Distribution of Reacted Sequences in Homopolymers

José J. González*

Institutt for teoretisk fysikk, Universitetet i Trondheim, 7034 Trondheim-NTH, Norway, and Institut für Festkörperforschung der Kernforschungsanlage, D-5170 Julich, Federal Republic of Germany

Klaus W. Kehr

Institut für Festkörperforschung der Kernforschungsanlage, D-5170 Jülich, Federal Republic of Germany. *Received January 1, 1978*

ABSTRACT: The theoretical analysis of reactions on homopolymers with nearest-neighbors cooperative effects lacked so far results for the distribution of reacted sequences. We derive the differential equations describing these distributions and give a complete formal solution. Solvable special cases are discussed. Additionally, the differential equations are solved numerically for the parameters appropriate for the periodate oxidation of amylose.

I. Introduction

It is well-established that periodate oxidated units in many polysaccharides inhibit the oxidation of unreacted nearest-neighbors through formation of hemiacetals.[1,2] The theoretical analysis of the pertinent model describing nearest-neighbor *cooperative* (i.e., inhibitory or activatory) effects in linear chains is fairly complete, both for homo-[3-8] and copolymers,[9-10] and successful applications of this model on homopolymeric[11] and copolymeric[12] polysaccharides exist. However, while both the extent of reaction and the distribution of sequences of *unreacted* units can be computed, to our knowledge nobody has yet been able to find the distribution of sequences of reacted units.[19] In this article, we contribute to the solution of this important problem by deriving the set of differential equations determining the average densities of reacted sequences for infinitely long homopolymers. We are able to give the exact solutions, too. But these exact expressions are of little practical interest for sequences having more than, say, five reacted units. It remains, therefore, to develop suitable approximation methods. Still, we are able to obtain numerical results for sequences of up to eight reacted units, but we do this by direct numerical integration of the differential equations.

Before entering into computational details, it is convenient to realize why sequence densities for unreacted units are considerably easier to derive than those for reacted units.

The point is the principle of independence of unreacted neighbors[9,10,12,13] is valid for the present model with nearest-neighbor cooperative effects.

The principle states that the probability of a given configuration of a polymer containing, somewhere, two unreacted adjacent units is the product of two probabilities, each referring to the state of one of the two parts of the polymer arising from a hypothetical partition between the two unreacted residues. The validity of the principle rests upon the obvious fact that correlations between the residues are introduced solely by the cooperative mechanism between neighbors *after* one of them has reacted.

Hence, for sequences of $l > 2$ units the corresponding densities at time t, $q_l(t)$, will satisfy

$$q_l(t) = q_2(t) \exp\{-k(l-2)t\} \tag{1}$$

because $l - 2$ units are uncorrelated. The rate constant, k, is defined as the probability per unit time that an unprotected unit will react. (Strictly speaking "protection" occurs only for inhibitory effects.) Altogether, only two sequence densities are independent, viz., $q_1(t)$ and $q_2(t)$. These can be easily found because they obey simple differential equations expressing their creation and destruction through the reaction process:[5-8,14]

$$\mathrm{d}q_1(t)/\mathrm{d}t = -kcq_1(t) + k(a + \tilde{a})q_2(t) + 2k\sum_{l=3}^{\infty} q_l(t) \tag{2}$$

$$\mathrm{d}q_2(t)/\mathrm{d}t = -k(a + \tilde{a})q_2(t) + k(a + \tilde{a})q_3(t) + 2k\sum_{l=4}^{\infty} q_l(t) \tag{3}$$

where ka ($k\tilde{a}$) is the reaction probability per unit time for a singly protected unreacted unit to the left (right) of the protecting unit, and kc is the reaction probability per unit time for an unreacted unit between two reacted ones. The reason for the simplicity of eq 2 and 3 is the absence of coagulation processes for sequences of unreacted units.

Reacted sequences do not enjoy anything like the property described by eq 1. On the contrary, the more units they contain the more correlations are present. An additional complication is that two reacted sequences separated by a single unreacted unit may coagulate by reaction of the separating unit.

