

Effect of Structure on the Thermal Decomposition of Polymers¹

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During recent years a considerable number of theoretical and experimental studies have been published on the kinetics and mechanism of the thermal decomposition of polymers. The treatment of depolymerization as a free-radical chain reaction involving the four basic steps of initiation, propagation, transfer, and termination seems adequate for a fairly complete understanding of the process in a large number of cases. Rate data now available are discussed from this point of view. It is shown that most of the characteristics of the thermal decomposition rate curves are a result of their basic structure and not of trace impurities. The magnitude of the rates and activation energies are, however, sensitive to trace structures or impurities. It is shown that intermolecular transfer will account for the rate behavior in a large number of polymers. In a relatively few other cases intramolecular transfer is indicated to be of more importance.

1. Introduction

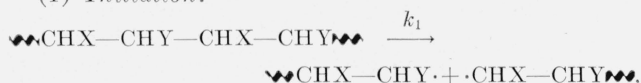
The hydrolytic degradation of polymers that are bonded by functional groups has been studied for a long time. For example, the mechanism of degradation of cellulose by dilute acid appears to be an attack of the reagent upon functional groups located at random. The kinetics of this type of random or near-random degradation are now well known [1].² Incidental to this mechanism are a very sharp initial drop in molecular weight of the polymers and the appearance of very little monomer until very late in the reaction.

In contrast, the degradation of vinyl polymers by heat shows a much wider variety of phenomena. The initial drop in molecular weight may be sharp or negligible, and the yield of monomer may be very small or nearly 100 percent. If monomer is formed, it usually is found even at the start of the reaction. In some cases, e. g., vinyl chloride, the main reaction observed is a stripping of side groups (here H and Cl atoms), leaving the carbon skeleton nearly intact. This stripping reaction [2,3] will not be considered further here.

There is fairly general agreement that the phenomena of most pyrolytic degradations of vinyl polymers require a free-radical chain mechanism. Several authors have developed special theories along this line [4,5]. A comprehensive theory was developed in several papers by Simha, Wall, and Blatz [6,7,8].

The necessary reaction steps, according to this scheme, are

(1) Initiation.



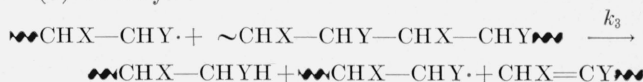
Modifications may involve end-groups, peroxidic fragments, etc.

(2) Propagation.

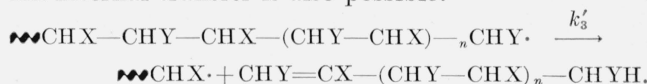


This is the reverse of the propagation step in free-radical polymerizations.

(3) Transfer.

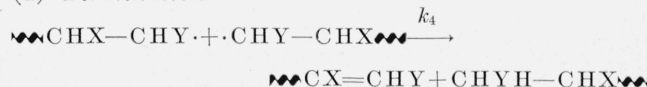


The relative importance of transfer is a principal distinction from the mechanism of polymerization and also from some other theories of degradation. An internal transfer is also possible:



Internal transfer can be treated formally as a special variety of propagation.

(4) Termination.



With the usual steady-state assumption, the rate equations can be solved in general, and solutions have been published for some extreme cases [6, 7, 8]. For intermediate cases, the labor of computation appears formidable.

It was necessary to consider the effects of the usual experimental procedure of conducting the pyrolysis in an open system, with continual volatilization of all products lying below some minimum molecular weight. The corresponding minimum degree of polymerization (DP) is denoted as L . The principal results are the appearance in some cases of an initial rate of volatilization and a maximum in the curve of rate against percent volatilized, both of which are greater the higher the limiting molecular weight for volatilization [7].

¹ This paper was presented in part before the 126th meeting of the American Chemical Society, September 1954.

² Figures in brackets indicate the literature references at the end of this paper.

