

Influence of Mixing Performance on Polymerization of Acrylamide in Capillary Microreactors

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Nonliving free radical polymerization of acrylamide was chosen as a model reaction to investigate the effect of mixing performance on the polymerization in capillary microreactors. The polymerization rate was enhanced by increasing the volumetric flow rate and the reaction temperature at a constant residence time. However, higher temperatures led to lower Mn and larger PDI. The reaction mixture viscosity increased significantly during the polymerization. Both diffusion and dispersion coefficients were calculated to evaluate the mixing performance in microreactors. The capillary microreactor with a larger inner diameter led to higher monomer conversions, lower Mn and larger PDI compared to the capillary microreactor with a smaller inner diameter, which could be explained through a heat balance analysis for the polymerization and the dispersion effect. Moreover, it was found that the addition of a pre-mixing stage minimized the effect of insufficient mixing between the initiators and the monomers on the polymerization. © 2017 American Institute of Chemical Engineers *AIChE J*, 64: 1828–1840, 2018

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Introduction

Microreactor technology is regarded as a promising process intensification strategy for chemical synthesis due to its unique characteristics, such as well-defined flow properties, high effective surface-to-volume ratio, enhanced heat- and mass-transfer rates, improved chemistry, and excellent process safety.^{1–3} With these advantages, polymers with low molecular weight distributions, well controlled molecular weight and structures, can be synthesized using microreactor technology.^{4–10}

Löwe et al. reported the preparation of poly(styrene) with narrow molecular weight distributions (polydispersity index of molecular weight distribution, PDI = 1.08–1.28) by living anionic polymerization method in a microreactor.¹¹ The reaction time was significantly reduced from several hours to several seconds when the batch reactor was replaced by the microreactor. Vandenbergh et al.⁸ synthesized a sequential multi-block-copolymer consisting of five consecutive acrylate blocks with controllable properties (number-average molecular weight, Mn = 3,1200 g/mol and PDI = 1.46) through the reversible addition fragmentation chain transfer (RAFT) polymerization in a continuous-flow microreactor within 20 min. Their results demonstrated the application potential of microreactors for synthesizing well-defined complex copolymers. Furthermore, the application of microreactors was extended into the preparation of polymer particles. Chu et al.¹² prepared monodisperse polymeric core-shell microparticles with hollow interiors in microreactors. The hole-shell structures could be

controlled by changing the flow rate ratio of different phases or doping nanoparticles into the inner phase for the core surface modification. Hornung et al. prepared a series of different polymers with the monomer (acrylamide, acrylate or vinyl acetate) conversion ranging from 80% to 100% at temperatures between 70 and 100°C using RAFT polymerization in microreactors.¹³ The values of PDI were controlled between 1.15 and 1.20 and the average molecular weights were similar to those obtained in the batch reactor. The microreactor technology provided a facile scale-up route for the RAFT polymerization, which is difficult for conventional batch processing because of the oxygen-sensitive nature of the RAFT process. Iwasaki et al. achieved a larger scale polymerization of methyl methacrylate (MMA) using a numbering-up strategy with an eight-microchannel reactor system.¹⁴ This microreactor system accomplished a continuous operation for 6 days to produce 4.0 kg of the polymer without any problems, indicating the application potential of microreactors for the industrial production of polymers.

As is well known, mixing represents an important phenomenon in many liquid-liquid reaction systems, for example, polymerization, precipitation, crystallization, self-catalysis, enzymatic catalysis, and so on, in which the mixing and the chemical reactions interact.^{15–17} Optimized mixing performance improves the contact of reactants and thus greatly influences selectivity, yield and quality of products. In particular, the improvement on the mixing performance may reduce the value of PDI and lead to more target products with desirable characteristics in many polymerization processes.^{5,7,18–20} The aforementioned studies on the polymerization processes conducted in microreactors focused on the optimization of operational conditions by adjusting the reactant concentration,

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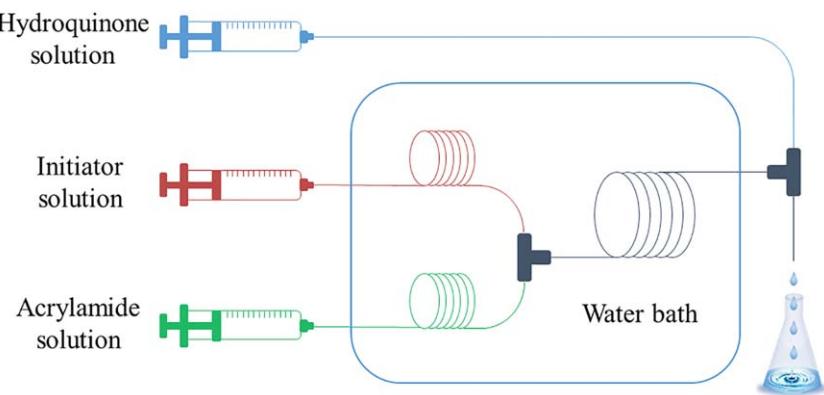


Figure 1. Schematic diagram of the microreactor system for synthesizing poly(acrylamide).

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the reaction temperature or the residence time, and they devoted to reducing the PDI value to minimize the product heterogeneity or controlling the microstructures of polymers to improve their performance in some circumstances. It was claimed that the efficient mixing in microreactors was utilized to synthesize polymers to control the product properties such as Mn and PDI in all these studies.

However, the mixing performance in the polymerization processes in microreactors was not evaluated systematically even it would be typically affected by a number of factors such as fluid properties, reactor structures, and operational conditions. In fact, the mixing process in the polymerization is much more complicated than that in small-molecule reaction systems due to the heterogeneity of monomers, radicals and polymer chains and the significant variation of fluid properties (e.g., viscosity) during the polymerization.

The mixing will play a crucial role in the reaction processes when the characteristic timescale of the chemical reactions involved is of the same magnitude or smaller than the timescale of the mixing process.²¹ In fact, the effect of mixing on the reaction processes can be judged by various dimensionless parameters such as the Fourier number (Fo), the Damköhler number (Da), the Peclet number (Pe), and others.^{15,22} In calculations of these parameters, the characteristic mixing time in reactors should be obtained and then compared with other characteristic times (e.g., the characteristic reaction time and the residence time). In polymerization processes, the production of polymers greatly affects the viscosity and substance diffusivity of the reaction mixture, resulting in the difficulty on accurately estimating the mixing time and characterizing the influence of the mixing performance on the polymerization performance in conventional reactors. With the aid of its fast heat transfer rate, microreactors provide an effective pathway for precise control over the reaction temperature on which the characteristic reaction time usually strongly depends according to the reaction kinetics. Moreover, the residence time (reaction time) can be easily controlled by changing the flow rate of the reaction mixture or the reactor volume.

Poly(acrylamide) is highly water-absorbent and has been widely applied in water treatment and processes like paper making and screen printing as a thickener and suspending agent. The hydrated poly(acrylamide) can be used as poly(acrylamide) gel electrophoresis and used in manufacturing soft contact lenses. More recently, poly(acrylamide) has been used as a subdermal filler for aesthetic facial surgery. Moreover, the polymerization mechanism of acrylamide is well

known and has been published by many reports.^{23–25} In this work, we chose the non-living free radical polymerization of acrylamide to poly(acrylamide) as the probe reaction to investigate the mixing influence on the polymerization in capillary microreactors. Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and sodium bisulfite (NaHSO_3) composed the redox initiator for this polymerization. The mixing characteristics associated with this polymerization in the capillary microreactors were analyzed. Various factors such as volumetric flow rate, residence time, reaction temperature, viscosity, capillary diameter and operational mode, which affect the reaction kinetics or the mixing efficiency and thus the polymerization in the capillary microreactor were investigated systematically. The polymerization performance was evaluated in terms of the monomer conversion (X), the number-average molecular weight of polymers and the polydispersity index of molecular weight distribution. The variation of reaction mixture viscosity with the conversion and its influences on the diffusion coefficients of monomers and polymers, and on the mixing performance in the capillary microreactor were characterized in details. The characteristic mixing time in the capillary microreactor was deduced with considering the effects of the viscosity variation and the produced polymers during the polymerization. A heat balance calculation for the polymerization in the capillary microreactor was conducted and the dispersion effect was evaluated to elaborate the effect of capillary diameter on the polymerization performance. Furthermore, a premixing stage as an alternative operational mode was added into the microreactor system to achieve optimized conditions with low values of PDI for the polymerization.

