

# Kinetic theory of directional isomerism in polymer chains: 1. Polymer microstructure

Deyue Yan and Xiaodong Hu

Department of Applied Chemistry, Shanghai Jiao Tong University, Shanghai, People's Republic of China

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This work deals theoretically with directional isomerism by means of a non-steady-state kinetic technique. The head-to-tail sequence length distribution, the concentrations of head-to-head and tail-to-tail enchainments and various dyad and triad fractions have been derived rigorously. Furthermore, the relationships between the microstructural parameters of the resultant polymer and the polymerization variables have been established. The chain structural parameters given in this work are different from those derived by way of statistics as reported by Cais *et al.* and other authors. The kinetic theory is amenable to every stage of polymerization with directional isomerism, whereas the probabilistic description is appropriate only for infinite chains. When the chain length of the polymer approaches infinity, the equations given by kinetics are simplified into those calculated from statistics.

(Keywords: directional isomerism; chain structure; sequence distribution; non-steady-state kinetics)

## INTRODUCTION

The structural parameters of polymer chains, such as the degree of polymerization and the sequence distribution, etc., are dependent on the polymerization processes. Both statistical and kinetic methods allow the study of these processes. From the well established theory of chain length distribution, we know that the probabilistic description of condensation polymerization is simpler and perfectly correct. However, the outcomes of the kinetic treatment are more precise and reliable for addition polymerization. So far as addition polymerization is concerned, we prefer the kinetic technique to the probability method.

The statistical theory of the sequence distribution in polymers has been developed by Coleman and Fox<sup>1</sup>, Bovey *et al.*<sup>2,3</sup>, Price<sup>4</sup> and others<sup>5-9</sup>. Since chain isomerism arises during addition polymerization, one of the present authors<sup>10</sup> has retreated the stereo-configurational sequences by means of non-steady-state kinetics for polymers generated in anionic polymerization, giving some significant information worthy of mentioning here. One basically important conclusion drawn from the kinetic theory is as follows: during a Bernoullian process the tacticity of the polymer chains formed remains constant; alternatively, for various Markovian processes the stereo-regularity of the polymer chains generated varies with the reaction time or monomer conversion, and finally reaches a certain limit. This theoretical prediction is confirmed by the experimental data<sup>11,12</sup>. Furthermore, in our work<sup>10</sup> all of the structural parameters of the polymer chain have been directly connected with the polymerization conditions, so the chain microstructure can easily be predicted in accordance with the reaction variables.

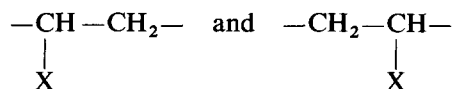
Recently, the non-steady-state kinetics approach to configurational sequences has been extended to deal with the microstructure of polydienes<sup>13,14</sup>, and the theoretical

conclusions have been corroborated qualitatively by n.m.r. and i.r. data<sup>15</sup>.

There is still another sort of structural isomerism in polymers involving head-to-tail, head-to-head and tail-to-tail addition of an asymmetrical monomer unit. A fine statistical description of directional isomerism was formulated by Meares<sup>16</sup> more than 20 years ago. In 1983, Cais *et al.*<sup>17</sup> made a probabilistic treatment as well, and demonstrated their application to fluorinated polymers. Both authors<sup>16,17</sup> restricted their attention to infinite chains because of the assumption of statistical stationarity. This paper studies the same problem in terms of the non-steady-state kinetic technique. The expressions for various chain structural parameters obtained are appropriate to every stage of the polymerization, and can be simplified into those derived from statistics when the polymer chain length approaches infinity. It is evident that the kinetic description of directional isomerism given in this work is superior to the probabilistic one, especially for oligomers.

## KINETIC DIFFERENTIAL EQUATIONS AND SEQUENCE DISTRIBUTION

Some monomeric units have a sense of direction in the polymer chains. For instance, with vinyl polymers the monomer can add as



Such a monomer is commonly denoted by HT, in which H means the head (the substituted carbon) and T indicates the tail (the unsubstituted carbon). In the polymerization of these monomers there are two different active species and four possible types of placements, resulting in three different chain microstructures, i.e.

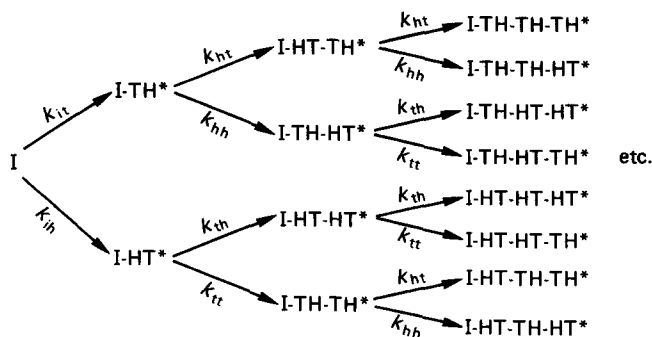


Figure 1 The reaction scheme

head-to-tail, head-to-head and tail-to-tail structures. For the anionic polymerization of these monomers without transfer and termination, the reaction scheme is shown in Figure 1.  $I$  denotes the residual concentration of initiator and the monomer concentration  $[HT]$  is omitted; the asterisk symbolizes the active site of the species. Here  $k_{it}$  and  $k_{ih}$  are the respective rate constants for the initiating molecules to attack the monomer producing two different species;  $k_{th}$  is one of the rate constants for chain propagation, subscripts t and h indicating that the head of the monomer adds to the growing species with unsubstituted carbon at the chain end;  $k_{tt}$ ,  $k_{hh}$  and  $k_{ht}$  have similar meanings.

We adopt the nomenclature shown in Table 1, where  $P_0^*$ ,  $Q_0^*$ ,  $P_n^*$ ,  $Q_n^*$ ,  $B^*$  and  $D^*$  represent respectively the pertinent active sequences at the chain end;  $P_n'$ ,  $Q_n'$ ,  $B'$  and  $D'$  denote respectively the relative terminated sequences except those at the chain end. Then, the set of kinetic differential equations adapted to the above scheme is as follows:

$$dI/dt = -(k_{it} + k_{ih})I[HT] \quad (1)$$

$$dP_0^*/dt = k_{it}I[HT] - (k_{ht} + k_{hh})P_0^*[HT] \quad (2)$$

$$dQ_0^*/dt = k_{ih}I[HT] - (k_{th} + k_{tt})Q_0^*[HT] \quad (3)$$

$$dP_1^*/dt = k_{ht}P_0^*[HT] + k_{ht}B^*[HT] - (k_{ht} + k_{hh})P_1^*[HT] \quad (4)$$

$$dP_n^*/dt = k_{ht}P_{n-1}^*[HT] - (k_{ht} + k_{hh})P_n^*[HT] \quad (5)$$

$$dQ_1^*/dt = k_{th}Q_0^*[HT] + k_{th}D^*[HT] - (k_{th} + k_{tt})Q_1^*[HT] \quad (6)$$

