

# Beyond Dispersity: Deterministic Control of Polymer Molecular Weight Distribution

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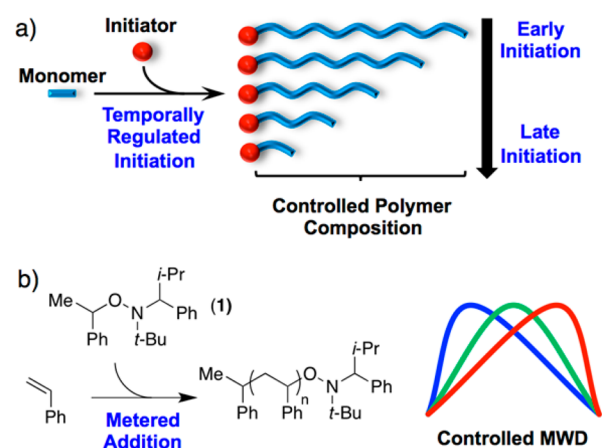
**S** Supporting Information

**ABSTRACT:** The breadth of the molecular weight distributions (MWD) of polymers influences their physical properties; however, no synthetic methods allow precise control of the exact shape and composition of a distribution. We report a modular strategy that enables deterministic control over polymer MWD through temporal regulation of initiation in nitroxide-mediated polymerization reactions. This approach is applicable to any controlled polymerization that uses a discrete initiator, and it allows the use of MWD composition as a parameter to tune material properties.

The dispersity ( $\bar{D}$ ) of a polymer sample, which is the ratio of the weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, has a profound influence on processability<sup>1,2</sup> and block copolymer properties.<sup>3–9</sup> However,  $\bar{D}$  is not a rigorous description of the distribution of polymer chain sizes in a given sample and provides information only about the relative span of molecular weights.<sup>10</sup> Importantly, variations in the shape of a molecular weight distribution (MWD) are postulated to have a marked influence on polymer properties as well.<sup>11</sup> Therefore, the development of a strategy to control absolute MWD composition would allow the investigation of the relationship between MWD shape and polymer function and facilitate the development of more robust materials for applications in areas such as nanolithography, photonics, filtration, and thermoplastic elastomers.<sup>12</sup> Herein, we report a modular synthetic strategy that provides predictable access to functional polymers with precisely defined MWDs.

Based on the importance of MWD on polymer properties, a small number of methods have been developed to govern  $\bar{D}$ . Blending polymers with various molecular weights is one strategy; however, the preparation of these materials is tedious, requiring the synthesis of multiple polymer samples.<sup>13–15</sup> Moreover, this protocol leads to multimodal compositions, which are undesirable. A second tactic involves the use of uncontrolled polymerizations to give dispersities of  $\sim 2$ . However, these methods provide no control over  $M_w$ ,  $\bar{D}$ , or the shape of the distribution.<sup>16–18</sup> Last, by taking advantage of polymer growth kinetics, Matyjaszewski and Hillmyer developed various methods to adjust  $\bar{D}$  in radical, ring-opening, and anionic polymerization.<sup>19–22</sup> Despite the control achieved by these methods, they modify only the relative breadth of the polymer chain lengths and provide no means for controlling the symmetry and shape of the final molecular composition.

We sought a modular strategy that would allow both fine-tuning of the breadth and shape of a distribution and control of  $M_n$  in a wide range of monomer types and polymerization classes. We envisaged that precise temporal generation of new polymer chains in a reaction would be a straightforward approach to address this challenge. Specifically, we reasoned that introducing initiators to a controlled polymerization reaction at specific times and rates would allow deterministic control over the exact molar quantities of individual polymer chain lengths in a final sample (Figure 1a). Importantly, this modular strategy would be



