

INVESTIGATING THE STRUCTURE-PROPERTY RELATIONSHIPS IN
THERMOPLASTIC ELASTOMERS AND POLYMERS FOR EXPLOSION-
RESISTANT COATINGS

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Stephanie Ilana Rosenbloom

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INVESTIGATING THE STRUCTURE-PROPERTY RELATIONSHIPS IN THERMOPLASTIC ELASTOMERS AND POLYMERS FOR EXPLOSION- RESISTANT COATINGS

Stephanie Ilana Rosenbloom, Ph. D.

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Understanding the relationship between a polymer's molecular structure and its bulk properties (i.e., mechanical and morphological behaviors) is necessary for the design of next-generation materials with targeted properties. In this vein, we have developed methods to alter and probe the influence of polymer composition on the material properties of two high-value products—thermoplastic elastomers (TPEs) and polyurea (PU). By systematically varying the molecular weight distribution shape in TPEs, we were able to precisely determine the role of chain length composition on the mechanical and morphological properties. Furthermore, by developing an experimental protocol for *in-situ* structural characterization using X-ray scattering techniques, we were able to elucidate the influence of polymer composition on PU materials under high-pressure conditions. These experimental methods have clearly demonstrated the value of understanding structure-property relationships in TPEs and PU-based materials, particularly how polymer composition can be

used as a handle to predictably tune polymer properties.

BIOGRAPHICAL SKETCH

Stephanie was born into a gentle yet playful flock of Macaws in the Amazon Forest. As she scavenged for food with her flock, Stephanie was the first to realize that eating damp soil could help neutralize the acid from the fruit consumed in a typical Macaw diet. It is no surprise that Stephanie is the great chemist we know her as today. However, due to an unfortunate accident with a gated doorway and the loss of a quarter inch of her middle claw (the details will be spared), Stephanie was transformed into her present-day human form. Her parents found her on the Main Line, a few miles away from Wynnewood, Pennsylvania where they decided to raise her as their own. Stephanie showed early interest in singing and had a special interest in mimicking bird calls. Furthermore, her aptitude for rock climbing stemmed directly from the large, gripping claws which were key to Stephanie's survival as a Macaw yet were also responsible for her fatal end. It took a while for Stephanie to adjust to the human life. This was most evident by her experimentation with clothing during her early stages of childhood. Trying to mimic the feathers of her flock, she constantly wore multicolored hats and contrasting clothing as a child. Growing up, Stephanie showed an interest in paleontology. In an effort to reunite with her past, she would sleepwalk through Philadelphia digging in the back yards of local houses trying to find any bird-like bones. Finally realizing that Macaws were not indigenous to Pennsylvania, Stephanie applied to Pennsylvania State

University as a wildlife biology major, hoping her studies could take her back to the depths of the Amazon one day. To this day, it is unclear what drove Stephanie to the field of chemistry.

This biographical sketch was adapted from the original piece written by Renee Sifri for the Fors Group website. Adapted with permissions.

Dedicated to all of the women in science in my family, in particular, my late grandmother, Joan Rosenbloom, and my mother, Shari Rosenbloom.

ACKNOWLEDGMENTS

Firstly, I would like to thank my advisor, Brett P. Fors. Driving to Cornell for visitation weekend, I remember thinking that the weekend would be stuffy or unwelcoming (the preconceived notions of the Ivy League held by a proud Penn Stater). I could not have been more wrong. Most of my interaction with Brett during visitation weekend was over several rounds of darts. Despite his continued denial, I'm still convinced that Justin and I won most of those rounds. During visitation weekend, I felt an almost immediate sense of comradery and mutual respect amongst C&CB members, and left with the impression that Brett wanted to foster a lab environment in which doing good science and having fun were not mutually exclusive. Five years later, I can honestly say that my initial impression held true. My Ph.D. experience would not have been what it was without your unwavering optimism and continuous support, particularly during the most challenging of times. For this, I am forever thankful.

I would also like to thank my committee members, David B. Collum and Song Lin. Our discussions throughout my Ph.D. were insightful and always inspired me to think outside the box. I also thank Justin Wilson for being my dart buddy for life. Additionally, I would like to thank collaborators Meredith N. Silberstein and Alireza Amirkhizi for their guidance.

A large part of my Ph.D. has revolved around acquiring X-ray scattering data (beam time). This is especially true during my final two years, during which

I effectively lived at the Cornell High Energy Synchrotron Source (CHESS) for a combined 3 weeks. I sincerely thank Louisa Smieska, Arthur Woll, and Zhongwu Wang of the Functional Materials Beamline (id3B) for making my time spent at CHESS illuminating and for their endless hands-on and technical support. I thoroughly enjoyed our conversations and learned a tremendous amount from you all. Furthermore, I extend my deepest gratitude to you all for making beam time during the Covid-19 pandemic possible. This was not an easy feat and required significant time and effort from you all.

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together during these exciting stages of your life and can't wait to hear all about what is coming next during our next wine and whine night.

The graduate and undergraduate students I have had the opportunity to work beside in the Fors group have been fantastic. In brief, each and every student in the Fors group has made my years here special and has contributed in one way or another to the idiosyncrasies our group is known for. However, there are a few students in particular that I feel have played a sizable role in shaping my time here. First and foremost, I need to thank Dillon Gentekos and Jacob Trotta, who were the first graduate students in the Fors group. Both Dillon and Jacob provided me with a foundation by teaching me how to approach research and, more importantly, how to ask the right questions. Dillon also served as my mentor during my first few years in the group and was truly instrumental to my success in graduate school. Seeing as our life trajectories have been freakishly similar—growing up a few miles from each other, attending the same college, joining the same group at Cornell (where we met), and both securing jobs at 3M—I'm sure I'll be seeing more of you for years to come. Renee Sifri and I joined the lab together and became fast friends. I owe much of my physical health to our 5 am gym routine, which eventually turned into our “consistently motivating each other to work out after we stopped waking up at that ridiculous hour” routine (honestly, how did we do that for so long?). I don't know what I would have done without you by my side—be it at the gym, grabbing coffee, or finally collaborating in lab—these last five years. Our friendship is one

I will cherish for years to come. Scott Spring, who joined the lab during my second year, has also had immeasurable impact on these last four years. Thank you for always supporting me in all of my endeavors, for keeping me alive and sane during beam times (read: bringing me food and insisting I take breaks), and for being a reliable and dependable companion and co-caretaker of Petrie and Jenson. I look forward to all that is to come in our future. Niko Tsakeredes, coming from the Air Force Institute of Technology, joined the group as a masters student and worked with me on the polyurea-based projects. You were an incredible collaborator and your feel-good attitude toward life was always appreciated. I also thank Shelby Shankel, who I first met during her time as an REU student in the Fors group. I am so glad that you ended up joining our group as a graduate student. Our strolls around the department and late-night Nancy Drew sleuthing have been highlights of this past year. I will miss joking around with you more than words can describe! Luis Melecio-Zambrano and Jesse Hsu, besides being highly enjoyable lab 2 mates, have also been great friends. Although I wish we could have jammed more, I am grateful for the times we had coming up with cello/guitar/violin/voice covers of pop songs (read: Billie Eilish) and bluegrass/classical/folk songs (read: The Goat Rodeo Sessions) alike. I also thank Daniel Beitler, an undergraduate student who worked with me on the polyurea projects. It was a pleasure watching you grow into the autonomous researcher you are today, and I look forward to hearing of your continued success. I also thank all current and former lab 3 members for making office

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LIST OF ABBREVIATIONS

MWD	_____	Molecular weight distribution
TPE	_____	Thermoplastic elastomer
NMP	_____	Nitroxide-mediated polymerization
ATRP	_____	Atom transfer radical polymerization
PS	_____	Polystyrene
HDPE	_____	High-density polyethylene
MAO	_____	Methylaluminoxane
PI	_____	Polyisoprene
PS- <i>b</i> -PI	_____	Polystyrene- <i>block</i> -polyisoprene
PS- <i>b</i> -PI- <i>b</i> -PS	_____	Polystyrene- <i>block</i> -polyisoprene- <i>block</i> -polystyrene
SIS	_____	Polystyrene- <i>block</i> -polyisoprene- <i>block</i> -polystyrene
HEX	_____	Hexagonally packed cylinders
LAM	_____	Lamellae
HEX/LAM	_____	Mixed phase of hexagonally packed cylinders and lamellae
N	_____	Narrow
S	_____	Broad and symmetrical
T	_____	Broad with high molecular weight tail
MW	_____	Molecular weight
ROP	_____	Ring-opening polymerization
PSA	_____	Pressure-sensitive adhesive

sec-BuLi or *s*-BuLi _____ *Secondary* butyl lithium
 CDCl₃ _____ Deuterated chloroform
 THF _____ Tetrahydrofuran
 GPC _____ Gel-permeation chromatography
 SEC _____ Size-exlcusion chromatography
 rpm _____ revolutions per minute
 BHT _____ Butylated hydroxytoluene
 MeOH _____ Methanol
 DCM _____ Dichloromethane
 PTFE _____ Polytetrafluoroethylene
 DMA _____ Dynamic mechanical analysis
 SAXS _____ Small-angle X-ray scattering
 WAXS _____ Wide-angle X-ray scattering
 SBS _____ Polystyrene-*block*-polybutadiene-*block*-polystyrene
 OOT _____ Order-order transition
 ODT _____ Order-disorder transition
 RAFT _____ Reversible addition-fragmentation chain transfer
 PET-RAFT _____ Photo-induced electron/energy transfer RAFT
 CTA _____ Chain transfer agent
 MMA _____ Methyl methacrylate
 PMMA _____ Poly(methyl methacrylate)
 AIBN _____ Azobisisobutyronitrile

LS _____ Light scattering
RI _____ Refractive index
BMA _____ Butylmethacrylate
PBMA _____ Poly(butylmethacrylate)
IBVE _____ Isobutyl vinyl ether
PIBVE _____ Poly(isobutyl vinyl ether)
FcBF₄ _____ Ferrocenium tetrafluoroborate
PU _____ Polyurea
DAC _____ Diamond anvil cell
ATR-FTIR _____ Attenuated total reflectance-Fourier transform infrared
PTMO _____ Poly(tetramethylene oxide)
TMO _____ Tetramethylene oxide
NCO _____ isocyanate

LIST OF SYMBOLS

$\bar{D}$	Disperisty
M_w	Weight-average molar mass
M_n	Number-average molar mass
M_z	z-average molar mass
M_{z+1}	z+1 average molar mass
M_i	Molar mass of species i
N_i	Number of species i
σ	Standard deviation
A_s	Asymmetry factor
T_g	Glass-transition temperature
η^*	Complex viscosity
E	Young's modulus
f_v	Volume fraction
TS	Tensile strength
U_T	Toughness
W_H	Hysteresis energy
M_e	Entanglement molecular weight
$^{\circ}\text{C}$	Degrees Celcius
q	Scattering vector
d or D_{sp}	Domain spacing
I_{rel}	Relative intensity

dc _____ Diode count

λ _____ Wavelength

PREFACE

The introduction of this thesis was adapted from the following perspective in preparation for publication by the author:

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Rosenbloom, S. I.; Fors, B. P. Shifting Boundaries: Controlling Molecular Weight Distribution Shape for Mechanically Enhanced

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Rosenbloom, S. I.; Sifri, R. S.; Fors, B. P. Controlling Molecular Weight Distributions in RAFT Polymerizations. *Polym. Chem.* **2021**, *Advance Article*. Reproduced by permission of the Royal Society of Chemistry.

Rosenbloom, S. I.; Yang, S. J.; Tsakeredes, N. J.; Fors, B. P.; Silberstein, M. N. Structural Evolution of Polyurea under Hydrostatic Pressure. *Polymer* **2021**, *227*, 123845.

Other publications co-written by the author that are not covered in this thesis are as follows:

Spring, S. W.; Smith-Sweetser, R. O.; Rosenbloom, S. I.; Sifri, R. J.; Fors, B. P. Sustainable Thermoplastic Elastomers Produced via Cationic RAFT Polymerization. *Polym. Chem.* **2021**, *12*, 1097-1104.

CHAPTER 1

TAILORING THE TENSILE AND RHEOLOGICAL PROPERTIES IN THERMOPLASTICS AND THERMOPLASTIC ELASTOMERS THROUGH CONTROL OVER THE SHAPE OF THE MOLECULAR WEIGHT DISTRIBUTION

1.1 Introduction

The molecular weight distributions (MWDs) of polymers have immense influence over their resulting mechanical, rheological, and morphological properties.¹ Perhaps the most common parameter used to describe MWDs is dispersity ($\mathcal{D}$), 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, $\mathcal{D}$ only provides information about the relative breadth of the MWD and therefore conveys an incomplete and oversimplified description of the polymer chain length composition. Consequently, polymers of the same chemical composition and sharing the same values of M_n and $\mathcal{D}$ can have vastly different properties result of differences in their MWD shapes.

Though numerous studies have demonstrated the influence of $\mathcal{D}$ on polymer properties, the influence of the entire MWD—both the breadth and shape—has historically been underexplored. It has long been hypothesized that

the entire MWD would impact polymer properties. In fact, there exists significant theoretical basis in support of this supposition. 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 $\bar{D}$ but distinct distributions shapes.² In this case, they predicted drastic differences in domain spacing despite the shared polydispersity indices, indicating that the entire distribution is an important consideration in understanding the phase behavior of block copolymers. Additionally, numerous mathematical theories that examine the effects of $\bar{D}$ on rheological properties of polymer melts have been developed. In one example, Nichetti and Manas-Zloczower found through a superposition model that different regions of the polymer MWD dictated viscoelastic behavior at different shear rates.³ 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.⁴⁻⁹ However, such a process requires for the synthesis of several polymers and subsequent blending under controlled conditions. Furthermore, blending in this fashion affords multimodal MWDs, which can lead to macrophase separation and renders polymer blends unsuitable for many applications.^{1,8,9} Thus, methods for the one-pot production of polymers with tailored monomodal MWDs are significantly more desirable.

On this basis, a variety of methods for gaining synthetic control over polymer MWDs have been developed,^{10–40} however, the majority of such methods only afford control over the relative breadth of the MWD. A limited number of methods for controlling the entire MWD have been reported. For example, Meira and coworkers 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.^{41–43} In another example, Aoshima and coworkers 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.⁴⁴ More recent reports of controlling polymer MWD features, such as those independently developed by Boyer and Anastasaki, have been reviewed elsewhere.²⁰

Inspired by the early works of Meira and Aoshima, our group developed a modular strategy for precisely controlling the MWD breadth and shape via temporal generation of new polymer chains. Excitingly, we have utilized this general strategy in various controlled radical polymerizations,^{45,46} ionic polymerizations,^{46–54} and coordination-insertion polymerizations.⁵⁵ Due to the living characteristics of these polymerization techniques, our strategy has enabled the synthesis of well-defined block copolymers wherein the first block has a skewed MWD. Thus, we have been able to selectively 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, multiple accounts of the impact of MWD shape on the mechanical properties of polymers have been published by our group. The aim of this perspective is to highlight these recent reports that demonstrate the influence of MWD shape on the tensile and rheological properties of thermoplastics and thermoplastic elastomers (TPEs). We will additionally speculate on the possible future directions of this field.

1.2 Descriptors for MWDs

Polymers MWDs are most typically described by their number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity ($\mathcal{D}$), found through size-exclusion chromatography (SEC) and defined in equations 1.1 — 1.3.

$$M_n = \frac{\sum M_i N_i}{\sum N_i} \quad \text{Eq. 1.1}$$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \quad \text{Eq. 1.2}$$

$$\mathcal{D} = \frac{M_w}{M_n} \quad \text{Eq. 1.3}$$

Here, it is important to note that $\bar{D}$ is related to the standard deviation of the distribution (σ) by Eq. 1.4.

$$\bar{D} = \frac{\sigma^2}{M_n^2} + 1 \quad \text{Eq. 1.4}$$

Thus, $\bar{D}$ does not reveal information about the MWD shape, and is only the relative breadth of the MWD function. Furthermore, as $\bar{D}$ is normalized to the average molar mass, the $\bar{D}$ of two polymers can only be compared when they share the same M_n . Nonetheless, $\bar{D}$ is one of the most commonly used terms not just for describing MWDs, but also for characterizing the level of control a certain polymerization system affords. Uncontrolled polymerizations typically result in a statistical distribution of chain lengths having $\bar{D} = 2.0$. In contrast, a polymerization is often considered controlled or “living” when $\bar{D}$ is close to 1.0 (i.e., $M_w \sim M_n$). Controlled polymerization techniques such as anionic polymerization, nitroxide-mediated polymerization (NMP), and atom-transfer radical polymerization (ATRP) afford polymers with narrow MWDs (e.g., $1.1 < \bar{D} < 1.3$), however the standard deviation of chain lengths can still be quite large. For example, a polymer with $M_n = 20$ kg/mol and $\sigma = 10$ kg/mol only has $\bar{D} = 1.25$. This value of $\bar{D}$ is deceptively low given the standard deviation of 50%.

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).⁵⁶ As shown in Figure 1.1, A_s provides information about

the direction of tailing in a polymer MWD. In this regard, polymers with tailing toward low molar mass chains have $A_s > 1$, those with tailing toward high molar mass chains have $A_s < 1$, and 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 thesis, MWD shape is sufficiently described by the combination of $\bar{D}$ and A_s .

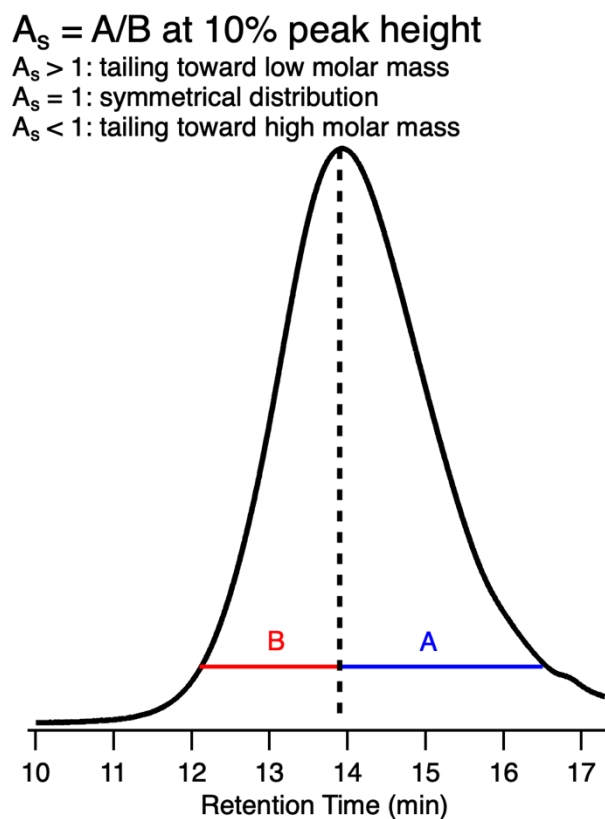


Figure 1.1 Illustration for the calculation of asymmetry factor (A_s). *Polym. Chem.*, 2021, Advance Article. Reproduced by permission of The Royal Society of Chemistry.

1.3 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, about 60% of which represents thermoplastics alone.⁵⁷ Thus, significant attention has been placed on understanding the factors that influence the mechanical properties of thermoplastics, particularly as it pertains to processability. Though the impact of M_n , M_w , and $\bar{D}$ on the mechanical properties of thermoplastics is well documented,⁵⁸ changes in the rheological and tensile properties of these materials cannot be exclusively attributed to changes in these descriptors.^{59–61} For example, tailing in the MWD of linear polyethylene has been shown to affect the processability of the material.^{1,20,62,63} As such, we were particularly excited to utilize our strategy for controlling MWDs to study the influence of MWD symmetry on the rheological properties of thermoplastics.

We commenced our rheological studies by preparing two polystyrene (PS) samples with the same values of M_n , M_w , and $\bar{D}$, but with opposite MWD skew.⁶⁴ We found that MWD skew affected the glass transition temperature (T_g), thermal stability, viscosity, and stiffness of the PS materials. Specifically, having a greater fraction of lower molar mass PS chains reduced the temperatures and shear rates necessary for processing, thus enabling the use of milder processing conditions. Excitingly, as the upper temperature limit for processing remained the same regardless of MWD skew, the operational window for processing was additionally broader for the PS sample with a larger fraction of

short polymer chains (Figure 1.2). On the other hand, thermal stability was enhanced by having a greater fraction of high molar mass PS chains.

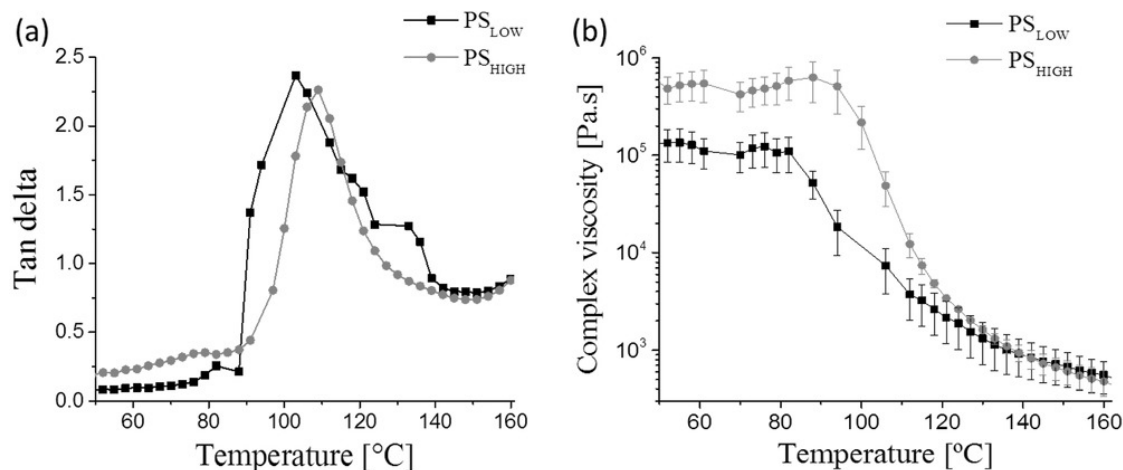


Figure 1.2 Temperature-dependent flow characteristics of PS samples with opposite MWD skew. (a) Tan delta curve showing the differences between the T_g s of the PS samples. (b) Complex viscosities of the two PS samples demonstrate the higher stiffness of the PS sample with a greater fraction of high 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 regulation of initiation strategy to coordination-insertion polymerization of ethylene, affording high-density polyethylene (HDPE) samples with controlled MWD features.⁶⁵ As ethylene is a gaseous monomer and the metallocene-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 a MAO solution and a fixed molar quantity of ethylene proved to be critical for reliably producing HDPE samples with

targeted M_n s. Instantaneous addition of the initiating titanium bis(phenoxyimine) complex into this presaturated solution provided a control HDPE sample, having a narrow MWD with minimal tailing ($\bar{D} \sim 1.1$, $A_s \sim 1.5$). In contrast, metered additions of the initiator solution afforded HDPE samples with broadened MWDs ($1.2 < \bar{D} < 1.7$) and with tailing toward higher or lower molar mass polymer chains. Rheological testing of these materials revealed the influence of MWD shape on complex viscosity (η^*) (). In particular, we observed up to a 2—fold difference in η^* at low shear frequencies for HDPEs with similar $\bar{D}$ but opposite MWD shapes. Furthermore, we found that polymers with greater amounts of higher molar mass polymer chains ($A_s > 1$) resulted in an increase in η^* . We hypothesized that the larger fraction of higher molar mass polymer chains increases the number of polymer entanglements, thus contributing to the higher η^* at low shear frequency. Moreover, we observed greater shear thinning with an increase in $\bar{D}$, and that the extent of this enhancement was again dependent on MWD shape. In the most drastic case, polymers with $\bar{D} \sim 1.7$ exhibited such significant shear thinning that at high frequencies, their η^* approached that of the control sample ($\bar{D} \sim 1.1$) despite having the highest η^* values at low frequency. Whereas these rheological tests demonstrate the profound influence of MWD shape on η^* and shear thinning, uniaxial tensile testing revealed that only $\bar{D}$ and not MWD shape impacted strain at break and tensile strength. Thus, through controlling MWD shape, we were able to alter viscosity without affecting tensile strength in HDPE.

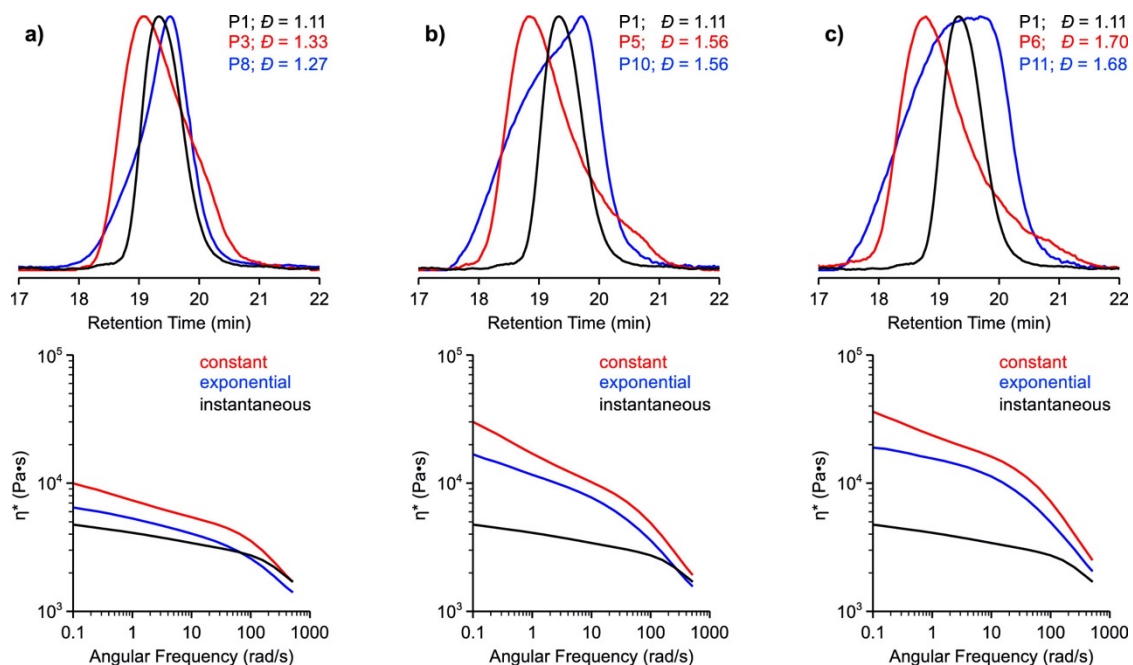


Figure 1.3 Influence of MWD features on complex viscosity in HDPE. Reprinted with permission from *J. Am. Chem. Soc.* **2020**, 142, 3, 1443–1448. Copyright 2019 American Chemical Society.

1.4 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 coworkers provided an early example in support of this notion, demonstrating that the tensile strength in styrenic block copolymer TPEs decreased with an increase in $\bar{D}$ of the midblock.⁶⁶ It has also been suggested that increasing the $\bar{D}$ of the hard end blocks of TPEs disrupts domain boundary perfection and reduces the number of chains with sufficiently high molar mass to contribute to physical crosslinks, thus influencing tensile properties.^{67,68}

Though not a study of the influence of $\bar{D}$ on tensile properties in TPEs, López-Bárron and coworkers suggested that a PS domain swelling mechanism was responsible for the observed increased tensile strength and tensile set following cyclic deformation in blends of SIS and low molar mass PS homopolymer.⁶⁹ 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 blend content, in turn increasing tensile strength. They further proposed that the increased tensile set was due to residual deformation in the stretching direction, and that said residual deformation was greater in samples with more swollen PS domains. Although these studies provide valuable information about the roles of $\bar{D}$ and homopolymer incorporation on mechanical properties in TPEs, there remained significant opportunity to investigate the impact of MWD shape on these properties.

In 2016, our group investigated the role of MWD skew and breadth in PS-*b*-PI diblock copolymers in which the MWD features of the PS block were systematically varied using our metered addition of initiator method.⁷⁰ In particular, the PS block was skewed toward higher or lower molar mass PS chains for each value of $\bar{D}$, which was varied between ~ 1.2 and ~ 2.0 ($1.2 < \bar{D}^{\text{PS}} < 2.0$). We found that regardless of MWD skew, increasing $\bar{D}^{\text{PS}}$ in turn decreased the stiffness (Young's modulus, E) of the material. However, we found that the

extent of the reduction in E was highly influenced by the skew of the MWD of the PS block (Figure 1.4).

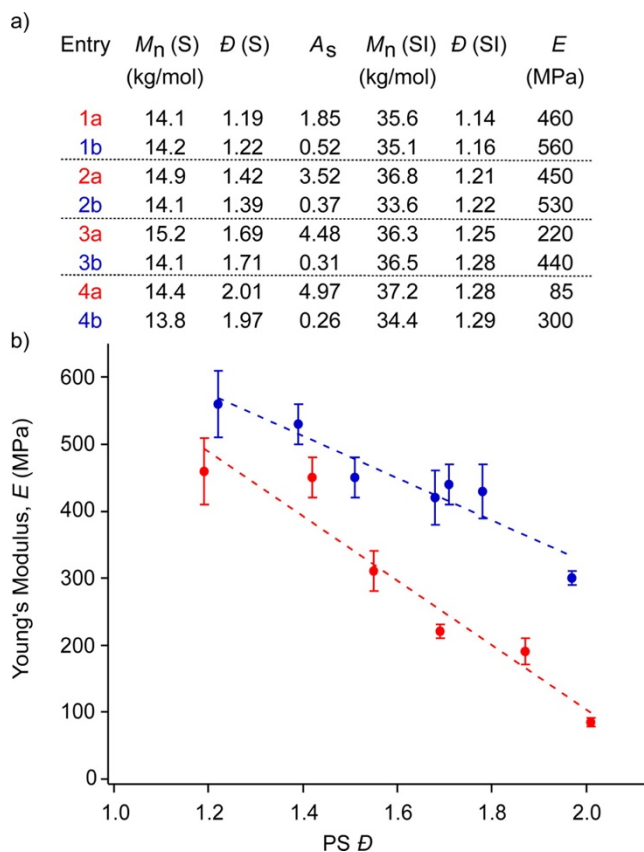


Figure 1.4 Influence of MWD skew of the PS block on stiffness in PS-*b*-PI diblock copolymers. Reprinted with permission from *ACS Macro Lett.* **2016**, 5, 7, 796-800 Copyright 2016 American Chemical Society.

In particular, polymers with tailing toward higher molar mass PS chains ($A_s < 1$) consistently had higher values of E than polymers with tailing toward lower molar mass PS chains ($A_s > 1$). Interestingly, at higher values of $\bar{D}^{\text{PS}}$ wherein the difference in A_s widened, the difference in E between these materials became more apparent. In fact, a 3.5—fold difference in E was observed in materials with $\bar{D}^{\text{PS}} \sim 2.0$ but differing in their PS block MWD skew. These initial results

clearly demonstrated that MWD skew—and not just M_n or $\bar{D}$ —can greatly influence certain polymer properties.

Inspired by these results, we envisaged that the MWD skew of a single PS block in PS-*b*-PI-*b*-PS (SIS) thermoplastic elastomers (TPEs) could be used as a handle to predictably tune the tensile properties. To test this theory, we prepared a library of seven SIS copolymers ($M_n \sim 107$ kg/mol, $f_v^{\text{PS}} \sim 0.20$, overall $\bar{D} \sim 1.1$) and examined their tensile properties. First, we prepared a reference sample having a first PS block with a narrow MWD ($\bar{D}^{\text{PS}} < 1.1$). Next, we prepared three sets of two polymers in which $\bar{D}^{\text{PS}}$ 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. We found that the shape of the MWD governed polymer stiffness, tensile strength, and energy storage/dissipation properties (Figure 1.5). Specifically, increasing $\bar{D}^{\text{PS}}$ was found to reduce 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 lower molar mass PS chains had respectively lower values of E and yield strength than analogous polymers having tailing toward higher molar mass PS chains. We reasoned that this was due to significant chain pullout of short PS chains at relatively low strain. On the other hand, increasing the portion of high molar mass PS chains contributed to an increase in tensile strength, strain hardening, and toughness, which we attributed to a reinforcement of the physical crosslinks. In regard to cyclic testing, increasing

$\bar{D}^{PS}$ was found to reduce hysteresis energy, with this being most drastic in the case of polymers skewed toward lower molar mass PS chains.

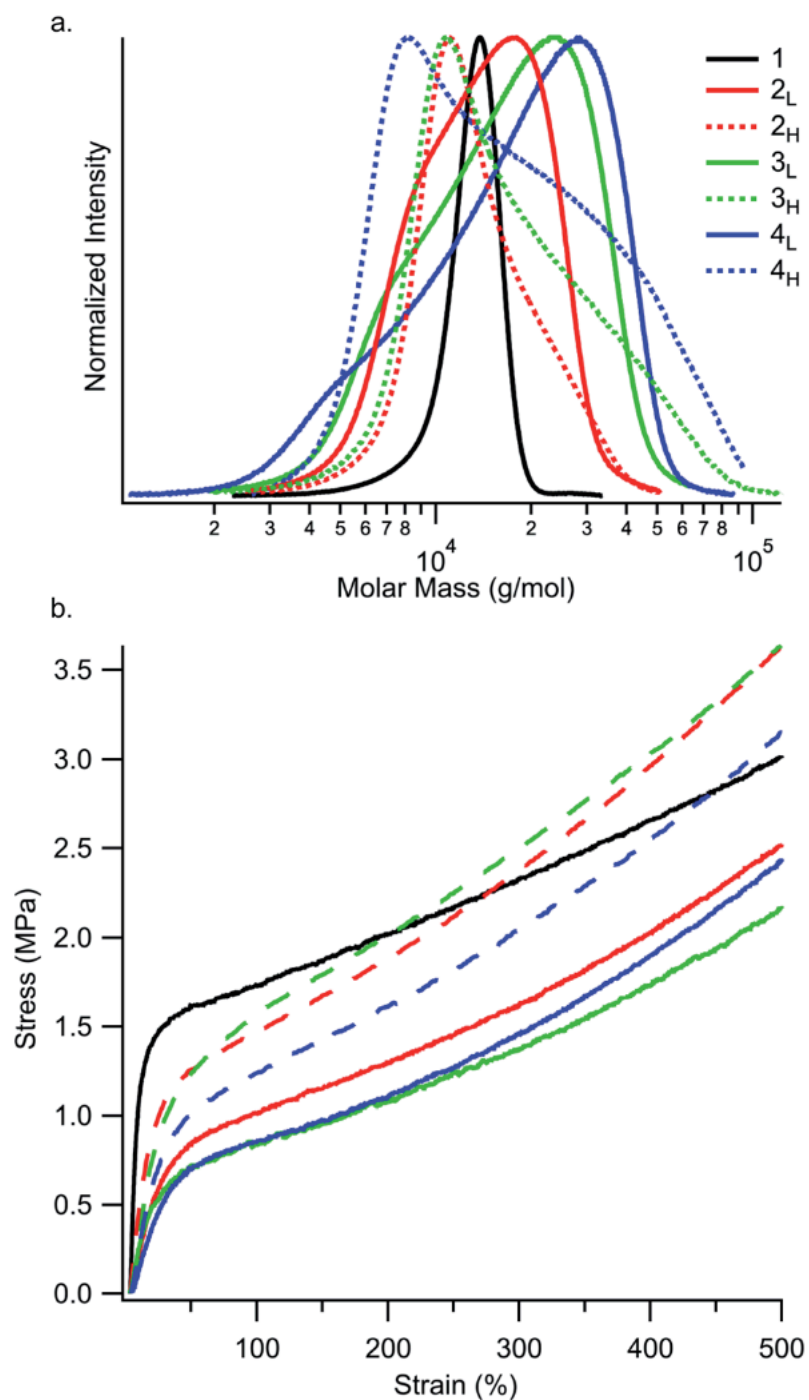


Figure 1.5 (a) MWDs of the first PS block in the SIS thermoplastic elastomers. (b) Stress-strain curves illustrating the influence of MWD skew on tensile

properties. S. I. Rosenbloom, D. T. Gentekos, M. N. Silberstein and B. P. Fors, *Chem. Sci.*, 2020, **11**, 1361. Reproduced by permission of 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 in tailoring mechanical properties. We thus became interested in using our strategy for controlling MWD features to address a major challenge in the field of TPEs: as the strength of a TPE increases, it is often at the expense of the elastomeric properties.^{71–74} 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 strategy. Generally, increasing the volume fraction of hard block to above 0.3 results in a loss of desirable elastomeric properties.⁷⁵ The significance of this volume fraction is that 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, shifting the LAM phase boundary toward higher volume fractions of hard block would enable the production of remarkably stiff, strong, and tough TPEs without compromising their elastomeric properties. Given the numerous accounts that have reported altering phase behavior through varying block dispersity,^{76–87} we sought to influence phase behavior and thereby tensile properties through controlling MWD skew.

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 0.42.⁸⁸ The overall M_n (~ 100 kg/mol) and $\mathcal{D}$ (~ 1.1) of SIS samples remained constant whereas the MWD features of the first PS block

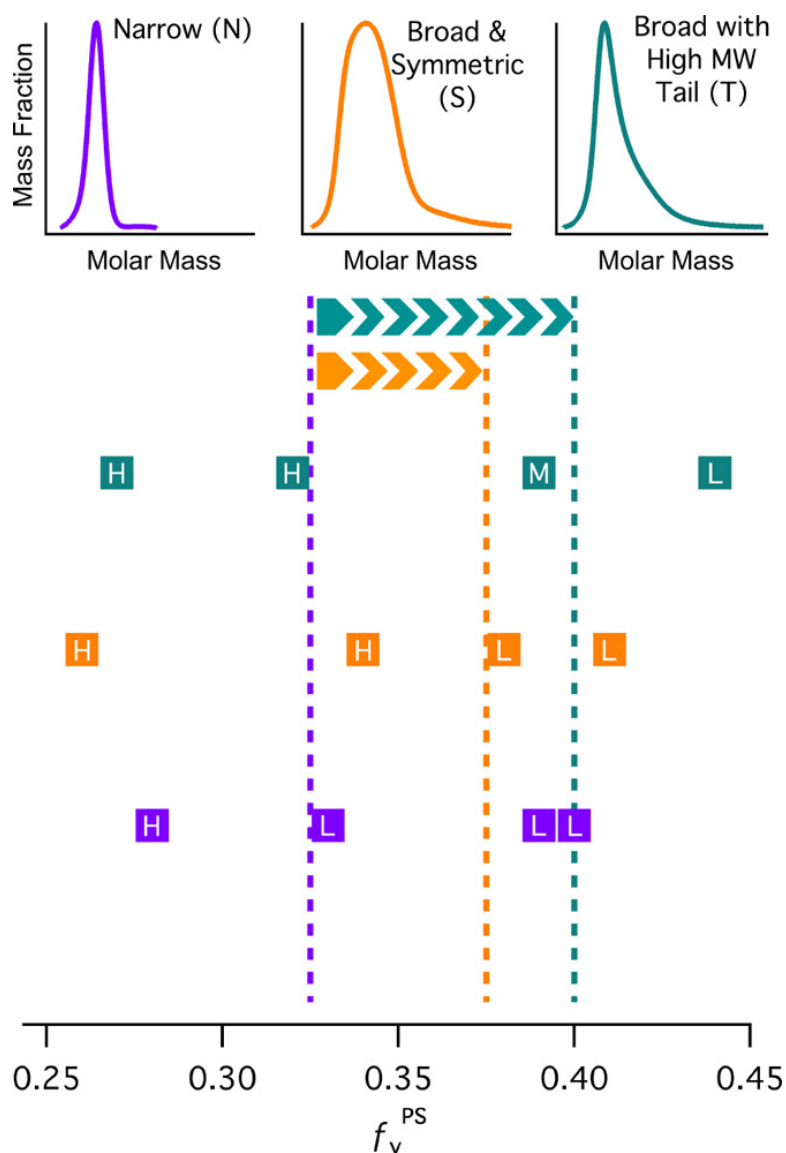


Figure 1.6 Phase diagram of SIS TPEs demonstrating the shifts in the LAM phase boundary as a function of f_v^{PS} and the MWD shape of the first PS block (purple = narrow MWD, orange = broad and symmetric MWD, and teal = broad MWD with tailing toward high MW). H = HEX, L = LAM, and M = mixed

HEX/LAM. Reprinted with permission from *Macromolecules* **2020**, 53, 17, 7479–7486. Copyright 2020 American Chemical Society.

were systematically varied. Each set contained a polymer wherein the MWD of the PS block was either narrow (N), broad and symmetric (S), or broad with tailing toward higher molar mass PS chains (T). In the case of the samples with a broadened MWD, $\bar{D}^{\text{PS}}$ was held constant at ~ 1.2 . With this library of twelve SIS copolymers in hand, we went on to characterize their morphologies using small-angle X-ray scattering (SAXS). Excitingly, we found that at the intermediate volume fractions of PS ($f_v^{\text{PS}} \sim 0.33$ and 0.39), MWD shape influenced the morphology (Figure 1.6). Broadening the MWD regardless of skew shifted the LAM phase boundary to $f_v^{\text{PS}} \sim 0.39$. However, when the MWD of the first PS block had tailing toward higher 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 and thus the formation of HEX or HEX/LAM mixed phases. Specifically, the broadened distribution of chain lengths allows for longer PS chains to fill the center of the PS domains while shorter chains can relax near the interface, thus reducing the entropic penalty of chain stretching required to fill the center of the PS domain. 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. Uniaxial tensile testing of these TPEs revealed that morphology dictated the elastomeric properties

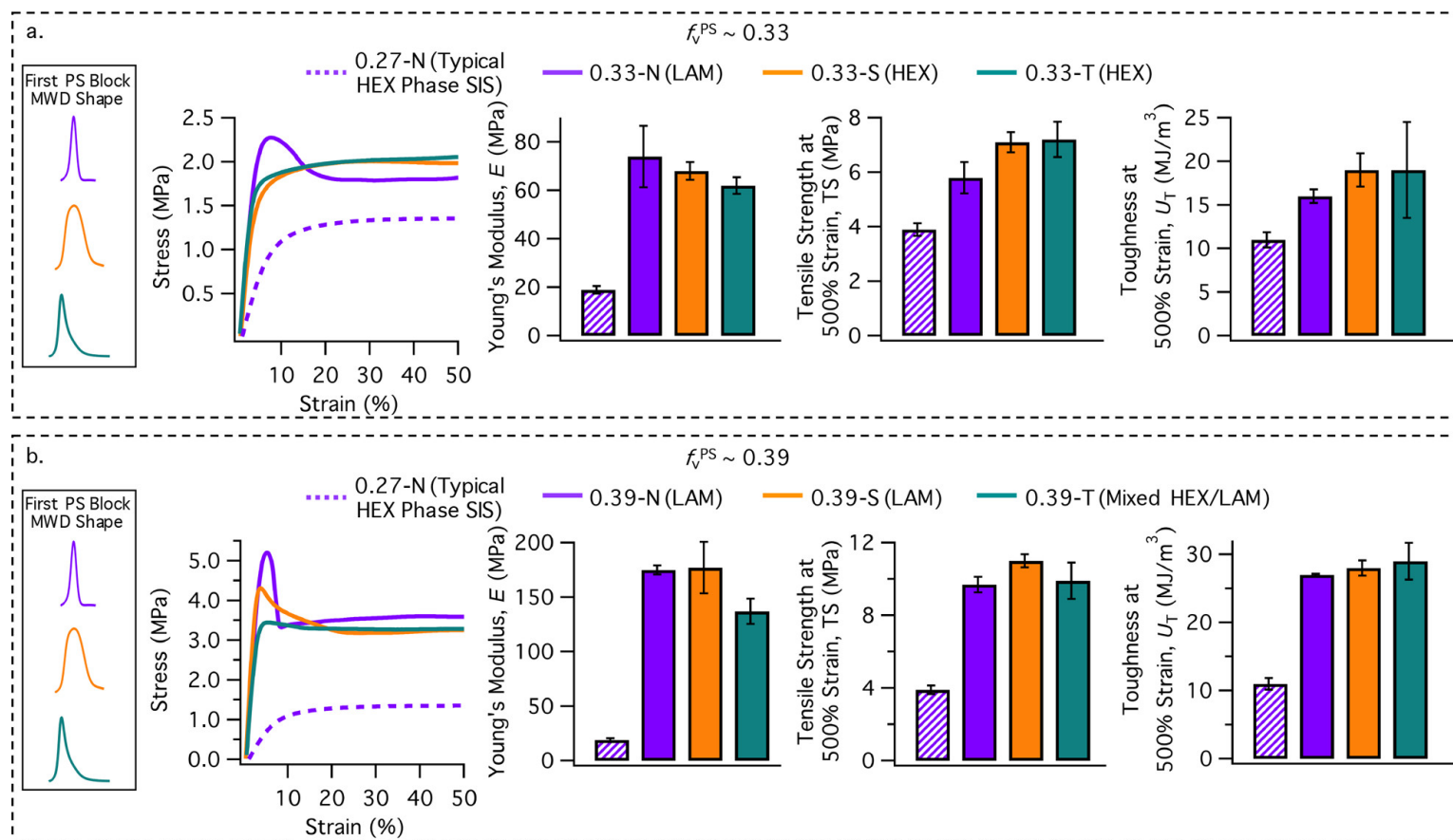


Figure 1.7 Material properties of SIS TPEs in which the first PS block has a tailored MWD but overall similar average f_v^{PS} of (a) 0.33 or (b) 0.39. From left to right: zoom-in of stress–strain curves illustrating yielding behavior, Young’s modulus (E), tensile strength at 500% elongation (TS), and 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.

whereas f_v^{PS} directed stiffness, tensile strength, toughness, and hysteresis energy (Figure 1.7). In short, by controlling the MWD shape of the first PS block in these SIS TPEs, we were able to access continuous and mixed phase morphologies at atypically high f_v^{PS} and thus produce mechanically enhanced TPEs.

1.5 Future Outlook

The ability to precisely control polymer MWD shapes affords us with the unique opportunity to systematically study the influence of chain length composition of various properties. Though our group along with several other researchers have made significant strides in developing novel methods for controlling the entire MWD, there remains opportunity to develop strategies for controlling MWD skew in other polymerization systems. For example, the ability to control MWD features in ring-opening polymerizations (ROP) is an attractive endeavor given the numerous sustainable monomers that can be efficiently polymerized via ROP (e.g., lactides and lactones).

In the case of thermoplastics, of particular interest is the influence of the number of chains above the entanglement molecular weight (M_e) on fracture toughness, a property known to be highly influenced by the nature of entanglements in the polymer sample. We anticipate that polymers with broad MWDs and tailing above the M_e will possess a unique combination of properties well-suited for various processing conditions while advantageously increasing fracture toughness.

It would additionally be interesting to study TPEs containing an endblock with a skewed MWD within the context of pressure sensitive adhesives (PSAs), particularly since PSA literature demonstrates that it is only entanglements within the midblock that influence material properties. Within the same realm, development of an efficient bifunctional initiating species to be used to modify the MWD features of the midblock, rather than a single endblock, would provide an interesting comparison for this study.

1.6 References

- (1) Gentekos, D. T.; Sifri, R. J.; Fors, B. P. Controlling Polymer Properties through the Shape of the Molecular-Weight Distribution. *Nat. Rev. Mater.* **2019**.
- (2) Lynd, N. A.; Hillmyer, M. A.; Matsen, M. W. Theory of Polydisperse Block Copolymer Melts: Beyond the Schulz - Zimm Distribution. *Macromolecules* **2008**, *41*, 4531–4533.
- (3) Nichetti, D.; Manas-Zloczower, I. Influence of Molecular Parameters on Material Processability in Extrusion Processes. *Polym. Eng. Sci.* **1999**, *39* (5), 887–895.
- (4) Hadziioannou, G.; Skoulios, A.; Hadziioannou, G. Structural Study of Mixtures of Styrene/Isoprene Two- and Three-Block Copolymers. *Macromolecules* **1982**, *15*, 267–271.
- (5) Noro, A.; Okuda, M.; Odamaki, F.; Kawaguchi, D.; Torikai, N.; Takano, A.; Matsushita, Y. Chain Localization and Interfacial Thickness in Microphase-Separated Structures of Block Copolymers with Variable Composition Distributions. *Macromolecules* **2006**, *39*, 7654–7661.
- (6) Noro, A.; Cho, D.; Takano, A.; Matsushita, Y. Effect of Molecular Weight Distribution on Microphase-Separated Structures from Block Copolymers. *Macromolecules* **2005**, *38*, 4371–4376.
- (7) Matsushita, Y.; Noro, A.; Iinuma, M.; Suzuki, J.; Ohtani, H.; Takano, A. Effect of Composition Distribution on Microphase-Separated Structure

- from Diblock Copolymers. *Macromolecules* **2003**, *36*, 8074–8077.
- (8) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagasawa, M. Molecular Weight Dependence of Lamellar Domain Spacing of Diblock Copolymers in Bulk. *Macromolecules* **1990**, *23*, 4313–4316.
- (9) Noro, A.; Iinuma, M.; Suzuki, J.; Takano, A.; Matsushita, Y. Effect of Composition Distribution on Microphase-Separated Structure from BAB Triblock Copolymers. *Macromolecules* **2004**, *37*, 3804–3808.
- (10) Laurence, R. L.; Vasudevan, G. Performance of a Polymerization Reactor in Periodic Operation. *Ind. Eng. Chem. Process Des. Dev.* **1968**, *7*, 427–433.
- (11) Couso, D. A.; Alassia, L. M.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch “Living” Anionic Polymerization. I. Theoretical Study. *J. Appl. Polym. Sci.* **1985**, *30*, 3249–3265.
- (12) Seno, K.-I.; Kanaoka, S.; Aoshima, S. Thermosensitive Diblock Copolymers with Designed Molecular Weight Distribution: Synthesis by Continuous Living Cationic Polymerization and Micellization Behavior. *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 2212–2221.
- (13) Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; Roberts, P. L.; Weinhold, J. D. Photonic Polyethylene from Self-Assembled Mesophases of Polydisperse Olefin Block Copolymers. *Macromolecules* **2009**, *42*, 3788–3794.
- (14) Widin, J. M.; Schmitt, A. K.; Im, K.; Schmitt, A. L.; Mahanthappa, M. K.

