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FPolymer: A Program for 3D Structure Generation and OPLS Topology of Polymers with High Molecular Mass

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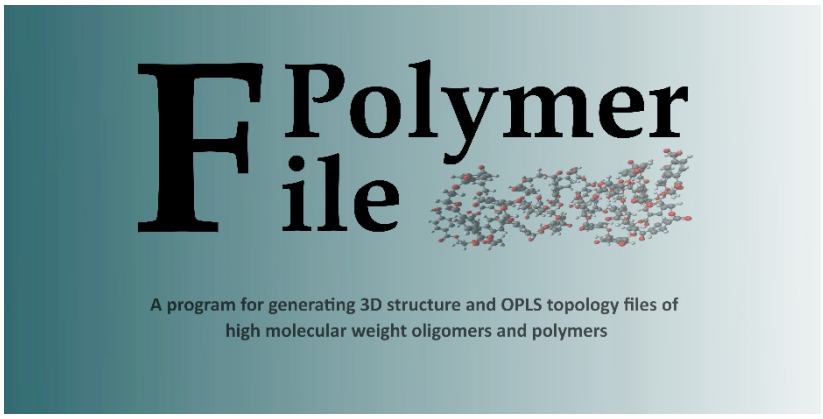
The need to study polymeric systems with high molecular masses by techniques such as molecular dynamics using free-use software, coupled with the difficulty of parameterizing such systems, led to the creation of the FPolymer program. This program was built in C++ language using the QT-creator framework and has a simple and intuitive interface. The main function of the program is to use previously parameterized trimers of any polymer to generate a structure with the number of repeating units indicated by the user. As output of the program, the user receives a file <file>.pdb containing the structure of the polymer and a file <file>.top with the topology prepared to perform youngest molecular dynamics in the GROMAS program.

Graphical abstract



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1. Introduction

With the great technological advance and expansion of the processing power of current [1] been presenting high quality and essential results in various areas. Molecular dynamics is a method based on classical mechanics and can be used for the study of large systems being mostly applied to the study of biochemical systems and consequently most force fields are developed for this purpose. Thus, studies of different systems need to be parameterized with the data from the chosen force field and this process is not always easy to be performed as in the case of polymers.

Polymers are the most used materials in the world and possess as one of their main characteristics the high molar mass that is responsible for many of their physical and chemical [2]. For a molecular dynamics study of a polymer to be able to reproduce experimentally obtained properties it is desirable that the number of repeating units be large enough to represent the extent of intermolecular and intramolecular interactions and this generates large molecules that are difficult to be parameterized by manual methods or with free tools.

Fortunately, there is the possibility of developing new programs and tools for automating these processes. The purpose of this article is to present the "FPolymer" a program written using QT/C++ with simple and user-friendly interface

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capable of generating files of polymeric molecule structures with indicated number of mere sums in PDB format and the corresponding topology file for molecular dynamics in the GROMACS [3] the OPLS-AA force field.

2. Material and Methods

For the development of this study and the creation of the FPolymer program, it was necessary to use tools and programming environment as the QT-creator framework in its version 4.14.2. The choice of this environment is linked to the ease of creating applications that can be easily compiled on multiple platforms without significant changes in source code, which facilitates the distribution of the final program.

FPolymer, in its first version, works by providing data previously obtained through the use of other programs such as ACPYPE [4] and MKTOP [5]. Using this software, trimer parameterization is performed, which are fragments of the desired polymers containing three mere scans with their proper terminations. The methodology used for parameterization consists in the creation of the trimer structure in molecular editing programs such as AVOGADRO [6] geometric optimization using classical methods. Also in AVOGADRO, in the extensions menu, an input file can be generated for MOPAC [7] semi-empirical methods such as AM1 [8], PM6 [9], PM7 [10], RM1 [11]. After the molecule has its structure optimized, the procedure described in the ACPYPE and MKTOP documentation is performed to obtain the topology files where the descriptions of each of the atoms within the chosen force field are located.

Data from topologies and structures are transcribed into the FPolymer database. Once the trimer data has been added to the program, you can generate the desired size structure.

The files generated by the program are a structure file in <file>.pdb and a topology file in <file>.top format. With these files it is possible to perform molecular dynamics using GROMACS.

In order to test the program and develop a protocol for the study of polymers by molecular dynamics, simulations were carried out with the polymer poly(ethylene terephthalate) (PET) according to the following protocol:

- Construction of the trimer structure through the AVOGADRO program.
- Parameterization of the trimer using the ACPYPE program.
- Add the trimer data to the program database.
- Creation of the polymer structure using the FPolymer program.
- Using GROMACS, perform creation and a triclinic box.
- Creating an index file.
- Performing a minimization using the Steepest Descent method.
- Minimization using the almost Newton L-BFGS method.
- Perform dynamics in 5ns vacuum.
- Re size the box and make it dodecadic.
- Generate position constraint file
- Solve the system.
- Performing a minimization using the Steepest Descent method with polymer position restriction.
- Performing a minimization using the Steepest Descent method without restriction of polymer position.
- Minimization using the almost Newton L-BFGS method.
- Perform a water dynamic.
- Perform dynamics of the 5n system
- Perform dynamics with heating ramp from 250K to 650K with a heating rate of 10K/ns.
- Use the "gmx energy "tool available in GROMACS to obtain related data on polymer interaction as a function of time.