Experimental Section

Materials

Acrylamide (AM, 99.0 wt %), carbamide ($\text{CO}(\text{NH}_2)_2$, 99.0 wt %), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 99.0 wt %), and sodium bisulfite (NaHSO_3 , 99.0 wt %) were analytical reagents (AR grade) and purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Hydroquinone ($\text{C}_6\text{H}_4(\text{OH})_2$) (AR, 99.0 wt %) and methanol (AR, 99.5 wt %) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals used in this study were not further purified.

Synthesis of poly(acrylamide)

Figure 1 shows the schematic diagram of the experimental setup for synthesizing poly(acrylamide). The material of the

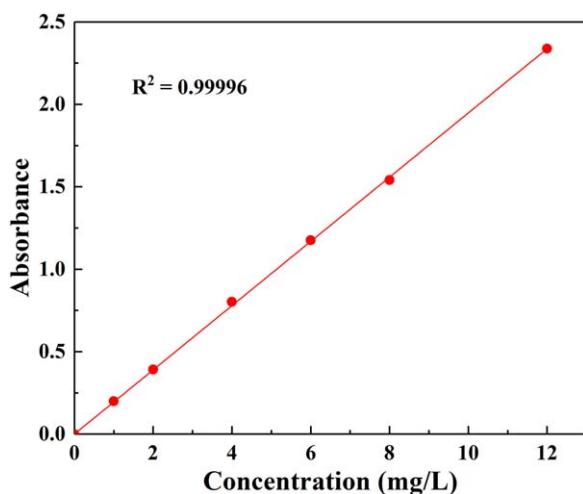


Figure 2. The maximum absorbance of acrylamide solutions with different concentrations at 197.4 nm.

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capillary microreactors is perfluoroalkoxy alkane (PFA) with a high degree of flexibility, transparency, and strength. PFA is a kind of hydrophobic polymer which is beneficial for minimizing the effect of the boundary layer of the flow in the PFA capillary. All the T-micromixer, the connectors and the capillary microreactor were immersed inside the water bath to maintain the set temperature. The aqueous solution of acrylamide (2.814 mol/L) and the aqueous solution of initiator were delivered into the microreactor system using two syringe pumps (New Era Pump System, NE-1200) at the same flow rates. These two solutions contacted and mixed in a T-micromixer, and then entered into the capillary microreactor inside which the polymerization occurred. The residence time was easily controlled by changing the flow rate of the reaction mixture or the capillary length. To completely quench the polymerization after exiting the capillary microreactor, an aqueous hydroquinone ($C_6H_4(OH)_2$) solution was fed to a second T-micromixer and contacted with the reaction stream from the capillary microreactor. The liquid sample was collected in a conical flask for further treatment. Poly(acrylamide) was extracted from the mixed solution by methanol for three times. These three extraction solutions were combined and then dried in vacuum at 25°C for 24 h. The solid Poly(acrylamide) was obtained and further treated for analysis.

Analytical procedure

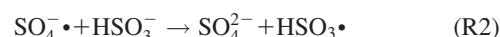
A UV/visible light spectrophotometer (UV-1800, Shimadzu, Japan) was used to measure the light absorption properties of the mixed solution collected at the outlet of the capillary microreactor to determine the conversion of acrylamide. The wavelength in the measurement was set as 197.4 nm with a maximum absorption of acrylamide. Figure 2 shows the maximum absorbance of aqueous acrylamide solutions with different concentrations at 197.4 nm wavelength. The linear correlation coefficient (R^2) for the curve was 0.99996, indicating that the amount of acrylamide remaining in the reaction mixture can be properly determined according to the Lambert-Beer law. Then the conversion of acrylamide was calculated. At least two measurements were performed for each sample, and the average values were taken for calculating the value of the monomer conversion.

A viscometer (DV2T, Brookfield) was used to measure the viscosity of the reaction mixture to determine the diffusion coefficients of monomers and produced polymers during the polymerization in the capillary microreactor. First, the reaction mixture from the capillary microreactor was collected in a tube placed inside an ice-water bath. Solid hydroquinone was put inside the tube for quenching the polymerization. The liquid sample was separated from the solid and then its viscosity was measured by the viscometer at the corresponding polymerization temperature controlled by a heating-cooling circulator (DC0506, -5°C~100°C, Shanghai FangRui Instrument Co., Ltd. China). The viscosity of the sample was determined by an average value of three measurements and it was considered as the viscosity of the reaction mixture with a certain monomer conversion.

The number-average molecular weight and the polydispersity index were determined by a gel permeation chromatography (GPC, Perkin Elmer series 200, American) with a combination of 10 μm PL gel, 300 × 7.5 mm mixed-B and mixed-C columns and equipped with a refractive index (RI) detector. Aqueous sodium nitrate ($NaNO_3$) solution (0.05 mol/L) was used as an eluent at a flow rate of 1.0 mL/min. The molecular weight was calibrated according to the standard samples of poly(acrylamide). The measurements were performed at 25°C. At least two measurements were performed for each sample, and the average values were taken as the final values of Mn and PDI.

Reaction mechanism of the acrylamide polymerization

A free radical polymerization mainly consists of three elementary reactions including chain initiation, propagation, and termination.²⁶ Free radicals for the acrylamide polymerization are produced in the redox initiator system presented as follows²⁷



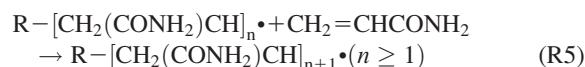
The formation of free radicals is mainly determined by the redox reaction (R1). In this main reaction, $S_2O_8^{2-}$ reacts with HSO_3^- to generate radicals of SO_4^\bullet and HSO_3^\bullet . A side reaction (R2) occurs between SO_4^\bullet and HSO_3^- to generate SO_4^{2-} and HSO_3^\bullet . This side reaction is a free radical transfer reaction and has no influence on the total free radical concentration. Another side reaction (R3) is a free radical termination reaction with two moles of HSO_3^\bullet forming one mole of $H_2S_2O_6$, which leads to the decrease of total free radical concentration. To suppress the second side reaction (R3), the mole ratio of $(NH_4)_2S_2O_8$ and $NaHSO_3$ was set as 1.2 in this study.

In the chain initiation reaction, the free radicals activate monomers to form monomer radicals expressed as reaction 4 (R4)



where R represents the free radicals of SO_4^\bullet or HSO_3^\bullet .

