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. 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 chaingrowth polymerization reactions even at a large scale.
Keywords: Polystyrene, Microchannels, Hybrid Stochastic Simulation Algorithm, Gillespie Algorithm, Free Radical Polymerization, Process Intensification.

Nomenclature

Average Percentage Error	APE	$(-)$
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_{tc}	$(kgm^{-3}s^{-1})$
Kinetic Constant for Chain Termination by Disproportionation	K_{td}	$(kgm^{-3}s^{-1})$
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}	$(m^6 mol^{-2}s^{-1})$
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	$(°K)$
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	(s)

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 of polymers. 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. Moreso, this computational technique can in turn result in both 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 could 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 towards the improvement 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 polymer. 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 performing 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 complex chemical reactions.

Furthermore, assuming α_0 the cumulative sum of propensity 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 uniform random distribution or URD. Moreso, the degree of discreteness of the simulation is also dependent on the numerical values of α_j, ξ_1 .The original Gillespie Algorithm (Direct Method) is then described according 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, 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 two (2) pseudorandom numbers ξ_1, ξ_2 from a URD or $\sim N(0,1)$. Again, 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 the propensity for the next reaction channel R_j such that:

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

STEP 5: Update the next 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 time of simulation t_f where: $n \geq t_f$. Else, repeat **STEP 2**.

There are some other variants of the GA or SSA. They do offer not only increased computational speed to the simulation of complex chemical reactions such as the FRP but also, they are robust enough to solve the problems associated with the CME representing complex chemical reactions. It is worth noting that the deterministic rate constants or kinetic constants were converted to stochastic rate constants based on the chemistry of the reaction illustrated in the equations below. According to the publication of Gillespie (2007), the kinetic constants were mathematically transformed into stochastic rate constants as follows in Equations 1 through to 4:

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 speed of computation by partitioning the chemical reactions of a given system 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 parallel computation of the stochastic and deterministic simulation of the FRP of styrene model. 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 10 minutes.

Usually, analytical solutions for a complex chemical reaction system such as the FRP of styrene produces over 100,000 stiff ODEs. Moreover, with approximate method like the application of method of moments (MoM), these large set of ODEs are reduced to a fewer number of non-stiff differential equations and differential algebriac euqations (or 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 within a predefined time of simulation. The HSSA computational steps are shown below::

STEP 1: Initiate the FRP of styrene model according to the chemistry of reaction in Table 1. Next, 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:

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

Give that given that $j = (1,2,3,\dots,N)$ and h_j is the number of instant combinations of reactants for reaction, R_j.

STEP 3: Generate two (2) pseudorandom numbers ξ_1, ξ_2 satisfying a URD or $\sim N(0,1)$.

STEP 4: Initiate the stochastic simulation in order to generate the stochastic trajectories by computing the next reaction time and propensity at $t \to t + \tau$ 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 time of simulation t_f where: $n \ge t_f$. 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 $t \rightarrow t + \tau$ using equations in **STEP 4** and the equation:

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

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 time of simulation t_f where: $\ge t_f$. 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 time of simulation t_f where: $n \ge t_f$. Else, repeat **STEP 3**.

STEP 10: Data frame Processing and Computation of the values of X, M_n , M_w, and PDI using Equation (15) to Equation (18).

Referring to **STEP 6** 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 exists 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 that may not capture a reaction channel R_j hence, the algorithm would compute extremely slowly. Therefore, from each iteration, the propensity at $\tau > 0$ 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 every R_j, which is sampled from a Poisson Random Distribution (PRD):

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

Thus, mimicking an explicit Euler iteration technique, the above Equation 5 approximates "leap" for the next chemical reaction system within a time τ which is given by:

$$X(t + \tau) = X(t) + \sum_{j=1}^{M} P_j \left(\alpha_j \tau \right) v_{ij} \tag{6}$$

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, is it assumed that the chain termination is predominantly by disproportionation thus the kinetic constant of termination by combination and disproportionation are related as follows:

$$K_{td} + K_{tc} \gg K_{td} \tag{6}$$

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, then the propensity of propagation for the chain growth reaction is given by:

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

Moreso, by definition β is the probability that a radial on an active chain will propagate rather than terminate.

From the chemistry of reaction in Table 1,

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

Or

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

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:

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

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

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

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

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

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

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, by definition assuming that the

concentration of $[M]$, $[I]$ are constant at low conversion, the probability that a dead chain is an $i -$ mer :

$$P(i) = \beta^{i-1}(1 - \beta) \tag{14}$$

From Equation 14, it can be shown by further mathematical derivation that the number- average and weight - average molecular weights as well as the polydispersity index are given by Equations 15, 16 and 17 respectively:

$$M_N = \frac{2M_s}{(1 - \beta)} \tag{15}$$

$$M_W = M_S \frac{(2 + \beta)}{(1 - \beta)} \tag{16}$$

$$PDI = \frac{M_W}{M_N} = \frac{2 + \beta}{2} \tag{17}$$

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

In addition, the monomer conversion for a monofunctional monomer is given by:

$$X = \frac{[M]_0 - [M]}{[M]_0} \tag{18}$$

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

3. Results and Discussions

The simulation of FRP of styrene was carried out by 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 simulation as reactor volume.

As shown in Table 2, the ratio between solvent and monomer were 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 were 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 (M_N) and weight-average molar mass (M_W) . For completeness, the referenced experimental and the HSSA simulation outcomes were compared. The results generated in Table 2 were used to validate the proposed HSSA model used in this work. Moreso, within a reaction time of 20 to 80 minutes, the Average Percentage Errors or APEs for both the monomer conversion (X) and polydispersity index (PDI) were 23.27%, 11.83% and 20.04%, 13.24% for this work and the referenced work respectively, when considering only the deterministic simulation of the FRP model.

Table 2 - A comparative table of results obtained from the HSSA and experimental results Fullin *et al*. (2015).

Table of results for $M_N(gmol^{-1})$, $M_W(gmol^{-1})$, PDI and X Operating temperature, $\mathbf{T}$ = 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
10008	14908	1.49	0.18	-	-	-	-	6768	13607	1.57	0.091
DETERMINISTIC SIMULATION **				**STOCHASTIC SIMULATION** **				**EXPERIMENTAL RESULTS** **			
M_N	M_W	PDI	X	M_N	M_W	PDI	X	M_N	M_W	PDI	X
6384	9471	1.49	0.24	-	-	-	-	5640	8223	1.68	0.391

* M/S = 60/40 v/v **OR** 41g / 59g, I=1g & Simulation time, t = 5mins.

** M/S = 60/40 v/v **OR** 41g / 59g, I=1g & Simulation time, t = 20mins.

Furthermore, referring to Table 2, it could be observed that the corresponding stochastic outcomes based on the predefined conditions could not be captured. Thus, this proves the effectiveness of the mill reactor used in the referenced experimental work for FRP of styrene. Moreso, the selectivity and optimization of the feeding conditions as well as operating temperatures deployed also ensured that predictions of polymer's end-use properties. However, for the purpose of scaling the polymerization reaction from a microscale to a macroscale, the initial conditions were adjusted for this work. By implementing a scale factor, k of 10^2 to the respective monomer, solvent and initiator input volumetric ratios as well as increasing the temperature correspondingly to 140℃; the following results were recorded in Table 3.

Again, as shown in Table 3, while there were observed deviations for the monomer conversion between the deterministic and stochastic result, the corresponding deviations for the PDIs were reportedly minimal. Moreso, as the reaction time increased, the observed deviation in terms of monomer conversion rates between the stochastic trajectories and corresponding deterministic profiles reduced. This behavioral pattern is captured in Figures 1 and 2. On the other hand, the molecular weight distribution or MWD were well distributed as shown in the Figures below. However, considering the adjusted operating condition, the MWD becomes narrower as shown in the results recorded in Table 3. Overall, as observed for both the deterministic and stochastic outcomes, the recorded PDIs were lesser than 1.50 thus, further indicating a narrow MWD. Therefore, it can be inferred that the polymer chains have a uniform size or length per molecule.

As earlier shown in the HSSA steps in Section 2.2, the HSSA comprises of three (3) separate stochastic trajectories that depicted different outcomes of the chemical reaction as shown in Figure 1 and Figure 2. In addition, the computation of an ensemble of 100 stochastic trajectories using the tau-leaping algorithm were carried-out, which are denoted by dashed green lines in Figures 1 and 2. The tau - leaping stochastic trajectory showed closer agreement with the corresponding deterministic profiles. It is worth noting that the deterministic trajectory or curve provides a "sanity" check to the corresponding stochastic trajectories obtained from every simulation.

Table 3 – Deterministic versus Stochastic simulation results of the HSSA.

Results for $M_N(gmol^{-1})$, $M_W(gmol^{-1})$, PDI and X Operating temperature, $\mathbf{T}$ = 140 ℃ Multiplicative Scale Factor, $\boldsymbol{k} = 10^2$							
DETERMINISTIC SIMULATION *				STOCHASTIC SIMULATION *			
M_N	M_W	PDI	X	M_N	M_W	PDI	X
2472	3605	1.46	0.87	4994	7387	1.48	0.14
DETERMINISTIC SIMULATION *				STOCHASTIC SIMULATION *			
M_N	M_W	PDI	X	M_N	M_W	PDI	X
1467	2096	1.43	0.94	2282	3318	1.45	0.30

* M/S = 60/40 v/v **OR** 41g / 59g, I=1g & Simulation time, t = 5mins.

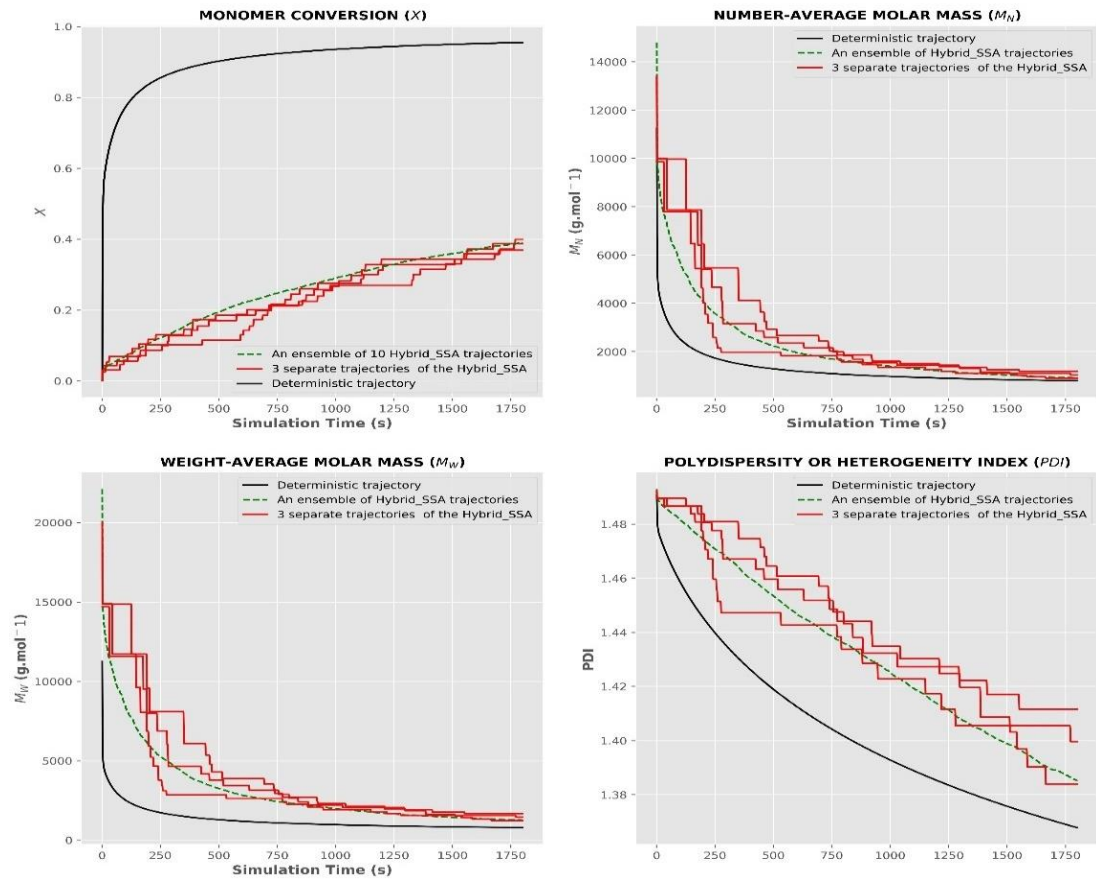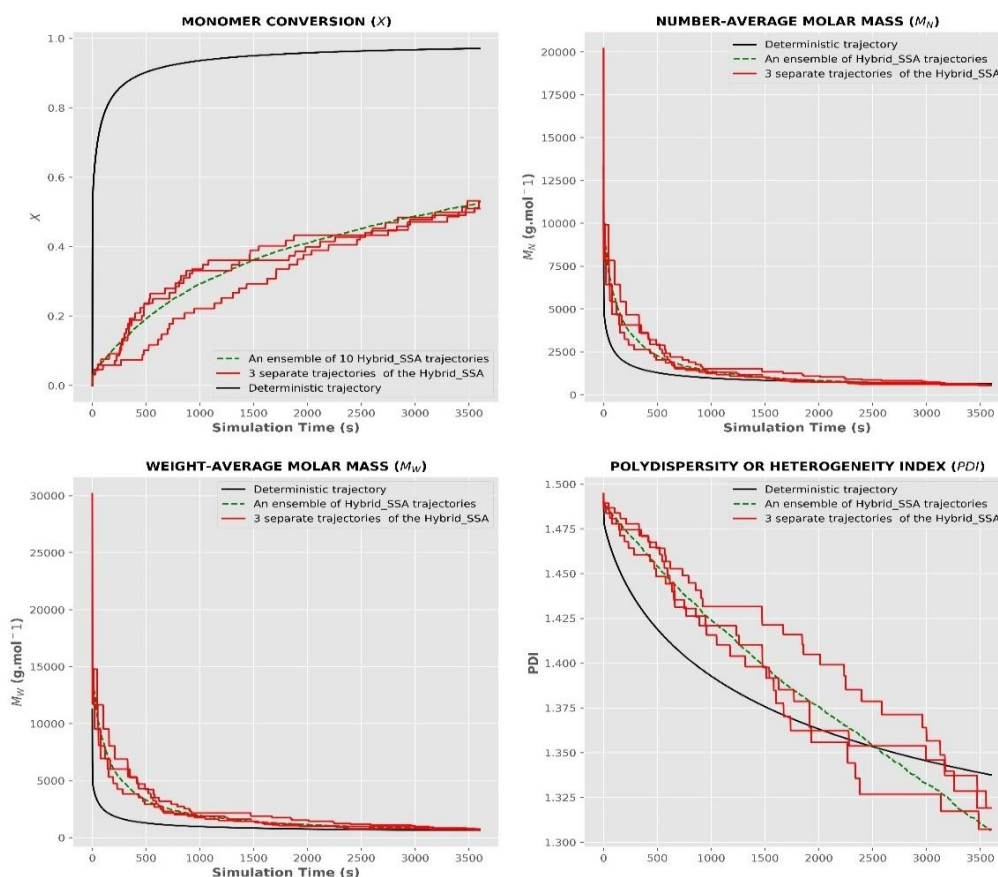** M/S = 60/40 v/v **OR** 41g / 59g, I=1g & Simulation time, t = 20mins.

Figure 1 - A graphical plot of the stochastic versus deterministic trajectories of the FRP of styrene in a microchannel (4mL). The green dashed line represents an ensemble of 100 stochastic trajectories. The initial value of the monomer (M) to solvent (S) in grammes = 41g/59g and initiator (I) = 1g. Operating temperature, T = 140℃, time, t = 30mins and a multiplicative scale factor, k = 10^2 .

Figure 2 - A graphical plot of the stochastic versus deterministic trajectories of the FRP of styrene in a microchannel (4mL). The green dashed line represents an ensemble of 100 stochastic trajectories. The initial value of the monomer (M) to solvent (S) in grammes = 41g/59g and initiator (I) = 1g. Operating temperature, T = 140°C, time, t = 60mins and a multiplicative scale factor, $k = 10^2$.

4. Conclusion

Therefore, it suffices to say that the HSSA provided a good prediction of the experiment. The mean polydispersity index (or PDI) 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 simulate the FRP reaction not only helps in understanding the reaction taking place in the 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

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