

## Effect of Four Neighboring Groups in Kinetics of Polymer Reactions

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### Synopsis

Assuming that the rate of reaction of an unreacted site in polymer reactions depends upon whether the two immediate neighboring sites on either side (four neighboring sites in all) are reacted or unreacted, differential equations were obtained giving the rate of change of  $N_n$  with time (where  $N_n$  is the number of sequences of  $n$  consecutive unreacted sites with a reacted site at both ends) and solved numerically with the help of a computer.  $N_n$  was obtained as a function of time and also as a function of  $M$ , the total number of unreacted sites. Three sets of values of  $k$  were tried, one of these relating to autocatalytic reaction, one to autoretarding reaction, and one to the null case in which the reaction rates do not depend upon the neighbors.

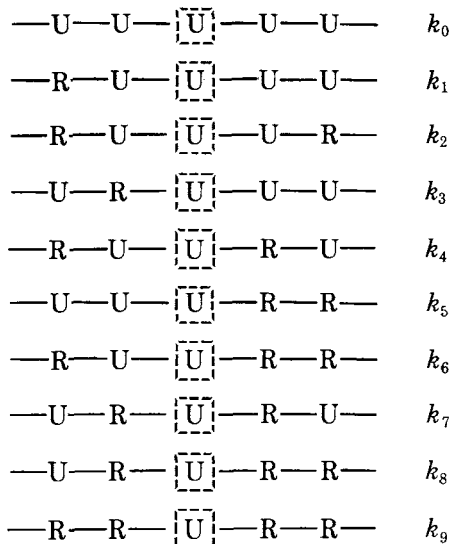
### INTRODUCTION

The reactivity of a site in relation to high polymer reactions can depend upon whether the neighboring sites are reacted or unreacted. Alfrey and Lloyd<sup>1</sup> derived recurrence relationships for runs of various lengths of unreacted sites and obtained numerical solutions for a truncated set of resulting differential equations. Arends<sup>2</sup> derived similar results based on probabilistic considerations, and obtained a theoretical solution for the number of sequences of a length of unreacted sites. Keller<sup>3</sup> found, based on certain assumptions, an expression for the fraction unreacted as a function of time. McQuarrie et al.<sup>4</sup> derived an exact solution. Keller<sup>5</sup> verified using a different method the results of Arends<sup>2</sup> and Keller.<sup>3</sup> Whereas the earlier studies related to irreversible reactions, Silberberg and Simha,<sup>6</sup> who considered reversible reactions with rates depending upon the state of its nearest neighbors, developed a procedure for getting the rate equations and obtained their solution under certain assumptions. In the present paper, the method of Alfrey and Lloyd<sup>1</sup> has been extended to the case where reactivity of a site is assumed to depend upon four neighboring sites, two on either side, but the study is restricted to irreversible reactions.

### OBTAINING THE DIFFERENTIAL EQUATIONS

In this case, the reaction rate can take ten different values. The extreme cases are when an unreacted site is flanked by (a) two unreacted sites on either side and (b) by two reacted sites on either side. Let the reaction rates in

these cases be  $k_0$  and  $k_9$ , respectively and those in the intermediate cases,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ ,  $k_6$ ,  $k_7$ , and  $k_8$ . The full scheme is indicated below, U denoting an unreacted site and R a reacted site.



Let  $N_n$  denote the number of sequences of  $n$  consecutive unreacted sites flanked by a reacted site at both ends. Such a sequence can be of three types: (a) flanked by a reacted site on either side, (b) flanked by a reacted site on one side and an unreacted site on the other side, and (c) flanked by an unreacted site on both sides. Let the number of sequences of types (a), (b), and (c) be  $N_{n,1}$ ,  $N_{n,2}$ ,  $N_{n,3}$ , respectively. For instance,  $N_1$ , which is the number of sequences of one unreacted site flanked by a reacted site at both ends, consists of  $N_{1,1}$  sequences of the type —R—R—U—R—R—,  $N_{1,2}$  sequences of the type —R—R—U—R—U— or —U—R—U—R—R—, and  $N_{1,3}$  sequences of the type —U—R—U—R—U—,  $N_1$  being equal to  $N_{1,1} + N_{1,2} + N_{1,3}$ .

The following differential equations are easy to derive:

$$dN_{1,1}/dt = -k_9N_{1,1} + 2k_6N_{2,1} + k_4N_{2,2}$$

$$\begin{aligned}
 dN_{1,2}/dt = & -k_8N_{1,2} + k_6N_{2,2} + 2k_4N_{2,3} + k_2(2N_{3,1} \\
 & + N_{3,2}) + 2k_1 \sum_{n=1}^{\infty} N_{n+3,1} + k_1 \sum_{n=1}^{\infty} N_{n+3,2}
 \end{aligned}$$

$$dN_{1,3}/dt = -k_7N_{1,3} + k_2(N_{3,2} + 2N_{3,3}) + k_1 \sum_{n=1}^{\infty} N_{n+3,2} + 2k_1 \sum_{n=1}^{\infty} N_{n+3,3}$$

