

Atom Transfer Radical Polymerization in Continuous Microflow: Effect of Process Parameters

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Received: 15 January 2014; accepted: 8 March 2014

We report on the synthesis of 2-(dimethylamino)ethyl methacrylate by atom transfer radical polymerization (ATRP) in tubular microreactors. Different process parameters, temperature, pressure, and shear rate, were considered to accelerate the reaction. Increase in temperature induced a faster reaction, but controlled nature of ATRP decreased past a threshold value that can be increased up to 95 °C by reducing the residence time. Positive effect of pressure was observed since significant increases in monomer conversion (+12.5 %) and molecular weight (+5,000 g/mol) were obtained. Moreover, polydispersity index was found to decrease from 1.52 at normal pressure to 1.44 at 100 bars. Benefit of pressure was more visible in smaller reaction space (smaller tube diameter). Finally, shear rate has quite an influence on the early stage of the polymerization and is expressed by an increase in the reaction rate. However, the effect was dimmed for long residence times.

Keywords: ATRP, microreactor, high pressure, polymerization

1. Introduction

Demand for low molecular weight distributions along with controlled architectures (e.g. block, branched) in free radical polymerizations triggered the development of different controlled radical polymerization techniques like nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation technique (RAFT). These techniques of polymerization rely on the dynamic equilibrium between propagating radicals and dormant species, thereby increasing the life of a growing chain from seconds to hours and making the reaction slower because of intermittent activation and deactivation processes [1]. However, fast controlled radical polymerizations are still highly desirable not only for throughput concerns but also for energy consumption and reduction of equipment size.

Recent findings show potentials of microreactors to carry out polymerization in a controlled way [2]. High interface and heat exchange surface per volume unit are the key factors for fast mixing and efficient heat transfers, respectively. These features of microreactors, in contrast to lab scale or large scale reactors [3], provide a better control from the beginning of reaction to achieve controlled macromolecular characteristics [4]. Efficient heat management and short diffusion pathways in microreactors unleash the possibility to carry out the reaction at new operating windows. Thus, it was found that anionic polymerization can be operated at room or even moderate temperatures compared to conventional cryogenic temperatures in macroscale reactors [5]. Controlled radical polymerization techniques in microreactors are not new and were reported by many authors [4c, 6]. However, accelerating these polymerization processes in microreactor without sacrificing their controlled characteristics has been surprisingly less studied. Recent findings suggest that controlled radical polymerizations (RAFT and ATRP) can be accelerated significantly by microreactors [4d, 7]. These findings rely purely on the primary characteristic of the microreactor, i.e. high surface to volume ratio. On the other hand, when a

batch polymerization is transferred to a continuous polymerization in microreactor, some additional process parameters like pressure and shear rate come into picture, which can significantly influence both the polymerization and polymer characteristics. In the short history of polymerization in microreactors, the effects of these parameters on polymerization were never studied thoroughly. Though, the effect of pressure was studied extensively in macro/batch reactors and significant acceleration of controlled radical polymerizations was observed [8]. However, these studies were performed under a very high pressure of 2,000–6,000 bars [9]. Need for specialized equipment and limited reaction volume limits the applicability of such high-pressure reaction of controlled radical polymerization other than research and academic purpose. Following the intuition and to bridge this gap, the effect of temperature, pressure (range of 100 bars), and shear rate on ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in microreactor are reported in this article. To the best of our knowledge, such studies concerning ATRP in microreactor have never been reported before.

