The Effect of Intramolecular Energy on the Conformation of Polymers by the Monte Carlo Methods

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ABSTRACT: The conformation of chain molecules is investigated by the "successive dimerization" technique. The three different models, the diamond lattice model, the GT-model of polyethylene and the modified GT-model of polyethylene, are used as the models for the polymer. The effect of intramolecular conformational energy is considered for the latter two models. A relation $\langle S^2 \rangle = aN^{1.20}$ is obtained in all the models.

KEY WORDS   Monte Carlo / Excluded Volume / Polyethylene / Random Walk / Conformation / Diamond Lattice /

The problem of the excluded volume effect in polymers has been treated by numerical methods using digital computers. The Monte Carlo calculation using a computer produces two kinds of problem.

(1) That of deciding which kind of model should be used to simulate the chain molecules. Most of the studies up to now have been performed by the restricted walks confined to a certain multidimensional lattice, but the relative stabilities of the real molecules due to intramolecular energy are not considered. Using a more realistic model, we estimate the intramolcular conformational energy for each conformation. The average dimensions are calculated by using the energy.

(2) That of discovering how the generation of a large number of nonintersecting random walks are accomplished. On the diamoned lattice, the number of steps in a walk N, which is attained in a reasonable number of samples, is a few hundreds by the direct Monte Carlo Methods. Wall and Erpenbeck[1] therefore devised the "sample enrichment" technique. With the help of this method they constructed walks up to $N=600$ on the same lattice. Then, to obtain much longer walks, one of the present authors[2]

devised the "successive dimerization" technique. The short self-avoiding walks are generated by the direct Monte Carlo Method, and are connected to each other as dimers. Two dimers are connected to give a tetramer, and two tetramers yields an octamer, and so on. By this method, 8192-step walks were obtained on a diamond lattice. However, for the more realistic model that takes the intramolecular energy into acount, a new extreme attrition has appeared according to the unbalanced weight by the Boltmann factor. For this reason, we could only construct a polyethylene chain with bond numbers up to 384 on the GT-model.

The Monte Carlo data could be well fitted by a relation of the form $\langle S_N{}^2 \rangle = aN^b$, where $\langle S_N{}^2 \rangle$ is the mean-square radius of gyration, and a and b are constants. The typical values of b being 1.50 for a two-dimensional lattice model, and 1.20 for a three-dimensional lattice model.[3] For the off-lattice model, at the present time it is reported only by E. Loftus and P. J. Gans[4] that the value of b is greater than the accepted values 1.20 for the lattice models. In the case of a very long chain, it is theoretically expected that the values of b must be 1.20 for any three-dimensional model.

In this paper the conformations of the model chain are studied by the successive dimerization technique of the Monte Carlo method with the intramolecular energy taken into account. The

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obtained values are discussed by comparing them with those of the diamond lattice model.

MODEL

The Monte Carlo calculation of nonintersecting random walks has been accomplished by specific lattice, nonlattice systems, etc. We then compare the three models, the diamond lattice model, the GT-model of polyethylene* and the modified GT-model of polyethylene. In the latter two models, the bond lengths and bond angles are fixed as shown in Table I. Three rotational isomeric states are chosen in the GT-model, i.e., trans (180°), gauche (60°), gauche' (300°), and seven states are chosen in the modified GT-model, i.e., trans (175, 180, 185°), gauche (55, 65°), gauche' (295, 305°); the angle for the cis form is taken to be 0°. The difference between the diamond lattice model and the GT-model lies in the existence of the hydrogen atoms,

Table I. Bondlengths and Bondangles

	Values
C—C	1.54 Å
C—H	1.08 Å
$\angle$CCC	109°28′
$\angle$CCH	109°28′
$\angle$HCH	109°28′

although both chains have the same skeletal chains. A form of the GT-model of polyethylene is shown in Figure 1. It is drawn in perspective by the plotter system at the Computer Center of the University of Tokyo.

