Configurational Properties of Polymethylene Chain by Direct Enumeration Method

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ABSTRACT: The configurational properties of the polymethylene chain have been deduced using the three-rotational isomeric state approximation combined with the direct enumeration method. The characteristic ratios for mean square end-to-end distance, $<R_n^2>$, and radius of gyration, $<S_n^2>$, are obtained using a graphical extrapolation method. The influence of short- and long-range interactions has been assessed. The validity of two types of contact distance has also been examined. The outer limit contact distances yield reasonable results and might be considered as appropriate to describe the polymethylene system. The normally allowed contact distances are shown to yield only rigid rod behavior. The effects of the variation in bond and rotational angles have been investigated using the outer limit contact distances.

A great deal of theoretical work has been carried out in the past decade relating molecular properties to chemical structure.[1,2] These studies cover a wide range of synthetic polymers. Homopolymers and stereochemical copolymers, such as, vinyl polymers of variable *d*, *l*, structure,[2] and diene polymers of variable cis, trans structure,[3,4] have been studied. Various properties, such as the mean square dimensional properties, higher moments of dimensional properties, dipole moments, optical properties, and probability functions have been calculated. An excellent review on this subject may be found in ref 1.

Flory and his collaborators have pioneered the mathematical techniques and methodology of obtaining the above mentioned properties and have applied them successfully to a variety of synthetic polymers.[1] In doing this, the isomeric state approximation has been extensively used. This effectively replaces the continuous rotational angles by a set of discrete values. In elucidating any given property, the statistical weights (which are related to the energy and the temperature by means of an exponential factor) are assigned to each nearest neighbor interaction.[5] The interactions are assumed to extend only a few bonds from the group of atoms in question. These interactions are classified as *first order*[6] if they involve the groups separated by three skeletal bonds (one rotational angle, ϕ) and as *second order* if the interacting pairs are separated by four skeletal bonds (two rotational angles). No effort has been made to include the long-range interactions or the so called excluded volume effect. Obviously, such inclusion leads to numerous mathematical difficulties. In order to compensate for short-range interactions, the statistical weights (or the energy values) at a particular temperature (θ temperature) are adjusted until the calculated value of the property coincides or nearly coincides with the experimental value. In performing these calculations few configurations with the number of bonds greater than 100 are generated on the computer. An asymptotic value, which is valid for long-chain molecules, is deduced using graphical techniques. Alternatively, an asymptotic value can also be obtained directly from the limiting mathematical equations.

We have undertaken a different approach. Using the direct enumeration technique, we have generated all the accessible configurations of a chain molecule consisting of only a few bonds. The excluded volume effect between two interacting pairs is explicitly taken into account by using a predescribed set of contact distances. An asymptotic value is then obtained by a graphical extrapolation method. It is often impossible, in a practical sense, using direct enumeration to generate configurations containing more than 14 bonds on a tetrahedral lattice. This is due to the computer time available. The direct enumeration technique has been successfully applied to a number of model systems in studying the excluded volume problem.[7,8] In applying this technique the mathematical approach which was developed by Flory and his associates[1] is not required.

In the present study, the configurational properties of polymethylene chain are obtained using the above mentioned technique. The isomeric state approximation model has been used. Asymptotic values are deduced using a graphical extrapolation method.

Theory

The model we adopt for the polymethylene chain is described by Flory.[1] Specifically, each skeletal bond is assumed to occur in any one of the three discrete rotational states. In the present case, these three rotational states are labeled trans (t), gauche positive (g^+) and gauche negative (g^-), which are assumed to occur at rotational angles $\phi = 0$, 120, and $-120°$, respectively. The bond angle, θ, was taken as 68°. The local coordinates of carbon and hydrogen atoms are computed by using the standard bond lengths and bond angles.[1,9] Many workers[9] have treated the carbon atom and the hydrogen atom(s) attached to that carbon atom (groups such as CH, CH_2, and CH_3) as a single unit. In the present work, the hydrogen atoms are separated from the carbon atoms and are treated as separate entities. Carbon atom 1 is placed at the origin of the Cartesian coordinate system, that is, bond 1 is made to lie along the *x* direction (see ref 1, Figure I-3). Bond 2 is added to bond 1, and the rotations around bond 1 are carried out by assigning three rotational states in a systematic way. The coordinates of each atom are then transformed from the local coordinate system to the reference system by means of a general transformation equation, which is

$$V^i = T_i(\phi_p, \theta)V \tag{1}$$

where the $T_i\,(\phi_p,\theta)$ is the transformation matrix

$$T_i(\phi_p, \theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\phi_p & -\cos\theta\cos\phi_p & \sin\phi_p \\ \sin\theta\sin\phi_p & -\cos\theta\sin\phi_p & -\cos\phi_p \end{bmatrix} \tag{2}$$

$$p = t,\ g^+,\ g^-$$

After having added four bonds, the excluded volume is checked between the nonbonded atoms. After each step a