2. Results and Discussion

2.1. Effect of Temperature on Polymerization in Microreactor.

It is well known that temperature has an accelerating effect on polymerization. On the other hand, termination rate also increases with temperature, resulting in polymer with broader molecular weight distribution. If the diffusion of monomer towards the growing chain can be facilitated to decrease termination, then significant acceleration can be achieved in a controlled way. Known for their diffusion driven mixing capability, microreactors have potentials for such requirements. Microreactors allow a broad range on reaction temperature as they can operate at higher temperatures owing to the large surface to volume ratio which guarantee nearly isothermal conditions. Considering these features, kinetics of ATRP of DMAEMA was studied in a microreactor at different temperatures. Polymerization rate increased significantly with temperature as shown in Figure 1 (Figure S7 in Supporting Information [SI]). Molecular weight of polymer obtained is very close to the theoretical values

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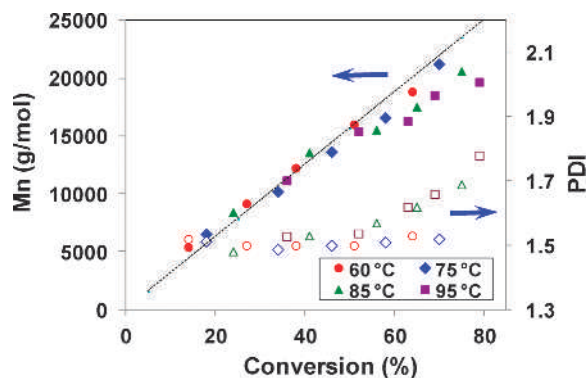


Figure 1. Evolution of molecular weight (M_n , filled symbols) and PDI (empty symbols) with conversion at different temperatures

for 60 °C and 75 °C indicating controlled characteristics of polymerization. However, difference between theoretical and actual molecular weight (M_n) starts to appear at polymerization temperature 85 °C and 95 °C after 30 min of residence time. More insight about the polymerization was seen when polydispersity indexes (PDIs) (Figure 1) obtained for different polymerization temperatures were compared. Significant increase in PDI was observed after 30 min of residence time, at high polymerization temperatures (i.e. 85 °C and 95 °C) indicating uncontrolled reaction. Dominating transfer reactions and auto initiation may be responsible for such uncontrolled behavior of ATRP. Considering the controlled characteristic and faster polymerization, 75 °C was chosen as the polymerization temperature for further investigations. However, for molecular weights around 15,000 g/mol, higher temperature seems to be a good alternative as it reduces the polymerization time significantly (see Figure S1 and Figure S7 in SI), without sacrificing the controlled nature of ATRP.

2.2. Effect of Pressure. Increase in conversion and molecular weight was observed with increase in pressure from 1 bar to 50 bars at different residence times as shown in Figures 2 and 3. M_n /conversion plot shown in Figure 3 indicates a controlled polymerization as the M_n obtained by gel permeation chromatography (GPC) lies close to theoretical values. A significant increase in conversion can be attributed partially to increased propagation rate constant with pressure [10]. Increased density of polymerizing solution with application of pressure can be another factor for increased conversion in microreactor. In literature, enough evidences are available indicating increased density of liquid and polymer solution with pressure [11]. As the polymerization was carried out in a continuous-flow microreactor, increased density under pressure leads to reduced

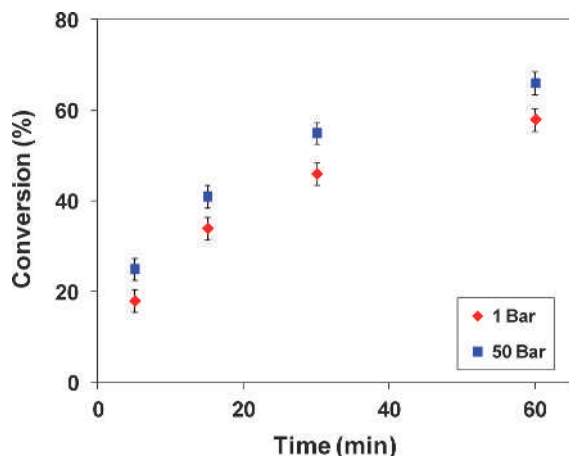


Figure 2. Conversion of DMAEMA under different polymerization pressures in a microreactor of 810 μm internal diameter and 3 m length

