Supplementary Information

Kinetic Investigation on the Cationic Polymerization of *o*-Phthalaldehyde: Understanding Ring-Expansion Polymerization

Anthony Engler, Paul A. Kohl*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States.

*Corresponding author: kohl@gatech.edu

1. General Experimental Details

Figure S1. Pictures of flow reactor parts. (a) syringe pump; (b) 316 stainless steel pipe, 1/16” OD x 0.014 in wall thickness; (c) PTFE luer-lock adapter and tubing, 12” long, 1/16” ID; (d) 316 stainless steel union tee for 1/16” OD pipe.

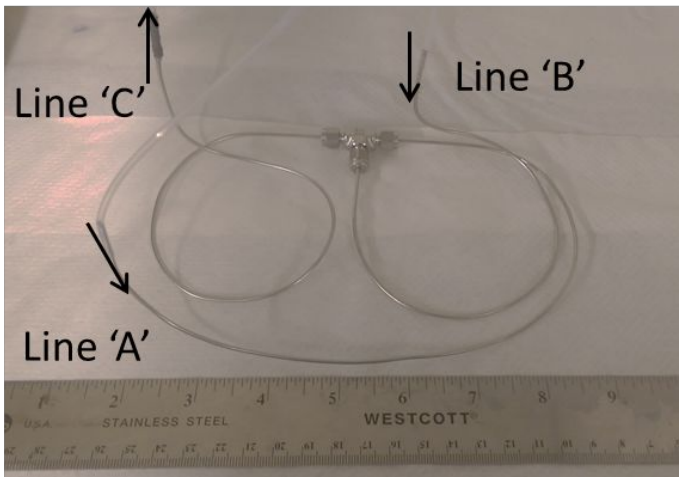

Figure S2. Picture of constructed stainless steel reactor portion.

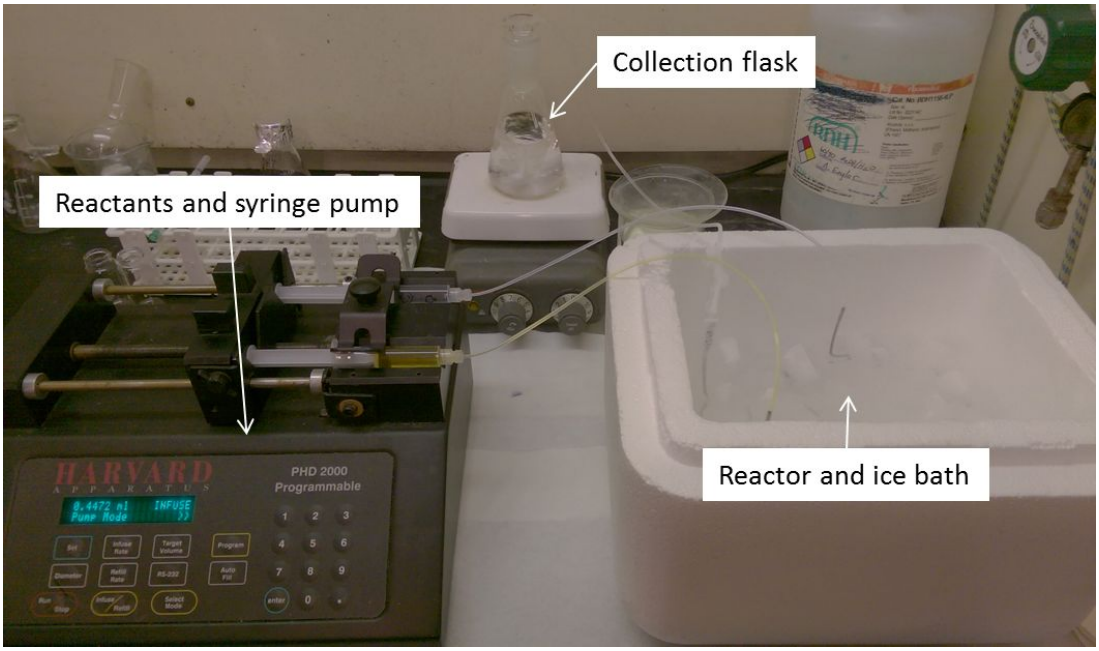

Figure S3. Flow reactor set up during operation.

Table S1. Flow reactor parameters. See Figure S2 for identification of segment lines.

Length of segment 'A'	12 in	Volume	187 µL
Length of segment 'B'	10 in		
Length of segment 'C'	10 in		
Internal diameter of steel pipes	876 µm		
Surface area-to-volume ratio of segment 'A'	4571 m^{-1}		

2. Polymerization data

Flow Polymerizations

Table S2. Polymerization data for the flow reactor experiments with [M]/[I] = 500 and T = -78°C.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
2.00	4.3	40.8	2.02
4.00	24.3	68.7	1.96
7.00	30.9	73.6	1.88
10.00	34.3	77.4	1.67
20.04	47.8	80.9	2.03
29.93	66.6	89	1.85
44.93	72.5	129	2.04
59.93	80.7	133	2.08
90.00	85.8	137	1.84
121.78	89.6	188	1.94

