

Supporting information
For
**Atom Transfer Radical Polymerization in continuous-microflow: effect of
process parameters**

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1. Reservoirs composition and flow rates

Compositions of two reservoirs, flow rates of the pumps to get desired residence times and reagent compositions for polymerization are given in Table S1 and S2. It is worthy to note that composition of reservoirs remains same irrespective of diameter of reactor, where only flow rates were changed to achieve desired residence time.

Table S1. Reservoir composition for linear PDMAEMA synthesis

	Reagents	Quantity
Reservoir 1	CuBr	0.1396 g
	Isopropanol	39.70 ml
	HMTETA	291.2 μ l
	<hr/>	
Reservoir 2	DMAEMA	37.16 g
	Initiator	173.4 μ l

Targeted degree of polymerization of linear PDMAEMA= 200.
Temperature of polymerization 75 °C.

Table S2. Flow rates for different residences time and different microreactor internal diameters.

Time (min.)	572 μm (6 meters)		876 μm (3 meters)		1753 μm (3 meters)	
	<i>R 1</i>	<i>R 2</i>	<i>R 1</i>	<i>R 2</i>	<i>R 1</i>	<i>R 2</i>
5			198.6	163.2		
15			66.1	54.4		
30			33.1	27.2		
60	14.1	11.6	16.5	13.6	66.2	54.5
120			8.3	6.8		

Note: All flow rates reported are in $\mu\text{l}/\text{min}$, R1 and R2 are reservoir 1 and reservoir 2 respectively. Flow rate was increased proportionately with increase in reactor length.

2. Rheological behaviour of polymerizing solution

Steady state shear viscosity of polymerizing solution at different polymerization times was determined by Anton Paar Physica MCR 301 rheometer (Paris, France). Concentric cylinder geometry with a conical end bob was used for this study. First the polymer solution was poured into the cup then the bob was lowered down to measuring position and temperature was raised till 75 °C. After reaching the set temperature, solution was allowed to stay at the set temperature for further 2 minutes. It allows getting 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.

2.1 Viscosity evolution as a function of shear rate

Steady state viscosity of polymerizing solution at different polymerization times was determined. It was observed that solutions remain Newtonian (flat curves) irrespective of polymerization time as shown in Figure S1, e.g. from the early stage of the reaction (5 min) till 2 hours.

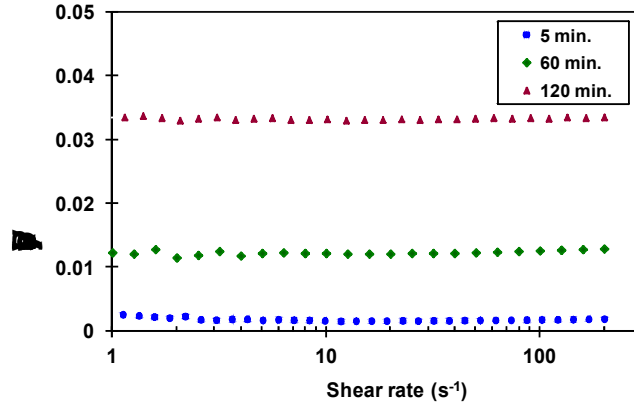


Figure S1. Steady state shear viscosity of DMAEMA polymerizing solution at different residence time

2.2 Intrinsic viscosity

Intrinsic viscosities of polymerizing solutions at 75 °C for 4 different residence times were determined. Viscosities of these 4 polymerizing solutions after successive dilutions (down to 25%) were determined as described in general procedure for rheological measurements (Figure S2). The crude polymerizing solutions were referred as 100% in Table S3. Solvent used for dilution was prepared by mixing Isopropanol and DMAEMA. Composition of diluting solvent was determined considering the conversion of DMAEMA at the particular polymerization time. Intrinsic viscosities for each solution were determined as described below in equations. Where, η is the polymer solution viscosity, η_0 is the solvent viscosity and η_{sp} is the specific viscosity.

$$\text{Specific viscosity } (\eta_{sp}) \uparrow \frac{\eta - \eta_0}{\eta_0} \quad (\text{S1})$$

$$\text{Intrinsic viscosity } [\eta] \uparrow \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C} \quad (\text{S2})$$

$$\text{Overlap concentration } (C^*) \uparrow \frac{1}{[\eta]} \quad (\text{S3})$$

From the above calculations concentration limits of the polymerizing solution was determined from C/C^* or when $C \times [\eta]$ reaches 1. It gives indication about the transition of polymerizing

solution from dilute to semi dilute regime. Its implication and impact on polymerization is explained in the main article.

