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Modelagem estocástica da microestrutura de homopolímeros e copolímeros em reatores batelada

Stochastic modeling of microstructure of homopolymers and copolymers in batch reactor

Modelado estocático de la microestructura de homopolímeros y copolímeros de reactor por lotes

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Resumo

Encontrar a microestrutura do produto gerado numa reação de polimerização é algo desejável do ponto de vista da ciência dos materiais, devido a associação entre a microestrutura e as propriedades físicas. Pela ciência deste fato, esse artigo possui o objetivo de utilizar a modelagem estocástica para obter a microestrutura e as principais informações de um conjunto de cadeias poliméricas geradas durante uma reação. A partir desses dados, o presente artigo contribui com a minimização de despesas experimentais, além da economia de tempo, devido ao fato de não serem necessários experimentos para descobrir as características do polímero obtidado sob determinadas condições de reação. Essas informações não podem ser encontradas por outras metodologias usuais para modelar reações químicas, como a forma determinística. Além disso, a partir de uma dada estrutura desejada, consegue-se obter as condições iniciais de concentração e temperatura para formação daquele produto. Este estudo foi realizado baseado nos métodos estocásticos de Monte Carlo, pelo qual busca-se replicar a aleatoriedade presente nas reações químicas. O algoritmo criado em linguagem C^{++} determina a variação do número de moléculas de cada espécie com o tempo, além da composição química, sequência de monômeros e tamanho das cadeias geradas. Esta abordagem aplica-se para homopolimerizações e copolimerizações de cadeia linear. Neste trabalho foi estudada a polimerização em reatores batelada do estireno para formar o poliestireno, além da copolimerização do estireno com o alfa-metil-estireno. Estas simulação foram caracterizadas por formar cadeias com pequenos blocos de monômeros.

Palavras-chave: Polímeros; Modelagem; Estocástico; Distribuições; Probabilidade.

Abstract

Find the microstructure of the product generated in a reaction of polymerization is desirable from a material science standpoint, due to the association between the microstructure and the physical properties. For the science of this fact, this paper aims to use stochastic modeling to obtain the microstructure and key information from a set of polymer chains generated during a reaction. From this data, the present article contributes to the minimization of experimental expenses, besides the saving of time, since no experiments are necessary to discover the characteristics of the polymer obtained under certain reaction conditions. This information cannot be found by other usual methodologies for modeling chemical reactions, such as the deterministic form. Also, from a given desired structure, the initial concentration and temperature conditions for forming that product can be obtained. This study was conducted based on Monte Carlo stochastic methods, by which we seek to replicate the randomness present in chemical reactions. The algorithm created in C^{++} language determines the variation of the number of molecules of each species with time, besides the chemical composition, the sequence of mere and size of the generated chains. This approach applies to straight-chain homopolymerizations and copolymerizations. In this paper, we studied the polymerization in styrene batch reactors to form polystyrene, in addition to the copolymerization of styrene with alpha-methyl styrene. These simulations were characterized by forming chains with small blocks of monomers.

Keywords: Polymers; Modeling; Stochastic; Distributions; Probability.

Resumen

Encontrar la microestructura del producto generado en una reacción de polimerización es deseable desde el punto de vista de la ciencia de los materiales, debido a la asociación entre la microestructura y las propiedades físicas. Para la ciencia de este hecho, este artículo tiene como objetivo utilizar el modelado estocástico para obtener la microestructura y la información clave de un conjunto de cadenas de polímeros generadas durante una reacción. A partir de estos datos, el presente artículo contribuye a la minimización de los gastos experimentales, además del ahorro de tiempo, debido al hecho de que no son necesarios experimentos para descubrir las características del polímero obtenido bajo ciertas condiciones de reacción. Esta información no puede ser encontrada por otras metodologías usuales para modelar reacciones químicas, como la forma determinista. Además, a partir de una estructura deseada dada, se pueden obtener las condiciones iniciales de concentración y temperatura para formar ese producto. Este estudio se realizó con base en los métodos estocásticos de Monte Carlo, por los cuales buscamos replicar la aleatoriedad presente en las reacciones químicas. El algoritmo creado en lenguaje C $^{++}$ determina la variación del número de moléculas de cada especie con el tiempo, además de la composición química, la secuencia de monomeros y el tamaño de las cadenas generadas. Este enfoque se aplica a las homopolimerizaciones y copolimerizaciones de cadena lineal. En este trabajo, se estudió la polimerización en reactores discontinuos de estireno para formar poliestireno, además de la copolimerización de estireno con alfa-metilestireno. Estas simulaciones se caracterizaron por formar cadenas con pequeños bloques de monómeros.

Palabras clave: Polímeros; Modelado; Estocástico; Distribuciones; Probabilidad.

1. Introduction

Polymers are macromolecules consisting of the covalent bond between smaller structural units called monomers. These units are low molecular weight molecules that bind during the polymerization reaction (Meyer & Keurentjes, 2005).

