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The Three-dimensional Structure of Macromolecules. I. The Conformation of Ethylene Polymers by the Monte Carlo Method

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The Monte Carlo method is employed on a high-speed digital computer in order to generate non-intersecting random chains simulating polymer molecules. For this purpose the GT-model of polyethylene is used. Suitable potential functions are used to calculate the energy and the probability of each chain conformation thus generated. The nonbonded-interaction energy is calculated by the Lennard-Jones "6—12" potential function. The average dimensions are then calculated by using this energy. It is suggested that the hydrogen atoms contribute largely to the statistical properties of the ethylene polymers.

The Monte Carlo procedure is used to simulate non-self-intersecting random walks on a high-speed digital computer. Most of the works up to this time have considered the restricted walks confined to a multidimensional lattice,[1] but the stability of the real molecule (intramolecular energy) is not considered.

Using a more realistic model, we estimate the intramolecular conformational energy of each conformation. The average dimensions are calculated by using this energy.

The lower members of the normal hydrocarbon series have been fully discussed in terms of "Conformation Analysis,"[2] "Molecular Geometry,"[3] *etc.* We use the results of these discussions, and then consider the higher members of the normal hydrocarbon series by means of the Monte Carlo Method.

Model

In this paper we discuss the GT-model of polyethylene. The fully-extended conformation of polyethylene is shown in Fig. 1. The hydrogen atoms are bonded to the ith carbon atom as H_i and H_i'. The backbone of the molecule is considered to begin with the atom H_0, continue on through n carbon atoms, and end with the atom H_{n+1}. All the bond lengths and bond angles are kept constant. The bond lengths are taken to be 1.08 Å for the C–H bonds and 1.54 Å for the C–C bonds, while all the bond angles are taken to be tetrahedral. We assume that each bond in a polyethylene molecule can exist in three rotational isomeric states, *trans*(180°), *gauche*(60°), and *gauche'*(300°). This model is equal to the diamond lattice model if we consider only the skeletal carbon atoms. The *trans* form is chosen with the probability of $p_T=1/2$, and the *gauche* forms, with the probabilities, $p_G=p_G'=1/4$.[*1]

Calculation

Steric hindrances are examined on the basis of

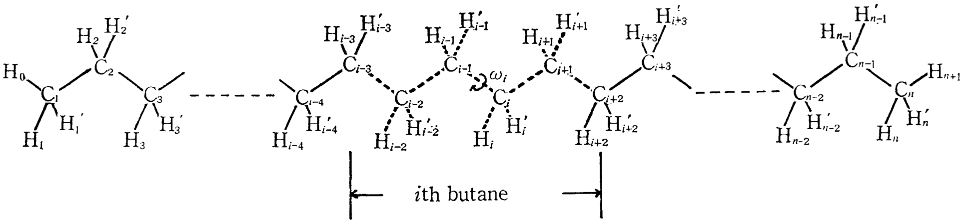

Fig. 1. The polyethylene molecule in the fully extended state.

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[1] F. T. Wall, S. Windwer and P. J. Gans, *Methods Computation Phys.*, **1**, 217 (1963).

[2] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966).

[3] E. J. Jacob, H. B. Thompson and L. S. Bartell, *ibid.*, **47**, 3736 (1967).

[*1] This operation is a method to get long chains rapidly, but the generated chain has an unequal *a priori* probability. This inequality is corrected when we calculate the average quantities (see Eq. (4)). However the inequality corresponds roughly to the energy difference between the *trans* and *gauche* forms so that the generated chains have comparable weights.

the van der Waals radii. When the nonbonded interaction energy (see next section) becomes positive, the whole molecule is discarded. Long, non-self-intersecting random walks are difficult to achieve even when the walks are confined to a lattice.[4] When the walks are off the lattice, this problem is much greater. In order to overcome this extreme attrition, use is made of the enrichment technique previously developed by one of the present authors.[5] The scheme of the program is as follows:

1) MAKE AN M-BOND CHAIN AT RANDOM. ($M=12$, FOR EXAMPLE).

2) IF THE NONBONDED INTERACTION ENERGY IS POSITIVE, 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 THE NONBONDED INTERACTION ENERGY IS POSITIVE, OUTPUT AND CLEAR BOTH THE N-BOND CHAINS AND THEN GO TO 1.

7) $N=2N$, AND GO TO 4.