Before we turn to the task of deriving the differential equations for sequences $r_l(t)$ of l reacted units, we list the well-known solutions[3-8,11-14] of eq 1–3

$$q_1(t) = 1 - y(t) - (2 - e^{-kt}) \exp[-k(a + \tilde{a})t - (2 - a - \tilde{a})(1 - e^{-kt})] \tag{4}$$

and for $l \geq 2$

$$q_l(t) = (1 - e^{-kt})^2 \exp[-k(a + \tilde{a})t - (2 - a - \tilde{a}) \times (1 - e^{-kt})] \exp[-(l-2)kt] \tag{5}$$

where the extent of reaction $y(t) \equiv 1 - \sum_{l=1}^{\infty} lq_l(t)$ is given by

$$y(t) = 1 + (a + \tilde{a} - c)^{-1}\Big\{-ce^{-kct} + (2c - a - \tilde{a}) \times \exp[-k(a + \tilde{a})t - (2 - a - \tilde{a})(1 - e^{-kt})] + (3c - c^2 - a - \tilde{a})e^{-kct}\int_0^{kt} \mathrm{d}s \times \exp[(c - a - \tilde{a} - 1)s - (2 - a - \tilde{a})(1 - e^{-s})]\Big\} \tag{6}$$

González and Hemmer[9,10,12,13] have shown how to find the results in eq 4–6 by an alternative method. By using the principle of independence of unreacted neighbors it turns out that all the q_l's can be expressed in terms of the

---

* Address correspondence to this author at Agder Ingeniør-og Distriktshøgskole, N-4890 Grimstad, Norway.

0024-9297/78/2211-0996$01.00/0

probabilities that at time t the left (right) terminal unit of a lattice is unreacted. These probabilities are very simple expressions; for a left terminal unit $\exp[-kat - (1 - a)(1 - e^{-kt})]$.

The layout of this article is as follows: in section II we derive and solve the differential equations determining the average densities of l reacted units, $r_l(t)$. Crucial to our analysis is the uniformity of distribution of reacted and unreacted sequences. Once this is proven, the differential equations for $r_l(t)$ readily follow. Alternatively, the same differential equations may be obtained by applying Felderhof's powerful theory,[15] which rests on a *Stosszahlansatz*. We comment upon the validity of Felderhof's Stosszahlansatz for the present model. Finally, in section III we predict the densities of sequences of up to eight reacted units for periodate oxidated amylose. Dr. T. Painter will try to carry out a suitable experiment to test our predictions.

II. Theory

As for the densities of unreacted units, $q_l(t)$, we set up differential equations for the densities of reacted units, $r_l(t)$, expressing their creation and destruction through the reaction process. The fate of a sequence of reacted units depends upon the length of the adjacent sequences of unreacted ones. We are thus led to find the probability of occurrence of two adjacent sequences of l reacted and m unreacted units, where $l, m = 1, 2, \ldots$ We contend that the reacted and unreacted sequences are *uniformly* distributed along the chain, i.e., that there is no correlation between the lengths of reacted and unreacted adjacent sequences. Our contention implies that the required probability equals $r_l(t)q_m(t)/\rho(t)$ for an infinitely long homopolymer, $\rho(t)$ being the total density of sequences:

$$\rho(t) = \sum_{l=1}^{\infty} r_l(t) = \sum_{l=1}^{\infty} q_l(t) = 1 - y(t) - \exp[-(a + \tilde{a})kt - (2 - a - \tilde{a})(1 - e^{-kt})] \quad (7)$$

Equation 7 is obtained in a straightforward way by using eq 4 and 5. To understand the expression $r_l(t)q_m(t)/\rho(t)$, we note that $r_l(t)[q_m(t)]$ is the probability of finding at an arbitrarily chosen place in the infinitely long polymer l $[m]$ contiguous reacted [unreacted] units bounded by unreacted [reacted] ones, while $q_m(t)/\rho(t)[r_l(t)/\rho(t)]$ equals the probability that an unreacted [reacted] sequence consists of precisely m $[l]$ units.

First we give an intuitive argument for the above contention: the number of constituents in a sequence of unreacted units cannot have influenced the formation of its adjacent reacted sequence, since any cooperative effect shaping the formation of the reacted sequence comes only from one of its constituents. Therefore, the conditional probability of finding a reacted sequence of l units given that it is adjacent to an unreacted sequence of m units is simply the probability that a reacted sequence consists of l units, i.e., $r_l(t)/\rho(t)$.

