

cording to some recent theories of the osmotic second virial coefficient in the limit of large excluded volumes, *i.e.*, for high molecular weight polymer molecules in thermodynamically "good" solvents, the ratio  $A_2\bar{M}_w^2/(\bar{R}_w^2)^{3/2}$  should attain an essentially constant value. Qualitatively the constancy of this ratio is an expression of the expectation that the interactions of polymer molecule pairs in such media resemble collisions of spheres whose volumes are proportional to  $(\bar{R}_w^2)^{3/2}$ . If, then, the volumes of the equivalent hydrodynamic spheres observed viscometrically are also proportional to  $(\bar{R}_w^2)^{3/2}$  the ratio  $A_2\bar{M}_w/[\eta]$  should be another constant.

The ratio  $A_2\bar{M}_w^2/(\bar{R}_w^2)^{3/2}$  is plotted against  $\log \bar{M}_w$  in the center graph of Fig. 7 for the ten polyvinylacetate fractions in methyl ethyl ketone. Over this molecular weight range the ratio is a constant equal to  $4.4 \times 10^{24}$ .

A plot of  $A_2\bar{M}_w/[\eta]$  against  $\log \bar{M}_w$  for the same system in the lower graph of Fig. 7 reveals a remarkably constant value, 1.39, for this ratio over the molecular weight range 246,000 to 3,460,000.

Here again data of Howard<sup>19</sup> have been used to extend the observations to lower molecular weight polymer fractions.

It may therefore be stated empirically that the thermodynamic interaction of a pair of high molecular weight polyvinylacetate molecules in methyl ethyl ketone is similar to the collision of spheres having effective volumes proportional to  $(R^2_w)^{3/2}$ . This observation, coupled with the validity of the equivalent hydrodynamic sphere treatment of limiting viscosity numbers, yields an empirical relation among the quantities  $A_2$ ,  $\bar{M}_w$  and  $[\eta]$ . It has been found<sup>40</sup> that this relation is valid for several polymers in thermodynamically good solvents, and similar magnitudes for the ratio  $A_2\bar{M}_w/[\eta]$  are observed.

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(40) E. F. Casassa, W. H. Stockmayer and R. L. Cleland, unpublished calculations.

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## The Depolymerization of Polymethylene and Polyethylene

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Depolymerization rates and molecular weight changes of polymethylene have been studied and mass spectrometric analyses of the volatile products obtained. The results are compared with those for commercial and radiation cross-linked polyethylene. Cross linking has little effect on the rate of depolymerization. The behavior of linear polymethylene approaches that predicted by theory for negligible depropagation and pronounced transfer. Provided a single type of intermolecular transfer occurs, the kinetics becomes then equivalent to a random depolymerization and the experimental results are analyzed on this basis. The rate exhibits a characteristic maximum as a function of conversion, which is absent in polyethylene but is predicted by theory. The differences are presumably connected with the branched structure of polyethylene. Current estimates of the amount of long and short branches lead to an increase of the initial rate over that of the linear polymer by a factor not exceeding five. These estimates do not explain the absence of a maximum rate for polyethylene. This seems to require more long branches or longer short branches.

### Introduction

The theory of free radical depolymerization previously developed leads to two competing modes of decomposition, namely, scission and rapid zip. Their relative importance determines the three observable quantities usually considered, *viz.*, the rate of conversion to volatiles,  $dC/dt$ , the decrease in degree of polymerization,  $dP_n/dC$ , and the yield of pure monomer in the volatiles.<sup>1</sup> Methyl methacrylate, and presumably  $\alpha$ -methylstyrene, represent one extreme, namely, preponderance of the zip. On the basis of the practically zero yield of pure monomer and the rapid molecular weight decrease, one expects polyethylene to represent the opposite extreme of an almost exclusive scission reaction, proceeding more or less at random. Yet the rate pattern does not conform to this picture. This may be attributed to the fact that the polyethylene molecule is structurally inhomogeneous because of the various types of branches formed during its synthesis.

(1) For a review see R. Simha, *Trans. N. Y. Acad. Sci.*, **14**, 151 (1952).

A study of the linear polymethylene was undertaken with this in mind. It is our purpose to compare the experimental results with those for commercial polyethylene, that is branched polymethylene, and with the prediction of the general theory of chain depolymerization.

The thermal degradation of polyethylene has been the subject of several recent investigations.<sup>2-6</sup> The experimental results are similar in the various studies but no completely satisfactory interpretation has been given, capable of explaining all the features of the decomposition, some of which appear contradictory. The depolymerization produces only negligible amounts of the monomer, ethylene. There is no main product. A broad spectrum of linear hydrocarbons is found, consisting mainly of a wax-like portion of average molecular weight 692.<sup>5</sup> The molecular weight of the residue drops

(2) L. A. Wall, *J. Research Natl. Bur. Standards*, **41**, 315 (1948).

(3) W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

(4) S. L. Madorsky, *J. Polymer Sci.*, **9**, 133 (1952).

(5) H. H. G. Jellinek, *ibid.*, **4**, 13 (1949).

(6) S. L. Madorsky, S. Straus, D. Thompson and L. Williamsou, *J. Research Natl. Bur. Standards*, **42**, 499 (1949).



of diazomethane with boron trifluoride etherate.<sup>11</sup> The polymer had an intrinsic viscosity  $[\eta]_0$  of 20 deciliters gram<sup>-1</sup> when measured in xylene at 120°. The viscosity measurements were made in Ubbelohde viscosimeters with enlarged reservoirs to permit dilution *in situ*.