In the chain propagation reaction, the monomer radicals attack monomers to form chain radicals, which can be expressed as reactions 5 (R5)



The chain termination reaction occurs mainly due to the disproportionation.²⁸ Two chain radicals form two polymers of

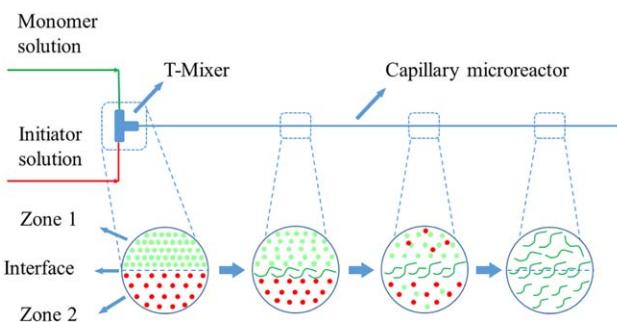
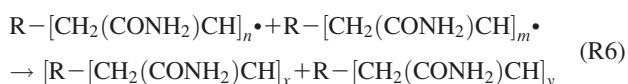


Figure 3. Schematic diagram of the acrylamide polymerization accompanied by the mixing at low flow rates.

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ploy(acrylamide) with different chain lengths, presented as reaction 6 (R6)



Results and Discussion

Mixing in the polymerization process in capillary microreactors

The monomer solution and the initiator solution contact in the T-micromixer and then enter into the capillary microreactor. The flow pattern during the acrylamide polymerization in the capillary microreactor was laminar due to relatively low Reynolds numbers, so the mixing process was driven by the radial diffusion. Figure 3 presents a schematic diagram of the acrylamide polymerization accompanied by the mixing at low flow rates in the radial direction. Two reaction regions in the capillary microreactor are, respectively, defined as Zone 1 and Zone 2, based on an assumption that there is an interface between the monomer solution and the initiator solution at the initial contact of these two reactive solutions. The chain initiation reaction only occurred at the interface initially. With the concentration gradient as a driving force, a part of monomer molecules and initial radicals crossed the interface and diffused to the other reaction zone when the mixing occurred. The monomers and the free radicals participated in the polymerization forming longer molecular chains at the interface, limiting the diffusion of monomers and initial radicals due to the effect of steric hindrance. In fact, the interface between the monomer solution and the initiator solution gradually became blurry and a new zone consisting of the poly(acrylamide) was formed as the polymerization proceeded. The diffusion coefficient of polymers is much lower than those of the monomers and the initial radicals,²⁹ leading to the increase of the heterogeneity during the polymerization. In Zone 1, a higher monomer concentration and a lower free radical concentration were obtained and thus led to produce polymers with longer molecular chains. In contrast, a lower monomer concentration and a higher free radical concentration existed in Zone 2, leading to produce the polymers with shorter molecular chains. The inhomogeneity of various substance concentrations between Zone 1 and Zone 2 in the capillary microreactor may resulted in a broad molecular weight distribution.

Effects of volumetric flow rate and residence time on the acrylamide polymerization

Flow rate is an important factor which can control the flow pattern and affect the mixing performance in micromixers and microreactors.^{15,30} The Reynolds number in microstructured devices is usually low due to their small characteristic dimensions and low volumetric flow rates, and therefore the flow in micromixers and microreactors is generally within the laminar flow regime.³¹ Engler et al. demonstrated that the laminar flow in a T-micromixer can be further distinguished among three flow regimes including stratified flow, vortex flow, and engulfment flow with the Reynolds number lower than 200.³² Both experimental and simulation results have proven that the increase of flow rate results in a higher mixing quality due to the increased vorticity and disturbance inside the T-junction of the T-micromixer.^{16,32}

Figure 4 shows the effects of the volumetric flow rate (q_v) and the residence time (t) on the monomer conversion. The same residence time could be obtained for different volumetric flow rates by applying capillaries with different lengths (L) at the same inner diameter. As shown in Figure 4, the monomer conversion increased significantly with the increase of the residence time. When the residence time was less than 2 min, there was no much difference of monomer conversions for different volumetric flow rates. In this polymerization process, the formation of initial free radicals needs high activation energy, and the chain initiation reaction rate is slow. With such a short residence time, the monomer conversion was rather low for all these volumetric flow rates ($X < 8\%$). The conversion increased with increasing the volumetric flow rate when the residence time was longer than 2 min. This illustrates that the intensified mixing performance provided by a higher volumetric flow rate is beneficial for accelerating the polymerization rate. With the increase of the volumetric flow rate, the

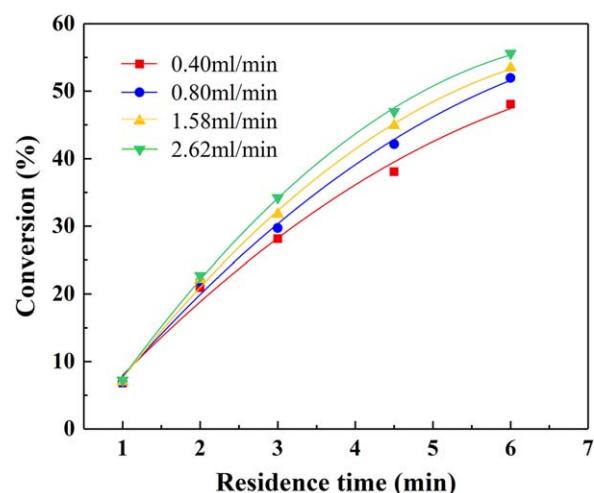


Figure 4. Effects of the volumetric flow rate and the residence time on the acrylamide conversion at different residence times (the inner diameter of capillary microreactor was 1.016 mm, the polymerization temperature was 40°C, and the values of Reynolds number were 12.9, 25.4, 50.8, and 84.7 corresponding to the volumetric flow rates of 0.40, 0.80, 1.58, and 2.62 mL/min).

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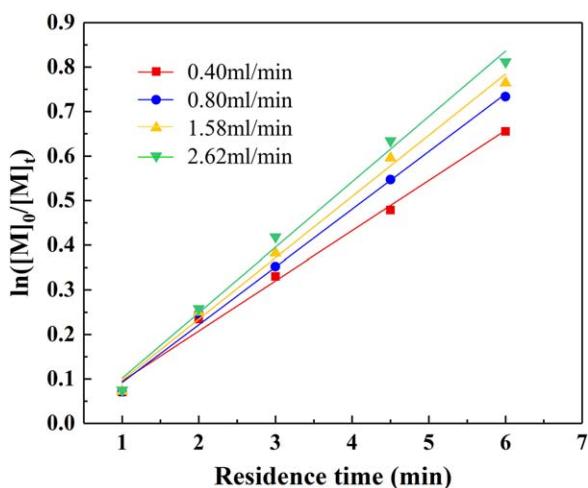


Figure 5. Effect of the volumetric flow rate on apparent polymerization kinetics (the slope values of fitting lines are 0.113, 0.130, 0.137, and 0.147 min^{-1} corresponding to the volumetric flow rates of 0.40 ml/min, 0.80 ml/min, 1.58 ml/min and 2.62 ml/min).

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flow pattern in the T-micromixer varied from the stratified flow to the vortex flow. This can be approximately judged from the Reynolds number, whose value was varied from 12.9 to 84.7. Here, the value of Reynolds number was calculated based on the simplified assumption that the fluid properties such as viscosity and density did not change at the early stage of the polymerization. However, the effect of the volumetric flow rate became weaker when the residence time was further prolonged (e.g., $t > 5 \text{ min}$). This is because the concentrations of free radicals and monomers decreased as the polymerization proceeded. Conversely, the cage effect became more significant as the polymerization proceeded.³³ Some monomers and free radicals were surrounded by the long polymer chains, which reduced the chain initiation efficiency and the polymerization rate.

