

# On the Relationship between the Characteristic Ratio of a Finite Chain, $C_n$ , and the Asymptotic Limit, $C_\infty$

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**ABSTRACT:** Often experiments with chains containing a finite number of bonds,  $n$ , are interpreted with the assumption that the characteristic ratio,  $C_n$ , is determined completely by  $C_\infty$  and  $n$ . This assumption is supported by some, but not all, textbook models for simple flexible chains. The freely jointed chain, freely rotating chain with fixed bond angle, and simple wormlike chain predict  $C_n = f(C_\infty, n)$ . These three models share the feature that the stiffness of the chain is specified by no more than one parameter. However, when more than one parameter affects the stiffness of the chain, as in the model with fixed bond angle and symmetric hindered rotation about independent bonds,  $C_n$  is no longer determined by  $C_\infty$  and  $n$  alone,  $C_n \neq f(C_\infty, n)$ . Since virtually all real chains have hindered rotation, they cannot be expected to have the dimensions given by  $C_n = f(C_\infty, n)$ . This conclusion is supported by numerical calculations using previously published rotational isomeric state models for polyethylene, polyisobutylene, and poly(dimethylsiloxane). Although these three polymers have similar values of  $C_\infty$ , they may have quite different values of  $C_n$ . This conclusion from the calculations is consistent with the observed behavior of polyisobutylene and poly(dimethylsiloxane), as reported by Arbe et al. (*Macromolecules* 2001, 34, 1281) and by Sluch et al. (*Macromolecules* 2003, 36, 2721). The finite  $n$  effect in these polymers is three times stronger for the mean square unperturbed radius of gyration than for the mean square unperturbed end-to-end distance.

## I. Introduction

Flexible homopolymers have mean square unperturbed end-to-end distances,  $\langle r^2 \rangle_0$ , directly proportional to the number of bonds,  $n$ , in the limit as  $n \rightarrow \infty$ . The characteristic ratio,  $C_n$ , for a chain with  $n$  bonds of length  $l$  approaches an asymptotic limit,  $C_\infty \equiv \lim_{n \rightarrow \infty} C_n$ .

$$C_n \equiv \langle r^2 \rangle_0 / nl^2 \quad (1)$$

Since experiments are performed using chains with  $n < \infty$ , there is interest in the nature of the approach of  $C_n$  to  $C_\infty$ . Unfortunately, several popular and simple models for chain molecules present a confusing picture of one of the most fundamental aspects of the relationship between  $C_n$  and  $C_\infty$ : Is  $C_n$  completely determined by  $C_\infty$ , or might two different chains that coincidentally have the same value of  $C_\infty$  nonetheless have different values of  $C_n$ ? Here we explicitly state the results for several of these popular models, and demonstrate what properties of the models controls their prediction about the uniqueness of the relationship between  $C_n$  and  $C_\infty$ .

A simple hypothesis, often coupled with the traditional definition of a Kuhn segment, or effective bond length, is that  $C_n$  is determined completely by  $C_\infty$  and  $n$ .

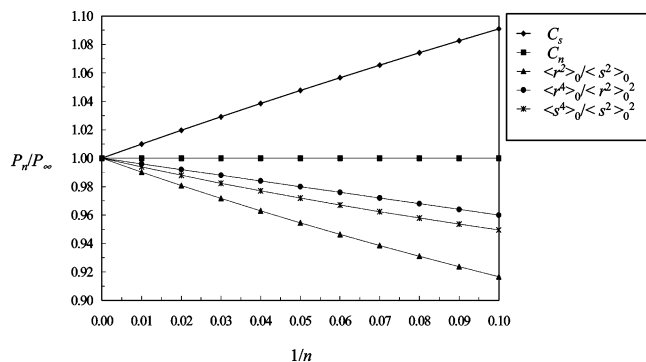
$$P_n = f(P_\infty, n) \quad (2)$$

Here  $P_n$  denotes a dimensionless ratio determined by the distribution of segments in the chain, and  $P_\infty$  denotes the limit for  $P_n$  as  $n \rightarrow \infty$ .  $C_n$  is one such