This paper focuses on radical polymerization reactions since, for this process to take place, the presence of a starting substance and the monomers that will form the polymeric chain is required. The initiator is the substance responsible for breaking down radicals, which in turn triggers the subsequent reactions.

The mechanism of radical polymeric reactions consists of joining up to four basic steps. The first step is called initiation, which involves the decomposition of the initiator in the radicals, as well as the reaction of the latter with the molecules of the monomers present. In this way, the first polymeric chains are formed, which initially have unit size.

The second step is related to propagation, in which the free monomer molecules randomly incorporate the chains already formed in the initiation step, which consequently increase in size (Zhang & Ray, 2001).

The third step of the reaction mechanism is the termination mechanism. This will occur when there is a reaction between the radicals of two polymer chains. In this case, the chains lose their ability to propagate, thus stabilization occurs. Termination reactions can be divided into two basic types: by combination or disproportionate.

Combination termination involves joining two polymeric chains into one, thus forming a new chain with a size equal to the sum of the two generating structures. Disproportionate termination occurs by transferring one radical from one polymer chain to another. Thus, the product has two inactive chains (Araujo & Pinto, 2013).

A fourth step will occur in the system if another compound is added to the process, a substance known as a capture agent. This agent is intended to decrease the number of active polymer chains available. Consequently, there is a slowdown in the propagation reaction, but termination reactions are also rarer. This capture step must be reversible, so the structure is only temporarily inactive.

To develop this research, we opted for stochastic modeling, which has its advantages over deterministic methodology, especially when it comes to polymers or media with a small number of molecules. In traditional modeling of chemical reactions, a system of differential equations develops, with each equation representing the change in concentration of each chemical species over time. However, when it comes to studying polymers, the number of distinct species involved tends to infinity, because each chain has its particular size and sequence of monomers. Therefore, a system of gigantic size coupled ordinary differential equations would be necessary, which cannot be solved even with the help of the best computers (Lemos, Melo, & Pinto, 2015).

This paper aims to characterize polymeric chains through probability distribution functions of the most relevant properties, such as chain size, blocks and chemical composition. Thus, the average values of each of these properties are obtained, as well as the variation in the number of molecules in the reactor over time. Thus, this study tends to make waste of time and reagents unnecessary to find polymers with the desired properties for a given application, because it finds the information necessary to obtain a predefined product.

Thus, the algorithm helps materials science, something that could not be obtained deterministically, due to the complexity of the studied environment, proving to be a great advance for this field.

2. Methodology

The development of this project starts with the implementation of C $^{++}$ algorithms based on random number generation (Fluendy, 1970). In these codes were developed data storage systems for the chains generated, information that, in turn, is transformed into text files.

The implementation of the algorithms is based on the Gillespie method (Gillespie, 1976), applied to batch reactors, considering the perfect mixture and isothermal. Firstly, algorithms for linear chain homopolymerizations are developed. Shortly thereafter these are generalized so that they can achieve copolymers.

2.1 Free radical homopolymerization

Radical homopolymerization is a single species polymerization mechanism in which the formation of chains is due to the presence of radicals in the medium. Since only linear chains will be generated in this section, chain size will be the only variable that will influence polymer properties. When homopolymerization proceeds freely, the process is usually rapid, due to the high chance of termination reactions occurring, since no capture agent is used in this case.

This type of polymerization can be defined by three steps: initiation, propagation, and termination, with disproportionate termination being applied here. The reaction steps are expressed in table 1:

Table 1- Reactive steps of free radical homopolymerization.

Stage	Kinetic mechanism	Kinetic constant
Initiation	$I \longrightarrow 2R$	$k_1 = 10^{-4}\ s^{-1}$
	$R+M \longrightarrow P_1$	$k_2 = 10^2\ l \cdot mol^{-1} \cdot s^{-1}$
Propagation	$P_i+M \longrightarrow P_{i+1}$	$k_3 = 10^2\ l \cdot mol^{-1} \cdot s^{-1}$

Termination	$P_i+P_j \longrightarrow L_i+L_j$	$k_4 = 10^6$ l·mol^{-1}·s^{-1}

Source: Meyer & Keurentjes (2005).

In table 1, R as radical, M as a monomer, P_i is an active polymeric chain of size i, while L_i is an inactive chain of size i. The kinetic constants are represented by the letter k, and the subindex is the number of each equation. In this type of polymerization, there are only two types of chains, which are termed as "living" or "dead". Living chains are those that can still undergo a propagation reaction, while dead ones are chains that have already undergone the termination reaction, so they cannot react with any monomer. To represent these two types of chains in the Dev C $^{++}$ program, two vectors were created: one for living chains and one for dead chains. As a representation methodology, P was defined as the vector that represents the living chains and L the vector that represents the dead chains. Regarding the operating conditions of the system, the temperature was set at 383 K, the volume at 10^{-18} l and a residence time of 100,000 seconds. Initially, the reactor had 6,020 initiator molecules and 6,020,000 monomer molecules.