The relationship between $\ln([M]_0/[M]_t)$ and the residence time is shown in Figure 5. $[M]_0$ and $[M]_t$ represent the initial concentration of acrylamide and the concentration of acrylamide after a certain residence/reaction time (t), respectively. The linear correlation coefficient (R^2) for each fitting line is

above 0.99, indicating that the acrylamide polymerization can be considered to be a pseudo-first order reaction. That is, the polymerization is first order with respect to acrylamide, which was also reported in previous works using a batch reactor for the acrylamide polymerization.^{23,34} Furthermore, an apparent polymerization rate constant (k_{app}) was determined as 0.147 min^{-1} through the slope of the fitting line for the flow rate of 2.62 mL/min. These results indicated that a higher mixing rate should be provided to obtain an intrinsic reaction kinetics of the acrylamide polymerization in the capillary microreactor.

Effect of the temperature on the acrylamide polymerization

The reaction temperature can be well controlled in microreactors, which is difficult to achieve in batch reactors especially for free radical thermopolymerization. In particular, the temperature will also evidently affect the mixing performance in microreactors for the mixing process driven by molecular diffusion.³⁵

Figure 6 shows the effect of the polymerization temperature (T) on the monomer conversion, Mn and PDI at the volumetric flow rate of 0.5 mL/min. The mixing process in the T-micromixer and the capillary microreactor was mainly dominated by molecular diffusion at low Reynolds numbers. Both the molecular diffusion and the collision between the monomer molecules and the free radicals were intensified due to the improved molecular motion accelerated by increasing the temperature. Thus, the monomer conversion increased with the increase of the temperature (Figure 6A). Whereas, the collision probability between various chain radicals increased at the same time leading to a rapid termination reaction rate. Therefore, the conversion of monomers did not further increase as the temperature was higher than 60°C. A maximum conversion of 89.0% could be obtained with the residence time of 12 min in the capillary microreactor. At higher temperatures, the radicals with short chains may contact and react with each other to form dead polymers before growing into long chain radicals, resulting in the decrease of Mn (Figure 6B). The PDI value increased with rising the temperature. This is attributed to the increasing collision probability between the chain radicals, which enhances the heterogeneity of the polymer products.^{36,37}

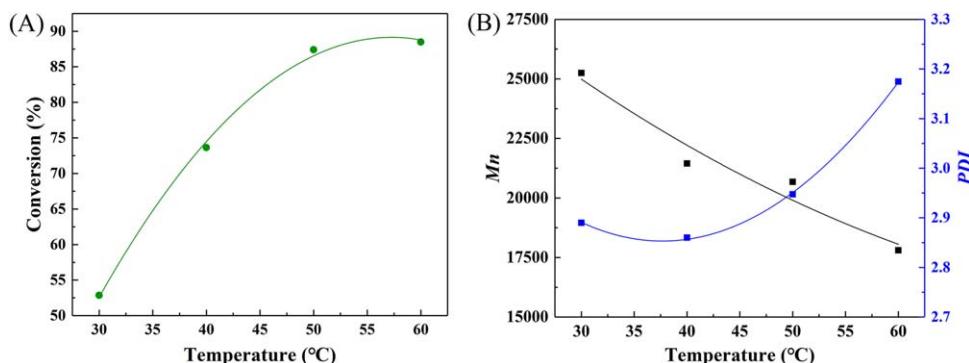


Figure 6. (A) Effect of the polymerization temperature on conversion; (B) Effect of polymerization temperature on Mn and PDI (the inner diameter of capillary microreactor was 1.016 mm, the volumetric flow rate was 1.00 mL/min, and the residence time was 12 min).

[Color figure can be viewed at wileyonlinelibrary.com]

Effect of the viscosity on the acrylamide polymerization

Viscosity is one of important physical properties of fluids, which greatly affects the mass transport in liquid systems.^{38–40} The viscosity of a reaction mixture in the polymerization strongly depends on the concentrations of monomers and produced polymers, the temperature and the molecular weight of polymers.^{41,42} The viscosity varies largely with the conversion of monomers during the polymerization. Figure 7 shows the viscosity variation of the reaction mixture collected from the capillary microreactor with the monomer conversion at different temperatures. The concentration of poly(acrylamide) increased with the increase of the monomer conversion as the polymerization proceeded. Some of polymer chains twined around each other leading to the poor mobility of these polymer chains. Therefore, the viscosity of the reaction mixture increased with the increase of the conversion. The viscosities at different polymerization temperatures became obvious with the increase of the conversion (e.g., $X > 40\%$). As is well known, the fluid viscosity decreased with the increase of the temperature.⁴³ This was a main reason for the reaction mixture viscosity decrease with increasing temperature in the capillary microreactor. Moreover, Mn is another important factor that affects the viscosity of the solution consisting of polymers. As mentioned before, higher polymerization temperatures led to the decrease of Mn. The friction between the polymers with smaller values of Mn was weaker than that between the polymers with larger values of Mn, resulting in the decrease of the reaction mixture viscosity for higher polymerization temperatures.

Figure 8 shows the Mn variation of the polymers collected from the capillary microreactor with the monomer conversion at different temperatures. For all temperatures, the value of Mn decreased with the increase of the monomer conversion. With a low monomer conversion or a short polymerization time, the longer polymer chains were easily formed because the available monomers for the chain propagation were sufficient. Both the monomer and initiator concentrations decreased as the polymerization proceeded. Thus, the free

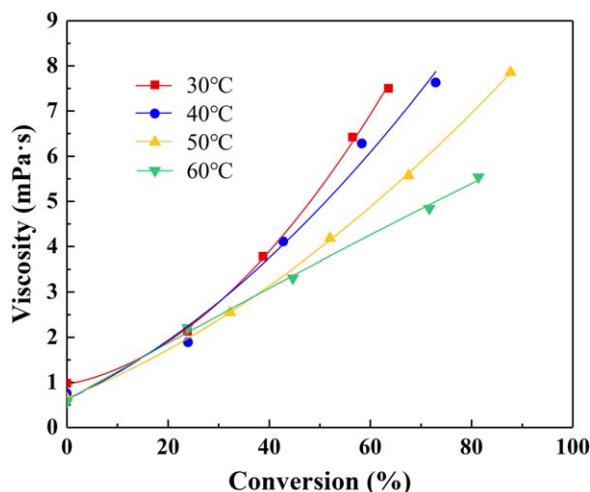


Figure 7. The viscosity variation of the reaction mixture collected from the capillary microreactor with the monomer conversion at different temperatures (the inner diameter of capillary microreactor was 1.016 mm and the volumetric flow rate was 1.00 mL/min).

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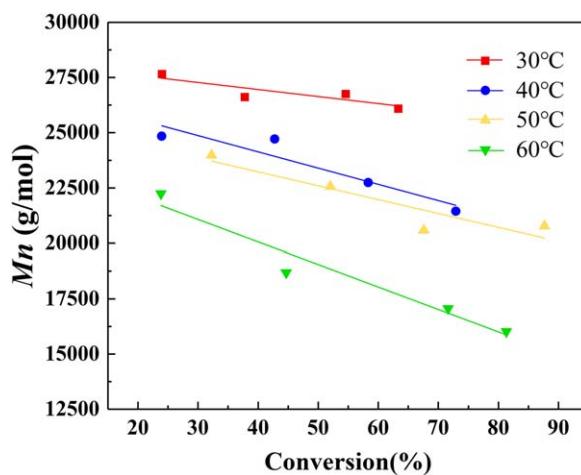


Figure 8. The Mn variation of the polymers collected from the capillary microreactor with the monomer conversion at different temperatures (the inner diameter of capillary microreactor was 1.016 mm, and the volumetric flow rates was 1.00 mL/min).

[Color figure can be viewed at wileyonlinelibrary.com]

radicals available for the chain initiation and the monomers available for chain propagation deceased, leading to the formation of polymers with shorter chains. Therefore, Mn decreased with the increase of the conversion.

