Study of a Model of the Polyethylene Chain. Comparison of the Rotational Isomerism Theory with Results Obtained by a Simulation of the Brownian Motion

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ABSTRACT: As part of our program on simulation of the Brownian motion of chain molecules, we have studied the conformational static and dynamic properties of a model of polyethylene. In the present paper we systematically derive the same properties by using the rotational isomer theory. As expected, there is a good agreement for the static properties like conformational averages and chain dimensions. In addition the local mobility of the chain has been favorably compared by the aid of the two approaches.

In order to study the dynamics of macromolecular chains, we have developed a model in which the chains, confined on a tetrahedral lattice, are submitted to random local motions involving three or four bonds.[1,2] By this means both static[3] and dynamic[4] properties of tetrahedral chains (i.e., chains without conformational interactions) have been studied, with allowances for the excluded volume effect.

Recently we have modified this model so as to describe more realistically polymers like polyethers and polyethylene.[5,6] The tetrahedral lattice description of the chains and of their movements is preserved, as it is not far from the actual geometry of linear polyethers. The major change is the introduction of conformational statistical weights. The energy of the conformations is taken into account during the generation of chains and also in the local-motion process, in order to keep the chain in its conformational equilibrium state. The statistical weights were chosen to account for the solution properties of polyethers.[7] For comparison, polyethylene (PE) has been studied with the same energy parameters, and the results are described here.

Briefly, a cycle in the Brownian motion simulation procedure is the following. A chain bond vector is selected at random, and the conformation of the adjacent bonds is examined to see whether a local jump is geometrically possible. If the movement is blocked, the cycle ends, otherwise, the energy difference ΔE between the final and initial states is assessed and the frequency of occurrence of the motion is weighted by the probability factor

$$p(\text{motion}) = \exp(-\Delta E/kT)/[1 + \exp(-\Delta E/kT)] \quad (1)$$

Special rules pertain to bonds at chain ends, but these need not be described here. Details of the simulation procedure are given elsewhere.[5,6] Because of the so-called pentane effect, the four-bond motion, which is important in our model for polyethers, is forbidden in PE chains. With the above described model, numerous static properties have been calculated both at the generation of chains and during the simulation of the motions. The local mobility and the dynamic properties of the whole chain have also been investigated.[5,6]

In this paper we compare our approach with the classic rotational isomerism theory. Based on the Ising model this theory was developed by Volkenstein,[8] Birshtein and Ptitsyn,[9] Lifson,[10] Nagai,[11] and Hoeve[12] and a great number of applications are given by Flory.[13] It has been proved very useful for studying the conformation-dependent properties of linear polymers. Here we can use either the formalism of Lifson,[10] as Gorin[7] did, or that of Flory.[13] The difference lies in the way of writing the statistical weight matrix: for Lifson

$$\mathbf{U}_L = \begin{vmatrix} 1 & p_g p_{tg} & p_g p_{tg} \\ p_{gt} & p_g p_{gg} & 0 \\ p_{gt} & 0 & p_g p_{gg} \end{vmatrix} \quad (2)$$

and for Flory

$$\mathbf{U}_F = \begin{vmatrix} 1 & p_g p_{tg} & p_g p_{tg} \\ 1 & p_g p_{gg}/p_{tg} & 0 \\ 1 & 0 & p_g p_{gg}/p_{tg} \end{vmatrix} \quad (3)$$

The two expressions are equivalent because $\mathbf{U}_L$ and $\mathbf{U}_F$ are related by a similarity transformation. Let us recall that p_g refers to the interaction between the extremities of a three-bond gauche sequence and p_{gg} and p_{tg} to the extremities of four-bond sequences gg and tg, respectively.

In the tetrahedral lattice description, $p_{g^+g^-} = 0$, because of the pentane effect. The parameters we have used in the simulation deduced from the van der Waals interaction at 20 °C are the following: $p_t = p_{tt} = 1$ (by convention), $p_g = 0.40$, $p_{tg} = 1.24$, and $p_{gg} = 2.50$. These parameters give

$$\mathbf{U}_L = \begin{vmatrix} 1 & 0.5 & 0.5 \\ 1.24 & 1 & 0 \\ 1.24 & 0 & 1 \end{vmatrix}$$

$$\mathbf{U}_F = \begin{vmatrix} 1 & 0.5 & 0.5 \\ 1 & 0.81 & 0 \\ 1 & 0 & 0.81 \end{vmatrix} \quad (4)$$

