

# Thermal Degradation of Polymers as a Function of Molecular Structure<sup>1</sup>

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When heated in a vacuum at temperatures of about 200° to 500° C, polymer chains break up into volatile fragments of various sizes, depending on the nature of the polymer. Some polymers, like poly-alpha-methylstyrene, yield the monomer exclusively. Other polymers, like polymethylene, yield a whole spectrum of fragments consisting of 2 carbon atoms in the chain to about 50 or more. Intermediate between these two types of polymers are those like polyisobutylene, which yield partly monomer and partly large fragments. The rates at which these fragments are formed and vaporized also vary for different polymers. On comparing rates of volatilization of a series of polymers at 350° C, we find that polytetrafluoroethylene is the most thermally stable polymer, having an initial rate of volatilization of 0.0000016 weight percent per minute, whereas poly-alpha-methylstyrene is the least stable, having a rate of volatilization of 230 percent per minute. These differences in the thermal behavior of polymers can be correlated with the molecular structure of the polymer and with the nature and frequency of side groups.

## 1. Introduction

When heated in a vacuum at temperatures of about 200° to 500° C, organic polymers usually degrade to yield molecular fragments of various sizes. Some polymers, like poly-alpha-methylstyrene and polymethyl methacrylate, yield almost exclusively the monomer, whereas other polymers, such as polymethylene, yield a whole spectrum of molecular fragments volatilizable at the temperatures employed. Intermediate between these two extremes are polymers like polyisobutylene that yield part monomer and part larger fragments. The rates of degradation are also different for different polymers. In the case of some polymers, degradation by heat, as expressed by loss of weight through volatilization, is almost complete in less than an hour at about 300° C, whereas in the case of others there is very little loss of weight during the same period, even at 450° C. The difference in the thermal behavior of polymers has been the subject of a number of papers by various authors in the last few years [1 to 12].<sup>2</sup>

In this investigation a systematic study was initiated to determine the effect of molecular structure of chains and side groups of polymers on the rate of their degradation and the nature and relative amounts of the volatile products obtained when these polymers are heated in a vacuum. The following polymers were used:

1. A pure grade of polymethylene,



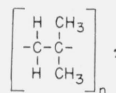
of high molecular weight prepared by the decomposition of diazomethane, using trimethyl borate as catalyst. This material is the same as was used in

<sup>1</sup> This work was performed as a part of the research project sponsored by the Federal Facilities Corporation, Office of Synthetic Rubber Research and Development Division, Polymer Science Branch.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

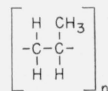
the study of melting transition of polymethylene [13]. Unlike polyethylene, this polymer consists of a nonbranched hydrocarbon chain.

2. Polyisobutylene,



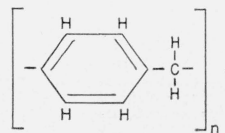
of high purity was obtained by repeatedly dissolving the commercial polymer in benzene and precipitating with methanol. It had a molecular weight of 1,500,000, as determined by light-scattering.

3. Polypropylene,<sup>3</sup>



A 90-g sample of number-average molecular weight of about 5,000 was reduced to 6 g of a higher molecular weight material by six fractionation steps. In each step the material was dissolved in benzene and then precipitated with acetone.

4. A pure grade of polybenzyl,<sup>4</sup>

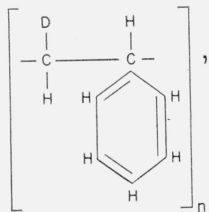


<sup>3</sup> The authors are indebted to C. M. Fontana, Socony Vacuum Co., for supplying this polymer.

<sup>4</sup> The authors are indebted to Daniel I. Livingston, Polaroid Corporation, for this polymer.

of molecular weight of  $4,300 \pm 10$  percent, as determined cryoscopically.

#### 5a. Poly-beta-deuterostyrene,



molecular weight 220,000 by light-scattering. The same material was used by Wall, Brown, and Hart [14] in their studies on pyrolysis of alpha- and beta-deuterostyrene polymers. The monomer used in the preparation of this polymer contained about 15 percent of normal styrene.

5b. Poly-beta-deuterostyrene of much higher molecular weight than 5a. The monomer used in its preparation contained only a few percent of normal styrene.

## 2. Apparatus and Experimental Procedure

The work described in this paper was carried out in two parts: (1) pyrolysis of polymer samples and fractionation of the volatile products, and (2) a study of rates of thermal degradation and the activation energies involved.

### 2.1. Pyrolysis

Pyrolysis experiments were carried out on polymethylene, polypropylene, polybenzyl, and poly-beta-deuterostyrene. Pyrolysis of polyisobutylene has been studied and described [5]. The apparatus consisted of a Dewar-like molecular still provided with a platinum tray resting on a platinum-wire-wound heater placed inside. This apparatus and the experimental procedure have been described [1, 5, 6]. Only a few salient points of the procedure will be recounted here. The samples were limited to a maximum of about 40 mg to avoid spattering that might occur if larger amounts were used. Polymethylene and polybenzyl were used in powdered form, polypropylene and poly-beta-deuterostyrene as solutions in benzene. In either case the samples were preheated in a vacuum for about  $1\frac{1}{2}$  hr at  $160^\circ\text{C}$ , and the volatiles were rejected before starting pyrolysis. In all experiments it took 45 min to heat the tray containing the sample to the pyrolysis temperature. This temperature was then maintained constant to about  $\pm 1.5$  deg C for 30 min. The following fractions were obtained: A residue, I, except when pyrolysis was carried to completion; a heavy fraction, II, volatile at the temperature of pyrolysis; a light fraction, III, volatile at room temperature. In some cases fraction III was separated by molecular distillation at  $-80^\circ\text{C}$  into a more volatile fraction, IIIA, and a less volatile fraction, IIIB. A gaseous fraction, IV, not condensable at liquid-nitrogen temperature, was also

collected. The weights of all these fractions were determined directly or indirectly. Fraction II was tested for average molecular weight by a micro-cryoscopic method in a suitable solvent. Fractions III, IIIA, and IIIB were analyzed in the mass spectrometer. Fraction IV amounted in all cases to less than 0.1 percent by weight of the sample, and was found on mass-spectrometer analysis to consist of a small amount of hydrogen mixed with air, carbon dioxide, and carbon monoxide.

### 2.2. Rates

Rates of degradation, as expressed by loss in weight of polymer samples when heated in a vacuum, were determined by means of a very sensitive tungsten helical-spring balance. The method and the apparatus used in this part of the work have also been described [7, 8, 9]. Samples were limited to 5 to 6 mg and were used in dry state, after preheating for several hours in a vacuum of about 100 mm at  $175^\circ\text{C}$  to a constant weight, in order to eliminate traces of solvents.