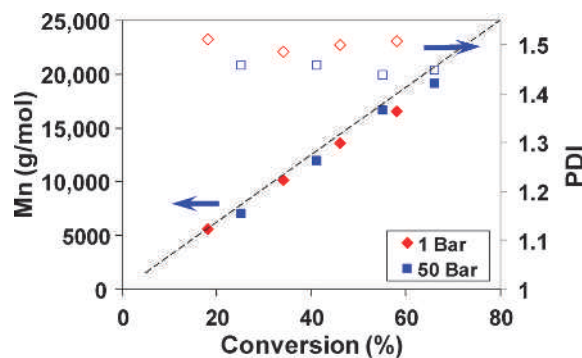


Figure 3. Effect of pressure on molecular weight (M_n , filled symbols) and PDI (empty symbols)

volumetric flow rate which results in higher residence times than the set ones. Therefore, increased polymerization rate cannot be only due to one of these two factors solely but rather it is due to the synergistic effect of both. Furthermore, unexpected PDI reduction was observed as shown in Figure 3 and Table 1 (entries 2 and 9, respectively) and may be explained by a decrease in the termination rate under higher pressures [12].

In order to have a clear idea about the impact of pressure on polymerization in micro dimension, polymerization was carried out in microreactors of 576, 876 and 1753 μm internal diameter. As shown in Figure 4, conversions obtained at 1 bar were nearly the same for all three diameters. Interestingly, an increase in conversion with pressure was observed for all three reactors but followed distinct paths. Moreover, a plateau at high pressure indicates a nonlinear relationship between pressure and conversion. This means that a significant increase in pressure is required to increase the conversion further. Evolution in M_n with pressure (Figure 5) followed the same trend as conversion. Higher propagation rates at higher pressures in conjunction with favorable radial diffusion of monomer in smaller diameter microreactor resulted in a faster kinetics.

In contrast, whatever the pressure and under similar residence time, larger diameter microreactors reduced conversion and M_n while increasing PDI (Figures 4 and 5). For Newtonian fluids flowing in a tubular pipe, diffusion theory of Taylor [13] predicts a more prominent axial diffusion for larger tube diameters which in turn induces a broader residence time distribution (RTD) [14]. For a controlled/“living” radical polymerization like ATRP, RTD will significantly affect the molecular weight distribution of synthesized macromolecules as all growing chains do not spend the same time in the reactor. Therefore, the broader the RTD, the higher is the PDI and the smaller the M_n and monomer conversion. These observations suggest that polymerization can be significantly accelerated, +12.5% in conversion within 1 h with moderate increase in pressure from 1 to 100 bars and reduction in tube diameter from 1753 to 576 μm .

2.3. Effect of Shear Rate on Polymerization. In a tubular geometry, the inner wall surface to volume ratio is inversely proportional to the inner tube radius. Thus, tubular microreactors are characterized by a much higher wall surface per volume unit than their macroscale counterparts (e.g. there is a factor of 8 between 1/16" and 1/2" tubes). Therefore, a good portion of the fluid flowing in a tubular microreactor experiences the shear at the wall which may, unlike in bigger tubes, affect significantly the overall polymer characteristics (molecular weight, PDI). Indeed, wall shear inside a microreactor cannot only alter mixing but may also change the conformation of macromolecules [15]. Elongated conformation of a growing polymer chain can make the reacting site more accessible for reaction than a coiled conformation. This condition can enhance the reaction rate as well as the control over the polymerization. Shear rate

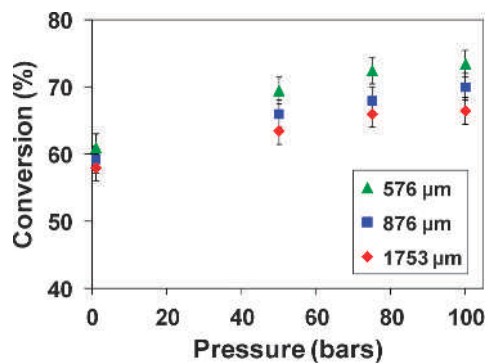
Table 1. Summary of monomer conversion and macromolecular characteristics obtained at different polymerization conditions and for different microreactor dimensions