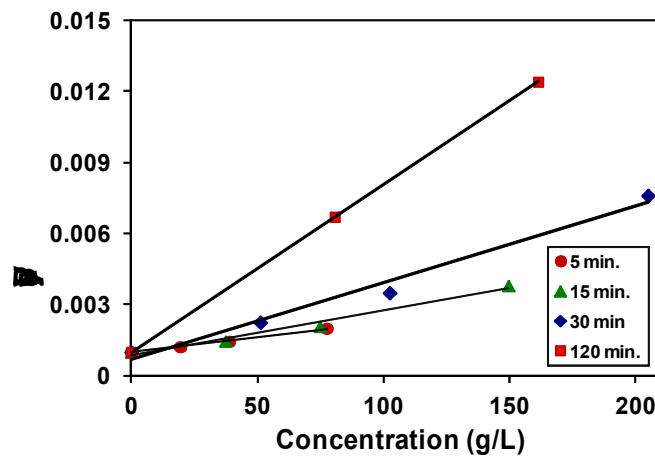


Figure S2. Plot showing viscosity of polymerizing solutions for different residence times and different dilutions.

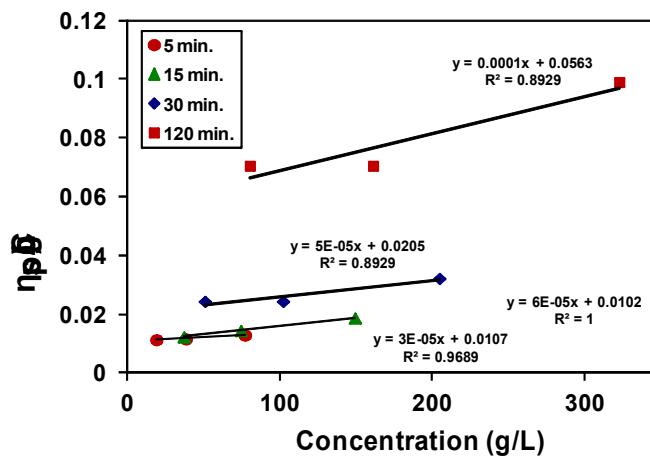


Figure S3. Plot used to determine intrinsic viscosity of polymerizing DMAEMA at different polymerization times.

Table S3. Detailed calculation to determine concentration limits of polymerizing DMAEMA in isopropanol at different polymerization times.

Residence time (min.)	Dilution factor	Concentration (g/L)	ζ (Pa.s)	η_{sp} (-)	η_{sp}/C (L/g)	$[\eta]$ (L/g)	$[C \times \eta]$ -
5	100%	77.51	0.00200	1.00	0.0129	0.0129	0.8
	50%	38.755	0.00145	0.45	0.0116	0.0116	
	25%	19.377	0.00122	0.22	0.0114	0.0114	
	0%					<u>0.0107</u>	

							<i>0</i>
15	100%	149.62	0.00380	2.80	0.0187	0.0187	
	50%	74.81	0.00208	1.08	0.0144	0.0144	
	25%	37.4	0.00146	0.46	0.0123	0.0123	
						<u>0.0102</u>	
	0%					<u>0</u>	1.5
30	100%	205	0.00760	6.60	0.0322	0.0322	
	50%	102.5	0.00350	2.50	0.0244	0.0244	
	25%	51.25	0.00225	1.25	0.0244	0.0244	
						<u>0.0205</u>	4.2
120	100%	323	0.03300	32.00	0.0991	0.0991	
	50%	161.5	0.01240	11.40	0.0706	0.0706	
	25%	80.75	0.00670	5.70	0.0706	0.0706	
		0				<u>0.0563</u>	18.2

3. High pressure polymerization in microreactors

Back Pressure Regulator (BPR) is the vital element of microreactor setup for high pressure polymerization. It was used to achieve desired pressure inside microreactor by closing or opening the knob of a metering valve (SS-SS1, Swagelok). Body of the valve is made up of stainless steel and working pressure range is up to 2000 psi (137 bars).

Desired pressure inside the microreactor was achieved in a stepwise increase as shown in Figure S4 as it was difficult to reach manually the desired pressure in one single step. In between each step increase the pressure was allowed to stabilize. It may take 30 min to 2.5 hours to reach the desired pressure depending on residence time. For longer residence times, longer time was needed to reach the new steady state as viscosity of the reactants evolves during a long period of time. Once the desired pressure was reached, polymerization was continued till the steady state ($2.5 \times$ residence times) of the reactor was reached. During polymerization the pressure varied within ± 2 bars for lower pressure and ± 2.5 bars for high pressure (100 bars). Polymerizations were carried out at 1 bar, 50 bars, 75 bars and 100 bars.

Three different microreactor diameters (576 μm , 876 μm , 1753 μm) of 3 meters length each were used to study the effect of pressure on polymerization while keeping the residence time the same for all reactors.