A proof of the contention is obtained by complete induction. We first observe that the present model can be obtained in terms of a slightly different description in which the variable n, equal to the number of attacks on the polymer units, plays the role of time (cf. ref 14). In the limit $n/N \rightarrow \text{constant} \times t$, $n \rightarrow \infty$, $N \rightarrow \infty$ (N = number of units of the polymer), the continuous time version is recovered. We now proceed to give a proof by complete induction in n. Obviously, for $n = 0$ it is trivially correct that the reacted and unreacted sequences are uniformly distributed along the chain, since the whole chain is unreacted. Let us assume that after $n > 0$ attacks the reacted and unreacted sequences are uniformly distributed along the chain. Then, because of the randomness of the attack and of the nearest-neighbor character of the cooperative effect, the probability that a given unreacted sequence is the affected one in the $(n + 1)$th attack is independent of how many reacted units are to its right (or left) side, and, since the sequences are uniformly distributed along the chain, the reaction occurs with identical probability for sequences of equal length. Hence, nothing occurs in the $(n + 1)$th attack that could disturb the uniform distribution of reacted and unreacted sequences and the contention follows.

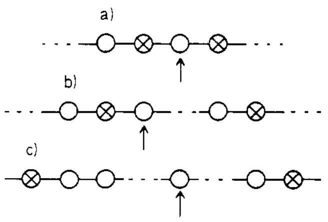

Figure 1. Typical processes contributing to the right-hand side of eq 8: (a and b) destruction of a reacted sequence of length 1 because of the reaction of an adjacent unit in an unreacted sequence of one or more units, respectively; (c) creation of a reacted sequence of length 1 because of the reaction of a nonterminal unit in an unreacted sequence.

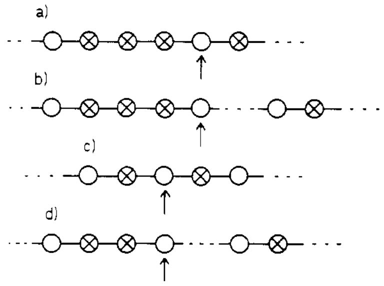

Figure 2. Typical processes contributing to the right-hand side of eq 9: (a and b) destruction of a reacted sequence of length $l = 3$ because of the reaction of an adjacent unit in an unreacted sequence of one or more units, respectively; (c) creation of a reacted sequence of length $l = 3$ because of the reaction of a single unit separating two reacted sequences; (d) creation of a reacted unit of length $l = 3$ because of the reaction of an adjacent unit to a reacted sequence of length $l = 2$.

The differential equations for the $r_l(t)$, $l = 1, 2, \ldots$, are now easily written down:

$$\mathrm{d}r_1(t)/\mathrm{d}t = -2kcr_1(t)q_1(t)/\rho(t) - k(a + \tilde{a})r_1(t)[1 - q_1(t)/\rho(t)] + k\sum_{m=3}^{\infty}(m - 2)q_m(t) \quad (8)$$

We describe the rhs of eq 8: The first and second terms express the destruction of a reacted sequence because of the reaction of an adjacent sequence of a single unreacted unit and of its adjacent unit in a neighbor unreacted sequence of two or more units. The last term expresses the appearance of a single reacted unit (Figure 1).

The differential equations for $l \geq 2$ are:

$$\mathrm{d}r_l(t)/\mathrm{d}t = -2kcr_l(t)q_1(t)/\rho(t) - k(a + \tilde{a})r_l(t)[1 - q_1(t)/\rho(t)] + kcq_1(t)\{\sum_{n=1}^{l-2} r_n(t)r_{l-n-1}(t)\}/\rho^2(t) + k(a + \tilde{a})[1 - q_1(t)/\rho(t)]r_{l-1}(t) \quad (9)$$

where the sum $\sum_{n=1}^{l-2}$ is empty for $l = 2$. As before, only the sum $a + \tilde{a}$ enters the equations (Cf. also ref 6 and 11). The interpretation of the rhs of eq 9 does not present any difficulty (cf. Figure 2).

We note that eq 8 and 9 can be solved successively for $l = 1$ upwards as linear inhomogeneous differential equations. For a given $l = 1, 2, \ldots$ they are of the form

$$\mathrm{d}r_l(t)/\mathrm{d}t = -Q_l(t)r_l(t) + S_l(t) \qquad (10)$$

where $Q_l(t)$ and $S_l(t)$ do not depend on $r_l(t)$ and can be found by first computing $r_1(t), r_2(t), \ldots, r_{l-1}(t)$.

