Free-Radical Polymerization of Methacrylic Acid: From Batch to Continuous Using Stirred Tank Reactors

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Abstract: In the last years important efforts have been made to convert the traditional batch polymer production to continuous. This transition allows to overcome most of the limitations of discontinuous or semi-continuous processes, such as environmental and safety issues and inadequate product quality. In this work we propose a model–based strategy to convert the solution free-radical polymerization of non-ionized methacrylic acid (MAA) from semibatch to continuous while preserving the product average molecular weight and polymer content. First, a purely kinetic model for the polymerization of MAA was validated for batch, semibatch and continuous stirred tank reactors (CSTR). Then, a basic optimization approach was applied to guide the transition of a selected semibatch process to a CSTR. This strategy results in a substantial productivity increase (5.1 times higher than in the original semibatch) while preserving the selected polymer average molecular weight and dry content. Finally, in order to reduce the residual monomer in the product leaving the CSTR, we simulated the addition of a tubular reactor. This was modelled introducing a small plug flow reactor in series to the CSTR. This approach represents an effective and robust tool for polymer manufacturers to assist switching their productions to continuous preserving their product portfolio.

KEYWORDS: Free-Radical Polymerization; Continuous Stirred Tank Reactor; From Batch to Continuous; Kinetic Modelling; Optimization; Poly(Methacrylic Acid)

1. Introduction

Polymers are industrially produced by means of different polymerization techniques depending upon the choice of the monomers and the desired final polymer features. Among them, one of the most important and established technique is free-radical polymerization (FRP)[1]. It can be performed either in homogeneous (*e.g.*, bulk and solution) or heterogeneous environment (*e.g.*, emulsion and

suspension) depending upon the monomer and polymer solubility in the continuous phase. Irrespectively of the conditions, FRP can be performed in discontinuous or continuous reactors[2].

Nowadays, the majority of the industrial processes of polymer production relies on batch or semibatch reactors, given their easy conduction and versatility of polymer grades. However, these traditional configurations are characterized by safety, environment, and cost limitations. In fact, discontinuous systems are typically characterized by poor productivity, mainly connected to the dead times required to load the reactor, recover the product, and clean the vessel. In addition, the big volumes required by the ever increasing polymer demand represent a substantial safety concern. In fact, in case of disastrous situations (*e.g.*, runaway, emissions, explosions etc.) the magnitude of the related risks would be extremely high. The adoption of a continuous process would allow to alleviate most of these limitations. In fact, the typically high productivity of a continuous system not only enables to intensify the production but also to reduce the monomer and solvent hold-up, the main source of safety and environmental risks.

The transition from discontinuous to continuous FRP is often accomplished with difficulties, in particular when the reproduction of the same process (*i.e.*, conversion, productivity, heat removal capacity, etc.) and product (*i.e.*, solid content, molecular weight distribution (MWD), nanoparticle size, etc.) features of the discontinuous reactor is essential. These difficulties are mainly attributed to the different fluid-dynamic and residence time distribution between discontinuous and continuous reactors, in addition to the difficulty in handling the viscous polymer mixture in a continuous configuration. All these considerations make the transition to continuous processes in the polymer field very challenging[3]–[5].

In this scenario, mathematical models can represent a very efficient tool to study and guide the implementation of continuous processes, enabling the identification of optimal operating conditions while saving time and experimental effort. For example, models have been successfully used to predict the transition of the solution polymerization of non-ionized acrylic acid[6], [7] or to study the impact of micromixing in the solution polymerization of methyl methacrylate (MMA) in a continuous stirred tank reactor (CSTR)[8]. This is a topic of primary interest from both academic and industrial points of view, as testified by several recent publications[6], [9], [10]. In particular, companies have interest in the production of large volumes of polymers always preserving their quality, in order not to alter their portfolio and ensure continuity in their business. In this context, one of the most industrially appealing product is poly(methacrylic acid) (PMAA) mainly due to the manifold applications that this polymer finds in the fields of organic coatings[11], [12], adhesives[13], [14], leather treatment[15], ion-exchange resins[16], textiles[17], and paper industries[18]. Aqueous solution FRP of MAA has been extensively studied in a wide range of concentrations, from 1% w/w

to bulk polymerization[19]–[21], but always considering batch or semibatch processes[22]–[24]. Indeed, to the best of our knowledge, a contribution focused on the relevant aspects of the transition from the traditional discontinuous processes to the continuous ones is still missing in literature.

In this work, we developed a model-based strategy for the transition of a semibatch MAA production to an intensified continuous process using a CSTR. In particular, we first developed and validated a purely kinetic model able to predict conversion and MWD of PMAA produced either in batch, semibatch or CSTR. The model was made of mass and population balance equations, with kinetic parameter values as measured by pulsed laser polymerization in previous studies on MAA. Namely, Lacík et al. were able to reliably estimate propagation as well as termination rate constants of MAA at different concentrations and ionization degrees, providing functional forms for these constants with wide range of validity [21], [25], [26]. Then, we applied this model to design the transition of a selected semibatch process to a continuous one using a CSTR with the constraint of providing the same weight-average molecular weight (Mw) and polymer content (PC) obtained in the semi-continuous process. A basic but robust optimization approach is adopted, exploring the process performances in terms of Mw, PC and productivity as a function of four different operating variables, namely inlet volumetric flow rate, inlet monomer, water, and initiator concentrations. Among the collected results, those providing minimum conversion of 98% and the highest productivity are selected. To reduce the concentration of the residual monomer leaving the CSTR to the value imposed by the current regulation, the use of a tubular reactor in series to the CSTR is finally examined.

With this approach, a substantial intensification of the process was achieved, while obtaining a product very similar to the one produced in semibatch reactors. Therefore, this strategy could represent a booster in the transition from batch to continuous polymer production.

2. Experimental section

2.1. Materials

Methacrylic acid (MAA, 99%), ammonium persulfate (APS, 98%), hydroquinone (≥99%) and acetonitrile (ACN, 99.9%, analytical grade) were purchased from Sigma Aldrich and used as received. Analytical grade water was used without further treatment.

2.2. Non-ionized methacrylic acid solution polymerization

2.2.1. Batch FRP

Different polymerizations were performed using MAA as monomer, APS as initiator and water as solvent. The monomer weight concentration was kept constant to 5% w/w for all the syntheses while the initiator to monomer weight ratio was varied in the range 0.5-3% weight based on monomer (wbm) in order to produce polymers with different molecular weights. In a typical polymerization

protocol, 2.5 g of MAA were solubilized in 45 g of distilled water. The solution was poured in a 100 mL round bottom flask equipped with a magnetic stirrer, purged with nitrogen for 30 minutes in order to remove the oxygen and then heated to 50 °C in an oil bath under stirring (500 rpm). Then 0.025 g of APS in 2.475 g of water were added to the flask by the use of a syringe and the reaction was let to occur for 5 hours. Samples were taken at regular time intervals, hydroquinone was added to quench the reaction and the conversion was evaluated via thermogravimetric analysis (described in Section 2.3.). For the measurements of the MWD, the samples were freeze-dried overnight using a Telstar Lyoquest freeze-drier at a pressure of 0.1 mbar and -56 °C and analysed via aqueous gel permeation chromatography (GPC) according to the procedure described in Section 2.4.

