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PART III

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## **THERMAL DEGRADATION STUDIES OF POLYMERS AT HIGH TEMPERATURES**

**S. L. MADORSKY, S. STRAUS, AND M. E. VACKS**

**NATIONAL BUREAU OF STANDARDS**

**NOVEMBER 1961**

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WADD TECHNICAL REPORT 59-64  
PART III

## **THERMAL DEGRADATION STUDIES OF POLYMERS AT HIGH TEMPERATURES**

*S. L. MADORSKY, S. STRAUS, AND M. E. WACKS*

*NATIONAL BUREAU OF STANDARDS*

*NOVEMBER 1961*

DIRECTORATE OF MATERIALS AND PROCESSES  
DELIVERY ORDER No. (33-616)-58-8  
PROJECT No. 7340

AERONAUTICAL SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

## FOREWORD

This report was prepared by the National Bureau of Standards under WADC Order No. (33-616) 58-8, Project No. 7340: "New Chemicals and Methods". The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division.

This report, "Thermal Degradation Studies of Polymers at High Temperatures", which covers the work carried out from February 1, 1960 to April 16, 1961, is divided into two Sections.

Section A. This Section, "Thermal Degradation of Polymers Up to 1200°C", was prepared by S. L. Madorsky and S. Straus of the Polymer Structure Section of the National Bureau of Standards. The present report represents the termination of this portion of the project.

Section B. This Section, "Degradation Studies of Mass Spectrometer Techniques", was prepared by Morton E. Wacks and Vernon H. Dibeler of the Mass Spectrometry Section of the National Bureau of Standards. This portion of the project is being continued into the next year.

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ABSTRACT

Section A: An investigation was made of the thermal degradation of polydivinylbenzene and a series of copolymers of styrene with divinylbenzene and with trivinylbenzene in the temperature range 346 to 450°C. One phase of this investigation involved a study of the relative thermal stability of these polymers and copolymers and of the qualitative and quantitative compositions of the degradation products. Another phase consisted of a study of rates and activation energies of thermal degradation of these materials. The results indicate a gradual increase of thermal stability of the copolymers as the amount of the crosslinking agents, divinylbenzene or trivinylbenzene, is increased. An investigation was also made of thermal degradation of polystyrene, polymethylene, polytetrafluoroethylene, poly- $\alpha$ -methylstyrene, polypropylene, polyisobutylene, and poly(methyl methacrylate), at temperatures up to 1200°C, in a vacuum and in helium at atmospheric pressure. The pyrolysis produce a greater fragmentation of the degradation products.

Section B: Instrumentation for the study of the basic processes occurring in the thermal degradation of organic material has been decided upon and obtained. Existing equipment has been modified to complement the newly acquired equipment. With this instrumentation the initial stages of degradation are to be studied. Some tests and specifications on the newly acquired Bendix Corporation time-of-flight mass spectrometer are discussed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



A. M. Lovelace  
Chief, Polymer Branch  
Nonmetallic Materials Laboratory  
Directorate of Materials and Processes

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## SECTION A

### THERMAL DEGRADATION OF POLYMERS AT TEMPERATURES UP TO 1200°C\*

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#### I. INTRODUCTION

The previous annual report<sup>1</sup> describes some studies on the thermal degradation in a vacuum of copolymers of styrene (St) with divinylbenzene (DVB) or with trivinylbenzene (TVB) in the temperature range of 346° to 450°C, also on the pyrolysis of simple vinyl polymers up to 1200°C. The main objective in the studies on copolymers was to determine the effect of crosslinking agents such as DVB and TVB on the thermal stability of polystyrene. The copolymers that were studied had the following compositions in weight percent: 98St - 2DVB; 75St - 25DVB; 52St - 48DVB; 44St - 56DVB, and 75St - 25TVB. Using a previously described method<sup>2</sup> of evaluating the relative thermal stability of a polymer, it has been found that the presence of 2% of DVB does not change appreciably the thermal stability of polystyrene. The addition of 25% increases the thermal stability by about 9°C. Additions of 48% or 56% DVB, or of 25% TVB, increase the thermal stability by 27°-35°C. In addition to these copolymers a study has also been made previously of pyrolysis of polymethylene in a vacuum and in helium in the temperature range 330° to 1200°C. The results indicated that the higher the temperature and pressure of pyrolysis the greater was the fragmentation of the degradation products.

All these studies have been extended and amplified during the past year to include not only the polymers and copolymers indicated above but also the following additional polymers: Polydivinylbenzene (PDVB), polystyrene, polytetrafluoroethylene, poly- $\alpha$ -methylstyrene, polypropylene, polyisobutylene, and poly(methyl methacrylate). The findings and conclusions of these studies are described in this report.

Most carbon-chain polymers begin to lose weight appreciably when heated in a vacuum in the temperature range 200° - 300°C, although polytetrafluoroethylene, which is the most

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\*Manuscript released by authors June 15, 1961, as an ASD  
Technical Report 59-64 Pt III.

stable of such polymers, does not begin to lose weight appreciably until about 400°C. However, all these polymers vaporize almost completely when heated above 500°C. We have previously chosen and used an arbitrary scale for measuring the relative thermal stability of this type of polymer.<sup>2</sup> This scale is based on a temperature of half life, designated as  $T_h$ , which is defined as the temperature at which a polymer loses half of its weight in 30 min of heating in a vacuum. For example, poly- $\alpha$ -methylstyrene, poly-(methyl methacrylate), polyisobutylene, polystyrene, polymethylene, and polytetrafluoroethylene have  $T_h$  values of 286°, 327°, 348°, 364°, 414°, and 509°C, respectively.<sup>2-4</sup> However, polymers such as polyacrylonitrile or poly(vinylidene fluoride), which develop double bonds or crosslinks or both during pyrolysis, or a polymer like polytrivinylbenzene, which is highly crosslinked to start with, do not vaporize completely even at temperatures far above 500°C; but instead they form more or less completely carbonized residues.<sup>5</sup> The  $T_h$  scale could not be used as a reliable measure of the relative thermal stability of these crosslinked polymers. A more appropriate scale of comparison in this case would be a measure of the amount of carbonaceous residue and the extent of carbonization of this residue.

The overall effect of a higher temperature of pyrolysis in a vacuum is that there is a greater fragmentation of the volatile products of decomposition. A similar effect is produced when the polymer is heated in a neutral atmosphere, such as helium. Pyrolysis studies in an air atmosphere have been avoided because the reaction of oxygen with the products of degradation would make it very difficult to interpret the purely thermal effect on the degradation of the polymers.

## II. EXPERIMENTAL

### 1. Apparatus and Procedures

Studies on the thermal degradation of PDVB and of copolymers of DVB and TVB with St consisted in pyrolyzing these materials, determining their relative thermal stability, and making qualitative and quantitative determinations of the products of degradation. In addition, the rates of thermal degradation were measured at various temperatures, and the overall activation energies of degradation were calculated on the basis of these rates by means of the Arrhenius equation. Studies on the thermal degradation of the simple vinyl polymers involved only pyrolysis of these materials at temperatures up to 1200°C and analysis of the volatile products of degradation.

The apparatus used in the pyrolysis studies was the same as that used in the pyrolysis of polytrivinybenzene (PTVB) and other polymers.<sup>1</sup> Samples weighing 15-30 mg were heated in a vacuum by quickly moving a preheated furnace into position surrounding the sample for pyrolysis. At temperatures below 500°C a 5-min period was used to heat up the sample from room temperature to the temperature of pyrolysis, followed by a 30-min period at the pyrolysis temperature. Fluctuation of the final temperature was  $\pm 2^\circ\text{C}$ . The residues were weighed, and the volatile products were collected and fractionated. The following volatilized fractions were obtained: a) a wax-like fraction, designated as  $V_{\text{pyr}}$ , volatile at the temperature of pyrolysis, but not at room temperature. It consisted of large molecular fragments deposited in the apparatus just beyond the hot zone; b) a light fraction,  $V_{25}$ , volatile at room temperature, collected in a liquid-nitrogen-cooled trap; and c) a gaseous fraction,  $V_{190}$ , not condensable at the temperature of liquid nitrogen. In some cases a fraction,  $V_{80}$ , volatile at the temperature of dry ice, was also collected. Analysis of fractions  $V_{25}$ ,  $V_{80}$ , and  $V_{190}$  was made by means of a mass spectrometer.

The rates of thermal degradation were measured in a vacuum by a gravimetric method, which makes use of a very sensitive tungsten spring balance having a sensitivity of about  $570\mu/\text{mm}$  of displacement. The apparatus and experimental procedure have been described in detail in an earlier publication.<sup>6</sup> Samples were limited to about 5 mg and were heated in a platinum crucible.

## 2. Materials Used

The copolymers were the same as those used by Winslow and Matreyek<sup>7\*</sup> in their pyrolysis work. The PDVB was prepared by heating a pure grade of DVB monomer in an evacuated and sealed 6-mm Pyrex tube in an oven at 80-90°C for 6 weeks. The tube was then opened, and the polymer, which was in the form of a rod, was heated further for 1 hr in an evacuated chamber at 120°C. A loss of 8%, presumably monomer, took place during this heating step, but no additional loss occurred on further heating at this temperature.

The following homopolymers were used:

- (a) Polystyrene. Thermally prepared. Molecular weight

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\*The authors are indebted to F. H. Winslow of Bell Telephone Laboratories for supplying them with samples of these copolymers.

230,000 as determined by the osmotic pressure method.

- (b) Polymethylene. A nonbranched high molecular weight material prepared by treating an ether solution of diazomethane with boron trifluoride etherate.
- (c) Polytetrafluoroethylene. A Teflon tape 0.07 mm thick. The molecular weight is not known, but estimated to be very high.
- (d) Poly- $\alpha$ -methylstyrene. A flaky material obtained from the Dow Chemical Company. It was prepared by low-temperature polymerization and had a molecular weight of 350,000 as determined by light scattering.
- (e) Polypropylene. A fine white powder, prepared by B. F. Goodrich Company using the Ziegler method. Its molecular weight was indicated as being between 50,000 and 100,000.
- (f) Polyisobutylene. A pure grade white gum, currently used as a National Bureau of Standards standard material for viscosity measurements. It had a weight average molecular weight of 1,560,000 as determined by the light-scattering method.
- (g) Poly(methyl methacrylate). Prepared from the monomer at room temperature without the use of catalysts. It had a molecular weight of 5,100,000 as determined by light-scattering.

### III. RESULTS FROM THERMAL DEGRADATION

#### 1. Copolymers of Styrene with Divinylbenzene and with Trivinylbenzene

a) Pyrolysis:- Polystyrene was found to decompose thermally in a vacuum<sup>7,8</sup> or in a neutral atmosphere<sup>5,9</sup> at temperatures up to 850°C by a mechanism consisting of random scissions of C-C chain bonds, followed by unzipping at the resulting free-radical chain-ends to yield monomers and also multiples of structural units of an average molecular weight of about 264. Under these conditions complete volatilization of the sample takes place, for example, at 400°C in about 30 min of heating. On the other hand, polytrivinylbenzene (PTVB),<sup>5</sup> in which the structural unit consists of a trifunctional styrene, when pyrolyzed under similar conditions

does not yield any appreciable amounts of either St or of TVB monomers. Instead, the volatile degradation products consist of a fraction containing a small amount of hydrogen and of saturated and unsaturated hydrocarbon fragments having from 1 to 11 carbons; a less volatile fraction consists of larger fragments having an average molecular weight of 372; and the residue consists of a carbonaceous material.

The mechanisms of degradation of this highly crosslinked polymer are assumed to be as follows: When a C-C bond in the short connecting links between the phenyl groups breaks, two reactions are possible: a) a transfer of hydrogen may take place at the site of break so that one end becomes saturated and the other unsaturated, and b) the two ends become free radicals. In the latter case the free radicals do not unzip to form monomers because of the crosslinkages that hold the phenyl groups at other points. Instead, the free radicals abstract hydrogen from the surrounding medium and become saturated. As the number of such scissions increases, fragments of various sizes, which may or may not contain phenyl groups, split off from the chain, abstract some hydrogen from the residue, and vaporize. The residue in the meantime becomes carbonized in the process through loss of hydrogen.

Intermediate between these two extremes are copolymers of St with DVB or with TVB. An investigation of the thermal behavior of such copolymers was carried out by Winslow and Matreyek in nitrogen at atmospheric pressure at temperatures up to about 550°C. They were interested primarily in the relative thermal stability of these copolymers and in the nature of the residues and therefore did not study the volatile products of degradation. An attempt was made in the present study to obtain information on the mechanism of thermal degradation of these copolymers through analysis of the volatile products of degradation. A study was also made of the degradation of PDVB. The present work, as in the case of most of our other work on thermal degradation of polymers, was carried out in a vacuum. In addition to a study of the nature of the volatile degradation products, the rates and activation energies of degradation were also included. Allowing for the differences in the experimental conditions, our results are in fairly good agreement with those of Winslow and Matreyek.

Fractions V<sub>pyr</sub> and V<sub>25</sub> were weighed, and the amount of V<sub>-190</sub> was determined from pressure, volume, and chemical composition data. Fractions V<sub>25</sub>, V<sub>-80</sub>, and V<sub>-190</sub> were analyzed in the mass spectrometer. Fraction V<sub>-190</sub> was very small, less than about 0.1% by weight, and was found to consist primarily of CO. This is similar to the results obtained previously<sup>8</sup> in the case of polystyrene.

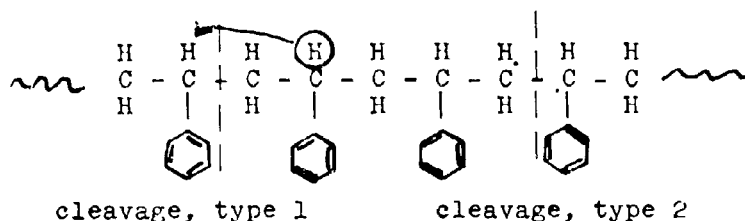


The relative thermal stabilities of PDVB and of copolymers of St with DVB and with TVB are shown in Figure 1. The data from which these curves are plotted are given in Table 1. Curves for polystyrene and PTVB are included in Figure 1 for comparison and are based on data obtained previously.<sup>3,5</sup> As can be seen from this figure, St-DVB copolymers containing only a small percentage of DVB have a thermal stability not much different from that of the styrene homopolymer. The copolymer containing 25% of DVB shows an increase in the stability over that of the polystyrene. Still greater quantities of DVB in the copolymers produce further increases in the thermal stability and when about 50% or more of DVB is present thermal stability is reached which is about equal to that of PDVB homopolymer. Polytrivinylbenzene (PTVB) has a higher thermal stability than that of the PDVB, and it requires only 25% of TVB in the St-TVB copolymer to equal the thermal stability of PDVB.

The relative amounts of volatilized fractions from the pyrolysis experiments on PDVB and the copolymers are given in Table 1. The V<sub>25</sub> fractions from a number of experiments on the copolymers were analyzed in the mass spectrometer, and the results are shown in Table 2. The mass spectrograph for fraction V<sub>25</sub> from PDVB was very complex and could not be interpreted completely. The results are therefore not indicated on the table. However, there was a definite indication of the presence of considerable amounts of toluene, benzene, styrene, and xylene. There was also a group of peaks in the mass-range of 112-118, corresponding to a compound C<sub>9</sub>H<sub>10</sub>.

