

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### The Kinetics of Thermal Decomposition of Polymers

J. Atkinson<sup>a</sup>; J. R. Maccallum<sup>a</sup>

<sup>a</sup> Department of Chemistry, St. Andrews University Fife, Scotland

**To cite this Article** Atkinson, J. and Maccallum, J. R.(1971) 'The Kinetics of Thermal Decomposition of Polymers', Journal of Macromolecular Science, Part A, 5: 5, 945 – 956

**To link to this Article:** DOI: 10.1080/00222337108061077

**URL:** <http://dx.doi.org/10.1080/00222337108061077>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## The Kinetics of Thermal Decomposition of Polymers

J. ATKINSON and J. R. MacCALLUM

*Department of Chemistry*

*St. Andrews University*

*Fife, Scotland*

### SUMMARY

The rate equations for the thermal decomposition of a polymer by a random scission reaction followed by evaporation of low molecular weight species are solved using a different approach to that used by previous workers. The results obtained are in agreement with their conclusions.

### INTRODUCTION

The confirmation of a postulated mechanism for a chemical reaction depends primarily on agreement between predicted and observed kinetic behavior. Although much research has been devoted to the study of the thermal decomposition of polymers [1, 2], there are relatively few examples for which the predicted and observed rate laws are in total agreement.

Two of the most important mechanisms of the thermal breakdown of polymers are 1) the scission of main chain bonds followed by a reverse polymerization resulting in high yields of monomer, and 2) evaporation of low molecular weight homologs produced as a result of random scission of the macromolecules. Decompositions incorporating both mechanisms can also occur.

Several papers have considered the first mechanism [3-6]. The outstanding treatment of the kinetics of weight loss by an evaporation mechanism is that of Simha, Wall, and Blatz [3, 4] which has been extended by Boyd and coworkers [5, 6]. Both these groups used sets of differential equations and one of the most significant conclusions was that the rate of loss of weight had a maximum value at 26.4% decomposition. The present paper is concerned with this particular mechanism, but uses a different approach to evaluate the kinetic equations.

### KINETIC ANALYSIS

The mechanism of decomposition is exactly that proposed by Simha et al. [3, 4]—random scission of the main chain bonds with rapid evaporation of any species of less than a prescribed degree of polymerization.

### LIST OF SYMBOLS USED

- $P_0$  Initial degree of polymerization of the sample.  
 $P$  Degree of polymerization of the sample at time  $t$ .  
 $W_0$  Initial weight of the sample.  
 $W$  Weight of the sample at time  $t$ .  
 $N$  Number of moles in the sample at time  $t$ .  
 $N_x$  Number of moles in the sample of degree of polymerization  $x$ .  
 $m$  Molecular weight of the repeat unit.  
 $t$  Time of reaction.  
 $k_s$  Rate constant for scission reaction.  
 $a$  Degree of polymerization of the largest molecule that can evaporate from the sample.

For a given sample, at any time, the following relationship applies

$$W = mNP \quad (1)$$

During the course of the reaction, the number of molecules, the weight of the sample, and the degree of polymerization all vary continuously with respect to time. Hence the following relationship must hold

$$\frac{1}{m} \frac{dW}{dt} = \frac{NdP}{dt} + \frac{PdN}{dt} \quad (2)$$

In the following kinetic analysis, the sample is assumed to have a "most probable" distribution of molecular sizes.

This is expressed mathematically by Eq. (3).

$$N_x = \frac{N'}{P'} \left( 1 - \frac{1}{P'} \right)^{x-1} \quad (3)$$

$N'$  and  $P'$  are the number of moles and degree of polymerization at time  $t$  if a complete distribution were present. In the case which considers an evaporatable size "a," these are not the experimental quantities and the above equation must be modified to incorporate the experimental values

$$N = \sum_{a+1}^{\infty} N_x$$

$$= \sum_{x=a+1}^{\infty} \frac{N'}{P'} \left( 1 - \frac{1}{P'} \right)^{x-1}$$

$$N = N' \left( 1 - \frac{1}{P'} \right)^a$$

$$P = \frac{\sum_{a+1}^{\infty} x N_x}{\sum_{a+1}^{\infty} N_x}$$

$$P = \frac{\sum_{a+1}^{\infty} x \frac{N'}{P'} \left( 1 - \frac{1}{P'} \right)^{x-1}}{\sum_{a+1}^{\infty} \frac{N'}{P'} \left( 1 - \frac{1}{P'} \right)^{x-1}}$$

$$P = P' + a$$

$$N = N' \left( 1 - \frac{1}{P-a} \right)^a$$

Substituting in Eq. (3)

$$N_x = \frac{N}{\left\{ 1 - \frac{1}{(P-a)} \right\}^a} \frac{1}{P-a} \left\{ 1 - \frac{1}{P-a} \right\}^{x-1} \quad (4)$$

