Article

Simulation of the Equilibrium Constant Effect on the Kinetics and Average Properties of Polystyrene Obtained by ATRP

Roniérik P. Vieira,[a] Andréia Ossig,[b] Janaína M. Perez,[b] Vinícius G. Grassi,[b]
Cesar L. Petzhold,[b] Augusto Peres,[c] João M. Costa[c] and Liliane M. F. Lona,[a]*

[a]*School of Chemical Engineering, University of Campinas, 13083-852 Campinas-SP, Brazil*

[b]*Chemistry Institute, Federal University of Rio Grande do Sul, 91501-970 Porto Alegre-RS, Brazil*

[c]*Center for Research and Development, PETROBRAS, 21941-915 Rio de Janeiro-RJ, Brazil*

Este artigo utiliza simulações para estudar o processo de polimerização radicalar via transferência de átomo por meio da análise do comportamento das espécies químicas (polímeros "vivos", "dormentes" e "mortos"). Para isso, um modelo matemático foi desenvolvido usando o método dos momentos, e os dados experimentais da polimerização de estireno, obtidos da literatura, foram utilizados para validá-lo. A partir disto, foram obtidos perfis de concentração destas espécies, que foram posteriormente usados para obter as propriedades médias dos polímeros (Mn e IPD). As propriedades foram avaliadas em diferentes valores da costante de equilíbrio (K_{eq}) e verificou-se que os valores na ordem de 10^{-7} e 10^{-9} proporcionam o melhor controle na estrutura dos polímeros. Esta pesquisa é, por isto, um ponto de partida para a escolha ideal do sistema catalítico, ligantes e iniciadores. Além disso, a técnica de modelagem apresentou-se como uma ferramenta de fácil implementação e bastante eficiente na análise do processo ATRP.

This article uses simulations to study the atom transfer radical polymerization by analyzing the behavior of the chemical species ("living", "dormant" and "dead" polymers). For this, a mathematical model has been developed using the method of moments, and experimental data from styrene polymerization, obtained from literature, were used to validate the model. From this point, the concentration profiles of all species were obtained, and later on, they were used to obtain the average properties of polymers (Mn and PDI). The properties were evaluated at different values of equilibrium constant (K_{eq}) and it was found that values around 10^{-7} and 10^{-9} provide a better control in the structure of polymers. Therefore, this study is a starting point for selecting the optimal catalytic system, binders and initiators. In addition, the modeling technique presented as a useful tool, being very effective on the analysis of ATRP processes.

Keywords: ATRP, equilibrium constant, controlled polymerization, kinetic simulation

Introduction

In recent years the interest on synthesize macromolecules with precisely controlled sizes and functionality has increased significantly, due to the applicability of these materials as microelectronics (all computers and mobile phones), textiles, food packaging, paints, health and beauty products, controlled drugs delivery and other biomedical materials.

A variety of these materials occurs due to structural characteristics, such as blocks copolymers, stars, telechelics, and (hyper) branched polymers. They can be synthesized using methods such as atom transfer radical polymerization (ATRP),[1] nitroxide-mediated polymerization (NMP),[2] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[3] The most powerful controlled polymerization technique is the atom transfer radical polymerization (ATRP), developed by Wang and Matyjaszewski, because it can be conducted efficiently at low temperatures and for various monomers.[1]

Simulations in chemical reaction engineering are used for different reasons during the investigation and development of a reaction process or system. In the initial stages, they are used to dissect and understand the process or system. By setting up a model and studying

*e-mail: liliane@feq.unicamp.br

the results from the simulations, engineers and scientists achieve the understanding and intuition required for further innovation. Once a process is well understood, modeling and simulations are used to optimize and control the process variables and parameters. These "virtual experiments" are run to adapt the process to different operating conditions.