Table I
Contact Distances (Å) Used to Check the Excluded Volume in Polymethylene Chain

Atomic pair	Normally allowed	Outer limit
C···C	3.2	3.0
C···H	2.4	2.2
H···H	2.0	1.9

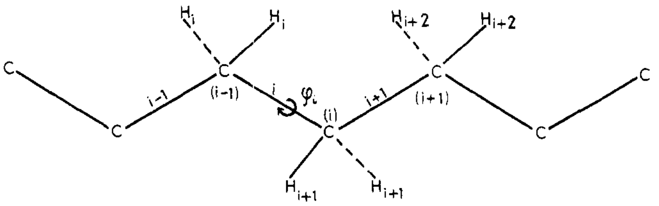

Figure 1. The planar conformation of a portion of a polymethylene chain. In the planar trans conformation, $\phi = 0°$. For the Cartesian framework, see ref 1, Figure I-3.

test for excluded volume is made. Using this procedure, a chain of a desired length is generated. Once the desired length is reached, the properties in question are computed. The hydrogen atoms attached to the *i*th carbon atom are treated as a part of a unit which consists of these two hydrogen atoms and the $(i + 1)$th carbon atom (see Figure 1). It is necessary to do so since rotation about the *i*th bond changes the coordinates of the hydrogen atoms attached to the *i*th carbon atom and the $(i + 1)$th carbon atom.

Method

The technique used to enumerate excluded volume polymethylene chain is based on the method developed by Martin.[10,11] Since the paper by Martin and ref 11 give a complete exposition of this method, it will not be discussed here. The program was run on a CDC 3600 machine, housed in the Computing Center at Adelphi University.

Results and Discussion

The computation has been carried out using two sets of contact distances given by Flory[12] (these contact distances are given in Table I). The mean square end-to-end distance $<R_n^2>$, the mean square radius of gyration $<S_n^2>$, and their characteristic ratios have been obtained. These properties are listed in Table II for normally allowed and outer limit contact distances, respectively. For comparison, the above mentioned properties were calculated without taking into account excluded volume and included in Table II. Two sets of contact distances were used in order to examine the validity of the contact distances in yielding the experimental characteristic ratio. In Figures 2 and 3, the asymptotic values are deduced using the graphical extrapolation technique. The characteristic ratios, $C_\infty = (<R_n^2>/nl^2)_\infty$ and $C_\infty' = (<S_n^2>/nl^2)_\infty$ (where n is the number of bonds in a chain molecule, and l is the bond length), and their ratios are tabulated in Table III. From these results, it is evident that the outer limit contact distances yield a characteristic ratio, C_∞, which is a little higher than the experimental value 6.7 at 140° (see ref 1, p 40). A slight increase in our calculated value can be explained in terms of long-range interactions. The experimental value, which is derived at the θ-point, accounts for only the short-range interactions, whereas, our calculated value accounts for the short-range as well as the long-range interactions. The difference between our calculated and experimental values (given by Flory), 7.16 − 6.7 = 0.4, may be attributed to the influence of long-range interactions. It is also important to stress how sensitive our results are to the chosen contact distances. This difference is not great in magnitude and may not be significant at all. Nevertheless, it indicates, to a certain extent, the influence of long-range interactions. A slight increase in the characteristic ratio for the mean square radius of gyration, C_∞', can similarly be explained in terms of the influence of long-range interactions. From this discussion, it is clear that, at least in the polymethylene chain, the short-range interactions are the dominant factors in determining the configuration of a polymer chain. Previously, Abe, *et al.*,[13] have matched the experimental ratio by using E_σ = 430–590 cal mol^{-1} and E_ω = 1700–2000 cal mol^{-1} for the same bond angle $\theta = 68°$, and the rotational angle $|\phi| = 120°$. The normally allowed contact distances generate very unreasonable results in two respects: (a) the characteristic ratios are very high, $C_\infty = 50.00$ and $C_\infty' = 2.857$; (b) and only nine configurations survive for each chain length. Therefore, the normally allowed contact distances, for the polymethylene chain, are unreasonable. The C_∞ and C_∞' for no exclusion can be predicted from the formulas, $C_\infty = (1 + \cos\theta)(1 - \cos\theta)^{-1}$ and $C_\infty' = \frac{1}{6}C_\infty$. By substituting $\theta = 68°$, one calculates C_∞ and C_∞' and obtains the values 2.198 and 0.366. Our calculated values (Table III) are in agreement with these predicted values. The C_∞ for the no exclusion case is 2.128. The difference between the experimental and the no exclusion values is 4.572,