dimensionless ratio. Other dimensionless ratios can be formulated from the mean square unperturbed radius of gyration,  $\langle s^2 \rangle_0$ , from higher even moments,  $\langle r^{2p} \rangle_0$  and  $\langle s^{2p} \rangle_0$ ,  $p = 2, 3, \dots$ , from the ratio of  $\langle r^2 \rangle_0$  and  $\langle s^2 \rangle_0$ , etc. Several simple models for chain molecules, including the freely jointed (FJ) chain, freely rotating (FR) chain with a single fixed bond angle, and simple wormlike chain, have values of  $C_n$  that conform to the hypothesis expressed in eq 2.

Most real chains exhibit more complex behavior, such that  $C_n$  is not given accurately by  $C_\infty$  and  $n$  alone, as illustrated by a comparison of polyisobutylene (PIB) and poly(dimethylsiloxane) (PDMS). These two polymers have similar values of  $C_\infty$ , but the finite  $n$  effect on the mean square dimensions is significantly stronger in PIB than in PDMS.<sup>1,2</sup> When this behavior of real chains goes unrecognized, unphysical results for local chain properties, such as bead size or segment length, can be obtained from interpretation with eq 2 of data obtained at finite  $n$ . The problem was recognized three decades ago, when a "shift factor" was introduced to improve the range of applicability of the wormlike chain model.<sup>3</sup>

Here we revisit the well-known analytical expressions for several textbook models of polymer chains, permits identification of the common feature of the FJ chain, FR chain, and simple wormlike chain that prompts their adherence to eq 2. Then consideration of the simple chain with fixed bond angle and independent bonds subject to symmetric hindered rotation identifies the feature that causes deviation from the behavior promised by this equation. It is then easily seen that real chains are not expected to obey eq 2. This expectation is verified by numerical calculations using previously published rotational isomeric state (RIS) models for polyethylene (PE), PIB, and PDMS.



**Figure 1.**  $P_n/P_\infty$  vs  $1/n$  for the FJ chain. From top to bottom at finite  $n$ , the property  $P$  is  $C_{s,n}$ ,  $C_n$ ,  $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$ ,  $\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2$ , and  $\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2$ .

## II. Models with $C_n = f(C_\infty, n)$

**The Freely Jointed Chain.** The mean square dimensions of a FJ chain are given by simple formulas that appear in textbooks.<sup>4</sup>

$$\langle r^2 \rangle_0 = n l^2 \quad (3)$$

$$\langle s^2 \rangle_0 = (1/6)(n+2)(n+1)^{-1} n l^2 \quad (4)$$

A dimensionless characteristic ratio analogous to  $C_n$  can be formulated from  $\langle s^2 \rangle_0$ .

$$C_{s,n} \equiv \langle s^2 \rangle_0 / n l^2 \quad (5)$$

Characteristic ratios at finite  $n$  are related to the asymptotic limits as suggested by eq 2.

$$C_n = C_\infty \quad (6)$$

$$C_{s,n} = (n+2)(n+1)^{-1} C_{s,\infty} \quad (7)$$

This form is also observed with  $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$  and dimensionless ratios that measure the widths of the distributions for  $r^2$  and  $s^2$ .<sup>5,6</sup>

$$\langle r^2 \rangle_0 / \langle s^2 \rangle_0)_n = (n+1)(n+2)^{-1} (\langle r^2 \rangle_0 / \langle s^2 \rangle_0)_\infty \quad (8)$$

$$\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2)_n = (5n-2)(5n)^{-1} (\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2)_\infty \quad (9)$$

$$\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2)_n = (19n^3 + 45n^2 + 32n - 6) \times [19n(n+1)(n+2)]^{-1} (\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2)_\infty \quad (10)$$

Comparison of the rates of convergence of  $P_n$  (where  $P$  denotes any of the dimensionless properties in eqs 6–10) to the Gaussian limit can be determined from  $P_n$  vs  $1/n$ . Even more informative is the evaluation of  $P_\infty^{-1} [dP_n/d(1/n)]$ , so that all of the lines have an intercept of 1 at  $1/n = 0$ , as shown in Figure 1. Casual inspection of this figure reveals that  $P_n$  is well approximated as being directly proportional to  $1/n$  for FJ chains with  $n > 10$ .