The viscosity of the reaction mixture increased with the increase of the conversion although Mn decreased as shown in Figures 7 and 8. This was due to the increase in the concentration of poly(acrylamide) during the polymerization. We doubted that the reaction mixture flowing inside the capillary microreactor might transform gradually from the Newtonian fluid to the non-Newtonian fluid during the acrylamide polymerization. Figure 9A shows the effect of the shear rate on the viscosities of the reaction mixtures from the capillary microreactor. With increasing the shear rate, the value of the viscosity changed very slightly for different monomer conversions. It indicated that the viscosity was independent of the shear rate. This is one of important characteristics of Newtonian fluids.⁴⁴ As shown in Figure 9B, the ratio of the shear stress to the shear rate was constant for reaction mixtures with various monomer conversions. These results again illustrated that the reaction mixture during the polymerization in the capillary microreactor was maintained as a Newtonian fluid.⁴⁵ It was attributed to the low molecular weight of the polymers ($M_n < 30,000$) synthesized in the capillary microreactor.

The effect of the viscosity on the acrylamide polymerization can be reflected by the diffusion coefficients of monomers and produced polymers in a more direct way. Wilke-Chang equation provides a theoretical expression for the calculation of diffusion coefficients in liquid phases expressed as Eq. 1³⁵

$$D_{AB} = 7.4 \times 10^{-8} \frac{T \sqrt{\varphi_B M_B}}{\eta V_A^{0.6}} \quad (1)$$

where D_{AB} represents the diffusivity of solute A in the solvent B, V_A is the molar volume of solute at its normal boiling point (cm^3/mol), T is the absolute temperature (K), η is the viscosity of solvent ($\text{mPa}\cdot\text{s}$), φ_B is a parameter for the molecular association in the solution, and M_B is the molecular mass of the solvent (g/mol), respectively.

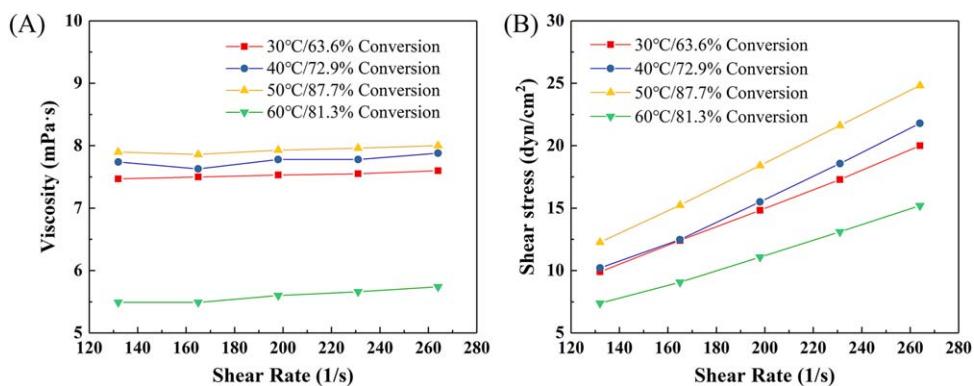


Figure 9. (A) Effect of the shear rate on the viscosities of the reaction mixtures from the capillary microreactor, (B) effect of shear rate on the shear stress for reaction mixtures with various monomer conversions.

[Color figure can be viewed at wileyonlinelibrary.com]

The viscosity variation results in the changes of diffusion coefficients, and thus the evaluation of mixing efficiencies during the polymerization in microreactors becomes tricky. With basically understanding the effects of the temperature, the conversion of monomer and the molecular weight of poly(acrylamide) on the viscosity of the reaction mixture (η_R), a power function is developed to predict the viscosity of the reaction mixture during the polymerization in the capillary microreactor

$$\eta_R = \varphi X^\varepsilon T^\beta M_n^\gamma \quad (2)$$

where φ is the pre-exponential factor, ε , β and γ are the exponents with respect to the monomer conversion, the temperature and the number-average molecular weight, respectively. The regression of the parameters of this model was performed with the software package Matlab R2014b. Next, nonlinear fitting was realized with the least-squares sense solver lsqcurvefit, and then the fitting values of φ , ε , β , γ and R-square were obtained, as shown in Table 1.

To evaluate the credibility of these fitting parameters, the experimental and predicted values of the viscosities of the reaction mixtures are compared, as shown in Figure 10. The relative deviations between the experimental and predicted values are found to be within $\pm 12\%$. It can be concluded that the above correlation can be used to accurately calculate the reaction mixture viscosity for predicting the diffusion coefficients during the acrylamide polymerization in the microreactor under the involved operational conditions.

Furthermore, the correlation (Eq. 2) was integrated into Eq. 1 and then the following equation could be obtained for calculating the diffusion coefficient of the monomers (D_{mo}) in the reaction mixture during polymerization

$$D_{mo} = 2.4667 * 10^{-4} \frac{T^{1.0127} \sqrt{\varphi_B M_B}}{X^{1.2193} M_n^{1.0518} V_{mo}^{0.6}} \quad (3)$$

where V_{mo} is the molar volume of the monomer at its normal boiling point (cm^3/mol).

With this equation for calculating the diffusion coefficient of monomers in hand, the characteristic mixing time (τ_{mix}) in

the capillary microreactor during the polymerization can be calculated by the Einstein-Smoluchovski equation with considering the flow pattern as a strictly laminar flow²²

$$\tau_{mix} = \frac{d_i^2}{4D} \quad (4)$$

where the inner diameter of the capillary (d_i) can be considered as the characteristic mass transport distance. It should be noted that only the transport of monomers is considered during the mixing process in this equation. In fact, the transport of monomer radicals and polymers with various chain lengths would affect that of monomers in this polymerization process.

The characteristic mixing time (τ_{mo}) with specific monomer conversion (X) and number-average molecular weight (M_n) can be calculated according to Eqs. 3 and 4

$$\tau_{mo} = 1.0135 * 10^5 \frac{d_i^2 X^{1.2193} M_n^{1.0518} V_{mo}^{0.6}}{T^{1.0127} \sqrt{\varphi_B M_B}} \quad (5)$$

The diffusion coefficient of the polymers (D_{po}) can be calculated by the Phillips model⁴⁶

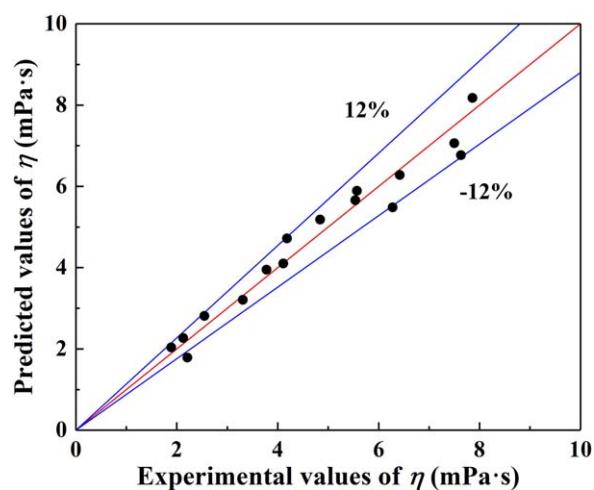


Figure 10. Comparison between the experimental values of the viscosities of the reaction mixtures versus the predicted values.