$$dN_{2,1}/dt = -2k_6N_{2,1} + 2k_5N_{3,1} + k_3N_{3,2}$$

$$\begin{aligned}
 dN_{2,2}/dt = & -(k_6 + k_4)N_{2,2} + k_5N_{3,2} + 2k_3N_{3,3} + k_1(2N_{4,1} + N_{4,2}) \\
 & + 2k_0 \sum_{n=1}^{\infty} N_{n+4,1} + k_0 \sum_{n=1}^{\infty} N_{n+4,2}
 \end{aligned}$$

$$dN_{2,3}/dt = -2k_4N_{2,3} + k_1(N_{4,2} + 2N_{4,3}) + k_0 \sum_{n=1}^{\infty} N_{n+4,2} + 2k_0 \sum_{n=1}^{\infty} N_{n+4,3}$$

$$\begin{aligned}
dN_{3,1}/dt &= -(2k_5 + k_2)N_{3,1} + 2k_5N_{4,1} + k_3N_{4,2} \\
dN_{3,2}/dt &= -(k_5 + k_3 + k_2)N_{3,2} + k_5N_{4,2} + 2k_3N_{4,3} + k_1(2N_{5,1} + N_{5,2}) \\
&\quad + 2k_0 \sum_{n=1}^{\infty} N_{n+5,1} + k_0 \sum_{n=1}^{\infty} N_{n+5,2} \\
dN_{3,3}/dt &= -(2k_3 + k_2)N_{3,3} + k_1(N_{5,2} + 2N_{5,3}) \\
&\quad + k_0 \sum_{n=1}^{\infty} N_{n+5,2} + 2k_0 \sum_{n=1}^{\infty} N_{n+5,3} \\
dN_{4,1}/dt &= -(2k_5 + 2k_1)N_{4,1} + 2k_5N_{5,1} + k_3N_{5,2} \\
dN_{4,2}/dt &= -(k_5 + k_3 + 2k_1)N_{4,2} + k_5N_{5,2} + 2k_3N_{5,3} + k_1(2N_{6,1} + N_{6,2}) \\
&\quad + 2k_0 \sum_{n=1}^{\infty} N_{n+6,1} + k_0 \sum_{n=1}^{\infty} N_{n+6,2} \\
dN_{4,3}/dt &= -(2k_3 + 2k_1)N_{4,3} + k_1(N_{6,2} + 2N_{6,3}) \\
&\quad + k_0 \sum_{n=1}^{\infty} N_{n+6,2} + 2k_0 \sum_{n=1}^{\infty} N_{n+6,3} \\
dN_{n,1}/dt &= -\{2k_5 + 2k_1 + (n-4)k_0\}N_{n,1} \\
&\quad + 2k_5N_{n+1,1} + k_3N_{n+1,2} \quad \text{for } n \geq 5 \\
dN_{n,2}/dt &= -\{k_5 + k_3 + 2k_1 + (n-4)k_0\}N_{n,2} + k_5N_{n+1,2} + 2k_3N_{n+1,3} \\
&\quad + 2k_1N_{n+2,1} + k_1N_{n+2,2} + 2k_0 \sum_{i=n}^{\infty} N_{i+3,1} + k_0 \sum_{i=n}^{\infty} N_{i+3,2} \quad \text{for } n \geq 5 \\
dN_{n,3}/dt &= -\{2k_3 + 2k_1 + (n-4)k_0\}N_{n,3} + k_1N_{n+2,2} \\
&\quad + 2k_1N_{n+2,3} + k_0 \sum_{i=n}^{\infty} N_{i+3,2} + 2k_0 \sum_{i=n}^{\infty} N_{i+3,3} \quad \text{for } n \geq 5 \quad (1)
\end{aligned}$$

To illustrate the method of getting these equations, we have only to consider the first of these equations.  $N_{1,1}$  is the number of sequences —R—R—U—R—R—. They can arise out of sequences —R—R—U—U—R—R— when either of the unreacted sites react and from sequences —R—R—U—U—R—U— when the fourth site from the left reacts. Decrements in  $N_{1,1}$  can arise only when the unreacted site of a sequence —R—R—U—R—R— reacts. Taking these three factors and the corresponding reaction rates, we get

$$dN_{1,1}/dt = -k_9N_{1,1} + 2k_6N_{2,1} + k_4N_{2,2}$$

In case, the total number of sites reacted and unreacted, to be denoted by  $S$ , is known, set (1) of equations can be reduced to a closed set which can be solved by following the method of Silberberg and Simha<sup>6</sup> for the irreversible case. In case  $S$  is not known, set (1) cannot be solved without additional equations and assumptions. For such a case, seven additional equations are obtained from set (1) for  $dL_j/dt$ ,  $dM_j/dt$ , and  $dM/dt$ , where  $L_j = \sum_{n=1}^{\infty} N_{n,j}$ ,  $M_j = \sum_{n=1}^{\infty} nN_{n,j}$ , and  $M = \sum_j M_j$  (where  $j = 1$  to 3). All the equations so obtained are rewritten in the following form:

$$dN_{1,1}/dt = -k_9N_{1,1} + 2k_6N_{2,1} + k_4N_{2,2}$$

$$dN_{1,2}/dt = -2k_1N_{1,1} - (k_1 + k_8)N_{1,2} - 2k_1N_{2,1} + (k_6 - k_1)N_{2,2} \\ + 2k_4N_{2,3} + (2k_2 - 2k_1)N_{3,1} + (k_2 - k_1)N_{3,2} + 2k_1L_1 + k_1L_2$$

$$dN_{1,3}/dt = -k_1N_{1,2} - (2k_1 + k_7)N_{1,3} - k_1N_{2,2} - 2k_1N_{2,3} \\ + (k_2 - k_1)N_{3,2} + (2k_2 - 2k_1)N_{3,3} + k_1L_2 + 2k_1L_3$$

$$dN_{2,1}/dt = -2k_6N_{2,1} + 2k_5N_{3,1} + k_3N_{3,2}$$

$$dN_{2,2}/dt = -2k_0N_{1,1} - k_0N_{1,2} - 2k_0N_{2,1} \\ - (k_0 + k_4 + k_6)N_{2,2} - 2k_0N_{3,1} + (k_5 - k_0)N_{3,2} \\ + 2k_3N_{3,3} + (2k_1 - 2k_0)N_{4,1} + (k_1 - k_0)N_{4,2} + 2k_0L_1 + k_0L_2$$

$$dN_{2,3}/dt = -k_0N_{1,2} - 2k_0N_{1,3} - k_0N_{2,2} - (2k_0 + 2k_4)N_{2,3} - k_0N_{3,2} \\ - 2k_0N_{3,3} + (k_1 - k_0)N_{4,2} + (2k_1 - 2k_0)N_{4,3} + k_0L_2 + 2k_0L_3$$

$$dN_{3,1}/dt = -(2k_5 + k_2)N_{3,1} + 2k_5N_{4,1} + k_3N_{4,2}$$

$$dN_{3,2}/dt = -2k_0N_{1,1} - k_0N_{1,2} - 2k_0N_{2,1} - k_0N_{2,2} \\ - 2k_0N_{3,1} - (k_0 + k_2 + k_3 + k_5)N_{3,2} \\ - 2k_0N_{4,1} + (k_5 - k_0)N_{4,2} + 2k_3N_{4,3} + (2k_1 - 2k_0)N_{5,1} \\ + (k_1 - k_0)N_{5,2} + 2k_0L_1 + k_0L_2$$

$$dN_{3,3}/dt = -k_0N_{1,2} - 2k_0N_{1,3} - k_0N_{2,2} - 2k_0N_{2,3} \\ - k_0N_{3,2} - (2k_0 + k_2 + 2k_3)N_{3,3} - k_0N_{4,2} \\ - 2k_0N_{4,3} + (k_1 - k_0)N_{5,2} + (2k_1 - 2k_0)N_{5,3} + k_0L_2 + 2k_0L_3$$

$$dN_{4,1}/dt = -(2k_5 + 2k_1)N_{4,1} + 2k_5N_{5,1} + k_3N_{5,2}$$

$$dN_{4,2}/dt = -2k_0N_{1,1} - k_0N_{1,2} - 2k_0N_{2,1} - k_0N_{2,2} - 2k_0N_{3,1} - k_0N_{3,2} \\ - 2k_0N_{4,1} - (k_0 + 2k_1 + k_3 + k_5)N_{4,2} - 2k_0N_{5,1} + (k_5 - k_0)N_{5,2} + 2k_3N_{5,3} \\ + (2k_1 - 2k_0)N_{6,1} + (k_1 - k_0)N_{6,2} + 2k_0L_1 + k_0L_2$$

$$dN_{4,3}/dt = -k_0N_{1,2} - 2k_0N_{1,3} - k_0N_{2,2} - 2k_0N_{2,3} - k_0N_{3,2} \\ - 2k_0N_{3,3} - k_0N_{4,2} - (2k_0 + 2k_1 + 2k_3)N_{4,3} - k_0N_{5,2} \\ - 2k_0N_{5,3} + (k_1 - k_0)N_{6,2} + (2k_1 - 2k_0)N_{6,3} + k_0L_2 + 2k_0L_3$$

$$dN_{n,1}/dt = -\{2k_5 + 2k_1 + (n - 4)k_0\}N_{n,1} + 2k_5N_{n+1,1} + k_3N_{n+1,2} \\ \text{for } n \geq 5$$

$$dN_{n,2}/dt = -2k_0 \sum_{i=1}^{n+2} N_{i,1} - k_0 \sum_{i=1}^{n+2} N_{i,2} - \{(n - 4)k_0 + 2k_1 + k_3 + k_5\}N_{n,2} \\ + k_5N_{n+1,2} + 2k_3N_{n+1,3} + 2k_1N_{n+2,1} + k_1N_{n+2,2} + 2k_0L_1 + k_0L_2 \\ \text{for } n \geq 5$$

$$dN_{n,3}/dt = -k_0 \sum_{i=1}^{n+2} N_{i,2} - 2k_0 \sum_{i=1}^{n+2} N_{i,3} - \{(n - 4)k_0 + 2k_1 + 2k_3\}N_{n,3} \\ + k_1N_{n+2,2} + 2k_1N_{n+2,3} + k_0L_2 + 2k_0L_3 \quad \text{for } n \geq 5$$