The well-known three-minima cosinusoidal rotational potential is replaced by a three minima square-well potential having energy zero in the trans states and 0.8 kcal/mol in the gauche states. It expresses the torsional energy. The nonbonded interactions are expressed by a Lennard—Jones "6—12" potential

$$U_{ij} = \frac{d_{ij}}{r_{ij}^{12}} - \frac{e_{ij}}{r_{ij}^{6}} \quad (1)$$

The sets of constants[6] in eq 1 are summarized in Table II.

Table II. The sets of potential function constants

Pair	d/kcal Å^{12} mol^{-1}	e/kcal Å^{6} mol^{-1}	r_{min}, Å
H····H	4.5×10^3	47	2.4
C····C	286×10^3	370	3.4
C····H	38×10^3	128	2.9

THE METHOD OF CALCULATION

A computer program embodying the model is written chiefly in FORTRAN IV and runs on
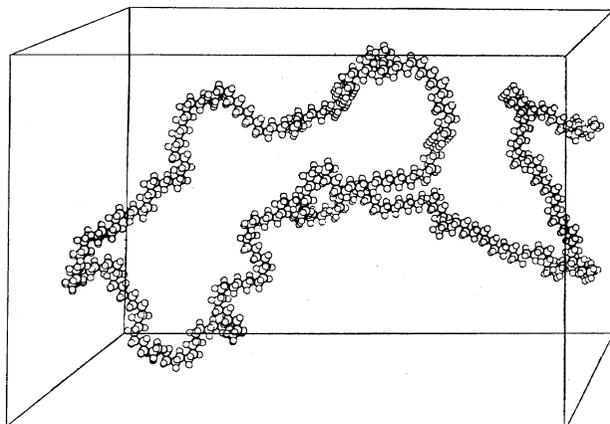
Figure 1. Schematic representation of a GT-model of Polyethylene: N, 384; S^2, 1086 Å^2; R^2, 2664 Å^2.

* This model is explained fully in the previous paper.[5]

the computer HITAC 5020E at Computer Center of the University of Tokyo.

The scheme of the program* to make chains without overlaps is as follows:

1 MAKE AN M-BOND CHAIN AT RANDOM.
2 IF THERE IS AN OVERLAP, GO TO 1.
3 $N=M$.
4 IF ANOTHER N-BOND CHAIN IS NOT STORED, STORE THE NEW CHAIN AND GO TO 1.
5 CONNECT THE STORED CHAIN TO THE NEW CHAIN AND MAKE A $2N$-BOND CHAIN.
6 IF THERE IS AN OVERLAP, OUTPUT AND CLEAR BOTH THE N-BOND CHAINS, AND GO TO 1.
7 $N=2N$, AND GO TO 4.

About the GT-model of polyethylene, the sterically allowed conformations are examined on the basis of the van der Waals radii.

RESULTS AND DISCUSSION

Random walks have been generated in the
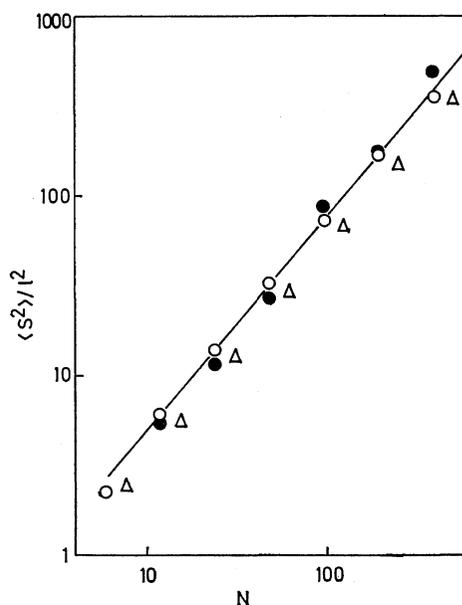
Figure 2. Values of $\log(S^2/l^2)$ vs. $\log N$: ($\triangle$), diamond lattice model; ($\bigcirc$), GT-model; ($\bullet$), mGT-model.