[Color figure can be viewed at wileyonlinelibrary.com]

Table 1. Simulated Values of φ , ε , β , γ and R-Square

φ	ε	β	γ	R-square
0.0003	1.2193	-0.0127	1.0518	0.9537

$$D_{po} = D_0 \exp(-\alpha c_{po}^v) \quad (6)$$

where c_{po} is the concentration of polymers, D_0 is the diffusion coefficient with the average value of $5 \times 10^{-11} (\text{m}^2 \cdot \text{s}^{-1})$ in the limit of low concentrations,⁴⁷ α is the parameter dependent on the polymer molecular weight for macromolecules, and v is the parameter with the value of 1 for polymers with low molecular weight ($M_n < 40,000$).⁴⁸

D_{po} can be further expressed as the following equation

$$D_{po} = D_0 \exp(-\alpha c_{A0} X) \quad (7)$$

According to Eqs. 4 and 7, the characteristic mixing time (τ_{po}) of the polymers with various chain lengths in the reaction mixture can be deduced, and the result leads to the following equation

$$\tau_{po} = \frac{d_i^2 \exp(\alpha c_{A0} X)}{D_0} \quad (8)$$

The existence of produced polymers hinders the diffusion of monomers due to its steric effects. Moreover, the monomer radicals with various chain lengths participate in the polymerization process, and its transport can be considered to be similar to that of polymers. The diffusion processes of the monomers, monomer radicals and polymers occurred at the same time once the polymerization was initiated. Considering the mutual effects of the transports of monomers, monomer radicals and polymers, the overall average characteristic mixing time (t_o) is determined by the maximum value of τ_{mo} and τ_{po} . Therefore, the following equation can be obtained

$$t_o = \max(\tau_{mo}, \tau_{po}) \quad (9)$$

According to Eqs. 5 and 8, t_o increases significantly with the increase of the monomer conversion. To achieve a high monomer conversion for the polymerization in the capillary microreactor, there would be a challenge that capillaries with rather long lengths should be provided for compromising the overall characteristic mixing time with a medium or high throughput. The capillary length required (L_{req}) for reaching a homogenous mixing condition for polymerization can be deduced as follows⁴⁹

$$t_{res} \geq t_o \quad (10)$$

$$t_{res} = \frac{\pi L d_i^2}{4 q_v} \quad (11)$$

$$L_{req} \geq \frac{d_i}{2} \times Pe \quad (12)$$

where t_{res} is the minimum residence timescale of the reaction mixture in the capillary microreactor and its value should exceed the characteristic mixing timescale for complete mixing, and l is the hydraulic diameter of the capillary microreactor. The Péclet number (Pe) is defined as⁴⁹

$$Pe = \frac{ul}{D} = \frac{ud_i}{2D} = \frac{2q_v}{\pi D d_i} \quad (13)$$

where u is the average linear velocity of the reaction mixture in the capillary microreactor. In our experiments, the conversion of 87.7% could be obtained with the capillary length of 15 m and the inner diameter of 1.016 mm at the residence time of 12 min and the polymerization temperature of 50°C. For typical conditions applied, the values of τ_{mo} and τ_{po} were 36.44 min and 84.97 min, respectively. Therefore, the value of t_o was equal to 84.97 min which was larger than that of t_{res} .

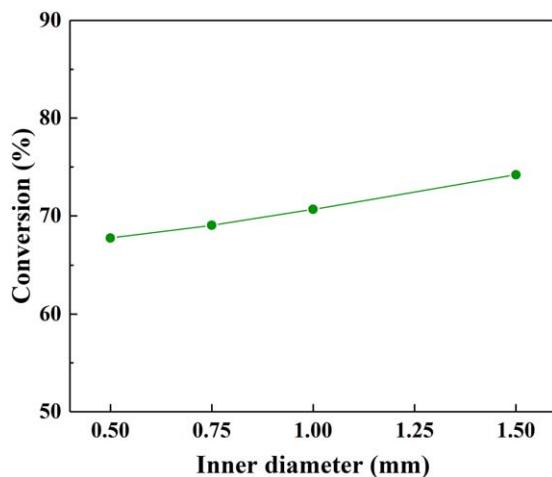


Figure 11. Effect of the capillary inner diameter on the monomer conversion at a constant residence time of 5 min.

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Moreover, the value of Pe is equal to 2.06×10^5 , and the required capillary length is 104.90 m if the homogeneous mixing needs to be achieved for such conditions (e.g., $X = 87.7\%$ and $T = 50^\circ\text{C}$). From the above calculation, it illustrated that the produced polymers, the monomer radicals, the monomers that did not participate in the polymerization still could not reach homogenous mixing when they reached the outlet of the capillary microreactor.

Effect of the capillary diameter on acrylamide polymerization

According to Eq. 9, the overall characteristic mixing time in the capillary microreactor can be shortened by reducing the inner radius of the capillary. Figure 11 shows the effect of the capillary inner diameter on the acrylamide polymerization at a constant residence time. Interestingly, it was found that the monomer conversion was improved with the increase of capillary diameter (Figure 11). As is well known, the free radical polymerization of acrylamide is a highly exothermic reaction. The capillary with a smaller inner diameter had a higher heat-transfer rate than the capillary with a larger inner diameter. Therefore, the heat produced in the polymerization could be removed more quickly from the capillary with a smaller inner diameter (e.g., $d_i = 0.508 \text{ mm}$). In other words, the temperature gradient possibly existed in the capillary with a larger diameter (e.g., $d_i = 1.548 \text{ mm}$).

The schematic diagram of a heat balance analysis for the polymerization in capillary microreactors is shown in Figure 12. The heat balance equation can be expressed as the following

$$Q_{total} = Q_{exchanged} + Q_{out} \quad (14)$$

where Q_{total} is the total heat released by the polymerization of acrylamide, $Q_{exchanged}$ is the heat removed through the exchange with the capillary wall, and Q_{out} is the heat taken to the outside of the capillary by the flow of the reaction mixture. Q_{total} can be expressed as

$$Q_{total} = q_v (-\Delta H) c_{A0} X_A \quad (15)$$

where ΔH is the enthalpy of the polymerization of acrylamide ($81.5 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$),⁵⁰ and c_{A0} is the initial concentration of monomers (1.407 mol/L).

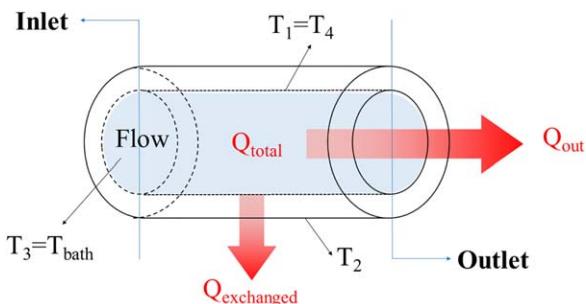


Figure 12. Schematic diagram of a heat balance analysis for the polymerization in microreactors.
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Due to the laminar flow characteristics within the capillary microreactor, the convection heat transfer could be neglected. Thus, $Q_{\text{exchanged}}$ can be calculated as follows

$$Q_{\text{exchanged}} = 2\pi\lambda L(T_1 - T_2)/\ln(r_2/r_1) \quad (16)$$

where λ is the thermal conductivity of the capillary with a value of $0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$,⁵¹ T_1 is the average temperature on the inner wall surface of the capillary, T_2 is the average temperature on the outer wall surface of the capillary and its value is considered to be the set temperature of the water bath (50°C), and r_1/r_2 is the outer/inner radius of the capillary, respectively. Q_{out} can be expressed as

$$Q_{\text{out}} = q_v\rho c_p(T_4 - T_3) \quad (17)$$

where ρ is the initial density of the reaction mixture, c_p is the specific heat capacity of water, T_3 and T_4 are the temperatures of the reaction mixture at the inlet and outlet of the capillary microreactor, respectively. Here, T_3 is considered as the set temperature of the water bath. Two pieces of tubing immersed inside the water bath for introducing the initiator and acrylamide solutions into the capillary microreactor through the T-micromixer were long enough for the heat exchange. Thus, the temperatures for the initiator and acrylamide solutions at the T-micromixer could reach the set temperature of the water bath. T_4 is considered as the average temperature on the inner wall surface of the capillary. After traveling along the capillary with a long distance, the temperature of the reaction mixture can be supposed to be the same as the average temperature on the inner wall surface of the capillary. Therefore, the following equation can be obtained

$$T_4 - T_3 = T_1 - T_2 \quad (18)$$

Equation 17 can be further transformed as the following

$$Q_{\text{out}} = q_v\rho c_p(T_1 - T_2) \quad (19)$$

The temperature difference between T_1 and T_2 is defined as ΔT

Table 2. List of the Temperature Difference Between the Outer and Inner Wall Surfaces of the Capillary Under Different Conditions

