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Coil Flow Inversion as a Route To Control Polymerization in Microreactors

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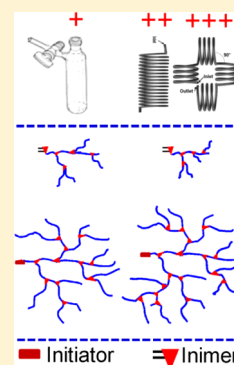
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S Supporting Information

ABSTRACT: Linear and branched polymers of 2-(dimethylamino)ethyl methacrylate (PDMAEMA) were synthesized in flow by atom transfer radical polymerization (ATRP) and self-condensing vinyl copolymerization adapted to ATRP, respectively, in capillary type stainless steel coiled tube (CT) microreactors. Coil flow inversion (CFI) was introduced to achieve better mixing and narrower residence time distributions during polymerization. This strategy was adopted to improve control over macromolecular characteristics and polymer architecture. Polydispersity index (PDI), as an overall indicator of control over polymerization, was significantly lower for CFI in the case of linear PDMAEMA, 1.39 compared to 1.53 for CT. For branched polymers containing up to 10 mol % of inimer, a reduced PDI was also obtained for CFI microreactor. As for the branching efficiency, it was found to follow the following trend CFI > CT > batch reactor.



1. INTRODUCTION

Application of microreaction technology in polymer synthesis dates back roughly to one decade¹ and has showed enormous potentials to produce polymers with well-defined characteristics. Microdevices derive these potentials from their high surface-to-volume ratio, small diffusion pathways, and large interfacial areas which give them the ability to overcome heat transfer and mixing limitations often encountered in their macroscale counterparts. Thus, microreactors and micromixers were found to be elements of choice when comes the need to increase the control of macromolecular characteristics. Ionic, free radical, controlled/“living” radical, and more recently enzyme-catalyzed polymerization reactions were carried out successfully in microreactors,^{2,3} the latter allowing an improved control over architecture and chemical composition.^{4–8} Their high surface-to-volume ratio also allowed considering new operating windows like higher temperatures, which permitted for instance to carry out extremely exothermic reactions (ionic polymerizations) at much more convenient conditions (noncryogenic).^{9–12}

Controlled radical polymerizations like ATRP can benefit a lot from the special features of microdevices in terms of conversion, molecular weight, and architecture. In the first ever reported experiment of ATRP in a microreactor, Beers and co-workers demonstrated the possibility to synthesize polymer libraries just by changing the flow rate or reactants' feed ratio.¹³ They were also able to synthesize well controlled block copolymers of

poly(ethylene oxide–2-hydroxypropyl methacrylate) by using a special design of a three-input–one-output chip reactor.¹⁴ Evidences were also reported that microreactors can accelerate a slow polymerization reaction like ATRP.¹⁵ Furthermore, microreactors were found to achieve higher branching structures compared to batch reactor.¹⁶ Finally, by using a continuous-flow microfluidic system, Beers and co-workers were able to produce a gradient solution of two comonomers for the synthesis of statistical-copolymer-brush gradient on a silicon substrate initially layered with an ATRP initiator.¹⁷ For most applications, ATRP catalyst need to be removed from the polymer solution. This downstream operation which is usually quite time-consuming may be eased and operated in flow within millireactors. One such example was reported by Zhu and co-workers, who used silica gel supported catalyst to pack a tubular millireactor (i.d. = 3.75 mm) for the ATRP synthesis of methyl methacrylate homo- and copolymers.^{18,19} However, the observed broadening of molecular weight distribution suggested the trapping of molecules in the pores and the difficulty encountered by polymer chains to reach catalytic sites with increasing viscosity. To alleviate this problem, Cunningham and co-workers used a copper tube millireactor (i.d. = 1.65 mm) for

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ATRP process.²⁰ Elemental copper of the tube was used as the source of catalyst and allowed a significant reduction of copper and ligand amounts.