### MOLECULAR POPULATION

If a molecule undergoes scission to produce two smaller molecules, then the molecular population increases by one. However, if the break occurs within a distance of "a" repeat units from either end, then the smaller of the two molecules of a size less than, or equal to, "a" evaporates and the molecular population is unchanged. There will also be a fraction of molecules which when broken at certain bonds will produce two fragments of size less than "a" with a resulting decrease in molecular population.

Thus

$$\frac{dN}{dt} = \text{rate of scission leading to an increase} \\ - \text{rate of scission leading to a decrease}$$

$$\frac{dN}{dt} = k_s [\text{total number of bonds which when broken lead to} \\ \text{and increase in population}]$$

$$-k_s [\text{total number of bonds which when broken lead} \\ \text{to a decrease in population}]$$

$$= k_s \sum_{x=2a+2}^{\infty} N_x(x - 2a - 1)$$

$$- k_s \sum_{x=a+1}^{x=2a} N_x(2a + 1 - x)$$

$N_x$  can be replaced using Eq. (4)

$$= k_s \frac{N}{(P - a)} \frac{1}{\left(1 - \frac{1}{P - a}\right)^a} \left\{ \sum_{x=2a+2}^{\infty} \left(1 - \frac{1}{P - a}\right)^{x-1} (x - 2a - 1) - \right. \\ \left. \sum_{x=a+1}^{x=2a} \left(1 - \frac{1}{P - a}\right)^{x-1} (2a + 1 - x) \right\}$$

By resolving the summations, the above equation reduces to:

$$= k_s \frac{N}{(P-a)} \frac{1}{\left(1 - \frac{1}{P-a}\right)^a} \left\{ (P-a)^2 \left(1 - \frac{1}{P-a}\right)^{2a+1} - (P-a) \left(1 - \frac{1}{P-a}\right)^a [2a - P + 1 + (P-a) \left(1 - \frac{1}{P-a}\right)^{a+1}] \right\}$$

This reduces to

$$\frac{dN}{dt} = kN(P - 2a - 1) \tag{5}$$

**Weight of Sample**

The rate of loss of weight,  $-dW/dt$ , is equal to the rate of production of volatile fragments multiplied by the weight of the volatile part.  $-dW/dt$  comprises three parts.

(a) Molecules for which  $x \geq 2a + 1$ . Any molecule in this range has  $2a$  bonds which, when broken, lead to one molecule which can evaporate and one which cannot.

Rate of loss of weight due to (a)

$$= k_s a(a+1) \frac{Nm}{P-a} \left\{ \frac{1}{\left(1 - \frac{1}{P-a}\right)^a} \right\} \sum_{x=2a+1}^{\infty} \left(1 - \frac{1}{P-a}\right)^{x-1}$$

$$= k_s a(a+1)Nm \left(1 - \frac{1}{P-a}\right)^a$$

From Eq. (1),  $Nm = W/P$ , therefore

$$-\frac{dW}{dt} = k_s \frac{W}{P} a(a+1) \left(1 - \frac{1}{P-a}\right)^a$$

(b) Molecules for which  $a + 1 \leq x \leq 2a$ . In this region, any molecule has  $(2a + 1 - x)$  bonds which on scission lead to complete removal of the molecule. When this occurs, the weight lost is equivalent to  $xm$ .

Rate of loss of weight due to (b)

$$\begin{aligned}
 &= k_s \frac{Nm}{(P-a)} \left( \frac{1}{1 - \frac{1}{P-a}} \right)^a \sum_{x=a+1}^{x=2a} \left( 1 - \frac{1}{P-a} \right)^{x-1} (2a+1-x)x \\
 &= k_s \frac{Nm}{P-a} \left( \frac{1}{1 - \frac{1}{P-a}} \right)^a \\
 &\quad \left\{ \left( 1 - \frac{1}{P-a} \right)^a [a(a+1) \left( 1 - \left( 1 - \frac{1}{P-a} \right)^a \right) (P-a)] \right. \\
 &\quad \left. - \sum_{n=2}^a \left( 1 - \frac{1}{P-a} \right)^{n-1} (n-1)n \right\}
 \end{aligned}$$

(c) Molecules for which  $a+2 < x < 2a$ . For this case, any molecule has  $2(x-a-1)$  bonds which on scission lead to the loss of one fragment, while the other remains in the sample.

