

Kinetic theory of directional isomerism in polymer chains: 2. Molecular-weight distribution

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In this work, polymerization with directional isomerism is studied theoretically by means of a non-steady-state method. The molecular-weight distribution function and some molecular parameters of the resulting polymer are rigorously derived. During the process of solving the kinetic differential equations, the Laplace transform and graph theory are employed. The theoretical results obtained are also applicable to anionic polymerization proceeding by a bimodal mechanism.

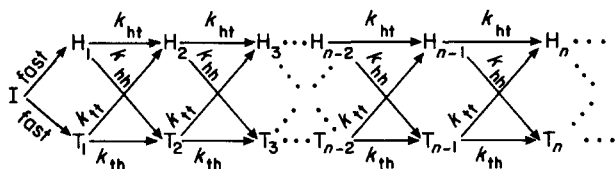
(Keywords: kinetics; isomerism; molecular weight distribution)

INTRODUCTION

Directional isomerism in polymer chains frequently occurs during the polymerization of some asymmetrical monomers, such as vinylidene fluoride¹, propylene oxide²⁻⁴ and phenyl glycidyl ether^{5,6}, and results in irregular sequences (head-to-head and tail-to-tail linkages) in the polymer chains. Several workers⁷⁻⁹ have studied, both experimentally and statistically, the chain microstructures of polymers with directional isomerism. In the first paper¹⁰ of this series, we dealt theoretically with the same problem in terms of a non-steady-state kinetic method, and connected the microstructural parameters of the polymer, such as the head-to-tail sequence distribution, average sequence length of head-to-tail structures, the concentrations of head-to-head and tail-to-tail enchainments and various dyad and triad fractions, with polymerization conditions, so that the microstructure of the resulting polymer can be predicted in accordance with reaction conditions. This work applies the same theoretical method to give rigorous expressions for the molecular size distribution and other molecular parameters for a polymerization with directional isomerism.

MOLECULAR SIZE DISTRIBUTION

For the anionic polymerization of asymmetrical monomers without transfer and termination, the reaction scheme can be given by:



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Here I denotes the initiator, and monomer M is omitted; H_n and T_n are the resultant n -mers with, respectively, the substituted and unsubstituted carbons at the growing chain ends; k_{ht} is one of the rate constants for chain propagation, subscripts h and t symbolizing that the tail (unsubstituted carbon) of a monomer adds to the growing species with substituted carbon at the chain end; k_{tt} , k_{th} and k_{hh} have similar meanings.

The set of kinetic differential equations corresponding to the scheme can be listed immediately:

$$dH_1/dt = -(k_{hh} + k_{ht})MH_1 \quad (1)$$

$$dH_n/dt = k_{ht}MH_{n-1} + k_{tt}MT_{n-1} - (k_{hh} + k_{ht})MH_n \quad (2)$$

$$dT_1/dt = -(k_{th} + k_{tt})MT_1 \quad (3)$$

$$dT_n/dt = k_{th}MT_{n-1} + k_{hh}MH_{n-1} - (k_{th} + k_{tt})MT_n \quad (4)$$

where *italics* are used to denote concentrations of the corresponding species, for simplicity of notation.

The initial conditions for the set of equations are:

$$M|_{t=0} = M_0 - I_0 \quad H_1|_{t=0} = H_0 \quad T_1|_{t=0} = T_0$$

$$H_{n>1}|_{t=0} = T_{n>1}|_{t=0} = 0$$

where I_0 and M_0 are the initial concentrations of the initiator and monomer respectively. In accordance with material balance and instantaneous initiation, we have:

$$\sum_{n=1}^{\infty} (H_n + T_n) = H_0 + T_0 = I_0 \quad (5)$$

Putting

$$x = \int_0^t M dt \quad (6)$$

equations (1)–(4) become:

$$dH_1/dx = -(k_{ht} + k_{hh})H_1 \quad (7)$$

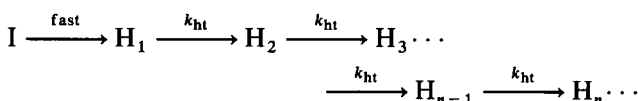
$$dH_n/dx = k_{ht}H_{n-1} + k_{tt}T_{n-1} - (k_{ht} + k_{hh})H_n \quad (8)$$

$$dT_1/dx = -(k_{th} + k_{tt})T_1 \quad (9)$$

$$dT_n/dx = k_{th}T_{n-1} + k_{hh}H_{n-1} - (k_{th} + k_{tt})T_n \quad (10)$$

A special case

When only one kind of propagation is overwhelmingly predominant in the polymerization, the reaction mechanism is:



which is the case of instantaneous initiation with no termination, that is, $k_{hh} = k_{th} = 0$, $T_{n \geq 0} = 0$ and $\sum_{n=1}^{\infty} H_n = H_0 = I_0$.

Then equation (17) becomes:

$$H_n = \frac{H_0 (k_{ht} x)^{n-1} e^{-k_{ht} x}}{(n-1)!} \quad (27)$$

which is exactly the standard Poisson distribution.

Subsequently, equations (23) and (24) can be simplified to:

$$\sum_{n=1}^{\infty} n N_n = I_0 (1 + k_{ht} x) \quad (28)$$

$$\sum_{n=1}^{\infty} n^2 N_n = I_0 (1 + 3k_{ht} x + k_{ht}^2 x^2) \quad (29)$$

Consequently, the number- and weight-average degrees of polymerization in this situation are respectively:

$$\bar{P}_n = 1 + k_{ht} x \quad (30)$$

$$\bar{P}_w = 1 + k_{ht} x + \frac{k_{ht}^2 x^2}{1 + k_{ht} x} \quad (31)$$

All the results obtained from the simpler case are in accordance with those in previous work^{13,14}.

DISCUSSION

To discuss the influence of reaction conditions on the molecular parameters of the resultant polymer, it is necessary to clarify the dependence of x on reaction conditions. From equation (23), the following formula is obtained:

$$y = \frac{I_0}{M_0} \left[\left(1 + \frac{\alpha}{\varphi} x \right) + \frac{\theta \gamma}{\varphi^2} (1 - e^{-\varphi x}) \right] \quad (32)$$

where y denotes monomer conversion. On the other hand, the relationship between x and polymerization time t may be derived from equations (6) and (23):

$$t = \int_0^x \frac{dx}{M_0 - I_0 [(1 + \alpha x / \varphi) + \theta \gamma (1 - e^{-\varphi x}) / \varphi^2]} \quad (33)$$

If we substitute initial conditions M_0 and I_0 into equation (32) or (33), x can be determined by iteration from monomer conversion y or reaction time t . Therefore, the molecular-weight distribution function, average molecular weight and dispersity may be plotted theoretically against y or M_0/I_0 , respectively.

Figure 1 gives differential MWD curves at various monomer conversions. Small shoulder peaks appear in the MWD curves, which are possibly related to the bimodal mechanism, i.e. the presence of two types of active species with different propagation rates in the reaction system. Obviously, the low-molar-mass tails of the derived distribution arise from the contribution of species T_n . The relation between the MWD and the ratio

