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A Statistical Derivation of the Average Degree of Polymerization in a Stirred Tank Reactor

Neil A. Dotson

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455. *Received December 27, 1988; Revised Manuscript Received February 14, 1989*

ABSTRACT: The statistical approach in its many forms has been a powerful tool in describing the structural evolution of nonlinear polymers but has been limited in its application to batch processes. This restriction is removed by considering the paradigm of A_f homopolymerization in a homogeneous stirred tank reactor. The number- and weight-average degrees of polymerization are derived from recursive arguments which properly account for the nonrandom combination of monomers caused by the residence time distribution. The results are in agreement with those derived from the kinetic equations. This route is not necessarily a simpler or more powerful approach than solution of the kinetic equations, but it does provide new insight into this particular problem, as well as demonstrating the versatility of the statistical approach.

Introduction

Stepwise polymers produced in a homogeneous continuous stirred tank reactor[1] (HCSTR) can exhibit significantly broader distributions than their counterparts produced in batch reactors. The homopolymerization of A_2 monomers serves to illustrate this. In a batch reactor, the molecular weight distribution is the most probable (or geometric) distribution:[1]

$$P_n = p^{n-1}(1-p) \qquad (1)$$

where P_n is the molar fraction of n-mers and p is the extent of reaction (the probability that a functional group has reacted). This distribution gives the following number- and weight-average degrees of polymerization:

$$\mathrm{DP_n} = \frac{1}{1-p} \qquad (2)$$

$$\mathrm{DP_w} = \frac{1+p}{1-p} \qquad (3)$$

The polydispersity of the polymer thus has an upper bound of two. The conversion is related to time, t, through the Damköhler number, Da, by the following relationship:

$$p = \frac{Da}{1+Da} \qquad (4)$$

where $Da = ktfc_{10}$, k is the rate constant for functional group (*not* monomer) reaction, f is the functionality of the monomer (here 2), and c_{10} is the initial monomer concentration.

In an HCSTR, on the other hand, the distribution takes a more complicated form[1]

$$P_n = \frac{(2n-2)!}{n!(n-1)!}\frac{p^{n-1}}{(1+p)^{2n-1}} \qquad (5)$$

which yields the following average degrees of polymerization:

$$\mathrm{DP_n} = \frac{1}{1-p} \qquad (6)$$

$$\mathrm{DP_w} = \frac{1+p^2}{(1-p)^2} \qquad (7)$$

Here, in contrast to the previous case, the polydispersity has no upper bound. The conversion is related to the relative rates of exit and reaction through the Damköhler number by the following relation:

$$p = 1 - \frac{(1+4Da)^{1/2}-1}{2Da} \qquad (8)$$

where $Da = k\theta fc_{10}$, c_{10} is the entering monomer concentration, and the mean residence time θ is the ratio of the volume of the reactor to the volumetric throughput rate.

Since for linear polymerizations broad distributions are easily obtained in an HCSTR, for nonlinear polymerizations one might expect the situation to be even more severe, such that the gel point could be advanced considerably. Several researchers have investigated the behavior of nonlinear polymerizations in HCSTRs. With regard to step polymerizations, the first work is that of Cozewith et al.,[2] which solved both the steady-state and start-up problems for A_∞ homopolymerization. For finite functionality systems, Gupta and co-workers[3-5] have analyzed HCSTRs in series, the effect of oscillations in feed, and the effects of intramolecular reaction. Hendriks and Ziff[6] have analyzed the problem starting with the Smoluchowski coagulation equation and have looked at different coagulation kernels, analyzing both A_2 and A_∞ homopolymerization (which describes as well the critical behavior of the A_f system). Nonlinear free-radical systems have also been studied.[7-11]

Common to all of these analyses is the use of the kinetic equations describing polymerization. This approach would seem necessary because the various statistical methods, which are so useful for describing nonlinear polymerizations, have been held (usually implicitly) to be valid only for batch polymerizations.[12,13] The nongeometric character of the distribution of eq 5 would thus seem to be beyond statistical reach, yet Biesenberger and Tadmor justify it with combinatoric reasoning.[1,14] Thus, this alleged restriction is not absolute. Nonetheless, the following question must be asked: how are the ideality assumptions (equal reactivity and independent reaction) violated, so that simple application of statistical methods is invalid? Then, is there a correct statistical route to the average properties? The paradigm of random step homopolymerization of f-functional monomers, analyzed by the recursive method,[15] serves to answer both questions, with the answer to the latter being "yes".