In the 2%-DVB copolymer the yield of the styrene monomer, C<sub>8</sub>H<sub>8</sub>, was greater than that from 100% polystyrene, which had previously been found to be about 40 weight % of the total volatilized part. The yield of styrene decreased with an increase of DVB content in the copolymer and disappeared altogether when the content of DVB reached about 50%. There was, however, considerable styrene monomer content in the volatiles from the 25%-TVB copolymer.

The mechanism of thermal degradation of the copolymers of St with DVB or with TVB can be visualized as follows: In polystyrene, cleavage of the chain ordinarily takes place at the weakest bonds, which are the C-C bonds in  $\beta$ -position to the double bonds in the phenyl groups--in this case the ones in the main chain.



The cleavage can be of two types. Type 1 results in the formation of one saturated and one unsaturated end; and type 2 produces two free radicals, which proceed to unzip to give monomer, dimer, and trimer.<sup>8</sup> The monomer collects with other small fragments in fraction  $V_{25}$ , while the dimer, trimer, etc., appear in fraction  $V_{\text{pyr}}$ . On the addition of a small amount of a crosslinking agent, such as 2% DVB, the unzipping to give dimer and trimer is somewhat blocked by the shortening of the free chain between crosslinks, and more of the monomer appears at the expense of the multiple units. However, with an increase of crosslinks in the chain by the addition of DVB or TVB, the formation of monomer units is blocked. This is the case with the copolymer containing 25% DVB, where the yield of monomer falls off, or with the copolymer containing 25% TVB, where the yields of monomer fall off even more. When the amount of the crosslinking agent is further increased, as in the case of copolymers containing 50% or more of DVB, no monomer is found among the volatile products.

There were no signs of carbonization of the degradation residues from copolymers with 2% or 25% of DVB. However, for copolymers containing higher percentages of DVB and also for the 25%-TVB copolymer and the PDVB, the volatilization curves begin to level off at about 80% to 90% loss (Figure 1), and carbonization of the residue takes place. The PTVB volatilization curve<sup>9</sup> begins to level off at about 53% loss, and the residue shows considerable carbonization.

b) Rates:- Pertinent data on rates of thermal degradation of PDVB and of copolymers of St with DVB and with TVB are shown in table 3. Cumulative percentages of volatilization for the copolymers and for PDVB are shown plotted in Figures 2, 4, 6, 8, 10, and 12. These curves of percentage loss versus time were used

in calculating the data for the rate curves, which are shown plotted in terms of percentage loss per minute as a function of cumulative percentage volatilization, in Figures 3, 5, 7, 9, 11, and 13. In calculating the activation energies of the polymer degradation reactions by means of Arrhenius equation, the maximum rates were used in all cases except for the 25%-TVB copolymer, where the initial rates obtained by extrapolation (Figure 11) were used. The results of these calculations are shown plotted in Figure 14 and the numerical values of the activation energies are given in Table 3. Data for PTVB<sup>5</sup> are shown for comparison. The activation energies seem to increase with an increase in content of the cross-linking agent in the copolymer. An activation energy for polystyrene was previously found to be 55 kcal/mole,<sup>10</sup> which is about the same as that for the copolymers having small percentages of DVB.

## 2. Polystyrene

It was shown in an earlier study<sup>5</sup> on pyrolysis of polystyrene at 362° and 850°C in a vacuum and in helium at atmospheric pressure that higher temperatures and higher pressures produce a greater fragmentation of the volatile products. This is shown in Table 4, which is based on Table 2 of Reference 5, recalculated in terms of weight percent of total volatiles.

This study has now been extended to temperatures up to 1200°C. The volatile products were collected and fractionated in the usual manner, and the more volatile fractions were analyzed in the mass spectrometer. Results of analysis for pyrolysis in a vacuum are shown in Table 5 and those for pyrolysis in helium at atmospheric pressure in Table 6. As can be seen from these tables, the yield of monomer C<sub>8</sub>H<sub>8</sub> generally decreases with a rise in the temperature of pyrolysis either in a vacuum or in helium, while the yields of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> generally increase. In comparing the results of pyrolysis in a vacuum with that in He, the degradation products in helium pyrolysis show greater fragmentation, particularly at the higher temperatures.

## 3. Polymethylene

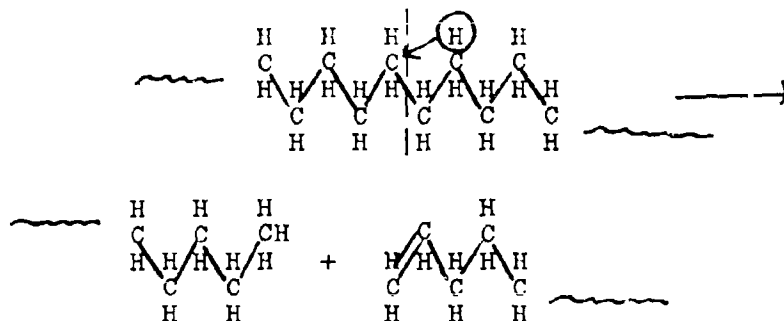
Of all carbon-chain polymers polymethylene is unique in that it has the highest ratio of hydrogen to carbon. It is very simple in structure and has a high thermal stability and a high activation energy for decomposition. A study of the behavior of this polymer

at high temperatures should therefore throw light on the mechanism of degradation of high-temperature polymers in general under similar conditions of pyrolysis. It has been studied previously<sup>8,10,11</sup> at temperatures below 500°C, and in the present work the temperature range has been extended to 1200°C.

Results of pyrolysis of polymethylene at 500°, 800°, and 1200°C, in a vacuum and also in helium at atmospheric pressure, are shown in Table 7. Results of previous pyrolysis<sup>4</sup> at 393° and 449° are also included in this table for comparison. As can be seen from this table, volatilization is almost complete above 500°C both in vacuum and in helium. The higher the temperature or pressure, the greater is the fragmentation of the volatile products. In the case of pyrolysis in helium the effect of temperature or pressure on the size of volatile fragments is somewhat masked in this table by the fact that the amounts of fractions  $V_{pyr}$  and  $V_{-190}$  are shown combined. We are dealing here with very small quantities of material, and it would have been very difficult to separate the gaseous products that are not condensable at the temperature of liquid nitrogen from the helium. The amount of  $V_{-190}$  was therefore calculated by difference, together with that of  $V_{pyr}$ .

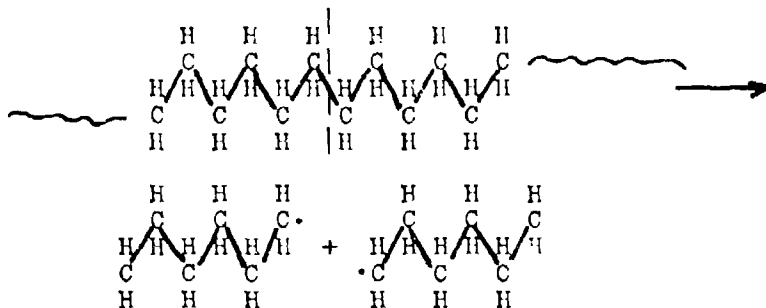
Results of mass spectrometer analysis of volatile products from pyrolysis of polymethylene in a vacuum at 500°, 800°, and 1200°C are shown in Table 8. The amounts of  $V_{pyr}$  are included in this table as part of the total volatiles. The heavier fragments predominate at the lower temperatures, while the reverse is true of the lighter fragments. The monomer,  $C_2H_4$ , is lacking at 500°C and increases to about 26% at 1200°C. In the pyrolysis of polymethylene at 800° and 1200°C the amount of monomer ( $C_2H_4$ ) is the most abundant volatile product, next to the  $V_{pyr}$  fraction, as shown in Table 8. This could be explained on the basis of two competing reactions taking place in the decomposition of this polymer by random scissions:

(1)

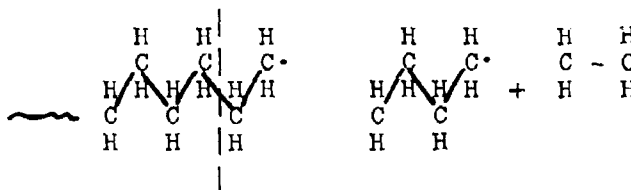


which produces one saturated and one unsaturated chain end, and the other reaction

(2)



which forms 2 free radicals. Each of the free radicals proceeds then to unzip to yield  $C_2H_4$ , thus,



At lower temperatures reaction (1) is predominant, while with the rise of temperature of pyrolysis reaction (2) asserts itself more and more. As a result, the yield of monomer increases in direct proportion to the temperature. At temperatures above  $1200^\circ$ , however, the monomer itself may break up to give  $C_2H_2 + H_2$ ,  $CH_4 + C$ , etc.

Table 9 shows comparative results of mass spectrometer analysis of volatile fractions from pyrolysis of polymethylene in a vacuum and in helium. Here the combined results of analysis of fractions V25 and V80 are shown. Since fraction V190 could not be collected for analysis in the helium experiments it is shown combined with fraction V<sub>pyr</sub> for all the experiments. This table shows some monomer at  $500^\circ C$  in the pyrolysis in helium. It also shows increasing amounts of monomer with increases in temperature and pressure, except in the case of pyrolysis in helium at  $1200^\circ$ . This can be explained on the ground that while the rate of scission increases with increased temperature, the rate of vaporization is slowed down with increased pressure. The latter circumstance would permit more

time for free radicals to unzip into monomer in the pyrolysis in helium. However, fraction V<sub>-190</sub> is not shown in this table, and some of the monomer produced in the pyrolysis in helium at 1200°C could have been in the V<sub>-190</sub> fraction.

#### 4. Polytetrafluoroethylene

Previous work<sup>11</sup> has shown that polytetrafluoroethylene (Teflon), when pyrolyzed in a vacuum at temperatures up to 538°C, yields about 95% monomer. The present work determines the effect of higher temperatures of pyrolysis on the nature and relative amounts of the volatile products. Pyrolysis was carried out at 500°, 800°, and 1200°C. Distribution of fractions is shown in Table 10, and analysis of the volatile products is shown in Table 11. In contrast with low-temperature pyrolysis, the higher temperatures yield, in addition to the monomer, some large molecular fragments collected in fraction V<sub>pyr</sub> (Table 10) and larger amounts of CF<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> (Table 11). It was postulated in our earlier work<sup>11</sup> that this polymer breaks up at free-radical ends of the chains by an unzipping process to yield mostly monomer. This unzipping, once started proceeds until the whole chain is consumed, so that large fragments (V<sub>pyr</sub>) do not appear among the volatile products. It is likely that at the higher temperatures some of the shorter free-radical chains evaporate before they have a chance to decompose into monomer, thus producing larger fractions of V<sub>pyr</sub>.

#### 5. Poly(-α-methylstyrene)

When heated in a vacuum at temperatures below 400°C, poly-α-methylstyrene decomposes almost completely into monomer.<sup>5</sup> The effect of a higher temperature on the distribution of fractions in the pyrolysis of this polymer is shown in Table 12. Considerable amounts of fractions V<sub>pyr</sub> and V<sub>-190</sub> are produced at the expense of fraction V<sub>25</sub>. This effect is even more clearly indicated in Table 13, where analysis of the volatile fractions from pyrolysis of the polymer are shown. The appearance of larger molecules found in fraction V<sub>pyr</sub> could be caused by the higher temperatures vaporizing some of these molecules before they have time to break up into the monomer by the unzipping process. The formation of small molecules found in V<sub>-190</sub> is most likely caused by cracking of the larger molecules in the hot zone of the apparatus.

#### 6. Polypropylene and Polyisobutylene

Pyrolysis of these two polymers in a vacuum has been studied previously at temperatures up to about 400°C. For polypropylene the yield of monomer-size molecules, fraction V<sub>25</sub>, is about 12%, and for polyisobutylene about 30%.<sup>12</sup> At higher temperatures fractions V<sub>25</sub> are produced in larger amounts, as shown in Tables 14 and 15. Analyses of the volatile fraction from pyrolysis of these two polymers are shown in Tables 16 and 17. As compared with pyrolysis at temperatures below 500°C,<sup>4,12,13</sup> the yields of monomers, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub>, are much higher at the higher temperatures.

#### 7. Poly(methyl methacrylate)

Poly(methyl methacrylate) decomposes on heating in a vacuum primarily into monomer at temperatures up to about 450°C.<sup>4</sup> However, when the temperature is raised to 1200°C considerable amounts of other fragments, both larger and smaller than the monomer, appear among the volatiles. Table 18 shows the distribution of volatile fractions for 500°, 800°, and 1200°C pyrolysis. The appearance of preponderant amounts of V<sub>-190</sub> at 1200°C is particularly notable and is mainly due to the formation of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>, as indicated in Table 19, which shows analysis of volatile products. It was found that fractions V<sub>25</sub> and V<sub>-190</sub> from pyrolysis at 800° and 1200°C, if allowed to stand for more than a day, tend to repolymerize and thus give misleading results. All the analyses of these two fractions were therefore made on the same day that they were produced and collected.

### IV. CONCLUSIONS

A polymer such as styrene can be greatly improved in thermal stability if it is copolymerized with a sufficient quantity of crosslinking agent such as divinylbenzene or trivinylbenzene. At higher temperatures and pressures the breakdown of the polymers produces greater fragmentation of the degradation products than at lower temperatures and pressures. At higher temperatures a fragment already formed might break up further while passing through the hot zone in the furnace. At higher pressures, a further breakup of a fragment could take place while its escape from the hot zone is retarded through collisions with other molecules. It is not clear from the present work whether the greater fragmentation at higher temperatures and pressures takes place during the primary reaction when the fragments break off the polymer, or in a secondary reaction after the fragments have already been formed.

## SECTION B

### DEGRADATION STUDIES BY MASS SPECTROMETER TECHNIQUES

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This past year has been spent primarily in deciding on and procuring the instrumentation necessary to obtain information applicable to the problem of understanding the basic processes of degradation. The resulting instrumentation is aimed at studying the degradation process by observing both steady-state conditions and transient phenomena from rapid reactions. The equipment, when completed and installed, will consist basically of a modified Consolidated Electrodynamics Corporation Model 21-103 mass spectrometer and a Bendix Corporation Model 14-101 mass spectrometer.

The CEC 21-103 has been modified by the addition of a heated inlet oven, micromanometer, pen recorder, Veeco ionization gauge and control chassis, and a vibrating reed electrometer. The existing electronics were modified to improve stability of operation, and a high resolution analyzer was installed after the existing magnet pole faces were reshaped to accept it. The existing wiring has been changed so that the instrument is electrically isolated from the laboratory power lines by means of a 7.5 kva isolation transformer, and all electronic circuitry is powered by a 3Kva constant voltage transformer. The mechanical circuits are electrically isolated from the electronic circuits. The electrical ground return is isolated and made via a stranded No. 4 copper wire connected to two 8-foot copper grounding rods placed directly in the ground outside the laboratory.

The Bendix Corporation mass spectrometer, Model 14-101, was delivered during April 1961. It has the following characteristics and specifications:

1. The spectrometer is supplied with the S-14-107 ion source which is capable of analyzing positive or negative ions produced at a 10 KC repetition rate or continuously.
2. The spectrometer is supplied with the M105-G6 multiplier for detection of positive or negative ions. This multiplier has six gate structures and associated anodes and an oscilloscope anode.



3. The spectrometer is equipped with six analog output chassis (five scanner chassis number 321 and one controller chassis number 311) for use with the six gated outputs of the M105-G6 multiplier.

4. The spectrometer uses an IFI model 395A wide band amplifier for amplifying the output of the scope anode of the M105-G6 multiplier.

5. The vacuum system pressure is monitored by a Veeco discharge gauge type DG-2-10, a Veeco ionization gauge and two Veeco thermocouple gauges. The associated control circuit is the Veeco model RG-3A.

