Computational study of tacticity effect in polypropylene structural properties using Rotational Isomeric State model

Author: Jordi Sans
*Secció de Química Física and IQTCUB, Facultat de Química, Universitat de Barcelona, Barcelona.**

Advisors: Pablo M. Blanco and Francesc Mas.

Abstract: Tacticity is the spatial orientation of the substituent groups along a polymeric chain. Its study is a matter of undeniable importance due to its effect on relevant physicochemical properties. In this thesis, it has been implemented Rotational Isomeric State (RIS) model and build up a methodology for studying polypropylene. The first and second neighbours interactions has been deeply studied to be able to acquire the parameters of the transfer matrices for polypropylene. It also has been necessary to perform *ab initio* calculations of models to obtain the parameters of the tranfer matrices. Monte Carlo simulations has been produced for isotactic and syndiotactic polypropylene to include excluded volume effects and overcome the limitations of RIS model. In conclusion, the results show that tacticity effect changes the structural properties of polypropylene.

I. INTRODUCTION

The study of the microscopic properties of polymers by means of statistical mechanics has been developed by Flory [1]. He proposed the Rotational Isomeric State (RIS) model that uses the method of transfer matrices aiming to compute the conformational properties of linear neutral polymers such as polyethylene, polyoximethylene, polyoxiethylene, etc. This methodology has also been used for calculating the microscopic properties of polypropylene and among other polymers in [2–4],

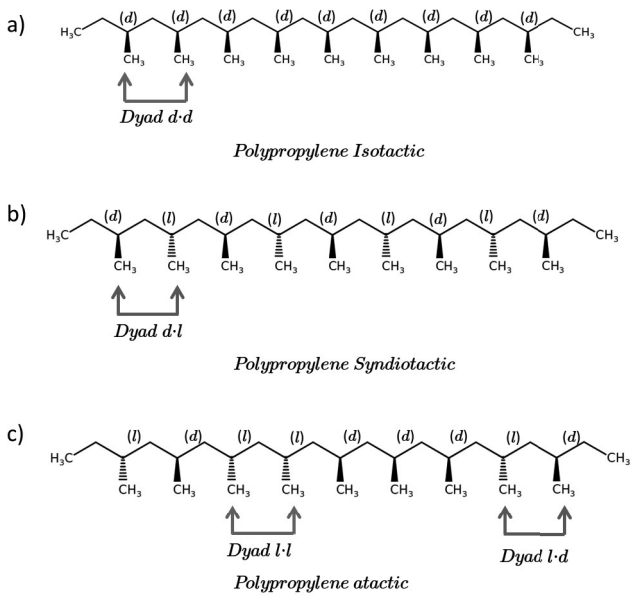

FIG. 1: An illustrative representation of the adjacent chiral centers along polypropylen chain is shown for isotactic, syndiotactic and atactic tacticities. The first one only presents the chiral center d which is repeated along the chain. The second one, presents a racemical dyad (dl), periodically repeated along the chain. Whereas, atactic polypropylene is characterised by a disorganized distribution of chiral centers within the macromolecule.

Tacticity is the relative stereochemistry of adjacent chiral centers within a macromolecule[6] .As it is shown in Fig (1a), an isotactic polymer presents one type of stereochemical center along the chain. In this case the relative position of the methyl is orientated towards the reader which is denoted by d, whereas the opposite direction is represented by l. In contrast, a syndiotactic polymer presents two chiral centers with opposite stereochemistry repeated periodically along the chain. For instance, a syndiotactic polypropylene is shown in Fig(1b). As observed in Fig(1c) the spatial orientation of the stereochemical centers in an atactic chain does not follow any specific order. The stereoregularity of a chain cannot be interconverted by means of conformational changes as stretching, bending, rotating or torsion motions of bonds in the polymeric chain and it only depends on its polymerization processes[7]. In the case of polypropylene, tacticity plays a fundamental role in its macroscopic properties[7]. As a case in point, isotactic polypropylene presents a crystalline structure and it is expected to have mechanical strength and chemical resistance. While syndiotactic presents a semicrystalline and flexible structure an atactic polypropylene has a gum-like form and it is a tacky material [5, 6]. Focusing on the study of polymer properties regarding its tacticity, polypropylene has been widely studied by[2][3][5][8] using techniques based in RIS model applying slightly changes. Asakura [2] and Nakajima[3] used RIS model to calculate the ratio characteristic for polypropylene and polyethylene. Bloqmvist[4] and Madkour[5] have used Monte Carlo technique applying RIS model to study the microscopic properties of polyesters and polypropylene respectively. Monte Carlo methods has been a fundamental tool to develop models for studying polymer properties such as SB (Site Bind-

*Electronic address: jsdfiguero@gmail.com

ing) [9] in this group. Furthermore, it also has been coupled with RIS to study the effect of protonation on the structural properties of polymers (Site Binding and Rotational Isomeric State, SBRIS model)[10, 11].

In consonance with the preceding works, the aim of this thesis is to develop a model to study the tacticity of polypropylene and to build up a methodology to model polymers with tacticity. In this thesis, the structural properties of polypropylene are analyzed. It is a neutral macromolecule which is described by the presence of methyl groups on its monomeric structure. These properties arise from the intramolecular interactions significantly modified by the presence of these side groups. The knowledge of nearest and second neighbours interactions is crucial, in order to implement the RIS model to predict the structural properties of polypropylene. As a matter of fact, the study of these interactions is realized on the rotational states of minimum energy (*trans*, *gauche+*, *gauche-*)(see Fig.(2)) which are the ones significantly populated. Furthermore, it has been done a classification of these interactions in terms of the distance between groups and the type of group. After that, a quantification of the interactions of nearest neighbours and second neighbours for the states of minimum energy given two consecutives dihedral angles has been quantified. It have been done performing *ab initio* calculations of model molecules. Finally, in order to compute the structural properties of polypropylene, Monte Carlo simulations in the canonical ensemble (N,V,T) based on RIS model are performed. Its main objective is to overcome the limitations of RIS model and to include the effect of excluded volume to the intramolecular interactions of the polymer.