## 3. Results

### 3.1. Pyrolysis

Results of pyrolysis experiments at various temperatures are shown in table 1. Fractions I, II, and III add up to 100-percent material balance because the gaseous fraction, IV, is very small. Polymethylene, like polyethylene, yields mostly fraction II. Polypropylene and polybenzyl yield more of fraction III and less of fraction II than polymethylene. Low and high molecular weight poly-beta-deuterostyrene (5a and 5b) yield a fraction III equal to 42.2 and 41.0 percent, respectively, of the total volatilized part, about the same as in the case of polystyrene.

Mass-spectrometer analyses of fraction III or IIIA are shown in tables 2, 3, 4, 5, and 6. In the case of polymethylene, fraction III was separated into IIIA, comprising 20 percent, and IIIB, 80 percent, of its total weight. This was done in order to facilitate mass-spectrometer analysis. As seen from table 2, the components of IIIA consist of saturated and unsaturated hydrocarbons up to and including six carbon atoms. Fraction IIIB was also analyzed in the mass spectrometer and was found to contain similarly saturated and unsaturated hydrocarbons, but of 7 to 12 carbon atoms.

On comparing table 2 with table 14 of reference [5],<sup>5</sup> which shows the mass-spectrometer analysis of fraction IIIA from polyethylene pyrolysis, we find that in the case of polymethylene this fraction has about twice as many double bonds as the corresponding fraction from polyethylene.

Polypropylene, like polymethylene, yields a large number of constituents in fraction III, and this fraction was therefore separated into subfractions IIIA and IIIB in the weight-percent ratio of 25:75.

<sup>5</sup> In this reference the ratio of IIIA to IIIB fraction for polyethylene is not shown. This ratio is the same (20:80) as for polymethylene.

Mass-spectrometer analysis of IIIA is shown in table 3 for three experiments. There is some disagreement in the analysis of this fraction from the three experiments, much more so than in the case of polymethylene reported in table 2. This difference does not seem to be due to a temperature effect. It is most likely due to experimental error

TABLE 1. *Pyrolytic fractionation of polymers*

| Experiment   | Temperature | Fractions of original sample |                                      |                                   | Fraction III of total volatilized part |
|--|-------------|------------------------------|--------------------------------------|-----------------------------------|--|
|  |             | I. Residue                   | II. Non-volatile at room temperature | III. Volatile at room temperature |  |
| Polymethylene <sup>a</sup>                             |             |                              |                                      |                                   |  |
|  | °C          | wt %                         | wt %                                 | wt %                              | wt %                                   |
| 1.....   | 393         | 92.8                         | 6.9                                  | 0.3                               | 4.1                                    |
| 2.....   | 407         | 71.5                         | 27.6                                 | .9                                | 3.3                                    |
| 3.....   | 410         | 70.8                         | 28.0                                 | 1.2                               | 4.1                                    |
| 4.....   | 415         | 52.5                         | ---                                  | ---                               | ---                                    |
| 5.....   | 419         | 29.7                         | 69.2                                 | 1.1                               | 2.4                                    |
| 6.....   | 425         | 23.0                         | 75.2                                 | 1.8                               | 2.3                                    |
| 7.....   | 444         | 1.5                          | 96.2                                 | 2.3                               | 2.4                                    |
| 8.....   | 449         | 2.9                          | 93.4                                 | 3.7                               | 3.9                                    |
| Average.....   |             |                              |                                      |                                   | 3.2±0.7                                |
| Polypropylene  |             |                              |                                      |                                   |  |
| 1.....   | 328         | 91.8                         | 6.7                                  | 1.5                               | 17.7                                   |
| 2.....   | 374         | 71.4                         | 24.4                                 | 4.2                               | 14.8                                   |
| 3.....   | 380         | 58.5                         | 35.7                                 | 5.8                               | 14.0                                   |
| 4.....   | 384         | 53.9                         | 39.4                                 | 6.7                               | 14.5                                   |
| 5.....   | 393         | 36.8                         | 54.3                                 | 8.9                               | 14.0                                   |
| 6.....   | 395         | 39.2                         | 62.8                                 | 8.0                               | 11.3                                   |
| 7.....   | 400         | 13.2                         | 76.9                                 | 9.9                               | 11.5                                   |
| 8.....   | 410         | 3.6                          | 85.3                                 | 11.1                              | 11.6                                   |
| Average.....   |             |                              |                                      |                                   | 13.7±1.7                               |
| Polybenzyl   |             |                              |                                      |                                   |  |
| 1.....   | 412         | 81.5                         | 16.9                                 | 1.6                               | 8.9                                    |
| 2.....   | 427         | 74.4                         | 23.3                                 | 2.3                               | 9.0                                    |
| 3.....   | 431         | 48.2                         | ---                                  | ---                               | ---                                    |
| 4.....   | 444         | 28.1                         | 67.5                                 | 4.4                               | 6.2                                    |
| 5.....   | 462         | 5.6                          | 89.1                                 | 5.3                               | 5.6                                    |
| Average.....   |             |                              |                                      |                                   | 7.4±1.5                                |
| Poly-beta-deuterostyrene of low molecular weight (5a)  |             |                              |                                      |                                   |  |
| 1.....   | 314         | 87.3                         | 7.8                                  | 4.9                               | 38.6                                   |
| 2.....   | 334         | 77.0                         | 13.7                                 | 9.3                               | 40.3                                   |
| 3.....   | 341         | 69.0                         | 19.7                                 | 11.3                              | 36.5                                   |
| 4.....   | 355         | 40.8                         | 33.9                                 | 25.3                              | 42.6                                   |
| 5.....   | 361         | 36.2                         | 36.7                                 | 27.1                              | 42.4                                   |
| 6.....   | 366         | 21.2                         | 44.2                                 | 34.6                              | 43.8                                   |
| 7.....   | 371         | 18.8                         | 46.0                                 | 35.2                              | 43.3                                   |
| 8.....   | 374         | 8.8                          | 51.9                                 | 39.3                              | 43.0                                   |
| 9.....   | 374         | 7.8                          | 50.5                                 | 41.7                              | 45.1                                   |
| 10.....  | 399         | 1.0                          | 52.7                                 | 46.3                              | 46.6                                   |
| Average.....   |             |                              |                                      |                                   | 42.2±2.3                               |
| Poly-beta-deuterostyrene of high molecular weight (5b) |             |                              |                                      |                                   |  |
| 1.....   | 345         | 98.8                         | (b)                                  | (b)                               | (b)                                    |
| 2.....   | 360         | 86.6                         | 8.0                                  | 5.4                               | 40.0                                   |
| 3.....   | 376         | 28.9                         | 40.8                                 | 30.3                              | 42.6                                   |
| 4.....   | 384         | 6.6                          | 55.8                                 | 37.6                              | 40.3                                   |
| Average.....   |             |                              |                                      |                                   | 41.0±0.6                               |

<sup>a</sup> The thermal-stability curve for polymethylene in figure 2 of reference [9] should have been drawn at 10 deg C above its present position.  
<sup>b</sup> Amount of volatiles is too small for accurate weighing.

