

NOTE

Comment on a Paper by Oyama and Shiokawa

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Oyama and Shiokawa¹ recently published a note showing the calculations of bond conformation and unperturbed dimension for the polyethylene (PE) chain by using a direct integration method. They adopted the formulation prescribed by Saito² some years ago. The eigenvalues and eigenfunctions of the intergral equation whose kernel corresponds to the statistical weight defined for a pair of neighboring bond rotations, were evaluated numerically by using a potential energy contour map. The results were compared with those derived from calculations based on the rotational isomeric state (RIS) approximation in which statistical weights are expressed by simple Boltzmann factors in the corresponding conformational energies. Satisfactory agreement was found for the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$. For the bond conformation, however, a somewhat higher estimate for the *trans* conformation was obtained when the RIS scheme was employed. These authors concluded from these results that the RIS scheme may be applicable for calculating $\langle r^2 \rangle_0$, but not bond conformation. They suggested that such a discrepancy may arise from the fact that, in the RIS scheme adopted in their treatment, no consideration was made of the shape of the potential energy surface.

In this note, I would like to point out that a more elaborate RIS scheme³ has been available, allowing the shape of the potential energy minima to be taken into account. According to the procedure developed by Suter and Flory,³ the conformational partition function z_ζ , average energy $\langle E \rangle_\zeta$, and averaged rotation angle $\langle \phi_i \rangle_\zeta$ for each rotational state ζ may be calculated by

$$z_\zeta = \int_\zeta \int \exp(-E/RT) d\phi_i d\phi_{i+1} \quad (1)$$

$$\langle E \rangle_\zeta = z_\zeta^{-1} \int_\zeta \int E \exp(-E/RT) d\phi_i d\phi_{i+1} \quad (2)$$

$$\langle \phi_i \rangle_\zeta = z_\zeta^{-1} \int_\zeta \int \phi_i \exp(-E/RT) d\phi_i d\phi_{i+1} \quad (3)$$

where ϕ_i and ϕ_{i+1} represent the rotation angles for a pair of consecutive skeletal bonds i and $i+1$, respectively. In the following treatment, the energies $E(\phi_i, \phi_{i+1})$ were taken from the conformational energy contour map given by Oyama and Shiokawa.¹ Boltzmann factors were calculated for each discrete set of ϕ_i and ϕ_{i+1} defined at 10° intervals and integrations were carried out according to the trapezoidal rule over the range $E \leq 5$ kcal mol⁻¹ as prescribed by the energy contour map. The partition functions z , average energies $\langle E \rangle$, and averaged angles $\langle \phi_i \rangle$ and $\langle \phi_{i+1} \rangle$ calculated at three temperatures for the four nonequivalent states are listed in Table I. The energies are expressed relative to E at the minimum for the *tt* state, and correspondingly the partition functions are given relative to a value of unity for this state. The averaged rotation angles are nearly independent of temperature.

Oyama and Shiokawa¹ used a 3×3 statistical weight matrix in their RIS treatment of the PE chain, which may be expressed customarily⁴ as

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (4)$$

Table I. Partition functions, average energies, and averaged rotation angles deduced from the potential energy contour map^a

Rotational state	z^b			$\langle E \rangle^c / \text{kcal mol}^{-1}$			$\langle \phi_i \rangle, \langle \phi_{i+1} \rangle^d / \text{deg}$		
	300 K	400 K	500 K	300 K	400 K	500 K	300 K	400 K	500 K
<i>tt</i>	1.000	1.000	1.000	0.64	0.85	1.04	0.0, 0.0	0.0, 0.0	0.0, 0.0
<i>tg</i> ⁺	0.340	0.430	0.495	1.21	1.42	1.60	0.8, 116.6	0.9, 116.4	0.9, 116.2
<i>g</i> ⁺ <i>g</i> ⁺	0.125	0.201	0.265	1.78	1.97	2.13	116.5, 117.0	116.4, 116.9	116.3, 116.7
<i>g</i> ⁺ <i>g</i> ⁻	0.005	0.018	0.038	3.86	3.93	3.98	108.9, -108.9	109.0, -109.0	109.1, -109.1

^a cf. Figure 1 of ref 1.

