Modeling of Anionic Polymerization in Flow With Coupled Variations of Concentration, Viscosity, and Diffusivity

Bruno Cortese, Timothy Noel, Mart H. J. M. de Croon, Simon Schulze, Elias Klemm, Volker Hessel

This paper explains the reasons behind the very low polydispersity index (PDI) obtained in living anionic polymerizations in microstructured reactors. From the results, it can be explained that a narrow molecular weight distribution can be obtained due to the presence of a highly segregated flow behavior, even in microflow conditions, provided that the mean residence time is high enough. This paper investigates the feasibility of a living anionic polymerization reaction under micro-fluidic conditions. This is accomplished using a multi-physics model that accounts for the changes in viscosity and diffusivity. These properties descend with the increase in weight of the polymer, and could not be uncoupled from hydrodynamics and mass transfer. The results of the model are used to understand the reasons behind the very low PDI that can be experimentally obtained in microflow conditions. This leads to the conclusion that the increased viscosity almost “suppresses” the diffusion of the monomer, even at the very short characteristic lengths of a micro-device. These conditions generate a fully segregated flow that yields an almost monodisperse polymer regardless of the effective residence time distribution encountered in the reactor.

1. Introduction

Anionic polymerization is a largely investigated research topic over the last decades and has also transferred to industrial practice. This technique owes an important status due to the capability of overcoming some of the usual limitations encountered with thermal and radical methods, i.e. theoretical lower limit if polydispersity index (PDI) (1.5 for radical polymerization) or difficulties in the synthesis of well defined co-polymers (high control over block lengths).[3-5]

Micro-flow chemistry and microstructured reactors (MSR’s) have proven in the past their capabilities in providing a high degree of control and safety over a wide range of reactions, both mass transfer limited and heat transfer limited.[6,7] Consequently, MSR’s have shown benefits in broad variety of applications, such as synthetic chemistry, process engineering, chemical biology, biology, and material science.
The synthesis of polymers is a well-known chemical reaction and has been extensively studied in the past. The actual reference market for polymers represents one of the largest, exceeding 2500 bn € per year in Europe. In the last decade, the application of MSR’s for polymerization reactions has received an increasing amount of interest due to their added value to the field. The main advantages of microfluidic systems for the synthesis of polymers, such as enhanced heat and mass transfer characteristics, can be attributed to the particular geometry and typical length scales of the devices. This avoids the presence of hotspots and poor homogeneity of initiation, which is usually encountered under typical batch conditions. As a result, polymers with better-defined characteristics can be obtained, i.e. controllable molecular weights and small PDI.

Previous studies from Serra et al. investigated and explained the possibility of synthesizing polymers in a micro-system via radical polymerization. Unfortunately, polymers produced with this method have a theoretical PDI limit of 1.5, making them non suitable for specialty applications, where often extremely narrow MW distributions are required (i.e. a PDI below 1.1). The technique normally used for the production of polymers with a low PDI is the so-called living-anionic-polymerization (LAP), which is able to yield the required monodispersity. Unfortunately, LAP of styrene, styrene derivatives and other vinyl-molecules usually have to be performed at very low temperatures and with long reaction time in batch conditions.

Previous studies from Yoshida et al., Kralisch et al., Lowe et al., and from Klemm et al. (which results are summarized in Table 1) show that LAP can indeed be performed in a MSR with results as good as the ones obtained in batch, namely down to PDI = 1.1 or lower. However, a thorough mechanistic rationale which could explain these results was not provided.

