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“Shaping” the Future of Molecular Weight Distributions in Anionic Polymerization

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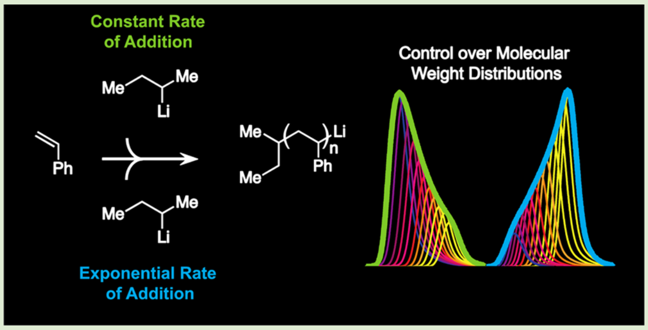
Supporting Information

ABSTRACT: Varying molecular weight distributions (MWDs) have the potential to precisely tune polymer properties, but this approach remains relatively unexplored owing to a lack of synthetic methods that provide control over the exact makeup of a distribution. Herein, we report a simple and highly efficient strategy for addressing this challenge through temporal regulation of initiation in the anionic polymerization of styrene. This method yields unprecedented control over the shape of the polymer MWD and facilitates the synthesis of diblock copolymers with controlled MWD compositions. Importantly, we show that the MWD symmetry has a marked influence on the stiffness of poly(styrene-*block*-isoprene) copolymers, which demonstrates that varying MWD shape is an effective method for altering polymer properties.



The dispersity (Đ) of a polymer sample is a key parameter in the control of material properties such as viscosity, processability, and all facets of block copolymer self-assembly.[1−14] However, Đ is the normalized standard deviation of the molecular weights in a polymer sample and, therefore, describes only the relative breadth of the molecular weight distribution (MWD).[15] Theoretical studies have looked beyond the breadth of MWD and suggested that distribution shape has a marked influence on polymer physical properties.[16,17] Therefore, synthetic methods that enable deterministic control over the exact distribution of chain lengths in a sample are needed to understand the full influence of MWD composition on polymer properties; these methods have the potential to facilitate the implementation of polymer distribution as a means to develop improved materials.

On this basis, multiple methods have been developed to modify MWDs in controlled polymerizations. The majority of these processes only give control over the relative breadth of the distribution;[9−13] however, a limited number have taken a step toward changing MWD shape. Specifically, Meira and co-workers have demonstrated that variation of monomer and initiator flow rates in continuous flow reactors imparted partial control over MWD shape.[18−21] Further, methods have been developed using pulsed initiation through photolysis or monomer/initiator feeds to give multimodal distributions.[22−24] Additionally, Aoshima and co-workers have tuned polymer composition through controlled termination processes.[25] Although these methods give partial control, new strategies are still needed to give precise regulation of MWD shape in living polymerization processes.

In an effort to realize deterministic control of MWD symmetry, we recently reported a method in which we used temporally controlled initiation in nitroxide-mediated polymerization (NMP) reactions.[26] Specifically, by controlling the addition of an alkyl nitroxide initiator to the polymerization of styrene, we predictably modulated polymer MWD shape while maintaining excellent control over number-average molecular weight (M_n) and Đ. Although this protocol afforded robust command of the MWD, several challenges need to be addressed to make this strategy more powerful and practical. For example, NMP processes inherently produce polymers with broader distributions, which limits how precisely the MWD can be defined through temporally controlled initiation.[27,28] Moreover, these radical polymerizations have limited substrate scopes and can be run only to partial conversions to get reasonable chain-end fidelities. Therefore, we sought a polymerization method that gives more precise control over MWD shape, is applicable to a wider array of monomer types, and provides higher-molecular-weight polymers. Additionally, we wanted a truly living polymerization process that would enable reactions to be run to full conversion, thereby providing access to the one-pot synthesis of block copolymers.

