

Supporting Information

Comprehensive control over molecular weight distributions through automated polymerizations

Maarten Rubens^{[a][b]} and Tanja Junkers^{[a][b]}

^aPolymer Reaction Design Group, Universiteit Hasselt, Martelarenlaan 42, 3500 Hasselt, Belgium.

^bPolymer Reaction Design Group, School of Chemistry Monash University 19 Rainforest Walk, Building 23, Clayton, Vic 3800 (Australia)

Content

Experimental Setup	S 2
Poly(Methyl Acrylate) with an M_n of 3000 g·mol ⁻¹ and a \mathcal{D} of 1.2, 1.3 and 1.4	S 3
Poly(Methyl Acrylate) with an M_n of 2500 g·mol ⁻¹ and a \mathcal{D} of 1.6	S 4
Poly(Methyl Acrylate) with an M_n of 2000 g·mol ⁻¹ and a \mathcal{D} of 1.2, 1.3 and 1.4	S 5

Experimental Setup



Figure 1: Overview of experimental setup to control molecular weight distribution through mixing. **1.** Chemyx Fusion 100 syringe pumps. **2.** Isothermal oil-bath containing continuous flow reactor. **3.** Switch valve to direct product stream to online-GPC or collection to flask. **4.** Collection vial. **5.** Online-GPC setup used for the autonomous optimization to a predefined molecular weight.

Poly(Methyl Acrylate) with an M_n of 3000 g·mol⁻¹ and a \bar{D} of 1.2, 1.3 and 1.4

M_n of 3000 g·mol⁻¹ and a \bar{D} of 1.21

Three pMA samples of DP 27, 38 and 51 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S1 for the individual fractions.

Table S1: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	<i>M_n</i>	<i>n (μmol)</i>
1	27	2675	10.91
2	38	3622	7.76
3	51	4741	5.74

M_n of 3000 g·mol⁻¹ and a \bar{D} of 1.30

Three pMA samples of DP 24, 41 and 63 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S2 for the individual fractions.

Table S2: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	<i>M_n</i>	<i>n (μmol)</i>
1	24	2416	12.23
2	41	3880	7.18
3	63	5774	4.60

M_n of 3000 g·mol⁻¹ and a \bar{D} of 1.41

Four pMA samples of DP 21, 35, 55 and 80 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S4 for the individual fractions.

Table S3: Degree of polymerization (DP) and amount required of 4 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	M_n	n (μmol)
1	21	2158	10.42
2	35	3363	0.84
3	55	5085	0.53
4	80	7238	0.36

Poly(Methyl Acrylate) with an M_n of 2500 g·mol⁻¹ and a \bar{D} of 1.6

Five pMA samples of DP 15, 25, 40, 65 and 100 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S5 for the individual fractions.

Table S4: Degree of polymerization (DP) and amount required of 5 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	M_n	n (μmol)
1	15	1642	10.00
2	25	2503	8.00
3	40	3794	5.60
4	65	5946	4.20
5	100	8960	1

Poly(Methyl Acrylate) with an M_n of 2000 g·mol⁻¹ and a \bar{D} of 1.2, 1.3 and 1.4

M_n of 2000 g·mol⁻¹ and a \bar{D} of 1.21

Three pMA samples of DP 18, 25 and 32 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S6 for the individual fractions.

Table S5: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	<i>M_n</i>	<i>n (μmol)</i>
1	18	1900	16.05
2	25	2503	11.76
3	32	3105	9.22

M_n of 2000 g·mol⁻¹ and a \bar{D} of 1.30

Three pMA samples of DP 16, 27 and 41 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S7 for the individual fractions.

Table S6: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	<i>M_n</i>	<i>n (μmol)</i>
1	16	1728	17.87
2	27	2675	10.91
3	41	3880	7.18

M_n of 2000 $\text{g}\cdot\text{mol}^{-1}$ and a \bar{D} of 1.4

Four pMA samples of DP 14, 24, 37 and 54 are synthesized with predetermined M_n according to the autonomous flow reactor system with targeted molecular weight and afterwards mixed together. See Table S7 for the individual fractions.

Table S7: Degree of polymerization (DP) and amount required of 4 pMA polymer samples to attain simulated MWD.

<i>Entry</i>	<i>DP</i>	M_n	n (μmol)
1	14	1556	15.10
2	24	2417	9.17
3	37	3536	5.98
4	54	4999	4.06