

MODELING AND PARAMETER ESTIMATION OF NITROXIDE MEDIATED LIVING FREE RADICAL POLYMERIZATION (NMRP) OF STYRENE

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Abstract

The aim of this work is to present a mathematical model for determination of molecular weight and polydispersity (PDI) of polymer with linear structure (Styrene) obtained from the polymerization in presence of a stable radical. This polymerization process, named nitroxide mediated radical polymerization (NMRP), emphasizes the production of polymers with highly controlled structure, narrow MWD and polydispersity index close to 1.0. In this work, the model proposed was able to simulate monomolecular and bimolecular NMRP process to different conditions of temperature and species concentrations. Model predictions are validate against experimental data. Results show that the simulated data predict the process rather well. Thus, the model is thought to have a potential in designing the proper conditions to improve the NMRP.

Keywords: Modeling, NMRP, Styrene

1. Introduction

Nitroxide mediated radical polymerization includes techniques that have attracted much attention in the last few years for providing high molecular weight polymers with low polydispersities and molecular weights increasing linearly with conversion. The basic control principle consists of introducing in the reacting system a species (typically a nitroxide stable radical) able to trap the propagating chains in reversible non-propagating species. The trapping reaction can be represented as follows:



where $[R^\circ]$ represents the propagating (or active) chain concentration and $[R-T]$ the trapped (or dormant) chain concentration. Because the above equilibrium is shifted strongly to the right side, the concentration of the active species is lower in the nitroxide- mediated polymerization than in conventional free radical polymerization. This significantly reduces in the concentration of the active chains makes bimolecular termination almost negligible (reduction in difusional effects). Thus, this reversible process results in the decrease of both the rate of termination reactions and the rate of polymerization. The second effect of this reversible reaction is that all living chains will have a nearly equal chance to grow, what provides a uniformity in chain length and a low polydispersity product.

The literature on the NMRP process is extensive and growing. Several research groups have proposed new synthesis routes and have been able to use new nitroxides and /or alkoxyamines (Fukuda et al.,1996 and Schulte et al.,2004). However, few researches have been concerned with the proposal of the detailed kinetic mechanism underlying the observed behavior (Fukuda et al.,1996, Veregin et al., 1996, Zhang and Ray, 2002, Bonilla et al., 2002).

To fully exploit the potential of these polymerization processes, in this paper, a detailed kinetic mechanism for the NMRP of polymer with linear structure (Styrene) is considered and the corresponding mathematical model, based on the method of moments, is derived. Namely, the model presented here will take account the thermal effect in the kinetics rates. For bimolecular process, it will be analyse the effect of temperature and radical/initiator ratio on molecular weights and polydispersities. For monomolecular process, it will be analyse the effect of radical ratio on conversion, molecular weights and polydispersities. Experimental data obtained from literature were used to validate the model.

2. Model Development

A kinetic model based on a detailed reaction mechanism for NMRP of Styrene for a batch reactor is presented (Mesa, 2003). The reaction mechanism includes the following reactions: chemical initiation, reversible nitroxyl ether decomposition, monomer dimerization, thermal initiation, propagation, reversible monomeric and polymeric alkoxyamine formation (production of dormant species), alkoxyamine decomposition, rate enhancement, transfer to monomer and dimer, as well as conventional termination.

Existing models reported in the literature are limited to specific kinetic modeling and, therefore, are not general tool for designing a practical process. In this study, the kinetic data obtained from diverse authors (Fukuda et al.,1996, Veregin et al., 1996, Zhang and Ray, 2002, Bonilla et al., 2002) had been adjusted according to Arrhenius equation. In that case, the thermal effect was included in the kinetics rates.

The method of moments (applied inclusively for the polymer radical molecules, dead polymer molecules and dormant polymer molecules) was used to obtain the molecular weight.

3. Research Results

3.1 Bimolecular Process

For bimolecular process, styrene polymerization with BPO as initiator and TEMPO as nitroxide radical was used, as case study, with the objective of validate the model.