TABLE 2. *Mass-spectrometer analysis of fraction IIIA collected at -80° C in the pyrolysis of polymethylene*

| Component       | Temperature of pyrolysis, ° C |            |             |            | Average     |
|-----------------|-------------------------------|------------|-------------|------------|-------------|
|                 | 398                           | 410        | 416         | 435        |             |
| Ethylene.....   | Mole % 18.3                   | Mole % 2.6 | Mole % 21.0 | Mole % 7.3 | Mole % 12.3 |
| Ethane.....     | 8.1                           | ---        | 9.1         | ---        | 4.3         |
| Propadiene..... | 1.6                           | 1.1        | 1.3         | 1.5        | 1.4         |
| Propylene.....  | 19.2                          | 22.8       | 19.0        | 21.9       | 20.7        |
| Propane.....    | ---                           | 2.9        | ---         | 11.4       | 3.6         |
| Butadiene.....  | 2.6                           | .6         | ---         | 5.4        | 2.1         |
| Butene.....     | 13.8                          | 15.5       | 7.3         | 15.5       | 13.0        |
| Butane.....     | 9.5                           | 11.4       | 9.6         | 14.4       | 11.2        |
| Pentadiene..... | 2.7                           | 3.3        | 2.3         | 2.7        | 2.8         |
| Pentene.....    | 8.5                           | 11.4       | 8.0         | 10.6       | 9.6         |
| Pentane.....    | 5.7                           | 7.4        | 5.7         | 5.6        | 6.1         |
| Hexadiene.....  | 1.4                           | 4.7        | 4.1         | ---        | 2.6         |
| Hexene.....     | 7.7                           | 15.9       | 11.3        | ---        | 8.7         |
| Hexane.....     | .9                            | .4         | 1.3         | 3.7        | 1.6         |
| Total.....      | 100.0                         | 100.0      | 100.0       | 100.0      | 100.0       |

TABLE 3. *Mass-spectrometer analysis of fraction IIIA collected at -80° C in the pyrolysis of polypropylene*

| Component       | Temperature of pyrolysis, ° C |            |            | Average    |
|-----------------|-------------------------------|------------|------------|------------|
|                 | 380                           | 395        | 410        |            |
| Acetylene.....  | Mole % ---                    | Mole % --- | Mole % 1.0 | Mole % 0.3 |
| Ethylene.....   | 5.4                           | 6.1        | 1.0        | 4.1        |
| Ethane.....     | 3.4                           | 1.9        | ---        | 1.8        |
| Propadiene..... | ---                           | 1.4        | .7         | .7         |
| Propylene.....  | 11.0                          | 2.7        | 7.1        | 6.9        |
| Butadiene.....  | .9                            | 1.1        | .5         | .8         |
| Butene.....     | 22.7                          | 9.2        | 18.5       | 16.8       |
| Butane.....     | 13.1                          | 12.7       | 12.7       | 12.8       |
| Isoprene.....   | ---                           | ---        | .8         | .3         |
| Pentadiene..... | .7                            | .8         | 2.4        | 1.3        |
| Pentene.....    | 20.3                          | 25.1       | 13.6       | 19.7       |
| Pentane.....    | 2.1                           | 18.9       | 12.5       | 11.2       |
| Hexadiene.....  | 3.7                           | 2.8        | .3         | 2.3        |
| Hexene.....     | 4.8                           | 9.5        | 18.8       | 11.0       |
| Hexane.....     | 7.7                           | 7.2        | 6.0        | 7.0        |
| Benzene.....    | 4.2                           | .6         | 4.1        | 3.0        |
| Total.....      | 100.0                         | 100.0      | 100.0      | 100.0      |

TABLE 4. *Mass-spectrometer analysis of fraction III obtained in the pyrolysis of polybenzyl*

| Component    | Temperature of pyrolysis, ° C |             |             | Average     |
|--------------|-------------------------------|-------------|-------------|-------------|
|              | 412                           | 431         | 444         |             |
| Toluene..... | Mole % 78.6                   | Mole % 77.6 | Mole % 69.5 | Mole % 75.3 |
| Benzene..... | 20.3                          | 21.3        | 29.6        | 23.7        |
| Xylene.....  | 1.1                           | 1.1         | .9          | 1.0         |
| Total.....   | 100.0                         | 100.0       | 100.0       | 100.0       |

TABLE 5. Mass-spectrometer analysis of fraction III obtained in the pyrolysis of poly-beta-deuterostyrene (5a)

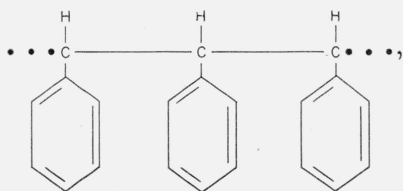
| Component                | Temperature of pyrolysis, ° C |             |             |             |             | Average     |
|--------------------------|-------------------------------|-------------|-------------|-------------|-------------|-------------|
|                          | 314                           | 334         | 355         | 361         | 399         |             |
| Beta-deuterostyrene..... | Mole % 85.3                   | Mole % 82.8 | Mole % 81.8 | Mole % 80.0 | Mole % 80.8 | Mole % 82.1 |
| Styrene.....             | 10.2                          | 11.1        | 11.1        | 10.2        | 11.3        | 10.8        |
| Toluene.....             | 4.5                           | 6.1         | 7.1         | 9.8         | 7.9         | 7.1         |
| Total.....               | 100.0                         | 100.0       | 100.0       | 100.0       | 100.0       | 100.0       |

TABLE 6. Mass-spectrometer analysis of fraction III obtained in the pyrolysis of poly-beta-deuterostyrene (5b)

| Component                | Temperature of pyrolysis, ° C |             | Average     |
|--------------------------|-------------------------------|-------------|-------------|
|                          | 376                           | 384         |             |
| Beta-deuterostyrene..... | Mole % 96.9                   | Mole % 96.8 | Mole % 96.8 |
| Deuterotoluene.....      | .2                            | .4          | .3          |
| Toluene.....             | 2.9                           | 2.8         | 2.9         |
| Total.....               | 100.0                         | 100.0       | 100.0       |

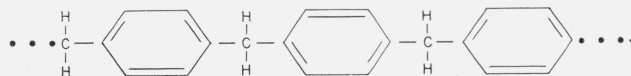
when dealing with quantities of the order of 1 mg. For example, the total time taken to separate fraction III into two subfractions by molecular distillation was only 2 min. A slight difference in the time from one sample to another might cause a difference in the composition of fraction IIIA or IIIB. In some experiments, IIIB was also analyzed in the mass spectrometer and was found to consist of saturated and unsaturated hydrocarbons containing 6 to 12 carbon atoms.

