Electronic Supplementary Material (ESI) for Polymer Chemistry.

Predictive Design of Polymer Molecular Weight Distributions in Anionic Polymerization

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Supporting Information

Experimental Section and Data Processing

Anionic Polymerization

All reactions were performed in a Unilab MBraun Glovebox with a nitrogen atmosphere unless otherwise noted. To a freshly flame-dried 20 mL scintillation vial, equipped with a magnetic stir bar, was added styrene (0.8 mL) and cyclohexane (6.9 mL). A previously prepared stock solution of *s*-BuLi (320 µL, 0.16 M in cyclohexane) was then drawn into a plastic syringe and mounted onto a New Era NE-4000 Double Syringe Pump. Once the needle was submerged into the polymerization mixture, the addition profile was initiated causing the solution to slowly turn bright orange. Once the addition rate program was run to completion and full monomer conversion was reached, the reaction was quenched with a small amount of BHT, immediately turning the reaction from bright orange to colorless. The reaction mixture was then sampled for SEC analysis. It is important to note that for 80, 100, and 120 min exponentially ramped additions, an initiator stock solution of 0.053 M was prepared and 960 µL was added to the polymerization mixture (total amount of cyclohexane was also reduced to 6.3 mL).

Size Exclusion Chromatography (SEC)

Each polymer sample was monitored by SEC analysis, using a Tosoh EcoSEC HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.35 mL/min using THF as eluent. Number-averaged molar mass (M_n), weight-averaged molar mass (M_w), and dispersity ($Đ$) were calculated from refractive index traces verse TSKgel polystyrene standards. Conversions were determined using a Varian 400 MHz NMR spectrometer in $CDCl_3$.

Data Processing

The data was recorded *via* SEC in the form shown in Figure 3A, where the refractive index response (proportional to concentration) is plotted as a function of the retention time for the case of the constant initiator addition during 60 min. The other initiator addition profiles will be discussed in detail in the Results and Discussion. In order to quantitatively compare this type of data to the modeling results, we performed the conversion steps exemplified in Figure S1. All the solid curves contain numerous points connected by straight lines and every hundredth data point is magnified as a solid blue dot.

We first convert the raw SEC retention time data into the logarithm MWD *via* the standard procedure of a calibration curve using polystyrene standards (Figure S1A-C). Next the molecular weight is converted to a linear scale to give weight fraction MWDs (Figure S1D-E) followed by transformation into the number fraction distribution (Figure S1F). The vertical axis, the refractive index detector response, is proportional to concentration and rewritten without any approximations using the following definition of the concentration of chains, N, of a given molecular weight, MW:

$$\frac{d\mathrm{wt}}{d\mathrm{MW}} = N(\mathrm{MW})\ . \tag{S1}$$

The data in Figure 3A, C and D are in arbitrary units and therefore needs to be normalized with a condition that all styrene monomer was converted to polymer chains,

$$P(k) = \frac{N(k)}{I_0} \frac{M_0}{\sum_{j=1}^{\infty} j \cdot N(j)}\ , \tag{S2}$$

where $k = \mathrm{MW}/\mathrm{MW}_0$, $k \in \mathbb{R}$, with MW_0 being the molecular weight of one repeat unit in the chain, M_0 the total initial concentration of styrene, and I_0 the total concentration of the initiator added into the system. The normalized data (fraction of chains of length k) are shown in Figure S1F. The primary concern with this data is that k is not an integer. Since the degree of polymerization of the polystyrene chains must be an integer value, the data are discretized before comparing to modeling results.