2.2.2. Semibatch FRP

These reactions were carried out varying both the initiator to monomer weight ratio and the monomer feeding time (FT) in order to validate the model under different conditions. As an example, 0.23 g of APS were dissolved in 49.77 g of distilled water and poured into a 100 mL round bottom flask equipped with mechanical stirrer. The mixture was purged with nitrogen for 30 minutes in order to remove the oxygen and placed in an oil bath at a selected temperature. In particular, for semibatch reactions two different temperatures were tested, namely 50 and 60 °C. In the meanwhile, 10 g of methacrylic acid were loaded in a syringe pump (New Era Pump systems, NE-300). Five different FT were implemented, 20, 30, 40, 50, and 120 minutes, respectively. Once the addition of the monomer was over, the polymerization was protracted in batch for further 30 minutes, in order to deplete all the residual monomer. To monitor conversion and MWD during time, samples were taken at regular times (*i.e.*, 0, 5, 10, 15, 25, 35, 50, 90, 120 minutes). Polymer molecular weights were analysed with the protocol described in Section 2.4 while the conversion was evaluated according to the procedure described in Section 2.3.

2.2.3. CSTR

A 100 mL round bottom flask was filled with 50 g of water. Nitrogen was bubbled for 30 minutes to remove oxygen and the flask was thermostated in a pre-heated oil bath at 60 °C. The flowrates of inlet and outlet streams were controlled by two peristaltic pumps (New Era Pump systems, NE-9000B). In a typical experiment, an inlet stream of 5 10^{-3} L/min with monomer concentration of 1.84 mol/L and initiator concentration of 3.97 10^{-2} mol/L was fed to the reactor. The outlet volumetric flow rate was adjusted in order to ensure constant reaction volume equal to 50 mL. The actual experimental discretization of the outlet flowrate predicted by the model is shown in **Figure S1**. Samples were taken at regular intervals in order to evaluate monomer conversion (Section 2.3) and polymer MWD following the same protocol described below. In order to reach the steady state conditions, the reaction experiment lasted 24 hours.

2.3. Thermogravimetric analysis

An Ohaus MB35 Moisture Analyser was used as already shown in literature[27]. 1 mL of the reaction mixture was sampled, immediately inhibited by adding 0.06 g of hydroquinone and weighted on an aluminium disk. Then, the disk was heated up to 160 °C in order to guarantee water and monomer evaporation. Finally, the dry polymer was used to calculate the monomer conversion according to **eqs. S1-S3** in **Table S1**.

2.4. MWD analysis by GPC

Aqueous gel permeation chromatography analysis was performed on a Jasco 2000 system. After freeze-drying the samples, they were dissolved at 5 mg mL^{-1} in 0.05 M Na_2SO_4/acetonitrile 80/20 v/v solution and filtered by means of 0.45 μm pore-size nylon membrane. The flow rate was set at 0.5 mL min^{-1} at the temperature of 35 °C with a guard column and three Suprema columns (Polymer Standards Service; particle size 10 μ m, pore sizes of 100, 1000, and 3000 Å).

The polymer MWD and mean values (*i.e.* weight-average molecular weight, Mw, and number-average molecular weight, Mn) were evaluated by size exclusion chromatography using poly(acrylic acid) (PAA) standards (16 – 1100 kDa) for the calibration curve. Therefore, the Mark-Houwink equation (**eq. 1**) was applied to determine the actual (PMAA) molecular weight.

$$k_1 M_{P,1}^{1+a_1} = k_2 M_{P,2}^{1+a_2} \qquad (1)$$

Here k and a are the Mark-Houwink parameters, which depend on the specific combination solvent-polymer and temperature, M_P is the polymer molecular weight, and the subscripts 1 and 2 indicate two different polymers (in our case, PAA and PMAA). Specifically, a = 0.86 and k = 0.004 mL/g and a = 0.65 and k = 0.0449 mL/g were used for PAA and PMAA, respectively [28]. These values correspond to temperature of 35 °C and mixed solvent at 0.05 M NaNO3/acetonitrile 80/20 v/v, a composition very similar to that of the eluent used in this work. Moreover, the same values can be applied in a range of molecular weight up to 1.1 10^6 Da, consistent with the results of this work.

The results provided by this analytic method, despite being reasonable for monomer conversion >30%, proved to be unreliable at low polymer content. Therefore, the ability of the model to predict the molecular weight distribution of the product was judged based on the data acquired at conversions higher than 30% only.

3. Model development and kinetic parameters

The kinetic scheme in **Table 1** is considered. Ammonium persulfate is used as thermal initiator; given the large reactivity of the initiator fragments, the primary radicals $R_1^{\bullet}$ are reported as reaction products. Active chains of any length ($R_n^{\bullet}$) undergo propagation, chain transfer to monomer and bimolecular termination, both by disproportionation and combination. Dead chains (P_n) are formed by termination reactions.

Table 1 Kinetic scheme for the solution polymerization of non-ionized methacrylic acid: initiation (2), propagation (3), bimolecular termination (4), and chain transfer to monomer (5) were considered.

Chain initiation	$I_2 \xrightarrow{k_d} 2R_1^{\bullet}$	$r_i = 2 \cdot f \cdot k_d \cdot I$	(2)
Propagation	$R_n^{\bullet} + M \xrightarrow{k_p} R_{n+1}^{\bullet}$	$r_p = k_p \cdot M \cdot R$	(3)
Termination by disproportionation	$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_{td}} P_n + P_m$	$r_t = (k_{tc} + k_{td}) \cdot R^2$	(4)
Termination by combination	$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_{tc}} P_{n+m}$		
Chain transfer to monomer	$R_n^{\bullet} + M \xrightarrow{k_{tr,M}} P_n + R_1^{\bullet}$	$r_{tr,M} = k_{tr,M} \cdot M \cdot R$	(5)

The values of all the rate constants are from the literature, mainly estimated by pulsed-laser polymerization: such values as well as the corresponding sources are summarized in **Table 2**. In case, the dependence on instantaneous monomer concentration, average chain length and reaction temperature are included. While the temperature dependence of monomer and water density is accounted for, the polymer density is assumed constant.

Table 2 Numerical values of the parameters in the rate laws and corresponding sources.