This is to be compared to the values given by Flory at 140 °C:

$$\mathbf{U}_F' = \begin{vmatrix} 1 & 0.54 & 0.54 \\ 1 & 0.54 & 0.05 \\ 1 & 0.05 & 0.54 \end{vmatrix} \quad (5)$$

The differences between (4) and (5) are effectively not as large as they might appear at first sight. The first rows of the $\mathbf{U}_F$ and $\mathbf{U}_F'$ matrices are almost the same when adjusted to the same temperature. In the second and third rows, Flory's model permits a small number of $g^{\pm}g^{\mp}$ conformations which are completely forbidden in our model, and it is known that even a weak proportion of such conformations strongly influences both chain dimensions[7] and dynamic properties.[4-6] However, in our model there is an increased frequency of $g^{\pm}g^{\pm}$ conformations, and this largely compensates for the exclusion of $g^{\pm}g^{\mp}$ sequences because it generates chain folds of a different kind. Physically, it may be argued that an enhanced $g^{\pm}g^{\pm}$ probability is favored by the van der Waals attraction between methylene

Table I
A priori Conformational Probabilities (%)

	P_t	P_g	P_{tt}	P_{tg}	P_{gg}	$P_{g^+g^-}$	P_{t_i}	P_{g_i}
Flory's model	59.7	40.3	32.0	54.9	11.9	1.0	53.8	46.2
Present model	54.8	45.2	28.8	52.1	19.1	0	52.5	47.5
Simulation results	55.1	44.9	29.2	51.7	19.1	0	52.6	47.4

Table II
Conformational Probabilities of Five- and Six-Bond Sequences

5-bond conf	ttt	ttg$^\pm$ g$^\pm$tt	tg$^\pm$t	tg$^\pm$g$^\pm$ g$^\pm$g$^\pm$t	g$^\pm$tg$^\pm$	g$^\pm$tg$^\mp$	g$^\pm$g$^\pm$g$^\pm$
P[C]	0.151	0.274	0.150	0.221	0.062	0.062	0.081
6-bond conf	tttt	tttg$^\pm$ g$^\pm$ttt	ttg$^\pm$t tg$^\pm$tt	ttg$^\pm$g$^\pm$ g$^\pm$g$^\pm$tt	tg$^\pm$tg$^\pm$ g$^\pm$tg$^\pm$t	tg$^\pm$tg$^\mp$ g$^\pm$tg$^\mp$t	
P[C]	0.080	0.144	0.158	0.116	0.071	0.071	
6-bond conf	g$^\pm$ttg$^\pm$	g$^\pm$ttg$^\mp$	tg$^\pm$g$^\pm$t	tg$^\pm$g$^\pm$g$^\pm$ g$^\pm$g$^\pm$g$^\pm$t	g$^\pm$tg$^\pm$g$^\pm$ g$^\pm$g$^\pm$tg$^\pm$	g$^\pm$tg$^\mp$g$^\mp$ g$^\pm$g$^\pm$tg$^\mp$	
P[C]	0.033	0.033	0.064	0.093	0.052	0.052	
6-bond conf	g$^\pm$g$^\pm$g$^\pm$g$^\pm$						
P[C]	0.034						

Table III
Conformational Probabilities (Comparison with the Simulation)

Conformation	t	tg$^\pm$t	tg$^\pm$g$^\pm$ g$^\pm$g$^\pm$t	g$^\pm$g$^\pm$g$^\pm$
P_{calcd}	0.548	0.150	0.220	0.081
P_{sim}	0.541	0.145	0.222	0.087

Table IV
Mean Energy and Standard Deviation

	Flory's model	Present model	Generation
E_k at 20 °C, kcal	12.8	5.9	6.6
σ, kcal	2.7	1.87	1.84

groups separated by four bonds when in this conformation, since the separation between them is then about 3.6 Å, corresponding roughly to the minimum of the potential energy function between two methyl groups.[7]

It should also be remarked that the statistical weights given in eq 3 are based on the energetics developed by us for polyethers and that another set of conformational energies could be chosen if our purpose were to produce the best model only for polyethylene.