$$dQ_n^*/dt = k_{th}Q_{n-1}^*[HT] - (k_{th} + k_{tt})Q_n^*[HT] \quad (7)$$

$$dB^*/dt = k_{tt} \left( Q_0^* + D^* + \sum_{n=1}^{\infty} Q_n^* \right) [HT] - (k_{ht} + k_{hh})B^*[HT] \quad (8)$$

$$dD^*/dt = k_{hh} \left( P_0^* + B^* + \sum_{n=1}^{\infty} P_n^* \right) [HT] - (k_{th} + k_{tt})D^*[HT] \quad (9)$$

$$dP_n'/dt = k_{hh}P_n^*[HT] \quad (10)$$

$$dQ_n'/dt = k_{tt}Q_n^*[HT] \quad (11)$$

$$dB'/dt = (k_{ht} + k_{hh})B^*[HT] \quad (12)$$

$$dD'/dt = (k_{th} + k_{tt})D^*[HT] \quad (13)$$

$$d \sum_{n=1}^{\infty} P_n^*/dt = k_{ht}(P_0^* + B^*)[HT] - k_{hh}[HT] \sum_{n=1}^{\infty} P_n^* \quad (14)$$

$$d \sum_{n=1}^{\infty} Q_n^*/dt = k_{th}(Q_0^* + D^*)[HT] - k_{tt}[HT] \sum_{n=1}^{\infty} Q_n^* \quad (15)$$

$$d[HT]/dt = -(k_{it} + k_{ih})I[HT] - (k_{ht} + k_{hh})[HT] \times \left( P_0^* + B^* + \sum_{n=1}^{\infty} P_n^* \right) - (k_{th} + k_{tt})[HT] \left( Q_0^* + D_0^* + \sum_{n=1}^{\infty} Q_n^* \right) \quad (16)$$

The initial conditions for the set of equations are:

$$I|_{t=0} = I_0 \quad [HT]|_{t=0} = [HT]_0 \quad P_{n \geq 0}^*|_{t=0} = 0 \\ Q_{n \geq 0}^*|_{t=0} = 0 \quad P_{n \geq 0}'|_{t=0} = 0 \quad Q_{n \geq 0}'|_{t=0} = 0$$

where  $I_0$  and  $[HT]_0$  are the initial concentrations of the initiator and monomer, respectively. By introducing the following variable transformation:

$$x = \int_0^t [HT] dt \quad (17)$$

the set of equations (1)–(16) can be transformed into a linear one. Solving these linear differential equations (cf. Appendix), we obtain:

$$\sum_{n=1}^{\infty} P_n^* = I_0 k_{ht} \left( \frac{c}{K_1} + \alpha_1 e^{-K_1 x} + \frac{\beta}{K_1 - K_3} e^{-K_3 x} + \frac{c + \beta}{K_1 - K_4} e^{-K_4 x} \right) \quad (18)$$

$$\sum_{n=1}^{\infty} Q_n^* = I_0 k_{th} \left( \frac{1-c}{K_2} + \alpha_2 e^{-K_2 x} - \frac{\beta}{K_2 - K_3} e^{-K_3 x} + \frac{1-c-\beta}{K_2 - K_4} e^{-K_4 x} \right) \quad (19)$$

$$B^* = I_0 k_{tt} \left[ \frac{1-c}{K_1} - \left( \frac{K_4}{K_1(K_1 - K_4)} - \alpha_1 \right) e^{-K_1 x} - \frac{\beta}{K_1 - K_3} e^{-K_3 x} + \frac{1-c-\beta}{K_1 - K_4} e^{-K_4 x} \right] \quad (20)$$

$$D^* = I_0 k_{hh} \left[ \frac{c}{K_2} - \left( \frac{K_4}{K_2(K_2 - K_4)} - \alpha_2 \right) e^{-K_2 x} + \frac{\beta}{K_2 - K_3} e^{-K_3 x} + \frac{c + \beta}{K_2 - K_4} e^{-K_4 x} \right] \quad (21)$$

where we have put

$$K_4 = k_{it} + k_{ih} \quad a = k_{ht}/K_1 \\ b = k_{th}/K_2 \quad c = k_{tt}/K_3$$

Table 1 Nomenclature

Notation	Sequences
$P_0^*$	I-TH*
$Q_0^*$	I-HT*
$P_n^*$	... HT-TH-TH-TH-TH-... TH-TH-TH*
$Q_n^*$	... TH-HT-HT-HT-HT-... HT-HT-HT*
$P_n'$	... HT-TH-TH-TH-TH-... TH-TH-TH-HT-...
$Q_n'$	... TH-HT-HT-HT-HT-... HT-HT-HT-TH-...
$B^*$	... HT-TH*
$D^*$	... TH-HT*
$B'$	... HT-HT...
$D'$	... TH-HT...

$$\alpha_1 = \frac{k_{it}K_1 - k_{tt}K_4}{K_1(K_1 - K_3)(K_1 - K_4)}$$

$$\alpha_2 = \frac{k_{ih}K_2 - k_{hh}K_4}{K_2(K_2 - K_3)(K_2 - K_4)}$$

$$\beta = \frac{k_{ih}k_{tt} - k_{it}k_{hh}}{K_3(K_3 - K_4)}$$

Subsequently, the size distribution functions for the active head-to-tail and tail-to-head sequence are derived:

$$P_n^* = I_0 \left[ (1-a)ca^n \Gamma_{K_1x}(n+1) - \frac{k_{it}\beta}{K_1 - K_3} \left( \frac{k_{ht}}{K_1 - K_3} \right)^n e^{-K_3x} \Gamma_{(K_1 - K_3)x}(n+1) + \frac{(K_4 - k_{hh})(c + \beta)}{K_1 - K_4} \left( \frac{k_{ht}}{K_1 - K_4} \right)^n e^{-K_4x} \Gamma_{(K_1 - K_4)x}(n+1) \right] \quad (22)$$

$$Q_n^* = I_0 \left[ (1-b)cb^n \Gamma_{K_2x}(n+1) + \frac{k_{hh}\beta}{K_2 - K_3} \left( \frac{k_{th}}{K_2 - K_3} \right)^n e^{-K_3x} \Gamma_{(K_2 - K_3)x}(n+1) + \frac{(K_4 - k_{tt})(1 - c - \beta)}{K_2 - K_4} \left( \frac{k_{th}}{K_2 - K_4} \right)^n e^{-K_4x} \Gamma_{(K_2 - K_4)x}(n+1) \right] \quad (23)$$

where

$$\Gamma_{Kx}(n) = e^{-Kx} \sum_{i=n}^{\infty} \frac{(Kx)^i}{i!}$$

or

$$\Gamma_{Kx}(n) = \frac{1}{(n-1)!} \int_0^x (Kx)^{n-1} e^{-Kx} d(Kx)$$

is the incomplete gamma function.