$$P_n/P_\infty = 1 + P_\infty^{-1} [dP_n/d(1/n)]_{1/n=0} (1/n) \quad (11)$$

The initial slopes of the lines in Figure 1 are measures of the steepness of the convergence of  $P_n$  to the Gaussian limit for the FJ chain.

$$C_\infty^{-1} [dC_n/d(1/n)]_{1/n=0} = 0 \quad (12)$$

$$C_{s,\infty}^{-1} [dC_{s,n}/d(1/n)]_{1/n=0} = 1 \quad (13)$$

$$(\langle r^2 \rangle_0 / \langle s^2 \rangle_0)_\infty^{-1} [d(\langle r^2 \rangle_0 / \langle s^2 \rangle_0)/d(1/n)]_{1/n=0} = -1 \quad (14)$$

$$(\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2)_\infty^{-1} [d(\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2)/d(1/n)]_{1/n=0} = -2/5 \quad (15)$$

$$(\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2)_\infty^{-1} [d(\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2)/d(1/n)]_{1/n=0} = -12/19 \quad (16)$$

$C_n$  is at the Gaussian limit at  $n \geq 1$ . The steepest final approaches to this limit, as judged by the absolute values of  $P_\infty^{-1} [dP_n/d(1/n)]_{1/n=0}$ , are seen with  $C_{s,n}$  and  $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$ . The former property approaches the limit from above, and the latter property approaches the limit from below. Also approaching the limit from below are  $\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2$  and  $\langle s^4 \rangle_0 / \langle s^2 \rangle_0^2$ . The width of the distribution for  $r^2$  approaches the Gaussian limit less steeply than the width of the distribution for  $s^2$ . The fact that  $C_n$  and  $C_{s,n}$  both become linear in  $1/n$  at sufficiently large  $n$  is a general property of unperturbed homopolymers.<sup>7,8</sup>

Not all attributes of the chain approach the Gaussian limit at the same rate, or from the same direction. Attainment of the Gaussian limit by any specific property, such as  $C_n$ , is a necessary, but not a sufficient, condition for rigorous adherence to Gaussian statistics.

**The Freely Rotating Chain.** The FR chain has mean square unperturbed dimensions expressed in terms of  $\alpha \equiv -\cos \theta$ , defined as the cosine of the supplement of the bond angle,  $\theta$ .<sup>9</sup> The well-known equations, which appear in textbooks and monographs (see, for example, Flory<sup>10</sup>), define limiting values that recover the usual relationship between  $C_\infty$  and  $C_{s,\infty}$ .

$$C_\infty = 6C_{s,\infty} = (1 + \alpha)(1 - \alpha)^{-1} \quad (17)$$

The initial slopes of  $C_n/C_\infty$  and  $C_{s,n}/C_{s,\infty}$  vs  $1/n$  are determined by  $\alpha$  (or, equivalently, by  $C_\infty$ ).

$$C_\infty^{-1} [dC_n/d(1/n)]_{1/n=0} = -X \quad (18)$$

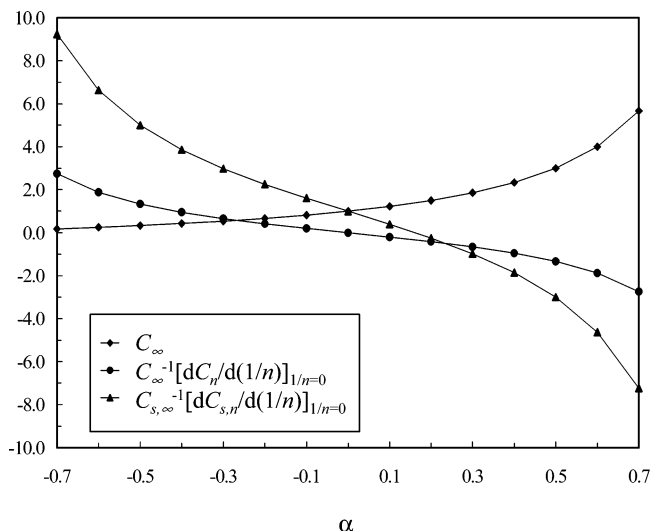
$$C_{s,\infty}^{-1} [dC_{s,n}/d(1/n)]_{1/n=0} = 1 - 3X \quad (19)$$