^b Expressed relative to a value of unity for the *tt* state.

^c Energies expressed relative to zero for the minimum in the *tt* state.

^d Rotation angles are measured from the *trans* state ($\phi_i = 0$).

Table II. Conformational energies and preexponential factors associated with statistical weights

	300 K	400 K	500 K
$E_\sigma / \text{cal mol}^{-1}$	570	560	550
$E_\omega / \text{cal mol}^{-1}$	2080	1960	1840
σ_0	0.92	0.91	0.89
ω_0	1.36	1.12	0.97

where the elements are indexed in the order *t*, *g*⁺, *g*⁻. In this study, the statistical weight parameters σ and ω are defined in terms of the conformational energies E_σ and E_ω , respectively:

$$\begin{aligned} \sigma &= \sigma_0 \exp(-E_\sigma/RT) \\ \omega &= \omega_0 \exp(-E_\omega/RT) \end{aligned} \quad (5)$$

The preexponential factors σ_0 and ω_0 represent the effective sizes of the associated potential energy minima. Values of E_σ , E_ω , σ_0 , and ω_0 were estimated from $\langle E \rangle$ and z given in Table I according to the procedure set forth by Suter and Flory.³ The results are summarized in Table II. As shown on the energy contour map,¹ the shapes of the potential energy minima for the *tt*, *tg*[±], and *g*[±]*g*[±] states are quite similar to each other except for the altitude of these minima. Correspondingly, the mean value of the preexponential factor σ_0 deduced by the analysis of these states is close to unity and stays nearly invariable over a wide range of temperature. The *g*[±]*g*[∓] state involves severe steric interactions, and the energy contour diagram calculated for this region consists of a doublet.¹ Values of $\langle \phi_i \rangle$ and

$\langle \phi_{i+1} \rangle$ obtained by taking averages over the entire domain are given in Table I. The corresponding energy $\langle E \rangle$, expressed relative to the *tt* state, varies from 3.2 to 2.9 kcal mol⁻¹ in the range 300 to 500 K: the magnitude of $\langle E \rangle$ thus found is close to the minimum value ($E_{\min} = 3.3$ kcal mol⁻¹) reported for this state.¹ The factor ω_0 decreases from 1.3₆ to 0.9₇ over the same temperature range. From these results, we adopt the following expressions for the temperature of 140°C:

$$\begin{aligned} \sigma &= 0.9 \exp(-560/RT) \\ \omega &= 1.1 \exp(-1940/RT) \end{aligned} \quad (6)$$

with RT expressed in cal mol⁻¹. Values of σ_0 and ω_0 depart from unity only by ca. 10%. This suggests that the effect arising from the dissimilarity of the shapes of the potential energy minima should be comparatively small in this polymer system.

In accordance with the treatment of Oyama and Shiokawa,¹ we assume an infinitely long chain ($n = \infty$) for which the largest-eigenvalue method can be applied. The largest eigenvalue of the matrix given in eq 4 takes the form⁴

$$\lambda = (1/2) \{ 1 + \sigma + \omega + \sqrt{[1 - \sigma(1 + \omega)]^2 + 8\sigma} \} \quad (7)$$

Bond conformations ($e.g., f_{\xi\eta}$) may be estimated for a consecutive pair of bonds according to the expression,

$$f_{\xi\eta} = \partial \ln \lambda / \partial \ln u_{\xi\eta} \quad (8)$$

where $u_{\xi\eta}$ denotes the (ξ, η) element of U in eq 4. Values of f calculated for the *tt*, *tg*[±] (*g*[±]*t*), *g*[±]*g*[±], and *g*[±]*g*[∓] conformations are listed in Table III. These results are in good agreement with those

Table III. Comparison of bond conformations estimated by various methods for the temperature of 140°C