Statistical (Recursive) Derivation

$\mathrm{DP_w}$. Consider the homopolymerization of f-functional monomers in an HCSTR operating at steady state, for which cyclization is prohibited and for which only monomer enters the reactor. To derive the weight-average de-

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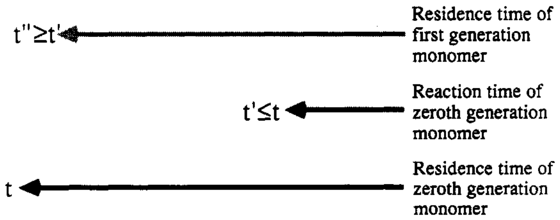

Figure 1. Illustration of the meaning of the times (or "ages") t, t', and t''.

gree of polymerization, we first grab a (zeroth-generation) monomer at random, so that we can write

$$\mathrm{DP_w} = 1 + fE(N_{\mathrm{A}}^{\mathrm{out}}) \tag{9}$$

where $E(N_{\mathrm{A}}^{\mathrm{out}})$ is the expected number of attached monomers looking out from a functional group.[15] We must realize two things: (1) the probability of any of the f-functional groups on the monomer having reacted is dependent upon the residence time of that monomer, and (2) the only correlation between the states of the different functional groups is the fact that they all share the same residence time. These two points correspond to violations of the equal reactivity assumption and the independent reactivity assumption, respectively. The source of these nonidealities, however, is not intrinsic to the reaction chemistry but rather to the reactor configuration.

As an HCSTR is perfectly mixed, the residence time distribution is described by an exponential distribution:

$$\rho(t)\ \mathrm{d}t = \frac{1}{\theta}e^{-t/\theta}\ \mathrm{d}t \tag{10}$$

Given a residence time t of the zeroth-generation monomer (see Figure 1), the probability of a functional group having reacted is given by the following:

$$p(t) = 1 - e^{-t/\tau} \tag{11}$$

where τ is the time scale for reaction, equal to $[k(1 - p)fc_{10}]^{-1}$, such that $\theta/\tau = Da(1-p)$. The overall conversion is thus given by

$$p = \int_0^\infty p(t)\ \rho(t)\ \mathrm{d}t = \frac{\theta}{\theta + \tau} = \frac{Da(1-p)}{1 + Da(1-p)} \tag{12}$$

which is consistent with eq 8.

Conditioning upon residence time, we can then write

$$E(N_{\mathrm{A}}^{\mathrm{out}}) = \int_0^\infty E(N_{\mathrm{A}}^{\mathrm{out}}|t)\ \rho(t)\ \mathrm{d}t \tag{13}$$

To evaluate $E(N_{\mathrm{A}}^{\mathrm{out}}|t)$, we must first condition upon the time t' at which the reaction occurred (see Figure 1):

$$E(N_{\mathrm{A}}^{\mathrm{out}}|t) = 1 - e^{-t/\tau} + (f-1) \times \int_0^t E(N_{\mathrm{A}}^{\mathrm{out}}|\text{one group reacted at time } t')\ \frac{1}{\tau}e^{-(t-t')/\tau}\ \mathrm{d}t' \tag{14}$$

where the weighting function in the integrand is the probability density of reaction at time t' given a residence time t, which is consistent with eq 11. To close the recursion, we must further condition upon the residence time t'' of the first generation monomer (see Figure 1):

$$E(N_{\mathrm{A}}^{\mathrm{out}}|t) = 1 - e^{-t/\tau} + (f-1)\frac{1}{\tau}e^{-t/\tau}\int_0^t \int_{t'}^\infty E(N_{\mathrm{A}}^{\mathrm{out}}|t'')\ \rho'(t''-t')\ \mathrm{d}t''\ e^{t'/\tau}\ \mathrm{d}t' \tag{15}$$

The recursion thus does not close algebraically, as it does in the case of a batch reactor,[15] but rather gives a double-integral equation.