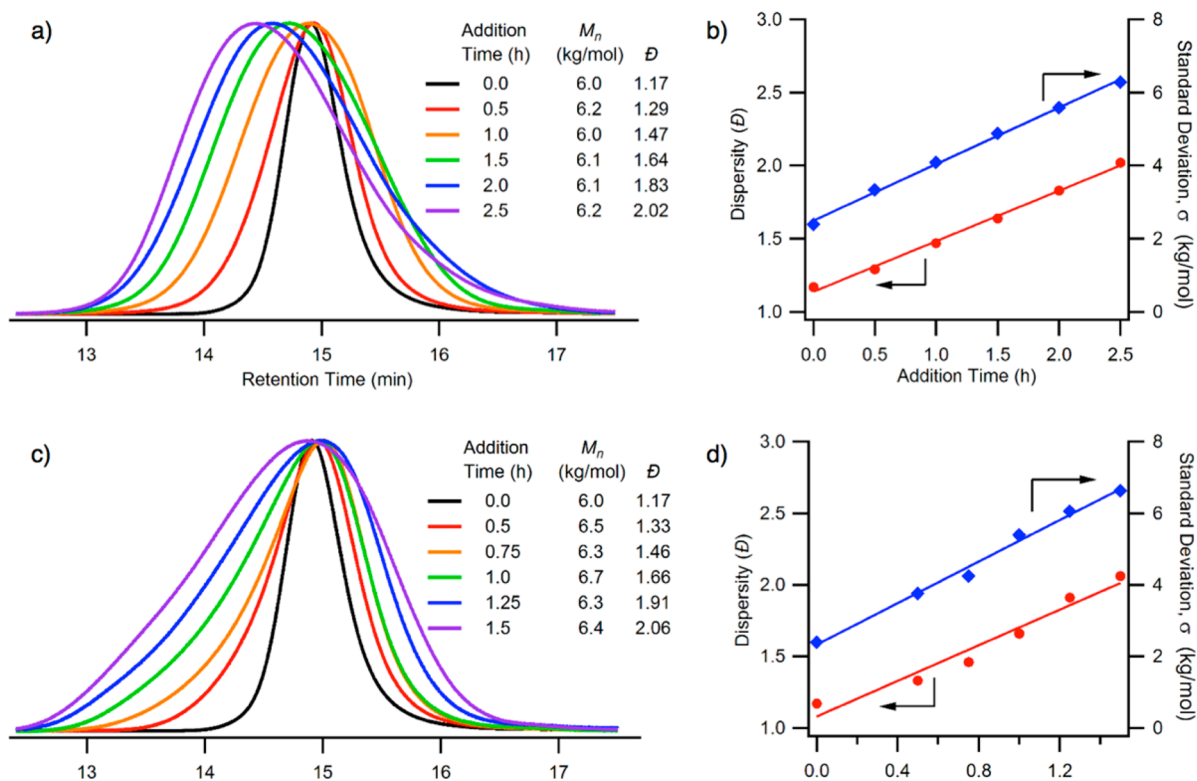
**Figure 1.** (a) Temporal regulation of chain initiation for deterministic control of the shape and composition of polymer molecular weight distributions (MWDs), and (b) the application of this strategy to nitroxide-mediated polymerizations through metered addition of **1**.

applicable to any controlled polymerization that uses a discrete initiating species and, therefore, would provide well-defined polymer compositions for an extensive set of functional materials.

Nitroxide-mediated polymerization (NMP) was selected to test our hypothesis because of its simplicity, functional group tolerance, and use of stable initiators.<sup>23–25</sup> Preliminary studies focused on regulating  $\bar{D}$  through metered addition of an alkyl nitroxide initiator (**1**) for the polymerization of styrene (Figure 1b).<sup>26</sup> The total molar quantity of initiator and the final conversion of the monomer were held constant for each polymerization, but the time of initiator addition was varied. Introducing the entire amount of **1** at the beginning of the reaction resulted in well-defined polystyrene (PS) with an  $M_n$  of

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**Figure 2.** Varying the breadth of polystyrene MWDs through (a,b) constant or (c,d) linearly increasing addition rates of **1**.

6.0 kg/mol and a  $\bar{D}$  of 1.17. Intriguingly, adding **1** at constant rates between 0.5 and 2.5 h effectively broadened the  $\bar{D}$  of the final polymers from 1.29 to 2.02 while maintaining  $M_n$  (Figure 2a). The size-exclusion chromatography (SEC) traces of these reactions show continuous monomodal MWDs where the molar mass at the peak maximum ( $M_p$ ) increases with addition time. These results clearly demonstrate that the breadth of a MWD can be broadened by controlling the relative rate of initiation to polymerization through metered addition of **1**.

For this same data, plotting  $\bar{D}$  versus time of initiator addition reveals a linear relationship (Figure 2b), which shows that MWD breadth can be predictably tuned. Moreover, because we have demonstrated that we can maintain  $M_n$  while regulating  $\bar{D}$ , we inferred that the absolute breadth of our distribution is precisely controlled.<sup>10,27</sup> In support of this inference, Figure 2b shows that standard deviation ( $\sigma$ ) increases linearly with addition time.