Bond conformation	RIS approximation			Integration method ^a
	Present method (eq 6)	Minimum energies (eq 9)	Mean energies (eq 10)	
f_i^b	0.626	0.609	0.605	0.618
f_g^b	0.374	0.391	0.395	0.382
f_{ii}	0.361	0.337	0.332	0.351
$f_{ig\pm} + f_{g\pm i}$	0.531	0.545	0.546	0.534
$f_{g\pm g\pm}$	0.098	0.110	0.112	0.101
$f_{g\pm g\mp}$	0.010	0.008	0.009	0.012

^a cf. Table I of ref 1.

^b Values of $\langle \cos \phi \rangle$ ($=f_i \cos \phi_i + f_g \cos \phi_g$) were calculated to be 0.459, 0.435, and 0.429 for eq 6, 9, and 10, respectively. The corresponding value deduced from the integration method¹ is 0.488.

estimated from the direct integration method by Oyama and Shiokawa.¹ Fractions of the conformer for a single bond, f_i and f_g , can be deduced therefrom, and are included in the table. Also given in the table are the results obtained alternatively by adopting simpler expressions for the statistical weight parameters in eq 4; *i.e.*, with the minimum energies,¹

$$\sigma = \exp(-550/RT) \quad (9)$$

$$\omega = \exp(-2200/RT)$$

and with the energies termed "mean" values,¹

$$\sigma = \exp(-540/RT) \quad (10)$$

$$\omega = \exp(-2030/RT)$$

As shown in the table, use of these alternative parameter sets yields very similar results with those derived from the more elaborate methods: *e.g.*, values of f_i ($=1 - f_g$) calculated as above all fall in the range 0.615 ± 0.011 . In this respect, the present results are at variance with those of Oyama and Shiokawa,¹ who obtained a somewhat higher content for the *trans* conformation ($f_i = 0.721 \pm 0.003$) when a parameter set such as those given in eq 9 and 10 was employed. Since the details of the computational procedure have not been reported,¹ the cause for this discrepancy can not be identified.

The characteristic ratio C_∞ for the unperturbed end-to-end distance and its temperature coefficient $d \ln C_\infty / dT$ were also calculated by using the parameter set given in eq 6. When geometrical pa-

rameters such as $\angle CCC = 112^\circ$, $\phi_i = 0$, and $\phi_{g\pm} = \pm 116.5^\circ$ were used, the following values calculated⁴ for an infinitely long PE chain were obtained: $C_\infty = 7.84$ and $d \ln C_\infty / dT = -1.23 \times 10^{-3} \text{ K}^{-1}$ at 140°C. These results⁵ should be compared with those obtained by adopting the energy parameters given by Oyama and Shiokawa.¹ Use of the parameter set for the minimum energy (eq 9) yielded $C_\infty = 7.65$ and $d \ln C_\infty / dT = -1.06 \times 10^{-3} \text{ K}^{-1}$ (140°C). The parameter set for the mean energy (eq 10) gave $C_\infty = 7.51$ and $d \ln C_\infty / dT = -1.10 \times 10^{-3} \text{ K}^{-1}$ (140°C). In these calculations, geometrical parameters were taken to be identical with those given above. Variation arising from the choice of the statistical weight parameter set is quite insignificant for either C_∞ or $d \ln C_\infty / dT$.

In summary, I would like to call attention to the fact that, in the RIS scheme developed by Flory,^{3,4} due consideration is given to the effect arising from the shape of the potential energy minima. The calculations presented in this note indicate, however, that the simple RIS treatment gives a satisfactory presentation of the bond conformation of the PE chain. This conclusion is at variance with Oyama and Shiokawa.¹ Allegra and Immirzi⁶ examined the Fourier series development of the statistical weight function, and concluded that their method should be preferable to the RIS treatment in such a case that the energy minima are flat and/or the energy barriers are low compared to RT . The same seems to apply to the integration method developed by Oyama and Shiokawa.¹

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