(I) Average Conformations of Infinite Chains

The a priori probabilities of the conformations of an infinite chain are easily calculated by using the rotational isomeric state model.[13] Let us call these probabilities P_t, P_g, P_{tt}, P_{tg}, P_{gg}, $P_{g^+g^-}$ and let P_{t_i}, and P_{g_i} be the a priori probabilities for an end conformation to be t or g, respectively. Table I shows the calculations as performed either with our set of statistical weights or with Flory's for comparison with the generation results. The very good agreement between these calculated values and those found by the simulation process indicates that the particular generation we have performed[5] does not introduce any appreciable bias into the conformation distribution. We observe also that the difference between the present model and Flory's is rather small; as mentioned before, there is some compensation between g$^\pm$g$^\pm$ and g$^\pm$g$^\mp$ conformations.

(II) Probabilities of Three- and Four-Conformation Sequences

By the aid of the a priori probabilities (Table I), one can calculate the probability of any conformational sequence inside an infinite chain. Let $[C]_n$ be a $(n + 2)$-bond conformation, which thus contains n individual conformations of three bonds: $C_1, C_2, C_3 \cdots C_{n-1}, C_n$. Its probability is given by:

$$P(C_n) = \prod_{i=1}^{n-1} P_{C_iC_{i+1}} \Big/ \prod_{i=2}^{n-1} P_{C_i} \qquad (6)$$

The results for 5-bond and 6-bond conformations are reported in Table II (recall that all the conformations containing g$^\pm$g$^\mp$ sequences have a zero probability).

A comparison with certain data of the simulation is possible (Table III). It concerns only those sequences able to move by a three-bond motion and the t conformations. The agreement is satisfactory. One may add two remarks. First, the "trans" proportion is lower in the simulation results, probably because of the noninfinite length of the chain. Also, the ggg and tgg sequences are favored to the detriment of tgt; this will be discussed below with the mobility effects.

(III) Conformational Energy of Chain

The statistical weights are related to the conformational energies in the standard way by the equation $E_\alpha = kT \log p_\alpha$, for conformational state α. Thus the average total energy of a chain can be calculated from the a priori probabilities. We may write

$$E = (N - 2)P_gE_g + (N - 3)(P_{tg}E_{tg} + P_{gg}E_{gg} + P_{g^+g^-}E_{g^+g^-}) \qquad (7)$$

if it is assumed that N is so large that the end effects are negligible. The results for 80-bond chains are shown in Table IV. The small discrepancy between calculation and generation results arises from the end effects. The larger energy obtained with Flory's model is due to the somewhat higher energy he assigns to gauche conformations and to the allowed g$^\pm$g$^\mp$ sequences which, although they are not very numerous, have rather high energies.

The standard deviation σ of the energy distribution has also been determined. Let P_{tg}' and P_{gg}' be the proportions of tg and gg conformations in a certain chain. For this chain the approximate energy is:

$$E/(N - 3) \simeq P_{tg}'(E_{tg} + \tfrac{1}{2}E_g) + P_{gg}'(E_{gg} + E_g) \qquad (8)$$

With the particular set of statistical weights we have used, $P_{tg}' = 1 - P_{gg}' - P_{tt}'$, and since E_{tt} is zero by convention we can

Table V
Characteristic Ratio

	Calcd 20 °C	Sim 20 °C	Flory 140 °C	Exptl 140 °C
R_0^2/Nl^2	6.0	6.3	6.8	6.6 to 6.8

Table VI
Sequences with Central tgt

Type of conformation	Conf probability, %	Energy diff between initial and final states
tt tgt tt	11.4	$2E_1$
tt tgt tg	10.3	$E_1 + E_2$
tt tgt gt	11.3	E_1
tt tgt g⁻t	11.3	0
tt tgt g⁻g⁻	8.3	$E_1 - E_2$
gt tgt tg	2.3	$2E_2$
gt tgt gt	5.1	E_2
gt tgt g⁻t	5.1	$E_2 - E_1$
gt tgt g⁻g⁻	3.8	0
tg tgt gt	2.8	0
tg tgt g⁻t	5.6	$-E_1$
tg tgt g⁻g⁻	4.1	$-E_2$
tg⁻ tgt g⁻t	2.8	$-2E_1$
tg⁻ tgt g⁻g⁻	4.1	$-E_1 - E_2$
g⁻g⁻ tgt g⁻g⁻	1.5	$-2E_2$

rewrite eq 8 as

$$E = \text{constant}(N-3)P_{tg}' = (\text{constant})n_{tg} \qquad (9)$$

where n_{tg} is the number of tg conformations of the chain. The standard deviation of E is thus proportional to that of n_{tg}.