Table 1. Summary of relevant literature regarding LAP in MSR.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Monomer</th>
<th>Temperature [K]</th>
<th>MW (up to) [g mol⁻¹]</th>
<th>PDI (down to)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[16]</td>
<td>Styrene</td>
<td>353</td>
<td>71 000</td>
<td>1.09</td>
</tr>
<tr>
<td>[18]</td>
<td>Styrene</td>
<td>320</td>
<td>75 000</td>
<td>1.06</td>
</tr>
<tr>
<td>[19]</td>
<td>Styrene</td>
<td>297</td>
<td>20 000</td>
<td>1.09</td>
</tr>
<tr>
<td>[20]</td>
<td>Styrene</td>
<td>297</td>
<td>7 000</td>
<td>1.1</td>
</tr>
</tbody>
</table>

This study simulates a LAP/retarded anionic polymerization (RAP) process, in a MSR taking into account the changes of almost all the relevant physical parameters in order to provide such missing explanation (i.e. identify the parameters and properties which express the biggest influence in determining the properties of the final product).

2. Model

Modeling studies must take into account the different processes happening into the investigated device and the effects they have on the final product. In the case of a chemical reactor, these can be summarized in the following set of equations after coupling with the appropriate reaction kinetic.

\[
\nabla \cdot u = 0
\]

\[
\rho \frac{du}{dt} + \rho (u \cdot \nabla u) = -\nabla p + \nabla \cdot (\eta(\nabla u + (\nabla u)^T))
\]

\[
\rho C_p \frac{dT}{dt} + \nabla \cdot (-k_h \nabla T) = Q - \rho C_p u \cdot \nabla T
\]

\[
\frac{dC_i}{dt} + \nabla \cdot (-D_i \nabla C_i + C_i u) = r_i
\]

where \( \rho \) is the density of the fluid, \( T \) is the temperature, \( u \) is the velocity vector, \( Q \) is the heat released/absorbed by the reaction, \( p \) is the pressure \( r_i \) is rate of formation/consumption of specie \( i \) and \( k_h \) is the heat transfer coefficient. Equations (1–4) are respectively the continuity equation, the Navier–Stokes equation, and the standard descriptions for heat and mass transfer.

It is known that all the phenomena described by Equations (1–4) are tightly coupled and have a strong influence on the outcome of the reaction. Other aspects that need to be accounted for a polymerization reaction are the sharp change in viscosity and the high heat release associated with the monomer conversion. All the governing equations must be solved simultaneously.
2.1. Reaction

The reaction considered is the LAP of styrene in toluene at 298 K in isothermal conditions (with an initial monomer concentration of 900 mol·m⁻³).

The simplified mechanism of the LAP can be summarized as in Figure 1. In clean conditions (i.e. in absence of impurities that can terminate the reaction), it proceeds until all the monomer is consumed. After this stage the polymer chain is still “alive” unless a termination (sometimes referred to as end-capping) reaction is performed. This peculiarity makes LAP an extremely useful technique for the synthesis of block-copolymers or for other specialty chemicals.

Another variation of this technique, which differs from the main one only by the initiator, is known as RAP. Carlotti et al. [21,22] demonstrated the possibility of working at higher T while controlling the kinetic regime of the reaction due to the initiator nature, which implies that a wider range of operating conditions can be chosen.

From a kinetic point of view, after the initiation step (which happens extremely fast) the reaction follows first order kinetics with respect to the monomer (for example see Baskaran et al.).

\[ r_i = k_i [\text{Initiator}]_0 [\text{Monomer}] \]  
\[ X = 1 - \frac{[\text{Monomer}]}{[\text{Monomer}]_0} \]  
\[ \text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum M_i N_i}{\sum M_i N_i} \]  

where in Equation (7) \( N_i \) represent the number of polymer molecules with a MW of \( M_i \) and \( \bar{M}_w \), and \( \bar{M}_n \), are respectively the weight average molecular weight and the number average molecular weight.

Starting from a molecular weight versus radius plot, \( M_i \) corresponds to the weight at the mesh node and \( N_i \) at the initiator (and therefore polymer) concentration; PDI is then calculated using data uniformly distributed along the radius.

2.2. Meshing and Geometry

All the simulations have been performed on a PC using the COMSOL 3.5a software.