Entry	Reactor length (meter)	Reactor diameter (μm)	Temp. ($^{\circ}\text{C}$)	Pressure (bar)	Shear rate ^a (s^{-1})	Residence time (min)	Conv. (%)	Mn (g/mol)	PDI
1	3	876	60	0.5–1	–	120	64	18,900	1.53
2	3	876	75	0.5–1	15.2	30	46	13,900	1.51
3	3	876	75	0.5–1	3.8	120	70	21,200	1.52
4	3	876	85	0.5–1	–	30	56	15,600	1.56
5	3	876	85	0.5–1	–	120	76	20,600	1.69
6	3	876	95	0.5–1	–	15	52	15,400	1.53
7	3	876	95	0.5–1	–	120	80	19,700	1.77
8	3	876	75	50	–	60	66	19,700	1.46
9	3	876	75	100	–	60	70	21,300	1.44
10	3	576	75	0.5–1	–	60	61	16,900	1.49
11	3	576	75	100	–	60	73.5	22,300	1.42
12	3	1753	75	0.5–1	–	60	58	15,300	1.58
13	3	1753	75	100	69.80	60	67	19,600	1.51
14	6	876	75	0.5–1	30.44	30	46.5	14,300	1.49
15	6	876	75	0.5–1	7.62	120	72	21,000	1.50
16	9	876	75	0.5–1	45.66	30	50	14,800	1.48
17	9	876	75	0.5–1	11.43	120	72	21,700	1.51
18	18	876	75	0.5–1	91.32	30	52	15,000	1.49
19	18	876	75	0.5–1	22.86	120	73	22,600	1.50

^a At wall.

was changed by increasing the length of reactor while keeping the residence time constant and was varied from 3.81 to 547.7 s^{-1} for 3 m length / 2 h residence time and 18 m length / 5 min residence time, respectively (see Table 1 and Supporting Information for detailed calculations). Increase in conversion was observed (Figure 6) with an increase in reactor length (i.e., an increase in shear rate). However, when the residence time increases, the relative gain in conversion for the longest reactor length diminishes. Rheological measurements were conducted to determine the intrinsic viscosity of the reactive solution for the following residence times: 5 min, 15 min, 30 min, and 2 h (see Supporting Information for details). From the obtained values, the product of concentration times intrinsic viscosity was found superior to 1 for residence times above 5 min. It can be concluded that the polymerization operates in the dilute regime up to 5 min and then in the semi-diluted regime [16]. This last regime is characterized by an overlapping of the hydrodynamic spheres of individual macromolecules while, in the dilute regime, there are no interactions in-between polymer chains. Therefore, the following explanation can be drawn and is qualitatively summarized in Figure 7. This figure shows the conformation of polymer chains when the residence time increases (i.e. for different monomer conversions) and when the length of the reactor is increased (i.e. for higher shear rates).

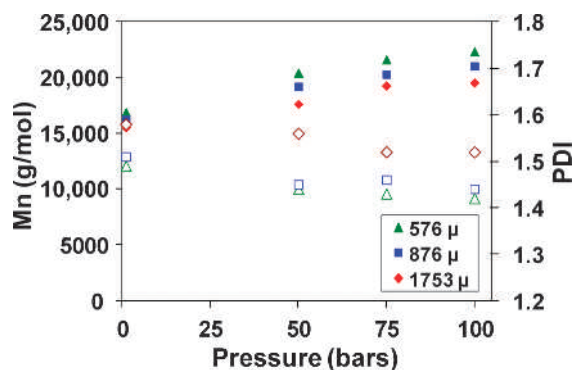
At the beginning, the polymerization solution contained a large amount of monomer (low conversion), and thus, polymer chains were quite short and the mean number-average chain length (DP_n) for all four reactors was equal to 43 for 5 min. Therefore, shear rate had little effect on the polymerization kinetics, and a marginal increase in conversion (+4 points)