$k_d/(s^{-1}) = 1.17e22 \cdot \exp(\frac{-21169}{T/K})$ $f = 0.5$	[29]
$k_p/(L \cdot mol^{-1} \cdot s^{-1}) = 4.1e6 \cdot \exp(\frac{-1880}{T/K}) \cdot (0.08 + 0.92 \cdot \exp\left(\frac{-5.3 \cdot w_{MAA}^0 \cdot (1-X)}{1 - w_{MAA}^0 \cdot X}\right) \cdot \exp(0.096 + \frac{0.11 \cdot w_{MAA}^0 \cdot (1-X)}{1 - w_{MAA}^0 \cdot X}))$	[25]

$k_t^{1,1}/L \cdot mol^{-1} \cdot s^{-1} = 2.29e12 \cdot \exp(\frac{-2640}{T/K})$ $if\ \overline{DP_n} \leq 68$: $\mathrm{k}_t/(L \cdot mol^{-1} \cdot s^{-1}) = k_t^{1,1} \cdot \overline{DP_n}^{-0.61}$ $if\ \overline{DP_n} > 68$: $\mathrm{k}_t/(L \cdot mol^{-1} \cdot s^{-1}) = k_t^{1,1} \cdot 68^{-0.444} \cdot \overline{DP_n}^{-0.166}$ $\mathrm{k}_{tc}/(L \cdot mol^{-1} \cdot s^{-1}) = 0.2 \cdot \mathrm{k}_t$ $\mathrm{k}_{td}/(L \cdot mol^{-1} \cdot s^{-1}) = 0.8 \cdot \mathrm{k}_t$	[19], [30], [31]
$\mathrm{C}_{tr,M} = \frac{\mathrm{k}_{tr,M}}{\mathrm{k}_p} = 5.37 \cdot 10^{-5}$	[19]
$\rho_M/g \cdot mL^{-1} = 1.0288 - 5.5568 \cdot 10^{-4} \cdot (T/°C) - 1.11132e \cdot 10^{-5} \cdot (T/°C)^2 + 1.0041 \cdot 10^{-7} \cdot (T/°C)^3$	[31]
$\rho_{H_2O}/(g \cdot mL^{-1}) = 0.9999 + 2.3109 \cdot 10^{-5} \cdot (T/°C) - 5.44807 \cdot 10^{-6} \cdot (T/°C)^2$	
$\rho_P/(g \cdot mL^{-1}) = 1.29$	[28]

In the table, T is the temperature, f the initiation efficiency, w_{MAA}^0 the mass fraction of MAA in solution in absence of polymer, $k_t^{1,1}$ the overall rate coefficient of bimolecular termination of two radicals of chain length one, $\overline{DP_n}$ is the number-average chain length of the radicals, X is the conversion, ρ_M, ρ_{H_2O} and ρ_P are the monomer, water and polymer densities, respectively. The pH of the reacting mixture was carefully monitored by an Accumet AP110 meter (FisherScientific). Since acidic values were measured at all conditions (pH = 2 - 3), the assumptions of fully protonated, non-ionic monomer and pH independent rate constants are quite accurate.

The applied model has been developed in a previous work[7]. The complete set of constitutive equations (material and population balances) is summarized in **Table S2** of SI, where **eq. S4-S9** are the material balances while the average molecular weight properties are evaluated through **eqs. S12** and **S14**. Note that it is also possible to evaluate the entire chain length distribution by solving the population balances **S11** and **S13** at selected chain length values. All these equations are applicable to the three reactor types under examination by proper adjustments.

4. Results and discussion

4.1. Model validation

The reliability of the model was assessed by simulating the experimental data from MAA polymerization in batch, semibatch and continuous processes.

The three batch experiments reported in **Table 3** were examined first.

Table 3 Experimental conditions of batch experiments.

Experiment	Monomer [% w/w]	Initiator [% wbm]	T [°C]
1	5	0.5	50
2	5	2.0	50
3	5	3.0	50

The monomer conversion predicted by the model is compared with the experimental data in **Figure 1a**. Using the parameters reported in **Table 2** with a minor increase (*i.e.* 4x) in the value of $k_{tr,M}$, the model predictions are quite in good agreement with the experiments, with deviations which are within the experimental error (7%). The polymerization rate increases at increasing initiator concentration, as expected, while auto-acceleration due to Trommsdorff effect is visible in all cases.

The experimental values of weight average molecular weight (Mw) and dispersity (Đ) for the batch experiments are depicted in **Figure 1b** along with the predictions provided by the model.

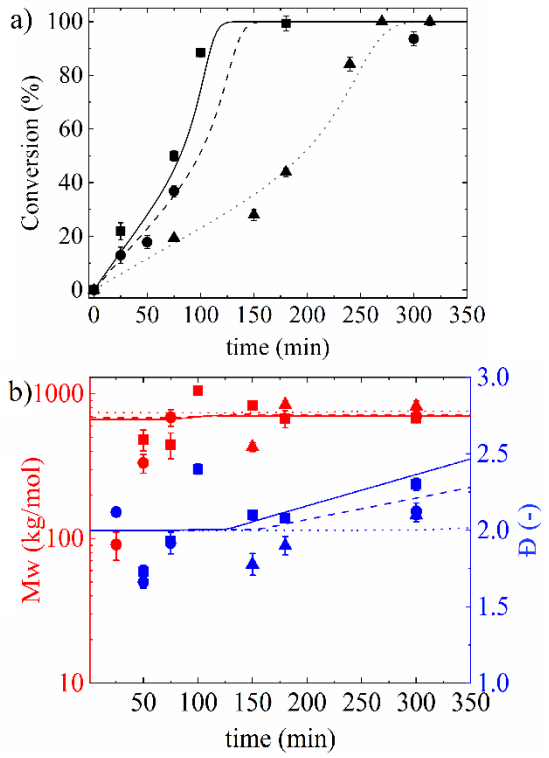

Figure 1 Model vs. experimental conversion profile (a) and MWD (b). The curves (model) and the symbols (experimental data) reported represent the profiles of experiments 1(… and ▲), 2 (--- and ●), and 3 (- and ■) in Table 3. The results shown are the average of three independent experiments with the error bars representing the standard deviation of the measurements.

The experimental point at 25 min is definitely not reliable for this system. In fact, when a chain transfer to monomer mechanism is the dominant termination, the Mw is expected to be constant throughout the polymerization, as predicted by the model. This inaccuracy was attributed to the poor reliability of the analytics at low monomer conversion (< 30%). On the other hand, it is possible to appreciate the good predictivity of the model in terms of both Mw and Đ at higher monomer conversion.

Moving on to the semibatch configuration, the most popular operating mode in polymer industry, a wide range of operating conditions was simulated. Specifically, we selected low, intermediate, and high initiator concentration (*i.e.* from 1 to 3% wbm), feeding time between 20 and 120 minutes, and temperature between 50 and 60 °C. All the experimental conditions are summarised in **Table 4**.