The distribution $\rho'(t''-t')$, which is the probability density that a monomer has a residence time t'' given that one of its groups reacted at t', is a function only of $t''-t'$ because the residence time distribution of a monomer, one group of which reacted at time t', is insensitive to the fact that it must have remained in the reactor for a subsequent period t'. The distribution is given by the following:

$$\rho'(t)\ \mathrm{d}t = \left(\frac{1}{\theta} + \frac{1}{\tau}\right)e^{-t/\tau}\ e^{-t/\theta}\ \mathrm{d}t \tag{16}$$

i.e., simply the (properly normalized) product of the probabilities of a functional group escaping both reaction and exit.

The double-integral equation can now be transformed to a second-order ordinary differential equation, and the result is

$$E''(N_{\mathrm{A}}^{\mathrm{out}}|t) - \frac{1}{\theta}E'(N_{\mathrm{A}}^{\mathrm{out}}|t) + \frac{f-2}{\tau}\left(\frac{1}{\tau} + \frac{1}{\theta}\right)\left(E(N_{\mathrm{A}}^{\mathrm{out}}|t) + \frac{1}{f-2}\right) = 0 \tag{17}$$

The character of the solution will differ depending on whether $f = 2$ or $f > 2$; this is to be expected, since a linear system is very different from a nonlinear one. Before proceeding to the solutions, though, we can answer the first question posed in the Introduction.

If we had naively assumed, in eq 14, that the first generation monomer was also randomly chosen, we would have written that

$$E(N_{\mathrm{A}}^{\mathrm{out}}|\text{one group reacted at time } t') = E(N_{\mathrm{A}}^{\mathrm{out}}) \tag{18}$$

The recursion would thus have closed algebraically, and we would have obtained

$$\mathrm{DP_w} = \frac{1 + \int_0^\infty p(t)\ \rho(t)\ \mathrm{d}t}{1 - (f-1)\int_0^\infty p(t)\ \rho(t)\ \mathrm{d}t} \tag{19}$$

which by eq 12 is simply the familiar *batch* reactor result.[15] Thus, we see that it is not merely the residence time distribution that is the source of the nonideality but rather that the residence time distribution forces nonrandom combination of monomers. That is, a monomer with a residence time t' does not combine with other monomers with a probability proportional to $\rho(t)$; rather, the residence time distribution of the first generation is different from the overall distribution. In fact, the expected residence time of a first generation monomer is $\theta(1 - (\tau/(\theta + \tau))^2)$, which is less than the value for the zeroth generation monomer, θ. The "skewing" of the residence time distribution will also occur for every successive generation, so the nonideality may be called a long-range effect. The problem can nonetheless be solved exactly, as shown below. (All results will be expressed in terms of the conversion p; see eq 8.)

I. The f = 2 Case. Under the initial condition $E(N_{\mathrm{A}}^{\mathrm{out}}|0) = 0$ and the restriction that $\mathrm{DP_w}$ must be finite, eq 17 is easily solved to yield

$$E(N_{\mathrm{A}}^{\mathrm{out}}|t) = \frac{\theta}{\tau}\left(\frac{1}{\tau} + \frac{1}{\theta}\right)t \tag{20}$$

The expected weight on a monomer thus grows *linearly* with residence time. Integrating according to eq 13, we find the weight-average degree of polymerization to be as in eq 7 before.

II. The $f > 2$ Case. The solution of eq 17 depends upon whether we are operating below, above, or at the critical conversion, p_c, or the corresponding critical Damköhler number, Da_c,

$$p_c = 1 - 2(f-2)\left(\left(1 + \frac{1}{f-2}\right)^{1/2} - 1\right) \qquad (21)$$

$$Da_c = \frac{1}{4(f-2)} \qquad (22)$$

as found from the discriminant of the characteristic equation. We will examine each case in turn.

A. $p < p_c$. With the initial condition that $E(N_A^{out}|0) = 0$ and the condition that as p (or Da) approaches zero DP_w must approach unity, the solution is

$$E(N_A^{out}|t) = \frac{1}{f-2}(e^{\lambda t} - 1) \qquad (23)$$

where

$$\lambda = \frac{1}{2\theta}\left(1 - \left(1 - 4(f-2)\frac{\theta}{\tau}\left(1 + \frac{\theta}{\tau}\right)\right)^{1/2}\right) \qquad (24)$$

In contrast to the linear A_2 homopolymerization, for the nonlinear case the expected weight on a monomer grows *exponentially* with residence time. The weight-average degree of polymerization is given by

$$DP_w = \frac{f}{(f-2)^2}\frac{1-p}{2p}((1-p) - ((1-p)^2 - 4(f-2)p)^{1/2}) - \frac{2}{f-2} \qquad (25)$$

in agreement with the solution that can be obtained from the kinetic equations (see Appendix).