Other slower polymerization reactions like nitroxide-mediated polymerization (NMP) and reversible addition–fragmentation chain transfer (RAFT) were also investigated in microreactors^{6,7,21–23} and exhibited same benefits when carried out in microdevices.

In spite of all these benefits and since mixing in continuous-flow microchannel- or capillary-based microreactors is mainly governed by mass diffusion, increased viscosity and diminished monomer concentration at higher conversion can trigger for (controlled) radical polymerizations unwanted termination reactions resulting in increased PDIs.¹⁵ Increasing solvent content is one of the possible strategies to overcome diffusion limitations as the increase in viscosity could be maintained low. However, such strategy will affect the throughput of microreactor negatively. Another strategy suggested in the literature was the use of patterned microreactors to enhance mixing inside microreactor during polymerization. However, fabrication of such patterned microreactors is not only difficult but also expensive.²⁴ Therefore, a simpler and robust alternative needs to be explored in order to expand the applicability of microreactors as well as to improve polymer quality. As a part of this effort to achieve a better control over polymerization in microreactor when the reactive medium viscosity is increasing, the flow inversion technique in capillary-based microreactor was considered in this study and its effect on polymerization kinetics and polymer characteristics of both linear and branched polymers investigated. Although the concept of flow inversion is not new in chemical engineering, it has been only investigated as heat exchanger in macroscale devices.^{25–27} Thus, effect of flow inversion was never experimentally investigated in micro-geometry for homogeneous polymerization reactions, although numerical studies have emphasized their benefit over straight tubular reactor.²⁸

2. EXPERIMENTAL SECTION

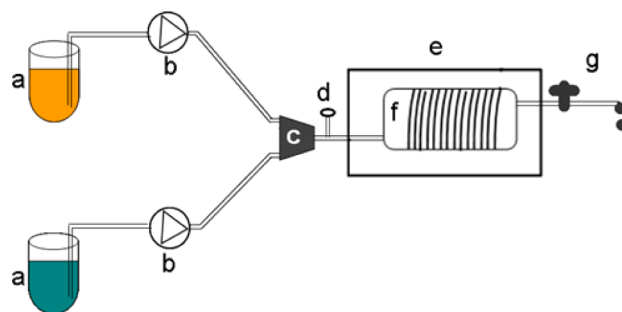
2.1. Materials. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (Sigma-Aldrich, Germany) was destabilized by passing through alumina column. Copper(I) bromide (CuBr) (Sigma-Aldrich) was washed in acetic acid, then repeatedly with methanol, and dried overnight under vacuum before use. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%) (Sigma-Aldrich, USA) and isopropanol (Sigma-Aldrich, France) were purchased and used as received. Ethyl 2-bromoisobutyrate (EBIB 98%) (Sigma-Aldrich, USA) was distilled and stored in argon before use. 2-(2-Bromoisobutyryloxy)ethyl methacrylate (BIEM) was used as an inimer for branched polymer synthesis. Hydroxyethyl methacrylate and 2-bromoisobutyryl bromide were used to synthesize BIEM as per the procedure described in the literature.²⁹ For the detailed procedure of BIEM synthesis, see Supporting Information section 1.0.

2.2. Polymerization in Batch Reactor. Linear and branched poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) were synthesized by ATRP or self-condensing vinyl copolymerization (SCVCP) adapted to ATRP using BIEM as an inimer. Polymerization was carried out for a targeted degree of polymerization (DP) of 100 in a Schlenk flask at 75 °C under an argon atmosphere using dimethylformamide (DMF) as a solvent. 6 mL of DMF, 5.36 mL of DMAEMA, 0.39 mL of inimer (for branched architecture), 100.2 μ L of HMTETA, and 0.048 g of CuBr were used for synthesis. Solution of DMF, HMTETA, and CuBr was purged with argon for 15 min to remove oxygen. Then degassed DMAEMA was added to the Schlenk, and argon purging was continued for further 5 min. Required quantity of inimer and initiator stored under argon atmosphere was added, and the Schlenk was immersed in a

preheated oil bath at 75 °C. Samples were withdrawn by syringe pumping at defined interval and cooled in ice to terminate the reaction.