In addition to comparison with data available in the literature, experimental thermal tests were also performed using Calorimetry and Exploratory Differential (DSC) equipment to obtain parameters of great importance for the polymer industry, they are the vitreous transition (Tg), crystallization temperature (Tc) and melting temperature (Tm) [12–14]. The experiments were carried out in an inert atmosphere with a heating rate of 10°C/min part going from room temperature to 370°C.

3. Results and Discussion

The process of parameterization of small molecules using programs such as ACPYPE and MKTOP has been widely tested and is widely used in recent years in various types of studies conducted in various areas and, therefore, its reliability is quite high. For this reason, the use of parameterized trimers for the generation of larger structures is a viable alternative.

Within the structure of the trimers there are all kinds of atoms that are present in the polymer whatever their size. This is because the polymer is nothing more than the repetition of n times the smallest basic unit that repeats, the so-called mere. Although a single mere can represent a polymer, there is a need to count the atoms that are present in the head and tail of the structure to close the valences leaving the complete structure and for this are represented the three types of structure as shown in Figure 1.

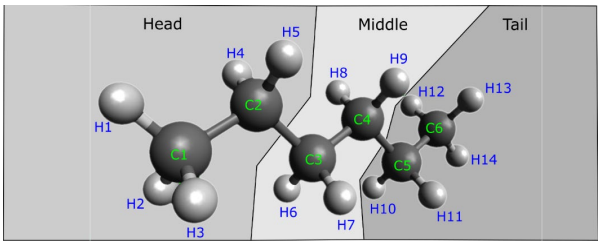

Fig. 1. Representation of a polyethylene trimer with the terminal hydrogens highlighting the structures of the mere heads, medium and tail.

The construction of the structure of a polymer fragment with 4 repeating units from the represented trimer consists of the insertion of the mere head followed by the repetition of the central mere twice added to the mere tail thus forming a structure with four meres. That is, in the case of polyethylene, carbons C3 and C4 and hydrogens H6, H7, H8 and H9 are repeated within the polymer chain without changes to form the structure of the desired size. This occurs with any polymer since one of its main characteristics is the presence of these

repeating units. Thanks to this fact it is possible to use the data generated in the parameterization of the trimers and enlarge to polymers of any size.

Within the topology file, the atoms of the central mere are repeated and renumbered as many times as necessary, and their identifications and parameters are maintained to generate the desired polymer topology. With the coordinate file, something similar occurs, the atoms of the central mere are repeated, and their positions are recalculated to generate the final file in pdb format.

The interface of the program is thought to be easy to usability making it possible to generate the desired files with a few clicks as shown in Figure 2.

The working details as well as all the extant functions of the program may change due to updates and for this reason are described in the documentation provided along with the binaries precompiled for Linux and Windows.

For the purposes of testing the systems generated by the program, calculations using the polymer poly(ethylene terephthalate) were performed. The choice of this polymer is mainly due to the fact that it is among the most used materials in the world and presents three thermal events of great interest for polymer industries. Thus, using the Polymer program, a PET oligomer was constructed with 25 units of repetition, which corresponds to a molar mass of 4800 g·mol^{-1}. Although it is a relatively low mass when it is considered that polymers of commercial interest have a mass exceeding 10000 g·mol^{-1}, the mass used already makes possible the measurement of intramolecular polymer-polymer interaction.

After creation, the oligomer is in linear format and after the minimization steps with subsequent realization of molecular dynamics of 5 ns in the vacuum, the polymer chain is curl. The simulation time for the polymer to reach the state envelop in vacuum may vary depending on the characteristics of the polymer.

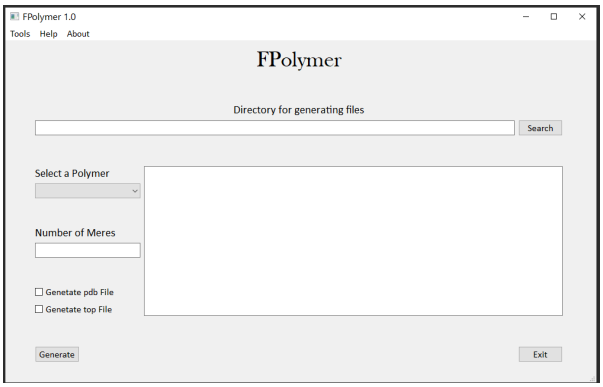

Fig. 2. FPolymer 1.0.0 program interface running on Windows 10.

