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### Simulation of Degradation Processes. III. Testing of Some Relations for Random Chain Scission

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## Simulation of Degradation Processes. III. Testing of Some Relations for Random Chain Scission

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### ABSTRACT

By means of the Monte Carlo method a course of random chain scission was simulated and the following were determined: the number-average molecular weight and the degree of polymerization of the system, the weight-average molecular weight and the degree of polymerization of the system, the number of molecules of degree of polymerization higher than an arbitrarily chosen value, and the number of molecules of a given degree of polymerization. Values obtained by simulation were compared with some analytical relations. Some hitherto unknown characteristics of the whole process have been established.

### INTRODUCTION

In a previous paper [1] a simple model was described which used the Monte Carlo method for simulation of changes in molecular weights of polymers. The distribution in tabular form was worked out on four assumptions:

1. The probability of scission of a molecule of degree of polymerization  $n_1$  is equal to its weight fraction.

2. The elementary steps move in the system at a constant velocity (one elementary step is a scission of one molecule).
3. The process is completely random.
4. The system is closed.

Depolymerization in the simultaneous formation of monomer was not considered.

It follows from Assumption 2 that the time of degradation is directly related to the number of calculated cycles. From Assumptions 1 and 3 it follows that the probability of scission of a molecule of polymerization degree  $n_i$  is  $p_i = N_i n_i / \sum N_i n_i$ , where  $N_i$  is the number of molecules of degree of polymerization  $n_i$ . The course of one calculation cycle performed by computer is apparent from the simplified scheme in Fig. 1.

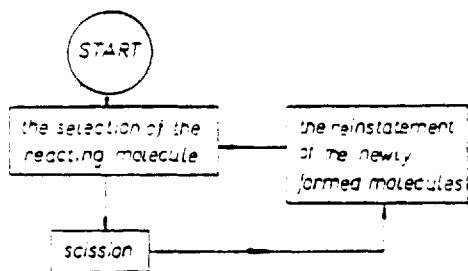


FIG. 1. Simplified calculation scheme.

From our model the following were derived:

1. The dependence on time of the number of molecules  $N_i$  of degree of polymerization  $n_i$

$$dN_i/dt = -k'v p_i \quad (1)$$

where  $k'$  is a constant and  $v$  is the velocity of the elementary steps.

Equation (1) was integrated in the limits 0 to  $t$  on the assumption that the starting molecular weight distribution is sufficiently narrow.

$p_i = N_i n_i / \sum N_i n_i$ ,  $v$  is constant, and  $k' = k \sum N_i n_i$ . The result was an equation for a first-order reaction:

$$N_{it} = N_{i0} \exp(-kvn_i t) \quad (2)$$

2. For

$$1/\bar{n}_{nt} - 1/\bar{n}_{n0} = Kt \quad (3)$$

where  $\bar{n}_{nt}$  and  $\bar{n}_{n0}$  are the number-average degree of polymerization of the system at times 0 and  $t$ , respectively, and  $K$  is a constant, and with the assumption that

$$\sum N_{it} = \sum N_{i0} + vt \quad (4)$$

it was derived that

$$K = v / \sum N_i n_i \quad (5)$$

and the average scission velocity of the chains of the whole molecular set at any given time is equal to

$$\bar{v} = K\bar{n}_n \quad (6)$$

The aim of this paper was to test some quantities which are expressed analytically and which are important for the characterization of a polymer in the course of random chain scission by applying the results obtained by the Monte Carlo method and to find some mutual relations.

## RESULTS AND DISCUSSION

To test the analytical relations by the application of results obtained by the Monte Carlo method, we shall assume that time

is numerically equal to the number of cycles calculated by computer.

The Dependence of the Number-Average Polymerization Degree of the System  $\bar{n}_n$  and the Number-Average Molecular Weight  $\bar{M}_n$  on Time

It is known that  $\bar{M}_n = M\bar{n}_n$ , where  $M$  is the molecular weight of a monomer unit. The determination of the dependence of  $\bar{n}_n$  on time therefore also determines the dependence of  $\bar{M}_n$ .

The value of the number-average polymerization degree  $\bar{n}_n$  in time  $t$  is equal to

$$\bar{n}_{nt} = \Sigma N_{i1} n_i / \Sigma N_{it} = \bar{n}_{n0} \Sigma N_{i0} / \Sigma N_{it} \quad (7)$$

where  $\Sigma N_{it}$  and  $\Sigma N_{i0}$  are the numbers of molecules in the system in time  $t$  and in time  $t = 0$ , respectively.

Substituting for  $\Sigma N_{it}$  from Eq. (4):

$$\bar{n}_{nt} = \bar{n}_{n0} (1 + vt, \Sigma N_{i0}) \quad (8)$$

The value of the elementary steps velocity  $v$  can be evaluated from Eqs. (3) and (5). Equations (7) and (8) are identical with the equations derived in Ref. 2 for the case of random cross-linking without cyclization.

Comparison with Results Obtained by the Monte Carlo Method

The dependence of  $1/\bar{n}_{nt} - 1/\bar{n}_{n0}$  on the number of calculated cycles given by computer for the simulated case is plotted in Fig. 2. For the simulated case, the value of the constant  $K$  in Eq. (3) is equal to (deduced from the graph in Fig. 2):  $K = 3.65 \times 10^{-3}$ . It follows from Eq. (5) that  $v = K \Sigma N_{i1}$ . For the simulated case,

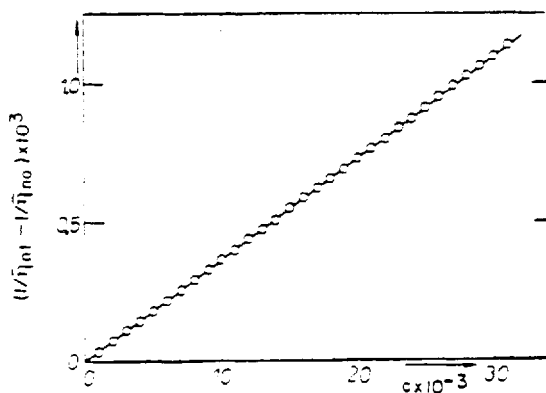


FIG. 2. Dependence of the difference  $1/\bar{n}_{nt} - 1/\bar{n}_{n0}$  on the number of cycles.

$\sum N_i n_i = 27,404,350$ , thus  $v = 1.0002588 \approx 1$ , which is in agreement with the assumption that at one calculated cycle on the computer one new molecule is formed as a result of scission of one randomly selected molecule into two parts.

For the simulated case it is thus possible to write Eq. (7) in the form

$$\bar{n}_{nt} = \sum N_i n_i / (\sum N_{i0} + t) \quad (9)$$

where  $t$  is the number of computed cycles. The dependence of the number-average polymerization degree  $\bar{n}$  on the number of computed cycles is shown in Fig. 3 for the simulated case.

The Dependence of the Weight-Average Polymerization Degree of the System  $\bar{n}_w$  and the Weight-Average Molecular Weight of System  $\bar{M}_w$  on Time

Since  $\bar{M}_w = M \bar{n}_w$ , we shall examine only the dependence of  $\bar{n}_w$  on time, where  $\bar{n}_w = \sum N_i n_i^2 / \sum N_i n_i$ . For a closed system  $\sum N_i n_i$  is

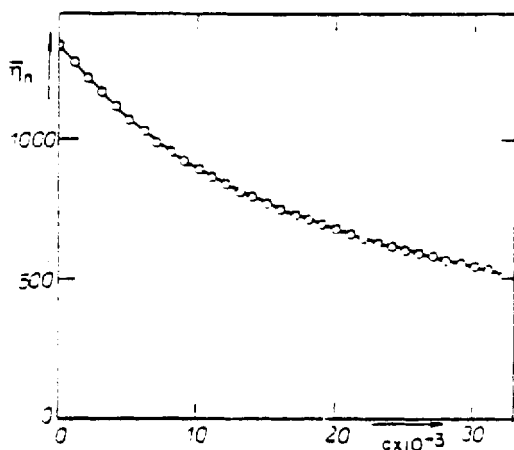


FIG. 3. Dependence of the number-average polymerization degree  $\bar{n}_n$  on the number of calculation cycles.

constant, so that only the term  $\sum N_i n_i^2$  varies with time. By selecting at random a molecule with a polymerization degree  $n_x = n_1 + n_2$  and splitting it at random into two molecules of polymerization degrees  $n_1$  and  $n_2$ , the value of  $\sum N_i n_i^2$  will decrease:

$$(\sum N_i n_i^2)_{t+\Delta t} = (\sum N_i n_i^2)_t - (n_1 + n_2)^2 + (n_1^2 + n_2^2)$$

$$\Delta \sum N_i n_i^2 = -2n_1 n_2$$

where  $\Delta t$  is the time needed for a scission of one randomly selected molecule.