**Figure 4.** Plot showing the effect of pressure on monomer conversion for different microreactor diameters at a polymerization time of 1 h

was observed at the lowest residence time (5 min). For 15 min residence time, molecular weight was increased (average DP_n = 71) and chains adopted a coiled conformation which under shear tend to be elongated as numerical studies reported in the literature [17]. Following our aforementioned discussion, it resulted in an increase in conversion, +10 points for the longest reactor in comparison with the shortest one. This result is in agreement with the findings of Agarwal et al. during polymerization of (poly (*p*-phenylene terephthalamide)) [18]. When the residence time was further increased, the gain in conversion for the longest reactor decreased and ultimately no significant effect of shear rate was observed for the highest residence time (2 h) which complies with similar observations made by Leveson et al. [19]. It is worthy to note that since the flow rate was reduced to accommodate higher residence times, the shear rate also reduced according to eq. S5 (Table 1), thus, explaining the observed behavior. As shown in Figure 8, Mn evolution followed the same behavior as monomer conversion for different shear rates. However, it is worthy to note that no significant difference in PDI was observed between samples polymerized at different shear rates.

3. Conclusion

Continuous-microflow ATRP of DMAEMA was carried out in tubular microreactor and variations of temperature, pressure, and reactor length were investigated to accelerate the reaction. Higher temperatures increase polymerization rate but, at the

**Figure 5.** Plot showing the effect of pressure on molecular weight (Mn, filled symbols) and PDI (empty symbols) for different microreactor diameters and for 1 h residence time

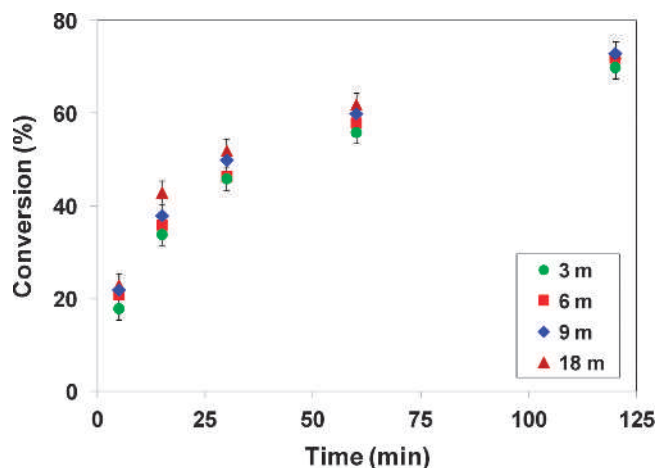


Figure 6. Conversion of DMAEMA with respect to the residence time for different reactor lengths

same time, lead to a broadening of the molecular weight distribution because termination reactions are also favored. A trade-off can be found considering the desired molecular weight. For low molecular weights (up to 17,000 g/mol), a temperature of 95 °C was beneficial to reduce the polymerization time by a quarter in comparison with 75 °C while still keeping a low PDI value (1.53 compared to 1.51). However, increase in PDI (from 1.51 to 1.76) was observed when molecular weights are above 17,000 g/mol.

High pressure (100 bars) in microreactor was found to accelerate the polymerization significantly (+12.5 % in monomer conversion compared to 1 bar) with an additional benefit of an improved control of the molecular weight distribution (PDI reduced from 1.52 to 1.44). However, pressure affects the polymerization kinetics quite differently upon reactor diameter as smaller diameters exhibit a higher polymerisation rate.

Finally, the effect of shear rate was found evident at low conversions and molecular weights due to an effective elongation of the polymer chains under the shear. However, past the critical entanglement molecular weight, which depends upon the polymer concentration (i.e., residence time), shear rate has less effect on the monomer conversion. Thus, it was demonstrated that, under given constraints, an ATRP microprocess can be significantly intensified by increasing the temperature and shear rate but, above all, by increasing the pressure.