6. The ion-accelerating voltage and multiplier voltage is supplied by a John Fluke regulated power supply model 405 N.

7. The spectrometer presents 10,000 complete mass spectra per second to an oscilloscope.

8. Each of the 10,000 mass spectra per second covers the mass range from 1 to 5000 atomic mass units.

9. Adjacent masses are partially resolved above mass 500 on the oscilloscope spectrum, and resolution is improved at lower masses. The spectrometer will resolve the mercury spectrum so that the peak height interference between adjacent masses as measured at mass 202 is:

<u>Type of Spectrometer Operation (electron beam ionization in all cases</u>	<u>Type of Spectrum Presentation</u>	<u>Peak Height Interference</u>
Pulsed	Recorder	less than 1.5%
Continuous	Recorder	less than 4.0%

The mass resolution on the oscilloscope will always be better than that shown on the recorded spectrum for the corresponding mode of spectrometer operation.

10. The ionizing electron energy is continuously variable from 0 to 100 volts.

11. When no sample is being introduced, the mass spectrometer will pump down to a pressure of at least  $5 \times 10^{-7}$  Torr, as measured with a hot filament ionization Gage.

12. The sensitivity of the mass spectrometer is such that an argon partial pressure in the ionization region of about  $2 \times 10^{-8}$  Torr produces a peak containing, on the average, one ion per cycle.

13. The relative sensitivity of the spectrometer is such that it has been able to detect the argon 36 and 38 isotopes in an air sample (34 and 6 parts per million respectively) as well as helium in air (5 parts per million).

14. The vacuum system includes: (a) a 12-inch-diameter chamber enclosing a well-type liquid nitrogen trap, (b) a six-inch-diameter gate valve, (c) a Freon-cooled baffle with the conductance of a 6-inch-diameter hole, and (d) a 6-inch metal mercury diffusion pump. The ion source is housed in a 3.3-inch tube welded to the side of the 12-inch diameter chamber.

15. The spectrometer can present either positive or negative ion spectra to an oscilloscope.

16. The spectrometer is equipped to analyze either positive or negative ions created outside the mass spectrometer.

17. The spectrometer is equipped with two side ports opposite the ion source and two side ports between the cold trap and multiplier.

18. The spectrometer is equipped to utilize an externally-created continuous ionizing beam such as a beam of light or a beam of particles (such as protons).

19. The spectrometer can record either the ratio of any two resolved mass peaks between 1 and 800 a.m.u. or a mass spectrum. Any portion of the mass spectrum between 1 and 800 a.m.u. can be recorded in a single sweep.

20. After a one-hour warmup, the trap current regulator will be capable of regulating (to  $\pm 0.1\%$ ) an average current of 0.1 to 0.3 microamp in the range of measured electron energy of 10 to 90 volts.

21. The difference between the ionization potentials of argon and neon shall be constant and reproducible to within  $\pm 0.25$  ev. The ionization potential shall be obtained by plotting the logarithm of the ion intensity vs. the energy of the ionizing electrons and extrapolating to essentially zero ion current. The

difference between the onset of these two curves when the slopes are normalized at 50 volts shall be the difference between the spectroscopic ionization potentials of argon and neon to  $\pm 0.25$  ev.

22. The positive ion mass spectrum of normal butane shall be reproducible as follows: The relative abundance of each ion in a mass spectrum shall not vary by more than  $\pm 2\%$  standard deviation of themselves or  $\pm 0.05\%$  standard deviation of the largest peak in each spectrum (whichever is greater). These results will be obtained when (a) the analog output system is used, (b) when the mass spectrum is obtained at a scan rate which will cover  $m/e$  10 to  $m/e$  100 in not less than 5 minutes, (c) when a recording system capable of being read to an accuracy of  $\pm 0.2\%$  of full scale is used, (d) when the liquid nitrogen trap is continuously maintained full, and (e) when the equivalent partial pressure of the largest peak of the sample spectrum in the ion source is equal to or greater than  $5 \times 10^{-7}$  Torr. Negative ion spectra will be qualitatively reproducible on the oscilloscope.

23. The sensitivity of the instrument shall not vary abruptly, and the ratio of peak height to partial pressure of the gas being ionized will not change during an 8-hour continuous period of operation by more than  $\pm 5\%$  for changes in the total partial pressure of the sample in the ion source within the range of  $10^{-6}$  to  $10^{-9}$  Torr, provided the spectrometer is preconditioned for a continuous period of 8 hours by a gas similar in nature to the sample.

24. The above specifications are to be met with the following operating conditions:

- A. 10 kc repetition rate
- B. electron gate pulse of 0.3 microseconds, average electron beam intensity 0.125 microamperes, except where otherwise noted.

This spectrometer has its own isolated and regulated voltage source similar to that previously described for the CEC 21-103 instrument. Auxiliary equipment for this spectrometer consists of the following:

- a. A six-channel recorder of the direct writing galvanometer type, matched to the six analog output circuits.

b. Oscilloscope with a Polaroid Land Camera attachment and a revolving drum camera.

c. High-speed ( $1/4$  second response) pen recorder.

d. dri-vac ion pump with speed of 25 l/sec air and 8 l/sec argon.

e. capacitor bank for energy storage of 4000 joules.

f. associated sample handling and introductory system.

The time-of-flight instrument provides data as a repetitive signal consisting of an amplitude and time variation. The individual signals represent the quantity of ions ( $m/e$  ratio), by the amplitude of the signal, as a function of the mass to charge ratio of the ions, by the time base of the signal. This information is obtained at a 10 Kc repetition rate and can be presented in one of several manners. The resulting information can then be recorded in one of several ways. The combination of output and recording system chosen will depend upon the experimental apparatus used with the instrument and the processes being monitored.

The output of the instrument is obtained from an electron multiplier. This multiplier has six gated outputs as well as the final scope output which is used to present the total mass spectrum to an oscilloscope. Each of the six gates can be applied at any time during a single cycle. When the gate is applied, the specific portion of the electron multiplier current due to a particular ion is deflected to a separate anode associated with that gate structure. Thus, a part of the electron current is subtracted from the total output. This portion is put through an associated electrometer circuit (analog system), and a signal proportional to the deflected electron beam current is available from a cathode follower output circuit. This signal can be presented to a pen recorder or galvanometer recorder for storage of information. If the gate pulse is constant in time for each cycle of the instrument, each of these six output channels represents the time-rate-of-change of a specific ion. This signal has a time constant associated with the electrometer-amplifier circuit and can be adjusted in the range of 10 milliseconds to 5 seconds. Since this is a subtraction phenomenon, the final signal which reaches the oscilloscope display now has these six ion peaks missing.

The total signal can alternatively be presented on an oscilloscope with the trace representing the entire mass range possible ( $m/e$  1-500 Amu) or any selected portion thereof. These data can be recorded from the oscilloscope by means of a revolving drum camera (which then records every cycle of the instrument) or a Polaroid Land Camera attachment which obtains a time average of several cycles to several thousand cycles, depending upon shutter speed. These methods give data on several ions, as a function of time (with the revolving drum camera every 100 microseconds, with the polaroid camera perhaps every minute. Individual ions can be followed continuously as a function of time for much longer periods by use of the oscilloscope or analog output system. If the oscilloscope is set for a very slow scan and the trace blanked except for the portion of the 10 Kc repeated signal corresponding to the ion of interest, the resulting envelope of the oscilloscope trace will represent the time-rate-of-change of ion intensity (of the ion in question).

A typical experiment might consist of carrying out a rapid reaction (about  $10^{-3}$  to  $10^{-5}$  seconds) and sampling the products with the instrument. The data consist of the initial transient species and the species characterizing the steady state of the system. The reaction onset, which could be an explosively rapid reaction, would trigger the oscillographic revolving drum camera which would record for approximately 1/50 sec. This would record about 200 total mass spectra representing the transient phenomena occurring during reaction. At or near the end of this period, the six analog circuits would be activated and the six signals fed to appropriate recording systems with preselected time constants. This would take over the gathering of information while the final information can be obtained by a mass scan with one of the analog systems recorded on a pen recorder or by photographing an oscillographic presentation of the total spectrum (this last step would also be the very first step so that the condition of the total system is known before, during and after the experiment).

The resultant data represent (a) the steady-state pre-reaction quiescent system, (b) the transient, very short-lived species during the reaction, (c) the longer-lived species, (d) the post-reaction quiescent steady state of the system. All of this information is known as an accurate function of time so that the data may be treated as kinetic information, time-concentration and rate-temperature correlations being the final data processing steps. The understanding of the pathways involved in going from

reactants to products will most certainly require more than one ion peak per compound so that a system of simultaneous equations will arise. The solution of these equations for every point in time chosen will represent the concentration of various compounds in the system being sampled at that particular time. With this information the kinetics of the reaction may possibly be understood.

During the latter half of March 1961 data were obtained in Cincinnati, Ohio, on the Bendix mass spectrometer being constructed for this research. These data consist of the results of a stability test as specified in Item 22 of the Characteristics and Specifications and a check on Item 21, the measured difference between the ionization potentials of neon and argon as compared to the spectroscopic value of this difference. Table 20 contains the results of a five-day test on Item 22. Of 10 runs, one was made each morning and one each afternoon during the five-day period. The standard deviation,  $\sigma$ , is the conventionally defined value

$$\sigma = \left[ \frac{\sum (x_i - \bar{x})^2}{N - 1} \right]^{1/2}$$

where  $x_i$  is the value of the quantity  $x$  for the  $i^{\text{th}}$  determination,  $\bar{x}$  is the average value of  $x$ ,  $[\bar{x} = \frac{\sum x_i}{N}]$ , and  $N$  is the number of determinations of the value  $x$ . Since the ion currents are normalized to the largest ion current ( $m/e=43$ ), to meet specifications all values of  $\sigma$  can be no greater than  $0.05/I$  where  $I$  is the normalized ion current. In general it is seen that the standard deviations of the average relative abundances of the ion (R.A.) fall close to or within the maximum allowable values ( $\sigma_{\text{max}}$ ).

Some determinations of the relative ionization potentials of Argon and Neon, as outlined in Item 21 of the specifications, gave values well within the tolerance specified (typical values were in the range of  $5.9_5$  ev to  $6.0_0$  ev while the spectroscopic

value is  $5.80_{\mu}$  ev). It appears that the instrument will be able to meet specifications upon delivery and probably will outperform the written specifications in several respects.

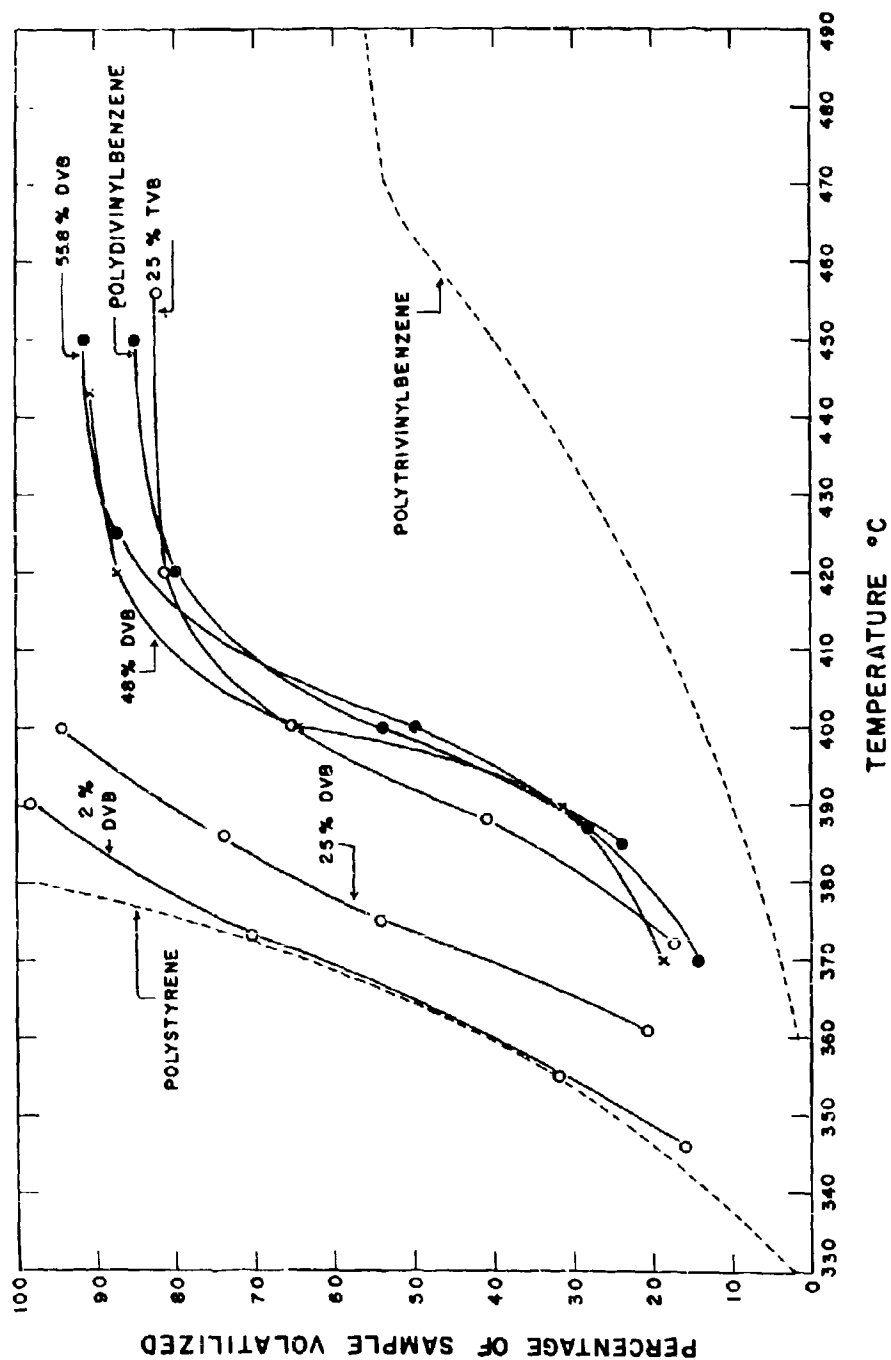


Figure 1. Relative thermal stability of polydivinylbenzene and polytrivinylbenzene and their copolymers with styrene