Figure 1 (a) shows predict profiles and experimental data for polydispersity versus conversion curves, for different temperatures. It is important to point out that previous experimental data published on styrene controlled polymerization show experimental evidence of large polydispersities at low conversions, similar to the ones predict by the model in our case study. Moreover, it was observed that the M_w/M_n stays close to 1.2.

The measured logarithmic conversion values and experimental data as a function of time, for different levels of nitroxide/initiator, are shown in Figure 1 (b). Note that at the higher TEMPO level, the induction period becomes very significant, as predict by the

model and observed by the experimental data. Similar observations have been found by Zhang and Ray (2002). Moreover, it was observed that the time required to reach a specific conversion value was higher for higher [TEMPO]/[BPO] ratio.

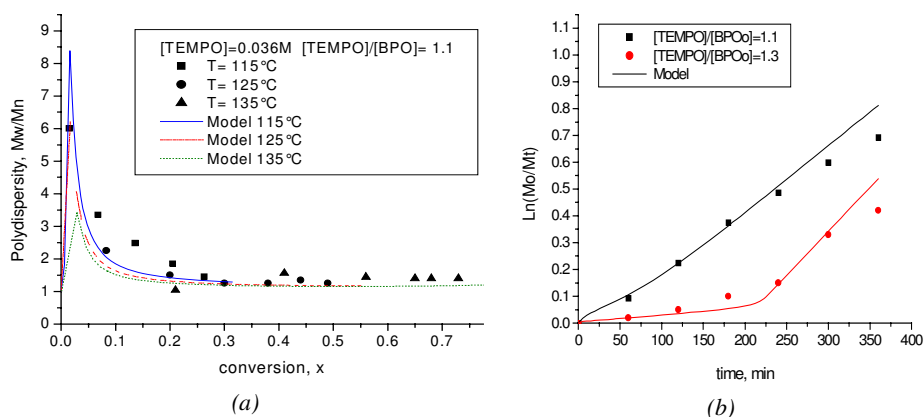


Figure 1 – Effect of temperature on polydispersity simulated and experimental data (a). Plots of $\ln(M_o/M)$ vs. time, Temperature = 125°C and [TEMPO] = 0.036M, $[M_o] = 8.7M$ (b). Experimental data provided by Veregin et al. (1996).

After the demonstration that the model proposed has been able to predict the experimental data reasonably well, the model will be applied for the polymerization of styrene, initiated by BPO and in presence of AT-298 as nitroxide radical. The process temperature was equal to 130°C and bath time equal to 6 hours.

It was observed that the initiator was completely consumed in the first minutes of the reaction. However, nitroxide radical was consumed after 50 minutes of the polymerization reaction starts. At this point, the concentration of monomer starts a sharper decreasing profile, due to the fact that the monomers start to be captured by the propagating chain (R°).

The concentration of dead chains ([P]) represented approximately 10% of the concentration of the dormant chains. The dead chains appear after that the nitroxide radicals are consumed, what indicates that the dead polymer chains come from live polymeric chain not captured by nitroxide radicals in the NMRP process. Then, NMRP can obtain “living” characteristic if exists enough quantity of nitroxide radical.

Figure 2 (a) expose the profile of propagation rate and nitroxide radical concentration with time. As observed, the higher propagation rate value was obtained when the nitroxide radical concentration reaches values nearly zero. After this point, the propagation rate falls until the end of the process. Indeed, the nitroxide radical concentration influences the radical concentration and the propagation rate.

Figure 2 (b) shows the behavior of some properties of polymer (M_n , M_w and PDI) in bimolecular NMRP process. The molecular weights reaches the minimum values before the time equal 50 minutes. After this time, the molecular weight increases due to activation of dormant chains. In addition, the polydispersity at the end of the reaction is 1.15, a low value when it is compared with the polydispersity obtained in free-radical polymerization (FRP), $PDI \geq 2.0$.