The initial condition being $r_l(0) = 0$ for all values of l, the solution of eq 10 is

$$r_l(t) = \int_0^t \mathrm{d}v\, S_l(v) \exp\left\{-\int_v^t \mathrm{d}u\, Q_l(u)\right\} \qquad (11)$$

We use eq 11 to give explicit results for $l = 1, 2$. First, using eq 5 one finds

$$\sum_{m=3}^{\infty} (m-2)q_m(t) = \exp[-(1 + a + \tilde{a})kt - (2 - a - \tilde{a})(1 - e^{-kt})] \qquad (12)$$

Using eq 8, 11, and 12 we then find:

$$r_1(t) = \int_0^{kt} \mathrm{d}v \exp\left\{-(1 + a + \tilde{a})v - (2 - a - \tilde{a})(1 - e^{-v}) - \int_v^{kt} \mathrm{d}u\, [a + \tilde{a} + (2c - a - \tilde{a})q_1(u)/\rho(u)]\right\} \qquad (13)$$

where $q_1(t)$ and $\rho(t)$ are given by eq 4 and 7.

Similarly, one finds

$$r_2(t) = (a + \tilde{a}) \int_0^{kt} \mathrm{d}v\, [1 - q_1(v)/\rho(v)] \times \exp\left\{-\int_v^{kt} \mathrm{d}u\, [a + \tilde{a} + (2c - a - \tilde{a})q_1(u)/\rho(u)]\right\} \times \int_0^v \mathrm{d}x \exp\left\{-(1 + a + \tilde{a})x - (2 - a - \tilde{a})(1 - e^{-x}) - \int_x^v \mathrm{d}s\, [a + \tilde{a} + (2c - a - \tilde{a})q_1(s)/\rho(s)]\right\} \qquad (14)$$

Clearly, the expression for $r_l(t)$ becomes very complicated with increasing l.

In some special cases, the $r_l(t)$ become simple expressions. Here, we discuss the following cases: (i) $a = \tilde{a} = c = 0$, i.e., total protection by reacted units; (ii) $a = \tilde{a} = c = 1$, i.e., absence of cooperative effects; (iii) $a = 1$, $\tilde{a} = 0$, $c = 0$, e.g., complete protection from one side, no cooperative effect from the other side. (i) When $a = \tilde{a} = c = 0$ only $r_1(t)$ is different from zero. One finds

$$r_1(t) = \tfrac{1}{2}\{1 - \exp[-2(1 - e^{-kt})]\} \qquad (15)$$

which equals the extent of reaction for this special case, as it should be. (ii) When $a = \tilde{a} = c = 1$ the simple and obvious result

$$r_l(t) = e^{-2kt}(1 - e^{-kt})^l \qquad (16)$$

is obtained. (iii) $a = 1$, $\tilde{a} = 0$, $c = 0$: in this case the differential equations simplify considerably, mainly due to the absence of the coagulation term. One finds from eq 8

$$r_1(t) = \tfrac{1}{2}(1 - e^{-2kt}) \exp[e^{-kt} - 1] \qquad (17)$$

The higher $r_l(t)$, $l \geq 2$, obey the equation

$$\mathrm{d}r_l(t)/\mathrm{d}t + ke^{-kt}r_l(t) = ke^{-kt}r_{l-1}(t) \qquad (18)$$

which is simplified by the ansatz

$$r_l(t) = \lambda_l(t) \exp[e^{-kt} - 1]$$

to

$$\mathrm{d}\lambda_l(t)/\mathrm{d}t = ke^{-kt}\lambda_{l-1}(t) \qquad (l \geq 2) \qquad (19)$$

We have $\lambda_1(t) = {}^1/_2[1 - \exp(-2kt)]$. Equation 19 is seen to have the solution

$$\lambda_l(t) = \frac{1}{l!}(1 - e^{-kt})^l - \frac{1}{(l+1)!}(1 - e^{-kt})^{l+1}$$