$$X = 2\alpha(1 + \alpha)^{-1}(1 - \alpha)^{-1} = (1/2)(C_\infty + 1) \times (C_\infty - 1)C_\infty^{-1} \quad (20)$$

The leading term of 1 in eq 19 is from the FJ chain, eq 13. The second term in eq 19,  $-3X$ , is the correction arising from the fixed bond angle. Since the FJ chain has  $C_\infty^{-1} [dC_n/d(1/n)]_{1/n=0} = 0$ , eq 12, the only nonzero term in eq 18 is the correction due to the fixed bond angle. This correction is less severe for  $C_n$  than for  $C_{s,n}$ .

Since  $X$  is determined completely by  $C_\infty$  in eq 20,  $C_n$  and  $C_{s,n}$  for the FR chain obey the hypothesis expressed in eq 2.

Figure 2 depicts the expressions in eqs 18 and 19, along with  $C_\infty$ , as a function of  $\alpha$ . Both initial slopes are negative if  $\alpha > 0.1623...$  (if  $C_\infty > 1.387...$ ). The initial slope for  $C_{s,n}/C_{s,\infty}$  vs  $1/n$  is more negative than the initial slope for  $C_n/C_\infty$  vs  $1/n$  if  $\alpha > 0.2360...$  (if  $C_\infty > 1.618...$ ). Since most real polymers have  $C_\infty > 2$ , the FR chains of greatest practical interest have  $C_n$  and  $C_{s,n}$  that approach their limiting values from below. If these



**Figure 2.**  $C_\infty$ ,  $[d(C_n/C_\infty)/d(1/n)]_{1/n=0}$ , and  $[d(C_{s,n}/C_{s,\infty})/d(1/n)]_{1/n=0}$  as a function of the cosine of the supplement of the bond angle,  $\alpha$ , for a FR chain.

chains have a finite number of bonds,  $C_n/C_\infty$  will be closer to 1 than will  $C_{s,n}/C_{s,\infty}$ . For this reason, the final approach of  $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$  to its limiting value of 6 is from above.

**The Wormlike Chain.** The simple wormlike chain, Porod–Kratky chain, or continuously curved chain has mean square dimensions expressed in terms of the persistence length,  $a$ , and the contour length,  $r_{\max}$ , with the latter quantity directly proportional to molecular weight.<sup>11–13</sup> Dimensionless ratios, in analogy to  $C_n$  and  $C_{s,n}$ , are obtained through division of  $\langle r^2 \rangle_0$  and  $\langle s^2 \rangle_0$ , respectively, by  $ar_{\max}$ . In the limit as  $r_{\max} \rightarrow \infty$ ,  $\langle r^2 \rangle_0$  and  $\langle s^2 \rangle_0$  approach limits of  $2ar_{\max}$  and  $(1/3)ar_{\max}$ , respectively. The expressions analogous to eqs 18 and 19 show that the approach to the asymptotic limit is specified completely by the persistence length,  $a$ .

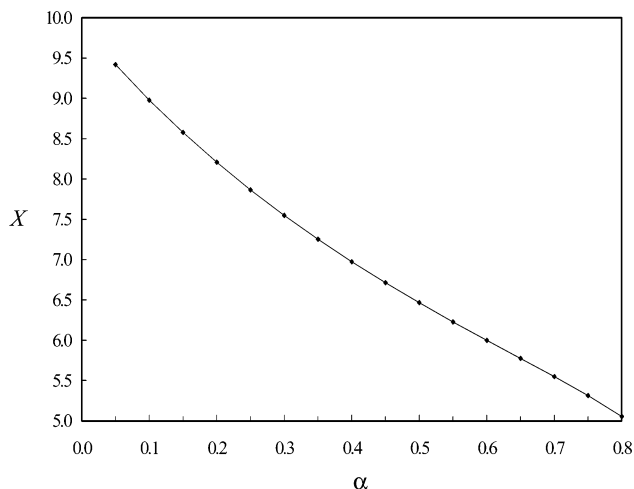
$$(\langle r^2 \rangle_0 / ar_{\max})_\infty^{-1} [d(\langle r^2 \rangle_0 / ar_{\max}) / d(1/r_{\max})]_{1/r_{\max}=0} = -a \quad (21)$$