Rate of loss of weight due to (c)

$$\begin{aligned}
 &= k_s \frac{Nm}{P-a} \cdot \left( \frac{1}{1 - \frac{1}{P-a}} \right)^a \sum_{x=a+2}^{2a} \left( 1 - \frac{1}{P} \right)^{x-1} (x-a-1)(x-a) \\
 &= k_s \frac{Nm}{P-a} \left( \frac{1}{1 - \frac{1}{P-a}} \right)^a \left( 1 - \frac{1}{P-a} \right)^a \sum_{n=2}^a \left( 1 - \frac{1}{(P-a)} \right)^{n-1} (n-1)n
 \end{aligned}$$

The expression for the total rate of loss of weight is the sum of the three parts (a), (b), and (c), and solves out as

$$-\frac{dW}{dt} = k_s \frac{W}{P} a(a+1) \quad (6)$$

Figure 1 illustrates a plot of  $(dW/dt)W_0$  vs.  $t$  for some values of  $P_0$  and  $a$ ,

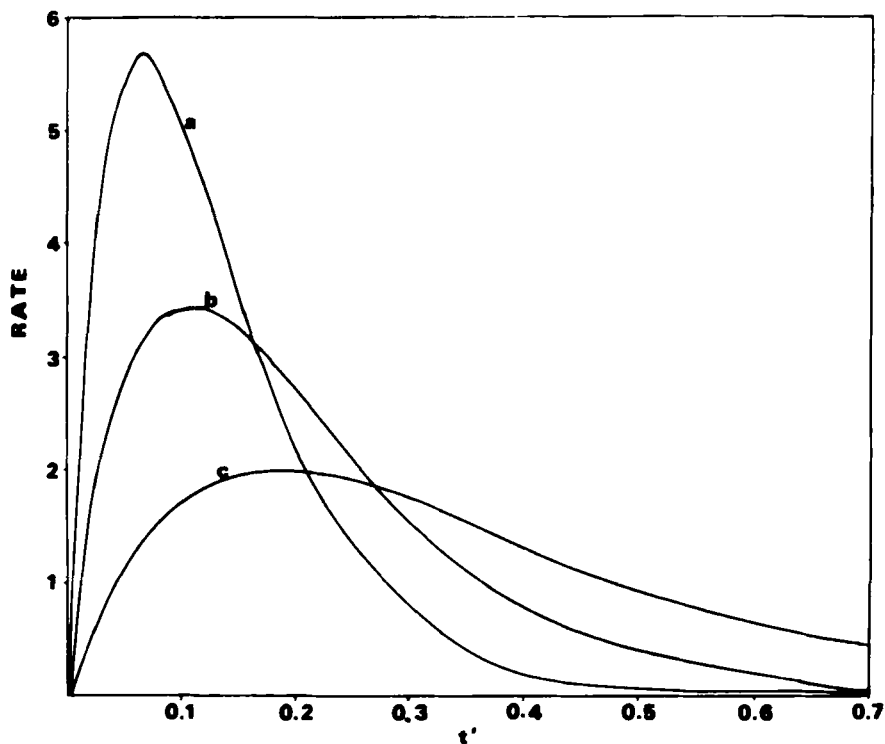


Fig. 1. Plot of rate in per cent per unit time vs.  $t'$  (equal to  $k_s t$ ). The absolute values of the rate and time parameters will depend on the value of  $k_s$ .  
Evaporatable length: (a),  $a = 15$ ; (b),  $a = 9$ ; (c),  $a = 5$ .

and Fig. 2 shows a plot of percentage weight vs. degree of polymerization for the same values of  $P_0$  and  $a$ .

### DEGREE OF POLYMERIZATION

From Eqs. (2), (5), and (6), the following expression can be deduced for the rate of change of degree of polymerization with respect to time