The modeled reactors are a series of cylindrical capillaries with different lengths and diameters (as listed in Table 2). The geometry has been simplified from 3D to 2D taking into account the symmetry of the reactor (as shown in Figure 2). The simplification allowed using a more refined mesh avoiding numerical diffusion problems and refining the grid where the sharpest variations in the properties occur.

Both free triangular mesh and structured quadrangular mesh have been tested on a sample reactor (number R2 in Table 2), a strong difference in the program performance has been observed between the two, with the mapped mesh showing a much higher numerical stability and shorter solution time.

For this reason all the subsequent calculations have been conducted using a mapped mesh, which has been refined until no discrepancy in the results was obtained.

2.3. Viscosity and Diffusivity

One of the specificities of a polymerization reaction is the variation of viscosity of the reactive solution, which can have an intensity of several orders of magnitude (depending on the weight of the synthesized macromolecule). In order to obtain the highest possible precision degree, it is absolutely necessary to account for this phenomenon.

We modeled the change in viscosity using the following procedure. From the definition of the specific viscosity of a polymer solution, we know that

\[ \eta_s = \frac{\eta_s - \eta_s}{\eta_s} \]  
\[ \eta = \eta_s(1 + \eta_{sp}) \]  

where \( \eta_{sp} \) is typical for the analyzed solute/solvent system.

The specific viscosity may be evaluated from the first terms of the virial expansion of the Huggins equation (as reported by McCormick).

\[ \eta_{sp} = [\eta]c + \kappa[\eta]c^2 \]  

where \( \kappa \) is typical for the analyzed solute/solvent system.

The intrinsic viscosity is a function of the molecular weight of the polymer.

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Figure 1. Simplified scheme of the living anionic polymerization of styrene.
following the Han equation:

\[ \eta = \alpha_1 \cdot M W^{\beta_1} \] (11)

where \( \alpha_1 \) and \( \beta_1 \) are characteristic for the polymer–solvent interaction.

Using the data sets reported in the previously cited publications, expanded with values reported by Kulicke and Kniewske,\(^{[25]} \) it is possible to obtain the correlation for the intrinsic viscosity.

Moreover, the local diffusion coefficient depends on the local viscosity; this aspect can be modeled considering that a comprehensive correlation for the diffusion coefficient (specific for every solute) as a function of the solution viscosity has been proposed by Hayduk and Cheng;\(^{[26]} \) this is reported below:

\[ D_{AB} = \alpha_2 \eta^{\beta_2} \] (12)

where \( \alpha_2 \) and \( \beta_2 \) are characteristics of the solute.

The dataset used to determine the parameters in Equation (12) are taken from Fan et al.\(^{[27]} \)

After regression of the data on the two correlations, the needed parameters have been obtained (as listed in Table 3).

### 2.4. Other Simplifications

It is known that the hydrodynamics of a reactive flow, as well as the kinetics of the reaction taking place, are influenced by the temperature. Nonetheless, MSR are also well known for their extremely high heat transfer capabilities, which have been proven for reactions that exhibit higher thermal production than the polymerization under investigation (e.g., ionic liquid synthesis or high-T epoxidation).\(^{[28,29]} \) We therefore decided to make use of the common assumption that the full reactor body and reactive mixture are in isothermal conditions.

Another simplification refers to the non-Newtonian behavior observed in polymer solutions.\(^{[30]} \) This has been neglected in this study due to the absence of reliable data to be used for regressions.

Finally, the reacting mixture has been considered as entering the reactor homogeneously mixed and already under laminar flow conditions. This can be justified if a RAP-like situation is taken into account, which allows for initiation to be separated from the mixing stage. The assumption is also valid for a “standard” LAP if the mixing stage is kept at a very low temperature.

### Table 2. Relevant data of the simulated geometries, mean refer to mean values of the property, \( C_0 \) refer to the monomer concentration at the inlet.

