Controlling the Shape of the Molecular Weight Distribution for Tailored Tensile and Rheological Properties in Thermoplastics and Thermoplastic Elastomers

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Abstract: Thermoplastics and thermoplastic elastomers compose roughly 80 percent of all polymeric materials manufactured today and play an important role in numerous sectors of modern society. While the effects of molecular weight and dispersity ($Đ$) on the tensile and rheological properties of these materials are well-known, only recent studies have evidenced the profound influence of the shape of the molecular weight distribution (MWD) on polymer properties. This development is largely due to the emergence of new synthetic strategies to control higher moments of the MWD. In this Perspective, we describe recent advancements by our group in understanding the effect of MWD shape on the mechanical and rheological properties of thermoplastics and thermoplastic elastomers. We highlight means to exploit MWD shape for improved processability and performance and discuss future directions in this field.

1. Introduction.

Molecular weight distributions (MWDs) have immense influence over the mechanical, rheological, and morphological properties of polymers.[1] Perhaps the most common parameter used to describe MWDs is dispersity ($Đ$), which is related to the standard deviation of chain lengths and is defined as the weight-average molecular weight (M_w) divided by the number-average molecular weight (M_n). However, $Đ$ only provides information about the relative breadth of the MWD and therefore conveys an incomplete description of the total composition of chain lengths. Consequently, polymers that share the same $Đ$, M_n, and chemical composition may have different MWD shapes and thus can exhibit vastly different properties (Figure 1).

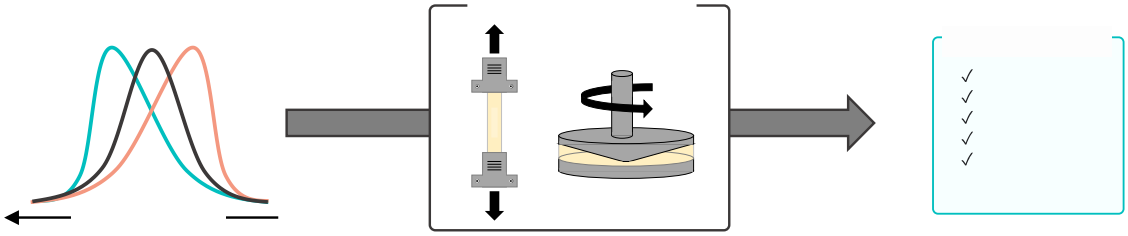

Figure 1. Tensile and rheological characterization reveal the effects of MWD shape on material properties.

A more comprehensive description of a polymer MWD can be achieved by analyzing the entire shape of the MWD, which is in part defined by the asymmetry factor (A_s).[2] As shown in Figure 2, A_s provides information about the direction of tailing in a polymer MWD. In this regard, polymers with tailing toward low or high molar mass chains have $A_s > 1$ or $A_s < 1$, respectively, while perfectly symmetrical MWDs have $A_s = 1$. Though A_s provides significantly more information about the shape of a MWD, this information is still limited. As such, it is often beneficial to analyze the higher moments of a MWD, such as skewness and kurtosis, representing the third and fourth standardized moments of a MWD, respectively. For the purposes of this perspective, MWD shape is sufficiently described by the combination of $Đ$ and A_s.

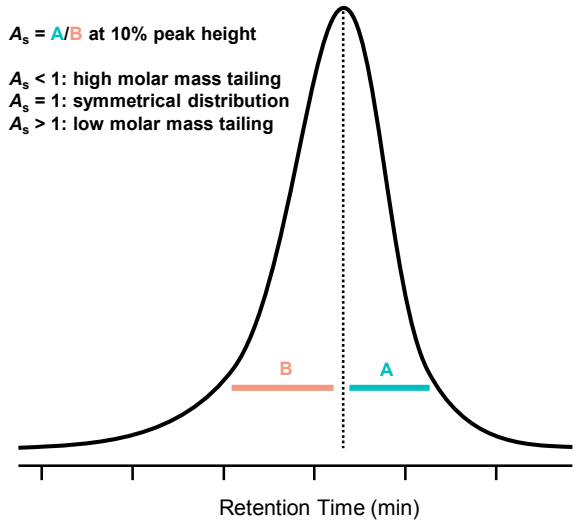

Figure 2. Illustration for the calculation of asymmetry factor (A_s), which is equal to the length of A divided by the length of B at 10% peak height.

