

# Supporting Information

## Controlling Molecular Weight Distributions through Photoinduced Flow Polymerization

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### EXPERIMENTAL SECTION

#### Materials

*N,N'*-dimethylacrylamide (DMAm, 99%) was purchased from Sigma-Aldrich. The monomer was deinhibited by percolation through basic alumina (Ajax Chemical, AR) column. Dimethylsulfoxide (DMSO, 99%) was supplied by Ajax Chemical and used as received. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine zinc (ZnTPP, 97 %) was obtained from Sigma-Aldrich and used as received. 2-(((dodecylthio)carbonylthio)thio)propanoic acid (DTPA, 97%) was obtained from Boron Molecular and used as received.

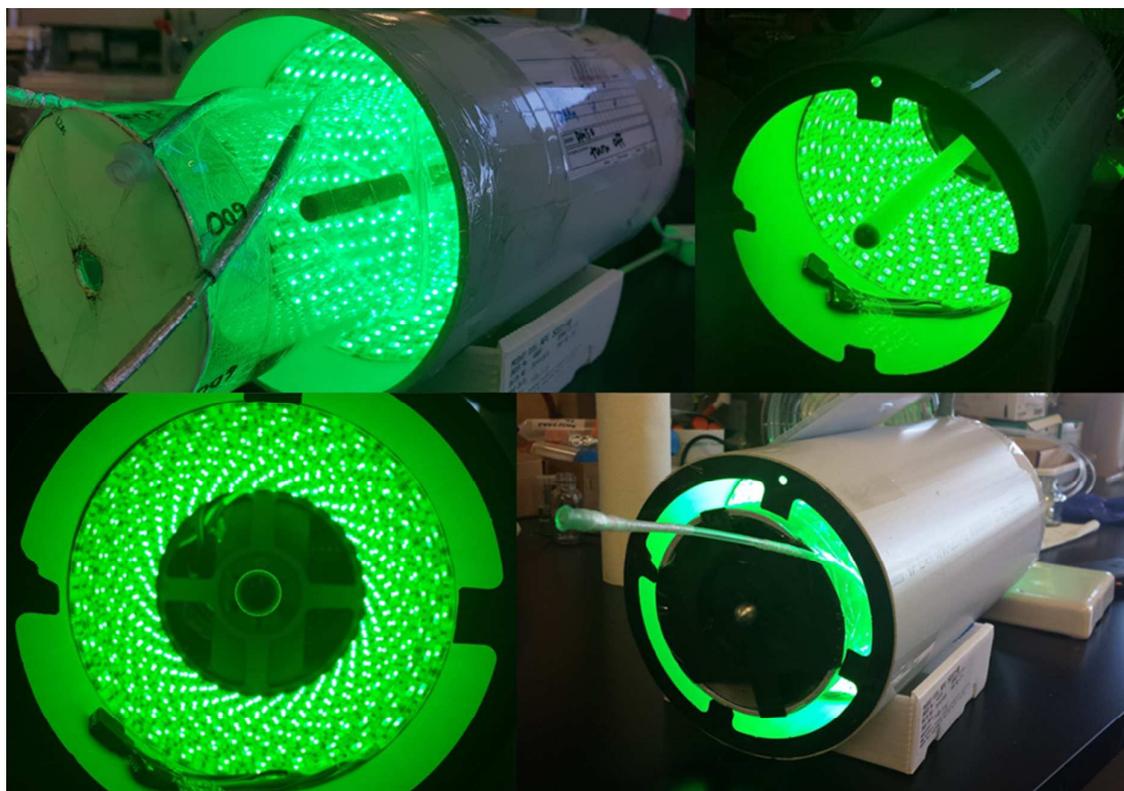
## Instrumentation

Gel Permeation Chromatography (GPC) was used to characterize synthesized polymer with dimethylacetamide (DMAc) as the eluent. The GPC instrument consists of Shimadzu modular system with an autoinjector, a Phenomenex 5.0  $\mu\text{M}$  bead sizeguard column (50 x 7.5 mm) followed by four Phenomenex 5.0  $\mu\text{M}$  bead size columns (105 , 104 , 103 and 102  $\text{\AA}$ ) for DMAc system. The DMAc GPC system was calibrated based on narrow molecular weight distribution polymethylmethacrylate standards with molecular weights of 200 to  $10^6$   $\text{g mol}^{-1}$ . Nuclear Magnetic Resonance (NMR) spectroscopy was carried out with Bruker Avance III with SampleXpress operating at 300 MHz for  $^1\text{H}$  using  $\text{CDCl}_3$  as solvent. Tetramethylsilane (TMS) was used as a reference. The data obtained was reported as chemical shift ( $\delta$ ) measured in ppm downfield from TMS.