$$dL_1/dt = (-k_9 + 2k_1 - 3k_0)N_{1,1} - k_3N_{1,2} + (2k_1 - 2k_0)N_{2,1} \\ + (k_4 - k_3)N_{2,2} + (2k_1 - k_2 - k_0)N_{3,1} + (4k_0 - 2k_1)L_1 + k_3L_2 - k_0M_1$$

$$dL_2/dt = (6k_0 - 4k_1)N_{1,1} + (k_3 - k_8)N_{1,2} - 2k_3N_{1,3}$$

$$\begin{aligned}
& + (4k_0 - 4k_1) N_{2,1} + (k_3 - k_4) N_{2,2} + (2k_4 - 2k_3) N_{2,3} \\
& + (2k_0 - 4k_1 + 2k_2) N_{3,1} + (4k_1 - 8k_0) L_1 - k_3 L_2 + 2k_3 L_3 + 2k_0 M_1 \\
dL_3/dt = & (3k_0 - 2k_1) N_{1,2} + (3k_0 - 2k_1 + 2k_3 - k_7) N_{1,3} \\
& + (2k_0 - 2k_1) N_{2,2} + (2k_0 - 2k_1 + 2k_3 - 2k_4) N_{2,3} \\
& + (k_0 - 2k_1 + k_2) N_{3,2} + (k_0 - 2k_1 + k_2) N_{3,3} \\
& + (2k_1 - 4k_0) L_2 + (-4k_0 + 2k_1 - 2k_3) L_3 + k_0 M_2 + k_0 M_3 \\
dM_1/dt = & (-45k_0 + 2k_1 + 2k_5 - k_9) N_{1,1} \\
& + (-34k_0 + 4k_1 + 2k_5 - 2k_6) N_{2,1} + (k_4 - k_3) N_{2,2} \\
& + (-23k_0 + 6k_1 - 3k_2) N_{3,1} - 12k_0 N_{4,1} - 6k_0 N_{5,1} - 2k_0 N_{6,1} \\
& + (56k_0 - 2k_5) L_1 - k_3 L_2 - (11k_0 + 2k_1 + k_3) M_1 \\
& - k_3 M_3 + k_3 M - 2k_0 (N_{9,1} + 3N_{10,1} + 6N_{11,1} + 10N_{12,1} + \dots) \\
dM_2/dt = & 42k_0 N_{1,1} + (-24k_0 + 2k_1 + k_3 + k_5 - k_8) N_{1,2} \\
& + (32k_0 - 2k_1) N_{2,1} + (-18k_0 + 3k_1 + 2k_3 - 2k_4 + k_5 - k_6) N_{2,2} \\
& + (2k_4 - 2k_3) N_{2,3} + (22k_0 + 2k_2 - 4k_1) N_{3,1} \\
& + (-12k_0 + 4k_1 - 2k_2) N_{3,2} + 12k_0 N_{4,1} - 6k_0 N_{4,2} \\
& + 6k_0 N_{5,1} - 3k_0 N_{5,2} + 2k_0 N_{6,1} - k_0 N_{6,2} \\
& - (52k_0 + 2k_1) L_1 + (30k_0 - k_1 - k_5) L_2 - 2k_3 L_3 \\
& - (16k_0 + 3k_1 + k_3) M_2 - (10k_0 + 2k_1 - 2k_3) M_3 \\
& + (10k_0 + 2k_1) M + 2k_0 (N_{9,1} + 3N_{10,1} + 6N_{11,1} + 10N_{12,1} + \dots) \\
& - k_0 (N_{9,2} + 3N_{10,2} + 6N_{11,2} + 10N_{12,2} + \dots) \\
dM_3/dt = & 21k_0 N_{1,2} + (-3k_0 + 2k_1 + 2k_3 - k_7) N_{1,3} \\
& + (16k_0 - k_1) N_{2,2} + (-2k_0 + 2k_1 + 4k_3 \\
& - 4k_4) N_{2,3} + (11k_0 - 2k_1 + k_2) N_{3,2} - (k_0 - 2k_1 + k_3) N_{3,3} \\
& + 6k_0 N_{4,2} + 3k_0 N_{5,2} + k_0 N_{6,2} - (26k_0 + k_1) L_2 \\
& + (4k_0 - 2k_1) L_3 - (5k_0 + k_1) M_1 - (6k_0 + k_1 + 2k_3) M_3 \\
& + (5k_0 + k_1) M + k_0 (N_{9,2} + 3N_{10,2} + 6N_{11,2} + 10N_{12,2} + \dots) \\
dM/dt = & (-3k_0 + 2k_1 + 2k_5 - k_9) N_{1,1} + (-3k_0 + 2k_1 + k_3 + k_5 - k_8) N_{1,2} \\
& + (-3k_0 + 2k_1 + 2k_3 - k_7) N_{1,3} + (-2k_0 + 2k_1 + 2k_5 - 2k_6) N_{2,1} \\
& + (-2k_0 + 2k_1 + k_3 - k_4 + k_5 - k_6) N_{2,2} + (-2k_0 + 2k_1 + 2k_3 - 2k_4) N_{2,3} \\
& + (-k_0 + 2k_1 - k_2) N_{3,1} + (-k_0 + 2k_1 - k_2) N_{3,2} \\
& - (k_0 - 2k_1 + k_2) N_{3,3} + (4k_0 - 2k_1 - 2k_5) L_1 \\
& + (4k_0 - 2k_1 - k_3 - k_5) L_2 + (4k_0 - 2k_1 - 2k_3) L_3 - k_0 M \dots \quad (2)
\end{aligned}$$