The rates of volatilization of polymethylene were obtained by the method previously described<sup>4</sup> which utilizes 5 to 10 mg. per run. The changes in molecular weight during decomposition were also determined. Samples of approximately 0.1 g. were pyrolyzed separately for various times in a highly evacuated system after which the intrinsic viscosities of the residue were measured. An apparatus described elsewhere,<sup>6</sup> essentially a single-stage molecular still, was also used. In this technique 20- to 60-mg. samples are used and the products separated into fractions according to their volatility. Four fractions are obtained; in what follows, volatile at -196° refers to the gas which passes through the liquid nitrogen trap, volatile at -80° to material which can be distilled out of the liquid nitrogen trap when it is warmed to Dry Ice temperature, volatile at 25° to material which distills out at room temperature, and volatile at temperature of pyrolysis to the remaining product. Residue denotes the material left in the tray of the molecular still when the pyrolysis is incomplete or when material undistillable at the pyrolysis temperature is obtained. The fractions volatile at -196° and -80° were analyzed in the mass spectrometer. The material volatile at 25° consisted of numerous hydrocarbons and quantitative analyses were not made. The number average molecular weight of the material volatile only at the pyrolysis temperature was determined cryoscopically.

### Results

The distribution of the pyrolysis products of polymethylene and polyethylene is shown in Table I. The data given represent averages of six or more

TABLE I  
DISTRIBUTION OF PRODUCTS FROM THERMAL DECOMPOSITION OF POLYMETHYLENE AND POLYETHYLENE

| Fraction                       | Polymethylene, wt. %       | Polyethylene, wt. %        |
|--------------------------------|----------------------------|----------------------------|
| Volatile at -196°              | Trace                      | Trace                      |
| Volatile at -80° <sup>a</sup>  | 0.6                        | 1.1                        |
| Volatile at 25°                | 2.5                        | 2.3                        |
| Volatile at temp. of pyrolysis | 96.9 ( $\bar{M}_n = 755$ ) | 96.6 ( $\bar{M}_n = 692$ ) |

<sup>a</sup> See Table II for analysis of these fractions.

runs. The results are quite similar except for the molecular weight of the least volatile fraction. In the polymethylene the product distribution is shifted considerably toward higher molecular weights. Table II presents average analyses of the

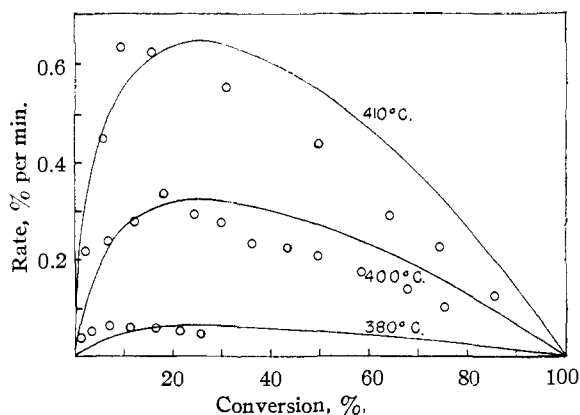


Fig. 2.—Rates of pyrolysis of polymethylene: — calculated, equation 1; O, experimental points.

(11) G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, 3701 (1952).

volatiles at -80° from four runs on each polymer. There is a noticeable increase of unsaturates in the polymethylene pyrolysis yielding 0.83 double bonds per molecule, about twice the amount found in the polyethylene products.

Figure 1 exhibits a schematic rate *versus* conversion curve for each of the two polymers. The polyethylene starts off at a high rate and drops off fast and then slowly. The polymethylene starts slow and goes through a maximum. Thus, at low conversions the rates are drastically different. It was considered possible that low molecular weight impurities might account for this difference. However, the insoluble, highly cross-linked polyethylene curves as the unirradiated material and also the previous commercial polyethylene.<sup>4</sup> This is good evidence that an actual difference in polymer structure is responsible for the large initial difference in the rate pattern observed. It is reasonable to assume that the large amount of branching in polyethylene is connected with this effect.

TABLE II  
VOLATILES AT -80° FROM THE PYROLYSIS OF POLYMETHYLENE AND POLYETHYLENE

| Component    | Polymethylene, mole % | Polyethylene, mole % |
|--------------|-----------------------|----------------------|
| Ethylene     | 12.2                  | 4.3                  |
| Ethane       | 4.3                   | 12.4                 |
| Propadiene   | 1.4                   | 0.3                  |
| Propylene    | 20.7                  | 5.2                  |
| Propane      | 3.6                   | 14.8                 |
| Butadiene    | 2.1                   | ...                  |
| Butene       | 13.1                  | 24.6                 |
| Butane       | 11.2                  | 19.1                 |
| Pentadiene   | 2.8                   | 0.4                  |
| Pentene      | 9.6                   | 7.5                  |
| Pentane      | 6.1                   | 6.2                  |
| Hexadiene    | 2.6                   | 0.3                  |
| Hexene       | 9.7                   | 3.2                  |
| Hexane       | 0.6                   | 1.2                  |
| Heptene      | ...                   | 0.2                  |
| Heptane      | ...                   | 0.4                  |
| Totals       | 100.0                 | 100.0                |
| Double bonds | 83.1                  | 47.0                 |

Detailed results on the rate of volatilization of polymethylene are presented in Fig. 2.