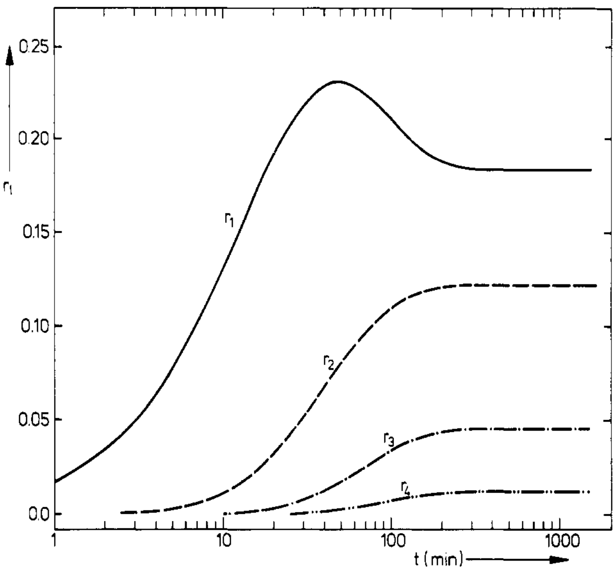

Figure 3. Distribution of reacted sequences $r_l(t)$ (l = 1–4) as a function of time for the model $a = 1$, $\tilde{a} = 0$, $c = 0$. The rate constant was chosen to be $k = 0.01875\ \mathrm{min}^{-1}$.

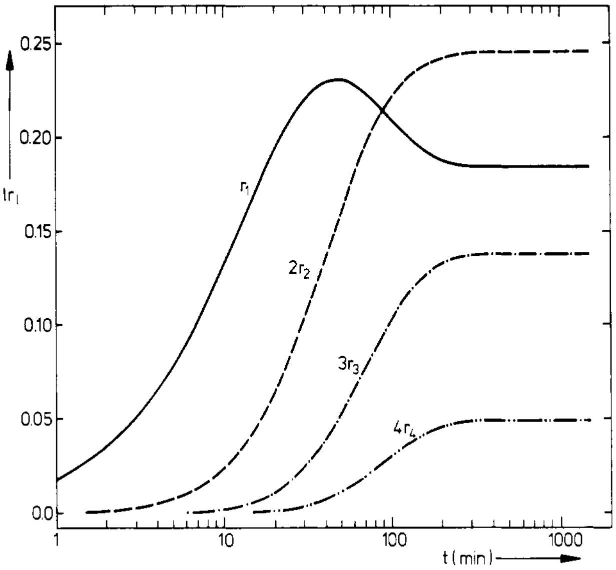

Figure 4. Contribution $l \times r_l(t)$ (l = 1–4) for the reacted sequences to $y(t)$ as a function of time for the model $a = 1$, $\tilde{a} = 0$, $c = 0$, with $k = 0.01875\ \mathrm{min}^{-1}$.

valid for all l. The densities of reacted sequences are then given by

$$r_l(t) = \exp[e^{-kt} - 1]\left\{\frac{1}{l!}(1 - e^{-kt})^l - \frac{1}{(l+1)!}(1 - e^{-kt})^{l+1}\right\} \qquad (20)$$

In Figure 3 we have plotted $r_l(t)$ for $l = 1, 2, 3, 4$ for this special case, and in Figure 4 $l \times r_l(t)$. One sees that the densities of the reacted units approach finite values for large times. In this case unreacted units survive on the limit $t \to \infty$, and the extent of reaction approaches $1 - e^{-1} < 1$. The quantity $l \times r_l(t)$ represents the relative number of reacted monomer units contributed by sequences of length l. It is seen that there are more reacted units on $l = 2$ sequences than in any other type of sequence for large times.

Our problem being a case of kinetics of a binary lattice, one expects that Felderhof's powerful theory[15] should be applicable. On comparing with ref 15 it is easy to recognize