In the case of polybenzyl, an attempt to separate fraction III into IIIA and IIIB showed that all the material appeared in IIIA. For this reason fraction III was analyzed as such. Mass-spectrometer analysis of this fraction is shown in table 4. The main constituents are toluene and benzene. If polybenzyl were to have the structure then it should

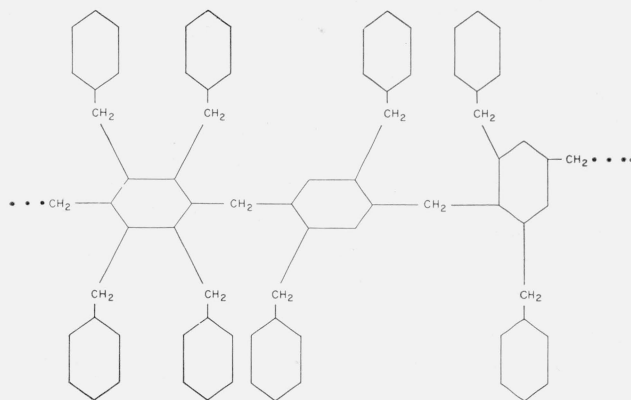


yield on pyrolysis stilbene as one of the volatile products. This compound was absent in fraction III. The vapor pressure of stilbene is given as 1 mm at 87.4° C for the *cis*- and at 113.2° C for the *trans*- variety [15]. After fraction III was separated by distillation at room temperature from the volatile products, another fraction was collected under conditions of molecular distillation at 80° C. This fraction, as shown by mass-spectrometer analysis, contained traces of toluene and benzene, but no

stilbene. Another argument against the above structure is the high thermal stability of polybenzyl, as shown below. It is concluded, on the basis of these facts, that the chain structure of polybenzyl is



Haas, Livingston, and Saunders [16], on the basis of infrared, X-ray, chemical, and other evidence, suggest the following as a part of the structure of polybenzyl:



Poly-beta-deuterostyrene, like polystyrene, poly-alpha-deuterostyrene, and poly-meta-methylstyrene [5, 6], yields a fraction III not separable into IIIA and IIIB. Mass-spectrometer analysis of fraction III for polymers 5a and 5b is shown in tables 5 and 6. The appearance of normal styrene among the components shown in table 5 is due to its presence in the polymer.

Results of molecular weight determination of fraction II from pyrolysis of four polymers are shown in table 7. The values for polyethylene and polyisobutylene were given in a previous publication [5] and are shown here for comparison. Poly-beta-deuterostyrene yields a low-molecular-weight fraction II, and, as in the case of the other polystyrenes, this fraction consists most likely of the dimer, trimer, and tetramer. These compounds have molecular weights 210, 315, and 420, respectively, as compared with the average molecular weight of 318 for fraction II.

TABLE 7. Average molecular weight of fraction II obtained in the pyrolysis of polymers

| Polymer                            | Solvent          | Average molecular weight |
|------------------------------------|------------------|--------------------------|
| Polyethylene.....                  | Benzene.....     | 692                      |
| Polymethylene.....                 | Camphor.....     | 755                      |
| Polypropylene.....                 | Cyclohexane..... | 854                      |
| Polyisobutylene.....               | do.....          | 543                      |
| Polybenzyl.....                    | Benzene.....     | 536                      |
| Poly-beta-deuterostyrene (5b)..... | Cyclohexane..... | 318                      |

### 3.2. Rates and Activation Energies of Thermal Degradation

In figures 1, 2, 3, and 4 the solid curves represent plots of percentage volatilization versus time at 4 to 5 different temperatures for polymethylene, polypropylene, polyisobutylene, and polybenzyl, respectively. All these curves show that at zero time, 1 to 3 percent (for polypropylene up to 7 percent) of the sample has already volatilized. This is due to the fact that it usually takes about 15 min to heat the crucible containing the sample from room temperature to the temperature of operation. During this time, depending on the temperature of operation, some of the material volatilized, and zero time indicated on the figures is the time the required temperature was reached. Logarithm to the base 10 of the

percentage residue at any given time is shown plotted against time in the broken lines in the four figures. These lines are straight, except for a slight break in the early stage of vaporization of the samples. This break occurs anywhere between 0 and 100 min from the start of the experiment, and may be due to disturbances of operation in the early stage or to some mechanism of initiation of degradation different from that operating during subsequent degradation, or to both of these causes combined. The slope of the main part of each line, when multiplied by 2.303, represents the rate constant of volatilization of any of these polymers at the given temperature [17]. The initial rates are obtained by extrapolating the main parts of the broken lines in figures 1, 2, 3, and 4, to zero time, and are the same as the rate constants.

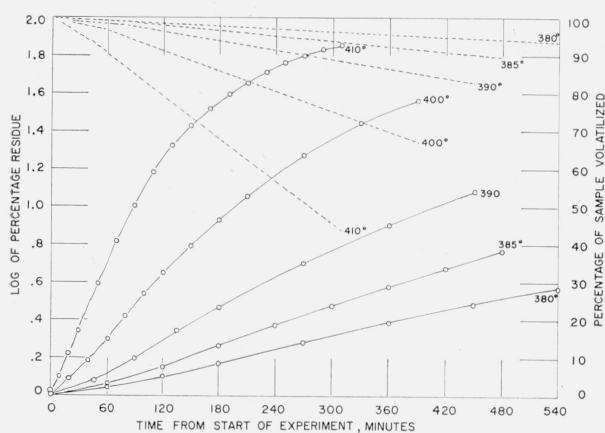


FIGURE 1. Thermal degradation of polymethylene.

—————, Percentage of sample volatilized versus time; -----, logarithm to the base 10 of percentage residue versus time.