The present results of theory can be surveyed in terms of several kinetic parameters:

$$\text{Reduced time, } \tau = k_1 t,$$

$$\text{Initial degree of polymerization} = N/2,$$

Transfer constant, $\sigma =$

$$\frac{\text{probability of transfer}}{\text{probability of initiation}} = k_3 R / 1,$$

where R has its usual meaning of radical concentration.

Approximate "zip" length, $Z, (1/\epsilon - 1),$

$$\begin{aligned} &= \frac{\text{probability of propagation}}{\text{probability of termination} + \text{transfer}}, \\ &= k_2 / k_4 R (1 + \sigma/2) \text{ for random initiation,} \\ &= k_2 / k_4 R [1 + \sigma/2(N-1)] \text{ for end initiation.} \end{aligned}$$

The zip represents that part of the kinetic chain length confined to the depropagation within a single molecule. It is analogous to the degree of polymerization in addition polymerization. Both become the actual kinetic chain length when transfer is absent.

The salient features of the theory are shown in figure 1, in which results for the extreme cases are compared. For all curves, σ is taken as zero. Nevertheless, the probable effect of transfer can be pointed out. In the figure the theoretical values for the rate of volatilization and for the relative degree of polymerization, both plotted as a function of conversion, are given for certain extreme cases. The values of the zip lengths are shown on the curves. From this

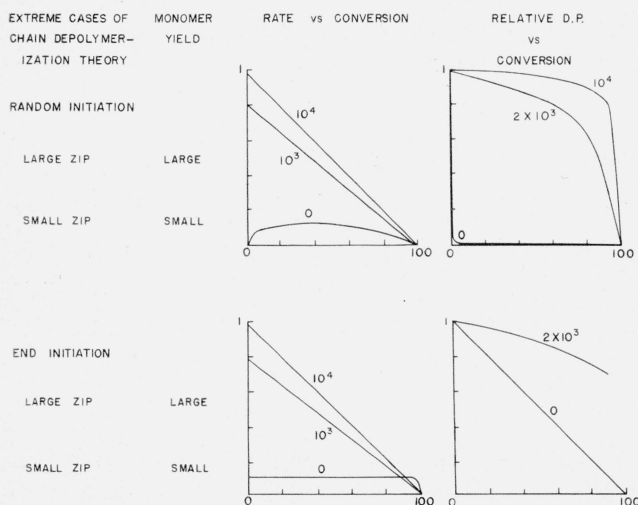


FIGURE 1. Theoretical results for extreme cases of the depolymerization theory.

Zip length values, $(1/\epsilon - 1)$, are shown on curves. $N=1,000$, $a=0$, and $L=4$, for all curves. For curves, zip=0, rate is multiplied by factor of 100 for random initiation and by 50 for end initiation. The conversion is represented by the abscissa for all curves shown.

figure one can compare the monomer yield, the rate of conversion, and the DP behavior for any combination of random- and end-initiation reactions with large or small zip. Regardless of method of initiation, large zip goes with a linearly decreasing rate curve, while the molecular weight curves are initially horizontal and above the diagonal. With random initiation and zero zip the rate and DP curves are those for simple random decomposition, the rate showing a maximum and the DP coinciding almost exactly with the axes of the ordinates and the abscissas. With end initiation zero zip produces a horizontal rate curve and a diagonal DP curve. Unless transfer occurs, end initiation cannot produce DP curves that drop below the diagonal. Introduction of transfer would tend to push the curves toward the random curves, i. e., those for the case of random initiation and zero zip. In this paper it will be seen, qualitatively at least, that molecular structures favorable for transfer reactions to occur on thermal decomposition give low monomer yields [9] and generally exhibit maximum-type rate curves.