2.2 Controlled radical homopolymerization

The basic difference between free and controlled radical homopolymerization is that in the controlled reaction there is the addition of a compound known as a capture agent. This has the function of forming a third type of chain, which in this paper will be named as "dormant". The name alludes to a chain that is neither dead nor alive so that it cannot propagate and cannot be terminated. However, as previously reported, this is a transient state. The formation of this new type of chain is intended to reduce the number of live chains available in the reaction medium, leading to a reduction in the number of dead chains generated, since the latter amount is proportional to the square of the number of live chains available in the system. Table 2 presents possible reactions in this system.

The nomenclature used in table 2 is similar to that used in table 1. It is worth mentioning the presence of two new symbols, one of them being X, this one represents the capture agent. And the other is compound Di, which represents a dormant chain of size i.

One change made from the previous algorithm is that in the termination step there is a combination of chains. Thus, when two chains react, the result will be a chain that is equal to the sum of the size of the reactant chains. This information, in turn, must be stored in a single element of the L vector.

Table 2- Reaction steps of controlled radical homopolymerization.

Step	Kinect mechanism	Kinetic constant
Initiation	$I \longrightarrow 2\mathrm{R}$	$k_1 = 1.370\cdot10^{-2}\ \mathrm{s}^{-1}$
	$R+M\longrightarrow P_1$	$k_2 = 1.596\cdot10^{3}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$
Propagation	$P_i+M\longrightarrow P_{i+1}$	$k_3 = 1.596\cdot10^{3}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$
Capture	$P_i+X\longrightarrow D_i$	$k_4 = 3.808\cdot10^{7}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$
	$P_i+\mathrm{X}\longleftarrow D_i$	$k_5 = 3.404\cdot10^{-4}\ \mathrm{s}^{-1}$
Termination	$P_i+P_j\longrightarrow L_{i+\mathrm{j}}$	$k_6 = 9{,}679\cdot10^{4}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$

Source: (Zhang & Ray, 2001).

This polymerization system involves the formation of polystyrene from N-oxyl-2,2,6,6-tetramethyl piperidine (TEMPO nitride) as a capture agent. For operating conditions, a temperature of 383 K, a volume of 10^{-17} l and a residence time of 800 seconds were set. Initially, the medium had 1,023 initiator molecules, 2,107 capture agents and 4,286,240 monomers.

Note that the amount of capture agents is approximate twice the number of initiators, this is due to the need to include an amount of nitroxide equal to the maximum number of radicals that can be generated. Thus, an equilibrium tends to be established, so that there is no lack or excess of nitroxide about the number of chains formed, avoiding efficient terminations.

2.3 Controlled radical copolymerization

To develop the copolymerization algorithm, a more robust program was created, to which several other reactions were added, as well as a different way of allocating the data of interest of the chains.

The number of reactions of this process increased mainly due to the presence of a second monomer, with several combinations for the propagation reaction. Table 3 presents the possible reactions for copolymerization:

Table 3- Reactive steps of controlled radical copolymerization.

Step	Kinect mechanism	Kinect constant
Initiation	$I \longrightarrow 2R$	$k_1 = 1.443\cdot10^{-1}\ s^{-1}$
	$R+M_1 \longrightarrow P_{1,0}$	$k_2 = 4.340\cdot10^{-2}\ l\cdot mol^{-1}\cdot s^{-1}$
	$R+M_2 \longrightarrow Q_{0,1}$	$k_3 = 2.547\cdot10^{1}\ l\cdot mol^{-1}\cdot s^{-1}$
Propagation	$P_{i,j}+M_1 \longrightarrow P_{i+1,j}$	$k_4 = 4.340\cdot10^{-2}\ l\cdot mol^{-1}\cdot s^{-1}$
	$P_{i,j}+M_2 \longrightarrow Q_{i,j+1}$	$k_5 = 1.659\cdot10^{-1}\ l\cdot mol^{-1}\cdot s^{-1}$
	$Q_{i,j}+M_1 \longrightarrow P_{i+1,j}$	$k_6 = 1.255\cdot10^{2}\ l\cdot mol^{-1}\cdot s^{-1}$
	$Q_{i,j}+M_2 \longrightarrow Q_{i,j+1}$	$k_7 = 2.547\cdot10^{1}\ l\cdot mol^{-1}\cdot s^{-1}$
Capture	$P_{i,j}+X \longrightarrow Z_{i,j}$	$k_8 = 3.799\cdot10^{1}\ l\cdot mol^{-1}\cdot s^{-1}$
	$P_{i,j}+X \longleftarrow Z_{i,j}$	$k_9 = 2.500\cdot10^{-3}\ s^{-1}$
	$Q_{i,j}+X \longrightarrow W_{i,j}$	$k_{10} = 2.290\cdot10^{-6}\ l\cdot mol^{-1}\cdot s^{-1}$
	$Q_{i,j}+X \longleftarrow W_{i,j}$	$k_{11} = 2.500\cdot10^{-3}\ s^{-1}$
Termiantion	$P_{i,j}+P_{m,n} \longrightarrow L_{i+m,j+n}$	$k_{12} = 4.074\cdot10^{1}\ l\cdot mol^{-1}\cdot s^{-1}$
	$Q_{i,j}+Q_{m,n} \longrightarrow L_{i+m,j+n}$	$k_{13} = 1.300\cdot10^{-5}\ l\cdot mol^{-1}\cdot s^{-1}$
	$P_{i,j}+Q_{m,n} \longrightarrow L_{i+m,j+n}$	$k_{14} = 2.300\cdot10^{-3}\ l\cdot mol^{-1}\cdot s^{-1}$