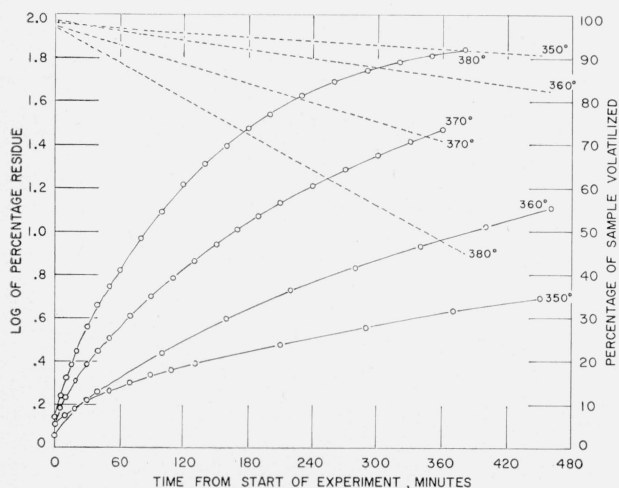


FIGURE 2. Thermal degradation of polypropylene.

—————, Percentage of sample volatilized versus time; -----, logarithm to the base 10 of percentage residue versus time.

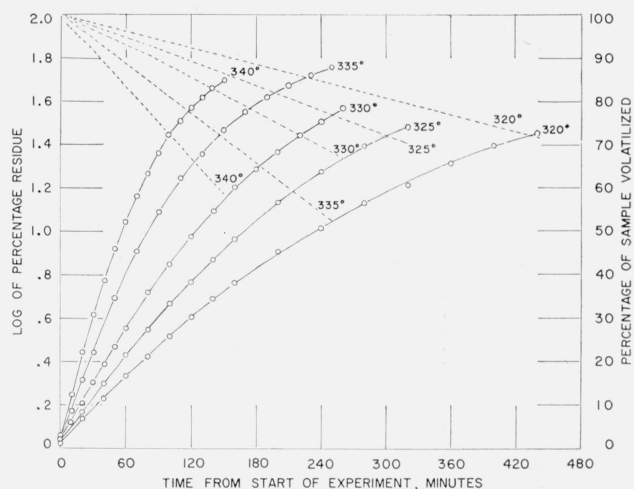


FIGURE 3. Thermal degradation of polyisobutylene.

—————, Percentage of sample volatilized versus time; -----, logarithm to the base 10 of percentage residue versus time.

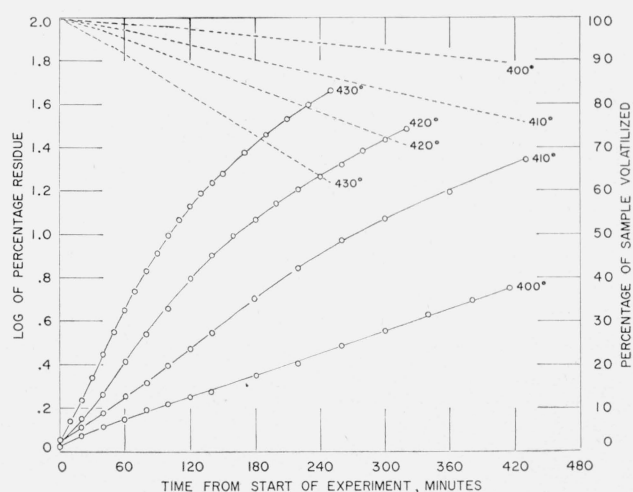


FIGURE 4. Thermal degradation of polybenzyl.

—————, Percentage of sample volatilized versus time; -----, logarithm to the base 10 of percentage residue versus time.

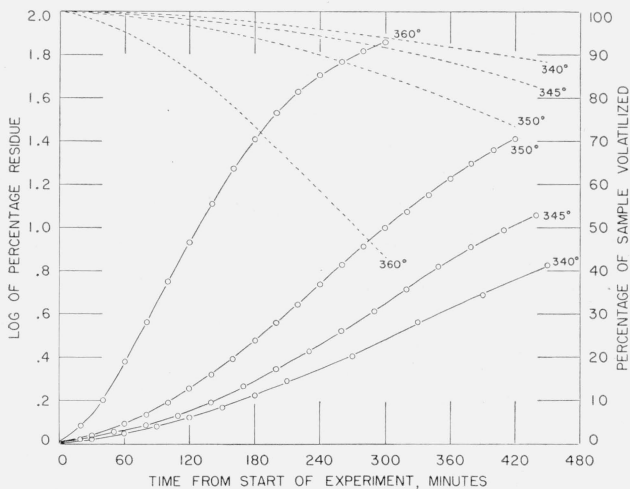


FIGURE 5. Thermal degradation of poly-beta-deuterostyrene (5b).

—————, Percentage of sample volatilized versus time; - - - - - , logarithm to the base 10 of percentage residue versus time.

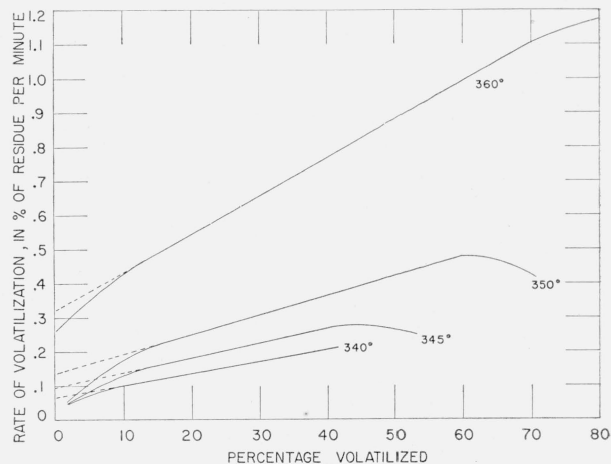


FIGURE 6. Rate of volatilization of poly-beta-deuterostyrene (5b), in percent of residue per minute, as a function of percentage volatilization.

—————, Percentage of sample volatilized versus time; - - - - - , logarithm to the base 10 of percentage residue versus time.