It follows that

$$d\bar{n}_w = -(2v/\sum N_i n_i) n_1 n_2 dt \quad (10)$$

When describing the method of chain scission simulation in Ref. 1 and in Ref. 3, it was stated that for a randomly selected molecule of degree of polymerization  $n_x$ , we should use a random number  $\rho$  from the population equidistributed in the range 0 to 1 and by its

use we should create the fragments  $n_1 = \rho n_x$  and  $n_2 = (1 - \rho) n_x$ . The product  $n_1 n_2$  shall then be equal to

$$n_1 n_2 = \rho(1 - \rho) n_x^2$$

According to the mean value theorem, the mean value of the product  $\rho(1 - \rho)$  in the region  $(\rho_0, \rho)$  is equal to

$$\frac{1}{\rho - \rho_0} \int_{\rho_0}^{\rho} \rho(1 - \rho) d\rho$$

which for the interval  $(0,1)$  gives the value  $1/6$ . Equation (10) can thus be expressed in the form

$$d\bar{n}_w = - (v/3 \sum N_i n_i) \bar{n}_w^2 dt \tag{11}$$

In order to integrate Eq. (11), we must substitute for  $n_x$ .

Case 1

Let us suppose that  $n_x = \bar{n}_w$ . Then

$$d\bar{n}_w = - (v/3 \sum N_i n_i) \bar{n}_w^2 dt \tag{12}$$

Integrating in the limits 0 to t, we obtain

$$1/\bar{n}_{wt} - 1/\bar{n}_{w0} = vt/3 \sum N_i n_i \tag{13}$$

Comparison with Results Obtained by the Monte Carlo Method

The dependence of  $\bar{n}_w$  on the number of computed cycles is apparent in Fig. 4 for the simulated case. For the simulated case we found from the graph in Fig. 2 the value  $K = v/3 \sum N_i n_i = 3.65 \times 10^{-8}$ , which makes it possible to evaluate the right-hand side of Eq. (13).



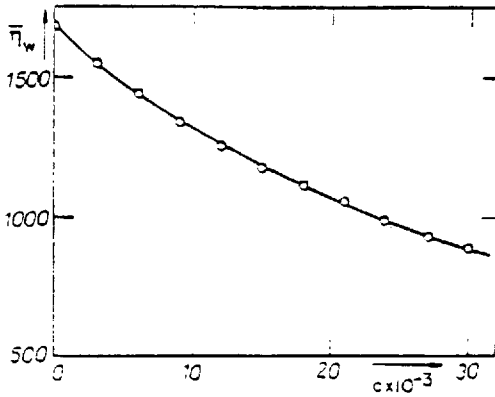


FIG. 4. Dependence of the weight-average polymerization degree  $\bar{n}_w$  on the number of calculation cycles.

The dependence of  $1/\bar{n}_{wt} - 1/\bar{n}_{w0}$  for values of  $\bar{n}_w$  calculated by the Monte Carlo method and the dependence of  $vt \cdot 3\sum N_i n_i$  on the number of cycles given by the computer is plotted for the simulated case in Fig. 5. This figure shows poor agreement between the values obtained by the Monte Carlo method and Eq. (13). For the dependence of  $\bar{n}_w$  on time during cross-linking without cyclization

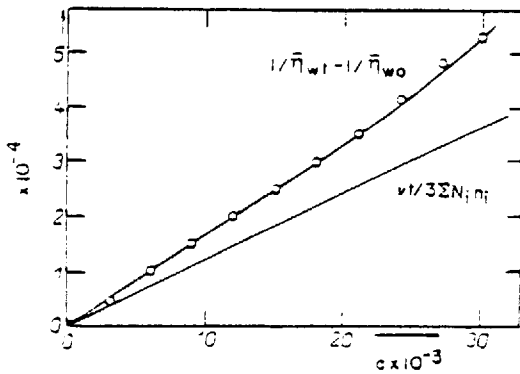


FIG. 5. Dependence of the difference  $1/\bar{n}_{wt} - 1/\bar{n}_{w0}$  and dependence of  $vt \cdot 3\sum N_i n_i$  on the number of calculation cycles.

we have shown in Ref. 2 that, in order to get better agreement with the results obtained by the Monte Carlo method, it is necessary to also express in the equation the change in the total number of molecules present in the system.

### Case 2

Let us suppose the dependence is in the form

$$\bar{n}_x^2 = \bar{n}_w^2 (\sum N_{i0}, \sum N_{it})^n$$

By substituting in Eq. (11) and integrating in the limits 0 to  $t$ , we obtain

$$\frac{1}{\bar{n}_{wt}} - \frac{1}{\bar{n}_{w0}} = \frac{1}{3\bar{n}_{n0}^{1-n}} \left[ \left( \frac{\bar{n}_{nt}}{\bar{n}_{n0}} \right)^{n-1} - 1 \right] \quad (14)$$

Comparison with results obtained for the simulated case by the Monte Carlo method shows that for Eq. (14) the most convenient value is  $n = -2, 3$ . Substituting this value for  $n$  in Eq. (14), we obtain

$$\frac{1}{\bar{n}_{wt}} - \frac{1}{\bar{n}_{w0}} = \frac{1}{3\bar{n}_{n0}} \left[ \left( \frac{\bar{n}_{nt}}{\bar{n}_{n0}} \right)^{-3/2} - 1 \right] \quad (15)$$

The difference  $1/\bar{n}_{wt} - 1/\bar{n}_{w0}$  for values calculated by the Monte Carlo method and the values of the right-hand side of Eq. (15) are plotted for the simulated case in relation to the number of cycles in Fig. 6.

For cross-linking it was shown [2] that for the simulated case it is possible to obtain excellent agreement between the equation and the results obtained by the Monte Carlo method if we assume that

$$\bar{n}_1 \bar{n}_2 = \bar{n}_w^2 (\sum N_{i0}, \sum N_{it})^{3/2}$$

Poorer agreement of Eq. (15) with the results obtained by the Monte Carlo method for chain scission, which can be noted in

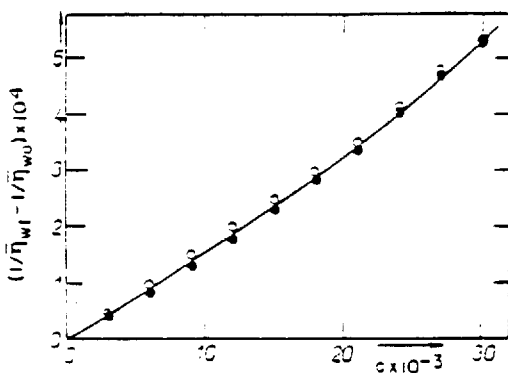


FIG. 6. Values of the difference  $1/\bar{n}_{wt} - 1/\bar{n}_{w0}$  (○) and values of the right-hand side of Eq. (15) (●) and dependence on the number of calculation cycles.

Fig. 6, is probably caused by  $\rho(1 - \rho)$ . The validity of Eq. (15) and the influence of  $\rho(1 - \rho)$  will be necessary to test for other forms of the distribution curve and for other values of  $\Sigma N_{10}$ .

### Number of Molecules of Polymerization Degree Higher Than the Randomly Chosen Value $n_i$ in Relation to Time

At random scission of polymers the degradation can be accompanied by dissolution of a part of the material with the lowest molecular weight. This case was studied by Mejzler [4] for two formerly published models of random degradation [5, 6]. Both of these models are limited by the condition of the starting molecular weight of the polymer and are, therefore, not general enough. We shall attempt to find relations valid for any form of distribution curve.