Table 4 Experimental conditions of semibatch experiments.

Experiment	Monomer [%]	Initiator [% wbm]	Temperature [°C]	Feeding time [min]
4	15	1	60	20
5	15	2	60	20
6	15	3	60	20
7	15	2	60	30

8	15	2	60	40
9	15	2	60	50
10	15	2	50	120

Figures 2a, 2c and **2e** show the comparison between experimental and predicted monomer conversion. The instantaneous conversion values are reported in **Figures 2b, 2d** and **2f**, defined as ratio between the produced polymer at time *t* and the monomer cumulatively fed to the reactor up to the same time *t*.

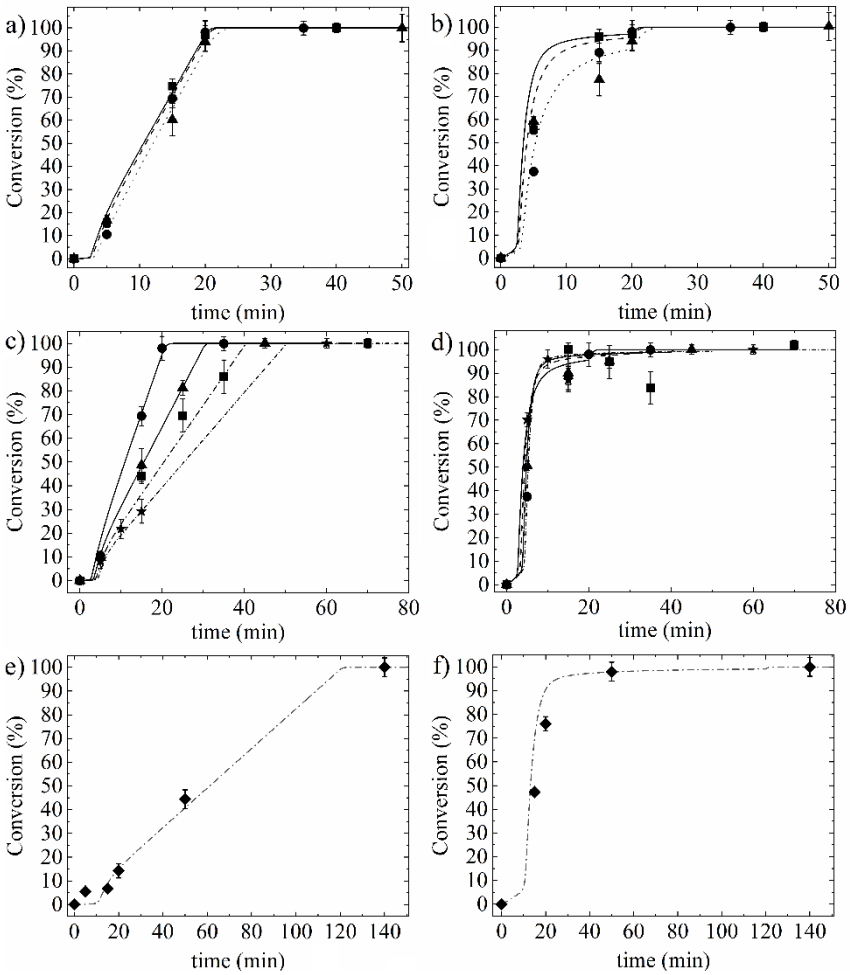

Figure 2 Simulated vs. experimental cumulative (a, c, e) and instantaneous (b, d, f) conversion for semibatch reactor. In the case of (a, b) same FT (20 minutes) and initiator concentration equal to 1% wbm (… and ▲), 2% wbm (--- and ●), 3% wbm (- and ■). (c, d) same initiator concentration (2%) and FT equal to 20 (- and ●), 30 (--- and ▲), 40 (- . - and ■) and 50 minutes (-.- and ★). (e, f) FT 120 minutes. The curves are the model results, the symbols are the experimental results. The results shown are the average of three independent experiments with the error bars representing the standard deviation of the measurements.

A good agreement is obtained in all cases with the same parameter values previously applied for the batch case. The further reaction time of 30 minutes is effective to reach complete conversion in all cases, as verified also by the model.

The comparison model-experiment in terms of Mw and $Đ$ is shown in **Figure 3**. Again, the agreement is good when retaining the scaling factor 4x for $k_{tr,M}$ evaluated for the batch experiments (**Figure S2**). A moderate impact of the initiator concentration on the average chain length is verified.

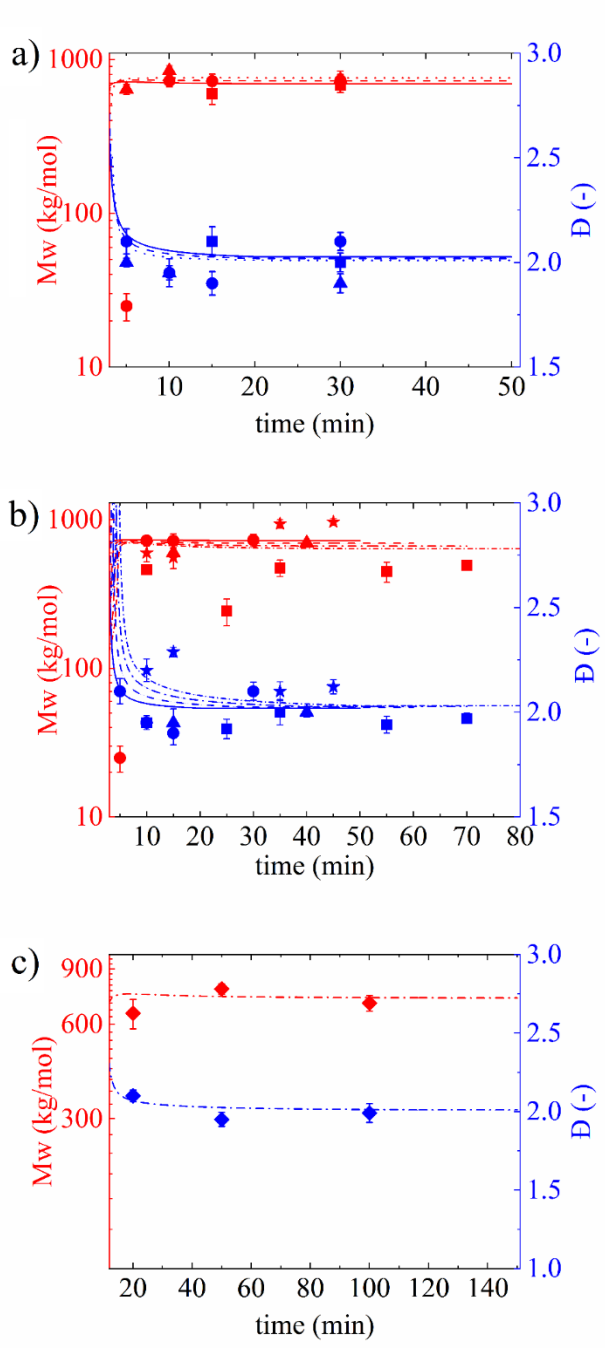

Figure 3 Model vs. experimental MWD average properties for semibatch reactor. (a) same FT (20 minutes) and initiator concentration equal to1% wbm (… and ▲), 2% wbm (--- and ●), 3% wbm (- and ■), (b) same initiator concentration (2%) and FT equal to 20 (- and ●), 30 (--- and ▲), 40 (- . - and ■) and 50 minutes (-.- and ★), (c) FT 120 minutes. Curves are model simulations, symbols are experimental data. The results shown are the average of three independent experiments with the error bars representing the standard deviation of the measurements.