Though numerous studies have demonstrated the influence of $Đ$ on polymer properties, the influence of the entire MWD—including both the breadth and shape—has historically been underexplored. It has long been hypothesized that the entire MWD would impact polymer properties. For example, Lynd, Hillmyer, and Matsen utilized self-consistent field theory to compare the theoretical phase behavior of two block copolymer melts having the same $Đ$ but distinct distribution shapes.[3] In this case, they predicted drastic differences in domain spacing despite the shared molecular dispersities, indicating that the entire distribution is an important consideration in understanding the phase behavior of block copolymers. Furthermore, multiple mathematical theories that examine the effects of MWD on rheological properties of polymer melts have been developed.[4–7] In one example, Nichetti and Manas-Zloczower found through a superposition model that by combining monodisperse polystyrene samples with different molecular weights, viscoelastic behavior at different shear rates could be dictated.[8] As such, development of synthetic methods for controlling the entire MWD shape have garnered significant interest.

A common method for producing polymers with tailored MWD compositions is post-polymerization blending.[9–14] However, such a process requires the synthesis of several polymers and subsequent blending under highly controlled conditions. Furthermore, blending in this fashion often affords multimodal MWDs and can lead to macrophase separation, rendering polymer blends unsuitable for many applications.[1,13,14] Thus, methods for the one-pot production of polymers with tailored monomodal MWDs are highly desirable.

On this basis, a variety of methods for gaining synthetic control over polymer MWDs have been developed.[15–46] Although the majority of early methods only afforded control over the relative breadth of the MWD, a limited number of such methods for controlling the entire MWD have been reported. For example, Meira and co-workers were able to impart MWD shape control in the anionic polymerization of styrene by oscillating the feed rates of monomer and alkyllithium initiator in continuous-flow reactors.[16–18] In another example, Aoshima and co-workers took advantage of controlled termination in a cationic polymerization, wherein the polymerization solution was metered into a solution of deactivating agent using a syringe pump.[19] More recently, Boyer and co-workers demonstrated control over polymer MWDs by altering the flow rates of a continuous flow PET-RAFT system,[20–22] and similarly, Junkers and co-workers independently developed an automated continuous flow radical RAFT process to tune the dispersity and shape of the MWD.[23,24] Notably, several recent mathematical models have also been developed to predictively synthesize tailored MWDs.[21,23,24,36,39,40,43,44]

In 2016, with inspiration from the early works of Meira and Aoshima, our group developed a modular strategy for precisely controlling MWD breadth and shape via temporal initiation, in which discrete chain-initiating species are added over time to a one-pot reaction for deterministic control over polymer chain length. We have utilized this general strategy in various controlled

radical polymerizations,[47,48] ionic polymerizations,[49–55] and coordination-insertion polymerizations.[56] Due to the living characteristics of these polymerization techniques, our strategy has enabled the synthesis of well-defined homopolymers as well as block copolymers—wherein the first block has a skewed MWD (Figure 3). Thus, we have been able to systematically study the influence of MWD shape on numerous polymer properties. Recently, our group reviewed other strategies for controlling MWD features and the influence of MWD shape on polymer properties.[1] Since then, we have published multiple accounts detailing the impact of MWD shape on the mechanical and rheological properties of thermoplastics and thermoplastic elastomers (TPEs). The aim of this perspective is to highlight these recent reports as well as provide insight on future directions in this field.

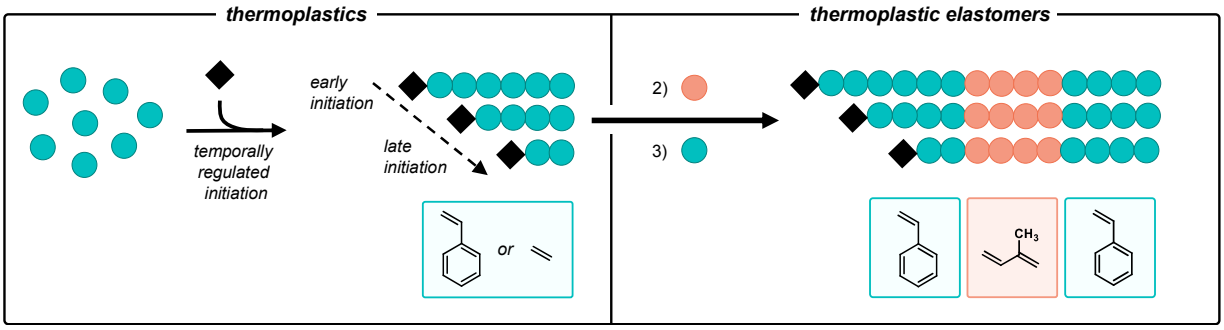

Figure 3. Depiction of our temporal initiation strategy to access tailored MWD shapes in thermoplastics and thermoplastic elastomers.