For the terminated head-to-tail and tail-to-head sequence and head-to-head and tail-to-tail enchainment, the following expressions are obtained:

$$P_n' = I_0 k_{hh} \left\{ \frac{a^n}{K_1} \left[ ck_{hh} \left( x - \frac{n+1}{K_1} \right) - c\beta + \left( 1 - \frac{k_{hh}}{K_4} \right) (c + \beta) \right] \Gamma_{K_1x}(n+1) + \frac{c\beta}{K_1 - K_3} \left( \frac{k_{ht}}{K_1 + K_3} \right)^n e^{-K_3x} \Gamma_{(K_1 - K_3)x}(n+1) - \frac{(K_4 - K_{hh})(c + \beta)}{K_4(K_1 - K_4)} \left( \frac{k_{ht}}{K_1 - K_4} \right)^n e^{-K_4x} \Gamma_{(K_1 - K_4)x}(n+1) + (1-a)c \left( \frac{k_{ht}}{K_1} \right)^n \frac{x^{n+1}}{n!} e^{-K_1x} \right\} \quad (24)$$

$$Q_n' = I_0 k_{tt} \left\{ \frac{b^n}{K_2} \left[ ck_{tt} \left( x - \frac{n+1}{K_2} \right) - (1-c)\beta + \left( 1 - \frac{k_{tt}}{K_4} \right) (1-c-\beta) \right] \Gamma_{K_2x}(n+1) - \frac{(1-c)\beta}{K_2 - K_3} \left( \frac{k_{th}}{K_2 - K_3} \right)^n e^{-K_3x} \Gamma_{(K_2 - K_3)x}(n+1) + (1-b)c \left( \frac{k_{th}}{K_2} \right)^n \frac{x^{n+1}}{n!} e^{-K_2x} \right\} \quad (25)$$

$$B' = I_0 k_{tt} \left[ (1-c)x - \left( \frac{K_4}{K_1(K_1 - K_4)} - \alpha_1 \right) (e^{-K_1x} - 1) + \frac{K_1\beta}{K_3(K_1 - K_3)} (e^{-K_3x} - 1) + \frac{K_1(1-c-\beta)}{K_4(K_1 - K_4)} (e^{-K_4x} - 1) \right] \quad (26)$$

$$D' = I_0 k_{hh} \left[ cx - \left( \frac{K_4}{K_2(K_2 - K_4)} - \alpha_2 \right) (e^{-K_2x} - 1) - \frac{K_2\beta}{K_3(K_2 - K_3)} (e^{-K_3x} - 1) + \frac{K_2(c + \beta)}{K_4(K_2 - K_4)} (e^{-K_4x} - 1) \right] \quad (27)$$

The size distribution function for the total head-to-tail sequence is:

$$P_n = P_n^* + P_n' \quad (28)$$

Similarly, for the total tail-to-head sequence, tail-to-tail and head-to-head enchainment, we have:

$$Q_n = Q_n^* + Q_n' \quad (29)$$

$$B = B^* + B' \quad (30)$$

$$D = D^* + D' \quad (31)$$

On the basis of the equations given above, the other microstructural parameters can be derived easily.

### THE OTHER MICROSTRUCTURAL PARAMETERS

In order to gain insight into the microstructure of polymers with directional isomerism, we need to obtain the various statistical moments for the growing and terminated sequences from the corresponding sequence size distribution functions, which are as follows:

$$\sum_{n=1}^{\infty} n P_n^* = I_0 k_{ht} \left( \frac{c}{k_{hh}} (1 - e^{-k_{hh}x}) - \frac{\beta}{k_{tt}} (e^{-K_3x} - 1) - \frac{c + \beta}{k_{hh} - K_4} (e^{-K_4x} - 1) \right) \quad (32)$$

$$\sum_{n=1}^{\infty} n Q_n^* = I_0 k_{th} \left( \frac{1-c}{k_{tt}} (1 - e^{-k_{tt}x}) + \frac{\beta}{k_{hh}} (e^{-K_3x} - 1) - \frac{1-c-\beta}{k_{tt} - K_4} (e^{-K_4x} - 1) \right) \quad (33)$$

$$\sum_{n=1}^{\infty} P_n' = I_0 k_{ht} \left[ \frac{c}{K_1} (k_{hh}x - 1) - \alpha_1 [a + (1-a)e^{-K_1x}] - \frac{\beta}{K_1 - K_3} [c + (1-c)e^{-K_3x}] + \frac{c + \beta}{K_1 - K_4} \left( 1 + \frac{k_{hh}}{K_4} (e^{-K_4x} - 1) \right) \right] \quad (34)$$

$$\sum_{n=1}^{\infty} Q'_n = I_0 k_{th} \left[ \frac{1-c}{K_2} (k_{tt} x - 1) - \alpha_2 [b + (1-b) e^{-K_2 x}] + \frac{\beta}{K_2 - K_3} [1 + c(e^{-K_3 x} - 1)] + \frac{1-c-\beta}{K_2 - K_4} \left( 1 + \frac{k_{tt}}{K_4} (e^{-K_4 x} - 1) \right) \right] \quad (35)$$

$$\sum_{n=1}^{\infty} nP'_n = I_0 k_{ht} \left( cx + \frac{c}{k_{hh}} (e^{-k_{hh} x} - 1) + \frac{(1-c)\beta}{k_{tt}} (e^{-K_3 x} - 1) + \frac{k_{hh}(c+\beta)}{K_4(k_{hh} - K_4)} (e^{-K_4 x} - 1) \right) \quad (36)$$

$$\sum_{n=1}^{\infty} nQ'_n = I_0 k_{th} \left( (1-c)x + \frac{1-c}{k_{tt}} (e^{-k_{tt} x} - 1) - \frac{c\beta}{k_{hh}} (e^{-K_3 x} - 1) + \frac{k_{tt}(1-c-\beta)}{K_4(k_{tt} - K_4)} (e^{-K_4 x} - 1) \right) \quad (37)$$