It is standard operation to obtain the variance of n_{tg} by twice differentiating the conformational partition function, just as a single differentiation leads to $\langle n_{tg}\rangle$. (See ref 13 p 78.) We thus obtain

$$\sigma_E = 0.213(N-3)^{1/2}\ \text{kcal/mol} \qquad (10)$$

For an 80-bond chain, σ_E is found to be 1.87 kcal, very close to the 1.84 kcal of the generated chains. A similar estimate for Flory's model gives 2.7 kcal. This relatively high value is of course due to the large conformational energies of g±g∓ and even g±g± sequences.

(IV) Dimensions of Chains

The calculation of chain dimensions in the rotational isomerism model has been extensively described[7,9-13] and need not be recalled here. Our results, in terms of the characteristic ratio, are presented in Table V.

Experimentally, the variation of the characteristic ratio in the temperature interval 110–190 °C is[13] given by d log $\langle R_0^2\rangle/\mathrm{d}T = -1.1 \times 10^{-3}$. The extrapolation of the results reported by Flory gives $\langle R_0^2\rangle/Nl^2 = 7.6$ at 20 °C for infinite chains. This is a relatively high value, but it could be lowed by several considerations: (1) the chains are not infinite[13] and (2) the experimental determinations of characteristic ratios and of their temperature dependence are made with a relatively high uncertainty, perhaps about 10%. For these reasons the disagreement is not very significant.

(V) Probabilities of Motions

In the present model, the only motions to be considered excepted at chain ends are three-bond motions. We have listed in Tables VI–VIII all the sequences of seven rotational states in which the central conformation may give rise to a motion, with their computed probabilities and the energy difference between the conformation and the final one, i.e., the new conformation if the motion is performed. For the sake of simplification we note that

$$E_1 = E_g + 2E_{tg}$$
$$E_2 = E_g + E_{gg} \qquad (11)$$

The conformations are grouped by two or four because it is not necessary to distinguish the sign of the central gauche conformation and the sense of the chain. For example, tg⁻tgtg⁻g⁻ holds for: tg⁻tg⁺tg⁻g⁻, tg⁺tg⁻tg⁺g⁺, g⁻g⁻tg⁺tg⁻t, and g⁺g⁺tg⁻tg⁺t.

A total of 29.8% of the conformations are able to move. In the present model, at 20 °C, E_2 equals zero, so that the energy difference can take only five values: $\pm E_1$, $\pm 2E_1$, and 0. The probability of occurrence of a motion from an inital state with null energy to a final state with energy E has been defined in our simulation[5,6] by eq 1 as

$$P(\text{motion}) = e^{-E/kT}/(1 + e^{-E/kT})$$

Table IX sums up, classified by energy change, the probabilities of the conformations and of the motions, and the percentage of motion per simulation cycle (i.e., the choice at random of a certain bond of the chain). The efficiency of the simulation, as measured by the mean probability of motions, 47.2%, appears higher than the value obtained by simulation, 32.3%. The reason is that we have a priori discarded the con-

Table VII
Sequences with Central tgg

Type of conf	Conf probability, %	Energy diff between initial and final states
tt tgg tt	18.4	$E_1 + E_2$
tt tgg tg⁻	8.3	$2E_2$
tt tgg gt	14.9	$E_1 - E_2$
tt tgg gg	10.9	$2(E_1 - E_2)$
gt tgg tt	8.3	$2E_2$
tg tgg tg⁻	3.8	$3E_2 - E_1$
gt tgg gt	6.7	0
gt tgg gg	4.9	$E_1 - E_2$
tg tgg tt	9.1	E_2
tg tgg tg⁻	4.1	$2E_2 - E_1$
tg tgg gt	7.4	$-E_2$
tg tgg gg	5.4	$E_1 - 2E_2$
tg⁻ tgg tt	9.1	$E_2 - E_1$
tg⁻ tgg tg⁻	4.1	$2(E_2 - E_1)$
tg⁻ tgg gt	7.4	$-E_1 - E_2$
tg⁻ tgg gg	5.4	$-2E_2$
g⁻g⁻ tgg tt	6.7	0
g⁻g⁻ tgg tg⁻	3.0	$E_2 - E_1$
g⁻g⁻ tgg gt	5.4	$-2E_2$
g⁻g⁻ tgg gg	4.0	$E_1 - 3E_2$