In the special case where  $k_0 = k_1 = k_2 = K_1$ ,  $k_3 = k_4 = k_5 = k_6 = K_2$  and  $k_7 = k_8 = k_9 = K_3$ , it amounts to assuming that the dependence of the reaction rate is only on the two adjacent sites (one on either side) which is the case discussed by Alfrey and Lloyd.<sup>1</sup> If the corresponding equations for this case are written and the equations for  $dN_{n,1}/dt$ ,  $dN_{n,2}/dt$ , and  $dN_{n,3}/dt$  are added, we get exactly the same results.

$N_{n,j}$ ,  $L_j$ ,  $M_j$ , and  $M$  in the above equations can be divided by  $S$  to give the appropriate fractions.  $M/S$ , which is  $\sum_{n=1}^{\infty} n (N_{n,1} + N_{n,2} + N_{n,3})/S$ , should be 1 initially. For the sake of convenience, we can assume without loss of

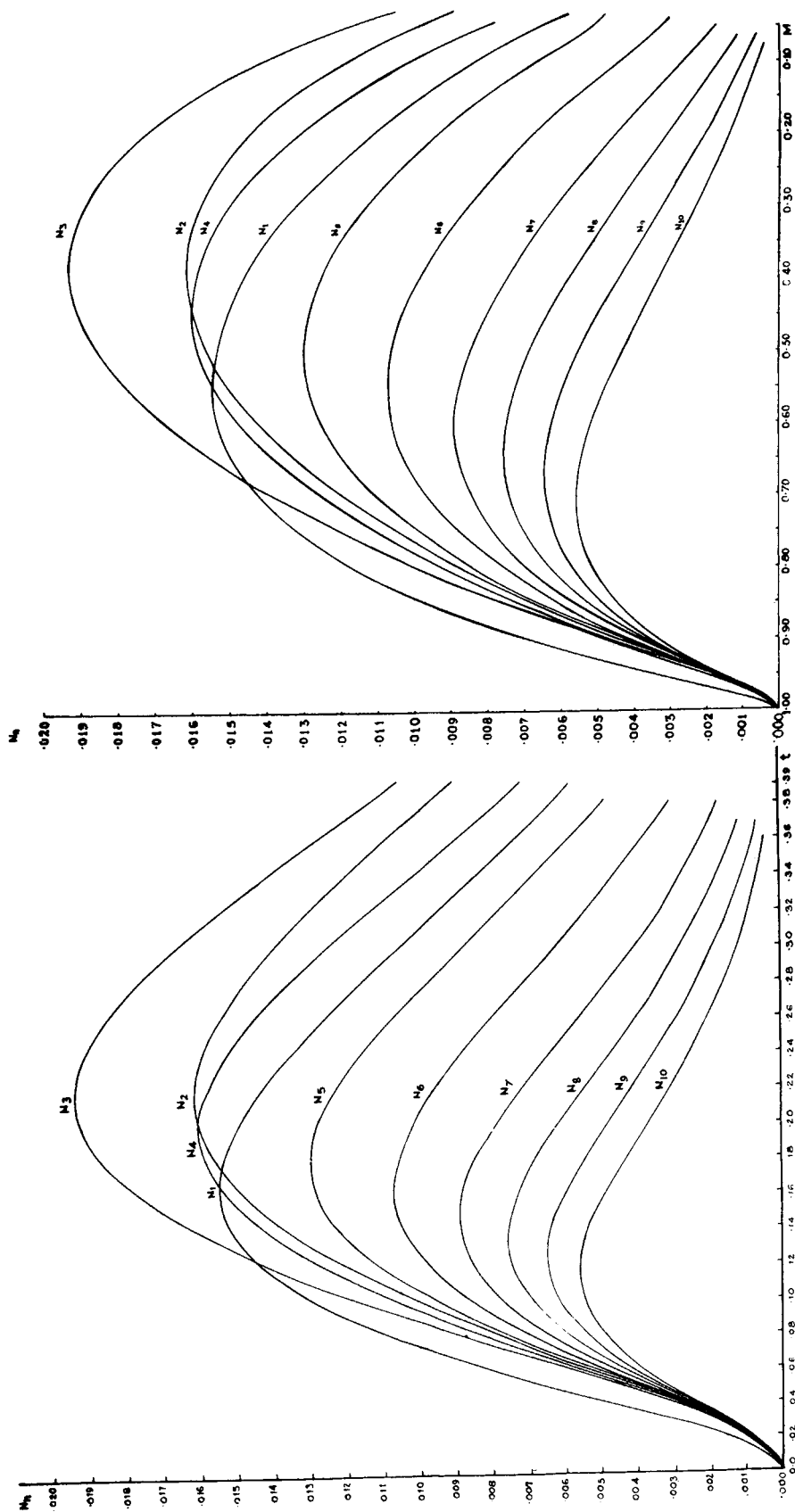


Fig. 1. Variation with time of  $N_n$  in autocatalytic reaction.

