

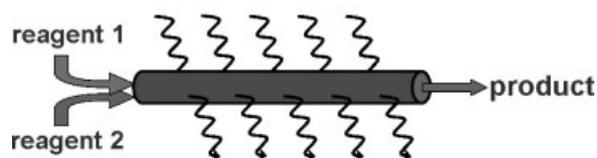
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Scale-Up of Microwave-Assisted Polymerizations in Continuous-Flow Mode: Cationic Ring-Opening Polymerization of 2-Ethyl-2-oxazoline

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Microwave-assisted polymerizations is a growing field of interest because the use of microwave irradiation instead of thermal heating was demonstrated to result in faster, cleaner, and higher yielding reactions. To overcome the one-at-a-time nature of preparing polymerizations in single microwave vials and the possible scale-up method for microwave-assisted polymerizations, the use of continuous-flow reactions under microwave irradiation seems to be ideal. In this contribution, we report for the first time the use of different continuous-flow microwave reactors for polymerizations, using the cationic ring-opening polymerizations of 2-ethyl-2-oxazoline as a model system. In addition, the observed broader molecular-weight distributions were correlated to residence time distributions of the continuous-flow reactors that were determined using methyl orange as the flow marker.

Continuous flow microwave-assisted polymerizations



Introduction

During the last several years, microwave irradiation has become a popular heat source for organic chemistry.^[1,2] The fast and direct heating offered by microwave irradiation leads to more homogeneous heat profiles compared to thermal heating. Generation of the energy

directly inside the reaction mixture and the higher accessible temperatures (by the use of closed reaction vessels) have resulted in cleaner and faster reactions. Microwave-assisted heating is based on dielectric heating, which is dependent on the ability of a material to absorb microwave energy and convert it into heat. The two main heating mechanisms are dipolar polarization and ionic conduction.^[3–5] The use of microwave irradiation in polymer chemistry is still a rather unexplored field of research.^[6] Nevertheless, it was already demonstrated that the use of microwave irradiation in polymer chemistry could result in accelerated polymerizations and could suppress side reactions.^[7] In order to make microwave-assisted polymerizations a fully accepted technology,

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scale-up possibilities have to be developed and investigated. Direct scaling of microwave-assisted chemistry in batch mode^[8–14] and continuous-flow reactors^[15–18] has already been demonstrated in organic chemistry. Direct scaling of microwave-assisted polymerizations in batch mode has been reported up to 250 and 400 mL scale in domestic microwave ovens equipped with reflux condensers.^[19,20] Recently, we reported for the first time, the direct scaling of a microwave-assisted polymerization process under pressure conditions in batch mode, namely the cationic ring-opening polymerization of 2-ethyl-2-oxazoline was scaled up to a 250-mL batch reaction.^[21] However, microwave-assisted polymerizations in a continuous-flow reactor have not been discussed in the literature to the best of our knowledge. Synthesis of well-defined polymers via living/controlled polymerization techniques requires not only a homogeneous heating profile, but also a homogeneous concentration profile through the entire polymerization mixture to ensure a narrow molecular weight distribution. Moreover, the higher viscosities that are generated in polymerization reactions (in contrast to organic synthesis) might lead to undesired concentration profiles in continuous-flow microwave-assisted polymerizations. In this contribution, we report and discuss our investigation on the microwave-assisted cationic ring-opening polymerization of 2-ethyl-2-oxazoline in various continuous-flow reactors. This polymerization system was chosen to evaluate the microwave-assisted continuous-flow set-ups, because this particular polymerization system has been studied extensively under microwave irradiation in batch mode. Therefore, the results obtained in continuous-flow mode can be directly compared to batch mode, allowing a better evaluation of the system.

Experimental Part

Materials and Instrumentation

Acetonitrile (Biosolve Ltd.) was dried over molecular sieves (3 Å) before being used as a polymerization solvent. 2-Ethyl-2-oxazoline (Aldrich) was distilled over BaO and stored under argon. Methyl tosylate (Aldrich) was distilled and stored under argon. Methyl orange (Merck) and concentrated hydrochloric acid (VWR 37%) were used as received.