The expressions for  $\sum_{n=1}^{\infty} P_n^*$  and  $\sum_{n=1}^{\infty} Q_n^*$  have been given in equations (18) and (19). Thus, the statistical moments of the total head-to-tail and tail-to-head sequences are:

$$\sum_{n=1}^{\infty} P_n = I_0 k_{ht} \left[ (1-a)cx + \alpha_1 (e^{-K_1 x} - 1) + \frac{c\beta}{K_1 - K_3} (e^{-K_3 x} - 1) - \left( 1 - \frac{k_{hh}}{K_4} \right) \left( \frac{c+\beta}{K_1 - K_4} \right) (e^{-K_4 x} - 1) \right] \quad (38)$$

$$\sum_{n=1}^{\infty} nP_n = I_0 k_{ht} \left( cx - \frac{\beta}{K_3} (e^{-K_3 x} - 1) + \frac{c+\beta}{K_4} (e^{-K_4 x} - 1) \right) \quad (39)$$

$$\sum_{n=1}^{\infty} Q_n = I_0 k_{th} \left[ (1-b)(1-c)x + b\alpha_2 (e^{-K_2 x} - 1) - \frac{(1-c)\beta}{K_2 - K_3} (e^{-K_3 x} - 1) - \left( 1 - \frac{k_{tt}}{K_4} \right) \left( \frac{1-c-\beta}{K_2 - K_4} \right) (e^{-K_4 x} - 1) \right] \quad (40)$$

$$\sum_{n=1}^{\infty} nQ_n = I_0 k_{th} \left( (1-c)x + \frac{\beta}{K_3} (e^{-K_3 x} - 1) + \frac{1-c-\beta}{K_4} (e^{-K_4 x} - 1) \right) \quad (41)$$

The average length of the head-to-tail and tail-to-head sequence is defined as:

$$\langle l \rangle = \frac{\sum_{n=1}^{\infty} nP_n + \sum_{n=1}^{\infty} nQ_n}{\sum_{n=1}^{\infty} P_n + \sum_{n=1}^{\infty} Q_n} \quad (42)$$

Substituting (38)–(41) into (42), the explicit expression for  $\langle l \rangle$  is derived (omitted here).

As the matter of fact, the head-to-tail and tail-to-head sequences cannot be discriminated by experimental data,

so we take them as one kind of orienticity sequence. Letting  $f(\text{H-T})$ ,  $f(\text{H-H})$  and  $f(\text{T-T})$  denote respectively the fractions of head-to-tail, head-to-head and tail-to-tail dyads, we obtain the following expressions:

$$f(\text{H-T}) = \frac{\sum_{n=1}^{\infty} n(P_n + Q_n)}{B + D + \sum_{n=1}^{\infty} n(P_n + Q_n)} = \{ [k_{th} + (k_{ht} - k_{th})c] K_3 K_4 x + K_4 \beta (k_{th} - k_{ht}) (e^{-K_3 x} - 1) + K_3 [k_{th} + (k_{ht} - k_{th})(c + \beta)] (e^{-K_4 x} - 1) \} / \{ [K_2 + (K_1 - K_2)c] K_3 K_4 x + K_4 \beta (K_2 - K_1) \times (e^{-K_3 x} - 1) + [K_2 + (K_1 - K_2)(c + \beta)] K_3 (e^{-K_4 x} - 1) \} \quad (43)$$

$$f(\text{H-H}) = \frac{D}{B + D + \sum_{n=1}^{\infty} n(P_n + Q_n)} = k_{hh} [c K_3 K_4 x - K_4 \beta (e^{-K_3 x} - 1) + K_3 (1-c-\beta) (e^{-K_4 x} - 1)] / \{ [K_2 + (K_1 - K_2)c] K_3 K_4 x + K_4 \beta (K_2 - K_1) \times (e^{-K_3 x} - 1) + [K_2 + (K_1 - K_2)(c + \beta)] K_3 (e^{-K_4 x} - 1) \} \quad (44)$$

$$f(\text{T-T}) = \frac{B}{B + D + \sum_{n=1}^{\infty} n(P_n + Q_n)} = k_{tt} [(1-c) K_3 K_4 x + K_4 \beta (e^{-K_3 x} - 1) + K_3 (c + \beta) (e^{-K_4 x} - 1)] / \{ [K_2 + (K_1 - K_2)c] K_3 K_4 x + K_4 \beta (K_2 - K_1) \times (e^{-K_3 x} - 1) + [K_2 + (K_1 - K_2)(c + \beta)] K_3 (e^{-K_4 x} - 1) \} \quad (45)$$

For the sake of convenience, let  $C(\text{H-TH-T})$ ,  $C(\text{T-TH-T})$ ,  $C(\text{H-TH-H})$  and  $C(\text{H-HT-T})$  be the respective numbers of the four kinds of triads, and  $f(\text{H-TH-T})$ ,  $f(\text{T-TH-T})$ ,  $f(\text{H-TH-H})$  and  $f(\text{H-HT-T})$  be the corresponding fractions of the different triads. Then

$$f(\text{H-TH-T}) = \frac{C(\text{H-TH-T})}{C(\text{H-TH-T}) + C(\text{T-TH-T}) + C(\text{H-HT-H}) + C(\text{H-HT-T})} \quad (46)$$

$$f(\text{T-TH-T}) = \frac{C(\text{T-TH-T})}{C(\text{H-TH-T}) + C(\text{T-TH-T}) + C(\text{H-HT-H}) + C(\text{H-HT-T})} \quad (47)$$

$$f(\text{H-HT-H}) = \frac{C(\text{H-HT-H})}{C(\text{H-TH-T}) + C(\text{T-TH-T}) + C(\text{H-HT-H}) + C(\text{H-HT-T})} \quad (48)$$

$$f(\text{H-HT-T}) = \frac{C(\text{H-HT-T})}{C(\text{H-TH-T}) + C(\text{T-TH-T}) + C(\text{H-HT-H}) + C(\text{H-HT-T})} \quad (49)$$

where

$$\begin{aligned}
 C(\text{H-TH-T}) &= \sum_{n=1}^{\infty} (n-1)(P_n + Q_n) \\
 &= I_0 \left[ [k_{\text{ht}}ac + k_{\text{th}}b(1-c)]x - k_{\text{ht}}\alpha\alpha_1(e^{-K_1x} - 1) \right. \\
 &\quad - k_{\text{th}}b\alpha_2(e^{-K_2x} - 1) \\
 &\quad + \frac{\beta}{K_3} \left( \frac{k_{\text{th}}^2}{K_2 - K_3} - \frac{k_{\text{ht}}^2}{K_1 - K_3} \right) (e^{-K_3x} - 1) \\
 &\quad \left. + \frac{1}{K_4} \left( \frac{k_{\text{ht}}^2(c+\beta)}{K_1 - K_4} + \frac{k_{\text{th}}^2(1-c-\beta)}{K_2 - K_4} \right) (e^{-K_4x} - 1) \right] \quad (50)
 \end{aligned}$$

$$\begin{aligned}
 C(\text{T-TH-T}) &= \sum_{n=1}^{\infty} Q'_n + \frac{k_{\text{ht}}}{K_1} B' \\
 &= I_0 k_{\text{tt}} \left[ (a+b)(1-c)x + a \left( \alpha_1 - \frac{K_4}{K_1(K_1 - K_4)} \right) \right. \\
 &\quad \times (e^{-K_1x} - 1) - b\alpha_2(e^{-K_2x} - 1) \\
 &\quad + \frac{\beta}{K_3} \left( \frac{k_{\text{ht}}}{K_1 - K_3} + \frac{k_{\text{th}}}{K_2 - K_3} \right) (e^{-K_3x} - 1) \\
 &\quad \left. + \frac{1-c-\beta}{K_4} \left( \frac{k_{\text{ht}}}{K_1 - K_4} + \frac{k_{\text{th}}}{K_2 - K_4} \right) (e^{-K_4x} - 1) \right] \quad (51)
 \end{aligned}$$

