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Conformational characteristics of polymeric chains with various degrees of rigidity

Summary — A simple model based only on steric constrictions of chain molecules is used to describe the conformational characteristics of polymer chains endowed with various degrees of rigidity. The effect of rigidity of bond rotations was studied in terms of the model in relation to chain molecule size; a rigidity criterion was thus obtained, based on the width of the interval of rotational angles. Other results suggested the scaling law between the size of the chain and the number of monomers to become modified with the degree of chain rigidity. Examples of scaling behavior are discussed. An additional parameter, helicity, which corresponds with the average rotation angle, is presented as helpful in understanding the structural characteristics of polymer chains.

Key words: rigidity of polymer chains, conformational characteristics, scaling law, helicity.

The conformational characteristics of the polymeric chains that constitute a specific material play a basic role in understanding their physical properties and structural characteristics [1]. As generally recognized, such conformational characteristics are determined by the rigidity and geometric characteristics of the covalent bonds that constitute the chain backbone, and by the relatively weak forces between and within the chains, different from the strong covalent forces that hold them as a single macromolecule [2].

However, because of their characteristic large lengths, monomer-monomer interactions along chains are strongly influenced by steric impediments and chain constrictions, and molecular potentials routinely used to describe very short chains are not generally adequate to describe the collective behavior of monomers in large chains. Accordingly, we have recently proposed a simplified model to obtain the conformational characteristics of polymeric chains based only on the steric constrictions between monomers [3]. The model predicts chain conformations by fixing bond lengths and angles, and by restricting the rotation angle to a previously determined interval associated to the angular displacements allowed by the steric constrictions of the considered chain. We demonstrated how strongly the amplitude of the rotation angle between monomers affected the dimensions of the chain, and a direct relationship between

this angular amplitude and the backbone rigidity was established.

In the present work, other aspects of the effect of the backbone rigidity on the conformational characteristics of chains are considered. A relationship between the scaling law for the radius of gyration as a function of the number of monomers and the chain rigidity is obtained. We show also that, for the same rigidity, the value of the average rotation angle between monomers, here named helicity, introduces a proportionality constant into the aforementioned law.

GENERAL DESCRIPTION OF THE MODEL

In our model we estimate polymer conformations by the basic steric constrictions between the monomers of the considered chains. This is achieved by limiting the rotation angle of any bond in the chain to a restricted interval $[\varphi_{i1}, \varphi_{i2}]$, or equivalently $[\varphi_a - \Delta\varphi, \varphi_a + \Delta\varphi]$, associated with short range interactions between the neighboring groups. Such angular restriction would represent the best fit to specific experimental situations, but in any case, the angular interval considered is included into the widest one associated with bond rotation in the very short chain (less than five monomers). Long-range interactions are considered by keeping apart any two backbone atoms in the chain by more than a characteristic contact distance D_c .

As shown schematically (Fig. 1), any particular chain is represented by the set $\{\vec{l}_i\}$ of bond vectors, \vec{l}_i , pointing from atom $i-1$ to atom i within the chain backbone. Associated with each bond vector \vec{l}_i , a pair of unit vectors,

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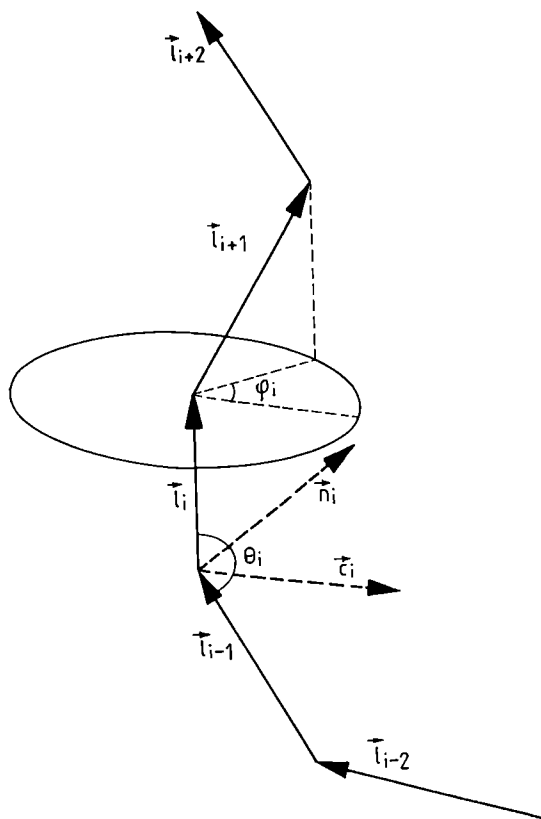