<table>
<thead>
<tr>
<th>Reactor ID</th>
<th>Diameter [mm]</th>
<th>Length [cm]</th>
<th>Aspect ratio</th>
<th>( u_{\text{mean}} ) [mm s(^{-1})]</th>
<th>( r_{\text{mean}} ) [mm s(^{-1})]</th>
<th>( C_0 ) [mol L(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1</td>
<td>3</td>
<td>30</td>
<td>1</td>
<td>30</td>
<td>0.93</td>
</tr>
<tr>
<td>R2</td>
<td>2</td>
<td>8</td>
<td>40</td>
<td>1</td>
<td>80</td>
<td>0.93</td>
</tr>
<tr>
<td>R3</td>
<td>4</td>
<td>8</td>
<td>20</td>
<td>1</td>
<td>80</td>
<td>0.93</td>
</tr>
<tr>
<td>R4</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>1</td>
<td>80</td>
<td>0.93</td>
</tr>
</tbody>
</table>

### Table 3. Parameters to be used in Equations (10–12).

<table>
<thead>
<tr>
<th>Equation</th>
<th>( k )</th>
<th>( \alpha_i )</th>
<th>( \beta_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.34</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>–</td>
<td>0.0092</td>
<td>0.7317</td>
</tr>
<tr>
<td>12</td>
<td>–</td>
<td>1.9084</td>
<td>−0.682</td>
</tr>
</tbody>
</table>
The last simplification is numerically driven; the most common boundary condition used in CFD calculations of liquids is the so-called “no-slip” condition, in which the fluid velocity is set at 0 at the wall. Unfortunately under the specific formulation used in this study to describe the viscosity and diffusivity of the species this boundary condition generates a polymer layer along the wall with a weight that increases infinitely. This makes it impossible for the system to converge. To avoid this problem a small slip condition has been implemented in the model, with a wall speed of 1% of the mean speed. This operation can also be more generally justified considering a previous publication of Barrat et al. [31]

3. Results and Discussion

The simulations have been run on the previously presented geometries (see Table 2). All the effects discussed below have been found almost identical in all the investigated geometries, and for this reason no specific references will be done.

3.1. Flow Profile

In all the studied geometries, the same velocity profile of the flow has been observed. The laminar flow exhibits a “normal” fully parabolic velocity profile both at the inlet and at the outlet of the reactor with only minor deviations. Conversely, the flow behavior along the reactor while the reaction is proceeding undergoes a series of modifications.

The initial parabolic profile slowly becomes sigmoidal (see Figures 3 and 4) with the speed of the central streamline increasing. After a maximum it changes back to the parabolic profile when almost full conversion is achieved.

We can explain this phenomenon with the different viscosities of the reactive mixture at different points, which in fact mimics the behavior of the co-current flow of two liquids with different viscosities. In this situation, the decrease in velocity that is observed in laminar flow going toward the wall leads to a non sharp RT along the radius for a given reactor length (this holds also with the modified boundary condition applied). Being the viscosity a function of the MW of the polymer, and the MW a function of the RT of the relevant streamline, a viscosity profile also develops, which leads to the aforementioned behavior (see Figure 5).

It is also possible to look at the flow velocity along the central streamline. Hereby, the linear velocity along the axis direction is increasing up to the point when the conversion become significant, after that the sharp increase in viscosity which originates from the increased MW leads to a reduction of the viscosity gradient and therefore of the velocity (see Figure 6).

No general indications can be given for the aforementioned “significant” conversion, because the exact value at which the phenomenon is observed depends from a fine interplay between: the initial concentration of monomer, the mean inlet velocity and the size of the reactor.

3.2. Diffusion

As it has been underlined in previous sections, due to the dependence of the viscosity on the MW, a profile is developing along the reactor. As presented in Equation (12) the diffusion coefficient depends from the viscosity, and therefore also a diffusivity profile is automatically imposed on the previous one. If this is combined with the concentration gradient of the monomer, we obtain one of the key aspects in the results explanation.