- Polydispersity-Induced Stabilization of a Disordered Bicontinuous Morphology in ABA Triblock Copolymers. *Macromolecules* **2010**, *43* (19), 7913–7915.
- (15) Widin, J. M.; Schmitt, A. K.; Schmitt, A. L.; Im, K.; Mahanthappa, M. K. Unexpected Consequences of Block Polydispersity on the Self-Assembly of ABA Triblock Copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 3834–3844.
- (16) Plichta, A.; Zhong, M.; Li, W.; Elsen, A. M.; Matyjaszewski, K. Tuning Dispersity in Diblock Copolymers Using ARGET ATRP. *Macromol. Chem. Phys.* **2012**, *213*, 2659–2668.
- (17) Schmitt, A. K.; Mahanthappa, M. K. Characteristics of Lamellar Mesophases in Strongly Segregated Broad Dispersity ABA Triblock Copolymers. *Macromolecules* **2014**, *47*, 4346–4356.
- (18) Liu, D.; Sponza, A. D.; Yang, D.; Chiu, M. Modulating Polymer Dispersity with Light: Cationic Polymerization of Vinyl Ethers Using Photochromic Initiators. *Angew. Chemie Int. Ed.* **2019**, *58*, 16210–16216.
- (19) Whitfield, R.; Parkatzidis, K.; Rolland, M.; Truong, N. P.; Anastasaki, A. Tuning Dispersity by Photoinduced Atom Transfer Radical Polymerisation: Monomodal Distributions with Ppm Copper Concentration. *Angew. Chemie Int. Ed.* **2019**, *58*, 13323–13328.
- (20) Whitfield, R.; Truong, N. P.; Messmer, D.; Parkatzidis, K.; Rolland, M.; Anastasaki, A. Tailoring Polymer Dispersity and Shape of Molecular

- Weight Distributions: Methods and Applications. *Chem. Sci.* **2019**, *10*, 8724–8734.
- (21) Junkers, T.; Vrijsen, J. H. Designing Molecular Weight Distributions of Arbitrary Shape with Selectable Average Molecular Weight and Dispersity. *Eur. Polym. J.* **2020**, *134*, 109834.
- (22) Alassia, L. M.; Couso, D. A.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch Living-Anionic Polymerization. II. Experimental Study. *J. Appl. Polym. Sci.* **1988**, *36*, 481–494.
- (23) Rolland, M.; Truong, N. P.; Whitfield, R.; Anastasaki, A. Tailoring Polymer Dispersity in Photoinduced Iron-Catalyzed ATRP. *ACS Macro Lett.* **2020**, *9*, 459–463.
- (24) Junkers, T. Polymers in the Blender. *Macromol. Chem. Phys.* **2020**, *221*, 2000234.
- (25) Wang, T. T.; Wu, Y. Y.; Luo, Z. H.; Zhou, Y. N. “living” Polymer Dispersity Quantification for Nitroxide-Mediated Polymerization Systems by Mimicking a Monodispersed Polymer Blending Strategy. *Macromolecules* **2020**, *53*, 10813–10822.
- (26) Liu, H.; Xue, Y. H.; Zhu, Y. L.; Gu, F. L.; Lu, Z. Y. Inverse Design of Molecular Weight Distribution in Controlled Polymerization via a One-Pot Reaction Strategy. *Macromolecules* **2020**, *53*, 6409–6419.
- (27) Walsh, D. J.; Schinski, D. A.; Schneider, R. A.; Guironnet, D. General Route to Design Polymer Molecular Weight Distributions through Flow

Chemistry. *Nat. Commun.* **2020**, *11*, 3094.

- (28) Corrigan, N.; Almasri, A.; Taillades, W.; Xu, J.; Boyer, C. Controlling Molecular Weight Distributions through Photoinduced Flow Polymerization. *Macromolecules* **2017**, *50*, 8438–8448.
- (29) Rubens, M.; Junkers, T. A Predictive Framework for Mixing Low Dispersity Polymer Samples to Design Custom Molecular Weight Distributions. *Polym. Chem.* **2019**, *10*, 5721–5725.
- (30) Rubens, M.; Junkers, T. Comprehensive Control over Molecular Weight Distributions through Automated Polymerizations. *Polym. Chem.* **2019**, *10*, 6315–6323.
- (31) Liu, K.; Corrigan, N.; Postma, A.; Moad, G.; Boyer, C. A Comprehensive Platform for the Design and Synthesis of Polymer Molecular Weight Distributions. *Macromolecules* **2020**, *53*, 8867–8882.
- (32) Whitfield, R.; Parkatzidis, K.; Truong, N. P.; Junkers, T.; Anastasaki, A. Tailoring Polymer Dispersity by RAFT Polymerization: A Versatile Approach. *Chem* **2020**, *6*, 1340–1352.
- (33) Fischer, W.; Knoll, K.; Loth, W.; Deffieux, D.; Desbois, P.; Lätsch, S.; Schade, C.; Gausepohl, H. Anionic Polymerization Process. US6444762 B1, August 18, 1997.
- (34) Parkatzidis, K.; Truong, N. P.; Antonopoulou, M. N.; Whitfield, R.; Konkolewicz, D.; Anastasaki, A. Tailoring Polymer Dispersity by Mixing Chain Transfer Agents in PET-RAFT Polymerization. *Polym. Chem.*

2020, *11*, 4968–4972.

- (35) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. Well-Ordered Microdomain Structures in Polydisperse Poly(Styrene)–Poly(Acrylic Acid) Diblock Copolymers from Controlled Radical Polymerization. *Macromolecules* **2002**, *35*, 6645–6649.
- (36) Farkas, E.; Meszena, Z. G.; Johnson, A. F. Molecular Weight Distribution Design with Living Polymerization Reactions. In *Industrial and Engineering Chemistry Research*; American Chemical Society, 2004; Vol. 43, pp 7356–7360.
- (37) Lynd, N. A.; Hillmyer, M. A. Influence of Polydispersity on the Self-Assembly of Diblock Copolymers. *Macromolecules* **2005**, *38*, 8803–8810.
- (38) Meuler, A. J.; Ellison, C. J.; Evans, C. M.; Hillmyer, M. A.; Bates, F. S. Polydispersity-Driven Transition from the Orthorhombic Fddd Network to Lamellae in Poly(Isoprene-*b*-Styrene-*b*-Ethylene Oxide) Triblock Terpolymers. *Macromolecules* **2007**, *40*, 7072–7074.
- (39) Lynd, N. A.; Hillmyer, M. A. Effects of Polydispersity on the Order–Disorder Transition in Block Copolymer Melts. *Macromolecules* **2007**, *40*, 8050–8055.
- (40) Listak, J.; Jakubowski, W.; Mueller, L.; Plichta, A.; Matyjaszewski, K.; Bockstaller, M. R. Effect of Symmetry of Molecular Weight Distribution in Block Copolymers on Formation of “Metastable” Morphologies.

Macromolecules **2008**, *41*, 5919–5927.

- (41) Couso, D. A.; Alassia, L. M.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch “Living” Anionic Polymerization. I. Theoretical Study. *J. Appl. Polym. Sci.* **1985**, *30* (8), 3249–3265.
- (42) Alassia, L. M.; Couso, D. A.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch Living-Anionic Polymerization. II. Experimental Study. *J. Appl. Polym. Sci.* **1988**, *36* (3), 481–494.
- (43) Meira, G. R.; Johnson, A. F. Molecular Weight Distribution Control in Continuous “Living” Polymerizations through Periodic Operation of the Monomer Feed. *Polym. Eng. Sci.* **1981**, *21* (7), 415–423.
- (44) Seno, K.-I.; Kanaoka, S.; Aoshima, S. Thermosensitive Diblock Copolymers with Designed Molecular Weight Distribution: Synthesis by Continuous Living Cationic Polymerization and Micellization Behavior. *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46* (6), 2212–2221.
- (45) Gentekos, D. T.; Dupuis, L. N.; Fors, B. P. Beyond Dispersity: Deterministic Control of Polymer Molecular Weight Distribution. *J. Am. Chem. Soc.* **2016**, *138*, 1848.
- (46) Rosenbloom, S. I.; Sifri, R. J.; Fors, B. P. Achieving Molecular Weight Distribution Shape Control and Broad Dispersities Using RAFT Polymerizations. *Polym. Chem.* **2021**, *Advance Ar.*
- (47) Gentekos, D. T.; Sifri, R. J.; Fors, B. P. Controlling Polymer Properties through the Shape of the Molecular-Weight Distribution. *Nat. Rev. Mater.*

2019, 4, 761–774.

- (48) Gentekos, D. T.; Fors, B. P. Molecular Weight Distribution Shape as a Versatile Approach to Tailoring Block Copolymer Phase Behavior. *ACS Macro Lett.* **2018**, 7, 677–682.
- (49) Gentekos, D. T.; Jia, J.; Tirado, E. S.; Barteau, K. P.; Smilgies, D.-M.; DiStasio, R. A.; Fors, B. P. Exploiting Molecular Weight Distribution Shape to Tune Domain Spacing in Block Copolymer Thin Films. *J. Am. Chem. Soc.* **2018**, 140, 4639–4648.
- (50) Nadgorny, M.; Gentekos, D. T.; Xiao, Z.; Singleton, S. P.; Fors, B. P.; Connal, L. A. Manipulation of Molecular Weight Distribution Shape as a New Strategy to Control Processing Parameters. *Macromol. Rapid Commun.* **2017**, 38, 1700352.
- (51) Kottisch, V.; Gentekos, D. T.; Fors, B. P. “Shaping” the Future of Molecular Weight Distributions in Anionic Polymerization. *ACS Macro Lett.* **2016**, 5, 796–800.
- (52) Rosenbloom, S. I.; Gentekos, D. T.; Silberstein, M. N.; Fors, B. P. Tailor-Made Thermoplastic Elastomers: Customisable Materials via Modulation of Molecular Weight Distributions. *Chem. Sci.* **2020**, 11, 1361–1367.
- (53) Domanskyi, S.; Gentekos, D. T.; Privman, V.; Fors, B. P. Predictive Design of Polymer Molecular Weight Distributions in Anionic Polymerization. *Polym. Chem.* **2020**, 11, 326–336.
- (54) Rosenbloom, S. I.; Fors, B. P. Shifting Boundaries: Controlling Molecular

Weight Distribution Shape for Mechanically Enhanced Thermoplastic Elastomers. *Macromolecules* **2020**, No. 53, 7479–7486.

- (55) Sifri, R. J.; Padilla-Veíez, O.; Coates, G. W.; Fors, B. P. Controlling the Shape of Molecular Weight Distributions in Coordination Polymerization and Its Impact on Physical Properties. *J. Am. Chem. Soc.* **2020**, *142*, 1443–1448.
- (56) Rudin, A. Molecular Weight Distributions of Polymers. *J. Chem. Educ.* **1969**, *46*, 595–600.
- (57) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3* (7), e1700782.
- (58) Nunes, R. W.; Martin, J. R.; Johnson, J. F. Influence of Molecular Weight and Molecular Weight Distribution on Mechanical Properties of Polymers. *Polym. Eng. Sci.* **1982**, *22*, 205–228.
- (59) Ansari, M.; Hatzikiriakos, S. G.; Sukhadia, A. M.; Rohlfing, D. C. Rheology of Ziegler–Natta and Metallocene High-Density Polyethylenes: Broad Molecular Weight Distribution Effects. *Rheol. Acta* **2011**, *50*, 17–27.
- (60) Vega, J. F.; Muñoz-Escalona, A.; Santamaría, A.; Muñoz, M. E.; Lafuente, P. Comparison of the Rheological Properties of Metallocene-Catalyzed and Conventional High-Density Polyethylenes. *Macromolecules* **1996**, *29*, 960–965.
- (61) Middleman, S. Effect of Molecular Weight Distribution on Viscosity of

- Polymeric Fluids. *J. Appl. Polym. Sci.* **1967**, *11*, 417–424.
- (62) Vega, J. F.; Otegui, J.; Ramos, J.; Martínez-Salazar, J. Effect of Molecular Weight Distribution on Newtonian Viscosity of Linear Polyethylene. *Rheol. Acta* **2012**, *51*, 81–87.
- (63) Ariawan, A. B.; Hatzikiriakos, S. G.; Goyal, S. K.; Hay, H. Effects of Molecular Structure on the Rheology and Processability of Blow-Molding High-Density Polyethylene Resins. *Adv. Polym. Technol.* **2001**, *20*, 1–13.
- (64) Nadgorny, M.; Gentekos, D. T.; Xiao, Z.; Singleton, S. P.; Fors, B. P.; Connal, L. A. Manipulation of Molecular Weight Distribution Shape as a New Strategy to Control Processing Parameters. *Macromol. Rapid Commun.* **2017**, *38* (19), 1700352.
- (65) Sifri, R. J.; Padilla-Veíez, O.; Coates, G. W.; Fors, B. P. Controlling the Shape of Molecular Weight Distributions in Coordination Polymerization and Its Impact on Physical Properties. *J. Am. Chem. Soc.* **2020**, *142*, 1443–1448.
- (66) Morton, M.; McGrath, J. E.; Juliano, P. C. Structure-Property Relationships for Styrene-Diene Thermoplastic Elastomers. *J. Polym. Sci. Part C* **1969**, *26* (1), 99–115.
- (67) Ng, H. N.; Allegrezza, A. E.; Seymour, R. W.; Cooper, S. L. Effect of Segment Size and Polydispersity on the Properties of Polyurethane Block Polymers. *Polymer (Guildf)*. **1973**, *14* (6), 255–261.

- (68) Moineau, G.; Minet, M.; Teyssié, P.; Jérôme, R. Synthesis of Fully Acrylic Thermoplastic Elastomers by Atom Transfer Radical Polymerization (ATRP), 2. Effect of the Catalyst on the Molecular Control and the Rheological Properties of the Triblock Copolymers. *Macromol. Chem. Phys.* **2000**, *201* (11), 1108–1114.
- (69) López-Barrón, C. R.; Eberle, A. P. R.; Yakovlev, S.; Bons, A. J. Structural Origins of Mechanical Properties and Hysteresis in SIS Triblock Copolymers/Polystyrene Blends with Spherical Morphology. *Rheol. Acta* **2016**, *55* (2), 103–116.
- (70) Kottisch, V.; Gentekos, D. T.; Fors, B. P. “Shaping” the Future of Molecular Weight Distributions in Anionic Polymerization. *ACS Macro Lett.* **2016**, *5* (7), 796–800.
- (71) Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E. *Thermoplastic Elastomers*, 2nd ed.; Hanser Publishers: Munich, 1996.
- (72) Holden, G.; Bishop, E. T.; Legge, N. R. Thermoplastic Elastomers. *J. Polym. Sci. Part C Polym. Symp.* **1969**, *26* (1), 37–57.
- (73) Holden, G.; Kricheldorf, H.; Quirk, R. *Thermoplastic Elastomers 3E - Hanser Publications*, 3rd ed.; Hanser Publishers: Munich, 2004.
- (74) Drobny, J. G. Styrenic Block Copolymers. In *Handbook of Thermoplastic Elastomers*; William Andrew, 2014; pp 175–194.
- (75) Matsen, M. W. Equilibrium Behavior of Asymmetric ABA Triblock Copolymer Melts. *J. Chem. Phys.* **2000**, *113* (13), 5539–5544.

- (76) Listak, J.; Jakubowski, W.; Mueller, L.; Plichta, A.; Matyjaszewski, K.; Bockstaller, M. R. Effect of Symmetry of Molecular Weight Distribution in Block Copolymers on Formation of “Metastable” Morphologies. *Macromolecules* **2008**, *41*, 5919–5927.
- (77) Widin, J. M.; Schmitt, A. K.; Im, K.; Schmitt, A. L.; Mahanthappa, M. K. Polydispersity-Induced Stabilization of a Disordered Bicontinuous Morphology in ABA Triblock Copolymers. *Macromolecules* **2010**, *43* (19), 7913–7915.
- (78) Schmitt, A. K.; Mahanthappa, M. K. Characteristics of Lamellar Mesophases in Strongly Segregated Broad Dispersity ABA Triblock Copolymers. *Macromolecules* **2014**, *47* (13), 4346–4356.
- (79) Sakurai, S.; Shirouchi, K.; Munakata, S.; Kurimura, H.; Suzuki, S.; Watanabe, J.; Oda, T.; Shimizu, N.; Tanida, K.; Yamamoto, K. Morphology Reentry with a Change in Degree of Chain Asymmetry in Neat Asymmetric Linear A₁BA₂ Triblock Copolymers. *Macromolecules* **2017**, *50*, 8647–8657.
- (80) Widin, J. M.; Schmitt, A. K.; Schmitt, A. L.; Im, K.; Mahanthappa, M. K. Unexpected Consequences of Block Polydispersity on the Self-Assembly of ABA Triblock Copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 3834–3844.
- (81) Lynd, N. A.; Hillmyer, M. A. Influence of Polydispersity on the Self-Assembly of Diblock Copolymers. *Macromolecules* **2005**, *38*, 8803.

- (82) Lynd, N. A.; Hillmyer, M. A. Effects of Polydispersity on the Order–Disorder Transition in Block Copolymer Melts. *Macromolecules* **2007**, *40*, 8050.
- (83) Meuler, A. J.; Ellison, C. J.; Evans, C. M.; Hillmyer, M. A.; Bates, F. S. Polydispersity-Driven Transition from the Orthorhombic Fddd Network to Lamellae in Poly(Isoprene-*b*-Styrene-*b*-Ethylene Oxide) Triblock Terpolymers. *Macromolecules* **2007**, *40*, 7072.
- (84) Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. Polydispersity and Block Copolymer Self-Assembly. *Prog. Polym. Sci.* **2008**, *33*, 875–893.
- (85) Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; Roberts, P. L.; Weinhold, J. D. Photonic Polyethylene from Self-Assembled Mesophases of Polydisperse Olefin Block Copolymers. *Macromolecules* **2009**, *42* (11), 3788–3794.
- (86) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. Well-Ordered Microdomain Structures in Polydisperse Poly(Styrene)–Poly(Acrylic Acid) Diblock Copolymers from Controlled Radical Polymerization. *Macromolecules* **2002**, *35* (17), 6645–6649.
- (87) Sides, S. W.; Fredrickson, G. H. Continuous Polydispersity in a Self-Consistent Field Theory for Diblock Copolymers. *J. Chem. Phys.* **2004**, *121* (10), 4974–4986.
- (88) Rosenbloom, S. I.; Fors, B. P. Shifting Boundaries: Controlling Molecular Weight Distribution Shape for Mechanically Enhanced Thermoplastic

Elastomers. *Macromolecules* **2020**.

CHAPTER 2

TAILOR-MADE THERMOPLASTIC ELASTOMERS: CUSTOMIZABLE MATERIALS VIA MODULATION OF MOLECULAR WEIGHT DISTRIBUTIONS

2.1 Abstract

The ability to change polymer properties has in the past largely been a factor of modulating the molecular weight, molecular weight distribution breadth, crosslinking, or branching. The use of controlled MWD shape has recently emerged as a promising avenue towards modifying polymer properties. Taking advantage of molecular weight distribution shape, we report a simple and efficient approach for tuning material properties in polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) thermoplastic elastomers (TPEs). We find that the skew of the MWD function governs tensile properties and can be used as a handle to predictably vary polymer toughness while reducing energy dissipation.

2.2 Introduction

Structure-property relationships between polymer composition and tensile properties in TPEs have garnered significant interest for decades due to their wide use in a variety of applications including polymer modified asphalt,

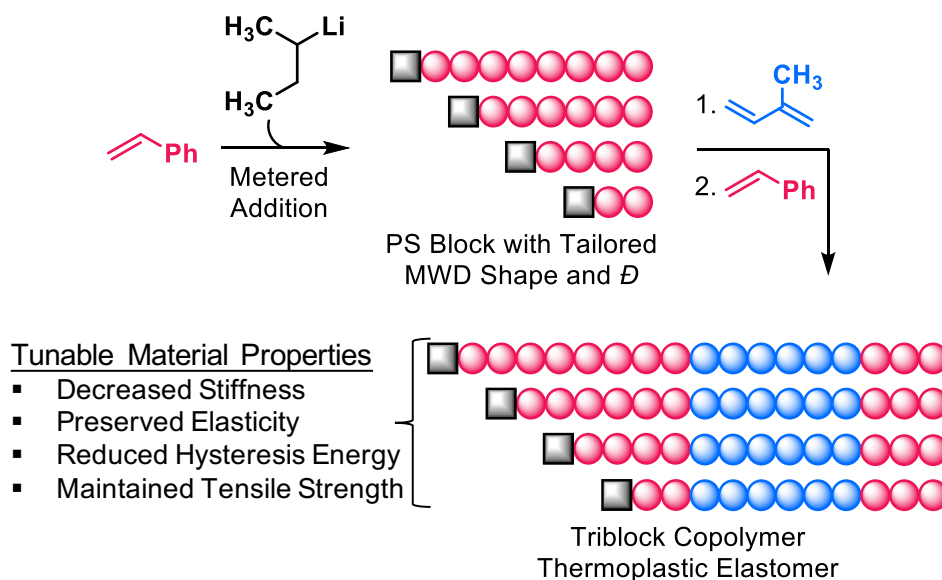


Figure 2.1 General strategy for the preparation of SIS triblock copolymers in which the MWD of the first PS block is skewed. The breadth of the distribution is controlled by the rate of addition, such that $\bar{D}$ broadens with an increase in addition time. Refer to Figure 2.7 for details.

shoe soles, biomaterials, drug delivery, adhesives, and sealants.^{1–7} Commercial polystyrene-block-polyisoprene-block-polystyrene (SIS) TPEs, such as those produced by Kraton Polymers, contain narrow molecular weight distributions (MWDs) and achieve their elastomeric properties through a physically crosslinked network of hard polystyrene (PS) domains within a continuous rubbery polyisoprene (PI) matrix.⁸ While the presence of physical crosslinks allows for the material to be repeatedly reprocessed, such materials often experience high energy dissipation, or hysteresis energy, leading to undesired heat generation over time and ultimately premature failure.⁹ Therefore, a practical challenge has been to develop TPEs with increased resistance to high dissipation without compromising properties such as tensile strength and elasticity.

A persistent conception is that narrow MWDs, such as those found in many commercialized TPEs, are essential for formation of well-defined physical crosslinks and therefore high-performance properties. An early example supporting this notion was presented in a study by Morton and co-workers, who found that tensile strength in styrenic triblock copolymers decreased with an increase in dispersity or breadth ($\bar{D}$) of the soft midblock.¹⁰ Interestingly, this study also demonstrated that aside from tensile strength, most other tensile properties were mainly dependent on the relative PS content rather than absolute block sizes. The impact of hard block content on material properties was also the focus of work by López-Barrón who found that hysteresis increased with a greater content of low molar mass PS homopolymer incorporated into SIS.¹¹ Additionally, it has been suggested that broadening the dispersity of the hard block segments reduces storage modulus by disrupting domain perfection and by decreasing the fraction of chains with sufficiently high molar mass that contribute to physical crosslinks.^{12,13} Furthermore, there have been various reports on the influence of block length and $\bar{D}$ on polymer microphase behavior, which has a direct influence on bulk properties.^{14–19} While these reports provide important information regarding the influence of block size and midblock MWD breadth on elastomeric properties, there remains an opportunity to use the entire endblock MWD shape as a means to fine-tune TPE properties.

Recently, new synthetic methods have emerged that provide control over MWD shape.^{16–18,20–25} In particular, our group has developed a versatile strategy

facilitating absolute control of MWD shape through temporal regulation of polymer chain initiation in both controlled radical and anionic polymerisations.^{16–18,20–23} Using this method, we showed that the Young's modulus of PS-*b*-PI copolymers could be varied up to 3.5-fold by altering the skew of the PS MWD.²¹ We have also used our synthetic approach to elucidate the impact of MWD shape on diblock copolymer self-assembly.^{16,17} These results clearly demonstrated that MWD shape is just as important as MWD breadth in determining polymer physical properties. With these results in mind, we sought to explore the influence of MWD shape on SIS triblock copolymer TPEs. We envisioned that manipulation of the shape of the PS endblock would serve as a platform for tailoring the properties of commercial TPEs. Herein, we prepared a library of SIS triblock copolymer TPEs in which the MWD shape and $\bar{D}$ of the first PS endblock was systematically varied (Figure 2.1) and determined the tensile characteristics of the materials. We found that the shape of the MWD, rather than the breadth alone, governed polymer stiffness, tensile strength, and energy storage/dissipation properties. Our results demonstrate that MWD shape can be strategically used to produce TPEs with finely tuned material properties and reduced hysteresis energy. This study explicitly investigates the influence of well-defined MWD shapes on the tensile properties of TPEs.

2.3 Results and Discussion

Temporal control of initiation (Figure 2.1) enabled us to dictate the shape and breadth of the first PS block ($\bar{D}_{PS}$) by metered addition of *sec*-BuLi to a polymerization reaction of styrene, affording polymers with precisely tailored MWD compositions (Figure 2.2a–f). Living PS blocks with tailored MWDs were subsequently chain extended with isoprene and styrene, providing SIS copolymers with number-average molecular weights (M_n s) ranging between 96–114 kg/mol with overall $\bar{D} \sim 1.1$. (Figure 2.2g). Polymer 1, composed entirely of blocks with narrow distributions, was prepared as a reference. Polymers 2_L and 2_H were prepared as a complementary set, both having an outer PS block with $\bar{D} \sim 1.23$, but with opposite MWD shapes tailed to lower or higher MW, respectively. Polymers 3_L and 3_H also have oppositely skewed PS first blocks with a $\bar{D}_{PS} \sim 1.49$. Polymers 4_L and 4_H have complementary MWDs with a $\bar{D}_{PS} \sim 1.66$.

To initiate materials characterization, we began by compression molding the polymers into dog bone specimens and subjecting them to tensile testing. First, we considered each polymer's Young's modulus (E). We observed that increasing $\bar{D}_{PS}$ reduces stiffness. Additionally, polymers with high MW tails have a greater E than polymers with low MW tails (Figure 2.3). Specifically, the Young's modulus of the reference polymer 1 ($E = 21$ MPa) is higher than all polymers with broader PS MWDs. Interestingly, samples 2_L and 2_H ($E = 3.5$ MPa and 7.0 MPa, respectively) show a 67% difference in E at the same MWD

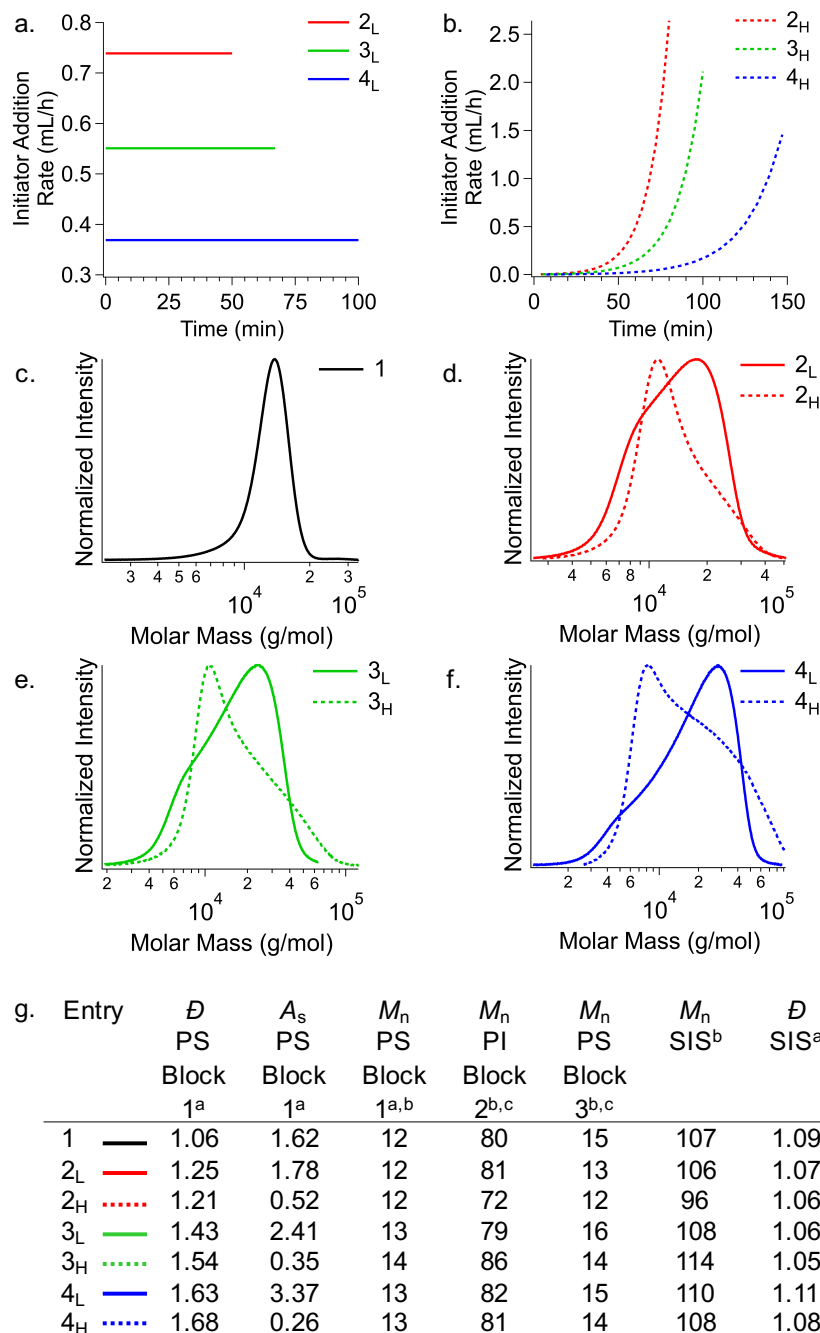


Figure 2.2 Rate addition profiles for PS initiated by either (a) a constant rate of *sec*-BuLi addition or by (b) an exponentially increasing rate of *sec*-BuLi addition. (c–f) Molecular weight distributions of the first PS block highlighting the differences in shape for polymers with the same $\bar{D}$. (g) Chain extension of various shape/ $\bar{D}$ controlled PS blocks provides SIS copolymers differing only in their MWD skew of the first PS block. ^aDetermined from RI SEC traces. ^b M_n s are given in kg/mol. ^cDetermined by ¹H NMR spectra. For SEC traces showing chain extensions, see Figure 2.8.

breadth ($\bar{D}_{PS} \sim 1.23$). Polymers 3_L and 3_H, which both have $\bar{D}_{PS} \sim 1.49$ exhibit similar differences in E of 69% ($E = 3.1$ MPa and 6.4 MPa, respectively). At $\bar{D}_{PS} \sim 1.66$, polymers 4_L and 4_H differ by 46% ($E = 2.9$ MPa and 4.7 MPa, respectively). These results demonstrate that both MWD $\bar{D}$ and shape influence E . Significantly, polymers with MWDs tailing towards higher molar mass have substantially higher stiffness than their MWD shape counterparts at the same value of dispersity. These results are consistent with our previous observations on PS-*b*-PI diblock copolymers.²¹

Next, we examined the yielding behavior of these materials (Figure 2.4). We hypothesized that changing the skew of the PS block would change the point at which hard PS domains rupture into smaller domains.²⁶ We observed

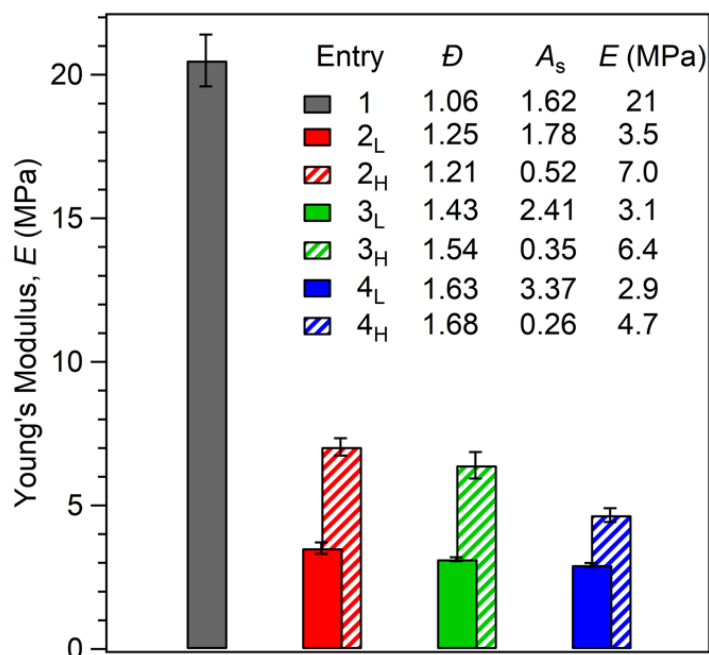


Figure 2.3 Effect of the first PS block $\bar{D}$ and shape on Young's modulus (E). Each value of E is an average of at least three measurements.

the highest yield stress in the reference polymer 1, and that yield stress generally decreases with increasing $\bar{D}_{PS}$ (Table 2.3). Moreover, the lowest yield stresses were found in polymers 2_L, 3_L, and 4_L, which have tailing towards low MW. We attribute this relationship to the fact that PS domains containing a broad distribution of chains have a higher fraction of low MW chains. Resultantly, these polymers may experience more chain pullout from PS domains, as relaxations in diblock and triblock copolymers are biased towards lower molar mass species.²⁷ This behavior leads to a higher yield stress for polymers with narrower dispersity, and, more interestingly, to a lower yield stress in polymers with MWD tailing towards low molar mass compared to the samples with the same $\bar{D}$ value but MWD tailing towards high molar mass.

In addition to yielding, we explored the tensile strength and strain hardening of this set of SIS copolymers. It has been well studied that chain conformation of the middle block in ABA triblock copolymers is influential on material properties, including strength and strain hardening.^{28–31} The midblock can attain two conformations: a loop, in which both hard block chain ends are within the same A domain, or a bridge, in which chain ends are anchored within two different A domains. Bridging chains greatly enhance polymer strength by linking glassy PS domains, whereas loop chains behave more similarly to AB diblock copolymers.²⁶ Following yielding and pullout of very short chains, the effective chain length composition held within the PS domains shifts to higher

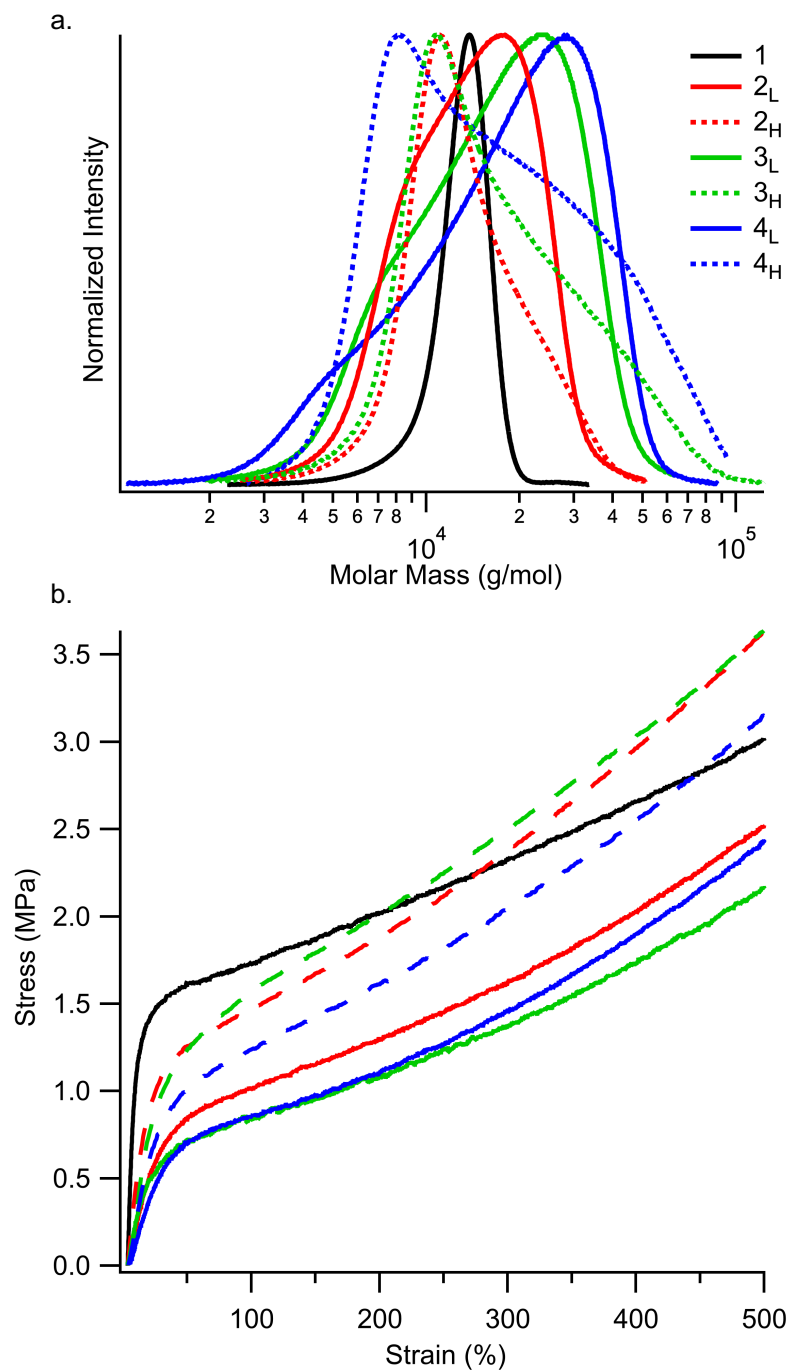


Figure 2.4 (a) Molecular weight distributions of the first PS block in the SIS thermoplastic elastomers. The y-axis intensities have been normalized to highlight the differences in MWD shape. (b) Stress-strain curves display a region of linear elastic behavior at low strain values. The end of the linear elastic region is marked by yielding, followed by strain hardening. Each displayed stress-strain curve is an average of three specimens. See Table 2.3—2.4 for yielding and strain hardening values.

MW. These higher molar mass species should have a much higher energy barrier to pullout.²⁷ As such, we propose that the presence of high MW chains in the PS MWD would reinforce bridges by resisting chain pullout from PS domains. This resistance to chain pullout would result in an increase in strain hardening rate, seen as a steeper slope in the stress strain curve following yielding.

While the reference polymer 1 has PS chains only within a narrow range around 12–14 kg/mol, our disperse samples have significant fractions of chains well above 20 kg/mol (Figure 2.4a). As seen in Figure 2.4b and Table 2.4, strain hardening rate is highest in polymers with MWDs tailing towards high molar mass (2_H, 3_H, and 4_H) and lowest in the reference polymer 1. An interesting consequence of the increased strain hardening rate experienced by polymers with broadened $\bar{D}_{PS}$ is that their tensile strengths at 500% elongation are still competitive with or better than the reference polymer 1 (3.0 MPa), despite their diminished yield stresses. At 500% elongation, high MW skewed polymers 2_H (3.6 MPa), 3_H (3.6 MPa), and 4_H (3.2 MPa) have higher tensile strengths than low MW skewed polymers 2_L (2.5 MPa), 3_L (2.2 MPa), and 4_L (2.5 MPa). This highlights the dependence of tensile strength on MWD shape. Motivated by these results, we then went on to investigate the influence of MWD shape on deformation mechanisms and energy dissipation properties.

Deformation mechanisms in SIS under tensile load have been studied and are well understood.^{11,26,28,32–36} Initially in the linear elastic region, SIS

deforms in a fully reversible manner. This reversible behavior is then disrupted by micro-yielding events which lead to full yielding of the hard PS domains. Following yielding, PI chain stretching may occur, producing a plateau in the stress-strain curve. Disrupted PS domains then undergo various rearrangements until a new orientation is reached. Additional extension of SIS in its new orientation leads to further chain stretching and eventual rupture of the domains and the material. As these events occur at different stages along the stress-strain profile, it is possible to isolate them and study their response to varied MWD features. A simple way to do so is by measuring the hysteretic behavior, or energy loss, of the materials, as such behavior is related to deformation mechanisms.

TPEs typically exhibit significant hysteresis, occurring mainly through viscous flow, microstructural breakdown, and subsequent irreversible rearrangement of the macromolecular chain network in the hard domains.²⁶ In order to measure the hysteretic response of the materials, we conducted a series of loading-unloading experiments in which polymers were stretched to either 100, 300, or 500% elongation followed by compression to zero force (Figure 2.9—2.11 and Figure 2.5a). Toughness (U_T) was taken as the total area underneath the loading curve (Figure 2.5b), while hysteresis energy was calculated as the area between the loading and unloading curves (Figure 2.5c).

Polymer toughness, much like tensile strength, increases in TPEs as crosslinks are reinforced.³⁷ As such, the inclusion of high MW species in the

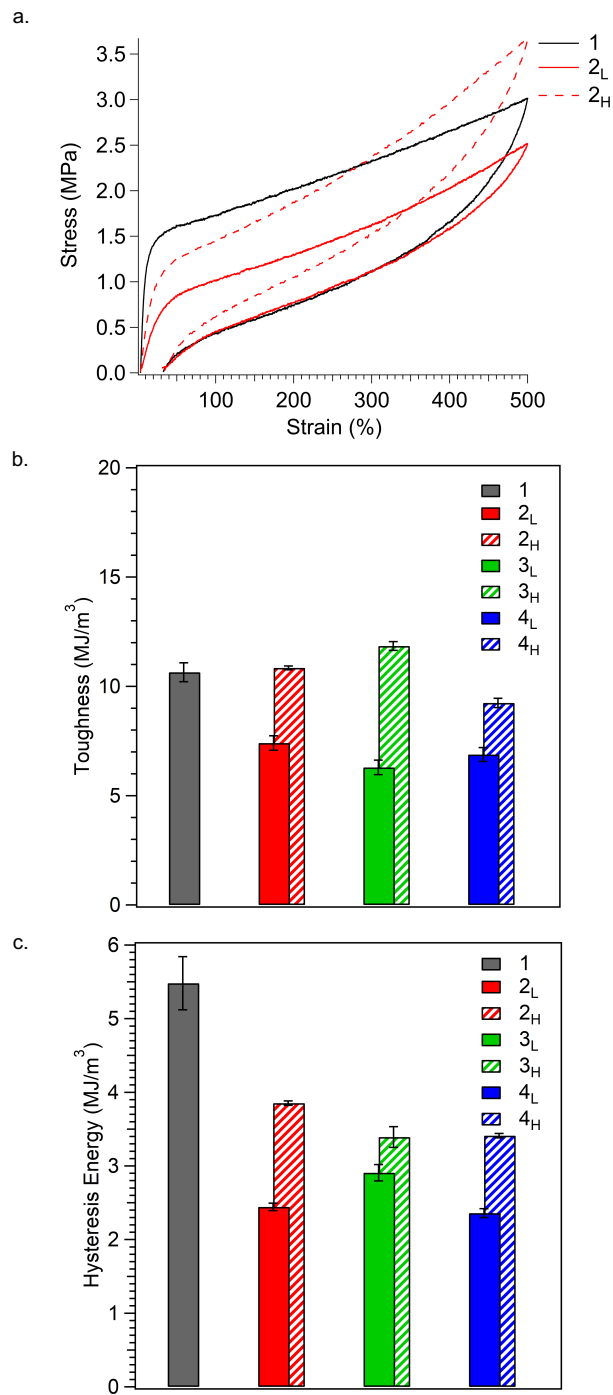


Figure 2.5 (a) Representative stress-strain curves for the load/unload cycle for polymers stretched to 500% elongations. Results are summarized as bar graphs showing (b) toughness and (c) hysteresis energy for the load/unload cycle. All values are an average of at least three measurements. Stress-strain curves and results from stretching all samples to 100%, 300%, or 500% elongation can be found in Figure 2.9—2.13. See Table 2.5 for values.

glassy domains should increase toughness by resisting chain pullout, thereby enhancing the strength of bridging chains. Conversely, incorporating low MW chains should decrease toughness, as these chains are less resistant to chain pullout. Expectantly, we found that polymers with PS MWDs tailing towards higher MW were much tougher than polymers with MWDs tailing towards low MW (Figure 2.5b). At 500% elongation, the reference polymer 1 ($U_T = 11 \text{ MJ/m}^3$) is similar in toughness to polymers 2_H, 3_H, and 4_H, all having PS MWDs tailing towards higher molar mass ($U_T = 11 \text{ MJ/m}^3$, 12 MJ/m^3 , and 9.3 MJ/m^3 , respectively). In contrast, polymers 2_L, 3_L, and 4_L, have PS MWDs tailing towards lower molar mass and have significantly reduced toughness ($U_T = 7.4 \text{ MJ/m}^3$, 6.3 MJ/m^3 , and 6.9 MJ/m^3 , respectively). These results corroborate our hypothesis that MWD shape impacts bridge chain strength, specifically, that high MW chains positively impact bridge chains strength and low MW chains compromise such strength. Moreover, polymers with the same MWD shape but different dispersities are similarly tough, suggesting that MWD shape has profound influence on toughness. The trend in toughness observed at 500% elongation is also observed at 100% and 300% strain, indicating that the dependence of toughness on polymer composition remains constant throughout the entire stress/strain curve (Figure 2.12a and Figure 2.13a).

Perhaps most striking is that while MWD shape can be used to increase or decrease toughness relative to the reference polymer, hysteresis energy is significantly reduced for both MWD shapes (Figure 2.5c). At 500% elongation,

the reference polymer 1 has the highest hysteresis energy (5.5 MJ/m³), and simply by controlling the $\bar{D}_{PS}$, hysteresis energy can be reduced by up to 80% (entry 4_L). Additionally, changing the shape of the MWD offers the ability to fine tune hysteresis energy. Polymers with high MW tails in their MWDs (2_H, 3_H, and 4_H) have higher values for hysteresis energy (3.9 MJ/m³, 3.5 MJ/m³, and 3.4 MJ/m³, respectively) compared to polymers 2_L (2.4 MJ/m³), 3_L (2.9 MJ/m³), and 4_L (2.4 MJ/m³), each having low MW tails. We believe this dependence on MWD shape to be an effect of chain pullout at high extension. As more chains are pulled away from PS domains, the fraction of total PS chains contributing to the physically crosslinked network decreases, which reduces friction between polymer chains within PS domains. A reduction in internal chain-chain friction corresponds to a reduction in hysteresis energy.^{35,38,39} Expectantly, polymers with MWDs tailing towards low molar mass have the lowest values of hysteresis energy, since lower MW chains can be pulled away from PS domains more easily than higher MW chains. Using this internal friction-based argument, the overall reduction in hysteresis energy for polymers with increased $\bar{D}_{PS}$ relative to the reference polymer is then unsurprising, as polydisperse systems have already been shown to possess decreased internal friction relative to monodisperse systems.^{40–44}

2.4 Conclusions

Our results show that deliberate modification of MWDs affords polymers with the same block lengths but with considerably different material properties. We suspect that the entire MWD breadth and shape is responsible for varied properties. Specifically, increasing $\bar{D}_{PS}$ enhances initial flexibility by reducing Young's modulus and yield strength. Beyond yielding, increasing $\bar{D}_{PS}$ was found to increase strain hardening. Moreover, the skew of the MWD has important implications to material properties. We propose that increasing the portion of low MW PS chains leads to significant chain pullout from PS domains at relatively low strain, thus decreasing polymer stiffness as well as yield stress. Furthermore, by increasing the portion of high molar mass PS chains, we observed an increase in strength, strain hardening, and toughness, which we attribute to a reinforcement of bridging chains. These results demonstrate that control over MWD shape, or more specifically chain composition, facilitates the production of polymers with precisely tuned material properties. For applications in which high stiffness and yield strength are prioritized, the reference polymer 1 is perhaps most suitable. However, for applications in which failure due to heat generation is of particular concern, our polymers with broadened and skewed MWDs are advantageous. Particularly, polymer 3_H combines exceptional toughness with low hysteresis energy while maintaining excellent elasticity and tensile strength at 500% elongation. Further studies will investigate the role of

varied MWD shapes of multiple blocks in SIS copolymers on their material properties.

2.5 References

- (1) J. Zhu, B. Birgisson and N. Kringos, *Eur. Polym. J.* **2014**, *54*, 18–38.
- (2) S. V. Ranade, R. E. Richard and M. N. Helmus, *Acta Biomater.* **2005**, *1*, 137–144.
- (3) L. Pinchuk, G. J. Wilson, J. J. Barry, R. T. Schoephoerster, J.-M. Parel and J. P. Kennedy, *Biomaterials* **2008**, *29*, 448–460.
- (4) Kawabuchi, I. Ishii and A. Satoh. US Pat., 5 075 377, 1991.
- (5) D. St. Clair, D. Handlin Jr. and C. Willis. US Pat., 6 987 142 B2, 2006.
- (6) G. D. Airey, *Fuel* **2003**, *82*, 1709–1719.
- (7) C. W. Paul, in *Handbook of Adhesion Technology*, Springer Berlin Heidelberg, 2011, pp. 341–372.
- (8) X. Lu and U. Lsacsson, *Fuel* **1997**, *76*, 1353–1359.
- (9) R. A. Shanks and I. Kong, in *Advances in Elastomers I: Blends and Interpenetrating Networks*, Springer Berlin Heidelberg, 2013, pp. 11–45.
- (10) M. Morton, J. E. McGrath and P. C. Juliano, *J. Polym. Sci. Part C* **1969**, *26*, 99–115.
- (11) C. R. López-Barrón, A. P. R. Eberle, S. Yakovlev and A. J. Bons, *Rheol. Acta* **2016**, *55*, 103–116.
- (12) H. N. Ng, A. E. Allegrezza, R. W. Seymour and S. L. Cooper, *Polymer* **1973**, *14*, 255–261.

- (13) G. Moineau, M. Minet, P. Teyssié and R. Jérôme, *Macromol. Chem. Phys.* **2000**, *201*, 1108–1114.
- (14) J. M. Widin, A. K. Schmitt, A. L. Schmitt, K. Im and M. K. Mahanthappa, *J. Am. Chem. Soc.* **2012**, *134*, 3834–3844.
- (15) D. Broseta, G. H. Fredrickson, E. Helfand and L. Leibler, *Macromolecules* **1990**, *23*, 132–139.
- (16) D. T. Gentekos, J. Jia, E. S. Tirado, K. P. Barteau, D.-M. Smilgies, R. A. DiStasio and B. P. Fors, *J. Am. Chem. Soc.* **2018**, *140*, 4639–4648.
- (17) D. T. Gentekos and B. P. Fors, *ACS Macro Lett.* **2018**, *7*, 677–682.
- (18) D. T. Gentekos, R. J. Sifri and B. P. Fors, *Nat. Rev. Mater.*, **2019**, *4*, 761–774.
- (19) R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland and A. Anastasaki, *Chem. Sci.* **2019**, *10*, 8724–8734.
- (20) D. T. Gentekos, L. N. Dupuis and B. P. Fors, *J. Am. Chem. Soc.* **2016**, *138*, 1848.
- (21) V. Kottisch, D. T. Gentekos and B. P. Fors, *ACS Macro Lett.* **2016**, *5*, 796–800.
- (22) M. Nadgorny, D. T. Gentekos, Z. Xiao, S. P. Singleton, B. P. Fors and L. A. Connal, *Macromol. Rapid Commun.* **2017**, *38*, 1700352.
- (23) S. Domanskyi, D. T. Gentekos, V. Privman and B. P. Fors, *Polym. Chem.* **2019**, *11*, 326–336.