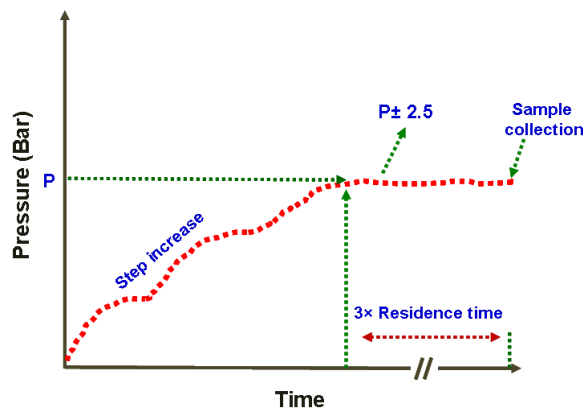


Figure S4. General strategy followed to achieve desired pressure in microreactor.

4. Reaction with different shear rates

Shear rate depends on flow rate/velocity of the fluid inside microreactor. In order to increase the shear rate without changing the residence time, length of the reactor was changed proportionately as shown in Figure S5. Shear rate at the wall of the reactor was calculated by using the formula given in equation S5 for Newtonian fluids (flow index n being equal to one as emphasized in §2.1) where $\dot{\gamma}_w$ is the shear rate at the wall, Q is the flow rate and R is the radius of the microtube reactor. Four different microreactor lengths of 876 μm internal diameter were used for these experiments. Maximum length of reactor received from supplier was 6 meters, therefore reactors were connected in series to get the desired length. For example, three CT microreactors of 6 meters length were connected to make a 18 meters length CT microreactor.

$$\dot{\gamma}_w \uparrow \frac{4Q}{\sqrt{R^3}} \frac{3n \dot{\gamma}_w}{4n} \quad \text{for power law fluids} \quad (\text{S4})$$

$$\dot{\gamma}_w \uparrow \frac{4Q}{\sqrt{R^3}} \quad \text{for Newtonian fluids} \quad (\text{S5})$$

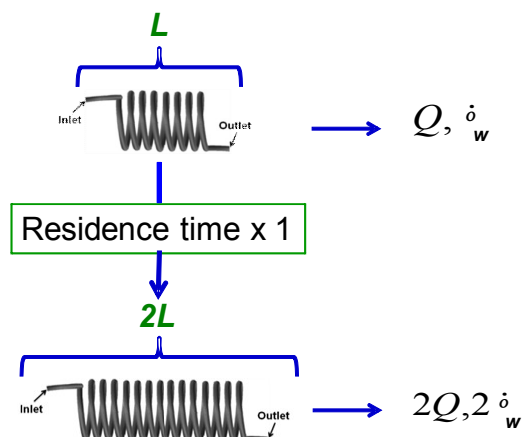


Figure S5. Strategy to achieve higher shear ($\dot{\gamma}_w$) rate at a given residence time (L is the length and Q the flow rate).

5. NMR analysis

5.1 Representative NMR spectra of polymerizing DMAEMA and conversion calculation

^1H NMR spectra of DMAEMA polymerizing solution was recorded in a Bruker 300 equipped with Top Spin software. A representative ^1H NMR spectra with protons used for conversion calculation is shown in Figure S6. Equation S6 was used for necessary calculation.

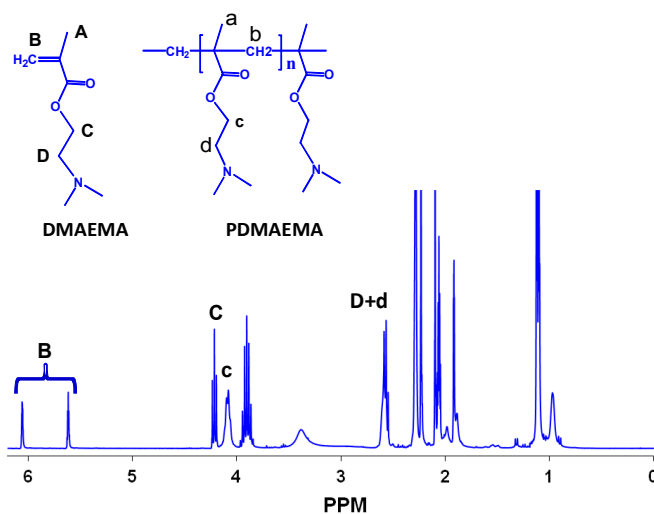


Figure S6. Representative NMR spectra of polymerizing DMAEMA.

$$\text{Conversion} = \frac{(D \hat{G} d) \dot{H} B}{D \hat{G} d} \quad (\text{S6})$$