Finally, the reliability of the model is verified in the case of a CSTR. Namely, four experiments are considered, whose recipe and operating conditions are reported in **Table 5**.

255

256 ***Table 5 Experimental conditions of CSTR experiments***

Experiment	Inlet Monomer [M]	Inlet Water [M]	Inlet Initiator [% wbm]	Inlet Volumetric Flow Rate [L/min]	Temperature [°C]
11	1.84	46.74	5.5	$5\ 10^{-3}$	60
12	1.82	46.86	2.0	$3\ 10^{-3}$	60
13	1.80	46.93	5.5	$3\ 10^{-3}$	60
14	1.78	47.01	1.0	$3\ 10^{-3}$	60

257

258 In all cases, the model predicts the kinetic behaviour (**Figure 4a**) as well as the average MWD
259 properties (**Figure 4b**) with acceptable accuracy. Note that all simulations have been carried out
260 without any further parameter adjustment, thus supporting the prediction ability of the model. Given
261 the wide range of reactor operating mode (from batch/semibatch to continuous) and explored
262 conditions (monomer contents up to 15% w/w, initiator concentration in the range 0.5-5.5% wbm,
263 and temperature between 50 and 60 °C), the model can be considered adequate to guide the transition
264 from semi-continuous to continuous operations.

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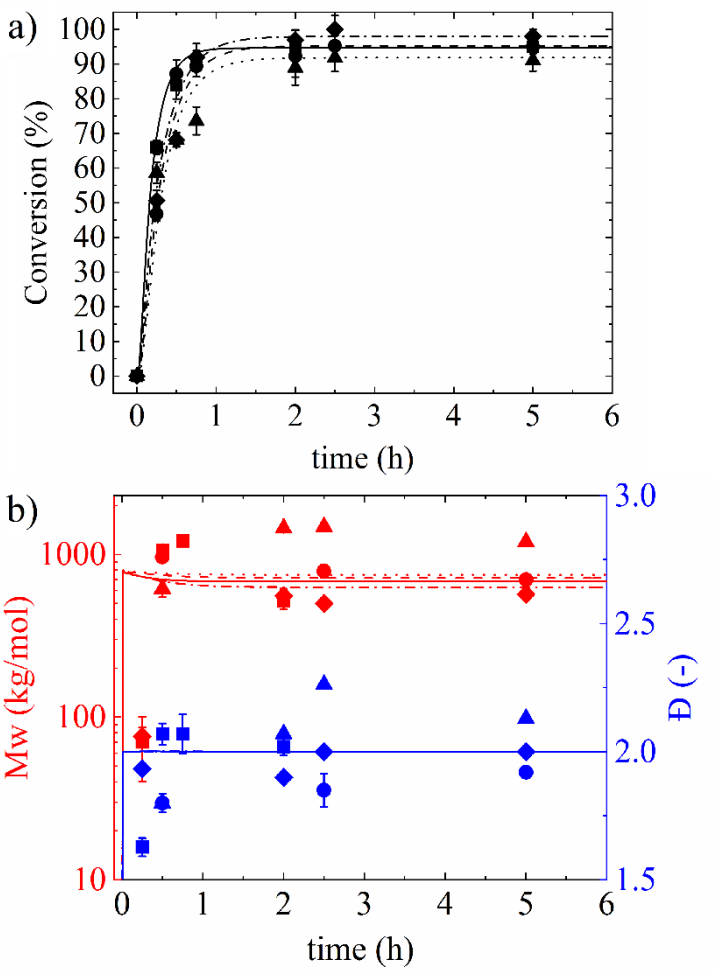

Figure 4 Model prediction vs. experimental conversion for the solution FRP of non-ionized MAA in a CSTR. The curves are model simulations, the symbols are experimental data. Conversion (a), Mw (b, red) and Đ (b, blue) values for experiment 11 (- and ■), 12 (--- and ●), 13 (-. and ♦), and 14 (… and ▲) (cf. Table 5). The results shown are the average of three independent experiments with the error bars representing the standard deviation of the measurements.

4.2. Converting a semibatch production to continuous

Focusing on a well-established polymerization process carried out in semibatch, we now consider the design of the operating conditions of the equivalent reaction carried out in a CSTR while ensuring the same polymer quality (*i.e.* final PC of 15% w/w and final Mw of 6.9 10^5 g/mol). We considered a specific reactor volume (50 mL) to analyse the realistic situation where stirred reactors with constant volume are available (those previously used in batch or semibatch production) and have to be converted into continuous configurations. According to the semibatch process, the initiator concentration is 0.5% wbm, with 15% w/w of monomer fed in 120 minutes and 30 minutes of post-reaction (final batch stage). The process performances are 100% of conversion and a final productivity of 1 10^{-3} g/min/mL considering 150 minutes as overall process duration. It is worth highlighting that this estimate is quite conservative since the actual productivity will be smaller. In

fact, a semibatch process is typically afflicted by considerable dead times (*i.e.* charging/discharging, cleaning, and others).

Procedurally, we used the rigorous model equations in order to select the best operating conditions able to reproduce in continuous the product obtained with the selected semibatch formulation. The system composed by **eqs. (S4)-(S10)** and **(S12)** accounts for 10 equations. Given the absence of active species (R_{in} and λ_1^{in}) and pre-formed polymer (P_{in} and $\mu_{j,in}$) fed to the reaction vessel, the number of unknowns is equal to 15 and so 5 degrees of freedom need to be set. Given the reactor volume, we defined an 11x2 matrix of reasonable values for the monomer and water inlet concentrations. Each couple of values was readily calculated by considering the required PC and 11 hypothetical values of monomer conversion in the range 95 - 100% (residual monomer smaller than 5% was considered) in **eq. (6)**:

$$\chi = \frac{PC}{\%M_{in}} \cdot 100 \qquad (6)$$

Thus, **eq. (6)** allows to obtain the mass percentage of monomer in the stream entering the reactor ($\%M_{in}$) and, consequently, the corresponding molar concentration (M_{in}). Since the inlet stream is only composed by monomer and water (initiator concentration can be neglected), the water concentration entering the reactor (W_{in}) is readily evaluated.