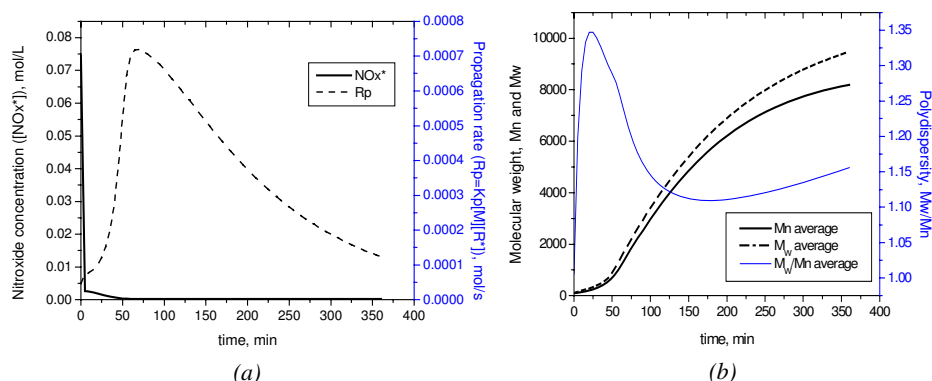


Figure 2- Profile of propagation rate and nitroxide radical concentration with time (a). Behavior of the properties of polymer (M_n , M_w , PDI) in bimolecular NMRP process (b).

3.2 Monomolecular Process

For monomolecular process, styrene polymerization with nitroxyl ether NO_{E-299} at $130^\circ C$ was used as case study for validate and test the model proposed.

Figure 3 (a) shows a comparison of model predictions and experimental data of conversion-time curves for styrene polymerization at the conditions mentioned above. In monomolecular process, differently of the displayed one in the bimolecular process, no evident induction times are observed, which favors reaching high enough conversion in less time.

Experimental data and model predictions for number average molecular weight are shown in Figure 3 (b). It was observed that for the polymerization with a higher content of NO_{E-299} , the plots of molecular weights versus conversion are linear even at high conversion, i.e., the system remains living in the case of the higher level of NO_{E-299} . In contrast, in the lower presence of the NO_{E-299} it was observed that the living character of the system is significantly reduced after 50% of monomer conversion.

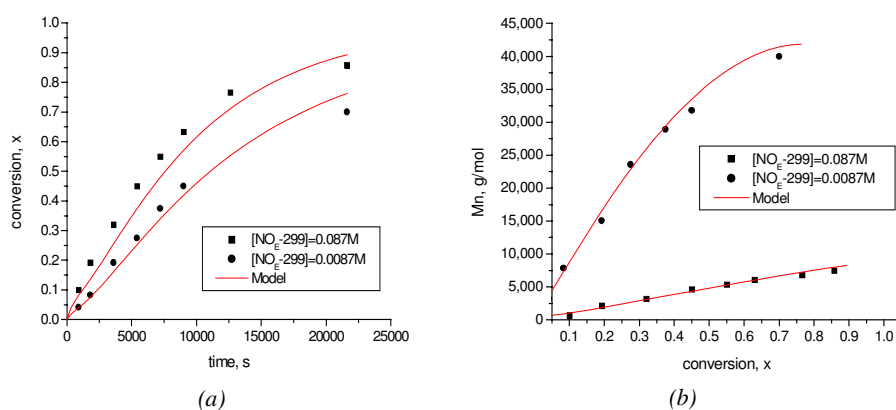


Figure 3. Conversion versus time for styrene polymerization at $130^\circ C$ (a). Plots of molecular weights vs. conversion for NMRP process at $130^\circ C$ (b). $[M_0] = 8.7 M$. Experimental data provided by Bonilla et al. (2002).

Having demonstrated that the kinetic model proposed is in good agreement with a variety of experimental data for NMRP, the model will be applied to an operation condition specified: bath time equal to 6 hours and reaction temperature equal to 130°C. In the monomolecular process the controller agent (NO_E -299) presents, in its decomposition, equal amounts of nitroxide radical and radical (active chains), that can initiate the polymerization process. Therefore, at the point when polymerization starts, the monomer concentration starts a decreasing profile, without the presence of an induction period time. Furthermore, it was observed that primary nitroxide radicals ($[\text{NO}_E]$) are consumed at low conversion (less than 10%).

The profiles presented by the active and dead chains are different of the observed in the bimolecular process. In the monomolecular process the dead chains appear since the beginning of the reaction, due to the fact that the induction period was not observed for this process. Moreover, it was observed that only a very small number of chains terminate by irreversible termination reaction (at 6 hours, $[\text{P}]=0.012 \text{ mol.L}^{-1}$). On the other hand, the alkoxyamines cleave homolytically, providing high initial concentration of radicals. However, in a very short time, the excess of the radicals recombine, leading to a new stationary concentration of active chains ($[\text{R}^\bullet]\approx 3.0\times 10^{-8} \text{ mol L}^{-1}$) and dormant chains ($[\text{RnONx}]\approx 0.085 \text{ mol L}^{-1}$).

In the same way as it was observed in the bimolecular process, the concentration of NO_E -299 determines implicitly the propagation rate, as exposed on Figure 4 (a). When the NO_E -299 concentration arrives to zero, the propagation rate arrives its higher value, but also, the activation-deactivation reaction starts to influence the process.

Figure 4 (b) shows that the average numerical and mass weights are different since the beginning of the process. The polydispersity offers a decreasing profile, arriving at a value of $\text{PDI}=1.15$ at the end of the bath time (6 hours).

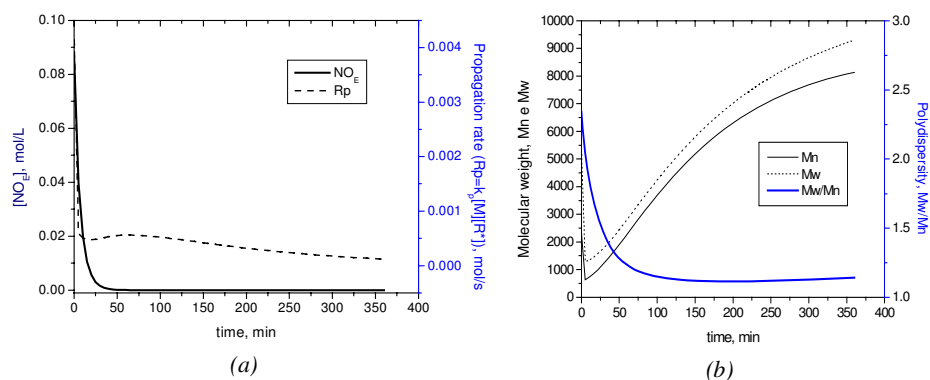


Figure 4- Profile of propagation rate and nitroxyl ether concentration with time (a). Behavior of the properties of polymer (M_n , M_w , PDI) in monomolecular NMRP process (b).

4. New Aspect

NMRP provides a variety of unique polymerization systems that are particularly interesting from the viewpoint of the production of polymers with highly controlled structure, narrow MWD and polydispersity index close to 1.0.

In this study, the thermal effect was included in the kinetics rates. Then, the model proposed was able to simulate monomolecular and bimolecular NMRP process to different conditions of temperature and species concentrations. Moreover, the model will be able to simulate the whole process of a NMRP run and predict the characteristics of the product.

5. Conclusion

The objective of this work was to present a comprehensive view on the polymerization of polymer with linear structure (styrene) in the presence of nitroxide radical (bimolecular process) and nitroxyl agent (monomolecular process). A detailed kinetic and mathematical model for NMRP was presented. On the basis of the experimental data exposed in the literature, the kinetic model proposed were validated. The results were perfectly consistent with the proposed kinetic scheme.

It was observed that temperature and nitroxide radical concentration affect the polymer properties and conversion. Moreover, the results showed that dead polymer chains come from live polymeric chain not captured by nitroxide radicals. Then, NMRP can obtain “living” characteristics if exists enough quantity of nitroxide radical.

Finally, the model proposed allows to obtain significant results in relation to productivity and product quality.

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