Polymerizations were performed in the CEM VoyagerTM monomode microwave and the Milestone FlowSYNTH multimode microwave. The CEM VoyagerTM is equipped with 2 pulse dampened HPLC pumps, a 17.2 bar back-pressure regulator, and the choice between three continuous-flow add-ons; a 10 mL tube reactor (System 1A), a 5 mL Teflon coil (System 1B), or a 10 mL glass coil (System 1C). The Milestone FlowSYNTH is equipped with a 200 mL continuous-flow tube reactor (System 2) with mechanical stirring (set to 30% stirring speed). The batch reference poly-

merization was performed using the Emrys Liberator monomode microwave synthesizer (Biotage, formerly PersonalChemistry). Polymerizations were performed under temperature control utilizing an optical fiber temperature sensor (CEM Teflon and glass coil), an IR temperature sensor (CEM tube reactor and Emrys Liberator) or an thermocouple (Milestone CSTR). Size exclusion chromatography (SEC) was measured on a Shimadzu system with an SCI-10A system controller, an LC-10AD pump, an RID-6A refractive index detector, an SPD-10A UV detector, and a PLgel 5 μm Mixed-D column with chloroform/triethylamine/2-propanol (94:4:2) as the eluent and the column oven set to 50 °C (polystyrene calibration). UV-Vis spectra were recorded on a Perkin Elmer Lambda-45 UV-Vis spectrophotometer.

Polymerizations

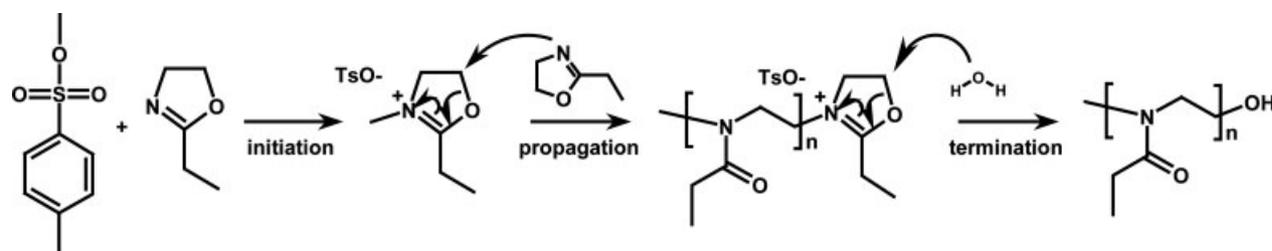
The polymerizations were performed with stock solutions of 4 M monomer concentration in acetonitrile and a monomer to initiator (methyl tosylate) ratio of 90 to 100. These polymerization stock solutions were heated to 140 °C under microwave irradiation with flow rates depending on the reactor volume resulting in a theoretical residence time of 1000 s. After at least 30 min equilibration time, the polymerization mixtures were quenched by the addition of water and the obtained polymers were analyzed by SEC. Furthermore, a 1 mL sample was taken from the stock solution and polymerized simultaneously with the Emrys Liberator monomode microwave synthesizer in batch mode as reference experiment.

Determination of Residence Time Distributions

The residence time distributions were investigated as follows. The continuous-flow microwave set-ups were rinsed for 60 min with acidified demineralized water. Subsequently, methyl orange was added to the inlet yielding a red stock solution and the system was further rinsed with this stock solution. Samples were collected at predefined time intervals. These samples were analyzed by UV-Vis spectroscopy and the absorbance at 505 nm was determined against time. The resulting data were fitted using a sigmoidal curve fit. The first derivative of this fit was taken as the residence time distribution.