Explicitly, as shown in Figure 1, the triad (T-TH-T) arises from the terminated tail-to-head sequence and a portion of the terminated tail-to-tail sequence. Similarly,

$$\begin{aligned}
 C(\text{H-HT-H}) &= \sum_{n=1}^{\infty} P'_n + \frac{k_{\text{th}}}{K_2} D' \\
 &= I_0 k_{\text{hh}} \left[ (a+b)cx - \alpha\alpha_1(e^{-K_1x} - 1) \right. \\
 &\quad + b \left( \alpha_2 - \frac{K_4}{K_2(K_2 - K_4)} \right) (e^{-K_2x} - 1) \\
 &\quad - \frac{\beta}{K_3} \left( \frac{k_{\text{ht}}}{K_1 - K_3} + \frac{k_{\text{th}}}{K_2 - K_3} \right) (e^{-K_3x} - 1) \\
 &\quad \left. + \frac{c+\beta}{K_4} \left( \frac{k_{\text{ht}}}{K_1 - K_4} + \frac{k_{\text{th}}}{K_2 - K_4} \right) (e^{-K_4x} - 1) \right] \quad (52)
 \end{aligned}$$

$$\begin{aligned}
 C(\text{H-HT-T}) &= \frac{k_{\text{hh}}}{K_1} B' + \frac{k_{\text{tt}}}{K_2} D' \\
 &= I_0 k_{\text{hh}} k_{\text{tt}} \left[ (2-a-b) \frac{x}{K_3} \right. \\
 &\quad + \frac{1}{K_1} \left( \alpha_1 - \frac{K_4}{K_1(K_1 - K_4)} \right) (e^{-K_1x} - 1) \\
 &\quad + \frac{1}{K_2} \left( \alpha_2 - \frac{K_4}{K_2(K_2 - K_4)} \right) (e^{-K_2x} - 1) \\
 &\quad + \frac{(K_1 - K_2)\beta}{K_3(K_1 - K_3)(K_2 - K_3)} (e^{-K_3x} - 1) \\
 &\quad \left. + \frac{1}{K_4} \left( \frac{1-c-\beta}{K_1 - K_4} + \frac{c+\beta}{K_2 - K_4} \right) (e^{-K_4x} - 1) \right] \quad (53)
 \end{aligned}$$

Tetrads and pentads can be, of course, derived from the statistical moments as well. However, their expressions are much more complicated than those of dyads and triads, and are omitted here.

#### DETERMINATION OF VARIABLE $x$ AND NUMERICAL COMPUTATION

All microstructural parameters given in the preceding sections depend on variable  $x$ . Therefore, it is important to determine the value of  $x$  from the polymerization conditions. From (16) and (17) we obtain:

$$\begin{aligned}
 [\text{HT}] &= [\text{HT}]_0 - I_0 \left[ [cK_1 + (1-c)K_2]x \right. \\
 &\quad + \frac{K_1 - K_2}{K_3} \beta (e^{-K_3x} - 1) \\
 &\quad \left. - \left( 1 - \frac{K_2 + (K_1 - K_2)(c+\beta)}{K_4} \right) (e^{-K_4x} - 1) \right] \quad (54)
 \end{aligned}$$

Substituting equation (54) into the definition of monomer conversion,  $y = ([\text{HT}]_0 - [\text{HT}]) / [\text{HT}]_0$ , gives:

$$\begin{aligned}
 y &= \frac{I_0}{[\text{HT}]_0} \left[ [cK_1 + (1-c)K_2]x + \frac{K_1 - K_2}{K_3} \beta (e^{-K_3x} - 1) \right. \\
 &\quad \left. - \left( 1 - \frac{K_2 + (K_1 - K_2)(c+\beta)}{K_4} \right) (e^{-K_4x} - 1) \right] \quad (55)
 \end{aligned}$$

On the other hand, the relationship between  $x$  and polymerization time  $t$  may be derived from equations (17) and (55):

$$t = \int_0^x \frac{dx}{[\text{HT}]_0} \quad (56)$$

By the aid of computer, it is rather easy to calculate the value of  $x$  from the initial concentrations of initiator and monomer, and monomer conversion or reaction time.

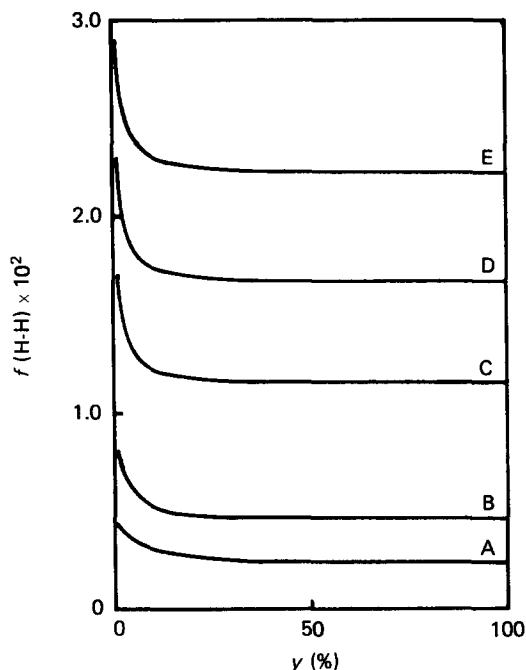
Consequently, we can estimate the microstructural parameters of polymers with directional isomerism from the polymerization conditions. For example Figures 2 and 3 show the dependences of the tail-to-tail and head-to-head dyad fractions on the monomer conversion at various propagation rate constants, which indicates that at the start of polymerization the fraction of head-to-head dyad declines and the fraction of tail-to-tail dyad increases, and the fractions of both dyads finally tend to the same equilibrium value. In contrast, the fraction of head-to-tail dyad is constant during the whole polymerization process, as shown in Figure 4.

The plots for the fraction of triads against the monomer conversion, as given in Figures 5-8, indicate that except for triad (H-TH-T) the other triads augment to various degrees with increasing monomer conversion.

