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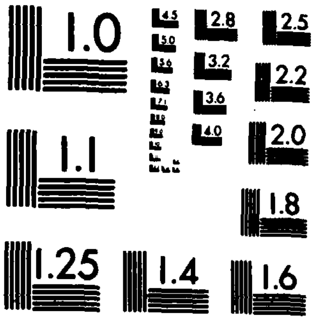

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The Molecular Weight Distribution for Molecules Requiring Rotational Diffusion Prior to Reaction

by

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The molecular weight distributions have been calculated for rigid rods which must rotate into a collinear conformation prior to reaction. The underlying assumptions include bimolecular reaction without by-product formation and a rotary diffusion parameter that is proportional to molecular length through the term $(i^{-N}+j^{-N})$ where i and j are rod lengths and N is an arbitrary parameter. To reduce the number of simultaneous differential equations that must be solved, an empirical scaling law is introduced which is independent of chain length. Essentially asymptotic values are obtained for number (over)

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Introduction

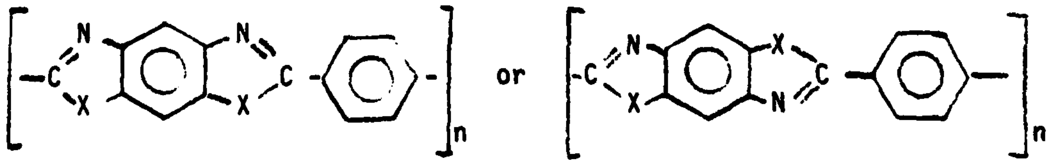
In 1939 Flory announced the principle of equal reactivity of polymer chains (1). The principle maintains that the ability of a chain molecule to form larger molecules is independent of the chain length. The argument was very significant at that time for two reasons: First, the existence of high molecular weight polymers was considered by some to be improbable. These proponents argued that the high molecular weight species must have a higher diffusion constant, relative to the lower molecular weight species, which would eventually limit the extent of polymerization. Studies on condensation-type polymers with random coils demonstrated the general validity of the principle of equal reactivity (2). The second significant result was that the distribution of molecular weights could be readily calculated from kinetic parameters that were independent of chain length.

The major significant deviations from this principle seem to occur only with very low molecular weight species where inductive or polarization effects can be transmitted across a small molecule. Indeed, Lenz (3) cites a number of cases where the reactivity of a functional group on a difunctional monomer depends on whether or not the other functional group has reacted. Challa (4) showed a similar effect on the rate of polymerization of poly(ethylene terephthalate) where the reactivity of the "monomer" bis(β-hydroxyethyl) terephthalate differs from that of higher oligomers and polymer. Peebles and Wagner (5) examined the transesterification kinetics of dimethyl terephtalate and ethylene glycol in the presence of a catalyst.

They concluded that the second transesterification reaction was some three times faster than the first transesterification reaction. The overall transesterification of the terephthalate monomer must somehow involve some type of molecular transition state containing the catalyst because attempts to verify the faster transesterification reaction with the partly transesterified material resulted in absolutely no reaction (6). Thus, the documented "violations" of the principle of equal reactivity seems to be restricted to very small chain segments of random coil molecules.

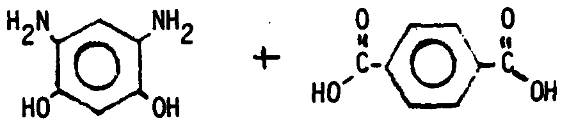
Several calculations have been made to determine how departures from the principle of equal reactivity would influence the molecular weight distribution of a polymer. Nanda and Jain (7) assumed that the second order reaction constant for a condensation polymer was proportional to the molecular weight of the formed polymer through the relation $k(1+\xi i)$, where k and ξ are constants and i is the number of monomers in a chain of length i, to obtain an analytical solution for the molecular weight distribution. Magat (8) developed simultaneous integral equations for stepwise polymerizations without termination for a number of conditions where the rate constant for propagation varied with chain length. His approaches are limited, however, in that the precise polymerization conditions must be specified before the equations can be evaluated.