Fig. 2. Variation of  $N_n$  with  $M$  in autocatalytic reaction.

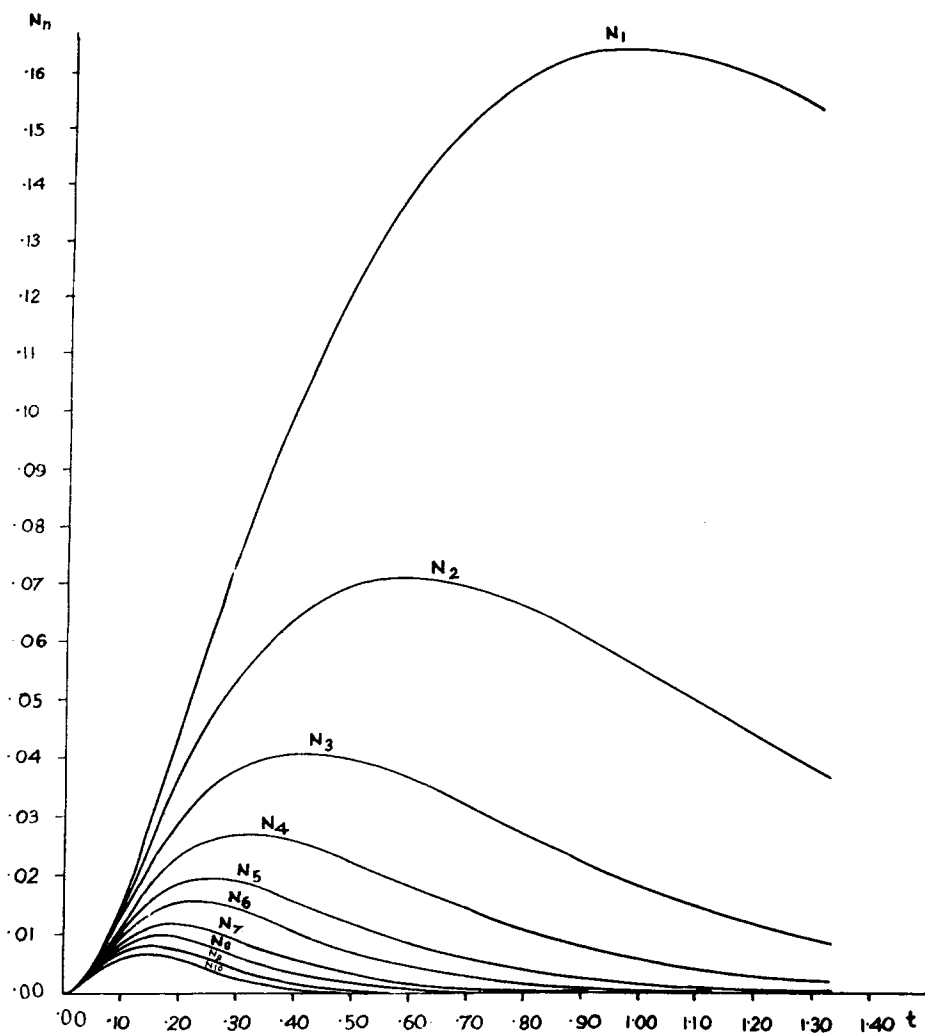


Fig. 3. Variation with time of  $N_n$  in null case.

generality that  $N_{n,j}$ ,  $L_j$ ,  $M_j$ , and  $M$  in eqs. (2) actually denote these quantities divided by  $S$ . For instance,  $N_{1,1}$  in the rest of paper will mean  $N_{1,1}$  as defined earlier divided by  $S$ .

### SOLUTION OF THE DIFFERENTIAL EQUATIONS

A set of equations  $dN_{n,j}/dt$ ,  $dL_j/dt$ ,  $dM_j/dt$ , and  $dM/dt$  (where  $n = 1$  to  $m$  and  $j = 1, 2, 3$ ) was taken up for solution. Since these would involve  $N_{m+l,j}$  (where  $l \geq 1$ ), it is not possible to solve them. Some additional assumptions are essential in order to close them. We have made the assumption that for each value of  $j$ , the sequence  $N_{m+r-1,j}$  ( $r \geq 0$ ) is in geometric progression (for example,  $N_{m,j}/N_{m-1,j} = N_{m+1,j}/N_{m,j}$ ) to eliminate extra terms and thus get a set of  $3m + 7$  differential equations of first order involving  $3m + 7$  unknown quantities  $N_{n,j}$ ,  $L_j$ ,  $M_j$ , and  $M$ , the constants involving only  $k_0, k_1, k_2, \dots, k_9$ .