Results and Discussion

The living cationic ring-opening polymerization of 2-oxazolines is a well-known procedure for the preparation of well-defined (co)polymers. The polymerization is initiated by the nucleophilic attack of the monomer onto an electrophilic initiator resulting in the formation of a cationic oxazolinium propagating species. The next monomer will react with this cationic species resulting in the formation of ring-opened poly(2-oxazoline). The addition of nucleophiles to the polymerization mixtures will lead to termination and end-capping of the polymer. This ideal polymerization mechanism is schematically depicted in



Scheme 1. Schematic representation of the mechanism of the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline with methyl tosylate as initiator.

Scheme 1. In practice, the cationic ring-opening polymerization of 2-oxazolines proceeds only in such a living manner under appropriate conditions that prevent the occurrence of chain transfer and chain termination reactions. Recently, optimization of the polymerization of 2-ethyl-2-oxazoline under microwave irradiation led to improved conditions with very good control over the polymerization process.^[22,23] However, optimization was performed at several milliliter scales, which would be insufficient for larger mechanical testing or finally even for commercial applications. Therefore, we have recently investigated the scale-up of this polymerization under pressure conditions in batch mode.^[21] Nevertheless, scale-up of pressurized microwave-assisted polymerizations in batch mode is limited due to safety issues and due to limitations in the penetration depth of the microwave irradiation.

In the current study, the continuous-flow microwave-assisted polymerization of 2-ethyl-2-oxazoline was investigated under pressure conditions. The use of a continuous-flow set-up would allow further scale-up in a safe manner and it would allow easy adaptation into commercial polymer synthesis, which is often done in continuous flow. The continuous-flow microwave systems that were used in the current study are shown in Figure 1. Three different continuous-flow set-ups were investigated for the polymerization in the CEM Voyager™ monomode microwave system (max. 300 W, Figure 1): a 10-mL flow cell (system 1A), a 5-mL Teflon coil (system 1B), and a 10-mL glass coil (system 1C). The tube reactor operates with an IR-temperature sensor, whereas both the coil reactors have the temperature probe attached to the outside of the coil implying that the actual internal temperature might be slightly higher. In addition, this continuous-flow microwave

reactor is equipped with two HPLC pumps that allow flow rates from as low as 0.01 up to 20 mL·min⁻¹ corresponding theoretically to the polymerization of 2.4 × 10⁻³ up to 4.6 mol 2-ethyl-2-oxazoline per hour. In addition, the two HPLC pumps can feed two different stock solutions, which could be used to separate the monomer and the initiator for more reactive systems. The pressure in the system results from a backpressure regulator that opens at 17.2 bar pressure. In addition, the polymerization was performed in a larger scale using the Milestone FlowSYNTH continuous-flow multimode microwave reactor (max. 1 000 W, system 2 in Figure 1). This system has a large continuous-flow reactor (200 mL) equipped with a mechanical screw stirrer. The reactor can be best described as a continuous stirred tank reactor (CSTR). An external pump provides flow rates from 12 to 130 mL·min⁻¹ corresponding to a monomer throughput from 2.88 to 31.2 mol per h. The temperature is monitored inside the tube reactor with a thermocouple element. Moreover, the



Figure 1. Pictures of the utilized microwave synthesizers: CEM Voyager™ equipped with a 10 mL tube reactor (system 1A), 5 mL Teflon coil (system 1B), or 10 mL glass coil (system 1C) and the Milestone FlowSYNTH equipped with a 200 mL CSTR (system 2).

Table 1. Details of the continuous-flow microwave synthesizers used.

Microwave system	Irradiation mode	Microwave power	Reactor	Stirring	Reactor volume	Flow rate
		W			mL	mL · min ⁻¹
1A	monomode	300	tube	–	10	0.01–20
1B	monomode	300	Teflon coil	–	5	0.01–20
1C	monomode	300	glass coil	–	10	0.01–20
2	multimode	1 000	CSTR ^{a)}	mechanical	200	12–130

^{a)}Continuous stirred tank reactor.

pressure in the system is regulated by a backpressure regulator that opens at 19.3 bar. In addition, the system is equipped with a cooling unit behind the reactor to ensure that the solvent is below its boiling point before leaving the reactor. The microwave field in this multimode device is less homogeneous than a monomode microwave reactor. To ensure a good mixing and homogeneous heating of the reaction mixture, a stirring screw is present inside the tube reactor. The most important parameters of the continuous-flow microwave systems that were used in this study are summarized in Table 1.