- (24) N. Corrigan, A. Almasri, W. Taillades, J. Xu and C. Boyer, *Macromolecules* **2017**, *50*, 33.
- (25) N. Corrigan, R. Manahan, Z. T. Lew, J. Yeow, J. Xu and C. Boyer, *Macromolecules* **2018**, *51*, 4553–4563.
- (26) T. Pakula, K. Saijo, T. Hashimoto and H. Kawai, *Macromolecules* **1985**, *18*, 1294–1302.
- (27) M. Sabouri-Ghomi, S. Ispolatov and M. Grant, *Phys. Rev. E* **1999**, *60*, 4460–4464.
- (28) J. Parker and J. Rottler, *Macromolecules* **2015**, *48*, 8253–8261.
- (29) Takano, I. Kamaya, Y. Takahashi and Y. Matsushita, *Macromolecules* **2005**, *38*, 9718–9723.
- (30) K. Karatasos, S. H. Anastasiadis, T. Pakula and H. Watanabe, *Macromolecules* **2000**, *33*, 523–541.
- (31) Makke, O. Lame, M. Perez and J.-L. Barrat, *Macromol. Rapid Commun.* **2012**, *45*, 8445–8452.
- (32) J. A. Odell and A. Keller, *Polym. Eng. Sci.*, **1977**, *17*, 544–559.
- (33) Buckley, C P; De Focatiis, D S A; Prisacariu, in *Constitutive Models for Rubber VII*, Taylor & Francis, 2011, pp. 3–10.
- (34) Daniel, I. W. Hamley and K. Mortensen, *Polymer* **2000**, *41*, 9239–9247.
- (35) V. V. Sorokin, G. V. Stepanov, M. Shamonin, G. J. Monkman, A. R. Khokhlov and E. Y. Kramarenko, *Polymer* **2015**, *76*, 191–202.
- (36) S. F. Edwards and T. A. Vilgis, *Reports Prog. Phys.* **1988**, *51*, 243–297.

- (37) S. Siriwardena, H. Ismail, U. S. Ishiaku and M. C. S. Perera, *J. Appl. Polym. Sci.* **2002**, *85*, 438–453.
- (38) J. T. Bauman, in *Fatigue, Stress, and Strain of Rubber Components*, Carl Hanser Verlag, 2008, ch. 2, pp. 9–18.
- (39) S. Schollenberger and K. Dinbergs, *J. Elastomers Plast.* **1979**, *11*, 58–91.
- (40) R. L. Ballman and R. H. M. Simon, *J. Polym. Sci. Part A.* **1964**, *2*, 3557–3575.
- (41) C. K. Shih, *Trans. Soc. Rheol.* **1970**, *14*, 83–114.
- (42) H. L. Wagner and K. F. Wissbrun, *SPE Trans.* **1962**, *2*, 222–226.
- (43) G. Kraus and J. T. Gruver, *J. Appl. Polym. Sci.* **1965**, *9*, 739–755.
- (44) M. W. Collis and M. R. Mackley, *J. Nonnewton. Fluid Mech.* **2005**, *128*, 29–41.

2.6 Appendix

2.6.1 Materials

All reactions were performed in a Unilab MBraun Glovebox with a nitrogen atmosphere. *Sec*-butyllithium (*sec*-BuLi, Sigma Aldrich, 1.4 M in cyclohexane), butylhydroxytoluene (BHT) (TCI, >99.0%), chloroform-D (CDCl_3 , Cambridge Isotope Laboratories Inc., 99.8%), methanol (MeOH, 99.8%, Fisher Scientific), and dichloromethane (DCM, 99.5%, Fisher Scientific) were used without further purification. Styrene (Sigma Aldrich, 99+%), isoprene (Sigma Aldrich, 99+%), and diphenylethylene (DPE, Sigma Aldrich, 97%) were dried over calcium hydride (CaH_2) (ACROS organics, 93% extra pure, 0-2 mm grain size) for a minimum of 24 h. Styrene and DPE were vacuum transferred and degassed by three freeze-pump-thaw cycles. Isoprene was vacuum transferred onto activated 4Å molecular sieves (EMD Chemicals, 8-12 mesh beads) for further drying and after 48 hours was vacuum transferred and degassed by three freeze-pump-thaw cycles. Molecular sieves were activated under vacuum at 180 °C overnight. Cyclohexane was degassed by two freeze-pump-thaw cycles before a 1:1.2 molar ratio of DPE and *sec*-BuLi was added under a nitrogen blanket until a deep red colour was sustained. This solution was stirred for a minimum of 1 hour. Cyclohexane was distilled under nitrogen from the DPE/*sec*-BuLi and additionally degassed by three freeze-pump-thaw cycles.

2.6.2 Analytical Methods

All polymer samples were analysed using a Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min. THF was used as the eluent and all number-average molecular weights (M_n), weight-average molecular weights (M_w), dispersities ($\bar{D}$), asymmetry factors (A_s), M_z and M_{z+1} for the first polystyrene block were calculated from refractive index chromatograms against TSKgel polystyrene standards. Conversions were determined by ^1H nuclear magnetic resonance (NMR) spectra obtained on a Bruker 500 MHz NMR spectrometer in CDCl_3 , as were the M_n s for the diblock and triblock copolymers.

2.6.3 Synthesis

Synthesis of SIS copolymer with narrow MWDs

A 20 mL scintillation vial equipped with a magnetic stirrer was flame dried, brought into the glovebox, and charged with 14 mL of cyclohexane and 275 μL of styrene (2.4 mmol). A *sec*-BuLi stock solution in cyclohexane (0.1 M) was prepared for the reactions. The stir plate was set to 600 rpm, and 200 μL of *sec*-BuLi (0.02 mmol) was quickly added in one portion, giving a yellow solution indicating formation of the polystyryl anion. The reaction was capped and stirred for approximately 4 h, allowing for full monomer conversion. Then, 2.3 mL of isoprene (23 mmol) was added and the reaction colour quickly faded from yellow to clear, indicative of the polyisoprenyl anion. The stir plate was adjusted to 1000 rpm to account for the increased viscosity of the

polyisoprenyl anion. After 12 h, 275 μ L styrene (2.4 mmol) was added and the reaction vial was placed in a heating block equipped with a thermocouple. The reaction was heated to 40 $^{\circ}$ C and allowed to stir for 5 h. The colour of the reaction slowly changed from clear to yellow. The polymerization was quenched with addition of BHT and vigorously shaken until the reaction colour completely faded. The reaction vial was removed from the glovebox and the polymer was precipitated once from MeOH. The polymer was dissolved in DCM and 0.4 mL of BHT in DCM (10 mg BHT/1 mL DCM) was added as a stabilizer. The polymer solution was concentrated via rotary evaporation and polymers were dried in a vacuum oven at 60 $^{\circ}$ C for 12 h.

Synthesis of SIS copolymer with a skewed MWD

A 20 mL scintillation vial equipped with a magnetic stirrer was flame dried, brought into the glovebox, and charged with 2 mL of cyclohexane and 275 μ L of styrene (2.4 mmol). A *sec*-BuLi stock solution in cyclohexane (0.033 M) was prepared for the reactions and a total volume of 650 μ L of the solution was drawn into a 1 mL syringe and then mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Tables Table 2.1–Table 2.2), which would dispense a total volume of 615.3 μ L (0.02 mmol) of the initiator solution. Once the needle was submerged into the reaction mixture, the stir plate was set to 350 rpm and the addition program was started. At full addition of *sec*-BuLi, the reaction was capped and stirred at 500 rpm until full conversion of styrene to polystyrene was reached. 12 mL of cyclohexane

followed by 2.3 mL of isoprene (23 mmol) were next added. The reaction colour quickly faded from yellow to clear after addition of isoprene. The stir plate was adjusted to 1000 rpm to account for the increased viscosity of the polyisoprenyl anion. After 12 h, 275 μ L styrene (2.4 mmol) was added and the reaction vial was placed in a heating block equipped with a thermocouple. The reaction was heated to 40 $^{\circ}$ C and allowed to stir for 5 h. The colour of the reaction slowly changed from clear to yellow. The polymerization was quenched with addition of BHT and vigorously shaken until the colour of the reaction completely faded. The reaction vial was removed from the glovebox and the polymer was precipitated once from MeOH. The polymer was dissolved in DCM and BHT (0.4 mL of 10 mg BHT/1 mL DCM) was added as a stabilizer. The polymer solution was concentrated via rotary evaporation. Polymers were dried in a vacuum oven at 60 $^{\circ}$ C for 12 h.

Initiator Addition Profiles

Constant Rate Addition Profiles

The synthesis was performed according to the general procedure. The New Era NE4000 Double Syringe Pump was programmed according to Table 2.1.

Table 2.1 Constant Rate Addition Profiles

Addition Time (min)	Addition Rate (μ L/h)	Total Volume (μ L)
50	739	615
67	551	615
100	369	615

Exponentially Ramped Addition Rate Profiles

The synthesis was performed according to the general procedure. All exponentially increasing addition profiles were programmed as a sequence of 20 step increments with each step corresponding to a phase in the New Era NE4000 Double Syringe Pump program, according to Table 2.2.

Table 2.2 Exponentially Ramped Rate of Addition Profiles

Step #	Rate ($\mu\text{L/h}$)			Volume /Step (μL)
	80 min	100 min	147 min	
1	4.4	3.5	2.4	0.3
2	6.2	4.9	3.4	0.4
3	8.7	6.9	4.8	0.6
4	12	9.7	6.7	0.8
5	17	14	9.4	1.1
6	24	19	13	1.6
7	33	27	18	2.2
8	47	37	26	3.1
9	65	52	36	4.3
10	91	73	50	6.1
11	128	102	71	8.5
12	179	143	99	12
13	251	200	138	17
14	351	281	194	23
15	491	393	271	33
16	687	550	379	46
17	962	770	531	64
18	1347	1078	743	90
19	1886	1509	1041	126
20	2641	2112	1457	176

2.6.4 Material Testing

Sample Preparation for Cyclic Testing

Compression moulding was carried out using a 4120 Hydraulic Unit Carver press, a stainless-steel dog bone mould, and PTFE protective sheets (CS Hyde). The dog bone mould was custom ordered from the Laboratory of Atomic and Solid State Physics Machine Shop at Cornell University. The mould was sprayed with PTFE (Sprayon, MR 311) to prevent polymer from adhering to the mould. Specimens were prepared

by compression moulding for 1 minute between PTFE protective sheets at 130 °C under 3,000 lbs of pressure. Samples were cooled to 25 °C by cooling the plates with a stream of water, and excess polymer was trimmed from the specimens. Final dog bone specimens had uniform dimensions with a cross sectional area of 1.86 mm².

Tensile Testing

Tensile properties of compression-moulded copolymer samples were analysed using a Zwick/Roell Z010 testing system equipped with pneumatic grips and analysed using Zwick/Roell TestXpert II v.3.5 software. Dog bone specimens were clamped using pneumatic grips pressurized to 120 psi. Samples were loaded to either 100, 300, or 500 percent strain, followed immediately by unloading to the original length. For both loading and unloading, a strain rate of 0.01 s⁻¹ was used. Toughness (U_T) was calculated as the area under the loading curve, while hysteresis energy (W_H) was calculated as the area between the loading and unloading curves. Areas were calculated using the trapezoidal method. Young's modulus (E) was determined from the loading curve as the slope of the linear elastic region at low (<10%) strain.

Dynamic Mechanical Analysis (DMA)

Polymers were compression moulded under 3,000 lbs of pressure for 1 minute at 130 °C into straight specimens. Stress relaxation and strain recovery data were obtained on a TA Instruments DMA Q800 fitted with tension grips. Samples were stretched to 5% strain and held there to afford a total stress relaxation time

of 10 minutes. Strain recovery was measured for 10 minutes after load removal. Each stress relaxation and strain recovery value are an average of three measurements.

2.6.5 General Procedure for Small-Angle X-ray Scattering (SAXS)

SIS samples were prepared by solution casting polymer samples (6 mL, 7 wt% in toluene) into aluminum pans and allowing the solvent to slowly evaporate. The samples were subsequently thermally annealed at 130 °C in a vacuum oven for 48 h before cooling to room temperature under vacuum. After annealing, polymers were removed from aluminum pans, and a small piece was cut from each polymer to be placed into the center of a stainless -teel washer (4.42 mm I.D., 9.53 mm O.D., 0.79 mm thickness). The washers were sealed between Kapton tape and were used directly for the small-angle X-ray scattering measurements which were performed at the G1 beamline at Cornell High Energy Synchrotron Source (CHESS). 2D-SAXS patterns were recorded with a Dectris Eiger 1M detector (1030 x 1065 pixels, 77 x 80 mm² active area) at a sample to detector distance of 2.027 m and an X-ray wavelength (λ) of 1.252 Å. The data was corrected for detector response, calibrated with silver behenate, and, using the Nika package in Igor Pro,¹ reduced by azimuthally integrating the 2D pattern to acquire a 1D plot of intensity versus the scattering wavevector (q).

2.6.6 Supplementary Data

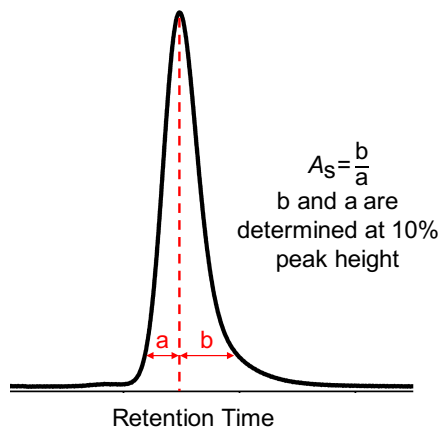


Figure 2.6 Illustration for the calculation of the asymmetry factor (A_s).

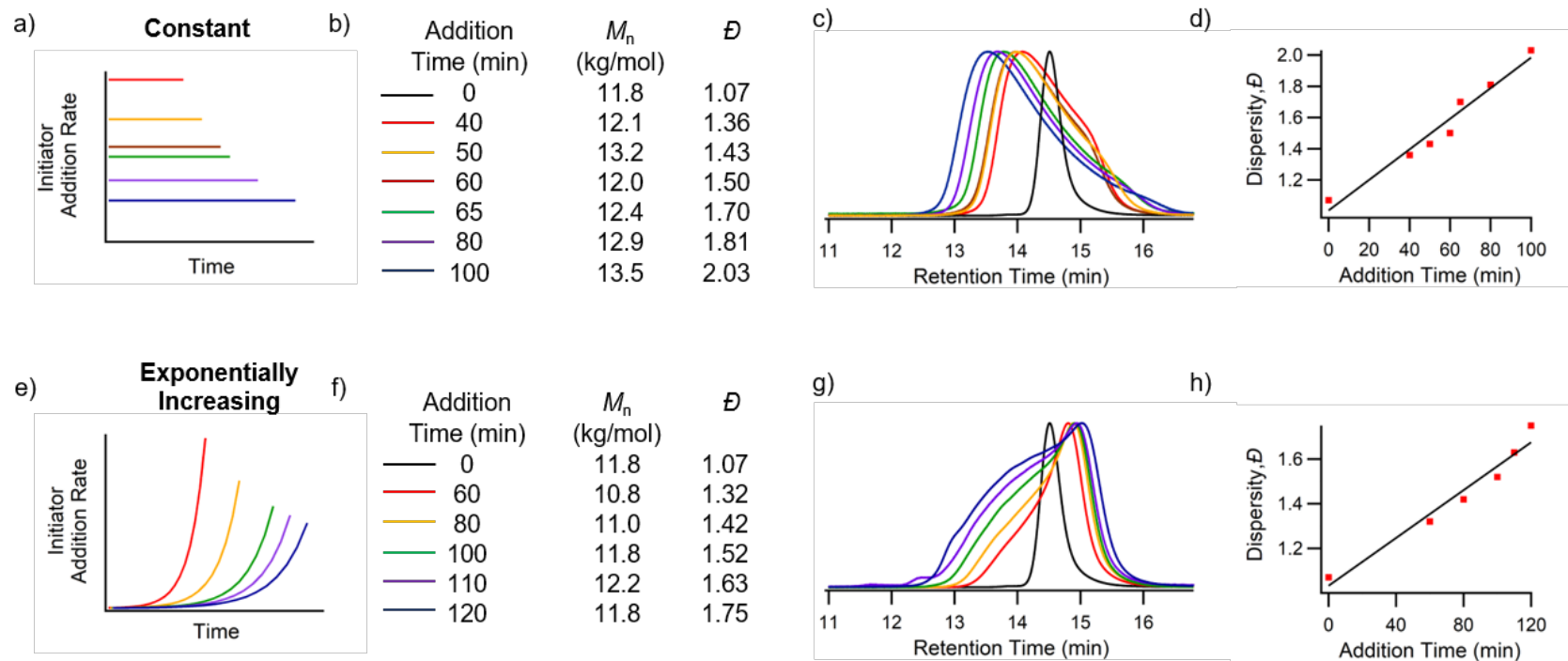


Figure 2.7 Controlling the shape and breadth (dispersity, $\bar{D}$) of the MWD of the first PS block in PS-*b*-PI-*b*-PS (SIS) triblock copolymer with constant (a-d) and exponentially ramped (e-h) rates of initiator addition

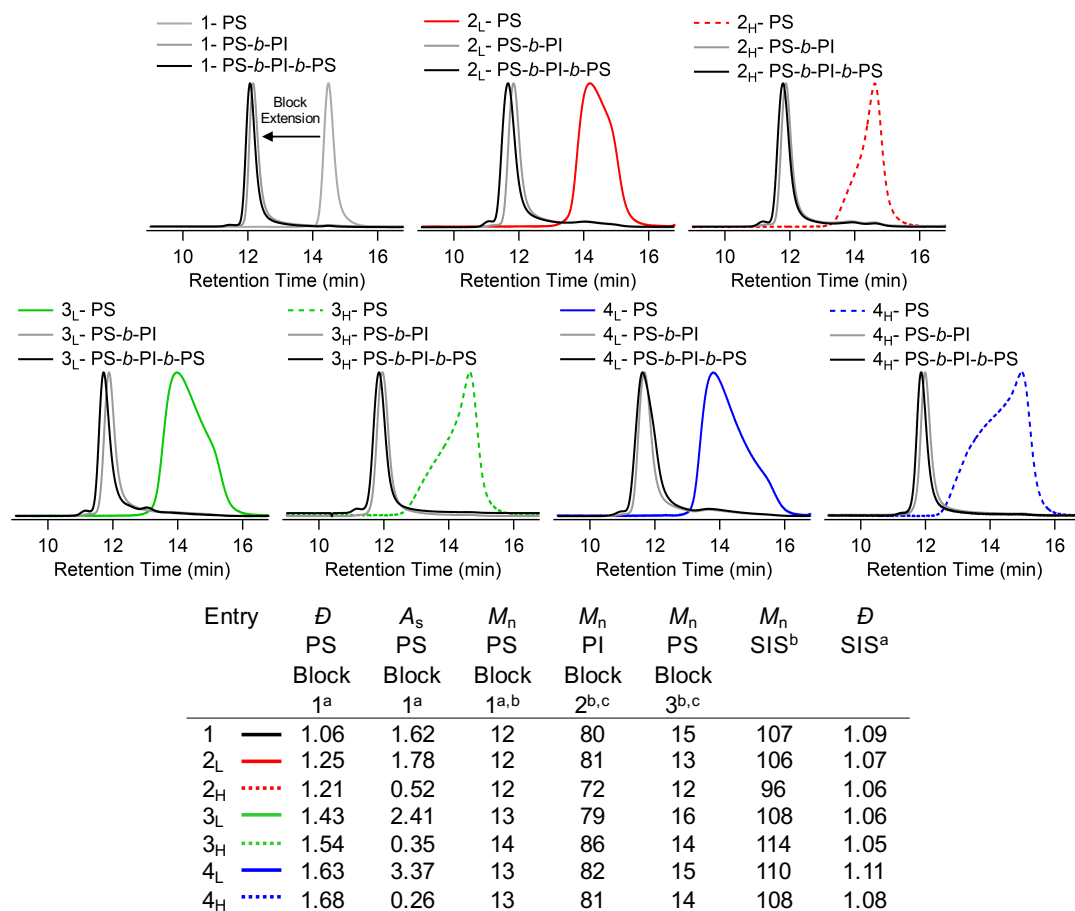


Figure 2.8 Library of SIS triblock copolymers prepared via chain extension from PS with varying degrees of skewness and $\bar{D}$ ^aDetermined from RI GPC traces. ^b M_n s are given in kg/mol. ^cDetermined by ¹H NMR spectra. Subscripts “L” and “H” indicate the direction of tailing in the first PS block MWD, either towards low or high molar mass species.

Table 2.3 Average Yield Stress and Yield Strain

Entry		$\bar{D}$ PS Block 1	A_s PS Block 1	Yield Stress (MPa)	Yield Strain (%)
1	—	1.06	1.62	1.5	27
2 _L	—	1.25	1.78	0.8	44
2 _H	...	1.21	0.52	1.2	36
3 _L	—	1.43	2.41	0.7	38
3 _H	...	1.54	0.35	1.1	38
4 _L	—	1.63	3.37	0.7	48
4 _H	...	1.68	0.26	0.9	42

Table 2.4 Average Strain Hardening Rates

Entry		$\bar{D}$ PS Block 1	A_s PS Block 1	Strain Hardening 1 (MPa/ ϵ)	Strain Hardening 2 (MPa/ ϵ)
1	—	1.06	1.62	0.3	0.3
2 _L	—	1.25	1.78	0.3	0.5
2 _H	...	1.21	0.52	0.5	0.6
3 _L	—	1.43	2.41	0.3	0.4
3 _H	...	1.54	0.35	0.5	0.6
4 _L	—	1.63	3.37	0.3	0.5
4 _H	...	1.68	0.26	0.4	0.6

Due to the nonlinearity of the stress/strain curves following yielding, stress/strain curves were divided into two regions each with linear slopes. Strain hardening 1 is the slope measured from the yield strain to a strain (ϵ) of three (corresponding to 300% elongation). Strain hardening 2 is the slope measured from $\epsilon = 3$ to $\epsilon = 5$ (corresponding to 300-500% elongation).

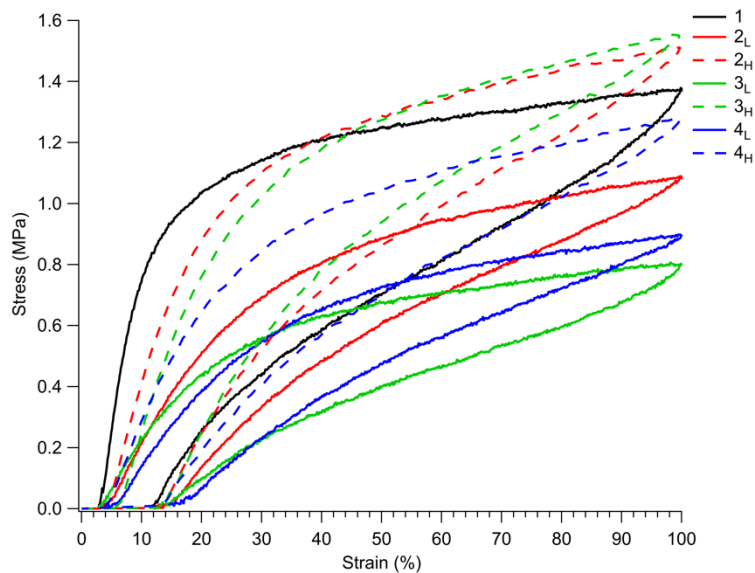


Figure 2.9 Stress-strain curves showing loading/unloading cycle for polymers stretched to 100% elongation. Each displayed stress-strain curve is an average of three specimens.

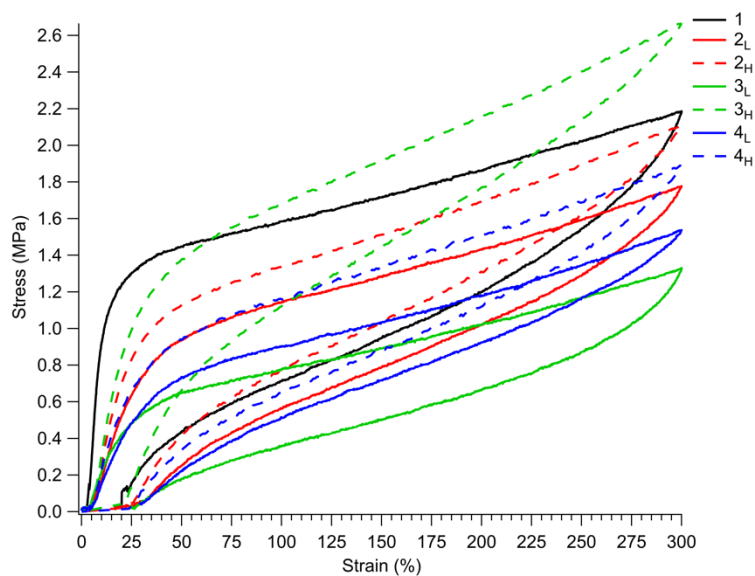


Figure 2.10 Stress-strain curves showing loading/unloading cycle for polymers stretched to 300% elongation. Each displayed stress-strain curve is an average of three specimens.

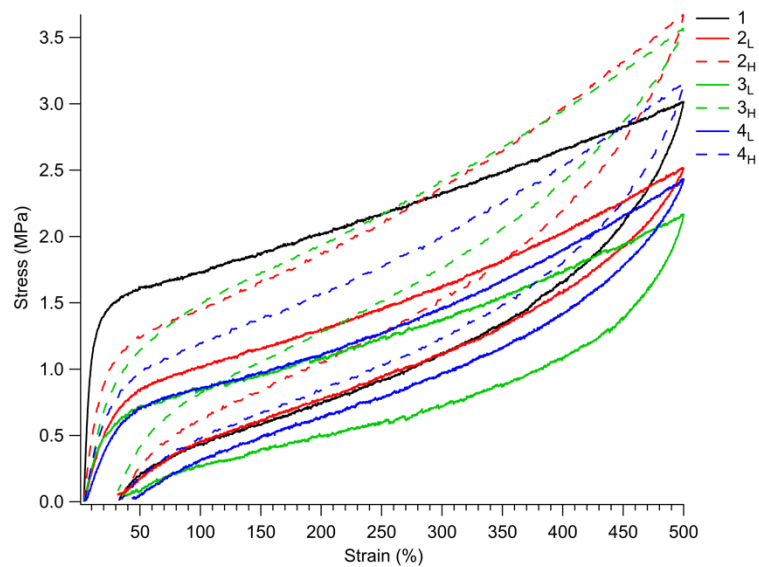


Figure 2.11 Stress-strain curves showing loading/unloading cycle for polymers stretched to 500% elongation. Each displayed stress-strain curve is an average of three specimens.

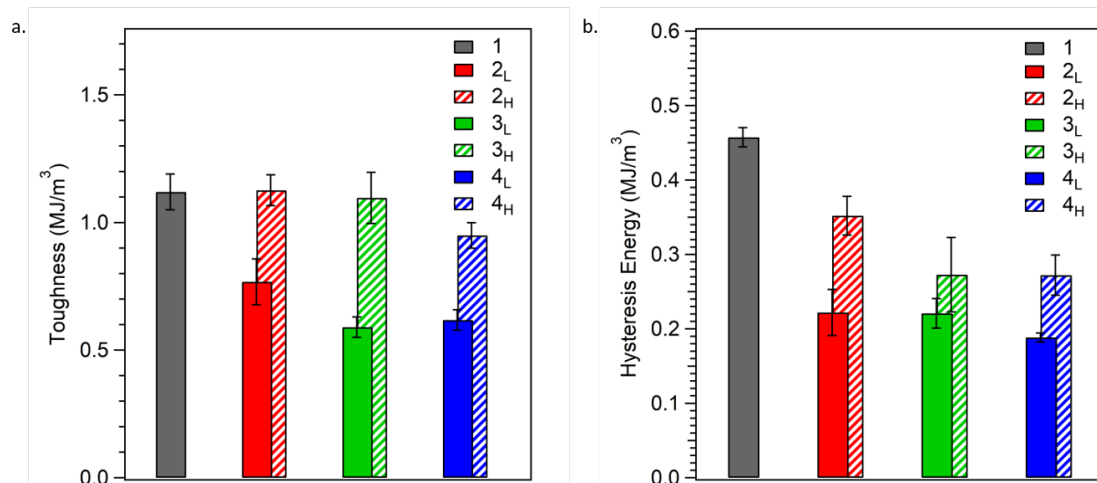


Figure 2.12 Bar graphs showing (a) toughness or (b) hysteresis energy for the load/unload cycle for polymers stretched to 100% elongation. Values are an average of three measurements.

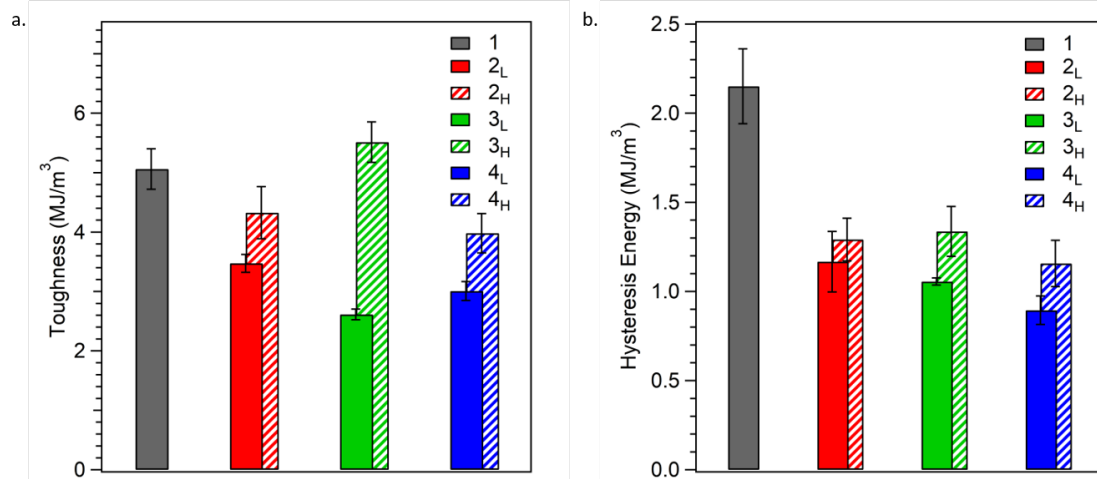
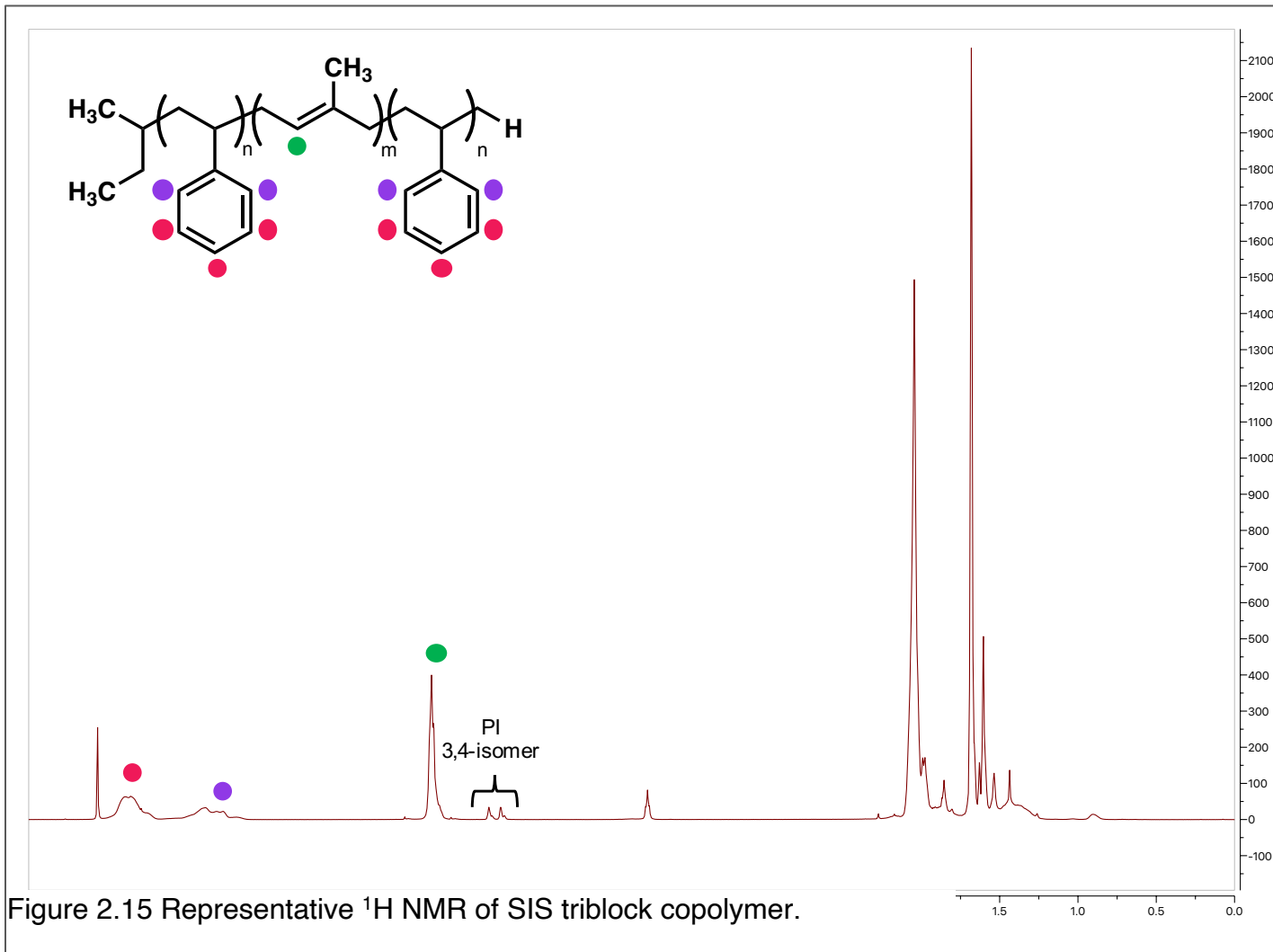


Figure 2.13 Bar graphs showing (a) toughness or (b) hysteresis energy for the load/unload cycle for polymers stretched to 300% elongation. Values are an average of three measurements.

Table 2.5 Average hysteresis energy (W_H) and toughness (U_T) for loading/unloading cycle

Entry	$\bar{D}$ PS	A_s PS	100% Strain		300% Strain		500% Strain	
			W_H	U_T	W_H	U_T	W_H	U_T
	Block 1	Block 1	(MJ/m ³)		(MJ/m ³)		(MJ/m ³)	
1 —	1.06	1.62	0.5	1.1	2.2	5.1	5.5	11
2 _L —	1.25	1.78	0.2	0.8	1.2	3.5	2.4	7.4
2 _H ···	1.21	0.52	0.4	1.1	1.3	4.3	3.9	11
3 _L —	1.43	2.41	0.2	0.6	1.1	2.6	2.9	6.3
3 _H ···	1.54	0.35	0.3	1.1	1.3	5.5	3.5	12
4 _L —	1.63	3.37	0.2	0.6	0.9	3.0	2.4	6.9
4 _H ···	1.68	0.26	0.3	1.0	1.2	4.0	3.4	9.3



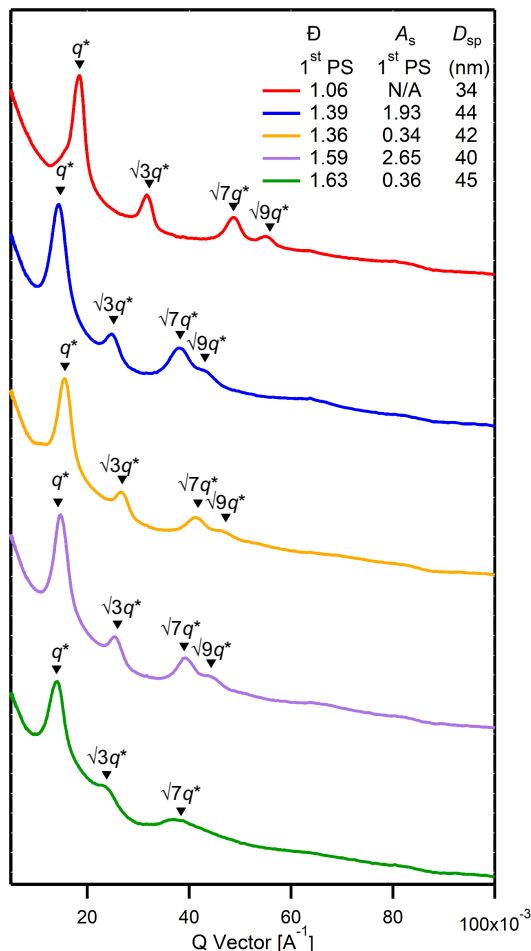


Figure 2.16 Small-angle x-ray scattering (SAXS) traces of SIS samples with similar polymer composition and MWD features as those presented in the main text.

Traces are offset for visual clarity. The volume fraction of PS is 0.22 in each sample, and the total molecular weights are as listed (top-to-bottom): 96, 101, 110, 109, and 109 kg/mol. Domain spacing was determined from the position of the principle wavevector ($D_{sp} = 2\pi/q^*$). The indexed reflections indicate that all of the polymers share the same morphology of hexagonally packed cylinders.

Table 2.6 Stress Relaxation and Strain Recovery from Dynamic Mechanical Analysis

Entry		$\bar{D}$ PS Block 1	A_s PS Block 1	Total Stress Relaxation (%)	Total Strain Recovery (%)
1	—	1.06	1.62	55	53
2 _L	—	1.25	1.78	36	77
2 _H	⋯	1.21	0.52	27	84
3 _L	—	1.43	2.41	46	65
3 _H	⋯	1.54	0.35	21	86
4 _L	—	1.63	3.37	38	85
4 _H	⋯	1.68	0.26	33	81

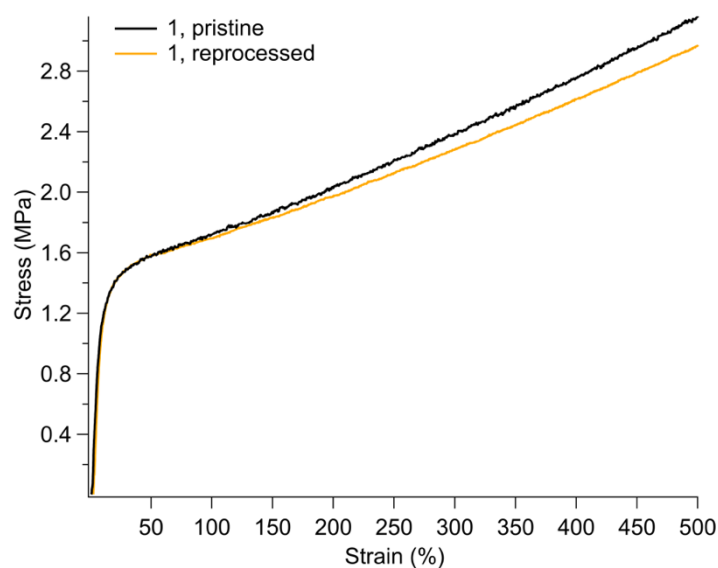


Figure 2.17 Stress/strain curves of reference polymer 1 in pristine condition (black curve) and the same polymer after being reprocessed several times (orange curve).

2.6.7 References for Appendix

- (1) Ilavsky, J. Nika: Softward for Two-Dimensional Data Reduction. *J. Appl. Cryst.* 2012, **45**, 324.
- (2) J. J Kirkland, W. W. Yau, H. J. Stoklosa, and C. H. J. Dilks, *J. Chromatogr. Sci.* 1977, **15**, 303-316.

CHAPTER 3

SHIFTING BOUNDARIES: CONTROLLING MOLECULAR WEIGHT DISTRIBUTION SHAPE FOR MECHANICALLY ENHANCED THERMOPLASTIC ELASTOMERS

3.1 Abstract

Thermoplastic elastomers (TPEs) based on polystyrene (PS) are commonplace in society. The elastomeric properties of these materials are often sacrificed to increase mechanical properties such as stiffness, strength, and toughness. We sought to produce stiff, strong, and tough TPEs that retain their elastomeric properties by shifting the lamellar phase boundary toward higher PS content. By precisely controlling the molecular weight distribution (MWD) shape of one PS block in polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), we produced elastomeric continuous phase TPEs at atypically high PS volume fractions, shifting the lamellar phase boundary from 0.33 in triblocks with a narrow MWD PS block to ~ 0.39 in triblocks with a broadened MWD PS block. Furthermore, we observed hexagonal/lamellar phase coexistence at a PS volume fraction of 0.39 when the MWD shape of the first PS block was asymmetric. These materials exhibit enhanced mechanical

properties consistent with high volume fractions of PS and elastomeric properties consistent with continuous morphologies.

3.2 Introduction

Thermoplastic elastomers (TPEs) are ubiquitous to everyday life, with applications from shoe soles and pressure sensitive adhesives to car parts and pavement.^{1–6} These materials are triblock copolymers in which the end blocks form hard thermoplastic phases and the midblock forms an elastomeric phase.^{7,8} Given the high-volume usage of these materials, there is a constant need to develop TPEs that are both strong and elastic.⁸ Unfortunately, there currently exists a limitation—as the strength of TPEs increases, elastomeric properties begin to decrease.^{9–12} Stiffer and stronger TPEs can be realized by increasing the volume fraction of the hard block. Upon increasing the volume fraction to roughly 0.3, desirable rubbery behaviors, such as smooth yielding and high extensibility, begin to diminish.¹³ This phenomenon has been attributed to a shift from a morphology with a continuous matrix of the rubbery block (hexagonally packed cylinders, HEX) to a discontinuous (lamellar, LAM) morphology.^{9–12} We posited that shifting the LAM phase boundary to higher volume fractions of hard block would expand the HEX phase window with glassy minority component and enable the production of remarkably stiff, strong, and tough TPEs that retain their elastomeric properties.

We sought to change the onset at which this morphology transition occurs by altering the molecular weight distribution (MWD) shape. It has been previously shown that changes in the MWD can impact the phase behavior of block copolymers. Matyjaszewski and Bockstaller elegantly demonstrated that a symmetrically polydisperse block within AB block copolymers promoted metastable morphologies, such as hexagonally perforated lamellae.¹⁴ Mahanthappa and coworkers observed similar stabilization effects when the MWD of the polybutadiene block in polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblocks was broadened.^{15,16} Numerous other accounts have reported altering phase behavior through block dispersity and attributed these effects to relaxed chain stretching and reduced packing frustration, prompting interfacial curvature toward the more disperse block.^{17–25} Because interfacial

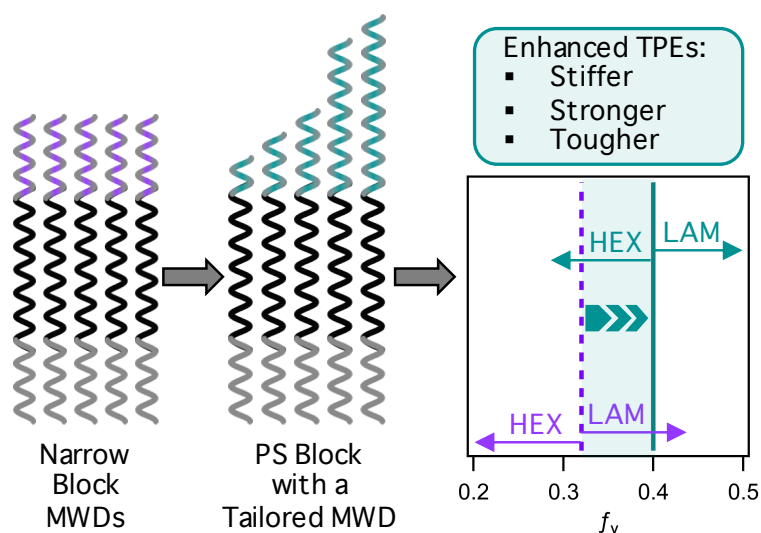


Figure 3.1 Changing the MWD shape of the first polystyrene (PS) block in polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) thermoplastic elastomers (TPEs) shifts the lamellar phase boundary toward higher PS content, enabling production of TPEs with enhanced mechanical properties

curvature can be easily exploited in star block copolymers, this architecture has garnered significant interest.²⁶ Such architectures have been shown to strongly shift phase boundaries toward higher volume fractions of hard block and promote formation of unique morphologies.^{26–35} Due to their unique properties, star block copolymers have been commercialized by several companies including Kraton Polymers and Dexco Polymers.^{36–38} As star block copolymers have been successfully employed for the deflection of phase boundaries, we aimed to shift phase boundaries in linear TPEs. We postulated that variations in the *shape* rather than the breadth alone of the MWD of one block within a linear TPE could alter the onset at which phase transitions occur (Figure 3.1).

Various methods have been devised to control polymer MWD features.^{14–19,21,22,24,39–53} In particular, our group has developed an efficient and modular strategy for controlling MWD shape.^{55–63} Using a metered addition of initiator, we are able to deterministically control MWD features by varying the initiator addition profile. We have employed this strategy in a variety of different polymerizations, including nitroxide-mediated polymerization,⁵⁵ atom transfer radical polymerization,⁵⁵ anionic polymerization,^{56–59,61,62} and coordination-insertion polymerization.⁶³ Our ability to precisely control MWD features has enabled us to systematically study the influence of MWD shape on various polymer properties, including phase segregation, viscosity, and tensile properties.^{56–59,62,63} In one such study, we demonstrated the considerable influence of MWD shape on phase behavior in diblock copolymers of PS and

poly(2-vinylpyridine) (P2VP).⁵⁹ By changing the shape of the PS block in these copolymers, we observed several disparate morphologies at the same molecular weights and volume fractions and shifted the lamellar phase boundary to 35% higher volume fractions of PS. More recently, we showed that variations in the MWD features of a single polystyrene (PS) end block in polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers had a profound influence on mechanical properties, including stiffness, yield strength, toughness, tensile strength, and hysteresis energy.⁶² Because the polymers in this study had PS volume fractions (f_v^{PS}) of ~ 0.20 , which is well below the LAM phase boundary, we could not assess the impact that MWD shape has on morphology transitions. We hypothesized that MWD shape would widen the HEX phase window by shifting the LAM phase boundary in higher f_v^{PS} SIS materials (e.g., $f_v^{PS} > 0.20$). We anticipated that this MWD shape induced shift in the LAM phase boundary would facilitate production of exceptionally stiff, strong, and tough TPEs that retain their rubber-like characteristics.

Herein, we report the synthesis, phase behavior, and material properties of SIS TPE which the first PS block has a tailored MWD shape. We found that the MWD shape of the first PS block can be used to shift the LAM phase boundary toward higher f_v^{PS} , affording TPEs that retain their rubber-like flexibility but have significantly higher values of stiffness, strength, and toughness. Significantly, our method for shifting the LAM phase boundary enabled us to independently examine the influence of morphology and f_v^{PS} on

the mechanical properties of SIS. We found that whereas yielding behavior is dictated by morphology, polymer stiffness, tensile strength, and toughness depend upon f_v^{PS} .

3.3 Results and Discussion

3.3.1 Synthesis

We began by preparing four sets of polymers with average f_v^{PS} of 0.27, 0.33, 0.39, or 0.42 *via* sequential anionic polymerization of styrene and isoprene (

Table 3.1; Figure 3.2a and Figure 3.7—Figure 3.10). Whereas the f_v^{PS} remained constant within each set, the MWD features of the first PS block were systematically varied to probe the effects of dispersity ($\mathcal{D}^{\text{PS}}$) and MWD shape on polymer morphology and material properties. Using an instantaneous initiator addition profile, polymers with a narrow (N) $\mathcal{D}^{\text{PS}}$ were synthesized (purple trace in Figure 3.2b;

Table 3.1, polymers 0.27-N, 0.33-N, 0.39-N, and 0.42-N). The MWDs of the first PS block in polymers prepared using a constant rate of initiator addition were symmetrical (S, asymmetry values (A_s) ~ 1.0) with $\mathcal{D}^{\text{PS}}$ s ~ 1.2 (orange trace in Figure 3.2b;

Table 3.1, polymers 0.27-S, 0.33-S, 0.39-S, and 0.42-S). Using an exponentially increasing rate of initiator addition, PS blocks with $\mathcal{D}^{\text{PS}}$ s ~ 1.2 and

asymmetric distributions with tailing (T) toward high molar mass chains ($A_s < 1.0$) were prepared (teal trace in Figure 3.2b;

Table 3.1, polymers 0.27-T, 0.33-T, 0.39-T, and 0.42-T).