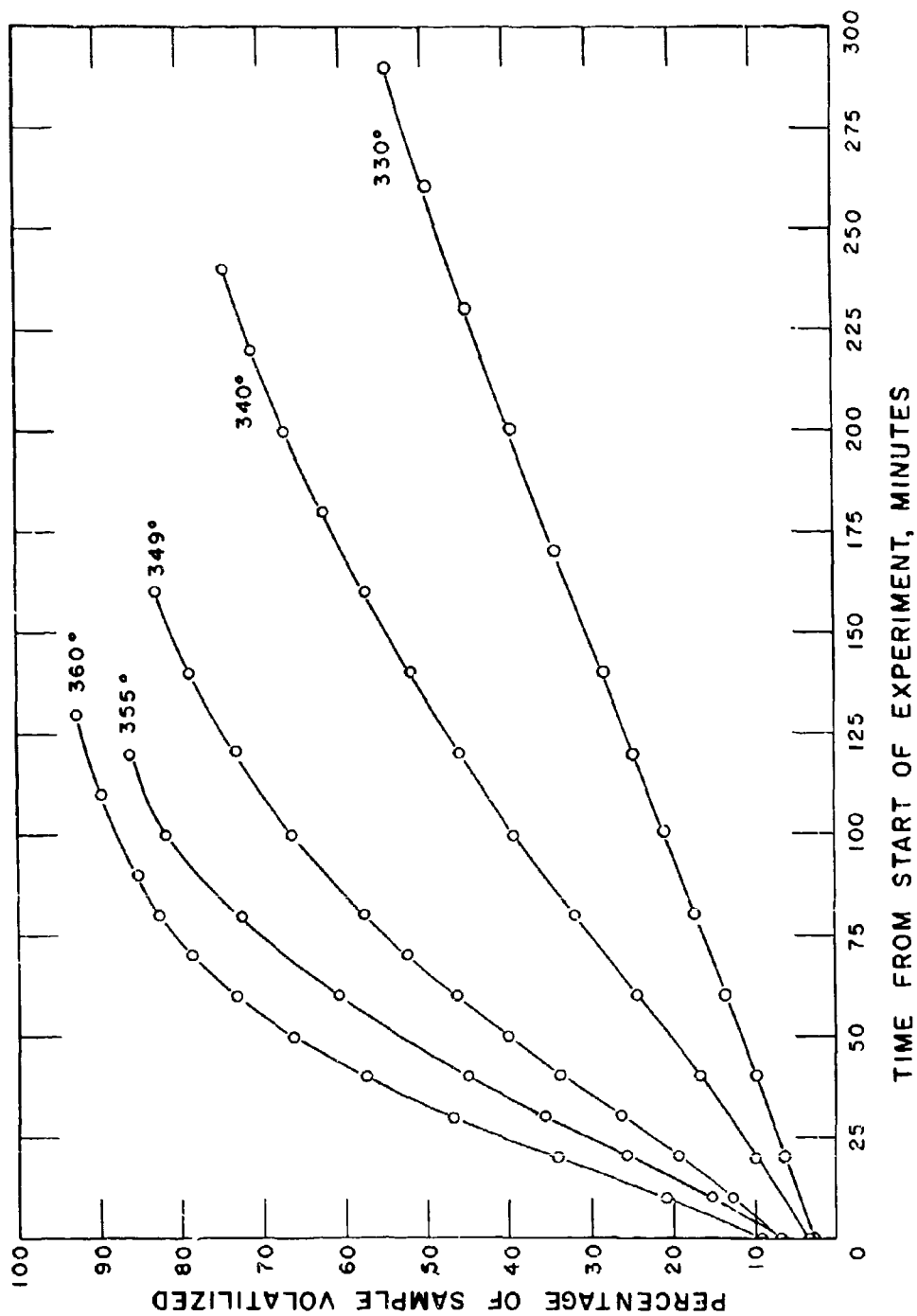


Figure 2. Thermal degradation of copolymer, 98% styrene-2% divinylbenzene

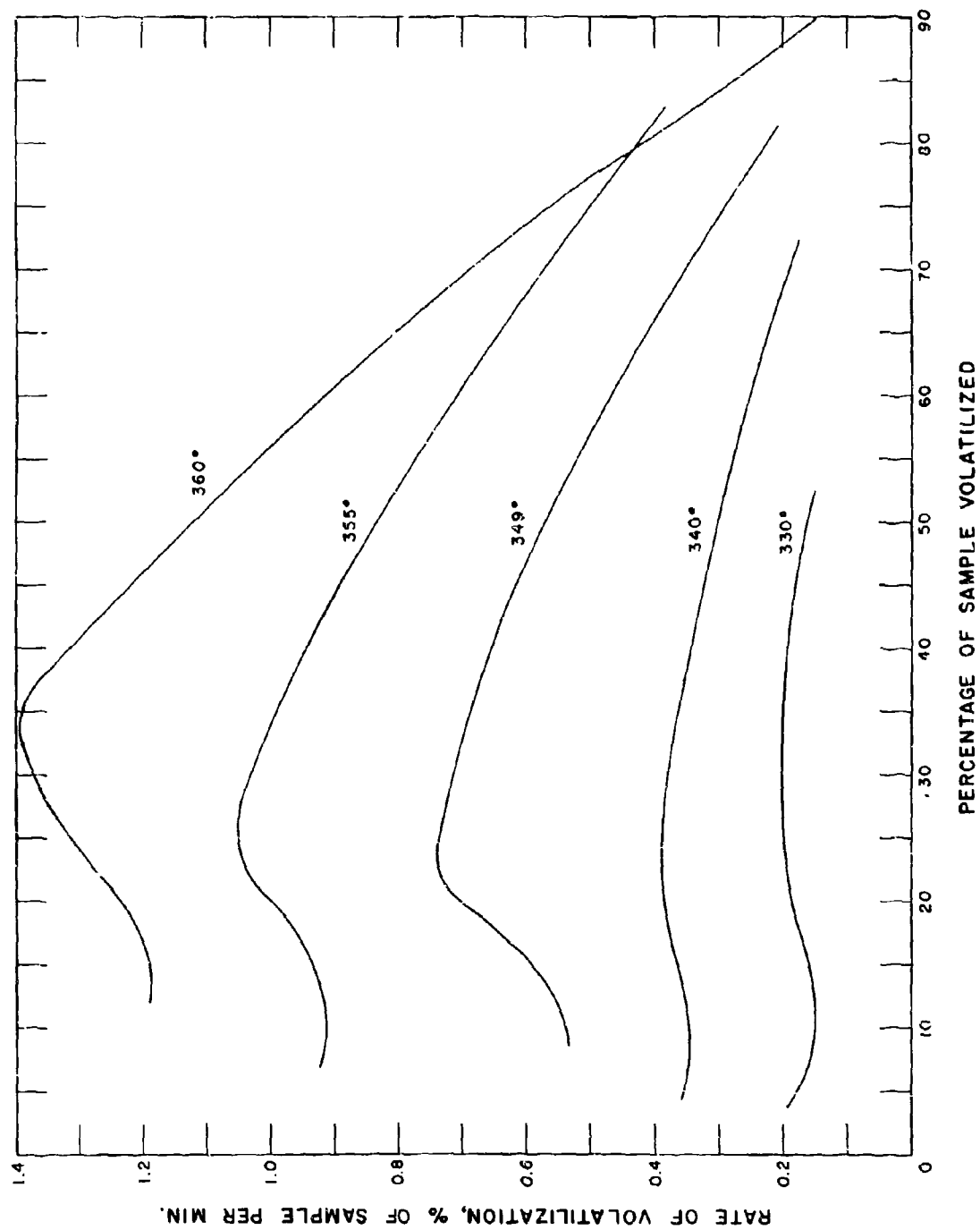


Figure 3. Rates of volatilization of copolymers, 98% styrene-2% divinylbenzene

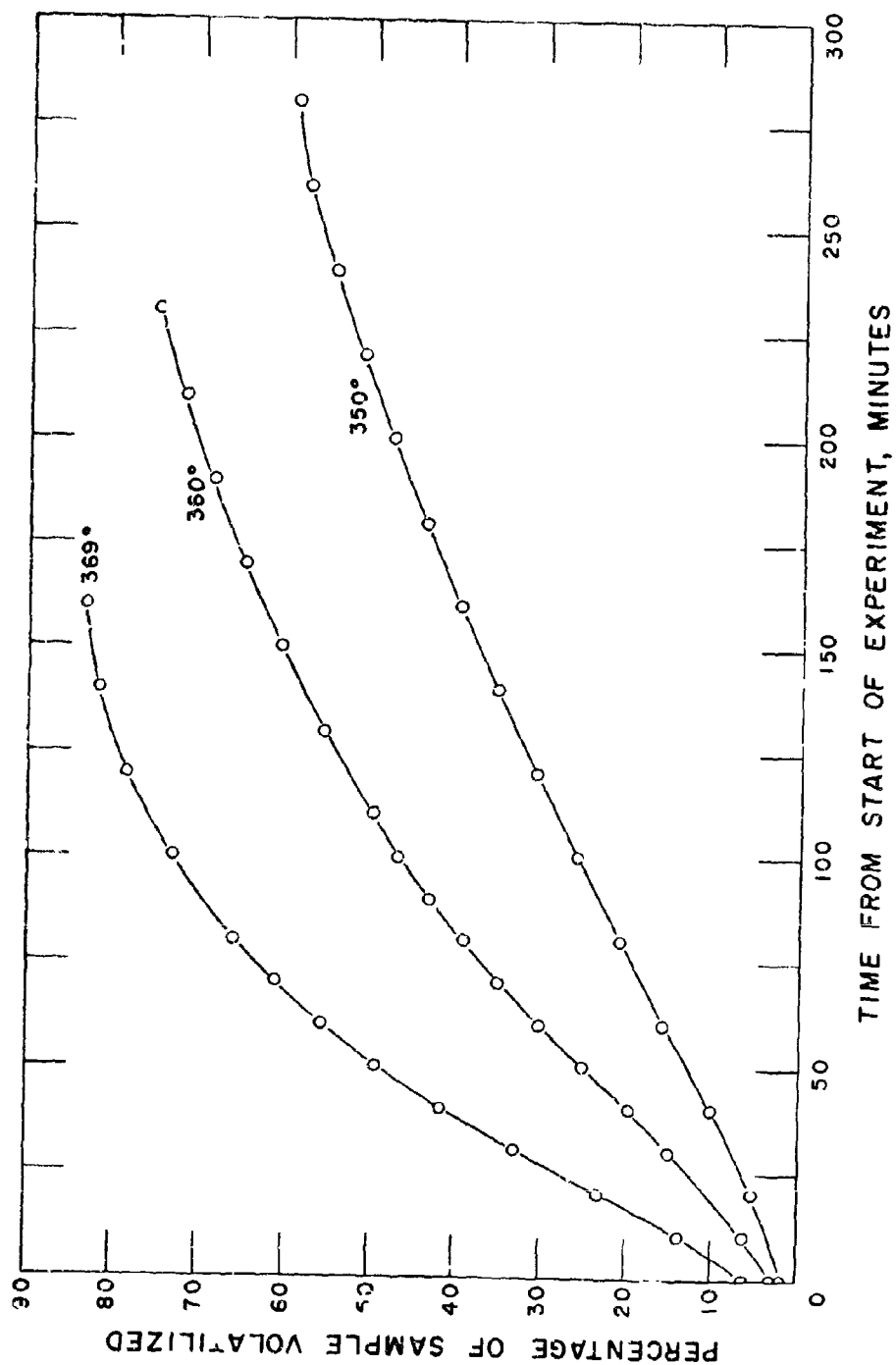


Figure 4. Thermal degradation of copolymer, 75% styrene-25% divinylbenzene

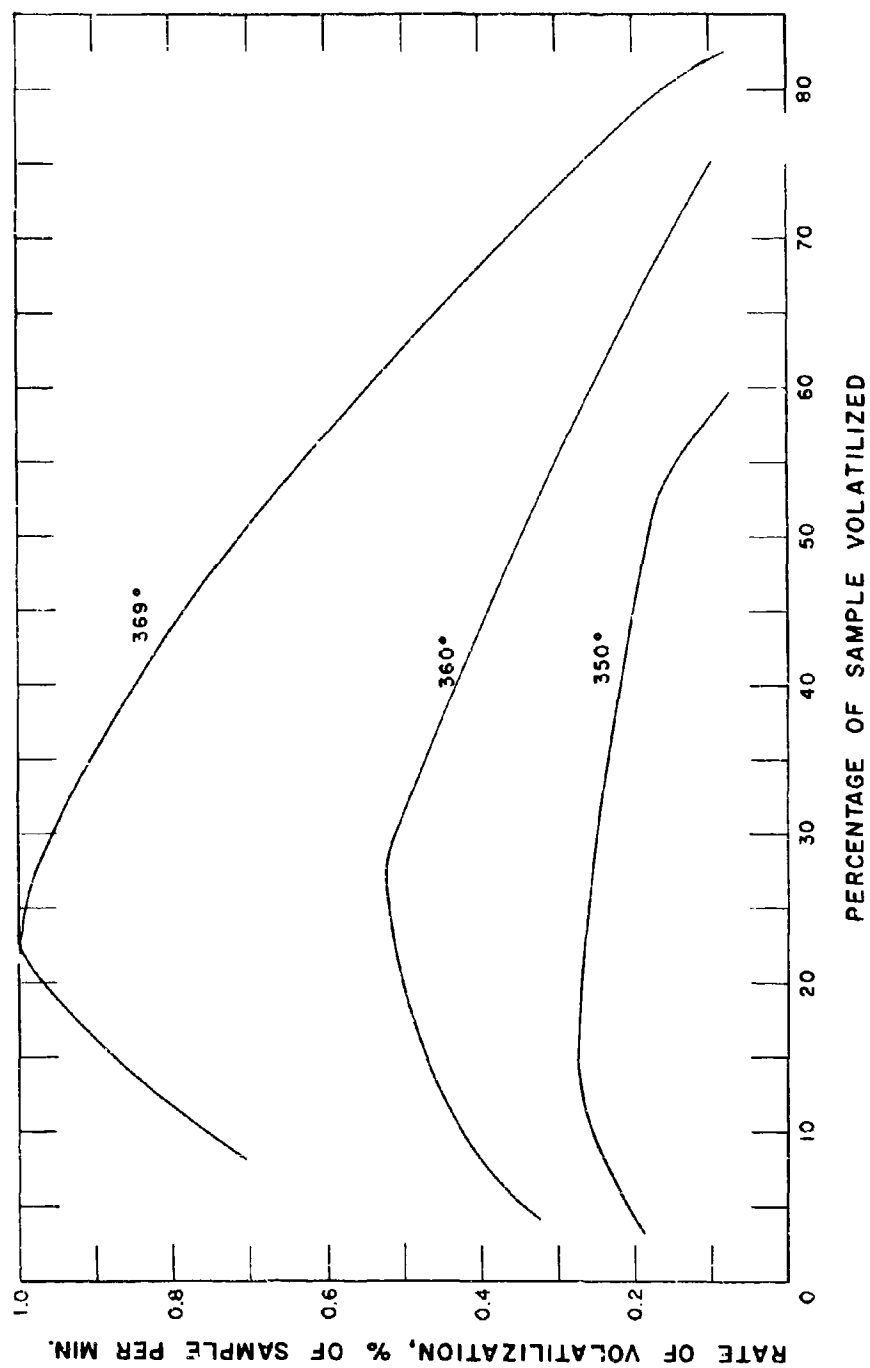


Figure 5. Rates of volatilization of copolymer, 75% styrene-25% divinylbenzene

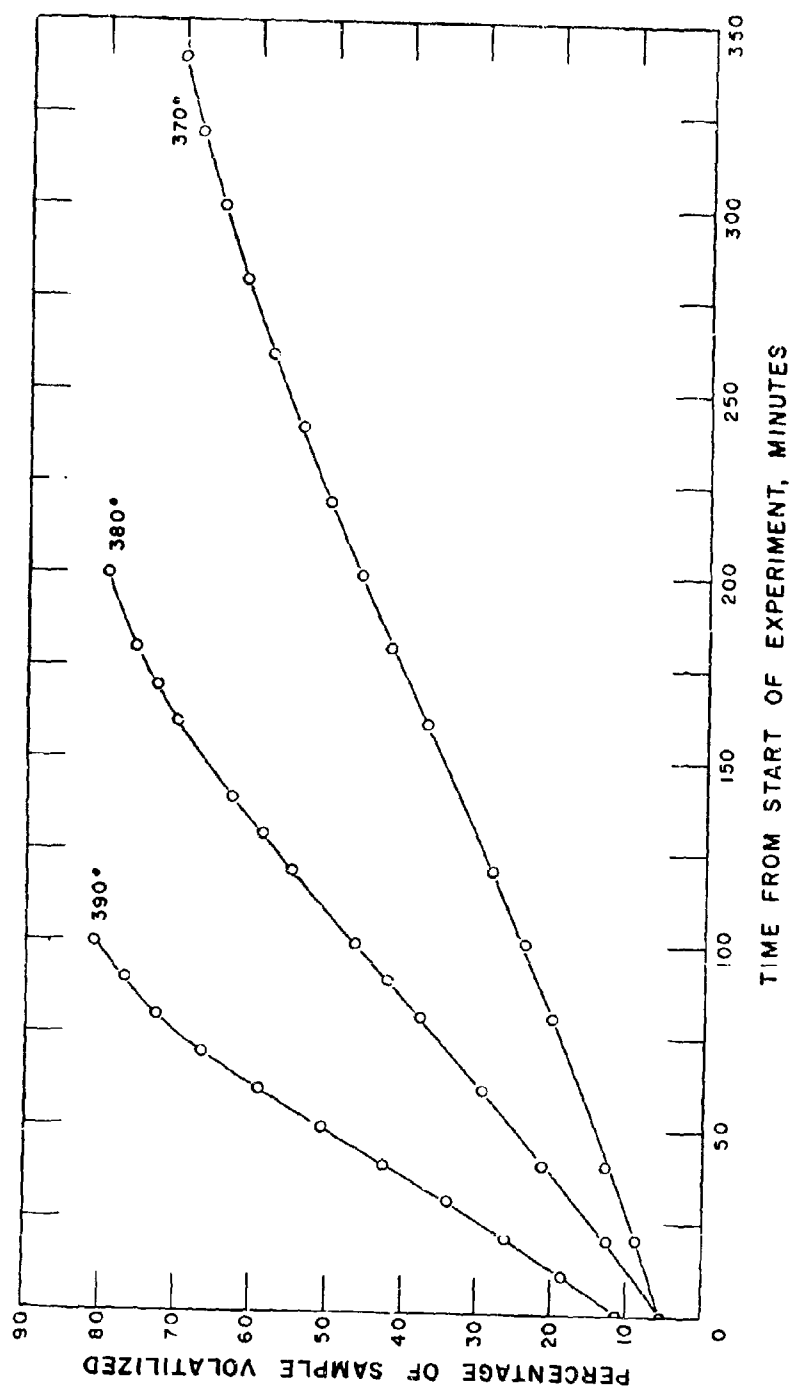


Figure 6. Thermal degradation of copolymer, 52% styrene-28% divinylbenzene

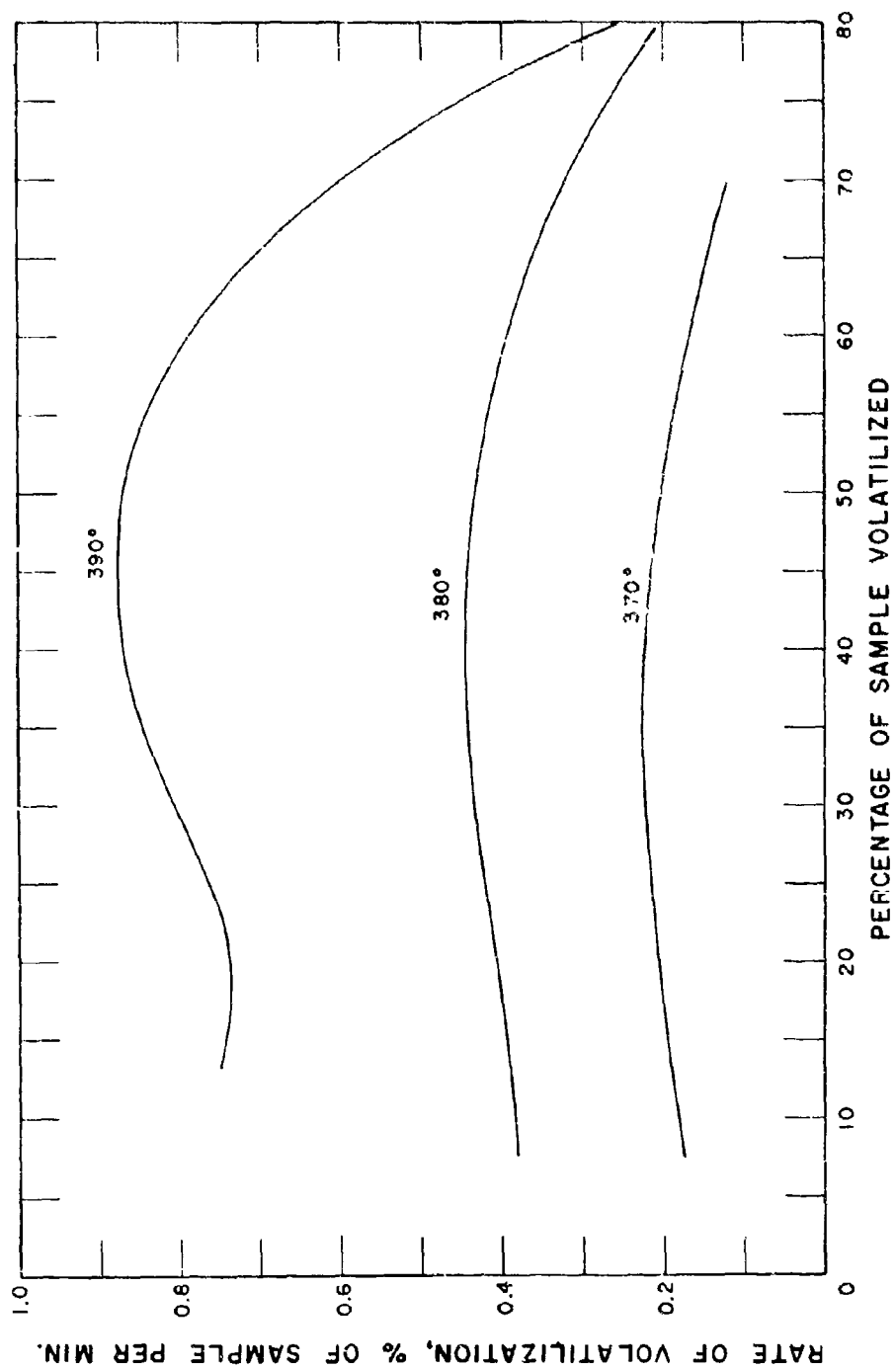


Figure 7. Rates of volatilization of copolymers, 52% styrene-48% divinylbenzene

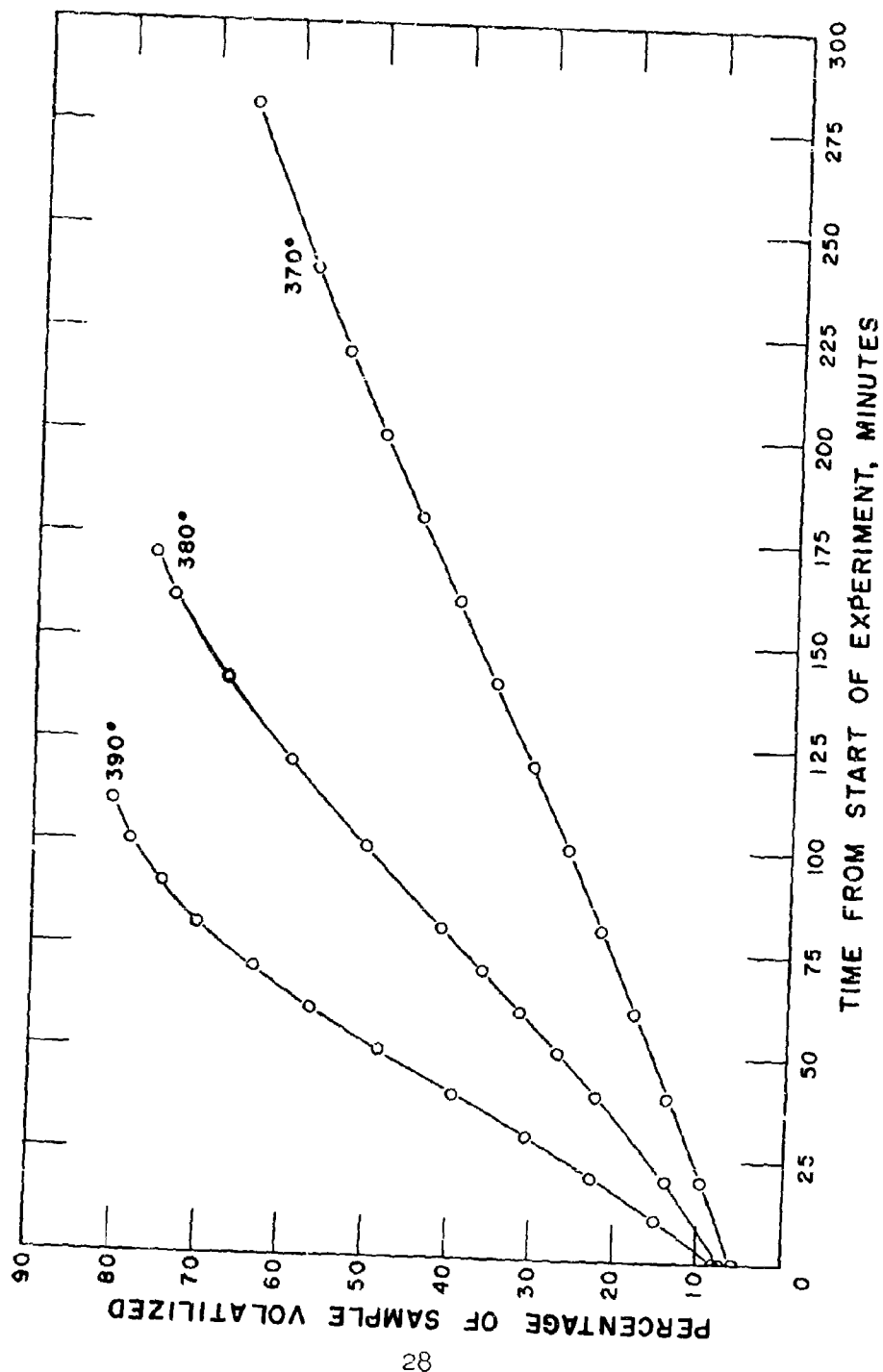


Figure 8. Thermal degradation of copolymer, 44% styrene-56% divinylbenzene

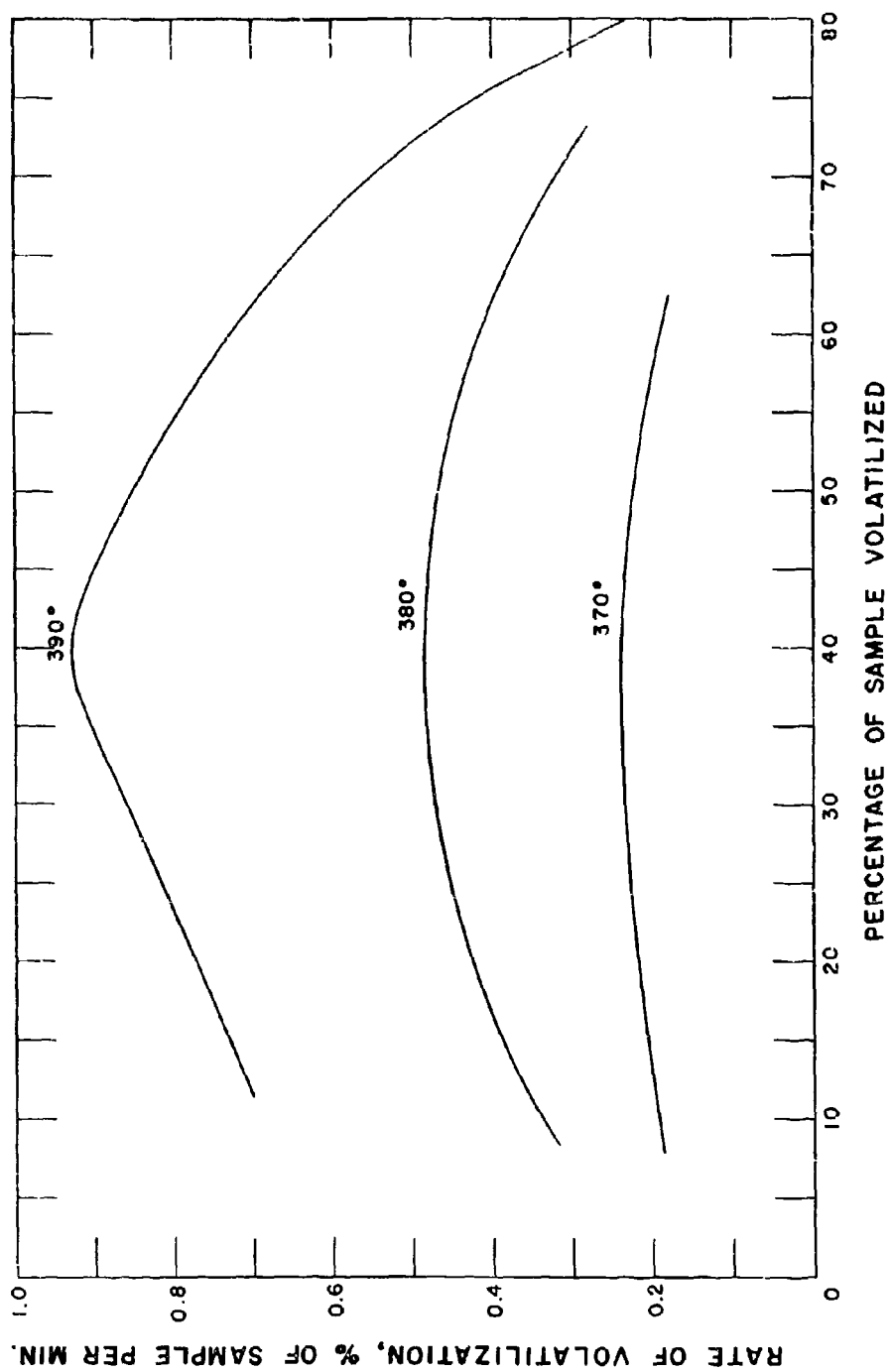


Figure 9. Rates of volatilization of copolymer, 44% styrene-56% divinylbenzene



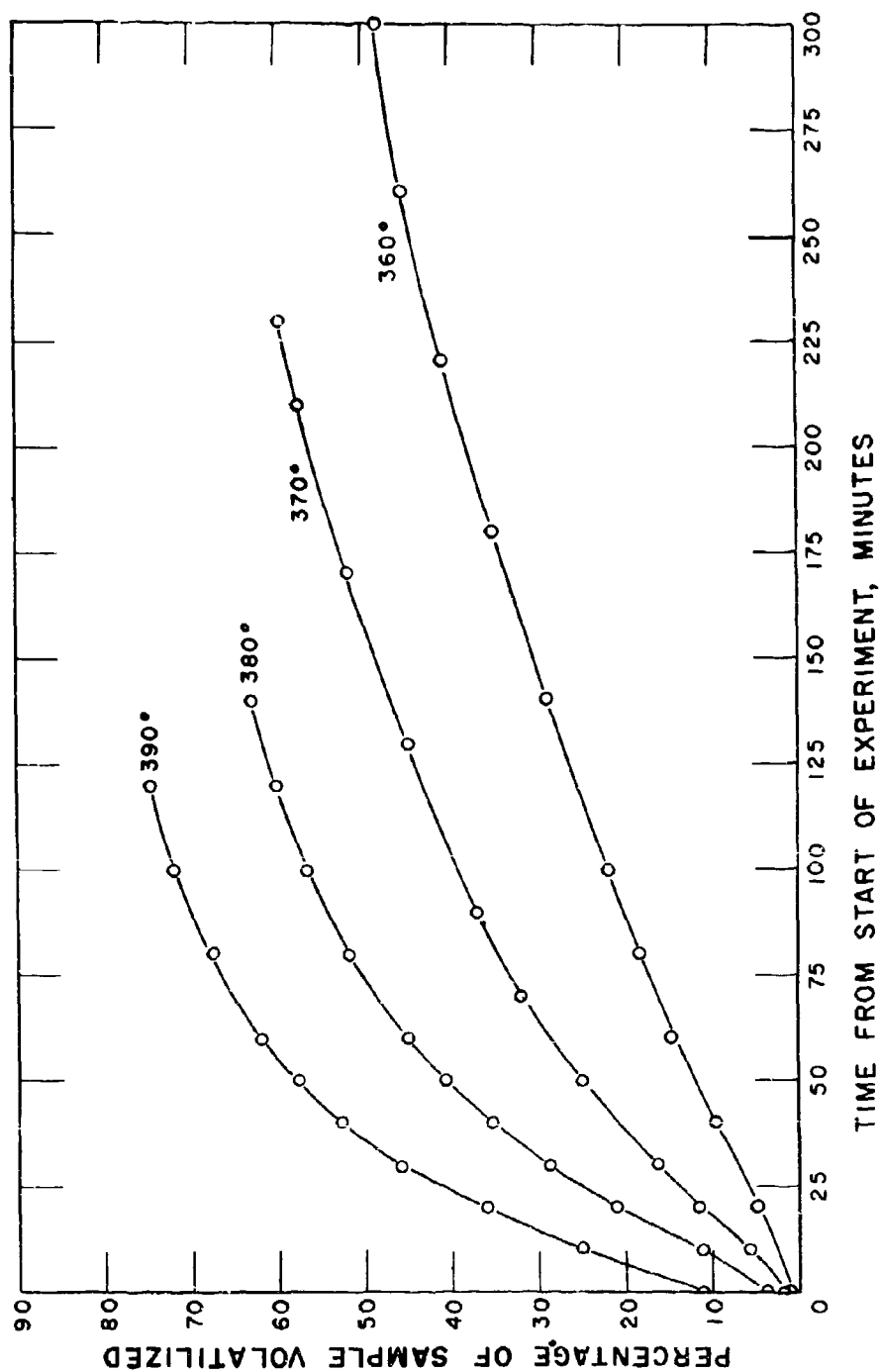


Figure 10. Thermal degradation of copolymer, 75% styrene-25% trivinylbenzene

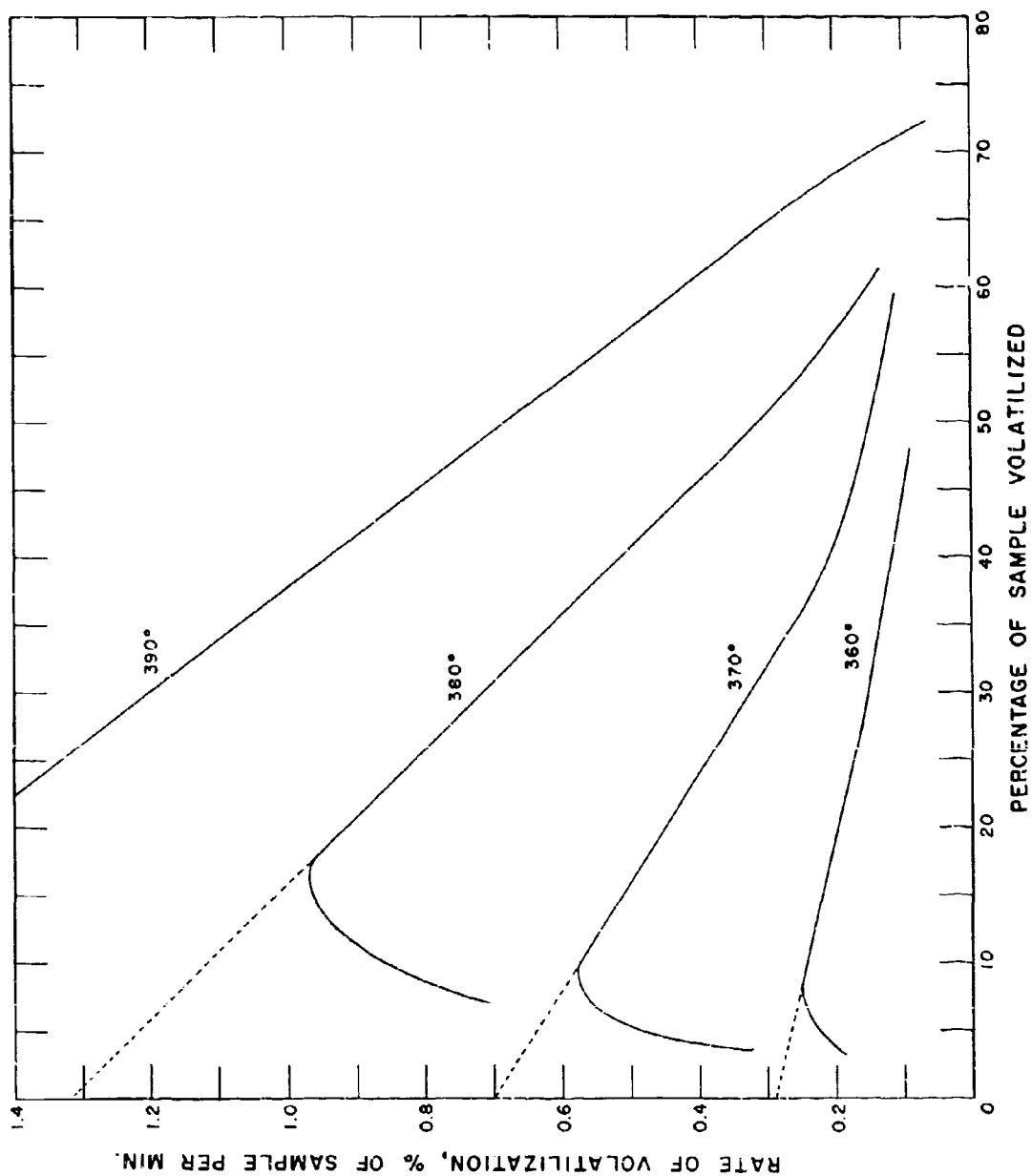


Figure 11. Rates of volatilization of copolymer, 75% styrene-25% trivinylbenzene

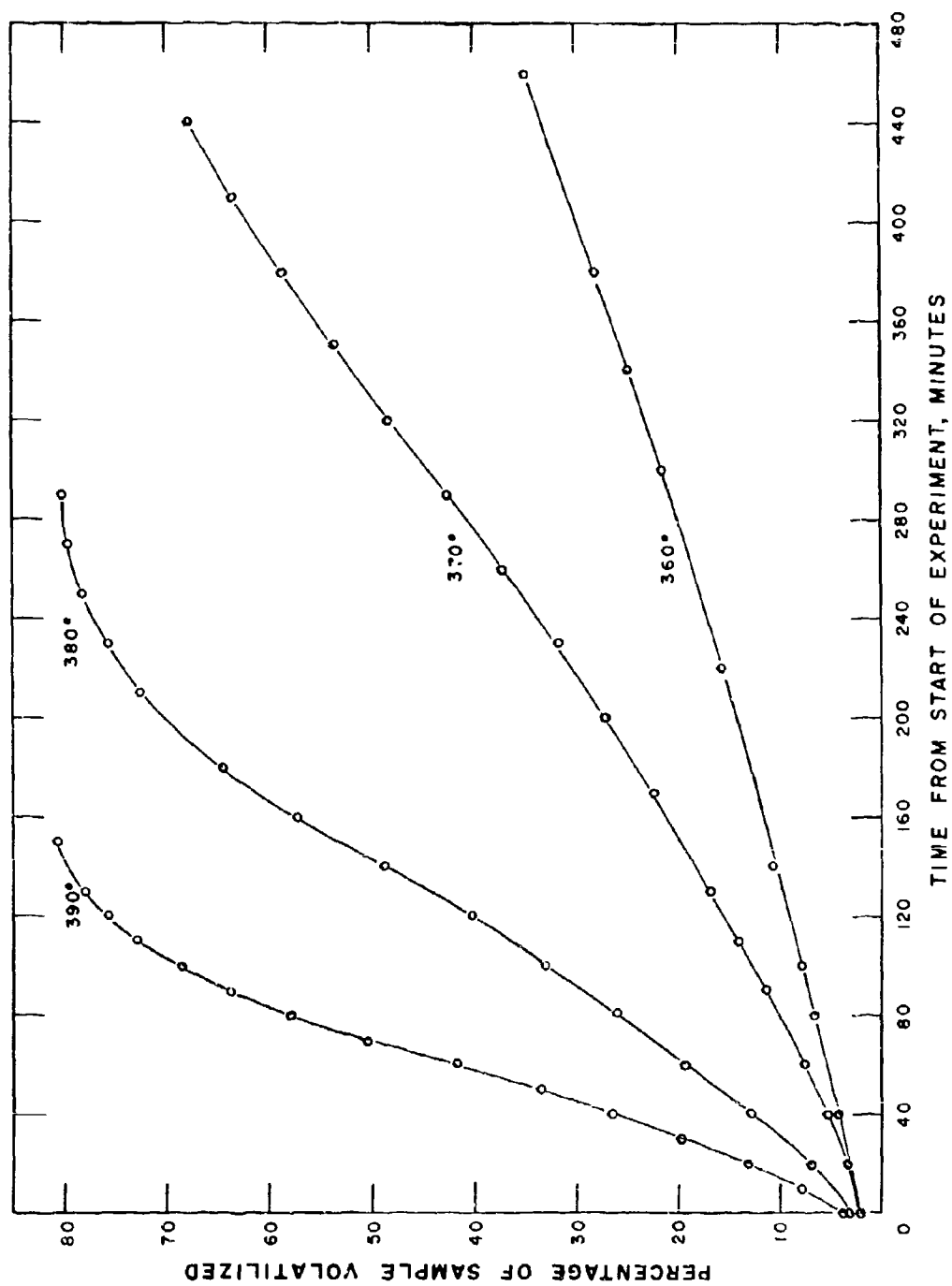


Figure 12. Thermal degradation of polydivinylbenzene

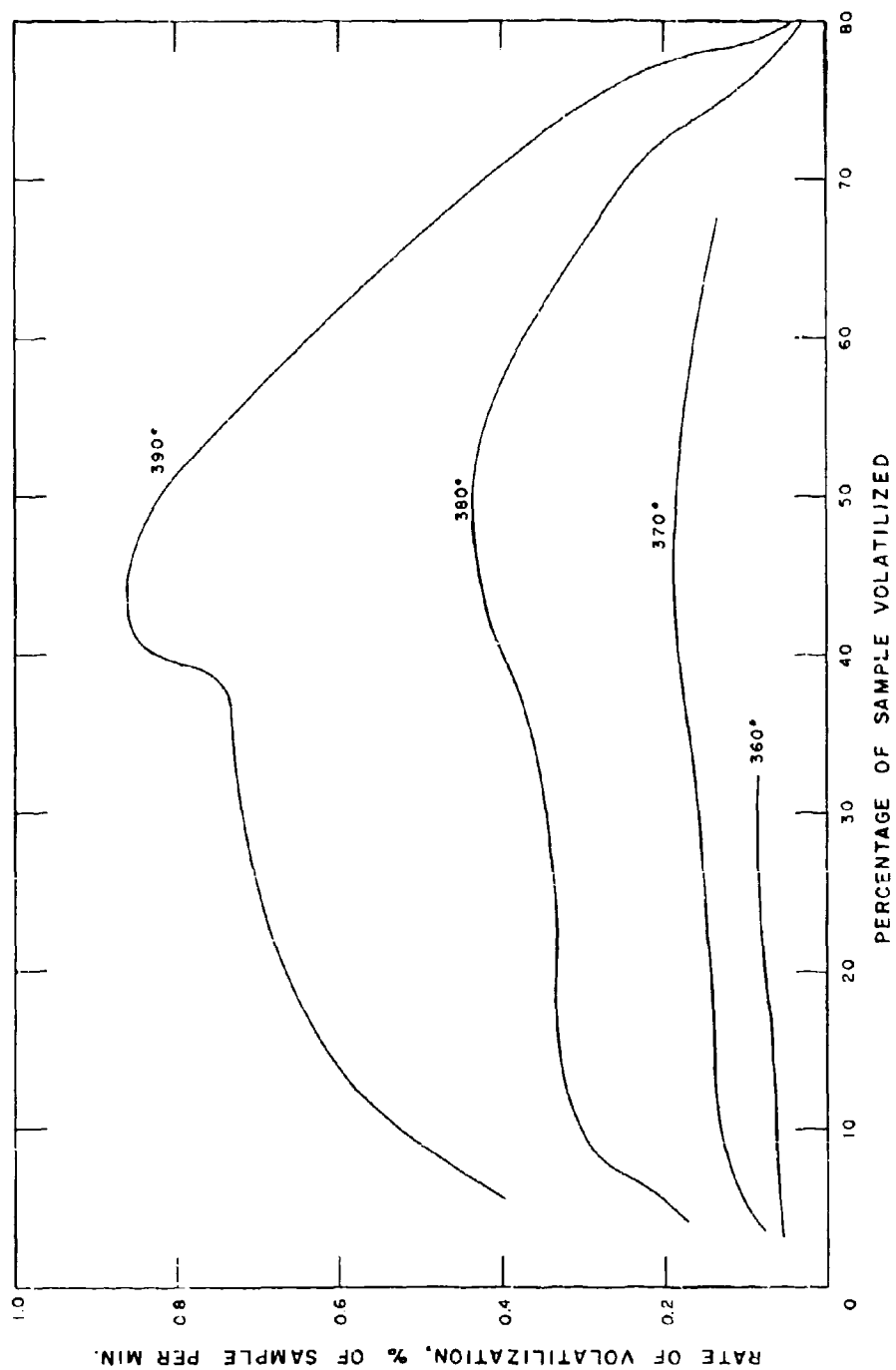


Figure 13. Rates of volatilization of polydivinylbenzene

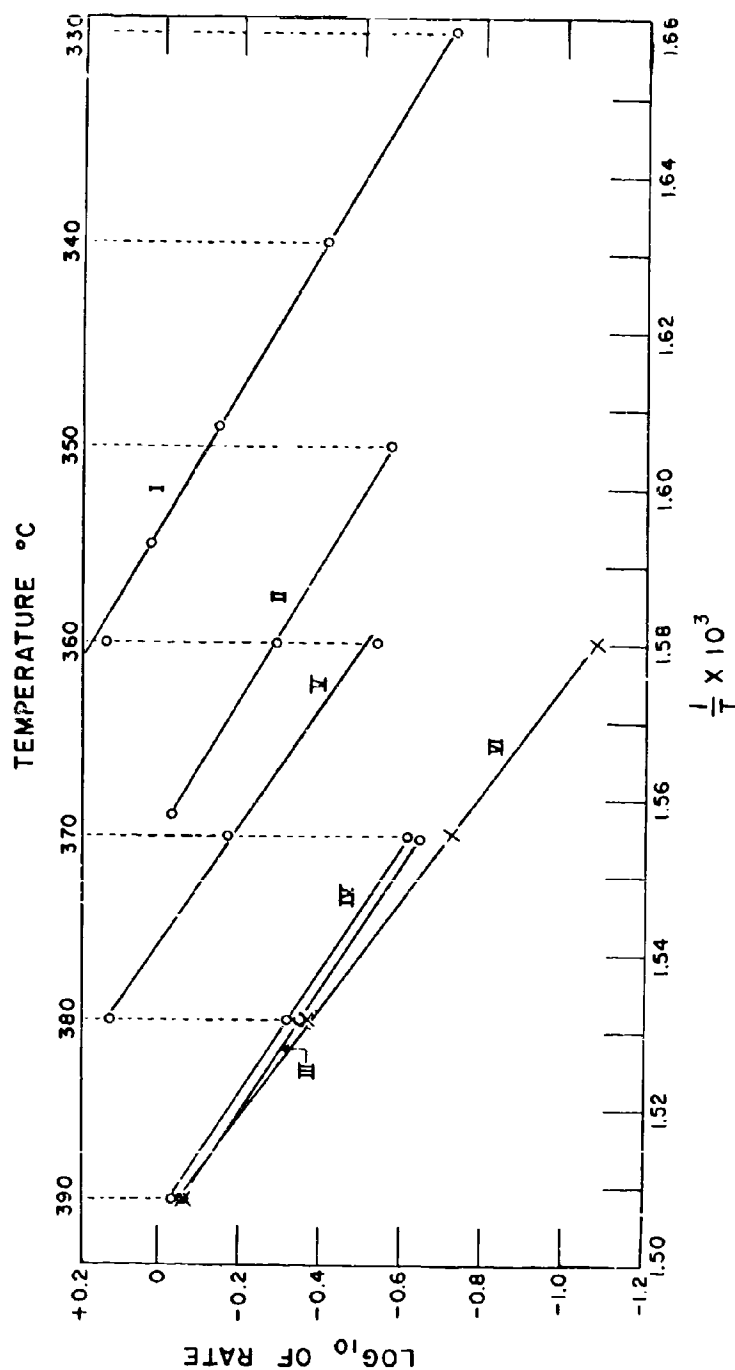


Figure 14. Activation energy curves for the thermal degradation of polydivinylbenzene and of copolymers of styrene with divinylbenzene and with trivinylbenzene  
 I, St, 98-DVB, 2%  
 II, St, 75-DVB, 25%  
 III, St, 52-DVB, 48%  
 IV, St, 44-DVB, 56%  
 V, St, 75-DVB, 25%  
 VI, Poly-DVB

TABLE 1  
PYROLYSIS OF COPOLYMERS OF STYRENE WITH  
DIVINYLBENZENE AND WITH TRIVINYLBENZENE

Copolymer	Temp.	Volatili- zation	Fractions, based on total volatilized	
			V <sub>pyr</sub>	V <sub>25</sub>
	°C	%	%	%
2% DVB	346	16.0	42.1	57.9
	355	32.2	42.7	57.3
	373	70.6	47.2	52.8
	390	98.3	48.1	51.9
25% DVB	361	20.7	43.0	57.0
	375	54.2	49.7	50.3
	386	73.9	49.1	50.9
	400	94.5	52.1	47.9
48% DVB	370	18.6	80.5	19.5
	390	31.1	87.4	12.6
	401	64.6	94.9	5.1
	420	87.5	96.0	4.0
	443	90.7	95.0	5.0
56% DVB	370	14.4	64.0	36.0
	387	28.4	77.4	22.6
	400	50.1	82.9	17.1
	425	87.3	93.2	6.8
	450	91.6	91.8	8.2
100% DVB	385	24.0	54.4	45.6
	400	53.8	67.1	32.9
	420	79.8	71.1	28.9
	450	84.7	81.0	19.0
25% TVB	372	17.3	69.0	31.0
	388	41.1	63.6	36.4
	400	65.6	77.8	22.2
	420	81.4	79.9	20.1
	450	82.0	83.7	16.3

TABLE 2  
ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS IN A VACUUM  
OF COPOLYMERS OF STYRENE WITH DIVINYLBENZENE  
AND WITH TRIVINYLBENZENE

Component <sup>a</sup>	2% DVB		25% DVB		48% DVB			56% DVB		25% TVB	
	346	390	386	400	370	390	443	400	450	400	420
	%	%	%	%	%	%	%	%	%	%	%
C <sub>3</sub> H <sub>6</sub>	-	-	0.8	-	-	-	-	-	-	0.8	0.4
C <sub>4</sub> H <sub>6</sub>	-	-	0.6	-	-	-	-	-	-	-	-
C <sub>5</sub> H <sub>10</sub>	-	-	-	-	-	-	-	0.7	0.6	-	-
C <sub>5</sub> H <sub>12</sub>	-	-	-	-	-	-	-	3.0	2.7	-	-
C <sub>6</sub> H <sub>6</sub>	-	0.4	1.5	0.5	-	-	-	-	-	0.4	0.4
C <sub>6</sub> H <sub>14</sub>	-	-	0.8	-	-	-	-	-	-	-	-
C <sub>7</sub> H <sub>8</sub>	0.6	1.4	2.8	2.7	-	-	-	-	-	2.7	3.0
C <sub>8</sub> H <sub>8</sub>	51.7	49.8	39.9	34.8	-	-	-	-	-	16.2	14.4
C <sub>8</sub> H <sub>10</sub>	2.0	-	0.9	1.4	-	0.5	0.6	1.0	1.2	1.3	1.4
C <sub>9</sub> H <sub>10</sub>	0.7	-	1.7	1.0	0.4	0.4	0.5	0.9	-	0.4	-
C <sub>9</sub> H <sub>12</sub>	2.1	-	0.7	0.8	0.7	0.8	0.6	0.9	0.9	-	-
C <sub>10</sub> H <sub>12</sub>	-	-	-	4.8	9.2	7.5	2.0	6.7	0.5	-	-
C <sub>10</sub> H <sub>14</sub>	0.8	-	1.0	1.1	8.9	2.9	0.6	1.7	0.5	-	-
Others <sup>b</sup>	0	0.3	0.2	0.8	0.3	0.4	0.7	2.2	1.8	0.4	0.5
Total of V <sub>25</sub>	57.9	51.9	50.9	47.9	19.5	12.6	5.0	17.1	8.2	22.2	20.1
V <sub>pyr</sub>	42.1	48.1	49.1	52.1	80.5	87.4	95.0	82.9	91.8	77.8	79.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

<sup>b</sup>Components in amounts of 0.3% or less are not shown individually in this table.

TABLE 3

RATES OF THERMAL DEGRADATION OF COPOLYMERS OF STYRENE  
WITH DIVINYLBENZENE AND WITH TRIVINYLBENZENE

Copolymer	Temp. °C	Heating duration min	Loss of weight		Activation energy kcal/mole
			Amount %	Rate %/min	
2% DVB	330	290	54	0.19	53
	340	240	74	0.39	
	349	160	83	0.74	
	355	120	86	1.05	
	360	130	93	1.39	
25% DVB	350	280	59	0.27	54
	360	230	75	0.52	
	369	160	83	1.00	
48% DVB	370	340	70	0.23	58
	380	200	80	0.45	
	390	100	81	0.88	
56% DVB	370	280	65	0.24	58
	380	170	76	0.48	
	390	110	81	0.93	
100% DVB	360	460	35	0.08	65
	370	440	68	0.19	
	380	290	80	0.44	
	390	150	81	0.86	
25% TVB	360	300	48	0.29	61
	370	230	60	0.70	
	380	140	63	1.32	
	390	120	75	- <sup>a</sup>	