We hypothesized that anionic polymerization would be the ideal reaction class with which to address the above challenges owing to its capacity to give narrow Đs, truly living nature and broad monomer scope.[29−35] Furthermore, for the anionic polymerization of styrene, Lynd and Hillmyer have successfully broadened polymer Đ up to 1.3 through a combination of metered initiator addition and temperature control.[9] BASF also patented a method that enabled the synthesis of broad polystyrene samples through controlled addition of monomer,

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initiator, and rate-retarding agents.[36] Although both of these reports did not control the MWD shape, they provided evidence that anionic polymerization would work well in our temporally controlled initiation strategy. Herein, we report the deterministic control of polymer MWDs for the anionic polymerization of styrene (Figure 1). This method imparts unprecedented control over MWD shape and opens the door to better understand the relationship between polymer chain-length composition and material properties. Using our new method, we demonstrate that the shape of the MWD in block copolymers has a significant influence on their physical properties, which clearly illustrates that MWD composition can be used to tune polymer function.

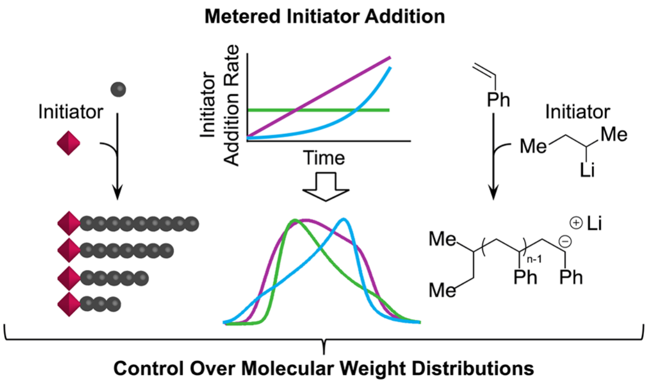
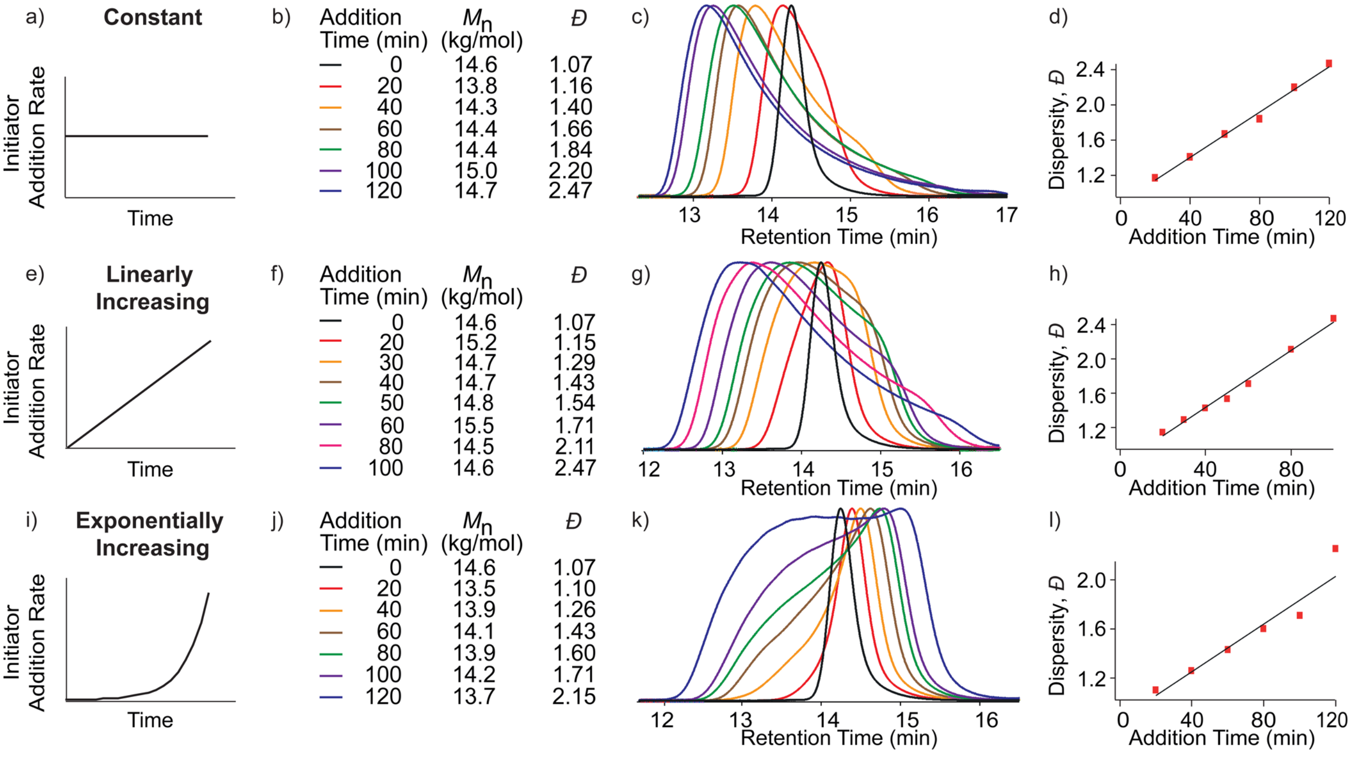