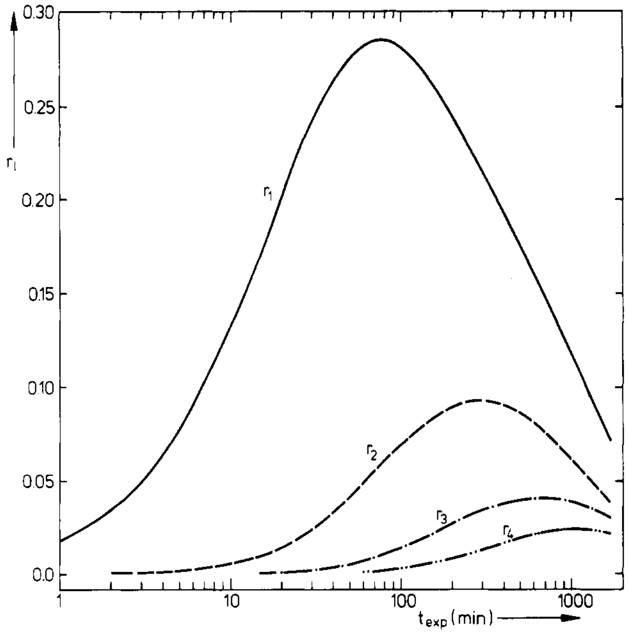

Figure 5. Distribution of reacted sequences $r_l(t)$ (l = 1-4) as a function of t_{exptl} for parameters appropriate for the experiment of Painter and Larsen[18] on amylose.

that Felderhof's Stosszahlansatz is only a slightly sharper version of the uniformity of distribution of average densities of unreacted and reacted sequences that was proven above. Hence, Felderhof's eq 42 should be expected to give our eq 8 and 9, as indeed is the case.

Finally, it should be clear that, once the q_l's and r_l's are known, the probability of occurrence of *any* sequence having reacted and unreacted units in an arbitrary order can be found by simple arithmetics. Indeed, the principle of independence of unreacted units and the uniform distribution of unreacted and reacted sequences provide the key.

III. Reacted Sequences in Amylose

The extent of reaction of periodate oxidated amylose is well-described by the present theory. This was shown by Monte-Carlo simulation[17] and by direct application of eq 6.[11]

Hence, it is tempting to predict the distribution of reacted sequences for amylose. We choose the conditions of the experiment previously analyzed[11,17] as they are given in ref 18. The constants appearing in our equations are: $k = 0.01875$ min^{-1}, $a + \tilde{a} = 0.46$, and $c = 0.0337$.

Instead of using the exact solutions of the type in eq 11, we have solved the differential eq 8 and 9 numerically by the Runge-Kutta-Merson method for l = 1-8. The accuracy of the method was controlled partly by comparing the values for $r_1(t)$ as obtained by direct numerical integration of eq 13 and by numerical solution of the differential eq 8. Another check for sufficiently small times is to evaluate

$$y(t) \simeq \sum_{l=1}^{8} l r_l(t)$$

and

$$\rho(t) \simeq \sum_{l=1}^{8} r_l(t)$$

and to compare with the exact results obtained through eq 6 and 7. Both checks suggest that the numerical solutions of the differential equations are accurate up to four significant digits.

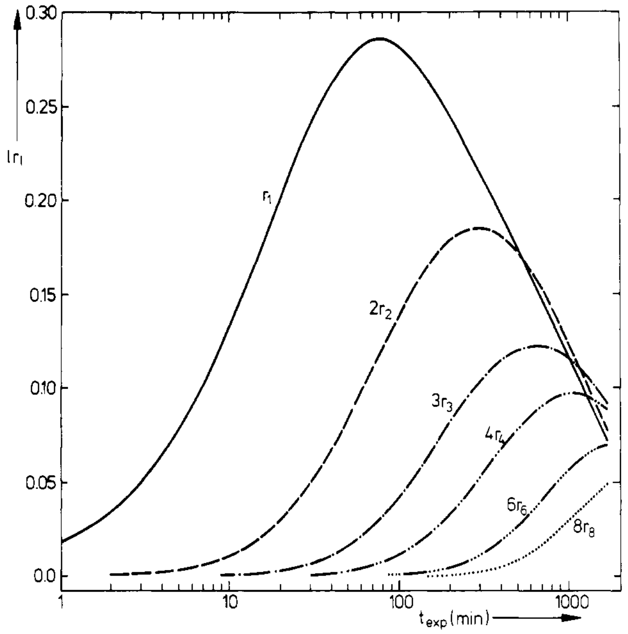

Figure 6. Contribution $l \times r_l(t)$ (l = 1-4, 6, 8) of the reacted sequences to $y(t)$ as a function of t_{exptl} for the parameters appropriate for the experiment of Painter and Larsen[18] on amylose.