The continuous-flow polymerizations were performed in these four different set-ups with the previously optimized polymerization conditions, namely polymerization with 4 M monomer concentration in acetonitrile at 140 °C, and a monomer-to-initiator ratio of around 100, whereby the flow rates were calculated to result in 1 000 s residence time (details are listed in Table 2). After microwave heating of the polymerization mixtures, water was added to terminate the cationic propagating species to prevent the occurrence of side-reactions. However, one should be aware of the fact that the polymerization temperatures

inside the continuous-flow reactors will have a gradient from ambient temperature to beyond the set temperature of 140 °C. The temperature before the position of the temperature sensor will be lower than 140 °C and after the sensor, the temperature will further increase due to additional microwave absorption. In addition, the monomode microwave synthesizers are not designed for such small coil reactors leading to temperature fluctuations that might influence the polymerization. The presence of such a temperature gradient is a major difference compared to microwave-assisted batch polymerizations that have a very homogeneous heat profile. Nevertheless, we have demonstrated previously that the polymerization of 2-ethyl-2-oxazoline results in well-defined polymers at temperatures from 80 up to over 200 °C. As a result, the presence of a continuous temperature gradient should not affect the structure of the final polymer as long as the temperature gradient is present only in the flow direction of the reactor. The continuous-flow polymerizations were allowed to equilibrate for at least 30 min. After this equilibration time, the polymerization mixtures were analyzed by ¹H NMR spectroscopy and size-exclusion

Table 2. Details of the microwave-assisted polymerization of 2-ethyl-2-oxazoline for different continuous-flow set-ups.

Microwave system	Flow rate	Monomer throughput	Reaction time ^{a)}	Conversion (¹ H NMR)	$\overline{DP}^b)$ (¹ H NMR)	$\overline{M}_{n,th}^c)$	$\overline{M}_{n,GPC}$	PDI _{GPC}
	mL · min ⁻¹	mol · h ⁻¹	s	%		Da	Da	$\overline{M}_w/\overline{M}_n$
1A	0.60	0.144	1 000	81	85	8 400	11 500	1.44
1B	0.30	0.72	1 000	96	89	8 800	12 400	1.33
1C	0.60	0.144	1 000	100	86	8 500	13 500	1.42
2	12	2.88	1 000	60	62	6 200	7 700	1.47
Batch reaction ^{d)}	–	^{e)}	1 000	100	89	8 800	14 800	1.14

^{a)}Theoretical reaction time calculated from the reactor volume and the flow rate; ^{b)}Degree of polymerization calculated from the polymer and initiator signals; ^{c)}Calculated from the degree of polymerization that was determined by ¹H NMR spectroscopy; ^{d)}The batch polymerization was performed in an Emrys Liberator monomode microwave synthesizer; ^{e)}The scale of the batch reaction was 4 mmol.

chromatography (SEC) to determine the monomer conversion, degree of polymerization (DP), and the molecular weight (distribution). The polymerizations in the batch reactor and the two coil reactors (Systems 1B and 1C) reached close to full conversion, whereas the tube (System 1A) and the CSTR (System 2) reached 80 and 60% conversion, respectively (Table 2). The resulting SEC traces are shown in Figure 2 together with a SEC trace of the reference polymerization in batch mode. The corresponding number average molecular weights (\bar{M}_n) and polydispersity indices (PDI) were calculated using a polystyrene calibration and are also listed in Table 2. In general, all the polymerizations revealed an \bar{M}_n higher than the theoretical value ($\bar{M}_{n,th} = 9\,000$ to $10\,000$ Da) due to the applied polystyrene calibration. The reference batch polymerization revealed a monomodal molecular weight distribution with a low PDI value of 1.14, indicative of a living polymerization, and the degree of polymerization was found to be 89 using ^1H NMR spectroscopy, which is close to the initial monomer to initiator ratio of 92. From the SEC traces it is obvious that the shape of the molecular weight distribution changes when the polymerization set-up is changed from batch mode to continuous-flow mode. The two coil-type reactors (Systems 1B and 1C) resulted in monomodal molecular weight distributions that are broadened compared to the batch reactor. This broadening is also evident from the higher PDI, whereby the thinner Teflon coil reactor (system 1B) resulted in a relatively well-defined polymer (PDI = 1.33). The tube reactor and the CSTR (systems 1A and 2) resulted in