2.3. Polymerization in Microreactor. Microreaction system consisted in a stainless steel tubular microreactor with other accessories as shown in Scheme 1. Thermoregulated oven was used to

Scheme 1. Schematic Representation of Microreactor Setup Used for Polymerization Comprising: Reagents Reservoirs (a), HPLC Pumps (b), HPIMM Micromixer (c), Pressure Sensor (d), Oven (e), Stainless Steel Microreactor (CT/CFI) (f), and Back-Pressure Regulator (g)^a



^aOperating conditions and reservoir compositions are detailed in the Supporting Information.

accommodate the required temperature. An interdigital multilamination micromixer (HPIMM, IMM, Mainz, Germany) was used to premix the two reactant streams prior the entrance of the microreactor. Flow rates were changed to get the desired residence time. Details of reservoir composition and flow rates are given in the Supporting Information (Tables S1a to S3b). Two Gilson 5 SC piston pumps were used to achieve accurate flow of degassed reagents from two reservoirs kept under a nitrogen atmosphere. Microreactor was flushed with degassed reagent for 5–7 min at a flow rate of 1 mL/min before to start the reaction, and then flow rate was reduced to get the targeted residence time. To suppress unwanted polymerization before microreactor, inlet tubing and micromixer were kept in ice. Pressure during polymerization was maintained within 1–1.5 bar with the help of a back-pressure regulator. Slight positive pressure maintained a uniform reaction condition and avoided any kind of drainage of reactant due to capillary action.

Microreactors used in this study are shown in Figure 1. Stainless steel coiled tube (CT) and coil flow inverter (CFI) reactors of 3 m length and

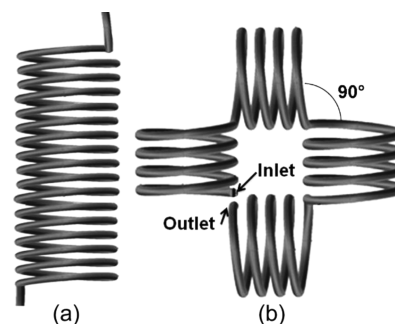


Figure 1. Coiled tube (a) and coil flow inverter (b) microreactors used in this study.

876 μ m internal diameter were used. CFI is a tubular microreactor having the same number of coils as in CT. However, 90° bends were introduced at equal interval in one direction as shown in Figure 1b. In this study CFI having three bends was used for polymerization. Equal numbers of coils were maintained between each bends.

2.4. Characterization Methods. Polymer samples were collected at the end of microreactor once the reaction reached its steady state.

During collection, samples were cooled by ice–water to terminate the reaction. Conversion and molecular weight were determined by proton NMR (Bruker 300 equipped with Topspin software) and gel permeation chromatography (GPC) respectively. A PL-GPC 120 platform equipped with a Shimadzu LC-10AD liquid chromatograph, a column (PL-gel 5 μ m 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 (DALS), and a PL refractive index detector—was used. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min at 35 °C. Narrow poly(methyl methacrylate) standards were used for calibration of GPC. Raw samples were used for determination of branching efficiency by GPC.