A new series of stiff rod-like polymers (9) have recently been synthesized and characterized with a repeating unit of the form



where the "X" atom can be oxygen, sulfur, or singly hydrated nitrogen.

The condensation of the functional groups



appears to occur simultaneously to form the benzobisoxazole because intermediate functionalities have not been detected by chemical or spectral means (9e). These observations suggest that the interacting molecules must be collinear (or nearly so) before reaction can take place. Furthermore, once reaction has commenced, the entire series of reactions to form the cyclic structure must occur quite rapidly. If such is the case, then the rate determining step is the ability of rods to rotate into a collinear configuration rather than the coupling step. Here the principle of equal reactivity is not violated; the reactivity of each end is independent of the length of the chain to which it is attached. The purpose of this paper is to calculate the molecular weight distribution for randomly oriented rod-like molecules which must diffuse or rotate into a collinear configuration prior to the coupling reaction.

Mathematical Development

The reaction between molecules of size i reacting with molecules of size j to form a molecule of size i + j irreversibly and without by-product

$$x_i + x_j \rightarrow x_{i+j} \qquad (1)$$

is postulated to have a rate of formation proportional to k $c_{ij}x_ix_j$ where k is the specific second order rate constant for coupling, c_{ij} is a function of the molecular lengths i and j and is a measure of the ability of molecules to become collinear, and x_i, x_j are the concentrations of molecules of size i and j.

To simplify the notation, the constant k is adsorbed into the time derivative. Thus from eq (1), the rate of formation of x_i is given by

$$\dot{x}_i = \tfrac{1}{2}\sum_{j=1}^{i-1} c_{j,i-j}x_jx_{i-j} - x_i \sum_{j=1}^{\infty} c_{ij}\, x_j \qquad (2)$$

The monomer x_1 is considered to react at the rate

$$\dot{x}_1 = - x_1 \sum_{j=1}^{\infty} c_{1j}\; x_j \qquad (3)$$

These rate formulas can be summed to give the following time derivative functions

$$\sum_{i=1}^{\infty} i\, \dot{x}_i = 0 \qquad (4)$$

line up?

since no by-product is formed.

$$\sum_{i=1}^{\infty} \dot{x} = -\tfrac{1}{2}\sum_{i=1}^{\infty} x_i \sum_{j=1}^{\infty} c_{ij}x_j \qquad (5)$$

line up?

$$\sum_{i=1}^{\infty} i^2\, \dot{x}_i = \sum_{i=1}^{\infty} i\, x_i \sum_{j=1}^{\infty} j\, c_{ij}\, x_j \qquad (6)$$

If the variable c_{ij} can be specified, then the molecular weight distribution and the moments of the distribution can in principal be determined by computer calculations.

Because many polymers have degrees of polmerization in excess of 100, and perhaps into the thousands or millions, it is not reasonable to solve the excessive number of simultaneous differential equations given by (2) and (3). However, if some type of scaling law can be found which will permit calculation of the distribution for a low number average molecular weight distributions, then computer calculations are feasible.

The generalized exponential distribution function

$$F(i,m,k) = my^{k/m}\, i^{k-1}[\exp(-yi^{m})]/\Gamma(k/m) \qquad (7)$$

Gk cap Γ

$$W(i,m,k) = my^{(k+1)/m}\, i^{k}[\exp(-yi^{m})]/\Gamma[(k+1)/m] \qquad (8)$$

where $\langle i\rangle_n = \Gamma\left[(k+1)/m\right]/y^{1/m}\Gamma(k/m)$,

can be rewritten in a scaling law form with $i/\langle i\rangle_n$ as the independent variable.

$$F(i,m,k)\langle i\rangle_n = \frac{mg^k}{\Gamma(k/m)}\left[\frac{i}{\langle i\rangle_n}\right]^{k-1}\exp\left[-(gi/\langle i\rangle_n)^m\right] \qquad (9)$$

$$W(i,m,k)\langle i\rangle_n = \frac{mg^k}{\Gamma(k/m)}\left[\frac{i}{\langle i\rangle_n}\right]^{k}\exp\left[-(gi/\langle i\rangle_n)^m\right] \qquad (10)$$

with $g = \{\Gamma[(k+1)/m]\}/\Gamma(k/m)$

This distribution is a generalized form of the Schulz distribution ($m = 1$), the Tung-Weibull distribution ($k = m-1$, $k > 0$), and a good approximation of the most probable distribution ($m = k = 1$) at large values of $\langle i\rangle_n$.