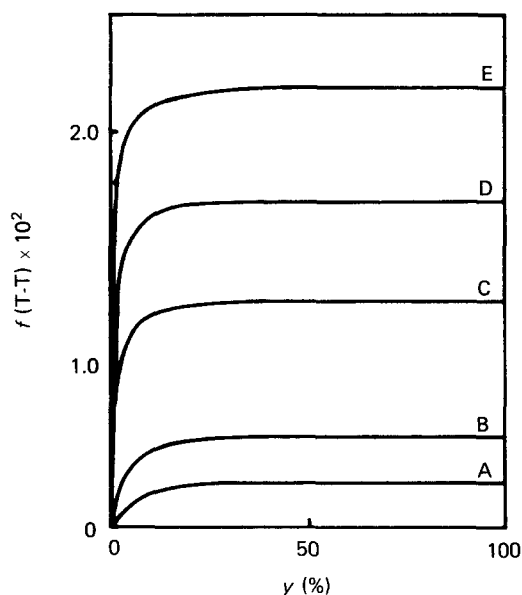
The weight distribution function of the head-to-tail sequence, defined as

$$W_n = n(P_n + Q_n) / \left( B + D + \sum_{n=1}^{\infty} nP_n + \sum_{n=1}^{\infty} nQ_n \right)$$

can be computed as well from the polymerization conditions. Figure 9 demonstrates that the higher the monomer conversion, the wider the sequence distribution. In addition, the initial concentration ratio of the initiator to monomer considerably affects the shape of the sequence distribution curve, as shown in Figure 10.



**Figure 2** The fraction of tail-to-tail dyad vs. monomer conversion at various propagation rate constants:  $k_{ht}=k_{th}=10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{it}=1.0 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{ih}=0.05 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $I_0=10^{-3} \text{ mol l}^{-1}$ ;  $[\text{HT}]_0=1.0 \text{ mol l}^{-1}$ ; and  $k_{tt}=k_{hh}=5.0$  (A), 10 (B), 30 (C), 50 (D) and  $80 \text{ l mol}^{-1} \text{ s}^{-1}$  (E)

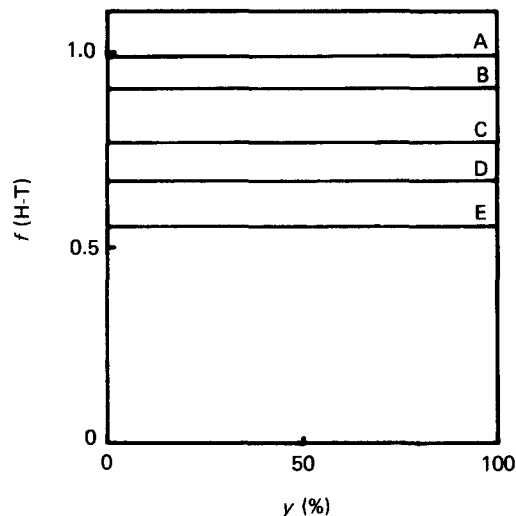


**Figure 3** The fraction of head-to-head dyad vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2

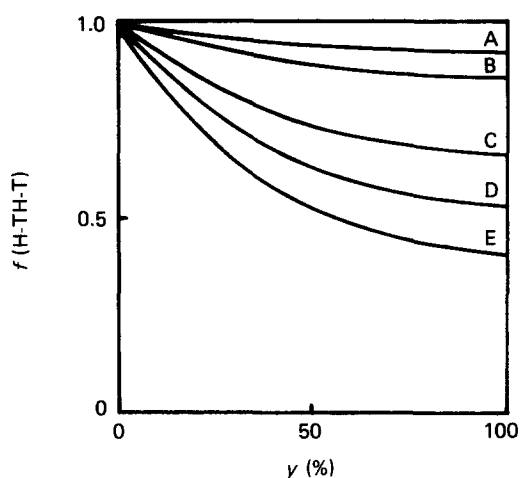
Similarly, Figures 11 and 12 illustrate respectively the effect of the initiation and propagation rate constants on the sequence distribution.

## DISCUSSION

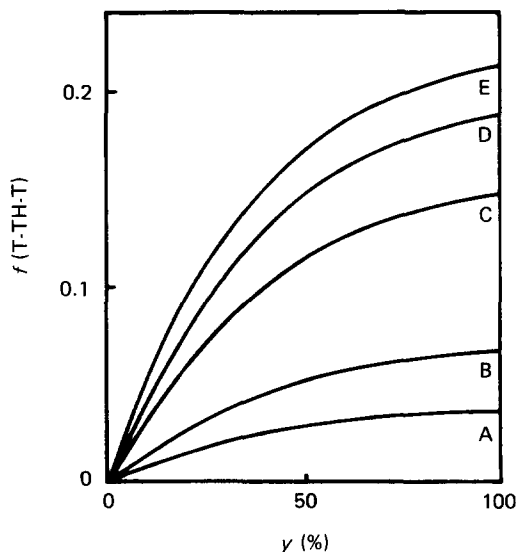
The dyad and triad functions have been derived by Meares using the probability method<sup>16</sup>. It is interesting that the formulae reported are simply the limits of the



**Figure 4** The fraction of head-to-tail dyad vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2



**Figure 5** The fraction of triad (H-TH-T) vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2



**Figure 6** The fraction of triad (H-HT-H) vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2

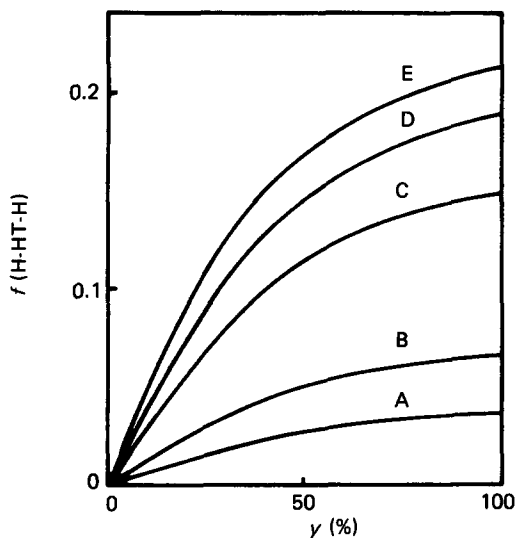


Figure 7 The fraction of triad (T-TH-T) vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2

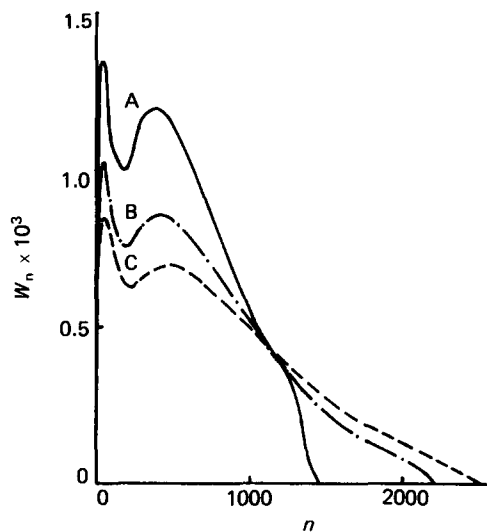


Figure 10 Curves of weight distribution for head-to-tail sequence at various initial concentration ratios of initiator to monomer:  $y=100\%$ ; (A)  $I_0/[HT]_0=10^{-3}$ , (B)  $I_0/[HT]_0=5 \times 10^{-4}$ , (C)  $I_0/[HT]_0=10^{-4}$ ; the others are identical with those in Figure 9