Figure 3 shows the variation of the relative intrinsic viscosity  $[\eta]/[\eta]_0$  of the residual polymer during the course of pyrolysis. The initial portion of the curve is not shown due to the very sharp initial drop in degree of polymerization which occurs at less than one per cent. conversion.

Due to the difference in the shape of the rate curves, Fig. 1, one may compare the rates in several ways. Obviously the initial rates are different by orders of magnitude. However, in the later stages they are quite close. In Fig. 4 the final rates linearly extrapolated to  $C \rightarrow 0$  are plotted as a function of temperature. On this basis polymethylene is only slightly more stable. The activation energies based on such extrapolations are 68 kcal. for polyethylene and 72 kcal. for polymethylene.

### Discussion

We have indicated previously the reasons for

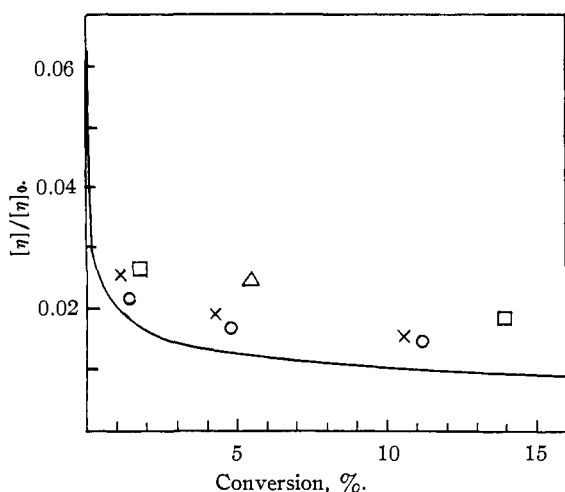


Fig. 3.—Relative intrinsic viscosity of the residue versus conversion in pyrolysis of polymethylene: —, calculated; experimental points,  $\Delta$ , 375°;  $\square$ , 380°;  $\times$ , 390°;  $\circ$ , 400°.

analyzing the depolymerization of polymethylene in terms of random theory. It yields the following expressions for the fractional conversion to volatiles,  $C$ , the rate of reaction  $dC/dt$ , and the number average degree of polymerization of the residue  $\bar{P}_n$  expressed in methylene units.<sup>8,12</sup>

$$\left. \begin{aligned} 1 - C &= (1 - \alpha)^L - 1 \left[ 1 + \frac{\alpha(N - L)(L - 1)}{N} \right] \approx (1 - \alpha)^L(1 + \alpha L) \\ \frac{dC}{dt} \frac{1}{k} &= (L - 1)(1 - C) - (1 - \alpha)^L \frac{(N - L)(L - 1)}{N} \approx \frac{\alpha L^2}{(1 + \alpha L)} (1 - C) \\ \lim_{t \rightarrow 0} \frac{dC}{dt} \frac{1}{k} &= \frac{L(L - 1)}{N}; \left[ \frac{dC}{dt} \frac{1}{k} \right]_{\max} \approx L/e; C_{\max} \approx 0.26 \\ \bar{P}_n/N &= \left[ 1 + \frac{\alpha(N - L)(L - 1)}{N} \right] / [1 + \alpha(N - L)] \approx \frac{(1 + \alpha L)}{(1 + \alpha N)} \end{aligned} \right\} (1)$$

Here  $k$  represents the over-all rate constant of the process. In terms of the elementary chain mechanism and the total radical concentration  $R$ , it is given by

$$k = k_1 + k_3 R \approx k_3 R = k_3 \left( \frac{I}{k_4} \right)^{1/2}$$

where  $I$  is the rate of initiation of active centers,  $k_3$  the rate constant for transfer,  $L$  the minimum chain length for pyrolysis, assuming that smaller molecules evaporate in preference to further pyrolysis,  $\alpha = 1 - e^{-kt}$  the fraction of carbon-carbon bonds, broken at time  $t$ , and  $N$  the initial degree of polymerization of the homogeneous polymer.

The approximate relations are valid for  $N \gg L \gg 1$ . From a comparison of the calculated molecular weight distribution of the volatiles,  $j < L$ , with the mass spectrometrically and cryoscopically observed distribution of products we concluded previously that  $L$  is between 70 and 80 for polyethylene,<sup>12</sup> so that the above inequalities are fulfilled. The data in Table I would indicate values higher by some 10% for polymethylene if we assume that the molecular weights of all fractions except the wax are the same as in polyethylene. For our future comparison an accurate knowledge of  $L$ , which is in itself a somewhat artificial quan-

(12) R. Simha and L. A. Wall, *J. Polymer Sci.*, **6**, 39 (1951).