Figure 1. Metered addition of *sec*-butyllithium in the anionic polymerization of styrene to tailor the shape and composition of the molecular weight distribution (MWD).

We began our studies by looking at the temporally controlled initiation of anionic polymerizations of styrene. Metering in a fixed amount of the initiator, *sec*-butyllithium (*s*-BuLi), at a constant rate to a solution of styrene in cyclohexane, we expected to observe the MWD broadening with increasing addition time while M_n remained unchanged (Figure 2a). Traditional reaction conditions, in which the full amount of the initiator is added at the beginning of the reaction, yielded a 14.6 kg/mol polystyrene (PS) sample with a narrow *Đ* of 1.07. In support of our hypothesis, the addition of the same molar quantity of *s*-BuLi at constant rates from 20 to 120 min broadened the *Đ* from 1.16 to 2.47 without changing M_n (Figure 2b). Size exclusion chromatography (SEC) traces of these reactions showed a shift in the peak maximum (M_p) to higher molecular weights and a clear broadening of the distribution as addition time increased (Figure 2c). Moreover, a linear relationship between initiator addition time and *Đ* was observed (Figure 2d). These results illustrate that temporally controlled initiation in the anionic polymerization of styrene enables predictable control over polymer *Đ* and M_n.

Next, we efficiently achieved our goal of controlling the shape of the distribution by modulating the initiator addition rate profile. Compared with polymer samples synthesized with constant rates of initiator addition, those produced with linearly increasing addition rates gave distributions that had less tailing and were significantly broader at 50% peak height (Figure 2e–h). Furthermore, drastically different peak shapes were obtained when exponentially increasing rates were used (Figure 2i–l). For these addition profiles, the SEC traces showed a decrease in M_p at longer addition times, with a tailing into higher molecular weights. These shapes are the antithesis of the polymer samples prepared with constant rates of addition and demonstrate that our method can be used to achieve drastically different MWD compositions. Notably, for both the linearly and exponentially increasing addition rates, excellent control over M_n was obtained



b)

Addition Time (min)	M_n (kg/mol)	*Đ*
0	14.6	1.07
20	13.8	1.16
40	14.3	1.40
60	14.4	1.66
80	14.4	1.84
100	15.0	2.20
120	14.7	2.47

f)

Addition Time (min)	M_n (kg/mol)	*Đ*
0	14.6	1.07
20	15.2	1.15
30	14.7	1.29
40	14.7	1.43
50	14.8	1.54
60	15.5	1.71
80	14.5	2.11
100	14.6	2.47