2. Discussion of Experimental Results

Over several years a large number of polymers have been pyrolyzed, and it is now interesting to apply the theory as far as possible in interpreting the experimental results. The experimental details and data referred to are those of Madorsky and coworkers [10]. Because changes in molecular weight were followed in only a few instances, they will not be discussed here. The basic data consist of volatilization as a function of time and also the composition of volatile products. From these data are derived curves of rates of volatilization versus percent conversion, and also activation energies and monomer yields. During the first few percent of reaction there is an uncertainty in the experimental data due to the time necessary for the sample to reach constant temperature. For this reason, the initial region of a curve should probably be given less weight when either the temperature, the rate of decomposition, or both are very high.

The volatilization curves of Madorsky et al were used unaltered when the experimental points were numerous and closely spaced. From plots of conversion to volatiles, c , against time, t , Madorsky takes $\Delta c/\Delta t$ for adjacent points as the rate dc/dt , and the average conversion, $C + \Delta C/2$, as the conversion. This has the advantage of exhibiting and even somewhat enlarging the scatter of experimental data. Where experimental points were less closely spaced, the data were plotted in a different manner, designed to secure the best empirical smooth curve. The plot of C versus t was roughly fitted to an arbitrary function, $C = a + bt$, or $C = ae^{-bt}$. For given values of t , the difference of ordinates, C (experimental) minus C (algebraic), was taken numerically to a sufficient number of decimal places. This relatively small difference C' was plotted against t , and the derivative dC'/dt taken graphically. For a given t the rate dC/dt was taken as dC/dt (algebraic) + dC'/dt , and the conversion C as C (algebraic) + C' . It is evident

that graphical errors and the exercise of judgment are concentrated in the relatively small and meaningless difference functions. No method gave satisfactory results in the initial part of the pyrolysis of one methyl methacrylate sample, where, because of the very rapid rate, few experimental points were secured until after a sudden change had taken place in the rate. The curves of rate versus conversion are shown in figures 2 to 6.

The polymers may be classed chemically as in table 1. For each polymer the monomer yield and activation energy for decomposition are also listed.

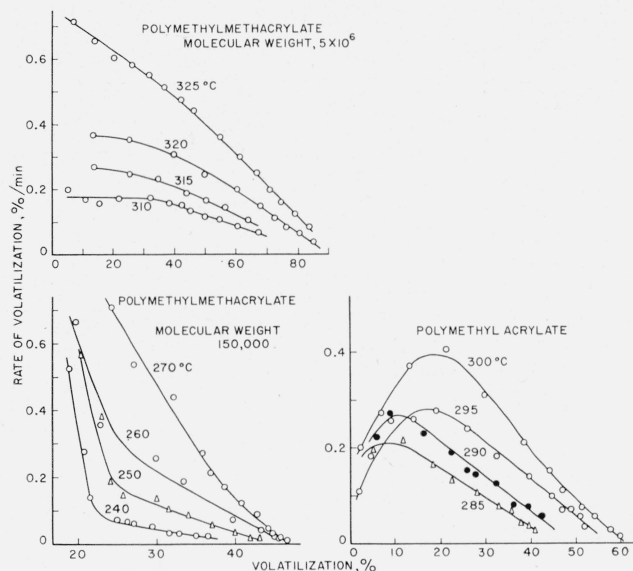


FIGURE 2. Volatilization rates for polymers of methyl methacrylate and methyl acrylate [10].