Source: Araújo & Pinto (2013).

The nomenclature used in table 3 is similar to that used in tables 1 and 2. However, it is noteworthy that the notation $P_{i,j}$ represents a chain that ends with the type 1 monomer, and which has i type 1 monomer and j type 2 monomers. This same reasoning extends to the other chains.

This reaction system refers to the styrene polymerization with alpha-methyl styrene, initiated with benzoyl peroxide (BPO) and uses TEMPO nitride as a capture agent. The temperature of the system was set at 408 K, volume 10^{-19} l and residence time 500,000 seconds. Initially, the medium had 103 initiator molecules, 212 capture agent molecules, 428,624 styrene molecules, and 92,798 alpha-methyl styrene molecules.

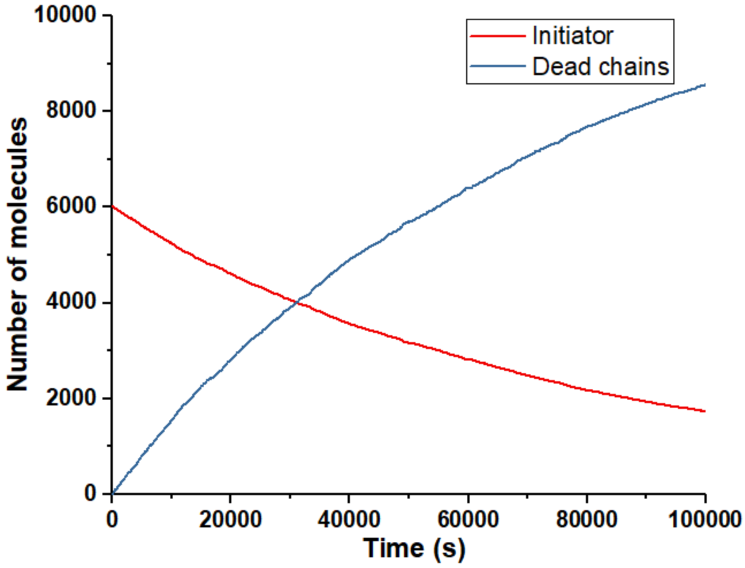
3. Results and Discussions

This section presents all the graphs obtained during modeling. These condense the information about the generated polymer chains.

3.1 Free radical homopolymerization

To define the composition of the reactor at all times, Figure 1 shows the variation in the number of initiators and dead chains over time.

Figure 1: Variation in the number of initiators and dead chains in the medium over time.

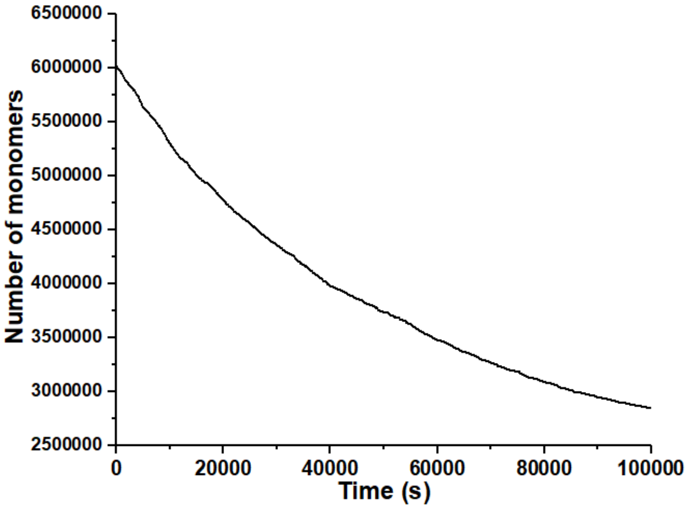


Source: Authors.

Figure 1 it is noticeable that the concentration of initiator molecules tends to decay over time. This fact was already expected due to the lack of replacement of these molecules in the system and their constant consumption. On the other hand, the number of dead chains is increasing and appreciable. This is due to the small number of living chains in the system, they do not appear on this scale, so it is possible to see that the chains are formed and then undergo a termination. Thus, the final product will have a small size polymeric structure.

To complete the information shown in Figure 1, Figure 2 shows the variation in the number of monomers over time.