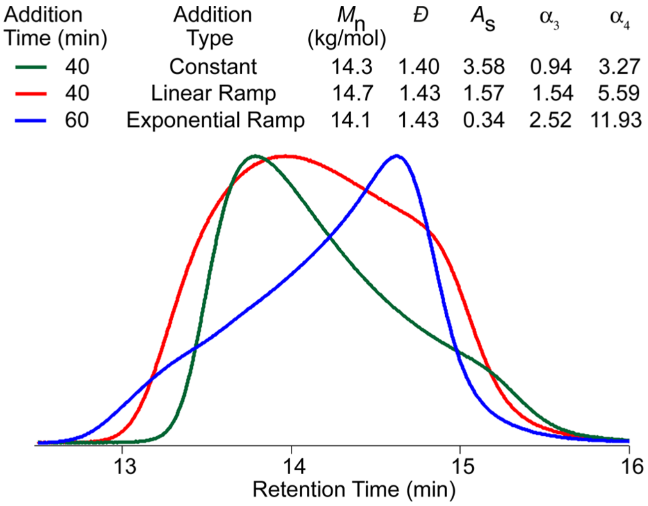
j)

Addition Time (min)	M_n (kg/mol)	*Đ*
0	14.6	1.07
20	13.5	1.10
40	13.9	1.26
60	14.1	1.43
80	13.9	1.60
100	14.2	1.71
120	13.7	2.15

Figure 2. Controlling the breadth and shape of polystyrene MWD distributions with constant (a–d), linearly ramped (e–h), and exponentially ramped (i–l) rates of initiator addition (a, e, and i are representative initiator addition profiles).

and a linear relationship between Đ and addition time was observed.

A major advantage of using temporally controlled initiation in anionic polymerizations is that vastly different MWD shapes are accessible even at relatively low Đs. We highlight this in Figure 3, which shows three SEC curves of PS samples that have Đs of ∼1.4 and M_ns of ∼14.5 kg/mol but were made with different initiator addition profiles. According to only M_n and Đ, these materials would be considered almost identical; however, there is little resemblance among these traces, which have asymmetry factor (A_s) values of 3.6, 1.6, and 0.3 corresponding to polymers made with constant, linearly increasing, and exponentially increasing addition rates, respectively (see Figure 3).[37] The overlay of these SEC traces illustrates the drastically variable shapes that can be accessed with our method.



Addition Time (min)	Addition Type	M_n (kg/mol)	Đ	A_s	α_3	α_4
🟩 40	Constant	14.3	1.40	3.58	0.94	3.27
🟥 40	Linear Ramp	14.7	1.43	1.57	1.54	5.59
🟦 60	Exponential Ramp	14.1	1.43	0.34	2.52	11.93

Figure 3. Three polymer samples with similar M_n and dispersity (Đ) values but drastically variable MWD compositions. α_3, skewness; α_4, kurtosis; A_s, asymmetry factor.

These MWDs can be further described by going beyond M_n and Đ values to the third (skewness, α_3) and fourth (kurtosis, α_4) moments of the distribution function.[38] Skewness describes the symmetry of the curve, whereas kurtosis indicates the amount of tailing on either side of the MWD around M_p. Both of these parameters, which further describe the shape of the distribution, are significantly different among the polymers made with the three initiator addition profiles.

Compared with temporally controlled initiation in NMP reactions, the anionic polymerizations permitted significantly higher levels of control over the shape of the distribution. For example, for PS polymers with Đ values of ∼1.4 made with NMP, A_s values ranged from 0.6 to 1.0 (compared with values of 0.3 to 3.6 for anionic polymerizations).[26] These results demonstrate that the inherently narrow MWDs afforded by anionic polymerization enable markedly better command of MWD shape, especially when Đ is below 1.7.