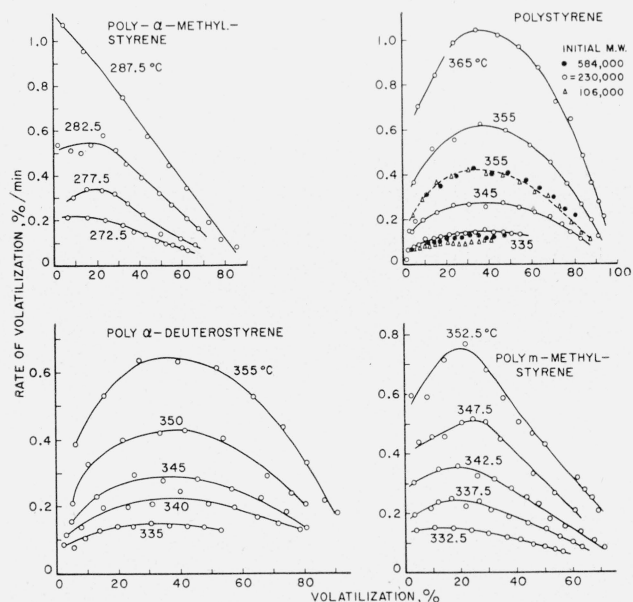


FIGURE 3. Volatilization rates for the styrene family of polymers [10].

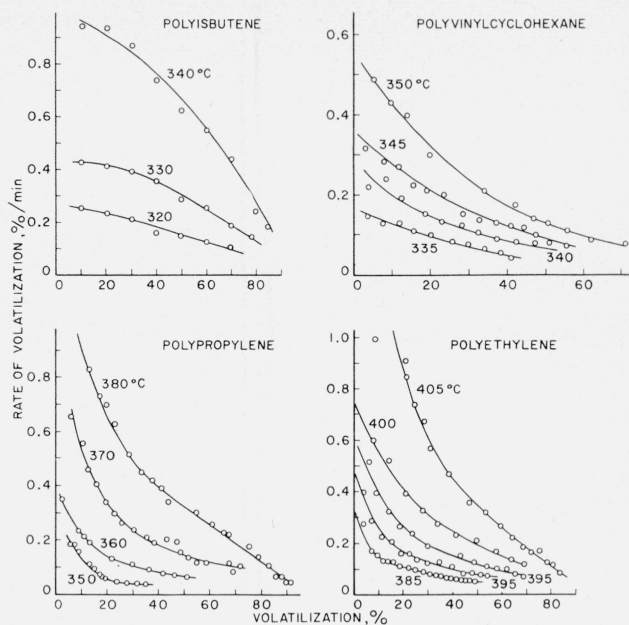


FIGURE 4. Volatilization rates for the aliphatic hydrocarbon polymers [10].

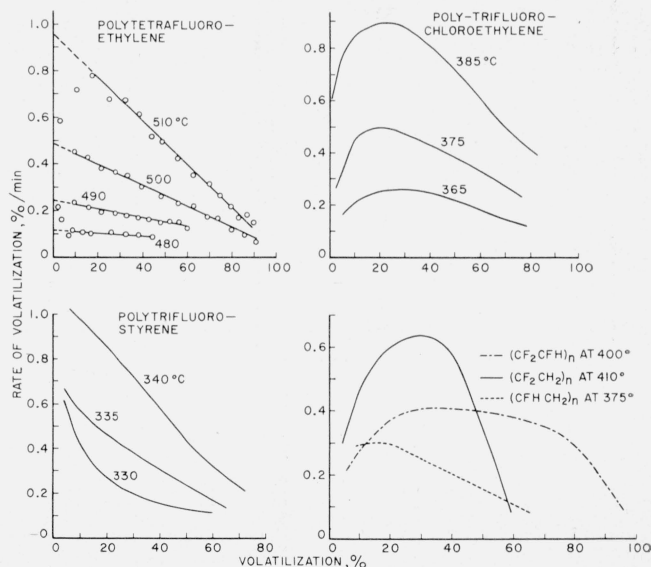


FIGURE 5. Volatilization rates for fluoro polymers [10].

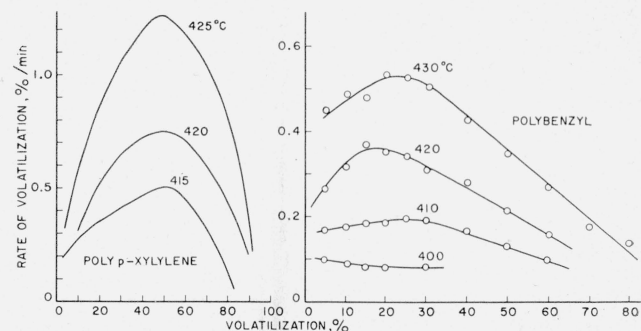


FIGURE 6. Volatilization rates for aromatic hydrocarbon polymers [10].