Energy Equations

The intramolecular conformational energy of each conformation is calculated by using the semi-empirical potential functions. The energy equation is:

$$E = U_{rot} + U_{nb} \qquad (1)$$

where:

$$U_{rot} = \sum_i U_{rot}(\omega_i) \qquad (2)$$

Table 1. The sets of potential function's constants

Atom pair	a (kcal·Å^{12}/mol)	b(kcal·Å^6/mol)	$r_{\min}$ (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

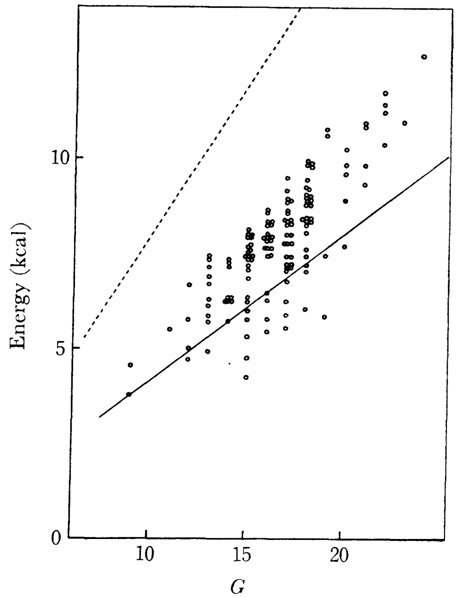

Fig. 2. Plot of total energy against number of *gauche* forms at $N=48$.
The dotted line indicates the energy which is calculated by Eq. (2). The molecules with equal value of $g\cdot\exp(-E/kT)$ at 300°K are equidistant from the solid line.

Table 2. Values of $\langle R^2\rangle$ (Å^2)

N	3	6	12	24	48	96	192
m[a]			256	148	163	39	13
$T=\infty$	10.7	35.0	107.8	308.2	863.8	2230.7	6624.8
$T=1000$°K	11.3	36.7	106.8	300.9	791.0	1811.9	4826.3
$T=360$°K	12.5	40.4	108.5	276.5	576.3	1343.3	3644.3
$T=340$°K	12.6	40.8	109.0	276.1	555.9	1313.7	3677.3
$T=320$°K	12.7	41.2	109.7	276.2	532.9	1281.6	3737.6
$T=300$°K	12.8	41.7	110.6	277.1	506.9	1247.4	3833.5
$T=280$°K	12.9	42.3	111.9	279.4	477.6	1212.2	3966.8
trans[b]	15.0	56.9	227.7	910.7	3642.7	14571.0	58284.0
F. R. [c]	10.8	24.9	53.4	110.3	224.1	451.8	907.1

a) Total number of sample chains.
b) All rotational angles take *trans* forms.
c) Theoretical values for free rotation.
$R^2/r^2=2N+3/2(-1+1/3^N)$, $r=1.54$Å

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[4] F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).

[5] K. Suzuki, This Bulletin, **41**, 538 (1968).

TABLE 3. VALUES OF $\langle S^2 \rangle$ (Å²)

N	3	6	12	24	48	96	192
m[a]			256	148	163	39	13
$T=\infty$	1.91	4.84	13.44	38.71	108.14	285.89	813.83
$T=1000$°K	1.94	4.99	13.61	38.99	102.25	225.15	684.53
$T=360$°K	2.01	5.29	14.47	38.51	80.52	176.21	551.73
$T=340$°K	2.02	5.32	14.12	38.59	78.86	174.04	544.55
$T=320$°K	2.03	5.35	14.19	38.72	77.12	171.63	535.03
$T=300$°K	2.03	5.39	14.28	38.92	75.31	168.90	522.33
$T=280$°K	2.04	5.44	14.39	39.21	73.45	165.82	506.37
trans[b]	2.17	6.52	22.33	82.41	316.41	1239.70	4907.80
F. R.[c]	1.91	4.10	8.70	18.09	37.01	74.93	150.81

a) Total number of sample chains.
b) All rotational angle take *trans* forms.
c) Theoretical values for free rotation.
$S^2/r^2=N/3-5/12+[7/6+3(-3+1/3^N)/8(N+1)]/(N+1)$, $r=1.54$Å

and with ω_i designating the rotation angle about the $C_{i-1}-C_i$ bond.

$$U_{nb}=\sum_{i<j}(a_{ij}/r_{ij}^{12}-b_{ij}/r_{ij}^{6}) \tag{3}$$

We assume that the polyethylene molecule ($C_n H_{2n+2}$) is formed by overlapping $n-3$ butanes in regard to the internal rotation energy. The energy difference between the one *trans* and the two *gauche* forms is taken as 0.8 kcal/mol from the experimental values of butane. The first term in Eq. (1) is a sum over this energy difference. The second term in Eq. (1) is a sum over the nonbonded interactions between atoms separated by six or more bonds (long-range interaction). In treating the nonbonded interaction, we have used the Lennard-Jones "6—12" potential functions.