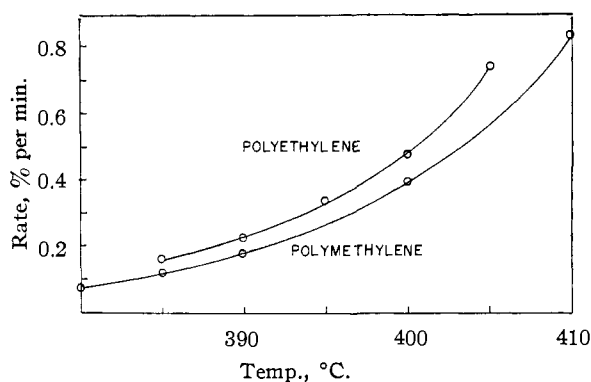


Fig. 4.—Comparison of the rates of decomposition of polymethylene and polyethylene versus temperature.

tity because of the assumed sharp transition between reaction and evaporation, is not necessary. The location of the maximum in equation 1 is completely unaffected by variations in  $L$ , as long as  $N \gg L$ , and other relations are only slightly modified, considering the accuracy of the observed rates and molecular weight changes.

We can make an independent estimate of the magnitude of  $L$  by extrapolating vapor pressure data on corresponding  $C_{20}$  to  $C_{30}$  hydrocarbons. One finds in this manner for a vapor pressure of

$10^{-4}$  mm. and  $T = 683^\circ \text{K.}$ ,  $L \approx 54$  to 64, which is in reasonable agreement with our previous kinetic estimate.

A thermodynamic effect must be considered in applying equation 1. Due to the lowering of the vapor pressure in the pyrolyzing mixture,  $L$  will gradually increase with conversion. This can be estimated from the free energy of dilution of the "solvent," that is, the  $L$ -mers in the mixture, by using familiar expressions and considering that the volume fraction of solvent is

$$v_1 = L n_L / \sum_{j=L}^N j n_j = \frac{L\alpha[2 + (N - L - 1)\alpha]}{[N + \alpha(N - L)(L - 1)]} \approx \frac{L\alpha(2 + N\alpha)}{N(1 + L\alpha)} \quad (2)$$

Assuming the validity of Harris' equation<sup>13</sup>

$$[\eta] = 1.35 \times 10^{-3} \bar{M}_n^{0.63} \quad (3)$$

which gives for our polymethylene  $N \approx 3 \times 10^5$ , one finds from the previous vapor pressure estimate and setting  $L = 70$  that for  $10^{-4} \leq \alpha \leq 5 \times 10^{-3}$  and  $1.7 \times 10^{-4} \leq C \leq 0.05$ ,  $21 \leq \Delta L \leq 9$  where  $\Delta L$  is the decrease in  $L$ . Thus  $L$  changes relatively slowly with conversion in the significant range of  $C$  between 0.01 and 0.05 (it must be remembered that at  $C = 0.05$ ,  $\bar{P}_n/N$  has already decreased to about  $10^{-3}$ ). We are justified within our limits of uncertainty to treat  $L$  as a constant parameter. Since the intercept,  $\lim_{t \rightarrow 0} dC/dt$ , varies as  $L^2$ , whereas the maximum depends on  $L$ , which is already nearly constant at the corresponding conversion, the initial

(13) I. Harris, *ibid.*, **8**, 353 (1952).

part of the  $dC/dt$  versus  $C$  curves (Fig. 2) will rise somewhat more steeply than is predicted for constant  $L$ . In this range of  $L$ -values the effect on the molecular weight drop will be negligible, as may be judged from Fig. 1 of reference 12.

These considerations show that extrapolated initial rates must be used with caution for the determination of rate constants and activation energies in the present systems. This is primarily due to the variation of  $L$  with conversion. The effect of temperature on  $L$  is small over the range of 40 or so degrees usually employed. These complications do not occur at the maximum.

The expression so far given apply to an initially homogeneous polymer. We must now gage the influence of an initial molecular weight distribution on the results. This can be done by a consideration of Montroll's equations for random degradation.<sup>14</sup> For simplicity let only monomer evaporate from the tray. If its initial mole fraction is  $n_1$ , and  $\bar{P}_n(0)$  denotes the initial number average degree of polymerization, one finds

$$\bar{P}_n = \frac{\bar{P}_n(0) + [\bar{P}_n(0) - 2]\alpha - n_1(1 - \alpha)}{1 + [\bar{P}_n(0) - 2]\alpha - n_1(1 - \alpha)}$$

$$C = \frac{2\alpha + \alpha^2[\bar{P}_n(0) - 2] + n_1[(1 - \alpha)^2 + 1]}{\bar{P}_n(0)} \quad (1a)$$

Comparing this result with that for a homogeneous polymer of D.P. =  $\bar{P}_n(0)$ , one finds, as anticipated, that, for a given  $\alpha$ ,  $\bar{P}_n$  (inhom.)  $>$   $\bar{P}_n$ , since the additional  $n_1$ -term is more important in the denominator than in the numerator. Of course, the conversion is also increased. Now if  $\bar{P}_n$  (inhom.) is to be  $f\bar{P}_n$ ,  $f > 1$ , the concentration  $n_1$  must obey the equation

$$n_1(1 - \alpha) = \frac{(f - 1)}{f} [1 + \alpha\bar{P}_n(0)]$$

This gives a meaningful result only for

$$\alpha \leq \frac{1}{(f - 1)\bar{P}_n(0) + f}$$

Thus the initial presence of small species can play a role at the very beginning of the reaction and for sizable proportions only. For  $L > 2$ , the  $n_1$  term is replaced by  $\sum_{i=1}^{L-1} in_i$  in the numerator and  $\sum_{i=1}^{L-1} n_i$  in the denominator of the first equation 1a. The initial conversion, however, will be more appreciably increased. Furthermore, the presence of low molecular weights in the range of  $2L$  to  $3L$  tends to shift the maximum rate to lower conversions.