If we select with probability  $p_x = \frac{N_x n_x}{\Sigma N_i n_i}$  a molecule of degree of polymerization  $n_x = n_1 + n_2$  and split it at random into two molecules of polymerization degree  $n_1$  and  $n_2$ , then, for an arbitrarily

chosen degree of polymerization  $n_x > n_i$ , three different cases may arise:

$$\text{Case 1: } n_1 < n_i$$

$$n_2 < n_i$$

$$\text{Case 2: } n_1 < n_i$$

$$n_2 > n_i$$

$$\text{Case 3: } n_1 > n_i$$

$$n_2 > n_i$$

Note: The case  $n_1$  or  $n_2 = n_i$  shall be dealt with in the following section.

### Case 1

The result is a decrease in the number of molecules larger than  $n_i$ . This can happen only if  $n_x$  is from the interval  $n_i < n_x < 2n_i$ .

The probability that from the random scission of one molecule of degree of polymerization  $n_x$  from the range  $n_i < n_x < 2n_i$ , two molecules of degree of polymerization lower than  $n_i$  are formed is equal to

$$p_1 = (2n_i - n_x)/n_x$$

The probability that any molecule of degree of polymerization  $n_x$  from the interval  $n_i < n_x < 2n_i$  will be randomly selected and by random scission two molecules are formed of degree of polymerization lower than  $n_i$ , will be the sum  $p_x p_1$  from  $n_x = n_i$  up to  $2n_i$ .

We can thus write for the number of molecules from interval  $n_i$  to  $2n_i$ :

$$\left( \sum_{n_x=n_i}^{2n_i} N_x \right)_{t-\Delta t} - \left( \sum_{n_x=n_i}^{2n_i} N_x \right)_t = - \sum_{n_x=n_i}^{2n_i} \frac{N_x (2n_i - n_x)}{\sum N_i n_i}$$

where  $\Delta t$  is the time needed for a scission of one molecule in the system. Then

$$\partial \sum_{\substack{N_x \\ n_x = n_1}}^{2n_1} = K \left( \sum_{\substack{N_x n_x \\ n_x = n_1}}^{2n_1} - 2n_1 \sum_{\substack{N_x \\ n_x = n_1}}^{2n_1} \right) \partial t \quad (16)$$

where  $K$  is a constant from Eq. (3).

Both terms of the right-hand side of Eq. (16) are not only decreasing as a result of the transfer of molecules into the area below  $n_1$ , but they can even increase by the scission of molecules of degree of polymerization higher than  $2n_1$  as a consequence of Case 2 or 3.

### Case 2

In this case the total number of molecules larger than  $n_1$  is not influenced. Their dislocation in the range above  $n_1$  is altered, however, and the total mass of molecules of degree of polymerization higher than  $n_1$  is decreasing. The probability that by random scission of a molecule of degree of polymerization from the range  $n_1 < n_x < 2n_1$ , one molecule will be formed of degree of polymerization lower and another molecule of degree of polymerization higher than  $n_1$  is

$$p_2 = 2(n_x - n_1)/n_x$$

The probability that by random scission of a molecule of degree of polymerization  $n_x > 2n_1$ , one molecule will be formed of polymerization degree higher and another of polymerization degree lower than  $n_1$  is

$$p_3 = 2n_1/n_x$$

By scission of a molecule of degree of polymerization  $n_x > 2n_1$  a molecule of degree of polymerization  $n_1 < n_x$  can be formed and, at the same time, a molecule of polymerization degree  $n_2$  from the range  $(n_1, 2n_1)$ .

If by scission of a molecule of degree of polymerization  $n_x$  it is desired to form a molecule of degree of polymerization  $n_1 < n_x$  and simultaneously a molecule of degree of polymerization  $n_2$  from the range  $(n_1, 2n_1)$ , then  $n_x$  must be from the range  $(2n_1, 3n_1)$ , etc. By this procedure the whole range of values  $n_x$  disintegrates for a given  $n_1$  from the point of view of Case 2 into a number of subranges whose limits are formed by the whole even multiples of degree of polymerization  $n_1$ , i.e., the values  $kn_1$  and  $k = 1, 2, \dots$

For  $k > 2$  it holds that the probability of scission of a molecule of degree of polymerization  $n_x$  from the range  $((k-1)n_1, kn_1)$ , with the simultaneous formation of a molecule of degree of polymerization  $n_1 < n_x$  and a molecule of degree of polymerization  $n_2$  from the range  $((k-2)n_1, (k-1)n_1)$ , is equal to

$$p_k = 2(kn_1 - n_x)/n_x$$

Mass transfers resulting from Case 2 are, therefore, fairly complicated.

### Case 3

The result in this case is an increase of the total number of molecules larger than  $n_1$ . This can only happen when  $n_x > 2n_1$ .

The probability of formation of two molecules of degree of polymerization higher than  $n_1$  by random scission of a molecule of degree of polymerization  $n_x > 2n_1$  is

$$p_4 = (n_x - 2n_1)/n_x$$

The probability that a molecule of degree of polymerization  $n_x > 2n_1$  will be randomly selected, and by random scission two molecules formed of degree of polymerization higher than  $n_1$ , is the sum  $p_{x,2}$  from  $2n_1$  to  $n_{1 \max}$ , so that for a change of the number of molecules of degree of polymerization higher than  $n_1$  as a result of Case 3 we can write

$$\sum_{n_x=n_1}^{n_{1 \max}} N_x = K \left( \sum_{n_x=2n_1}^{n_{1 \max}} N_x n_x - 2n_1 \sum_{n_x=2n_1}^{n_{1 \max}} N_x \right) \quad (17)$$

where  $K$  is a constant from Eq. (3).

As a result of Case 3 there are again complicated mass transfers in the region above  $n_1$ .

Two molecules from the range  $\langle n_1, 2n_1 \rangle$  can be formed by scission of a molecule of degree of polymerization  $n_x$  as per Case 3 only when  $n_x$  is from the range  $\langle 2n_1, 4n_1 \rangle$ , etc. Two molecules of a degree of polymerization from the range  $\langle 2^{a-2}n_1, 2^{a-1}n_1 \rangle$  can, therefore, be formed only when  $n_x$  is from the range  $\langle 2^{a-1}n_1, 2^a n_1 \rangle$ , while  $a = 2, 3, \dots$ . The probability that by scission of a molecule of degree of polymerization  $n_x$  from the range  $\langle 2^{a-1}n_1, 2^a n_1 \rangle$ , two molecules will simultaneously be formed of degree of polymerization from the range  $\langle 2^{a-2}n_1, 2^{a-1}n_1 \rangle$  is equal to

$$p_{a2} = (n_x - 2^{a-1}n_1) / n_x$$

One molecule of degree of polymerization from the range  $\langle n_1, 2n_1 \rangle$  can be formed by scission of a molecule of polymerization degree  $n_x$  as per Case 3 only when  $n_x > 4n_1$ , so that one molecule of degree of polymerization from the range  $\langle 2^{a-2}n_1, 2^{a-1}n_1 \rangle$  can only be formed

when  $n_x > 2^a n_1$ . The probability that by random scission of one molecule of degree of polymerization  $n_x > 2^a n_1$ , one molecule will be formed from the range  $(2^{a-2} n_1, 2^{a-1} n_1)$  is equal to

$$p_{a1} = 2^{a-1} n_1 n_x$$

### Simultaneous Course of Cases 1 to 3

Case 2 does not influence the number of molecules of degree of polymerization higher than  $n_1$ . The change in the number of molecules higher than  $n_1$  is given, therefore, by the summation of the right-hand sides of Eqs. (16) and (17):

$$d \sum_{n_x=n_1}^{n_1 \max} N_x = K \left( \sum_{n_x=n_1}^{n_1 \max} N_x n_x - 2n_1 \sum_{n_x=n_1}^{n_1 \max} N_x \right) dt \quad (18)$$

where  $K$  is a constant from Eq. (3).

The determination of the dependence of  $\sum_{n_x=n_1}^{n_1 \max} N_x n_x$  on time in the

simultaneous course of Cases 1 to 3 is difficult. In order to solve Eq. (18) we shall assume the dependence in the form  $\sum_{n_x=n_1}^{n_1 \max} N_x n_x = C_x \exp(\lambda t)$ .