Table III. Values of S^2/l^2 [a]

GT-Model of polyethylene											
N	6	12	24	48	96	192	384				
S^2/l^2	2.277	6.114	13.79	32.51	73.03	170.5	351.5				
N_s				2449	699	182	76				
σ				12.23	23.46	75.5	207.5				
Modified GT-model of polyethylene											
N	6	12	24	48	96	192	384				
S^2/l^2	2.277	5.482	11.60	27.24	88.08	177.2	498.4				
N_s				2462	702	150	70				
σ				7.84	21.12	24.6	184.6				
Diamond lattice model											
N	8	16	32	64	128	256	512	1024	2048	4096	8192
S^2/l^2	2.444	5.560	12.78	29.31	67.37	153.4	350.3	787.0	1740.	3747.	7943.
N_s						4235	1072	256	307	102	38
σ						65.0	145.9	325.0	797.	1509.	2666.

[a] l, bond length; T, 300°K; N_s, number of samples; σ, dispersion.

diamond lattice model, the GT-model of polyethylene and the modified GT-model of polyethylene by the successive dimerization technique.

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* This scheme may "overflow" the capacity of the computer, and there should be an additional scheme, which treats the overflow.

Mean Dimension

Monte Carlo estimations of the mean-square radius of gyration $\langle S_N^2 \rangle$ are more precise than the mean-square end-to-end distance $\langle R_N^2 \rangle$. The values obtained to $\langle S_N^2 \rangle$ are given in Table III and the relation between $\langle S_N^2 \rangle$ and N is shown

in Figure 2. The results obtained for $\langle S_N^2 \rangle$ may be expressed by an equation of the form

$$\langle S_N^2 \rangle = aN^b \qquad (2)$$

where a and b are constants.

On the diamond lattice model, where 8192 steps were attained, the exponent b was quite close to 1.20 over the range $N > 8$. The model in the range satisfies the postulate in the theories, which conclude that $b = 1.20$ for all the three-dimensional models.[7]

The range tends to recede towards larger N in the bulky or stiff chains. However, the result on the GT-model shows the recession is small, and the b-value is 1.20 in the range $12 < N < 384$. We may expect the range to extend further as in the diamond lattice model.

The difference in a-values between the diamond lattice model and the GT-model is attributed to the difference in thickness due to the existence or nonexistence of the hydrogen atoms.

The result on the modified GT-model have a larger fluctuation and we cannot give it a different character from that of GT-model.

Attrition Coefficient

The nature of the intersections accompanying the dimerization is expressed by Alexandrowicz[8] to the attrition coefficient

$$\frac{W_N}{\Omega} = cN^{-k} \qquad (3)$$

where W_N is the number of samples remaining after dimerization of $N/2$ step-chains, and Ω is the number of trial dimerizations. Our results for the attrition coefficient (Table IV) suit this equation. In Figure 3 the results for the attrition

coefficients $\log(W_N/W_{N/2})$ of the 4-choice cubic lattice by Alexandrowicz and the diamond lattice model and the GT-model of polyethylene are shown to be proportional to $\log N$. These three sets of data produce three parallel lines. The constant k is 0.165 in this calculation. So the difference in model only affects the constant
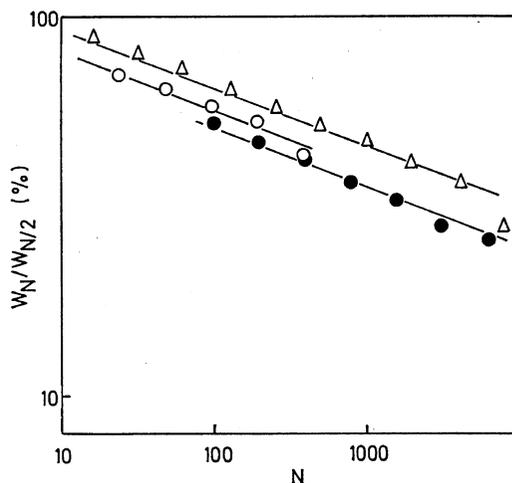
Figure 3. Values of $\log(W_N/W_{N/2})$ vs. $\log N$: ($\triangle$), diamond lattice model; ($\bigcirc$), GT-model; ($\bullet$), cubic lattice model.[8]