TABLE 8. Experimental data on rates of thermal degradation of polymers

| (1)  | (2)                                    | (3)                                    | (4)                                       | (5)  | (6)  | (7)               |      |      |      |
|--|--|--|---|--|--|-------------------|------|------|------|
| Polymer  | Temperature                            | Duration of experiment                 | Total volatilized                         | Time after start of experiment when break in the logarithm of residue-versus-time curve occurs | Initial rate of volatilization                 | Activation energy |      |      |      |
| Polymethylene<br>$\left[ \begin{array}{c} \text{H} \\   \\ -\text{C}- \\   \\ \text{H} \end{array} \right]_n$  | ° C<br>380<br>385<br>390<br>400<br>410 | min<br>540<br>480<br>450<br>390<br>310 | %<br>28.4<br>38.1<br>54.1<br>78.2<br>92.8 | min<br>20<br>100<br>80<br>60<br>40   | %/min<br>0.063<br>.109<br>.178<br>.413<br>.860 | } 76              |      |      |      |
| Polypropylene<br>$\left[ \begin{array}{c} \text{H} \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right]_n$  | 350<br>360<br>370<br>380               | 450<br>460<br>360<br>380               | 34.9<br>55.4<br>73.6<br>92.0              | 80<br>80<br>40<br>20   | 0.069<br>.158<br>.338<br>.666                  |                   | } 61 |      |      |
| Polyisobutylene<br>$\left[ \begin{array}{c} \text{H} \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array} \right]_n$   | 320<br>325<br>330<br>335<br>340        | 440<br>320<br>260<br>250<br>150        | 72.6<br>74.2<br>78.4<br>87.8<br>85.1      | 0<br>80<br>80<br>0<br>30   | 0.268<br>.431<br>.612<br>.869<br>1.278         |                   |      | } 52 |      |
| Poly-beta-deuterostyrene (5b)<br>$\left[ \begin{array}{c} \text{D} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \\   \quad   \\ \text{H} \quad \text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right]_n$ | 340<br>345<br>350<br>360               | 450<br>440<br>420<br>300               | 41.5<br>53.0<br>70.6<br>93.0              | -----<br>-----<br>-----<br>-----   | 0.065<br>.095<br>.135<br>.320                  |                   |      |      | } 59 |
| Polybenzyl<br>$\left[ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{C}_6\text{H}_5-\text{C}- \\   \\ \text{H} \end{array} \right]_n$   | 400<br>410<br>420<br>430               | 414<br>430<br>320<br>250               | 37.7<br>67.0<br>74.3<br>82.9              | 100<br>60<br>40<br>50  | 0.118<br>.265<br>.438<br>.723                  |                   |      |      |      |

In figure 5 the curves of percentage volatilization plotted against time for poly-beta-deuterostyrene (5b), just as for polystyrene and poly-alpha-deuterostyrene [7, 8], show points of inflection. The broken lines in figure 5 for the logarithm of percentage residue plotted against time are curved and could not be used for calculating the rate constants. However, the initial rates are obtained by extrapolating the straight parts of the curves shown in figure 6. These lines were obtained by plotting rates of volatilization, expressed in percentage of residue per minute versus percentage of volatilization, as was done in the case of polystyrene and poly-alpha-deuterostyrene [7, 8].

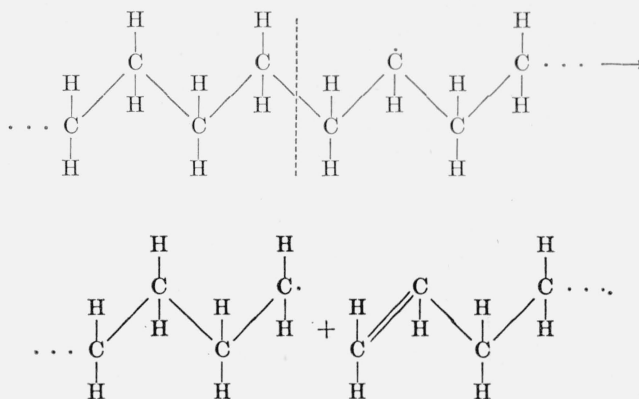
Experimental conditions and results of rate studies are shown in table 8. In column 5 of table 8, the time, in minutes after the start, at which the break in the broken line for each rate experiment occurs is given. The initial rates are given in column 6. The activation energy was calculated from the initial rates by means of Arrhenius' equation [7]. These activation energies are shown in the last column of table 8.

#### 4. Discussion

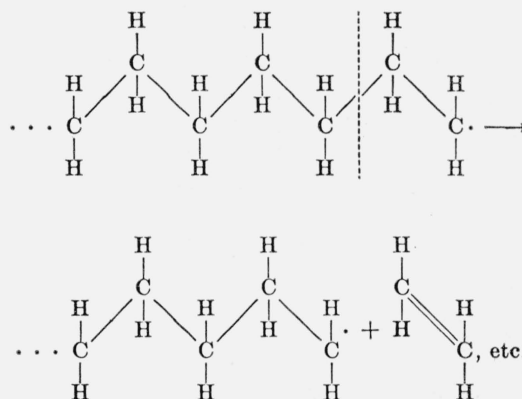
On the basis of experimental data on thermal degradation of polymers that have accumulated during the past few years, some conclusions can be drawn as to the mechanism of this type of degradation. It was found in the case of polyethylene [12] that even at temperatures below those at which appreciable loss by volatilization occurs, a drop in molecular weight of the polymer takes place. In the case of polystyrene [7, 14], poly-alpha- and poly-beta-deuterostyrene [14], polyisobutylene [18], high molecular weight polymethyl methacrylate [19], and polymethylene [10], it was found that at temperatures at which volatilization of the degradation products takes place, a more or less rapid drop in the molecular weight of the polymer takes place during the first few percentage losses, followed by a more gradual drop. This initial decrease in molecular weight under the influence of heat may be due to the presence of weak links caused by some foreign elements or groups of elements, such as O, O<sub>2</sub>, and OH, which become incorporated in the chain during polymerization [4]. Such an assumption is legitimate because it is very difficult to carry out any polymerization in the absence of foreign materials.

The pattern of breakup of polymers, beyond the initial stage of degradation, varies with the nature of the polymer and the nature and frequency of side groups. A free-radical mechanism for the depolymerization of polymers has been proposed by Simha, Wall, and Blatz [20]. One of the important steps in this mechanism is intermolecular abstraction of hydrogen by free radicals. A free radical, which is formed initially through thermal breaks of the chains or through some other mechanism, abstracts a hydrogen from a polymer chain with which it happens to come in contact. This free radical becomes saturated in this action; the chain from which the hydrogen

was abstracted breaks, for example, in the case of polymethylene, in the following manner:



A double bond thus forms at one chain end at the break and a free radical at the other. However, instead of going through the step of abstraction, a free radical may break up into monomers:



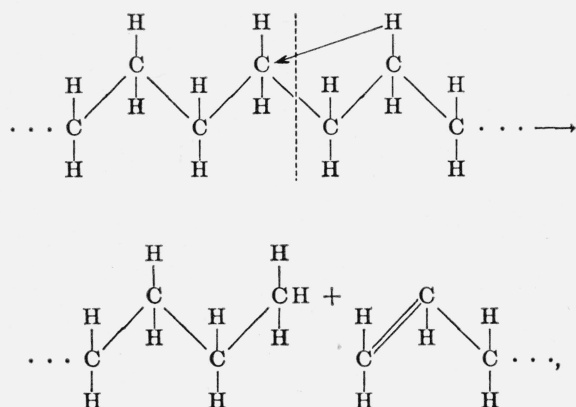
As to which of these two modes of reaction a free radical will follow depends on two factors: (1) the reactivity of the radical for abstracting hydrogen, and (2) the presence of hydrogen atoms susceptible to abstraction along the polymer chain. The reactivity of a free radical depends on its structure.