Since the emergence of the ATRP process, few researches on process modeling were developed.[4-14] For example, Zhu developed a mathematical model for the ATRP kinetics using the method of moments.[8] Butte *et al.* compared the kinetic models of MNP and ATRP for styrene polymerization.[11] Zhang and Ray proposed a mathematical model for controlled radical polymerization in stirred tank reactors, which provides a tool for process development in design issues.[13]

All these works reported above give us a set of tools that provide a preliminary analysis of the process with respect to the average properties of polymers, such as the average molecular weights and polydispersity indexes. However, only an analysis considering the concentration profiles of each chemical species provides a detailed understanding of the manner in which the polymerization occurs. Once the kinetics and also the concentrations of the species involved play an important role in the control of polymerization, a perfect understanding of these topics becomes indispensable.

The objective of this paper is to examine the effect of the equilibrium constant (K_{eq}) on the concentration profiles of all species involved (monomer, "living", "dead" and "dormant" polymers) through simulations of ATRP and to observe how it affects the polymerization kinetics and the control of the system.

Unlike other studies in the literature, the key contribution of this research is to give detailed information of all species of polymer chains under three equilibrium constants to help readers understand the mechanism of ATRP and choose the best catalytic system (if they already know equilibrium constants of catalytic system).

Methodology

The mathematical model has been developed considering the reaction mechanism with the steps: initiation, propagation, chain transfer and termination. The mechanism is expressed by Equation 1 to 7.[15]

Initiation:

$$RX + C \xleftrightarrow{ka_0 / kda_0} R^{\bullet} + XC \tag{1}$$

$$R^{\bullet} + M \xrightarrow{ki} P_1^{\bullet} \tag{2}$$

Propagation:

$$P_n X + C \xleftrightarrow{Keq=\frac{ka}{kda}} P_n^{\bullet} + XC \tag{3}$$

$$P_n^{\bullet} + M \xrightarrow{kp} P_{n+1}^{\bullet} \tag{4}$$

Chain transfer:

$$P_n^{\bullet} \xrightarrow{ktr} P_n \tag{5}$$

Termination by combination:

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{ktc} P_{m+n} \tag{6}$$

Termination by disproportionation:

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{ktd} P_m + P_n \tag{7}$$

In the above equations, *RX* represents the initiator, *C* is the catalyst, *XC* is the catalyst in the oxidized state, *M* is the monomer, P_nX is the dormant polymer, $P_n^{\bullet}$ is the living polymer, P_n is the dead polymer.

A population balance was developed for each species involved in the process (monomer, "living", "dormant" and "dead" polymers), considering an isothermal batch reactor as system. After that, the method of moments (Equation 8 to 10) was used to obtain the profiles of populations.[16] This method was chosen because it can be used to predict the average properties of polymers with branched and linear chains, being more versatile than instantaneous method, that can be used only for polymers with linear chains.[13] Usually the method of moments generates a system of equations with high stiffness, and in this work the Adams-Moulton method was used to solve the system of equations. Table 1 provides the physical meanings of population moments of order "zero".

$$\mu_r = \sum_{n=1}^{\infty} n^r \left[P_n^{\bullet} \right] \tag{8}$$

$$\lambda_r = \sum_{n=1}^{\infty} n^r \left[P_n \right] \tag{9}$$

$$\delta_r = \sum_{n=1}^{\infty} n^r \left[P_n X \right] \tag{10}$$

In these equations, μ_r represents the moment of order "r" for the living polymer, λ_r is the moment of order "r" for the dead polymer, δ_r is the moment of order "r" for dormant polymer, r is the order (in this case 0, 1 and 2), *n* is the length of the polymer chain, $[P_n^{\bullet}]$ is the living polymer concentration, $[P_n]$ is the concentration of dead polymer and $[P_nX]$ is the concentration of dormant polymer.

Table 1. Physical meanings of population moments of order "zero"[16]

Moment	Physical meaning
μ_0	Total concentration of living polymers ($\sum_{n=1}^{\infty}[P_n^{\bullet}]$).
λ_0	Total concentration of dead polymers ($\sum_{n=1}^{\infty}[P_n]$).
δ_0	Total concentration of dormant polymers ($\sum_{n=1}^{\infty}[P_nX]$).