$$-\frac{dP}{dt} = k_s(P - a - 1)(P - a) \quad (7)$$



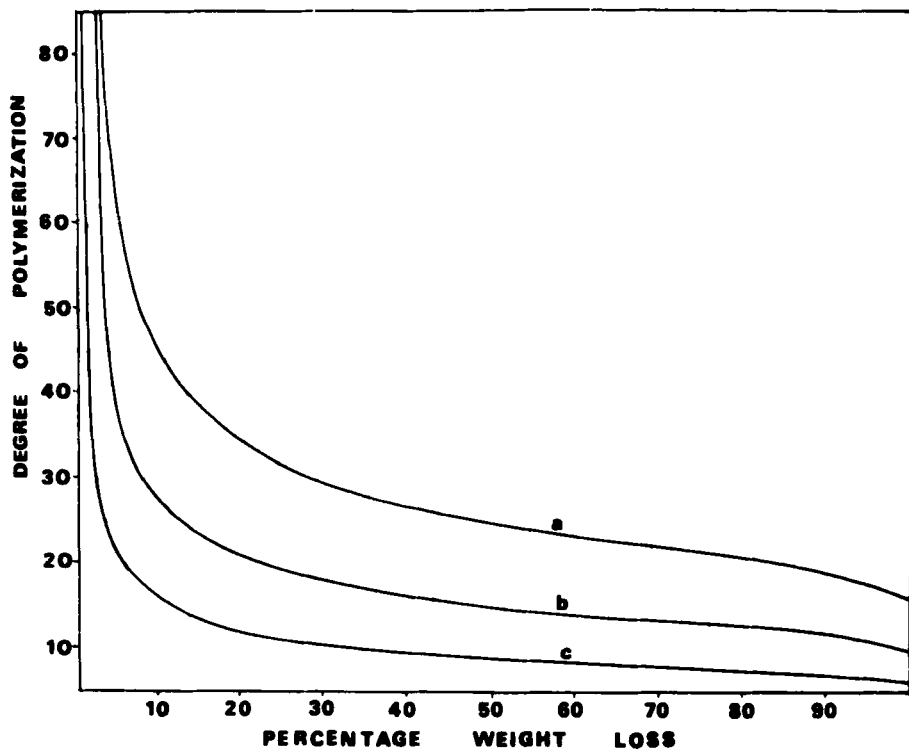


Fig. 2. Plot of degree of polymerization,  $P_0$ , vs. percentage change in weight. Values for "a" are (a) 15, (b) 9, and (c) 5.  $P_0$  values of 500, 1000, or 2000 make no significant difference to the curves.

The rate Eq. (7) can readily be integrated, resulting in the following expression for  $P$  in terms of  $t$

$$P = a + 1 + \frac{1}{\frac{ekt}{C} - 1} \quad (8)$$

where

$$C = \frac{P_0 - a - 1}{P_0 - a}$$

Figure 3 shows a plot of  $1/P$  vs.  $t$  for various values of  $P_0$  and  $a$ . For most

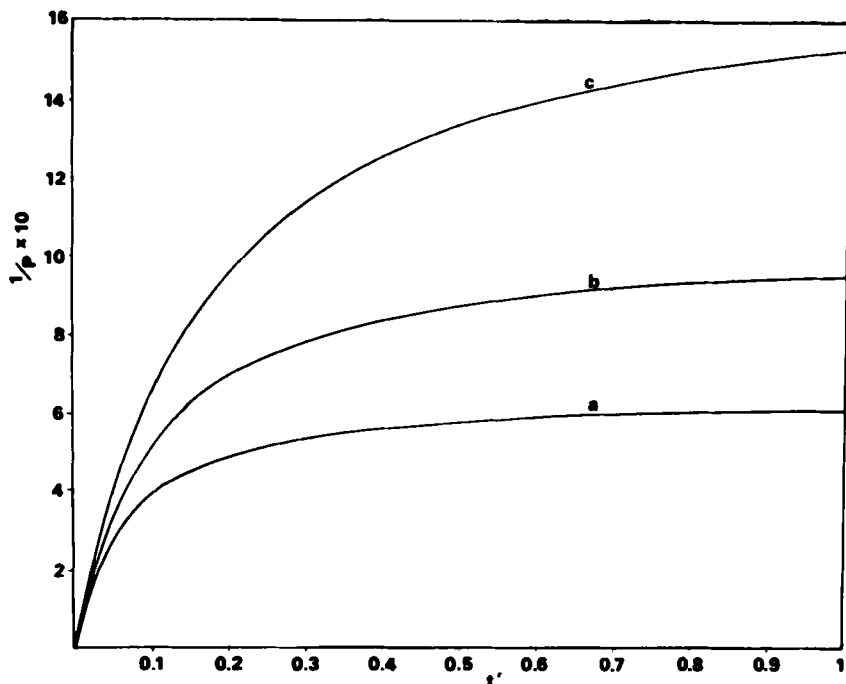


Fig. 3. Plot of reciprocal degree of polymerization versus  $t'$  (equal to  $k_{st}$ ).  $P_0$  values of 500, 1000, or 2000 make no significant difference to the curves for which "a" has the values (a) 15, (b) 9, and (c) 5.

cases C can be regarded as equal to 1; however, for the limiting case of  $t = 0$ , it must be present.