2. Influence of MWDs on Thermoplastics

The global annual production of plastics has drastically increased from 2 million metric tons in 1950 to a staggering 407 million metric tons in 2015, of which the majority represents thermoplastics alone.[57,58] Thus, significant attention has been placed on understanding the factors that influence the mechanical properties of thermoplastics, particularly as they pertain to processability. Though the impact of M_n, M_w, and $Đ$ on the mechanical properties of thermoplastics is well documented,[59] rheological and tensile properties cannot be exclusively attributed to these

three descriptors.[60–62] For example, tailing in the MWD of linear polyethylene has been shown to affect the processability of the material.[1,25,63,64] As such, we were particularly interested in utilizing our strategy for controlling MWDs to systematically study the influence of MWD symmetry on the rheological properties of thermoplastics.

We began our rheological studies by preparing two polystyrene (PS) samples with the same values of M_n, M_w, and $Đ$, but with opposite MWD skew.[51] We found that samples with a greater fraction of high molar mass PS chains and a low-molecular-weight tail ($A_s > 1$) exhibited a higher glass transition temperature (T_g), thermal stability, viscosity, and stiffness. Conversely, having a greater fraction of lower molar mass PS chains and a high-molecular-weight tail ($A_s < 1$) reduced the temperatures and shear rates necessary for processing, thus enabling the use of milder processing conditions. Furthermore, as the upper temperature limit for processing remained the same regardless of MWD skew, the operational window for processing was broader for the PS sample with a larger fraction of short polymer chains (Figure 4).

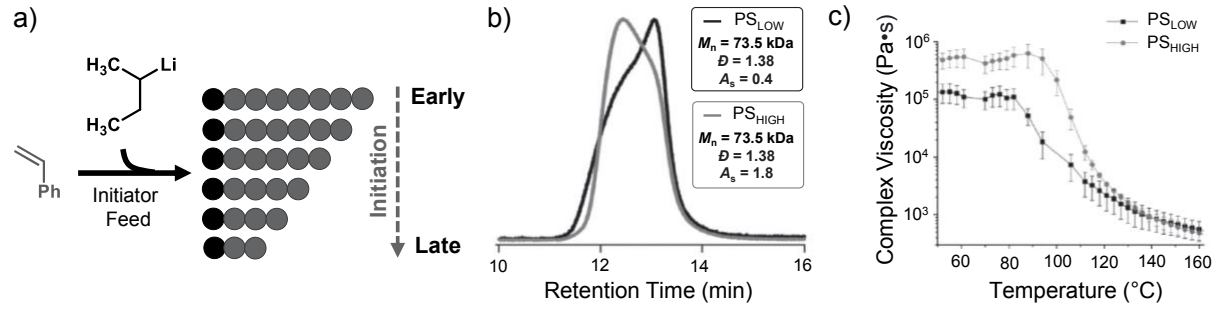

Figure 4. Temperature-dependent flow characteristics of PS samples with opposite MWD skew. (a) Temporal initiation strategy used to synthesize polystyrene samples with skewed MWDs (b) MWDs of samples exhibiting tailing toward high or low molecular weight (c) Complex viscosities of the two PS samples, demonstrating the higher viscosity of the PS sample with a greater fraction of high molar mass PS chains compared to the PS sample with a greater fraction of low molar mass PS chains. Reprinted with permission from *Macromol. Rapid Commun.,* **2017**, 1700352.

More recently, we extended our temporal initiation strategy to coordination-insertion polymerization of ethylene to afford high-density polyethylene (HDPE) samples with controlled

MWD features.[56] Because ethylene is a gaseous monomer and the metal-catalyzed polymerization required the use of methylaluminoxane (MAO) as a co-catalyst, this represented an entirely new challenge given that our previous studies on controlling MWD features involved addition of a discrete initiating species into a solution of liquid monomer in solvent. Presaturating toluene with an MAO solution and a fixed molar quantity of ethylene proved to be critical for reliably producing HDPE samples with targeted M_ns. Instantaneous addition of the initiating titanium bis(phenoxyimine) complex into this presaturated solution provided an HDPE sample with a narrow MWD and minimal tailing ($Đ \sim 1.1$, $A_s \sim 1.5$). In contrast, metered additions of the initiator solution afforded HDPE samples with broadened MWDs ($1.2 < Đ < 1.7$) and with tailing toward higher or lower molar mass polymer chains (Figure 5a). Rheological testing of these materials revealed a significant influence of MWD shape on complex viscosity (η*). We observed up to a 2—fold difference in η* at low shear frequencies for HDPEs with opposite MWD shapes, but similar $Đ$s and M_ns, where polymers with greater amounts of low molar mass chains ($A_s < 1.5$) exhibited a lower η* (Figure 5b). We hypothesize that the larger fraction of low molar mass polymer chains decreases the number of polymer entanglements, thus contributing to the lower η* at low shear frequency. Moreover, we observed greater shear thinning with an increase in $Đ$, where the extent of this enhancement was again dependent on MWD shape (Figure 5c-e). In the most drastic case, polymers with $Đ \sim 1.7$ exhibited such significant shear thinning at high frequencies that their η* approached that of the control sample ($Đ \sim 1.1$), despite having the highest η* values at low frequency (Figure 5e). Whereas these rheological tests demonstrated the profound influence of MWD shape on η* and shear thinning, uniaxial tensile testing revealed that only $Đ$ and not MWD shape impacted strain at break and tensile strength. Thus, through altering MWD shape