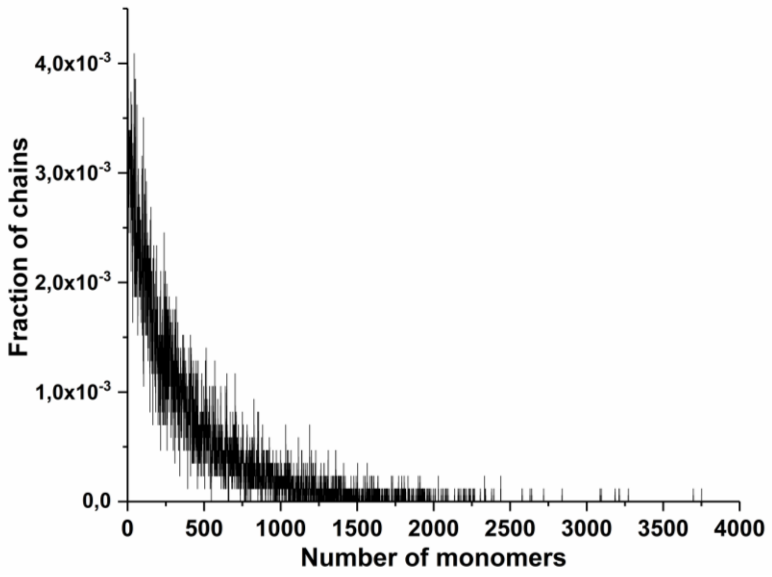
Figure 2: Variation in the number of monomers over time.



Source: Authors.

Figure 2 shows that about 50% of the monomers present at the beginning of the process are consumed. This can be seen as inefficient, thus requiring a separation process to recover these monomers and use them later. In contrast, this large number enables initiation and propagation reactions. The biggest benefit that stochastic modeling can bring to this case is the supply of the chain size distribution at the end of the polymerization, which is fundamental for determining the properties of the formed product. Figure 3 presents this information:

Figure 3: Chain size distribution.



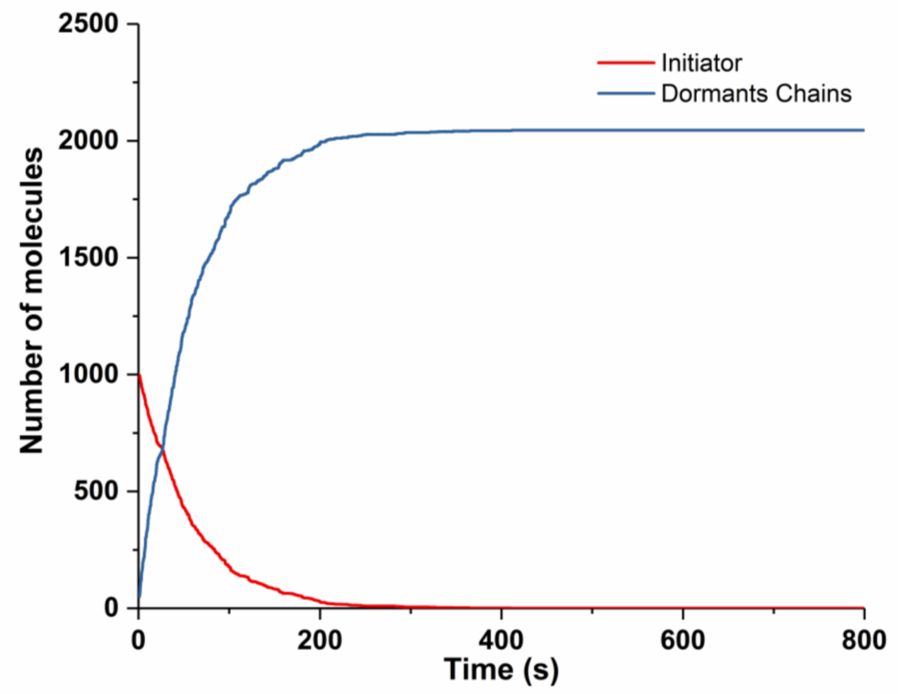
Source: Authors.

Figure 3 the great tendency to form small chains with less than 2,500 monomers is noticeable, even though the largest chain in the system has more than 3,500 monomers. From the algorithm, it was possible to find an average chain size of 703.27 monomers.

3.2 Controlled radical homopolymerization

This topic will also be presented first the variation of the number of molecules over time, but later will be informed beyond the molar distribution of the chains, will also be a possible representation on a mass basis. This last approach was possible because it is a real system, different from the first topic. Firstly, Figure 4 shows the variation in the number of initiators and dormant chains over time.