By solving Eq. (18) we obtain

$$\sum_{n_x=n_1}^{n_1 \max} N_x = \frac{K}{2Kn_1 + \lambda} \sum_{n_x=n_1}^{n_1 \max} N_x n_x - C \exp(-2Kn_1 t) \quad (19)$$

where  $\lambda$ ,  $C$ , and  $K$  are constants. Substituting  $\text{const} = K/(2Kn_1 + \lambda)$ , the equation becomes



$$\sum_{n_x = n_i}^{n_i \max} N_x = \text{const} \sum_{n_x = n_i}^{n_i \max} N_x n_x - C \exp(-2Kn_1 t)$$

### Comparison with Results Obtained by the Monte Carlo Method

Since Case 3 can only take place on the condition that  $n_x > 2n_1$ , it is possible to eliminate the incidence of Case 3 by a suitable choice of  $n_1$ . Cases 1 and 2 cannot be separated. The incidence of Case 2 is, however, largely limited to the highest degrees of polymerization in a given distribution.

For our model the starting distribution contained degrees of polymerization from the range (500,3700). The range  $n_1$ , for which no  $n_x > 2n_1$  exists, is therefore, for the distribution under scrutiny, the range  $n_1 > 1850$ .

For testing purposes we chose three different values of  $n_1$ .

1.  $n_1 = 3000$ . For the simulated course the region of highest degree of polymerization where the scission occurs mostly according to Case 1.
2.  $n_1 = 2000$ . Cases 1 and 2 occur, but not Case 3.
3.  $n_1 = 500$ . Cases 1, 2, and 3 occur simultaneously.

In Figs. 7 and 8 the course for the dependence of  $\Sigma N_1 n_1$  on time as obtained by the Monte Carlo method is plotted on a logarithmic scale. It shows that the application of the assumption  $\Sigma N_x n_x = C_x \exp(\lambda t)$ , which we used in the integration of Eq. (18), is correct because the dependence on time in the logarithmic scale is linear.

As long as Eq. (18) describes the real dependence of  $\Sigma N_x n_x$  on time, Eq. (19) should also be valid, since the assumption  $\Sigma N_x n_x = C_x \exp(\lambda t)$  holds good.

The right-hand side of Eq. (19) has two terms. We shall first attempt to plot the values of  $\Sigma N_x$ , obtained by the Monte Carlo method, against the values of  $\Sigma N_x n_x$ . These dependencies are

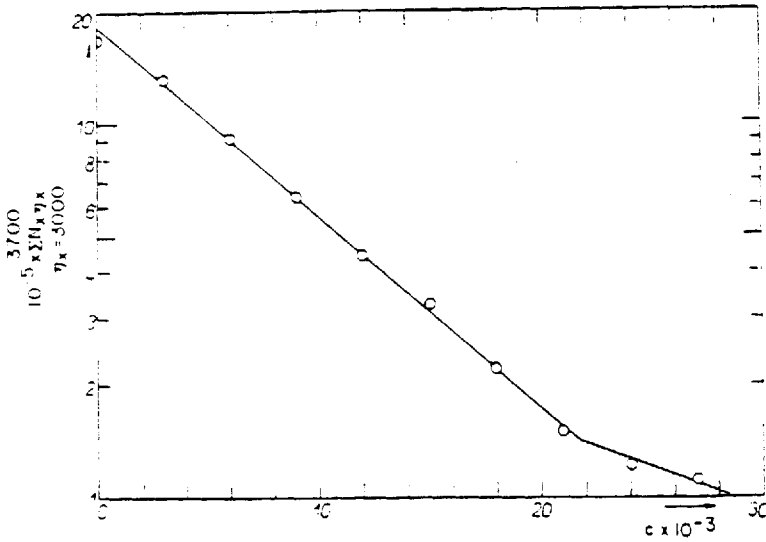


FIG. 7. Dependence  $\sum_{n_x=3000}^{3700} N_x n_x$  on the number of calculation cycles.

graphed in Figs. 9 to 11. The dependence in Fig. 9 is quite linear, the dispersion of points in Fig. 10 slightly greater, while the dependence in Fig. 11 is at first sight more complicated than the foregoing dependencies.

It follows from Figs. 9 and 10 that in the region where  $n_x > 2n_1$  does not exist, the influence of  $C \exp(-2Kn_1 t)$  in Eq. (19) is very small (i.e., C is near zero) for the simulated case so that the course in this simulated case can be expressed with a fair accuracy by

$$\sum_{n_x=n_1}^{n_i \max} N_x = \text{const} \sum_{n_x=n_1}^{n_i \max} N_x n_x \tag{20}$$

where the constant of proportionality is  $K, (2Kn_1 + \lambda)$ .

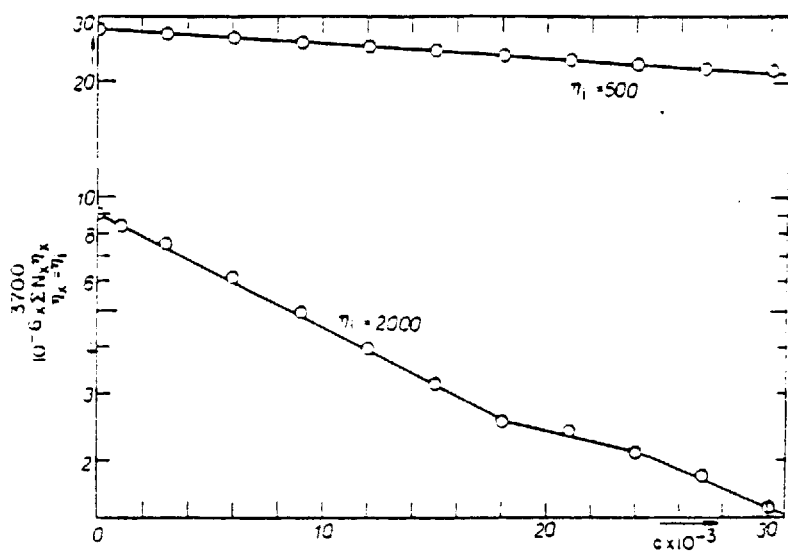


FIG. 8. Dependence  $\sum_{n_x=n_1}^{3700} N_x n_x$  on the number of cycles for  $n_1 = 500$  and 2000.

The value of the proportionality constant in Eq. (20), deduced from Fig. 9, is  $3.085 \times 10^{-4}$ ; that from Fig. 10 is  $4.025 \times 10^{-4}$ .

Since  $\text{const} = K/(2Kn_1 - \lambda)$ , then  $\lambda = K(1, \text{const} - 2n_1)$ . As noted before, the dependence of  $\sum N_x n_x$  on  $\sum N_x n_x$  for the simulated case is linear in the range  $n_x > 2n_1$ , hence

$$1, \text{const} \doteq (\sum_{n_x=n_1} N_x n_x / \sum_{n_x=0} N_x) = \bar{n}_{n_1 0}$$

Then

$$\lambda \doteq K(\bar{n}_{n_1 0} - 2n_1) \quad (21)$$

which makes it possible to obtain the value  $\lambda$  for the simulated case in a given area. The dependence of values of  $\lambda$  on  $n_1$  is plotted for

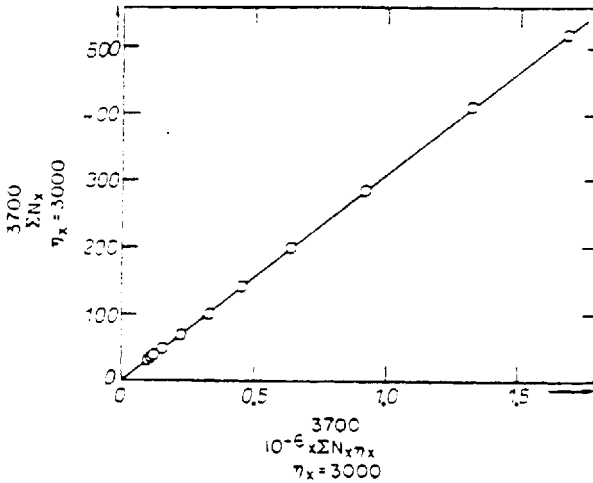


FIG. 9. Dependence of values  $\sum_{n_x=3000}^{3700} N_x$  on values  $\sum_{n_x=3000}^{3700} N_x n_x$

this simulated case in Fig. 12. As it is apparent from the figure, we can express this dependence for the model case by a linear equation

$$\lambda = k_\lambda n_i + q_\lambda \tag{22}$$

where  $k_\lambda$  and  $q_\lambda$  are constants. After evaluation of the constants we obtain for the simulated case

$$\lambda = -(4.7 \times 10^{-9} n_i) + (4 \times 10^{-5}) \tag{23}$$

Since for the simulated case Eq. (21) is valid, it must also hold that

$$\bar{n}_{nio} = k_n n_i + q_n \tag{24}$$

where  $k_n$  and  $q_n$  are constants.