During our studies, we noticed that the majority of the constant and linearly increasing initiator addition rates afforded polymers for which SEC traces showed precipitous peak edges at low molecular weights. We postulated that this outcome was a result of abrupt stops in initiator addition, which caused the distribution to decline sharply to baseline with shorter addition times. To investigate this hypothesis, we monitored one of the polymerizations in which the initiator was added at a constant rate over 40 min. The SEC curves of the polymer before the end of the addition showed a smooth return to baseline (Figure 4). However, time points after the addition showed the emergence of the peak edge, which grew as the polymerization proceeded. This experiment provided straightforward evidence to support our hypothesis.

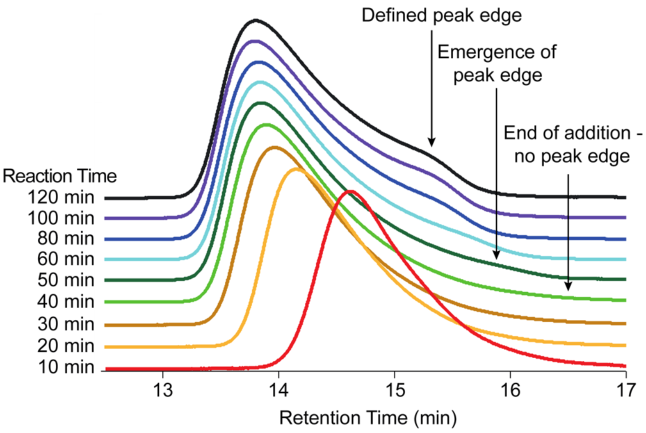
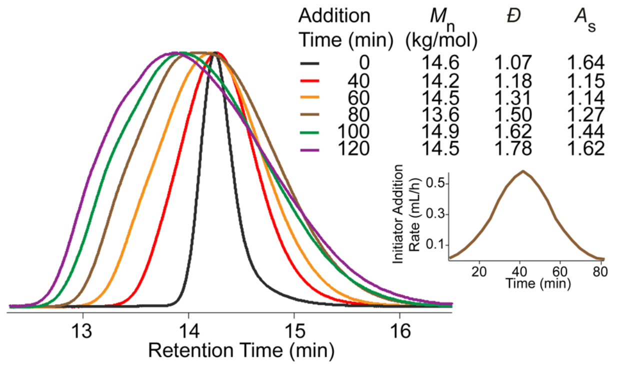


Figure 4. Size exclusion chromatography curves at indicated time points with a 40 min constant rate addition.

We reasoned that the observed peak edge could be removed by gradually decreasing the initiator addition rate at the end of the process. Using bell-shaped addition profiles, we obtained nearly symmetrical PS distributions that had no discernible peak edges (Figure 5). These data further demonstrate that MWD shape and composition can be precisely tuned by simply modulating the addition profile of the initiator.



Addition Time (min)	M_n (kg/mol)	Đ	A_s
⬛ 0	14.6	1.07	1.64
🟥 40	14.2	1.18	1.15
🟧 60	14.5	1.31	1.14
🟫 80	13.6	1.50	1.27
🟩 100	14.9	1.62	1.44
🟪 120	14.5	1.78	1.62

Figure 5. Size exclusion chromatography curves of a bell-shaped initiator addition profile. Inset: rate (mL/h) vs time (min) of an 80 min addition profile.

The living nature of anionic polymerizations allows these reactions to run to full conversion and enables the one-pot synthesis of diblock copolymers.[9,39] Taking advantage of these features, we synthesized a series of poly(styrene-*block*-isoprene) copolymers (PS-*b*-PI) in which both the shape and the Đ of the PS block varied (Figure 6a).[40] In all cases, efficient chain extension of our compositionally controlled PS samples with isoprene gave well-defined PS-*b*-PI copolymers.