Thus,  $\text{R}\overset{\cdot}{\text{C}}\text{H}$ , for example, is more reactive than  $\text{R}\overset{\cdot}{\text{C}}\text{H}_2$ .

[2]. As to the susceptibility of hydrogen on the chain, one attached to a tertiary carbon is more susceptible than a hydrogen attached to a secondary carbon in the chain.

Another mechanism of depolymerization can be visualized [8, 21] if we assume that a thermal break in a chain takes place simultaneously with an intramolecular transfer of hydrogen from the same chain

at the point of the break. Thus, taking again polymethylene as an example,



resulting in one saturated and one unsaturated end in the two parts of the chain. In the case of polymethylene, polyethylene, or polyvinylcyclohexane, where there is a large supply of hydrogen atoms attached to carbons in the chain or in the side groups, thermal breaks, proceeding as above, will result in the formation of large fragments, so that most of the volatiles from thermal degradation will be in fraction II. For poly- $\alpha$ -methylstyrene, polymethyl methacrylate, or polytetrafluoroethylene, where some or all of the hydrogen atoms are substituted by methyl groups or fluorine, thermal breaks result in two radicals formed at the break. These radicals proceed to break into monomers by a chain reaction. As a result, most of the volatiles are found in fraction III. Between these two extremes are polymers like polyisobutylene, which yield part monomer and part large fragments.

The fact that free radicals, in the case of polymethylene, for example, do not yield an appreciable amount of monomer is explained by Simha, Wall, and Blatz as due to a higher rate of transfer as compared to the rate of monomer formation. In the mechanism of thermal breaks, involving intramolecular transfer, scarcity of monomer in thermal degradation of polymethylene is evident from the nature of the thermal scission in which the free radicals become immediately saturated.

In table 9 the yield of fraction III is shown in weight and mole percent for 13 polymers. Four of these polymers have been studied in the present work; the rest were investigated previously. These polymers are arranged in two groups. In the first group, polymethylene has no side groups, polyethylene has side groups, or branches, at infrequent intervals, polypropylene has a hydrogen on every other carbon in the chain replaced with a methyl group, polyisobutylene has both hydrogens on every other carbon replaced with methyl groups, and polytetrafluoroethylene has all hydrogen atoms replaced with fluorine. Polymethylene and polyethylene yield the smallest amount of fraction III.

TABLE 9. Yield of monomeric fraction in thermal degradation of polymers as a function of structure and side groups

| Polymer                                 | Yield of monomeric fraction in percentage of total volatilized part |        | Reference |
|---|---|--------|-----------|
|   | wt %  | Mole % |           |
| Group 1                                 |   |        |           |
| Polymethylene.....                      | 3   | 21     | [5]       |
| Polyethylene.....                       | 3   | 21     |           |
| Polypropylene.....                      | 14  | 57     | [5]       |
| Polyisobutylene.....                    | 32  | 78     |           |
| Polytetrafluoroethylene.....            | 100   | 100    | [9]       |
| Group 2                                 |   |        |           |
| Polyvinylcyclohexane.....               | 6   | 25     | [6]       |
| Polybenzyl.....                         | 7   | 31     | [1]       |
| Polystyrene.....                        | 42  | 65     |           |
| Poly- $\beta$ -deuterostyrene (5a)..... | 42  | 68     | [6]       |
| Poly- $\alpha$ -methylstyrene.....      | 52  | 77     |           |
| Poly- $\beta$ -deuterostyrene.....      | 70  | 86     | [6]       |
| Poly- $\alpha$ -methylstyrene.....      | 100   | 100    | [6]       |
| Polymethyl methacrylate.....            | 100   | 100    | [6]       |

This amount is the same for each polymer. For the other polymers of this group, there is a progressive increase of fraction III with increase of the number of replaced hydrogen atoms. It should be pointed out here, in connection with polytetrafluoroethylene, that when hydrogen and fluorine are both present on the chain, there is a tendency for some of the hydrogen to combine with fluorine to give HF [9].

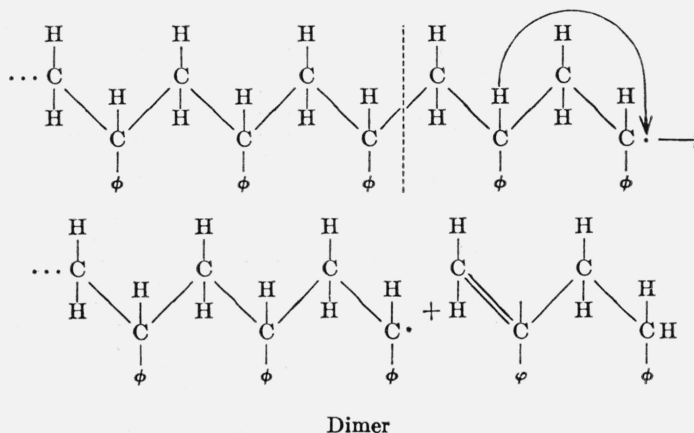
In the second group of polymers we find polyvinylcyclohexane yielding only a little more of fraction III than polymethylene or polyethylene. Although here every other carbon in the chain has a cyclic group replacing hydrogen, the cyclic group itself has hydrogen available for abstraction during a thermal break, so that there is little chance for monomer formation. Polybenzyl, judging from the fact that there was no stilbene in the volatile products and that it has a high thermal stability, should have a structure in which the chain consists alternately of a phenyl and a  $\text{CH}_2$  group, as pointed out before. Abstraction in such a polymer is difficult, and as a consequence, thermal breaks should result in formation of monomers. On the other hand, it is hard to see how a monomer could form from a free radical end in polybenzyl. The 31 mole percent of fraction III actually formed in the pyrolysis consists mainly of toluene and benzene and of a small amount of xylene. All these compounds require hydrogen for their formation, and this hydrogen must come by stripping the chain somewhere. Actually, the residue varied in color from light brown to almost black, depending on the extent of degradation.