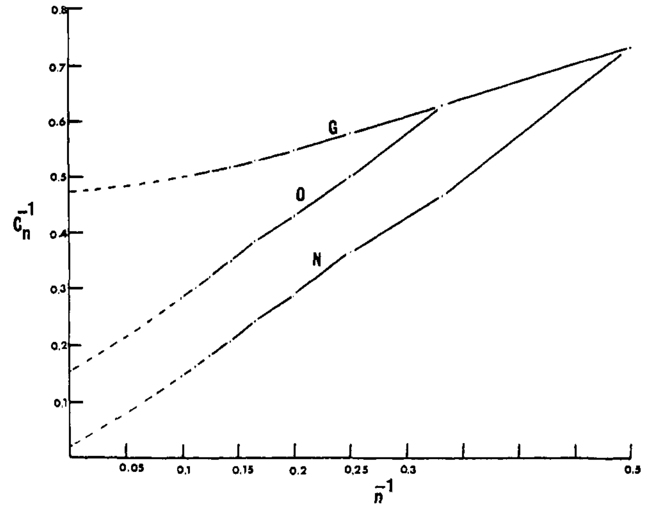

Figure 2. Plot of C_n *vs.* n^{-1} for Gaussian (G), outer limit (O), and normally allowed (N) contact distances. C_∞ are deduced by the graphical extrapolation method (dotted lines).

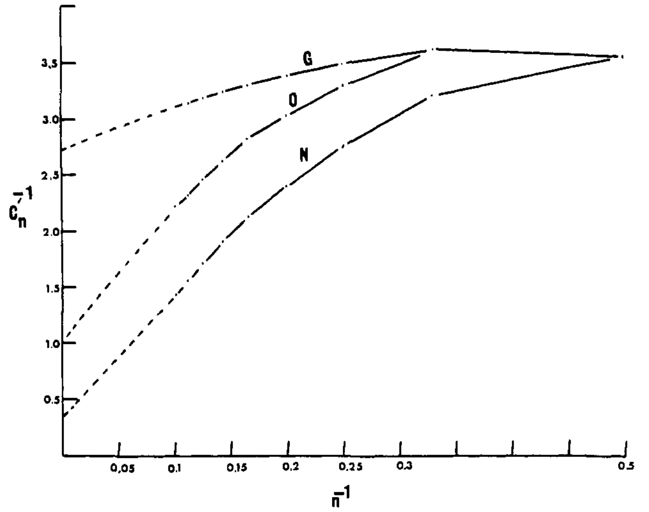

Figure 3. Plot of C_n' *vs.* n^{-1} for Gaussian (G), outer limit (O), and normally allowed (N) contact distances. C_∞' are deduced by the graphical extrapolation method (dotted lines).

Table II
Listings of the Characteristic Ratios for No Exclusion, Normally Allowed Contact Distances, and Outer Limit Contact Distances

Chain length	No exclusion			Normally allowed			Outer limit		
	No. of config	C_n	C_n'	No. of config	C_n	C_n'	No. of config	C_n	C_n'
2	9	1.375	0.264	9	1.375	0.264	9	1.375	0.264
3	27	1.593	0.277	9	2.166	0.312	27	1.593	0.277
4	81	1.728	0.287	9	2.750	0.362	63	2.000	0.303
5	243	1.818	0.296	9	3.500	0.416	153	2.331	0.330
6	729	1.880	0.303	9	4.124	0.471	369	2.607	0.355
7	2,187	1.925	0.309	9	4.856	0.527	891	2.875	0.380
8	6,561	1.959	0.314	9	5.498	0.582	2,151	3.110	0.404
9	19,683	1.985	0.318	9	6.220	0.639	5,193	3.318	0.426
10				9	6.873	0.695	12,521	3.511	0.447
11				9	7.589	0.752			
12				9	8.247	0.808			