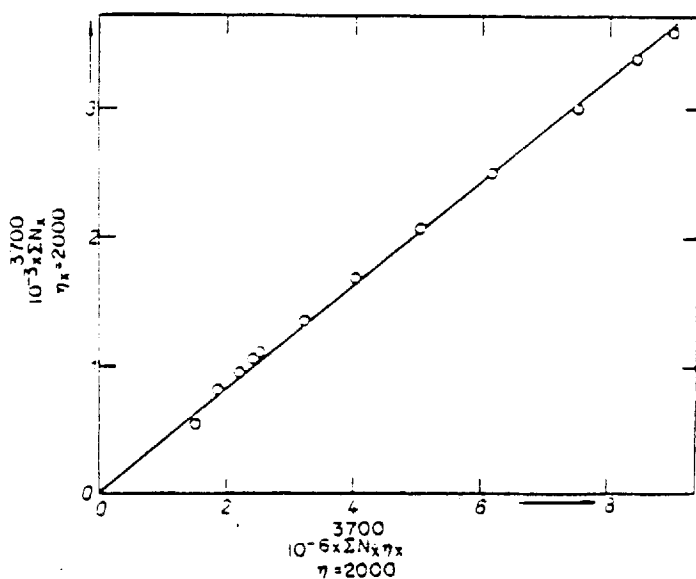


FIG. 10. Dependence of values  $\sum_{n_x=2000}^{3700} N_x$  on values  $\sum_{n_x=2000}^{3700} N_x n_x$

Substituting Eq. (24) into Eq. (21) and comparing with Eq. (22), we obtain

$$k_n = k_\lambda K - 2$$

$$q_n = q_\lambda K$$

Thus by substituting values from Eq. (23) we obtain for the simulated case  $k_n = 0.712$  and  $q_n = 1096$ .

The dependence of  $\bar{n}_{n10}$  on  $n_1$  is plotted in Fig. 13. We note in this figure that the dependence for the simulated case is really linear. The values of constants deduced from Fig. 13 are  $k_n = 0.72$

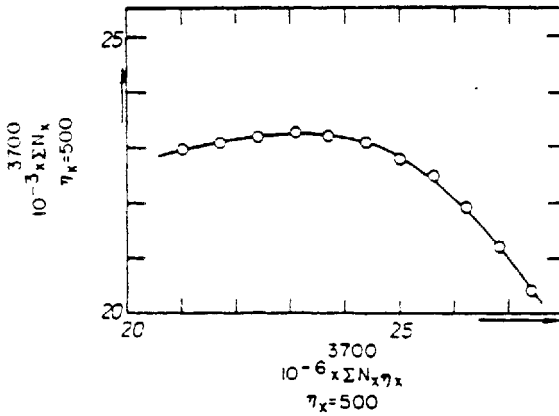


FIG. 11. Dependence of values  $\sum_{n_x=500}^{3700} N_x$  on values  $\sum_{n_x=500}^{3700} N_x n_x$

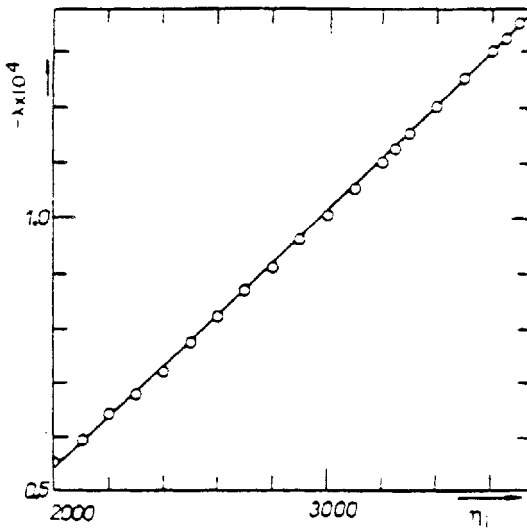


FIG. 12. Dependence of values of constant  $\lambda$  on polymerization degree  $n_1$ .

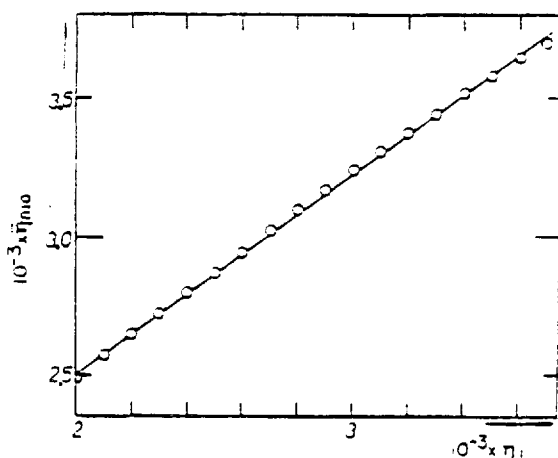


FIG. 13. Dependence of the number-average polymerization degree of molecules bigger than  $n_i$  (indicated by  $\bar{n}_{nio}$ ) on polymerization degree  $n_i$ .

and  $q_{\bar{n}} = 1060$ , which is in good agreement with the values obtained by Eq. (23).

Since the dependence of  $\bar{n}_{nio}$  on  $n_i$  is given by the shape of the distribution curve, so also is the validity of Eq. (24) and, consequently, of Eq. (22) limited to some special cases, e.g., to the simulated case.

On the basis of only one simulated case it is difficult to decide the range in which Eq. (20) is valid for any arbitrary distribution, i.e., whether the value of the constant  $C$  in Eq. (19) depends solely on the occurrence of Case 3 or whether it depends also on the form of the distribution curve.

Let us go now to Fig. 11. The dependence of  $\Sigma N_x$  on  $\Sigma N_x n_x$  is more complicated for  $n_i = 500$  than the dependence in Figs. 9 and 10.

In Eq. (19) we shall therefore also investigate the influence of  $C \exp(-2Kn_1 t)$ . For the simulated case the dependence of  $\Sigma N_x$  on  $\Sigma N_x n_x$  and on time for  $n_i = 500$  is expressed by Eq. (19) which, after evaluation of the constants, has the form

$$\sum_{n_x=500}^{3700} N_x = 1.344 \times 10^{-3} \sum_{n_x=500}^{3700} N_x n_x - 1.64 \times 10^4 \exp(-3.549 \times 10^{-5}t) \quad (25)$$

Equation (25) expresses the dependence of  $\Sigma N_x$  on  $\Sigma N_x n_x$  and on time with an accuracy greater than  $\pm 1\%$  as compared with values obtained by the Monte Carlo method for  $n_1 = 500$ .

For the tested course both the assumption  $\Sigma N_x n_x = C_x \exp(\lambda t)$  and Eq. (19) in the whole range of degrees of polymerization are valid. Also valid is Eq. (18), whose validity we endeavored to test. It will also be necessary to test the validity of Eqs. (18) and (19) for other shapes of distribution curves and with other numbers of molecules present in the system.

Since  $\Sigma N_x n_x = C_x \exp(\lambda t)$  holds good and so does Eq. (19), we can adjust Eq. (19) and use the relation  $\Sigma N_x n_x = C_x \exp(\lambda t)$  to obtain

$$\frac{1}{\bar{n}_{nio}} - \frac{1}{\bar{n}_{nit}} = \frac{C}{C_x} \{1 - \exp[-(2Kn_1 - \lambda)t]\} \quad (26)$$

After further adjustment of Eq. (26) we obtain

$$\bar{n}_{nit} = \bar{n}_{nio} [1 - C_1(1 - e^{C_2 t})] \quad (27)$$

where  $C_1 = \bar{n}_{nio} C / C_x$  and  $C_2 = -(2Kn_1 + \lambda)$ . Equation (27) describes the dependence of a number-average degree of polymerization of molecules with a degree of polymerization higher than the arbitrarily chosen value  $n_1$  on time as long as Eq. (19) and the relation

$\Sigma N_x n_x = C_x \exp(\lambda t)$  is valid.