TABLE 1. Pyrolysis of polymers

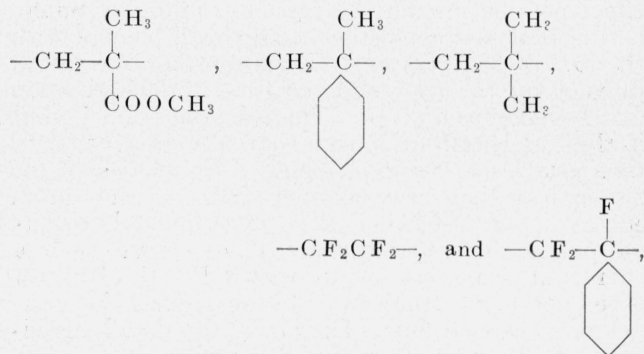
Polymer	Structure	Monomer yield	Activation energy	Rate at 350° C
Acrylates:		<i>wt %</i>	<i>kcal</i>	<i>wt %/min</i>
Methyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOCH}_3 \end{array}$	>95	55 to 32	5.2 to 220
Methyl acrylate	$\begin{array}{c} \text{H} \\ \\ \text{CH}_2-\text{C}- \\ \\ \text{COOCH}_3 \end{array}$	2	37	~10
Styrenes:				
α -Methylstyrene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	>95	58	228.0
α -Deuterostyrene	$\begin{array}{c} \text{D} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	70	58	0.268
<i>m</i> -Methylstyrene	$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_4-\text{CH}_3 \end{array}$	52	59	.900
Styrene	$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	42	58	.235
β -Deuterostyrene	$\begin{array}{c} \text{H} \\ \\ -\text{CHD}-\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	42	-----	-----
Aliphatic hydrocarbons:				
Isobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	~20	52	2.4
Propylene	$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	2	61	0.069
Ethylene (linear) (polymethylene)	$-\text{CH}_2-\text{CH}_2-$	0.1	70	.004

TABLE 1. *Pyrolysis of polymers—Continued*

Polymer	Structure	Monomer yield	Activation energy	Rate at 350° C
Aliphatic hydrocarbons—Continued Ethylene (branched)-----	$-\text{CH}_2-\text{CH}_2$	wt % .025	kcal 70	wt %/min .008
Vinyl cyclohexane-----	$ \begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{H} \\ \diagup \quad \diagdown \\ \text{H}_2 \quad \text{H}_2 \\ \diagdown \quad \diagup \\ \text{H}_2 \quad \text{H}_2 \\ \diagup \quad \diagdown \\ \text{H}_2 \end{array} $	≈. 1	52	.450
Fluorocarbons:				
Tetrafluoroethylene-----	$-\text{CF}_2\text{CF}_2-$	>95	80	2×10^{-6}
Trifluorostyrene-----	$ \begin{array}{c} \text{F} \\ \\ -\text{CF}_2-\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array} $	75	67	2.4
Trifluorochloroethylene-----	$-\text{CF}_2\text{CFCl}-$	28	66	0.044
Trifluoroethylene-----	$-\text{CF}_2\text{CFH}-$	<1	53	.046
Vinylidene fluoride-----	$-\text{CF}_2\text{CH}_2-$	<1	-----	-----
Vinyl fluoride-----	$-\text{CH}_2\text{CHF}$	<1	-----	-----
Aromatic chains:				
<i>p</i> -Xylylene-----	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$	0 (?)	76	.002
Benzyl-----	$-\text{C}_6\text{H}_5-\text{CH}_2-$	0	53	.006
Phenyl-----	$-\text{C}_6\text{H}_5-$	0	-----	-----