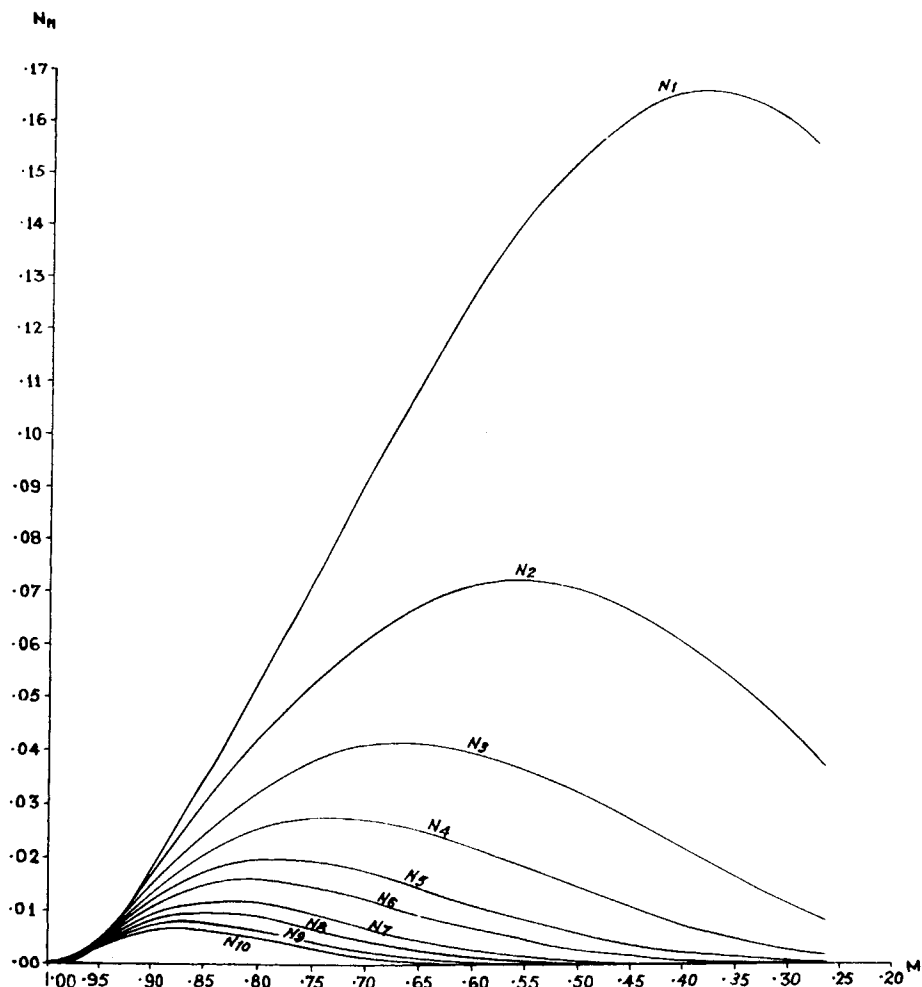


Fig. 4. Variation of  $N_n$  with  $M$  in null case.

Assuming various sets of values for  $k$ , numerical solutions were attempted for  $m = 10$  with the help of a computer (IBM-7044) using Runge Kutta Gill's method (Ralstan and Wilf<sup>7</sup>) appropriately modified. During the course of computation it became necessary to make a further assumption, viz.  $N_{9,1}/N_{9,2} = N_{10,1}/N_{10,2}$ .

## RESULTS AND DISCUSSION

The various sets of values for the  $k$ 's tried are given in Table I:

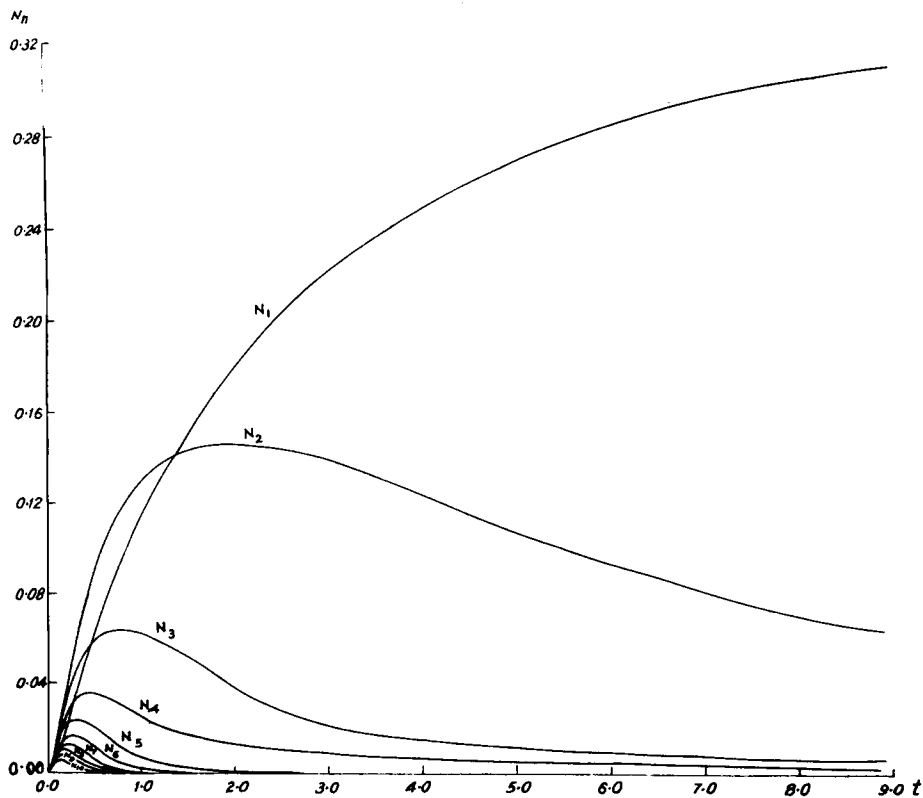
Set I relates to an autocatalytic reaction, whereas set III relates to an auto-retarding reaction. In set II, the reaction rates are independent of neighboring sites. Graphs showing  $N_1, N_2, \dots, N_{10}$  against time and against  $M$  for sets I, II, and III as obtained by solving differential eqs. (2) are given in Figures 1 to 6.