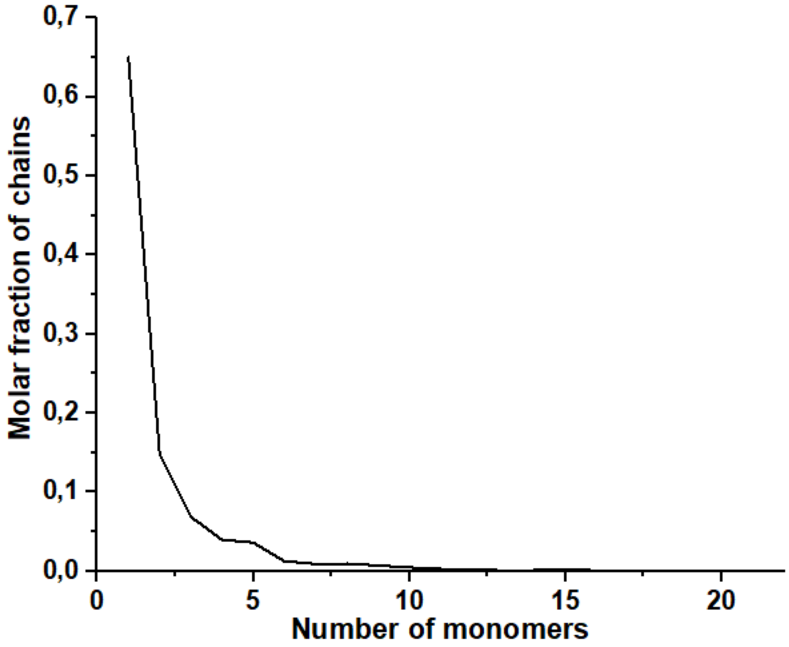
Figure 4: Variation in the number of initiators and dormant chains over time.



Source: Authors.

For this system, it was pertinent to analyze the number of initiators molecules and dormant chains over time. This is due to some facts, such as that the starter molecules were consumed quickly, before 300 seconds of process, so new chains were not produced after this time, because the concentration of radicals present in the system was zero. It is noteworthy that the number of dormant chains has become constant due to the very nature of the reverse reaction to capture, which rarely happens. The number of living and dead chains in the system was null because all formed chains were quickly captured, thus forming a static system. Figure 5 shows the molar size distribution of the formed chains.

Figure 5: Molar size distribution of chains.

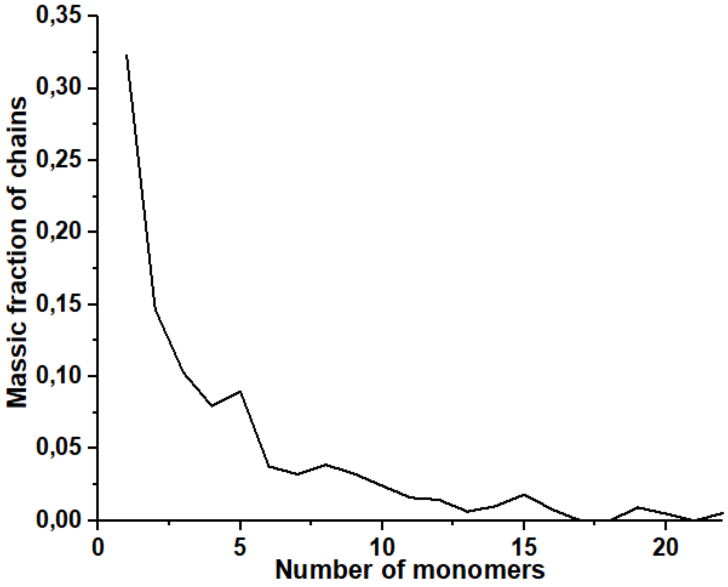


Source: Authors.

By associating the information presented in Figures 4 and 5, it is noted that the propagation step was strongly affected by the rapid capture of living chains, so that the chains could not exceed the size of 10 monomers. Based on Figure 5, it is also observed that 65% of the chains are unit size, so it can be concluded that the capture agent prevents chain propagation, which may not be interesting depending on the application. Through the algorithm, it was possible to determine that the average chain size, in this case, was 2.02 monomers. With the styrene molar mass, it was possible to find that the average molar mass of the medium was 210.38 g·mol^{-1}.

To quantify the due weight of each chain size in the total mass of the system, the mass distribution was also generated in this case. Figure 6 shows the greater relevance of the larger chains in the total mass of the medium and a consequent decrease in the contribution of the smaller chains.

Figure 6: Massic size distribution of chains.

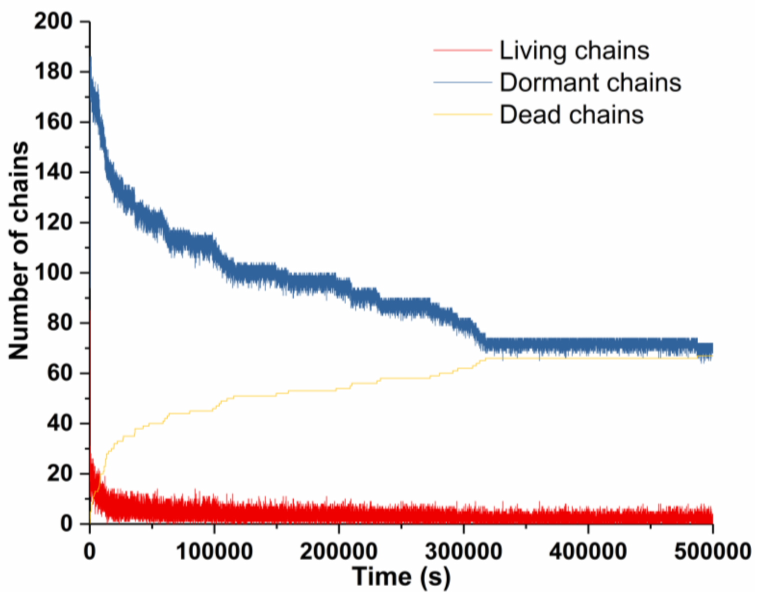


Source: Authors.

3.2 Controlled radical copolymerization

The study of copolymerizations is more complex than in previous cases. In this system, it was relevant to quantify the variation of the chemical composition of the chains over time, besides the size of the formed blocks and their number. Figure 7 shows the variation in the number of chains over time:

Figure 7: Variation in the number of living, dead and dormant chains over time.

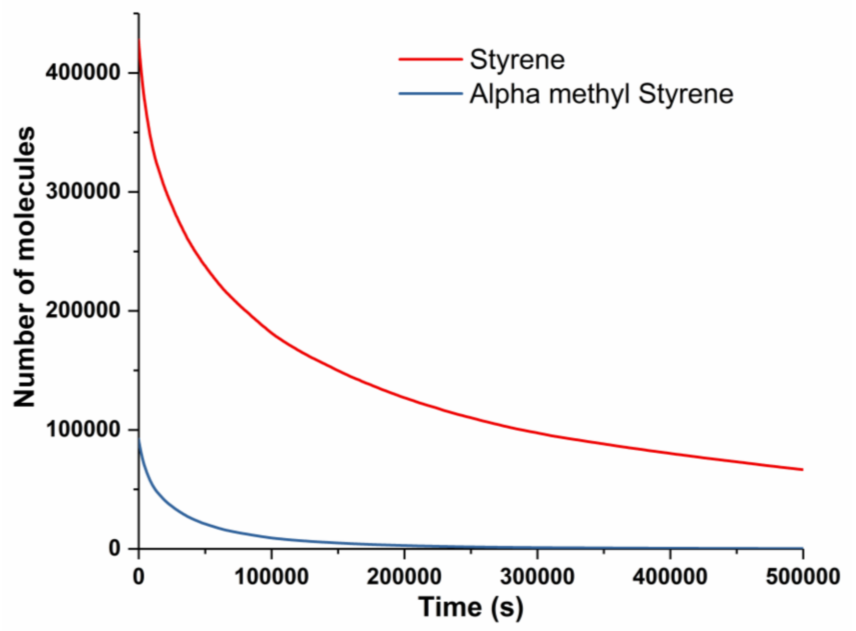


Source: Authors.

From the analysis of Figure 7, it is noticed that the number of living chains in the system is much smaller than the others. Q-type living and dormant chains were not represented due to their negligible number during the process. This fact can be explained by a brief analysis of the kinetic constants, which present lower values than for the others.

Figure 7 also shows that the number of dormant chains tends to decrease over time until it stabilizes, and that of dead chains is always increasing. This is due to the reversibility of capture reactions, the irreversibility of deaths and the reduction in the number of initiators and living chains in the system. Also, the kinetic constants of the termination reactions favor such a scenario. Figure 8 shows the change in the number of monomers over time:

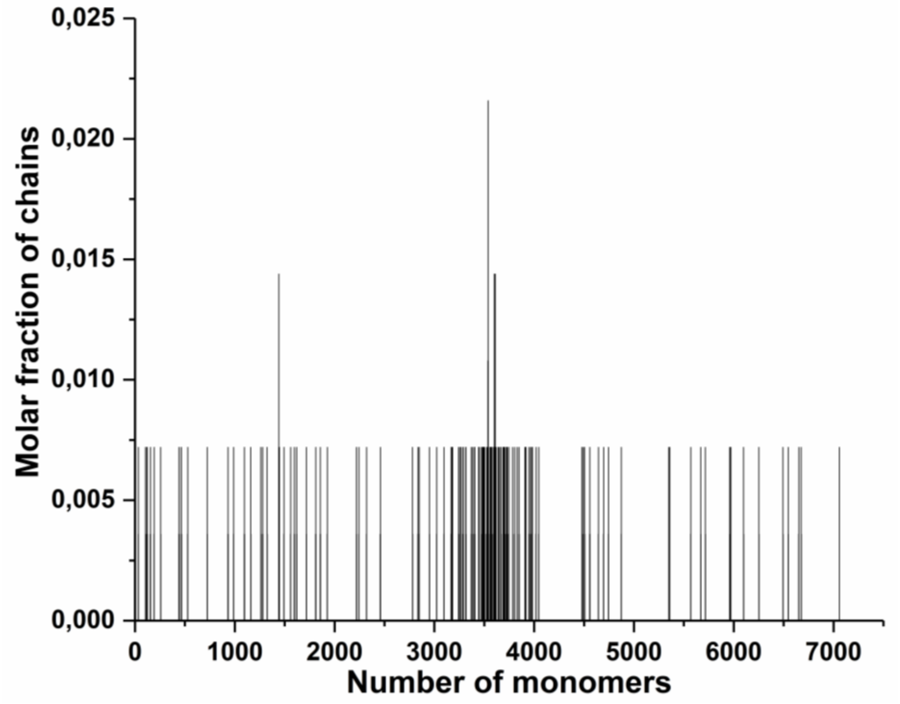
Figure 8: Variation in the number of living, dead and dormant chains over time.