## Continuous Flow Photoreactor

The photoreactor is comprised of an outer PVC pipe to which LED strips are attached. (**Figure S1**) An inner PMMA pipe is used to attach the FEP tubing which the reaction mixture flow through. The full dimensions of the photoreactor can be found in our previous work.<sup>1</sup>

The flow reactor utilised 5050 SMD LEDs at 60 LEDs per meter, set to green (525-535 nm, 3.8  $\text{W/m}^2$  max intensity at FEP tube surface) for a standard reaction, drawing a maximum power of 14.4  $\text{W/m}$ , at 12-24 V. The wavelength of blue light was 455-465 nm, and red light was 625-635 nm, and the maximum intensity at the FEP tube surface was 5.5  $\text{W/m}^2$  and 2.7  $\text{W/m}^2$  for blue and red lights, respectively, measured using a Newport 843-R power meter. The total LED coil length inside the tubular reactor was 10 m. A New Era NE-1000 multi-phaser syringe pump was used in conjunction with NormJect 9.65 mm and 15.9 mm inside diameter syringes to inject solutions into a 1/16 inch inside diameter FEP tubing purchased from John Morris Scientific. PVDF luer valve connectors, Y connectors and straight connectors used were also purchased from John Morris Scientific. The total tubing length was calculated to be  $\sim 0.3$  m ( $\sim 600$   $\mu\text{L}$ ) and the flow rate was set to 6.667  $\mu\text{L}/\text{min}$  for a 90 minute residence time, in a typical reaction; other flow rates are calculated as such. All reactions were performed at room temperature (measured as 22  $^\circ\text{C}$ ).



**Figure S1.** Flow reactor used for polymer synthesis. Clockwise from top left: inner PMMA pipe with FEP tubing, outer PVC pipe with LEDs, complete reactor setup, front view of outer PVC tubing with LEDs.

### Reaction setup

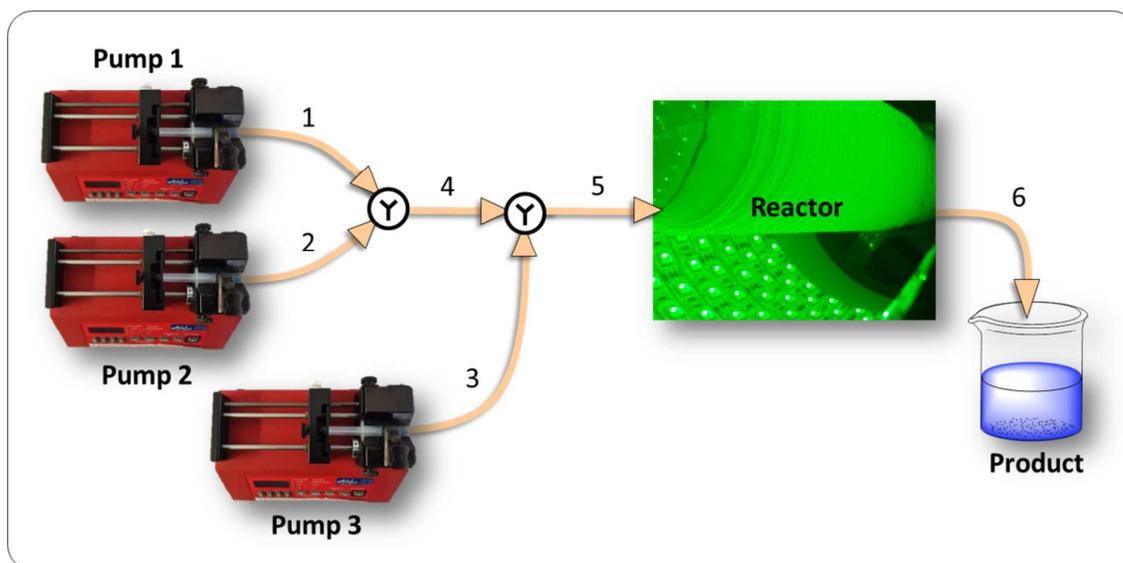
Throughout this study three different reaction setups were used to inject the PET-RAFT reaction mixtures into the previously described photoreactor. The reaction setups differ in the number of pumps needed to introduce the reagents into the photoreactor, and include one, two, and three pump systems. The one pump system is comprised of a single pump which was used to continuously inject a homogenized reaction mixture into the photoreactor from a syringe. (**Figure S4**) The one pump system was used for the kinetic study, and for controlling MWDs in the residence time, light intensity, and irradiation wavelength experiments (vide infra).