2.1. Monomer Yields

The occurrence of transfer, either inter or intra, offers a chance of forming nonmonomeric material and should, therefore, reduce the monomer yield. It would seem plausible that if one type of transfer occurred in a given system, the other would also occur to some degree. It is also likely that a small amount of intermolecular transfer would be more noticeable on the DP changes than on the monomer yield. From experience with small molecules, tertiary hydrogen atoms are especially readily removed in a transfer reaction. Experience with chain transfer in polymerization suggests that chlorine atoms are also vulnerable. Transfer will be favored by active radicals, and less likely with resonance-stabilized or sterically hindered radicals. The higher monomer yields in the various chemical classes are experienced with the structures



which are all devoid of tertiary hydrogen. The importance of location in the tertiary position is shown further by the comparison of α -deuterostyrene with β -deuterostyrene [12]. Substitution of tertiary H by D reduces transfer and raises monomer yield

from 42 to 70 percent, whereas substitution of a methylenic β -hydrogen has no marked effect. The lower monomer yield of polytrifluorochloroethylene is considered to be related to the vulnerability of the Cl atom to transfer.

The class of styrenes all show relatively high monomer yields. Although transfer is favored by the tertiary hydrogens present in most members, it is presumably lessened because of the relatively stable radicals involved.

Polymers of the aliphatic hydrocarbon class all show relatively low monomer yields even when tertiary hydrogen is absent. The activity of the alkyl radicals appears to compensate for the lack of tertiary hydrogens. As some estimates give a reactivity ratio of tertiary/primary of only 10/1, the compensation required is not great. Vinyl cyclohexane has a multitude of secondary hydrogens on the cyclohexyl group, as well as the tertiary hydrogen. Nevertheless, the order of monomer yield increased with methyl substitution. Substituent groups act in at least two ways: (1) by blocking specific positions and (2) by activating specific positions and weakening the main chain, thus affecting the temperature of decomposition and indirectly the rate of transfer. In general, with the exception of polytetrafluoroethylene, higher temperature of decomposition is associated with low monomer yield, which is due to more transfer.

2.2. Activation Energies

The activation energy for initiation E_1 is the largest, but not always the only important, contribution to the over-all activation energy. The activation energy for propagation is not as low as in polymerization because it will be at least as large as the thermochemical heat of polymerization, usually 10 to 20 kcal per mole of monomer. For methyl methacrylate the over-all energy of activation varies from 32 to 55 kcal, depending on the molecular weight and history of the polymer. This is an indication that initiation sometimes occurs at particular labile groups, the nature of which depends upon the polymerization catalyst and similar details. However, an important effect pointed out on theoretical grounds by Simha [13] is that the activation energy will change with the DP of the polymer. Equations for the initial rates of volatilization and variation in the activation energy have been given. The essential point is that if the zip length is longer than the polymer DP, then activation energy is equal to E_1 , whereas if the zip is less than the polymer DP, the activation energy is $E_1/2 + E_2 - E_4/2$. Experimental results on polymethyl methacrylate have shown such a change in activation energy with DP [14]. In most other polymers, studies of the rate versus DP have not been carried out. Therefore, the detail significance of the energies reported is not clear.

Except for the acrylate class the activation energies are often not very far below the usual carbon-carbon bond strength of 80 kcal, and may reflect initiation by a random break of a carbon-carbon bond. The highest activation energies are found for tetra-

fluoroethylene, 80 kcal, and ethylene, 70 kcal. Substitution in the chain lowers the activation energy. There is a regular sequence 70, 61, 52 for ethylene, propylene, and isobutylene, respectively; but among the styrenes the extra methyl of α -methylstyrene seems to have no effect.