II. THEORETICAL BACKGROUND

A given conformation of a polymer chain is defined by a set of dihedral angles $\{\phi\}$. The conformation which acquires a fragment of that chain depends on its rotational energy profile. This potential energy profile, as shown in Fig.(2), is given by the set of interactions that presents each conformation in the given interval of angles. Moreover, it is shown the rotational profile of a butane molecule where the states of minimum energy are represented by the conformations *trans* (t), *gauche+*(g+) and *gauche-*(g-). The representation of this energy profile in terms of probability, sets a significant statistical weight on those conformations which are in the states *trans*, *gauche+* and *gauche-*. The average of butane conformations in thermal equilibrium outside of the energy minima can be considered neglegible. Based on this observation, the RIS model [1], describes the rotational profile as three discrete states that significantly represent the conformation that can adopt a given chain. Moreover, it is considered that the conformation of a fragment given by a dihedral is correlated with the precedent dihedral angle.

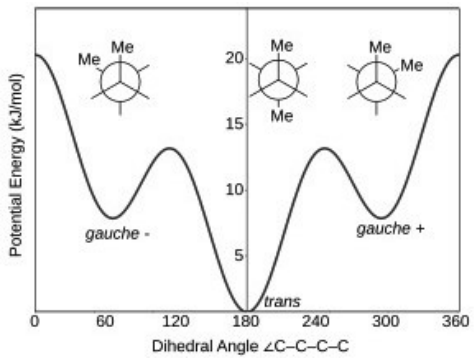

FIG. 2: Rotational profile of butane molecule. It allows to study the nearest neighbours steric factors for a polyethylene chain, given the rotational states of minimum energy (*trans*, *gauche+*, *gauche-*).

This loss of correlation allows to define the energy of a polymer as the sum of the rotational energy of each of the N bonds

$$E(\{\phi\}) = \sum_{i=2}^{N-1} E_i(\phi_{i-1}, \phi_i) \tag{1}$$

Where the conformational energy of each bond is function of the preceding and its dihedral angle. Therefore, the partition function of a polymeric chain is given by

$$Z_N = \sum_{\{\phi\}} \exp\Big(\frac{-E(\{\phi\})}{k_{\mathrm{B}}T}\Big) = \sum_{\{\phi\}} \Omega(\{\phi\}) \tag{2}$$

$$\Omega(\{\phi\}) = \prod_{i=2}^{N-1} u_i = \prod_{i=2}^{N-1} \exp\Big(\frac{-E(\phi_{i-1}, \phi_i)}{k_{\mathrm{B}}T}\Big) \tag{3}$$

Where the statistical weight (Ω) of a conformation is defined by the product of the Boltzmann factors of the rotational state of each bond(u_i). The probability of a conformation is given by

$$P(\{\phi\}) = \frac{\Omega(\{\phi\})}{Z} \tag{4}$$

The problem of calculating the partition function using the equation (2) is that one has to sample all the configurations. In order to solve this problem, it is employed the transfer matrix technique [1]. A well-known technique used in statistical mechanics for 1-dimensional systems allows to define in a recursive way the partition function of N bonds with the partition function of *N-1*.

$$Z_N = \boldsymbol{T} Z_{N-1} \tag{5}$$

Using Eq.(5) it is possible to calculate the partition function of N bonds as the product of transfer matrices that define each bond using as a starting row vector $\boldsymbol{q} = (1, 0, 0)$ and an ending vector $\boldsymbol{p} = (1, 1, 1)^T$.

$$Z_N = \boldsymbol{q}\left[\prod_{i=2}^{N-1}\boldsymbol{T}_i\right]\boldsymbol{p} \tag{6}$$

Eq.(6) is useful to calculate the properties of a polymeric chain but its limitation is that it does not account for long range interactions. Fig.(3) shows a transfer matrix where each of the elements are the Boltzmann factors defining a rotational state of bond i involving two consecutive dihedral angles. These Boltzmann factors depend, on the main interactions given a rotational state.

For example, the transfer matrix regarding polyethylene (PE) interactions is given by [1]:

$$\boldsymbol{T}_{PE} = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{pmatrix} \tag{7}$$

Where σ is the Boltzmann factor that comes from the difference of energy between *gauche* and *trans* states, where all the chain in *trans* position is the reference state. ω is the Boltzmann factor that describes the interaction when two consecutive dihedral angles are in *gauche+* and *gauche-*. ψ is the Boltzmann factor that describes the interaction occurring when both dihedral angles are in *gauche-* position. In the case of polyethylene, as the same type of bond is periodically repeated along the polymeric chain, its partition function only depends on the product of N-2 transfer matrices given a polyethylene of N bonds and two terminal

$$Z_N = q\boldsymbol{T}_{PE}^{N-2}p \tag{8}$$

III. COMPUTATIONAL METHODOLOGY

A. Classification of interactions of polypropylene

As shown in Fig.(1), polypropylene is a macromolecule that presents methyl side groups in its monomeric structure. Within RIS model, two different kinds of bonds can be differentiated in a polypropylene chain. As shown in Fig.(4), each bond presents an important difference regarding the neighbours interactions. The rotation around

$$\boldsymbol{T_i} = \begin{array}{c|ccc} \Phi_i = & t & g^+ & g^- \\ \hline \Phi_{i-1} = t & u_{tt} & u_{tg^+} & u_{tg^-} \\ g^+ & u_{g^+t} & u_{g^+g^+} & u_{g^+g^-} \\ g^- & u_{g^-t} & u_{g^-g^+} & u_{g^-g^-} \end{array}$$

FIG. 3: An example of transfer matrix for RIS model. It contains the Boltzmann factors involving the rotational states of two consecutives dihedral angles(ϕ_{i-1} ϕ_i). These Boltzmann factors are considered the most populated statistical weights in the rotational energy profile.