Figure 2 shows a comparison between observed and calculated rates  $dC/dt$  as function of  $C$ , equation 1, for various temperatures. The two sets were fitted to each other by making the heights of the respective maxima identical and setting  $L = 72$ . The experimental points are seen to be relatively close to the theoretical curves. The chief differences are the shift of the observed maximum rate to lower conversions and the nearly linear decay beyond the extreme. It should be added that with the above normalization procedure, the result is only slightly dependent on the choice of an  $L$ -value within a large range of variation. This procedure

yields the following expression for the rate constant

$$k = 1.93 \times 10^{16} e^{-68,100/RT} \text{ (sec.}^{-1}\text{)} \quad (4)$$

Figure 3 exhibits the corresponding comparison of theory and experiment for the intrinsic viscosity by converting calculated degrees of polymerization with the aid of equation 3. An  $L$ -value of 72 was used throughout. This results in a sharper drop than is observed. The choice of a larger  $L$  would raise the curve, but there is no apparent justification for such an assumption. In spite of the deviations between observed and calculated molecular weights in Fig. 3, the extremely sharp drop in chain length strongly indicates an essentially random degradation. No other polymer so far studied approaches this kind of behavior except possibly polyethylene. Molecular weight-conversion curves are not available for this polymer. So far normal polystyrene comes closest to this situation.

An alternative and more sensitive procedure for testing the theory is based on the time dependence of the molecular weight. From the last of equations 1 we obtain the following relation when  $N \gg L$

$$\frac{1}{\bar{P}_n} - \frac{1}{N} = \frac{1 - e^{-kt}}{1 + L(1 - e^{-kt})} \quad (1b)$$

When  $L$  is of the order of unity, this plot is linear in time for  $\alpha \ll 1$ , which can mean appreciable extents of conversion. Otherwise this linearity, which is usually taken as a characteristic of random depolymerization, holds only for a very limited range. This is shown in Fig. 5. There we have plotted the function above (unbroken lines), using again  $L = 72$  and the rate constants  $k$ , equation 4, obtained previously from the rates of volatilization. As anticipated from Fig. 3, the experimental curves bend over more rapidly than the theoretical ones. The deviations are smallest at the higher temperatures and small times. Considering that these data come from two independent sets of measurements and involve a conversion to number average degree of polymerization, the extent of agreement seems rather remarkable. A better fit (see dashed lines) can be obtained by varying  $L$  empirically. The values of the parameter  $L$  required are quite large and vary inversely with the temperature of thermal decomposition. Since there is at the moment no apparent theoretical basis for this result, further experimentation is desired, particularly a study of the effect of initial molecular weight.

Thus it is seen that the over-all pattern in polymethylene does not appreciably deviate from a random scission. We have already evaluated certain factors which are not considered in the theory, equation 1. In an attempt to account for remaining discrepancies one might consider some additional factors magnified in our case by the sharp initial change in molecular weight. If the over-all reaction is diffusion-controlled, then the rate of evaporation of  $j$ -mers,  $j < L$ , should first be slower than is calculated. This, as well as the thermodynamic mixing-effect, reduces the initial effective  $L$ -value, and if at all, tends to shift  $(dC/dt)_{\max}$  to higher conversions. This would be counteracted by a reduction in surface, but there is no reason to assume

(14) E. W. Montroll, THIS JOURNAL, 63, 1215 (1941).