3. RESULTS AND DISCUSSION

3.1. Linear Polymer Synthesis. Increase in viscosity during polymerization in microreactor limits the diffusion of reacting species, resulting in a poor control over polymerization especially at high monomer conversions.¹⁵ To overcome such limitation and reduce residence time distribution inside microreactor, a simple alternative like flow inversion was considered. A marginal increase (~ 3 –5%) in monomer conversion was observed in case of CFI microreactor compared to CT (Figure 2). Because of the

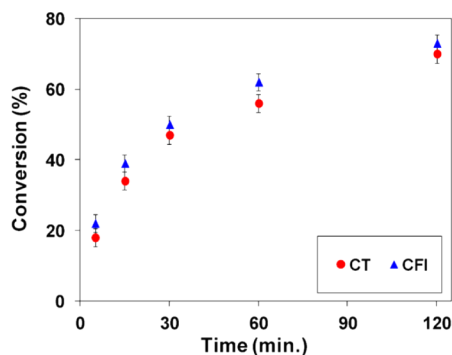


Figure 2. Plot showing the effect of microreactor geometry on conversion of DMAEMA for linear polymers synthesis.

presence of 90° bends in a microreactor (Figure 1b), direction of flow changes after a given interval, which brings the growing chains near the wall to the center and vice versa.²⁵ A reactor having such characteristics will not only improve mixing during flow but also will reduce residence time distribution (RTD) (Figure S3) in the reactor as described in sections 4 and 5 of the Supporting Information.

Improved mixing reduces concentration gradients and allows polymer chains growing equally throughout the length of microreactor. On the other hand, reduced RTD ensures equal residence time of molecules inside the reactor which is a prerequisite in controlled radical polymerizations for producing macromolecules with narrow chain length distributions. Polymers synthesized in CFI were found to have higher molecular weights (M_n), up to +2000 g/mol compared to CT (Figure 3). Gain in M_n was observed at each residence time (Figure. S4). Effect of improved mixing and narrow RTD was evident from reduced polydispersity index (PDI) as shown in Figure 3 and entries 1, 2 of Table 1.

3.2. Branched Polymer Synthesis. More clear evidence about mixing and its effect on the synthesis of branched polymers were obtained during polymerization in different reactors, i.e. batch, CT, and CFI. Elution traces (Figure 4) of batch polymerization of branched polymers with 5 mol % inimer

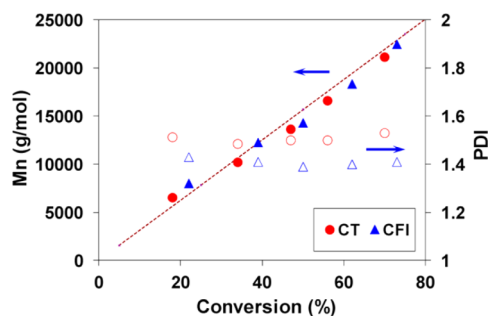


Figure 3. Evolution of molecular weight (M_n , filled symbols) and PDI (empty symbols) with respect to monomer conversion for different microreactor geometries.

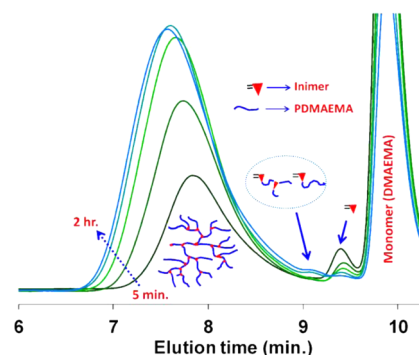


Figure 4. GPC elution traces of branched polymers obtained after 5 min to 2 h in a batch reactor.

indicates a rapid disappearance of the peak corresponding to inimer for 1 h polymerization time. This suggests major portion of BIEM (inimer) molecules has reacted, either as a monomer or as an initiator.

From ^1H NMR analysis, it was found that 56% (Figure S5) of BIEM molecules had their double bond reacted, meaning that inimer was incorporated into a growing chain as a monomer. Thus, it can be concluded with the support of NMR spectra (see Supporting Information) that a significant proportion of the inimer (44%) has acted like an initiator. This explains the appearance of a broad peak at low molecular weights region of elution traces at 1 h polymerization time, corresponding to the formation of oligomers initiated by BIEM molecules and having a double bond at one chain ends. These oligomers can be considered as a macromonomer, but their incorporation in the main branched structure will be impeded by steric hindrance and slow diffusion coefficient.