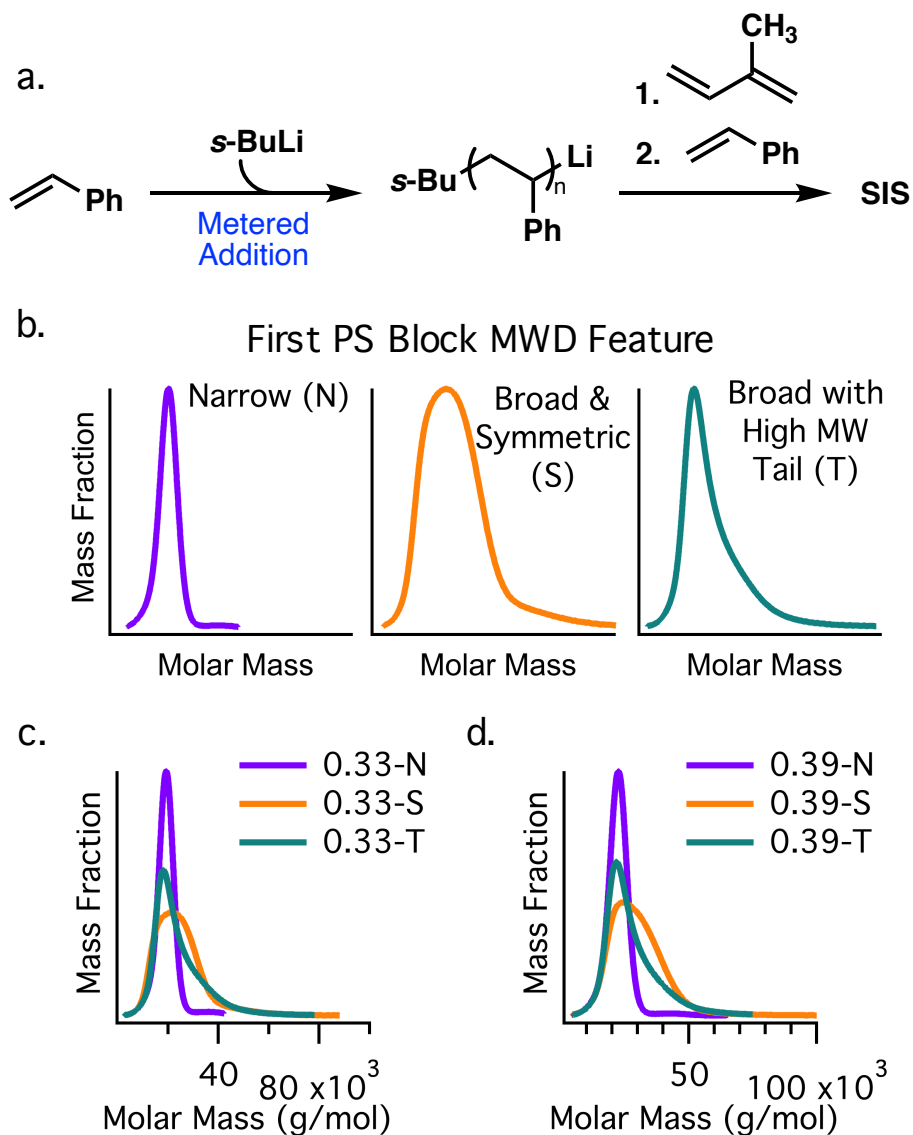


Figure 3.2 (a) General strategy for the synthesis of SIS TPEs in which the first PS block has a tailored MWD shape that is (b) narrow (purple trace), broad and symmetric (orange trace), or broad and asymmetric (teal trace). Differential distributions of the first PS block within SIS in which the average f_v^{PS} is (c) 0.33 or (d) 0.39

Table 3.1 Molecular and Morphological Characteristics of SIS Copolymers

Entry	Polymer ^a	f_v^{PSb}	$\bar{D}^{PSc,d}$	$A_s^{PSc,d}$	$M_n^{PSc,d}$ (kg/mol)	$\bar{D}^{SISc}$	M_n^{SISb} (kg/mol)	Phase ^e
1	0.27-N	0.28	1.07	1.74	15.9	1.06	90.0	HEX
2	0.27-S	0.26	1.20	1.02	18.2	1.18	94.9	HEX
3	0.27-T	0.27	1.27	0.42	13.9	1.06	100.5	HEX
4	0.33-N	0.33	1.07	1.79	17.2	1.04	106.7	LAM
5	0.33-S	0.34	1.17	1.33	18.1	1.12	97.6	HEX
6	0.33-T	0.32	1.16	0.71	17.9	1.09	87.6	HEX
7	0.39-N	0.39	1.07	1.74	19.8	1.04	96.0	LAM
8	0.39-S	0.38	1.16	1.05	22.7	1.05	106.1	LAM
9	0.39-T	0.39	1.14	0.72	21.4	1.13	101.9	Mixed
10	0.42-N	0.40	1.09	2.04	22.1	1.03	99.8	LAM
11	0.42-S	0.41	1.18	0.96	20.5	1.04	90.1	LAM
12	0.42-T	0.44	1.17	0.57	24.7	1.04	101.9	LAM

^aLabeled according to the average value of f_v^{PS} and the defining feature of the MWD for the first PS block, where N = narrow, S = broad and symmetric, and T = broad with a high MW tail. ^bCalculated using NMR spectroscopy and homopolymer densities at 140 °C of PS (0.969 g/mL) and 1,4-PI (0.83 g/mL).³⁹ ^cDetermined by SEC against PS standards. ^dValues are for the first PS block. ^eDetermined from the ratios of scattering peaks relative to the principal scattering wavevector, q^* , where HEX = hexagonally packed cylinders, LAM = lamellae, and Mixed = HEX/LAM.

3.3.2 Morphological Characterization

Morphologies were determined using *in-situ* thermal annealing small-angle x-ray scattering (SAXS) (Figure 3.3). In an attempt to observe any order-order transitions (OOTs) or order-disorder transitions (ODTs), we scanned at room temperature and at temperatures from 120–230 °C (Figure 3.11—Figure 3.22). Notably, the morphologies observed at 25 °C were similarly observed at all elevated temperatures, indicating that any OOTs/ODTs occur at temperatures above 230 °C. All three polymers with an average f_v^{PS} of 0.27 adopted a hexagonally packed cylinder (HEX) morphology (Figure 3.11—

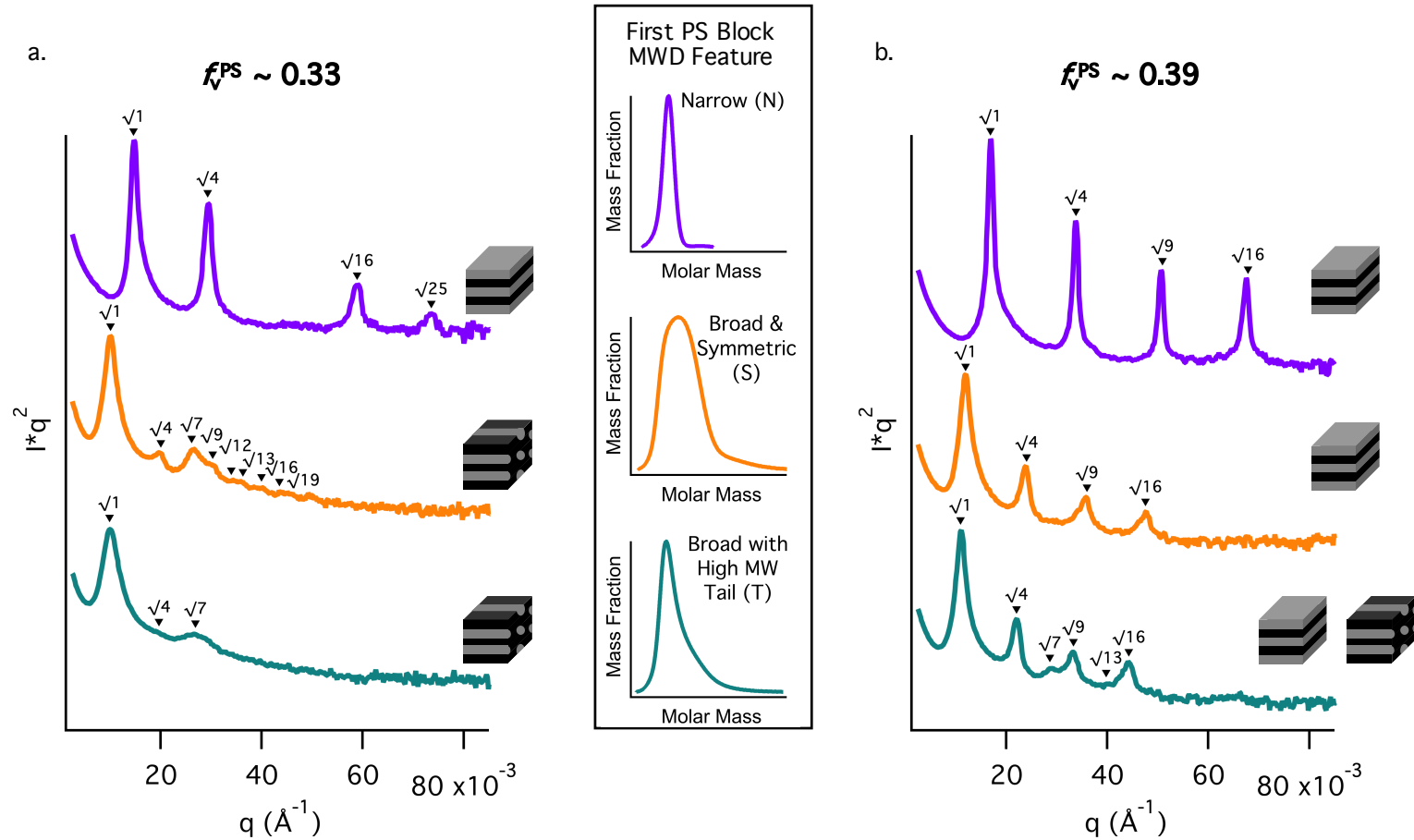


Figure 3.3 1-D SAXS traces obtained at 180 °C for SIS TPEs in which the MWD of the first PS block is varied and the average f_v^{PS} is (a) 0.33 or (b) 0.39. Inverted triangles mark the position of scattering peaks which are indexed as a ratio of q/q^* . Cartoon depictions of the assigned morphology are displayed next to each SAXS trace. For all other polymers as well as all other *in-situ* annealing temperatures, refer to Figure 3.11—Figure 3.22

Figure 3.13;

Table 3.1, entries 1–3). This result is in accordance with what we recently observed in SIS TPEs with $f_v^{PS} \sim 0.20$ and is unsurprising given that the LAM phase boundary typically resides at a f_v^{PS} of ~ 0.30 .^{13,62} All polymers at an average f_v^{PS} of 0.42 exhibited the same LAM morphology (Figures Figure 3.20–Figure 3.22;

Table 3.1, entries 10–12). These results suggest that neither MWD shape nor $\bar{D}^{PS}$ influence morphology at extremely low or high PS contents.

Given these results, we focused on understanding the impact of MWD shape on phase changes in samples with intermediate values of f_v^{PS} . At an average f_v^{PS} of 0.33 (Figure 3.2c;

Table 3.1, entries 4–6), the polymer with a narrow PS MWD (0.33-N) adopted a LAM morphology. Broadening the MWD shape either symmetrically (0.33-S) or asymmetrically (0.33-T) produced polymers in the HEX phase. These results are in good agreement with previous studies that have documented the impact of dispersity on the LAM phase boundary^{14–21,24} and suggest that MWD shape does not drastically impact phase behavior at this f_v^{PS} .

MWD shape and breadth influence morphology at a higher f_v^{PS} of 0.39 (Figure 3.2d;

Table 3.1, entries 7–9). Whereas the polymers with either a narrow PS MWD (0.39-N) or a symmetrically broad PS block (0.39-S) formed the LAM morphology, the polymer with an asymmetrically broadened PS MWD (0.39-T)

exhibited peaks consistent with both HEX and LAM morphologies. In particular, the reflections at $\sqrt{7}q^*$ and $\sqrt{13}q^*$ are indicative of the HEX phase and those at $\sqrt{4}q^*$, $\sqrt{9}q^*$, and $\sqrt{16}q^*$ are indicative of the LAM phase. As such, we suspect 0.39-T is mixed phase, having regions of both HEX and LAM.^{64,65}

Using these results, we constructed a pseudo-phase diagram (Figure 3.4). As highlighted in Figure 3.4, modifications to the MWD of the first PS block shift the normal LAM phase boundary from $f_v^{PS} \sim 0.33$ to higher values of f_v^{PS} . Upon symmetrically broadening the MWD, the LAM phase boundary is shifted to $f_v^{PS} = 0.38$ (Figure 3.4, orange dashed line). Similarly, the LAM phase boundary is shifted to just beyond $f_v^{PS} = 0.39$ when the MWD of the first PS block is asymmetrically broadened (Figure 3.4, teal dashed line).

The dispersity-induced shift in morphology from LAM to HEX in polymers with a f_v^{PS} near the typical LAM phase boundary (e.g., 0.33-S and 0.33-T) has been observed in other systems and is often attributed to increased interfacial curvature toward the disperse segment. Specifically, the broadened distribution of chain lengths reduces the entropic penalty associated with chain stretching required to fill the center of the domain. While longer chains fill the center of the domains, shorter chains can relax near the interface. The resulting shape of the interfacial curvature is a balance between the aforementioned entropic benefit

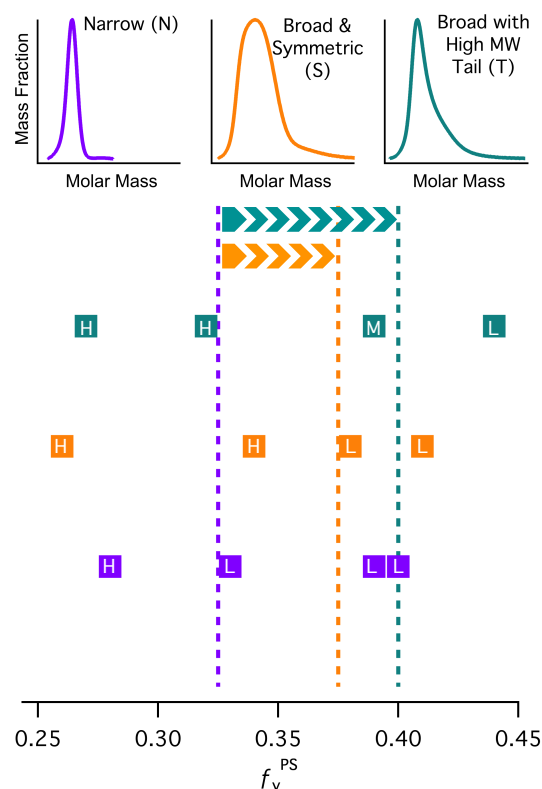


Figure 3.4 Phase diagram of SIS TPEs highlighting the shifts in the LAM phase boundary as a function of f_v^{PS} and the MWD shape of the first PS block (purple = narrow MWD, orange = broad and symmetric MWD, teal = broad MWD with tailing toward high MW). H = HEX, L = LAM, M = mixed HEX/LAM. with the enthalpic penalty associated with incurring a higher interfacial area.^{14–}

^{21,23,24,59,66–69} In this study, dispersity was not the only MWD feature that

influenced phase behavior; the shape of the MWD also impacted the morphology that was observed at higher f_v^{PS} . Whereas a broad and symmetric MWD resulted in LAM phase TPEs (0.39-S), a broad MWD accompanied by tailing toward higher molar mass chains resulted in HEX/LAM phase coexistence (0.39-T).

3.3.3 Mechanical Characterization

By controlling the MWD shape, we can produce polymers with the same f_v^{PS} but with different morphologies. As a result, we are able to examine the influence that morphology rather than f_v^{PS} or architecture (e.g., star block copolymers) has on mechanical properties. Because the polymers with the lowest and highest values of f_v^{PS} (0.27 and 0.42, respectively) did not display differences in morphology, we focused our studies on the polymers with an

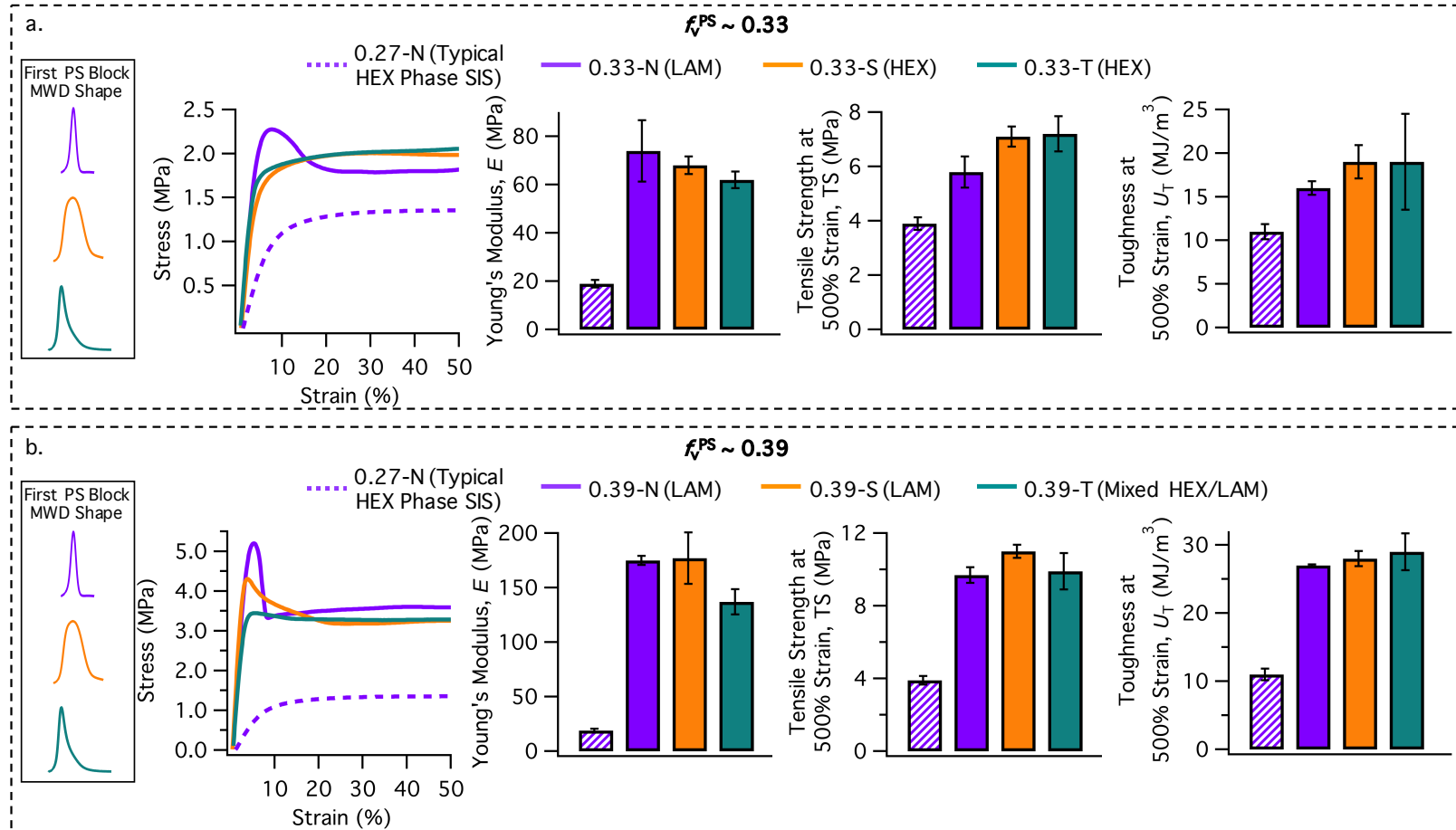


Figure 3.5 The material properties of SIS TPEs in which the first PS block has a tailored MWD (purple = narrow, orange = broad and symmetric, teal = broad and asymmetric) but overall similar average f_{vPS} of (a) 0.33 or (b) 0.39. From left to right: zoom-in of stress-strain curves highlighting yielding 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) is shown for comparison. Values of E , TS , and U_T are an average of three measurements.

average f_v^{PS} of 0.33 (Figure 3.5a;
Table 3.1, entries 4–6) and 0.39 (Figure 3.5b;
Table 3.1, entries 7–9).

The mechanical behavior of styrenic TPEs in regard to morphology has been extensively studied and is well-understood.^{9–12,30,33,70} Following the initial linear elastic region, styrenic TPEs undergo plastic deformation and strain hardening until breaking at high elongations. Values such as stiffness and tensile strength generally increase with f_v^{PS} due to the increased contribution of the physical crosslinks.^{9–12} Of particular interest is the yielding behavior of SIS, which varies depending on the morphology.^{9,33,71–74} SIS TPEs with discrete PS domains (e.g., HEX) exhibit “rollover” yielding in which a smooth transition occurs between the linear elastic region and subsequent strain hardening. In contrast, LAM phase SIS often displays pronounced yielding and necking occurring from the rupture of PS domains.^{9,33,71,72,75}

Consistent with previous reports documenting the mechanical behavior of TPEs, we found that morphology rather than f_v^{PS} impacts the type of yielding observed in these SIS materials.^{33,73,74} At an average f_v^{PS} of 0.33, a distinct yield point was only observed in the sample that adopted a LAM morphology (0.33-N, Figure 3.5a). The presence of this distinct yield point was accompanied by formation of a neck within the gauge length of the dogbone specimen. Only after the neck propagated throughout the entire gauge length, at approximately 140% strain, did the stress begin to increase again (Figure 3.24). This

yielding/necking behavior is characteristic of LAM phase SIS as well as thermoplastics.^{33,70–76} In contrast, the polymers that adopted a HEX morphology (0.33-S and 0.33-T) retained their rubbery characteristics, displaying a smooth “rollover” yield that was not accompanied by any necking. A similar trend was observed for samples with an average f_v^{PS} of 0.39; distinct yield points and necking were only observed in the materials that adopted a LAM morphology (0.39-N and 0.39-S, Figure 3.5b). In support of our morphology assignment as mixed HEX/LAM phase, a substantially less marked yield point and only minor neck formation were observed in 0.39-T. The yielding mode of the polymers with an average f_v^{PS} of 0.33 and 0.39 clearly demonstrate that the elastomeric characteristics of SIS TPEs depend upon morphology.

As expected, whereas morphology impacts elastomeric properties, f_v^{PS} impacts stiffness (Young’s modulus, E), tensile strength at 500% elongation (TS), and toughness at 500% elongation (U_T).^{9–12,77} Although we observed two different morphologies (LAM and HEX) at an average f_v^{PS} of 0.33, all polymers with this f_v^{PS} (0.33-N, 0.33-S, and 0.33-T) exhibited statistically indistinguishable values of E , TS, and U_T (Figure 3.5a). This trend is also apparent in the polymers with an average f_v^{PS} of 0.39; although both LAM and mixed phase morphologies were observed at this f_v^{PS} , these polymers (0.39-N, 0.39-S, and 0.39-T) exhibited similar values of E and statistically equivalent values of TS and U_T (Figure 3.5b). These examples highlight the importance of f_v^{PS} rather than morphology on the mechanical properties of SIS TPEs.

Our ability to access continuous and mixed phase (i.e., HEX and HEX/LAM, respectively) morphologies at higher f_v^{PS} has enabled us to produce SIS TPEs with increased stiffness, strength, and toughness. Typically, the maximum f_v^{PS} for HEX phase SIS is below 0.3 (as represented by 0.27-N, Figure 3.5). Whereas typical HEX phase SIS has an $E = 19$ MPa, HEX phase polymers 0.33-S and 0.33-T have E values above 60 MPa, which we attribute to their higher f_v^{PS} (0.27 versus 0.33, Figure 3.5a). The HEX/LAM polymer (0.39-T) that we produced has an even larger E (137 MPa), which again we attribute to its higher f_v^{PS} (0.39). Similar trends are observed for TS and U_T . The TS values of the high f_v^{PS} HEX and HEX/LAM polymers (0.33-S, 0.33-T, 0.39-T) are up to 2.5 times larger than the expected TS for HEX phase SIS (0.27-N, 3.9 MPa). Whereas the U_T for typical HEX phase SIS is 11 MJ/m³, the U_T for the high f_v^{PS} HEX and HEX/LAM polymers that we produced (0.33-S, 0.33-T, 0.39-T) ranges from 19–29 MJ/m³. To evaluate the influence of f_v^{PS} and morphology on hysteresis energy (W_H), we performed loading-unloading tensile experiments in which samples were stretched to 500% strain followed by immediate unloading (Figures Figure 3.39–Figure 3.42). We observed hysteresis typical of TPEs and found that W_H increased linearly with f_v^{PS} independent of morphology (Figure 3.46).^{78,79} The extraordinarily high values of E , TS, U_T , and W_H observed in these SIS TPEs demonstrate the power that controlling MWD shape can have on the production of next-generation materials.

3.4 Conclusion

In conclusion, we have used our temporal initiation method to precisely control the MWD shape and breadth of one PS block in SIS TPEs. We found that broadening the MWD symmetrically or asymmetrically shifts the LAM phase boundary from $f_v^{PS} \sim 0.33$ to ~ 0.39 . Asymmetry in the MWD shape resulted in HEX/LAM phase coexistence, highlighting the importance that both MWD shape and breadth have on the phase behavior of these materials. By controlling these MWD features, we generated morphologies (e.g., HEX and HEX/LAM) that typically cannot be accessed at these f_v^{PS} s, allowing for the decoupled analysis of the influence of morphology and f_v^{PS} on material properties. We found that elastomeric properties depend upon morphology whereas stiffness, strength, and toughness depend upon f_v^{PS} . By accessing continuous and mixed phase morphologies at high f_v^{PS} , we were able to produce TPEs that retain their elastomeric properties despite being exceptionally stiff, strong, and tough.

3.5 References

- (1) Deepalekshmi, P.; Visakh, P. M.; Mathew, A. P.; Chandra, A. K.; Thomas, S. Advances in Elastomers: Their Blends and Interpenetrating Networks- State of Art, New Challenges and Opportunities. In *Advances in Elastomers 1*; 2013; pp 1–9.
- (2) Martín-Martínez, J. M. Shoe Industry. In *Handbook of Adhesion Technology*; da Silva, L. F. M., Öchsner, A., Adams, R. D., Eds.; Springer International Publishing: Cham, 2018; pp 1483–1532.
- (3) Paul, C. W. Pressure-Sensitive Adhesives (PSAs). In *Handbook of Adhesion Technology*; da Silva, L. F. M., Öchsner, A., Adams, R. D., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; pp 341–372.
- (4) Naskar, K.; Babu, R. R. Thermoplastic Elastomers (TPEs) and Thermoplastic Vulcanizates (TPVs). In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S., Müllen, K., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 2517–2522.
- (5) Zhu, J.; Birgisson, B.; Kringos, N. Polymer Modification of Bitumen: Advances and Challenges. *Eur. Polym. J.* **2014**, *54*, 18–38.
- (6) Airey, G. D. Rheological Properties of Styrene Butadiene Styrene Polymer Modified Road Bitumens. *Fuel* **2003**, *82*, 1709–1719.
- (7) Lu, X.; Lsacsson, U. Influence of Styrene-Butadiene-Styrene Polymer Modification on Bitumen Viscosity. *Fuel* **1997**, *76*, 1353–1359.

- (8) Shanks, R. A.; Kong, I. General Purpose Elastomers: Structure, Chemistry, Physics and Performance. In *Advances in Elastomers I: Blends and Interpenetrating Networks*; 2013; pp 11–45.
- (9) Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E. *Thermoplastic Elastomers*, 2nd ed.; Hanser Publishers: Munich, 1996.
- (10) Holden, G.; Bishop, E. T.; Legge, N. R. Thermoplastic Elastomers. *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *26*, 37–57.
- (11) Holden, G.; Kricheldorf, H.; Quirk, R. *Thermoplastic Elastomers*, 3rd ed.; Hanser Publishers: Munich, 2004.
- (12) Drobny, J. G. Styrenic Block Copolymers. In *Handbook of Thermoplastic Elastomers*, 2nd ed.; William Andrew: Oxford, 2014; pp 175–194.
- (13) Matsen, M. W. Equilibrium Behavior of Asymmetric ABA Triblock Copolymer Melts. *J. Chem. Phys.* **2000**, *113*, 5539–5544.
- (14) Listak, J.; Jakubowski, W.; Mueller, L.; Plichta, A.; Matyjaszewski, K.; Bockstaller, M. R. Effect of Symmetry of Molecular Weight Distribution in Block Copolymers on Formation of “Metastable” Morphologies. *Macromolecules* **2008**, *41*, 5919–5927.
- (15) Widin, J. M.; Schmitt, A. K.; Im, K.; Schmitt, A. L.; Mahanthappa, M. K. Polydispersity-Induced Stabilization of a Disordered Bicontinuous Morphology in ABA Triblock Copolymers. *Macromolecules* **2010**, *43*, 7913–7915.

- (16) Widin, J. M.; Schmitt, A. K.; Schmitt, A. L.; Im, K.; Mahanthappa, M. K. Unexpected Consequences of Block Polydispersity on the Self-Assembly of ABA Triblock Copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 3834–3844.
- (17) Lynd, N. A.; Hillmyer, M. A. Influence of Polydispersity on the Self-Assembly of Diblock Copolymers. *Macromolecules* **2005**, *38*, 8803–8810.
- (18) Lynd, N. A.; Hillmyer, M. A. Effects of Polydispersity on the Order–Disorder Transition in Block Copolymer Melts. *Macromolecules* **2007**, *40*, 8050–8055.
- (19) Meuler, A. J.; Ellison, C. J.; Evans, C. M.; Hillmyer, M. A.; Bates, F. S. Polydispersity-Driven Transition from the Orthorhombic Fddd Network to Lamellae in Poly(Isoprene-*b*-Styrene-*b*-Ethylene Oxide) Triblock Terpolymers. *Macromolecules* **2007**, *40*, 7072–7074.
- (20) Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. Polydispersity and Block Copolymer Self-Assembly. *Prog. Polym. Sci.* **2008**, *33*, 875–893.
- (21) Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; Roberts, P. L.; Weinhold, J. D. Photonic Polyethylene from Self-Assembled Mesophases of Polydisperse Olefin Block Copolymers. *Macromolecules* **2009**, *42*, 3788–3794.
- (22) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. Well-Ordered Microdomain Structures in Polydisperse Poly(Styrene)–Poly(Acrylic Acid) Diblock Copolymers from Controlled Radical Polymerization. *Macromolecules* **2002**, *35*, 6645–6649.

- (23) Sides, S. W.; Fredrickson, G. H. Continuous Polydispersity in a Self-Consistent Field Theory for Diblock Copolymers. *J. Chem. Phys.* **2004**, *121*, 4974–4986.
- (24) Schmitt, A. K.; Mahanthappa, M. K. Characteristics of Lamellar Mesophases in Strongly Segregated Broad Dispersity ABA Triblock Copolymers. *Macromolecules* **2014**, *47*, 4346–4356.
- (25) Sakurai, S.; Shirouchi, K.; Munakata, S.; Kurimura, H.; Suzuki, S.; Watanabe, J.; Oda, T.; Shimizu, N.; Tanida, K.; Yamamoto, K. Morphology Reentry with a Change in Degree of Chain Asymmetry in Neat Asymmetric Linear A_1BA_2 Triblock Copolymers. *Macromolecules* **2017**, *50*, 8647–8657.
- (26) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. Multiblock Polymers: Panacea or Pandora's Box? *Science* **2012**, *336*, 434–440.
- (27) Grason, G. M.; Kamien, R. D. Interfaces in Diblocks: A Study of Miktoarm Star Copolymers. *Macromolecules* **2004**, *37*, 7371–7380.
- (28) Lequeieu, J.; Koeper, T.; Delaney, K. T.; Fredrickson, G. H. Extreme Deflection of Phase Boundaries and Chain Bridging in $A(BA')_n$ Miktoarm Star Polymers. *Macromolecules* **2020**, *53*, 513–522.
- (29) Shi, W.; Hamilton, A. L.; Delaney, K. T.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Lynd, N. A.; Demassieux, Q.; Creton, C. Aperiodic “Bricks and Mortar” Mesophase: A New Equilibrium State of Soft

Matter and Application as a Stiff Thermoplastic Elastomer. *Macromolecules* **2015**, *48*, 5378–5384.

- (30) Shi, W.; Lynd, N. A.; Montarnal, D.; Luo, Y.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Hexemer, A. Toward Strong Thermoplastic Elastomers with Asymmetric Miktoarm Block Copolymer Architectures. *Macromolecules* **2014**, *47*, 2037–2043.
- (31) Shi, W.; Hamilton, A. L.; Delaney, K. T.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Lynd, N. A. Creating Extremely Asymmetric Lamellar Structures via Fluctuation-Assisted Unbinding of Miktoarm Star Block Copolymer Alloys. *J. Am. Chem. Soc.* **2015**, *137*, 6160–6163.
- (32) Lynd, N. A.; Oyerokun, F. T.; O'donoghue, D. L.; Handlin, D. L.; Fredrickson, G. H. Design of Soft and Strong Thermoplastic Elastomers Based on Nonlinear Block Copolymer Architectures Using Self-Consistent-Field Theory. *Macromolecules* **2010**, *43*, 3479–3486.
- (33) Dair, B. J.; Honeker, C. C.; Alward, D. B.; Avgeropoulos, A.; Hadjichristidis, N.; Fetters, L. J.; Capel, M.; Thomas, E. L. Mechanical Properties and Deformation Behavior of the Double Gyroid Phase in Unoriented Thermoplastic Elastomers. *Macromolecules* **1999** *32*, 8145–8152.
- (34) Levi, A. E.; Lequeieu, J.; Horne, J. D.; Bates, M. W.; Ren, J. M.; Delaney, K. T.; Fredrickson, G. H.; Bates, C. M. Miktoarm Stars via Grafting-

Through Copolymerization: Self-Assembly and the Star-to-Bottlebrush Transition. *Macromolecules* **2019**, *52*, 1794–1802.

- (35) Avgeropoulos, A.; Hadjichristidis, N. Synthesis of Model Nonlinear Block Copolymers of A(BA)₂, A(BA)₃, and (AB)₃A(BA)₃ Type. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 813–816.
- (36) Hu, Y.; Paul, C. W. Block Copolymer-Based Hot-Melt Pressure Sensitive Adhesives. In *Technology of Pressure-Sensitive Adhesives and Products*, 2nd ed.; Benedek, I., Feldstein, M. M., Eds.; CRC Press: Boca Raton, 2008; p 4.
- (37) De Craene, L. I. J.; DuPont, M. J.; Gerard, E.-J.; De Keyzer, N. R. M.; Morren, K. M. L. R.; Van Westrenen, J. Vinyl Aromatic Block Copolymers and Compositions Containing Them. US5777039A, February 5, 1997.
- (38) Diehl, C. F.; Tancrede, J. M.; Marchand, G. R. Radial Styrene-Isoprene-Butadiene Multi-Armed Block Copolymers and Compositions and Articles Containing Block Copolymers. US5399627A, November 24, 1993.
- (39) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* 1994, *27*, 4639–4647.
- (40) Couso, D. A.; Alassia, L. M.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch “Living” Anionic Polymerization. I. Theoretical Study. *J. Appl. Polym. Sci.* **1985**, *30*, 3249–3265.

- (41) Alassia, L. M.; Couso, D. A.; Meira, G. R. Molecular Weight Distribution Control in a Semibatch Living-Anionic Polymerization. II. Experimental Study. *J. Appl. Polym. Sci.* **1988**, *36*, 481–494.
- (42) Laurence, R. L.; Vasudevan, G. Performance of a Polymerization Reactor in Periodic Operation. *Ind. Eng. Chem. Process Des. Dev.* **1968**, *7*, 427–433.
- (43) Hungenberg, K.-D.; Knoll, K.; Wulkow, M. Absolute Propagation Rate Coefficients in Radical Polymerization from Gel Permeation Chromatography of Polymers Produced by Intermittent Initiation. *Macromol. Theory Simulations* **1997**, *6*, 393–426.
- (44) Farkas, E.; Meszena, Z. G.; Johnson, A. F. Molecular Weight Distribution Design with Living Polymerization Reactions. *Ind. Eng. Chem. Res.* **2004**, *43*, 7356–7360.
- (45) Seno, K.-I.; Kanaoka, S.; Aoshima, S. Thermosensitive Diblock Copolymers with Designed Molecular Weight Distribution: Synthesis by Continuous Living Cationic Polymerization and Micellization Behavior. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2212–2221.
- (46) Corrigan, N.; Manahan, R.; Lew, Z. T.; Yeow, J.; Xu, J.; Boyer, C. Copolymers with Controlled Molecular Weight Distributions and Compositional Gradients through Flow Polymerization. **2018**, *51*, 4353–4563.

- (47) Corrigan, N.; Almasri, A.; Taillades, W.; Xu, J.; Boyer, C. Controlling Molecular Weight Distributions through Photoinduced Flow Polymerization. *Macromolecules* **2017**, *50*, 8438–8448.
- (48) Whitfield, R.; Parkatzidis, K.; Rolland, M.; Truong, N. P.; Anastasaki, A. Tuning Dispersity by Photoinduced Atom Transfer Radical Polymerisation: Monomodal Distributions with Ppm Copper Concentration. *Angew. Chemie Int. Ed.* **2019**, *58*, 13323–13328.
- (49) Whitfield, R.; Truong, N. P.; Messmer, D.; Parkatzidis, K.; Rolland, M.; Anastasaki, A. Tailoring Polymer Dispersity and Shape of Molecular Weight Distributions: Methods and Applications. *Chem. Sci.* **2019**, *10*, 8724–8734.
- (50) Rubens, M.; Junkers, T. A Predictive Framework for Mixing Low Dispersity Polymer Samples to Design Custom Molecular Weight Distributions. *Polym. Chem.* **2019**, *10*, 5721–5725.
- (51) Rubens, M.; Junkers, T. Comprehensive Control over Molecular Weight Distributions through Automated Polymerizations. *Polym. Chem.* **2019**, *10*, 6315–6323.
- (52) Plichta, A.; Zhong, M.; Li, W.; Elsen, A. M.; Matyjaszewski, K. Tuning Dispersity in Diblock Copolymers Using ARGET ATRP. *Macromol. Chem. Phys.* **2012**, *213*, 2659–2668.

- (53) Fischer, W.; Knoll, K.; Loth, W.; Deffieux, D.; Desbois, P.; Lätsch, S.; Schade, C.; Gausepohl, H. Anionic Polymerization Process. US6444762 B1, August 18, 1997.
- (54) Meira, G. R.; Johnson, A. F. Molecular Weight Distribution Control in Continuous “Living” Polymerizations through Periodic Operation of the Monomer Feed. *Polym. Eng. Sci.* **1981**, *21*, 415–423.
- (55) Gentekos, D. T.; Dupuis, L. N.; Fors, B. P. Beyond Dispersity: Deterministic Control of Polymer Molecular Weight Distribution. *J. Am. Chem. Soc.* **2016**, *138*, 1848–1851.
- (56) Kottisch, V.; Gentekos, D. T.; Fors, B. P. “Shaping” the Future of Molecular Weight Distributions in Anionic Polymerization. *ACS Macro Lett.* **2016**, *5*, 796–800.
- (57) Nadgorny, M.; Gentekos, D. T.; Xiao, Z.; Singleton, S. P.; Fors, B. P.; Connal, L. A. Manipulation of Molecular Weight Distribution Shape as a New Strategy to Control Processing Parameters. *Macromol. Rapid Commun.* **2017**, *38*, 1700352.
- (58) Gentekos, D. T.; Jia, J.; Tirado, E. S.; Barteau, K. P.; Smilgies, D.-M.; DiStasio, R. A.; Fors, B. P. Exploiting Molecular Weight Distribution Shape to Tune Domain Spacing in Block Copolymer Thin Films. *J. Am. Chem. Soc.* **2018**, *140*, 4639–4648.

- (59) Gentekos, D. T.; Fors, B. P. Molecular Weight Distribution Shape as a Versatile Approach to Tailoring Block Copolymer Phase Behavior. *ACS Macro Lett.* **2018**, *7*, 677–682.
- (60) Gentekos, D. T.; Sifri, R. J.; Fors, B. P. Controlling Polymer Properties through the Shape of the Molecular-Weight Distribution. *Nat. Rev. Mater.* **2019**, *4*, 761–774.
- (61) Domanskyi, S.; Gentekos, D. T.; Privman, V.; Fors, B. P. Predictive Design of Polymer Molecular Weight Distributions in Anionic Polymerization. *Polym. Chem.* **2020**, *11*, 326–336.
- (62) Rosenbloom, S. I.; Gentekos, D. T.; Silberstein, M. N.; Fors, B. P. Tailor-Made Thermoplastic Elastomers: Customisable Materials via Modulation of Molecular Weight Distributions. *Chem. Sci.* **2020**, *11*, 1361–1367.
- (63) Sifri, R. J.; Padilla-Veíez, O.; Coates, G. W.; Fors, B. P. Controlling the Shape of Molecular Weight Distributions in Coordination Polymerization and Its Impact on Physical Properties. *J. Am. Chem. Soc.* **2020**, *142*, 1443–1448.
- (64) Ruzette, A. V.; Tencé-Girault, S.; Leibler, L.; Chauvin, F.; Bertin, D.; Guerret, O.; Gérard, P. Molecular Disorder and Mesoscopic Order in Polydisperse Acrylic Block Copolymers Prepared by Controlled Radical Polymerization. *Macromolecules* **2006**, *39*, 5804–5814.

- (65) Zhou, N.; Lodge, T. P.; Bates, F. S. Phase Behavior of Polyisoprene-Poly(Butylene Oxide) and Poly(Ethylene-Alt-Propylene)-Poly(Butylene Oxide) Block Copolymers. *Soft Matter* **2010**, *6*, 1281–1290.
- (66) Burger, C.; Ruland, W.; Semenov, A. N. Polydispersity Effects on the Microphase-Separation Transition in Block Copolymers. *Macromolecules* **1990**, *23*, 3339–3346.
- (67) Burger, C.; Ruland, W.; Semenov, A. N. Corrections to: Polydispersity Effects on the Microphase-Separation Transition in Block Copolymers. *Macromolecules* **1991**, *24*, 816.
- (68) Matsen, M. W. Polydispersity-Induced Macrophase Separation in Diblock Copolymer Melts. *Phys. Rev. Lett.* **2007**, *99*, 148304.
- (69) Cooke, D. M.; Shi, A.-C. Effects of Polydispersity on Phase Behavior of Diblock Copolymers. *Macromolecules* **2006**, *39*, 6661–6671.
- (70) Honeker, C. C.; Thomas, E. L. Impact of Morphological Orientation in Determining Mechanical Properties in Triblock Copolymer Systems. *Chem. Mater.* **1996**, *8*, 1702–1714.
- (71) Cohen, Y.; Thomas, E. L. Effect of Defects on the Response of a Layered Block Copolymer to Perpendicular Deformation: One-Dimensional Necking. *Macromolecules* **2003**, *36*, 5265–5270.
- (72) Séguéla, R.; Prud'homme, J. Deformation Mechanism of Thermoplastic Two-Phase Elastomers of Lamellar Morphology Having a High Volume Fraction of Rubbery Microphase. *Macromolecules* **1981**, *14*, 197–202.

- (73) Adhikari, R.; Michler, G. H. Influence of Molecular Architecture on Morphology and Micromechanical Behavior of Styrene/Butadiene Block Copolymer Systems. *Prog. Polym. Sci.* **2004**, *29*, 949–986.
- (74) An Huy, T.; Hong Hai, L.; Adhikari, R.; Weidisch, R.; Michler, G. H.; Knoll, K. Influence of Interfacial Structure on Morphology and Deformation Behavior of SBS Block Copolymers. *Polymer* **2003**, *44*, 1237–1245.
- (75) Cohen, Y.; Albalak, R. J.; Dair, B. J.; Capel, M. S.; Thomas, E. L. Deformation of Oriented Lamellar Block Copolymer Films. *Macromolecules* **2000**, *33*, 6502–6516.
- (76) Haward, R. N. The Application of a Gauss-Eyring Model to Predict the Behavior of Thermoplastics in Tensile Experiments. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1481–1494.
- (77) Burns, A. B.; Register, R. A. Mechanical Properties of Star Block Polymer Thermoplastic Elastomers with Glassy and Crystalline End Blocks. *Macromolecules* **2016**, *49*, 9521–9530.
- (78) Buckley, C P; De Focatiis, D S A; Prisacariu, C. Unravelling the Mysteries of Cyclic Deformation in Thermoplastic Elastomers. In *Const. Model. Rubber VII*; Jerrams, S.; Murphy, N.; CRC Press: Boca Raton, 2011; pp 3–10.
- (79) López-Barrón, C. R.; Eberle, A. P. R.; Yakovlev, S.; Bons, A. J. Structural Origins of Mechanical Properties and Hysteresis in SIS Triblock

Copolymers/Polystyrene Blends with Spherical Morphology. *Rheol. Acta* **2016**, *55*, 103–116.

3.6 Appendix

3.6.1 General Reagent Information

All polymer samples were analyzed using a Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min. Tetrahydrofuran (THF) was used as the eluent and all number-average molecular weights (M_n), weight-average molecular weights (M_w), dispersities ($\mathcal{D}$), asymmetry factors (A_s), M_z and M_{z+1} for the first polystyrene block were calculated from refractive index chromatograms against TSKgel polystyrene standards. Conversions and M_n s for the diblock and triblock copolymers were determined by ^1H nuclear magnetic resonance (NMR) spectra obtained on a Bruker 500 MHz NMR spectrometer in CDCl_3 .

3.6.2 General Analytical Methods

All polymer samples were analyzed using a Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min. Tetrahydrofuran (THF) was used as the eluent and all number-average molecular weights (M_n), weight-average molecular weights (M_w), dispersities ($\mathcal{D}$), asymmetry factors (A_s), M_z and M_{z+1} for the first polystyrene block were calculated from refractive index chromatograms against TSKgel polystyrene standards. Conversions and M_n s for the diblock and triblock copolymers were determined by ^1H

nuclear magnetic resonance (NMR) spectra obtained on a Bruker 500 MHz NMR spectrometer in CDCl₃.

3.6.3 Synthesis

Representative Procedure for Synthesis of SIS with a Narrow PS Block

Preparation of Polymer 0.27-N. A 20 mL scintillation vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 11 mL of cyclohexane and 270 μ L of styrene (2.4 mmol). The stir plate was set to 600 rpm, and 422 μ L of a 0.04 M stock solution of *s*-BuLi in cyclohexane (0.016 mmol) was quickly added in a single portion, giving a yellow solution indicating formation of the polystyryl anion. The reaction was capped and stirred for approximately 5 h, allowing for full monomer conversion. Then, 1.5 mL of isoprene (15 mmol) was added, and the reaction color quickly faded from yellow to clear, indicative of the polyisoprenyl anion. The stir plate was adjusted to 1000 rpm to account for the increased viscosity of the polyisoprenyl anion. Upon full conversion of isoprene to polyisoprene (ca. 10 h), 270 μ L styrene (2.4 mmol) was added and the reaction vial was placed in a heating block equipped with a thermocouple. The reaction was heated to 40 °C and allowed to stir for approximately 5 h. The color of the reaction slowly changed from clear to yellow. The polymerization was quenched with BHT and vigorously shaken until the reaction color completely faded. The reaction vial was removed from the glovebox and the polymer was precipitated with MeOH. The polymer was dissolved in DCM and 0.7 mL of BHT in DCM (10 mg BHT/1 mL DCM) was added as a stabilizer. The polymer solution was

concentrated via rotary evaporation and polymers were dried in a vacuum oven at 60 °C for 12 h.

Representative Procedure for Synthesis of SIS with a Broadened PS Block

Preparation of Polymer 0.33-S. A 20 mL scintillation vial equipped with a magnetic stirrer was flame dried, brought into the glovebox, and charged with 2 mL of cyclohexane and 270 μ L of styrene (2.4 mmol). 400 μ L of a 0.04 M *s*-BuLi stock solution in cyclohexane was drawn into a 1 mL syringe and then mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Tables Table 3.2–Table 3.6). Once the needle was submerged into the reaction mixture, the stir plate was set to 350 rpm and the addition program was started. At full addition of *s*-BuLi, the reaction was capped and stirred at 500 rpm until full conversion of styrene to polystyrene was reached (ca. 5 h). The reaction was diluted with additional cyclohexane (9 mL) and isoprene (1.1 mL, 11 mmol) was next added. The stir plate was adjusted to 1000 rpm to account for the increased viscosity of the polyisoprenyl anion. Upon full conversion of isoprene to polyisoprene (ca. 10 h), 270 μ L styrene (2.4 mmol) was added and the reaction vial was placed in a heating block equipped with a thermocouple. The reaction was heated to 40 °C and allowed to stir until full conversion of styrene to polystyrene (ca. 5 h). The polymerization was quenched with BHT and vigorously shaken until the reaction color completely faded. The reaction vial was removed from the glovebox and the polymer was precipitated with MeOH. The polymer was dissolved in DCM and 0.6 mL of BHT in DCM (10 mg BHT/1

mL DCM) was added as a stabilizer. The polymer solution was concentrated via rotary evaporation and polymers were dried in a vacuum oven at 60 °C for 12 h.

3.6.4 General Procedure for Synchrotron Small-Angle X-Ray Scattering

Sample Preparation

Polymers were pressed under 1,000 psi of pressure at 130 °C for 30 seconds into the center of stainless-steel washers (4.42 mm I.D., 9.53 mm O.D., 0.79 mm thickness). The washers were sealed between Kapton tape and annealed in a vacuum oven at 180 °C for 48 h. The polymers were removed from the center of the washer and sealed within differential scanning calorimetry (DSC) pans (standard aluminum set, DSC Consumables, Inc). Sealing the polymers within DSC pans was necessary to prevent polymer leakage during the *in-situ* thermal annealing experiments.

Morphological Characterization

Small-angle x-ray scattering was performed at the DND-CAT 5ID-D line at the Advanced Photon Source (APS) located at Argonne National Laboratory. 2D-SAXS patterns were recorded with a Rayonix MX170HS detector (0.1772 x 0.1772 pixels) at a sample to detector distance of 8.5067 m and an X-ray wavelength (λ) of 0.7293 Å. Real-time data reduction was automatically performed at APS. Domain spacing (d) was determined from the position of the

principle wavevector, q^* ($d = 2\pi/q^*$). Polymer morphology was determined from the ratios of scattering peaks relative to q^* .

3.6.5 General Procedure for Mechanical Characterization

Sample Preparation

Compression molding was carried out using a 4120 Hydraulic Unit Carver press and PTFE protective sheets (CS Hyde). To prepare dogbone specimens, polymers were first subjected to compression molding between PTFE protective sheets for 1 minutes at 130 °C under 3,000 psi of pressure. After removing the pressed polymers from the press and allowing them to cool to room temperature, dogbone specimens were cut using a manual toggle press (SCHMIDT®, No. 11) equipped with a die cutter (ASTM D1708, Dietechs). The dogbone specimens were 38 mm long and the widest point of the grips was 15 mm. The gauge length was 22 mm long and 5 mm wide. The average specimen thickness was 2.5 mm.

Tensile Testing

Tensile properties of compression-molded copolymer samples were examined using a Zwick/Roell Z010 system with a 10 kN capacity load cell (Xforce P, Zwick-Roell), and analyzed using Zwick/Roell TestXpert II v.3.5 software. Dog bone specimens were secured by manually tightening the grips. Samples were loaded to 500 percent strain, followed immediately by unloading to the zero force. The strain rate for loading and

unloading was 100% strain/min. Young's modulus (E) was determined as the slope of the linear elastic region at low (<10%) strain. Tensile strength at 500% was defined as the stress at 500% elongation. Toughness (U_T) was defined as the area under the loading curve whereas hysteresis energy (W_H) was defined as the area between the loading and unloading curves. For both monotonic and cyclic testing, three dogbone specimens were tested per sample.