Table S3. Polymerization data for the flow reactor experiments with [M]/[I] = 300 and T = -78°C.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
2.00	23.7	34.2	2.47
4.00	40.4	50.5	2.32
7.00	51.5	66.2	2.01
10.00	57.1	63.6	1.81
20.04	70.5	64.8	1.74
29.93	77.6	77.8	2.29
44.93	82.5	81.7	2.16
59.93	85.8	99.2	2.10
80.34	88.9	101	1.81
100.05	92.2	137	1.87

Table S4. Polymerization data for the flow reactor experiments with [M]/[I] = 160 and T = -78°C.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
1.00	8.97	66.7	2.24
2.00	45.5	126	2.10
4.00	56.1	139	2.07
7.00	78.9	170	2.08
10.00	85.9	198	2.01

20.04	90.4	244	2.06
29.93	92.3	252	2.26
44.93	94.3	276	1.94

Table S5. Polymerization data for the flow reactor experiments with [M]/[I] = 50 and T = -78°C.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
0.50	6.67	91.6	2.22
1.00	45.3	130	2.11
2.00	65.6	140	2.33
4.00	85.6	144	2.37
7.00	91.4	177	2.14
10.00	94.4	277	2.13

Table S6. Polymerization data for the flow reactor experiments with [M]/[I] = 160 and T = -57°C. Sample with τ_R = 1.00 did not have enough material for a GPC sample. Data points below the thick horizontal line are beyond the linear portion of the reaction and highlight the pinching reaction affects.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
1.00	0.28	-	-
2.00	30.3	87	2.14
4.00	48.3	106	2.03
7.00	55.9	120	2.15
10.00	56.9	85.8	2.08
20.00	55.5	68.5	1.95

Table S7. Polymerization data for the flow reactor experiments with [M]/[I] = 160 and T = -67°C.

τ_R (s)	Yield (%)	M_n (kDa)	Đ
1.00	2.91	40	2.87
2.00	37.3	122	2.14
4.00	62.4	154	2.20
7.00	70.3	155	2.17
10.00	78.7	174	2.09

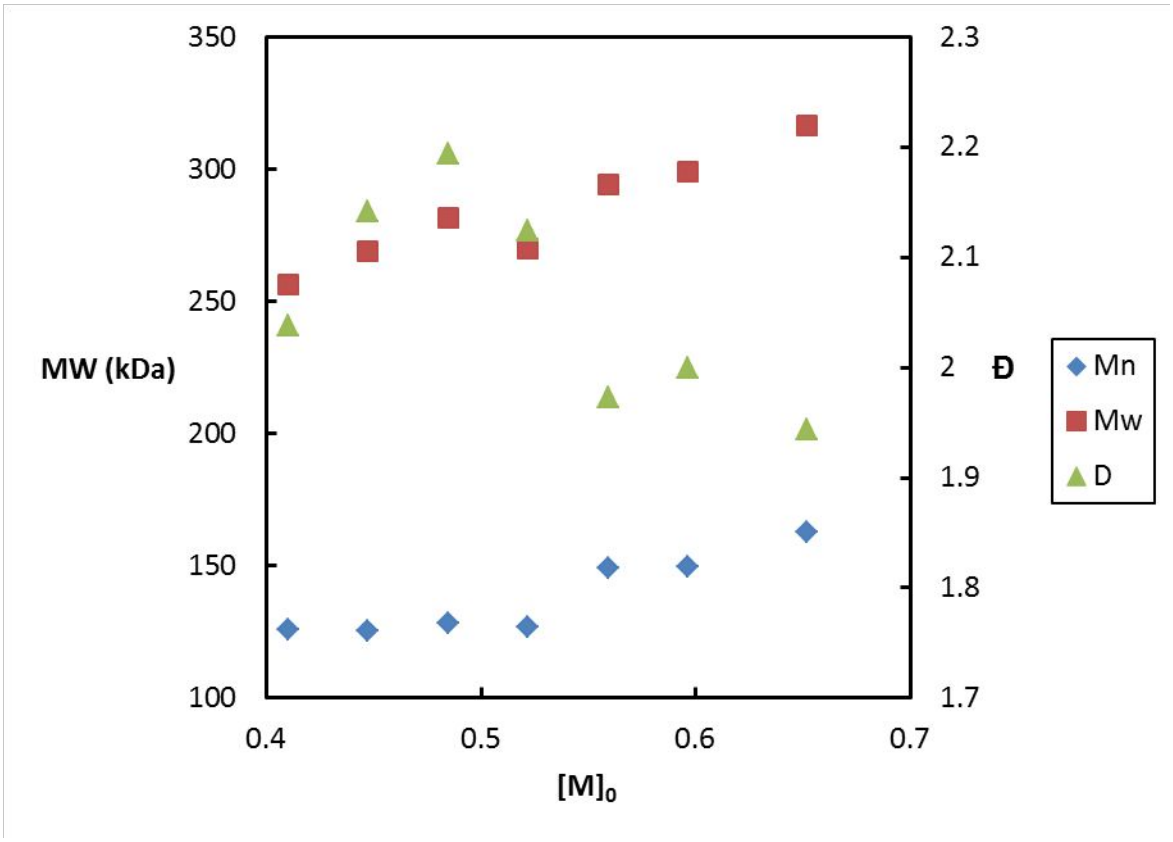

Figure S4. Equilibrium batch polymerization data systematically varying the $[M]_0$ values to show that large polymer is formed before this kinetics transition, and therefore likely not due to cyclic critical concentrations as given by Jacobson-Stockmayer theory.