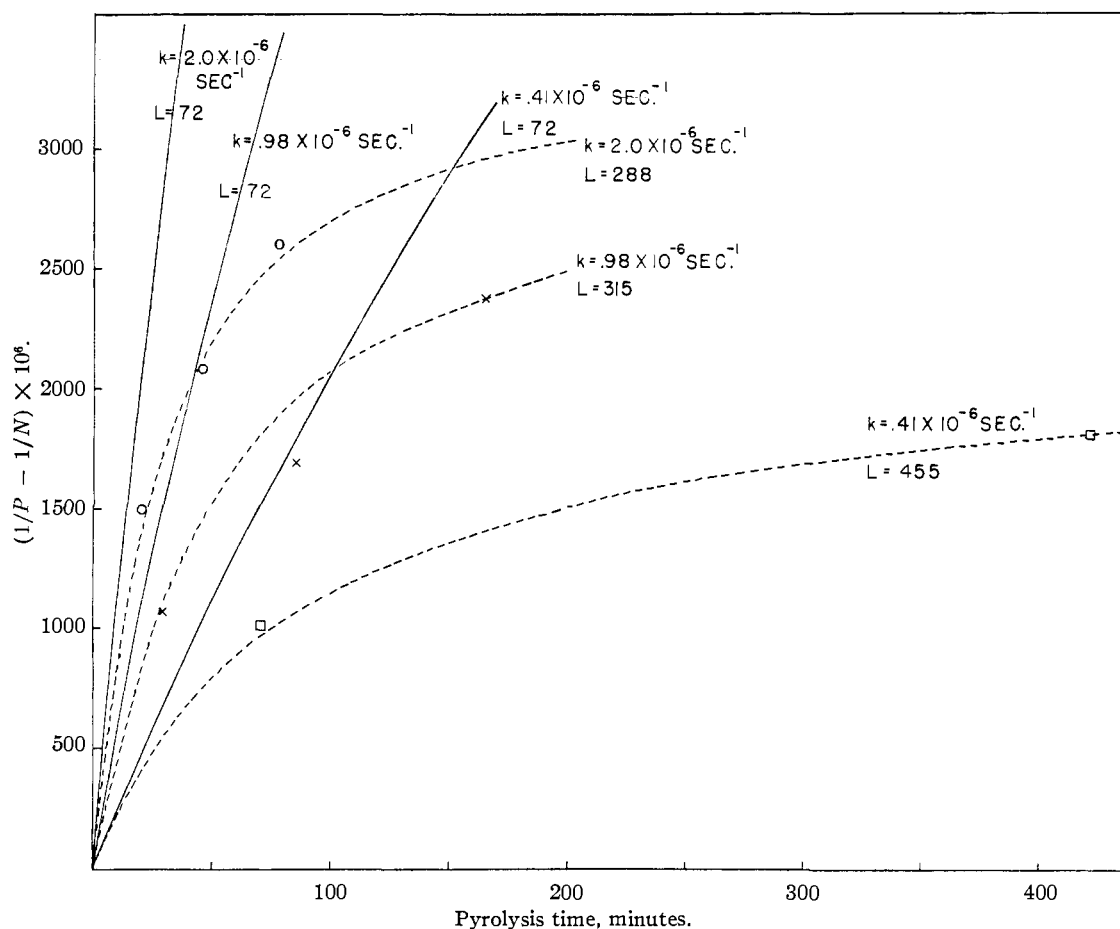


Fig. 5.—Reciprocal of the degree of polymerization minus the reciprocal of initial D.P. versus time: —, calculated, equation 1b; ----- fitted to experimental points by adjusting  $L$ ; experimental points, O, 400°; X, 390°; □, 380°.

such, since we are dealing with a polymer melt. It has furthermore been assumed that all individual rate constants are independent of conversion. It is well known that particularly the termination rates can become diffusion controlled in vinyl polymerization at higher conversions. We have previously suggested the reverse of this effect as a possible factor in the interpretation of the pyrolysis of polymethyl methacrylate,<sup>8</sup> the polymer par excellence for the occurrence of the gel effect in polymerization. Considering the activity of the radical in the present case and the rapid change in molecular weight, this effect may well be operating to yield a gradually decreasing radical concentration and hence over-all rate  $k$ . This causes a shift in the maximum to the left, possibly the consistently smaller observed rate at higher conversions and a slower molecular weight drop. Finally, there may be an increase of the intermolecular transfer rate  $k_3$  with decreasing molecular weight working in the other direction. Such variations in the rate constants could be introduced into the theory.

It remains to analyze the differences in the rates for polyethylene and polymethylene. This requires a calculation of  $C$  and  $dC/dt$  for the branched structure indicated by recent investigations<sup>15</sup> with

(15) M. J. Roedel, *THIS JOURNAL*, **75**, 6110 (1953); W. M. D. Bryant and R. C. Voter, *ibid.*, **75**, 6113 (1953); F. W. Billmeyer, Jr., *ibid.*, **75**, 6118 (1953).

“weak” links at the branch points. However, the number of secondary C-H and C-C bonds greatly outweighs the increased reactivity of the tertiary structures, except at the very beginning. The increased number of chain ends due to the numerous branches is the more important factor. We cannot give an accurate extrapolation of the observed rates; however it is to be expected that the differences are most pronounced in the limit  $t \rightarrow 0$  (see Fig. 1), and for that case one can at once write down the expression for  $dC/dt$ . In equation 1 we had for a linear chain

$$\lim \frac{dC}{dt} \frac{1}{k} = 2 \sum_{i=1}^{L-1} i \frac{Q_N(0)}{NQ_N(0)} = \frac{L(L-1)}{N}$$

The sum is proportional to the weight of material obtainable from one chain by breaking either of the first  $(L-1)$  bonds at one end, which leads to the initial volatilization. This is multiplied by the number of chains and divided by the total initial weight. In the same manner the short branches contribute terms

$$\frac{S(S+1)}{2} \frac{b}{N} + \frac{k_1}{k} \frac{Sb}{N}$$

where  $S < L$  is the chain length of the branches assumed to be of uniform size and  $b$  their number per chain, and  $k_1/k$  the ratio of rates for tertiary and secondary C-C bonds. It is understandable that

the irradiated sample gives the same rate since the number of chain ends is not altered if the only change is the production of cross links. Assuming  $S = 4$ ,<sup>15</sup>  $b \approx N/30$ ,<sup>13,15</sup>  $k_1/k \approx 3$  and  $N \approx 3 \times 10^8$ ,  $L = 72$ , the  $S$ -terms are only 43% of the first one, the reason being the small weight of the branches. The two contributions are equal for  $N \approx 10^4$ . The long chain branching<sup>15</sup>  $S \geq L$  is more important on a weight basis, each branch increasing the initial rate by 50%. Thus all branching effects arising from the proposed picture may increase the rate corresponding to a linear polymer by a factor of about 3 to 5. Clearly the greatly reduced initial rate in polymethylene arises from its large molecular weight, that is the small number of chain ends. Assuming equality of the  $k$  values, this gives rise to a factor of the order of  $10^2$  in the rates. Equation 1 indicates that at finite conversions the dependence of  $dC/dt$  on  $N$  is much less pronounced.