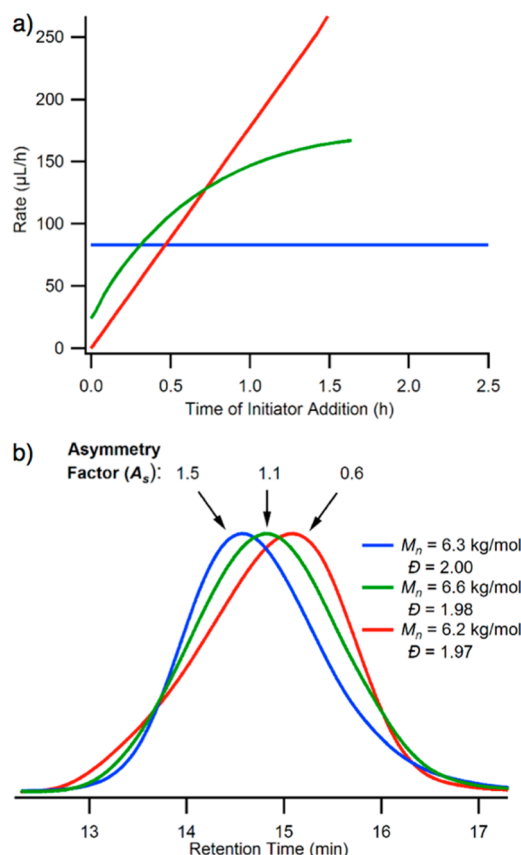
Encouraged by the excellent control observed when adding **1** at a constant rate, we next investigated the ability to regulate the shape of a MWD. We expected that modulation of the addition rate throughout the course of the reaction would give precise control over the degree of polymerization of the polymer chains in our final material and, therefore, would dictate the shape of the distribution. To investigate this hypothesis, in a procedure analogous to the reactions above, we added a set quantity of **1** at linearly increasing addition rates; we expected that these addition rate profiles would shift the overall peak shape to lower molecular weights. Indeed, all reactions gave polymers with similar  $M_n$  values, and  $\bar{D}$  and  $\sigma$  both increased linearly with addition time (Figure 2c,d). More important, the SEC traces revealed that the  $M_p$  values for these polymers remain relatively constant; this result is a direct contrast with the values for polymers produced through constant addition rates of **1**, in which  $M_p$  shifted to higher molecular weights with increasing  $\bar{D}$ . These results

illustrate that the shape of a MWD can be systematically varied while  $M_n$  and  $\bar{D}$  are controlled.

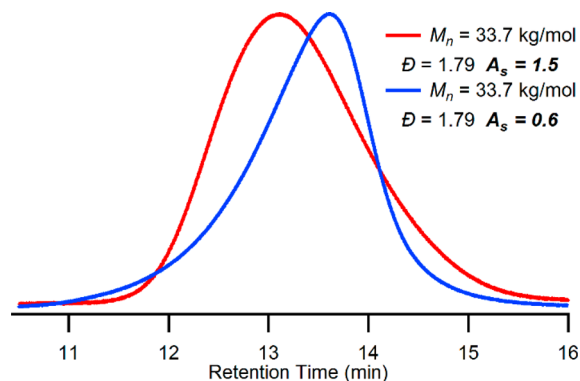
To highlight more thoroughly the differences in MWD shapes that can be accessed with this method, we synthesized more symmetrical distributions by using a nonlinearly increasing addition rate of **1** and compared them to the distributions of the polymers discussed above. Strikingly, gel permeation chromatograph traces of materials from three different addition classes (Figure 3a) shows polymers with similar  $M_n$  and  $\bar{D}$  values but significantly disparate chain length compositions (Figure 3b). Clearly these polymers cannot be distinguished by using  $M_n$  and  $\bar{D}$ , and therefore, we used asymmetry factor ( $A_s$ ) as a metric to identify the MWD differences, where values of  $\sim 1$  signified symmetrical peaks, and values of  $>1$  or  $<1$  indicated distributions skewed to higher or lower molecular weights, respectively.<sup>28</sup> Figure 3b illustrates that  $A_s$  accurately depicted the MWD shapes using a single parameter, with the three PS samples having  $A_s$  values of 1.5, 1.1, and 0.6. It should be noted that skewness and kurtosis, which are higher moments of the distribution, can also be used to describe MWD shape (see Supporting Information).<sup>29</sup>

Importantly, by changing the total molar quantity of **1**, various  $M_n$  values can be predictably targeted while maintaining excellent control over the breadth and shape of the MWD (see Supporting Information for details). For example, Figure 4 shows two polymers with molar masses of 34 kg/mol and  $\bar{D}$  values of 1.79 but with variable MWD shapes.