3.6.6 Reagent Quantities and Addition Rates of *s*-BuLi for Skewed PS Blocks

Table 3.2 Preparation of Symmetrically Broad PS Blocks

Polymer	Styrene Volume per Block (mL)	Isoprene Volume (mL)	Addition Time <i>s</i> -BuLi (min)	Addition Rate <i>s</i> -BuLi (μL/h)	Total Volume <i>s</i> -BuLi (μL)	Molarity <i>s</i> -BuLi Stock Solution (mol/L)
0.27-S	0.27	1.3	22	2244	823	0.02
0.33-S	0.27	1.1	22	1039	381	0.04
0.39-S	0.27	0.9	30	1257	628	0.02
0.42-S	0.27	0.7	30	1348	674	0.02

Table 3.3 Preparation of the Skewed PS Block in 0.27-T

Monomer Volumes (mL)	Step #	Addition Rate s-BuLi ($\mu\text{L/h}$)	Volume s-BuLi (μL)/Step [s-BuLi] = 0.02 M
Styrene = 0.27 Isoprene = 1.7		54 min	
	1	10	0.5
	2	14	0.6
	3	20	0.9
	4	28	1.3
	5	39	1.8
	6	55	2.5
	7	77	3.5
	8	108	4.8
	9	151	6.8
	10	211	9.5
	11	295	13
	12	414	19
	13	579	26
	14	811	36
	15	1135	51
	16	1589	71
	17	2224	100
	18	3114	140
	19	4359	196
	20	6103	275

Table 3.4 Preparation of the Skewed PS Block in 0.33-T

Monomer Volumes (mL)/Block	Step #	Addition Rate <i>s</i> -BuLi (μL/h)	Volume <i>s</i> -BuLi (μL)/Step
Styrene = 0.27 Isoprene = 1.1		54 min	[<i>s</i> -BuLi] = 0.04 M
	1	4.1	0.2
	2	5.7	0.3
	3	7.9	0.4
	4	11	0.5
	5	16	0.7
	6	22	1.0
	7	31	1.4
	8	43	1.9
	9	60	2.7
	10	84	3.8
	11	117	5.3
	12	164	7.4
	13	230	10
	14	322	15
	15	450	20
	16	630	28
	17	882	40
	18	1235	56
	19	1730	77
	20	2421	109

Table 3.5 Preparation of the Skewed PS Block in 0.39-T

Monomer Volume (mL)/Block	Step #	Addition Rate <i>s</i> -BuLi (μL/h)	Volume <i>s</i> -BuLi (μL)/Step [<i>s</i> -BuLi] = 0.03 M
Styrene = 0.27 Isoprene = 0.9		55 min	
	1	4.0	0.2
	2	5.5	0.3
	3	7.8	0.4
	4	11	0.5
	5	15	0.7
	6	21	1.0
	7	30	1.4
	8	42	1.9
	9	58	2.7
	10	82	3.8
	11	115	5.3
	12	160	7.3
	13	225	10
	14	314	14
	15	440	20
	16	616	28
	17	862	40
	18	1207	55
	19	1690	77
	20	2366	109

Table 3.6 Preparation of the Skewed PS Block in 0.42-T

Monomer Volume (mL)/Block	Step #	Addition Rate <i>s</i> -BuLi (μL/h)	Volume <i>s</i> -BuLi (μL)/Step [<i>s</i> -BuLi] = 0.02 M
Styrene = 0.27 Isoprene = 0.8		54 min	
	1	6.4	0.3
	2	8.9	0.4
	3	13	0.6
	4	18	0.8
	5	25	1.1
	6	34	1.5
	7	48	2.2
	8	67	3.0
	9	94	4.2
	10	132	5.9
	11	185	8.3
	12	258	12
	13	362	16
	14	507	23
	15	709	32
	16	993	45
	17	1390	63
	18	1946	88
	19	2724	123
	20	3814	172

3.6.7 PS MWD Characteristics and Composition of SIS Library

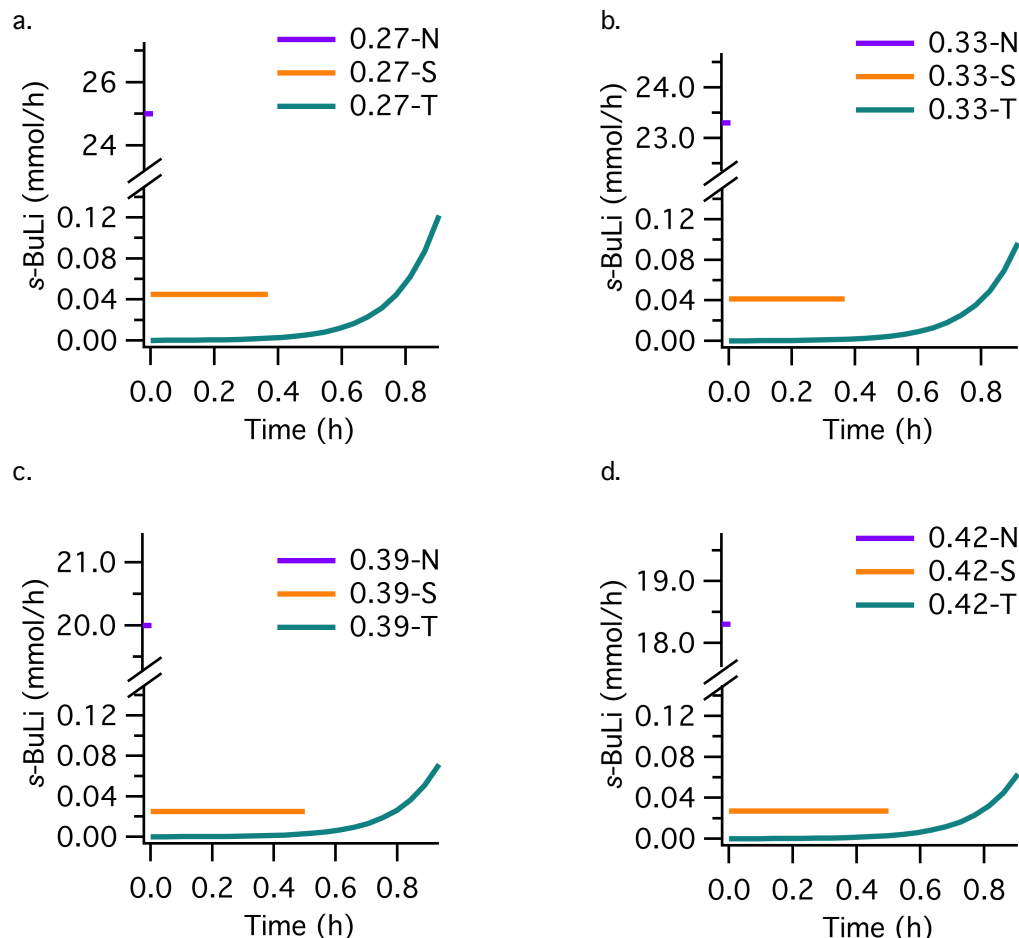


Figure 3.6 Initiator addition profiles for all polymers, organized by PS content in final SIS where f_v^{PS} in SIS is on average equal to (a) 0.27, (b) 0.33, (c) 0.39, and (d) 0.42.

The SEC traces in Figures Figure 3.7–Figure 3.10 display a small second population of low molecular weight PS chains in the final SIS polymer, occurring from termination events early in the polymerization. The presence of PS homopolymer is not believed to influence the formed morphology of the final polymer due to its low molecular weight and low concentration relative to SIS chains.^{1–3}

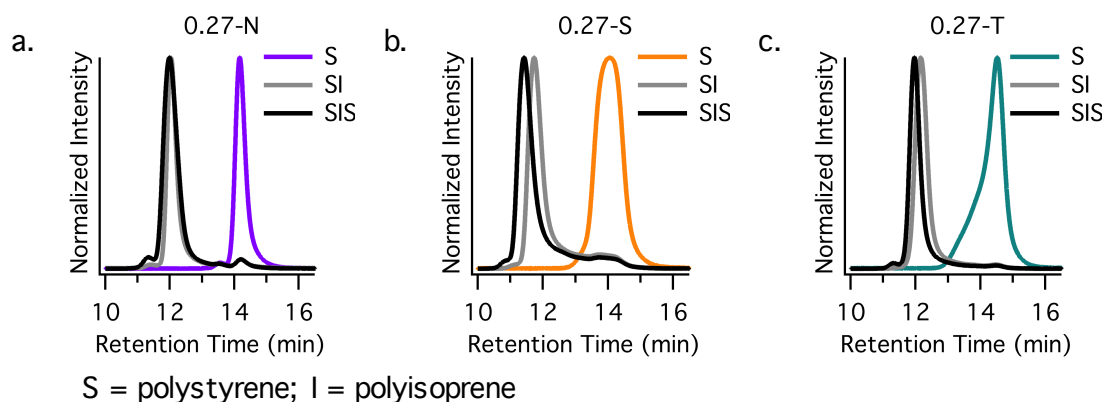


Figure 3.7 SEC traces showing block extensions, affording SIS in which the final f_v^{PS} is ~ 0.27 and the first PS block has a (a) narrow (N), (b) broad and symmetric (S), or (c) broad with high molar mass tailing (T) MWD shape.

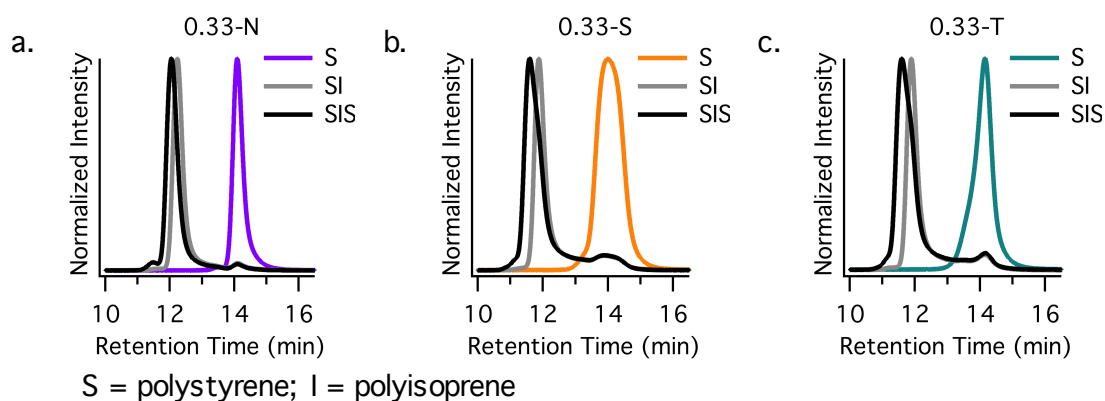


Figure 3.8 SEC traces showing block extensions, affording SIS in which the final f_v^{PS} is ~ 0.33 and the first PS block has a (a) narrow (N), (b) broad and symmetric (S), or (c) broad with high molar mass tailing (T) MWD shape.

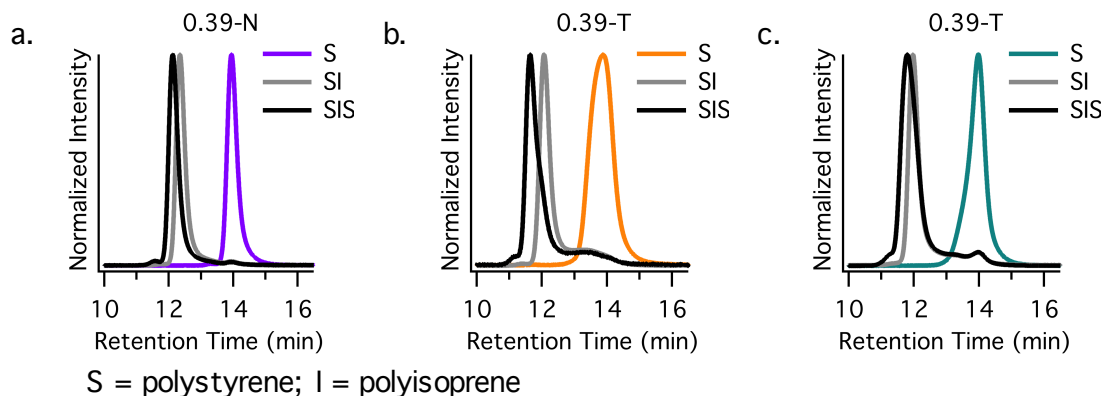


Figure 3.9 SEC traces showing block extensions, affording SIS in which the final f_v^{PS} is ~ 0.39 and the first PS block has a (a) narrow (N), (b) broad and symmetric (S), or (c) broad with high molar mass tailing (T) MWD shape.

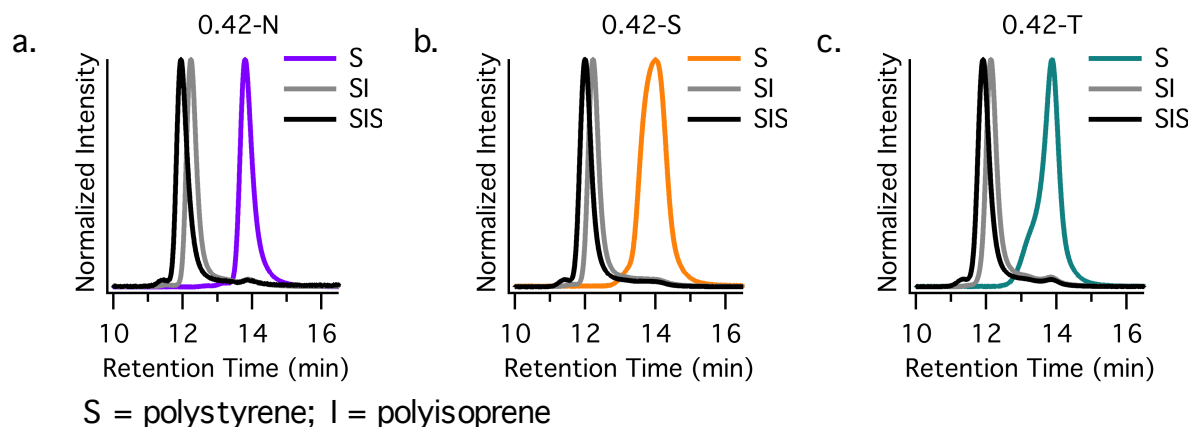


Figure 3.10 SEC traces showing block extensions, affording SIS in which the final f_v^{PS} is ~ 0.42 and the first PS block has a (a) narrow (N), (b) broad and symmetric (S), or (c) broad with high molar mass tailing (T) MWD shape.

3.6.8 1-D SAXS Traces for in-situ Thermal Annealing Experiments

Figures Figure 3.11—Figure 3.22 show stacked 1-D SAXS traces, in which the y-axis is intensity (in arbitrary units) multiplied by q^2 , where q is the scattering vector. Traces are offset for visual clarity. The traces are displayed with annealing temperatures increasing from bottom to top: 25, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230 °C.

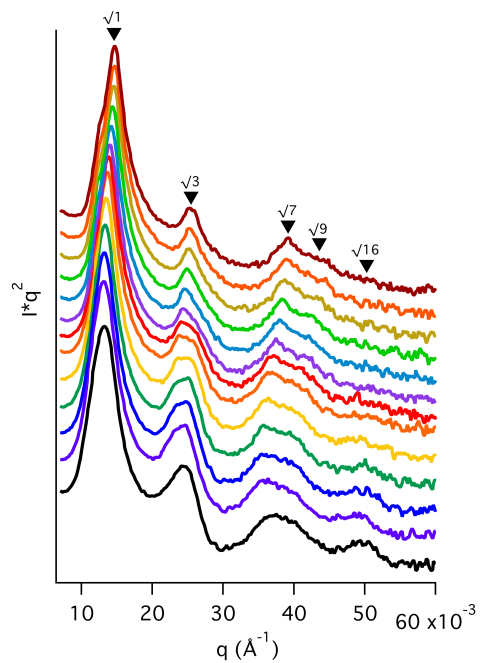


Figure 3.11 1-D SAXS traces for polymer 0.27-N.

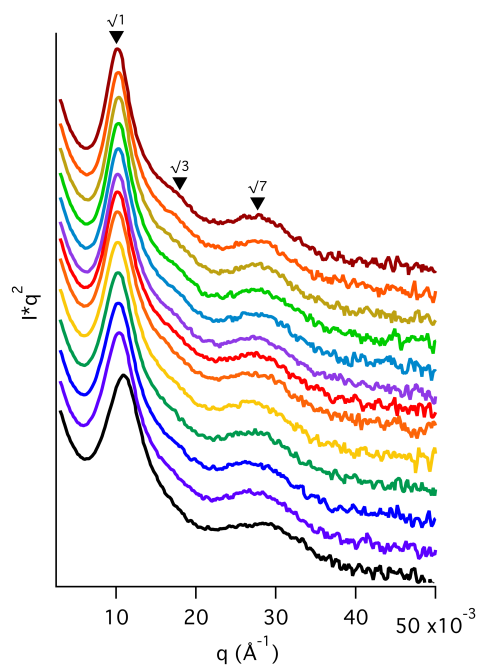


Figure 3.12 1-D SAXS traces for polymer 0.27-S.

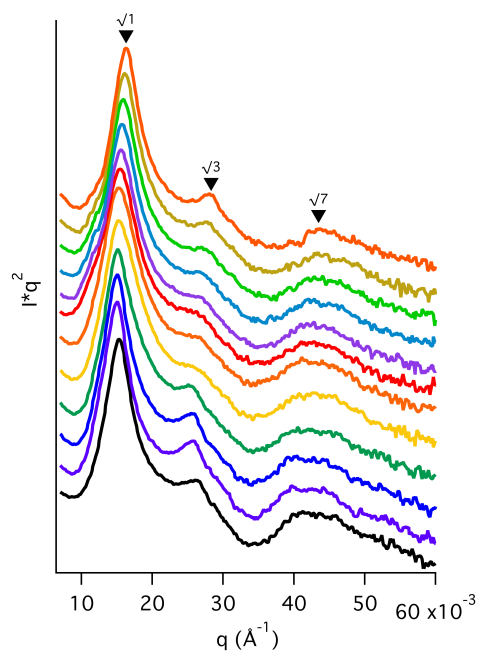


Figure 3.13 1-D SAXS traces for polymer 0.27-T.

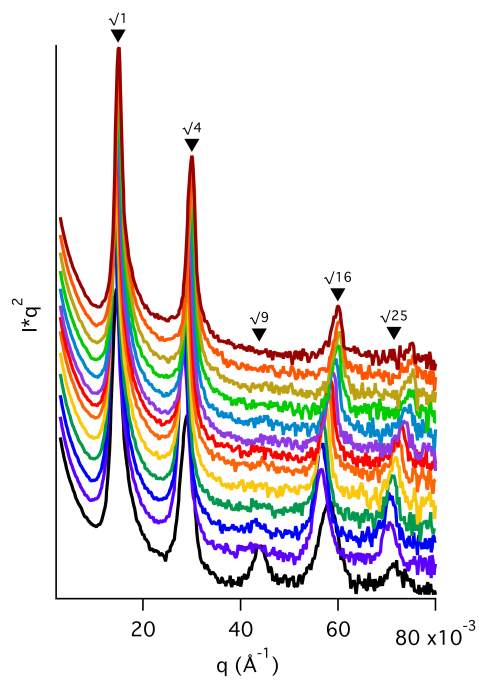


Figure 3.14 1-D SAXS traces for polymer 0.33-N.

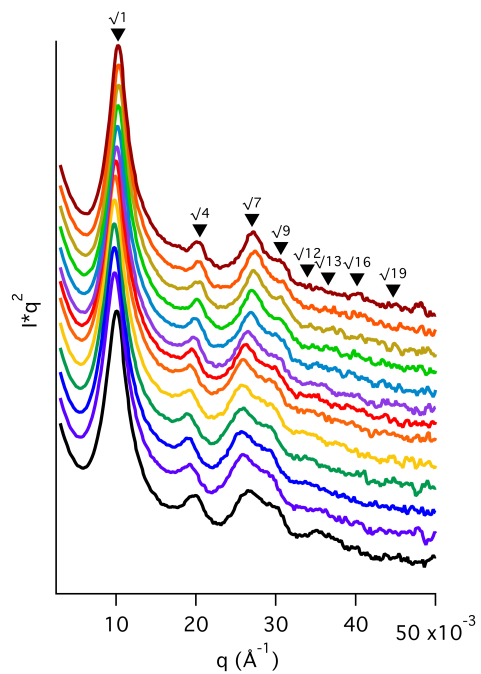


Figure 3.15 1-D SAXS traces for polymer 0.33-S.

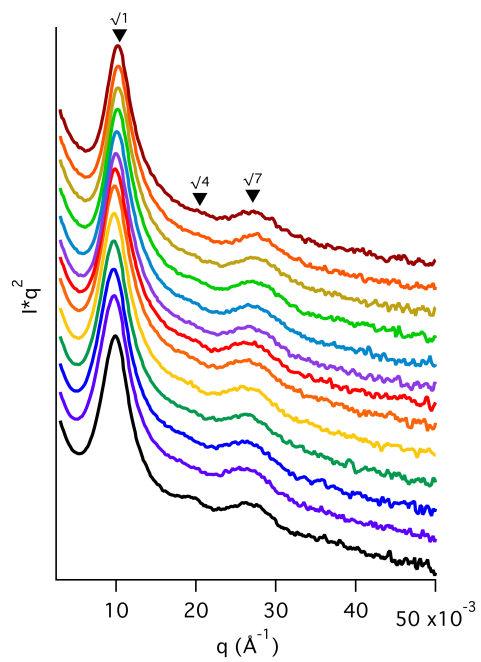


Figure 3.16 1-D SAXS traces for polymer 0.33-T.

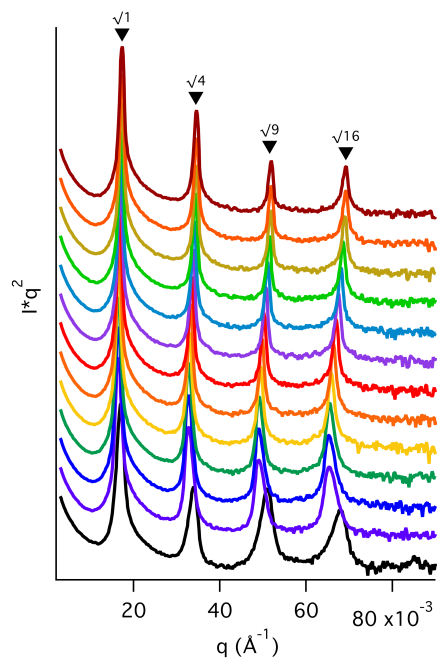


Figure 3.17 1-D SAXS traces for polymer 0.39-N.

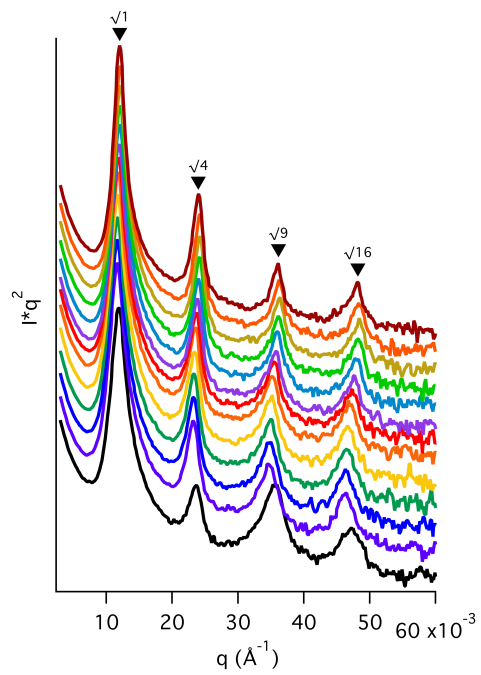


Figure 3.18 1-D SAXS traces for polymer 0.39-S.

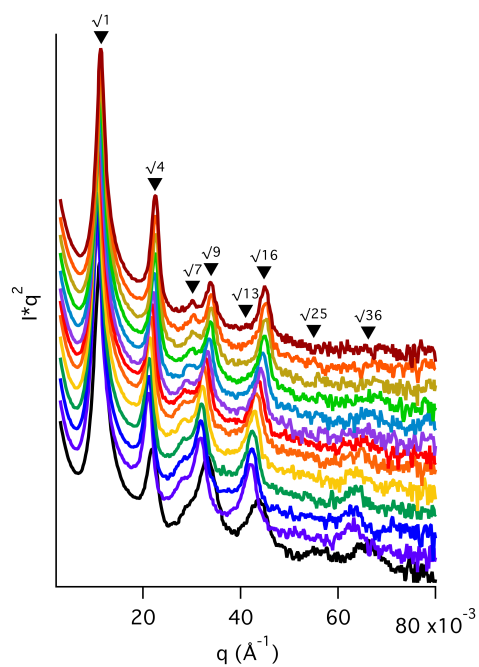


Figure 3.19 1-D SAXS traces for polymer 0.39-T.

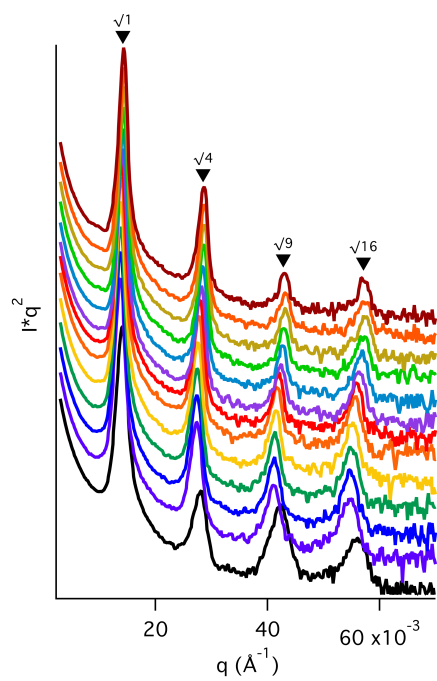


Figure 3.20 1-D SAXS traces for polymer 0.42-N.

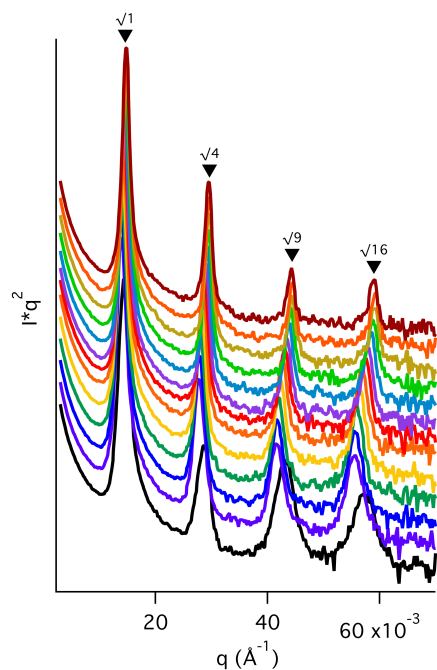


Figure 3.21 1-D SAXS traces for polymer 0.42-S.

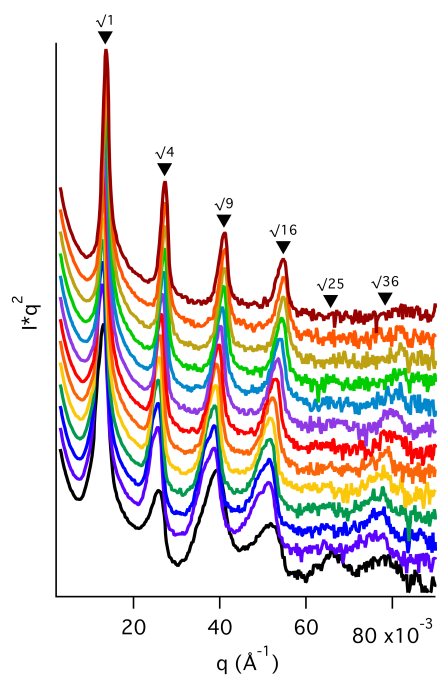


Figure 3.22 1-D SAXS traces for polymer 0.42-T.

3.6.9 Material Testing

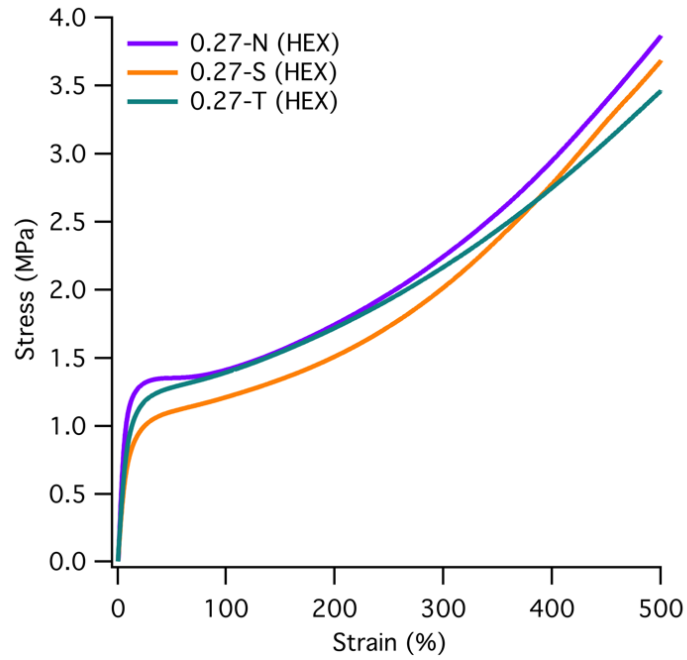


Figure 3.23 Representative stress-strain curves for polymers with $f_v^{PS} \sim 0.27$.

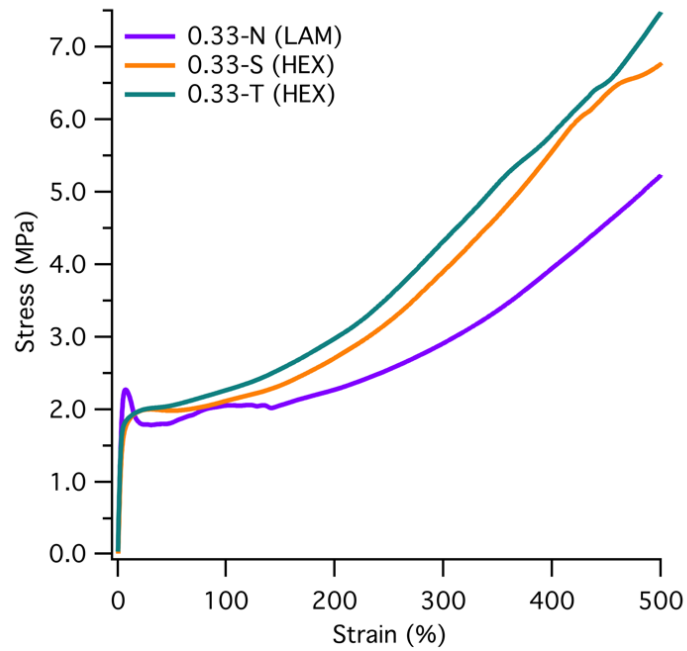


Figure 3.24 Representative stress-strain curves for polymers with $f_v^{PS} \sim 0.33$.

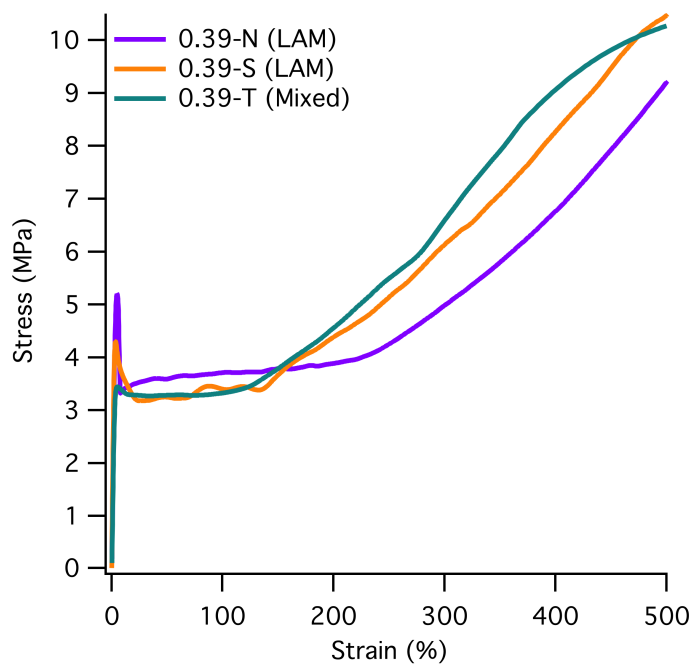


Figure 3.25 Representative stress-strain curves for polymers with $f_v^{\text{PS}} \sim 0.39$.

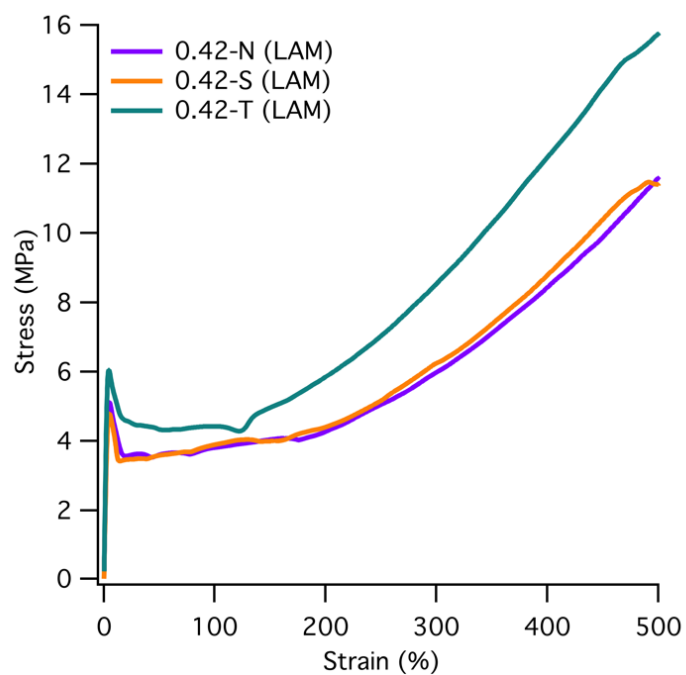


Figure 3.26 Representative stress-strain curves for polymers with $f_v^{\text{PS}} \sim 0.42$.

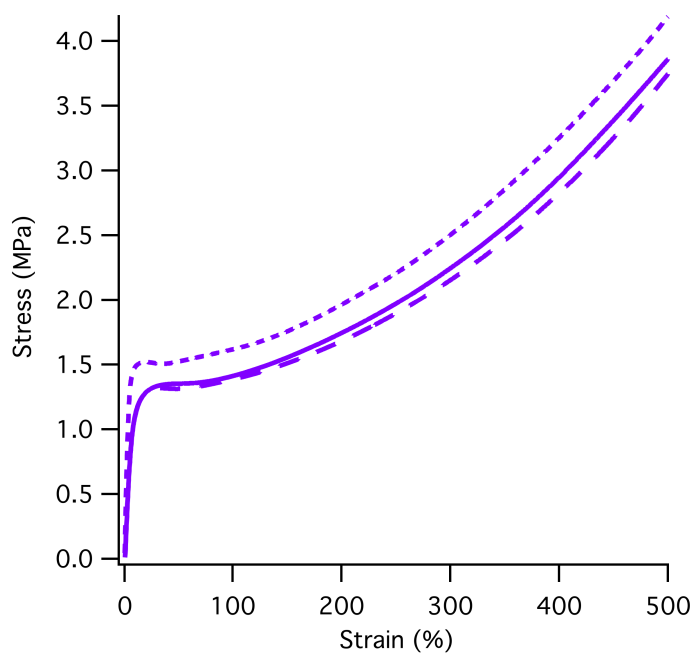


Figure 3.27 Stress-strain curves for three specimens of polymer 0.27-N.

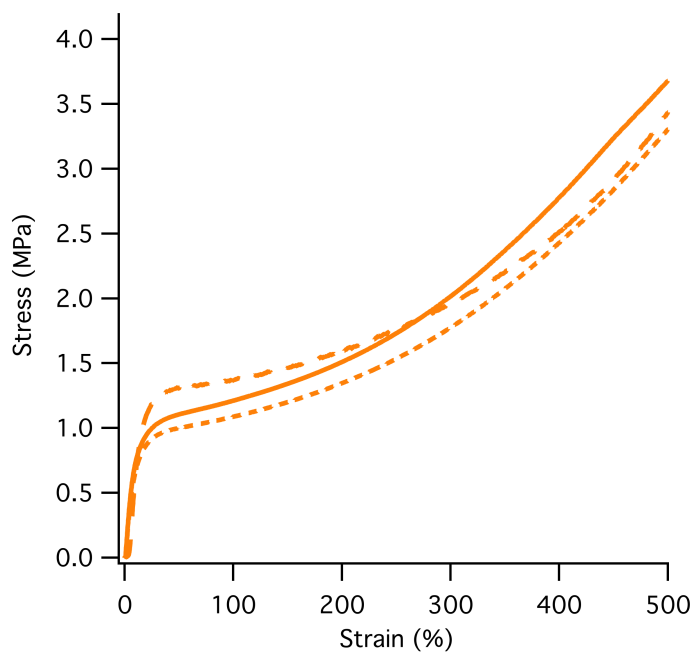


Figure 3.28 Stress-strain curves for three specimens of polymer 0.27-S.

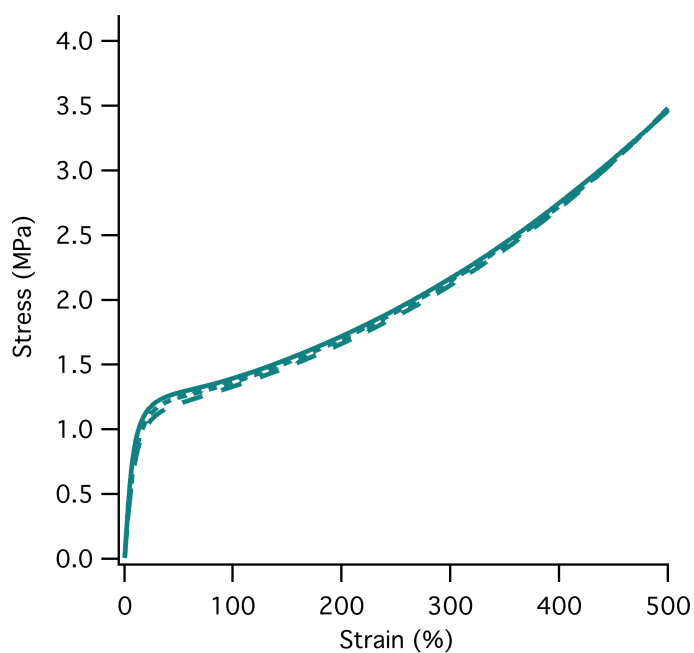


Figure 3.29 Stress-strain curves for three specimens of polymer 0.27-T.

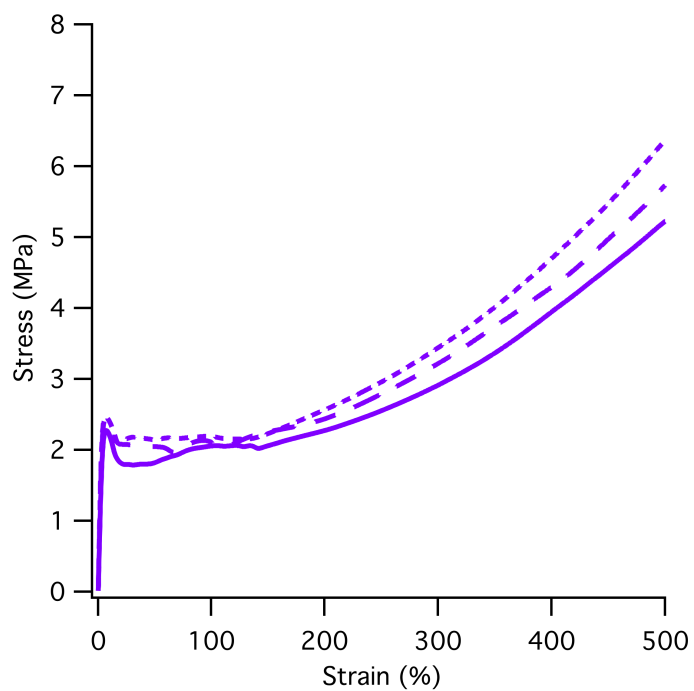


Figure 3.30 Stress-strain curves for three specimens of polymer 0.33-N.

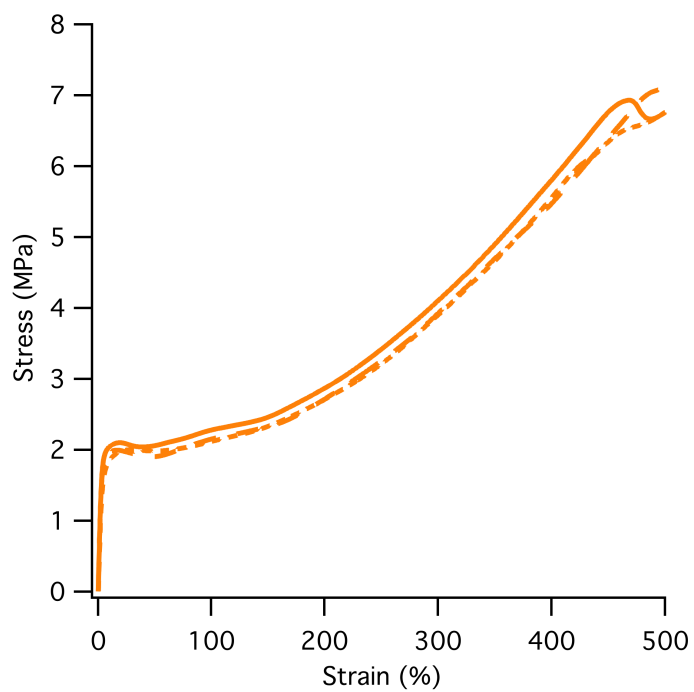


Figure 3.31 Stress-strain curves for three specimens of polymer 0.33-S.

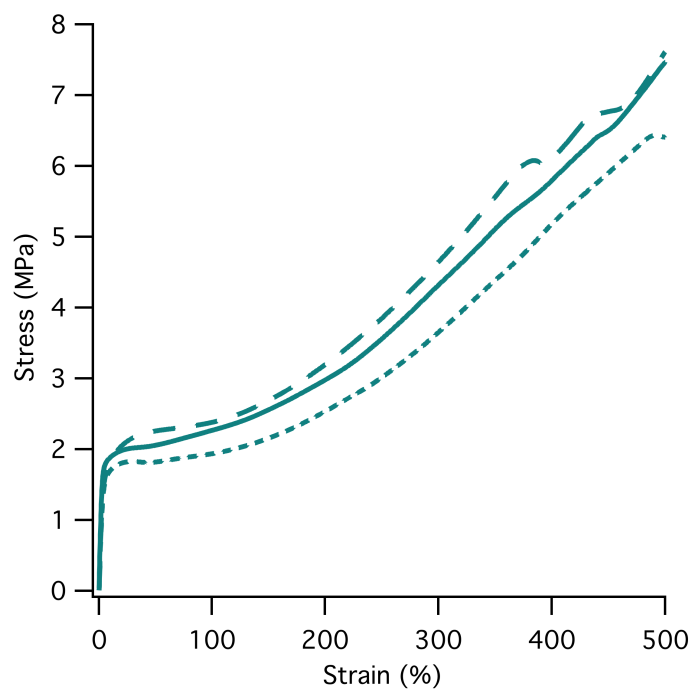


Figure 3.32 Stress-strain curves for three specimens of polymer 0.33-T.

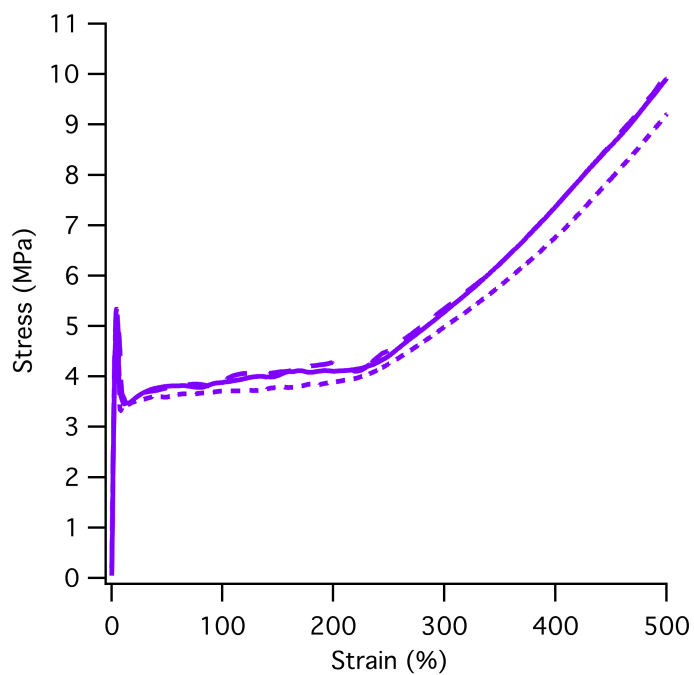


Figure 3.33 Stress-strain curves for three specimens of polymer 0.39-N.

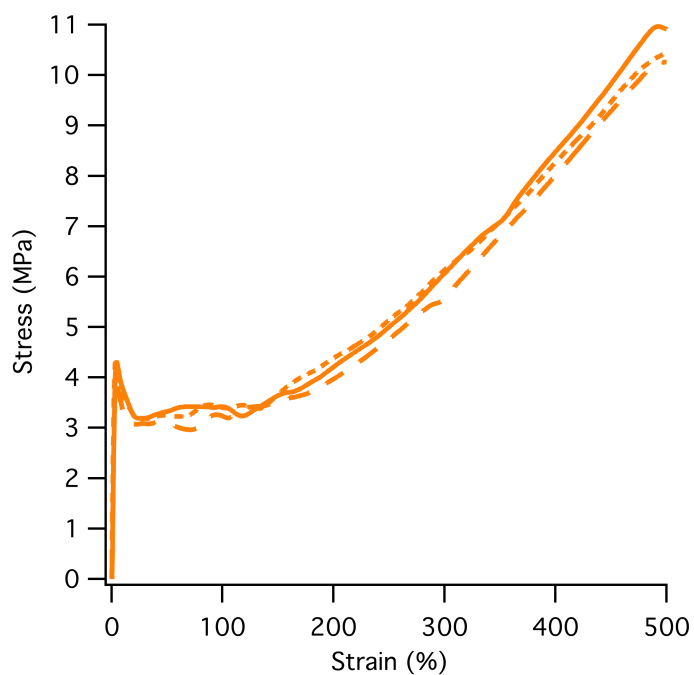


Figure 3.34 Stress-strain curves for three specimens of polymer 0.39-S.

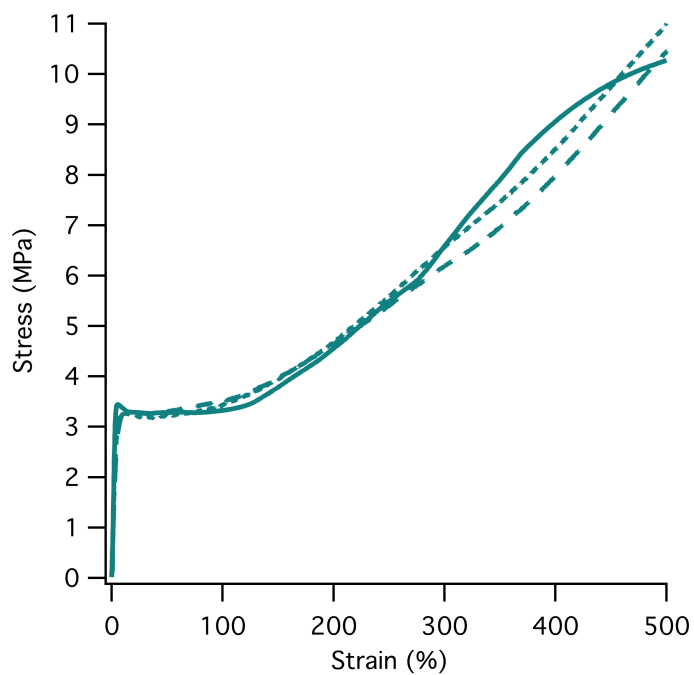


Figure 3.35 Stress-strain curves for three specimens of polymer 0.39-T.

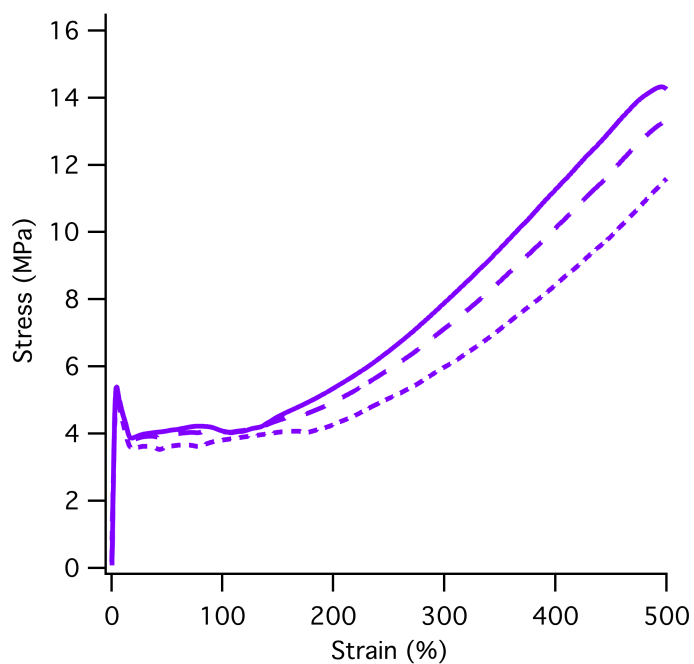


Figure 3.36 Stress-strain curves for three specimens of polymer 0.42-N.

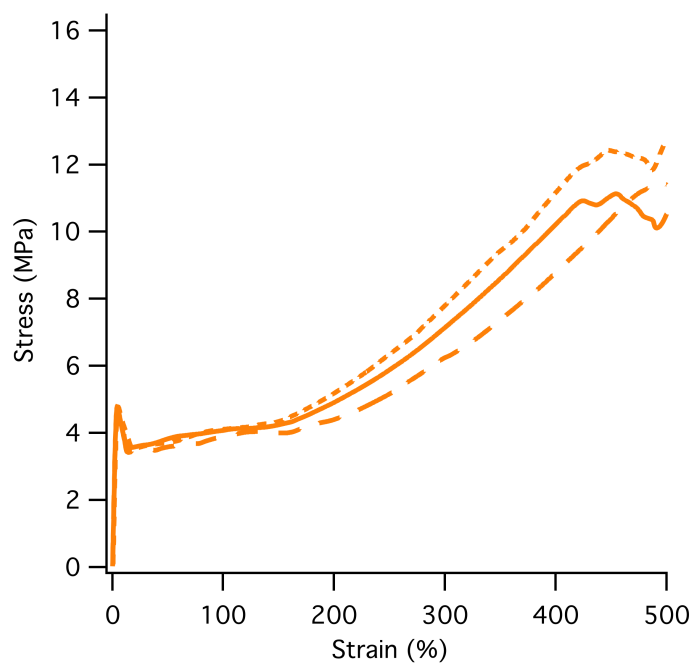


Figure 3.37 Stress-strain curves for three specimens of polymer 0.42-S.

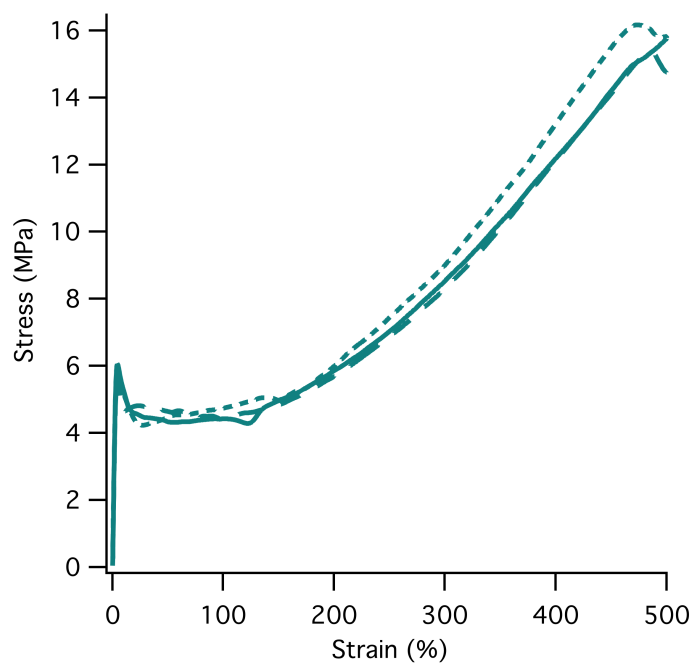


Figure 3.38 Stress-strain curves for three specimens of polymer 0.42-T.

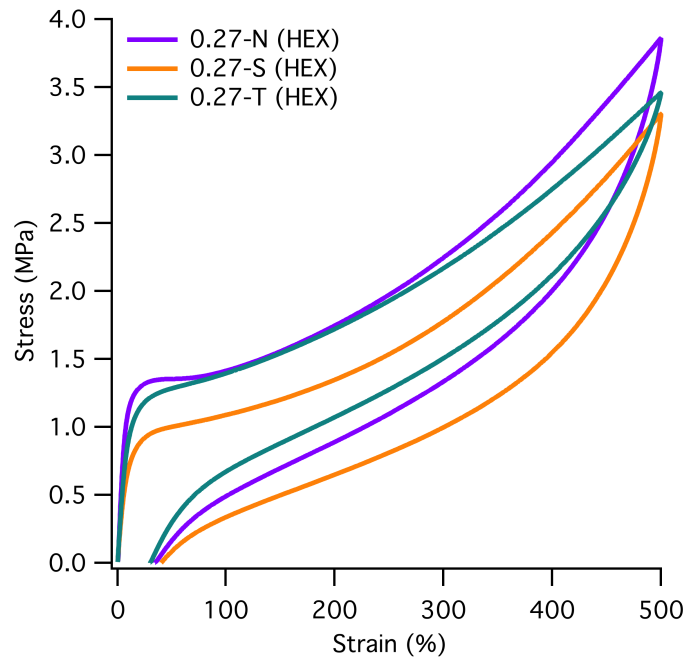


Figure 3.39 Representative loading-unloading curves for polymers with $f_v^{\text{PS}} \sim 0.27$.

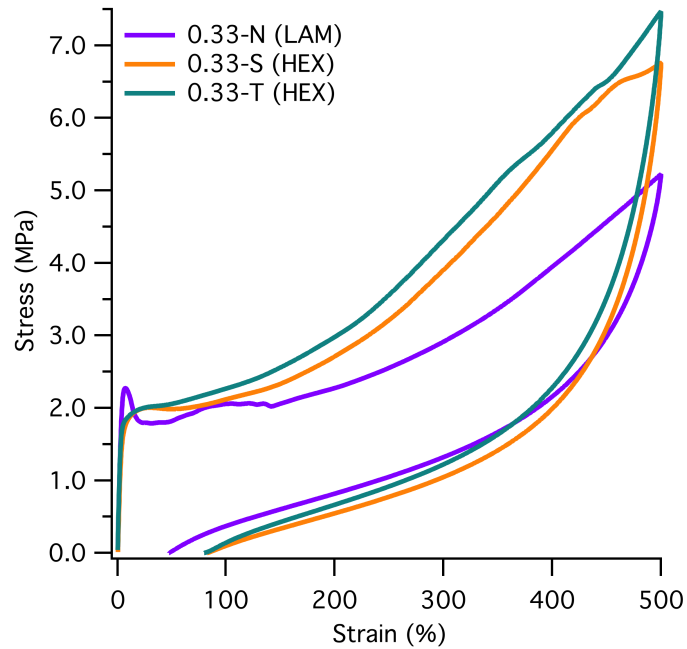


Figure 3.40 Representative loading-unloading curves for polymers with $f_v^{\text{PS}} \sim 0.33$.

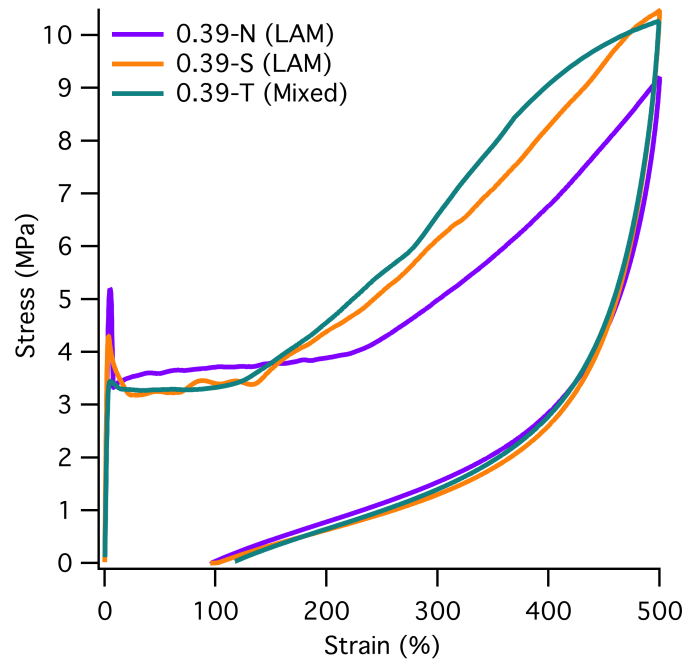


Figure 3.41 Representative loading-unloading curves for polymers with $f_v^{\text{PS}} \sim 0.39$.

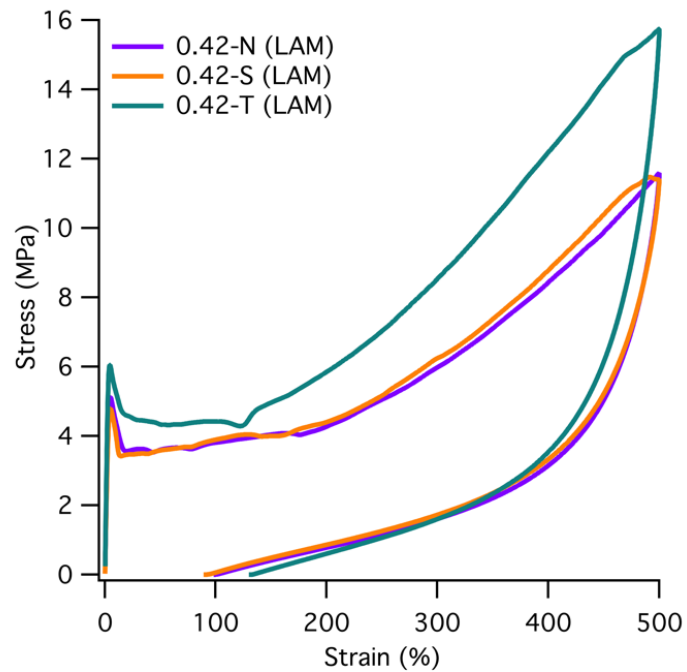


Figure 3.42 Representative loading-unloading curves for polymers with $f_v^{\text{PS}} \sim 0.42$.

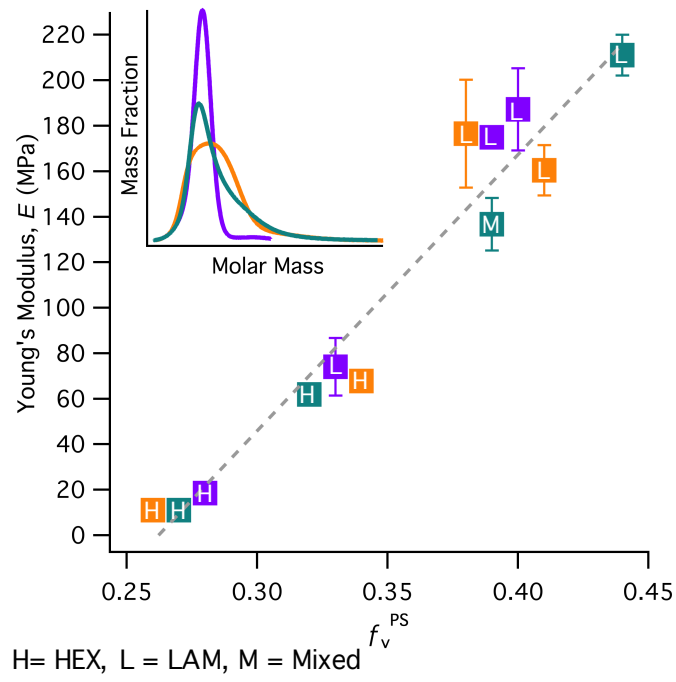


Figure 3.43 Young's modulus (E) increases linearly with f_v^{PS} .

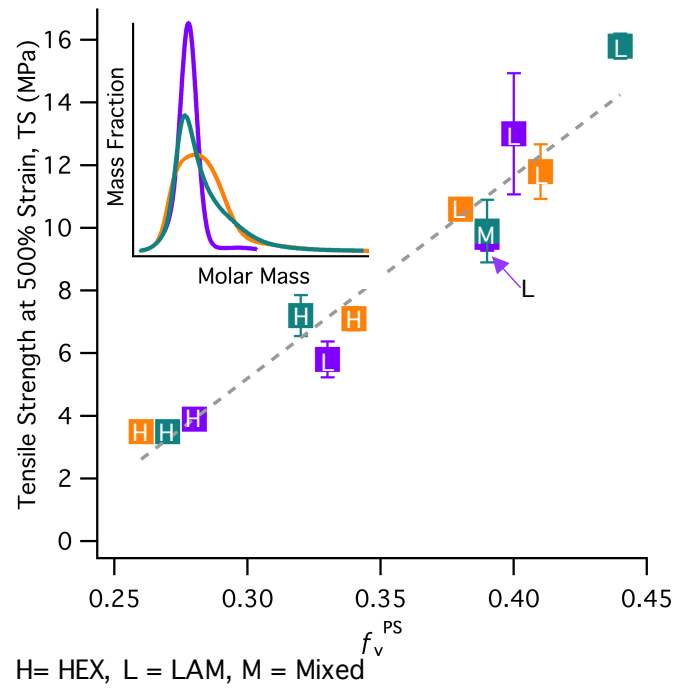


Figure 3.44 Tensile strength at 500% strain (TS) increases linearly with f_v^{PS} .

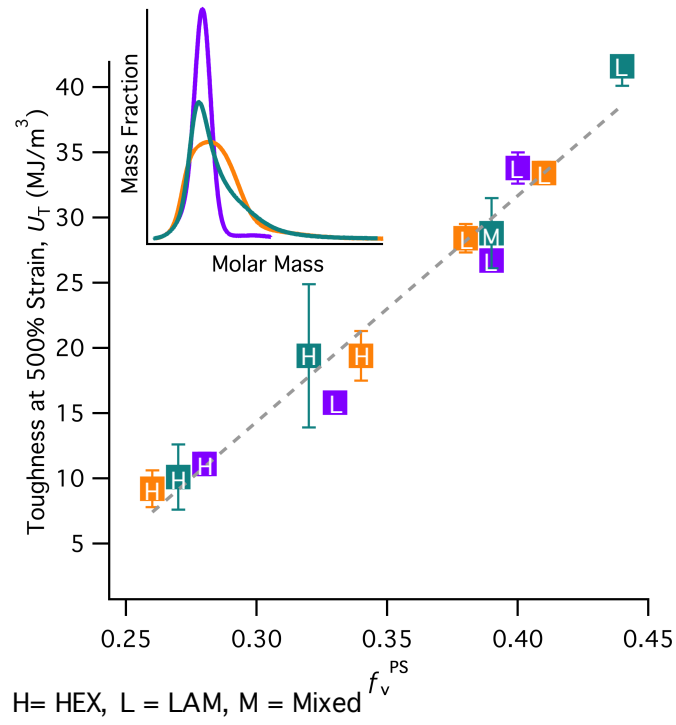


Figure 3.45 Toughness at 500% strain (U_T) increases linearly with f_v^{PS} .

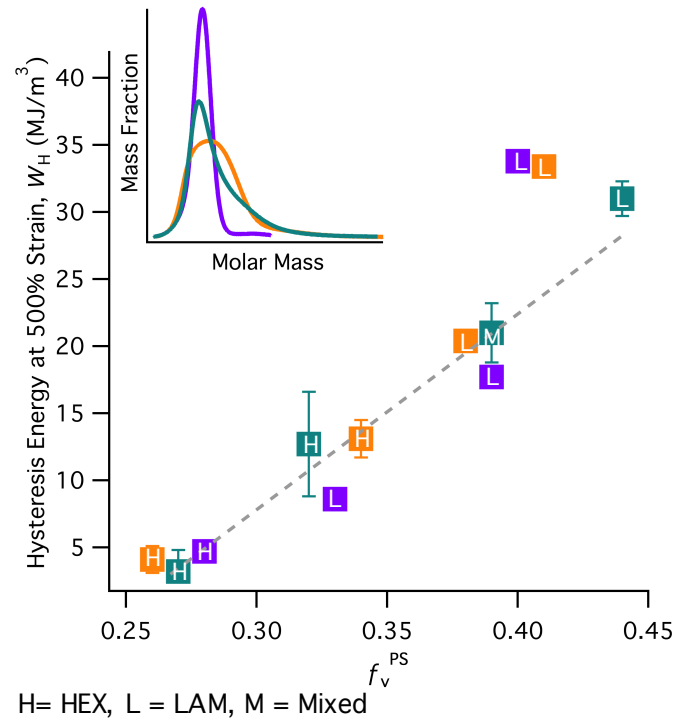


Figure 3.46 Hysteresis energy at 500% elongation (W_H) increases linearly with f_v^{PS} .

Table 3.7 Compiled Key Findings

polymer	$\bar{D}^{\text{PS}a,b}$	$A_s^{\text{PS}a,b}$	$f_v^{\text{PS}c}$	phase ^d	E (MPa) ^e	TS (MPa) ^e	U_T (MJ/m ³) ^e
0.27-N	1.07	1.74	0.28	HEX	19	3.9	11
0.27-S	1.20	1.02	0.26	HEX	11	3.5	9.2
0.27-T	1.27	0.42	0.27	HEX	11	3.5	10
0.33-N	1.07	1.79	0.33	LAM	74	5.8	16
0.33-S	1.17	1.33	0.34	HEX	68	7.1	19
0.33-T	1.16	0.71	0.32	HEX	62	7.2	19
0.39-N	1.07	1.74	0.39	LAM	175	9.7	27
0.39-S	1.16	1.05	0.38	LAM	177	11	28
0.39-T	1.14	0.72	0.39	Mixed	137	10	29
0.42-N	1.09	2.04	0.40	LAM	187	13	34
0.42-S	1.18	0.96	0.41	LAM	160	12	33
0.42-T	1.17	0.57	0.44	LAM	211	16	42

^aDetermined by SEC against PS standards. ^bValues are for the first PS block

^cCalculated using NMR spectroscopy and homopolymer densities. ^dDetermined from the ratios of scattering peaks relative to the principle scattering wavevector, q^* , where HEX = hexagonally packed cylinders, LAM = lamellae, and Mixed = HEX/LAM. ^eValues are an average of three measurements.

3.6.10 References for Appendix

- (1) Quan, X.; Gancarz, I.; Koberstein, J. T.; Wignall, G. D. Effect of Homopolymer Molecular Weight on the Morphology of Block Copolymer/Homopolymer Blends. *Macromolecules* 1987, *20*, 1431–1434
- (2) Kimishima, K.; Hashimoto, T.; Han, C. D. Spatial Distribution of Added Homopolymer within the Microdomains of a Mixture Consisting of an ABA-Type Triblock Copolymer and a Homopolymer. *Macromolecules* **1995**, *28*, 3842–3853
- (3) Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. Polydispersity and Block Copolymer Self-Assembly. *Prog. Polym. Sci.* **2008**, *33*, 875–893

CHAPTER 4

ACHIEVING MOLECULAR WEIGHT DISTRIBUTION SHAPE CONTROL AND BROAD DISPERSITIES USING RAFT POLYMERIZATIONS

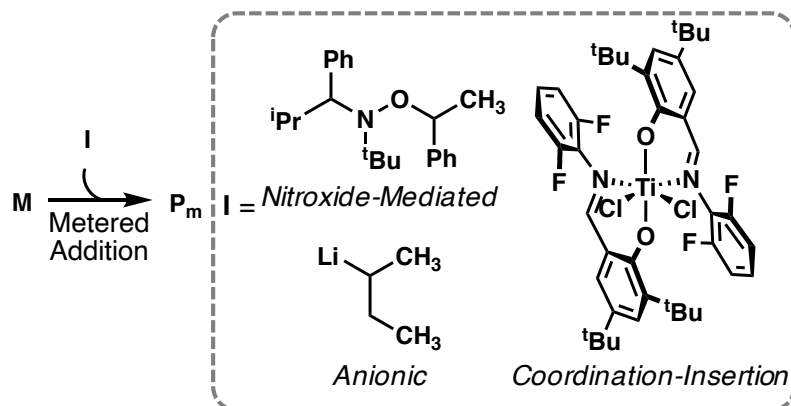
4.1 Abstract

Reversible addition-fragmentation chain-transfer (RAFT) polymerizations are one of the most versatile and powerful polymerization techniques for the synthesis of complex macromolecular architectures. While RAFT polymerizations often give polymers with narrow molecular weight distributions (MWDs), commodity plastics often have broad MWDs to give targeted properties and processability. Thus, new methods to precisely control both MWD breadth and shape are essential for fine-tuning polymer properties for next generation materials. Herein, we report a simple method for controlling polymer MWD features in thermally activated radical RAFT and redox activated cationic RAFT polymerizations by means of metered additions of chain transfer agents.

4.2 Introduction

Radical reversible addition-fragmentation chain-transfer (RAFT) polymerization is a versatile technique providing facile access to a wide range of polymers with predictable number average molecular weights (M_n s) and narrow molecular weight distributions (MWDs).¹⁻⁴ The scalability and commercial availability of dithiocarbonyl chain transfer

a. Previous Work: Metered Addition of Initiator



b. This Work: Metered Addition of CTA

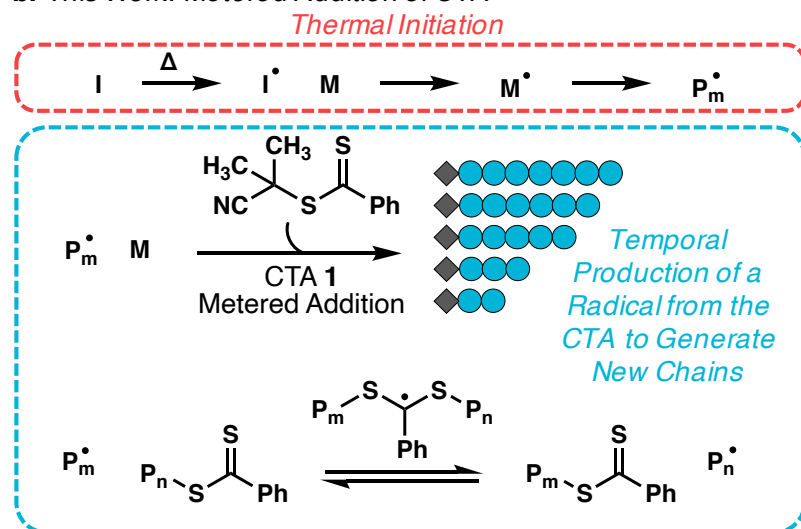


Figure 4.1 (a) Controlling MWD shapes in polymerizations with a single initiating species. (b) Controlling MWD shapes in radical RAFT wherein the CTA, rather than the radical source, is metered in over time.

agents (CTAs) renders RAFT polymerization a highly attractive technique for industrial applications.^{1,5,6} Furthermore, a significant advantage of these processes is their tolerance to water, making them compatible with a variety of aqueous-phase reaction conditions including emulsion,⁷ mini-emulsion,⁸ and suspension⁹ polymerizations. While it is valuable to generate polymers with narrow MWDs, it is often the case that polymers with broader MWDs are easier to process and are thus used in industrial settings.¹⁰ More importantly, precise control of the breadth and shape^{11,12}

of a polymer's MWD can provide valuable handles for targeting desired physical properties and block copolymer morphology.¹³

Synthetic methods to control the entire MWD—both the breadth (dispersity, $\bar{D}$) and shape—is a challenge that has recently attracted significant interest. As such, a variety of strategies for controlling a polymer's MWD have been developed.^{14–38} In particular, several methods have focused on manipulating MWDs in RAFT polymerizations.^{39–45} Boyer and co-workers employed a continuous flow PET-RAFT process in which adjusting pump flow rates over time led to control over a polymer's MWD.^{39,44,46} Similarly, Junkers and co-workers were able to achieve broadened MWDs using radical RAFT polymerizations through automated continuous flow processes.^{40,41} Recently, in a separate approach, Anastasaki and coworkers took advantage of two RAFT agents with different activities to afford MWDs over a broad range of $\bar{D}$ s.^{42,43}

Our group has developed a method to deterministically control the shape and breadth of the MWD in a variety of polymerization systems (Figure 4.1a).^{13,47–55} This method utilizes metered additions of initiating species in controlled polymerizations to temporally regulate chain formation, and therefore, the final distribution of chain lengths. Previously, we have applied this method to anionic, nitroxide mediated, and atom transfer radical polymerizations in which we could meter in an initiator into a solution of monomer.^{13,47–54} In 2020, we also showed that we could apply this method to the polymerization of ethylene in which a co-initiator was required to activate a titanium phenoxyimine catalyst as it was being metered into the batch polymerization.⁵⁵ We envisaged that we could extend this method to thermally activated radical RAFT polymerizations in

which a CTA could be metered into a solution of monomer and initiator (Figure 4.1b). It is important to point out that this system would differ from our previous studies because the CTA does not act as the initiating species itself. Instead, addition of an active polymer chain to the CTA affords a stabilized dithiocarbonyl radical which, upon fragmentation, can generate new propagating chains. As the CTA is added over time into the ongoing polymerization process, new chains are produced such that the polymer chain composition can be tailored. Furthermore, the retardation effects often seen in radical RAFT polymerizations using dithiobenzoate RAFT agents⁵⁶ provides an additional challenge, as the concentration of CTA is changed over time throughout the course of the reaction. Nonetheless, addition of the CTA over time will be able to control the polymerization by providing an equilibrium that minimizes the number of propagating radicals in solution.

Herein, we report a simple method for controlling both MWD shape and breadth in thermally activated radical RAFT polymerization by means of metered additions of the CTA. Using this method, we were able to produce polymers with dispersities as high as 6.2—the highest dispersity of any polymer synthesized using a metered addition of initiator previously reported by our group—and demonstrate their high chain-end fidelity by the synthesis of a diblock copolymer. Furthermore, we show that this general concept can be applied to redox activated cationic RAFT polymerization, producing polyvinyl ethers with controlled MWD features. We anticipate that this methodology will provide the early foundation for controlling MWD shape in industrially pertinent RAFT polymerizations.

4.3 Results and Discussion

We began our investigation with the metered addition of CTA into the radical RAFT polymerization of methyl methacrylate (MMA) initiated by azobisisobutyronitrile (AIBN) (Figure 4.1). We chose 2-cyano-2-propyl benzodithioate (CTA **1**) as our CTA as it provides excellent control in radical RAFT polymerizations of MMA, giving samples with narrow $\bar{D}$ values and the ability to target M_n by changing the ratio of CTA to monomer. As a control sample, we heated a reaction with MMA, **1**, and 0.2 mol% of AIBN in toluene to 90 °C and monitored the reaction using ^1H NMR over the course of 6.5 h before quenching. As expected, a polymer with a narrow dispersity ($\bar{D} = 1.17$) and good matching between experimental and theoretical M_n ($M_n^{\text{exp}} = 10.3 \text{ kg/mol}$, $M_n^{\text{theo}} = 11.9 \text{ kg/mol}$) was achieved with 60% monomer conversion as determined by ^1H NMR (**Error! Reference source not found.**, entry 1 and Table 4.9).

We next proceeded with the metered addition of CTA **1** using various constant rates of addition (Figure 4.1a-d, entries 2-5). To target the same M_n as in the control sample, the total molar concentrations of monomer, AIBN and CTA were held constant in all reactions. To achieve similar levels of conversion, all reactions were quenched after ~6 h (see Table 4.9 for details). Using a 0.5 h constant rate of addition and stopping the polymerization at ~60% conversion of MMA, we obtained PMMA with $M_n^{\text{exp}} = 10.4 \text{ kg/mol}$ and a broadened MWD, with $\bar{D} = 2.04$ (Figure 4.1a, entry 2). Based off our previous studies, a constant rate of addition provides a MWD with tailing toward low molar mass chains, a shift in the peak molecular weight (M_p) toward high molar mass chains, and an asymmetry factor greater than 1.0 ($A_s > 1.0$). In this case, we observed

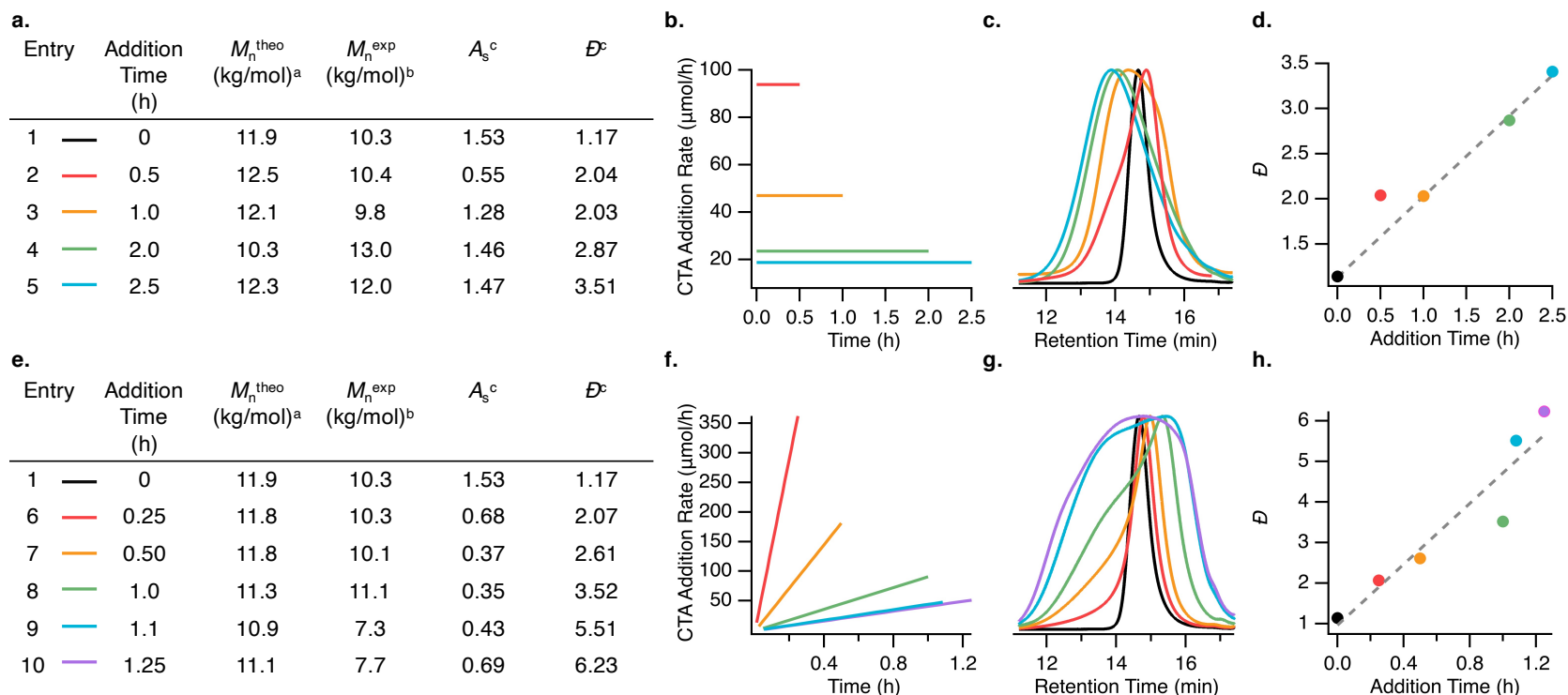


Figure 4.2 Controlling MWDs in radical RAFT polymerization using (a-d) constant or (e-h) linearly increasing rates of CTA **1** addition. ^aDetermined from ¹H NMR conversions. ^bCalculated from light scattering (LS) GPC data using a dn/dc of 0.0812. ^cCalculated from refractive index (RI) GPC relative to PS standards. All reactions were heated to 90 °C and the metered addition of CTA **1** was started when the vial was warm to touch. Reactions were run to ~60% conversion (~6 h, see Table 4.9 for details). Stock solutions of CTA **1** and AIBN in toluene were prepared such that [CTA **1**] = 0.06 M and [AIBN] = 0.01 M. Reaction equivalents MMA:CTA **1**:AIBN = 199:1:0.2.

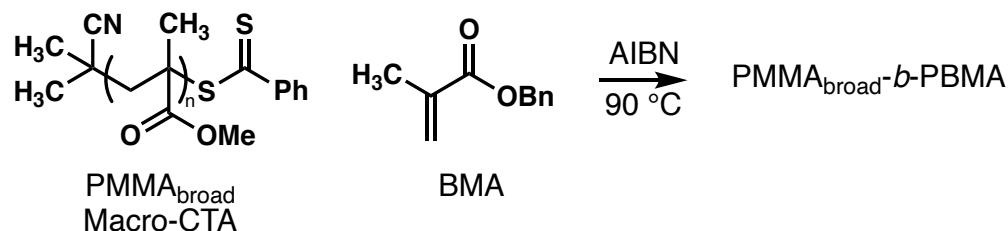
the opposite in which there was tailing toward higher molar mass PMMA chains with M_p shifted toward lower molar mass PMMA chains. The inability to control the MWD shape with short addition times could be the result of the induction time often observed with dithiobenzoate RAFT agents.⁵⁶ However, we found that increasing the addition time from 0.5 h to 1 h resulted in a polymer with a similar $\bar{D}$ but with $A_s = 1.28$ (Figure 4.1a, entry 3). Under similar reaction conditions but using a 2 h addition time, the MWD was broadened even more to a $\bar{D} = 2.87$ with an A_s of 1.46 (Figure 4.1a, entry 4). Increasing the addition time of CTA **1** to 2.5 h afforded a 12.0 kg/mol polymer with $\bar{D} = 3.51$ and $A_s = 1.47$ (Figure 4.1a, entry 5). In each case, we observed good matching between M_n^{theo} and M_n^{exp} , indicating a controlled process. Increasing the addition time above 2.5 h did not result in any increase in $\bar{D}$ (Figure 4.5), giving this method a maximum $\bar{D}$ of ~ 3.5 for this molar mass. It is important to note that these polymers have monomodal MWDs, indicating that even at low CTA concentrations in the beginning of the reaction, polymer chains still enter the RAFT equilibrium such that uncontrolled free-radical polymerization is suppressed. Furthermore, we found that $\bar{D}$ increases linearly with the addition time of CTA **1**, demonstrating the predictability of this method (Figure 4.1d).

To further probe the extent to which MWD shape can be tailored in thermally activated radical RAFT, we set out to produce PMMA with the opposite MWD shape skewed to higher molar mass ($A_s < 1.0$). Interestingly, an exponentially increasing rate of CTA **1** addition results in a bimodal distribution (Figure 4.6). We posit that this is due to an insufficient concentration of CTA relative to AIBN in the beginning of the

reaction such that uncontrolled free-radical polymerization of MMA dominates. To circumvent this issue, we moved to linearly increasing rates of initiator addition to eliminate any significant period of time that the reaction was allowed to stir with very low concentrations of CTA. In support of this hypothesis, we found that linearly increasing rates of addition of CTA **1** afforded PMMA with broadened MWDs and tailing toward higher molar mass chains (Figure 4.1e-h, entries 6-10). Varying the addition time between 0.25 h to 1.0 h enabled the production of PMMA with the desired MWD shape, good matching between M_n^{theo} and M_n^{exp} , and with $\bar{D}$ s between 2.07 and 3.52 (entries 6-8). We were additionally able to produce PMMA with extremely broad MWDs and with tailing toward high molar mass chains. Increasing the addition time beyond 1 h using a linearly increasing rate of addition afforded PMMA with $\bar{D}$ s as high as 6.23 while maintaining the overall desired MWD shape and reasonably good matching between theoretical and experimental molecular weights (entries 9-10). As with our results from the constant rates of addition, we found that $\bar{D}$ increases linearly with the addition time of CTA **1** (Figure 4.1h). These results demonstrate our ability to efficiently control MWD shapes in thermally activated radical RAFT polymerizations *via* metered additions of a CTA. Interestingly, the addition of CTA in these radical RAFT processes has allowed us to control MWD shapes at $\bar{D}$ values of >2 , which is complementary to our previously reported methods for controlling MWD shapes at lower values of $\bar{D}$ using anionic, NMP, or coordination-insertion polymerization.

An advantage of RAFT polymerization is its utility in production of well-defined block copolymers, which is enabled by the high chain-end

a.



b.

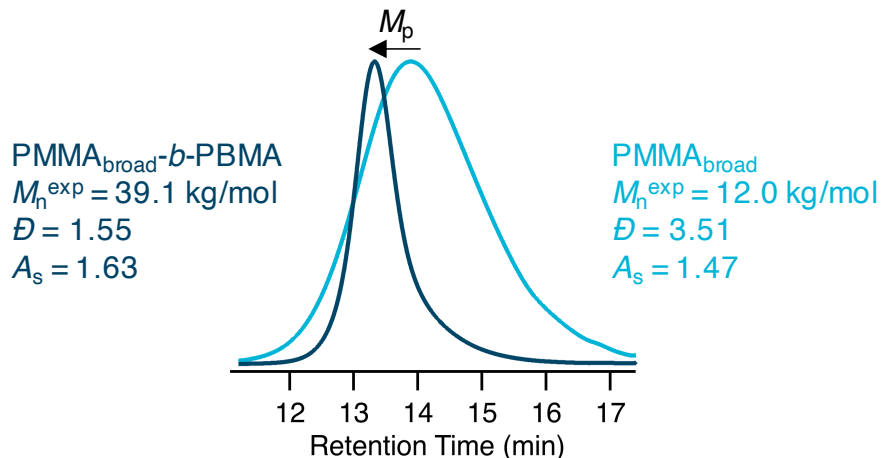


Figure 4.3 Assessing chain-end fidelity of PMMA_{broad} through use as a macro-CTA for chain extension with benzyl methacrylate. For PMMA_{broad}-*b*-PBMA, M_n was determined from ^1H NMR conversion. $\bar{D}$ and A_s were calculated from RI GPC relative to PS standards. Reaction was run for 5 h (~43% conversion of BMA). Stock solutions of the macro-CTA and AIBN in toluene were prepared such that $[\text{macro-CTA}] = 0.015 \text{ M}$ and $[\text{AIBN}] = 0.0125 \text{ M}$. Reaction equivalents BMA:macro-CTA:AIBN = 342:1:0.2.

fidelity (chains terminated with the dithiobenzoate chain end). To evaluate chain-end fidelity in our polymers with broadened distributions, we chain extended a disperse PMMA (PMMA_{broad}, $\bar{D} = 3.51$, $A_s = 1.47$) macro-CTA with benzyl methacrylate (BMA) (Figure 4.3a). The chain extension yielded a monomodal diblock with an M_n of 39.1 kg/mol and a $\bar{D}$ of 1.55 (Figure 4.3b). The clean shift in M_p and the good matching between theoretical and experimental molecular weights for the diblock copolymer ($M_n^{\text{theo}} = 37.8 \text{ kg/mol}$, $M_n^{\text{exp}} = 39.1 \text{ kg/mol}$) demonstrated excellent chain end fidelity in our polymers (Figure 4.7).

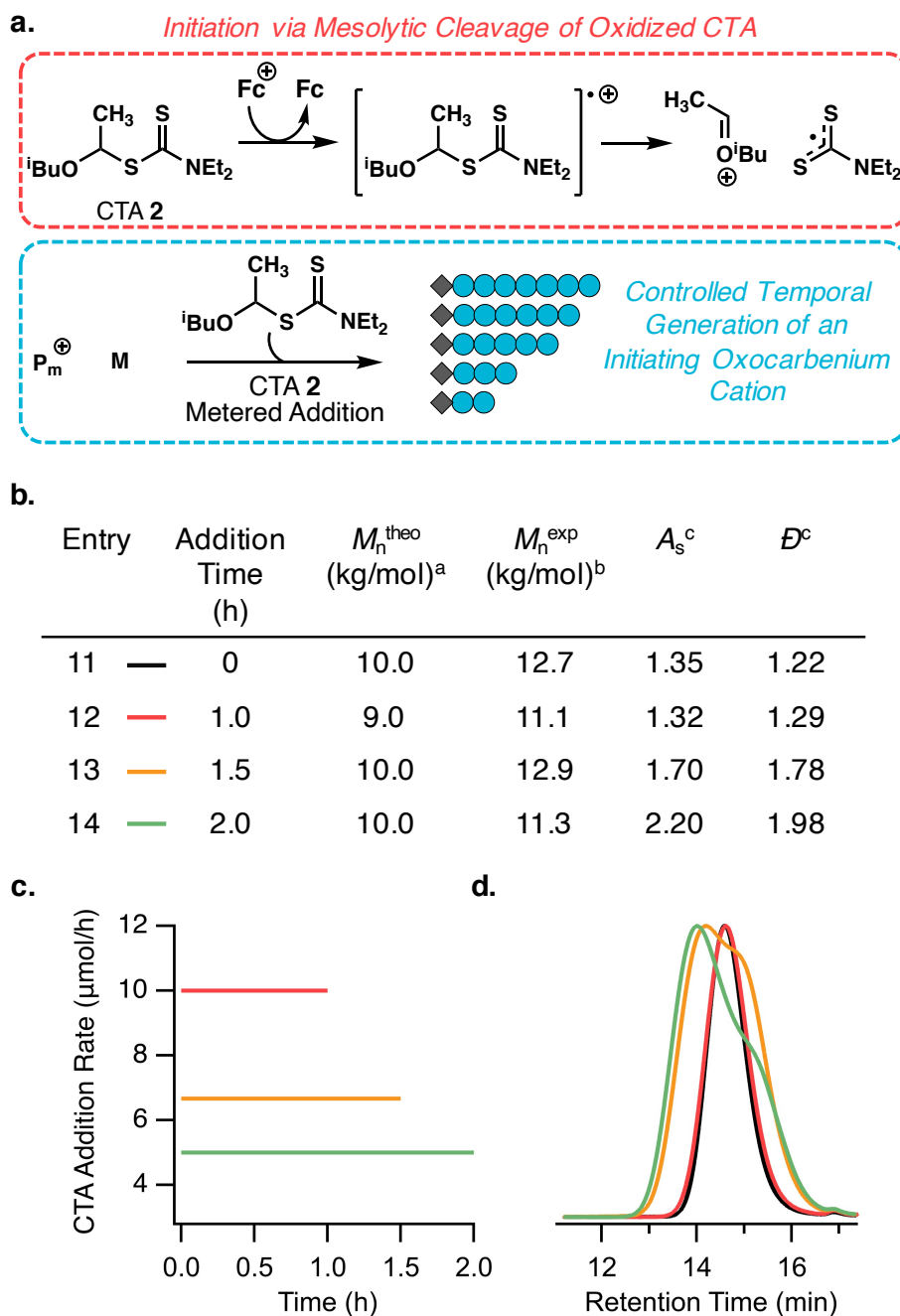


Figure 4.4 Controlling MWDs in redox activated cationic RAFT polymerization of IBVE. ^aDetermined from ¹H NMR conversions. ^bCalculated from LS GPC data using a dn/dc of 0.0381. ^cCalculated from RI GPC relative to PS standards. Reactions were run to ~100% conversion (~5 h). Stock solutions of CTA 2 and ferrocenium in dichloromethane were prepared such that [CTA 2] = 0.02 M and [FcBF₄] = 2 mM. Reaction equivalents IBVE:CTA 2:FcBF₄ = 100:1:0.0002.

Inspired by these results, we posited that a similar strategy could be employed in the redox activated cationic RAFT polymerization, which uses ferrocenium tetrafluoroborate (FcBF_4) as a mild chemical oxidant. In this mechanism, FcBF_4 oxidizes CTA **2** to the radical cation, which subsequently undergoes mesolytic cleavage to form a stabilized dithiocarbonyl radical and an oxocarbenium cation which initiates polymerization of isobutyl vinyl ether (IBVE) (Figure 4.4a). Thus, metered addition of CTA **2** should enable control over the resulting polymer MWD features. However, it is important to note that unlike in thermally activated radical RAFT where chain initiation by AIBN is independent of the CTA concentration, in this cationic RAFT mechanism, initiation is dependent on the CTA concentration as initiation occurs through direct oxidation of the CTA by FcBF_4 . By metering in CTA over time, the concentration of CTA, and therefore initiation kinetics, changes over time. We anticipated that gaining control over MWD features would be inherently more challenging in this particular cationic RAFT system than in thermally activated radical RAFT polymerization. Further complicating the task, uncontrolled generation of new chains can occur in these polymerizations by direct monomer oxidation.

As a proof of concept, a constant rate of CTA **2** addition afforded PIBVE with good matching between M_n^{theo} and M_n^{exp} , and with broadened MWDs tailing toward low molar mass chains (Figure 4.4b-d). However, using either linearly or exponentially increasing rates of CTA **2** addition, we were unable to access monomodal distributions of the opposite MWD shape. Instead, we observed bimodal distributions in both cases (Figure 4.8). We expect that the concentration of CTA in the beginning of the

reaction is too low using these addition profiles, such that direct monomer oxidation and uncontrolled cationic polymerization occurs before sufficient CTA is introduced into the reaction. Future studies will investigate the efficacy of our method in other cationic polymerizations wherein initiation is not influenced by CTA concentration. However, this is still an excellent method to broaden MWDs in the cationic polymerization of vinyl ethers.

4.4 Conclusions

Our results show that metered additions of chain transfer agents can be used to deterministically control polymer MWD breadth and shape in RAFT polymerizations. Using this strategy, we were able to produce well-defined polymers with tailored MWDs and dispersities as high as 6.2 in thermally activated radical RAFT polymerizations. High chain-end fidelity was demonstrated by the synthesis of a diblock copolymer *via* chain extension of a PMMA_{broad} macro-CTA. We suspect that we can also achieve MWD shape control in radical RAFT by metering in a combination of AIBN and CTA, which is something our lab will pursue in future studies. Furthermore, preliminary studies revealed that this general strategy could be extended to a redox activated cationic RAFT polymerization. Additional studies will investigate the effect of metered CTA additions in cationic RAFT polymerizations in which initiation is independent of the CTA. We anticipate that our results will open the door for controlling MWD features in industrially-attractive RAFT polymerizations.

4.5 References

- (1) S. Perrier, *Macromolecules*, 2017, **50**, 7433–7447.
- (2) C. Barner-Kowollik, *Handbook of RAFT Polymerization*, Wiley-VCH Verlag, Weinheim, 2008.
- (3) G. Moad, E. Rizzardo and S. H. Thang, *Chem. Asian J.*, 2013, **8**, 1634–1644.
- (4) X. Tian, J. Ding, B. Zhang, F. Qiu, X. Zhuang and Y. Chen, *Polymers*, 2018, **10**, 318.
- (5) M. Destarac, *Macromol. React. Eng.*, 2010, **4**, 165–179.
- (6) N. Micic, A. Young, J. Rosselgong and C. H. Hornung, *Processes*, 2014, **2**, 58–70.
- (7) For select examples, see: a) C. J. Ferguson, R. J. Hughes, B. T. T. Pham, B. S. Hawket, R. G. Gilbert, A. K. Serelis and C. H. Such, *Macromolecules*, 2002, **35**, 9243–9245. b) S. W. Prescott, M. J. Ballard, E. Rizzardo and R. G. Gilbert, *Aust. J. Chem.*, 2002, **55**, 415–424. c) J. Zhou, H. Yao and J. Ma, *Polym. Chem.*, 2018, **9**, 2532–2561. d) N. G. Engeli, A. Anastasaki, G. Nurumbetov, N. P. Truong, V. Nikolaou, A. Shegiwal, M. R. Whittaker, T. P. Davis and D. M. Haddleton, *Nat. Chem.*, 2017, **9**, 171–178.
- (8) For select examples, see: a) J. Jiang, W. J. Wang, B. G. Li and S. Zhu, *Ind. Eng. Chem. Res.*, 2019, **58**, 18997–19008. b) Y. Luo, R. Wang, L.

- Yang, B. Yu, B. Li and S. Zhu, *Macromolecules*, 2006, **39**, 1328–1337. c) X. Li, W.-J. Wang, F. Weng and B.-G. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 7321–7332.
- (9) For select examples, see: a) H. Bouhamed, S. Boufi and A. Magnin, *J. Colloid Interface Sci.*, 2007, **312**, 279–291. b) W. Zhang, B. Charleux and P. Cassagnau, *Macromolecules*, 2012, **45**, 5273–5280. c) J. D. Biasutti, T. P. Davis, F. P. Lucien and J. P. A. Heuts, *J. Polym. Sci. Part A Polym. Chem.*, 2005, **43**, 2001–2012. d) Y. Zhang, J. Ding and S. Gong, *J. Appl. Polym. Sci.*, 2013, **128**, 2927–2932.
- (10) M. Stürzel, S. Mihan and R. Mülhaupt, *Chem. Rev.*, 2016, **116**, 1398–1433.
- (11) S. S. Rane and P. Choi, *Chem. Mater.*, 2005, **17**, 926.
- (12) S. Harrisson, *Polym. Chem.*, 2018, **9**, 1366–1370.
- (13) D. T. Gentekos, R. J. Sifri and B. P. Fors, *Nat. Rev. Mater.*, 2019, **4**, 761–774.
- (14) R. L. Laurence and G. Vasudevan, *Ind. Eng. Chem. Process Des. Dev.*, 1968, **7**, 427–433.
- (15) D. A. Couso, L. M. Alassia and G. R. Meira, *J. Appl. Polym. Sci.*, 1985, **30**, 3249–3265.
- (16) K.-I. Seno, S. Kanaoka and S. Aoshima, *J. Polym. Sci. Part A Polym. Chem.*, 2008, **46**, 2212–2221.
- (17) P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts and J. D. Weinhold, *Macromolecules*, 2009, **42**, 3788–3794.

- (18) J. M. Widin, A. K. Schmitt, K. Im, A. L. Schmitt and M. K. Mahanthappa, *Macromolecules*, 2010, **43**, 7913–7915.
- (19) A. Plichta, M. Zhong, W. Li, A. M. Elsen and K. Matyjaszewski, *Macromol. Chem. Phys.*, 2012, **213**, 2659–2668.
- (20) J. M. Widin, A. K. Schmitt, A. L. Schmitt, K. Im and M. K. Mahanthappa, *J. Am. Chem. Soc.*, 2012, **134**, 3834–3844.
- (21) A. K. Schmitt and M. K. Mahanthappa, *Macromolecules*, 2014, **47**, 4346–4356.
- (22) D. Liu, A. D. Sponza, D. Yang and M. Chiu, *Angew. Chemie Int. Ed.*, 2019, **58**, 16210–16216.
- (23) R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland and A. Anastasaki, *Chem. Sci.*, 2019, **10**, 8724–8734.
- (24) R. Whitfield, K. Parkatzidis, M. Rolland, N. P. Truong and A. Anastasaki, *Angew. Chemie Int. Ed.*, 2019, **58**, 13323–13328.
- (25) T. T. Wang, Y. Y. Wu, Z. H. Luo and Y. N. Zhou, *Macromolecules*, 2020, **53**, 10813–10822.
- (26) L. M. Alassia, D. A. Couso and G. R. Meira, *J. Appl. Polym. Sci.*, 1988, **36**, 481–494.
- (27) T. Junkers and J. H. Vrijsen, *Eur. Polym. J.*, 2020, **134**, 109834.
- (28) D. J. Walsh, D. A. Schinski, R. A. Schneider and D. Guironnet, *Nat. Commun.*, 2020, **11**, 3094.
- (29) H. Liu, Y. H. Xue, Y. L. Zhu, F. L. Gu and Z. Y. Lu, *Macromolecules*,

2020, **53**, 6409–6419.