The next question to consider is the form of the function c_{ij} which determines the ability of the molecules to rotate into a collinear conformation. Doe and Edwards (9) suggest that the rotational diffusion constant of a rod depends on $(\ln i)/i^3$ in dilute solution and higher inverse powers of i in more concentrated solutions, whereas Bird (10) suggests that the rotation of a rigid dumbbell depends on the square of the length (i^2). The assumption can then be made that if rod $\underline{i}$ were held fixed in space while rod $\underline{j}$ was allowed to rotate freely, then the rate of rotation would be proportional to j^{-N}, where $\underline{N}$ is an adjustable parameter. If rod $\underline{j}$ were held fixed and rod $\underline{i}$ allowed to rotate, the rate is proportional to i^{-N}. The overall average rate is then

$$c_{ij} = (i^{-N} + j^{-N})/2 \qquad (11)$$

linear

This equation can then be substituted into the set of simultaneous differential equations 2 - 6. The initial concentration of monomer, x_1 was selected to be unity. Initially, x_1 was taken as the independent variable. A set of $\underline{K}$ simultaneous differential equations $\dot{x}_i/\dot{x}_{ind}$, where $\dot{x}_{ind}$ is the change in concentration with time of the independent variable, was set up for solution by a computer. The value of $\underline{K}$ was selected to be large enough so that $\sum ix_i > .999$ over the range of integration considered. A Runga-Kutta method was used to obtain values of x_i, from $\underline{i}$ = ind to $\underline{i} = \underline{K}$. After each integration, an interger value of $\underline{L} = 0.8K$ was tested to see whether $Lx_L < 0.0005$. If the test failed, a larger value of $\underline{K}$ was selected, the program retreated to the results obtained on a previously performed integration, and computation continued. This procedure allowed only a small number of equations to be solved at the beginning of the solution, but as $\langle i \rangle_n$ increased, more equations were solved, and hence more computer time required. Also, as $\langle i \rangle_n$ increased, values of x_{ind} decreased and eventually became too small to permit reliable values of $\dot{x}_i/\dot{x}_{ind}$ to be computed as evidenced by fluctuations in x_{ind}. As x_{ind} approached this limiting value, a new independent variable was selected and concentrations of all $\underline{i}$ variables below x_{ind-1} were arbitrarily set to zero. Extensive testing of this procedure by choosing various values of $\underline{i}$ for the independent variable exhibited no effect on the calculated distribution provided that $x_{ind} < x_{max}$.

Results

Integration of eq's 2, 3, 5 and 6 were performed for integer values of N in eq 11 as a function of conversion. Values of $<i>_n$ varied from unity (initial condition) to $<i>_n$ values in excess of 50. From the x_i values so computed, values of $x_i<i>_n/\Sigma x_i$ were obtained. For all values of N used, except for N = 0 (the most probable distribution) the scaling law held to within the precision of the data when $<i>_n$ values exceeded ten. The results are presented in Fig.'s 1 and 2 for the distribution as a function of $i/<i>_n$ and in Fig. 3 for the heterogenity index $<i>_w/<i>_n$ as a function of conversion.

Discussion

The empirical observation that the scaling laws $F(i)\langle i\rangle_n$ and $W(i)\langle i\rangle_n$ are functions only of $i/\langle i\rangle_n$ means that inexpensive computer calculations can be performed to evaluate these functions at small values of $\langle i\rangle_n$. The function can then be used directly to evaluate the molecular weight distributions for large values of $\langle i\rangle_n$. This technique can be used for other schemes relating kinetics to reactor designs, etc. where numerical calculations are required.