4. Experimental

4.1. Materials. ATRP of DMAEMA was followed in this study. DMAEMA (Sigma-Aldrich, Germany) was destabilized

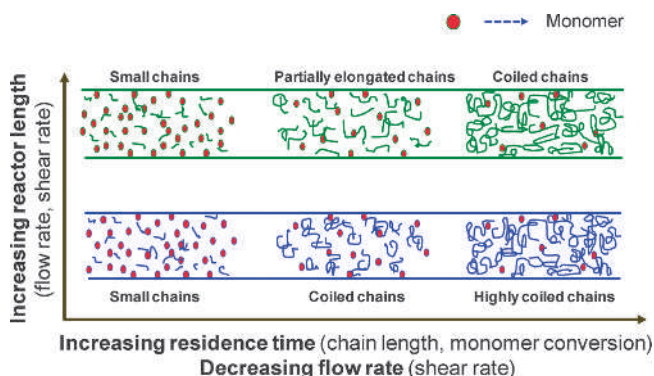


Figure 7. Schematic drawings of the polymer chains conformation as a function of residence time and reactor length

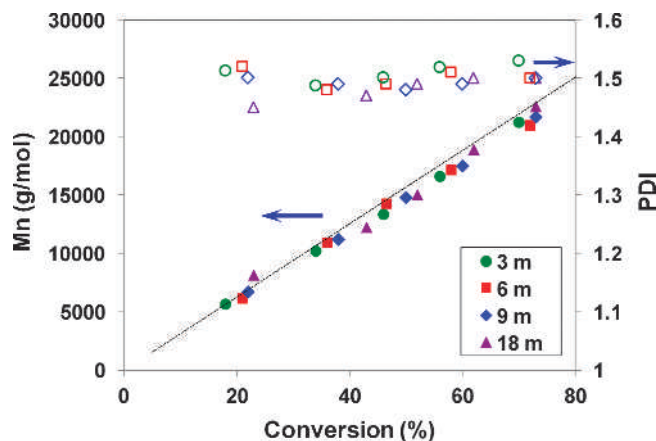
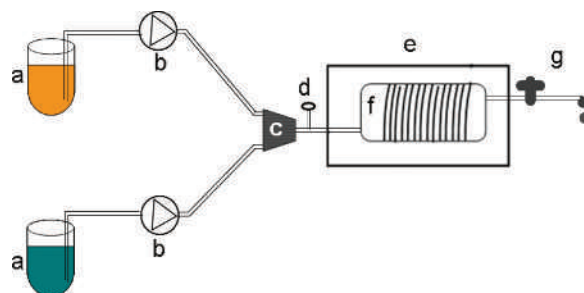


Figure 8. Evolution of molecular weight (M_n , filled symbols) and PDI (empty symbols) with respect to residence time for different reactor lengths

by passing through basic and neutral alumina column. Copper (I) bromide (CuBr) (Sigma-Aldrich, USA) was purified by washing with glacial acetic acid and then with methanol repeatedly. Washed CuBr was then dried overnight under vacuum before use. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%) (Sigma-Aldrich, USA) and isopropanol (Sigma-Aldrich, France) were used as received. Ethyl 2-bromoisobutyrate (EBIB, 98%) was purchased from Sigma-Aldrich (USA) and was distilled before use. Tetrahydrofuran (Chromasolv Plus) was purchased from Sigma-Aldrich UK and used as received.

4.2. Protocol of Polymerization. Microreaction system consisted in a stainless steel tubular microreactor with other accessories as shown in Scheme 1. Microreactor was housed inside a thermo regulated oven, and all other components of the micro-reaction system were kept outside the oven. An interdigital multilamination micromixer (HPIMM, IMM, Mainz, Germany) was used to premix the two reactant streams prior the entrance of the microreactor. HPIMM was chosen as the micromixer from our previous experiences [6c, 20]. Flow rates of reactants were maintained in such a way that the ratio of monomer, ligand, CuBr, and initiator just before entering the microreactor was maintained at 200:1.1:1:1. For details of composition of reservoirs and flow rates, see Table S1 and Table S2 of Supporting Information. As shown in Scheme 1, two reservoirs were used to supply reactants after they were degassed by nitrogen for 20 min. Two 307 HPLC Gilson (Paris, France) piston pumps were used to supply reactants to the microreactor. Before the start of reaction, reactor was flushed with degassed reagents at a flow rate of 1 mL/min to remove any trace of oxygen. Time of flushing depends on the length and diameter of the reactor. For