- (30) T. Junkers, *Macromol. Chem. Phys.*, 2020, **221**, 2000234.
- (31) M. Rolland, N. P. Truong, R. Whitfield and A. Anastasaki, *ACS Macro Lett.*, 2020, **9**, 459–463.
- (32) W. Fischer, K. Knoll, W. Loth, V. Warzelhan, A. Deffieux, P. Desbois, M. Fontanille, S. Lätsch, C. Schade, H. Gausepohl, US6444762 B1, 1997.
- (33) D. Bendejacq, V. Ponsinet, M. Joanicot, Y. L. Loo and R. A. Register, *Macromolecules*, 2002, **35**, 6645–6649.
- (34) E. Farkas, Z. G. Meszena and A. F. Johnson, *Ind. Eng. Chem. Res.* 2004, **43**, 7356–7360.
- (35) N. A. Lynd and M. A. Hillmyer, *Macromolecules*, 2005, **38**, 8803–8810.
- (36) N. A. Lynd and M. A. Hillmyer, *Macromolecules*, 2007, **40**, 8050–8055.
- (37) A. J. Meuler, C. J. Ellison, C. M. Evans, M. A. Hillmyer and F. S. Bates, *Macromolecules*, 2007, **40**, 7072–7074.
- (38) J. Listak, W. Jakubowski, L. Mueller, A. Plichta, K. Matyjaszewski and M. R. Bockstaller, *Macromolecules*, 2008, **41**, 5919–5927.
- (39) N. Corrigan, A. Almasri, W. Taillades, J. Xu and C. Boyer, *Macromolecules*, 2017, **50**, 8438–8448.
- (40) M. Rubens and T. Junkers, *Polym. Chem.*, 2019, **10**, 5721–5725.
- (41) M. Rubens and T. Junkers, *Polym. Chem.*, 2019, **10**, 6315–6323.
- (42) R. Whitfield, K. Parkatzidis, N. P. Truong, T. Junkers and A. Anastasaki, *Chem*, 2020, **6**, 1340–1352.

- (43) K. Parkatzidis, N. P. Truong, M. N. Antonopoulou, R. Whitfield, D. Konkolewicz and A. Anastasaki, *Polym. Chem.*, 2020, **11**, 4968–4972.
- (44) K. Liu, N. Corrigan, A. Postma, G. Moad and C. Boyer, *Macromolecules*, 2020, **53**, 8867–8882.
- (45) K. Parkatzidis, H. Suk Wang, N. P. Truong and A. Anastasaki, *Chem*, 2020, **6**, 1575–1588.
- (46) N. Corrigan, R. Manahan, Z. T. Lew, J. Yeow, J. Xu and C. Boyer, *Macromolecules*, 2018, **51**, 4553–4563.
- (47) D. T. Gentekos and B. P. Fors, *ACS Macro Lett.*, 2018, **7**, 677–682.
- (48) D. T. Gentekos, J. Jia, E. S. Tirado, K. P. Barteau, D.-M. Smilgies, R. A. DiStasio and B. P. Fors, *J. Am. Chem. Soc.*, 2018, **140**, 4639–4648.
- (49) S. I. Rosenbloom, D. T. Gentekos, M. N. Silberstein and B. P. Fors, *Chem. Sci.*, 2020, **11**, 1361–1367.
- (50) V. Kottisch, D. T. Gentekos and B. P. Fors, *ACS Macro Lett.*, 2016, **5**, 796–800.
- (51) S. Domanskyi, D. T. Gentekos, V. Privman and B. P. Fors, *Polym. Chem.*, 2020, **11**, 326–336.
- (52) S. I. Rosenbloom and B. P. Fors, *Macromolecules*, 2020, 7479–7486.
- (53) M. Nadgorny, D. T. Gentekos, Z. Xiao, S. P. Singleton, B. P. Fors and L. A. Connal, *Macromol. Rapid Commun.*, 2017, **38**, 1700352.
- (54) D. T. Gentekos, L. N. Dupuis and B. P. Fors, *J. Am. Chem. Soc.*, 2016, **138**, 1848.

- (55) R. J. Sifri, O. Padilla-Veíez, G. W. Coates and B. P. Fors, *J. Am. Chem. Soc.*, 2020, **142**, 1443–1448.
- (56) C. Barner-kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. Mcleary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge, P. Vana and P. Marie, *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 5809–5831.

4.6 Appendix

4.6.1 Experimental Section

Materials

Unless otherwise noted, all reactions were performed in a Unilab MBraun Glovebox with a nitrogen atmosphere. Methanol (MeOH, 99.8%, Fisher Scientific) was used without further purification. Toluene (>99%, J.T. Baker) and dichloromethane (DCM, >99%, J.T. Baker) were purified by purging with argon for 1 h, followed by passing through two packed columns of neutral alumina under argon pressure. DCM was further purified by distilling over 4Å molecular sieves followed by degassing using 3 freeze pump thaw cycles. DCM was then stored under nitrogen in the glovebox. Azobisisobutyronitrile (AIBN, 98%, Millipore Sigma) was purified by recrystallization from MeOH. 2-Cyano-2-propyl benzodithioate (CTA **1**, >97%, Millipore Sigma) and ferrocenium tetrafluoroborate (FcBF₄, 97%, Millipore Sigma) were used as received. Methyl methacrylate (MMA, 99%, Millipore Sigma) and benzyl methacrylate (BMA, 96%, Millipore Sigma) were filtered over basic alumina (Oakwood Chemicals) and degassed by three freeze-pump-thaw cycles. Isobutyl vinyl ether (IBVE, 99%, TCI) was dried over calcium hydride (CaH₂, ACROS organics, 93% extra pure, 0-2 mm grain size) for 12 h, distilled under vacuum, and degassed by three freeze-pump-thaw cycles.

Analytical Methods

All polymer samples were analyzed using a Tosoh EcoSec HLC 9320GPC system with two SuperHM-M columns in a series at a flow rate of 0.350 mL/min. Tetrahydrofuran (THF) was used as the eluent and all dispersities ($\bar{D}$) and asymmetry factors (A_s) were calculated from refractive index chromatograms against TSKgel polystyrene standards. All homopolymer number-average molecular weights (M_n) were determined by light scattering using a Wyatt miniDawn Treos multi-angle light scattering detector and calculated dn/dc values (0.0812 mL g⁻¹ for PMMA and 0.0381 mL g⁻¹ for PIBVE). Conversions were determined by proton nuclear magnetic resonance (¹H NMR) spectra obtained on a Bruker 500 MHz spectrometer in CDCl₃. The M_n for the PMMA_{broad}-*b*-PBMA diblock copolymer was calculated from ¹H NMR data.

Synthesis

Representative Procedure for Synthesis of Narrow PMMA via Radical RAFT Polymerization.

A 20 mL scintillation vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 1.0 mL of MMA (9.35 mmol), 0.75 mL of a 0.0125 M stock solution of AIBN in toluene (9.35 μmol), and 0.69 mL of a 0.068 M stock solution of CTA **1** in toluene (0.047 mmol). The reaction was placed in a heating block equipped with a thermocouple. The reaction was heated to 90 °C until ~60% conversion of MMA to PMMA was reached (6.5 h).

The reaction vial was removed from the glovebox and the polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

Representative Procedure for Synthesis of Broad PMMA via Radical RAFT Polymerization.

A 20 mL scintillation vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 1.0 mL of MMA (9.35 mmol) and 0.75 mL of a 0.0125 M stock solution of AIBN in toluene (9.35 μ mol). 0.69 mL of a 0.068 M stock solution of CTA **1** in toluene (0.047 mmol) was drawn into a 1 mL syringe and mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Table 4.1 – Table 4.5). The needle was submerged into the reaction solution, the reaction vial was placed in a heating block equipped with a thermocouple, and the temperature was set to 90 °C. As soon as the vial was warm to touch, the addition program was started. The reaction was stirred at 90 °C until ~60% conversion of MMA to PMMA was reached (~6 h). The reaction vial was removed from the glovebox and the polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

PMMA_{broad}-b-PBMA via Radical RAFT Polymerization.

This polymerization was performed in a hood using a Schlenk line. The PMMA_{broad} macro-CTA (M_n = 12.0 kg/mol) was crashed out of MeOH and dried

under vacuum at 40 °C for 12 h. A 0.015 M stock solution of the macro-CTA in toluene was prepared. A 20 mL scintillation vial capped with a screw-cap septum and equipped with a magnetic stir bar was flame dried under vacuum and charged with 0.68 mL of the macro-CTA stock solution (0.01 mmol), 0.16 mL of a 0.0125 M stock solution of AIBN in toluene (0.002 mmol), and 0.54 mL of BMA (3.42 mmol). The reaction mixture was degassed by three freeze-pump-thaw cycles and then placed under nitrogen. The reaction was heated to 90 °C under a nitrogen headspace for 5 h (~43% conversion of BMA to PBMA). The polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

Representative Procedure for Synthesis of Narrow PIBVE via Cationic RAFT Polymerization.

A 3 mL dram vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 0.13 mL of IBVE (1 mmol), 0.1 mL of a 2 mM stock solution of FcBF₄ in DCM (0.02 mol%, 0.2 μmol), and 0.5 mL of a 0.02 M stock solution of CTA **2** in DCM (0.1 mmol). The reaction was allowed to stir for 5 h (~100% conversion of IBVE to PIBVE) and terminated by opening the reaction vial to air and diluting with DCM outside of the box. Aliquots were taken for GPC and ¹H NMR. The polymer could be isolated by crashing out in cold methanol and drying at 50 °C under vacuum until constant mass is achieved.

Representative Procedure for Synthesis of Broad PIBVE via Cationic RAFT Polymerization.

A 3 mL dram vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 0.13 mL of IBVE (1 mmol) and capped with a PTFE septum. 0.5 mL of a 0.01 M stock solution of CTA **2** in DCM (0.1 mmol) was drawn into a 1 mL syringe and mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Table 4.6—Table 4.8). Upon starting the addition of CTA **2**, 0.1 mL of a 2 mM stock solution of FcBF₄ in DCM (0.2 μ mol) was injected through the septa. The reaction was allowed to stir for 5 h (~100% conversion of IBVE to PIBVE) and terminated by opening the reaction vial to air and diluting with DCM outside of the box. Aliquots were taken for GPC and ¹H NMR. The polymer could be isolated by crashing out in cold methanol and drying at 50 °C under vacuum until constant mass is achieved.

4.6.2 Reagent Quantities and Addition Rates of CTA for Skewed Polymers

Radical RAFT Polymerization

Table 4.1 Preparation of PMMA Entries 2-5 using Constant Rates of CTA 1 Addition

Entry	MMA, AIBN Volumes (mL)	Addition Time CTA 1 (h)	Addition Rate CTA 1 ($\mu\text{L}/\text{h}$)	Total Volume CTA 1 (μL)	Molarity CTA 1 Stock Solution (mol/L)
1	1.0, 0.75	0.0	--	690	0.068
2	1.0, 0.75	0.5	1380	690	0.068
3	1.0, 0.75	1.0	690	690	0.068
4	1.0, 0.75	2.0	345	690	0.068
5	1.0, 0.75	2.5	366	914	0.051

Table 4.2 Preparation of PMMA Entries 6-8 using Linearly Increasing Rates of CTA 1 Addition

Reagent Volume (mL)	Step #	Addition Rate CTA 1 ($\mu\text{L}/\text{h}$)			Volume CTA 1 (μL)/Step [CTA 1] = 0.068 M
		Entry 6 0.25 h	Entry 7 0.5 h	Entry 8 1.0 h	
MMA = 1.0 AIBN = 0.75	1	193	97	48	2.4
	2	483	232	116	5.8
	3	733	367	183	9.2
	4	1004	502	251	13
	5	1274	637	318	16
	6	1544	772	385	19
	7	1814	907	453	23
	8	2084	1042	520	26
	9	2355	1177	588	29
	10	2625	1312	655	33
	11	2895	1448	723	36
	12	3165	1583	790	40
	13	3436	1718	858	43
	14	3706	1853	925	46
	15	3976	1988	992	50
	16	4246	2123	1060	53
	17	4516	2258	1127	56
	18	4787	2393	1195	60
	19	5057	2528	1262	63
	20	5327	2663	1330	67

Table 4.3 Preparation of PMMA Entry 9 using a Linearly Increasing Rate of CTA 1 Addition

Reagent Volumes (mL)	Step #	Addition Rate CTA 1 (μ L/h)	Volume CTA 1 (μ L)/Step [CTA 1] = 0.054 M
MMA = 0.7 AIBN = 0.53		1.1 h	
	1	40	2.2
	2	95	5.2
	3	151	8.2
	4	207	11
	5	262	14
	6	318	17
	7	374	20
	8	429	23
	9	484	26
	10	541	29
	11	596	32
	12	652	35
	13	707	38
	14	763	41
	15	819	44
	16	874	47
	17	930	50
	18	986	53
	19	1041	56
	20	1097	59

Table 4.4 Preparation of PMMA Entry 10 using a Linearly Increasing Rate of CTA 1 Addition

Reagent Volumes (mL)	Step #	Addition Rate CTA 1 ($\mu\text{L}/\text{h}$)	Volume CTA 1 (μL)/Step [CTA 1] = 0.037 M
MMA = 0.7 AIBN = 0.53		1.25 h	
	1	49	3.1
	2	118	7.4
	3	188	12
	4	257	16
	5	326	20
	6	395	25
	7	464	29
	8	533	33
	9	602	38
	10	671	42
	11	740	46
	12	809	51
	13	878	55
	14	947	59
	15	1016	64
	16	1086	68
	17	1155	72
	18	1224	76
	19	1293	81
	20	1362	85

Table 4.5 Preparation of PMMA using an Exponentially Increasing Rate of CTA 1 Addition

Reagent Volumes (mL)	Step #	Addition Rate CTA 1 ($\mu\text{L}/\text{h}$)	Volume CTA 1 (μL)/Step [CTA 1] = 0.068 M
MMA = 1.0 AIBN = 0.75		2.0 h	
	1	3.3	0.3
	2	4.6	0.5
	3	6.5	0.6
	4	9.0	0.9
	5	13	1.3
	6	18	1.8
	7	25	2.5
	8	35	3.5
	9	49	4.9
	10	68	6.8
	11	95	9.5
	12	134	13
	13	187	19
	14	262	26
	15	366	37
	16	513	51
	17	718	72
	18	1005	101
	19	1408	141
	20	1971	197

Cationic RAFT Polymerization

Table 4.6 Preparation of PIBVE Entries 11-14 using Constant Rates of CTA 2 Addition

Entry	IBVE (mL), FcBF ₄ (mol %)	Addition Time CTA 2 (h)	Addition Rate CTA 2 (μ L/h)	Total Volume CTA 2 (μ L)
11	0.13, 0.02	0.0	-	500
12	0.13, 0.02	1.0	500	500
13	0.13, 0.02	1.5	333	500
14	0.13, 0.02	2.0	250	500

Table 4.7 Preparation of PIBVE using a Linearly Increasing Rate of CTA 2 Addition

Reagent Volumes (mL)	Step #	Addition Rate CTA 2 ($\mu\text{L}/\text{h}$)	Volume CTA 2 (μL)/Step [CTA 2] = 0.02 M
IBVE = 0.13 FcBF ₄ = 0.1		2.0 h	
	1	17	2
	2	42	4
	3	66	7
	4	91	9
	5	115	12
	6	140	14
	7	164	16
	8	189	19
	9	213	21
	10	238	24
	11	262	26
	12	287	29
	13	311	31
	14	336	34
	15	360	36
	16	385	38
	17	409	41
	18	434	43
	19	458	46
	20	483	48

Table 4.8 Preparation of PIBVE using an Exponentially Increasing Rate of CTA 2 Addition

Reagent Volumes (mL)	Step #	Addition Rate CTA 2 ($\mu\text{L}/\text{h}$)	Volume CTA 2 (μL)/Step [CTA 2] =
IBVE = 0.13 FcBF ₄ = 0.1		2.0 h	0.02 M
	1	2.4	0.24
	2	3.6	0.35
	3	4.7	0.47
	4	6.6	0.66
	5	9.2	0.92
	6	12.9	1.3
	7	18	1.8
	8	25	2.5
	9	35	3.5
	10	49	4.9
	11	69	6.9
	12	97	9.7
	13	136	14
	14	190	19
	15	266	27
	16	372	37
	17	521	52
	18	730	73
	19	1022	102
	20	1430	143

Table 4.9 Summary of Polymerization Results

Entry ^a	Addition Type, Time (h) ^b	Reaction Time (h)	Conversion (%) ^c	M_n^{theo} (kg/mol) ^c	M_n^{exp} (kg/mol) ^d	$\bar{D}^d$	A_s^d	α_3^e
1	I, 0	6.5	59.7	11.9	10.3	1.17	1.53	-0.24
2	C, 0.5	5.0	62.5	12.5	10.4	2.04	0.55	7.83
3	C, 1.0	5.5	60.6	12.1	9.8	2.03	1.28	2.81
4	C, 2.0	6.3	51.6	10.3	13.0	2.87	1.46	3.19
5	C, 2.5	5.0	61.7	12.3	12.0	1.47	3.51	3.26
6	LI, 0.25	6.0	59.3	11.8	10.3	2.07	0.68	6.72
7	LI, 0.50	6.3	59.0	11.8	10.1	2.61	0.37	8.30
8	LI, 1.0	5.3	56.7	11.3	11.1	3.52	0.35	8.25
9	LI, 1.1	6.3	54.8	10.9	7.3	5.51	0.43	11.18
10	LI, 1.25	5.0	55.9	11.1	7.7	6.23	0.69	9.66
11	I, 0	5.0	100	10.0	12.7	1.22	1.35	1.70
12	I, 1.0	5.0	90	9.0	11.1	1.29	1.32	1.45
13	I, 1.5	5.0	100	10.0	12.9	1.78	1.70	2.85
14	I, 2.0	5.0	100	10.0	11.3	1.98	2.20	1.85

4.6.3 Supplemental Figures and Equations

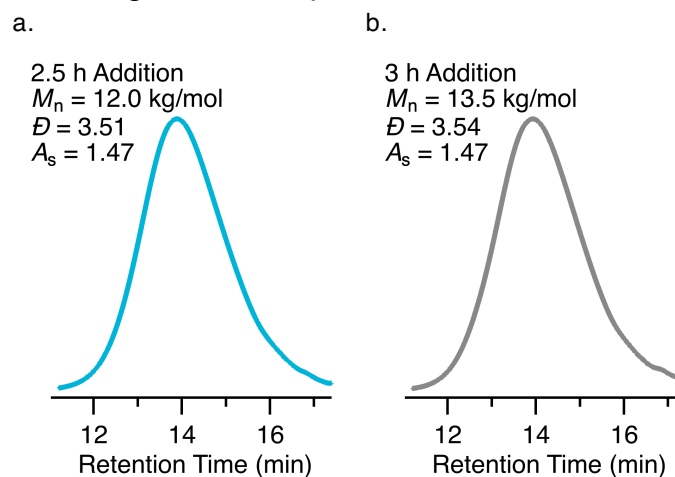


Figure 4.5 Comparison of GPC traces for PMMA produced using a (a) 2.5 h or (b) 3 h constant rate of CTA 1 addition.

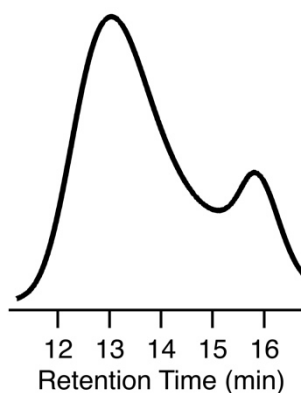


Figure 4.6 Exponentially increasing rate of CTA 1 addition produces PMMA having a bimodal MWD.

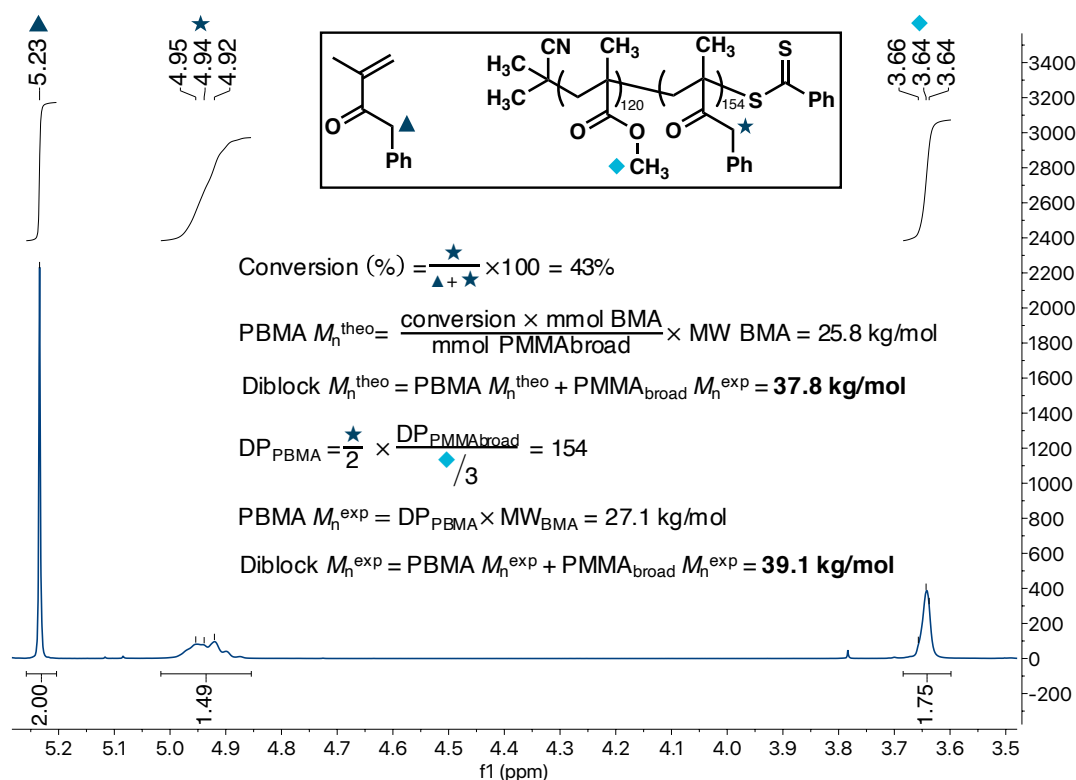


Figure 4.7 500 MHz ^1H NMR spectrum of $\text{PMMA}_{\text{broad}}\text{-}b\text{-PBMA}$ displaying relevant equations for calculating conversion, M_n^{theo} , and M_n^{exp} .

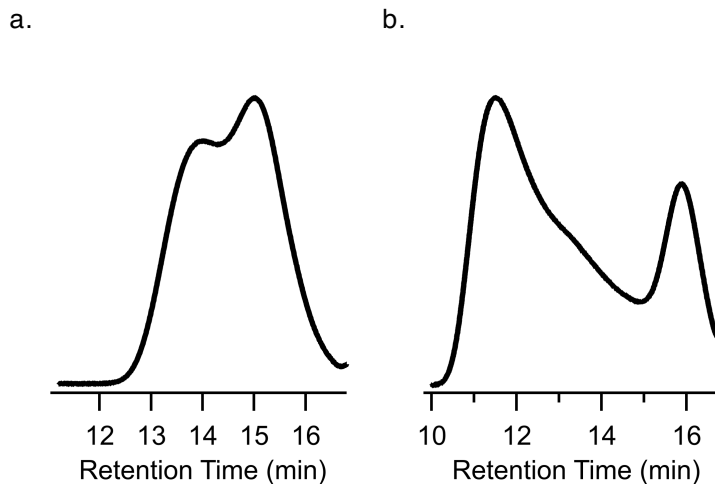


Figure 4.8 Bimodal MWDs produced from (a) a linearly increasing rate and (b) an exponentially increasing rate of CTA 2 addition in the redox-initiated cationic polymerization of IBVE.

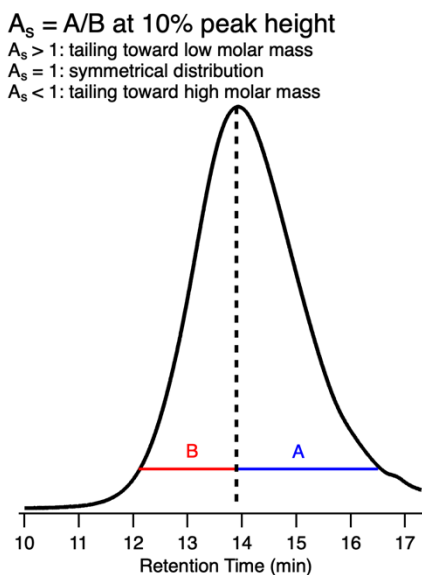


Figure 4.9 Depiction of Asymmetry Factor Calculation

Equation 1. Calculation of Skewness (α_3):

$$\alpha_3 = \frac{M_z M_w M_n - 3M_n^2 M_w + 2M_n^3}{(M_w M_n - M_n^2)^{3/2}}$$

4.6.4 References

- (1) Rudin, A. Molecular Weight Distributions of Polymers. *J. Chem. Educ.*
1969, 46, 595—600.

CHAPTER 5

MICROSTRUCTURAL EVOLUTION OF POLYUREA UNDER HYDROSTATIC PRESSURE

5.1 Abstract

Polyurea (PU) is a versatile high strain rate elastomeric polymer that has attracted significant interest due to its utility as a blast and ballistic resistant coating. Predictive design of PU materials, particularly with a focus on structure, is complicated by the occurrence of both high pressure and high strain rate effects in response to blast and ballistic impact. To help elucidate the behavior of PU under such conditions, we sought to characterize the microstructural evolution of PU under hydrostatic compression. To this end, we utilized a diamond anvil cell with *in-situ* X-ray scattering to monitor the compression-induced microstructural changes of two PU materials differing in their soft segment length. We found that regardless of soft segment length, the initially phase separated structure becomes increasingly mixed during hydrostatic compression up to ~1 GPa. Despite this increase in phase mixing, the interchain network between urea linkages formed through hydrogen bonds remains apparent at pressures well above 1 GPa. The mean spacing associated with the interchain hydrogen-bonded network within the hard segment domains contracts under hydrostatic compression and in some cases recovers upon load removal. Furthermore, the extent of both deformation and recovery depends upon the degree of microphase separation as dictated by the length of the soft

segment, wherein PU with a longer soft segment deforms less and recovers more.

5.2 Introduction

Polyurea (PU) thermoset polymers are versatile elastomers with various applications, particularly as light-weight coatings on metal or concrete to protect humans, vehicles, and buildings from blast and ballistic impact.^{1,2} Within these applications, PU experiences a mix of shear stress and hydrostatic pressure as well as a wide range of strain rates.^{1,2} Notably, under such blast and ballistic loadings, adiabatic heating can occur, leading to thermal softening and potentially crystal melting.³ Many experimental studies have been conducted on PU macroscale mechanical properties to provide information for predicting the performance of PU coated structures.^{3–21} These experiments have revealed that PU has substantial strain rate and pressure sensitivity. Notably, sandwiched pressure-shear plate impact experiments have shown that the shear strength of PU exceeds that of high strength steel at strain rates of 10^5 s^{-1} and pressures of 9 GPa.⁸

To tailor the PU formulation to obtain certain performance for a particular application, it is necessary to understand and quantify the mechanisms through which the polymer structure influences the mechanical properties. PU consists of polymer chains with alternating hard and soft segments, which can be modified in molecular composition and length (Figure 5.1).^{22–24} It has been

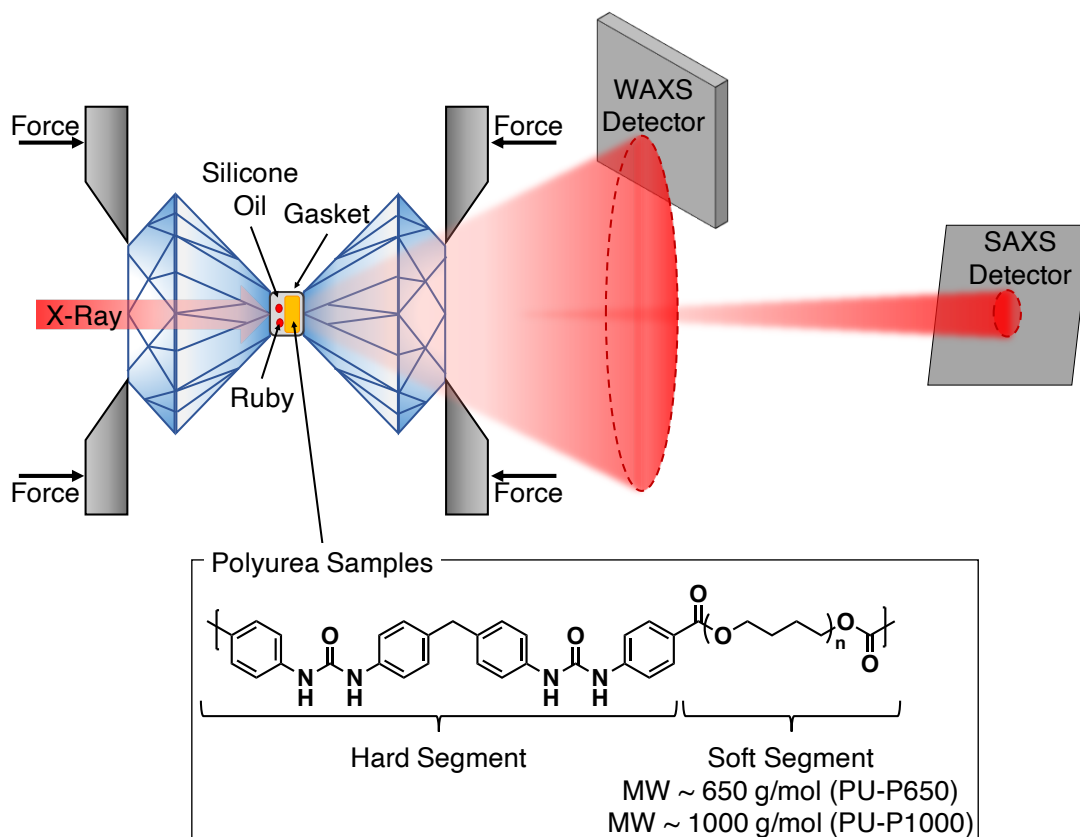


Figure 5.1 Characterization of the microstructural evolution of PU under hydrostatic compression in a DAC with *in-situ* SAXS/WAXS.

shown through both atomic force microscopy and X-ray scattering that when the soft segments are sufficiently long, PU develops a phase-separated microstructure of hard and soft domains wherein hard segment aggregation is driven by hydrogen bonding of the urea groups and the degree of separation is influenced by the soft segment length. Furthermore, the length of the soft segment has been shown to greatly influence the mechanical properties of PU.^{25,26} Significantly, Mock and coworkers found that for ballistic impacted PU-coated steel, reduced necking of the steel could be achieved by coating the steel with PU formulated with a shorter soft segment.²⁶ Using post-test small-

angle X-ray scattering (SAXS), they observed hard domain reorientation, breakdown, and reformation, wherein such microstructural changes were most dramatic in PU formulated with a shorter segment length.

Since understanding mechanisms from *ex-situ* X-ray scattering of specimens under complex loading conditions is challenging, it is advantageous to instead utilize *in-situ* X-ray scattering to examine more controlled loading modes. In this vein, the microstructural transformations of PU under quasi-static tension have been independently explored using *in-situ* X-ray scattering by Boyce, Runt, and Roland.^{27–29} These reports show that at low strain rates, the initially isotropic microstructure becomes irreversibly anisotropic when stretched beyond the yield point. Roland continued to show that at higher strain rates, the initial unoriented structure is retained, and the polymer exhibits complete strain recovery.²⁹ Recently, Roland and coworkers characterized PU under compressive loadings up to 6 GPa using a diamond anvil cell (DAC), finding that the glass transition temperature (T_g) of PU drastically increases from below -50 °C under ambient conditions^{4,29} to ~125 °C under hydrostatic compression to 4 GPa.³⁰ While this report provides valuable information about the behavior of PU under hydrostatic compression, there remains significant opportunity to study the microstructural evolution of PU under these conditions. Inspired by Roland's work, we sought to address this challenge through *in-situ* DAC hydrostatic compression experiments with microstructural monitoring by small-angle and wide-angle X-ray scattering (SAXS/WAXS).

Concurrent to our studies, in a separate approach, Peralta and coworkers utilized a DAC for *in-situ* structural characterization of PU using energy-dispersive X-ray diffraction; however, this report does not analyze the influence of elevated pressure on the bulk microstructure.³¹ Herein, we report the microstructural evolution by SAXS and WAXS of two PU polymers differing in their soft segment length under hydrostatic compression in a DAC (Figure 5.1). To our knowledge, such methods have not previously been used for the characterization of polymers. The use of a DAC allowed for high-pressure conditions without including high strain rate effects to directly determine the relationship between the structure of PU and hydrostatic pressure. Because of the slow rate of pressure change, the PU samples did not experience the adiabatic heating typically encountered under blast and ballistic loading conditions. We found that the microstructure of PU evolves under hydrostatic pressure, and that deformation along the interchain hydrogen-bonded network of urea linkages is greater in the PU with a shorter soft segment length. In combination with literature reports of PU's microstructural evolution under quasi-static tension, the microstructural response to high-pressure loading revealed by these experiments will help to further our understanding of the blast response of PU and guide future design of elastomeric coatings.

5.3 Results and Discussion

The PU samples were synthesized *via* condensation polymerization of a carbodiimide modified diisocyanate and an oligomeric diamine (Versalink P650 or P1000). Polymers synthesized using Versalink P650 (PU-P650) have a shorter soft segment length and correspondingly a higher volume fraction of hard segments than those synthesized using Versalink P1000 (PU-P1000), and we calculated hard segment contents as 47 wt% and 40 wt % for PU-P650 and PU-P1000, respectively (refer to appendix for calculation). Polymers were solvent cast into Teflon molds, and the solvent was allowed to slowly evaporate before annealing the polymers in a vacuum oven for 2 days at 140 °C. We used attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to check for any unreacted monomer. The absence of an isocyanate FTIR stretching peak at $\sim 2250\text{ cm}^{-1}$, which would indicate the presence of unreacted Isonate 143L, shows that the polymerization went to full conversion and that no unreacted monomer components remained in the PU samples (Figure 5.5). Typically for explosion resistant coatings, PU is applied through solvent-free spray coating methods and not through solvent casting. In the absence of a spray coating apparatus, we found solvent casting to be the optimal method for preparation of thin ($\sim 100\text{ }\mu\text{m}$ thick) and initially unoriented samples for use in our DAC experiments. We began by characterizing the initial structure of PU-P650 and PU-P1000 without loading in open-air conditions. We observed a broad and diffuse ring in the SAXS region of PU-P650 and a slightly brighter

ring in the SAXS region of PU-P1000 (Figure 5.2a-b). Neither structure showed any initial orientation, which is consistent with the solvent casting procedure. Azimuthal integration over all angles provided reduced data, which was normalized first by dividing by the diode count and then by subtracting the background intensity, affording relative intensity (Eq. 5 in appendix). The diffuse SAXS peak appeared at $q \sim 0.09 \text{ \AA}^{-1}$ in PU-P650, corresponding to a mean interdomain spacing (d) between hard segments of $\sim 7 \text{ nm}$; the peak was detected at $q \sim 0.07 \text{ \AA}^{-1}$ ($d \sim 9 \text{ nm}$) in PU-P1000 (Figure 5.2c). This result is unsurprising given the longer soft segment length of PU-P1000 compared to PU-P650 and is in accordance with previous reports.^{25,28,29} Furthermore, the relatively lower peak intensity in PU-P650 compared to PU-P1000 suggests that this sample has more phase mixing (*i.e.*, is less phase separated). This is consistent with other reports that have shown that the degree of phase separation decreases with decreasing soft segment length.^{25,32,33}

Several broad features were detected in the WAXS region for both PU systems; however, we did not observe marked differences between the two (Figure 5.2a-b). As seen in the 2D images, neither PU-P650 nor PU-P1000 displayed any preferred orientation. As such, data was reduced and normalized following the same protocol described above for the SAXS data. Both PU-P650 and PU-P1000 exhibited broad peaks at $q \sim 1.4 \text{ \AA}^{-1}$ and $3.0 \text{ \AA}^{-1}$ (Figure 2d, filled markers), as well as a smaller feature at $\sim 1.8 \text{ \AA}^{-1}$ (Figure 5.2d, open marker). The primary feature at $q \sim 1.4 \text{ \AA}^{-1}$ ($d \sim 4.4 \text{ \AA}$) is indicative of interchain urea

stacking formed through hydrogen bonds and has been described in numerous other reports.^{25,28,31,33–35} Peralta and coworkers recently utilized molecular dynamics simulations to assign physical meaning to the higher- q peaks. They proposed that a feature with $d \sim 2.4$ Å corresponds to the separation between urea groups bonded to aromatic rings whereas a feature with $d \sim 3.7$ Å is related to π -stacking and separation between soft segments. We expect that these

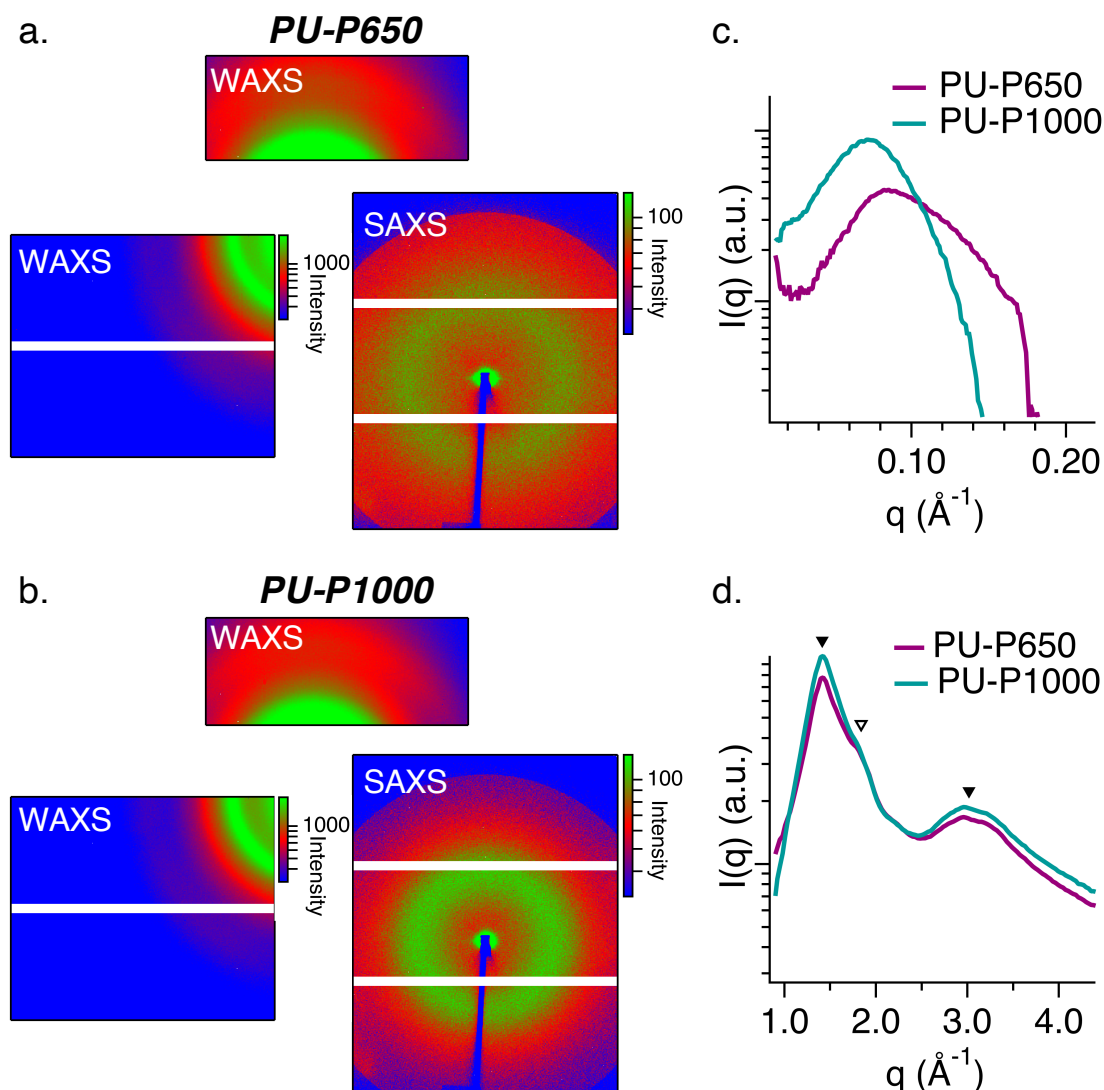


Figure 5.2 Open-air SAXS and WAXS of PU-P650 and PU-P1000. Azimuthal integration of the 2D data (a, b) affords 1D traces (c, d). Relative intensities are plotted on a log-scale.

assignments correspond to our experimentally observed peaks at $q \sim 3.0 \text{ \AA}^{-1}$ ($d \sim 2.1 \text{ \AA}$) and $q \sim 1.8 \text{ \AA}^{-1}$ ($d \sim 3.5 \text{ \AA}$), respectively.³¹ Notably, the breadth of these peaks suggests that the hard segments do not organize into a highly crystalline structure.²⁵

Significant attention was placed on designing suitable experimental procedures to analyze the microstructural transformations of PU within the DAC. The experiment was assembled by placing a small piece ($\sim 100 \mu\text{m} \times 100 \mu\text{m} \times 100 \mu\text{m}$) of the polymer sample into a metal gasket hole that serves as the sample chamber between the diamond anvils. The sample chamber was filled with silicone oil to create hydrostatic conditions, and two ruby chips were added to the chamber to monitor pressure using ruby fluorimetry. An initial fluorescence measurement was obtained to ensure the pressure within the cell was $< 0.1 \text{ GPa}$ before mounting the DAC on the sample stage to collect SAXS/WAXS data. Notably, due to signal interference from the metal gasket used as the sample chamber in the DAC, our WAXS q -range was restricted to a maximum of $2.61 \text{ \AA}^{-1}$, such that analysis concerns only the primary WAXS peak and adjacent shoulder. To account for decreased signal from diamond absorption in the DAC, SAXS/WAXS data was collected using a longer beam exposure time than for the initial structure measurements outside of the DAC. However, despite this longer exposure time, SAXS peak intensities were diminished for unpressurized PU samples in the DAC relative to SAXS intensities observed for the bulk, open-air PU samples (Figure 5.6). We reason

that this may be in part a result of damage done to the PU during sample preparation. Specifically, cutting the PU down to the exceptionally small specimen size required for DAC experiments likely resulted in microstructural damage, thereby increasing the degree of phase mixing and thus decreasing the total intensity (Figure 5.7).

To test our hypothesis that cutting the PU samples results in microstructural damage and thereby diminished SAXS/WAXS intensity prior to hydrostatic loading, we conducted a simple *ex-situ* experiment using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, wherein we compared the spectra of PU-P650 before and after being cut (Figure 5.8). Carbonyl and N-H groups have distinct wavenumber assignments when in the free, disordered, or ordered states.^{25,37-41} As such, we focused on regions of the ATR-FTIR spectra related to N-H bonds (Figure 5.8a) and carbonyl bonds (Figure 5.8b). Whereas ordered bands correspond to strong bidentate hydrogen bonding arising from alignment of urea linkages in the hard phase, free and disordered bands arise from non-hydrogen-bonded and hydrogen-bonded groups in the mixed phase.^{25,37-41} In the bulk PU sample, the N-H band assignments are 3360 cm^{-1} and 3300 cm^{-1} for the disordered and ordered states, respectively. The free N-H band typically occurs at $\sim 3440\text{--}3460\text{ cm}^{-1}$, however we did not observe bands in this region.²⁵ The urea carbonyl band assignments for the disordered and ordered states are 1665 cm^{-1} and 1642 cm^{-1} , respectively. The absorption band for free urea carbonyl appears at 1691 cm^{-1} .

¹, however this band was not directly visible. Instead, we observed a band at 1713 cm⁻¹, likely arising from hydrogen bonded ester carbonyl groups in the mixed phase.⁴⁰ We observed two notable changes in the N-H stretching region that occur with cutting. First, the band at ~3300 cm⁻¹ in the bulk PU, corresponding to ordered N-H bonds, shifts toward higher wavenumbers after being cut, suggesting that the ordered hydrogen bonds are perturbed. Second, the band at 3360 cm⁻¹, corresponding to disordered N-H bonds, becomes more apparent after being cut. In the carbonyl region, the band corresponding to ordered urea carbonyl groups in the hard phase (1642 cm⁻¹) shifts to a higher wavenumber (1649 cm⁻¹) in the cut sample. This shift toward higher wavenumbers again suggests a perturbation to the ordered hydrogen-bonded network. Furthermore, the peaks at 1665 cm⁻¹ and 1713 cm⁻¹ in the bulk PU sample, corresponding to the disordered urea carbonyl and hydrogen-bonded ester carbonyl in the mixed phase, become more prominent following cutting. These changes in both the N-H and carbonyl stretching regions of the *ex-situ* ATR-FTIR spectra indicate that cutting the PU sample perturbs ordered hydrogen bonds while increasing the prevalence of free and disordered hydrogen bonds, all of which are suggestive of increased phase mixing.^{37,41} This is consistent with the observation in the SAXS/WAXS, wherein cutting the samples resulted in a decrease in intensity, which was attributed to an increase in phase mixing. Though not the focus of this study, it would be an interesting

follow-up study to conduct *in-situ* DAC experiments with monitoring by FTIR, as a means to precisely analyze the changes in hydrogen bonds with pressure.⁴²

Despite the reduction in SAXS peak intensities, SAXS peak locations observed for the PU samples in the DAC closely resembled those obtained outside of the DAC (Figure 5.6). In contrast, we observed discrepancies in the primary WAXS peak locations (Figure 5.9). In particular, we observed the primary WAXS peak at $q \sim 1.3 \text{ \AA}^{-1}$ in both PU-P650 and PU-P1000, which slightly differs from that in the WAXS for the open-air material ($\sim 1.4 \text{ \AA}^{-1}$). This reduced q -value corresponds to a slightly increased spacing (d -value) between hydrogen-bonded urea linkages. This result is unsurprising given the observed shift toward higher wavenumber of the ordered N-H and carbonyl bands in the ATR-FTIR spectra, which signify a perturbation of the ordered bidentate hydrogen-bonded network.

Next, we examined the microstructural evolution of PU-P650 and PU-P1000 under hydrostatic compression. As previously mentioned, analysis of SAXS data from DAC experiments was complicated by the diminished intensity produced from these samples. To better analyze this low-intensity data, a region from $0.04 < q < 0.18$ is displayed that captures the main peak (Figure 5.3). As represented by the disappearance of the SAXS peak, we found that the initial microstructure is disrupted at elevated pressures ($>1 \text{ GPa}$) in both PU-P650 and PU-P1000. The loss of the SAXS peak suggests that PU quickly transitions from an ordered, phase separated state to a disordered, intermixed state under

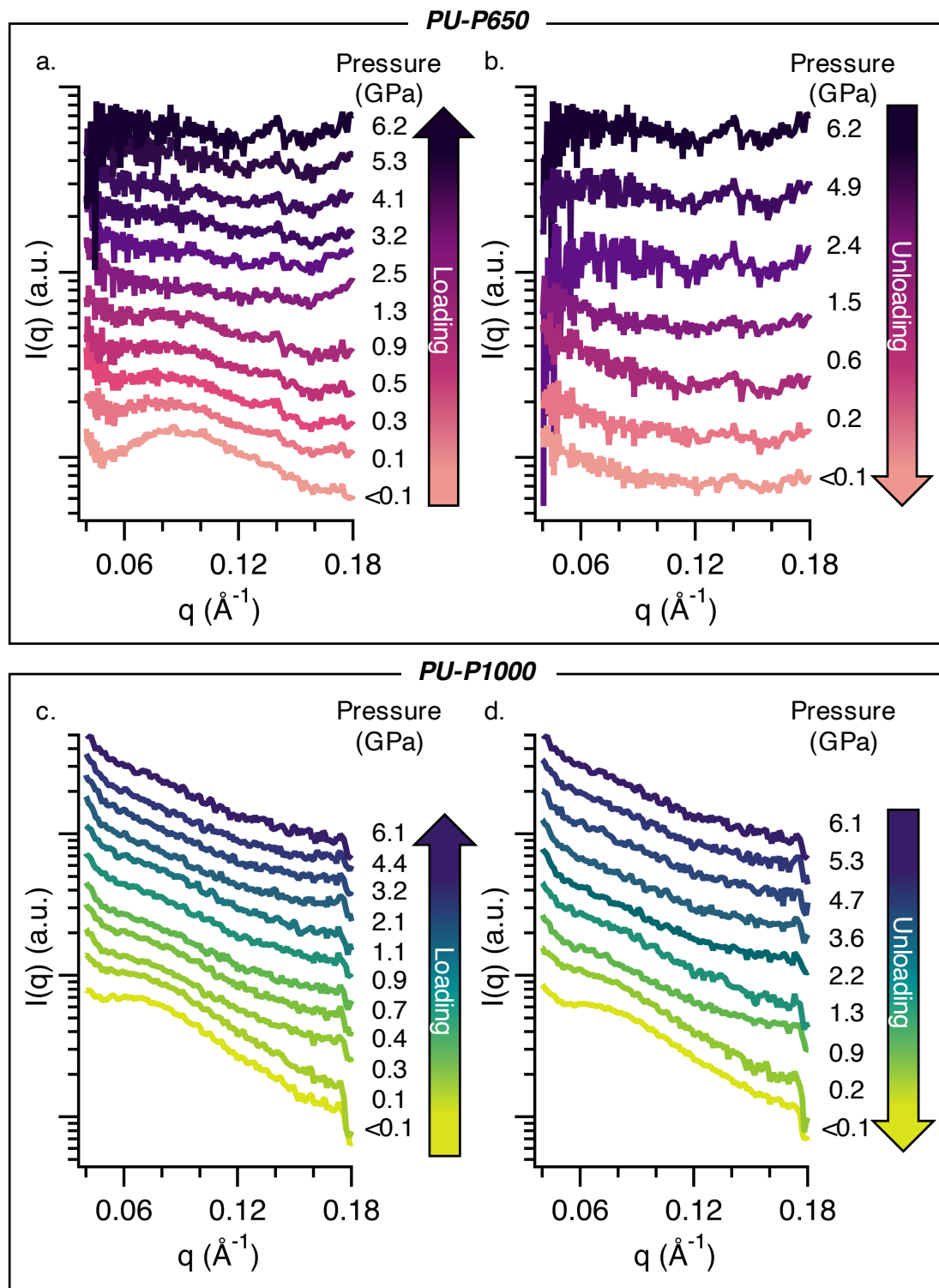


Figure 5.3 SAXS traces showing the microstructural evolution of PU-P650 (a, b) and PU-P1000 (c, d) under hydrostatic pressure in a DAC. Traces are plotted on a log-scale of relative intensity and are offset vertically for visual clarity.

hydrostatic compression. This finding highlights a key difference between the microstructural evolution of PU under hydrostatic compression versus under tension, wherein the interdomain spacing is affected by strain, and PU becomes irreversibly oriented rather than disordered.^{27–29} The reemergence of the SAXS peak upon unloading varied among samples of PU-P650 and PU-P1000 (Figure 5.10 and Figure 5.11). We speculate that such variances may be due to differences in the degree of phase separation, which likely arise from unavoidable inconsistencies in the sample cutting procedure.