$$(\langle s^2 \rangle_0 / ar_{\max})_\infty^{-1} [d(\langle s^2 \rangle_0 / ar_{\max}) / d(1/r_{\max})]_{1/r_{\max}=0} = -3a \quad (22)$$

As with the FR chain, this simple model implies obedience to the form of eqs 2,  $\langle r^2 \rangle_0 / ar_{\max} = f(\langle r^2 \rangle_0 / ar_{\max})_\infty, r_{\max})$ . At finite  $r_{\max}$ , the mean square dimensions are a function solely of the length of the chain, expressed as  $n$  or  $r_{\max}$ , and a parameter that describes the stiffness, either  $C_\infty$  or  $a$ .

### III. Chains with $C_n \neq f(C_\infty, n)$

**Simple Chain with Fixed Bond Angle and Symmetric Hindered Rotation about Independent Bonds.** The mean square unperturbed dimensions of a simple chain with independent bonds, bond angles fixed at  $\theta$ , and bonds subject to symmetric hindered rotation can be expressed in terms of  $n$ ,  $\alpha$ , and  $\eta$ , where  $\eta = \langle \cos \phi \rangle$ , with  $\phi$  being the torsion angle.<sup>14–16</sup> Following Flory, we adopt here the convention that  $\phi = 0$  for a trans placement.<sup>16</sup> Symmetric hindered rotation means  $E(\phi) = E(-\phi)$ , where  $E$  is the torsion energy. The discussion is confined to chains with  $0 < \eta < 1$ , so that a chain remains flexible and has a net preference for



**Figure 3.**  $X$ , defined by eq 24, for simple chains with  $C_\infty = 10$  and independent bonds subject to symmetric hindered rotation. The cosine of the supplement of the bond angle is denoted by  $\alpha$ . The hindered internal rotation changes with  $\alpha$ , via eq 23, so that  $C_\infty$  remains constant.

conformations that are more expanded than the FR chain with the same bond angle.

$$C_\infty = 6C_{s,\infty} = (1 + \alpha)(1 - \alpha)^{-1}(1 + \eta)(1 - \eta)^{-1} \quad (23)$$

Equations 18 and 19 apply to this chain, but  $X$  is now given by a more complicated expression than eq 20.

$$X = 2(\alpha - 1)(\alpha + 1)^{-1}(\eta - 1)(\eta + 1)^{-1}[(\alpha\eta + \lambda_1) \times \lambda_1(1 - \lambda_1)^{-2} - (\alpha\eta + \lambda_2)\lambda_2(1 - \lambda_2)^{-2}](\lambda_1 - \lambda_2)^{-1} \quad (24)$$

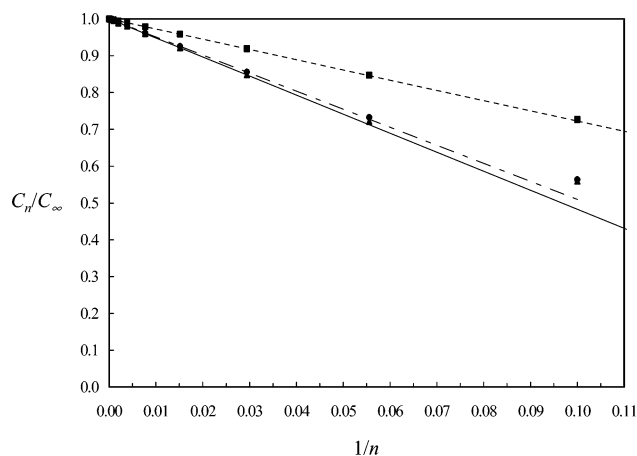
$$\lambda_{1,2} = (1/2)\{\alpha(1 - \eta) \pm [\alpha^2(1 - \eta)^2 + 4\eta]^{1/2}\} \quad (25)$$