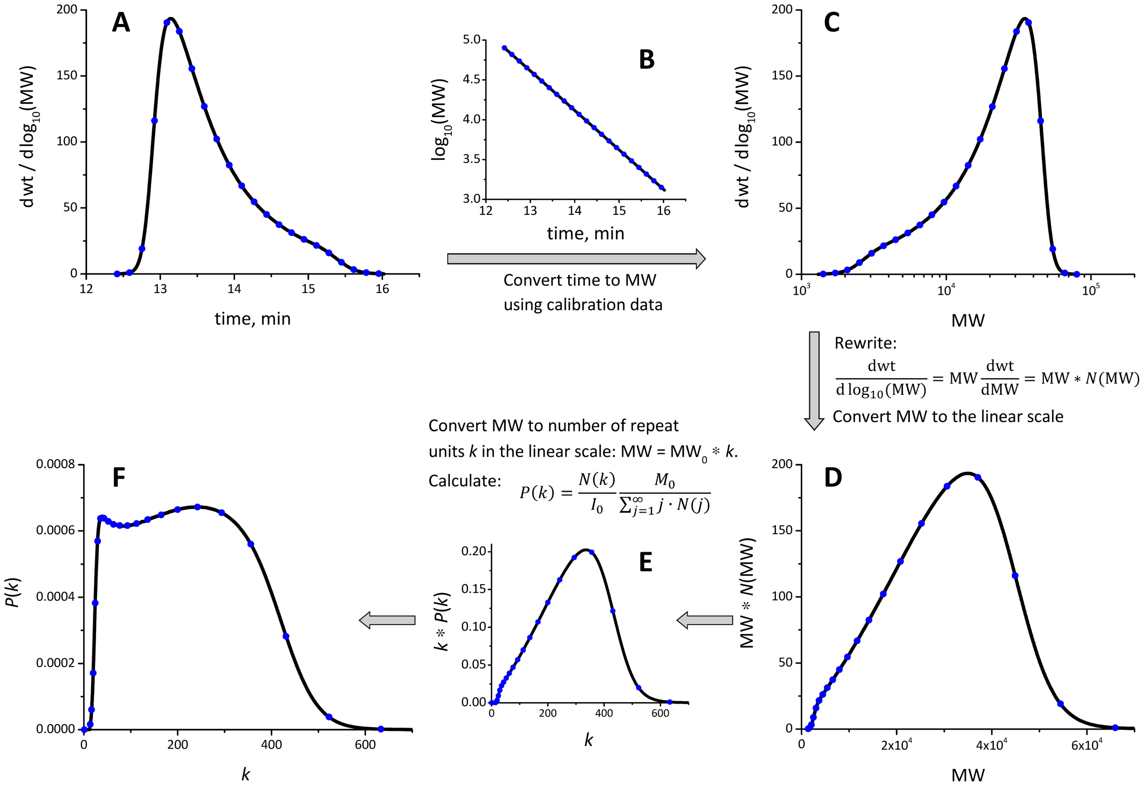

Figure S1. (A) Data recorded by the SEC instrument for the 60 min constant rate initiator addition profile. The solid curves contain numerous points connected by straight lines and every hundredth data point is magnified as a solid blue dot. (B) Calibration experiment with a known molecular weight distribution sample. (C), (D), (E) The experiment data, identical to panel (A), converted according to the procedures detailed in text.

To re-discretize the data from Figure S1F, it is convenient to prepare the cumulative chain fraction as a function of the chain length (Figure S2A):

$$\sum_{j=1}^{k_j \le i} P(k_j)\,, \tag{S3}$$

where j is the index of the data points in Figure S1F. Next, preserving the cumulative chain fraction function, Equation (S3) determines the new distribution of chain fractions as a function of integer values of chain length, $i \in \mathbb{N}$ (Figure S2B). The latter plot is converted into the weight fraction of chains (Figure S2C) for further comparison with the modeling results.