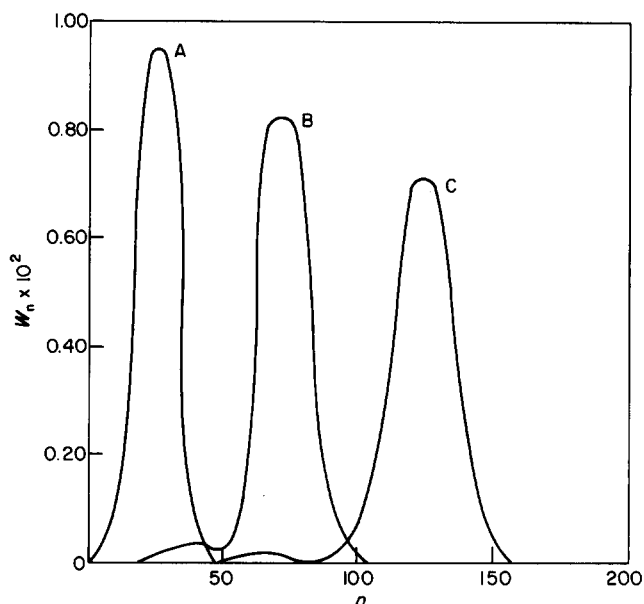


Figure 1 The theoretical curves of molecular-weight distribution at various monomer conversions, y : $W = nN_n / \sum_{n=1}^{\infty} nN_n$, $H_0 = 0.004 \text{ mol l}^{-1}$, $T_0 = 0.001 \text{ mol l}^{-1}$, $k_{ht} = 200 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{th} = 100 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{hh} = k_{tt} = 2 \text{ mol}^{-1} \text{ s}^{-1}$, $M_0 = 1.0 \text{ mol}$; (A) $y = 10\%$, (B) $y = 30\%$, (C) $y = 50\%$

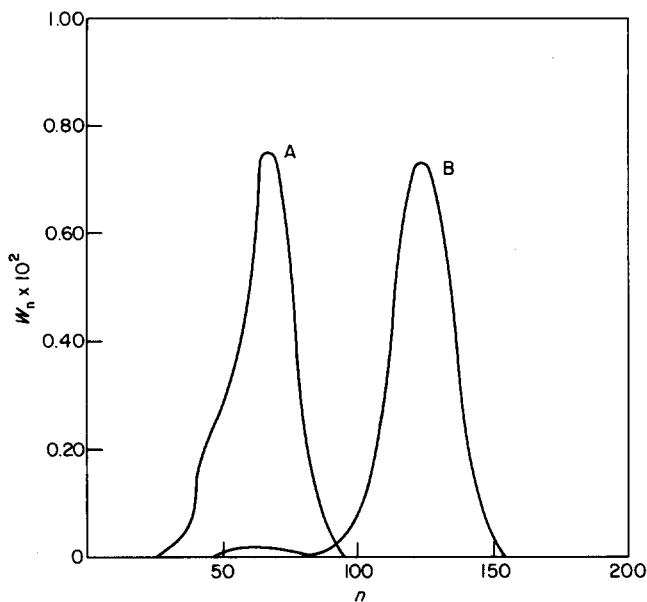


Figure 2 The theoretical curves of molecular-weight distribution for different values of M_0/I_0 : $y = 50\%$; (A) $M_0/I_0 = 100$, $H_0 = 0.008 \text{ mol l}^{-1}$, $T_0 = 0.002 \text{ mol l}^{-1}$; (B) $M_0/I_0 = 200$, $H_0 = 0.004 \text{ mol l}^{-1}$, $T_0 = 0.001 \text{ mol l}^{-1}$; other parameters are identical with those of Figure 1

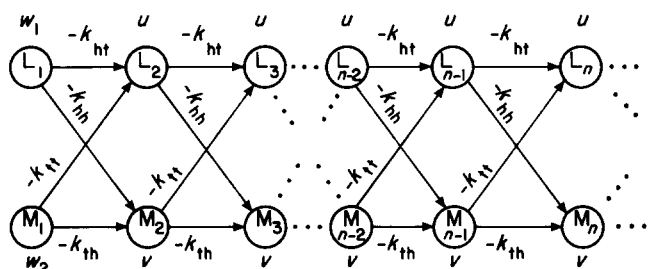
of M_0 to I_0 is shown in Figure 2. The MWDs in both Figures 1 and 2 are very narrow and the ratios of \bar{P}_w to \bar{P}_n approach 1.0, which demonstrate that the bimodal nature of the mechanism does not affect the homogeneity of the living polymer generated from an anionic polymerization. This theoretical conclusion is in agreement with the pertinent experimental data reported hitherto. Numerous anionic polymerizations with bimodal mechanisms have been reported to date, which should be amenable to the kinetic scheme given in this work. An experimental test of our theory will be published in the third part of this series.