Table III
Asymptotic Values for the Characteristic Ratios and the Exponents Given in Equation 4

	$C_\infty = (\langle R_n^2\rangle\lvert nl^2)_\infty$	$C_\infty' = (\langle S_n^2\rangle\lvert nl^2)_\infty$	C_∞'/C_∞	ϵ
Normally allowed	50.000	2.857	0.057	2.0
Outer limit	7.143	1.176	0.165	1.28
No exclusion	2.128	0.364	0.171	1.0

Table IV
The Summary of the Characteristic Ratios at Various Rotational Angles

θ, deg^{-1}	$\lvert\theta\rvert$, deg^{-1}	$C_\infty = \langle R_n^2\rangle\lvert nl^2$	$C_\infty' = \langle S_n^2\rangle\lvert nl$	C_∞'/C_∞	ϵ
	100	13.333	1.428	0.107	1.50
	110	9.524	1.250	0.131	1.36
	115	8.000	1.200	0.150	1.32
	120	7.143	1.176	0.165	1.28
68	121	~16.666	~2.380	0.143	1.68
	122	~16.666	~2.380	0.143	1.68
	123	~16.666	~2.380	0.143	1.68
	124	~16.666	~2.380	0.143	1.68
	125	~200 (>20)	~4.0 (>2.0)	0.020	2.0
60		13.333	1.428	0.102	1.50
62		11.114	1.333	0.120	1.40
64	120	9.709	1.250	0.129	1.34
66		8.333	1.190	0.143	1.30
68		7.143	1.176	0.165	1.28
69		~50.00	~2.38	0.048	1.98

which might be attributed to short-range interactions. The characteristic ratios for mean square radius of gyration, C_∞', have been listed in column 3 of Table III. The value of C_∞' has been obtained as 1.176 for the outer limit contact distances. Jernigan and Flory[14] have calculated $C_\infty' = 1.145$ and predicted that $C_\infty'/C_\infty = 0.166$. Our calculations also show that the value of this ratio is 0.165 for the outer limit contact distances, which is in agreement with their results. However, it is higher than the Monte Carlo and the direct enumeration studies on various lattice models.[8]

There are two main differences between our calculations and those of Flory and his associates. (a) Flory and his associates have generated few chains with number of bonds greater than 100, using the predeveloped mathematical equations, whereas, we have generated all the possible chains consisting of only a few bonds without using the mathematical equations. (b) They have used the energy as a variable parameter (to compensate the short-range interactions) in order to obtain an agreement between the experimental and theoretical property, whereas, we have used the contact distances as a variable parameter, and the excluded volume effect has been accounted for explicitly.

Both calculations have been based on the same rotational isomeric state approximation, which rests on the conformational energy treatment. The limitations and the significance of conformational energy has recently been discussed by Flory.[15]

From the above discussion we conclude that the outer limit contact distances are more reasonable in describing the experimental characteristic ratio of the polymethylene chain. Using these contact distances, we have examined the effect of variation of the bond angle, θ, and the rotational angle, ϕ, on C_∞ and C_∞'. The results are summarized in Table IV. It is obvious that the effect of θ is more severe than the effect of ϕ.

The excluded volume parameter, ϵ, in the following equation

$$\langle X_n^2\rangle \cong an^\epsilon;\ \langle X_n^2\rangle = \langle R_n^2\rangle \text{ or } \langle S_n^2\rangle \tag{3}$$

which is applicable to long chain polymer molecules, has been evaluated by using the ratio method.[8] An approximate equation that is used to calculate the exponent is

$$\epsilon_n \approx n\left[\frac{\langle X_{n+1}^2\rangle}{\langle X_n^2\rangle} - 1\right] \tag{4}$$

where $0(n^{-1})$ terms have been neglected in the binomial ex-expansion. The ϵ ($=\epsilon_\infty$) values are then obtained by plotting ϵ_n vs. n^{-1} as shown in Figure 4, and the asymptotic values

