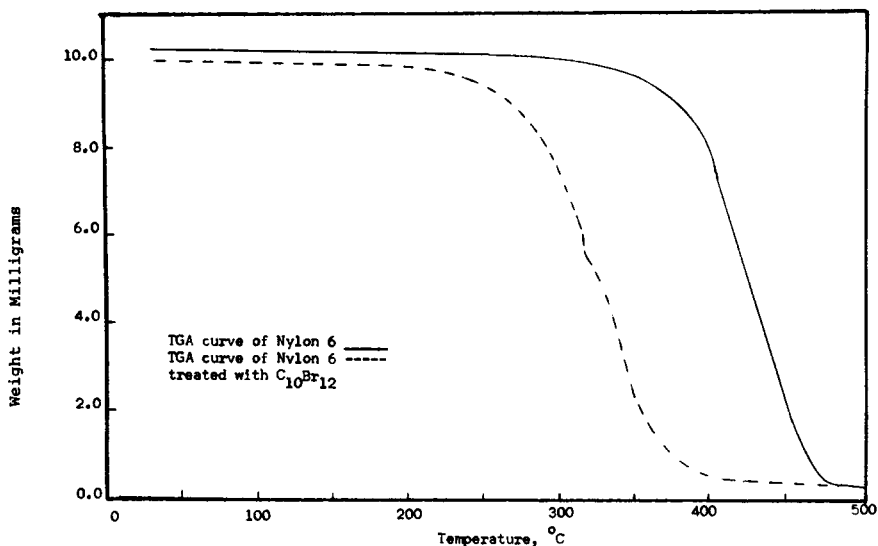


Fig. 13. Plot of the thermogravimetric analysis (TGA) curve of Nylon 6 compared to the TGA curve of Nylon 6 treated with $C_{10}Br_{12}$. Samples were decomposed at a heating rate of $6^{\circ}C/min$.

and $20^{\circ}C$ per minute (Figs. 13 and 14). Activation energy and order of reaction were calculated for the various samples (Table I). The kinetic data showed excellent agreement between the samples. Order of reaction approached first order for each of the samples, and the activation energy was approximately 46 kcal/mole in each case.

Reimschuessel and Dege¹³ in their investigation of the effect of heat on nylon 6 mentioned the possibility of hydroperoxides effecting the thermal decomposition of the polymer. Due to the high temperatures at which nylon 6 is extruded and its exposure to oxygen during processing, oxidation products such as hydroperoxides may be present. In order to determine whether such oxidation products were effecting the decomposition reaction in this study, a sample was preheated to $275^{\circ}C$ and cooled to room temperature before decomposing. At these temperatures, the oxidation prod-

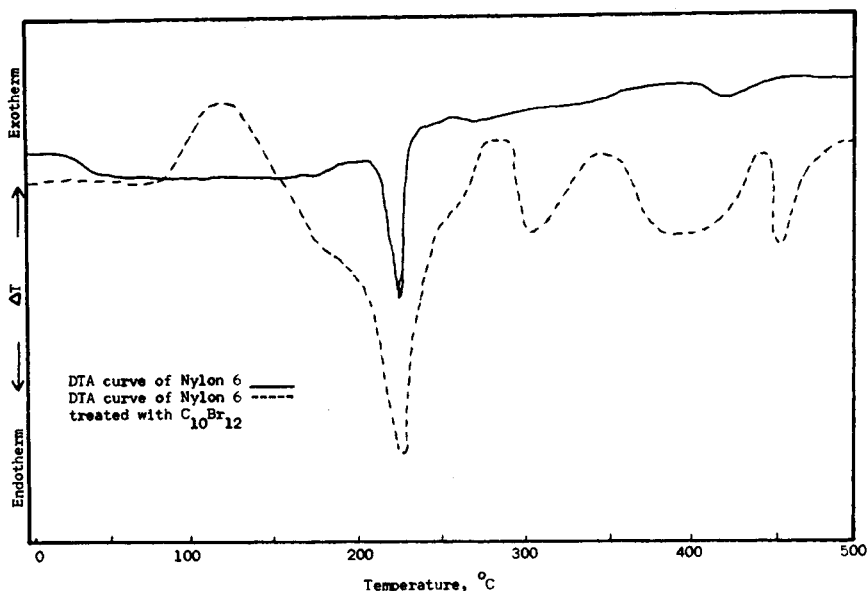


Fig. 14. Plot of the differential thermal analysis (DTA) curve of Nylon 6 compared to the DTA curve of Nylon 6 treated with $C_{10}Br_{12}$.