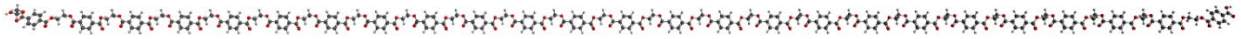

Fig. 3. PET oligomer structure with 25 mers and a total of 262.65 Å in length generated with the FPolymer program.

To verify if the packed structure is in equilibrium, the graph of the variation of the energy of the systems over time is verified, a stable profile suggests the stabilization of the system as shown in Figure 4.

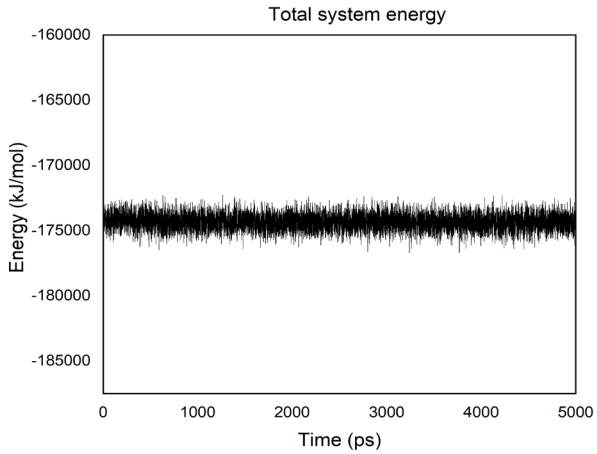

Fig. 3. Graph of system energy over time for PET oligomer dynamics in vacuo.

Energy stabilization indicates that the system structure is balanced and ready for the next step. For the study carried out it was of paramount importance that the polymer was in this state because thus several molecular interactions are established, and their energies can be quantified. Through this energy it is possible to identify some properties of the polymer. The structure obtained is presented in Figure 5.

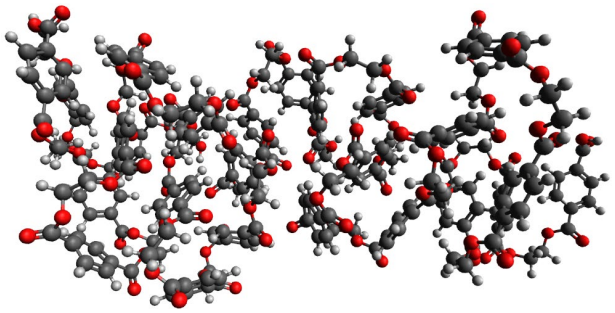

Fig. 4. Structure of the PET oligomer with 25 mere curl after molecular dynamics of 5 ns in the vacuum.

The structure was used for a new sequence of calculations where, this time, it was placed in a water drop and the whole process of minimization was carried out again plus a dynamic of waters and later a loose dynamic of 10 ns to balance the system. From the result of this dynamic, a calculation was performed using the annealing method where a heating rate of 250K to 650K was established over a period of 40 ns which corresponds to 10k/ns controlled by the thermostat of Berendsen. At the end of the dynamics, the polymer-polymer interaction over time was analyzed.

Analyzing the data from the chart we see that and 70°C is observed the first thermal event for PET. In the DSC curve it is possible to notice a change in the baseline of the curve caused by a second-order transition characteristic of the Tg of the polymers. At this same temperature, for the data we have a change in the profile of the curve. At 126°C in the DSC curve is observed at Tc, this event is slightly less clear in the theoretical data and is slightly displaced appearing at 150°C. This variation is acceptable since the process occurs in a

temperature range and the nature of the thermal process to which the material is being subjected beyond the thermal history of the sample. And finally, we see in the DSC curve the melting temperature Tm around 245°C, in the data obtained by molecular dynamics we have this event appearing through the new change of curve profile at 255°C which is also acceptable since the process occurs in a temperature range and not at a single point.

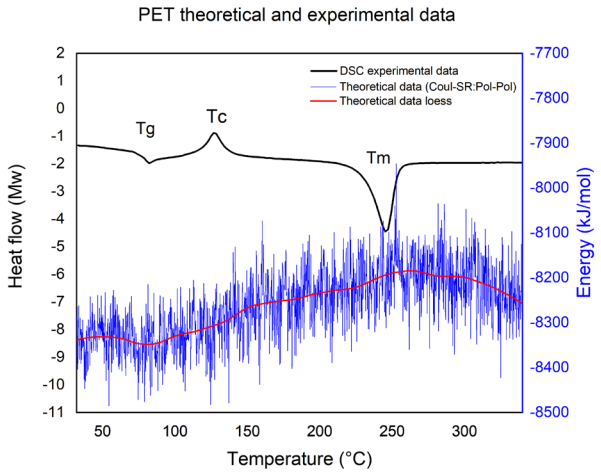

Fig. 5. Graph relating thermal events observed in experimental CSD curve with variation in the curve profile of Coulomb energy variation as a function of temperature obtained through theoretical molecular dynamics data.