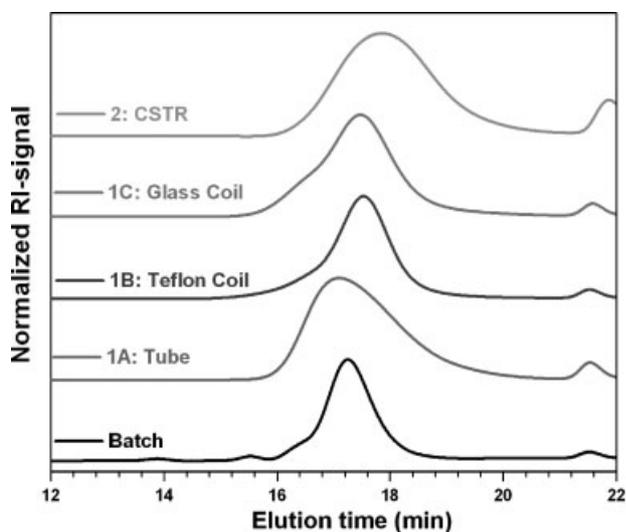


Figure 2. SEC traces of the poly(2-ethyl-2-oxazoline)s that were obtained after at least 30 min equilibration time utilizing the different continuous-flow microwave reactors. In addition, the SEC trace of a reference microwave-assisted polymerization in batch mode is shown.

polymers with broader molecular weight distributions than the coil reactors (Figure 2). The SEC curves of the tube reactor and the CSTR are similar with a broad peak maximum. The continuous-flow coils (systems 1B and 1C) will have a laminar flow inside (based on the very thin diameter and the low flow rate) causing higher flow rates in the center of the coil compared to closer to the wall.^[24] The glass-tube reactor without stirring (system 1A) is assumed to have a laminar flow as well based on the very low flow rate. Nonetheless, the broader diameter of this tube compared to the coils might result in more pronounced diffusion effects. The large tube reactor (system 2) has a coarse screw stirrer that could result in a turbulent flow. Therefore, it is proposed that the observed differences in molecular weight distribution for the coil and the tube/CSTR reactors might be caused by the difference in flow as well as in diffusion. For the investigated living polymerization system, fluctuations in residence time can have a strong effect on the molecular weight distribution since longer residence time can result in the addition of more monomer units. In contrast, organic reactions do not suffer so much from residence time fluctuations since a reaction between reagents A and B will still lead to the formation of product C, whereby only the yield might be affected. The reason for the observed broadening of the molecular weight distributions in continuous flow was further studied by determining the residence time distributions of the different continuous-flow microwave reactors using an aqueous solution of methyl orange at ambient temperature. Although the viscosity and temperature of the mixture will influence the residence time distribution as well as the flow type (laminar or turbulent), this aqueous model system was chosen since it is expected to have a viscosity that is in between the viscosity of the monomer solution (start of the polymerization) and the viscosity of the polymer solution (end of the polymerization). Although these differences will influence the flow in the reactors, the determined residence time distributions will provide a better understanding of the different flow reactors. To determine the residence time distributions, the continuous flow systems were first flushed with water, and at time zero methyl orange was added to the stock solution. From this point on, samples were taken from the outlet of the reactor and the change in UV-absorption at 505 nm, which is the absorption of methyl orange, was measured with time. The resulting curves were fitted by a sigmoidal curve fit (assuming symmetry) and the first derivatives of these fits were taken as the residence time distribution (Figure 3). The peak maxima and the half-peak widths from these residence time distributions are listed in Table 3. The peak maxima are a measure of the average residence times for the complete continuous flow systems including pumps, inlet and outlet tubing as well as the continuous flow reactor. In fact, these peak maxima might