alone, we were able to modulate the viscosity of HDPE for easier processing without affecting the tensile strength of the material.

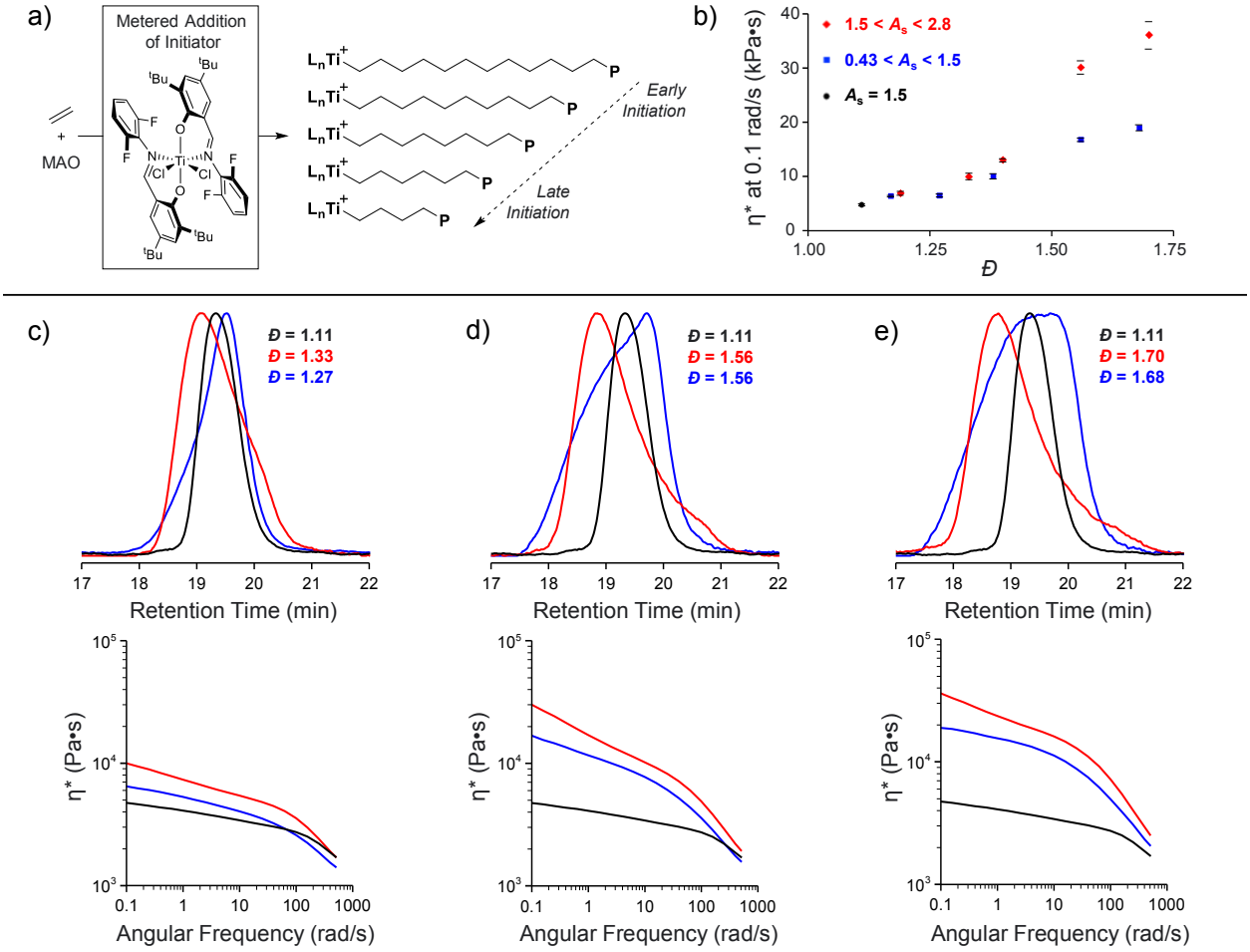

Figure 5. Influence of MWD features on complex viscosity in HDPE. (a) Temporal initiation strategy used to synthesize polyethylene samples (M_n ~ 80 kg/mol) with skewed MWDs (b) Complex viscosity vs. dispersity plot demonstrating a two-fold viscosity increase in samples with $Đ$ ~ 1.7 and opposite MWD skews (c-e) MWDs and complex viscosity vs. angular frequency plots for samples of three different dispersities but opposite MWD skews. Reprinted with permission from *J. Am. Chem. Soc*. **2020**, *142*, 3, 1443–1448. Copyright 2019 American Chemical Society.

3. Influence of MWDs on Thermoplastic Elastomers

A common perception in TPE literature is that narrow MWDs are crucial to the formation of well-defined physical crosslinks which afford the material with its characteristic properties such as high elongation at break and toughness. Morton and co-workers provided an early example in

support of this notion, demonstrating that the tensile strength in styrenic block copolymer TPEs decreased with an increase in $Đ$ of the midblock.[65] It has also been suggested that increasing the $Đ$ of the hard endblocks disrupts domain boundary perfection and reduces the number of chains with sufficiently high molar mass to contribute to physical crosslinks, thus influencing tensile properties.[66,67] Though not a study on the influence of $Đ$, López-Bárron and co-workers suggested that a domain swelling mechanism was responsible for an observed increase in tensile strength and tensile set following the blending of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) with a low molar mass polystyrene (PS) homopolymer.[68] They posited that the low molar mass PS homopolymer swelled the triblock copolymer PS domains such that the energy required to deform the polymer samples increased with increasing homopolymer content, which in turn increased the tensile strength. They further proposed that the increased tensile set was due to residual deformation in the stretching direction, which was greater in samples with more swollen PS domains. Although these studies provide valuable information about the effects of homopolymer incorporation on TPE mechanical properties, there remained significant opportunity to investigate the impact of MWD shape on these properties.