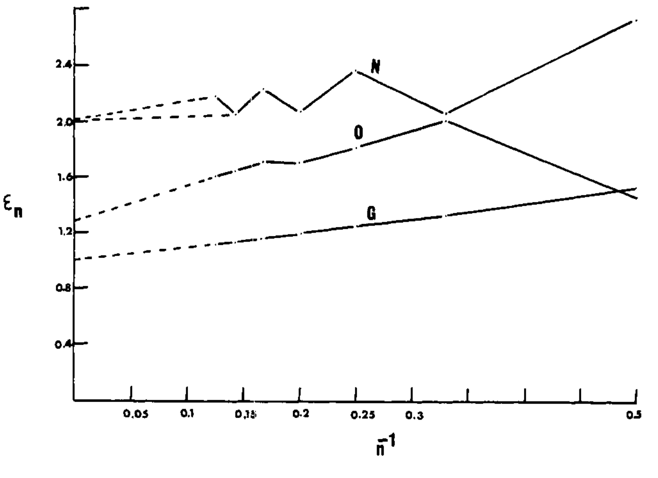

Figure 4. Plot of ϵ_n *vs.* n^{-1} for Gaussian (G), outer limit (O), and normally allowed (N) contact distances. The ϵ_∞ are obtained by extrapolation technique (dotted lines). The ϵ_n are calculated from eq 4 for the mean square end-to-end distance.

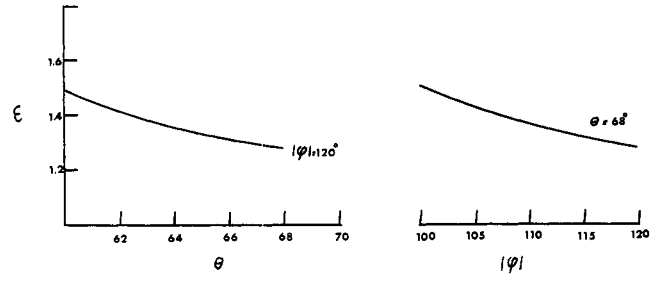

Figure 5. The variation of ϵ (the exponent in the mean square end-to-end distance) with θ and ϕ.

are listed in the last column of Table III. The $\epsilon \approx 1.0$ for the Gaussian limit (no exclusion) and $\epsilon \approx 1.28$ for the outer limit contact distances have been obtained. The self-avoiding random walks on various lattice models[7,16] have suggested that the asymptotic value of ϵ be about 1.20. Off-lattice model studies[17] indicate the value is not restricted to 1.20 but varies as the bond rotation angle varies. The values obtained for off-lattice studies are very close to that obtained for the polymethylene chain with outer limit contact distances. Thus it is probable to speculate that the off-lattice models might approximate the simple real polymer systems, such as polymethylene chain. It is very interesting to note that $\epsilon = 2.0$ for normally allowed contact distances. This value can only occur for rigid rod configurations. Our results show that when normally allowed contact distances are employed for the excluded volume condition only rigid rod configurations survive. An examination of models shows that one can obtain nine rigid rod backbones at each chain length (Table II) in agreement with our results. We also note that our results predict rigid rod behavior when $\theta = 69°$ and $|\phi| = 120°$, and $\theta = 68°$ and $|\phi| = 125°$. Figure 5 explains how the ϵ value may depend on θ and ϕ. The ϵ values for all the angles are listed in the last column of Table IV. The exponent for the mean square radius of gyration cannot be estimated due to its nonconvergence (Figure 6).

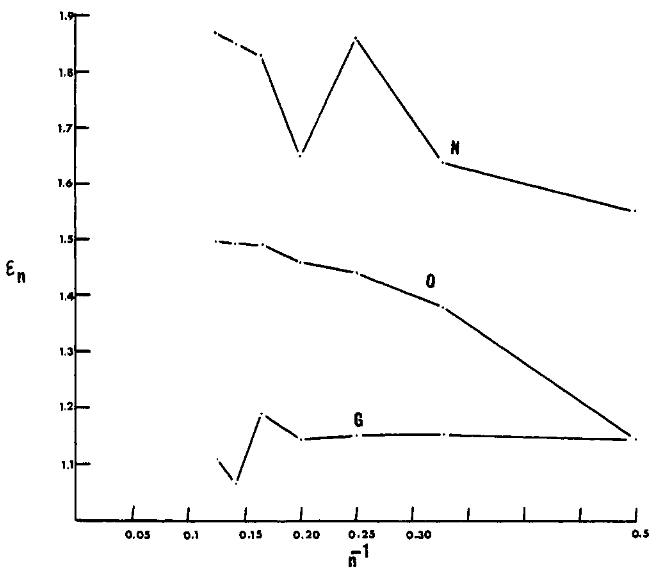

Figure 6. Plot of ϵ_n *vs.* n^{-1} for Gaussian (G), outer limit (O), and normally allowed (N) contact distances. The ϵ_n values refer to the mean square radius of gyration.

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