With the above series of copolymers in hand, we set out to investigate the influence of MWD shape and breadth on the Young's modulus (E) of the material (Figure 6b).[41−44] For all samples, materials in which the PS MWD shape was tailing to higher molecular weights (A_s < 1) had E values that were

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a)

Entry	M_n (S) (kg/mol)	$Đ$ (S)	A_s	M_n (SI) (kg/mol)	$Đ$ (SI)	E (MPa)
1a	14.1	1.19	1.85	35.6	1.14	460
1b	14.2	1.22	0.52	35.1	1.16	560
2a	14.9	1.42	3.52	36.8	1.21	450
2b	14.1	1.39	0.37	33.6	1.22	530
3a	15.2	1.69	4.48	36.3	1.25	220
3b	14.1	1.71	0.31	36.5	1.28	440
4a	14.4	2.01	4.97	37.2	1.28	85
4b	13.8	1.97	0.26	34.4	1.29	300

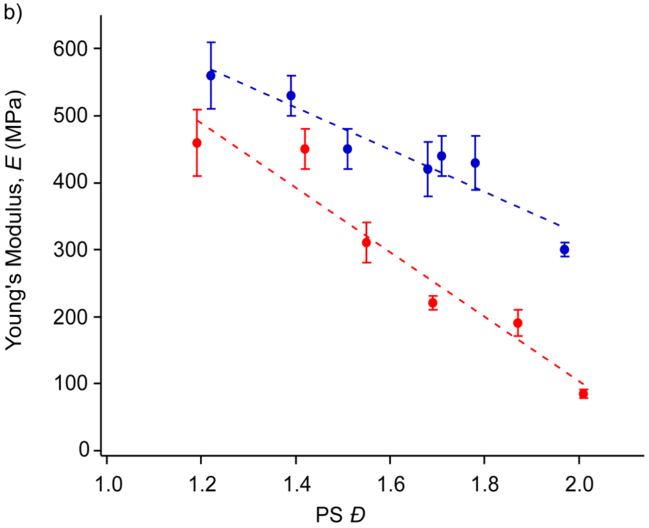

Figure 6. (a) Poly(styrene-*block*-isoprene) block copolymers with varying polystyrene (PS) MWD shapes and Young's moduli (E) determined with dynamic mechanical analysis. (b) Plot of PS $Đ$ vs E (MPa): blue circles indicate PS blocks with asymmetry factor (A_s) values of <1; red circles indicate PS blocks with A_s values of > 1; S = PS; SI = poly(styrene-*block*-isoprene). Each E value is an average of at least four measurements.

consistently higher than those of samples with shapes tailing to lower molecular weights ($A_s > 1$). This difference in E between the two MWD shapes increased as $Đ$ increased or as the difference in A_s values widened between the samples. For example, two samples in which the $Đ$ of the PS block was ∼1.2 with A_s values of 1.9 and 0.5 gave E values of 460 and 560 MPa, respectively; a moderate 1.2-fold increase in E. Remarkably, when we switched to two samples that had PS $Đ$s of ∼2.0 with A_s values of 5.0 and 0.3, we observed E values of 300 and 85 MPa, respectively. In this case, the change in E was 3.5-fold between the samples, which clearly shows that the MWD shape and composition have a significant influence. Moreover, these results demonstrate that the MWD shape is just as important, if not more important, than the breadth of the distribution and can effectively be used as a parameter for tuning material function.

In summary, we have developed a robust method for precisely tailoring MWD shape by temporally regulating initiation in the anionic polymerization of styrene. The truly living nature of this anionic polymerization allows the synthesis of materials with similar M_n and $Đ$ values but drastically different polymer compositions and provides facile access to block polymers. Taking advantage of our new method, we synthesized a library of PS-*b*-PI copolymers with various PS MWD shapes. Significantly, we found that MWD symmetry had a considerable influence on the stiffness of the material, which shows that MWD shape is a key parameter influencing polymer properties. This simple and modular approach offers unparalleled levels of control and gives access to a wide array of functional materials with systematically deviating polymer compositions. It also provides a platform for further fundamental studies of the influence of MWD shape on polymer properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00392.

> General experimental considerations, experimental procedures, initiator addition rate profiles, and additional supporting data (PDF).

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Notes

The authors declare no competing financial interest.

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