In the two pump system, the syringe attached to the first pump contained RAFT agent solvated in DMSO, while the syringe on the second pump contained DMAM and ZnTPP (in DMSO). Both pumps continuously injected their respective solutions into the photoreactor and the streams were mixed through a mixing Y-piece. (**Figure S3**) While the two pump system was able to alter the RAFT:monomer ratio, the total concentration of monomer and catalyst was not able to be fixed. The two pump system was used for mixing experiments (vide infra).

The three pump system used during this experimentation is shown in **Figure S1**, and includes 3 pumps, 6 sections of FEP tubing connected with mixing Y-pieces and the aforementioned photoreactor. The syringe attached to the first pump contained DTPA solvated in DMSO, the syringe on the second pump contained pure DMSO, and the syringe in the third pump contained DMAM and ZnTPP (in DMSO). Pumps 1 and 2 were used to alter the RAFT agent concentration while maintaining the total flow rate of solvent, while pump 3 injected the monomer and catalyst solution at a constant flow rate. The three pump system was able to alter the RAFT concentration while maintaining the total concentrations of both the monomer and catalyst. The three pump system was used to control MWDs.

### **General Procedure for the Synthesis of Poly *N,N*-Dimethylacrylamide (PDMAM) via PET-RAFT Polymerization in a three pump continuous flow reactor**

DTPA (17.1 mg, 48.8  $\mu\text{mol}$ ) was dissolved in DMSO (1709  $\mu\text{L}$ , 1880 mg, 24.1 mmol) inside a 4 mL glass vial, then drawn into a new 3 mL NormJect syringe (syringe 1). DMSO (7000  $\mu\text{L}$ , 7700 mg, 98.6 mmol) was drawn into a new NormJect 10 mL syringe (syringe 2). A mixture of DMAM (1920  $\mu\text{l}$ , 1.847 g, 18.63 mmol) and 632  $\mu\text{L}$  of ZnTPP stock solution in DMSO at 1 mg/mL (0.632 mg, 0.93  $\mu\text{mol}$  ZnTPP & 632  $\mu\text{L}$ , 695.2 mg, 8.90 mmol DMSO) was drawn into a new 3 mL NormJect syringe (syringe 3). Excess solution was drawn into each syringe to ensure the pump injected solutions from the syringes within their correct operating range. The syringes were fastened to their corresponding New Era NE-1000 multi-phaser syringe pump (pumps 1, 2 & 3) and connected to the FEP tubing rig using luer valve connectors. The syringes were then covered with aluminium foil to prevent light exposure to the reactant solution.



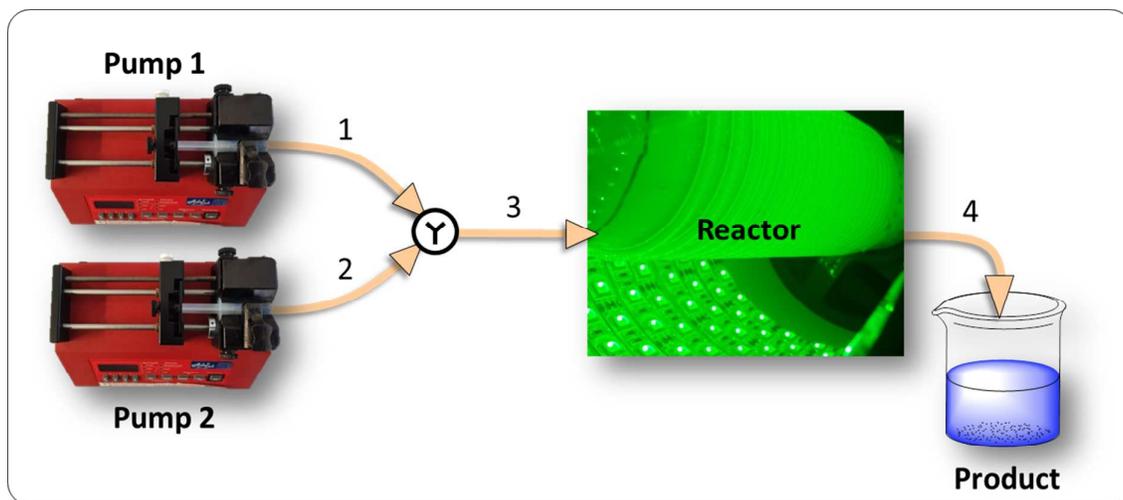
**Figure S2.** Reaction setup for three pump fully automated production of controlled MWDs and stream numbers. Stream 1: concentrated RAFT agent solution; Stream 2: Pure solvent; stream 3: monomer and catalyst (in solvent) solution; stream 4: diluted RAFT agent solution; stream 5: mixed reagent solution; stream 6: polymer product.