2.3. Rates of Volatilization

The method of plotting experimental data has varied considerably in the literature. In order to illustrate the situation, especially with regard to random decomposition, figure 7 shows theoretical curves for over-all random decomposition (solid-line curves). They show random theory when plotted as rate in percentage of original material (lower curve) and rate in percentage of material remaining at the various stages (upper curve). Because experimental data often scatter to some degree, it is evident that when points at low conversion are given little weight, straight lines such as the dashed lines in the figure, may fit the experimental data very well.

With curves such as the theoretical ones, true initial points are practically impossible to measure. Final points are likewise impossible to measure both because of the shape of the curves and because in practice no reaction is 100 percent pure. Thus, curves of the upper type tend to drop, as indicated by the dotted curve in upper right of figure, because there is invariably a finite residue of carbon or ash. It is evident that the maximum-type plot and the use of the maximum rate should give the best esti-

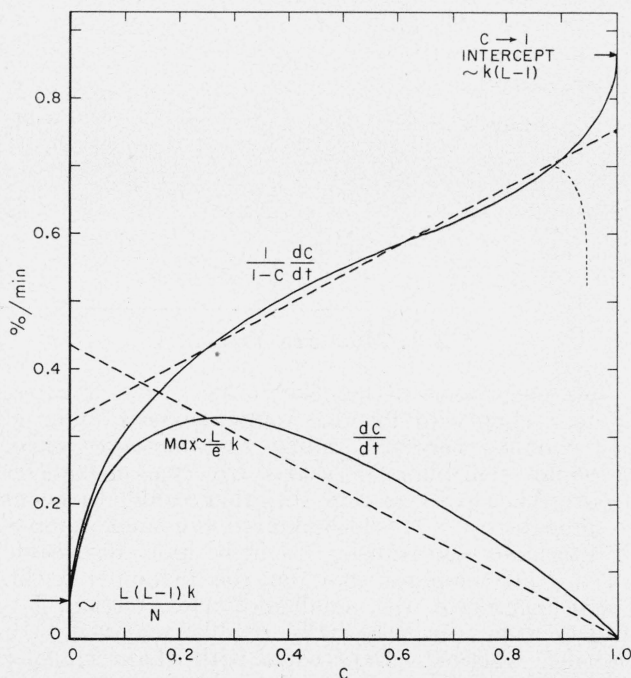


FIGURE 7. Comparison of two methods of plotting the rates of volatilization.

—, Theoretical curves for random degradation, $N=1,000$, $L=72$, and $k=10^{-2}$ min $^{-1}$. Upper-curve rate is percentage of instantaneous residue, lower-curve rate is percentage of initial material; - - - - - , misleading ways of extrapolating experimental data; , behavior when a finite quantity of ash or residue is present.

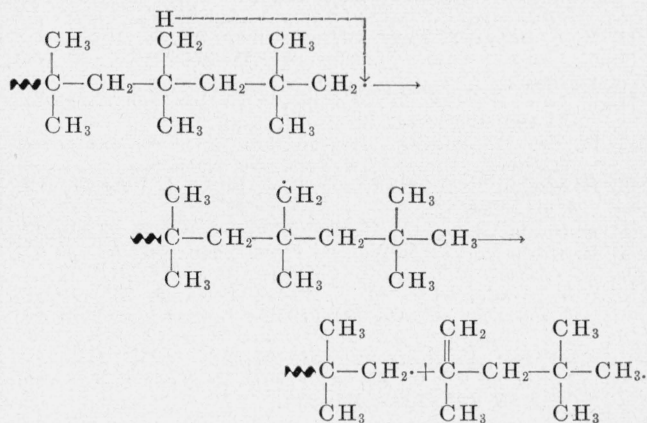
mates of rate constant and the activation energy. A knowledge of L , which is the DP of the smallest molecule that decomposes in order to volatilize, is required for precise evaluation of the defined rate constant, k . The value of L is easily estimated from product analysis. Fortunately, activation energies taken by the use of the initial points of the dashed lines cannot be greatly in error. However, rates obtained in this manner have doubtful significance and obscure the elucidation of the actual mechanism. In this article all rates plotted are in units of weight percent of original sample per minute, dC/dt . Thus a significant comparison can be made.