We envisaged that the MWD skew of a single PS block in SIS thermoplastic elastomers could be used as a handle to predictably tune tensile properties. To test this theory, we prepared a library of seven SIS copolymers (M_n ~ 107 kg/mol, volume fraction of PS (f_v^{PS}) ~ 0.20,) and examined their tensile properties (Figure 6a).[53] First, we prepared a reference sample having a first PS block with a narrow MWD ($Đ^{PS} < 1.1$). Next, we prepared three sets of two polymers in which $Đ^{PS}$ was approximately 1.23, 1.49, or 1.66 and the MWD of the first PS block was skewed either toward lower or higher molar mass PS chains (Figure 6b). We found that the MWD shape of the first PS block governed polymer tensile strength and strain hardening (Figure 6c), stiffness (Figure

6d), toughness (Figure 6e), and energy storage/dissipation properties (Figure 6f). Specifically, increasing $Đ^{PS}$ was found to reduce Young's modulus (E) and yield strength while increasing strain hardening. More interestingly, the direction of tailing in the PS block greatly influenced the tensile properties. For example, polymers with tailing toward high molar mass PS chains ($A_s < 1$) had higher values of E and yield strength than analogous polymers having tailing toward low molar mass ($A_s > 1$). We reasoned that this was due to significant chain pullout of short PS chains at relatively low strain. Additionally, samples with PS chains tailing toward high molar mass exhibited an increase in tensile strength and strain hardening as well as toughness, which we attributed to a reinforcement of physical crosslinks at high strain. Upon cyclic testing, an increased $Đ^{PS}$, as compared to the reference sample, was found to reduce hysteresis energy, where this reduction was most drastic in the case of polymers skewed toward lower molar mass PS chains.

