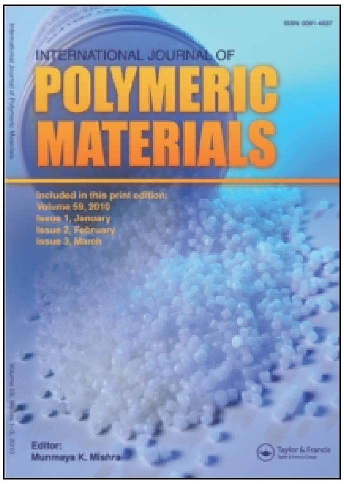

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Ocampo, M. A. and Castaño, V. M.(2001) 'A Simple Model for the Conformational Characteristics of Polymeric Chains', International Journal of Polymeric Materials, 49: 1, 51 — 57

To link to this Article: DOI: 10.1080/00914030108035866

URL: http://dx.doi.org/10.1080/00914030108035866

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 51–57
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A Simple Model for the Conformational Characteristics of Polymeric Chains

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(Received 18 July 1999; In final form 7 January 2000)

A simple model, based on the role played by steric constrictions in chain molecules, is presented aimed to obtain the conformational characteristics of polymeric chains. The model has been run in a simple personal computer and the obtained results show potential usefulness to simulate polymeric structures as well as a structure generator for other models. The model was applied to study the effect of the rigidity of bond rotations on the size of chain molecules, the results obtained in this calculation explain the behaviour of chain sizes when dissolved in different solvents.

Keywords: Polymeric chains; Conformation; Model; Steric constrictions

INTRODUCTION

The general properties of polymeric materials arise from relevant characteristics of the monomeric units from which synthesis is made, and from the way these units are conformed along their three-dimensional chain-like structure [1]. Such arrangements are influenced by the relatively weak forces between and within the chains, different from the covalent forces that hold the chain, as well as by the conditions in which a specific material is formed.

Chain entanglements, crystallization and solvation effects are among the factors that determine the way in which monomers behave

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in a given chain [2]. Because of these, molecular potentials used to describe very short chains (less than five monomers) are not generally adequate to describe the collective behaviour of monomers in large chain molecules. Furthermore, chain steric constrictions and the overall low chain mobilities keep polymeric materials far from thermodynamic equilibrium conditions. All these aspects of the problem are usually not considered in standard calculations of polymeric structures, and render unnecessary the introduction of complicated models for such calculations.

Steric constrictions between groups attached to consecutive monomers in a chain, as well as those arising from interactions between separate monomers happen to be the basic and gross interactions within a chain. These interactions are very important because they primarily restrict the number of possible configurations in a chain. Other contributions would consist of relatively small variations of the interacting potentials of less importance from the point of view of the gross characteristics of the chain structure.

In this work we propose a model that restricts chain conformation only by the steric restrictions to chain conformations. The model is then used to obtain chain conformations with up to 20000 bonds and is run to obtain the statistics of the radius of gyration for several sets of parameters representing different degrees of chain rigidity. It is observed that the amplitude of rotations around a central value is the basic factor in determining chain flexibility. A further insight into this result explains why solvation interactions can change chain sizes by limiting or widening the angle of rotation between consecutive monomers in a chain. It can also be seen that the correction of our results by small variations of the rotational potential can only rigidize further the chain backbone to give larger end-to-end size of the chains than those predicted by merely steric considerations.

FUNDAMENTALS OF THE MODEL

As has extensively cited in the literature, basic conformation of polymeric chains is well accounted for by keeping bond lengths and angles constant along modeled chains [3]. Only bond rotations, measured by the dihedral angles between the planes defined by consecutive pairs of bonds, are typically considered. Particular conformations for chains with N bonds ($N+1$ backbone atoms) are determined by the set of $N-2$ consecutive dihedral angles following the first two bonds in one of the chain extremes. To determine what values these angles adopt, a Boltzmann probability factor is usually introduced to weigh dihedral angles energies in agreement with the corresponding equilibrium thermodynamic distribution [3,4]. A common practice considers the preferential orientations so associated with the well-defined isomeric states and reduces the problem to the evaluation of probabilities for specific angle sequences, those corresponding to the *trans* and the two *gauche* configurations [5]. Self-avoiding conformations are considered to take free volume contributions into account and must be properly introduced to obtain realistic conformations and their corresponding physical properties [6].

Real polymeric chain conformations depend strongly on the processes followed to obtain a specific material and, in practical cases, strict equilibrium conditions are seldomly attained. Because of this, we consider it convenient to maintain only the most basic aspects of the problem for a gross estimate of polymer configurations.

In this work we model such elements as the steric constrictions of the particular chain, this is done by limiting the rotation angle of any bond in the chain to a restricted interval $[\varphi_{i1}, \varphi_{i2}]$, or equivalently $[\varphi_0, \varphi_0+\Delta\varphi]$, associated to short range interactions between neighbouring groups. Such angular restriction would represent the best fit to specific experimental situations, but in any case, it is included in the widest interval associated to the inner chain bond rotation dictated by the short chain case. Long range interactions are considered by keeping apart any two backbone atoms in the chain by more than a characteristic contact distance D_c.

Any particular chain is represented by the set $\{\mathbf{l}_i\}$ of bond vectors, $\mathbf{l}_i$, pointing from atom $i-1$ to atom i in the chain backbone. Associated with each bond vector $\mathbf{l}_i$, a pair of unit vectors, $\mathbf{n}_i$ and $\mathbf{c}_i$, perpendicular to each other and to $\mathbf{l}_i$, are introduced;

$$\mathbf{n}_i = \frac{\mathbf{l}_i \times \mathbf{l}_{i-1}}{\operatorname{Sin}\theta_i}, \quad \theta_i, \text{being the } i\text{-th bond angle}$$

$$\mathbf{c}_i = \mathbf{n}_i \times \mathbf{l}_i,$$

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

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

$$\mathbf{l}_{i+1} = -\mathrm{Cos}\ \theta_{i+1}\ \mathbf{l}_i + \mathrm{Sin}\ \theta_{i+1}(\mathrm{Cos}\ \varphi_i\, \mathbf{c}_i - \mathrm{Sin}\ \varphi_i\, \mathbf{n}_i),$$

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

It can be seen, from Figure 1, that the all *trans* planar conformations correspond to the case $\varphi_i = 0$ for any i, and that the case $0 < \varphi_i < \pi/2$ corresponds to right-handed backbones.

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 in the xz plane. All other bonds are constructed by randomly selecting a rotation angle between φ_{i1} and φ_{i2}, and by checking

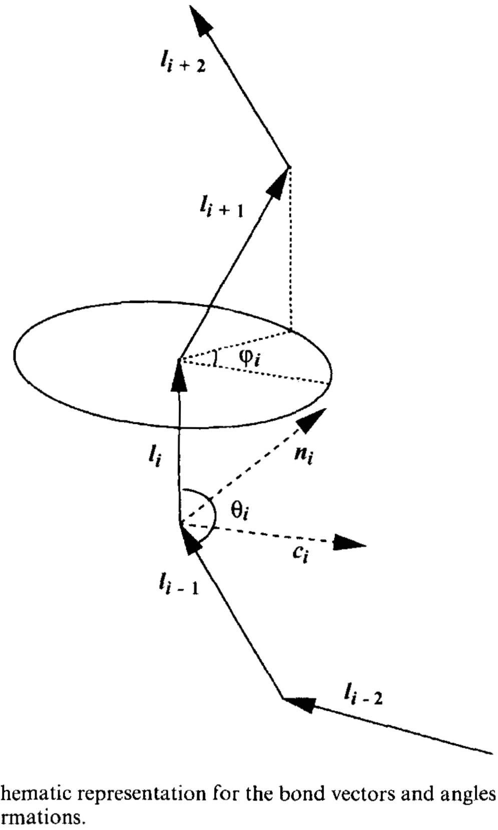

FIGURE 1 Schematic representation for the bond vectors and angles used to calculate our chain conformations.

that the distances from the $i+1$ atom position to the first i positions are larger than D_c. To reduce the number of distances checking, if D_c is larger than the bond length checking is restricted to $i-j$ positions, where j represents the number of bonds after which D_c can be surpassed.

RESULTS AND DISCUSSION

Our algorithm was run in a 100 MHz personal computer through a conventional program written in Basic language. The main objectives of the proposed model, namely, to avoid chain overlapping while keeping its simplicity, are well accounted for by more of a hundred of types of structures, in which φ_0 and $\Delta\varphi$ were varied along their allowed intervals, and N varied regularly from 125 to 2,000 and for specific cases up to 20,000. Figure 2 shows the xy plane projection of some conformations grown with our algorithm. They are shown with a same scale and it can be seen the effect of increasing $\Delta\varphi$ on the chain straightness, and therefore the chain size.

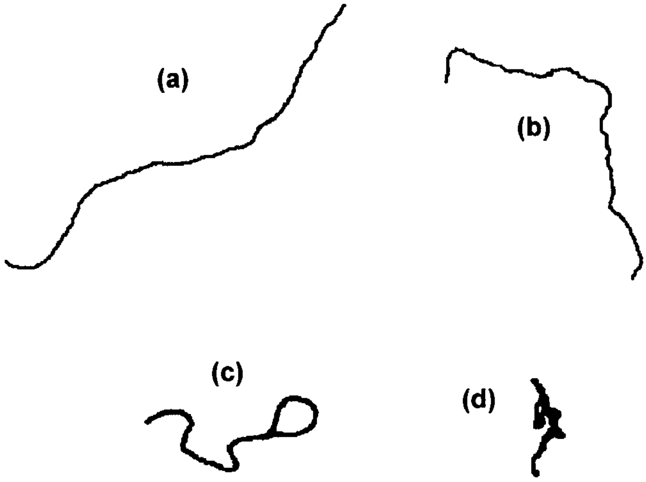

FIGURE 2 xy plane projection of some conformations grown with our algorithm. They are shown at the same scale. It can be seen the effect of increasing $\Delta\varphi$ on the chain straightness and size; $\varphi_0=0$, (a) $\Delta\varphi=\pi/18$, (b) $\Delta\varphi=\pi/9$, (c) $\Delta\varphi=\pi/6$, (d) $\Delta\varphi=\pi/3$. θ is taken as the tetragonal angle.

Computing times to obtain a specific chain conformation varied between few seconds for the smaller chains up to about 20 minutes for a 20000 bond chain, they increase no linearly with the number of monomers in most of the cases. Main differences are associated to the probability of growing chain segments that tend to close over themselves causing big numbers of chain overlapping, and so of repeated calculations, this happens more easily in the case of chains with $\varphi_0 + \Delta\varphi/2$ close to π and small $\Delta\varphi$, *i.e.*, those chains tending to close over themselves forming ring-type structures.

Our model is useful by itself, since generated chain structures are realistic; have no overlapping and are as random as they can be, restricted only by the imposed steric hindrances. It can also be useful as a chain structure generator for other models intended to get more real structures by allowing them to relax under a process simulator, as those used in molecular dynamic calculations.

Figure 3 shows the radius of gyration for chains with fixed φ_0 and varied $\Delta\varphi$. It is evident from it that the size of the chain molecule is greatly reduced for values of $\Delta\varphi$ over $\pi/6$. For values of $\Delta\varphi$ larger than $\pi/3$, which closely coincides with the case in which isomeric descriptions are important for most of the polymers, size variations are

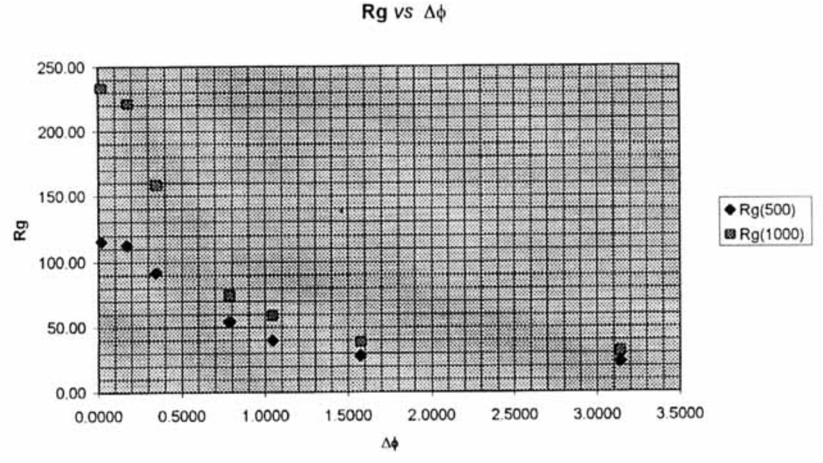

FIGURE 3 Radius of gyration for bond chains with 500 and 1000 monomers. The dihedral angle between consecutive monomers is varied between 0 and π, while φ_0 is kept fixed at 0. θ is taken as the tetragonal angle.

greatly reduced. This result is important because typical calculations consider isomeric structures as the basic ones to calculate big chains and so they can easily change from a rigid regime to a flexible one by changing the relative weighs associated with each isomeric state.

From the point of view of solvation mechanisms, the well known experimental fact that chain sizes diminish with the poorness of the solvent in which it is embedded, suggests that good solvents locally couple with the chain in such a way that angular mobility between monomers is strongly reduced. This would be in good agreement with a "zipper type" mechanism of coupling between solvent and chain molecules. This idea is also in good agreement with the fact that extreme rigidity of the chain backbone is required in the crystalline state, or in high strength polymeric materials.

CONCLUSIONS

Our simple model is shown to be potentially useful in obtaining good conformational characteristics of chain molecules, it can be used by itself, or can be employed as a good generator for single chains in a solvent, or in situations representing mean field conditions. A further procedure to relax the calculated structures, considering more detailed interactions, could result in a more realistic configuration, hopefully with a reduced added effort.

The application of our model to a series of varying rigidity chains helps to give a good explanation of the behaviour of the observed sizes of chain molecules according to the quality of the used solvent.

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