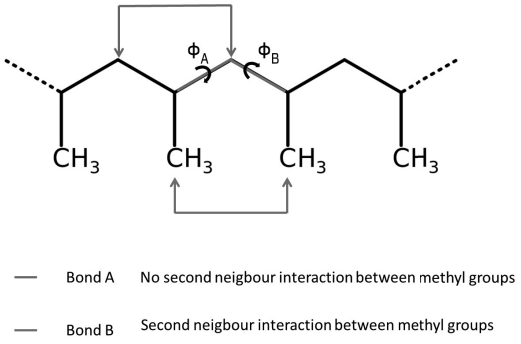

FIG. 4: Polypropylene fragment showing which bonds are object of study. The bond A does not present second neighbour methyl-methyl interactions whereas the bond B presents them.

bond B presents methyl-methyl second neighbours interactions that does not present the bond A. Moreover, regarding Fig.(4), the transfer matrices of bond A depend on the stereochemistry of one group whereas for bond B they depend on the stereochemistry of both methyls in a dyad. Then, bond A is described by matrices $\boldsymbol{T}_d$ and $\boldsymbol{T}_l$. Whereas bond B is described by matrices $\boldsymbol{T}_{dd}$,$\boldsymbol{T}_{ll}$,$\boldsymbol{T}_{dl}$,$\boldsymbol{T}_{ld}$.

In order to obtain these transfer matrices it is necessary to classify polypropylene interactions.To perform this task, a program has been developed, its scheme is shown in Fig.(6). It deduces which substituents are in contact in the rotational states of minimum energy within

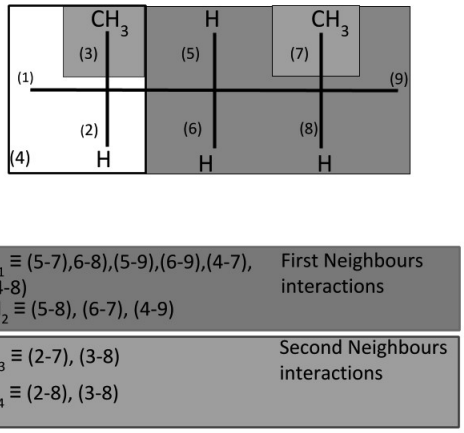

FIG. 5: A Fischer representation of the dyad dd in tt conformation Fig.(1). The classification of the interactions is done by means of the distance between groups. d_1 and d_2 helps to classify the nearest neighbours interactions whereas d_3 and d_4 helps to distinguish the second neighbours interactions.

two consecutive dihedral angles for each conformation.

The substituents are separated in groups depending on the distance between them (see Fig.(5)). These distances are previously chosen and the whole process helps to better understand the main contributions to the energy of each rotational state in the RIS Model. The distances d_1 and d_2 help to differentiate among interactions of nearest neighbours. In contrast, d_3 and d_4 make a distinction among second neighbours interactions. d_1 represents the groups in *gauche* positions but d_2 represents de groups in *trans* position. While d_3 represents "*cis*" interactions and d_4 "*trans*" interactions.

Therefore, depending on the tacticity of polypropylene, its partition function is defined using the transfer matrix that comes from the local interactions present in the dyads of Fig.(1). From Eq.(6), it is possible to define the partition function of each tacticity. For isotactic, syndiotactic polypropylene, the partition function is calculated as follows:

$$Z_{PP_{isotactic}} = \boldsymbol{q}\left[\boldsymbol{T}_d\boldsymbol{T}_{dd}\right]^{\frac{N-2}{2}}\boldsymbol{p} \tag{9}$$

$$Z_{PP_{syndiotactic}} = \boldsymbol{q}\left[\boldsymbol{T}_d\boldsymbol{T}_{dl}\boldsymbol{T}_l\boldsymbol{T}_{ld}\right]^{\frac{N-2}{4}}\boldsymbol{p} \tag{10}$$

The periodicity that presents both types of tacticities allows to define both partition functions (Eq.(9) and Eq.(10)). But as atactic polypropylene presents randomly distributed adjacent chiral centers its partition function has to be computed by the whole matrix product (Eq.(6)) taking into account which chiral center is described in each value of the index. The transfer matrices are deduced and defined in further sections of this thesis.

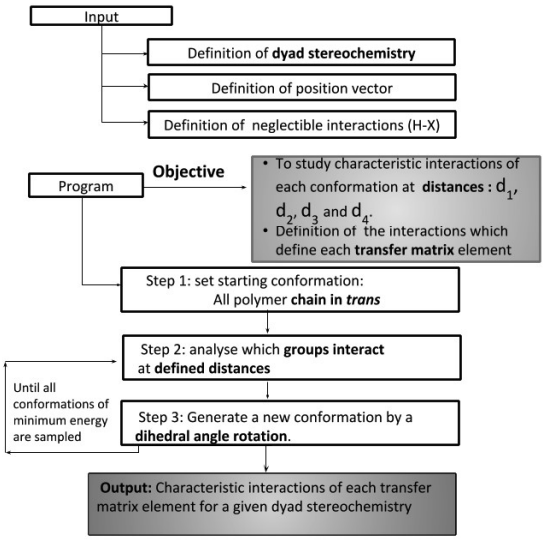

FIG. 6: Scheme of the program used for classifying the interactions regarding a stereochemical dyad (Fig.(1)). The classification of the interactions is done by means of the distance between groups. d_1 and d_2 helps to classify the nearest neighbours interactions whereas d_3 and d_4 helps to distinguish the second neighbours interactions.

Finally, this study leads to better understand the Boltzmann factors given in the rotational states of Fig.(3) for each of the dyads. Necessary to compute Eq.(6).

B. Calculations of Boltzmann factors for polypropylene

Once the previous analysis has been done, it is necessary to calculate the interactions of the rotational states (*trans*,*gauche+* and *gauche-*). In order to compute them, the molecules 2,5-methylheptane and 4-methylheptane have been prepared using Avogadro [12]. The molecules have been chosen because they can reproduce the local interactions. The chain is represented by an ethyl group, in order to differentiate from the methyl side group . The preparation of this structures have been done by constructing one of the stereochemical dyads in Fig(1). After that, the energy of each of the structures coming from each of the rotational states of minimum energy within two consecutive dihedral angles have been minimized. This process of minimization of energy have been done using a molecular dynamics algorithm that uses the General Amber Force Field (GAFF). It is necessary to minimize the energy in order to converge faster to the stationary state of minimum energy.

For quantum calculations the Gaussian 09 [13] package has been used to perform calculations of a perturbational method of second order (MP2) with a basis 6-31G(d,p). Its objective is to compute the state of minimum energy which has been achieved by calculating the frequencies at temperature 418.15 K using as a solvent diphenyl ether using a SMD method. For this solvent and temperature polypropylene is known to be at its Flory temperature where the polymer is close to an ideal behaviour within the Flory-Huggins theory of polymer solutions. [3] [**?**]. The equations used for calculating the parameters from the set of energies coming from the set of Boltzmann rotational states are given in the appendix section.