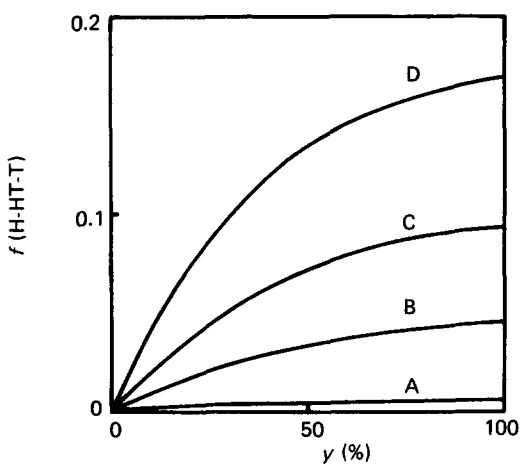


Figure 8 The fraction of triad (H-HT-T) vs. monomer conversion at various propagation rate constants. Reaction conditions are identical with those in Figure 2

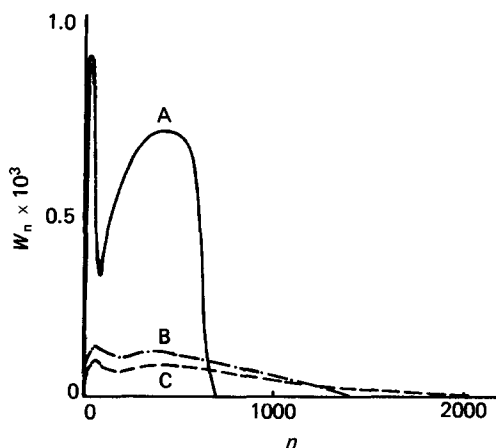


Figure 11 Curves of weight distribution for head-to-tail sequence at various initiation rate constants:  $y=100\%$ ; (A)  $k_{it}=0.4 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{ih}=0.02 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (B)  $k_{it}=1.0 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{ih}=0.05 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (C)  $k_{it}=2.0 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{ih}=0.1 \text{ l mol}^{-1} \text{ s}^{-1}$ ; the others are identical with those in Figure 9

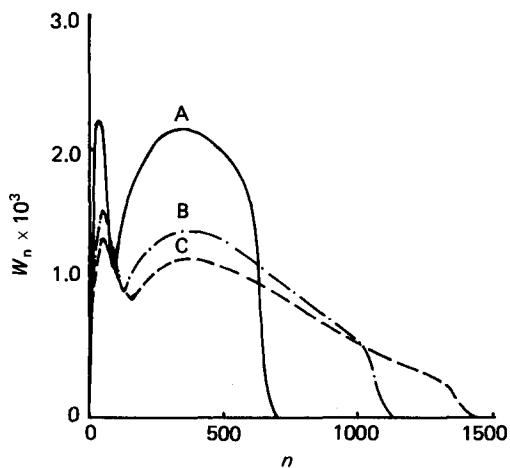


Figure 9 Curves of weight distribution for head-to-tail sequence at various monomer conversions:  $k_{ht}=10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{hh}=k_{tt}=2.01 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (A)  $y=50\%$ , (B)  $y=80\%$ , (C)  $y=100\%$ ; the others are identical with those in Figure 2

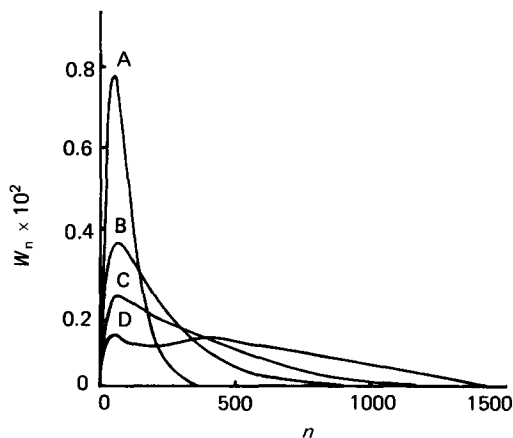


Figure 12 Curves of weight distribution for head-to-tail sequence at various propagation rate constants:  $y=100\%$ ; (A)  $k_{ht}=100 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (B)  $k_{ht}=300 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (C)  $k_{ht}=500 \text{ l mol}^{-1} \text{ s}^{-1}$ ; (D)  $k_{ht}=10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ ; the others are identical with those in Figure 9

pertinent expressions in this work:

$$\lim_{x \rightarrow \infty} f(\text{H-T}) = \frac{a+b-2ab}{2-a-b} \quad (57)$$

$$\lim_{x \rightarrow \infty} f(\text{H-H}) = \frac{(1-a)(1-b)}{2-a-b} \quad (58)$$

$$\lim_{x \rightarrow \infty} f(\text{T-T}) = \frac{(1-a)(1-b)}{2-a-b} \quad (59)$$

where the fractions of head-to-head and tail-to-tail dyads are identified with each other in the case  $x \rightarrow \infty$ .

Similarly, for triads we have:

$$\lim_{x \rightarrow \infty} f(\text{H-TH-T}) = \frac{a^2+b^2-ab(a+b)}{2-a-b} \quad (60)$$

$$\lim_{x \rightarrow \infty} f(\text{T-TH-T}) = \frac{(a+b)(1-a)(1-b)}{2-a-b} \quad (61)$$

$$\lim_{x \rightarrow \infty} f(\text{H-HT-H}) = \frac{(a+b)(1-a)(1-b)}{2-a-b} \quad (62)$$

$$\lim_{x \rightarrow \infty} f(\text{H-HT-T}) = (1-a)(1-b) \quad (63)$$

As is known, the statistical description of directional isomerism suffers from the limitation of a stationary assumption suitable for polymers with infinite chain length. The non-steady-state kinetic theory not only throws comprehensive light on the whole polymerization process without any presumptions, but also connects the molecular parameters with the reaction conditions, so that one can predict the chain microstructure from the initial conditions. The experimental test of the theory will be reported in later communications of this series.