Because a region can exist where  $C \neq 0$  and, consequently, also  $C_1 \neq 0$  (for the simulated case the region  $n_1 \geq 2000$ ), there can also exist a region of higher molecular weights, for which the number-average degree of polymerization is constant irrespective of degradation time by random chain scission.



Dependence of the Number of Molecules  $N_i$  of  
Polymerization Degree  $n_i$  on Degradation Time

In the foregoing section we did not deal with the case where  $n_1$  or  $n_2 = n_i$ . This case is, nevertheless, important for expressing the dependence of the number of molecules of degree of polymerization  $n_i$  on time.

In Ref. 1 we deduced the dependence of the number of molecules of degree of polymerization  $n_i$  on time in the form of Eq. (1) as

$$dN_i/dt = -k'v p_i \quad (1)$$

where  $k'$  is a constant and  $v$  is the velocity of the elementary steps. For random chain scission there exists no region in which the starting distribution of molecular masses is sufficiently narrow. Equation (2) then holds good exactly only for the highest degree of polymerization. For all other degrees of polymerization we have to assume that the probability  $p_i$  in Eq. (1) is composed of the number  $p_{i-}$ , i.e., the probability that a molecule of degree of polymerization  $n_i$  will be randomly selected for scission, and the probability  $p_{i+}$ , i.e., the probability that by random scission of some molecule larger than  $n_i$  a molecule of degree of polymerization  $n_i$  will be formed. Hence Eq. (1) must be written for random chain scission as

$$dN_i/dt = k'v (p_{i-} - p_{i+}) \quad (28)$$

The probability  $p_{i-}$ , i.e., the probability that a molecule of polymerization degree  $n_i$  will be randomly selected for scission, is

$$p_{i-} = N_i n_i / \sum N_i n_i$$

The probability  $p_{i+}$ , i.e., the probability that by random scission of a randomly selected molecule of degree of polymerization  $n_j > n_i$  a molecule will be formed of degree of polymerization  $n_i$ , is a probability composed of two parts:

1. The probability that for scission a molecule of degree of polymerization  $n_j$  will be selected is equal to  $p_j = N_j n_j / \sum N_i n_i$ .
2. The probability that by random scission of a molecule of degree of polymerization  $n_j > n_i$ , a molecule of degree of polymerization  $n_i$  will be formed is equal to  $p_{ji} = 2/n_j$ .

The probability  $p_{i+}$  is then

$$p_{i+} = \sum_{n_j=n_i+1}^{n_i \max} p_j p_{ji} = 2 \sum_{n_j=n_i+1}^{n_i \max} N_j \sum_{n_i} N_i n_i$$

Substituting into Eq. (28), we obtain

$$dN_i/dt = k'K \left( -N_i n_i + 2 \sum_{n_j=n_i+1}^{n_i \max} N_j \right) \quad (29)$$

where  $K$  is a constant from Eq. (3).

In order to integrate Eq. (29) we must substitute for  $\sum N_j$ . The number of molecules of degree of polymerization higher than the arbitrarily chosen value was dealt with in the foregoing section. It suffices then to express  $\sum N_x$  in Eq. (19) by means of assumption  $\sum N_x n_x = C_x \exp(\lambda t)$  as a function of time, to substitute into Eq. (29), and to adjust to obtain

$$dN_i/dt + C_1 N_i = C_2 \exp(\lambda t) + C_3 \exp(-2Kn_i t) \quad (30)$$

where

$$C_1 = k'Kn_i$$

$$C_2 = 2k'K^2 C_X / (2Kn_i + \lambda)$$

$$C_3 = 2k'KC$$

$C$  is a constant from Eq. (19).

By solving Eq. (30) and adjusting, we obtain

$$N_i = \text{const}' \sum_{n_j=n_i+1}^{n_i \text{ max}} N_j n_j + C' \exp(-2Kn_i t) \quad (31)$$

where

$$\text{const}' = \frac{2k'K^2}{(2Kn_i + \lambda)(k'Kn_i + \lambda)}$$

$$C' = \frac{2k'C}{n_i(k' - 2)}$$

As can be seen, Eq. (31) is in agreement, with the exception of the constant values, with Eq. (19). It is necessary, however, to point out that both Eq. (19) and Eq. (31) were deduced on the assumption that  $\sum_x N_x n_x = C_X \exp(\lambda t)$ , which is valid for the simulated case but whose general validity has not been proved.

#### Comparison with Relations Published Thus Far

Simha [7], Tobolsky [8], and Conley [9] have, in their equations for the change in the number of molecules of a given degree of

polymerization in relation to time. only one constant  $k$  instead of two constants ( $k'$ ,  $K$ ) introduced in Eq. (29), and instead of  $n_i$  they have  $n_i - 1$  so that their equations, expressed by the symbols used in this paper, have the form

$$dN_i/dt = k \left[ -(n_i - 1)N_i + 2 \sum_{n_j=n_i+1}^{n_i \max} N_j \right]$$

The difference from our Eq. (29) is thus insignificant.

Saito [10] published an integro-differential equation which, after transcription to the symbols used in this paper and after replacing the integral by summation, has the form:

$$dN_i/dt = -N_i n_i + 2 \sum_{n_j=n_i+1}^{n_i \max} N_j$$

Compared to our Eq. (29), it assumes a value for constant  $k'K$  of 1.

#### Comparison with Results Obtained by the Monte Carlo Method

Estimation of Value of Constant  $k'$  in Eq. (1).  
As already noted, Eq. (2) is valid for random chain scission only for the highest degree of polymerization in a given distribution. The highest degree of polymerization in this simulated case is  $n_i = 3700$ ;  $N_{3700}$  is, however, too small for this case (less than 100). For the dependence of  $N_{3700}$  on time, one can expect a considerable dispersion of points.

Equation (2) should, however, be approximately valid even for a wider region of the highest degree of polymerization. The region of the highest degree of polymerization for this simulated case is  $n_i \geq 3000$ . We can thus transcribe Eq. (2) into the form

$$\ln \left( \frac{\sum_{n_i=3000}^{3700} N_{i0}}{\sum_{n_i=3000}^{3700} N_i} \right) = k'n_i t \quad (32)$$

Plotting the dependence on a logarithmic scale derived from the first part of the dependencies in Fig. 14, the value of  $k\bar{v}n_i = 1.184 \times 10^{-4}$ .

Substituting for  $n_i$  a usual arithmetical mean, i.e., the value 3350, we obtain  $k\bar{v} = 3.53 \times 10^{-8}$ . Since  $k\bar{v} = k'K$ , where  $k'$  is a constant in Eq. (1) and  $K$  a constant in Eq. (3), and since the value of constant  $K$  in Eq. (3) as deduced for the simulated case in Fig. 2 is  $K \approx 3.65 \times 10^{-3}$ , it is possible to estimate that the value of the constant  $k'$  for random chain scission is equal to 1, which is in agreement with the assumption that one computed cycle means the selection and scission of one molecule.

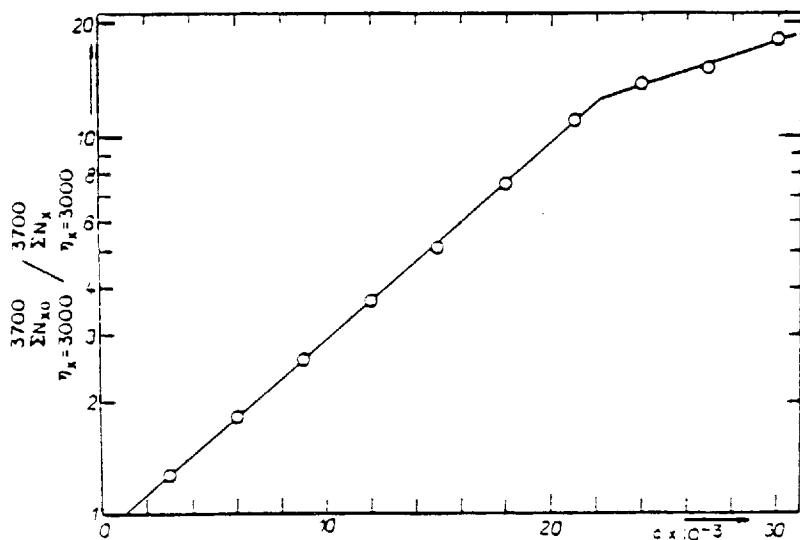


FIG. 14. Dependence of  $\ln \left( \frac{\sum_{n_i=3000}^{3700} N_{i0}}{\sum_{n_i=3000} N_i} \right)$  on the number of cycles.