The material balance for the monomer and the equations of population moments generate a system of ordinary differential equations that was solved numerically through a computer program developed in Fortran and using the LSODE subroutine.[17] This subroutine uses the Adams-Moulton method to solve initial value problems. This method was chosen because it is very effective to deal with high stiffness in the differential equations system, which is quite common in polymerization engineering problems.

The polymers' average properties were also calculated (Equation 11 to 14). Experimental data from Fu's research and co-workers were used,[6] in order to obtain a model validation.

Number average molecular weight:

$$\overline{Mn} = MW_M\left(\frac{\mu_1 + \lambda_1 + \delta_1}{\mu_0 + \lambda_0 + \delta_0}\right) \tag{11}$$

Weight average molecular weight:

$$\overline{Mw} = MW_M\left(\frac{\mu_2 + \lambda_2 + \delta_2}{\mu_1 + \lambda_1 + \delta_1}\right) \tag{12}$$

Polydispersity index:

$$PDI = \frac{\overline{Mw}}{\overline{Mn}} \tag{13}$$

Monomer conversion:

$$X = 1 - \frac{[M]}{[M]_0} \tag{14}$$

In order to validate the model, a styrene bulk polymerization at 110 °C was considered, using $[M]_0 = 15$ mol L^{-1}, methyl-2-bromopropionate as initiator and bromide copper (I) with N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as catalyst system, in a ratio of 50:1:1:1 among them.[6] The set of kinetic rate constants considered in this work are summarized in Table 2.

Table 2. Kinetic rate constant for simulation of styrene ATRP at 110 ºC obtained from Fu *et al.*[6]

Kinetic rate constant	Value / (L mol^{-1} s^{-1})
k_p	1571
k_a	1.1
k_{da}	1.1×10^7
k_{t0}	3.132×10^8
k_{tc}	$0.99k_t$
k_{td}	$0.01k_t$
k_{tr}	0.22

Results and Discussion

Validation of the model with experimental data from literature

As viscosity of the system increase during polymerization, a gel effect correlation (Equation 15), proposed by Zhang and Ray, was considered in this work. In Equation (15), k_{t0} is the kinetic rate constant at zero conversion, and it is assumed that the termination rate constant, k_t, varies with the weight fraction polymer (w_p).[13]

$$k_t = k_{t0}\exp(-0.4404w_p - 6.362w_p^2 - 0.1704w_p^3) \tag{15}$$
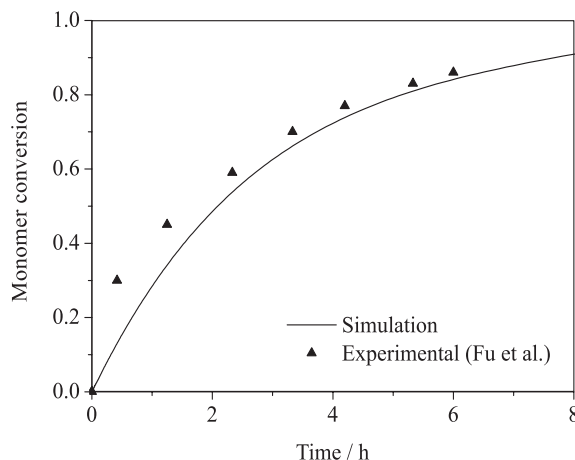

Figure 1. Comparison of experimental data from Fu *et al.*[6] and the simulation of this work for the monomer conversion versus time.

Figure 1 shows a good agreement between experimental data and simulation results for the monomer conversion versus time. It can be observed that the model fits better the experimental data for higher conversions value and presents a slight deviation at low conversions, when the rate of polymerization is faster.

Fu *et al.* studied ATRP system characterized by very low solubility limits and experimental data on these limits are provided with solvent.[6] However, the model presented

in this work neglects these solubility limits for the ATRP catalyst in both its activated and deactivated forms. Due to these solubility limits, the polymerization rate and the effect of reaction conditions on the ATRP process will change for sure.