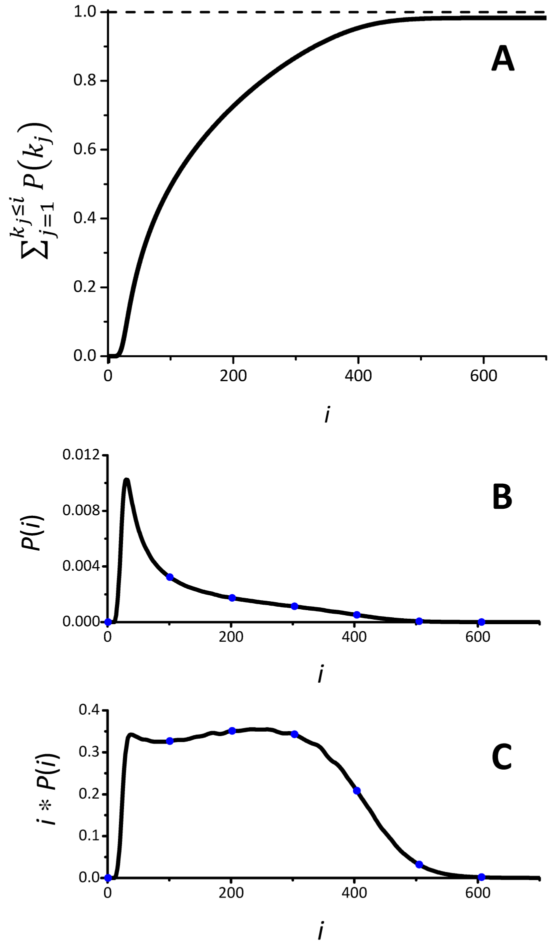

Figure S2. (A) Cumulative chain fraction as a function of the chain length. (B) distribution of chain fractions as a function of the chain length, $i \in \mathbb{N}$. (C) Chain fractions multiplied by the length of the chains in that fraction, see text for detail. Identically to Figure 3, the solid curves in (B) and (C) contain numerous points connected by straight lines and every hundredth data point is magnified as a solid blue dot.

Calibration Curve for the Transformation of Retention Time to Molar Mass

The calibration curve for size-exclusion chromatography (SEC) data was obtained using Tosoh TSKgel polystyrene (PS) standards. The relationship between the logarithm of molar mass and retention time is a third order polynomial shown in Equation S4:

$$\log MW = At^3 + Bt^2 + Ct + D , \tag{S4}$$

where *MW* is the molar mass of the polymer chain, *t* is in minutes, $A = -0.0034$, $B = 0.1350$, $C = -2.2554$, and $D = 18.6905$.

Numerically Determined Effective Rate Constant from Figure 5

$$k_p(i) = 0.0806\left(108.6 - 107\sqrt{\frac{600}{i+600}} - e^{-0.0002(i-100)^2}\right)\left(9 + \frac{500^3}{i^3+500^3}\right) \tag{S5}$$

Initiator Addition Rate Profiles

Initiator addition rates from Figure 1 have been used previously and are reported elsewhere.[1] The initiator addition rates from Figure 2 are reported in Tables S1 – S5.

Table S1. Figure 2A Black

Step Number	Rate (µL/h)	Volume (µL)
1	240.8	160.5
2	126.9	4.7
3	177.9	6.5
4	249.6	9.2
5	348.8	12.8
6	489.5	17.9
7	683.9	25.1
8	958.3	35.1
9	1342	49.2

Table S2. Figure 2A Red

Step Number	Rate (µL/h)	Volume (µL)
1	160.5	160.5

2	84.6	4.7
3	118.6	6.5
4	166.4	9.2
5	232.6	12.8
6	326.3	17.9
7	455.9	25.1
8	638.8	35.1
9	894.4	49.2

Table S3. Figure 2A Green

Step Number	Rate (µL/h)	Volume (µL)
1	120.4	160.5
2	63.4	4.7
3	88.9	6.5
4	124.8	9.2
5	174.4	12.8
6	244.7	17.9
7	341.9	25.1
8	479.1	35.1
9	670.8	49.2

Table S4. Figure 2B 30 min Linearly Decreasing Initiator Addition

Step Number	Rate (µL/h)	Volume (µL)
1	1247	31.2
2	1184	29.6
3	1120	28.0
4	1056	26.4
5	992.8	24.8
6	929.2	23.2
7	865.6	21.6

8	801.8	20.0
9	738.2	18.4
10	674.4	16.8
11	610.8	15.3
12	547.2	13.7
13	483.4	12.1
14	419.8	10.5
15	356	8.9
16	292.4	7.3
17	228.8	5.7
18	165.0	4.1
19	101.4	2.5
20	37.6	1.0

Table S5. Figure 2B 60 min Linearly Decreasing Initiator Addition

Step Number	Rate (µL/h)	Volume (µL)
1	623.8	31.2
2	592.0	29.6
3	560.1	28.0
4	528.3	26.4
5	496.4	24.8
6	464.6	23.2
7	432.8	21.6
8	400.9	20.0
9	369.1	18.4
10	337.2	16.8
11	305.4	15.3
12	273.6	13.7
13	241.7	12.1
14	209.9	10.5

15	178.0	8.9
16	146.2	7.3
17	114.4	5.7
18	82.5	4.1
19	50.7	2.5
20	18.8	1.0

Additional Modeling Results

Here we show that MWDs can be predicted from arbitrary initiator addition profiles, demonstrating the numerical modeling capability of this approach (Figure S3 and Figure S4). In these simulated reactions the initiator was added according to the profiles shown in the insets. These profiles are simulated as 50-step initiator addition rate profiles in a similar fashion the experiments described in the main text. The code for modeling of MWDs from initiator addition profiles is attached to the Supporting Information as a separate file.