It can be further noted in Fig. 14 that in the region of the highest molecular weights, the dependence of  $N_i$  on time is really approximately expressed by Eq. (2). Further, there is noticeable break in the dependence on time which we have already observed in time dependence of  $\sum N_{i0}$  in Figs. 7 and 3.

Estimation of the Values of Constants in Eq. (31).  
Constant  $C'$  in Eq. (31) is equal, as pointed out already, to

$$C' = \frac{2k'C}{n_1(k' - 2)}$$

Since  $k' = 1$ ,

$$C' = -2C n_1$$

where  $C$  is a constant from Eq. (19). For the model case it was found in the preceding section that the value of constant  $C$  is usually near 0, so that  $C \exp(-2Kn_1t)$  in Eq. (19) can, in a wider region, be neglected. Only for a region of lower degree of polymerization is  $C$  great enough to make the influence of  $C \exp(-2kn_1t)$  in Eq. (19) noticeable.

We see now that  $C' = -2C n_1$ , while the value  $n_1$  is of the order of  $10^3$ . It will most likely be possible to neglect the influence of  $C' \exp(-2Kn_1t)$  in the whole region of the degrees of polymerization of the simulated case.

Constant  $const'$  in Eq. (31) is equal to

$$const' = \frac{2k'K^2}{(2Kn_1 - \lambda)(k'Kn_1 + \lambda)}$$

Since  $k' = 1$ ,

$$const' = \frac{2K^2}{(2Kn_1 - \lambda)(Kn_1 + \lambda)}$$

and it may thus be expected that the value of the constant  $const'$  in Eq. (31) will greatly depend on the value  $\lambda$  in the relation  $\Sigma N_j n_j = C_x \exp(\lambda t)$ . In Figs. 7 and 8 it is apparent that both the value of  $C_x$  and the value of  $\lambda$  are not constant in the whole interval of times tested, but that they change, mostly discontinuously.

It is therefore to be expected that there will be discontinuous changes in the values of the constant  $\text{const}'$  also.

Verification of the Estimate of Values of Constant  $C'$  and Constant  $\lambda'$ . Since for the simulated case we used a distribution in a tabular form, where the values of polymerization degree  $n_i$  were changing by  $\Delta n_i = 50$ , Eq. (31) can have the form

$$N_i = \text{const}' \sum_{n_j = n_i - 50}^{n_i} N_j n_j - C' \exp(-2Kn_i t) \quad (33)$$

1. As far as  $C' \exp(-2Kn_i t)$  in Eq. (33) can be neglected, the dependence of  $N_i$  on  $\sum N_j n_j$  must be linear.
2. As far as  $\text{const}'$  is strongly dependent on  $\lambda$ , we may expect sudden changes in the dependence of  $N_i$  on  $\sum N_j n_j$ .

In order to verify 1 and 2, we shall choose one example from each region as we did in the preceding section. We shall again assume the lowest values for  $n_j$ : A,  $n_j = 3000$ ; B,  $n_j = 2000$ ; and C,  $n_j = 500$ . We shall examine the values: A,  $N_{2950}$ ; B,  $N_{1950}$ ; and C,  $N_{450}$ .

If we plot the values found by the Monte Carlo method for  $N_i$  against the values of  $\sum N_j n_j$  (see Figs. 15 through 17), we see that both Assumptions 1 and 2 for constants  $C'$  and  $\text{const}'$  are fulfilled. Since Assumptions 1 and 2 are fulfilled, we can transcribe Eq. (33) to

$$N_i = \text{const}' \sum_{n_j = n_i - 50}^{n_i} N_j n_j = \text{const}' C'_x \exp(\lambda' t)$$

and, further adjustment,

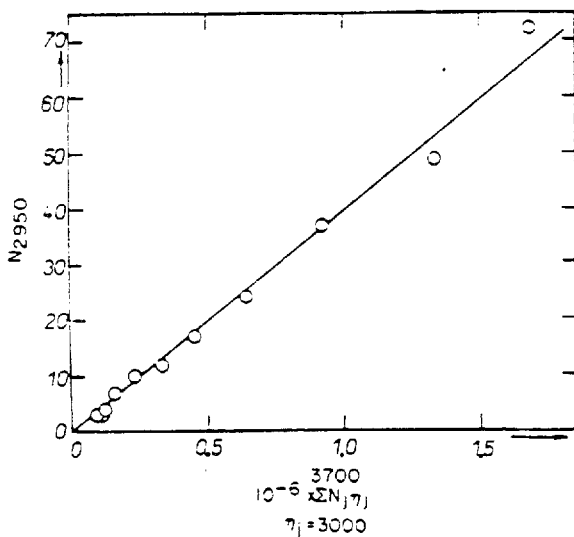


FIG. 15. Dependence of  $N_{2950}$  on  $\sum_{j=3000}^{3700} N_j n_j$ .

$$\ln(N_i n_i) = \lambda' t - C^+ \tag{34}$$

where  $C^+ = \ln(\text{const}' C' n_i)$ .

The Dependence of  $N_i$  on Time. It was shown [2] that it is convenient to plot the values of  $N_i n_i$  ( $N_i n_i$  is directly related to the weight fraction of a polymer of degree of polymerization  $n_i$ ). The dependence of  $\ln(N_i n_i)$  on time could then be expressed for a random chain scission by Eq. (34), while we can expect that the values of both  $C^+$  and  $\lambda'$  will change in some regions.

The dependence of  $\ln(N_i n_i)$  on time for the simulated case is plotted in Figs. 18 and 19. Figure 18 shows the dependence for a



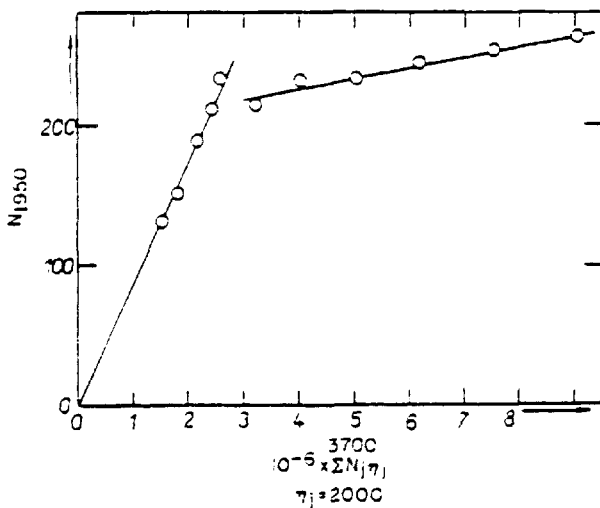


FIG. 16. Dependence of  $N_{1950}$  on  $\sum_{n_j=2000}^{3700} N_j n_j$ .

degree of polymerization in the range from 250 to 750; Fig. 19 shows the same dependence for a degree of polymerization from 1000 to 3100. It is apparent in these figures that there exist regions in which the dependence of  $\ln(N_1 n_1)$  on the number of cycles is linear, as well as regions where both  $C^+$  and  $\lambda'$  change their values. From these figures it can be further noted that changes of  $C^+$  and  $\lambda'$  for the same degree of polymerization  $n_1$  can occur several times during degradation.

In Figs. 20 and 21 there are only regions for which the dependence of  $\ln(N_1 n_1)$  on time is linear. From these linear regions we can determine the values of the constant  $\lambda'$ .