C. Monte Carlo simulations

The use of RIS model to calculate the polymer structural properties presents the counterpart of not considering excluded volume intramolecular interactions. Therefore, in order to overcome the limitations of RIS model, Monte Carlo simulations considering excluded volume are produced[11][10]. In Fig.(7) there is a representation of excluded volume interactions that exhibits a polymer distinguishing them from short range interactions. These

long range interactions are modeled by means of a hard-sphere potential.

$$F_{LR}(r_{ij}) = \begin{cases} 0 & \text{if } r_{ij} \geq R_i + R_j \\ \infty & \text{if } r_{ij} < R_i + R_j \end{cases} \quad (11)$$

Its purpose is to reject a conformation when the distance between two chain atoms i and j is lesser than the sum of their atomic radius $(R_i + R_j)$. It is not considered a long range interaction when two atoms are separated for a distance smaller than six bonds.

As shown in the scheme of Fig.(8), the starting conformation of a Monte Carlo simulation of polypropylene is characterized by all the bonds in the chain in *trans* conformation.

Then, in each Monte Carlo step, the conformation of one randomly chosen bond is changed applying a rotation of ± 60 °. Which corresponds to the three rotational states of minimum energy shown in Fig(2). As RIS model is being applied, only these significantly populated rotational states are considered. The free energy computed in Monte Carlo simulations is divided in two parts, the part coming from the short range interactions (F_{SR}) and the part coming from the long range interactions(F_{LR}).

$$F = F_{SR} + F_{LR} \quad (12)$$

But, when the atomic radius is set to zero, the modeled polymer only presents accurately described short range interactions. As explained in Fig(8), the conformational change is accepted when it minimize the free energy of the system. Nevertheless, if the new conformation does not minimize the free energy, it is accepted with a probability given by one of the Boltzmann factors in a transfer matrix Fig(3). Therefore, the probability of acceptance not only depends on the actual dihedral angle but also depends on the preceding dihedral angle. The transfer matrices that are used for calculating conformational changes depend on the dyads used of the tacticity of polypropylene Fig(1). For isotactic polypropylene, the transfer matrices $\boldsymbol{T}_{dd}, \boldsymbol{T}_{d}$ have been used. Whereas, for syndiotactic polypropylene, the transfer matrices $\boldsymbol{T}_{dl}, \boldsymbol{T}_{ld}, \boldsymbol{T}_{d}, \boldsymbol{T}_{l}$ have been used. For atactic polypropylene both types of transfer matrices are necessary to calculate its structural properties.

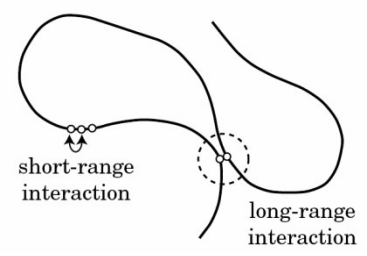

FIG. 7: Representation of a polymeric chain presenting excluded volume interactions (long range interactions). It is also shown the difference between the short-ranged interactions and the long range interactions.

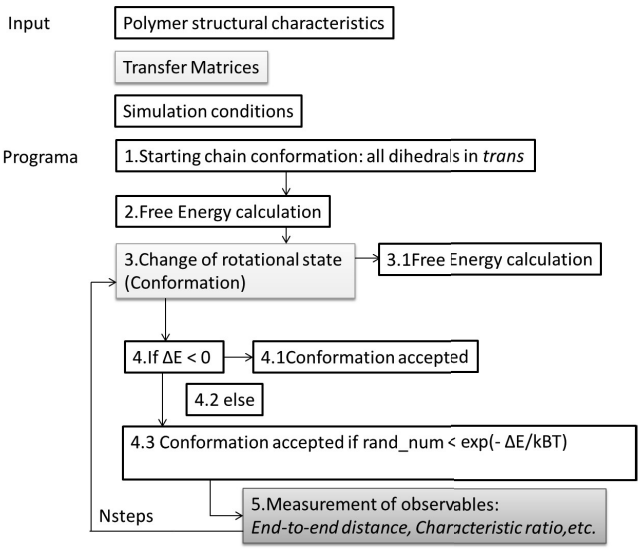

FIG. 8: A scheme explaining the Monte Carlo program used for calculating the structural properties of polypropylene for each tacticity.

Regarding the computation step of Fig(8), once a conformation is accepted, it is calculated the end-to-end distance, characteristic ratio. The end-to-end distance $(< r^2 >)$ of a polymeric chains is computed as the thermal average of as the distance between the first atom and the last atom of the chain.

$$< r^2 > =< (r_0 - r_f)^2 > \quad (13)$$

Where r_0 and r_f are the spatial positions of the first and the last atom of the chain. The characteristic ratio of the chain is also computed.

$$C_\infty = lim_{N\to\infty} \frac{< r^2 >}{Nl^2} \quad (14)$$

Where l is the bond length. It measures the deviation of the end-to-end distance from the Freely Jointed Chain model. Finally, the simulations have been performed for temperature of 418,15 K. It reproduces the conditions of a theta solvent for diphenyl ether [3]. The length of the simulations have been 10^7 Monte Carlo steps, the bond length is 1.557 Å. The bond angle is given by 112.85°. The atomic Radius for the carbon atoms with methyl chains have a length of 2.195 Å. The atomic radius for the methylene groups have a length of 1.095 Å. Both radius have been measured using Avogadro [12] as the distance from the carbon atom to the distance of a hydrogen atom of methylene or methyl groups.