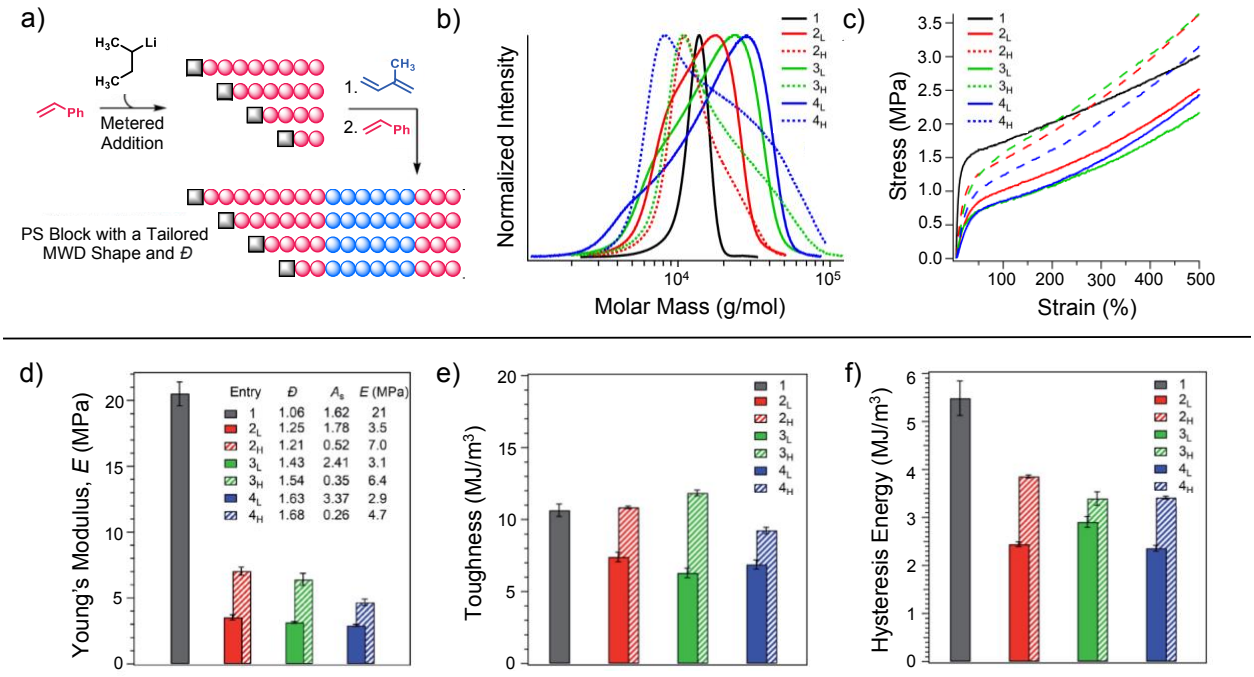

Figure 6. (a) Temporal initiation used to synthesize SIS thermoplastic elastomers (M_n ~ 107 kg/mol) with a skewed PS first block (b) MWDs of the first PS block in SIS thermoplastic elastomers (M_n ~ 13 kg/mol) (c) Stress–strain curves illustrating the influence of MWD skew on tensile properties (c) Young's modulus, (e) toughness, and (f) hysteresis energy of the reference

sample and those of different dispersities skewed toward high or low molecular weights. Reproduced from Ref. 53 with permission from the Royal Society of Chemistry.

Our study of the influence of MWD features on SIS TPEs highlighted the importance of considering the skew of the MWD when tailoring mechanical properties. We thus became interested in using our strategy to control MWD features to address a major challenge in the field of TPEs—increasing the strength of TPEs while leaving their elastomeric properties intact.[69–72] A common strategy for producing stiffer and stronger TPEs is to increase the volume fraction of the hard block; however, there exists a limit to this approach. Generally, increasing the volume fraction of the hard block to above 0.3 results in a loss of desirable elastomeric properties.[73] This volume fraction is significant because it is typically where a shift from a morphology with a continuous matrix of the rubbery block (*e.g.*, hexagonally packed cylinders, HEX) to a discontinuous morphology (*e.g.*, lamellar, LAM) is observed. In principle, by shifting the LAM phase boundary toward higher volume fractions of hard block, one would enable the production of remarkably stiff, strong, and tough TPEs without compromising their elastomeric properties. Given the numerous accounts that have reported tuned phase behavior through varying block dispersity,[26–42,74–77] we sought to influence phase behavior and thereby tensile properties through controlling MWD skew.