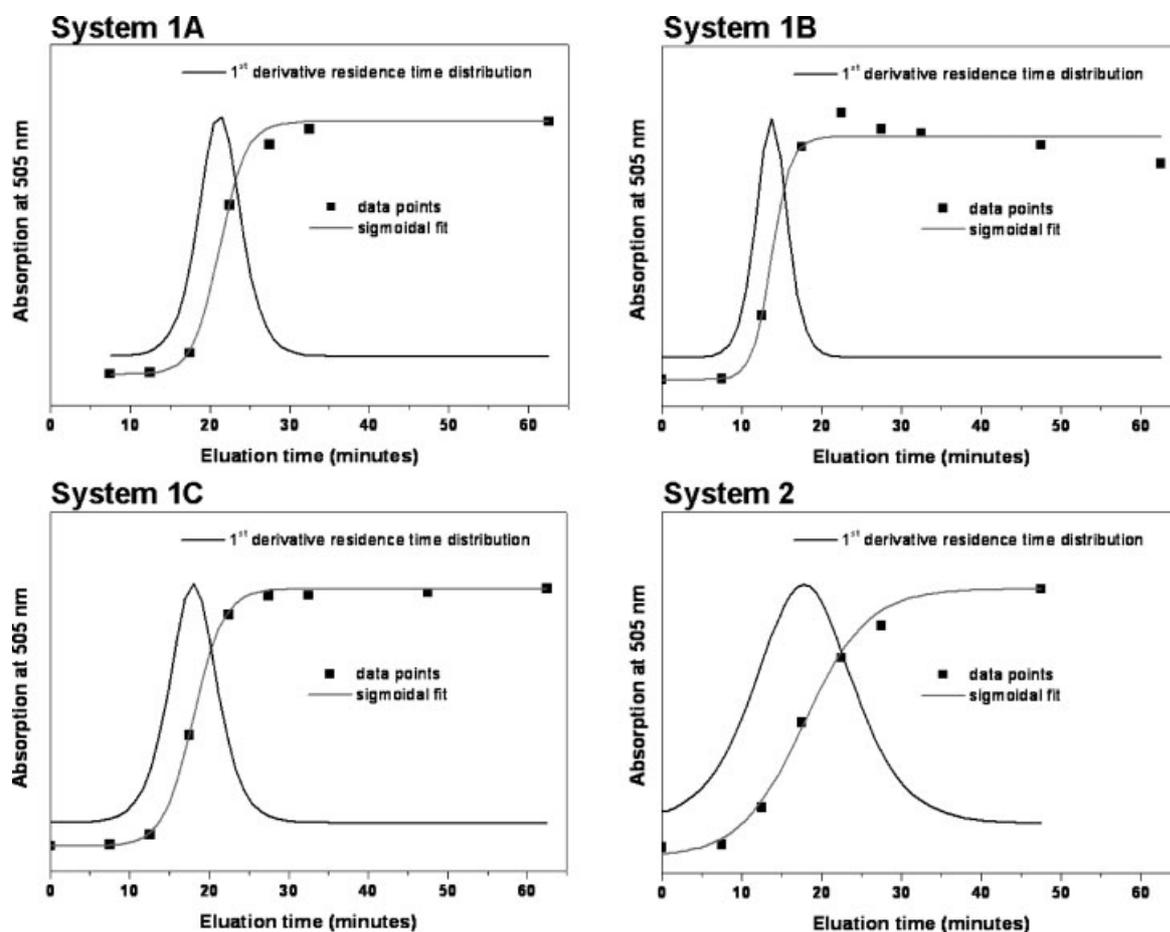


Figure 3. Residence time distributions that were determined for the different continuous-flow microwave systems using methyl orange as the flow marker. The data were fitted using sigmoidal curve fitting and the first derivatives of these fits were taken as residence time distributions.

