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Stochastic Modelling and Simulation of Free Radical Polymerization of Styrene in Microchannels using a Hybrid Gillespie Algorithm

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Abstract

Most recently, the production of polystyrene by Free Radical Polymerization (FRP) via microchannels has been a subject of core interest due to the efficiency of a micro- or milli-reactor brings. In addition, especially in pilot experimentations, a micro or milli-reactor has been known widely to be efficient in monitoring the microstructural end-use features or properties of the polymer as the chain propagates and ultimately terminates. However, the limitations posed by using micro or milli-reactors in process intensification such as clogging of pores can be a bottleneck when tracking the common phenomena associated with FRP such as cage, gel, and glass effects. In this work, the simulation of the synthesis of polystyrene in FRP via microchannels is computed using a robust and time-efficient hybrid Gillespie Algorithm (GA) or Hybrid Stochastic Simulation Algorithm (HSSA). The obtained results of the end-use properties of polystyrene such as Monomer conversion(X), Polydispersity Index(PDI), Number-Average Molar Mass (M_n) and Weight Average Molar Mass (M_w) were compared to experimental data. The simulation results agree well with the experimental results reported in this work. Hence, stochastic simulations prove to be an effective tool in making decisions in the context of process intensification of chain growth polymerization reactions even at a large scale.

Keywords: Polystyrene, Microchannels, Hybrid Stochastic Simulation Algorithm, Gillespie Algorithm, Free Radical Polymerization, Process Intensification.

Nomenclature

Chemical Master Equation	CME	$(-)$
Dead Polymer Concentration	D°	$(mol.m^{-3})$
Differential Algebraic Equation	DAE	$(-)$
Free Radical Polymerization	FRP	$(-)$
Gillespie Algorithm	GA	$(-)$
Monomer Conversion	X	$(-)$
Hybrid Stochastic Simulation Algorithm	HSSA	$(-)$
Stochastic Simulation Algorithm	SSA	$(-)$
Initiator Concentration	I	$(mol.m^{-3})$
Initiator Efficiency	f	$(-)$
Kinetic Constant for Chain Initiation	K_i	$(mol^{-1}s^{-1})$
Kinetic Constant for Chain Propagation	K_p	$(kgm^{-3}s^{-1})$

Kinetic Constant for Chain Termination by Combination	K_{trM}	$(kgm^{-3}s^{-1})$
Kinetic Constant for Chain Termination by Disproportionation	K_{trM}	$(kgm^{-3}s^{-1})$
Kinetic Constant for Chain Transfer to Monomer	K_{trM}	$(kgm^{-3}s^{-1})$
Kinetic Constant for Chain Transfer to Solvent	K_{trS}	$(kgm^{-3}s^{-1})$
Kinetic Constant for Initiator dissociation	K_d	(s^{-1})
Kinetic Constant for Thermal Initiation	K_{iterm}	$(m^6mol^{-2}s^{-1})$
Live Polymer Concentration	P°	$(mol.m^{-3})$
Long Chain Approximation	LCA	$(-)$
Monomer Concentration	M	$(mol.m^{-3})$
Number-Average Molar Mass	Mn	$(gmol^{-1})$
Operating Temperature	T	$(^{\circ}K)$
Ordinary Differential Equation	ODE	$(-)$
Polydispersity Index	PDI	$(-)$
Pseudo Steady-State Hypothesis	PSSH	$(-)$
Quasi-Steady State Approximation	QSSA	$(-)$
Radical Concentration	R°	$(mol.m^{-3})$
Solvent Concentration	S	$(mol.m^{-3})$
Uniform Random Distribution	URD	$(-)$
Weight-Average Molar Mass	Mw	$(gmol^{-1})$

List of Symbols

Molecular Species	X_i	$(-)$
Number of Moles of the Reacting Species	N	$(moles)$
Number of Reaction Combinations	h_j	$(-)$
Rate of Polymerization	β	$(molm^{-3}s^{-1})$
Reaction Channel	R_j	$(-)$
Reaction Propensity	α_j	$(-)$
Reaction Volume	V	(m^3)
Simulation or Residence time	t	(min)
State Vector	v_{ij}	$(-)$
Stochastic Constant	c_j	$(-)$
Time Interval or Leap	τ	(sec)

1. Introduction

In recent years, the synthesis of polystyrene via Free Radical Polymerization (FRP) in microchannels continues to probe into the increasing level of macromolecular details. Moreover, among many recently published literatures, Dagmar et al. (2015) further validate that the performance of polymeric materials depends on the control over the polymer microstructure during the reaction steps. One of the pivotal applications of the micro- or milli- reactor technology is that it bridges the gap between the synthesis of the end-use features of the polymer at the microscale and macroscale. Furthermore, Vianna et al. (2007) proposed the utilization of continuous flow processes to improve polystyrene's flow dynamics as there were stochastic perturbations observed. Hence, the importance of stochastic modelling and simulation of a chain growth polymerization reaction in microchannels cannot be overemphasized. This will in turn result in both a high reproducible molecular weight distribution and improved productivity.

According to Gillespie (2007), an ensemble of the stochastic trajectories obtained within the bounds of statistical confidence can reveal the latent behavior of a chemical reaction system at small molecular copy numbers. Thus, from a microscopic perspective, this information can be used to predict the key end-use features of the polymer as feeding conditions are varied. This technique in monitoring a chain growth reaction is vital at a pilot level since such reactions constitute both fast and slow reaction steps. Furthermore, the reproducibility of the simulation results or outcomes at small molecular scales is of pivotal relevance to improving the polymer's final properties. The main aim of the work is to find an effective, robust, and scalable approach to simulating Free Radical Polymerization (FRP) of Styrene in microchannels by mimicking a micro- or milli-reactor volume. The specific objectives are:

I. To investigate the statistical discrepancies between experimental and simulated results by considering each successive growing chain length per macromolecule of the end-use polystyrene. This implies the application of a simulation technique that does not apply Long-Chain Approximation (LCA) or Quasi-Steady State Approximations (QSSA). As earlier suggested by Higham (2008), mathematical models rely on modelling assumptions.

II. To apply a Hybrid Stochastic Simulation Algorithm (HSSA) that has the capacity of a parallel simulation of both a stochastic and deterministic simulation. The resulting deterministic trajectory for every feed condition provides a 'sanity' check for the corresponding stochastic trajectories.

2. Stochastic Simulation and Modelling Technique

According to Hahl et al. (2016), by comparing the application of the deterministic and stochastic simulations, stochastic simulation of the kinetics of complex chemical systems like the FRP has proven to be an effective technique for having a clearer understanding of the given chemical system at low molecular copy numbers. Furthermore, Meimaroglou et al. (2014) initially suggested that each simulation technique has its advantages and limitations, which influence their choice regarding the problem at hand. As illustrated in section 2.2, the Hybrid Stochastic Simulation Algorithm (HSSA) is applied in the simulation of the FRP of styrene because of its capacity to perform parallel stochastic and deterministic simulations to capture both the fast and slow dynamics of the reaction and in addition, the robustness to simulates the chain growth reaction up to $2^{31}-1$ of the chain length per macromolecule.

2.1 Gillespie Algorithm (GA)

As earlier published by Gillespie (1976), the Gillespie Algorithm (GA) which is also known as Stochastic Simulation Algorithm (SSA), was introduced to predict or simulate the exact realizations of biochemical or cellular reactions that involve interactions of millions of molecular species. Although computationally expensive, it effectively solves the intractable nature of the Chemical Master Equation (CME) that governs chemical reactions.

To reemphasize, α_0 the cumulative sum of propensity is after an iteration is completed and α_j is the respective propensity for every reaction channel, R_j. The value of τ is a function of the cumulative sum of propensities α_j of the successive chemical reactions taking place within the time interval, $d\tau$ and a variable, ξ_1 which is generated from a URD. Hence, the degree of discreteness of the simulation is dependent on the numerical values of α_j, ξ_1 . The original Gillespie Algorithm (Direct Method) is further described in the following steps:

STEP 1: Initialize the simulation time, t and state vector, v_{ij}. Where v_{ij} is the product of the molecular species, X_i and reaction channels, R_j.

STEP 2: Compute the cumulative sum of propensities for every reaction channel, R_j for $j = (1,2,\dots,M)$ using the equation:

$$\alpha_0 = \sum_{j}^{M} c_j h_j$$

STEP 3: Compute a pseudorandom number ξ_1 from a URD or $\sim U(0,1)$ and compute the next reaction time $t \rightarrow t + \tau$ using the equation :

$$\tau = \frac{1}{\alpha_j} \ln\left(\frac{1}{\xi_1}\right)$$

STEP 4: Compute a pseudorandom number ξ_2 from a URD or $\sim U(0,1)$ and compute the propensity for the next reaction channel R_j using such that:

$$\frac{1}{\alpha_0} \sum_{j=1}^{M-1} \alpha_j \le \xi_2 > \frac{1}{\alpha_0} \sum_{j=1}^{M} \alpha_j$$

STEP 5: Update the reaction system such that:

$$X \leftarrow X + v_{ij} \quad \& \quad t \leftarrow t + \tau$$

The iteration or computation continues until the number of iterations n exceed the predetermined criterion and time of simulation t_f where: $n \ge t_f$. Else, repeat **STEP 2**.

There are some other variants of the GA or SSA. They offer not only increase computational speed to the simulation of complex chemical reactions such as the FRP but also, robust enough to solve the problems associated with the CMEs representing the chemical reaction system. It is worth noting that the deterministic rate constants or kinetic constants are converted to stochastic rate constants based on the chemistry of the reaction. According to the publication of Gillespie (2007), the kinetic constants were mathematically transformed into stochastic rate constants as follows:

For unimolecular reactions:

$$K^{Experimental} = K^{Stochastic} \tag{1}$$

For bimolecular reactions between different species:

$$K^{Experimental} = \frac{K^{Stochastic}}{V.N} \tag{2}$$

For bimolecular reactions between same species:

$$K^{Experimental} = \frac{2K^{Stochastic}}{V.N} \tag{3}$$

For termolecular reaction among same species:

$$K^{Experimental} = \frac{6K^{Stochastic}}{V.N} \tag{4}$$

Where V is the reactor volume and N the number of moles of the reacting species.

2.2 Application of the Hybrid Stochastic Simulation Algorithm (HSSA)

Haseltine and Rawlings (2002) earlier proposed the idea of the Hybrid Stochastic Simulation Algorithm (HSSA) used in this work. It aims at improving accuracy and increasing computational speed by partitioning the reaction into fast and slow components or simply by applying "Stochastic Partitioning". As shown in the computational steps below, the program of the FRP of styrene was developed and simulated by using the gillespy2 python module earlier developed by Abel et al. (2017). The program allows the parallelization of the stochastic and deterministic simulation of the FRP of styrene model using Jupyter notebook or Google Colab. With C^{++} integration, the version 1.7.0 of the gillespy2 python library is computationally robust and scalable for a number of complex chemical reaction systems such as the FRP with up to a chain length of $2^{31} - 1$ per macromolecule. This resulted to a high-speed computation for every varying input or feeding condition for a maximum of approximately 3 minutes.

The deterministic trajectory obtained from every simulation was produced to provide a "sanity check" for an every multiple stochastic trajectories generated. Usually, analytical solutions for a complex chemical reaction system such as the FRP of styrene produces over 10,000 stiff ODEs. Moreover, with approximate method like the application of MOMENTS, these large set of ODEs are reduced to a fewer number of non-stiff differential equations and DAEs of index 1. This reduces the accuracy of the prediction of the polymer's end use properties. Nonetheless, it is worth noting that the HSSA used in this work combines ODE and SSA solvers for the chain growth reaction mechanism for every propensity change without partitioning the system. It can be further employed to track the polymer's end use properties for an increasing number of chain lengths. The HSSA computational steps are shown below:

STEP 1: Initiate the FRP of Styrene model by defining the initial state, v_{ij} and simulation time, t. Also, define the microchannel volume and initial reaction kinetic parameters.

STEP 2: By applying the respective stochastic constants, c_j from Equation 1 to Equation 4, compute the cumulative propensities for every reaction channel, R_j for each of the chain growth reaction depicted in Table 1 using the equation:

$$\alpha_0 = \sum_{j}^{M} c_j h_j$$

STEP 3: Generate two pseudorandom numbers ξ_1, ξ_2 satisfying a URD or $\sim U(0,1)$.

STEP 4: Initiate the stochastic simulation in order to generate the stochastic trajectories by computing the next reaction time and propensity at $t \rightarrow t + \tau$ using equations:

$$\tau = \frac{1}{\alpha_j} \ln\left(\frac{1}{\xi_1}\right) \quad and \quad \frac{1}{\alpha_0}\sum_{j=1}^{M-1} \alpha_j \le \xi_2 > \frac{1}{\alpha_0}\sum_{j=1}^{M} \alpha_j$$

STEP 5: Update the reaction system such that:

$$X \leftarrow X + v_{ij} \quad \& \quad t \leftarrow t + \tau$$

The iteration or computation continues until the number of iterations n exceed the predetermined criterion and time of simulation t_f where: $n \geq t_f$. Else, repeat **STEP 3**.

STEP 6: Initiate the stochastic simulation to generate an ensemble of 100 stochastic trajectories by computing the “leaping” time and propensity at $t \to t + \tau$ using equations in **STEP 4** and the equation:

$$\lambda = \frac{e^{-\alpha_j \tau}\left(\alpha_j \tau\right)^k}{k!}$$

STEP 7: Update the reaction system such that:

$$X \leftarrow X + \lambda \quad \& \quad t \leftarrow t + \tau$$

The iteration or computation continues until the number of iterations n exceed the predetermined criterion and time of simulation t_f where: $\geq t_f$. Else, repeat **STEP 3**.

STEP 8: Initiate the deterministic simulation to generate the deterministic trajectory by integrating the ODEs from the same reaction system for every fired reaction channel R_j and reaction time according to equations in **STEP 4**.

STEP 9: Update the reaction system such that:

$$X \leftarrow X + v_{ij} \quad \& \quad t \leftarrow t + \tau$$

The iteration or computation continues until the number of iterations n exceed the predetermined criterion and time of simulation t_f where: $n \geq t_f$. Else, repeat **STEP 3**.

STEP 10: Dataframe Processing and Computation of the values of X, M_n ,M_w, and PDI using Equation (14) to Equation (17).

Referring to **STEP 10** of HSSA above, it is worth noting, that this technique sacrifices the exact simulation for an approximate simulation that is quicker to compute. The ‘leaping condition’ holds when there exist an infinitesimal time step $\tau > 0$, which is small enough to represent each reaction channel in the chemical reaction system. Furthermore, instead of computing the next infinitesimal time step for the next reaction, R_j,the algorithm ‘leaps’ forward in time following a Poisson Random Distribution (PRD) by updating the population of the respective molecular species in one step. Furthermore, the appropriate size of the ‘leap’ determines the accuracy of the algorithm thus, the larger the size of the ‘leap’, the higher the speed of implementation. In contrast, a small ‘leap’ denotes many steps or iterations may not capture a reaction channel R_j hence, the algorithm would compute extremely slowly. Therefore, from each iteration the propensity $\tau > 0$ will be a function of the leaping time with the number of occurrences k_j (or frequency of an event occurring within the defined 'leap') for everyR_j, sampled from a Poisson Random Distribution (PRD):

$$\lambda = \frac{e^{-\alpha_j \tau}\left(\alpha_j \tau\right)^k}{k!} \tag{5}$$

2.3 Simulation of the FRP of styrene reaction

In this work, the chemical reaction is mainly made-up initiation, propagation, chain transfer, and termination steps. A phenomenological model for the Free Radical Polymerization (FRP) of styrene is shown below:

Table 1- Chemistry of Reaction for the FRP of Styrene.

Reaction Step (#)	**Annotation**	**Chemistry of Reaction**
1	Initiator Dissociation	$I \xrightarrow{K_d} 2R^{\bullet}$
2	Chemical Initiation	$R^{\bullet} + M \xrightarrow{K_i} P_1^{\bullet}$
3	Thermal Initiation	$3M \xrightarrow{K_{iterm}} R_1^{\bullet} + R_2^{\bullet}$
4	Chain Propagation by Thermal Initiation	$R_1^{\bullet} + M \xrightarrow{4K_p} P_2^{\bullet}$
5	Chain Propagation by Thermal Initiation	$R_2^{\bullet} + M \xrightarrow{4K_p} P_3^{\bullet}$
6	Chain Propagation	$P_n^{\bullet} + M \xrightarrow{K_p} P_{n+1}^{\bullet}$
7	Chain Transfer to Monomer	$P_n^{\bullet} + M \xrightarrow{K_{trM}} D_n + P_1^{\bullet}$
8	Chain Transfer to Solvent	$P_n^{\bullet} + S \xrightarrow{K_{trS}} D_n + P_1^{\bullet}$
9	Termination by Combination	$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{K_{tc}} D_{n+m}\ (*)$
10	Termination by Disproportionation	$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{K_d} D_n + D_m\ (*)$

$(*)$ Where m$\neq n$. It worth noting that m ,n are different chain lengths of the growing polymer.

In this work, the kinetic constant of termination by combination and dissociation are related as follows:

$$K_{td} = 99K_{tc} \tag{6}$$

Applying Flory statistical distribution, the molecular weight distribution (MWD), polydispersity index (PDI) and monomer conversion (X) in terms of the dead polymer, D_n when termination is by disproportionation ($K_{td} + K_{tc} \gg K_{td}$), then the propensity of propagation for the chain growth reaction is given by:

$$\beta = \frac{(\text{Rate of Propagation})}{(\text{Rate of Propagation}) + (\text{Rate of Termination of Chain})} \tag{7}$$

From the chemistry of reaction in Table 1,

$$\beta = \frac{\left(K_p M R^{\bullet}\right)}{\left(K_p M R^{\bullet}\right) + \left(K_{trM} M R^{\bullet}\right) + \left(K_{trS} S R^{\bullet}\right) + \left(K_{td}\left(R^{\bullet}\right)^2\right)} \tag{8}$$

Or

$$\beta = \frac{\left(K_p M\right)}{\left(K_p M\right) + \left(K_{trM} M\right) + \left(K_{trS} S\right) + \left(K_{td} R^{\bullet}\right)} \tag{9}$$

Where $R^{\bullet}$ is the formed radicals in the chain growth reaction.

Considering chain initiation by only chemical initiation and the rate of termination of chain or the net rate of disappearance of radicals of the growing polymer chain:

$$\sum_{i=1}^{\infty} -r_i = -2fK_d I_2 + K_{td}(R^{\bullet})^2 \tag{10}$$

Applying Pseudo Steady State Hypothesis (PSSH) the Equation (27), the net free radical concentration is given by:

$$\sum_{i=1}^{\infty} -r_i = -2fK_d I_2 + K_{td}(R^{\bullet})^2 = 0 \tag{11}$$

$$R^{\bullet} = \left(\frac{2K_d f I_2}{K_{td}}\right)^2 \tag{12}$$

Upon substituting Equation (12) into Equation (9) :

$$\beta = \frac{\left(K_p M\right)}{\left(K_p M\right) + \left(K_{trM} M\right) + \left(K_{trS} S\right) + \left(2K_{td} f I_2\right)^{\frac{1}{2}}} \tag{13}$$

The initiator, solvent, styrene monomer, live and dead polymer are denoted by I, S, M, P , and D respectively. In addition, the respective kinetic constant for initiator dissociation, chemical, thermal initiation, propagation, transfer to monomer, transfer to solvent, termination by combination and disproportionation are $K_d, K_i, K_{iterm}, K_p, K_{trM}, K_{trS}, K_{tc}$ and, K_{td}. The constant f at the chemical initiation reaction step is referred as initiator's efficiency, which ranges between $0.2 < f \leq 0.7$.

Since,β is a function of time and when chain transfer is negligible then, the monomer conversion rate can be simply be obtained assuming, $\beta = X$. Alternatively, the monomer conversion for a monofunctional monomer is given by:

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

Where $[M]_0$,$[M]$ are the original monomer concentration and the unreacted monomer concentration after a certain period of time.

Thus, the number-average molecular weight is given by:

$$M_n = \frac{M_s}{1 - X} \tag{15}$$

M_s is the molecular mass of styrene monomer (M_s = 104.15 g/mol)

Again, the weight-average molecular weight is:

$$M_w = M_s \frac{(1+X)}{(1-X)} \tag{16}$$

Dividing Equation (16) by (15), the polydispersity index is computed as follows:

$$PDI = \frac{M_w}{M_n} \tag{17}$$

1. Results and Discussions

The simulation of FRP of styrene was carried out adhering to the same feeding conditions in the experiment performed by Fullin et al. (2015) to validate the HSSA. The styrene monomer was polymerized in a Syrris Asia 120 microreactor with a volume of 4 ml, which was also adopted in the HSSA as reactor volume. The same operating temperatures used in the experiment were also applied in the simulation, which was 100˚C and 115˚C respectively. In addition, the kinetic constants used were also reported in the experiment.

As shown in Table 2 and 3, the ratio between solvent and monomer was chosen to match the empirical correlation already presented in the same experiment by Fullin et al. (2015). The initial concentration of Styrene monomer, Toluene solvent and Benzoyl peroxide Initiator was fed into the milli-reactor in integral volumetric ratios. The respective volumetric ratios of monomer to solvent were 60/40, 40/60 and 30/70. The same empirical correlation was also applied in the HSSA in order to compute the monomer conversion (X), polydispersity index(PDI), number-average molar mass (Mn) and weight-average molar mass(Mw). Again, from Table 2 and 3, for a volumetric ratio of 60/40 and 40/60, the numerical results obtained provided a good correlation with the earlier performed experiment with residence times of 5 and 40 minutes as shown.

The numerical deviation of the stochastic simulations from the experimental results for the number-average molar mass (Mn) and weight-average molar mass (Mw) were larger when compared to the corresponding monomer conversion (X) and polydispersity index (PDI) because the former is an extrinsic property of the end-use polymer which depended on the initial feeding conditions whereas, the latter are intrinsic properties. Moreover, in the HSSA simulation, the input values were measured in terms of whole number ratios, as the HSSA is a discrete stochastic process. As earlier reported in the performed experiment, the feeding amounts of the monomer(M), solvent(S) and initiator (I) were measured as non-integer amounts or in grammes.

As earlier shown in the HSSA, the parallel simulations of the HSSA involved three separate stochastic trajectories that depicted different outcomes of the chemical reaction within the limit of a one-standard-deviation envelop as shown in Figure 1 and Figure 2. Also, an ensemble of 100 Tau-Leaping HSSA trajectories denoted by dashed green lines using the TauLeapingCSolver of the gillespy2 python library was also produced as illustrated in Figure 1 and Figure 2 The stochastic trajectories produced by the TauLeapingCSolver showed closer agreement with the respective deterministic trajectories.

Considering, Figure 1, the degree of stochasticity of the three trajectories of the HSSA was more pronounced as shown in the graph for M_n and M_w when compared to X and PDI as they were almost spreading out of the statistical confidence interval. This trend was more evident specifically in the upper region of the statistical interval denoted by the dashed blue lines. Again, the disparity between the stochastic and deterministic simulation could also be seen from the small deviation of the 100 ensembles of the Tau-Leaping HSSA trajectories denoted by the green dashed line from the black curve representing the deterministic simulation. It is worth noting that, the deterministic trajectory or curve provides a "sanity" check to the corresponding stochastic trajectories obtained from every simulation.

In the case of Figure 2, the level of stochasticity was higher as shown in the graph. In a similar fashion, the three HSSA trajectories deviated out of both ends of the confidence interval as the simulation proceeded when considering the outcomes of the M_n and M_w . This behaviour can be further observed as the 100 ensembles of the Tau-Leaping HSSA denoted by the green dashed line deviated from the deterministic trajectory as the simulation progressed. In addition, the degree stochasticity of three HSSA trajectories for X and PDI was higher at the beginning of the simulation however; they later aligned partially to the deterministic curve.

Table 2 - A comparative table of results obtained from the HSSA and Experiment with initiator concentrations of $5v$ and $1g$ respectively.

Results for $M_n(gmol^{-1})$, $M_w(gmol^{-1})$, PDI and X								Operating Temperature ,$T = 100$℃			
DETERMINISTIC SIMULATION (*)				STOCHASTIC SIMULATION (*)				EXPERIMENTAL RESULTS (*)			
M_n	M_w	PDI	X	M_n	M_w	PDI	X	M_n	M_w	PDI	X
457.44	810.72	1.61	0.61	339.15	574.16	1.51	0.55	6768	13607	1.57	0.091

(*) Monomer/Solvent = 60/40v/v & Simulation time, t = 5mins

Table 3 - A comparative table of results obtained from the HSSA and Experiment with initiator concentrations of $1v$ and $2g$ respectively.

Results for $M_n(gmol^{-1})$, $M_w(gmol^{-1})$, PDI and X								Operating Temperature ,$T = 100$℃			
DETERMINISTIC SIMULATION (*)				STOCHASTIC SIMULATION (*)				EXPERIMENTAL RESULTS (*)			
M_n	M_w	PDI	X	M_n	M_w	PDI	X	M_n	M_w	PDI	X
1577.19	3050.24	1.76	0.76	1606.75	3109.36	1.75	0.76	8907	16747	1.88	0.478

(*) Monomer/Solvent = 40/60v/v & Simulation time, t = 40mins

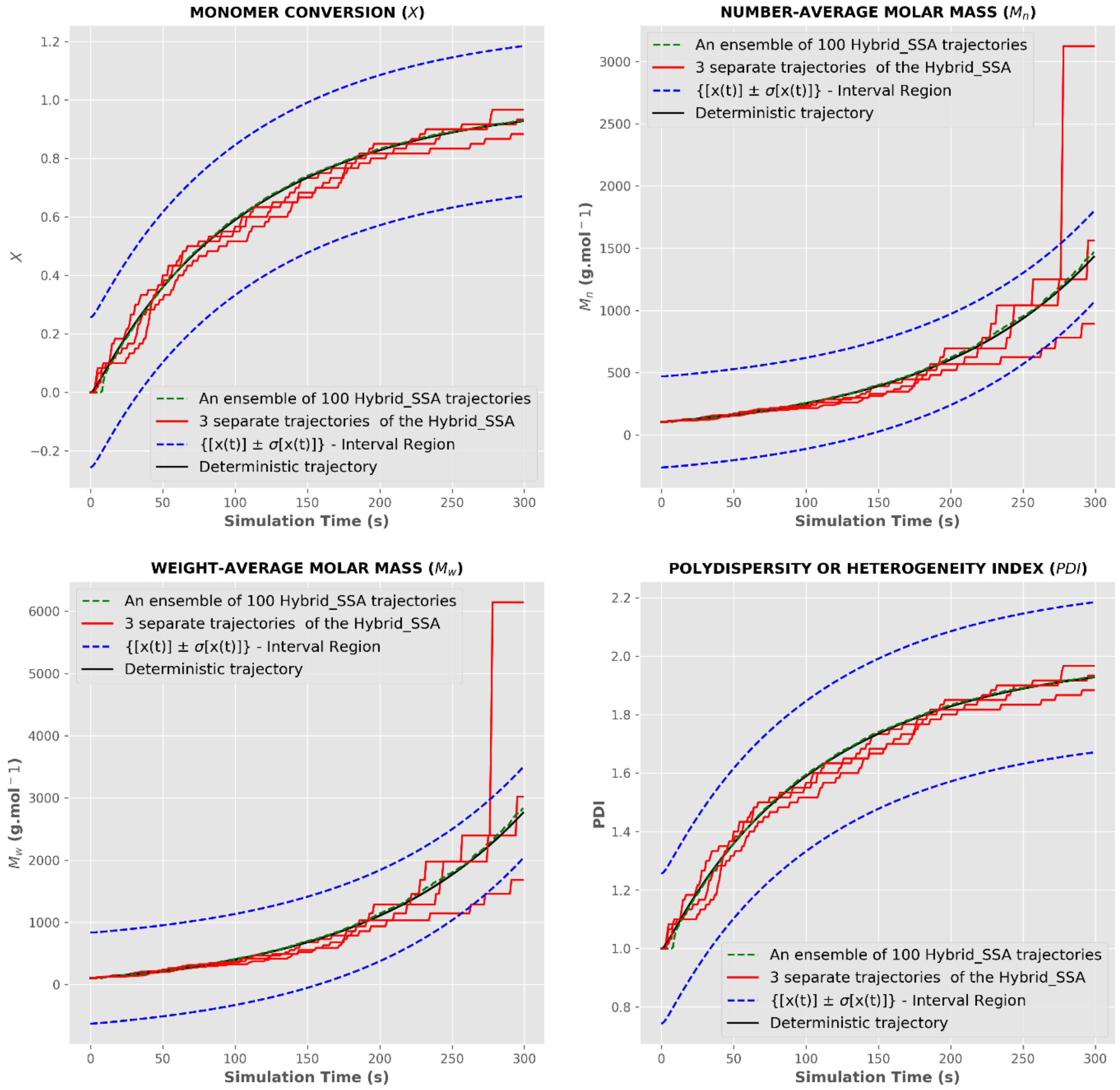

Figure 1- HSSA simulation results with volumetric ratio of monomer to solvent as 60/40 v/v for 5 minutes with the conditions defined in Table 2.

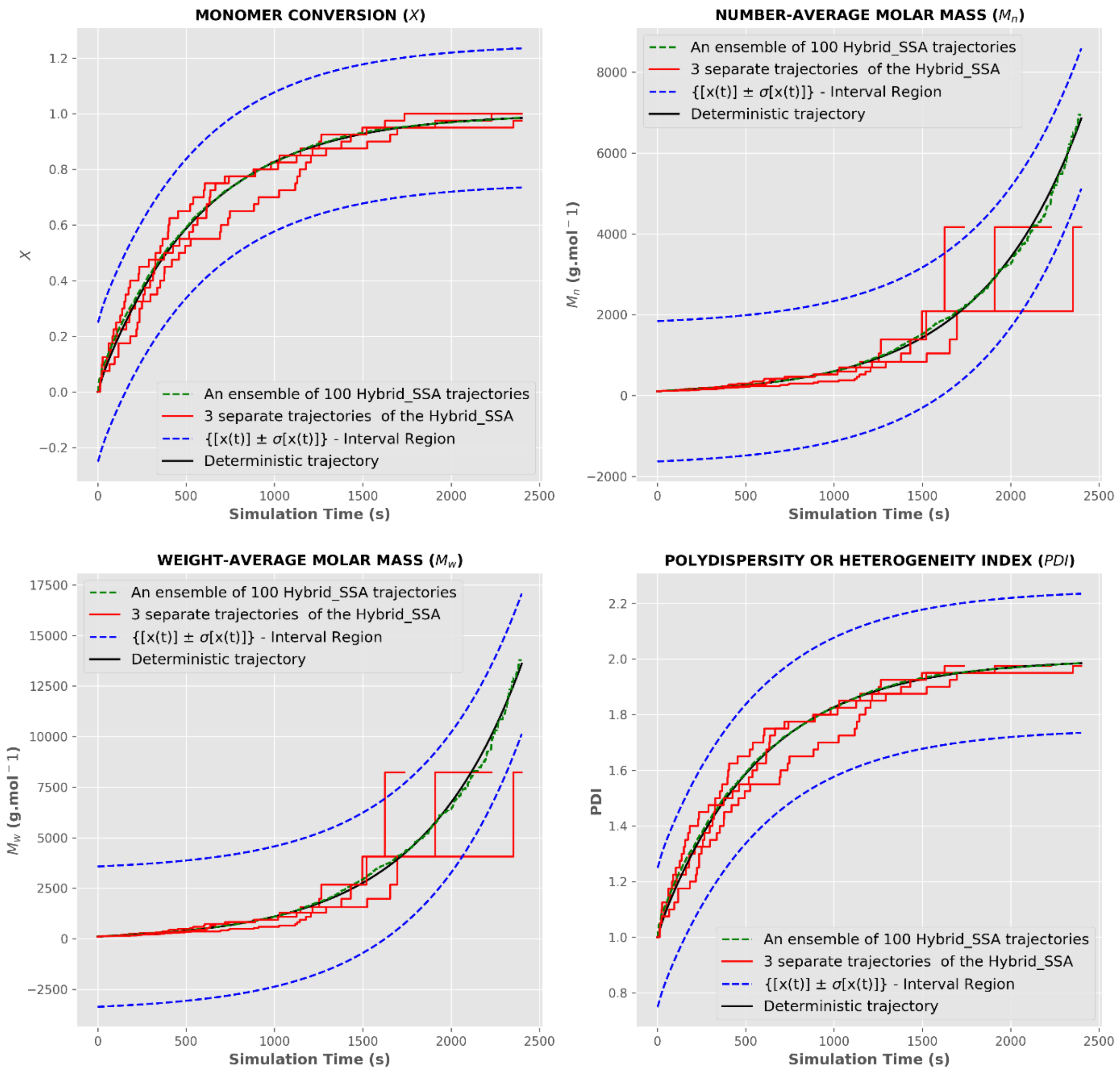

Figure 2- HSSA simulation results with volumetric ratio of monomer to solvent as 40/60 v/v for 40 minutes with the conditions defined in Table 3.

2. Conclusion

Therefore, it suffices to say that the HSSA provided a good prediction of the experiment. The mean P DI was close to 1.5, which implies perfect mixedness of the reaction constituents with the milli-reactor. However, non-idealities due to viscosity variations, fouling of the milli-reactor and, micromixing processes may cause numerical deviations from a standpoint of the experimental situation. Therefore, the application of the HSSA to the simulation of the FRP reaction not only helps in understanding the reaction in microchannels at a micro-scale but is also, applicable in scaling up the process with better productivity while ensuring good end-use polymer qualities.

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Conflict of interest

The authors declare they have no conflict of interest

References

Abel, J., Drawert, B., Hellander, A. and Petzold, L. (2017). Gillespy: A Python package for stochastic model building and simulation. *IEEE Life Sciences Letters*, 2(3), 35-38. https://doi.org/10.1109/LLS.2017.2652448

Dagmar, R.D., Paul, H.M., Pieter, D., M.F., Marie-Françoise & R. Marin, G.B. (2015). Model-based design of the polymer microstructure: Bridging the gap between polymer chemistry and engineering. *Journal of Polymer Chemistry*, 6(40), 7081-7096. https://doi.org/10.1039/c5py01069a

Fullin, L., Melloni, E. and Vianna, A.S.J. (2015). Solution styrene polymerization in a millireactor. *Journal of* Chemical Engineering and Processing: Process Intensification, 98, 1-12. https://doi.org/10.1016/j.cep.2015.09.017

Gillespie, D.T. (1976). A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *Journal of Computational Physics*, 22(4), 403–434. https://doi.org/10.1016/0021-9991(76)90041-3

Gillespie, D.T. (2007). Stochastic simulation of chemical kinetics. Annual *Review of Physical Chemistry*, 58, 35–55. https://doi.org/10.1146/annurev.physchem.58.032806.104637

Hahl, S. K. and Kremling, A. (2016). A comparison of deterministic and stochastic modeling approaches for biochemical reaction systems: On fixed points, means, and modes. *Frontiers in Genetics Journal*, 6, 157. https://doi.org/103389/fgene.2016.00157

Haseltine, E.L. and Rawlings, J.B. (2002). Approximate simulation of coupled fast and slow reactions for stochastic chemical kinetics. *Journal of Chemical Physics*, 117(15), 6959-6969. http://dx.doi.org/10.1063/1.1505860

Higham, D. J. (2008). Modeling and simulating chemical reactions. *The Journal of Society for Industrial and Applied Mathematics*, 50(2), 347-368. https://doi.org/10.1137/060666457

Meimaroglou, D. and Kiparissides, C (2014). Review of Monte Carlo methods for the prediction of distributed molecular and morphological polymer properties. *Journal of Industrial and Engineering Chemistry Research*, 53(22), 8963-8979. https://doi.org/10.1021/ie4033044

Vianna, A. D.S., Biscaia, E.C and Pinto, J.C. (2007). A stochastic flow model for a tubular solution polymerization reactor. *Journal of Polymer Engineering and Science*, 47(11), 1839–1846. https://doi.org/10.1002/pen.20893