The use of living processes in our method is a major advantage that enables further derivatization of the final polymers to form functional materials. Specifically, the excellent chain-end fidelity in NMP reactions gives facile access to block copolymers. To provide evidence that we maintained the nitroxide chain ends in our polymerization reactions, we used two PS samples with identical  $M_n$  and  $\bar{D}$  values but different MWDs and chain-



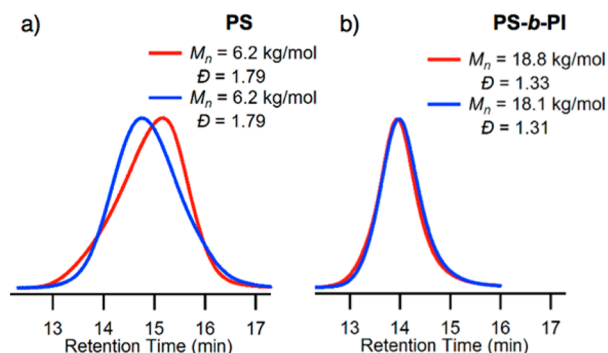
**Figure 3.** Synthesis of polymer samples with similar  $M_n$  and  $\bar{D}$  values but variable MWD shapes. (a) Addition rate profile of **1** and (b) size-exclusion chromatography (SEC) traces of the three polystyrene samples.



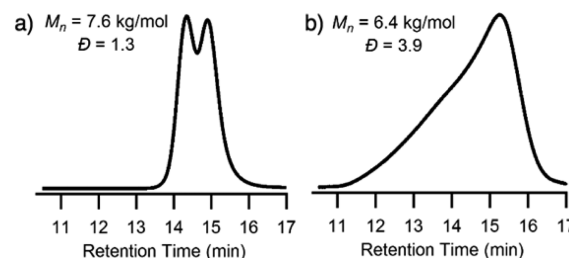
**Figure 4.** Targeting higher-molecular-weight polystyrene while maintaining control over the shape and breadth of the MWD.

extended them with isoprene.<sup>30,31</sup> In both cases we observed efficient formation of poly(styrene-*b*-isoprene) block copolymers without remaining macroinitiator (Figure 5). In addition, to show the modularity of this approach a bifunctional nitroxide initiator was utilized to grow poly(styrene-*b*-valerolactone) block copolymers while controlling MWD shape (see Supporting Information for details).<sup>32</sup>

We emphasize that this method is not limited to the synthesis of monomodal polymers with  $\bar{D}$  values of  $<2$ . By adjusting the rate of addition of **1**, we can unambiguously make PS with multimodal distributions or dispersities up to  $\sim 4.0$  while controlling  $M_n$  (Figure 6). We anticipate that this adjustability



**Figure 5.** Chain extension of polystyrene (PS) macroinitiators synthesized via temporally regulated initiation to give poly(styrene-*b*-isoprene) (PS-*b*-PI) polymers.



**Figure 6.** Synthesis of polystyrene samples with (a) a bimodal MWD or (b) a  $\bar{D}$  of 3.9 by using temporally regulated initiation.

will prove useful in tuning polymer processability, and it further exemplifies the versatility of our approach.

In summary, we have developed a method for precisely controlling the  $M_n$ ,  $\bar{D}$ , and shape of a polymer MWD by temporally regulating chain initiation in a controlled NMP process. Using this protocol, we prepared various PS samples that are indistinguishable based solely on the mean and breadth of their MWDs but have variable chain-length compositions. This modular strategy, which should be applicable in any controlled polymerization process that uses a discrete initiating species,<sup>33</sup> will enable the synthesis of materials that are defined beyond dispersity and will facilitate fundamental studies of polymer MWD shape and physical properties. We anticipate that this general method will change the way MWD is viewed and allow distribution shape to be used as a parameter to tune material function.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13565.

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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