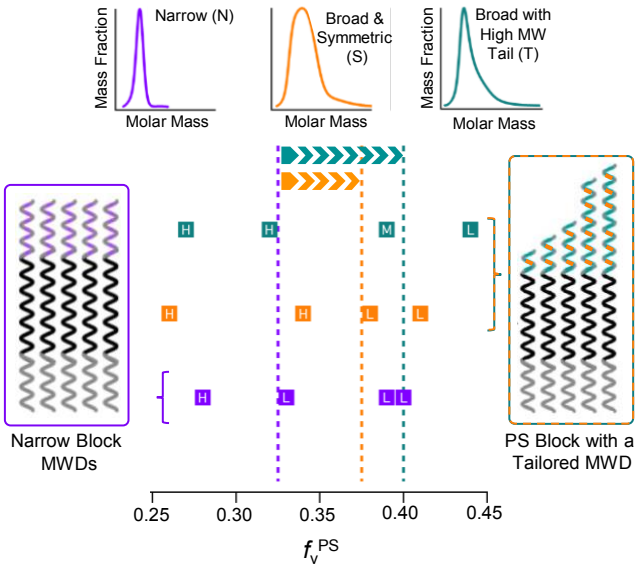

Figure 7. Phase diagram of SIS TPEs (M_n ~ 100 kg/mol) demonstrating the shifts in the LAM phase boundary as a function of f_v^{PS} and the MWD shape of the first PS block (purple = narrow MWD, orange = broad and symmetric MWD, and teal = broad MWD with tailing toward high MW). H = HEX, L = LAM, and M = mixed HEX/LAM. Reprinted with permission from *Macromolecules* **2020**, 53, 17, 7479–7486. Copyright 2020 American Chemical Society.

Using a similar synthetic strategy as in our previous SIS study, we prepared four sets of SIS triblock copolymers wherein the average f_v^{PS} was either 0.27, 0.33, 0.39, or 0.42.[55] The overall molecular weight of SIS samples remained constant (M_n ~100 kg/mol) whereas the MWD features of the first PS block were systematically varied. Each set contained a polymer wherein the MWD of the PS block was either narrow (N, $Đ^{PS}$ = 1.1), broad and symmetric (S, $Đ^{PS}$ = 1.2, A_s = 1), or broad with tailing toward higher molar mass PS chains (T, $Đ^{PS}$ = 1.2, A_s < 1). With this library of twelve SIS copolymers in hand, we proceeded to characterize their morphologies using small-angle X-ray scattering (SAXS). We found that at the intermediate volume fractions of PS (f_v^{PS} ~ 0.33 and 0.39), MWD shape influenced the morphology (Figure 7). Broadening the MWD regardless of skew shifted the LAM phase boundary to f_v^{PS} ~ 0.39. Moreover, when the MWD of the first PS block had tailing toward high molar mass PS chains, we observed phase coexistence between the HEX and LAM phases. We reasoned that broadening the MWD of the PS block

promoted interfacial curvature, favoring the formation of HEX or HEX/LAM mixed phases. Specifically, a broadened distribution of chain lengths would allow for longer PS chains to fill the center of the PS domains while shorter chains could relax near the interface, thus reducing the entropic penalty of chain stretching required to fill the center of PS domains. The extent of the resultant interfacial curvature is thus a balance between the entropic benefit of decreased chain stretching and the enthalpic penalty accompanied with an increase in interfacial area.

As hypothesized, we found that morphology dictated the elastomeric properties, whereas f_v^{PS} determined stiffness, tensile strength, and toughness (Figure 8). Uniaxial tensile testing revealed a distinct yield point in samples exhibiting a LAM morphology. In contrast, a smooth elastomeric "rollover" yield was observed in samples with a HEX or HEX/LAM mixed phase morphology. Across all samples, a larger f_v^{PS} resulted in a higher stiffness, tensile strength, and toughness. Therefore, by controlling the MWD shape to access continuous and mixed phase morphologies at atypically high f_v^{PS} (*e.g.*, HEX at $f_v^{PS} = 0.33$ and HEX/LAM at $f_v^{PS} = 0.39$), we were able to produce TPEs with significantly enhanced mechanical properties.