Fig. 1. Schematic representation of the bond vectors and angles used to calculate our chain conformations

\bar{n}_i and \bar{c}_i , perpendicular to each other and to \bar{l}_i , are introduced;

$$\bar{n}_i = \frac{\bar{l}_i \times \bar{l}_{i-1}}{\sin \theta_i} \quad (1)$$

where: θ_i is the i -th bond angle.

$$\bar{c}_i = \bar{n}_i \times \bar{l}_i \quad (2)$$

\bar{n}_i is perpendicular to the plane formed by \bar{l}_{i-1} and \bar{l}_i , and $\{\bar{l}_i, \bar{c}_i, \bar{n}_i\}$ is a right-handed basis of unit vectors.

The \bar{l}_{i+1} vector is generated by:

$$\bar{l}_{i+1} = -\cos \theta_{i+1} \bar{l}_i + \sin \theta_{i+1} (\cos \varphi_i \bar{c}_i + \sin \varphi_i \bar{n}_i) \quad (3)$$

where: φ_i is a random angle chosen within the interval $[\varphi_{i1}, \varphi_{i2}]$.

In our calculations, the first bond is directed along the positive z -axis, and the second one, restricted by the fixed bond angle θ_i , is chosen to lie in the xz -plane. All other bonds are constructed by randomly selecting a rotation angle between φ_{i1} and φ_{i2} , and by checking that distances from the $i+1$ atom position to the first i positions are larger than D_c .

RESULTS AND DISCUSSION

Reproduced from [3], Figure 2 shows the radius of gyration, R_g , for two chains differing in length with

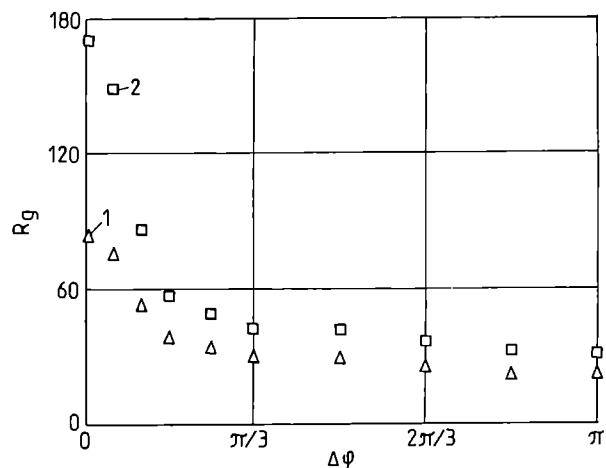


Fig. 2. Radius of gyration for bond chains with (1) 500 and (2) 1000 monomers. The dihedral angle interval between consecutive monomers, $\Delta\varphi$, is varied between 0 and π , while φ_n is kept fixed at $\pi/3$

fixed φ_n and varying $\Delta\varphi$. It is evident from Fig. 2 that the size of the chain molecule reduces steeply for values of $\Delta\varphi$ between $\pi/12$ and $\pi/3$. For values of $\Delta\varphi$ larger than $\pi/3$, size variations are greatly reduced. Rigidity regimes can be separated, through the interval width for bond rotations; according to our results, high rigidity is obtained at $\Delta\varphi < \pi/12$, semi-rigidity is obtained at $\pi/12 \leq \Delta\varphi \leq \pi/3$, and the flexible regime occurs at $\Delta\varphi > \pi/3$. Many examples of chains in the solution are found in the literature for the flexible and the semi-rigid cases of chains [4, 5], the highly rigid cases are mainly associated with highly ordered fibers and some biological chains [6, 7].

A set of computer experiments were performed aimed at obtaining the radius of gyration as a function