Neglecting these limits was a simplification made intentionally, once this study aims to investigate the behavior of chemical species in a bulk polymerization and not in a solution polymerization, as in the research of Fu and co-workers. Nevertheless, experimental data show a very good agreement with the simulation for the evolution of molecular weight and PDI, as shown in Figure 2 and Figure 3, respectively.

Figure 2. Comparison of experimental data from Fu *et al.*[6] and the simulation of this work for the average molecular weight development versus conversion.

Figure 2 shows that the number average molecular weight evolves linearly as the monomer conversion is increased. This is in agreement with a typical living polymerization.[18,19] In ATRP polymerization nearly all propagating chains have the same lifetime, starting at essentially the same time and growing with negligible occurrence of chain-breaking reactions until high conversion of monomer is reached.[20] Nevertheless, at high conversion, the polymerization rate decreases significantly, such that normal termination is not sufficiently suppressed, showing characteristics of a conventional free radical polymerization, i.e., the chain-breaking reactions become high enough to promote a slight deviation from linearity in the evolution of molecular weight, especially in higher order kinetics.[19]

Once the mathematical model takes into account the termination and chain transfer in its mechanism, the slight deviation from linearity at high conversions (above 50%) can be attributed to that. Nevertheless, it is important to note that this deviation is very small, confirming the expected for a typical controlled polymerization.
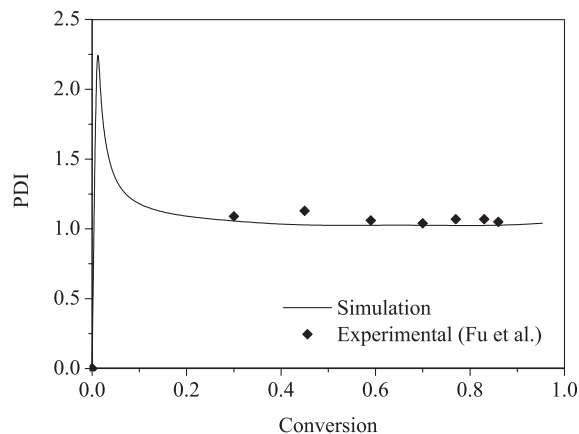

Figure 3. Comparison of experimental data from Fu *et al.*[6] and the simulation of this work for the polydispersity index versus conversion.

Figure 3 shows that the ATRP process can maintain a good control of the polydispersity index (PDI lower than 1.5). The model fits the experimental data, so that it may be a good approximation to represent the system. The mathematical model considers a generic mechanism to represent any ATRP process and the computational program was developed in a generic way, being possible to use it for different kinds of monomer, initiators, binders and catalysts. Thus, this model can be used to represent any ATRP process since all parameters are known. Moreover, one can use the model to estimate parameters (kinetic constants, for example) for a specific system and promote the optimization and process scale up.

Influence of K_{eq} in the concentration profiles of reaction components

For a detailed understanding of the ATRP process, an analysis of concentration profiles of all components involved is necessary. The equilibrium constant of the ATRP process refers to the ratio between the kinetic constant of activation and deactivation of the catalytic species. Figure 4 discusses the equilibrium constant's influence on the profile of "living" polymers.
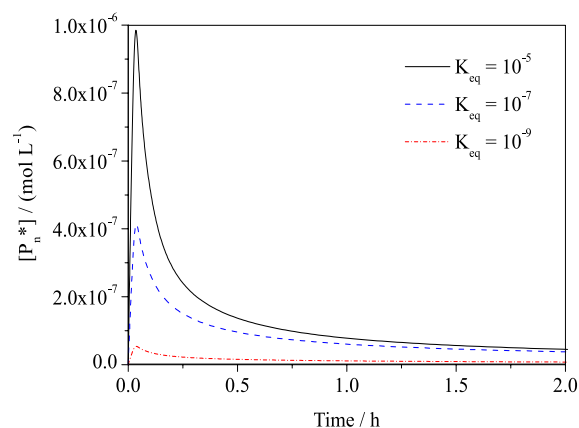

Figure 4. Influence of K_{eq} on the living polymer concentration.