Similarly, by substituting the P derived in Eq. (8) in Eq. (6), we can deduce the following expression for W in terms of t

$$W = \frac{W_0 [(a + 1)e^{kt} - ac](P_0 - a)}{P_0 e^{(a + 1)kt}} \quad (9)$$

To test for the possible existence of a maximum value for the rate of loss of weight,  $-dW/dt$  is differentiated with respect to time and set equal to zero. From this, it can be shown that the maximum rate of loss of weight occurs when the degree of polymerization has a value of  $2a + 1$ .

The percentage decomposition corresponding to this maximum value for

the rate of loss of weight can be calculated by integration of  $dP/dW^*$  and substituting  $P = 2a + 1$  in the resulting equation

$$\frac{dP}{dW} = \frac{(P - a - 1)(P - a)P}{Wa(a + 1)}$$

Integration of this equation between the limits  $W_0$  to  $W$  and  $P_0$  to  $P$  yields the following expression

$$\ln \frac{W}{W_0} = (a + 1) \ln \frac{(P_0 - a)}{(P - a)} + a \ln \frac{(P - a - 1)}{(P_0 - a - 1)} + \ln \frac{P}{P_0} \quad (10)$$

By substitution of  $P = 2a + 1$  in Eq. (10), the expression reduces to

$$\frac{W}{W_0} = \frac{(2a + 1)}{P_0} \frac{(P_0 - a)^{a+1}}{(a + 1)} \left\{ \frac{a}{(P_0 - a - 1)} \right\}^a$$

The percentage degradation,  $[1 - (W/W_0)] \times 100$ , corresponding to the maximum rate of loss of weight for various "a" and  $P_0$  values, is summarized in Table 1.

## CONCLUSIONS

The relationship obtained by the above treatment is in good agreement with previous work although a different approach has been used. It seems possible that by using the above techniques the kinetics of more complex mechanisms can be analyzed, in particular the occurrence of unzipping along with evaporation.

Turning to practical applications, it would seem that none of the thermal decomposition reactions of polymeric materials so far studied proceeds by a simple scission-and-evaporation mechanism. Recent evidence [7] has shown that linear alkanes of degree of polymerization greater than 47 evaporate without undergoing chemical change. On this basis the maximum rate of

---

\* $\frac{dP}{dW} = \frac{dP}{dt} / \frac{dW}{dt}$ ; both  $\frac{dP}{dt}$  and  $\frac{dW}{dt}$  are continuous functions and hence the above manipulation can be made.

Table 1

a	$P_0$	$(1 - W/W_0) \times 100$
1	100	25.00
3		26.13
4		26.18
5		26.20
6		26.18
7		26.14
10		25.90
20		24.30
1	500	25.00
5		26.32
10		26.38
11		26.38
12		26.38
13		26.38
20		26.35
1	1000	25.00
5		26.32
10		26.39
15		26.40
16		26.40
17		26.40
20		26.40

loss of weight by the above mechanism would occur at a D.P. of 95, which is very much lower than is encountered experimentally.

The standard method of following the thermal breakdown of a polymer is by thermogravimetry, whereby the sample is weighed as its temperature is progressively increased. Wall, Flynn, and Straus [7] have demonstrated

that "a," the D.P. of the largest fragment which can evaporate, is itself a complicated function of temperature, and this factor must be taken into account when Eq. (6) is applied to data collected during programmed thermogravimetry.

#### REFERENCES

- [1] N. Grassie, *The Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956.
- [2] S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley (Interscience), New York, 1964.
- [3] R. Simha, L. A. Wall, and P. J. Blatz, *J. Polym. Sci.*, **5**, 615 (1950).
- [4] R. Simha and L. A. Wall, *J. Phys. Chem.*, **56**, 707 (1952).
- [5] R. H. Boyd, *J. Chem. Phys.*, **31**, 321 (1959). R. H. Boyd and T. P. Lin, *J. Chem. Phys.*, **31**, 773, 778 (1959).
- [6] R. H. Boyd, *J. Polym. Sci., Part A-1*, **5**, 1573 (1967).
- [7] L. A. Wall, J. H. Flynn, and S. Straus, *J. Phys. Chem.*, **74**, 3237 (1970).

*Accepted by editor December 21, 1970*

*Received for publication January 13, 1971*