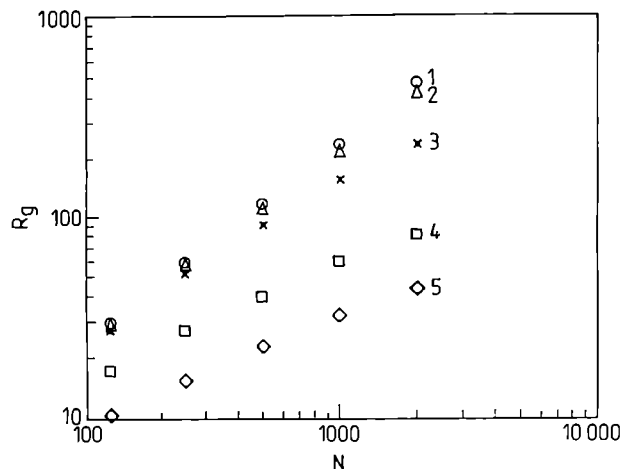


Fig. 3. Radius of gyration as function of N ; $\Delta\varphi$ is equal to: 1 — $\pi/180$, 2 — $\pi/18$, 3 — $\pi/9$, 4 — $\pi/3$, 5 — 2π a different scaling law $R_g \sim N^\alpha$ is obtained for each value of $\Delta\varphi$. In each graph, φ_n is fixed at π

Table 1. Scaling exponent for the R_g vs. N relationship as function of $\Delta\varphi$

$\Delta\varphi$ ($\varphi_n = 0$)	α
Compacted systems	1/3
2π	0.51
$\pi/3$	0.53
$\pi/9$	0.68
$\pi/18$	0.95
$\pi/180$	1.00

of the number of monomers in the chain, for several values of $\Delta\varphi$ (or rigidities). Results are graphically summarized in Fig. 3, which shows that R_g scales differently with large N 's at different values of $\Delta\varphi$. Table 1 gives the α scaling exponent in the $R_g \sim N^\alpha$ relationship, including, as a reference, the value $\alpha = 1/3$ which corresponds to a hypothetical chain packed in such a way that no volume is left unoccupied. Clearly, for a real polymer, α must always be larger than $1/3$; at the most, it can be 1. The case $\alpha = 1$ corresponds to perfectly rigid chains ($\Delta\varphi = 0$), *i.e.* to helical conformations, for which the chain size grows linearly with N . The calculated value of α for $\Delta\varphi = 2\pi$ corresponds well with the analytical value obtained by Flory [8] for what he called the freely rotating chain model, with no-self-avoiding considerations. The remaining values of α for $0 < \Delta\varphi < 2\pi$ fit well between these extreme cases and show that the R_g vs. N scaling law depends on chain rigidity. Although very large values of N have not been obtained due to a prohibitively large increase in computing time, the range considered covers well the usual experimental molecular weights (for which $N < 2000$).

In order to verify that $\Delta\varphi$ is indeed the driving factor for the α scaling exponent in the $R_g(N)$ relationship, we also run a set of computer experiments in which we fixed $\Delta\varphi$ and let φ_n vary. Figure 4 shows the R_g vs. N relationship for these cases. Both rigid and semi-rigid cases are presented, and since the $\Delta\varphi$ equal to 0 and to 2π are trivial cases, it can be considered that the parallelism between the $R_g(N)$ graphs, for different values of φ_n and fixed $\Delta\varphi$, reflects that $\Delta\varphi$ is the parameter which determines the α exponent in the scaling law for $R_g(N)$.

A pictorial way to visualize the present results is to think on the helical conformations, corresponding to $\Delta\varphi = 0$, as a basic structure, and then to start $\Delta\varphi$ to grow up.

The basic helical structures are built up by considering a constant rotation angle, φ_n , along the chain. The value of this angle determines how fast the chain extension grows as monomers are added to it, the slower growing rates corresponding to the values that approach π as much as the characteristic contact distance, D_c , allows it. The helix will degenerate in the *all-trans* conformation for $\varphi_n = 0$. However, in any case, the size of the chain will be proportional to N , apart from a small correction due to the small separation of each \vec{l}_i vector from the exact geometrical axis of the structure. The