Then, for each couple of monomer and water concentration, we arbitrarily varied the remaining degrees of freedom, namely Q_{in} and I_{in}, in the range 2.08 10^{-1} - 10 mL/min for Q_{in} (corresponding to a mean residence time from a minimum value of 5 min to a maximum value of 240 min) and 0.1 - 6% wbm for the initiator. Namely, to scan all possible combinations inside the selected range of values, a square calculus mesh of 30x30 has been applied, solving numerically the non-linear system of model equations in their steady state version for each specific combination of Q_{in} and I_{in}. An example of the model output in terms of PC and Mw obtained at conversion of 95% is shown in **Figure S3**. The same approach was applied to each one of the 11 combinations water-monomer inlet concentrations mentioned above, resulting in a set of PC and Mw surfaces fully equivalent to those in the figure. The intersections between such surfaces and the planes representing the target values of PC and Mw (blue planes in **Figure S3**) correspond to two curves, providing all pairs of values of Q_{in} and I_{in} fulfilling one or the other target. At each specific conversion, the optimal values are finally found as the intersection between these two curves, as summarized in **Table S3**. Notably, the values in the table correspond to conversion values from 95 to 98%, since no solution is found at imposed conversion values larger than 98%. These results are also shown in **Figure 5** in terms of conversion

and productivity as a function of the mean residence time: the expected trade-off between such two quantities is found, since large residence times result in high conversions but low productivity.

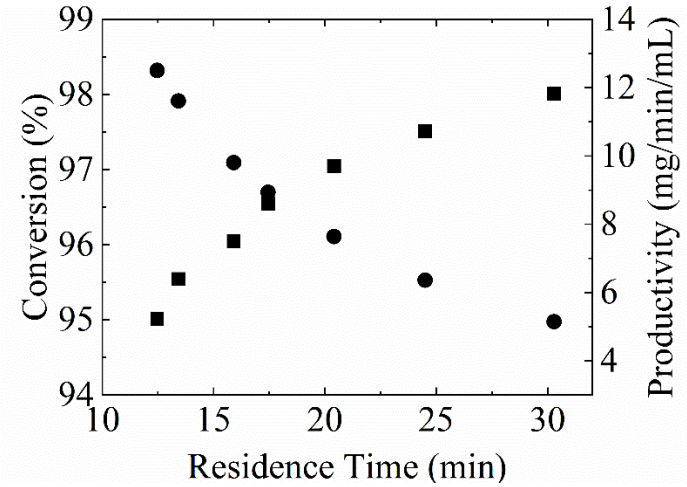

Figure 5 Conversion (■) and productivity (●) vs. average residence time in a CSTR. Each symbol corresponds to specific values of inlet monomer, water, and initiator concentrations, and inlet volumetric flow rate which guarantee the desired polymer content of 15% and weight-average molecular weight of 6.9 10^5 g/mol.

Assuming maximum conversion (98%) as the strongest requirement, a productivity of 5.1 10^{-3} g/min/mL is evaluated at mean residence time of 30.3 minutes, with a favourable productivity ratio between CSTR and semibatch equal to 5.1. As expected, the produced polymer is fulfilling the selected quality targets (polymer content and weight average molecular weight). On the other hand, according to the dominant termination mechanism, its polydispersity is very close to 2 and the entire molecular weight distribution is very close to that produced in the starved semibatch reactor, as shown in **Figure S4**. Therefore, much higher productivity is obtained without affecting the product quality. Nonetheless, very high conversions are of paramount importance in industry in order to minimize the residual monomer. As a matter of fact, several strategies able to reduce the monomer content below the limits imposed by the regulatory agencies are available. In the case of methacrylic acid the most conservative critical threshold of residual monomer is 100 ppm[32]. An effective approach to monomer depletion is the use of a short tubular reactor in series to the main CSTR. This unit ensures the necessary reaction volume for reducing the monomer concentration at limited increase of fix costs (usually its volume is small).

To simulate this reactor configuration, a plug flow reactor (PFR) in series to the CSTR was considered, with inlet flow rate equal to the output flow rate of the CSTR along with the possible increasing of the reaction temperature. The reaction mixture with final conversion equal to 98% is considered as input to the PFR (see **Table S3**, entry 7). The residual monomer concentration as a

function of the reactor volume is reported in **Figure 6** for 3 reaction temperatures, *i.e.* 60, 80 and 90 °C.

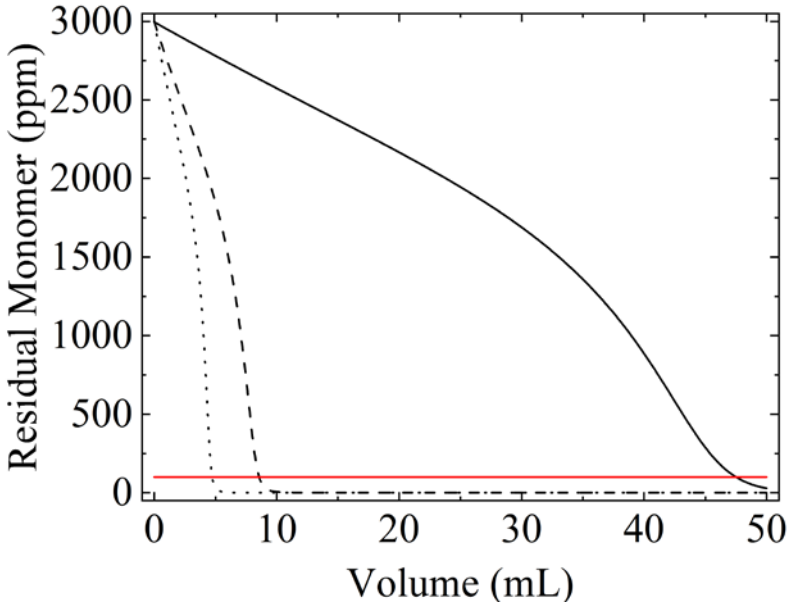

Figure 6 Residual monomer concentration vs. PFR volume. The curves represent different temperatures of the tubular reactor, which increase as: 60°C (-), 80°C (- -), 90°C (..). The horizontal red line indicates a residual monomer equal to 100 ppm, set as target.

As expected, the PFR volume necessary to reduce the residual monomer concentration below the critical value of 100 ppm (red line) depends on the reactor temperature. In particular, performing the reaction at the same temperature of the CSTR (*i.e.* 60°C) leads to a large-volume PFR, very close to the CSTR one (50 mL). Such reactor size would increase the total fix costs thus vanishing the productivity improvement previously achieved with the CSTR configuration. On the other hand, carrying out the reaction at higher temperatures dramatically reduces the tubular reactor volume up to 5 mL at 90°C, as clearly shown in **Figure 6**, making this strategy appealing and economically viable for the depletion of the residual monomer.