Although interchange of  $\alpha$  and  $\eta$  has no effect on  $C_\infty$  or  $C_{s,\infty}$ , as can be seen from the form of eq 23, that interchange alters the values of  $\lambda_1$  and  $\lambda_2$  via eq 25 and hence the values of  $X$ , via eq 24. Values of  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$  and  $C_{s,\infty}^{-1}[dC_{s,n}/d(1/n)]_{1/n=0}$ , via eqs 18, 19, and 24, cannot be determined from  $C_\infty$  alone. The simple behavior seen with the FR chains, where these two derivatives are determined completely by  $C_\infty$ , is lost when the bonds are subject to hindered internal rotation.

The potential size of the effect is illustrated in Figure 3. All of the chains considered in this figure have  $C_\infty = 10$ , which is close to the experimental  $C_\infty$  for several real chains, such as atactic polystyrene<sup>17–19</sup> and isotactic poly(methyl methacrylate).<sup>20,21</sup> When  $\alpha = 1/3$ , the value of  $\eta$  is  $2/3$ . At other values of  $\alpha$ , a new value of  $\eta$  is calculated from eq 23 so that  $C_\infty$  is unchanged. The figure depicts the values of  $X$ , calculated from eq 24 for each combination of  $\alpha$  and  $\eta$ . These values of  $X$  vary by nearly a factor of 2 over the range of  $\alpha$  covered in the figure.

Two chains with the same value of  $C_\infty$  may have different values of  $C_n$  for finite  $n$ , if symmetric hindered rotation leads to different values of  $\langle \cos \phi \rangle$ . The steepness of the final approach of  $P_n/P_\infty$  to its limit at  $1/n = 0$  cannot be deduced from  $C_\infty$  alone if the bonds in the chain are subjected to hindered internal rotation. These chains have more complex behavior than the simple expectation promised by eq 2.

**Rotational Isomeric State Models for Real Chains.** The literature contains RIS models for hun-



**Figure 4.**  $C_n$  vs  $1/n$  for RIS models of PE<sup>20</sup> (triangles), PIB<sup>21</sup> (circles), and PDMS<sup>22</sup> (squares). The straight lines depict the initial slopes. The slopes and intercepts of the straight lines are listed in Table 1.

**Table 1. Numerical Results from RIS Models**

| polymer | RIS model | $C_\infty = 6C_{s,\infty}$ | $C_\infty^{-1} \times [dC_n/d(1/n)]_{1/n=0}$ | $C_{s,\infty}^{-1} \times [dC_{s,n}/d(1/n)]_{1/n=0}$ |
|---------|-----------|----------------------------|--|--|
| PE      | ref 23    | 6.81                       | -5.2   | -16  |
| PIB     | ref 24    | 6.61                       | -4.9   | -14  |
| PDMS    | ref 25    | 6.29                       | -2.8   | -8   |

dreds of polymer structures.<sup>22</sup> It will suffice to examine only three of these models that have nearly the same value of  $C_\infty$ . Can such models have different values of  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$ , as suggested in Figure 3 by simple chains with independent bonds subject to symmetric hindered rotation?