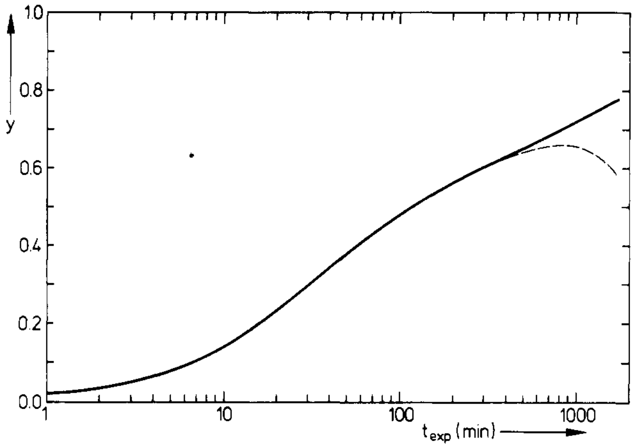

Figure 7. Extent of reaction $y(t)$ of amylose as a function t_{exptl} for the parameters appropriate for the experiment of Painter and Larsen. The dashed line indicates the contribution of the sequences having up to eight reacted units.

In order to account for the loss of the oxidation agent during the reaction we have converted times t into "experimental" times t_{exptl} through the equation[11,12]

$$t_{\text{exptl}} = c_1 \int_0^t d\tau/(c_1 - c_2 y(\tau)) \qquad (21)$$

where c_1 and c_2 are the initial concentration of periodate and of monomer units. The relation between t_{exptl} and t for the conditions of the experiment of Painter and Larsen[18] has been evaluated in ref 11 and the known values of t have been used in this paper.

The results are given in Figure 5 for $r_l(t)$ (l = 1-4) and in Figure 6 for $l \times r_l(t)$ (l = 1-4, 6, 8). For completeness we show in Figure 7 the extent of reaction $y(t)$, cf. ref 11. Since now $c \neq 0$ the smaller reacted sequences disappear for larger times, in favor of larger sequences. This is also seen in Figure 7. However, the reader should notice that up to quite large times short reacted sequences, especially single reacted units, dominate. For instance, after 120 min, when half of the amylose chain units have reacted, $y \simeq 50\%$, the contribution from sequences with four or more reacted units to the extent of reaction is less than 1.5%.

Even after 1320 min, when about 75% of the units are oxidized, only 16% of the oxidized units are found in sequences with more than eight oxidized units. A similar conclusion can be drawn from Figure 6. It shows that up to $t_{\text{exptl.}} \simeq 630$ min the sequences with one reacted unit contribute more to $y(t)$ than any other type of sequences, and up to $t_{\text{exptl}} \simeq 1150$ min the sequences with two reacted units have the largest contribution to $y(t)$.

As previously shown by one of us,[11] the extent of reaction of periodate oxidated amylose is well described by the present model of nearest-neighbor cooperative effects. Hence, it will be very interesting to see whether experiments confirm the validity of the theory to describe sequences of reacted units. Dr. T. Painter will attempt to carry out an experiment to this effect.

Acknowledgment. This work was incited by a discussion remark from Professor B. U. Felderhof. Therefore we are especially indepted to him. One of us (J.J.G.) would like to thank the Institut of Festköperforschung der Kernforschungsanlage, Jülich, for hospitality, and Norges Tekniske Høgskoles Fond, Norway, for financial support.