When the value of N in equation 11 is nonzero, the rate of polymerization $\Sigma \dot{x}_i$, eq 5, decreases with increasing conversion. As N increases, the rate of polymerization decreases at a faster rate. Both the scaled mole fraction and weight fraction distributions show a maximum in the range $i/\langle i\rangle_n$ of 0.6-0.7, the maximum shifting to higher values with increasing N. The breadth of the distribution, however, becomes narrower, and reaches an asymptotic value at $\langle i\rangle_n$ values of approximately 10. The application of these calculations to the observed distributions of Poly([benzo(1,2-d:5,4-d') bisoxazole-2,6 -diyl] -1,4-phenylene) has been discussed by Cotts and Berry (9e).

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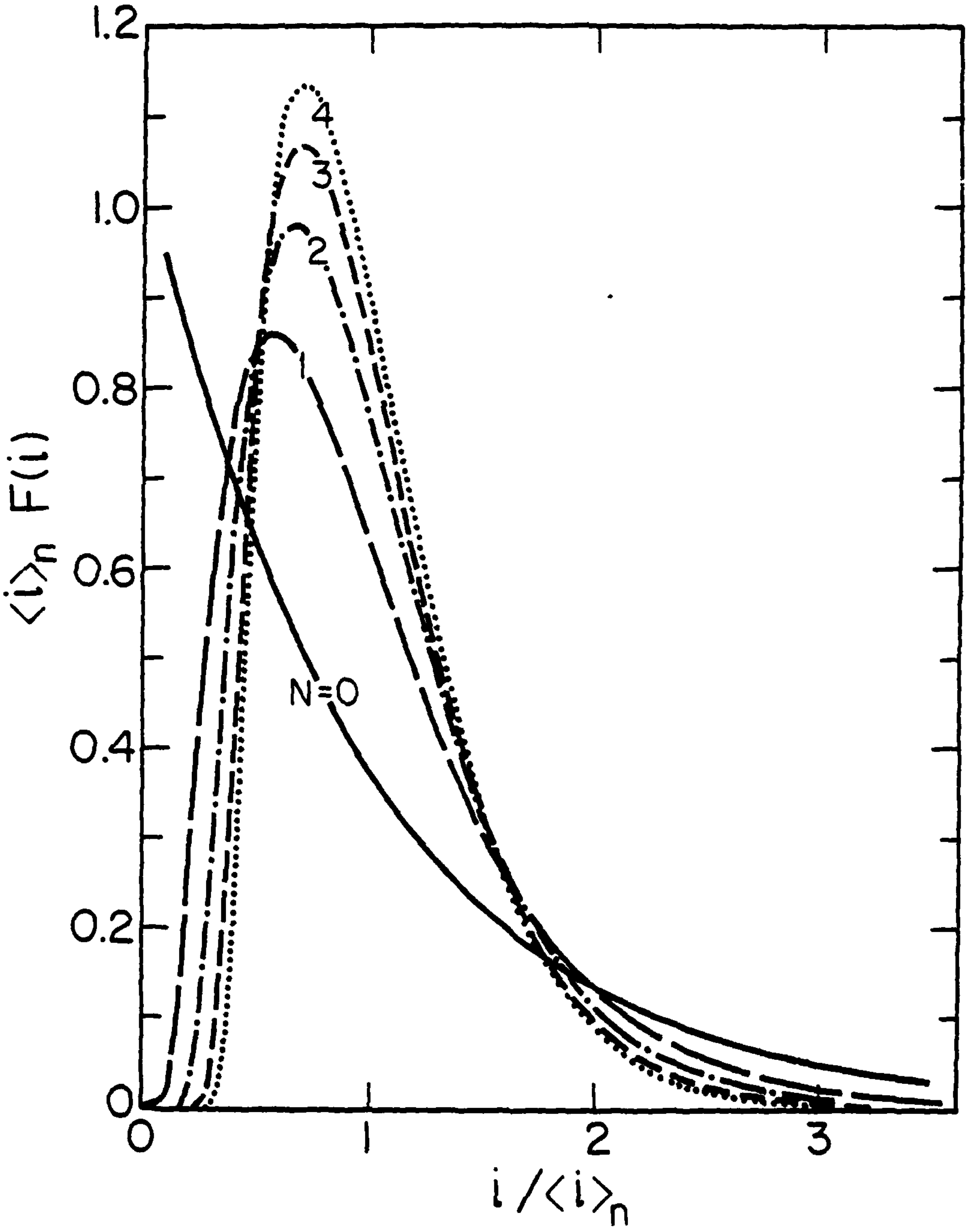
Legend for Figures