Streams 1, 2, and 3 (**Figure S2**) were filled with the solutions from syringes 1, 2, and 3, respectively. The pumping programs for pumps 2 and 3 were then started when both streams reached the first Y connector. Pump 3 was then started once the diluted RAFT agent solution reached the Y connector after stream 4. All pumps were set to automatically inject the reagent solutions at the designated rates and volumes (see “reaction flow rates” below). After irradiation inside the photoreactor, the reaction mixture was collected using a 4 mL glass vial covered in aluminium foil to avoid further reaction. The resulting mixture was shaken vigorously using a vortex mixer for 15 seconds before analysis by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and GPC (DMAc) to determine the conversions and molecular weight distributions.

### Two pump system

For the two pump system, reaction mixtures were prepared, drawn into syringes, and fastened to corresponding pumps in the same manner as the three pump system (*vide supra*). Stream 1 was then filled

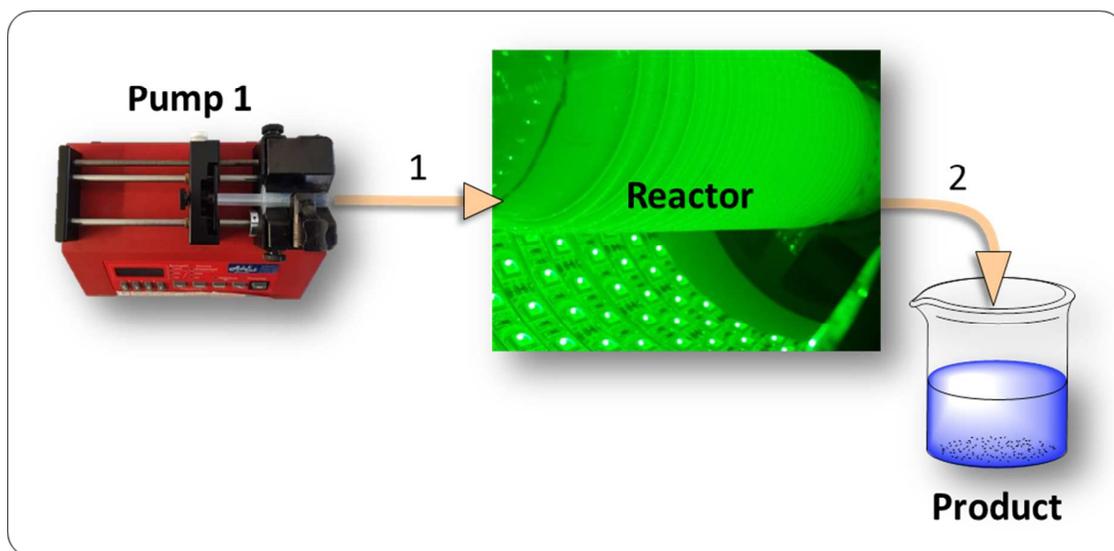
with the RAFT agent in DMSO solution until the liquid reached the Y connector. **(Figure S3)** Stream 2 was filled with the monomer and catalyst (in DMSO) solution until the liquid reached the Y connector. Both pumps were then started, and set to automatically inject the reagent solutions at the designated rates and volumes (see “reaction flow rates” below). Collection and sample preparation was identical to the three pump system.



**Figure S3.** Reaction setup for two pump fully automated production of controlled MWDs and stream numbers. Stream 1: RAFT agent in DMSO; Stream 2: monomer and catalyst (in solvent) solution; stream 3: mixed reagent solution; stream 4: polymer product.

### One pump system

For the one pump system, a single reaction mixture was prepared in a 4 mL glass vial and mixed using a vortex mixer to ensure homogeneity. The reaction mixture was then drawn into a 3 mL NormJect syringe which was then fastened to the pump. **(Figure S4)** The pump was then started, and set to automatically inject the reagent solution at the designated rates and volumes (see “reaction flow rates” below). Collection and sample preparation was identical to the two and three pump systems.



**Figure S4.** Reaction setup for one pump fully automated production of controlled MWDs and stream numbers. Stream 1: mixed reagent solution; stream 2: polymer product.

### Reaction flow rates

The flow rates and syringe contents for all reactions performed in this study are shown below.

**Table S1:** Flow rates, volumes and syringe contents for the fully automated residence time distribution system outlined in **Figure 5, b**.