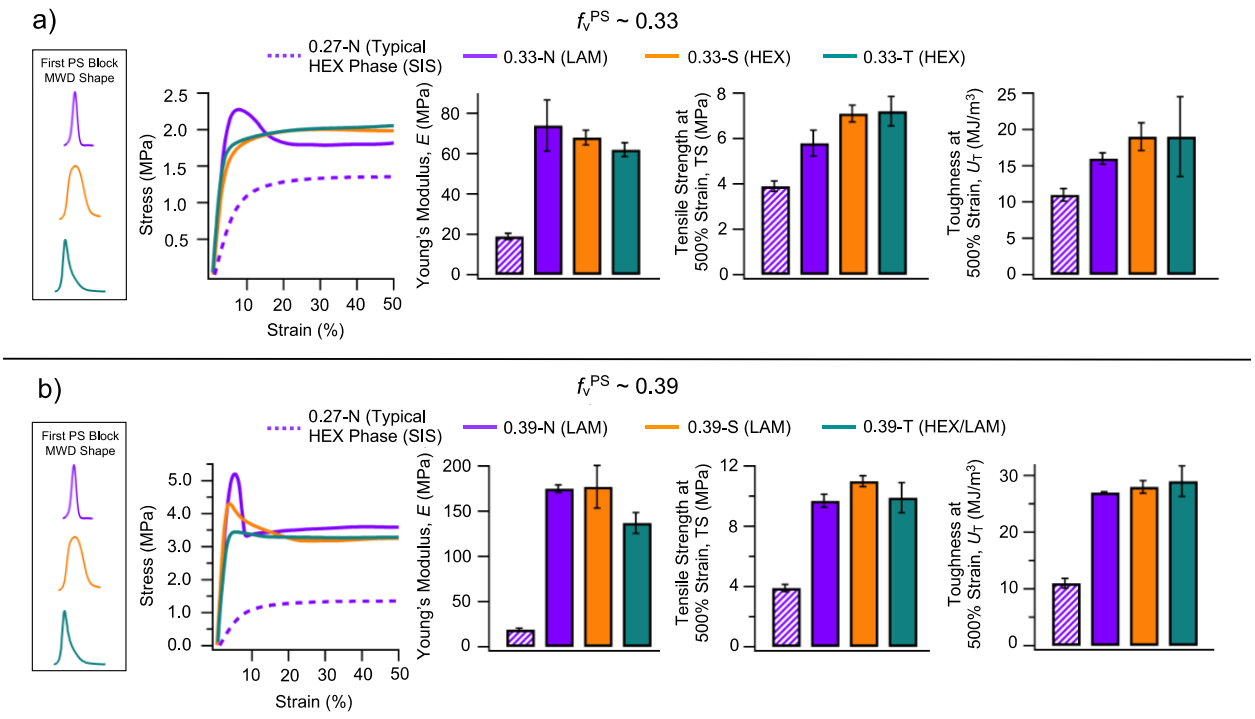

Figure 8. Material properties of SIS TPEs in which the first PS block has a tailored MWD but an overall similar M_n and average f_v^{PS} of (a) 0.33 or (b) 0.39. From left to right: zoom-in of stress–strain curves illustrating yielding behavior, Young's modulus (E), tensile strength at 500% elongation (TS), and toughness at 500% elongation (U_T). Data for a typical HEX phase SIS TPE (0.27-N, purple dash) are shown for comparison. Reprinted with permission from *Macromolecules* **2020**, 53, 17, 7479–7486. Copyright 2020 American Chemical Society.

4. Future Outlook

The ability to precisely control polymer MWD shape has afforded the unique opportunity to selectively study the influence of chain length composition on polymer properties. Though our group, along with several other researchers, have made significant progress in developing novel methods to control the entire MWD, there remains an opportunity to develop strategies for controlling MWD skew in additional polymerization systems. For example, the ability to control MWD features in ring-opening polymerizations (ROPs) is an attractive endeavor given the numerous biorenewable monomers (*e.g.*, lactones and carbonates) that can be efficiently polymerized via ROP for degradable and biocompatible materials. Notably, it is conceivable that control over biodegradation or the release of bioactive compounds for drug delivery may be

achieved by altering the MWD shape of these polymers. In the case of thermoplastics, of particular interest is the distribution of chains above and below the entanglement molecular weight (M_e) and its influence on fracture toughness, a property known to be highly influenced by the number of entanglements in a polymer sample. We anticipate that polymers with a broad MWD and tailing that spans the M_e may possess unique combinations of properties well-suited for various processing conditions while exhibiting increased fracture toughness. It would additionally be interesting to study TPEs containing a midblock with a skewed MWD, particularly because pressure sensitive adhesive (PSA) literature demonstrates that entanglements within the midblock greatly influence material properties.[78] In this case, development of an efficient bifunctional initiating species to modify the MWD of the midblock rather than a single endblock may prove advantageous. Overall, we anticipate that tailored MWDs, and the development of methods to access them, will continue to elucidate polymeric materials with highly tuned properties for improved performance and application.

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While the effects of molecular weight and dispersity on the tensile the rheological properties of polymers are well-known, only recent studies have evidenced the profound influence of the shape of the molecular weight distribution (MWD). In this Perspective, we describe recent advancements in understanding the effect of MWD shape on the mechanical and rheological properties of thermoplastics and thermoplastic elastomers, highlight means to exploit MWD shape for improved processability and performance, and discuss future directions in this field.

*S. I. Rosenbloom, J. H. Hsu, and B. P. Fors**

Controlling the Shape of the Molecular Weight Distribution for Tailored Tensile and Rheological Properties in Thermoplastics and Thermoplastic Elastomers

ToC figure: