SOLUTION STYRENE POLYMERIZATION IN A MILLIREACTOR

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ABSTRACT – The innovative characteristics of microreactors allow producing new materials. The present work analyses the behavior of the Syrris ASIA millireactor for the solution polymerization of styrene. The polymerizations were performed at 100°C, using benzoyl peroxide as initiator and toluene as solvent. Different monomer to solvent ratios and initiator quantities have been tested, besides varying the residence time from 5 to 80 minutes. The variations of the parameters involved gave conversions from 9% to 70%, with MW ranging from 6,000 to 60,000 g/mol. No plugging happened, allowing more aggressive and well controlled applications. A first attempt of modeling was made, using a PFR model and the method of moments to compute the mean distribution. This simplified model gave a good forecast of conversion and average MW for the more diluted experiments, but partially deviated for higher monomer contents, with larger PDIs, meaning a greater discrepancy from plug flow for the millireactor.

1. INTRODUCTION

Microstructured reactors are devices with three-dimensional structures, whose inner dimensions are under a millimeter in size, and more specifically between ten and a hundred micrometers. Process parameters such as pressure, temperature, residence time and flow rate are more easily controlled in reactions that take place in small volumes (Jähnisch *et al.*, 2004). Wegner *et al.* (2011) defined a new category in which to classify reactors that present diameters between 500 μm and a few mm: millireactors. Millireactors have smaller surface to volume ratio but can also present advantages compared to the microreactors, with improved flow capacities (thus higher productivity), lower pressure drops and lower tendency to block. Clogging, in fact, is one of the most serious concerns in dealing with small diameter tubes.

Iwasaki and Yoshida (2005) already performed polymerizations with a 0.5 mm reactor and concluded that microreactors are quite effective for molecular weight distribution control for highly exothermic free radical polymerization, while improvements are less evident for less exothermic ones. Rosenfeld *et al.* (2007) carried out continuous TIPNO-mediated styrene polymerizations in toluene in a 900 μm i.d. stainless steel tube reactor: he also verified a better reaction control of high exothermic reactions. In 2011 Mandal *et al.* studied a coiled configuration of a 2 mm millireactor and observed a higher conversion and satisfactory polymer molecular weights, due to a better mixing caused by the reactor curves.

In the present work the behavior of the Syrris "Asia 120" reactor in relation to the styrene free-radical polymerization was studied. The device presents an i.d. of 0.5 mm, that is geometrical characteristics which are not conventional in industry, and a 20.37 m length. The potential advantages of carrying out exothermic reactions were evaluated, and resulted in a good control over conversions and polymer properties. The styrene polymerization was performed in toluene (benzoyl peroxide as initiator); the presence of solvent was required in order to use quite aggressive reaction conditions: solvent, in fact, decreases the overall viscosity, thus preventing the reactor from plugging.

2. FUNDAMENTALS

For the styrene polymerization, the kinetic scheme assumed includes chemical and thermal initiation, propagation, chain transfer to monomer and solvent, and termination only by combination. For the gel effect contribution, the formula by Hui and Hamielec (1972, apud CABRAL, 2003) was applied. The volume change during the reaction can be also introduced in the model through a contraction factor, ϵ, whose definition can be found in the work by Tulig and Tirrell (1981). Since the reactor is supposed to operate isothermally, no energy balance is required.

The method of moments was employed to calculate the number and mass average molecular weight, defining the moments of order k as:

$$\lambda_k = \sum_{n=1}^{\infty} n^k [R_n \cdot] \qquad \mu_k = \sum_{n=1}^{\infty} n^k [D_n] \qquad (1,2)$$

Tubular reactors behavior is commonly modeled as a PFR, in the most simplified case: this simple model will be used as a first approach to simulate the reactor performance.

Equations 3-12 report the mass balances to be solved for the polymerization in the millireactor:

$$\frac{d(c_{init})}{dz} = -\frac{1}{v_z} k_d c_{init} + \frac{1}{v_z} \frac{c_{init} Q_{sty_0} \epsilon}{A} \frac{d\chi}{dz} \qquad (3)$$

$$\frac{d(c_{sty})}{dz} = \frac{1}{v_z} \left[-2 f k_d c_{init} - (k_p + k_{tm}) c_{sty} \lambda_0 - k_{ti} c_{sty}^3 \right] + \frac{1}{v_z} \frac{c_{sty} Q_{sty_0} \epsilon}{A} \frac{d\chi}{dz} \qquad (4)$$

$$\frac{d(c_{tol})}{dz} = \frac{1}{v_z} \left(-k_{ts} c_{tol} \lambda_0 \right) + \frac{1}{v_z} \frac{c_{tol} Q_{sty_0} \epsilon}{A} \frac{d\chi}{dz} \qquad (5)$$

$$\frac{d(\lambda_0)}{dz} = \frac{1}{v_z} \left[2 f k_d c_{init} - k_t \lambda_0^2 + k_{ti} c_{sty}^3 \right] + \frac{1}{v_z} \frac{\lambda_0 Q_{sty_0} \epsilon}{A} \frac{d\chi}{dz} \qquad (6)$$

$$\frac{d(\lambda_1)}{dz} = \frac{1}{v_z} \left[2 f k_d c_{init} + k_p c_{sty} \lambda_0 + (k_{ts} c_{tol} + k_{tm} c_{sty})(\lambda_0 - \lambda_1) + k_{ti} c_{sty}^3 - k_t \lambda_0 \lambda_1 \right] +$$
$$\frac{1}{v_z} \frac{\lambda_1 Q_{sty_0} \epsilon}{A} \frac{d\chi}{dz} \qquad (7)$$

$$\frac{d(\lambda_2)}{dz} = \frac{1}{v_z}\left[2fk_d c_{init} + k_p c_{sty}(\lambda_0 + 2\lambda_1) + (k_{ts}c_{tol} + k_{tm}c_{sty})(\lambda_0 - \lambda_2) + k_{ti}c_{sty}^3 - k_t\lambda_0\lambda_1\right] + \frac{1}{v_z}\frac{\lambda_2 Q_{sty_0}\epsilon}{A} \tag{8}$$

$$\frac{d(\mu_0)}{dz} = \frac{1}{v_z}\left[(k_{ts}c_{tol} + k_{tm}c_{sty})\lambda_0 + k_t\frac{\lambda_0^2}{2}\right] + \frac{1}{v_z}\frac{\mu_0 Q_{sty_0}\epsilon}{A}\frac{d\chi}{dz} \tag{9}$$

$$\frac{d(\mu_1)}{dz} = \frac{1}{v_z}\left[(k_{ts}c_{tol} + k_{tm}c_{sty})\lambda_1 + k_t\lambda_0\lambda_1\right] + \frac{1}{v_z}\frac{\mu_1 Q_{sty_0}\epsilon}{A}\frac{d\chi}{dz} \tag{10}$$

$$\frac{d(\mu_2)}{dz} = \frac{1}{v_z}\left[(k_{ts}c_{tol} + k_{tm}c_{sty})\lambda_2 + k_t(\lambda_1^2 + \lambda_0\lambda_2)\right] + \frac{1}{v_z}\frac{\mu_2 Q_{sty_0}\epsilon}{A}\frac{d\chi}{dz} \tag{11}$$

$$\frac{d(\chi)}{dz} = -\frac{V}{n_{sty_0} - V_{sty_0}c_{sty}\epsilon}\frac{dc_{sty}}{dz} \tag{12}$$

3. MATERIALS AND METHODS

3.1. Reactor description

The Syrris microreactor used was composed of various modules:

1. The tubular reactor, with a total volume of 4 mL, an i.d. of 0.5 mm and a length of 20.37 m, formed by a Teflon tube rolled on a heated cylinder.
2. The bottles pressurizing modulus, where reagents were charged under continuous nitrogen flux, in order to pressurize the bottles and to avoid oxygen in the reaction.
3. The heater, which permitted to set temperatures up to 125 °C.
4. The syringe pumps modulus, where two syringes for each pump (two in total) allowed a feed injection into the reactor from 10 μl/min up to 2.5 ml/min (that means a residence time ranging from 1 min 36 s to 400 min).

In each experiment, only one injection pump was used, which meant that the reagents mixture happened before the feed entrance. Each unit was connected through Teflon tubes. Before starting each experiment, the heater unit was set to a constant temperature of 100 °C and toluene was run through the reactor, in order to condition it and to remove all the possible residuals. This procedure was adopted at the end of each experiment, too, to clean all the tubes: it is crucial to do it early, in order to prevent the polymer from cooling out, solidifying and eventually clogging the reactor. Figure 1 reports the reactor operation scheme.
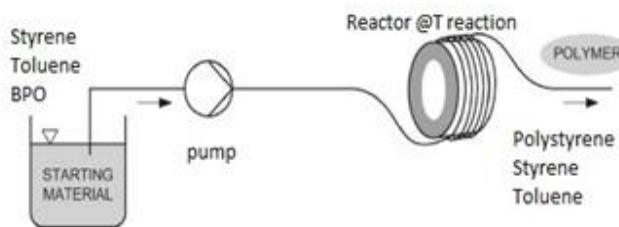

Figure 1 - Reactor operation scheme.

3.2. Reagents preparation

The experiments were done without any sort of additional purification, and reagents were used as received:

a) Styrene (S), used as monomer, liquid. BASF, industrial purity;
b) Toluene (T), used as solvent, liquid. Vetec, 99.5%;
c) Benzoyl peroxide, used as initiator, white solid powder. Arkema, 75%;
d) Methanol (MET), used to precipitate the polystyrene formed, liquid. Vetec, 99.8%;
e) Tetrahydrofuran (THF), used in the GPC analysis, liquid. J. T, Baker, 99.997%;
f) Nitrogen (N2), used to remove oxygen, gaseous. White Martins, Industrial purity;
g) Acetone (ACE), used to clean laboratory glassware, liquid. Synth, 99.5%.

The reactional solution was prepared by weighing the masses of the monomer, solvent and initiator, in order to obtain about 100 g of solution.

The ratio between solvent and monomer was chosen so that it could be possible to use empirical correlations already present in literature. Cabral *et al.* (2004) calculated in their work the dependence of solution density on reaction conversion for the following toluene to styrene volumetric ratio: 60/40, 50/50, 40/60, 30/70. The same empirical correlation was assumed here in order to deduce conversions from density values.

Two sets of experiments were performed: experiments 1 to 4 had a volumetric ratio 40/60, while experiments 5 to 8 had a ratio 60/40. Initiator mass and feed flow were the two variables to be varied to obtain polystyrenes with different properties. In the experimental conditions shown later on, residence times instead of flow rates will be reported.

3.3. Samples collection and analysis

The reagents were mixed and put in the bottle which feeds the syringe pump; the pump was set to different pumping velocities, varying the residence time τ of the reactive solution, too. The temperature was always set to 100°C. After waiting for about three τ, in order to reach steady-state, a sample was collected and its density was measured.

From this sample, the polymer was separated from the solution with the addition of methanol; then, in a becker, the polymer was dried under agitation and under a flux of nitrogen which helped the evaporation of styrene, toluene and alcohol.

The resulting powder was collected and a very small quantity of it was analyzed through GPC, after dissolution in THF. The equipment used was a multidetector *ViscotekGPCmaxVE2001*, with 3 columns of 8 mm diameter and pore diameter of 10^3Å. The instrument calibration was made by using the standard PS-105K. The aforementioned GPC employs three detectors: RI detector, LALS and RARS detector and IV detector.

3.4. Numerical simulation

To better understand and predict the behavior of the millireactor, a PFR model was chosen to solve the mass balances in the *Matlab* environment. Equations 3 to 12 resulted to be stiff. The resolution of the system was performed by using the ODE15s solver, which uses an implicit resolution method and is appropriated for stiff problems. The kinetic constants used are reported in Vianna Jr. (2011).

4. RESULTS AND DISCUSSION

The experimental results of the eight different conditions performed are presented in Tables 1 and 2: the first one reports conversions results, while the second one molecular weights results.

Table 1 – Experimental Conversions.

Conversion	Toluene/Styrene 60/40 v/v						Conversion	Toluene/Styrene 40/60 v/v				
	X Run1	X Run2	X Run3	X Run4	X Run5	$X_{average}$		X Run1	X Run2	X Run3	X Run4	$X_{average}$
Exp 1 τ=5 min m_{init}=1 g	0.0896	0.093	0.083	0.098		**0.091**	**Exp 5** τ=40 min m_{init}=1.5 g	0.462	0.473	0.5		**0.478**
Exp 2 τ=20 min m_{init}=1 g	0.241	0.266	0.312	0.268	0.275	**0.272**	**Exp 6** τ=40 min m_{init}=1 g	0.397	0.411	0.433		**0.414**
Exp 3 τ=20 min m_{init}=2 g	0.372	0.408	0.37	0.413		**0.391**	**Exp 7** τ=80 min m_{init}=1 g	0.56	0.658	0.722	0.61	**0.638**
Exp 4 τ=20 min m_{init}=0.5 g	0.158	0.18	0.187	0.198		**0.181**	**Exp 8** τ=80 min m_{init}=0.2 g	0.233	0.234	0.361	0.29	**0.279**

Table 2 – Experimental Molecular Weights.

MW [kg/kmol]	Toluene/Styrene 60/40 v/v				MW [kg/kmol]	Toluene/Styrene 40/60 v/v			
	Mn PD 1st Analysis	Mn PD 2nd Analysis	Mn PD 3rd Analysis	$Mn_{average}$ $PD_{average}$		Mn PD 1st Analysis	Mn PD 2nd Analysis	Mn PD 3rd Analysis	$Mn_{average}$ $PD_{average}$
Exp 1 τ=5 min m_{init}=1 g	6919 1.63	6616 1.51		**6768 1.57**	**Exp 5** τ=40 min m_{init}=1.5 g	10280 1.56	8770 1.92	7670 2.27	**8907 1.88**
Exp 2 τ=20 min m_{init}=1 g	5892 1.874	6463 1.7	7408 1.84	**6587 1.80**	**Exp 6** τ=40 min m_{init}=1 g	8615 2.77	10264 1.59	8886 2.4	**9255 2.22**
Exp 3 τ=20 min m_{init}=2 g	5210 1.47	6069 1.45		**5640 1.46**	**Exp 7** τ=80 min m_{init}=1 g	13388 1.73	11927 1.88	14169 1.65	**13786 1.86**
Exp 4 τ=20 min m_{init}=0.5 g	10334 1.67	11905 1.85	12354 1.51	**11531 1.68**	**Exp 8** τ=80 min m_{init}=0.2 g	35385 1.61	24375 1.78	33472 2.05	**31077 1.81**

By comparing the first group of four experiments with the second one, a general rise of conversion, molecular weights and PDI is observed. This is due to the fact that the monomer concentration is higher and, in case of conversion, reactions happen for longer τ. The PDI probably rises due to the chain transfer reactions between polymer and solvent or monomer, that happen for greater τ; a possible not perfect mixing within the reagents; a stronger gel effect (due to the higher monomer concentration), that reduces the termination reaction more sharply.

4.2. Comparison with model results

In Tables 3, 4, 5 and 6 experimental and *Matlab* results are compared for each experiment.

Table 3 – Experimental vs. Model Data: Exp1 (left); Exp2 (right)

Experimental Average Conversion			Model Conversion			Experimental Average Conversion			Model Conversion		
0.091			0.09			0.272			0.298		
GPC Average MW			Model MW			GPC MW			Model MW		
Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD
6768	10607	1.57	8775	13106	1.5	6587	11876	1.8	8976	13422	1.5

Table 4 – Experimental vs. Model Data: Exp3 (left); Exp4 (right)

Experimental Average Conversion			Model Conversion			Experimental Average Conversion			Model Conversion		
0.391			0.408			0.181			0.216		
GPC Average MW			Model MW			GPC MW			Model MW		
Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD
5640	8223	1.46	6155	9157	1.49	11531	19330	1.68	8976	13422	1.5

Table 5 – Experimental vs. Model Data: Exp5 (left); Exp6 (right)

Experimental Average Conversion			Model Conversion			Experimental Average Conversion			Model Conversion		
0.478			0.623			0.414			0.528		
GPC Average MW			Model MW			GPC MW			Model MW		
Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD
8907	16747	1.88	12046	18208	1.51	9255	20497	2.22	15000	22786	1.52

Table 6 – Experimental vs. Model Data: Exp7 (left); Exp8 (right)

Experimental Average Conversion			Model Conversion			Experimental Average Conversion			Model Conversion		
0.638			0.753			0.279			0.4		
GPC Average MW			Model MW			GPC MW			Model MW		
Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD	Mn	Mw	PD
13786	25571	1.86	16683	26233	1.57	31077	56368	1.81	39895	65383	1.64

The model seems to overestimate the conversion obtained, as well as M_w and M_n, and the simplifications made had the consequence of underestimating the polydispersity index. In fact, its theoretical instantaneous value in a polymerization in which termination happens only by combination is 1.5.

5. CONCLUSIONS

In conclusion, polymerization reactions are well controlled (with low PDI values) by the millireactor Asia, besides satisfactory conversions values were achieved (considering the reactor small size), and no fouling occurred. A successful polymerization control allows a reactor of such characteristics being scaled up and employed in greater productivities, since it ensures good polymers qualities.

The PFR model represented the experimental results partially, due to its simplifications. A possible explanation of high conversion values estimated in the second four experiments can be associated to the gel effect correlation: as Cabral *et al.* (2004) already pointed out, the formula is derived from a bulk styrene polymerization and it may need to be softened in case of modeling solution polymerizations. PDIs were always close to 1.5, due to the model choice, which implies perfect mixedness along the reactor section; however, non-idealities due to viscosity variations and micromixing processes may cause deviations from this situation. Future studies on this reactor should be oriented to develop RTD experiments, in order to verify its fluid dynamics.

6. NOMENCLATURE

List of abbreviations

GPC gel permeation chromatography
i.d. internal diameter
IV intrinsic viscosity (detector)
LALS low angle light scattering
ODE ordinary differential equation
PD or PDI polispersity index

PFR plug flow reactor
PS polystyrene
RALS right angle light scattering
RI refractive index
THF tetrahydrofuran
TIPNO tert-butyl isopropyl phenyl nitroxide

List of symbols

A reactor area, $[m^2]$

$c_{init}, c_{sty}, c_{tol}$ initiator, styrene and toluene concentrations, $[mol\ m^{-3}]$

$[D_n]$ dead polymer concentration of a molecule having n repeat units, $[mol\ m^{-3}]$

f initiator efficiency

k_d rate constant for initiation in presence of the gel and glass effects, $[s^{-1}]$

k_p, k_t, k_{tm}, k_{ts} rate constants for propagation, termination with gel effect, chain transfer to monomer and solvent $[m^3 mol^{-1}s^{-1}]$

k_{ti} thermal initiation rate constant, $[m^6 mol^{-2}s^{-1}]$

Mw weight average molecular weight of polymer, $[kg/kmol]$

MW molecular weight, $[kg/kmol]$

n_{sty_0} initial moles of styrene, $[mol]$

Q volumetric flow rate, $[m^3 s^{-1}]$

Q_{sty_0} initial styrene volumetric flow rate, $[m^3 s^{-1}]$

$[R_n \cdot]$ living polymer concentration of a molecule having n repeat units, $[mol\ m^{-3}]$

T temperature of the reaction mixture, $[K]$

v_z fluid velocity in the axial direction, $[m\ s^{-1}]$

m_{init} initiator mass, $[g]$

Mn number average molecular weight of polymer, $[kg/kmol]$

Greek letters

ϵ volume contraction factor

$\lambda_k(k = 0,1,2), \mu_k(k = 0,1,2)$ moment of live and dead polymer, $[mol\ m^{-3}]$

V volume of liquid at conversion x, $[m^3]$

V_{sty_0} initial volume of styrene, $[m^3]$

z reactor length coordinate, $[m]$

τ residence time, $[min]$

χ monomer conversion (molar) at residence time τ

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