The sets of constants[6] in Eq. (3) are summarized in Table 1.

Results and Discussion

The influence of the nonbonded interaction energy on the total intramolecular energy is shown in Fig. 2. The unstabilization by *gauche* forms is fully compensated by the nonbonded interaction energy.

$\langle R_N^2\rangle$ and $\langle S_N^2\rangle$. The mean-square end-to-end distance, $\langle R_N^2\rangle$, and the mean-square radius of gyration, $\langle S_N^2\rangle$, are calculated by an equation of the form:

$$\langle J_N^2\rangle=\sum_i J_i^2 g_i \exp(-E_i/kT)/\sum_i g_i \exp(-E_i/kT) \tag{4}$$

where N is the number of C–C bonds and is equal to $n-1$, where J represents R or S, and where g is the weight which corrects the uneven selection.*2 These values are calculated only with carbon atom coordinates. The variation in the molecular dimension with the temperature is calculated by changing the temperature in the Boltzmann factor, $\exp(-E_i/kT)$.

These results fit an equation of the form:

$$\langle J_N^2\rangle=kN^{\alpha} \tag{5}$$

where k and α are constants.

The results are summarized in Tables 2 and 3. Figure 3 shows plots of $\log\langle S_N^2\rangle$ *vs.* $\log N$ at

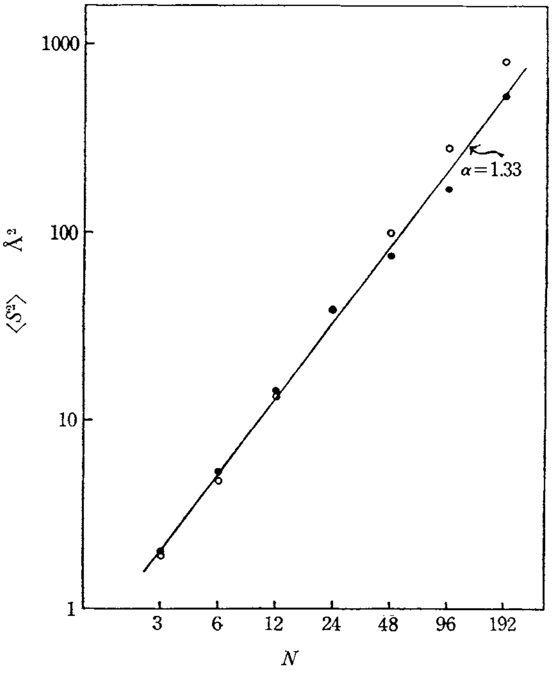

Fig. 3. Values of $\langle S^2\rangle$ *vs.* N on a log-log plot.
○ $T=\infty$
● $T=300$°K

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[6] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **45**, 2091 (1966).

*2 The values of g_i are calculated by means of the number of *gauche* forms G; $g_i=(p_T/p_G)^G$. We adopted the uneven selection in order to have a narrow distribution of $g\cdot\exp(-E/kT)$.

TABLE 4. VALUES OF $(\log\langle R_{2N}^2\rangle - \log\langle R_N^2\rangle)/\log 2$

N	3	6	12	24	48	96	192
$T=\infty$	1.705	1.622	1.516	1.487	1.369	1.570	
$T=1000$°K	1.693	1.543	1.495	1.394	1.196	1.413	
$T=360$°K	1.697	1.426	1.349	1.060	1.221	1.440	
$T=340$°K	1.699	1.419	1.340	1.010	1.241	1.485	
$T=320$°K	1.702	1.413	1.332	0.948	1.266	1.544	
$T=300$°K	1.706	1.407	1.325	0.871	1.299	1.620	
$T=280$°K	1.711	1.403	1.321	0.773	1.344	1.710	
trans[a]	1.928	2.000	2.000	2.000	2.000	2.000	
F. R.[b]	1.100	1.086	1.057	1.033	1.018	1.009	

a) All rotational angles take *trans* forms. b) Theoretical values for free rotation.