B. $p = p_c$. Here we obtain

$$E(N_A^{out}|t) = \frac{1}{f-2}(e^{t/2\theta} - 1) \qquad (26)$$

which in turn gives DP_w as follows:

$$DP_w = 2\frac{f-1}{f-2} \qquad (27)$$

Thus, the largest DP_w to be obtained is 4, for $f = 3$; as f approaches infinity, the largest DP_w goes to 2.[2] Thus, despite the broad distributions, we do not obtain high polymer.[3] (The polydispersity here is deceptively low, for at any Damköhler number all moments above a critical moment are divergent.[6])

C. $p > p_c$. For this case, the roots of the characteristic equation are complex, and thus the solution is of the form

$$E(N_A^{out}|t) = e^{t/2\theta}\left\{c_1 \sin\left(\frac{t}{2\theta}\left(4(f-2)\frac{\theta}{\tau}\left(1 + \frac{\theta}{\tau}\right) - 1\right)^{1/2}\right) + c_2 \cos\left(\frac{t}{2\theta}\left(4(f-2)\frac{\theta}{\tau}\left(1 + \frac{\theta}{\tau}\right) - 1\right)^{1/2}\right)\right\} - \frac{1}{f-2} \qquad (28)$$

where c_1 and c_2 are constants. This equation makes no physical sense, as it allows $E(N_A^{out}|t)$ to be negative. Indeed, DP_w is found to be given by eq 25 and thus itself to have an imaginary component. We thus conclude either that steady-state operation is not possible for $p > p_c$[2] or that the steady state is a gelling one.[6] Practically, of course, gelation would make operation of an HCSTR impossible anyway, such that from an engineering viewpoint p_c gives the critical conversion (and hence Da_c) above which steady-state operation is not possible.

DP_n. The number-average degree of polymerization can always be calculated from simple stoichiometric reasoning, being related only to the number of reacted groups and not to the details of connectivity. Thus,

$$DP_n = \frac{1}{1 - (f/2)p} \qquad (29)$$

in agreement with the result from the kinetic equations (see Appendix).

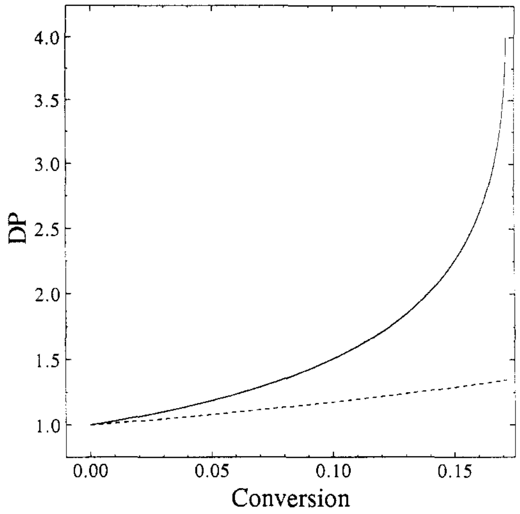

Figure 2. Average degree of polymerization versus conversion in an HCSTR, $f = 3$. (—) DP_w, (- - -) DP_n.

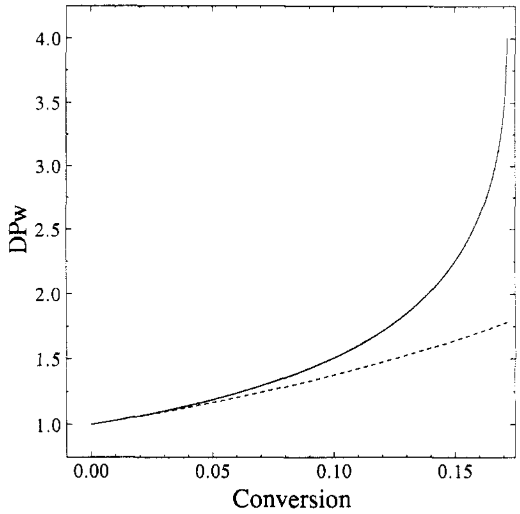

Figure 3. Weight-average degree of polymerization versus conversion, $f = 3$. (—) HCSTR, (- - -) batch.