IV. DISCUSSION AND RESULTS

A. Deduction of transfer matrices for polypropylene

The procedure that has been described in Fig.(5) and its results given in the appendix has been fundamental to deduct the parameters of the transfer matrices of polypropylene. The output of this program provides the interacting groups in the rotational states of minimum energy. After that, it classifies them in the previously defined distances $d1$, d_2, d_3, d_4. Therefore, this analysis gives a qualitative description of which groups produce the steric interactions of each of the transfer matrices. Before explaining the meaning of each parameter, the reference state is set when at distance d_1 there is a steric interaction between two chains and at distance d_2 there is a steric interaction between a chain and a methyl group. As there are 6 types of adjacent chiral centers, the previous described interactions are found in different positions of the transfer matrices defining bond A and bond B. The Boltzmann parameter η represents the first neighbours interactions when there are both chains at distance d_2 (*trans* position), and there are a chain and a methyl group at d_1(*gauche* position)(see rotational state $u_t t$ Appendix A Fig.(a) , Fig.5). The Boltzmann parameter τ represents the first neighbours interactions when there are both chains at distance d_1 (gauche position) and there are a chain and a methyl group at distance d_1 (gauche position)(see rotational state u_{tg+} Appendix A Fig.(a) . The Boltzmann parameter ω_{3cc} is given by sterical interactions of the chain substituents at distance d_3. The Boltzmann parameter ω_{3cr} is given by sterical interactions of the chain and the side group at distance d3. The Boltzamnn parameter ω_{3rr} is given by the sterical interaction of both substituents at distance d_3.As the interactions given by the distance 4 (d_4) almost do not contribute to the sterical interaction of each of the parameters, they have been neglected. Because at (d_4) the groups are pointing in opposite directions, therefore their sterical interaction is minimal. (see Fig.(4)). As a result, the transfer matrices that are used for calculating the partition functions of isotactic polypropylene, syndiotactic polypropylene and atactic polypropylene are given by :

$$\boldsymbol{T}_d = \begin{pmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega_{3cr} \\ \eta & \omega_{3cc} & \tau \end{pmatrix} \tag{15}$$

$$\boldsymbol{T}_l = \begin{pmatrix} \eta & \tau & 1 \\ \eta & \tau & \omega_{3cc} \\ \eta & \tau\omega_{3cc} & 1 \end{pmatrix} \tag{16}$$

$$\boldsymbol{T}_{dd} \begin{pmatrix} \eta\omega_{3rr} & \tau\omega_{3cr} & 1 \\ \eta & \tau\omega_{3cr} & \omega_{3cc} \\ \eta\omega_{3cr} & \tau\omega_{3cc}\omega_{3cr} & \omega_{3cr} \end{pmatrix} \tag{17}$$

$$\boldsymbol{T}_{ll} = \begin{pmatrix} \eta\omega_{3rr} & 1 & \tau\omega_{3cr} \\ \eta\omega_{3cr} & \omega_{3cr} & \tau\omega_{3cc}\omega_{3rr} \\ \eta & \omega_{3cc} & \tau\omega_{3cr} \end{pmatrix} \tag{18}$$

$$\boldsymbol{T}_{dl} = \begin{pmatrix} \eta & \tau\omega_{3rr} & \omega_{3rc} \\ \eta\omega_{3rr} & \tau\omega_{3rc}^2 & \omega_{3cc} \\ \eta\omega_{3rc} & \tau\omega_{3cc} & 1 \end{pmatrix} \tag{19}$$

$$\boldsymbol{T}_{ld} = \begin{pmatrix} \eta & \tau\omega_{3rr} & \omega_{3rc} \\ \eta\omega_{3rr} & \tau\omega_{3rc}^2 & \omega_{3cc} \\ \eta\omega_{3rc} & \tau\omega_{3cc} & 1 \end{pmatrix} \tag{20}$$

The qualitative analysis given by Flory [1] in the case of polypropylene chains is consonant with the results obtained in our analysis. However, the fact that the second neighbours have been clearly identified (see groups at distances d_3 appendix A) permits to classify the ω factors by the name of the interacting substituents.

B. Calculation of Boltzmann factors for Polypropylene

In order to compute the values for the interacting parameters defined in the previous section, two different model molecules has been chosen. The free energy of each rotational state of the model molecules has been substracted from the free energy of the reference state, previously defined. Then, setting the difference of energy equal to the quantum calculations obtained using the RIS model it possible to calculate the value of the parameters. The Equations system that calculate these parameters are in Appendix (B) and the Table 1 gives the values of the parameters that have been obtained regarding each of the transfer matrices Eq.(15)-Eq.(20).

Parameters	η	τ	ω_{3cc}	ω_{3cr}	ω_{3rr}
d	1.33	0.558	0.0957	-	-
l	1.33	0.558	0.0957	-	-
dd	1.33	0.558	0.284	0.0403	0.0558
ll	1.33	0.558	0.284	0.0403	0.0558
ld	1.33	0.558	0.0783	0.171	0.0377
dl	1.33	0.558	0.0783	0.171	0.0377

TABLE I: The value of the parameters obtained given in the transfer matrices for Eq.(15)-Eq.(20)

The first neighbours parameters are the same for all the transfer matrices. The second neighbours parameters obtained in table 1, present different values depending on the adjacent stereochemical centers. One reason could be that they are involving in an effective way different types of interactions. Furthermore, the sterical interaction ω_{3cr} and ω_{3rr} from the transfer matrices d and l do not exist.

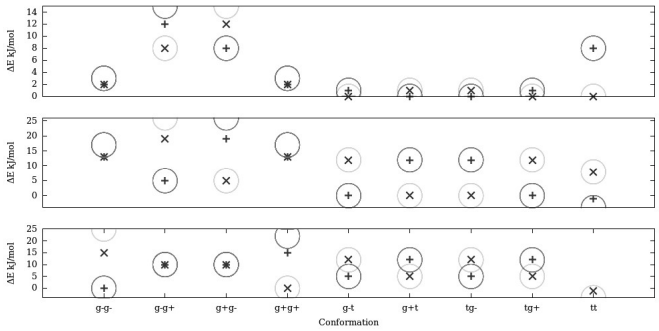

FIG. 9: the free energy computed by means of the parameters of interaction(crosses) and the energy computed by means of quantum calculations is done(circles). In the plot from the top, green circles and magenta circles respectively represent d and l stereochemistry. In the plot from the middle, green and magenta circles respectively represent dd and ll stereochemistry . The bottom plot, the green and magenta circles respectively represent dl and ld stereochemistry .