The presence of a maximum rate in random depolymerization of linear chains is indicative of a maximum number of chain ends. This number is equal to  $2Q_N(0)N/(eL)$  and consequently is smaller than the initial number for a branched molecule with the same  $N$  if the average distance between branch points is less than  $L$ . However, this does not appear to be sufficient to account for the absence of a maximum in the branch system, unless the amount of long chain branching, the lengths of the short branches or the ratio  $k_1/k$  is greater than has hitherto been assumed,<sup>16</sup> or there is an appreciable inverse gel effect in the kinetic picture. It is not obvious that this effect should be more pronounced in polyethylene than in polymethylene.

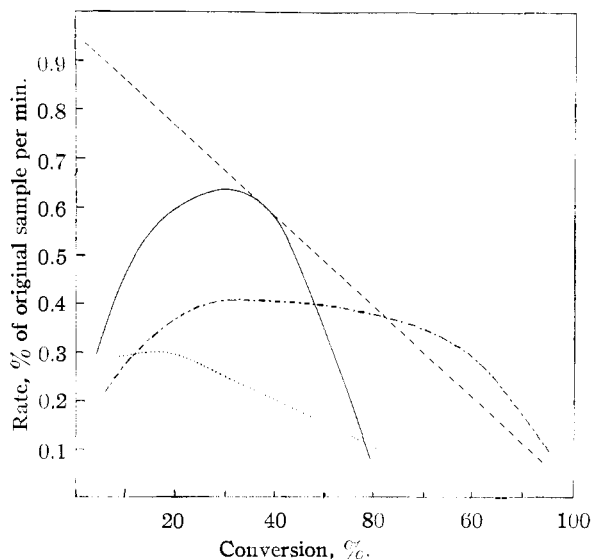


Fig. 6.—Rates of decomposition for fluorinated ethylene polymers: ---,  $(CF_2CF_2)_n$  at  $510^\circ$ ; - - - - - ,  $(CF_2CFH)_n$  at  $400^\circ$ ; —,  $(CF_2CH_2)_n$  at  $410^\circ$ ; ·····,  $(CFHCH_2)_n$  at  $375^\circ$ .

(16) As long as the number of bonds in the main chain exceeds that in the side chains and the process is random, the total number of molecules with chain length greater than  $L$  will first increase on degradation and therefore a maximum will result. This condition would require  $S$ -values of at least 12–15, if  $b$  is  $N/30$ , or  $1/6$  of the total number of branches as chains  $\geq L$  with  $S = 4$ , if no maximum is to appear.

Furthermore, cross linking did not affect the rate. We recall in this connection that polystyrene, another linear polymer, does show a maximum.

One more word concerning the discrepancies in reported activation energies of polyethylenes. The values of 60 to 70 kcal. found by Oakes and Richards<sup>8</sup> and obtained by observing the decrease in molecular weight, that is, the decrease in the number of bonds, should correspond more closely to the value of 68 kcal. found by Madorsky<sup>4</sup> which is based on high conversion rates (see Fig. 1). The same treatment of the data yields 72 kcal. for polymethylene. For polyethylene he calculated 45 kcal. from the initial part of the rate curve. Jellinek,<sup>5</sup> by measuring initial rates, found 45 to 66 kcal. depending on molecular weight. It is very likely that the different samples used by Jellinek differed in the degree of branching and hence a material with few branches would have given the higher activation energy.<sup>17</sup> On this basis the apparent discrepancies in activation energies of polyethylene seem to be related to the amount of branching.

The present study has shown that the mechanism of decomposition of polymethylene and polyethylene is similar to that of low molecular weight paraffinic hydrocarbons. In essence, the transfer step occurs to the exclusion of any depropagation. By contrast, it is seen in Fig. 6<sup>18</sup> that polytetrafluoroethylene degrades by a totally different mechanism, which is also evident from the fact that the only important product is the monomer. Here depropagation is the predominant reaction. Transfer cannot readily occur due to the larger C–F bond strengths. Replacing one fluorine atom in the monomer unit by hydrogen drastically changes the picture, Fig. 6. The rate immediately shows a maximum and presumably this is due to a large increase in the transfer probability because hydrogen in each unit is available for abstraction. Very little monomer is obtained. A second and third substitution of fluorine by hydrogen shows similar results. There is an additional effect, however, in these partially fluorinated polymers since another type of reaction occurs which yields hydrogen fluoride. It is produced at the greatest rate from the polyvinylidene fluoride. The less fluorinated polymer stops volatilizing at approximately 60 to 70% conversion due to this side reaction and a carbonaceous residue remains. The incorporation of hydrogen also decreases the decomposition temperature from  $\approx 500$  to  $\approx 400^\circ$ , where polyethylene has an approximately equivalent rate of decomposition, see Fig. 1.

This demonstrates that whenever the polymer structure favors transfer, a maximum type curve will be obtained provided an essentially linear structure is involved. Branching gives a continuously decreasing rate, qualitatively similar to that resulting from a reverse propagation mechanism. This of course does not imply such a mechanism in polyethylene. The present work has pointed

(17) According to the designation in reference 13 the degree of branching should be highest for Jellinek's sample with the lowest activation energy.

(18) S. L. Madorsky, *J. Research Natl. Bur. Standards*, **51**, 327 (1953).

out the differences between branched and linear depolymerizing systems. What is obviously needed now are kinetic studies on polymers with known branch concentrations and lengths. At this time

two types of structures look promising to us, namely, copolymers of diazomethanes with higher diazo derivatives and polymers of deuterioethylene. WASHINGTON, D. C., NEW YORK, N. Y.