		STEP			
		1	2	3	4
Volume ( $\mu\text{L}$ )	PUMP No.	1383	563.0	164.0	300.0
Rate ( $\mu\text{L}/\text{min}$ )	1	30.00	15.00	10.00	5.000
Syringe Contents					
<b>Pump 1</b>					
<b>DTPA (mg)</b>	<b>DMSO (<math>\mu\text{L}</math>)</b>	<b>ZnTPP in DMSO @ 1 mg/mL (<math>\mu\text{L}</math>)</b>			<b>DMAm (<math>\mu\text{L}</math>)</b>
10.3	4003	247			750

**Table S2:** Flow rates, volumes and syringe contents for the fully automated residence time distribution system outlined in **Figure 5, c**.

		STEP				
		PUMP No.	1	2	3	4
Volume ( $\mu\text{L}$ )	1	2800	600.0	200	300	
Rate ( $\mu\text{L}/\text{min}$ )		30.00	15.00	10.00	5.000	
Syringe Contents						
Pump 1						
DTPA (mg)	DMSO ( $\mu\text{L}$ )	ZnTPP in DMSO @ 1 mg/mL ( $\mu\text{L}$ )			DMAm ( $\mu\text{L}$ )	
10.3	4003	247			750	

**Table S3:** Flow rates, volumes and syringe contents for the fully automated intensity alteration experiment outlined in **Figure 6, a**.

		STEP		
		PUMP No.	1	2
Volume ( $\mu\text{L}$ )	1	1500	600.0	
Rate ( $\mu\text{L}/\text{min}$ )		6.667	6.667	
Wavelength (nm)		530	530	
Intensity ( $\text{W}/\text{m}^2$ )		0.3	3.8	
Syringe Contents				
Pump 1				
DTPA (mg)	DMSO ( $\mu\text{L}$ )	ZnTPP in DMSO @ 1 mg/mL ( $\mu\text{L}$ )		DMAm ( $\mu\text{L}$ )
5.1	2203	197		600

**Table S4:** Flow rates, volumes and syringe contents for the fully automated wavelength alteration experiment outlined in **Figure 6, b**.

		STEP		
		PUMP No.	1	2
Volume ( $\mu\text{L}$ )	1	600.0	2400	
Rate ( $\mu\text{L}/\text{min}$ )		8.000	8.000	
Wavelength (nm)		460	630	
Intensity ( $\text{W}/\text{m}^2$ )		4.2	1.4	
Syringe Contents				
Pump 1				
DTPA (mg)	DMSO ( $\mu\text{L}$ )	ZnTPP in DMSO @ 1 mg/mL ( $\mu\text{L}$ )		DMAm ( $\mu\text{L}$ )
5.1	2203	197		600

**Table S5:** Flow rates, volumes and syringe contents for the fully automated concentration variation experiment outlined in **Figure 7, a**.

	PUMP No.	STEP				Syringe Contents	
		1	2	3	4		
Volume (μL)	1	124.9	83.63	56.15	37.78	DMSO (μl)	DTPA (mg)
Rate (μL/min)		2.082	1.394	0.936	0.630		
Volume (μL)	2	115.3	156.6	184.0	202.4	DMSO (μL)	
Rate (μL/min)		1.921	2.609	3.067	3.374		658
Volume (μL)	3	59.81	59.81	59.81	59.81	DMAm (μl)	ZnTPP @ 1 mg/ml in DMSO (μl)
Rate (μL/min)		0.997	0.997	0.997	0.997		

**Table S6:** Flow rates, volumes and syringe contents for the fully automated concentration variation experiment outlined in **Figure 7, b**.

	PUMP No.	STEP				Syringe Contents	
		1	2	3	4		
Volume (μL)	1	552.6	328.4	195.9	117.2	DMSO (μl)	DTPA (mg)
Rate (μL/min)		3.070	1.824	1.088	0.651		
Volume (μL)	2	328.5	552.6	685.1	763.9	DMSO (μL)	
Rate (μL/min)		1.825	3.070	3.806	4.244		2330
Volume (μL)	3	319.0	319.0	319.0	319.0	DMAm (μl)	ZnTPP @ 1 mg/ml in DMSO (μl)
Rate (μL/min)		1.772	1.772	1.772	1.772		

**Table S7:** Flow rates, volumes and syringe contents for the fully automated number of chains experiment outlined in **Figure 8**.