100% TVB	394	2,640	39	0.03	73
	420	210	45	0.28	
	430	140	46	0.59	
	440	80	48	1.22	

<sup>a</sup>Rate at this temperature was too fast, and the accuracy of the extrapolated initial rate was therefore in doubt.



TABLE 4

ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS OF POLYSTYRENE  
IN A VACUUM AND IN HELIUM

Component <sup>a</sup>	At 362°C		At 850°C	
	In Vac.	In He	In Vac.	In He
	%	%	%	%
C <sub>2</sub> H <sub>4</sub>	0	0	0	17.7
C <sub>2</sub> H <sub>6</sub>	0	0	0	1.6
C <sub>3</sub> H <sub>4</sub>	0	0	0.5	0.6
C <sub>6</sub> H <sub>6</sub>	0	20.5	37.1	18.4
C <sub>7</sub> H <sub>8</sub>	2.1	3.1	3.8	16.6
C <sub>8</sub> H <sub>8</sub>	40.9	31.4	26.6	17.1
V <sub>pyr</sub>	57.0	45.0	32.0	28.0
Total	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

TABLE 5

ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS OF POLYSTYRENE  
IN A VACUUM

Component <sup>a</sup>	at 400°C		at 500°C		at 800°C			at 1200°C	
	No.1	No.2	No.3	No.4	No.5	No.6	No.7 <sup>b</sup>	No.8	No.9
	%	%	%	%	%	%	%	%	%
C <sub>2</sub> H <sub>2</sub>	-	-	-	-	-	-	-	2.3	-
C <sub>2</sub> H <sub>4</sub>	-	-	-	-	-	1.6	2.8	5.6	4.7
C <sub>3</sub> H <sub>4</sub>	-	-	-	-	-	0.4	0.7	0.4	0.8
C <sub>3</sub> H <sub>6</sub>	-	-	-	-	-	-	-	-	1.0
C <sub>6</sub> H <sub>6</sub>	1.9	2.2	1.5	0.5	0.8	1.6	3.8	3.1	2.1
C <sub>7</sub> H <sub>8</sub>	4.0	3.7	1.1	3.4	1.8	3.9	8.9	2.5	2.8
C <sub>7</sub> H <sub>11</sub>	-	-	0.4	-	0.5	-	-	0.6	-
C <sub>8</sub> H <sub>8</sub>	46.6	50.2	56.4	51.4	47.4	47.5	27.2	24.0	28.4
C <sub>8</sub> H <sub>11</sub>	-	-	0.3	-	0.3	-	-	0.3	-
C <sub>9</sub> and up	0.4	0.5	4.5	6.1	21.8	22.2	-	16.6	17.1
V <sub>pyr</sub>	47.1	43.4	35.8	38.6	27.4	22.8	56.6	44.6	43.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.<sup>b</sup>Time of collection was 1 hr instead of the usual 3 hrs.

TABLE 6  
ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLYSTYRENE IN HELIUM

Component <sup>a</sup>	At 500°C			At 800°C			At 1200°C
	No.10	No.11	No.12	No.13	No.14	No.15 <sup>b</sup>	No.16
	%	%	%	%	%	%	%
C <sub>2</sub> H <sub>2</sub>	0.1	-	-	-	-	0.1	0.6
C <sub>2</sub> H <sub>4</sub>	-	-	3.5	8.5	5.8	5.9	2.6
C <sub>2</sub> H <sub>6</sub>	-	-	-	-	0.4	0.3	0.2
C <sub>3</sub> H <sub>4</sub>	-	-	-	0.2	-	-	-
C <sub>4</sub> H <sub>10</sub>	-	3.5	-	-	-	0.1	-
C <sub>5</sub> H <sub>10</sub>	-	-	4.1	-	-	-	-
C <sub>6</sub> H <sub>6</sub>	0.7	1.4	2.4	16.2	15.5	20.9	12.5