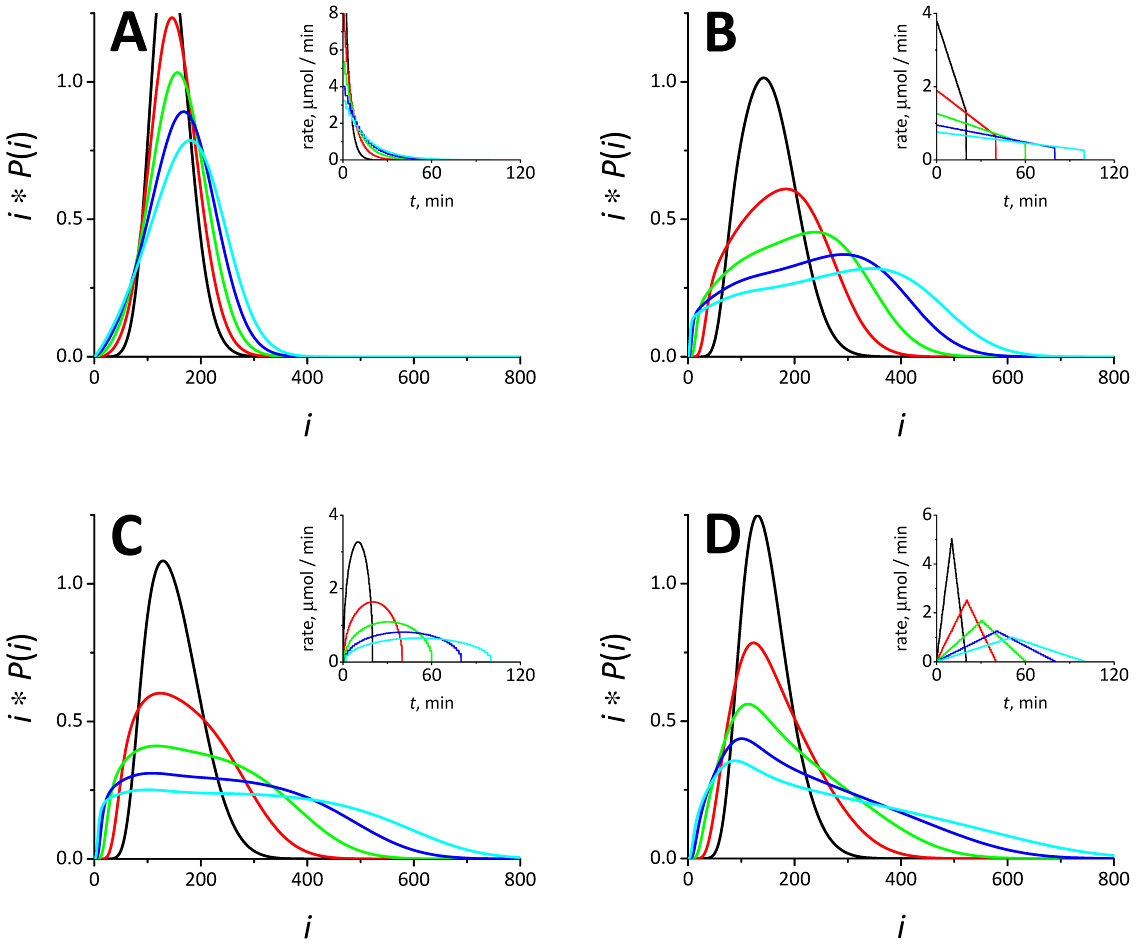

Figure S3. Sets of predicted, numerically calculated, distributions with the initiator addition rates shown in the insets (initiator addition rates not performed experimentally).