Scheme 1. Schematic of microreaction setup used for polymerization showing reservoirs (a), HPLC pumps (b), HPIMM micromixer (c), pressure sensor (d), oven (e), stainless steel microreactor (f), and back pressure regulator (g). Operating conditions and reservoir compositions are detailed in Supporting Information



example a 3-meter length microreactor of 810 μm internal diameter was flushed for 5–7 min. Then, flow rates were reduced to achieve the targeted residence time, which was varied from 5 min to 2 h. To prevent polymerization in the supply tubing, ice was used for cooling inlet tubing and micromixer, whereas water circulation was used to cool down the pump head. Cooling is crucial for long residence times (1 h and 2 h) to avoid unexpected polymerization. During polymerization, pressure inside the reactor was maintained within 1–1.5 bars with the help of a back pressure regulator attached at the end of the microreactor. It helps in providing uniform reaction condition and unwanted drainage of reactants from microreactor due to capillary action and expansion of solvent during heating.

The back pressure regulator was the most important component to study the effect of pressure on polymerization in microreactor. In this study, the effect of pressure was investigated at 50, 75, and 100 bars. Different microtube diameters were used to have a clear idea on the effect of pressure on polymerization. The effect of shear rate on polymerization was studied by using microreactors of 876 μm internal diameters and length varying from 3 to 18 m. Flow rates were changed to achieve the same residence in all microreactors investigated. More details can be found in Supporting Information.

4.3. Analysis. Once the reaction reached its steady state, polymer samples were collected at the exit of microreactor and reaction was terminated by cooling in ice. Crude polymer solution collected from microreactor was used to determine the molecular weight and PDI by GPC. PL-GPC 120 Platform (Polymer Laboratories, Church Stretton, UK) equipped with a Shimadzu LC-10 AD liquid chromatograph, a column (PL-gel 5 μm MIXED-C, Polymer Laboratories, 300 mm), and four online detectors: a Knauer K-2501 UV detector (operating at 254 nm), a single capillary viscometer (length, 20 cm; inner diameter, 0.5 mm), a dual angle-light scattering detector (MALS), and a PL-Refractive Index detector, were used for this purpose. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min, at 35 °C. Apparatus was calibrated with narrow linear polymethyl methacrylate (PMMA) standards. Cirrus GPC software (Polymer Laboratories, Church Stretton, UK) was used to process the data obtained from detectors. Conversion of monomer was determined by ^1H NMR (Bruker 300 equipped with TopSpin software) using deuterated acetone as the solvent. See Supporting Information for details regarding polymerization protocol and analysis.

Steady state shear viscosity of polymerizing solution at different polymerization time was determined by Anton Paar Physica MCR 301 Rheometer. Concentric cylinder geometry with a conical end bob was used for this study. Crude polymer solution was poured into the cup, then the bob was lowered down to measuring position, and temperature was raised to 75 °C. After reaching the set temperature, the solution was allowed to stay at the set temperature for further 1 min. It allows to get uniform temperature throughout the solution before the beginning of test. Steady state shear was applied with a range from 0.1 to 200 s^{-1} , and viscosity of the solution was recorded. Values below the limiting torque value for the geometry were excluded from the analysis. Detailed analyses of rheological data are given in Supporting Information.

Acknowledgments. Authors would like to thank Christophe Sutter, Christophe Melart, and Sebastien Gallet for their valuable

help during the experiments. The financial supports by Agence Nationale de la Recherche grant n° 09-CP2D-DIP² is greatly appreciated.

Supporting Information

Electronic Supplementary Material (ESM) with additional information on experimental details and results is available in the online version at: doi: 10.1556/JFC-D-14-00003.

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