It is known that the diffusion can be expressed as:

$$\nabla_j c = D_{AB} \Delta c$$  \hspace{1cm} (13)

And that the diffusivity for smaller species is much higher than the one for bulky species (as a rule of thumb). For
this reason, we assumed that the polymer is not diffusing (and therefore the initiator is not diffusing), while the monomer is free to follow the concentration gradient. It should be noted that even if the approximation appears rough, there is in fact no concentration gradient for the polymer; this arises from the fact that all the polymer chains were considered equal in terms of diffusion and that, due to the homogeneous mixing at the inlet assumption, there is no radial gradient at any point of the reactor. Moreover, the diffusivity of the macro-molecules will be around one order of magnitude smaller than the one of the monomer. Therefore, by combining the low diffusion coefficient and the small driving force we can neglect this aspect.

A higher driving force (concentration gradient) is present in the part of the reactor, which exhibits the higher conversion (consuming the monomer). Conversely, this area is also the one that exhibits the smaller diffusion coefficient, due to a high viscosity. In all the investigated reactors, the diffusion profile can be easily indentified (Figure 7), and it is possible to notice how it follows the flow profile.

In fact, the only area of the reactor that can undergo a “relevant” diffusion effect is the “interphase” between high and low MW polymers, but only in the small parts where the viscosity has not suppressed the diffusion by means of a low diffusion coefficient.

A more straightforward way to evaluate the impact of diffusion can be done by re-expressing Equation (13) as in Equations (14 and 15). It then becomes explicit that the molar flow due to diffusion is affected by two contrasting effects, i.e. a diffusion coefficient decreasing with increasing polymer weight and a driving force increasing with concentration differences, both of them triggered by the same event (the increasing conversion of the monomer).

\[
\nabla | \nabla \cdot C = D_{AB}(X) \Delta C(X)
\]

where

\[
\begin{align*}
\frac{\partial D_{AB}}{\partial X} & < 0 \\
\frac{\partial \Delta C}{\partial X} & > 0
\end{align*}
\]

This leads to a situation in which the relative magnitude of the different increases play a role in the determination of the effective diffusive flux. But, even more important, a mitigation-like behavior on the impact of diffusion is present, and is important also at the small characteristic lengths that are typical of microreactors.

Finally, we evaluated the impact of the monomer diffusion on the reaction outcome. From the numerical solution of the model, we identified diffusive fluxes up to 0.03 mol m\(^{-2}\) s\(^{-1}\) (in the very worst case), against an initial concentration of monomer of 930 mol m\(^{-3}\); the difference

\[
\begin{align*}
\text{Figure 5. Radial viscosity profiles at different lengths (percentage of reactor length in the legend).} \\
\text{Figure 6. Axial velocity profile along the central streamline.} \\
\text{Figure 7. Diffusion profile (white high, black low) for geometry R2.}
\end{align*}
\]
between the two values is of 5 orders of magnitude (mol-wise), which leads to the conclusion that the effect of diffusion is almost uninfluential, unless very long residence time are used.

This effect can be confirmed as well by use of the Fourier number \( (F_o) \) defined as follow:

\[
F_o = \frac{D_{AB} \tau}{l^2}
\]  

(16)

where \( l \) is the relevant length-scale of the system.

It is known that diffusion starts to exhibit a relevant behavior when \( F_o \) is above 0.1, and that is dominant when \( F_o \) is above 1.\[^{[32]}\] It should of course be pointed out that the use of \( F_o \) makes sense only in situations that preserve a concentration difference as a driving force along the reactor. Therefore to obtain a proper approximation the length used for the reactor should be the one that allows reaching full conversion (around 99%) and the time to be used is the mean residence time at that length (same goes for the diffusion coefficient).

With these data it is possible to calculate \( F_o \), which shows a value of \( 10^{-2} \), confirming the absence of any relevant diffusion effect.