Figure 1. The scaled mole fraction of polymer as a function of $i/\langle i\rangle_n$ for various values of N in eq 11

Figure 2. The scaled weight fraction of polymer as a function of $i/\langle i\rangle_n$ for various values of N in eq 11

Figure 3. The heterogeneity index $\langle i\rangle_n/\langle i\rangle_n$ as a function of $\langle i\rangle_n$ and N.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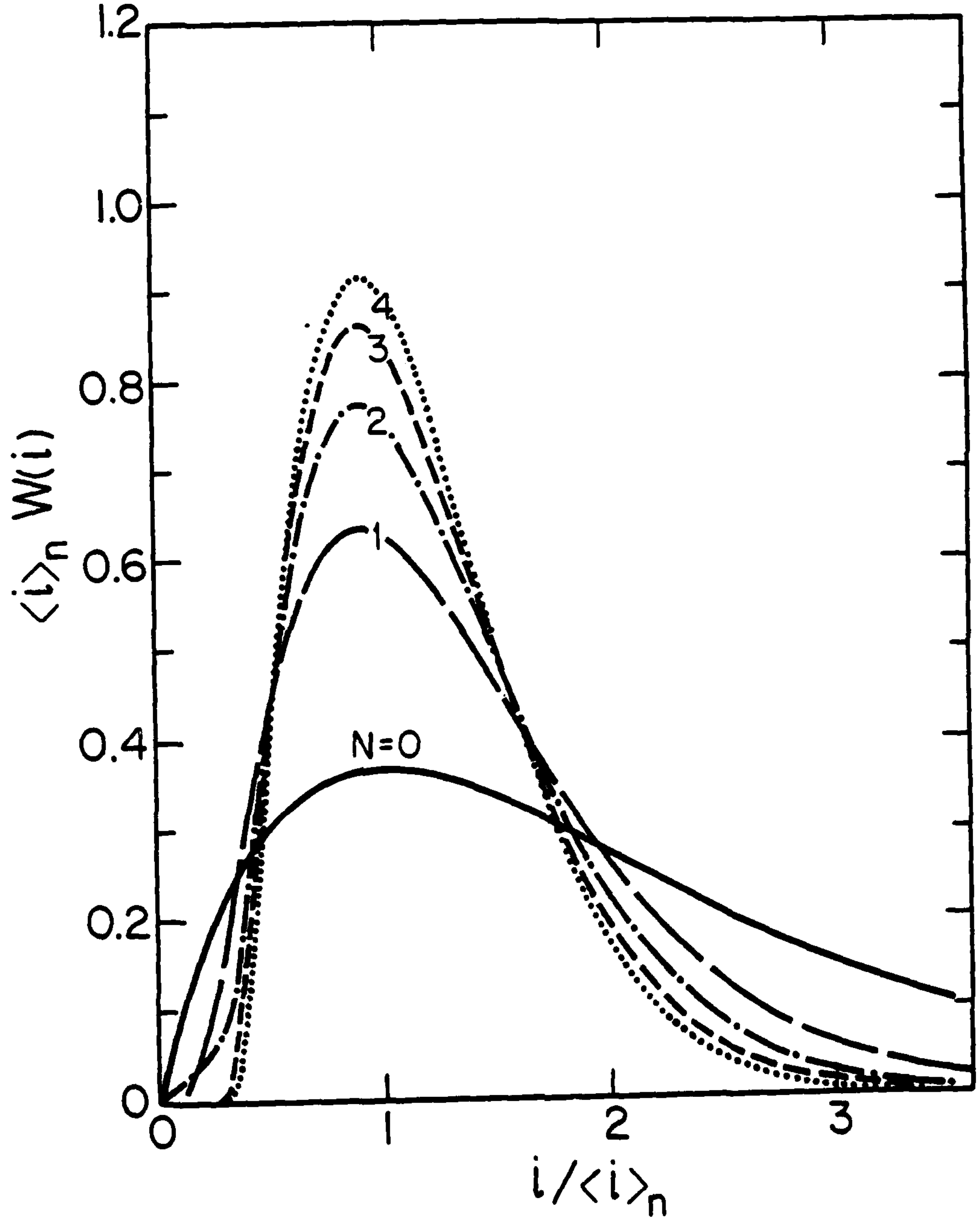
N=0