However, an increase in the reactor temperature in presence of unreacted monomer may alter the final polymer properties since short chains are formed because of the very low monomer amount. For this reason, we compared the MWD of the polymer leaving the PFR in the worst scenario (*i.e.* temperature equal to 90°C) with the one of the polymer leaving the CSTR (see **Figure S5**). As can be seen from the figure, no significant change in polymer MWD is observed. Moreover, considering to use an empty tube with a diameter of 5 mm and a volume of 5 mL (the value necessary in the case of 90°C), it is possible to calculate the length of the reactor that is equal to 25.5 cm. These small values coupled with the fast monomer depletion and the preservation of polymer quality support the industrial feasibility of the proposed process.

5. Conclusions

The transition from batch to continuous of non-ionized methacrylic acid free radical polymerization has been explored taking advantage of a kinetic model of the polymerization reaction. The model reliability has been confirmed by comparison between the model simulations and experimental data collected in batch, semibatch as well as in continuous (CSTR) reactors. Then, the validated model was applied to design the operating conditions suitable to convert a semibatch process into a continuous one under the constraints of constant polymer quality (same average properties of molecular weight) and same polymer content.

For a defined space of operating conditions, the maximum monomer conversion in the continuous case is smaller than the complete conversion actually achieved in semibacth and equal to 98%. On the other hand, a substantial improvement in the process productivity is found, with productivity ratio between CSTR and semibatch equal to 5.1. In order to reduce to the minimum the residual monomer in the final product, the use of a tubular reactor in series to the CSTR was also examined and modelled through a PFR. Different monomer concentrations at the outlet of the tubular reactor can be achieved on the basis of the given tubular reactor volume and reaction temperature.

Supplementary Information

Electronic supporting information are available at the publisher's website and include the discretization of the outlet volumetric flow rate adopted for the CSTR model validation, the equations used to evaluate the experimental conversion profiles in the three reactor configurations, the mathematical model of the MAA solution polymerization process, the mathematical evaluation of the formula that relates conversion, polymer content and inlet monomer concentration, the results of the deterministic approach fixing a conversion of 95%, the recipes obtained through the basic optimization procedure presented, the MWD of the products obtained from the selected semibatch process and its conversion to a CSTR and the MWD of the products obtained from the selected CSTR process and the one after the PFR.

Conflicts of interest

The authors report no competing interests for this work.

Bibliography

[1] P. Nesvadba, *Radical Polymerization in Industry*. 2012.

[2] J. Ilare and M. Sponchioni, "From batch to continuous free-radical polymerization: Recent

advances and hurdles along the industrial transfer," *Adv. Chem. Eng.*, pp. 1–29, 2020, doi: 10.1016/bs.ache.2020.07.005.

[3] I. Rossetti and M. Compagnoni, "Chemical reaction engineering, process design and scale-up issues at the frontier of synthesis: Flow chemistry," *Chem. Eng. J.*, vol. 296, pp. 56–70, 2016, doi: 10.1016/j.cej.2016.02.119.

[4] D. Kohlmann, M. Chevrel, S. Hoppe, D. Meimaroglou, D. Chapron, P. Bourson, C. Schwede, W. Loth, A. Stammer, J. Wilson, P. Ferlin, L. Falk, S. Engell and A. Durand, "Modular, Flexible, and Continuous Plant for Radical Polymerization in Aqueous Solution," *Macromol. React. Eng.*, vol. 10, no. 4, pp. 339–353, 2016, doi: 10.1002/mren.201500079.

[5] J. R. Richards and J. P. Congalidis, "Measurement and control of polymerization reactors," *Comput. Chem. Eng.*, vol. 30, no. 10–12, pp. 1447–1463, 2006, doi: 10.1016/j.compchemeng.2006.05.021.

[6] M.-C. Chevrel, S. Hoppe, D. Meimaroglou, L. Falk, and A. Durand, "Continuous Pilot-Scale Tubular Reactor for Acrylic Acid Polymerization in Solution Designed Using Lab-Scale Rheo-Raman data," *Macromol. React. Eng.*, vol. 10, no. 4, pp. 354–363, 2016, doi: 10.1002/mren.201500058.

[7] J. Ilare, M. Sponchioni, G. Storti, and D. Moscatelli, "From batch to continuous free-radical solution polymerization of acrylic acid using a stirred tank reactor," *React. Chem. Eng.*, vol. 5, no. 11, pp. 2081–2090, 2020, doi: 10.1039/D0RE00252F.

[8] S. Fathi Roudsari, F. Ein-Mozaffari, and R. Dhib, "Use of CFD in modeling MMA solution polymerization in a CSTR," *Chem. Eng. J.*, vol. 219, pp. 429–442, 2013, doi: 10.1016/j.cej.2012.12.049.

[9] A. Durand and S. Engell, "Batch to Conti Transfer of Polymer Production Processes," *Macromol. React. Eng.*, vol. 10, no. 4, pp. 308–310, 2016, doi: 10.1002/mren.201600031.

[10] C. Schoppmeyer, H. Vermue, S. Subbiah, D. Kohlmann, P. Ferlin, and S. Engell, "Operation of Flexible Multiproduct Modular Continuous Polymerization Plants," *Macromol. React. Eng.*, vol. 10, no. 4, pp. 435–457, 2016, doi: 10.1002/mren.201500044.

[11] G. Montesissa, A. Olivieri, and G. Scapellato, "Alkyd resins modified with acrylic or methacrylic acid for use in water based paints," US3894978A, 1975.

[12] A. K. Khan, B. C. Ray, and S. K. Dolui, "Preparation of core-shell emulsion polymer and

optimization of shell composition with respect to opacity of paint film," *Prog. Org. Coatings*, vol. 62, no. 1, pp. 65–70, 2008, doi: 10.1016/j.porgcoat.2007.09.022.

[13] C. E. Frank, G. Kraus, and A. J. Haefner, "Butadiene–Methacrylic Acid Copolymers as Rubber-to-Steel Adhesives," *Ind. Eng. Chem.*, vol. 44, no. 7, pp. 1600–1603, 1952, doi: 10.1021/ie50511a033.

[14] B. Loomans, N. Opdam, T. Attin, D. Bartlett, D. Edelhoff, R. Frankenberger, G. Benic, S. Ramseyer, P. Wetselaar, B. Sterenborg, R. Hickel, U. Pallesen, S. Mehta, S. Banerji, A. Lussi and N. Wilson, "Severe Tooth Wear: European Consensus Statement on Management Guidelines," *The Journal of Adhesive Dentistry*, vol. 19, no. 2. pp. 111–119, 2017, doi: 10.3290/j.jad.a38102.