	PUMP No.	STEP				Syringe Contents	
		1	2	3	4		
Volume (μL)	1	40.24	59.82	92.78	159.3	DMSO (μl)	DTPA (mg)
Rate (μL/min)		3.484	1.920	1.324	1.010		
Volume (μL)	2	9.674	70.22	199.8	499.0	DMSO (μL)	
Rate (μL/min)		0.699	2.254	2.285	3.164		779
Volume (μL)	3	158.3	158.3	158.3	158.3	DMAm (μl)	ZnTPP @ 1 mg/ml in DMSO (μl)
Rate (μL/min)		2.484	2.484	2.484	2.484		

**Table S8:** Flow rates, volumes and syringe contents for the fully automated system outlined in **Figure 9**.

step	Pump 1		Pump 2	
	Rate ( $\mu\text{L}/\text{min}$ )	Volume ( $\mu\text{L}$ )	Rate ( $\mu\text{L}/\text{min}$ )	Volume ( $\mu\text{L}$ )
1	16.69	28.0	66.76	112.0
2	19.32	32.42	64.12	107.6
3	21.96	36.84	61.49	103.2
4	24.59	41.26	58.85	98.74
5	27.23	45.68	56.22	94.32
6	29.86	50.11	53.58	89.89
7	32.50	54.53	50.95	85.47
8	35.13	58.95	48.31	81.05
9	37.77	63.37	45.67	76.63
10	40.40	67.79	43.04	72.21
11	43.04	72.21	40.40	67.79
12	45.67	76.63	37.77	63.37
13	48.31	81.05	35.13	58.95
14	50.95	85.47	32.50	54.53
15	53.58	89.89	29.86	50.11
16	56.22	94.32	27.23	45.68
17	58.85	98.74	24.59	41.26
18	61.49	103.16	22.0	36.84
19	64.12	107.58	19.3	32.42
20	66.8	112.00	16.7	28.00
Syringe Contents				
Pump 1		Pump 2		
DTPA (mg)	DMSO ( $\mu\text{L}$ )	ZnTPP in DMSO @ 1 mg/mL ( $\mu\text{L}$ )	DMAm ( $\mu\text{L}$ )	
41.8	1500	180	1120	

**Generation of theoretical GPC curves**

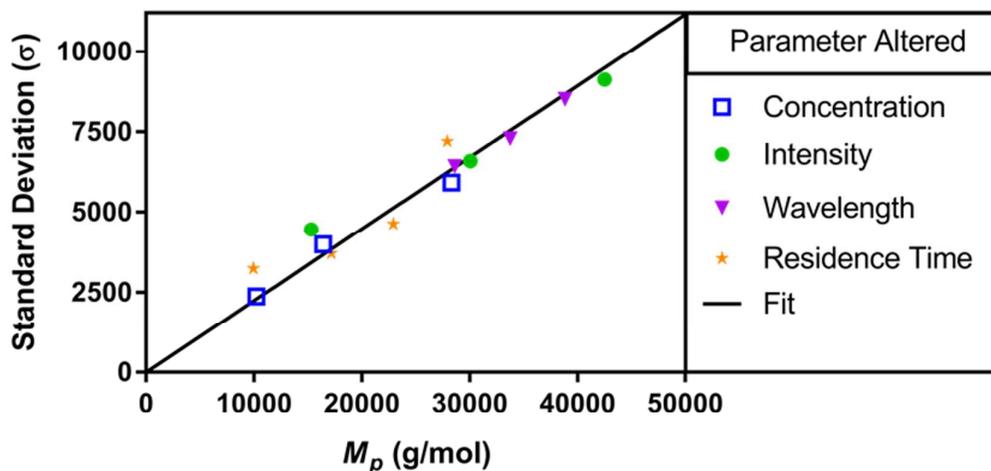
The theoretical MWDs generated in this study are intended to be a rough guide for the experimentally produced MWDs. More precise calculations are required to generate more realistic theoretical MWDs. In order to produce theoretical MWDs for PDMAm polymers in this study we first assumed that our individual homopolymer fractions formed normal distributions at all molecular weights. Theoretical normal

distributions can then be produced given a known mean and standard deviation. The mean was taken as the  $M_p$  of PDMAm polymers and the standard deviation was calculated experimentally through analysis of the full width at half maximum of monomodal polymer fractions produced in this study.

To estimate the standard deviation of polymers produced in this study, thirteen PDMAm homopolymer fractions from the concentration, intensity, wavelength, and residence time alteration experiments (**Figure 1-3**) were analyzed. The full width at half maximum (FWHM) was calculated for these thirteen samples, which is related to the standard deviation,  $\sigma$ , by the following equation:

$$FWHM = 2\sigma \cdot \sqrt{2 \ln(2)} \approx 2.355 \sigma$$

The calculated standard deviations were then plotted against the peak molecular weights ( $M_p$ ) of each sample. (**Figure S5**) The standard deviation was found to linearly increase with  $M_p$  with a gradient of 0.223. This standard deviation value was used for the calculation of theoretical MWDs. To produce curves of multimodal distributions, the curves based on these normal distributions were then superimposed on each other and normalized to generate the theoretical MWD.