From Figure 4, it is clear that the living polymers concentration had a sharp increase in the first minutes of reaction. This happens in other controlled polymerization, like nitroxide mediated radical polymerization.[2] In the first minutes of reaction, the generation of free radicals, due to the dissociation of initiator, is faster than the step in which the controller traps the chain, making the concentration of radicals increase rapidly. After a while, more chains become dormant, reducing the radical concentration. After two hours, there was a significant reduction in radical concentration. This is in agreement with a typical living polymerization in which all living polymer chains are maintained in a reduced concentration due to the addition of dormant species.[20]

It is noteworthy that, in a typical ATRP process, the equilibrium constant is around 10^{-7}. One can obtain other results by varying this experimental conditions,[21] however, if the equilibrium constant is higher than 10^{-7} (like 10^{-5}, in Figure 4) the polidispersity become bigger than 1.5 (see Figure 9); and if the equilibrium constant is lower than 10^{-7} (like 10^{-9}, in Figure 4), the rate of polymerization become very slow (see Figure 7). Figure 5 expresses the influence of K_{eq} in the dormant polymer.
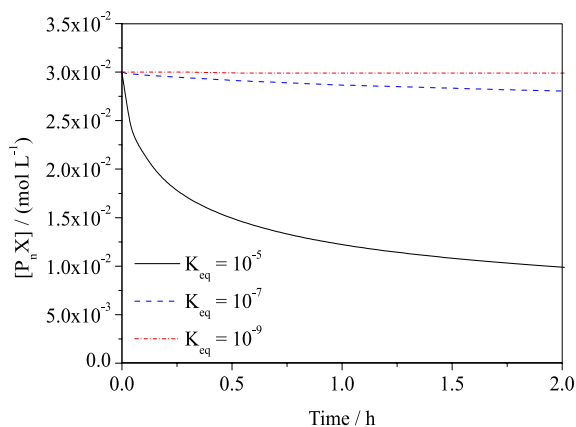

Figure 5. Influence of K_{eq} on the dormant polymer concentration.

From Figure 5, we can see a drastic change in the concentration of dormant polymer during the process when the equilibrium constants are changed. Firstly, in a typical ATRP ($K_{eq} = 10^{-7}$ and 10^{-9}), the concentration of dormant polymer shows a slight decrease. This fact suggests that the control provided by the addition of dormant species is occurring effectively. Moreover, by increasing the equilibrium constant, the concentration of dormant species reduces drastically (see larger ratio $K_{eq} = 10^{-5}$). In addition, from Figure 5, one can get a sense of the polymer functionality at any moment of the reaction, what means that the concentration of functional polymers can be obtained. Several works address the terminal functionality using the ATRP process.[22,23]

Figure 6 expresses the influence of K_{eq} in the dead polymer concentration. The literature discuss that in a successful ATRP, the dead polymer concentration during the process is negligible.[24] It is quite evident for the $K_{eq} = 10^{-7}$ and 10^{-9} (see Figure 6). In this case, the dead polymer concentration does not reach 2×10^{-3} mol L^{-1}, confirming what is expected in theory. Unlike this, when equilibrium constant increases, the dead chains concentration tends to increase significantly, approaching a conventional radical polymerization process.
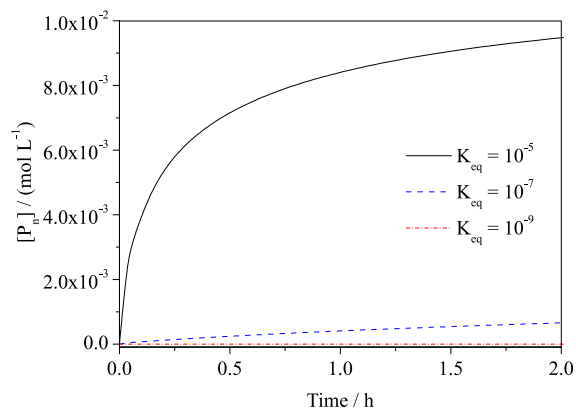

Figure 6. Influence of K_{eq} on the dead polymer concentration.