C <sub>7</sub> H <sub>8</sub>	5.5	12.5	10.2	7.7	7.2	8.9	1.3
C <sub>7</sub> H <sub>11</sub>	0.9	-	-	0.6	-	-	-
C <sub>8</sub> H <sub>8</sub>	52.7	49.1	29.8	8.8	12.5	3.7	0.6
C <sub>8</sub> H <sub>10</sub>	-	-	-	-	0.8	-	-
C <sub>8</sub> H <sub>11</sub>	0.4	-	-	-	-	-	-
C <sub>9</sub> and up	4.5	5.1	-	18.0	18.0	-	7.6
V <sub>pyr</sub>	35.2	28.4	50.0	40.0	39.8	60.1	74.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

<sup>b</sup>Time of collection was 1 hr instead of the usual 3 hrs.

TABLE 7

## PYROLYSIS OF POLYMETHYLENE IN A VACUUM AND IN HELIUM

Expt. No.	Weight of Sample	Temp.	Volatil- ization	Fractions, based on total volatilized			
				V <sub>pyr</sub>	V <sub>25</sub>	V <sub>-80</sub>	V <sub>-190</sub>
	mg	°C	%	%	%	%	%
1 (in vac)	-	393-449	7.2-98.5	94.0-98.5	2.4	0.8	Trace
2 " "	17.2	500	99.4	94.1	4.7	1.2	Trace
3 " "	17.9	800	99.5	77.8	11.0	11.0	0.2
4 " "	25.0	1200	98.2	41.3	10.6	37.1	11.0
5 (in He)	17.9	500	99.2	82.9 <sup>a</sup>	10.0	6.2	a
6 " "	18.7	800	97.9	56.1 <sup>a</sup>	18.0	25.9	a
7 " "	15.9	1200	95.3	61.6 <sup>a</sup>	14.6	23.8	a

<sup>a</sup>For pyrolysis in helium, values for V<sub>pyr</sub> and V<sub>-190</sub> were combined.

TABLE 8  
ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLYMETHYLENE IN A VACUUM<sup>a</sup>

Component <sup>c</sup>	At 500°C	At 800°C	At 1200°C
	No. 2 <sup>b</sup>	No. 3 <sup>b</sup>	No. 4 <sup>b</sup>
	%	%	%
H <sub>2</sub>	-	0.1	0.2
CH <sub>4</sub>	-	0.1	3.6
C <sub>2</sub> H <sub>2</sub>	-	-	3.3
C <sub>2</sub> H <sub>4</sub>	-	5.5	26.4
C <sub>2</sub> H <sub>6</sub>	0.1	0.3	0.9
C <sub>3</sub> H <sub>4</sub>	0.1	0.2	2.7
C <sub>3</sub> H <sub>6</sub>	0.1	2.9	8.0
C <sub>3</sub> H <sub>8</sub>	0.2	-	0.5
C <sub>4</sub> H <sub>6</sub>	0.3	0.9	7.1
C <sub>4</sub> H <sub>8</sub>	0.3	3.9	3.1
C <sub>4</sub> H <sub>10</sub>	0.1	0.4	-
C <sub>5</sub> H <sub>8</sub>	-	0.5	1.8
C <sub>5</sub> H <sub>10</sub>	0.8	2.2	-
C <sub>6</sub> H <sub>6</sub>	-	0.1	1.1
C <sub>6</sub> H <sub>10</sub>	-	0.6	-
C <sub>6</sub> H <sub>12</sub>	1.9	2.4	-
C <sub>6</sub> H <sub>14</sub>	-	0.3	-
C <sub>7</sub> and C <sub>8</sub>	2.0	1.8	-
V <sub>pyr</sub>	94.1	77.8	41.3
Total	100.0	100.0	100.0

<sup>a</sup>Results of analysis of V<sub>25</sub>, V<sub>-80</sub>, and V<sub>-190</sub> were combined.

<sup>b</sup>Expt. Nos. are the same as in Table 7.

<sup>c</sup>Components are in weight percent of total volatiles.