It is worthy to note that the initial consumption rate of BIEM double bond (as determined by ^1H NMR) is higher than that of DMAEMA irrespective of reactor type (Figure S5) and that for long polymerization times (after 30 min) this rate somehow diminishes and becomes lower than for DMAEMA. This decrease in rate may be ascribed for the formation of these macromonomers since for long polymerization times, the remaining double bonds coming from the inimer are mainly located at the end of macromonomers. Such double bonds have a lower probability to react than the double bond of a free molecule of DMAEMA due to steric hindrance of macromonomers. Mixing can also affect the polymerization and architecture of the branched polymer. Easy and faster diffusion increases the probability of macromonomers to react with a growing branched chain. On the opposite, slow diffusion will make oligomers

Table 1. Summary of Linear and Branched PDMAEMA Characteristics Synthesised after 2 h in Different Reactors

entry	mol % BIEM	reactor type	M_n (g/mol)	PDI	$M_{w,RI}$ (g/mol)	$M_{w,MALS}$ (g/mol)	$M_{w,RI}^a/M_{w,MALS}$	unreacted C=C ^b (%)
1	0	CT	21042	1.54	32404			
2	0	CFI	22574	1.40	31603			
3	5	batch	3156	2.48	8172	9150	0.86	27.4
4	5	CT	3477	2.35	8170	10770	0.75	23.4
5	5	CFI	3618	2.20	8140	11770	0.69	20.6
6	10	batch	1814	2.8	5124	8836	0.58	18.1
7	10	CT	2100	2.56	5220	10004	0.52	15.4
8	10	CFI	2218	2.50	5567	12160	0.46	14.1

^a $M_{w,RI}$ and $M_{w,MALS}$ are the weight-average molecular weights obtained by refractive index (RI) or by multiangle light scattering (MALS) detectors.

^bDetermined by ¹H NMR (Figure S8).

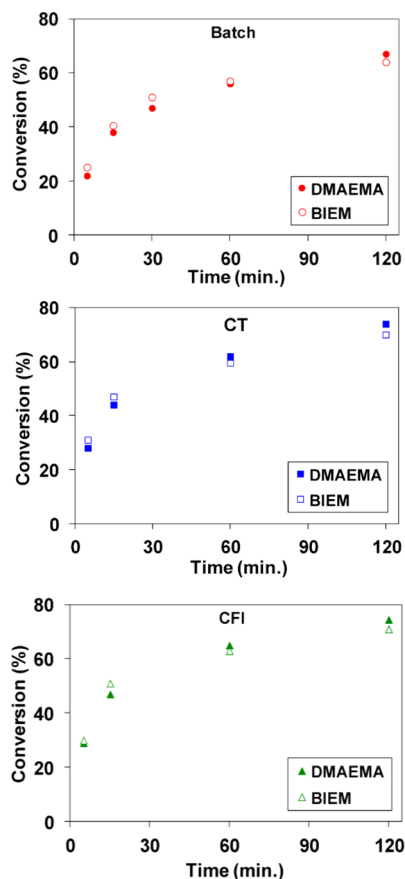


Figure 5. Relative conversions of DMAEMA and BIEM in batch (a), CT (b), and CFI (c) at different polymerization times.

growing as a separate chain and results in lower molecular weight polymers and higher polydispersity at a given polymerization time. This argument was supported by Figure S6 where conversion of inimer at anytime in CFI was higher than the conversion achieved in batch reactor. As a result, the molecular weight of branched polymers synthesized in microreactors is higher at a given polymerization time as shown in Figure 6. Another consequence is the lower proportion of macro-monomers/oligomers for CT and CFI as seen in the GPC traces of Figure 7a where the peak at low molecular weights is barely visible. The overall consequence is a reduced PDI for these two microreactors (Figure 6) compared to batch reactor. It worthy to mention that this observation remains valid for higher BIEM composition (i.e., 10 mol % inimer, Figure 7b and Table 1). Note that higher molecular weights observed in microreactors