6. Conversion at different polymerization temperature

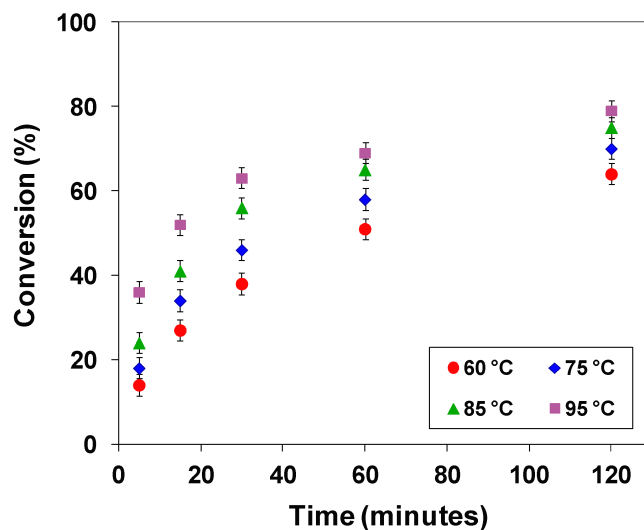


Figure S7. Conversion of DMAEMA in a 3 m length microreactor at different polymerization temperatures and 1-1.5 bars.

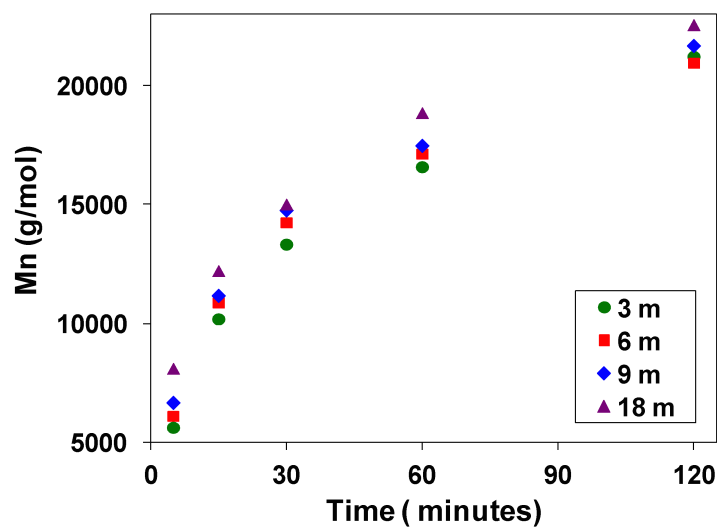


Figure S8. Evolution of molecular weight (Mn) with time for different microreactor lengths.

7. Main operating parameters and relevant results

Table S4. 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 (bars)	Shear rate* (s^{-1})	Residence time (minute)	Conv. (%)	Mn (g/mol)	PDI
1	3	876	60	1-1.5	7.62	120	64	18900	1.53
2	3	876	75	1-1.5	91.2	5	18	5600	1.51
3	3	876	75	1-1.5	30.4	15	34	10200	1.48
4	3	876	75	1-1.5	15.2	30	46	13900	1.51
5	3	876	75	1-1.5	3.8	120	70	21200	1.52
6	3	876	85	1-1.5	30.44	30	56	15500	1.56
7	3	876	85	1-1.5	7.62	120	76	20600	1.69
8	3	876	95	1-1.5	60.88	15	52	15400	1.53
9	3	876	95	1-1.5	7.62	120	80	19700	1.77
10	3	876	75	50	15.22	60	66	19700	1.46
11	3	876	75	100	15.22	60	70	21300	1.44
12	3	576	75	0.5-1	15.22	60	61	16900	1.49
13	3	576	75	100	15.22	60	73.5	22300	1.42
14	3	1753	75	0.5-1	15.22	60	58	15300	1.58
15	3	1753	75	100	15.22	60	67	19600	1.51
16	6	876	75	1-1.5	182.64	5	21	6100	1.52
17	6	876	75	1-1.5	60.88	15	36	10900	1.48
18	6	876	75	1-1.5	30.44	30	46.5	14300	1.49
19	6	876	75	1-1.5	7.62	120	72	21000	1.50
20	9	876	75	1-1.5	273.93	5	22	6700	1.48
21	9	876	75	1-1.5	91.32	15	38	10900	1.49
22	9	876	75	1-1.5	45.66	30	50	14800	1.48
23	9	876	75	1-1.5	11.43	120	72	21700	1.51
24	18	876	75	1-1.5	547.9	5	23	8100	1.45
25	18	876	75	1-1.5	182.64	15	43	12200	1.47
26	18	876	75	1-1.5	91.32	30	52	15000	1.49
27	18	876	75	1-1.5	22.86	120	73	22600	1.50