be a better estimate for the reaction time than the ones given in Table 2, since the exact volume of these continuous-flow reactors was not known. Nevertheless, systems 1A, 1C, and 2 revealed peak maxima of more than 15 min, which is more than the required polymerization time of ≈ 15 min. Although the Teflon coil (System 1B)

revealed a peak maximum of only 13.8 min, the polymerization reached full conversion, which might indicate that the average reaction temperature exceeded 140°C . In addition, from a combination of the PDI values and the half-peak width, it is evident that a broader residence time distribution results in a broader molecular weight distri-

Table 3. Details of the residence times for the different continuous-flow set-ups.

Microwave system	Flow rate	Monomer throughput	Theoretical residence time ^{a)}	Residence time, peak maximum ^{a)}	Residence time, half-peak width ^{a)}
	$\text{mL} \cdot \text{min}^{-1}$	$\text{mol} \cdot \text{h}^{-1}$			
1A	0.60	0.144	16.7	21.5	6.1
1B	0.30	0.72	16.7	13.8	4.4
1C	0.60	0.144	16.7	18.0	6.9
2	12	2.88	16.7	17.7	14.2

^{a)}Residence time parameters are given in minutes.

bution. The thinner Teflon coil (system 1B) showed a significantly narrower residence time distribution compared to the thicker glass coil (system 1C), whereas the CSTR (System 2) showed the broadest distribution. Moreover, the very broad residence time distribution of the CSTR explains the lower monomer conversion since a significant part of the polymerization mixture is less than 10 min in the reactor. A closer look at the sigmoidal curve fits shows that the data points of the tube reactor and the CSTR are below the fitted curve at longer residence times. These deviations indicate that the symmetric sigmoidal curve fit is a rough estimation of the actual residence time distributions. This observation will be investigated in more detail in future studies that will include simulations of the different continuous-flow microwave reactors.

Conclusion

The continuous-flow microwave-assisted polymerization of 2-ethyl-2-oxazoline under pressure was investigated using different continuous-flow microwave reactors to overcome the problems related to scale-up in batch mode including safety issues and the maximum microwave-penetration depth. The continuous-flow polymerizations were performed in two different flow coils and in a small tube as well as a CSTR. It was found that all the continuous-flow microwave polymerizations resulted in broader molecular weight distributions compared to a microwave-assisted polymerization in batch mode. The continuous-flow coils resulted in monomodal molecular weight distributions with relatively sharp peak maxima, whereas the tube reactor and the CSTR revealed molecular weight distributions with broad peak maxima. The thinnest Teflon coil reactor resulted in a relatively well-defined polymer with a PDI of 1.33. It is proposed that the observed differences in the resulting polymers are caused by the different flow profiles in the different types of reactors, namely laminar in the flow coils as well as the tube reactor and turbulent in the CSTR, whereby the larger diameter of the tube reactor might facilitate diffusion leading to a broader peak maximum. Nevertheless, this will be investigated in further detail in future investigations that will include theoretical calculations and predictions of the flow profiles as well as the resulting residence time and molecular weight distributions. In addition to the polymerizations, the residence time distributions of the different continuous-flow reactors were investigated using methyl orange as the flow marker. It was found that the thin continuous-flow coil resulted in the narrowest residence time distribution and the CSTR revealed the broadest distribution. The width of the residence time distribution could be correlated to the observed PDIs, which indicates that the broadening of

molecular weight distributions is indeed caused by the residence time distributions in the flow reactors. However, the observed difference in the molecular weight distribution for the different reactor set-ups (coil or tube/CSTR) could not be directly correlated to the observed residence time distributions. Nevertheless, a larger deviation of the data points from the sigmoidal fit was observed for the tube reactor and the CSTR, which might explain the observed differences.

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