TABLE I

	I	II	III
$k_0$	1.0	1.0	1.00
$k_1$	2.0	1.0	0.50
$k_2$	4.0	1.0	0.25
$k_3$	5.0	1.0	0.20
$k_4$	10.0	1.0	0.10
$k_5$	10.0	1.0	0.10
$k_6$	20.0	1.0	0.05
$k_7$	25.0	1.0	0.04
$k_8$	50.0	1.0	0.02
$k_9$	100.0	1.0	0.01

If the percentage unreacted ( $M$ ) can thus be computed for a large number of sets of reaction rates and if for a polymer reaction the fraction unreacted can be experimentally determined at various points of time, it should be possible to get some estimates of the reaction rates. If the reaction rates can thus be estimated, it is possible to have an idea of the number of sequences of

Fig. 5. Variation with time of  $N_n$  in autoretarding reaction.

the type  $N_1, N_2, \dots$  at any point of time and the structure of the product at any stage of conversion.

It would not be possible to comment specifically on the results depicted in Figures 1 to 6 since they would depend on the reaction rates assumed. But in general, heterogeneity is seen to be much more pronounced in the autocataly-

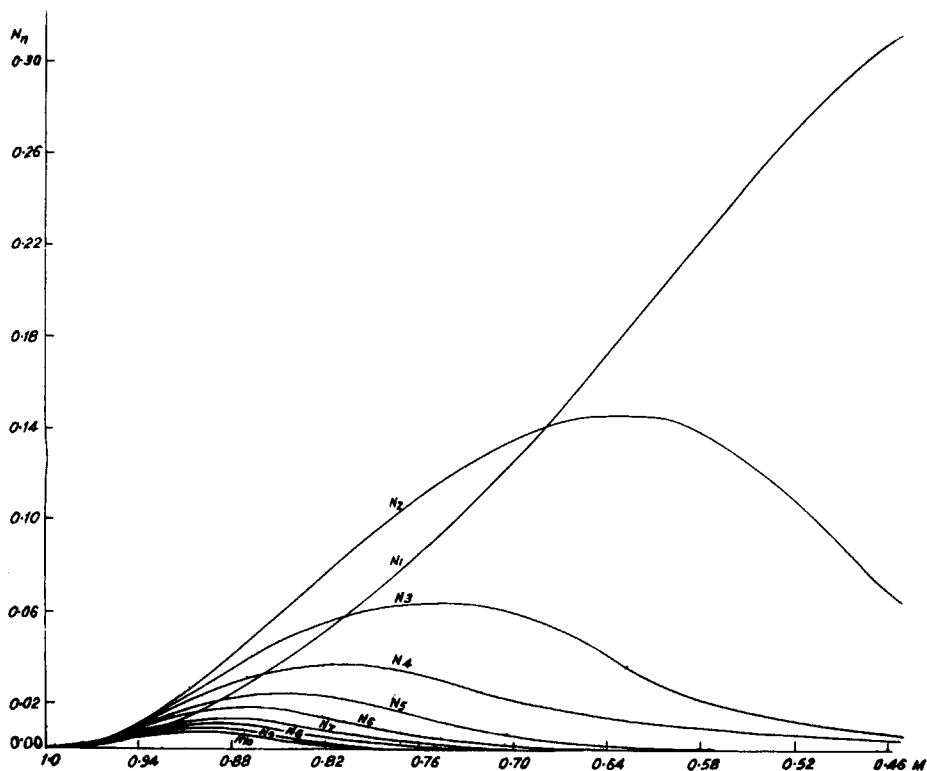


Fig. 6. Variation of  $N_n$  with  $M$  in autoretarding reaction.

tic case. For instance, from Figures 2, 4, and 6, it is seen that by the time 50% reaction has taken place, in the autocatalytic case all the sequences  $N_n$  ( $n = 1, 10$ ) are present in fairly large numbers, whereas it is not so in the autoretarding case.

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