ucts, if any, should be destroyed. The preheated sample was then decomposed at a heating rate of $6^{\circ}\text{C}/\text{min}$ and the kinetic data were determined. Comparison of activation energy and order of reaction (Table I) with the original samples shows a close agreement. These results indicate that oxidation products are not effecting the decomposition of the nylon 6.

As was previously stated, the kinetic parameters for the nylon 6 samples were determined at three different temperature rates to ensure reliability. In this same manner, the activation energy and order of reaction were calculated for the samples treated with the brominated flame retardants. The addition of the hexabromobiphenyl to the nylon 6 caused the activation energy to be lowered to 38 ± 3 kcal/mole, or a decrease of 8 kcal. Order of reaction remains the same, approximately first order (Table II). These kinetic data are in agreement with the thermogravimetric analyses which show a decrease in activation energy accompanying a decrease in decomposition temperature. The close agreement of order of reaction for both the treated and untreated samples indicate that the mechanism of decomposition is the same in both cases. This point is further substantiated by the fact that ϵ -caprolactam is the major decomposition product for all the samples. The flame retardant appears to be reacting in the condensed phase to catalyze the decomposition so that activation energy and decomposition temperature are lowered.

Samples of nylon 6 treated with $C_{10}Br_{12}$ exhibited similar behavior to that of the samples treated with hexabromobiphenyl (Table II). The activation energy was lowered to approximately 30 ± 3 kcal/mole or a

TABLE II
Kinetic Parameters of Nylon 6 Treated with Brominated Flame Retardants Determined
by Ratio Method at Various Heating Rates

Sample	Heating rate, °C/min	Reaction order	Activation energy, kcal/mole
Nylon 6	6	.93 ± .04	46 ± 3
Nylon 6	10	.96 ± .04	46 ± 3
Nylon 6	20	.94 ± .04	47 ± 3
Nylon 6 with hexabromobiphenyl	6	1.02 ± .04	38 ± 3
Nylon 6 with hexabromobiphenyl	10	1.04 ± .04	38 ± 3
Nylon 6 with hexabromobiphenyl	20	1.02 ± .04	37 ± 3
Nylon 6 with C ₁₀ Br ₁₂	6	.96 ± .03	29 ± 3
Nylon 6 with C ₁₀ Br ₁₂	10	.98 ± .03	31 ± 3
Nylon 6 with C ₁₀ Br ₁₂	20	.96 ± .03	31 ± 3

decrease of 16 kcal from the untreated nylon 6. The reaction remained approximately first order. Again the decrease in decomposition temperature as seen on the TGA curve is accompanied by a decrease in activation energy. The C₁₀Br₁₂ appears to be reacting in the same manner as the hexabromobiphenyl, that is, catalyzing the decomposition in the condensed phase, but not changing the decomposition mechanism.

SUMMARY AND CONCLUSIONS

The investigation has shown the following points:

1. ϵ -Caprolactam is the main product of the thermal decomposition of nylon 6.
2. ϵ -Caprolactam remains the main product of decomposition when nylon 6 is treated with hexabromobiphenyl or C₁₀Br₁₂.
3. Two brominated flame retardants cause a decrease in decomposition temperature of the nylon 6.
4. A condensed phase reaction takes place between the nylon 6 and the flame retardants.
5. Activation energy is also lowered due to the presence of the flame retardants.
6. Order of reaction remains the same for all the samples.

The observations indicate that the brominated compounds should not be effective flame retardants for nylon 6. An efficient flame retardant would induce the production of noncombustible products or slow down the production of combustible compounds. These brominated compounds catalyze the decomposition by lowering the decomposition temperature while the decomposition products remain the same. The rate of fuel production is increased by the catalyzing effect of the brominated compounds

in the condensed phase. This reaction may offset the radical inhibition of the Br. in the vapor phase.

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