The same analysis can be performed using the short-range Lenard-Jones interaction energy as shown in the graph in Figure 7.

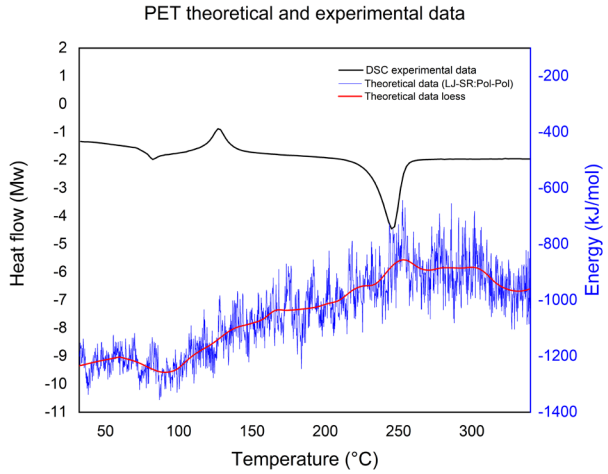

Fig. 7. Graph relating thermal events observed in experimental CSD curve with variation in the profile of the Lenard-Jones energy variation curve as a function of the temperature obtained through theoretical molecular dynamics data.

The relationship between the experimental data and the theoretical data was already expected, as the thermal properties of polymers are related to the existing intramolecular and intermolecular interaction energies. Other parameters that can be obtained from the theoretical data such as Radius of Gyration, Solvent Accessible Area and Pol-Water Hydrogen Bonding can be used to extract information about the thermal behavior of polymers and all these parameters have information, even if indirect, of the interaction between the polymeric chains responsible for their thermal properties. The only care in using this data is that it can be more difficult to identify the desired property because in most cases there is a lot of noise as shown in Figure 8.

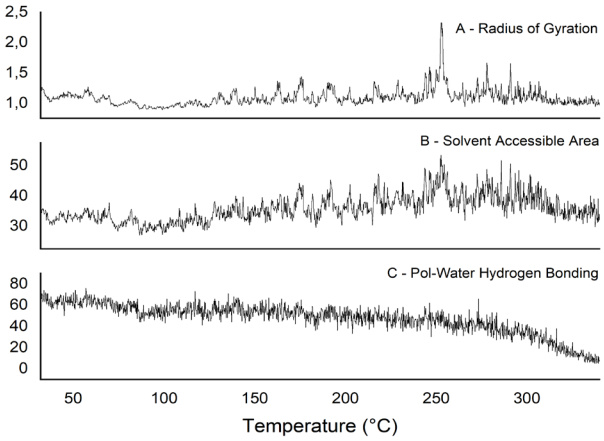

Fig. 8. Radius of Gyration (Figure 8-A), Solvent Accessible Area (Figure 8-B) and Pol-Water Hydrogen Bonding (Figure 8-C) graphs obtained with the molecular dynamics of the PET oligomer.

Another fact to be aware of is that observing the graphs in Figure 8-A and Figure 8-B, it is possible to see a stabilization trend from about 310°C.

The big challenge is to get theoretical data that represents these interactions well, and the first step is to get the ability to create models with the right size easily and quickly. The FPolymer program was created with for this purpose and is promising in creating models for various types of studies. Pre-compiled binary files for all major platforms are available for download from GitHub **https://github.com/FabricioUliana/FPolymer**.

4. Conclusions

The great difficulty of the study of polymeric materials by molecular modeling techniques is the difficulty of constructing models large enough to simulate in a satisfactory way the intermolecular and intramolecular interactions present in the real systems. The FPolymer program was developed to be an alternative to facilitate and enable this process by generating systems with hundreds of mere systems quickly. The program has a user-friendly and easy-to-use graphical interface and allows the insertion of any polymer into your database. In the tests performed with pet polymer interesting results were obtained showing that in addition to FPolymer, the protocol for calculating molecular dynamics presented proved to be quite adequate for the identification of some of the most important thermal properties of the polymers that are Tg, Tc and Tm.

Supporting Information

FPolymer 1.0.0 user manual.

Author Contributions

Fabricio Uliana – Conceptualization, Methodology,

Investigation, Formal analysis, Software. Eloi Alves da Silva Filho – Supervision, Methodology, Conceptualization, Project administration. Arlan da Silva Gonçalves – Methodology, Conceptualization, Formal analysis, Software. Vadilson Malaquias dos Santos - Formal analysis, Methodology. Mateus Uliana – Software, Methodology.

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