Fig 1



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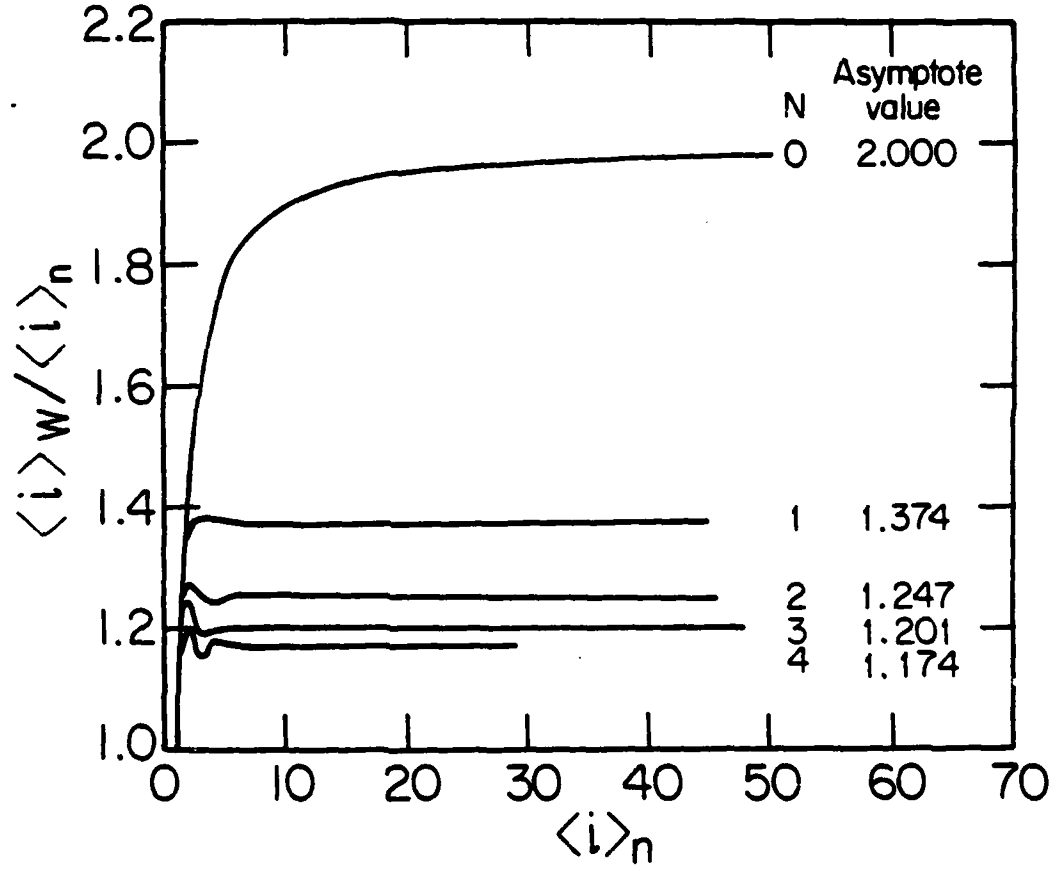
N=0

Fig 2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60
70
$\langle i \rangle_n$
N
Asymptote value
0 2.000
1 1.374
2 1.247
3 1.201
4 1.174

Fig 3

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