It is interesting to noted that, in Figure 4, for $K_{eq} = 10^{-7}$ and $K_{eq} = 10^{-5}$, the radical concentration profiles are almost the same for both cases, however a lot of radicals become dead polymers when $K_{eq} = 10^{-5}$ (see Figure 6), differently from the case when $K_{eq} = 10^{-9}$, in which a reduction of radical concentration due to termination is very slow (tending to zero).

This results in only a small percentage of chains undergoing irreversible radical-radical termination that removes the functionality from the chain ends. However, this small amount of termination leads to a buildup of excess deactivator. Thus, favoring deactivation further over radical-radical termination and thereby enhancing control. This scenario is termed the persistent radical effect and has been shown by Fischer[25,26] and ourselves,[19] to be operating in both ATRP and NMP.

Figure 7 deals with the influence of K_{eq} on the monomer conversion. An initial examination of Figure 7 shows that as the equilibrium constant increases there is also an increase in the monomer conversion versus time. Thus, it is confirmed that the polymerization rate tends to be lower in controlled radical polymerization. For a low equilibrium constant ($K_{eq} = 10^{-9}$), it is apparent a drastic reduction in the rate of polymerization, causing the total monomer conversion lasts hours. Figure 8 compares the average molecular weights obtained in different numerical values of K_{eq}.
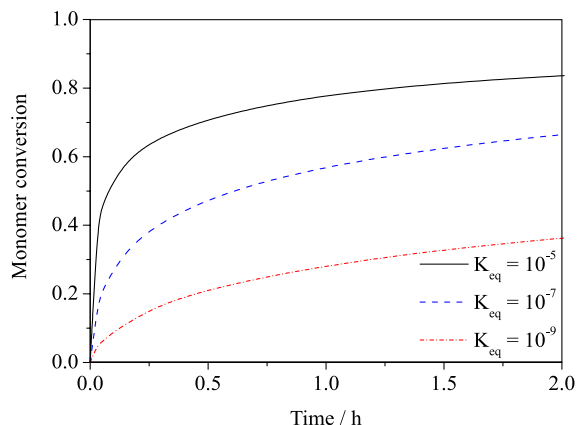
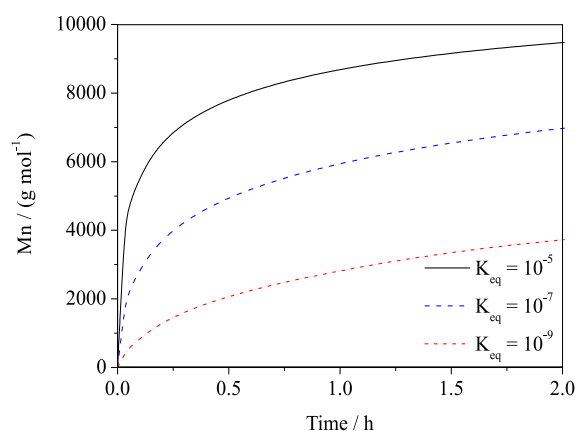**Figure 7.** Influence of K_{eq} on the monomer conversion.

Figure 8. Influence of K_{eq} on the molecular weight development as a function of time.

Figure 9. Influence of K_{eq} on the polydispersity index as a function of time.

Analyzing Figure 8, we see that as equilibrium constant is increased, there is a slight increase in the number average molecular weight ($K_{eq} = 10^{-5}$; Mn = 9500 in 2 hours of reaction). Unlike to this, in low equilibrium constant, the polymers obtained will have low molecular weight ($K_{eq} = 10^{-9}$; Mn = 3700 in 2 hours of reaction). Figure 9 expresses the influence of K_{eq} on the polydispersity index.