TABLE 5. VALUES OF $\langle S^2\rangle/\langle R^2\rangle$

N	3	6	12	24	48	96	192
$T=\infty$	0.178	0.138	0.125	0.126	0.125	0.128	0.123
$T=1000$°K	0.171	0.136	0.127	0.130	0.129	0.124	0.142
$T=360$°K	0.162	0.131	0.133	0.139	0.140	0.131	0.151
$T=340$°K	0.161	0.131	0.129	0.140	0.142	0.132	0.148
$T=320$°K	0.160	0.130	0.129	0.140	0.145	0.134	0.143
$T=300$°K	0.159	0.129	0.129	0.140	0.149	0.135	0.136
$T=280$°K	0.158	0.129	0.129	0.140	0.154	0.137	0.128
trans[a]	0.145	0.115	0.098	0.090	0.087	0.085	0.084
F. R.[b]	0.177	0.164	0.163	0.164	0.165	0.166	0.166

a) All rotational angles take *trans* forms. b) Theoretical values for free rotation.

$T=\infty$ and at $T=300$°K.

α, the exponent in Eq. (5), is calculated by the equation:

$$\alpha = (\log\langle J_{2N}^2\rangle - \log\langle J_N^2\rangle)/\log 2. \qquad (6)$$

These values are summarized in Table 4.

$\langle S_N^2\rangle/\langle R_N^2\rangle$. Table 5 lists the $\langle S_N^2\rangle/\langle R_N^2\rangle$ ratios for the different values of N obtained in this study. These values are small compared with the values determined in a previous investigation.[7] The major reason for this may be the influence of hydrogen atoms.

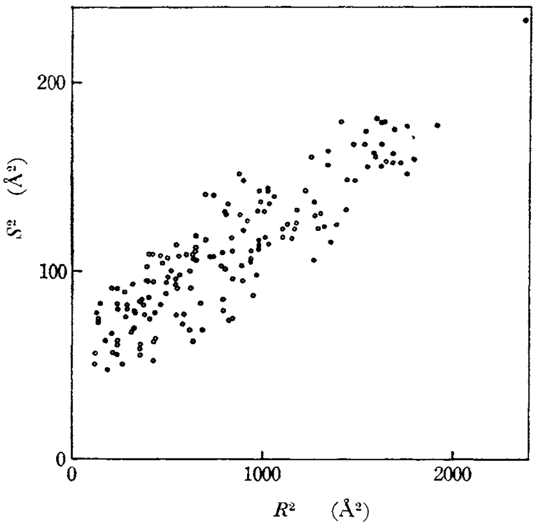

Fig. 4. Plot of S^2 against R^2 at $N=48$.

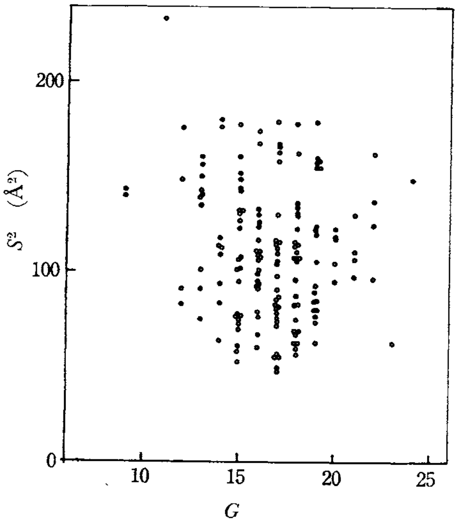

Fig. 5. Plot of S^2 against number of *gauche* forms at $N=48$.

The variation in R^2 with S^2 is shown in Fig. 4.

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[7] S. Windwer, *J. Chem. Phys.*, **43**, 115 (1965).

It is noticeable in Fig. 3 that the temperature coefficient of the dimensions is reversed between $N=24$ and $N=48$. This means that the average dimensions of the long ethylene polymer are affected more strongly by the "long range" interaction than by the "short range" interaction. In this case the van der Waasl attraction is stronger than the *trans-gauche* energy difference. Figure 5 shows that the number of *gauche* forms has little effect on the dimensions.

Our model is a simple one compared with real molecules, but the use of much more realistic models would not alter the general features of the result; the long-range interaction, including interactions by the solvent, will overcome the short-range interaction at the early stage of the chain length.