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## ALTERNATIVE DIFFUSION-BASED KINETIC MODELING FOR FREE-RADICAL POLYMERIZATION REACTIONS

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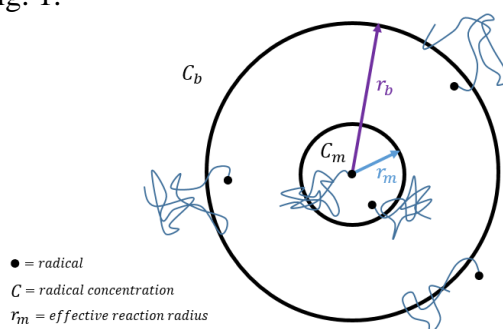
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**Abstract** – In pursuance of improving polymerization simulations, a diffusion-based model for free-radical polymerization was studied. The proposed model is based on the Diffusion-Control mechanism presented by Achilias and Kiparissides [1] with changes that adjusted the monomer conversion to better represent the experimental data. The main modifications include the initiator's efficiency, the estimation of the reaction probability factor for two radicals in proximity, the assumption of the quasi-steady-state approximation and the use of alternative expressions for the polymerization kinetic constants. The major advantage of using a diffusion-controlled model is the glass and the gel effects are backed up by transport phenomena instead of critical breaking points. The simulation was implemented for the polymerization of methyl methacrylate (MMA) with azobisisobutyronitrile (AIBN) as the initiator in the conditions presented in literature [1] to enable a proper comparison of the results.

**Keywords:** *Diffusion-Controlled Polymerization, Free-Radical Polymerization, Polymerization Kinetic Modeling, Poly(Methyl Methacrylate).*

### Introduction

The polymerization process is defined by the synthesis of an organic macromolecule formed from the reaction of small repeating units (monomers). Since the formation of the macromolecules changes the viscoelasticity of the reaction medium, the polymer chains mobility is affected over time, resulting in the well-known glass and gel effects [2]. To mathematically assess these effects, many authors resort to empirical models [2-5]. Nonetheless, Achilias and Kiparissides [1] developed a general mathematical framework for modeling free-radical polymerization reactions based on diffusion properties of the chemical species involved in the polymerization process. The authors' model adjusts the propagation and the termination kinetic parameters according to some parameter such as the total quantity of radicals, the diffusion coefficient of the species and the relative distance between active molecules as shown in Fig. 1.



**Figure 1** – Schematic representation of the reaction radius of the polymerization.  $C_b$  is the radical concentration at a given radius  $r_b$  and  $C_m$  is the radical concentration at  $r_m$ . Adapted from Uliana [6].

Although gel and glass effect are well known in free-radical polymerization reactions, the literature lacks empirical gel and glass effect expressions for copolymerization systems, specially the ones conducted in suspension. Modeling the suspension polymerization of the poly(vinyl acetate-co-methyl methacrylate) (P(VAc-co-MMA)) is a challenge we intend to overcome. The model devised by Achilar and Kiparissides [1] has shown a considerably good performance in representing the variation of total radical quantity, but some imprecisions can still be identified when analyzing the conversion over time. Hence, this work aims to improve the before mentioned diffusion-based model for a better prediction of methyl methacrylate polymerization experimental data as a first step for the modeling of P(VAc-co-MMA).

## Methodology

### Kinetic Modeling

For the kinetic modeling, only the initiation, the propagation, the radical transfer to monomer and the termination by combination and disproportionation were considered. Table 1 presents each respective chemical reaction expression.

**Table 1** – Considered polymerization chemical equations.

Reaction	Equation
Initiation	$I \xrightarrow{k_d} 2R^\bullet + G \uparrow$ (1) <span style="margin-left: 20px;"><math>R^\bullet + M \xrightarrow{k_i} P_1^\bullet</math> (2)</span>
Propagation	$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$ (3)
Radical Transfer to Monomer	$P_n^\bullet + M \xrightarrow{k_{fm}} D_n + P_1^\bullet$ (4)
Termination by Combination	$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} D_{n+m}$ (5)
Termination by Disproportionation	$P_n^\bullet + P_m^\bullet \xrightarrow{k_{td}} D_n + D_m$ (6)

The method of moments [7] was applied to the differential equations obtained from the above-mentioned reactions, where  $\lambda_i$  accounts for the “live” polymer chains and  $\mu_i$  accounts for the “dead” polymer chains. In addition, it was assumed the system is in accordance with the quasi-steady-state approximation for the primary and the “live” chains radicals, resulting in the equations shown in Table 2.

**Table 2** – Implemented polymerization kinetic equations.

Analyzed Factor	Equation
Primary Radical concentration ( $R^\bullet$ )	$R^\bullet = \frac{2fk_d}{k_i M}$ (7)
Zeroth Live Moment ( $\lambda_0$ )	$\lambda_0 = \sqrt{\frac{k_i R^\bullet M}{k_{tc} + k_{td}}}$ (8)
First Live Moment ( $\lambda_1$ )	$\lambda_1 = \sqrt{\frac{k_i R^\bullet M + k_p M \lambda_0 + k_{fm} M \lambda_0}{k_{fm} M + (k_{tc} + k_{td}) \lambda_0}}$ (9)
Second Live Moment ( $\lambda_2$ )	$\lambda_2 = \sqrt{\frac{k_i R^\bullet M + k_p M (2\lambda_1 + \lambda_0)}{k_{fm} M + (k_{tc} + k_{td}) \lambda_0}}$ (10)
Volume (V)	$\frac{dV}{dt} = -V_0 \epsilon \left( k_i R^\bullet + \lambda_0 (k_p + k_{fm}) \right) (1 - X)$ (11)
Monomer concentration (M)	$\frac{dM}{dt} = -k_i R^\bullet M - (k_p + k_{fm}) M \lambda_0 - \frac{M}{V} \frac{dV}{dt}$ (12)
Initiator concentration (I)	$\frac{dI}{dt} = -k_d I - \frac{I}{V} \frac{dV}{dt}$ (13)
Zeroth Dead Moment ( $\mu_0$ )	$\frac{d\mu_0}{dt} = (k_{td} + 0.5k_{tc}) \lambda_0^2 + k_{fm} M \lambda_0 - \frac{\mu_0}{V} \frac{dV}{dt}$ (14)
First Dead Moment ( $\mu_1$ )	$\frac{d\mu_1}{dt} = (k_{td} + k_{tc}) \lambda_0 \lambda_1 - \frac{\mu_1}{V} \frac{dV}{dt}$ (15)
Second Dead Moment ( $\mu_2$ )	$\frac{d\mu_2}{dt} = (k_{td} + k_{tc}) \lambda_0 \lambda_2 + k_{tc} \lambda_1^2 + k_{fm} M \lambda_2 - \frac{\mu_2}{V} \frac{dV}{dt}$ (16)

Obs.:  $\epsilon$  is the volume concentration factor [1];  $X$  is the reaction conversion;  $f$  is the initiator's efficiency.

### Diffusion Effect Over Kinetic Constants

Differently from Achilias and Kiparissides [1], this model maintains the initiator's efficiency constant at 0.58 through the reaction. On the other hand, the propagation and termination kinetic parameters ( $k_p$ ,  $k_{tc}$  and  $k_{td}$ ) dependence on diffusion phenomena is kept. The equations representing the glass and gel effect through diffusion properties and other related information are shown in Table 3.

**Table 3** – Equations that characterize the diffusion effect over the kinetic parameters and related information.

Diffusion effect equations	
$k_p = \frac{k_{p0}}{(1+\tau_{Dp}/\tau_{Rp})}$ (17)	$\tau'_{Dp} = \frac{r_m^2}{3D_{pe}}$ (24)
$\tau_{Dp} = \frac{r_m^2}{3D_m}$ (18)	$\tau'_{p_p} = \frac{1}{k_{tc0}\lambda_0}$ (25)
$\tau_{p_p} = \frac{1}{k_{p0}\lambda_0}$ (19)	$D_{pe} = F_{seg}D_p$ (26)
$r_m = r_t$ (20)	$D_p = D'_p \left(\frac{M'_w}{M_w}\right) \exp \left[ -\frac{\gamma}{\xi_{13}} \left( \frac{w_m V_m^* + w_p V_p^* \xi_{13}}{V_f} \right) - \frac{1}{V_f} \right]$ (27)
$D_m = D_{m0} \exp \left[ -\gamma \frac{V_m^* M_{jm}}{V_f} \left( \frac{w_m}{M_{jm}} + \frac{w_p}{M_{jp}} \right) \right]$ (21)	$k_{tc,Res} = A k_p M$ (28)
$k_{tc} = k'_{tc} + k_{tc,Res}$ (22)	$A = \frac{8 \pi \delta^3 N_A \sqrt{J_c}}{3000}$ (29)
$k'_{tc} = \frac{k_{tc0}}{(1+\tau'_{Dp}/\tau'_{Rp})}$ (23)	$\frac{1}{j_c} = \frac{1}{j_{c0}} + \frac{2\phi_p}{X_{c0}}$ (30)

Obs.: The  $D$  variables are the different diffusion coefficients; The unspecified parameters can be found in Achilias and Kiparissides[1].

Alternatively, the kinetic parameters initial values and  $k_{td}$ 's dependence on  $k_{tc}$  were taken from different references, as demonstrated in Table 4. The subscription 0 indicates kinetic parameter values that don't include the diffusional effect.

**Table 4** – Initial value for the polymerization's kinetic parameters and  $k_{td}$ 's dependence on  $k_{tc}$ .

Equation	Source
$k_{p0} = 4.92(10^5) 60 \exp[-4353/(RT)]$ [L/(mol.min)] (31)	Mahabadi and O'Driscoll [8]
$k_{tc0} = 9.80(10^7) 60 \exp[-701.0/(RT)]$ [L/(mol.min)] (32)	Mahabadi and O'Driscoll [8]
$k_{td} = k_{tc} 3.956(10^{-4}) \exp[4090/(RT)]$ [L/(mol.min)] (33)	Louie et al. [9]
$k_{fm} = 4.66(10^9) 60 \exp[-76290/(RT)]$ [L/(mol.min)] (34)	Peklak et al. [10]
$k_d = 6.32(10^{16}) \exp[-30660/(RT)]$ [1/min] (35)	Achilias and Kiparissides [1]

Obs.:  $R$  is the ideal gas constant in [cal/(mol.K)], with the exception of  $k_{fm}$  that used [J/(mol.K)].

For the estimation of  $F_{seg}$ , a particle swarm optimization algorithm was implemented in Python language and the objective function ( $Fobj$ ) was defined as the sum of the square difference between the conversion data from the proposed model and from the experimental data.

### Model Implementation

The simulation was programed in Python language where the differential equations system was solved with the *integrate.ode* method from the *scipy* library. The chosen integration algorithm was the "dopri5" that consists on an explicit fifth-order Runge-Kutta.

For better analyses and comparison of the models, the considered monomer was MMA and AIBN was the initiator. Additionally, the reaction's initial conditions are the same as in Achilias and

Kiparissides [1] with the exception of the initial volume, that was not discussed in their work, since the model equations were written with dependence on its component's concentration, instead of their molar quantities. These conditions are presented in Table 5.

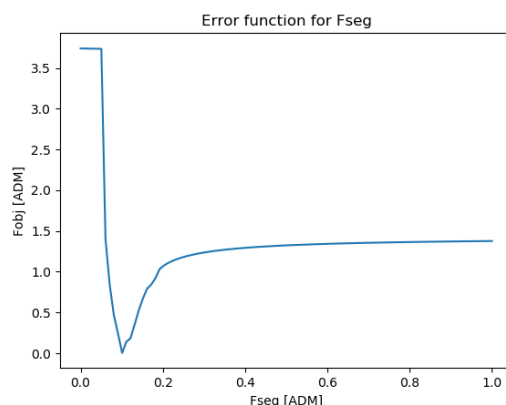
**Table 5** – Reaction's initial conditions.

Volume (V)	Monomer concentration (M)	Initiator concentration (I)	Temperature (T)
1.0 [L]	8.811 [mol/L]	0.01548 [mol/L]	70 [°C]

Obs.: All moment related variables had their initial conditions set to zero; thermal variation wasn't considered, therefore the temperature was kept constant throughout the reaction.

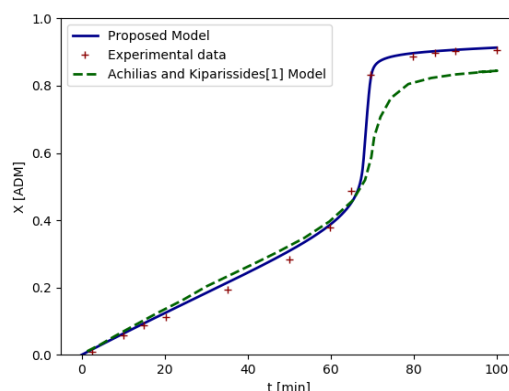
## Results and Discussion

The behavior of the objective function for the Fseg estimation is demonstrated in Fig. 2 and it was used to establish the variable range for the PSO implementation.



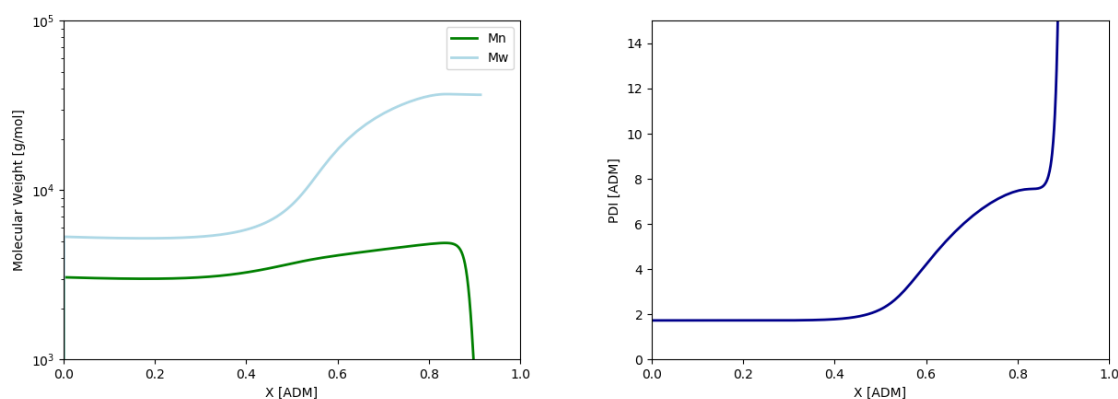
**Figure 2** – Error function related to the experimental data for various values of Fseg.

The optimal value found was  $F_{seg} = 0.102$  and the proposed model is shown in Fig. 3. As it can be seen, the proposed model gives a more precise prediction of the reaction conversion over time in comparison to Achilias and Kiparissides' [1] model for the polymerization of MMA with AIBN as initiator.



**Figure 3** – Reaction conversion over time for the proposed model, Achilias and Kiparissides' [1] model and experimental data over time (data taken directly from the scientific paper).

The number- and weight-average molecular weight ( $M_n$  and  $M_w$ , respectively) and the polydispersity index (PDI) are shown in Fig. 4. These results imply that the model is consistent, since  $M_w$  is always greater than  $M_n$ . Besides,  $M_n$  drops considerably for high conversion values, which illustrates the gel effects' significance. This can also be verified by the PDI sudden growth.



**Figure 4** – Molecular Weight over conversion (left) and Polydispersity Index (PDI) over time (right).

## Conclusions

An alternative diffusion-based model for free-radical polymerization reactions has been developed. The model was initially based on Achilias and Kiparissides' [1] model with the main following modifications: the initiator's efficiency was kept constant throughout the reaction; the parameter that accounts for the reaction probability for two radicals in proximity ( $F_{seg}$ ) was estimated through the particle swarm optimization algorithm; the quasi-steady-state approximation was assumed for the primary and the "live" polymers radicals (QSSA). Furthermore, the polymerization kinetic constants used in the model were acquired from different references.

The simulation applied to the polymerization of MMA with AIBN as initiator rendered a closer approximation of experimental monomer conversion data when compared with the results presented in Achilias and Kiparissides' [1] work.

For the near future, it is intended to implement the same alternative diffusion-based model to the suspension copolymerization of poly(vinyl acetate-co-methyl methacrylate) with the proper modifications.

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