According to Figure 9, it can be seen that the polydispersity indexes tend to unity for the values of $K_{eq} = 10^{-9}$ and $K_{eq} = 10^{-7}$. Comparing these two values, it can be seen that the lower equilibrium rate constant gives
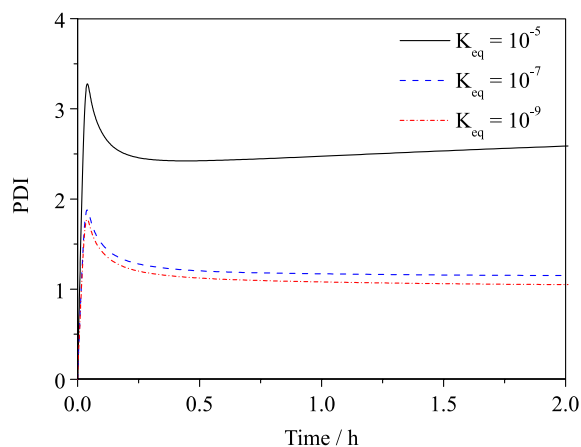
lower values of PDI, being the control more effective as described by Fischer.[25] In contrast, for high equilibrium constant values ($K_{eq} = 10^{-5}$) the PDI values deviate from the unit in a progressive manner.

The difference on the PDI when considering $K_{eq} = 10^{-7}$ and $K_{eq} = 10^{-9}$ is very small, however the polymerization rate is very fast when $K_{eq} = 10^{-7}$ is considered (see Figure 7). All simulation profiles have to be analyzed together in order to choice the ideal K_{eq}. This analysis is summarized in Table 3.

From the analysis of Table 3, it is evident that the equilibrium constant around 10^{-7} is more suitable for ATRP process, since it provides higher values of molecular weight and low polydispersity index. Also, the total conversion of monomer is achieved in less curing time (65 % in two hours of polymerization, according to Figure 7). This account for the majority of the researches available in the literature that adopt for catalytic systems values of K_{eq} in this order of magnitude. Nevertheless, many studies in the literature address the applicability of other values of equilibrium constant to obtain a specific material characteristic.

For example, Schroender *et al.* estimated K_{eq} for different catalyst systems.[21] The values for this constant ranged from 10^{-9} to 10^{-5}. Thus, this work can be a good reference for selecting the catalyst system to obtain a

Table 3. Summary of result analysis

Variable	$K_{eq} = 10^{-9}$	$K_{eq} = 10^{-7}$	$K_{eq} = 10^{-5}$
$[P_{living}]$	Very low	Low	Low
$[P_nX]$	Keep constant	Decreases a little	Decreases very much
$[P_{dead}]$	Very low	Low	Increases very much
Conversion	Slow	Fast	Too fast
Mn	Very low	Increases	Increases
PDI	Very close to unity	Close to unity	Increases

material with specific characteristics. The materials of low molecular weight and PDI close to unity, for example, are widely used in biomedical and pharmaceutical field.[27,28] Thus, a catalyst system with K_{eq} about 10^{-9} would be appropriate for this synthesis.

On the other hand, several other applications require materials with higher molecular weights and low PDI, for example, specific applications in the automotive industry and aerospace.[29] In this case, a higher value of K_{eq} is more appropriate because, in addition to providing these macromolecular characteristics, also influence the velocity and yield of reaction, once a greater amount of material must be produced to meet the high demand. Therefore, an initial analysis of K_{eq} for the ideal choice of initiator and catalyst system becomes an indispensable tool for the effective control of the polymerization and the future application of the material.

Conclusion

An analysis of the simulation data of styrene ATRP was carried out in this work using a kinetic mathematical model considering the method of moments. We evaluated the influence of equilibrium constant on the concentration profiles of all species ("living", "dormant" and "dead" polymer) involved in the process and also the influence on the average properties (Mn and PDI) in the formed polymers. The results suggest that an equilibrium constant around 10^{-7} and 10^{-9} would be ideal for a controlled synthesis using ATRP. Therefore, the analysis proposed in this work becomes a starting point for an optimal choice of catalyst, binder and initiator. Plus provide the readers details of the behavior of chemical species involved in the process, which differentiates it from most of the works that discuss only the average properties. Furthermore, the modeling and simulation technique used in this work can be an easy and comprehensive tool for the analysis and design of chemical reactors, once it is robust and represent different ATRP systems (different monomers, catalyst and initiators), if the parameters are known.

Acknowledgement

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