Discussion

For the sake of illustration, we examine the $f = 3$ case; all of the conclusions drawn, however, are independent of f (for $f > 2$). The steady-state values of the number- and weight-average degrees of polymerization are shown in Figure 2, which emphasizes that high polymer is simply not obtained in a single HCSTR. However, while DP_w is finite (and in this case equal to four) at the critical conversion, it should be noted that dDP_w/dp is infinite. Insight can also be gained from comparison of the HCSTR results with those from a batch reactor;[15] we can compare based on either conversion or Damköhler number. For DP_w, Figures 3 and 4 show these comparisons; on either basis, the HCSTR product exhibits a higher DP_w than the batch reactor product, as expected. This is obviously not due to increased conversion at a given Da; indeed, Figure 5 shows that the DP_n for the HCSTR product is lower than that from a batch reactor at the same Da, indicating a correspondingly lower conversion. (A comparison of DP_n

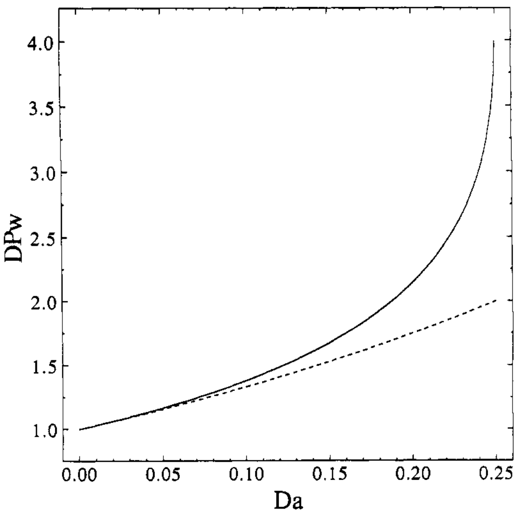

Figure 4. Weight-average degree of polymerization versus *Da*, $f = 3$. (—) HCSTR, (- - -) batch.

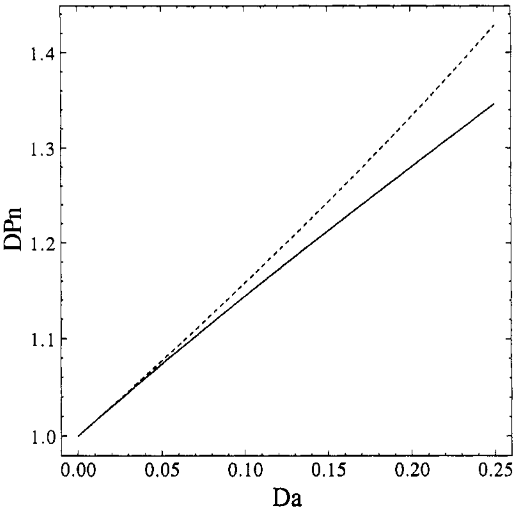

Figure 5. Number-average degree of polymerization versus *Da*, $f = 3$. (—) HCSTR, (- - -) batch.

on the basis of conversion is not shown, because there is no difference between the two on this basis.)

In conclusion, the recursive method has been extended to HCSTRs, proper care being taken to account for residence time distribution and the accompanying nonrandom reaction. The results obtained are in agreement with kinetic derivations, and although this derivation is not necessarily simpler or more powerful than the kinetic derivation (indeed, we have only solved the steady-state situation), it does offer insight into how the structure changes with residence time of the monomer. More importantly, it demonstrates the power of the statistical method to account, rigorously, for nonideality, in this case a violation of both the independent and equal reactivity assumptions enforced by the reactor configuration. While the ideas presented here could be extended to other more practical chemical systems (e.g., $A_f + B_2$) or to other types of reactors, perhaps they will find greater utility in the analysis of nonidealities intrinsic to the reaction chemistry.