Table IV. Values of attrition coefficient

GT-Model of polyethylene

N	24	48	96	192	384
$W_N/W_{N/2}$	0.68	0.63	0.57	0.52	0.42

Modified GT-model of polyethylene

N	24	49	96	192	384
$W_N/W_{N/2}$	0.69	0.65	0.57	0.43	0.47

Diamond lattice model

N	16	32	64	128	256
$W_N/W_{N/2}$	0.87	0.78	0.71	0.62	0.56
N	512	1024	2048	4096	8192
$W_N/W_{N/2}$	0.50	0.46	0.40	0.36	0.27
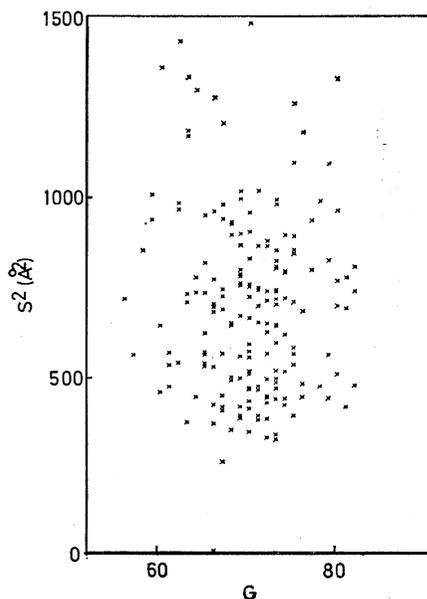
Figure 4. Plots of S^2 against the number of *gauche* forms G, at $N = 192$ of GT-model.
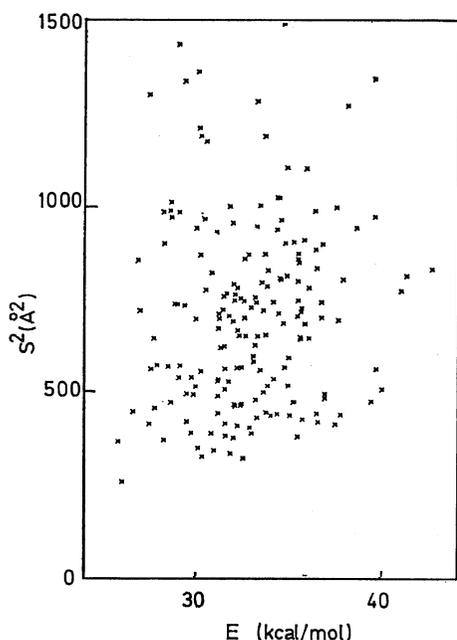
Figure 5. Plots of S^2 against the intramolecular energy E, at $N=192$ of GT-model.

Figure 6. Plots of R^2 against S^2, at $N=96$ of GT-model.

c, and the constant c depends primarily on the short-range interaction. The long-range interaction affects largely the constant k, and seems to be the same for any model.

R^2, S^2, G and E

Figure 4 shows that the dimensions of a chain molecule, rich in *gauche* forms G, are not necessarily smaller than those of the *trans*-rich molecule. The intramolecular energy E has no correlation with S^2 as shown in Figure 5. The variation in R^2 with S^2 is shown in Figure 6. In the case of a random flight chain, the relation between $\langle S^2 \rangle_R$ and R^2 is expressed by Hermans and Overbeek.[9]

The mean-square radius of gyration $\langle S^2 \rangle_R$ with R fixed

$$\langle S^2 \rangle_R = \frac{1}{12} Na^2 \left(1 + \frac{R^2}{Na^2} \right) \qquad (4)$$

and in the case of unperturbed chain

$$\langle S^2 \rangle_R = \frac{1}{12} \langle R^2 \rangle \left(1 + \frac{R^2}{\langle R^2 \rangle} \right) \qquad (5)$$

For the free rotation of fixed bond angles θ

$$\langle R^2 \rangle = \frac{1 - \cos\theta}{1 + \cos\theta} a^2 N \qquad (6)$$

This relation is shown as the solid line in Figure 6. These figures would give valuable information about the characteristics of chain molecules.

The Monte Carlo calculation for the GT-model of polyethylene in the present scheme cannot be extended further due to the heavy requirement of computer time—for example, 100 walks of $N=192$ required 4 hr. As we would have longer chains in the realistic model, which included the intramolecular energy, we should have a new method to make a walk.

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