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APPENDIX

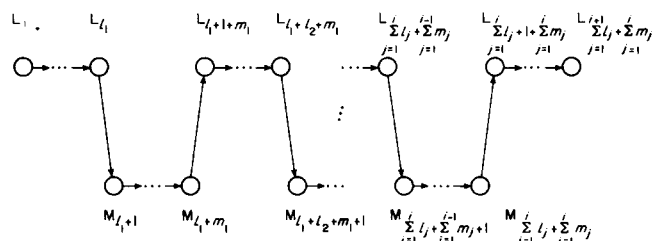
In equation (16), the coefficient matrix relates to the topology of this algebraic set, which is represented by the following graph:



In this graph, a vertex corresponds to a diagonal element in the triangular matrix, and an edge diverting from a vertex to the next is connected with one of the non-diagonal elements. Two initial vertices L_1 and M_1 have weights of $(\lambda + k_{hh} + k_{ht})/H_0$ and $(\lambda + k_{th} + k_{tt})/T_0$, respectively. Each of the vertices L_2, L_3, \dots, L_n possesses equal weight $(\lambda + k_{hh} + k_{ht})$, and each of M_2, M_3, \dots, M_n has the same weight $(\lambda + k_{th} + k_{tt})$. The weight of the edge diverting from vertex L_n to L_{n+1} or from vertex M_n to M_{n+1} , where $n \geq 1$, is $-k_{ht}$ or $-k_{th}$. The weight of the cross edge connecting vertex L_n with vertex M_{n+1} or vertex M_n with L_{n+1} is $-k_{hh}$ or $-k_{tt}$. In accordance with the graph theory rule^{11,12}, the root L_n or M_n is determined by the paths from vertices L_1 and M_1 to vertex L_n or M_n . The contribution of each path to the expression for L_n or M_n is a fraction with a factor $(-1)^{n-1}$, of which the numerator is a product composed of all edge weights in the path under consideration, and the denominator is a product of all vertex weights in the same path. Summarizing all of the contributions of every path, L_n and M_n can be derived. Let us consider the solution to L_n first.

There are two different initial vertices, L_1 and M_1 , which lead to vertex L_n . It is straightforward to see that there are n vertices and $n-1$ edges in every path from vertex L_1 to L_n . We assume that i pairs of edges go up and down between L-type and M-type vertices in the

path, of which i edges have identical weight $-k_{hh}$ and the other i edges possess equal weight $-k_{tt}$, where $i=0, 1, 2, \dots, (n-1)/2$ or $n/2-1$ (when n is odd, $i=(n-1)/2$; otherwise $i=n/2-1$). Then such a path from vertex L_1 to L_n can be shown as follows:



Let $l = \sum_{j=1}^{i+1} l_j$ and $m = \sum_{j=1}^i m_j$, where $n-i > l \geq i+1$, then $l+m=n$, which means there are l L-type vertices, m M-type vertices and i pairs of edges connecting the different kinds of vertices in the path. Based on the graph-theory rule described in the previous paragraph, the contribution of the path is:

$$\frac{(-1)^{n-1} (-k_{hh})^i (-k_{tt})^i (-k_{ht})^{\Sigma_1} (-k_{th})^{\Sigma_2}}{[(\lambda + k_{ht} + k_{hh})/H_0](\lambda + k_{ht} + k_{hh})^{\Sigma_3} (\lambda + k_{th} + k_{tt})^{\Sigma_4}}$$

$$= \frac{H_0}{k_{ht}} \left(\frac{k_{hh} k_{tt}}{k_{ht} k_{th}} \right)^i \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^l \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-i}$$