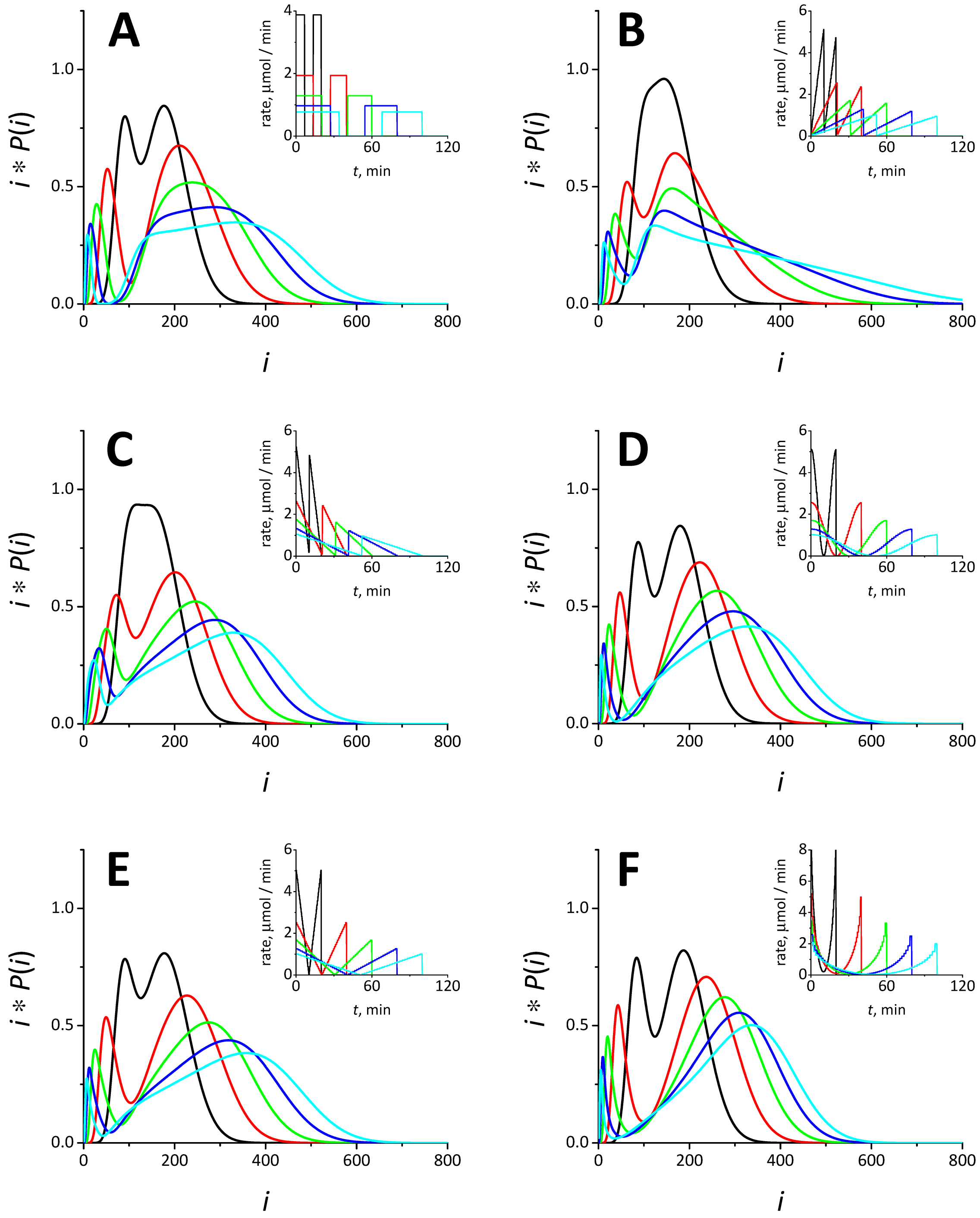

Figure S4. Numerical calculations to give bimodal distributions, with the initiator addition rates shown in the insets (the initiator addition rates not performed experimentally).

References:

1) Kottisch, V.; Gentekos, D. T.; Fors, B. P. *ACS Macro Lett*. **2016**, 5, 796.

2) Worsfold, D. J.; Bywater, S. Anionic Polymerization of Styrene. *Can. J. Chem.* **1960**, 38, 1891