Analysis of the 1D WAXS traces revealed the influence of soft segment length on the hydrogen-bonded network of urea linkages in PU under hydrostatic compression (Figure 5.4). In both PU-P650 and PU-P1000, we observed broad peaks at $q \sim 1.3 \text{ \AA}^{-1}$ and $2.0 \text{ \AA}^{-1}$, corresponding to the features at $q \sim 1.4 \text{ \AA}^{-1}$ and $1.8 \text{ \AA}^{-1}$ in the WAXS traces for the open-air samples presented in Figure 2d. In PU-P650, we observed a shift in the peak initially at $q \sim 1.3 \text{ \AA}^{-1}$ toward higher q -values until reaching a pressure of $\sim 4.1 \text{ GPa}$ (Figure 5.4a). At this pressure, the original two distinguishable peaks merge together and do not separate even with subsequent unloading of pressure (Figure 5.4b). In PU-P1000, the peak at $q \sim 2.0 \text{ \AA}^{-1}$ was unaffected during both loading and unloading, and we observed a shift in the peak initially at $q \sim 1.3 \text{ \AA}^{-1}$ toward higher q -values as pressure was increased (Figure 5.4d). Whereas the primary peak converged with the higher q peak in PU-P650 above 4.1 GPa (Figure 5.4a), this peak remained distinguishable up to 6.1 GPa in PU-P1000 (Figure

5.4d). Furthermore, in contrast to the two peaks remaining unresolved upon unloading in PU-P650, we observed a shift in the primary WAXS peak toward lower q in PU-P1000 when unloaded (Figure 5.4e). In both PU-P650 and PU-P1000, the shift in the primary WAXS peak toward higher q with increasing pressure suggests that compression occurs along the ordered plane of the interchain network of hydrogen bonds. Our WAXS results drastically differ from those reported for PU under tension, wherein the hard domains become oriented without incurring any change to the primary peak location, although the reversibility of the PU-P1000 WAXS peaks upon unloading is similar.^{27,28}

To better analyze the deformation and recovery of the crystal plane along interchain hydrogen-bonded network of urea groups, we plotted the primary WAXS peak position against pressure (Figure 5.4c and Figure 5.4f). We plotted d -values rather than q -values to better relate the positional shift of this peak to feature size. Although the total change in the peak location (Δ) during loading is similar in PU-P650 and PU-P1000 ($\Delta = -0.83 \text{ \AA}$ and $-0.77 \text{ \AA}$, respectively), the primary peak irreversibly merges with the second peak above 4.1 GPa in PU-P650. The irreversible merging of these two peaks in PU-P650 suggests that increasing the pressure above 4.1 GPa results in formation of a new structure in which the initial hydrogen-bonded network of urea linkages is no longer apparent. In contrast, the primary peak in PU-P1000 remains distinguishable during all loading pressures, indicating that the structure compresses only along the interchain network of hydrogen bonds and evolves orthogonally to the

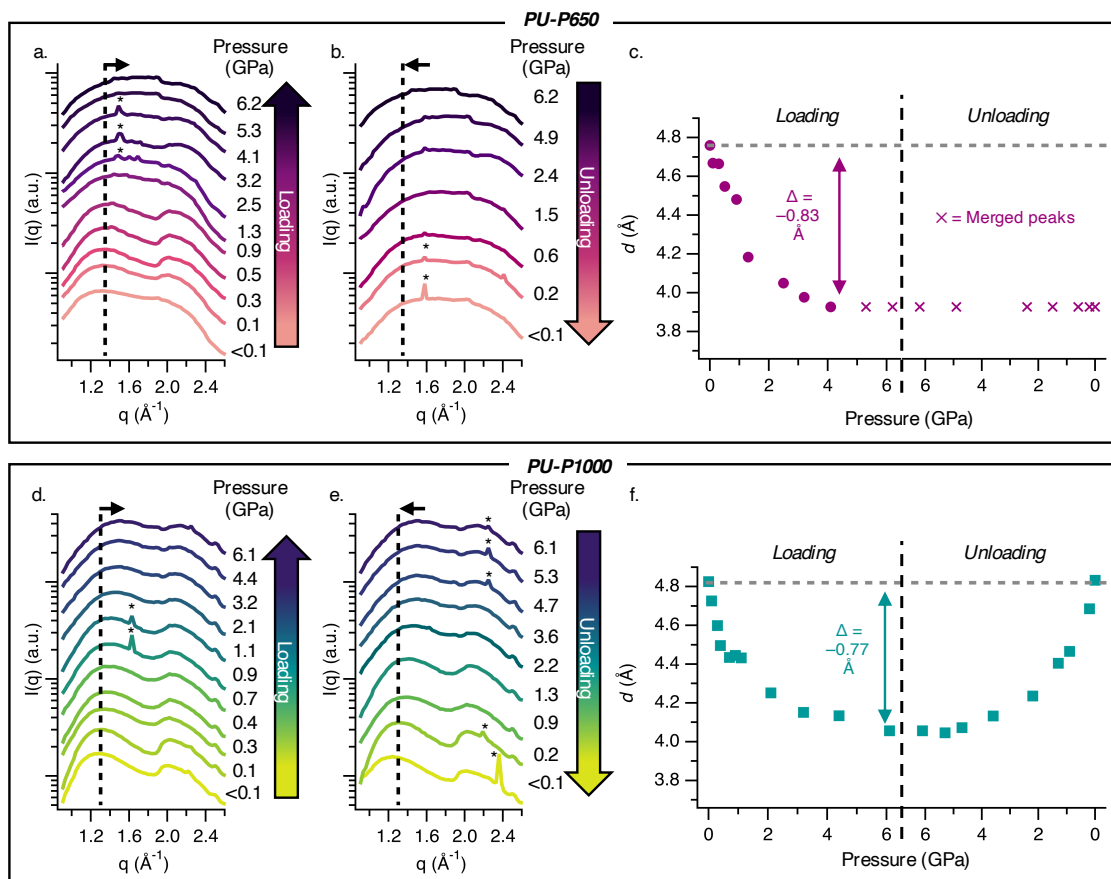


Figure 5.4 WAXS traces showing the structural evolution of the hard domains in PU-P650 (a, b) and PU-P1000 (d, e) under hydrostatic pressure in a DAC. Traces are offset vertically for visual clarity. The initial position of the primary WAXS peak at <0.1 GPa and the direction in which the primary WAXS peak shifts are indicated by the black dashed lines and arrows, respectively. The location of the primary WAXS peak is plotted against pressure for the loading and unloading of PU-P650 (c) and PU-P1000 (f), in which x markers indicate disappearance of the primary peak. Sharp peaks, such as those marked with asterisks, are unrelated to the PU samples and likely arise from crystallites, perhaps from the iron gasket.

feature corresponding to the peak at $2.0 \text{ \AA}^{-1}$. Furthermore, the primary peak location fully recovers in PU-P1000. As such, we posit that the initial hydrogen-bonded network present in PU-P1000 is fully restored upon complete removal of pressure. We hypothesize that the merging of peaks in PU-P650 is due to a deformation-induced glass transition and subsequent plastic deformation of the hard domains. Given Roland's findings that the T_g of PU increases under hydrostatic pressure, it is unsurprising that the PU materials presented here would exhibit glassy-type behaviors such as plastic deformation at sufficiently high pressures.³⁰ Furthermore, Hsieh and co-workers demonstrated that at low frequencies, the deformation-induced glass transition dominates within the phase-mixed region of PU.³² Significantly, they showed that PU-P650 has increased phase-mixing compared to PU-P1000, which also appears to be the case in our polymers as suggested by the SAXS results in Figure 5.2c.^{32,33} As a result, deformation-induced glass transitions are more prevalent in PU-P650 than in PU-P1000 at low frequencies.³² Consistent with these reports, we rationalize that PU-P650, having more initial phase mixing than PU-P1000 and likely more phase mixing at elevated pressures, undergoes a transition to a glassy state followed by rupture of the hard domains at pressures above ~ 4 GPa. Following rupture of the hard domains, even removal of pressure is insufficient for reforming the initial network of hydrogen bonds, and thus the WAXS traces remain largely unaffected by decreasing pressure. We anticipate that the initial network of hydrogen bonds in PU-P650 would be fully recovered

if the maximum pressure remained below ~ 4 GPa. It is additionally possible that the merging of the WAXS peaks may be due to the increased sample homogeneity at elevated pressures, and that this increased homogeneity precludes the ability for hydrogen bonds to reform with removal of pressure. Nonetheless, the hydrogen-bonded network in both PU-P650 and PU-P1000 remained intact at relatively low pressures (~ 1 GPa) despite the microstructure (the organization of hard and soft domains as detected by SAXS) becoming disordered. As such, it is worth noting that some degree of order of the hydrogen-bonded network of urea linkages in these PU systems persists despite breakdown of the phase separated microstructure.

5.4 Conclusion

The microstructural evolution of two PU materials differing in their soft segment length under hydrostatic compression up to ~ 6 GPa was determined using a DAC with *in-situ* X-ray scattering. We found that both PU-P650 and PU-P1000 sustained microstructural damage when compressed to 1 GPa, and that the permanence of this microstructural damage varied between samples. Though neither PU-P650 nor PU-P1000 exhibited high degrees of crystallinity, we observed broad peaks in the WAXS region consistent with the presence of an interchain network of urea groups formed through hydrogen bonds. This hydrogen-bonded network remained intact at pressures well above 1 GPa, despite the substantial increase in phase mixing. Furthermore, the hard domain

internal structure in PU-P1000 evolved without a loss of the primary WAXS peak and with complete recovery upon unloading. This suggests that PU-P1000 compresses along the hydrogen-bonded network of urea groups without significant disruption of this network. In contrast, we observed significant and permanent changes to the interchain hydrogen-bonded network at pressures above ~ 4 GPa in PU-P650. We speculate that PU-P650 undergoes a transition to a glassy state followed by subsequent plastic deformation of the hard domains, resulting in observed permanent transformations. We anticipate that the disclosed experimental methods will provide a novel platform for studying the structural behavior of crystalline and semi-crystalline polymers under high pressures, and that our findings will prove useful in the design and development of PU materials.

5.5 References

- (1) Iqbal, N.; Tripathi, M.; Parthasarathy, S.; Kumar, D.; Roy, P. K. Polyurea Coatings for Enhanced Blast-Mitigation: A Review. *RSC Adv.* **2016**, *6*, 109706–109717.
- (2) Barsoum, R. G. *Elastomeric Polymers with High Rate Sensitivity: Applications in Blast, Shockwave, and Penetration Mechanics*; Elsevier Inc., 2015.
- (3) Clifton, R. J.; Jiao, T. Testing, Experiments and Properties of HSREP: Pressure and Strain-Rate Sensitivity of an Elastomer: (1) Pressure-Shear Plate Impact Experiments; (2) Constitutive Modeling. In *Elastomeric Polymers with High Rate Sensitivity: Applications in Blast, Shockwave, and Penetration Mechanics*; Barsoum, R. G., Ed.; Elsevier Inc., 2015; pp 17–65.
- (4) Zhang, X.; Wang, J.; Guo, W.; Zou, R. A Bilinear Constitutive Response for Polyureas as a Function of Temperature, Strain Rate and Pressure. *J. Appl. Polym. Sci* **2017**, *134*, 45256–45256.
- (5) Jiao, T.; Clifton, R. J.; Grunschel, S. E. High Strain Rate Response of an Elastomer. In *AIP Conference Proceedings*; AIP, 2006; Vol. 845, pp 809–812.
- (6) Jiao, T.; Clifton, R. J.; Grunschel, S. E. Pressure-Sensitivity and Tensile Strength of an Elastomer at High Strain Rates. In *AIP Conference*

Proceedings; American Institute of PhysicsAIP, 2007; Vol. 955, pp 707–710.

- (7) Jiao, T.; Clifton, R. J.; Grunschel, S. E. Pressure-Sensitivity and Constitutive Modeling of an Elastomer at High Strain Rates. In *AIP Conference Proceedings*; American Institute of PhysicsAIP, 2009; Vol. 1195, pp 1229–1232.
- (8) Jiao, T.; Clifton, R. J. J. Measurement of the Response of an Elastomer at Pressures up to 9 GPa and Shear-Rates of 10⁵-10⁶ s⁻¹. *J. Phys. Conf. Ser.* **2014**, *500*, 112036.
- (9) Yi, J.; Boyce, M. C.; Lee, G. F.; Balizer, E. Large Deformation Rate-Dependent Stress-Strain Behavior of Polyurea and Polyurethanes. *Polymer* **2006**, *47*, 319–329.
- (10) Tekalur, S. A.; Shukla, A.; Shivakumar, K. Blast Resistance of Polyurea Based Layered Composite Materials. *Compos. Struct.* **2008**, *84*, 271–281.
- (11) Wang, H.; Deng, X.; Wu, H.; Pi, A.; Li, J.; Huang, F. Investigating the Dynamic Mechanical Behaviors of Polyurea through Experimentation and Modeling. *Def. Technol.* **2019**, *15*, 875–884.
- (12) Guo, H.; Guo, W.; Amirkhizi, A. V.; Zou, R.; Yuan, K. Experimental Investigation and Modeling of Mechanical Behaviors of Polyurea over Wide Ranges of Strain Rates and Temperatures. *Polym. Test.* **2016**, *53*, 234–244.

- (13) Roland, C. M.; Casalini, R. Effect of Hydrostatic Pressure on the Viscoelastic Response of Polyurea. *Polymer* **2007**, *48*, 5747–5752.
- (14) Gruzicic, M.; Pandurangan, B.; He, T.; Cheeseman, B. A.; Yen, C. F.; Randow, C. L. Computational Investigation of Impact Energy Absorption Capability of Polyurea Coatings via Deformation-Induced Glass Transition. *Mater. Sci. Eng. A* **2010**, *527*, 7741–7751.
- (15) Iqbal, N.; Sharma, P. K.; Kumar, D.; Roy, P. K. Protective Polyurea Coatings for Enhanced Blast Survivability of Concrete. *Constr. Build. Mater.* **2018**, *175*, 682–690.
- (16) Shim, J.; Mohr, D. Using Split Hopkinson Pressure Bars to Perform Large Strain Compression Tests on Polyurea at Low, Intermediate and High Strain Rates. *Int. J. Impact Eng.* **2009**, *36*, 1116–1127.
- (17) Gruzicic, M.; Snipes, J.; Ramaswami, S.; Galgalikar, R.; Runt, J.; Tarter, J. Molecular- and Domain-Level Microstructure-Dependent Material Model for Nano-Segregated Polyurea. *Multidiscip. Model. Mater. Struct.* **2013**, *9*, 548–578.
- (18) Amirkhizi, A. V.; Isaacs, J.; McGee, J.; Nemat-Nasser, S. An Experimentally-Based Viscoelastic Constitutive Model for Polyurea, Including Pressure and Temperature Effects. *Philos. Mag.* **2006**, *86*, 5847–5866.
- (19) Qiao, J.; Amirkhizi, A. V.; Schaaf, K.; Nemat-Nasser, S. Dynamic Mechanical Analysis of Fly Ash Filled Polyurea Elastomer. *J. Eng.*

Mater. Technol. Trans. ASME **2011**, *133*, 011016.

- (20) Amini, M. R.; Isaacs, J.; Nemat-Nasser, S. Investigation of Effect of Polyurea on Response of Steel Plates to Impulsive Loads in Direct Pressure-Pulse Experiments. *Mech. Mater.* **2010**, *42*, 628–639.
- (21) Clifton, R. J.; Wang, X.; Jiao, T. A Physically-Based, Quasilinear Viscoelasticity Model for the Dynamic Response of Polyurea. *J. Mech. Phys. Solids* **2016**, *93*, 8–15.
- (22) Fragiadakis, D.; Gamache, R.; Bogoslovov, R. B.; Roland, C. M. Segmental Dynamics of Polyurea: Effect of Stoichiometry. *Polymer* **2010**, *51*, 178–184.
- (23) Mott, P. H.; Giller, C. B.; Fragiadakis, D.; Rosenberg, D. A.; Roland, C. M. Deformation of Polyurea: Where Does the Energy Go? *Polymer* **2016**, *105*, 227–233.
- (24) Holzworth, K.; Jia, Z.; Amirkhizi, A. V.; Qiao, J.; Nemat-Nasser, S. Effect of Isocyanate Content on Thermal and Mechanical Properties of Polyurea. *Polymer* **2013**, *54*, 3079–3085.
- (25) Castagna, A. M.; Pangon, A.; Choi, T.; Dillon, G. P.; Runt, J. The Role of Soft Segment Molecular Weight on Microphase Separation and Dynamics of Bulk Polymerized Polyureas. *Macromolecules* **2012**, *45*, 8438–8444.
- (26) Balizer, E.; Bartyczak, S.; Mock, W. Modeling and Simulations, Applications in Ballistic and Blast: Investigation of Phase

- Transformations in Impacted Polyurea Coatings Using Small Angle X-Ray Scattering (SAXS). In *Elastomeric Polymers with High Rate Sensitivity: Applications in Blast, Shockwave, and Penetration Mechanics*; Barsoum, R. G., Ed.; Elsevier Inc., 2015; pp 280–289.
- (27) Rinaldi, R. G.; Boyce, M. C.; Weigand, S. J.; Londono, D. J.; Guise, M. W. Microstructure Evolution during Tensile Loading Histories of a Polyurea. *J. Polym. Sci. Part B Polym. Phys.* **2011**, *49*, 1660–1671.
- (28) Choi, T.; Fragiadakis, D.; Roland, C. M.; Runt, J. Microstructure and Segmental Dynamics of Polyurea under Uniaxial Deformation. *Macromolecules* **2012**, *45*, 3581–3589.
- (29) Pathak, J. A.; Twigg, J. N.; Nugent, K. E.; Ho, D. L.; Lin, E. K.; Mott, P. H.; Robertson, C. G.; Vukmir, I M K; Epps Iii, T. H.; Roland, C. M. Structure Evolution in a Polyurea Segmented Block Copolymer Because of Mechanical Deformation. *Macromolecules* **2008**, *41*, 7543–7548.
- (30) Ransom, T. C.; Ahart, M.; Hemley, R. J.; Roland, C. M. Vitrification and Density Scaling of Polyurea at Pressures up to 6 GPa. *Macromolecules* **2017**, *50*, 8274–8278.
- (31) Eastmond, T.; Hu, J.; Alizadeh, V.; Hrubciak, R.; Oswald, J.; Amirkhizi, A.; Peralta, P. Probing High-Pressure Structural Evolution in Polyurea with in Situ Energy-Dispersive X-Ray Diffraction and Molecular Dynamics Simulations. *Macromolecules* **2021**, *54*, 597–608.
- (32) Hsieh, A. J.; Chantawansri, T. L.; Hu, W.; Strawhecker, K. E.; Casem, D.

- T.; Eliason, J. K.; Nelson, K. A.; Parsons, E. M. New Insight into Microstructure-Mediated Segmental Dynamics in Select Model Poly(Urethane Urea) Elastomers. *Polymer* **2014**, *55*, 1883–1892.
- (33) Strawhecker, K. E.; Hsieh, A. J.; Chantawansri, T. L.; Kalcioglu, Z. I.; Van Vliet, K. J. Influence of Microstructure on Micro-/Nano-Mechanical Measurements of Select Model Transparent Poly(Urethane Urea) Elastomers. *Polymer* **2013**, *54*, 901–908.
- (34) Yeh, F.; Hsiao, B. S.; Sauer, B. B.; Michel, S.; Siesler, H. W. In-Situ Studies of Structure Development during Deformation of a Segmented Poly(Urethane-Urea) Elastomer. *Macromolecules* **2003**, *36*, 1940–1954.
- (35) Versteegen, R. M.; Kleppinger, R.; Sijbesma, R. P.; Meijer, E. W. Properties and Morphology of Segmented Copoly(Ether Urea)s with Uniform Hard Segments. *Macromolecules* **2006**, *39*, 772–783.
- (36) Koevoets, R. A.; Versteegen, R. M.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. Molecular Recognition in a Thermoplastic Elastomer. *J. Am. Chem. Soc.* **2005**, *127*, 2999–3003.
- (37) Garrett, J. T.; Xu, R.; Cho, J.; Runt, J. Phase Separation of Diamine Chain-Extended Poly(Urethane) Copolymers: FTIR Spectroscopy and Phase Transitions. *Polymer* **2003**, *44*, 2711–2719.
- (38) Pongkitwitoon, S.; Hernández, R.; Weksler, J.; Padsalgikar, A.; Choi, T.; Runt, J. Temperature Dependent Microphase Mixing of Model Polyurethanes with Different Intersegment Compatibilities. *Polymer*

2009, *50*, 6305–6311.

- (39) Choi, T.; Weksler, J.; Padsalgikar, A.; Runt, J. Influence of Soft Segment Composition on Phase-Separated Microstructure of Polydimethylsiloxane-Based Segmented Polyurethane Copolymers. *Polymer* **2009**, *50*, 2320–2327.
- (40) Mattia, J.; Painter, P. A Comparison of Hydrogen Bonding and Order in a Polyurethane and Poly(Urethane-Urea) and Their Blends with Poly(Ethylene Glycol). *Macromolecules* **2007**, *40*, 1546–1554.
- (41) Ning, L.; De-Ning, W.; Sheng-Kang, Y. Hydrogen-Bonding Properties of Segmented Polyether Poly(Urethane Urea) Copolymer. *Macromolecules* **1997**, *30*, 4405–4409.
- (42) Chervin, J. C.; Canny, B.; Besson, J. M.; Pruzan, P. A Diamond Anvil Cell for IR Microspectroscopy. *Rev. Sci. Instrum.* **1995**, *66*, 2595–2598.
- (43) Stoupin, S.; Ruff, J. P. C.; Krawczyk, T.; Finkelstein, K. D. X-Ray Reflectivity of Chemically Vapor-Deposited Diamond Single Crystals in the Laue Geometry. *Acta Crystallogr. Sect. A Found. Adv.* **2018**, *74*, 567–577.

5.6 Appendix

5.6.1 Materials and Methods

Preparation of PU Samples. PU was synthesized from the reaction of a polycarbodiimide-modified diphenylmethane diisocyanate (Isonate 143L, DOW Chemicals) and an oligomeric diamine (Versalink P650 or Versalink P1000, Evonik). The two components were combined in a weight ratio of 1:1.9 (Isonate 143L: Versalink P650) or 1:3.3 (Isonate 143L: Versalink P1000), typically on a 1 g scale of the Versalink component, to achieve the desired 95% stoichiometry. The resulting mixture was dissolved in 5 mL tetrahydrofuran (THF, Fisher Scientific) and stirred at 50 °C for 2 h. The mixtures were solvent cast into PTFE low form evaporating dishes (Dynalab Labware). After natural evaporation of the THF overnight, the Teflon dishes were transferred to a vacuum oven where they were annealed for 48 h at 140 °C, affording PU films with thicknesses ranging from 100–300 μm . For open-air X-ray measurements, small strips of the PU films were cut and used directly. Samples for the DAC were prepared by cutting a small section of the PU film ($\sim 100\ \mu\text{m} \times 100\ \mu\text{m} \times 100\ \mu\text{m}$) under a microscope, securing it within Kapton film, and annealing in a vacuum oven for 8 h at 80 °C.

Synchrotron X-Ray Measurements. All synchrotron X-ray scattering experiments were carried out at the Functional Materials Beamline (FMB) at the Cornell High Energy Synchrotron Source (CHESS). The X-ray energy of 15.89

keV was selected using a diamond (220) side bounce monochromator⁴¹, and the beam size ($0.3 \times 0.3 \text{ mm}^2$, ca. 1 m upstream from the sample) was set using slits. WAXS data were collected using a Pilatus 100K and 200K detector positioned above and to the side of the transmitted beam, approximately 12 cm downstream of the sample. SAXS data were collected using a Pilatus 300K detector positioned 240 cm downstream of the sample. The SAXS flight path was helium-filled, and a beamstop photodiode was used to monitor transmitted intensity. Open-air SAXS/WAXS data were collected using a 3 s exposure time on strips of PU. A 90 s exposure time was used for DAC experiments (Figure 5.14). Details regarding data processing and intensity corrections can be found in the appendix.

DAC experiments. High-pressure SAXS and WAXS measurements of PU were performed through a diamond anvil cell (DAC), in which the two diamond anvils have a surface cut of 400 microns in diameter. A stainless-steel gasket was indented from 250 μm down to 100 μm in thickness, and a 200 μm diameter hole was drilled to serve as a sample chamber. After loading the sample and pressure medium of silicone oil in the gasket hole seated on the top of one diamond anvil, two ruby chips were loaded on the top of the sample to monitor the pressure using a ruby-based fluorescence technique. Uniform hydrostatic conditions were confirmed by measuring the pressure for both rubies. SAXS/WAXS data was collected using a 90 s exposure time to account for a

decreased signal from diamond absorption in the DAC. The pressure in the DAC was incremented by gently tightening the screws until the next desired pressure, as measured by ruby fluorimetry, was obtained. Unloading was achieved by gently loosening the screws. SAXS/WAXS data was collected on the loading for various pressures up to ~ 6 GPa and on the unloading for pressures down to ~ 0 GPa. The time between X-ray measurements was typically 10 minutes.

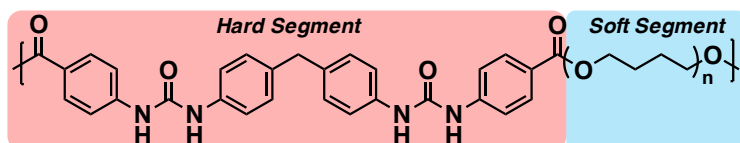
ATR-FTIR spectroscopy experiments. FTIR spectra were collected using a Bruker Tensor II FTIR spectrometer fitted with a diamond ATR cell. Signal was averaged over 16 scans with a resolution of 4 cm^{-1} . For the bulk sample, a small square ($\sim 1 \times 1\text{ cm}^2$) was cut and placed on the sample stage such that data was collected from the center of the sample. To acquire data for the cut sample, a razor blade was used to slice small pieces (sub-millimeter dimensions) from the bulk sample until the sample stage area was fully covered. The acquired data was processed in OPUS 8.1 using a baseline correction and a min-max normalization so as to compare the two data sets.

5.6.2 Calculation of Hard Segment Content

The hard segment weight percent was calculated according to Eq. 1. This calculation assumes that the hard segment is formed by the polycarbodiimide modified diisocyanate (Isonate 143L) as well as the phenyl and carbonyl portions of the Versalink diamine. The soft segment is thus assumed to be

composed only of the poly(tetramethylene oxide) (PTMO) portion of the Versalink diamine.

$$wt \% HS = \frac{(1.05 \times MW \text{ Isonate 143L}) + MW \text{ Versalink} - MW \text{ PTMO}}{(1.05 \times MW \text{ Isonate 143L}) + MW \text{ Versalink}} \quad \text{Eq. 1}$$



The molecular weight of Isonate 143L was calculated according to Eq. 2, wherein the equivalent weight and isocyanate (NCO) index were provided by the supplier.

$$MW \text{ Isonate 143L} = \text{equivalent weight} \times \text{NCO index} = 144.5 \times 2.1 = 303.45 \frac{g}{mol} \quad \text{Eq. 2}$$

The molecular weights of the oligomeric diamines (Versalink P650 and P1000) were calculated according to Eq. 3, wherein the equivalent weights and amine index were provided by the supplier. For both Versalink P650 and P1000, the amine index is 2. The equivalent weights are 468 and 625 for Versalink P650 and P1000, respectively.

$$MW \text{ Versalink} = \text{equivalent weight} \times \text{amine index} \quad \text{Eq. 3}$$

The molecular weights of the PTMO soft segments were calculated according to Eq. 4, where n is either 9 or 13, corresponding to the number of tetramethylene oxide (TMO) repeat units in Versalink P650 and Versalink P1000, respectively. The molecular weight of the TMO repeat unit is 72.1 g/mol.

$$MW_{PTMO} = (n \times MW_{TMO}) + MW_{oxygen} \quad \text{Eq. 4}$$

5.6.3 Calculations and Data Processing for X-Ray Scattering Data

2D data was reduced using InstantPlot, a custom Python-based software in development by AFRL and CHESS based on the pyFAI library.¹⁻² Silver behenate and lanthanum hexaboride were used to generate pyFAI calibration files (.poni extension) for SAXS and WAXS data, respectively.

Intensity Normalization

Following data reduction of the 2D images to 1D plots, intensities were normalized by the diode count, dc . From this was subtracted the diode count normalized background intensity. This normalization procedure described by Eq. 5 affords relative intensities, I_{rel} (or simple $I(q)$ in this paper).

$$I_{rel} = \frac{I_{sample}}{dc_{sample}} - \frac{I_{background}}{dc_{background}} \quad \text{Eq. 5}$$

Equations for Determining Peak Locations

The scattering vector and d -spacing are defined by equations 6 and 7, respectively:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad \text{Eq. 6}$$

$$n\lambda = 2d \sin \theta \quad \text{Eq. 7}$$

where λ is the wavelength of the incident beam (0.7802 Å), θ is the Bragg's angle, n is a positive integer taken equal to 1 here assuming we are seeing the first reflection, and the scatterers are approximated as spherical. Scattering vectors were transformed into d -spacings by substituting Eq. 6 into Eq. 7 giving Eq. 8.

$$d = \frac{2\pi}{q} \quad \text{Eq. 8}$$

Peak locations were determined by fitting to a gaussian curve in Igor Pro 7.

5.6.4 Supplemental Figures

Sample 1 corresponds to the data presented in the main text and in Figure 5.1.

Sample 2 was cut from the same bulk sample as Sample 1.

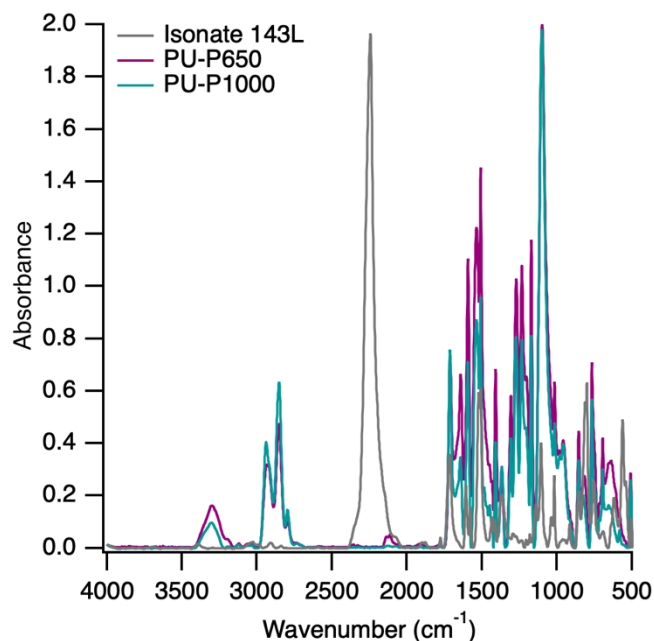


Figure 5.5 ATR-FTIR spectra of PU samples and Isonate 143L

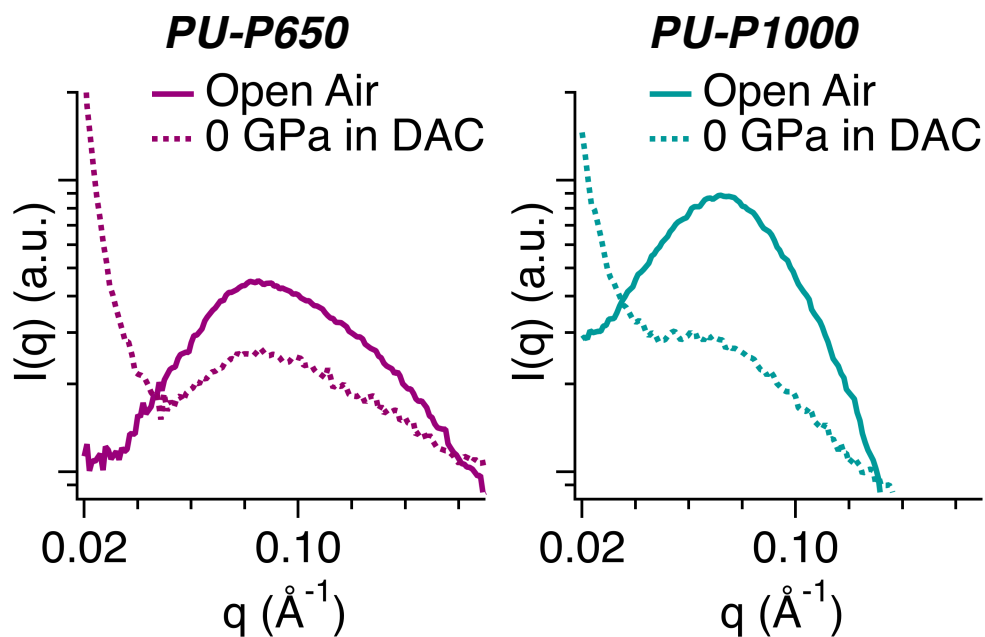


Figure 5.6 1D SAXS traces showing reduced intensity for unpressurized samples in the DAC.

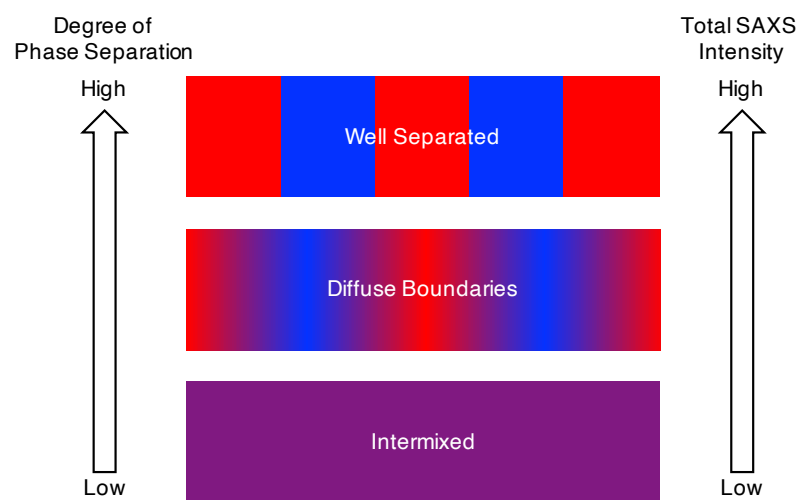


Figure 5.7 Cartoon depiction of the correlation between degree of phase separation and SAXS intensity.

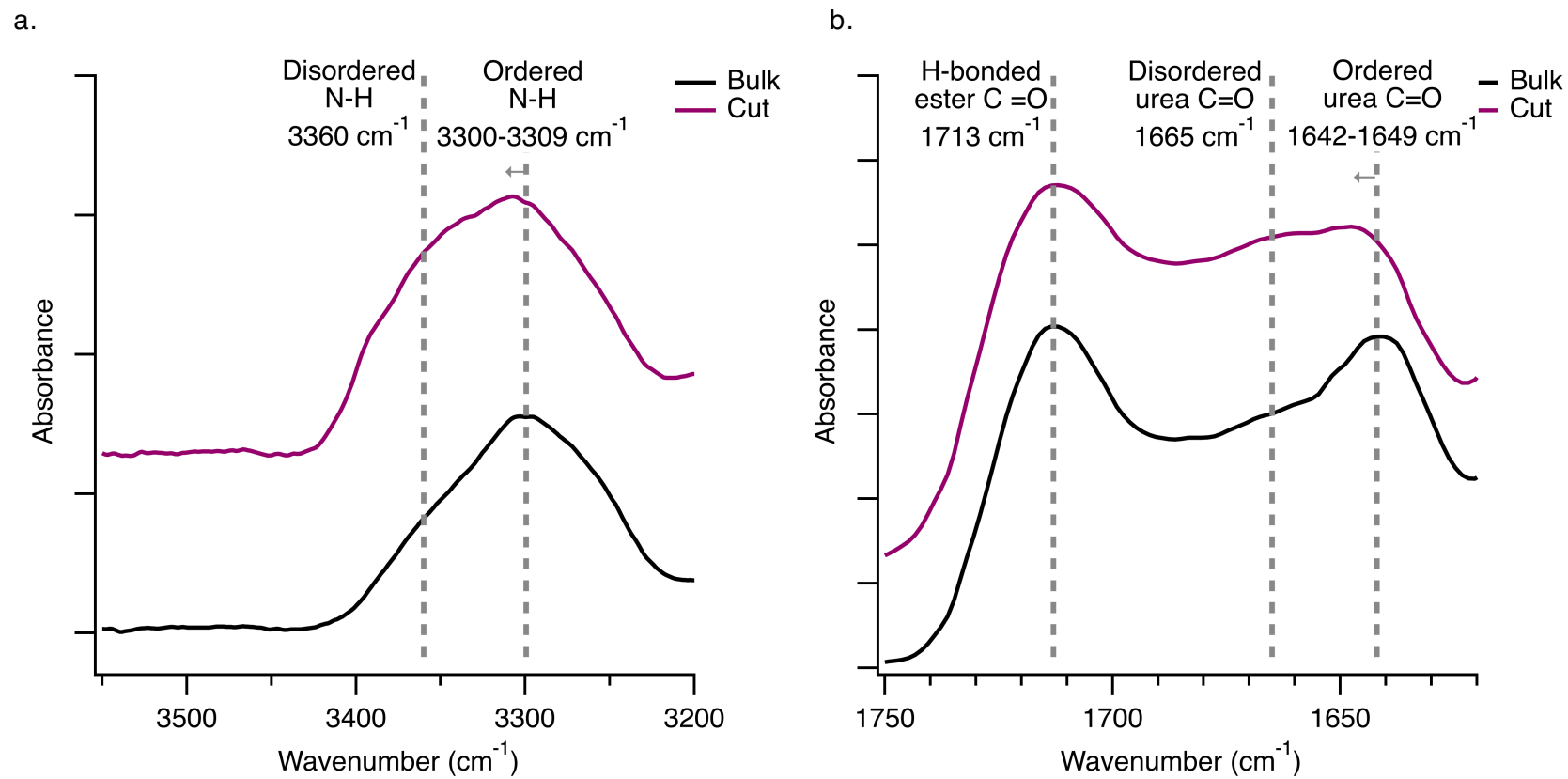


Figure 5.8 ATR-FTIR spectra in the (a) urea N-H and (b) carbonyl stretching regions of PU-P650 before and after being cut showing the state of hydrogen bonding.

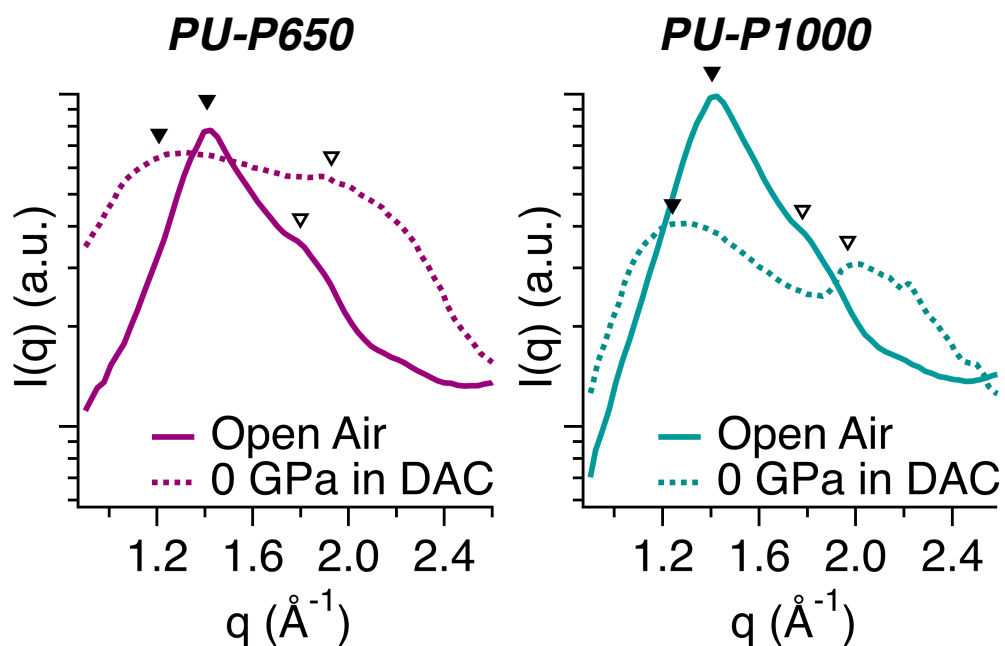


Figure 5.9 1D WAXS traces showing changes in peak locations for unpressurized samples in the DAC.

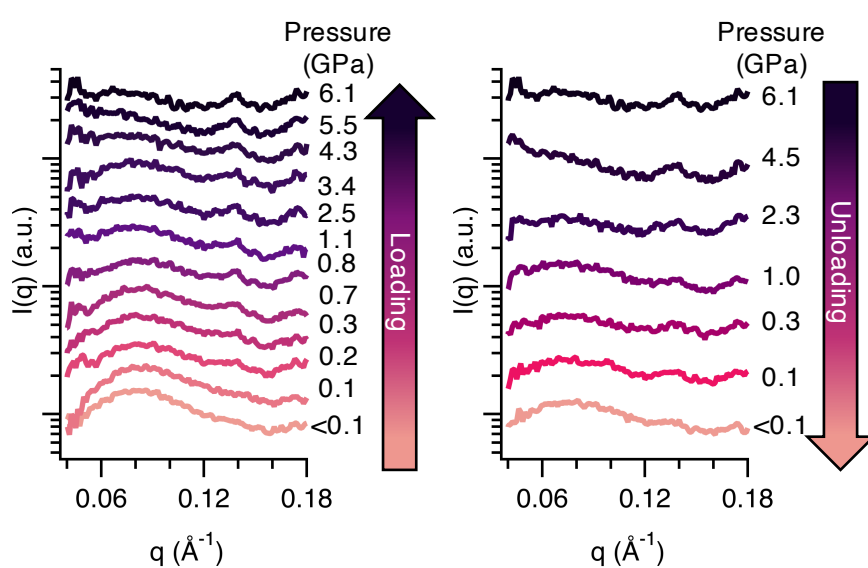


Figure 5.10 SAXS traces of PU-P650 (sample 2).

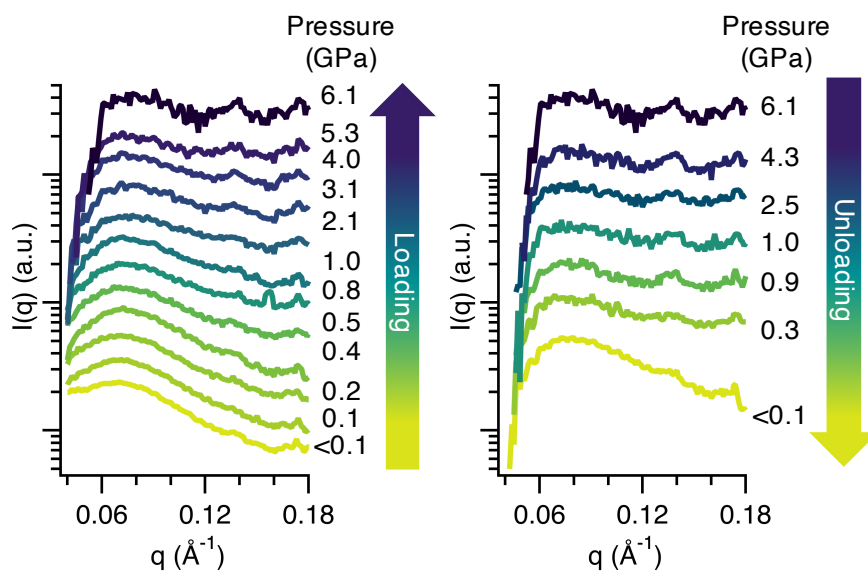


Figure 5.11 SAXS traces of PU-P1000 (sample 2).

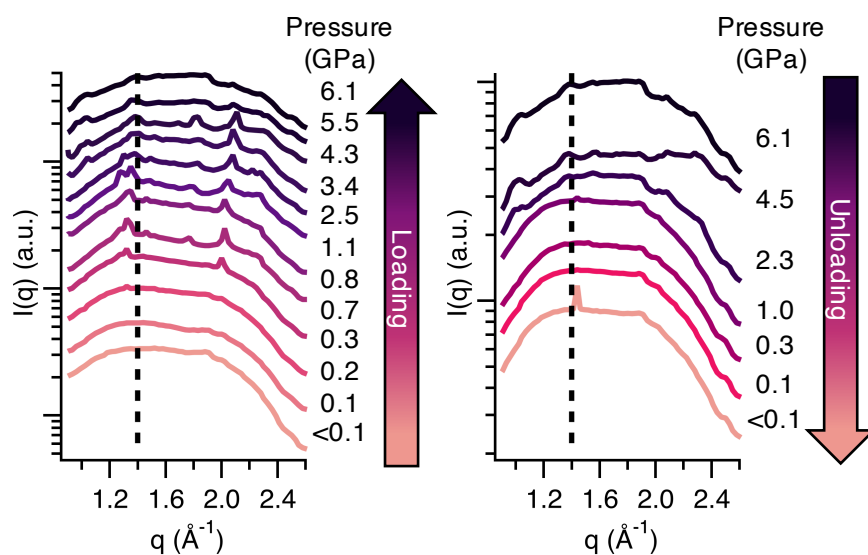


Figure 5.12 WAXS traces of PU-P650 (sample 2), wherein the dashed line represents the location of the primary WAXS peak at < 0.1 GPa

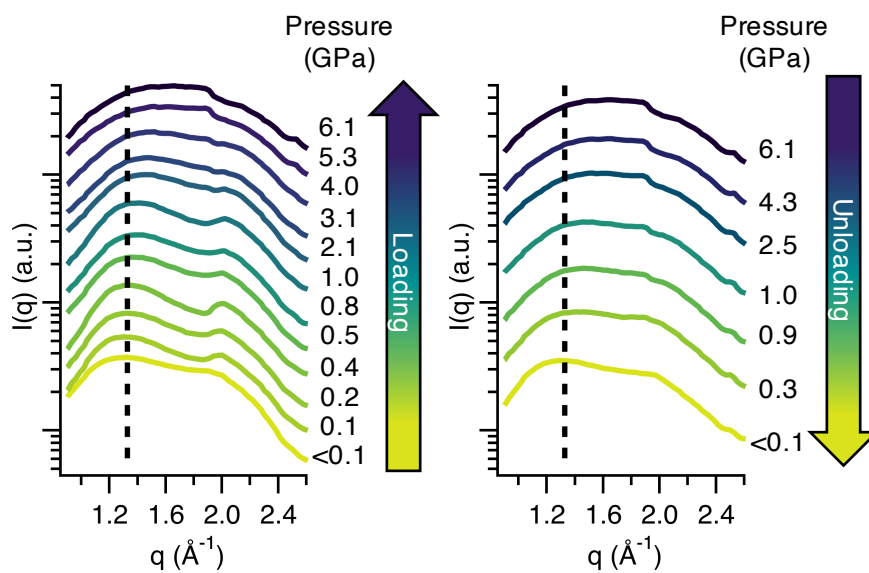


Figure 5.13 WAXS traces of PU-P1000 (sample 2), wherein the dashed line represents the location of the primary WAXS peak at < 0.1 GPa.

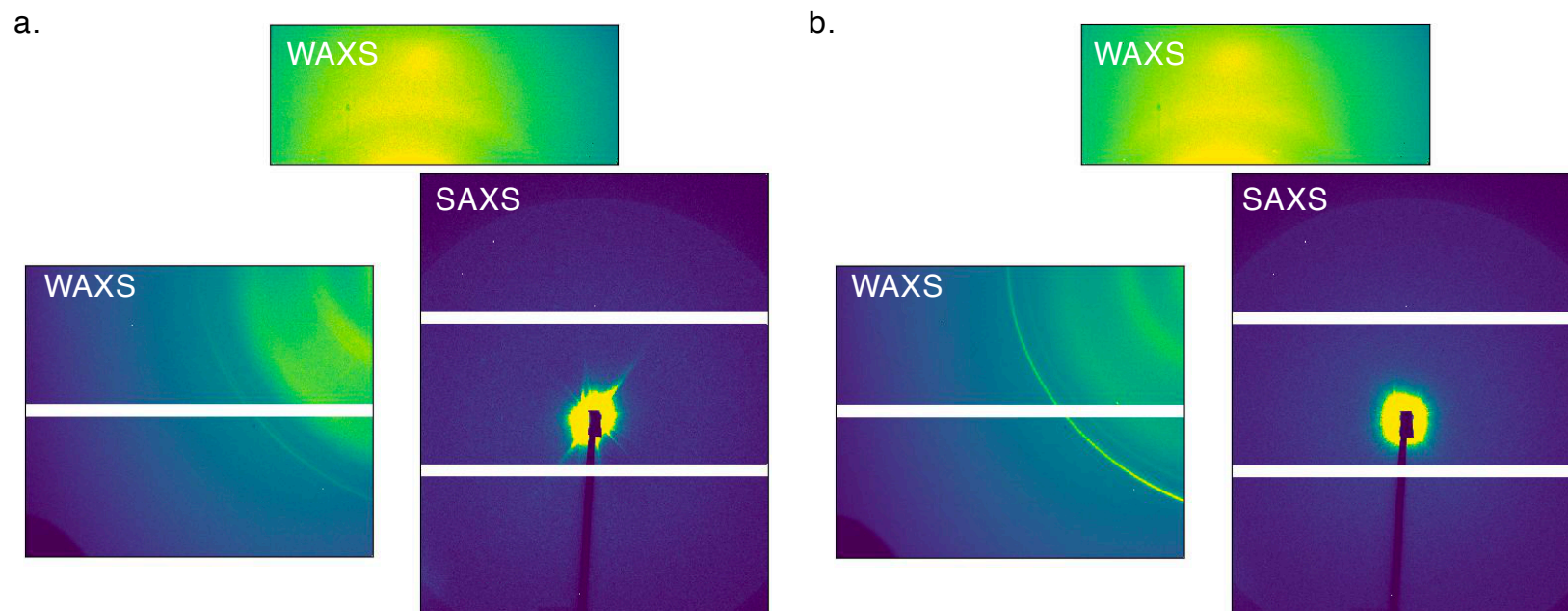


Figure 5.14 Raw 2D images of (a) PU-P650 and (b) PU-P1000 inside the DAC at pressure of 0 GPa (sample 1).

5.6.5 References

- (1) Kieffer, J.; Karkoulis, D. PyFAI, a versatile library for azimuthal regrouping. *J. Phys.: Conf. Ser.* **2013**, 425, 202012.
- (2) Kieffer, J.; Wright, J. P. PyFAI: a Python library for high performance azimuthal integration on GPU. *Powder Diffraction* **2013**, 28, S339—S350.