## APPENDIX 1

From equations (1)–(17) we obtain the set of linear differential equations:

$$dI/dx = -(k_{it} + k_{ih})I \quad (A1)$$

$$dP_0^*/dx = k_{it}I - (k_{ht} + k_{hh})P_0^* \quad (A2)$$

$$dQ_0^*/dx = k_{ih}I - (k_{th} + k_{tt})Q_0^* \quad (A3)$$

$$dP_1^*/dx = k_{ht}(P_0^* + B^*) - (k_{ht} + k_{hh})P_1^* \quad (A4)$$

$$dP_n^*/dx = k_{ht}P_{n-1}^* - (k_{ht} + k_{hh})P_n^* \quad (A5)$$

$$dQ_1^*/dx = k_{th}(Q_0^* + D^*) - (k_{th} + k_{tt})Q_1^* \quad (A6)$$

$$dQ_n^*/dx = k_{th}Q_{n-1}^* - (k_{th} + k_{tt})Q_n^* \quad (A7)$$

$$dB^*/dx = k_{tt}\left(Q_0^* + D^* + \sum_{n=1}^{\infty} Q_n^*\right) - (k_{ht} + k_{hh})B^* \quad (A8)$$

$$dD^*/dx = k_{hh}\left(P_0^* + B^* + \sum_{n=1}^{\infty} P_n^*\right) - (k_{th} + k_{tt})D^* \quad (A9)$$

$$dP'_n/dx = k_{hh}P_n^* \quad (A10)$$

$$dQ'_n/dx = k_{tt}Q_n^* \quad (A11)$$

$$dB'/dx = (k_{ht} + k_{hh})B^* \quad (A12)$$

$$dD'/dx = (k_{th} + k_{tt})D^* \quad (A13)$$

$$d \sum_{n=1}^{\infty} P_n^*/dx = k_{ht}(P_0^* + B^*) - k_{hh} \sum_{n=1}^{\infty} P_n^* \quad (A14)$$

$$d \sum_{n=1}^{\infty} Q_n^*/dx = k_{th}(Q_0^* + D^*) - k_{tt} \sum_{n=1}^{\infty} Q_n^* \quad (A15)$$

$$d[\text{HT}]/dx = -(k_{ih} + k_{it})I - (k_{ht} + k_{hh})\left(P_0^* + B^* + \sum_{n=1}^{\infty} P_n^*\right) - (k_{th} + k_{tt})\left(Q_0^* + D^* + \sum_{n=1}^{\infty} Q_n^*\right) \quad (A16)$$

The corresponding initial conditions become:

$$\begin{aligned} I|_{x=0} &= I_0 & [\text{HT}]|_{x=0} &= [\text{HT}]_0 \\ P_{n \geq 0}^*|_{x=0} &= 0 & Q_{n \geq 0}^*|_{x=0} &= 0 & Q_{n \geq 0}'|_{x=0} &= 0 \\ P'_{n \geq 0}|_{x=0} &= 0 & Q'_{n \geq 0}|_{x=0} &= 0 \end{aligned}$$

Obviously, the polymerization system undergoes the following constraint condition:

$$P_0^* + Q_0^* + B^* + D^* + \sum_{n=1}^{\infty} P_n^* + \sum_{n=1}^{\infty} Q_n^* = I_0 - I \quad (A17)$$

By solving equations (A1)–(A3), we obtain:

$$I = I_0 e^{-(k_{it} + k_{ih})x} \quad (A18)$$

$$P_0^* = \frac{I_0 k_{it}}{k_{ht} + k_{hh} - k_{ih} - k_{it}} (e^{-(k_{it} + k_{ih})x} - e^{-(k_{ht} + k_{hh})x}) \quad (A19)$$

$$Q_0^* = \frac{I_0 k_{ih}}{k_{th} + k_{th} - k_{ih} - k_{it}} (e^{-(k_{it} + k_{ih})x} - e^{-(k_{th} + k_{tt})x}) \quad (A20)$$

Combining equations (A8), (A9), (A14), (A15) and (A16), we obtain the set of linearly independent equations:

$$d \sum_{n=1}^{\infty} P_n^*/dx = k_{ht}P_0^* - k_{hh} \sum_{n=1}^{\infty} P_n^* + k_{ht}B^* \quad (A21)$$

$$d \sum_{n=1}^{\infty} Q_n^*/dx = k_{th}[I_0 - (I + P_0^*)] - (k_{th} + k_{tt}) \sum_{n=1}^{\infty} Q_n^* - k_{th}\left(B^* + \sum_{n=1}^{\infty} P_n^*\right) \quad (A22)$$

$$dB/dx = k_{tt}[I_0 - (I + P_0^*)] - (k_{ht} + k_{hh})B^* - k_{tt}\left(B^* + \sum_{n=1}^{\infty} P_n^*\right) \quad (A23)$$

Equations (A21)–(A23) can be written as:

$$d\mathbf{Y}/d\mathbf{X} = \mathbf{A}\mathbf{Y} + \mathbf{f}(\mathbf{X}) \quad (A24)$$

where

$$\mathbf{Y} = \begin{pmatrix} \sum_{n=1}^{\infty} P_n^* \\ \sum_{n=1}^{\infty} Q_n^* \\ B^* \end{pmatrix}$$

$$\mathbf{A} = \begin{pmatrix} -k_{hh} & 0 & k_{ht} \\ -k_{th} & -k_{th} - k_{tt} & -k_{th} \\ -k_{tt} & 0 & -k_{tt} - k_{ht} - k_{hh} \end{pmatrix}$$

$$\mathbf{f}(\mathbf{X}) = \begin{pmatrix} k_{ht}P_0^* \\ k_{th}[I_0 - (I + P_0^*)] \\ k_{tt}[I_0 - (I + P_0^*)] \end{pmatrix}$$



The solution of (A24) is:

$$Y = P e^{BX} C + \int_0^X P e^{B(X-S)} P^{-1} f(S) dS \quad (A25)$$

where  $P e^{BX} C$  is the general solution of the homogeneous equation corresponding to (A25), and

$$P = \begin{pmatrix} 0 & 1 & k_{ht}(k_{th} - k_{hh}) \\ 1 & 0 & k_{th}(k_{tt} - k_{ht}) \\ 0 & -1 & -k_{tt}(k_{th} - k_{hh}) \end{pmatrix}$$

$$B = \begin{pmatrix} -k_{ht} - k_{hh} & & \\ & -k_{th} - k_{tt} & \\ & & -k_{tt} - k_{hh} \end{pmatrix}$$

$P^{-1} =$

$$\begin{pmatrix} 0 & -k_{tt}(K_1 - K_3) & -k_{ht}(K_1 - K_3) \\ (K_1 - K_3)(K_2 - K_3) & k_{th}(K_2 - K_3) & k_{th}(K_2 - K_3) \\ 0 & 1 & 1 \end{pmatrix}$$

and  $C$  is a zero matrix which is determined by the initial conditions. In the matrix  $P^{-1}$ , we have put

$$K_1 = k_{ht} + k_{hh}, \quad K_2 = k_{th} + k_{tt} \quad \text{and} \quad K_3 = k_{tt} + k_{hh}.$$

Therefore, the solution of (A24) is the expressions (18)–(20). By substituting (18)–(20) into (A17), equation (21) can be derived.

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