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## NOTES

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### Gases Liberated during the High Voltage Electron Irradiation of Polyethylene

BY ELLIOTT J. LAWTON, P. D. ZEMANY AND J. S. BALWIT

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The irradiation of polyethylene with high energy electrons causes a liberation of hydrogen and volatile hydrocarbons, presumably due to the breaking of C-H and C-C bonds. The radicals and ions thus formed are capable of reacting further to form, (1) cross-linked material and (2) depolymerization products. Both reactions occur simultaneously in the material. The predominant reaction appears to favor the formation of cross-linked material.<sup>1</sup> Usually the nature of the reactions are deduced by the physical properties of the remaining bulk irradiated material. However, the gaseous products that are concomitantly produced in the reactions can be examined and will lead to a further understanding of the mechanism. Both approaches should result in the same deductions.

Charlesby has reported similar findings for polyethylene irradiated in an atomic pile.<sup>2</sup> He reported that hydrogen accounted for 98% of the total volume of the gas liberated and that the remaining gas consisted almost entirely of methane and ethane with smaller amounts of propane and butane.

The experiments described in this note were undertaken to determine the nature of the gases liberated from polyethylene when bombarded with high energy electrons in order to confirm some of the previous findings.<sup>1,2</sup>

#### Experimental

The source of high energy electrons used in the experiments was the General Electric Research Laboratory 800 kv. (peak) resonant transformer cathode ray unit.<sup>3,4</sup>

The gas liberated during the irradiation was subsequently analyzed with a mass spectrometer.

The polyethylene was of commercial grade and had a molecular weight of about 19,000. The test sample consisted of a stack of four 1-inch squares cut from 0.003 inch thick sheet and had an initial weight of 0.1988 g.

The test sample was sealed into a thin-wall glass bulb that could be connected to the spectrometer vacuum system through a ground glass taper joint. Attached to the thin bulb were two side arms, one of which served as a cold trap and the other contained a pressure gage.

The bulb was blown to a diameter of about 5 cm. from

AO fernico sealing type glass. The volume of the total system was 140 cc. The polyethylene samples were first loaded through the glass side arm, and the bulb then sealed to the rest of the system. The equivalent absorber thickness of the combined bulb wall and polyethylene sample was about 76 mg./cm.<sup>2</sup>, which value is in the range of penetration of the electron beam where the irradiation dose is nearly uniform throughout the thickness.

Condensable products liberated during irradiation were collected in the cold trap, which was held at liquid nitrogen temperature during the irradiation.

Preliminary to each irradiation exposure, the sample and glassware were outgassed by heating them while connected to the vacuum system. The thin bulb was heated to approximately 90° by means of infrared lamps. The bulb and sample were usually heated for several hours. In addition, most of the remainder of the glassware was vigorously heated by torching. At the end of the outgassing cycle, the pressure was usually zero, both with the trap at room temperature and at liquid nitrogen temperature. Gas pressure was measured with a thermistor type gage.<sup>5</sup>

During the irradiation period the trap was held at liquid nitrogen temperature so that the gas pressure indicated was that of the non-condensable fraction. By comparing the pressure readings with and without coolant on the traps, it was possible to determine the total pressure and the pressure corresponding to the volatile hydrocarbon products.

Irradiation dose measurements were made with a specially constructed air ionization chamber. The dose is expressed in roentgen units. The roentgen by definition is the amount of irradiation to produce 1 e.s.u. of charge in one cc. of standard air. The absorption of one roentgen corresponds to the liberation of  $1.6 \times 10^{12}$  charges, or ion pairs, in one gram of air, and it is assumed in one gram of polymer. On the basis of 32.5 e.v. per ion pair, this is equivalent to the absorption 83.8 ergs./g.

#### Discussion and Results

The pressure of the non-condensable gas, which was found to be hydrogen, was observed to increase linearly with the amount of irradiation. This is to be expected as the number of cross-links, as determined by swelling and tensile measurements, was found to increase nearly linearly with irradiation.<sup>1</sup> The data also indicates that the pressure of both the non-condensable and condensable gases is nearly a linear function of the irradiation dose up to a total dose of  $16 \times 10^6$  roentgen. The pressure of the gases liberated by an irradiation dose of  $16 \times 10^6$  roentgen was 1660  $\mu$  and 360  $\mu$  for the non-condensable and the condensable fractions, respectively. The near linear relationship holds in the case of the non-condensable fraction for irradiation doses up to  $200 \times 10^6$ , but not for the condensable fraction, as the yield of condensable gas was considerably less than expected. The decrease may in part be due to reabsorption of condensables by the polyethylene during the pressure measurement

(5) S. Dushman, "Vacuum Technique," p. 329.

(1) E. J. Lawton, A. M. Bueche and J. S. Balwit, *Nature*, **172**, 76 (1953).

(2) A. Charlesby, *Proc. Roy. Soc. (London)*, **A215**, 203 (1952).

(3) E. J. Lawton, W. D. Bellamy, *et al.*, *Tappi*, **34**, 113 (1951).

(4) J. A. Knowlton, G. R. Mahn and J. W. Ranftl, *Nucleonics*, **11**, 64 (Nov. 1953).