TABLE 9  
COMBINED ANALYSIS OF FRACTIONS V<sub>25</sub> AND V<sub>-80</sub> FROM PYROLYSIS  
OF POLYMETHYLENE IN A VACUUM AND IN HELIUM

Component <sup>a</sup>	At 500°C		At 800°C		At 1200°C	
	in vac	in He	in vac	in He	in vac	in He
	No.2 <sup>b</sup>	No.5	No.3	No.6	No.4	No.7
	%	%	%	%	%	%
CH <sub>4</sub>	-	-	-	0.2	3.1	0.1
C <sub>2</sub> H <sub>2</sub>	-	-	-	0.4	2.9	0.6
C <sub>2</sub> H <sub>4</sub>	-	2.1	5.4	11.9	22.3	16.2
C <sub>2</sub> H <sub>6</sub>	0.1	0.8	0.3	2.2	0.8	1.5
C <sub>3</sub> H <sub>4</sub>	0.1	0.1	0.2	0.2	2.1	-
C <sub>3</sub> H <sub>6</sub>	0.1	2.2	2.8	5.8	6.4	3.9
C <sub>3</sub> H <sub>8</sub>	0.2	0.8	-	0.6	0.4	-
C <sub>4</sub> H <sub>2</sub>	-	0.3	-	0.3	-	0.3
C <sub>4</sub> H <sub>6</sub>	0.3	0.5	0.9	1.7	5.4	1.3
C <sub>4</sub> H <sub>8</sub>	0.3	1.5	3.9	3.6	2.4	0.7
C <sub>4</sub> H <sub>10</sub>	0.1	0.3	0.4	0.3	-	-
C <sub>5</sub> H <sub>6</sub>	-	-	0.1	0.7	-	0.5
C <sub>5</sub> H <sub>8</sub>	-	0.6	0.5	1.8	1.2	0.4
C <sub>5</sub> H <sub>10</sub>	0.8	1.0	2.1	2.0	-	-
C <sub>6</sub> H <sub>6</sub>	-	0.1	0.1	7.2	0.6	11.4
C <sub>6</sub> H <sub>10</sub>	-	1.2	0.6	1.2	-	-
C <sub>6</sub> H <sub>12</sub>	1.9	1.5	2.4	1.4	-	-
C <sub>6</sub> H <sub>14</sub>	-	0.8	0.3	0.3	-	-
C <sub>7</sub> and C <sub>8</sub>	2.0	3.3	2.0	2.1	0.1	1.5
V <sub>pyr</sub> + V <sub>-190</sub>	94.1	82.9	78.0	56.1	52.3	61.6
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

<sup>b</sup>Expt.Nos. are the same as in Table 7.

TABLE 10  
PYROLYSIS OF POLYTETRAFLUOROETHYLENE IN A VACUUM

Expt. No.	Wt. of Sample	Tempe- rature	Volatil- ization	Fractions, based on total volatilized <sup>a</sup>	
				V <sub>pyr</sub>	V <sub>25</sub>
	%	°C	%	%	%
1	24.7	500	17.2	0	100
2	20.2	500	16.1	0	100
3	14.1	800	99.7	0	100.
4	8.6	800	100	1.8	98.2
5	10.9	1200	100	11.8	88.2
6	10.7	1200	100	15.9	84.1

<sup>a</sup>Fraction V<sub>-190</sub> appeared in trace amounts.

TABLE 11

ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLYTETRAFLUOROETHYLENE IN A VACUUM

Component <sup>a</sup>	At 500°C		At 800°C		At 1200°C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
	%	%	%	%	%	%
HF	0	0	0	0	0.2	0.5
CF <sub>4</sub>	1.5	1.2	1.6	1.8	1.7	2.6
C <sub>2</sub> F <sub>4</sub>	94.8	95.1	92.5	89.9	81.0	75.2
C <sub>3</sub> F <sub>6</sub>	3.7	3.7	5.9	6.5	5.3	5.8
V <sub>pyr</sub>	0	0	0	1.8	11.8	15.9
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.



TABLE 12  
PYROLYSIS OF POLY( $\alpha$ -METHYLSTYRENE)  
IN A VACUUM

Expt, No.	Wt. of Sample	Temp.	Amt. of vol- atilization	Fractions, based on total volatilized		
				V <sub>pyr</sub>	V <sub>25</sub>	V <sub>-190</sub>
	mg	°C	%	%	%	%
1	10.2	500	99.0	0	100	0
2	11.3	500	99.4	0	100	0
3	8.0	800	100.0	11.2	88.7	0.1
4	10.1	800	100.0	5.4	94.3	0.3
5	7.9	1200	98.7	34.3	54.2	11.5
6	8.2	1200	99.4	32.6	61.1	6.3

TABLE 13

ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLY( $\alpha$ -METHYLSTYRENE) IN A VACUUM

Component <sup>a</sup>	At 500°C		At 800°C		At 1200°C	
	No.1	No.2	No.3	No.4	No.5	No.6
	%	%	%	%	%	%
H <sub>2</sub>	-	-	0.1	0.1	1.7	1.3
CH <sub>4</sub>	-	-	.3	.3	5.6	3.1
C <sub>2</sub> H <sub>2</sub>	-	-	-	-	.8	.7
C <sub>2</sub> H <sub>4</sub>	-	-	.5	.1	3.8	3.2
C <sub>3</sub> H <sub>4</sub>	-	-	.8	.3	1.0	1.8
C <sub>3</sub> H <sub>6</sub>	-	-	.8	.2	.7	.4
C <sub>4</sub> H <sub>4</sub>	-	-	-	-	.5	1.9
C <sub>6</sub> H <sub>6</sub>	-	-	2.0	1.1	9.3	13.3
C <sub>7</sub> H <sub>8</sub>	-	-	.4	.3	6.1	3.6
C <sub>8</sub> H <sub>8</sub>	-	-	-	-	2.6	4.2
C <sub>9</sub> H <sub>10</sub>	100.0	100.0	83.9	92.2	33.6	33.9
V <sub>pyr</sub>	0	0	11.2	5.4	34.3	32.6
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

TABLE 14

## PYROLYSIS OF POLYPROPYLENE IN A VACUUM

Expt. No.	Wt. of Sample	Temp.	Volatilization	Fractions, based on total volatilized		
				V <sub>pyr</sub>	V <sub>25</sub> <sup>a</sup>	V <sub>-190</sub>
	mg	°C	%	%	%	%
1	10.0	400	76.5	76.7	23.3	trace
2	10.5	400	82.4	79.2	20.8	trace
3	11.0	500	99.6	82.4	17.6	trace
4	9.6	800	100.0	29.6	70.3	0.1
5	9.4	1200	98.9	22.4	75.8	1.8
6	40.8	1200	98.9	31.7	53.7	14.6

<sup>a</sup>Includes V<sub>-80</sub> fraction.

TABLE 15

## PYROLYSIS OF POLYISOBUTYLENE IN A VACUUM

Expt. No.	Wt. of Sample	Temp.	Volatilization	Fractions, based on total volatilized		
				V <sub>pyr</sub>	V <sub>25</sub>	V <sub>-190</sub>
	mg	°C	%	%	%	%
1	15.9	400	99.3	53.3	46.7	0
2	14.1	400	98.6	57.5	42.5	0
3	17.0	500	99.4	51.1	47.8	1.1
4	15.8	500	99.4	52.1	46.9	1.0
5	13.8	800	99.6	3.6	94.8	1.6
6	12.9	800	99.2	3.1	94.5	2.4
7	14.1	1200	98.6	14.7	66.8	18.5
8	14.0	1200	97.5	7.6	73.3	19.1

TABLE 16  
ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLYPROPYLENE IN A VACUUM

Component <sup>a</sup>	At 100°C		At 500°C	At 800°C	At 1200°C	
	No.1	No.2	No.3	No.4	No.5	No.6
	%	%	%	%	%	%
H <sub>2</sub>	-	-	-	.1	.1	.4
CH <sub>4</sub>	.1	.1	-	.4	2.6	9.6
C <sub>2</sub> H <sub>2</sub>	.1	.1	-	.3	6.3	4.3
C <sub>2</sub> H <sub>4</sub>	.4	.3	.4	6.0	13.1	19.0
C <sub>2</sub> H <sub>6</sub>	.3	.3	.3	.7	1.0	.9
C <sub>3</sub> H <sub>4</sub>	.6	.4	.3	3.4	8.5	6.5
C <sub>3</sub> H <sub>6</sub>	.6	.6	.4	17.9	18.4	12.6
C <sub>3</sub> H <sub>8</sub>	.5	.5	.6	2.3	1.9	.6
C <sub>4</sub> H <sub>4</sub>	-	-	-	.7	2.3	2.4
C <sub>4</sub> H <sub>6</sub>	-	-	-	3.0	5.1	4.1
C <sub>4</sub> H <sub>8</sub>	2.5	1.7	.6	12.4	8.1	2.9
C <sub>4</sub> H <sub>10</sub>	1.8	1.3	.7	1.3	0.5	-
C <sub>5</sub> H <sub>6</sub>	-	-	-	.5	.8	1.0
C <sub>5</sub> H <sub>8</sub>	.8	.6	.6	3.0	2.1	.8
C <sub>5</sub> H <sub>10</sub>	3.3	3.8	2.0	10.2	4.1	.3
C <sub>5</sub> H <sub>12</sub>	3.1	2.2	3.0	1.9	-	-
C <sub>6</sub> H <sub>6</sub>	-	-	-	-	1.6	2.9
C <sub>6</sub> H <sub>10</sub>	.7	.5	.7	1.7	.7	-
C <sub>6</sub> H <sub>12</sub>	4.0	3.7	3.0	4.6	.4	-
C <sub>6</sub> H <sub>14</sub>	.2	1.4	1.9	-	-	-
C <sub>7</sub> H <sub>16</sub>	2.2	1.8	1.0	-	-	-
C <sub>9</sub> H <sub>18</sub>	2.1	1.5	1.4	-	-	-
C <sub>10</sub> H <sub>20</sub>	-	-	.7	-	-	-
V <sub>pyr</sub>	76.7	79.2	82.4	29.6	22.4	31.7
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

TABLE 17

ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLYISOBUTYLENE IN A VACUUM

Component <sup>a</sup>	At 400°C		At 500°C		At 800°C		At 1200°C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
	%	%	%	%	%	%	%	%
H <sub>2</sub>	-	-	-	-	-	-	2.7	1.6
CH <sub>4</sub>	-	-	-	-	1.2	-	17.6	10.1
C <sub>2</sub> H <sub>2</sub>	-	-	-	-	0.8	1.1	6.8	7.3
C <sub>2</sub> H <sub>4</sub>	-	-	0.9	0.6	2.7	5.0	9.6	13.6
C <sub>2</sub> H <sub>6</sub>	-	-	-	-	-	-	1.6	1.2
C <sub>3</sub> H <sub>4</sub>	0.5	-	1.1	1.6	3.0	5.4	14.9	16.5
C <sub>3</sub> H <sub>6</sub>	-	-	-	-	-	-	0.9	1.0
C <sub>3</sub> H <sub>8</sub>	-	-	0.7	1.3	-	-	4.8	4.4
C <sub>4</sub> H <sub>4</sub>	-	-	-	-	2.1	1.3	4.5	4.2
C <sub>4</sub> H <sub>6</sub>	-	-	-	-	-	0.7	4.5	5.9
C <sub>4</sub> H <sub>8</sub>	35.6	31.5	38.0	34.9	72.7	65.3	10.6	15.3
C <sub>4</sub> H <sub>10</sub>	0.7	0.7	-	-	-	-	-	-
C <sub>5</sub> H <sub>6</sub>	-	-	-	-	-	0.5	1.0	1.9
C <sub>5</sub> H <sub>8</sub>	-	-	0.7	-	-	-	0.7	2.4
C <sub>5</sub> H <sub>10</sub>	-	-	-	-	5.7	1.7	-	1.1
C <sub>6</sub> and up	9.9	10.3	7.4	9.5	8.2	15.9	5.1	5.9
V <sub>pyr</sub>	53.3	57.5	51.2	52.1	3.6	3.1	14.7	7.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.

TABLE 18

## PYROLYSIS OF POLY(METHYL METHACRYLATE) IN A VACUUM

Expt. No.	Wt. of Sample	Temp.	Volatilization	Fractions, based on total volatilized		
				V <sub>pyr</sub>	V <sub>25</sub>	V <sub>-190</sub>
	mg	°C	%	%	%	%
1	10.3	500	100	3.6	96.4	0
2	9.9	500	100	2.3	97.7	0
3	8.5	800	100	11.2	88.7	0.1
4	11.3	800	100	8.8	91.1	.1
5	9.8	1200	100	5.0	29.4	65.6
6	9.8	1200	100	8.2	26.2	65.6

TABLE 19  
ANALYSIS OF VOLATILE PRODUCTS FROM PYROLYSIS  
OF POLY(METHYL METHACRYLATE) IN A VACUUM

Component <sup>a</sup>	At 500°C		At 800°C		At 1200°C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
H <sub>2</sub>	-	-	-	-	.9	1.1
CH <sub>4</sub>	-	-	-	-	5.9	6.3
C <sub>2</sub> H <sub>2</sub>	-	-	-	-	2.6	3.5
C <sub>2</sub> H <sub>4</sub>	-	-	.7	.7	5.3	4.7
C <sub>2</sub> H <sub>6</sub>	-	-	-	-	1.4	1.1
C <sub>3</sub> H <sub>4</sub>	.7	1.0	.3	1.4	6.7	6.6
C <sub>3</sub> H <sub>4</sub> O	-	-	.3	.8	-	-
C <sub>3</sub> H <sub>6</sub>	-	-	.1	.7	3.2	5.6
C <sub>3</sub> H <sub>6</sub> O	-	-	.3	-	-	-
C <sub>4</sub> H <sub>4</sub>	-	-	.4	-	1.2	.5
C <sub>4</sub> H <sub>6</sub>	-	-	.3	-	1.4	3.0
C <sub>4</sub> H <sub>8</sub>	-	-	2.0	1.0	1.3	2.0
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	93.0	95.4	80.5	83.1	16.5	9.3
C <sub>5</sub> H <sub>8</sub>	-	-	.3	-	-	-
C <sub>5</sub> H <sub>10</sub>	-	-	1.0	1.0	.7	2.0
C <sub>5</sub> H <sub>12</sub>	-	-	.7	-	-	-
C <sub>6</sub> H <sub>6</sub>	.1	-	.2	-	1.8	1.9
CO	2.3	.8	.6	1.8	31.3	31.4
CO <sub>2</sub>	.3	.5	1.1	.7	9.8	12.8
V <sub>pyr</sub>	3.6	2.3	11.2	8.8	5.0	8.2
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Components are in weight percent of total volatiles.



TABLE 20  
STANDARD DEVIATIONS OF IONS FROM n-BUTANE

m/e	R.A.	$\sigma_{\text{obs}}$ %	$\sigma_{\text{max}}$ %
2	1.19	4.92	4.10
12	.15	16.3	23.22
13	.22	12.0	22.73
14	.67	5.85	7.69
15	4.20	3.43	2.00
16	1.51	8.00	3.13
25	.61	2.11	8.77
26	7.05	3.15	2.00
27	35.32	1.10	2.00
28	34.77	1.24	2.00
29	41.22	1.17	2.00
30	1.10	3.78	4.42
37	.49	8.13	10.63
38	1.63	5.10	3.13
39	14.48	2.34	2.00
40	2.41	3.29	2.12
41	29.49	1.28	2.00
42	13.86	2.34	2.00
43	100.00	-	-
44	3.19	2.83	2.00
50	.77	1.62	6.76
51	1.00	4.90	5.05
52	.35	9.17	14.71
53	1.09	3.11	4.67
54	.33	13.89	15.15
55	1.23	6.40	4.07
56	1.09	11.23	4.59
57	2.95	3.42	2.00
58	21.43	1.62	2.00
59	.85	7.37	5.62

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