where

$$\Sigma_1 = \sum_{j=1}^{i+1} (l_j - 1) \quad \Sigma_2 = \sum_{j=1}^i (m_j - 1)$$

$$\Sigma_3 = \sum_{j=1}^{i+1} (l_j - 1) \quad \Sigma_4 = \sum_{j=1}^i m_j$$

In the path there are l L-type vertices, $(n-l)$ M-type vertices and i pairs of edges connecting one kind of vertex with another. Accordingly there are

$$\binom{l-1}{i} \binom{n-l-1}{i-1}$$

arrangements of the vertices and edges. In other words, there are

$$\binom{l-1}{i} \binom{n-l-1}{i-1}$$

paths having the same contribution to L_n . Therefore, we obtain the total contributions of all the paths from L_1 to L_n :

$$L_n^1 = \frac{H_0}{k_{ht}} \left[\left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^n + \sum_{i=1}^{(n-1)/2 \text{ or } n/2-1} \sum_{l=i+1}^{n-i} \binom{l-1}{i} \binom{n-l-1}{i-1} \times \left(\frac{k_{hh} k_{tt}}{k_{ht} k_{th}} \right)^i \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^l \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-i} \right] \quad (\text{A.1})$$

L_n^1 denotes the contribution of all the paths from vertex L_1 to L_n . Similarly, L_n^2 , the contribution of all the paths

from vertex M_1 to L_n , is:

$$L_n^2 = \frac{T_0}{k_{hh}} \sum_{i=1}^{(n-1)/2 \text{ or } n/2-1} \sum_{l=i}^{n-i} \binom{l-1}{i-1} \binom{n-l-1}{i-1} \times \left(\frac{k_{hh}k_{tt}}{k_{ht}k_{th}} \right)^i \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^l \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-l} \quad (\text{A.2})$$

Consequently, we have:

$$L_n = L_n^1 + L_n^2 = \frac{H_0}{k_{ht}} \left[\left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^n + \sum_{i=1}^{(n-1)/2 \text{ or } n/2-1} \sum_{l=i+1}^{n-i} \binom{l-1}{i} \binom{n-l-1}{i-1} \times \left(\frac{k_{hh}k_{tt}}{k_{ht}k_{th}} \right)^i \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^l \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-l} \right] + \frac{T_0}{k_{hh}} \times \sum_{i=1}^{(n-1)/2 \text{ or } n/2-1} \sum_{l=i}^{n-i} \binom{l-1}{i-1} \binom{n-l-1}{i-1} \times \left(\frac{k_{hh}k_{tt}}{k_{ht}k_{th}} \right)^i \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^l \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-l} \quad (\text{A.3})$$

Equation (A.3) can be transformed into:

$$L_n = \frac{H_0}{k_{ht}} \left[\left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^n + \sum_{i=1}^{n-1} \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^i \right]$$

$$\times \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-l} F(1-l, l-n, 1, K) \Big] + \left(\frac{T_0}{k_{hh}} - \frac{H_0}{k_{ht}} \right) \sum_{i=1}^{n-1} \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^i \times \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^{n-l} F(1-l, l+1-n, 1, K) \quad (\text{A.4})$$

Similarly, the contribution of all the paths from vertices L_1 and M_1 to vertex M_n is:

$$M_n = \frac{T_0}{k_{th}} \left[\left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^n + \sum_{i=1}^{n-1} \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^i \times \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^{n-l} F(1-l, l-n, 1, K) \right] + \left(\frac{H_0}{k_{tt}} - \frac{T_0}{k_{th}} \right) \sum_{i=1}^{n-1} \left(\frac{k_{th}}{\lambda + k_{th} + k_{tt}} \right)^i \times \left(\frac{k_{ht}}{\lambda + k_{ht} + k_{hh}} \right)^{n-l} F(1-l, l+1-n, 1, K) \quad (\text{A.5})$$

By making use of the inverse Laplace transform¹⁵, equations (A.4) and (A.5) can be converted into equations (17) and (18), respectively.