Except for the hydrocarbon polymers in figure 4 the rate curves in figures 2, 3, 5, and 6 show that maximum-type rate curves appear when the structure allows transfer, and this effect coincides with low monomer yield. It is evident, qualitatively at least, that intermolecular transfer affords the most general mechanistic explanation of the results. There are, however, many unexplained features. At the lower temperatures the distinction between the various curves diminishes. This is believed to be a result of the larger importance of diffusion at these temperatures. Therefore, in this discussion, the greatest weight is placed on the curves obtained at the highest temperature in each case.

The rate curves for polyisobutylene, polypropylene, polyvinyl cyclohexane, and polyethylene all show no maxima, although none give very high monomer yields. All yields are lower than that of monomer from polystyrene. However, it has been previously shown experimentally that the absence of a maximum in the rate of pyrolysis of polyethylene is due to the presence of branching [15]. When linear samples of polymethylene made from diazomethane are pyrolyzed, maximum-type curves are produced [15]. Commercial linear polyethylene and polyamides also give rate curves with maxima very similar to that for random theory [11].

Theoretical treatment of the degradation of branched structures on a statistical basis and the use of various ratios for the rate constant for breaking bonds at and near the branched points versus those between branched points could not eliminate the maximum in the rate curves without going to unreasonable values for the ratios of constants for bond cleavage [16]. The situation is, then, that the low monomer yield indicates transfer, whereas the rate curves for these hydrocarbon polymers suggest long zip lengths, and the branch structure with a statistical type of treatment does not produce other than maximum-type curves. The only readily apparent alternative is that intramolecular transfer predominates. In polymers of isobutene, vinyl cyclohexane, propylene, and branched polyethylene the structure must favor an internal isomerization such as that used by Kossiakoff and Rice [17] in order to fit with theory the thermal decomposition results of relatively small aliphatic hydrocarbons. Their isomerization is essentially the same process as the first part of our intramolecular transfer. For polyisobutylene it is suggested that

the following process of radical isomerization, followed by cleavage, i. e., intramolecular transfer, occurs to an appreciable extent;



The formation of the neopentyl radical would occur if the isomerized radical cleaves by the alternate path available. Neopentane is found in the pyrolysis of polyisobutene in an amount of 2 weight percent of the polymer decomposed. Intramolecular transfer is not limited to only the process depicted, but is assumed to occur in such a manner as to produce trimer, tetramer, etc., and other products, as well as the dimer depicted. An interesting point in this mechanism is that usually the depropagating radical is assumed to be the one where the odd electron is located on the carbon with the substituents. Here the primary and more active radical appears to be the most likely intermediate. Consideration of models suggests that the tertiary radical would have little chance of reaction except by disproportionation and depropagation.

In the polyethylene studied, branches must also effectively lead to greater kinetic zip lengths by increasing the probability of intramolecular transfer at the expense of intermolecular transfer. The polypropylene that was used was prepared with $\text{AlBr}_3\text{-HBr}$ as catalyst and is probably highly branched [18]. A study of linear polypropylene would be desirable to establish whether branches are responsible for the nonexistence of a maximum here.

3. Conclusions

On qualitative grounds it is evident that the pyrolytic behavior of polymers studied is a result of their basic structure and not of trace impurities or structures, at least within certain limits. Furthermore, the degree of intermolecular transfer is a deciding factor, and occurs to a significant extent in a large number of polymers. On the other hand, it is apparent that the ratio of inter- to intramolecular transfer is quite sensitive to detailed molecular structure. The exact evaluation of inter- versus intramolecular transfer will require extensive investigation of products, rate and DP versus conversion, and the dependence of the latter two quantities on the initial molecular weight.

4. References

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WASHINGTON, October 15, 1957.