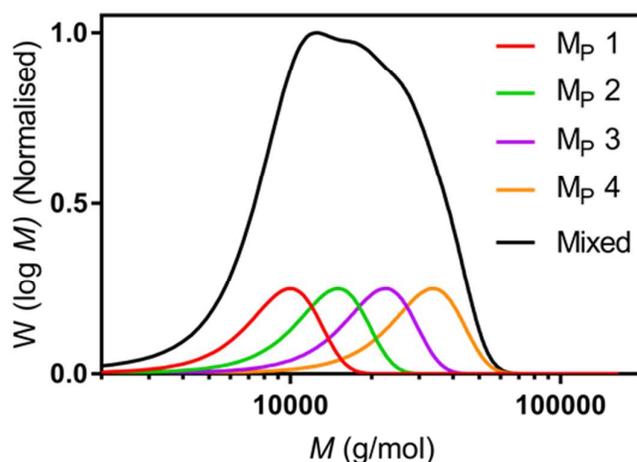


**Figure S5.** Standard deviation ( $\sigma$ ) vs peak molecular weight ( $M_p$ ) for PDMAm samples.

### Calculation of required volume ratios for manual mixing experiments

For the GPC unit used in this study, the response of the RI detector is proportional to the mass concentration of polymer eluted at any specific elution time. Therefore, in order to generate an equal GPC response over a particular MW range, equal mass concentrations of polymer at each molecular weight (elution time) are required. Assuming polymer density is constant with molecular weight, equal volumes of polymer at each target  $M_p$  were required. As the response is generated from superimposition of four monomodal polymer fractions in this study, only a nearly equal response over the MW range is attainable. If more monomodal polymer fractions are available for mixing, the response can become closer to the ideal case, with an equal response over the defined MW range.

In order to simplify calculations, four model monomodal polymers with a standard deviation of  $0.223 \cdot M_p$  (vide supra) were superimposed to generate a model MWD representative of the entire mixture. For instance, **Figure S6** shows four theoretical MWDs for monomodal polymer fractions, and the resulting Theoretical MWD generated by their superimposition.



**Figure S6.** Theoretically derived GPC traces for monomodal and mixed PDMAm samples.

The overall curve shown in **Figure S6** assumes equal conversion for all four monomodal polymer fractions. If the conversion of the monomodal polymer fractions is not equal, the theoretical volume fractions must be multiplied by a factor to account for the reduced polymer volume in the lower monomer conversion fractions. E.g. to produce an equal GPC response for two polymer fractions containing 50 % and 100 % monomer conversion, respectively, the volume of the 50 % monomer conversion fraction is required to be double the volume of the fraction with 100 % conversion. Since the molecular weight (retention time) scale is base 10 logarithmic for this setup, the monomodal polymer fractions were targeted to have equal spacing on the logarithmic scale. The  $M_p$ 's, conversions and volume fractions of polymers used in the manual mixing experiment (**Figure 4**) are shown in **Table S9**.

**Table S9.** Peak molecular weights, conversions and volume fractions for monomodal PDMAm fractions used in the manual mixing experiment shown in **Figure 5**.

Peak Number	$M_p$ (kg/mol)	$\alpha$ (%)	Vol. fraction
1	27.9	84	0.278
2	22.9	71	0.111
3	17.2	50	0.267
4	9.9	26	0.344

#### Calculation of volume fractions for equal number of chains

As per the equations of Clay and Gilbert, the number of chains distributions in this study were generated by dividing each GPC response by the square of the molecular weight at that response.<sup>2</sup> (**Equation 1**) As such, in order to generate a MWD with an equal number of chains at each MW the volume of each monomodal polymer fraction was calculated as:

$$\text{Volume fraction at } M_{p,i} = \frac{M_{p,i}^2}{\sum_{i=1}^n M_{p,i}^2}$$

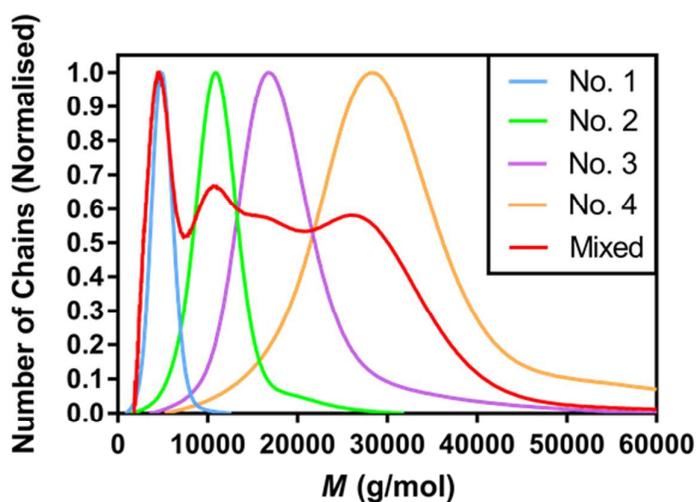
Where  $M_p$  is the peak molecular weight.