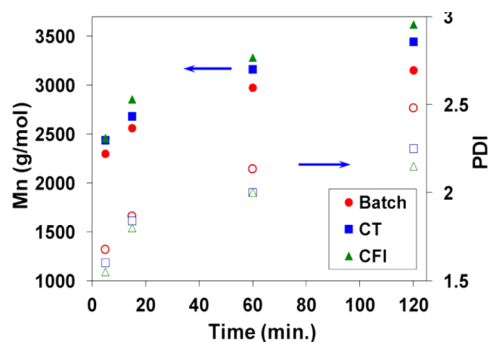


Figure 6. Evolution of molecular weight (M_n , filled symbols) and PDI (empty symbols) with time in different reactors.

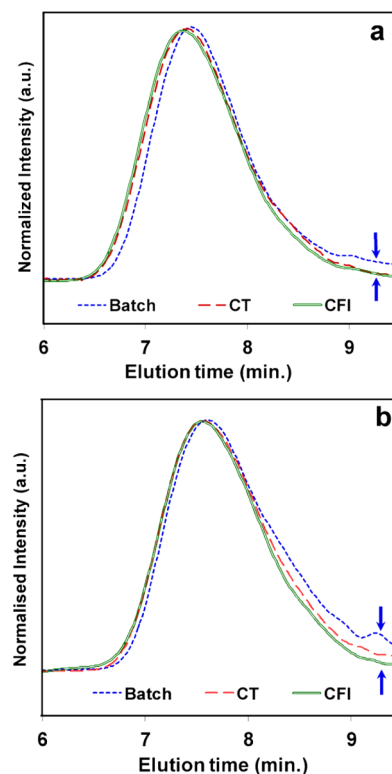


Figure 7. GPC elution traces of branched polymers synthesized in different reactors at 5 mol % (a) and 10 mol % (b) of inimer after 2 h of polymerization time.

also result from higher DMAEMA conversions (Figure 5 and Table S6).

Additional information is provided by the first-order plot of polymerization rate (Figure 8). At the early stage of the

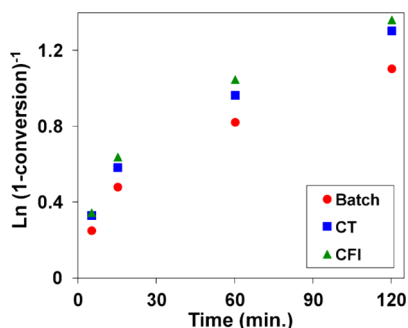


Figure 8. Overall monomer conversion (DMAEMA + BIEM) with respect to the polymerization time for different reactors.

polymerization (5 min), the continuous-flow mode (irrespective of the geometry of the tubular microreactor (CFI or CT)) promotes an efficient initiation though the concentration of initiating species should be the same for all reactors. Later on (after 5 min) and for each reactor, the downward curvature indicates a decrease in number of propagating sites due to the incorporation of macromonomers (initiated by inimer) into a growing chain. However, a clear trend is to be seen in between the three reactors: CFI leading always to the highest conversion index while the batch reactor exhibiting the lowest. Furthermore, the discrepancy between batch and microscale reactors is getting higher as the polymerization time increases. This discrepancy may originate from a slower diffusion of chemical species in batch reactor while a shorter diffusion pathway (small diameter) and effect of 90° bends for the CFI enhance diffusion of species as discussed in section relative to linear polymers.