References and Notes

(1) T. Painter and B. Larsen, *Acta Chem. Scand.*, **24**, 813 (1970).
(2) M. F. Ishak and T. Painter, *Acta Chem. Scand.*, **25**, 3875 (1971).
(3) J. B. Keller, *J. Chem. Phys.*, **37**, 2584 (1962); **38**, 325 (1963).
(4) T. Alfrey, Jr., and W. G. Lloyd, *J. Chem. Phys.*, **38**, 322 (1963); **39**, 1903 (1963).
(5) D. A. McQuarrie, J. P. McTague, and H. Reiss, *Biopolymers*, **3**, 657 (1965).
(6) A. Silberberg and R. Simha, *Biopolymers*, **6**, 479 (1968). See also P. Rabinowitz, A. Silberberg, R. Simha, and E. Loftus, *Adv. Chem. Phys.*, **15**, 281 (1969).
(7) E. A. Boucher, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2295 (1972); *J. Chem. Soc., Faraday Trans. 2*, **69**, 1839 (1973).
(8) J. J. Gonzâlez, P. C. Hemmer, and J. S. Høye, *Chem. Phys.*, **3**, 228 (1974).
(9) J. J. Gonzâlez and P. C. Hemmer, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 645 (1976).
(10) J. J. Gonzâlez and P. C. Hemmer, *J. Chem. Phys.*, **67**, 2496 (1977); **67**, 2509 (1977).
(11) J. J. Gonzâlez, *Biophys. Chem.*, **2**, 23 (1974).
(12) J. J. Gonzâlez, Avhandling for den tekniske doktorgrad, Trondheim, 1977, and *Macromolecules*, in press.
(13) P. C. Hemmer and J. J. Gonzâlez, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 321, (1977).
(14) B. Widom, *J. Chem. Phys.*, **44**, 3888 (1966); **58**, 4043 (1973).
(15) B. U. Felderhof, *J. Stat. Phys.*, **6**, 21 (1972).
(16) T. H. Barron, R. J. Bawden, and E. A. Boucher, *J. Chem. Soc., Faraday Trans. 2*, **70**, 651 (1974).
(17) O. Smidsrød, B. Larsen, and T. Painter, *Acta Chem. Scand.*, **24**, 3201 (1970).
(18) T. Painter and B. Larsen, *Acta Chem. Scand.*, **24**, 2724 (1970).
(19) Barron, Bawden, and Boucher[16] have analyzed another model, the random pairwise occupation of a linear array. They were able to derive the distribution of reacted sequences as a function of time. Their model is, for an infinite lattice, equivalent to our special case with complete inhibition of neighbor units.

Studies on the Deformation Mechanism of Polyethylene Spherulites by the Orientation Distribution Function of Crystallites[1a]

Masaru Matsuo,*[1b] Kazumi Hirota,[1b] Kenichi Fujita,[1c] and Hiromichi Kawai[1c]

Department of Textile Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992, Japan, and the Department of Polymer Chemistry, Faculty of Engineering, Kyoto University 606, Japan. *Received August 9, 1977*

ABSTRACT: A deformation mechanism of a polyethylene spherulite under uniaxial stretching is discussed on the basis of the crystallite orientation distribution function obtained by the distribution functions of a reciprocal lattice vector of 13 crystal planes. The distribution functions for each crystal plane at the extension ratio $\lambda = 1.4$ are observed in detail by X-ray diffraction. The result is actually demonstrated that the evaluation of the deformation mechanism already suggested by many authors is correct. That is, the crystallite orientation distribution function reflects the fact that the deformation mechanism is dependent upon the rotation of crystallites around their own *b* axes associated with the lamellar rotation in the equatorial region as well as around their own *a* axes associated with the rotation of crystallites within lamellae in the meridian region. Moreover, the orientation distribution function of the crystal *c* axes has a peak around polar angle $\theta_j = 30°$, which has never been observed directly because of the weak intensity of X-ray diffraction. On the other hand, the preferential orientation of crystal *c* axes is found to be dependent upon the distribution of a principal stress having the highest magnitude in the stretching direction. This relation suggests that since tie-chain molecules are strained, the crystal *c* axes orient gradually parallel to the stretching direction.

I. Introduction

There have been a number of papers[2-16] concerning the deformation mechanism of polymer spherulites. Quantitative investigations have been reported for polyethylene spherulites by Stein et al.,[3,4] Kawai et al.,[6,8,14,15] and Moore.[10] They compared the experimental results observed from X-ray diffraction technique with the theoretical ones calculated from the model considering the orientation of crystallites or/and that of crystal lamellae in addition to the affine deformation of the spherulite. The evaluation for their comparison is classified into two methods. One is in terms of the second-order orientation factors of orientation distribution functions of principal axes of the crystal unit cell $F_{20}{}^{j}$ ($j = a, b, c$).[3,4,6,8,10] The other is in terms of the orientation distribution functions of the reciprocal lattice vector of the crystal plane.[14-16] The former is only due to an apparent aspect of the orientation distribution, and one cannot discuss the crystal orientation in detail. However, it may suffice for the characterization of simple textures. Theoretical investigations of general arrangements of crystallites were mainly carried out by Wilchinsky[17,18] and Sack.[19] Their investigations have demonstrated that it is possible to deduce from other data the value of the second-order orientation factor of a plane whose diffraction is too weak to observe. The latter is a direct comparison between the experimental and theoretical distribution functions reflecting the deformation mechanism. Hence, the latter is superior to the former.