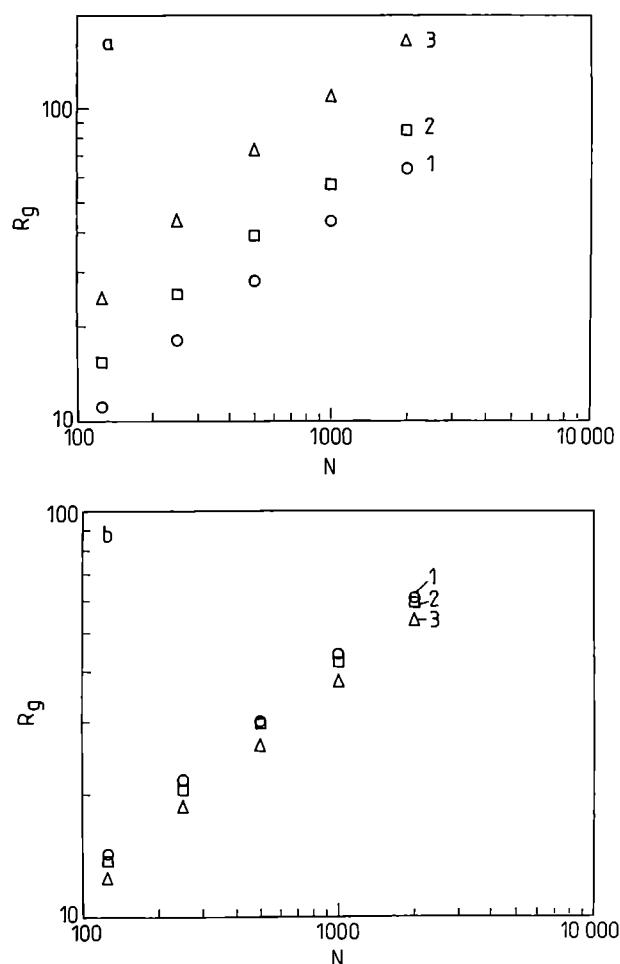


Fig. 4. Radius of gyration as function of N ; φ_n is equal to: 1 — $\pi/6$, 2 — $\pi/3$, 3 — π ; $\Delta\varphi$ is fixed at (a) $\pi/6$, semi-rigid case, or (b) $\pi/2$, flexible case

overall extension increase of the helices will always be in a straight geometry and the linear scaling between R_g and N settles naturally.

If we now grow $\Delta\varphi$ to a small value (as compared to π), the small mobility given to φ allows the overall growing of the chain to separate from the straight geometry, however, for sufficiently small $\Delta\varphi$ the helical nature of the structure is not altered because the local axis tilting cannot be large enough and so, close turns of the chain cannot be produced. Strong randomization of the structure is limited because the local radius of curvature for the still recognizable axis of the structure cannot be too small. In fact, for the great majority of structures, deviations from the original straight geometries are restricted by the random character of the growing process, which tends to compensate turns in the structure on either side. So, although the R_g vs. N relationship becomes non-linear, departure from such type of scaling is reduced, and although its precise nature is not clear, it would be presumably the same for any value of φ_n .

For $\Delta\varphi$ close to $\pi/6$, the helical nature of the chain structures can be preserved only in a very crude manner, strong deviations from the linearity between R_g and

N set in, mainly due to the possibility of getting large turns of the overall structure, associated with fluctuations in the random character of the φ_i sequences for two or more consecutive monomers. Finally, for larger values of $\Delta\varphi$, the helical nature of the chains is completely lost, a strong randomization of the structures sets in and the statistics for the overall sizes of the structures becomes essentially the same.

In the light of the presented results, chain stiffness factors [9] must be cautiously interpreted because, although given definitions correctly assign it to restrictions in the angular rotation interval, they also assume a quadratic relationship between R_g and N . As we have seen, for the case in which the rotation angle is restricted to a continuous single interval, as occurs in rigid chain polymers, R_g can scale differently with N , and the stiffness evaluation must consider both, the R_g vs. N scaling law and the R_g ratio for experimental and θ -conditions, and the result obtained will reflect φ -statistics through φ_n and $\Delta\varphi$.

The randomness of bond rotation within the model interval [$\varphi_n - \Delta\varphi$, $\varphi_n + \Delta\varphi$], is of course of great concern to the present discussion, however, the introduction of such restrictions for the rotation angle, allows the identification of the rigidity ($\Delta\varphi$) and the helicity (φ_n), apart from others, as the important characterizing parameters to typify the kind of disorder associated with polymeric chains. Any physical situation in which φ -correlations exist is beyond the scope of the present results, but comparison to the ideas here discussed could presumably help us identify the effect that some correlations can introduce.

CONCLUSIONS

By using a simple model, a dependence on bond rigidity, associated with the amplitude of the angular variation of the dihedral angle, was found for the scaling law

between the chain size and the number of monomers in a polymeric chain. An additional parameter, namely the helicity, which corresponds with the average rotation angle, is also a useful parameter to understand the structural characteristics of polymeric chains. Although simple, this approach enabled us to study the loss of helicity due to increased freedom of bond rotation.

The model in its present form does not take account for the situations when the loss of rigidity is caused by the loss of helicity at few places along the chain, however, the results obtained illustrate the important effects of restricted bond rotation and set intuitive and pictorial views on the conformation of chains in general situations, useful for understanding chain rigidity at different scales.

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