Table VIII
Sequences with Central ggg

Type of conf	Conf probability, %	Energy diff between initial and final states
tt ggg tt	7.4	$2E_2$
tt ggg tg⁻	6.7	$3E_2 - E_1$
tt ggg gt	12.0	0
tt ggg gg	8.8	$E_1 - E_2$
g⁻t ggg tg⁻	1.5	$4E_2 - 2E_1$
g⁻t ggg gt	5.4	$E_2 - E_1$
g⁻t ggg gg	4.0	0
tg ggg gt	4.8	$-2E_2$
tg ggg gg	7.1	$E_1 - 3E_2$
gg ggg gg	2.6	$2E_2 - 4E_1$

Table IX
Possibilities of Motions According to the Energy Change

Energy diff	Conf probability, %	Probability of motion, %[a]	% motion/ simulation cycle
$-2E_1$	0.85	72.6	0.61
$-E_1$	5.44	61.9	3.37
0	11.66	50	5.83
E_1	9.35	38.1	3.56
$2E_1$	2.49	27.5	0.68
Total	29.79	47.19	14.06

[a] See eq 1.

formations which would have given the sterically forbidden conformation g^+g^-. But these cases were accounted for in the simulation as rejected by energy condition. In Table X, we reintroduce the probabilities of such conformations and obtain a correction factor of 0.66.

Incidentally, we observe that the conformations whose three-bond motions are favored are ggg, tgg, and tgt in decreasing order. We have already found that the simulation seems to favor slightly the conformations themselves in the same order. So it is possible that the simulation process tends to enrich the chains in the conformations which are most able to move. However, this effect is very small. Finally the efficiency of the simulation, defined as the ratio of performed motions/tentative motions, amounts to 31.1% by the above calculation, as compared with 32.3% by the simulation.

The ratio (number of motions/cycle of the simulation) is 14.1% (calculated) or 14.6% (simulation). This value is close to the 14.8% one obtains for a tetrahedral lattice chain without energy weighting.

Conclusion

We have tested the model developed in the simulation of chain Brownian motion by using the rotational isomer theory. A straightforward application to the polyethylene chain allowed us to show the consistency of the model with respect to conformational properties and even to local dynamic behavior. A similar analysis could have been done for any of the polyethers we have studied, but the complexity of the chain backbone would have made the calculations far more tedious, and the final conclusions would have been expected to be the same. The agreement between these two quite different approaches to conformational properties gives strong support to the simulation model.

Table X
Influence of Blocked Conformations

Type of conf	A = conf probability, %	B = probability of the conf able to move	B/A
tgt	15.01	9.01	0.60
tgg	22.05	14.75	0.67
ggg	8.10	6.04	0.75
Total	45.16	29.80	0.66

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Verification of the Long-Range and Localized Dynamics of Molecules in an Amorphous Polymer Matrix

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ABSTRACT: The neutron incoherent quasi-elastic scatter from polypropylene oxide certainly shows two quasi-elastic components, one in the rubber and the second in the glass below 200 K. Overall the dependence of broadening on momentum transfer is consistent with the origin of the high-temperature component as local main chain wriggling and the low-temperature component from hindered internal rotation of the methyl group. Although the effects observed demonstrate the qualitative aspects of the rotational isomeric model, better experimental results are required at low temperatures to enable the scattering law and the activation energy for methyl group rotation to be evaluated with precision comparable to that achieved in the measurement of torsional frequencies.

Molecular theories of polymerized materials are based on the rotational isomeric model.[1] An individual chain is built up of a series of small repeat units, the geometry of each unit being essentially that of the corresponding small molecule. The backbone of the polymer chain is a sequence of σ bonds, sometimes interspersed by bonds of higher order, and the backbone subtends atoms or side groups to make up the complete macromolecule. In the crystalline state, the model chain can assume a planar zig-zag form (achieved for example by a sequence of trans rotational conformers about the σ bonds in a carbon–carbon or carbon–oxygen chain) or a regular helical form (which requires, for example, a specific sequence of gauche rotational conformation about main σ chain bonds). In amorphous states more random conformations are required. The model satisfies this requirement by internal rotations about the main chain bonds, which are correlated