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Appendix: Derivation of DP_w and DP_n from Kinetic Equations for $f > 2$

The kinetic equation describing the polymerization is essentially Smoluchowski's coagulation equation with source and sink terms[6] and with a kernel appropriate to A_f homopolymerization:[16]

$$\frac{dc_n}{dt} + \frac{c_n - c_{n0}}{\theta} = \frac{k}{2}\sum_{i+j=n}[(f-2)i + 2][(f-2)j + 2]c_i c_j - k[(f-2)n + 2]c_n\sum_{i=1}^{\infty}[(f-2)i + 2]c_i \quad \text{(A1)}$$

where c_{n0} is the entering n-mer concentration. The first three moments, μ_i ($i = 0, 1, 2$), of the distribution evolve according to the following expressions:[17]

$$\frac{d\mu_0}{dt} + \frac{\mu_0 - \mu_{00}}{\theta} = -k\{(1/2)(f-2)^2\mu_1^2 + 2(f-2)\mu_1\mu_0 + 2\mu_0^2\} \quad \text{(A2)}$$

$$\frac{d\mu_1}{dt} + \frac{\mu_1 - \mu_{10}}{\theta} = 0 \quad \text{(A3)}$$

$$\frac{d\mu_2}{dt} + \frac{\mu_2 - \mu_{20}}{\theta} = k\{(f-2)^2\mu_2^2 + 4(f-2)\mu_2\mu_1 + 4\mu_1^2\} \quad \text{(A4)}$$

where μ_{i0} is the entering ith moment. The concentration of unreacted functional groups [A] (which equals $(f-2)\mu_1 + 2\mu_0$) obeys the following equation:

$$\frac{d[A]}{dt} + \frac{[A] - [A]_0}{\theta} = -k[A]^2 \quad \text{(A5)}$$

For steady-state operation (i.e., the time derivatives vanish) and only monomer entering ($\mu_{00} = \mu_{10} = \mu_{20} = c_{10}$), solution of the above (algebraic) equations gives

$$\mu_0 = \left(1 - \frac{f}{2}\left(1 - \frac{(1 + 4Da)^{1/2} - 1}{2Da}\right)\right)c_{10} \quad \text{(A6)}$$

$$\mu_1 = c_{10} \quad \text{(A7)}$$

$$\mu_2 = \left(\frac{f(1 - 4(f-2)Da)^{1/2}}{2Da(f-2)^2} - \frac{2}{f-2}\right)c_{10} \quad \text{(A8)}$$

From eq A5, the conversion is found to be given by eq 8, and when $DP_w = \mu_2/\mu_1$ and $DP_n = \mu_1/\mu_0$ are defined, eq 25 and 29 are obtained.

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Interpretation of the Mean-Square Dipole Moment of Poly(A–B) by Use of the Mean-Square End-to-End Distance for Its Didymous Partner

Neal A. Neuburger and Wayne L. Mattice*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909.
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ABSTRACT: For chains of the type A–B–A–B–...–A, with n bonds of length l between A and B and n bond dipole moment vectors of length m pointing from A to B, there is a didymous chain, which is defined such that $C' = D$ and $D' = C$, where $C = \langle r^2\rangle_0/nl^2$ and $D = \langle \mu^2\rangle_0/nm^2$ for the real chain and primes denote these ratios for the didymous chain. Thus the behavior of the mean-square dipole moment, $\langle \mu^2\rangle_0$, for the real chain can be deduced from the behavior of the mean-square end-to-end distance, $\langle r^2\rangle_0$, for the didymous chain. An understanding of the relationship between the real chain and its didymous partner therefore sheds insight into the relationship between C and D for the real chain. The didymous chain is described here for bonds subject to independent symmetric rotational potentials and for bonds subject to interdependent symmetric 3-fold rotation potentials. In the former case, it is sufficient to simply replace each bond angle by its supplement. In the latter case, one must also make the assignments $\psi' = \omega$ and $\omega' = \psi$, where ψ and ω are the statistical weights for the second-order interactions in g^+g^+ and g^+g^- states, respectively, in the real chain.