Three well-known polymers, PE, PIB, and PDMS, are adopted for this purpose. The literature contains several RIS models for each of these polymers.<sup>22</sup> The specific models used here are due to Abe et al.<sup>23</sup> for PE, DeBolt and Suter for PIB,<sup>24</sup> and Flory et al.<sup>25</sup> for PDMS. Calculations for PE use a bond angle of  $112^\circ$ , three rotational isomeric states with  $\phi$  of 0 and  $\pm 120^\circ$ , and 0.55 and 0.092 for the statistical weights denoted by  $\sigma$  and  $\omega$ , respectively. PIB is treated using four rotational isomeric states with  $\phi$  of  $\pm 25^\circ$  and  $\pm 120^\circ$ , bond angles of  $110^\circ$  and  $124^\circ$  for  $\text{CH}_2\text{-C-CH}_2$  and  $\text{C-CH}_2\text{-C}$ , respectively, and 0.007, 0, and 0 for the statistical weights denoted by  $\xi$ ,  $\gamma$ , and  $\delta$ , respectively. For PDMS, we use bond angles of  $110^\circ$  and  $143^\circ$  for  $\text{O-Si-O}$  and  $\text{Si-O-Si}$ , respectively, three rotational isomeric states with  $\phi = 0$  and  $\pm 120^\circ$ , and 0.286, 0.286, and 0.06 for the statistical weights denoted by  $\sigma$ ,  $\sigma'$ , and  $\delta$ , respectively. The lengths of the C-C and Si-O bonds, 0.154 and 0.164 nm, respectively, are irrelevant. Calculations of  $C_n$  were performed with the program listed in Appendix C of Mattice and Suter.<sup>26</sup> The values of  $C_{s,n}$  were calculated with an analogous program in which the  $7 \times 7$  generator matrix appropriate for  $s^2$  replaces the  $5 \times 5$  generator matrix that is appropriate for  $r^2$ .<sup>27</sup>

The  $C_n$  calculated from the RIS models are depicted by the data points in Figure 4. The asymptotic limits, which are listed in Table 1, are  $6.55 \pm 0.26$ . The straight lines in Figure 4 denote  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$ . Their values, along with  $C_{s,\infty}^{-1}[dC_{s,n}/d(1/n)]_{1/n=0}$ , are also listed in Table 1. PE and PIB exhibit nearly the same final approach to their asymptotic limits, but this approach is significantly steeper than the one seen with PDMS, where  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$  is only 53% of the value for PE. The difference in the behavior of the RIS models

**Table 2. Sensitivity Test for the Individual Parameters,  $w$ , in the RIS Models**

| polymer           | RIS model | $w$                                | RIS value   | $\partial(\ln C_\infty)/\partial(\ln w)$ | $\partial(\ln  A )/\partial(\ln w)^a$ |
|-------------------|-----------|------------------------------------|-------------|--|---------------------------------------|
| PE                | ref 23    | $\theta$                           | $112^\circ$ | 4.5                                      | 3.1                                   |
|                   |           | $\phi_g^b$                         | $120^\circ$ | -2.2                                     | -3.2                                  |
|                   |           | $\sigma$                           | 0.55        | -0.43                                    | -0.16                                 |
|                   |           | $\omega$                           | 0.092       | -0.083                                   | -0.038                                |
| PIB <sup>d</sup>  | ref 24    | $\theta_{\text{CH}_2\text{CCH}_2}$ | $110^\circ$ | 3.8                                      | 2.9                                   |
|                   |           | $\theta_{\text{CCH}_2\text{C}}$    | $124^\circ$ | 0.86                                     | -0.076                                |
|                   |           | $\phi_t^c$                         | $25^\circ$  | 0.38                                     | 0.41                                  |
|                   |           | $\phi_g^b$                         | $120^\circ$ | -2.3                                     | -2.2                                  |
|                   |           | $\xi$                              | 0.007       | 0.0007                                   | 0.017                                 |
| PDMS <sup>f</sup> | ref 25    | $\theta_{\text{SiOSi}}$            | $143^\circ$ | -3.5                                     | -8.9                                  |
|                   |           | $\theta_{\text{OSiO}}$             | $110^\circ$ | 5.6                                      | 8.6                                   |
|                   |           | $\phi_g^b$                         | $120^\circ$ | 0.23                                     | 2.6                                   |
|                   |           | $\sigma$                           | 0.286       | 0.26                                     | 0.92                                  |
|                   |           | $\sigma'$                          | 0.286       | 0.068                                    | 0.10                                  |
|                   |           | $\delta$                           | 0.06        | -0.055                                   | -0.19                                 |

<sup>a</sup> All values of  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$  are negative. The absolute value is denoted by  $|A|$ . <sup>b</sup> The gauche states have torsion angles of  $\pm\phi_g$ . <sup>c</sup> The two "trans" states have torsion angles of  $\pm\phi_t$ .

for PDMS and PIB in Table 1 is consistent with the experimentally observed behavior of these polymers.<sup>1,2</sup>

For each polymer in Table 1,  $C_{s,n}$  approaches its limit more steeply than does  $C_n$ . The initial slopes are related by a factor of 3.

$$C_{s,\infty}^{-1}[dC_{s,n}/d(1/n)]_{1/n=0} = 3C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0} \quad (26)$$

This relationship is seen also with the simple wormlike chain, eqs 21 and 22. Equations 18–20 for the FR chain support the hypothesis that eq 26 may be "universal" in the limit as  $C_\infty$  becomes sufficiently large. Equation 26 is not obeyed by the FJ chain, eqs 12 and 13, and by FR chains with small values of  $C_\infty$ .

The actual values of  $C_n$  are reproduced to within 1% by the straight lines in Figure 4 down to  $n$  of about 20 for PE or PIB, and to  $n$  of 10 for PDMS. Equation 11 is robust when applied to  $C_n$  for these three polymers, provided the correct value of  $P_\infty^{-1}[dP_n/d(1/n)]_{1/n=0}$  is used. The correct value of this derivative is not determined by  $P_\infty$  alone.

Small variations in the parameters in the RIS models yield some insight into the origin of the differences in the values of  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$  for these three polymers. The change in any parameter in the RIS model affects  $C_\infty$  and  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$ , as shown in Table 2. With only one exception, a change that increases  $C_\infty$  causes  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$  to become more negative. The strongest effects in these three polymers, as judged by the absolute values of the partial derivatives, are seen upon changes in the bond angles. Analysis of additional polymers will be required before one can determine whether this conclusion is broadly applicable to real polymers.

#### IV. Concluding Remarks

The simple expectation from eq 2 is an attribute of models that include zero or one parameter that describes the stiffness of the simple chain. The FJ chain is the model with zero such parameters. The FR and simple wormlike chains are examples of models with one such parameter, the fixed bond angle  $\theta$  and the persistence length  $a$ , respectively.

When the stiffness of the chain is characterized by two or more parameters, the model no longer adheres



to the simple expectation from eq 2. The simple chain with symmetric hindered rotation is the prototype. Most real chains have a more complicated description of their hindered rotation. The torsion potential may be asymmetric, as in vinyl polymers, and the bonds may be interdependent, as is true for the great majority of real polymers. Errors will occur if eq 2 is assumed to apply to such real chains. An example would be the use of  $C_\infty$  and a persistence length to estimate  $C_n$  using the simple wormlike chain model. It may be dangerous to use  $C_\infty$  to estimate the bead size for a spring and bead model. Long ago, this problem with the simple wormlike chain model motivated the incorporation of a "shift factor" in order to improve agreement between the model and the behavior of real chains of finite molecular weight.<sup>3,28-32</sup> The "shift factor" introduces another parameter into the model, which permits a more accurate fitting of the model to experimental data. A new parameter can be introduced into the wormlike chain in other ways, as in the helical wormlike chain.<sup>33-37</sup> The helical wormlike chain allows coupled rotations.<sup>38</sup>

The RIS model provides an accurate description of  $C_n$  for real chains, at all values of  $n$ . It does not support the hypothesis expressed in eq 2, but instead finds  $C_n \neq f(C_\infty, n)$ . The expression  $C_n/C_\infty = 1 + C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}(1/n)$  can work remarkably well down to quite small values of  $n$ . For PE, PIB, and PDMS, the finite chain effect is three times stronger for  $\langle s^2 \rangle_0$  than for  $\langle r^2 \rangle_0$ , as judged by the relationship between  $C_{s,\infty}^{-1}[dC_{s,n}/d(1/n)]_{1/n=0}$  and  $C_\infty^{-1}[dC_n/d(1/n)]_{1/n=0}$ . This relationship may hold for all flexible chains with sufficiently large values of  $C_\infty$ .

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