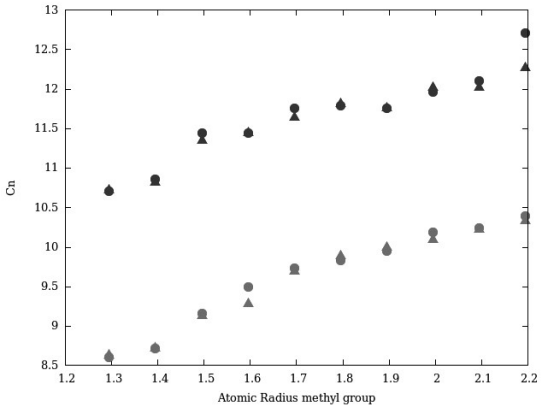

FIG. 10: This plot shows the variation of the characteristic ratio in function of the atomic radius of the methyl group. For Isotactic polypropylene, the red triangles and circles respectively represent the contribution of only the atomic radius of methyl group and the contribution of the atomic radii of methylene and methyl group. For syndiotactic blue triangles and circles respectively represent the contribution the atomic radius of only the methyl group and the contribution of the atomic radii of methylene and methyl group.

In order to prove that these parameters properly reproduce the free energy computed for the dyads shown in Fig.(1), a comparison of the energy computed by the parameters and the energy computed by quantum calculations (section (3b)) is done in Fig.(9).

It is observed that the energies with minor value computed using the parameters agree with the energy computed using quantum calculations. Whereas, the energies with higher value are somehow underestimated. The parameters with higher energy represent statistical weights close to zero, therefore, their contribution still have a similar value. However, since the conformations with higher energy have a small statistical weight this energetic difference can be considered negligible.

C. Monte Carlo simulations

In order to study the effect of the atomic radius in the characteristic ratio(Eq.(14)). Monte Carlo simulation have been performed varying the radii of methylene and methyl groups and only varying the radius of the methyl group. As it is observed in Fig.(10) syndiotactic polypropylene (blue circles and triangles) shows greater value of the ratio characteristic than isotactic polypropylene (red circles and triangles). As it is expected, as the atomic radius of methyl group increases, the number of folded states is reduced, therefore the end-to-end distance of the polymer increases and consequently its characteristic ratio. As a result, it is obtained that the main contribution of the excluded volume effect to the characteristic ratio is due to the methyl group (greatest atomic radius).

Before, studying the characteristic ratio in function of the number of bonds, the atomic radius of both methylene and methyl groups has been measured using Avogadro [12]. The distance between the carbon atom of the backbone of the polymer to the hydrogen atom has been chosen as the atomic radius of methylene.The distance between the carbon atom of the backbone of the polymer and the hydrogen atom of the methyl group has been chosen as its atomic radius. The values of atomic radii for methylene and methyl groups are 2.195 Å and 1.095 Å respectively. In Fig.(11) the representation of the characteristic ratio in function of the number of bonds shows syndiotactic polypropylene (blue squares) obtains higher values than isotactic polypropylene (red squares) considering only short range interactions. Adding excluded volume effects to isotactic (red triangles) and syndiotactic

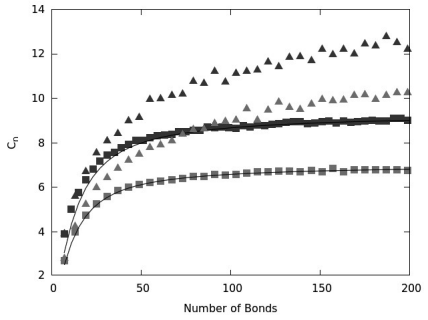

FIG. 11: This graphic shows the dependence of the characteristic ratio in function of the number of atoms for isotactic (red squares) polypropylene and syndiotactic (blue squares) polypropylene. Moreover it compares the effect of the excluded volume on the characteristic ratio for isotactic (red triangles) and syndiotactic (blue triangles) polypropylene. Finally it shows that Monte Carlo simulations give the same results as analytic RIS model calculations for isotactic and syndiotactic (solid black line).

(blue triangles) the ratio characteristic for syndiotactic also is higher than isotactic.

It is important to note that if we obtain the characteristic ratio using the analytical expression of RIS model without excluded volume, this agrees with the Monte Carlo simulations made by isotactic (red squares) and syndiotactic polypropylene (blue squares) Fig.(11). Finally, the solid black line denotes the analytical calculation of RIS model for isotactic polypropylene and syndiotactic polypropylene. Therefore it denotes that the Monte Carlo simulations are perfectly suitable for reproducing polypropylene properties using RIS model.

The results obtained from Monte Carlo simulations show how the tacticity effect changes the structural properties of polypropylene. Furthermore, the results obtained for isotactic polypropylene (red squares) can be compared with the experimental results given by Nakajima .et.al [3] (see section 3B). From the experimental for isotactic polypropylene the $C_n = 5.93$ while in Monte Carlo simulations only considering short range interactions it is obtained a $C_n = 6.7$(red squares). The experimental value is close to the value of short range interactions because in the Flory temperature in the limit of an infinite polymeric chain the excluded volume effect is negligible. But this effect is important when it is considered a dilute polymeric solution and the effect increases as the concentration of polymer decreases[14]. Therefore, the excluded volume effect using a hard sphere potential overestimates the value of C_n for isotactic polypropylene. In [3] there are no results for syndiotactic polypropylene. The same tendency is observed using experimental techniques [5] but using a different solvent and temperature.

V. CONCLUSIONS

The program developed to understand the sterical interactions between groups, has settled a methodology to classify and understand the main interactions for each conformational state and stereochemistry.This allowed to define the minimal needed parameters to construct the transfer matrices necessary to use RIS model in PP. A new methodology to estimate the value of the parameters from quantum calculations have been prepared.The agreement of the energies computed using the obtained parameters and the energies calculated quantum mechanically prove that these parameters can reproduce the local interactions of polypropylene. The results obtained regarding the Monte Carlo simulations show that tacticity effect changes the characteristic ratio of polypropylene and therefore it cannot be neglected. For the case of isotactic ($C_n = 6.77$) polypropylene, the number of folded conformations is greater than syndiotactic ($C_n = 9.01$) polypropylene. As it is expected, Monte Carlo simulations (blue and red squares) fulfill the calculations of the theoretical RIS model (black solid line). Moreover, excluded volume interactions reduce the number of folded conformations, incrementing the characteristic ratio of both isotactic and syndiotactic polypropylene. Focusing on the excluded volume effect, it is observed from the results of that the characteristic ratio mainly depends on the methyl group (greatest value of atomic radius 2.195 Å).

