

NOTE

## Reexamination of McQuarrie's Solution on the Kinetic Theory of Polymer-Analogous Reaction

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In a very recent review,<sup>1</sup> Platé and Noah recommended the theory proposed by McQuarrie<sup>2</sup> to be the most exact kinetic theory on polymer-analogous reactions of a sufficiently long homopolymer having the nearest-neighbor effects. By the polymer-analogous reaction, we mean the reaction of the substituent functional groups of a polymer with reagents low in molecular weight without any change in the degree of polymerization.<sup>3</sup> Although this theory is almost as exact as that of Boucher,<sup>4</sup> the final equations for expressing the extent of a reaction as a function of time appear to differ from each other. McQuarrie's equation involves two integral terms, while Boucher's one consists of a non-integral term and an integral term relating to the isolated unreacted units. Thus the properties of the McQuarrie equation are difficult to examine and numerical evaluations are difficult to make. We have examined McQuarrie's formulation and found a procedure by which a simpler equation can be obtained from it. The present paper deals with this derivation.

The formulations by the above authors are based on the assumption of the nearest-neighbor effects for the irreversible reaction of the first-order. In this case, three rate constants are sufficient to characterize the reaction kinetics. They are  $k_0$ ,  $k_1$ , and  $k_2$ , *i.e.*, the rate constants of unreacted units with zero, one, and two reacted nearest-neighbors, respectively.

McQuarrie defined two kinds of unreacted sequences; a)  $j$ -clusters: the sequence of  $j$ -unreacted

units flanked by two reacted units, and b)  $j$ -tuplet: the sequence of  $j$ -unreacted units flanked either by unreacted or by reacted units. Let  $p_j$  be the probability of finding a  $j$ -cluster in the chain and  $q_j$  be the probability of finding a  $j$ -tuplet in this chain. Thus the following set of equations at time ( $t$ ) can be obtained,

$$q_j = \sum_{i=0}^{N-j} (i+1) p_{i+j} \quad (1)$$

$$p_j = q_j - 2q_{j+1} + q_{j+2} \quad (2)$$

$$dq_1/dt = -k_0q_3 - 2k_1(q_2 - q_3) - k_2(q_1 - 2q_2 + q_3) \quad (3)$$

$$dq_j/dt = -2k_1(q_j - q_{j+1}) - k_0[(j-2)q_j + 2q_{j+1}] \quad (j \geq 2) \quad (4)$$

where  $N$  is the maximum length of the sequence of unreacted units. These equations comprise the McQuarrie formulation.

The solution of eq 4 for  $j \geq 2$  can be written in the following simple form,<sup>5</sup>

$$q_j = \exp(-jk_0t) \exp[2(k_0 - k_1)\{t - (1 - e^{-k_0t})/k_0\}] \quad (5)$$

There is no doubt about the validity of eq 1—5.

McQuarrie derived the expression for the fraction of unreacted units ( $q_1$ ) by substituting  $q_2$  and  $q_3$  from eq 5 into eq 3 and solving the resultant first-order linear differential equation. The result is,

$$q_1 = \exp(-k_2 t) \left[ 2(k_2 - k_1) e^{2(k_1 - k_0)/k_0} \right. \\ \times \int e^{(k_2 - 2k_1)t} \exp(Ae^{-k_0 t}) dt \\ \left. + (2k_1 - k_0 - k_2) e^{2(k_1 - k_0)/k_0} \int e^{(k_2 - k_0 - 2k_1)t} \right. \\ \left. \times \exp(Ae^{-k_0 t}) dt + C \right] \quad (6)$$

where  $C$  is the integration constant and  $A = 2(k_0 - k_1)/k_0$ . Equation 6 is the function examined below.

Now our problem is to obtain an expression for  $q_1$  other than eq 6 by using eq 1–5. To make the final expression as compact as possible, let us change the variable ( $t$ ) by  $s = \exp(-k_0 t)$  and let  $\alpha = k_1/k_0$ , and  $\beta = k_2/k_0$ . Then, eq 5 can be expressed in a simpler form as follows,

$$q_j = s^{j+2\alpha-2} \exp[2(\alpha-1)(1-s)] \quad (7)$$

From eq 1 and 2 with  $j=1$  and eq 6, we get,

$$q_1 - p_1 = 2q_2 - q_3 = \sum_{i=2}^N ip_i \\ = (2-s)s^{2\alpha} \exp[2(\alpha-1)(1-s)] \quad (8)$$

This is applicable for  $j \geq 2$ .

By differentiating eq 2 with respect to  $t$  at  $j=1$ , we obtain

$$dp_1/dt = dq_1/dt - 2dq_2/dt + dq_3/dt \quad (9)$$

With the help of eq 1, 3, and 4, eq 9 can be transformed as follows.

$$dp_1/dt = 2k_0(q_3 - q_4) + 2k_1(q_2 - 2q_3 + q_4) \\ + k_2(q_1 - 2q_2 + q_3) = 2k_0 \sum_{i=3}^N p_i \\ + 2k_1 p_2 - k_2 p_1 \quad (10)$$

This differential equation is identical to that derived by Boucher for the isolated unreacted units. Thus, eq 10 leads to,

$$p_1 = 2s^\beta \int_s^1 (1-x)[\alpha(1-x) + x]^{2\alpha-\beta-1} \\ \times \exp[2(\alpha-1)(1-x)] dx \quad (11)$$

Equation 7 plus eq 11 given the result we sought and is identical with the equation given by Boucher<sup>4</sup> and others.<sup>6,7</sup>

The properties of eq 11 is still cannot be examined as well as those of eq 8, however. For this to be possible, eq 11 must be modified by partial integration as follows,

$$p_1 = (1-s)^2 s^{2\alpha-1} \exp[2(\alpha-1)(1-s)] \\ + (2\alpha - \beta - 1) s^\beta \int_s^1 x^{2\alpha-\beta-2} (1-x)^2 \\ \times \exp[2(\alpha-1)(1-x)] dx \quad (12)$$

It is certainly at once evident that the second term of the right-hand side of eq 12 becomes zero at  $\beta = 2\alpha - 1$ . Under this condition, it can be shown that the resulting binary copolymer satisfies the conditions required for the Markov chain of the first-order.<sup>8</sup> Hence the integral term in eq 12 represents the extent of deviation from the Markov chain of the first-order. Since eq 12 is the solution for the isolated unreacted units, the deviation is limited to these special unreacted units. This unique property of  $q_1$  cannot be obtained from eq 6 unless transformed to eq 11 or 12.

It is concluded that eq 8 plus 11 (or 12) is superior to the equation derived by McQuarrie, *i.e.*, eq 6.

## REFERENCES

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