[15] S. N. Jaisankar, S. Ramalingam, H. Subraman, R. Mohan, P. Saravanan, D. Samanta and A. Mandal "Cloisite-G-methacrylic acid copolymer nanocomposites by graft from method for leather processing," *Ind. Eng. Chem. Res.*, vol. 52, no. 4, pp. 1379–1387, 2013, doi: 10.1021/ie300290g.

[16] B. Saha and M. M. Sharma, "Esterification of formic acid, acrylic acid and methacrylic acid with cyclohexene in batch and distillation column reactors: Ion-exchange resins as catalysts," *React. Funct. Polym.*, vol. 28, no. 3, pp. 263–278, 1996, doi: 10.1016/1381-5148(95)00092-5.

[17] S. Alay Aksoy, C. Alkan, M. S. Tözüm, S. Demirbağ, R. Altun Anayurt, and Y. Ulcay, "Preparation and textile application of poly(methyl methacrylate-co-methacrylic acid)/n-octadecane and n-eicosane microcapsules," *J. Text. Inst.*, vol. 108, no. 1, pp. 30–41, 2017, doi: 10.1080/00405000.2015.1133128.

[18] S. B. Vitta, E. P. Stahel, and V. T. Stannett, "The Preparation and Properties of Acrylic and Methacrylic Acid Grafted Cellulose Prepared by Ceric Ion Initiation. Part I. Preparation of the Grafted Cellulose," *J. Macromol. Sci. Part A - Chem.*, vol. 22, no. 5–7, pp. 579–590, 1985, doi: 10.1080/00222338508056624.

[19] M. Buback, P. Hesse, R. Hutchinson, P. Kasa, I. Laci, M. Stach, and I. Utz, "Kinetics and modeling of free-radical batch polymerization of nonionized methacrylic acid in aqueous solution," *Ind. Eng. Chem. Res.*, vol. 47, no. 21, pp. 8197–8204, 2008, doi: 10.1021/ie800887v.

[20] S. Beuermann, M. Buback, P. Hesse, R. A. Hutchinson, and I. Lacı, "Termination Kinetics of the Free-Radical Polymerization of Nonionized Methacrylic Acid in Aqueous Solution," pp. 3513–3520, 2008.

[21] S. Beuermann, M. Buback, P. Hesse, and S. Kukuc, “Propagation Rate Coefficient of Non-ionized Methacrylic Acid Radical Polymerization in Aqueous Solution . The Effect of Monomer Conversion,” pp. 41–49, 2007, doi: 10.1002/masy.200750205.

[22] E. J. Fischer, G. Storti, and D. Cuccato, “Aqueous Free-Radical Polymerization of Non-Ionized and Fully Ionized Methacrylic Acid,” *Processes*, vol. 5, 2017, doi: 10.3390/pr5020023.

[23] Y. J. Katsuhiro, Iwase, Kazunori Miyuki, Sasaki Keigo, Watanabe Harumi, “METHOD FOR PRODUCING METHACRYLIC RESIN,” JP2018035225A, 2016.

[24] H. Junichi Yoshida, K. Watanabe, and M. K. Iwase, Keigo Sasaki, “METHACRYLIC RESIN,” US 10174145 B1, 2019.

[25] S. Beuermann, M. Buback, P. Hesse, and I. Lacík, “Free-radical propagation rate coefficient of nonionized methacrylic acid in aqueous solution from low monomer concentrations to bulk polymerization,” *Macromolecules*, vol. 39, no. 1, pp. 184–193, 2006, doi: 10.1021/ma051954i.

[26] S. Beuermann, M. Buback, P. Hesse, R. A. Hutchinson, S. Kukučková, and I. Lacík, “Termination kinetics of the free-radical polymerization of nonionized methacrylic acid in aqueous solution,” *Macromolecules*, vol. 41, no. 10, pp. 3513–3520, 2008, doi: 10.1021/ma7028902.

[27] N. Manfredini J. Ilare, M. Invernizzi, E.Polvara D. Contreras Mejia, S. Sironi, D. Moscatelli and M. Sponchioni, “Polymer nanoparticles for the release of fragrances: How the physico-chemical properties influence the adsorption on textile and the delivery of limonene,” *Ind. Eng. Chem. Res.*, 2020, doi: 10.1021/acs.iecr.0c02075.

[28] J. E. Mark, “Polymer data handbook,” *Oxford Univ. Press*, 1999.

[29] C. Costa, A. Alberton, A. Santos, M. Fortuny,P. Araújo, C. Sayer and J. Pinto,, “Kinetic Parameters of the Initiator Decomposition in Microwave and in Conventional Batch Reactors - KPS and V50-Case Studies,” *Macromol. React. Eng.*, vol. 9, no. 4, pp. 366–373, 2015, doi: 10.1002/mren.201500013.

[30] J. Barth and M. Buback, “SP-PLP-EPR study into the termination kinetics of methacrylic acid radical polymerization in aqueous solution,” *Macromolecules*, vol. 44, no. 6, pp. 1292–1297, 2011, doi: 10.1021/ma102278n.

[31] N. F. G. Wittenberg, M. Buback, and R. A. Hutchinson, “Kinetics and Modeling of Methacrylic Acid Radical Polymerization in Aqueous Solution,” *Macromol. React. Eng.*, vol.

7, no. 6, pp. 267–276, Jun. 2013, doi: 10.1002/mren.201200089.

[32] E. Commission, “European Union Risk Assessment Report,” 2002. [Online]. Available: https://echa.europa.eu/documents/10162/f0b94b4b-a87b-442b-b647-8ff56895c92c.

Table of Contents for

Free-Radical Polymerization of Methacrylic Acid: From Batch to Continuous Using Stirred Tank Reactors

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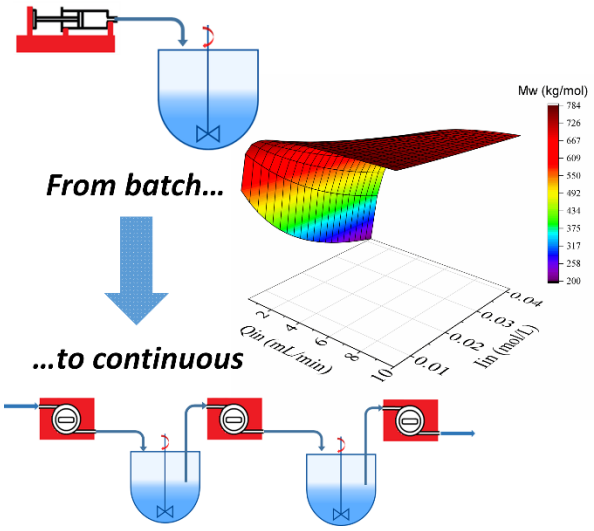

Model-assisted optimization to convert a semibatch poly(methacrylic acid) production to continuous preserving the same average molecular weight and dry content.