No.	d_i (mm)	d_o (mm)	L (m)	X	ΔT (°C)
1	0.508	1.588	10.0	0.677	0.085
2	0.762	1.588	11.8	0.690	0.126
3	1.016	1.588	10.0	0.707	0.138
4	1.548	3.175	5.10	0.742	0.553

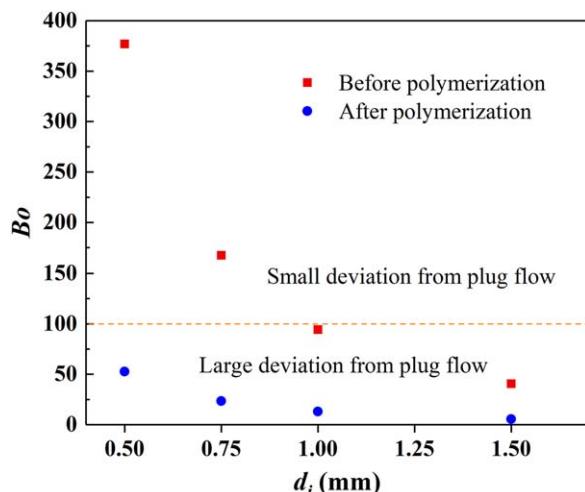


Figure 13. The calculated values of Bo before/after polymerization.

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$$\Delta T = T_1 - T_2 \quad (20)$$

These equations (Eqs. 14–20) lead to the following equation for calculating ΔT

$$\Delta T = \frac{q_v(-\Delta H)c_{A0}X}{\frac{2\pi\lambda L}{\ln(r_2/r_1)} + q_v\rho c_p} \quad (21)$$

According to the experimental conditions (e.g., q_v , r_1 , and r_2) and results (e.g., X), the values of ΔT can be obtained, as shown in Table 2.

As can be seen from Table 2, ΔT increases with the increase in the inner diameter of the capillary. Although the temperature difference between the outer and inner wall surfaces of the capillary was very small, it indicated that a radial temperature gradient existed inside the capillary microreactor. The radial temperature gradient inside the capillary microreactor with a larger inner diameter was higher than that inside the capillary microreactor with a smaller inner diameter. As discussed above, the flow pattern in the capillary microreactor during the polymerization of acrylamide was laminar. The polymerization firstly occurred at the interface where the monomers and the initiators contacted with each other. The initial interfacial area in the capillary with a larger inner diameter was larger, leading to more hot spots appearing in the interface due to the fact that the polymerization of acrylamide was highly exothermic. The heat produced from the reaction resulted in the radial temperature gradient and meanwhile accelerated the polymerization of acrylamide. Therefore, the capillary microreactor with a larger the inner diameter resulted in a higher monomer conversion.

The conversion difference indicated that the concentration gradient was different with the inner diameter variation, which might lead to the flow profile and dispersion effect difference.

Table 3. List of Parameters with Different d_i in the Polymerization Process

No.	d_i (mm)	L (m)	L_{full}	S_L (m ²)	D'
1	0.508	10.0	1.458	0.051	0.006
2	0.762	11.8	3.870	0.090	0.020
3	1.016	10.0	5.831	0.102	0.025
4	1.548	5.1	6.902	—	—

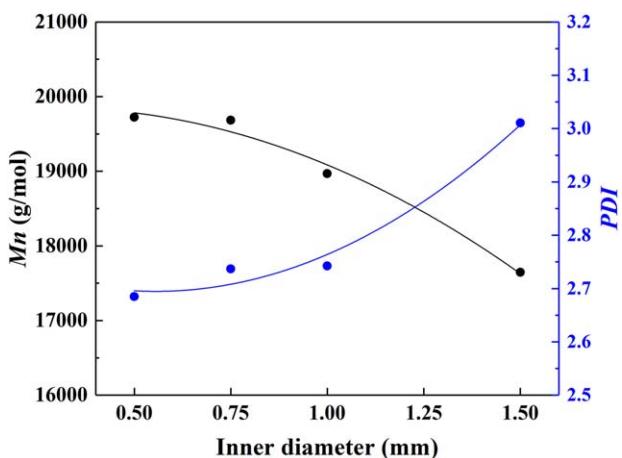


Figure 14. Effect of the capillary inner diameter on Mn and PDI at a constant residence time of 5 min.

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Microreactors are typically described as plug flow reactors. However, the plug flow in a channel is only valid when the radial diffusion is much faster than convective mass transport along the channel length.^{21,52} The Bodenstein number (Bo) in a dispersion model, provided by Taylor and Aris,^{21,53,54} describes the ratio of convection to dispersion and provides a general method to estimate the deviation from plug flow

$$Bo = \frac{uL}{D'} = \frac{4\phi D_a t}{d_i^2} \quad (22)$$

Here, the diffusion coefficient D_a is represented by the average diffusion coefficient of monomers in the reaction mixture concerning the beginning and end of the polymerization, which can be calculated from Eq. 1. D' is the Taylor dispersion coefficient which typically is equal to the axial diffusivity in small-scale flow systems. The parameter ϕ is related to the channel geometry, which is 48 for channels with circular cross-sections. Small deviations from plug flow can be seen in flow systems with $Bo > 100$, while large deviations from plug flow can be observed with $Bo < 100$.

To investigate the flow profile variation with d_i , the value of Bo was calculated and the results are shown in Figure 13. Bo decreased with enlarging d_i . For the initial reaction mixture, $Bo > 100$ when d_i was 0.508 mm or 0.762 mm revealing that small deviations from plug flow existed and the dispersion effect was limited. While $Bo < 100$ when d_i was 1.016 mm or

1.548 mm indicating that deviations from plug flow were enhanced and the dispersion effect could not be ignored. The value of Bo decreased at the outlet of the microreactor comparing with that at the inlet of the microreactor because of the decrease of the diffusion coefficient. That is, the deviations from plug flow increased gradually with the polymerization proceeding.

The Taylor dispersion coefficient can be further expressed as the following

$$D' = \frac{S_L^2}{4\phi D_a t^2} = \frac{uLd_i^2}{4\phi D_a t} \quad (23)$$

where S_L is defined as the area of the maximum quadrat cross-section along the axial direction in the channel ($S_L = Ld_i$). As illustrated by Eq. 23, a larger diffusion coefficient, a longer residence time, a smaller inner diameter and a longer length of the capillary are beneficial for eliminating the dispersion effect. For experiments, the capillary length was accordingly shortened when the capillary diameter became larger to maintain a constant residence time in various capillary microreactors. D' is a quadratic function of d_i , indicating that the sensitivity of the dispersion effect to d_i is higher compared to L . It should be noted that the aforementioned dispersion model is based on an assumption that the channel length is long enough to achieve fully developed flow.²¹ The guideline for its application is presented as

$$\frac{L_{\text{full}}}{d_i} \geq 0.04 \frac{ud_i}{D_a} \quad (24)$$

where L_{full} is the channel length needed for a fully developed flow. In our experiments, capillary microreactors with various diameters and lengths were applied for the polymerization, and thus the proper application of the Taylor dispersion model was evaluated. For the capillary with 1.548 mm inner diameter, the value of L was smaller than that of L_{full} , indicating that the flow had not fully develop in the polymerization. According to experimental conditions, the value of D' with different d_i was calculated according to Eq. 23 and listed in Table 3.