Source: Authors.

Figure 8 shows an abrupt variation in the number of two monomers used, which is due to the great tendency of the chains to undergo the propagation reaction. This predisposition happens because monomers are in large numbers in the system, besides the possibility of being incorporated by 6 types of reactions. Note that after 200,000 seconds monomer 2 practically runs out, leading to the belief that the "tail" of the chains will preferably be formed of styrene monomers. To switch composition only at the beginning. This is mainly due to the initial concentration difference the medium has undergone. Figure 9 presents the distribution function for the size of the formed chains.

Figure 9: Distribution function between the number of monomers and the fraction of chains.

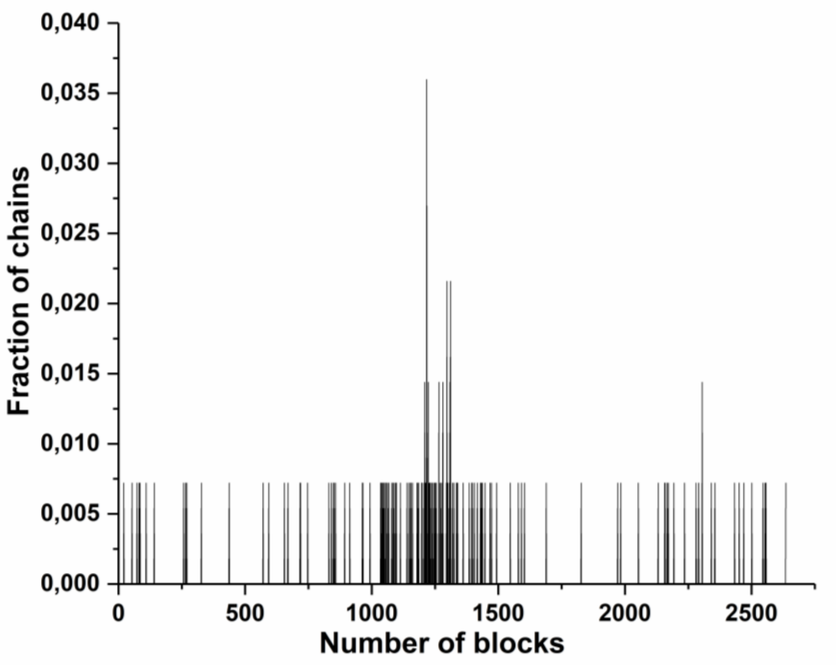


Source: Authors.

Figure 9 reveals information about the size of the chains formed in the system. It is noticeable that most of them are concentrated in a central range of less than 5,000 and more than 2,000. However, it is worth mentioning the presence of chains with more than 7,000 monomers. Due to the small number of chains in the system, there are few sizes with more than just one string composing their set. Based on these data it was possible to find out that the average number of monomers in a chain was 3,270.56. The count of the number of blocks per chain is shown in Fig. 10 as a distribution function.

From Figure 10 it becomes apparent that most chains have from 500 to 2,000 blocks, however, it is worth noting the presence of chains with more than 2,500 blocks. This leads to the conclusion that there was a large alternation in propagation reactions between type 1 and type 2 monomers, given that the average chain length was 3,270.56 monomers.

Figure 10: Relation between the number of blocks and fraction of chains.



Source: Authors.

4. Final considerations

This paper fulfilled its objective, which was to characterize polymer chains through probability density functions. The algorithm used can be directly applied by scientists to develop new materials. Especially for the creation of straight-chain polymers with one or more monomers, generated in temperature-controlled batch reactors. This last condition is very common with current technology. This is a breakthrough in saving time and burden on reagents.

The present paper can be further explored for other types of polymerization reactions as a mechanism of complexation. Given the limitation of the c ++ language to create data arrays with only up to 7 dimensions, methods for modeling chains with more branches may deviate from the methodology of this paper but would be achievable through modeling with graph networks. Also, prospects include the addition of energy balances by quantifying the enthalpy variation produced by each reaction, making it possible to locate possible temperature gradient regions, which are common in polymerization reactors.

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