Introduction

A chain in which the atoms alternate between A and B, with a dipole moment vector of nonzero length colinear with each bond and pointing from A to B, is one of the simplest macromolecules with a permanent dipole moment. A fragment of this chain is depicted in Figure 1. Its unperturbed mean-square end-to-end distance and unperturbed mean-square dipole moment, denoted by $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$, respectively, are conveniently expressed by two dimensionless characteristic ratios defined as

$$C = \langle r^2\rangle_0/nl^2 \tag{1}$$

$$D = \langle \mu^2\rangle_0/nm^2 \tag{2}$$

where n is the number of bonds, l is the length of the bond vector, and m is the length of the bond dipole moment vector. Vectors of length l are connected head-to-tail, but vectors of length m are connected head-to-head and tail-to-tail, as shown in Figure 1. In the special case where the bonds are freely jointed, $C = D = 1$. In general, however, these two characteristic ratios have different values. In many models for real chains, $C > 1 > D$.

Added insight into the influence of the local structure on D can be obtained by investigation of a molecule that we call the didymous chain. In this work, primes will be appended to the properties of the didymous chain. The word "didymous" carries the connotation of "twin" in biology. We prefer the uncommon word "didymous" to the more common word "twin" because the relationships between the real chain and its didymous partner are

$$C' = D \tag{3}$$

$$D' = C \tag{4}$$

It is not their values of C, and their values of D, that are identical. Rather it is C' that behaves as D and D' that behaves as C. Definition of the relationship between a real chain and its didymous partner therefore provides additional insight into the relationship between C and D for the real chain. The relationship is trivial if the chain is freely jointed, because then $C = D = C' = D' = 1$, and the real chain is identical with the didymous chain. For more realistic models, however, the real chain is not identical with the didymous chain. The treatment here will first consider chains with bonds subject to independent symmetric rotation potentials and then chains with bonds subject to interdependent symmetric 3-fold rotational potentials.

Independent Symmetric Rotation Potential

When the internal bonds are subject to identical independent rotation potentials, the generator matrix formalism for C and D for poly(A–B) terminated with A at each end takes the blocked form[1]

$$C = n^{-1}l^{-2} \times \\ [1 \quad \mathbf{0}]\left\{\begin{bmatrix} 1 & 2\mathbf{l}^{\mathrm{T}}\langle \mathbf{T}_{\mathrm{A}}\rangle & l^2 \\ \mathbf{0} & \langle \mathbf{T}_{\mathrm{A}}\rangle & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\begin{bmatrix} 1 & 2\mathbf{l}^{\mathrm{T}}\langle \mathbf{T}_{\mathrm{B}}\rangle & l^2 \\ \mathbf{0} & \langle \mathbf{T}_{\mathrm{B}}\rangle & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\right\}^{n/2}\begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix} \tag{5}$$

$$D = n^{-1}m^{-2} \times \\ [1 \quad \mathbf{0}]\left\{\begin{bmatrix} 1 & 2\mathbf{m}_{\mathrm{A}}^{\mathrm{T}}\langle \mathbf{T}_{\mathrm{A}}\rangle & m^2 \\ \mathbf{0} & \langle \mathbf{T}_{\mathrm{A}}\rangle & \mathbf{m}_{\mathrm{A}} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\begin{bmatrix} 1 & 2\mathbf{m}_{\mathrm{B}}^{\mathrm{T}}\langle \mathbf{T}_{\mathrm{B}}\rangle & m^2 \\ \mathbf{0} & \langle \mathbf{T}_{\mathrm{B}}\rangle & \mathbf{m}_{\mathrm{B}} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\right\}^{n/2}\begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix} \tag{6}$$

where $\mathbf{0}$ denotes a rectangular null block such that the initial row and last column contain five elements and the square matrices are of dimensions 5 × 5. The transpose of each bond length vector is $\mathbf{l}^{\mathrm{T}} = [l \quad 0 \quad 0]$. Subscripts are appended to each bond dipole moment vector, $\mathbf{m}$, and each averaged transformation matrix, $\langle \mathbf{T}\rangle$. The bond dipole moment vectors are $\mathbf{m}_{\mathrm{A}}^{\mathrm{T}} = [m \quad 0 \quad 0]$ and $\mathbf{m}_{\mathrm{B}} = -\mathbf{m}_{\mathrm{A}}$. The two averaged transformation matrices will differ if $\theta_{\mathrm{ABA}} \neq \theta_{\mathrm{BAB}}$, where θ denotes the supplement of the bond angle specified by the subscript.

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