E.g. for four monomodal polymer fractions with different peak molecular weights:

**Table S10.** Example calculation of the volume fractions required to produce a polymer sample with an approximately equal number of chains over the range of the lowest to highest  $M_p$ 's.

<b>Fraction No.</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b><math>M_p</math></b>	10000	15000	22500	33750
<b><math>M_p^2</math></b>	100000000	225000000	506250000	1139062500
<b><math>\Sigma M_p^2</math></b>	1970312500			
<b>Volume fraction</b>	0.051	0.114	0.257	0.578

To demonstrate this, four monomodal PDMAm polymer fractions were produced and mixed in the ratio as shown in **Table S10**. **Figure S7** shows the results of manually mixed PDMAm polymers. Although the first fraction appears overexpressed, the number of chains appears relatively constant over the range of 8-33 kg/mol. The monomer conversion of each of the PDMAm polymer fractions was ~85 %. Again, if the conversion of the monomodal polymer fractions is not equal, the theoretical volume fractions must be multiplied by a factor to account for the altered volume in such fractions.



**Figure S7.** Normalized number distributions for monomodal and manually mixed PDMAM sample.

### Skewness, Kurtosis and Dispersity of Controlled MWDs

**Table S11** contains information on the skewness, kurtosis and dispersity of polymer samples produced in this study. The kurtosis and skewness were calculated through equations described by Rudin.<sup>3</sup>

**Table S11.**  $M_n$ ,  $M_p$ , Kurtosis ( $\alpha_3$ ), skewness ( $\alpha_4$ ), and dispersity of poly(DMAM) produced in photoinduced flow polymerisation.

Entry	Corresponding Figure	$M_n$ (kg/mol)	$M_p$ (kg/mol)	$\alpha_3$	$\alpha_4$	$\mathcal{D}$
1	Figure 4, 1	10.8	9.1	0.21	2.84	1.14
2	Figure 4, 2	17.8	15.7	-0.25	2.88	1.09
3	Figure 4, 3	23.5	20.5	0.30	4.24	1.09
4	Figure 4, 4	28.6	23.6	0.70	5.27	1.16
5	Figure 4, Mix	19.7	14.6	1.39	6.02	1.32
6	Figure 5a	29.6	25.9	0.45	4.64	1.10
7	Figure 5b	27.5	22.0	1.43	8.94	1.18

8	Figure 5c	16.3	17.1	1.23	6.23	1.21
9	Figure 7a	23.8	19.3	1.17	5.81	1.22
10	Figure 7b	50.2	32.3	3.72	32.51	1.80
11	Figure 8	26.0	20.4	1.50	8.22	1.35

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### Calculation of Reynolds number

The Reynolds number (Re) is defined as:

$$\text{Re} = \frac{\rho \cdot u \cdot L}{\mu}$$

Where:

$\rho$  is the fluid density (kg/m<sup>3</sup>)

$u$  is the fluid velocity (m/s)

$L$  is the length of tubing (m)

$\mu$  is the dynamic viscosity (kg/m/s)

Assume the dynamic viscosity for liquid mixtures can be calculated through the following equation<sup>4</sup>:

$$\ln(\mu) = \sum_{i=1}^n \frac{1}{n} \cdot (x_i + \phi_{vi}) \cdot \ln(\mu_i)$$

Where:

$x_i$  is the mole fraction of component  $i$

$\phi_{vi}$  is the volume fraction of component  $i$

$\mu_i$  is the dynamic viscosity of component  $i$

For a 20/80 volume/volume ratio of DMAm/DMSO (standard experimental ratio) the dynamic viscosity is found to be 0.002098 kg/m/s.

Also for a 20/80 volume/volume ratio of DMAM/DMSO, assume the density is a constant  $1072.4 \text{ kg/m}^3$  (numerical average). The density will increase due to volume contraction during the polymerization, but constant density is a fair assumption for this back of the envelope calculation.<sup>5</sup>

For a 0.3 m length of FEP tubing, a reaction time of 90 minutes (standard experimental time) gives a velocity,  $u$ , of  $5.55 \times 10^{-5} \text{ m/s}$ .

As such, the Reynolds number for a typical polymerization is initially 8.51. This value is well within the laminar region.<sup>6</sup> Moreover, as the polymerization proceeds, the dynamic viscosity increases, which decreases the Reynold number. Therefore our polymerization should be in the laminar regime for the entire reaction duration.

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