As shown in Figure 14, the value of Mn increased and the value of PDI decreased with reducing the capillary inner diameter. The capillary with a smaller inner diameter provided a shorter diffusion distance for the transport process, which was beneficial for obtaining higher mixing efficiencies in comparison with the capillary with a larger inner diameter. Moreover, the dispersion effect became more remarkable in the capillary microreactor with a larger inner diameter (see Table 3), which

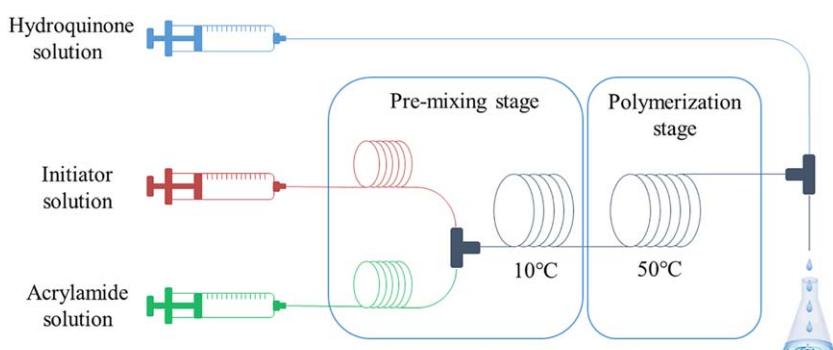


Figure 15. Schematic diagram of the microreactor system with a pre-mixing stage and a polymerization stage for synthesizing poly(acrylamide).

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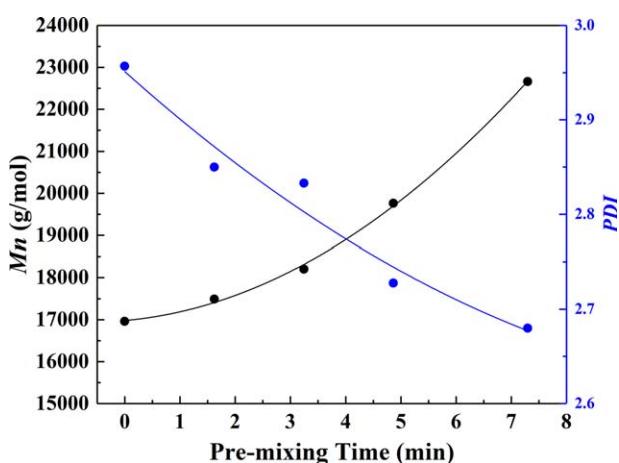


Figure 16. Effect of the pre-mixing time on Mn and PDI (the inner diameter of capillary microreactor was 1.016 mm, the polymerization temperature was 50°C, the volumetric flow rate was 1.00 ml/min, and the polymerization time was 7 min).

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further enhanced the inhomogeneity of the reaction condition for the polymerization, leading to a decrease of Mn and an increase of PDI.

Effect of premixing time on acrylamide polymerization

Mass transport phenomena are rather complex during the polymerization, and this complexity is possibly further aggravated by the variation of rheological property.^{42,55,56} Most of free radical polymerization processes are kinetically fast, and whether they are mixing-controlled systems strongly depends on reactors and operational conditions.^{57,58} As shown in our experimental results, the effect of insufficient mixing on the polymerization is not trivial, and its elimination should be paid enough attention even the polymerization is conducted in microreactors. Currently, this was also reported by other researchers.⁵⁹

A pre-mixing stage with a long capillary was added before the reaction stage to minimize the effect of insufficient mixing on the acrylamide polymerization, as shown in Figure 15. It should be noted that the temperature was set to 10°C to avoid any polymerization in the premixing process of the initiator solution and the monomer solution. The polymerization only occurred in the reaction stage at higher temperatures. The premixing was driven by the molecular diffusion and the reaction mixture in this stage could be considered as the Newtonian fluid. Therefore, the characteristic mixing time can be calculated by Eq. 4. The values of diffusion coefficient and characteristic mixing time in the capillary for the pre-mixing stage were, respectively, determined to be $6.221 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ and 6.7 min at 10°C. Figure 16 shows the variations of Mn and PDI with different pre-mixing times. As the premixing time increased, the mixing between the monomers and the initiators tended to be completed. A longer premixing time was beneficial for both the increase of Mn and the decrease of PDI. In the case of the pre-mixing time longer than the characteristic mixing time, the mixing between the monomers and the initiators should theoretically be completed. This should result in the formation of homogeneous polymers with long chains. On the contrary, incomplete mixing would lead to the formation

of chains with the different lengths. However, the values of PDI for this case with theoretically complete mixing was still much larger than 1, which were close to those for the free radical polymerization of butyl acrylate in microreactors performed by Iwasaki and Yoshida.⁶⁰ This was mainly attributed to the characteristics of free radical polymerization in solution. The heterogeneity of the solution can be minimized by the pre-mixing strategy. However, it cannot be totally eliminated because the chain propagation is still not well controlled during the polymerization resulting in large values of PDI of the produced polymers.

Conclusions

The influence of mixing performance on the nonliving free radical polymerization of acrylamide in capillary microreactors was investigated. The mixing process during the polymerization in the capillary microreactor was analyzed according to the flow characteristics. A higher flow rate was beneficial for improving the mixing between the initiators and the monomers and thus the polymerization rate. A higher temperature was also found to improve the mixing performance and the monomer conversion in the polymerization. However, higher polymerization temperatures led to lower values of Mn and larger values of PDI. The measurement on the viscosity of the reaction mixture with different monomer conversions at various temperatures was conducted. The viscosity of the reaction mixture significantly increased with the increase of the monomer conversion. Nevertheless, the reaction mixture in the capillary microreactor during the polymerization still belonged to the Newtonian fluid because of the low molecular weight of the produced poly(acrylamide). Both diffusion coefficients of the monomers and the polymers were correlated with the monomer conversion, the viscosity of the reaction mixture during the polymerization. With the diffusion coefficients of the monomers and the polymers in hand, the average characteristic mixing time in the capillary microreactor during the polymerization was further deduced with considering the mutual effects of the transports of monomers, monomer radicals, and polymers. The monomer conversion of 87.0% could be obtained with the capillary length of 15 m at the residence time of 12 min and the reaction temperature of 50°C. However, the produced polymers and the residual monomers still could not achieve homogenous mixing in the capillary microreactor according to the calculation of the characteristic mixing time.

The monomer conversion was improved with the increase of the capillary diameter. A heat balance for the polymerization in the capillary microreactor was analyzed to explain the effect of the capillary diameter on the polymerization performance. The radial temperature heterogeneity became higher and more hot spots existed inside the capillary microreactor with a larger inner diameter, leading to a higher monomer conversion. Moreover, the flow profile estimation indicated that the deviations from plug flow increased with enlarging the capillary diameter and with the polymerization proceeding according to the calculation of the Bodenstein number. The dispersion effect indicated by the Taylor dispersion coefficient aggravated the inhomogeneity of the reaction condition in capillary microreactors, which was more significant in the microreactor with a larger inner diameter. Thus, poly(acrylamide) synthesized in the capillary microreactor with a smaller inner diameter led to larger values of Mn and lower values of PDI than those in the capillary microreactor with a

larger inner diameter. The addition of a premixing stage minimized the effect of insufficient mixing between the initiators and the monomers in the polymerization. It was found that Mn increased and PDI decreased with the increase of the premixing time.

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