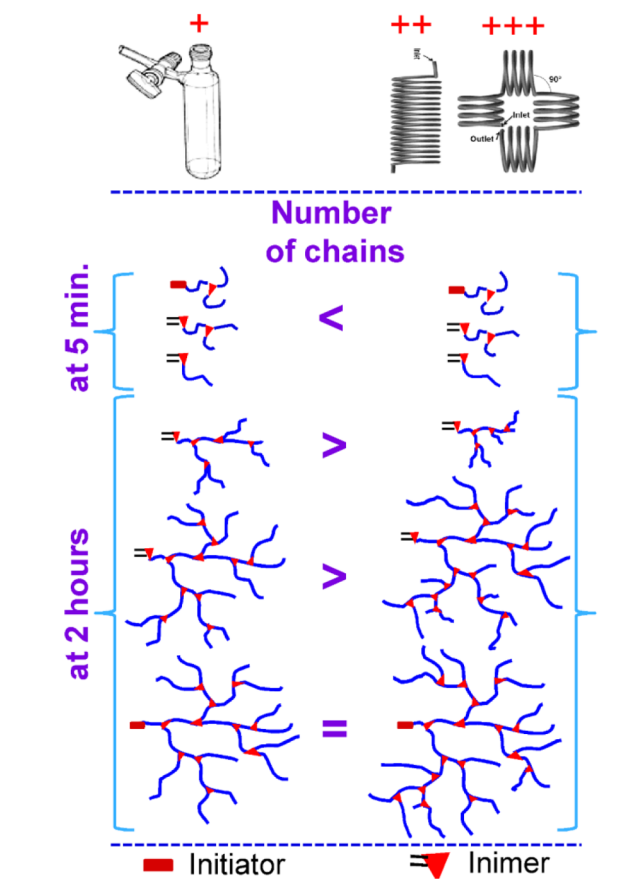
Moreover, incorporation of inimer into a growing chain may result in a branching point. One can define an apparent branching efficiency defined as the percentage of BIEM incorporated in the branched structure. Thus, this parameter is simply calculated from the complement of the percentage of unreacted BIEM C=C bonds as seen by NMR analysis (Table 1). Unfortunately, NMR analysis on purified polymer cannot discriminate among the incorporated inimers which has led to a branching point. However, it is likely that the higher the apparent branching efficiency, the higher will be the number of branching points. The ratio between M_w as determined by refractive index detector (RI) and M_w determined by multiangle light scattering detector (MALS) ($M_{w,RI}/M_{w,MALS}$) was used as a qualitative indicator of branching efficiency³⁰ at a given inimer content and is listed in Table 1. Interestingly, whatever the BIEM composition, a better branched structure was obtained in CFI compared to other two reactors.

Considering the above observations from GPC and ¹H NMR analysis, a simple schematic drawing is proposed in Scheme 2 to explain the main difference between the mechanisms of branched polymer synthesis in batch and continuous-microflow reactors.

4. CONCLUSION

This work aimed at comparing different geometries of capillary-type microreactors to highlight the effect of mixing on ATRP linear and branched synthesis. Compared to the standard coiled tube geometry (CT), a simpler alternative like flow inversion (CFI) was used for the first time in microreaction to reduce the mass diffusion limitation rising from the increased viscosity at

Scheme 2. Schematic Comparison of Branched Polymer Synthesis in Batch and Microreactors after 2 h Polymerization Time



high conversion. Thus, improved mixing condition in CFI was found to be quite effective to reduce PDI of synthesized linear PDMAEMA. Diffusion-driven mixing and its impact on branched polymer characteristics were clearly visible when polymerization in the different microreactors were compared. Improvement in branching efficiency from batch to CFI microreactor showed more controlled incorporation of branching points in polymer chain evidencing that flow inversion can be an effective tool to improve control over polymer characteristics.

■ ASSOCIATED CONTENT

Supporting Information

(1) BIEM synthesis; (2) reservoir composition and flow rates for linear and branched polymer synthesis in microreactors; (3) monomer conversion calculation by ¹H NMR; (4) residence time distribution of CT and CFI microreactors; (5) mixing phenomena in CFI microreactor; (6) molecular weight evolution during polymerization; (7) precipitation procedure of polymer; (8) determination of dn/dc of branched polymer; (9) determination of unreacted double bonds in branched polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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