### 3.3. Conversion

Due to the previously discussed behavior of the system (speed of streamlines and segregated behavior) the monomer concentration exhibits a large radial gradient. Recalling Equation (5) an exponential decay of concentration over time is expected for each streamline, while the intensity against length varies as a function of the linear velocity. This behavior is shown in Figure 8, where the monomer concentration versus length is shown for different radial positions on geometry R2 (where the arrow indicates lines progressively closer to the reactor center).

The aforementioned pattern (first order like concentration profile) is clearly recognizable, as well as the intensity of the concentration versus length variation, which overlay the velocity profiles previously discussed.

The same behavior shown for R2 can be found in all the other studied geometries.

### 3.4. PDI Evolution

Finally, the PDI has been considered, which is the most important indicator to measure the quality of the product. It should be noted that for a LAP the theoretical PDI is exactly 1. In this case, all the monomer chains grow at the very same rate, and there are no termination effects. Nonetheless the PDI that is obtained experimentally is between 1.05 and 1.11.

Two considerations can then be drawn; the first being the evolution of the PDI along the length of the reactor and the second being the theoretical value that can be obtained under reasonable conversions (e.g., 99%).

In Figure 9, the general trend observed in the evolution of PDI is reported. It can be seen that the initial PDI value (at low reactor length) is extremely high, due to the high RT
difference observed between the central streamline and the external one. In addition, the PDI is monotonically decreasing along the reactor length (and therefore at increasing conversions).

This can be explained by the absence of consecutive and parallel reactions. When the polymer chains have consumed all the monomer around them, they do not undergo any other transformation, and following increases in the MW are due only to other monomer feed provided by diffusion. As discussed in the previous section, this aspect is prevented by the low diffusivity connected with the high viscosity observed in these parts of the reactor, and therefore a quasi-fully segregated behavior appears.

From a more general point of view, the lowest PDI that can be simulated is a value of 1.03, which is very close to the experimental data reported by Yoshida, Kralsich, Lowe, and Klemm.\textsuperscript{[16–20]}

4. Conclusion

During this study, a numerical interpretation of a LAP/RAP in a MSR reactor has been performed by means of CFD simulations with parameters dependent from the obtained MW. The results obtained theoretically indicated that a low PDI (<1.03) can be obtained by use of MSR in the synthesis. Our results are in satisfactory accordance with the ones available from the literature on similar systems investigated experimentally.

More in depth, it has been demonstrated that the narrow MWD that can be obtained descends from the presence of a highly segregated flow behavior, even if the reaction is performed in MSR, which are well known for their high mass transfer capabilities.

The use of the Fo number as a different method for confirmation of the results allows to confirm that the system is not in a Taylor–Aris dispersion dominated regime, but in a segregation dominated regime, at least for residence times below a minimum that can be calculated for each reactor diameter.

Also, evidence has been found regarding a very fine interplay between the reactor geometry, the kinetics and the polymer solution properties, which exhibit an extremely relevant role on the final product quality.

Nomenclature

Acronyms

- CFD: computational fluid dynamic
- LAP: living anionic polymerization
- MSR: microstructured reactor
- MW: molecular weight
- MWD: molecular weight distribution
- PDI: polydispersity index
- RAP: retarded anionic polymerization
- RT: residence time
- RTD: residence time distribution

Symbols

- $C$: concentration
- $D_{AB}$: diffusion coefficient
- $T$: temperature
- $t$: time
- $p$: pressure
- $Q$: heat
- $r$: reaction rate
- $u_{\text{mean}}$: mean inlet linear velocity
- $X$: conversion
- $k$: reaction rate constant

Greek Symbols

- $\eta$: viscosity
- $[\eta]$: intrinsic viscosity
- $\eta_{sp}$: specific viscosity
- $\alpha_i$: parameter
- $\beta_i$: parameter
- $\kappa$: parameter
- $\rho$: density
- $\tau$: residence time

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