All values of the constant  $\lambda'$  determined from Figs. 20 and 21 for the simulated case are plotted on  $n_1$  in Fig. 22. It is apparent from Fig. 22 that the values of  $\lambda'$  in this simulated case can be joined by lines (indicated by numbers 1 to 6), so that the dependence of  $\lambda'$  on the degree of polymerization probably has the form

$$\lambda' = k' n_1 - q'$$

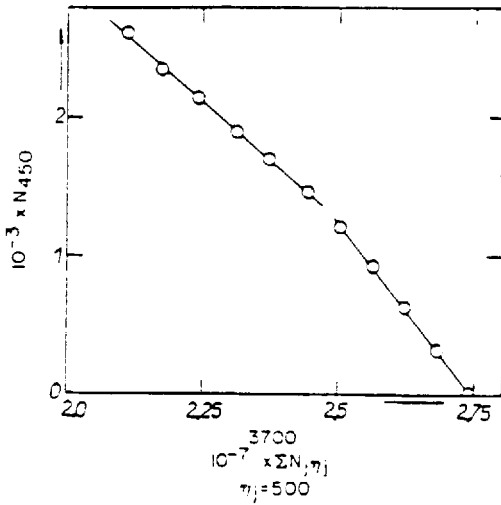


FIG. 17. Dependence of  $N_{450}$  on  $\sum_{n_j=500}^{3700} N_j n_j$ .

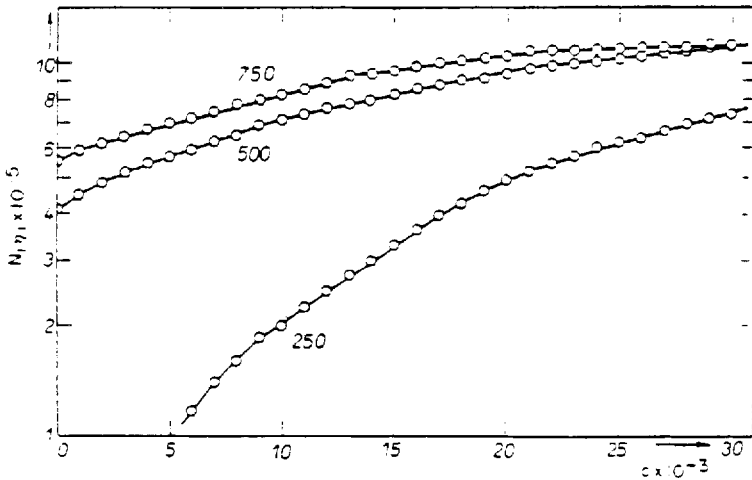


FIG. 18. Dependence of  $\ln(N_i n_i)$  on the number of calculation cycles.

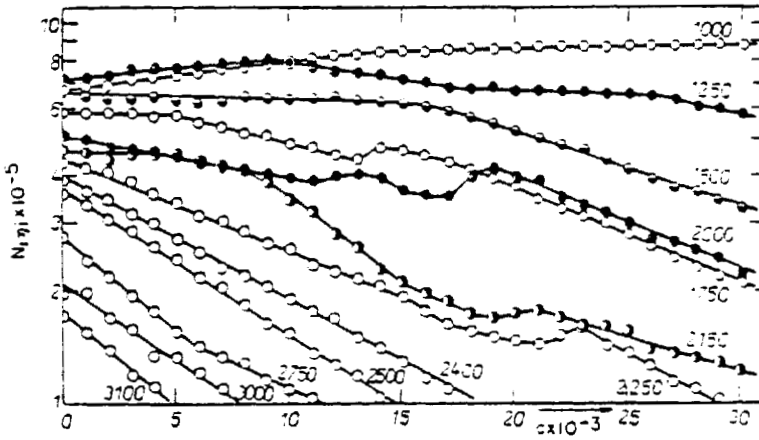


FIG. 19. Dependence of  $\ln(N_1 n_1)$  on the number of calculation cycles.

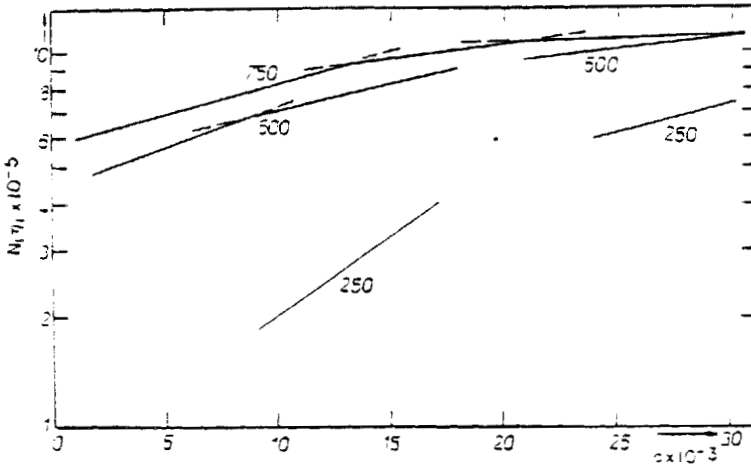


FIG. 20. Dependence of  $\ln(N_1 n_1)$  on the number of calculation cycles.

The values of  $k'_\lambda$  and  $q'_\lambda$  for all six lines in Fig. 22 are given in Table 1.

The values of the quotients resulting from dividing  $k'_\lambda$  and  $q'_\lambda$

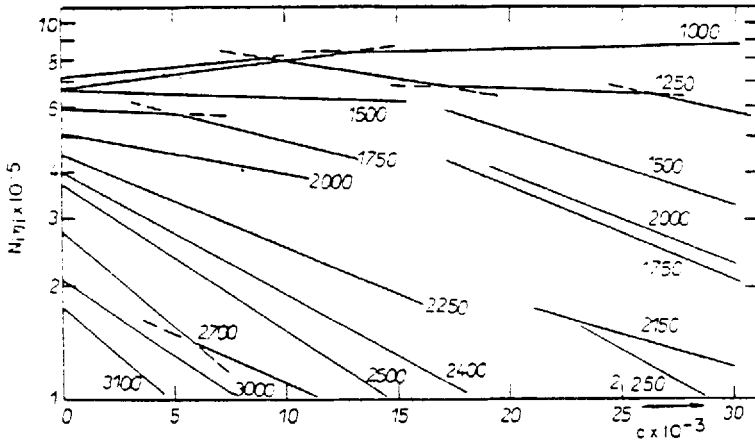


FIG. 21. Dependence of  $\ln(N_i n_i)$  on the number of calculation cycles.

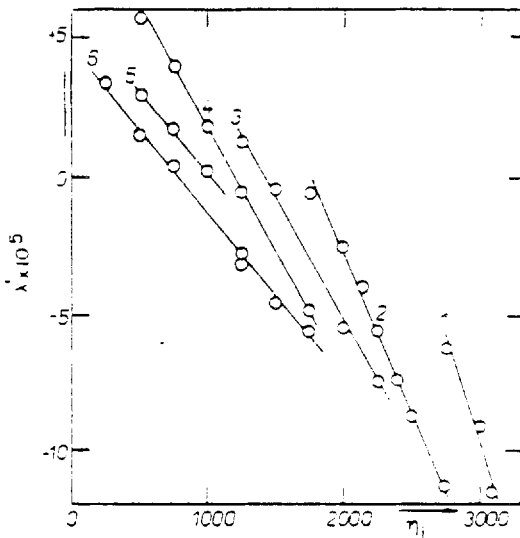


FIG. 22. Dependence of values of constant  $\lambda'$  on polymerization degree  $n_i$ .

TABLE 1. Values of  $k'_\lambda$  and  $q'_\lambda$  for the Model Case

Number	$k'_\lambda \times 10^4$	$q'_\lambda \times 10^3$	$k'_\lambda/k_\lambda$	$q'_\lambda/q_\lambda$
1	-15.5	37.1	3.3	9.3
2	-11.6	20.4	2.5	5.1
3	-9.1	12.9	1.9	3.2
4	-9.1	11.1	1.9	2.8
5	-5.7	6.0	1.2	1.5
6	-6.1	4.9	1.3	1.2

by the values of  $k_\lambda$  and  $q_\lambda$  from Eq. (23) shows that we cannot exclude the values of  $N$  in Eq. (34), for they are in some way "quantized" as a result of the final number of molecules in the system.

### CONCLUSION

A detailed study of the course of random chain scission simulated by the Monte Carlo method has shown some hitherto unknown characteristics of the whole process and has made it possible to test the validity of some equations.

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