Polystyrene, poly- $\beta$ -deuterostyrene, poly- $\alpha$ -methylstyrene, and poly- $\alpha$ -deuterostyrene all yield considerable amounts of monomer. Although these polymers have the same amount of hydrogen atoms on the chain as polypropylene, the yield of monomer is much greater here, particularly if we consider the fact that fraction III for polypropylene, as seen from table 3, has very little monomer, whereas for polystyrenes it is almost all monomer (tables 5 and 6 and references [1, 5, 6]). Apparently



the phenyl group, because of steric hindrance, reduces the tendency of the hydrogen atoms on the chain to transfer intramolecularly during a thermal scission. This results in an increased yield of monomer. The low average molecular weight of fraction II from these styrene polymers (table 7 of

the present paper and table 2 of reference [8]) indicates that this fraction consists chiefly of the dimer, trimer, and tetramer. As pointed out in a previous paper [8], the dimer, trimer, and tetramer could form, along with monomer, in the same chain reaction, at a free radical end, as follows:



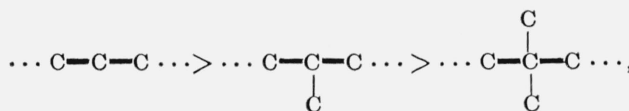
Substitution of a beta-hydrogen with deuterium does not affect the monomer yield; substitution of a hydrogen on the phenyl group with a methyl group increases this yield; substitution of an alpha-hydrogen with deuterium increases the monomer yield considerably. When the alpha-hydrogen is substituted with a methyl group, the monomer yield reaches 100 percent. Hydrogen on the tertiary carbon (alpha-position) is more susceptible to transfer than that on a secondary carbon (beta-position) [20], and blocking the alpha-position with a deuterium atom or with a methyl group favors the formation of monomer at the expense of dimer, trimer, or tetramer. In polymethyl methacrylate the monomer is the only volatile product of degradation. Steric hindrance, caused here by the ester group, and blocking of the alpha-hydrogen with a methyl group, produce the same effect on monomer yield as in the case of poly-alpha-methylstyrene.

Table 10 shows a series of 13 polymers arranged in the order of rates of thermal degradation at 350° C. Five of these polymers have been the subject of the present investigation; the others were studied previously [7, 8, 9]. Actually, the rates of only a few polymers were measured at 350° C; the other rates were studied at temperatures either below or above 350° C. In these latter cases the rates corresponding to 350° C were calculated from the actual rates measured at other temperatures, by means of Arrhenius' equation, in the form of

$$\log_{10} k_1 = -\frac{E \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}{2.303R} + \log_{10} k_2,$$

where  $k_1$  and  $k_2$  are rates, in percent, of original sample per minute at corresponding absolute temperatures  $T_1$  and  $T_2$ ,  $R$  is the gas constant in calories, and  $E$  is the activation energy, in calories.

Polymer chains when heated tend to break at their weakest points. The strength of a C—C bond in a chain follows the order given below:



the bond shown as a heavy line being the one under consideration. Thus, breaks will occur more readily in bonds adjacent to a tertiary or quaternary carbon in the chain.

A bond in the beta-position to a double bond in the chain, or in its side groups, is another source of weakness in a C—C bond in the chain. An abundance of hydrogen on a chain facilitates saturation of the free-radical ends formed during a thermal break. When all the hydrogen atoms on the chain are replaced with fluorine atoms, this saturation does not take place due to the greater strength of the C—F bond as compared with the C—H bond.

With these considerations of bond weaknesses in mind, we find in table 10 that polytetrafluoroethylene is the most thermally stable polymer. Next to this polymer is polymethylene, which has only secondary carbons in the chain and an abundance of hydrogen atoms on the carbons. Polybenzyl occupies a position below polymethylene in this table. At a temperature of about 400° to 420° C, polybenzyl is actually more stable than polymethylene, but because of a lower activation energy than in the case of polymethylene, the position is reversed at a lower temperature. The phenyl group, which is here a part of the chain, seems to impart stability to it, perhaps through resonance. Polyethylene has an abundance of hydrogen on the chain and a few tertiary carbons. Its position in the series is next

TABLE 10. Rates of thermal degradation of polymers in a vacuum at 350°C

| Polymer                            | Volatilization, in percent, of original sample | Reference |
|------------------------------------|--|-----------|
|                                    | <i>%/min</i>                                   |           |
| Polytetrafluoroethylene            | 0.000002                                       | [9]       |
| Polymethylene                      | .004   | -----     |
| Polybenzyl                         | .006   | -----     |
| Polyethylene                       | .008   | [7]       |
| Polypropylene                      | .069   | -----     |
| Poly- $\beta$ -deuterostyrene (5b) | .14  | -----     |
| Polystyrene                        | .24  | [7]       |
| Poly- $\alpha$ -deuterostyrene     | .27  | [8]       |
| Polyvinylcyclohexane               | .45  | [8]       |
| Poly-meta-methylstyrene            | .90  | [8]       |
| Polyisobutylene                    | 2.4  | -----     |
| Polymethyl methacrylate            | 5.2  | [8]       |
| Poly- $\alpha$ -methylstyrene      | 230  | [8]       |

to polymethylene and polybenzyl. Next comes polypropylene, with every other carbon in the chain of a tertiary type. Next in the series are poly-beta-deuterostyrene, polystyrene, poly-alpha-deuterostyrene, and poly-meta-methylstyrene, with every other carbon being of a tertiary type and every bond in beta-position to a double bond in the phenyl group. Polyvinyl cyclohexane, with every other carbon in the chain of tertiary type and an abundance of hydrogen available for transfer, occupies a position between two polystyrenes. Polyisobutylene and polymethyl methacrylate, both having every other carbon in the chain of the quaternary type, come next, with very high rates of volatilization. Finally, poly-alpha-methylstyrene, with every other carbon in the chain of the quaternary type and every bond in the chain in beta-position to a double bond in a phenyl group, is the most thermally unstable polymer of the series.

Thus, we see from a study of a number of polymers that the pattern of their thermal degradation, the types and relative amounts of the volatile products produced in pyrolysis, and their stability in a vacuum, in the temperature range of about 200° to 500° C, are functions of their molecular structure and of the kind and frequency of side groups.

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WASHINGTON, June 14, 1954.