VI. APPENDIX

A. Classification of interactions

In this section it is shown the output of the program that classifies the sterical interactions between groups given the type of bond A and bond B in the Fig.(4). The Model molecules that have been used for reproducing the different interactions of bonds A and B have been drawn in the same output.

```
Starting Configuration ---> tt rotational state

 a) d·d

  R H R
C-|-|-|-C -------> Polypropylene (tt rotational state)
  H H H

 C R  tt  d1     C R  tg+ d1     C C  tg- d1
 C C  tt  d2     C C  tg+ d1     C R  tg- d2
 R R  tt  d3     R C  tg+ d3     R C  tg- d4
                 R R  tg+ d4

 C R  g+t d1     C R  g+g+ d1    C C  g+g- d1
 C C  g+t d2     C C  g+g+ d1    C R  g+g- d2
 C R  g+t d3     C C  g+g+ d3    R C  g+g- d3
 R R  g+t d4     R R  g+g+ d3    C C  g+g- d4
                 R C  g+g+ d4
                 C R  g+g+ d4

 C R  g-t d1     C R  g-g+ d1    C C  g-g- d1
 C C  g-t d2     C C  g-g+ d1    C R  g-g- d2
 C R  g-t d4     C R  g-g+ d3    C C  g-g- d3
                 C C  g-g+ d4



b) l·l

  H H H
C-|-|-|-C -------> Polypropylene ( tt rotational state)
  R H R

 C R  tt  d1     C C  tg+ d1     C C  tg- d1
 C C  tt  d2     C R  tg+ d2     C R  tg- d1
 R R  tt  d3     R C  tg+ d4     R C  tg- d3
                                 R R  tg- d4

 C R  g+t d1     C C  g+g+ d1    C C  g+g- d1
 C C  g+t d2     C R  g+g+ d2    C R  g+g- d1
 C R  g+t d4     C C  g+g+ d3    C R  g+g- d3
                                 C C  g+g- d4

 C R  g-t d1     C C  g-g+ d1    C C  g-g- d1
 C C  g-t d2     C R  g-g+ d2    C R  g-g- d1
 C R  g-t d3     R C  g-g+ d3    R R  g-g- d3
 R R  g-t d4     C C  g-g+ d4    C C  g-g- d3
                                 C R  g-g- d4
                                 R C  g-g- d4
```

c) d·l

```
  R H H
C-|-|-|-C -------> Polypropylene (tt rotational state)
  H H R
```

C R tt d1	C C tg+ d1	C C tg- d1
C C tt d2	C R tg+ d2	C R tg- d1
R R tt d4	R C tg+ d3	R R tg- d3
		R C tg- d4
C R g+t d1	C C g+g+ d1	C C g+g- d1
C C g+t d2	C R g+g+ d2	C R g+g- d1
R R g+t d3	C C g+g+ d3	C R g+g- d3
C R g+t d4	R C g+g+ d4	R C g+g- d3
		R R g+g- d4
		C C g+g- d4
C R g-t d1	C C g-g+ d1	C C g-g- d1
C C g-t d2	C R g-g+ d2	C R g-g- d1
C R g-t d3	C C g-g+ d4	C C g-g- d3
		C R g-g- d4

d) l·d

```
  H H R
C-|-|-|-C -------> Polypropylene (tt rotational state)
  R H H
```

C R tt d1	C R tg+ d1	C C tg- d1
C C tt d2	C C tg+ d1	C R tg- d2
R R tt d4	R R tg+ d3	R C tg- d3
	R C tg+ d4	
C R g+t d1	C R g+g+ d1	C C g+g- d1
C C g+t d2	C C g+g+ d1	C R g+g- d2
C R g+t d3	C C g+g+ d3	C C g+g- d4
	C R g+g+ d4	
C R g-t d1	C R g-g+ d1	C C g-g- d1
C C g-t d2	C C g-g+ d1	C R g-g- d2
R R g-t d3	R C g-g+ d3	C C g-g- d3
C R g-t d4	C R g-g+ d3	R C g-g- d4
	C C g-g+ d4	
	R R g-g+ d4	

e) ·d·

```
  H R H
C-|-|-|-C -------> Polypropylene (tt rotational state)
  H H H
```

R C tt d1	C C tg+ d1	C C tg- d1
C C tt d2	R C tg+ d1	R C tg- d2
R C g+t d1	C C g+g+ d1	C C g+g- d1
C C g+t d2	R C g+g+ d1	R C g+g- d2
	C C g+g+ d3	C C g+g- d4
R C g-t d1	C C g-g+ d1	C C g-g- d1
C C g-t d2	R C g-g+ d1	R C g-g- d2
	C C g-g+ d4	C C g-g- d3

f) ·l·

```
  H H H
C-|-|-|-C -------> Polypropylene (tt rotational state)
  H R H
```

R C tt d1	C C tg+ d1	C C tg- d1
C C tt d2	R C tg+ d2	R C tg- d1
R C g+t d1	C C g+g+ d1	C C g+g- d1
C C g+t d2	R C g+g+ d2	R C g+g- d1
	C C g+g+ d3	C C g+g- d4
R C g-t d1	C C g-g+ d1	C C g-g- d1
C C g-t d2	R C g-g+ d2	R C g-g- d1
	C C g-g+ d4	C C g-g- d3

FIG. 12: The title of each subsection is referred to the stereochemistry of the model molecule. Following the title there is a fischer representation of the model molecule in the trans trans rotational state. Each matrix element contains the steric interactions between groups, the rotational state and the distance between groups. Where R and C are describing the methyl group and chain respectively.

B. Calculation of parameters

This subsection shows the set of equations that have been used for calculating the parameters of all the transfer matrices. Model structure: 4(d)-methylheptane

$$E(\eta) = \Delta E_{11} \tag{21}$$

$$E(\tau) = \Delta E_{12} + E(\eta) \tag{22}$$

$$E(\omega_{3cc}) = \Delta E_{32} - E(\eta) \tag{23}$$

The interactions ω_{3cr} and ω_{3rr} does not exist in the rotational states of this structure as can be seen in appendix 1a).

Model structure: 4(l)-methylheptane

$$E(\eta) = \Delta E_{11} \tag{24}$$

$$E(\tau) = \Delta E_{12} \tag{25}$$

$$E(\omega_{3cc}) = \Delta E_{23} + E(\eta) \tag{26}$$

The interactions ω_{3cr} and ω_{3rr} does not exist in the rotational states of this structure as can be seen in appendix 1a).

Model structure: 2(d),5(d)-dimethylheptane

The nearest neighbours parameters $E(\eta)$ $E(\tau)$ are obtained and averaged from the structures 4(d)-methylheptane, 4(l)-methylheptane.

$$E(\omega_{3cc}) = \Delta E_{23} + E(\eta) \tag{27}$$

$$E(\omega_{3cr}) = \Delta E_{22} - E(\tau) + E(\eta) \tag{28}$$

$$E(\omega_{3rr}) = \Delta E_{11} - E(\eta) \tag{29}$$

The interactions ω_{3cr} and ω_{3rr} does not exist in the rotational states of this structure as can be seen in appendix 1a).

Model structure: 2(l),5(l)-dimethylheptane

The nearest neighbours parameters $E(\eta)$ $E(\tau)$ are obtained and averaged from the structures 4(d)-methylheptane, 4(l)-methylheptane.

$$E(\omega_{3cc}) = \Delta E_{32} + E(\eta) \tag{30}$$

$$E(\omega_{3cr}) = \Delta E_{13} - E(\tau) \tag{31}$$

$$E(\omega_{3rr}) = \Delta E_{11} - E(\eta) \tag{32}$$

Model structure: 2(d),5(l)-dimethylheptane

The nearest neighbours parameters $E(\eta)$ $E(\tau)$ are obtained and averaged from the structures 4(d)-methylheptane, 4(l)-methylheptane.

$$E(\omega_{3cc}) = \Delta E_{23} - E(\tau) \tag{33}$$

$$E(\omega_{3cr}) = \Delta E_{21} - E(\eta) \tag{34}$$

$$E(\omega_{3rr}) = \Delta E_{32} - E(\eta) - E(\tau) \tag{35}$$

Model structure: 2(l),5(d)-dimethylheptane

The nearest neighbours parameters $E(\eta)$ $E(\tau)$ are obtained and averaged from the structures 4(d)-methylheptane, 4(l)-methylheptane.

$$E(\omega_{3cc}) = \Delta E_{23} - E(\tau) \tag{36}$$

$$E(\omega_{3cr}) = \Delta E_{31} - E(\eta) \tag{37}$$

$$E(\omega_{3rr}) = \Delta E_{21} - E(\eta) - E(\tau) \tag{38}$$

VII. ACKNOWLEDGEMENTS

I would like to thank Pablo M. Blanco, Dr. Sergio Madurga and Dr. Francesc Mas for their dedication and support to help me to understand the most in the matter of investigation.

Finally, I want to thank my family, my closest friends and especially Anna Bosch, Raul Santiago, Oriol Piqué, Martí Lopez and Lorena Vega for encouraging me in the most difficult moments of the master.

This thesis could not have been accomplished without all of you.

VIII. BIBLIOGRAPHY

[1] Flory, P.L. *Statistical Mechanics of Chain Molecules*; John Wiley: New York, (1969).

[2] Asakura, T.; Ando, I. and Nishioka A. "Calculation of the Characteristic Ratio of Polypropylene Containing Chemical Inversions (Head-to-Head and Tail-to-Tail Units)". Makronzol. Cliem. **177**: 1493-1500 (1976)

[3] Nakajima, A. and Saijyo, A. "Unperturbed Chain Dimensions of Isotactic Polypropylene in Theta Solvents". J. Polym. Sci. A **6**: 735-744 (1968).

[4] Bloqmvist, J.; Pietila, L-O. and Mannfors B. "RIS Metropolis Monte Carlo studies of some aliphatic main chain and side group polyesters". Polymer **42**: 109116 (2001)

[5] Madkour, T.M and Soldera, A."Tacticity induced molecular microstructure dependence of the configurational properties of metallocene-synthesized". Eur. Polym. J.**37**: 1105-1113 (2001).

[6] Huimin, S. and Langmui, X. "An Introduction of Structure, Synthesis and Safety Concerning Polypropylene Applications".Nova Science Publisher (2013).

[7] Cowie, J.M.G; Arrighi V.Polymers: *Chemistry and Physics of Modern material*. 3rd ed. CRC press, (2007)

[8] Madkour, T. M.; Goderis, B.; Mathot, V.B.F. and Reynaers, H. "Influence of chain microstructure on the conformational behavior of ethylene-1-olefin copolymers. Impact of the comonomeric mole content and the catalytic inversion ratio." Polymer **43** (2002) 2897-2908

[9] Borkovec, M. and Koper, G. "Binding of Metal Ions to Polyelectrolytes and Their Oligomeric Counterprts: An Application of a Generalized Potts Model". *J.Phys.Chem* **105**: 6666-6674 (2001)

[10] Garcés, J.L; Madurga, S. and Borkovec, M. "M.Coupling of conformational and ionization equlibria in linear poly(ethylenimine): A study based on site binding/ rotational isomeric state (SBRIS) model". *Phys. Chem. Chem. Phys.*: **16**, 4626-4638 (2014).

[11] Blanco, P.M.; Madurga, S.; Mas, F.; Garcés, J.L. "Coupling of Charge Regulation and Conformational Equilibria in Linear Weak Polyelectrolytes: Treatment of Long Range Interactions via Effective Short-Ranged and pH-Dependent Interaction Parameters". Preprints 2018060300, (2018).

[12] Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E. and Hutchison, G. R.; Avogadro: An advanced semantic chemical editor, visualization, and analysis platform J. Cheminformatics (2012), 4:17.

[13] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W. and Schlegel, H. B.;*et. al.*; Gaussian, Inc., Wallingford CT, 2013.

[14] Zubiaga, H.A.*Macromolculas*; GREFOL,S.A: Madrid (1982)